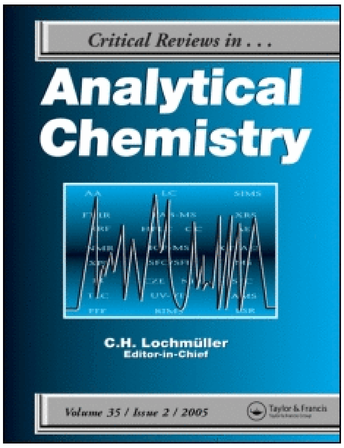

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MULTIELEMENT CONCENTRATION FOR TRACE ELEMENTS

Author: **K. Bächmann**
Department of Inorganic and Nuclear Chemistry
Technical University
Darmstadt, Federal Republic of Germany

Referee: G. Tölg
Laboratory of High Purity Materials
Max Planck Institute of Metal Research
Schwäbisch Gmünd, Federal Republic of Germany

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I. INTRODUCTION

In order to avoid misunderstanding, it is necessary to give clear definitions about the three terms used in the title: "multielement", "trace element", and "concentration".

It is difficult to give a definition for the term "multi" as is used in analytical chemistry, but in this paper we will use it for cases where at least more than two elements are to be determined. The determination of several trace elements in one sample is of growing interest due to the development of new fields. In multielement analysis one can differentiate between a "sequential analysis", which means that each single element is determined using the most suitable method, or a "simultaneous analysis" where all the elements are determined at the same time with one method. In the first case one uses enough "sample volume" or "amount" which is high enough for a number of analyses. In the second case the determination is less time-consuming, but the method which is chosen cannot be optimized for all the elements which are of interest.

Table 1 lists some of the fields and matrices for which the analysis of a number of elements is either necessary or at least advantageous. The matrices 1 to 3 are characteristic examples for high-purity materials. It is possible to differentiate between examples where the concentrations of all trace elements are important (for example, HNO_3) since the supplier does not know which trace elements might interfere in the user's problem, and examples where only the concentration of certain elements are important.

In the case of trace elements in wave guides, they are the only elements of interest which absorb the light of the wavelength which is used. In pure aluminum elements which change, the electrical conductivity might be of interest. In environmental studies especially, trace elements with toxic properties are of interest. However, in some cases when correlation studies are carried out, it is necessary to determine in air, for example, such elements as Na and Cl which could be produced by sea water or Br which is probably from automobile exhaust and is correlated with Pb levels. Furthermore, in environmental studies an elemental analysis is not satisfying, since the toxicity is strongly dependent on the species.

In cases 10 and 11 it is useful to determine trace elements which are characteristic for a substance in order to identify objects by pattern analysis. Table 2 shows that the term "trace analysis" in connection with multielement analysis has to cover a rather broad range from fg to mg. However, since this review article deals with the "concentration" of trace elements, it can be assumed that low amounts of traces play a more important role because high amounts can often be determined by pure instrumental methods without any concentration step. A multielement concentration would be much easier when elements with similar chemical behavior should be separated, but a property as light absorption or toxicity is in most cases not correlated with similar chemical behavior.

The term "concentration" needs a more extensive discussion. Concentration can be relative or absolute. Absolute concentration is the decrease of the mass of the sample, e.g., by evaporation or by extraction into a small volume of an organic phase from a large volume of aqueous phase. Relative concentration does not necessarily mean only a decrease of mass or volume, but an increase in the mass ratio of the trace elements to the main components (e.g., using coprecipitation with $Fe(OH)_3$ as a separation step for Co

Table 1
EXAMPLES FOR MULTIELEMENT TRACE ANALYSES

Field	Matrix	Trace elements	Detection range
Pure substance	e.g., SiO_2	Ti, V, Cr, Mn, Fe, Cu, Ni, Co	1—10 ng/g
Pure substance	Al	Zn, Cd, Fe, Ni, Co, Zr, Hf, Ta	ng/g—μg/g
Pure substance	HNO_3	Cl^-, NO_3^-, SO_4^{2-}, Ag, Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sn, Sr, Ti, Tl, V, Zn, Zr	10 ng/g—0.5 μg/g
Uptake of trace Elements in plants	Biological sample	Na, K, Cs, Rb, Ca, Sr, Ba, Fe, Co, Ni, Mo, Se, As, Sb, Cr	pg/g—mg/g
Clinical diagnosis	Biological sample	Co, Cr, Ni, Fe, Pb, Cd, Mo	fg/g—μg/g
Geochemistry (prospection)	Water, rock, or soil	U, Mg, Ca, Mn, Ni	pg/g—mg/g
Environmental study (air chemistry)	Aerosols	Pb, Cd, Hg, Fe, Cr, Ni, Cu, Na, Cl	$\mu g/m^3$
Water analysis	Water	Pb, Cd, Hg, Ni, Se, As	pg/g—μg/g
Food analysis	Biological sample	Pb, Cd, Hg, Ni, Se, As	pg/g—μg/g
Forensic chemistry	All types	Cr, Ni, V, Fe, Cu, Zr, K	pg/g—μg/g
Archaeology	e.g., ceramics	Na, Ca, Fe, Ti, Al, Mn, Mg	μg/g—mg/g
Radio ecology	Water, air, biological samples	Cs-137, Pu-239, J-131, Sr-9o, Ra-226, etc.	fCi—μCi

Table 2
CLASSIFICATION OF CONCENTRATION FOR TRACE ELEMENTS ACCORDING TO INITIAL AND SECOND PHASE

Initial phase	Second phase	Method of concentration
Solid	Gas	Evaporation of trace elements or matrix elements; volatilization by reaction with a reactive gas
Solid Liquid	Gas	Gas chromatography
Liquid	Liquid	Solvent extraction of trace elements or matrix elements
Liquid	Liquid	Extraction chromatography
Liquid	Solid	Sorption of trace elements or matrix
Liquid	Solid	Precipitation and coprecipitation of trace elements or matrix
Liquid	Solid	Electrolytic deposition of trace elements or matrix
Liquid/solid	Liquid/solid	Selective dissolution of trace elements of matrix

from Na will not necessarily change the mass, but the ratio Co/Na will increase so that this is a relative concentration of Co to Na). Relative concentration is always connected with a separation step. In many cases, for example, extraction, it is possible to simultaneously carry out an absolute concentration. Concentration can be expressed by the concentration coefficient K:

$$K = \frac{m_{IE}}{m_M} \Big/ \frac{m^o_{TE}}{m^o_M} \qquad (1)$$

where m_M and m^o_M are the amounts of matrix before and after concentration and m_{TE} and m^o_{TE} are the amounts of trace element before and after concentration. The reciprocal value $1/K = S$ is defined as separation coefficient

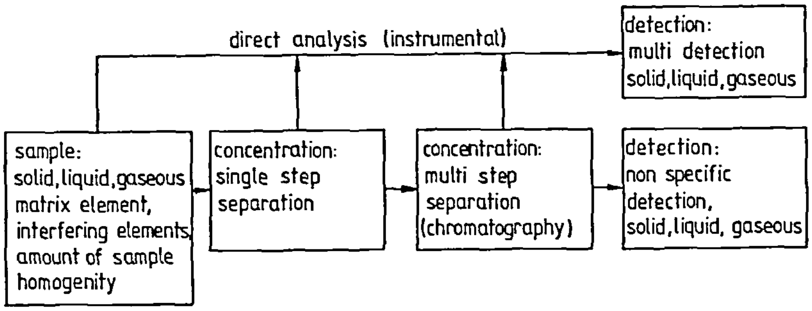


FIGURE 1. The correlation between sample, concentration, and detection method.

$$S = \frac{m_M}{m_{TE}} \bigg/ \frac{m_M^o}{m_{TE}^o} \qquad (2)$$

If only part of the matrix is removed, the term "enrichment" is used.

Depending on the reason for the separation and on the detection method, the S or K values which are desirable are quite different. Extreme cases are the complete removal of the matrix elements, whereas all the trace elements of interest are left. Another extreme case is the complete separation of several single trace elements. In most practical analyses, especially in multielement analyses, it is desirable to carry out group separations or concentrations which are just enough for the required aim (determination of a number of elements with a tolerable error). The sample form, the preconcentration, and the detection method have to be viewed as a unity. In Figure 1 the correlation between sample concentration and detection method is shown schematically. A given sample form or amount requires certain concentration techniques, and the concentration techniques are advantageously connected with certain detection methods.

As long as an analysis is possible without systematic errors, one will choose a direct method. Concentration is always time-consuming and complicates the analysis. Furthermore, there is a risk of loss of trace elements or of contamination with trace elements. Reagents of high purity and specially equipped laboratories increase the cost of analysis. Therefore, a decision to do a concentration will be taken only when a direct method is not possible. A number of reasons can be listed in favor of a concentration step. The most important reason for concentration is that the detection limit of the analytical method is higher than the concentration of the trace element in the sample. A very simple method could be followed, e.g., for liquid samples, with evaporation of the solvent.

A second reason for concentration is the interference by the matrix element or other elements. In this case, at least a relative concentration of the analyte to the interfering element is necessary, but most separations are connected with an absolute concentration also. Since the sensitivity of analytical instruments is improved every year, the interference of the matrix or other elements is becoming more important than the first reason of a detection limit (which is too low). It is not possible to make any precise statements about the concentrations of the matrix or major contituents which cause interference. When the interference is due to spectral reasons, e.g., the overlapping of peaks or the tungsten background in X-ray fluorescence or the compton background in γ-spectroscopy, then it is possible to calculate for a given detection arrangement the maximum permissible concentration of the interfering elements. Interference which is due to chemical reactions (e.g., during the temperature program in the graphite tube of a flameless atomic absorption spectrometer) can only be measured and a limit of "interference concentration" determined, but it is not possible to extrapolate this result to another sample, since a third component might be involved in the chemical reaction so that the limit of interference is a function of several parameters. Concentration may also play a role in homogenization or in sampling of representative samples. If trace elements are nonhomogeneously distributed, e.g., in soil, rock, or plants, then a representative sample must be quite large. Since a large sample cannot be used for the determination, an aliquot has to be taken, which is only possible when the sample is completely homogenized. When small traces are to be determined, one will take advantage of the large sample and try to separate the trace element. In some cases homogenization is not possible before the sample has been fused or dissolved. Such a case is the determination of plutonium in soils. The plutonium adheres to fairly large particles so that by, milling and homogenizing 1 g of the sample, the plutonium level still might be tenfold times that in a second sample of 1 g. For such cases, the concentration step is simultaneously the step of homogenizing.

Another reason for a complete separation is the application of a sequential detection method in cases where only small amounts of the sample are available. For example, if emission spectroscopy with a scanning spectrometer is used, the trace elements should be separated by a chromatographic method in order to have time between the different elution times of the elements to change the wavelength.

A further important point in favor of a concentration step preceding the determination is an improvement in calibration. The closer that sample and reference materials are to being identicals the more accurate is calibration. This means for concentration that a complete separation without the presence of any other elements could be an optimum condition for using a calibration standard. On the other hand, the advantage of an easier and seemingly more accurate calibration might be outweighed by the disadvantage of possible losses during the concentration. Therefore, either the reference material has to be run through the same concentration procedure or the separation has to be 100%, or it is a reproducible and known factor, respectively. The most elegant method of determining the yield of a separation is the addition of radioactive-labeled elements and compounds.

The separation method may be classified into three main groups:

1. Separation of the trace elements (compounds) of interest
2. Separation of the matrix element (compound)
3. Separation of a major interfering element (compound)

A classification of concentration methods is possible according to different parameters, such as the type of process, the type of driving force, or the type of phases.

In Table 2 the different concentration methods are listed according to the initial phase and the second phase. An important point is the concentration or separation during the sampling procedure. Dry-ashing and freeze-drying is a concentration step in which the bulk of water is removed. In biological samples, the removal of water leads to a high absolute concentration. A further concentration is obtained by burning the organic components to CO_2 and H_2O. Dry-ashing at higher temperatures may cause an undesirable loss of volatile compounds or elements such as Hg, As, Sb, Br, I, Cl, etc. Furthermore, one must pay attention to the sorption of trace elements during the dissolution of a sample when part of the sample is not dissolved.

In the context of this review, it is not possible to go into details of the concentration which takes place during different sample procedures. It seems necessary, however, to draw attention to desirable and undesirable concentration during sample pretreatment.

In this review, it is not possible to give a complete summary of this rather extensive field. I will therefore try to present on one hand a summary of the state-of-the-art, and show the future trends by interpreting the newest developments.

II. CONCENTRATION METHODS

A. Extraction and Extraction Chromatography

Extraction is used most frequently as the concentration method. This method is quite simple and rapid and can be applied to many different problems as a selective separation, a group separation, or matrix separation. A great number of monographs, reviews, and papers were published in the last year.[1-7] This review will be restricted, therefore, to a very general survey; and to the consideration of the special problems which are involved in group separations (multielement analysis), the special problem of the determination of low concentrations, and the topic of extraction chromatography.

The major reasons for the rapid growth of interest in extraction methods for preconcentration is (1) its intrinsic simplicity and (2) time-consuming steps are avoided. When multielement analysis is necessary, the optimum conditions would be a separation of all the elements of interest from all interfering elements. This is possible only when elements which are chemically similar are to be analyzed. In the near future it should be possible in some instances, but not always, to use mixed complexing agents. Sachdev and West[40] and Sachdev et al.[41] employed an ethyl propionate solution of diphenylthiocarbazone, 8-hydroxyquinoline, and pentane-2,4-dione for the extraction of aluminum, beryllium cadmium, cobalt, copper, iron(II), lead(II), nickel, silver, and zinc. Frei et al.[85] developed a multielement extraction system for cadmium, cobalt, copper, nickel, and zinc in water samples based upon picolinaldehyde, 2-quinolylhydrazone, and 3-methylbutane-1-ol. With the knowledge of more equilibrium constants and kinetic data as a function of all parameters which are important for extraction, it should be possible in the near future to mathematically devise an increasing number of mixed systems which are suitable for a given analytical problem. One of these calculations is given by Bajo[43] about the optimal experimental conditions for liquid-liquid extractions with diethyldithiocarbamic acid. Since a great number of equilibric constants have been determined, it seems to be fruitful to carry out more optimization calculation in order to start a simplifying of the available extraction literature. In many cases it is enough to separate only the matrix or some interfering elements using a high-capacity extracting system.

An important point for the choice of the extracting phase, usually organic, is the detection system. For example, when atomic absorption or atomic emission in a flame is used, the nebulizing properties are extremely important. A very high volatility solvent (as with diethyl ether) has the disadvantage that uncontrolled loss due to the high vapor pressure may occur. A second point connected with the choice of the detection system is the enhancement effects compared with the aqueous solution. Most of the extensively used organic solvents give a reduction in mean droplet diameter, which in turn leads to improved atomization efficiency. Guto and Sudo[42] have, therefore, concluded that the number of concomitant elements which may be tolerated is larger in organic solvents than in aqueous solutions.

It is possible to differentiate extractions based on chelate complexes, ion-association complexes, and the extraction of molecules.

Table 3 summarizes the most important traditional chelating reagents (e.g., dithiocarbamates, dithizone, acetylacetone, 8-hydroxyquinoline), together with some newer and promising reagents. There are a great number of parameters which influence the extraction such as the organic phase, the pH-value, and other ions which are present (e.g., by salting effect and masking agents — EDTA, SCN^-, $S_2O_3^-$, F^-, CN^-, tartrate,

Table 3
CHELATING AGENTS FOR CONCENTRATION OF TRACE ELEMENTS BY EXTRACTION

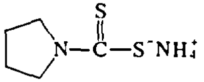
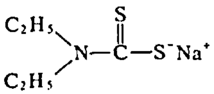
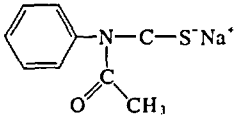
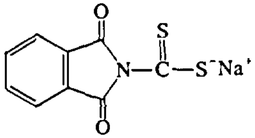
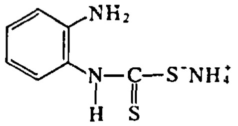
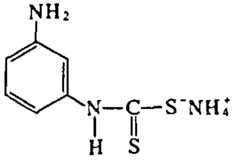
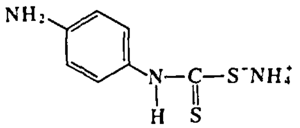
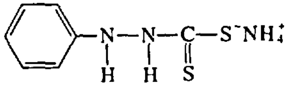
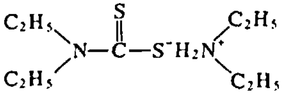
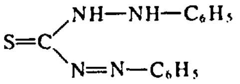
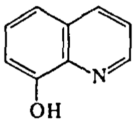
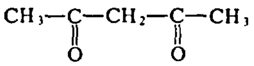
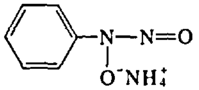
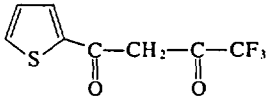
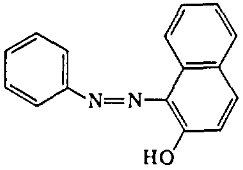
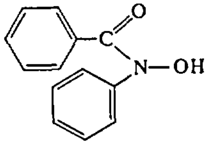
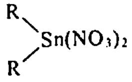
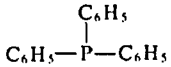
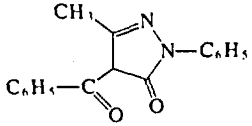
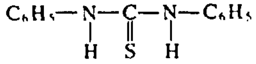
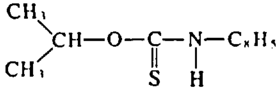
Common or abbrev	Chemical name	Formula	Elements which are extracted (more than 50% are extracted)	Organic phase	Ref.
APDC	Ammonium pyrrolidine dithiocarbamate ammonium-tetramethylen-dithiocarbamate		V, Cr, Fe, Cs, Ni, Cu, Zn, Ga, Ge, As, Nb, Mo, Tc, Ru, Rh, Pd, Ag, In, Sn, W, Re, Os, Ir, Pt, Au, Hg, U	$CHCl_3$, CCl_4	1, 2 8—12
NaDDC	Sodium diethyldithio-carbamate		Ti, V, Cr, Mn, Fe, Co, Ni Cu, Zn, Ga, As, Se, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, W, Au, Hg, Tl, Pb, Bi, U, Pu	$CHCl_3$, CCl_4	13—16, 57, 58, 82
Na-N, N′-ph acetyl-DC	Sodium-*N*, *N*′phenyl-acetyl-dithiocarba-mate		V, Mn, Fe, Cs, Ni, Cu, Zn, As, Se, Mo, Ru, Rh, Rd, Ag, Cd, Sb, Te, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	8
Na-N, N′-ph C	Sodium-*N*, *N*′-phtalyl-dithiocarbamate		Fe, Cr, Ni, Cu, Zn, As, Se, Mo, Rh, Pd, Ag, Cd, Sn, Sb, Te, Pt, Au, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	8
NH_4-*o*-amin yl- DC	Ammonium-*o*-amino-phenyl dithiocarbamate		Cr, Mn, Fe, Co, Ni, Sn, Zn, As, Se, Mo, Pd, Ag, Cd, In, Sn, Te, Ir, Pt, Au, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	17
NH_4-*m*-ami yl- DC	Ammonium-*m*-amino-phenyl-dithiocarbamate		V, Cr, Fe, Co, Ni, Cu, Zn, Se, Mo, Pa, Cd, In, Sn, Te, Ir, Pt, Au, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	17

Table 3 (continued)
CHELATING AGENTS FOR CONCENTRATION OF TRACE ELEMENTS BY EXTRACTION

Common na abbreviati	Chemical name	Formula	*Elements which are extracted (more than 50% are extracted)*	Organic phase	Ref.
NH_4-*p*-aminoph DC	Ammonium-*p*-amino-phenyl dithiocarbamate		V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Pd, Ag, Cd, In, Sn, Te, Ir, Pt, Au, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	17
NH_4-anilino DC	Ammonium-anilino-dithiocarbamate		V, Fe, Co, Ni, Cu, Zn, Mi, Pd, Ag, Ca, In, Sb, Te, W, Ir, Pt, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	18—21
DADC	Diethyl-ammonium-diethyl-dithio-carbamate		V, Cr, Mn, Fe, Co, Zn, Ga, Ge, As, Se, Mn, Pd, As, Cd, In, Sn, Sb, Te, W, Pt, Hg, Tl, Pb, Bi	$CHCl_3$, CCl_4	18—21, 34, 35
Dithizone	Diphenylthiocarbazone		Mn, Fe, Co, Ni, Cu, Zn, Ga, Pd, As, Cd, In, Sn, Te, Pt, Au, Hg, Tl, Pb, Bi, Po	$CHCl_3$, CCl_4	13, 24, 27, 33
Oxine	8-Hydroxiquinoline		Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Aq, Cd, In, Sn, Sb, Ba, La, Hf, W, Hg, Tl, Pb, Bi, Ce, Nd, Sm, Er, Th, Pa, U, Pu	$CHCl_3$, C_6H_6-toluene	1, 31
ACAC	Acetylacetone	 $CH_3-\underset{\underset{O}{\parallel}}{C}-CH_2-\underset{\underset{O}{\parallel}}{C}-CH_3$	Be, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Zr, Mo, Ru, Pd, In, Sn, Hf, Hg, Tl, Pb, Bi	Acetylacetone, benzene, acetylacetone, $CHCl_3$	25, 28, 29
Cupferron	Ammoniumphenyl-nitrosohydro-xylamine		Ti, V, Fe, Co, Cu, Al, Ga, Nb, Mo, Pd, Fn, Sn, Sb, Pb, Bi, Co, Th, Pa, U	$CHCl_3$, MIBK, ethylacetate	32

TTA	Thenoyltrifluoroacetone		Be, Al, Ca, Sc, Cr, Mn, Fe, Ga, Ni, Cu, Sr, Y, Zr, Mo, Pd, In, Sn, Cs, La, Hf, W, Pt, Tl, Pb, Bi, Po, Ce, Eu, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm	CCl_4	26, 38
PAN	1-(2-Pyridylazo)-2-naphtol		Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Rh, Pd, As, Cd, In, Sn, La, Ir, Pt, Hg, Pb, Bi, Co, En, Th, U	$CHCl_3$	33, 37
BPH	*n*-Benzoyl-*n*-phenyl-hydroxylamine		Be, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Ge, Y, Zr, Nb, Mo, In, Sn, Sb, La, Hf, Ta, W, Re, Hg, Tl, Pb, Bi, Co, Nd, Th, Pa, U, Pu	$CHCl_3$, benzene	30
	Dialkyltin dinitrates $R = C_8H_{17}, C_9H_{19}$	 $R_2Sn(NO_3)_2$	PO_4^{3-}, AsO_4^{3-}, SeO_4^{2-}, SeO_3^{2-}		47
	Triphenyl phosphine	 $(C_6H_5)_3P$	Ag, Au		23, 48, 49
	1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5		Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, Cm, Eu	$CHCl_3$/ethanol	x 36, 50, 51
	Diphenylthiourea	 $C_6H_5-NH-C(=S)-NH-C_6H_5$	Ag, Au, Pd, Pt, Ru, Rh, Ir, Cu, Tl		22, 52—54
	O-Isopropyl-*N*-ethylthiocarbamate		Ag, Hg, Pt, Pd	$CHCl_3$	x 55, 56

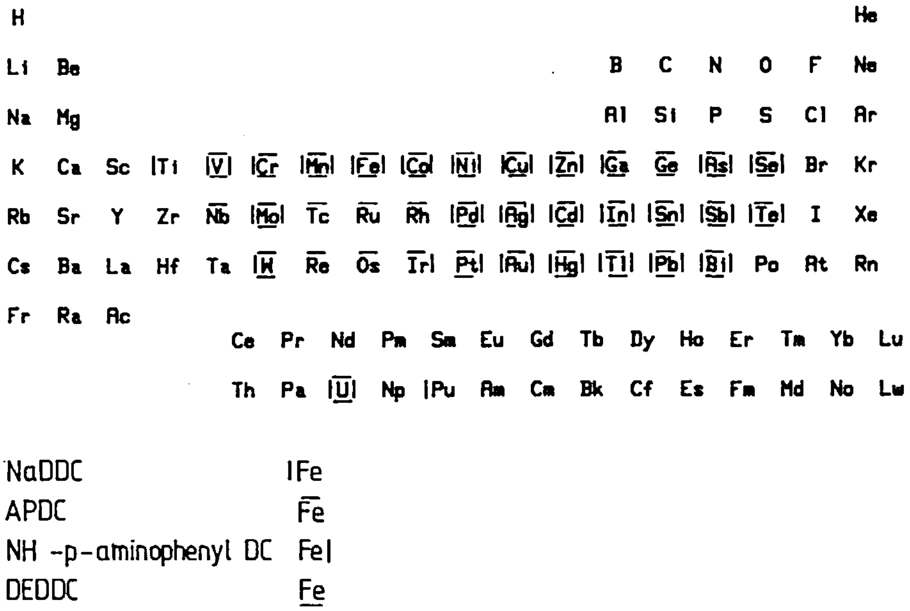


FIGURE 2. Extraction of trace elements with dithiocarbamates.

citrate). Although the traditional reagents have been investigated very extensively, there is still work going on with these reagents, which is partly due to the fact that the number of parameters is so high and all analytical problems are different.

One of the main requirements is that the matrix is not extracted itself. Figures 2 to 4 show that in most of the samples, no interference by the matrix element occurs when alkaline or alkaline earths are the matrix elements or in the analyses of water, acids, and biological systems. Figures 2 to 4 demonstrate only in a qualitative way which elements are extracted. Since there is always a large excess of the matrix element, it is possible that after one extraction step the absolute amount of the matrix element is still higher than the absolute amount of the trace elements, even if the extraction coefficients differ by a factor of 100.

In multielement analysis it is often interesting to determine all trace elements in a sample — for example, in biological samples or pure materials. In this case it is interesting to extract all trace elements, with the exception of the matrix elements. Figures 2 and 3 show that the use of chelating agents extracts most of the metals. APDC is the most comprehensive, that is, the least selective, reagent. Any additional selectivity which might be desirable can be obtained by controlling the pH-value, the organic phase, masking agents, etc. Since a great number of extraction procedures are worked out for molecular absorption or for atomic absorption of one single element, special highly selective methods have been investigated. Table 4 lists the extracting systems in which metal-solvent complexes are formed with organic compounds.

Figure 5 summarizes the elements extractable with organic compounds, which form complexes (as lewis-base) with the metal cation (as a Lewis acid). In some cases, the formation of ion association complexes plays a role (amines). From the point of view of selectivity, this class of extracting compounds is comparable to the chelating complexes.

Ion-association extraction procedures are capable of extracting higher absolute weights of metal ions in small volumes of solution than in organic chelate extraction procedures. Therefore, it is frequently possible to undertake the extraction of the bulk

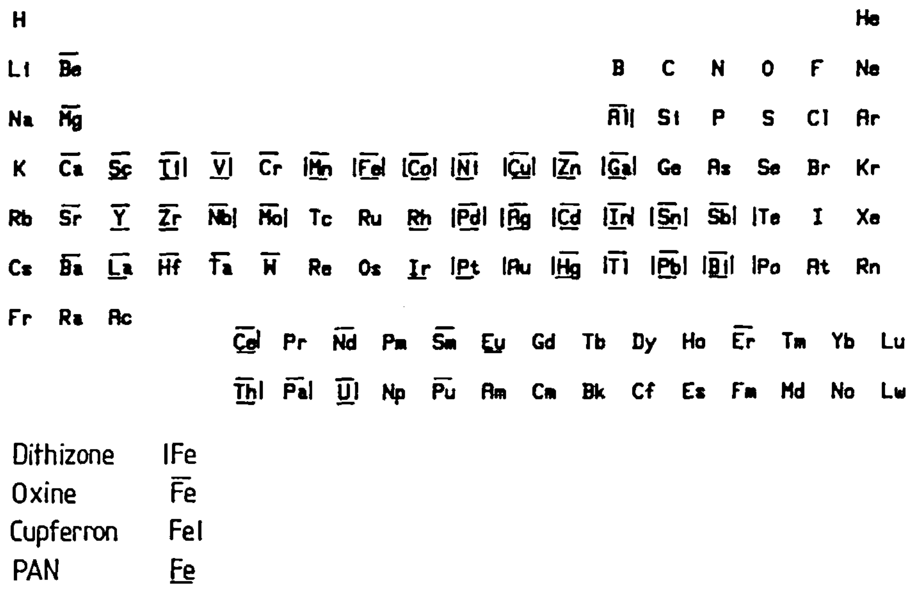


FIGURE 3. Extraction of trace elements with dithizone, oxine, cupferron, and PAN.

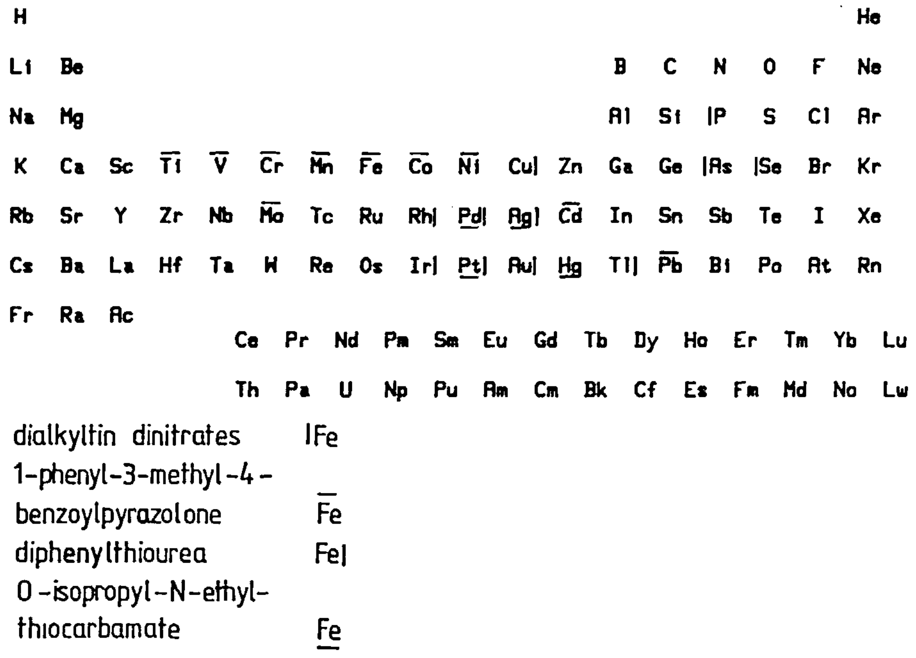


FIGURE 4. Extraction of trace elements with dialkyltin dinitrates, 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5, diphenylthionrea, and D-isopropyl-*N*-ethyl-thiocarbamate.

matrix elements and to leave the analyte elements in the original aqueous solution. This is a typical relative concentration step, but not an absolute concentration step.

Metal chelates are less convenient for the purpose of matrix extractions. One of the new reagents is *O*-isopropyl-*N*-ethylthiocarbamate.[44] The reagent is liquid, missible with

Table 4
EXTRACTION OF THE METAL CATIONS AS METAL-SOLVENT COMPLEX

Solvent	Organic phase	Aqueous phase	Elements	Ref.
tri-isooctylamin	tri-isooctylamin/xylene	1—8 n HCl, HNO_3, H_2SO_4	Hg, Au, Bi, Cd, Ga, In, Nb, Os, Pa, Re, Pt, Tc, Te, U, V, Zn, Np, Pu	59
tri-*n*-butylphosphate (TBP)	TBP, TBP/benzene, TBP/hexane, TBP/isooctane,	1—8 n HCl or HNO_3	Au, Fe, Ga, Ge, Hg, In, Mo, Nb, Pa, Re, Sb, Sc, Ta, Tc, Te, Tl, U, V, W, Zn, Cr, Np	60—62, 94
di-2-ethylhexyl-phosphoric acid (D2EHPHA)	0.75 m D2EHPHA/ petrolether	1—11 n HCl, HNO_3	As, Fe, Ga, Ge, Hf, Mo, Nb, Os, Sb, Sc, Ta, Ti, W, Y, Zr, R.E.	65
tri-*n*-octylphosphinoxide (TOPO)	5% TOPO/tuluene TOPO/4-methyl-pentane-2-one	1—8 n HCl, HNO_3	Au, Bi, Cr, Fe, Hf, Hg, In, Mo, Nb, Os, Sn, Tc, Th, Ti, U, V, Zn, Zr, Sb	63, 66, 79
di-*n*-butyldithio-phosphoricacid (DBDTPA)	0.2 m DBDTPA/CCl_4	1—6 n HCl, H_2SO_4	Ag, Au, Bi, Cd, Cu, Hg, In, Pb, Pd, Se, Tl, Zn	62, 67, 68

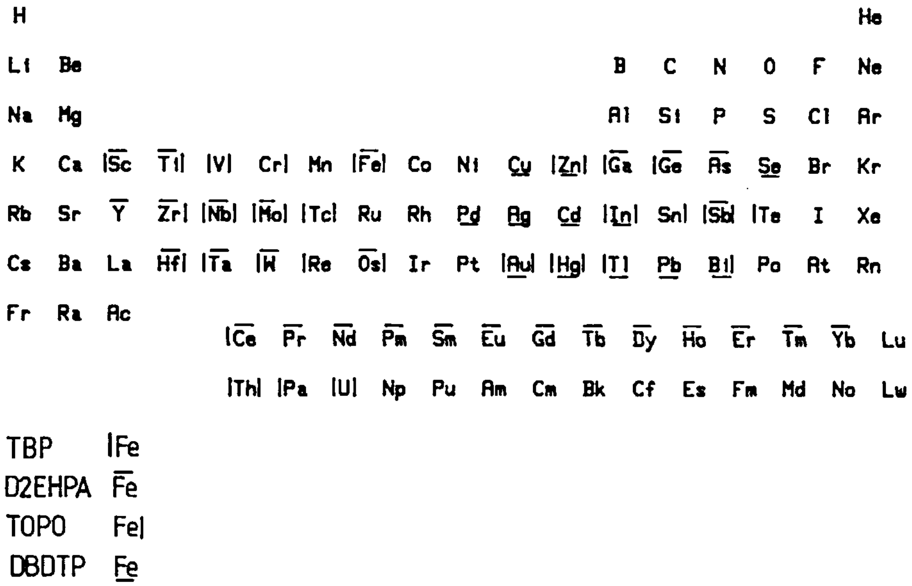


FIGURE 5. Extraction of trace elements with TBP, D2EHPA, TOPO, and DBDTP.

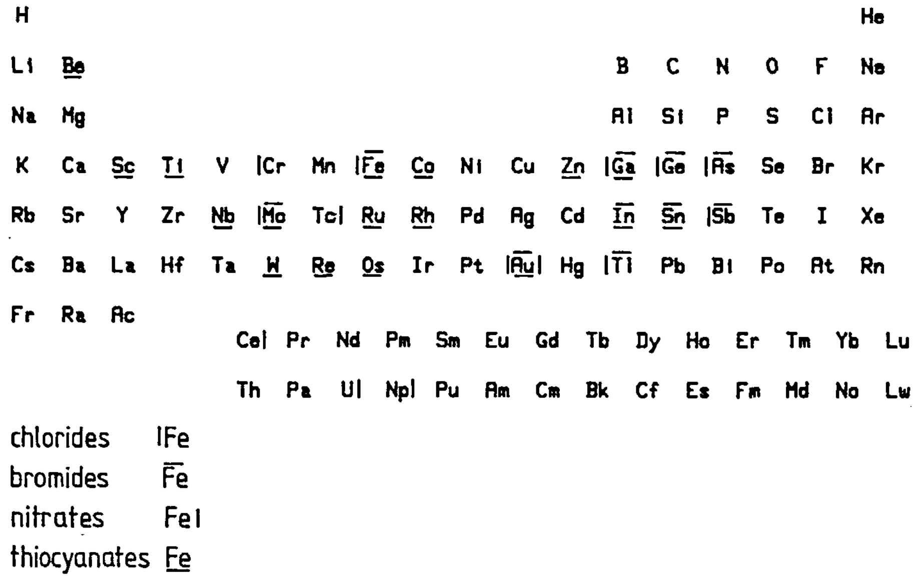


FIGURE 6. Extraction of trace elements as undissociated molecules (chlorides, bromides, nitrates, thioisocyanates).

organic solvents, and has high capacity. Silver is extracted very well. Mercury, platinum, palladium, and some gold are also extracted, whereas most of the other elements remain in the aqueous phase.

Figure 6 and Table 5 summarizes the extracting systems of undissociated molecules. These extractions are not very interesting for the extraction of many trace elements at the same time, since under given experimental conditions the number of extracted elements

Table 5
EXTRACTION OF UNDISSOCIATED MOLECULES

Group which is extracted	Organic phase	Aqueous phase	Elements	Ref.
Chlorides	Isopropyl ether, CCl_4 4-methylpentane, methylisobutylketone (MIBK) amylacetate, cyclohexanone	6 n HCl	Fe, Ga, Ge, As, Mo, Sb, Au, Tl,	64, 69, 70, 71, 80, 95
Bromides	Diethyl ether, benzene, diisopropyl ether	5 n HBr	Fe, Ga, As, Mo, In, Sn, Sb, Au, Tl	72, 73, 96
Iodides	Diethyl ether, benzene, isopentol,	6.9 n HI	As, Cd, Sn, Sb, Au, Hg, Tl, Bi	74, 81, 84
Fluorides	Diethyl ether	20 m HF	Nb, Ta, P, Ge, As, Se, Sb, Te	75
Nitrates	Diethyl ether	8 n HNO_3	Ce, U, Np, Au, Tc	76
Thiocyanates	Diethyl ether, 4-methylpentane-2-one	0.5 n HCl	Be, Sc, Ti, Fe, Co, Zn, Ga, Nb, Mo, Ru, Rh, In, Sn, W, Re, Os, Au	77, 78

Table 6
IMPURITIES IN AQUEOUS PHASES AND ORGANIC SOLVENTS USED FOR EXTRACTION ($\mu g/g$)[a]

Element	HCl	HNO_3	$NaOH$	EDTA	CCl_4	$CHCl_3$	$HClO_4$	Water
Al	0.01	0.005	0.05	0.3	—	—	—	<0.002
As	0.005	0.001	0.5	—	—	—	—	—
Ca	0.05	0.05	1	0.1	—	—	0.05	<0.0003
Cd	—	0.005	—	<0.2	—	—	0.005	<0.007
Co	0.005	0.—01	0.01	<0.1	—	—	0.01	0.02
Cr	0.001	0.07	—	<0.1	—	—	—	0.0002
Cu	0.005	0.005	0.01	0.02	0.01	0.01	0.005	<0.002
Fe	0.02	0.0μ	0.05	0.1	0.1	0.1	0.01	<0.0005
Mg	—	—	0.2	0.01	—	—	0.01	<0.0002
Mn	—	0.005	0.05	0.02	—	—	0.01	<0.0005
Mo	—	—	—	0.02	—	—	—	—
Ni	0.005	0.005	0.01	0.1	—	—	0.01	<0.0002
Pb	0.005	0.005	0.01	0.2	0.05	0.01	0.01	<0.003
Zn	0.005	0.005	0.05	2	0.05	0.05	0.005	<0.002

[a] Values from different producers of ultrapure reagents and from different publications.

is quite low — often only one element. However, this fact can be used for the removal of a large excess of the interfering matrix element. Thus the determination of trace metals in iron metal can be reached by extracting most (about 99%) of the iron from a 6 *M* HCl solution of the metal into ether. Many metals — for example, bismuth, aluminum, cadmium, cobalt, beryllium, lead, manganese, nickel, and silver—are not extracted and can be determined in the remaining aqueous phase.

There is also a lack of systematic investigations about the detection limits for different extraction systems depending, for example, on the natural background (Table 6) of elements in acids, organic solvents, masking agents, etc. Because the element detectability for many solvent extraction procedures (plus detection system) is very low, contamination and loss of trace elements are a severe problem. In the context of this paper, it is not possible to write about contamination during sampling and preparation of the sample. This is a general problem which is often very difficult to handle compared to the contamination in form of impurities in the reagents. Provided the complexing reagent is not itself excessively extracted into the organic solvent phase, it may be possible to remove impurities from salting-out reagents, buffers, and complexing reagents by a preliminary preextraction. This extraction does not help when impurities are in the organic phase itself. Redistillation may help to decrease the contamination level of the organic phase.

Another problem of extraction as a concentration step is the loss of trace elements from solution via adsorption on the walls of the sample container. Many reports of losses of elements have been published,[97] but it is difficult to make useful generalizations. The adsorption is a function of time, pH-value, composition of the solution, and surface properties. The treatment of a surface can change the properties considerably so that each surface has its own "history". In many cases "conditioning" means treatment of the wall container with a solution of similar composition to help avoid losses. A general survey of the problem of contamination and losses is given by Zief and Mitchell.[86]

Besides the natural background for example, wall effects may also play a role. It is important that, for very low concentrations, the extraction coefficients are not valid. A general rule for the limit of extraction is a concentration of 0.1 ng/mℓ. For example, it

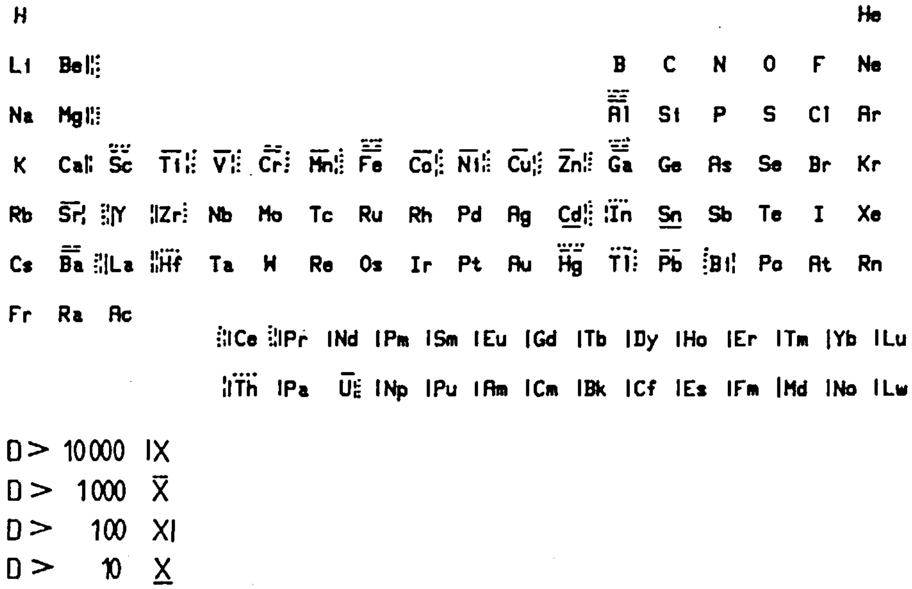


FIGURE 7. Distribution coefficients D for ion exchange between Dowex 50 W-X8 and 0.2 n HCl[108] (——), 0.2 n HNO_3[109] (---), and 0.2 n H_2SO_4[110] (···).

has been found that 2 ng Cr(VI) were extracted from 10 mℓ of 2N HCl with MIBK only at the 87% level, whereas 20 ng Cr(VI) are extracted under the same experimental conditions to a 96% level.[45] Similar results were found in an investigation of the extraction of cobalt. An evaluation and comparison of the different extracting agents can be carried out according to four parameters: the type of sample, the detection limits which are expected, the capacity which is necessary, and the detection method. For example, a high acid concentration (HCl or HNO_3) might be favorable for an extraction with TBP, whereas it is likely to destroy a chelating reagent. An adjustment of the pH-value is connected with an addition of further impurities, and dilution changes the absolute concentrations. After a fusion or charring process the sample normally is dissolved in an acid (HCl, HNO_3, $HClO_4$).

Table 6 summarizes impurities in aqueous phases and organic solvents. Since the type of acid, as well as the concentration for the dissolution, is not necessarily the most suitable acid for extraction of all elements, it might be necessary to use different aqueous phases (depending on the acid and the pH-value) and different extraction reagents or mixtures. In this case, it has been quite difficult to give more than approximate rules about the application of the different systems. Therefore, an analytical problem usually is tested more with a feeling than with a calculation of all the parameters and requirements.

In context with Figure 7, it has been discussed that in multielement analysis in certain cases a multistage separation — or even chromatographic separation (with several hundred of plates) — might be preferable. In this technique a column is packed with a solid support that holds an organic stationary phase. For the extraction, an aqueous phase is added with the analytes, and the separation takes place by a multistage extraction.

Extraction chromatography is important for three cases:

1. The determination of very low concentrations
2. The use of an unspecific detector
3. The use of an atomic spectrometer in a scanning mode

Sometimes the phases are reversed so that the aqueous phase is stationary, and elution is performed with an organic phase. Normally the stationary phase is more polar then the mobile phase; if the opposite is true, the process is called "reversed-phase chromatography".

Compared to modern, high-pressure liquid extraction chromatography of organic compounds, the state-of-the-art for separation of metal ions or anions is still far behind. However, the high separating power of extraction chromatography is illustrated by the separation of adjacent rare earths.[46]

A review of liquid extraction chromatography is given by Schwedt.[6] It must be differentiated between liquid-liquid partition chromatography and liquid-solid adsorption chromatography. The latter can be classified as well as sorption methods (Section II.B.2). We will summarize all liquid chromatographic methods with organic phases in this chapter and treat the liquid chromatographic methods with an aqueous mobile phase in addition to, for example, a chelate functional group as solid phase in Section II.B.2.

Another classification of methods is possible by the type of flow. The mobile phase can flow only by gravitational forces or it can be used as a forced or even high-pressure flow. The flow is determined by column dimensions, the grain size of the stationary phase, and the optimum time of a separation. The importance of liquid partition chromatography will increase with the development of high-efficiency columns and with new detection possibilities. The application of AAS and AES as detection systems in chromatography will open new possibilities in multielement analysis.

Special precautions have to be taken in extraction chromatography as to the purity of the organic solvents. Distilled spectroquality solvents have been introduced that are characterized by maximum absorbance specifications in the UV region.

The separated elements and stationary and mobile phases are listed in Table 7. Difficulties will arise when the bulk material has to be separated from low concentrations of trace elements. Therefore, HPLC is more suitable as a second concentration step after the removal of the matrix. A bibliography of inorganic applications of extraction chromatography up to 1971 is given by Escherich and Drent.[39]

B. Sorption Methods of Concentration

1. General Remarks

The three possible sorption mechanisms are adsorption, ion exchange, and complex formation. A classification between ion exchange and complex formation is often difficult. In both cases, a skeletal structure of a polystyrene-divinylbenzene copolymer, cellulose, or silicagel is used, together with a functional group. This group can either form a chemical bond with a clathrate compound; or the trace element can move into the interstices without exchanging an ion or replace the trace element with anion. The simplest case is physical adsorption.

As to the technique, one may differentiate between the bulk or slurry procedure and the column procedure (chromatography). Either the trace elements are "sorbed", or the matrix is sorbed. In the first case, the trace elements can be "desorbed" or the sorbent incinerated. A third variant is a determination of trace elements together with the sorbent material, in cases where the sorbent does not interfere. For all three cases, it is important that the sorbents are of high purity for the determination of small concentrations of trace elements.

2. Ion Exchange (Polymer Resins)

Ion exchange with COOH and SO_3H as the functional group on polymer resins for cation exchange and with NR_3OH or $RN(CH_3)_2$ as the functional group for anion

Table 7
LIQUID EXTRACTION CHROMATOGRAPHY FOR SEPARATION OF TRACE ELEMENTS

Matrix	Elements	Chromatographic system	Detection	Ref.
Water	Zr, Hf	Reversed phase: acetophenone	Photometry	98
Uranium solution	Metals	Reversed phase: TBP	AAS	99
Molybdenite concentrates flue dust	Re	Reversed phase: PTFA + tributylphosphate	UV-227 nm	100
	Cu, Ni, Pb, Hg, Co, Se, Cr	Reversed phase: LiChrosorb RP8/methanol-water diethyldithiocarbamates	UV/VIS-spectrometry	101
	Cu, Ni, Pd	Reversed phase: kieselgel/acetonitril-diethyletherpetrolether tetradentate β-ketoamine chelates	UV-254 nm	102
	Ni, Cu	Reversed phase: tetradentate β-ketoamine chelates	UV-254 nm	103
	Se	Reversed phase: nucleosil 10-C_{18}/acetonitril/chlor piazselenol	UV, fluorimetry	104
	Hg	Reversed phase: dibenzo-18-crown-6 complexes	UV-254 nm	105
	Cu, Hg, Ni, Cu, Zn, Cd	Reversed phase: LiChrosorb/benzene, cyclohexanole, DDTC, or benzylmethyl DTC	UV	106
	Zn, Cd, Hg	Silica gel with Agdithizonate/*o*-dichlorobenzene/dithizone	—	107

exchange is now an almost "classical" separation method for single elements or groups of elements.

Using tables of distribution coefficients as a function of the pH-value, the anion concentration and the total ion strength it is possible to calculate the optimum conditions for a separation. The presentation in Figure 7 shows that group separations are possible in four groups:

1. Lanthanides, actinides, Zr, La, Y
2. Sr, Ba, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, U
3. Be, Mg, Ca
4. Cd, Sn

These groupings are shifted when the concentration of the HCl is changed. When a separation of trace elements from the matrix element is desired, the capacity of the ion exchange resin has to be high enough for the concentration of the matrix element. Due to the higher amount of resin, this leads to an increase of the contamination.

Table 8 summarizes examples for recent work on ion exchange with polymer resins. There are two important trends for the future: an increase in efficiency by the application of high pressure and the use of more sophisticated and often selective detectors.

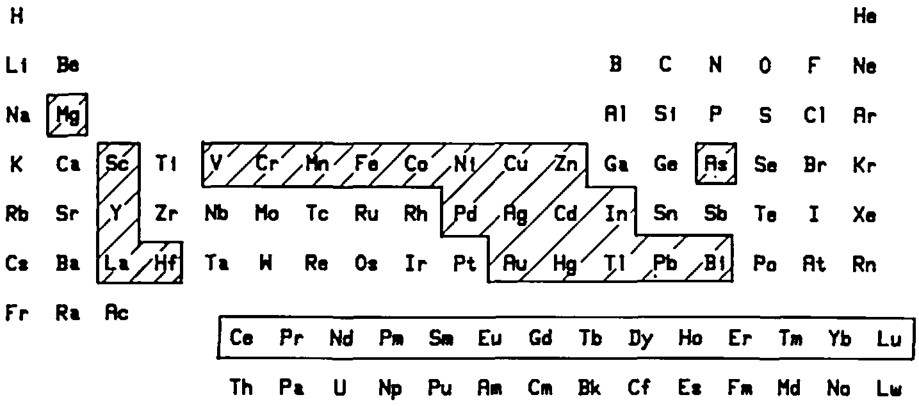
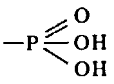


FIGURE 8. Trace elements which have been separated by adsorption.

Table 8
EXAMPLES FOR ION EXCHANGE CHROMATOGRAPHY OF TRACE ELEMENTS USING POLYMER RESIN

Matrix	Elements	Detection method	Ref.
Manganese nodules	Metals	AAS	112
Geological matrix	Be	AAS	113
Natural waters	Trace elements	AAS, fluorimetry	114
Silicates	Metals	AAS	115
Meteorites	Pt-group	Photometry	116
Plant leaves	Cu, Zn	NAA	117
Urine, blood	Pb, Cd	AAS	118
Rocks	La, Yb, Pb	NAA	119
Pure bismuth	Cu, Cd, Pb	Stripping, voltametry	120
Sea water	Mo, W	Photometry	121
Molybdenum	Alkali earth metals	OES, AAS	122
Tungsten	Na, K, Mg, Ca	AAS	123

Since ion exchange at polymer resin is carried out either in acidic or basic medium, it is especially important to purify the acids and bases in question. The best results are obtained by subboiling distillation[124-126] (i.e., for HCl, HNO_3, $HClO_4$, H_2SO_4 and HF) or by isothermal isopiestic distillation. Special care has to be taken when low concentrations of trace elements are to be determined by the ion exchange. Maximum specifications of most resins for copper, iron, and lead impurities are approximately 50, 500, or 10 ppm. The resins can be purified by eluting contaminants with a solution of Na_2EDTA. Besides changing selectivity by altering the eluent, changes in resins are possible. For example, when the sulfonic acid group in a conventional strong cation resins is replaced by phosphoric acid,



$$-P(=O)(OH)OH$$

a resin is formed with high affinity for removal of lead, copper, zinc, cadmium, or manganese.[127]

Table 9
EXAMPLES FOR INORGANIC ION EXCHANGE OF TRACE ELEMENTS

Matrix	Ion exchange compound	Elements	Detection method	Ref.
Water	AgCl	I^-, I_2	Radioactivity	128, 129
Fission products	CdS	Tc	Radioactivity	130
Biological material	$Sb_2O_5 \cdot \times H_2O$	Na, K	NAA	
	Zirconium phosphate	P		131
Fission products	Antimony(V)-hexacyanoferrat(II)	Sr	Radioactivity	132
Fission products	Titanium hexacyanoferrat	Cs	Radioactivity	133
Water	$TiO_2 \times H_2O$	UO_2^{2+}	Spectrophotometrically	134
Water	$(CePO_4)_2(HPO_4)_{0.74}(SO_4)_{0.26}$	Na, K, Rb, Cs, Li, Ag	Radioactivity	174, 175, 176

Another interesting approach for higher selectivity is the introduction of tetraphenylborate as a functional group for the separation of alkali ions[130,138] into a polystyrene resin. The disadvantage of the tetraphenylborate compound is the instability below pH 4 and above pH 9.

Fritz and Meyers[155] have introduced the arsenic acid and separated Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn.

In some special cases, an anion exchange resin can be used for the removal of the matrix: in H_2SO_4 uranium(VI), chromium(VI), and molybdenum(VI) can be separated.[110] In HCl, bismuth, cadmium, chromium(VI), polonium(IV), platinum(IV), rhodium(IV), antimony(III), and tellurium(IV) can be separated.[111]

3. Inorganic Ion Exchange

Inorganic substances serving as an ion exchange material are much less important than organic substances. In most cases the matrix and the functional group are identical. Natural ones are zeolites and clay minerals, which consist of an aluminosilicate lattice. The synthetic molecular sieves have properties similar to the zeolites. Other important synthetic inorganic compounds are hydrated oxides (e.g., $TiO_2 \cdot xH_2O$, $ZrO_2 \cdot xH_2O$), hydrated phosphates (e.g., $Ti(HPO_4)_2 \cdot xH_2O$) and hydrated hexacyanoferrates (e.g., $Ti(OH)(HFe(CN)_6) \cdot H_2O$. The main disadvantage of inorganic ion exchange is the high content of all trace element contamination and the difficulties of purification.

For multielement trace analysis in a number of cases, a separation of the matrix element is possible. Thus, titanium hexacyanoferrate shows a high selectivity for cesium ions, which is probably due to the attraction to the interstices between the octahedral groups of the cyanoferrate ions. However, the main separation mechanism is exchange of H^+ ions or adsorption. These processes are much more suitable for trace element analysis than the exchange of ionic compounds using, for example, $BaSO_4$ or AgCl. These latter compounds are able to exchange Ba^{2+} with Sr^{2+}, and Cl^- with I^-, respectively.

In these substances, one cation is exchanged for the other so that a possible matrix interference might be exchanged for another matrix interference. The exchange with ionic crystals can also be classified as a precipitation (Section II.B.5).

Table 9 cites examples for the ion exchange of trace elements with inorganic ion exchangers. Because of the risk of contamination by impurities in the inorganic exchange material, this method is preferred for the separation of radioactive products. Of the examples, the separation of Na, K, and P[131] from biological material in neutron activation analysis is important. (In neutron activation analysis of biological substances,

Table 10
DIFFERENT ADSORPTION SYSTEMS FOR PRECONCENTRATION OF TRACE ELEMENTS

Elements which are adsorbed	Activated carbon (chelated with 8-hydroxyquinoline) % adsorbed[135,136]	Silicic acid (chelated with APDC) % adsorbed[137]	Activated carbon (pM 7)[140]
Zn	90—100	>95	85
Cu	80—90	>95	96
Ni	90—100	95	88
Co	90—100	>95	70
Fe	90—100	95	70
Mn	90—100	—	98
Cr	90—100	—	—
Sc	56	—	—
Se	0	—	—
Ag	30	—	92
Cd	95	95	96
Sb	0—20	—	—
Hf	96	—	—
Re	>99	—	—
Hg	90—100	—	—
Pb	80—90	>95	92
Ba	≈0	—	—
Ca	<10	—	—
Mg	Variable	—	98
Li, Na, K, Cs	0	—	—
Rare earths	86—99	—	—

the sodium and potassium content is a problem due to the high concentration and the high activation.)

4. Adsorption

Adsorption processes have been used successfully for the preconcentration of trace elements. Activated charcoal[135,136,140-142,148,149] and highly dispersed silicic acid[137] have been used as trace collectors. Activated charcoal behaves as an anion exchanger (it selectively adsorbs, e.g., anionic complexes of noble metals) as well as a cation exchanger (oxidized charcoal after treatment with nitric acid). Oxidized charcoal will preferably adsorb multicharged ions (e.g., in columns packed with oxidized charcoal, alkaline earth metals are concentrated compared with alkali metal salts).

Table 10 lists typical yields for activated carbon or activated carbon and silicic acid, together with a chelate-forming reagents. An adsorbent with a large surface area can be used without any additive when the pH-value is high enough to form hydroxides, but in this case the matrix element should not hydrolyze. When chelate-forming compounds are added, either solubles or insolubles compounds with the trace elements are formed. The soluble compounds are much better adsorbed than the ions themselves since the physical adsorption with the large molecule is higher. The explanation for the high yield with insoluble chelates is probably a coagulation of colloids which is favored in the presence of the activated carbon. Another type of interesting adsorbent is the silver halides, together with chelate-forming compounds.[143-146] In this case it is difficult to differentiate between "adsorption" and "coprecipitation". Sometimes the process which takes place might also

Table 11
BACKGROUND CONCENTRATIONS OF TRACE ELEMENTS IN THE ADSORPTION MATERIAL[137]

	Concentration of trace element (μg/g)		
Element	Activated charcoal	Aerosil R 972	Aerosil 380
Ag	<0.2	<0.2	<0.2
Bi	<2	<3	<2
Cd	<0.1	<0.1	<0.08
Co	<0.6	<0.4	<0.3
Cr	1.3	<2	<1
Cu	18	<0.2	<0.1
Fe	156	1.6	1.1
Ga	<4	<4	<3
In	<2	<2	<2
Mg	90	0.7	<0.08
Mn	150	<0.2	<0.2
Ni	1.9	<0.5	<0.4
Pb	2.3	<1	<0.9
Tl	<1	<1	<0.8
Zn	3.4	0.3	0.4

Note: The values with < are the guaranteed limits of purity.[139]

be classified as a sorption process by complex formation with a chelate resin (Section II.2.5). This is the case when glass surfaces are used on which chelates are fixed.

After the adsorption, the subsequent procedure depends on the detection method and detection limits. For XRFA and AAS, a direct determination is possible. For XRFA, thin supports of activated carbon are preferable. In AAS, the carbon powder can be used without interference. For other methods, it is necessary to dissolve the adsorbed trace elements with acids again.

Table 11 shows[137] background values for the trace elements in the adsorbents. For a number of elements, the highly dispersed silicic acid has lower background values.

In Table 12, examples are given for adsorption as the concentration method. As to the elements separated, this method seems to be most suitable for the multicharged transition metals. Adsorption chromatography for inorganic trace elements has never been developed extensively since the efficiency of a separation using activated carbon, silicic acid, Al_2O_3, $CaCO_3$, $Ca(OH)_2$, $CaSO_4$, MgO, etc. is not very high. Physical adsorption is more suitable for a single-step separation than for a chromatographic separation.

5. Complex Formation with Chelate Resins

Chelate resins either in a packed column or in the form of an impregnated filter (membranes) are gaining more and more importance as preconcentrating agents. The sorption can also be carried out under static conditions, but for eliminating traces from large volumes, a column is preferable. An important point is the comparison of a single-step extraction with chelating agents and the use of chelating resins.

Schmuckler[183] has compared, therefore, the interaction of Cu with the monomer of benzyl iminodiacetic acid and with Dowex-A-1 (chelex 100 is a chelating resin which contains iminodiacetic acid). It was found that the monomer forms a complex with two molecules, whereas the chelating resin forms a 1:1 complex (Figure 9). This is easily understood since only five of eight aromatic rings in the polymer are substituted by the

Table 12
EXAMPLES FOR THE CONCENTRATION OF TRACE ELEMENTS BY ADSORPTION

Adsorbens	Matrix	Trace elements	Ref.
Activated carbon + 8-hydroxyquinoline	Water	Zn, Cu, Ni, Co, Fe, Mn, Cr, Sc, Cd, Hf, Re, Hg, Pb, R.E.	135, 136
Silicic acid + APDC	Al, Mg, Ga	Bi, Cd, Co, Cu, Fe, In, Ni, Pb, Zn	137
Activated carbon	Water	Ag, Bi, Cd, Co, Cu, Fe, In, Mg, Mn, Ni, Pb, Zn	140
Activated carbon + Na DDC	Water	Ag, Cd, Co, Cu, In, Ni, Pb, Tl, Zn	141
Activated carbon + xylenolorange	Ag, Tl	Bi, Co, Cu, Fe, In, Pb	142
AgBr + biscyclohexanone oxalyldihydrazone	Pb, Ni	Cu	143
AgI + EDTA	Ag	Hg	144
AgCl, AgBr, AgI, AgSCN + 1.10-phenanthroline	Water	Fe, Ni, Co, Cu, Pb, Bi, Tl, Au, Hg, Zn, Pd, V	145
AgI + 1.10-phenanthroline	Mn	Fe, Co, Ni, Cu, Zn, Cd, Pb, Bi, Tl	146
Glass + APDC	Water	Cr, Fe, Co, Ni, Cu, Zn, As, Hg, Pb	147

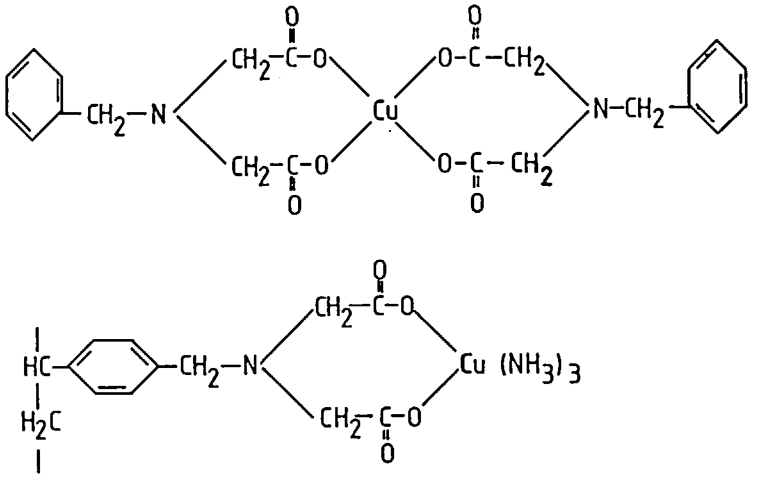


FIGURE 9. Monomer and polymer complex of Cu with benzyl iminodiacetic acid.[183]

ligand.[184] The coordination number 6 is maintained by other ligands. In the interaction of Pd with benzylthiouronium hydrochloride and with a polyisothiouronium ion exchanger in contrast to the Dowex-A-1 with Cu a 1:2, molar interaction takes place since every aromatic ring is substituted with a thiourea molecule (Figure 10). These two examples show that because of the difference in stoichiometry, the extraction behavior and that of the chelating resins are not comparable. A second effect which has to be taken into account is the difference in kinetic behavior between the complex formation of a chelate

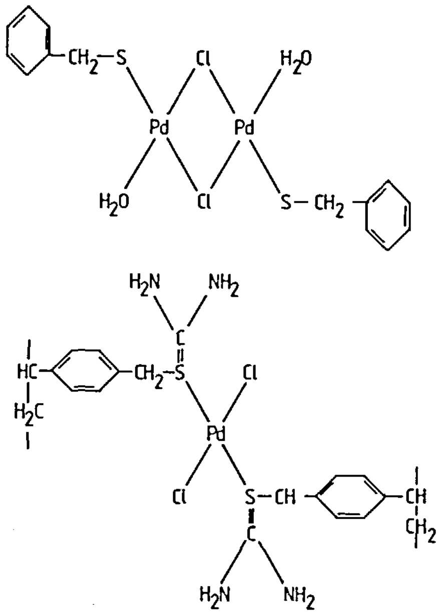


FIGURE 10. Monomer and polymer complex of Pd with benzylthiouronium.[183]

compound fixed to a resin or desolved in a solvent. Although liquid-liquid extraction of trace elements by using a chelating agent such as APCD often provides sufficient concentrations, the chelate-resin system is more efficient for very low amounts. Because the degree of extraction decreases when the aqueous-to-organic phase volume ratio is increased, the concentration factor which can be achieved is limited. Furthermore, a quantitative separation ability is limited by the difference in extraction coefficients. Thus, not only are chelating resins simpler to use and less time-consuming than solvent extraction but the concentration factors are much higher.

Table 13 summarizes typical examples for chelate resins which have been synthesized and tested. As the matrix cellulose, polystyrol and silica gel are used. Instead of silica gel, small glass balls can be used. The elements in the second column have been separated from various matrices. In some cases, the chelate resins are highly selective; in other cases, most of the trace elements are sorbed. The sorbed elements are desorbed, or the elements are determined directly on the chelate resin — e.g., by X-ray fluorescence. In the latter case, the knowledge of the concentration of the trace elements in the chelate resin before the separation is important in determining the detection limit.

Smits and van Grieken[153] have demonstrated, using 2,2′-diaminodiethylamine on cellulose, how much influence the reagents have on the "blank" values. (Table 14). The synthesis of resins with immobilized chelates is in the first stage of development. Since almost every functional group can be introduced, and even mixed resins are applicable, it should be possible to optimize each separation problem. Until now, only part of the exchange coefficients for the different elements and all possible parameters have been determined. In Table 15, Burba et al.[169] give some examples for functional groups (fixed to a cellulose skeleton). Fritz and Meyers[155] have used a very special inorganic functional group for ion exchange. The arsenic group was introduced, producing an ion exchange resin which was used for the separation of uranium from other heavy metals and for the separation of thorium from other heavy metals.

Table 13
TRACE ELEMENT SEPARATION USING CHELATING ION EXCHANGE RESINS

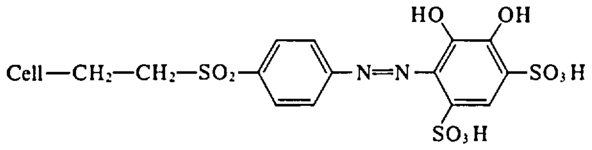
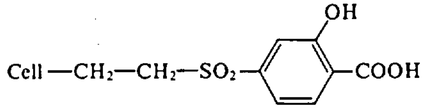
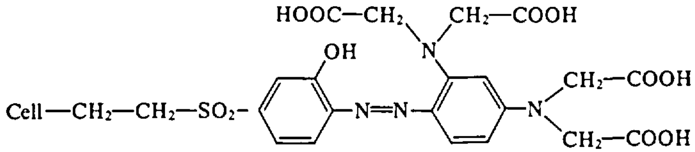
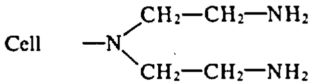
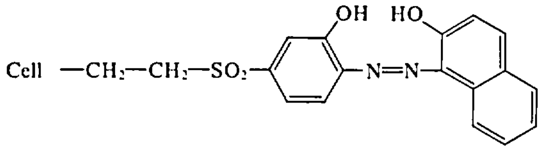
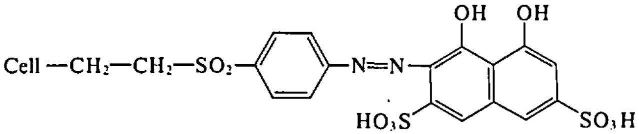
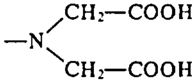
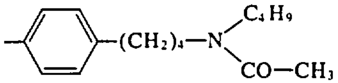
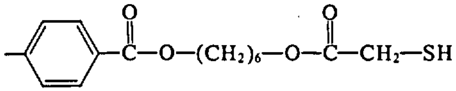
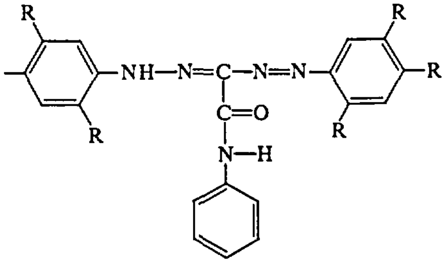
Exchanging resins	Chemical name of the chelating group	Cations which have been investigated	Ref.
	1,2 Dihydroxy benzene-3,5-disulphonic acid (Tiron)	Fe, Cu, Hg, Ba, Sr, Ca, Mg	150
	Salicylic acid	Te, Fe, U, Cu, (Ag, Sr, Co, Ni, Y, In)	151, 152
	1-(2-Hydroxyphenylazo)-2,4-phenylenediamine-*N,N,N',N'*-tetraacetic acid	La, Lu	156
	2,2'-Diamino-diethylamine	Eu, Cr, Co, Fe, Co, Pb, n, Zn, Cu (pH > 5)	153
	1-(2-Hydroxyphenylazo)-2-naphtol (Hyphan)	Fe, Cu, Zn, Pb, U	154, 158

Table 13 (continued)
TRACE ELEMENT SEPARATION USING CHELATING ION EXCHANGE RESINS

Exchanging resins		Chemical name of the chelating group	Cations which have been investigated	Ref.
		Chromatropic acid	Fe, Cu, Zn, Sr	157
Polystyrol divinylbenzyl (Dowex-A-1, Chelex 100)		Iminodiacetic acid	Mn, Co, Zn, Eu, Fe, Cu, Hg, Cd, Ni, Pb	159—162
Polystyrol divinylbenzyl			U	163
Polystyrol divinylbenzyl			Ag, Au, Hg, Bi	163
Polystyrol		1,5-Diphenyl-3-phenyl carbamolformazane	Pd and other noble metals	159

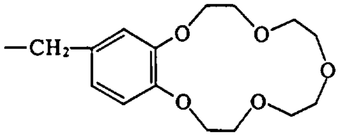
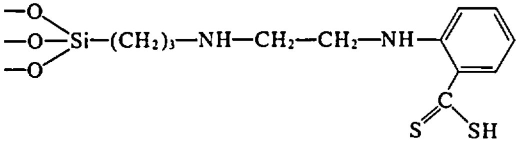
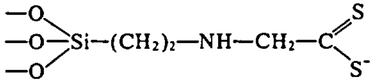
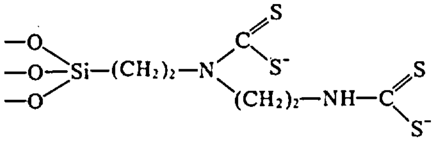
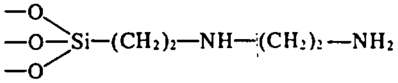
Polystyrol		Benzo-15-krone-5	Na, K, Cs, Ca, Sr, Ba	164
Silica gel			U, Cu, Ni, Co, Zn, Hg, As	165
Silica gel			Cu, Co, Ni, Zn, Fe	166—168
Silica gel			Cu, Co, Ni, Zn, Fe	166—168
Silica gel			Cu, Co, Ni, Zn, Fe	166—168

Table 14
INORGANIC BLANK IMPURITIES IN THE CELLULOSE FILTERS PREPARED WITH DIFFERENT CHEMICALS

Blank impurity levels (and standard deviations per measurement) (ng cm^{-2})

	A	B	C	D	E	F	G
			Purified DMF and $POCl_3$ from				
Element	Whatman-41 cellulose filters	Unpurified DMF, Merck $POCl_3$	Merck	UCB	Baker	Riedel de Haën	Final cel-DEN filters
Fe	98(25)	150(12)	100(16)	130(7)	120(30)	130(9)	156(45)
Cu	16(3)	50(30)	24(6)	32(2)	21(2)	26(4)	23(6)
Zn	3(2)	63(52)	12(11)	27(2)	13(3)	16(3)	46(17)
Pb	<6	19(7)	<6	<6	<6	<6	<6
Br	8(3)	9(4)	<6	14(2)	410(148)	11(10)	<6

[a] DMF, dimethylformamide.

From Smits, J. and van Grieken, R., *Anal. Chim. Acta,* 88, 97, 1977. With permission.

Table 15
SEPARATION AND DETERMINATION OF TRACE ELEMENTS BY CELLULOSE EXCHANGERS WITH DIFFERENT FUNCTIONAL GROUPS

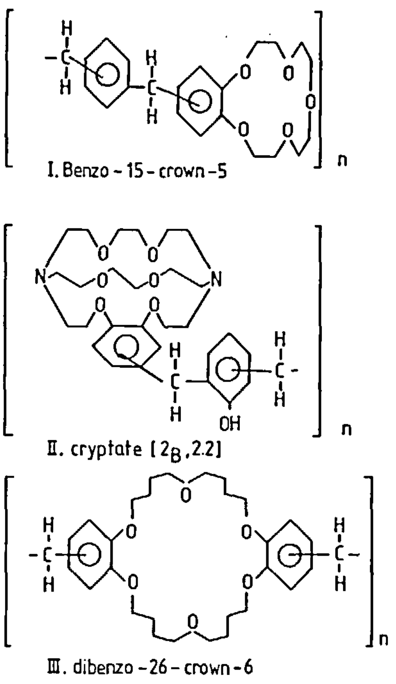
Functional group	Trace elements
Brenzcatechin	Nb, Ti, Fe
Alizarin	Al, In, Th, Zr
Chinalizarin	Al, Ga, In, Sc, U
Pyrogallol	Bi, Nb, Sb, Ta
Glyoxalbis(2-hydroxyanil)	U
PAR	Pb, Co, U
TAM	Hg
5-(4-Dimethylaminobenzyliden)-rhodanin	Hg, noble metals
Arsenazo III	Hf, Th, U, lanthanides

From Burba, P., Röber, M., and Lieser, K. H., *Angew. Makromol. Chem.,* 66, 131, 1978. With permission.

The efficiency of concentration of elements by chelate resins also depends on speciation of the trace elements. For example, in sea water it is not correct to use a standard addition procedure either with active or inactive traces since the recovery measurement is prone to error. Part of the element will not be present as free ionic species, but in a colloidal or complexed form and will not equilibrate in the same fashion as "free" ionic species will.

6. *Exchange With Crown Ethers*

In recent years a great number of exchangers with cyclic polyethers as anchor groups have been prepared by condensation, substitution, and polymerization reactions.[171-173]



I. Benzo - 15 - crown-5

II. cryptate [2_B,2.2]

III. dibenzo -26 - crown-6

FIGURE 11. Examples of typical crown ethers.[171]

The selectivity for different salts depends on the cation, the anion, the solvent, and the size of the ring and also on the type and basicity of the hetero atom (*O, N, S*). Typical structures are shown in Figure 11.[171]

Comparing the crown ether exchangers with other commercially available exchangers shows the following advantages of the ethers: high resistance to chemicals, temperature, and radiolysis; neutral ligands as the anchor group; and the binding of ions is facilitated in solvents less polar than water, e.g., methanol.

For some ions, the cyclic polyethers show preference — e.g., potassium is more strongly bound in exchangers I and II than the other alkali ions. The exchangers have a broad application in multielement analysis, such as the separation of cations with a common anion (especially alkaline and alkaline earth metals, heavy and precious metals), anions with a common cation (halides and pseudohalides), separation of radionuclides, and the determination of water. Table 16 summarizes the selectivity series in water and methanol. The stability sequences of the exchangers in methanol and water correspond with those of the monomer complexes. Typical separations are shown in Figures 12 and 13.

The detection limits depend on the detector used in the separation. They range from the microgram to picogram levels. Usually a differential refractometer, together with a fraction collector, is used. However, there is a lack of practical experience as to the interference of elements and the influence of matrices. With a few exceptions, the investigations are in the stage of scientific basic research, but there might be very interesting applications in the future.

7. *Ion Chromatography*

Ion chromatography (IC) is a new ion-exchange, liquid chromatographic technique developed by Small et al.[335] of the Dow Chemical Co. With this technique, it is possible to solve the problem of separation and detection of highly acidic or basic ions. In Table 17

Table 16
SELECTIVITY SERIES IN WATER AND METHANOL

Exchanger	Solvent	Alkali metal ions	Ions	Alkaline earth metal ions	Alkylammonium chlorides
§-C(2_B.2.2)	Water	$K^+ > Na^+ > Rb^+ > Cs^+ > Li^+$	$SCN^- = I^- > Br^- > Cl^-$	No uptake	—
	Methanol	$K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$	$SCN^- = I^- > Br^- > Cl^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ for Cl^-, Br^- $Sr^{2+} = Ca^{2+} > Ba^{2+} > Mg^{2+}$ for SCN^-, I^-	No uptake
§-DB-21-C-7	Water	$Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$	$SCN^- > I^- > Br^- > Cl^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} = Mg^{2+}$	—
	Methanol	$Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$	$SCN^- = I^- > Br^- > Cl^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	Only monomethyl- and monoethylammonium chlorides are taken up
§-DB-24-C-8	Water	$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$	$SCN^- > I^- > Br^- > Cl^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	—
	Methanol	$Cs^+ > Rb^+ > K^+ > Na^+ \gg Li^+$	$SCN^- > I^- > Br^- > Cl^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	No uptake
§-B-15-C-5 (phenol)	Water	$K^+ > Na^+ = Rb^+ > Cs^+ > Li^+$	$OH^- > SCN^- = I^- > PO_4^{3-} > NO_3^- = SO_4^{2-} > Br^- > Cl^- > F^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	—
	Methanol	$K^+ > Rb^+ > Na^+ > Cs^+ \gg Li^+$	$OH^- > SCN^- > I^- = PO_4^{3-} > NO_3^- > Br^- > Cl^- > F^-$	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	Methyl > ethyl- > n-propyl = n-butyl-substituted; mono- > di- > tri- > tetra-substituted for methyl- and ethylammonium chlorides
§-DB-18-C-6	Water	$K^+ > Rb^+ > Na^+ > Cs^+ \gg Li^+$	$SCN^- > I^- > NO_3^- > Br^- > Cl^- > PO_4^{3-} = OH^- > F^- = SO_4^{2-}$	$Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	—
	Methanol	$K^+ > Rb^+ > Na^+ > Cs^+ \gg Li^+$	$SCN^- > I^- > NO_3^- = Br^- > Cl^- > OH^- = PO_4^{3-} > F^-$	$Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	Methyl- > ethyl- = n-propyl- > n-butyl-substituted; mono- > tetra- > di- > tri-substituted for methylammonium chlorides; mono- > tetra- > tri- > di-substituted for ethylammonium chlorides

From Blasius, E., Janzen, K. P., Luxenberger, H., Nguyen, V. B., Klotz, H., and Stockemer, J., *J. Chromatogr.*, 167, 307, 1978. With permission.

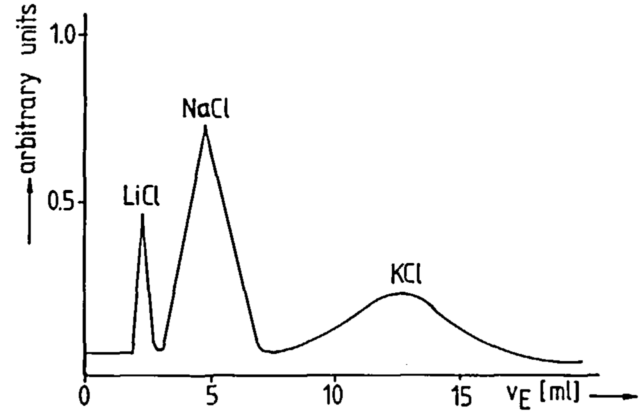


FIGURE 12. Separation of 0.006 mg LiCl, 0.035 mg NaCl, and 0.08 mg KCl by elution with water.[173]

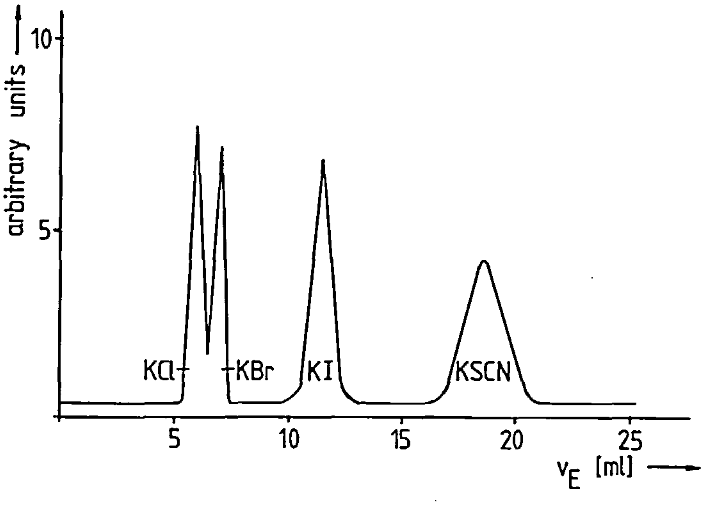


FIGURE 13. Separation of 0.42 mg KCl, 0.60 mg KBr, 1.60 mg KI, and 1,77 mg KSCN by elution with water.[173]

are summarized ions which have been successfully separated and detected. A detailed description of IC is given in References 177 and 178. Using high pressure, the power of high-speed liquid chromatographic separation can now be applied to analytical problems involving the ions in Table 17.

The instrumentation involves a pumping station, an eluent, an injection valve, an ion-exchange separation column, an ion-exchange suppressor column, and a conductivity cell. The function of the suppressor columns is to convert the eluent (solvent system) to a less conductive species while converting sample ions in a conductive form. By this method, conductometric detection of the sample ions in a low conductivity background is possible.

In the case of cation analysis, the HCl eluent is converted to water while the sample ions are converted to strongly conducting basic forms. The linear response range extends from a few parts per billion to approximately 50 to 100 ppm (using 100 $\mu \ell$ injection

Table 17
IONS SEPARATED AND DETECTED BY IC INORGANIC IONS

Ammonium
Arsenate
Azide
Bromate
Bromide
Calcium
Carbonate
Cesium
Chlorate
Chloride
Chromate
Dithionate
Fluoride
Hypochlorite
Iodate
Iodide
Lithium
Magnesium
Nitrate
Nitrite
Ortho-phosphate
Potassium
Rhenate
Rubidium
Sodium
Strontium
Sulfate
Sulfite
Tetrafluoroborate
Thiocyanate
Thiosulfate

From Rich, W. E. and Wetzel, R. A., *Monitoring Toxic Substances,* ACS Symp. Ser. No. 94, 1979, 234. With permission.

Table 18
LIMITS OF DETECTION

Ion	Standard conditions (100 μℓ injection loop)	Modification 1 (1 mℓ injection loop)	Modification 2 (concentration column)
F	20	5[a]	1[a,b]
Cl	25	5	1[a,b]
NO$_2$	50	10	2
PO$_4$	200	20	2
NO$_3$	150	20	1
SO$_4$	100	10	1
J	500	150	20[b]
Na	10	1[a]	1[a]
NH$_4$	50	10	2 bis 5[b]
K	75	5	2 bis 5[b]
Ca	500	50	10
Mg	250	25	5

[a] Limited by the background.
[b] Estimated values in demineralized water.

From Janzen, K. H., *Laborpraxis Nr.,* 3, 2, 1978. With permission.

volume). It was possible to determine concentrations of Cl$^-$ as low as 1 μg/ℓ. Limits of detection are given in Table 18.[178] If one ion is present in excess, e.g., Cl$^-$ in ocean water, then it is necessary to use a cation exchange resin in the silver form after the injection. H$^+$X$^-$ and Y$^+$OH$^-$ must be highly ionic ($pK < 7$) in order to obtain sensitive detection. Since ions with $pK > 7$ are not detected, the interference from other ions are rather low. For example, cations of transition metals generally precipitate as hydroxides.

A typical separation of anions is shown in Figure 14,[177] and a typical separation of cations is shown in Figure 15. Until now, the most interesting application of ion chromatography seems to be the analysis of environmental water samples such as drinking water, rain water, or river water as to the anions.[179-181]

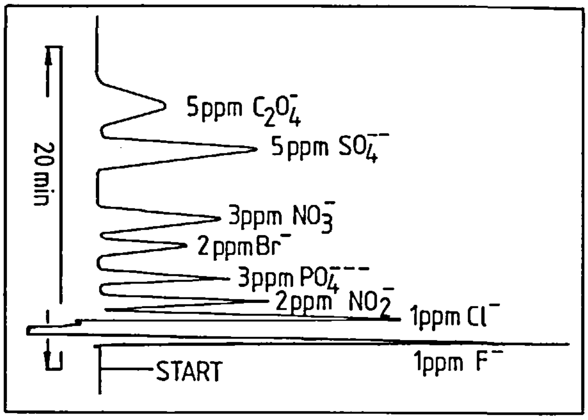


FIGURE 14. Separation of anions by ion chromatography (IC).[177]

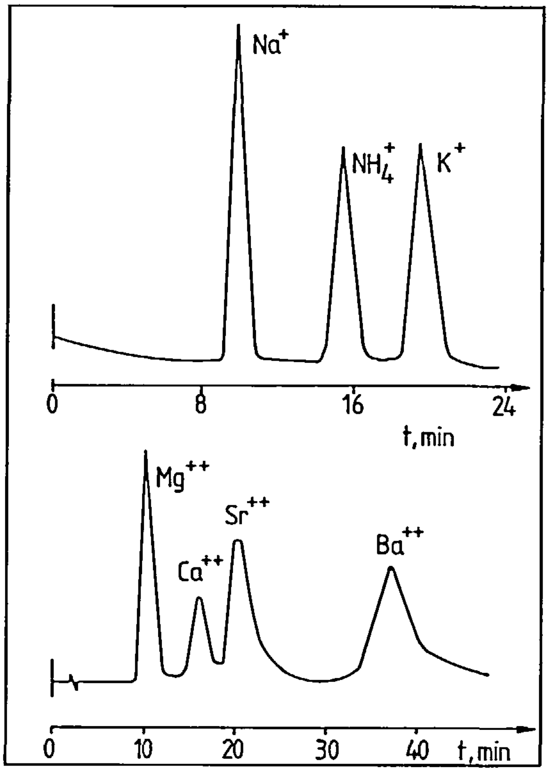


FIGURE 15. Separation of alkali and alkali earth ions by ion chromatography.[177]

C. Evaporation, Volatilization, and Gas Chromatography

1. General Remarks

Most of the preparation steps in analysis such as wet or dry ashing or concentrating by boiling belong to this group. The term "evaporation" will be used when a substances is

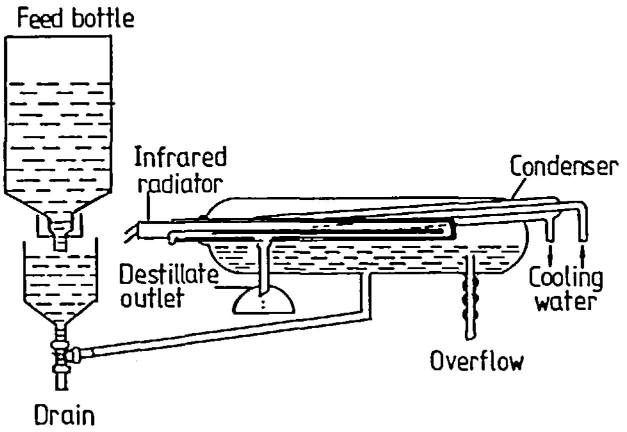


FIGURE 16. Subboiling still (vitreous silica).[86]

evaporated by heating without any reaction. In cases where a reaction is used in order to form volatile compounds, the term "volatilization" will be used. The separation methods which uses the gaseous phase have the advantage of low contamination. The disadvantage is that heterogeneous reactions are involved, and the chemical behavior in the gas phase (which is often not known) makes the separation of trace elements unpredictable.

2. *Evaporation of Liquids*

Removal of the matrix from the liquid sample is widely used. Either part of the matrix is evaporated in order to increase the concentration of the trace elements, or the matrix is completely evaporated in the absence or presence of a collector. Examples are the analysis of water, acids, organic liquids, and inorganic low boiling liquids such as silicon tetrachloride.

Figure 16 shows a characteristic arrangement for the so-called sub- or non-boiling evaporation.[86] For the ultratrace analysis in liquids, special care has to be taken as to the "clean room" conditions and to the adsorption losses on vessels with large surfaces.

A very simple enrichment method involving evaporation consists of impregnating a filter paper with the solution to be analyzed, and subsequent drying.[182,186-191] Some authors applied the ring-oven technique and obtained sensitivities at the parts per million level.[185] A systematic study in order to optimize all the sample preparation steps with respect to sensitivity, accuracy, precision, speed, simplicity, and economy has been carried out by Smits and van Grieken.[182] For the determination they used energy dispersive X-ray fluorescence and found that the optimal target preparation procedure consists of spotting a sample volume within a hydrophobic wax ring on a Whatman-41 filter, and drying with an unheated airstream from underneath. On a confined area of 6.2 cm^2, 1.5 mℓ water is spotted by this technique. The average relative standard deviation amounted to 12%. Table 19 lists optimal detection limits. This method cannot be applied to very concentrated solutions because of crystal formation on the bottom of the filter.

3. *Volatilization Out of Liquids*

Volatilization from water has become an important concentration step for the mercury determination and hydride evolution methods, especially for atomic absorption spectrometry. This method has a number of advantages; high enrichment factors (e.g.,

Table 19
OPTIMAL DETECTION LIMITS WHEN ONE 1.5-mℓ ALIQUOT IS SPOTTED WITHIN A HYDROPHOBIC RING (29-mm DIAMETER) ON A WHATMAN® FILTER AND ANALYZED FOR 2000 S

	Detection limit as secondary target (ppb)			
Element	Ge	Mo	Sn	Nd[a]
K	293	1096		
Ca	124	563		
Ti	45	219		
V	39	148		
Cr	37	112		
Mn	28	88		
Fe	35	72		
Ni	38	39	110	
Cu	65	40	93	
Zn	49	31	77	
As		30	65	
Se		29	54	
Br		30	56	
Rb		31	53	
Sr		35	57	
Zr			64	
Mo			69	
Ag			91	1165
Cd				1432
Sb		4846[b]		3687
Cs		980[b]		12920
La		553[b]		
Eu		250[b]		
Ta		87[b]	255[b]	
Hg		66[b]	127[b]	
Tl		73[b]	140[b]	
Pb		67[b]	130[b]	

[a] Unlike the other targets, the available Nd-target was not matched with a filter of the same material.

[b] With L-radiation; K X-rays were counted in all other cases.

From Smits, J. and van Grieken, R., *Anal. Chim. Acta*, 88, 97, 1977. With permission.

Hg can be separated from a large volume such as 1 ℓ of water); no matrix effect since only a small number of elements form volatile hydrides (As, Se, Te, Sb, Bi, Sn, Ge, Pb, and Hg as atoms); and high atomization yields since Hg is already present as atoms and the hydrides are easily decomposed.

There are three different ways of introducing the gaseous compounds into a detection system, especially into a flameless AAS, which is the most often applied by coupling with a hydride generator (Figure 17):

1. The hydride is generated and introduced into the detector. This method requires a fast generation and release of the hydride. Therefore, the sample volume is limited.

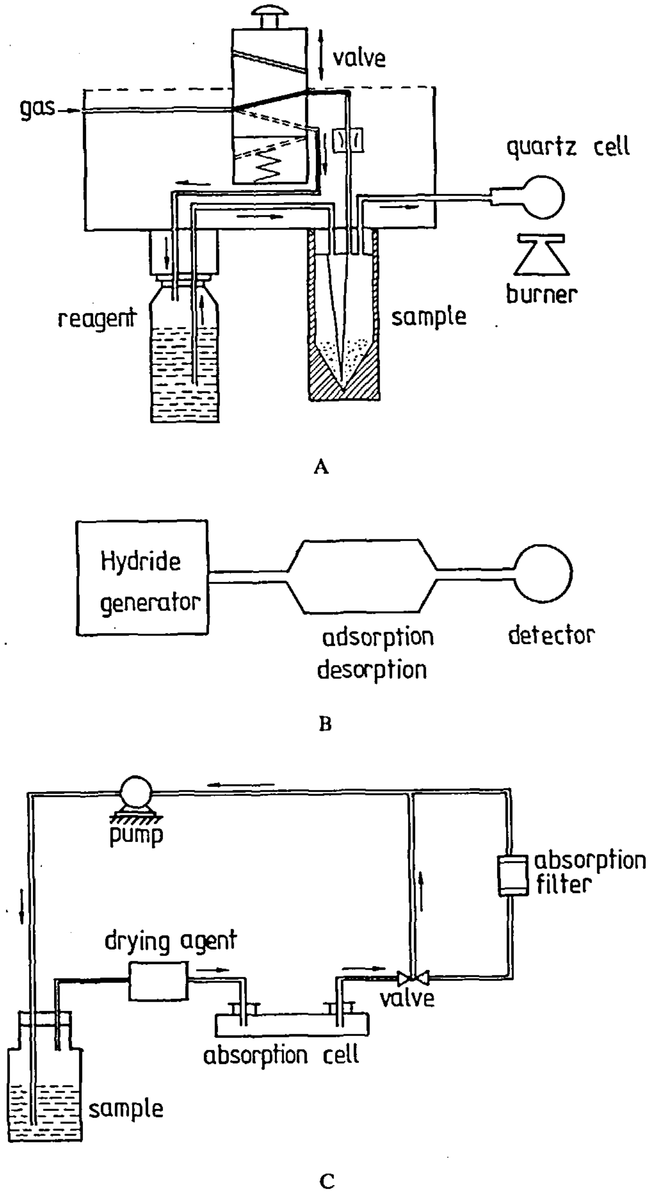


FIGURE 17. Arrangement for the hydride (Hg) evolution out of liquids and the coupling to detectors.

2. The hydride is generated and trapped before the detector. In this case, the releasing time is not important, and a high enrichment can be achieved. After the complete adsorption, the compound is desorbed and determined.
3. The gaseous analyte is pumped in a cycle through the detector, e.g., an atomic absorption cell.

The most frequent application of gas evolution out of liquids is the determination of Hg.[192,193] The atomic vapor is produced by reduction with $SnCl_2$ or $NaBH_4$. By using a sophisticated sequential, specific absorption tube system, different species of mercury in air such as $HgCl_2$, $(CH_3)_2Hg$, Hg, and CH_3HgCl can be determined.

Table 20
EVOLUTION OF ELEMENTS OUT OF LIQUIDS

Matrix	Elements	Reduction solution	Remarks	Ref.
Ocean water	Hg	$SnCl_2$	Enrichment on gold foil 10 ng/ℓ	194
Water	Hg	$SnCl_2$	0.1 ng or 0.02 ppb	193
Water	Pb	$NaBH_4$, $K_2Cr_2O_7$ tartaric acid	10 μg/ℓ	196
Foodstuff	Sb, As, Sn	$NaBH_4$	As 2 μg/g; Sb 2 μg/g; Sn 10 μg/ℓ	197
Water	Sb, Pb, Te, Sn, As, Bi, Se	$NaBH_4$, $K_2Cr_2O_7$ tartaric acid	—	198
Natural water	As(III), As(V)	$NaBH_4$	Selective, sequential evolution of different species	199
Plant tissue	B	Methanol	24.5 μg/g	200
Air particulate	Sn	$NaBH_4$	0.05 ng/mℓ	
Organic matrix	Bi	$NaBH_4$	2.4 ng	201
Rocks	Se, As, Sb	H_3PO_4, NaBr	Evolution as bromides; determination by NAA	202

When hydrides are formed, a number of parameters influence the formation, the transport, and the decomposition in an atomic absorption cell or the adsorption in a trap before the cell. Therefore, the conditions for each element should be optimized. Much more important is the problem of interference by other elements in the solution such that the hydrides are not completely vaporized. A careful study about the influence of different ions on the signal of selenium has been carried out by Meyer et al.[260]

The volatile sensitivity can be kept constant partly by the addition of a high acid concentration.[203] Therefore, complex matrixes — for example, biological matrices with low concentrations of trace elements — have to be investigated very carefully with respect to parameters which influence the evolution. Table 20 summarizes some examples for the evolution of Hg, hydrides, bromides, and the boron methylester. The detection limits are often given by the impurities in the reduction reagents such as $NaBH_4$ or $SnCl_2$.

4. Volatilization or Evaporation Out of Solid Samples

Evaporation out of solid samples is a method which was developed 20 years ago by Geilmann and co-workers.[204,205,207-209] Table 21 lists some typical examples. In these examples, one or two volatile elements are evaporated out of a nonvolatile matrix. Zaidel et al.[216] and Mandelstam et al.[217] have used this method for the analysis of pure nuclear material. The determination of C, S, and O in metals by melting of metals and vacuum degassing also belongs to this technique of concentration, but will not be treated in this article.

The above-mentioned examples are developed for the determination of only one or a very small number of elements. In order to extend this method, a volatilization is necessary that involves a reaction of the sample with a reactive gas (e.g., HCl) and the formation of a great number of volatile compounds. A second possibility is to volatilize the matrix. In order to avoid trace element losses, the evaporation temperature should be as low as possible, but then the evaporation of large samples demands a lot of time. Matrices such as iodine, arsenic, antimony, zinc, and mercury are easily evaporated. We have investigated the evaporation of such matrices as Na_2CO_3, K_2CO_3, H_3BO_3, which are used in the production of wave guides.[218] From 30 mg samples, Na_2CO_3, and K_2CO_3 are evaporated at 990° C in 2 hr in an inert gas stream or in an oxygen stream, whereas the trace elements Co, Cr, Cu, Mn, Fe, and Ni, remain in the evaporation cuvette. Sodium is

Table 21
TYPICAL EXAMPLES FOR THE SEPARATION OF TRACE ELEMENTS USING EVAPORATION OUT OF SOLID SAMPLES

Matrix	Element	Temperature (°C)	Yield (%)	Amount	Gas Stream	Ref.
ZnO	Cd	300—750	100	2—3000 ng	H_2N_2	204
Compounds	Zn	1000—1200	100	μg—mg	H_2	205
Al, Ga, In	Zn	1000—1150	91.0	20—1000 ng	H_2	206
Bauxite	Be	1000	100	5—100 ng	O_2	207
Bauxite	Zn	1150	100	30 μg	H_2	208
Solid samples	Tl	1000	100	2—1000 ng	H_2	209
Cu	Se	1000	96.7	2 μg	—	210
Cu	Se	1150	100	1 ng	O_2	211
Al	Cd, Zn	600—700	100	20 pg	H_2/Ar	212
Aerosol	Cd	600—700	100	0.15—0.25 μg	H_2/N_2	213
Rock	Bi, Cd, Tl	1000—1200	95—100	10—100 pg	H_2/N_2	214
Plant	Pb	1000	100	ng—μg	H_2	215

From Spachidis, C. and Bächmann, K., *Z. Anal. Chem.*, 300, 343, 1980. With permission.

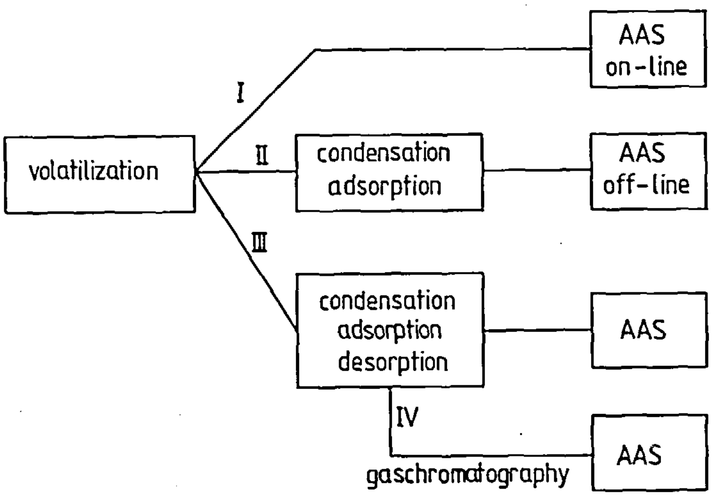


FIGURE 18. Different coupling possibilities of volatilization to AAS.

either evaporated as atoms in the inert gas stream or as Na_2O_2 in an oxygen stream. Potassium is evaporated as K_2O.

H_3BO_3 can be evaporated at 180°C in a stream of water vapor or at 900°C in an argon stream. A separation of Na and K out of biological samples also seems to be possible.[219]

A separation of volatile chlorides has been carried out from pure aluminum.[212,220,221] Zilverstain[222] has volatilized Fe, Ni, Co, Al, Ti, Sn, Mn, In, Ga, and Be from high-purity silica. In cases where the trace elements are volatilized, the condensation or adsorption is carried out either in a graphite cuvette (which can be used for AES or AAS) or on a foil or disk. Also, the use of graphite cups is possible. The type of the trap depends on the detection mode.

Figure 18 shows the different ways of coupling volatilization with atomic absorption spectrometry. The volatilization can be improved by carrying out more than one

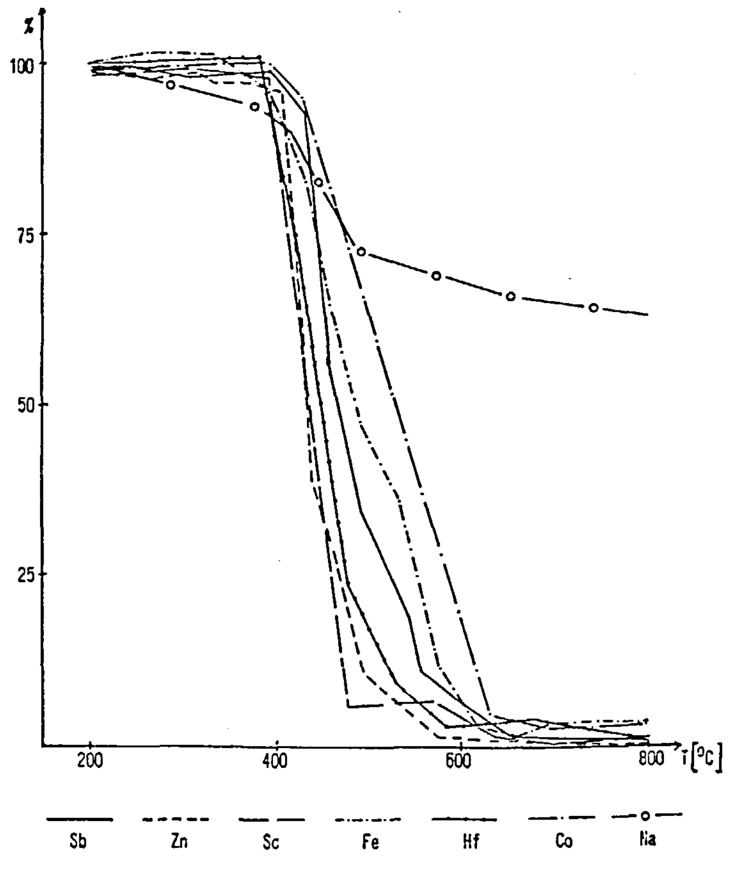


FIGURE 19. Volatilization of trace elements with HCl out of high-purity aluminum.[221]

volatilization. Figures 19 and 20 show the duplicate volatilization of trace elements out of pure aluminum.[221]

Evaporation and volatilization of trace elements is a separation method which, because of the complex behavior, is far from being understood. Complex formation in the gas phase, as has been shown in the case of $AlCl_3$ with NaCl or $ScCl_3$, makes it quite difficult to predict the separation. In practical cases, the separation process is often a mixture of distillation, physical and chemical adsorption chromatography, and different reaction rates. Also, the condensation and adsorption of very low concentrations of trace elements is often incomplete. However, in cases where this technique can be applied, the detection limits are very low.

5. *Gas Chromatography of Metal Chelates and Metal Organic Compounds*

A number of reviews summarizing the investigation of gas chromatography of metal chelates and metal organic compounds have been published.[6,224-229] There are more than 1000 publications on this subject, but most of these papers deal with basic research on chelate compounds or the separation of substances. Only a small number of studies have been carried out on the practical application of gas chromatography to inorganic trace analysis. The reason for this neglect is that there have been some general problems, such as low thermal stability and the interaction between the compound used for analysis and the column packing. In recent years, the development of special detectors, (the electron

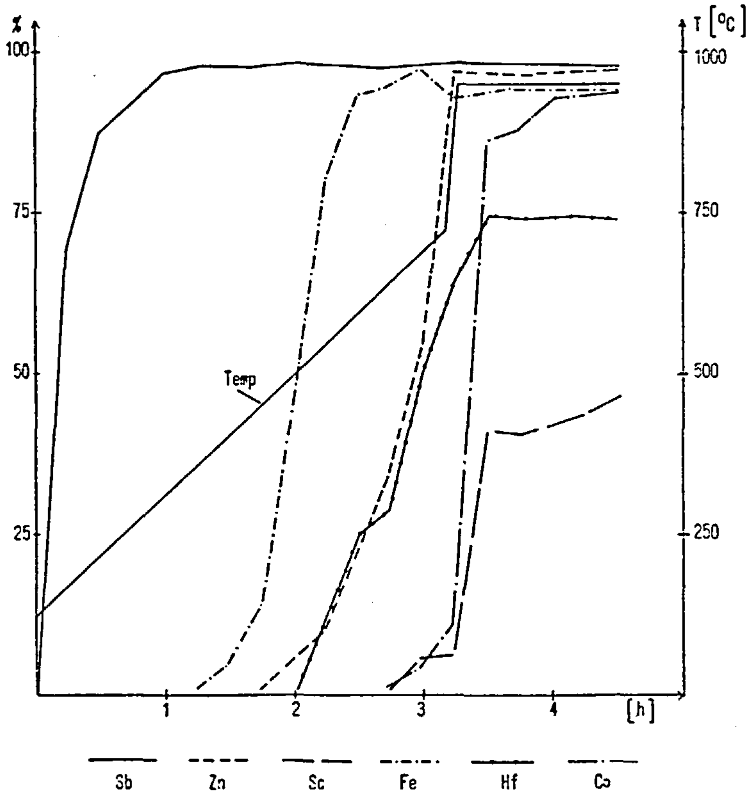


FIGURE 20. Second volatilization of the condensed compounds in an Ar/HCl-stream.[221]

capture detector (ECD), the flame photometry detector (FPD), and the microwave emission detector (MED), has stimulated the investigation of gas chromatography.

The interactions between polar metal chelates and the packed chromatographic column which produce elution curves with tailing can be reduced by a careful conditioning of the column and by deactivating the supporting material. The decomposition at higher temperature can be depressed by the presence of a carrier gas containing the ligand vapor.[230,231] Often the use of metallic columns (stainless steel, copper, nickel) can lead to reactions of the column walls with the compounds examined, or may catalyze the decomposition of the compounds so that inert material, such as PTFE (Teflon®) and borosilicate glass columns, is necessary.

Table 22 summarizes examples of gas chromatographic separations with quantitative analyses. The main group is the metal chelates with β-diketones and similar ligands. The polyfluorinated β-diketones such as ligands give more highly volatile derivatives and can be detected with high sensitivity with an electron capture detector.

Another group of compounds which are interesting for gas chromatography are ternary complexes from fluorinated β-diketones and organic solvent molecules, such as dimethylformamide or di-*n*-butylsulfoxide. These ternary complexes show a higher stability than binary complexes.

Figure 21A gives a survey of the elements which form complexes with β-diketones or their derivatives. Even the rare earth metals can be separated using the "ligand vapor gas

Table 22
TYPICAL EXAMPLES OF TRACE ELEMENT SEPARATION USING THE GAS CHROMATOGRAPHY OF CHELATES OR ORGANOMETAL COMPOUNDS

Matrix	Elements	Chelate forming compound	Detection method	Ref.
CCl_4, benzene	Bi, Pb, In, Co	Dithiocarbamates	FID, ECD	240—242
$CHCl_3$	Hg, Cd, Ni, Cu, Zn			
MIBK	Ho, Dy, Tb, Gd	Trifluoroacetylacetonates	TCD	232
—	Tl, Se, Te, Hg, As, Sb, Bi, Sn	Phenyl compounds	FID	243
Blood	Cr	1,1,1-Trifluoro-2,4-pentanedione	MED	244
Air	Pb	Alkyl compounds	MED	245
—	Cu, Ni, Pd	Propylentrifluoro-acetylacetonate	dc, Argon plasma	246
—	Cr	Acetylacetonates, trifluoroacetylacetonates, hexafluoro-acetylacetonates	FID and MED	247
—	Be	Trifluoroacetylacetonates	ECD	248
Biological	Se	5-Nitropiazoselenol	ECD	249

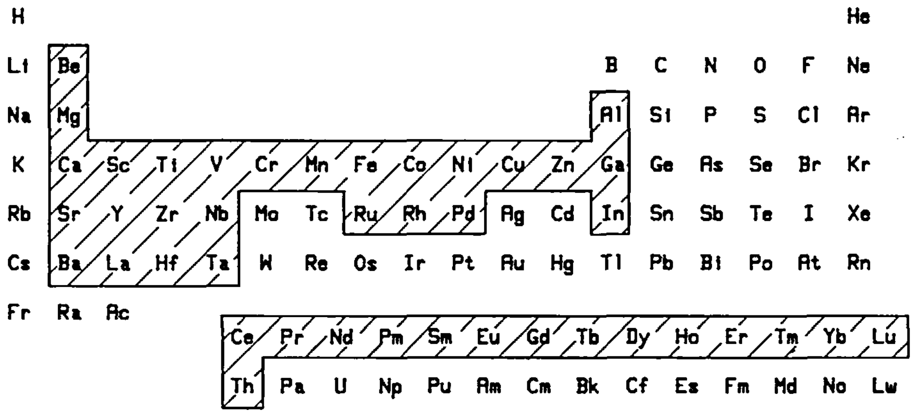


FIGURE 21. Elements which form volatile complexes with β-diketones.

chromatographic" (LVGC) method, which means that the trifluoro-acetylacetone is added to the carrier gas.

Figure 22 shows a separation of lanthanides[232] such as trifluoroacetylacetonates.

A great number of organometallic compounds based on as alkyl- and acryl-compounds and cyclopentadion, have been used in inorganic chromatography. Recently, sulfur-containing metal chelates and nonfluorinated diethyldithiocarbamates[240-242] of relatively low volatility have been successfully applied in gas chromatographic multielement analysis. Figure 22B shows a separation of trace elements such as dithiocarbamates.[240] The different possibilities of interference by the other elements present in the solution are illustrated by the different equilibriums which are involved: normally the chelate is formed in the aqueous phase and extracted into an organic solvent. The extraction is described by the following equation:

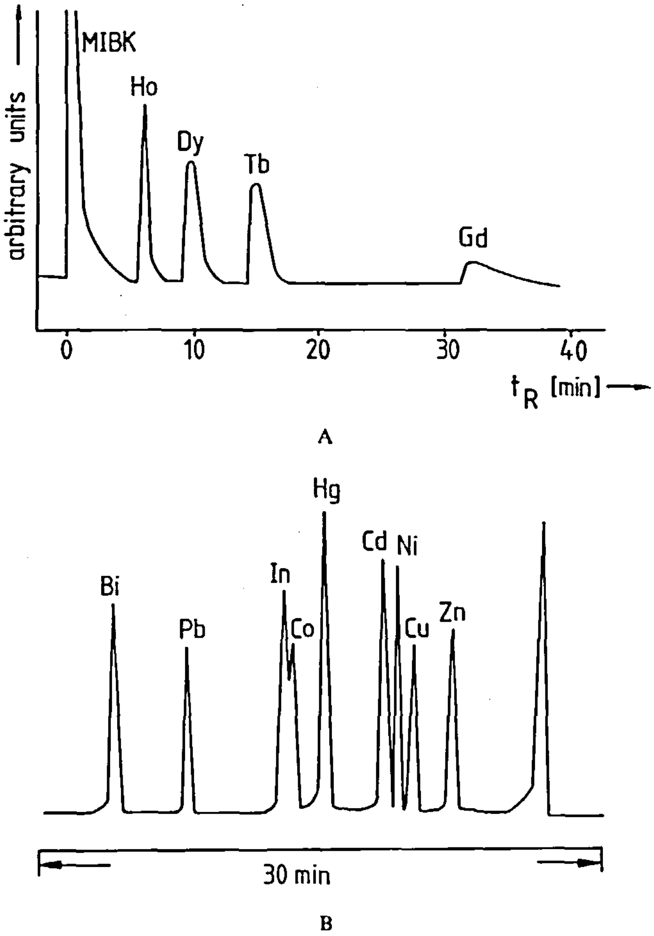


FIGURE 22. (A) Gas chromatogram of TFA chelates of Gd, Tb, Dy, and Ho. Column: Chromosorb W® loaded with 0.2% PEG-20M and 1.8% Silicone® OV-17 and kept at 240° C; carrier gas: He (including 0.41 mℓ of HTFA) at 41 mℓ/min; detector: thermal conductivity.[232] (B) Gas chromatogram of di-(trifluoroethyl)dithiocarbamates (1 µg/µℓ): column OV-25 on Chromosorb®. 120 to 210° C: column 900 × 2 mm; FID.[240]

$$Me^{P+} + p\,(HL)_o \rightleftharpoons (MeL_p)_o + pH^+ \qquad (1)$$

with Me^{P+} = metal concentration in the aqueous phase $(HL)_o$ = chelate forming agent in the organic phase $(MeL_p)_o$ = metal chelate in the organic phase p = coordination number, valency. The constant for the equilibrium (extraction constant) is given by the following expression:

$$K = \frac{(MeL_p)_o \cdot (H^+)^P}{(Me^{P+})(HL)_o^P} \qquad (2)$$

K is composed by the following constants:

Table 23
SUITABLE VOLATILE COMPOUNDS FOR THE CONCENTRATION OF TRACE ELEMENTS

Type of compound	Elements which form suitable volatile compounds (25 to 950°C)
Chlorides	Ti, Zr, Hf, V, Nb, Ta, (Cr), Mo, W, Tc, Re, Mn, Fe, Ru, Os, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te, Po, Ce
Fluorides	Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, Re, Ru, Os, Rh, Ir, Hg, Si, Ge, Sn, P, As, Sb, Bi, S, Se, Te
Oxides	S, Se, Te, Po, (As), Tc, Re, Ru, Os, (Mo, W), Zn, Cd, Hg
$AlCl_3$-complexes	Lanthanides, actinides, Ca, Sr, Ba, Ra, Fe, Co, Ni, Cu, Pd, Pa, Mo
Elements	Noble gases, halogenes, O, S, Se, Te, Po, N, P, As, Sb, Bi, Sn, Pb, Tl, Zn, Cd, Hg, (Li, Na, K, Rb, Cs, Fr)

From Bächmann, K. and Rudolph, J., *Radioanal. Chem.*, 32, 243, 1976. With permission.

$$Q_{HL} = \frac{(HL)_o}{(HL)} \text{ distribution coefficient for the chelate forming agent}$$

$$^{Q}MeL_p = \frac{(MeL_p)_o}{(MeL_p)} \text{ distribution coefficient for the metal chelate}$$

$$^{K}MeL_p = \frac{(MeL_p)}{(Me^{p+})\cdot(L^-)^p} \text{ stability constant of the metal chelate}$$

$$K_{HL} = \frac{(H^+)\cdot(L^-)}{(HL)} \text{ dissociation constant of the chelate forming agent}$$

Therefore,

$$K = \frac{^{K}MeL_p \cdot K^p_{HL} \cdot {}^{Q}MeL}{Q^p_{HL}} \tag{3}$$

The extraction has to be optimized as to the pH-value and the use of a buffering solution. The extraction also depends on the volume ratio of aqueous and organic phase. This is important since a small volume of organic phase would result in a less quantitative extraction but higher preconcentration.

The main disadvantage of the use of chelates or organic metallic compounds for a gas chromatographic separation is that at very low concentrations, losses on the column lead to high systematic errors.

6. Gas Chromatography of Inorganic Compounds

Table 23 summarizes the elements[223] which form volatile compounds when the temperature is as high as 1000°C. Most of the elements form volatile halides; some of the elements form volatile oxides or $AlCl_3$-complexes.

In Table 24, organic gas chromatography is compared with inorganic gas chromatography. The main difference is that inorganic gas chromatography as defined above is used for the quantitative determination of elements and not the determination of molecules. Therefore, it is possible to form suitable volatile compounds. A second characteristic feature is the use of a reactive mobile phase. Reactive gases influence the separation in three different ways:

Table 24
COMPARISON OF INORGANIC AND ORGANIC CHROMATOGRAPHY

	Detection and identification	Stationary phase	Mobile phase
Inorganic gas chromatography	Preferable selective detectors	SiO$_2$, graphite salts	Ar/Cl$_2$, HCl, CCl$_4$, Br$_2$, BBR$_3$, O$_2$, AlCl$_3$
Organic gas chromatography	Often unselective detectors and use of retention times	Organic compounds	Ar, N$_2$, (inert gases)

Table 25
SEPARATION OF TRACE ELEMENTS USING INORGANIC GAS CHROMATOGRAPHY

Group and Reactive gas	Stationary phase	Elements	Detection	Ref.
Fluorides	PTFE, KELF	Te, I, Mo, Np, Tc, Pu, Sb, Nb, Ru	ECD	250
Chlorides	As InCl$_3$-TlCl, fused salts	Zr, Ti, Ta, Sn, Sb, Nb, Mo, Hf, Fe, As, Al	FPD	251
Chlorides	Graphite, LiCl-KCl	Nb, Ta, Zr, Hf	FPD	252
Chlorides	Silicone, oil DC 550, etc.	Si, Ge, P, As, Sn	TCD	253
Fluorides	PTFE	Mo, W, Ta, Nb, Sb, As	TCD	254
Bromides, iodides	Fused salts	Sn, P, Ti, As, Al, Fe, Si, Ge, Ta, Nb	TCD, FPD	222
Chlorides	Quartz, graphite, NaCl, KCl, SrCl$_2$ YCl$_3$, etc.	Nb, Mo, Tc, Zr, Te	Radioactivity	255, 256, 258, 259
Chlorides	Quartz, graphite, NaCl, KCl, SrCl$_2$, YCl$_3$, etc.	Re, Ta, Tl, Ga, Cd, Pb, In, Sn, Po, Bi, Sb, Pa, Hf, Zr, Os, Te, Tc	Radioactivity	257
Bromides	Quartz, NaBr, KBr., etc.	Sn, Sb, Nb, Te, Bi, Mo, Zr, In, Tc	Radioactivity	260
Oxides	Quartz	Ru, Te, Re, Os, Ir	Radioactivity	234

1. Volatile molecules which are decomposed on walls to form a nonvolatile compound (e.g., PuCl$_4$ → PuCl$_3$) can react again, forming the volatile compound.
2. The properties of the stationary phase may change by the adsorption of the reactive mobile phase.
3. The reactive gas reacts with impurities in the gas — for example, O$_2$ in argon — so that interfering reactions are avoided. BBr$_3$ and CCl$_4$, especially at higher temperatures, act as scavengers for H$_2$O or O$_2$.

In Table 25, some typical separations are compiled: In a number of studies, the separation of volatile hydrides[300,308] has been studied. In most cases, the hydrides were generated from aqueous solution by the addition of sodium borohydride. After trapping a Porapak Q column was used[300] for the separation of GeH$_4$, AsH$_3$, SnH$_4$, and SbH$_3$. The oven was temperature-programed at 8°C min^{-1} from 75 to 120°C.

Detection limits for 5 mℓ samples with the freeze-trap method are: Ge (1 ppb); Sn (10 ppb); As (2 ppb); Sb (20 ppb). The detection was in some cases carried out by a katharometer detector. Before the detector, the hydrides passed through a furnace at

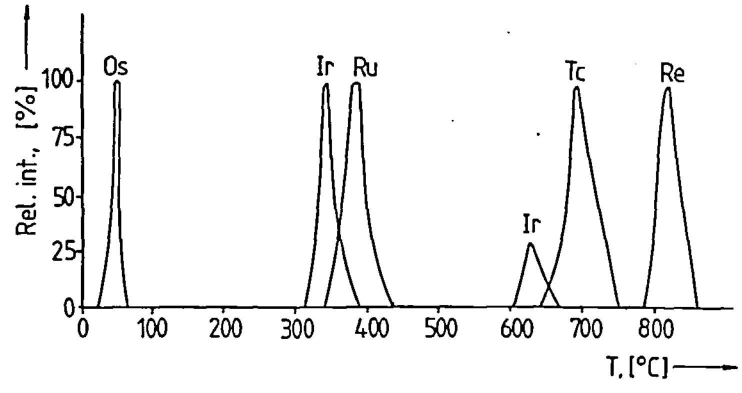


FIGURE 23. Separation of volatile oxides at a quartz surface.[234,235] Heating rate: 20°/min.

1000°C to decompose them and to measure only the H_2-gas. Also, dual flame ionization, atomic absorption, and mass spectrometric detectors have been used.

Whereas the hydrides are separated gas chromatographically at rather low temperatures, the oxides and halides are separated at high temperatures — also in a temperature-programed mode. A separation of trace elements using gas chromatography is especially advantageous without any fusion process, but with a direct volatilization. The elements Te, Re, Os, Ru, and Ir (as is shown in Figure 23) are separated as oxides.[234,235]

A great number of studies have been carried out, using the halides. Metal halides react with the usual liquid or solid phases and with metallic parts of the gas chromatographic system at higher column temperatures. It is therefore necessary to use inert material. Special precautions have to be taken in order to avoid any traces of oxygen or moisture from the carrier gas and stationary phase. The necessity of constructing gas chromatographs which work at high temperatures and a number of technological problems have made inorganic gas chromatography unattractive. However, the requirement of the separation of very low concentrations, together with an elimination of contamination, makes it necessary to develop new methods which fulfill these requirements. Gas phase separation is especially suitable for extreme conditions as given by low concentrations.

A typical separation of chlorides is shown in Figure 24.[236] The problem of inert stationary phases is solved by using quartz, graphite, and salts, such as NaCl, KCl, CsCl, $SrCl_2$, $BaCl_2$, $CaCl_2$, $MgCl_2$, YCl_3, and others.

Bromides are separated by using NaBr, KBr, etc. as stationary phase. Taking $AlCl_3$ and forming complexes with chlorides, it is possible to separate even adjacent lanthanides.[238] In Figure 25 are compiled the elements which form volatile complexes with $AlCl_3$. A typical example of a separation is shown in Figure 26.

A modification of gas chromatography is thermochromatography.[235,237,239] In this method, the different elements are deposited in a tube with a temperature gradient. Figure 27 shows an example of a tube with a temperature gradient the different zones are coated with different stationary phases. The deposited compound can be desorbed or decomposed by heating up and carrying out a sequential analysis.

7. *Gas Chromatography of Anions*

Due to the nonvolatility of anions, the application of gas chromatography to the analysis of inorganic anions is a relatively new field. Derivatization reactions are

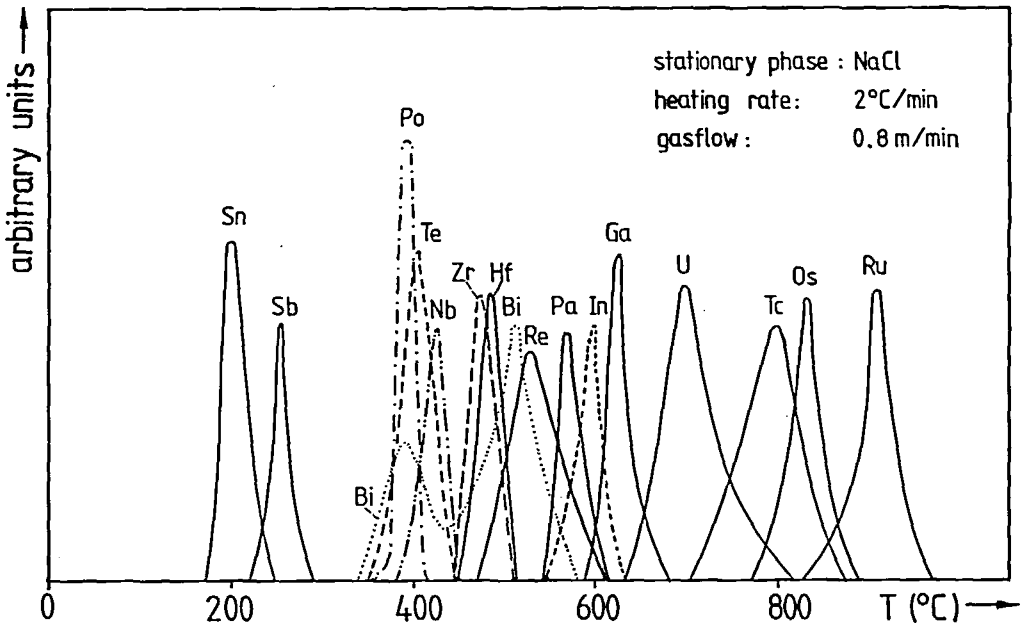


FIGURE 24. Temperature programed gas chromatographic separation (stationary phase NaCl, heating rate 2° C/min, mean carrier gas flow 0.8 m/min.[236])

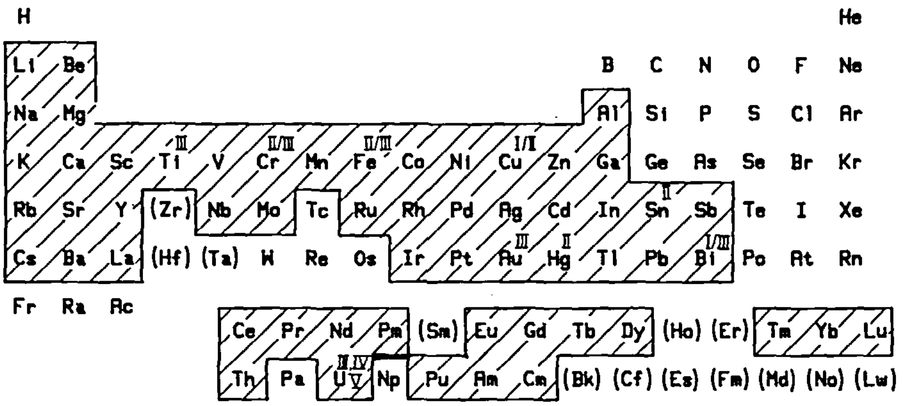


FIGURE 25. Elements which form volatile complexes with $AlCl_3$.[233]

necessary to form volatile compounds which can be separated by gas chromatography. Ideally, the derivatization products should have low polarity and should not react with the stationary phase of the columns. Characteristic reaction products are esters, substitution or addition products with organic compounds, anhydrides, the elements, and the acids or other inorganic compounds. Table 26 summarizes a number of these types of reactions:[261]

1. A reagent for a number of anions is trimethylchlorosilane (TMCS) or triethylchlorosilane (TECS) or bistrimethylsilylfluoroacetamide (BSTFA). Derivatives from the

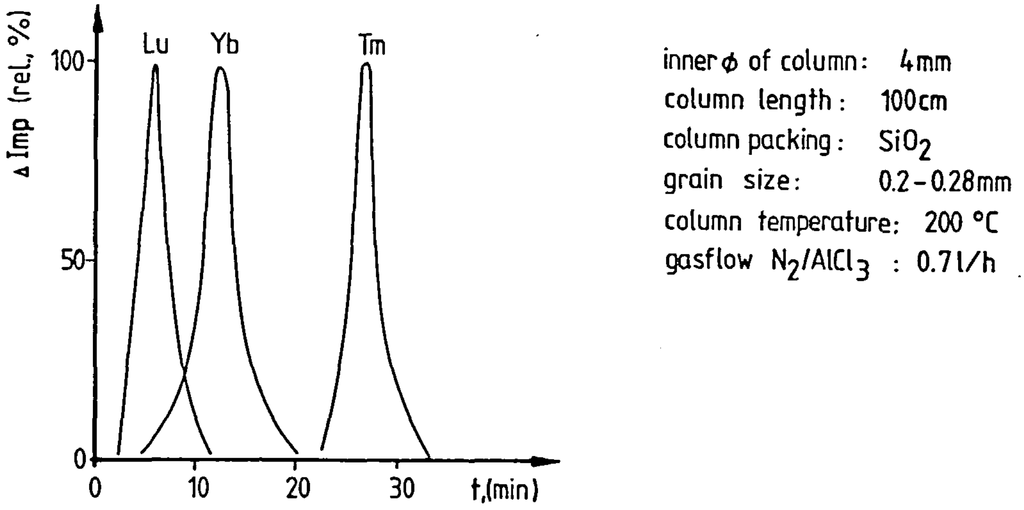


FIGURE 26. Separation of lanthanide chloride-aluminum chloride complexes at a quartz surface (180° C) 1 m column.[238]

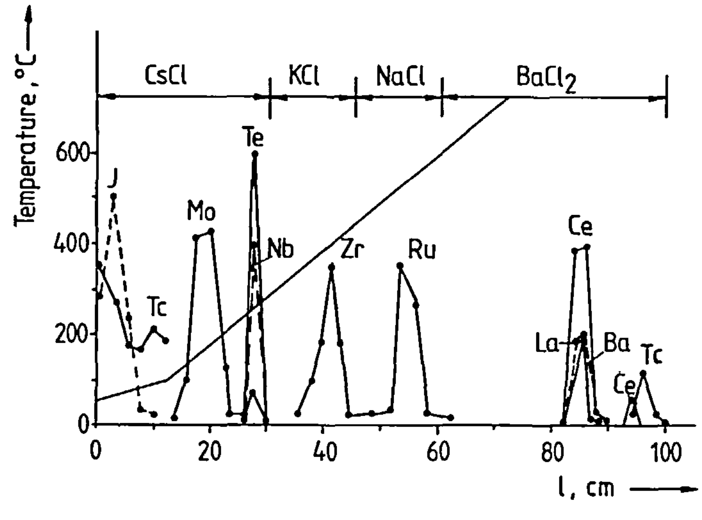


FIGURE 27. Chromatographic separation of chlorides using a temperature gradient and different wall coatings.[236,237]

following anions have been formed:[261] AsO_3^{3-}, AsO_4^{3-}, $(CH_3)_2AsO_2^-$, BO_3^{3-}, CO_3^{2-}, $C_2O_4^{2-}$, PO_3^{3-}, PO_4^{3-}, SO_4^{2-}, SiO_4^{4-}, VO_4^{3-}, F^-.

2. Addition to double bonds or epoxides: for example, the acids HCl, HBr, HI, and HF. Especially with HCl we could show that by adding HCl to an epoxide and using a second derivatization agent (HFBA), 100 fg of HCl can be determined.[271-273]
3. Substitution or organic molecules: Br^-, I^- (using the halogens), NO_2^-, NO_3^-.
4. Formation of acids: S^{2-}/H_2S; when HI is added to a solution, S in any form is reduced so that H_2S is produced.
5. Formation of anhydrides: From CO_3^{2-} and SO_3^{2-}, CO_2 and SO_2 can be produced and separated.

Table 26
ANIONS DETERMINED BY GAS CHROMATOGRAPHY

Anion	Derivative	Sample matrix	Stationary phase	Detector	Ref.
AsO_3^{3-}	$(TMS)_3AsO_3$	H_2O	SE-30, OV-17	FID, MS	262
AsO_4^{3-}	$(TMS)_3AsO_4$	H_2O	SE-30, OV-17	FID, MS	262
$(CH_3)_2AsO_2^-$	$(CH_3)_2AsI$	H_2O	DC-200	EC	263
	$(CH_3)_2AsO_2(TMS)$	Solid salt	SE-30	FID	263
BO_3^{3-}	$(TMS)_3BO_3$	H_2O	SE-30, OV-17	FID, MS	262
Br^-	$BrCH_2CH_2OH$	H_2O	EGS	FID	264
	CH_3Br	H_2O	Poropak Q	TC	265
CN^-	CNCl	Blood, urine	Halcomid M-18	EC	
CO_3^{2-}	$(TMS)_2CO_3$	H_2O	SE-30, OV-17	FID, MS	262
	CO_2	Solid salt	Poropak Q	TC	266
$C_2O_4^{2-}$	$(TNS)_2C_2O_4$	H_2O	SE-40, OV-17	FID, MS	262
Cl^-	$ClCH_2CH_2OH$	H_2O	EGS	FID	264
	CH_3Cl	H_2O	Poropak Q	TC	265
F^-	$(C_2H_5)_3SiF$	H_2O	DC-550	FID	
	CH_3F	H_2O	Poropak Q	TC	265
I^-	ICH_2CH_2OH	H_2O	EGS	FID	264
	CH_3I	H_2O	Poropak Q	TC	265
NO_2^-	$C_6H_5NO_2$	H_2O	Apiezon M	EC	267
NO_3^-	$C_6H_5NO_2$	H_2O	Apiezon M	EC	267
PO_3^{3-}	$(TMS)_3PO_3$	H_2O	SE-30, OV-17	FID, MS	262
PO_4^{3-}	$(TMS)_3PO_4$	H_2O	DC-430	TC	268
S^{-2}	H_2S	Solid salt	Poropak Q	TC	266
SCN^-	CNBr	H_2O	Poropak Q	EC	269
SO_3^{2-}	SO_2	Solid Salt	Poropak Q	TC	266
SO_4^{2-}	$(TMS)_2SO_4$	H_2O	SE-30, OV-17	FID, FPD, MS	262
SiO_4^{4-}	$(TMS)_4SiO_4$	Solid salt	SE-30	FID	270
$Si_2O_7^{6-}$	$(TMS)_6Si_2O_7$	Solid salt	SE-30	FID	270
VO_4^{3-}	$(TMS)_3VO_4$	H_2O	SE-30, OV-17	FID, MS	262

6. Formation of inorganic derivatives: $PhHgNO_3 + Cl^- \rightarrow PhHgCl + NO_3^-$. Since the product PhHgCl is volatile and easily extractable, a separation is possible and one way of determining the Hg is with atomic absorption.

D. Electrochemical Methods for Preconcentration

A rather classical method of enrichment is electrodeposition on disks, foils, tubes, or wires. Table 27 summarizes characteristic examples for electrochemical methods. The surface material of the support depends on the subsequent determination method.

For XRFA with thin layers, a disk or foil is suitable. The material of the foil should have a low Z, e.g., polyethylene or carbon. For AES or AAS, a material which can be heated up for the desorption is suitable. Especially elegant is the solution of Volland et al.[280,281] where they used graphite tube as the cathode, which can be used directly for flameless atomic adsorption. For the determination of very low concentrations the electrolysis times need to be increased considerably (up to 50 hr), and a limit of concentration is reached which cannot be lowered. In a hydrodynamic flow[280,281] with a small distance between the cathode and anode, the electrolytic deposition is improved. Volland et al.[280,281] with a hydrodynamic flow system could deposit ng of Fe, Co, Zn, Bi in the absence of a matrix, which is also electrolytically deposited. The only added reagent after the fusion was NH_4OH so that the contamination risk is rather low.

Table 27
EXAMPLES FOR ELECTRODEPOSITION AS PRECONCENTRATION METHOD

Matrix	Elements electrodeposited	Support	Analytical method	Ref.
Seawater	Pb, Co, Ni	Pyrolytic graphite-coated tubes	AAS	279
Water	Ni, Cu, Zn	End face of a graphite rod	XRF	278
Water	Cu, Au	Platinum wire	microprobe	277
2-Propanol-water	Co, Ni, Cu, Zn, Cd	Al-foil	XRF	276
Water	Cd, Ni, Zn	Graphite disk	XRF	275
Water	Fe, Ce, Zn, Bi	Graphite tube	MIP, AAS	280, 281
Water	Ag, Bi, Cd, Hg, Pb, Se, Te, Tl, Zn	Pt-spiral-filament	AAS	274

Table 28
EXAMPLES FOR COPRECIPITATION AS PRECONCENTRATION METHOD

Matrix	Elements coprecipitated	Precipitate	Analytical method	Ref.
Standard reference material	Fe, Cr, Co, Cu, Ni	Hydroxide + diethyldithiocarbamate + Ti	XRFA	282
Water	Hg, Ag, Cu, Bi, Pb, Cd, Te	ZnS, MnS, CuS, PbS	XRFA, AAS	283
Aqueous solution	Co, Ni, Cu, Fe, Mn, Cr	Hydroxide + diethyldithiocarbamate + Ti	XRFA	284
Aqueous solution	Cr, Fe, Co, Ni, Cu, Zn, As, Hg, Pb	Ammonium pyrrolidine dithiocarbamate	XRFA	285
Water	Fe, Cu, Zn, Se, Cd, Sn, Te, Hg, Pb	Polyvinylpyrrolidone-thionalide	XRFA	286
Phosphate containing matrices	Zn, Cu, Pb, Mn	$Fe(OH)_3$	XRFA	287
Aluminum containing matrices	Ca, Fe, Mn, Si, Ti, V, Zn	$Zr(OH)_4$	AAS	288

E. Coprecipitation and Matrix Precipitation

Table 28 summarizes typical examples for coprecipitation and matrix precipitation. The method of coprecipitation is closely related to the method of adsorption when insoluble compounds are adsorbed. The choice of the precipitating agent depends on the elements to be analyzed, on the matrix, and on the analytical method. In multielement

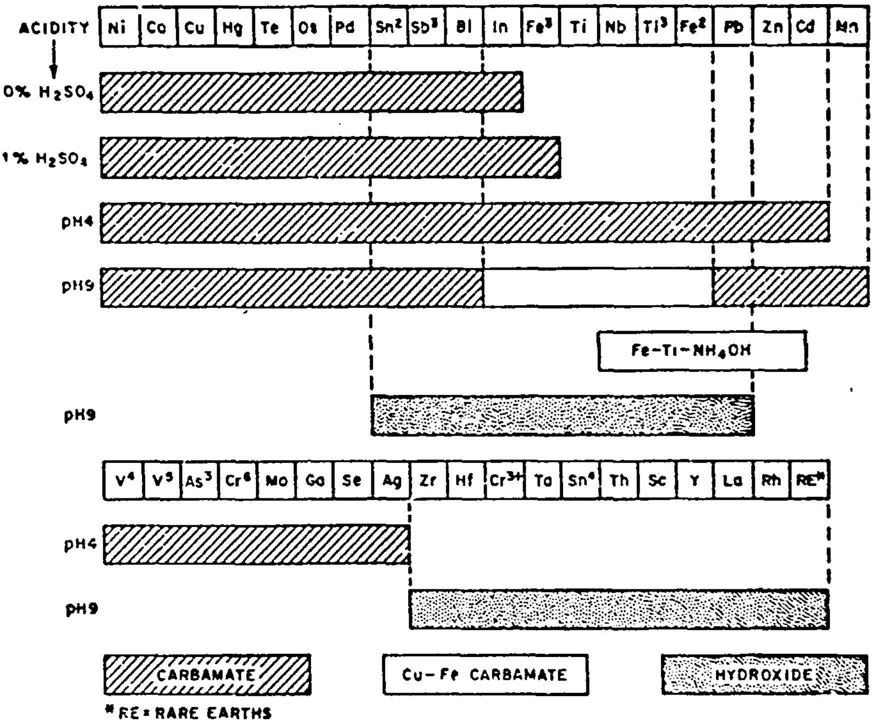


FIGURE 28. Conditions for coprecipitation of trace elements with carbamate and ammonium hydroxide.

analysis, a broad spectrum precipitating system is of interest as, for example, hydroxides or organic complex-forming agents. A second requirement is a high purity of the precipitating agent. The last requirement is the adaption to the analytical method. For XRFA the precipitation should form a thin and uniform layer. Confinement of the entire sample to a small area which is equivalent to the size of the milliprobe X-ray beam, provides advantages. The X-ray fluorescence intensities from the trace elements are increased, and [283] the scattering from the supporting filter is low. Disam et al.[283] have used sulfides and form the precipitate by filtering the solution through a preformed precipitation. The advantage of this method is that a preformed precipitation can be produced much more uniformly.

An interesting modification is the matrix precipitation. Jackwerth and Willmer[289] have precipitated Cu as CuS with thioacetamide and determined Cd, Co, Fe, In, Mn, Ni, Pb, Tl, and Zn in the residual solution. The trace elements in strontium and barium salts were determined after precipitation of the matrices as nitrates.[300] Jackwerth has also determined trace elements in silver after precipitation of the matrix.[301,303,304]

Figure 28 shows that selective separations of groups of elements are possible by controlling the pH at which precipitation occurs. Thus, the first 11 elements can be separated from as much as 1 g of manganese in 1% H_2SO_4. Conditions for the selective separations of trace elements are described by Luke.[306]

The processes which play a role in coprecipitation are quite complex and are of a chemical and physical nature. Physical adsorption, colloidal effects (adsorption due to the electrical charge), and cocrystallization are responsible for the coprecipitation. Compared with extraction, the selectivity and sensitivity of coprecipitation is poorer.

Table 29
METHOD OF PRECONCENTRATION BY PARTIAL DISSOLUTION OF THE MATRIX

Matrix	Trace element	Analytical method	Ref.
Zinc	Ag, Au, Bi, Co, Cu, Fe, Ni, Pb, Pd	AAS	293
Tin	Ag, Au, Bi, Cu, Pd	AAS	289
Indium	Ag, Au, Bi, Cd, Co, In, Ni, Pb, Pd, Sn, Tl	Different	289
Aluminum	Bi, Cd, Ga, In, Pb, Tl, Zn	AAS	295
Gallium	Ag, Au, Bi, Cu, Fe, Hg, Ni, Pb, Pd, Sn, Zn	AAS	296, 298
Mercury	Au, Pd	Photometry	291
Cadmium	Ag, Au, Bi, Cu, Ni, Pb, Pd	AAS	294, 297

Precipitation is suitable for determining amounts between micrograms and picograms and depends sometimes on the amount. Thus, it is possible to precipitate micrograms of Be with calcium phosphate, whereas nanograms of Be are only 70% precipitated. In some cases, the precipitating agent is removed after the precipitation. For example, mercury can be removed as its bromide after precipitation of trace elements on mercury sulfide. The organic precipitating agent can be removed by incineration or by solution in an organic solvent.

F. Partial Dissolution of the Matrix

In Table 29, some examples for the method of selective dissolution of the matrix which has been developed by Jackwerth and co-workers are given.[290-299] The samples are amalgamated by addition of mercury and then dissolved in acids. Most of the matrix metal, together with the traces which are less noble, is dissolved, whereas the electrochemical nobler traces remain in the residue. The recovery rates are mostly higher than 90%.

G. Thin-layer Chromatography, Paper Chromatography, Electrophoresis

In chapter Sections II.B.1 and II.B.2, extraction and sorption methods have been described, either as a single concentration step or as a multistage separation on a column. The process of extraction and sorption can also be used on a planar stationary phase. Included in this type of separation is electrophoresis, even if the migration in an electrical field is a completely different separation process. The advantages of these methods are simplicity, the use of selective spray reagents for detection, and the possibility of automatization of quantitative evaluation by scanning methods. Furthermore, compared with liquid chromatography it is possible to separate several samples side by side. The disadvantage of these methods are difficulties in quantitative determination and the background of trace elements in the stationary phase. In Table 30 are compiled examples for the paper and thin-layer chromatography of trace elements.[6] The stationary phases are either solids as silica gel or liquids on a solid support for distribution chromatography. Metal ions are separated on impregnated paper. Organic chelating reagents or inorganic substances are useful for impregnation.

The detection limits range from the microgram level down to the nanogram level. For quantitative analyses a great number of different methods are used such as planimetry

Table 30
PAPER AND THIN-LAYER CHROMATOGRAPHY OF TRACE ELEMENTS

Element	Chromatography	Detection	Detection limit	Ref.
Cs, Rb	PC: as picrates	Elution: photometry	5 μg	25
Cu, Co	PC: as 2-hydrazinothiazole derivatives	Planimetry	0.1—6 μg	308
Ag, Cu, Pb, Cd	PC + Fe or Pb diethyldithiocarbamate (precipitation-chromatography)	Visual	0.05—0.2 μg	309
Zr, Hf	PC + NH_4NO_3 (ascending PC)	+ Arsenazo III	μg-Range	310
Zr, Nb	PC + methylene-bis(di-*n*-hexyl) phosphine oxide	+ 8-Hydroxychinoline	Zr μg-range	311
U (acetato complex)	DEAE (cellulose)anion-exchanger	+ K_3 $Fe(CN)_6$ (ringoven)	ng-Range	312
Zn, Cd, Co, Fe	Cellulose + liquid ion-exchanger	+ PAN (densitometry)	1 μg	313
Fe, Co, Mn, Ni, Zn, Co, Rh, Pb, Cd, Hg	TLC: silica gel, as tetraphenylporphyrin chelates	Visual	10^{-10} moles	314
Ni, Cu, Co, Mn	TLC: silica gel, as PAN-chelates	Elution: photometry	0.4 ppm	315
F, Cl, Br, J	TLC: silica gel + starch binder fluorescent reagent	Visual: + bromcresol purple	1—2 μg	316
Cu, Cu, Ni, Fe	TLC: Al_2O_3 combination of ringoven and circular chromatography	Visual: + rubeanic acid, + KSCN	5—10 ng	317

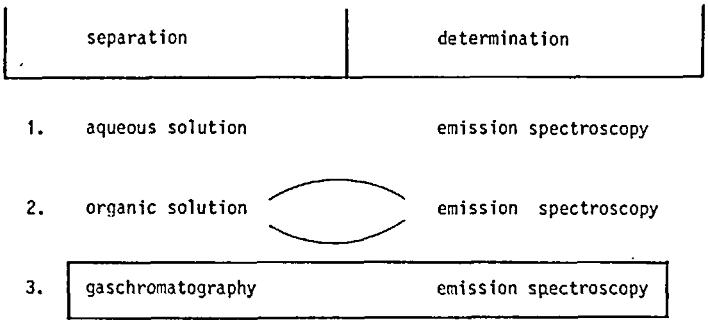


FIGURE 29. Different types of connection between concentration method and detection method.

and photodensitometry of colored substances (with or without spraying), diffuse reflectance spectrometry, fluorimetry, radiometry, and flame photometry. A special technique is the ring-oven method,[185,318] in which a chromatogram of a drop is developed in a circle. The separation efficiency of thin-layer chromatography was shown by Hohmann and co-workers,[319] who separated all rare earth nitrates in the tri-*n*-butylphosphate/aqueous nitrate system.

Electrophoresis is not very extensively investigated for the separation of trace elements, but it was shown[320-322] that adjacent lanthanides and actinides can be separated completely.

The disadvantage of paper chromatography and thin-layer chromatography for practical analyses is that only small amounts can be separated so that trace element/matrix separation is impossible or, at least, difficult. These methods are more suitable for the separation of trace elements themselves. Also, the quantitative evaluation, with the exception of radiometric determination, needs improvement.

III. COMBINATION OF CONCENTRATION METHOD AND DETECTION METHOD

A. General Remarks

It is possible to differentiate between different types of connecting of separation and determination (Figure 29). If emission spectroscopy is used for the determination, and the sample is in the form of an aqueous solution, the method of separation leading to the aqueous solution is not important. (This is not valid for the interference of other elements which are in the solution and are separated with different separation factors, when different methods are used.) In the case of an organic solution, the signal for an element depends on the organic solvent which has been used for the extraction so that it is necessary to optimize the best organic solvent for the determination and the best organic solvent for the extraction. In the third type of connection, separation and determination are combined in one instrument (chromatography). In this case, the conditions for the separation of the trace elements as an inert gas and the streaming velocity has to be adapted to the conditions for the determination. Furthermore, it is not possible to have a completely free choice of the detection method. If it is desirable to use several detection methods, combinations of the first type are the best.

A second point for the choice of the combination of the separation method and the detection method is that both methods should give the same precision. The combination of a high-precision determination with a low-precision separation, and vice versa, does

Table 31
COMBINATION OF ATOMIC SPECTROSCOPY WITH DIFFERENT CONCENTRATION METHODS

Method	Remarks	Ref.
Extraction	Most frequently used, especially with flame atomic absorption; partly enhanced signals in organic solvents	2
Precipitation and coprecipitation	In case of a coprecipitation of the trace elements, a dissolution is necessary	282—288, 300—306
Electrolysis	Very elegant method when the trade elements are electrodeposited directly in a graphite tube	280, 281
Volatilization	Especially developed for the evolution of hydrides of an aqueous solution (As, Se, Te, Bi, Sb, Sn, Pb)	197—199, 218, 220, 221, 260
Extraction chromatography; sorption chromatography	The combination of AAS and AES with liquid chromatography is not very elegant	6
Gas chromatography	The combination of AAS and AES (ICP or MIP excitation) is not very developed, but is rather promising for the future	3, 218, 220, 221

not make sense. The same considerations are valid for the background of the elements which are analyzed. There is no point in combining a separation method that has a high contamination with a detection method which allows the determination of very low amounts, and vice versa.

B. Determination by Atomic Absorption and Emission Spectroscopy

The problems of the combination of AAS and AES with a concentration step are almost the same as when flame spectroscopy or plasma spectroscopy is carried out. In flameless atomic adsorption, some special problems arise. Atomic absorption or emission spectroscopy is most frequently combined with solvent extraction as the preconcentration step or with concentration steps which lead to an aqueous solution. In recent years, the combination with volatile products (volatilization, evaporation, or evolution) has been developed more and more. Compared with atomic spectroscopy of solutions, the atomic spectroscopy of gaseous products results in much less interferences. In a solution, a number of processes such as evaporation, decomposition, etc., leads to formation of atoms, whereas in the gas phase only the dissociation of molecules leads to atoms, which is a process not very dependent on the other molecules. In Table 31, the different combinations are summarized.

An interesting combination of gas chromatography and AAS is shown in cases where different species of one element are to be determined,[326,327,331,332] whereas gas chromatography of different elements is better combined with a multichannel emission spectrometer.

C. Determination by X-ray Fluorescence Spectroscopy

For X-ray fluorescence, the samples should be preferably in a solid state after the concentration. Therefore, if a preconcentration in an aqueous or organic solution has been carried out, it is necessary to add a precipitation or electrodeposition step.

The intensity of the fluorescent X-radiation is a complicated function of the matrix. The intensity of the emitted X-ray is influenced by absorption and enhancement effects from elemental interactions and physical effects resulting from variations in particle size and surface.

When thick samples are used, the exciting radiation is completely absorbed and fusing with sodium borate or mixing with silica gel are recommended methods for obtaining a uniform matrix. The matrix should consist of elements with a low Z in order to avoid interferences. An evaluation of an X-ray fluorescence spectrum either by standards or by calculations is rather complicated when elements with a $Z > 20$ form the matrix. Therefore, a separation of the matrix elements and the trace elements is the aim of concentration steps in X-ray fluorescence analysis. Instead of thick samples, another form of the sample is to use a thin layer, which should be uniform and adherent to a thin support which does not interfere. Table 19 shows that elements in a thin layer can be analyzed in the nanogram range. Special excitation such as with a small angle or with polarized X-ray, lowers the detection limits even more.

Table 32 compiles examples for concentration steps which produce thin layers. The three methods which are used are precipitation, adsorption, and electrolytic deposition. A future development might be condensation of volatile compounds.[328] Thin-layer XRFA is especially applied for routine analysis of a great number of elements since precipitation and X-ray fluorescence can be carried out rather rapidly. Some restrictions as to the accuracy have to be taken into account.

D. Determination by Spark Source Mass Spectroscopy

Spark source mass spectroscopy is an extremely useful multielement survey method, *primarily because virtually all elements in the periodic table can be detected. At the same* time, it is possible to determine metallic and nonmetallic elements (halogen, oxygen, nitrogen, sulfur, phosphorus, etc.). Methods for the preparation of different samples for spark source analysis were reviewed by Guthrie.[329]

The preconcentration step should consist of a separation of the trace elements from the matrix and a deposition of the trace elements on an electrode.

There are a great number of other ionization processes which can be used thermal ionization, field desorption ionization, electron impact ionization after evaporation from a Knudsen cell, laser microprobe, and secondary ion mass spectrometry (SIMS). Most of these methods are restricted to special problems, such as surface analysis, and are more suitable for a direct application without any concentration step.

E. Determination by γ-spectroscopy (Activation Analysis)

The advantage of neutron activation analysis for multielement trace determination is the high accuracy and precision when an instrumental analysis without separation is carried out. Since some elements are activated very strongly due to the neutron capture cross section and the half-life, it is not necessarily the matrix element which has to be separated, but other elements which interfere in most of the γ-spectra.

In biological samples especially, sodium, potassium, and phosphorus cause interferences. Therefore, for multielement analysis of typical systems (for example, biological samples), group separation has been developed. Figure 30 shows an example of a group separation for processing SRM 1571 orchard leaves.[330] Figure 31 shows an example of group separations for volatile elements.[334]

In activation analysis, differentiation can be made between trace concentration before irradiation compared to after irradiation. A separation before irradiation nullifies the advantage of activation analysis in that no blank correction is necessary. Nevertheless, in some cases separations are carried out before irradiation in order to avoid the production and handling of high activities. Also, in cases where short-lived nuclides have to be measured and there is, therefore, no time for a separation after the irradiation is left, separations prior to the irradiation are applied. If short-lived nuclides are involved, special procedures have to be developed which are fast enough.

Table 32
CONCENTRATION METHODS FOR XRFA

Matrix	Elements	Concentration or absolute amount	Method	Ref.	Remarks
Aqueous solution	Cu, Zn, Ni	2—100 ng/mℓ	Electrolytic deposition	278	
Aqueous solution	Au, Cu	0.3·3 ng	Electrolytic deposition	277	Microprobe
Aqueous solution	Cr, Fe, Co, Ni, Cu, Zn, As, Hg, Pb	20 ng	Chelate formation and bonding to a glass surface	147	
Aqueous solution	Hg, Ag, Cu, Bi, Pb, Cd, Sn, As, Se, Te, Zn, Cr, Ni	ng/ℓ	Precipitation as metalsulfide layers	280, 281	
Aqueous solution	Mn, Co, Ni, Cu, Zn, Rb, Sr, Pb	ng/mℓ	Chelex-100 ion exchange membrane	3	80—90% capacity limited, due to Na^+ and K^+ content in natural water
Aqueous solution	Fe, Cr, Co, Cu, Ni	9—330 ng	Coprecipitation with $Ti(OH)_4$	3	Spot of 1.27 mm
Aqueous solution		1—5 ng/mℓ	Chelate formation on activated carbon	136	
Aqueous solution	69 Elements	μg-level	Coprecipitation	305	
Propanol/H_2O	V, Cr, Fe, Co, Ni, Cu, Zn, Ag, Cd, Pt, Au, Hg	10—300 ppb	Electrodeposition	276	

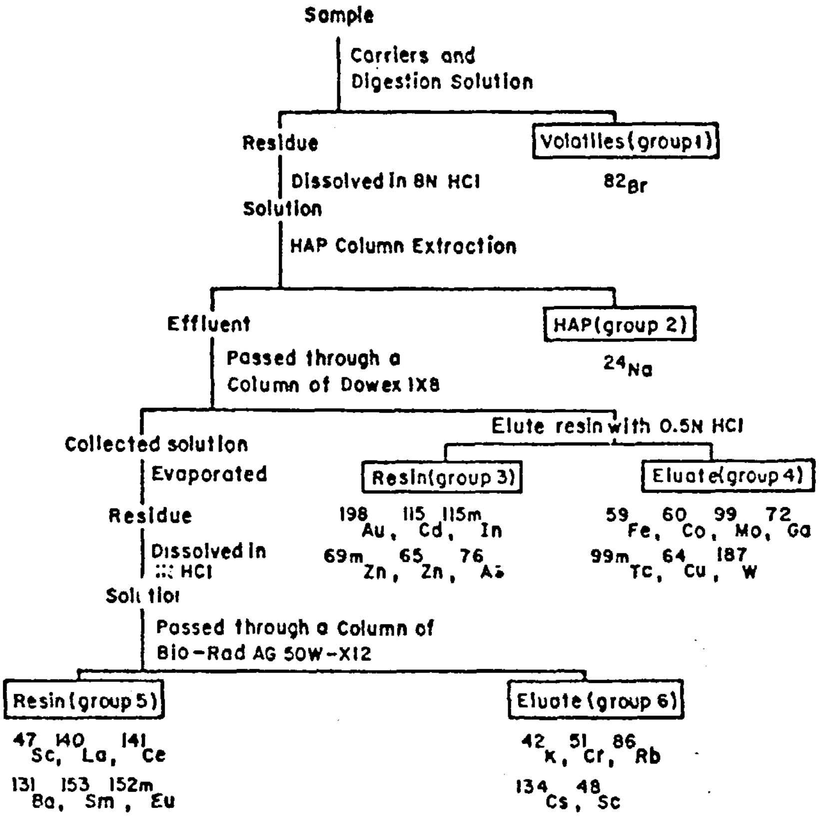
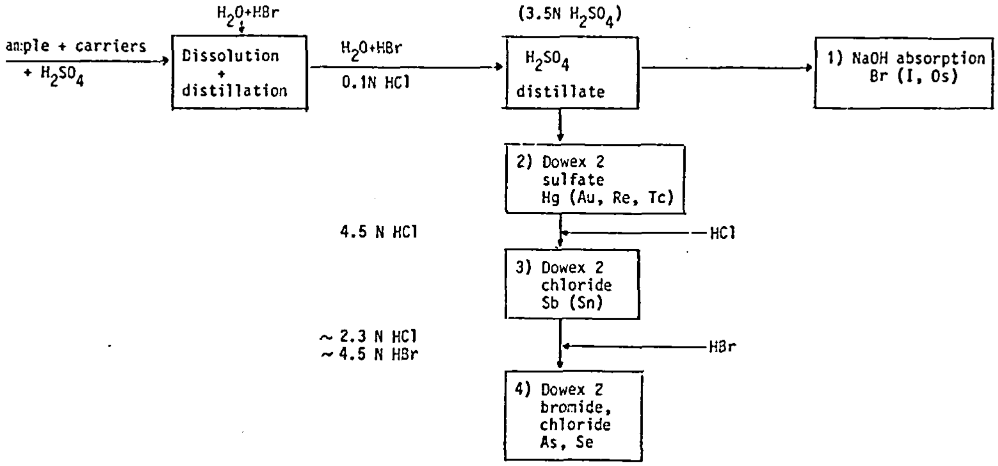


FIGURE 30. Radiochemical group separations by ion exchange. (From Morrison, G. H. and Potter, N. M., *Anal. Chem.*, 44, 839, 1972. With permission.)



Group 1) NaOH absorption: ^{32}Br (yield 92 %)
Group 2) Dowex 2 sulfate: ^{197}Hg, ^{203}Hg (yield 96 %)
Group 3) Dowex 2, chloride: ^{122}Sb (yield 97 %)
Group 4) Dowex 2, bromide, chloride: ^{76}As, ^{75}Se (yield 90 and 85 %, resp.)

The yields are given for Samsahl's automatic separation system (see section IV-B).

FIGURE 31. Group separation for volatile elements.

IV. COMBINATION OF CONCENTRATION METHOD AND SAMPLE SYSTEM

For the choice of the concentration method a great number of parameters are important, especially the type of sample and the elements which are to be determined and their concentration (absolute amount). Therefore, it is not possible to make more than some general remarks about suitable combinations of the concentration method and sample system.

In Table 33, the most important systems are summarized. Natural waters, biological samples, geological samples, and air samples show a certain similarity as to the composition of the matrix. The reason is that in these matrices the abundance of the elements in the crust of the earth play an important role. Therefore, the difference in the choice of the preconcentration step is governed more by the aim of the analysis and the elements to be determined. Survey routine analysis — e.g., of river water — will be restricted to the more abundant toxic elements, and the requirements of sensitivity and accuracy are not too high. For routine analysis, the time and the cost is an important factor. It is not possible to suggest concentration methods for the analysis of high-purity substances since each problem is different.

In the analysis of biological samples, especially when basic research is carried out, it is possible that the separation of very rare elements in microsamples is required. In this case, a time-consuming, chromatographic separation may be chosen. Another point which is common to the first four systems is that often not only the concentration of the element is important, but also knowledge of the chemical state (speciation). In this case, prior to the preconcentration, separation steps which take account of chemical state have to be carried out.

V. COMPARISON AND CHOICE OF CONCENTRATION METHODS

The choice of a concentration method (see Table 34) in multielement trace analysis depends on a number of parameters:

1. Matrix elements and major constituents
2. Elements to be determined
3. Concentration of the trace elements
4. Sample form and amount of sample
5. Accuracy and precision
6. Time necessary for the concentration
7. Detection methods which are available

The last point is often decisive since the equipment in a laboratory and the effectiveness of a certain concentration method will force one to choose what may not be the best method.

The great demand to carry out multielement analysis for a large number of samples will stimulate the development of concentration methods which can be fully automatized. In principle, it should be possible to automate all separation procedures by microprocessor units. Until now, the automation of instrumental analysis is much greater than the automation of preconcentration steps. The most difficult point in multielement trace concentration is to find a method which is suitable to separate all trace elements which are to be determined. As has been shown already in Table 1, the trace elements often have a quite different chemical behavior.

Table 33
POSSIBLE CONCENTRATION METHODS FOR DIFFERENT MATRICES

Matrix	Matrix elements	Elements to be determined	Concentration methods	Detection method
Natural waters	Na, Mg, Ca, K, Si	Environmental relevant elements	Routine concentration methods which use an aqueous solution	AAS, AES, XRFA
Biological samples	K, Ca, Na, Fe, Si	Environmental relevant elements, essential elements, biochemical relevant elements	Fusion and production of aqueous solutions; often less sample weight	AAS, NAA, AES, XRFA (higher sensitivity than in water)
Geological samples	Si, Al, Fe, Ca, K, Na, Mg	Geological relevant elements, environmental elements	In most cases preconcentration is avoided; since all fusion processes lead to aqueous solutions, the separation is in natural waters	XRFA, NAA
Air samples	Al, Fe, Mn, Ti, Na, K, Cl, S	Environmental relevant elements	For dust the same concentration steps are suitable as for soils	XRFA, NAA, AAS
High purity material	Metals, wave guides, semiconductor	Elements which change certain physical properties, e.g., the electrical conductivity	Different, depending on the matrix	High sensitivity

Table 34
COMPARISON OF DIFFERENT CONCENTRATION METHODS

Concentration method	Number of elements element groups	Contamination	Time for the concentration	Remarks
Extraction	All elements	Medium, depending on the purity of the organic phase	Rapid	Most frequently used; can be combined with most of the detection methods
Extraction chromatography			Slow	Special application
Ion exchange	All elements	Medium	Slow	Not frequently used
Adsorption	All elements except of low charged elements	High	Rapid	Low selectivity
Chelate resin	Special elements	Medium	Slow	Special applications
Crown ether	Anions, alkaline, and alkaline earths	Medium	Slow	Suitable for alkaline elements
Ion chromatography	Anions	Medium	Slow	The best method for anions
Volatilization	Only volatile elements	Low	Medium	Suitable for very long concentrations; application in speciation
Gas chromatography	Almost all elements except of alkaline elements and alkaline earths	Low	Slow	Suitable for very long concentrations; application in speciation
Electrochemical methods	Special elements	Depending on support	Slow	Special application
Coprecipitation	Almost all elements	High, depending on the precipitation agent	Rapid	Low selectivity
Matrix precipitation	Almost all elements	High, depending on the precipitation agent	Medium	Low selectivity
Partial dissolution	Special elements		Medium	Low selectivity
Thin layer chromatography, paper chromatography	Almost all elements	High, depending on the purity of the stationary phase	Slow	Application in speciation

The search for an optimum separation method should, in the future, be more and more a problem which is solved by using a computer. Until then, less elegant ways must be used. For example, the data on extraction (extraction coefficients as a function of all parameters) are so numerous that a choice of a separation procedure is often done more by intuition than by using the available theoretical knowledge.

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