RADIOACTIVATION ANALYSIS

By E. N. Jenkins, M.Sc., A.R.I.C.,
and A. A. Smales, B.Sc., F.R.I.C.
(Atomic Energy Research Establishment,
Harwell, nr. Didcot, Berks.)

Introduction

In radioactivation analysis the weight of the required element in a sample is determined by measuring the intensity of induced radioactivity, rather than by measuring, say, the optical density of a coloured solution, the weight of a precipitate, or the volume of reagent consumed during a titration. The intensity of induced radiation is directly proportional, other things being equal, to the weight of the required element and is, of course, independent of the state of chemical combination of the element. The assay of certain ores for uranium and of fertilisers for potassium are common industrial examples of quantitative chemical analysis by measurement of radioactivity. The α-, β-, and γ-radiation from ^{238}U and its decay products, and the β- and γ-radiation from ^{40}K (of 0·012% abundance in natural potassium), are examples of natural or spontaneous radioactivity: only twelve elements of atomic number 92 or less show any such appreciable spontaneous radioactivity in the naturally occurring mixture of isotopes. Most of the remaining elements can, however, be converted into artificially radioactive isotopes by appropriate nuclear bombardment or " activation ". The process of nuclear bombardment of a weighed sample, normally together with a standard, followed by measurement of the intensity of the induced radiation, constitutes radioactivation analysis. Normally the method includes the isolation and purification of the required artificially radioactive isotope or mixture of isotopes by specific chemical operations, often performed in the presence of milligram amounts of an inactive isotopic carrier added after the activation: in favourable cases this isolation is not required and the final measurement is made on the intact sample. In either case the mass of the required constituent, Y, in the sample is finally calculated by the simple equation:

Mass of Y in sample =

$$\text{Mass of Y in standard} \times \frac{\text{Radiation intensity from Y in sample}}{\text{Radiation intensity from Y in standard}}$$

Radioactivation analysis is applicable in principle to almost all the elements, though a few of them present great difficulty. In general, the distinctive features of the method are its extreme sensitivity, its freedom from contamination by reagents, the ease with which both the sample and the standard may be activated at the same time, and the possibility in certain cases of preserving the samples intact through the analysis.

Experimental methods

The methods and techniques involved in radioactivation analysis will be discussed with particular reference to a specific and important example, the determination of small quantities of arsenic in biological material.[1]

Sampling and Activation.—A feature of radioactivation is the minimum pretreatment received by the sample before activation. Chemical treatment, say, for concentration of the arsenic or for the removal of interfering elements, or for the oxidation of organic matter, is rarely necessary at this stage. The physical preparation of the sample consists only of weighing it into a suitable irradiation container such as a quartz or Polythene ampoule, which is then sealed. Refractory minerals may require preliminary crushing and grinding to aid their eventual dissolution. Just as in any other sensitive analytical method, extreme care must be taken to avoid contamination of the sample at this stage. In particular, the laboratory and balance used when weighing out samples must be segregated from the main chemical laboratory where radiochemical operations will be carried out involving macroquantities, *e.g.*, of arsenic, as carriers.

The most widely used method of activating the sample and standard is to place them, side by side, within the high flux of thermal and fast neutrons and γ-rays, provided by a nuclear reactor. This process is usually called a " pile irradiation ". Most of the nuclear reactions useful in radioactivation analyses can be induced by the thermal neutrons : occasional use can be made of the fast-neutron component of the pile flux. Alternative methods of providing an intense neutron flux, or bombardment with deuterons or other charged particles, will be mentioned later. In the example we have chosen, the activation of arsenic by pile irradiation, the appropriate nuclear reaction is :

$$^{75}\mathrm{As}(n,\gamma)^{76}\mathrm{As}\ (t_{\frac{1}{2}} = 26{\cdot}8\ \text{hr., } \beta\text{- and } \gamma\text{-active})$$

and it proceeds with a cross-section (for thermal neutrons) of 4·1 barns. An important feature of nuclear reactors, particularly those of the graphite moderated type (*e.g.*, B.E.P.O., Harwell), is their capacity for the simultaneous irradiation of several hundreds of small samples (including standards if required). The practical details of the irradiation of samples in B.E.P.O. have been discussed fully in a review by Smales.[2] The irradiation facilities are available to outside workers and information can be obtained from the Isotope Division, A.E.R.E., Harwell.[3]

Given adequate facilities for the irradiation of analytical samples, the analyst will next be interested in the quantitative laws governing the growth of induced activity in the sample and the standard and its decay on removal from the irradiation device. Generally speaking, it seems fair to remark that activation of a minor constituent by thermal neutrons is influenced far less by the nature of the solid or liquid matrix than is the case with

[1] Smales and Pate, *Analyst*, 1952, **77**, 196.

[2] Smales, *Atomics*, 1953, **4**, No. 3, 55.

[3] " Radioactive Materials and Stable Isotopes ", Catalogue No. 3, Isotope Division, Atomic Energy Research Establishment, Harwell, near Didcot, Berks., 1954.

spectrometric arc or spark excitation. This implies that radioactivation analysis stands in much less need of specially prepared standards than direct emission or mass spectrometry. Normally the sample may be irradiated side by side with a primary chemical standard, say, a pure metal or oxide, or a small volume of a standard solution. However, it is not always permissible to assume that the effective neutron flux is uniform throughout the combination of sample and standard. Apart from possible local variations in pile flux (which could be tested for by irradiating a number of specimens simultaneously), a variation in flux may be introduced through neutron absorption (self-shielding) by the required constituent or by others. Fortunately, many common matrix materials (Si, O, C, H, Al) have low total absorption cross-sections for neutrons of thermal or of intermediate energy.[4] The absorption by a minor constituent would not normally be excessive, and the standard could be appropriately diluted to an equally low concentration of absorbing centres. Where the matrix material or a major constituent of it is opaque to thermal neutrons, then the sample weight must be restricted to the minimum. The complete calculation of the self-shielding factor for a given matrix in a given shape, integrated over the whole spectrum of pile neutrons, would be a formidable task and only approximate solutions have been put forward.[5] A useful preliminary assessment can be made using the simple exponential equation, $f = f_0 e^{-N\sigma r}$, where f_0, f are the incident and attenuated fluxes, N the number of absorbing centres per cm.^{3}, r the radius of a spherical sample, and σ the total atomic neutron absorption cross-section [4] for the complete spectrum of pile neutrons at the point of irradiation (not merely the cross-section for thermal neutrons). Attention has recently been drawn again by Plumb and Lewis [6] to the effect of neutrons of " resonance " energies. Any contribution by neutrons of intermediate energy to the total self-shielding effect will be reduced if the irradiations are carried out (at considerable loss of sensitivity) in the thermal column of the reactor. In all cases the practical effect of self-shielding in a given sample and/or standard could be judged by simultaneous irradiation of a number of samples of different weights or dilutions.

The growth of induced activity during irradiation follows the law :

$$I^0{}_{\mathrm{B}} \text{ (dis. min.}^{-1}\text{)} = 60W_{\mathrm{A}}.\theta.6{\cdot}02.10^{23}.\sigma_a.10^{-24}.f[1 - \exp(-0{\cdot}693t/t_{\frac{1}{2}})]/M_{\mathrm{A}}$$

where $I^0{}_{\mathrm{B}}$ = induced radioactivity due to product B, $t/t_{\frac{1}{2}}$ = ratio of irradiation time to half-life of B, W_{A} = mass of target element A, θ = fractional abundance of a specific isotope, σ_a = activation cross-section (in barns) for that specific isotope, M_{A} = atomic weight of the element A, and f = activating flux of neutrons per cm.^{2} per sec.

The expression $[1 - \exp(-0{\cdot}693t/t_{\frac{1}{2}})]$ is often called the " growth

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[4] Hughes and Harvey, " Neutron Cross Sections ", B.N.L. 325, U.S. Govt. Printing Office, Washington 25, D.C., 1955.

[5] Keyes, U.S. Atomic Energy Commission Unclassified Report No. A.E.C.D.-3000, 1950.

[6] Plumb and Lewis, *Nucleonics*, 1955, **13**, No. 8, 42.

factor ". It has a value of 0·5 for an irradiation time equal to the half-life of the product ; for longer periods of irradiation it rises more slowly to a limiting value of 1·0. Practically, an irradiation for 5 half-lives induces almost a saturation activity, of magnitude controlled solely by the factors W_A, θ, σ_a, M_A, and f. Under these conditions, and with the values, $W_A = 10^{-6}$ g., $f = 10^{12}$ cm.$^{-2}$ sec.$^{-1}$ (appropriate for irradiations in B.E.P.O.), the previous equation reduces to :

$$I^o{}_B = 3{\cdot}6 \times 10^7 \sigma_a \theta / M_A$$

This equation is convenient in making a rapid preliminary assessment of activation possibilities.

The decay of the induced activity, starting as soon as the irradiation ceases, follows the law :

$$I^d{}_B = I^o{}_B \exp\,(-\,0{\cdot}693d/t_{\frac{1}{2}})$$

where $I^d{}_B$ is the residual radioactivity of B after a time d.

In the specific case of arsenic, irradiation almost to saturation would require at least 5 days ; at the end of this period the induced activity, due to ^{76}As, from 10^{-6} g. of arsenic in the sample may be calculated as follows :

$$I^o{}_B = 3{\cdot}6 \times 10^7 \times 4{\cdot}1 \times 1{\cdot}00/75 = 1{\cdot}96 \times 10^6 \text{ dis. min.}^{-1}\ \mu\text{g.}^{-1}$$

Twenty-four hours after the end of the irradiation, the residual activity would still be about 1×10^6 dis. min.$^{-1}$.

Radiochemical Purification.—Immediately after irradiation, the sample is normally subjected to radiochemical purification in order to isolate the required product, *e.g.*, ^{76}As, free from extraneous radioactivity. For example, the irradiation of 10^{-6} g. of arsenic in 1 ml. of blood for 5 days would yield, not only 2×10^6 dis. min.$^{-1}$ of ^{76}As, but also 4×10^7 dis. min.$^{-1}$ of 37-min. ^{38}Cl and 2×10^8 dis. min.$^{-1}$ of 14·8-hr. ^{24}Na. Rather than undertake the labour of the quantitative separation and purification of 10^{-6} g. of arsenic, with the attendant risks of losses such as those due to absorption on precipitates, the analyst adds 50 mg. of inactive arsenic as a carrier for the radioactive ^{76}As. Provided that the mixture can now be treated so as to bring all arsenic atoms, normal and radioactive, into the same chemical form—say, as arsenate—the subsequent chemistry need not be quantitative. The problem of the quantitative recovery of 10^{-6} g. of arsenic (or it could well be 10^{-10} g., for radioactivation analysis has been applied at this low level) is replaced by that of purifying 50 mg. of arsenic, with quantitative determination of the chemical yield, that is, the percentage recovery of the added arsenic carrier. In the specific example of the determination of arsenic in biological material, the arsenic in the sample might be present as $AsO_2{}^{-1}$, $AsO_3{}^{3-}$, $AsO_4{}^{3-}$, As^{3+}, or as an organic compound. The carrier was added as sodium arsenite, followed by a wet oxidation of the sample and added carrier with hydrogen peroxide, nitric acid, sulphuric acid, and perchloric acid.

The radiochemical purification of the induced activity, in the presence of the carrier, involves normal chemical procedures such as precipitation, distillation, solvent extraction, ion exchange, and chromatography. An operation frequently of use consists of " scavenging " traces of unwanted elements from solution by forming in it a strongly adsorptive precipitate, *e.g.*, of ferric hydroxide, antimony sulphide, or barium sulphate. It is, of course, restricted to conditions such that the carrier element remains in solution. The purification need not be too time-consuming ; the operations may be carried out on a semimicro-scale and permit the use of a clinical centrifuge as a rapid alternative to filtration. Again, small losses due to incomplete transference of solutions or to incomplete precipitation are adjusted by final measurement of the chemical yield. It has been found possible to purify the relatively short-lived isotope ^{233}Th (half-life, 22·1 min.) from very high initial extraneous β-activities due to uranium, zirconium, yttrium, and rare-earth elements within two hours of the irradiation and dissolution of the sample.[7] The purification of arsenic in irradiated biological material or germanium oxide included several precipitations as the metal with ammonium hypophosphite, distillation under oxidising conditions to remove germanium while the arsenic remains in the acid mixture, and distillation of arsenic as arsenious chloride under reducing conditions. Useful accounts of the radiochemical purification of a variety of elements have been published by Meinke,[8] by Coryell and Sugarman,[9] and by Kleinberg.[10] During the radiochemical purification of the induced activity from the sample, the standard will require similar, but possibly less extensive, treatment. At the very minimum, the standard must be taken into solution together with carrier, and then precipitated and weighed for determination of chemical yield in exactly the same chemical form as the end-product of the purification of the sample. In our example, arsenic was finally precipitated from acid solution with ammonium hypophosphite, washed with water, and dried under a radiant heater.

In the example followed above, inactive ^{75}As was converted by neutron capture into the β- and γ-active ^{76}As, which was purified, after admixture with arsenic carrier, by chemical procedures specific for arsenic. It should be pointed out that cases arise where the product of pile irradiation is not identical chemically with the target element—cf. oxygen and uranium, among others, in the Table (p. 94). In the determination of uranium utilising the fission of ^{235}U, it is convenient to add barium carrier to the irradiated sample and to carry out chemical procedures which are specific for barium, not for uranium.[11]

Measurement of Source.—The mounting and counting of the carrier precipitates bearing radiochemically pure, induced activity demand only

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[7] Jenkins, *Analyst*, 1955, **80**, 301.

[8] Meinke, U.S. Atomic Energy Commission Unclassified Reports Nos. A.E.C.D.-2738, 1949, and -3084, 1951.

[9] Coryell and Sugarman, " The Fission Products, Book 3 ", National Nuclear Energy Series, Vol. IV–9, McGraw-Hill, New York, 1951.

[10] Kleinberg, U.S. Atomic Energy Commission Unclassified Reports No. LA-1566, 1953 and LA-1721, 1954.

[11] Smales, *Analyst*, 1952, **77**, 778 ; Seyfang and Smales, *ibid.*, 1953, **78**, 394.

an elementary knowledge of radiochemistry.[12] It is usually convenient to make the precipitates into a slurry on circular aluminium trays about an inch in diameter. Considerable attention must be paid to obtaining a uniform thickness over the tray; in the most precise work the thickness should be so far as possible similar for the sample and the standard.

With the counting equipment at present commercially available in this country the ultimate sensitivity of radioactivation analysis is best attained by counting β-particles rather than γ-photons. Simple β-counting equipment, comprising a lead-shielded, end-window Geiger tube, a power pack to give up to 1800 v, a pre-amplifier, and a scaling unit costs only a few hundred pounds and is becoming widely available. Doubtless, γ-counting will in future assume greater prominence, with the improvement of techniques—possibly this may include a reduction in the present high background of scintillation crystals and the provision of inexpensive and stable multichannel pulse-analysers. At the moment the chief interest in γ-measurements lies in γ-spectroscopy,[13] usually with moderately intense sources, to select individual γ-energies and avoid much of the necessity for chemical separations. Examples of this approach will be given below.

Measurement of the β-activity of the sample and standard is best regarded as measurement of a ratio between two sources of similar composition and thickness, at identical counting geometry. In this way many of the potential errors of absolute β-counting (variations in self-absorption, self-scattering, back-scattering, external absorption) are avoided. β-Particles of maximum energy below 0·2 Mev require special mounting and counting techniques, and in some cases a gas-flow proportional counter is used with the sample mounted internally with 2π geometry. Most of the elements listed in the Table with favourable sensitivity can be determined by making the final measurements with an end-window Geiger tube, preferably of the mica-window EHM2 type.

One fundamental aspect of measuring radioactivity must be stressed—the statistical nature of the radioactive process causes variations to appear between successive measurements on the same sample (even where decay loss is insignificant over the duration of the experiment). The standard deviation of a series of repeated measurements is an index of this variability and is numerically equal to the square root of the average number of particles or photons recorded during each measurement (*not* the square root of the count *rate*). The statistical fluctuations in measurements of radioactivity need not introduce large errors, provided that the counting periods are prolonged so as to include 10,000 counts; the standard deviation is then 100, *i.e.*, the coefficient of variation is 1%.

The lower limits of reasonably precise measurement are governed by the efficiency of the counter and by the natural background of the equipment—owing to radioactive elements in the constructional materials and to cosmic

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[12] Cook and Duncan, "Modern Radiochemical Practice", Oxford Univ. Press, Oxford, 1952.

[13] Owen, *Atomics*, 1953, **4,** No. 1, 5; No. 2, 34; Connally and Lebœuf, *Analyt. Chem.*, 1953, **25,** 1095; Peirson, *Nature*, 1954, **173,** 990.

radiation. Reasonable limits are 100 dis. min.$^{-1}$ for β-emitters where the maximum β-particle energy exceeds 0·2 Mev, 1000 dis. min.$^{-1}$ for isotopes emitting softer β-radiation, and 1000 photons min.$^{-1}$ for γ-emitters. The upper limit of precise measurement can be extended at will by taking only a small known fraction of the purified carrier for the actual measurement of radioactivity.

In the above discussion, we have assumed that the chemical treatment of the sample after addition of the carrier isolated the required activity completely free from extraneous activities. Much of the reliability of radioactivation analysis arises from the ease with which this assumption can usually be checked. The radiochemical purity of the final precipitates isolated from sample and standard respectively may, in the first instance, be checked by a series of decay measurements. After appropriate corrections, the count rates at various intervals are plotted on a logarithmic scale against time on a linear scale. Successive count rates obtained during the decay of a single radiochemically pure isotope will lie on a straight line of slope related to the half-life. Alternatively, the penetrating power of the β-radiation may be measured through a series of aluminium absorbers of increasing thickness, with correction for any concomitant decay. The corrected count rates are again plotted on a logarithmic scale, but against the absorber thickness on a linear scale. The shape of the absorption curve is characteristic of the β-spectrum of a particular isotope and may be closely compared with standard curves recorded with especially purified isotopes under the same conditions. The penetrating power of any γ-radiation emitted by the isolated radioactive isotope may be measured through a series of lead absorbers : a scintillation counter would normally be used as a detector. Finally, the characteristic γ-spectrum of the isotope can be recorded by means of a sodium iodide scintillation spectrometer [13] (see Figure) provided that the source is of reasonable intensity (with present equipment, including a single-channel pulse analyser, at least 1000 photons min.$^{-1}$ are required to obtain reasonable results). The record may be compared with standards.

In certain cases the purified induced activity may be a mixture of radioactive isotopes, *e.g.*, the irradiation of cerium under the conditions defined in the footnotes to the Table would give ^{141}Ce (33 days, 0·58 Mev β, 0·145 Mev γ) together with ^{143}Ce (33 hr., 1·39 Mev β, 0·035, 0·126, 0·160, 0·289, 0·356, 0·660, and 0·720 Mev γ). The test of radiochemical purity remains that of comparing the sample and the standard under similar conditions.

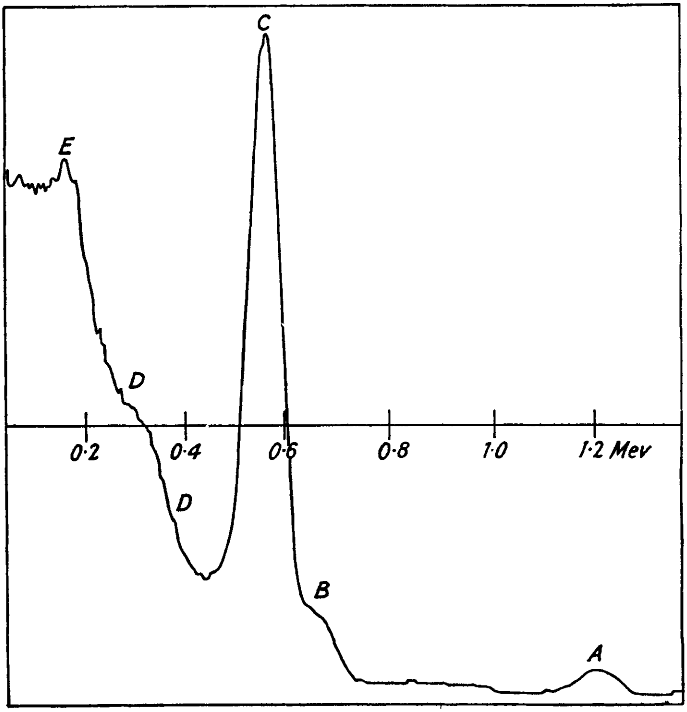
It is not expected that each of the three parameters, half-life, shape of β-absorption curve, and shape of γ-spectrometer record, can in every case be precisely determined : for example, several activities listed in the Table decay only comparatively slowly. In general, enough characteristic results may be gathered to establish the required degree of purity.

The practical steps in a normal radioactivation analysis may now be summarised :

1. Simultaneous activation of weighed quantities of sample and standard.
2. Dissolution of sample and standard, each in the presence of carrier.

3. Treatment of sample and standard to bring the induced activity and the carrier into the same chemical form in a homogeneous mixture.

4. Chemical purification of carrier in the solution from the sample (and possibly also from the standard) until the induced activity is radiochemically pure.



γ-Spectrum of ^{76}As.

A, Photoelectric γ-capture peak at 1·21 Mev.
B, „ „ „ „ 0·65 Mev.
C, „ „ „ „ 0·55 Mev.
D, Compton continuum due to γ of 0·55 Mev.
E, Back-scatter peak due to γ of 0·55 Mev.

5. Determination of the chemical yields of carrier for the sample and standard severally.

6. Comparison of the intensity of radioactivity of suitably mounted sources prepared from sample and standard, under identical counting conditions, with appropriate corrections for chemical yield, decay, dead-time losses in the counter, etc.

7. Confirmation of the radiochemical purity of the isolated induced activities by measuring (*a*) the rate of decay, (*b*) the shape of the β- and possibly the γ-absorption curves, and (*c*), in suitable cases, the characteristic γ-spectrometer record.

Limitations caused by conflicting nuclear processes

In the preceding discussion it was assumed that ^{76}As, the illustrative example, could be formed in the sample, as in the standard, only by thermal neutron activation of the required element, arsenic. However, in certain rather special cases, the required activity may be induced by neutron bombardment of some element *other* than arsenic. This hardly ever occurs except when the required element is accompanied in the sample by a large excess of an element differing from it by only one or two units of atomic number. Nuclear reactions of the (n,p) or (n,α) type may then induce an activity in the foreign element identical with that of the product of the (n,γ) reaction of the target element. A more subtle case arises when a foreign element of atomic number one unit less than that of the required element is actually transmuted into the latter by the succession of an (n,γ) reaction and β-decay. Examples of each of the above type of interference are given below. Each case relates to activation using pile neutrons.

(*a*) During determination of traces of sodium in aluminium the fast neutron component of the pile flux induces the reaction, $^{27}\mathrm{Al}(n,\alpha)^{24}\mathrm{Na}$ [cf. $^{23}\mathrm{Na}(n,\gamma)^{24}\mathrm{Na}$]. Measurements made by Salmon [14] show that the spurious sodium activity introduced in this way is equivalent to 81 p.p.m. of sodium for irradiations near the centre of B.E.P.O. (1954).

(*b*) Le Claire, Gregory, and Smales [15] attempted the estimation of traces of ^{40}A in sylvite (KCl) minerals by neutron activation to ^{41}A (this determination would be significant in estimating the ages of such minerals). The estimation is subject to prohibitive interference from the reaction, $^{41}\mathrm{K}(n,p)^{41}\mathrm{A}$ [cf. $^{40}\mathrm{A}(n,\gamma)^{41}\mathrm{A}$].

(*c*) Smales and Pate [16] have shown that the following sequence of reactions occurs during the activation of germanium : $^{74}\mathrm{Ge}(n,\gamma)^{75}\mathrm{Ge}(t_{\frac{1}{2}}$ 1·37 hr.) ; ^{75}Ge (β decay) ^{75}As (stable) ; $^{75}\mathrm{As}(n,\gamma)^{76}\mathrm{As}(t_{\frac{1}{2}}$ 26·8 hr.). However, insufficient arsenic is produced by transmutation from the germanium to introduce appreciable error into the determination of arsenic in germanium dioxide at the 0·05 p.p.m. level, when the irradiations are made for 15 hours at a flux of 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$.

It must be emphasised that the limitations described in this section become apparent only in rather special cases where one is trying to determine traces of an element in the presence of a very large excess of an element which adjoins it in the Periodic Table, the cross-sections for (n,p), (n,α) reactions or the yield of the combined $(n,\gamma\,;\ \beta)$ reaction being normally extremely low.

The (n,p) and the (n,α) reaction are normally due to the fast-neutron component of the pile flux and can often be avoided if the irradiations are carried out in the thermal column. This irradiation facility provides a substantially lower flux than that near the centre of the pile, and the analyses are correspondingly less sensitive.

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[14] Salmon, United Kingdom Atomic Energy Authority Unclassified Report No. A.E.R.E. C/R 1324, 1954.

[15] Le Claire, Gregory, and Smales, personal communication.

[16] Smales and Pate, *Analyt. Chem.*, 1952, **24**, 717.

The production of spurious ^{76}As from germanium during the determination of traces of arsenic in 1 g. samples of germanium dioxide depends on the time of irradiation and on the square of the neutron flux : although the error is $+$ 0·08 p.p.m. for 75 hours' irradiation at 2×10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$, it falls to $+$ 0·0001 p.p.m. for 10 hours' irradiation at 2×10^{11} neutrons cm.$^{-2}$ sec.$^{-1}$. At this reduced flux and irradiation time the method retains adequate sensitivity for the analysis of 0·001 p.p.m. of arsenic.

General discussion of radioactivation analysis for trace elements

Irradiation of 10^{-6} g. of arsenic under standard conditions has been calculated (p. 84) to yield 2×10^{6} dis. min.$^{-1}$. 100 dis. min.$^{-1}$ can be measured with reasonable precision when normal β-counting equipment is used. After allowance for minor losses due to decay, incomplete chemical recovery, etc., the lower limit of satisfactory analysis for arsenic may be set at 10^{-10} g., and Smales and Pate [16] have measured arsenic at this level in distilled water. It is well known that the measurement of radioactivity permits the detection of extremely minute quantities of the natural radioactive series : the analyst may now extend the scope of highly sensitive radioactivity measurements to include species which are themselves inactive, but which acquire induced activity on neutron activation. By reason of this intrinsic sensitivity, radioactivation analysis is particularly suited to the determination of trace elements, *i.e.*, elements present in a sample at a concentration of 100 p.p.m. or less.

The utility of an analytical method can be assessed by answering the questions :

(*a*) What property is measured ? (*b*) What elements can be determined and to what lower limits ? (*c*) Is the element determined identified with certainty ? (*d*) Can several elements be determined simultaneously ? (*e*) How reliable are the quantitative results ?

(a) What Property is measured ?—Radioactivation, like emission or mass spectrometry, is a method of determining elements, irrespective of their state of combination. Chemical bonds are frequently broken during neutron and γ-ray bombardment. That is, radioactivation does not disclose the chemical form in which an element occurs in a sample, and it cannot be used for determination of specific compounds.

It has just been stated that radioactivation is a method of determining elements, but, strictly, it determines a specific isotope of the element : that is, radioactivation analysis for, say, dysprosium proceeds through a measurement of the induced activity due to the product of the reaction, ^{164}Dy(n,γ)^{165}Dy. Now the abundance of ^{164}Dy in naturally occurring dysprosium is 28·47%, the other important stable isotopes being those of mass 156, 158, 160, 161, 162, and 163. None of those isotopes is directly measured. Radioactivation has, of course, been used as a method of isotopic-abundance analysis, *e.g.*, by measuring the ratio ^{235}U : total uranium for enriched and for depleted uranium metal.[11] These are favourable cases, however, and, in general, radioactivation is very much less versatile than mass spectrometry for isotopic analysis.

(b) What Elements can be determined and to what Lower Limits?—On p. 92 the limit of sensitivity of radioactivation analysis for arsenic was discussed on the assumption that the sample was irradiated to saturation at a flux of 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$ and that 100 dis. min.$^{-1}$ of induced activity due to ^{76}As can be isolated and measured. It is instructive to extend this discussion over the entire range of chemical elements.

A practical definition of sensitivity might be taken as that weight of element which on irradiation at a flux of 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$ to saturation or for one month (whichever is the shorter), followed by decay for 2 hours, gives 100 dis. min.$^{-1}$ of residual induced activity.

The Table sets out the absolute weights of various elements which one could expect to measure : the corresponding concentrations depend on the sample weight—in general, 1 g. would be a fair figure, possibly rather more for solids and rather less for liquids. The coefficient of variation of single analyses for a given element would be about 10% if the sample and the background could each be measured for an hour. The flux of 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$ assumed in calculating the results given above is appropriate for irradiations carried out near the centre of a graphite-moderated natural-uranium reactor of the B.E.P.O. type. Higher fluxes (available over a smaller effective volume) are available in water-moderated reactors of similar or higher power rating, *e.g.*, figures of 7×10^{13} and 5×10^{14} have been quoted for the Canadian heavy-water reactor at Chalk River [17] and for the American light-water-moderated Materials Testing Reactor at Idaho.[17] Heavy-water reactors now under construction at Harwell [18] should in time provide irradiation facilities which will extend the sensitivities quoted in the Table by a factor of nearly 100.

In certain cases elements listed with poor sensitivities in the Table may be analysed more readily by other methods of activation or detection. The most important alternative to pile irradiation is the use of a cyclotron beam of protons or deuterons. The disadvantages compared with pile irradiation are the limited cross-sectional area of the beam and the limited degree of penetration of charged particles into solid samples. The radioactivation analyses of carbon in steel, by von Ardenne and Bernhard and others,[25] and in organic compounds by Süe,[26] exemplify a cyclotron-induced reaction which could not have been brought about in the pile, namely, $^{12}\mathrm{C}(d,n)^{13}\mathrm{N}$ (9·9-min. 1·2 Mev positron emitter).

Basile and others [27] used the 22 Mev betatron at the G. Roussy Institute, Villejuif, France, for the radioactivation analysis of oxygen down to a 6 mg. level in organic compounds and down to 0·1% in aluminium metal, by using the reaction $^{16}\mathrm{O}(\gamma,n)^{15}\mathrm{O}(t\frac{1}{2}$ 2·1 min. 1·7 Mev $\beta^{+})$. These workers indicated

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[17] " Catalogue of Nuclear Reactors ", C.R.R.-590, Atomic Energy of Canada, Ltd., Chalk River, Ontario, 1955.

[18] " First Annual Report of the United Kingdom Atomic Energy Authority, 1954–55 ", H.M.S.O., London, 1955.

Estimated sensitivities of radioactivation analyses by irradiation in a natural uranium graphite-moderated reactor (for notes, see pp. 96, 97). [a, g]

Element	Activated form	Half-life	Estimated sensitivity (g.)	Notes
Actinium * .	Parent ^{227}Ac	22 y., 1% α	5×10^{-13}	*
Aluminium .	^{28}Al	2·3 min.	Poor	K 0·8
Antimony. .	^{122}Sb	2·8 d.	1×10^{-10}	
	with ^{124}Sb	60 d.		
Argon . . .	^{41}A	1·8 hr.	5×10^{-10}	
Arsenic . .	^{76}As	26·8 hr.	5×10^{-11}	
Astatine * .	Parent ^{210}At	8·3 hr., EC, 0·20% α	1×10^{-16}	*
Barium . .	^{139}Ba	85 min.	1×10^{-9}	
Beryllium. .	^{10}Be	$2{\cdot}7 \times 10^{6}$ y.	Poor	K 0·11
Bismuth . .	^{210}Bi	5·0 d.	5×10^{-8}	
Boron . . .	^{12}B	0·03 sec.	Poor	$K < 0{\cdot}4$
Bromine . .	$^{80\text{m}}$Br + ^{80}Br	4·6 hr.	1×10^{-10}	
	with ^{82}Br	35·9 hr.		
Cadmium . .	^{115}Cd	54 hr.	1×10^{-9}	
	with ^{117}Cd	2·9 hr.		
	and $^{115\text{m}}$Cd	43 d.		
Cæsium . .	^{134}Cs	2·3 y.	5×10^{-10}	
Calcium . .	^{45}Ca	152 d.	1×10^{-7}	
Carbon . .	^{14}C	5580 y., soft β	Poor	K 10^{-4}
Cerium . .	^{141}Ce	32 d.	1×10^{-9}	
	with ^{143}Ce	33 hr.		
Chlorine . .	^{38}Cl	37·3 min.	5×10^{-9}	
Chromium. .	^{51}Cr	27 d., EC, 3% γ	1×10^{-7}	
Cobalt . . .	^{60}Co	5·2 y.	5×10^{-10}	
Copper. . .	^{64}Cu	12·8 hr., EC, 58% $\beta^- + \beta^+$	1×10^{-10}	To give 100 $(\beta^- + \beta^+)$ min.$^{-1}$
Dysprosium .	^{165}Dy	2·3 hr.	1×10^{-12}	
Erbium . .	^{171}Er	7·5 hr.	1×10^{-10}	
Europium . .	$^{152\text{m}}$Eu	9·3 hr., β, EC	1×10^{-12}	
Fluorine . .	^{20}F	12 sec.	Poor	K 0·05
Francium * .	Parent ^{223}Fr	21 min.	1×10^{-18}	*
Gadolinium .	^{159}Gd	18·0 hr.	5×10^{-10}	
Gallium . .	^{72}Ga	14·1 hr.	1×10^{-10}	
Germanium .	^{75}Ge	82 min.	5×10^{-9}	
	with ^{77}Ge	12 hr.		
Gold . . .	^{198}Au	2·7 d.	5×10^{-12}	
Hafnium . .	^{181}Hf	45 d.	5×10^{-10}	
Helium . .	^{5}He	(unknown)		
	^{3}H	12·4 y., soft β	5×10^{-6}	n,p on ^{3}He [b]
Holmium . .	^{166}Ho	27·2 hr.	5×10^{-12}	
Hydrogen . .	^{3}H	12·4 y., soft β	Poor [c]	K 1×10^{-5}
Indium . .	^{116}In	54 min.	1×10^{-11}	
	with ^{114}In–$^{114\text{m}}$In	50 d.		
Iodine . . .	^{128}I	25 min.	1×10^{-9}	
Iridium . .	^{194}Ir	19 hr.	1×10^{-11}	
	with ^{192}Ir	75 d.		
Iron . . .	^{59}Fe	45 d.	1×10^{-7}	
Krypton . .	^{85}Kr	4·4 hr.	5×10^{-11}	

Element	Activated form	Half-life	Estimated sensitivity (g.)	Notes
Lanthanum	^{140}La	40 hr.	5×10^{-11}	
Lead	^{209}Pb	3·3 hr.	5×10^{-6}	
Lithium	^{8}Li	0·8 sec.	Poor	K 0·4
,,	n,α : ^{3}H	12·4 y., soft β	5×10^{-10}	
,,	^{18}F	112 min., β^{+}	Possibly $< 10^{-6}$	^{d}
Lutecium	^{177}Lu	6·8 d.	5×10^{-12}	
	with ^{176}Lu	3·7 hr.		
Magnesium	^{27}Mg	9·6 min.	5×10^{-5}	
Manganese	^{56}Mn	2·6 hr.	1×10^{-11}	
Mercury	^{203}Hg	48 d.	1×10^{-9}	
Molybdenum	^{99}Mo	67 hr.	1×10^{-8}	
Neodymium	^{147}Nd	11·6 d.	5×10^{-10}	
	with ^{149}Nd	1·8 hr.		
Neon	^{23}Ne	40 sec.	Poor	K 0·02
Nickel	^{65}Ni	2·6 hr.	1×10^{-8}	
Niobium	^{94m}Nb	6·6 min. IT, β (0·1%)	5×10^{-2}	To give 100 β min.$^{-1}$
Nitrogen	^{16}N	7·3 sec.	Poor	K 2×10^{-6}
Osmium	^{193}Os	31 hr.	1×10^{-9}	
	with ^{191}Os	16 d., soft β		
Oxygen	^{19}O	29 sec.	Poor	K 2×10^{-6}
	or ^{18}F	112 min., β^{+}	5×10^{-7}	^{d}
Palladium	^{109}Pd	13·4 hr.	1×10^{-10}	
Phosphorus	^{32}P	14·3 d.	5×10^{-10}	
Platinum	^{197}Pt	18 hr.	1×10^{-9}	
	with ^{199}Pt	31 min.		
Polonium *	Parent ^{210}Po	138 d. α	1×10^{-16}	*
Potassium	^{42}K	12·4 hr.	1×10^{-9}	
Praseodymium	^{142}Pr	19·3 hr.	5×10^{-11}	
Promethium *	Parent ^{147}Pm	2·6 y.	5×10^{-14}	*
Protactinium *	Parent ^{231}Pa	$3·4 \times 10^{5}$ y., α	1×10^{-11}	*
Radium *	Parent ^{226}Ra	1620 y., α	5×10^{-13}	*
Radon *	Parent ^{222}Rn	3·8 d., α	5×10^{-18}	*
Rhenium	^{188}Re	17 hr.	1×10^{-11}	
	with ^{186}Re	91 hr.		
Rhodium	^{104m}Rh–^{104}Rh	4·3 min.	5×10^{-3}	
Rubidium	^{86}Rb	19 d.	5×10^{-10}	
	with ^{88}Rb	18 min.		
Ruthenium	^{105}Ru	4·5 hr.	1×10^{-9}	
	with ^{103}Ru	40 d.		
Samarium	^{153}Sm	46 hr.	1×10^{-11}	
Scandium	^{46}Sc	85 d.	5×10^{-11}	
Selenium	^{81m}Se–^{81}Se	57 min.	5×10^{-8}	
	with ^{81}Se	17 min.		
Silicon	^{31}Si	2·6 hr.	1×10^{-8}	
Silver	^{110m}Ag–^{110}Ag	270 d.	5×10^{-9}	
Sodium	^{24}Na	15 hr.	1×10^{-10}	
Strontium	^{89}Sr	54 d.	1×10^{-7}	
Sulphur	^{35}S	87 d., soft β	5×10^{-7}	
	or ^{32}P	14·3 d.	5×10^{-8}	^{e}
Tantalum	^{182}Ta	111 d.	1×10^{-10}	
Technetium *	Parent ^{98}Tc	$\geqslant 10^{7}$ y.	Poor	*
,,	^{99m}Tc	6 h., IT, γ	Possibly sensitive	^{f}
Tellurium	^{127}Te	9·3 hr.	5×10^{-9}	
	with ^{129}Te	70 min.		

Table continued on next page.

Element	Activated form	Half-life	Estimated sensitivity (g.)	Notes
Terbium . .	^{160}Tb	73 d.	5×10^{-11}	
Thallium . .	^{204}Tl	2·7 y.	1×10^{-8}	
Thorium . .	^{233}Th	22 min.	5×10^{-9}	
	or ^{233}Pa	27·4 d.	1×10^{-10}	
Thulium . .	^{170}Tm	129 d.	5×10^{-11}	
Tin. . . .	^{121}Sn	27 hr.	5×10^{-9}	
	with ^{123}Sn	40 min.		
Titanium . .	^{51}Ti	6 min.	1×10^{-2}	
Tungsten . .	^{187}W	24 hr.	5×10^{-11}	
Uranium . .	^{239}U	23·5 min.	1×10^{-8}	
	or ^{239}Np	2·3 d.	1×10^{-10}	
	or ^{140}Ba	12·8 d.	5×10^{-9}	Fission of ^{235}U
Vanadium . .	^{52}V	3·7 min.	Poor	*K* 9
Xenon . . .	^{133}Xe	5·3 d.	5×10^{-9}	
	with ^{135}Xe	9·2 hr.		
Ytterbium .	^{175}Yb	4·2 d.	5×10^{-11}	
Yttrium . .	^{90}Y	61 hr.	1×10^{-10}	
Zinc . . .	^{69}Zn	52 min.	5×10^{-9}	
Zirconium . .	^{97}Zr	17 hr.	1×10^{-7}	
	with ^{95}Zr	65 d.		

Notes to Table : (*a*) The sensitivities given in the Table have been rounded to the nearest 5 times an integral power of 10. The irradiations are assumed to have been carried out at a thermal neutron flux of 10^{12} cm.$^{-2}$ sec.$^{-1}$ for one month (or to saturation if this period is less) and to have been followed by a two-hours' delay during which radiochemical purification is carried out, with quantitative yield. In rare cases where the fast neutron component of the pile flux is used, *e.g.*, to induce the S(*n,p*) reaction, the sensitivities given apply to the neutron distribution at the centre of the B.E.P.O. reactor at Harwell. The radiochemically pure sources are assumed to be counted under an end-window Geiger counter, at an efficiency of 10% for β-particles or positrons of maximum energy $> 0{\cdot}2$ Mev and of 1% for β-particles of lower energy (tabulated as " soft β "). These efficiencies are deemed to include self-absorption effects in the sources. In the rare cases where the only suitable activated form decays only through isomeric-transition (IT) or electron-capture (EC) processes, it is assumed that the source is γ-counted under a scintillation counter at 10% efficiency ; the sensitivity limit has then been set at a weight sufficient to give 10^3 γ-photons min.$^{-1}$ (rather than 10^2 particles min.$^{-1}$ as in β-counting) to allow for the higher background normally characteristic of the γ-counter. It is impossible in one compact table to indicate *all* the possibilities of pile activation : the data presented here relate particularly to the possibilities of conducting highly sensitive analyses within two hours of irradiation. In some cases the analyses could be carried out (with some loss of sensitivity) by using longer-lived isotopes, *e.g.*, analysts not working near a pile might not wish to use the 52-min. ^{69}Zn for zinc analysis at 5×10^{-9} g., but could still use a 14-hr. ^{69m}Zn or a 250-day ^{65}Zn at a level of perhaps 10^{-7} g. or more. These possibilities can only adequately be appreciated by consulting the tables of nuclear data.

Elements marked * occur in Nature as radioactive isotopes of reasonable specific activity, or else the only known forms are artificially prepared isotopes, in which case the isotope of greatest half-life has been selected. Many of these elements are α-emitters : because of the much lower background the sensitivity of α-counting is about 100 times that of β-counting, but a proportionately longer time must be spent on the counting periods to attain reasonable precision.

The Table is based upon the General Electric Company's Chart of the Nuclides,[19] and upon the " Table of Isotopes " by Seaborg and others.[20]

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[19] " Chart of the Nuclides ", General Electric Company, Schenectady, New York, 4th Edn., 1952.

[20] Hollander, Perlman, and Seaborg, *Rev. Mod. Phys.*, 1953, **25**, 469.

(*b*) The abundance of ^{3}He in normal helium has been assumed to be $1{\cdot}3 \times 10^{-4}$ %. The ^{3}He(n,p) reaction could detect 5×10^{-12} g. of enriched ^{3}He.

(*c*) The ^{2}H$(n,\gamma)^{3}$H reaction would be moderately sensitive as a means of analysis of enriched deuterium, with a sensitivity of 1×10^{-5} g.

(*d*) The possibility of radioactivation analysis for lithium or oxygen by means of ^{18}F arises from the sequence, ^{6}Li$(n,\alpha)^{3}$H, ^{16}O$(^{3}$H$,n)^{18}$F. The sensitivity given by Osmond and Smales [21] for oxygen applies to the determination of oxygen in finely divided ($< 50\ \mu$) metallic beryllium, intimately mixed with an excess of lithium fluoride. In principle the reactions could be applied also to the determination of lithium.

(*e*) The ^{32}S$(n,p)^{32}$P reaction requires a neutron energy of at least 1 Mev. The flux of fast neutrons in pile irradiations may be increased by placing the sample inside a hollow uranium cylinder : under these conditions the yield in this reaction in the B.E.P.O. pile increases [22] by a factor of seven—the sensitivity of the sulphur determination would then be about 1×10^{-8} g. This fast neutron reaction is included in the Table to illustrate the possibilities of using neutron-induced reactions other than the (n,γ) reaction. A possible advantage of a method for sulphur based on ^{32}P is the ease of measuring the 1·7 Mev β-radiation rather than the 0·17 Mev β-radiation from ^{35}S. An obvious disadvantage is the parallel production of ^{32}P by (n,γ) reaction on any phosphorus in the sample, which necessitates a separate analysis. The interference from phosphorus might be greatly reduced by the use of a cadmium screen to absorb the thermal neutrons.

(*f*) Herr,[23] and Alperovitch and Miller,[24] have obtained preliminary evidence for the presence of a long-lived ^{98}Tc in mineral samples, by activation to $^{99\mathrm{m}}$Tc. It is not yet possible to state the sensitivity of the method in terms of the mass of ^{98}Tc.

(*g*) When sensitivity, calculated according to the convention adopted, is particularly low, the value of the function $K = 100\theta\sigma_a/M_{\mathrm{A}}$, has been tabulated, as well as the half-life. Certain elements show a high K value, and the poor sensitivity is entirely due to the very short or very long half-life.

the possibility of extending the method to carbon and nitrogen, activated to 20-min. ^{11}C and 10-min. ^{13}N respectively.

The use of the pile or of the cyclotron or betatron discussed so far in this Review has been to produce an activated isotope which can be isolated chemically and measured, *e.g.*, by using a Geiger–Müller counter, after the irradiation has ceased. This intention is sometimes frustrated by the overlong or overshort half-life of the product. An alternative approach is to measure each activating collision actually during irradiation. This has been adopted by Gaudin and Pannell [28] in measuring beryllium down to 1—2 p.p.m. in minerals, by counting the prompt neutrons emitted during the reaction, ^{9}Be$(\gamma,n)2^{4}$He. In the specific case of ^{9}Be, the threshold for the photoneutron reaction is below 2 Mev, and a portable γ-source (60d-^{124}Sb, max. γ-energy 2·04 Mev) is adequate for the irradiation. The prompt neutrons are counted by means of a boron trifluoride pulse ionisation chamber. The principle of the instantaneous detection of activating collisions has been extended to pile-irradiations. A natural limitation is the requirement that the measuring device must be very sensitive to the required nuclear event

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[21] Osmond and Smales, *Analyt. Chim. Acta*, 1954, **10**, 117.

[22] Whitehouse and Putman, " Radioactive Isotopes ", Oxford Univ. Press, Oxford, 1953, p. 124.

[23] Herr, *Z. Naturforsch.*, 1954, **9**a, 907.

[24] Alperovitch and Miller, *Nature*, 1955, **176**, 299.

[25] von Ardenne and Bernhard, *Z. Physik*, 1944, **122**, 740.

[26] Süe, *Compt. rend.*, 1953, **237**, 1696.

[27] Basile, Huré, Lévêque, and Schuhl, *ibid.*, 1954, **239**, 422.

[28] Gaudin and Pannell, *Analyt. Chem.*, 1951, **23**, 1261.

and yet remain insensitive to the pile flux of slow and fast neutrons and γ-photons. In principle, a pulse ionisation chamber might be used to determine traces of, say, boron, lithium, or uranium,[28a] all of which eject heavily ionising particles (α-particles, tritons, or fission fragments) when irradiated with neutrons. The sample would be contained within the counting chamber. Actual analyses for each of these elements have, in fact, been made by using a nuclear emulsion as detector. The sample is evaporated from a microdrop (commonly 0·001 ml.) on to a metallic support which is irradiated in close contact with a sensitive emulsion. The emulsion is then developed and fixed and the photographic record is examined under a microscope. It is possible to distinguish tracks due to α-particles, tritons, or fission fragments from the shorter tracks due, for example, to protons. The reactions involved are : (i) $^{10}B(n,\alpha)^{7}Li$ (used by Faraggi, by Mayr, and by Loveridge and Smales, to determine boron down to 2×10^{-9} g.).[29] (ii) $^{6}Li(n,\alpha)^{3}H$ (used by Picciotto and Van Styvendael to determine lithium down to 10^{-11} g.).[30] (iii) $^{235}U(n$, fission) (used by Curie and Faraggi to study the localisation of uranium on the surface of polished mineral specimens).[31]

Of the 82 elements which are not naturally radioactive with high specific activity, all but hydrogen seem susceptible to radioactivation analysis in favourable circumstances. Beryllium, boron, carbon, and oxygen, although unsuited to neutron activation, may be activated by other means. Aluminium, fluorine, neon, niobium, rhodium, titanium, and vanadium, while susceptible to activation by thermal neutrons, give relatively short-lived isotopes which would decay prohibitively during moderately prolonged radiochemical separations.

(c) Is the Element determined identified with certainty?—The specificity of radioactivation analysis is high. It relies on three, and sometimes four, characteristics, *viz.*, the specific radiochemical purification, the half-life of the product, the maximum β-energy as determined from aluminium absorption measurements, and, in favourable cases, the γ-spectrum.

(d) Can several Elements be determined simultaneously?—It is obviously possible to irradiate an unknown sample for, say, 1 month and then to take it into solution add carriers, separate the groups, and isolate specific compounds. This technique would not normally be considered as valuable a means of qualitative analysis as the simultaneous recording of a wide range of elements by emission or mass spectrometry. In certain cases it is feasible to carry out analyses for a limited range of elements after a single irradiation of a sample and a mixed standard : for instance, Smales and others during their analyses of marine sediments and of rock samples, separated 2·5-hr. ^{65}Ni, 12·9-hr. ^{64}Cu, and 5·2-y. ^{60}Co in that order.[32]

[28a] Stewart and Bentley, *Science*, 1954, **120,** 50.

[29] Faraggi, Kohn, and Doumerc, *Compt. rend.*, 1952, **235,** 714 ; Mayr, *Nucleonics*, 1954, **12,** No. 5, 58 ; Loveridge and Smales, unpublished work at Harwell.

[30] Picciotto and Van Styvendael, *Compt. rend.*, 1951, **232,** 855.

[31] Curie and Faraggi, *ibid.*, p. 959.

[32] Smales, Geneva Conference on Peaceful Uses of Atomic Energy, August, 1955, Paper 770.

The simultaneous analysis for several trace elements by irradiation followed by direct estimation of individual disintegration rates without radiochemical separations is sometimes feasible, provided that the activity due to the main constituents is not excessive. The individual trace elements may be recognised by resolving the gross decay curve or, with much greater certainty, by a combination of decay studies and γ-spectroscopy. For example, Smales [32] irradiated a sodium–potassium alloy for a long time and then allowed two weeks for decay; subsequent γ-spectroscopy without chemical separation revealed ^{134}Cs (γ-energies 0·59, 0·80 Mev), ^{110}Ag (0·88, 1·36, 1·48 Mev), and ^{87}Rb (1·09 Mev). In these cases identification was by γ-energy only, as the products were long-lived. The quantitative analyses revealed Ag 100 p.p.m., Rb 5 p.p.m., and Cs 0·1 p.p.m., the last figure being actually obtained in a separate analysis which included a radiochemical purification. In a similar study Morrison and Cosgrove [33] irradiated silicon for 3 days, then measured ^{69}Zn, ^{76}As, ^{187}W, ^{59}Fe, ^{24}Na, ^{42}K, and ^{182}Ta by direct γ-scintillation spectrometry.

(e) How reliable are the Quantitative Results?—The precision of results (an index of the reproducibility of repeated individual analyses) must be distinguished from the absolute accuracy, or closeness of the mean value to the truth.

Radioactivation, like the other general methods of trace analysis, should give a coefficient of variation of no worse than 10% for single determinations, at an adequate level of trace element, *i.e.*, at the levels for the various elements quoted in the Table. By careful work at somewhat higher levels the coefficient of variation can be lowered to 1%. The possibilities of very precise radioactivation analysis have been demonstrated by Seyfang's determination [34] of the isotopic content of depleted and enriched uranium : this analysis, which involves measuring the fission product ^{140}Ba produced on pile-irradiation of the ^{235}U constituent, is similar in principle to a trace-element analysis, and the method was originally used to determine traces of natural uranium. In Seyfang's most recent work, 7 portions of natural uranium, as the oxide U_3O_8, were simultaneously irradiated, then treated chemically, and the final barium sulphate sources were β-counted, each source recording about 50,000 counts in 4 minutes. The series of 7 corrected counts showed a coefficient of variation of only 0·5%. The statistical errors in the determination of the counting rates account for 0·4% *i.e.*, for most of the observed variation. It may be estimated that the analysis of an unknown sample by simultaneous irradiation of one portion of sample and one portion of standard should be subject to a coefficient of variation of 0·7%, in these particular conditions.

The precision attainable by a given trace-element method normally decreases as the amount of the required constituent present becomes smaller. The precision at any given level depends, not only on the intrinsic sensitivity of the method, but also on a factor present in greater or smaller degree in all trace-element analytical methods, namely, the " background ". The

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[33] Morrison and Cosgrove, *Analyt. Chem.*, 1955, **27**, 810.

[34] Seyfang, *Analyst*, 1955, **80**, 74 ; cf. ref. 11.

" background " may take the form of contamination collected from reagents or the atmosphere, as in absorptiometry and certain other methods, or of the residual current in polarography, or of the electronic noise level in recording spectrometry, or of the extraneous radioactivity due to cosmic radiation, etc., in radioactivation analysis. Strictly, it is not the absolute level of the background, but rather the fluctuation between one measurement and another, which is the limiting factor.

One of the most restrictive types of background is that set by contamination from impurities in reagents. This often remains a problem even after reagents of the highest quality have been subjected to further elaborate purification.

The radioactivation method avoids errors introduced by impure reagents and it remains to take adequate precautions against surface contamination by, *e.g.*, atmospheric dust during the physical preparation of the sample. This method, like any other, is still subject to a background, which however is normally of a low level : it is the intrinsic background of the shielded counting assembly, normally of the order of 10 counts per minute for an end-window Geiger–Müller tube of 1 inch diameter ; its relative insignificance for many trace analyses is illustrated by the facts that even the minute weights of various elements listed in the Table would normally give a count rate (due to sample plus background) of 20 counts per minute, and that the coefficient of variation of the background (for an hour's counting) would be as little as 4%.

Next must be discussed the absolute accuracy of the method, *i.e.*, the degree to which the experimentally determined level of the trace constituent, obtained as the mean of many analyses with high reproducibility, approaches the truth. This is sometimes expressed as the bias (positive or negative) of the method. In many methods of analysis, including radioactivation, the sample is compared directly or indirectly with a standard. If then there is adequate precision, the absolute accuracy of the method depends on the availability of a suitable standard, *i.e.*, one whose composition is accurately known to an accuracy exceeding the maximum accuracy of the trace-element determination. This requirement is often met by weighing out elements or compounds of known composition, or by dispensing solutions of such reference substances. Further, the behaviour of the standard in colour development, excitation, activation, etc., must exactly parallel that of the trace constituent in the sample. For example, a sample of finely ground rock might be excited for say 40 seconds by a graphite arc for emission spectrometry : volatilisation of a trace constituent from the rock matrix might then not be matched in a parallel excitation of, say, a solid dilution of the oxide of the element in graphite or silica.

Radioactivation is independent, within reasonable limits, of the nature of the solid matrix of the sample provided that the weight and concentration of the sample and the standard are sufficiently low to avoid the self-shielding errors discussed on p. 85. This arises because radioactivation is a nuclear process, and does not involve considerations of the volatility of atomic species, their adhesion to other species, or the excitation behaviour of their external electrons. Direct radioactivation followed by measurement of disintegration rate, all on the intact solid sample and accompanied by a parallel analysis of a standard, should approach absolute accuracy. The standard could be a pure element or compound or a liquid or solid dilution. In this hypothetical case, it has been supposed that the disintegration rate of the activated product could be measured directly on the solid sample (and on the standard) without loss due to self-absorption or interference due to foreign activities. This ideal has been attained in certain instances, such as the direct γ-spectrometer measurements (pp. 99, 103). More generally, the sample must be dissolved after irradiation and a carrier added, followed by radiochemical purification of the element concerned. The radioactivation method will retain high accuracy—if the activated species passes completely into true solution, without loss by volatility, adsorption, or persistent traces of insoluble residues, and if the dissolved species undergoes complete isotopic exchange with the added carrier.

Summarising, the radioactivation method should give a low bias in those favourable cases where it can be applied without radiochemical separation. In its more general applications its accuracy is as good as that of the mass-spectrometer isotope-dilution method, and greater than that of direct emission or mass spectrometry. It is very valuable as a method for the standardisation of samples, *e.g.*, rock samples containing trace elements, which can then be used as standards for emission or mass spectrometry (see below).

Practical applications of radioactivation analysis to the determination of trace elements

There are four major fields where analysis of trace elements is required, namely, geochemistry, biology, physics of the solid state, and nuclear physics.

Geochemistry.—Geochemistry requires reliable analysis of the distribution of the elements, often only in minute amounts, throughout the earth's crust, the oceans, and meteorites. The analytical results provide essential data for the theorist and are occasionally of immediate practical interest, as in geochemical prospecting, *i.e.*, detection of trace elements in neighbouring soils, vegetation, and waters. Brown and Goldberg [35] used radioactivation in analyses of iron meteorites for gold, gallium, rhenium, and palladium ; and Reed and Turkevitch [36] used it for uranium. By its use Morris and Brewer [37] determined gallium in blende, and Long [38] and later workers determined tantalum in minerals. Smales [39] has reported the determination of nickel, copper, cobalt, palladium, gold, and rubidium in samples of granite and diabase which have had world-wide circulation as standards in rock

[35] Brown and Goldberg, *Science*, 1949, **109**, 347; Goldberg and Brown, *Analyt. Chem.*, 1950, **22**, 308.

[36] Reed and Turkevitch, *Nature*, 1955, **176**, 794.

[37] Morris and Brewer, *Geochim. Cosmochim. Acta*, 1954, **5**, 134.

[38] Long, *Analyst*, 1951, **76**, 644.

[39] Smales, *Geochim. Cosmochim. Acta*, 1955, **8**, 300.

analysis. The same author [11] determined traces of uranium in monazite, zircon, and dunite, and Jenkins [7] determined thorium in similar materials. Determination of traces of uranium and thorium in igneous rocks, *e.g.*, granite, is important in attempts to estimate the age of the earth's crust (the radioactivation analyses would of course require to be supplemented by an alternative and more sensitive method of determination of lead—preferably by the mass-spectrometer isotope-dilution technique). In a different method of dating, applicable to potassium minerals, Moljk, Drever, and Curran [40] determined ^{40}A by radioactivation. Herr [23] and (independently) Alperovitch and Miller [24] recently published preliminary evidence for the occurrence of a long-lived ^{98}Tc in Nature, based on neutron activation and detection as ^{99m}Tc.

Smales and Wiseman [41] have discussed the origin of the nickel found in deep-sea sediments, which Pettersson and Rotschi [41a] had ascribed to the deposition of meteoritic dust. Radioactivation analysis for nickel, copper, and cobalt in representative samples of globigerina ooze, red clay, and oceanic rocks from the Atlantic, the Pacific, and the Indian Ocean showed that the ratios nickel : cobalt, nickel : copper, and copper : cobalt were not those accepted for meteorites (13·1, 92, and 0·14 respectively) and were very close to the normal ratios for igneous rocks (3·5, 1·1, and 3·0 respectively).

Recent Harwell determinations, by radioactivation, of trace elements in sea-water include arsenic,[42] rubidium, cæsium,[43] and strontium.[44]

Biology.—Biological work often necessitates determining major constituents in minute samples, *e.g.*, sodium and potassium in single nerve fibres.[45]

Trace analysis is of great importance in studies of the metabolism of potentially toxic elements and of elements which appear to be essential to an organism. In certain cases determination of non-radioactive traces may be sounder than the alternative of following the distribution and excretion of an added radioactive tracer, for sensitive systems may conceivably be modified by the radiation. This objection does not apply to activation of the samples after the required metabolic process has taken place. Harrison and Raymond [46] point out that administration of radioactive isotopes, while giving valuable information on the relative retention and distribution of elements, cannot give information on the absolute excretion rates of these elements. Radioactivation has been applied to problems of animal metabolism by Tobias and Dunn [47] who studied the distribution of gold throughout the tissues of a mouse, 30 days after administration of 1×10^{-5} g.

[40] Moljk, Drever, and Curran, *Nucleonics*, 1955, **13**, No. 3, 44.

[41] Smales and Wiseman, *Nature*, 1955, **175**, 464.

[41a] Pettersson and Rotschi, *Geochim. Cosmochim. Acta*, 1952, **2**, 81.

[42] Smales and Pate, *Analyst*, 1952, **77**, 188.

[43] Smales and Salmon, *ibid.*, 1955, **80**, 37.

[44] Hummel and Smales, *Analyst*, in the press.

[45] Keynes and Lewis, *Nature*, 1950, **165**, 809.

[46] Harrison and Raymond, *J. Nuclear Energy*, 1955, **1**, 290.

[47] Tobias and Dunn, U.S. Atomic Energy Commission Unclassified Report No. A.E.C.D.-2099B.

of inactive gold, and by Harrison and Raymond [46] who studied the fæcal and urinary excretion of strontium and barium from a human subject on a normal diet.

Smales and Pate illustrated the potentialities of radioactivation in the study of arsenic metabolism by carrying out analyses on the individual organs of a normal mouse.[1]

Few applications of radioactivation analysis appear to have been made to studies of the metabolism of trace elements during plant growth. The sensitivity of this method is adequate (at a flux of 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$) to measure submicrogram amounts of P, Ca, K, Cs, Fe, Mn, Cu, Zn, Mo, Co, or Cl : it is interesting that the method is not as sensitive as microbiological assay for molybdenum.[48] Boron would require a specialised technique (see p. 98), and nitrogen and magnesium could be determined at present only at relatively high levels. In certain cases the radioactivation method, which determines the *mass* of the trace element, may usefully supplement microbiological methods, which determine the *availability* of the element. The determination of cæsium and rubidium in seaweed by Smales and Salmon [43] showed that these elements are enriched with respect to sodium, compared to the corresponding values for sea-water.

Physics of the Solid State.—This includes problems as to the effect of trace impurities on electrical, optical, and mechanical properties of solids. For example, the electrical properties of semiconductors such as germanium and silicon are profoundly changed by the presence of 1 part in 10^9 of copper or nickel. The scope of the various methods of trace analysis in the semiconductor field has recently been reviewed by one of us.[49] Radioactivation has been used for the analysis of arsenic [16] down to 0·005 p.p.m., and for nickel [32] down to 0·1 p.p.m. in germanium, by Smales and his co-workers ; for rare earths, antimony, molybdenum, copper, and zinc in germanium oxide and metal at 0·1 p.p.m. by Jakovlev,[50] and for copper in germanium to 0·001 p.p.m. by Szekely.[51] Arsenic and copper have been determined by Smales [32] and by James and Richards [52] in silicon down to 0·0001 p.p.m. In some cases it is now possible to measure a range of elements simultaneously, as discussed on p. 98, by γ-spectrometry on the activated sample. This approach has been followed by Smales [32] * and by Morrison and Cosgrove.[33]

Trace analyses by means of radioactivation have given important results in the study of phosphors and luminescent solids and of γ-dosimeter glasses : *e.g.*, Delberg, Glendenin, and Yuster [53] measured thallium down to 10^{-6} g. in potassium iodide crystals, Grillot [54] measured 10^{-6} g. of copper and

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[48] Nicholas, *Analyst*, 1952, **77**, 629.

[49] Smales, *J. Electronics*, 1955, **1**, 327.

[50] Jakovlev, Geneva Conference on Peaceful Uses of Atomic Energy, August, 1955, Paper 632.

[51] Szekely, *Analyt. Chem.*, 1954, **26**, 1500.

[52] James and Richards, *Nature*, 1955, **175**, 769.

[53] Delbecq, Glendenin, and Yuster, *Analyt. Chem.*, 1953, **25**, 350.

[54] Grillot, *Compt. rend.*, 1952, **234**, 1775 ; cf. Bancie-Grillot and Grillot, *ibid.*, 1953, **237**, 171.

* Cf. also ref. 49.

chlorine in zinc sulphide powders, and Peirson [55] has identified and measured manganese as an impurity in metal phosphates of possible application to dosimeter preparation.

In the metallurgical field, traces of various impurities have been determined by radioactivation in high-purity iron,[56, 32] aluminium,[57] and magnesium [58] metal.

Nuclear Physics.—The application of nuclear physics to the atomic-energy project has set high standards of purity for such basic materials as uranium, thorium, graphite, light and heavy water, beryllium, zirconium, and plutonium. For example, traces of strong neutron-absorbers such as cadmium, boron, lithium, or the rare earths cannot be tolerated in the uranium rods, the aluminium cans, or the graphite moderator of the B.E.P.O. reactor. Among other methods, radioactivation analysis has been used at Harwell for the determination of the individual rare earths [59] and of vanadium [60] in graphite, of hafnium in zirconium,[61] of oxygen in beryllium,[21] and of magnesium, chromium, rubidium, cæsium, silver, antimony, strontium, and cobalt in a sodium–potassium alloy of possible interest as a reactor coolant.[62]

Practical applications of radioactivation analysis on intact samples

The first distinctive feature of radioactivation analysis is its extreme sensitivity, already discussed. The second important feature has only been touched on above, that is, the analysis of *intact* samples. This concept of non-destructive analysis has implications which extend even to industrial processing.

There are at least four reasons for interest in an analytical method which might be applied non-destructively.

(*a*) If it is very rapid and can be made automatic, it could be applied to automatic process-control, *e.g.*, to sorting of mineral mixtures. Or it may be used in process control by providing a human controller with rapid information. This information need not always be of the highest precision provided it is prompt.

(*b*) Certain samples are non-consumable by reason of their historical, scientific, or other interest, or they may be highly toxic.

(*c*) In certain cases any chemical treatment of the sample may be suspect, owing to potential loss of the required constituent by, *e.g.*, volatilisation during acid digestion.

(*d*) It is sometimes possible to derive information about the spatial or surface distribution of the required constituent in an intact sample.

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[55] Peirson, unpublished work at Harwell.

[56] Albert, Caron, and Chaudron, *Compt. rend.*, 1953, **236,** 1030.

[57] *Idem, ibid.*, 1951, **233,** 1108.

[58] Atchison and Beamer, *Analyt. Chem.*, 1952, **24,** 1812.

[59] Cornish, U.K. Atomic Energy Authority Report, A.E.R.E. C/R 1224, 1953.

[60] Smales and Mapper, U.K. Atomic Energy Authority Report, A.E.R.E. C/R 607, 1950.

[61] Smales and Fullwood, unpublished work.

[62] Smales, Geneva Conference on Peaceful Uses of Atomic Energy, August, 1955, Paper 766. Cf. ref. 32.

Radioactivation analysis offers advantages in each of these four fields. In most cases the induced activity is measured by its γ-radiation, which is normally able to penetrate the intact solid without prohibitive loss by self-absorption. The increasing use of γ-scintillation spectrometers [13] facilitates the specific recognition of characteristic γ-energies. It should be emphasised that this type of application accepts each sample very much on its own merits, and the user must be aware of potential interference by extraneous induced activities—that is, it is less universally applicable than the normal sequence of radioactivation analysis including radiochemical purification. Nevertheless, in specific instances it is invaluable. The potentialities are illustrated by the following examples :

(i) Rapid routine analysis (automatic or otherwise) will normally measure a major constituent rather than a trace element, and great interest will attach to short-lived induced activities (many of the data in the Table are irrelevant in this respect, and the full compilations should be consulted). Gaudin and his co-workers [63] investigated the activities induced in 150 specimens of 51 different mineral species by irradiation for 2·5 seconds in a pile at 10^{12}—10^{13} neutrons cm.$^{-2}$ sec.$^{-1}$. The γ-activities were measured 30 seconds after irradiation. Under these conditions, even oxygen and fluorine give significant activities. The authors concluded that it should be possible to separate felspars from iron minerals, copper minerals from pyrites, or galena from limestone, but they stress that each ore-body would present a specific problem as the activities induced in a given mineral species varied considerably from one sample to the next owing to the varying content of impurities. Industrial application of this type of work would require a portable (or readily accessible) neutron source—Gaudin concludes that a flux of about 100 times that offered by curie-level radium–beryllium sources is desirable. It seems possible that this gap can be closed, both by the use of more sensitive γ-counters (a sodium iodide scintillation counter would give about 100 times the sensitivity of the Geiger–Müller tube used by Gaudin) and by the development of neutron sources of higher flux. For example, a large antimony–beryllium source might be prepared by pile irradiation of a massive compact, or large sources of the Be(α,n) type might become available by the use of cheaper α-emitters than radium. Further, particle accelerators might be designed specifically to offer moderate neutron fluxes (by bombardment of an appropriate target) at a reasonable capital cost.

(ii) Radioactivation analysis is being applied currently in the authors' laboratories [64] to the rapid determination of plutonium in metallic and other inorganic compounds by pile-irradiation for 5 seconds, followed by quantitative measurement of a specific γ-emitting fission product, *e.g.*, ^{131}I (0·36 Mev) or ^{140}Ba–La (1·60 Mev), by means of a scintillation spectrometer. In certain cases the quantitative measurement can be carried out with moderate precision by use of an inexpensive ionisation chamber (radiation monitor) without discrimination between individual γ-emitting fission products. Chemical methods are, of course, available for the analysis of such materials,

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[63] Gaudin, Senftle, and Freyberger, *Eng. Min. J.*, 1952, **153,** No. 11, 95, 174.

[64] Atkins, Phillips, and Jenkins, unpublished work.

but radioactivation is quicker and avoids excessive handling of a toxic material.

Again, several workers have determined the arsenic content of human hair in medicolegal analyses. Griffon and Barbaud [65] measured the induced ^{76}As activity without chemical separation, at various points along intact hairs. This approach might be useful in demonstrating relatively high levels of arsenic content, if backed up by γ-spectrometry and decay studies to provide a specific identification. It would have the virtue of preserving the specimen intact as a legal exhibit.

(iii) Examples of the application of radioactivation to the analysis of silicon semiconductors by direct γ-spectrometry immediately after irradiation have been given on p. 99. This technique avoids possible loss, *e.g.*, of arsenic, during chemical dissolution.

(iv) Autoradiography of uranium and thorium inclusions in polished mineral specimens has been carried out by placing a sensitive emulsion against the surface and recording the tracks of the ionising α-particles. Curie and Faraggi [31] extended this method by irradiating the specimen and emulsion, in mutual contact, in the Chatillon pile. The densely ionising recoil fragments from the fission of uranium atoms left heavy tracks and served to distinguish uranium from thorium segregations, in polished granite samples. Further applications of activation analysis to autoradiography have either involved direct irradiation of the sample and the emulsion as above, or have brought the sample and the emulsion into contact after irradiation. The method has been used in studying the segregation of uranium and of lithium in minerals,[31, 30] of arsenic,[66] boron,[67] and carbon [68] in steels, of lithium [69] and possibly boron and iodine [70] in biological samples, and of sulphur, phosphorus, and chlorine- and bromine-containing organic compounds on paper chromatograms.[71]

The autoradiography of an activated sample need not be confined to the use of contact emulsions or films. The γ-emitting centres on the active surface could be made to form an image on a distant film by the use of a γ-sensitive pin-hole camera : it appears that a resolution of at least $\frac{1}{4}$ inch can be achieved.[72] Alternatively, the surface may be scanned by a lead-shielded collimator, and the activity at any given spot recorded.

Conclusions

Radioactivation analysis is extremely sensitive for a large number of the elements and in this respect may be compared with emission and mass

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[65] Griffon and Barbaud, *Compt. rend.*, 1951, **232**, 1455.

[66] Kohn, " Radioisotope Conference, 1954 ", Butterworths, London, 1954, Vol. II, p. 68.

[67] Faraggi, Kohn, and Doumerc, *Compt. rend.*, 1952, **235**, 714.

[68] Curie, *J. Phys. Radium*, 1952, **13**, 497.

[69] Ficq, *Compt. rend.*, 1951, **233**, 1684.

[70] Mayr, *Nucleonics*, 1954, **12**, No. 5, 58.

[71] Winteringham, Harrison, and Bridges, *ibid.*, 1952, **10**, No. 3, 52 ; Schmeiser and Jerchel, *Angew. Chem.*, 1953, **65**, 366, 490.

[72] Mortimer, Anger, and Tobias, U.S. Atomic Energy Commission Unclassified Report No. U.C.R.L.-2524, 1954.

spectrometry. The ubiquitous traces of contaminants in most chemical reagents do not normally cause difficulties in radioactivation : this is perhaps its most distinctive feature. The ease with which both the sample and the standard may be activated at the same time and under closely similar conditions makes the method valuable in the calibration of reference samples, later to be used as standards for other methods such as emission spectroscopy. Activation is best carried out in the high flux of thermal neutrons within a nuclear reactor. At least 50 reactors [17] of various types were known to be operating in 1955, including several comparatively inexpensive low-power reactors which are suitable for use as neutron sources by universities and industrial research organisations.

The chief significance of radioactivation analysis will probably be its contribution to the measurement of trace elements : a secondary interest may be that of rapid, industrial, control analyses on intact samples.