Journal of Analytical Chemistry, Vol. 59, No. 10, 2004, pp. 912–929. Translated from Zhurnal Analiticheskoi Khimii, Vol. 59, No. 10, 2004, pp. 1014–1032.

REVIEWS

Filters for the Preconcentration of Elements from Solutions

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Received April 5, 2004

Abstract—The main techniques for the preconcentration of elements on thin-layer filters are considered: sorption on filters with noncovalently immobilized reagents, bonded groups, and "mechanically" fixed sorbents and the extraction of elements on filters as poorly soluble and polymeric forms previously formed in solution. The matrix of the filters is cellulose, synthetic polymers of the linear and branched structures, synthetic fibers, reversed-phase silica gels, foamed polyurethanes, etc. The variation of the nature of the bonded group or the reagent introduced into the solution, the matrix material, and the technique for the immobilization of groups provides the preconcentration of elements with regard to the peculiarities of test materials and the method for the subsequent determination of elements. Methods for the determination of elements in different samples including preconcentration on filters are considered.

Many works deal with the sorption preconcentration of elements from solutions. Preconcentration is performed using inorganic and organic polymer sorbents with different chemical and mechanical properties: powdered, fibrous, sorption filters, etc. Sorbents of each type have some advantages and disadvantages. For example, sorption on fibrous sorbents is characterized by high rate; however, the capacity of these sorbents is rather low. Flow analysis systems mostly employ columns with powdered sorbents and sorption filters are virtually not used, because a narrow zone of the concentrate must be obtained in flow etc.

The use of thin-layer filters for the preconcentration of elements from solutions is reasonable in so-called combined off-line analysis methods, which involve the determination of elements directly in the solid concentrate. The performance characteristics of these methods are primarily controlled by the quality of the surface of samples; the thickness and density of samples are also important. For example, the high sensitivity of the X-ray fluorescence (XRF) determination of elements is attained in the analysis of concentrates on thin-layer organic polymer filters, because the fluorescence of elements incorporated in these filters (C, N, H, and O) is beyond the recorded spectrum and the small thickness and low density of these materials minimize the absorption and scattering of the primary and fluorescence radiation [1]. An increase in the sensitivity on using thin-layer concentrates was also observed in the radiometric determination of α and soft β emitters [2] and in the determination of elements by diffuse reflectance spectrometry (DRS) [3].

Because of low backpressure, high flow rates through the filters are readily attained, which, in principle, makes it possible to rapidly attain high concentration coefficients and thus to improve the sensitivity of the determination of elements in solutions [4]. For the same reason, filters are used for the separation of suspended and dissolved forms of elements [4].

In this review, we made an effort to systematize the data published on the use of sorption filters for the preconcentration of elements from solutions.

An exact definition of the term *filter* is absent in the literature: in the majority of works such terms as *membrane*, *disk*, *membrane filter*, etc., are used along with the term *filter*. According to the IUPAC nomenclature for membranes and membrane processes, a membrane is a structure having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces [5]. Membranes can have different structures and thicknesses, be neutral or charged, synthetic or prepared from natural materials. In spite of the fact that the above definition of the membrane is the most general, in this review we used the term *filter*, because it accounts for the technique of the experiment in the dynamic mode (filtration). Depending on the area of application, different classifications of filter are given in the literature, and their mechanical, chemical, and structural properties and peculiarities are described in detail.

To improve the efficiency of the preconcentration of elements, the surface of filters is frequently modified with different compounds. On the modification, the surface charge can change, and reagents responsible for the interaction with different forms of elements can be incorporated in the material of the filters. We distinguished four types of filters for the preconcentration of elements from solutions; this classification forms the basis of this review:

filters with noncovalently immobilized reagents;

filters with bonded groups;

filters with "mechanically" fixed sorbents;

filters for the extraction of poorly soluble forms of elements.

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FILTERS WITH NONCOVALENTLY IMMOBILIZED REAGENTS

The noncovalent immobilization of reagents at the surface of filters is frequently used for preparing thin-layer sorbents. The simplicity of obtaining impregnated filters and the possibility of changing one reagent with another make it possible to solve different problems. However, the relatively weak fixing of the reagents immobilized by this technique at the surface of filters and, as a consequence, their partial washing out on the contact with a solution are the main disadvantages of impregnated filters.

It is reasonable to classify noncovalently immobilized filters according to the nature of the bond that occurs between the immobilized reagent and the matrix of the filter. It is also important to consider techniques that are used for fixing reagents at the surface of filters.

Reagents can be noncovalently immobilized at the surface of a filter through both specific and nonspecific interactions. These interactions between the reagent, which occurs in the solution in the ionic or molecular form, and the surface of the filter lead to the formation of hydrogen, dipole–dipole, and ionic bonds. Hydrophobic reagents can be also applied to the surface of a filter by the exclusion of molecules from polar solvents (commonly from water); in this case, a so-called distribution mechanism is realized [6, 7]. The charge redistribution effect (dipole generation) in groups or atoms with nonuniformly distributed charge density manifests itself only at short distances. These dipoles interact with other permanent dipoles, and dipole–dipole interactions occur. Permanent dipoles can also affect neutral groups inducing dipoles in them. This induction dipole–dipole interaction is weaker then ordinary dipole–dipole interaction. In the absence of groups or atoms with permanent dipoles [hydroxyl (–OH), carbonyl (C=O), or halide (I, Br, Cl, or F)], electron density fluctuations produce statistic dipoles, which give rise to very weak dispersion forces. Stronger specific interactions lead to the formation of hydrogen bonds. It is known that only the most electronegative atoms are capable of hydrogen bonding. The strength of bonds increases with the electronegativity of interacting atoms. Oxygen and nitrogen form hydrogen bonds with energies in the range from 15 to 29 kJ/mol depending on the type and state of interacting atoms [5].

Commonly, none of the above mechanisms occurs in pure form, and mixed mechanism are observed that are largely controlled by the nature of the matrix. Synthetic polymers, reversed-phase silica gels, foamed polyurethanes (FPU), and cellulose (powdered or as filter paper) are used as matrices for preparing filters with noncovalently immobilized reagents.

Filters based on synthetic polymers. Filter sorbents are frequently prepared using synthetic polymers of linear or spatial structures: polystyrene, polyethylene, different styrene copolymers, polyvinylchloride, and cellophane with ion-exchange groups introduced at the stage of synthesis [8, 9]. These ion exchangers commonly exhibit low selectivity, and their capacity with respect to element ions is rather low. To overcome these disadvantages, ion-exchange filter membranes are modified with different reagents, commonly complexing. In this case, the ion-exchange mechanism of the sorption of dissociated reagent molecules commonly occurs [10]. The sorption of organic reagents with granulated ion exchangers was studied in several works [10–12], where the dependence of the sorption of reagents on the nature of the adsorbed reagent and the bonded ionogenic group and on the pH of the solution was examined. The sorption of complexing reagents on ion-exchange filters has not been studied in detail; however, an analogous mechanism of fixing the reagents can be assumed. In the impregnation of ion exchangers, it is important to preclude sorption at the functional analytical group, because this can hinder the subsequent formation of element complexes in the sorbent phase.

Azorhodanines, sulfochlorophenolazothiopropiorhodanine (tyrodine), and Sulfonitrophenol M were immobilized on a polyamide membrane that was a microporous polymer material containing the amide group, and on filters with phosphate and vinylpyridine groups [13–15]. The amount of immobilized reagent was determined by spectrophotometry. In the sorption of reagents from aqueous, acetone, and ethanol solutions on a polyimide membrane and cation-exchange filters, the color the reagents on the supports was close to the color of the reagents in solutions. This means that functional groups of the reagents responsible for complexation in the immobilized forms remain “free”. However, the use of the proposed modified filters for the preconcentration and determination of elements involved some difficulties because of the low sorption capacity and partial washing out of reagents and their complexes of metal ions [14].

A large group of filters was developed on the basis of “filled” materials [11, 16–19]. Filters prepared from fibers “filled” with finely dispersed cation and anion exchangers (particle size of the sorbents was 5–10 μm) were treated with solutions of reagents that are used for the photometric determination of an element. In some works, this procedure was performed after the preconcentration of elements from solutions.

Disks of polyacrylonitrile fiber filled with anion exchangers differing in basicities and impregnated with Arsenazo I were used for the preconcentration of uranium(VI) [19]. The immobilization of the reagent was possible because of the presence of two $–SO_3H$ groups in its molecule. The strength of fixing the reagent at anion exchangers was estimated by the value of the diffuse reflectance signal after the sorption of uranium(VI) ions. It was found that the analytical signal decreases with increasing basicity of the anion exchanger, evidently because of binding arsono groups on the anion exchangers of medium and high basicity, which hinders the formation of uranium complexes in the sorbent phase. Therefore, for solving the problem in hand, it is recommended to use a weakly basic anion exchanger in the chloride form. The recovery of the reagent was 35%; the concentration of the reagent was 7×10^{-6} mol/g of the filter.

For the preconcentration of palladium from chloride solutions, disks of the same fiber, which was filled with finely dispersed ion exchangers KU-2 and KB-4 and the anion exchanger with benzimidazole groups A-5, were modified with reagents of the *p*-nitrosamine group (*p*-nitrosodiethylaniline*, p*-nitrosodimethylaniline, and *p*-nitrosodiphenylaniline), derivatives of bisazochromotropic acid, and triphenylmethane dyes [18]. It was found that reagents are rather strongly retained only on the fibrous materials filled with KU-2, and the maximum analytical signal in the spectrophotometric determination of palladium is attained with the use of nitrosodiethylaniline. The concentration of the reagent in the disk was determined by the change in the absorbance of the sorbent after immobilization. The capacity of the sorbent with respect to the reagent determined from the sorption isotherm was 5 mmol/g of the filter or 10 mmol/g of KU-2. The time for attaining a constant analytical signal at the concentration of palladium of 1×10^{-8}–5×10^{-6} M was 2–10 min.

Filters based on silica gels with bonded alkyl groups. The mechanism of the sorption of organic compounds on “reversed-phase” silica gels was studied in many works. It was demonstrated that regent molecules are both adsorbed at the outer surface of the bonded layer and distributed inside this layer; the interaction of fragments of reagent molecules with residual silanol groups is also possible [20]. According to the data from [21], the distribution mechanism makes the major contribution to the retention of hydrophobic molecules of organic reagents. The authors found that the hydrophobicity of reagents (azo compounds, macrocyclic compounds, β-diketones, etc.) correlates with the capacity of the modified sorbents based on hydrophobized silica gel.

Hydrophobic forces responsible for the transfer of compounds from the aqueous phase to the solid phase are the forces of specific repulsion between nonpolar atomic groups and water molecules. The thermodynamics of these processes is primarily controlled by the change in the entropy of the system related to the structure features of water as a condensed system. On the transfer of a hydrophobic compound from the aqueous phase to the organic phase, the destructuration of water occurs and the entropy of the system increases, i.e., the entropy factor plays an important role in the total free energy balance. The efficiency of the extraction of a compound is estimated using the distribution coefficient of this compound in the water–octanol system and sometimes merely using the solubility in water. For surfaces with alkyl groups, the capacity of fixing the same compounds decreases upon decreasing the number of carbon atoms (sorption on C_1–C_{16} silica gels was studied) [21].

The sorption of reagents prone to protolytic reactions, e.g., hexaoxacycloazochrom and 1-(2-pyridylazo)-2-naphthol on hydrophobized silica gels substantially depends on the pH of the solution. The reagents are efficiently extracted only under conditions where molecular forms of the reagents dominate, which confirms the substantial contribution of the distribution mechanism. However, a contribution of the sorption of the regents because of specific interaction between hydroxy groups of the reagent and residual silanol groups of silica is also possible in this case [21, 22].

Filters based on alkylsilica gel (with a thickness of 0.5 mm and standard composition: 90 wt % SiC_{18} and 10 wt % polytetrafluoroethylene; particle size 8 μm; pore size 60 Å [23–28]) (Empore^{TM}3M) were modified with macrocyclic, organic phosphorus-containing, and azo compounds: decyl-18-crown-6 [23], hexathia-18-crown-6-tetraone [24], hexathia-18-crown-6 [25], dicyclohexyl-18-crown-6, 11-hydroxynaphthacene-5,12-quinone [21, 26], Salphen [27], tri-*n*-octylphosphine, triphenylphosphine oxide, tri-*n*-butyl phosphate, hexaoxacycloazochrom [21, 28], and 1-(2-pyridylazo)-2-naphthol [22]. Modified filters were used for the dynamic preconcentration of elements from solutions [22–28].

Filters based on foamed polyurethane. The high sorption efficiency of foamed polyurethanes with noncovalently immobilized organic and inorganic reagents, in particular when foamed polymers were simultaneously plasticized, is primarily caused by their cellular membrane-like structure, which provides the access of extracted molecules inside the sorbent, the combination of various hydrophilic (urethane, amide, urea, ester, and ether) and hydrophobic (hydrocarbon and aromatic) active centers and reactive terminal toluidine groups. The variety of functional groups in the flexible polymeric chain of foamed polyurethanes offers wide possibilities for intermolecular interactions of different energies and chemical nature and significantly affects the physicochemical properties of these polymers [21, 29, 30]. Thus, diethyldithiocarbamate, pyrrolidinedithiocarbamate, 4-(2-pyridylazo)resorcinol, 1-(2-pyridylazo)-2-naphthol, dithizone, diphenylcarbazide, dimethylglyoxime, diacetylmonoxime benzothiazolylhydrazone, cyanates, etc., were fixed on foamed polyurethane disks for the preconcentration of elements [21].

Filters based on cellulose. Impregnated sorbents are frequently obtained by the modification of papers [21, 31]. The paper matrix is the natural polymer, cellulose, whose chemical composition and molecular structure are controlled by peculiarities of the biochemical synthesis. The polymer consists of repeated 1,5-anhydroglucopyrazone units linked through the 1,4-β-D-glucoside bond. The large specific surface area of cellulose, its fibrous structure, and the presence of reactive hydroxy groups in its composition provide the immobilization of a large number of organic and inorganic reagents at its surface. However, the mechanism of the interaction of cellulose with different compounds and resulting bonds are frequently treated ambiguously [32].

The techniques and mechanisms of the immobilization of different reagents on cellulose (Table 1) were considered in detail in [31]. Before the immobilization of reagents, paper was wetted in water and slightly dried. In the authors' opinion [31], this technique leads to the more complete displacement of water from submicroscopic capillaries of cellulose and to the loosening of fibers. Next, the paper was treated with solutions of ion pairs of the azo derivatives of pyrocatechol and trihydroxyfluorones with cetylpyridinium and complexes of the reagents with metal ions [33]. After drying this paper, the reagents were strongly fixed in pores of the cellulose paper. An analogous process known as inclusion was used for preparing "reactive" cellulose [32]. Modified papers were used for the preconcentration of Al, Mo(VI), Ti(IV), W(VI), and V(V) from aqueous solutions.

It was assumed that the high concentration of azo compound molecules at the surface of ordinary cellulose is due to the orientation of adsorbate molecules parallel the polar surface of cellulose [34]. At the next stage, the reagent diffuses to the depth of the intermicellar space of cellulose, loses there its hydrate shell, and forms an aggregate.

Hydrophobic dithiocarbamates [35], triphenylarsine chloride, and tetraphenylarsine bromide [36] were used as paper-modifying reagents.

The noncovalent immobilization of reagents is performed in the both static and dynamic modes. Modified sorbents were obtained, e.g., merely by wetting the support in a reagent solution at the constant ionic strength and the experimentally selected pH [21, 31]. For the immobilization of reagents poorly soluble in water, their solutions in organic solvents were used, or the reagents were applied as a finely dispersed powder [31]. Either single-stage or multistage immobilization was used. The multistage immobilization of reagents was performed for preparing a protective layer and for the successive immobilization of different reagents or the synthesis of an analytical chromogenic reagent at the surface of the filter. In the former case, after drying the support was repeatedly wetted, e.g., in a solution of polyvinyl alcohol, gelatin, and other film-forming compounds and dried again [21, 31].

A technique was proposed for the noncovalent immobilization of trioctylamine (TOA) on filters [37, 38]. Cellulose blue-ribbon filters were treated with a 5% solution of paraffin in hexane in the presence of 0.20–0.25 M trioctylamine. The concentration of nitrogen in the filter was 0.3–0.4 mmol/g. These filters were used for the extraction of Au(III), Pd, and Pt(IV) from chloride solutions of complex composition.

Table 1. Reagents for paper impregnation [31]

Impregnated reagents	Analytes
Poorly soluble organic reagents:	
trihydroxyfluorones	Ge, Hf, Mo, Sb, Sn, Ta, Ti, W, Zr
azo derivatives of pyrocatechol	Al, Ga, Mo, Ti, V, W
1-(2-pyridylazo)-2-naphthol	Co, Cu, Fe, Ni, Zn
dimethylglyoxime	Ni
dithizone	Ag, Cd, Hg, Pb, Zn
nitrosonaphthols	Co, Fe, Cu
dimethylaminobenzylidenerhodanine	Ag, Au, Hg, Pt
Poorly soluble complex salts:	
hexacyanoferrates(III)	Fe(II), Cl^-, Br^-, I^-

Chromatographic paper was treated with a solution of 1-(2-pyridylazo)-2-naphthol in ethanol, next the reagent was fixed with a latex emulsion of styrene and butadiene, and the paper was dried at 90°C [39]. The ion-exchange capacity of the filter was 0.012 mmol. The filters were used for the preconcentration of nickel and copper from aqueous solutions.

Paper was impregnated with a solution of a silver salt and, after drying, with a solution of sodium chromate [21]. The resulting indicator paper was used for the test determination of chloride.

A polyvinylchloride membrane was wetted with solutions of chelating agents 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine) [40] and bathophenanthroline [30] and dried.

Xylenol Orange was immobilized on filters of polyacrylonitrile fiber filled with a finely dispersed anion exchanger in the course of formation by the treatment with a 10^{-5}–10^{-3} M aqueous solutions of the reagent for 15–30 min. The concentration of the reagent at the surface of the filter was determined by spectrophotometry [16].

Techniques for the immobilization of reagents on foamed polyurethane were proposed. The immobilization of liquid reagents, e.g., tributyl phosphate, trioctylamine, and di-(2-ethylhexyl)phosphoric acid is attained by holding FPU disks in the corresponding reagent [21, 29]. Foams obtained by this technique contained 50 to 80 wt % reagent. Solid chelating agents were immobilized on foamed polyurethane by the treatment of the support with a solution of the reagent in a nonvolatile organic solvent (plasticizer) or with a solution in a highly volatile solvent and subsequent drying. In both cases, the solubility of the reagent must be sufficiently high. Tributyl phosphate and α-dinonyl phosphate were used as plasticizers [29].

In the dynamic mode, filters were modified using standard filtration devices or chromatographic columns, through which solutions of reagents in the corresponding solvent were passed after fixing the filters [23–28].

SiC_{18} filters were modified in the dynamic mode with solutions of decyl-18-crown-6 in methanol [23], hexathia-18-crown-6-tetraone in dimethyl sulfoxide [24], hexathia-18-crown-6 in acetonitrile [25], etc. Modified filters were used for the preconcentration of Ag, Hg(II), and Sr from aqueous solutions. Filters were treated with methanol and acetonitrile to remove impurities, next solutions of reagents were passed through the filters at a flow rate of 10 mL/min, and after that the solvent was removed at a temperature of 60°C. Both reagents and metal complexes were quantitatively desorbed from the surface of filters with 5 mL of 0.1 M $Na_2S_2O_3$ or 5% HNO_3.

Cu(II), Fe(III), and Ni were preconcentrated from nitric acid solutions using filters of polyacrylonitrile fiber filled with the KU-2 cation exchanger, which were modified in flow with solutions of potassium thiocyanate, dimethylglyoxime, and sodium diethyldithiocarbamate [17].

Polytetrafluoroethylene filters (Millipore) with a pore size of 3.0–5.0 μm, porosity of 60–85%, and thickness of 25–200 μm were impregnated with α-hydro-ω-hydroxypoly-(oxy-1,4-butanediyl) (molecular mass 1000 ± 50 g/mol) [41, 42]. For this purpose, 3–5 mL of the molten reagent was passed through the filter at 65°C in the dynamic mode. The data of electron microscopy demonstrated that the surface of the filter remains porous after the treatment with the reagent; from this fact, the authors came to a conclusion on the impregnation mechanism: the molten reagent penetrates into the pores and after cooling coats their inner surface. The sorption capacity of the filters with respect to gold was 0.5 mg per milligram of the immobilized reagent. The authors of the works used modified filters for the dynamic preconcentration of Au(III), Pd, and Pt(IV) from aqueous solutions.

Thus, filters with noncovalently immobilized reagents were obtained by the modification of filters of synthetic polymers, reversed-phase silica gels, cellulose, and foamed polyurethanes (Table 2). These filters have found widest acceptance in simple and rapid methods that combine preconcentration and obtaining colored forms of elements.

FILTERS WITH BONDED GROUPS

In the covalent modification of sorbent filters, a functional group responsible for the interaction with ions of elements and chemically bonded to the matrix is introduced into the composition of the matrix. Functional groups can be introduced into a polymer matrix by chemical conversions or are formed in the course of the synthesis of the polymer sorbent. The majority of works describe the preparation of filters with complexing groups [44–50, 70–77], which exhibit high selectivity for the extracted elements and good kinetics of sorption interaction. The sorption properties of these filters depend on the nature of functional groups and physical and chemical properties of the polymer matrix. In Table 2, filters with bonded groups are systematized by the types of the polymer matrix and the functional group. Cellulose, synthetic polymers of linear and branched structures (styrene copolymers, polyethylene, polyvinylchloride, and other fibers) were used as polymer matrices for obtaining these filters.

The directed development of complexing sorbents of new types can be performed on the basis of the structure of the complex of the given element with a monomeric ligand and the strength of the metal–ligand bond. The success of complexation with an organic ligand depends on the ability of the ligand to fill the coordination polyhedron optimum for the given element. In turn, this ability depends on the type of the donor atoms of functional groups of the ligand and the conformational flexibility of these atoms, which is primarily controlled by the possibility of the distortion of bond angles and bond lengths of these functional groups. Unlike the complexation in solutions, the flexibility of the donor atoms of functional groups of the ligands bonded to the polymer matrix is limited by both the conformational rigidity of the matrix and the length and conformational flexibility of the ligand spacer (fragment of the molecule bonding the polymer matrix to the complexing group). The density of the distribution of functional groups on the polymer is important for the complexation of the bonded monodentate ligand. In addition, the sorbent capacity can decrease because of the cross-linking of polymeric chains in the course of the formation of complexes of ligands located at neighboring chains of the polymer [68].

The observed decrease in the stability constants of the complexes of elements with bonded ligands in comparison with corresponding monomeric ligands [69] is primarily due to the distortion of the resulting coordination polyhedron of the element. Probably, an increase in the coordination flexibility of the donor atoms of the functional groups of sorbents leads to a decrease in steric hindrances in the formation of the coordination sphere required for the given element. It is expected that, for a monodentate ligand with a relatively high density of functional groups and sufficient length of the spacer, the conformational flexibility of donor atoms will be controlled by the conformational flexibility of the spacer. In contrast, at a sufficient length of the spacer and its conformational flexibility, complexation depends on the density of functional groups. Thus, elements do not commonly form coordinatively saturated complexes with monodentate ligands fixed on silica gel. Because of the features of the structure of this matrix, the density of functional groups on it is rather low [20]. The use of polymers whose modification can yield a high density of functional groups provides the conditions for the formation of coordinatively saturated complexes. For example, cellulose and cross-linked polystyrene are among these polymers.

Table 2. Preconcentration of elements from solutions on filters

Analytes	Test material	Introduced reagents (sorbent)	Filter matrix	Determination method	References
Filters with noncovalently immobilized reagents					
Au, Cu, Hg, Pd, Pt	Acidic solutions	Azorhodanines, tyrodine, Sulfonitrophenol M	PA	DRS	[13–15]
Sr	Solutions of alkali and alkaline-earth metals	Decyl-18-crown-6	Si–C_{18}	AAS	[23]
Al, Mo, Ti, V, W	Waters	Ion pairs of azo derivatives of pyrocatechol and trihydroxyfluorones with cetylpyridinium and their chelates with metal ions	C	DRS	[33]
Ag, Bi, Co, Fe	Biological and environmental materials	Metal diethyldithiocarbamates	C	Test method	[35]
Os	Ores	Salts of triphenylarsine and tetraphenylarsine	C	XRF	[36]
Cu, Fe	Potable and natural waters	Bathocuproine, bathophenanthroline	PVC	SP	[40]
Hg	Natural waters	Diethylammonium diethyldithiocarbamate	FPU	XRF	[43]
Filters with bonded groups*					
Au, Pd, Pt	Ores	α-Hydro-ω-hydroxypoly-(oxy-1,4-butanediyl)	PTFE	AAS	[41, 42]
Co, Cr, Cu, Fe, Ga, Mn, Ni, Ti, Zn	Biological materials	Iminodiacetic acid	C	XRF	[44]
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, РЗЭ	Natural and sewage waters	Diethylenetriaminepentaacetic acid	C	XRF	[45, 46]
As, Cr, Mo, Se, W, V	Tap and melt waters	Diethylenetriamine	C	XRF	[47]
As, Cd, Cu(II), Hg, Pb, Se, Te	Natural and sewage waters, biological materials	Dithiocarbamates	C	XRF	[45]
Cu, Fe,Hg, Sr, Zn	Natural waters	Chromotropic acid	C	XRF	[48]
РЗЭ	Sea waters	8-Hydroxyquinoline	PAN	ICP MS	[47]
Co, Cu, Fe, Ni, Pb, Zn	Natural and sewage waters	1-(2-Hydroxyphenylazo)-2-naphthol	C	XRF	[48]
Cu, K, Mn, Ni, Pb, Rb, Sr, Zn	Natural waters	Iminodiacetic acid	CSDVB	XRF	[48, 49]
Cd, Co, Cu, Fe, Ni, Pb	Natural and sewage waters	2-Aminopyridine, semicarbazide, thiosemicarbazide, hydroxylamine hydrochloride, L-aspartic acid, urea	PE	XRF, AAS	[50]
Filters with “mechanically” fixed sorbents					
Pd	Chloride solutions	CSDVB with amidoxime and hydrazidine groups	PAN	SPS	[51]
Pd	Chloride solutions	*p*-Nitrosodiethylaniline immobilized on CSDVB with –SO_3H groups	PAN	DRS	[18]
Au	Ores, rocks	CSDVB with amino groups	C	XRF, NAA	[52]
Ag, Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mn, etc.	Alloys, metals, and biological materials	CSDVB with sulfo and carboxy groups	C	XRF	[53]
I^-, SO_4^{2-}, $Cr_2O_7^{2-}$, VO_3^-, etc.		CSDVB with trimethylamino and amino groups	C		

Table 2. (Contd.)

Analytes	Test material	Introduced reagents (sorbent)	Filter matrix	Determination method	References
*Filters for the extraction of polymeric and poorly soluble forms of elements***					
Fe	Waters	Bathocuproine and Zephiramine	NC	SP	[54]
Be	Natural waters	Chromazurol S and hexadecyltrimethylammonium bromide	GF	SPS	[55]
C	Biological materials	Ammonium and hexadecyltrimethylammonium diethyldithiocarbamates and sulfosalicylic acid	NC	SP	[56]
Ge	Natural waters	Phenylfluorone and Zephiramine	NC	SPS	[57]
Cu, Fe, Hg, Zn	Sodium chloride	Sodium diethyldithiocarbamate	CD	XRF	[58]
As, Cr, Pb, Th, Ti	Natural waters	Aluminum hydroxide	CD	XRF	[59]
Ti, V	Biological materials	Lead pyrrolidinedithiocarbamate	C	NAA	[60]
Au, Bi, Co, Cu, Fe, Hg, Nb, Ni, Pd, Se, Ta, Ti, V, W, Zr	Natural and sewage waters, biological materials	Sodium diethyldithiocarbamate, 1,10-phenanthroline, desferrioxamine B, and perfluorooctanoic acid	C	XRF	[62]
Ag	Sea water	Cobalt pyrrolidinedithiocarbamate	PC	ETAAS	[61]
Be, Cd, Cr, Cu, Ni, Pb	Natural waters	Zirconium hydroxide	CD	ETAAS	[63]
As, Cr,	Waters	Iron dibenzyldithiocarbamate	C	XRF	[64]
Cd, Co, Cu, Fe, Ni, Pb, Zn	River water	Molybdenum pyrrolidinedithiocarbamate	PC	XRF	[65]
As, Sn	Natural waters	Nickel pyrrolidinedithiocarbamate	G	ETAAS	[66]
Heavy and noble metals	Alloys	Sodium diethyldithiocarbamate and perfluorooctanoic acid	CD	XRF	[67]

Note: List of abbreviations:

Filter materials: PA polyamide, SiC $_{18}$ reversed-phase silica gels, C cellulose, PVC polyvinylchloride fiber, PTFE polytetrafluoroethylene, FPU foamed polyurethanes, PE polyethylene, PAN polyacrylonitrile fiber, CSDVB copolymer of styrene and divinylbenzene, NC nitrocellulose, GF glass fiber, CD cellulose derivatives, PC polycarbonate, and G glass. Preconcentration mode: B batch; D dynamic.

* Corresponding monomeric reagents that were used for the introduction of groups.

** Reagents that were used for the formation of poorly soluble forms.

For the modification of a polymer matrix with polydentate ligands that can alone saturate the coordination sphere of the element, the requirements of the high density of functional groups and the sufficient length of the spacer become less stringent. The ability to complexation in this case is controlled by the ability of the ligand to fill the coordination polyhedron of the adsorbed element, i.e., the conformational flexibility of the bonded polydentate ligand. In the limiting case, at the high conformational flexibility of this group and the matrix, the difference between the complexation of the monomer in the solution and the corresponding polymer must be substantially smaller.

Table 3. Capacity of sorption filters (μmol/g) for some elements [71]

Element	EDTA filters	IDA filters	MIDA filter
Pb	160	218	127
Cu(II)	336	202	106
Mg	160	109	109
Ca	325	109	109
Zn	209	157	69
Co(II)	197	171	53

Cellulose is most frequently used as the polymer matrix for the preparation of sorption filters with bonded groups [44–47, 70–74]. The reactivity of the hydroxyl groups of cellulose allows the synthesis of different complexing sorbents. Unlike the majority of synthetic polymers, cellulose exhibits high permeability and specific surface area, which simplifies its modification and improves the kinetic characteristics of sorbents based on cellulose. As seen in Table 3, cellulose filters with nitrogen-, oxygen-, and sulfur-containing functional groups, namely the groups of iminodiacetic acid (IDA filters) [44], methyliminodiacetic acid

(MIDA filters) [70], ethylenediaminetetraacetic acid (EDTA filters) [71–73], diethylenetriaminepentaacetic acid [45, 46], triethylenetetraaminepentaacetic acid [74], diethylenetriamine [45], dithiocarbamates [45, 47], chromotropic acid [48], sulfosalicylic acid [48], 8-hydroxyquinoline [47], 1-(2-hydroxyphenylazo)-2-naphthol [48], 4-(2-pyridylazo)resorcinol [48], 1-(2-pyridylazo)-2-naphthol [47], etc., were obtained.

IDA, MIDA, and EDTA filters were used for the group preconcentration of Ca, Cd, Co, Cu(II), Fe(III), Hg(II), Mg, Ni, Pb, and Zn from aqueous solutions [44, 70, 71]. The procedure of the synthesis of these filters included the preparation of chlorinated cellulose ($POCl_3$ in dimethylformamide, 60°C), which was subsequently treated with solutions of corresponding monomeric reagents. The comparison of the capacities of the obtained filters demonstrated (Table 3) that EDTA filters have the highest capacity and MIDA filters have the lowest capacity. Elements were preconcentrated on the filters in the dynamic mode at pH 3 from 100 mL of a solution (recovery was 60–100%, $K_{\mathrm{conc}} = 100$). In agreement with the stability constants of the complexes of metal ions with methyliminodiacetate and ethylenediaminetetraacetate groups of the filters, the recovery decreased from lead to calcium: Pb > Cu(II) > Mg ≅ Ca.

IDA filters were also used for the dynamic preconcentration of Co, Cr(III), Cu(II), Fe, Ga, Mn(II), Ni, Ti(IV), and Zn from urine. At pH 6.0–7.5, all of the elements were extracted quantitatively except chromium and manganese, for which the recovery was 73 and 57%, respectively [44].

Cellulose filters with chromotropic acid groups were proposed for the preconcentration of trace Cu(II), Fe(III), Hg(II), Sr, and Zn from water [48]. For the introduction of the functional group, *p*-aminophenylcellulose $R{-}NH_2$ was synthesized and treated with a mixture of HCl and $NaNO_2$ to obtain $R{-}N_2^+Cl^-$, and chromotropic acid was added to the reaction product. The concentration of the functional groups in the resulting sorbent was 0.2 mmol/g. It was demonstrated that for the sorption of iron(III) at pH 1.5 the equilibrium is attained within 10 s.

Fe(III), Th, Sc, Y, Zr(IV), and lanthanide ions were extracted from solutions obtained after the decomposition of monazite on cellulose filters with 2-hydroxypolyiminodiacetate groups. It was demonstrated that the elements can be desorbed from the filters with a 0.03 M CH_3COONa/HCl solution [75].

Filters with 1-(2-hydroxyphenylazo)-2-naphthol groups were proposed for the extraction of Co, Cu(II), Fe(III), Ni, Pb, and Zn from natural and sewage waters [48, 76]. The sorption capacity of the filters was 0.3–1.0 mmol/g.

An approach to the development of sorbents with increased efficiency was proposed; the approach consists in increasing the conformational flexibility of the bonded complexing ligand at the surface of the cellulose matrix [45, 46, 68]. Filters containing conformationally flexible amine (DETA filters) aminocarboxylic (DETATA filters), aminomethylphosphonic, and dithiocarbamate groups (DTC filters) were synthesized. It was demonstrated that at the surface of the sorbent elements form complexes analogous in composition and structure to the complexes of these elements with corresponding monomeric reagents in solutions. The characteristics of the proposed filters are presented in Table 4.

Table 4. Characteristics of sorption filters with conformationally flexible groups [45]

Filters	Capacity, μmol/g	Preconcentrated elements
DETA	0.1–0.2	As(V), Cr(VI), Mo, Se(VI), V(V), W
DETATA	0.3–0.7	Cd, Co, Cr(III), Cu(II), Fe(III), Mn(II), Ni, Pb, V, Zn, rare-earth elements
DTC	0.1–0.2	As(III), Cd, Cu(II), Hg(II), $HgCH_3$(I), Pb, Se(IV), Te(IV)

DETATA filters were found to be the most efficient (Table 4) [45, 46]. The range of elements efficiently extracted with DETATA filters in the dynamic mode is rather wide: about 33 elements. The main salt components of waters (alkali and alkaline earth metals) are removed by this preconcentration by 99%. Cd, Co, Cr(III), Cu(II), Fe(III), Mn(II), Ni, Pb, V(IV), and Zn are quantitatively extracted at pH 3–8 from 0.1–1.0 L of a solution at a flow rate of 10–14 mL/min. The preconcentration of metals from a sample of water with a volume of 500 mL on a DETATA filter with a diameter of 22 mm requires no more than 30 min; K_{conc} is up to 1.2×10^4. It was demonstrated that sodium (200 g/L), calcium (20 g/L), and magnesium (30 g/L) chlorides do not interfere with the quantitative extraction of trace elements.

DETA filters can extract heavy metals by two mechanisms [45, 47]. Copper, nickel, and some other elements form stable amine complexes and are extracted from neutral solutions. AsO_4^{3-}, CrO_4^{2-}, MoO_4^{2-}, SeO_4^{2-}, VO_3^-, and WO_4^{2-} are extracted from weakly acidic solutions by the ion-exchange mechanism. It was demonstrated that arsenic(V) can be quantitatively extracted on DETA filters from 50–1000 mL of a solution at pH 4. The recovery of arsenic drastically decreased in the presence of salt components even in insignificant concentrations (0.001 M $CaCl_2$ and NaCl).

Filters with dithiocarbamate groups were proposed for the preconcentration of As(III), Cd, Co, Cu(II), Fe(III), Hg(II), Ni, Zn, Pb, Se(IV), and Te(IV) from biological materials and natural and potable water. The elements were extracted at pH 2 from 1 M HCl in the presence of potassium iodide from a volume of 100 mL at a flow rate of the solution of 1 mL $min^{-1}cm^{-2}$ [45].

Unlike cellulose, synthetic polymers of linear and branched structures are less frequently used for the preparation of filters with bonded groups, although they are a convenient matrix for the synthesis of many complexing sorbents. Evidently, this is due to technological features: the difficulties in preparing filters with a developed surface.

It was demonstrated that Chelex-100 filters (polymer matrix, copolymer of styrene and divinylbenzene) containing complexing groups of iminodiacetic acid can be used for the extraction of Co, Cu(II), Mn(II), Ni, Pb, Sr, and Zn from waters [48, 49]. The capacity of the filter for zinc was 0.066 mmol. Elements were preconcentrated on double sorption filters from 200 mL at pH 7–8 and the flow rate of the sample < 10 mL/min; K_{conc} was 1250; the recovery was 68–92%. In the presence of sodium (43 mM), the recovery of lead and strontium decreased to 60–70% and the recovery of copper and manganese decreased to 55%; in the presence of calcium ions (50 μM), the recovery of all elements decreased to 3%.

For the extraction of uranium from natural waters, membranes based on the Chelex-100 sorbent were placed at the bottom of a vacuum filtering device and covered with a filter protecting the membrane from suspension particles, and 250 mL of a test solution was passed [30].

Polyethylene filters with groups of (1) *L*-aspartic acid, (2) 2-aminopyridine, (3) semicarbazide, (4) thiosemicarbazide, (5) thiourea, and (6) hydroxyl groups were used for the extraction of Cd, Co, Cr(III), Cu(II), Fe(III), Ni, and Pb from natural waters [50]. The introduction of complexing groups was preceded by the copolymerization of styrene and maleic anhydride on a polyethylene film in a nitrogen atmosphere under the action of γ-rays from ^{60}Co at 50°C. The capacity of the sorbents was 2.3 mmol/g for copper (1), 2.5 mmol/g for lead (2), 2.5 mmol/g for copper (3), and 2.4 mmol/g for iron (6). The elements were extracted from a solution heated to 70°C at pH 5. The filters were kept in the solution for 30–45 min. The structure and stoichiometry of the complexes that were formed in the filter phase were studied by infrared spectrometry.

Filters of polyacrylonitrile fiber with 8-hydroxyquinoline groups were used for the dynamic preconcentration of rare-earth elements from sea water [77]. The capacity of the filters for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu was 23–28 mmol/g. The elements were preconcentrated from 250–1500 mL of water at pH 3–8 and the flow rate of the sample of 10 mL/min; K_{conc} was 300; the recovery was above 95%. Na, K, Mg, and Ca chlorides at concentrations of 20, 0.5, 2.5, and 0.5 g/L, respectively, did not decrease the recovery of rare-earth elements. It was demonstrated that the elements can be desorbed from the filters with 5–10 mL of 1 M HCl/0.1 M HNO_3.

Thus, filters with covalently immobilized complexing and/or ionogenic groups are also used for the preconcentration of elements from solutions. Sorption filters based on cellulose with nitrogen-, oxygen-, and sulfur-containing functional groups are used most frequently. However, the synthesis of these filters is commonly difficult and laborious.

FILTERS WITH “MECHANICALLY” FIXED SORBENTS

The filters prepared by the introduction of finely dispersed sorbents into a particular, commonly polymer matrix are considered as a separate group. A large group of these filter sorbents is formed by “filled” sorbents, which are a nonwoven cloth of a neutral fibrous polymer, polyacrylonitrile, in which finely dispersed granules of ion exchanger with functional groups are “mechanically” retained [18, 19, 51, 78]. These sorbents are characterized by large specific surface area and good kinetic properties, which makes them particularly attractive for the preconcentration of elements in the dynamic mode. Filters of any size can be easily prepared of a cloth.

POLYORGS 33-N filters ($d = 2.5$ cm, $m = 0.06$ g, $l = 0.13$ cm) of fiber “filled” with a sorbent with amidoxime and hydrazidine groups were proposed in [51]. The thickness of fibers in the swollen sate was 30–100 μm; the particle size of the filler was 10–70 μm; the concentration of the filler in the fiber was 50%. The sorbent possessed anion-exchange and complexing properties: it quantitatively and selectively extracted platinum-group metals from 1 M HCl and Cd, Co, Cu(II), Ni, Pb, rare-earth and other elements from neutral solutions.

Filters of fiber “filled” with the POLYORGS 11-N sorbent with heterocyclic amine groups were proposed for the extraction of gold and platinum-group metals from solutions obtained after the decomposition of ores and rocks [78]. It was demonstrated that elements can be preconcentrated in the batch mode (sorption time 10–30 min) and in the dynamic mode (flow rate of the solution 20 mL/min). In the dynamic mode, Au, Pd, and Pt(IV) are extracted quantitatively, and Ir(IV) and Rh(III) are extracted by 40%. From 0.1–1 M HCl, this sorbent selectively extracted Au, Ir, Pd, Pt, and Rh in the presence of significant concentrations of Cu(II) (50 g/L), Co and Ni (100 g/L), Sn(II) (90 g/L), and Fe(III) (20 g/L).

Another group of filters was obtained by introducing finely dispersed particles of ion exchangers into cellulose fiber [8, 9]. Ion exchangers based on the copolymers of styrene with divinylbenzene and acrylic acid with divinylbenzene with acidic ($-SO_3H$, $-COOH$, $-OH$, and $-PO_3H_2$) or basic [$-N^+(CH_3)_3$] groups were used (Table 5). The disadvantages of these filters were low selectivity and capacity and a rather low equilibration rate [36, 52, 79].

Table 5. Cellulose filters with "mechanically" fixed ion exchangers [9]

Type	Ion exchanger	Functional group	Form	Capacity	
				mmol/g	mmol/cm^2
Amberlite SA-2	Amberlite IR-120	$-SO_3H$	Na	1.9	0.03
Amberlite SB-2	Amberlite IRA-400	$-N^+(CH_3)_3$	Cl	1.5	0.02
Amberlite WA-2	Amberlite IRC-50	–COOH	H	4.6	0.06
Amberlite WB-2	Amberlite IR-4B	$-NH_2$; >NH	OH	3.0	0.04

Gold(III) was extracted from chloride solutions obtained after the decomposition of different ores and rocks on cellulose filters containing the finely dispersed styrene–divinylbenzene copolymer with amino groups. The recovery of gold from 250 mL of a test solution was no higher than 30% [52]. Cu(II), Fe(III), Ni, and Zn were also adsorbed along with gold; these elements were desorbed from the filter with 50 mL of 2.4 M HCl.

Amberlite SA-2 cellulose filters with the introduced Amberlite IR-120 cation exchanger containing $-SO_3H$ groups were used for the preconcentration of Cu(II), Mn(II), Ni, Zn, and Pb from solutions obtained after the decomposition of biological materials [79]. The capacity of the filters for iron was 0.25 mequiv. The ions were extracted from the solution at pH 2–3.

It was demonstrated that Amberlite SA-2 and Amberlite WA-2 cellulose filters (with introduced cation exchangers) can be used for the dynamic preconcentration of Ag, Al, Ba, Bi, Ca, Cd, Co(II), Cr(III), Cu(II), Fe(III), La, Mn(II), Ni, Pb, Sr, Ti(IV), U(VI), Y, and Zn and Amberlite SB-2 and Amberlite WB-2 filters (with anion exchangers) can be used for the dynamic preconcentration of Br^-, $Cr_2O_7^{2-}$, $Fe(CN)_6^{4-}$, HPO_4^{2-}, I^-, MnO_4^-, MoO_4^{2-}, $PtCl_6^{2-}$, SO_4^{2-}, and VO_3^- in the analysis of alloys, metals, and biological materials [53]. The capacity of the Amberlite SA-2, Amberlite WA-2, Amberlite SB-2, and Amberlite WB-2 filters was 1.9–2.0, 4.6–5.0, 1.5–1.6, and 4.0–4.2 mequiv/g, respectively. Ions were extracted from 40 mL of a solution; the solution was multiply passed through the filter at a rate of 100 mL/min, and the number of cycles must be at least seven. Alkali metals suppressed the sorption of other cations; therefore, they were separated before the preconcentration. The selectivity series in the extraction of anions on anion-exchange filters was as follows: citrates > sulfates > oxalates > iodides > nitrates > chromates > bromides > thiocyanates > chlorides > formates > hydroxides > acetates.

The extraction of Ba, Cd, Cu(II), Fe(III), Hg(II), and Ni on analogous ion-exchange filters (Whatman P-81 and Amberlite SA-2, WA-2, and SB-2) was studied depending on the pH of the solution [36]. After the selection of the preconcentration conditions, these filters were suggested for use in the analysis of environmental samples. Uranium was preconcentrated from natural waters on Whatman P-81 filters.

Indicator papers obtained by the treatment of cellulose paper with precipitates of hexacyanoferrates(II, III) [80] and diethyldithiocarbamates [35] were used for the test determination of Ag, Bi, Co(II), Cu(II), Fe(II, III), and Hg(II) in biological and environmental materials. These precipitates were fixed on cellulose paper with a polymer film.

Other techniques of the "mechanical" application of sorbents to the surface of filters are also known. For example, a membrane filter was treated with metal sulfides (ZnS, MnS, CuS, and PbS) in the batch mode [30]. The thickness of the metal sulfide layer was 300–400 nm. Trace amounts of Ag, Bi, Cd, Cu(II), Hg(II), Pb, and Te(IV) were preconcentrated on these filters from natural and sewage waters.

Thus, filters with "mechanically" applied sorbents are used for the preconcentration of elements from solutions. However, complicated techniques are sometimes necessary for preparing these filters.

FILTERS FOR THE EXTRACTION OF SUSPENDED PARTICLES AND POORLY SOLUBLE FORMS OF ELEMENTS

In some cases analytes occur in aqueous test solutions in the form of poorly soluble compounds as solid particles or polymers. For example, in natural waters heavy metals can form soluble complexes and precipitate forming suspensions and bottom sediments. The compounds contained in natural water can be roughly divided into two categories: dissolved components and solid particles of organic and inorganic origin. Conventionally, all insoluble particles that are retained on a filter with a pore sized above 0.45 μm are assigned to suspended compounds [81]. Precipitation, which is among the oldest preconcentration methods, still finds use in the preconcentration of elements from solutions as poorly soluble and polymeric forms [8, 30].

Filters for the extraction of suspended forms of elements. Suspended forms are commonly separated by membrane filtration [5, 82, 83] (Table 6). This approach to the determination of suspended particles of trace elements is widespread, although ultrafiltration involves high risks of both sample contamination and losses of elements.

Table 6. Determination of the forms of elements (trace amounts) in natural waters with the use of membrane filtration [83]

Water	Elements	Filters, pore size	Determination method
River, sea	Hg, Zn, Co	Nuclear-track filters, 0.45 μm	Nuclear-physics methods
River, sea	Aluminum	Polycarbonate filters, 0.1–0.4 μm	CP, AAS
River	32 elements	Nuclear filters, 0.05 and 0.45 μm	NAA
River	Fe, Al	Polymer filters, 0.1 and 1.4 μm	ICP AES

Preconcentration of elements on filters as polymeric and poorly soluble forms. For the preconcentration and separation of elements as high-molecular forms, aqueous solutions of different water-soluble polymers (polyethyleneimine, polyethylene glycol, poly-*N*-vinylpyrrolidone, polyacrylic acid, etc.) were introduced into the analyzed sample [83]; the concentration of the polymer in the solution was commonly no higher than 1–4%. On passing the obtained solution through a polymer membrane, high-molecular complexes of elements are retained at its surface or in a minimum volume of the aqueous solution over the surface of the membrane.

The preconcentration of trace impurities by precipitation as poorly soluble forms is rarely used: the concentration of elements is so low that the solid phase is not formed [30]. For this purpose, it is more reasonable to use coprecipitation with organic or inorganic collectors. Trace elements were preconcentrated from solutions with the use of poorly soluble ion pairs consisting of a bulky organic cation and/or anion [52–57, 79–84]; complexing compounds (low- and high-molecular) [58, 85–88]; some indifferent compounds [30]; and hydroxides, sulfides, sulfates, chlorides, and phosphates [30, 59, 89]. The advantage of organic coprecipitants over inorganic consists in their higher efficiency and selectivity and the simplicity of the subsequent processing of the concentrate: an organic compound can be easily burned or dissolved in an organic solvent [30]. Table 2 presents examples of organic and inorganic collectors proposed for the preconcentration of elements on filters.

The following techniques of coprecipitation are used: the introduction of a macrocomponent and the corresponding reagent–precipitant (either inorganic or organic), partial precipitation of the matrix (macrocomponent is present in the sample), the introduction of an organic compound in an organic solvent miscible with water (after dilution with water, the coprecipitant precipitates carrying complexes of trace elements with it). Depending on the physicochemical properties of the components and experimental conditions, coprecipitation proceeds through the sorption of the element at the surface of the collector, the formation of isomorphous mixed crystals and mixed chemical compounds, occlusion, and mechanical capture, and all these processes can occur simultaneously [30].

Elements are most frequently coprecipitated with the use of water-insoluble precipitates with a large surface area, which are commonly obtained in the batch mode. The selection of the collector also accounts for the requirements of the method for the subsequent determination, e.g., collectors that do not introduce spectral interferences are preferable in atomic-emission analysis. After finishing the formation of precipitates, the solid phase is separated by filtration.

The precipitated forms of elements are extracted from solutions using different filters of natural and synthetic polymers: cellulose [90], nitrocellulose [61], polycarbonate [61], ceramic [91], polytetrafluoroethylene [92], fused silica [93], and glass [94].

A series of works [54–57, 84] deals with the precipitation of elements from solutions as ion pairs formed by complex ions of elements with organic reagents and surfactants. For the determination of arsenic, silicon, and phosphorus, ion pairs of molybdoarsenic heteropoly acid with tetrapentylammonium chloride, molybdosilicic acid with Malachite Green, and molybdophosphoric acid with dodecyltrimethylammonium chloride, respectively, were precipitated and extracted on a filter [54]. Analogously, Chromazurol S and hexadecyltrimethylammonium bromide were used for the preconcentration of beryllium [55], 1-(2-pyridylazo)-2-naphthol and dodecyltrimethylammonium chloride were used for the preconcentration of cadmium [54], nitroso-R salt and benzyldimethyltetradecylammonium bromide (Zephiramine) were used for the preconcentration of cobalt [54], phenylfluorone and hexadecyltrimethylammonium chloride were used for the preconcentration of chromium(VI) [84], diethyldithiocarbamate and hexadecyltrimethylammonium chloride were used for the preconcentration of copper(II) [56], 4,7-diphenyl-1,10-phenanthrolinedisulfonate and Zephiramine were used for the preconcentration of iron(II) [54], phenylfluorone and Zephiramine were used for the preconcentration of germanium(IV) [57], potassium thiocyanate and Malachite Green were used for the preconcentration of palladium [54], and Arsenazo III and cationic surfactants were used for the preconcentration of uranium(VI) [54]. The concentration coefficients in the extraction of the elements were 10–400. The precipitates were separated from the solutions by filtration through a nitrocellulose filter with a pore diameter of 0.2–0.45 μm. It was demonstrated that filter concentrates can be dissolved in organic solvents (dimethylformamide, dimethyl sulfoxide, and 2-methoxyethanol) or in concentrated inorganic acids.

The majority of works describing the use of complexing coprecipitants for the extraction of trace com-

Table 7. Effect of the composition of filters and the pore size on the recovery (*R*, %) of elements in the presence of 3-hydroxy-4-[(6-hydroxy-*m*-tolyl)azo]naphthalenesulfonic acid [102]

Filters (diameter, mm; pore size, μm)	Co(II)	Cr(III)	Cu(II)	Fe(III)	Pb
Nitrocellulose (47; 0.45)	97 ± 2	100 ± 2	100 ± 1	100 ± 1	100 ± 2
Nitrocellulose (20; 0.25)	96 ± 3	98 ± 3	95 ± 2	99 ± 3	98 ± 2
Cellulose acetate (47; 0.45)	78 ± 3	100 ± 3	100 ± 2	95 ± 3	100 ± 2
Cellulose ester (47; 0.45)	56 ± 2	100 ± 1	90 ± 2	100 ± 2	100 ± 3

ponents from solutions deal with the use of dithiocarbamates [30, 58, 85–88]. Ions of many elements form stable complexes with dithiocarbamates; hence, dithiocarbamates of primary and secondary amines, diamines, and hydrazines and dithiocarbamate esters were used for the extraction [85]. Commonly elements were precipitated in the batch mode, which is accompanied by the sorption of dithiocarbamates at the walls of glassware and leads to long-term and laborious experiments. In our opinion, these disadvantages can be surmounted by performing the experiment in the dynamic mode, which makes it possible to form insoluble precipitates in the flow directly before the filter. This approach holds promise as experimentally confirmed in several works, which demonstrated that hydrophobic compounds of elements formed in the flow can be extracted on filters [95], on microcolumns [96], and in a knotted reactor [4, 97, 98].

A method was proposed in [95] for the preconcentration of As(III), Bi, Cd, Co, Cu, Fe(III), Ni, Pb, Se(IV), V(V), and Zn from water and soil on cellulose and hydrophobized filters as pyrrolidinedithiocarbamate (PDTC) complexes obtained in the flow after mixing the flows of the reagent (0.7–1.0 mL/min) and the sample (3.0–3.2 mL/min). It was found that elements are nearly quantitatively ($R = 90–100\%$) extracted from 50–100 mL of a sample at the total flow rate up to 25 mL/min at pH 5 (Cd, Co, Cu, Fe(III), Ni, Pb, V(V), and Zn) and from 2 M HCl (As(III), Bi, and Se(IV)) at the concentration of the reagent of 0.1%; $K_{\text{conc}} = (1–2) \times 10^3$. The mechanism of the extraction of PDTC complexes on cellulose and modified cellulose filters was studied. It was demonstrated that small amounts of PDTC complexes (0.1–0.5 μg) are adsorbed at the surface of cellulose and paraffinized filters. The extraction of relatively large (5–50 μg) amounts of elements is due to the mixed sorption and filtration mechanism.

Sodium pyrrolidinedithiocarbamate was used for the preconcentration of Cu(II), Fe(III), Ni, Pb, and Zn from rain water. The recovery of elements was 100%; $K_{\text{conc}} = 1000$ [86]. The coprecipitation of elements was performed from 25 mL of a sample at pH 3–7 by the addition of 500 μg of cobalt. It was demonstrated that the change in the pore size of nuclear filters from 0.2 to 0.45 μm and holding PDTC complexes of metals in the solution for 100 h does not affect the efficiency of the extraction of elements on the filter.

A method was proposed for the preconcentration of Cu(II), Hg(II), V(IV), and Zn on filters from natural waters [87]. The quantitative extraction of PDTC complexes ($R = 92–95\%$) on a filter was attained from 100 mL of a sample at pH 4 after the addition of 200 μg of iron(III).

For the preconcentration of 0.01–10 mg/L Cd, Co, Hg(II), Pb, and Zn from a saturated sodium chloride solution, 20 mL of a freshly prepared 1% aqueous solution of sodium diethyldithiocarbamate was added to 250 mL of the initial solution [58]. The precipitate was held for 10 min and then separated by filtration through a membrane filter with a pore size of 0.6 μm.

Uranium(VI) was preconcentrated from 500 mL of river water as dibenzyldithiocarbamate (DBDTC) at pH 4 [88]. In this case, up to 15% of uranium is not extracted in the presence of humic acids, and up to 50% is not extracted in the presence of fulvic acids. For the quantitative extraction of uranium ($K_{\text{conc}} = 94\%$), a water sample was irradiated with an ultraviolet lamp and iron(III) was introduced to precipitate Fe(DBDTC)_3. Alkali and alkaline-earth metals, chloride, and sulfate (up to 100 mg/L) did not affect the extraction of uranium.

Elements were also precipitated and coprecipitated from solutions on filters with the use of other complexing reagents: thionalide [99], 1-(2-pyridylazo)-2-naphthol [100], dithizone [30], 8-hydroxyquinoline [101], bathocuproine [30], dimethylglyoxime [30], α-benzyldioxime [30], and 3-hydroxy-4-[(6-hydroxy-*m*-tolyl)azo]naphthalenesulfonic acid [102]. The last reagent was used for the extraction of Co, Cr(III), Cu(II), Fe(III), and Pb from mineral, river, and tap waters; $K_{\text{conc}} = 150–250$ was attained [102]. The reagent was introduced into 30–50 mL of a sample at pH 8, within 10 min the precipitate was filtered off and dissolved in 0.5 mL of concentrated HNO_3 at 80°C. The effect of the composition of filters and the pore size on the efficiency of the extraction of elements was demonstrated (Table 7). Alkali and alkaline-earth metals, chloride, and sulfate (50 mg/L) did not interfere with the quantitative extraction of elements.

Cd, Cu(II), Fe(III), Mn(II), and Zn ions were preconcentrated on filters from natural waters as 1-(2-pyridylazo)-2-naphthol complexes. After the introduction of the reagent into 20–1000 mL of a sample at pH 10, 50 μg of Ni was added [103].

Elements were also preconcentrated on filters by coprecipitation with inorganic precipitates, although the efficiency of the extraction in this case was commonly lower than in the case of the use of organic coprecipitants. Thus, aluminum hydroxide was used for the coprecipitation of As(V), Cr(III), Pb, Th, and Ti(IV) from natural waters [59]. Coprecipitation was performed at pH 7.3 from 200 mL of a sample in the presence of 1 mg of the collector for 1 h; the recovery was 98% (Cr, Pb, Th, and Ti) and 50% (As, Cu, U, and Zn); $K_{\text{conc}} = 2 \times 10^4$. This method is unsuitable for the preconcentration of elements from sea water, because alkaline-earth metals contained in large concentrations also transfer to the precipitate.

Sulfides are undoubtedly the most efficient among inorganic collectors [89]. For example, nanogram amounts of cadmium were coprecipitated as sulfide from river and sea waters at pH 4 from 200 mL of a sample. In this case, the collectors were sulfides of elements that occur in the solution in higher concentrations than cadmium: iron, copper, etc. The precipitate was filtered off on a nitrocellulose filter with a pore size of 0.45 μm and dissolved in 2 mL of 0.05 M HNO_3.

Thus, the precipitation and especially coprecipitation of elements with organic and inorganic collectors and the subsequent separation of the precipitates on filters provide high concentration coefficients ($\geq 10^4$) and the possibility of the group and individual preconcentration of elements in the batch and dynamic modes; the selective extraction of elements is attained by the selection of corresponding reagents and coprecipitation conditions. An undoubted advantage of this preconcentration method is the possibility to extract elements in a wide concentration range, because the “capacity” of filters in this case is unlimited.

The efficiency of the preconcentration of elements on filters of different types was estimated by comparing the concentration coefficients, the capacities of filters, and the time of preconcentration. The largest concentration coefficients ($K_{\text{conc}} = 500–10^4$) were attained in the extraction of elements on filters with bonded groups and on filters that extract previously obtained forms of elements. Weak fixing of the reagent on the filter on its noncovalent immobilization precludes the preconcentration of elements from large volumes of solutions (above 50–100 mL), which leads to smaller counteraction coefficients ($K_{\text{conc}} \approx 20–400$). When desorption or the dissolution of the filter concentrate was performed, the concentration coefficients were smaller ($K_{\text{conc}} = 7–400$) than in the direct determination of elements in the filter phase because of the use of excess solvent irrespective of the type of the filter; the time of the determination and the probability of losses of elements increased.

It was demonstrated that the quantitative extraction of elements from solutions (R = 90–100%) can be attained on filters of all types.

The sorption capacities of the filters of different types could be hardly compared because these data are not presented in many works. The filters that extract the forms of elements previously obtained in the solution are not characterized by sorption capacity. The maximum amounts of elements extracted on filters with noncovalently and covalently immobilized reagents in the majority of cases are comparable and vary in the range 50–2000 μg per filter.

The time of the preconcentration of elements on filters is commonly 5–30 min.

METHODS FOR THE DETERMINATION OF ELEMENTS IN ENVIRONMENTAL AND TECHNICAL MATERIALS INCLUDING PRECONCENTRATION ON FILTERS

Many different combined methods using filters were proposed for the determination of elements in environmental and biological materials and technical solutions. After preconcentration, elements were determined directly on the filters by XRF spectrometry, neutron activation analysis (NAA), and spectrophotometry (SP) [13, 57, 62, 104–106]; in the other cases filter concentrates were decomposed or elements were desorbed. In the resulting solutions, elements were determined by atomic-absorption spectrometry (AAS), electrothermal atomic-absorption spectrometry (ETAAS), and inductively-coupled plasma atomic-emission spectrometry (ICP AES) (mass spectrometry (MS)) [54, 107–109].

Sorption–X-ray fluorescence methods. The development of compact and relatively inexpensive XRF spectrometers provided the wide use of this multielement analytical method for the determination of elements in soils, geological samples, plant materials, and many other samples. However, the sensitivity of the XRF method is insufficient for the determination of trace elements in waters and solutions, and the preconcentration is required.

The performance characteristics of the XRF determination of elements is substantially affected by the composition and quality of the surface of emitter samples, which are responsible for the absorption and scattering of the primary and fluorescence radiation. The majority of sorption–XRF methods for the determination of elements involve conventional techniques for the preparation of concentrate samples: molding pellets [36] and applying a layer of the sorbent concentrate to membrane or cellulose filters [110]. These procedures failed to provide a uniform distribution of the concentrate over the surface and the bulk of the sample; as a result, relatively thick emitters were obtained, and the sensitivity of the combined method was decreased. To improve the sensitivity of the determination, thin-layer methods of analysis are finding increasing application

Table 8. Detection limits (%) of noble metals in different matrices by the X-ray fluorescence method [36]

Element	Molybdenum oxide	Niobium oxide	Nickel sulfide	Ion exchanger	Cellulose	Sorption filter	Polymer sorbents
Au	–	–	–	3.6×10^{-3}	6.0×10^{-5}	1.0×10^{-5}	1.3×10^{-3}
Pd	2.0×10^{-3}	1.0×10^{-3}	6.0×10^{-4}	1.5×10^{-3}	1.2×10^{-4}	4.0×10^{-5}	4.2×10^{-4}
Pt	4.8×10^{-4}	9.0×10^{-4}	2.4×10^{-3}	5.3×10^{-3}	6.0×10^{-5}	2.0×10^{-5}	1.3×10^{-3}
Rh	8.0×10^{-3}	4.0×10^{-3}	7.0×10^{-4}	1.7×10^{-3}	1.0×10^{-4}	9.0×10^{-5}	3.6×10^{-4}
Ru	7.0×10^{-4}	6.0×10^{-4}	6.8×10^{-4}	1.7×10^{-3}	8.0×10^{-5}	5.0×10^{-5}	3.5×10^{-4}

[1]. Therefore, of great interest are the works where elements are preconcentrated using "light" (cellulose) filters, which provide larger concentration coefficients (above 10^4) [36] (examples are given in Table 8). However, in this case adequate reference samples can be hardly prepared [111]. The peculiarities of the formation of the analytical signal in the XRF determination of elements extracted on filters by different techniques with the distribution of elements over the surface and in the bulk of the filters were studied in [112]. It was demonstrated that the sensitivity of the XRF determination with the extraction of elements at the surface of cellulose filters is 1.2–1.6 times higher than at the uniform distribution of elements in the bulk of the same filters.

A sorption–X-ray fluorescence method was developed for the determination of As(III), Bi, Cd, Co, Cu, Fe(III), Ni, Pb, Se(IV), V(V), and Zn in waters and soil extracts [95, 113]. Elements were extracted from solutions on cellulose filters as PDTC complexes formed in the flow before the filter. The calibration plots are linear in the range 5–50 μg of the element per filter. The detection limits of elements in waters calculated from the 3*s*-value at the preconcentration from 100 mL of a solution were 0.001–0.040 mg/L; RSD was no higher than 10%.

The XRF method was also used for the determination of Co(II), Cu(II), Fe(III), Ni, Zn, and Pb in rain water after the extraction of elements on filters as PDTC complexes [86]. The detection limits of elements in waters were 0.6–1.7 μg/L; RSD < 4%.

Cu(II), Fe(III), Mn(II), Ni, and Zn ions in biological materials were determined by the XRF method after the decomposition of organic samples, precipitation of diethyldithiocarbamates, and their extraction on filters [104]. The determination of elements was performed by the K_α lines; the detection limits were 0.6–1.7 μg per filter; RSD was no higher than 7%.

An XRF method was proposed for the determination of Au, Bi, Co(II), Cu(II), Fe(II), Hg(II), Ni, Pd, Ti(IV), V(V), and W(VI) in waters. Sodium diethyldithiocarbamate, 1,10-phenanthroline, desferrioxamine B, and perfluorooctanoic acid were used for the preconcentration of elements on filters [62]. The concentration coefficient was 500, which provided low detection limits (1×10^{-8} M) of elements by the XRF method. The calibration plots were linear in the concentration range 5×10^{-7}–1×10^{-5} M; RSD was no higher than 5%.

As(V), Cr(III), Pb, Th, and Ti(IV) ions were determined in natural waters by the XRF method after the coprecipitation with aluminum hydroxide and the separation of the precipitate on a filter [59]. The detection limits of elements were 0.2–0.8 μg/L; RSD was no higher than 6%.

A sorption–XRF method was developed for the determination of gold and platinum in chloride solutions obtained after the decomposition of ores and rocks; the method includes the preconcentration of the chloride complexes of elements on cellulose filters with noncovalently immobilized trioctylamine [38]. The calibration plots are linear in the range 5–50 μg of the element per filter. The detection limits of elements in ores and rocks calculated by the 3*s*-value were 3×10^{-5}–8×10^{-5}%; RSD ≤ 8%.

Sorption–spectrophotometric methods. The sensitivity and reproducibility of the determination of small amounts of elements by sorption–spectrophotometric methods can be improved only by the elimination of the effects of light absorption and scattering by the concentrate sorbent, nonuniformity of the distribution of sorbent particles in size and shape, and the different thickness of the absorbing layer. Many of the above problems were solved by the replacement of powdered sorbents with sorption filters. Many sorption–spectrophotometric methods for the determination of elements in solutions involving preconcentration on filters were proposed in recent years. In these methods, photometric reagents also participate in the preconcentration of elements and provide the formation of colored compounds on filters. The main advantages of these methods are their high sensitivity and rapidness, the possibility of the visual detection of the analytical signal, and the simplicity of the selection of the reagent.

It was demonstrated that the use of azorhodanines is a promising technique for obtaining colored compounds in the solid phase [13–15]. Rapid and sensitive methods for the determination of Ag, Au, Cu(II), Hg(II), Pd, and Pt(IV) in solutions with the detection limits 1–3 μg/mL were developed with the use of membranes and disks of polyamide filled with a finely dispersed cation exchanger and impregnated with azorhodanines and azothiopropiorhodanines [13]. The change in the color of disks was estimated visually (test method) and by the change in diffuse reflection coefficients (diffuse reflectance spectrometry).

Germanium(IV) was determined in natural waters by the spectrophotometric method after obtaining the colored complex of phenylfluorone in the presence of Zephiramine in the filter phase [57]. The calibration plots are linear at the amounts of germanium 0.1–0.26 μg; the detection limit of germanium was 1.9 ng; RSD was no higher than 1.3%.

A sorption–spectrophotometric method was developed for the determination of beryllium in natural waters with the preliminary coprecipitation of the element with Chromazurol S and hexadecyltrimethylammonium bromide and the extraction on a filter [55]. The concentration of beryllium in waters was 0.12–3.52 μg/L; the detection limit was 13 ng/L.

It was demonstrated that palladium can be determined by the sorption–spectrophotometric method in solutions of complex composition with the use of cellulose filters impregnated with trioctylamine and the subsequent formation of the colored compound of palladium with 4-(2-pyridylazo)resorcinol on the filter [114]. Palladium was determined on filters by diffuse reflectance spectrometry, by chromaticity measurements, and using a test scale. The relative standard deviation of the results of the determination of palladium was no higher than 5% in the entire linearity range of the calibration plot (0.5–10.0 μg of palladium per filter). The absolute detection limit of palladium with the use of diffuse reflectance spectrometry was 0.08 μg of palladium per filter. For the visual detection of the analytical signal with the use of a test scale, the minimum reliably detected amount of palladium on the filter was 0.5 μg.

A sorption–spectrophotometric method was proposed for the determination of palladium and uranium(VI) in solutions [18, 19]. Elements were preconcentrated on disks of polyacrylonitrile fiber filled with a strongly acidic cation exchanger with immobilized *p*-nitrosodiethylaniline. The detection limit of palladium in solutions was 5×10^{-9} M.

Sorption–neutron-activation methods. In combined analytical methods including off-line sorption preconcentration, it was found more preferable to use filter sorbents rather than the same sorbents as powders. This was caused by the necessity of performing different operations with the obtained concentrates before the determination stage, e.g., drying, transferring into the detection device, treatment with reagents, etc. These advantages of filters over powdered sorbents clearly manifest themselves in sorption–neutron-activation methods for the determination of elements: filter concentrates are more conveniently packed for the subsequent irradiation and divided into parts, the probability of losses of the irradiated material is decreased, etc.

Titanium(IV) and vanadium(V) were determined in biological materials by the neutron-activation method after preliminary coprecipitation with $Pb(PDTC)_2$ and $Bi(PDTC)_3$ and extraction on filters [60]. The amount of elements was determined by measuring the γ-radiation of short-lived isotopes ^{51}Ti and ^{52}V. The analytical ranges were 105–130 ng/mL for Ti and 1.3–6.5 ng/mL for V; the detection limits were 70 and 0.7 ng/mL, respectively.

As(III, V), Se(IV, VI), and Sb(III, V) were determined by the sorption–NAA method in natural waters [105]. Elements were coprecipitated with $Pb(PDTC)_2$, and the resulting precipitate was filtered off. The detection limits of elements in solutions were 0.1–1.0 ng/L.

Sorption–atomic-absorption methods. AAS methods (with flame and electrothermal atomization) are also used for the determination of elements after desorption or after the decomposition of the filter concentrate and directly in the filter concentrate with the use of electrothermal atomization.

A method was proposed for the determination of cadmium in biological materials, waters, soils, and rocks; the method includes the preconcentration of cadmium by coprecipitation as the diphenylguanidinium salt of the cadmium complex of Cadion S and 2,4-dinitroaniline [81]. After ashing the filter concentrate and dissolving the salt residue, cadmium was determined by atomic-absorption spectrometry.

Silver was determined in sea water by the Sorption–atomic-absorption method including coprecipitation with cobalt pyrrolidinedithiocarbamate and the extraction of the precipitate on a polycarbonate filter [61]. Silver was determined in the solution after the treatment of the filter with the precipitate with 210 μL of concentrated HNO_3. The detection limit of silver was 0.1 ng/L.

A method was developed for the determination of chromium(VI) in natural and tap waters [54]. Chromium was coprecipitated with phenylfluorone and cetyltrimethylammonium bromide. The resulting precipitate was collected on a nitrocellulose filter and dissolved in 2-methoxyethanol. Chromium was determined by atomic-absorption spectrometry. The linearity range of the calibration plot was 10–60 μg/L; the detection limit of chromium in waters was 0.06 μg/L at $K_{\mathrm{conc}} = 20$.

Co(II), Cr(III), Cu(II), Fe(III), and Pb were preconcentrated from mineral, river, and tap waters using 3-hydroxy-4-[(6-hydroxy-*m*-tolyl)azo]naphthalenesulfonic acid; the precipitate was filtered off and dissolved in 0.5 mL of concentrated HNO_3 at 80°C; elements were determined by atomic-absorption spectrometry [102]. The detection limits were 0.06–2.5 μg/L; RSD was no higher than 10%.

Thus, the preconcentration of elements on filters is used in many combined and hybrid analytical methods. The advantage of this preconcentration method over the others are particularly clear when elements are determined by the X-ray fluorescence and spectrophotometric methods. In this case, the preparation of thin-layer samples provides an increase in the sensitivity of the determination not only because of preconcentration, but also because of the minimization of the absorption and scattering of radiation.

REFERENCES

1. Kalinin, B.D. and Plotnikov, R.I., *Zavod. Lab.*, 1996, vol. 64, no. 2, p. 16.
2. Kashirin, I.A., Ermakov, A.I., Malinovskiy, S.V., *et al.*, *Appl. Radiat. Isot.*, 2000, vol. 53, p. 303.
3. Zolotov, Yu.A., Dorokhova, E.N., Fadeeva, V.I., *et al.*, *Osnovy analiticheskoi khimii* (Basic Analytical Chemistry), vol. 2: Metody khimicheskogo analiza (Methods of Chemical Analysis), Moscow: Vysshaya Shkola, 2000.
4. Fang, Zh., *Flow Injection Separation and Preconcentration,* New York: Weinheim, 1993.
5. Mulder, M., *Basic Principles of Membrane Technology*, Kluwer, 1991. Translated under the title *Vvedenie v membrannuyu tekhnologiyu*, Moscow: Mir, 1999.
6. Vol'kenshtein, M.V., *Biofizika* (Biophysics), Moscow: Nauka, 1988, p. 104.
7. Thurman, E.M. and Mills, M.S., *Solid-Phase Extraction: Principles and Practice*, Chemical Analysis: A Series of Monographs of Analytical Chemistry and Its Application, Ed. Winefordner, J.D., Ed., New York: Wiley, 1998, vol. 147.
8. Mizuike, A., *Enrichment Techniques for Inorganic Trace Analysis*, Berlin: Springer, 1983. Translated under the title *Metody kontsentrirovaniya mikroelementov v neorganicheskom analize*, Moscow: Khimiya, 1986.
9. Marhol, M., *Ion Exchangers in Analytical Chemistry*, Prague: Academia, 1982. Translated under the title *Ionoobmenniki v analiticheskoi khimii*, Moscow: Mir, 1986.
10. Brykina, G.D., Krysina, L.S., and Ivanov, V.M., *Zh. Anal. Khim.*, 1988, vol. 43, no. 9, p. 1547.
11. Savvin, S.B. and Mikhailova, A.V., *Zh. Anal. Khim.,* 1996, vol. 51, no. 1, p. 49 [*J. Anal. Chem.* (Engl. Transl.), 1996, vol. 51, no. 1, p. 42].
12. Yoshimura, K. and Waki, H., *Talanta*, 1985, vol. 32, no. 5, p. 345.
13. Gur'eva, R.F. and Savvin, S.B., *Usp. Khim.,* 1998, vol. 67, no. 3, p. 236.
14. Gur'eva, R.F. and Savvin, S.B., *Zh. Anal. Khim.*, 2000, vol. 55, no. 3, p. 280 [*J. Anal. Chem.* (Engl. Transl.), 2000, vol. 55, no. 3, p. 249].
15. Gur'eva, R.F. and Savvin, S.B., *Zh. Anal. Khim.*, 1997, vol. 52, no. 3, p. 247 [*J. Anal. Chem.* (Engl. Transl.), 1997, vol. 52, no. 3, p. 217].
16. Trutneva, L.M., Shvoeva, O.P., and Savvin, S.B., *Zh. Anal. Khim.*, 1989, vol. 44, no. 10, p. 1804.
17. Shvoeva, O.E., Trutneva, L.M., and Savvin, S.B., *Zh. Anal. Khim.*, 1994, vol. 49, no. 6, p. 574.
18. Shvoeva, O.P., Trutneva, L.M., Likhonina, E.A., and Savvin, S.B., *Zh. Anal. Khim.*, 1991, vol. 46, no. 7, p. 1301.
19. Shvoeva, O.P., Trutneva, L.M., and Savvin, S.B., *Zh. Anal. Khim.*, 1989, vol. 44, no. 11, p. 2084.
20. Lisichkin, G.V., Kudryavtsev, G.V., Serdan, A.A., Staroverov, S.M., and Yuffa, A.Ya., *Modifitsirovannye kremnezemy v sorbtsii, katalize i khromatografii* (Modified Silicas in Sorption, Catalysis, and Chromatography), Moscow: Khimiya, 1986.
21. Zolotov, Yu.A., Ivanov, V.M., and Amelin, V.G., *Khimicheskie test-metody analiza* (Chemical Test Methods of Analysis), Moscow: Editorial URSS, 2002.
22. Morozko, S.A. and Ivanov, V.M., *Zh. Anal. Khim.*, 1996, vol. 51, no. 6, p. 631 [*J. Anal. Chem.* (Engl. Transl.), 1996, vol. 51, no. 6, p. 580].
23. Mojtaba Shamsipur and Farhad Raoufi, *Mikrochim. Acta*, 2001, vol. 137, p. 163.
24. Yadollah Yumini, Naader Alizadeh, and Mojtaba Shamsipur, *Anal. Chim. Acta*, 1997, vol. 355, p. 69.
25. Mojtaba Shamsipur and Mohammad Hossein Mashhadizadeh, *Fresenius' J. Anal. Chem.*, 2000, vol. 367, p. 246.
26. Mojtaba Shamsipur, Armen Avanes, Mohammed Kazem Rofouei, *et al.*, *Talanta*, 2001, vol. 54, p. 863.
27. Zahra Ghasemi, Fatemeh Basiripour, Tahereh Poursaberi, *et al.*, *Int. J. Environ. Anal. Chem.,* 2001, vol. 81, p. 233.
28. Mojtaba Shamsipur, Ali Reza Ghiasvand, and Yadollah Yamini, *Anal. Chem.*, 1999, vol. 71, p. 4892.
29. Dmitrienko, S.G., *Doctoral (Chem.) Dissertation*, Moscow: Moscow State Univ., 2001.
30. Zolotov, Yu.A. and Kuz'min, N.M., *Kontsentrirovanie mikroelementov* (Preconcentration of Microelements), Moscow: Khimiya, 1982.
31. Amelin, V.G., *Doctoral (Chem.) Dissertation*, Vladimir: Vladimir State Univ., 1998.
32. Klenkova, N.I., *Struktura i reaktsionnaya sposobnost' tsellyulozy* (The Structure and Reactivity of Cellulose), Leningrad: Nauka, 1976.
33. Amelin, V.G. and Ivanov, V.M., *Zh. Anal. Khim.*, 2000, vol. 55, no. 4, p. 411 [*J. Anal. Chem.* (Engl. Transl.), 2000, vol. 55, no. 4, p. 367].
34. Jiles, C., in *Adsorption from Solution at the Solid–Liquid Interface*, Parfitt, G.D. and Rochester, C.H., Eds., London: Academic, 1983. Translated under the title *Adsorbtsiya iz rastvorov na poverkhnosti tverdykh tel*, Moscow: Mir, 1986, p. 403.
35. Amelin, V.G., *Zh. Anal. Khim.*, 1999, vol. 54, no. 10, p. 1088 [*J. Anal. Chem.* (Engl. Transl.), 1999, vol. 54, no. 10, p. 963].
36. Shestakov, V.A. and Petrukhin, O.M., *Zh. Anal. Khim.,* 1987, vol. 42, no. 6, p. 965.
37. Gordeeva, V.P., Ermakov, A.I., and Tsizin, G.I., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2003, vol. 44, no. 3, p. 183.
38. Pisareva, V.P., *Cand. Sc. (Chem.) Dissertation*, Moscow: Moscow State Univ., 2003.
39. Sidakov, T.A., Lobanov, F.I., Stefanov, A.V., and Makarov, N.V., *Zavod. Lab.*, 1985, vol. 51, no. 9, p. 12.
40. Saito, T., *Talanta,* 1994, vol. 41, no. 5, p. 811.
41. Oleschuk, R. and Chow, A., *Talanta*, 1998, vol. 45, p. 1235.
42. Oleschuk, R. and Chow, A., *Talanta*, 1997, vol. 44, p. 1371.

43. Braun, T. and Abbas, M.N., *Anal. Chim. Acta*, 1984, vol. 160, p. 277.
44. Ping, L., Matsumoto, K., and Fuwa, K., *Anal. Chem.*, 1983, vol. 55, p. 1819.
45. Tsizin, G.I., Seregina, I.F., Sorokina, N.M., *et al.*, *Zavod. Lab.*, 1993, vol. 59, no. 10, p. 1.
46. Varshal, G.M., Velyukhanova, T.K., Pavlutskaya, V.I., *et al.*, *Int. J. Environ. Anal. Chem.*, 1994, vol. 57, p. 107.
47. Smits, J., Nelissen, J., and Van Grieken, R., *Anal. Chim. Acta*, 1979, vol. 111, p. 215.
48. Myasoedova, G.V. and Savvin, S.B., *Khelatoobrazuyushchie sorbenty* (Chelating Sorbents), Moscow: Nauka, 1984.
49. Van Grieken, R.E., Bresseleers, C.M., and Vanderborght, B.M., *Anal. Chem.*, 1977, vol. 49, no. 9, p. 1326.
50. Abd El-Rehim, H.A., Hegazy, E.A., El-Hag, and Ali , A., *React. Funct. Polym.,* 2000, vol. 43, p. 105.
51. Zakharchenko, E.A., Myasoedova, G.V, and Nikashina, V.A., *Sorbts. Khromat. Prots.*, 2001, vol. 1, no. 3, p. 448.
52. Green, T.E., Law, S.L., and Campbell, W.J., *Anal. Chem.*, 1970, vol. 42, no. 14, p. 1749.
53. Campbell, W.L., Spano, E.F., and Green, T.E., *Anal. Chem.*, 1966, vol. 38, no. 8, p. 987.
54. Goto, K. and Taguchi, S., *Anal. Sci.*, 1993, vol. 9, p. 6.
55. Nukatsuka, I., Ohba, T., Ishida, H., *et al.*, *Analyst,* 1992, vol. 117, p. 1513.
56. Endo, M., Suzuki, K., and Abe, S., *Anal. Chim. Acta*, 1998, vol. 364, p. 13.
57. Nukatsuka, I., Takahashi, K., Ohzeki, K., and Ishida, R., *Analyst*, 1989, vol. 114, p. 1473.
58. Holynska, B. and Bisiniek, K., *J. Radioanal. Chem.*, 1976, vol. 31, p. 159.
59. Eltayeb Mohamed, A.H. and Van Grieken, R.E., *Anal. Chim. Acta*, 1992, vol. 268, p. 177.
60. Lavi, N. and Alfassi, Z.B., *J. Radioanal. Nucl. Chem., Lett.,* 1988, vol. 126, no. 5, p. 361.
61. Bloom, N.S. and Crecelius, E.A., *Anal. Chim. Acta,* 1984, vol. 156, p. 139.
62. Igarash, S., Takahashi, A., Veki, Y., and Yamaguchi, H., *Analyst,* 2000, vol. 125, p. 797.
63. Nakamura, N., Oka, H., Ishii, M., and Sato, J., *Analyst*, 1994, vol. 119, no. 6, p. 1397.
64. Leyden, D.E., Dolbach, K., and Ellis, A.T., *Anal. Chim. Acta*, 1985, vol. 171, p. 369.
65. Pik, A.L., Cameron, A.J., Eckert, L.M., *et al.*, *Anal. Chim. Acta*, 1979, vol. 110, p. 61.
66. Zhang, Q., Minami, H., Inoue, S., and Atsuya, I., *Fresenius' J. Anal. Chem.,* 2001, vol. 370, p. 860.
67. Takahashi, A., Igarashi, S., Ueki, Y., and Yamaguchi, H., *Fresenius' J. Anal. Chem.,* 2000, vol. 368, p. 607.
68. Zolotov, Yu.A., Tsizin, G.I., Formanovskii, A.A., *et al.*, *Koord. Khim.*, 1992, vol. 18, nos. 10–11, p. 1113.
69. Moyers, E.M. and Fritz, J.S., *Anal. Chem.,* 1977, vol. 49, p. 418.
70. Gennaro, M.C., Sarzanini, C., Mentasti, E., and Baiocchi, C., *Talanta*, 1985, vol. 32, no. 10, p. 961.
71. Gennaro, M.C., Mentasti, E., and Sarzanini, C., *New J. Chem.*, 1986, vol. 10, no. 2, p. 107.
72. Häubl, G., Wegscheider, W., and Knapp, G., *Angew. Makromol. Chem.*, 1984, vol. 121, p. 209.
73. Tsizin, G.I., Formanovskii, A.A., Mikhura, I.V., *et al.*, *Zh. Neorg. Khim.,* 1990, vol. 35, no. 4, p. 960.
74. Burba, P., Rocha, J., and Klockow, D., *Fresenius' J. Anal. Chem.*, 1994, vol. 349, p. 800.
75. Sasaoka, N., Morishige, K., Shigematsu, T*., et al.*, *Bunseki Kagaku*, 1987, vol. 36, no. 4, p. 261.
76. Coetzee, P.P. and Lieser, K.H., *Fresenius' J. Anal. Chem.*, 1986, vol. 323, p. 257.
77. Wen, B., Shan, X., and Xu, S., *Analyst,* 1999, vol. 124, p. 621.
78. Myasoedova, G.V., Antokol'skaya, I.I., Kubrakova, I.V., *et al.*, *Zh. Anal. Khim.*, 1986, vol. 41, no. 10, p. 1816.
79. Kingston, H. and Pella, P.A., *Anal. Chem.,* 1981, vol. 53, no. 2, p. 223.
80. Amelin, V.G., *Zh. Anal. Khim.*, 1999, vol. 54, no. 9, p. 991 [*J. Anal. Chem.* (Engl. Transl.), 1999, vol. 54, no. 9, p. 880].
81. *Povedenie rtuti i drugikh tyazhelykh metallov v ekosistemakh: Analiticheskii obzor. Ch. 1. Fizikokhimicheskie metody opredeleniya soderzhaniya rtuti i drugikh tyazhelykh metallov v prirodnykh ob"ektakh* (The Behavior of Mercury and Other Heavy Metals in Ecosystems: Analytical Review. Part 1: Physicochemical Methods for the Determination of Mercury and Other Heavy Metals in Natural Samples), Novosibirsk: Akad. Nauk SSSR, 1989.
82. Brock, T., *Membrane Filtration, A Users Guide and Reference Manual*, Madison: Sci. Tech., 1983. Translated under the title *Membrannaya fil'tratsiya,* Moscow: Mir, 1987.
83. Spivakov, B.Ya., Shkinev, V.M., and Geckeler, K.E., *Pure Appl. Chem.,* 1994, vol. 66, no. 3, p. 631.
84. Piying, G., Ruolan, F., Huaizhu, Z., and Zhigiang, L., *Anal. Lett.*, 1998, vol. 31, no. 6, p. 1095.
85. Byr'ko, V.M., *Ditiokarbamaty* (Dithiocarbamates), Moscow: Nauka, 1984.
86. Alvarez, A.M., Alvarez, J.R.E., and Alvarez, R.P., *J. Radioanal. Nucl. Chem.*, 2000, vol. 245, no. 3, p. 485.
87. Pradzynski, A.H., Henry, R.E., and Stewart, J.S., *J. Radioanal. Chem.*, 1976, vol. 32, p. 219.
88. Caravagal, G.S. and Mahan, K.I., *Anal. Chim. Acta*, 1982, vol. 135, p. 205.
89. Hiraide, M., Chen, Z., and Kawaguchi, H., *Talanta*, 1996, vol. 43, p. 1131.
90. Iwasaki, K., *Anal. Chim. Acta*, 1979, vol. 100, p. 67.
91. Yuan Shi, Britten Stephen, and Pal Uday, *Proc. Electrochem. Soc.*, 1997, vol. 95, no. 124, p. 294.
92. Kyotani, T. and Iwatsuki, M., *Analyst*, 1998, vol. 123, p. 1813.
93. Aneva, Z., Stamov, S., and Kalaydjieva, I., *Anal. Lab.*, 1997, vol. 6, no. 2, p. 67.
94. Jung Yong-June, Choi Jong-Moon, Choi Hee-Seon, and Kim Young Sang, *J. Korean Chem. Soc.*, 1996, vol. 40, no. 12, p. 724.
95. Gordeeva, V.P., Statkus, M.A., Tsysin, G.I., and Zolotov, Yu.A., *Talanta*, 2003, vol. 61, no. 3, p. 315.

96. Anthemidis, A.N., Zachariadis, G.A., and Stratis, J.A., *Talanta*, 2001, vol. 54, p. 935.
97. Ivanova, E. and Adams, F., *Fresenius' J. Anal. Chem.*, 1998, vol. 361, p. 445.
98. Nielsen, S. and Hansen, E.H., *Anal. Chim. Acta*, 1998, vol. 366, p. 163.
99. Panayappan, R., Venezky, D.L., Gilfrich, J.V., and Birks, L.S., *Anal. Chem.*, 1978, vol. 50, no. 8, p. 1125.
100. Ohzeki, K., Toki, C., and Ishida, R., *Analyst*, 1987, vol. 112, p. 1689.
101. Nukatsuka, I., Munakata, T., Œhzeki K., and Ishida R., *Analyst,* 1993, vol. 118, no. 8, p. 1071.
102. Soylak, M., Divrikli, U., Elci, L., and Dogan, M., *Talanta*, 2002, vol. 56, p. 565.
103. Watanabe, H., Berman, S., and Russell, D.S., *Talanta*, 1972, vol. 19, p. 1363.
104. Holynska, B. and Jasion, J., *J. Radioanal. Nucl. Chem., Lett.,* 1986, vol. 105, no. 2, p. 71.
105. Sun, Y.C. and Yang, J.Y., *Anal. Chim. Acta,* 1999, vol. 395, p. 293.
106. Smagunova, A.N., Tarasenko, S.V., Bazykina, E.N., and Karpukova, O.M., *Zh. Anal. Khim.,* 1979, vol. 34, no. 2, p. 388.
107. Britske, M.E., *Atomno-absorbtsionnyi spektral'nyi analiz* (Atomic-Absorption Spectral Analysis), Moscow: Khimiya, 1982.
108. Hudnik, V., Gomiscek, S., and Gorenc, B., *Anal. Chim. Acta*, 1978, vol. 98, p. 39.
109. Hasegawa Shin-Ichi, Kobayashi Takeshi, Sato Koichi, *et al.*, *Nippon Kinzoku Gakkaishi*, 1999, vol. 63, no. 8, p. 1064.
110. Taher, M.A., Puri, S., and Puri, B.K., *Talanta*, 1997, vol. 45, p. 411.
111. Waetjen, U., Kriews, M., and Dannecker, W., *Fresenius' J. Anal. Chem.*, 1993, vol. 345, p. 261.
112. Statkus, M.A., Gordeeva, V.P., Maiorova, E.N., *et al.*, *Zavod. Lab.,* 2004, vol. 70, no. 3, p. 3.
113. Gordeeva, V.P., Statkus, M.A., Sorokina, N.M., *et al.*, *Zh. Anal. Khim.*, 2002, vol. 57, no. 8, p. 834.
114. Gordeeva, V.P., Kochelaeva, G.A., Tsizin, G.I., *et al.*, *Zh. Anal. Khim.*, 2002, vol. 57, no. 8, p. 820.