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NEUTRON ACTIVATION AND HIGH RESOLUTION GAMMA SPECTROMETRY — ACTIVATION ANALYSIS

D. H. RETIEF*, C. W. VAN WYK†, J. TURKSTRA‡.

I. Fundamentals of Radioactivation

(A.) *Introduction*

RADIOACTIVE elements always have been present on earth, but they were first detected only towards the end of the nineteenth century. In 1896 Becquerel and Marya Sklodowska, later to become the celebrated Madame Curie, made a chance discovery that a photographic plate is activated by uranium salts. They surmised that the activation of the emulsion is due to a form of radiation of which the exact nature was still unknown. During the following decades a number of natural radioactive substances were isolated. Knowledge gained from the work that followed resulted in the classification of the radiations emitted by radioactive substances:

(i) Alpha (α)—particles.
An alpha-particle consists of two protons and two neutrons bound together in the stable component of the helium nucleus and carries a positive electric charge of two units.

(ii) Beta (β)—particles.
The beta-particles are identical with electrons and each particle carries one unit of negative electric charge.

(iii) Gamma (γ)—rays.
The gamma-ray is a quantized unit of electromagnetic energy with properties very similar to that of very high frequency x-rays.

In 1934 the famous husband and wife team, Frederic and Irene Curie-Joliot, discovered that radioactivity can be induced in non-radioactive substances by irradiation with α-particles. After the discovery of the neutron by Chadwick in 1932, Fermi (1934) showed that the number of artificially produced radioactive substances (radionuclides) can be greatly increased by neutron activation.

Thus the value of neutron activation as an analytical research tool became apparent, and in 1936 Hevesy and Levi pioneered its use for this purpose. Due to the lack of suitable radiation sources and sensitive gamma spectrometers, it developed slowly. Since the second world war nuclear reactors as a source rich in neutrons have become available and helped to solve the problem. In addition the remarkable advance in the field of elec-

*Dental Research Unit of the University of the Witwatersrand and Council for Scientific and Industrial Research, Johannesburg.

†Department of Dentistry, University of the Witwatersrand, Johannesburg.

‡Chemistry Division, Atomic Energy Board, Pelindaba.

tronics has resulted in the development of sensitive gamma spectrometers, the other basic requirement of neutron activation analysis.

(B.) *The Principle of Neutron Activation*

This depends on the reaction of neutrons with the nuclei of atoms. The sample to be analysed is exposed to neutron bombardment. Some of the atoms in the sample will interact with the bombarding particles and may be converted into different isotopes of the same element or isotopes of different elements. In many cases the isotopes produced are radioactive. The radioactive isotopes (radionuclides) decay and in the process may emit, amongst others, gamma-rays which are high-energy electromagnetic radiations. The energy of the released gamma-ray is characteristic of the nucleus from which it is emitted and the intensity of the induced radioactivity is proportional to the weight of the element, all other conditions being equal.

Neutrons can enter the nucleus without being repelled by the positively charged protons because they carry no charge. Under the same conditions, neutrons do not react to the same extent with different nuclei. The tendency of a nucleus to react with neutrons is called the activation cross-section and is expressed by σ (sigma) and is measured in barns (1 barn = 10^{-24} cm^2). The neutron cross-section varies over a wide range for different nuclei such as:

Element	*Thermal Neutron Absorption Cross-section in Barns*
Cd	2500
Pt	195
Ag	63
Br	6·7
Na	0·53

The activation cross-section, which depends on the neutron energy, is also proportional to the probability that the bombarding particles will activate the target nuclei.

Depending on the energy of the neutrons, they react with nuclei in various ways. Neutron capture is the reaction with the greatest probability for thermal neutrons—that is, neutrons that are produced in nuclear reactors [(n, γ) reaction]. Because such a nucleus contains an excess of neutrons, it leads in most cases to unstable nuclei. These usually decay by beta emission and may be accompanied by the emission of gamma rays.

If the nucleus of an atom A with atomic weight m and atomic number z captures a neutron n, the reaction may be represented as follows:

$$ {}^{m}_{z}A + {}^{1}_{0}n \longrightarrow {}^{*m+1}_{z}A \quad \text{———(1)} $$

${}^{*m+1}_{z}A$ is an isotope of ${}^{m}_{z}A$ and is in the exited (metestable) state. It almost immediately decays to ${}^{m+1}_{z}A$ in the ground state by the emission of prompt gamma rays.

$$ {}^{*m+1}_{z}A \longrightarrow {}^{m+1}_{z}A + \gamma \quad \text{———(2)} $$

$$ (1) + (2) \quad {}^{m}_{z}A + {}^{1}_{0}n \longrightarrow {}^{m+1}_{z}A + \gamma $$

or $\quad {}^{m}_{z}A\ (n, \gamma)\ {}^{m+1}_{z}A.$

In most cases the product of neutron capture is a radioactive isotope. Such a nucleus contains an excess of neutrons and may transfer one of these into a proton plus an electron.

$$ n \longrightarrow p^{+} + e^{-}. $$

The electron being unable to remain in the nucleus, is emitted as a β-particle while the resulting nucleus has its atomic number increased by one and thus becomes the nucleus of a different element. The emission of β-particles may be accompanied by gamma rays as shown below.

$$ {}^{m+1}_{z}A \xrightarrow[\text{with or without } \gamma\text{-rays}]{\text{emission of } \beta\text{-particles}} {}^{m+1}_{z+1}B $$

The energy of the β- and γ-emissions is characteristic of the emitting nucleus, and thus

$$^{23}_{11}\text{Na}\ (n, \gamma)\ ^{24}_{11}\text{Na} \xrightarrow[1 \cdot 38\ \text{MeV}\gamma]{1 \cdot 39\ \text{MeV}\beta} {}^{24}_{12}\text{Mg}$$

The induced radioactivity can be measured in terms of rate of decay of the radioactive atoms present. The rate at which these radioactive nuclei disintegrate depends on the number present at any one time and is expressed by the following relationship:

$$\frac{dN^*}{dt} = \lambda N^* \qquad (3)$$

Where N^* = the number of radioactive atoms at any time t,

λ = the radioactive disintegration constant which is characteristic of the radioactive nuclei under consideration.

Integration of (3) gives:

$$N^* = N_0 e^{-\lambda t} \qquad (4)$$

Where N_0 = the number of radioactive atoms present at time t = o.

If $t\frac{1}{2}$ represents the time during which the number of radioactive atoms decreases to half the number originally present—that is, when $N^* = \frac{1}{2} N_0$

then $\frac{1}{2} N_0 = N_0 e^{-\lambda t\frac{1}{2}}$

$$\frac{1}{2} = e^{-\lambda t\frac{1}{2}}$$

$$t\tfrac{1}{2} = \frac{\ln 2}{\lambda}$$

$$t\tfrac{1}{2} = \frac{0.693}{\lambda} \qquad (5)$$

$t\frac{1}{2}$ is a function of λ and is therefore a nuclear constant. It is known as the half-life of the radio isotope and is a specific characteristic of the nucleus which decays. When a radio isotope is produced at a constant rate, the rate of increase in the quantity of the isotope is the difference between the rate of its production and the rate of its decay.

$$\text{Thus } \frac{dN^*}{dt} = P - \lambda N^* \qquad (6)$$

Where P = the production rate of the radioactive nuclei. The production rate is proportional to the neutron flux, the nuclear cross-section and the number of target atoms and is given by the following equation:

$$P = f \sigma N$$

where f = the neutron flux in neutrons . cm^{-2}. sec^{-1},

σ = the neutron-activation cross-section in cm^2,

N = the number of inactive target atoms.

$$\therefore \frac{dN^*}{dt} = f \sigma N - \lambda N^* \qquad (7)$$

Integration over the period of irradiation gives:

$$N^* = \frac{f \sigma N (1-e^{\lambda t})}{\lambda} \qquad (8)$$

The number of radioactive atoms in a sample increases until their rate of formation just equals their rate of decay. In practice it may take too long for this equilibrium to be reached and the operator settles for an irradiation time which gives him sufficient gamma-activity to measure accurately. The half-life of the radionuclide does not control the inherent sensitivity of the method, except in so far as it becomes a practical limitation. In the case of the long-lived emitters the irradiation time has to be so long in order to obtain sufficient activity for accurate measurement that it is not a practical proposition. On the other hand the half-lives of some of the radioisotopes formed are too short to allow for removal from the reactor and subsequent counting. The activity in disintegrations per second of the N^* atoms at time t is

$$A_t = \lambda N^*$$

$$= f \sigma N (1-e^{\lambda t}) \qquad (9)$$

$$\text{Where } N = \frac{\theta\ W \times \text{Avogadro's number}}{M}$$

Where θ = fractional abundance of the isotope concerned,

W = weight of element with atomic weight M,

and Avogadro's number = $6 \cdot 02 \times 10^{23}$

Therefore equation (9) may be written as follows:

$$A_t = \frac{f \sigma \theta W (1-e^{\lambda t})\ 6 \cdot 02 \times 10^{23}}{M}$$

By making use of the absolute disintegration rate, the magnitude of the flux, the activation cross-section and the half-life of the resulting radionuclide, a calculation can be made to determine the absolute mass of the component which is being investigated. The knowledge of the flux and activation cross-section is, however, not always accurate. In addition the absolute disintegration rate cannot be determined with sufficient accuracy. In practice these difficulties are overcome by using a comparative procedure. The samples to be analysed are simultaneously irradiated with standard specimens containing known proportions of the elements under investigation. The mass of X, the constituent to be determined, is obtained as follows:

$$\frac{\text{Mass of X in unknown}}{\text{Mass of X in standard specimen}} = \frac{\text{Total activity from element X in unknown}}{\text{Total activity from element X in standard specimen}}$$

(C.) *Nuclear Reactions*

When an atomic nucleus is bombarded with nuclear particles, a wide range of nuclear reactions can take place depending on the nature of the bombarding particle as shown below:

Bombarding Particle	*Possible Nuclear Reaction*
(i) Thermal Neutrons $V_0 = 2200$ m/sec	(n, γ)
(ii) Fast neutrons $V_0 \simeq C$ (speed of light)	(n, 2n), (n, p), (n, α), (n, γ)
(iii) Charged particles (protons and deuterons)	(p, n), (p, d), (p, γ), (d, n), (d, p)
Charged particles with energy E 100KeV $<$ E $<$ 10MeV	(p, n), (p, p), (α, α), (d, d)
(iv) Electromagnetic radiation	(γ, n), (γ, p), (γ, d)

II. THE SOURCE OF BOMBARDING PARTICLES

(A) *Nuclear Reactor Neutron Sources*

The neutron source with the greatest flux is the nuclear reactor, and this is the most common method of irradiation used in activation analysis. In most research reactors a flux of 10^{12} to 10^{14} thermal neutrons .cm^{-2}.sec^{-1} can be obtained. An important characteristic of a nuclear reactor is the accessability to the neutrons in its core. A reactor is equipped with a pneumatic-rabbit system by means of which samples to be irradiated can readily be inserted into the core and withdrawn after irradiation.

(B) *Non-Reactor Neutron Sources*

(i) *Nuclear Accelerators and Neutron Generators.* Charged particles (protons and deuterons) are accelerated to an appropriate energy and allowed to strike a tritium target. The neutrons are produced by a secondary reaction:

$$^{3}H\ (p, n)\ ^{3}He$$
$$^{3}H\ (d, n)\ ^{4}He$$

In this manner, up to 10^{10} fast (approximately 14 MeV) neutrons per second can be obtained.

(ii) *Isotopic Neutron Sources.* By mixing beryllium intimately with high-energy gamma emitters (Sb-124) or with alpha emitters (Am-241) a laboratory source of neutrons can be obtained by the (γ, n) and (α, n) reactions on beryllium:

$$^{9}Be\ (\gamma, n)\ ^{8}Be$$
$$^{9}Be\ (\alpha, n)\ ^{12}C.$$

A low neutron flux of approximately 10^{1} thermal n.cm^{-2}.sec^{-1} is obtained. The isotopic neutron sources are not suitable for trace-element analysis but can be useful for rapid macro-analysis.

(iii) *Spontaneous fission neutron sources.* Such as ^{252}Cf which emits neutrons in its decay scheme.

(C) *Activation by Particles Other than Neutrons*

The most efficient charged particles for activation are deutrons and tritons, but protons and α-particles are quite frequently used (see nuclear reactions). Cyclotrons and van de Graaff machines are used for the production of these bombarding particles.

III. COUNTING EQUIPMENT

(A) *Beta-activity*

The β-activity can be measured with a Geiger-Müller or proportional counter. The operation of both detectors is based on the fact that incoming β-particles cause ionization in a gas-filled tube. This gives rise to electrical impulses which can, after amplification, be indicated on a scaler.

(B) *Gamma-activity*

In the case of γ-spectrometry the gamma-rays can be measured with a scintillation counter or a semiconductor detector. Incident gamma-rays cause light photons in the scintillation crystal which in most instruments consists of a NaI(Tl) crystal. The scintillation detector emits flashes of light or scintillations each time a gamma-ray passes through it. The flashes are detected by a photo-multiplier tube which converts them into electrical impulses. The more energetic the gamma-ray the brighter the flash and consequently the higher the voltage of the electrical pulse. The pulses are amplified and then passed through a multichannel differential analyser.

The scintillation counters have been superseded by the semiconductor detectors because of their superior resolution. A semiconductor detector consists of a lithium drifted germanium detector, Ge (Li), which is obtainable in different volumes. It may be regarded as an ionisation chamber in which the sensitive volume is a solid instead of a gas. An incident gamma-photon (gamma-ray) produces a certain amount of ionisation charge in the detector which gives a pulse of current in an external circuit—a pre-amplifier. The latter converts the ionisation charge into a voltage pulse. The pulse is then amplified to a level suitable for detection by a multichannel analyser.

In both methods of gamma-ray detection described, the multichannel analyser groups all the pulses of the same energy into their respective channels. These may be recorded electronically on the screen of an oscilloscope, graphically with a point plotter, printed digitally or recorded on a magnetic tape. The heights of the pulses in the different channels are proportional to the number of incident gamma-photons and therefore a measurement of the concentration of the elements.

IV. PRACTICAL STEPS IN ACTIVATION ANALYSIS

(A) *Select the best nuclear reaction*

The (n, γ) reaction or neutron capture is the reaction with the greatest probability for thermal or slow neutrons produced in a nuclear reactor. If the activation cross-section for thermal neutrons is too small for a particular element, activation by fast neutrons or charged particles (protons or α-particles) should be considered.

(B) *Choose a radiation facility*

See under II—the source of bombarding particles.

(C) *Preparation of the sample prior to irradiation*

Special care must be taken in the preparation of the sample to prevent its contamination prior to irradiation. It may also be necessary to remove elements that emit interfering radiation by chemical means.

(D) *Irradiation of the sample*

The sample is irradiated with the neutron source selected. The time of irradiation depends on the sensitivity desired, the activation cross-section involved and the half-life of the radioisotope produced. In some cases it is possible to employ a non-destructive analysis which involves direct measurements of the activity of the irradiated sample without prior chemical separation. The high resolution obtained with the solid-state detectors (germanium/lithium) often eliminates the need for chemical separation.

(E) *Chemical separation after irradiation*

Chemical separation (destructive analysis) of the irradiated sample is not always necessary, but if it is, the separation technique must be efficient so that the elements can be recovered quantitatively for counting.

(F) *Counting of the irradiated sample*

The irradiated sample or the fractions obtained after chemical separation are subjected to gamma spectrometry.

(G) *Interpretation of the data*

If the composition of different materials is to be compared the "nuclear-fingerprints" may be used. They are obtained from the gamma spectra of the samples.

If a qualitative analysis is required, the counting apparatus is calibrated with standard samples of known radioisotopes and the energies of photo-electric peaks read from the calibration curve. Tables, available in all nuclear laboratories, enable the investigator to identify the radioisotope. If a quantitative analysis is required the data is compared with that obtained from samples containing known quantities of the elements concerned and irradiated simultaneously with the unknown sample.

V. THE ADVANTAGES OF ACTIVATION ANALYSIS

Activation analysis is the most sensitive analytical method available for many elements. It is also a relatively rapid method; even if chemical separation has to be carried out an experienced operator can analyse a number of samples daily.

Contamination with analytical materials *after* irradiation has no effect because the concentration of the element in the sample is determined only by its radioactivity. Hence it rarely poses a problem.

VI. THE LIMITATIONS OF ACTIVATION ANALYSIS

Like any other analytical method, activation analysis has its limitations.

The half-life of some of the radionuclides formed is so short that it is difficult to record the activity after removal from the reactor. Elements in this category include He, Li, B, N, O and F, which have half-lives measured in seconds or even less. The long-lived radioisotopes such as Be and C also present certain difficulties; their low radioactivity makes the accurate determination of their activity difficult due to technical problems.

The activation cross-sections of some elements for thermal neutrons, such as H and Pb, are so low that irradiation with high energy neutrons or even charged particles may give more favourable results.

As heat is produced in a nuclear reactor and by the neutron reaction, unless the sample is stable at the particular temperature to which it is exposed it will decompose. In addition structural damage and decomposition of a sample may occur as it is exposed to neutrons and gamma-rays in a nuclear reactor. This decomposition may produce gas, the pressure of which can break even the sealed containers.

Although the n, γ reaction is the main one to occur with the thermal neutrons in a nuclear reactor, other nuclear reactions may take place with the slow neutrons as well as the fast neutrons and gamma-rays that are present in a reactor.

In practice this means that the radionuclide being used as a measure of the mass of a certain element may in fact be formed from quite a different element. For example the determination of arsenic by irradiation depends on the formation of ^{76}As from ^{75}As by the following nuclear reaction:

$$^{75}_{33}\text{As} + {}^{1}_{0}\text{n} \longrightarrow {}^{76}_{33}\text{As}$$

^{76}As, however, may be produced by several other nuclear reactions starting from elements other than arsenic.

Such as $$^{76}_{34}\text{Se} + {}^{1}_{0}\text{n} \longrightarrow {}^{76}_{33}\text{As} + {}^{1}_{1}\text{H}$$

(n, p) reaction

or $$^{79}_{35}\text{Br} + {}^{1}_{0}\text{n} \longrightarrow {}^{76}_{33}\text{As} + {}^{4}_{2}\text{He}$$

(n, α) reaction

The (n, p) and (n, α) reactions, however, have a much lower cross-section than the (n, γ) reaction. In practice this limitation only becomes apparent in the determination of trace elements in the presence of macroquantities of the adjacent elements in the periodic table.

VII. THE APPLICATION OF ACTIVATION ANALYSIS

The inherent high sensitivity of neutron activation for many elements makes this method extremely suitable for the determination of traces of them.

It is extensively used to determine the composition of geological samples and meteorites. Activation methods have been developed for the determination of traces of elements in pure metals, and equipment has been designed for the analysis of the crust of the moon.

In the biological sciences it is frequently used—for example in the determination of trace-elements in human blood and tissues. The accuracy of this analytical method has led to its use in the medico-legal field. Hair, even hundreds of years old, can be analysed successfully for arsenic and other residues. It has even been used to identify the geographical source of opium by identifying the trace-elements the poppy plants absorb from the different soils in which they grow.

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A QUALITATIVE AND COMPARATIVE STUDY OF ELEMENTS IN TEETH BY NEUTRON ACTIVATION AND HIGH RESOLUTION GAMMA SPECTROMETRY

I. INTRODUCTION

As the exact mineral composition of teeth often has to be known, improved methods for the detection and quantitive analysis of the elements they contain continually are being sought. In 1937 Lowater and Murray[1] detected nineteen elements by spectrographic methods; and later Swift[2] found a large number quantitively by means of spark source mass spectrometry. A further advance was the use of electron probe x-ray microanalysis by Suga *et al*[3] to determine the topographical distribution of some of the elements present.

A recently developed sensitive analytical method—neutron activation followed by gamma-ray spectrometry—may be used as a qualitative and quantitative method for analysis of elements in teeth. Söremark and Samsahl[4,5,6] employed it for the analysis of trace-elements in enamel, dentin and calculus. The samples were irradiated for 20 hours in a neutron flux of approximately 2 x 10^{12}n.cm^{-2}.sec^{-1}. The activated samples were subjected to a chemical group separation followed by gamma spectrometric analysis. A NaI(Tl) scintillation crystal was used as a detector. Eleven elements (Ca, P, Na, Cl, Zn, Sr, Br, Mn, Cu, W and Au) were determined quantitatively, and an additional eight long-lived radioisotopes qualitatively. This work was continued by Söremark and Lundberg[7], who determined six of these long-lived radioisotopes (Pb, Cr, Ag, Fe, Co and Pt) quantitatively by employing a higher neutron flux of approximately 6·5 x 10^{13}n.cm^{-2}.sec^{-1}.

The inherent high sensitivity of neutron activation analysis for many elements makes this method suitable for the analysis of trace-elements. Since Ge (Li) semiconductor detectors[8] with a superior resolution have superseded the Na I (Tl) scintillation counters for the detection and measurement of gamma-rays, this method has become even more versatile. The high resolution permits studies of complex gamma spectra in much more detail and has made possible the non-destructive