RADIOACTIVATION ANALYSIS IN A NUCLEAR REACTOR

G. B. COOK

Isotope and Research Division, A.E.R.E., Harwell, U.K.

L'analyse par radioactivation est une méthode très efficace qui permet de déterminer les quantités de nombreux éléments présents à l'état de traces sans que, généralement, le gros de l'échantillon perturbe gravement les opérations. La sensibilité, qui est grande pour de nombreux éléments, dépend de ce que, avec les flux de neutrons et les détecteurs dont on dispose, il est possible d'induire dans un microgramme, et même dans une quantité moindre d'un grand nombre d'éléments, des quantités de radioisotopes faciles à déterminer. Les facteurs qui influent sur la sensibilité, dans l'équation fondamentale de l'activation sont: le flux de neutrons, la section efficace d'activation des neutrons lents et, dans une moindre mesure, la période du radioisotope produit. Il n'est cependant pas possible de faire des analyses exactes en recourant à l'equation fondamentale pour le calcul des résultats, parce qu'on ne connaît pas avec une précision suffisante la valeur numérique des différents facteurs. Pour surmonter cette difficulté, un poids connu de l'élément recherché (désigné ci-après par T, pour abréger) est irradié avec l'échantillon, ce qui permet d'établir un rapport entre le taux de désintégration et le poids de T, et d'appliquer ce rapport au taux de désintégration de T constaté dans l'échantillon.

Après activation, on peut recourir à deux méthodes d'analyse différentes. Si les principaux éléments composant l'échantillon possèdent des radioisotopes à période courte (par exemple, Al ou Si, *etc.*), on peut les laisser se désintégrer de manière à pouvoir examiner les traces des radioisotopes à longue période que présentent les impuretés, sans perturbations dues à des quantités importantes d'autres isotopes. En pareil cas, on pourra, à l'aide d'un spectromètre à scintillation, mesurer une émission éventuelle de rayons gamma, sans avoir à détruire l'échantillon. Toutefois, de tels cas sont exceptionnels; le plus souvent, le traitement chimique s'impose. Les quantités d'oligo-éléments sont trop faibles pour permettre une simple manipulation chimique; c'est pourquoi on ajoute, après dissolution de l'échantillon, un poids connu de T inactif (généralement de 10 à 50 mg) comme entraîneur. Il faut que l'entraîneur et la trace soient ramenés à un même état chimique (s'il existe plusieurs possibilités); on sépare et on épure T de manière à le rendre chimiquement et radiochimiquement pur. Il n'est pas nécessaire que le processus de séparation soit quantitatif, puisqu'on peut déterminer le rendement chimique. Enfin, on détermine la radioactivité de T par un moyen approprié et on la compare à celle d'un poids connu du produit type.

On peut apercevoir, dans cette méthode, plusieurs sources d'erreurs. Une des plus importantes est celle qui résulte de l'absorption des neutrons. Si l'échantillon ou l'étalon contient des quantités appréciables d'un élément à grande section efficace de capture de neutrons, le flux de neutrons au centre peut différer sensiblement de ce qu'il est à la surface, de sorte que les conditions moyennes auxquelles l'échantillon et l'étalon sont exposés risquent de ne pas être les mêmes, ce qui entraîne des erreurs. D'autre part, la plupart des irradiations se produisent dans des réacteurs où il existe un flux appréciable de neutrons rapides (énergie supérieure à 1 MeV). Ceux-ci peuvent entrer en réaction avec les principaux éléments de l'échantillon (surtout par des réactions (n,p) et (n,α)) et constituer, dans certains cas, le même produit radioactif que celui qui résulte de l'action des neutrons lents sur une trace d'impureté stable Si donc l'élément recherché a un nombre atomique qui est inférieur de 1 ou 2 à celui de l'un quelconque des principaux constituants, des erreurs peuvent se produire du fait qu'il y aura une apparente impureté à l'état de trace, provoquée par les neutrons rapides.

En plus de sa haute sensibilité, la méthode par radioactivation présente un certain nombre d'autres avantages, dont un des plus importants est qu'il n'est nécessaire de faire de correction d'après témoin. L'auteur signale d'autres avantages et inconvénients.

GENERAL PRINCIPLES

As is well known, the equation relating the radioactivity induced in an isotopic species subjected to a constant flux of neutrons (f) with the number of atoms of that species in the target is

$$A_X = f\sigma_a \mathcal{N}_X (1 - e^{-\lambda t}) \tag{1}$$

where $\mathcal{N}_X$ is the number of target atoms of type X with an activation cross-section for the bombarding particles of σ_a, A_X the disintegration rate of the radioisotope produced from X as a result of the bombardment, λ its disintegration constant and t the time of bombardment. As $\mathcal{N}_X$ is related to mass by Avogadro's number and the atomic weight, the disintegration rate may be related to mass, and hence the possibility of analytical use. If some typical figures are substituted in the equation above, one of the great advantages of radioactivation as a method of analysis, its high sensitivity, becomes obvious. Let us take the case of sodium irradiated in a reactor with a flux of thermal neutrons of 10^{12} cm^{-2} sec^{-1}, a value that is readily available today. The activation cross-section is 0.54×10^{-24} cm^{-2}, and we will assume that the detector of radiation has an overall efficiency of 10 per cent. Assuming 1 count per second detected to be significant, then $10 = 10^{12} \times 0.54 \times 10^{-24} \times \mathcal{N}(1 - e^{-\lambda t})$. The radioisotope of sodium produced, ^{24}Na, has a half-life of 15 h so that for an irradiation time of 3 days, the term $(1 - e^{-\lambda t})$ or $(1 - e^{-0.693 t/t_{\frac{1}{2}}})$ equals $(1 - e^{-3.3})$ or $(1 - 0.036)$ which we can call 1. Therefore $\mathcal{N} = 10^{13}/0.54$ or 1.85×10^{13} atoms or 7×10^{-10} g of sodium.

The equation shows that the sensitivity is directly proportional to both σ_a and the flux. Many isotopes have activation cross-sections appreciably higher than that of sodium and the sensitivity is correspondingly greater. In some cases, however, the cross-section is much lower and sensitivity may be reduced to that of earlier methods, although with a flux value of 10^{12} neutrons cm^{-2} sec^{-1}, this is not often the case. Even in such cases, improvement can be obtained by increasing the neutron flux, and values of 10^{13} and even 10^{14} can be obtained, although not readily.

The half-life of the radioisotope produced enters into the sensitivity in two ways. Firstly, it is included in the term $(1 - e^{-\lambda t})$. If the half-life is short compared with the irradiation time, this factor tends to 1, but the length of irradiation has practical limits (irradiations longer than 1 month become inconvenient), so that if the half-life is long compared with the irradiation time, $(1 - e^{-\lambda t})$ is appreciably less than 1. For example, it has the value of only 0.01 for ^{60}Co ($t_{\frac{1}{2}} = 5.2$ years) for a month's bombardment. After irradiation, the manipulations required before making a measurement of the radioactivity must not take so long that an appreciable fraction of the nuclide decays. Thus if a time corresponding to three half-lives is required, a loss of sensitivity by a factor of eight occurs. Since some procedures are quite time-consuming this can be a serious limitation for radioisotopes with half-lives of about 30 min or less, but in certain cases where manipulation is a minimum, elements with isotopes of half-lives less than 1 min have been analysed.

EXPERIMENTAL METHODS

Whilst, theoretically, the amount of an element can be determined from equation (1) above, the experimental uncertainties in the values are so great that a much simpler and more accurate comparative method is always used. The sample is irradiated with a " standard ", a known weight of the element sought. The two, usually in the same container, are thus subjected to the same irradiation conditions. From the disintegration rate per unit weight of element from the standard, the determined disintegration rate of the element sought from the sample may be converted to weight by simple proportions.

Treatment of the sample before irradiation is relatively simple, but great care, of course, must be taken to avoid accidental contamination, as with any method of trace analysis. Samples are often sealed in polythene containers for short irradiations (up to a few days) or in silica for longer times.

Non-destructive analysis

After irradiation, all elements of the sample are radioactive. The half-lives of the various activities produced will, of course, depend on the composition, but in certain cases the half-life of the main bulk of the sample is much shorter than those of some of the trace impurities. After a suitable decay period, therefore, only the trace elements remain active. This happens for instance in the trace analysis of super-pure aluminium ($t_{\frac{1}{2}} = 2\cdot3$ min) and silicon ($t_{\frac{1}{2}} = 2\cdot6$ h) which are industrially important. Advantage is taken of this fact to carry out a rapid, non-destructive analysis of the samples, since the trace impurities can now be measured directly[1–4]. Some means of discriminating between the various activities must be available since several are usually involved. For β-particle emitters, this is possible by half-life and β-absorption curve resolution, but this tends to be cumbersome and time consuming. The most suitable technique is γ-ray analysis using the γ-ray scintillation spectrometer. With this instrument, the characteristic γ-energies (and their abundances) of a given nuclide can be recognized and quantitative estimates made of the amount of radiation detected either from the photoelectric peak height or its area on the pen-recorder tracing, using the standard to normalize the determined quantity to weight. However, since a γ-ray energy is not a unique identification of a nuclide, some further assurances of identity may be necessary. These can be provided by the detection of the other γ-rays known to be emitted by the nuclide, if its decay scheme is complex, and from half-life determinations.

When using the single-channel pulse analyser, the sensitivity of detection using the γ-scintillation spectrometer is less by a factor of at least 20 than that of methods involving determination of β-particles. Some gain in sensitivity is obtained by using a multichannel pulse analyser, particularly when applied to short-lived isotopes as these decay appreciably during the time of a scan by the single-channel instrument. The attractions of this approach to activation analysis are so obvious that further improvements both in reliability and price of instruments are to be expected.

17

In an attempt to overcome some of the difficulties mentioned above, Putman and Taylor[5] devised a method whereby the greater activity on the base material can be eliminated to reveal the γ-trace of the impurity. Two sodium iodide scintillation counters are used and their outputs are balanced and subtracted electronically from each other, so that when identical radioactive samples are viewed by both, the net output is nil. If now two samples, one differing from the other only by the presence of a trace impurity, are irradiated together and the γ-activity examined as above, the resultant record is that of the trace impurity. This was shown to be quite practical in an investigation of the amount of selenium retained by a glass, using the contaminated glass as one sample and the untreated glass as the other. Clearly, this method is somewhat restricted in application, but may be of use in special cases and is perhaps worthy of further investigation.

Method involving chemical separation

The majority of samples cannot be examined by γ-ray spectroscopy alone because of the residual radioactivity from the main bulk of the sample. In this case, a chemical separation is necessary. After irradiation, the sample is dissolved in a suitable medium and a small, known quantity (usually 10–50 mg) of the trace element in question is added to the solution to act as a " carrier " so that chemical manipulations, such as precipitation, not possible with the original 10^{-6} g or less, can be performed.

Steps must now be taken to ensure that the carrier and trace are brought to the same chemical state, if several exist, for obvious reasons. Then some predetermined chemical separation is performed which will yield the element sought in a chemically and radiochemically pure state. The separation need not be quantitative as correction for chemical losses can easily be made from the initial and final weight of carrier. The estimation of the chemical yield is usually made gravimetrically, although other means are not excluded. The β- and γ-activities of the sample are now determined by suitable means and the radiochemical purity of the specimen can be verified by half-life, β- and γ-energy determinations. If the activity of the standard is determined with the same apparatus, the many possible sources of error due to scattering of radiation are eliminated. A possible exception to this is the correction for self-absorption in the precipitate. This too can be avoided by ensuring that the sample and standard precipitate have the same weight, but care is needed if the β-energy is very low (*e.g.*, ^{35}S, ^{14}C), because small differences in weight may have appreciable effects. The sensitivity by β-particle determination for elements which can be analysed by radioactivation has been compiled and published by Smales and Jenkins[6].

In certain cases where a chemical procedure is required it is possible to shorten the analysis by using a simple separation which removes the main radioactive component from the trace activity. The determination of the amount of trace activity is now carried out by γ-spectroscopy where resolution of the γ-components of the mixture acts as a further stage of separation. This can appreciably shorten the analysis as chemical procedures are usually multistage processes. We have found this very useful for biological samples where sodium (as sodium-24) is nearly always present.

SOURCES OF ERROR

As in all methods of analysis, certain sources of error, other than faults of commission, must be recognized.

Secondary nuclear effects

In the reactor, radioactivation analysis depends on the fact that an element, T, captures a neutron to form the nuclide (T + 1), from the disintegration rate of which the mass of T can be determined. If (T + 1) can be formed by means other than this reaction, errors will be introduced. Production of (T + 1) is possible in several ways. Firstly, if (T + 1) is a fission product of uranium or other fissile material, traces of these elements will introduce (T + 1) in an amount unrelated to the mass of T present. Secondly, some isotopes capture slow neutrons to yield a radioactive isotope which decays not to a stable species, but to another radioactive one. If this should be (T + 1), analysis is impossible, and even if it is another isotope of T, the amount may be sufficient to interfere with the measurement of the small amount of (T + 1). Thirdly, all reactors have a flux of fast neutrons which are sufficiently energetic to cause nuclear reactions involving the emission of a charged particle, so that a change of element is involved. Thus, in the B.E.P.O. reactor at Harwell, copper-64 is produced by the (n,p) reaction on pure zinc, in an amount equivalent to that which would be produced from 700 parts per million of natural copper in the zinc[7]. Similarly, (n,α) reactions occur, though usually with lower yield than for (n,p) reactions. For instance, the ^{27}Al (n,α) ^{24}Na reaction occurs to an extent equivalent to 80 parts/ million of natural sodium[8]. On the other hand, there was no interference from the ^{109}Ag (n,p) ^{109}Pd reaction in the analysis of palladium in silver[1]. In determining trace elements which are one or two atomic numbers less that any major component of the sample (*i.e.*, equivalent to the (n,p) and (n,α) reactions respectively), the possibility of an error from this cause must be considered although it may be negligible. Since the ratio of fast to slow neutrons varies with the type of reactor and with the irradiation position in the reactor, each case must be treated on its own merits. Some information does exist about the cross-sections of such reactions with pile neutrons but it is by no means complete or consistent[7, 9].

A less common effect is the production of the trace impurity by successive neutron capture. This was noted some time ago by Smales *et al.*[10] in the analysis of arsenic in germanium transistor material. Natural arsenic (^{75}As) is determined by the production of ^{76}As, but at the same time stable germanium-74 produces ^{75}Ge which decays by β-particle emission to form ^{75}As which in turn is another route to the formation of the required ^{76}As. The order of magnitude of these effects is an error of $+0.08$ parts/million of arsenic for a 75 h irradiation at 2×10^{12} neutrons cm^{-2} sec^{-1} but only $+0.0001$ parts/million for 10 h at 2×10^{11} neutrons cm^{-2} sec^{-1}. However, as reactors of high flux (10^{13} neutrons cm^{-2} sec^{-1} and greater) are becoming available, greater attention must be directed to this possibility, as the effects vary as the square of the flux.

Another factor which may be appreciable, but probably only occasionally, even in high flux reactors, is the destruction of the required product of

neutron capture by a further event. Thus natural gold-197 produces gold-198, which has a half-life of 2·7 days, but a slow neutron capture cross-section of 19,000 barns, and gold-199, which is also radioactive, can be detected in appreciable quantities in many gold-198 preparations. This effect is also dependent on the square of the neutron flux, the time of irradiation and the capture cross-section of the radioactive isotope, which is known in only a few cases.

The effects noted above can usually be recognized and in some cases eliminated. If the element sought is known to be a fission product, the presence of the other fission products can be used to indicate the presence of uranium, if this itself is not recognized. Tables of radioisotopes will indicate whether isotopes of the trace element can be formed from components of the sample, provided the composition is known. This will also indicate whether formation by (n,p) or (n,α) reactions is a possibility. Should this be the case, irradiation in a purely slow neutron flux is indicated, although this means a severe loss of sensitivity, because pure slow neutron fluxes comparable with the heteroenergetic fluxes within the core of a reactor are not available. It is also possible to correct for such effects by irradiation of the samples and standards in neutron fluxes with different ratios of fast to slow neutrons, and solving two simultaneous equations. This inevitably introduces a greater error than normal, since two determinations are involved, and will fail experimentally if the amount of T + 1 formed from T is much smaller than that from other sources. The remaining two effects, depending as they do on the square of the flux, will be recognized from results obtained from irradiations at different fluxes.

Neutron shielding effects

A basic condition of the radioactivation method is that the sample and standard are irradiated under identical conditions. If, however, the sample has components of high neutron capture cross-section, the neutron flux at the centre of the sample will be significantly less than that at the surface, and the average flux to which the sample is subjected is different from that of the non-absorbing standard. This difficulty may be minimized by using as small a sample as possible, but is best overcome by constructing a correction curve from samples of known composition. In the worst case another analytical technique must be sought. If the standard has a high cross-section, the difficulty is overcome by using a weight so small that neutron self-shielding is insignificant. This is most easily done by irradiating a very dilute solution of the standard.

This we prefer to dilution with solid as pure water is more readily available than a pure solid. Various formulae have been derived to calculate the neutron self-shielding cross-sections[1, 11], but these are dependent on the shape of the sample and are usually based on the thermal neutron absorption cross-section. Pile neutrons are, however, not truly thermal in energy and many isotopes have pronounced resonance absorption effects just above the thermal energy region. We find it best to use the formula only as a guide to the order of magnitude of the effect and to determine experimentally the maximum concentration below which such effects can be neglected. Plumb and Lewis[12] have also pointed out that the differential

absorption of resonance neutrons can cause differences in the proportions of radionuclides from different isotopes of the same element in samples of different sizes.

FAST PARTICLE ACTIVATION ANALYSIS IN REACTORS

The majority of radioactivation analyses in the pile depend on the (slow neutron, gamma) reaction. Occasionally it is possible to use other reactions which occur in the pile. Thus, although sulphur can be analysed by the production of sulphur-35, the cross-section for the reaction is low, the half-life of ^{35}S is relatively long and the β-particles are of low energy ($E_{max} = 0\cdot167$ MeV). There is also interference from the chlorine (n,p) sulphur-35 reaction. On the other hand, the yield of phosphorus-32 by the ^{32}S (n,p) ^{32}P reaction is relatively high, and in fact the sensitivity is greater for the latter method. Experimentally, there is the added advantage that the energetic β-particles of ^{32}P are measured ($1\cdot7$ MeV). However, in this case, ^{32}P can also be produced by ^{31}P (n,γ) reaction so that the phosphorus content of the sample must be known. Alternatively, this can be determined by irradiation of samples and standards in two positions of differing flux ratios of fast to slow neutrons and solving two simultaneous equations. Another example is the analysis of nickel by the ^{58}Ni (n,p) ^{58}Co reaction, which has a relatively high cross-section, and in this case, we have the advantage that cobalt-58 cannot be produced by neutron capture in natural cobalt contamination.

Another interesting example was demonstrated by Osmond and Smales[13]. Lithium-6 on irradiation with slow neutrons disintegrates to produce energetic alpha and tritium particles by the reaction ^{6}Li (n, ^{3}H) ^{4}He. The triton has an energy of $1\cdot78$ MeV, sufficient to cause further nuclear reactions. In this case, it was used to estimate oxygen by the amount of fluorine-18 ($t_{\frac{1}{2}} = 112$ min) produced by the ^{16}O (^{3}H, n) ^{18}F reaction. The method consists of irradiating an intimate mixture of a suitable lithium compound (LiF was used) with the finely divided sample, in this case beryllium metal containing a trace of oxide. A limiting sensitivity of 5×10^{-7} g of oxygen has been given, but several experimental difficulties exist. Thus the lithium compound must be free of oxygen to these limits, and the effects of grain size of the sample must be controllable, as the penetrating power of the recoil triton in matter is very small. In principle, the same reaction could be used to estimate lithium, although the direct estimation by the amount of tritium produced is more sensitive[6].

The cyclotron and betatron have also been used as the activating source for radioactivation analysis. The experimental difficulties are much greater than with a reactor and these problems will not be discussed here.

ADVANTAGES OF THE METHOD

Although some emphasis has been placed on the errors arising in activation analysis, it should not be thought that these effects are serious in the majority of analyses. Perhaps the most important general interference is likely to arise from a high neutron absorption cross-section of the sample itself (such conditions in the standard are easily dealt with), but

it is fortunate that many of the common matrix materials, silicon, oxygen, carbon, hydrogen, aluminium and iron, have low total absorption cross-sections for neutrons of thermal and intermediate energies.

Activation analysis has the following advantages:

(1) For a wide variety of elements (some seventy elements have been investigated and a useful bibliography is available[14]) the sensitivity is high and is amenable to simple calculation (a comparison of the sensitivities of other methods of trace analysis with radioactivation has also been made[15]).

(2) The specificity is high, since a chemical process can be devised which is unique for the element in question, and the success of the operation can be checked by measurements of the half-life and β- and γ-ray energies of the radioisotope concerned.

(3) The method is free from reagent blank corrections, as only the constituents of the irradiated sample will be radioactive and only the radio-active content is determined.

(4) There is in general little interference from the matrix with the requirements for special standards.

(5) The chemical procedure need not be quantitative.

(6) The chemical manipulations are carried out with semi-micro amounts of carrier (e.g., 10–50 mg) rather than with micro- and submicrogram amounts.

On the debit side of the ledger we have the following facts:

(1) Few laboratories have suitable irradiation facilities within immediate reach of a reactor, a fact which restricts the use of the method when short-lived isotopes only are formed.

(2) Certain samples cannot be accepted as they might endanger the safety of the reactor, e.g., volatile organic liquids which might decompose under the action of the intense gamma and neutron bombardment, building up dangerous pressures in the sealed sample containers.

(3) Certain matrices become highly radioactive, emitting penetrating radiation, so that the facilities of a laboratory suitable for handling relatively high levels of radioactive materials are required.

It can be seen that the objections to the method are not very restrictive, and although it is unfortunate that several important elements such as oxygen, carbon, nitrogen, and fluorine cannot be analysed adequately, the application to other elements is a powerful addition to the analytical armoury.

References

[1] Y. V. Yakovlev, A. I. Kulak, V. A. Ryabukhin and R. S. Rytchkov. "The determination of trace impurities in pure materials by radioactivation analysis ", *Report of the Second United Nations Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1958, A/CONF/ 15/P/2023

[2] R. E. Connally. "Instrumental methods of gamma ray spectrometry ", *Anal. Chem.* **28**, 1847 (1956)

[3] P. Iredale. "An impurity analysis of aluminium by radioactivation and scintillation spectrometry ", *U.K. Atomic Energy Authority Report*, A.E.R.E. El/M.96, H.M.S.O., London, 1957

[4] L. Salmon. "Gamma-ray spectroscopy applied to radioactivation analysis. Part I. Introduction and nuclear data ", *A.E.R.E. C/R.* 2377 (1), H.M.S.O., London, 1959

[5] J. L. Futman and W. H. Taylor. "On the subtraction of gamma-ray spectra as a tool in radioactivation analysis ", *J. Appl. Radiation and Isotopes*, **1**, 315 (1957)

[6] E. N. Jenkins and A. A. Smales. "Radioactivation analysis ", *Quart. Rev. (London)* **X** (1), 83 (1956)

[7] C. E. Mellish, J. A. Payne and R. L. Otlet. "The production of threshold reactions in a graphite reactor ", *Radioisotopes in Scientific Research*, Vol. 1, p. 35, Pergamon Press, London, 1958
"Flux and cross-section measurements with fast fission neutrons in B.E.P.O. and D.I.D.O.", *U.K. Atomic Energy Authority Report*, A.E.R.E. I/R.2630, H.M.S.O., London, 1958

[8] L. Salmon. "The extent of the fast neutron effect on the determination of sodium in aluminium by activation in the Harwell pile ", *U.K. Atomic Energy Authority Report*, A.E.R.E. C/R.1324, 1954

[9] R. S. Rochlin. "Fission neutron cross-sections for threshold reactions ", *Nucleonics*, **17**, (1), 54 (1959)

[10] A. A. Smales and B. Pate. "The determination of submicrogram quantities of arsenic by radioactivation. Part I. General method and application to germanium dioxide ", *Anal. Chem.* **24**, 717 (1952)

[11] R. Keyes. "Estimation of self-absorption in neutron irradiated samples ", *U.S. Atomic Energy Comm. Report*, A.E.C.D. 3000, 1950

[12] R. Plumb and J. E. Lewis. "How to minimise errors in neutron activation analysis ", *Nucleonics*, **13**, (8), 42 (1955)

[13] R. G. Osmond and A. A. Smales. "The determination by radioactivation analysis of the oxygen content of powdered metals with particular reference to beryllium ", *Anal. Chim. Acta*, **10**, 117 (1954)

[14] D. Gibbons, B. A. Loveridge and R. J. Millett. "Radioactivation Analysis, a Bibliography ", *United Kingdom Atomic Energy Authority Report*, A.E.R.E. I/R.2208, 1957

[15] W. W. Meinke. "Trace element sensitivity; comparison of activation analysis with other methods ", *Science*, **121**, 177 (1955)

DISCUSSION

J. HOSTE (*Belgium*): Have you any experience in the use of γ-spectrometers to suppress or compensate for Compton effects, which obscure results where a mixture of gamma energies is involved?

G. B. COOK (*U.K.*): We have little experience of coincidence arrangements using the two-crystal systems of the Pierson type. I believe they are of little advantage in purely quantitative work. Single-crystal systems have proved adequate for our needs.

D. GIBBONS (*U.K.*): We consider that the extra time required to match up the responses of the anthracene and sodium iodide crystals used in the Compton-effect subtraction spectrometer of the Pierson type, and the increased statistical error involved, more than offset the advantages of the system compared with techniques using simple radiochemical separations in combination with single-channel spectrometry. The double-crystal system is excellent for qualitative work where it is necessary to identify, say, five gamma-emitting impurities, but their actual separation and quantitative measurement are best done by chemical processes.

We have also used coincidence spectrometry, not for the purpose of suppressing Compton effects, but for measuring radioisotopes emitting similar gamma energies. Although the technique is very useful for such purposes, its sensitivity is not great because its overall efficiency is the product of the efficiencies of the two detectors.

P. Leveque (*France*): In the quantitative determination of radioisotopes, using either single or multi-channel gamma spectrometers, was the quantity determined on the basis of peak heights or peak areas, and how were the highest-energy Compton effects compensated for?

What experimental set-up was used to avoid the many corrections needed in determining beta activity? In France, a filter-paper method of preparing the specimens and standard samples has overcome many difficulties; the same correction for self-absorption could be applied to both.

It has been found in France that the results over a series of determinations on a given material varied by more than the statistical counting error. I wonder whether, in using very small samples as suggested in the paper, there is not a considerable error, arising from non-homogeneity of the sample, which is superimposed on the statistical counting error, so that the results are less precise than expected.

G. B. Cook (*U.K.*): Determination methods using peak height and peak area have been compared, and the peak-height determination has been found to yield a higher overall variation. The peak-area determination method is therefore better.

The high-energy Compton effect is compensated for by the empirical method of extrapolating from before to after the Compton-effect peak.

The samples are usually mounted by means of a suspension or slurry of the precipitates in a suitable solvent. The suspension is poured onto an aluminium tray and the solvent is evaporated off. For many substances, this method produces a good uniform layer; an important exception is silver chloride. The coagulated precipitate normally used does not meet the needs of the radiochemist, and in connection with fission products analysis a modified technique has been developed to produce finely divided silver chloride which gives the uniform precipitate required for beta-particle analysis.

The filter-paper method has also been used in the United Kingdom and has been found to give a uniform area of precipitate.

I agree that the overall error in the determination of uranium by fission-products analysis is given as 0·5 per cent against an expected statistical error of 0·4 per cent. Clearly there are still a number of uncontrollable factors involved, and the remedy is to exercise careful attention to detail throughout the process. In addition to statistical randomness, it is necessary to take into account randomness on the part of the analyst, perhaps particularly when, as frequently happens, radioactivation analysis is performed by physicists, who are not necessarily fully conversant with the techniques of chemical analysis.

H. Seligman (*I.A.E.A.*): I believe that the errors mentioned in the paper often depend on the availability of fast neutrons, which varies from reactor to reactor and also from place to place within a given reactor.

Has any radioactivation analysis work been done with fast neutrons only, in order to obtain (n,α) and (n,p) reactions, particularly the latter? Very large fluxes would, of course, be needed, but such fluxes should now be available.

G. B. Cook (*U.K.*): In the graphite-moderated reactor, there is a rapid (exponential) fall of the fast/slow neutron ratio in the reflector to the edge of the biological shield. Thus it is possible to find irradiation positions where the fast-neutron flux is very low, but the slow flux is also so low that it is doubtful whether sufficient sensitivity could be secured. In the heavy-water-moderated reactor all irradiation positions are in the reflector. Fluxes of 5×10^{12} neutrons cm^{-2} sec^{-1} to less than 1×10^{12} neutrons cm^{-2} sec^{-1} are obtainable.

I have no special experience with very high fast-neutron fluxes, except with the flux in B.E.P.O., which, in any case, is not particularly high for the ^{32}S (n,p) ^{32}P technique.

A. H. W. Aten (*Netherlands*): The correction for the Compton continuum in gamma spectra is not an important point in radioactivation analysis applications, since the observed spectrum only has to be interpreted as the sum of the essentially known spectra of the various pure components. It is, however, very important in determining the energy and intensity of gamma spectral lines. A satisfactory technique has been developed by overall measurement of a series of long-lived standard nuclides (*e.g.*, ^{203}Hg, ^{137}Cs, ^{54}Mn, ^{65}Zn and ^{22}Na), from which the shape of substantially pure gamma lines may be obtained. Starting with the line of highest energy, each gamma-line is " peeled off " in turn by adjusting the shape of the photo-peak to the observed standard shape and subtracting the Compton contribution. The method permits as many as fifteen gamma lines in a single spectrum to be " peeled off " and is very accurate, provided that great attention is paid to the purity of the calibrated nuclides and also to the stability of the instruments.

Back-scatter peaks due to the different physical forms of specimens are avoided by ensuring that as many aspects as possible of the experimental arrangement are reproducible. The samples should be kept small and in the same position, and it is especially important that the electronic instruments employed should be reliable so that there are no changes of sensitivity during the measurements.

P. Leveque (*France*): In a recent publication of mine on the determination of uranium a correction has been made for the products of fast neutron fission of ^{238}U. Applying this method to the figures given in a United Kingdom paper on uranium determination, I have calculated that the fast-neutron flux in B.E.P.O. is about 12 per cent of the thermal flux.

G. B. Cook (*U.K.*): We have calculated the fast thermal flux ratio by determining the slow neutron flux using the $^{23}Na(n,\gamma)$ ^{24}Na reaction and the fast neutron flux using either the $^{32}S(n,p)$ ^{32}P or $^{58}Ni(n,p)$ ^{58}Co reactions. The fast thermal ratio was 17–20 per cent.

W. W. Meinke (*U.S.A.*): The point raised about the counting error being greater than the statistical error is at least partly explicable in terms of random behaviour of the electronic apparatus. Results begin to exceed the statistical deviation after samples have been irradiated for several hours.

Dr Cook has pointed out that many laboratories do not have ready access to neutron sources, which is an important disadvantage when the radio-nuclides to be determined have short half-lives. I should like to draw

attention to the fact that certain companies in the United States and the United Kingdom are developing neutron generators based on the reaction of deuterons of relatively low energy on tritium to give essentially mono-energetic neutrons of 14 MeV with a flux after thermalization of about 10^9 neutrons cm^{-2} sec^{-1}, which is sufficient to induce measurable activation of microgramme quantities of such elements as vanadium. The same reaction has been used for some years but on relatively large and costly Van de Graaf machines. New compact neutron generators will shortly be available at a price (about US$20,000) comparable with that of a good mass spectrometer and, of course, much lower than that of reactors. The targets are of tritium adsorbed on zirconium foil and sealed in generator tubes which have a life of several hundreds of hours, sufficing for many kinds of work though not for work involving irradiation for several weeks. A replacement tube will cost about US$500.

With regard to Dr Seligman's request for information about fast neutron activation, a paper by Turner in *Analytical Chemistry* describes the use of 14 MeV neutrons to induce (n,p) reactions in aluminium and silicon. A similar process applied to oxygen in water has also been described by Fall of Harwell.

G. W. REED (*U.S.A.*): Concerning the question by Dr Seligman on the application of fast neutrons in activation studies I should like to offer the following.

At the Argonne National Laboratory we have facilities in the CP-5 heavy-water reactor which permit

(1) irradiations with almost purely thermal neutrons inside the graphite moderator;

(2) irradiations at higher fluxes and with a high percentage of epi-thermal neutrons in thimbles adjacent to fuel rods; and

(3) irradiations inside a specially constructed fuel element where maximum fission spectrum (unmoderated) neutrons are available.

We have used this last facility to measure the amount of ^{204}Pb in meteorites *via* the reaction

$$^{204}Pb(n,2n)^{203}Pb \xrightarrow{\epsilon, \ e^-, \ \gamma} {}^{203}Tl$$
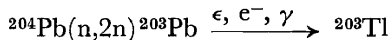
Since ^{208}Pb gives ^{209}Pb *via* (n,γ) we are thus able to measure the $^{208}Pb/^{204}Pb$ ratio.

The sensitivity is about 10^{-6} g/g. That is, enough activity is produced in 10^{-6} g of lead in this type of irradiation (the thermal flux is about 2×10^{13} neutrons cm^{-2} sec^{-1}) to be determined with a small overall counting error. The radiations are measured both *via* beta and scintillation counting. A monitor is always measured simultaneously so that a quantitative determination is made. The results obtained by both counting techniques agree quite well.

One critical aspect of the lead measurements lies in the timing. Exhaustive chemistry was necessary—and time consuming—since ^{209}Pb ($t_{\frac{1}{2}} = 3\cdot3$ h) can only be measured from its beta activity. ^{203}Pb decays by orbital electron capture, and photons, as well as conversion electrons, were measured. Samples counted were always less than $0\cdot8$ mg/cm^2 to

avoid the necessity for making self-absorption corrections. Some of the results are compared with mass spectrometrically measured ratios in *Tables 1* and *2*. The errors associated with the ratios are larger than our statistical errors, possibly because of systematic errors, inhomogeneity in samples, *etc.*

Table 1.   Lead in sulphide phase of iron meteorites
(Concentrations in g/10^8 g of sample)

Activation analysis	^{204}Pb	^{208}Pb	$^{208}Pb/^{204}Pb$
Canyon Diablo	$9 \cdot 2 \pm 0 \cdot 1$	267 ± 2	$28 \cdot 8 \pm 1 \cdot 0$
	$10 \cdot 5 \pm 0 \cdot 2$	293 ± 3	$27 \cdot 6 \pm 1 \cdot 0$
Toluca	$10 \cdot 8 \pm 0 \cdot 2$	311 ± 6	$28 \cdot 8 \pm 3 \cdot 1$
			$28 \cdot 2 \pm 0 \cdot 7$
*Mass spectrometry**			
Canyon Diablo		1050	29·44
Henbury		292	29·54
			29·49

* Claire Patterson, "Age of meteorites and the earth", *Geochim. et Cosmochim. Acta*, **10**, 230 (1956).

Table 2.   Isotopic composition of lead in some
chondritic meteorites

Meteorite	$^{208}Pb/^{204}Pb$	Literature*
Nuevo Laredo	59 ± 8	67·97
Indarch	$26 \cdot 8 \pm 1 \cdot 2$	
Mighei	$31 \cdot 1 \pm 1 \cdot 2$	
Orguiel	$30 \cdot 3 \pm 1 \cdot 2$	
Average Troilite	$28 \cdot 2 \pm 0 \cdot 7$	29·49

* Claire Patterson, "Age of meteorites and the earth", *Geochim. et Cosmochim. Acta*, **10**, 230 (1956).

K. Ljunggren (*Sweden*):   In addition to the Pierson method of Compton-effect suppression mentioned by Dr Hoste, more sensitive spectrometry may be secured by the use of a fairly fast coincidence circuit with a resolving time of 10^{-8} to 10^{-7} sec for measuring cascaded gamma rays and also for determining positron emitters.

Has Dr Cook any figures on the ultimate accuracy of radioactivation analysis?

G. B. Cook (*U.K.*):   An error of ± 5 per cent is an accepted accuracy. This figure may be improved upon in very special circumstances, but that is not to be expected from an analysis technique which it is hoped to make into a routine service.

A. H. W. Aten (*Netherlands*):   Reference has been made to the measurement of the fast neutron flux in a reactor by the (n,p) reaction on sulphur ($^{32}S(n,p)^{32}P$).   In this connection it may be of some interest to know that the use of the (n,p) reaction on phosphorus-31 gives identical results.

27

However, the short half-life of ^{31}Si makes this reaction much more sensitive for short irradiations. The ratio of the cross-sections has been checked by irradiating samples of sulphur and phosphorus in different activation positions, and found to be quite constant throughout the reactor. Thus, the P–Si reaction could be substituted for the S–P reaction in all cases, and with advantage where short irradiations are concerned.

G. W. LEDDICOTTE (*U.S.A.*): The facilities available to the analytical chemist at Oak Ridge provide a total flux of the order of 10^{12} neutrons cm^{-2} sec^{-1} in the graphite reactor and 10^{14} to 10^{15} neutrons cm^{-2} sec^{-1} in the O.R. research reactor.

With regard to the fast (epi-cadmium and above) neutron flux, the two reactors provide fluxes of the order of 10^9 and 10^{12} neutrons cm^{-2} sec^{-1} respectively at an energy of 2·3 MeV, 5×10^8 and 1×10^{11} neutrons cm^{-2} sec^{-1} respectively at 6·8 MeV, and 10^8 and 10^{10} neutrons cm^{-2} sec^{-1} respectively at 8·3 MeV and above. These fluxes are used for the determination of nickel and titanium.

With regard to γ-spectrometry, Oak Ridge is using a crystal gamma discriminatory system with two crystals, not of different substances but both of sodium iodide of differing thickness. By permitting loss of high energies, the wafer crystal emphasizes the low energies. Used with multi-channel analysers, the system can be employed for the semi-quantitative analysis of various constructional materials and seems to be quite a promising technique.

I agree with Dr Cook that ± 5 per cent is generally acceptable as an indication of the accuracy of the method, but in many cases a larger error must be accepted.

PH. ALBERT (*France*): I wonder if there is an irradiation position in a reactor where the (n,α) reaction for the determination of sodium in aluminium does not occur. Using extremely pure " zone-melted " aluminium, we have observed in the El.2 reactor at Saclay that an apparent sodium content of 0·2 parts/million could be measured, and we wonder whether this value represented the extent of occurence of the (n,α) reaction, or the minimum concentration of sodium in " zone-melted " aluminium.

With regard to the determination of sulphur by the ^{32}S(n,p)^{32}P reaction, it has been stated that not only phosphorus but also chlorine could be a substantial source of error, as it, too, yielded phosphorus-32 (^{35}Cl(n,α)^{32}P).

In connection with the determination of elements with low effective cross-sections for neutrons, or excessively short half-lives, Gill at Harwell has determined boron in silicon by protons and Albert and Sue have determined carbon in iron and aluminium by deuterons. This indicates, I think, that the use of accelerators—not necessarily very powerful ones—by chemists is a promising line of work. It seems that oxygen, carbon and nitrogen might be determined with great sensitivity in this way.

The possible errors, referred to by Dr Leveque, due to heterogeneity of the samples may be avoided by using fairly large samples (about 1 g) and subsequently performing the analysis on aliquot parts.

F. GIRARDI (*Italy*): The use of plastics such as nylon and polythene for the capsules containing the samples has given rise to much difficulty at

Chalk River, especially with sulphur and phosphorus determinations, because they strongly adsorb active material from the target. Nylon capsules have in some cases acquired an activity of more than 10,000 counts/min.

I agree with the statement that the presence of chlorine might interfere with sulphur determination using the $^{32}S(n,p)^{32}P$ reaction. The effective cross-section for the latter has been measured at Chalk River as 2·0 mb; thus the effective cross-section for the $^{35}Cl(n,\alpha)^{32}P$ reaction of 0·79–0·8 mb is relatively large.

G. B. Cook (*U.K.*): I have used polythene capsules for short irradiations in a reactor without particular difficulty, though I agree that their use is restricted. Quartz capsules are used for longer exposures.

I agree about the interference of chlorine with sulphur determinations which represents a further disadvantage of the $^{32}S(n,p)^{32}P$ reaction in addition to the ^{31}P interference mentioned in my paper.

D. Mapper (*U.K.*): May I refer Dr Albert to the paper by L. Salmon[*] entitled: " The extent of the fast neutron effect on the determination of sodium in aluminium by activation in the Harwell pile "?

Reverting to the merits of gamma-spectrometry, it is clear that during this conference the relative advantages of gamma-spectrometry, with and without radiochemical separation will be discussed extensively. We are particularly concerned with the determination of traces of many elements, whose gamma-emitting intensities are minute compared with the gross gamma-activity in the bulk of the sample. In such cases radiochemical separations *must* be performed. Even in the case of a simple determination like that of arsenic in very pure silicon, it has been shown[†] that the contributions to the measured ^{76}As photo-peak from ^{122}Sb and ^{64}Cu, due to the presence of antimony and copper, could introduce serious errors, even though the decay of the photo-peak is followed for some time, if the determination is made entirely without previous radiochemical separations.

In order to eliminate the Compton continuum, the Harwell group uses large crystals, which minimize the Compton effect and increase the photo-peak.

C. Garavelli (*Italy*): I have found that the error in peak-height determination is about 15 per cent, whereas in the case of peak-area determination it is 6–8 per cent. If the curve is obtained without a rate-meter by interpolation between the plots representing the number of counts detected on each channel, about half the overall variation is due to the uncertainty of interpolation.

D. Gibbons (*U.K.*): We have also found that simple peak-height measurements give an error of 10–15 per cent, scaler measurements give 7–10 per cent and peak-area measurements 5 per cent or even better, depending on the stability of the equipment used.

---

[*] *A.E.R.E. C/R.*1324 (1954).

[†] A. D. Smales, D. Mapper, A. J. Wood and L. Salmon. " The determination by radioactivation of trace quantities of arsenic, antimony and copper in pure silicon ", *A.E.R.E. C/R* 2254, (1957).

J. COLARD (*Belgium*): We have used activation analysis and gamma spectrometry for the measurement of small quantities of impurities of the order of parts per million, in liquids. Traces of vanadium and sodium in mineral oils in various stages of purification have been measured. Chemical manipulations on the samples were avoided, both before irradiation, so as not to introduce further impurities, and after irradiation in view of the short half-life of vanadium-52 (3·76 min). Gamma spectrometry has been used in order to avoid interference from other impurities.

We have found the limit of detection for vanadium to be 0·005 parts/million using a sample of 10 cm^3 which has been irradiated for 5 min at a flux of 2×10^{12} neutrons cm^{-2} sec^{-1}. The limits for sodium and manganese were found to be 0·05 parts/million and 0·007 parts/million respectively. The reproducibility at these limits is about 25 per cent and 5–10 per cent for higher concentrations.