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Radiochemistry for neutron activation analysis

Lecture notes

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Definitions:

Nuclear Chemistry: The application of procedures and techniques common to chemistry to study the structure of the nucleus and to define the nature of the fundamental particles.

Radiochemistry: The application of the phenomenon of radioactive decay and techniques common to nuclear physics to solve problems in the field of chemistry.
Radiochemistry: The chemistry of radioactive substances.

Introduction

The main characteristics of neutron activation analysis (NAA)are:

1. Multi-element capability
2. Sensitivity for many elements
3. General good selectivity
4. No effects of the chemical binding of the analyte element
5. Absence or at least minimisation of the blank value
6. Relatively minor matrix effects
7. Ability to analyse samples up to a few grams thus reducing problems by inhomogeneities
8. Possibility to add carrier after irradiation allowing to work in more controlled conditions and to determine the chemical yield of the chemical operations
9. Good traceability
10. Independence of the physical basis of the technique, viz. a basis that differs substantially from the basis of other trace-element analytical techniques

An analytical method should be fit for purpose, i.e., its performance parameters, such as detection limit, uncertainty of measurement, the turn-around time and cost of analysis should be optimised according to the required (customer) needs.

The detection limit in units of mass fraction, m_D, is given by:

$$m_D = \frac{L_D}{K} \tag{1}$$

where L_D is the detection limit expressed by the signal magnitude (e.g., a number of counts in γ-ray spectrometry) and K is a calibration factor (a number of counts per mass unit) obtained in NAA by:

$$K = \frac{N_A \theta_a \gamma_a}{M_a} SDC(G_{th}\phi_0\sigma_{0,a} + G_{e,a}\phi_e I_{0,a}(\alpha)\varepsilon_{\gamma,a}Y_a) \tag{2}$$

It is obvious from Eq. (1) that the detection limit m_D can be decreased both by increasing K and decreasing L_D (e.g., namely background, e.g., due to matrix activities, such as ^{24}Na, ^{42}K, ^{82}Br, ^{32}P in NAA of biological and environmental samples, interferences in γ-ray

spectrometry, nuclear interference reactions, etc.) and by performing both. Therefore, it appears advantageous to consider the optimisation of m_D by a comprehensive analysis of Eq. (2). The optimisation can be done using both physical and chemical means.

1. Physical optimisation

2. Chemical optimisation

   Chemical separation is usually the most effective way of minimizing the m_D value, because it allows removal of interfering components with decontamination factors of up to $5x10^7$. Obviously, such an improvement of the signal-to-background ratio can hardly be achieved using any of the physical means mentioned above. Separation can be performed either after or prior to irradiation (radiochemical or pre-irradiation separation, respectively). Both approaches have their merits and shortcomings. The main advantages of the radiochemical mode of separation are the retention of the essentially blank-free nature of analysis, the possibility to perform trace element radiochemistry under controlled conditions by inactive carrier additions, and the ease of measuring the chemical yield, either by the carrier budgeting or the radiotracer method. However, radiochemical separation is associated with a radiation burden on personnel and there are time limitations when separation of short-lived isotopes ($T_{1/2}$ in the order of several minutes) is to be performed.
   The advantages of pre-irradiation separation are that they avoid any extensive handling of radioactive materials, there are no time limitations and there is the possibility of speciation analysis. However, pre-irradiation separation suffers from the same problems as other trace analytical methods, i.e., the problem of blank, the risk of contamination, irregularities of the behaviour of elements at very low concentrations (colloid formation, sorption on surfaces, co-precipitation, etc.), and little control over the chemical yield of separation. Nowadays, the increased availability of high-purity chemicals and clean laboratories result in a reduction of the problem of contamination and highly variable blank values for many elements. Still, for NAA applications the use of pre-irradiation separation may be preferred in the cases where the risk of contamination is generally not very high, where time limitations are severe and where speciation is of prime interest.

Possible problems: Creation of artefacts, mainly due to contamination and/or losses during sampling and sample handling. Solutions: development of facilities, techniques and procedures to minimise these unwanted effects, e.g. via clean rooms, laminar flow benches, metal-free tools, and high purity chemicals.

The unique advantage of radiochemical neutron activation analysis (RNAA) is that pre-irradiation handling is limited to a subsampling step, possibly a drying step (lyophilisation), to end with packing in a vial. These steps can be fully kept under control when working under class 100 conditions and using appropriate measures, e.g., thoroughly cleaned vessels and metal free tools, e.g., platinum needles, titanium or quarts knives. After irradiation of the samples in the nuclear reactor, any fortuitous external addition of trace elements is harmless, since it is not radioactive and thus not detected. The validity of the data is by no means jeopardised by non-radioactive contamination.

Full sensitivity of neutron activation analysis cannot be attained unless post-irradiation separations are used. This is particularly true for medical samples, where the background in the gamma-spectrum is high due to e.g., 24Na and 82Br, and where many trace element of interest are present in quite low concentration, displaying only very small peaks.

Pre-separations do not only allow singling out a specific species, but it also may concentrate the analyte (e.g., copper, iodine and mercury) and/or reduce the levels of interfering elements. This implies that post-irradiation separations become simpler, or are even not necessary any more. Although pre-separations are avoided as much as possible because of the loss of the blank-free characteristics, they are used already for a long time. For instance, when the half-life of the radionuclide of interest is too short lived for extensive radiochemistry, e.g., ^{52}V and ^{28}Al in the determination of vanadium and aluminium respectively. Pre-separations are also used for purpose of concentration, and preferentially at the same time removing interfering elements. Even with the loss of the blank free character, RNAA with pre-separations may be competitive or superior, when dealing with elements or radionuclides that activate quite well, e.g., iridium, thorium in human tissues, or iodine in foodstuffs.

RNAA may also be of interest for determination of radionuclides, which are difficult to measure at low levels due to their associated long half-lives. Even when direct radioactivity determination and/or mass spectrometry may be feasible, RNAA is attractive as independent method to compare with. RNAA with the associated powerful characteristic of the possibility to perform a determination of the radiochemical yield has been applied for measurement of ^{129}I. RNAA may also be used when isotopically enriched materials are used for metabolic studies, e.g., with calcium isotopes.

An additional advantage of RNAA facilities and expertise is that these also may be used for production and application of radioactive tracers. These are quite useful in developing and testing of analytical procedures, e.g., for unravelling trace-element physiology or for pre-concentrations and speciation. In both latter cases one may use radionuclides isotopic with the analyte of interest to determine the chemical yield of the chemical separation, e.g., ^{227}Th is applied in the separation and concentration of ^{232}Th from bone material.

Strategies of radiochemical separation

The strategy of radiochemical separation always depends on the elements of interest, their chemical and nuclear properties and their concentrations (amounts) to be measured. It went through changes over the years, mainly due to improvements of the counting facilities available. With the advent of γ-ray spectrometry using semiconductor detectors, the requirements for radiochemical purity of the separated fractions were reduced significantly. Very simple radiochemical separations became popular, especially in analysis of biological and environmental samples, consisting of removal of the major activities of ^{24}Na, ^{42}K, and ^{32}P using selective sorption on inorganic ion exchangers. Later, this approach turned out to be unsatisfactory, because the m_D values of most essential and trace elements were not sufficiently low. A more extreme approach was the design of complex procedures for separation of up to 40 elements into 10 to 15 groups, mostly using ion exchange chromatography. This was abandoned due to its labour and counting time requirements. Presently, simple, well-balanced group separation schemes designed by taking into account both chemical and nuclear characteristics of the relevant radionuclides for their measurement by γ-ray spectrometry are more frequent, as well as the separation of single elements. The latter approach is usually necessary for the determination of elements forming short-lived radionuclides. Emphasis should be given to the determination of the chemical yield in each separation procedure, mostly using radiotracers, to minimize the uncertainty of the results.

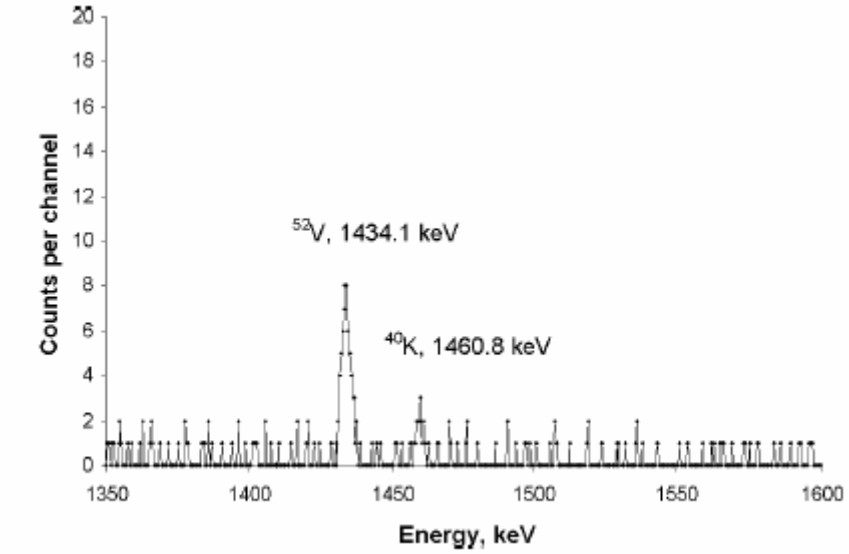
Non-destructive versus radiochemical approach

The tendency to replace radiochemical separation by a non-destructive approach in NAA, if feasible, has become more common in recent years. Examples include the determination of several elements, such as antimony, arsenic, cadmium, and mercury at the ng.g^{-1} range by means of both INAA (or ENAA) followed by CSC and RNAA, iodine determination by ENAA and RNAA, silicon using activation with fast neutrons (FNAA) followed by CSC and RNAA, etc. It is instructive to compare those approaches in terms of detection limit and uncertainty of measurement. For instance, the detection limit of silicon in biological materials by the FNAA-CSC method yielded a value of 12 μg.g^{-1}, while that of RNAA was 0.5 μg.g^{-1}. The m_D value for the iodine determination in diet samples by ENAA varied between 10 ng.g^{-1} to 40 ng.g^{-1}, depending on the chlorine, bromine and manganese contents, while that of RNAA was 0.5 for identical samples and irradiation in the same reactor. The consequence is that the uncertainty of the results obtained by ENAA was significantly higher compared with those achieved by RNAA. This may be considered typical for the situation where either approach can be used. Clearly, when low-uncertainty results are required, e.g., in certification analyses of reference materials, an RNAA procedure may be preferred if there is a possibility to use either approach.

Unique position of RNAA

There are several elements whose low-level determination by non-nuclear and/or non-destructive activation methods is associated with severe difficulties due to a variety of interferences. One of these elements is vanadium. However, the complete removal of interfering radionuclides can be achieved using an RNAA procedure designed for low-level

determination of vanadium in various biological matrices. The conditions of RNAA were as follows: 250 mg of freeze-dried blood was irradiated at a neutron fluence rate of $4x10^{16}$ $m^{-2}s^{-1}$ for 12 minutes, wet-ashed in a mixture of H_2SO_4+HNO_3+$HclO_4$, vanadium was extracted with 0.2% N-benzoylphenylhydroxylamine (N-BPHA) in toluene from 2 $moldm^{-3}$ HCl (total processing time 8 minutes) and the activity of ^{52}V was counted using a 120 cm^3 HPGe well-type detector for 7 minutes. In this case, the analytical radionuclide ^{52}V has a virtually zero background and the (low) uncertainty of its measurement is governed only by the counting statistics of the peak and not of the background. For this and other reasons the most reliable values of blood-, serum- and urinary vanadium that are currently considered reference values for an occupationally non-exposed population have been determined mostly by RNAA. Only one laboratory succeeded in this demanding analytical task by employing NAA with pre-irradiation separation and one by high-resolution inductively coupled plasma mass spectrometry (ICP-MS). Low-level determination of fluorine is also difficult as there is only a limited choice of analytical methods capable of achieving this task, including INAA.



Selection of γ-ray spectrum of a separated vanadium fraction in RNAA of blood. The peak corresponds to ~ 0.05 ng cm^{-3} of V

Competitive role of RNAA

In addition to improvements of non-destructive activation methods, especially NAA, analytical techniques capable of determining a great number of elements at trace and ultratrace levels have developed remarkably in last two decades. Among them various modes of atomic absorption spectrometry and X-ray fluorescence analysis, inductively coupled plasma optical emission spectrometry (ICP-OES), and ICP mass spectrometry (ICP-MS) can be mentioned. Currently, these methods are replacing radiochemical activation analysis in many fields, where NAA, PAA and CPAA used to have a dominant position, due to the expanded availability of measurement devices and the need for a high throughput of samples. It can be expected that this trend will continue in the near future and additional instrumentation improvements for these techniques will appear. However, the theoretical background of these techniques is not as well developed compared to activation analysis. There will always be a need for an independent technique for quality control purposes. Thus, radiochemical activation analysis, especially RNAA, with its competitive features in terms of achievable detection limits will remain a technique of choice to check, independently, the accuracy of results and/or to complement results obtained by the above techniques. In the

field of biological and environmental samples, the results for quite a number of elements at trace and ultratrace levels, such as antimony, arsenic, cesium, chromium, cobalt, gold, manganese, mercury, molybdenum, nickel, rubidium, scandium, selenium, vanadium, thorium, and uranium measured by RNAA will be the more reliable ones. The same can be said about the rare earth elements and some noble metals in geological and cosmochemical samples, phosphorus and other elements in metallic and high-tech matrices. RNAA will also remain an attractive alternative for the determination of naturally-occurring and/or man-made radionuclides which are difficult to measure at low levels due to their long half-lives, such as ^{53}Mn, ^{99g}Tc, ^{129}I, even when direct radioactivity measurement and/or mass spectrometry may be feasible. Recently, a favorable mode of determination of ^{238}U, ^{232}Th, ^{230}Th, ^{237}Np and ^{231}Pa by RNAA, was demonstrated which yielded advantage factors of up to 10^7 compared to radiometric analysis and also suggested a new approach to radioisotopic analysis of U (^{234}U, ^{235}U, ^{238}U) and Th (^{228}Th, ^{230}Th, ^{232}Th) using α-spectrometry in combination with prior NAA.

Conclusions

In general, radiochemical activation analysis and specifically RNAA provides lower detection limits compared with other, especially physical, means of the optimisation in NAA. These detection limits are unique in some cases and highly competitive compared with other trace element analytical techniques. Therefore, RNAA should preferably be used when low-uncertainty determination is required, such as in quality control of other techniques and in the field of chemical metrology, e.g., in the certification of reference materials. It can also be expected that the performance of other analytical techniques will further improve, such as for high-resolution ICP-MS. However, no technical (instrumentation) improvement can help in solving the chemical problems of trace element analysis, namely the analytical blank and irregularities of chemical behaviour of elements at very low concentrations. These problems can be avoided in RNAA and the quality features of this method should not be underestimated. Clearly, there will be further opportunities to exploit the advantages and importance of RNAA in the future. For this purpose, the maintenance and further development of knowledge and experience in radiochemical separation is needed, contrary to recent trends.

Radiochemical analysis procedures

Radiochemical separation becomes necessary when it is impossible to determine the activity of a radionuclide of interest by direct radiometric techniques. This occurs when the activity of the radionuclide is close to the detection limit of the direct technique or when the sample matrix interferes with the measurement. The interference may be due to the absorption of the radioactive emissions by the sample matrix or the presence of other radionuclides that emit particles or electromagnetic radiation of similar energy to the radionuclide of interest. When a radiochemical separation is required, a suitable procedure must be chosen. The general requirements of such a procedure are as follows:

- The radionuclide of interest is isolated in high yield and with high purity
- The radioactive emissions are detected with as high an efficiency as possible, taking into account background considerations
- The analysis of a wide range of material types and radionuclide concentrations should be achievable.

Pre-treatment

Wet and dry ashing techniques are commonly employed to remove organic constituents and convert samples into an inorganic form, which is more readily solubilised. These ashing procedures also function as a pre-concentration step. Dry ashing is normally carried out at temperatures between 300 ºC and 550 ºC and the selection of conditions must take into account the sample matrix and radionuclides of interest. Losses ov volatile or semi-volatile radionuclides will occur to a greater or lesser extent. Went ashing techniques using mineral acids and/or oxidising reagents such as hydrogen peroxide can eliminate some of disadvantages of dry ashing.

Solubilisation

The dissolution of samples containing radionuclides can be achieved either by total dissolution or leaching. The purpose of the analysis and final use of the analytical data should always be a consideration in the choice of the dissolution procedure, and the objective should be to ensure that quantitative extraction is achieved.

Total dissolution procedures either rely on treatments with mineral acids or fusion with a suitable flux to solubilise the material. Various combinations of mineral acids have been employed for dissolution and these usually consist of nitric, perchloric and hydrofluoric acids. The use of heated pressure vessels and microwave ovens provide a very efficient approach. Fusion techniques have been used for total solubilisation of resistant materials and require the samples to be thoroughly mixed with the flux and heated to high temperatures (800 ºC - 1000 ºC) to disrupt mineral matrices. Acid dissolution of the fused melt is the final process in this procedure. Fusion procedures are commonly employed to eliminate preparation losses of

semi-volatile radionuclides by subjecting the sample to an alkaline fusion to remove organic material.

Separation and pre-concentration

As a rule, methods for separating substances utilise differences between the distribution coefficients of the individual constituents of a mixture between two phases. Three modifications of the separation methods are possible:

1. The major constituent is isolated from the sample, whereas the traces remain in solution – a macro-micro separation
2. Trace constituents are isolated from a solid or dissolved sample, major constituents being retained in solution – a micro-macro separation
3. Trace constituents are separated from one another after isolation – a micro-micro separation.

A method of separation is characterised by:

- The separation factors of the constituents of the mixture to be analysed
- The specificity or selectivity of the separation
- The rate of process
- The ease of performance and availability of equipment
- The suitability for further treatment of the isolated fraction of the constituents to be determined
- The coefficient of enrichment

We can distinguish two modifications of the separation process:

1. Specific isolation of a single constituent from a mixture. It is associated with a macro-micro separation in which the macro constituent is specifically isolated with no trace elements carried along. Or separation of specifically one trace element if it is the only one to be determined.
2. Group separation of all the trace elements from a mixture. It usually seeks to separate simultaneously all the trace elements to be determined, with the sample matrix retained unaffected.

Masking

Masking of constituents of the sample, which may interfere with the separation, can make a separation more or even completely specific. A masking agent is a substance which reacts to form stable complexes with constituents which interfere with the main reaction of the component to be isolated or determined.

Contamination problems

- From the atmosphere – avoidance (air-conditioning, glove boxes), laboratory equipment
- Laboratory vessels and containers – glass, quartz, platinum, plastics, cleaning
- Reagents – water, reagents, solutions

Precipitation and co-precipitation

Precipitation is formation of a separable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it. Precipitates are usually contaminated with foreign ions present in the solution although these ions would not themselves have been precipitated under the given experimental conditions. This phenomenon is called co-precipitation. Direct separations are not possible for traces, because the amounts involved are too tiny to handle, but separation of trace constituents by co-precipitation on a collector (carrier) intentionally added to the solution has been found to be practicable and extremely useful.

1. Crystalline precipitates form in two or three distinct crystallisation stages: nucleation, crystal growth, and aging.
2. The mechanism of formation of colloidal precipitates differs from that for crystalline precipitates. In colloidal precipitates, there is a continuous transition from particles characteristic of true molecular solutions, through those separable only by ultrafiltration, to macroscopic aggregates. A hydrophilic precipitate has a strong affinity for water, is reluctant to flocculate, difficult to wash, apt to incorporate numerous substances and hard to separate by filtration. Hydrophobic colloids have a low affinity for water and produce aggregates, which are easy to flocculate by adding a small amount of a suitable electrolyte.
3. Co-precipitation is the incorporation of impurities into a precipitate by substances, which under experimental conditions are usually soluble in the liquid phase. This term is usually used to all instances when trace constituents are precipitated together with a collector. The mechanism of co-precipitation is usually considered to include mixed-crystal formation, occlusion and adsorption.
    a. Mixed-crystal formation involves substitution of ions in the crystal lattice of the carrier by co-precipitating ions. When both ions are about the same size, mixed crystals can be formed at all ratios of the two ions to form true mixed crystals. Mixed crystals can also be formed with ions considerably differing in size, but then the amount of the co-precipitated ion is limited. Co-precipitation is favoured when the precipitation process attains equilibrium very slowly.
    b. Occlusion involves mechanical entrapment of foreign ions and solvent molecules at the surface of the precipitate during the rapid growth of its crystals.
    c. The mechanism of adsorption depends on the surface of the resulting precipitate.

Application of precipitation and co-precipitation

1. Separation of the major sample constituent (matrix) by precipitation

    In trace analysis precipitation is useful only for macro-micro separations, i.e. for removing the major constituent of a sample, if this interferes with the subsequent determination of traces. The precipitation conditions can be chosen so that a considerable amount of the major constitutient can be precipitated without causing losses, by co-precipitation, of the

trace constituents to be determined subsequently. Examples: lead removal, as major constituent, by HCl; AgCl removal; BiI removal.

2. Co-precipitation of trace elements with inorganic collectors (carriers)

   One can separate a large group of trace elements or isolate one specific trace constituent. Collectors: sulphides, hydroxides, manganese dioxide, halides.

3. Co-precipitation of trace elements with organic collectors (carriers)

   Two reagents are usually used together. One is able to form complexes with the metal ions to be separated; it may be a chelating agent or a simple anion (e.g. thiocyanate, chloride, bromide or iodide), which forms anionic complexes with the ions to be separated. The other must be an organic compound, which is sparingly soluble in water.

4. Electro deposition

   Electrolysis, whether normal or "internal" may be used for precipitation of components of a solution.

Volatilisation of substances

A classic example is the determination of impurities in distilled water after the water as the major constituent has been distilled off. In trace analysis of inorganic materials either the matrix or trace elements are separated, depending on which is more volatile; they are never separated by fractional distillation. There are generally two possibilities:

- Direct distillation of one or more trace constituents from the sample.
- Conversion of the constituents of the sample into chemical species, which can be separated by virtue of the difference in their volatilities (usually fluorine, chlorine, bromine, and the hydrogen halides).

1. Direct distillation of the sample matrix

   This procedure has been used primarily for analysing certain high-purity metals and high-purity volatile compounds. Examples are: separation of Zn, Cd, Se, and Na at temperatures of 500, 400, 460 and 350 ºC, respectively. Evaporation of Hg selenide; in a quartz beaker, at 400 ºC, the selenide sublimes completely, and the trace impurities remain intact in the beaker.

2. Distillation of the sample matrix

   Elements such as As, Cr, Ge, Os, Rh, Ru, Sb, and Sn can be distilled from solution as the chlorides or bromides.

3. Isolation of trace constituents

   Elements of concern are directly distilled and afterwards collected e.g. in a cooled receiver. Examples are Sb, As, Bi, Ge, In, Cd, Pb, Hg, Tl and Te in a stream of hydrogen at 1000 ºC. Volatile hydrides and halides can be distilled off.

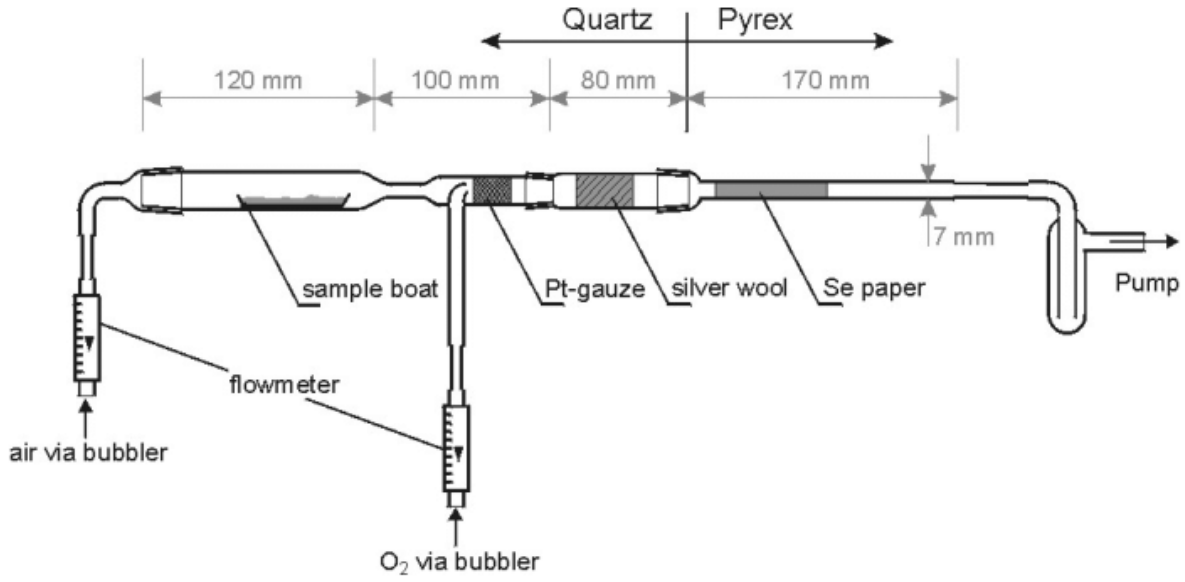


Fig. 1: Isolation of Hg

4. Ashing of organic matrices

Determination of inorganic constituents in organic materials requires removal of the organic matter, because it would either interfere with, or simply preclude, analytical reactions. The simplest way to remove organic matter is to ash or oxidise it. Carbon and hydrogen are oxidised to carbon dioxide and water, and organic nitrogen is mainly liberated as free nitrogen. Since all the products are gasses, ashing may be considered to be a method based on volatilisation. It should meet the following requirements:

- It should be quantitative: all the organic matter should be oxidised and volatilised, and the inorganic portion should remain quantitatively as the residue.
- It should be rapid: in routine analyses of large numbers of samples the rate of ashing greatly affects the time and cost of the analysis.
- It should be feasible in a simple and inexpensive apparatus.
- No trace constituent must be lost from or introduced into (as an extraneous impurity) the sample examined.

Wet ashing

It was introduced to avoid losses due to volatilisation of trace constituents. Most frequently, a sulphuric acid-nitric acid mixture is used. Also perchloric acid is useful because its oxidation potential is higher than that of sulphuric acid. At the same time perchlorates are, in general, more soluble than sulphates. Hydrogen peroxide has long been applied as an additive to promote ashing.

Liquid – liquid extraction

This is a process of transferring a chemical compound from one liquid phase to a second liquid phase, immiscible with the first one. One phase is usually water and the other a suitable organic solvent. In terms of extractability, inorganic compounds may be tentatively classed into the two groups:

- Compounds, which occur in the aqueous phase as undissociated covalent species, e.g. I_2, Br_2, halides of some metals, e.g. $AgCl_3$, $AsBr_3$, and some oxides, e.g. OsO_{34}.
- Ionic compounds

Three main mechanisms for extraction of inorganic cations may be distinguished, namely extraction of chelates, of ion pairs, and of co-oerdinatively solvated salts. In trace analysis for inorganic species, two main types of extraction systems can be distinguished: (1) the species extracted are uncharged covalent compounds (e.g. chelates) or (2) the species extracted are electrovalent compounds (e.g. anionic complexes, ion pairs with amines, and co-ordinatively solvated salts).

1. Chelate systems.

   Chelates are uncharged covalent compounds. They are complexes of a metal ion with a multidentate ligand which occupies two or more co-ordination sites, and in which rings are formed. A stable ring is often formed when the ligand contains a charged group, which can form an electrovalent bond with the metal, and also an electron-donating group, which can form a covalent bond with the metal. Typical charged groups are –OH, –COOH, =NOH, =NH. Typical electron donating groups are (usually contain O, N, S) =O, –O–, –N=, =S.

2. Ion-association extraction systems.

   These are systems in which the compounds extracted may be a variety of species; non-solvated co-ordination salts, solvated co-ordination salts and anion complexes are the most important in separation processes. An important group of ion-association compounds for separation processes are the anionic complexes. Such complexes are fiormed by certain transition metals with halide or pseudohalide ions (e.g. CN^-, SCN^-).

- Co-ordinatively solvated salts

An extractive separation in trace analysis will have one of the following three aims:

- Extraction of the major component, to allow the impurities left in aqueous phase to be determined.
- Isolation of a group of elements which are to be determined.
- Selective isolation of a single element from the material to be analysed.

Ion exchange chromatography

This is a mode of chromatography in which ionic substances are separated on cationic or anionic sites of the packing. In ion exchange chromatography, charged substances are separated via column materials that carry an opposite charge. The sample ion (and usually a

counter ion) will exchange with ions already on the ionogenic group of the packing. Ion-exchangers are insoluble solid materials, which contain exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions initially present in an electrolyte solution when an ion-exchanger is brought into contact with it. Substances containing exchangeable cations are called cation-exchangers and those containing exchangeable anions are called anion-exchangers.

1. Inorganic ion exchangers

   Inorganic ion-exchangers are natural (clays, zeolite-type minerals, etc.) and synthetic (synthetic zeolites, molecular sieves, hydrous multivalent metal oxides, heteropoly acid salts, etc.) compounds. Zeolites are crystalline aluminosilicates with ion-exchange properties. Heteropoly-acid salts are e.g. molybdophosphates, molybdoarsenates, molybdosilicates, etc. Most widely used are the synthetic ion-exchange resins, which have as charge carriers ionogenic groups bonded to a framework (matrix) that is a three-dimensional network of hydrocarbon chains.

2. Organic ion exchangers

   a. Cation exchangers

      Synthetic organic cation-exchangers are cross-linked polyelectrolytes, which consist of a three-dimensional network of hydrocarbon chains carrying groups such as sulphonate, carboxylate, phenolate, phosphonate, and others. The properties of an ion-exchanger depend on the nature and number of functional groups, the degree of ionisation, the type and extent of cross-linking in the matrix, and the configuration of the functional groups. Ion-exchangers are synthesised by condensation or polymerisation. Condensation type is e.g. obtained by sulphonation of phenol and subsequent condensartion with formaldehyde: Amberlite IR-100, Dowex-30. Polymerisation type is e.g. based on a styrene-divinyl-benzene copolymer: Dowex 50, Zerolit 225, Amberlite IR-120.

   b. Anion-exchangers

      Condensation-type anion exchange resins are prepared e.g. by condensing aromatic amines with formaldehyde or aliphatic polyamines with aldehydes. Polymer type anion exchange resins are mostly based on S-DVB coplymers. Examples are Amberlite IRA-400, Dowex 1.

Extraction chromatography

The stationary phase is an extractant, which coats or is bonded to a porous hydrophobic support, and the mobile phase is a suitable solution of an acid, base or salt. As stationary phase supports are silica gel, Hostaflon, Teflon, etc. The most used extractants are tributyl phosphate, methyl isobutyl ketone, TOPO, etc.

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