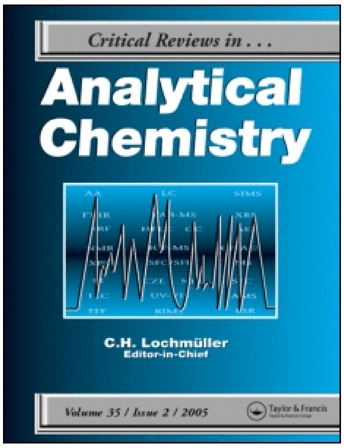

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Zolotov, Yu A. , Bodnya, V. A. , Zagruzina, A. N. and Freiser, Henry(1982) 'Application of Extraction Methods for the Determin of Small Amounts of Metals', Critical Reviews in Analytical Chemistry, 14: 2, 93 — 174

To link to this Article: DOI: 10.1080/10408348208542772

URL: http://dx.doi.org/10.1080/10408348208542772

APPLICATION OF EXTRACTION METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF METALS

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I. INTRODUCTION

Like other separation and preconcentration methods, solvent extraction plays a secondary, but very important role in analytical chemistry. Its significance can be judged by the known fact that in many cases, if not in the majority of cases, direct analysis methods do not enable one to determine all the necessary elements in their wide range of concentrations without interference from other components present in the sample. Preliminary separation and preconcentration of elements are the essential stages of analyses, especially when determining small amounts of metals. Among the separation and concentration methods, solvent extraction holds a very prominent place.

Extraction is a universal method. In fact, at present there are no elements that cannot be extracted from an aqueous solution into an organic solvent. Also, it can be employed for very different concentrations of elements — from concentrations of a radio isotope without a carrier to several moles per liter. Solvent extraction is a fast and simple process; it generally demands simple equipment, and can be easily automated if necessary. Significant successes of the theory of extraction, synthesis and detailed studies of new extractants, and the vast available data on extraction of metals make it possible to determine, with sufficient reliability, the conditions for the extraction and separation of elements. Presently, these conditions are generally selected with rich perception; about 20 years ago the selection was often guided by empirical data.

With the exception of different variants of chromatography, extraction is most frequently employed for analytical separation and concentration of metals. Extraction, like different chromatographic methods, is used presently not only for the separation and preconcentration of elements, but also as an integral part of "hybrid" methods of analysis based on a combination of separation (concentration) and subsequent determination methods. If modern gas chromatography can serve as a standard model for such processes, including chromatographic separation of elements, then extraction-photometric or extraction-atomic-absorption methods, when the determination is carried out in the extract itself, are examples of similar methods involving extraction.

A great number of papers and even books are dedicated to the use of solvent extraction for the determination of small amounts of metals. In the present review we shall restrict ourselves mainly to the approximately 1300 papers published in the past 5 to 6 years. For various reasons, not all of these 1300 papers have been used in this review. Slightly heavier reference has been made to the papers published in Russian for the reason that they may be less known to a foreign reader due to the language barrier. We have also included many of our works in the field.

The problem concerning use of extraction for the determination of trace elements has been dealt with in a number of monographs, manuals, and reviews.[1-11] Some books and reviews related to this problem have been published in the last few years. In the monograph by Valkovic,[12] trace determination methods including extraction have been considered. Zolotov and Kuzmin[13] have gathered data on extraction of metals by the use of acylpyrazolones. The reviews by Marcus[14] and Zolotov[15] are dedicated to the general problems of extraction (theory, classification of systems, etc.) Levin and Kletenik[16] have reviewed some information on the extraction of chelates.

We shall remark upon reviews dedicated to certain particular problems concerning application of ammonium pyrrolidine dithiocarbamate for the determination of trace metals in water,[17] properties and use of fourteen 1-phenyl-3-methyl-4-acyl-5-pyrazolones,[18] extraction of metals by carboxylic[19] and violuric acids,[20] use of basic dyes,[21] diphenylguanidine,[22] amines,[23] 4-(2-pyridylazo)-resorcinol,[24] and organic compounds of phosphorous.[25] Hala[26] has published an interesting review on the extraction of metals from water-organic phases which treats mainly extraction systems containing a solvent that mixes both with the aqueous and organic phases. In this review he has made an attempt to classify such systems according to the type of the extracted compound, and also to estimate the effect of different factors on the metal extraction process. The separation methods used in chemical analysis including solvent extraction are discussed in the monograph by Miller.[27] The separation methods employed in radiochemical analysis are available in the review by Irving.[28]

II. GENERAL CHARACTERISTICS OF EXTRACTION METHODS

A. History

Extraction is a very old process. In 1825, bromine was extracted from an aqueous solution in an organic solvent.[29] Extraction of thiocynates by diethyl ether was described and used by Braun for analytical and preparative purposes in the sixties of the last century.[30,31] He extracted molybdenum using diethyl ether and showed how to analyze mixtures containing different elements (iron-cobalt, platinum group metals). The method of extracting iron (III) with diethyl ether from solutions of hydrochloric acid was proposed in 1892,[32-34] which like the extraction of molybdenum thiocyanate is still used. One of the first reports on the extraction of chelate compounds was published in 1900.[35] The author of this paper extracted chromium using a solution of diphenylcarbohydrazide in benzene. In 1917, Baudisch and Furst studied the extraction of cupferronates.[36] The work done by Fischer in the twenties of this century on extraction of complexes with dithizone was of great importance. His studies revealed a dependence of element distribution on the concentration of reagent, metal, and hydrogen ions. Beside this, his studies had practical significance for analytical chemistry. Except for the distribution law established by Bertelot, Jungflesch, and Nernst back in the last century, Kolthoff and Sandell initiated a quantitative description of the extraction process (from the view point of chemistry) and, in 1941, published a simple equation describing extraction of chelate compounds.[38] Irwing and William developed this theory further.[39] Rydberg, Connick et al., Fomin and Maiorova, Dyrssen and Sillen developed extraction methods for the study of the complexing process in solutions, which have been generalized.[40,41] In 1957, Rozen[42] published a theoretical description of extraction of metals by neutral extractants of the tributyl phosphate type.

Extraction found extensive application in the postwar years, especially beginning from the mid fifties. The works on nuclear technology gave impetus to the development of the extraction method. This led to the emergence and wide application of new phosphoryl-containing extractants (in particular of tributyl phosphate) and also of high-molecular weight amines. Later these extractants found use in analytical chemistry. Other extractants, for example chelate-forming reagents (hydroxyoximes, hydroxyquinoline and its analogues, and others) and partially the salts of quarternary ammonium bases, used in analytical chemistry found, on the contrary, their widest application in industry. In the fifties, when extraction was already widely applied, many important problems related to its chemistry remained unresolved. As it is now clear, some processes were not interpreted correctly. However, the subsequent studies explained the chemistry of the majority of important extraction processes.

The extraction method continues to be developed at a fast rate. The statistics of publications bear witness to this. More than 20,000 scientific papers have been dedicated to the extraction of inorganic compounds. As shown by the scientometric analysis of the publications,[43] the fraction of works done by one or two authors is decreasing and of those where the number of authors is three or more is increasing. This reflects that different specialists are enlisted for solving extraction problems.

B. Theory: Classification of Extraction Systems

1. Theoretical Bases of Extraction

Extraction is a complex physico-chemical process. It is not possible to make proper use of it without understanding the chemical basis of the method. The chemical theory of extraction lies at the boundary of different fields of science — chemical thermodynamics, theory of solutions, chemical kinetics, and coordination chemistry. The selection of extractants demands the use of achievements of organic chemistry.

The main task of extraction chemistry is to learn how to convert a metal into a compound which can be completely and selectively extracted. Hence, it is necessary to select this compound, to find optimal conditions of its formation, and to choose a suitable solvent. All this requires detailed investigations, the study of the chemistry of processes, and determination of different relationships. Now we have acquired the knowledge of the fundamentals of the chemistry of almost all the extraction processes used. Also, it has now become possible to pre-estimate the behavior of metals in the extraction systems. In other words, the chemistry of solvent extraction has made tremendous advances.

Now we shall list the conditions under which a metal passes from an aqueous solution into an organic solvent. Extraction is possible if the solubility of metal compounds in organic solvent is higher than in water. Here, it may be noted that in actual systems metal can exist in the form of different compounds and, often, the desired compounds usually absent in the initial water solution are formed during extraction. For this reason it is not always clear which compound is to be considered when studying solubilities. However, in general the above mentioned holds.

General rules for selection of extraction systems have been made. Charged compounds cannot pass into an organic solvent. If the metal is present in the form of ions, they must first be changed into an uncharged complex or an ion associate with a counter ion. In other words, it is necessary to neutralize the charge. In the extraction of ion associates the absolute value of the ion charge plays a significant part, as extraction generally decreases with an increase in the charge. Under similar conditions the extraction of singly-charged ions is better than those of doubly-charged and especially triply-charged ions. The compound to be extracted should be hydrophobic in nature and, hence, its molecules should not contain such hydrophilic groups as free hydroxyl or carboxyl groups. Solvation by the molecules of the extractant solvent favors extraction. In this case the nature of the latter plays a decisive role. Finally, the size of the molecules of the compound to be extracted is also important for this case. Generally, the large molecules are better extracted because they destroy the structure of water. High stability of the complexes to be extracted is often thought to favor extraction.

Extraction is a two-phase heterogeneous process and the phase rule can be applied to it. The distribution of substance between two liquid phases should adhere to the distribution law, which states that at constant temperature and pressure the ratio of equilibrium concentrations of the substance in two immiscible phases is a constant value that does not depend on the total concentration of the substance (this value is called the distribution constant). The range of application of this law is very limited. It holds if the substance exists in both phases in the same form, and the form does not vary with concentration. This condition is rarely fulfilled during metal extraction; the metal compounds generally participate in different chemical transformations — complexation, hydrolysis, polymerization, ionic aggregation, and others. This is the reason why the ratio of metal concentrations in organic and aqueous phases often vary with concentration.

The extraction process can be described as a normal two-phase chemical reaction; a large majority of extraction reactions are reversible, i.e., the law of mass action can be applied to them. Thus we can talk about the extraction reaction equilibrium constant which is called the extraction constant.

2. Classification of Extraction Methods and Processes Types of Extracting Compounds

Extraction techniques have been classified using various schemes. For example, the classification based on the nature of relative movement of two phases is essential for specialists in chemical engineering. Here, one can talk about batch, semicounterflow or counterflow extraction. But, if the classification has been done according to the type of extractants used, the basis of extraction by neutral, acidic and basic extractants must be used.

The classification based on the nature of extracting compounds is very important for the estimation of the chemistry of extraction processes. The extracting compounds can be divided into two groups: non-ionized compounds and ion associates. The following more complete classification details these groups of compounds.

Covalent neutral compounds of type I_2, $AsBr_3$, OsO_4 — For extraction of these types of compounds, of special importance is the relative solubility which should be more in the organic phase than in the aqueous one. The practical interest to these compounds results from the fact extraction of these compounds can be quite selective if use is made of inert non-polar solvents, say carbon tetrachloride or benzene. For example, arsenic in the form of AsI_3 is quite selectively separated with benzene from iodine solutions, and germanium in the form of $GeCl_4$ from chlorine solutions.

Chelates — The complexes of metals and beta-diketones, 8-hydroxyquinoline, dithizone, and hydroxyoximes can serve as examples of chelate compounds — a thoroughly studied class of compounds, the extraction theory of which is rather fully developed. Complexes with alkyl phosphoric and similar acids, and also with carboxylic and naphthenic acids, are grouped with chelates.

Neutral coordinatively solvated (mixed) complexes — Here, we list the complexes of metals with mixed coordination sphere containing inorganic ligand and neutral extraction reagent. The compounds $PdCl_2L_2$, where L is a neutral sulfur-containing reagent, or $ScCl_3\ (TBP)_3$ where TBP stands for the tributyl phosphate molecule, or $UO_2(NO_3)_2\ (TBP)_2$ can serve as examples of these complexes. Such compounds are extracted only with reagents capable of entering into the inner coordination sphere of the complex. Depending on the type of the metal, reagents with different active atoms are applied. For alkali earth and rare-earth metals, zirconium, uranium, and other hard metals, use is made of oxygen-containing extraction reagents; for soft platinum metals, mercury, and bismuth, use is made of sulfur-containing reagents. Both these types of reagents can be used for transition d-elements.

These three groups of compounds form a class of nonionized extractable compounds. All others belong to ion associates.

Coordinatively nonsolvated ion associates — These are analogous for instance to the associates formed by the large tetraphenylarsonium cation with the large and coordinatively nonsolvated perrhenate-ion. The salts of quarternary ammonium bases with nonsolvated metal-containing anions can also be grouped into this class by slightly stretching the classification. The typical compounds of this group are better extracted by using, as a rule, high polarity organic solvents.

Mineral acids — These acids are extracted only with sufficiently basic solvents capable of combining with protons, for example amines or oxygen-containing solvents having quite high electron-donor ability, i.e., such as tributyl phosphate and others.

Complex metal-containing acids and their salts — These compounds are of the type H_nMX_{m+n}, where M stands for metal, X represents a single-charged electronegative ligand (for example fluoride, chloride, cyanide, nitrate), and m signifies the metal ion charge. Examples of these compounds are: $HFeCl_4$, $HNbF_6$, and $HInI_4$. The complex acids are extracted only with highly basic oxygen-containing extractants — ketones, ethers, esters, etc., or with amines. Inert organic solvents like benzene or chloroform do not extract them. Extraction of metal-containing acids is employed for separating tantalum, gold, indium, cadmium, molybdenum, iron, antimony, and many other metals. The heteropoly acids used for separating silicon, phosphorous, and molybdenum can also be classed with complex acids.

Other ionic associates — This group is formed of those compounds which for one or another reason cannot be classified into the groups mentioned earlier.

C. Extraction Techniques

For the determination of small amounts of metals one usually employs batch extraction in separatory funnels. Very rarely, recourse is taken to semicounterflow or counterflow extraction and the Craig method. In the last few years extraction chromatography has come into importance; the extraction of low-melting extractants and the use of three-phase extraction systems play a less important role. Among the methods based on chemical nature rather than on the extraction techniques, mention must be made of synergistic effects often observed in the mixtures of reagents, of the exchange extraction when a complex with some other metal is used as an extractant, of substoichiometric extraction, and of the use of mutual effects of metals in the extraction process.

1. Extraction Chromatography

A detailed treatment of this technique is available in the book edited by Braun and Ghersini.[44] Extraction chromatography, which successfully brings extraction chemistry into concord with chromatographic techniques, has acquired vital analytical importance. It makes possible the separation of trace amounts of elements very close in properties and also the concentration of these traces. In the majority of cases, use is made of the extraction systems with ionic associates and neutral mixed complexes, but sometimes chelates are also employed though they are less convenient due to kinetic difficulties.

In certain cases the extraction chromatography has an advantage over the usual extraction process.[45,46] The multiple repeating of elementary extraction events enables the separation of elements with similar properties. Use can also be made of organic solvents that form stable emulsions. The component distribution coefficients can be determined from the elution curves; this is essential in those cases when it is difficult to determine them by usual methods. To the advantages of extraction chromatography must be added the high degree of absolute concentration and the fact that experiment can be carried out under stable sterile conditions; this results in small fluctuations of the blank when compared with usual extraction methods. The extraction chromatography process can be easily controlled. Its capabilities show themselves very vividly in separating elements of like properties (i.e., lanthanides, actinides, zirconium-hafnium, niobium-tantalum, etc.). Rational selection of the extraction system, composition of the aqueous phase, introduction of masking agents, oxidants, reducing agents, and also proper control of separation conditions which depend directly on the chromatographic column parameters, i.e., the thickness of the equivalent theoretical plate and the number of such plates enables good separation to be obtained.

Theoretical principles of this technique are described in many fundamental works.[44,47] Some methods of calculating chromatographic column parameters in terms of elementary plates or layers are also known.[47,48]

A number of specific requirements are imposed upon the carriers of the immobile phase.[44] They should easily wet the immobile phase and retain it in sufficient amounts. Also, the immobile phase must not be stripped from the carrier by the mobile phase flow. The carrier should be chemically inert; it should not swell and dissolve in the extractant and absorb the components of the mixture to be separated. It should have uniformly distributed particles, sufficiently developed surface, and ensure phase motion through the column at the required rate. No less important are the particle size, density, strength, and porosity. Finally, the carrier should be readily available. Waterproof silica gel, polytrifluorochlorethylene, polytetrafluoroethylene (Teflon®) and others have found wide application. Block porous Teflon® which enables columns to be prepared with stable parameters is advantageous.[49-51]

Extraction chromatography can be employed for concentrating trace elements. The concentrated microelements are separated under such conditions that the difference in distribution coefficients is sufficiently large (at least ten times). In this case the matrix elements pass through the column practically without being absorbed, whereas the microelements of interest are retained. Glukhov et al.[52] isolated gold from complex solutions (particularly from natural waters) containing 21 cations. He used a 0.5 *M* benzene solution of petroleum sulfides to coat porous Teflon® tablets. Only gold and palladium were absorbed from 0.5 *M* HCl solutions. The determination was concluded with neutron activation. Alimarin et al.,[53] upon analyzing pyrite, used a mixture of tridecylamine in toluene and of hydrochloric acid for concentrating indium and cadmium and their subsequent separation. As a carrier of the immobile phase they used Teflon®. Indium and gallium present in different fractions of eluate were determined by polarography.

2. *Use of Three-Phase Systems*

This is an interesting technique. In certain extraction systems the organic phase is divided into two phases. One of them — often very small in volume — contains practically all the extracted element. This phase can be isolated and used directly for spectrochemical or atomic-absorption analysis. Zhivopistsev and Petrov (U.S.S.R.) have proposed several such methods. A few of them are discussed below.

For the determination of silver in dilute solutions (5×10^{-9} *M*) the metal was concentrated in the bottom phase of the three-phase extraction system.[54] The third phase appeared upon extracting silver from thiocyanate solutions using diantipyrylmethane or its halogen derivatives in chloroform or dichlorethane.

Petrov et al.,[55,56] for the determination of germanium, concentrated this element also in the bottom phase of the three-phase extraction system. In this case, germanium was first extracted in a usual manner, for example, in the form of a salt of oxalate-germanate-ion with hexyldiantipyrylmethane[55] or in the form of germanium chloride using kerosen,[56] and then the third phase was formed by adding petroleum ether[55] or diantipyrylmethane iodide dissolved in chloroform.[56] This enabled a spectrochemical determination to be carried out without mineralizing the extract. The described techniques are quite selective (many transition and non-transition metals are no barrier to them) and have small determination limits for germanium (0.5 to 1.0 μg).

Mercury was extracted from an aqueous phase containing 0.02 to 0.05 M H_2SO_4 and 0.3 M CCl_3COONa with the use of a diantipyrylmethane solution in dichlorethane.[57] Thereafter, petroleum ether was added to the extract and the bottom phase was collected for mercury determination. These very authors have proposed a method for concentrating indium using a similar technique.[58]

A three-phase system was suggested for concentrating thorium.[59] At the same time thorium is effectively separated from REE, Be, Cd, Zn, Cu, Ni, Co, Ga, Bi, Sb, Mo and W. The methods of concentrating tantalum[60] and zirconium[61] are based on this very principle.

3. *Melt Extraction*

Some extraction reagents easily melt at elevated temperatures and such melts are often used for extraction. Another method involves the use of easily fusible neutral substances (naphthalene, diphenyl) into the melt of which the extraction reagent is dissolved. In both cases the mixture, after extraction is cooled and the solidified extract is separated. For example, a method has been proposed for concentrating Nb, Ta, Hf and Zr by extracting them from water solutions using melts of 8-hydroxyquinoline, benzoylacetone, or dibenzoylmethane.[62] Lobanov et al.[63] extracted metals prior to their spectrochemical determination using the melt of 8-hydroxyquinoline. After cooling, the solid phase was dissolved in chloroform and then evaporated in the presence of carbon powder which was later subjected to spectrochemical analysis. They determined Al, Ag, Au, Bi, Co, Cr, Cu, Fe, Ga, Mn, Ni, Pb, and Sb by this method.

Melt extraction has some advantages over usual extraction.[64] It is convenient in those cases when the subsequent determination method demands solid concentrate as in the case of X-ray fluorescence analysis. The solid concentrate (solid extract) is pressed into a tablet which is analysed. At elevated temperature and in the presence of large amounts of molten extractant, the reactions, in a number of cases, proceed rather completely and at a faster rate than in usual extraction.

4. *Gel Extraction*

As an organic phase use may be made of a gel of non-ionized surface-active substance (SAS).[65-67] On adding a certain amount of non-ionic SAS into an aqueous solution and heating it up to a temperature exceeding the cloud point of the used SAS, the system separates into two phases — a miceller solution and a gel. The gel effectively entraps the extracting complexes and, therefore, it is removed from the system. After dissolution, it is used in a photometric determination. In particular, the determination of nickel with 1-(2-thiazolylazo)-2-naphthol is based on this principle.[65,66] But the non-ionic SAS Triton X-100 used in these works did not prove to be quite as good because its cloud point is very high (above 70° C). That is why such an effective technique as centrifugal separation cannot be employed for gel separation. Watanabe and co-workers[67] used another SAS — nonylphenyl ether of polyoxyethylene PONPE-7.5 — that has a very low cloud point. This made possible the use of centrifugal separation for the gel that ensured a quantitative separation of the phases. A similar method has been developed for the determination of zinc in tap water using PAN.

5. *Use of Mixtures of Extractants and Different Additives (Synergistic Effects)*

Here we shall talk about extraction in systems where the mixture of extractants makes it possible to obtain much higher values of distribution coefficients than expected from the additivity law. This procedure has long been known and is widely employed for extracting chelates of alkali earth elements, lanthanides, actinides, and also some metals (cobalt, nickel, manganese, zinc, and sometimes copper). As a second extractant, use is generally made of neutral monodentate compounds having significant donor ability: tributylphosphate, and analogous to it pyridine and other aromatic amines. These additives most often enter into the inner sphere of the central atom of the metal; mixed complexes are formed which contain anions of the chelate-forming reagent and the reagent-additive. The increase in extraction is often caused by the substitution of water molecules that could remain in the inner sphere, and by the decrease in the hydrophilicity of the complexes.

Several examples can be listed. For spectrophotometric determination of uranium, extraction was performed using a benzene solution of acetylacetone and pyridine.[68] Copper was pre-extracted in the form of a chelate with isonitrosoacetylacetone in the presence of pyridine for its spectrophotometric determination in steel and the alloys of non-ferrous metals.[69] At pH 5.6-10 cadmium forms a mixed complex with thiothenoyltrifluoroacetone and 1,10-phenanthroline (bidentate reagent) which is subsequently extracted with xylene; this technique was employed prior to the spectrophotometric determination.[70] Many other methods of a similar nature are known. Synergistic extraction is applied in combination not only with photometry, but also with atomic absorption or gas chromatography determination.

6. Exchange Extraction

Extraction selectivity in a number of cases is increased by using another metal complex as a reagent extractant. The classical example of this is the complex of copper with diethyldithiocarbamate dissolved in an organic solvent. The metal present in the parent complex can be substituted only by that element for which the extraction constant is larger than that of the replacable element (provided the charges of metal ions are equal). For each reagent, metals can be arranged in such an order that each metal would substitute all those to the right of it. For example, for cupferron the metals have been arranged in the following order: Mo(VI), Fe(III), Ga, Cu(II), In, and Al. If copper cupferronate is used as an extractant, then indium and aluminium will not be extracted, and molybdenum, iron, and gallium will replace copper and thus go into the organic phase. Sometimes the use of complexes as reagents offers some other advantages also, for example, copper cupferronate does not undergo any changes during storage and extraction, unlike cupferron.[71]

Exchange extraction of chelates is often employed in radiochemical analysis methods. Thus, in the radioactivation determination of copper, use was twice made of exchange reactions.[72] First, the interfering radioactive impurities were extracted from the irradiated sample solution using a chloroform solution of nickel diethyldithiocarbamate and then copper was extracted using a bismuth diethyldithiocarbamate solution. Thereafter, the radioactivity of the extract was measured. Pernicka et al.[73] determine Ag, Au, Cd, and Cu in sulfide ores by the use of neutron activation. After extracting arsenic in the form of $AsCl_3$, all the above listed metals were removed from 0.5 M $HClO_4$ using a chloroform solution of zinc diethyldithiocarbamate, and the gamma-spectra of the extract were recorded on a high-resolution spectrometer.

Exchange extraction is convenient in those cases when the determinable metal does not have suitable radioactive isotopes or when non-radioactive elements are determined by radiochemical methods. For example,[74] in the determination of mercury(II), the aqueous solution containing sulfuric acid and sodium bromide was shaken up with a carbon tetrachloride solution of zinc dithizonate labelled with ^{65}Zn isotope. Mercury was determined by the lowering of the activity of the organic phase; this method enables mercury to be determined up to 0.2 μg. A theory of such exchange reactions has been developed by Zolotov, Spivakov, and Alimarin.[75-78]

7. Substoichiometric Extraction

This technique requires lower amounts of reagent than needed by stoichiometry; this enables the selectivity to be increased. Substoichiometric extraction is employed almost exclusively in the analysis methods based on radioactivity, and, therefore, it is considered elsewhere in the present review.

D. Extractants

The present day task of finding and studying new extractants resides in increasing the selectivity of their action, preferably on the basis of the theory of selectivity which is still to be developed. General principles related to the selection of extractants are discussed in the works of Zolotov and Petrukhin.[79,80]

A convenient way of selecting extractants is based on the principle of hard and soft bases and acids. It is known that according to this conception hard bases react preferably with hard acids and soft bases with soft acids. Extractants usually play the role of bases, oxygen-containing extractants being hard, and sulfur- or phosphorus(III)- containing compounds soft ones. Extractants with an active nitrogen atom have intermediate behavior. As to metal ions, they can be divided into three groups — hard, borderline, and soft acids. For instance:

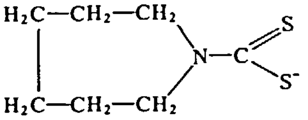
Hard acids:Li(I),Na(I),K(I),Be(II),Mg(II),Ca(II),Sr(II),Mn(II),Zn(II),
Al(III),Sc(III),Ga(III),In(III),La(III),Ce(III),Cr(III),
Co(III),Fe(III), Ti(IY),Zr(IY),Th(IY),Ce(IY),Hf(IY),Sn(IY),
Nb(Y), Ta(Y), UO_2^{2+}, VO^{2+}, MoO^{3-}
Borderline
acids: Fe(II),Co(II),Ni(II),Cu(II),Pb(II),Sn(II),Sb(III)
Soft acids:Cu(I),Ag(I),Au(I),Tl(I),Pd(II),Cd(II),Pt(II),Hg(II),
Tl(III),Au(III),Pt(IY),Te(IY)

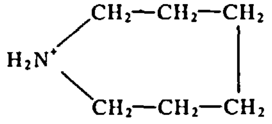
Thus, it is reasonable to use oxygen-containing extractants for hard metal ions and sulfur- or phosphorus(III)-containing compounds for extracting soft ones. Borderline metal ions can be extracted with various extractants, but O- or N-containing compounds often extract these metals quite well.

For the determination of trace metals diverse extractants are used. Among them are anionic (cationic exchange), cationic (anionic exchange), and neutral extractants (which often form mixed complexes). In reagents that form complexes with metals, generally O, N, S, and rarely P(III) and Se, act as active atoms. Use is also made of mono- and polydentate complex-forming reagents.

Extraction involving the use of cationic exchange extractants enjoys wide application. Sufficient information on the use of 8-hydroxyquinoline, beta-diketones, hydroxamic acids, hydroxyazo compounds, dioximes, dithiocarbamates, dithizone, dithiophosphates, and xanthates as cation-exchange extractants is available in the books by Stary,[2] Zolotov,[4] and others.[6,8,9]

The ammonium pyrrolidine.dithiocarbamate (APDTC) — methylisobutyl ketone system has found extensive use in analysis; many methods of analysing water, biological, and other objects have been developed with the use of this system. Hexamethylene ammonium hexamethylenedithiocarbamate is successfully used as an alternative to APDTC.[81,82]





Extraction of 32 elements from 0.1 to 10.0 M HCl solution containing potassium ethylxanthate was studied by Donaldson,[83] who ascertained that out of the studied elements Pd(II), As(III), Se(IV), and Te(IV) are completely extracted throughout the studied interval of HCl concentrations. Other elements such as Rh(III), Ru(III), Ir(IV), Os(IV), Ce(III, IV) and others are either not extracted or are extracted partly at a particular acid concentration. For example, germanium is partially extracted from 6 to 10 M HCl in the form of chloride complexes.

Group extraction of about 40 elements has been studied with the use of dithiocarbamine acid ester.[84] Transition metals of periods IV and V of the Periodic System as well as thallium can be extracted from 6 to 10 M HCl solution. Co, Ni, and post-transition metals — Bi, Cd, In, Hg, Pb, Tl, Zn — can be extracted from thiocyanate solutions containing 1 M HCl. Gold is selectively extracted from thiocyanate solutions. Using the obtained data, Byrko and co-workers[84] have suggested atomic absorption methods for selective and group determination of elements.

The possibilities of analytical application of thio-beta-diketones are discussed in the work of Uhlemann et al.[85]

1-Phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP) and its analogues are suitable for group concentration of a number of elements. Several spectrochemical methods of determining impurities in sodium hydroxide and many other substances have been developed based on the use of this reagent. It is also employed for selective extraction of certain elements prior to atomic absorption, photometric, or luminescence determination. Zolotov and Kuzmin[13] have generalized in their recent monograph more than 100 works dedicated to the application of this reagent. Of interest are the chelate-forming extractants which are stable free radicals (see IV,I).

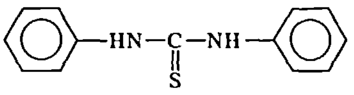
The extraction properties of the complex anion $\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2\,Co\cdot(CoB_2)\}^-$ have been studied in relation to alkali metals.[86] The obtained data suggest that the compounds of this anion are good extracting agents for selective separation of alkali metals in nitrobenzene (as ionic pairs).

Among anionic exchange extractants, dinonyl- and dioctyltin dinitrates $R_2Sn(NO_3)_2$, where $R = C_8H_{17}$ or C_9H_{19}, have a unique ability to extract multicharge anions. With the use of these reagents the phosphate and arsenate are well extracted; the extraction of doubly charged selenite and selenate is worse, though not bad; many single-charged anions are not extracted.[87,88] This differentiates organotin extractants from practically all known extractants. Methods of preconcentrating phosphorus, arsenic, and selenium, and in particular the extraction photometric methods of determining phosphorus in vanadium have been developed based on the use of these reagents.[89]

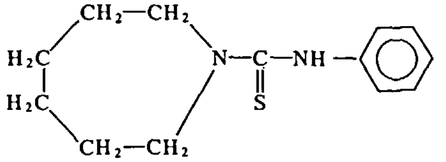
Hanif et al.[90] studied the extraction of 40 elements from thiocyanate solutions using 2-hexylpyridine in benzene. They studied the HCl concentration effect also and established that only Au(III), Mo(VI), Fe(III), Hg(II), Tc(VII), Zn(II), and As(III) were extracted with high distribution coefficient. These data may be used as a basis for concentrating these elements.

Various neutral extractants forming coordinately solvated complexes (mixed complexes) and certain ionic associates have found extensive application. For the extraction concentration of chalcophile metals, in particular for silver and platinum group metals, Zolotov et al.[91-93] recommend the use of diphenylthiourea (I)[91] and hexamethylenphenylthiourea (II).[92,93] These reagents enable noble metals to be concentrated and separated from non-ferrous metals. A spectrochemical method has been developed for the determination of all noble metals except osmium in solutions after decomposing natural and technological materials containing large amounts of nickel, cobalt, iron, manganese, zinc, and moderate quantities of copper.[94] It involves the extraction preconcentration of noble metals in the form of complexes with diphenylthiourea after treating the solution with stannous chloride. The detection limits are 1 to 100 ppb. Diphenylthiourea has also been used for concentrating silver traces in rocks, ores, and concentrates,[95,96] and also copper, silver, and thallium in chemical reagents;[97] in both cases the elements were determined by atomic absorption method.

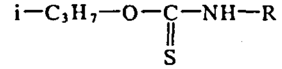
Mention may also be made of O-isopropyl-N-ethylthiocarbamine and O-isopropyl-*N*-methylthiocarbamine (III). Their behavior has been studied in detail, and several methods have been proposed for the separation and concentration of elements.[91,98,99] The reagents are liquids which are mixed with organic diluents, that is why they have a large capacity. They extract silver very well. In O-isopropyl-N-ethylthiocarbamine extraction of silver from 1 *M* HNO_3 solution, only mercury, platinum, palladium, and gold are partially extracted together with silver. All other elements remain in the aqueous phase.



I



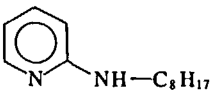
II



$i{-}C_3H_7{-}O{-}\underset{\underset{S}{\|}}{C}{-}NH{-}R$

III

$R = CH_3, C_2H_5$



IV

In one extraction about 99.98% of the silver is extracted using a 2 *M* chloroform solution of the reagent — that is, silver is completely extracted. Use of this fact has been made in developing the spectrochemical method of determining 23 impurities in high-purity silver.[100] The detection limits are 0.2 to 50 ppb and the enrichment factor is 50. A similar method is based on the application of the methyl derivative.[101] Both compounds have also been exploited for the determination of small amounts of silver in minerals and ores.[102]

Information on extraction of metals with the use of neutral sulfur-containing extractants has been reviewed in our recent monograph.[103]

A proposal was made to use triphenylphosphine for selective concentration of gold and silver traces, followed by atomic absorption determination of gold in minerals and cyanide solutions[104] and of silver in rocks, ores, and minerals.[105,106] The characteristic property of this reagent is that it reacts preferably with metal ions which are weak acids.[107]

2-Octylaminopyridine (IV), synthesized in one of our laboratories, has proved to be a quite suitable reagent for platinum metals; it extracts iridium very well.[108]

A mention may also be made of a comparitively new class of organic analytical reagents — macrocyclic organic compounds containing electron-donor heteroatoms in the ring.[109] Crown ethers containing oxygen atoms as heteroatoms have found extensive application. These compounds usually react with alkali and alkali earth metals, the reaction being quite specific. For example, a new and specific extraction photometric reagent — 4-(picrylamino)-benzo-15-crown-5 — has been proposed for calcium.[110,111] A suitable procedure enables microgram amounts of calcium to be determined in the presence of ten times as much Rb and large amounts of Li, Na, Cs. Yoshio et al.[112] have suggested the use of the ammonium complex of 18-crown-6 or the dicyclohexyl derivative of the latter dissolved in dichloroethane for solvent extraction of cobalt thiocyanate. Subsequent photometric evaluation makes it possible to determine cobalt. The ion associate is extracted in the pH range of 1 to 7, and extraction proves to be quite selective. The presence of Cd, Cu, Ni, Sn(III), Pb, and Zn does not hinder the determination, but presence of iron (III) does.

A method of separating barium (concentration about 10^{-4} *M*) from 100-times the amount of calcium is described in the work of Takeda and co-workers.[113] It is based on the extraction of barium in the presence of picric acid using a nitrobenzene solution of 1,4,7,10,13,16-hexaoxacyclooctadecane.

Sevdic et al.[114] have proposed a method involving selective extraction of silver and mercury (II) from picric and mineral acids using nitrobenzene solutions of a macrocyclic ether — 1,4,8,11-tetrathiocyclotetradecane. Silver and mercury can be extracted with concentrations 10^{-7} to 10^{-8} up to 10^{-4} *M*, respectively, followed by their separation. Cobalt, zinc, and cadmium are not extracted.

Extraction of a number of metals, mainly transition metals, into chloroform in the presence of aliphatic derivatives ($n\text{-}C_4H_9 \ldots n\text{-}C_9H_{19}$ of arsenic acid has been studied by Pietch and Gilani.[115] The extraction mechanism has not been explained, but the results point to the possibility of separating a number of metals.

III. BASIC TRENDS OF USING EXTRACTION IN ANALYTICAL CHEMISTRY

Extraction is primarily used for the separation and preconcentration of trace amounts of elements prior to their determination. The terms "separation" and "preconcentration" need clarification, for the reason that it is difficult to draw distinct boundaries between these concepts.

Separation may include: (1) separation of comparable amounts of elements; (2) relative concentration, if the determinable elements are to be separated from the main components of the sample, the latter being rejected; and (3) purification, if the main component is to be retained after rejecting the impurities. Despite the analogy between these techniques, they have certain specific features that determine the selection of extractants and separation conditions. Here, we also talk about absolute concentration, by which is meant the transfer of substance from a large volume of an aqueous phase into a small volume of the organic solvent. Absolute concentration is but rarely applied in the analysis of waters, acids, or alkalies.

Extraction is also applied as a method of studying chemical processes that proceed in aqueous solutions: hydrolysis, polymerization, complexation; the discussion of these processes is beyond the scope of the present review.

A. Separation of Mixtures of Elements

The difference in composition and stability of resulting compounds is the main factor that governs separation. The most simple case is the separation of the required element from the elements that do not react at all with the extracting agent. For example, it is not difficult to separate mercury and bismuth from zirconium and aluminium with the use of dithizone because neither zirconium nor aluminium react at all with dithizone. Antimony (V) can be separated from arsenic (V), which is not extracted at all in this system, by methylisobutylketone from HCl solution.

A more typical case is when all separable elements are extracted, but to different extents. Here, separation is achieved by varying the conditions, i.e., pH, concentration of the components of the system including the extractant, etc. Thus, Fe(III), Al and Mn(II) are extracted under definite conditions as 8-hydroxyquinolinates; they can be separated by varying the pH: iron is extracted at $pH = 2.8$, aluminum at $pH = 5.0$, manganese at $pH = 10$. Using 2-mercapto-benzo-gamma-thiopyrone, cobalt can be extracted with ethylacetate at $pH = 7$, nickel with chloroform at $pH = 8$ to 10;[116] thereafter suitable photometric measurements are taken. In a like manner, chromium and manganese are determined in steels.[117]

In order to separate aluminum and indium from gallium and thallium (III), the latter were extracted with benzene from HCl solutions containing prometazin;[118] the chloride complex of thallium (III) is extracted quantitatively in the form of an ionic associate from 2 *M* HCl, and the corresponding gallium complex from HCl solutions of molar concentration five and more; aluminum and indium remain in the aqueous phase. By varying the concentration of iodide ions, mercury, bismuth, and cadmium can be separated by extracting them from iodide solutions.[119]

The effective way of separating elements is to change their oxidation state. Thus, in separating elements with oxygen-containing solvents and amines, good results are obtained by reducing iron into the nonextractable bivalent state; gallium is readily extracted. Thallium and platinum when oxidised to the tri- and tetravalent states, respectively, can be extracted with dithizones, whereas many other dithizonates pass over to the organic phase.

Another factor that governs the selectivity is the use of a different extractant. From this viewpoint, powerful extractants do not always give good results. Indium and gallium are easily separated from chloride solutions with relatively weak extractants — ethers — which separate only gallium, but ketones or tributylphosphate — extractants having large extraction ability — favor the extraction of indium.

Finally, sufficient experience has been gained in masking those elements which are to be left in the aqueous phase. Sometimes, several masking agents are introduced. For example, at $pH = 8$ indium hydroxyquinolate is practically selectively extracted from the aqueous solution containing ascorbic acid, potassium cyanide, and ammonium chloride. From the solution containing uranium, aluminum can be extracted in the form of a complex with hydroxyquinoline by introducing carbonate ions, which bind uranium into the nonextractable complex.

One thing which is clear is that it is not necessary to extract the element to be determined; in a number of cases the interfering elements are extracted. Such techniques have found extensive application. For example, when determining bismuth in different materials,[120] the interference of iron is eliminated by extracting the latter from weakly alkaline media using bisacetylacetoethylenediamine in chloroform; thereafter, bismuth is determined photometrically in the aqueous phase using sulfobenzopyrogallol. Cobalt, iron, and zinc can be separated from nickel with the use of aliphatic derivatives of bissulfonium.[121] In the fluorimetric determination of cerium[122] with 8-hydroxyquinoline-5-sulfoacid the interference of permanganate was eliminated by extracting the latter with tetraphenyl arsonium chloride solution in chloroform.

Complete separation is often achieved not at the extraction stage, but by back extraction. Such a method of separating mixtures of certain metals is described in the work of Ivanova et al.[123] They studied the back extraction of metal cupferronates from the chloroform or isoamyl alcohol phase using HCl or NH_3 solutions. As one would expect, in the majority of cases, back extraction of metals into the aqueous phase increases with HCl or NH_3 concentration and decreases as the concentration of cupferron is increased in the organic phase. But some cupferronates behave in a different manner. For example, titanium and zirconium cupferronates are not back extracted with HCl; iron and tin cupferronates are back extracted only from a chloroform phase. Aluminum cupferronate is not stripped from chloroform, but from isoamyl alcohol only with concentrated HCl. On the basis of this and similar data, analysis procedures involving suitable separation schemes have been developed for a number of seignette-electric materials.

Of importance are also the exchange and substoichiometric extractions (see II. C. and IV. G.).

B. Preconcentration of Trace Elements

Preconcentration is necessary in those cases when the sensitivity of the employed method is insufficient for the determination of trace elements present in the sample. It ensures the removal of matrix or a large part of it and, sometimes, a number of interfering trace elements. In the concentrate the relative concentration of trace elements is much higher than in the parent sample. Beside this, the possibility of increasing the sample weight involved in the concentration process enables the amounts of determinable elements to be increased. As a result, the detection limit of trace elements may be lowered, sometimes very significantly, i.e., by hundred or thousand times. This is the major, but far from being the only reason that preconcentration is extensively applied.

Preconcentration is almost necessary when trace elements are non-homogeneously distributed in the sample. The representative sample in this case should be quite large; direct analysis of such a sample is difficult particularly if the determination method demands a small sample, as, for example, spark source mass spectrometry or spectrochemical analysis. Concentration with preliminary dissolution, fusion, etc., and with the recovery of a small amount of concentrate facilitates the preparation of a representative sample in many cases. A classical example of this is fire melting. It enables gold and other irregularly distributed noble metals in the sample to be concentrated from large sample weights of natural materials. Homogenization of the sample can, of course, be attained by subjecting the sample to other treatments.

Preconcentration alleviates calibration, particularly when standard reference materials are not available. It enables monotypical concentrates to be obtained for the analysis of diverse samples (in this case it is not necessary to have standard reference samples for all materials to be analysed). Concentration with complete separation from the matrix is highly desirable for the analysis of toxic, radioactive, or very costly materials. Besides, internal standards can be easily introduced, if necessary, during sample decomposition and preconcentration. Sometimes, concentration permits the number of trace elements which can be determined by the used method to be increased, or makes it possible to use this method of determination.

These merits make preconcentration an important stage of the trace analysis. Despite the progress made in developing sensitive instrumental methods of direct analysis, the importance of preconcentration is not decreasing. On the contrary, its possibilities are widening through the use of new combinations with determination methods.

On the other hand, preconcentration leads to prolonged and complicated analysis. This is associated with the possibility of losing material (incomplete preconcentration) or of introducing impurities. In some cases the number of determinable trace elements decreases in comparison with direct analysis; besides, it calls for special working techniques, high-purity reagents, specially equipped laboratories, and specific materials for the equipment. Nevertheless, the advantages of this technique usually outweigh the disadvantages.

Preconcentration is done in diverse ways. As mentioned earlier, its two forms are absolute, and relative. Trace elements are transferred from the large mass of the sample into a small one by absolute concentration. Relative concentration increases the ratio between trace elements and the main macroelements (in this case, the solvent is not considered as a macrocomponent). Relative concentration is a process of separating components very different in their concentration. Often it is employed to replace the matrix that hinders determination by a suitable collector, usually of less mass.

Individual or group preconcentration of trace elements is accomplished depending on the results to be obtained. Preconcentration is carried out either by removing the matrix or by isolating necessary trace elements. It is more convenient to remove the matrix when using multielement determination methods, say spectrochemical analysis. Quite often, the matrix is removed for analysing high-purity metals. If the matrix contains several elements that form complex compounds (geological and biological objects), it is better to isolate the trace elements. Sometimes, complete separation of the matrix is not necessary (here, it is appropriate to use the term "enrichment" of the matrix). But in the majority of cases another "matrix" is conveniently obtained by concentration which meets the subsequent determination requirements, simplifies calibration, etc. Some such collectors are sufficient for the determination of trace elements by several methods. For example, graphite powder as a collector can be analysed using spectrochemical or flameless atomic absorption methods.

Many ways of preconcentrating of impurities are known.[124] Proper selection of the concentration technique is very important and depends primarily on the nature of the matrix.[124,125] Extraction is one of the main concentration techniques. A review of these techniques is available in the book *Extraction Concentration*.[9] The successes made in this direction are also reflected in the review by Kuzmin.[126] The problem has also received attention in many reviews. Thus, Umezaki[127] and Pinta[128] have generalized the experience of using extraction for the determination of metal traces in water and for the analysis of high-purity mineral acids. Extraction concentration methods are suitable either for gathering trace elements in the extract or for extracting the matrix. These methods are universal, simple, and fast. Extraction usually ensures high concentrating efficiency.

Often trace elements are group-concentrated using usual reagents like 8-hydroxyquinoline, dithizone, dithiocarbamates, and in particular diethyl- and pyrrolidine dithiocarbamates. In order to recover the maximum number of elements, extraction is carried out at several pH values or by using a mixture of reagents. For example, a method is known for the determination of 18 impurities in highly pure alkali metal halides using a mixture of cupferron, sodium diethyldithiocarbamate, and trioctylphosphineoxide.[129] All the 18 elements are extracted at pH = 8 to 9; thereafter, the extract is evaporated in the presence of graphite and analysed spectrochemically. The reagents are so chosen that under metal extraction conditions they do not dissolve the organic phase. Trioctylphosphineoxide passes into the extract, but does not interfere with the spectrochemical determination of elements.

Many examples of group extraction exist. A few more will be given here to illustrate the utility of the method. A solution of 2-naphthylbismuthol in cyclohexanone is used for concentrating copper, lead, zinc, and cadmium in the presence of large amounts of cobalt, manganese, molybdenum, and nickel.[130] Iron (III) is extracted, though. The naphthhydrazide of nicotinic acid[131] was used as a group reagent for concentrating copper, molybdenum, vanadium, zirconium, titanium, and iron for further determination of these elements by radiochemical, atomic absorption, or photometric methods. A salicyclic acid solution in chloroform containing 1,10-phenanthroline can be used for group isolation of copper, cobalt, iron, and nickel. Substitution of phenanthroline by pyridine suppresses the extraction of iron (III).[132] Group concentration of alkali earth metals can be accomplished with benzoylphenylhydroxylamine.[133] Its solutions in chloroform enable the metals to be extracted with concentrations to 10^{-3} *M*.

Among theoretical problems of extraction of significance for the recovery of trace elements by removal of the matrix from the aqueous solution, the two important ones are the problem concerning the effect of unextractable compounds of the matrix (due to salting out, masking, complex-formation, etc.), and the problem related to the effect of the distribution of the trace component as a function of its concentration.

Extraction of the matrix is also of great importance in analytical practice.[134] The organic phase in this case should have a large capacity and the extraction should be quite selective such that the necessary trace elements are completely left behind in the aqueous phase. For this purpose the chelates are less suitable due to their limited solubility in organic solvents, but different ionic associates, coordinatively solvated compounds, and coordinatively unsolvated compounds with covalent bonds prove to be quite suitable.

For example, for the determination of rare-earth metals in rocks and meteorites by the radioactivation method the large mass of iron was extracted with diethyl ether or amylacetate,[135] but Dolgorev et al.[136] removed matrix elements with the use of chloroform solution of diantipyrilmethane. For the photometric determination of tungsten present in rhenium the large amounts of the latter was extracted with a chloroform solution of tribenzylamine.[137] In the photometric determination of molybdenum present in ferromolybdenum, the interfering effect of iron was eliminated by extracting iron with a benzene solution of acetylacetone and pyridine.[138] In spectrochemical and neutrone activation analysis of high-purity tin, tin was extracted with di-2-ethylhexylphosphoric acid.[139] In the spectrochemical analysis of high-purity mercurous iodide, mercury was removed by extracting it with a dichlorethane solution of di-n-butyl sulphide.[140] Many more examples of extraction preconcentration can be found in Section V.

An important problem when extracting the matrix is the behavior of trace elements. After working for several years on this problem we have found a regular and theoretically substantiated suppressing extraction of trace elements, which favors concentration by this method.[9] Such a suppression takes place during extraction of metal complex acids ($HFeCl_4$, $HNbF_6$, etc.) with oxygenated solvents of high enough polarity. For example, the distribution coefficient (D) of thallium(III) in the extraction with a mixture of dibutyl ether (10%) and 1,2-dichloroethane from 10 *M* HCl is 10 but in the presence of 0.1 *M* (extractable) iron(III) it is 0.08. The suppression is connected with the dissociation of complex acids — $HFeCl_4$ and $HTlCl_4$ in this example — in the organic phase. Dissociation gives rise to conditions that favor the display of the common-ion effect. It can be explained most simply as follows. The equation of the extraction of a complex acid of the trace metal is

$$H^+ + A^- = H^+_{(o)} + A^-_{(o)}$$

Then

$$K_{ex} = [H^+]_o[A^-]_o[H^+]^{-1}[A^-]^{-1}$$

Here A^- is the complex metal halide anion. If $[A^-]_o/[A^-] = D$, then

$$D = K_{ex}[H^+][H^+]_o^{-1}$$

The value of $[H^+]$ is high and practically constant. If extraction and dissociation of HCl are negligible in comparison with extraction and dissociation of the $HFeCl_4$, then $[H^+]_o$ depends only on the concentration of iron in the organic phase. Therefore, the value of D for trace metal (thallium) will be smaller in the presence of the matrix element than in its absence.

The suppression of trace metal extraction can also be obtained in the extraction of metal complex anions with high molecular weight amines and quarternary ammonium salts.

We shall illustrate this effect with some more examples. For concentration, use can be made of the mutual suppression of the extraction of Nb, Ta, and Zr from halide solutions by using aliphatic amines.[141] Zolotov[142] describes how the extraction of niobium and zirconium from fluoride solutions containing large amounts of tantalum can be suppressed. At pH = 8 to 9 chromium (III) suppresses the extraction of nickel and cobalt 8-hydroxyquinolinates in the presence of tartrates.[143] Presence of iron (III) in large amounts suppresses the extraction of americium and europium with TOA solutions in different organic solvents.[144] The extraction suppression of tin (IV) from a hydrochloric acid medium with n-butyl-acetate in the presence of large amounts of antimony (V) was used for isolating nanogram amounts of tin in the analysis of antimony pentachloride.[145]

In a number of cases the undesired coextraction of trace components is possible. As to metal complex acids, coextraction takes place if organic solvents of low polarity are used. The cause of coextraction may be association of complex acids in the organic phase. The conductivity in dibutyl or di-isopropyl ethers depends anomalously on the concentration of metal acids which is obviously caused by the formation of complex ion aggregates such as ion triplets or quadruplets. If mixed ion aggregates are formed which include matrix and trace metals we shall obtain the coextraction of the trace component.

Coextraction takes places sometimes for metals prone to formation of hydroxy complexes. For example, germanium is coextracted with iron (III) if high-molecular fatty acids, say caprylic acid, are used as extractants.[146] It is quite probable that different metal hydroxy complexes are formed which are polymeric in nature and contain germanium atoms as one of the monomer units. Coextraction of molybdenum with iron (III) using caprylic acid solution in kerosene as an extractant can be applied for the determination of molybdenum in sea and waste waters.[147]

C. Combination of Different Separation and Concentration Methods

For the analysis of samples of complex composition, often the use of extraction alone does not ensure isolation of the required element or effective separation of the mixture. In such cases extraction is applied in combination with other separation methods. In general, this, of course, is undesirous because it complicates the analysis.

A combination of coprecipitation and extraction methods was used to concentrate germanium.[148] First, germanium was coprecipitated with copper hydroxide and the precipitate was treated with a 2M carboxylic acid (C_6-C_9) in an inert diluent. Copper went into the organic phase and germanium was determined in the aqueous solution. For the analysis of high-purity tin the impurities were concentrated by applying double extraction and zone melting.[149]

Extraction and chromatographic concentration techniques were jointly applied for the determination of uranium and neptunium content ($\geqslant 3$ μg/g) in metallic plutonium,[150] and for the activation determination of rhenium in molybdenum.[151] Smet and coworkers[152] have proposed a procedure of separating trace elements from rocks and minerals into four groups with subsequent determination by activation. The procedure combines ion-exchange chromatography of fluoride solutions and extraction of a number of trace elements with tributylphosphate.

A quite complicated method for group isolation and subsequent separation of Cu, Ni, Co, Zn, and Cd has been proposed by Rozycki et al.[153] The indicated metals are first extracted from sodium chloride solutions with diethylthiocarbamate in chloroform. After mineralizing the extract, copper is extracted from 0.5*M* HCl using dithizone. The remaining metals, i.e., Co, Ni, Zn, Cd, are separated from other elements possibly present by coprecipitating them with lanthanum hydroxide; the precipitate is then treated with ammonia in the presence of ammonium chloride. From the ammonia solution cobalt is extracted as 1-nitro-so-2-naphtholate using isoamyl alcohol, and nickel is extracted at $pH = 7$ with a chloroform solution of dimethylglyoxime. Cadmium and zinc left over in the aqueous phase are separated by extracting their thiocyanate complexes with methylisobutylketone; cadmium is then back extracted. Thus, the separation procedure involves several operations. This threatens loss of determinable impurities that may tend to lower the accuracy and to worsen the determination limit. In our opinion, such procedures are not very successful and their use should be avoided, if possible.

IV. COMBINATION OF TRACE ELEMENTS EXTRACTION TECHNIQUES WITH THEIR SUBSEQUENT DETERMINATION METHODS

A. General

The ways of combining extraction concentration with subsequent determination methods can be divided into two groups. In the first group extraction is used only as the help stage, and the trace elements after extraction are transferred into the aqueous solution by back extraction or mineralizing the extract. In so doing the nature of the extractant or solvent does not practically affect the analytical signal of trace element which is determined in "usual" aqueous solution. In the second group the trace elements are determined directly in the extract (sometimes after changing it either by adding other solvents into it or by other ways). The nature and concentration of the extractant in this case can produce effects on the magnitude and even on the nature of the analytical signal. Here, we deal not merely with subsequent application of two techniques — separation and determination — but in the limiting case actually with new methods referred to as hybrid ones. For example, in the atomic absorption analysis of organic extracts, several important properties associated with different viscosities of organic solvents compared to water, and their combustibility show up very vividly and lead to changes in the mechanism of flame processes. An almost similar picture is observed upon combining extraction with photometric determination, if the determination is carried out directly in the organic phase. Polarographic analysis of organic extracts also differs from the polarography of aqueous solutions.

Furthermore, it may be mentioned that it is reasonable to combine group extraction — isolation and concentration — with multielement determination methods, and vice versa. The monoelement determination method, for example photometric or kinetic, demands, in many cases the use of individual extraction for the isolation and determination of the trace element.

Extraction can be conveniently combined with many determination methods. Among them are photometric, luminescence; atomic absorption, emission spectrochemical, X-ray fluorescence methods, the methods based on radioactivity, and also electrochemical, kinetic, and other methods. Of large importance are the extraction photometric and extraction atomic absorption methods. Table 1 shows percentage of publications devoted to these combinations in the period 1975-1979.

Table 1
PERCENTAGE OF PUBLICATIONS DEVOTED TO COMBINATIONS OF EXTRACTION WITH DETERMINATION METHODS*

Determination methods	%
Photometric methods	60
Atomic absorption methods	15
Radioactivity-based methods	8
Luminescence methods including X-ray fluorescence methods	7
Emission spectrochemical methods	3
Polarographic methods	3
Other methods	4

* (About 1100 papers were published in the period 1975–1979)

As may be seen from this table, the maximum number of publications are devoted to the combination of extraction with photometric determination. This is related to a better theoretical knowledge of the photometric method, to the availability of diverse photometric reagents (many of which have been studied in detail), and to the availability of equipment. Also, these techniques can be realized rather easily. It is also significant to note that the extensive application of extraction in analytical chemistry is historically associated with its use for photometric determination of elements, say with dithizone. Next to them are the extraction atomic absorption methods; at the present time a very large number of papers are devoted, in particular, to the combination of extraction with flame atomic absorption.

B. Photometry

Usually, for photometric determination monoelement concentration is applied, or several elements are extracted subsequently. The matrix in this case is rarely extracted. Often, for preconcentration, use is made of the reagent which forms a colored complex with the element to be determined. Nevertheless, discrete techniques are also employed, i.e., two reagents are used: at the first stage, the most selective reagent is used for separating trace element and, thereafter, a reagent is introduced into the extract which may not be selective, but should be more suitable from the viewpoint of photometry. This varient is more often realized after back extraction or the destruction of extract.

Extraction photometric methods are illuminated in many monographs, manuals, and reviews, for example in the books by Sandell and Onishi,[154] Marczenko,[155] Holzbecher et al.,[156] and Bloom.[157] The extraction photometric methods of determining a number of trace elements (Ag, V, Co, Cu, Mo, Mn, and others) are considered in the book by Busev.[158]

Often several metals as complexes are transfered into the extract. If they have different absorption spectra, then several metals can be readily determined without taking recourse to further separation. This is how the complexes of ruthenium (III) and osmium (VIII) were extracted with acetothioacetanilide,[159] and of copper and nickel with a 2-hydroxyoximes.[160] In a like manner, niobium and molybdenum were extracted with a chloroform solution of TBP.[161]

Sometimes, more complicated procedures are employed. For example, Gurtler[162] extracted molybdenum and tungsten in the following manner. The metals were first concentrated by extracting their complexes with 2-benzoynoxime into chloroform from a solution of sodium chloride, and then the extract was mineralized. After dissolving the residue, the thiocyanate complexes of molybdenum (V) and tungsten (V) were extracted with diisopropyl ester and the absorbance was recorded at 405 (tungsten) and 490 (molybdenum) nm. The described techniques are quite interesting. Nevertheless, the possibilities of selecting such reagents are very limited.

Often, the excess reagent in the organic phase interferes with the extraction photometric determination of element because the absorption spectra of the reagent and the extractable complex can overlap. In this case the reagent can be back extracted with an aqueous solution of suitable composition. Usually, solutions with increased pH are used. Thus, excess monothiothenoyltrifluoroacetone can be removed from the organic phase by washing the latter with the solution of borates (pH = 10), and copper is determined in the extract.[163] By using a suitable buffer solution (pH = 12), excessive amounts of thiobenzoylacetone are removed from the copper complex.[164] Excess acetylacetonate is removed from beryllium acetylacetonate solutions using a 0.1 *M* NaOH solution.[165] Beaupre et al.[166] used a HCl solution to extract 2-pyridyl-2-thienyl-beta-ketoxime from the corresponding complex of cobalt (III), because the complex is kinetically inert. It is evident that acids can also be used to separate the reagents from all complexes of this type.

The improvement in determination limits of extraction photometric methods is of great importance. This is mainly achieved with the use of reagents, the complexes of which are characterized by high molar absorption coefficients. For example, the use of Michler thioketone[167] enables one to determine nanogram amounts of mercury, and 2-(2-thiazolylazo)-5-dimethylaminophenol is a highly sensitive reagent for the determination of vanadium.[168] The methods employing extraction of ionic associates with different dyes usually have excellent detection limits.

Another way of improving the sensitivity involves extraction of mixed, multicomponent compounds of different natures. The examples of this are the methods of determining cobalt,[169] rhenium,[170] vanadium,[171] tungsten,[172] zirconium.[173] Extraction of the uranium(VI) complex with N-phenyl-2-naphthohydroxamic acid and gossypol[174] enables 0.1 μg of the metal to be determined in 1 mℓ of the organic phase. The use of similar compounds tends at times not only to improve the detection limit, but also the determination selectivity; this is illustrated with the example of vanadium (V) determination.[175] This element forms extractable mixed complexes with N-hydroxy-N-p-chlorophenyl-N′-(2-methyl-4-chlorophenyl)-benzamidine and thiocyanate or azide. Manganese, chromium, titanium, zirconium, molibdenum and tungsten do not interfere; iron(III) can be masked by the sodium phosphate.

It is not always possible to select a reagent or a group of reagents which simultaneously ensures high specificity and high sensitivity. That is why one often tries to combine the techniques. One such combination, as mentioned earlier, consists in extracting the determinable trace element and carrying out the photometric reaction in the extract phase with another reagent. For example, aluminum can be extracted in chloroform using 2-hydroxy-2-dibutylphosphineoxypropionic acid; after adding an alcohol solution of xylenol orange into the extract,[176] the absorbance is measured. Cadmium can be extracted from iodide solutions using capriquat; the photometric reaction with PAN is then carried out in the organic phase.[177] Pyatnitsky and co-workers[178] separated iron from large amounts of cobalt and nickel by extracting them with a chloroform solution of benzoic acid, and determined iron in the extract by the thiocyanate reaction.[178] Similar methods have been described for Ga,[179] In,[180] Mn,[181] Mo(V),[182] Os(IV),[183] Sn(IV),[184] Ti,[185] U(VI),[186] V(V),[187] and Zn.[188]

A varient of this method is the technique when the extract is shaken with the aqueous solution of the reagent for carrying out photometric reaction. This is how gallium was determined.[189,190] Mirza[190] first extracted gallium with a xylene solution of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 and then mixed the extract with an aqueous solution of rhodamine B containing HCl. For the determination of niobium,[191] the extract containing niobium benzoylphenylhydroxylaminate was first treated with aqueous solution of lumogallion, and then the absorbance was recorded. The same technique was used for the determination of cadmium.[192]

There is another way of carrying out photometric reaction in a medium containing several solvents, say in water-organic media. For this, use is usually made of those solvents (for example, acetone, alcohol, etc.) which homogenize the mixture. Pollock[193] extracted thorium and uranium using a cyclohexane solution of trioctylphosphine oxide; as a homogenizing solvent ethanol was added to the extract from a part of which thorium was determined using thoron, while from the other part uranium was determined with the use of PAN. In a similar manner, Kabrt[194] determined zirconium.

Often double extraction is applied. The first extraction serves to separate the determinable impurity from interfering components, while the second, after back extraction, is directly used for the extraction photometric determination. For example, Donaldson[195] extracted gold (III) from HCl solutions to separate it from many other metals using a mixture of 4-methyl-2-pentanol and benzene (3:1), back extracted with ammonia solution and then extracted into chloroform in the form of a compound with 2-furyldioxime and pyridine. Bublik et al.[196] determined bismuth in concentrates and alloys by the extraction photometric method according to the reaction with potassium xanthate after its back extraction from a chloroform solution of diethylthiocarbamate. A similar scheme was used for the determination of cerium in the presence of iron and manganese,[197] uranium,[198,199] and zinc.[200,201]

The methods based on the schematic: extraction-back extraction-photometric determination in aqueous phase have found extensive use. Such methods can be classed with extraction photometric methods only conditionally. Here, mention may be made of several such methods, although it is beyond doubt that the first stage of the scheme involved — that is, extraction, — serves only the purpose of separation. By this scheme, neptunium (IV) and plutonium (IV) are determined in solutions.[202] Both metals are first extracted with xylene solution of HTTA, back extracted with HNO_3, and then reacted with arsenazo III. For the determination of osmium in the presence of accompanying ions it is selectively removed in the form of OsO_4 into CCl_4 and back extracted with o-arsanilic acid which at the same time acts as the photometric reagent.[203] Small amounts of palladium can be determined by extracting its PAR complex with methyl isobutyl ketone followed by back extraction with EDTA solution ($pH = 10.5$). and photometric determination.[204] Rhenium in molybdenum concentrates can be determined by extracting perrhenate with acetone in the presence of large amounts of alkalies and by back extracting with water; thereafter, 2-furyldioxime is used as the photometric reagent.[205] A similar scheme was followed for the determination of scandium,[206] tin,[207] tellurium,[208] thorium,[209,210] thallium,[211] titanium,[212] uranium,[213] vanadium,[214] and zirconium.[215]

Sometimes it is recommended to mineralize the extract or to remove the solvent by evaporation prior to photometric determination. This complicates the analysis and may result in the loss of the element to be determined. Such a treatment is justified in those cases when the extractant or the solvent significantly affects the photometric reaction, thereby deteriorating its analytical parameters. For example, cobalt traces are first recovered with the use of chloroform solution of 2-nitroso-1-naphthol, the solvent is removed by evaporation and then cobalt is determined by reacting it with 2-pyridine-2-thienyl-β-ketoxime.[216] Similar procedure was followed for the determination of molybdenum[217] which was first extracted into chloroform as a complex with 2-benzoinoxime and the extract was mineralized; thereafter, molybdenum was determined photometrically in the form of a compound with gallein and papaverine. Dupuis and Holland[218] determined a trace of palladium in the presence of large amounts of Co, Cu, Fe, and Ni by extracting with 4-heptanone oxime, mineralizing the chloroform extract, and photometric determination with di-2-pyridylketoxime.

Different oxidation states of metal can be determined by extraction photometric methods. Fadrus and Maly[219] have described a procedure of determining iron (II) and (III); the procedure of determining chromium (III) and (VI) is available in the work of Fujii et al.[220] These procedures are based on alternate extraction of different metal forms. For instance, iron (II) is first extracted and then iron (III) is reduced in aqueous solution; thereafter, extraction is repeated. A method has also been proposed for the determination of thallium (I) in the presence of its organic derivative — dimethylthallium; this method permits determination of both forms.[221] First, the total content of thallium is determined by extracting its complex with PAN and by photometric measurement of the extract. Then, in the second portion of the solution to be analysed, thallium (I) is masked by EDTA and dimethylthallium is removed and determined with PAN.

By visualizing future developments of extraction photometric methods, it can be said that the tendency associated with the search of new selective and sensitive reagents will retain its prime importance. The macrocyclic reagents hold much promise in this respect. The methods incorporating photometric reactions in organic phase after preliminary extraction of metal with the aim of separating or concentrating it will probably acquire importance. The use of surface-active substances also seems to be quite interesting and promising.

C. Luminescence

Luminescent methods of determining trace elements (mainly fluorescence) have found extensive application in analytical chemistry, as well as in combination with extraction separation and preconcentration techniques. Concurrent with traditional sources of fluorescence excitation (UV-emitters), lasers are presently used.

Fluorimetric methods are known to have very good detection limits and high selectivity. The extraction-luminescence methods have considerable promise. For example, Savina et al.[222] have shown that by combining extraction with low-temperature luminescence the determination limit of thallium is considerably improved (to 1 ng/mℓ), and the determination becomes more selective, as in the case of bismuth detection in the presence of antimony.[223] In these methods the nature of the luminescent compound is of great significance. The type of fluorescence excitation source is less important. Thus, Zorov et al.[224] studied the determination conditions for indium and thallium by the fluorescence of ionic associates of their bromide complexes with rhodamines B and 6G. The extract was excited using a xenon lamp or a nitrogen-based pulsed laser. For both metals the detection limits were found to be almost equal irrespective of the excitation source and amounted to 1 ng/mℓ for rhodamine B and 0.1 to 0.2 ng/mℓ for rhodamine 6G. In actual practice different types of mercury lamps are used as fluorescence excitation sources, because they are readily available and simple in design and operation.

Often in extraction fluorimetric methods advantage is taken of the extraction of multicomponent compounds, particularly of mixed ligand complexes.[225]

Recourse is made to exchange reactions when none of the ion-partners is capable of fluorescence. This is how Bloom et al.[226] determined antimony. The metal was first extracted with benzene as an ion associate of $SbCl_6^-$ with crystalline violet, and then the cation of the associate was exchanged for ethylrhodamine B. The minimum determinable amount was 0.02 μg; Au, Tl, Cu hindered the determination. Bloom et al. have suggested similar procedures for the determination of gold,[227] mercury,[228] rhenium,[229] and thallium;[230] Shumova has proposed a method for the determination of tin.[231] Note that all these elements cannot be determined in the presence of each other because of their similar behavior during extraction.

There is no need to carry out exchange reactions if the extractable ionic associate has a fluorescent component. For example, Grigoryan et al.[232] extracted gold as an ionic pair with rhodamine 6G using butylacetate. The determination limit was 0.02 μg of gold per milliliter.

In fluorimetric techniques, the separation of elements is often of significant importance to preclude their mutual effect upon measuring the signal. Separation is effected by all known techniques (removal of matrix, selective extraction of trace elements, concurrent reactions of complex formation in aqueous phase, etc.). For example, for the analysis of high-purity gold Kasiura[233] extracted the matrix from 2M HCl using diisopropyl ether. The impurities remained in the aqueous phase; they were separated by extraction and ion-exchange chromatography techniques. A few of them were determined fluorimetrically.

In the considered references the extraction fluorimetric methods have been used in a variant when fluorescence of the extract is measured. Other methods are also available, in which extraction is used as a separation or preconcentration technique and fluorimetric determinations are carried out after back extraction or mineralization of the extract. According to this scheme, cadmium was determined in polymetallic sulfide ores,[234] gallium in metallic aluminum,[235] rhenium in ores and alloys,[236] and zinc in portland cement.[237] In the determination of trace elements in natural waters[238] a provision has been made for fluorimetric treatment after mineralization of the extract.

In the majority of cases the use of ionic associates and mixed ligand complexes forms the basis of extraction-fluorimetric methods. These compounds are used not only in accordance with the requirements and possibilities of extraction chemistry, but often prove to be the compounds whose fluorescence can be registered.

D. Atomic Absorption Spectrophotometry

Extensive development of extraction atomic absorption methods is related not only to the known merits of the atomic absorption method as such (good detection limit, selectivity, sufficiently high accuracy), but also to the advantages of using this spectroscopic method together with extraction separation of elements to be determined. The combination is generally achieved in the variant extraction-flame atomic absorption, with direct nebulization of the extract into the flame. The advantages of such methods in comparison with the determination of elements in aqueous solution resides in improving the detection limit and accelerating and simplifying the analysis. Also, the following operations are eliminated: evaporation of extracts, back extraction, and other operations which result in the increase of the correction factor for the blank experiment in the determination of common elements. Sometimes, the use of an appropriate organic solvent enables the determination to be carried out without the use of a combustible gas. Extraction is also employed in combination with flameless atomic absorption determination. The selectivity of atomic absorption determination enables a group of trace elements to be extracted; therefore, group extraction is applied along with monoelement extraction of metals.

The extraction atomic absorption methods are discussed in the monograph "Solvent Extraction in Flame Spectroscopic Analysis" by Cresser,[239] in the book *Extraction Concentration*[9] and in a number of reviews.[240,241] The extraction atomic absorption methods of determining noble metals,[242] and other elements present in iron-containing materials[243] have been covered in the reviews dedicated to some particular problems.

In these methods, different extraction techniques and systems are employed. Extensive use is made of extraction of chelates, i.e., of complexes with hydroxyquinoline, beta-diketones, xanthate, and particularly with dithiocarbamates. Chloroform or carbon tetrachloride and also benzene, due to its toxity, are less suitable for use as a solvent. Suitable solvents are methyl isobutyl ketone (MIBK) and butyl acetate. The ammonium pyrrolidine dithiocarbamate -methyl isobutyl ketone system is of great importance for group extraction of trace elements. Equipment is available for automatic extraction concentration; the use of Technicon equipment enables one to process 60 samples per hour.[244] Another variant of extraction and preconcentration technique developed for use in combination with a six-channel atomic fluorescence spectrophotometer makes possible the processing of 25 samples in an hour.[245] The so-called "injection" method is of great utility in the atomic absorption determination of small amounts of substances and in the analysis of concentrates.[246]

Now we shall consider some examples of group extraction for subsequent flame atomic absorption determination. D'angiuro et al.[247] determined Cd, Co, Cu, Pb and Mn after extracting them as pyrrolidine dithiocarbamates in MIBK. The detection limits for Cd and Co equaled 0.01; for Cu, 0.03; for Pb, 0.05; and for Mn, 0.005 μg/mℓ. Dornemann et al.[248] have suggested a fast method of determining nanogram amounts of heavy metals in aqueous solutions, which is based on the extraction of their hexamethylene dithiocarbamate complexes using mixture of xylene and diisopropyl ketone (3:7). Busev and his associates[130,249] employed extraction for the determination of Cd, Cu, Pb, and Zn in nickel alloys and in the salts of cobalt and nickel using solution of naphthylbismutol in cyclohexane. Vanova et al.[250] used 1-phenyl-3-methyl-4-benzoylpyrazolone-5 as a group extractant for the determination of Co, Cu, Fe, Mn, Ni, and Zn. Extraction of Ag, Bi, Cd, Cu, and Pb iodides with MIBK and the subsequent introduction of the extract into flame makes possible the determination of these elements quite selectively and with high sensitivity. For example, the determination limit of Cd equals 0.005 μg/mℓ, and that of Cu, 0.016 μg/mℓ.[251] Cadmium, copper, lead, and zinc were determined after extracting their ionic associates with MIBK.[252]

Extraction of copper as a chelate with PAN using dibutyl ether can serve as an example of individual (monoelement) extraction for the determination in flame.[253] Chambers and McClellan[253] extracted cadmium in the form of dithizonate using MIBK. The detection limits of copper and cadmium were found to be 0.01 and 0.1 ng/mℓ, respectively. The elements were extracted separately.

Extraction is used, although more rarely, in combination with flameless AA determination. The application of this type of atomization lowers the detection limits of metals by several times and sometimes by an order of magnitude or more. Examples of this can be found in the works devoted to the determination of gold.[254,255] However, for the comparison of detection limits of flame and flameless methods, it is necessary to account for the analysis procedure as a whole. For example, Surles and Tuschall[256] have made a comparitive study of the methods of determining heavy metals in sea water. They also compared the flameless (without concentration) and flame (with extraction concentration) methods of AAS. The latter has advantages over the former as far as detection limits, accuracy, and reproducibility of results are concerned. Obviously, the methods have not been compared correctly because two factors were changed simultaneously: determination technique and sample preparation (concentration was used only in one procedure). Menshikov et al.[257] used pulse atomizers based on graphite furnances HGA-72 and HGA-74, and the atomizer of type "furnance-flame" (C_2H_2-air). Different atomization methods have been compared for the determination of gold in geological materials. Gold was concentrated by extracting it from 2 *M* HCl with organic sulfides in toluene, and the detection limits (μg/mℓ) were found to be 8×10^{-4} for HGA-72, 10×10^{-4} for HGA-74, and 5×10^{-4} for furnance-flame(referred to 1%

absorption). Thus, the application of "furnance-flame" type atomizers results in an insignificant increase in the detection limit, whereas they have a number of other significant advantages, i.e., they are simple in design, and, hence, cost less for the same detection limit.

Flameless methods of atomization are often employed for the determination of sum of heavy metals. Jan Tsu Kal and Young[258] concentrated heavy metals by extracting pyrrolidine dithiocarbamates with MIBK. They then treated the extract with nitric acid and introduced the back extract into the atomizer. The detection limits were found to be 0.02 (Ag), 0.03 (Cd), 0.05 (Cr, Cu), 0.2 (Fe), 0.1 (Ni), and 0.03 (Pb, Zn) μg/mℓ. Danielsson et al.[259] extracted dithiocarbamates of Cd, Co, Cu, Fe, Ni, Pb, Zn with trichlortrifluorethane in the analysis of sea water. After treating the extract with concentrated nitric acid, they introduced the back extract into the atomizer. For this same purpose, Lee and Burrell[260] extracted dithizonates with chloroform. In the analysis of ground water, Kasterka et al.[261] concentrated heavy metals by extracting their diethyl dithiocarbamates with amyl acetate. The extracts containing Bi, Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn were introduced into the atomizer. Fuller[262] determined some heavy metals in lead glasses. After decomposing the samples he extracted metal traces either in the form of complexes with 4,7-diphenyl-1,10-phenanthroline (using MIBK), or as diethyl dithiocarbamates (after precipitating lead in the form of $PbSO_4$).

In many cases, the use of flameless AAS necessitates mineralization of the extract.

Extraction in combination with emission flame photometry is in less use now. Small amounts of gadolinium in heavy water,[263] of molybdenum in steels,[264] and of sodium in tellurium[265] have been determined.

E. Emission Spectroscopy

Solvent extraction has paramount significance for spectrochemical analysis. In employing this determination method preconcentration is necessary when direct analysis does not permit achieving desirable relative detection limit, and also in other cases. It is expedient to remove the matrix if it hinders determination of trace elements as a result of superposition of spectral lines or due to an unfavorable excitation potential of the matrix metal. It is useful to convert the analysed samples into one physicochemical form, as this enables one series of reference samples to be used. Besides, the increase in the concentration of trace elements in the concentrate compared to the sample eliminates the need of using unreliable reference samples with low content of determinable elements. Preconcentration makes it possible to decrease the variations in spectrochemical analysis results due to uneven distribution of trace elements in the sample. This motivates extensive application of the considered combination.

It is wise to employ group preconcentration of all trace elements to be determined. If the emission spectrum of matrix elements is quite simple and the physicochemical properties of the matrix are favorable to the spectrochemical determination of trace elements, then complete removal of the matrix is not necessary; it is sufficient to carry out enrichment. In any event, the concentrate must be available in a form convenient for direct excitation of the spectrum of traces which should be concentrated in a small mass collector.

Preconcentration of trace elements prior to spectrochemical determination is carried out by different methods — extraction, chromatographic, precipitation, distillation, and other techniques. The methods involving preconcentration are sometimes called the "chemico-spectral methods" (a Russian term), or one talks about spectrochemical analysis with chemical enrichment. The extraction spectrochemical methods represent one of the variants of chemico-spectral analysis. In this variant, the extract is often evaporated on a collector, mineralized at elevated temperature, and the spectrum is excited by one of the known techniques. (DC or AC arc, spark discharge, and other).

The collector should be a substance stable on storage and nonhygroscopic; it should give a simple emission spectrum of elements that enter into its composition. The substance of the collector should be readily available in a reproducible form which may be achieved through a small number of operations. It is desirable that the substance should be relatively nonvolatile; this ensures uniform entry of trace elements into the discharge. Charcoal (graphite) powder, often with the addition of sodium chloride, satisfies this requirement. Many procedures have been developed based on the use of this collector.

The techniques involving extraction separation of the matrix have found extensive application. They are convenient for spectrochemical analysis, as it is easier to leave behind many determinable elements in the aqueous phase than to select conditions for their transfer into the extract. This can be illustrated with several examples. For the determination of heavy metal impurities (10^{-4} to $10^{-6}\%$) in metallic gold, Cordis et al.[266] extracted gold from halide solutions using MIBK; the raffinate was evaporated with charcoal powder and analysed. Kondratenko et al.[267] made recourse to the isolation of the matrix on analysing extra pure tin. This element was isolated from HBr solutions with di-2-ethylhexylphosphoric acid, and then the trace impurities (Ag, Al, Be, Bi, Ca, Cd, Co, Cu, Fe, Mn, and others) were determined (10^{-7} to $10^{-6}\%$). Organophosphorous extractants were also used in the analysis of plutonium.[268] Moroshkina et al.[269] spectrochemically determined niobium, tantalum, zirconium, and hafnium ($\geqslant 10^{-5}\%$) in steels after extracting the iron as halide complexes with a mixture of diethyl ether and chloroform. The detection limits are rather low — about 10^{-7} to 10^{-6} g. In the determination of rare-earth elements in steels, iron was separated by extracting it with TBP;[270] the sensitivity of the method is however not very good ($10^{-3}\%$ Ce, La, Nd, Y). For the determination of rare-earth elements in plutonium oxides the microcomponents were extracted from a hydrochloric acid medium using a chloroform solution of trioctylamine.[271]

Extraction of determinable microcomponents is also often used. Wieteska et al.[272] have developed an extraction spectrochemical method for the determination of traces of Ag, Al, Bi, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in highly pure lithium hydride. The impurities are concentrated as 8-hydroxyquinolinates or diethyldithiocarbamates using isoamyl alcohol at pH = 5.8. These extractants, diluted with chloroform, were used for the determination of heavy metals (10^{-4} to 10^{-6} %) in pore solutions.[273] Krivenkova et al.[274] have developed a method for the determination of Bi, Cd, Cu, Pb, Sb, Sn, and Zn in steels; the determination procedure envisages extraction of iodide complexes of metals from sulfuric acid medium, subsequent back extraction with hydrogen peroxide and sulfuric acid solutions, and spectrochemical determination by the fractional distillation method using KI as a carrier. The detection limits are 10^{-4} to 10^{-6} %. Mishchenko et al.[275] have described a method of determining impurities in highly pure oxides of rare-earth elements; the impurities are concentrated by extracting 8-hydroxyquinilinates or 8-mercaptoquinolinates. Gold, palladium, and platinum present in polymetallic ores and sulfide concentrates can be determined after group extraction with 3,5-diphenyl-1-thiocarbamidopyrazoline in $CHCl_3$;[276] the extract is concentrated by evaporating on carbon powder, and analysed. The works of Gindin et al.[277,278] are also devoted to the determination of noble metals; here, the possibility of using organic sulfides has been discussed in particular.[277] Lazovin et al.[279] used extraction of chromium (III) thiocyanate complexes with diantipyrilmethane in chloroform for its determination in solutions. For small contents of chromium it is recommended to evaporate the extract in the presence of graphite powder, to mineralize by calcination at 600° C, and to analyse by the spectrochemical method. Crampurohit and Kaimal[280] employed a similar procedure for the determination of iron in diammonium phosphate; they extracted the metal with chloroform in the form of 8-hydroxyquinolate. Chelnokova et al.[281] studied extraction concentration of trace elements with the use of antipyrine dyes. They recommend the use of chrompyrazole I for concentrating Co, Mo, W, and Zn from thiocyanate solutions, and chrompyrazole II for concentrating Bi, Cd, and Hg from iodide solutions. The extracts, thereafter, are analysed. Judelevic et al.[282] have considered a number of problems related to the application of preconcentration in spectrochemical analysis of highly pure substances, in particular of extraction preconcentration. One of the techniques used by them resides in extracting microimpurities from molten metal with the use of a metal halide melt.

In the given examples the residue obtained after mineralization or raffinate is analysed rather than the extract. The application of extraction as a concentration method is however useful in all cases. Besides, direct introduction of an extract into a charge is associated with technical difficulties and this is apparently not always considered. But cases are known where this has been achieved. Thus, Zheleznova and Tarasevich[283] studied the effect of certain parameters on analysis results with the aim to improve the detection limit and to increase the accuracy of the aerosol spark method. In particular they studied the effect of air pressure on the evaporation and spectra excitation processes when chloroform extracts are sprayed into the spark discharge. The extracts contained 8-hydroxyquinolinates or diethylthiocarbamates of Al, Ag, Ga, Co, Cu, Pb, Mn, Ni, and Ti. Kreshkov et al.[284] have described a method of analysing natural iron-containing sulfides of Au, Sb, Ga, Mo, and Tl. After dissolving the sample, iron (III) is removed by multistage extraction using diethyl ether. Thereafter, the impurities to be determined are extracted from 6 *M* HCl with ethyl acetate, and the extract is sprayed into the spark discharge. Kushkarev et al.[285] have proposed an extraction spectrochemical technique for the determination of impurities in metallic selenium.

F. X-Ray Fluorescence

Group concentration is often used in X-ray fluorescence analysis. The concentrate is usually prepared as a solid sample which can be directly analyzed. After extraction, the extract is generally mineralized and the trace elements are collected on cellulose powder or on silica gel with functional groups grafted to it. Other techniques are also employed. For example, the extract is placed on a filter paper and dried. Thus, for the determination of indium in aluminium alloys,[286] the chloroform extract of indium diethyldithiocarbamate ($\geqslant 0.3\ \mu g/m\ell$) was put on a paper which after drying was placed in the holder of the spectrometer chamber. Mercury was determined in a similar manner by analysing the chloroform extract of mercury dithizonate.[287] This general technique is widely employed in preparing samples.

The samples analyzed by Lobanov[288] were prepared in a different manner. The extract containing 8-hydroxyquinolinates of metals to be determined was diluted with a chloroform solution of polyvinylbutylmetacrylate. The obtained mixture was poured on the surface of metallic mercury and the solvent was removed by heating under a small vacuum until a foil was formed which was placed in a spectrometer.

Extraction can now be carried out with fusible extractants at elevated temperature; the solid concentrate (after cooling) can be immediately converted into a tablet and analyzed. In a similar manner, Co, Cr, Cu, Fe, Ni, and Zn present in fresh water and organic materials were determined.[289] These metals were concentrated by extracting with the melt of 8-hydroxyquinoline.

For the determination of gold and silver in copper-containing materials,[290] the metals to be determined were extracted with a triphenylphosphine solution in the melt of an eutectic mixture of naphthalene-diphenyl. The analysis sample was prepared by pouring the melt into a brass ring lying on a polished surface. The naphthalene-diphenyl eutectic melt was also used for the determination of microgram amounts of molybdenum;[291] 1-phenyl-3-methyl-4-benzoylpyrazolone-5 was used as an extractant. Andreeva et al.[292]

have proposed an extraction X-ray fluorescence procedure for the determination of a number of rare-earth elements (La, Eu, Sm, Yb, Nd) in various materials, using a melt of monocarboxylic fatty acids (C_{17}-C_{20}) and permits of determination of 10^{-1} to 10^{-4} % of rare-earths.

Nekhaev et al.[293] determined hafnium and zirconium in molybdenum alloys after separating them from the matrix with a chloroform solution of diantipyrilmethane. For the determination of niobium and zirconium in the presence of titanium, it is recommended to extract them from the latter with a cyclohexane solution of tri-n-octylphosphinoxide.[294] They are then back extracted with an oxalic acid solution and the back extract is analyzed. For the determination of small amounts of uranium (0.005 to 0.2 mg/mℓ) in phosphoric acid solutions,[295] the X-ray fluorescence method can also be used after extraction concentration using the mixture of di-(2-ethylhexyl) phosphoric acid and TOPO in kerosene.

G. Radioanalytical Determination

Methods of determining small amounts of metals, which combine extraction with radioactivity measurements, are in common use. Basically, these methods involve excitation of radioactivity by irradiating the sample with neutrons, other elementary particles, or gamma-rays (activation analysis), as well as with the use of commercial radioactive isotopes of metals for their determination by the isotope dilution method or by other similar techniques.

Extraction separation and concentration is of great importance in neutron activation analysis.[296] It permits concentrating traces by two principal ways: before, and after irradiation.

Removal of the matrix before irradiation is necessary if it is strongly activated and the formed radio isotopes have long half-lives. Highly activating microcomponents which need not to be determined can also be separated by concentration. For example, Allen and Steinnes[297] determined niobium in geological materials in the following manner: niobium before irradiation was removed from the fluoride-sulfate solution with MIBK, back extracted with a hydrogen peroxide solution, and then irradiated; after irradiation the radioactivity of ^{95}Nb was measured. For the neutron activation determination of gold, copper, and mercury in sea water, Lo et al.[298] preconcentrated these metals in a chloroform solution of lead dithiocarbamate, washed the extract with water to remove sodium, evaporated the solvent, and then irradiated the residue in a reactor. The concentration of determinable elements was found from the activities of ^{198}Au, ^{64}Cu, and ^{197}Hg.

Concentration before irradiation however eliminates one of the main advantages of activation analysis — absence of the blank correction. This advantage is valid if concentration is done after irradiation. Both variants are used in analytical chemistry, but the second one is more often employed.

Tamura[299] determined cobalt in nickel alloys. After irradiating and dissolving the sample he extracted cobalt diethyldithiocarbamate with benzene from the aqueous phase (pH 5 to 6), washed the organic phase with potassium cyanide and mercuric chloride solutions, and measured the activity of ^{60}Co on a gamma-spectrometer. Argollo and Schilling[300] have proposed a procedure for the simultaneous determination of gallium and germanium in volcanic rocks. After irradiating and dissolving the sample, germanium is extracted with carbon tetrachloride from 9 M HCl. Thereafter, the acidity of the raffinate is reduced down to 6 M and gallium is extracted with diisopropyl ether. The determinable elements are then stripped from the extracts with water, and the activities of ^{72}Ga and ^{77}Ge are measured. The detection limits for Ga and Ge are found to be 0.0005 and 0.01 ppm, respectively. Das and Bhattacharya[301] have developed a method for the determination of gold and tungsten in geological samples. Gold is first extracted with MIBK and then, after acidification of the raffinate, tungsten is removed using undiluted TBP. Another method of determining gold is based on extraction separation of ^{198}Au from the irradiated sample with 4-(5-nonyl)-pyridine in 1 *M* H_2SO_4.[302] The extraction yield of gold amounts to more than 93%. Iqbal et al.[303] have studied extraction of gold traces with chloroform solution of diphenyl-2-pyridylmethane. Gold is quite selectively removed from 1 *M* HCl; use may be made of this fact for the separation of gold in neutron activation determination. This procedure has been tested for artifical mixtures containing Al, Ce, Co, Fe, Mg, Mn, Na, Ni, and Zn. Vlasov and Perezhogin[304] determined the concentration of sodium (10^{-5} to 10^{-3}%) in tantalum ethylate. The sample after irradiation was hydrolyzed with nitric acid and tantalum was extracted from the fluoride solution with TBP. The activity of ^{24}Na was measured in the raffinate.

The application of modern gamma-spectrometers appreciably enlarges the possibilities of the activation analysis, particularly for group determination of elements. For example, Gilbert et al.,[305] used a high-resolution gamma-spectrometer for the determination of about 30 impurities in metallic silver after extraction separation of the matrix with a benzene solution of dibutylsulfide. Present-day equipment does not call for the necessary removal of each of the determinable radioisotopes; often it is sufficient to divide them into groups. Kusaka et al.[306] divide the determinable elements into four groups. Extraction is carried out with pyrrolidine dithiocarbamate. Division into groups is accomplished by varying the acidity and the composition of aqueous phases. Group separation of trace elements by extraction was used by Alimarin and co-workers[307] in neutron activation analysis of volcanic waters. For similar purposes, Yang et al.[308] used dinonylnaphthalene sulfonic acid as an extractant.

In activation analysis, use is often made of substoichiometric separation by extraction. Jaskolska[309] employed substoichiometric extraction of antimony from an irradiated sample for its determination in germanium. N-Benzoyl-N-phenylhydroxylamine (BPHA) was used as an extractant. The gamma-activity of the ^{122}Sb isotope was measured. When the concentration of antimony is small (of the order of 10^{-7} %), it is necessary to preisolate antimony from germanium by extraction with diisopropyl ether; antimony is then back extracted. Substoichiometric extraction has also been used for the determination of antimony in metallic zinc.[310] After dissolving the irradiated sample, antimony (V) is partially reduced to antimony (III) which is extracted with BPHA solution in $CHCl_3$. Thereafter, the activity of the raffinate is measured and the concentration of antimony in the sample is calculated. Mitchell et al.[311] separated gold substoichiometrically from the solution of irradiated sample using tri-n-octylphosphine sulfide in cyclohexane. Shigematsu and Kudo[312] separated substoichiometrically a number of heavy metals (Ag, Au, Co, Cr, Cu, Sb) present in zinc selenide after irradiating the sample. Different reagents were used: for gold, rhodamine B; for silver and copper, dithizone; for chromium, sodium diethyldithiocarbamate; for cobalt, 1-nitroso-2-naphthol; and for antimony, cupferron.

For the determination of trace amounts of gallium,[313] the solution of the sample to be analyzed was irradiated and a carrier was introduced. Thereafter, gallium was substoichiometrically extracted with a cyclohexane solution of tri-n-octyl-phosphine oxide. The activity of ^{72}Ga was measured in the extract. Yakovlev et al.[314] used tri-n-octylamine for substoichiometric extraction of molybdenum (VI); molybdenum was preliminarily extracted from the solution of the irradiated sample (H_2SO_4, HCl) with amyl acetate. Kudo et al.[315] determined impurities of copper, manganese, and platinum in optical glass. For the determination of copper (II) and platinum (II) use was made of substoichiometric extraction with dithizone. Manganese was determined in the usual manner; it was extracted with thenoyltrifluoroacetone after isolating copper.

Extraction is an important separation technique used in isotopic dilution and other radioisotopic methods. In this case, use is generally made of substoichiometric extraction. For instance, after adding the indicator^{197,203}Hg in the solution of the sample submicrogram amounts of mercury can be determined by substoichiometric extraction with silver diethyldithiocarbamate solution.[316] Gold (III), palladium (II), hydrochloric and nitric acids strongly hinder the process. Kudo et al.[317] have proposed a complicated procedure for the determination of indium in metallic cadmium and tin, which involves multistage extraction isolation of the ^{114m}In isotope from the irradiated sample. Finally, indium is extracted with substoichiometric amounts of sodium diethyldithiocarbamate. The application of substoichiometric extraction in combination with isotope dilution or radiometric correction methods has made it possible to suggest a highly sensitive procedure for the determination of titanium (monolauryl phosphoric acid is used as an extractant), the detection limit being 1 to 2 μg/mℓ.[318] This procedure was used for the determination of titanium in hafnium and zirconium. Hoentsch and Flachowsky[319] have suggested a substoichiometric extraction procedure for the determination of silver in semiconducting materials, in which silver is isolated as dibenzyldithiocarbamate. The procedure envisages introduction of the radioactive indicator (^{110m}Ag) into the sample, and extraction of silver at 5°C with 10^{-5} *M* zinc dibenzyldithiocarbamate solution in carbon tetrachloride. It ensures a detection limit of 1 μg/mℓ with 2 to 4% relative error. Grosheva et al.[320] used substoichiometric extraction isolation, which involves the use of 8-mercaptoquinoline, in combination with the isotope dilution method for the determination of Co, Cr, Mn, and Zn. The detection limits were found to be 3×10^{-8} g, 5×10^{-7} g, 1.5×10^{-8} g, and 2×10^{-8} g for Co, Cr, Mn, and Zn, respectively. In a similar manner they determined mercury, cobalt, copper, and zinc using 8-mercaptoquinoline.[321] Sichkar and Shamaev[322] used substoichiometric extraction by dithizone in combination with the radiometric correction method for the determination of $\sim 10^{-4}$ % bismuth in alloys. Rao et al.[323] used brilliant green for substoichiometric separation and subsequent determination of thallium (III). The sensitivity of the method is quite high ($\leqslant$1 μg), the relative error being 2 to 3%. For the determination of chromium, Kudo et al.[324] suggest to extract it substoichiometrically from the aqueous solution containing EDTA and cerium (IV) sulfate. They used diethyldithiocarbamate as an extractant and MIBK as a solvent. The activity of ^{51}Cr was registered in the extract. For the determination of gold by the isotope dilution method, Chermette et al.[325] extracted the metal from chloride solutions (pH $<$ 2) with chloroform solution of copper diethyldithiocarbamate. Mercury hinders the determination.

Extraction is also used in methods based on the measurement of natural radioactivity. As an example, the reader may be referred to the procedure of determining plutonium traces in soils.[326] It combines several separation techniques: plutonium is separated from uranium by precipitating it with barium sulfate. In order to isolate trivalent actinides and thorium, it is recommended first to extract them with plutonium (IV) using Aliquat-336, and then to back extract with nitric (actinides) and hydrochloric (thorium) acids. Thereafter, plutonium is back extracted with a mixture of hydrochloric and oxalic acids, electrolytically precipitated, and its concentration is determined from the measured alpha-activities of ^{236,238,239,240}Pu isotopes.

H. Electrochemical Determination

Polarographic analysis of extracts containing trace elements is commonly used. Such a combination of methods speeds up analysis, as it is not necessary to decompose the extract or to perform a back extraction. Besides, the selectivity of polarographic determination is compounded with that of extraction preconcentration. The procedure usually consists of the following. The determinable element or the group of elements are isolated by extraction. The extract is analysed polarographically; for this, use is made of different polarographic methods (classical DC, oscillographic and AC polarography, and other ways, including stripping variants).

If the organic solvent has a sufficiently high dielectric constant and polarity, then a suitable background electrolyte is introduced into the extract and the voltammetric characteristics of the organic solution are recorded by a suitable method. When the organic solvent does not conform to these requirements, the extract is diluted with other solvents, for example with acetone or methanol, and a background electrolyte is added; thereafter, the measurements are taken. In some instances, the measurements are taken in mixed water-organic solutions. Additional introduction of a polar solvent into the extract gives, of course, poorer detection limits, and in this sense impairs the analysis procedure. But, on the other hand, the range of extraction systems and, hence, of the determinable elements by the considered methods is considerably extended. The first review of extraction polarographic methods was published in 1967.[327]

We shall now consider some of the extraction polarographic methods of determining metals which have been suggested in the last few years. Karbainov and Karbainova[328] have proposed a procedure for the determination of antimony in high-purity solutions of sodium chloride and hydrochloric acid. They separated antimony from the solution by extracting its diethyldithiocarbamate with chloroform in the presence of EDTA and KI. Polarographic analysis of the extract enables 5×10^{-6} % antimony to be determined in the solution, the relative error being 10 to 15 %. Kopanskaya and Odobesku[329] used oscillographic polarography for the determination of antimony in semiconducting alloys. The metal was separated from disturbing elements by extracting it with benzene from a bromide solution. The extract was polarographically analyzed after adding to it a solution of LiCl in anhydrous acetic acid. Nincakova and Kosturiak[330] have proposed a method for the determination of cadmium in mixtures of metals. It is extracted from a thiocyanate solution with pyridine. This enables microgram amounts of cadmium to be determined in the presence of a number of metals that are recovered almost in the same range of potentials. Nevertheless, excessive amounts (10-times) of Ag, Hg, Cu, and Pb hinder the determination.

Fujinaga and Nagaosa[331] extracted cadmium with acetonitrile as a thiocyanate complex using ammonium sulfate as salting out agent. Further polarographic analysis of the extract enable 2×10^{-7} to 2×10^{-5} g-ion per liter of Cadmium Cd to be determined. Fujinaga and Puri[332] extracted oxinates of cadmium (pH 7 to 10) and lead (pH 9 to 12) with molten naphthalene for their polarographic determination. After extraction, the melt was dissolved in dimethylformamide and analyzed. The calibration curve is a straight-line in the interval 0 to 112 μg Cd and 0 to 207 μg Pb in 10 mℓ. For the extraction polarographic determination of cadmium and tin in high-purity iron, Karbainov and Tarzemyanova[333] have given conditions for the extraction of separable impurities and for polarographic analysis. Good results are obtained upon extracting metals from a sulfuric acid solution in the form of iodide complexes. Ethanol is good diluent for the extract. Stripping voltammetry was used. The determinable elements (Cd, Bi, Zn) were concentrated by different extraction methods; the procedure enables one to determine 10^{-7} % impurities. Fujinaga and Lee[335] have shown that it is possible to determine cadmium, cobalt (II), and iron (II) from a mixture containing all of them. The metals are extracted at 15° C with n-butyl alcohol as oxinates. A butyl alcohol solution of $LiClO_4$ is added to the extract which is then analyzed polarographically. Kitagawa et al.[336] extracted copper oxinate with MIBK followed by polarographic analysis of the extract for the determination of copper. For the same purpose, copper 8-mercaptoquinolinate was extracted with naphthalene melt.[337] Zhiyangulova[338] has studied in more detail the copper (II)-8-mercaptoquinoline-naphthalene melt system. After dissolving the cooled melt in dimethylformamide, polarographic analysis of the obtained solution makes it possible to determine 5×10^{-7} % Cu. Commensurable amounts of Sb (III), Bi(III), Cd, Co(II), Fe(III), Pb, Ni, V, Zn do not affect the determination. This procedure was employed for the determination of copper in soils and tap water.[338] Kozirod and

Shukin[339] determined copper in natural waters after extraction concentration with dithizone. The combination of extraction with polarographic measurements in the extract enabled 10^{-3} to 10^{-5} % Cu to be determined in cadmium sulfate without separating the matrix.[340] Microgram amounts of indium can be determined after extracting the oxinate with the melt of naphthalene.[341]

Tilyupo et al.[342] have proposed an oscillopolarographic method of determining lead in extracts. Carbon tetrachloride was used to extract lead in the form of a complex with heptylxanthate. The extract was diluted with ethyl alcohol and analyzed polarographically using LiCl as a supporting electrolyte. The determination limit was found to be 4 μg. Tran Churong et al.[343] have shown that it is possible to determine lead at the same background after extracting 8-hydroxyquinolinate with ethylacetate. Bhowal and Umland[344] determined molybdenum polarographically after extracting it as *N*-benzoyl-*N*-phenylhydroxylaminate. The studies of polarographic behavior of oxinates of some metals in organic solvents have revealed the possibility of determining molybdenum in ethyl acetate or in its mixture with methanol.[345] When analyzing steels, Penz[346] determined niobium after extracting it from a 4 *M* HCl solution using a chloroform solution of 2-benzoinoxime. Oxalates, phosphates, nitrates, fluorides, and sulfides hinder the separation of niobium. The presence of ascorbic acid ensures against extraction of chromium (VI), tungsten (VI), and vanadium (V); molybdenum is first precipitated with 2-benzoinoxime and then filtered. The extract containing niobium is evaporated; the residue is dissolved in a mixture of sulfuric and hydrochloric acids and niobium is determined polarographically. Podkorytova et al.[347] have suggested an extraction polarographic technique for the determination of 10^{-7} to 10^{-5} % nickel and zinc in high-purity cadmium.

Golimowski et al.[348] have developed a method for the determination of heavy metals (Cd, Fe, Pb, Ni, Zn) in the wastes of the copper-production industry. Copper is first isolated by electrolysis, and then the metals to be determined are extraction concentrated as diethyldithiocarbamates. The extract is mineralized and metals are determined by polarographic or spectrophotometric methods. Katagawa et al.[349] have studied the polarographic behavior of a number of metals in the extracts of their chelates. Iron (III) acetylacetonate yields a reversible single-electron wave, and this enables iron (III) to be determined by the extraction polarographic method. 8-Hydroxyquinolinates of copper (II), pyrrolidinedithiocarbamates of copper (II), lead, and zinc behave in a like manner in MIBK medium. When analyzing metallic vanadium,[350] the impurities (10^{-3} to 10^{-4} % Al, Cd, Cr, Mo, Ni, and Zn) are first concentrated by extracting the diethyldithiocarbamates with chloroform, and then they are determined polarographically. Budnikov et al.[351] have studied the polarographic behavior of heavy metals in anhydrous solutions after extracting diethyldithiophosphates with toluene. They have proposed several extraction techniques for the determination of certain metals when present together — for example in combinations of Pb-Tl, As-Bi-Pb, Co-Ni.

Palladium was determined in the electrolyte used for palladium coating, which contained excessive amounts of tin.[352] For this purpose it was isolated by exchange extraction using a toluene solution of copper diethyldithiocarbamate. The extract was diluted with an ethanol solution of $LiClO_4$, and analyzed polarographically; 7×10^{-6} g-ion Palladium per liter can be determined by oscillographic polarography. For the extraction polarographic determination of palladium and nickel, Fujinaga and Puri[353] extracted their dimethylglyoxymates with molten naphthalene. The polarographic behavior of tin complexes with *N*-benzoyl-*N*-phenylhydroximic acid has been studied in the $CHCl_3$-CH_3OH medium in the presence of $LiClO_4$.[354] An extraction polarographic analysis technique has been suggested which enables 7×10^{-7} to 2×10^{-5} *M* tin to be determined in the presence of excess amounts of foreign metals and complexing substances. Only Mo(VI), Ti(IV), and V(V) hinder the determination.

Irutsu et al.[355] have determined uranium in sea waters by stripping voltammetry after its extraction concentration with acetylacetone solution of trioctylphosphine oxide. The procedure permits determination of $\geq 5 \times 10^{-9}$ *M* uranium (VI). Small amounts of uranium (1 to 100 ppb) have been determined by Keil,[356] whose technique depends on nitrate reduction reaction catalyzed by uranium, and involves the use of differential pulse polarography. Uranium is preconcentrated by extracting it with chloroform solution of triphenylarsine oxide and then back extracted with Na_2CO_3 solution. Gold (III), iron (II) and chromium (VI) strongly hinder the determination. Fujinaga and Lee[357] have shown that it is possible to use acetylacetone as an extractant and at the same time as a solvent for subsequent determination of uranium (VI) and.iron (III) in the extract when they are present together. It is of interest that, depending on extraction conditions (pH of the aqueous phase), the uranium complex in acetylacetone can give rise to one or two reduction waves.

It is understood that the application of extraction in combination with polarography is not limited to the above extraction polarographic methods, including polarographic analysis of extracts. Extraction is employed as a usual method of separation and concentration of metals which are determined in aqueous solution. Belova et al.[358] have determined arsenic (10^{-6} to 10^{-5} %) in metallic gallium and gallium chloride by inversion AC polarography. After extracting arsenic from halide solutions, it is back extracted with water and then determined in a usual manner. Savostin et al.[359] have determined microamounts of gallium after extracting it from 7 *M* hydrochloric acid with a benzene solution of dibutylamidobutylphosphate. Gallium is back extracted and determined polarographically. Large amounts of aluminum, iron (II), copper, and zinc are not extracted; excessive amounts of aluminum also suppress extraction of antimony (III). Tin (IV), iron (III), and arsenic (V) hinder the determination.

An indirect extraction-polarographic method of determining mercury has also been developed.[360] This method is based on the exchange reaction between carbon tetrachloride solution of bismuth (III) diethyldithiocarbamate and the aqueous bromide complex of mercury (II). An amount of bismuth equivalent to that yielded by the exchange reaction is determined in aqueous solution by stripping voltammetry, which serves to calibrate the method. Katsura[361] has extracted uranium (VI) with chloroform as an ionic associate obtained in the presence of sodium benzoate and tetradecyldimethylbenzyl ammonium chloride. Uranium is back extracted with sulfuric acid (0.5 *M*) and then determined polarographically. The calibration curve is close to a straight-line in the range from 10^{-4} to 10^{-3} *M* uranium. Mercury (II) and copper (II) interfere with the determination. Mikhailova et al,[362] used heavy metal extraction for the determination of Bi, Cd, Cu, Pb, Zn in niobates, tantalates, and oxides of tantallium (V) and niobium (V). The determinable metals are back extracted with hydrochloric acid and then determined by usual polarographic techniques. The technique enables 10^{-5} to 10^{-6}% of Bi, Cd, Cu, Pb, Zn to be determined.

Karlsson and Gorton[363] have proposed an extraction coulometric method of determining iron. According to this method, iron (III) is first extracted with diisopropyl ether and then titrated with iodine which is generated coulometrically at a constant potential. The detection limit equals 1 μg/mℓ. Kletenik and co-workers[364] have formulated the conditions and discussed future prospects of conductrometric titration of extracts for the determination of small amounts of metals. The possibilities of the method have been illustrated by determining gold (III). Gold is extracted from hydrochloric acid using a heptane solution of TBP. Thereafter, the electrical conductivity of the extract is measured and the concentration of gold is determined from the calibration curve. Under optimal conditions 10^{-6} to 10^{-7} *M* gold can be determined. This method is of interest also for the reason that the coextracting impurities which do not contribute to the conductivity of the organic phase are no barrier to determination. For example, uranium (VI) is simultaneously extracted with gold (III) but it does not hinder the determination as it forms non-ionic compounds.

I. Other Methods

Electron spin resonance (ESR) is infrequently used in inorganic analysis. The main reason for this is that the number of metals in stable oxidation states which yield ESR signal are limited. True, complexes of paramagnetic ions can be obtained, in which the central atom has an anomalous degree of oxidation. Such complexes were obtained by Solozhenkin et al.[365] who extracted Pt, Pd, Ir, and Ag in the form of bis-dithio-2-diketonate or dithiocarbamate complexes using mixture of dichlorethane and chloroform (1:1). They then transferred the central atoms of the complexes present in the extract into paramagnetic oxidation states — Pt(III), Pd(III), Ag(II), etc. — and measured the ESR signal. The detection limits were found to be: 2 μg/mℓ for silver, 4 μg/mℓ for palladium, and 20 μg/mℓ for platinum. It is not so easy to obtain similar oxidation states in the stable state, and, for this reason, this technique hardly finds wide application.

The technique involving the use of compounds that contain free stable radical (spin labelled reagents) as extractants has a better future. Such compounds have, besides a spin label, the complexing groups, and can react with metal ions including diamagnetic ions, and hence, they can be used with ESR for analytical purposes. Zolotov et al.[366] have studied the properties of a number of reagents labelled with nitroxyl radicals, and the possibilities of their analytical application for the determination of zinc. The extractants readily separate zinc into the organic phase, in which the ESR signal of the complex can be measured. The common disadvantage of these methods is the isolation of excess reagent from the complex. To accomplish this, a chromatographic method was used. A procedure has been developed for the determination of zinc with spin labelled potassium xanthate.[367] Its detection limit can be 0.01 μg zinc per milliliter but the application of this method presents difficulties due to the unstability of the reagent and the complex. Solozhenkin et al,[368] used the same reagent to determine palladium, mercury, and silver. The technique depends on the extraction of complexes with chloroform, and on measuring the ESR signal of the extract.

Extraction properties of spin labelled beta-diketone have been studied in respect to 26 metals by extraction chromatography with reversed phases.[369] Maximum extraction is observed for mercury, cadmium, copper, lead, silver, and iron. For iron and copper, extraction by usual methods has been studied and the extraction constants, partition constants, and the stability constants of complexes have been determined.

The extractable complexes containing two molecules of nitroxyl reagent are biradicals, the ESR spectra of which can differ from that of the spin labelled reagent. Under these conditions the ESR signal can, in principle, be measured in the presence of the reagent without removing the latter. Thus, the reaction between palladium and 4-hydrooxyiminomethyl-2,2,5,5-tetramethyl- 3-imidazoline-1-oxyl (HL) was studied.[370] Palladium is extracted with chloroform in the form of the PdL_2 complex. One of the ESR spectrum lines of this biradical was used for quantitative determination of palladium with an error of ± 2.5% for concentrations from 5×10^{-5} to 5×10^{-4} *M*, and with an error of ± 5% for concentrations from 5×10^{-6} to 5×10^{-5} *M*.

For the quantitative determination of copper, use has also been made of the biradical formation process, but in a different manner.[371] Upon reacting copper (II) with 2,2,6,6-tetramethyl-1-iminoxyl-4-xanthate, a complex of copper (I) is formed with a radical and a biradical dixanthogenide. The complex and the biradical are extracted with carbon tetrachloride, and the signal of one of the ESR spectrum lines of the biradical, which does not coincide with ESR signal lines of the complex, is measured in the organic phase. The intensity of the corresponding ESR line in the extract can be taken to be a measure of concentration of copper in the solution to be analyzed. The detection limit if found to be 2 μg/mℓ.

The analytical sensitivity of organic radicals is quite high if modern ESR spectrometers are used. Therefore, further studies in this direction can lead to the development of new methods of determining metals, characterized by very low detection limits.

Preconcentration techniques have been used in combination with *spark source mass spectrometry.* The trace elements, after their removal from the matrix, are deposited on a collector — high-purity aluminium oxide.[372] For the determination of eight trace elements in steel, they are first extracted from a thiocyanate solution with MIBK, and then back extracted with dilute sulfuric acid and evaporated on alumina. After calcination, the concentrate is analyzed using a mass spectrometer with double focusing. A like procedure has been developed for the determination of impurities in sulfuric acid, detection limits being 10^{-7} to 10^{-5}%. An alternate method is also used for determination of traces of noble metals in natural and industrial samples. Noble metals are extracted from a HCl solution, containing copper and other non-ferrous metals, as complexes with hexamethylenephenylthiourea; at the same time copper (I) is extracted. The extract is evaporated and calcinated, and the concentrate is obtained on copper oxide or copper sulfide which is then analyzed. Copper does not hinder the determination.

Spark source mass spectrometry enables very small amounts of at least 60 to 70 elements to be determined. Therefore, it is expeditious to use this method in combination with concentration techniques which involve the removal of the matrix.

Use is also made of other variants of mass spectrometry. Osaki et al.[373] have determined the total concentration of chromium in sea waters using mass spectrometric variant of the isotope dilution method. A known amount of stable ^{50}Cr (VI) is added to the sample and chromium pyrrolidinedithiocarbamate is extracted with chloroform. The extract is mineralized and the residue is analyzed by mass spectrometry. The detection limit equals 1 ng of chromium per liter. Matsmoto et al.[374] have proposed an extraction mass-spectrometric method of determining mercury in a purely hybrid form. A solution containing ^{198}Hg is added to the solution of the sample, and mercury iodide is extracted from sulphuric acid solution with MIBK. Thereafter, 1 μℓ of the extract is introduced into the ion source of mass spectrometer.

Kletenik et al.[375] have evaluated the possibilities of the *extraction magnetometric method* of analyzing extracts, which consists in measuring the magnetic moment of organic phase after extraction of paramagnetic ion complexes: Fe(III)-TBP, and Co(III)-di-(2-ethylhexyl)phosphoric acid. The measurements of magnetic moments enables one to determine small amounts of Fe(III) and Co(III) in extracts (~ 10^{-5} *M*). However, the magnetic moment of extracts is weakly dependent on concentration (i.e., poor sensitivity), and, therefore, the measurements must be taken with high precision. From this viewpoint, the possibilities of using the proposed method are not quite clear.

An extraction *photoacoustic method* of determining cadmium has been suggested by Oda et al.[376] The metal is extracted with chloroform as the dithizonate and the extract is exposed to an argon laser ray. The photoacoustic signal is detected by a piezoelectric ceramic, the response of which is linear in the range from 0.05 to 50 ng Cd/mℓ. It is probable that with the development of the photoacoustic spectroscopy technique such methods will grow further.

Otto et al.,[377] the authors of the review devoted to *catalytic methods* of determining traces, suggest that the use of these methods together with extraction is highly desirable: such a combination makes it possible to significantly increase the determination selectivity. But the application of extraction catalytic methods is faced with several difficulties: metals in the extract are present not in the form of free aqua-ions, but as complexes.

The catalytic activity of complexes and the nature of their action on the indicator reaction in the organic solvent may altogether be different compared to aqueous solutions. Also, a number of other difficulties are encountered. But for those cases, when one succeeds in surmounting these difficulties, extraction-catalytic methods of determining traces have also been developed. These methods are characterized not only by their good detection limits, but also by high selectivity. A number of such cases have been considered in the review by Otto et al.[377] Their list can be extended.

Otto et al.,[377] the authors of the review devoted to *catalytic methods* of determining Copper is extracted with chloroform in the form of a mixed complex with salicyalate and pyridine. Subsequently, copper is determined by the oxidation reaction of sulfamic acid with hydrogen peroxide in a chloroform-ethanol medium, which is catalysed by a copper complex. Otto and Muller[379] have proposed a selective and sensitive method of determining iron traces (5×10^{-6} to $10^{-3}\%$) in cobalt, copper, and nickel salts. This method is based on a MIBK extraction of iron from 7 *M* LiCl. Subsequently, iron is determined by the indicator oxidation reaction of p-phenetidine with hydrogen peroxide in the presence of 1,10-phenanthroline. The reaction is carried out in the extract. Jordanov et al.[380] have developed a very sensitive method of determining rhenium (VII). The study of conditions under which rhenium (VII) is reduced with stannous chloride in the presence of HCl and H_2SO_4, and of the effect of complex-formation (SCN-dimethylglyoxime, alpha-furyldioxime) has made it possible to suggest an extraction-catalytic procedure of determining rhenium, which is characterized by its detection limit of 1 pg.

There are other trends of using extraction in catalytic methods. For example, for the catalytic determination of traces of copper the product obtained by oxidizing o-aminophenol with air oxygen was extracted with chloroform.[381] The oxidation products were found to be highly colored ($\epsilon_{414} \simeq 10^5$). This technique has made it possible to suggest a very sensitive method of determining nanogram amounts of copper in tap and river waters.

Tananaiko et al.[382] proceeded in a like manner. They extracted the oxidation products in the lusegenine-copper(II)-hydrogen peroxide system with benzene and measured the absorbance of the extract. This method is less sensitive (20 to 120 ng Cu/mℓ) than the earlier mentioned one,[381] because the lusegenine oxidation products have an $\epsilon_{420} \simeq 1.5 \times 10^4$. It is evident that extraction in the considered cases[381,382] will yield better results if the reaction products are selectively removed. Other researchers have also published the results of their studies related to the use of extraction in catalytic methods.[383-386] However in these cases extraction was used as an auxiliary method, that is, as a method for selective removal of the determinable metal from a mixture of more or less complex composition. The extract is decomposed or the element back extracted, and then the determination is carried out in an aqueous solution. In this manner, silver was determined after extracting it with dithizone;[383] cobalt was determined after extracting the cobalt (III) 1-nitroso-2-naphtholate.[384] Manganese was determined catalytically after extracting all interfering elements as complexes with PAN.[385]

The number of publications dedicated to extraction catalytic methods is not very large. But these methods seem to have a bright future, as all three ways of using extraction in catalytic methods will, apparently, prove useful.

V. EXTRACTION OF SMALL AMOUNTS OF DIFFERENT ELEMENTS OF MAJOR INTEREST

Here, we shall list (without making any reference) the most commonly used and well-known methods for the extraction of each of the given elements. This will be usually followed by some recently proposed techniques for the separation of these elements. The latter information is not exhaustive, since many methods of separating these elements are listed in the earlier sections of this review. The extraction methods of separating different elements are discussed in many monographs and manuals, for example in the books of the series "Analytical Chemistry of Elements" which was first published in Moscow in 1960.

Aluminum. Microamounts of aluminum are not often extracted; in most cases the elements that hinder the determination of aluminum are removed by extraction. But if aluminum is to be extracted, then usually its chelates with 8-hydroxyquinoline, cupferron, and rarely with β-diketones are used. This is how Kuchkarev et al.[387] determined aluminum in selenium by the spectrochemical method; aluminum acetylacetonate was pre-extracted with chloroform and then the graphite rod was impregnated with the extract; AC arc was used to excite the emission spectrum. The complex of aluminum in the ethyl ether solution of 2,4-dioxo-4-(4-hydroxy-6-methyl-2-pyrone-3-yl)butyric acid is extracted with chloroform; Drevenkar et al.[388] used extraction for fluorescence determination of this element (0.5 μg/mℓ). For the photometric determination of aluminum, Miftakova et al.[176] extracted this element in chloroform as a compound with hydroxy-α-dibutylphosphineoxido propionic acid.

Antimony. Antimony (V) is often extracted from HCl solutions with different oxygen-containing solvents in the form of the complex acid $HSbCl_6$. MIBK is a convenient solvent.[389,390] For the atomic-absorption determination of antimony in geological materials, McHugh and Welsch[389] extracted this element from HCl solution with MIBK, and sprayed the extract into an acetylene-air flame; they determined $10^{-4}\%$ antimony with an error of 2 to 8%. For the extraction-photometric determination of antimony it is often extracted in the form of ionic associates $R^+SbCl_6^-$, where R^+ stands for the cation of the basic dyes, for example rhodamine B.[391]

Antimony (III) can be extracted from HCl solution with oxygen-containing solvents or amines in the form of $HSbCl_4$. Other suitable solvents are also used to extract antimony (III) from H_2SO_4 solution of potassium iodide, bromide, or chloride as SbI_3, $SbBr_3$, or $SbCl_3$. Extraction of $SbCl_3$ with benzene followed by back extraction with the use of EDTA solution was employed for atomic-absorption determination of antimony in atmospheric dust.[392] The method of separating antimony and tin depends on the extraction of their bromide complexes from H_2SO_4 solution with a mixture of octane and toluene. Antimony (III) bromide was extracted for the oscillopolarographic[329] and photometric[393] determination of this element (antimony iodide can also be separated for photometric determination).

The complexes of antimony (III) are conveniently extracted with dithiocarbamates (pentavalent antimony is not extracted). On this principle is based, for example, the method of separate atomic-absorption determination of Sb(III) and Sb(V) in natural and waste waters;[394] pyrrolidinedithiocarbamate and MIBK were used, respectively, as reagent and solvent. For the atomic-absorption determination of antimony use was also made of extraction with diethyldithiocarbamate.[395] For the polarographic determination, antimony was extracted as diethyldithiocarbamate with chloroform.[328] Antimony (III) is extracted also in the form of chelates with xanthates,[396] *N*-benzoyl-*N*-phenylhydroxylamine,[309,310] and cupferron.[312]

Arsenic. The most commonly used methods for extraction separation of this element are based on the recovery of its neutral halides ($AsCl_3$, $AsBr_3$, or AsI_3) with inert solvents like carbon tetrachloride, chloroform, or benzene. Arsenic trichlorides can be extracted from 8 to 12 *M* HCl solution with these solvents, only germanium is extracted along with arsenic. Arsenic (III) dithiocarbamates can also be extracted from H_2SO_4 solutions (pentavalent arsenic is not extracted). Methods of extracting arsenic (V) are also known.

For example, molybdo-arsenic heteropoly acid is separated from acid solutions with n-butyl alcohol; separation can also be effected with organotin compounds. Dioctyl or dinonyltin dinitrates extract arsenic (V) with a high distribution coefficient and quite selectively; chloroform can serve as a solvent.[87,88]

For the flameless atomic-absorption determination of arsenic in water and urine, it was extracted from 12 *M* HCl solution as AsI_3 and then back extracted with water or a potassium dichromate solution.[397] Extraction of arsenic trihalides (mainly AsI_3) was used for the polarographic determination of this element.[358]

Barium. It seems that no good methods of extracting barium are available. Recently it has been shown that macrocylic compounds can possibly be used to extract barium. Takeda et al.[113] have proposed a procedure for the atomic-absorption determination of barium in the presence of large amounts of calcium, including extraction of barium in the form of compounds with 18-crown-6 ether. After extraction, barium is back extracted with HNO_3 and then determined in the acetylene-nitrous oxide flame.

Beryllium. It is generally extracted in the form of acetylacetonate (and rarely as β-diketonates) with benzene or carbon tetrachloride. The presence of EDTA enables one to make this method selective. This is shown, for example, in the work of Ackermann and Konig[165] who extracted beryllium at pH 6 to 7. At this pH value, microgram amounts of beryllium are extracted and aluminum in excessive amounts — 100 to 200 times as much is no hindrance. Other metals hinder the extraction to a lesser extent. Ultrasmall amounts of beryllium can be concentrated by extracting it with a mixture of acetylacetone and chloroform.[398] Vilcsek and Lohmann[399] extracted beryllium in the form of acetylacetonate for its flameless atomic-absorption determination in space materials. Prior to atomization, they back extracted beryllium from the organic phase with HCl. The detection limit was found to be 1.7 ng/g (for a sample weight of 50 to 200 mg). Jauniaux et al.[400] have suggested an extraction atomic-absorption method for the determination of beryllium in aluminum ($> 10^{-3}\%$) and copper ($> 2 \times 10^{-4}\%$). Beryllium is extracted with acetylacetone in MIBK from the saturated solution of sodium chloride containing EDTA.

The extraction systems based on β-diketones were used for the atomic-absorption determination of beryllium, and also for some heavy metals.[401] Drevenkar et al.[388] propose the use of the ethyl ether solution of 2,4-dioxo-4-(4-hydroxy-6-methyl-2-pyrone-3-yl)butyric acid for the spectrofluorimetric determination of beryllium (0.5-2.0 μg/mℓ). Gladilovich et al.[402] used 2-hydroxy-3-naphthioc acid for the determination of beryllium in silicate rocks and alloys of copper. The beryllium complex was extracted with n-butanol from a slightly acidic aqueous solution containing EDTA, and the extract was subjected to fluorimetric analysis. Thus, 1-4 μg beryllium can be determined in 50 mℓ of the extract. Wicks and Burka[403] used the above-mentioned reagent for the fluorimetric determination of beryllium. The metal was preconcentrated by extracting it with a chloroform solution of acetylacetone, and then the fluorescent complex of 2-hydroxy-3-naphthioc acid was used. The detection limit was found to be 0.05 μg.

Bismuth. Bismuth (III) is usually extracted in the form of cupferronate, dithizonate, or dithiocarbamates. Extraction of diethyldithiocarbamate in the presence of tartrate, cyanide, or EDTA from alkaline solutions is a specific method of separating this element; chloroform or carbon tetrachloride can be used as solvent. Examples of the use of diethyldithiocarbamate can be found in the works of Donaldson[196] and Karlsson and Gorton[362] who determined bismuth spectrophotometrically (by the iodide method) and polarographically. Tsalev et al.[404] determined bismuth in tungsten trioxide by extracting its complex with hexamethylenedithiocarbamate in butyl acetate, followed by atomic-absorption determination in the flame. The detection limit was found to be $6 \times 10^{-5}\%$. Inui et al.[405] used zinc dibenzyldithiocarbamate for the extraction atomic-absorption determination of bismuth in aluminum and solders. Sufficiently high amounts of bismuth were determined (≃ 0.3% in aluminium and 0.06% in solders); this, apparently, does not fully characterize the possibilities of this method. Ficklin and Ward[406] have developed a flameless atomic-absorption method for the determination of bismuth in soils and rocks. According to this method, the metal is first concentrated in MIBK as the pyrrolidinedithiocarbamate, and then the extract is introduced into a graphite atomizer; the detection limit is $5 \times 10^{-6}\%$. Bismuth dithizonate was extracted for the determination of this element by the radiometric adjustment method;[322] bismuth xanthates were extracted for the spectrophotometric determination.[196]

Another known method is the extraction of the bismuth iodide complex from an acidic medium, for example with isoamyl acetate. The complex is extracted as a compound with chrompyrazol II (antipyrine dye). Dolgorev et al.[407] used dithiopyrylmethane to concentrate bismuth. The chemistry of the extraction of bismuth halide complexes with different extractants has been studied in detail by Raman laser spectroscopy and partially by IR-spectroscopy in a series of our works (confer, for instance[408]).

Cadmium. It is generally extracted as chelates with dithiocarbamates, dithizone, and other chelate-forming reagents (often in the presence of donor-active additives), and also from iodide solutions of this element with oxygen-containing solvents or amines.

Extraction of ethylxanthate with MIBK was used for atomic-absorption determination of cadmium; large amounts of aluminum, cobalt, chromium, iron, and nickel hinder the extraction.[409] Cadmium diethyldithiocarbamate was used for separations for polarographic determination of this metal.[334,362] Very small amounts of cadmium were extracted with chloroform as the dithizonate and were determined by photoacoustic spectroscopy.[376] Prior to polarographic determination in an organic solvent, cadmium was extracted as hydroxyquinolinate with butanol[335] or with molten naphthalene.[332]

Solutions of cinnamic acid in chloroform containing pyridine and other organic bases of this type were used to extract cadmium prior to atomic-absorption determination.[410] The extract was diluted with methanol or ethanol, and introduced into a propane-air flame. The detection limit was found to be 0.01 μg/mℓ; this value is less by 3 to 5 times than that obtained upon atomizing aqueous solutions.

The extraction-fluorimetric determination of cadmium is based on the extraction of its mixed ligand complex with 8-mercaptoquinoline and 1,10-phenanthroline or pyridine.[411] For the determination of cadmium in the presence of zinc (1:100), Stolyarov and Firyulina[412] extracted, with chloroform, the complexes of the metal with 1,10-phenanthroline and dibromfluorescein. A minimum amount of 1.5×10^{-7} *M* cadmium was determined. By combining xylene extraction of the cadmium complex with thiothenoyltrifluoracetone in the presence of 1,10-phenanthroline and the flame atomic-absorption measurement of signal, $2 \times 10^{-4}\%$ cadmium in metals can be determined.[413]

Different amines — tetrabutyl ammonium,[414] tribenzylamine,[192] capriquat[177] can be used to extract cadmium iodide complexes. For a polarographic determination, cadmium was extracted as the thiocyanate complexes.[330,331]

Calcium. No good specific methods of separating calcium are known. It is often isolated from others by leaving it behind in the aqueous phase after the extraction of other elements. Calcium can be extracted as its chelate with azo-azoxy BN reagent.[415-417] Extraction is carried out in an alkaline medium with carbon tetrachloride in the presence of tributylphosphate. Conditions can be created under which strontium and barium will not be practically extracted.[418] Calcium in the presence of magnesium can be determined fluorimetrically after benzene extraction of the ionic associate formed with 5,7-dinitro-8-hydroxyquinoline and rhodamine B.[419]

Chromium. A review of extraction separation methods for chromium is available in the book by Lavrukhina and Yukina.[420] Chromium (VI) is often extracted from HCl solutions with MIBK and other oxygen-containing solvents or amines; apparently, $HCrO_3Cl$ is extracted. For example, Kudo et al.[324] proceeded in this manner for the neutron activation determination of chromium; they used MIBK as the solvent. Another method involves extraction of perchromic acid from a weakly acidic medium in the presence of hydrogen peroxide. Thus, in the analysis of waste waters chromium was extracted as perchromic acid with MIBK, and the extract was introduced into a flame for AA determination.[421,422]

The thiocyanate complexes of chromium are also completely extracted. Jong and Brinkman[423] have proposed a method for separately determinating chromium (III) and (VI) in sea waters. The method is based on subsequent extraction of chromium (VI) (pH 2) and chromium (III) (pH 6 to 8) from thiocyanate solutions with Aliquate-336 solution in toluene. It ensures detection limits of 0.01 and 0.03 μg/mℓ for Cr(III) and Cr(VI), respectively. The total content of chromium can also be determined after oxidizing Cr(III) with ammonium persulfate. Another example of the use of chromium thiocyanate is its extraction with diantipyrilmethane in chloroform for the spectrochemical determination of this element.[279]

Extraction of chromium (III) chelates has a number of distinguishing features. The substitution reactions occuring in the internal sphere of the hydrated ion Cr^{3+} proceed very slowly. That is why, under ordinary conditions extraction equilibrium is often not achieved, or it is attained after a long time. But methods of accelerating the extractions are also known. Chromium dithiocarbamates, for example diethyldithiocarbamate, were extracted with MIBK for the determination of chromium in waste waters,[424] zinc selenide[312] and other objects[324,425-427] (determination is usually carried out by atomic-absorption spectroscopy). The detection limit of chromium in sea waters was found to be $4 \times 10^{-8}\%$; chromium in amounts of $\geqslant 5$ μg can be determined in pulps.[427] According to Hiiro et al.,[425] the detection limit is improved if for atomization and excitation use is made not of flame but of a graphite furnance. In the latter case, $2 \times 10^{-9}\%$ chromium can be determined. Extraction of chromium pyrrolidinethiocarbamate with chloroform was used to determine this element in sea waters by mass spectrometry.[383] Potassium benzyl xanthate was used to extract chromium (III) with MIBK.[428] It was possible to determine 0.02 μg of chromium per milliliter. Inoue et al.[429] have suggested a method for the determination of Cr(VI) traces in the presence of large amounts of Cr(III). The method is based on the MIBK extraction of the ionic associate formed by the cationic complex of chromium with dimercaptomaleonitrile and tetrabutyl ammonium bromide; its detection limit is 0.15 μg/mℓ. Some researchers have also made use of 8-mercaptoquinoline[320] and cupferron.[220]

Cobalt. It can be extracted by diverse methods, but the classical method of extracting small amounts of cobalt involves the use of 1-nitroso-2-naphthol or 2-nitroso-1-naphthol. Thus, 1-nitroso-2-naphthol was used for the kinetic determination of cobalt in inorganic products used in the optical glassmaking industry[384] and for the activation determination in zinc selenide (with substoichiometric separation);[312] 2-nitroso-1-naphthol was used for the photometric determination.[216] On the basis of a comparative study, it is recommended[430] to determine cobalt after chloroform extraction of its complex formed with PAN; many heavy metals (Ag, Al, Cd, Cr, Fe, Mn, and others) are no hindrance to the determination. Extraction of 8-hydroxyquinolinate with butanol was used for polarographic determination of cobalt.[335] Extraction of chelates with sulfur-containing reagents — diethyldithiocarbamate[299] (activation determination) and other dithiocarbamates, for example with hexamethylenedithiocarbamate for the analysis of sea water[431] — also holds a prominent place. Cobalt dithizonate is separated at pH 6 to 8 and the formed chelate, similarly to the nitrosonaphtholate, is not destroyed by dilute hydrochloric acid, unlike a number of other dithizonates. Cobalt (as well as nickel) was determined in biological objects by the atomic-absorption method after extracting the ethylxanthate complexe with MIBK.[432] Nickel and cobalt can be separated during extraction, because the former is extracted at lower pH values (5.5 to 9.8) than the latter (6.5 to 11.5). Chromium (III) hinders the extraction of cobalt. The detection limits are 0.04 μg of cobalt per milliliter and 0.01 μg of nickel per milliliter. For the extraction-magnetometric determination of cobalt, Kletenik et al.[375] extracted this element as a complex with di-(2-ethylhexyl)dithiophosphoric acid. Substoichiometric separation of cobalt for its determination by the isotope dilution method was carried out using 8-mercaptoquinoline,[320,321] and 2-pyridyl-2-thienyl-β-ketoxime was used for the spectrophotometric determination of cobalt in natural waters,[216] in pure iron and in iron salts.[166]

Extraction of cobalt compounds with azide and pyridine using MIBK was employed for the spectrophotometric determination of cobalt.[169] The thiocyanate complex was extracted also with the solution of 4-(5-nonyl)pyridine in benzene, and the aqueous phase contained potassium thiocyanate and free mineral acid.[433]

Copper. Many extraction separation methods are available for copper; extraction of this element, particularly in the form of chelates, is being extensively studied. Extraction of copper as diethyldithiocarbamate and other dithiocarbamates has become important in analytical chemistry. Often separation of copper in the form of a chelate with DEDTC is followed by the determination of its concentration in the extract by the photometric method. Other chelates are dithizonates and oximates (benzoinoximate and salicylaldoxymate) which are of importance in the extraction of small amounts of copper. Hydroxyoximes have found industrial application as extractants of copper (extractants of the type LIX).

Copper diethyldithiocarbamate was extracted for the determination of this element by the polarographic[362] and the neutron-activation method (in sea water);[298] in the latter case, zinc diethyldithiocarbamate was used as the reagent. For the atomic-absorption determination of copper in high-purity iron[434] and in sea water, copper was extracted as hexamethylenedithiocarbamate with butyl acetate.

Extraction of the dithizonate was used for neutron-activation determination of copper in zinc selenide[312] and in high-purity optical glass;[315] in both cases substoichiometric extraction was employed. Dithizonate was extracted for polarographic determination of copper in natural waters[339] and for flameless atomic-absorption determination of copper in sea water;[435] in the latter work 0.4 to 0.9 ng/mℓ of copper was determined. Maeda and Tanaka[436] used a method for the determination of copper (a few μg/ℓ) in river and sea waters, which involves extraction of the element with dithizone in carbon tetrachloride followed by back extraction and atomic-absorption determination. It is quite possible that if the authors had nebulized the extract into a flame they would have succeeded in improving the detection limit.

Having extracted copper ethylxanthate with MIBK, Aihara and Kiboku[409] selected conditions for atomic-absorption determination of microamounts of the element. The drawback of this method is that large amounts of Al, Co, Cr(III), Fe(III), and Ni interfere with the determination at the extraction stage. It has been shown that substoichiometric extraction of copper with 8-mercaptoquinoline in chloroform is possible, and use of this can be made for the determination of copper by the isotope dilution method.[321] For polarographic determination, Toropova et al.[337] extracted copper mercaptoquinolinate in molten naphthalene. Monothiothenoyl trifluoroacetone in cyclohexane was used for extraction separation of copper from iron (III) and for its subsequent photometric determination.[163] Under definite conditions, selective separation of Cu(II) from other metals can be ensured with the use of monothiodibenzoylmethane.[437] Copper (II) is separated from nickel, cobalt, iron (III), cadmium, and zinc at pH 6 by extracting its complex with thiobenzoylacetone,[164] but Ag(I), Hg(II), Pd(II) and some anions are also extracted. Use may be made of cadmium di-2-ethylhexyldithiophosphate for selective separation of copper from the accompanying elements for its determination in complex materials;[438] but in the presence of gold and bismuth it is necessary to back extract copper with a 3 *M* HNO_3 solution.

Zelyukova et al.[439] determined copper in rare earth elements by the atomic-absorption method after extracting the 8-hydroxyquinolinate with isobutyl alcohol. Using the acetylene-air flame, it is possible to determine 0.01 μg of Cu in 1 mℓ of the extract. Berenguer-Navarro et al.[440] also recommend the use of this technique; they add an emulsifier — polyethyleneglycol ester of nonylphenol — into the extract prior to atomization. The 8-Hydroxyquinolinate was extracted with methylisobutylketone for the polarographic determination of copper in the extract.[336]

For selective separation of copper use was made of hydroxyoximes R – C(= NOH) – R′, where R stands for the cyclic hydrocarbon radical with OH-group present at position 2, and R′ denotes the aliphatic group. Use was made of hydroxyoxime solutions in kerosene; cycloalkylmonocarboxylic acids were added into the aqueous phase to improve extraction. Hydroxyoximes LIX 70 and LIX 65N in kerosene or heptane were used for the atomic-absorption and photometric determination of copper.[160]

A method has been developed for the determination of copper in the gaseous effluents of industrial enterprises;[442] the solution of 1,1,1-trifluor-6-methylheptane-2,4-dione in benzene is used as the extractant.

An extraction atomic-absorption method of determining copper in aluminum-based alloys has been suggested by Stephens and Felkel;[443] the thiocyanate complexes of copper are extracted with propylenecarbonate from saturated solutions of NaCl, and the extract is nebulized in the flame.

Kish and Buletsa[444] have proposed a method for selective separation of copper in chlorobenzene from an aqueous solution containing 0.01 *M* KI and 5×10^{-4} *M* cation red basic dye 2S (pH 3); excessive amounts (10^5-times) of Al, As, Ga, Ge, rare earth elements, Zn, Zr, and other elements are no hindrance to subsequent photometric determination of copper. A method for selective separation of copper (I) with the use of 2,2-biquinoxaline is also described in the work of Yatsenko and Sidorov.[445] Janssen et al.[446] have determined traces of copper in steels by the atomic-absorption method after extraction concentration. Patil et al.[447] have proposed a multistage method of separating copper for its determination in steels and alloys.

Gallium. Extraction of the gallium chloride complex $GaCl_4^-$ with oxygen-containing solvents or mixtures of highly basic oxygen-containing compounds (TBP, diantipyrilmethane and others) with inert solvents is of great importance. In actual practice, diisopropyl ether or amyl acetate is often used as the solvent, and 6 *M* HCl as the aqueous phase. For the determination of traces of gallium by the neutron activation method, gallium was extracted from a HCl solution with tri-n-octylphosphineoxide solution in cyclohexane,[313] and diisopropyl ether;[300] substoichiometric extraction was used in the former case. For atomic absorption determination of gallium, it was extracted from HCl solutions with dibutylamidobutyl phosphate in benzene;[359] in this case small amounts of Al, Zn, Fe(II), and Cu are not extracted, but Sn(IV) and to a large extent Fe(III), As(V), and Sb(III) are co-extracted. Savostin et al.[448] have proposed to extract gallium from 6 *M* HCl solution with monoamidophosphate in benzene for the separation of Ga-Al and Ga-In pairs. The use of 4-methyl-2-pentanol enables Ga to be isolated from In and Tl(III);[449] the method has been tested for comparitively large amounts ($\geqslant$ 5 mg), but may, apparently, be applied also for small concentrations. Banateanu and Costinescu[450] have proposed a sensitive photometric method for the determination of gallium in minerals. The method depends on benzene extraction of the ionic associate of chlorgallate with pironine G from 6 M HCl, and can be used for concentrations of 0.01 to 2.0 μg of gallium per milliliter.

Often 8-hydroxyquinolinate and other chelates of gallium are extracted. For the analysis of bauxite and silicate rocks, De Dipak et al.[451] extracted gallium cupferronate with MIBK. For the photometric determination of gallium with rhodamine B, this element is first extracted in the form of complexes with 1-phenyl-3-methyl-4-benzoylpyrazolone-5[190] and thenoyltrifluoracetone.[179]

Germanium. The best method of extraction separation of germanium resides in separating this metal as $GeCl_4$ from 9 to 10 *M* HCl solutions with carbon tetrachloride or other inert organic solvents. This method is used extensively. For example, Shcherbov et al.[452] used this technique for the fluorimetric determination of germanium with rezarson, and Argollo and Schilling[300] for the neutron activation determination of this element in rocks; carbon tetrachloride was used in both cases. For the atomic absorption determination of germanium, it was first extracted with n-butyl ether from 8 *M* HCl, and then the extract, prior to its introduction into the C_2H_2-N_2O flame, was emulsified with concentrated HCl.[453] The authors of this work believe that the technique enabled them to lower the detection limit by 5 times, compared to the generally employed direct atomization of MIBK-based extract into a flame.

Gold. In analytical practice, extensive use is made of extraction separation of gold (III) in the form of its chloride or bromide complexes AuX_4^- ($X = Cl^-$, Br^-) with oxygen-containing solvents, for example ethers or esters. Thus, gold can be separated with great ease and speed from many transition and noble metals by extracting it from 3 *M* HCl with a mixture of 4-methyl-2-pentanol and benzene (3:1); should the need arise, gold can be readily back extracted with a 0.5 *M* solution of ammonia.[454]

The extraction of gold was studied in Au(III)-HCl-cyclopentanol or cyclohexanol systems with its atomic absorption determination.[455] Primary emphasis was given to the study of the effect of the aqueous phase acidity as well as of the diluents (hexane, benzene, toluene, xylene). The use of diluents favors quantitative separation of gold and widens the range of complete extraction of gold up to 10 *M* HCl. It has been noted that 100-fold amounts of Fe(III) impair the extraction of gold. Although this investigation has no practical application, the results may be of significance for further studies in this direction.

Bazhov et al.[255] extracted gold from HCl solutions with isoamyl alcohol for the atomic absorption determination of this element in geological materials (gold content being $\geq 5 \times 10^{-7}\%$). For this purpose, a "furnance-flame" atomizer was used, the operating conditions of which were so regulated that the solvent would evaporate completely or partially before the aerosol enters into the flame. Use was also made of different flames of the type propane-butane-air or isoamyl alcohol-air. In the case of partial or complete removal of the solvent and the application of an isoamyl alcohol-air flame, the detection limit is 5×10^{-4} μg of gold per milliliter with a relative standard deviation of 0.04 to 0.06.

Gold was extracted from HCl solutions with oxygen-containing solvents for its neutron activation determination in geological samples (MIBK),[301] for its conductometric determination in the extracts (TBP in heptane),[364] and for its photometric determination with 2-furyldioxime and pyridine (4-methyl-2-pentanol).[195] Gold chloride complexes are extracted also with amines: diphenyl-2-pyridylmethane,[303] 4-(5-nonyl)-pyridine,[302] and rhodamine B[312] for the neutron activation determination.

In chloride solutions, gold (III) also forms mixed neutral complexes $AuCl_3L$, particularly with soft sulfur-containing extractants — organic sulfides, substituted thioureas, and also with triphenylphosphine. A number of extraction methods have been developed on the basis of this property. Thus, gold was extracted with dibutylsulfide in toluene for its atomic absorption determination in rocks.[456] The flameless variant (HGA-74 furnance) proved to be more sensitive (10^{-7}%) than the flame one (acetylene-air, 2×10^{-6}%). Sizykh et al.[457] determined ultra-traces of gold in rocks by the spectrochemical method after also extracting it with dibutylsulfide. Glukhov et al.[458] also used this reagent for the extraction of gold. The solution of petroleum sulfides in toluene was used for the flame and flameless atomic absorption determination of gold.[254] In the flame variant the detection limit is 2×10^{-2} μg/mℓ or 10^{-2} g/t and in the flameless variant, (2 to 6) $\times$ 10^{-4} μg/mℓ or 10^{-4} g/t. This procedure has been used for the analysis of rocks, pyrities, thermal waters, and plant ashes. Glukhov et al.[459] have compared several radiochemical methods of determining gold in rocks, ores, and minerals, which involve the use of neutron activation. Gold was separated from the sample with organic sulfides at different stages of analysis (before and after irradiation) and by different methods including those which involve substoichiometric extraction and isotope dilution. The detection limits differ insignificantly. Good results (1×10^{-10} g/g) were obtained using substoichiometric extraction of gold from sample weights of 0.1 to 0.3 g or by extracting gold in a usual manner from sample weights of 25 to 30 g.

Diphenyldithiourea was used to extract noble metals including gold prior to their determination by the spectrochemical and atomic absorption methods. Bazhov and Sokolova[96] determined gold in ores, rocks, and in the products obtained on treating them with diphenylthiourea in butylacetate. Even the use of low-temperature propane-butane-air flame enabled them to detect 2×10^{-6}% silver and 2×10^{-7}% gold in the samples by the AA determination method.

For substoichiometric neutron activation determination of gold in waste waters, gold was extracted with tri-n-octylphosphine sulfide in cyclohexane.[311] Gold is extracted well also as compounds with O-isopropyl-N-alkylthiocarbamines.[92,99] A method of selective concentration of gold from cyanide solutions with the use of ethyl ether solutions of hexamethylenedithiocarbaminic acid has been described by Byr'ko et al.[84] The method of extracting gold with triphenylphosphine, proposed by Serebryany et al.,[104] was used for their atomic absorption[104] and X-ray fluorescence determination.[290]

Gold (III) is extracted also in the form of chelates. The distinguishing feature of this element is that it forms chelates of unusual composition because of the less suitable charge to coordination number ratio for Au(III). The formation of an unusual chelate AuL_3 with bidentate monobasic reagent is practically impossible due to the non-availability of coordination sites (coordination number 4); therefore, the compounds of the type $AuL_2^+X^-$, $AuLX_2$, or of other types are formed. The complexes of the type AuL_3 can be formed only in those cases when not all the molecules of the reagent are bidentate ones. The detailed studies of gold (III) chelates, carried out by us from this viewpoint, have shown that the chelates with diethyldithiocarbamate, dithizone, and 8-mercaptoquinoline are "cations".

For the neutron-activation determination of gold in sea waters, it was first concentrated with zinc diethyldithiocarbamate solution in chloroform, and then the solvent was evaporated prior to irradiation.[298] Substoichiometric extraction with copper diethyldithiocarbamate and zinc dibenzyldithiocarbamate was used to determine gold by the radioisotope method.[319,325] For the spectrochemical determination of gold, the use of three-phase extraction systems is recommended.[460,461] The methods combine selective extraction of gold by any of the known methods with subsequent conversion of a two-phase system into a three-phase one (for details refer to the works of Petrov et al.[55,56]). Mineralization of the bottom phase, in which gold is concentrated, is not necessary. The methods are noted for their selectivity and good detection limit (0.5 to 1.5 μg of gold.)

Indium. Very often the iodide and bromide complexes of indium are extracted from the solutions of corresponding acids with oxygen-containing solvents, for example with diethyl ether. For this purpose, use is also made of basic dyes; in this case indium can be determined either by the photometric or by the luminescent method. Extraction of chelates — dithiocarbamates, β-diketonates, and others — is also employed.

For a photometric determination, indium was extracted with benzene as an ionic pair of $InBr_4^-$ with ethylrhodamine B from a H_2SO_4 solution.[462] Less than 2 μg of indium can be determined by this method, but small amounts of Tl, Pt, Hg, Fe, Sb, Sn, Ga, and large amounts of copper hinder the determination.

Extraction of acetylacetonate and then of diethyldithiocarbamate was used for substoichiometric neutron-activation determination of indium in metallic tin and cadmium.[317] X-Ray fluorescence determination of indium in aluminum alloys was carried out after extracting it as diethyldithiocarbamate with chloroform.[286] A triple complex of indium with 8-mercaptoquinoline and acetate, which can be extracted with chloroform, was used for the fluorimetric determination of this element.[463] Extraction of 8-mercaptoquinolinate with molten naphthalene was used for the polarographic determination of indium.[341] For a fluorimetric determination, indium was extracted with butyl alcohol as a complex with lumogallion;[464] the detection limit is 0.02 μg/mℓ, aluminum and gallium hinder the determination. Separation of indium as a complex with xylenol orange and 2-brombutyric acid was used for the photometric determination of this element.[180]

Iron. The most important method is the extraction of Fe (III) as $HFeCl_4$ from HCl solutions with oxygen-containing solvents, although the extraction is not very selective. This method is used in different ways. Thus, the selective determination of small amounts of Fe(II) can, in a number of cases, be raised by pre-extracting Fe(III) with MIBK[465] or with mesityl oxide.[466] For the atomic-absorption determination of iron (10^{-3} to 10^{-2}%) in materials with a non-ferrous base, it can be extracted with mesityl oxide.[467] Kletenik et al.[363] extracted iron with diisopropyl ether and titrated the extract with iodide generated at a particular potential. Iron can also be extracted with amines. For the atomic-absorption determination of less than 10^{-4}% iron in titanium tetraiodide, it was separated from a chloride-iodide solution with trioctylamine in a mixture of MIBK and toluene (1:1).[468]

Extraction of thiocyanate complexes of Fe(III) with oxygen-containing solvents or amines is also well-known. For the atomic-absorption determination of iron in waste waters, it was extracted from thiocyanate solutions with butyl acetate in the presence of zephyramine.[469]

Iron (III) is nicely extracted also as chelates. For example, for the determination of this element in rocks, it was extracted as a complex with *N*-phenylnaphthohydroximic acid.[470] Use is made of extraction of the acetylacetonate (pH 1 to 2) and other β-ketonates as well as the 8-hydroxyquinolinate or cupferronate. Thus, extraction of the acetylacetonate was used for the polarographic determination of iron in extracts.[349,357] During determination of cerium, iron was extracted as a complex with benzoyltrifluoracetone.[197] Extraction of the 8-hydroxyquinolinate, which was studied in greater detail, was employed for the spectrochemical determination of iron in ammonium phosphate.[280] Zolotov et al.[471] have developed a sensitive procedure for the atomic-absorption determination of iron (0.1 to 10 μg/mℓ) in solutions; the procedure depends on the extraction of the ionic associate which is formed by reacting the cationic dithizone complex of Fe(III) and the tetraphenylborate anion; the extract is then introduced into the flames.

As far as Fe(II) is concerned, it is more often extracted as ionic associates formed by the cationic complexes of Fe(II) with 2,2′-dipyridyl, or 1,10-phenanthroline and its derivatives. Extraction of the compound formed with 1,10-phenanthroline was used for a fast photometric determination of Fe(II) and Fe(III) when both were present in the same sample (they are separated with nitrobenzene in the presence of perchlorate).[219]

The Fe(II) complex formed with 8-hydroxyquinoline was extracted with n-butyl alcohol for subsequent polarographic determination of iron in the extract.[335] For the photometric determination of iron in waters, the compounds of Fe(II) formed with pyrogalol red and zephyramine were extracted.[472]

Lead. Extensive use is made of extraction of lead dithizonate; usually it is followed by photometric determination of the metal. This classical method is currently employed in combination with other determination methods, for example with atomic-absorption. Lead is readily extracted as dithiocarbamates and in the form of chelates with other sulfur-containing reagents. Other chelates as well as the iodide complex of lead can also be extracted.

Lead dithizonate was extracted with carbon tetrachloride for the atomic-absorption determination of submicrogram amounts of the metal in water;[473] before introduction into the atomizer, lead was back extracted with HCl. Extraction of lead dithizonate was also used for the analysis of alkalies.[474] The atomic-absorption determination limit is $5 \times 10^{-4}\%$ for a sample weight of 1g. Extraction of lead dithiocarbamate is often employed for its determination in environmental samples, for example the diethyldithiocarbamate was separated with MIBK for the analysis of sea bottom deposits by atomic-absorption.[475] This chelate was separated and used for the polarographic determination of lead.[362] For this purpose, use was also made of the extraction of the heptylxanthate with carbon tetrachloride,[342] and of 8-hydroxyquinolinate with ethyl acetate.[343] For the atomic-absorption determination of lead in air, it was extracted from weakly alkaline media with solutions of diphenylcarbazone and pyridine in toluene; the absolute detection limit was found to be 0.05 μg.[476]

Extraction of β-diketonates and like compounds is not very characteristic for lead. Nevertheless, it has been shown that it is possible to separate its complexes formed with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 and its capryl analog.[477,478] The former reagent was used for the atomic-absorption determination of lead in aerated water (citrate and ammonium sulfate were introduced, MIBK was used as solvent);[477] the extract was introduced into an acetylene-air flame. The procedure enables $5 \times 10^{-6}\%$ lead to be detected in the sample with a relative error of about 3%. Al, Co, Cu hinder the determination. Using the latter reagent, lead was determined in copper and zinc by the same method;[477] MIBK was used as solvent.[478] Small amounts of Fe(II) caused the analysis results to be too low, but the presence of large amounts of Cd, Ni, Zn, and Cu (exceeding by 50 or more times the concentration of lead) does not have a perceptible effect on results.

Manganese. Although Mn(VII) can be extracted as ionic associates of the anion MnO_4^-, for example with tetraphenylarsonium or pyridinium, use is often made of the extraction of Mn(II) in the form of its chelates. Upon separation of dithiocarbamates, manganese is oxidized and forms Mn(III) complexes; possibly, oxidation will also take place on using other sulfur-containing reagents. Sometimes, manganese 8-hydroxyquinolinate is extracted.

Dithiocarbamates are separated for the determination of manganese in environmental and other samples. Thus, tetramethylenedithiocarbamate was extracted with MIBK for the atomic-absorption determination of manganese in natural waters.[479] The ethanol solution of the reagent was added into the extract to stabilize it. Although this causes the detection limit to be slightly poorer, it improves other characteristics of the method. Extraction of the diethyldithiocarbamate was employed for the photometric determination of manganese with other reagents.[181] Aihara and Ishii[480] are of the opinion that small amounts of manganese ($\leqslant 1$ μg/mℓ of the extract) can be determined by atomic-absorption after extracting the manganese complex with benzylxanthate followed by the introduction of the extract into a flame. The procedure is not only fairly sensitive, but selective also; the presence of Au, Cd, Co, Cu, and Zn is no hindrance to the determination. Extraction of 8-mercaptoquinoline was used to determine manganese by the isotope dilution method in the substoichiometric variant.[320] For the determination of manganese in steels or solutions, Taga et al.[481] pre-extracted the metal as the ionic associate. To the solution containing $\leqslant 10$ μg manganese was added the solution of 2-[2-(oxyamino)-1-methylpropylidine]-*N*-phenylhydrazincarbothioamide in dimethylformamide, and after a achieving pH $\simeq 10$, manganese was extracted with tetrabutylammonium in MIBK. The extract was introduced into the acetylene-air flame.

Sometimes, manganese β-diketonates are extracted. Usually, they are hydrated in the inner coordination sphere, and, therefore, extraction is possible only in the presence of donor-active solvents or specially introduced synergistic additions. Thenoyltrifluoracetonate was extracted for the neutron activation determination of manganese in optical glass.[315] Kato[482] has proposed a sensitive atomic-absorption method for the determination of manganese (1.6 $\mu g/m\ell$) which involves extraction of manganese with thenoyltrifluoracetone solution in MIBK. It is however not selective. Besides Fe(III), which can be preseparated, Cr, Hf, Nb, Ni, Rh, Sn, Ti, and Zr in particular hinder the determination. The presence of fluorides, cyanides, and thiocyanates is also undesirable. When determining cerium, manganese was separated as a complex with benzoyltrifluoracetone.[197] Small amounts of manganese were separated also after extracting its complex with 1-phenyl-1-benzoyl-3-methyl-pyrazolone-5 in MIBK.[483]

Mercury. Extraction of mercury (II) dithizonate is, apparently, the most important method of separating mercury; it is well-known that the colored dithizonate is used also for the photometric determination of this element in the extract. A large number of papers are dedicated to mercury dithizonate. Among the latest publications, we would refer the reader to the work of Curry and Menon.[74] For the determination of traces of mercury, it (together with other elements) was extracted with dithizone in carbon tetrachloride followed by back extraction with a H_2SO_4 solution of NaBr. The aqueous phase, which contains mercury (II), was treated with zinc dithizonate (^{65}Zn) in carbon tetrachloride and the content of mercury in the parent sample was measured as a function of the decrease in radioactivity of the extract. A method for neutron activation determination of mercury in coal has been described;[484] the coal sample is irradiated, decomposed, and mercury is extracted with dithizone; thereafter, the intensity of γ-radiation of ^{197}Hg is measured in the extract. The X-ray fluorescence determination involved extraction of mercury dithizonate with chloroform and subsequent evaporation of extract drops on a filter paper.[287]

Often, mercury dithiocarbamates are extracted, in particular diethyldithiocarbamate. Mercury is extracted with a very high extraction constant, it being larger than the extraction constants of other elements. That is why as extractants, use is made of chelates of other metals and exchange reactions are conducted. For example, for indirect polarographic determination, mercury was extracted with bismuth diethyldithiocarbamate in carbon tetrachloride.[360] For the determination of mercury by the isotope dilution method, the element to be determined was extracted substoichiometrically with silver diethyldithiocarbamate in chloroform.[316] Mercury (as well as silver and copper) was extracted with lead diethyldithiocarbamate in chloroform for its activation determination in sea water; extraction was carried out before irradiation.[298] Among other sulfur-containing chelate-forming reagents used for the extraction of mercury, mention may be made of 8-mercaptoquinoline, which is employed, in particular, for substoichiometric separation of this element when determined by the isotope dilution method,[321] and of spin-labelled xanthate when determined by the ESR method.[368] This method, but with the involvent of spin-labelled β-diketone, was used in our work.[369]

Another commonly used method for the separation of Hg(II) consists in extracting stable mercury iodide complexes HgI_2 and HgI_3^- with different solvents. For example, iodide complexes were separated with MIBK for the determination of mercury by the isotope dilution method with mass spectrometric control,[374] and to concentrate small amounts of mercury with the use of Chrompyrazole II.[281] Mixed thiocyanate complexes of mercury were extracted with different reagents of the pyridine type.[485,486] Thus, the $Hg(Py)_2(SCN)_2$ complex is separated with 5-(4-pyridyl)nonane. Extraction was used to determine mercury by the atomic-absorption method.[485]

Molybdenum. Very often this element is extracted as chelates with 2-benzoinoxime (0.01-2 M HCl), 8-hydroxyquinoline, hydroxamic acids and other reagents. Also, for analytical purposes molybdenum is separated in the form of a chloride complex or molybdate with different oxygen-containing extractants and amines. Thiocyanate complexes of Mo(V) are also extracted.

For the photometric determination of molybdenum, the 2-benzoinoximate was pre-extracted as a triple compound with gallein and papaverine[217] and as a thiocyanate complex.[162] For extraction and polarographic determination, molybdenum was extracted as the 8-hydroxyquinolinate[345] and the *N*-benzoyl-*N*-phenylhydroxylaminate,[344] and for X-ray fluorescence determination — as the chelate of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 with a molten eutectic mixture of naphthalene and diphenyl.[291] For the determination of molybdenum in rocks and scheelite ores by radioactivation, molybdenum was first extracted from a HNO_3 solution of the irradiated sample with a 50% benzene solution of di-(2-ethyl-hexyl)phosphoric acid, and then the accumulated ^{99m}Tc was back extracted with 7 *M* HNO_3.[397] The γ-activity of the back extract was measured. Molybdenum was extracted with a caprylic acid solution in kerosene in the presence of Fe(III), which was introduced into the system to improve extraction of molybdenum; this method was employed to determine molybdenum in sea and waste waters.[147] The method of extracting molybdenum with toluene-3,4-dithiol is also well-known.

The work of Gurtler[162] can serve as an example of the use of extraction of the molybdenum (V) thiocyanate complex, in which molybdenum was extracted with diisopropyl ether in the presence of $SnCl_2$ for its spectrophotometric determination. Molybdenum can also be extracted with trioctylamine from a H_2SO_4 solution (pH ~ 1).[314] Plotnikova et al.[487] studied a number of extraction systems (acetylacetone-chloroform, diethyldithiocarbamate-chloroform, SCN^--isoamyl acetate, and Cl^--diethyl ether) with the aim to select among them the best system for the fluorimetric determination of molybdenum with Alizarin red.

Nickel. Extraction of nickel chelates with dimethylglyoxime is the most extensively used method of separating nickel. Thus, for the polarographic determination of nickel, its chelate was separated with molten naphthalene.[353] Commercial 2-hydroxyoximes (LIX 65N and LIX 70) were used to extract nickel from ammonia solutions for the subsequent photometric determination of this element in the extract.[160] For the atomic-absorption of nickel it was extracted as a complex with PAN;[430] nickel can be determined in the presence of cobalt. The method of separating small amounts of nickel from large amounts of Fe (II), which involve extraction of bromcapronates in the presence of amines, is described in the work of Sukhan et al.[488] This method has been used for the analysis of steel samples. For the atomic-absorption determination of nickel in aluminum and waste waters, the metal ($\leqslant 1$ μg of nickel per milliliter) was extracted from weakly acidic thiocyanate solutions with trioctylmethyl ammonium chloride in isopropyl acetate; milligram amounts of bismuth, cadmium, cobalt, and iron hinder the determination.

Niobium. The most important method of extracting niobium consists in separating its fluoride complex with different extractants, in particular with oxygen-containing ones. This method permits isolation of niobium (and tantalum) from many other elements, and also separation of niobium and tantalum. For this purpose, use was made of tetraphenylarsonium chloride,[490] high-molecular weight amines in HCl media,[491] and diantipyrilmethane and its derivatives in the presence of hydrofluoric acid.[492] It is very difficult to decide between these techniques. It may only be mentioned that, by judging from the data reported by Ivanov and Degtev,[491] the use of high-molecular weight amines enables niobium to be isolated from a large number of accompanying elements. Beside this, it has been noted that the lifetime of aqueous solutions of separable elements ("aging of solutions") has an effect on separation results. The increase in "aging" time tends to impair separation.

Niobium, for the determination of impurities in it, was extracted from HF-sulfate solutions with tributylphosphate, cyclohexanone, or petroleum sulfoxides.[493] For the radioactivation determination of niobium in geological materials, it was isolated (prior to irradiation) from a HF-H_2SO_4 solution with MIBK.[297] Kuchumov and Renard[494] have proposed an original technique for the atomic absorption determination of niobium and tantalum in technological and waste solutions; the determinable metals are extracted from a HF-H_2SO_4 medium with MIBK, and the extract is introduced into a flame. Microgram amounts of Ta have an appreciable effect on the results of atomic absorption determinations. To eliminate this effect, large amounts of tantalum (0.5 g/l) were added to the sample to be analyzed and to the reference solutions. The detection limit was found to be 1 μg/mℓ (Nb) and 0.5 μg/mℓ (Ta) with a relative error of 5 to 10%.

Other complexes of niobium are also extracted. Ponosov et al.[495] concentrated niobium from aqueous solutions containing sulfuric and tartaric acids and hydrogen peroxide with a solution of undecyldiantipyrilmethane in chloroform. Carbon tetrachloride and petroleum ether are added to the extract, and the bottom phase is removed for the determination of niobium. A method of determining small amounts of Nb and Ta, which involves preconcentration of elements by extracting them from oxalate solutions with tetraoctylammonium bromide, has been described by Tayursky and Shastina.[496] Information concerning the application of mixed ligand complexes in the analytical chemistry of niobium and tantalum has been reviewed by Elinson.[497]

Use is also made of extraction of chelates with *N*-benzoyl-*N*-phenylhydroxylamine (from concentrated HCl),[191] and with 2-benzoyloxime.[346]

Platinum metals. Group isolation and concentration of these metals is often necessary. For this purpose, use is made of a number of reagents, particularly of substituted thioureas, and *p*-octylaniline. Zolotov et al.[92] have proposed a method of concentrating these metals with diphenyldithiourea; platinum metals present in the concentrate are determined by the spectrochemical method. Use has also been made of other substituted thioureas, in particular of 1,1-hexamethylene-3-phenylthiourea.[94] Using this reagent, Savel'eva and Khairulina[498] concentrated platinum metals ($<10^{-3}$%) prior to their atomic absorption determination. For this very purpose, use was made of group extraction with *S*-(1-decyl)-*N,N*-diphenylisothiourea bromide in diisobutylketone.[499] In this case, other metals [Bi(III), Cd, Fe(III), Se(IV), Sn(II), and Zn] were also extracted under certain conditions from HCl solutions, which, however, are removed from the extract by washing it with HCl solutions. Unfortunately, this results in partial loss of iridium. The extract is then introduced into a flame. *p*-Octylaniline is a good group extractant for concentration of platinum metals.[500-504]

Byr'ko et al.[276] used 3,5-diphenyl-1-thiocarbamidopyrazoline to concentrate gold, palladium, and platinum. This method was used to analyze polymetallic ores and sulfide concentrates. Radushev and Ackermann[505] concentrated platinum metals by extracting them with 1-phenyltetrazolinethion-5 solution in chloroform.

Borshch et al.[506] propose the use of di-2-ethylhexyldithiophosphoric acid to concentrate iridium and other platinum group metals. Because of the inertness of iridium complexes it is necessary to add a reagent in the aqueous phase, for example as a solution in acetone, and then to heat and separate the extracting complex with suitable organic solvents. Extraction of tin-bromide complexes of platinum metals with organophosphorous compounds was studied systematically in an effort to develop methods for their group and selective concentration.[507] A total of 56 compounds were studied. The ethyleneamides of dialkylphosphoric acids and oxides of tertiary phosphines were found suitable for group concentration, while amides of phosphoric acid and phosphinic acids extract platinum selectively, and thiophosphoric acid esters are selective in respect to palladium. Metals like copper, nickel, iron, cobalt, and a number of other metals are no hindrance to the extraction of platinum metals with organophosphorous compounds.

The extraction separation methods for platinum metals also hold an important place. Rakovsky and co-workers[508] have proposed a method of separating Pd, Pt, and Ir which involves extraction of their di-o-tolylthiourea complexes with dichlorethane. Separation is based on different rates of formation of extracting compounds.

The work of Diamantatos and Verbeeck[509] is dedicated to extraction separation of Pt, Pd, Rh, Ir, and Au. Separation is effected both by varying extraction conditions (acidity and composition of the aqueous phase) and by selecting different extractants. Good separation is obtained. The extraction-radiometric methods of determining palladium, copper, and silver with sodium diethyldithiocarbamate, labelled ^{32}P, have been described by Ganiev et al.[510] Gilberg and co-workers[511] have recommended suitable methods for the determination of palladium and silver with organic sulfides. Merkulov and Bogomolova[512] determined platinum and gold in the intermediate metallurgical products by the activation method. First, the determinable metals were extracted from the sample solution and then amounts of the daughter isotopes — ^{100m}Ag for the determination of palladium and ^{199}Au for the determination of platinum — were measured. Ahmad et al.[513] proceeded in a different manner for the activation determination of Pd, Pt, Ir, and Au in geological materials. First, gold was extracted from the HCl solution of the sample with diethyl ether, and then Pd, Pt, and Ir were extracted from the raffinate with a solution of di-*n*-heptylsulfoxide in 1,1,2-trichloroethane. Thereafter, all the determinable elements were back extracted; at this stage, they were separated, isolated in the elementary state, and the activities of precipitates were measured.

For the determination of the same noble metals, Gilbert et al.[514] used the extraction-radiometric methods in the classical variant. The irradiated sample was dissolved in 0.5M HCl and gold and palladium were extracted with a benzene solution of petroleum sulfides. Direct measurement of the activity of the extract (^{109}Pd, ^{198}Au) enabled the content of Au and Pd to be determined. Further, platinum was extracted from the raffinate with a 2-nonylpyridine-*N*-oxide solution in dichlorethane, and then Ir with alkylaniline. The activity of the extract (^{197}Pt, ^{192}Ir) provided information on the content of platinum and iridium.

Rakhimov et al.[515] have suggested a slightly different scheme for the determination of these metals when all of them are present. For the separation of elements and their isolation from the accompanying elements, use is made of both extraction (with the application of TBP and cationic surface active compounds) and chromatographic methods. In our opinion, the method used by Gilbert et al.[514] is simpler than the one suggested by Rakhimov et al.[515]

For the activation determination of iridium (10^{-5} to 10^{-7}%) in ores, concentrates, and rocks,[516] the sample is irradiated, melted, dissolved, and gold and palladium are extracted from the solution with a benzene solution of petroleum sulfides. Iridium is then separated from the raffinate with alkylamines, and the activity of $^{192,194}Ir$ is measured in the extract.

Palladium has a rich extraction chemistry; many extraction methods have been developed for its separation. Among them are the methods of extracting palladium from 0.1 to 0.3 *M* HCl with dimethylglyoxime (Fujinaga and Puri[353] extracted Pd with molten naphthalene), other oximes, and related compounds.[218,370] Deshmukh and Kharat[517] propose to isolate palladium from copper by extracting the former with 2′-hydroxy-4-methoxy-5′-methylchalconeoxime solution in isobutanol at a pH of 1. Walker and Holland[518] used 4-heptanoneoxime to separate palladium from copper, and also to isolate small amounts of palladium from gram amounts of Ni and Fe. Less than 0.2% Cu, Ni, and Fe are coextracted with palladium into chloroform from 1 *M* HCl. Dupuis and Holland[519] used this separation method for the determination of palladium in sulfide concentrate. Microgram amounts of Pd can also be isolated from large amounts of Pt(IV) by extracting it with alkylketones.[520] Palladium can be determined by the atomic absorption method after extracting the metal as isonitrosoacetanilide complex with MIBK and introducing the extract into a flame.[521] For a high degree of concentration, a detection limit of 0.5 ng of palladium per milliliter can be achieved. Good reagents for palladium are isonitrosobenzoylacetone[522] or *N*-pyridyl-*N*-benzoylthiourea.[523] Sawanti and Haldar[524] have suggested a method for the neutron activation determination of Pd in the mixtures of noble metals. The solution of the irradiated sample (<1 *M* in HCl) is treated with ethyl-α-isonitrosoacetylacetate, palladium is back extracted with 1 *M* HCl, hydroquinone is added to the back extract and heated to remove gold and osmium. After removing the precipitate, palladium is again extracted from acetic acid medium and the radioactivity of the extract is measured. Shcherbov and co-workers[525] propose to use a fluorescent reaction for palladium, which involves extraction of palladium complexes with heterocyclic amines and halogen derivatives of fluorescein. The detection limit amounts to 0.15 μg Pd in 8 mℓ of the extract. Paramagnetic (free radical) xanthate was used to determine palladium by the ESR method.[368] Diethyldithiocarbamate of copper was used for the polarographic determination of palladium.[352] Use was also made of dithioketone.[365]

For the neutron activation determination of palladium in silver,[526] the sample, after irradiation, is dissolved electrochemically in HNO_3 and palladium is separated with 8-hydroxyquinoline solution in chloroform. The activity of ^{109}Pd is measured in the extract. The detection limit is 5×10^{-7} g.

Petrov et al.[527,528] propose to extract Pd and Pt from a H_2SO_4 solution containing KBr and hexyldiantipyrilmethane in the form of suitable ionic associates with a mixture of chloroform, carbon tetrachloride, and hexane. Rubeska et al.[529] determined palladium by the flameless atomic absorption method (the detection limit being 2×10^{-10}g) after extracting the metal with dibutylsulfide. For the atomic absorption determination of palladium in catalysts, it was extracted as a complex with 1,10-phenanthroline;[530] palladium was removed with TOA from HCl solution for its determination in uranium.[531]

Apart from the earlier mentioned methods, many other methods can be used to extract platinum. For example, for the neutron activation determination of platinum in silver and intermediate metallurgical products, it was extracted with 2-nonylpyridine-oxide;[532] for the spectrochemical determination in polymetallic ores and sulfide concentrates, platinum was concentrated with 3,5-diphenyl-1-thiocarbamidopyrazoline in chloroform.[276] Platinum (II) dithizonate can be extracted and used for analytical purposes.[315] Platinum was also concentrated with decyl-*bis*-(1-phenyl-2,3-dimethylpyrazolone-5-yl)-methane from a H_2SO_4 solution in the presence of KI; a mixture of kerosene, chloroform, and carbon tetrachloride served as the solvent.[528]

Osmium is extracted as OsO_4, for example with carbon tetrachloride, prior to its photometric determination with o-arsanilic acid[203] or TBP from HCl solutions.[183] For the photometric determination of osmium, it was extracted from an Os(VIII) solution with chloroform as a compound with acetothioacetanilide, the extracted complex was found to be colored.[159] Rhodium was separated as a compound with di-o-tolylthiourea in the presence of tin (II) chloride for its subsequent photometric determination.[533]

Ionov et al.[534] have developed a procedure of determining platinum metals in high-purity platinum, which involves the use of extraction separation and concentration methods. Procedures of determining noble metals in copper are described in the work of Yovaerts et al.[535] The methods of determining platinum metals in metallic silver are discussed in other works.[532,536,537] Clay et al.[242] have published a review on the AA analysis of materials containing noble metals, in which are given in particular the extraction separation and concentration methods for these elements.

Potassium. The most interesting method of extracting potassium resides in using macrocyclic compounds — crown ethers, and in particular dibenzo-18-crown-6 and its substitutes. Crown ethers are neutral compounds; therefore, the potassium-containing compounds represent large cations. They can be extracted with polar solvents by introducing bulky hydrophobic anions, for example picrate, into the system. Thus, the potassium complex formed with dibenzo-18-crown-6 or polynactine was extracted using dichlorethane in the presence of an anion — anilinenaphthalenesulfonate.[226] The solution to be analyzed was mixed with an anilinonaphthalenesulfonate solution and the mixture was introduced into the flow (1.2 mℓ/min) of the solution of one of the complexing reagents in dichlorethane. Fluorescence was excited and registered in the flow. Excessive amounts of sodium (10-times) are no hindrance to the determination of 4×10^{-4} *M* potassium. Kina et al.[538] have described another variant for the extraction fluorimetric determination of potassium.

Rare-earth metals. Very often one faces the problem of extraction separation and concentration of all the rare-earth elements. When analyzing aluminum oxide. Sizonenko et al.[539] separated rare-earth elements and Y from a weakly acidic media by extracting them with a chloroform solution of 1-phenyl-3-methyl-4-benzoylpyrazolone-5. The conditions under which the rare-earth elements are extracted from phosphate-containing solutions and concentrated with diantipyrylmethane have been studied.[540] Zaitsev et al.[541] have developed a procedure for the neutron activation determination of rare-earth elements in rocks, which involves concentration of determinable elements from HCl solutions with diantipyrilmethane. The solution of the liquid anion-exchanger Amberlite LQ-2 in xylene completely removes Sc, Th, U(VI), and Zr from H_2SO_4 solutions; rare-earth elements and Y remain in the aqueous phase.[542]

Separation of rare-earth elements from each other and isolation of individual rare earths from the mixture of non-rare-earth elements is a more important problem. For separating a mixture of rare-earth elements in the presence of macroamounts of U(VI), Tomazic and Branica[543] applied multistage counter-current extraction using di-2-ethylhexylphosphoric acid. The separation conditions (the concentration of HNO_3 in water and in toluene) were selected on the basis of experimental data on extraction under ordinary conditions. In the course of the process uranium remained in the organic phase and the REE in the aqueous phase; the latter elements were gradually separated. According to the data obtained by Tomazic and Branica, this method of separating REE has definite advantages compared with extraction chromatography.

Nastasi and Lima[544] applied the counter-current method to separate rare-earth elements with the use of a tetracycline chloride solution in benzyl alcohol. The La-Tu pair is completely separated in a ten stage process, but not less than 23 stages are needed for the separation of Pr, Eu, and Yb. Shevčhuk et al.[545] have determined conditions under which La and Y can be separated by extracting their thiosulfate complexes with solutions of primary alkylamines (the C_{10}-C_{12} fraction) in chloroform. The interdependence of extraction ability with respect to REE (with the example of Ce and Nd) and the structure of higher tertiary amines has been studied.[546] The steric factors play a dominant role in the extraction from nitrate solutions. Ce and Nd were better separated with methyl-n-diheptyl- and methyl-n-dioctylamine. Kopyrin et al.[547] have studied the effect of different complexones on the separation of Ce and Eu in the same extraction systems. With diethylenetriaminepentacetic acid in the aqueous phase, the maximum separation factor (2000 to 3000) was achieved for the Ce-Eu pair. Mishchenko et al.[548] have suggested an extraction fluorimetric method of determining europium, which depends on the toluene extraction of the metal complex formed with naphthonic acid and 1,10-phenanthroline. The detection limit is 5×10^{-10} M, but no information on the selectivity is given. Extraction of different-ligand complex of Eu with 1,10-phenanthroline and salicyclate was used for its determination in mineral waters.[549] The accompanying elements were separated by electrolysis on a mercury cathode.

Matveets et al.[550] determined europium (1 to 1.5 ng/mℓ) and samarium (5 to 3000 ng/mℓ) fluorimetrically after benzene extraction of the three-component complex of metals formed with 1,10-phenanthroline and thenoyltrifluoracetone. An extraction complexometric method of determining Y is described in the work of Kalmykova et al.[551] Diantipyrilmethane in chloroform and thiocyanate media were used to separate Y from Ti and Fe. The variation in the acidity of the aqueous phase enabled first Ti and Fe to be removed from it, and then Y. Ce (III) traces can be separated from Ce (IV) by separating them with solutions of *N*-oxides of trioctylamine and 4-(5-nonyl)-pyridine in benzene and xylene. Good results are obtained upon extracting then from 0.01 to 0.1 M solutions of mineral acids, and with more than 0.25 M solutions of *N*-oxides in organic solvents. For the determination of cerium in rocks, it was extracted as a complex with *N*-phenylnaphthohydroxamic acid.[470]

Rhenium. It is usually extracted as a perrhenate ReO_4^-, but extraction of other compounds, in particular of low-oxidation-state chelates of this element, is also extensively used.

Perrhenates can be extracted from acidic, neutral and alkaline solutions with oxygen-containing solvents, amines, or different large organic or complex cations, for example with tetraphenylarsonium or nitron. Rochet[121] has suggested a method of separating Re (VII) from impurities by extracting perrhenate from 0.25M H_2SO_4 with a mixture of mesityl oxide and benzene. For the determination of rhenium in shales and molybdenites (5×10^{-7}%) it was concentrated with methyl ethyl ketone.[553] For this purpose, use was made of extraction with an Aliquat-336 solution in MIBK;[554] rhenium was extracted with sodium perchlorate solution, the back extract was treated with solutions of sodium dodecylsulfonate in heptane and of potassium ethylxanthate in carbon tetrachloride to remove the interfering elements, and the activity of ^{186}Re was measured in the extract.

The perrhenate can be extracted from strongly alkaline solutions with acetone, because it is salted out with alkali in a separate phase (confer, for instance[205]). A number of methods for the fluorimetric determination of rhenium, which are based on extraction of perrhenate as ionic associates with Rhodamines, have been described by Grigoryan et al.[555,556] They have also discussed methods of determining rhenium in ores with a detection limit of 0.02 µg/mℓ of the extract. Solomatin et al.[557] have suggested an indirect method of determining rhenium in alloys. After dissolving the alloy, Re(VII) is separated with dichlorethane as an ionic associate formed with ferrocenium cation. Rhenium was determined by the AA method using the iron absorption line. The detection limit was found to be equal to 0.22 µg/mℓ. Senise and Silva[558] extracted the ionic associate of perrhenate with the cation complex, which was formed by reacting copper azide and 2,2′-dipyridyl, for the determination of rhenium; rhenium was indirectly determined by AA.

Pavlova et al.[559] have proposed an activation method for the determination of rhenium in rocks. Prior to irradiation, the solution of the sample is treated with H_2O_2 and pyridine. The organic phase is evaporated and the residue is dissolved in water; the obtained solution is passed through a U-shaped column containing Dowex 50W8 in the H-form. $HReO_4$ kept in the eluate is neutralized with ammonia, evaporated and irradiated with thermal neutrons, and the γ-activity of ^{186}Re is measured. Extraction of rhenium complexes with thiocyanate, dimethylglyoxime, and 2-furyldioxime was studied by Iordanov et al.[380] For the photometric determination of rhenium, its thiocyanate complex was extracted with hexamethylenephosphoramide.[170]

Scandium. Of the publications dedicated to the extraction of scandium, we shall point out only two. The thiocyanate complex of this metal was extracted with mesityl oxide for subsequent photometric determination.[206] Kononenko et al.[560] have developed a method for the extraction fluorimetric determination of scandium in REE oxides (>0.04%), which is based on the extraction of ionic associates with benzene, xylene, etc., that are formed in the presence of salicyclic acid or 2-phenyl-quinoline-4-carbonic acid and Rhodamine B. The detection limit was found to be 0.007 to 0.02 μg.

Selenium. It is quite often extracted with sulfur- and nitrogen-containing reagents, forming chelates or other compounds. For this purpose, use can also be made of dithiocarbamates; for example, Kamada et al.[561] have described a procedure of using diethyldithiocarbamate for the AA determination of selenium in waters.

A procedure for fluorimetric determination of selenium (10^{-4} to 4×10^{-2} %) in sulfides, which involves a cyclohexane extraction of selenium (IV) complexes formed with diaminophenol, has been described by Michael et al.[562] Copper and lead hinder the determination to an appreciable extent, that is why they should be separated prior to the determination. For the AA determination of selenium in metallurgical samples, Ohta and Suzuki[563] extracted the selenium complexes formed by 3,3′-diaminobenzidine with toluene. The extract was introduced into an atomizer — that is, into a molybdenum tube. The detection limit was found to be (2 to 5) $\times 10^{-11}$ g. Organotin compounds in the form of solutions in organic solvents were used to concentrate Se (IV and VI).[564] In this case, selenium can be separated from tellurium. Of interest is the extraction of organoselenium compounds which are formed by reacting Se (IV) with unsaturated hydrocarbons in HCl solutions. The extraction is quite selective.[565]

Silver. Many methods are known for the extraction separation of this element. They are based mainly on the use of chelates with sulfur-containing reagents, and of mixed neutral complexes (coordinatively solvated compounds).

Extraction of silver dithizonate continues to hold an important place. This method was used, for example, to isolate silver prior to its kinetic determination,[383] to separate silver substoichiometrically for its determination by activation analysis.[312] Upon developing a method for fluorimetric determination of silver traces in metallic copper,[566] good results were obtained by extracting silver with dithizone from a solution (pH 3 to 5) containing EDTA, by back extracting with bromide solutions followed by fluorimetric determination with butylrhodamine B or pyronine M.

Extraction of dithiocarbamates is also extensively used. Diethyldithiocarbamate was extracted for the determination of silver by the ESR method (silver was oxidized to the paramagnetic bivalent state prior to its determination).[365] For the AA determination of silver in silicates, silver diethyldithiocarbamate was extracted with benzene.[567] The detection limit was found to be 10^{-6}% (graphite furnance). Ryabinina and Lazareva[568] determined Ag, Cd, and Cu in sea waters by extracting them as diethyldithiocarbamates with chloroform. Zinc dibenzyldithiocarbamate served as an extractant in the determination of silver by the radiochemical method, using its substoichiometric extraction.[319] For the determination of silver in sea water, it was extracted with hexamethylenedithiocarbamate.[431] Use is also made of extraction of silver xanthate, for example, with MIBK from weakly acidic media;[569] spin-labelled xanthate was used to determine silver by the ESR method.[368]

Many papers are dedicated to the extraction of silver with organic sulfides obtained synthetically as well as isolated from petroleum. Extraction is commonly used, particularly in the U.S.S.R., to separate silver prior to its determination by atomic absorption, neutron activation, and others. Khlebnikova and Torgov[570] have shown that it is possible to achieve a sufficiently low AA determination limit for silver (~0.003 μg/mℓ) provided it is separated from a HNO_3 medium with a solution of petroleum sulfides in toluene, and the extract is nebulized into the toluene-air flame. For the neutron activation determination of noble metal impurities in silver, the matrix was extracted first with the solution of tertiary dodecylmercaptan in toluene, and then with the solution of dioctylsulfide in benzene.[537]

Zolotov et al.[571] have recommended certain methods for selective extraction of silver with chloroform solutions of *N N'*-diphenylthiourea or *O*-isopropyl-*N*-ethylthiocarbamine. Under the conditions found by the authors, only mercury is extracted along with silver; with the use of the second reagent, mercury is poorly separated from H_2SO_4 solutions. For the AA determination of silver, it was extracted with diphenylthiourea.[572] It has been shown that the flameless variant enables the determination limit to be lowered by about three orders — 5×10^{-4} μg of gold per milliliter compared with 0.1 μg/mℓ (when nebulization is carried out in a flame). For the neutron activation determination of silver in natural objects,[573] the sample was irradiated, dissolved, and the metal was extracted from 2 *M* H_2SO_4 with a diphenylthiourea solution. Thereafter, the activity of ^{110m}Ag was measured in the extract.

As an extractant for silver the use of triphenylphosphine was recommended. The silver compound formed with this extractant was extracted with MIBK for the atomic absorption determination of this element.[107] Extraction of the complex with triphenylphosphine in the melt of the eutectic mixture of naphthalene and diphenyl was used for the X-ray fluorescence determination of silver.[290] In order to concentrate silver for its AA determination in natural and industrial objects, Basargin et al.[574] extracted into cyclohexanone the ionic associate formed by the anion-complex of silver with 4-sulfobenzeneazorhodamine (pH 1-2) and triphenylguanidinium. Such a method makes it possible to determine both comparatively small (10^{-5}%) and relatively large (0.1%) amounts of silver in samples.

Strontium. There are not many good methods for the extraction separation of strontium. The main task resides in developing methods that would permit extraction of strontium in the presence of significant amounts of calcium. It is not improbable that for this purpose the crown ethers will be of interest. Strontium can be isolated from cesium and potassium by extracting the ionic associate with tetraphenylborate into nitrobenzene or hexane containing trioctylphosphine oxide.[575] Shtefek et al.[576] have proposed a method for the radiometric determination of strontium which involves extraction with hydrophobic boron-containing anions in the presence of polyethyleneglycol.

Thallium. As thallium (III), this metal is extracted completely and selectively from weak HCl and HBr solutions with oxygen-containing solvents or extractants that supply large organic cations. This can be illustrated with some examples.

Bohmer and Pille[577] used the fluorescence property of thallium chloride in MIBK for the determination of thallium in rocks and soils. For the photometric determination, thallium was extracted with mesityl oxide from 1 *M* HCl-1 *M* LiCl, and $TlCl_4^-$ was converted in the extract into an associate with brilliant green.[211] The associate formed with $TlCl_4^-$ and the brilliant green were extracted with benzene for the determination of thallium by the isotope dilution method.[323]

Schnepfe[578] has suggested a method for the determination of thallium in silicate rocks. Thallium (I) is preseparated from the solution of the sample with dithizone solution in chloroform. After back extracting thallium with HNO_3, it is oxidized to thallium (III) which is separated from HCl as an ionic associate formed with Rhodamine B, and the extract is measured with a photometer. The detection limit is 0.01 μg/g of the rock.

Thallium (I) is nicely extracted as chelates, for example as the dithizonate. Kirchmann and Huber[221] have suggested a method of successive spectrophotometric determination of thallium (I) and dimethylthallium which is based on the extraction of complexes with PAN.[221]

Tantalum. The best method of extracting tantalum, including its separation from niobium, is the separation of its fluoride complex (often from the solutions of the type HF-H_2SO_4, HF-HCl) with oxygen-containing solvents, amines, or extractants containing a reactive large organic cation. For example, for the AA determination of tantalum in the presence of noble metals, it was pre-extracted with MIBK from HF-HCl solutions.[468] For the determination of impurities in tantalum, the matrix element was separated from fluoride-sulfate solution with TBP, cyclohexanone, or a mixture of petroleum sulfoxides.[493] Nikolaev et al.[579] used sulfoxides to concentrate tantalum. For the activation determination, Bakhmatova et al.[580] and Cbrusnik and Posta[581] propose to extract tantalum from fluoride solutions as the ionic associates with brilliant green. The methods are characterized by good detection limits (1 to 2 μg Ta) and a relative error of 2 to 3%. Elinson[497] has described a method for extraction photometric determination of tantalum and niobium. The main organic reagents used for the extraction photometric determination of tantalum are listed in the work of Podchainova et al.[582]

Tellurium. Usually tellurium (IV) is extracted from halides, particularly from chloride solutions, with oxygen-containing solvents. First the interfering elements, for example Fe(III), are removed and then, by varying the conditions, tellurium is extracted. Thus, Marke and Jettmar[583] first separated Fe, Au, Tl, Ga, Sn, and many other metals from HCl solution with diisopropyl ether, and then saturated the aqueous phase with NaF and extracted tellurium (IV) with di-n-octylsulfoxide in tetrachlorethane.

Using double concentration, Nazarenko et al.[584] determined tellurium in ores by AA: first, a relative concentration was achieved under oxidizing conditions (the major amount of iron was removed from HCl medium with MIBK) and then absolute concentration by extracting Te(IV) from a HCl solution with the same solvent. The method enables tellurium to be determined practically in all samples of raw minerals with a concentration of not less than $6 \times 10^{-6}\%$. Chao et al.[585] have suggested an equally sensitive method for the AA determination of tellurium in geological objects, which involves extraction with MIBK. In steels, tellurium was determined by extracting it with TOPO solution in MIBK.[586] For the photometric determination of tellurium in pure selenium, it was extracted with MIBK from HCl solution.[208]

Tellurium (IV) can be concentrated also with chloroform in the presence of dithiopyrylmethane and perchlorate.[587] This method enables $2 \times 10^{-4}\%$ tellurium to be determined in nickel ores by the photometric method. Donaldson[588] has suggested a composite method of separating tellurium in the analysis of concentrates and brasses. The method envisages co-precipitation of tellurium with $Fe(OH)_3$ and subsequent extraction into chloroform as ethylxanthate. The use of diethyldithiocarbamate permits extraction of tellurium (IV) for subsequent AA determination in waters.[589] Kulev[590] has suggested a neutron activation method for the determination of uranium in geological objects, which involves separation of ^{132}Te as a fission product. The method envisages separation of ^{132}Te from the irradiated sample by combining precipitation of tellurium in the elementary state and extraction in the form of diethyldithiocarbamate. The detection limit of uranium in this manner is 10^{-7} g.

Thorium. The nitrate complexes of thorium are completely extracted and, therefore, they are often used to separate this element. Thorium can be separated from REE and Y by extracting it from a HNO_3 medium with solutions of the *N*-oxide of 5-(4-pyridyl)-

nonane.[591] Thorium and scandium were separated in the nitrate system with diantipyrilmethane.[592] For the photometric determination of thorium with arsenazo III in technological solutions of the REE industry[210] and with thoron in ores,[193] the determinable element was pre-extracted from HNO_3 solutions with TBP in carbon tetrachloride[210] and with TOPO in cyclohexane.[193]

Thorium is also separated from HCl solutions; thus, for the determination of thorium traces in REE and their compounds, it was separated from HCl solutions with triisoamylphosphine oxide solutions.[593] For the photometric determination of thorium with arsenazo III, it was pre-extracted with *n*-butylamine from H_2SO_4 solution.[209]

Thorium can be concentrated with dibutyl ether of phenylsulfonilamidophosphoric acid.[594] A method of extracting thorium with TTA solutions in organic solvents is also known (for details, refer to the work of Kondrateva et al.)[593]

Tin. Tin (IV) can be extracted from thiocyanate solutions. For example, in the photometric determination of tin with propylfluoron, the thiocyanate complex was pre-extracted with antipyrene.[184] The iodide complex was isolated for the polarographic determination of tin in the extract.[333] The use of bromide systems and of di-2-ethylhexylphosphoric acid as extractants enabled tin to be separated from large amounts of alkalies, alkali earths, and many heavy metals.[595] On the basis of this, a method has been developed for the determination of tin in unrefined and high-purity indium. For the determination of tin in standard samples of rocks by the neutron activation method, the metal was extracted with diisopropyl ether from thiocyanate solutions.[596] After evaporating the extract, tin was separated as the sulfide and the γ-activity of ^{117m}Sn was measured. The detection limit was found to be equal to 0.01 μg Sn.

Tin (IV) chelates are generally "cationic" in nature. Therefore, they can be extracted either by introducing other ligands (of chloride, etc.) into the internal sphere of tin, which form mixed complexes (for example, of the type SnA_2X_2, where A stands for the anion of chelate-forming reagent, X is the inorganic anion), or the anionic associates of the type $SnA_3^+X^-$. In the latter case, for the X^- it is desirable to have a large hydrophobic anion. Chelates of this type are formed by reacting tin (IV) with 8-hydroxyquinoline and other reagents.

Among the works devoted to the practical application of extraction of tin chelates, we shall mention those in which BPHA has been used for the polarographic[354] and photometric[207] determination of tin.

Titanium. An effective method of separating and determining titanium depends on extraction and photometric measurement of its mixed complex with thiocyanate and diantipyrilmethane. Other extractants, for example mesityl oxide,[312] are also used to extract titanium from thiocyanate solutions. For the determination of titanium in steels and silicozirconium, it was extracted from chloride and thiocyanate solutions with a tetraethyldiamideheptylphosphate solution in toluene.[597]

Pyatnitsky and Simonenko[598-600] separated titanium using mixed compounds that are formed in the systems containing 2-brombutyric acid and 1-phenyl-3-methylpyrazolone-5 (for separating titanium from vanadium, chromium, cobalt, nickel),[598,599] and benzohydroxamic acid — tetrabrompyrocatechol.[600] Using monoaurylphosphoric acid in hexane, titanium was extracted substoichiometrically from a H_2SO_4 solution for its determination using isotope dilution and radiometric correction methods.[318,601]

Practically in one stage, titanium is selectively separated from solutions of complex composition by extracting the complex with isobutanol, which is formed with thymolphthalecsone.[602] This method was used for analyzing steels, cast irons, and aluminum.

Tungsten. In the review by Ivanov et al.[603] the use of extraction in the analytical chemistry of tungsten has been considered with a view to separate and determine it by different methods. Extensive use is made of extraction of the thiocyanate complex of tungsten (V) with MIBK and other solvents. For example, extraction is employed for the AA determination of tungsten.[604] Tungsten can be separated from molybdenum by extracting it from thiocyanate solutions with the salts of quaternary ammonium bases.[605] In this case the elements which are to be separated are first reduced with tin(II) chloride to W(V) and Mo(III). The chloride complexes of tungsten (VI) can also be extracted with TBP.[301] Small amounts of tungsten are extracted as heteropolycompounds, particularly as phosphotungstic acid; thus, Yatirajam and Dhamija[606] used this method for the analysis of industrial and natural samples.

Among tungsten chelates, mention must be made of the compound formed with 2-benzoinoxime and used for the photometric determination of this element.[162] Korrey and Goulden[607] determined tungsten in natural waters by AA; for this, they extracted the metal into MIBK as a complex formed with benzoinantioxime. In order to stabilize the extract, a solution of ephedrine in MIBK was added to it; after 2 to 3 hr the extract was nebulized into the C_2H_2-N_2O flame. Tsykhansky et al.[608] propose to determine tungsten in rocks and minerals spectrographically after extracting tungsten as a complex with 5,7-dibrom-8-hydroxyquinoline. For the determination of tungsten in metallic zirconium, the former was preseparated by extracting it as benzhydroxamate with a mixture of isobutanol and chloroform (1:1).[609] Large amounts of tungsten, when determining rhenium in it, were separated as chelates with BPHA.[610] Good results can be obtained upon separating tungsten with solutions of 3-hydroxy-2-methyl-1-phenyl-4-pyridone in chloroform.[611] Only vanadium was extracted along with tungsten, although the range of studied elements was not sufficiently wide.

Extraction of ionic associates with chloroform has been studied, the cationic part of which contains tungsten, trioxyfluorone and antipyrine, and the anions of strong acids serve as counter ions;[172] these associates have been used for the photometric determination of tungsten.

Uranium. The separation method for uranium (VI) consists in extracting $UO_2(NO_3)_2$ solvated with oxygen-containing extractants — ketones or esters including phosphoric acid esters. Extraction is easily carried out from solutions with low HNO_3 concentration, not exceeding 1 *M*, because on extracting from solutions with high acid concentration other metals are also extracted, and as a result the selectivity is impaired. The anionic complexes of uranium (VI) formed with nitrate, chloride, sulfate, acetate are extracted with amines and salts of quaternary ammonium bases. Beside this, uranium (VI) and (IV) are extracted as chelates including those formed with phosphorous-containing chelate-forming extractants.

Uranyl nitrate was extracted with TOPO solution in cyclohexane for the photometric determination of uranium in ores with PAN.[193] Examples of extraction of anion complexes with amines are: separation with an Aliquat-336 solution in xylene from solutions with high concentration of LiCl for the photometric determination of uranium in sea water with arsenazo III;[213] and extraction with trialkylamine in benzene also from HCl solutions for the photometric determination of uranium with chlorphosphonazo III.[186] Uranium was extracted from the sulfate solution with TOA for its subsequent photometric determination with 8-hydroxyquinoline.[198] Phenylarsenoxide in chloroform was used as extractant.[356] In the analysis of ores, uranium was determined after extracting it with MIBK from perchlorate, halide, and other solutions in the presence of calcium nitrate used as salting out agent.[612]

Uranium (VI) acetylacetonate was extracted for the photometric determination of uranium in the organic phase.[357] Acetylacetone in the presence of TOPO was used to extract uranium prior to its polarographic determination in sea water.[355] Budesinsky[613] has suggested a method of separating uranium by extracting it from neutral solutions with dibenzoylmethane in benzene. For the determination of uranium in rocks, it was extracted as a complex with *N*-phenylnaphthohydroximic acid.[470] For a photometric determination, use was made of synergistic extraction of uranium (VI) with the same acid in the presence of gossypol.[174] Konstantinova et al.[614] determined uranium in ores photometrically after extracting the metal with solutions of TOPO and benzoic acid in benzene, and subsequent mineralization of the extract. Uranium was determined by the polarographic method after extracting its anionic benzoate complex in the presence of tetradecyldimethylbenzyl ammonium.[361] The colored anionic complex of uranium formed with arsenazo III is extracted in the presence of diphenylguanidine with butanol; use of this property has been made for the extraction photometric determination of uranium in waste waters.[199]

Uranium was extracted with di-(2-ethylhexyl)phosphoric acid in the presence of TBP for its photometric determination in phosphate rocks and phosphoric acid,[615] and also to determine this element by the fluorimetric method;[616] uranium was extracted also in the presence of TOPO for its X-ray fluorescence determination in phosphoric acid solutions.[295]

Vanadium. It is best extracted as chelates, for example, with 8-hydroxyquinoline, cupferron, BPHA, β-diketones. Several methods of extracting vanadium are given in the review by Svehla and Tolg.[617]

For the AA determination of vanadium, the extract obtained on separating vanadium cupferronate with di-*n*-butyl ether was nebulized into a flame.[618] Large amounts of iron and copper were preseparated by extracting their cupferronates at much higher pH values of the aqueous solution. The detection limit of vanadium varied from 0.05 to 10 μg/mℓ. Vanadium traces in air ($3 \times 10^{-6}\%$) were determined by extracting cupferronate with MIBK.[619] The extract was mineralized and subjected to atomization; tin hinders the determination of vanadium. On determining rhenium in vanadium the latter was separated by extracting its complex formed with BPHA;[610] for the determination of vanadium in rocks, it was separated as a compound with *N*-phenylnaphthohydroximic acid.[470] Kojima et al.[620] determined vanadium in silicates by AA using synergistic extraction of the vanadium complex formed with β-isopropyltropolone with dibutyl ether containing butanol. The extract was introduced into a flame. Large amounts of iron were preseparated with ion-exchange chromatography. Shcherbakova et al.[621] have described several methods of separating vanadium with β-diketones, they have found out conditions under which vanadium (V) and (IV), when both of them are present, can be determined by extracting them as complexes with PMBP, chloroform containing amylalcohol is used as the solvent. The vanadium-2-(2-thiazolilazo)-5-dimethylaminophenol complex was extracted with chloroform for the photometric determination of vanadium.[168]

8-Hydroxyquinoline forms a mixed chelate with vanadium (V) in the presence of alcohols, which is used for the photometric determination of vanadium or alcohols. Thus, Kojima et al.[620] extracted vanadium hydroxyquinolinate with MIBK in the presence of ethyl alcohol.

Buenafama and Lubkowitz[622] have suggested a sensitive neutron activation method for the determination of nanogram amounts of vanadium in geological materials, metals, and alloys. Prior to irradiation, molybdenum is removed from the solution of the sample by passing the solution through a column containing an anion-exchange resin. From the eluate, vanadium is extracted with solutions of BPHA, 8-hydroxyquinoline or tri-*n*-butylamine in MIBK. The extract is then irradiated and the activity is measured.

Other vanadium compounds are also used. For an extraction photometric determination, vanadium was extracted in the form of mixed compounds formed with thiocyanate (or azid) and hydrochloride of *N*-hydroxy-*N*-*p*-chlorphenyl-*N'*-(2-methyl-4-

chlorphenyl)-benzamidine,[175] with *N*-hydroxy-*N,N'*-diarylbenzamidines, and anisaldehyde.[171] Busev et al.[187] extracted vanadium from a solution (pH of 1.5) with TOA dissolved in benzene, and after adding tribrompyrogallol into the extract determined vanadium by the photometric method.

Extraction of the mixed pyridine-thiocyanate complex of vanadium (II) enables vanadium to be separated from many interfering elements; vanadium is reduced with zinc amalgam in H_2SO_4.[214]

Zinc. The classical method of extracting zinc as dithizone is extensively used for its photometric determination by the same reagent. For the determination of zinc in soils, it was concentrated by dithizonate extraction followed by back extraction.[623] Diethyldithiocarbamate is used to separate zinc from other metals and for absolute concentration; this method was used, for example, for the polarographic determination of zinc in niobates and tantalates of alkali metals and other objects.[362] Zinc was extracted substoichiometrically with 8-mercaptoquinoline for its determination by the isotope dilution method.[320,321] Spin-labelled xanthate was used to determine zinc in the extract by the ESR method.[366]

Zinc is nicely determined by the AA method after extracting the complex formed with organic bases of the pyridine type; cinnamic acid in chloroform was used as the solvent.[410] The extract is diluted with methyl or ethyl alcohol, and introduced into a propane-butane-air flame. The detection limit (0.01 μg/mℓ) is improved by 3 to 5 times compared .to the case when the aqueous solution is nebulized into the flame.

Shevchuk et al.[624] determined zinc (10^{-4} to 10^{-5}%) in steels by AA after extracting chloroform complexes of zinc with TOA solution in MIBK. A TOA solution in chloroform was used to extract zinc for its photometric determination in aluminum and nickel by the dithizonate method.[200] Halide and thiocyanate complexes of zinc were extracted using *bis* (4-ethyl-3,5-dipropyl-1-pyrazolyl)methane in the form of coordinatively solvated compounds; thereafter, zinc was determined by the dithizone method in cadmium chloride.[201] Extraction of zinc from thiocyanate solutions with MIBK was used for the determination of this element in ores, concentrates, and cements.[625]

Zirconium. It can be extracted from nitrate and chloride solutions with TBP or similar extractants. For example, for the photometric determination of zirconium with xylenol orange, it was extracted from 9 *M* HCl with a TBP solution in benzene.[194] Zirconium was separated from titanium by TOPO extraction in cyclohexanone.[294] The pyridine complex was extracted with chloroform.[215] By extracting zirconium with the *N*-oxide of 4-(5-nonyl)-pyridine and TOA in xylene from HCl and nitrate solutions, it can be separated from uranium and fission products.[626] Zirconium can be isolated from Mg, Zn, Ni, Fe, Al, U, and Th by extracting it from HCl media with TOA solutions in benzene.[627] When analyzing zirconium, the rare-earth elements can be concentrated by separating the matrix elements through extraction into the third phase which is formed under definite conditions in the system: aqueous solution — chloroform and benzene mixture, also containing diantipyrilmethane. The rare-earth elements remain in the aqueous solution and can be determined, for example, by the spectrochemical method.

For the subsequent photometric determination of zirconium, the mixed complex with BPHA and methylthymol blue was extracted with butanol.[173] Zirconium can be separated from many elements by extracting it from 4-6 *M* HCl or 3-4 *M* $HClO_4$ with a TTA solution in benzene.

Solovkin and Yagodin[629] have considered the interdependence of the ionic state of zirconium in aqueous solutions and its behavior when extracted in different systems. This review is concerned mainly with the technological aspects, but shall prove useful for analysts engaged in the field of trace analysis.

VI. EXTRACTION IN THE ANALYSIS OF SELECTED SAMPLES

Extraction is extensively used as a separation and preconcentration method in the analysis of different materials. It is often employed in combination with other techniques (distilation, coprecipitation, etc.) serving the same purpose; examples of such combinations can be found in the earlier sections of this report.

Here, we shall briefly consider in short the application of extraction for the determination of small amounts of metals in environmental samples, natural mineral samples, metals, alloys, and inorganic compounds including high-purity inorganic substances.

A. Environmental Samples

The problem of analyzing environmental samples (natural waters, industrial wastes, air, etc.) is very acute at the present time. This is related to the intensification of human activity in industry and agriculture. As a result of this, many harmful substances enter into the environment which produce undesirable effects on living organisms and their surroundings. Beside this, the increased content of a number of substances does not permit, for example, repeated use of water for industrial purposes — i.e., it presents difficulties in having a closed cycle.

Numerous impurities enter into natural waters. That is why the analysis of natural waters and of waste waters that enter into them receives great attention. It seems that waters as an object of analysis should not present many difficulties. But trace elements can be present in waters in diverse states; they can exist as simple ions or complexes with different organic substances including vital products of living organisms. Trace elements can be occluded or adsorbed with suspended matter, and as organic and inorganic suspensions. The salt content in waters can be too high. All these factors have appreciable effects on separation and concentration processes of metals. Without taking into account these factors, it is impossible to obtain reliable results. The suspensions present in water are either dissolved and then extraction-concentrated or are separated by centrifugation or filtration and the precipitate is mixed with the concentrate of trace elements and analyzed.

Very often the determinable trace elements are present in water as soluble complex compounds formed with natural and technological organic substances, and also as colloids. When analyzing sea waters, it is necessary to add a small amount of acid into sample solution; it is expedient to store and transport the sample in polyethylene or Teflon® containers. Use of certain methods permits direct concentration of trace elements without treating the water to stabilize; for example, heavy metals can be extracted, without subjecting the water to any treatment, as hexamethyleneammonium hexamethylenedithiocarbamate complexes with butylacetate (see above). This, as a rule, calls for the destruction of the complexes present initially. The water is treated with oxidants — for example with persulfate. This problem has still more significance in the analysis of surface and fresh waters. Complexing of metal ions with humic and fulvic acids and with other organic substances present in waters has a strong effect on the degree of extraction of trace elements. Complete determination is generally possible only after the destruction of these organic substances.

A number of reviews are dedicated to the methods used in the analysis of different waters,[127,630-634] in which much thought has been given to the application of extraction for the separation and concentration of metals. The number of experimental works related to the use of extraction in the analysis of waters is very large; we shall list only a few of them.

In the analysis of waters with carbamates use was made of group concentration by extraction.[397,568] Mamontova et al.[635] separated nanogram amounts of cadmium and lead from natural waters by extracting their pyrrolidinedithiocarbamates into MIBK followed by flameless AA determination in the extract. When analyzing river waters, Tweetan and Knoeck[636] extracted trace heavy metals as their diethyldithiocarbamates in isoamyl alcohol. The detection limits were found to be $\geqslant 2\ \mu g$ of metals (Cd, Cu, Fe, Pb, Mn, and Zn) in 1 mℓ of water. A slightly more complicated procedure was used by Korkisch and Sorio[238] to analyze waters for the concentration of heavy metals. Apart from the extraction of trace elements as diethyldithiocarbamates, use is made of an anion exchanger to isolate the interfering anions; only after this the AA determination is carried out. Copper, silver and cobalt can be extracted with butyl acetate as hexamethylenedithiocarbamates.[431] This method has been used for the analysis of sea water. Kirnade and Van[637] concentrated gold, copper, and mercury from sea water by extracting them with lead diethyldithiocarbamate. The sample was first filtered through a membrane filter and then boiled in a condensation flask with a mixture of concentrated HNO_3 and HCl to destroy the organic and colloidal forms. Then the metals were determined by the neutron activation method.

Extensive use is made, as before, of dithizone for concentration. We shall mention the works of Smith and Windom[638] and Armannsson[639] in addition to the earlier referred, above mentioned papers on the determination of copper and zinc.[436] Extraction of dithizone was used to concentrate a number of heavy metals (Cd, Cu, Ni, Zn, and others) in the analysis of sea water. The combination of extraction and AA determination enabled nanogram amounts of the above mentioned metals to be determined. The application of dithizone in the analysis of water is not limited only to these works.

Use is also made of chelate-forming extractants — β-diketones, oximes, organic acids, etc. Koumtris et al.,[640] for example, suggest the use of 2,2′-dipyridyl-2′-pyridylhydrazone for the determination of cobalt in waters (by the extraction photometric method). The method permits determination of cobalt at a level of 1ppb. Pyatnitsky et al.[641] have described a method for the group concentration of metals (Cd, Co, Cu, Ni, and Zn) in the analysis of natural waters, which involves extraction with chloroform solution of enanthic acid and benzoylhydrazine. At pH 6 to 8 and for the ratio of phase volumes $V_{H_2O}: V_{CHCl_3} \leqslant 20$ group separation of earlier mentioned metals is observed. Trace elements were concentrated by extracting them from a weakly acidic medium with a mixture of 8-hydroxyquinoline and diethyldithiocarbamate.[642] The extract was evaporated in the presence of charcoal powder and determined spectrographically in an AC arc. Pakhol'chuk and Andrianov[147] have suggested a method for the determination of molybdenum; an iron chloride solution (0.1 mg of iron per milliliter) is added to the waste water sample, the pH is raised to 7.5 to 8, and the solution with the precipitate is treated with 1 *M* solution of caprylic acid in kerosene. Molybdenum is determined after back extraction in the aqueous phase.

Often, use is made of extraction systems based on ionic associates for the analysis of waters. For separate determination of Cr(III) and Cr(VI) in sea water, they were extracted with an Aliquat-336 solution in toluene after adding ammonium thiocyanate.[423]

Kim et al.[643,644] have suggested a method for the determination of molybdenum, rhenium, and tungsten in soils, sediments, and natural waters. The method is based on the extraction of thiocyanate complexes of Mo(V), Re(V), and W(V) from HCl media with tricaprylmethylammonium chloride solutions (Amberlite LAI) in chloroform. The extract is nebulized into a flame. Iron, copper, manganese, palladium, and zinc slightly hinder the determination. Yoto and Unohara[489] extracted nickel from waste waters with trioctylammonium chloride into isopropyl acetate. Significant amounts (>1 mg) of cadmium, cobalt, bismuth, and iron appreciably hinder the determination. Aliquat-336 was used as an extractant in the separation of uranium (VI) from sea water with diethylbenzene.[645] The aqueous phase must contain 3.5 *M* LiCl and 0.2 *M* HCl. Finally, the determination is carried out photometrically with arsenazo III. Thorium, hafnium, zirconium, rare-earth elements are no hinderance to the determination.

B. Natural Minerals

The elements whose concentration in the solid sample does not exceed 0.01% are generally considered to be trace elements as applied to geological materials. The determination of trace elements in these samples is a quite difficult task because of different compositions of the samples, forms in which micro- and macroelements exist, non-uniform distribution of traces, the impossibility of preparing standard samples of all possible natural mineral materials. The use of methods involving chemical decomposition of samples, isolation and concentration of trace elements often appreciably alleviates the analysis.[646,647] Among the methods used to separate and concentrate traces present in the considered materials, extraction holds a significant place.

In the analysis of geological samples, extraction is employed to separate the determinable elements; in so doing, the matrix elements are never extracted. This is dictated by the presence of large number of trace elements having diverse chemical properties.

Several AA methods have been suggested for the determination of heavy metals in different mineral materials. Armannsson[648] extracted small amounts of Co, Cu, Ni in rocks and deposits from HCl solutions with chloroform as their dithizonates. Cd and Zn, which are left behind in the aqueous phase, were determined by AA. The extract was mineralized and, after dissolving the residue in 2 *M* HCl, determined by the AA method. Nakagawa[649] proceeded in a slightly different manner to determine Ag, Bi, Cd, Co, Cu, and Ni in similar objects. First, large amounts of iron were separated by extracting its bromide complex into MIBK, and then the determinable elements were extracted with a diethylammonium diethyldithiocarbamate solution in MIBK.. Using an acetylene-air flame, $10^{-5}\%$ of the above-mentioned metals can be determined with sufficient accuracy. Viels[650] determined Ag, Bi, Cd, Cu, Pb, and Zn in geological samples after extracting them with tricaprylmethylammonium chloride (Aliquat-336) into MIBK. For the determination of Co, Cu, and Ni, Chowdhury et al.[651] used 2-nitroso-1-naphtholates of these metals. Hannaker and Hughes[652] have suggested a method for multi-element AA analysis of geological materials after separating iron and manganese. Different types of extraction systems (ionic associates and chelates) are used for sequential extraction of several metals, the mutual presence of which does not hinder their AA determination.

Very often extraction is used to determine uranium by different methods. In the analysis of ores, Pakans et al.[612] separated this element from perchlorate, halide, and other solutions with MIBK in the presence of a salting out agent — calcium nitrate. Agrawal et al.[470] used *N*-phenylnaphthohydroxamic acid to separate uranium from the solutions obtained after decomposing rocks; separation was achieved, in particular, of vanadium, iron, and cerium. For the determination of uranium in phosphate rocks, it was separated with di(2-ethylhexyl)-phosphoric acid in TBP after oxidizing iron (II).[615] Alder and Das[653] have suggested an indirect method of determining uranium (IV), which is based on the reduction of copper (II) to copper (I) with uranium (IV). Thereafter, Cu(I) is combined into a complex with 2,9-dimethyl-1, 10-phenanthroline, extracted as an ionic associate, and, after back extraction, determined in a flame. The detection limit is 4 to 9 μg. The same authors have suggested a method for the determination of uranium in geological samples, which is based on the same principle.[654] Steinnes[655] used tributylphosphate to separate uranium from nitrate solutions for its determination in ultramorphic rocks by the neutron activation method.

Table 2
EXAMPLES OF THE USE OF EXTRACTION FOR THE SEPARATION OF GOLD FOR ITS DETERMINATION IN NATURAL MINERAL MATERIALS

Material analyzed	Extractant	Aqueous phase	Method of determination	Detection limit	Ref.
Pyrite, arsenopyrite	Isoamyl alcohol	HCl	AAS	—	656
Rocks and ores	Diphenylthiourea (chloroform)	6 *M* HCl, $SnCl_2$	ES	$1 \times 10^{-6}\%$	94
	MIBK	HCl	AAS	$5 \times 10^{-6}\%$	657
Silicate rocks	Hexyldiantipyrylmethane (benzene)	1—3 *M* HCl	ES	0.2 μg	658
Rocks	MIBK	1.5 *M* HCl	AAS	0.01 μg/mℓ	659
Rocks, ores, and ore treatment products	Trialkylbenzyl ammonium chloride (benzene)	0.1—0.25 *M* HCl	AAS	0.005 μg/mℓ	660
Copper sulfide ores and flotation products	MIBK	$HCl + HNO_3$	AAS	$1 \times 10^{-5}\%$	661
Polymetallic ores, sulfide concentrates	3,5-Diphenyl-1-tricarbamidopyrazoline (chloroform)	4—5 *M* HCl	ES	—	662
Ores	Cyclic sulfoxides	HF	AAS	0.3 μg/mℓ	663
Ores	Isoamyl alcohol	$HCl + HNO_3$	AAS	—	664
Rocks and minerals	Dibutylsulfide(toluene)	1 *M* HCl	ES	0.005 μg	665
Geological materials	MIBK	$HCl + HNO_3$	NAA	—	301
	MIBK	HCl	AAS	$<5 \times 10^{-5}\%$	652
Silicate rocks	Nickel diethyldithiocarbamate (chloroform)	—	NAA	—	666
Rocks and their treatment products	Amylacetate	Br_2, HCl	AAS	$1 \times 10^{-5}\%$	667

Some examples of the use of extraction for the determination of gold in geological materials are given in Table 2.

Donaldson[668] has suggested a method of determining antimony in ores, concentrates, and other materials, including extraction of its xanthate with chloroform; antimony is then determined by the spectrophotometric method in the form of iodide. For the neutron activation determination of molybdenum in scheelite-tungsten ores and rocks, it was extracted, after irradiating the sample, with a benzene solution of di(2-ethyl-hexyl)-phosphoric acid.[669] Tellurium was extracted with MIBK from a HCl solution for its AA determination in ores.[670]

A few more examples of the use of extraction for the determination of small amounts of elements can be found in Table 3.

C. Metals, Alloys and Inorganic Compounds

Unlike geological samples, these materials are usually simple in composition: the matrix contains one or two, and rarely three elements. That is why, in the determination of impurities and alloying elements in such materials, extraction is used not only to separate trace elements but also to remove the matrix elements. The second method is often employed in the analysis of pure metals. Some examples are given in Table 4. Many more techniques of this type have been considered in the books by Zilbershtein[691] and Yudelevich et al.[692]

Table 3
EXAMPLES OF THE USE OF EXTRACTION FOR THE DETERMINATION OF TRACE ELEMENTS IN NATURAL MINERAL MATERIALS

Material analyzed	Trace elements to be extracted	Extractant	Aqueous phase	Method of determination	Detection limit	Ref.
Basalt, granite	Tl	Diisopropyl ether	1 *M* HBr	AAS	$5 \times 10^{-6}\%$	671
Bauxites	Sc	Diantipyrylmethane (chloroform, benzene)	0.5 *M* HCl + KI	ES	1—3 μg	672
Galenites	Sb	MIBK	8.3 *M* HCl	AAS	—	673
Limestones	Ag,Bi,Cd,Cu,Pb	MIBK	H_3PO_4 + KI	AAS	0.6—0.005 μg/mℓ	674
Loparite	Th	Methyldiantipyryl methane (benzene)	6 *M* HNO_3	ES	<15 μg	675
Different materials	Mo	α-Benzoinoxime (chloroform)	1—3 *M* HCl	AAS	0.01 g/t	572
	Bi	Dithizone (chloroform)	pH 3	ES	$10^{-7}\%$	677
	Co,Cu	Diethyldithiocarbamate (CCl_4)	pH 8—9	AAS	10^{-10}-10^{-12}g	678
	Sc	Phenol (benzene)	9 *M* HBr + HF	AAS	$6 \times 10^{-6}\%$	679
	Te	MIBK	6 *M* HCl	AAS	$2 \times 10^{-10}\%$	680
Rocks and other materials	Ag	Triisooctyl phosphate (MIBK)	HNO_3	AAS	$5 \times 10^{-6}\%$	681
		Diphenylthiourea (chloroform)	1 *M* HCl	ES	0.01 μg	665
		Dithizone (MIBK)	$HClO_4$	AAS	5 μg/g	689
		Triphenylphosphine (benzene)	1 *M* HCl	AAS	0.01 g/t	105
		Triphenylphosphine (MIBK)	HNO_3-H_3PO_3	AAS	—	106
Rocks	Bi	MIBK	KI	AAS	10 ng/g	683
Geological materials	Co,Ni,Cu	Diethyldithiocarbamate	pH 6	AAS	$5 \times 10^{-4}\%$	684
Shales	As	Benzene	12 *M* HCl	Inversion voltammetry	$6 \times 10^{-5}\%$	685

Often, for the analysis of metals and their compounds use is also made of extraction of trace elements; some examples of this are given in Table 5.

We shall point to the studies on the analysis of some covalent halides. Rigin[698] has suggested an interesting method of concentrating impurities when analysing germanium tetrachloride. First, one is concerned with a three-phase system. A HCl solution is introduced between the $GeCl_4$ layer and the organic phase, which does not permit the $GeCl_4$ layer to come in contact with the organic phase. The solution of TTA and TBP in methyl isobutyl ketone is used as the extractant. Thus, Cu, Fe, Zn, Sc, and As can be concentrated. Orlova et al.[697] have suggested an extraction AA procedure for the determination of impurities in some metals in titanium tetrachloride. The impurities (V, Mo, Fe) are extracted from the HCl solution of $TiCl_4$ or from the same solution with a TOA solution in toluene in the presence of NH_4I (Cu, Zn). The extract is diluted with acetone (5:1) prior to its atomic absorption determination. This procedure makes it possible to determine $2 \times 10^{-6}\%$ Zn, $5 \times 10^{-6}\%$ Fe and Cu, $1 \times 10^{-5}\%$ Mo, and $2 \times 10^{-5}\%$ V.

Table 4
EXAMPLES OF THE USE OF EXTRACTION FOR THE REMOVAL OF MATRIX IN THE ANALYSIS OF METALS AND INORGANIC COMPOUNDS

Material analyzed	Elements to be extracted	Elements to be concentrated	Extractant	Method of determination	Ref.
High-purity mercury	Hg	22 elements	Dibutylsulfide	ES	686
Ancient silver coins	Ag(Au,Cu)	Na,Mn,Ni,As,Sb, Co,Sn,In	Bismuth diethyldithiocarbamate	NAA	687
High-purity palladium		26 elements	Diamylsulfide	ES	688
Niobium, tantalum	Nb,Ta	12 elements	TBP, cyclohexanone, petroleum sulfides	—	493
Steels	Fe	Nb,Ta,Hf,Zr	Mixture of diethyl ether and chloroform	ES	269
High-purity tin	Sn	Ag,Al,Ba,Be,Bi,Ca, Cd,Co,Cr,Cu,Fe, Ga,Mg,Mn,Ni, Pb,Te,Zn	Di-2-ethylhexyl	ES, NAA	139
Antimony chloride	Sb	Bi,Fe,Cd,Co,Mg, Cu,Ni,Pb,Zr	Dichlordiethyl ether	AAS	689
Yttrium oxide	Y	Ni,Pb,Fe,Co,Cr, Cu,Mn,Al,Ca, Mg,Si	Triisoamylphosphine oxide	ES	690

Table 5
EXAMPLES OF THE USE OF EXTRACTION FOR THE SEPARATION OF DETERMINABLE TRACE ELEMENTS IN THE ANALYSIS OF METALS AND INORGANIC COMPOUNDS

Metal/inorganic compound analyzed	Extractable and determinable trace elements	Extractant	Aqueous phase	Method of determination	Ref.
High-purity platinum	Ag	Triphenylphosphine (benzene)	5 *M* HCl pH 10	AAS	693
Titanium alloys	Pd	Diethyldithiocarbamate (chloroform)	pH 9.5 (Tartrate and EDTA)	PFA	694
Steels and other alloys	Cu	Lead diethyldithiocarbamate (chloroform)	—	AAS	446
Tungsten compounds	Cu,Fe,Ni,Co, Mg,Al,Pb, Mn,Zn	Hydroxyquinoline	Ammonia solution	ES	695
	62	Hexamethylene dithiocarbamate hexamethylene ammonium (butyl acetate)	pH 5.3; H_2O_2	AAS	696
Titanium tetrachloride	V,Mo,Fe,Cu,Zn	Trioctyamine (toluene)	HCl, NH_4I	AAS	697

Titanium tetrachloride and arsenic trichloride were analyzed for impurities using extraction separation and AA determination.[699] When analysing $TiCl_4$, the impurities are separated with isoamyl alcohol at a pH of ~5, and then aspirated into a flame. The detection limits were: V, 0.2%; Fe, 0.03%; and Cu, 0.004%. In the case of $AsCl_3$, some impurities (Se, Te) were determined after separating them from a 7 *M* HCl solution with

MIBK; the remaining elements (Cd, Mg, Cu, Zn) were determined in this raffinate after evaporating it and dissolving the residue in isopropyl alcohol. The extraction systems based on ionic associates and using protonated amines as ion-pair have also been used for the determination of iron[469] in titanium tetraiodide.[468] A detection limit of less than $10^{-4}\%$ has been achieved.

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