CHAPTER II

THEORY

2.1 Neutron Activation Analysis

2.1.1 Principle

Neutron activation analysis (NAA) is a nuclear method of elemental analysis in which the elements in a sample to be analysed are made radioactive by irradiation with neutrons and the induced radioactive species are then identified and measured. The amount of a given neutron activation product that is formed during neutron irradiation is directly proportional to the amount of its parent isotopes. Measurement of the radionuclide provides a measure of the total concentration of the parent element.

The basic equation for activation is

$$W = \frac{AM}{a\sigma\phi N_{av} (1 - e^{-\lambda t_1})} \quad \ldots\ldots\ldots\ldots\ldots (2.1)$$

Where W = weight of element irradiated (gm)

A = induced activity at the end of irradiation (disintegrations/sec.)

M = atomic mass of that element

a = isotope abundance of the target nuclide

σ = the activation cross section for the nuclear reaction concerned (cm^2)

ϕ = flux of neutrons used in the irradiation (neutrons/cm^2-sec.)

N_{av} = Avogadro's number

λ = the decay constrant of the induced radionuclide ($sec.^{-1}$)

t_1 = irradiation time (sec.)

From the abave equation it is obvious that the dectection sensitivity for a given element can be improved by increasing the neutron flux and/or the irradiation time. The relative detection sensitivities for all of the elements in the periodic table are a function of their activation cross section for the nuclear reaction concerned, the decay constant of the induced radionuclide, the atomic weight of that element and the fractional abundance of the particular isotope of the element concerned. When a cooling time t_2 is applied, the equation 2.1 is changed to :-

$$W = \frac{AM}{a\sigma\phi N_{av} (1 - e^{-\lambda t_1}) e^{-\lambda t_2}} \quad \ldots\ldots\ldots (2.2)$$

The actually measured count rate R, expressed in counts per minute, is proportional to A as

$$R = \frac{60\, E \Omega p A}{4\pi} \qquad \ldots\ldots\ldots\ldots\ldots (2.3)$$

Where E = effeciency of the detector for the radiation measured

Ω = spatial angle of the detector towards the sample

P = fraction of the total number of disintegrations that decays under emission of the radiation to be measured.

The quantitative determination of an element by NAA is based on the equal specific activity of the element in the sample and a standard of known weight, irradiated during the same time in the same neutron flux. Again, the geometry of the sample and standard is the same during both irradiation and measurement.

The following equation is then obtained :-

$$W_x = \frac{R_x \cdot f_x}{R_s \cdot f_z} W_s e^{\lambda (t_x - t_s)} \qquad \ldots\ldots\ldots\ldots (2.4)$$

Where W_x and W_s are the weight of the element in sample and standard respectively

R_x and R_s are respective count rates of sample and standard

f_x and f_s are respective relative flux factors

t_x and t_z are the time after the end of the irradiation of which sample and standard are counted.

The NAA method does not distinguish between various physicochemical forms of an element in a particular sample, but provides a measure of its "total" concentration. However, if different physicochemical specimens of the same element are seperated prior to the neutron irradiation, this method can provide a measure of each specific form.

The characteristic γ - radiation of the radioactive nuclide is usually measured with NaI(Tl) detectors or Ge(Li) detectors, connected to a multichannel analyser to sort gamma's of different energy. Ge(Li) detector has relative higher resolving power but lower efficiency than NaI(Tl) crystals. A photopeak is usually supposed to begin when the different between the number of counts in one channel and that in the previous channel, Ri exceeds the value $2\sqrt{Ri}$. The end of the peak is marked by the channel with the lowest number of counts compared to the next one. Also, the base line is usually assumed to be straight line. Then the net peak area, due to the substraction of the continuum from the total peak area and the continuum is

$$N = T - \tfrac{1}{2} n (Ri + Rn) \quad \ldots\ldots\ldots\ldots\ldots (2.5)$$

Where N = net peak area

T = total peak area = $\sum_{i=1}^{n} Ri$

Ri and Rn = number of counts in the first channel and the last channel respectively

n = peak width

In practice, the fundamental steps in a typical NAA are :-

a) Irradiation weighted quantities of the sample and standard in suitable containers for a sufficient time to give adequate radioactivity for the element to be determined. Some times preconcentration step has been performed before the irradiation.

b) After the irradiation, instrumental neutron activation analysis (INAA) is accomplished by simply counting the samples and standards with Ge(Li) and/or NaI(Tl) gamma-ray spectrometers at optimum time following the irradiation to directly measure elements producing short, intermediate and long-lived neutron activated products.

c) If INAA dose not provide the desired sensitivity, radiochemical seperation of the activated products of interest from the interfering radionuclides has to be done before counting.

d) Compare the radioactivity of the samples and standards under indentical counting conditions, making decay correction, flux distribution correction, compton back ground correction as necessary.

e) To ensure that the gamma-ray being measured is due solely to the radionuclide of interest, check the half-life of the activity to be certain that it is decaying at the proper rate. Futher confirmation may be desired when the radionuclide emits more that one gamma ray per disintegration, in this case both the energies and relative intensities can be used for verification.

Expressions for the limit of qualitative detection, LD which is defined as the net signal level which may be a priori expected to lead to detection and the limit of quantitative determenation, LQ - the level at which the measurement precision will be satisfactory for quantitative determination, in terms of the continuum back ground (B), have been given in ref [14] as following :-

$$L_D = 4.65\ \sigma(B) \quad \ldots\ldots\ldots\ldots\ldots (2.6)$$

$$L_Q = 14.1\ \sigma(B) \quad \ldots\ldots\ldots\ldots\ldots (2.7)$$

Where $\sigma(B) = {}^{n}/_{2}\sqrt{Ri + Rn}$ $\ldots\ldots\ldots\ldots\ldots (2.8)$

Futher modification has been achieved [15] as following :-

a) For absolute amounts of the element to be determined

$$\left[L_D\right]_M = \frac{4.65}{A_{sp}}\sigma(B) \quad \mu g. \quad \ldots\ldots\ldots (2.9)$$

$$\left[L_Q\right]_M = \frac{14.1}{A_{sp}}\sigma(B) \quad \mu g. \quad \ldots\ldots\ldots (2.10)$$

b) For relative amounts of the element in a sample

$$\left[L_D\right]C = \frac{4.65}{A_{sp}.G}\sigma(B) \quad \mu g./g. \quad \ldots\ldots\ldots (2.11)$$

$$\left[L_Q\right]C = \frac{14.1\ \sigma(B)}{A_{sp}.\ G} \quad \mu g./g. \quad \ldots\ldots (2.12)$$

Where A_{sp} = specific activity of the radionuclide concerned

and G = total weight of the sample.

For a constant measurement efficency, the value of $[L_D]_M$ and or $[L_Q]_M$ depends upon the activation condition, the cooling time and type of sample as due to the continuum back ground level. The limit of qualitative detection for a fix conditional INAA is given in table 2.1.

Table 2.1 INAA-limit of qualitative detection for 68 elements in the absence of interfering activities [16]

(For $\phi = 10^{13}$ n./cm^2-sec. $t_1 = 5$ hr, $t_2 = 0$ $t_{count} = 100$ min. with 40 cm^3 Ge(Li) detector at 2 cm. abave the crystal.

Limit of detection (µg.)	Element
$1 - 3 \times 10^{-7}$	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

Table 2.1 (Cont.)

Limit of detection (μg.)	Element
$1 - 3 \times 10^{-4}$	Sc, Ge, Sr, Te, Ba, Nd, Ta
$4 - 9 \times 10^{-4}$	Cl, Se, Cd, Gd, Tb, Tm, Hg, 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, Nb
$4 - 9 \times 10^{-1}$	no report
1 - 3	Fe
4 - 9	Si
10 - 30	S, Pb

Finally, NAA offers a few important advantages over the other analytical techniques, which make it worthwhile to look for an extension of its application in water analysis. The attractive features are :-

a) The method is very sensitive for many elements.

b) Matrix effects during irradiation and measurement are usually negligible or can be eleminated by a simple way.

c) After activation, the method is not subjected to interference by non radioactive contamination.

d) Often, a number of elements can be determined simultaneously.

2.2 Preconcentration and Decontamination in Radioanalysis [17]

2.2.1 General

The scope of any analytical method may be enhanced by preconcentration of the compound of interest and the elemination of interferences. Often these steps may be combined. Obviously, preconcentration makes sense only if the sample material can not be analysed as such. This depends on

a) the limit of determination, $(L_Q)_M$ expressed in µg.

b) the maximum of volume or weight, V_1 or G_1 which can be handled, in ml or gm.

c) the expected concentration level, $\bar{C_o}$, expressed in µg/ml or µg/gm.

If the limit of determination for the untreated material is $(L_Q)_M$, the scope of the analysis with out preconcentration is given by

$$V_1 \cdot \bar{C_o} > (L_Q)_M \quad \ldots\ldots\ldots\ldots (2.13)$$

or $$G_1 \cdot \bar{C_o} > (L_Q)_M \quad \ldots\ldots\ldots\ldots (2.14)$$

If this condition is not fulfilled it may be reached by

a) increasing the concentration or

b) lowering the limit of determination.

The concentration steps may be defined by four criteria :-

a) Concentration factor

b) Decontamination factor

c) Recovery

d) Specificity

Which are thus briefly expressed as following :-

a) Concentration factor

A concentration procedure reduces the original volume or weight, V_o or G_o to new values V_1 or G_1, under constant, preferably quantitative, it thus follows from equations (2.13) and (2.14) that

$$X.V_1.\bar{C}o = V_1 \bar{C}_1 \geqslant (L_Q)_M \quad \ldots\ldots\ldots\ldots (2.15)$$

or

$$X.G_1.\bar{C}o = G_1\bar{C}_1 \geqslant (L_Q)_M \quad \ldots\ldots\ldots\ldots (2.16)$$

Where X stands for the concentration factor and $\bar{C}_1$ for the average concentration in the concentrated aliquots.

The actual concentration of the individual samples will vary around the estimated average. If this variation follows a Poisson - distribution, $\sigma(\bar{C}_o) = \sqrt{\bar{C}_o}$ and 99% of the sample will be

covered by the analysis if equations 2.15 or 2.16 hold,

$$X.V_1.[\bar{C}_o - 2.5\sqrt{\bar{C}_o}] \geqslant (L_Q)_M \quad \ldots\ldots\ldots\ldots (2.17)$$

$$X.G_1.[\bar{C}_o - 2.5\sqrt{\bar{C}_o}] \geqslant (L_Q)_M \quad \ldots\ldots\ldots\ldots (2.18)$$

The blank caused by the preconcentration step posseses a third condition :-

$$\frac{\text{blank}}{\text{mass of analyte}} = \frac{\text{blank (in } \mu\text{g.)}}{X.V_1.\bar{C}_o} \text{ or } \frac{\text{blank } (\mu\text{g.})}{X.G_1.\bar{C}_o} \quad 1/p \quad \ldots\ldots (2.19)$$

The minimal acceptable value of p depends on the uncertainty in the blank. A reasonable practical choice is $p = 2$. When the blank is caused by the reagents solely it is obvious that

$$1/p \geqslant [\text{blank concentration}].\left[\frac{\text{Mass of reagent}}{\text{Mass of analyte}}\right] \quad \ldots\ldots (2.20)$$

b) Decontamination factor

The elemination of interferences which is caused by the preconcentration step may be expressed in terms of the decontamination factor Y, defined as the double ratio

$$Y = \left[\frac{\text{Concentration of element of interest}}{\text{Concentration of interference}}\right]_{\text{after/before}}$$

$$\ldots\ldots\ldots\ldots (2.21)$$

In general the value of $(L_Q)_M$ depends on that of Y. In spectrometric techniques a net peak area is obtained by subtraction of a continuum background which is due to the interferences. Moreever, the peak involved may be interfered by a similar peak of the interfering compound.

Seperation by a numerical technique will cause an extra uncertainty and thus increase $(L_Q)_M$. If it is required that the peak of interest is at least as strong as that of the interference a minimal value of Y can be defined.

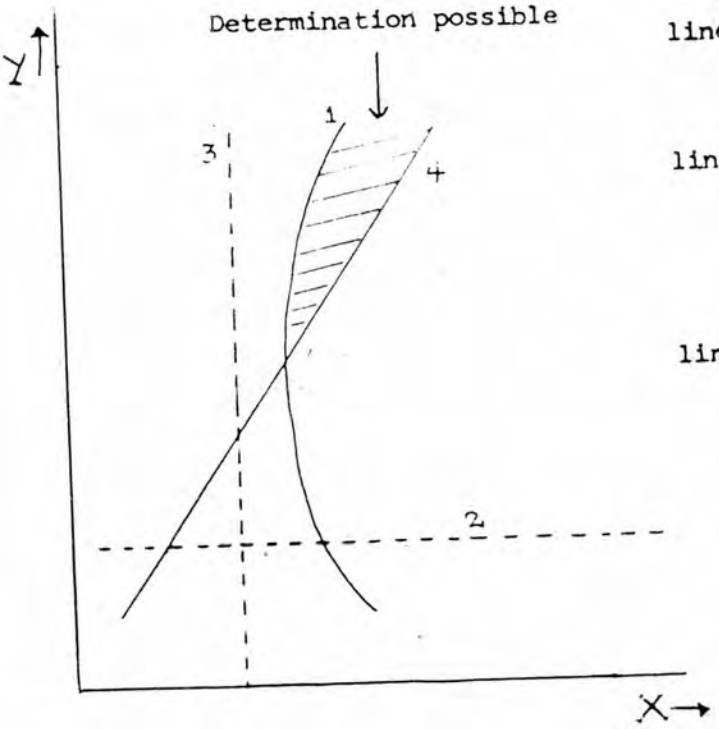
The relation between X and the minimal value of Y is "the X-Y line" in an X-Y graph. The shape of this line depends on the preconcentration procedure. A typical X-Y graph is given in fig. 2.1

For each material there exists a minimal representative sample weight which imposes a minimal X value depending on the maximal sample weight or - volume which can be handled. This is represented by a vertical line in the X-Y graph.

Finally, the maximal weight which can be handled in activation analysis due to irradiation facilities and counting limitations depends on Y. In trace analysis this relation is usually a simple proportionality. In the X-Y diagram this becomes "the decontamination line". Its shape depends on the sample material and the irradiation.

In the X-Y diagram in fig. 2.1, the area which represents the analytical possibilities lies right of the line 1 and 3 and abave

the line 2 and 4. In addition to these requirements equation 2.19 has to be fulfilled.



line 1 = X-Y line

line 2 = lower limit of Y to peak seperation

line 3 = lower limit of X set by representative sample

line 4 = Decontamination line

Fig. 2.1 Principle of the X-Y diagram.

c) Recovery

The recovery R is defined as 100 (amount collected)/ (amount present). One may consider R as a function of the ratio P = (Mass of reagent)/ (mass of analyte) as shown in fig. 2.2. In the ideal case of a complete reaction and with a stoichiometric ratio α has

$$R = \frac{100 \cdot P}{\alpha} \qquad \ldots\ldots\ldots\ldots\ldots (2.22)$$

Then the equation 2.16 becomes

$$^{1}/_{r} \quad \text{(blank concentration)} \frac{\alpha . R}{100} \quad \ldots\ldots\ldots \quad (2.23)$$

Thus for a quantitative recovery and a given value of α the choice of r sets the maximal acceptable value of the blank concentration in the reagent.

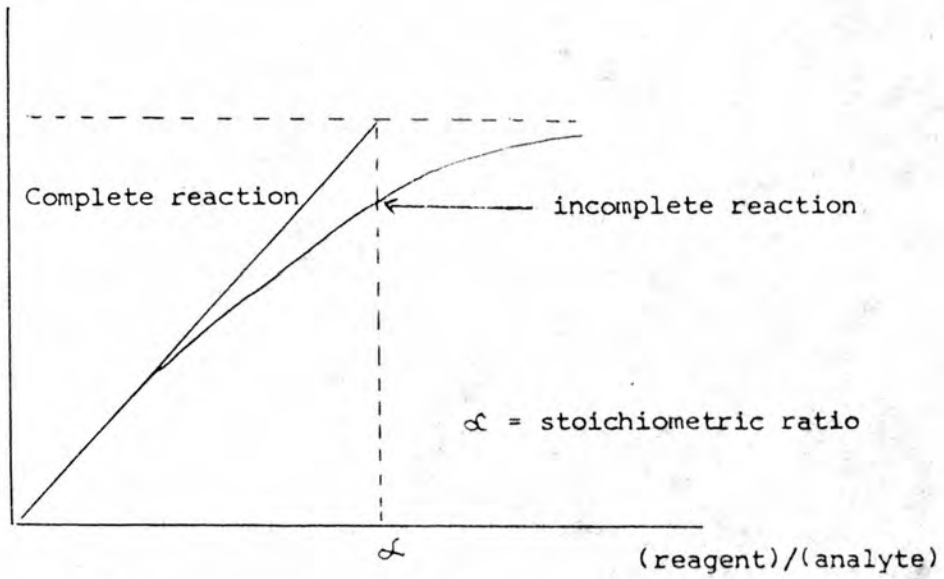


Fig. 2.2 The recovery as a function of the ratio mass of reagent and analyte.

d) Specificity

The determination of the isolated compound should be free of an appreciably bias due to interferences. The specificity for compound i, Si, may be defined as

$$Si = \frac{100\ Ki\,[A]i}{\sum Ki\,[A]i} \qquad \ldots\ldots\ldots\ldots (2.24)$$

Where Ai is the mass of the analyte i and Ki corresponding specific sensitivity.

2.2.2 Choice of the procedure in application to radioanalysis

The procedure which is followed in choosing a preconcentration/purification step is shown schematically in table 2.2. It is iterative by nature as $(L_Q)_M$ depends on Y. Whether the chosen procedure is feasible or not depends on the blank.

In activation analysis two additional closely related factors have to be considured :-

a) The half-life of the radionuclide involved.

b) The dose-rate at the time of handling.

The maximal amount of sample which can be handled may increase by elimination of interfering radionuclides if the dose-rate during handling is the governing factor.

Table 2.2 Scheme for the iterative choice of preconcentration procedure