PRECONCENTRATION IN INORGANIC TRACE ANALYSIS

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Abstract - Preconcentration in trace analysis lowers the detection limit,
simplifies the treatment of a representative sample, facilitates
calibration, reduces the need for various standard reference samples and
frequently involves separation of the matrix in analysis of toxic,
radioactive and expensive materials.   In this paper, the types of
preconcentration are considered and quantitative characteristics which
describe it are noted.   The main methods of preconcentration are discussed:
solvent extraction, sorption, precipitation and co-precipitation,
evaporation, ashing, directed crystallization, electrochemical methods,
fire-assay, partial dissolution of the matrix and so on.   A comparison of
preconcentration methods is made.   Rational combinations of concentration
methods and subsequent methods of determination are of great importance.
In these cases, the number of elements to be determined, the nature of the
concentrate, and the overall error connected with the concentration and
determination stages should be taken into consideration.   Examples of
successful combinations are given: solvent extraction - spectrochemical
analysis, solvent extraction - atomic absorption, and others.   Peculiarities
of preconcentration in analysis of high-purity substances and natural
waters are also considered.

Preconcentration is used if the detection limit of the analytical technique is higher than
the concentration of trace elements in the sample.   Concentration often involves separation
of the matrix or the bulk of it, and sometimes a number of interfering minor constituents as
well.   In a prepared concentrate, the relative concentration of trace elements is usually
higher than in the initial sample.   Moreover, the possibility of increasing the amount of
sample analysed means that the absolute amounts of elements to be determined can also be
increased.   As a result, it is possible to reduce the detection limit of trace elements
(sometimes very significantly; by a factor of 100 or 1000).   This is the main but not the
only reason for the widespread use of preconcentration.

Preconcentration is almost essential if trace elements are non-homogeneously distributed in
the material.   In this case, a representative sample must be quite large; it is difficult
to analyse it directly, especially if the method of determination needs a small sample as,
for instance, spark-source mass-spectrometry or spectrochemical analysis.   To take a
classical example: the fire-assay technique concentrates gold and other noble metals, which
are non-homogeneously distributed in ores, rocks, etc., from very large samples.   In many
other cases, preconcentration with preliminary dissolution and production of a small volume
of concentrate facilitates the preparation of a representative sample.   Samples can also
be homogenized during other operations, of course.

Concentration facilitates calibration, especially if there is a lack of standard reference
materials.   It makes it possible to obtain concentrates with identical matrices in analysis
of quite different materials, for example, concentrates on carbon powder in spectrochemical
analysis.   Reference samples are prepared as concentrates of the same type.   There is then
no necessity to have standard reference materials for all substances analysed.

Preconcentration with exhaustive removal of the matrix is desirable in the analysis of toxic,
radioactive or,if the matrix can be recovered,very expensive materials.   Moreover, it is
convenient to add elements as internal standards, if necessary, during decomposition of the
sample and concentration.   Sometimes, preconcentration allows an increase in the number of
trace elements which can be determined by a selected technique or makes it possible for the
determination technique to be used at all.

These advantages of preconcentration make it an important part of trace analysis.   In spite
of the progress in sensitive instrumental methods of direct analysis, the significance of

concentration does not diminish.   On the contrary, its possibilities increase, particularly because of new combinations with methods of determination.

On the other hand, preconcentration increases the analysis time and complicates the analysis. It may also lead to losses of microelements to be determined or to contamination.   The number of trace elements determinable is sometimes lower than by direct analysis.   Special working procedures, reagents of high purity, specially equipped laboratories and special materials for equipment are necessary.   However, the advantages outweigh the disadvantages.

Preconcentration can be absolute or relative.   In absolute preconcentration, trace elements are transferred from a large mass of sample into a small mass, e.g. by evaporation or by solvent extraction into a small volume of an organic phase.   Relative preconcentration increases the mass ratio of trace elements to main components (the solvent is not considered as a major component in this case).   Relative preconcentration involves at least partial separation of the components when their concentrations differ very much.   Its main aim is often to exchange the matrix for a suitable collector (generally of smaller mass) to prevent its interference in the determination.   In some cases, it is difficult to define a boundary between absolute and relative preconcentration.

Depending on the purpose, trace elements can be concentrated selectively or in groups and either separation of the matrix or separation of the trace components can be used.   Removal of the matrix is reasonable if used in combination with multielement determination techniques, e.g. spectrochemical analysis, but only if the matrix is of simple composition.   Matrix removal is used especially in analysis of high-purity metals.   If the matrix contains several elements forming complex compounds (geological and biological materials), it is better to separate the trace elements.   Sometimes, there is no need to remove the matrix completely; the process is then called "enrichment".   However, it is usually more profitable to change to another matrix which better meets the demands of the subsequent determination, simplifies a calibration, etc.   Several such collectors are suitable for determinations by different techniques.   For instance, carbon powder can be analysed by a spectrographic method or by flameless atomic-absorption spectrophotometry.

Three quantitative characteristics are used for description of preconcentration: recovery, concentration coefficient and separation coefficient.   The meaning of these characteristics is clear from Table 1.

TABLE 1. Main terms for preconcentration

Recovery (R)	$R = Q_T/Q_T^O$, where Q_T and Q_T^O are respectively the quantities of trace element in the concentrate and in the sample. It is usually expressed as a percentage.
Concentration coefficient (K)	$K = (Q_T/Q_M)/(Q_T^O/Q_M^O)$, where Q_M^O and Q_M are respectively the amounts of matrix before and after preconcentration. If $R = 100\%$ then $K = Q_M^O/Q_M$.
Separation coefficient (S)	$S = (Q_M/Q_T)/Q_M^O/Q_T^O) = 1/K$.

General aspects of preconcentration have been considered in a number of reviews and monographs(1-8).

PRECONCENTRATION METHODS

Many different methods are used for analytical preconcentration.   They can be classified according to the nature of the separations used, first into chemical and physical methods (Table 2) and then according to the number and nature of the phases involved in the separation process.   Methods based on distribution of species between two immiscible phases are the most important, because one of the phases can concentrate the trace elements.   Such a classification is given in Table 3.   However, there are methods based on separation in one phase, e.g. electrodialysis, diffusion methods.

The methods vary in importance, of course.   The IUPAC commission on microchemical techniques and trace analysis has compared separation and concentration methods used in 188 laboratories in many countries for determination of impurities in chemical reagents(9).   Solvent extraction, ion-exchange, precipitation of complexes, distillation and sublimation, and

TABLE 2. Chemical and physical methods of preconcentration

Chemical and physico-chemical methods	Physical methods
Solvent extraction methods	Evaporation (distillation sublimation)
Sorption methods	Directed crystallization
Precipitation, coprecipitation	Zone melting
Ashing and other methods with chemical decomposition of a sample	
Partial dissolution of a matrix	
Electrochemical methods	

TABLE 3. Methods of preconcentration of trace elements, based on the distribution between two phases

Phase		Methods of preconcentration
Concentrate of trace elements	Matrix	
Liquid	Liquid	Solvent extraction of trace elements
		Solvent extraction of a matrix
		Distribution chromatography
Solid	Liquid	Sorption of trace elements
		Coprecipitation of trace elements
		Electrolytic deposition and cementation of trace elements
Liquid	Solid	Sorption of a matrix
		Precipitation of a matrix
		Electrolytic deposition of a matrix
		Selective dissolution of trace elements by solvents
		Directed crystallization
		Zone melting
Gas	Liquid	Evaporation of trace elements
Liquid	Gas	Evaporation of a matrix, wet ashing
Gas	Solid	Evaporation of trace elements
Solid	Gas	Sublimation of a matrix
		Evaporation of a matrix - after chemical treatment (dry ashing etc.)

electrolysis are used the most frequently in 79, 21, 18, 8 and 5 laboratories respectively. It is expedient to consider some of these methods in more detail.
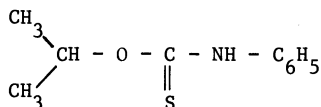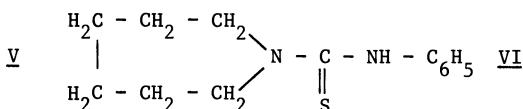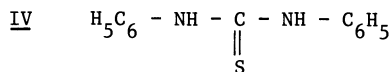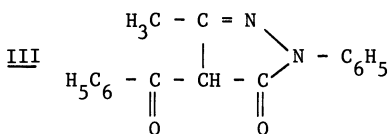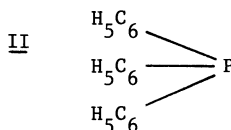
Solvent extraction methods.   These are particularly convenient.   They may be used for separation (selective or group) of trace elements into the extract or for matrix extraction. Wide scope, simplicity and rapidity are important advantages of these methods.   Solvent extraction usually ensures high efficiency of concentration.   These methods are reviewed in our book "Solvent Extraction Preconcentration"(8).

Various systems are used in extraction of trace elements, chelate systems being most frequently used.   Trace element separation is possible if the matrix does not react with the

reagent used, e.g. in analysis of water, acids, alkali metal salts, metal compounds which can be converted into anionic form in the extraction.   8-Hydroxyquinoline, dithizone and dithiocarbamates, particularly diethyl- and pyrrolidinedithiocarbamates, are conventional reagents for group concentration.

In order to extract the maximum number of elements, the extraction may be carried out successively at several pH values or with a mixture of reagents.   For instance, a procedure has been developed for determining 18 elements as impurities in alkali metal halides of high purity by using a mixture of cupferron, sodium diethyldithiocarbamate, and trioctylphosphine oxide(10).   All 18 elements are simultaneously extracted at pH 8-9, then the extract is evaporated on carbon powder and analysed spectrographically.   These reagents were chosen because under the extraction conditions they do not transfer into the organic phase (except for the trioctylphosphine oxide, which remains in the extract but does not interfere with the determination).

Several new reagents have been suggested for extraction concentration of trace elements. Dialkyltin dinitrates, e.g. dinonyl and dioctyl (I) possess unique power for extraction of highly charged oxo-anions: they extract phosphate and arsenate best of all, selenite and selenate not quite so well although satisfactorily, and extract singly-charged anions poorly(11,12).   In this respect the organotin extractants differ from all other known extractants.   Procedures have been developed with these extractants for preconcentration of phosphorus, arsenic, and selenium, e.g. the extractive-photometric determination of phosphorus and arsenic in vanadium.

I $\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array}$ $Sn(NO_3)_2$

  $R = C_8H_{17}, \ C_9H_{19}$

II $\begin{array}{c} H_5C_6 \\ H_5C_6 \\ H_5C_6 \end{array} P$

III $\begin{array}{c} H_3C - C = N \\ | \qquad \diagdown \\ H_5C_6 - C - CH - C \diagup N - C_6H_5 \\ \parallel \qquad \parallel \\ O \qquad O \end{array}$

IV $H_5C_6 - NH - C - NH - C_6H_5$
       $\qquad\qquad\qquad \parallel$
       $\qquad\qquad\qquad S$

V $\begin{array}{c} H_2C - CH_2 - CH_2 \\ | \qquad\qquad\qquad \diagdown \\ H_2C - CH_2 - CH_2 \diagup N - C - NH - C_6H_5 \\ \qquad\qquad\qquad\qquad \parallel \\ \qquad\qquad\qquad\qquad S \end{array}$

VI $\begin{array}{c} CH_3 \\ \diagdown \\ CH - O - C - NH - C_6H_5 \\ \diagup \qquad\qquad \parallel \\ CH_3 \qquad\qquad S \end{array}$
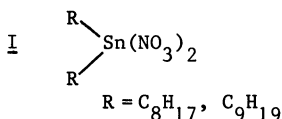
Triphenylphosphine (II) has been proposed in our laboratory for selective preconcentration of traces of gold and silver followed by atomic-absorption determination, and used for gold in minerals and cyanide solutions(13) and silver in rocks, ores, and minerals(14).   The special property of this reagent is its ability to react with metal ions which are "soft" acids(15).

1-Phenyl-3-methyl-4-benzoylpyrazolone-5 (benzoylpyrazolone, III)(16) may be used for group concentration of some elements.   Figure 1 illustrates the pH ranges within which some elements are extracted (17).   Spectrographic methods have been worked out for determining impurities in sodium hydroxide and some other materials with this reagent.   It is also used for selective extraction of some elements before atomic-absorption(18), photometric and luminescence determination.   More than 100 papers have been written on the use of this reagent, and recently its use has been reviewed(16).

Diphenylthiourea (IV) and hexamethylenephenylthiourea (V) have been suggested for solvent extraction concentration of chalcophilic elements, particularly silver and the platinum-group metals.   These reagents make it possible to concentrate noble metals and separate them from non-ferrous metals.   Thus, a spectrographic procedure has been developed for determining all the noble metals, except for osmium, in the solutions obtained after decomposition of natural and technological materials containing large amounts of nickel, cobalt, iron, manganese, zinc and moderate amounts of copper(19).   The procedure involves extraction preconcentration of noble metals with diphenylthiourea after treatment with tin(II) chloride.   The limits of detection are 1-100 ppM (parts per milliard).   Diphenylthiourea has been used for preconcentration of trace amounts of silver in rocks, ores and concentrates(20), and of copper, silver, and thallium in chemical reagents(21); the elements were determined by atomic-absorption.
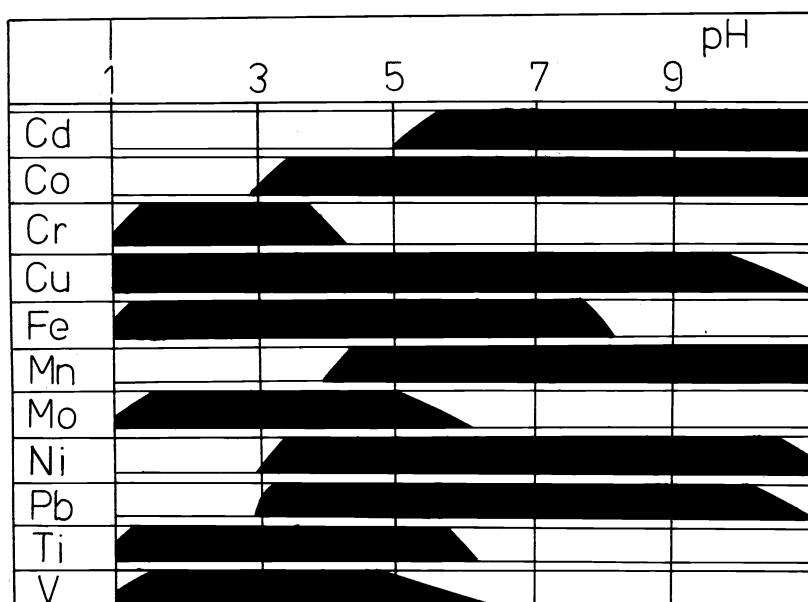
Fig. 1 Extraction of metal complexes with benzoylpyrazolone
(organic phase: chloroform plus ethanol).

Important factors in separation of trace elements from the matrix in aqueous solution are the
effects of the unextracted matrix components (salting-out, masking, etc.), and the effect of
the trace component concentration on its distribution coefficient. There are some
interesting problems still to be solved in this field.

Extraction of the matrix is also of great importance in analytical practice. In this case,
the capacity of the organic phase has to be high and the extraction has to be sufficiently
selective for the trace elements to remain completely in the aqueous phase. Metal chelates
are less convenient for the purpose because of their moderate solubility in the organic phase,
but various ion-association complexes, coordinatively solvated compounds, and molecular
compounds are quite suitable. The effect of the extracted matrix on the behaviour of the
trace elements is an interesting and important general problem. Undesirable coextraction of
trace components is possible in some cases. We have investigated this problem for several
years and established the principles for enhancement and suppression of microelement
extraction which favours concentration by this method(22,23).

Many extractants are used for matrix extraction. $\underline{O}$-Isopropyl-$\underline{N}$-ethylthiocarbamate (VI) is
one of the new reagents(24). Its extractive power has been examined in detail, and several
separation and preconcentration procedures have been developed. The reagent is liquid,
miscible with organic solvents and has high capacity. It extracts silver very well. Only
mercury, platinum, palladium and in part gold are extracted together with silver from 1$\underline{M}$
nitric acid; other elements remain in the aqueous phase. A single extraction of silver with
2$\underline{M}$ reagent in chloroform is 99.98% complete. It has been used to develop a spectrochemical
procedure for determining 23 elements as impurities in high-purity silver(25). The limits
of detection were 0.2 - 50 ppM, the concentration factor being 50.

Usually solvent extraction ensures a concentration factor of not greater than 50 - 100. In
this respect, extraction chromatography, which is being intensively developed(26),
gel-extraction(27) and utilization of three-phase systems(28) are more promising. This last
method is of interest. Two organic phases are formed in some systems, one of which, small
in volume, contains practically the whole of the element extracted. This phase may be
separated and directly used for spectrochemical or atomic-absorption analysis. Several such
procedures have been proposed, mainly by Zhivopistsev and Petrov(29,30).

Sorption Methods   Numerous sorption methods of preconcentration are used, based on different
sorption mechanisms: simple adsorption, ion-exchange, complex formation. Ion-exchange
methods, which often involve complex formation, are of particular interest. The necessity
to work with large solution volumes makes it difficult to use the usual high molecular-weight
synthetic ion-exchangers, but the technique is utilized in many laboratories, especially the
procedures with microcolumns. Static, dynamic, and chromatographic variants of ion-exchange
separation may be used for preconcentration. Microelements or the matrix can be separated.
If trace elements are sorbed, they can be desorbed or the sorbent incinerated; however, the

latter procedure is possible only if a high-purity sorbent is used.   If very pure sorbents are available, direct spectrochemical (or other) analysis of the sorbent-concentrate is helpful.   Such a procedure is used by Otmakhova et al., at Tomsk University(31-33).   They have developed, for example,a procedure for determining impurities in boron anhydride(31). This compound is dissolved in a mixture of water and glycerol; the glyceroboric acid formed is not sorbed by ion-exchangers.   Cu, Ni, Cr and other trace impurities are sorbed on a cation-exchanger in a microcolumn, then the ion-exchanger is placed in a Teflon mortar, sodium chloride is added, the mixture is ground, and a drop of concentrated sulphuric acid is added.   The destroyed ion-exchanger is ground with alcohol and analysed spectrographically.

Rare-earth elements present as impurities in uranium metal have been concentrated by a two-stage ion-exchange procedure(34).   The rare earths were first separated from the bulk uranium by sorption from a sulphate solution on a column of KU-2 cation-exchanger and eluted with hydrochloric acid.   The second stage consisted in sorption of the uranium residue as its chloro complex on the anion-exchanger Dowex 1x8; the rare earths were not sorbed in this case.   As a result, gadolinium, europium, and samarium as impurities could be determined by the luminescence technique at levels down to 0.02 ppM.

Complex formation is also used in ion-exchange concentration to mask elements which are not to be sorbed and to transform the elements of interest into a well-sorbed form.   Numerous chelate-forming organic reagents may be used for this purpose, besides the usual inorganic ligands.   For instance, to concentrate traces of Cu, Zn, and Cd on a conventional anion-exchanger, they were transformed into their anionic complexes with 2-(3'-sulphobenzoyl)-pyridine-2-pyridylhydrazone(35).   The concentration coefficient was 300.

Complexes of trace elements are adsorbed well by active charcoal under certain conditions. This adsorbent behaves as an anion-exchanger in aqueous solution, e.g. it selectively adsorbs anionic complexes of noble metals.   On the other hand, oxidized charcoal, (treated with nitric acid for example) is a cation-exchanger and adsorbs multicharged cations well.   The adsorption properties of oxidized charcoals have been examined in detail by Tarkovskaya et al. in Kiev(36,37).   Columns packed with oxidized charcoal make it possible to concentrate alkaline earth metal impurities from solutions of alkali metal or ammonium salts.   Active charcoal can also concentrate metal chelates, e.g., diethyldithiocarbamates; this is used for preconcentration of traces of chalcophilic metals.
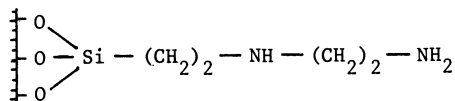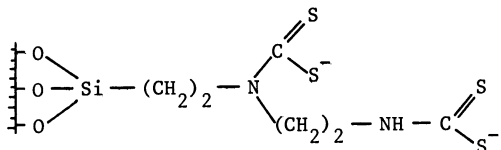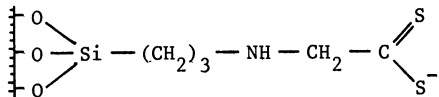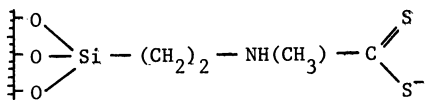
In our opinion, several chelate resins are very promising.   The great number of analytical reagents available and the extensive information on their reactions with the elements make it possible to prepare polymer resins containing various selective and non-selective reaction groupings.   There are already some achievements in this field.   Examples of chelate resins synthesized in the Vernadsky Institute are given below.   Sorbent I adsorbs palladium and platinum, sorbent II adsorbs copper(38-40).   Resins of the Chelex 100(41) and XAD(42) types and others have been studied.
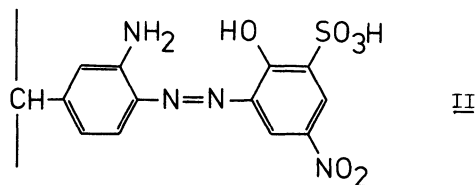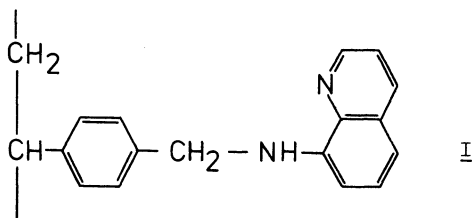
Various inorganic sorbents are being investigated - hydroxides, sulphides, phosphates etc. For example, copper and gold are completely concentrated from 6M hydrochloric acid on copper sulphide.   The sorbents used for concentration of trace elements have to be of high purity; this is not easy to ensure.

Inorganic sorbents "inoculated" with functional groups are hybrids of inorganic sorbents and synthetic chelate resins.   They are an interesting type of sorbent for preconcentration.

Leyden(43-45) has developed procedures for preconcentrating ions on silica gel or small glass balls with complex-forming groups immobilized on their surface.   Such groups are shown below.

$$\begin{array}{l} O \\ O \end{array}\!\!\!\!\searrow Si - (CH_2)_2 - NH(CH_3) - C \diagup\!\!\!\!\!\!^{S}_{\searrow S^-}$$

$$\begin{array}{l} O \\ O \end{array}\!\!\!\!\searrow Si - (CH_2)_3 - NH - CH_2 - C \diagup\!\!\!\!\!\!^{S}_{\searrow S^-}$$

$$\begin{array}{l} O \\ O \end{array}\!\!\!\!\searrow Si - (CH_2)_2 - N \diagup^{C \diagup\!\!^{S}_{\searrow S^-}}_{(CH_2)_2 - NH - C \diagup\!\!^{S}_{\searrow S^-}}$$

$$\begin{array}{l} O \\ O \end{array}\!\!\!\!\searrow Si - (CH_2)_2 - NH - (CH_2)_2 - NH_2$$

The diethyldithiocarbamate group ensures sorption of cations, and the diamine group that of anions.   The method of introduction of these groups (silylation) is original.   The sorption of trace elements is sufficiently complete under static conditions, but for isolating traces from a large volume the column method is preferable, although in this case it is better to use glass balls instead of silica gel.   After the sorption, the glass or silica gel particles are mixed with an equal amount of powdered cellulose and pressed, and the tablet is analysed by X-ray fluorescence.   Elements can be extracted from very dilute solutions, e.g. selenium from 2 litres of water, at the level of 10 ng/ml.

Co-precipitation and matrix precipitation   Co-precipitation of trace elements with a collector and matrix precipitation are undoubtedly important methods of preconcentration.   In order to co-precipitate trace elements, amorphous precipitates of high activity (hydroxides, sulphides and others) are most frequently used.   Co-precipitation on such precipitants may be considered as a heterogeneous ion-exchange or chemical reaction which leads to formation of a solid solution or of chemical compounds of the microcomponent with the matrix compound.   There are several large research groups in the Soviet Union which study profoundly the mechanism of co-precipitation on such collectors.

The choice of collector is determined by many factors.   It is very important that the collector is a pure substance completely adsorbing trace elements on a small mass of precipitate. A specific demand if spectrochemical analysis is to be used is that elements with simple emission spectra should be used as collectors, e.g. aluminium and zinc hydroxides but not iron(III) or manganese.   Sometimes, it is convenient to use as collector a compound of an element which can later be removed by evaporation or other simple method.   For example, mercury was removed as its bromide after precipitation of trace elements on mercury sulphide(46).   Some trace components are easily reduced to the elementary state and co-precipitated, e.g. with elementary tellurium or mercury.

It is not always necessary to introduce a collector into the solution;   some of the matrix may be used instead.   Such concentration procedures have been developed by Chuiko(47,48), Jackwerth(49) and other chemists.   This approach is particularly suitable in the case of hydroxides.   It is sometimes necessary to control the charge of the trace elements e.g. by transforming them into complex anions, because in the separation of part of the matrix as a slightly soluble crystalline compound, the precipitate surface develops a positive charge. However, hydroxides adsorb hydroxyl ions and, hence, this rule does not apply to them.

Organic co-precipitants are very interesting.   They were introduced into analytical practice in the fifties mainly by Kuznetsov(50-52).   Organic collectors are easily removed, there are many of them, there is less uncontrolled co-precipitation of foreign microcomponents and matrix compounds, and unlike solvent extraction, the consumption of organic reagent may be

very small. In the case of atomic-absorption or photometric determination, the collector may
not need to be incinerated but can be dissolved in a suitable organic solvent and the
solution used directly for the analysis. 8-Hydroxyquinoline, cupferron and many other reagents
are used as co-precipitants; they are often combined with inert co-precipitants of the
naphthalene type. Many examples of concentration with organic co-precipitants are given in
the book by Kuznetsov and Akimova(52). Among recent works, there are papers on concentration
of a number of elements on germanium and aluminium salicylfluoronates(53), or preconcentration
of gold and palladium with dithizone followed by flameless atomic-absorption(54).

Precipitation of the matrix, leaving the trace elements concentrated in the solution, demands
large amounts of reagents, causes high blank values, and is laborious. A large mass of
precipitate promotes losses of trace elements by co-precipitation. These disadvantages can
be avoided however, in some cases. Many procedures have been based on matrix precipitation.
For example, in the analysis of high-purity lead, its precipitation as the nitrate from
concentrated nitric acid is probably the best method of concentrating the impurities(55).
Other procedures of this type have been developed by Karabash, e.g. precipitation of bismuth
iodide in spectrochemical determination of impurities in bismuth(56).

<u>Evaporation methods</u> These are used in several ways: simple thermal evaporation of trace
elements, evaporation of trace elements after conversion into volatile compounds, and
sublimation or distillation of the matrix directly or after chemical conversion of the matrix
into volatile forms. Simple thermal evaporation is accompanied by relatively low
contamination; the degree of contamination increases when reagents are used for preparation
of volatile compounds, especially compounds of the matrix. There may be losses of the
elements to be determined, in all cases, particularly during matrix evaporation. One or
several elements will usually be concentrated during evaporation of the trace components.
Group concentration of all trace elements in the residue is achieved when the matrix is
evaporated (with or without a collector).

Evaporation of traces from a solid matrix demands careful crushing, which is a drawback of the
method. Moreover, the sample should be small (50 - 100 mg). Evaporation in vacuum is
effective for many impurities but is a more complicated technique. Evaporation in a carrier-
gas stream is sometimes used. The volatilization of certain elements by use of a flow of
hydrogen chloride at moderate temperature in the analysis of high-purity silica is a good
example(57). In this case, Fe, Ni, Co, Al, Ti, Sn, Mn, In, Ga, Be are evaporated and
determined by the spectrographic method. The elements are condensed in a small cap of pure
carbon, cooled by water. Meyer <u>et al</u>.(58) have developed a very sensitive method of
determination of selenium in high-purity copper by using gas chromatography after
volatilization in a stream of oxygen. The condensate of selenium dioxide is converted into
5-nitrodiazoselenol which is extracted with toluene and determined by gas chromatography.
Evaporation is often applied to isolation of mercury vapours, particularly before atomic-
absorption determination(59,60).

Evaporation of the matrix is utilized if it is more volatile than the trace elements to be
determined. It is usually difficult to perform a simple evaporation at atmospheric pressure;
the evaporation rate increases with temperature but the temperature must not exceed 800°C as
there is a danger of losses of trace elements and oxidation of matrix elements. However, at
low temperatures, evaporation of a large sample demands much time. Only matrices such as
iodine, arsenic, antimony and zinc can be easily evaporated. Therefore, it is common to
resort to use of reduced pressure, or an inert carrier gas or (more frequently) various
chemical reactions transforming the matrix into a more volatile form. Dry ashing, the
combustion of organic substances and carbonaceous materials in an atmosphere of air or oxygen,
is simple and the most widely used technique. It is also often used as the final stage of
a concentration begun by other methods. Ashing of the matrix is possible in the presence or
absence of a collector; the losses of trace elements are lower in the presence of a collector,
e.g. carbon powder. Combustion allows the removal of the above-mentioned substances and
sulphur, arsenic, selenium and osmium. Besides oxygen, hydrogen fluoride, hydrogen chloride,
chlorine and carbon monoxide may serve as the combustion atmosphere, forming volatile fluorides,
chlorides and carbonyls respectively. Carbonyls, especially nickel carbonyl, are formed
only at high temperature and pressure; carbon monoxide and the carbonyls themselves are
toxic.

Removal of the matrix from the liquid into the gaseous phase is widely used. Its most usual
application is evaporation of a large volume of test liquid in the presence or absence of a
collector, e.g. in analysis of water, acids, organic liquids, and some inorganic liquids such
as tin or silicon tetrachloride. Wet ashing of organic or biological substances also belongs
to this group; the technique requires large amounts of reagents and is accompanied by
contamination but gives lower losses of trace elements than dry ashing does.

<u>Electrochemical methods</u> Typical examples are electrolytic deposition on solid metal,
graphite or mercury electrodes, cementation, etc. One practical method consists in
electrolytic deposition of trace elements on carbon discs or cores which are then directly
used for spectrochemical or flameless atomic-absorption determination. Krasil'shchik
<u>et al</u>.(61-64) in the Institute of Chemical Reagents (Moscow) have collected trace elements on

carbon discs 4 mm in diameter and 1 mm thick, fixed by special supports or at the end of a
carbon rod (Fig. 2).   The deposition is made on the cathode, the anode being a platinum wire.
The elements separated are then determined by spectrochemical methods with a carbon rod as the
electrode.   The method is used for the analysis of alkali metal and aluminium compounds,
organic acids etc.; the Bi, In, Cd, Co, Cu, Ni, Pb, Zn and Mn contents have been determined.
A similar method was used in another series of papers(65-67) for determination of trace
elements by flameless atomic-absorption spectrometry.   A platinum or tungsten wire or a
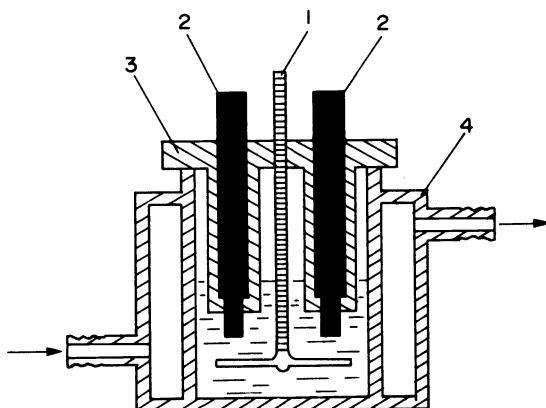graphite electrode was used as an electrode.

Fig. 2   Electrolytic cell for the collection of trace elements on carbon rods.

1 - platinum anode;   2 - graphite cathodes; 3 - Teflon holder;
4 - quartz cell.   The arrows show the direction of water flow.

My colleagues in the Vernadsky Institute have studied in detail the reduction of rare earths
at a mercury cathode in the presence of citrates.   Different rates of reduction are used
for concentration of several rare earths in analysis of compounds of high-purity europium
and ytterbium, for concentration of europium from compounds of other rare earths, aluminium
and basalts.

Electro-osmosis may be used for concentration of ions from very dilute solutions and from
non-electrolyte solutions.   With use of membranes made of alumina and polytetrafluoroethylene,
it is possible to reach concentration coefficients of $10^3 - 10^4$ and trace element recovery
of $85 - 99\%(68,69)$.

There is a special group of electrochemical concentration methods which are used in inverse
voltammetry(70).   Some of these methods will be considered in the next section.

Crystallization methods   These concentration techniques (directed crystallization and zone
melting) require no reagents(71).   The advantages of these methods are their universal
applicability, ease of automation, and low degree of contamination if the process is carried
out in a closed atmosphere and at a not very high temperature.   If necessary, the main part
of the material analysed may be recovered for use.   The disadvantage of the methods is that
the efficiency decreases at low concentrations of the elements to be separated, especially
if they are isomorphous with the main compounds;   moreover, the methods are time-consuming.

In the USSR, the method of directed crystallization has been studied in detail.   The ingot is
completely melted and then crystallized from one end;   during the crystallization, the
impurities concentrate in that part of the ingot which crystallizes last.   Directed
crystallization requires much simpler apparatus than zone melting.   Besides crystallization
from high-temperature melts, it is possible to use directed crystallization of water – salt
eutectics and crystallohydrates.   For this purpose, it is possible to apply, for example, the
automatic device shown in Figs. 3 and 4(72).   In the Khar'kov Institute of Monocrystals, a
number of methods have been developed for concentration of impurities in metal halides.
Vertical directed crystallization has been used, during which the melt is mixed by the intense
natural convection.

Selective dissolution of the matrix   Jackwerth uses an original method of concentration which
consists of a partial dissolution of the matrix in conditions under which the impurities do
not pass into the solution but remain in the residual matrix.   For instance, during
concentration of trace elements from high-purity zinc, the zinc sample (up to 100 g) is
covered   with 1 – 5% of mercury and then the zinc is dissolved in hydrochloric acid until
only a small residue is left, in which Bi, Cd, Co, Pb, Ni, Sn, Tl, In, Ag, Au and Pd are
concentrated(73).   Similar methods have been worked out for analysis of cadmium, lead (after
fire assay), gallium and aluminium (Table 4).   In the case of aluminium, the recovery is
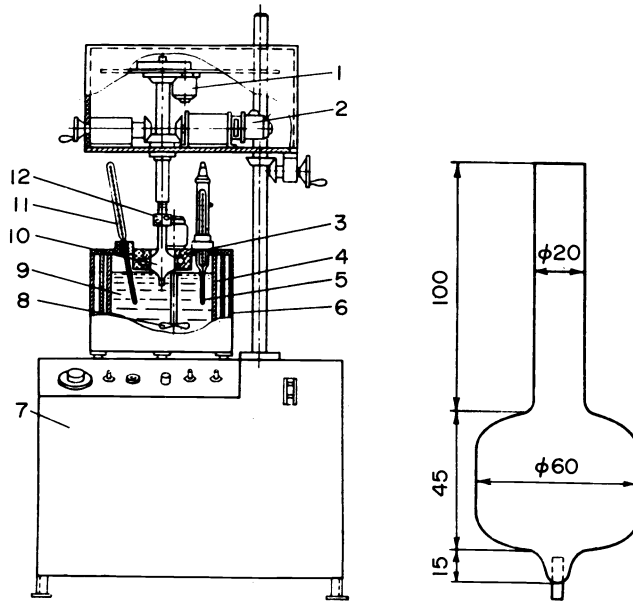over 95%, and the concentration coefficient about 10^3.

Fig. 3 Unit for directed crystallization of aqueous solutions

       1 - rotation drive motor; 2 - vertical drive motor; 3 - resistance
       heater; 4 - evaporator of the cold-air unit; 5 - contact thermometer;
       6 - cooling chamber; 7 - control unit; 8 - stirrer; 9 - antifreeze;
       10 - sample container; 11 - control thermometer; 12 - clamp.

Fig. 4 Container for directed crystallization (dimensions are given in mm).

TABLE 4. Methods of concentration of trace elements from high purity
         metals by partial dissolution of a matrix

Matrix	Trace element	Methods 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*	Noble metals	Atomic absorption	75
Gallium	Ag,Au,Bi,Cu,Fe,Hg,Ni, Pb,Pd,Sn,Zn	Atomic absorption	76
Mercury	Au,Pd	Photometry	77
Cadmium	Ag,Au,Bi,Cu,Ni,Pb,Pd	Atomic absorption	78

* After fire melting

Fire melting (fire assay) is a special type of preconcentration. It combines decomposition
of the sample and concentration of noble metals, e.g. into molten lead, in one operation.
As a result, the noble metals are separated from other elements and a large representative
sample can be used for analysis of ores and rocks. The concentration coefficient reaches
values of 100 - 1000. The classic fire assay is now believed not to be very effective,
because of the low sensitivity and difficulties in separating noble metals. However, fire
melting as a method of decomposition and concentration is convenient in combination with
modern highly sensitive techniques such as spectrography or neutron-activation analysis.

Fire melting is of importance for analysis of samples in which the noble metal contents are 1 – 1000 ppM. The old method of concentration into lead ensures satisfactory results only for gold, silver, platinum and palladium. Nowadays, tin, metal and nickel sulphide are used instead of lead. Conditions for concentrating iridium and rhodium have also been found. Unfortunately, the theory of fire melting has been very badly developed, but it is the oldest method of concentration other than evaporation.

Other preconcentration methods Flotation can be used both for separation of the matrix and isolation of trace elements. The matrix can be floated after its precipitation, in order to avoid filtration. The isolation of silver(79), vanadium(80) and a group of nine elements(81) from sea-water illustrates separation of trace components. Ultrafiltration, lyophilic drying and other methods are also applied.

As mentioned above, several methods of concentration may be used successively and sometimes original combinations of methods are applied. Thus, in the analysis of organic and biological materials, ashing almost always follows microelement concentration by some methods. There are many examples of the successive use of solvent extraction and sorption, precipitation and flotation, extraction and ashing, etc. Andrianov and Poladyan(82) have concentrated germanium, combining its co-precipitation on iron(III) hydroxide with a subsequent iron extraction by a kerosene solution of fatty acids. Germanium is co-extracted with the iron, which is directly separated from the hydroxide precipitate; it is of interest that the degree of germanium co-extraction decreases with increasing time of phase contact.

In the Vernadsky Institute, a combined method of concentration of noble metals for analysis of natural and industrial materials has been developed(83). Traces of noble metals are co-precipitated on copper sulphide from the solution after sample decomposition in the presence of mercaptobenzothiazole. In the second stage, the elements to be determined are separated from copper by sorption on a chelate resin. After concentration, the noble metals are determined by spectrochemical, atomic-absorption or neutron-activation methods.

The comparison of concentration methods This is a difficult problem. It can hardly be done without reference to the type of material analysed and the method of analysis of the concentrate. If these factors are taken into consideration, the results of the comparison may be quite different. Yudelevishch and Shelpakova(84) have compared solvent extraction of the matrix, distillation, ion-exchange and directed crystallization as methods of trace-element concentration in the analysis of high-purity antimony. The impurities in the concentrate were determined by spectrochemical methods. On the basis of all the characteristics used, solvent extraction of the matrix was the best technique. The concentration coefficient is an important characteristic of a preconcentration method. An attempt was made to compare concentration methods with respect to this parameter (Fig.5). However, it should be emphasized that this is only one parameter; others are often no less important.

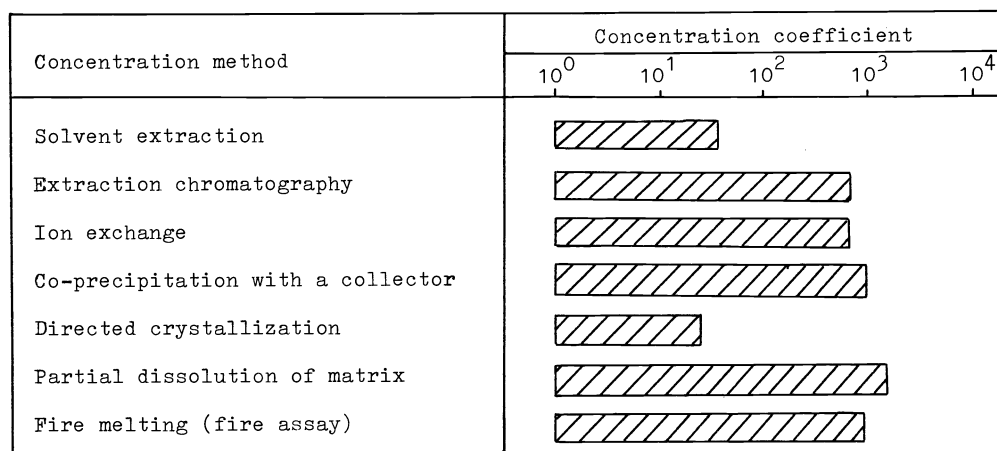| Concentration method	Concentration coefficient 10^0 10^1 10^2 10^3 10^4
Solvent extraction	▨
Extraction chromatography	▨
Ion exchange	▨
Co-precipitation with a collector	▨
Directed crystallization	▨
Partial dissolution of matrix	▨
Fire melting (fire assay)	▨

Fig.5 Values of concentration coefficients attainable with various
        methods of preconcentration.

COMBINATION OF PRECONCENTRATION AND DETERMINATION

Let us consider rational combinations of preconcentration methods with methods of determination. Naturally, it is reasonable to combine multi-elemental determination methods with methods of group concentration. A collector (matrix for the concentrate) should meet as fully as

possible the demands of the selected determination method: carbon powder for spectrographic
analysis, organic extracts for flame atomic-absorption spectrometry, etc.   There is no point
in combining a high-precision determination method with a concentration method which does not
give good precision, and vice versa.

Two groups of analytical techniques can be distinguished, which result from combination of
concentration and determination.

In the techniques of the first group, the concentration and determination are not closely
connected; in this case, more or less independent methods of concentration and determination
are used.   The properties of the concentrate do not substantially affect the determination.
In such a case it is relatively unimportant which type of concentration method is used –
ion-exchange, solvent extraction with subsequent stripping etc.   In the last case, for
example, the analyst will have an aqueous solution as the concentrate, and this reflects the
history of the sample treatment to only a small degree.   Such a solution can be analysed
by various techniques.   It is clear that combinations of such a type (used for a long time
and very widely) do not have any special peculiarities which should be discussed in detail.

Sometimes, however, the properties of the concentrate strongly affect the determination.
Specific peculiarities of the combination appear in these cases.   We no longer deal simply
with successive use of two methods: a new system appears.   For example, although for flame
atomic-absorption analysis of aqueous solutions it is not very important by what method the
elements being determined were separated, important peculiarities appear during the atomic-
absorption analysis of organic extracts.   These are connected with the different viscosity
of organic solvents in comparison with water, their combustibility, and changes in the
mechanisms of processes in the flame.   These peculiarities are so noticeable that it has
become necessary to treat such methods differently from the usual ones.   The same picture
arises in combination of solvent extraction with photometric determination, if the determination
is done directly in the organic phase.

In recent years, attempts have been made to combine extraction separation with direct
polarography of the extracts.   It is obvious that polarography of such organic solutions
differs from the polarography of aqueous solutions.

We may also speak about the close combination of separation and determination in a somewhat
different sense.   We know that the processes of separation and determination can sometimes
be combined in one instrument, as, for instance, in gas chromatographs.   An analogous
combination is achieved in modern high-pressure liquid chromatographs.   The expediency of
distinguishing methods is most clearly exemplified by gas chromatography.   To what category
of methods should gas chromatography be assigned?   To methods of separation? Of course:
a typical chromatographic separation is accomplished in the instrument.   Perhaps to
determination methods?   In fact, analytical gas chromatographs are not used for separation as
such but for analysis of mixtures, i.e. in the end for identification and determination of
the components of the mixture.   The combined methods of the second group may be called
hybrid methods.

Let us now consider particular combinations of preconcentration with some of the most
important methods of determination.

Spectrochemical analysis   Concentration is of great importance in this connection and has
been used in this technique for more than 25 years; the papers by Gorbach and Pohl were
among the first(85-89).   Preconcentration is used when direct analysis does not yield the
necessary relative detection limit, as well as in the other cases considered above.   It is
expedient to separate the matrix if it hinders the determination of trace elements by
overlap of spectral lines or if its excitation potential is unfavourable.   It is useful to
convert samples into the same physicochemical form so that a universal series of reference
samples may be used.   A further advantage of preconcentration is that it is no longer
necessary to use reference samples with a very low content of element to be determined, which
are known not to be reliable.   There is less fluctuation in the results because of uneven
distribution of trace elements in the sample(2).   For these reasons this combination is
widely used.   In the USSR, such combinations are called chemico-spectrographic methods
(Karabash).

Group concentration of the trace elements to be determined is advantageous in these methods.
If the emission spectra of the matrix elements are sufficiently simple and the physicochemical
properties of the matrix are favourable for spectrographic determination of trace elements,
it is not necessary to separate the matrix completely; enrichment suffices.   In any case,
the concentrate   should be in a form convenient for direct excitation of the spectrum of
the traces, which should be concentrated in a small mass of collector or on a small electrode
surface.

What demands are made on the collector (matrix of the concentrate) in spectrochemical analysis?
It should be stable on storage, non-hygroscopic, have a simple emission spectrum, and be
easily· obtainable in a reproducible form as a result of a small number of simple operations.

Preferably it should have relatively low volatility: this favours the uniform supply of trace elements into the discharge zone. Carbon (graphite) powder satisfies these requirements. Very many chemico-spectrographic methods have been based on the use of this collector. Methods worked out in our laboratory (Table 5) may serve as an example.

TABLE 5. Some chemico-spectrographic methods

Material analysed	Method of preconcentration	Trace elements	Detection limit, ppM	Reference
High-purity silver	Extraction of matrix	Al,As,Ba,Be,Bi,Ca,Cd, Co,Cr,Cu,Fe,Ga,In,Mg, Mn,Ni,Pb,Sn,Te,Tl,V, Zn,Zr	1 - 20	25
Steel	Extraction of trace elements	Bi,Cd,Cu,Pb,Sb,Sn,Zn	10 - 1000	90
Aqueous solutions	Extraction of trace elements	Cd,Co,Cr,Cu,Fe,Mn,Mo, Ni,Pb,Ti,V	-	17
Sodium iodide	Extraction of trace elements	Ag,Al,Bi,Ca,Cd,Co,Cr, Cu,Fe,Mg,Mn,Mo,Ni,Pb, Sb,Sn,Ti,Zn	1 - 100	10
Solutions after decomposition of ores and concentrates	Extraction of trace elements	Ag,Au,Ir,Pd,Pt,Rh,Ru	10 - 1000	19
	Sorption on CuS and chelate resin	Ag,Au,Ir,Pd,Pt,Rh,Ru	1 - 100	83
Aluminium,gallium, indium phosphide	Co-precipitation on Bi_2S_3, $Bi(OH)_3$, In_2S_3	Ag,Au,Cd,Co,Cr,Cu,Mn, Ni,Pb,Sn,Zn	1 - 100	91

One method(90) may be considered in more detail. Small impurities (0.01 - 1 ppM) of antimony, tin, lead, bismuth, zinc, cadmium and copper in steel were determined. These elements were extracted with methyl isobutyl ketone from a 1M solution of ammonium iodide in 2.3M sulphuric acid and back-extracted with 15% hydrogen peroxide in 2.5M sulphuric acid, and the aqueous solution obtained was evaporated with 10 mg of carbon powder. The concentrate was heated at $350 - 400^{\circ}C$. Spectrographic determination was accomplished by fractional distillation with potassium iodide as carrier. The detection limits with a spectrograph of mean dispersion were 0.01 - 1 ppM, the relative standard deviation was 9 - 36%. The use of a high-dispersion spectrograph allows the detection limits to be lowered to 0.001 - 0.1 ppM.

There is a concentration technique specific for spectrochemical analysis - the method of evaporation, the prototype of which was the method of fractional distillation(92). The technique has been developed in two variants by Zaidel et al.(73) and Mandelstam et al.(94) for the analysis of pure nuclear materials: evaporation in air and under vacuum. A refractory powder sample, especially of oxides, is placed in a small graphite vessel (Fig.6) and heated by a high-intensity current in a graphite furnace between graphite side-plates attached to water-cooled copper electrodes. The vapours of the evaporating trace elements condense on the cooled graphite or copper capsule, which subsequently serves as one electrode of the arc for the spectrographic analysis. A two-stage evaporation may be used for analysis of samples of medium volatility, for example silicon. A small cooled graphite vessel serves as receiver in the first stage, and in the second, the trace elements are evaporated from the small vessel onto the capsule-electrode. This technique ensures a more efficient removal of the matrix. In a number of methods, a volatile matrix, e.g. molybdenum or chromium oxide, is preliminarily converted into a non-volatile one (the corresponding carbide).

Atomic-absorption spectrometry This technique is most frequently combined with preconcentration by means of solvent extraction followed by flame atomic-absorption with direct spraying of the extract into the flame. The advantage of such methods in comparison with the use of aqueous solutions lies in the lower detection limit, and the greater speed and simplicity of the analysis. The evaporation of extracts, back-extraction etc., which lead to larger blank corrections in determination of abundant elements, are avoided. Sometimes, if an organic solvent that burns well is used, there is even no need for a combustible gas. Concentration is also used in combination with flameless atomic-absorption.

The selectivity of the atomic-absorption method permits group concentration to be used for trace elements. Hydroxyquinoline, β-diketones, xanthates and especially dithiocarbamates
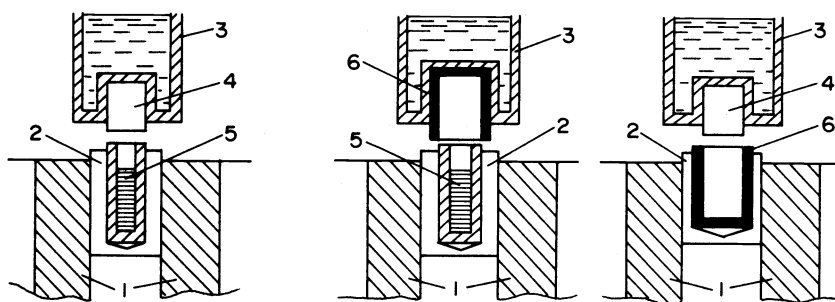
Fig. 6   Device for sample-heating and condensation of trace elements
         in the one-step (A) and two-step (B) evaporation methods.

         1 - graphite side-plates of water-cooled copper electrodes;
         2 - graphite crucible;   3 - water-cooled copper holder;
         4 - capsule for receiving the condensate;   5 -   small
         graphite beaker with sample powder;   6 - small glass receiver
         for the first condensate.

are widely used for this purpose.   As solvents, chloroform or carbon tetrachloride are
unsuitable because of their combustion characteristics, and so is benzene owing to its
toxicity (women are prohibited from using benzene for routine analysis in the USSR).
Suitable solvents for flame atomic-absorption are methyl isobutyl ketone (MIBK) or butyl
acetate.   The system of ammonium pyrrolidinedithiocarbamate (APDTC) and MIBK is of great
importance for group extraction of trace elements;   many methods for the analysis of waters
and biological and other materials have been developed with use of this system.   Typically(95)
lead and cadmium are extracted directly from wine;   sugars and acids contained in the wine
are not extracted.

Instead of APDTC, hexamethyleneammonium hexamethylenedithiocarbamate(VII) has been successfully
used.
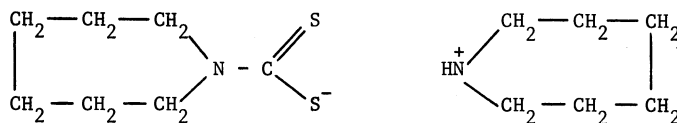
VII

The reagent is synthesized from haxamethyleneimine which is a byproduct of nylon production
and readily available(96).   Several methods have been developed with use of this reagent,
for example for determination of Co, Cu, Fe, Mn, Ni, Pb and Zn in sea-water(97).

Devices for automatic extractive concentration have been developed, and in particular the
Technicon instruments allow work with up to 60 samples per hour(98).   Automatic extractive
concentration has also been combined with a six-channel atomic-fluorescence
spectrophotometer(99).   The so-called "injection" method for atomic-absorption determination
of small amounts of matter and for the analysis of concentrates is also useful(100).

Some atomic-absorption methods for trace elements in various materials have been developed
in our laboratory (Table 6).   The combination of extraction and atomic-absorption has been
considered in more detail elsewhere(8,105).

<u>X-Ray fluorescence analysis</u>   In this case, group concentratration, and more rarely individual
concentration, is used and the concentrate should preferably be a solid which can be analysed
directly.   Otherwise, several operations must be successively performed.   Thus for example,
extracts are often decomposed and the trace elements sorbed on cellulose powder or silica
gel carrying functional groups.   It is more convenient to do the extraction with low-melting
reagents at increased temperature.   In this case, the solidified concentrate may at once be
pressed into a tablet and analysed.   Leyden(43-45) used the sorption of trace elements on
silica gel or glass pellets with reagents immobilized by silylation for the analysis of water.

TABLE 6. Examples of atomic-absorption methods for trace elements
          after extraction concentration

Trace elements determined	Material analysed	Main extraction reagent	Detection limit ppM	References
Ag	Rocks,ores,concentrates	Diphenylthiourea	0.01	20
Ag,Cu,Tl	Metal halides (chemicals)	Diphenylthiourea	0.001 – 0.1	20
Ag	Rocks,ores,minerals	Triphenylphosphine	0.01	15
Au	Minerals, cyanide solutions	Triphenylphosphine	1	14
Cu,Fe,Mo,V,Zn	Titanium tetrachloride	Trioctylamine	0.02 – 0.2	101
Bi,Cd,Cu,Pb, Sb,Sn,Zn	Steel	Trioctylamine	0.1 – 1	102
Fe	Sodium and potassium halides	Dithizone,sodium tetraphenylborate	–	103

Spectrophotometric determination   Combinations of concentration, especially extractive, with
spectrophotometry in the visible and ultraviolet regions are widely known.   Individual
concentration steps or successive separations of several elements are usually used.   The
matrix is very rarely separated in this case.   Most frequently, the reagent used for
concentration also gives a coloured complex with the element to be determined.   However, two
reagents may also be used: first, the most selective reagent is used for the separation and
then,for the determination, a reagent which may not be selective but is the most suitable for
the photometry is employed.   The second reagent may also be added after back-extraction or
mineralization of the extract.   The concentration of Cu, Zn, Cd, Hg, Mn and Ni as their
complexes with 1-(2-pyridylazo)-2-naphthol (PAN) by use of a transparent membrane consisting
of poly(vinyl chloride), tricresyl phosphate and PAN is of interest(106).   The membrane is
placed in the solution being analysed, taken out, washed, dried and measured photometrically.
The absorbance of the membrane depends on the metal concentration.   Some extraction-
photometric methods developed in the Vernadsky Institute are given in Table 7.

TABLE 7.   Some extraction-photometric methods

| Trace element determined	Reagent	Solvent	Materials analysed	Detection limit,ppM	Reference
Hg	Astraflocsin FG	Benzene	Zinc,cadmium;waters	0.01 – 20	107
Cd	1,4-Dimethyl-1,2,3-triazoline-(3-azo-4)-N,N-dimethylaniline	Mixture of benzene and cyclohexanone	Zinc sulphate,oxide; zinc metal	5 – 14	108
Co	Acid Monochrome Green S	Butanol	Gallium metal	0.1 – 5	109
Nd	1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5,5,7-dibromo-8-hydroxyquinoline	Chloroform	Lithium niobate	–	110
Si	Trioctylamine(as molybdosilicate)	Chloroform	CdSiAs$_2$	–	111
Al	Salicylal-o-amino phenol	Tributyl-phosphate	Sodium iodide, Mohr's salt	0.01 – 1*	112
Au	8-Mercaptoquinoline, trichloroacetic acid	Chloroform	Aluminium nitrate, nickel metal	0.01 – 0.1	113

* Fluorimetric determination

Spark-source mass-spectrometry   In our laboratory preconcentration has been used in a new combination with this technique.   After separation of the matrix, trace elements are collected on high-purity alumina as a collector.   For the separation of traces, we have used solvent extraction.   In a method for analysis of steel(114), eight elements were extracted with MIBK from iodide solution, then back-extracted with a dilute solution of sulphuric acid containing hydrogen peroxide;   the solution obtained was evaporated in the presence of Al_2O_3.   After ignition, the concentrate was analysed with a mass spectrometer.   A similar method has been developed for the determination of impurities in sulphuric acid.   Another variant was suggested for the determination of traces of noble metals in natural and industrial materials(115).   The noble metals were extracted as complexes with hexamethylenephenylthiourea from hydrochloric acid solution containing copper and other non-ferrous metals, copper being extracted simultaneously as copper(I).   The extract was evaporated and ignited, as a result of which a concentrate on copper oxide was obtained which was then analysed.   Copper does not interfere with the determination.

With spark-source mass-spectrometry it is possible to determine very small quantities of at least $60 - 70$ elements, and therefore it is expedient to use it with concentration methods based on removal of the matrix.

Neutron-activation analysis   There are two distinct ways of trace concentration in this method: before irradiation and after it.   Separation of the matrix before irradiation is necessary if it is strongly activated and the radioisotopes formed have long half-lives. In the concentration, trace components which are strongly activated (but are not to be determined) may also be separated.   However, concentration before irradiation nullifies one of the main advantages of activation analysis – that a blank correction is unnecessary.   This advantage is still valid, however, in the case of concentration after irradiation.   In analytical practice, both variants are used but the second more frequently.

Electrochemical methods of analysis   Again there are two main ways of using preconcentration. The first is electrochemical stripping analysis.   Trace elements are first concentrated electrochemically on a solid or mercury electrode, then determined during anodic dissolution. In the case of cations, a metallic precipitate may be obtained on the electrode which may, for example, be a glassy carbon electrode which is chemically stable and mechanically firm. In the determination of anions, one concentration method used consists in the formation of a film of a sparingly soluble compound of the electrode material (e.g. silver) with the anion concerned.

Toropova et al. at Kazan University have shown that oxidation – reduction reactions between the compounds of the elements being determined and metallic mercury may be used for concentration of trace amounts.   The reactions occur on the surface of a mercury drop without its external polarization.   For example, some selenium and tellurium compounds are involved in reactions of the type:

$$H_2SeO_3 + 4Hg + 4HCl \rightarrow Se + 2Hg_2Cl_2 + 3H_2O \ .$$
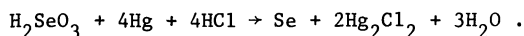
The reactions are possible owing to the change in the formal oxidation – reduction potentials of the corresponding systems.   The value of the electrodissolution current of the reaction products during the subsequent cathodic polarization of the stationary mercury microelectrode may be used as an analytical signal for the determination of the elements concentrated.

Polarography of extracts containing trace elements is another possibility.   Before the polarographic determination, a background electrolyte and a solvent-homogenizer, for example methanol, are introduced into the extract.   Such a combination accelerates the analysis as it eliminates the necessity to decompose the extract or to use a back-extraction.   Besides that, the selectivity of the polarographic determination reinforces the selectivity of the extractive concentration.   For example, we have worked out a method of determining an alloying indium additive in a complicated semiconductor $CdSiAs_2$(116).   Indium is extracted as its chelate with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 at pH 1.2 into chloroform. Cadmium and arsenic do not affect the indium extraction.   Ammonium bromide in methanol is used as supporting electrolyte.   Vydra(117) in Czechoslovakia and Pyatnitsky(118) in the USSR have made a series of such investigations.   The first review of extractive-polarographic methods was published by Kuzmin, Zolotov and Karbainov in 1967(119);   there are now several such reviews.

"Double" concentration, as used by Karbainov at the Tomsk Polytechnical Institute, is interesting(120).   It combines extractive concentration with subsequent electrochemical concentration on an electrode.   In this variant, both the techniques mentioned above are combined.

CONCENTRATION IN THE ANALYSIS OF PARTICULAR MATERIALS

It is desirable to consider briefly how concentration is used in the analysis of some important materials.   Concentration is especially widely used for analysis of high-purity

materials, natural waters and geological samples.

High-purity substances   In analysis of these the demands on purity of air, apparatus, reagents, etc. are particularly rigorous.   Sometimes, concentration methods which require no reagents are preferable: thermal evaporation of the matrix, crystallization techniques, etc.   The history of the pure materials should be taken into consideration when a concentration method is chosen: as a rule, the concentration method must be different from the method which was used for purification of the substance.

The problem of the blank is of special importance in the analysis of pure materials. Generally, this is determined by using the same conditions and quantities of reagents as for the concentration procedure, but without introduction of the material being analysed.   A correction for the blank is applied to the result of the analysis.   Such a blank experiment is often carried out but it is not always correct.   The degree of contamination and losses of trace elements may not be the same in the presence of the sample as in the blank experiment. Moreover, a residue of matrix in the sample concentrate may change the conditions for trace determination in comparison with the concentrate from the blank experiment, where such a matrix residue is absent.   Ways have been suggested for over-coming this contradiction, but they will not be discussed here.   It is sufficient to mention that they are based on the use of various weights of samples.

Tölg's opinions and experience(6,7) in eliminating and diminishing errors connected with preconcentration are of interest.   He suggests a close combination of decomposition, concentration and detection, in both time and space, preferring to use a single closed vessel. The use of micro and ultramicro techniques is also useful.

In the analysis of high-purity materials, various methods of concentration and combinations with determination methods are used.   In the USSR, chemico-spectrographic techniques are of great importance; extractive photometric methods are also extensively applied.

Natural waters   These form another important group of samples for which concentration is widely employed.   Without going into detail, we can emphasize the significance of the chemical state of trace elements in water (speciation) which is not always taken into consideration.   Very often, trace elements are present in water as soluble compounds with organic substances of both natural and technological origin and also as colloids.

In the analysis of sea-water, it is of importance to acidify the water directly after sampling, and to store and transfer the samples in polyethylene or Teflon bottles.   Some methods allow direct concentration of trace elements without preliminary treatment of the water, e.g. Cu, Co, Zn, Mn, Cd and In may be extracted as their complexes with hexamethyleneammonium hexamethylenedithiocarbamate by butyl acetate without any pretreatment. However, descruction of the compounds originally present is usually required.   The water is treated with oxidizing agents such as persulphate.

In the analysis of fresh surface water, this problem is more important.   Complex formation of metal ions with humic and fulvic acids and other organic substances present in the water very strongly affects the recovery during concentration of trace elements by solvent extraction, sorption or co-precipitation.   Quantitative concentration is usually possible only after preliminary destruction of these organic substances.

CONCLUSION

Finally it should be emphasized that the problems of analytical preconcentration have not been fully considered in this review.   Accuracy and precision of analysis and the effect of concentration on these characteristics, the control of concentration efficiency, the proper description of concentration methods, etc. were not discussed.

There are still significant problems to be solved.   Among these are the automation of preconcentration, its closer combination with decomposition of the sample and final determination of trace elements, and the development of new simple and rapid concentration methods needing no reagents.

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