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IV. ISOTOPENMETHODEN

Neutron Activation Analysis as an Analytical Tool

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Zusammenfassung

In vielen Ländern werden heute Kernreaktoren zu Forschungszwecken erbaut. Diese Reaktoren geben dem Analytiker Mittel zur Durchführung außerordentlich empfindlicher Anylasenmethoden in die Hand. Die meisten Kernreaktoren stellen eine intensive Quelle thermischer Neutronen dar und können zur Aktivierung einer großen Zahl von Elementen durch die $(n\gamma)$-Reaktion verwendet werden. Die auf diese Weise gebildeten Radioelemente werden radiochemisch gereinigt, worauf die charakteristische Strahlung, die sie aussenden, gemessen werden kann. Einer allgemeinen Einführung, die noch andere Methoden der Aktivierung erwähnt, folgt eine Diskussion über die Prinzipien der Neutronenaktivierungsanalyse und der dabei praktisch verwendeten Schritte. Es werden besondere Vorteile, wie das Fehlen von «blank»-Beiträgen der Reagenzien, erwähnt und mögliche Fehlerquellen, vor allem nuklearen Ursprungs, sowie die große Präzision und Empfindlichkeit dieser Methode behandelt.

Die heute verwendeten Zählmethoden werden erwähnt, wobei besonders die γ-Spektrometrie hervorgehoben wird. Diese wichtige neue Technik wird sowohl zur Identifizierung als auch zur Messung von γ-strahlenden Radioelementen verwendet. Sie vermindert sehr oft die Anforderungen bei den radiochemischen Trennungen oder macht sie in günstigen Fällen sogar ganz überflüssig. Zur Illustration dieser Ausführungen werden schließlich aus den zahlreichen Gebieten, in denen Neutronenaktivierung erfolgreich verwendet wurde, einige Beispiele näher betrachtet und diskutiert.

Introduction

Neutron activation analysis was first used by Hevesy and Levi[1] in 1936, and since then it has been widely used in many fields of pure and applied research. Neutron activation is a particular case of the general method of radioactivation analysis. In the latter method, particles such as deuterons, protons and neutrons, or radiation such as γ-photons, can be used to bring about the activation; but the most widely used method is that utilising the slow or thermal neutrons produced in nuclear reactors. The post-war construction of high neutron flux nuclear reactors, has enabled the chemist to apply a highly sensitive and specific method of analysis for the determination of minute quantities of a large number of elements (e.g. 10^{-9} to 10^{-10} g As).

Numerous articles and reviews[2,3,4,5] have dealt with its applications and advantages, and indeed a recent symposium in Vienna, organised by the I.A.E.A., was devoted entirely to the field of 'Radioactivation Analysis'.[6] Its application in the biological field has been reviewed by Loveridge and Smales,[7] and the most recent general account is that by Atkins and Smales.[8] A detailed survey of neutron activation analysis in geochemistry is given by Mapper,[9] and particular geochemical applications have been reviewed by Reed.[10] A bibliography on radioactivation analysis has been published by Gibbons *et al.*,[11] but this only covers the literature to June, 1957.

The experimental facilities for the irradiation of samples in most research nuclear reactors are easily

[1] G. Hevesy and H. Levi, *Kgl. Danske Videnskab Selskab, Math.-Fys. Medd. 14* (1936) No. 5.

[2] G. E. Boyd, *Anal. Chem. 21* (1949) 335.

[3] A. A. Smales, in *Trace Analysis* (J. H. Yoe und H. J. Koch jr., Editors), Wiley, New York 1957, p. 518.

[4] E. N. Jenkins and A. A. Smales, *Quart. Rev. Chem. Soc.* (London) *10* (1956) 83.

[5] U. Schindelwolf, *Angew. Chem. 70* (1958) 181.

[6] *I. A. E. A. Bull. 1* (1959) No. 2, p. 11.

[7] B. A. Loveridge and A. A. Smales, in *Methods of Biochemical Analysis* (D. Glick, Editor), Interscience, New York 1957, p. 225.

[8] D. H. F. Atkins and A. A. Smales, in *Advances in Inorganic Chemistry and Radiochemistry* (H. J. Emeléus and A. G. Sharpe, Editors), Academic Press, New York 1959, p. 315.

[9] D. Mapper, in *Methods in Geochemistry* (A. A. Smales and L. Wager, Editors), Interscience, New York 1960, p. 297.

[10] G. W. Reed, in *Researches in Geochemistry* (P. H. Abelson, Editor), Wiley, New York 1959, p. 458.

[11] D. Gibbons, B. A. Loveridge and R. J. Millet, *A. E. R. E. Report I/R. 2208, U. K. A. E. A.* (1957).

available to all potential users. Irradiations can be carried out, for example, in nuclear reactors in the U.K., U.S.A., France, etc., and it is assumed that facilities will shortly be available in the 10 MW heavy-water cooled and moderated reactor being built at Würenlingen, Switzerland.

Outline of Method

Activation analysis is a method of determining elements; and for some elements, a particular isotope. In neutron activation analysis the amount of an element present in a sample is determined by irradiating the sample with neutrons, and then measuring the intensity of the characteristic radioactivity induced in the element. The intensity of this induced radioactivity is directly proportional, other factors remaining constant, to the amount of the element, irrespective of its state of chemical combination. The simplest and most important nuclear reaction which is utilised in activation analysis, is the (n,γ) reaction, brought about by thermal neutrons produced in nuclear reactors.

When an element is bombarded with neutrons, the rate of growth of the number of radioactive atoms, is given by the equation:

$$\frac{dN^*}{dt} = f\sigma N - \lambda N^*, \qquad (1)$$

where N = number of target atoms,
N^* = number of radioactive atoms formed,
f = constant neutron flux in neutrons/cm²/second,
σ = isotopic cross-section for the particular nuclear reaction and energy distribution of neutrons used, in cm²,
t = time in seconds,
λ = radioactive decay constant for the radioactive species formed.

The cross section, σ, of a nucleus can be regarded both as the 'target area' it presents to an approaching neutron, and as a measure of the probability that a neutron will strike and interact with the nucleus. Cross-sections are measured in square centimetres and the unit of magnitude is the 'barn', which is equal to 10^{-24} cm². For thermal neutrons the variation in cross section of different nuclides is very large,[12] e. g. the isotopic activation cross section for ^{23}Na is 0·53 barns and that for ^{115}In is 145 barns. Thermal neutron reaction cross sections are normally listed for 0·0253 eV neutrons, even though the actual measurements were usually made with neutrons of wide energy spread. Excitation curves, which show the variation of cross section with neutron energy for all the elements, have been collected in readily accessible form by HUGHES and SCHWARTZ.[13]

Equation (1) becomes on integration

$$\lambda N^* = f\sigma N\,(1 - e^{-\lambda t}). \qquad (2)$$

Hence the amount of radioactivity, A_t, in disintegrations per second exhibited by the atoms N^*, produced up to a time t, is given by

$$A_t = \lambda N^* = f\sigma N\,(1 - e^{-0{\cdot}693\,t/T}) \qquad (3)$$

since the half life, T, of the radionuclide formed is given by

$$\lambda = \frac{0{\cdot}693}{T}.$$

Hence for a weight W grams of an element of atomic weight M, where the particular isotope undergoing the (n,γ) reaction has a fractional abundance θ, we have:

$$A_t = 6{\cdot}02 \times 10^{23} f\sigma\theta \frac{W}{M}\,(1 - e^{-0{\cdot}693\,t/T}). \qquad (4)$$

The term in parentheses in equation (4), $(1 - e^{-0{\cdot}693\,t/T})$ is called the 'saturation factor' or 'growth factor', S. It is seen that for values of t very long compared with T, that $S = 1$, and when $t = T$, then $S = 0{\cdot}5$.

The maximum or saturation activity is obtained for an irradiation time of more than seven half lives, and is then A_∞, where

$$A_\infty = 6{\cdot}02 \times 10^{23} \times f\sigma\theta \frac{W}{M}. \qquad (5)$$

When the irradiation is stopped, the active species will decay with its own characteristic half-life, T.

From equation (4), it is seen that provided the magnitude of the flux, the activation cross section, the half-life and the time of the irradiation are known, a knowledge of the absolute disintegration rate should enable the mass of the element to be determined. In actual practice a comparative procedure is used, in which the sample, and a standard containing a known quantity of the element being determined, are carried together through the same irradiation, chemical separations and final counting.

Although activation is a tremendously sensitive method of trace analysis, there are no difficulties caused by working with minute amounts of trace elements. It is usual to add milligram quantities of the inactive element when the irradiated sample is being dissolved and this use of a 'carrier' simplifies the subsequent chemistry. It also avoids the necessity of quantitative recovery at each stage of the chemical separation, since the final determination of the 'yield' enables corrections to be made for any losses.

Practical Procedure

The following steps outline the procedure that is normally used:

(1) The samples and standards are weighed, separately, into silica ampoules, which are sealed, placed in aluminium containers, and then irradiated in the nuclear reactor for a suitable time.
(2) After irradiation, the samples are dissolved in the presence of known amounts of the inactive element (or elements) being determined.

[12] D. J. HUGHES, *Neutron Cross Sections*, Pergamon, London 1957.
[13] D. J. HUGHES and R. B. SCHWARTZ, *Neutron Cross Sections*, BNL-325, U.S. Govt. Printing Office, Washington (D.C.), 2nd ed. 1958.

(3) Chemical exchange between the active tracer and the inactive carrier is ensured and then a number of separations are carried out, in which the element, or usually some compound of the element, is isolated having been radiochemically purified.
(4) A convenient aliquot of the standard is also prepared in a similar way.
(5) The final precipitates from the samples and standards are mounted on weighed (aluminium) counting trays and the chemical yield is determined.
(6) The samples and standards are now counted under identical conditions in the appropriate counting equipment.
(7) Radiochemical purity is confirmed by measuring the half life of the particular nuclide, where possible, and by determining the energies of the β-particles or γ-rays that it emits.

The mass of the element X, is then calculated, using the equation:

$$\frac{\text{Mass of X in sample}}{\text{Mass of X in standard}} = \frac{\text{Total } \textit{corrected} \text{ activity produced by radionuclide in sample}}{\text{Total } \textit{corrected} \text{ activity produced by radionuclide in standard}}$$

An important advantage which activation analysis has over many other methods of trace analysis, is that it is unaffected by the normal 'blank' difficulties contributed by reagents and equipment. If any *inactive* trace amounts of the element being determined are picked up during the chemical operations, the quantity added is negligibly small compared with the milligram amounts of inactive carrier already present. This freedom from blank difficulties makes it all the more important, therefore, to avoid any possible contamination of the samples before their irradiation, and rigorous precautions to this end must be taken.[3]

Sources of Error

Provided the samples and standards are subjected to precisely the same irradiation conditions any *external* variation in the flux intensity or neutron spectrum will affect them equally. The position which the irradiation container occupies must not be one in which any significant flux gradient normally exists, since the samples and standards may often be 1 to 2 cm apart. It is usual to irradiate all samples and standards in duplicate, at least.

However, *internal* variations of the flux, within the samples and standards, caused by 'self-shielding' due to large cross sections or 'resonances' can introduce serious errors. Self-shielding occurs when excessive absorption of neutrons takes place, such that the effective neutron flux is no longer uniform throughout the combination of sample and standard.

Thus where a major constituent of the sample has a large cross section, the sample weight must be restricted to a minimum. If necessary, the samples can be diluted with relatively low cross section material such as alumina, magnesia or silica. It is usually more satisfactory that the standards should be in the form of dilute solutions, so that only microgram amounts of the elements being determined are irradiated.

A further effect which can cause self-shielding errors is that of 'resonance capture', where strongly selective absorption of neutrons takes place, at specific neutron energies. ^{115}In for example, has an activation cross section of 145 barns, but at a neutron energy of 1·46 eV, the cross section rises to a value of 3×10^4 barns. It is often overlooked that although many elements have a low total cross section for thermal neutrons, they may still possess large resonance peaks for neutrons of intermediate energy. The thermal neutrons in a nuclear reactor have a Maxwell-Boltzmann energy distribution. However, in addition to thermal neutrons, there are fast and intermediate energy neutrons, the fast neutrons having energies above 0·1 MeV.

PLUMB and LEWIS[14] have drawn attention to the resonance effect in the case of antimony. They noted that although the total cross section for antimony was only 6·4 barns, resonance peaks at neutron energies of 5, 15 and 21 eV caused self-shielding effects in solid standards of elemental antimony. A similar effect in the case of caesium was observed by CABELL and SMALES[15]. The large resonance for caesium at intermediate neutron energies, caused observable self-shielding effects, when solid standards of caesium chloride were irradiated. However, when dilute solutions of caesium chloride (up to 10 mg per g) were irradiated, self-shielding effects were negligible.

Any contribution to the total self-shielding by intermediate and fast neutrons will be reduced, if the irradiations are carried out in the thermal column of the reactor, but in this position the intensity of the thermal flux is much lower.

Radiochemical Techniques and Measurement of Radioactivity

Some samples become quite 'hot' during an irradiation and consequently may require cautions handling in the early stages of an analysis. However, once the initial separations of the elements being determined have been made, the intensity of radioactivity handled is at the tracer level only.

The method of dissolving the samples are those normally used in analytical chemistry, except that it is advisable to add the inactive carrier (or carriers, if more than one element is being determined) at the earliest possible stage of the dissolution, and to ensure that chemical exchange between the activated trace element and the inactive carrier has taken place. The particular radiochemical separation used will depend on the nature

[14] R.C. PLUMB and J.E. LEWIS, *Nucleonics 13* (1955) No. 8, p. 42.
[15] M.J. CABELL and A.A. SMALES, *Analyst 82* (1957) 390.

of the sample, but methods such as ion-exchange, solvent extraction, distillation and precipitation are all widely used, and in this respect activation analysis uses the same techniques as in normal radiochemistry.[16] The final radiochemically purified precipitate must be suitably mounted and prepared for counting. Liquid counting methods may also be used if necessary.

Since the essence of the activation method is comparison of the sample and standard under identical counting conditions, the measurement of the activity is consequently straightforward. It is not possible here to go into detail concerning the various types of β- and γ-counting equipment that are used in activation analysis, but it should be noted that only simple and comparatively inexpensive equipment is all that is required. CORNISH and GEISOW[17] have given an account of the instrumentation capable of dealing with all types of β- and γ-counting and they also discuss the use of automatic counting equipment, which considerably simplifies the task of counting.

In addition to counting the sample and standard, it is necessary to verify the characteristic properties of the radionuclide being measured. Usually this involves measuring the half-life, maximum β-energies and γ-energies. These values for all the radioactive nuclides are tabulated by STROMINGER *et al.*,[18] who also give valuable information on decay schemes.

The radiochemical purity of the final precipitates are checked by a series of decay measurements, providing the half-life is not prohibitively long. In certain cases the activity may be due to a mixture of isotopes e.g. irradiated germanium would give, when measured on an end-window β-counter, 82 minute $^{75}Ge(\beta^-)$, 12 hour $^{77}Ge(\beta^-, \gamma)$ and 11·4 day $^{71}Ge(e^-)$, in addition to 40 hour $^{77}As(\beta^-)$, which is formed from the decay of ^{77}Ge. In this case simple comparison of the decay curve obtained from the sample with that obtained from the standard is sufficient to confirm radiochemical purity.

Absorption measurements with aluminium absorbers and subsequent graphical analysis will enable the maximum β^--energy to be determined. DUNCAN and THOMAS[19] have compared three β^--absorption methods of measurment, indicating the relative value of each. Again, the most suitable technique in activation analysis is the direct comparison of the absorption curves obtained on the samples with that from the standard. The use of the γ-spectrometer to record the spectra of γ-emitters is also an invaluable aid in confirming radiochemical purity.

γ-Scintillation Spectroscopy

A discussion of the instrumentation and application of γ-scintillation spectroscopy in neutron activation has been given by CONALLY and LEBŒUF,[20] and CROUTHAMEL.[21] An outline of γ-ray spectroscopy as used in trace analysis has also been given by KOCH.[22] It will only be possible to deal with this subject briefly, but it is a technique of increasing importance in neutron activation. It is usual to use a single thallium-activated sodium iodide crystal, in conjunction with a photo-multiplier tube, and its associated electronic equipment. A single-channel pulse height analyser is usually used, but greater sensitivity and a considerable saving in time can be obtained by using the more expensive multi-channel pulse analysers (or 'kicksorters'), now commercially available.

In γ-spectroscopy a particular radionuclide, if it emits γ-radiation, can be identified and measured by its characteristic photopeak. An example of the spectrum produced by 12 hour ^{77}Ge is shown in Figure 1. HEATH[23] has catalogued the γ-ray spectra of numerous radionuclides. SALMON[24] has also given a tabular summary of nuclear data relevant to neutron activation, together with experimentally determined γ-ray spectra of radionuclides produced by neutron absorption. The latter author also discusses the interpretation of a gamma spectrum, originating from the photoelectric absorption. Compton scattering and pair production effects.

The most impressive use of the γ-spectrometer has been in the determination of a number of elements, by direct measurement on the irradiated sample, without any chemical treatment. The main difficulty is in eliminating interference caused by the presence of other

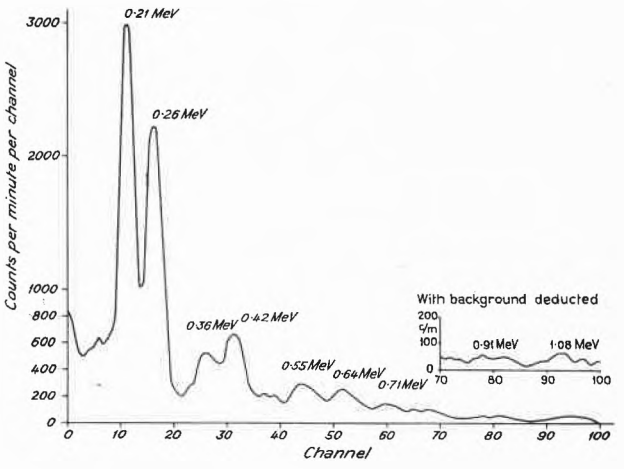

Fig. 1. Gamma-ray spectrum of 12 hour ^{77}Ge, using 3″ × 3″ NaI(Tl) crystal and 99-channel analyser

[16] P.C. STEVENSON and H.G. HICKS, in *Ann. Rev. Nuclear Sci. 3* (1953) 221 (J.G. BECKERLY, Editor).
[17] F.W. CORNISH and J.C.H. GEISOW, *Trans. Soc. Instr. Technol. 11* (1959) No. 2, p. 77.
[18] D. STROMINGER, J.M. HOLLANDER and G.T. SEABORG, *Rev. Mod. Physics 30* (1958) 585.
[19] J.F. DUNCAN and F.G. THOMAS, *Nucleonics 15* (1957) No. 10, p. 82.
[20] R.E. CONALLY and M.B. LEBŒUF, *Anal. Chem. 25* (1953) 1095.
[21] C.E. CROUTHAMEL, *Applied Gamma-Ray Spectrometry*, Pergamon, London 1960.
[22] H.W. KOCH, in *Trace Analysis* (J.H. YOE and H.J. KOCH jr., Editors), Wiley, New York 1957, p. 413.
[23] R.L. HEATH, *A.E.C. Report IDO-16408, U.S.A.E.C.* (1957).
[24] L. SALMON, *A.E.R.E. Report AERE C/R 2377 (1), U.K.A.E.A.* (1959).

γ-emitting nuclides, produced in the sample during the activation process. In measuring long-lived nuclides, this difficulty can be eliminated to some extent by allowing the shorter lived γ-emitters to decay.

Half-life measurements should be made by following the decay of particular photopeaks. It is necessary to exercise care, however, when two radionuclides emitting γ-photons of nearly equal energy are present in the same relative intensity and also have comparable half-lives. Unless these photopeaks can be resolved by the crystal, then further radiochemistry is required in their separation.

The main application of this new technique has been in the determination of trace impurities in pure metals, and particularly in semi-conductor materials, such as very pure silicon. Examples of this work will be given later.

It is seen that there are two approaches to activation analysis: the chemical separation method and the direct spectrometric determination with little or no chemical pretreatment. Which method is chosen will depend on the nature of the sample being analysed, and the instrumentation available. Generally speaking the greater sensitivity is obtained using the chemical separation method, but it is, of course, more time consuming. Usually, a judicious combination of the two methods produces the best results, since γ-spectrometry often eliminates the need for the thoroughgoing radiochemical purification that total β- or total γ-counting demands.

Sensitivity

As a method of analysis for trace elements, neutron activation has a high sensitivity. The practical limits of detection for a large number of elements are the most favourable of all existing methods of trace analysis. The sensitivity of the method has been discussed by MEINKE,[25] and JENKINS and SMALES.[4] Table I, which shows the estimated sensitivity for a number of elements, has been adapted from the latter reference.

Table I: Estimated sensitivities for some selected elements, irradiated in a flux of 10^{12} neutrons/cm^2/second

Element	Activated Form	Half-life	Sensitivity in grams
Pb	^{209}Pb	3·3 hr.	5×10^{-6}
Fe	^{59}Fe	45 days	1×10^{-7}
Bi	^{210}Bi	5·0 days	5×10^{-8}
Ni	^{65}Ni	2·6 hr.	1×10^{-8}
Zn	^{69}Zn	52 min.	5×10^{-9}
Hg	^{203}Hg	48 days	1×10^{-9}
Co	^{60}Co	5·2 y.	5×10^{-10}
Cu	^{64}Cu	12·8 hr.	1×10^{-10}
As	^{78}As	26·8 hr.	5×10^{-11}
Mn	^{56}Mn	2·6 hr.	1×10^{-11}
Au	^{198}Au	2·7 days	5×10^{-12}
Dy	^{165}Dy	2·3 hr.	1×10^{-12}

[25] W. W. MEINKE, in *Trace Analysis* (J. H. YOE and H. J. KOCH, Editors), Wiley, New York 1957, p. 619.

From equation (4), using the published values for cross sections, it is possible to calculate the radioactivity induced in an element for any time of irradiation. A practical definition of sensitivity is taken as being the weight of an element, which on irradiation in a flux of 10^{12} neutrons/cm^2/second, to saturation or for one month (whichever is the shorter), followed by decay for two hours, will give a minimum counting rate of double the background on the most suitable counting instrument for the measurement of the induced activity. Allowing for the different counting efficiencies, this means in practice, 100 disintegrations/minute for β-emitters above 0·2 MeV, 1000 disintegrations/minute for β-particles of lower energy and for γ-emitters. Table I presents the absolute weights for some selected elements calculated on this basis.

Nuclear Limitations

The problems arising from self-shielding during the irradiation have been considered above. A further limitation which must be considered is that due to nuclear reactions, other than the predominant (n,γ) reaction, caused not only by thermal neutrons, but by fast neutrons and γ-radiation. This means, in practice, the possibility that the radionuclide which is being used to determine a particular element present in the sample, may in fact be formed by a nuclear process on a totally different element. The determination of arsenic in germanium, first reported by SMALES and PATE,[26] will be used as an illustration.

When arsenic is irradiated, it undergoes the reaction $^{75}\mathrm{As}(n,\gamma)^{76}\mathrm{As}$. It is possible for ^{76}As to be formed by several other reactions, starting with elements *other than arsenic*, thus:

(1) $^{76}_{34}\mathrm{Se} + {}^{1}_{0}n \rightarrow {}^{76}_{33}\mathrm{As} + {}^{1}_{1}\mathrm{H}$ [(n,p) reaction]

(2) $^{79}_{35}\mathrm{Br} + {}^{1}_{0}n \rightarrow {}^{76}_{33}\mathrm{As} + {}^{4}_{2}\mathrm{He}$ [(n,α) reaction]

(3) (a) $^{74}_{32}\mathrm{Ge} + {}^{1}_{0}n \rightarrow {}^{75}_{32}\mathrm{Ge} \rightarrow {}^{75}_{33}\mathrm{As} + \beta^-$ $T = 82$ min.

(b) $^{75}_{33}\mathrm{As} + {}^{1}_{0}n \rightarrow {}^{76}_{33}\mathrm{As}$ [(n,γ) followed by β-decay and (n,γ)]

(4) (a) $^{76}_{34}\mathrm{Se} + \gamma \rightarrow {}^{75}_{33}\mathrm{As} + {}^{1}_{1}\mathrm{H}$

(b) $^{75}_{33}\mathrm{As} + {}^{1}_{0}n \rightarrow {}^{76}_{33}\mathrm{As}$ [(γ,p) followed by (n,γ)]

(5) $^{77}_{34}\mathrm{Se} + \gamma \rightarrow {}^{76}_{33}\mathrm{As} + {}^{1}_{1}\mathrm{H}$ [(γ,p) reaction]

In the determination of arsenic in germanium, SMALES and PATE[26] showed that the production of 'spurious' ^{76}As is dependent both on the time of irradiation and the square of the neutron flux. By choosing the optimum time of irradiation, the 'spurious' arsenic is kept sufficiently low so that the arsenic can still be determined at the 0·01 p.p.m. level.

It will be observed that these interfering reactions arise from the presence of elements differing by one or two units of atomic number from the element to be

[26] A. A. SMALES and B. D. PATE, *Anal. Chem. 24* (1952) 717.

determined. In general, because of the low values for the cross sections of (n,p), (n,α) and (γ,p) reactions, these limitations only become apparent when trace elements are being determined in the presence of a very large excess of the adjacent elements. The use of the thermal column eliminates the (n,p) and (n,α) reactions, which are normally due to the fast neutron component of the reactor flux, but with loss of sensitivity.

Another type of complicating nuclear process can best be discussed by considering the determination of cobalt in steels containing large amounts of nickel.[27] The cobalt is measured by utilising the reaction $^{59}Co(n,\gamma)^{60}Co$, and any spurious 5·2 y. ^{60}Co produced by $^{60}Ni(n,p)^{60}Co$ is not serious. However, the cross section for the reaction $^{58}Ni(n,p)^{58}Co$, forming 27 day ^{58}Co is comparatively large, and since ^{58}Ni is present to the extent of 68% in naturally occurring nickel, ^{58}Co will be formed in addition to ^{60}Co.

If the final counting is made without energy discrimination (by using an end-window G.M. counter), then the 0·47 MeV β^+'s of ^{58}Co will be counted with the 0·31MeV β^-'s of ^{60}Co, and a spuriously high cobalt content will be obtained. For steels, in which the ratios of Ni/Co are often as high as 100, the error could be serious.

Since these isotopes, ^{60}Co and ^{58}Co, cannot be separated chemically, the final counting must be in a way which will differentiate between these two contributions. Thus, the γ-spectrometer could be used to distinguish between the 1·17 and 1·33 MeV γ-photons of ^{60}Co and the 0·51 and 0·81 MeV γ-photons of ^{58}Co. Or counting methods involving absorption measurements would distinguish the different energy β-particles.

Precision and Accuracy

Many methods of trace analysis possess high sensitivity, but 'blank' contributions often reduce their precision. Activation does not suffer from this disadvantage, and SEYFANG[28] has demonstrated that high precision can be achieved in activation analysis, in his work on the determination of ^{235}U in pure U_3O_8, of natural isotopic compositon. The ^{235}U content was determined with a coefficient of variation of only $\pm 0{\cdot}53\%$, of which the statistical errors in the counting rates accounted for $\pm 0{\cdot}44\%$. It is clear that activation analysis should give a coefficient of variation of no worse than 10% for a single determination, at the levels for the different elements listed in Table I.

The absolute accuracy of the activation method is best shown by analysing samples whose *trace* element content is accurately known. Such samples are, however, extremely difficult to obtain but where work has been carried out in this way the results obtained have been satisfactory. The results reported by SMALES, MAPPER and WOOD[27] on the determination of nickel, copper and cobalt in British Chemical Standard Steels confirm the accuracy of the activation method, and indeed the activation method for cobalt is now used as a referee method for testing the accuracy of conventional methods.[29]

Since the accuracy of activation analysis depends ultimately, as in all other comparative methods of analysis, on the validity of the standards, these must be prepared with the utmost care. The possibility of errors, such as self-shielding and conflicting nuclear reactions, have been mentioned earlier. Provided these errors are eliminated and no losses of trace element occur during the disolution, then the accuracy of the activation method is high.

Applications of Neutron Activation

It is impossible to cover all the numerous fields in which activation analysis has proved of value. The large number of papers published each year indicate the increasing application of the activation method in all branches of chemistry. The following is merely to indicate briefly some of the more important uses to which activation has been put.

A survey of neutron activation in analytical chemistry has been given by LEDDICOTTE *et al.*,[30] in which they discuss the work of the Oak Ridge National Laboratory, U.S.A., in this field. They have determined 70 elements in many different sample materials, over the last six years. JARVIS and MACKINTOSH[31] have discussed activation analyses of interest to atomic energy programmes as carried out in Canada. YAKOVLEV *et al.*[32] have reported on the Russian work in this field, describing the determination of trace impurities in pure materials such as silica, germanium, bismuth, antimony, silver, etc. ALBERT[33] has described in detail a chemical separation scheme for many elements in high purity materials such as aluminium.

Semi-conductor materials such as silicon and germanium, have attracted much attention because of their importance in the manufacture of transistors. Neutron activation has been successfully applied by numerous workers[26, 34, 35, 36, 37] in investigating the trace element content of these materials. Silicon is particularly suitable for direct spectrometric examination, since the half-life of ^{31}Si is only 2·6 hours. To achieve the lowest sensiti-

[27] A.A. SMALES, D. MAPPER and A.J. WOOD, *Analyst 82* (1957) 75.
[28] A.P. SEYFANG, *Analyst 80* (1955) 74.
[29] B.I.S.R.A. Report, *J. Iron Steel Inst. 191* (1959) 236.
[30] G.W. LEDDICOTTE *et al.*, *Proceedings of the Second U.N. International Conference on Peaceful Uses of Atomic Energy 28* (1958) 478.
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vities, however, chemical separations are required, and it is usual to employ a combination of radiochemical separations and γ-spectrometry.

Table II: The arsenic, copper and antimony contents of very pure silicon samples

Sample	As p.p.m.	Cu p.p.m.	Sb p.p.m.
H	0·005 0·005 0·002	0·001 0·003	0·006 0·002 0·006
I	0·004 0·003 0·002 0·002	0·003 0·003	0·002 0·002 0·001 0·009
J	0·004 0·002 0·004 0·003	0·009 0·009 0·006 0·009	0·003 0·001 0·001 0·001

The arsenic, copper and antimony contents of some very pure silicon samples, obtained by SMALES *et al.*,[36] are shown in Table II. These elements were separated radiochemically and β-counted, whereas the results for tantalum, zinc, and copper, shown in Table III, were obtained by direct γ-spectrometric determination, using either single or multi-channel kicksorters.

Table III: The tantalum, zinc and copper contents of three silicon samples by direct determination on the γ-spectrometer

Sample	Ta p.p.m.	Zn p.p.m.	Cu p.p.m.
D	–	106	3·1
E	28	–	–
J	–	3·0	*very low*

LOVERIDGE and SMALES[7] have reviewed the applications of activation analysis in biochemistry. An example of some biological work is the determination of arsenic in hair, tissue, blood, etc. by SMALES and PATE.[38] STONE and REIFFEL[39] have determined sodium, potassium and phosphorus in milligram samples of human muscles.

An interesting example of the use that can be made of secondary reactions is provided by the work of OSMOND and SMALES[40] in the determination of oxygen in beryllium. The metal powder is mixed with pure lithium fluoride and irradiated in the reactor, when the following reactions occur:

(a) $^{6}Li\,(n,\alpha)\,^{3}H$,
(b) $^{16}O\,(^{3}H,n)\,^{18}F$.

The secondary tritons are used to form 1·87 hour ^{18}F from the oxygen present in the metal. The fluorine is chemically separated as lead chlorofluoride, and the 0·65 MeV positrons are counted. A further development in this determination is that reported by COLEMAN and PERKIN,[41] in which the beryllium metal was irradiated with 14·5 MeV neutrons and they measured the 7·4 second ^{16}N activity produced in the reaction $^{16}O\,(n,p)\,^{16}N$. The fast neutrons were produced by bombarding a tritiated zirconium target with 500 KeV deuterons, and fluxes of 10^{10} neutrons/second were obtained. Oxygen contents in the range 0·01 to 2·0% were measured.

GEBAUHR and MARTIN[42] have determined trace contaminants in pure phosphorus by activation and LELIAERT, HOSTE and EECKHAUT[43] have reported on activation analysis using an internal standard.

Activation methods are being extensively used in geochemistry, and references[9, 10] should be consulted for greater detail of this research. The earliest example of activation work to geochemical problems, is that of BROWN and GOLDBERG[44] in 1949, who determined the gallium and palladium content of iron meteorites. HUMMEL and SMALES[45] have used both isotope dilution and activation methods to determine the concentration of strontium in North Atlantic sea-water.

Important recent work on trace elements in meteoritic material is that reported by EHMANN and HUIZENGA[46] on the determination of bismuth, thallium and mercury in stone meteorites, and that by REED *et al.*[47] on determining bismuth, lead and thallium in stone meteorites. The lead was determined by utilising the $^{204}Pb\,(n,2n)\,^{203}Pb$ reaction, brought about by the fast neutron flux in an enriched fuel rod of the Argonne Heavy Water Pile, CP-5.

SMALES *et al.*[48] have determined the trace elements, copper, arsenic, antimony, germanium and chromium in iron meteorites, using chemical separations and γ-spectrometry. SMALES, MAPPER and WOOD[27] have also determined copper, nickel, and cobalt in rocks, meteorites and marine sediments, and on the basis of these results were able to refute the suggestion that the high nickel content of cores taken from deep-sea sediments, was due to a meteoritic origin.[49]

[38] A. A. SMALES and B. D. PATE, *Analyst 77* (1952) 196.
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[47] G. W. REED, K. KIGOSHI and A. TURKEVICH, *Proceedings of the Second U. N. International Conference on Peaceful Uses of Atomic Energy 28* (1958) 486.
[48] A. A. SMALES, D. MAPPER, J. W. MORGAN, R. K. WEBSTER and A. J. WOOD, *Proceedings of the Second U. N. International Conference on Peaceful Uses of Atomic Energy 2* (1958) 242.
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A further extension of this work has been reported by SMALES, MAPPER and WOOD[50] in the investigation of the possible 'cosmic origin' of black magnetic spherules obtained from deep sea-cores, and from other terrestrial sources. The extremely sensitive activation method enabled a few micrograms only of these spherules to be analysed for their nickel, copper and cobalt content, and a clear distinction could thus be drawn between spherules closely similar in chemical composition to iron meteorites and those in which no such similarity existed. As little as 0·03 μg of nickel, 0·0006 μg of copper and 0·01 μg of cobalt were determined in some of the spherule samples.

Conclusions

The present review has been devoted to neutron activation, as carried out in nuclear reactors, but it should be remembered that other radioactivation methods, utilising protons, deuterons, high energy γ-photons, and high energy neutrons, can often be used for those elements, for which ordinary activation is unsuitable. ATKINS and SMALES[8] review this aspect of activation analysis and a recent paper by GILL[51] deals with the proton activation analysis of microgram amounts of boron in silicon.

The limitations, as well as the advantages, of activation analysis have been dealt with, but it should be quite clear that activation analysis is an outstanding addition to modern methods of trace element analysis. Its chief advantages are very high sensitivity, freedom from reagent 'blank' difficulties, high specificity, and comparatively simple radiochemical operations not requiring quantitative separations. It has already played an important part in many branches of chemistry and with the greater availability of nuclear reactors and the extension of facilities for their experimental use, the applications of the activation method will clearly increase.

[50] A. A. SMALES, D. MAPPER and A. J. WOOD, *Geochim. Cosmochim. Acta 13* (1958) 123.

[51] R. A. GILL, *A.E.R.E. Report, AERE C/R 2758, U.K.A.E.A.* (1958).