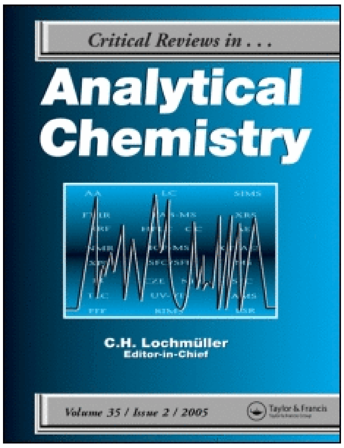


Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Chelating Sorbents in Analytical Chemistry

G. V. Myasoedova; S. B. Savvin; E. Blasius

To cite this Article Myasoedova, G. V. , Savvin, S. B. and Blasius, E.(1986) 'Chelating Sorbents in Analytical Chemistry', Critical Reviews in Analytical Chemistry, 17: 1, 1 — 63

To link to this Article: DOI: 10.1080/10408348608542791

URL: http://dx.doi.org/10.1080/10408348608542791

CHELATING SORBENTS IN ANALYTICAL CHEMISTRY

Authors: **G. V. Myasoedova**
S. B. Savvin
V. I. Vernadsky Institute of Geochemistry
and Analytical Chemistry
U.S.S.R. Academy of Sciences
Moscow, U.S.S.R.

Referee: E. Blasius
Anorganische Analytik und Radiochemie
University of Saarlandes
Saarbrücken, West Germany

I. INTRODUCTION

The importance of chelating sorbents in analytical chemistry has risen substantially in recent years. To a considerable extent this is explained by the fact that the methods of concentrating and separating chemical elements are widely used when they are determined in various objects. Sorption methods are distinguished by simplicity of implementation. They are convenient for concentrating from any, including large, volumes of solution, and are easily combined with different methods of elements determination. Owing to these advantages, the methods of concentration by sorption are successfully used in analytical chemistry.[1] Concentration and separation with the help of chelating sorbents is characterized by a high selectivity and effectiveness which assures an increase in sensitivity and reliability of the subsequent determination of elements by different chemical, physicochemical, and physical methods.[2]

Chelating sorbents, also designated as chelate resins and chelating ion exchangers, have been known for a long time.[3] To synthetize ion exchangers having selective properties with respect to individual ions or groups of ions, certain groups of atoms capable of selectively interacting with the elements are introduced into polymeric matrices. Numerous organic reagents are used for this purpose. These are well-known from the practice of analytical chemistry and are applied to separate, isolate, and determine elements. For instance, chelating sorbents were synthetized with the help of 8-hydroxyquinoline, chromotropic and salicylic acids, pyrogallol, β-diketones, and many other compounds. However, the sorptive properties of sorbents obtained at the early stages of investigations in this field proved to be worse than could have been expected; they had insufficient selectivity and sorptive capacity and a low sorption rate.[3-5]

Vast experience has now been accumulated in the synthesis of chelating sorbents; the characteristic features of their interaction with metal ions during sorption have been studied. Certain progress has been made in the field of polymeric matrices synthesis. All this has made it possible to synthetize chelating sorbents with better characteristics.[2,6]

Numerous chelating sorbents with various chemically active groups fixed on different matrices are known today. Synthetic and natural compounds, mineral carriers, etc., are used as polymeric matrices. Chelating sorbents are obtained in the form of pearls, powders, particles of different shape, films, filters, plates, tubes, catcher, tapes, etc.

The most widely known chelating sorbents are based on polymeric organic matrices. They belong to a wider class of complexing ion exchangers (complexites) whose characteristic feature is the ability to manifest during sorption complexing properties with respect to metal ions. Strictly speaking, chelating sorbents are assumed to form chelate rings in the sorbent phase during the sorption of metals. However, the possibility for such rings to be formed during sorptions on sorbents containing complexing groups depends on numerous factors. In the case of sorbents containing units with groups of atoms capable of chelating, e.g., iminodiacetate, 8-hydroxyquinoline, and other groups, the formation of chelate rings during sorption is more obvious and probable. However, the coordination properties of sorbents and the possibility of chelate rings being formed in the phase of sorbents are radically affected not only by the nature of chemically active groups in the sorbents but also by the physical nature of the polymeric matrix, steric factors, sorption conditions, etc. Chelate rings can be formed with the participation of donor atoms situated in one unit of polymeric matrix, the matrix chain, and nearby complexing groups in the neighboring units of polymeric sorbent. Most likely this is why, in the sorption of metal ions, chelate rings can be formed on numerous complexing sorbents.[7] This may explain the terminological ambiguity existing in the literature. The term frequently used is "chelate resins", which seems to be too narrow, since today, along with the traditional resin-type polymeric matrices, matrices of various other types and structures are used, e.g., cellulose, fibers, etc. The term "chelating sorbents" or "ion exchangers", appears to be broader and more correct.

At present, investigations in the field of the synthesis and application of chelating sorbents are intensively conducted in many countries. New sorbents are synthetized with different functional groups and are based on new polymeric matrices. The properties and structure of sorbents are studied, as well as the sorption mechanism and the processes of element ions complexing in the sorbent phase, new methods are continually developed for the concentration and separation of elements. Every year numerous publications appear dealing with the synthesis, study, and application of chelating sorbents. In spite of all this, chelating sorbents are still insufficiently used in the practice of analytical chemistry. One of the reasons for this may be the complexity of the synthesis of chelating sorbents.

In the present review, an attempt has been made at summing up the data from the literature regarding chelating sorbents and of that which is of interest for analytical chemistry. The principal physicochemical and analytical properties of chelating sorbents are examined, and their fields of application are described. Some practical recommendations are given, as well as examples of their use in inorganic analysis. The main attention is focused on the new promising sorbents, as well as the works of Russian authors who are less known to scientists in other countries. Publications and patents mainly describing the synthesis of chelating complexes are not dealt with in this review.

II. GENERAL CHARACTERISTICS OF CHELATING SORBENTS

The properties of chelating sorbents and their analytical possibilities depend on many factors. The most important characteristic is the nature of chemically active groups capable of forming complexes with the ions of metals in solution. Also essential is the nature of the polymeric matrix, as well as the methods of the synthesis of sorbents.

To characterize the properties of chelating sorbents it is necessary to investigate their acidic and basic properties, complexing capacity, and selectivity with respect to metal ions, depending on conditions, kinetic properties, and possibility of regeneration, etc. All these characteristics are usually taken into account when choosing the chelating sorbents with whose help the elements are supposed to be concentrated or separated.

A. Chelating Groups

The groups taking part in the formation of chelate rings usually include nitrogen, oxygen, and sulfur atoms. Nitrogen can be present in the form of a primary, secondary, or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide, and other groups. Oxygen is usually in the form of phenol, carboxyl, ketone, aldehyde, phosphoryl, and some other groups; sulfur is usually in the form of thiol, thioester, thiocarbamate, and disulfide groups, etc. Such groups can be introduced into the polymeric matrix by means of its chemical transformations or by the synthesis of sorbents with the participation of monomeric ligands.

The introduction of specific complexing groups into the polymeric matrix makes them capable of reacting with metal ions, owing to the coordination bond. Under favorable conditions, chelate rings are formed.

Chelate groups are usually capable of interacting with a large number of elements, but the stability of the formed complexes differs and depends on sorption conditions. This difference is used for selective concentration and separation of elements. At present, chelating sorbents with different groups are known. Table 1 shows examples of chelating groups of sorbents and the elements for which sorption these sorbents have been used.

B. Polymeric Matrices

At present, various polymeric compounds are used as matrices for the synthesis of chelating sorbents: polymers of linear and three-dimensional structure obtained by polycondensation and polymerization, and natural organic polymers, synthetic fibers, etc. Most widely used are sorbents based on copolymers styrene-divinylbenzene. In recent years, cellulose, copolymers based on vinylpyridines, methacrylates, and acrylonitrile, etc., have found an ever increasing use as polymeric matrices.

Polystyrene of linear structure has been used for the synthesis of a number of chelating sorbents, mainly polyazo compounds.[41,42] These sorbents are colored fine-grained products, they have a high sorptive capacity, and good kinetic properties. They are used for selective concentration and separation of elements in the analysis of different substances. For instance, a polystyrene-azoarsenazo sorbent has been synthetized based on polystyrene with a molecular weight of 1000. This sorbent was used in developing methods of concentrating U, Th, REE, Zr, Hf, Nb, Ta, Pa, Am, Cm, and other elements.[41,42,48-52] Based on this matrix, sorbents with PAR,[22] imidazole,[2] azorhodanine,[47] 8-mercaptoquinoline,[2] sulfonitroaminophenol,[24] and other groups[2] have also been synthetized.

Copolymers of styrene with divinylbenzene have been used to synthetize numerous chelating sorbents. Of great practical importance today are styrene copolymers with a macroporous structure, which, distinct from gel structure, provides for better permeability of the matrix, facilitating the synthesis of sorbents based on them and ensuring high kinetic properties.[7] Styrene copolymers with divinylbenzene have been used to synthetize numerous chelating sorbents, including the widely known sorbents with iminodiacetate groups: Chelex 100, Dowex® A-1, and many others.[2,3]

The properties of chelating sorbents obtained with the use of styrene copolymers with divinylbenzene depend on many factors, particularly the properties of the polymeric matrix itself, its structure, degree of cross linkage, etc.[7] The sorptive capacity and selectivity of sorbents based on styrene copolymers depend also on the method of synthesis, type and degree of homogeneity of functional groups introduced into the copolymer, etc. The sorbents based on styrene copolymers are usually characterized by a high stability in acid and alkaline solutions. Along with divinylbenzene, other compounds are also used as cross-linking agents.[7]

In recent years, hydrophilic porous polymers have found an ever-increasing application as polymeric matrices. For instance, a number of sorbents that are of interest for the concentration and separation of elements have been synthetized from macroporous copolymers of glycidyl-methacrylate with ethylene-dimethacrylate (GMA-EDMA); specifically those with iminodiacetate, ethylenediamine, mercapto, and other groups.[53,54] Copolymers of hydroxyethyl-methacrylate with ethylene-dimethacrylate (SPHERON) have been used to obtain sorbents with groups of 8-hydroxyquinoline, salicylic acid, and thiol groups. The sorbents based on this matrix are distinguished by their hydrophility, a high degree of porosity, and large internal surface, which ensures a rapid attainment of equilibrium during sorption[55-62].

Many different types of chelating sorbents have been synthetized based on cellulose,[63,64]

Table 1
CHELATING SORBENT GROUPS FOR SELECTIVE PRECONCENTRATION OF ELEMENTS

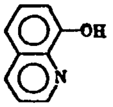
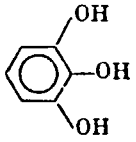
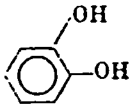
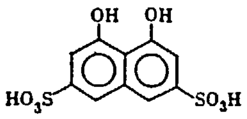
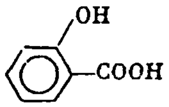
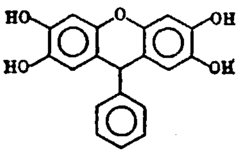
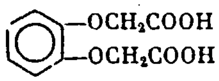
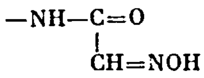
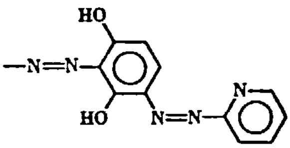
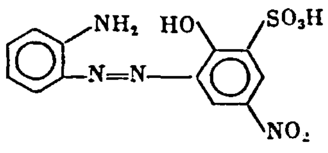
Chelate groups	Elements	Ref.
	Cu,Co,Ni,Mn,Mg,Hg,Al,U	8—10
	B,Be,Mg,Zn,Nb,Ta,Zr,Hf,Bi,U	11—13
	B,Be,Ga,Ge,Sn,Ti,Nb,Mo,W,U	11,12
	Fe,Cu,Zn,Ti	14,15
	Cu,Cd,Co,Ni,Mn,Fe,U	16—18
	Ge	19
	Zr	20
 $-NH-\underset{CH=NOH}{\underset{\mid}{C}}=O$	Pd	21
	Pb,Co,Cu,Pd, rare-earth metals	22,23
	Pd,Pt,Au,Cu	24—27

Table 1 (continued)
CHELATING SORBENT GROUPS FOR SELECTIVE PRECONCENTRATION OF ELEMENTS

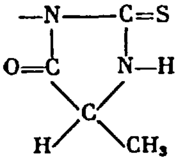
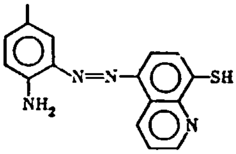
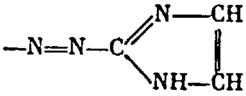
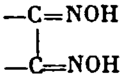
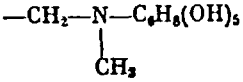
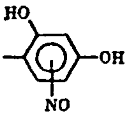
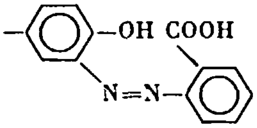
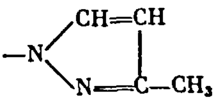
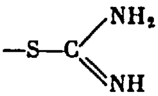
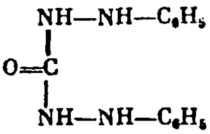
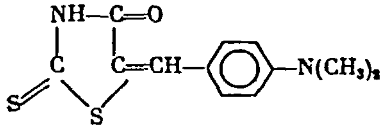
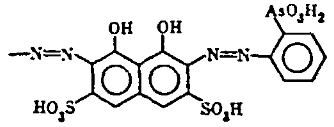
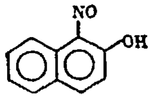
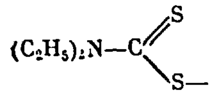
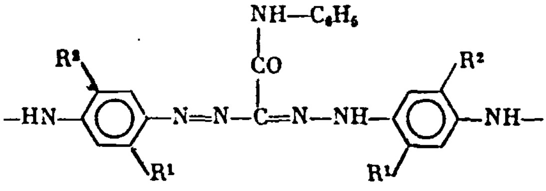
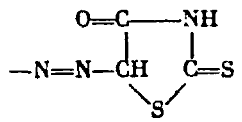
Chelate groups	Elements	Ref.
	Hg	28
	Pd,Pt,Rh,Ir,Ru,Os,Au,Ag	25—27
	Pd,Pt,Rh,Ir,Ru,Os,Au,Ag	2
 $\begin{array}{l}-\mathrm{C{=}NOH}\\ \;\vert\\ -\mathrm{C{=}NOH}\end{array}$	Cu,Cd,Zn,Ni,Pd	3
 $-CH_2-\underset{CH_3}{\underset{\vert}{N}}-C_6H_8(OH)_5$	B	30
	Cu,Co,Fe	31
	Be,Ca,Sr,Fe	32
	Pd,Pt,Rh,Ir,Ru,Os,Au,Ag	33,34
	Pd,Pt,Rh,Ir,Ru,Os,Au,Ag,Hg	35—37
 $\begin{array}{l}NH-NH-C_6H_5\\ \vert\\ O{=}C\\ \vert\\ NH-NH-C_6H_5\end{array}$	Cr	38

Table 1 (continued)
CHELATING SORBENT GROUPS FOR SELECTIVE PRECONCENTRATION OF ELEMENTS

Chelate groups	Elements	Ref.
	Pt,Pd,Os,Au,Ag	12,39,40
	Rare-earth metals, U,Th,Zr,Hf,Nb,Ta,Pa,Am,Cm,Pu	41,42
	Pd,U	43
 $(C_2H_5)_2N{-}C(=S){-}S{-}$	Rare-earth metals,Th,Mo,W,Fe,Cr,Os,Hg	44,45
	Pd,Hg,Ag	46
	Pd,Pt,Rh,Ir,Ru,Au,Ag	25,47

which is a hydrophilic porous polymer with reactive groups. Different kinds of cellulose are used in the synthesis, e.g., "bead", fine-crystalline, and fibrous such as cotton fabrics and paper. The chelating sorbents based on cellulose are characterized by high kinetic properties, they are convenient for sorption and subsequent determination of elements directly in the sorbent phase.[66]

In recent years fibrous sorbents have attracted great interest. Sorbents obtained from fibrous materials have a large surface for contact between solution and sorbent, as well as high kinetic properties, and convenience in handling. Fibrous sorbents are used with special success in concentrating microelements from natural waters.[67-69] Chelating sorbents are synthetized with the help of cellulose[70,71] and synthetic fibers based on polyvinyl alcohol,[72,73] polyacrylonitrile,[69,74] and others.[69,75]

Other polymers are also used as polymeric matrices for the synthesis of chelating sorbents, these include: polyethylene polyamines,[76,77] polyvinyl alcohol,[78] acrylonitrile copolymers,[79] and many other polymers.[80-84] In those cases when the synthesis of sorbents is accomplished with the participation of monomeric ligands, the polymeric matrix is formed in the course of the synthesis of the sorbent itself. Numerous chelating sorbents are obtained in this manner,

Table 2
CHELATING SORBENTS TO BE MADE BY CONDENSATION OF MONOMER CHELATE COMPOUNDS

Monomer compounds	Elements	Ref.
Metha-aminophenol	Pd, Pt	95
Gossipol and gossipol resin	Cu, Co, Ni	96
Macrocyclic compounds	Alkali, alkali-earth, and transition metals	93, 94, 97, 98
2-Mercaptobenzothiazol	Sb, Ni, Hg	2
2-Hydroxyacetophenone	Cu, Co, Zn, Mn, Fe	99
3-Hydroxy-2-naphthoine acid	Ca, Mg, Cu, Co, Zn, Ni	100
8-Hydroxyquinoline	Cu, Co, Zn, Ni, Fe, Al, U, Ca, Mg	8, 9, 101—103
PAR	Cu, Co, Al, Zn, Zr, V, Fe, Ni, U	23
Pyrogallol	B, Be, Zr, Hf, Nb, Ta	11
Pyrocatechol	B, Be, Ga, Sn, Mo, W, Th, U, Sb, Ca, Mg, Cu, Co, Zn, Ni	11, 100
Resacetophenone	Cu, Co, Al, Fe	104
α-Resolcylic acid	Cu, Pb, Ca, Mg	114
Resacetophenoxime	Cu	105
Salicylic acid	Fe, U	18, 106—108
Compounds with N- and P-donor atoms	Co, Ni, Mn, Fe, Hg	109, 110
Tannin	Cu, Cd, Zn, Pb, Hg, Ag	111
α-Furyldioxime	Cu, Cd, Zn, Co, Ni, Pd	112
Chromotropic acid	Ti	113

e.g., by polycondensation of phenols and amines with aldehydes, copolymerization of vinyl compounds with chelating groups, and other methods.[2,3,6]

C. Methods of Synthesis

Principal methods of synthesis of chelating sorbents are polycondensation with the participation of monomeric compounds containing chelating groups and polymer transformations. Also used are copolymerization of vinyl compounds with chelating groups and other techniques. Polycondensation is the simplest method of synthesis of the sorbents. The most widely used method, however, is that of the polymer transformations of prefabricated polymeric matrices. Different matrices are used for this purpose, and the chemical reactions on these matrices make it possible to introduce different chelating groups into the polymers.

The methods used to synthetize sorbents exert a great influence on their properties: sorption capacity, selectivity, stability, kinetic characteristics, etc. The methods of synthesis of the chelating sorbents and the influence of the conditions of synthesis on their properties have been examined in numerous works.[3,7,79,85-87] We shall confine ourselves here to a brief description of the most frequently used methods and some examples.

1. Polycondensation

Chelating sorbents are synthetized with the help of different compounds, especially polyphenols and amines which, when interacting with aldehydes in the presence of catalysts, form polymeric compounds containing chelating groups. Depending on the nature and ratio of the initial components, the condensation results in polymers of linear, branched, or three-dimensional structure. To improve the mechanical properties of polycondensates, the synthesis is often conducted in the presence of a cross-linking agent, e.g., resorcinol, urea, etc.[3,14,86]

Numerous chelating sorbents have been obtained by the polycondensation method. Examples of monomeric ligands used in the synthesis of sorbents are given in Table 2. The shortcomings of sorbents obtained with the help of condensation include: uncertainty of the structure of polymers, insufficient selectivity, slow sorption rate, etc. However, when the condensation is performed in specific conditions, in a hermetically sealed vessel or inside the grains of polymerization polymers, sorbents with better sorptive properties can be obtained. As exemplified by sorbents with 8-hydroxyquinoline groups, it was possible to synthetize sorbents with satisfactory and reproducible characteristics. These sorbents have been used to separate a number of elements.[88,89] The polycondensation method is still being used for the synthesis of new chelating sorbents.[90-94]

2. *Polymer Transformations*

This method is based on the chemical transformations of chemically active groups in polymeric matrices. Such groups are either contained in the polymeric matrix, e.g., in cellulose, or specially introduced into it. For instance, chloromethyl, amino, and other groups are introduced into the polystyrene matrix. Reactive groups of such polymers, when interacting with monomeric compounds, ensure certain chelating groups of being incorporated in the polymer. As a result, the polymer acquires a capability of interacting with the elements by means of complexing, with the polymer matrix not undergoing any substantial changes.

Polymer-like transformations are widely used in the synthesis of chelating sorbents. A large number of well-known sorbents have been obtained with the help of this method. Here, we shall only mention some of the most frequently used methods of synthetizing sorbents by means of polymer-like transformations, using some polymeric matrices as examples.

Sorbents based on polystyrene of linear structure are most often synthetized using its amino-derivative obtained by polystyrene nitration followed by its reduction to aminopolystyrene. Chelating groups are introduced by aminopolystyrene diazotization and coupling the diazo-derivative with various compounds containing chelating groups. This method was used to obtain a number of polyazo compounds applied as chelating sorbents for concentration and separation.[22,41,42] Also used for the synthesis of sorbents was the possibility of azo-coupling aminopolystyrene with diazotized amino compounds, the polymers obtained in this case contain aminoazooxy and other groups capable of interacting selectively with the elements during sorption.[24,25]

Similar reactions are also used to synthetize sorbents based on copolymers styrene-divinylbenzene[14,27,29,92] Also, often used for the synthesis of sorbents based on this matrix are their chloromethylation reactions followed by the interaction of chloromethylate copolymers with different monomeric compounds containing the chelating groups. Chloromethylate styrene copolymers have been used to obtain numerous well-known chelating sorbents, including those with iminodiacetate,[3] dithiocarbamate,[44] thioamide,[36] methylpyrazol,[33,34] and macrocyclic groups.[93,94]

Reactions of chloroacetyl, carboxyl, nitryl, epoxy, and other groups in polymeric matrices are also used for the synthesis of chelating sorbents.[3,14,87] In some rare cases such groups are introduced into monomeric compounds containing chelating groups. The interaction of these compounds with polymeric matrices can also result in chelating sorbents. This kind of method was applied, for example, to synthetize sorbents with 8-hydroxyquinoline groups.[115-116]

In the synthesis of chelating sorbents based on cellulose, the reactivity of its hydroxylic groups is usually utilized. The synthesis of sorbents often starts with obtaining different cellulose derivatives: aminobenzene, tosyl, epoxy, cyanuric cellulose, etc. These derivatives interact with the corresponding monomeric compounds containing chelating groups. In this way, for example, cellulose sorbents were obtained with the groups of iminodiacetic, anthranilic, aminophenylarsonic acids, and others.[64,117-119] Similar reactions are used to synthetize chelating sorbents based on other hydroxyl-containing polymeric matrices, e.g., sephadexes,[82,120,121] polyvinyl alcohol,[82] and others.[122]

Widely used for the synthesis of chelating sorbents are cellulose derivatives containing amino and hydroxyphenyl groups. Cellulose amino-derivatives are diazotized and coupled with various compounds containing chelating groups, e.g., pyrocatechol, pyrogallol, salicylic acid, arsenazo I, etc. Cellulose sorbents with such groups have been studied and are used for different purposes.[2,6,12,64,65] Hydroxyphenyl-derivatives of cellulose have been used for the synthesis of the well-known Hyphan sorbent, applied to determine a number of microelements in natural waters,[123-125] and especially to determine uranium.[126,127]

The sorptive capacity of chelating sorbents obtained by the method of polymer transformations on prefabricated polymeric matrices depends on the nature of the matrix and the degree of the substitution of its reactive groups at all stages of synthesis. Such transformations proceed with a higher effectiveness on polymers of linear structure. For instance, if we take sorbents synthetized on different matrices with the arsenazo groups, the highest sorptive capacity is seen in sorbents based on polymers of linear structure.[2] To synthetize chelating sorbents with a higher capacity, the chelating groups are sometimes introduced into a matrix of a polymer of linear structure; these reactions can often be conducted in aqueous and aqueous-organic solutions. The polymer is then cross-linked to obtain an insoluble sorbent stable in solutions.[79]

In some cases these chelating sorbents are used without cross-linking, and they are usually applied onto the surface of inert carriers, e.g., aluminum oxide[128,129] and others.[130]

3. *Polymerization of Vinyl Compounds Containing Chelating Groups*

This method of synthesis is widely used to produce ion-exchange and complexing sorbents.[3,7,14] An example is vinylpyridine sorbents that have found extensive application.[7,131] The synthesis of these sorbents is accomplished by polymerizing vinyl compounds containing, for example, chelating groups of vinyl-8-hydroxyquinoline[95,132] or imidazazole-carboxylic acids,[133,134] etc.,[3,135] with divinyl compounds. This method of synthesis makes it possible to obtain sorbents of high capacity and a uniform structure of the polymer. In practice, however, it is used comparatively infrequently, which is probably caused by the necessity and difficulty of synthetizing vinyl compounds containing chelating groups.

4. *Other Methods*

The synthesis of sorbents by means of different methods usually results in sorbents with a complex and nonuniform structure. This is associated with the quality of initial products, conditions of synthesis, possible side reactions, etc.[3,7] A more homogeneous structure is characteristic of sorbents of monofunctional nature; however, even in these cases, structural nonuniformity is noted to exist, which affects the sorptive properties, and the selectivity of sorbents among them.[3,136] Sorbents with a more uniform structure, assuring a certain selectivity, are synthetized with the help of special techniques. For example, by cyclopolymerization of certain compounds, sorbents are obtained in which the monomeric ligands and polymers based on them have chelating properties and a homogeneous polymer structure, displaying a very high selectivity.[137,138]

Of special interest are methods of synthetizing sorbents which are designed for particular metal ions. This technique consists of using a linear ligand that exhibits a selectivity for specific ions. The ligand forms a complex and fixate by means of intermolecular cross-linking, resulting in a rigid three-dimensional structure of the polymer. The metal contained in the polymer is washed out, e.g., with the help of an acid; the polymer in this case preserves its ability to sorb predominantly the same metal ion that was used in the synthesis.[139-143] Sorbents of such type, however, are presently not used in the practice of analytical chemistry.

D. Physicochemical Properties

The effectiveness of chelating sorbents and their value for analytical practice are deter-

Table 3
ACIDIC-BASIC PROPERTIES OF SORBENTS WITH IMINODIACETIC GROUPS

Sorbents	pK_{a_1}	pK_{a_2}	pK_{N_1}	pK_{N_2}
ANKB-50	4.8±0.1	9.2±0.2	1.60±0.05	0.17±0.01
ANKB-10	5.8±0.1	8.6±0.2	1.55±0.05	0.15±0.01
Wofatit MC 50	4.2±0.1	9.7±0.2	0.76±0.02	0.42±0.02

mined by the physicochemical properties of the sorbents: acidic, basic, kinetic properties, selectivity, sorptive capacity, and others. These properties depend on the type of functional groups in the sorbent, the nature of matrix, and the conditions of sorption.

1. Acidic and Basic Properties

Chelating sorbents are usually polyfunctional. Along with chelating groups, they also contain ion-exchange groups, e.g., sulfonic groups. The sorptive properties and selectivity of sorbents are affected by the state of all ionogenic groups contained in the polymeric sorbent.[7]

Acidic and basic properties of chelating sorbents are usually characterized by determining the content of chelating groups and the dissociation constants. The data of potentiometric titration are often used for this purpose. Dissociation constants of functional groups are usually calculated from the Henderson-Hasselbach equation. The value of the dissociation constants of functional groups in polymeric sorbents in many cases proves to be sufficiently close to those contained in monomeric ligands.[5,144,145] However, the polymeric nature of sorbents, simultaneous presence of groups of acidic and basic nature, heterogeneity of the polymer, and other factors, can produce a substantial effect on the acidic and basic properties of the sorbent and the values of dissociation constants of the groups contained in it.[3,7,147] Many chelating sorbents are polyampholites. Groups of basic (viz., pyridine and others) and acidic nature (carboxylic, phosphonic, arsonic, etc.) can be present in sorbents with different ratios, depending on the method of synthesis. Separate determination of the dissociation constants of groups in such sorbents encounters certain difficulties. In this case special techniques are applied, e.g., potentiometric titration with the determination of counter ions in the phase of the sorbent.[147] To characterize the acidic and basic properties of sorbents of the polyaminocarboxylic type, the protonation constants of the sorbent groups were determined using an equation accounting for the interaction of all the solution components with the sorbent phase.[148-150]

Dissociation constants of the functional groups in chelating sorbents are given in several publications. As an example, in Table 3 they are given the values of dissociation constants for some single-type sorbents containing imidoacetate groups.[147] It is seen from these data that the values of dissociation constants depend significantly on the matrices and the method of synthesis (ANKB and Wofatit MC 50 sorbents) and the degree of functional groups heterogeneity (ANKB-50 and ANKB-10 monofunctional sorbents).

To establish the acidic and basic properties of polyampholites, other physicochemical methods are also used, e.g., IR spectroscopy and others.[7,151-153]

2. Sorptive Capacity

The ability of a polymeric sorbent to sorb a certain quantity of metal ions from solution is determined by the content of chemically active groups in the sorbent. Chelating sorbents can also contain, along with complexing groups, ion-exchange groups that can also take part in the sorption under certain conditions. Therefore, the total exchange capacity of a sorbent reflects the sorptive possibilities of all the functional groups in the sorbent. In characterizing the chelating groups, the most important parameter is the sorptive capacity, reflecting the interaction of the metal with the sorbent, resulting from complex chelate formation. The sorptive capacity of chelating sorbents is therefore often determined under the conditions when metal sorption is accomplished as a result of complexing.

The sorptive capacity values for different chelating sorbents differ greatly. The theoretical value of sorptive capacity in chelating sorbents must be equivalent to the content of complexing groups. In actual fact, it also depends on the nature of the polymeric matrix, structural peculiarities of sorbent, and sorption conditions. The sorptive capacity of sorbents often proves to be much lower than its theoretical value; this is caused by steric effects when complexing is taking place in the sorbent phase, poor kinetic properties, etc. In other cases, the experimental sorptive capacity value can be higher than the theoretical one, which is explained by the possibility of additional coordination of the metal ion with donor atoms in the sorbent phase, and formation of polynuclear complexes on the solid phase, etc. The value of sorptive capacity can be affected by the state of the functional groups under certain conditions.[2,3,7]

A high sorptive capacity is usually characteristic of chelating sorbents based on linear polymeric matrices, caused by a more complete conversion of active groups at the synthesis stage and a more favorable arrangement of ligand groups for the complexes to be formed in the sorbent phase during sorption. In the case of sorbents with cross-linked structure, the sorptive capacity depends on the way the functional groups are introduced, the matrix structure, degree of cross-linking and flexibility of the polymer skeleton, mutual arrangement of complexing groups, and their location relative to the matrix chain.[7] Highly important is the swelling of sorbents and their kinetic properties. Chelating sorbents based on copolymers of a hydrophilic nature and macroporous structure have a high sorptive capacity.[154]

Chelating sorbents based on cellulose, as a rule, do not have a high sorptive capacity, which is determined by the content of hydroxyl groups in cellulose.

The sorptive capacity of chelating sorbents is expressed in different units: milligrams, grams, millimoles, and milligram-equivalents per gram of sorbent. The values of sorptive capacity for some individual sorbents are given in Section III of this review when describing their analytical characteristics.

3. Complexing Properties and Selectivity

The complexing properties and selectivity of chelating sorbents are determined by the nature of chemically active groups contained in the sorbent. Introduction of certain complexing groups into the polymeric matrix imparts to it the ability to interact with the elements via coordination bonds; this was shown when studying numerous complexing sorbents. With the help of potentiometric, IR, UV, ESR spectroscopy and other methods, the coordination of metal ions with donor atoms in the phase of numerous sorbents was established.[136,155-159] In a number of cases it was shown that during the sorption of metal ions the interaction resulted in the formation of chelate rings.[7,160-165] Theoretical aspects of the coordination chemistry of chelating sorbents have been recently examined.[159]

The complexing processes taking place during the sorption of metal ions by chelating sorbents are usually considered within the framework of the coordination chemistry of low-molecular compounds. Indeed, the complexing capacity of sorbents adheres to the laws governing the behavior of the corresponding monomeric ligands.[7,17,166,167] This analogy is highly useful in the practical sense, and in the synthesis of sorbents and their application for selective sorption of metal ions. At the same time, there exist quite substantial differences in the complexing of macromolecular and low-molecular ligands, which is primarily caused by the polymeric nature of macromolecular ligands and the resulting peculiarities of the interaction with metal ions in solution.[3,7,92,166,168-171]

Table 4
STABILITY CONSTANTS OF METAL COMPLEXES WITH CHELATING GROUPS OF SORBENTS

Sorbents	lgK	Ref.
IDA	9.01 (Cu),7.01 (Ni),6.21 (Zn), 6.11 (Co),2.11 (Mg)	3
ANKB-50	6.4±0.3 (Cu), 5.5±0.3 (Ni)	136
	7.4±0.1 (Ce), 7.2±0.1 (Yb)	136
ANKB-10	6.9±0.1 (Cu), 5.7±0.1 (Ni), 7.04±0.06 (Ce), 6.92±0.05 (Yb)	136
Sorbent with EDTA-groups	18.2 (Cu), 17.1 (Zn), 17.0 (Co), 15.5 (Cd), 9.2 (Ca), 8.8 (Mg), 8.2 (Sr)	173
Sorbent with OXIN-groups	17.6 (Cu), 14.3 (Ni), 14.0 (Zn), 12.5 (Co)	8
	8.49 (Cu), 6.64 (Ni)	170
Polystyreneazo-arsenazo	5.7 (Ca), 8.9 (La)	144

The peculiarity characterizing the complexing of polymeric sorbents with metal ions manifests itself in the composition and stability of the complexes formed in the polymer phase. Most probable for chelating sorbents is the coordination of metal ions with one coordination center of the sorbent. Vacant bonds of the metal are usually filled by the monomeric ligands or the water molecules present in solution.[3,158,172]

The stability of complexes formed in the phase of chelating sorbents is characterized by means of calculating their stability constants. Different methods are used for this purpose.[7] The values of stability constants are approximate, but they are highly useful in estimating the selectivity of sorbents and their analytical potentialities. Also very useful are the indirect methods of assessing the relative stability of complexes formed during sorption; these are pH of decomplexing, the method of competitive ligands, and others.[7,144,172-174]

Stability of the complexes formed by metal ions with the groups of chelating sorbents in a number of cases is lower than that of the corresponding monomeric ligands. The reason for this lies in large energy expenditures needed for the complexing of polymeric sorbents. For instance, such a regularity was established for the sorbents with iminodiacetate and 8-hydroxyquinoline groups.[158,170] In some individual cases, an increase in the strength of complexes was observed, resulting from the interaction with the groups of sorbents, as compared to monomeric compounds, e.g., in the formation of mixed complexes in the phase of the sorbents, and in the cases when the complexing is taking place with the participation of ligands present in solution.[157,158,172] Table 4 shows, as an example, the values of stability constants for the complexes formed by metal ions during sorption on some chelating sorbents.

The difference in the stability of complexes formed in the sorbent phase during sorption is reflected in their selectivity with respect to individual elements. This serves as the basis for selective concentration and separation of elements. A general notion of the selectivity can be obtained from the selectivity series produced on the basis of comparing the sorptive capacity, distribution coefficients, and stability constants, etc. The selectivity of chelating complexes with respect to different ions is quantitatively expressed as the ratio of the distribution coefficients of these ions or their stability constants.[2,7,63]

The selectivity of chelating sorbents depends on the conditions of sorption: pH of solution, concentration and state of metal ions in solution, and presence of salts and ligands in solution. A characteristic feature of chelating sorbents is the preservation of their high selectivity with respect to individual ions in the presence of large quantities of other salts. Generally speaking, the ionic strength of solutions exerts a substantial effect on the complexing processes in sorption with chelating sorbents, since it influences the state of metal ions and the sorbent functional groups, swelling, and other properties of the sorbents. In some cases the effect of ionic strength is so high that changes in the selectivity series are observed.[3,7] On the whole, however, chelating sorbents preserve their selectivity in the presence of salts.[63] This is of great practical importance as chelating sorbents are often used to extract microelements from complex solutions, e.g., to concentrate the traces of elements from natural waters.

The difference in the selectivity of chelating sorbents with respect to metal ions increases in the presence of complexing compounds; this is used in the separation of elements.

4. *Kinetic Properties*

Application of chelating sorbents depends, to a considerable extent, on their kinetic characteristics. If the sorbent is highly selective and has sufficient sorptive capacity but poor kinetic properties, its application for concentration may prove ineffective, especially in the separation of elements.

Kinetic properties of chelating sorbents are mainly determined by the nature and properties of the polymeric matrix. That is why great attention in the synthesis is especially given to the polymeric matrix. Used to an ever increasing extent as polymeric matrices are high-porosity polymers with a well-developed surface and high hydrophilic properties, different copolymers with a macroporous structure, cellulose, fibrous materials, etc. For instance, the time needed for the equilibrium to be reached when the sorption is conducted on sorbents obtained from cellulose and glycolmethacrylate gels amounts to a few minutes,[60,175] while on other sorbents it can reach several hours.

Chelating sorbents are also synthetized with the help of special techniques that make it possible to produce sorbents with improved kinetic properties. For instance, hydrophilic groups are introduced into the polymer[92] and certain conditions are maintained during the synthesis.[79,88]

The kinetic regularities of metal ion sorption by chelating sorbents have been studied to a comparatively small extent. It has been noted that the stage determining the rate of the sorption process on chelating sorbents can be either diffusion[8,162,176,177] or the chemical reaction.[179] This depends on the properties of polymeric sorbent, metal ion, and the sorption conditions. Also possible is a mixed mechanism of sorption and variation of the rate-determining stage of the process when the sorbent is filled with the metal ion.[7,179] Cellulose sorbents are usually characterized by the external diffusion sorption mechanism. It has been noted, however, that the rate of the process can also be determined by the chemical reaction.[63]

The sorption rate is greatly affected by the pH of solution, ionic strength, temperature, and concentration of the sorbed metal ions.[7,63,177]

The kinetic properties of chelating sorbents are characterized by determining the values of effective diffusion coefficients, half-time of exchange (50% sorption), and other parameters. For instance, the internal diffusion coefficients in the sorption of nickel (II) on a sorbent with picoline groups amount to $2.3 \cdot 10^{-7}$ cm^2/sec,[164] of copper (II) on Dowex® A-1 — $1.7 \cdot 10^{-6}$ cm^2/sec, palladium (IV) on polyisothiuronium sorbent — $5.0 \cdot 10^{-6}$ cm^2/sec.[162]

Internal diffusion coefficients in the sorption of copper (II) and silver (I) on a fibrous sorbent with 2 mercaptobenzothiazole groups are $1.3 \cdot 10^{-11}$ and $0.3 \cdot 10^{-11}$ cm^2/sec, respectively.[181] At present, much attention is given to the mathematical description of the kinetics of the absorption of metal ions accompanied by complexing in the sorbent phase. In particular, a numerical solution of a set of corresponding equations has been proposed, and relationships have been obtained to be used in calculating the sorption rates and diffusion coefficients.[182-184] In a number of cases, a satisfactory coincidence of experimental and calculated data has been obtained.[185-186]

When comparing the kinetic properties of different chelating sorbents, one can arrive at the conclusion that the sorbents with the best characteristics are those based on hydrophilic macroporous copolymers and cellulose, as well as fibrous materials.

Sorbents based on synthetic fibers are successfully used for different purposes.[6,187] Recently, a new type of chelating sorbent has been proposed, e.g., fine fibrous materials with a porous structure inside in which very fine particles (up to several microns) of chelating sorbent are located.[68,188] These sorbents have a selectivity corresponding to that of the chelating polymer located inside the fiber, but, distinct from granular sorbents, they have very good kinetic properties; the time needed to reach the equilibrium amounts to a few minutes. The structure of such fibrous material makes its use as filters of different shape possible. For the sorption to be achieved in a dynamic regime, the sorbent layers are placed on one another until the desired height is reached. Sorbents of this kind are especially convenient for concentrating elements from large volumes of solutions, followed by determining the sorbed elements directly on the sorbent. For instance, a fibrous sorbent of this type, POLYORGS XI, has been used to concentrate gold and silver from natural waters.[188]

5. *Other Properties*

Of great importance, when chelating sorbents are used in inorganic analysis, is the chemical and mechanical stability of sorbents, the possibility of their regeneration and repeated use, the form of sorbent (particles, fibers, filters, etc.), and other properties. In some cases sorption and desorption can be conducted at elevated temperatures and in highly radioactive solutions. All this is also important when chelating sorbents are used. These properties mainly depend on the nature and structure of the polymeric matrix. Numerous sorbents, especially those on cross-linked matrices, have a sufficient stability in acid and alkaline solutions and can be used for sorption at heating; repeated use of such sorbents is also possible. Less stable are the sorbents based on cellulose, especially in highly acidic and alkaline solutions;[190-192] polymeric sorbents with a linear structure are partially soluble.[79,126,189] Some sorbents of the formaldehyde resin type have insufficient stability, especially in alkaline solutions.[11,23] Chemical stability of chelating sorbents depends not only on the matrix, but also on the type of chelating groups. Some sorbents have reductive properties, which can cause the precipitation of sorbed metals and worsen the sorptive properties of sorbents.[193] The presence of strong oxidizers in solution can result in irreversible changes in the sorptive capacity and selectivity of chelating sorbents. For instance, considerable changes in sorptive properties were observed when chelating sorbents with iminodiacetate groups were used in nitric acid solutions.[194]

The possibility of regeneration and repeated use of chelating sorbents depends on the nature of chelating groups and the stability of the complexes formed by metal ions in sorbent phase. Also of importance in this case are the peculiarities of the polymeric matrix of the sorbent, a possibility for simultaneous processes to be taking place during sorption and other factors.

In the case of very stable complexes being formed in the sorbent phase, desorption may become altogether impossible or difficult to achieve, e.g., in the sorption of noble metals.[96] That is why chelating sorbents are often used only once, and determinations are performed directly in the sorbent phase.[196,197] In other cases, e.g., when iminodeacetate sorbents are used, the sorbed metals are usually desorbed with acids.[3]

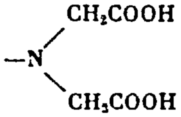
III. ANALYTICAL PROPERTIES OF INDIVIDUAL CHELATING SORBENTS

Different parameters are used to characterize the analytical properties of chelating sorbents. These include the values of total exchange and sorptive capacity for individual metals in specific conditions, selectivity series, separation factors, distribution coefficients, and time to establish equilibrium. The fields of application of these sorbents in analytical chemistry are also usually recommended.

Widely used at present in analytical practice are sorbents with iminoacetate groups. Known today are numerous sorbents of this type synthetized on the basis of various polymeric matrices. Such sorbents as Chelex 100, Dowex® A-1, and Wofatit MC 50 have acquired practical importance. ANKB-10, ANKB-35, ANKB-50, and other sorbents based on styrene copolymers containing imidoacetate groups have also been synthetized and studied.[37,155,198-200] The assortment of chelating sorbents has recently expanded considerably. Numerous new sorbents have appeared which are of interest for analytical applications. Given below are the analytical characteristics of individual chelating sorbents that are already applied in chemical practice or recommended for these purposes. Names and brands, structures of chelating groups, and characteristics of sorbents are given in accordance with the cited works.

Sorbent: Chelex 100

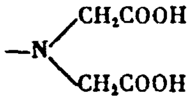
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene. The sorbent is produced as pearls of spherical shape used as granules with a size of 50 to 400 mesh and as filters containing the sorbents fixed on them,[201,202] as well as catcher with the sorbent.[203,204] The sorptive capacity with respect to Cu (II) is 2.9 mg-eq/g. The sorbent is used for group concentration of microelements when they are determined in natural waters.[175,205-212,221] It is also used to determine Cu, Ni, Zn, Pb, and other elements in rocks, ores, and other objects,[213-215] as well as separation of a number of elements.[216-218]

Sorbent: Dowex® A—1

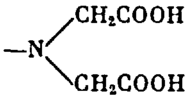
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene. The sorbent is produced as pearls of spherical shape with a size of 50 to 100 mesh. The sorptive capacity with respect to Cu (II) is 2.9 mg-eq/g. Selectivity sequence of the sorbent is Cr (III) > Fe (III) > Pd (II) > Cu (II) > Hg (II) > Ni (II) > Pb (II) > Zn (II) > Co (II) > U (VI) > REE > Ga (III) > Al (III) > Fe (II) > Mn (II) > Ca (II) > Mg (II) > Sr (II) > Ba (II).[3] The sorbent is used to concentrate microimpurities when they are determined, as well as to purify the solutions of salts, acids, alkalis, and other compounds.[3,5,219,220] It is also used to concentrate microelements when they are determined in natural waters[221-224] and rocks,[225,226] as well as used to separate Am and Cm,[227] and for other purposes.[228-230]

Sorbent: Wofatit MC 50

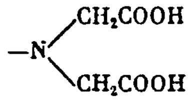
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene. The sorptive capacity of the sorbent with respect to Cu (II) amounts to 0.78 mol/ℓ. The sorbent is used to concentrate heavy metals from natural and sewage waters,[231,232] extract Fe (III) and Ti (IV) from solutions of aluminum salts,[233] concentrate a number of elements when they are determined in tungsten,[234] and separate noble metals from nonnoble ones.[235]

Sorbent: ANKB—50

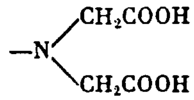
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene. The sorptive capacity of the sorbent with respect to Cu (II) amounts to 3.2 mg-eq/g.[7] Acidic, basic, and sorptive properties of the sorbent have been studied with respect to Cu, Ni, and REE.[136,147,158,198,236,237]

Sorbent: GMA — EDMA — IDAA

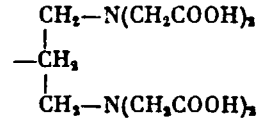
Chelating group:



Polymeric matrix: glycidylmethacrylate-ethylene dimethacrylate copolymers of macroporous structure. The sorbent is manufactured as spherically shaped granules having a particle diameter of 125 to 150 μm and is stable in acidic and alkaline solutions.[155,238] The sorptive capacity (mmol/g) of the sorbent with respect to Cu (II) is 1.15, Fe (III) is 1.14, Co (III) is 1.0, Ag (I) is 1.0, Al (III) is 0.92, Ni (II) is 0.89, U (VI) is 0.88, Mn (II) is 0.87, Zn (II) is 0.79, Pb (II) is 0.78, Rh (III) is 0.15, Pd (II) is 0.16, and Pt (IV) is 0.12. The selectivity series at pH 5 is Cu (II) > Fe (III) > Co (III) > Al (III) > Ni (II) > Mn (II) > Ag (I) > Zn (II) > Pb (II) > U (VI). The amount of time to establish equilibrium in sorption is 20 to 30 min. The sorbent is recommended for the concentration of Ag, Pb, and other elements[155] and the separation of platinum elements.[238,239]

Sorbent with Propylene-Diamine-Tetraacetate Groups

Chelating group:

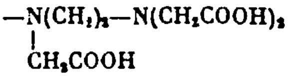


$$\begin{array}{l} \quad CH_2{-}N(CH_2COOH)_2 \\ \quad | \\ {-}CH_2 \\ \quad | \\ \quad CH_2{-}N(CH_2COOH)_2 \end{array}$$

Polymeric matrix: copolymers of styrene with divinylbenzene of macroporous structure. The sorbent is manufactured as light-brown pearls stable in acidic and alkaline solutions at standard conditions. The sorptive capacity of the sorbent amounts to 0.45 to 0.55 mmol/g. The selectivity series is Zr (IV) > Th (IV) > U (VI) > Cu (II) > Bi (III) > Ni (II) > Fe (III) > Zn (II) > Co (II) > Mn (II) > Mg (II). The sorbent is recommended for concentrating microelements from seawater and the separation of elements.[240]

Cellulose Sorbent with EDTA Groups

Chelating group:

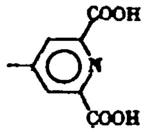


$$\begin{array}{l} {-}N(CH_2)_2{-}N(CH_2COOH)_2 \\ \;| \\ \;CH_2COOH \end{array}$$

Polymeric matrix: "bead" cellulose. The sorbent is used as 0.40 to 0.63 mm granules in swollen state. The sorptive capacity of the sorbent with respect to Cu (II) is 0.90 in static conditions, and 1.01 mmol/g in dynamic conditions. The sorbent is stable in neutral and acid solutions, and in alkaline solutions it is hydrolyzed with a decrease in sorptive capacity. Characterized by good kinetic properties it is recommended for selective concentration of microelements.[190,241]

Sorbent with 2,6-Pyridine-Dicarboxylic Acid Groups

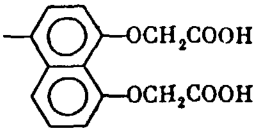
Chelating group:



The sorbents are obtained from polyaminostyrene (sorbent A), polyethyleneimine (sorbent B), and polycondensation with the participation of 2,6-pyridine-dicarboxylic acid (sorbent C),[241,242] all consisting of chemically and mechanically stable particles. The sorptive capacity (mg-eq/g) of the sorbents with respect to Cu (II) is 3.76 (A), 4.91 (B), and 4.50 (C); with respect to Ca (II) it is 3.58 (A), 4.18 (B), and 1.52 (C). The sorbents are recommended for Ca (II) and Sr (II) separation. Most suitable for this purpose is the sorbent obtained from polyethyleneimine (B).[241]

Sorbent with Groups of 1,8-Dihydroxynaphthalene-*O,O*-Diacetic Acid

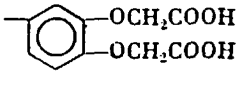
Chelating group:



The sorbent is obtained by the polycondensation of 1,8-dihydroxynaphthalene with formaldehyde with simultaneous partial substitution of hydrogen in OH-groups by acetic acid groups. The sorbent is a fine-grained dark-brown or black product mechanically stable in swollen state. The sorptive capacity of the sorbent with respect to Zr (IV) is 0.5 mmol/g. The sorbent is recommended for Zr (IV) and Hf (IV) separation, as well as the separation of Zr (IV) — U (VI), Zr (IV) — Ti (IV), Zr (IV) — Th (IV), Zr (IV) — Ce (IV), Zr (IV) — Be (II), Zr (IV) — Be (II), Zr (IV) — Pb (II), Zr (IV) — La (III), Zr (IV) — Fe (III) — Mg (II).[243]

Sorbent with Pyrocatechol-*O,O*-Diacetic Acid Groups

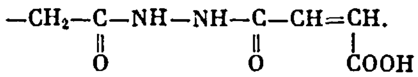
Chelating group:



The sorbent is obtained by the polycondensation of pyrocatechol-*O,O*-diacetic acid with formaldehyde and pyrocatechol, followed by the esterification of OH-groups with monochloroacetic acid. The sorbent is stable in acidic media, and in alkaline media it is colored but mechanically stable. The sorptive capacity of the sorbent depends on the ratio of the initial components. The amounts of sorptive capacity varies with the element, e.g., (mmol/g) with respect to Zr (IV), 1.95 to 4.5, and Cu (II), 1.7 to 2.6 (at pH 5). The sorbent is selective to Zr (IV) and is recommended for the separation of Zr (IV) from Mg, Cu, Ni, Al, Y, La, Ti (IV), U (VI), Fe (III) and also the separation of La (III) — Zr (IV), Ti (IV) — Zr (IV), U (VI) — Zr (IV), Fe (III) — Zr (IV) and Zr (IV) — Nb (V).[20]

Sorbent with Dimaleyl Succinic Dihydrazide Groups

Chelating group:

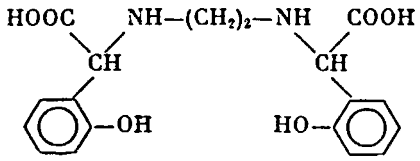


$$-CH_2-\underset{\underset{O}{\|}}{C}-NH-NH-\underset{\underset{O}{\|}}{C}-CH{=}\underset{\underset{COOH}{|}}{CH}.$$

Polymeric matrix: copolymer of styrene with divinylbenzene maleic anhydride. The sorbent is selective with respect to heavy metals in a series of Cu > Ni > Zn > Co > Fe (II) > Mg. The sorptive capacity with respect to Cu (II) is 3.2 mg-eq/g. The sorbent is recommended for selective concentration of heavy metals from solutions containing the salts of alkaline and alkaline-earth metals and for separation.[244]

Sorbent Polystyrene — Chel-1

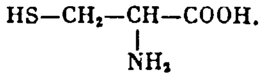
Chelating group:



Polymeric matrix: copolymer of styrene with divinylbenzene (2 or 3%) of gel and macroporous structure. The sorbent is used as 0.1 to 0.2 mm pearls. The sorptive capacity is 1.5 mmol/g.[245] The sorbent is recommended for the separation of Cu — Zn and Cu — Pb at pH 2.5.[39]

Sorbent with Cysteine Groups

Chelating group:

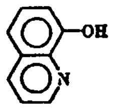


$$HS{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH.$$

Polymeric matrix: polyacrylonitrile copolymer. The sorbent has a high selectivity with respect to Ag, Hg, Au, and Pt. The sorptive capacity (mmol/g) of the sorbent to Ag (I) is 0.97, Hg (II) is 0.65, Au (III) is 1.22, and Pt (II) is 0.39. The sorbent is recommended for selective concentration and separation of these metals,[246] as well as Mo and W.[247]

Sorbents with 8-Hydroxyquinoline Groups

Chelating group:

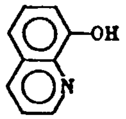


(1) The sorbent is obtained by the polycondensation of 8-hydroxyquinoline and resorcinol with formaldehyde as described in Reference 88, and consists of particles of 22 to 60 mesh size in swollen state. The sorbent is also stable in acidic and alkaline solutions. The sorptive capacity (mmol/g) with respect to Al (III) is 1.1, V (V) is 2.5, W (VI) is 2.7 (pH 4.0); Co (II) is 1.1, Ni (II) is 1.7, Zn (II) is 2.3 (pH 5.4); Cu (II) is 3.6 (pH 5); Fe (III) is 2.0 (pH 3.0); and Zr (IV) is 1.4 (pH 5.4).[88] The sorbent is used to separate pairs of elements, e.g. Cu — Fe, Cu — Ni, Cu — Co, Co — Zn, and other mixtures.[89]

(2) Polymeric matrix: copolymers of styrene with divinylbenzene (7.5%) of macroporous structure. The sorbent consists of brown pearls stable in acid solutions. The total exchange capacity of the sorbents amounts to 3.6 and 2.4 mg-eq/g (depending on the conditions of synthesis). The sorptive capacity of the sorbent with respect to Hg (II) is 3.62 and 1.22 mmol/g in 0.1 *M* HCl and 2.70 and 0.98 mmol/g in 0.1 *M* HNO_3. The sorbents are highly selective to Hg (II) and Cu (II)[10]; similar sorbents have been described in Reference 248. Depending on the method of synthesis, the sorbents are selective to Cu (II) and Hg (II) or only to Hg (II). A similar sorbent is used to concentrate Cd, Zn, Pb, Cu, Fe, Mn, Ni, and Co when they are determined in seawater.[249]

Sorbent: SPHERON OXIN

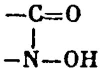
Chelating group:



Polymeric matrix: copolymers of glycolmethacrylate with glycol monomethacrylate of macroporous structure. The sorbent is used as particles of 20 to 63 μm in size. The sorptive capacity (mg/g) of the sorbent with respect to Mn (II) is 4.82, Al (III) is 3.35, Pb (II) is 46.5, Zn (II) is 13.9, Cd (II) is 20.5, Co (II) is 10.1, Ni (II) is 10.7, Fe (III) is 19.7, and Cu (II) is 16.6.[60] The time to establish equilibrium in sorption is 5 to 10 min, with distribution coefficients reaching 10^5. The sorbent is used to concentrate U, Co, Fe, Mn, Ni, and Pb from solutions of salts and for separation.[58,62]

Polyhydroxamic Sorbent

Chelating group:

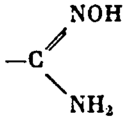


$$\begin{array}{l}-\mathrm{C{=}O}\\ \;\;\,|\\ -\mathrm{N{-}OH}\end{array}$$

Polymeric matrix: copolymers of acrylonitryl-ethylacrylate with divinylbenzene (5%). The sorbent is used as particles of 50 to 100 mesh size. The sorptive capacity (mmol/g) of the sorbent with respect to Cu (II) is 3.0 (pH 4), Au (III) is 4.0 (pH 1), and Ag (I) is 1.2 (pH 1). Quantitative extraction is achieved for Au (III) from 0.5 *M* HNO_3, Ag (I) from 0.05 *M* HNO_3, as well as from neutral solutions. The sorbent is recommended to extract Au and Ag from potassium cyanide solutions and Au from river water.[250]

Polyacrylamide Oxime Sorbent

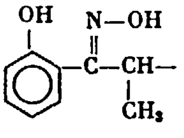
Chelating group:



Polymeric matrix: copolymer of acrylonitrile with divinylbenzene. The sorbent is used as particles of 60 to 80 mesh size. In alkaline solutions the sorbent is brownish-yellow and in acidic solutions it is white. The sorptive capacity of the sorbent (mmol/g, at pH 5) with respect to Ti (IV) is 1.00, V (V) is 0.90, Cr (VI) is 0.84, Mn (II) is 0.13, Co (II) is 0.34, Ni (II) is 0.40, Cu (II) is 1.45, Zn (II) is 0.38, Cd (II) is 0.19, Hg (II) is 1.07, Pb (II) is 0.72, (pH 2) Fe (II) is 0.24, and Fe (III) is 0.75. The sorbent is recommended for the concentration of Fe, Cu, Cd, Pb, and Zn when it is determined in sea and fresh waters[251] and is used to determine Al, Ti, V, Cu, Fe, and Si in extra-high-purity graphite.[252]

Sorbent with Hydroxyoxime Groups

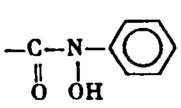
Chelating group:



Polymeric matrix: copolymer of styrene with divinylbenzene of macroporous structure. The sorbent is used as pearls of 250 to 325 mesh size and is selective to Cu (II) at pH > 3.5 and Mo (VI) in 0.1 *N* H_2SO_4. It is recommended for the separation of Cu and Mo from a large number of elements with the exception of Fe (III) and U (VI) and is used to determine copper and molybdenum in alloys with the help of a high-performance chromatograph.[253]

N-Phenylhydroxamic Sorbent

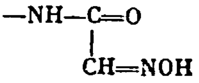
Chelating group:



Polymeric matrix: copolymer of styrene with divinylbenzene of macroporous structure. The sorbent is selective to Nb (V), Mo (VI), Sn (IV), U (VI), Sb (III), Zr (IV), and W (VI) in 2 *M* HCl and selective to Cu at pH 4 and is recommended for the separation of these elements.[254]

Sorbents with Isonitrozoacetamide Groups

Chelating group:

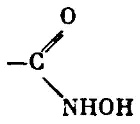


$-\mathrm{NH}-\underset{\substack{|\\ \mathrm{CH{=}NOH}}}{\mathrm{C}}{=}\mathrm{O}$

Polymeric matrices: polycondensate based on metha-aminophenol and formaldehyde and copolymers of styrene with divinylbenzene (2%). The sorptive capacity (mg-eq/g) of the sorbents with respect to Cu (II) is 5 (pH 5.6) and Pd (II) is 4.5 (1 *M* HNO_3). Selectivity of the sorbents decreases in the following series: Pd $\gg$ Hg $\gg$ U (VI) $\gg$ Cu $\gg$ Ag $\gg$ Pb $>$ Fe, Al $>$ Ni $>$ Zn $>$ Co $>$ Ca $>$ Mn $\gg$ Mg. The sorbents are recommended for the separation of Pd from Ag, and Pd from Ni, Cu, and Fe.[21]

Cellulose Fibrous Sorbent with Hydroxamic Groups

Chelating group:

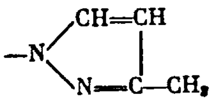


Polymeric matrix: cellulose. The sorbent is stable in neutral and acidic solutions, and soluble in alkaline solutions. The sorptive capacity of the sorbent is 2.13 mg-eq/g and acquires coloration when it interacts with metals such as Fe (III) — reddish brown, Cu (II) — yellowish green, and Au (III) — grey. A noticeable color reaction with the sorbent occurs in the case of the following metals with a concentration of 10 μg in 0.05 mℓ: Ag (I), Al (III), Bi (III), Cd (II), Cr (III), Hg (II), La (III), Mn (III), Mn (II), Ni (II), Pd (II), Sb (III), Th (IV), Ti (III), U (VI), and Zr (IV). The sorbent has the highest selectivity with respect to Fe (III) and is recommended to detect and concentrate elements when they are determined in the environment.[191]

Cellulose sorbent with hydroxamic and amidoximic groups (Komplexit TsG) is recommended for chromatographic separation of a number of cations.[255,275]

Sorbent: PVB-MP

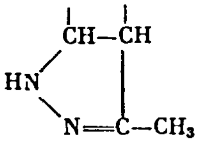
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene (8.12 to 20%) of macroporous structure. The sorbent consists of pearls (0.25 to 0.5 mm) of spherical shape, which are pale yellow in color and stable in acidic and alkaline solutions, when the solutions are heated to ~100°C. The sorptive capacity of the sorbent (with 8% divinylbenzene) with respect to Ag (I) is 263 (0.5 M HNO_3) and Au (III) is 660 mg/g (1 M HCl).[33,34] The sorbent is selective to Pd, Pt, Rh, Ir, Ru, Os, Au, and Ag and is recommended for the concentration of these elements from acidic solutions containing Cu, Ni, Co, Fe, Al, and other elements.[34,257] The sorbent is also used to determine noble metals in copper-nickel ores, industrial solutions, and other products.[196,258-263]

Sorbent: POLYORGS VI

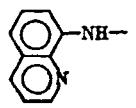
Chelating groups:



Polymeric matrix: polyvinylene fiber. The sorbent consists of brown fibers which are stable in acidic and neutral solutions at temperatures up to ~100°C. The sorptive capacity (mg/g in 1 M HCl) of the sorbent with respect to Pt is 20, Pd is 48, Ir is 30, Au is 219, and Ag is 80 (0.5 M HNO_3). The sorbent is highly selective to noble metals in highly acidic solutions and is recommended for selective concentration of Pd, Pt, Rh, Ir, Ru, Os, Au, and Ag.[264,265] It is also used to determine these elements in complex natural and industrial substances.[257,264]

Sorbent: ChMS-8AQ

Chelating groups:

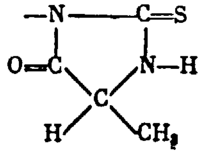


Polymeric matrix: copolymers of styrene with divinylbenzene (8%) of macroporous structure. The sorbent consists of spherical granules (0.25 to 0.5 mm) which are greyish yellow in color and stable in highly acidic solutions. The sorptive capacity (mg/g in 3 M HCl) of the sorbent with respect to Pd (II) is 110 in static conditions, Pd (II) is 20, and Au (III) is 100 in dynamic conditions. The sorbent is selective to Pd, Pt, and Au, it is recommended for selective concentration of these elements, and used to determine Rh in alloys of noble metals.[25,267]

Sorbents with similar groups have been synthetized and studied. They are based on sephadexes[121] and glycidyl methacrylate — ethylene dimethacrylate copolymers.[268]

Sorbent with Thiohydantoinyl Groups

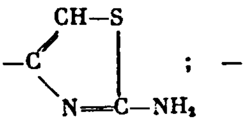
Chelating group:

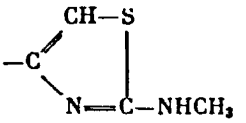


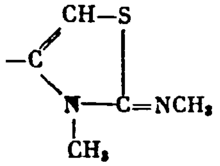
Polymeric matrix: copolymers of styrene with divinylbenzene, of macroporous structure. The sorbent consists of yellow granules and is stable in acidic and alkaline solutions. The sorptive capacity of the sorbent with respect to Hg (II) is 1.9 mmol/g. The selectivity series of the sorbent is Hg (II) > Cu (II) > Cd (II) > Zn (II) > Co (II) > Ni (II) > Mg (II). The sorbent is also recommended for selective concentration of mercury.[28]

Sorbents with Thiazole and Thiazoline Groups

Chelating groups:



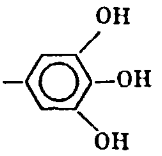




Polymeric matrix: copolymers of styrene with divinylbenzene of macroporous structure. The sorptive capacity of the sorbents with respect to Hg (II) is 1.8 to 2.8 mmol/g (0.1 *M* HCl). The sorbents are highly selective to Hg (II), are stable in acidic and alkaline solutions, and are recommended to concentrate mercury from seawater.[269]

Cellulose Sorbent with Pyrogallol Groups

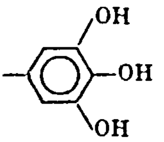
Chelating group:



Polymeric matrix: cellulose. The sorptive capacity of the sorbent is 0.3 mmol/g. The sorbent is selective to U (VI), Cu (II), Zn (II), Fe (III), and Sb (III); Sb (V) is not sorbed. It is also recommended to determine microelements in tap water and to separate Sb (III) and Sb (V).[12,13]

Pyrogallolformaldehyde Resin

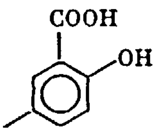
Chelating group:



The sorbent is obtained by polycondensating pyrogallol with formaldehyde in the presence of the acid by the method described in Reference 11. The sorbent constitutes a dark-brown powder, stable in acidic and neutral solutions; in alkaline solutions it is dissolved. The sorbent is also recommended to concentrate Be, Ge, Sn, Zr, Hf, Nb, Ta, Mo, and W[11] and is used to determine these elements in ores, minerals, steels, and natural waters.[270-272]

Cellulose Sorbent with Salicylic Acid Groups

Chelating group:

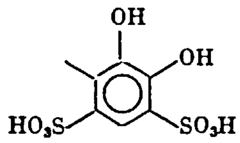


Polymeric matrix: cellulose (fibrous or microcrystalline). The sorptive capacity depends on the method of synthesis and amounts to 0.04 to 0.7 mg-eq/g.[273] The sorbent manifests its highest selectivity to Fe (III) and Th (IV) and is recommended for the concentration of Ag, Sr, Co, Ni, Cu, U, Y, Zn, Fe (III), and Th. It is used to separate Fe (III) and Cu (II) and Cu (II) and Ni (II).[274] In the sorption of microelements, the sorbent acquires coloration which can be used for their determination.[275,276]

Sorbents with similar groups have also been obtained based on copolymers of styrene,[16,277] methacrylate gels,[61] and by polycondensation of salicylic acid with formaldehyde.[18,106-108]

Sorbent: Tiron-Cellulose

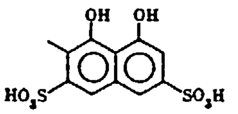
Chelating group:



Polymeric matrix: cellulose (microcrystalline). The sorptive capacity is 0.2 mmol/g. The time for sorption equilibrium is in the order of 3 min.[278] The sorbent is selective to Fe (III), Cu (II), and Hg (II), and it also sorbs alkaline-earth metals with the selectivity decreasing in the following series: Ba (II) > Ca (II) > Sr (II) > Mg (II). The sorbent is recommended to concentrate these metals from solutions of alkali-metal salts.[274] A sorbent with similar groups has been synthetized based on copolymers of styrene with divinylbenzene (3%) of macroporous structure.[245]

Sorbent: Chromotrop-Cellulose

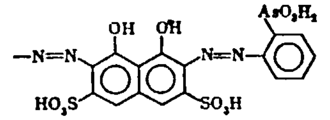
Chelating group:



Polymeric matrix: cellulose. The sorbent is used as filters obtained from 50 mg of sorbent, with a filter diameter of 31 mm. The sorptive capacity of the sorbent is 0.075 mg-eq/g. Equilibrium in sorption of Fe (III) at pH 1.5 is established after 10 sec. The time needed for full concentration by filtering 100 mℓ of solution is 10 min. The sorbent is recommended to concentrate Fe, Cu, Zn, Sr, and other elements from water for subsequent X-ray fluorescent determination directly on the filter.[15]

Sorbent: Polystyreneazoarsenazo (Polyarsenazo)

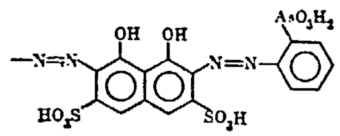
Chelating group:



Polymeric matrix: aminopolystyrene of linear structure. The sorbent is made of fine-grained particles (0.1 mm) stable in acidic and neutral solutions; in alkaline solutions the sorbent is partially soluble.[42] The sorptive capacity (mmol/g) of the sorbent with respect to Cu (II) is 2.1 (pH 5), La (III) is 1 (pH 5), and Zr (IV) is 0.4 (5 *M* HCl)[41]. The sorbent is recommended for selective concentration of U, Th, REE, Zr, Hf, Nb, Ta, Pa, Am, Cm, and other elements.[40-42] It is also used to determine microimpurities in rocks;[48] to concentrate Am and Cm;[52] separate Pa from Fe, U, Zr, Nb, Th, and Po;[51] and to separate La and Ca.[144]

Fibrous Sorbent with Arsenazo Groups

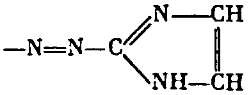
Chelating group:



Polymeric matrix: cellulose fiber. The sorbent consists of black fibers which are stable in acidic and neutral solutions. It manifests selectivity to U, Th, REE, Zr, Hf, and other elements and is recommended for selective concentration of microelements from solutions with a high concentration of the salts of alkalis and alkaline-earth metals. The sorbent is also used to determine uranium in seawater,[70] as well as uranium and thorium in sedimentary rocks.[2]

Sorbent: Polystyreneazoimidazole

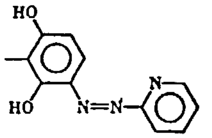
Chelating group:



Polymeric matrix: aminopolystyrene of linear structure. The sorbent is made of dark-red powder which is stable in acidic and alkaline solutions at temperatures up to ~100°C. The sorptive capacity (mg/g in 2 *M* HCl) of the sorbent with respect to Au (III) is 340, Rh (III); Ir (IV), and Ru (IV) is 12.5; Pd (II) is 18.4; and Ag (I) is 107 (0.5 *M* HNO_3). The sorbent is highly selective to noble metals in acidic solutions in the presence of copper, iron, and other elements, and is recommended for selective concentration of noble metals from solutions containing salts of Fe (III) and other nonnoble metals.[2]

Sorbent Polystyreneazo - PAR

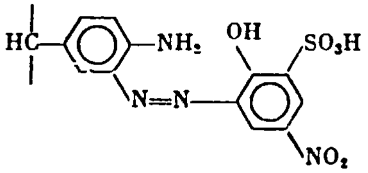
Chelating group:



Polymeric matrix: aminopolystyrene of linear structure. The sorbent is a dark-brown powder which is insoluble in neutral and acidic solutions. The sorptive capacity of the sorbent with respect to Cu (II) is 1.6 (pH 5) and 0.9 mmol/g (pH 2).[22] The sorbent is selective to Cu, Nb, U, and La and is used to concentrate microelements when they are determined in rocks.[36]

Sorbent: Polynitroxaminazo

Polymer unit with chelating group:

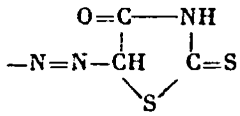


Polymeric matrix: aminopolystyrene of linear structure. The sorbent is a dark-brown powder which is insoluble in neutral and acidic solutions. The sorptive capacity of the sorbent with respect to Pd (II) is 94 mg/g (10 *N* H_2SO_4). The sorbent is recommended for the separation of Pd and Au from Rh and Ir and is used to determine rhodium in metallic palladium.[24]

A chelating sorbent with similar groups, based on the polymeric matrix consisting of copolymer of styrene with divinylbenzene (8%) of macroporous structure, is selective to copper in the presence of Fe (III) and other elements in acidic solutions (pH 1 to 2). The sorptive capacity of the sorbent with respect to Cu (II) (0.1 *N* H_2SO_4) is 32 (in static) and 20 mg/g (in dynamic conditions). The sorbent is recommended for selective concentration of copper.[27]

Sorbent: Polystyreneazorhodanine

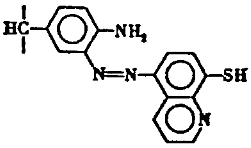
Chelating group:



Polymeric matrix: aminopolystyrene of linear structure. The sorbent is a yellow powder which is stable in acidic and neutral solutions at temperatures up to ~100°C. The sorptive capacity (mg/g) of the sorbent with respect to Pt (II) is 19.5, Pd (II) is 22.0, and Au (III) is 197 (1 *M* HCl).[47] The sorbent has selective properties with respect to noble metals in the presence of Fe, Ni, Co, Cu, and other elements,[29] and is used to determine noble metals in natural materials.[47]

Sorbent Polythioxine (Polystyrene Azo-8-Mercaptoquinoline)

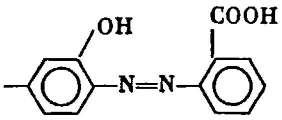
Chelating group: (possible structure)



Polymeric matrix: aminopolystyrene of linear structure. The sorbent is a dark-brown powder which is stable in acidic and neutral solutions. The sorptive capacity of the sorbent with respect to Pd (II) in 1 *N* HCl is 300 mg/g. The sorbent is selective to noble metals in acid solutions in the presence of Cu, Ni, Co, Fe, and other elements, and is recommended for selective concentration of Pd, Pt, Rh, Ir, Au, and Ag.[2,125]

Sorbent with Groups of $\overset{\approx}{O}$-(2-Hydroxyphenylazo) Benzoic Acid

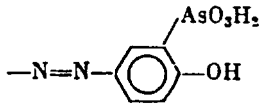
Chelating group:



Polymeric matrix: copolymer of 4-hydroxypolystyrene with divinylbenzene (3%). Used as pearls of 100 to 200 mesh size. The sorptive capacity is 3.2 mmol/g. The sorbent is selective to Fe (III) and alkaline-earth metals and is recommended for selective concentration of iron and for K — Ca, Ca — Sr, Be — Al separation.[32,279,280]

Sorbent Polystyrene Azo-$\overset{\approx}{O}$-Hydroxyphenylarsonic Acid

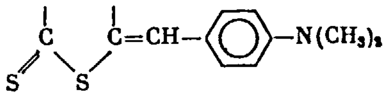
Chelating group:



Polymeric matrix: aminopolystyrene of linear structure. The sorbent is a yellow powder which is stable in neutral and acidic solutions. Total exchange capacity with respect to KOH is 2.8 mg-eq/g. The sorbent is selective to tantalum in the presence of niobium in 10 *M* H_2SO_4 and is recommended for concentration and separation of microquantities of tantalum from niobium.[50]

Sorbent: Polystyrene — DMBAR

Chelating group:



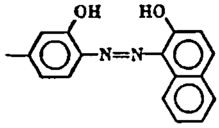
Polymeric matrix: copolymer of styrene with divinylbenzene (2 and 3%) of gel and macroporous structure. The sorbent is used as 0.1 to 0.2 mm pearls and the sorptive capacity is

1.4 mmol/g.[245] The sorbent is recommended for Ag — Cu, Ag — Pb, Hg — Zn, and Hg — Cd separation at pH 2.[39]

Sorbents with similar groups have been obtained based on cellulose.[12,40]

Sorbent: Hyphan — Cellulose

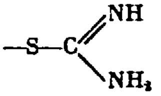
Chelating group:



Polymeric matrix: cellulose (fine-crystalline, "bead", fibrous, cotton fabric). In H^+-form the sorbent is bright red. The sorptive capacity of the sorbent is 0.3 to 1.0 mmol/g (depending on the type of cellulose).[63] The sorbent is recommended for selective concentration of Co, Cr, Cd, Cu, Fe, Hg, Mn, Mo, Ni, Pb, U, and Zn from solutions of alkaline and alkaline-earth metals and is used to determine these elements in river, sea, drinking and mineral waters,[123-126] as well as solutions of salts.[276]

Sorbent: SRAFION NMRR

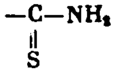
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene (2%). The sorbent is made of pale-yellow pearls. The sorptive capacity (g/ℓ at pH 0.5) of the sorbent with respect to Au (III) is 150, Pt is 65, Pd is 58, Ir is 25, and Rh is 25.[35,284] The sorbent is selective to noble metals and mercury and is used for group concentration of noble metals when they are determined in rocks, ores, meteorites, lunar soil, steels, and biological substances.[283-285,287,288] Also used as disks and filters,[213,289] the sorbent finds application in determining Mo[286] and Cu[45] and purifying solutions from Hg.[37] A sorbent with similar chelating groups has been synthetized based on copolymers of styrene with divinylbenzene of macroporous structure.[36,290]

Sorbent: Mtilon T

Chelating group:

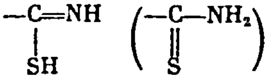


$$-\underset{\underset{S}{\|}}{C}-NH_2$$

Polymeric matrix: copolymer of cellulose with acrylonitrile of fibrous structure. The sorbent is made of yellow fibers which are stable in acidic (up to 1 *M* HCl) and neutral solutions. It manifests selectivity to noble metals and mercury in acid solutions. The sorptive capacity (mg/g in 1 *N* HCl) of the sorbent with respect to Pt is 97.5, Pd is 93.0, Rh is 20.0, and Ir is 72.5. The sorbent is recommended for selective concentration of noble metals and mercury, and is used to determine Pt, Pd, Rh, Ir, Ru, and Au in different objects.[192,291,292]

Sorbent PVA Fiber with Thioamide Groups

Chelating group:



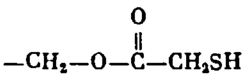
$$-\underset{\underset{SH}{|}}{C}{=}NH \quad \left(-\underset{\underset{S}{\|}}{C}-NH_2\right)$$

Polymeric matrix: copolymer of polyvinyl alcohol with acrylonitrile of fibrous structure.

The sorbent consists of golden-brown fibers which are stable in highly acidic solutions. The sorptive capacity of the sorbent with respect to Pd (II) in 2 *N* HCl is 1.5 mg-eq. The selectivity of the sorbent decreases in the following series: Pd (II) > Pt (II) > Ru (III) > Ir (IV) > Rh (III). The sorbent is recommended for selective concentration of the metals of platinum group from solutions with a high salt background and for the separation of Pt (II) and Rh (III)[72,293-295] and is used in analysis of alloys.[72]

Sorbents with Thioglycolate Groups

Chelating group:



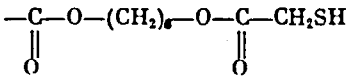
$$-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2SH$$

Polymeric matrix: copolymers of styrene with divinylbenzene of macroporous structure. The sorbent is used as pearls with a size of 150 to 200 mesh. The sorptive capacity of the sorbent with respect to Ag (I) is 1.39 to 1.77 mmol/g. The sorbent is stable in acidic solutions and is less stable at high pH and in the presence of oxidizers and Cu (II) salts. It exhibits the highest affinity to Hg (II), and in 0.1 *M* $HClO_4$ it sorbs Ag (I), Hg (II), Bi (III), Sn (IV), and Au (III), at pH 4 — Mg, Ca, Ba, Zn, Cd, Pb, Ni, Mn, Co, Cu, Fe (II), U (VI), La, and Th. The sorbent is also recommended to separate Pb — Bi — Hg; Sn, As — Sb; and Zn — Cd — Pb mixtures.[193]

A sorbent with similar groups, based on macroporous copolymers of acrylonitrile with divinylbenzene, is highly selective to Ag (I), Hg (II), Au (III), and Bi (III). A sorbent based on saccharose methacrylate gels with thioglycolate groups is selective to Ag (I) and Hg (II).[296]

Sorbent with Hexylthioglycolate Groups

Chelating group:

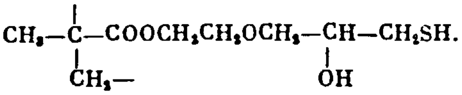


$$-\underset{\underset{\displaystyle O}{\|}}{C}-O-(CH_2)_6-O-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2SH$$

Polymeric matrix: copolymer of styrene with divinylbenzene of macroporous structure. The sorptive capacity (mmol/g) of the sorbent with respect to Ag (I) is 1.93, Hg (II) is 0.99, and Bi (III) is 0.75. The sorbent is highly selective to Ag, Hg, Bi, Au and is recommneded for the separation of these elements.[297]

Sorbent: SPHERON TIOL

Polymer unit with chelating group:

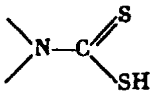


$$CH_3-\underset{\underset{\displaystyle CH_2-}{|}}{\overset{|}{C}}-COOCH_2CH_2OCH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2SH.$$

Polymeric matrix: copolymer of glycolmethacrylate with glycolmonomethacrylate of macroporous structure. Used as 40 to 63 m particles. The sorptive capacity of the sorbent with respect to Hg (II) is 0.5 to 1.0 mmol/g in 0.05 *M* HCl. The sorbent is highly selective to Hg, Sb, Bi, As, Ag, Cu, and Pt in highly acidic solutions (1 to 3 *M* H_2SO_4 or HCl). It is used for selective concentration of Hg, As, Sb, and Bi, as well as to determine them with the help of the atomic absorption method by introducing the sorbent suspension into the graphite atomizer.[56,57,59]

Sorbents with Dithiocarbaminate Groups

Chelating group:

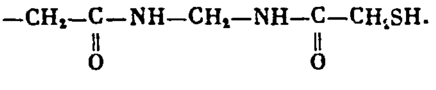


(1) Polymeric matrix: microcrystalline cellulose. The sorbent is stable in acid solutions. Its sorptive capacity (mg/g) with respect to Hg (II) is 370 (pH 4.3), Cr (VI) is 155 (pH 2.6), Ag (I) is 120 (pH 5.2), Se (IV) is 86 (pH 3.2), Cu (II) is 15 (pH 5.4), and Pb (II) is 9.5 (pH 5.9). The sorbent is also recommended for selective concentration of metals from water solutions.[298]

(2) Polymeric matrix: polyamines. The sorptive capacity of the sorbent (mg/g) with respect to Ag is 200, Hg is 54, Cu is 21, Sb is 4, Pb is 3.9, and Cd is 1. Selectivity of the sorbent decreases in the following series: Ag > Hg > Cu > Sb > Pb > Cd > Ni > Zn > Co[299] and is recommended for the concentration of heavy metals.[300,301]

Sorbent: (Poly[*N*-Acryloylaminomethyl] Mercaptoacetamide)

Polymer unit with chelating group:

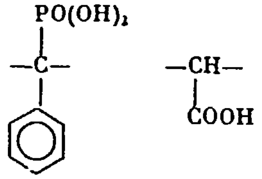


$$-CH_2-\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\underset{\underset{O}{\|}}{C}-CH_2SH.$$

Polymeric matrix: polyacrylamide. The sorptive capacity of the sorbent (mg/g) at pH 5.5 with respect to Mn (II) is 8.8, Fe (II) is 33, Co (II) is 41, Ni (II) is 67.5, Cu (II) is 82.5, Zn (II) is 111, Ag (I) is 421, Cd (II) is 146, Hg (II) is 602, Pb (II) is 342, and U (VI) is 300. The sorbent is oxidized during the sorption of Cu (II), Ag (I), and Hg (II); its selectivity corresponds to the series: Zn < Cd < Pb < Cu < Hg; and it is recommended to concentrate heavy metals.[302,303]

Sorbents with Phosphonic Acid Groups

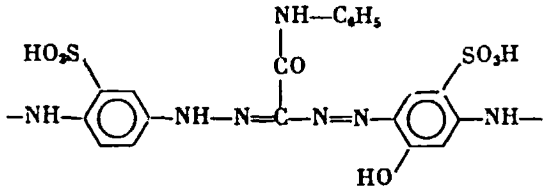
Chelating group:



Polymeric matrix: copolymers of α-phenylvinylphosphonic acid with acrylic acid. The sorptive capacity of the sorbents is 5.7 mg-eq/g. Their selectivity decreases in the series: Th (IV) > Sc (III) > Fe (III) > U (IV) > Me (II). The sorbent is recommended for Fe — Co; Fe — Ni; Zn, Cd, Cu — U; Cu, Cd, Zn — REE, Sc; REE — Th, Sc separation.[304]

Sorbent with Formazane Groups

Chelating group:

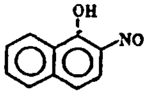


Polymeric matrix: copolymers of styrene with divinylbenzene of macroporous structure. The sorptive capacity of the sorbent (mmol/g in 0.01 *M* HCl) with respect to Ru (III) is 0.03, Rh (III) is 0.1, Pd (II) is 0.75, Ir (IV) is 0.43, Pt (II,IV) is 0.54, Au (III) is 0.90 (0.1 *N* HCl), Ag (I) is 0.92 (0.01 *N* H_2SO_4), Hg (II) is 0.63, U (VI) is 0.61 (acetate buffer). The sorbent is highly selective to Hg, Pd, Ag, and other noble metals and is recommended for the separation of Pd from Co and Ni.[46]

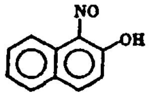
Sorbents with similar groups have been obtained based on cellulose[46,306] and saccharosomethylacrylate gels.[122]

Sorbents with 1-Nitrozo-2-Naphthol and 2-Nitrozo-1-Naphthol Groups

Chelating groups:



I

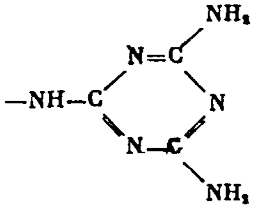


II

Polymeric matrix: copolymer of styrene with divinylbenzene (8%) of macroporous structure. The sorptive capacity of the sorbent with chelating group I with respect to Pd (II) is 0.67 mmol/g in 1 *M* HCl and is recommended for the separation of U and Pd from Cr, Mn, Co, Fe, Ni, Cu, Zn, Cd, Hg, and Al.[43] The chelating sorbent with group II is characterized by stability in acidic and alkaline solutions and is recommended for Pd (II) — Pt (IV); Pd (II) — Ag (I), Pb (II); and U (VI) — V (V) separation and extraction of microelements from seawater.[307]

Sorbent with 2,4,6-Triamino-1,3,5-Triazine Groups

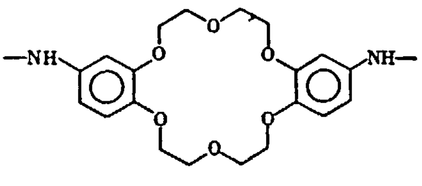
Chelating group:



Polymeric matrix: copolymer of styrene with divinylbenzene (3%). The sorbent is used as pearls with a size of 0.08 to 0.20 mm and is selective to Cu (II), Hg (II), Cd (II), and Ag (I). The sorbent also sorbs SO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, and CrO_4^{2-} anions.[308]

Sorbents with Diaminodibenzo-18-Crown-6 Groups

Chelating group:

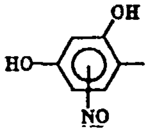


Polymeric matrices: polyamide isophthalic acid I[309,310] and cellulose II.[311] The sorbent with matrix I is used as particles of 200 to 400 mesh size. The sorptive capacity of the sorbent is 1.92 mg-eq/g. The sorbent is selective to potassium and is recommended for selective concentration of potassium, e.g., from seawater and for the separation of potassium and sodium.[309,310]

The sorbent with matrix II has the sorptive capacity of 0.25 mmol/g. Its selectivity in aqueous solutions of iodides decreases in the series: K > Na > Ba > Zn > Ca, and in 50% methanol — Ba > K > Na > Ca > Zn. No significant difference in selectivity is observed.[311] Sorbents with similar groups have been described in Reference 312.

Sorbent with Nitrozoresorcinol Groups

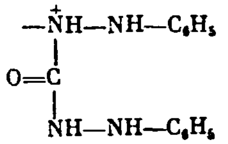
Chelating group:



Polymeric matrix: copolymers of styrene with divinylbenzene (7%). The sorbent consists of brown pearls with a size of 35 to 100 mesh. The total exchange capacity of the sorbent is 7 mg-eq/g. The sorbent manifests affinity to Fe, Cu, Co, Hg, Ni, Zn, Cd, and Mn; and it is the most selective to Cu and Fe. The sorbent is also recommended for concentrating cobalt from seawater and separating cobalt and iron.[31]

Sorbent with Diphenylcarbazide Groups

Chelating group:

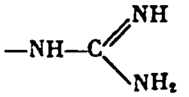


$$\begin{array}{l} \quad -\overset{+}{N}H-NH-C_6H_5 \\ \quad\ \ | \\ O=C \\ \quad\ \ | \\ \quad NH-NH-C_6H_5 \end{array}$$

Polymeric matrix: copolymers of styrene with divinylbenzene (6%) of macroporous structure. The sorptive capacity of the sorbent with respect to Cr (VI) at pH 1 is 12.85 mg/mℓ in dynamic conditions. It reduces Cr (VI) to Cr (III), and when the sorbent is regenerated it is eluted with Cr (III). The sorbent is also recommended for selective concentration of chromium.[38]

Guanidine Sorbent

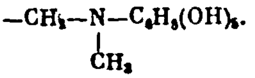
Chelating group:



Polymeric matrix: copolymer of styrene with divinylbenzene (2%). The sorbent is used as 10 to 30 μm pearls, it manifests affinity to Pd (II) and Pt (II) and is recommended for the separation of Pd from Pt.[313]

Sorbent with *N*-Methylglucamine Groups

Chelating group:

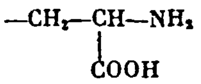


$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-C_6H_8(OH)_5.$$

Polymeric matrix: copolymer of styrene with divinylbenzene. The sorptive capacity of the sorbent with respect to boron is 1.35 mg-eq/g. The sorbent is recommended for boron concentration from neutral and alkaline solutions.[30,314]

Sorbent with Phenylalanine Groups

Chelating group:

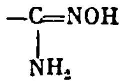


$$-CH_2-\underset{\displaystyle COOH}{\underset{|}{CH}}-NH_2$$

Polymeric matrix: copolymers of styrene with divinylbenzene (7.5%) of macroporous structure. The sorbent is used as 60 to 100 mesh pearls and is stable in acidic and alkaline solutions. The sorptive capacity of the sorbent with respect to Cu (II) is 1.4 (at pH 4) and 1.7 mmol/g (at pH 7). It is highly selective to copper and mercury and is used to concentrate copper when it is determined in seawater and to separate Cu — Co and Cu — Ni.[315]

Sorbent: POLYORGS VII

Chelating group:



$$-\underset{\displaystyle NH_2}{\underset{|}{C}}=NOH$$

Polymeric matrix: polyacrylnitrile fiber. The sorbent is a yellow fiber and is selective to heavy metals in the presence of alkaline and alkaline-earth metals. In highly acidic solutions it selectively sorbs noble metals. The sorptive capacity (mg/g) with respect to Au (III) is 144, Pt (IV) is 188, Pd (II) is 130, Ir (IV) is 45 in 1 *M* HCl, Ag (I) is 148 in 0.5 HNO_3, Cu (II) is 144 (pH 3.6), Co (II) is 150 (pH 6.6), Fe (III) is 160 (pH 1.9), Cd (II) is 103 (pH 6.3), Cr (III) is 31 (pH 3.7), Pb (II) is 425 (pH 3.0), and V (IV) is 50 (pH 2.8). The sorbent is recommended for sorptive concentration of heavy metals when they are determined in natural and waste waters and to determine noble metals in industrial products.[68]

Sorbent: POLYORGS IX

Chelating group: $-CH_2-SH$

Polymeric matrix: polyaminophenolic condensate. The sorbent is a brown powder, and its sorptive capacity (mg/g) with respect to Ag (I) is 638 (0.5 *M* HNO_3); Au (III) is 210, Pd (II) is 44, Pt (IV) is 93, Sb (III) is 40, and As (III) is 37 (1 *M* CHl); The sorbent is recommended for the concentration of Sb (III), (V), and As (III), and (V) in natural waters.[197]

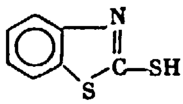
Sorbent: POLYORGS XI

Chelating group: $-N= \quad -NH$

The sorbent is a white laminate fibrous material stable in highly acidic, neutral, and weakly alkaline solutions. The filament thickness is 30 to 40 μm and its particle size is 5 to 10 μm. The total exchange capacity with respect to HCl is 2.14 mg-eq/g. The sorbent is selective to noble metals and its sorptive capacity (mg/g) with respect to Pd (II) is 170, Pt (IV) is 200, Rh (III) is 150, Ir (IV) is 280, and Au (III) is 990 in 1 *M* HCl. The sorbent is also recommended for concentrating noble metals from acid solutions as well as Au and Ag from seawater.[188]

Sorbent: POLYORGS XII

Chelating group:

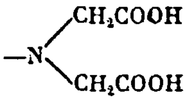


Polymeric matrix: polyaryl-amide fiber. The sorbent is a black fiber which is stable in acidic and alkaline solutions. The sorptive capacity (mg/g) with respect to Ag (I) is 355 (0.5 *M* HNO_3); Au (III) is 630 (1 *M* HCl); Hg (II) is 542 (0.1 *M* HNO_3); and Cu (II) is 76 (0.5 *M*

NaCl, pH ~ 5). The sorbent is recommended for the concentration of Au and Ag, as well as other metals from natural waters.[68]

IDA — Cellulose Filters

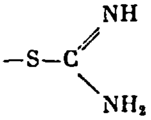
Chelating group:



Polymeric matrix: Watman 41 cellulose filters, diameter 47 cm, weight 0.16 g. The sorptive capacity (μmol/g) with respect to Cd (II) and Co (II) is 171; Cu (II) is 202; Ni (II) is 184; Zn (II) is 157 at pH 3; Pb (II) is 218 (pH 5); and Hg (II) is 88 (pH 9). The sorbent is recommended for concentrating these metals from natural waters.[319]

Sorbent: MONIVEX

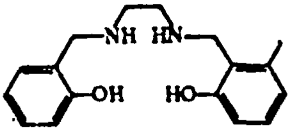
Chelating group:



Polymeric matrix: macroporous styrene divinylbenzene. The sorbent is selective to noble metals in 2 to 6 *M* HCl. The sorptive capacity (mg/g) in 1 *M* HCl with respect to Pt (II) is 309, Pd (II) is 185.5, Au (III) is 566, Ru (IV) is 112.8, Rh (III) is 97, and Ir (IV) is 185.5. The sorbent is recommended for selective concentration of platinum-group metals from hydrochloric acid solutions.[36]

Sorbent with *N,N'*-Bis(2-Hydroxybenzyl)-Ethylenediamine Groups

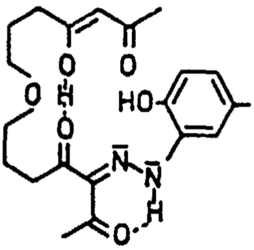
Chelating group:



Polymeric matrix: copolymer styrene divinylbenzene (2%) of porous structure. The sorbent is selective to Au (III) in acidic and alkaline solutions and to Pd (II) and Pt (IV) in the region of pH 3 to 5. Its selectivity series in the acidic solution is Au (III) > Pd (II) ≈ Pt (IV) > Cu (II) ≈ Ni (II); and in the alkaline solution it is Au (III) > Cu (II) ≈ Ni (II) > Pd (II) ≈ Pt (IV). The sorbent can be used to separate Au, Pd, and Pt from Cu and Ni.[316]

Sorbent with Groups of 8-Oxo-2,4,12,14-Tetraoxopentadecane

Chelating group:



Polymeric matrix: cellulose. The sorptive capacity with respect to Fe (III) is 1 mmol/g (pH 2.2). The sorbent is selective to U, Cu, Fe, and Ni in aqueous solutions and seawater-like model solutions.[317]

IV. USE OF CHELATING SORBENTS IN INORGANIC ANALYSIS

A. Application

In analytical chemistry, chelating sorbents are mainly used for selective concentration and separation of elements during the stages of analysis preceding the identification of elements by different methods. Preconcentration is necessary to enable element determination in various natural or industrial objects.[1,65] Sorption with chelating sorbents is very promising in this respect. A high effectiveness and selectivity of the extraction of microelements from solutions of complex composition, simple implementation, and possibility of extracting elements from large volumes of solution in combination with different identification methods, make it possible to use these methods for various analytical applications.[2,3,67,195]

Chelating sorbents are effectively used for the separation of elements, including those very similar in properties, which is highly important for their reliable and accurate determination.

Chelating sorbents are also used to remove traces of elements from salt, acid, alkali solutions, complexing agents, and organic solvents, which is of great practical importance in analysis.[3,37,320]

1. Selective Concentration

The possibility of selective sorption of certain elements in the presence of others is based on the different stability of complexes formed by the element ions with the chelating groups of the sorbent. Normally, chelating sorbents can react with a large variety of elements, but the stability of the resultant complexes differs and depends on the experimental conditions. The stronger the bond between the elements of interest and the sorbent groups, the more selective is the concentration method. By choosing an appropriate sorbent with the specific chelating groups and the optimum sorption conditions, one can obtain the required selectivity with respect to a certain element or a group of elements. For instance, the polystyrene-azoarsenazo can be used to concentrate numerous metal groups, resulting in their separation from alkaline and alkaline-earth metals at pH $\sim$ 6.[48] In highly acidic solutions the same sorbent is used for selective concentration of U, Th, Pa, Am, Cm, and other elements.[41,42] Selectivity in concentration can be improved by optimizing the temperature and adding masking compounds, etc.[2,3] A high selectivity is reached by combining sorptive concentration by means of chelating sorbents with other concentration methods, e.g., coprecipitation,[262] extraction,[321,322] and fire assaying.[258,259]

2. Separation of Elements

The difference in the selectivity of chelating sorbents with respect to certain element ions is used for their separation. Sorbent selectivity is determined by the nature of chelating groups and depends on the experimental conditions. Under specific conditions the sorptive capacity of sorbents with respect to certain ions can differ substantially; the distribution coefficients may vary within several orders of magnitude. In such cases the elements can be separated by means of selective sorption of one or several of them. For instance, separation of copper (II) and iron (III) can be effected by sorption of copper with a sorbent containing aminoazohydroxy groups;[27] and separation of silver (I), gold (III), and mercury (II) from other elements by sorption on the polystyrene-DMBAR sorbent.[39]

Effectiveness of separation by means of chelating sorbents also depends on the physicochemical properties of the polymeric matrices and largely on their kinetic characteristics.[63,171]

Elements exhibiting a high affinity to the chelating groups of sorbent can be separated by successive elution of sorbed metals with acids and complexing agents. Numerous element mixtures can be separated by this technique owing to the different stability of complexes formed by the metal ions in the sorbent phase. Useful for this purpose are, e.g., sorbents containing iminodiacetate,[3] 8-hydroxyquinoline,[89] hydroxame,[250,324-326] and other groups.[2,6,323,327] In the presence of complexing agents, the difference in the strength of metal bonding to sorbent groups increases. This fact is of high practical importance, but is utilized comparatively infrequently. This is probably associated with the specific complexing behavior of elements during sorption, caused by the polymeric nature of the sorbent matrix, heterogeneity of functional groups, and other factors.[3,7,327]

Separation of elements with similar properties is a difficult problem. It has been possible, however, to synthetize sorbents suitable for separation by using ligands which have different complexing activity with respect to similar elements. For instance, a sorbent containing 1,8-dihydroxynaphthalene-*O,O*-diacetic acid groups was synthesized for the separation of zirconium and hafnium;[234] and a sorbent containing pyridine-2,6-dicarboxylic acid groups was synthesized for the separation of calcium and strontium.[241]

B. Some Aspects of the Application of Chelating Sorbents

Chelating sorbents are finding an ever increasing application in practical analytical chemistry. Sorptive concentration has been found to be particularly useful in determining the microelements in natural water, ores, minerals, and pure substances. Chelating sorbents have been effectively used to determine rare and noble metals in various objects.[2,6,195,257]

Numerous element concentration and separation methods using chelating sorbents have now been developed. The procedures involved are rather simple and similar to those employed with other types of sorbents. They have some specific features, however, which may have a considerable influence on the effectiveness of chelating sorbents. For instance, the choice of the type of sorbent and its preparation for particular concentration or separation is highly important. The solution must likewise be prepared in an appropriate manner. Also of great importance is the sorption technique, as well as the possibility and necessity of desorption of elements. All of these factors are influenced by the requirements to the method, the nature of the material to be analyzed, and the methods of subsequent analysis.

1. The Choice of Sorbent and its Preparation

Concentration is usually carried out with a view to recover selectively one element or a group of elements with partial or total separation from the other components. The choice of chelating sorbents capable of solving this problem is usually governed by the properties of their functional groups. Much information can be derived from the selectivity series and analogy of the polymeric sorbent properties with those of monomeric ligands. However, the properties of a given sorbent as a whole, and not only those of its functional groups, must be taken into account when choosing a particular sorbent. Applicability of the selected sorbent to a particular system is usually estimated by carrying out concentration or separation of elements in model solutions.

Usually, the sorbent has to be prepared prior to work, e.g., it is swollen in water or another appropriate solution and pyrified from possible impurities. It is then converted into the certain chemical form. One must take into account its stability in acidic and alkaline solutions, since some sorbents may undergo rapid degradation in them. It is also necessary to choose the concentration or separation procedure most appropriate for a given system, as well as the method of determining the sorbed elements.

2. Preparation of Solutions

The required selectivity in the concentration or separation is achieved only within a specific pH interval and sometimes in the presence of complexing agents. The state of element ions in those solutions is an important factor, especially in the sorption of easily hydrolyzable elements and elements tending to produce polymeric and inert forms; for instance, noble metals must be converted into their chloride complex ion forms.[195,257] When microelements are determined in natural water, the latter should be treated to labilize the bound forms of metal ions.[67,328,329]

The completeness of recovery may be strongly affected by the concentration and composition of salts in the solution during the process of concentration. If necessary, the solutions are diluted; sometimes, a part of the macrocomponents are first separated.[202,258]

3. Concentration and Separation Techniques

The techniques by which sorption or separation with the help of chelating sorbents are achieved can be static, dynamic, or chromatographic. The chromatographic technique exists in column and thin-layer variants. Other methods used are multiple filtration through special thin filters, disks, and membranes. This technique is particularly useful for fast concentration of microelements from natural waters, followed by their determination directly on the filters or membranes by means of X-ray fluorescence or neutron activation methods.[202,213,330-332]

The static regime of sorption is (batch method) often used for selective concentration with the help of chelating sorbents. The method is simple and assures an even distribution of elements in the sorbent. It requires a small quantity of sorbent for its implementation, and is therefore preferable in some cases. Batch sorption is also convenient when it is unnecessary or expedient to desorb the elements after concentration or separation, as well as when sorption is performed in heated solutions, and in some other cases.

The dynamic (column) sorption technique is preferable for concentration from large volumes of solution (1 to 5 and more liters) and for the separation of elements. The chelating sorbent in the form of pearls, fibers or small particles is placed into the column or special cells.[3,203,204,405] To improve their filtering properties, the fine-grained and high-swelling sorbents are mixed with inert material;[77,334] soluble polymeric sorbents are applied on an appropriate carrier as thin films.[128-130,189]

Some special techniques are used to improve the element recovery effectiveness. For instance, the microelements to be determined in natural waters are concentrated on the Chelex 100 sorbent in a special vessel — ''separatory-column'' permitting static and dynamic sorption to be performed one after the other.[210,333,335] Gold was determined in natural materials by sorption on a special paper filter which carried the SRAFION NMRR sorbent. The filter was freely suspended in solution and kept there for 16 hr. Gold was determined directly on the filter. The simplicity, high selectivity, and reliability of this concentration technique which has made many hard analytical operations unnecessary, have permitted it to be used for gold determination in large samples of the analyzed material.[283]

In the TLC method, chelating sorbents are used as finely dispersed fractions premixed with cellulose;[34,336] also used are specially synthesized cellulose-based sorbents containing chelating groups.[119]

4. Concentration and Separation Conditions

The principal parameters of sorptive concentration or separation are as follows: pH or acidity of solution, ratio of sorbent mass to solution volume, volume or height of the column, and contact time or solution flow rate. These are usually determined experimentally. Some practical recommendations are given in Reference 3.

The optimum pH interval is selected on the basis of data describing the relationships between the degree of sorption, sorptive capacity or element distribution coefficients, and the solution pH. Such data are usually obtained on model solutions containing all the components, including alkaline and alkaline-earth metal salts. The reason is that the state of ions in solution and degree of extracting the interesting elements are affected not only by the nature but also by the concentration of other metals in solution, as well as the total concentration of salts present in solution.[3,7,63,337] For selective concentration, the pH interval is chosen in such a way as to minimize the effect of the other components; in separation the optimum pH interval is the one with the maximum difference in degree of sorption of the elements to be separated. Satisfactory separation is achieved when the distribution coefficients differ by not less than two orders of magnitude; in this case sorption is performed on a thin layer of sorbent and when the elution rate is high enough.[63] For instance, in static concentration of elements with the Hyphan sorbent, complete recovery (> 90%) is achieved for elements whose distribution coefficients are $>10^5$ (per 0.1 g of sorbent in 1000 mℓ of solution). In the column process, quantitative extraction from large volume (5 ℓ) of solution on small quantities of the same sorbent (2 to 5 g) can be achieved if the distribution coefficients are within 10^4 to 10^5.[125]

The contact time and solution flow rate in the column depend on the physicochemical properties of sorbent, primarily on its kinetic properties. Chelating sorbents based on porous hydrophilic matrices allow the concentration to be carried out with high flow rates, e.g., up to 30 mℓ/min on cellulosic sorbents. Fibrous sorbents are particularly promising in this respect.[70,124-126,188] Several interrelated parameters are to be simultaneously taken into account in choosing the optimum concentration conditions, especially in the column experiments, viz., concentration of elements in solution, solution volume, sorbent mass and volume, and flow rate. Conditions experimentally determined to be good for one system may prove inapplicable for another. Therefore, calculation methods of optimizing the concentration conditions are of great interest. Such methods have been developed and are used in choosing the conditions of concentration with the help of ion exchangers, as described in Reference 338. The method is based on the theory that with a minimum of experimental data, e.g., the diffusion and distribution coefficients, one can determine the concentration parameters for the preassigned experimental conditions. This makes it possible to choose the optimum conditions for any system; optimum solution and sorbent volume, contact time, and flow rate. This approach, for example, has been effectively used to determine the optimum conditions of copper concentration from seawater with the AN-31 anion-exchange resin for its subsequent analysis; sorbent mass 1 g, flow rate 600 mℓ/h, and contact time 1.5 hr.[338]

For chelating sorbents, the calculation of optimum concentration conditions is a more difficult task due to the more complex sorption mechanism. It has been shown for copper and silver, however, that it is possible in principle to choose the concentration conditions in this case too. Fibrous POLYORGS VIII was used as the chelating sorbent. The calculations were based on the following experimental data: (1) the distribution coefficients over the linear portions of the sorption isotherms equal to 4.5×10^3 (Cu) and 4×10^3 (Ag) for 1 mg/ℓ concentrations of Cu (II) and Ag (I); (2) the internal diffusion coefficients equal to 1.3×10^{-11} (Cu) and 0.3×10^{-11} (Ag) cm^2/sec; and (3) the column cross sections equal to 0.38 and 0.52 cm^2 at maximum sorbent compaction of 0.36 g/mℓ. These data were used to calculate the conditions of copper and silver concentration from 0.5 *M* NaCl solutions which assured degrees of extraction equal to 90% for Cu and 95 and 99% for Ag. Satisfactory agreement between the experimental and the calculated data confirms the possibility of calculating the conditions of the concentration of elements.[181]

The possibility of using the results of calculations to choose the conditions of the separation of elements with the help of chelating sorbents has also been demonstrated for the case of separating lanthanum and calcium on the polystyrene-azoarsenazo sorbent.[144] However, the calculations involved are rather complicated, and their application has so far been limited.

5. *Determination of Elements After Concentration and Separation*

Preconcentration of elements, followed by their determination, is of great importance since it determines to a great extent the effectiveness of the method as a whole.[1] After sorptive concentration or separation, the elements can be determined either directly in the sorbent phase, its decomposition residue, the eluent solution after desorption, or the effluent after the solution has been passed through the sorbent. From the practical viewpoint, determination of elements directly on the sorbent is the most convenient, since it eliminates further treatment of the sorbent, desorption, and ashing, etc. The methods most widely used for this purpose are those of X-ray fluorescence and neutron activation analysis.[66,339-341] In recent years, the atomic absorption method with electrothermal atomization of sorbent suspension has found an ever increasing application.[55,196,197,342,343] An indispensable requirement concentration is, along with high selectivity, a high purity of sorbents.

Atomic emission spectrometry is often used for the determination of elements in the residue left after the "dry" ashing of sorbent. In this way, e.g., noble metals are determined in various objects.[259,260] Also used are the methods of "wet" decomposition of sorbents prior to their determination with, e.g., a mixture of HNO_3, H_2SO_4, and $HClO_4$[258,262,290] or by other means.[252,353] The analysis is then carried out in solutions by different methods. These methods are used to determine the elements after desorption or in the effluent following their separation from other metals; these include spectrophotometry, atomic absorption spectrometry, electrochemical, catalytic, and other methods.

Given below are a few examples of combining sorptive concentration with the help of chelating sorbents and the most commonly used determination methods.

Atomic absorption method is the most widely used to determine elements in different objects after preliminary sorptive concentration. Most frequently, this combination is used for the analysis of natural waters. The analysis is usually performed in solutions following the elution of elements with acids, e.g., such sorbents as Chelex 100,[207,209,322,333,345,347] Dowex® A-1,[346] ANKB-2,[348] Hyphan,[347] and others.[67,344,353] The elements are determined in flame or with electrothermal atomization; the latter method is used either in solutions[347] or in aqueous suspension of the sorbent.[349,351,352] The atomic absorption technique with the elements being determined when sorbent suspension is injected into a graphite atomizer has been used in determining microelements in natural water with preliminary concentration on Chelex 100[343,345] and POLYORGS IX[188] sorbents, to determine platinum-group metals in complex natural materials using the PVB-MP sorbent,[196] as well as to determine As, Bi, and Sb sorbed on SPHERON TIOL,[61] and in determining copper,[345] aluminum,[343] lead,[349] and chromium[350] in various objects.

The neutron activation method is also rather frequently used to determine elements in various objects in combination with preliminary sorptive concentration with the help of chelating sorbents. The method is accurate and sensitive, but saltwater matrix is not well suited for this method. The extremely high concentrations of alkali and alkaline-earth metals and halogens make direct analysis difficult or impossible. The use of chelating sorbents makes it possible to minimize or even eliminate the effect of macroelements. For instance, in the analysis of natural water it becomes unnecessary to work with liquid samples; the effect of sodium, chlorine, and bromine is eliminated; the determination sensitivity is improved; the required radiation dose is reduced, etc.[341]

Preconcentration of elements from unirradiated samples makes it possible to use large quantities of analyzed material and irradiate small quantities of sorbent for subsequent determinations, which makes it unnecessary to work with highly active samples.[283,341] The major requirements to the chelating sorbents used for this purpose are high selectivity with respect to and purity of the elements to be determined. If the chelating sorbent is used at the stage of radiochemical treatment of irradiated samples, its purity is of little importance; selectivity becoming the critical property.

Sorptive concentration with the help of chelating sorbents is used in combination with the neutron activation trace analysis of natural waters,[115,124,129,201,224,334,357] and determination of noble[284,285,287,354] and some other elements[47,355] in various materials.

X-ray fluorescence methods are highly efficient for the determination of trace elements in samples preconcentrated on chelating sorbents.[66,339,340] Sorbents in the form of filters or disks, which do not require any special preparation of the sorbent for analysis, are very suitable for this application.[123,125,282] In other cases, fine-grained sorbent fractions are mainly used and pressed into pellets with the addition of a binder. If necessary, the prepared concentrates can be stored for long periods of time.[213]

When the elements are determined by means of X-ray fluorescence, preliminary sorptive concentration can be performed both in static and dynamic conditions.[213,354,355] A technique has been proposed to concentrate microelements using a sorbent encased in a plastic catcher in the shape of a small cylindrical capsule heated and pressed after sorption. The pellet obtained in this way was subjected to X-ray fluorescence or neutron activation analysis.[203,204,356] The combination of X-ray fluorescence analysis with preliminary concentration on a chelating sorbent has most widely been used in determining the microelements in natural waters[124,175,204,331,356] and noble metals in different objects.[213,283]

The atomic emission spectrometry is mainly used to determine noble metals[259,260,262,263,265,291] and to identify certain microelements in natural industrial objects.[47,48,270] The chelating sorbent in this case is usually ashed in a muffle, and the residue is analyzed. The ashing is performed at temperatures ranging from 500 to 600°C to prevent possible loss of elements.[258,260] Buffer mixtures or spectral carbon are added before or after the sorbent ashing,[260,270] and in some cases the sorbent is decomposed with acids, and the solution is evaporated to dryness on a carbon electrode.[263] In the inductively coupled plasma atomic emission spectrometry, the chelating sorbent is treated with 30% H_2O_2 and HNO_3[252] or aqueous suspension of the sorbent is injected into a plasma.[352]

Spectrophotometry is used to determine elements after their sorptive concentration and desorption with an appropriate eluent, as well as in solutions after the sorption of interfering elements. To determine, for example, uranium and other microelements, the sorption is conducted on Chelex 100 or Dowex® A-1 sorbents, and then the sorbed elements are desorbed with an acid and identified through spectrophotometry.[358-362] Rhodium is determined directly in the effluent after the separation of other noble metals by sorption on chelating sorbents.[25,34,72,267] Spectrophotometry is also used in determining some other elements including Mo, V, Cr, U, and others[2,70,253] after their sorptive concentration.

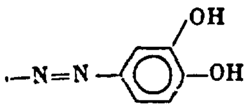
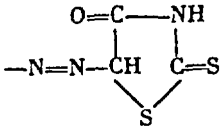
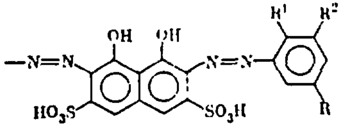
One of the rapid methods of semiquantitative estimation of metals concentration is their direct determination by the color reaction taking place in the sorbent phase when metals interact with the chelating groups of the sorbent. Cellulose-based sorbents are particularly suitable for this purpose. For instance, a cellulose sorbent containing hydroxame groups reacts with metals to form characteristically colored products, which is recommended for their detection in various objects of the environment.[191] A cellulose sorbent with salicylic acid groups has been used for chromatographic separation and determination of Fe (III), U (VI), and Cu (II) by the coloration of column sections filled with this sorbent; the detection limits for these elements are 0.2 μg Fe, 5 μg U, and 10 μg Cu.[275] The colored zone on such sorbents can be used for visual estimation of the quantity of sorbed metal.[276]

Cellulose sorbents with groups capable of reacting with elements to form colored zones are very convenient for the concentration and separation of elements by means of TLC.[119] Very effective, in particular, are sorbents containing monoazo and bisazo groups. The properties of monomeric reagents containing these groups are well known. They have been widely used in spectrophotometry, e.g., arsenazo III, sulfonitrophenol M, sulfochlorophenolazorhodanine, etc.[121] Cellulose sorbents containing similar groups can react with the same elements.[119] The reaction conditions and selectivity are also similar in both cases. Examples of the use of such sorbents for the identification and separation of elements are given in Table 5. Sensitivity of the visual determination of elements in the sorbent phase is 0.1 to 0.3 μg.

Such cellulose sorbents have been used in specially developed procedures for determination of palladium,[363] silver,[118] and some heavy metals.[364]

Some other methods are also used for element determination after concentration or sep-

Table 5
CHELATING SORBENTS ON CELLULOSE BASIS FOR DETECTION AND SEPARATION OF ELEMENTS BY TLC

Chelating groups of sorbents	Mobile phase	Elements to be detected	Ref.
	pH5 pH 1—5 pH1 1 *N* HCl	Zn(II) Cr(III), Cr(VI), Fe(II), Fe(III), V(IV), V(V) Cu(II), Ni(II), Co(II), Fe(III) Cr(VI), Fe(III), V(IV)	364
	0.01 EDTA	Ag	118
			
R=H, R^1=AsO_3H_2, R^2=H	H_2O 4 *M* HCL	Cu, Th, Hf, U Th	119
R=NO_2, R^1=OH, R^2=SO_3H	H_2O 1 *M* H_2SO_4 1 *M* HCl	Cu Pd Nb	119, 363
R=Cl, R^1=OH, R^2=SO_3H	H_2O 1 *M* HCl	Cu, In, Ga, Al, V Zr, Hf, Nb	113

aration on chelating sorbents. For instance, anodic stripping voltammetry is used to determine Cu, Pb, Zn, and Cd in seawater after sorptive concentration on Chelex 100[328,365] and Dowex® A-1 sorbents.[223] Catalytic methods have been used to identify platinum-group metals in rocks; the concentration was performed on the PVB-MP sorbent.[258] Before determination of Fe, Cd, Zn, Cu, Ni, Pb, and U they were concentrated on Chelex 100 and then analyzed by the spark source mass spectrometry.[210]

C. Chelating Sorbents in the Analysis of Different Objects

1. Natural Waters

Chelating sorbents are widely used for the concentration of microelements from natural waters, owing to their ability to remain highly selective in the sorption of elements from solutions containing high concentrations of alkaline and alkaline-earth metal salts. Natural waters, including the sea, rivers, mineral waters, etc., constitute complex solutions of salts which, in addition to the mineral components (NaCl, $MgSO_4$, etc.), contain various organic compounds, whereby microelements may occur in various forms and concentrations.[366,367] Therefore, preparation of water prior to concentration becomes an important stage in the analysis. Normally, water samples are filtered through membrane filters or centrifuged, and only then concentrated. If necessary, water is preserved by acidifying to pH 1 to 2 or by freezing.[210,368,369] The storage and transportation of water prior to its concentration is also of great importance.[370] For sorptive concentration to be effective, it is necessary to purity vessels, reactants, and atmosphere; special attention must be given to sorbent purity. To remove impurities, the sorbents are pretreated with solutions of acids, complexons, etc.[210,357,371]

The microelements occurring in water in different forms are converted into a labile state which assures their more complete extraction by sorption. For instance, water is first acidified, and then the solution pH is adjusted to the required value, or exposed to UV light, boiled with oxidants, etc.[367,371] The recovery of microelements desorbed after concentration from natural waters may be incomplete due to the possible pollution of water with, e.g., soaps, detergents, oils, etc.[361]

Concentration of microelements from natural water by sorption on chelating sorbents can be performed both by batch and column methods. The batch method is normally used for small water samples of 100 to 500 mℓ. It is particularly advantageous when the microelements are determined directly in the sorbent phase after concentration, since small quantities of sorbent are used in this case; the sorbed elements are more uniformly distributed in the sorbent, etc.[213]

Column concentration is used chiefly for large sample volumes of 1 to 5 ℓ and more. If sorbents based on hydrophilic and porous matrices are used, the concentration can be performed with very high solution flow rates, e.g., 30 to 50 mℓ/min.[70,282]

Fibrous sorbents hold great promise for the concentration of microelements from natural waters. The large surface area and high kinetic properties of these sorbents, the possibility of using them in different sorption modes, as filters, films, etc., are used in concentrating and determining various microelements.[120,125,126]

Numerous publications, including reviews, describe different techniques of concentrating the microelements from natural waters with the help of chelating sorbents.[6,67] Here, we shall give some examples of the use of certain sorbents to determine microelements in different types of natural waters.

The most frequently used sorbent is Chelex 100. Most methods involve the concentration of a group of microelements. For instance, numerous techniques have been described of concentrating Cd, Zn, Pb, Cu, Fe, Mn, Co, Cr, and Ni from seawater for their subsequent determination by means of spectrometry atomic absorption with electrothermal atomization. The elements are concentrated from 100-mℓ water samples preacidified, treated with hydrogen peroxide, and exposed to UV light. The sorption is performed in a special vessel.[333]

A similar procedure was used to determine Fe, Mn, Cu, Zn, and Ni in seawater by emission spectrometry with inductively coupled plasma,[372] and to determine certain microelements by the spark source mass spectrometry.[210]

Columns packed with Chelex 100 mixed with an inert material were used for neutron activation determination of microelements in sea and river water. This assured a constant flow rate when large water volumes (1 to 4 ℓ) have to be analyzed.[334] The use of a special Chelex 100-packed catcher made it possible to determine toxic metals after their sorption from natural water directly on the sorbent by neutron activation and X-ray fluorescence methods.[356]

Filters with a thin layer of fine-grained Chelex 100 sorbent fixed on them have also been used to concentrate microelements from natural waters. This technique is used in the X-ray fluorescence determination of some microelements in drinking water[202] and uranium in ground water.[175,206]

Sorptive concentration of microelements on Chelex 100 sorbent is used in the flow-injection system with on-line ion exchange preconcentration for the determination of trace amounts of heavy metals in seawater by atomic absorption.[318] Sorption on Chelex 100 is also used to determine Mo, U, Cu, and other elements in combination with spectrophotometry, anodic stripping voltammetry, and other methods.[67,175,322,360] In Reference 361, the effect of certain surfactants and other water pollutants on the extraction of microelements by sorption on Chelex 100 has been investigated. The authors have shown that certain pollutants are adsorbed on the sorbent surface but do not have any significant effect on the degree of extraction. The degree of their desorption is, however, decreased, which distorts the determination results.

Along with Chelex 100, other sorbents containing iminodiacetate groups, e.g., Dowex® A-1,[346,352,359,363] and Wofatit MC 50,[232] have been used to concentrate microelements from natural waters.

There have been numerous studies concerning the application of the cellulose-based sorbent Hyphan in the concentration of microelements from natural waters.[124-127,282] This sorbent, characterized by high selectivity with respect to heavy metals in solutions containing alkaline and alkaline-earth metal salts, has high kinetic properties and can be used both in the batch and column sorption. Microelements can be determined after the concentration either directly on the sorbent or in solution after their desorption with acids. Hyphan-cellulose is particularly suitable for multielement analysis by the X-ray fluorescence and neutron activation methods.[123,125,171] Hyphan-cellulose is used in many methods of microelements determination in various types of natural waters, viz., drinking, river, mineral, sea, etc.[123,124,126,282,374,375]

Traces of elements are concentrated from natural waters with the help of cellulose-based sorbents containing other chelating groups such as pyrogallol,[40] chromotropic[15] and 2(3)-alanine- *N*,*N*-diacetic acid groups,[375] dithiocarbaminate,[201] diamine,[331,332] and others.[376,377]

Cellulose sorbents are used in the form of filters, "bead", microcrystalline powder, or fibers. Fibrous cellulose sorbents are especially convenient for large water samples. For instance, cellulose sorbents with arsenazo groups[70] and Hyphan[126,282] have been used to concentrate uranium from large volumes of seawater.

Chelating sorbents with different groups are used to determine traces of toxic metals in natural waters. For instance, sorbents with dithiocarbamate and mercapto groups have been used to concentrate mercury (II) traces.[201,376] An effective method of concentrating mercury dissolved in natural waters is based on the use of ASH sorbent.[128,129] This sorbent is applied as a thin film onto Al_2O_3; mercury is then determined directly in the solid phase by neutron activation method.

The SPHERON TIOL sorbent is employed for atomic absorption spectrometry of As, Sb, and Bi in river water with the sorbent suspension being injected into the electrothermal atomizer.[61] The POLYORGS IX sorbent containing nitrogen and sulfur atoms in its functional groups has been developed for the concentration of As and Sb from natural water; the elements are determined by atomic absorption spectrometry with electrothermal atomization of sorbent suspension.[197]

Cadmium is determined in natural waters with the help of different chelating sorbents: Chelex 100, Dowex® A-1, Hyphan, Polyacrylamidoxyme, and others.[67] A procedure has been developed for the sorptive concentration of cadmium with the help of fibrous POLYORGS VII sorbent containing amidoxyme groups in the analysis of mineral waters. Cadmium is determined in solution after desorption with nitric acid, using the flameless atomic absorption method. Detection limit is 0.0008 μg/ℓ.[378] Fibrous sorbents with amidoxyme groups are also promising for the concentration of other microelements from natural waters,[68] uranium among them.[69,379]

Some examples of the use of chelating sorbents in the concentration of microelements from natural waters are given in Table 6.

2. *Geological Objects*

In the analysis of ores, rocks, minerals, and other objects, difficulties are often encountered when it becomes necessary to determine traces of metals, especially rare and noble ones. Rare metals are usually contained in very small quantities in such objects, and therefore preliminary concentration is required for them to be reliably determined.[1] Large samples usually have to be taken for analysis, and when dissolved they form rather large volumes of solutions containing large concentrations of salts. Chelating sorbents make it possible to selectively extract the required elements from such complex solutions. This improves the sensitivity and reliability of determinations and simplifies the analysis and reference sample preparation.[2]

Chelating sorbents are effectively used to determine noble metals in various minerals objects. Many different types of chelating sorbents are known today which are selective with respect to noble metals.[195,257] Numerous procedures have been developed to concentrate microquantities of gold, silver, platinum-group metals, and especially for the concentration of all the noble elements to be subsequently determined by different methods.[2,388]

Noble metals are usually concentrated with the help of chelating sorbents from highly acidic solutions, which raises their selectivity in the presence of salts of nonnoble elements. Different methods are used to dissolve solid samples, depending on the nature of the sample and its mass, etc. Often, mixtures of mineral acids are used as solvents, samples are fused with sodium peroxide, and other techniques are employed.[389] Fire assaying of samples makes it possible to dissolve large volumes of analyzed material and facilitate subsequent sorptive recovery of noble metals.[259] Sometimes the solutions have to be specially treated prior to sorption in order to convert the noble metals into more active and complex forms. Most frequently, such elements are sorbed from hydrochloric acid solutions.[388]

Chelating sorbents based on copolymers of styrene divinylbenzene, PVB-MP, and SRAFION NMRR, as well as fibrous sorbents POLYORGS VI and Mtilon T, are mostly used for group concentration of noble metals. Sorbents PVB-MP (POLYORGS IV) and POLYORGS VI contain methylpyrazol groups. Their high selectivity with respect to noble metals is due to the fact that in highly acidic solutions noble metals can react with these functional groups while other metals, usually accompanying noble metals, cannot react with them in these conditions.[3,26] The sorption is performed by batch method from 1 to 2 *M* HCl solutions. For a more complete extraction of all the platinum-group metals, including rhodium and iridium, solutions with the PVB-MP sorbent are boiled.

After concentration, noble metals are determined in the left after the ashing of the sorbent at 500 to 600°C[260] or decomposition with a mixture of HNO_3, H_2SO_4, and $HClO_4$ acids.[261] Noble metals can also be determined, after concentration, directly in the solid phase. For instance, a method has been developed for atomic absorption determination of platinum-group metals with electrothermal atomization of the PVB-MP sorbent suspension.[196]

Table 6
EXAMPLES OF USE OF CHELATING SORBENTS FOR THE DETERMINATION OF TRACE METALS IN NATURAL WATERS

Sorbents	Trace metals to be determined	Water analyzed	Methods of determination[a]	Ref.
Chelex 100	Fe, Cu, Zn, Cd, Ni, Pb, Mn, Co	Sea	AAS	202, 209, 211, 333, 345, 380
	V, Cr, Mo	Sea	SP	360
	Co	Sea	Luminescence	381
	Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Sc, U, V, Zn	Sea	NNA	172
	Fe, Cd, Zn, Cu, Ni, Pb, U	Sea	SSMS	210
	Cu, Cd, Co, Ni, Pb	Sea	Polarography	205, 382
	U	Ground	RFA	175, 206
	U	Sea	SP	360
	Cd, Zn	Sea and river	NNA	357
	Cu, Zn, Fe, Mn, Ni	Sea	SSMS	372
	Mo	Sea and other	AAS	322
	Mo	Natural	SP	383, 384
	Zn, Cd, Pb, Hg	Sea and river	RFA and NAA	203, 204
Dowex® A-1	Cu, Cd, Co, Pb, Hg, In	Natural	NNA	201, 224
	Cu, Cd, Zn, Pb	Sea	Voltammetry	223
	Cu, Cd, Ni	Sea	AAS	346
	Mo, V	Highly saline	AAS	222
ANKB-2	Cu, Zn, Co, Ni, Cr, Mn	Mineral	AAS	348
Sumichelate Q10	Hg	River and drinking	AAS	300
ALM-125	Hg	Sea and river	AAS	301
Sorbent with diethyldithiocarbaminate groups	Hg, Cu, Zn	Sea	NAA	201
Polyacrylamidoxime	Cu, Cd, Zn, Pb, Fe	Sea and river	AAS and voltammetry	251
Hyphan-cellulose	U, Co, Cr, Cu, Fe, Mo, Ni, Pb, Zn, Hg, Mn	River, mineral and other	RFA, NNA	124—127, 282
Cellulose fiber with arsenazo groups	U	Sea	SP	70
Chromotrop-cellulose	Cu, Zn, Hg, Fe, Sr	Low saline	RFA	15

Table 6 (continued)
EXAMPLES OF USE OF CHELATING SORBENTS FOR THE DETERMINATION OF TRACE METALS IN NATURAL WATERS

Sorbents	Trace metals to be determined	Water analyzed	Methods of determination[a]	Ref.
DEN-filters	Cr, Fe, Co, Ni, Eu, Hg, Pb, U, Ag, Cd	Sea and other	RFA	331
SRAFION NMRR	Au, Ag	River and waste	Complexometry	290
SPHERON TIOL	As, Sb, Bi	River	AAS	61
SPHERON OXIN	Fe, Ni, Cu, Zn, Pb, Cd, Mn	Natural	RFA	380
Piperazindithiocarbamat-cellulose	Au, Ag, Al, Cr, Cu, Co, Fe, Eu, La	Natural	NNA	387
ASH	Hg	River	NNA	128, 129
Pyrogallolformaldehyde resin	Be, Ta, Nb, Zr, Hf	Natural	ES	2

SP — specrophotometry; AAS — atomic absorption spectrometry; NNA — neutron activation analysis; RFA — X-ray fluorescence; SSMS — spark source mass spectrometry; ES — emission spectrometry.

The procedures of concentrating noble metals by sorption on PVP-MP are applicable when they are determined in copper-nickel,[259,260] chromite and molybdenite ores,[196] rocks,[258] and other objects.[262,263]

POLYORGS VI is used for the concentration of gold and platinum-group metals when they are determined in complex materials; it may be preceded by copper-nickel fire assay of the analyzed ore.[259,388]

Also used to determine small quantities of noble metals in various geological objects is the SRAFION NMRR sorbent. The sorption in this case is carried out in slightly acidic solutions. For instance, this sorbent is used in neutron-activation analysis of silver in ores,[285] of platinum-group metals, gold and silver in rocks, minerals, and lunar samples.[284,287,354] This sorbent has also been used for X-ray fluorescence determination of gold in silicate rocks and ores.[213,283] Paper disks with SRAFION NMRR sorbent fixed on them were used to concentrate gold from large ore samples (up to 200 g). The procedure is simple and can be easily combined with subsequent X-ray fluorescence and neutron activation determination methods.[213] To improve the selectivity of gold extraction in the analysis of meteorites and lunar samples, the sorptive concentration was conducted on the SRAFION NMRR sorbent from an organic medium consisting of extracts obtained by extraction of haloid complexes of gold with ethylacetate.[321]

Noble metals are concentrated with the help of other kinds of chelating sorbents as well. These include Mtilon T, polystyreneazorhodanine, and fibrous sorbents containing thioamide groups, etc.[6,195,257]

Chelating sorbents are also successfully used to concentrate and separate other elements in geological objects. For instance, group concentration of microelements has been carried out with polystyrene-azoarsenazo and polystyreneazo-PAR sorbents in the analysis of carbonate and silicate rocks;[48] and Chelex 100, in the determination of Cu, Ni, Zn, and Cd in silicate rocks[215,226] and other objects;[213] pyrogallolformaldehyde resin has been used to determine Be, Nb, Ta, and Zr in ores and minerals;[270] and cellulose sorbent with arsenazo groups, in the determination of U and Th in carbonate rocks.[390]

SRAFION NMRR is used to determine molybdenum[286] and copper[45] in geological objects.

Dowex® A-1 is used for the separation of U, Th, and REE before their determination in monazite.[225] Chromatographic separation of U (VI), Th (IV), and Zr (IV) with the help of a sorbent with propylene-diamine tetracetate groups is used in the spectrophotometric determination of these elements in ores.[240] Some examples of the use of chelating sorbents for the analysis of various objects are given in Table 7.

3. *Industrial Materials*

When elements are determined in industrial materials they often also require preliminary concentration or separation. Such objects are quite diversified and include technological solutions and concentrates, metals, alloys, salts, and other products. Concentrations of the elements of interest in these materials may vary from traces to dozens percent. Chelating sorbents are used both for the concentration of microquantities of elements from solutions containing macrocomponents and for the sorption of macrocomponents separated from the microelements, as well as for separating the elements themselves. For instance, Wofatit MC-50 has been used to concentrate Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb, and Zn for them to be determined in metallic tungsten; these elements are sorbed at pH 9.5 to 10.5; and the sorbed metals are eluted with 1 M H_2SO_4 and determined by the atomic absorption method.[234] Chelex 100 has been used to determine Se and Te in copper; the sorbent rapidly and completely sorbs copper; and selenium and tellurium are determined in solution after separation of copper by voltammetry.[385]

Chelating sorbents are very promising for the analysis of technological solutions. For instance, concentration of noble metals from complex technological solutions with the help

Table 7
EXAMPLES OF THE USE OF CHELATING SORBENTS IN THE ANALYSIS OF NATURAL MINERAL MATERIALS

Sorbents	Elements to be determined	Material analyzed	Methods of determination	Ref.
PVB-MP(POLYORGS IY)	Pt, Pd, Rh, Ir, Ru, Os, Au	Ores, Rocks, and other	ES	259, 260, 262, 263
	Pd, Rh, Ir	Rocks	Catalytic	258
	Pt, Pd, Rh, Ir	Ores	AAS	196
Mtilon T	Pt, Pd, Rh, Ir, Ru, Au	Sulfide ores	ES	291
POLYORGS VI	Pt, Pd, Rh, Ir, Ru, Au	Ores	ES	388
Polystyreneazorhodanin	Pt, Pd, Rh, Ir, Ru, Au	Ores	ES	47
SRAFION NMRR	Pd, Pt, Ir, Ru, Os	Ores, rocks, mineral, and other	NNA	284, 287, 354
Pyrogallolformaldehyde resin	Be, Ta, Nb, Zr, Hf	Ores, minerals	ES	270
Polystyreneazoarsenazo	Pb, Ga, Cr, Ni, Be, Y, V, Yb, Mo, Sc, Zr, Co, Zn, Ti, Mn, Nb	Carbonate rocks	ES	48
Cellulose fiber with arsenaso groups	U, Th	Rocks	SP	390
Chelex 100	Cu, Cd, Zn, Ni	Silicate	AAS	215, 226
	Co, Ni, Bi	Geological objects	RFA	213

of highly selective sorbents makes it possible to determine these elements in a wide interval of concentrations, and simplifies and accelerates analysis.

Methods have been developed for the concentration of noble metals from technological solutions with the help of chelating sorbents PVB-MP,[260,261] POLYORGS VI,[265] Mtilon T,[292] and others.[195]

Alloys have been analyzed with the help of ChMS-8AQ,[25,26,267] polynitroxaminazo,[24] and a fibrous sorbent with thioamide groups.[72] They sorb gold, palladium, and platinum and allow them to be separated from rhodium when the latter is to be determined.

The sulfohydryl sorbent has been used to determine a number of elements in various industrial products. Sorptive concentration on it is conducted by the column method. Using mineral acids of different concentrations, one can separate the interesting elements to be subsequently determined by the neutron activation method in a column or in eluates.[355]

Procedures have also been described to concentrate microimpurities with the help of chelating sorbents for their determination in salts, pure substances,[252] and waste catalysts.[399] Table 8 gives some illustrations of the use of chelating sorbents for analysis of industrial materials.

4. *Other Objects*

The fact that it is possible to use chelating sorbents for the analysis of various objects, other than those mentioned above, is demonstrated by examples described in literature. For instance, the Chelex 100 sorbent has been used to determine toxic metals in foodstuffs;[214] and polydithiocarbaminate and polyacrylamidoxyme sorbents have been used to identify a number of elements in coal, fuel oil, shale oil, and other samples.[394] Chelex 100[396,397] and SRAFION NMRR[287] are used to determine certain elements in biological materials.

Application of chelating sorbents is quite promising in the determination of heavy metals in sewage waters. For instance, sorptive concentration of Cu, Cd, Ni, Zn, and Cr (III) with the help of the fibrous sorbent POLYORGS VII allows the entire process, including sorption, desorption, and sorbent regeneration, to be performed within 1 hr, which can be utilized in express automatic analysis of sewage.

Chelating sorbents are also of interest in the concentration and separation of transuranium elements. For instance, the polystyreneazoarsenazo sorbent has been used to concentrate Pa,[51] Am, and Cm;[52] sorbent Dowex® A-1 has been used for the separation of Am and Cm;[227] and certain phosphorus- and nitrophosphorus-containing sorbents have been used for the separation of Cm and Cf.[398]

Sorbents containing macrocyclic ligand groups hold great promise for the analysis of various objects.[94,312,400,401]

V. CONCLUSIONS

Today, chelating sorbents are intensively investigated in many countries. New effective sorbents are synthesized on the basis of various polymeric matrices. Porous hydrophilic matrices attract ever growing attention since they impart high kinetic characteristics to chelating sorbents. Theoretical aspects of the sorption of elements, accompanied by their complexing in the sorbent phase, are now given great attention. This will help in understanding more profoundly the mechanisms of sorption with chelating sorbents and enable them to be used more effectively in the practice of analytical chemistry.

At present, chelating sorbents are mainly used in inorganic analysis to determine microelements in natural waters, geological and biological objects, and industrial materials. Highly promising is the use of such sorbents for the determination of toxic metals in the environment and sewage waters.

Preliminary concentration with the help of chelating sorbents raises the sensitivity and

Table 8
EXAMPLES OF THE USE OF THE CHELATING SORBENTS IN THE ANALYSIS OF INDUSTRIAL MATERIALS

Sorbents	Elements to be determined	Material analyzed	Methods of determination	Ref.
Chelex 100	Ba	NaCl	RFA	391
	Se, Te	Copper	Voltammetry	385
Dowex® A-1	Ca	LiCl, NaCl	Compexometry	392
	Ca	NaCl	AAS	219
	Ca	Thorium	AAS	395
Wofatit MC 50	Ca, Cu, Mg, Mn, Pb, Zn	Tungsten	AAS	234
SPHERON OXIN	Cu, Fe, Mn, Pb	NH_4Cl	AAS	62
Hydrooxime sorbent	Cu, Mo	Steels, alloys	SP(HPLC)	253
Sorbent with sulfhydryl groups	Cu, Zn, Cd, Hg, As, Sb, Cr	Industrial material	NNA	355
Dithiocarbaminate sorbent	Al, Ti, V, Cu, Fe, Si	High-pyrity graphite	ICP-ES	252
PVB-MP (POLYORGS IV)	Pt, Pd, Rh, Ir, Ru, Os, Au	Technological solution and other materials	ES	259, 260
	Pd, Pt		RFA	2, 388
	Pd, Pt, Rh, Ir		AAS	261
Mtilon T	Pt, Pd, Rh, Ir, Ru, Au	Technological solutions	ES	291, 293
Polynitroxaminaso	Rh	Palladium	SP	24
ChMS-8-AQ	Rh	Alloys	SP	25, 267
POLYORGS VI	Pt, Pd, Rh, Ir, Ru, Au	Technological materials, solutions and other	ES	265
PVA-fiber with thioamide groups	Pt, Rh	Alloys	SP	72
POLYORGS V	Pt, Pd, Rh, Ir, Au	Industrial materials	ES and NNA	393

reliability of determining the elements in various samples, facilitates preparation of reference samples, and accelerates analysis procedures. High selectivity and effectiveness of chelating sorbents, together with their high kinetic properties, make it possible to use them for sorptive concentration and separation in automatically controlled solution assaying systems in combination with different instrumental analysis techniques.

Chelating sorbents are also highly promising for the extraction of valuable metals from natural and waste waters and in hydrometallurgical processes. The possibility of using chelating sorbents to extract metals from seawater is being studied in many countries. A particularly high number of publications deal with uranium recovery from seawater.

Sorbents based on fibrous polymeric matrices are regarded as highly promising for metal concentration and extraction from solutions.

REFERENCES

1. **Zolotov, Yu. A., and Kuzmin, N. M.,** *Preconcentration of Microelements*, Khimia, Moscow, 1982 (in Russian).
2. **Myasoedova, G. V. and Savvin, S. B.,** *Chelating Sorbents*, Nauka, Moscow, 1984 (in Russian).
3. **Hering, R.,** *Chelatbildende Ionenaustauscher*, Akademie-Verlag, Berlin, 1967.
4. **Myasoedova, G. V., Eliseeva, O. P., and Savvin, S. B.,** Chelate sorbents in analytical chemistry (a review), *Zh., Anal. Khim.*, 26, 2172, 1971.
5. **Schmuckler, G.,** Chelating resins — their analytical properties and application, *Talanta*, 12, 281, 1965.
6. **Myasoedova, G. V. and Savvin, S. B.,** New chelating sorbents and their analytical applications, *Zh. Anal. Khim.*, 37, 499, 1982.
7. **Saldadze, K. M. and Kopylova-Valova, V. D.,** *Complex-Forming Ion Exchangers*, Khimia, Moscow, 1980 (in Russian).
8. **Orlova, N. N., Tolmachev, V. N., and Simonenko, E. A.,** Investigation of sorption kinetic of metal ions by means of complexing oxinresorcinol-formaldehyde resin, *Vysokomol. Soed.*, 14B, 335, 1972.
9. **Tolmachev, V. N., Orlova, N. N., and Maksyutina, L. I.,** Investigation of interaction of polymers containing oxin group with metal ions, *Vysokomol. Soed.*, 12A, 1379, 1970.
10. **Vernon, F. and Eccles, H.,** Chelating ion-exchangers containing 8-hydroxyquinoline as the functional group, *Anal. Chim. Acta*, 63, 403, 1973.
11. **Myasoedova, G. V. and Bolshakova, L. I.,** Concentration of elements by sorption on phenol-formaldehyde resins, *Zh. Anal. Khim.*, 23, 504, 1968.
12. **Burba, P., Röber, H.-M., and Lieser, K. H.,** Synthese von Celluloseaustauschern mit chelatbildende funktionelle Gruppen. III, *Angew. Makromol. Chem.*, 66, 131, 1978.
13. **Tscholakowa, J., Burba, P., Gleitsmann, B., and Lieser, K. H.,** Cellulose exchangers with pyrogallol as anchor group, *Z. Anal. Chem.*, 300, 121, 1980.
14. **Sinyavskii, V. G.,** *Selective Exchangers*, Tekhnika, Kiev, 1967 (in Russian).
15. **Lieser, K. H., Röber, H.-M., and Burba, P.,** Separation of trace elements from water by means cellulose exchanger filters and their determination by X-ray fluorescence analysis using radionuclide excitation, *Z. Anal. Chem.*, 284, 361, 1977.
16. **Kolesnikova, B. M., Gulyaeva, N. I., and Zadneprovskaya, V. I.,** A study of sorption of some metal ions by means coplexantes with azosalicylic acid and azo-p-crezol group on basis macroporous styrene-divinylbenzene copolymers, *Vest. Kharkov. Univ.*, N. 202, 56, 1980.
17. **Kolesnokova, B. M. and Tolmachev, V. N.,** Investigation of metal ion exchange in system: Cu and Cd, Cu and Ni, Cu and Ca on complex-forming polymer-polystyreneazosalicylic acid (PSASA), *Izv. Vyssh. Uchebn. Zav., Khim. Khim. Tekhnol.*, 16, 570, 1973.
18. **De Geiso, R. C., Donaruma, L. C., and Tomic, E. A.,** Chelation ion exchange properties of a salicylic acid-formaldehyde polymer, *Anal. Chem.*, 34, 845, 1962.
19. **Hrbkova, E.,** Selective ion exchanger for germanium, *Sb. VŠCHT Praze*, 6, 411, 1962.
20. **Blasius, E. and Kynast, G.,** Zr(IV)-spezifischer Chelataustauscher auf Brenzcatechin-O,O-diessing Saüre-Basis, *Z. Anal. Chem.*, 203, 321, 1964.
21. **Sýkova, V. and Dubský, F.,** Selective ion exchangers with isonitrozoacetamide functional groups. I,II, *Collect. Czech. Chem. Communs.*, 37, 33, 1504, 1972.
22. **Eliseeva, O. P., Savvin, S. B., and Gracheva, R. F.,** Chelate sorbents based on aminopolystyrene and resorcinol azoderivatives, *Zh. Anal. Khim.*, 25, 45, 1970.

23. **Eccles, H. and Vernon, F.**, Chelating ion-exchangers containing 4-(2-pyridylazo)-resorcinol as functional group, *Anal. Chim. Acta*, 66, 231, 1973.
24. **Dedkov, Yu. M., Eliseeva, O. P., Ermakov, A. N., Savvin, S. B., and Slotintseva, M. G.**, Study of the sorption of precious metals on the ion-exchanger containing the o-hydroxy-o′-aminoazogroups, *Zh. Anal. Khim.*, 27, 726, 1972.
25. **Savvin, S. B., Antokolskaya, I. I., Myasoedova, G. V., Bolshakova, L. I., and Shvoeva, O. P.**, Chelate sorbents for concentration and separation of noble metals, *J. Chromatogr.*, 102, 287, 1974.
26. **Malofeeva, G. I., Myasoedova, G. V., and Volynets, M. P.**, Sorption methods of concentrating noble metals, *Mikrochim. Acta*, 1, 391, 1978.
27. **Myasoedova, G. V., Bolshakova, L. I., and Savvin, S. B.**, Concentration and separation of elements on chelate sorbents. Selective concentration of copper, *Zh. Anal. Khim.*, 28, 2324, 1973.
28. **Sugii, A. and Ogawa, N.**, Preparation and properties of a macroreticular resin containing thiohydantonnyl groups, *Chem. Pharm. Bull.*, 24, 1349, 1976.
29. **Myasoedova, G. V., Bolshakova, L. I., Shvoeva, O. P., and Savvin, S. B.**, Selective sorbents for Pd, Pt, Rh and Au based on copolymers of styrene with divinylbenzene, *Zh. Anal. Khim.*, 28, 1550, 1973.
30. **Pinou, F., Deson, J., and Rosset, R.**, Properties specific to boron ion-exchanger Amberlite® XE 243, *Bull. Soc. Chim. France*, 8, 3454, 1968.
31. **Sugii, A. and Ogawa, N.**, Preparation and properties of chelating resin containing the nitrosoresorcinol group, *Talanta*, 26, 970, 1979.
32. **Blasius, E. and Fallot-Burghardt, W.**, Separation of traces of iron from concentrated salt solutions using a chelate exchanger based on o-(2-hydroxyphenylazo)benzoic acid, *Z. Anal. Chem.*, 251, 180, 1970.
33. **Myasoedova, G. V., Antokolskaya, I. I., Shvoeva, O. P., Bolshakova, L. I., and Savvin, S. B.**, A selective sorbent for concentrating noble metals, *Talanta*, 23, 866, 1976.
34. **Antokolskaya, I. I., Myasoedova, G. V., Bolshakova, L. I., Ezernitskaya, M. G., Volynets, M. P., Karyakin, A. V. and Savvin, S. B.**, A sorbent for the noble metals based on the copolymer of styrene and 3(5)-methyl-pyrazol, *Zh. Anal. Khim.*, 31, 742, 1976.
35. **Koster, G. and Schmuckler, G.**, Separation of noble metals from base metals by means of a new chelating resin, *Anal. Chim. Acta*, 38, 179, 1967.
36. **Warshawsky, A., Fieberg, M. M., Mihalik, P., Murphy, G., and Ras, Y. B.**, The separation of platinum group metals in chloride media by isothiouronium resins, *Sep. Purif. Methods*, 9, 209, 1980.
37. **Ke, J. P. and Thibert, R. J.**, Kinetic determination of mercury in natural and biological materials, *Mikrochim. Acta*, 417, 1973.
38. **Dore, M., Jelenc, R., and Lumbroso, R.**, Synthese d'une Resine Complexante du Chrome Hexavalent, *Bull. Soc. France*, N.1-2, 312, 1976.
39. **Griesbach, M. and Lieser, K. H.**, Separation of heavy metals by means chelating exchangers on basis of polystyrene, *Z. Anal. Chem.*, 302, 181, 1980.
40. **Bauman, A. J., Weetall, H. H., and Weliky, N.**, Coupled ligand chromatography, applications to trace element collection and characterization, *Anal. Chem.*, 39, 932, 1967.
41. **Savvin, S. B., Eliseeva, O. P., and Rozovskii, Yu. G.**, Chelate resins on basis of aminopolystyrene and monoazoderivatives of chromotropic acid, *Dokl. Acad. Nauk SSSR*, 180, 374, 1968.
42. **Savvin, S. B., Rozovskii, Yu. G., and Eliseeva, O. P.**, Synthese of polyazo-compounds on basis of polyaminostyrene and derivatives of chromotropic acid, *Vysokomol. Soed.*, 10B, 41, 1968.
43. **Grosh, J. P. and Das, H. R.**, Preparation and properties of a new chelating resin containing 1-nitroso-2-napthtol as the functional group, *Talanta*, 28, 274, 1981.
44. **Hiratani, K., Onishi, Y., and Nakagawa, R.**, Reaction with metal ions of chloromethylated polystyrene resin containing dithiocarbamate group, *J. Appl. Polym. Sci.*, 26, 1475, 1981.
45. **Gladney, E. S.**, Copper determination in standard materials by neutron activation and Srafion NMRR anion-exchange resin, *Anal. Chim. Acta*, 91, 353, 1977.
46. **Grote, M. and Kettrup, A.**, Formazans as functional groups of chelating ion exchanger, *Z. Anal. Chem.*, 295, 366, 1979.
47. **Basargin, N. N., Rozovskii, Yu. G., Zharova, V. M., Volchenkova, V. A., Mikhaelyan, A. I., Gorshkov, V. V., and Oyuun, Zh.**, *Organic Reagents and Chelate Sorbents in Analysis of Mineral Objects*, Nauka, Moscow, 1980, 82 (in Russian).
48. **Dorokhova, E. M., Shvoeva, O. P., Cherevko, A. S., and Myasoedova, G. V.**, Chemical-spectrographic determination of microelements as impurities in carbonate rocks using chelate sorbents, *Zh. Anal. Khim.*, 34, 1140, 1979.
49. **Savvin, S. B.**, *Organic Reagents of Group Arsenazo III*, Atomizdat, Moscow, 1971 (in Russian).
50. **Savvin, S. B., Myasoedov, B. F., and Eliseeva, O. P.**, Separation of microimpurities of thantalum from niobium by sorption on chelate resins, *Zh. Anal. Khim.*, 24, 1023, 1969.
51. **Myasoedov, B. F., Eliseeva, O. P., and Savvin, S. B.**, Selective sorption of protactinium on aminopolystyrene azoderivative chelating resin, *J. Radioanal. Chem.*, 2, 369, 1969.

52. **Myasoedov, B. F. and Molochnikova, N. P.**, A procedure for concentrating americium and curium combined with their separation from plutonium and fission products using a chelating resins, *J. Radioanal. Chem.*, 5, 67, 1970.
53. **Kálal, J., Kálalová, E., Jándrova, L., and Švec, F.**, Use of macroporous glycidil methacrylate-ethylene dimethacrylate copolymer modified by diethylamine for the separation of Pt(IV), Pw(II) and Rh(III), *Angew. Makromol. Chem.*, 115, 13, 1983.
54. **Janák, K. and Janák, J.**, Chelating ion exchangers with bonded 8-quinolinol on a glycidyl methacrylate gel, *Collect. Czech. Chem. Communs.*, 48, 2352, 1983.
55. **Slovák, Z.**, Direct sampling of ion-exchanger suspensions for atomic absorption spectrometry with electrothermal atomization, *Anal. Chim. Acta*, 110, 301, 1979.
56. **Slovák, Z. and Dočekal, B.**, Sorption of arsenic, antimony and bismuth on glycolmethacrylate gels with bound thiol groups for direct sampling in electrothermal atomic absorption spectrometry, *Anal. Chim. Acta*, 117, 293, 1980.
57. **Slovák, Z. and Dočekalova, H.**, Electrothermal atomization of mercury in the presence of thiols, *Anal. Chim. Acta*, 115, 111, 1980.
58. **Slovák, Z. and Slovákova, S.**, Use of hydrophilic glycolmethacrylate gels with bound 8-hydroxyquinoline in trace analysis, *Z. Anal. Chem.*, 292, 213, 1978.
59. **Slovák, Z., Smrž, M., Dočekal, B., and Slovákova, S.**, Analytical behaviour of hydrophilic glycolmethacrylate gels with bound thiol groups, *Anal. Chim. Acta*, 111, 243, 1979.
60. **Slovák, Z., Slovákova, S., and Smrž, M.**, Analitische Eigenschaften von hydrophilen Glykolmethacrylate. Polymeren mit chemisch gebundenen 8-Hydroxychinoline, *Anal. Chim. Acta*, 75, 127, 1975.
61. **Slovák, Z., Slovákova, S., and Smrž, M.**, Analitische Eigenschaften von hydrophilen Glykolmethacrylate Gelen mit chemish gebundener Salicylsäure, *Anal. Chim. Acta*, 87, 149, 1976.
62. **Slovák, Z. and Toman, J.**, Use of hydrophilic glycolmethacrylate gels with bound 8-hydroxyquinoline in trace analysis, *Z. Anal. Chim.*, 278, 115, 1976.
63. **Lieser, K. H.**, New ion exchangers, preparation, properties and application, *Pure Appl. Chem.*, 51, 1503, 1979.
64. **Wegscheider, W. and Knapp, G.**, Preparation of chemically modified cellulose exchangers and their use for the preconcentration of trace elements, *Crit. Rev. Anal. Chem.*, 11, 79, 1981.
65. **Marhol, M.**, Ion exchangers in analytical chemistry, Academia, Prague, 1982.
66. **Van Griken, R. E.**, Preconcentration methods for the analysis of water by X-ray spectrometry techniques, *Anal. Chim. Acta*, 143, 3, 1982.
67. **Myasoedova, G. V., Schcherbinina, N. I., and Savvin, S. B.**, Sorption preconcentration of trace elements for their determination in natural waters, *Zh. Anal. Khim.*, 38, 1503, 1983.
68. **Savvin, S. B. and Myasoedova, G. V.**, Chelate-forming sorbents for preconcentration and separation, in 2nd USSR-Japan Jt. Symp. Analytical Chemistry, Moscow, July 1 to 10, 1984. 155.
69. **Sakane, K., Katoh, S., Sugasaka, K., Takai, N., Seno, M., Itagaki, T., and Ouchi, H.**, Preparation of the fibrous absorbent containing amidoxime group and absorptivity for uranium, in Int. Meet. on Recovery of Uranium from Seawater, Tokyo, 1983, 79.
70. **Ryzhova, L. V., Myasoedova, G. V., Chitrov, L. M., Stepanets, O. V., and Chakimchodzaev, N.**, Determination of uranium in seawater with preconcentration by chelating sorbent, *Radiokhimiya*, 22, 284, 1980.
71. **Lieser, K. H., Breitniesser, E., Burba, P., Röber, M., and Spatz, R.**, Multielement trace analysis of solid and liquid samples by X-ray fluorescence, *Mikrochim. Acta*, 1, 363, 1978.
72. **Simanova, S. A., Bobritskaya, L. S., Kukushkin, Yu. N., and Kalontarov, I. Ya.**, Application of modified PVA-fibre for separation Pt and Rh in "rich" products, *Zh. Prikl. Khim.*, 54, 514, 1981.
73. **Bobritskaya, L. S., Simanova, S. A., Kukushkin, Yu. N., Kalontarov, I. Ya., and Yastrebunskii, A. A.**, Preparation and properties of modified sulphur-containing PVA-fibre as sorbent for platimum metals, *Zh. Prikl. Khim.*, 57, 343, 1984.
74. **Kazakevich, Yu. E., Goncharova, N. A., Strukova, I. M., and Emets, L. V.**, Investigation of the sorption of nonferrous metals by complexing fibrous ionites, *Zh. Anal. Khim.*, 38, 2257, 1983.
75. **Miyamatsu, T.**, Fibrous ion-exchangers and its application, *J. Soc. Fiber Sci. Technol. Japan*, 39, 7, 1983.
76. **Balakin, V. M. and Glukhikh, V. V.**, Synthesis of new ionites by interaction of polyamine anionites with 8-hydroxyquinoline and formaldehyde, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 18, 1466, 1975.
77. **Barnes, J. H., Bates, C., and Hartley, F. R.**, The removal of heavy metals from aqueous solution using a recoverable poly [N-dithiocarboxylate)-iminethene] column, Hydrometallurgy, 10, 205, 1983.
78. **Mateescu, M. A., Schell, H. D., Dimonie, M., Bentia, T., Dimitriu, C., and Maior, O.**, Sure perlförmige Ionenaustauscher des vernetzten Polyvinylalkohols. I, *Rev. Roum. Chim.*, 26, 117, 1981.
79. **Vernon, F.**, Preparation and properties ion exchange resins, *Chem. Ind.*, 634, 1977.

80. **Culberson, C. H., Liang, Y.-J., Church, T. M., and Wood, R. H.**, A chelating gel for collection of copper from seawater, *Anal. Chim. Acta*, 139, 373, 1982.
81. **Bektenov, N. A., Yergozhin, Ye.Ye., and Menligaziev, E. Sh.**, Investigation of sorption ability of exchangers to metal ions, *Izv. Akad. Nauk. Kaz. SSR, Ser. Khim.*, 45, 1983.
82. **Myasoedova, G. V., Savvin, S. B., and Uryanskaya, N. I.**, Chelate sorbents based on cyanur derivatives of cross linked dextran gels and polyvinyl alcohol, *Zh. Anal. Khim.*, 26, 1820, 1971.
83. **Hyashi, S., Aoyama, K., Yamada, R., and Kotsuji, K.**, Synthesis of ionite on basic sephadex with hydroxamic groups and its properties, *Bunseki Kagaku*, 31, 473, 1982.
84. **Pesavento, M., Soldi, T., Ferruti, P., Barbucci, R., and Benvenuti, M.**, Effect of the crosslinking agent on protonation, and metal ions complexing abilities, of ion exchange resins with poly(amido-amine) structure, *J. Polym. Sci.*, 28, 3361, 1983.
85. **Kahovec, J.**, Chelating and complexon polymers, *Chem. Listy*, 75, 398, 1981.
86. **Blasius, E. and Brozio, B.**, Chelating ion-exchange resins, *Chelates Anal. Chem.*, 1, 49, 1967.
87. **Janák, K. and Janák, J.**, Chemically bound analytical organic reagents, *Chem. Listy*, 75, 466, 1981.
88. **Vernon, F. and Nyo, K. M.**, Synthesis optimization and properties of 8-hydroxyquinoline ion-exchange resins, *Anal. Chim. Acta*, 93, 203, 1977.
89. **Vernon, F. and Nyo, K. M.**, Metal separation on an oxine chelating ion exchange resin, *J. Inorg. Nucl. Chem.*, 40, 887, 1978.
90. **Kapadia, R. N. and Dalal, A. K.**, Synthesis and physicochemical studies of some new amphoteric ion exchangers, *J. Appl. Polym. Sci.*, 27, 3793, 1982.
91. **Dalal, A. K. and Kapadia, R. N.**, Absorption properties of some phenolfurfural type chelating ion-exchange resins, *Indian J. Technol.*, 20, 500, 1982.
92. **Parrish, J. R.**, Chelating resins from 8-hydroxyquinoline, *Anal. Chem.*, 54, 1890, 1982.
93. **Altschuler, G. N. and Talovskaya, N. V.**, Sorption of chloride sodium and potassium by means of crown polymers, *Izv. Sib. Otd. Akad. Nauk. SSSR Ser. Khim. Nauk*, 6, 94, 1982.
94. **Blasius, E. and Janzen, K.-P.**, Preparation and application of polymers with cyclic polyether anchor groups (including application in analytical ion chromatography), *Pure Appl. Chem.*, 54, 2115, 1982.
95. **Sýkora, V., Dubský, F., and Protivová, S.**, Selective sorption of platinum metals on weakly basic anion exchangers, *Sb. VŠCHT Praze*, H13, 185, 1978.
96. **Doncheva, E. F., Fatkhullaev, E., Dzhalilov, A. T., and Askarov, M. A.**, Synthesis and studies of cation exchangers based on gossipol and gossipol resin with aldehydes, *Uzb. Khim. Zh.*, 52, 1978.
97. **Blasius, E., Janzen, K.-P., Keller, M., Lander, H., Nguyen-Tien, T., and Scholoten, G.**, Austauscher mit cyclischen Polyethern als Ankergruppen. I. Herstellung, *Talanta*, 27, 107, 1980.
98. **Blasius, E., Janzen, K.-P., Adrian, E., Klein, W., Klotz, H., Luxenburger, H., Mernke, E., Nguyen, V. B., Nguyen-Tien, T., Rausch, R., Stokemer, J., and Toussaint, A.**, Austanscher mit cyclischen Polyethern als Ankergruppen. II. Anvendung, *Talanta*, 27, 127, 1980.
99. **Patel, M. N. and Patel, J. B.**, Ion exchange properties of poly-(5-acetyl-4-hydroxy-1,3-phenylene)-1,2-ethanediyl with bivalent ions, *J. Ind. Chem. Soc.*, 58, 491, 1981.
100. **Kapadia, R. N. and Dalal, A. K.**, Preparation and absorption properties of phenol-acetaldehyde type chelating ion exchange resins, *Ind. J. Chem.*, 19A, 280, 1980.
101. **Bernhard, H. and Gross, F.**, Chelataustauscher auf der Grundlage des 8-Hydroxychinolins and ihre Verwendung für analytische Trenmingen, *Mikrochim. Acta*, 426, 1966.
102. **Dalal, A. K. and Kapadia, N. R.**, Preparation and absorption properties of phenol-acetaldehyde type chelating ion exchange resins, *Ind. J. Technol.*, 18, 430, 1980.
103. **Vernon, F. and Nyo, K. M.**, Metal-metal chelating ion-exchange processes on 8-hydroxyquinoline and 8-hydroxyquinaldine resins, *Sep. Sci. Technol.*, 13, 263, 1978.
104. **Parmar, J. S., Patel, M. R., and Patel, M. M.**, Resacetophenone-formaldehyde resins, *Angew. Makromol. Chem.*, 93, 11, 1981; 105, 75, 1982.
105. **Sýkora, V. and Dubský, F.**, Selective ion-exchange resin on basis resacetophenoxime. Preparation of resin and its main characters, *Collect. Czech. Chem. Communs*, 32, 3342, 1967.
106. **Vyas, M. V. and Kapadia, R. N.**, Synthesis and physico-chemical studies of some new amphoteric ion-exchangers, *Ind. J. Technol.*, 18, 411, 1980.
107. **Joshi, R. M. and Patel, M. M.**, Chelation ion exchange properties of salicylic acid-urea-formaldehyde copolymers, *Proc. Ind. Acad. Sci. Chem. Sci.*, 91, 351, 1982.
108. **Patel, S. D., Patel, H. S. and Patel, S. R.**, PAS-formaldehyde polymer as a polymeric ligand, *J. Macromol. Sci.*, A16, 1335, 1981.
109. **Petrov, K. A., Treshchalina, L. V., Chizhov, V. M., and Nesterchuk, A. I.**, Synthese and properties of ion-exchange resins with aminophosphonic, aminophosphanate and aminophosphinic groups, *Vysokomol. Soedin.*, 18A, 1540, 1976.
110. **Polikarpov, Yu. M., Esina, G. N., Smirnov, A. V., Makarova, S. B., Medved', T. Ya., and Kabachnik, M. I.**, New phosphororganic polyamphoteric ionites with diaminoalkylphosphonate groups, *Izv. Akad. Nauk SSSR Ser. Khim.*, 2117, 1978.

111. **Randall, J. M., Hautala, E., and McDonald, G.**, Binding of heavy metal ions by formaldehyde polymerized peanut skins, *J. Appl. Polym. Sci.*, 22, 379, 1978.
112. **Szczepaniak, W. and Kubera, G.**, Complexforming ion-exchanger with dioxime groups, *Chem. Analit. (Poland)*, 15, 1009, 1970.
113. **Lewandowski, A. and Szczepaniak, W.**, Selective resin specific to titanium ions, *Chem. Stosow.*, 7, 603, 1963; *Ref. Zh. Khim.*, 16629, 1964.
114. **Imaizumi, H.**, Absorption and separation of several metal ions on resorcinol-formaldehyde resin, α-resorcylic acid-formaldehyde resin and other chelating resins, *J. Chem. Soc. Japan, Chem. Ind. Chem.*, 1075, 1983.
115. **Buano, J. A., Karin, R. W., and Fashing, J. L.**, The rapid separation of trace metals from neutron-activated saline matrices by chelation on poly-5-vinyl-8-hydroxyquinoline column, *Anal. Chim. Acta*, 80, 327, 1975.
116. **Donya, A. P., Sokhina, S. I., and Sinyavskii, V. G.**, Introduction of 8-hydroxyquinoline links into polyaminostyrene chain, *Ukr. Khim. Zh.*, 48, 1087, 1982.
117. **Tolmachev, V. N., Miroshnik, L. V., Chaikina, E. A., and Galbraikh, L. S.**, Investigation of complexing process of cellulose derivative containing complex forming groups, *Vysokomol. Soedin.*, 13B, 454, 1971.
118. **Myasoedova, G. V., Volynets, M. P., Koveshnikova, T. A., Belyeav, Yu. I., and Dubrova, T. V.**, Use of modified cellulose for determination of microgram amount of silver, *Zh. Anal. Khim.*, 29, 2252, 1974.
119. **Volynets, M. P., Egorov, E. V., and Myasoedova, G. V.**, Use of new modified sorbents for separating inorganic ions, *Zh. Anal. Khim.*, 26, 1434, 1971.
120. **Myasoedova, G. V., Savvin, S. B., and Makarova, S. B.**, Chelate sorbents on the basis of dextran gels cross-linked with epichlorhydrin, *Zh. Anal. Khim.*, 25, 1859, 1970.
121. **Myasoedova, G. V., Eliseeva, O. P., Savvin, S. B., and Uryanskaya, N. I.**, Concentration and separation of elements on chelate sorbents. Sorption and separation of Pd, Pt, Rh and Au, *Zh. Anal. Khim.*, 27, 2004, 1972.
122. **Gruber, H.**, *Chelatharze mit Formazan-Ankergruppen auf Basis von Saccharosemethacrylaten*, *Monatsh. Chem.*, 112, 587, 1981.
123. **Burba, P. and Lieser, K. H.**, Energiedispersive Röntgenfluorescenzanalyse von Schwermetallspuren (Mn, Fe, Co, Ni, Cu, Zn, Ta, Pb, U) in mineral Wässern nach Abtrennung am Celluloseaustauscher Hyphan, *Z. Anal. Chem.*, 297, 374, 1979.
124. **Burba, P., Lieser, K. H., Neitzer, V., and Röber, H.-M.**, Preconcentration and determination of trace elements in fresh water and sea water, *Z. Anal. Chem.*, 291, 273, 1978.
125. **Burba, P. and Lieser, K. H.**, Abtrennung von Spurenelementen an einem Celluloseaustauscher mit 1-(2-hydroxyphenylaso)-2-naphthol (Hyphan) als funktioneller Gruppe und nachfolgende Bestimmung durch Röntgenfluorescenzanalyse, *Z. Anal. Chem.*, 286, 191, 1977.
126. **Burba, P. and Lieser, K. H.**, Abtrennung von Uran aus natürlichen Wässern mit dem Celluloseaustauscher Hyphan, *Z. Anal. Chem.*, 298, 373, 1979.
127. **Lieser, K. H. and Gleitsmann, B.**, Separation of heavy metals, in particular uranium, from sea water an auchor group of high selectivity, *Z. Anal. Chem.*, 313, 203, 1982.
128. **Krämer, H. J. and Neidhart, B.**, Selective enrichment of trace elements using an aniline-sulphur resin, *Radiochem. Radioanal. Lett.*, 22, 209; 23, 295, 1975.
129. **Krämer, L. J. and Neidhart, B.**, Determination of trace amounts of dissolved mercury compounds by instrumental neutron activation analysis following a selective preconcentration, *J. Radionanal. Chem.*, 37, 835, 1977.
130. **Zlatkis, A., Bruening, W., and Bayer, E.**, Poly-(triaminophenolglyoxal) as a chelating polymer in the determination of traces of nickel, *Anal. Chim. Acta*, 56, 399, 1971.
131. **Korshak, V. V., Zubakova, L. B., and Osokina, M. P.**, Studies of complexing ability of ionites containing pyridine, *Tr. Mendeleev. Inst.*, 89, 95, 1975.
132. **Manecke, G. and Aurich, H.-P.**, Synthese and chemische Eigenschaften einiger Copolymerisate von 8-hydroxy-5-vinylchinoline-Derivaten amphotere Kationenaustauscher, *Makromol. Chem.*, 148, 19, 1971.
133. **Manecke, G. and Schlegel, R.**, Polymer Imidazol-Carbonsäuren. Darstellung and Eigenschaften einiger vernetzten Polyvinylimidazolcarbonsäure, *Makromol. Chem.*, 174, 3191, 1976.
134. **Maneche, G. and Schleger, R.**, Über das Schwermetallionenbindungsvermögen von Chelatharzen mit 4,5-Dicarboxyimidazolyl-Gruppen, *Makromol. Chem.*, 179, 19, 1978.
135. **Maneche, G. and Rühl, G.-S.**, Darstellung und Eigenschaften von Chelatharzen mit Pyrazol-3,4-dicarbonsäure bzw. 1,3,5-Triazol-4,5-dicarbonsäure als Ankergruppen, *Makromol. Chem.*, 180, 103, 1979.
136. **Matorina, N. N., Shepetyuk, L. V., Kagiyants, S. M., Karlina, L. V., Kryuchkova, O. V., and Chmutov, K. V.**, Influence of chemical unhomogenation on sorption properties of iminodiacetic ionites, *Zh. Phys. Khim.*, 52, 1735, 1978.
137. **Hodgkin, J. H.**, Synthesis of metal chelating polymers, *Chem. Ind.*, 153, 1979.

138. **Guise, B.,** Metal selective-exchange resins, *Polym. News*, 9, 52, 1983.
139. **Kabanov, V. A., Efendiev, A. A., Orudzhiev, D. D., and Samedova, N. M.,** Synthese und investigation of complexing sorbent with tuned to ion sorption, *Dokl. Acad. Nauk SSSR*, 238, 356, 1978.
140. **Kabanov, V. A., Efendiev, A. A., and Orudzhiev, D. D.,** Complex-forming polymeric sorbents with macromolecular arrangement favourable for ion sorption, *Vysokomol. Soedin.*, 12A, 589, 1979.
141. **Kabanov, V. A., Efendiev, A. A., and Orudzhiev, D. D.,** Complex-forming polymeric sorbents with macromolecular arrangement favorable for ion sorption, *J. Appl. Polym. Sci.*, 24, 259, 1979.
142. **Nishide, H. and Tsuchida, E.,** Selective adsorption of metal ions on poly(4-vinylpyridine) resins in with the ligand chain is immobilized by cross linking, *Makromol. Chem.*, 117, 2295, 1976.
143. **Nishide, H., Deguchi, J., and Tsuchida, E.,** Adsorption of metal ions on crosslinked poly-(4-vinylpyridine) resins prepared with a metal ion as template, *J. Polym. Sci. Polym. Chem. Ed.*, 15, 3023, 1977.
144. **Shvoeva, O. P., Sorochan, A. M., Savvin, S. B., and Myasoedova, G. V.,** Preconcentration and separation of elements on chelate sorbents. Calculation of conditions for separation of lanthanum and calcium on polyarsenazo. *Zh. Anal. Khim.*, 35, 1074, 1980.
145. **Eger, C., Anspach, W. M., and Marinsky, J. A.,** The coordination behaviour of Co, Ni, Cu and Zn in a chelating ion-exchange resin. I, II, *J. Inorg. Nucl. Chem.*, 1899, 1911, 1968.
146. **Krasner, J. and Marinsky, J.,** Iminodiacetic group dissociation in chelating ion-exchanger, *J. Phys. Chem.*, 67, 2559, 1963.
147. **Matorina, N. N., Shepetyuk, L. V., Karlina, L. V., Chelyscheva, O. V., Kagiyants, S. M., and Chmutov, K. V.,** Acidic-basic properties of iminodiacetic amphoteric ionites, in *Sorption and Chromatography*, Nauka, Moscow, 1979, 122 (in Russian).
148. **Szabadka, Ö., Burton, K. W., and Inczedy, J.,** Modelling of chelating resin protonation equilibria, *J. Chromatogr.*, 201, 59, 1980.
149. **Szabadka, Ö., Burton, K. W., and Inczedy, J.,** Preparation and study of chelating resins. I, II, *Acta Chim. Acad. Sci. Hung.*, 109, 189, 1982.
150. **Szabadka, Ö.,** Study of chelating resins. I, II, *Talanta*, 29, 177, 183, 1982.
151. **Kargman, V. B., Kopylova, V. D., Saldadze, K. M., Shvarts, A. L., Suvorova, L. N., and Ivanova, I. I.,** Investigation acidic-basic equilibria of amphoteric ionites with picoline acid and pyridine groups, *Zh. Phys. Khim.*, 55, 1034, 1981.
152. **Tarasova, E. G., Vozdivizhenskii, V. F., and Dadabaev, A. F.,** Sorption mechanism of different ions by means of ANKB-10, *Zh. Phys. Khim.*, 52, 2081, 2617, 1978; 53, 423, 1979.
153. **Kargman, V. B., Shvarts, A. L., Zalkind, G. I., Kopylova, V. D., Zviadadze, G. N., Konovalova, B. E., and Saldadze, K. M.,** Peculiarity of acidic-basic and coordinate interaction of pyridine polyampholites, *Zh. Phys. Khim.*, 55, 2364, 1981.
154. **Kálalová, E., Beiglová, V., Kálal, J., and Švec, F.,** Sorption properties of macroporous chelate-forming resin from the copolymer glycidyl methacrylate-ethylenedimethacryalte containing iminodiacetic groups, *Angew. Makromol. Chem.*, 72, 143, 1978.
155. **Mekvabashvili, G. V., Kotov, Yu. I., Kopylova, V. D., Kalichevskii, O. V., and Saldadze, K. M.,** Character of sorption of transition metals by means of ionites AN-61 and ANKB-10, *Zh. Prikl. Khim.*, 56, 1288, 1983.
156. **Kukushkin, Yu. N., Simanova, S. A., Kálalová, E., Melgunova, L. G., Radová, Z., Kálal, J., and Švec, F.,** Character of sorption of platinum metals by means copolymere glycidyl methacrylate-ethylenedimethacrylate and diethylamine, *Zh. Prikl. Khim.*, 52, 2207, 1979.
157. **Shvarts, A. A., Molochnikov, L. S., Ivanova, T. M., Zviadze, G. N., Radionov, B. K., and Dzevitskii, B. E.,** Investigation of complexing ability of polyampholites containing nitrogen-phosphor by X-ray electron spectroscopy, *Zn. Phys. Khim.*, 57, 2292, 1983.
158. **Dubyna, A. M., Miroshnik, L. V., and Tolmachev, V. N.,** Investigation of physico-chemical properties of vanadium and molybdenum macrocomplexes by means of cellulose copolymer containing hydroxamine and amidoxime groups, *Vysokomol. Soedin.*, 18B, 526, 1976.
159. **Sahni, S. K. and Reedijk, J.,** Coordination chemistry of chelating resins and ion exchangers, *Coord. Chem. Rev.*, 59, 1, 1984.
160. **Hoek, P. J. and Reedijk, J.,** Coordination of transition-metals by chelating cation-exchange resins, *J. Inorg. Nucl. Chem.*, 41, 401, 1979; 42, 1759, 1980.
161. **Skobeleva, V. I., Gribanova, I. N., Villevald, G. V., Dolenko, G. N., and Oglezneva, I. M.,** Interaction of Pt(IV) with sulphur-nitrogen containing sorbents, *Zh. Phys. Khim.*, 56, 1212, 1982.
162. **Schmuckler, G.,** Complex formation in ion exchangers, in *Essay on Analytical Chemistry*, Pergamon Press, Oxford, 1977, 371.
163. **Yergozhin, Ye. Ye., Nurkhodshaeva, Z. A., Rafikov, S. R., and Prodius, L. N.,** High permeable nitrogen and phosphorous-containing ionites on the base of macro-network copolymers, *Vysokomol. Soedin.*, 21, 2248, 1979.

164. **Shcherbinina, N. I., Belyaeva, V. K., Myasoedova, G. V., Marov, I. N., and Savvin, S. B.,** A study of copper (II) sorption by means of fibrous sorbent and state of copper ions in sorbent phase by ESR method, *Zh. Neorg. Khim.*, 30, 959, 1985.

165. **Furman, E. G., Dabaev, A. Yu, and Mokryshev, A. I.,** IR-Investigation of structure and mechanism of sorption on ampholite ANKB-10, *Zh. Phys. Khim.*, 51, 2499, 1977.

166. **Trostyanskaya, E. B. and Nefedova, G. Z.,** Insoluble polyelectrolyte with functional groups, *Vysokomol. Soedin.*, 7, 1767, 1965.

167. **Tolmachev, V. N., Miroshnik, L. V., and Lugovaya, Z. A.,** Determination of ion exchange equilibrium constant on cellulose containing hydroxamine groups, *Vysokomol. Soedin.*, 14B, 389, 1972.

168. **Dyatlova, N. M., Temkina, B. Ya., and Kolpakova, I. D.,** *Complexons*, Khimia, Moscow, 1970 (in Russian).

169. **Zubakova, L. B., Nikiforova, L. Ya., Korshak, V. V., Alferova, A. V., and Leikin, Yu. A.,** Sorption of silver from water solution by means of N, -O- and S-containing sorbents, *Zh. Prikl. Khim.*, 50, 96, 1977.

170. **Utlelov, B. A., Yergozhin, Ye. Ye., Mukhitdinova, B. A., and Rafikov, S. R.,** Complexing properties of ionites on the basis of hydroxyquinoline, *Vysokomol Soedin.*, 20, 471, 1978.

171. **Vernon, F.,** Metal separation by chelating ion exchange, *Acta Polym.*, 30, 740, 1979.

172. **Loevenschuss, H. and Schmuckler, G.,** Chelating properties of the chelating ion exchanger Dowex®-A-1, *Talanta*, 11, 1399, 1964.

173. **Inczedy, J. J.,** Ion-exchange chromatography and complex formation. Separation of metal ions, *Proc. Anal. Div. Chem. Soc.*, 15, 49, 1978.

174. **Marton-Schmidt, E., Inczedy, J. J., Laki, Z., and Szabadka, Ö.,** Separation of metal ions in ion-exchange resin with ethylenediamine functional groups, *J. Chromatogr.*, 201, 73, 1980.

175. **Hathaway, L. R. and James, G. W.,** Preconcentration of uranium in natural waters for X-ray fluorescence, in *Advantages in X-ray Analysis*, Denver, 1976, 453.

176. **Paramonova, V. I., Akopov, G. A., and Kochevanova, L. A.,** Ion exchange kinetic on phosphorous acid sorbents with different form of particles, *Radiokhimiya*, 9, 642, 1967.

177. **Švec, F., Kálal, J., Kálalová, E., and Marek, M.,** Kinetics of chemical reactions of metal ions with functional groups of glycidyl methacrylate-ethylenedimethacrylate copolymers by ethylenediamine, *Angew. Makromol. Chem.*, 87, 95, 1980.

178. **Heitner-Wirguin, C. and Kendler, J. J.,** Kinetic behaviour of chelating resins with phosphoric functional groups, *J. Inorg. Nucl. Chem.*, 33, 3119, 1971.

179. **Tolmachev, V. N., Kolesnikova, B. M., Gulyaeva, N. I., and Mugabo, L.,** Investigation of velocity of copper exchange on macroporous complexing ionite polystereneazo-p-crezol, *Vestn. Khark. Univ.*, 23, 1981.

180. **Chmutov, K. V., Kalinichev, A. I., and Semenorskaya, T. D.,** Approximate solution of the equations of the kinetics of ion exchange in complexing ionites, *Dokl. Acad. Nauk SSSR*, 239, 650, 1978.

181. **Shvoeva, O. P., Shcherbinina, N. I., Myasoedova, G. V., Sorochan, A. M., Senyavin, M. M., and Savvin, S. B.,** Preconcentration of copper and silver from salt solutions on a fibrous sorbent, *Zh. Anal. Khim.*, 38, 221, 1983.

182. **Kalinichev, A. I., Kolotinskaya, E. V., and Semenovskaya, T. D.,** Computerized analyses of the diffusion processes in complexing ionites, *J. Chromatogr.*, 243, 17, 1982.

183. **Kalinichev, A. I., Kolotinskaya, E. V., and Pronin, A. Ya.,** Number solution of the sum of the kinetics of the ion exchange accompanied complex formation, *Zh. Phys. Khim.*, 53, 506, 1979.

184. **Kalinichev, A. I., Semenovskaya, T. D., Kolotinskaya, E. V., Pronin, A. Ya., and Chmutov, K. V.,** Investigation of the kinetics of ion-exchange processes accompanied by complex formation, *J. Inorg. Nucl. Chem.*, 43, 787, 1981.

185. **Semenovskaya, T. D., Kalinichev, A. I., Shcherbik, L. K., and Chmutov, K. V.,** Sorption kinetics of complexing macroporous ionites, *Zh. Phys. Khim.*, 52, 1748, 1978.

186. **Semenovskaya, T. D. and Avgul, V. T.,** Influence of selectivity on exchange speed in complexing ionites, *Zh. Phys. Khim.*, 54, 1206, 1980.

187. **Volf, L. A., Emets, L. V., Kostrov, Yu, A., Perepechkin, L. P., and Shamolina, I. I.,** *Fibres with Special Properties*, Khimia, Moscow, 1980 (in Russian).

188. **Shvoeva, O. P., Kuchava, G. P., Myasoedova, G. V., Savvin, S. B., Bannykh, L. N., Zhukova, N. G., Grishina, O. N., and Mezhirov, M. S.,** Sorption of gold and silver on POLYORGS XI-N sorbent, *Zh. Anal. Khim.*, 40, 1606, 1985.

189. **Zlatkins, A., Bruening, W., and Bayer, E.,** Determination of gold in natural waters at the part per billion level by chelation and atomic absorption, *Anal. Chem.*, 41, 1692, 1969.

190. **Kahovec, J., Matějka, Z., and Štamberg, J.,** EDTA ester of bead cellulose, a fast-kinetics chelating sorbent, *Polym. Bull.*, 3, 13, 1880.

191. **Grdinić, V. and Kujundžić, N.,** Hydroxamine cellulose fibre as a chelating cation exchanger, *Croat. Chem. Acta*, 54, 109, 1981.

192. **Tolmachev, V. N., Gubenko, E. P., Lischevskaya, M. O., and Ischenko, I. K.,** Investigation of some properties of graft cellulose copolymer with polyacrylthioamide, *Izv. Vyssh. Ucheb. Zaved., Khim., Khim. Tekhnol.*, 19, 97, 444, 1976; 18, 1460, 1975.
193. **Phillips, R. J. and Fritz, J. S.,** Chromatography of metal ions with a thioglycolate chelating resin, *Anal. Chem.*, 50, 1504, 1978.
194. **Pfrepper, G.,** Stability of ion exchangers against treatment with nitric acid and radiation. II. Change in sorption properties of Dowex®-A-1, Chelex 100, Wof MC 50 after treatment with nitric acid, *J. Chromatogr.*, 198, 257, 1980.
195. **Myasoedova, G. V. and Malofeeva, G. I.,** Sorption methods of concentrating the noble metals, *Zh. Anal. Khim.*, 34, 1626, 1979.
196. **Kubrakova, I. V., Varshal, G. M., Sedykh, E. M., Myasoedova, G. V., Antokolskaya, I. I., and Shemarykina, T. P.,** Determination of platinum metals in complex natural samples with electrothermal atomization by heating of sorbent, *Zh. Anal. Khim.*, 38, 2205, 1983.
197. **Kasimova, O. G., Shcherbinina, N. I., Sedykh, E. M., Bolshakova, L. I., and Myasoedova, G. V.,** Preconcentration of antimony and arsenic on a chelating sorbent POLYORGS IX for atomic absorption determination, *Zh. Anal. Khim., 39, 1823, 1984.*
198. **Galitskaya, N. B., Yaroshenko, T. F., Lobachev, A. A., Panchenko, L. T., Nefedova, G. Z., Khavchenko, N. S., Zastavnii, A. M., and Stebneva, I. T.,** Synthese of monofunctional iminodiacetate polycomplex, *Vysokomol. Soedin.*, 19B, 680, 1977.
199. **Yergozhin, Ye. Ye., Khalikova, V. K., and Mukhitdinova, V. A.,** Iminodiacetate derivatives of polyvinyl benzylamine and their chelating properties, *Vysokomol. Soedin.*, 26, 1577, 1984.
200. **Sinyavsky, V. G., Kornienko, R. A., Gorokhvatskaya, N. I., Atamanenko, I. D., and Kurilenko, O. D.,** Synthesis and properties of complexing ionite-cross-linked polystyrene amine diacetic acid, *Ukr. Khim. Zh.*, 50, 97, 1984.
201. **Bergerioux, C., Blanc, J.-P., and Haedi, W.,** Preconcentration of environmental trace elements on organic support for neutron activation and high resolution photon spectrometry, *J. Radioanal. Chem.*, 37, 823, 1977.
202. **Van Gricken, R. E., Bresseless, C. M., and Vanderborgh, V. M.,** Chelex 100 ion-exchange filter membranes for preconcentration in X-ray fluorescence analysis of water, *Anal. Chem.*, 49, 1326, 1977.
203. **Clanet, F. and Deloncle, R.,** Compressible chelating resin column for the determination of trace elements by X-ray fluorescence spectrometry, *Anal. Chim. Acta*, 117, 343, 1980.
204. **Clanet, F., Deloncle, R., and Popoff, G.,** Trace toxic metals determination in natural waters using X-ray fluorescence spectrometry on a chelating resin captor, *Analusis*, 9, 276, 1981.
205. **Abdullah, M. L., El-Rayis, O. A., and Riley, J. P.,** Re-assessment of chelating ion-exchange resins for trace metal analysis of sea water, *Anal. Chim. Acta*, 84, 336, 1976.
206. **Hathaway, L. R. and James, G. W.,** Use of chelating ion-exchange resin in the determination of uranium in ground water by X-ray fluorescence, *Anal. Chem.*, 47, 2035, 1975.
207. **Kingston, H. M., Barnes, I. L., Brady, T. J., Rains, T. C., and Champ, M. A.,** Separation of eight transition elements from alkali and alkaline earth elements in estuarine and sea water with chelating resin and their determination by graphite furnace atomic absorption spectrometry, *Anal. Chem.*, 50, 2064, 1978.
208. **Kingston, H. M. and Pella, P. A.,** Preconcentration of trace metals in environmental and biological samples by cation exchange resin filter for X-ray spectrometry, *Anal. Chem.*, 53, 223, 1981.
209. **Lamathe, J.,** A selective method of elution for the extraction of heavy metals from sea waters on a chelating resin, *Anal. Chim. Acta*, 104, 307, 1979.
210. **Mykytiuk, A. P., Russell, D. S., and Sturgeon, R. E.,** Simultaneous determination of iron, cadmium, zinc, copper, nickel, lead and uranium in seawater by stabile isotope dilution spark source mass spectrometry, *Anal. Chem.*, 52, 1281, 1980.
211. **Riley, J. P. and Taylor, D.,** Chelating resins for the concentration of trace elements from sea water and their analytical use in conjuction with atomic absorption spectrophotometry, *Anal. Chim. Acta*, 40, 479; 41, 175, 1968.
212. **Cutter, G. A.,** Selenium in reducing waters, *Science*, 217, 829, 1982.
213. **Blount, C. W., Leyden, D. E., Tomas, T. L., and Guill, S. M.,** Application of chelating ion exchange resins for trace element analysis of geological samples using X-ray fluorescence, *Anal. Chem.*, 1045, 1973.
214. **Menke, H.,** Investigation of a method for the determination of lead, cadmium, mercury, arsenic and tellurium in food by means of X-ray fluorescence analysis, *Z. Anal. Chem.*, 286, 31, 1977.
215. **Uchida, T., Nagase, M., Kojima, I., and Iida, C.,** A simple decomposition and chelating resin separation for the determination of heavy metals in silicates by atomic absorption spectrometry, *Anal. Chim. Acta*, 94, 275, 1977.
216. **Brajter, K. and Grabarek, J.,** Application of thriethylentetramine to the separation of metal ions on selective exchange resin chelex 100, *Talanta*, 23, 876, 1976.
217. **Brajter, K. and Miazek, J.,** Investigations on the effect of aqueous acetone medium on separation of metal ions on chelex 100 — exchanger, *Talanta*, 28, 759, 1981.

218. **Brajter, K. and Grabarek, J.**, Application of thriethylentetramine and 1,2- and 1,3-diaminopropane in the separation of metal ions on chelex 100 ion-exchanger, *Analyst*, 103, 632, 1978.

219. **Hiroi, K. and Schinohara, T.**, Ion-exchange concentration on chelating resin and atomic absorption spectrophotometric determination of trace amount calcium in high pyrity sodium chloride, *Bull. Sea Water Sci. Jpn.*, 34, 20, 1980.

220. **Turse, R. and Rieman, W.**, Concentrating traces of copper from 1 *M* ammonium chloride, *Anal. Chim. Acta*, 24, 202, 1961.

221. **Holynska, B.**, The use of chelating ion exchanger in conjunction with radioisotope X-ray spectrometry for determination of trace amounts of metals in water, *Radiochem. Radioanal. Lett.*, 17, 313, 1974.

222. **Mareček, J., Braunova, I., and Vachtová, J.**, Determination of molybdenum, vanadium and chromium in brines by atomic-absorption spectrophotometry, *Chem. Prům.*, 33, 429, 1983.

223. **Le Meur, J.-F. and Courtot-Coupez, J.**, Dosage de traces d'elements lourds dissous dans léau de mer par spectrophotometrie d'absorption atomique et relissolution anodique sur electrote d'argen amalgame, *Bull. Soc. Chim. France*, 1, 929, 1973.

224. **Matteheus, A. D.**, The determination of indium in sea water, *Anal. Chim. Acta*, 51, 287, 1970.

225. **Iyer, S. G., Padmanabhan, P. K., and Venkateswarlu, Ch.**, Use of Dowex® A-(H$^+$) and Zeokar-b 226 (H)$^+$ for the sequential separation of uranium, thorium and rare earths in monazite, *Sep. Sci.*, 12, 205, 1977.

226. **Uchida, T., Nagase, M., and Iida, Ch.**, Determination of copper in silicates using chelating resin after decomposition with teflon vessel, *Anal. Lett.*, 8, 825, 1975.

227. **El-Sweify, F. and Alis, A.**, Chromatographishe Am/Cm Trennung in schwach sauren oxidierenden Medien in der wässeringen und dem chelatbildende Austauscher Dowex®-A-1 un dez tationaren Phase, *J. Radioanal. Chem.*, 60, 353, 1980.

228. **Maura, G. and Rinaldi, G.**, Detection of traces of transition metals by formation of peroxy compounds and sorption on a chelating resin, *Anal. Chim. Acta*, 53, 446, 1971.

229. **Talašek, V., Mostecký, I., Vošta, J., Eliášek, J., and Matějka, Z.**, Separation of non-ferrous metals from solution containing calcium by means of weakly acid and chelate ionites, *Chem. Prům.*, 22, 69, 1972.

230. **Iyer, S. G. and Venkateswarlu, Ch.**, Precipitation ion exchange separation of cadmium from zinc and other cations, *Ind. Chem. J.*, 21, 216, 1982.

231. **Csővàri, M., Horvath, A., and Hohmann, J.**, Application of chelating resin Wofatit MC-50 for concentration of heavy metals from natural water, in 4th Symp. Ion Exchange: Abstr. Siofok, Lake Balaton, Hungaru, 1980, 161.

232. **Herrion, G., Bode, K., and Gelbrecht, G.**, Spurenkonzentrirung aus Wasser mittels Čhelationen Austauscher, *Z. Anal. Chem.*, 23, 36, 1983.

233. **Hering, R. and Ertel, W.**, Quantitative Abtrennung des Aluminiums von Eisen (III) und titan (IV) am Chelonit Wofatit MC 50, *Z. Chem.*, 12, 345, 1972.

234. **Henrion, G., Gelbrecht, J., Hoffmann, T., and Marquardt, D.**, Die AAS-Spurenbestimmung in Wolfram nach Abtrennung am Chelatharz Wofatit MC 50, *Z. Chem.*, 21, 192, 1981.

235. **Knothe, M.**, Separation of cations from solution of platinum metals by complex exchange Wofatit MC-50, *Isotopenpraxis*, 18, 241, 1982.

236. **Kagiyants, S. M., Matorina, N. N., Kryuchkova, O. V., and Chmutov, K. V.**, Sorption isotherms of Cu(II) and Ni(II) on ANKB-10 different concentrations of hydrogen ions, *Zh. Phys. Khim.*, 52, 199, 1978.

237. **Matorina, N. N., Shepetyuk, L. V., Karlina, L. V., and Chmutov, K. V.**, Sorption of Ni(II) by means of ANKB-50 in different concentration of hydrogen ions, *Zh. Phys. Chem.*, 52, 1454, 1978.

238. **Kálalová, E. and Spičaková, H.**, A sorbent with diethylamino and iminodiacetic acid functional groups and its application for separation of rhodium and platinum, *Zh. Neorgan. Khim.*, 27, 2316, 1982.

239. **Kálalová, E. and Spičaková, H.**, A sorbent with iminodiacetic acid functional groups and its application to the isolation of platinum metals, *Sb. VŠCHT Praze*, 27, 105, 1982.

240. **Moyers, E. and Fritz, J. S.**, Preparation and analytical application of a propylendiaminetetraacetic acid resin, *Anal. Chem.*, 49, 418, 1977.

241. **Blasius, E. and Brozio, B.**, Pyridin-2,6-dicarbonsäure-Austauscher für die Trennung Ca^{2+}/Sr^{2+}, *J. Chromatogr.*, 18, 572, 1965.

242. **Blasius, E. and Brozio, B.**, Erdalkaliselektiver Komplexonaustauscher auf Pyridin-2,6-dicarbonsäure-Basis, *Z. Anal. Chem.*, 192, 364, 1963.

243. **Blasius, E. and Brozio, B.**, Chelataustauscher auf 1,8-Dihydroxy-naphthalin-O,O -diessigsäure-Basis zu Abtrennung des Zirconiums von Hafniums and anderen Elementen, *J. Radioanal. Chem.*, 2, 55, 1969.

244. **Blasius, E. and Laser, M.**, Selektive und spezifische Ionenaustauscher auf Hydrasidbasis, *J. Chromatogr.*, 11, 84, 1963.

245. **Griesbach, M. and Lieser, K. H.**, Properties of chelating ion-exchangers on the basis of polysterene, *Z. Anal. Chem.*, 302, 109, 1980.

246. **Liu, Ch.-Y. and Sun, P.-Y.**, Preparation and analytical properties of a chelating resin containing cycteine groups, *Anal. Chim. Acta*, 132, 187, 1981.

247. **Liu, Ch.-Y. and Sun, P.-Y.**, Separation and concentration of molybdenum (VI) and tungsten (VI) with chelating ion-exchange resins containing sulphur ligands, *Talanta*, 31, 353, 1984.
248. **Sugii, A., Ogawa, N., and Hisamitsu, H.**, Preparation and properties of chelating resins containing 8-hydroxyquinoline, *Chem. Pharm. Bull.*, 26, 798, 1978.
249. **Willie, S. N., Sturgeon, R. E., and Berman, S. S.**, Comparison of 8-quinolinol-bonded polymer supports for the preconcentraiton of trace metals from sea water, *Anal. Chim. Acta*, 149, 59, 1983.
250. **Vernon, F. and Zin, W. M.**, Sorption and separation of gold and silver by polyhydroxamic acid, *Anal. Chim. Acta*, 123, 309, 1981.
251. **Collela, M. B., Siggia, S., and Barnes, R. M.**, Synthesis and characterization of a poly(acrylamidoxime) metal chelating resin. Polyacrylamidoxime resin for determination of trace metals in natural waters, *Anal. Chem.*, 52, 967, 2347, 1980.
252. **Mahanti, H. S. and Barnes, R. M.**, Analysis of highpurity graphite for trace elements by inductively coupled plasma atomic emission spectrometry after chelating resin concentration, *Anal. Chem.*, 55, 403, 1983.
253. **King, J. N. and Fritz, J. S.**, Separation of metal ions using an aromatic o-hydroxyoxime resin, *J. Chromatogr.*, 153, 507, 1978.
254. **Phillips, R. J. and Fritz, J. S.**, Synthesis and analytical properties of *N*-phenilhydroxamic acid resin, *Anal. Chim. Acta*, 121, 225, 1980.
255. **Tolmachev, V. N. and Miroshnik, L. V.**, Chromatographic separation of metal ions by means of a graft cellulose copolymer containing complex-forming groups of hydroxamic acid amidoxime (complexit TsG), *Zh. Anal. Khim.*, 30, 895, 1975.
256. **Miroshnik, L. V., Dubyna, A. M., and Tolmachev, V. N.**, Application of cellulose complexite in chromatography, *Zh. Anal. Khim.*, 37, 1897, 1982.
257. **Myasoedova, G. V., Antokolskaya, I. I., and Savvin, S. B.**, New chelate-forming sorbents for noble metals, *Talanta*, 32, 1105, 1985.
258. **Davydova, I. Yu., Kuznetsov, A. P., Antokolskaya, I. I., Nikolskaya, N. N., and Ezukova, Z. A.**, Determination of platinum group metals in rocks using a combined preconcentration procedure, *Zh. Anal. Khim.*, 34, 1145, 1979.
259. **Danilova, F. I., Fedotova, I. A., and Nazarenko, R. M.**, Fire assay-chemical-spectrographic determination of platinum metals and gold in sulphide copper-nickel ores and production of their processing, *Zavod. Lab.*, 48, 9, 1982.
260. **Danilova, F. I., Fedotova, I. A., Rozdukhova, I. A., Myasoedova, G. V., and Antokolskaya, I. I.**, Chemical-spectrographic determination of the noble metals in copper-nickel ores and products of their processing, *Zh. Anal. Khim.*, 33, 2191, 1978.
261. **Savel'eva, A. N. and Khairulina, N. P.**, Flameless atomic absorption determination of platinum, palladium, rhodium and iridium, *Zh. Anal. Khim.*, 33, 1380, 1978.
262. **Myasoedova, G. V., Malofeeva, G. I., Shvoeva, O. P., Illarionova, E. V., Savvin, S. B., and Zolotov, Yu.A.**, Sorption preconcentration of the noble metals, *Zh. Anal. Khim.*, 32, 645, 1977.
263. **Pavlenko, L. I., Popova, I. A., Marcheva, E. V., Myasoedova, G. V., and Malofeeva, G. I.**, Chemical-spectrographic determination of platinum metals, *Zh. Anal. Khim.*, 35, 717, 1980.
264. **Myasoedova, G. V., Antokolskaya, I. I., Danilova, F. I., Fedotova, I. A., Grinkov, V. P., Ustinova, N. V., Naumenko, E. A., Danilova, E. Ya., and Savvin, S. B.**, Application of POLYORGS VI as sorbent for concentration of metals from industrial solutions, *Zh. Anal. Khim.*, 37, 1578, 1982.
265. **Naumenko, E. A., Danilova, E. Ya., Emets, L. V., Volf, L. A., Antokolskaya, I. I., and Myasoedova, G. V.**, Selective fibre-sorbent for platinum metals and gold, *Khim. Volok.*, 44, 1985.
266. **Myasoedova, G. V., Antokolskaya, I. I., Emets, L. V., Danilova, E. Ya., Naumenko, E. A., Fedotova, I. A., Danilova, F. I., Seraya, V. I., Mushii, R. Ya., Volf, L. A., and Savvin, S. B.**, POLYORGS VI as new fibrous sorbent for noble metals, *Zh. Anal. Khim.*, 37, 1574, 1982.
267. **Myasoedova, G. V., Antokolskaya, I. I., Bolshakova, L. I., Shvoeva, O. P., and Savvin, S. B.**, Sorption and separation of Pd, Pt, Rh, Ir and Au by means of resin based on a copolymer of styrene and 8-aminoquinoline, *Zh. Anal. Khim.*, 29, 2104, 1974.
268. **Jeličková, A. and Švec, F.**, 8-Aminoquinoline modified copolymer glycidyl methacrylate-ethylene dimethacrylate and its sorption properties, in *Selective Polymeric Sorbents*, Praque meetings on macromolecules, 1982, M34-1.
269. **Sugii, A., Ogawa, N., and Nashizume, H.**, Preparation and properties of macromolecular resins containing thiasol and thiasoline groups, *Talanta*, 627, 1980.
270. **Moroshkina, T. M., and Vanaeva, L. V.**, Chemico-spectrographic determination of niobium, tantalum, zirconium, hafnium and beryllium in minerals and ores, *Zh. Anal. Khim.*, 25, 2374, 1970.
271. **Moroshkina, T. M., Myasoedova, G. V., and Vanaeva, L. V.**, Concentration of microamounts of niobium, tantalum and beryllium by sorption of the pyrogallol-formaldehyde resin, *Zh. Anal. Khim.*, 24, 698, 1969.

272. **Moroshkina, T. M. and Serbina, A. M.**, Sorption concentration of microcontents of some metals and their spectrographic determination, *Zavod, Lab.*, 43, 1468, 1977.

273. **Lieser, K. H., Förster, M., and Burba, P.**, Effect of the conditions of preparation on the properties of a cellulose exchanger containing salicylic acid as a functional group, *Z. Anal. Chem.*, 284, 199, 1977.

274. **Burba, P. and Lieser, K. H.**, Properties of a cellulose exchanger containing salicylic acid as functional group. Separation on a cellulose exchanger with salicylic acid as functional group, *Z. Anal. Chem.*, 279, 17; 280, 289, 1976.

275. **Burba, P. and Lieser, K. H.**, Chromatography on cellulose exchangers. Microdetermination of Fe^{3+}, UO_2^{2+} and Cu^{2+} ions in aqueous solutions by means of small separation columns, *Z. Anal. Chem.*, 291, 205, 1978.

276. **Förster, M. and Lieser, K. H.**, Separation of traces of heavy metals from concentrated salt solution by means of chelating cellulose exchangers, *Z. Anal. Chem.*, 309, 177, 1981.

277. **Tolmachev, V. N., Kolesnikova, B. M., Gulyaeva, N. I., and Murav'eva, O. M.**, Physico-chemical investigation of macroporous polystyreneazosalicylic acid and polystyrene-p-crezol, *Vest. Kharkov. Univ.*, 84, 1982.

278. **Burba, P., Griesbach, M., and Lieser, K. H.**, Synthesis and properties of a cellulose exchanger with 1,2-dihydroxybenzene-3,5-disulphonic acid (Tiron) as a functional group, *Z. Anal. Chem.*, 284, 257, 1977.

279. **Blasius, E. and Fallot-Burghardt, W.**, Kapazitat and Edalkaliselektivität des Chelataustauschers auf Basis o-(2-hydroxyphenylazo) benzoesäure, *Angew. Makromol. Chem.*, 12, 167, 197, 1970.

280. **Blasius, E., Janzen, K.-P., and Fallot-Burghardt, W.**, Abtrennung des Be(II) vom Al(III) and Chelataustauschers auf der Basis von o-(2-hydroxyphenylazo)benzoesäure, *Talanta*, 18, 549, 1971.

281. **Burba, P., Dyck, W., and Lieser, K. H.**, Abtrennung and energiedispersive RFA gelöster Schwermetallspuren, speziell in Trinkwässern, mittles chelatbildende Celluloseaustauscher, *Vom Wasser*, 54, 227, 1980.

282. **Burba, P., Gleitsmann, B., and Lieser, K. H.**, Separation and X-ray fluorescence analysis of dissolved uranium from natural water by means of chelating cellulose ion-exchangers (natural water samples as example), *Z. Anal. Chem.*, 289, 28, 1978.

283. **Green, T. E., Law, S. L., and Cambel, W. J.**, Use of selective ion-exchange paper in X-ray spectrography and neutron activation. Application to the determination of gold, *Anal. Chem.*, 42, 1749, 1970.

284. **Nadkarni, R. A. and Morrison, G. H.**, Determination of the noble metals in geological materials by neutron activation analysis, *Anal. Chem.*, 46, 232, 1974.

285. **Nadkarni, R. A. and Morrison, G. H.**, Determination of silver in rocks by neutron activation analysis, *Anal. Chem.*, 47, 2285, 1975.

286. **Nadkarni, R. A. and Morrison, G. H.**, Determination of molybdenum by neutron activation and Srafion NMRR ion exchange resin, *Anal. Chem.*, 50, 294, 1978.

287. **Nadkarni, R. A. and Morrison, G. H.**, Neutron activation determination of noble metals using a selective group separation scheme, *J. Radioanal. Chem.*, 38, 435, 1977.

288. **Susen, J. P.**, Simultaneous determination of the noble metals in geological material by radiochemical neutron activation analysis, *Analyst*, 105, 1157, 1980.

289. **Gregorowicz, Z., Stec, H., and Ciba, J.**, Use of blotting-paper collectors for the separation and X-ray fluorescent determination of traces of heavy metals (Cu, Hg, Ag) in water and waste water, *Z. Anal. Chem.*, 303, 381, 1980.

290. **Warshawsky, A. and Ehrlich-Rogozinski, S.**, Determination of silver and mercury bond to polystyrene incorporating isothiourea group, *Microchem. J.*, 22, 362, 1977.

291. **Danilova, F. I., Orobinskaya, V. A., Parfenova, V. S., Nazarenko, R. M., Khitrov, V. G., and Belousov, G. E.**, Chemical spectrographic determination of the platinum metals and gold in copper-nickel alloys obtained by smelting copper-nickel ores, *Zh. Anal. Khim.*, 29, 2142, 1974.

292. **Karpova, A. F., Litvinskaya, I. I., Kashlinskaya, S. E., Khardina, V. K., and Kunilova, N. M.**, Determination of microamounts of the noble metals in technological solutions, *Zh. Anal. Khim.*, 29, 2279, 1974.

293. **Simanova, S. A., Bobritskaya, L. S., Kukushkin, Yu. N., Kalontarov, I. Ya., Marunov, R. M., and Asrorov, Ya.**, About mechanism of platinum metal sorption by means of modified PVA-fibre, *Zh. Prikl. Khim.*, 54, 764, 1981.

294. **Simanova, S. A., Kalontarov, I. Ya., Bobritskaya, L. S., Melgynova, L. G., and Kukushkin, Yu. N.**, Sorption of platinum metals from hydrochloric acid and chloride-sulphate solutions by means of modified PVA-fibre, *Zh. Prikl. Khim.*, 51, 1871, 1978.

295. **Simanova, S. A., Kukushkin, Yu. N., Kalontarov, I. Ya., Maksimova, V. N., and Melgynova, L. G.**, Sorption of platinum metals from hydrochloric acid solution by means of modified fibre containing sulphur, *Zh. Prilk. Khim.*, 50, 519, 1977.

296. **Gruber, H.**, Chelating resins with sulphur containing auchor groups based on saccrosemethacrylate gels, *Monatsh. Chem.*, 11, 747, 1981.

297. **Moyers, E. M. and Fritz, J. S.**, Separation of metal ions using a hexylthioglycolate resin, *Anal. Chem.*, 48, 1117, 1976.
298. **Imai, S., Muroi, M., and Hamaguchi, A.**, Preparation of dithiocarbamate cellulose derivatives and their adsorption properties for trace elements, *Anal. Chim. Acta*, 113, 139, 1980.
299. **Dingman, J. F., Gloss, K. M., Milano, E. A., and Siggia, S.**, Concentration of heavy metals by complexation on dithiocarbamate resins, *Anal. Chem.*, 46, 774, 1974.
300. **Minagawa, K., Takizawa, Y., and Kifune, I.**, Determination of very low levels of inorganic and organic mercury in natural waters by col-vapor atomic absorption spectrometry after preconcentration on chelating resins, *Anal. Chim. Acta*, 115, 103, 1980.
301. **Yamagami, E., Tateishi, S., and Hashimoto, A.**, Application of a chelating resin to the determination of trace amounts of mercury in natural waters, *Analyst*, 105, 491, 1980.
302. **Deratani, A. and Sebille, B.**, Metal ion extraction with a thiol hydrophilic resin, *Anal. Chem.*, 53, 1742, 1981.
303. **Deratani, A. and Sebille, B.**, Preparation and characterization of a polyacrylamide resin containing thiol groups. Study of the reversible Zn(II) fixation, *Makromol. Chem.*, 182, 1875, 1981.
304. **Marhol, M., Chmelíček, J., Alovidinov, A. B., and Kočkarova, Ch. U.**, Selective properties and analytical use of an ion-exchange resin based on α-phenylvinilphosphonic acid, *J. Chromatogr.*, 102, 89, 1974.
305. **Grote, M. and Kettrup, A.**, The separation and enrichment of palladium. *Z. Anal Chem.*, 300, 280, 1980.
306. **Kettrup, A., Grote, M., and Sechardri, T.**, Präparation und praktische Erprobung selektver Ionenaustauscher zur Anreicherung von Metallionen, *Forchungsber. Landes Nordhei-Westfalen*, 23, 1982.
307. **Grosh, J. P., Pramanick, J., and Das, H. R.**, Preparation and properties of a new chelating resin containing 2-nitroso-1-naphthol, *Talanta*, 28, 957, 1981.
308. **Lieser, K. H. and Thybush, D.**, Preparation and properties of polysytrene exchanger with 2,4,6-triamino-1,3,5-triazine as auchor group, *Z. Anal. Chem.*, 306, 100, 1981.
309. **Igawa, M., Ito, I., and Tanaka, M.**, Separation of alkaline metal ions by crown either polymer, *Bunseki Kagaku*, 29, 580, 1980.
310. **Igawa, M., Tanaka, M., Abe, Yu., Yamaguchi, M., and Yamabe, T.**, Separation of potassium and sodium by polyamide crown resin, *Bull. Soc. Sea Water Sci. Jpn.*, 33, 331, 1980.
311. **Djamali, M. G., Burba, P., and Lieser, K. H.**, Synthese und Eigenschaften eines Celluloseaustauschers mit diaminodibenzo-18kzow-6 als Ankergruppe, *Angew. Makromol. Chem.*, 92, 145, 1980.
312. **Laskorin, B. N., Zhukova, N. G., Polyakova, O. P., Kudrya, T. N., Shchepalina, N. M., Tashmukhamedova, A. K., and Rodionova, G. S.**, Synthese and investigation of polymeric macroporous polyether, *Zh. Prikl. Khim.*, 57, 583, 1984.
313. **Gulko, A., Feigenbaum, H., and Schmuckler, G.**, Separation of palladium (II) and platinum (II) chlorides by means of a quanidine resin, *Anal. Chim. Acta*, 59, 397, 1972.
314. **Kunin, R. and Preuss, F.**, Selective to boron ion-exchanger, *Indust. Eng. Chem. Prod. Res. Dev.*, 3, 304, 1964.
315. **Sugii, A., Ogawa, N., Katayama, J., and Hida, T.**, Preparation and analytical properties of a chelating resin containing phenylalanine groups, *Talanta*, 29, 263, 1982.
316. **Djamali, M. G. and Lieser, K. H.**, Synthese and Eigenschaften eines chelatbildenden Austauscher mit N,N'-bis-(2-hydroxybenzyl)-ethylendiamin als Ankergruppe auf der Basis von Polystyrol, *Angew. Makmol. Chem.*, 113, 129, 1983.
317. **Fischer, H.-J. and Lieser, K. H.**, Selektive Abtrennung von Uran aus simuliertem Meerwasser an einem Celluloseaustauscher mit 8-Oxa-2,4,12,14-tetraoxopentadecan als chelatbildende Ankergruppe, *Angew. Makromol. Chem.*, 112, 1, 1983.
318. **Fang, Zh., Ružicka, J., and Hansen, H.**, An efficient flow-injection system with on-line ion-exchange preconcentration for the determination of trace amounts of heavy metals by atomic absorption spectrometry, *Anal. Chim. Acta*, 164, 23, 41, 1984.
319. **Gennaro, M. C., Baicocchi, C., Campi, E., Mentasti, E., and Arugo, R.**, Preparation and characterization of iminodiacetic acid-cellulose filters for concentration of trace metal cations, *Anal. Chim. Acta*, 151, 339, 1983.
320. **Mahanti, H. S. and Barnes, R. M.**, Purification and analysis of calcium carbonate with a poly(dithiocarbamate) resin, *Appl. Spectrosc.*, 37, 401, 1983.
321. **Sundberg, L. L.**, Direct absorption of solvent extracted gold on a chelating ion exchange resin, *Anal. Chem.*, 47, 2037, 1975.
322. **Ternerio, M. and Gracia, I.**, Determination of trace amounts of molybdenum in natural waters by solvent extraction — atomic absorption spectrometry after chelating ion-exchange preconcentration, *Analyst*, 108, 310, 1983.
323. **Pohlandt, C. and Fritz, J. S.**, Separation of metal ions on a new amide resin, *J. Chromatogr.*, 176, 189, 1979.

324. **Vernon, F. and Eccles, H.,** Chelating ion-exchangers containing N-substituted hydroxyl amine functional groups, *Anal. Chim. Acta,* 77, 145, 79, 229, 1975.
325. **Vernon, F. and Eccles, H.,** Hydroxamic acids. Colomn separation of metals on a hydroxamic acid resin, *Anal. Chim. Acta,* 82, 369; 83, 187, 1976.
326. **Vernon, F. and Kyffin, T. W.,** Iron, copper and uranium separation on Duolite CS-346 resin, *Anal. Chim. Acta,* 94, 317, 1977.
327. **Saldadze, K. M. and Kopylova, V. D.,** Chromatography by means of complexites, *Zh. Vses. Khim. Mendeleev Obtsth.,* 28, 58, 1983.
328. **Battley, G. E. and Florence, T. M.,** A novel scheme for the classification of heavy metal species in natural waters, *Anal. Lett.,* 9, 379, 1976.
329. **Burba, P. and Wilemer, P. G.,** UV-photolysis as sample pretreatment for the analytical multielement enrichment especially on chelating ion exchangers, *Z. Anal. Chem.,* 313, 222, 1982.
330. **Blount, C. W., Chanmell, R. E., Leyden, D. E., Van Grieken, R. E., Bresseleers, C. M., and Vanderborgh, B. M.,** Chelex 100 ion-exchange filter membranes for preconcentration in X-ray fluorescence, *Anal. Chem.,* 49, 1326, 1977.
331. **Smits, J. and Van Grieken, R. E.,** Enrichment of trace anions from water with 2,2′-diaminoethylamine cellulose filters, *Anal. Chim. Acta,* 123, 9, 1981.
332. **Röber, H.-M., Burba, P., and Lieser, K. H.,** Darstellung hochreiner Chelat-Celluloseaustauscher und ihre Verarbeitung zu Filtern, *Angew. Makromol. Chem.,* 85, 137, 1980.
333. **Sturgeon, R. E., Berman, S. S., Desaulniers, A. H., and Russell, D. S.,** Preconcentration of trace metals from sea water for determination by graphite furnace atomic-absorption spectrometry, *Talanta,* 27, 85, 1980.
334. **Chul, L., Bae, K., Choug, L. J., and Soon, C. K.,** The use of a chelating resin column for preconcentration of trace elements from sea water in their determination by neutron-activation analysis, *Talanta,* 24, 241, 1977.
335. **Sturgeon, R. E., Berman, S. S., Desaulniers, A. H., Mykytiuk, A. P., Moharen, J. W., and Russell, D. S.,** Comparison of methods for the determination of trace elements in sea water, *Anal. Chem.,* 52, 1585, 1980.
336. **Berger, J.-A., Meyniel, G., and Petit, J.,** Chromatographi sur couches minces de resine complexante exhangeuse de cations a groupements amino-diacetate, *Bull. Soc. Chim. France,* 3176, 1964.
337. **Shvoeva, O. P., Myasoedova, G. V., and Savvin, S. B.,** Concentration and separation of elements on chelate sorbents. On the sorption of iridium in the presence of macrocomponents, *Zh. Anal. Khim.,* 31, 2158, 1976.
338. **Senyavin, M. M.,** *Ion Exchange in Technology and Analysis of Neorganic Substances,* Khimia, Moscow, 1980 (in Russian).
339. **Lambrev, V. G., Ivanova, M. M., Koftyuk, V. A., and Kuzmin, N. M.,** Chromatographic separation and preconcentration in neutron-activation analysis, *Zh. Anal. Khim.,* 38, 138, 1983.
340. **Lobanov, F. I., Yanovskaya, I. M., and Makarov, N. V.,** Chemical X-ray fluorescence analysis of trace elements, *Uspekhi Khim.,* 52, 854, 1983.
341. **Greenberg, R. R. and Kingston, H. M.,** Trace element anaylsis of natural water samples by neutron activation analysis with chelating resin, *Anal. Chem.,* 55, 1160, 1983.
342. **Nakano, K., Takado, T., and Kakuta, T.,** Atomization by direct heating of metal-adsorbed ion-exchange resin in atomic absorption spectrometry, *Bunseki Kagaku,* 28, 325, 1979.
343. **Isozaki, A., Kawakami, T., and Utsumi, S.,** Electrothermal atomic absorption spectrometry for aluminum by direct heating of aluminum-adsorbed chelating resin, *Bunseki Kagaku,* 31, E311, 1982.
344. **Fritz, J. S. and Moyers, E. M.,** Concentration and separation of trace metals with an arsonic acid resin, *Talanta,* 23, 590, 1976.
345. **Isozaki, A., Soeda, N., and Utsumi, S.,** A sensitive atomic absorption spectrometric method for copper employing the direct introduction of chelating resin into carbon tube atomizer, *Bull. Soc. Jpn.,* 54, 1364, 1981.
346. **Frache, R., Baffi, F., and Dadone, A.,** The determination of heavy metals in the Ligurian sea. II. The geographical and vertical distribution of Cd, Cu and Ni, *Deep-Sea Res.,* 27A, 1079, 1980.
347. **Baffi, F., Frache, R., and Dadone, A.,** A comparison between the preconcentration methods for the determination of the chemical form of cadmium in inshore sea water by atomic absorption spectrophotometry with electrothermal atomization, *Ann. Chim. (Ital.),* 74, 385, 1984.
348. **Gogichayshvili, B. A., Dzhincharadze, G. G., and Seperteladze, M. D.,** Determination of trace element contents in some mineral waters of Georgia with the use of chromatographic concentrating, *Izv. Gruz. Acad. Nauk Ser. Khim.,* 4, 116, 1978.
349. **Isozaki, A., Fikuda, Y., and Utsumi, S.,** Electrothermal atomic absorption spectrometry for lead by direct heating of lead-adsorbed chelating resin, *Bunseki Kagaku,* 31, 404, 1982.

350. **Isozaki, A., Kumagai, K., and Utsumi, S.,** An atomic absorption spectrometric method for the individual determination of chromium (III) and chromium (VI) by atomization of chromium from a chelating resin in a graphite tube, *Anal. Chim. Acta,* 153, 15, 1983.
351. **Isozaki, A., Soeda, N., Okutani, T., and Utsumi, S.,** Flameless atomic absorption spectrophotometry of copper by the introduction of chelating resin in carbon tube atomizer, *J. Chem. Soc. Jpn. Chem. Ind. Chem.,* 549, 1979.
352. **Watson, A. E. and Moore, G. L.,** Determination of traces of noble metals adsorbed onto an ion-exchange resin by its direct injection into an ICP source, *S. Afr. J. Chem.,* 37, 81, 1984.
353. **Hayashi, S., Aoyama, K., Yoshimura, K., Shieda, T. D. K., and Kotsuki, K.,** Concentration and separation of different metals by means of xantohynated Sephadex, *J. Chem. Soc. Jpn. Chem. Ind. Chem.,* 1273, 1984.
354. **Das, H. A., Janssen, R., and Zonderhuis, J.,** Determination of iridium in rocks, *Radiochem. Radioanal. Lett.,* 8, 257, 1971.
355. **Jewett, G. L., Himes, R. P., and Anders, O. U.,** Chemical separation techniques for neturon activation analysis used at the Dow Chemical Co., *J. Radioanal. Chem.,* 87, 813, 1977.
356. **Clanet, F., Delocle, R., and Popoff, G.,** Chelating resin catcher for capture preconcentration and determination of toxic metal traces (Zn, Cd, Hg, Pb) in waters, *Water Res.,* 15, 591, 1981.
357. **Litman, R., Mallet, J., and Notini, B. R.,** Simultaneous isolation and concentration of zinc and cadmium from natural water, *Radiochem. Radioanal. Lett.,* 45, 347, 1980.
358. **Florence, T. M. and Farrar, Y.,** Spectrophotometric determination of uranium with 4-(2-pyridylazo)resorcinol, *Anal. Chem.,* 35, 1613, 1963.
359. **Ohnishi, K., Hori, Y., and Tomari, Y.,** Rapid spectrophotometric determination of uranium traces, *Bunseki Kagaky,* 26, 74, 1977.
360. **Pakalns, P.,** Separation of uranium from natural waters on chelex-100 resin, *Anal. Chim. Acta,* 120, 289, 1980.
361. **Pakalns, P., Batley, G. E., and Cameron, A. J.,** The effect of surfactants on the concentration of heavy metals from natural waters on Chelex 100 resin, *Anal. Chem.,* 29, 333, 1978.
362. **Sulcek, F. and Povandra, P.,** Photometric determination of uranium in waters after ion-exchange separation, *Collect. Czech. Chem. Commun.,* 32, 3140, 1967.
363. **Volynets, M. P., Myasoedova, G. V., Ermakov, A. N., Savvin, S. B., and Fomina, T. V.,** Selective concentration and detection of microgram amounts of palladium on the modified cellulose, *Zh. Anal. Khim.,* 26, 1432, 1971.
364. **Myasoedova, G. V., Volynets, M. P., Akimova, T. G., Bolshakova, L. I., Dubrova, T. V., Savvin, S. B., and Ermakov, A. N.,** Separation and determination of Cu, Co, Ni, Zn, Cr, Fe and V by TLC on cellulose sorbent with group azopyrokatechol, *Zh. Anal. Khim.,* 41, 662, 1986.
365. **Florence, T. M. and Batley, G. E.,** Removal of trace metals from sea water by chelating resin, *Talanta,* 22, 201, 1975; 23, 179, 1976.
366. **Bruland, K. W.,** Trace elements in sea water, *Chem. Oceanogr.,* 8, 157, 1983.
367. **Florence, T. M. and Batley, G. E.,** Chemical speciation in natural waters, *Crit. Rev. Anal. Chem.,* 9, 219, 1980.
368. **Grepink, B.,** Investigation of methods and sources of error in trace element analysis in surface waters using the determination of chromium and mercury as examples, *Pure Appl. Chem.,* 56, 1477, 1984.
369. **Rusmussen, L.,** Determination of trace extraction techniques and atomic absorption spectrometry, *Anal. Chim. Acta,* 125, 117, 1981.
370. **Florence, T. M.,** The speciation of trace elements in waters, *Talanta,* 29, 345, 1982.
371. **Brondi, M., Dall, A. M., Ghiara, E., and Gragnani, R.,** Trace element analysis in natural water, in Heavy Metals Environ. Int. Conf. Heidelberg, 1983, 204.
372. **Berman, S. S., LcLaren, J. W., and Willie, S. N.,** Simultaneous determination of five trace metals in seawater by inductively coupled plasma atomic emission spectrometry with ultrasonic nebulization, *Anal. Chem.,* 52, 488, 1980.
373. **Lieser, K. H., Burba, P., Calmano, W., Dyck, W., and Heues, E.,** Separation of trace elements from natural water and waste water, *Mikrochim. Acta,* II, 445, 1980.
374. **Lieser, K. H., Quandt, S., and Gleitsmann, B.,** Separation of heavy metals from natural waters using inorganic sorbents, *Z. Anal. Chem.,* 298, 378, 1979.
375. **Luterotti, S. and Grdinic, V.,** Collection of traces of cadmium (II)-ion on 2(3)-alanin-N,N-diacetic acid cellulose, *Croat. Chem. Acta,* 55, 321, 1982.
376. **Egawa, H., Kuroda, T., and Shiraishi, N.,** Determination of traces of "methyl-mercury" in sea water using chelating resins, *J. Chem. Soc. Jpn., Chem. Ind. Chem.,* 685, 1982.
377. **Goldback, L. and Lieser, K. H.,** Separation of toxic heavy metals from solutions by means of chelating cellulose exchangers, *Z. Anal. Chem.,* 311, 183, 1982.

378. **Myasoedova, G. V., Shcherbinina, N. I., Svanidze, Z. S., Varshal, G. M., and Myasoedov, B. F.,** Sorption concentrating of cadmium for atomic absorption determination in mineral waters, *Zh. Anal. Khim.*, 41, 477, 1986.
379. **Vernon, F.,** Chelating ion exchangers. The Synthese and use of poly (hydroxamic acid) resins, *Pure Appl. Chem.*, 54, 2151, 1982.
380. **Moore, R. M. and Burton, J. D.,** Concentration of dissolved copper in the eastern Atlantic Ocean 23°N to 45°N, *Nature (London)*, 264, 241, 1976.
381. **Marino, D. F. and Ingle, J. D.,** Ion exchange separation of cobalt from alkaline earth and selected transition metals with lophine chemiluminescence detection, *Anal. Chem.*, 53, 292, 1981.
382. **Abdullah, M. L. and Royle, L. G.,** The determination of copper, lead, cadmium, nickel, zinc and cobalt in natural waters by pulse polarography, *Anal. Chim. Acta*, 58, 283, 1972.
383. **Ficklin, W. H.,** The separation of tungstate and molybdate by ion chromatography and its application to natural waters, *Anal. Lett.*, 15, 865, 1982.
384. **Nakagawa, H. W. and Ward, F. N.,** New and refined methods of trace analysis useful in geochemical exploration. Determination of molybdenum in natural water and brines after separation using a chelating resin, *Geol. Surv. Bull.*, 65, 1975.
385. **Hamilton, T. W., Ellis, J., and Florence, T. M.,** Determination of selenium and tellurium in electrolytic copper by anodic stripping voltammetry at a gold film electrode, *Anal. Chim. Acta*, 110, 87, 1978.
386. **Brykina, G. D., Stefanov, A. V., Okuneva, G. A., Alexeeva, V. A., and Nikitin, Yu. S.,** X-Ray fluorescence determination of heavy metals in natural waters after sorption group preconcentration on spheron oxine, *Zh. Anal. Khim.*, 39, 1750, 1984.
387. **Imai, S., Muroi, M., Hamaguchi, A., and Koyama, M.,** Preconcentration of trace elements in natural water with cellulose piperazindithiocarbamate and determination by neutron activation analysis, *Anal. Chem.*, 55, 1215, 1983.
388. *Separation and Determination of Noble Metals*, Vernadskii Inst. Acad. Nauk SSSR, Moscow, 1981 (in Russian).
389. **Ginzburg, S. I., Ezerskaya, N. A., Prokof'eva, I. V., Fedorenko, N. V., Shlenskaya, V. I., and Belskii, N. K.,** *Analytical Chemistry of Platinum Metals*, Nauka, Moscow, 1972 (in Russian).
390. **Khakimhodzhaev, N., Savvin, S. B., Myasoedova, G. V., Pachadzhanov, D. N., and Mukhamedzhanov, M.,** Determination of uranium and thorium in sediment rocks, *Geokhim. Anal. Metody Izucheniya Veshchest. Sostava Osad. Porod* (Moscow), 140, II, 1974.
391. **Blount, C. W., Morgan, W. R., and Leyden, D. E.,** Preparation of pellets from ion-exchange resins for direct analysis of metal ions by X-ray spectroscopy, *Anal. Chim. Acta*, 53, 463, 1971.
392. **Olsen, R. L., Diehl, H., Collins, P. F., and Elelstad, R. B.,** Determination of calcium in lithium salts, *Talanta*, 7, 187, 1961.
393. **Myasoedova, G. V., Antokolskaya, I. I., Bolshakova, L. I., Danilova, F. I., Fedotova, I. A., Varhal, E. B., Rakovskii, Ye. E., and Savvin, S. B.,** POLYORGS V — a new selective sorbent for noble metals, *Zh. Anal. Khim.*, 37, 1837, 1982.
394. **Mahanti, H. S. and Barnes, R. M.,** Determination of trace elements in coal and other energy related materials by inductively coupted plasma emission spectrometry after collection on poly(dithiocarbamate) resin, *Anal. Chim. Acta*, 149, 395, 1983.
395. **Iyer, S. G., Padmanabhan, P. K., Lakshmi, T. S., and Venkateswarlu, Ch.,** Separation of traces of calcium from thorium on Zeokarb 226 and Dowex® A-1, *Indian J. Chem.*, 20A, 428, 1981.
396. **Agarwal, M., Bennett, R. B., Stump, I. G., and D'Auria, J.,** Analysis of urine for trace elements by energy dispersive X-ray fluorescence spectrometry with a preconcentraiton chelating resin, *Anal. Chem.*, 47, 924, 1975.
397. **Pakarinen, P., Pallon, J., and Akselsson, R.,** Ion exchange chromatography as a selective pre-concentration method for PIXE analysis of urine, *Nucl. Instrum. Meth. Phys. Res.*, B231, 168, 1984.
398. **Dedov, V. D., Kalinichenko, B. S., Nikolenko, L. N., Slabkaya, L. D., and Trukhlyaev, P. S.,** Izuchenie sorp. svoistv sint. fosforsod. kationitov, Kurchatov Inst. Preprint, Moscow, 1976.
399. **Yokoyama, T., Kikuch, A., Kimuta, T., and Suzuki, T.,** Selective separation of molybdenum (V)/ vanadium (V) using chelating resins with amine-N-acetic acid functional side chains, *J. Chem. Soc. Jpn. Chem. Ind. Chem.*, 363, 1983.
400. **Barabanov, V. A. and Davydova, S. L.,** Macromolecular macrocycle compounds, *Vysokomol. Soedin.*, 24A, 899, 1982.
401. **Davydova, S. L. and Barabanov, V. A.,** Polymers with macrocycle functional groups and their complex compounds: bonding of ions, small molecules and polymers, *Koor. Khim.*, 6, 823, 1980.