

PROBLEMS, LIMITATIONS, AND FUTURE TRENDS IN THE ANALYTICAL
CHARACTERIZATION OF HIGH-PURITY MATERIALS

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Abstract - In materials science, solid state physics, and many other fields of modern technology there is rapidly increasing interest in obtaining accurate analytical data. In addition to the determination of the concentration of traces of an element in the bulk material, information on its distribution within the sample or on the surface of the sample is required. The analytical chemist is always faced with new problems showing the limitations of his methods. In extreme trace analysis the systematic errors inherent in the methods frequently cause the analytical results to be incorrect by several orders of magnitude.

The first part of this contribution deals with the sources and the identification of such errors.

In the second part examples from the author's laboratory of how to obtain accurate results in extreme trace metal analysis will be presented.

In all the methods discussed, optimized decomposition and separation steps - checked by means of radioactive tracers if possible - are combined with a suitable technique for determination of the isolated trace element.

The samples are preferably decomposed in a special pressure bomb, with highly purified acids. The trace elements are then separated from the matrix by conversion into gaseous products or by electrolytical deposition in a hydrodynamic system.

The final determination is accomplished by using very sensitive spectrometric methods, e.g. furnace atomic absorption spectrometry (FAAS), optical emission spectrometry (OES) with microwave induced plasma (MIP) and hollow-cathode excitation.

Dust-free laboratories, chemically inert materials for construction of the necessary apparatus, highly purified reagents, and special micro-techniques are very important factors in reducing systematic errors. Furthermore, new developments in the field of extreme trace analysis will only be successful if at least two independent methods are available to solve a certain analytical problem and thus provide a cross-check of the accuracy of the results.

It must be pointed out that only by the application of such expanded multi-step procedures to a variety of different matrices is it possible to be sure of the composition of standard reference materials for instrumental multi-element methods (e.g. mass spectrometry and instrumental activation analysis).

AIMS OF THE ANALYSIS OF HIGH-PURITY MATERIALS

All naturally occurring chemical elements are known to be ubiquitous, and to be found in all materials. Their concentrations in a matrix vary very widely, however. Moreover they can be decreased considerably by purification procedures. Consider the extremely high standards of purity demanded for e.g. the purest metals, semi-conductors, reactor materials, or ultrapure chemicals or reagents. The purity actually aspired depends on the particular use to be made of the material. Either the impurities must impart to the material defined mechanical, electrical, magnetic or optical properties, or resistance to chemicals, temperature, and radiation ("purity according to a particular purpose"), or they must cause no undesired physical and chemical effects ("limits of purity"). Nowadays limits of concentration of about 10^{-10} % are considered possible, but even below this range foreign atoms can cause physical effects in a crystal lattice by interactions with structural defects.

Reliable trace analysis must face reality, however. Routine analytical work can satisfactorily control at best a concentration range down to 10^{-4} %. The uncertainty associated with the determination of lower levels increases exponentially as the order of magnitude decreases. Further problems arise if only a limited amount of sample is available (< 1 g) for the bulk analysis, or if local distributions of foreign atoms, e.g. on grain boundaries or on the surface, are to be investigated. The absolute amounts of impurities to be determined are then in the ng, pg or even in the fg range (Ref. 1,2). We may no longer start with the idea that the results obtained with only a single method are accurate, even if they are reproducible.

The systematic errors inherent in analytical methods are very difficult to discern and become increasingly significant as the absolute amount of the element to be determined decreases. The most important condition for statistical treatment of the errors - that they should be normally distributed - often does not hold. In these extreme ranges the true values can be higher or lower by several orders of magnitude than the average values calculated from collections of data by the usual statistical methods, as is being shown more and more often by comparative interlaboratory analyses.

GENERAL ASPECTS OF EXTREME TRACE ANALYSIS

These problems just mentioned mean that for analyses at ng/g and pg/g levels the approach and working techniques must differ from those for $\mu\text{g/g}$ analysis.

I think that it would be generally agreed that direct instrumental multi-element procedures, e.g. solid state mass spectrometry (SSMS), optical emission spectrometry (OES), X-ray fluorescence analysis (XRF), instrumental activation analysis (IAA), and others are still handicapped by enormous difficulties in ng/g and pg/g analyses although they increasingly outstrip the less economical solution methods. In many cases these direct procedures do not have sufficient power of detection, but more seriously, the very complex methodical errors inherent in the excitation of the samples are all associated with interferences by the matrix and concomitant elements as shown in Fig. 1, upper section. The separation and very sensitive detection of the signals from the

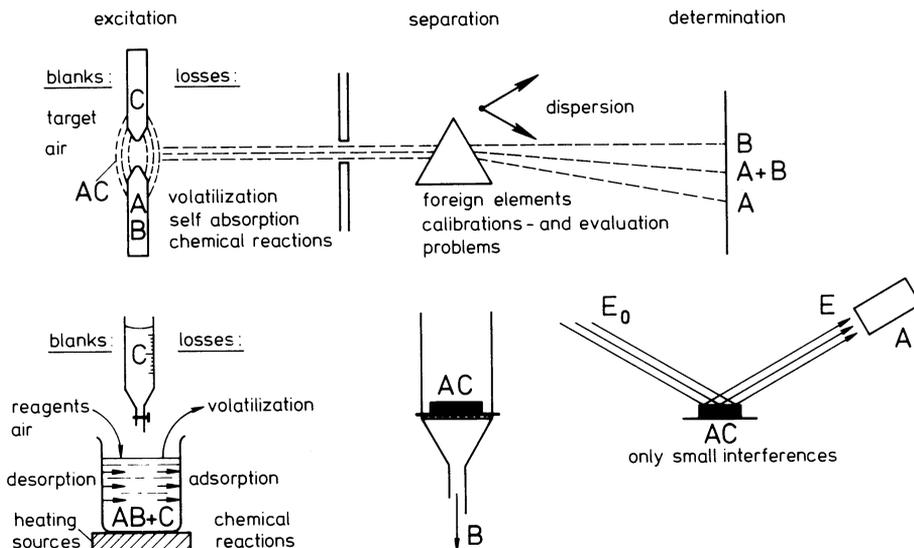


Fig. 1. Sources for systematic errors inherent in direct analysis procedures (above) and multi-stage procedures (below).

elements is much less of a problem. Even today, there is only a slight chance of obtaining accurate information if there is a lack of reliable reference samples, which must be very similar in composition to the sample to be analysed. It is imperative to check the accuracy of direct instrumental procedures with independent ones, easy to calibrate, where the trace elements are separated from the matrix and concomitant element before their determination.

For that reason we have to give priority to the development of these so called "multi-stage combined procedures". Moreover they are also suitable for preparing reliable standard samples.

There is no doubt that these procedures, consisting of the digestion, enrichment, and determination steps (see Fig. 1, lower section), are subject to a number of systematic errors, the avoidance of which requires great effort. First of all, there are the blanks or the interactions of the interfaces with the very small absolute amounts to be determined - these are adsorption and desorption effects or volatilizations - which may influence, and set a boundary, for the detection limits and the reliability, especially in connection with solution procedures (Ref. 3,4). The decomposition of the sample (including the trace elements) and the taking and preparation of the sample, are particularly subject to systematic errors. Therefore, this report deals mainly with methods to avoid these errors.

In the following I summarize once again some basic rules (Ref. 1-5);

1. All apparatus and tools must be made of an inert material. This requirement is only approximately met by noble metals, quartz, graphite, PTFE, and polypropylene. The purity and stability limits of these materials are, however, now well known.
2. Only the purest reagents and auxiliary materials available should be used and even then in minimum amounts. Thus, the choice of reagents is restricted to only a few in addition to water, HF, HCl, HNO₃, H₂O₂, aqueous ammonia, and some organic reagents and solvents. Additional special reagents have to be purified for each special case at the cost of time and effort.
3. Contamination from laboratory air has to be excluded. This criterion can be satisfied nearly completely by using substantially "dust-free" and "dust-controlled" working places, where the concentrations of especially abundant elements of laboratory dust can be reduced by at least a factor of 1000.
4. The decomposition and separation steps should be carried out in reaction vessels of minimal surface area and coupled as closely as possible, and at temperatures as low as possible.
5. Decomposition and separation must take place without loss of the elements to be determined. A careful determination of the efficiency is therefore indispensable and if possible should be done by use of radioisotopes.
6. Naturally, the method of determination itself plays an important role. The problem of making the method as sensitive as possible is invariably connected with the problem of transferring very small quantities of material into excitation areas which should be as small as possible. The techniques of classical micro and ultra-micro analysis have proved especially useful (Ref. 6,7).

By following these rules it has proved possible in many cases to detect impurities in the ng/g range in high-purity materials (metals, semiconductors, glass-ware, reagents etc.) with a high degree of precision and accuracy. The following examples present some multi-stage procedures, developed in our laboratory, which make this concept understandable.

EXAMPLES OF MULTI-STEP PROCEDURES

Combined decomposition and enrichment procedures by means of the gas phase
Especially convenient conditions for multi-stage procedures exist if the trace elements to be determined (e.g. B (Ref. 1), C (Ref. 8), N, O (Ref. 9), Si (Ref. 2), Se (Ref. 10,11), Hg (Ref. 3), Bi (Ref. 12)) can be liberated as a gas during the decomposition of the sample and so separated in the vapour phase from the nearly non-volatile matrix elements (e.g. Be, Al, Fe, Nb, Ta, W, Mo). The ideal case would be for the sample to be melted by excitation in a high-frequency field while freely suspended, i.e. without a crucible, without contact with other working materials, and with no need for reagents or auxiliary materials (Ref. 9), see Fig. 2.

This technique is preferable for the determination of gases (e.g. H, N, O) in high-melting metals (e.g. Nb, Ta, W, Mo). When the levitation melting procedure is used, blanks can be reduced by 1-2 orders of magnitude in comparison with the conventional hot extraction procedures.

For the determination of total nitrogen and oxygen in high-purity niobium the nitrogen is directly removed from the metal melt by ultra high vacuum and the oxygen by reaction with a hydrocarbon (e.g. acetylene). The isolated gases can be determined nearly without problems by means of a quadrupole mass spectrometer if its resolution is sufficient to separate nitrogen and carbon monoxide which have nearly the same mass number. With a high resolution instrument (resolution about 3000) both gases can be determined if their amounts do not differ by more than one order of magnitude. In the determination of nitrogen, the accuracy of the method can be verified with two independent

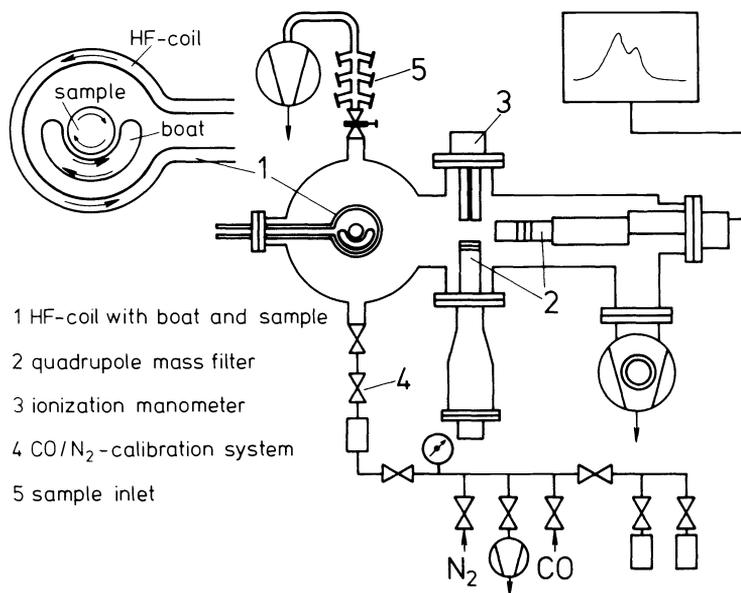


Fig. 2. Apparatus for the quadrupole mass spectrometric determination of oxygen and nitrogen (ppm- and ppb-range) in metals of high-purity after levitation melting

methods - the micro-Kjeldahl (Ref. 13) and the residual resistance method (Ref. 9), (see Fig. 3), but for the determination of oxygen a reference method is not yet available. The procedure, which allows reliable detection of as little as 0.05 ppm of nitrogen has reached practically the detection limit of a nitrogen determination by means of photon activation analysis (Ref. 14).

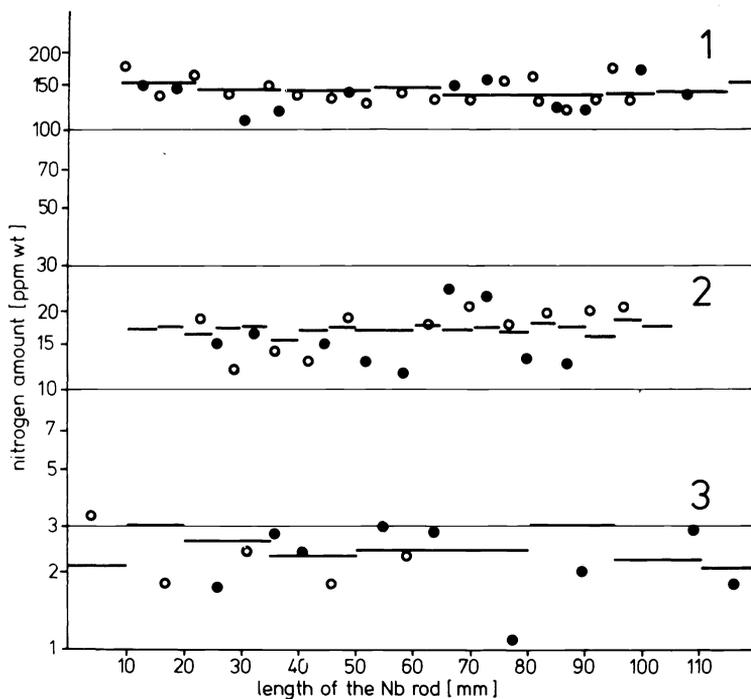


Fig. 3. Comparison of nitrogen contents in N-doped niobium rods. — residual resistance; ● ultra high vacuum extraction; ○ micro-Kjeldahl method

This procedure, hitherto the only available for the determination of very small nitrogen contents in metals, can now be checked for accuracy by an independent reference procedure. The next example deals with the as yet unsolved problem of the determination of ng/g levels of boron in ultrapure metals. Boron can be separated in ng-quantities as BF_3 from the matrix if the sample can be dissolved in a mixture of purest HF and HNO_3 . The BF_3 evolved is transferred by a carrier gas out of the PTFE-decomposition vessel into the receiver of determination digestion apparatus (see Fig. 4) in the same way as SiF_4 or H_2SiF_6 are transferred in the determination of silicon traces in metals (Ref.) 6. Before the emission spectrometric (see Fig. 5) it is necessary to separate and concentrate the boron from the hydrofluoric acid distillate.

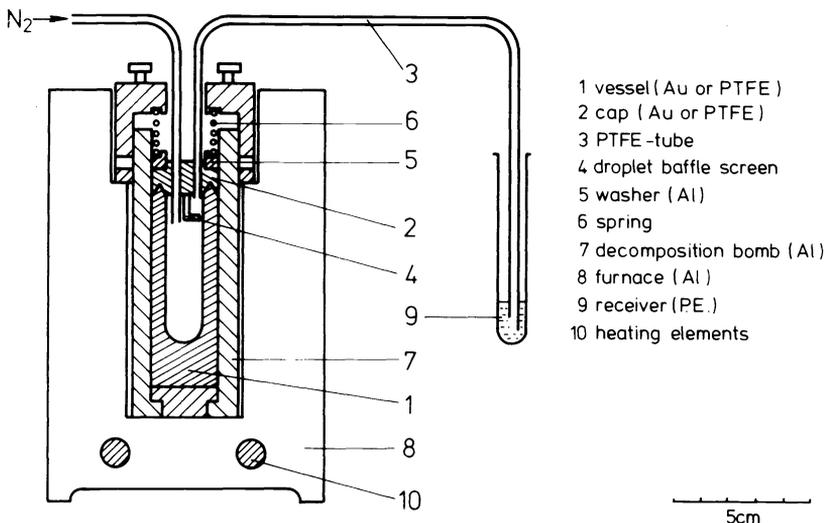


Fig. 4. Apparatus for the separation of B- and Si-traces as BF_3 and SiF_4 , respectively, from metal matrices

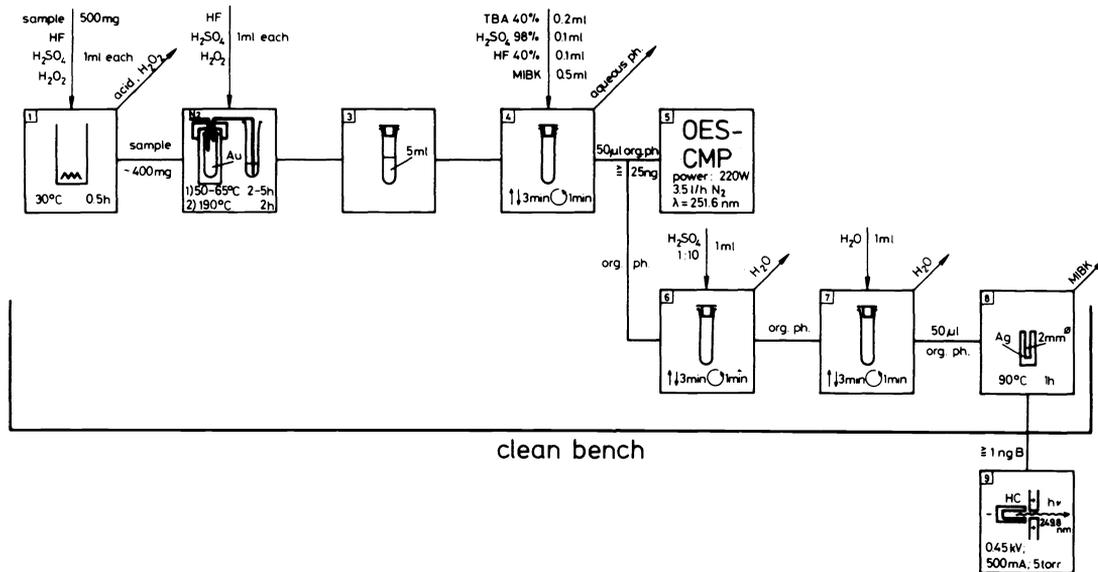


Fig. 5. Emission-spectrometric determination (CMP and hollow-cathode excitation) of traces of B in metals after volatilization (BF_3) and extraction (BF_4 -TBA/MIBK)

This is done by extracting it as the BF_4 -tetrabutylammonia complex (BF_4 -TBA) with methyl isobutyl ketone (MIBK). The organic phase is then directly sprayed into a microwave induced nitrogen plasma (CMP), (detection limit: 25 ng) (Ref. 15). Another possibility is to excite the boron in a hollow cathode after evaporation of the solvent (detection limit: 0.05 ng) (Ref. 16). The systematic errors that restrict the detection limit are inherent mainly

in the decomposition and separation steps and could be reduced if the two steps could be combined. Of course sample preparation, decomposition, and purification of the dissolving acids must be done under clean-room conditions. Combined decomposition and separation procedures using the gas phase are often applicable for the determination of elements which can be volatilized at temperatures up to about 1000 °C from non-volatile matrices. Table 1, taken from Rudolf and Bachmann (Ref. 17) is useful for orientation. Many of these procedures have been used to solve trace analytical problems since W. Geilmann introduced them (Ref. 18), but we can now recognize the limits of this analytical principle (Ref. 3).

Table 1. Elements and compounds suitable for separation via the gaseous phase according to K. Bächmann and I. Rudolf.

Type of compound	Elements which form suitable volatile compounds (25 - 950 °C)
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)
Oxides	S, Se, Te, Po, (As), Tc, Re, Ru, Os, (Mo, W), Zn, Cd, Hg
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
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
AlCl ₃ complexes	Lanthanides, Actinides, Ca, Sr, Ba, Ra, Fe, Co, Ni, Cu, Pd, Pa, Mo

Volatile trace elements may react with matrix constituents to give non-volatile thermally stable compounds or may interact with the materials (e.g. quartz, ceramics, graphite) of the vaporization apparatus. Hence it is indispensable to check the recoveries systematically. The dynamic techniques of vaporization analysis hitherto used, where the volatile components are transported by a carrier gas and subsequently condensed on a cold finger or in a capillary, fail mainly because the trace elements or their compounds (e.g. Hg, BiCl₃, SeO₂, As₂O₃) can no longer be trapped quantitatively on small condensation areas.

Condensation of the volatilized components together with the carrier gas has proved more effective in these cases (see Fig. 6) (Ref. 6, 10).

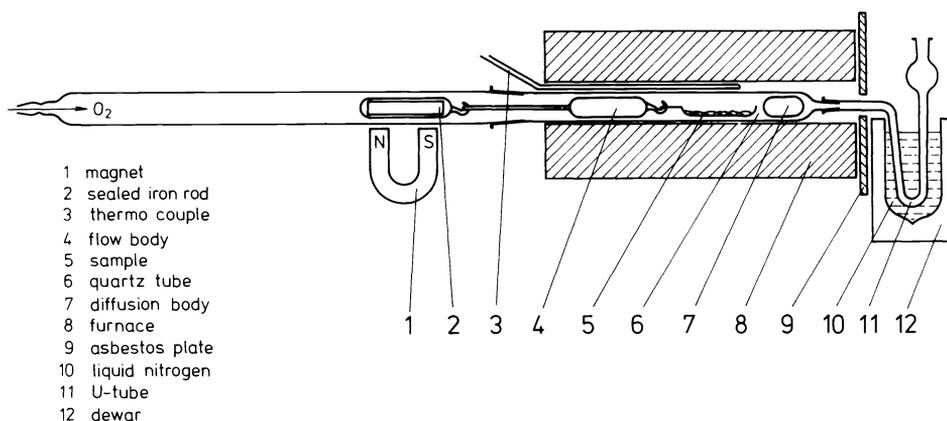


Fig. 6. Separation of ng amounts of Se in metals by volatilization as SeO₂

Recent applications of this vaporization technique for the determination of down to 0.1 ng/g of Se in ultrapure Cu, Ag, Au, Bi, Pb (Ref. 11) substantiate its capability.

In special cases, a static technique is to be preferred, involving vaporization without carrier gas in a quartz tube extended to a capillary (see Fig.7).

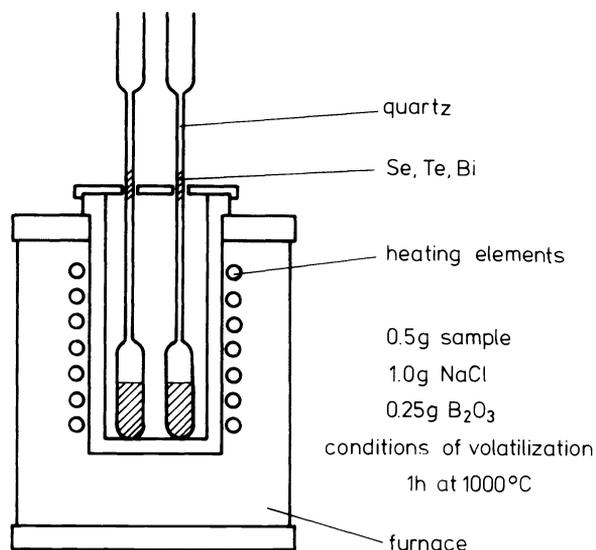


Fig. 7. Arrangement for the volatilization of Bi, Te, Se from a siliceous matrix into a quartz capillary

Radiochemical yield determinations have shown that with this simple principle $\geq 95\%$ of pg amounts of e.g. Se, Te, and Bi can be separated as chlorides from siliceous materials and enriched by deposition on a very small area of the capillary. After dissolution of the condensation products in small, known volumes of acids (50-100 μ l) the elements can be determined reliably and very sensitively by furnace atomic absorption spectrometry (FAAS) (see Fig. 8) (Ref. 12).

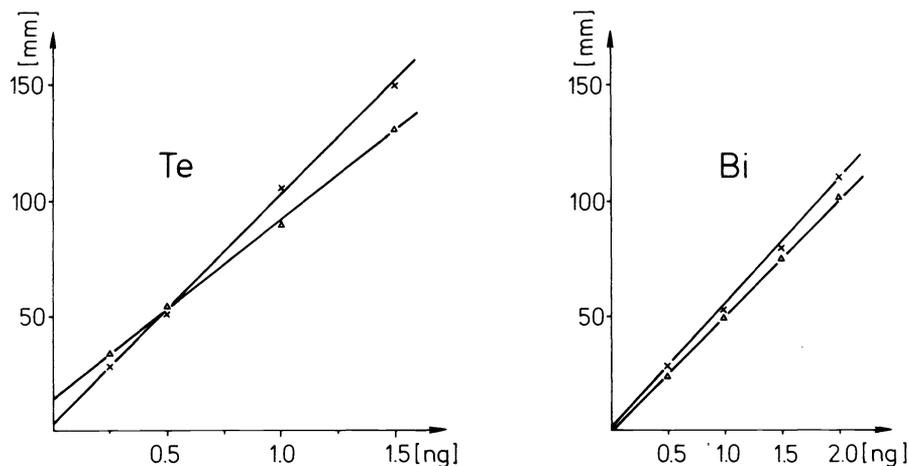


Fig. 8. Calibration curves for the determination of Te and Bi by FAAS (enrichment after volatilization of halide compounds)

x = 2 N HNO₃ standard solution

△ = 300 mg sample (glass) and addition of standard solution and 1 g B₂O₃/NaCl (1:4).

Decomposition procedures

When sample decomposition and separation of trace elements cannot be combined, both stages have to be optimized separately. The idea of combining both stages should be kept in mind, however.

Decomposition with acids is the most universal. Only easily volatilized acids such as HF, HCl, HNO₃ can be obtained extremely pure by subboiling point distillation or isothermal distillation (Ref. 7, 19). They should be preferred to higher boiling acids such as HClO₄, H₂SO₄, or H₃PO₄. In order to use minimum amounts of acids and minimize volatilization of elements and gain of impurities, decomposition techniques in the vapour phase (Ref. 20, 21) or in pressure digestion vessels (Ref. 22-24) or combinations of both (Ref. 25, 26) should be applied (see Fig. 9). Attention has to be paid to the stability of the vessel.

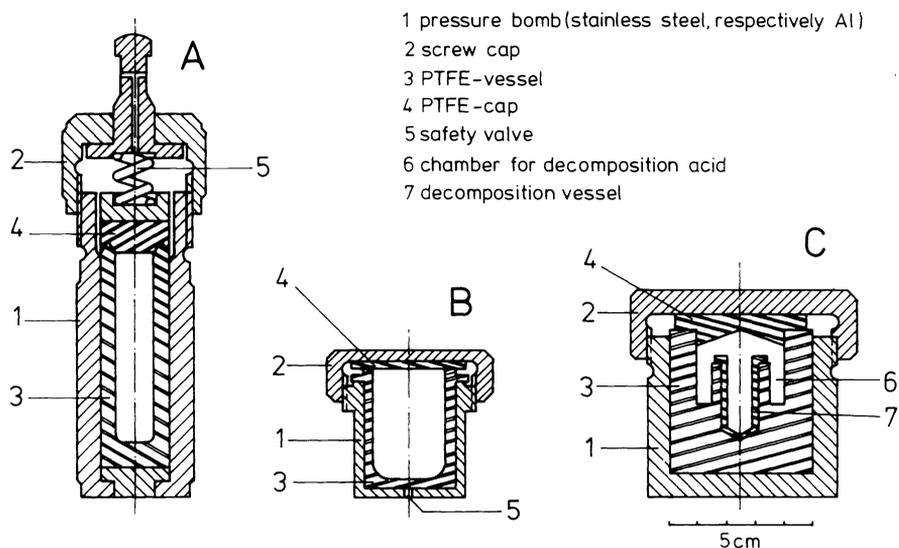


Fig. 9. Arrangement for acid decomposition under pressure
 A) after Kotz et al.; B) after Bernas; C) after Woolley.

materials, especially when pressure decomposition is applied.

Depending on the problem, noble metals, quartz, PTFE, or glassy carbon may be used. Care must be taken when PTFE is employed. Commercially available qualities of PTFE may contain impurities which diffuse little by little from the material into the digestion solution when PTFE is attacked under pressure, making it impossible to measure an accurate blank. Cleaning operations that may last for days are therefore necessary when Si, Cd, Hg, Fe are to be determined for example. Glassy carbon too, is not completely resistant to oxidizing acids. As, however, it is heated at temperatures above 2000 °C during the manufacturing process, the amount of easily volatilized impurities such as Hg, Cd, Pb, Sb should be less than those of Si, Al, Fe, B and other non-volatile elements. Glassy carbon may therefore in many cases be used instead of PTFE. The decomposition vessels should be shaped in such a way that all subsequent separation steps (e.g. co-precipitation, or liquid-liquid extraction) can be done in the same vessel to minimize systematic errors caused by adsorption effects and introduction of foreign elements. We prefer the pressure decomposition system (Ref. 24) developed in our laboratory.

For metallic matrices anodic dissolution procedures may be advantageous since they can be used at low temperatures and with a minimum of reagents. A vessel made of glassy carbon serves as anode and the cathode is made of purest graphite (see Fig. 10). The electrolyte depends on the matrix to be dissolved. For the dissolution of high purity niobium a solution of purest methanol saturated with purest ammonium chloride was shown to be suitable (Ref. 27).

Decompositions by fusion with B₂O₃, KHSO₄, NaOH, Na₂CO₃, and other reagents should be applied only when acid decompositions fail. Important reasons for not using fusion decomposition are: 1) the relatively large amounts of non-

volatile elements present as impurities in the fluxes require enormous expenditure of time on purifying operations, 2) interactions of the melt with the crucible material are not only difficult to prevent but may also result in both serious contamination and losses.

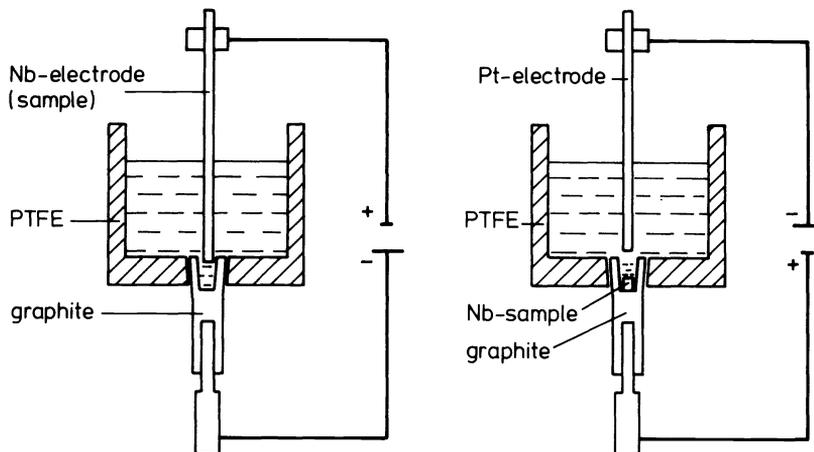


Fig. 10. Arrangement for the electrolytical dissolution of niobium (current density: 0.15 A/dm^2 ; electrolyte: methanol saturated with NH_4Cl).

After either acid decomposition or fusion the enrichment of the elements usually has to be achieved separately. An exception is the dissolution procedure for metals, in which the trace elements to be determined are enriched by electrochemical cementation on the less noble sample during the dissolution process. If the dissolution process is interrupted when a very small part of the sample remains undissolved (partial dissolution), the trace elements that have undergone cementation can be determined directly under certain circumstances in the presence of the small residue of matrix, as shown by Jackwerth and co-workers in numerous experiments (Ref. 28, 29).

Special separation and enrichment procedures

Most of the conventional principles of separation and enrichment (e.g. coprecipitation, liquid-liquid extraction, ion-exchange) that can be combined with the sample dissolution are subject to several systematic errors, mainly losses by irreversible adsorption of the ions onto the cell walls. These may, however, be partly compensated by introduction of the elements concerned when these occur in high concentration in the laboratory air, the reagents and the vessel materials.

Though the blanks may often be reduced by working in clean rooms, using high-purity reagents and inert working materials, optimizing the surface geometry, and pretreating the cell walls, the limitations of these methods are clearly to be seen. It is also very difficult to make the interferences reproducible.

Radiochemical yield determinations can be applied to ascertain adsorption losses if radionuclides of the elements to be determined with suitable half-life and specific activity are available. This expedient, however, is only helpful for those elements giving blanks which are negligible compared to the concentration range to be determined.

This explains our efforts to find techniques less prone to interferences, for isolating trace elements from digestion solutions. Two promising techniques will be briefly presented.

The first is based on electrolytic enrichment of trace elements (e.g. Hg, Cu, Bi, Pb, Cd, Fe, Zn, Ni and Co) occurring in non-deposited matrix elements (e.g. Be, Zr, Nb, W). It has already been shown that pg quantities of Bi, and ng quantities of Fe, Co, and Zn are deposited quantitatively within a short time from a fairly large electrolyte volume (about 50 ml). The mass transport in the electrolyte is not effected by stirring of the solution or rotation of the cathode, but by means of a hydrodynamic system. Figure 11 shows the arrangement. The electrolyte is circulated rapidly by means of a PTFE-membrane pump (5) through a cathode cylinder made of graphite (2). The Pt/Ir anode is

placed concentrically in the graphite cylinder cathode. The very small distance of 0.7 mm between cathode and anode allows electrolysis with high current densities of about 1 A/dm^2 . The high circulation rate of the electrolyte (20 ml/min) in the narrow electrolysis cell nearly completely avoids the interference caused by H_2 development. Thus, more than 98 % of the Bi in an ammonium fluoride solution containing 0.01 ng of Bi/ml could be deposited on the cathode (Ref. 30).

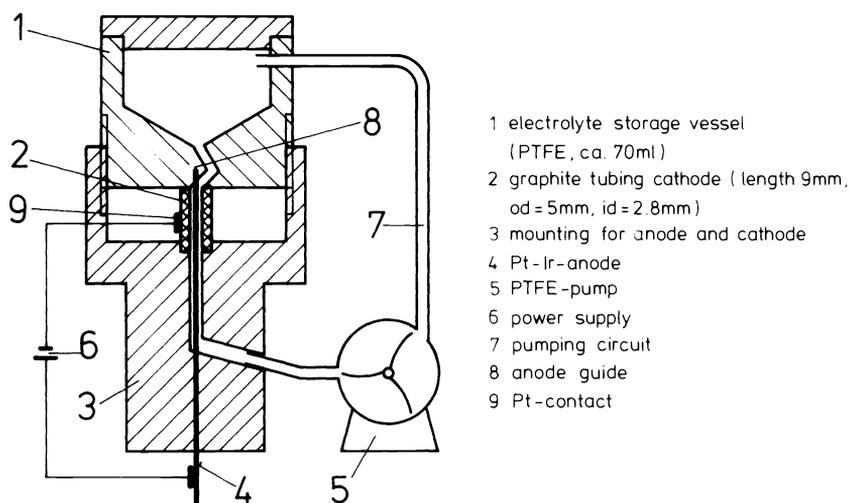


Fig. 11. Electrolysis in the hydrodynamic flow system.

It is obvious that the geometry of the cathode should be tubular so that the metals deposited inside the cathode can be determined directly by, for example, furnace atomic absorption spectrometry (FAAS, Maßmann micro-technique) (see Fig. 12 A). Emission spectrometric and activation analytical determinations can also be applied. The tubular graphite is used directly as a furnace for the atomization.

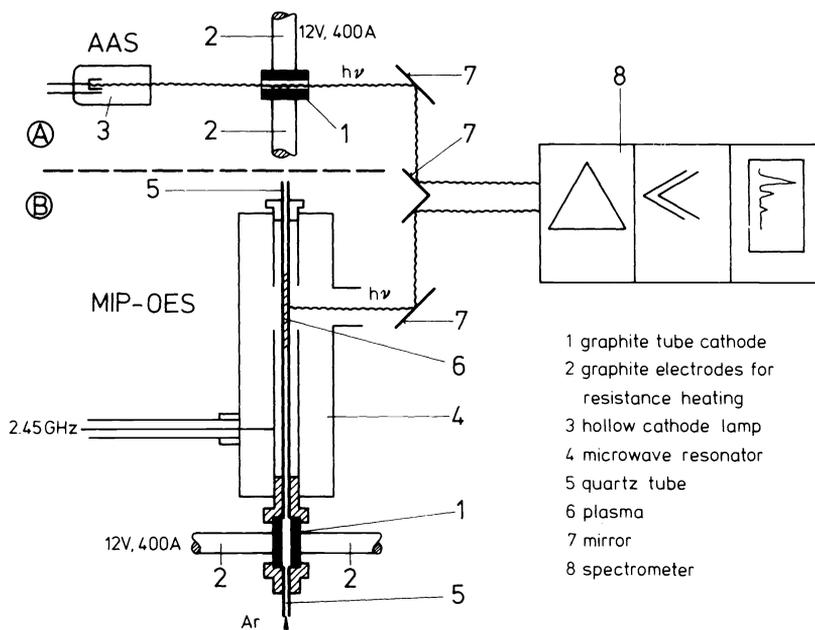


Fig. 12. Determination of traces of elements by furnace atomic absorption spectrometry (FAAS) and optical emission spectrometry (OES) after electrolytical deposition in a graphite tube cathode.
 A: FAAS; B: MIP/OES.

Thus, the detection limit can be improved by at least one order of magnitude relative to the conventional solution technique. Since the deposited elements are already present in the metallic state, dissociation and reduction processes (which may strongly affect the detection limit) are not necessary. In consequence of this, the multi-stage process for the determination of electrolytically depositable trace elements in purest niobium can be divided into the following operations: Decomposition of the sample with a minimum volume of high-purity HF in a PTFE pressure vessel, neutralization of the excess of acid with purest aqueous ammonia, electrolysis of the digestion solution diluted to 50 ml, and the determination of the elements by FAAS. Another technique (see Fig. 12 B) allows simultaneous determination of several elements deposited on the cathode. The elements, evaporated by heating the graphite cathode, are transferred into a microwave induced argon plasma, established in a quartz capillary which is attached to the furnace where the elements are excited to emission. Preliminary investigations yielded detection limits as low as 1 ng for many elements.

The second enrichment technique is based on a simple precipitation exchange. The trace elements in the digestion solution are drawn slowly through various thin layers, covering a PTFE membrane filter in a Hahn-filter funnel. These layers consist of freshly prepared precipitates of metal sulphides (e.g. ZnS, MnS), hydroxides, carbonates, phosphates, etc. or chelate-complexes (Ref. 3, 31). The exchanger layer retains all those elements for which the corresponding compounds have a lower solubility product or higher stability constant than the exchanger compound. Figure 13 indicates the scheme for enrichment of the elements of the hydrogen sulphide group in a zinc sulphide layer. Since the amount of the exchanger is only small (about 300 µg) and the material itself is well characterized and alters only slightly during the exchange process, any influence of the exchanger should be reproducible and an appropriate correction is possible.

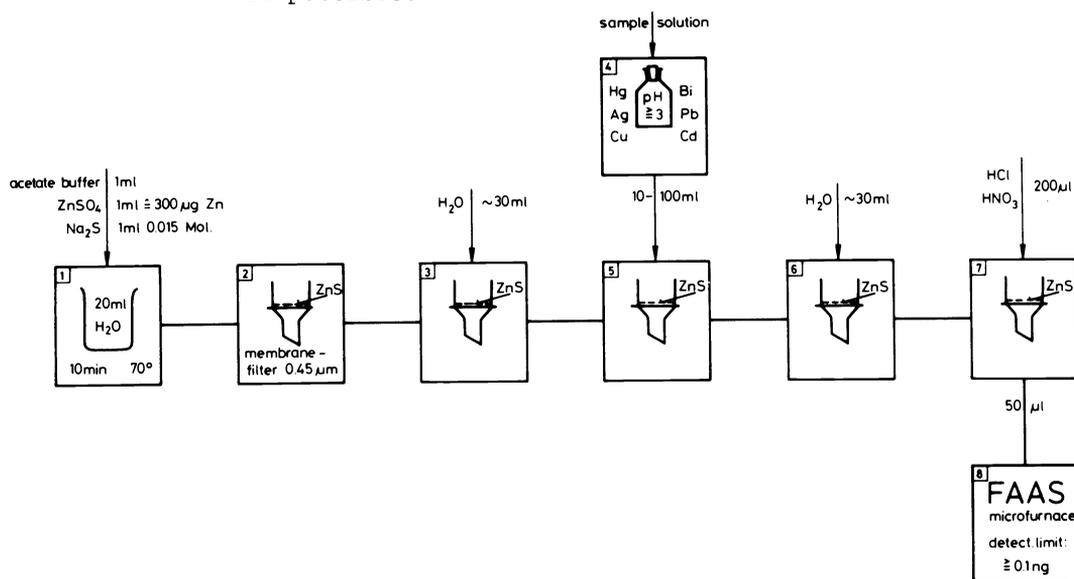


Fig. 13. FAAS determination of Ag, Bi, Pb, Cd after enrichment by precipitation exchange (ZnS)

For the determination of the enriched elements by FAAS, the exchanger is dissolved directly off the filter with a minimum volume of a suitable acid. Since PTFE membrane filters are permeable to aqueous solutions only when wetted with alcohol or acetone before use they are completely impermeable to the acid. The determination by FAAS is free from interferences (see Fig. 14).

In a similar way a filter covered with activated carbon retains trace elements that form complexes with organic reagents; the matrix and other elements not forming such complexes can pass the filter (Ref. 32, 33).

Both principles - precipitation exchange and sorption on activated carbon - serve as valuable supplemental techniques.

Anions down to the ng and pg range (e.g. phosphate, bromide, iodide, cyanide, sulphide) can also be enriched by precipitation exchange (Ref. 34-36) as will

be shown in the last example, the determination of traces of phosphorus in high-purity niobium (Ref. 36).

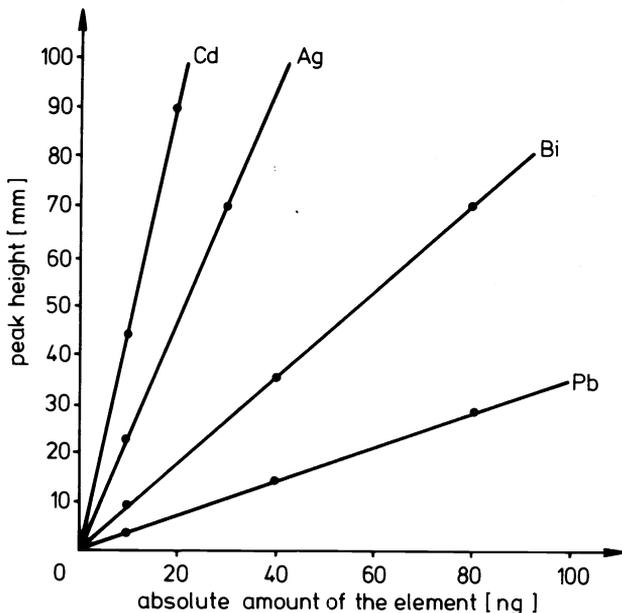


Fig. 14. Exchange of elements on a thin ZnS layer (aqueous solution) and determination by furnace atomic absorption spectrometry (FAAS) with optical excitation conditions.

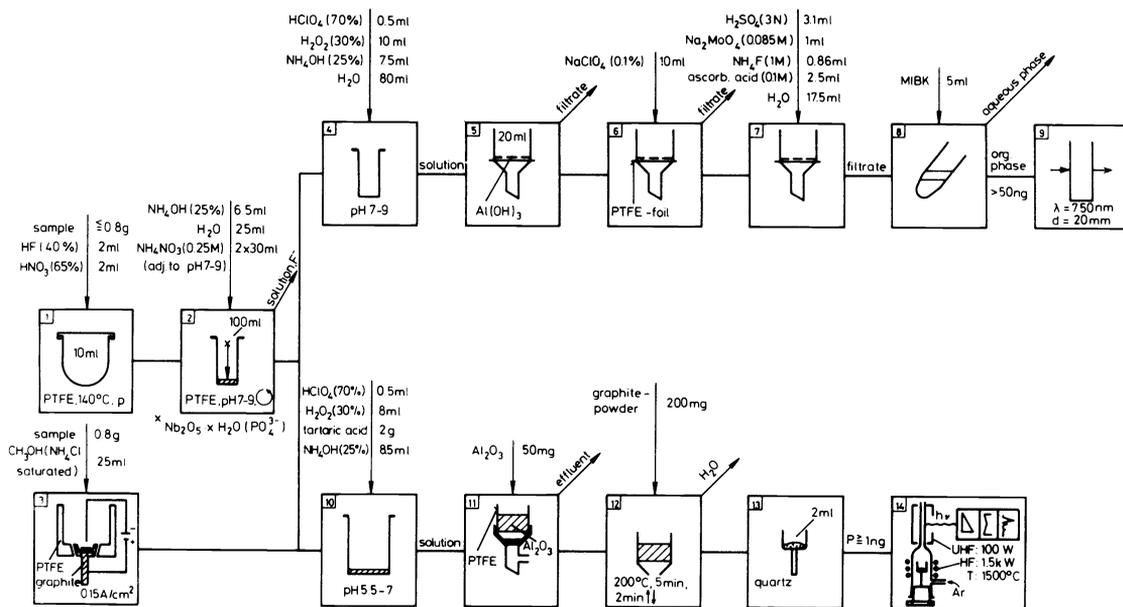


Fig. 15. Flow chart for a photometric (heteropoly blue method) and an emission spectrometric (MIP) determination of phosphorus in high-purity niobium in the upper and the lower ng range after separation of the phosphate with precipitation exchange techniques

As all known determination procedures for phosphorus are interfered with by niobium and HF - which is needed to dissolve the metal - even at low concentrations, isolation as phosphate is indispensable. The current separation techniques have been found to fail. They give inadequate yields, are too cumbersome, or give high blanks. However, we have succeeded in separating the phosphate with a thin layer of Al(OH)₃. Figure 15 illustrates the multi-stage procedure. The metal is dissolved either in purest HF in a PTFE pressure vessel, or anodically. The niobium has to be precipitated as niobic acid with

aqueous ammonia to remove excessive HF. In that step the phosphate is completely co-precipitated, as has been checked by radiochemical experiments using ^{32}P . After decantation of the fluoride solution from the centrifuged precipitation, the niobic acid is dissolved in H_2O_2 and HClO_4 and the solution is filtered through the $\text{Al}(\text{OH})_3$ exchanger layer. The pH dependent exchange can be optimized to give a phosphate recovery higher than 95 %. The sensitive determination of the phosphate in this $\text{Al}(\text{OH})_3/\text{PO}_4^{3-}$ system presents no problems. The determination procedure depends on the determination range. Quantities of phosphate higher than 50 ng can be determined most easily spectrometrically by formation of molybdophosphoric acid (MPA) and its reduction to "molybdenum blue". A more sensitive method is indirect determination through FAAS applied to the molybdenum in the molybdophosphoric acid.

This procedure requires, however, a careful separation of the molybdophosphoric acid from the excess of molybdate reagent by extraction with MIBK, and this additional step decreases the precision. Such difficulties explain our efforts to find a less troublesome but still sensitive emission spectrometric procedure. Its principle will be described only briefly. The phosphate is isolated by means of an $\text{Al}(\text{OH})_3$ layer or a small Al_2O_3 column. The column or layer material is then dried, mixed with graphite powder and heated to about 1500 °C with high-frequency heating in an apparatus arranged so that the elemental phosphorus produced is volatilized directly into a microwave induced argon plasma where it is excited to emit specific radiation (POH excitation). This last example also demonstrates that the success of a multi-stage procedure depends on optimization of all the individual steps with due regard to the chemistry of the system.

Determination procedures after isolation of the elements

Though certain determination procedures such as FAAS and solution-OES with microwave induced plasma excitation were favoured in the samples just given it was not intended to give the impression that these procedures are always the best. For the determination of the elements after their isolation, any method is suitable which will give sufficiently good detection limits (in ng or pg range), high selectivity and low systematic errors. Instrumental procedures, such as those already mentioned, AAS, electrochemical procedures, and gas chromatography of chelates have equal status with many methods of classical ultramicro analysis such as titration procedures with electrochemical, or visual endpoint detection, spectrophotometry, and fluorimetry (Ref. 7). The most suitable procedure will be dictated by the nature of the particular analytical problem.

Future developments, however, are likely to be in the direction of multi-element determination rather than single-element determination. In analysis of ultrapure materials which are very expensive, there is not only the economical question to be considered but also the fact that only a limited amount of sample material will be available. Therefore, one is obliged more and more to try to isolate groups of elements for their subsequent simultaneous determination.

In this connection solution-OES will undergo a renaissance because there are now some very constant light-emission sources since the new excitation sources such as high-frequency and ultra-high-frequency plasmas have been introduced (Ref. 37-41).

In direct simultaneous solution-OES in the ppm range we can recognize clear advantages in favour of the inductively coupled plasma excitation (ICP) because there are fewer interferences by concomitant elements than with capacitive microwave plasma (CMP) and microwave induced plasma (MIP) excitation (Ref. 41-42). However, this is by no means the case in extreme trace analysis, where the matrix must then be separated for the reasons already stated.

Excitation with hollow-cathode lamps also has good prospects in some special cases as shown in Table 2, indicating some detection limits. The results were obtained with a gold cathode having a very small hole of only 2 x 15 mm in which the sample solutions were evaporated to dryness before the determination of the elements. The reasons for the remarkable sensitivity are the high current density used and the long residence probability of the elements in the plasma (Ref. 16). In special cases the hollow-cathode can be made from the metal sample to be analysed (e.g. Au, Cu, Ag, Al, Be). The detection limits are sometimes even better than those of instrumental neutron activation analysis.

New prospects for multi-element determinations in solution are offered by chelate gas chromatography, used hitherto only for single element determinations (e.g. Be, Cr, Se) (Ref. 43, 44).

Table 2. Detection power of the hollow cathode
 Cathode material: Au; cathode geometry: depth = 15 mm,
 $\phi = 2$ mm, excitation conditions: U = 500 V, I = 500 mA

Element	[ng] absolut	= [ng/ml]	Element	[ng] absolut	= [ng/ml]
Be	0.05	1	As	7.0*	140*
B	0.15	3	Zr	0.4	8
Mg	0.05	1	Nb	2.0	40
Al	1.0*	20*	Mo	0.3	6
Si	0.2	4	Cd	0.25*	5*
Sc	0.1	2	In	0.15*	3*
Ti	0.3	6	Sb	2.0	40
V	0.2	4	Te	10.0	200
Cr	0.03	0.6	W	6.0	120
Mn	0.2	4	Tl	0.2*	4*
Co	0.2	4	Pb	1.5*	30*
Zn	1.0*	20*	Bi	2.0*	40*

*the most intensive line is not measurable

Recently Neeb et al. (Ref. 45-47) succeeded in separating and determining several elements (e.g. Cu, Cd, Zn, Ni, Co, Fe) in the form of the dialkyl-dithiophosphinato or O,O'-dialkyldithiophosphato and diethyldithiocarbamate chelates in the ng and pg range. Since the formation of stable complexes of heavy metals in aqueous solutions is pH-dependent, and since these complexes can be easily extracted into organic solvents, there are numerous possibilities for versatile extractive pre-enrichments followed by separations by gas chromatography and determination with very sensitive detector systems such as flame ionization, electron capture, microwave-induced plasma spectrometry.

DIRECT INSTRUMENTAL PROCEDURES

Though the use of direct instrumental procedures was initially approached very cautiously, they are the procedures of the future once reliable standardized reference materials for the extreme trace range have been obtained. The path propagated here and based on multi-stage procedures is by no means the only one. More prevalent is the statistical evaluation of collections of data obtained by interlaboratory comparative analyses and the correlation of the significantly most probable prediction with the true value. As already stressed, however, this procedure must be applied with great caution to the extreme trace range. Further, there are still too few laboratories concerned with the analysis of ultrapure materials for statistical methods to be applied. The situation can best be described by means of an example of a comparison of data which has recently been attempted in our country with a high purity sample of aluminium (see Table 3). The laboratories taking part used the spark source mass spectrometry (SMS) and instrumental neutron activation analysis and though the activation data agreed quite well, those obtained by SMS deviated considerably. Unfortunately the compilation has great gaps which underline again the difficulty of obtaining reliable data and standard samples. These premises apply in much higher degree to many other ultrapure materials, for statistical comparison of methods and statistical optimizations such as those extensively used in the conventional metal and environmental analysis.

For routine use of direct instrumental multi-element procedures to provide more than a mere assessment of orders of magnitude for all elements present, a lot of effort has to be expended. At present, instrumental activation analysis and mass spectrometry are the most promising direct instrumental procedures. Activation analysis may claim the more favourable prospects with regard to accuracy and provides a wide choice for excitation, with thermal and fast neutrons, charged particles and photons (Ref. 48). As, however, all excitation and activation conditions depend strongly on the matrix, and capture cross-sections vary by several orders of magnitude, it offers only a partial solution to the problem.

Table 3. Interlaboratory comparison of a high-purity Al-sample (selection of elements)

Element	Method - results in ppm -						
	INAA* (Lab.1)	INAA (Lab.2)	INAA (Lab.3)	INAA (Lab.4)	SMS** (Lab.5)	SMS (Lab.6)	SMS (Lab.7)
Cr	0.03	0.03	0.04	0.03	-	-	1.0
Cu	-	-	0.8	0.6	0.1	0.2	0.25
Fe	0.5	0.5	2	0.5	0.7	7	0.5
Ga	0.2	0.2	0.2	-	0.5	1.3	-
Mn	0.5	1.5	0.05	0.08	0.2	0.2	0.2
Na	0.07	0.1	0.2	-	-	-	-
Sb	0.45	0.8	0.25	0.5	0.5	0.2	-
Sc	0.09	0.09	0.05	0.11	0.05	-	0.5
Zn	0.5	1.5	2	0.56	0.5	0.5	2.0

*INAA = instrumental neutron activation analysis
**SMS = spark source mass spectrometry

For universality, mass spectrometry has to be preferred. Up till now, however, the reliability is lower, but is capable of development. Laser (Ref. 49, 50) and ion-excitation (Ref. 51-54) have proved to give more constant excitation conditions than the spark excitation commonly used. The main advantage of the new excitation sources is, however, that with the probe scanning techniques, distribution analyses with high local resolution on the surface and in the bulk are possible.

This contribution can be summarized as follows: The analysis of high-purity materials is at the beginning of its development, if its present stage is compared with the final aim. The ultimate aim is to be able to detect impurities in a high-purity matrix down to levels at which they cause practically no more changes in the properties of the material. The current problems are, however, essentially more realistic. The task is still to master reliably the ng/g range. This will only be achieved by coordinating purposeful all aspects of trace analysis. Multi-stage procedures which optimally involve chemical and physical approaches will be an indispensable help.

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REFERENCES

1. G. Tölg, Mikrochim. Acta (Wien), Suppl. 7, 1-26 (1977).
2. G. Tölg, Talanta 21, 327 - 345 (1974).
3. G. Tölg, Naturwissenschaften 63, 99-110 (1976).
4. G. Tölg, Z. Anal. Chem. 283, 257-267 (1977).
5. G. Tölg, Talanta 19, 1489-1521 (1972).
6. G. Tölg, Pure and appl. Chem. 44, 645-670 (1975).
7. G. Tölg, Elemental Analysis with Minute Samples, in Comprehensive Analytical Chemistry; C.L. Wilson and D.W. Wilson (Eds.) Vol. III, Elsevier Publ. Comp. New York, -London, -Amsterdam (1975).
8. P. Schoch, E. Grallath, P. Tschöpel and G. Tölg, Z. Anal. Chem. 271, 12-22 (1974).
9. M. Winterkorn, K. Schulze and G. Tölg, Mikrochim. Acta (Wien), Suppl. 7, 27-39 (1977).
10. A. Meyer, E. Grallath, G. Kaiser, G. Tölg, Z. Anal. Chem. 281, 201-209 (1976).
11. A. Meyer, Ch. Hofer, and G. Tölg, Z. Anal. Chem., in press.
12. P. Grünwald, I. Liem, P. Tschöpel and G. Tölg, Anal. Chim. Acta in preparation.
13. W. Werner and G. Tölg, Z. Anal. Chem. 276, 103-110 (1975).
14. Ph. Albert, Die Bestimmung des Stickstoffgehaltes hochschmelzender Metalle, Informationsheft Nr. 90, Büro Eurisotop, Brüssel (1974).

15. G. Kölblin, P. Tschöpel and G. Tölg, Z. Anal. Chem., in preparation.
16. P. Faßmann, P. Tschöpel and G. Tölg, Z. Anal. Chem., in preparation.
17. J. Rudolph and K. Bächmann, J. Radioanal. Chem. **32**, 243-263 (1976).
18. W. Geilmann, Z. Anal. Chem. **165**, 251-268 (1959).
19. M. Zief, J.W. Mitchell, Contamination Control in Trace Elemental Analysis, J. Wiley Publ., New York (1976).
- 19a. Th.J. Murphy, The Role of the Analytical Blank in Accurate Trace Analysis, in Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis Vol. 1, National Bureau of Standards Special Publication No. 422, 509-539, Washington (1976), Ed. Ph. D. LaFleur.
20. Kh. Zil'bershtein, M.M. Piruytko, O.N. Nikitina, Yu. F. Fedorov and A.N. Nenarokov, Zav. Lab. **29**, 1266 (1963).
21. J.W. Mitchell and D.L. Nash, Analyt. Chem. **46**, 326-328 (1974).
22. J. Ito, Bull. Chem. Soc. Japan **35**, 225 (1962).
23. B. Bernas, Analyt. Chem. **40**, 1682-1686 (1968).
24. L. Kotz, G. Kaiser, P. Tschöpel and G. Tölg, Z. Anal. Chem. **260**, 207-209 (1972).
25. J.F. Woolley, Analyst **100**, 896-898 (1975).
26. V.Z. Krasil'shchik, Zav. Lab. **42**, 153 and 279 (1976).
27. M. Mantel, A. Aladjem, and R. Nothmann, Anal. Lett. **9**, 671-676 (1976).
28. R. Höhn and E. Jackwerth, Spectrochim. Acta **29B**, 225-229 (1974) and Z. Anal. Chem. **282**, 21-23 (1976).
29. E. Jackwerth and J. Messerschmidt, Z. Anal. Chem. **274**, 205-206 (1975) and Anal. Chim. Acta **87**, 341-351 (1976).
30. G. Volland, P. Tschöpel and G. Tölg, Anal. Chim. Acta **90**, 15-23 (1977).
31. A. Disam, P. Tschöpel and G. Tölg, Z. Anal. Chem. in preparation.
32. E. Jackwerth, Z. Anal. Chem. **271**, 120-125 (1974).
33. E. Jackwerth, and H. Berndt, Anal. Chim. Acta **74**, 299-307 (1975).
34. W. Eckhardt, G. Herrmann and H.-D. Schüssler, Z. Anal. Chem. **226**, 71-88 (1967).
35. P. Tschöpel, A. Disam, V. Krivan and G. Tölg, Z. Anal. Chem. **271**, 106-117 (1974).
36. M.-Hsiung Yang, G. Kaiser, G. Tölg, paper presented at the Int. Symp. on Microchemical Techniques, Davos, 22.-27.5. 1977 Switzerland, publication in preparation.
37. V.A. Fassel and R.N. Kniseley, Analyt. Chem. **46**, 1110 A-1120 A (1974) and Analyt. Chem. **46**, 1155A-1164A (1974).
38. S. Greenfield, H. McD. McGeachin and P.B. Smith, Talanta **22**, 1-15 (1975), Talanta **22**, 553-567 (1975) and Talanta **23**, 1-14 (1976).
39. P.W.J.M. Boumans, Z. Anal. Chem. **279**, 1 (1976).
40. P.W.J.M. Boumans, Proc. Analyt. Div. Chem. Soc. **14**, 143-149 (1977).
41. P. Tschöpel, Plasma Excitation in Spectrochemical Analysis in Wilson & Wilson's Comprehensive Analytical Chemistry, G. Svehla (Ed.), Elsevier Publishing Comp, Amsterdam-Oxford-New York, in press.
42. P.W.J.M. Boumans, E.J. De Boer, F.J. Dahmen, H. Hölzel, and A. Meier, Spectrochim. Acta **30B**, 449-469 (1975).
43. H. Rüssel and G. Tölg, Fortschr. chem. Forsch. **33**, 1-74 (1972).
44. R.S. Juvet and S.P. Cram, Analyt. Chem. **46**, 101R-124R (1974).
45. A. Tavlaridis and R. Neeb, Naturwiss. **63**, 146-147 (1976).
46. A. Tavlaridis and R. Neeb, Z. Anal. Chem. **282**, 17-19 (1976).
47. A. Kleinmann and R. Neeb, Z. Anal. Chem. **285**, 107-109 (1977).
48. G. Tölg, J. Less-Common Metals **43**, 157-167 (1975).
49. R.A. Bingham and P.L. Salter, Analyt. Chem. **48**, 1735-1740 (1976).
50. Yu. A. Bykovskii, T.A. Basova, V.I. Belousov, V.M. Gladskoi, V.V. Gorshkov, V.G. Degtyarev, I.D. Laptev, and V.N. Nevolin, Zh. analit. Khim. **31**, 2092-2096 (1976).
51. H. Liebl, Analyt. Chem. **46**, 22A-30A (1974).
52. Ch. A. Evans, Jr., Analyt. Chem. **47**, 818A-829A and 855A-866A (1975).
53. H.W. Werner, Mikrochim. Acta (Wien), Suppl. **7**, 63-83 (1977).
54. H. Liebl, Mikrochim. Acta (Wien), in press.