CHIMIA

Volumen 21 Fasc. 3 1967 Pag. 113–144

Radiochemische Methoden in der analytischen Chemie II

Die erste Folge dieser Reihe erschien im Heft 1/1967 der *Chimia*

Neutron Activation Analysis

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Summary

Activation analysis is a technique of elementary analysis in which samples are exposed to a high flux of neutrons, and the radioactivity induced in selected elements is compared with that produced in known standards. It has the following advantages: (1) wide applicability, (2) sensitivities ranging from 10^{-6} to 10^{-14} g, (3) absence of reagent contamination, (4) built-in checks on reliability, (5) possibility of determining individual isotopes, (6) reasonable cost. Its disadvantages include: (1) It is only a method of elementary analysis. (2) It needs a source of neutrons. (3) It is inapplicable to most of the lighter elements which activate to nuclides of short half-life.

Current trends in activation analysis include automation of techniques and the development of laboratory neutron sources. Applications are doubling every 3.3 years, notably in the fields of semi-conductor research, metallurgy, geochemistry, cosmochemistry and inorganic biochemistry.

Activation analysis is a technique of elementary analysis which makes use of one of the nuclear reactions by which elements are synthesised in the interior of stars. It involves exposing samples to a high flux of neutrons, for example in an atomic reactor. Any nuclide can capture a neutron by the (n,γ) process, e.g.

$$^{55}\mathrm{Mn} + {}^{1}n \rightarrow {}^{56}\mathrm{Mn} + \gamma$$

If the nuclide formed is radioactive, it can be separated chemically or physically and its radioactivity measured. For example, in the case of manganese, the nuclide ^{56}Mn emits beta and gamma rays and has a half-life of 2.6 hours. The gamma-rays from ^{56}Mn may be physically isolated by using a gamma-spectrometer, which sorts out gamma-rays according to their energy. Alternatively the radiomanganese can be chemically separated from all other induced activities, and its beta or gamma radiation can then be counted.

Advantages and disadvantages

Activation analysis has a number of advantages which make it outstanding if not unique among techniques of analysis. These are listed and discussed below, together with the corresponding disadvantages:

1. The technique is applicable to 75 of the 81 stable elements. It cannot be used for B, Be, C, H, He, and Li, because these elements are activated to very short-lived or very long-lived nuclides. Certain other elements, namely Al, Cl, F, I, Mg, N, Nb, Ne, O, Rh, Ti and V, yield nuclides with half-lives of less than 1 hour on neutron irradiation, and so can only be determined near a source of neutrons.

2. The sensitivity of the technique is generally in the submicrogram region. The amount of radioactivity produced in any nuclide depends on its cross-section, abundance and atomic weight as well as on the flux and energy of neutrons available: these factors are usually fixed. The radioactivity produced may conveniently be adjusted by varying the activation period, and the delay between activation and counting. In practice, good results are obtained by setting the activation period equal to the half-life of the nuclide of interest. There is a simple formula which can be used calculate the approximate activity induced in any nuclide, which is:

Specific activity

$$= 0.62\ \Phi \sigma f A^{-1} (0.5)^{t'/t_{1/2}} \left[1 - (0.5)^{t/t_{1/2}}\right] \text{ dis sec}^{-1}\text{g}^{-1}$$

where Φ is the neutron flux in n cm^{-2} sec^{-1}
σ is the cross section of the nuclide in barns
f is the fractional abundance of the nuclide
A is the atomic weight of the nuclide
t is the activation period
t' is the time between activation and counting
$t_{1/2}$ is the half life of the nuclide

On applying this formula to the case of manganese, using a flux of 10^{14} neutrons cm^{-2} sec^{-1} and setting $t = t' = t_{1/2}$, one finds a specific activity of 3.7×10^{12} dis sec^{-1}g^{-1}, which implies that 10^{-14} g of manganese should be detectable. The sensitivity is not as good as this for most other elements, but even so it is usually better than all other techniques in many cases.

3. Reagent contamination is no problem in activation analysis, since only radioactive contaminants can affect the result. This is a big advantage over wet chemical techniques, where large volumes of acids are needed to dissolve samples.

4. There are several independent nuclear parameters which can be measured to check whether an analysis has been correctly performed. For example, the half-life, beta spectrum and gamma spectrum of the separated nuclide can be compared with known standards to ensure that the right nuclide is in fact being counted. Few other techniques have a built-in check of this kind to ensure that no systematic errors occur.

5. The method can be used to determine individual isotopes, and in a few cases competes with mass spectrometry in precision. For example, it can be used to determine both ^{235}U and ^{238}U in a sample of uranium.

6. Apart from the activation process, activation analysis can be carried out in an ordinary laboratory provided fume hoods, rubber gloves and a few lead bricks are available. Only rarely does an activated sample constitute a radiation hazard, as for example does activated sea water. Provided that the usual precautions are taken with regard to spillage, ingestion and waste disposal, the modifications required to carry out activation analysis in an ordinary laboratory are simple and inexpensive.

Counting equipment is the most expensive item required, but where radiochemistry is employed this need cost no more than other analytical instruments such as spectrophotometers. Simple equipment, suitable for counting beta and gamma radiation, might cost between 5000 and 10000 Swiss Francs. Sophisticated automatic equipment capable of plotting gamma spectra would cost at least ten times this sum, but is not essential for small analytical laboratories.

Few laboratories can afford to buy a reactor (costing at least 1 million Swiss Francs) or a neutron generator solely for activation analysis. But reactors are now working all over the world, and space in them can be hired at reasonable terms. It has been said that no part of the world is more than four hours flying time from a reactor, and operators of experimental reactors will often allow experimenters to carry out activation analyses with short-lived nuclides in adjacent laboratories.

Three disadvantages of activation analysis—the short-lived nuclides of some elements, radiation hazards, and proximity to reactors—have already been mentioned. The biggest disadvantage is the inherent one that the technique is only a method of elementary analysis, and gives no information on how the elements are chemically combined. For example, activation has been used to determine iodine in blood, but it does not distinguish between free iodide ions, iodinated amino-acids and thyroglobulin, or iodine bound to protein. The precision of the technique is less than $\pm$ 10% and usually less than $\pm$ 5%, which is adequate for most applications.

Discussion of technique

An actual analysis can be divided into five stages as follows:

1. Collection of sample and preparation of standard.
2. Canning for activation.
3. Activation by neutrons.
4. Radiochemical separation.
5. Determination of radioactivity.

Stage 4. can sometimes be eliminated.

Collection of sample

It is obvious that samples should be handled as little as possible and that operations such as grinding or sieving should be avoided. Drying in a dust-free atmosphere may be carried out to save reactor space, which is expensive. Samples should be handled with plastic instruments, and if necessary their surfaces should be etched with suitable acids after activation to remove surface contamination. Activation analysis can determine traces of contaminants which could not be detected by any other known method.

Preparation of standards

Standards are best prepared by weight. An aqueous solution containing an accurately known concentration of the element sought should be freshly made up; 50 mg l^{-1} is a convenient concentration. About 1 drop of this solution is then weighed into a clean container, which may then be sealed or the water evaporated prior to sealing. The containers used for samples and standards should be the same to avoid the possibility of different neutron absorption.

Canning for activation

The three commonly used canning materials are aluminium, silica and polyethylene. Aluminium foil can be folded or formed into many shapes and is resistant to high neutron fluxes and high temperatures. It activates to give 2.3 minute ^{28}Al and 15 hour ^{24}Na, which are strong gamma-emitters, so that it is unsuitable for short irradiations. Silica containers are readily sealed, and are also resistant to high neutron fluxes and high temperatures. They activate to give 2.6 hour ^{31}Si which is a beta-emitter but has no gamma ray. Silica is the purest and best canning material for long irradiations, but is rather bulky. Polyethylene can be obtained even purer, and is the ideal canning material for short irradiations. It is, however, melted by temperatures exceeding 108 °C and rendered brittle by exposure to more than 2×10^{17} neutrons cm^{-2}.

Activation by neutrons

Most applications use reactor neutrons, and while these have a range of energies the thermal neutrons, that is, those with energies around 0.025 eV, are the most effective in activation. Large reactors have neutron

fluxes ranging from 10^{12} to 10^{15} neutrons cm^{-2} sec^{-1}, and even higher fluxes can be obtained for periods of a few milliseconds in pulsed reactors. Reactor temperatures vary considerably, and should be measured if polyethylene containers are used. The flux gradient may be quite steep in small reactors, in which case cans should be spun during activation to ensure that all parts receive the same flux of neutrons.

The cross-sections of many nuclides have peaks at particular neutron energies. Ideally they should be activated by neutrons of these energies, but in practice this can only be achieved by reducing the neutron flux and hence the sensitivity. Neutrons can be produced at fluxes of up to 10^{11} neutrons cm^{-2} sec^{-1} in laboratory neutron generators, though the volume receiving this flux is smaller than that available in reactors. These neutrons have an energy of 14 MeV and produce different nuclear reactions from thermal neutrons. If they are slowed down to thermal energies the flux is considerably reduced.

Minor hazards may arise when liquids are irradiated in sealed containers, as the gases liberated may create a high pressure.

Radiochemical separations

Radiochemistry is needed to obtain the maximum sensitivity from activation analysis. By adding known amounts of inactive carrier, and determining the amount of this recovered at the end of a separation scheme, the chemistry can be simplified. In the first place it can be carried out on the milligram scale instead of the submicrogram scale, so that precipitates are easily seen. Secondly the chemistry need not be quantitative, which is a big advantage.

Techniques have been evolved to separate all the known elements in radiochemically pure states and these are applicable to all but the shortest lived nuclides. It is possible to carry out seven chemical steps in as little as one minute using specially designed apparatus. Several laboratories now have semi-automatic separation schemes, usually based on ion-exchange, which are able to separate about twenty different elements. Complete radiochemical separations are not always necessary if gamma spectrometry is used.

Determination of radioactivity

The final analysis is made by comparing the count-rates from a sample and standard which have been treated in the same way. Counting may be carried out using Geiger counters, Scintillation counters or solid state detectors. While some authors recommend the elimination of radiochemistry and its replacement by gamma spectrometry, this is a one-sided approach and every case should be taken on its merits. In practice it is rarely possible to determine more than 20 elements in a sample by gamma spectrometry alone, and this may involve three irradiations for different periods of time. Pure beta-emitters such as ^{32}P and ^{35}S cannot be determined by this method. Gamma spectrometry is useful for determining one or a few elements in a large number of samples. Radiochemistry must be employed when a large number of elements are to be determined in one or relatively few samples.

Current trends in activation analysis

The most obvious current trends are the development of laboratory neutron sources and the automation of both physical and chemical techniques of separation. Laboratory neutron sources have been and are still being improved, but are still not competitive with reactor neutrons where the latter are available. The gamma spectrometers available today are greatly superior to those of five years ago, but they are also far more expensive, and their price may put off would-be users of the method. However, the stage has already been reached where analyses for some elements, for example sodium and chlorine, could be carried out entirely automatically at the rate of many thousands per week. Such analyses would involve a reactor, a gamma spectrometer and a computer, and despite the expense of these items the analyses could be done at a competitive cost.

Automation of radiochemical methods has been slower but is likely to prove rewarding. Unfortunately the fastest separation technique, gas chromatography, is not applicable to most elements which form involatile compounds.

Applications of activation analysis

Since its first application in 1936, the number of papers on activation analysis have doubled every 3.3 years, so the subject is growing fast. It is impossible to mention all the applications here.

The semi-conductor industry has greatly benefitted from activation analysis, which is able to determine otherwise undetectable traces of up to 60 elements in pure crystals of silicon, germanium etc. Unfortunately one impurity of great interest, boron, cannot be detected by neutron activation.

In metallurgy, activation has been used in prospecting for ores of rare metals, as well as in distinguishing closely related pairs of metals such as zirconium and hafnium, or niobium and tantalum. Especially noteworthy are the efforts of Albert and co-workers in determining the impurities in very pure samples of aluminium, iron and zirconium. These metals are suitable matrices for activation, since they themselves activate to either short-lived or long-lived nuclides giving rise to relatively small radiation hazards.

The fields of geochemistry and cosmochemistry have been revolutionised by the application of activation analysis during the last 15 years, and it is fair to say that

most of our knowledge of the abundances of the rare elements in meteorites and in the earth's crust has been revised during this period. The new data has supported novel theories concerning the origin of elements in stars.

Inorganic biochemistry has also been given a new lease of life by the technique, which is able to determine elements whose presence was previously only inferred. As yet, however, only one element has been proved to be essential to life as an indirect result of activation analysis.

Archaeologists are beginning to realise the potentialities of the technique, especially the non-destructive gamma spectrometry. Forensic scientists are also interested in sensitivity of activation for poisonous elements such as arsenic, and for determining barium and antimony in gunpowder stains. A bizarre development is the determination of five elements in man *in vivo*, using an extremely low flux of neutrons and a refined gamma spectrometer.

References

The literature of activation analysis is now rather bulky and only a few items in it can be mentioned here. The following books have been written recently on the subject.

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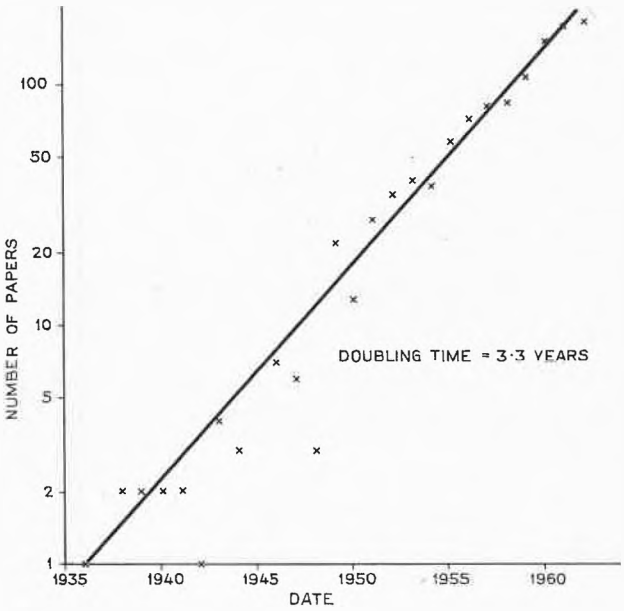

Fig. 1. Rate of increase of activation analysis literature