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PRECIPITATION OF MAJOR CONSTITUENTS FOR TRACE PRECONCENTRATION : POTENTIAL AND PROBLEMS[†]

Prepared for publication by

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Precipitation of major constituents for trace preconcentration: Potential and problems

Summary - The success of the separation of trace components by precipitation of the matrix depends not only on the quantitatively definable properties of the matrix and the trace constituents, but also on many marginal conditions. These produce effects which cannot as a rule be described numerically, and which impede the development of general rules for the choice of appropriate working parameters.

In this report an attempt is made to derive simple rules for trace enrichment. The application of the rules is illustrated with examples from the literature. A compilation of publications is tabulated dealing with the application of matrix precipitation to the simultaneous separation of several elements from pure metals.

1. INTRODUCTION

Nearly all methods that are applicable to trace preconcentration make use of the different distribution of compounds between two easily separable phases. For this purpose, the phases are either formed by the components to be separated, after transformation into appropriate compounds, or auxiliary phases are produced between which the distribution equilibria are established. In general, the effectiveness of the recovery of trace components has to be determined. Even when the equilibrium constants of the distribution reactions, usually involving several partial equilibria, are known, the success to be expected can usually only be predicted roughly. Experience shows that the smaller the trace concentration, and the larger the difference in concentration between the trace component and matrix, the less satisfactory are the theoretical predictions of distribution equilibria (ref. 1).

Precipitation, one of the oldest methods of separation, is used in trace separation methods. The sample solution serves as an auxiliary phase, within which the second phase is produced by adding a reagent so that certain components of the sample are more or less selectively precipitated. When traces are to be determined, an auxiliary (collector) phase must normally be precipitated simultaneously so that there is sufficient precipitate containing the trace component to be filtered or centrifuged conventionally. In precipitations of this kind, calculation of the extent of precipitation of a trace component on the basis of tabulated solubilities normally gives very inaccurate predictions. Deviations from calculated solubility equilibria arise particularly at the trace level from a variety of side reactions, and interaction with sample components and container surfaces which normally would be considered inert. The rate of precipitation also greatly influences the efficiency of trace precipitation and, unless slow precipitation is achieved, distributions based on equilibrium calculations cannot be expected to be valid (ref. 2). Nevertheless trace separation by coprecipitation is amongst the most useful methods for multielement separation from a large variety of sample materials, because of the high concentration factors achievable and its relative simplicity.

The effectiveness of trace separation methods based on the *precipitation of the main components* must be judged quite differently. In such cases, the same co-precipitation effect may now be the cause of losses of trace components. In the course of time, rules as to the choice of precipitation conditions have been formulated, on the basis of experimental observation, which must be adhered to for achieving quantitative separations (ref. 3). The successful separation of the matrix by precipitation therefore requires knowledge of likely perturbing factors and of possible ways to removing them or at least minimizing them. For this, it is important to know the nature and concentration of the traces which are to be separated.

In the present report the most important observations concerning precipitation and coprecipitation reactions are collated and discussed. The goal is an attempt to obtain rules, the systematic observation of which will render the success of trace separation by matrix precipitation less dependent on chance. These rules are illustrated by selected applications. Finally procedures for multielement recovery from pure metals by matrix precipitation are tabulated. The nomenclature of methods of precipitation and coprecipitation has been published previously (ref. 4,5).

2. PROPERTIES OF PRECIPITATED COMPOUNDS

For gravimetry the precipitates produced should be sufficiently pure to give no analytical error. This is also true for the separation of traces by matrix precipitation. Extensive investigations of various stages of precipitate formation (supersaturation, nucleation, crystal growth, ageing) (ref. 6-8) have led to an understanding of the influence of conditions on particle size and precipitate purity. In general, precipitates of larger particle size are of greater purity.

2.1 Solubility

The calculation of solution equilibria of precipitates requires knowledge of the solubility and solubility product (K_{sp}) of the precipitated compound. The solubility product, in turn, requires information on the stoichiometry and composition of the compound. This is problematical with many precipitates, particularly "hydroxides" and sulphides, where their composition and structure vary with the precipitation conditions (ref. 6,9,10). Particle size and ageing processes also significantly affect the solubility of a precipitate. Similar problems arise in the dissolution of precipitates, where side reactions (e.g. hydrolysis, formation of complexes) can also be expected, and in general, precipitation and dissolution of a given compound cannot be assumed to be reciprocal (ref. 11).

The application of K_{sp} values to trace analytical separation methods must therefore be viewed with caution, since in the definition of solubility product, ideal equilibrium conditions are assumed. Furthermore the precipitate may dissolve as molecules as well as ions (ref. 12), but such solubility is not measured by the conductimetric or potentiometric techniques often used to evaluate solubility products. Care must therefore be taken to ensure that the solubility values take into account both ionic and molecular solubility, i.e. solubility as ionic species and as undissociated molecules, respectively. It is often quite likely that the molecular solubility of a sparingly soluble compound is much greater than the ionic solubility. This is especially true for the almost insoluble sulphides and hydrated oxides (ref. 11), where not only molecular solubility but soluble complex formation make an important contribution to solubility.

2.2 Particle size

The particle size of a precipitate is governed by the relative rates of nucleation and particle growth, as well as by the concentration of precipitating species. Nuclei are the smallest particles of precipitate which can grow spontaneously. Their formation is termed nucleation, and is a necessary initial stage in the precipitation process. Detailed considerations of this process have been given by various authors (ref. 6,7,13,14). Although different nucleation mechanisms have been proposed, they all require concentrations of precipitating species significantly in excess of their saturation solubility (i.e. appreciable supersaturation) in order for nucleation to begin. Additionally, nucleation may involve only precipitate species (homogeneous nucleation) or may involve sub-microscopic impurity particles (heterogeneous nucleation). The former is a higher energy process, requires a much higher concentration of precipitating species than the latter, and tends to produce a much greater concentration of very small precipitate particles. If solutions are sufficiently concentrated, colloidal suspensions are obtained.

In order to produce large precipitate particles, therefore, homogeneous nucleation should be avoided or minimized. This can often be achieved by restricting the concentrations of the species involved in precipitate formation but for many compounds, such as hydrated oxides or sulphides, homogeneous nucleation occurs at such low concentrations as to make this impractical. In such situations, the use of precipitation from homogeneous solution, which greatly restricts the instantaneous concentrations of precipitant, can be very beneficial (ref. 15).

The solubility of very small particles (< 0.1 μm diameter) is greater than that of large particles of the same material. Therefore, if small precipitate particles are obtained, it is often possible to increase their size by an "ageing" process, because when a suspension is heated, the small particles tend slowly to dissolve and redeposit on the larger, less soluble particles.

2.3 Purity

The incorporation into precipitates of other components of a sample solution can occur in a number of ways, the most important being:

- (a) mechanical or adsorptive inclusion of the mother solution within disordered lattice regions or pores or enclosed spaces within crystal aggregates or gels;
- (b) adsorption of ions or molecules on the particle surface;
- (c) inclusion of "foreign" ions in the crystal lattice (formation of mixed crystals);
- (d) exchange of surface lattice ions by "foreign" ions.

The inclusion of foreign ions into the crystal lattice is thermodynamically predictable (see 3.3). However, such predictions are based on equilibrium conditions as is implied in solubility product calculations. Thus, as the rate of particle growth increases, there is an

increased deviation from equilibrium conditions, and decreased discrimination between the precipitation of the major component and "foreign" species (ref. 16). Thus, species which are being concentrated in the precipitate by co-precipitation are less efficiently separated from the matrix under conditions of rapid particle growth such as are achieved at high reactant concentrations. Likewise, attempts to precipitate the matrix whilst leaving trace species in solution are less efficient under conditions of rapid particle growth.

3. CAUSES OF PRECIPITATE CONTAMINATION

The main goal of the early studies of coprecipitation was to establish which ions are coprecipitated under certain conditions and why. The question as to which elements are not coprecipitated, which is more important to the trace analyst, was deemed less interesting. As is shown below, however, there are several very efficient procedures for multi-element concentration in which the matrix is precipitated to separate it from trace analytes. It is worthwhile, therefore, trying to clarify the coprecipitation mechanisms to establish if and how it will be possible to precipitate main constituents without contaminants.

Mechanical occlusion of impurities is not discussed here because specific predictions, other than that an increase in precipitation rate will result in an increase in irregular and defective crystal growth, are difficult to formulate.

3.1 Induced precipitation; post-precipitation

Induced precipitation is the simultaneous or nearly simultaneous precipitation of at least two compounds, the more soluble of which would not have precipitated had the other compound also not been precipitated. Classical examples are the induced precipitation of ammonium lead sulphate by barium sulphate (ref. 17,18) and of lithium by sodium iron(III) periodate (ref. 19).

A form of induced precipitation can be observed when trying selectively to precipitate individual major components from a solution of a complex matrix. In such cases, the precipitated compound may cause a simultaneous or delayed precipitation of other components. If the induced precipitation is delayed, it is called post-precipitation. For instance, some metal sulphides are first precipitated free of zinc from an acidic solution containing this element, but zinc is increasingly precipitated with increasing time of contact of the solution with the precipitate (ref. 20).

3.2 Adsorption

Adsorption of trace components is very important in trace analysis, especially at extremely low concentrations. Precipitate particles normally carry a surface electrical charge because of a selective adsorption of cations or anions. The charged surface can adsorb, with some selectivity, foreign ions of opposite charge, which also contaminate the precipitate (ref. 21-24). The extent of adsorption increases with the charge density on the precipitate and on the adsorbing ions. The charge density depends on the available surface area and the concentration of primary adsorbing ion. Adsorption on other surfaces may be a source of analyte loss in trace analysis.

It is not surprising that the literature contains contradictory statements about the effect of precipitation parameters on adsorption. For instance, increasing the temperature is reported to increase (ref. 25) or decrease (ref. 26,27) the adsorption of metals ions on silver halide and other precipitates. Acidity is said to diminish the adsorption of bismuth ions (ref. 21,22) on silver halides or to have no observable effect (ref. 28). Such apparently conflicting statements usually arise from the use of different experimental conditions.

The process of "adsorption", therefore, in the context of precipitate contamination, is complicated, and no clear rules can be established. The Paneth-Fajans-Hahn adsorption rule, which is useful as a first indication of likely coprecipitation effects, is not without exceptions, and cannot be interpreted quantitatively. Experimental verification of such behaviour of traces and precipitates therefore remains indispensable for reliable analytical application. Two features are clear, however. First, if adsorption is a required part of the analytical process, it is normally desirable to achieve the maximum adsorptive surface area, so that large reactant concentrations should be used during precipitation. Second, adsorption can occur on a pre-formed precipitate as well as one formed in the presence of the trace contaminant. Thus, "collection" of trace components can be achieved by addition of a pre-formed precipitate.

3.3 Bulk coprecipitation (mixed crystal formation)

The basic difference between adsorption and bulk coprecipitation is that in the former the coprecipitated traces are bound to the surface of the precipitated particle, whereas in the latter they are distributed throughout the particle. Thus adsorbed contaminants can often be dissolved from the particle surface by appropriate reagents, but those bound within the crystal lattice are essentially immobilized and can only be eliminated by dissolving the particle (ref. 21).

Incorporation of impurities into the crystal lattice implies distortion of the lattice. Thus the extent of coprecipitation is likely to be greater, the more easily the impurity is incorporated into the lattice i.e. the greater the similarity in ionic charge and size and crystal morphology between the major precipitate and the coprecipitated species. However, lack of similarity in these criteria does not exclude the occurrence of bulk coprecipitation, it merely limits its extent. For example, traces of lead are incorporated into the silver chromate lattice (ref. 29) in spite of the fact that lead and silver ions have different charges and lead and silver chromates have different crystal morphologies.

Bulk coprecipitation is an important as adsorption for trace analytical purposes because considerable separation factors can be achieved. The extent of bulk coprecipitation can be described mathematically mainly on the basis of two mechanisms, resulting in homogeneous and heterogeneous (logarithmic) distribution. These are briefly described below, but have been discussed in detail by Usedowski (ref. 30).

If a greater proportion of the trace impurity is precipitated than of the main component, this is an "enrichment system", and the ratio of impurity to main component in solution decreases during the precipitation process. As this ratio controls the degree of coprecipitation, the latter becomes increasingly small as the precipitation proceeds. In a "derichment system", the opposite situation obtains.

3.3.1 Homogeneous distribution. To obtain a homogeneous distribution of foreign ions throughout the lattice, the precipitate must be formed very slowly, at constant temperature and volume. The entire solid phase must remain in thermodynamic equilibrium with the surrounding solution during the whole of the crystal growth process. Thus the speed of recrystallization must be at least as great as the speed of growth of the crystals, so that mixed crystals with a homogeneous distribution of the trace species are formed, although the ratios of main and trace components deposited continually change during the precipitation. If these ideal conditions prevail, the concentrations of the trace (t) and main component (M) in the crystal (c) and the solution (s) at any stage during the precipitation are as follows (ref. 31):

$$[t]_c/[M]_c = K_{t,M}[t]_s/[M]_s$$

$K_{t,M}$ is the separation factor, which remains constant over the entire course of the precipitation for which the distribution process is valid. In an enrichment system, $K_{t,M}$ is > 1 , and for an appreciable enrichment of the trace component in the precipitate $K_{t,M} > 100$. Fig. 1 shows the relationship between trace and main component concentrations in the precipitate during the precipitation process. In normal analytical situations it is unlikely that sufficient time or experimental control will be available to ensure that the conditions allow continuous redistribution of an impurity throughout the crystal, even if it is possible. Thus homogeneous distribution is likely to be rare in such circumstances.

3.3.2 Heterogeneous (logarithmic) distribution. Such a distribution is obtained when no internal reorganization of the crystal lattice occurs during crystal growth. Thus each layer of crystal is in equilibrium with the solution present at the time it is laid down. As the solution composition and, especially, the trace:main component ratio, continually change during precipitation, the distribution of the trace impurity throughout the crystal is not homogeneous, but logarithmic (ref. 32).

$$\log \{ [t]_t/[t]_i \} = \lambda \log \{ [M]_t/[M]_i \}$$

where $[t]$ and $[M]$ are as above, initially (i) or after precipitation has continued for time t , and λ is the logarithmic distribution coefficient. Again, for trace enrichment, $\lambda > 100$ is desirable (Fig. 1). Fig. 1 also shows that a greater separation is achieved for a given distribution coefficient, when logarithmic rather than homogeneous distribution is achieved.

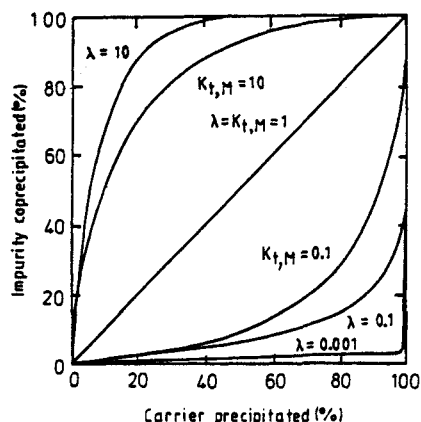


Fig. 1. Dependence of proportion of impurity precipitated with proportion of carrier precipitated for homogeneous and heterogeneous coprecipitation.

Logarithmic distribution is more common than homogeneous distribution (ref. 18); normally, however, incomplete redistribution of impurity within the crystal occurs, so that an intermediate distribution equation will hold.

3.3.3 Effect of precipitation rate. Both distribution equations assume equilibrium conditions, either at the crystal/solution interface, or, more rarely, throughout the complete solution/crystal system. Under analytical conditions, the rate of precipitation is likely to be too fast to allow such equilibria to be established. Several investigators have shown that λ is a function of precipitation rate (ref. 16,33,34), and that $\lambda \rightarrow 1$ as the rate increases i.e. the process becomes less discriminating.

For the most effective analytical separations to be based on bulk coprecipitation, therefore, it is necessary to ensure that the value of λ is as different from unity as is feasible, by carrying out the precipitation slowly. Precipitation from homogeneous solution has been shown to provide a very effective control of the precipitation rate (ref. 15,35,36).

3.4 Conclusions

here is still much to be learnt about the mechanisms of trace coprecipitation. Effects like adsorption or formation of mixed crystals are difficult to elucidate, so that it is usually impossible to predict accurately the behaviour of trace components in the presence of precipitates. Behaviour must be established experimentally, for each set of experiment conditions, but it must be emphasized that it is unreliable to extrapolate behaviour under such a set of conditions to other circumstances. Frequently it is necessary to control the reliability of procedures based on matrix precipitation by means of independent methods of separation and determination or by analysis of reference materials.

4. APPLICATIONS OF MATRIX PRECIPITATION IN TRACE ANALYSIS

The choice of a separation and preconcentration method in trace analysis depends on numerous well-documented considerations. These include the following, which increase in importance the smaller the trace concentration.

4.1 Blank problems

In general, procedures have to be favoured which allow the use of the minimum amounts of reagents which can be purified in a simple way (ref. 37). The use of large amounts of reagents generally causes high and often variable blank values resulting in an increase of the lower detection limit. Thus, the improvement in detection limits obtained by the use of a preconcentration procedure may be partly or completely counteracted by an increase in blank scatter. Frequently, procedures for separating major components will need larger amounts of reagents than those for traces, and buffer solutions and complexing agents for the matrix components may be required. Additionally, during trace analysis, the necessary transfer of the matrix into a rather large volume of a second phase or the concentrating of the resulting matrix-free solution is often accompanied by high blanks.

The "cementation" of metallic main components by reduction with metals of very low redox potentials is similar to the use of normal precipitants. This method, however, often cannot be recommended for trace analysis because of the high blank values to be expected because in addition to the ions of the reducing metal (e.g. Al, Mg, Zn), ions of impurities in these metals also dissolve.

4.2 Interactive effects

When separating matrix components, the partition behaviour of trace species depends on the composition and concentration of the sample solution, as described above. Often during evaporation, extraction, precipitation or chromatography of real samples, trace concentrations are decreased, sometimes to zero. Such effects are usually difficult to control, and extended experimental work is required to achieve some understanding of them. The influence of such effects on the analytical results can best be established by analyzing reference materials or by comparing the results with those of independent reference procedures.

4.3 Universality

In general the efficiency of procedures in which matrix components are precipitated in order to concentrate traces strongly depends on stringently following the established, optimized procedures. Changes in sample solution volume, reagent concentrations, reaction time, temperature etc. may affect the efficiency of the separation.

In spite of the many problems, procedures are nevertheless often applied in which the major components are separated from trace analytes and removed. This is usually necessary because certain matrix elements react undesirably with most of the common chelating agents. Therefore it is extremely difficult to find suitable conditions which allow freedom of interference for separation of trace analytes from, for example, a large excess of matrix components such as Ag^+ , Cu^{2+} , Hg^{2+} , Pb^{2+} or Bi^{3+} . In such cases it is more productive to try

to find a means of selectively precipitating the matrix. Such precipitation is mostly brought about with simple precipitants; chelating agents, in general, are too expensive to be used for precipitating main components.

Such precipitations have some advantages. They can relatively easily be carried out by trained technicians in a normal wet chemistry laboratory, provided that the basic requirements of trace analysis and the demands for clean working conditions are met. This simplicity of execution, however, should not obscure the complicated mechanisms which cause every new application to become an adventure which may be rich in surprises!

5. GUIDELINE FOR AVOIDING SORPTION LOSSES

Below, some guidelines are formulated which, during the development and application of preconcentration techniques by precipitation of the matrix, may be useful for avoiding losses of traces by sorption. Such guidelines are already known from gravimetry; they originate from general analytical experience of the sorption behaviour of trace elements onto freshly precipitated materials.

Guideline 1: Select the conditions for a matrix precipitate to ensure that particles with the smallest possible specific surface are obtained.

Guideline 2: Select the conditions for a matrix precipitation so that the trace components of interest would not precipitate if present in a much larger concentration or if present alone in the sample solution.

Guideline 3: Do not precipitate the matrix quantitatively if an excess of the precipitant causes sorption of the trace components of interest.

Guideline 4: Convert trace ions which are likely to be sorbed onto the precipitate into complexes which will not be sorbed.

Additionally, it should be borne in mind that the precipitation behaviour of trace concentrations of almost insoluble compounds cannot be deduced from their solubility products. Finally, volatile reagents that can be purified easily, e.g. by isothermal distillation, should be used as precipitants. In this way the blanks are kept low and trace concentrates can be obtained by evaporation of the precipitant under "clean" conditions (ref. 37).

6. EXAMPLES TO ILLUSTRATE THE GUIDELINES

The application of the guidelines in Section 5 are illustrated below with some examples of multi-element preconcentration. Only the principles and the results of the matrix separation methods are described. The detailed analytical procedures should be sought in the original literature (Section 7).

6.1 Precipitates with small specific surfaces

There is a direct correlation between the size of particles and the purity of a precipitate (Section 2.3). Therefore it is often better to precipitate a matrix component as a compound of greater solubility, and usually of greater particle size, than to select only sparingly soluble precipitates. Also, the precipitation process should be controlled in such a way that the formation of nuclei and crystal growth proceed sufficiently slowly so that the precipitate obtained has large particles and is as pure as possible. Traces, however, may be lost by mixed crystal formation, even under these optimal conditions.

Example: Precipitation of the matrix ions M^{2+} ($M = Pb, Sr, Ba$) as $M(NO_3)_2$.

A typical example of the preconcentration of numerous elements according to Guideline 1 is a method described by Ustimov *et al.* in which lead as a matrix element is precipitated as lead nitrate (ref. 38,39). The procedure is based on the fact that the high solubility of lead nitrate in water (0.52 g ml^{-1}) decreases in 65% nitric acid to a value which is lower, for example, than that of lead chloride in water (ref. 40). The sample of lead metal (e.g. 10 g) is dissolved in (1+1) nitric acid. On evaporation of water, the nitric acid concentration increases and the solubility of lead nitrate decreases simultaneously in a nearly linear fashion. When precipitation starts the solubility is still relatively large, so well-formed, highly pure crystals of a few mm diameter are slowly formed.

Two processes control the precipitation rate, the decrease in the solution volume and the increase of the nitric acid concentration. Precipitation stops when the nitric acid-water azeotrope (ca. 65% HNO_3) is obtained. Only 30 mg of lead remains dissolved in 100 cm^3 of this acid mixture, but >95% of the following elements remain in the solution: Ag, Al, Bi, Cd, Co, Cu, Fe, Ga, In, K, Mg, Na, Ni, Pd, Tl and Zn. These elements can be separated from the lead matrix simply by decantation from the precipitated lead nitrate; their concentration may be increased by further evaporation of the solution.

Lead chloride and sulphate precipitated under the same circumstances would coprecipitate larger proportions of the trace components than lead nitrate. Because other separation methods (e.g. extraction, evaporation, chromatography) can hardly be applied to the lead matrix, precipitation as lead nitrate is probably the best procedure for multi-element trace concentration from lead and its compounds.

Of more than 30 metal nitrates only strontium and barium nitrates show similar solubility behaviour in nitric acid to lead nitrate (ref. 41). All the other nitrates are much more soluble in nitric acid than in water, because of nitrate complex formation. Traces of strontium and barium are coprecipitated completely with lead nitrate, because the nitrates of these elements have the same type of crystal lattice (T^a_h) and the lattice constants are similar. Likewise strontium and barium as main components can be separated as nitrates from numerous elements (ref. 41), but not from lead.

A similar technique, in which the solubility of a compound decreases upon change in composition of a solvent, is the precipitation of matrix aluminium as $AlCl_3 \cdot 6H_2O$ by introducing hydrogen chloride gas into a water/diethyl ether mixture (ref. 42-45). Alkali and alkaline earth metals and magnesium as major components can also be separated in a similar manner (ref. 46).

6.2 Prevention of trace precipitation

To minimize coprecipitation, the precipitation conditions for the matrix should be chosen so that even much higher concentrations of the trace analytes would not precipitate if they were alone in solution. This means, for example, that the pH of the sample solution should be such that only the major component reacts significantly with the precipitant, and the trace species remain in solution. Similar discrimination can be achieved by addition of auxiliary complexing agents, redox agents etc. (ref. 47).

The search for the most appropriate conditions for precipitation is difficult because the range of conditions in which precipitation occurs depends on different parameters, such as the concentration of the main components and the temperature. The initial turbidity, for example, in the precipitation of zinc hydroxide occurs at a pH lower by 4 for $100 \text{ mg Zn}^{2+} \text{ cm}^{-3}$ than for $100 \text{ } \mu\text{g Zn}^{2+} \text{ cm}^{-3}$. If a precipitant forms stable, soluble complexes with the trace analytes but not with the matrix species, coprecipitation can be avoided by the use of a large excess of the reagent. Thus in the precipitation of matrix iron(III) with ammonia, traces of Ag, Cd, Co, Cu, Ni and Zn remain in solution as amines.

Example: Precipitation of matrix copper(II) ions as copper(II) sulphide.

There are many reasons why metal sulphide precipitations are not very suitable for matrix separations. Hydrogen sulphide is a particularly unselective precipitant, so that many trace metals are coprecipitated. Additionally metal sulphides have particularly low solubilities. The addition of hydrogen sulphide often produces precipitates of ill-defined composition, with large amounts of colloidal particles of large surface area. This results in very strong sorption of cations and anions. Furthermore the low solubilities make it difficult to increase the selectivity of the precipitation reaction by adding auxiliary reagents. It is not surprising, therefore, that sulphides are more usually used as versatile collector precipitates. The number of elements which can be precipitated decreases as the acidity of a solution is increased. This is also true for the number of elements which coprecipitate with a metal sulphide, and for the amounts coprecipitated.

To separate copper without loss of trace analytes from the solution, Guideline 2 indicates that the acidity of the sample solution should be adjusted with hydrochloric acid so that just sufficient copper is precipitated, but traces of elements having larger solubility products remain mostly in solution. The effect of acidity upon preconcentration efficiency for several metal ions in the $\mu\text{g g}^{-1}$ range is given in Fig. 2. The amount of separated matrix is 1 g of copper. According to Fig. 2, the trace elements behave only approximately in the way that would be expected from their solubility products.

To separate the matrix copper as a precipitate with the smallest possible specific surface area and to obtain a solution that contains the trace analyte which is as free as possible of residual matrix, the following conditions for precipitation were chosen:

- The precipitant (HS^-) is formed in homogeneous solution by hydrolysis of thioacetamide.
- The matrix copper is precipitated from boiling solution.
- Precipitate and mother liquor are separated immediately after precipitation.
- The filtrate is acidified with nitric acid to remove the excess of thioacetamide and its hydrolysis products during the evaporation process.

If 1 g of copper is precipitated in this way as copper(II) sulphide from 3M hydrochloric acid, the recovery from the filtrate of 1-50 μg of Cd, Co, Fe, In, Mn, Ni, Pb and Zn is > 90%. Traces of elements which form sulphides less soluble than copper(II) sulphide coprecipitate nearly completely with the matrix (ref. 48).

6.3 Incomplete matrix precipitation

From the start of precipitation through the equivalence point to when an excess of precipitant is present, the location of the trace species may change several times between solution and precipitate. Complicated sorption curves are obtained especially if major components are precipitated as almost insoluble ionic compounds which acquire an electrically charged surface by adsorption. As discussed in Section 3.2 this charge leads to the

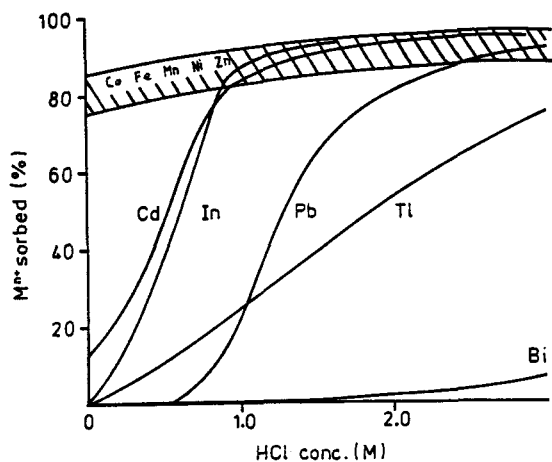


Fig. 2. Effect of acidity on the sorption of trace metal ions M^{n+} on CuS .

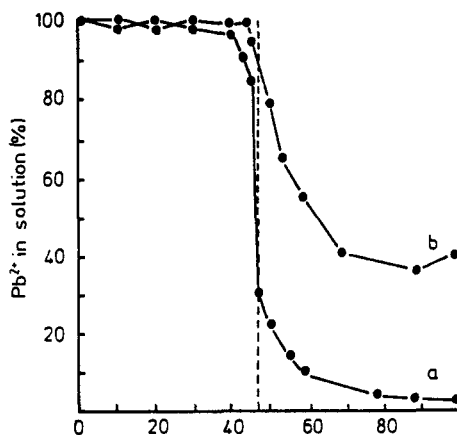


Fig. 3. Effect of HCl concentration on the adsorption of trace Pb^{2+} on 5 g Ag^+ precipitated as $AgCl$: (a) room temperature; (b) boiling temperature.

adsorption of foreign ions from the sample solution. Precipitates bearing a positive charge due to adsorption of their common cations have a tendency for "secondary adsorption" of foreign anions, and *vice versa*. At the isoelectric point losses of traces of cations or anions by electrostatic adsorption are not to be expected. This isoelectric point, however, is difficult to achieve experimentally, because it does not always coincide with the equivalence point of a precipitation process. Additionally, other sorption processes which are not controlled by electrical charge may occur even at the isoelectric point.

Effects similar to a charge-controlled sorption process also occur when trace elements and matrix react with a precipitant, with the trace compounds formed being more soluble than that with the matrix. Whilst some matrix remains unprecipitated this prevents the precipitation of the trace compounds, almost until the equivalence point is reached. Only after this stage, upon addition of further precipitant, are the trace compounds precipitated together with the small amount of residual matrix. So, very often it is not possible to distinguish whether coprecipitation of certain elements is caused by adsorption, depending on the electrical charge of the precipitate, or by the similar solubilities of matrix and trace compounds. In many cases both mechanisms may be involved simultaneously (ref. 28). Therefore, in such circumstances, in order to concentrate large numbers of trace species with recoveries as high as possible, a partial precipitation of the matrix should be attempted (Guideline 3). The matrix which remains in the filtrate may be eliminated without significant loss of the trace elements by a second, similar precipitation step.

Example: Precipitation of matrix silver as silver chloride.

There are several important reasons in trace analysis why hydrochloric acid is well suited for the precipitation of silver. It can be purified easily by isothermal distillation. Silver chloride is easily filtered, and is sufficiently insoluble to allow a quantitative separation of the matrix silver yielding, upon concentration of the filtrate, a trace concentrate which is nearly free of matrix. There are only a few other slightly soluble metal chlorides, so it is possible to precipitate the matrix with high selectivity. Because of the surface charge on the precipitate, it is unavoidable that traces coprecipitate to different extents upon addition of an excess of precipitant (ref. 24). Bismuth, Cd^{2+} , Hg^{2+} , Pb^{2+} , Pd^{2+} , Tl^+ and Tl^{III} , especially, coprecipitate in this way, whereas Ca^{3+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Ga^{3+} , In^{3+} , La^{3+} , Mn^{2+} , Ni^{2+} , Rh^{III} , Sn^{IV} , Th^{4+} , UO_2^{2+} and Zn^{2+} remain nearly quantitatively in solution.

The adsorption process is largely reversible with respect to a change of the electrical charge; it depends little on the acidity of the solution, and the fractions of adsorbed traces decrease as the temperature increases. As an example of the behaviour of trace elements which can be adsorbed by silver chloride, Fig. 3 shows the extent of adsorption of traces of lead. It begins just before the equivalence point, at room temperature or near the boiling point of water. The equivalence point is marked by the vertical dotted line. Such diagrams suggest a way of avoiding coprecipitation losses. Most the trace elements which normally are sorbed remain in solution if only about 90% of the silver is precipitated, at a temperature near the boiling point. If the subsequent trace determination is likely to be affected by the silver remaining in solution after the filtration of the silver chloride, this residual silver may be precipitated almost quantitatively in a second, similar 90% precipitation step without substantial sorption of the trace species. High recoveries of many trace species are obtained by this two-step matrix precipitation (ref. 49).

6.4 Formation of non-adsorbable complexes

As has been described, coprecipitation of some trace elements onto hydrated iron(III) oxide can be prevented by formation of ammine complexes. If charge-controlled adsorption of cations is the reason for losses during the enrichment process, or if cations are lost by formation of mixed crystals, it may be possible to increase the recovery by complexation of the traces to be enriched. This has been studied in detail for precipitates of silver and thallium(I) halides (ref. 28,50).

The proposed complexation technique is effective especially if adsorbable trace cations are converted into complex anions. In such cases, by using an anionic precipitant in excess, the sign of the charge on the precipitate and the trace complexes are the same and adsorption is prohibited. In some cases, however, it is found that a few elements which previously were not sorbed as cations now are coprecipitated as complex anions. Fortunately this phenomenon only occurs during that part of the precipitation process when the matrix has not been separated completely (ref. 28). Provided that such premature adsorption processes are sufficiently reversible, the sorbed trace complexes dissolve again when the equivalence point of the precipitation reaction is passed. Of course, success in preventing trace losses is achieved only if complexing agents are used which preferably react with the traces whereas the matrix element remains essentially unaffected.

Example: Precipitation of matrix thallium as thallium(I) iodide in the presence of EDTA.

Compared with the silver halides, thallium(I) halides acquire less charge by adsorption of their common ions. Accordingly the number of adsorbable metal cations, and their adsorption rates, are less than for silver halides. For the separation of matrix thallium, precipitation of thallium iodide may be used because of its low solubility. Selectivity, however, is not very high because traces of Bi, Cd, Cu, Pb, Ag, Au, Pd and Pt are removed by the precipitate in the separation process. Noble metals and silver are sorbed irreversibly, possible after reduction, whereas the other ions mentioned are sorbed by a reversible charge-controlled process. At higher concentrations, the formation of slightly soluble iodides should also be considered.

EDTA is very suitable for conversion of Bi^{3+} , Cd^{2+} , Cu^{2+} and Pb^{2+} to anionic complexes. Chelates of the doubly and triply charged trace cations have pK (stability constant) values between 16 and 28 and therefore they are far more stable than the thallium(I)-EDTA complex ($pK = 5.8$). This enables practically complete complexation of the traces by using only a small concentration of EDTA; a 10^6 -fold excess of thallium(I) does not interfere. Obviously, with regards to the pH sensitivity of the pK values, the precipitation should be carried out in a nearly neutral solution. Instead of hydriodic acid an alkali metal iodide should therefore be used, which in turn is the reason why the resulting filtrate cannot be concentrated without producing residues of alkali metal salts.

The influence of EDTA on the sorption behaviour of trace species is shown in Fig. 4 for bismuth. This cation is lost completely after addition of an excess of precipitant, whereas, the anionic EDTA chelate of bismuth remains quantitatively in solution. Other cations capable of sorption behave in the same way. This technique thus allows the following elements to be separated from matrix thallium with recoveries $>95\%$: Al, Bi, Cd, Co, Cu, Fe, Ga, In, La, Mg, Mn, Ni, Pb, Sn, Th, U and Zn. The noble metals are lost even in the presence of EDTA (ref. 50).

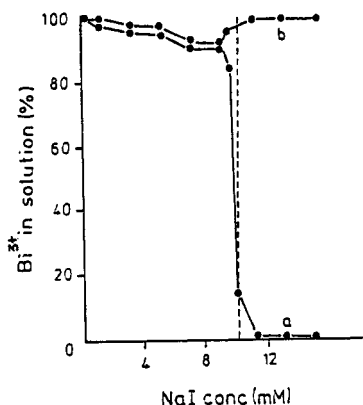


Fig. 4. Effect of NaI concentration on the adsorption of trace Bi^{3+} on 2 g Tl^+ precipitated as TlI : (a) Bi^{3+} cations; (b) Bi^{3+} -EDTA anions.

7. TABULATION OF PROCEDURES INVOLVING MATRIX PRECIPITATION

The publications given in Table I concerning matrix precipitation for multi-element preconcentration from pure metals have been obtained mostly from *Analytical Abstracts* and the abstracts in *Fresenius Zeitschrift für Analytische Chemie*. In most of them the quoted preconcentration method is combined with a spectrochemical or radiochemical measurement step.

The lack of details in these abstracts restricts the specification of data about the procedures (recoveries, precision, accuracy etc). So, for application of any of the quoted methods, consultation of the original papers is recommended.

TABLE I. Matrix precipitation for multielement preconcentration. (el) = electrolytic deposition.

Matrix Element	Precipitated Form	Preconcentrated Trace Element	Reference
Ag	Ag	As, Cd, Cu, Fe, Ga, In, Mn, Ni, Pb, Tl, Zn	51
	Ag (el)	Au, Co, Mn, Ni, Sb, Sn	52
	AgCl	Cd, Co, Cu, Ni, Zn	53
	AgCl	Cd, Cu, Fe, Mn, Ni, Pb, Zn	27
	AgCl	Bi, Cu, In, Pb, Sb, Zn	54
	AgCl	Co, Cr, Fe, Mn, Ni	55
	AgCl	Al, Au, Ca, Co, Cu, Fe, Hg, Ir, Mg, Mn, Ni, Os, Pd, Pt, Rh, Ru	56
	AgCl	As, Au, Cu, Sb	57
Al	AlCl ₃ .6H ₂ O	Ag, Bi, Cd, Cr, Cu, Ni, Pb, Zn	43
	AlCl ₃ .6H ₂ O	Cu, Fe, Mg, Mn, Si, Ti	44
	AlCl ₃ .6H ₂ O	Cr, Cu, Fe, Ga, Mg, Mn, Ni, V, Zn	45
Au	Au	"numerous elements"	58
	Au	26 elements	59
	Au (el)	As, P, Si	60
Bi	BiI ₃	Al, Ba, Ca, Cd, Co, Cr, Fe, In, Mg, Mn, Mo, Ni, Te, Ti, V, Zn	61
	BiOBr	Al, Ca, Cd, Co, Cu, Fe, Ga, In, Mg, Mn, Ni, Ti, Zn	62
	BiONO ₃	Ag, Al, Cd, Cu, Mg, Mn, Ni, Pb	63
Cd	Cd (el)	Co, Mn, Ni, Zn	64
Cu	Cu (el)	Bi, Pb, Sn	65
	Cu (el)	Fe, Mn, Ni, Sb, Sn, Zn	66
	Cu (el)	Ag, As, Au, Cd, Co, Cr, Cs, Fe, Ga, Hf, Hg, In, La, Mn, Mo, Ni, P, Rare Earth Metals, Rb, S, Sb, Sc, Se, Te, Th, U, Zn	67
	Cu (el)	Ag, Al, Au, Ba, Bi, Ca, Cd, Co, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Pt, Sb, Sn, Ti, V, Zn	68
	CuS	Cd, Co, Fe, In, Mn, Ni, Pb, Ti, Zn	48
Ge	GeO ₂	As, Au, Cd, Cu, Hg, Sb, Zn	69
	GeO ₂	Ag, As, Au, Cd, Co, Cu, Fe, Ga, Hg, In, Pb, Re, Zn	70
Hg	Hg	Alkali Metals, Alkaline Earth Metals, Al, As, Be, Bi, Cd, Cr, Co, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Sb, Sn, Te, Ti, Tl, Zn	71
Mo	Mo- α -benzoin	Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Ni, Pb, Sb, Sn, Ti, V, Zn	72
Os	Os	Au, Fe, Ir, Pd, Pt	73

Matrix Element	Precipitated Form	Preconcentrated Trace Element	Reference	
Pb	Pb(NO ₃) ₂	Ag, Al, As, Bi, Ca, Cd, Co, Cu, Fe, In, Mg, Na, Ni, Sb, Tl, Zn	38	
	Pb(NO ₃) ₂	Ag, Al, As, Bi, Ca, Cd, Co, Cu, Fe, Ga, In, Mg, Na, Ni, Sb, Tl, Zn	39	
	Pb(NO ₃) ₂	Ag, Al, Bi, Cd, Co, Cu, Fe, Ga, Hg, In, K, Mg, Mn, Na, Ni, Pd, Tl, Zn	40	
	PbCl ₂	Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, La, Mg, Mn, Mo, Na, Ni, P, Pd, Pt, Sb, Si, Sn, Sr, Tl, U, Zn	74	
		Ag, Al, Au, Bi, Cd, Co, Cu, Fe, Ga, In, K, Mg, Mn, Na, Ni, Pd, Sb, Tl, Zn	40	
	PbSO ₄	Cd, Zn	75	
	PbSO ₄	Ag, As, Bi, Cu, Fe, Mg, Sb, Sn, Zn	76	
	PbSO ₄	Cd, Cu, Zn	77	
	PbSO ₄	Cd, Co, Cu, Fe, Ga, In, Zn	78	
	PbSO ₄	Ag, Al, As, Bi, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Mo, Na, Ni, Sb, Sn, Te, Tl, V, Zn	47	
		Al, Bi, Ca, Cd, Co, Cu, Fe, Ga, Hg, In, Mg, Mn, Na, Ni, Pd, Sb, Zn	40	
	Pd	Pd	Cd, Co, Fe, Hg, Ru, Zn	79
		Pd-dimethylglyoxime	Co, Fe	73
Pd-dimethylglyoxime		"impurities"	80	
Pt	Pt	Cu, Fe, Ni, Pb, Te	81	
	Pt	Ag, Cd, Co, Fe, Hg, Ru, Zn	82	
	Pt (e1)	As, P, Si	60	
	(NH ₄) ₂ PtCl ₆	As, Sb	83	
	(NH ₄) ₂ PtCl ₆	Se, Te	84	
	(NH ₄) ₂ PtCl ₆	"impurities"	80	
	(NH ₄) ₂ PtCl ₆	Ag, Bi, P, Sb	85	
Se	Se	As, Cu, Fe, Zn	86	
	Se	As, Cu, Sb, Te	87	
	Se	As, Cd, Cu, Fe, Ga, Hg, In, Sb, Te, Tl	88	
	Se	As, Cu, Sb, Te	89	
	Se	Mo, P, S, W, Zn	90	
Te	Te	Al, As, Bi, Cd, Co, Cr, Cu, Fe, Ga, In, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Ti, Tl, V, W, Zn	91	
	Te	As, Cu, Sb, Se	89	
	Te	Mo, P, S, W, Zn	90	
	Te	Cd, Zn	92	
	TeO ₂	Ag, Al, As, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Na, Ni, Pb, Sb, Si, Sn, Tl, Zn	93	
	TeO ₂	Co, Ni	94	
	TeO ₂	Cd, Cu, Zn	84	
Th	Th-oxalate	Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Sb, Sn, Ti, V, Zn	95	
	Th-hydrogen peroxide	Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Zn	95	
Zr	Zr-mandelic acid	"impurities"	96	

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