CHAPTER II

THEORY OF NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis (NAA) is a method of elemental analysis in which various elements present in a sample are detected quantitatively by means of the radiations emitted by neutron-induced radioactivities in the sample. Each radioisotope can be identified by means of the type and energy of its radiations, and the half life with which it decays. The concentration of an element in a sample can be determined by using comparative method. In this method, the activity of the element (radionuclide or radioisotope) in the sample and a standard of known weight are compared.

2.1 Neutron Source (61)

There are many sources of neutrons such as isotope neutron source, accelerator and nuclear reactor. The major source of neutrons is the nuclear reactor, which operates on the principle of fission chain reactions in U-235. The fission neutron energy spectrum in the reactor is very wide, ranging from 0.001 eV (electron volt) to 15 MeV (Million electron volt). The neutrons can be broadly classified as

2.1.1 Thermal neutrons

Thermal neutrons have energies in the range of 10^{-3} to 0.5 eV; mean 0.025 eV. The thermal neutron cross-section for many elements are high, especially in (n,γ) reaction, thus thermal neutron activation analysis is an extremely sensitive method for most elements.

2.1.2 Epithermal neutrons

This type of neutrons have energies in range 0.5 eV to 0.5 MeV

2.1.3 Fast neutrons

These neutrons have energies in range 0.5-15 MeV or higher. The fast neutrons can be used to produce reactions of the type $(n,2n)$, (n,α), (n,p) and (n,n).

2.2 Nuclear Reaction (62)

When nucleus of element is bombarded with neutron, nuclear-reaction will happen, which depends on the type of neutron. Typical reactions may be classified as **follows:**

2.2.1 Neutron-gamma reaction: (n,γ) reaction

A target nucleus B bombarded with low-energy neutrons (often thermal neutrons) may be transformed into a radioisotope of the target element, C, with the emission of a γ-ray photon. This target element and its radioisotope usually cannot be separated chemically.

$$ {}^{A}_{Z}B + {}^{1}_{0}n \longrightarrow {}^{A+1}_{Z}C + \gamma $$

The common notation of this type of reaction is B (n,γ) C and typical reaction is ${}^{23}_{11}\mathrm{Na}\ (n,\gamma)\ {}^{24}_{11}\mathrm{Na}$. This (n,γ) reaction usually use in the neutron activation analysis.

2.2.2 Neutron-proton reaction: (n,p) reaction

A target nucleus B bombarded with high-energy neutrons (often fast neutrons) may be changed to a radioisotope of new element, C, with the emission of a proton. This element and **the** radioisotope of new element may be separated chemically, thus this reaction is usually used in the production of a radioactive element.

$$^{A}_{Z}B + {}^{1}_{0}n \longrightarrow {}^{A}_{Z-1}C + {}^{1}_{1}P$$

The common notation of this type of reaction is **B(n,p)C** and typical reaction is $^{32}_{16}S$ (n,p) $^{32}_{15}P$

2.2.3 Neutron-alpha reaction: (n,α) reaction

A target nucleus B bombarded with fast neutrons may receive enough energy to eject an α-particle and a radioisotope of new element, C. This reaction is not used in neutron activation analysis and the production of radioisotope element because it is difficult to occur.

$$^{A}_{Z}B + {}^{1}_{0}n \longrightarrow {}^{A-3}_{Z-2}C + {}^{4}_{2}\alpha$$

The common notation of this reaction is B (n,α) C and typical reaction is $^{27}_{13}Al$ (n,α) $^{24}_{11}Na$.

There are other nuclear reactions such as neutron-neutron reaction: (n,2n), neutron-fission reaction: (n,f).

2.3 The Theory of Neutron Activation Analysis (2,61-64)

2.3.1 Principles of Neutron Activation Analysis

In neutron activation, a very small fraction of the element to be determined is converted into a radioactive nuclide. Rate of formation of radioactive nuclide **depends** on the thermal neutron flux (ϕ), the neutron capture cross section of the target nuclei (σ), the numbers of target nuclide (N) and the fraction isotopic abundance of target element (express in %), f.

The rate of formation of any radioactive nuclide is given by the equation

$$P = N\sigma\phi \qquad (2.1)$$

in which N = the number of target nuclides present in the sample

σ = the neutron capture cross section of the target nuclei, in barn (1 barn = 10^{-24} cm^2)

ϕ = the thermal neutron flux, in neutrons $cm^{-2}.sec^{-1}$

P = the rate of formation of radioactive nuclide

While the radioactive nuclide is formed, the former radioactive nuclide also decays at the same time. The disintegration rate of radioactive nuclides, $\frac{dN^*}{dt}$, is dependent on the number of radioactive nuclides present at any time and is expressed by the relationship

$$\frac{dN^*}{dt} = -\lambda N^* \qquad (2.2)$$

where N^* = the number of radioactive nuclides at any time, t.

λ = the radioactive disintegration constant

$= 0.693 / t_{1/2}$

$t_{1/2}$ = half life of the radioactive nuclide which is the time required for half of the initially present radionuclide to disintegrate.

Thus, at any given time during a steady irradiation, the net rate of formation of such radioactive nuclide

$$\frac{dN^*}{dt} = P-\lambda N \qquad (2.3)$$

When this equation (2.3) is integrated, the solution is

$$N^* = \frac{P}{\lambda}(1-e^{-\lambda ta}) + No^* e^{-\lambda ta} \qquad (2.4)$$

where No* = the number of radioactive nuclides present initially, is zero

ta = irradiation time or activation time (λ and ta should be in the same unit)

thus at $t_a = 0$; $N^* = \frac{P}{\lambda}(1-e^{-\lambda ta})$ (2.5)

Given, Ao is the activity (disintegration rate of radionuclide) of that particular species of radioactive nuclide just at the end of the irradiation, **expressed** in disintegration per second.

From equation (2.2)

$$Ao = \lambda N^* \qquad (2.6)$$

Thus, equation (2.5) can **be written in the following equation,**

$$Ao = P(1-e^{-\lambda ta}) \qquad (2.7)$$

or

$$Ao = N\sigma\phi(1-e^{-\lambda ta}) \qquad (2.8)$$

The number of target nuclides present in the sample can be calculated from the following equation

$$N = N_o W f / M \qquad (2.9)$$

where N_o = Avogadro's number (6.022×10^{23}) atoms/gram-atom)

W = the weight of element present in the sample

f = the fraction isotopic abundance of particular target stable isotope of the element

M = atomic weight of the element

Thus, equation (2.8) can be written as

$$A_o = \frac{N_o W f \sigma \phi}{M} (1-e^{-\lambda t_a}) \qquad (2.10)$$

In general, however, the activity will not be determined until a time tw after the bombardment has ended, so that the radioactive nuclides produced will have decayed by a factor $e^{-\lambda t_w}$. Hence

$$A = \frac{N_o W f \sigma \phi}{M} (1-e^{-\lambda t_a})\, e^{-\lambda t_w} \qquad (2.11)$$

or

$$W = \frac{A M e^{\lambda t_w}}{N_o f \phi \sigma (1-e^{-\lambda t_a})} \qquad (2.12)$$

where A = the activity of radioactive nuclides at any time, tw

tw = decay time or waiting time (λ and tw should be in the same unit)

The concentration of an element in sample can be calculated from the equation (2.12). But some of the above parameters, such as neutron flux (ϕ), the neutron capture cross section of the target(σ)

can not be accurately measured. Thus, the comparative method is available because it eliminates any uncertainty in the parameters σ, ϕ and λ. In the comparative method, an element X in a sample and a known amount of the same element X as a standard are irradiated together, and both sample and standard are counted under exactly the same conditions by the same radiation detector. The equation by the comparative method is as follows:

$$\frac{\text{weight of element X in sample}}{\text{weight of element X in standard}} = \frac{\text{Ax in sample} \cdot e^{\lambda \text{tw sample}}}{\text{Ax in standard} \cdot e^{\lambda \text{tw standard}}}$$

2.3.2 The Technique of Neutron Activation Analysis

There are two main forms of the neutron activation analysis method, i.e.

2.3.2.1 Instrumental Neutron Activation Analysis (Non-destructive Analysis): INAA

In INAA, no chemistry is performed on the sample after it has been activated, the sample is merely activated together with the standard and then counted on the gamma-ray spectrometer after a suitable decay time. This form of the method is nondestructive.

2.3.2.2 Radiochemical Neutron Activation Analysis:RNAA

In RNAA, after the completion of irradiation the suitable chemical reactions steps, such as extraction, distillation, precipitation and ion-exchange, are carried out to isolate the activated elements of interest individually from other activated interfering elements. Then the activities of isolated element and standard are compared. This radiochemical-separation form of the method is destructive of the sample.

Pre-irradiation chemical separations (separate first and then irradiate) are also used in NAA work, but usually only when they are absolutely necessary because contamination easily **occurs.** This method is used only if other matrix elements, upon activation, seriously interfere with the INAA detection of a very short-lived induced activity of interest.

2.3.3 Sensitivity of Neutron Activation Analysis

Sensitivity of this method is defined as the smallest amount of element that can be determined under the given conditions. This sensitivity can be improved with increasing induced specific activity (activities per gram of element). From equation 2.11 it can be written:

$$\text{specific activity} = \frac{A}{W} = \frac{N_o f \sigma \phi}{M} (1 - e^{-\lambda ta})\, e^{-\lambda tw} \quad (2.14)$$

In connection to equation 2.14, the specific activity will be greater when:

- the higher the thermal-neutron flux (ϕ)
- the higher the neutron capture cross-section of target isotope (σ)
- the lower the atomic weight of the element (M)
- the shorter the half-life ($t_{1/2}$) of the radioisotope product (for a limited irradiation time, ta)
- the longer the irradiation time

and - the higher the fractional isotopic abundance (f) of the target stable isotope

Owing to the wide ranges in the various values of σ, f and $t_{1/2}$ and to a lesser extent in the various values of atomic weight, the various induced specific activities-for any combination of ϕ and ta-vary widely. In fact, considering the activities of practical use, they vary from the lowest value to the highest values. Thus, in the NAA method, some elements can be determined with very high sensitivity, most with very good sensitivity, and some only with rather modest sensitivity.

One factor that affects the sensitivity of the method is the efficiency of the detector. This efficiency is defined as

$$\%\ \text{efficiency} = \frac{\text{measured activities}}{\text{true activities}} \times 100 \qquad (2.15)$$

Therefore, the higher the efficiency of the detector, the greater the sensitivity of the method will be.

The efficiency of thermal neutron production of a reactor also affected this sensitivity. The higher the thermal neutron flux, the higher sensitivity is found. Finally, the sensitivity depends on the irradiation time and decay time used in each procedure.

2.3.4 The Limit of Detection (Detection Limit or Detection Sensitivity)

The limit of detection is defined as the smallest amount of the element which can be determined accurately under the given conditions.

The limit of detection depends upon the weight of sample, the irradiation time (when thermal neutron flux is constant) and the counting time (when the efficiency of counting equipment is constant). The higher values of these parameters, the lower value of the limit of detection (or the higher sensitivity of the method) is obtained. The limit of detection of 68 elements investigated by Guinn and Hoste (63) is shown in table 2.1

2.4 Advantages of Neutron Activation Analysis. (2,63-64)

2.4.1 It is very sensitive for many elements.

2.4.2 The problem of sample contamination by impurities in chemical reagents used in the analysis is eliminated, since normally no reagents are added until after sample activation.

2.4.3 Samples can be analyzed nondestructively, by simply irradiation with neutrons and then examining the activated sample by means of gamma-ray spectrometry. The analyses are very rapid and require small quantity of sample.

2.4.4 A number of elements can be determined simultaneously.

2.4.5 It is not necessary to separate the test element from interfering elements quantitatively because it can be corrected from the added radioisotope (as carrier).

2.4.6 It can be used in both qualitative and quantitative analyses because the nuclear properties of radioactive isotope, such as half life, type of radiation, and gamma energy are uniquely characteristic of that isotope.

2.5 Disadvantages of Neutron Activation Analysis. (2,63-64)

2.5.1 It only measures the total weight of an element and takes no account of different states of combination.

2.5.2 Intense irradiation of organic material and liquids causes always difficulties and is often impossible.

2.5.3 It can not determine all the elements in periodic table, especially the elements with atomic number less than 10, such as H, C, etc.

2.5.4 Working with radioactive sample implies safety precautions.

2.5.5 It requires well trained personnel.

2.5.6 Instruments used, e.g. neutron source, counting equipments, etc. are expensive.

2.6 Errors in Neutron Activation Analysis. (2,61)

2.6.1 Flux Variation During Irradiation

Flux variation can be divided into three groups: variations in time, variations in positions and flux depression inside the sample. Flux variations with time and with position are caused by the reactor operation and by the differences in the distance to the reactor-core, respectively. These types of flux variations can be eliminated by using flux monitors.

Flux depression is caused by absorption of neutrons in the container material and by self-shielding inside the sample. The first effect can be eliminated by using the same type of container throughout one experiment. Self-shielding occurred in the sample which contains large amount of high cross section elements such as B and Cd. As succeeding layers of the sample absorb particles, the residual flux becomes less and this results in the inside of the sample becoming less active than the outside. If the self-shielding does not occur, or occurs to a lesser extent, in the standard as compared to the sample, then different specific activities will result in the two materials, and the errors in the analysis will be dependent on the difference in the two self-shielding effects. To minimize this error, sample and standard should have similar compositions, concentration and matrix.

2.6.2 Interference by Nuclear Reactions

Interferences in NAA are of two types as follows:

(1) Interference from other radionuclides, e.g. the 280 KeV peak of Hg-203 has interference from the 279 KeV γ-energy of Se-75. This interference can be eliminated by specific radiochemical separations in which the interfering radionuclides are removed from the element of interest.

(2) Interference from two or more different nuclear reactions producing the same radionuclide, e.g.

$^{27}Al(n,\gamma)\,^{28}Al$ when n is the thermal neutron

$^{28}Si(n,p)\,^{28}Al$ when n is the fast neutron

$^{31}P(n,\alpha)\ ^{28}Al$ when n is the fast neutron

This interference is usually produced by fast neutron reactions. Thus, it can be eliminated by irradiating samples in thermal column or wrapping samples with Cd-sheet.

2.6.3 Preparation of Standards and Samples.

The error may arise due to the sample and standard having different composition, concentration and type of containers. If standard material is hygroscopic, it will cause the error in weighing.

The contaminations and the losses of some volatile elements from the samples during freeze drying and irradiation are the main sources of error during the sample preparation. These errors are eliminated by preparing the sample in a "clean room" where no chemicals and reagents are stored, and by using clean containers and tools.

2.6.4 Counting Error

The origins of counting errors are as follows:

(1) Uncertainty in the preset counting time: It is obviously impossible to count all samples on the same counter at the same time. Thus, a correction by mathematics using the published half-life for the particular radioisotope may be applied for this decay.

(2) Self absorption in the sample being counted. In simple terms this means that all the radiations produced in the

sample do not manage to escape from it. The proportion which is lost in this way depends on the energy of the radiation (often occurs with low-energy γ-rays) and on sample thickness (the more thickness, the more self absorption). To minimize this error, samples and standards must be thin and have same thickness.

(3) The counting errors of back-scattering and self-scattering are easily eliminated; the former by counting all samples on containers of uniform thickness and material; the latter by controlling sample size.

(4) Variation in geometrical efficiency and errors due to scattering by air and shielding materials: They are normally eliminated by counting all samples at a fixed distance from the counter.

(5) Efficiency of detection: The electronic equipment used for radioactivity measurements is not absolutely stable and the apparent efficiency of detection may vary from time to time. This causes the error in analysis.

Table 2.1 INAA Detection sensitivities for 68 elements-in the absence of interfering activities (63)

(For $\phi_{th} = 10^{13} n\ cm^{-2} sec^{-1}$, ta = 5hr max, tw = 0, t-count = 100 min max, 40 cm^3 Ge(Li)detector, 2cm distance)

Detection sensitivity	Element
(μg)	
$1-3 \times 10^{-7}$	In, Eu, Dy
$4-9 \times 10^{-7}$	Ho
$1-3 \times 10^{-6}$	Mn, Sm, Au
$4-9 \times 10^{-6}$	Ru, Lu, Re, Ir
$1-3 \times 10^{-5}$	Co, Cu, Ca, As, I, Cs, La, Er, W, Hg, U
$4-9 \times 10^{-5}$	Na, V, Br, Ru, Pd, Sb, Yb, Th
$1-3 \times 10^{-4}$	Sc, Ge, Sr, Te, Ba, Nd, Ta
$4-9 \times 10^{-4}$	Cl, Se, Cd, Gd, Tb, Tm, Hf, Pt
$1-3 \times 10^{-3}$	Al, Zn, Mo, Ag, Sn, Ce, Os
$4-9 \times 10^{-3}$	K, Ti, Cr, Ni, Rb, Y, Pr
$1-3 \times 10^{-2}$	Mg
$4-9 \times 10^{-2}$	Zr
$1-3 \times 10^{-1}$	F, Ca, Nb
$4-9 \times 10^{-1}$	**no report**
1-3	Fe
4-9	Si
10-30	S, Pb