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Concentration Methods for the Determination of Trace Elements

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Methods of concentrating trace constituents are discussed, and the quantitative parameters used to describe them are defined. The main methods of concentration (extraction, sorption, coprecipitation, evaporation, etc.) are examined and compared. Rational combinations of methods of concentration and methods of determination of trace elements are recommended, and successful examples of such combinations are quoted. Special aspects of concentration methods applicable to the analysis of high-purity materials and of natural waters are discussed. 114 references.

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I. INTRODUCTION

Preliminary concentration is used when the relative detection limit of an analytical method is higher than the real concentration of the trace elements in the sample. Concentration allows the matrix (or most of it) to be removed, together with a number of interfering micro-components. The concentrate thus obtained contains a higher relative concentration of the micro-elements than the initial sample. Furthermore the larger sample size made possible by the adoption of concentration methods also ensures that larger absolute amounts of the micro-elements are available for analysis. As a result the detection limit can be lowered by a considerable amount, often 100- or 1000-fold. This is the main (but not the only) reason for the widespread adoption of concentration methods.

Preliminary concentration is almost unavoidable if the trace elements are inhomogeneously distributed in the sample. A representative sample in this case must be large, and direct analysis of such a large sample may be difficult, especially when the chosen method of determination requires a small sample (e.g. mass-spectrometric analysis, or emission spectrometry). The preparation of a small concentrate from a solution or a melt of a relatively large sample often provides a representative sample for analysis: for example, assay melting can be used to concentrate gold and other precious metals unevenly distributed in large samples of naturally occurring materials.

Concentration also facilitates calibration, especially when suitable standard samples are not available. It yields concentrates of a single type for the analysis of different types of material: for example, concentrates on carbon powder for spectroscopic analysis. The reference samples are produced as concentrates in the same form, and special standards for each type of material become unnecessary. Concentration with complete removal of the matrix is very desirable in the analysis of toxic, radio-active, or very expensive materials. Furthermore suitable internal standards can be conveniently introduced (if required) during the decomposition and concentration of the sample. Concentration sometimes extends the range of the trace elements which can be determined by a chosen method of analysis.

Because of all these advantages, concentration is an important step in the determination of trace elements. Its importance has not decreased as a result of the development of new, highly sensitive direct analysis methods. On the contrary, its perspectives are continually expanding, especially in combination with new methods of determination.

On the other hand concentration makes the analysis more laborious and complicated. It can lead to a loss of sample, or to contamination from outside. In some cases fewer micro-elements can be analysed than by direct analysis, and special operating procedures are needed (high-purity reagents, specially equipped laboratories, special materials or apparatus). However the advantages of concentration methods far outweigh their disadvantages.

Concentration methods cover a wide range of variants. It is important to distinguish absolute and relative concentration. Absolute concentration transfers the trace elements from a large mass of sample into a smaller mass, as for example when a solvent is evaporated or when the trace elements are extracted into a small volume of organic phase. Relative concentration increases the ratio of the trace element to the main macro-component (in this case the solvent is not treated as a macro-component). Relative concentration is a separation of components present at very different concentrations; its main aim often is to replace an interfering matrix by a suitable collector (usually of smaller mass). In some cases (e.g. in concentration by zone melting methods) the boundary between absolute and relative concentration is blurred, and concentration of both types is assumed to occur.

Both individual and group concentration of the elements can be carried out as required. Concentration involves either removing the matrix or separating the wanted trace components. Removal of the matrix is convenient for the simultaneous determination of several trace elements (for example, by spectroscopic analysis), but only if the matrix has a simple composition. Removal of the matrix is most frequently used in the analysis of high-purity metals. If the matrix consists of several elements combined as a compound (as in geological and biological samples) it is often simpler to separate the trace elements. Sometimes it is not necessary to remove the matrix completely (in this case we use the term "enrichment"). However in most cases it is best to concentrate the wanted element into a different matrix which satisfies the special requirements of the chosen method of determination, which makes calibration easy, etc. Some of these collectors can be used for determining micro-elements by several methods. For example, graphite powder can be analysed spectroscopically or by flameless atomic absorption.

The general problems underlying the pre-concentration of trace elements have been discussed in a number of review articles and monographs[1-8].

The three quantitative parameters used to describe concentration methods—the extent of extraction, the concentration coefficient, and the separation coefficient—are defined as follows: 1) the extent of extraction $R = Q_T/Q_T^0$, where Q_T and Q_T^0 are the quantities of the micro-element in the concentrate and in the sample respectively; 2) the concentration coefficient $K = (Q_T/Q_M)/(Q_T^0/Q_M^0) = Q_T Q_M^0/Q_M Q_T^0$, where Q_M^0 and Q_M are the amounts of matrix before and after the concentration respectively (obviously, for $R = 100\%$ we have $K = Q_M^0/Q_M$); 3) the separation coefficient $S = (Q_M/Q_T)/(Q_M^0/Q_T^0) = Q_M Q_T^0/Q_M^0 Q_T$ (so that $S = 1/K$).

II. CONCENTRATION METHODS

Many different methods are used for analytical concentration. The most rational classification of these methods is in terms of the nature of the separation process used. First of all we distinguish between chemical (or physicochemical) and physical methods of concentration. Among the chemical and physicochemical methods we include extraction and sorption methods, precipitation and coprecipitation, ashing and other methods of decomposing the sample, partial dissolution of the matrix, leaching, and electrochemical methods. The physical group of methods includes evaporation (e.g. distillation, sublimation), directional crystallisation, zone melting, and some other concentration techniques.

Methods can be classified also according to the number and type of phases involved. Among the most important methods of concentration are those based on the distribution of solutes between two immiscible phases, such that one phase becomes a concentrate of the trace element. This classification is expanded in Table 1. However there are also methods based on separation in a single phase (electrodialysis and diffusion methods).

Table 1. Methods of concentrating trace elements based on the distribution of compounds between two phases.

Phases*		Concentration methods
concentrate	matrix	
Liquid	liquid	extraction of trace elements, extraction of the matrix, distribution chromatography
Solid	liquid	sorption of trace elements, coprecipitation of minor constituents, electrolysis and cementation of trace elements
Liquid	solid	sorption of the matrix, precipitation of the matrix, electrolysis of the matrix, leaching of trace elements by solvents, directional freezing and zone melting
Gas	liquid	evaporation of trace elements
Liquid	gas	evaporation of the matrix and wet ashing
Gas	solid	evaporation of trace elements
Solid	gas	sublimation of the matrix, evaporation of the matrix after chemical conversion (dry ashing etc.)

*Phases present during and after concentration are quoted.

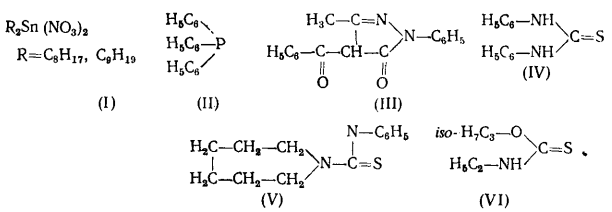
Of course, not all the methods are equally important. The IUPAC Commission for Microchemical Methods and Trace Analysis compared the methods of separation and concentration used in 188 laboratories throughout the world to determine impurities in chemical reagents[9]. The methods most generally used were found to be extraction (79 laboratories), ion exchange (21), precipitation of complexes (18), distillation and sublimation (8), and electrolysis (5). We shall discuss these methods in some detail, in approximately the same order.

1. Extraction Methods

Extraction methods are among the most convenient. They can be used either to transfer trace elements into the extract (individually, or in groups) or to remove the matrix. Important advantages of these methods are their universality, simplicity, and speed. Extraction usually offers very efficient concentration. Extraction methods are reviewed in Ref.8.

Various extraction systems are used for trace elements, though chelating agents are the commonest. Extraction of the trace element is possible only if the matrix does not react with the chosen reagent, as in the analysis of waters, acids, alkali, alkali metal salts, and metal compounds, which exist as anions during the extraction. Common reagents for group concentration include hydroxyquinoline, dithizone, and dithiocarbamates (especially diethyl- and pyrrolidinedithiocarbamate). In order to extract the largest possible number of elements extraction with a given reagent can be carried out at several pH values, or alternatively a mixture of different reagents can be used. For example, a method of determining 18 impurities in very pure alkali metal halides by extraction with a mixture of Cupferron, sodium diethyldithiocarbamate, and trioctylphosphine oxide has been reported[10]. All 18 elements are extracted simultaneously, and the extract is evaporated on graphite powder and analysed spectroscopically. Reagents which do not themselves become extracted by the organic phase under the condition of the metal extraction are chosen. Trioctylphosphine oxide goes into the extract, but it does not interfere with the spectroscopic determination of the elements.

Several new reagents for the concentration of trace elements by extraction have been proposed in recent years. The dinitrates of dinonyl- and dioctyltin (I) have a unique capacity for extracting multiply-charged anions. These reagents quantitatively extract phosphate and arsenate; sulphate, selenite, and selenate are removed less completely but still to an acceptable extent, and singly charged anions are only slightly extracted[11,12]. Organotin extractants are unlike any other previously known reagent: by using these materials methods of concentrating phosphorus, arsenic, and selenium have been developed, and in particular an extraction–photometric method of determining phosphorus and arsenic in vanadium[12].



Triphenylphosphine (II) has been recommended for the selective concentration of traces of gold and silver, followed by atomic-absorption analysis of the gold (in minerals and in cyanide solutions[13]) and of the silver (in ores and minerals[14]). A special feature of this reagent is its affinity for metal ions showing weak acid properties (according to Pearson's classification[15]).

1-Phenyl-3-methyl-4-benzoylpyrazol-5-one (III) can be used[16,17] for the group concentration of several elements. Spectroscopic methods of determining impurities in sodium hydroxide and other materials have been developed by applying this reagent. It can be used also for the selective extraction of certain elements before atomic-absorption[18], photometric, or luminescence analysis. The applications of this reagent are discussed in a recent monograph[16].

Diphenylthiourea (IV) and hexamethylenephenylthiourea (V) have been suggested for the concentration by extraction of chalcophilic metals, especially silver and metals of the platinum group. These reagents can be used to concentrate the precious metals and to separate them from non-ferrous metals. For example, a spectroscopic method of determining all the precious metals (except osmium) in solutions of natural or industrial materials containing large amounts of nickel, cobalt, iron, manganese, and zinc, and smaller amounts of copper, has been developed[19]. The method includes a preliminary concentration of the precious metals by extraction as diphenylthiourea complexes after treating the solution with tin(II) chloride: the limit of detection is 10^{-7}–10^{-5}%. Diphenylthiourea has been used to concentrate traces of silver in ores and in mineral concentrates[20], and also traces of copper, silver, and thallium in chemical reagents[21]. In both cases the elements were determined by atomic absorption spectroscopy.

The most important theoretical problems in the extraction of trace elements from a matrix in aqueous solution are the effect of other components of the matrix (salting-out, masking complex formation, etc.) and the concentration dependence of the distribution coefficient of the trace element. These problems offer some interesting topics for research.

Removal of the matrix is also very important in analytical practice. In this case the capacity of the organic phase must be large, and the extraction must be extremely selective (to ensure that the trace elements remain fully in the water phase). Chelates are not so attractive for this type of extraction, because their solubility in organic solvents is limited: the most suitable extraction forms are ionically associated, co-ordination solvated, and molecular compounds. An interesting and important general problem is the effect of the matrix being extracted on the behaviour of the trace element. In many cases undesirable co-extraction of the trace elements is observed. This problem has been studied for several years in the writer's laboratory[22,23]: rational and theoretically sound methods of suppressing co-extraction of trace elements have been developed.

Many different reagents have been used for extracting the matrix. Among the newer extractants we should mention *O*-isopropyl-*N*-ethylthiocarbamate (VI).[24] The extraction properties of this compound have been studied in detail, and several methods of separating and concentrating elements have been developed as a result. The reagent is a liquid, miscible with organic solvents, and therefore its capacity is large. Silver is extracted particularly well by reagent (VI). The only elements co-extracted with silver from a 1 *M* nitric acid solution are mercury, platinum, palladium, and (partly) gold. All the other elements remain in the water phase. A single-stage extraction by a 2 *M* solution of the reagent in chloroform removes 99.98% of the silver: i.e. the extraction is quantitative. This allows the determination of 23 impurities in high purity silver by a spectroscopic method[25]. With a concentration coefficient $K = 50$ the limits of detection are 2×10^{-6}–5×10^{-6}%. *O*-isopropyl-*N*-methylthiocarbamine is even more useful, because it is more easily available.

Ordinary extraction methods give a concentration coefficient not greater than 50–100. Improvements in this direction can be expected from current work on extraction chromatography[26], gel extraction (see, for example, Ref.27), and three phase extraction systems[28].

The latter method requires some explanation. In some extraction systems the organic phase separates into two layers, one of which (often very small in volume) contains practically the whole of the extracted element. This phase can be separated and used directly for spectroscopic or atomic absorption analysis. Several methods of this type have been proposed (see, for example, Refs.29 and 30).

2. Sorption Methods

Sorption methods of concentration rely on various types of sorption: physisorption, ion exchange, and chemisorption (with complex formation). The ion exchange methods are particularly important.

The use of conventional synthetic resins for ion exchange is complicated by the need to handle large volumes of solution, but nevertheless the method is used in many laboratories. Static, dynamic, and chromatographic variants of ion-exchange separation can be used to concentrate trace elements. Either the trace element or the matrix can be removed. If the trace elements are sorbed, they can be recovered for analysis by desorption or by ashing the sorbent (if a very high purity sorbent is available). Alternatively, concentrates on very pure sorbents can be analysed directly by spectroscopic or other methods. This approach is favoured in Refs.31–33 for the determination of impurities in boric anhydride[31] and other materials. The boric anhydride is dissolved in a mixture of glycerol and water, and the resulting glycerol complex of boric acid is not sorbed by the resin. The Cu, Ni, Cr, and other impurities are adsorbed on a cation-exchange resin in a micro-column, then the resin is transferred to a Teflon mortar, ground with sodium chloride, and treated with a drop of concentrated sulphuric acid. The decomposed resin is taken up in alcohol and analysed spectroscopically.

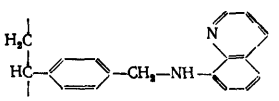
Rare-earth element impurities in metallic uranium have been determined by a two-stage ion-exchange concentration method[34]. The impurities were first sorbed (and thus separated from the main bulk of the uranium) from a sulphate solution on a column containing a cation exchanger. The rare earth elements were then eluted with a solution of hydrochloric acid. In the second concentration stage the uranium residues were sorbed as the chloro complex on an anion exchanger, while the rare earth elements were not sorbed. Impurities of gadolinium, europium, and samarium, can be determined in this way (using a luminescence method of end-analysis) at concentrations as low as 2×10^{-6}%.

Complex formation in ion-exchange concentration is used also to prevent unwanted elements from being sorbed, and to convert the wanted elements into an easily sorbed form. In addition to the normal inorganic ligands, many organic chelating reagents are found useful in this work. For example, traces of Cu, Zn, and Cd have been concentrated[35] on an ordinary anion exchanger by first converting them into 2(3′-sulphobenzoyl)-pyridine-2-pyridylhydrazone complexes. A concentration coefficient as high as 300 was obtained in this way.

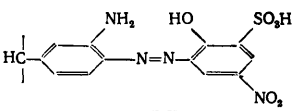
Under certain conditions trace-element complexes are readily sorbed by active carbon. This sorbent is known to behave as an anion exchanger in aqueous solutions: for example, it can selectively absorb anionic complexes of the precious metals. On the other hand oxidised carbon (i.e. carbon treated, for example, with nitric acid) acquires the properties of a cation exchanger and readily sorbs multiply-charged cations. The sorption properties of oxidised carbon towards Ag^+ have been studied in detail[36,37], and it was found that columns packed with oxidised carbon can be used to concentrate alkaline-earth metal impurities from solutions of alkali metal or ammonium salts. Active carbon can concentrate also metal chelates such as diethyldithiocarbamates. This property is used for concentrating traces of chalcophilic metals.

Synthetic chelating resins offer some very attractive possibilities. The existence of a very large number of organic analytical reagents, and the extensive information available on their interaction with various elements, can be used to synthesise resins incorporating special groups of different types,

for both selective and group reactions. Some examples of chelating resins are shown below: the sorbent (VII) takes up palladium and platinum, the sorbent (VIII), copper[38-40].



(VII)

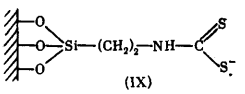


(VIII)

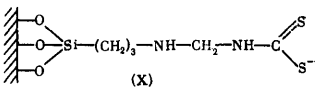
Resins of the Kelex-100,[41] XAD,[42] and other types have been studied and are now being used.

Many inorganic sorbents such as hydroxides, sulphides, and phosphates are being intensively studied. For example, copper and gold can be fully concentrated on copper sulphide from a 6 *M* solution of hydrochloric acid. However very pure inorganic sorbents are needed for the concentration of trace elements, and these materials are not readily available in a very pure form.

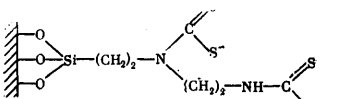
Sorbents containing grafted organic functional groups can be treated as a "hybrid" between inorganic sorbents and synthetic chelating resins. Leiden[42-45] has developed methods of concentrating ions on silica gel or on very small glass spheres with complex-forming groups of types (IX)–(XII) immobilised on their surface.



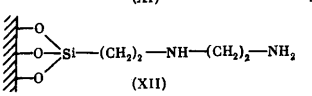
(IX)



(X)



(XI)



(XII)

The diethyldithiocarbamate group in reagents (IX)–(XI) assists the sorption of cations, the diamine group in (XII) the sorption of anions. Trace elements are sorbed fairly quantitatively even in the static variant. When traces have to be separated from a large volume of sample the column variant is used, and in this case the glass micro-spheres are better than silica gel. After sorption the glass of silica gel particles are mixed with an equal volume of powdered cellulose and pressed into a pellet which is analysed by X-ray fluorescence. Elements can be extracted from very dilute solutions: for example, selenium from 2 litre of water at a concentration of 2 ng ml^{-1}.

3. Coprecipitation and Precipitation Methods

The coprecipitation of the trace elements with a collector and the precipitation of the matrix are among the most important methods of pre-concentration of impurities. Trace elements are usually coprecipitated on amorphous precipitates of large surface area (hydroxides, sulphides, etc.). Coprecipitation on these carriers can be treated as a heterogeneous ion-exchange or chemical reaction leading to the formation of a solid solution or of chemical compounds between the trace component and the collector.

The choice of collector is dictated by various factors. It must be pure, and able to carry the wanted trace element on a small mass of the collector. A special requirement for spectroscopic end-determinations is that the emission spectrum must be as simple as possible: thus Al and Zn hydroxides are preferable to Fe and Mn hydroxides. A compound of a metal which can subsequently be removed by evaporation or other simple means makes a very convenient collector. For example, a mercury sulphide collector used for the coprecipitation of trace elements was removed as the bromide[46]. Some trace components are easily reduced to the elemental state and coprecipitated, for example, with elemental tellurium or mercury.

The collector does not necessarily have to be added to the solution: it can be part of the matrix. This type of concentration method was studied by Chuiko[47,48], Jackwerth[49], and others. The method is specially convenient with hydroxides. In the deposition of other precipitates the charge on the trace elements has to be "controlled", for example by converting them into complex anions. This is because when part of the matrix is precipitated as an insoluble crystalline compound the surface of the precipitate is usually positively charged. On the other hand nydroxides tend to sorb hydroxyl ions, and are not included in this rule.

Some very interesting organic coprecipitants were introduced into analytical practice in the 1950's, mainly by Kuznetsov and Myasoedova[50-52]. Organic collectors are easily eliminated, they are available in a variety of forms, and they minimise the uncontrolled coprecipitation of unwanted trace elements and of the matrix. In contrast to extraction methods, these organic reagents are needed in small amounts only. In the case of atomic-absorption or photometric end-determination the collector can be dissolved in a suitable organic solvent instead of being ashed: the solution thus obtained can be used directly for analysis. Hydroxyquinoline, Cupferron, and other reagents have been used as coprecipitants; they can be used in conjunction with indifferent coprecipitants of the naphthalene type. Many examples of concentration by using organic coprecipitants are quoted in Kuznetsov and Akimova's monograph[52]. Among the more recent work we should note that concentration of a large number of elements on germanium and aluminium salicylfluoronates[53], and the concentration of gold and palladium with dithizone before flameless atomic-absorption determination[54].

Deposition of the matrix leaving the trace elements in solution requires large amounts of reagents, usually involves a relatively large "blank" correction, and can be laborious. The large mass of precipitate can cause loss of the trace elements by coprecipitation. However in special cases many of these difficulties can be avoided, and many methods of concentration by precipitation of the matrix have been proposed. For example, in the analysis of high-purity lead the best method of concentrating impurities is to precipitate the lead as its nitrate from concentrated nitric acid solution[55]. Various methods of this type were developed by Karabash and coworkers[56], such as precipitation of bismuth iodide in the spectroscopic analysis of impurities in bismuth.

4. Evaporation Methods

Several variants of the evaporation method are used: simple thermal evaporation of the trace elements, evaporation after conversion of the trace elements into volatile compounds, and sublimation or distillation of the matrix either directly or after chemical reactions to convert it into volatile compounds.

Simple thermal evaporation is relatively free from contamination, but when reagents are used to produce volatile compounds the contamination problem increases, especially in the case of volatilisation of the matrix. Loss of the wanted elements is always possible, and can be serious when the matrix is evaporated. Usually only one element (or a small number of elements) is concentrated in the impurity evaporation variant. Evaporation of the matrix produces group concentration of the trace elements in the residue (either with or without a collector).

The evaporation of traces from a solid matrix requires the sample to be very finely divided, and this is a serious drawback of the method. Furthermore only small samples can be handled (50–100 mg). For many impurities vacuum distillation is effective, but it makes the method more complex. Evaporation of the trace elements in a stream of carrier gas has also been used. In the analysis of high-purity silicon dioxide the trace elements have been distilled in a stream of hydrogen chloride (an example of the removal of impurities at relatively low temperatures[57]). In that experiment the following impurities were distilled off and determined spectrometrically: Fe, Ni, Co, Al, Ti, Sn, Mn, In, Ga, and Be. The elements were condensed on a pure graphite tube which was cooled with water. Meyer and coworkers[58] developed a very sensitive method of determining selenium in high-purity copper by gas chromatography after evaporating the impurity in a stream of oxygen. The condensate (selenium dioxide) was converted into 5-nitropiaselenole [by reaction with 4-nitro-o-phenylene diamine, (Ed of Translation)], which was extracted with toluene and determined gas-chromatographically. The evaporation method is often used to evolve mercury vapour, especially before atomic-absorption analysis (see, for example, Refs.59 and 60).

Evaporation of the matrix is used when the matrix is much more volatile than the impurity elements being analysed. Under atmospheric pressure simple evaporation of the matrix can be difficult: the rate of evaporation increases with temperature, but temperatures in excess of 800 °C are not recommended because of the danger of losing the trace elements and of oxidising the matrix elements. However the evaporation of a large sample at low temperature is very time-consuming. The only matrices which are easily removed by evaporation are iodine, arsenic, antimony, and zinc. Both vacuum evaporation and evaporation in a stream of inert gas have been used, but the commonest variant is evaporation after chemical reactions to convert the matrix into a more volatile form. A simple and widely used method is dry ashing, i.e. combustion in air or in a stream of oxygen (in the case of organic materials and carbons). Ashing is often used as the final stage of a concentration procedure involving a different method. Ashing of the matrix is possible either in the presence or in the absence of a collector. The collector (e.g. graphite powder) helps to minimise the loss of trace constituents. Sulphur, arsenic, selenium, and osmium can also be removed by combustion. In addition to oxygen, the following can be used as chemical agents: hydrogen fluoride, hydrogen chloride, chlorine, and carbon monoxide. These produce volatile fluorides, chlorides, and carbonyls respectively. The carbonyls (e.g. nickel carbonyl) are formed under difficult conditions, and both carbon monoxide and the carbonyls are highly toxic.

Removal of the matrix from the liquid into the gas phase is widely used in practice. The commonest application of this method is the evaporation of a large liquid sample for analysis, with or without a collector: for example in the analysis of water, acids, liquid organic compounds, and a series of liquid inorganic compounds such as tin or silicon tetrachlorides. A similar method is the wet ashing of organic compounds, which requires large amounts of reagents and therefore suffers from contamination problems, but usually results in losses of trace elements lower than those produced by dry ashing.

5. Electrochemical Methods

Electrochemical methods are used occasionally (electrolysis on a solid electrode (metal or carbon), or on a mercury electrode, cementation, etc.). One of the most practical variants of this method is the electrolytic deposition of the trace elements on graphite disks or rods, which are used directly for spectroscopic or flameless atomic-absorption determination. Some workers[61–64] have deposited the trace elements either on carbon disks 4 mm in diameter and 1 mm thick, attached to a special holder, or on the end-face of a carbon rod (Fig.1). Deposition occurs at the cathode, and a platinum wire is used as the anode. The separated trace elements were then determined spectroscopically, using the carbon rod as the arc electrode. This method has been used in the analysis of compounds of the alkali metals, aluminium, organic acids, etc., in which Bi, In, Cd, Co, Cu, Ni, Pb, Zn, and Mn were determined. In another series of experiments[65–67] a similar method of concentration was used to determine trace elements by flameless atomic absorption spectroscopy. The trace elements were deposited on a platinum or tungsten wire, or on a graphite electrode.

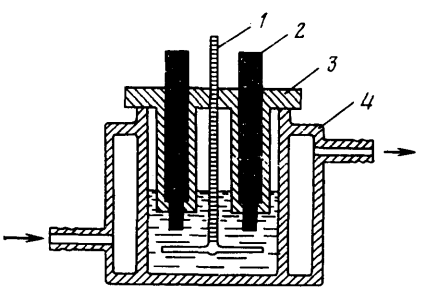


Figure 1. Electrolytic cell for depositing impurities on carbon rods: *1*) platinum anode, *2*) graphite cathodes, *3*) Teflon holder, *4*) quartz cell. Water circulation indicated by arrows.

The electro-osmosis method[68,69] is useful for concentrating ions from very dilute solutions, or from solutions of non-electrolytes. When membranes of aluminium oxide and polytetrafluoroethylene are used the concentration coefficient can be as high as 10^3–10^4, and the extent of extraction of the trace components is 85–99%. A special group of electrochemical concentration methods has been used as the basis of the inverse voltammetry method[70]. We shall refer to some of these methods below.

6. Crystallisation Methods

The reagentless concentration methods include the crystallisation methods (directional freezing and zone melting[71]).

The advantages of these methods are their universal application to all trace elements (i.e. they are group methods), the ease of automation, and the freedom from contamination (if the process is carried out in a closed apparatus at not too high temperature). Most of the sample can be recovered and re-used if necessary. However the methods have also some shortcomings: they are time-consuming, and the segregation coefficient tends to decrease at very low concentrations of the element being analysed, especially if this element is isomorphous with the main component.

The directional freezing method consists in melting the ingot completely and allowing it to crystallise from one end: as the crystallisation proceeds the impurities concentrate in the last part of the ingot to freeze. Directional freezing is much easier to carry out than zone melting. It can be applied to water–salt eutectics and crystal hydrates as well as to high-temperature melts. Various methods of concentrating impurities in metal halides have been developed at the All-Union Single Crystals Institute in Khar'kov (see, for example, Ref.72). Vertical directional freezing is used, and the melt is stirred by the strong convection currents.

7. Partial Dissolution of the Matrix

An unusual concentration method developed by Jackwerth[73] relies on dissolving part of the matrix under conditions such that the impurities do not go into solution but remain in the residue of the matrix. This is done by amalgamating the surface of metallic sample being dissolved. For example, in order to concentrate the impurities in high-purity zinc the sample (up to 100 g) is coated with 1–5% of the mercury. The zinc is then dissolved in hydrochloric acid until only a small residue is left, containing the Bi, Cd, Co, Pb, Ni, In, Tl, Sn, Ag, Au, and Pd in a concentrated form. Similar methods have been developed for the analysis of cadmium, lead (after assay melting), gallium, and aluminium (Table 2). In the case of aluminium[74] the extent of extraction of the impurities was >95%, and the concentration coefficient was ~10^3.

Table 2. Methods of concentrating trace elements in high-purity metals by partial dissolution of the matrix.

Matrix	Trace elements to be concentrated	Method of determination	Reference
Zinc	Ag, Au, Bi, Cd, Co, In, Ni, Pb, Pd, Sn, Tl	various	73
Aluminium	Bi, Cd, Ga, In, Pb, Tl, Zn	atomic absorption	74
Lead*	Precious metals	atomic absorption	75
Gallium	Ag, Au, Bi, Cu, Fe, Hg, Ni, Pb, Pd, Sn, Zn	atomic absorption	76
Mercury	Au, Pd	photometric	77
Cadmium	Ag, Au, Bi, Cu, Ni, Pb, Pd	atomic absorption	78

*After assay melting.

8. Assay Melting

Assay melting is a special form of pre-concentration. It combines, in a single operation, decomposition of the sample and concentration of the precious metals (for example, in molten lead). The result is a separation of the precious metals from their accompanying elements, which enables a large (and therefore representative) sample to be used in the analysis of ores and products of ore treatment. Concentration coefficients of 10^2–10^3 can be obtained. Assay melting is a convenient method of separation and concentration when combined with one of the modern, high-sensitivity methods of determination such as spectroscopic or activation analysis. Assay melting is valuable for the analysis of samples containing 10^{-7}–10^{-4}% of the precious metals. The method of concentrating the wanted elements into molten lead gives good results in the determination of gold, silver, platinum, and palladium. Metallic tin, and nickel sulphide, have been used as an alternative to lead. Conditions for concentrating iridium and rhodium have been found. The theory of assay melting continues to be poorly developed, though this is the oldest method of concentration (not counting evaporation).

9. Other Methods

Other methods have been used for the pre-concentration of trace elements. One of these is flotation, which can be used either to extract the matrix or to extract the trace components. The matrix can be floated after being precipitated, as an alternative to filtration. Examples of the separation of trace components by flotation include the extraction of silver[79], vanadium[80], and a group of nine elements[81] from seawater. Ultrafiltration, lyophilic drying, thermo-diffusion, and other methods have also been used.

As stated above, several concentration methods are often used in series, sometimes in unorthodox combinations. In the analysis of organic and biological materials the concentration of trace elements by any method is usually preceded by ashing. There are many examples of the combined use of extraction and sorption, precipitation and flotation, extraction and ashing, etc. Andrianov and Poladyan[82] concentrated traces of germanium by combining coprecipitation on iron(III) hydroxide with extraction of the iron by solutions of fatty acids in light petroleum. The germanium was co-extracted with the iron from the hydroxide precipitate.

A combined method of concentrating precious metals for their determination in natural and industrial materials has been developed[83]. After decomposition of the sample the traces of precious metals are coprecipitated from solution on copper sulphide in the presence of 2-mercapto-benzotriazole. In a second concentration stage the wanted elements are separated from the copper by sorption on a chelating sorbent. After concentration the precious metals are determined by spectral, atomic-absorption, or neutron activation methods.

10. Comparison of Methods

It is difficult to arrange the methods of concentrating trace components in order of merit. No comparison is significant without reference to the type of sample and to the method of analysis of the concentrate. However if allowance is made for these factors the order of merit can change radically. Yudelevich[84] compared matrix extraction, distillation, ion exchange, and directional freezing as methods of concentrating trace elements in the analysis of high-purity antimony with spectroscopic end-determination. From the sum of the indicators he concluded that matrix extraction is the best method of concentration.

The concentration coefficient is one of the main characteristics of concentration methods. The writer has tried to compare methods on the basis of this indicator (Fig.2). However it is important to note that this is only one of the relevant indicators: the other coefficients can be equally important on occasions.

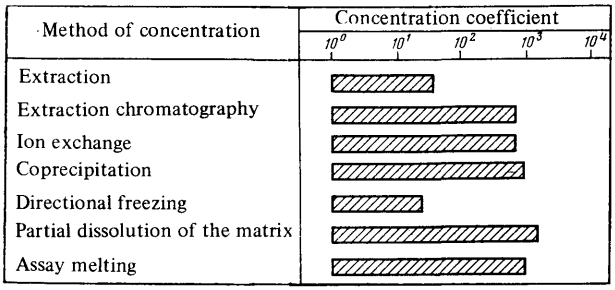


Figure 2. Concentration coefficients achieved by using various methods of pre-concentration.

III. COMBINED CONCENTRATION AND DETERMINATION METHODS

We shall now discuss rational ways of combining concentration methods and methods of end-determination, Evidently, non-specific (multi-element) determination methods should be used in conjunction with group concentration methods. The collector (i.e. the matrix of the concentrate) should be chosen so as to satisfy the requirements of the method of determination as far as possible: thus graphite powder is best for spectroscopic analysis, an organic extract for flame atomic-absorption spectroscopy, etc. It is useless to combine a high-precision method of determination with a method of concentration lacking adequate reproducibility, or *vice-versa*.

We can distinguish two groups of analytical procedures resulting from the combination of a concentration method and a determination method. In the first group the concentration and determination are not specially related: more or less independent methods of concentration and of determination are applied sequentially. The determination is not significantly affected by the properties of the concentrate. In these cases the method chosen for the concentration is immaterial from the standpoint of the determination: ion exchange, extraction (with or without re-extraction), or other methods are all equally suitable. The concentrate to be used in the determination can be, for example, an aqueous solution bearing little similarity to the original sample. Such a solution can be analysed by a variety of methods. Clearly, combinations of concentration and analysis methods of this type do not need to be specially discussed, though they have been used for a very long time and their applications are very widespread.

However on occasions the properties of the concentrate do have a substantial effect on the subsequent determination. In these cases we have to consider the special features of the combination, which can no longer be treated simply as the application of two methods in succession: a new qualitative aspect has appeared. For example, whereas with flame atomic-absorption analysis of aqueous solutions the method of extracting the trace elements is unimportant, substantial effects are observed in the atomic-absorption analysis of organic extracts. These effects arise from the difference in viscosity between organic solvents and water, and of course from the fact that the former are combustible. These differences can substantially affect the mechanism of processes in the flame. The effects are so marked that the methods are often placed in a class of their own. The situation is very similar in the combined extraction and photometric determination procedure when the organic phase is used directly for the determination. There have been recent attempts at combining extraction with direct polarographic analysis of the extract. Evidently the polarography of these organic solutions differs very substantially from the polarography of aqueous solutions.

The very close link between separation and determination methods is evident also from a different standpoint. Combinations of separation and determination methods in a single apparatus have been described (e.g. in gas chromatographs). Comparable unification is achieved in modern high-pressure liquid chromatographs. The need to separate the methods within a particular group is demonstrated most clearly by the gas chromatographic approach. Combined procedures of the second group can be termed hybrid methods.

We shall now discuss some specific examples of the combination of a pre-concentration method with some of the most important methods of determination.

Concentration is very important when *spectral analysis* is used: it has been applied for the past 25 years since the work of Semples, Pohl, and others[85,89]. Concentration is resorted to when direct analysis cannot reach the required limit of detection, and also for other reasons mentioned above. It is desirable to remove the matrix fully when its presence interferes with the determination of the trace elements because of overlapping spectral lines or if the excitation potential of the main element is unfavourable. All the samples should be converted into the same physicochemical form, so that a single series of reference standards can be used. The greater concentration of the trace elements in the concentrate (as compared with the original sample) avoids the need to use unreliable reference standards with extremely low concentrations of the wanted elements. Concentration also minimises the fluctuations of the spectroscopic results produced by uneven distribution of the trace elements in the sample[2]. All these reasons account for the very wide use currently made of these particular combinations. (In the USSR these combinations are termed chemico-spectral methods).

Group concentration of all the wanted trace elements is very desirable in these methods. In some cases complete removal of the matrix is unnecessary, and enrichment is sufficient. However the concentrate must always be in a form suitable for direct excitation of the spectrum of the trace elements: these elements must be concentrated on a small mass of the collector or on a small-area electrode.

Spectral analysis places a number of special requirements on the collector (i.e.on the matrix of the concentrate). It must be stable when stored, non-hygroscopic, and its constituent elements must have a simple emission spectrum. The collector material must be easily prepared in a reproducible form by a small number of simple operations. It should also be relatively involatile to ensure uniform access of the trace elements to the electric discharge during the spectral analysis. All these requirements are met by carbon (graphite) powder, often used in a mixture with sodium chloride. Very many specific methods of chemico-spectral analysis based on the use of this collector have been developed. Examples are given in Table 3.

One of the methods listed in Table 3 deserves special mention[90]. The aim was to determine small impurities (10^{-6}–10^{-4}%) of antimony, tin, lead, bismuth, zinc, cadmium, and copper in alloy steels. The above elements were extracted by methyl isobutyl ketone from a solution of 1 *M* ammonium iodide and 2.3 *M* sulphuric acid, and they were then re-extracted by 15% hydrogen peroxide into a 2.5 *M* solution of sulphuric acid. The re-extract was evaporated to dryness

with 10 mg of graphite powder, and the final concentrate was baked at 350–400 °C. The spectral determination was carried out by a fractional distillation method, using potassium iodide as a carrier. The limits of detection on a medium-dispersion spectrograph were 10^{-6}–10^{-4}%, the relative standard deviation 0.09–0.36. By using a high-dispersion spectrograph the limit of detection could be lowered to 10^{-7}–10^{-5}%.

Table 3. Examples of spectroscopic determinations with pre-concentration of the trace elements*.

Sample	Method of concentration	Elements to be concentrated	Limit of detection, %	Refs.
High-purity silver	matrix extraction	Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Ga, Fe, In, Mg, Mn, Ni, Pb, Sn, Te, Tl, V, Zn, Zr	10^{-7}–$2\cdot10^{-6}$	25
Alloy steels	trace element extraction	Bi, Cd, Cu, Pb, Sb, Sn, Zn	10^{-6}–10^{-4}	90
Aqueous solutions	trace element extraction	Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V	—	17
Sodium iodide	trace element extraction	Ag, Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Ti, Zn	10^{-7}–10^{-5}	10
Solutions from dedompn. of ores and concentrates	trace element extraction	Ag, Au, Ir, Pb, Pt, Rh, Ru	10^{-6}–10^{-4}	19
Ditto	sorption on CuS and chelating resin	Ag, Au, Ir, Pd, Pt, Rh, Ru	10^{-7}–10^{-5}	83
Aluminium, gallium gallium arsenide, indium phosphide	coprecipitation on Bi_2S_3, $Bi(OH)_3$, In_2S_3	Ag, Au, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Zn	10^{-7}–10^{-5}	91
Ores and minerals	trace element extraction	Au, Ag	$5\cdot10^{-8}$–$5\cdot10^{-5}$	92

*Powdered graphite used as collector in all cases.

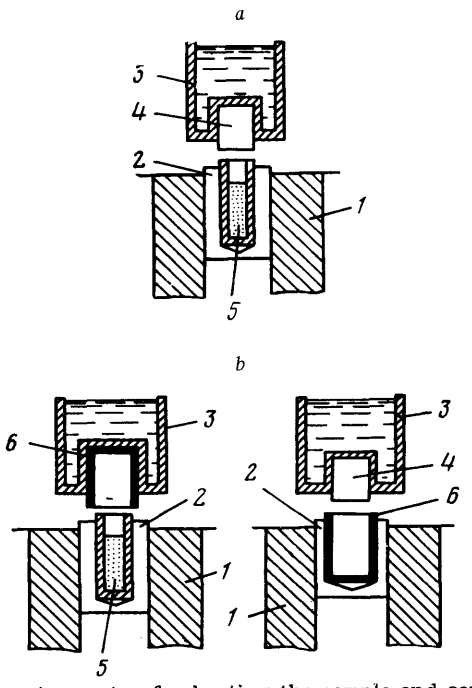


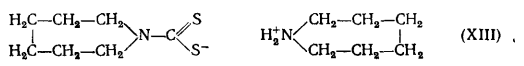
Figure 3. Apparatus for heating the sample and condensing the elements in the one-stage (*a*) and two-stage (*b*) method of evaporation: *1*) graphite flanges of water-cooled copper electrodes, *2*) graphite crucible, *3*) water-cooled holder for condensate receivers, 4) condensate capsule, 5) graphite beaker containing powdered sample, *6*) first condensate receiver.

A specific concentration procedure for spectral analysis is the evaporation method, a classical example of which is the fractional distillation method[93]. The evaporation method was proposed[94,95] for the analysis of pure materials used in the atomic energy industry. Two variants were described: evaporation in air and in a vacuum. An infusible powdered sample (usually oxides) is placed in a graphite cup (Fig.3) and heated by passing a heavy current through a graphite heater pressed between the graphite flanges of two water-cooled copper electrodes. The vapours of the evaporating trace elements are condensed on a cooled graphite or copper capsule which is then used as a spectrographic electrode. With samples of intermediate volatility (for example, silicon) a two-stage distillation of the trace elements can be carried out: the first stage uses a cooled graphite cup as the collector, and in the second stage the trace elements are distilled from this cup to the capsule electrode. This procedure offers a more complete separation of the matrix. Some workers have converted volatile matrices (for example, molybdenum or chromium oxide) into involatile carbides before this procedure.

The combination of pre-concentration and *atomic absorption spectrometry* is most often exploited in the extraction–flame atomic absorption variant, with direct atomisation of the extract into the flame. The main advantages of this method (as compared with the determination of elements in aqueous solution by atomic absorption) are a lower limit of detection and a faster and simpler analysis. The method avoids evaporation of the extracts, re-extraction, and other operations which result in higher blank corrections when widely occurring elements are being determined. In some procedures, using a highly combustible organic solvent, even the fuel gas can be dispensed with. Concentration is used also in conjunction with flameless atomic-absorption spectroscopy.

The high selectivity of the atomic-absorption determination allows the group concentration of the trace elements (for example, into an extract). Therefore group extraction is used as an alternative to individual extraction. The extraction of chelates is widely used for this purpose (i.e. complexes with hydroxyquinoline, β-diketones, xanthogenates, and especially dithiocarbamates). Chloroform and carbon tetrachloride, like benzene, are now rarely used as solvents because of their toxicity. Suitable solvents for flame atomic-absorption spectroscopy are methyl isobutyl ketone (MIBK) and butyl acetate. The ammonium pyrrolidinedithiocarbamate (PDTC)–methyl isobutyl ketone system is widely used for the group separation of trace elements, and many methods of analysis of waters, biological samples, and other materials have been based on this system. For example, Anders and Hailer[96] describe a method of direct extraction of cadmium and lead from wine which does not extract the sugars and acids of the wine.

Some workers[97,98] have successfully used hexamethylammonium hexamethylenedithiocarbamate (XIII) instead of PDTC:



(XIII)

This reagent is prepared from hexamethyleneimine, which is obtained as a side-product in the manufacture of Nylon and is therefore readily available. Several methods using this reagent have been developed, including the determination of Co, Cu, Fe, Mn, Ni, Pb, and Zn in sea-water[98].

Automatic apparatus for concentration by extraction has become available commercially: in particular, the model marketed by the firm "Technicon" has a throughput of 60 samples per hour[99]. Another variant of concentration by

extraction, developed for use in conjunction with a six-channel atomic fluorescence spectrophotometer, can handle 25 samples per hour[100]. Another useful method for determining traces of various elements and for analysing concentrates has been termed the "injection" method[101].

Typical atomic-absorption methods of determining trace elements in various materials are listed in Table 4. The special features of the combination of extraction and atomic absorption are discussed in detail in the recent monograph[58,105] and review literature[106].

Table 4. Examples of atomic-absorption determination with pre-concentration of trace elements by extraction.

Elements to be determined	Sample	Main extraction reagent	Detection limit, %	Refs.
Ag	minerals, ores, concentrates	diphenylthiourea	10^{-6}	20
Ag, Cu, Tl	metal halides	diphenylthiourea	10^{-7}—10^{-5}	21
Ag	ores and minerals	triphenylphosphine	10^{-6}	15
Au	minerals, cyanide solutions	triphenylphosphine	10^{-4} (2×10^{-3} $\mu g\ ml^{-1}$)	14
Cu, Fe, Mo, V, Zn	titanium tetrachloride	trioctylamine	$2 \cdot 10^{-6}$—$2 \cdot 10^{-5}$	102
Bi, Cu, Fe, Pb, Sb, Sn, Zn	alloy steels	trioctylamine	10^{-5}—10^{-4}	103
Fe	sodium and potassium halides	dithizone, sodium tetraphenylborate	—	104

In *X-ray fluorescence analysis* group concentration is used more often than individual concentration. In this case the concentrate should be a solid, which can be analysed directly. If the concentrate is liquid several additional operations are required: for example, after extraction the organic phase is often decomposed and the trace elements are sorbed on cellulose powder or on silica gel with grafted functional groups. Whenever possible the extraction is carried out with low-melting extractants at high temperature: the concentrate can then be simply pelleted and analysed. In some methods[43-45] of water analysis the trace elements are sorbed on silica gel microspheres with grafted chelating groups.

A widely used combination is concentration (usually by extraction) followed by *spectrophotometric determination* in the visible and u.v. regions of the spectrum. Individual concentration is often employed, or several elements are extracted sequentially. The matrix is very seldom removed in these methods. Usually the same reagent which gives a coloured complex is used also for concentrating the trace element. However two different reagents are used on occasions: a selective reagent is used first, to extract the trace element, and then a reagent not necessarily selective but having the most favourable photometric properties is added to the extract. This latter variant usually implies re-extraction, or decomposition of the extract. We should mention a method of concentrating copper, zinc, cadmium, mercury, manganese, and nickel as their 1-(2-pyridylazo)-2-naphthol (PAN) complexes: concentration occurs on an optically transparent membrane consisting of poly(vinyl chloride), tricresyl phosphate, and PAN.[107] The membrane is immersed into the solution for analysis, it is washed and dried, and its optical absorption is measured with a photometer.

Pre-concentration methods have been used also in combination with *spark source mass spectrometry*[108,109]. After being separated from the matrix (by extraction) the trace elements are deposited on a collector (usually high-purity alumina). In a determination[108] of eight trace elements in steel the impurities were extracted from an iodide solution into methyl isobutyl ketone, and they were then re-extracted by a dilute solution of sulphuric acid in the presence of hydrogen peroxide and evaporated on alumina. The concentrate was baked and analysed with a double-focussing mass spectrometer. A similar method was developed to determine impurities in sulphuric acid. A different, more specialised variant was proposed[109] for the determination of traces of the precious metals in both natural and technical materials. The precious metals are extracted from a solution in hydrochloride acid containing copper and other non-ferrous metals in the form of their hexamethylenephenylthiourea complexes. Copper(I) is co-extracted by this reagent. The extract is evaporated and baked to give a concentrate on copper oxide suitable for direct analysis in the mass spectrometer, since copper does not interfere with this determination.

Spark source mass spectrometry can be used to determine small quantities of at least 60—70 elements, and therefore it is most conveniently combined with concentration methods relying on removal of the matrix.

Concentration is used also in *activation analysis*. There are two basically different methods of concentrating trace elements in this method: concentration before irradiation and concentration after irradiation. Removal of the matrix before irradiation is essential when strong activation of the matrix would otherwise occur with production of long-lived radioisotopes. The concentration procedure can be used also to remove trace components liable to be strongly activated which are not being determined. However concentration before irradiation invalidates the main advantage of activation analysis: the absence of a blank correction. On the other hand this advantage is retained when concentration is carried out after irradiation. Both methods are used in analytical practice, though the second is by far the more common.

Two main types of pre-concentration method can be identified also in *electrochemical methods* of analysis. The first is inverse voltammetry. The trace elements are pre-concentrated electrochemically on a solid or a mercury electrode, and they are then determined by anodic dissolution. Cations produce a metallic deposit on the electrode: this deposit is conveniently handled by using a vitreous carbon electrode, which is chemically stable and mechanically strong. The concentration method used in the determination of anions consists in forming a film of an insoluble compound on a metallic (e.g. silver) electrode by the reaction between the electrode material and the anion being determined.

The alternative approach is polarography of extracts containing the trace elements. A background electrolyte and a homogenising solvent (for example, methanol) are added to the extract before polarographic analysis. This combination makes the analysis faster by avoiding the need for decomposition of the extract or for re-extraction. Furthermore it combines the selectivity of the polarographic method with that of concentration by extraction. For example, a method of determining indium doping impurities in the compound semiconductor $CdSiAs_2$ has been described[110]: the indium is extracted by chloroform at pH 1.2 as its chelate with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one, and the cadmium and arsenic do not interfere with the extraction of indium. A solution of ammonium bromide in methanol is used as background electrolyte. Several developments of this type have been reported[111,112]. The first review of extraction-polarographic methods was published in 1939,[113] and it was followed by several other reviews.

An interesting "double" concentration is described by Karbainov[114]: concentration by extraction is followed by electrochemical concentration on an electrode. Both the approaches mentioned above are used in this variant.

IV. CONCENTRATION METHODS IN THE ANALYSIS OF SPECIFIC SUBSTANCES

It is interesting to examine the special features of concentration methods in the analysis of some important materials. In most cases concentration is applied in the analysis of high-purity materials, natural waters, and geological samples.

In the analysis of high-purity materials the purity of the air, of the glassware, of the apparatus, and of the reagents is of the utmost importance. Methods of concentration which do not require the use of reagents are often preferred (thermal evaporation of the matrix, crystallisation methods, etc). When choosing a concentration method it is important to know the previous history of the pure sample: if possible the concentration method should be different from the purification method used in the preparation of the sample.

The blank problem has a special significance in the analysis of pure materials. Usually the blank experiment includes all the reagents used in the concentration experiment, in the same amounts and under the same conditions, but without the sample for analysis. The amount of the wanted element determined in the blank experiment is a correction which is subtracted from the analysis result. Blank experiments of this type are often carried out, but they are not entirely correct: the degree of contamination by (or of loss of) the trace element in the presence of the main constituent of the sample may not be the same as in the blank experiment. Furthermore the residue of the matrix in the real concentrate may produce conditions for the determination of the trace element different from those which apply to the concentrate of the blank experiment, which is free from these residues. Several ways of overcoming these inconsistencies have been proposed, but space does not allow us to discuss them here. We will only stress the importance of using a method capable of handling different weights of the sample for analysis.

There are interesting reports[6,7] of the avoidance or minimisation of errors introduced by concentration methods. One of the recommended procedures involves very close integration (in both time and space) of the decomposition, concentration, and detection stages, preferably within a single enclosure. The adoption of micro- and ultra-micro methods is also recommended.

Natural waters are another important type of material whose analysis involves concentration methods. Without going into this problem in depth, we shall only stress the importance of the state of the trace elements in the water, which is often ignored. Often the trace elements are present as soluble complexes with naturally occurring or industrial organic substances, or alternatively they can be present as colloids.

Some methods allow direct concentration of the trace elements without previous treatment of the water: for example, Cu, Co, Zn, Mn, Cd, and In can be extracted as their complexes with hexamethyleneammonium hexamethylenedithiocarbamate without any preliminary operation. However in most cases a preliminary decomposition of the complexes is required, and the water is therefore treated with an oxidising agent (e.g. persulphate).

The complex formation problem is even more important in the analysis of surface fresh waters. The complexes formed by metal ions with humic and fulvic acid and with other organic compounds present in natural waters can strongly influence the extent of concentration of the trace elements achieved by extraction, sorption, and coprecipitation methods. Full concentration is usually possible only after decomposition of these organic materials.

In conclusion we note that this review has dealt with only a small part of the problem of the analytical concentration of trace elements. No mention was made, for example, of the validity and the reproducibility of the analysis, or of the effect of the concentration procedure on these characteristics, of the problem of controlling the degree of concentration, of the need to specify the concentration method used, etc. Among the important problems still to be solved are the development of automated methods of concentrating trace elements, the creation of unified procedures for the decomposition of the sample and the concentration and final analysis of the trace elements, and the development of new, simple, and rapid reagentless methods of concentration.

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