Chapter II

THEORY

2.1 Basic Concepts of Activation Analysis

The basic principle of activation analysis is that a stable isotope, when irradiated by neutrons or charged particles, can undergo a nuclear transformation to produce a radioactive nuclide.

Stable isotopes can undergo a variety of nuclear transformations. A reaction used extensively in activation analysis is the neutron-gamma (n, r), which is illustrated as examples in equations (2-1) and (2-2)

$$_{33}As^{75} + {}_{0}n^{1} = {}_{33}As^{76} + {}_{0}r^{0} \qquad (2\text{-}1)$$

$$_{55}Cs^{133} + {}_{0}n^{1} = {}_{55}Cs^{134} + {}_{0}r^{0} \qquad (2\text{-}2)$$

The above reactions are usually expressed simply as As^{75} (n, r) As^{76} and Cs^{133} (n, r) Cs^{134}.

The (n, r) reaction is primarily a thermal-neutron (0.025 ev.) reaction, although it can occur with neutrons of other energies. The neutron is captured by a target atom, and one or more gamma rays are emitted (delayed gamma). Since no change of the atomic number occurs, the radioelement retains the chemical identity of the target element.

Although the (n, r) reaction is the most widely applied nuclear reaction for activation analysis, a number of other reactions are important.

In the (n, p) reaction, which requires neutrons with higher-than-thermal energies, a neutron enters a target nucleus with sufficient energy to cause a proton to be released. The atomic number is reduced by one, thereby converting the target atom into a different element as

$$_{16}S^{32} \; (n, p) \; _{15}P^{32}$$

The (n, α) reaction, like the (n, p) reaction, usually requires high-energy neutrons. In the (n, α) process, a neutron enters a target atom and causes an α - particle to be emitted. The atomic number of the target atom is reduced by two as $_{13}Al^{27}(n, \alpha)_{11}\,Na^{24}$

Other reactions which have found some use include (n, 2n), (p, n), (d, p), (d, n), (d, α), (α, n), (α, p), etc.

2.2 Neutron Activation Analysis

This method involves exposing the sample to be analyzed to a high flux of neutrons. The interaction of neutrons with the elements in the sample produces radioisotopes that can be identified by their characteristic decay rates, types and energies of emitted radiations. The amount of a radioisotope produced is proportional to the amount of stable isotope present in the sample and is given by the well-known activation equation:

$$A = N \sigma \phi \, (1-e^{-\lambda t}) \qquad (2\text{-}3)$$

where :

A = induced activity at the end of irradiation, dps.

N = number of target atoms present

σ = cross section of an element, cm^2

ϕ = neutron flux, n/cm^2- sec.

t = irradiation time

λ = decay constant of product nuclide = $\frac{0.693}{T_{1/2}}$

$T_{1/2}$ = half-life of product nuclide

Half-life ($T_{1/2}$) and irradiation time (t) must be in the same units of time. N can be calculated by means of the following relation.

$$N = \frac{N_o \cdot w.f}{At.\ Wt.}$$

where :

N_o = Avogadro's number, atoms/mole

w = weight of element, gm.

f = fractional isotopic abundance of the target nuclide

At. Wt. = atomic weight of the element being considered.

Substituting N into equation (2-3), the following equation is obtained:

$$A = \frac{N_o\ w\ f\ \phi\ \sigma}{At.\ Wt.} (1-e^{-\lambda t}) \quad (2-4)$$

It is evident from the activation equation that the maximum value of A is $A = N\sigma\phi$. This value is called the saturation activity, and it can theoretically be achieved when the term ($e^{-\lambda t}$) becomes zero. The term ($1-e^{-\lambda t}$) is called the saturation factor, and its value

depends on the period of irradiation and the half-life of the neutron-induced radioisotope. The values of the saturation factor lie between zero and one. For periods of irradiation of 0.25, 1, 2, 3, 5 and 10 times the half-life of the radioisotope, the values of saturation factors correspond to approximately 0.16, 0.5, 0.75, 0.87, 0.97 and 0.999, respectively.

Theoretically, it is possible to calculate the quantities of various elements present in a sample from equation (2-4). However in practice, this equation is not used because the exact value of neutron flux is not know. There is a fluctuation in the magnitude of neutron flux with time and with the location of the sample at the time of irradiation. Moreover the reaction cross section of an element is not known with sufficient accuracy and it is not always easy to determine the absolute disintegration rate A. Therefore, in order to eliminate this discrepancy and other errors caused by matrix effect and interference phenomenon, a solution containing mixed standards of known concentrations of all the elements of interest is irradiated under identical conditions along with the samples. Then, by comparing the count rate of standard with that of the sample, one can determine the quantity of each element in the sample by using the relation :

$$\frac{\text{weight of element sample}}{\text{weight of element in standard}} = \frac{\text{count rate of sample}}{\text{count rate of standard}}$$

This comparison technique eliminates many of the uncertainties in the absolute procedure.

2.3 Instrumental Neutron Activation Analysis (INAA)

In activation analysis there is a choice between instrumental techniques, in which the irradiated sample is measured nondestructively, and a technique involving chemical procedures where the constituents of the sample are separated before measurement. The latter method provides lower limits of detection (better sensitivity) but the separation methods are usually tedious and complicated. The instrumental technique with the support of a lithium-drifted germanium detector and a multichannal analyzer is well suited as a multielement analysis method. If the analysis is performed under optimum irradiation-, decay-, and counting times, the sensitivities for several elements can be raised and upto about 20 elements could be analysed simultaneously in water samples.

2.4 Sensitivity

When one is considering the use of an analytical technique, it is usually important to have imformations about the limits of detection or sensitivities of the technique for a given element of chemical species. From the activation equation, it could be seen that there is definitely an amount of activity or disintegration rate of a radioisotope below which accurate detection becomes questionable. In other words, it is necessary to have a certain minimum amount of activity **A** in order to obtain reliable results with the presently available radiation

detection equipment. From equation (2-4), if the irradiation is carried out for a sufficient number of half-lives and the activity is determined within a small fraction of half-life after irradiation ceases, the sensitivity of the method will be greater, the higher the efficiency of the detection equipment, the lower the atomic weight of the element, the greater its activation cross-section, the greater its isotopic abundance, and the greater the flux of bombarding particles.

With the high-flux nuclear reactors available for irradiation today, NAA is the most sensitive method for a large number of elements. The limits of detection for some elements are shown in Table 2-1, which is prepared from the data reported by Buchanan[1].

All of these tabulated limit of detection are situations in which the levels of interfering activitives are negligible, or become so by decay or via suitable radiochemical separations before counting. An attempt has been tried by V.P. Guinn to estimate limits of detection to instrumental NAA of matrices that exhibit very large levels of interfering activities[2].

---

1 Buchanan, J.D., "Activation Analysis with a TRIGA Reactor". Proc. 1961 Intl. Conf. Modern Trends in Activation Analysis, Texas A & M Univ. College Station, 15-16, 72 (1961)

2 Guinn, V.P., "Instrumental Neutron Activation Analysis. Limits of detection in the Presence of Interferences". Journal of Radioanalytical Chemistry. 15, 473-477 (1973)

Table 2-1 Detection limits for some elements by NAA (flux = 10^{13} n/cm^2-sec) irradiation time = 1 hr.)

Detection limit (ppb)	Elements
0.0009	Mn, In
0.003	Co, Ir
0.009	Br, Au
0.03	V, Cu, As, Ag, I, W
0.09	Na, Sr, Sb, Cs, La, U
0.3	Al, Cl, K, Se, Hg
0.9	Si, Ni, Rb, Cd, Ba, Pt
3.0	P, Zn, Mo, Sn
9.0	Mg, Ca, Bi
30.0	Cr, Zr
900.0	Fe

2.5 Errors in the Method of Activation Analysis

As the technique of activation analysis has its own special advantages, so it has its own particular set of errors. Fortunately, these errors are comparatively few and can, in general, be minimized if not eliminated.

2.5.1 Errors Due to Different Fluxes

The main source of error is due to the fact that standard and sample are not exposed to the same neutron flux. Neutron flux variations are possible as function of time and irradiation position.

For these reasons standards and samples are irradiated together in one container. It is then necessary to make sure that the samples and standards are as close together as possible.

2.5.2 Interfering Nuclear Reactions

As an (n, p) reaction on element Z + 1 or an (n, α) reaction on element Z + 2 can give the same reaction product as an (n, r) reaction on element Z, it is obvious that the presence of element Z + 1 or Z + 2 can interfere in the determination of element Z. The interference will obviously be more or less serious, depending on the relative concentrations of the target nuclides in the sample, on the ratio fast/thermal flux and on the ratio of the cross sections involved. Fortunately, the cross sections for (n, p) and (n, α) reactions are generally quite low compared to the (n, r) cross sections, so that these reactions normally (not always) cause serious interference only in the presence of macro-quantities of the interfering elements. This interference will, of course, be less important or even negligible if the irradiation is carried out in a well thermalized neutron region, such as the thermal column.

2.5.3 Interferences from High Compton Levels

The peak of interest can be superimposed if the Compton levels in the pulse-height spectra is high. This is caused by interactions of gamma-rays of higher energy than the peak of interest.

2.5.4 Other Errors

If the activity of the standard differs considerably from that of the sample, errors are possible due to different relative count losses. If possible, the activities for standards and samples should be of the same order of magnitude.

In the comparison technique, the geometry of counting of standard and sample should be the same. In many cases, standards are used as dilute solutions. If such a solution is not freshly prepared, adsorption of the element of interest on the container walls is possible. As a general rule, the dilute solutions should be prepared just before use.

2.6 Semiconductor Detectors

A detector which has proved to be extremely useful in gamma ray spectroscopy is the semiconductor detector. Fig. 2-1 shows the cross section of a coaxial type Ge (Li) detector which is produced by allowing lithium to diffuse into the sides of a germanium single crystal and this then drifts towards the center.

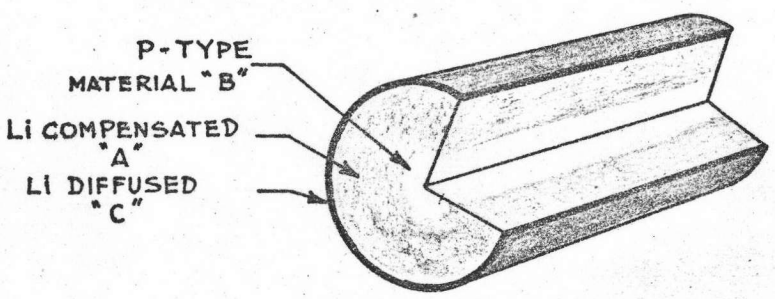

Fig. 2-1 Cross section of a Ge (Li) detector.

In Fig. 2-1 The compensated (intrinsic) region is labelled as "A", the p-type (undrifted) material in the conter as "B" and the n-type material (lithium diffused) on the outside as "C". The high mobility of lithium in germanium and silicon makes the storage and operation of such detectors at very low temperature compulsory. This is provided by a cryostat which consists of a reservoir for the cooling medium, or liquid-nitrogen dewar, and a vacuum chamber for the detector.

2.6.1 Energy Resolution of a Ge (Li) Detector

The limitation of the energy resolution of a Ge (Li) detector comes principally from the statistical fluctuation in the number of ion pairs created for a given energy E. The reason for this fluctuation is that only part of the energy lost by gamma-rays is expended for ionization, a portion is dissipated in heating the lattice structure of the crystal. While no fluctuation should be observed in the energy required for ionization, normal statistical fluctuations can be expected in that portion of the total energy lost in heating the lattice structure.

The ratio of the observed mean square fluctuation in the number of ionization events or the variance $(\delta)^2$, to the number of ionization events or yield (Y) is defined as the Fano factor. If the average number of electron volts necessary to form an electron-hole pair in germanium is given by ϵ, then

$$Y = \frac{E}{\epsilon} \qquad (2\text{-}5)$$

and the Fano factor is

$$F = \frac{\sigma^2}{\frac{E}{\epsilon}} \qquad (2\text{-}6)$$

Fano factor values of below 0.15 have been reported recently[3]. To obtain a value for the resolution in keV, equation (2-6) is solved for the root mean square variance or σ, and the result converted to electron volts. When σ is multiplied by ϵ, one gets

$$\epsilon\sigma = \epsilon\left(\frac{EF}{\epsilon}\right)^{1/2} = (\epsilon EF)^{1/2} \qquad (2\text{-}7)$$

The energy resolution of a Ge (Li) detector system is commonly expressed as the full width at half maximum (FWHM) of a peak in an energy spectrum. For spectral peaks with a Gaussian shape ΔE(FWHM) corresponds to 2.35 times the root mean square of the nergy spread. Hence if ϵ is 2.9×10^{-3}keV/ion-pair, ΔE, in keV for radiation of energy E (keV), becomes

$$\Delta E = 2.35(0.0029EF)^{1/2}$$

$$= 0.1286\ (EF)^{1/2}$$

for germanium at 77°K.

---

3 Bilger, H.R., and Mann, H.M., IEEE NS-13(3), 1967.

2.6.2 Efficiency of a Ge (Li) Detector

Ge (Li) detectors are mainly used as gamma-ray spectrometers for the medium energy region (40 keV to 2 MeV) where the photoelectric cross section is high in comparison to the cross section for pair production. Knowledge of the full-energy-peak efficiencies over this range must be known before information about the intensities of gamma-transitions can be obtained. The full-energy-peak efficiency is defined as the probability that a gamma-ray of a given energy will be recorded. The experimental determination of the absolute full-energy-peak efficiency is easy, only gamma-ray sources of known strength and reproducible detector geometries are necessary.

004745

I 17358541