ACTIVATION ANALYSIS

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I. Introduction

The determination of elements by means of their natural radioactivity has been an established analytical method for a number of years. While it possesses distinct advantages in certain cases, the method is limited to those naturally occurring radioactive elements which show a readily perceptible level of activity.

The discovery by Curie and Joliot (*19*) that radioactivity could be induced in a number of light elements by bombardment with alpha particles enabled the range of this method to be extended. Fermi (*23*) greatly increased the number of elements that could be activated artificially by using neutrons, which had been slowed down by passage through water or paraffin wax, as projectiles. It is primarily the method of activation first investigated by Fermi that has enabled activation analysis to develop into the highly sensitive analytical tool it is today.

Activation analysis consists in the determination of the amount of an element present in a sample by measuring the intensity of activity induced in that element by bombardment with suitable nuclear projectiles. With some reservations which will be discussed below, the activity induced is proportional to the amount of element present and is independent of its chemical state. In practice a standard is usually irradiated with the sample and the measured intensities of their radiation compared. This technique, known as comparative activation analysis, has the advantage that the absolute value of the flux of activating particles and the activation cross section for the nuclear reaction induced need not be known. In certain cases the activities may be compared without chemical separation, but frequently the method contains steps designed to isolate the required element in a pure state prior to measuring its activity. The necessary chemical operations are normally carried out in the presence of an inactive isotopic carrier added after the activation.

Whether separation is carried out or not, the mass of the element X determined in the sample, is given by the equation:

$$\frac{\text{mass of } X \text{ in sample}}{\text{mass of } X \text{ in standard}} = \frac{\text{radiation intensity from } X \text{ in sample}}{\text{radiation intensity from } X \text{ in standard}}.$$

Activation analysis was first applied by von Hevesy and Levi two years after the discovery of artificial radioactivity (*36*). Determination of 0.1% dysprosium in rare earth mixtures was made by activation with neutrons from a 300-millicurie radium emanation-beryllium neutron source. The 2.3-hr half-life induced activity due to Dy^{165} was compared with that induced in mixtures of known dysprosium content. A similar method was used to determine europium in gadolinium.

Further advances were necessarily limited until the development of the high-voltage accelerating machine, and, of greater importance, the advent of the nuclear reactor. The high charged particle or neutron flux obtainable from these sources has extended the range of elements susceptible to activation analysis and greatly increased the sensitivity of the method. At present more than 60 elements have been determined successfully, many of them in the submicrogram region.

The bulk of the published work on activation analysis has been concerned with neutron activation and this, the more general technique, will be dealt with in some detail. Activation with charged particles will be considered in Section VII.

II. Irradiation

If the sample containing the element to be determined is placed in a homogeneous flux of neutrons, some may be captured by the target nuclei to produce radioactive isotopes. These compound nuclei are unstable, having a definite probability of decay, and some will disintegrate during the bombardment. As a result, concentration of the radioactive species will increase until it is such that the rate of formation is equal to the rate of decay.

The rate of formation is given by $f\sigma N$, where f is the activating flux in particles per square centimeter per second, σ is the activation cross section in square centimeters for the reaction, and N the number of nuclei of the isotope involved. The rate of decay is λN^*, λ being the decay constant of the radioactive species of which N^* atoms are present. The over-all rate of growth is then given by:

$$dN^*/dt = f\sigma N - \lambda N^*. \tag{1}$$

Integration over the irradiation period t gives:

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

At the end of the irradiation the activity A_t in disintegrations per second from the N^* unstable atoms present is λN^*, and therefore:

$$A_t = \lambda N^* = f\sigma N(1 - e^{-\lambda t}). \tag{3}$$

The decay constant is related to the half-life of the nuclide, $T_{½}$, by the expression:

$$\lambda = 0.693/T_{1/2}. \tag{4}$$

Substituting for λ in Eq. (3)

$$A_t = f\sigma N(1 - e^{-0.693t/T_{1/2}}). \tag{5}$$

The expression within parentheses is termed the growth or saturation factor and reaches a maximum value of unity for infinitely long irradiations when

$$A_t = A_{t=\infty} = f\sigma N. \tag{6}$$

A value of 0.5 for the saturation factor is obtained for irradiations of one half-life and is proportionately smaller for shorter irradiations. Irradiation for ten half-lives gives a value of the saturation factor of 0.999, but except in the case of very short-lived isotopes it is seldom worthwhile to irradiate for periods longer than one half-life, as thereafter long-lived activities formed by neutron capture in extraneous impurities in the sample build up at a greater rate than the desired isotope.

Equation 5 can be simplified by replacing the number of atoms N by $W\phi/M$, where W is the weight of the element present, ϕ is the abundance of the isotope activated, and M the chemical atomic weight. If σ, the activation cross section, is expressed in barns (1 barn is equal to 10^{-24} square centimeters) it reduces to

$$A_t = W\phi\sigma f\, 6.02 \times 10^{23} \times 10^{-24}(1 - e^{-0.693t/T_{1/2}})/M \tag{7}$$

all variables being related to the final radioactivity of the nuclide formed.

It must be stressed that when this formula is used to find the total radioactivity of an irradiated element it must be applied to each isotope of the element in turn.

Values for the growth factor are conveniently obtained from a prepared graph, such as that of Smales (*82*), or from a nomogram (*96*).

As soon as the sample is removed from the activating flux, its initial activity A_0 will commence to decay exponentially, the activity $A_{t'}$, after a time t', being given by

$$A_{t'} = A_0e^{-0.693t'/T_{1/2}}. \tag{8}$$

With elements of short half-life, the sensitivity of the method, besides being dependent on the flux and activation cross section, will also depend on the time which must elapse between the termination of activation and the measurement of the activity. With short-lived nuclides this period frequently determines the over-all sensitivity of the method.

Fluctuations in the neutron flux can lead to errors caused by an unequal degree of activation in the samples and standards. The effects may be minimized by irradiating samples and standards very close together. More important are variations caused by progressive reduction of the effective neutron flux through either samples or standards due to the presence of elements having a high capture cross section for neutrons of the particular energy range in the irradiation position. To some extent this self-shielding effect can be eliminated by taking small samples and diluting the standards with material of low cross section (e.g., water, silica, alumina, or sucrose). Some idea of the extent of self-shielding to be expected can be obtained by means of the equation

$$f = f_0e^{-N\sigma r} \tag{9}$$

where f_0 and f are the initial and attenuated flux, N the number of absorbing centers per cubic centimeter, r the radius of a spherical sample, and σ the total neutron absorption cross section for the complete energy spectrum.

In a discussion of the errors in neutron activation analysis Plumb and Lewis (*72*) deal with the effect of self-shielding by resonance neutrons. Neutrons emitted during the fission of U^{235} have energies ranging from 0 to about 15 Mev. The energy of the faster neutrons is reduced by collision with a moderating material (graphite or light or heavy water) until they have a Maxwellian distribution of energy around 0.025 ev and are described as thermal. Most of the reactions utilized in activation analysis are of the (n,γ) type and are induced by thermal neutron capture. As the neutron energy is increased from the thermal region, the capture cross section for the (n,γ) reaction decreases as the inverse of the neutron velocity ($1/V$ law), although a very high cross section is often obtained over a small energy range (*40*). These resonance peaks as they are called are superimposed on the otherwise linear variation of cross section with $1/V$, and occur in the intermediate or epithermal region of the energy spectrum, 0.1 ev to about 50 kev. At higher energies the $1/V$ law no longer holds, and the cross section does not change with energy. However, at these higher energies reactions such as (n,p) and (n,α) become of increasing importance and these can cause complications, as will be considered below.

If the element being determined or a constituent of the sample matrix material has a high capture cross section for thermal or resonance neutrons, possible errors due to self-shielding cannot be ignored.

The level at which self-shielding errors become significant may be measured by irradiating increasing weights of the material under investigation either as solids of similar general shape or in solution. After irradiation the specific activity due to the unstable nuclides in each of the samples is measured. If this is constant and does not increase with dilution self-shielding is insignificant. A progressive decrease in specific activity with increasing sample weight is indicative of self-shielding. Cabell and Smales (*12*) used this technique in an investigation of the self-shielding effect in the caesium and rubidium chloride standards used in the determination of these elements in materials of geological interest. In the determination of sodium at the submicrogram level in lithium Smales and Loveridge (*85*) measured the extent of self-shielding resulting from the high cross section (67 barns) of the matrix material. With samples weighing 50-100 mg a mean negative error of between 10 and 20% was observed.

The contribution to neutron activation by resonance neutrons alone can be determined by irradiating two identical samples of the element of high cross section, one wrapped in thin cadmium foil. Cadmium is practically opaque to thermal neutrons ($\sigma = 20{,}000$ barns), so that any activity induced in the wrapped sample must be due to neutrons of energies other than thermal.

Self-shielding of resonance neutrons can be minimized by irradiating in the graphite-loaded column (thermal column) of the pile. Here the contribution by neutrons of energies greater than thermal is considerably reduced.

III. Radiation Sources

The sensitivity of activation analysis is directly proportional to the particle flux employed. In consequence it is the aim of the analyst interested in trace element determinations to obtain the highest possible flux, which for neutron activation is found together with certain other advantages in the nuclear reactor. Table I contains a list of some research reactors, with their fuels, moderators, and the thermal fluxes obtainable from them (*13*). The value for DIDO has been added.

TABLE I

THERMAL NEUTRON FLUX AVAILABLE FROM SOME NUCLEAR REACTORS

Reactor	Fuel	Moderator	Flux (neutrons/cm^2/sec)
BEPO (England)	Natural uranium	Graphite	2×10^{12}
BNL (Brookhaven, U.S.A.)	Natural uranium	Graphite	5×10^{12}
X-10 (Oak Ridge, U.S.A.)	Natural uranium	Graphite	1.1×10^{12}
NRX (Canada)	Enriched uranium	D_2O	6.8×10^{13}
MTR (Idaho, U.S.A.)	Enriched uranium	H_2O	5×10^{14}
LITR (Oak Ridge, U.S.A.)	Enriched uranium	H_2O	4×10^{13}
DIDO (England)	Enriched uranium	D_2O	1×10^{14}

Particle accelerating machines may also be used in the production of neutrons by secondary reactions. In general the steady flux is lower than that listed for nuclear reactors. If thermal neutrons are required, moderation is usually carried out by allowing the neutrons to pass through paraffin. Table II includes some results for a number of typical particle accelerators (*34*, *101*).

TABLE II

NEUTRON FLUX AVAILABLE FROM ACCELERATING MACHINES

Type	Particle and target	Ion current and particle energy	Neutron emission (neutrons/sec)	Approximate thermal flux in moderator (neutrons/cm^2/sec)
Cyclotron	Be^9 (*d*,*n*) B^{10}	1 ma, 8 Mev	3×10^{13}	1×10^{11}
Van de Graaff	Be^9 (*d*,*n*) B^{10}	50 μa, 2 Mev	1×10^{10}	5×10^{8}
Cockcroft-Walton	T (*d*,*n*) He^4	100 μa, 250 kev	1×10^{9}	1×10^{8}
Betatron	*e*-U	3 μa, 80 Mev	2×10^{10}	1×10^{8}
Linear accelerator (Harwell)	*e*-U	25 ma, 14 Mev	4×10^{14}	—

Neutron activation analysis using low-level laboratory sources of neutrons has received some attention, although because of the low fluxes available the sensitivity of the method is greatly reduced. Meinke and Anderson (*57*) have explored the possibility of using them for precise work. Table III contains results for neutron emission from some laboratory sources (*2*, *103*).

The figures in Table III refer to unmoderated neutrons. Sources containing radium and antimony require shielding, because of the intense gamma radiation emitted. Pu^{239}-Be and Po^{210}-Be sources have the advantage in that their decay is practically free from gamma emission, and consequently much less shielding is required. Po^{210} suffers from the disadvantage of a short (138 day) half-life. The same disadvantage applies to the photoneutron source listed, although this may be reactivated by pile irradiation.

TABLE III

NEUTRON EMISSION FROM LABORATORY NEUTRON SOURCES

Type	Reaction	Half-life	Neutron emission (neutrons/curie/sec)
Pu^{239}-Be	$Be^9(\alpha,n)C^{12}$	24,400 yr	1.4×10^7
Ra^{226}-Be	$Be^9(\alpha,n)C^{12}$	1,622 yr	1.3×10^7
Po^{210}-Be	$Be^9(\alpha,n)C^{12}$	138 days	2.6×10^6
Sb^{124}-Be	$Be^9(\gamma,n)Be^8$	60 days	3.2×10^6

IV. Experimental

A. PREPARATION OF SAMPLES

In activation analysis, as in all trace element determinations, care must be exercised to avoid contamination. One of the advantages of activation analysis is that the manipulation prior to irradiation of the sample is minimized. Contamination by inactive material after irradiation is unimportant, provided it does not take place in amounts sufficient to affect the chemical yield. The restrictions imposed on neutron activation by self-shielding mentioned above may necessitate the use of small samples and either liquid or solid dilutions of the pure standard material to overcome the difficulty.

In research reactors where the operating temperature is low, short irradiations may be performed in polythene provided that liquids are not used. Where long irradiations are necessary, or for small volumes of liquids, it is customary to seal samples and standards in silica ampoules.

B. Radiochemical Purification

Normally, as soon as possible after completion of the irradiation the sample is subjected to radiochemical purification designed to isolate the required product free from foreign activities.

With products of short half-life the time necessary for achieving the radiochemically pure final source for activity measurement must be as short as possible if the method is to show high sensitivity. As the activated nuclide is frequently present at the microgram or submicrogram level, a quantitative separation from many times its weight of the sample matrix material would present great difficulty. Instead it is customary to add inactive isotopic carrier at the milligram level and, after ensuring that chemical exchange takes place between it and the active nuclide, to isolate the required element by specific chemical steps. These steps need not be quantitative; the percentage recovery of the carrier can be determined at the end of the experiment and the measured activity corrected to 100% chemical yield. Care must be taken that exchange between the carrier and the irradiated material is initially complete.

Radiochemical purification of the induced activity in the presence of carrier involves chemical operations such as precipitation, distillation, solvent extraction, chromatography, and ion exchange. While the chemistry performed on the carrier and sample should be designed to isolate the material in a pure state, a useful operation frequently carried out is scavenging. Strongly adsorptive precipitates such as ferric hydroxide, lanthanum fluoride, and antimony sulfide may be formed in the solution. These precipitates, by coprecipitation, occlusion, and surface adsorption can be used to remove unwanted traces of activity. A scavenging agent should be chosen that will not carry down appreciable amounts of the carrier from solution. An alternative method is to add "hold-back" carriers for the unwanted traces of activity and precipitate the required element in their presence.

Activation analysis has the advantage over other methods of trace element determination, in that after irradiation it is insensitive to contamination by inactive material. However, where nuclides of long, or moderately long, half-life are estimated in a radiochemical laboratory precautions must be taken to prevent contamination with residual activity from previous analyses.

A number of accounts of methods used in the radiochemical purification of a variety of elements has been published (*17, 51, 52, 55, 56*).

In the chemical separation it is advisable for the standards to be taken into solution with carrier, precipitated, weighed for chemical yield determination, and the radioactivity measured in exactly the same form as the sample. Where pure standard materials are employed it may not be necessary to subject the standards to the entire radiochemical purification. It is important, however, that the final source should be in the same form and contain approximately the same weight of material as those derived from the sample in order to minimize self-scatter and self-absorption errors. If the chemical yields and consequently the source weights differ considerably, corrections for self-absorption may be made from an experimentally determined curve.

C. SOURCE PREPARATION

After the final precipitation stage in the radiochemical purification, the compound of activated element and carrier is mounted in a form suitable for the measurement of the radiation emitted from the unstable nuclei present. If the final assay of activity is by beta counting, care must be exercised in the selection of a suitable compound for the source and in ensuring that it is evenly spread on the counting tray. The choice of a compound for the source material is governed by the chemistry of the element and in cases such as the alkali metals, niobium, and tantalum the lack of suitable compounds is an added complication. Where a number of compounds are available the final choice should be made after consideration of the following points. The compound selected should be stoichiometric and should have a low solubility in order to prevent excessive losses in the final precipitation. Elements of high atomic number should be avoided in the source as far as possible and this is of particular importance with nuclides emitting soft beta particles (those with a maximum energy of not greater than 0.5 Mev). Since it is frequently convenient to dry the source under an infrared heating lamp the compound selected should be or become thermally stable, at least to the maximum temperature likely to be encountered. Finally, the dry source should not be loose and powdery so that it is difficult to handle or so coarse-grained that an evenly spread source cannot be obtained.

A number of techniques have been employed for source mounting. The source material may be slurried on to a weighed circular aluminum tray with a little alcohol or water. The process need not be quantitative. Solvent is removed from the tray, conveniently by surface heating under an infrared heating lamp. In another widely used technique the source precipitate may be deposited onto a small circle of filter paper by suction, dried, and fixed to a suitable backing material of low atomic number before counting. The source may also be deposited onto a metal disk or filter paper circle fitted into a demountable centrifuge tube. A good method which is unfortunately not generally applicable is electrodeposition directly onto the counting tray. Details of these and other techniques will be found in text books on radiochemistry (*15, 24*).

D. Activity Measurements

It has already been mentioned that difficulties are to be expected in counting sources of nuclides emitting soft beta particles. These difficulties increase as the maximum energy decreases, and with beta particles whose maximum energy is less than 0.2 Mev special mounting and counting techniques are required. However, the majority of determinations can be carried out with comparatively simple and inexpensive equipment. The minimum essential consists of a lead-shielded end-window Geiger-Muller tube, a power pack able to deliver up to 2000 volts, a preamplifier, and a scaling unit.

It has been assumed that the chemical procedure used to isolate the element after the addition of carrier has been successful, and the final product is free from all extraneous activity. Frequently the reliability of this assumption can be verified without a great deal of difficulty, by the application of some or all of the following checks: (1) determination of the half-life; (2) determination of the maximum beta energy; (3) examination of the gamma spectrum.

1. If short-lived nuclides are produced during activation, measurements of the count rate can be made for a period of several half-lives and decay curves constructed. After corrections for the background and dead time of the counter, successive counts can be plotted on a logarithmic scale against time expressed linearly. Provided that the activity is pure and no daughter activities grow into the sample, the resultant plot will be a straight line whose slope is related to the half-life of the nuclide, those derived from samples and standards being parallel. However, frequently more than one isotope of an element is produced during irradiation. Thus during the neutron irradiation of antimony, beta activities of half-life 2.8 days due to Sb^{122} and 60 days due to Sb^{124} are formed and a plot of the count rate against time results in a composite decay curve. In comparative activation analysis, where pure standard activities are obtained, the resolution of such a decay curve is not usually necessary, but occasionally the presence of foreign activity may necessitate resolution in an attempt at identification. In a limited number of cases encountered in activation analysis daughter activities may grow into the pure activity isolated and a composite decay curve will result. Smales (*81*) used fission product Ba^{140} in the determination of U^{235} by neutron activation in materials of geological interest. This isotope has a half-life of 12.8 days and decays by beta emis-

sion (maximum energy 1.02 Mev) to daughter La^{140}, half-life 40.2 hr, maximum beta energy 2.20 Mev. The characteristic nature of the growth-decay curve in such cases may actually aid identification.

2. With long-lived isotopes or where the half-lives of two nuclides are sufficiently close to make resolution difficult, absorption measurements are frequently made.

Positive or negative beta particles emitted from unstable nuclides (as opposed to conversion electrons) have energies ranging from a maximum, E_{MAX}, to zero with an average energy of approximately one-third of the maximum. In view of the complex energy spectrum the maximum energy is usually determined by absorption methods. A number of techniques have been described, depending on the activity present in the sample and the required accuracy (*21*). An additional method may be applied if a check on the radiochemical purity of the sample rather than an energy determination is sufficient. The absorber curve for the sample may be superimposed over that for the radiochemically pure standard obtained under the same conditions. If no gross contamination is present the two plots will be identical in shape.

3. Emission of a beta particle or positron from a parent element often leaves the daughter in an excited state, excitation energy being lost by the emission of a monoenergetic gamma ray photon or photons. Measurement of the characteristic gamma spectrum which is associated with the nuclear event is often a help in the identification or determination of the nuclide. Alternatively, examination of the gamma spectrum may be used as an additional check on the purity of the source.

Owing to the low efficiency of detection (rarely more than 1%) of gamma radiation by a Geiger-Muller tube, a scintillation counter is normally used for this purpose. Scintillation counters employing large crystals of organic materials such as naphthalene or anthracene have been used as phosphors with detection efficiencies of better than 10%. A phosphor of higher atomic number such as sodium iodide, activated by the presence of about 1% of thallium iodide, will give better efficiency and is usually employed. The phosphor crystal is mounted in optical contact with a photomultiplier tube, pulses from which are amplified and fed into a scaler.

The energy of gamma radiation can, like that of beta particles, be determined by means of an absorber curve using a scintillation counter as detector. However, on account of the greater penetrative powers of gamma radiation, lead rather than aluminum absorbers are used. If sufficient activity is present in the sample a single-channel gamma spectrometer may be employed (*14, 68, 70, 71*) and the energy spectrum compared with that obtained from standards. If the activity level from the sample is too low for it to be examined on the single channel gamma spectrometer, a multichannel instrument can be used (*25, 43, 104*).

The application of some or all of these checks on the purity of the isolated activity coupled with the specific radiochemical purification render the over-all specificity of activation analysis high.

In the past the greatest sensitivity attainable in activation analysis has been found in beta counting. The background of a conventional shielded beta counter is of the order of ten counts per minute, because of cosmic radiation and the materials used in the construction of the counter and castle. The large crystals used for gamma scintillation counters still suffer from a high background caused by traces of potassium in the crystals and by the difficulty of shielding them from extraneous radiation. However, gamma counting in a single channel of a gamma spectrometer can rival beta counting in sensitivity and should become of importance in activation analysis as these instruments become increasingly available.

E. GAMMA SPECTROMETRY

After irradiation it is quite feasible to take the sample into solution in the presence of carriers and isolate a series of radiochemically pure compounds for counting. This in fact has been done by Smales *et al.* (*86*), who determined 2.5-hr half-life Ni^{65}, 12.9-hr half-life Cu^{64} and 5.3-yr half-life Co^{60} in rocks, marine sediments, and meteorites by neutron activation. These workers are currently estimating ten elements in similar materials (*89*).

The advantage of this method is obvious where it is essential to obtain as much information as possible about trace element abundances on limited amounts of irreplaceable material such as meteorites.

Direct estimation of a number of elements without separation is a perfectly feasible method provided that the activity induced in the matrix material during irradiation is not excessive. Resolution of decay curves alone is not likely to be widely applicable, but if this is accompanied by gamma spectroscopy the utility of the method is considerably extended. Morrison and Cosgrove (*63*) determined Zn^{69}, As^{76}, W^{187}, Fe^{59}, and Na^{24} in neutron irradiated silicon by direct gamma scintillation spectrometry. Smales (*84*) neutron irradiated samples of a sodium-potassium alloy and, after allowing two weeks for decay, direct gamma spectrometry revealed the presence of Cs^{134} (0.59, 0.80 Mev γ), Ag^{110} (0.88, 1.36, 1.48 Mev γ), and Rb^{87} (1.09 Mev γ). Quantitative analysis gave 100 ppm of silver and 5 ppm of rubidium. In a separate analysis which included a radiochemical purification, 0.1 ppm of caesium was obtained. A two-crystal gamma spectrometer was employed by Iredale (*44*) in an examination of "superpure" aluminum after pile irradiation. With this instrument he was able to detect and determine manganese, copper, sodium, antimony, and scandium.

Salmon (*78*) has extended the applicability of the method of direct gamma spectroscopy by the determination of cobalt in iron using gamma-gamma coincidence measurements. Fe^{59}, half-life 46 days, emits gamma photons of energy 1.12 and 1.30 Mev, while 5.3 yr half-life Co^{60} emits gamma photons of 1.16 and 1.32 Mev. Clearly it would be impossible to differentiate between the two nuclides on a conventional spectrometer. Fe^{59} can decay in two distinct ways, each way being associated with its own gamma ray photon. Co^{60}, however, has only one mode of decay and the gamma photons associated with it are emitted within a very short time of each other. By counting the coincident pairs of gamma rays Salmon was able to differentiate between cobalt and iron, and by this method he determined cobalt at the 0.02 to 0.25% level in steels after pile irradiation.

F. Measurements During the Activating Collision

The measurement of radiations emitted during the activating collision is a method that has been applied in a number of cases where the sensitivity of neutron activation analysis is otherwise poor.

One method, of particular interest for the light elements, utilizes the prompt photoneutron emission which follows gamma irradiation. This method is not generally applicable without some apparatus for producing high-energy gamma rays. But, in the cases of beryllium and deuterium, the thresholds for the (γ,n) reaction are sufficiently low to enable a laboratory source of gamma radiation to be used. Gaudin and Pannell (*26*) determined beryllium at the 1-2 ppm level in low-grade ores by irradiating the samples with gamma ray photons from Sb^{124} (maximum energy 2.11 Mev, half-life 60 days) and counting the neutrons emitted after moderation in paraffin wax in boron trifluoride-filled neutron detectors. The threshold value for the reaction $Be^9(\gamma,n)2He^4$ is 1.63 Mev. Haigh (*31*) utilized the reaction $D^2(\gamma,n)H^1$, gamma threshold 2.2 Mev, for the determination of deuterium in relatively pure liquids, using a Na^{24} source of 15.0-hr half-life and maximum gamma energy 2.76 Mev. After moderation in paraffin the neutrons were counted in boron-lined ionization chambers. Any beryllium, which has a lower gamma threshold, in the samples would emit neutrons under these conditions.

The extension of the techniques of measuring the radiation emitted during the activating collision to pile irradiation requires a method of detection sensitive to the nuclear event but relatively insensitive to the pile neutron and gamma flux. Stewart and Bentley (*97*) estimated uranium extracted from sea water by irradiating the sample in a neutron beam in the counting chamber of a fission fragment counter.

A more common technique employs a nuclear emulsion to detect the radiation. The sample is irradiated in close proximity to a sensitive emulsion, which is subsequently developed, fixed, and examined under the microscope. In this way it is possible to distinguish tracks due to alpha particles, fission fragments, etc. Faraggi *et al.* (*22*) and Mayr (*54*) used this technique to determine boron by the $B^{10}(n,\alpha)Li^7$ reaction down to a level of 2×10^{-9} gm. Lithium at the 10^{-11}-gm level was determined by Picciotto and van Styvendael (*69*) by the reaction $Li^6(n,\alpha)H^3$ and Curie and Faraggi (*18*) studied the distribution of uranium in the surface of polished mineral specimens by the U^{235} (n,f) reaction.

G. Precision and Accuracy

Before any discussion of the precision and accuracy of activation analysis, it is important that the distinction between them should be appreciated. Precision is an index of the reproducibility of repeated individual analyses, whereas accuracy is a measure of the closeness of the mean value to the truth.

Although many papers give data from which the precision of the method they describe can be calculated, with the exception of that of Seyfang (*79*) little work has been done specifically with the object of attaining high precision in activation analysis. The isotopic content of depleted and enriched uranium had been determined by Seyfang and Smales by means of the fission product Ba^{140} produced during pile irradiation (*80*). Seyfang, using the same method, showed that the precision could be improved by paying more attention to the weighing and counting procedures. The following points were considered:

1. By weighing the uranium oxide samples and barium sulfate sources to the nearest 0.05 mg the error was ±0.1% or less.
2. Precautions taken with the counting equipment enabled repeat counts from a pulse oscillator to be recorded with a coefficient of variation of ±0.1%.
3. The paralysis time of the counting set up was adjusted to 300 ±2 μ sec, thereby enabling accurate coincidence corrections to be made.
4. Hysteresis in the Geiger counter was eliminated by placing the source under the window for several minutes before counting started.

Seven portions of natural uranium as the oxide U_3O_8 were irradiated, processed chemically after the addition of barium carrier, and the barium sulfate sources counted for 4 min (approximately 50,000 counts). The coefficient of variation on a single result was found to be ±0.53% of which 0.44% was due to statistical variations in the count rate.

The precision of activation analysis is, when all other variables have been eliminated, limited by statistical variations in the counting rate. Consequently the precision will tend to decrease as the amount of element estimated and the activity present in the final source derived from it becomes smaller. However, statistical variations in the counting rate are rarely of importance except at extreme sensitivity and then the effect can be minimized by increasing the counting period.

Determinations of the accuracy of activation analysis are complicated by the lack of suitable standard materials whose trace element content has been unequivocally established. Smales *et al.* (*86*), in the determination of nickel, cobalt, and copper in iron meteorites and other materials, tested the accuracy of their method by the analysis of commercially available standard steel samples. Satisfactory agreement was obtained between the activation results and the published values for nickel and copper, but in many cases the cobalt content by activation differed widely from the published figure (see Table IV). Results for the cobalt content determined by an absorptiometric method using tetraphenyl arsonic acid which confirmed the activation results were published in the same paper. More recently Bagshawe (*4*) independently confirmed the activation values for cobalt with results obtained with an absorptiometric method using nitroso-R salt.

TABLE IV

COBALT RESULTS ON STANDARD STEELS

Alloy steel number	Published average Co content	Co content by activation	Co content by absorptiometry	
			Tetraphenyl arsonic acid	Nitroso-R salt
251	0.018	0.070	0.073	0.070
252	0.015	0.043	0.043	0.042
253	0.012	0.031	0.030	0.032
254	0.010	0.027	0.027	0.029
255	0.006	0.019	0.020	0.020
256	0.016	0.031	0.031	0.034

While steel samples may be used as reasonable alternatives to iron meteorites in accuracy determinations they would not be as suitable in comparisons with silicate rocks. A granite G1 and a diabase W1 have been suggested as international standards for the determination of the major and minor constituents of igneous rocks. A number of workers using several separate methods including neutron activation have determined the

TABLE V

RUBIDIUM IN G1 AND W1

Analyst	Method	Rb found (ppm)	
		G1	W1
Smales and Webster (*94*)	Stable isotope dilution	214	21.3
Cabell and Smales (*12*)	Neutron activation	219	21.4
Herzog and Pinson (*35*)	Stable isotope dilution	216	28.5
Horstman (*37*)	Flame photometry	205	19
		204	25

rubidium content of G1 and W1. Table V taken from Smales and Webster (*93*) contains some published results for the rubidium content.

The accuracy of the activation analysis method when applied to sea water has been checked by comparison with other methods in the case of rubidium and strontium. The rubidium content (Table VI) of a sample of sea water has been investigated by Smales and Salmon (*92*) using neutron activation and by Smales and Webster (*94*) with an isotope-dilution method.

TABLE VI

RUBIDIUM IN SEA WATER

Analyst	Method	Rb content (μg/liter)
Smales and Webster	Stable isotope dilution	121.4 ± 5
Smales and Salmon	Neutron activation	120 ± 10

Hummel and Smales (*42*) determined the strontium content of sea water by neutron activation, isotope dilution using Sr^{84}, and a tracer technique with Sr^{89} (see Table VII).

TABLE VII

STRONTIUM IN SEA WATER

Method	Strontium content (mg/liter)
Stable isotope dilution	8.1 ± 0.1
Neutron activation	8.1 ± 0.3
Tracer technique	8.0 ± 0.1

From the published results for the accuracy of activation analysis applied to three widely different matrix materials it will be seen that the accuracy compares very favorably with other modern techniques. The case of cobalt is particularly interesting, inasmuch as the results obtained by activation analysis indicated the unreliability of conventional analytical methods when applied to this estimation at low levels.

V. Conflicting Nuclear Processes

Limitations may be imposed on activation analysis by conflicting nuclear processes. These have been mentioned above as becoming of increasing importance in neutron activation when the particle energy increases above that necessary to bring about the required interaction.

In the nuclear reactor the normal reaction used in activation analysis is the (n,γ) induced by thermal neutrons but there are several routes by which a nuclide A of atomic number Z and mass M may be produced:

1. A_{Z}^{M-1} (n,γ) A_{Z}^{M}
2. A_{Z+1}^{M} (n,p) A_{Z}^{M}
3. A_{Z+2}^{M+3} (n,α) A_{Z}^{M}
4. A_{Z}^{M+1} $(n,2n)$ A_{Z}^{M}
5. A_{Z}^{M+1} (γ,n) A_{Z}^{M}
6. A_{Z+1}^{M+1} (γ,p) A_{Z}^{M}

The following are indirect methods of forming the radio-nuclide:

7*a*. A_{Z-1}^{M+1} (n,γ) $A_{Z-1}^{M} \xrightarrow{\beta} A_{Z}^{M}$
7*b*. A_{Z-1}^{M-2} (n,γ) $A_{Z-1}^{M-1} \xrightarrow{\beta} A_{Z}^{M-1}$ (n,γ) A_{Z}^{M}

Isotopes of elements of intermediate mass number may be formed by nuclear fission of heavy elements.

8. Heavy elements (n,f) fission products

The more important of these reactions will be considered below. Reactions *2*, *3*, and *4* are brought about by the fast neutron flux in the pile, which flux Mellish *et al.* (*59*) calculated to be 0.17 of the slow flux in the center of the Harwell pile (BEPO). Fortunately, however, the cross sections for these reactions are usually considerably lower than those for normal (n,γ) reactions induced by thermal neutrons. Contributions brought about by (n,p) and (n,α) reactions can often be greatly reduced, as mentioned previously, by irradiating in the thermal column of the reactor, with some loss of sensitivity. Reaction *4*, $(n,2n)$, is produced by energetic neutrons and is not of great importance since its occurrence does not lead to a change in atomic number. The same argument will apply to reaction *5*, (γ,n), which will result in the same mass change as reaction *4*. Reaction *6*, (γ,p), is potentially more serious as it will result in a change in atomic number and as in the case of reactions *2* and *3* it must be recognized as a potential source of interference when one element is being determined in the presence of a considerable excess of an element one or two units higher in atomic number.

Smales *et al.* (*86*) in the determination of nickel, cobalt, and copper by neutron activation deal with possible interference by neutron-induced reactions other than (n,γ). They conclude that interference is unlikely except in the case of cobalt, where the cross section $Ni^{58}(n,p)Co^{58}$ is known to be high (*58*). Co^{58} is a 71-day half-life positron emitter (0.48 Mev), while Co^{60} is a 5.3 yr half-life beta emitter (0.31 Mev), so that if at the end of the experiment the isolated cobalt activity is counted without energy discrimination, any Co^{58} present will be counted as Co^{60} and lead to a spurious result. For irradiations not exceeding 70 days, during which period the growth of activity with time is linear for both isotopes, they calculate that the ratio of the measured beta activity from Co^{58} and Co^{60} derived from equal masses of nickel and cobalt is 0.0007. Such interference will be within the limits of experimental error, but when nickel to cobalt ratios are high, interference becomes serious and the authors describe the following methods for overcoming the difficulty:

(a) The activities of the cobalt isolated from standard and sample are compared by measuring the areas under the Co^{60} 1.16- and 1.32-Mev peaks on the gamma spectrometer.

(b) Irradiation in the thermal column of BEPO reduces the Co^{60} activity by a factor of about ten, but due to the very much smaller energetic component of the neutron flux that for Co^{58} is reduced to a much greater extent.

The formation of different isotopes of the same element by (n,γ) and (n,p) reactions considered in the previous paragraph presents a more straightforward problem than that where the same nuclide is formed by these conflicting reactions. An example of this is the determination of the A^{40} content of potassium minerals, the ratio K^{40}/A^{40} being of importance in age determinations. Attempts were made to determine the A^{40} content by neutron activation, utilizing the reaction $A^{40}(n,\gamma)A^{41}$, but it was found that the method was subject to prohibitive interference by the (n,p) reaction $K^{41}(n,p)A^{41}$. The difficulty was overcome by Moljk *et al.* (*60*), who separated the argon prior to activation. The purity of the separated argon was checked by irradiating a monitoring sample of the pure gas. The latter contains the isotope A^{36} which undergoes (n,γ) reaction to give 35-day half-life A^{37} which decays by K and L electron capture. Any atmospheric argon present in the gas separated from potassium minerals can be detected by this long-lived activity after the 1.82-hr A^{41} activity has decayed. With this method it was possible to measure 30-40 $\times 10^{-9}$ gm of A^{40} at the lower limit.

The determination of sodium in pure aluminum by the reaction $Na^{23}(n,\gamma)Na^{24}$ is complicated by the reaction $Al^{27}(n,\alpha)Na^{24}$ brought about by the fast component of the neutron flux spectrum. Salmon (*77*) determined the contribution to the sodium content by this reaction in BEPO by irradiating identical samples and standards normally and in the thermal column. The difference in the sodium content determined by these two methods gives the apparent sodium content derived from the (n,α) reaction. Salmon found this value to be 81 ppm under the conditions of the experiment.

Although it would be expected that the combined yields of $(n,\gamma;\beta)$ and $(n,\gamma;\beta;n,\gamma)$ reactions would be very low, interference in highly unfavorable cases has been recorded. Smales and Pate (*91*) during the determination of arsenic in germanium dioxide by the $As^{75}(n,\gamma)As^{76}$ reaction showed that the following sequences of reactions occur:

$$Ge^{74}_{32} \quad (n,\gamma) \quad Ge^{75}_{32} \xrightarrow{\beta} As^{75}_{33} \quad (n,\gamma) \quad As^{76}_{33}$$

and

$$Ge^{76}_{32} \quad (n,\gamma) \quad Ge^{77}_{32} \xrightarrow{\beta} As^{77}_{33}.$$

The production of As^{76} from germanium does not introduce appreciable error in the determination at the 0.05 ppm arsenic level when irradiations are made for 15 hr at a flux of 10^{12} neutrons/cm^2/sec. As^{77}, which is also a fission product, can be differentiated from As^{76} by counting through an absorber (approximately 800 mg of aluminum per square centimeter) because of the large difference in their maximum beta energies—As^{76}, 2.97 Mev; As^{77}, 0.7 Mev. However, the sensitivity of the method is somewhat reduced because of the high background of Bremsstrahlung produced by the interaction between the As^{77} 0.7-Mev beta particles and the absorber.

A further example of interference caused by a succession of (n,γ) reactions followed by beta decay is found in the determination of phosphorus in silicon by the $P^{31}(n,\gamma)P^{32}$ reaction when an apparent phosphorus content is caused by

$$Si^{30}_{14} \quad (n,\gamma) \quad Si^{31}_{14} \xrightarrow{\beta} P^{31}_{15} \quad (n,\gamma) \quad P^{32}_{15}.$$

Kant *et al.* (*50*) and James and Richards (*47*) calculated the phosphorus that would be produced under the conditions of irradiation. Kant *et al.* found that corrections were negligible for irradiation periods of 15 days if the phosphorus initially present is greater than 0.1 ppm.

The presence of uranium in a sample exposed to a flux of thermal neutrons can cause errors if the nuclide or nuclides determined are fission products or are isotopic with them. Hudgens and Dabagian (*39*) determined zirconium in zirconium-hafnium mixtures by separating the Nb^{95}, daughter of Zr^{95} formed by n,γ reaction, after the addition of carrier. Contributions from fission product niobium (Nb^{95}) can be allowed foı by irradiating a further sample, isolating fission product Ba^{140} and from the fission yield curve making allowance for radioactive niobium derived from any uranium impurity.

A further example of interference by fission is given by Seyfang and Smales (*80*) who were faced with the problem of determining the U^{235} content of mixtures of the naturally occurring isotopes. Contributions to the fission product Ba^{140} used in the estimation from the fast fission of U^{238} were greatly reduced by irradiating samples in the thermal column of BEPO. Any decrease in sensitivity was compensated for by increasing the irradiation period.

VI Applications of Neutron Activation Analysis

Applications of activation analysis are to be found in all the major fields where analytical chemistry is employed. Some of the unique properties of the method have rendered its contributions in the field of trace element analysis invaluable.

Perhaps the greatest single difference between activation analysis and other trace element methods lies in the virtual freedom of the activation method from contamination after irradiation. While this is of obvious importance in all fields of trace element analysis, it is of particular importance in the biological field. If conventional analytical methods are used the first stages in the analysis often consist in the destruction of large amounts of organic matter with the attendant risk of loss and contamination.

In the determination of sodium, potassium, and phosphorus in milligram samples of human muscle, Stone and Reiffel (*98*) avoided the possibility of contamination by irradiating intact samples after drying at 100°C for about 20 hr. After irradiation no chemical separation was employed, the sodium 2.76-Mev gamma photons and the potassium 3.6-Mev beta particles being counted through suitable absorbers to eliminate foreign activities. Eight to fourteen days were allowed for the sodium and potassium activities to decay before P^{32}, half-life 14.3 days, was counted. A similar technique of irradiating the intact dried sample had been used by Smales and Salmon (*92*) in a determination of the rubidium and caesium content of seaweeds and other materials, and a particularly striking example is the determination of arsenic in broad beans where the pod was irradiated unopened (*90*).

Information as to the fate of strontium in the animal and plant organism is of particular interest at the present time. Harrison and Raymond (*33*) developed a rapid method for determining the metabolism of strontium and barium without interference from calcium. After short irradiation in BEPO, samples were chemically treated and the isotopes were gamma counted using a scintillation counter. More recently strontium and barium have been determined in bone by Sowden and Stitch (*95*). Strontium at the 5-60 ppm level has been determined in animal tissue by Brooksbank, *et al.* (*10*) while Bowen (*8*) has determined strontium and barium in sea water and marine organisms.

The determination and the investigation of the metabolism of both toxic and nontoxic elements in the animal and plant organism have been investigated by activation methods and because of the medical and legal aspects associated with it, that of arsenic has received much attention. The distribution of arsenic in hair was first investigated by Griffon and Barbaud (*28, 29*). No separation was employed by these workers, who determined the location of the ingested element by traversing the length of the hair with a well-screened Geiger counter. This method has the advantage of leaving the sample intact at the end of the investigation. However, it is not entirely free from objection, due to the presence of other induced activities in the material and a quite general technique was described by Smales and Pate (*90, 91*) who determined the element in biological materials such as hair, nails, urine, and blood from normal human subjects, and the internal organs of a mouse.

Activation analysis may be regarded as an alternative to tracer techniques in the study of trace element metabolism. The activation method does not suffer from the disadvantage of possible radiation damage to the biological system inherent in the use of radioactive tracers. A further disadvantage in the use of tracers has been pointed out by Harrison and Raymond (*33*). They state that while giving valuable information as to the relative retention and distribution of trace elements, no absolute information as to their excretion rates is obtained.

The sensitivity of analytical methods for trace elements needs to be high, and ideally the reaction or property utilized should be entirely specific. The sensitivity of activation analysis is dependent on the element estimated and in many cases it is extremely high. Specificity is covered by three parameters, half-life of the nuclide produced, its maximum beta energy, and its gamma spectrum.

The analytical requirements of the electronics industry engaged in the production of semiconductor materials such as silicon and germanium and the problems associated with production of the high-purity materials required by the atomic energy and other projects, necessitate analytical methods of high sensitivity and specificity. The characteristics of semiconductor materials are highly dependent on the presence of traces of impurities such as copper, gallium, antimony, and others. Smales (*83*) has reviewed some of the analytical methods available for the determination of trace elements present as impurities in semiconductors. No one method is suitable for all the problems in this field, but owing to its high sensitivity and specificity activation analysis has been able to make a valuable contribution.

Arsenic at the 0.1-ppm level in germanium dioxide has been determined by Smales and Pate (*91*) after neutron irradiation in BEPO, while the uptake of impurities from a graphite crucible used in the melting of germanium has been studied by Morrison (*62*). Traces of copper in germanium were measured by Szekely (*100*). The standards employed in this work were artificially prepared mixtures of copper (1 ppm) in germanium. Copper, zinc, antimony, molybdenum, and the rare earths in germanium and its oxide at the 0.1-ppm level have been determined by Jakovlev (*45*).

Phosphorus in the range 0.004 to 2.0 ppm and arsenic have been determined by James and Richards (*46, 47*) in the transistor material silicon. Kant *et al.* (*50*) also determined iron, copper, zinc, gallium, arsenic, silver, cadmium, indium, antimony, thallium and bismuth in the range 10^{-2} to 10^{-5} ppm by neutron activation. A combination of radiochemical separation and direct gamma spectrometry has been used by Smales *et al.* (*87*) for the determination of arsenic, antimony, and copper as well as other elements, at the parts per thousand million level in pure silicon.

Hudgens and Cali (*38*) have described a determination of antimony at the parts per million level in zirconium oxide. Distillation and solvent extraction were used in the radiochemical purification and antimony was mounted, prior to counting, by electrolysis onto platinum foil. Atchison and Beamer (*3*) have determined arsenic, phosphorus, copper, sodium, strontium, calcium, and chromium in pure magnesium.

A method for the determination of the oxygen content of powdered metals, and in particular beryllium, has been described by Osmond and Smales (*67*). The metal powder is mixed with lithium fluoride and irradiated with neutrons when the reactions below take place:

$$1.\ \mathrm{Li}_3^6 + n_0^1 \rightarrow \mathrm{He}_2^4 + \mathrm{H}_1^3$$

$$2.\ \mathrm{O}_8^{16} + \mathrm{H}_1^3 \rightarrow \mathrm{F}_9^{18} + n_0^1$$

F^{18}, which is a 0.65-Mev positron emitter, is isolated, purified, and mounted as lead chlorofluoride. Good agreement between this and conventional methods was obtained for the oxygen content of beryllium.

Activation analysis has been applied to some of the problems connected with the study of luminescent solids and phosphors. Grillot (*30*) determined 10^{-8} gm of copper in solids at different stages in the preparation of luminescent substances and Bancie-Grillot and Grillot (*5*) determined chlorine in zinc sulfide. The thallium content of potassium iodide crystals has been measured by Delbecq *et al.* (*20*), and an accuracy of 5% at the microgram level claimed.

Trace quantities of uranium in aluminum were determined by Mackintosh and Jervis (*53*). Two methods were described, one utilizing fission product barium while the other used the reaction $U^{238}(n,\gamma)U^{239}$, half-life 23.5 min. In the latter case, after simple chemistry, uranium was mounted as the diuranate. Fairly good agreement was obtained between the two methods, that using U^{239} being the more sensitive and requiring shorter irradiation periods.

While high sensitivity has been obtained in the examination of pure materials, a far more rigorous test of the activation method is found in its application to materials of a more complex matrix. Emission and X-ray spectrometry and direct spark source mass spectrometry are all restricted by the lack of suitable standards when applied to materials of complex composition. Provided that precautions are taken to avoid self-shielding errors radioactivation is largely independent of the nature of the matrix material. It is this advantage which has enabled activation analysis to prove such an invaluable tool in geochemistry.

Cabell and Smales (*12*) have described the application of neutron activation to the determination of rubidium and caesium in international standard rocks, lepidolites, samples from the Skaergaard Intrusion of East Greenland, and some stony meteorites. Smales and Salmon (*92*) had previously determined the same two elements in sea water after a preliminary concentration on an ion exchange resin, and directly in other materials of geochemical interest.

Strontium determinations in soils, sea water, etc., have the same topicality as similar determinations in biological materials. The strontium and barium content of a number of soils and plants has been determined by Bowen and Dymond (*9*). They found that strontium was preferentially absorbed with respect to calcium by plants from most of the soils considered while barium was taken up much less readily.

Neutron activation was used by Smales *et al.* (*86*) to determine the nickel, cobalt, and copper contents of rocks, marine sediments, and meteorites. In a more recent paper these workers discuss the application of this method to "cosmic" and other magnetic spherules. Radioactivation was particularly suitable in this case as the available weight of samples lay within the range of 10-250 μg (*88*). From the nickel/copper, nickel/cobalt, copper/cobalt, and nickel/iron ratios observed they were able to establish a close similarity between meteoritic material and the spherules obtained from deep-sea cores. Spherules obtained from River Danube sand and from the roof of a collecting station off the coast of Sweden gave quite different ratios and indicated a different origin for these materials.

Gold contents which varied from about 400 μg/meter^3 for English coastal water to about 15 μg/meter^3 for waters from the Bay of Biscay were obtained by Hummel using neutron activation (*41*). The amount of gold and rhenium in iron meteorites has been determined by Goldberg and Brown (*27*). The use of milligram amounts of the elements as standards necessitated corrections for self-shielding due to the high neutron capture cross sections of these elements.

The gallium and palladium content of iron meteorites has been investigated by Brown and Goldberg (*11*). The elements were determined on separate samples after irradiation in the Argonne pile. Morris and Brewer (*61*) modified the method of Brown and Goldberg for the determination of gallium in blende.

Neutron irradiation has been employed in a number of cases to determine isotope abundance or to investigate the existence of isotopes where theory has indicated that this is possible.

The determination of isotopic abundance by means of an (n,p) reaction induced by thermal neutrons has been described by Coon (*16*). Variations in the He^3 content of helium gas depending on its source had been recorded and Coon was able to confirm these with gas obtained from wells and from air by means of the reaction $He^3(n,p)H^3$ whose cross section for thermal neutrons is approximately 5,000 barns. A search for Si^{32} in natural silicon was conducted by Turkevich and Tomkins (*102*). Theory had indicated that Si^{32} might be a beta-stable isotope and occur in natural silicon in small, undetected amounts. Neutron-irradiated quartz was examined radiochemically for 25-day half-life P^{33}, the daughter of Si^{33} formed by (n,γ) reactions on the sought isotope. However, only P^{32}, probably formed from impurities, was detected and assuming a cross section for the $Si^{32}(n,\gamma)Si^{33}$ reaction of 0.05 barns an upper limit of $4 \times 10^{-6}\%$ results for the abundance of Si^{32} in natural silicon. Subsequent work has shown Si^{32} to be an approximately 300-yr half-life beta emitter.

The geochemistry of uranium and thorium has excited considerable interest on account of their strategic importance. Smales determined uranium in rocks by neutron activation followed by isolation of fission product Ba^{140} (*81*). Interference from the fast fission of any thorium present in the sample and from beta-emitting barium isotopes formed by (n,γ) reaction is discussed and methods of overcoming the difficulties are described. The uranium content of two iron meteorites was determined by

Reed and Turkevich (*73*). Uranium was estimated as fission product Ba^{140} and as the beta-emitting Np^{239} formed by the reaction $U^{238}(n,\gamma)U^{239}$ followed by beta decay to Np^{239}. Approximately 100 cpm of the long-lived alpha emitter Np^{237} were added to enable a calculation of the neptunium chemical yield. Stone meteorites were examined by Hamaguchi *et al.* (*32*) using the same technique. In addition barium was determined in the sample.

Small quantities of thorium in geological samples have been determined by Jenkins (*48*). Thorium was estimated as the beta-emitting isotope Th^{232}, half-life 22.1 min., formed by irradiation in BEPO. In view of the short half-life a rapid procedure for chemical purification had to be developed if adequate sensitivity was to be obtained. Chromatographic separation on an aluminum oxide-cellulose column was the method successfully applied. Thorium in stone meteorites has been estimated by Bate *et al.* (*7*). Pa^{233}, the 27.4-day half-life daughter of Th^{233}, was used in this estimation. Although this resulted in a reduced sensitivity, greater time was available for the chemical processing. Rona (*75*) measured the isotopic ratio Th^{232}/Th^{230} in uranium minerals. Thorium was separated from the uranium mineral and the Th^{232} content was determined by activation analysis. Th^{230} was measured by alpha-particle counting.

VII. Activation Analysis with Charged Particles

It has been stated that the bulk of the published work on activation analysis has been concerned with the more general technique of neutron activation. A low probability of neutron activation or an overlong or overshort half-life of the activated species produced can, however, result in poor sensitivity for the method. This is the case with a number of the lighter elements such as beryllium, aluminum, carbon, nitrogen, and oxygen. In a number of these cases a satisfactory alternative may be found in activation by charged-particle bombardment (*65*).

The problems in this field of activation analysis are in many respects more complicated than those found in neutron activation. The positive potential barrier around the atomic nucleus prevents interactions below a certain minimum threshold value. Above this value a law of the $1/V$ type which holds for neutrons is not operative; the cross section of the reaction increases rapidly with particle energy until, as with neutrons of higher energies, new competing reactions become significant and the reaction yield falls off. Reactions with charged particles which involve the ejection of a further charged particle from the compound nucleus usually have a lower probability of taking place than those which result in the production of neutrons, since the charged particles formed from such interactions must penetrate the electrostatic barrier to escape from the parent nucleus. Deuteron reactions of the (d,n) type usually have a higher cross section than those induced by protons or alpha particles.

The simultaneous occurrence of several different nuclear reactions which lead to a variety of products is a feature of activation by charged particles. This may be exemplified by the following reactions which may occur in deuteron bombardment:

1. A_Z^M (d,t) A_Z^{M-1}
2. A_Z^M (d,p) A_Z^{M+1}
3. A_Z^M (d,α) A_{Z-1}^{M-2}
4. A_Z^M (d,n) A_{Z+1}^{M+1}
5. A_Z^M $(d,2n)$ A_{Z+1}^{M}

For a given energy of bombardment all these reactions tend to take place to a certain extent. At low energies the (d,n) reaction frequently predominates, while the (d,p), (d,α), (d,t), and $(d,2n)$ reactions become increasingly important as the deuteron energy is increased. This complexity compares unfavorably with thermal-neutron activation where frequently one reaction occurs to the virtual exclusion of all others.

Self-shielding during irradiation is of much greater importance with charged particles, whose range in matter is short, than with neutrons. It is customary to use targets sufficiently thick to absorb the whole of the radiation, but even if this technique is employed the physical shape and composition of samples and standards is of great importance. Because the whole of the particle beam is absorbed in the top few millimeters of the sample large amounts of heat are released and an efficient system of cooling must be devised if the sample is not to be affected (*74*).

The protons, deuterons, or alpha particles used are obtained from accelerating machines, although lower fluxes of alpha particles may also be obtained by the decay of suitable nuclides. The particle flux obtainable from an accelerating machine may be estimated from the ion beam currents quoted in Table II. One microampere of protons or deuterons will correspond to 6.3×10^{12} ions per sec, while the same beam current of alpha particles will contain one-half of this number.

The large amount of energy released in charged-particle bombardment tends to exclude this method where thermally labile organic or biological materials are employed as targets. However, Odeblad (*64*) was able to determine sodium in urine and other elements in biological materials by means of the weak source of alpha particles (160 millicuries) derived from the decay of Po^{210}. A similar source of alpha particles has been used to determine aluminum by the reaction $Al^{27}(\alpha,n)P^{30}$—half-life 2.5 min (*66*).

Boron, which under these conditions gives 10.3-min half-life N^{13}; and magnesium, which gives 2.4-min half-life Al^{28}, should be absent.

Due to the long half-life of C^{14} it is not feasible to determine carbon by neutron irradiation. Süe has used the reaction $C^{12}(d,n)N^{13}$ for its determination in organic matter (*99*). Samples of approximately 100 μg were sealed in silica microtubes and irradiated for periods of 5 min in the deuteron beam from a cyclotron when the following reactions occurred:

1. $O^{16}(d,n)\ F^{17}$ half-life 1.1 min
2. $Si^{30}(d,p)\ Si^{31}$ half-life 2.65 hr
3. $C^{12}(d,n)\ N^{13}$ half-life 10 min

Fifteen minutes were allowed for the fluorine activity to decay before plotting the decay curve of N^{13} and Si^{31}. The curve was resolved and it was found that 100 cpm of N^{13} corresponded to 0.31 μg of carbon. Activity due to Si^{31} was used as a measure of beam strength in this experiment. Albert *et al.* (*1*), in a determination of carbon in steel by this method, separated the nitrogen formed by Kjeldahl distillation and liquid-counted the nitrogen in the distillate. They state that the sensitivity is improved by this method.

Deuterons of 3 Mev were used by Sagane *et al.* (*76*) to reveal the presence of 10 ppm of sodium in aluminum.

The potential value of high-energy electron-producing machines such as the linear accelerator for activation analysis must not be overlooked. Here photonuclear reactions (γ,n) can be used, either to produce a high neutron flux (as most charged-particle machines can by choice of a suitable reaction), or directly on samples. This may well be valuable, particularly for some light element determinations.

The direct determination of oxygen in organic materials and metals by the reaction $O^{16}(\gamma,n)O^{15}$, half-life 2.1 min, 1.7 Mev positron, using a 22 Mev betatron has been described and the possibility of extending the method to carbon and nitrogen discussed by Basile and co-workers (*6*). Six milligrams of oxygen in organic materials and 0.1% in aluminum has been quoted as a lower limit for the sensitivity of the method.

VIII. Conclusion

Activation analysis is a powerful addition to the armory of modern analytical chemistry. Its sensitivity for many elements is already very high, as can be seen from a few examples listed in Table VIII (and of course the higher fluxes now becoming available with the development of more advanced reactors means even higher sensitivity) adding a new dimension to the older methods and being matched at present only by the

TABLE VIII

ESTIMATED SENSITIVITIS FOR SOME ELEMENTS IN NEUTRON ACTIVATION

Element	Radionuclide formed	Half-life	Estimated sensitivity* (gm)
Dy	Dy^{165}	2.3 hr	1×10^{-12}
Eu	Eu^{152m}	9.2 hr	1×10^{-12}
Au	Au^{198}	2.7 day	5×10^{-12}
In	In^{116}	54 min	1×10^{-11}
Mn	Mn^{56}	2.6 hr	1×10^{-11}
As	As^{76}	26.5 hr	5×10^{-11}
La	La^{140}	40 hr	5×10^{-11}
W	W^{187}	24.1 hr	5×10^{-11}
Cu	Cu^{64}	12.8 hr	1×10^{-10}
Ga	Ga^{72}	14.1 hr	1×10^{-10}
Ta	Ta^{182}	111 day	1×10^{-10}
Na	Na^{24}	15 hr	1×10^{-10}
Cs	Cs^{134}	2.3 yr	5×10^{-10}
Co	Co^{60}	5.3 yr	5×10^{-10}
P	P^{32}	14.3 day	5×10^{-10}
Rb	Rb^{86}	18.6 day	5×10^{-10}
Ba	Ba^{139}	85 min	1×10^{-9}
Hg	Hg^{203}	47 day	1×10^{-9}
Cl	Cl^{38}	37.3 min	5×10^{-9}
U	Ba^{140}	12.8 day	5×10^{-9}
Mo	Mo^{99}	68 hr	1×10^{-8}
Ni	Ni^{65}	2.6 hr	1×10^{-8}
Cr	Cr^{51}	27.8 day	1×10^{-7}
Sr	Sr^{89}	50 day	1×10^{-7}
Ca	Ca^{45}	164 day	1×10^{-7}
S	S^{35}	87.1 day	5×10^{-7}

* Estimated using slow neutron flux of 10^{12} neutrons/cm^2/sec, irradiation period of one month or saturation, whichever is less, a 2-hr period for radiochemical processing, and 100% chemical yield (*49*).

mass spectrometer-isotope dilution method. But there is even another advantage over this latter method, an advantage which becomes increasingly important with increasing sensitivity; freedom from contamination and reagent "blank" difficulties. Only those who have actual experience with this problem when trying to operate at the submicrogram level can really appreciate the importance of the contribution made by activation analysis.

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