

EXPERIENCE IN THE U.S.A. ON THE USE OF RADIOACTIVATION ANALYSIS

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Aux Etats-Unis, de nombreux chercheurs dans diverses branches de la science se servent maintenant de la radioactivation qu'ils considèrent comme un outil utile et commode aux fins d'analyse élémentaire. Leurs travaux ont consisté surtout jusqu'à présent à déterminer des concentrations de l'ordre du microgramme ou des concentrations encore plus faibles, d'éléments divers contenus dans des échantillons de substances biologiques, de produits pharmaceutiques, d'engrais, de substances chimiques fines, de produits alimentaires, de carburants, de verre, de matières céramiques, de métaux, de minéraux, de peintures, de dérivés du pétrole, de résines, de sols, de substances toxiques, d'eau et d'autres matières.

Il existe de nombreux types de sources neutroniques, mais la plupart des analyses faites au cours de ces recherches l'ont été au moyen de réactions neutroniques produites soit par une source de faible intensité, soit par un accélérateur, soit dans un réacteur. Dans certains laboratoires et notamment au Laboratoire national d'Oak Ridge, on se sert de l'analyse par radioactivation neutronique de façon presque courante. Le Service des analyses par activation de la Division des analyses chimiques du laboratoire a résolu des problèmes d'analyse nombreux et difficiles au moyen des flux neutroniques produits dans les réacteurs d'Oak Ridge.

Le mémoire a pour objet d'exposer les connaissances que les chercheurs des Etats-Unis ont acquises en employant cette technique. Il est consacré en partie à l'emploi, presque courant, de l'activation neutronique dans le cadre du programme d'Oak Ridge et donne des détails sur la façon dont d'autres chercheurs ont appliqué cette méthode à l'étude de problèmes spéciaux. Dans chaque cas, l'auteur indique par quels moyens les substances étudiées ont été irradiées et comment les substances irradiées ont été ensuite traitées. En outre, il décrit des procédés d'essai sans altération des matériaux et de séparation radiochimique ainsi que les méthodes et l'appareillage utilisés dans la métrologie des radio-nuclides. Dans tous les cas, il indique le degré de précision de la mesure pour chaque application.

Radioactivation analysis has become a well-established analytical method in the United States of America, and is being used on an increasing scale by many American researchers in analysis problems requiring a most sensitive and specific technique. This paper cites in a cursory way the applications that this method is finding in many different analytical problems. Significantly, most of these applications have been concerned with problems in elemental microanalysis; however, applications in macroanalysis and isotopic analysis have also been made. In addition, radioactivation analysis has been used as a complementary method to other analytical techniques employed in analysis problems of elemental segregation and diffusion, and in the determination of particle-size distributions.

THEORY

Excellent discussions of the overall theory of radioactivation analysis are available¹⁻³. The basic principles might be briefly stated by indicating that a sample, when placed in a nuclear particle source, is subjected to a bombardment, or irradiated, by the nuclear particles of that source so that

the element or elements to be determined are transformed into unstable isotopes or radioactive nuclides. Each radionuclide decays with a particular mode of decay and radioactive emission and by virtue of these characteristics it may be detected. A measurement of the radioactivity of a nuclide by applying counting procedures, usually, but not always, after suitable chemical separation, is then a measure of the mass of the stable isotope(s) of the element present in the sample being analysed. The characterization or identification of the radionuclide chosen to complete an analysis is made by examining its nuclear radiations and half-life by some type of counting method.

Most research workers find it practical to irradiate and process simultaneously both the sample being analysed and a weighed standard of the desired element or elements. This practice has minimized such problems as those concerned with an accurate measurement of the nuclear particle flux and the determination of the absolute disintegration rate of the observed radioactivity. Boyd's¹ formula is most generally applied to obtain the concentration of the element being determined:

$$\frac{\text{activity of unknown}}{\text{weight of unknown}} = \frac{\text{activity of standard}}{\text{weight of standard}}$$

Here, a relative counting of the radioactivity in the standard and unknown samples is made. The standard and unknown are usually counted in sequence and under similar counting conditions. After corrections for weight and radioactive decay in each sample, a direct comparison of their radioactivities can be used to measure the element concentration.

ADVANTAGES AND LIMITATIONS OF THE RADIOACTIVATION ANALYSIS METHODS

Although radioactivation analysis may be used to estimate qualitatively and quantitatively the concentration of a major elemental constituent in a sample matrix, it has been most often used as a microanalytical method. In this area, most of the American researchers using radioactivation analysis methods have done so because the trace element concentrations were beyond detection by other analytical methods. Radioactivation analysis, particularly with neutrons, generally possesses limits of measurement that are potentially more sensitive than those that can be obtained by other analysis methods. *Table 1* gives Morrison's comparison⁴ of the limits of measurement for various analytical chemistry methods.

Table 1. A comparison of the limits of measurement of various methods of trace element analysis⁴

<i>Method</i>	<i>Limits of measurement (%)</i>
Gravimetric	10 ⁻²
Volumetric	10 ⁻²
Colorimetric	~10 ⁻⁵
Spectrographic	~10 ⁻⁵
Mass spectrographic	~10 ⁻⁵
Radioactivation	10 ⁻⁸ -10 ⁻¹⁰

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Table 2. Quantitative determination of trace elements in metals and alloys by neutron radioactivation analysis

	Smallest concentration determined* (parts/million)	Limit of measurement (parts/million)† at neutron flux		Limits of measurement (parts/million) by other methods ⁶			
		5×10^{11}	10^{13}	Copper spark	Flame spectrometer	Colour reaction	Amperometric titration
Sb	0.4	0.004	0.0002	5		0.03	10
As	0.1	0.002	0.0001	5		0.1	0.4
Ca	5	4	0.2	0.1	0.03		100
Cd	1	0.05	0.003	2	20	0.01	5
Cs	0.1	0.03	0.002	0.5	1		
Cl	2	0.03	0.002				10
Cr	1	0.2	0.01	0.05	1	0.02	1
Co	0.05	0.02	0.001	0.5	10	0.03	100
Cu	1	0.007	0.004	0.2	0.1	0.03	10
Ga	13	0.007	0.0004	1	1		
Au	0.3	0.003	0.0002	0.2	200		
Hf	10	0.02	0.001	0.5			
Fe	0.2	9	0.45	0.5	2	0.05	2
Mn	0.1	0.0006	0.0003	0.02	0.1	0.001	0.0003
Mo	1	0.1	0.005	0.05	30	0.1	5
Ni	0.5	9	0.45	0.1	10	0.04	0.5
P	2	0.02	0.001	20		0.01	15
K	1	0.08	0.004	0.1	0.01		100
Se	0.2	0.02	0.003				200
Si	2	1	0.05	0.1		0.1	
Ag	0.2	0.1	0.005		0.5	0.1	1
Na	7	0.007	0.0004	0.1	0.002		
S	10	4	0.01				5
Ta	2	0.007	0.0004	1			
Sn	6	0.2	0.01		10		2
W	0.2	0.003	0.0002	0.5		0.4	
U	0.06	0.01	0.0005	1	10	0.7	
Zn	1.5	0.04	0.002	2	2000	0.02	10
Zr	5	0.3	0.02	0.1		0.1	

* By the Oak Ridge National Laboratory Activation Analysis Group.

† Based on measurement of 40 disintegrations per second of radioactivity produced in an irradiation at a neutron flux (neutrons $\text{cm}^{-2} \text{sec}^{-1}$) indicated for a "saturation" or one-week irradiation, whichever is shorter.

Table 2 shows Leddicotte's⁵ interpretation of the possibilities of the neutron activation analysis for trace element impurities in metals and alloys. The comparison study by Meinke⁶ in which the limits of measurement of neutron radioactivation has been compared with that obtained by several other methods of analysis has been used in part to compile Table 2. These comparisons show that a radioactivation analysis method using neutrons as the nuclear particles may be inherently more sensitive than most other analytical methods. Increased neutron fluxes, *i.e.*, greater than 10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$, will greatly enhance the limits of measurement by neutron radioactivation.

Radioactivation analysis is a most specific analysis method in that the radionuclide of an element produced by a nuclear particle irradiation disintegrates in a manner unique only to that radioactive species. The characteristic half-life of the radionuclide and the type of radiations emitted in its decay are never exactly duplicated by any other radionuclide product so that it is possible to detect and identify the radioactivity of interest without too much difficulty.

Radioactivation analysis is also greatly favoured because of its almost complete freedom from the spurious contamination that is most common with other analytical methods. Unless the trace element is added to the sample in some manner *before* the nuclear particle irradiation, contamination in very high orders of magnitude can be tolerated without seriously affecting the analysis.

The limitations of radioactivation analysis have been recognized. Smales⁷ classifies these as being physical, chemical and nuclear. The heat tolerance and the effective physical area available for irradiation are usually considered as physical limitations. Typical examples of irradiation facilities used in radioactivation analysis are given elsewhere in this report. With regard to heat tolerance, the activation analysis programme at the Oak Ridge Laboratory frequently uses a water-cooled irradiation facility in which it is possible to irradiate gaseous, liquid, and solid samples that can withstand temperatures of 40°–50°C.

Smales⁷ has stressed the importance of structural damage and decomposition processes during irradiation, and effectively describes compensations to be considered to take care of this limitation. In addition, all the experimenters using radiochemical analysis methods for the isolation of the desired radioactivity in the work described here recognize the need for obtaining a radiochemically pure, *i.e.*, free of radioactive contaminant, separated radionuclide to complete an analysis. Each in his own way has established the "best" separations method for his particular problem and gives a description of his method for each example that is cited.

With regard to nuclear limitations, each experimenter has also considered these in the light of the type of analysis that is required to complete his problem. Most sample materials when analysed have been found to be virtually transparent to the impinging nuclear particles. However, in those instances where the sample contains a relatively large amount of some material of high cross-section, a neutron particle flux attenuation, or slowing-down of the particles as they pass through the sample, can result in a lower production of radioactivity than would be expected, since the inner portion of the sample is exposed to a lower nuclear particle flux than the outer portion. The presence of appreciable absorption, or self-shielding, can be compensated for either (1) by employing a smaller sample in analysis, or (2) by diluting the sample with a diluent of low cross-section, or (3) by using comparator or standard samples made up to contain a known amount of the element determined for in a mixture containing an amount of the nuclear particle absorbing material equal to that contained in the unknown sample, or (4) by correcting for self-shielding by means of a suitable calibration curve, separated by the use of standard. Mullins *et al.*⁸ in their work on determining trace elements in zirconium-cadmium alloys by neutron radioactivation analysis have used the technique of adding to the standard sample an amount of cadmium equivalent to that in the unknown samples being irradiated. The Activation Analyses Group at O.R.N.L.⁹ in its investigations on the determination of trace selenium in biological materials and trace cobalt in metals and alloys has shown that small errors can result from self-shielding even if milligram amounts of these elements are used as comparator samples. The results of this study

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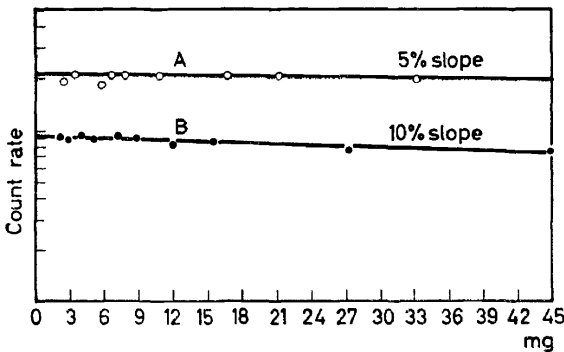


Figure 1. Self-shadowing effects during a neutron irradiation: A, $^{74}\text{Se}(n,\gamma)^{76}\text{Se}$;
B, $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$

are given in Figure 1. Similarly, Guinn and Wagner¹⁰ recently reported the results obtained in the analysis of a series of organic samples of increasing chlorine content and show a typical calibration curve used in their study.

In those areas of nuclear limitation concerned either with the production of the same radionuclide by some other type of nuclear reaction, or by a second nuclear particle reaction upon the stable decay product of the radionuclide produced by an original nuclear reaction, it has been possible to use a pre-irradiation separation of the trace element by chemical means with a subsequent irradiation of the separated materials, or irradiations in a flux area of a nuclear particle source essentially free of the type of nuclear particle capable of producing an additional amount of the desired radionuclide, or differential counting techniques. For example, the Activation Analyses Group at O.R.N.L.⁹ has used thallium sulphide as a carrier agent for manganese-55 in order to determine microgram amounts of manganese in iron. The radioactivity produced by the primary nuclear particle reaction $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$ is greatly distorted by the amount of radioactivity produced in the reaction $^{56}\text{Fe}(n,p)^{56}\text{Mn}$. Thus, by putting the unknown sample into solution and adding a known amount of thallium as a carrier reagent, and subsequently precipitating the thallium plus manganese as a sulphide, and then irradiating the separated sulphide in a neutron flux for several hours, it was possible to determine microgram concentrations of manganese in an iron sample. Following the irradiation, the $^{56}\text{Mn}(t_{1/2} = 2.56 \text{ h})$ was separated by a radiochemical analysis method. Similar pre-separation techniques must be used if phosphorus is to be determined in silicon and its compounds. Long irradiation intervals are required in a radioactivation analysis for ^{31}P and appreciable amounts of $^{32}\text{P}(t_{1/2} = 14.3 \text{ d})$ radioactivity can be produced by the radioactivation of the stable ^{31}P formed from the decay of $^{31}\text{Si}(t_{1/2} = 2.6 \text{ h})$ produced in the activation of ^{30}Si by the neutron reaction $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$.

An example of the production of the same radionuclide by another nuclear reaction is found in the work of Leddicotte and Reynolds¹¹ and Plumb and Silverman¹² on determining microgram amounts of sodium in aluminium. The primary nuclear reaction is $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$; however, copious quantities of $^{24}\text{Na}(t_{1/2} = 15 \text{ h})$ are also produced by the fast neutron reaction, $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$. In these investigations, it was possible to eliminate

this fast neutron interference by irradiating in an area of the Oak Ridge Graphite Reactor completely free of high energy neutrons. Although thermal neutron flux levels of somewhat smaller magnitude were used, the limits of measurement, parts/million, were increased by the use of samples of large size (2–10 g).

As a further example of another nuclear limitation, it is known that wherever microgram amounts of arsenic are being determined in germanium and germanium tetrachloride by the thermal neutron reaction $^{75}\text{As}(n,\gamma)^{76}\text{As}$, compensation must be made for the production of ^{77}As ($t_{1/2} = 40$ h) by the neutron reaction $^{76}\text{Ge}(n,\gamma)^{77}\text{Ge} \xrightarrow{\beta^-, \gamma} ^{77}\text{As}$. This difficulty has been resolved by differentiating between the radiations emitted by the two arsenic isotopes by means of counting techniques involving both beta and gamma counting. Green and Kafalas¹³ report on the use of neutron radioactivation analysis to determine trace arsenic in purified germanium. Samples from this study were analysed by the Activation Analyses Group at Oak Ridge National Laboratory and the results obtained showed that arsenic-75 in concentrations as small as 6.3×10^{-10} mole fraction of arsenic trichloride could be easily determined by this technique.

As these examples show, it is possible to overcome most of the inherent problems based upon nuclear limitations.

RADIOACTIVATION ANALYSIS METHODS

Any nuclear particle reaction producing a radionuclide can be used in radioactivation analysis. In the United States, alpha particles, protons, deuterons and fast and thermal neutrons have been used as the activity particles. It is significant that radioactivation by use of charged particles from a charged particle accelerator such as a cyclotron has had little use after 1950. At this time, reactor facilities were becoming available to most researchers and the rigid requirements on the type and size of samples that could be irradiated were relaxed. The heat dissipated within the accelerator chamber and the small area of the beam define these requirements. Another difficulty that greatly limits the charged particle method is that many different nuclear reactions can occur simultaneously during an irradiation, so that competitive reactions greatly influence the facility with which an element could be determined. Thus, the availability of the high neutron flux from various nuclear reactions, and the ease with which neutrons could be produced from targets inserted into Van de Graaff accelerators, have made it possible for most American scientists to promote neutron radioactivation analysis.

Research workers in the geographical areas in proximity to the reactor facilities of the U.S. Atomic Energy Commission have found much use for neutron radioactivation analysis in their problems. However, the most significant effort in neutron radioactivation analysis has been that accomplished at the Oak Ridge National Laboratory. Here, the advantages in the use of this method of analysis for problems arising in the research and development efforts of the Laboratory were soon realized, and in 1950 an Activation Analyses Group was formed within the Laboratory's Analytical Chemistry Division¹⁴. This analysis group has done considerable research

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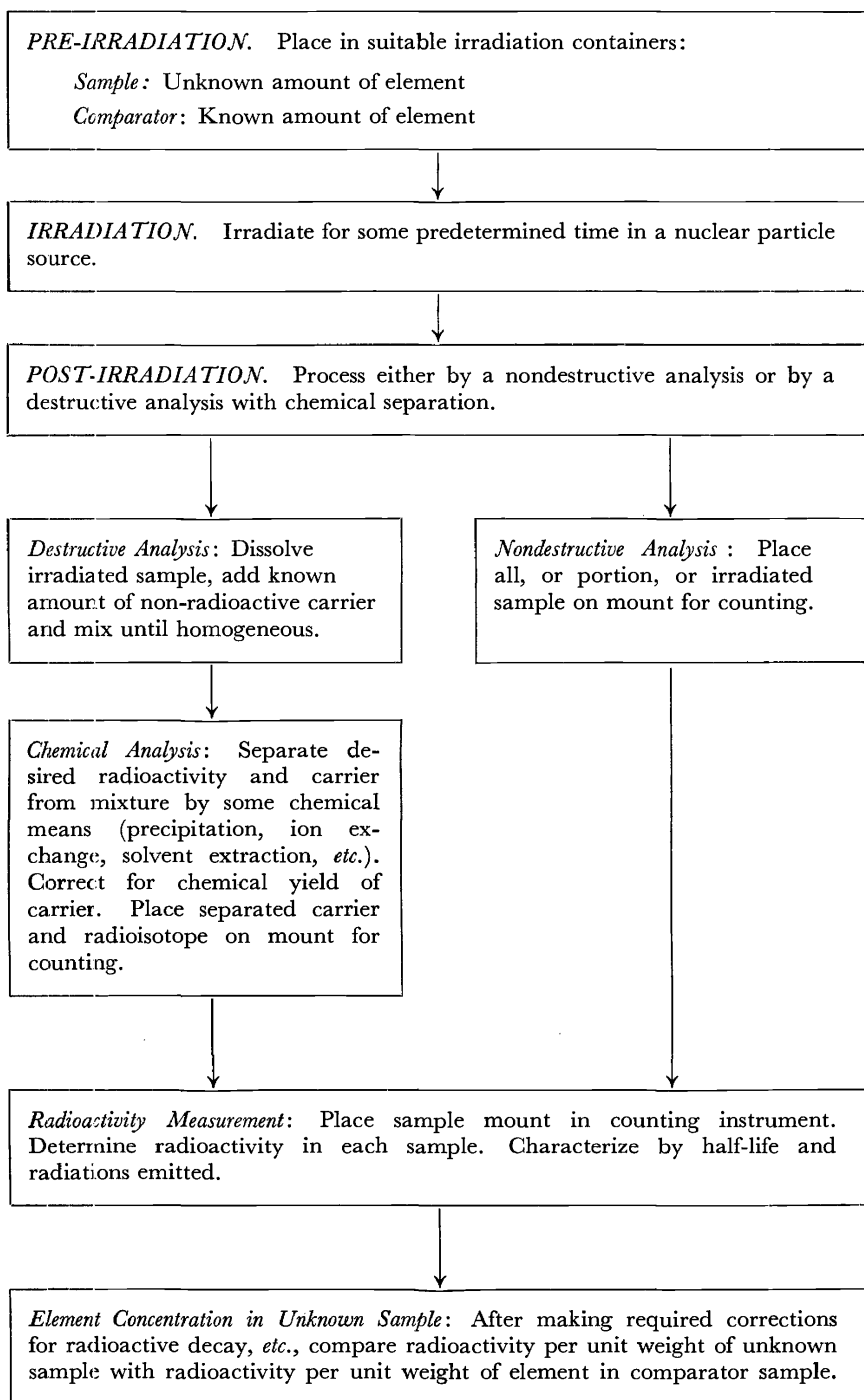


Figure 2. A typical procedure for radioactivation analysis

and development in neutron radioactivation analysis and, in addition to assisting in the Laboratory's programme, it provides a service analysis for industry, various research organizations and government agencies, particularly those with problems in trace element determinations. Thus, a considerable number of the applications in neutron activation analysis by this analysis group will be presented throughout this paper.

GENERAL PROCEDURE OF ANALYSIS

Most of the American investigators, particularly those involved in elemental microanalysis, follow an activation analysis procedure similar to that shown in *Figure 2*.

In almost all investigations, the sample materials as they are received are placed in some type of irradiation container. A typical irradiation facility used in neutron radioactivation analysis at the Oak Ridge National Laboratory is shown in *Figure 3*. Many different types of containers have been found suitable for use in radioactivation analysis and can be chosen for any particular experiment.

The period of irradiation is usually determined by the half-life of the radionuclide and the accessibility of a nuclear particle flux. However, in general, arbitrary values of at least one half-life or one week, whichever is shorter, is the basis for most analyses, especially those being completed by neutron radioactivation analysis.

The post-irradiation processing of an irradiated sample is usually dependent upon the desires of the analyst and the radioactivity measuring equipment available in his laboratory. Radiochemical procedures have been most frequently used; however, at the O.R.N.L. a considerable number of analyses are being completed by nondestructive methods¹⁵.

From radioactivation analysis have evolved many useful radiochemical methods based upon techniques involving precipitation, ion exchange,

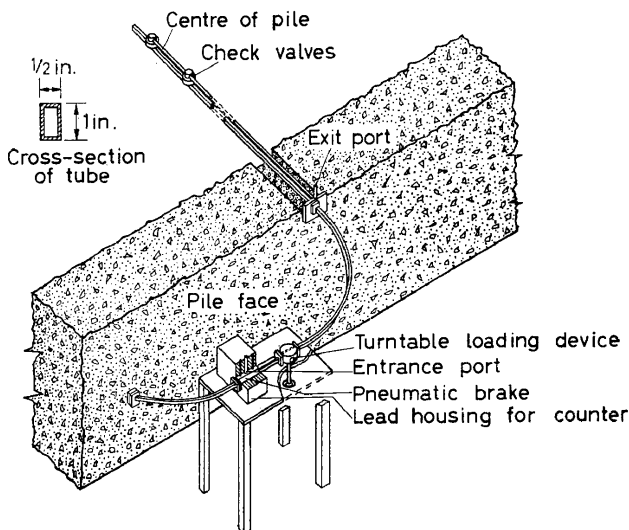


Figure 3. Fast pneumatic tube—Oak Ridge National Laboratory

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solvent extraction, electrolysis, *etc.* Typical precipitation radiochemical analysis methods used in determining the constituents of aluminium-base alloys have been reported by Brooksbank *et al.*¹⁶ Excellent examples of other quantitative analysis methods can be found in many of the references given to this report. Another report¹⁷ has provided the outline of a qualitative analysis scheme that is used routinely in neutron radioactivation analysis at the Oak Ridge National Laboratory. The Oak Ridge group⁹ has also found much use for the ion-exchange techniques given by Kraus *et al.*¹⁸ and Gilbert *et al.*¹⁹ in its radioactivation analysis applications.

In the measurement of the radioactivity, the beta radiations from a radioisotope after its isolation can be measured best by means of a Geiger counting technique. The recently developed technique of gamma scintillation spectrometry can be used in conjunction with radioactivation analysis to determine many of the isolated radionuclides. The principles of this method have been described elsewhere^{4, 20}. Typical spectral data obtained by this method are given in several reports^{10, 21-24}.

The general analysis method outlined above results in the greatest sensitivity. Modifications of the method certainly can be instituted to increase this sensitivity.

SCOPE OF APPLICATION

Solid, liquid and gaseous materials are now being analysed by radioactivation analysis methods. Submicrogram and microgram concentrations of at least seventy-five of the elements have been determined in these investigations. Applications in macroanalysis are also reported and the use of radioactivation analysis, particularly with neutrons, as a complementary method to other analysis techniques has also been reported.

This discussion concludes with a description of selected examples of the applications being made by American scientists of radioactivation analysis methods. Where appropriate, the information is given in tabular form.

Charged particle radioactivation analysis

American work on charged particle radioactivation analysis has been somewhat more limited than on the Continent. This is probably caused by the fact that more nuclear reactors have been available and much work has gone into these efforts, while charged particle accelerators have been used in basic research programmes. As early as 1938, Seaborg and Livingood²⁵ used cyclotron deuterons for determining gallium in iron, copper in nickel and iron in cobalt. King and Henderson²⁶ used alpha particles to determine small amounts of copper in silver. A summary of these applications is presented in *Table 3*.

Table 3. Charged particle radioactivation analysis

<i>Analysis for</i>	<i>Reaction</i>	<i>Material analysed</i>	<i>Element found</i>	<i>Ref.</i>
Ga	$^{69}\text{Ga}(\text{d},\text{p})^{70}\text{Ga}$ $^{71}\text{Ga}(\text{d},\text{p})^{72}\text{Ga}$	Iron	10^{-6} g	25
Fe	$^{58}\text{Fe}(\text{d},\text{p})^{59}\text{Fe}$	Co_3O_3	10^{-6} g	25
Cu	$^{63}\text{Cu}(\alpha,\text{n})^{66}\text{Ga}$	Ag	10^{-5} g	26

Radioactivation analysis with high intensity alpha sources

Reiffel²⁷ reports on the use of a 30-curie polonium source to initiate an (α, n) reaction upon beryllium-9 to determine microgram concentrations of beryllium. A prompt gamma of 4.5 MeV is given off which is measured by gamma counting. A typical apparatus used in this analysis has been described by Reiffel.

Radioactivation analysis with neutrons

Many uses for neutron activation analysis have been found by American scientists. In most instances, quantitative analyses have been completed by the use of neutrons from different neutron sources. However, the O.R.N.L. group⁹ has used reactor neutrons in many qualitative applications in this radioactivation analysis method. Some of these have been completed by qualitative schemes similar to that outlined elsewhere¹⁷ while other analyses have been completed by nondestructive or direct radioactivity measurement methods¹⁵. One of the examples given in this description was concerned with the determination of trace elements in beryllium metal. *Figure 4* shows the results obtained in an analysis by means of a gamma scintillation spectrometer equipped with a multichannel analyser and by radioactive decay measurements. More recently, Leddicotte and Bate²⁸ have used similar methods of analysis by means of a 200-channel analyser to determine qualitatively trace elements in tobacco, limestone, zinc ore, cement, graphite and sand.

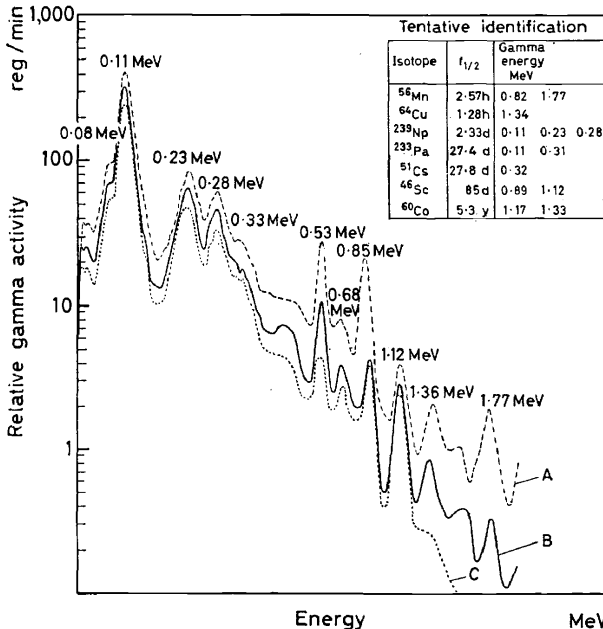


Figure 4. Activation analysis of beryllium metal. Irradiation period: 155 h. Flux: 6.5×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. Instrument: 20-channel gamma scintillation spectrometer. Crystal: solid NaI. Spectra recorded: A, 11 h; B, 30 h; C, 52 h after reactor discharge

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Table 4. Fast neutron radioactivation analysis

Neutron energy (MeV)	Nuclear source	Flux (neutrons cm ⁻² sec ⁻¹)	Analysis for	Neutron reaction	Material analysed	Element content (g)	Ref.
14.0	Low voltage accelerators (100-250 kV), D-T reaction	5 × 10 ⁷	Si	²⁸ Si(n,p) ²⁸ Al	SiO ₂	0.4	29
14.0	Low voltage accelerators (100-250 kV), D-T reaction	5 × 10 ⁷	Al	²⁷ Al(n,α) ²⁴ Na	Al ₂ O ₃	0.4	29
2.3	Reactor	10 ⁹ -10 ¹⁰	S	³² S(n,p) ³² P	HF, fluoride salts	10 ⁻⁶	52
4.5	Reactor	>10 ⁹	Ni	⁵⁸ Ni(n,p) ⁵⁸ Co	Soils, metals, ores	10 ⁻⁶	52
8.3	Reactor	>10 ⁹	Ti	⁴⁶ Ti(n,p) ⁴⁶ Sc	Metals	10 ⁻⁶ -10 ⁻⁶	52
	Reactor	10 ⁸ -10 ¹⁰	Al	²⁷ Al(n,α) ²⁴ Na	Water	<10 ⁻⁶	30

Although most of these applications have been made with slow or thermal neutrons, examples of fast neutron radioactivation are beginning to be reported. Turner²⁹ has determined silicon and aluminium with fast neutrons produced by an accelerator. Leddicotte *et al.*³⁰ have recently used fast neutrons from a reactor to determine trace sulphur, nickel, titanium and aluminium (see Table 4). In addition to fast neutron reactions, Bate and Leddicotte³¹ have been using *tritons* produced in the interaction of neutrons with ⁶Li in the nuclear reaction ⁶Li(n,α)³H, to determine microgram concentrations of oxygen in lithium, zirconium, aluminium and tantalum metals by the secondary nuclear reaction ¹⁶O(n,t)¹⁸F. Fluorine-18 decays with positron emission and a half-life of 112 min.

APPLICATIONS OF NEUTRON RADIOACTIVATION ANALYSIS

Use of accelerators as neutron sources

Low voltage accelerators of the Cockroft-Walton and Van de Graaff types have been used in a number of radioactivation analysis applications. In particular, the fast neutrons produced at voltages of 100-200 kV and with a deuterium-tritium target have been used for determining silicon and aluminium²⁹. The results of this work are given in Table 4.

Prolific neutron outputs are obtainable from Van de Graaff positive-ion accelerators by means of the ⁹Be(d,n)¹⁰B reaction. Burrell and Gale³² have tabulated the limits of measurements for irradiations at a flux of 10⁹ neutrons cm⁻² sec⁻¹. Typical information obtained in the use of this method of radioactivation analysis by several other research workers^{10, 33} is given in Table 5.

Use of low intensity neutron sources

Meinke and Anderson³⁴ have used a 25 mg radium-beryllium neutron source to develop a method for the activation analysis of rhodium, silver and indium in concentrations of 1 per cent or more. In another study, Meinke and Anderson³⁵ have reported on the determination of europium

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Table 5. The use of Van de Graaff accelerators in radioactivation analysis

Material analysed	Element determined	Obs. conc. (parts/million)	Ref.
Brominated polymers	Br	20-40	33
Synthetics	Cl	10 ² -10 ³	33
NH ₄ I, CaI ₂	I	50-66	33
NH ₄ F, NaF, LiF, Organics	F	10 ³ -10 ⁵	33
Polymers	Cl	3-190	10
Re-forming catalysts	Pt, Cl	10 ⁸	10
Inhibited sulphuric acid	Na, As	10 ⁸	10

in the presence of samarium and of dysprosium in the presence of holmium by use of similar equipment and techniques. De and Meinke²⁴ have recently used a 1-5 curie antimony-beryllium source and nondestructive methods based upon gamma scintillation spectrometry to analyse silver-cobaltic oxide, silver-lead iodide, copper and aluminium in synthetics, sodium iodide in various mixtures with other salts, manganese in ferromanganese and in various other mixtures. More recently Strain *et al.*³⁶ have been using americium-boron, americium-beryllium and radium-beryllium sources and an irradiation time of 1 h or less to determine a number of elements in concentrations of 0.1 per cent or less. Typical results from this unpublished study are given in Table 6.

Table 6. Neutron radioactivation analysis with low intensity neutron sources*

Element	Irradiation time	Units per minute† from the detection of 1 mg of element
Sc	1 min	54.3
Co	10 min	2.8
Mn	1 h	17.2
Cu	1 h	1.0
²³⁸ U	0.5 h	20.0
Na	1 h	0.2
Al	5 min	1.0

* J. E. Strain *et al.*, O.R.N.L. Activation Analyses Group.

† Detection limits for gamma scintillation count at discrete gamma energies. Count rate expressed as total scaler unit counts in channel of maximum energy. 1 unit = 16 counts per minute.

All of these studies would indicate that apparatus employing low intensity neutron sources can be applied to many analysis problems concerned with determining many different elements in which these occur in macro concentrations. Less time for analysis, smaller sample sizes and, in many instances, non-destructive analysis of sample material can result from the use of such apparatus.

Use of reactor neutrons

The application of large reactor neutron sources is well defined. Boyd¹, Taylor and Havens² and Leddicotte and Reynolds^{3, 37}, in particular, have based much of their descriptions of radioactivation analysis upon the use of the prolific sources of neutrons from a nuclear reactor. Leddicotte and Reynolds³⁷ and Leddicotte³⁸ have described the types of sample materials to which neutron radioactivation analysis can be applied.

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Applications in biochemistry

Table 7 shows the use of neutron radioactivation analysis in biochemistry by a number of investigators. Its use in medical research is most prominent; however, some work has already begun on its applications to the problems of nutrients, plant ecology, etc.

Table 7. Neutron radioactivation analysis applications in biochemistry

<i>Element determined</i>	<i>Material analysed</i>	<i>Element found (g)</i>	<i>Ref.</i>
<i>In medical research</i>			
Na	Blood serum	10^{-2}	39
	Muscle		40, 41
	Bone		42
	Blood vessels		43
K	Tissue	10^{-2}	44
	Muscle		40, 41
P	Tissue	10^{-4}	44
	Muscle		40, 41
Cl	Blood vessels	10^{-4}	43
	Tissue		44
Sb	Tissue	$10^{-7}-10^{-6}$	44
	Tissue		$10^{-8}-10^{-5}$
As	Tissue	$10^{-9}-10^{-6}$	44
	Tissue		$10^{-8}-10^{-5}$
Br	Tissue	$10^{-6}-10^{-5}$	44
	Tissue		10^{-6}
Cd	Tissue	$10^{-6}-10^{-5}$	44
	Tissue		$10^{-7}-10^{-4}$
Cs	Tissue	$10^{-7}-10^{-6}$	44
	Tissue		$10^{-5}-10^{-4}$
Cu	Tissue	$10^{-9}-10^{-5}$	44
	Tissue		$10^{-6}-10^{-5}$
Ni	Tissue	$10^{-6}-10^{-5}$	44, 45
	Bone		46
Zn	Tissue	$10^{-6}-10^{-3}$	44, 47
	Tissue		$10^{-6}-10^{-5}$
Zr	Tissue	10^{-6}	44
	Tissue		22
I	Blood proteins	$10^{-10}-10^{-6}$	44, 48
	Tissue		$10^{-8}-10^{-6}$
Au	Tissue	$10^{-8}-10^{-6}$	49, 50
<i>Other biochemistry applications</i>			
Co	Plant ash	10^{-9}	51
	Sugar cane		$10^{-7}-10^{-6}$
	Faeces		$10^{-8}-10^{-6}$
V	Plant ash	10^{-9}	51
	Soybean meal, yeasts, kidney powders		$10^{-8}-10^{-5}$
Se	L-cystine	10^{-6}	53, 54
	Sugar cane		55
Cu	Sugar cane	10^{-6}	52
	Grasses and grains		$10^{-4}-10^{-3}$
Fe	Grasses and grains	$10^{-4}-10^{-3}$	52
	Sugar cane		$10^{-7}-10^{-6}$
Mo	Sugar cane	$10^{-7}-10^{-6}$	52

Applications in petrochemistry

An extensive study of at least twenty trace elements in petroleum and similar materials has been recently completed by the Activation Analyses Group at O.R.N.L.⁹ A report of this work is now being compiled. Typical information obtained in the neutron radioactivation analysis of nickel in silica-alumina catalysts is given in Table 8. The data obtained are compared with those from the analysis of the same material by other methods. Work by other researchers^{10, 45, 56} also shows the usefulness of neutron radioactivation analysis in trace element determinations in

Table 8. Determination of nickel in silica-alumina catalysts

Sample	Nickel per cent by weight					
	Neutron activation analysis	Chemical colorimetric	Electrolysis colorimetric	Chemical gravimetric	Spec.	X-ray
A Base material	0.00095	0.00045	0.00065			
Base + 0.005%	0.0052	0.005	0.0056			
Base + 0.01%	0.0114	0.010	0.0104			
Base + 0.018%	0.0224	0.0197	0.0190			
D	0.0075			0.0090	0.0110	0.008
E	0.0145			0.0140	0.0170	0.0170
F	0.0120			0.0110	0.0090	0.0130

petrochemicals. In particular Guinn's report¹⁰ shows the possibilities of the method in analysing on a routine basis, and with nondestructive techniques, some twenty-seven different elements in petrochemicals. Many of these can be analysed in concentrations as small as a few parts per million.

Applications in metallurgy

Most of the applications of neutron activation analysis have been made in determining trace elements in metals and alloys. One of these^{5,7} has been used in studies concerned with the reduction of the iron and nickel contents of zirconium iodide by a floating zone purification of zirconium. The data obtained by the Activation Analyses Group at O.R.N.L.⁹ were used in the preparation of the curve given in Figure 5 to show the distribution of nickel as a function of displacement after several passes of the molten zone. More recently this analysis group has been concerned with the determination of trace impurities in ultra-pure semiconductor materials and in silicon and its compounds⁵. Typical data obtained in some of this work are given in Table 9. In addition to this work, Leddicotte *et al.*^{5,2}

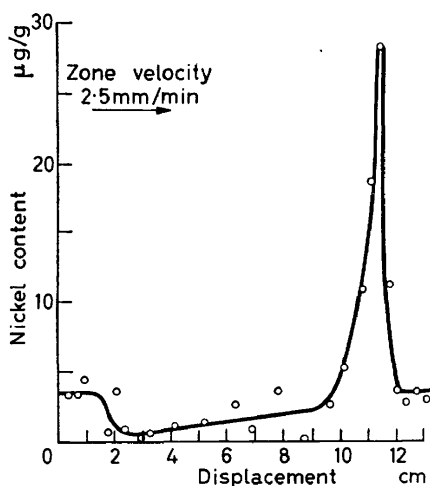


Figure 5. Nickel content as a function of displacement after six passes of the molten zone

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Table 9. Radioactivation analysis of trace elements in semi-conductor materials

<i>Material</i>	<i>Analyses for</i>	<i>Element found</i> (parts/million)
Trichlorosilane	Cu	0.4×10^{-3}
	Na	25.0×10^{-3}
	Mg, Ti, Al, Fe, Sn	$< 15 \times 10^{-3}$
	Ag, Sb, Mn, As	$< 10^{-3}$
Arsenic	Se	0.37, 0.36, 0.38
	Te	12.12
	S	69.6, 64.1 5.0, 6.7
Gallium	Na	268, 260
	Zn	25, 26
	Sn	1.0
	Cu	2.0
	Pt	3.2
	In	0.17
	W	0.018
Hg	0.68	

Table 10. Some applications of radioactivation analysis in metallurgy

<i>Element determined</i>	<i>Material</i>	<i>Element content</i> (g)	<i>Ref.</i>
Au	Silicon	10^{-7} – 10^{-6}	58
Zn	Silicon	10^{-4}	59
	Aluminium	10^{-3}	16
	Tungsten	10^{-5}	60
As	Silicon	10^{-6}	59
	Tungsten	10^{-6}	60
	Germanium	10^{-4}	61
W	Silicon	10^{-7}	59
	Titanium	10^{-6}	23
Fe	Silicon	10^{-5}	59
	Tungsten	10^{-4}	60
K	Silicon	10^{-7}	59
	Tungsten	10^{-6}	60
Na	Silicon	10^{-8}	59
	Tungsten	10^{-6}	60
	Germanium	10^{-5}	61
Ta	Silicon	10^{-6}	59
Cu	Aluminium	10^{-5}	59
	Aluminium	10^{-6} – 10^{-4}	16
	Tungsten	10^{-6}	60
	Germanium	10^{-4} – 10^{-6}	61, 62
Cr	Aluminium	10^{-6}	59
	Tungsten	10^{-4}	60
O	Metals	10^{-4} – 10^{-6}	31
Mn	Beryllium	10^{-5} – 10^{-4}	45
Ti	Aluminium	10^{-3}	16
Mo	Tungsten	10^{-6}	60
Sn	Tungsten	10^{-4}	60
	Germanium	10^{-6}	61
Ga	Aluminium	10^{-6}	45
	Zr-Hf	10^{-2}	63

have reported many other applications at the Oak Ridge National Laboratory.

Applications of neutron activation analysis in the field of metallurgy by other American investigators are shown in *Table 10*.

Applications in geochemistry

Important studies have been undertaken to determine trace elements in meteorites, ores, soils, waters, *etc.* by neutron activation analysis. Typical applications are given in *Table 11*.

Table 11. Applications of neutron radioactivation analysis in geochemistry

<i>Element determined</i>	<i>Type of sample</i>	<i>Element content (g)</i>	<i>Ref.</i>
Au	Meteorites	10^{-7} - 10^{-6}	64
Re	Meteorites	10^{-6}	65
K (as ^{41}A)	Minerals	(Age dating)	66
Th	Thorium meteorites	10^{-11}	67
	Stone meteorites	10^{-8}	68
	Ores, water, soils	10^{-8} - 10^{-6}	69
	Minerals	10^{-9}	70
U	Stone meteorites	10^{-8}	71
	Phosphate ores		72
Bi	Stone meteorites	10^{-10}	73
Pb	Stone meteorites	10^{-7}	73
Tl	Stone meteorites	10^{-10}	73
Mn	Water	10^{-6}	74
Various	Water	10^{-10} - 10^{-5}	75

Miscellaneous applications

Miscellaneous applications of neutron radioactivations include the analysis of 10^{-9} g of antimony in zirconium oxide⁷⁶. Cosgrove *et al.*⁷⁷ have used neutron radioactivation for the determination of 10^{-6} g of chloride, 10^{-6} g of iodide and 10^{-9} g of bromide in studies of the luminescent qualities of zinc sulphide phosphorus. Brooksbank *et al.*⁴⁵ also report on determining 10^{-5} - 10^{-6} g of cadmium in vinylite resins. Sayre *et al.*²¹ have used neutron activation analysis and gamma scintillation spectrometry to determine the presence of Al, Mn, Na, La, Sm, Cr, Sc, Cs, Fe, Co and Eu in ancient pottery. Rona *et al.*⁷⁴ have determined 10^{-6} g of manganese in oceanographic studies.

In addition to these analyses, Leddicotte⁷⁸ has determined the isotopic ratio of ^{235}U to ^{238}U in shales, and Rona⁷⁰ has used neutron radioactivation analysis for $^{232}\text{Th}/^{230}\text{Th}$ isotopic ratios. Emery and Leddicotte⁷⁹ have used neutron radioactivation analysis in the determination of trace argon in gaseous mixtures.

Radioactivation analysis as a complementary technique

A number of analytical methods have been complemented by radioactivation analysis. Benson⁵¹ reports on its use as a complement to radioautography of tissue specimens. Leddicotte *et al.*⁸⁰ have used it to assist in the analysis of particle size distribution in thorium oxide and uranium

oxide samples, and it has been used in studies of particle size distributions in multicomponent systems.⁸¹ In addition, Leddicotte and Bate⁸² have used it in studying the diffusion rates of chromium in Inconel in contact with corrosive solutions. Schultz *et al.*⁸³ have used radioactivation analysis to measure gear wear in various types of lubricants. Each of these applications is aptly described in these reports and data are presented for each application.

References

- ¹ G. E. Boyd. "Method of activation analysis", *Anal. Chem.*, **21**, 355 (1949)
- ² T. I. Taylor and W. W. Havens, Jr. "Neutron spectroscopy for chemical analysis. III", *Nucleonics*, **6**, No. 4, 54 (1950)
- ³ G. W. Leddicotte and S. A. Reynolds. "Activation analysis with the Oak Ridge reactor", *Nucleonics*, **8**, No. 3, 62 (1951)
- ⁴ G. H. Morrison. "Neutron activation analysis for trace elements", *Appl. Spectroscopy*, **10**, No. 2, 71 (1956)
- ⁵ G. W. Leddicotte. "Activation analysis for the determination of trace impurities in Group III-V elements and their compounds", paper presented at Battelle Memorial Institute, February 10, 1959. To be published.
- ⁶ W. W. Meinke. "Trace element sensitivity: Comparison of activation analysis with other methods", *Science*, **121**, No. 3137, 177 (1955)
- ⁷ A. A. Smales. "The scope of radioactivation analysis", *Atomics*, **4**, No. 3, 55 (1953)
- ⁸ W. T. Mullins, J. E. Strain, J. H. Oliver and G. W. Leddicotte. Unpublished data
- ⁹ Activation Analyses Group, Analytical Chemistry Division, Oak Ridge National Laboratory, Union Carbide Nuclear Company, Oak Ridge, Tennessee. Unpublished results
- ¹⁰ V. P. Guinn and C. D. Wagner. "Instrumental neutron activation analysis", Paper 772, American Chemical Society Meeting, Boston, Massachusetts, April, 1959. To be published in *Analytical Chemistry*
- ¹¹ G. W. Leddicotte and S. A. Reynolds. "The determination of the alkali metals by neutron activation analysis", O.R.N.L.-1623, October, 1953.
- ¹² R. C. Plumb and R. H. Silverman. "Activation analysis determines the sodium content of aluminum alloys", *Nucleonics*, **12**, No. 12, 29 (1954)
- ¹³ M. Green and J. A. Kafalas. "The purification of germanium", *J. Chem. Soc.*, **1955**, 1604
- ¹⁴ *Isotopics, United States Atomic Energy Comm. (Oak Ridge)*, **2**, No. 2 (Apr. 1952)
- ¹⁵ G. W. Leddicotte and S. A. Reynolds. "Nondestructive methods of analysis for radioactive nuclides", paper given at American Chemical Society National Meeting, San Francisco, California, April, 1958
- ¹⁶ W. A. Brooksbank, G. W. Leddicotte and J. A. Dean. "Neutron activation analysis of aluminum-base alloys", *Anal. Chem.*, **30**, 1785 (1958)
- ¹⁷ D. W. Moeller, G. W. Leddicotte and S. A. Reynolds. "Radionuclides in reactor cooling water", *J. San. Eng. Div., Amer. Soc. Civ. Eng.*, **SA2**, 11 (1959)
- ¹⁸ K. A. Kraus and F. Nelson. *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, **7**, 113-135 (1956)
- ¹⁹ H. G. Hicks, R. S. Gilbert, P. L. Stevenson and W. H. Hutchin. "The quantitative behavior of a number of metals with an ion exchange resin, Dowex 2", LRL-65 (December, 1953)
- ²⁰ W. J. Price. *Nuclear Radiation Detection*, pp. 162-211, McGraw-Hill, Inc., New York (1958)
- ²¹ E. V. Sayre, A. Murrenhoff and C. F. Weick. "The nondestructive analysis of ancient potsheds through neutron activation", *Brookhaven Nat. Lab., BNL-508 (T-122)* (April 1, 1958)
- ²² D. C. Borg. "Application of activation analysis to biological and medical research", Paper 841, 2nd International Conference of the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958
- ²³ W. A. Brooksbank, G. W. Leddicotte and S. A. Reynolds. "Determination of trace elements in titanium by neutron activation analysis", *Anal. Chem.*, **28**, 1033 (1956)
- ²⁴ A. K. De and W. W. Meinke. "Activation analysis with an antimony-beryllium source", *Anal. Chem.*, **30**, 1474 (1958).
- ²⁵ G. T. Seaborg and J. Livingood, "Artificial radioactivity as a test for minute traces of elements", *J. Am., Chem. Soc.* **60**, 1784 (1938)

- ²⁶ D. T. P. King and W. J. Henderson. "Radioactive isotopes of indium from alpha bombardment of silver", *Phys. Rev.*, **56**, 1169 (1939)
- ²⁷ L. A. Reiffel. "Measurement and control methods using radiation", Paper 827, 2nd United Nations International Conference of the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958
- ²⁸ G. W. Leddicotte and L. C. Bate. Oak Ridge National Laboratory. Unpublished data
- ²⁹ S. E. Turner. *Anal. Chem.*, **28**, 1457 (1956)
- ³⁰ G. W. Leddicotte and J. F. Emery. Unpublished data
- ³¹ L. C. Bate and G. W. Leddicotte. "The determination of oxygen by radioactivation analysis", Paper No. 40, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 3-7, 1958
- ³² E. A. Burrell and A. J. Gale. *Activation Analysis with Van de Graaff Neutron Sources*, High Voltage Engineering Corporation, Cambridge, Mass. (1954)
- ³³ G. J. Atchison and W. H. Beamer. "Neutron activation analysis with the Van de Graaff accelerator", *Anal. Chem.* **28**, 237 (1956)
- ³⁴ W. W. Meinke and R. E. Anderson. "Activation analysis using low level neutron sources", *Anal. Chem.*, **25**, 778 (1953).
- ³⁵ W. W. Meinke and R. E. Anderson. "Activation analysis of several rare earth elements", *Anal. Chem.*, **26**, 907 (1954)
- ³⁶ J. E. Strain, J. H. Oliver and G. W. Leddicotte. Unpublished data
- ³⁷ G. W. Leddicotte and S. A. Reynolds. "The determination of trace elements by neutron radioactivation analysis", *A.S.T.M. Bull.*, No. **188**, p. 29 (February, 1953)
- ³⁸ G. W. Leddicotte. "Activation analysis—What can it do for you?", *Nucleonics* **14**, No. 5, 46 (1956)
- ³⁹ R. P. Spencer, T. G. Mitchell and E. R. King. "Neutron activation analysis of sodium in blood serum", *J. Lab. Clin. Med.*, **50**, 646 (1957)
- ⁴⁰ L. Reiffel and C. A. Stone. "Neutron activation analysis of tissue; Measurement of sodium, potassium and phosphorus in muscle", *J. Lab. Clin. Med.*, **49**, 286 (1957).
- ⁴¹ J. D. Williams, B. M. Ansell, L. Reiffel, C. A. Stone and R. M. Kark. "Electrolyte levels in normal and dystrophic muscle determined by neutron activation", *Lancet*, **1**, 464 (1957).
- ⁴² R. Druyan, T. G. Mitchell and E. R. King. "Neutron activation analysis in the determination of bone sodium". To be published
- ⁴³ L. Silver. Unpublished data
- ⁴⁴ G. W. Leddicotte and W. T. Mullins. Unpublished data
- ⁴⁵ W. A. Brooksbank, G. W. Leddicotte and H. A. Mahlman. "Analysis for trace impurities by neutron activation analysis", *J. Phys. Chem.*, **57**, 815 (1953)
- ⁴⁶ W. B. Savachuck. "A comparison of bone growth in normal and strontium-treated rats", *J. Dental Research*, **38**, No. 1, 49 (1959)
- ⁴⁷ H. J. Koch, Jr., E. R. Smith, N. F. Shimp and J. Connor. "Analysis of trace elements in human tissues", *Cancer*, **9**, 499 (1956)
- ⁴⁸ A. M. Brues and O. H. Robertson. "Estimation of thyroglobulin iodine by slow neutron irradiation", *Argonne Nat. Lab. Quart. Rep. ANL-4108*, p. 104 (1947)
- ⁴⁹ C. A. Tobias and R. S. Dunn. "Analysis of microcomposition of biological tissue by means of induced radioactivity", AECD-2099B (1948)
- ⁵⁰ C. A. Tobias and R. W. Dunn. "Analysis of micro-composition of biological tissues by means of induced radioactivity", *Science*, **109**, 109 (1949)
- ⁵¹ A. A. Benson. "Application of the nuclear reactor in biochemical analysis: Neutron activation chromatography", Paper 858, 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958
- ⁵² G. W. Leddicotte, W. T. Mullins, L. C. Bate, J. F. Emery, R. E. Druschel and W. A. Brooksbank, Jr., Paper 927, 2nd United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958
- ⁵³ K. Schwarz and C. M. Foltz. "Factor 3 potencies of selenium compounds", *Federation Proc.*, **17**, No. 1 (March, 1958)
- ⁵⁴ E. L. Hove, G. S. Fry and K. Schwarz, "Ineffectiveness of factor 3-active selenium compounds in muscular dystrophy of rabbits on vitamin E-free diets", *Proc. Soc. Exp. Bio. Med.*, **98**, 27 (1958)
- ⁵⁵ K. Schwarz, J. A. Stesney and C. M. Foltz. "Relationship between selenium traces in L-cystine and protection against dietary liver necrosis", *Metabolism*, **8**, No. 1, 88 (1959)

EXPERIENCE IN THE U.S.A. ON RADIOACTIVATION ANALYSIS

- ⁵⁶ G. F. Shipman and O. I. Milner. "Determination of arsenic in hydrocarbon reforming catalysts by neutron activation", *Anal. Chem.*, **30**, 210 (1958)
- ⁵⁷ G. D. Kneip, Jr. and J. O. Betterton, Jr. "Floating zone purification of zirconium", *J. Electrochem. Soc.*, **103**, 684 (1956)
- ⁵⁸ G. Bemski and J. D. Struthers. "Gold in silicon", *J. Electrochem. Soc.*, **105**, 588 (1958)
- ⁵⁹ G. H. Morrison and J. F. Cosgrove. "Activation analysis of trace impurities in silicon using scintillation spectrometry", *Anal. Chem.*, **27**, 810 (1955)
- ⁶⁰ J. F. Cosgrove and G. H. Morrison. "Activation analysis of trace impurities in tungsten using scintillation spectrometry". To be published
- ⁶¹ G. H. Morrison and J. F. Cosgrove. "Activation analysis of trace impurities in germanium using gamma scintillation spectrometry", *Anal. Chem.*, **28**, 320 (1956)
- ⁶² G. Szekely. "Determination of traces of copper in germanium by activation analysis", *Anal. Chem.*, **26**, 1500 (1954)
- ⁶³ J. E. Hudgens and H. J. Dabagian. "Radioactivation determination of zirconium in Zr-Hf mixtures", *Nucleonics*, **10**, 25 (1952)
- ⁶⁴ H. S. Brown and E. Goldberg. "Radiometric determination of gold and rhenium", *Anal. Chem.*, **22**, 308 (1950)
- ⁶⁵ H. Brown and E. Goldberg. "The neutron pile as a tool in quantitative analysis. Gallium and palladium content of iron meteorites", *Science*, **109**, 347 (1949)
- ⁶⁶ A. Moljik, R. W. P. Drever and S. C. Curran. "Neutron activation applied to potassium-mineral dating", *Nucleonics*, **13**, 44 (1955)
- ⁶⁷ G. L. Bate, H. A. Potratz and J. R. Huizenga. "Thorium in iron meteorites: A preliminary investigation", *Geochim. et Cosmochim. Acta*, **14**, 118 (1958)
- ⁶⁸ G. L. Gate, J. R. Huizenga and H. A. Potratz. "Thorium content of stone meteorites", *Science*, **126**, 612 (1957)
- ⁶⁹ G. W. Leddicotte and H. A. Mahlman. "Determination of microgram and submicrogram quantities of thorium by neutron activation analysis", Paper 542, 1st United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1956
- ⁷⁰ E. Rona. "A method to determine the isotopic ratio of thorium-232 to thorium-230 in minerals", *Trans. Am. Geophys. Union*, **38**, 754 (1957)
- ⁷¹ H. Hamaguchi, G. W. Reed and A. Turkevich. "Uranium and barium in stone meteorites". To be published
- ⁷² H. A. Mahlman and G. W. Leddicotte. "Determination of microgram and submicrogram quantities of uranium by neutron activation analysis", *Anal. Chem.*, **27**, 823 (1955)
- ⁷³ G. W. Reed, K. Kigoski and A. Turkevich. "Activation analysis for heavy elements in stone meteorites", Paper 953, 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958
- ⁷⁴ E. Rona, D. W. Hood, L. K. Akers and L. Muse. "Determination of manganese in sea water". To be published
- ⁷⁵ R. S. Blanchard and G. W. Leddicotte. "The analysis of drinking water by neutron activation", Paper 796, 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958
- ⁷⁶ J. E. Hudgens, Jr. and P. J. Cali. "Determination of antimony by radioactivation", *Anal. Chem.*, **24**, 171 (1952)
- ⁷⁷ J. F. Cosgrove, R. P. Bastian and G. H. Morrison. "Determination of traces of mixed halides by activation analysis", *Anal. Chem.*, **30**, 1872 (1958)
- ⁷⁸ G. W. Leddicotte. Unpublished data
- ⁷⁹ J. F. Emery and G. W. Leddicotte. Unpublished data
- ⁸⁰ G. W. Leddicotte, J. P. McBride, H. H. Miller and R. E. Druschel. "Particle size analysis by radioactivation", ORNL-2160 (1958)
- ⁸¹ L. C. Bate and G. W. Leddicotte. "An evaluation of the particle-size distribution in multicomponent systems", *U.S. Atomic Energy Comm. Report TID-7568* (Pt. 3), p. 43 (April, 1959)
- ⁸² G. W. Leddicotte and L. C. Bate. Unpublished data
- ⁸³ W. W. Schultz, H. D. Briggs, R. A. Derves, E. E. Goodale, D. H. Morley, J. P. Neissel, R. S. Rochlin and V. V. Verbinski. "The use of activation in making isotope techniques more available to industry", Paper 819, 2nd United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, 1958

DISCUSSION

G. B. COOK (*U.K.*): What safety factors do you impose on samples so that they should not endanger the reactor? I am thinking, for instance, of organic liquids and solids which may also be inflammable and which, under the action of the intense ionizing radiation, may decompose and build up dangerous pressures in sealed containers.

G. W. LEDDICOTTE (*U.S.A.*): The containers used satisfy the requirements of the Reactor Safeguards Committee. They are never filled to more than about one-third of their volume so that sufficient room is left to allow for pressure effects. By July 1960, there will be a vertical facility with a cross-section of about 4 in. surrounded by a shield to permit the pouring in of liquid nitrogen or water.

J. HOSTE (*Belgium*): When chemical separations are required after activation it is of advantage to use specific reagents to speed up the process and reduce contamination. Copper, for instance, can be extracted specifically with isoamyl alcohol as the diquinolyl complex. As regards the difficulties mentioned in connection with the isolation and purification of chromium, the chromium can be isolated by distillation as CrO_2Cl_2 from perchloric acid through which hydrogen chloride is passed. The yield is quantitative. Other volatile chlorides such as those of arsenic, antimony and tin can be removed before the CrO_2Cl_2 distillation.

W. W. MEINKE (*U.S.A.*): I should be interested to hear further details about the pricing of radioactivation analysis.

P. LEVEQUE (*France*): The fee in France is 50 new French francs per analysis, including the irradiation. The price is not a cost price; as the method is relatively new, the price has been fixed as low as possible.

G. W. LEDDICOTTE (*U.S.A.*): The price in the United States was originally fixed on an analysis-hour basis. The original price was \$35 per element, taking into account the analytical time and the cost of buying neutrons at the reactor. More recently, a price of \$16 has been fixed for any irradiation service; monitoring would cost a further \$35, bringing the total to \$51 per irradiation. The object is to cover costs and, once a procedure becomes routine and can be taken over by commercial firms, the general policy is to discontinue the service.

D. GIBBONS (*U.K.*): There is no fixed scale of charges for the Harwell industrial activation analysis service. The charge for each analysis is made up of the cost of the radiation plus the cost of the experimental work in terms of the number of man-hours involved in the actual analysis. No charge is made for development work, which is regarded as research. We are not prepared, however, to undertake routine repetitive analyses for a large number of samples. Under such circumstances it would be in the interest of the user to set up his own laboratory. The average cost for the last 250 samples was £5 each. This may seem rather low, but the majority of irradiations have included up to about six samples so that the contribution of the irradiation charge per sample is small. Our irradiation charges have been increased and I estimate that the average charge will in future be £6 to £8 per sample and this will, of course, be higher for a single analysis and lower for multiple analyses.