

CHAPTER II

THEORY



2.1 Basic Concepts. (1, 2, 4)

When a sample is exposed to a flux ϕ of neutrons, each isotope present in the sample undergoes nuclear reaction with the incident neutrons at a rate given by the equation:

$$\text{Rate of reaction} = N\phi\sigma \dots\dots\dots(2.1)$$

where N = the number of target nuclei in the sample.

σ = cross-section/nucleus

ϕ = neutron flux

and $N = \frac{mN_0}{A}$

where A = atomic weight of the element.

m = weight of the element.

N_0 = Avogadro's number.

With thermal neutrons, the only reaction possible is neutron capture. This type of reaction is (n, γ) reaction, since one or more gamma-ray photons are emitted by the newly-formed nucleus promptly after neutron capture. In (n, γ) reactions the product nucleus is one of the same element, but with a mass number one unit higher than before capture. The product nucleus may be another stable isotope of the element, or it may be a radioisotope of that element. Only the latter case is of use in activation analysis. For example, ordinary magnesium consists of three stable isotopes, in fixed proportions 78.8% Mg^{24} , 10.1% Mg^{25}

and 11.1% Mg^{26} . Their thermal neutron capture cross-section are 0.03, 0.27 and 0.03 barn respectively (1 barn = 10^{-24} cm²). Neutron capture by Mg^{24} forms only stable Mg^{25} , neutron capture by Mg^{25} forms only stable Mg^{26} , but neutron capture by Mg^{26} forms radioactive Mg^{27} , which decays by beta particle emission and gamma-ray emission with a half-life of 9.5 minutes.

Fast neutron reactions.

If fast neutron (energy > 1 Mev) are also incident upon the sample, reactions other than (n, γ) reaction may also occur. The most common fast neutron-induced reactions are (n, p) , (n, α) and $(n, 2n)$ reactions. With (n, p) reaction the incident fast neutron is captured, but a proton is then promptly ejected. The product isotope (stable or radioactive) has the same mass number as the original nucleus, but an atomic number one unit lower, it is an isotope of a different element.

In $(n, 2n)$ reaction, the product nucleus is an isotope of the original element, but with a mass number one unit lower. Fast neutron cross-sections not only differ from one isotope to another, but also depend on the neutron energy.

Approach to saturation.

If the product isotope in a given case is radioactive, some will be decaying even while the irradiation is going on. If irradiation is continued long enough, a steady state will be approached in which the rate of formation of the radioisotope equals its rate of decay. This situation is often termed "saturation activity". Further irradiation

does not increase the activity of that particular radioisotope in the sample, as long as the neutron flux remains the same. If, however, irradiation is discontinued before saturation is achieved, the induced activity of the particular radioisotope in question will be less than the saturation activity, and will be given by the equation:

$$A_0 = N\sigma\phi \left[1 - \exp(-0.693t_i / t_{1/2}) \right] \text{ dps.} \quad \dots\dots(2.2)$$

where t_i = duration of the neutron exposure.

$t_{1/2}$ = half-life of the radioisotope.

the parenthetical, or "saturation" term of equation (2.2) has numerical values ranging from zero at $t_i = 0$, to unity as $t_i \rightarrow \infty$. At t_i values of 1, 2, 3, 4 times $t_{1/2}$, the saturation term has values of $\frac{1}{2}$, $\frac{3}{4}$, $\frac{7}{8}$, $\frac{15}{16}$ - - - - -. Thus it is seldom worth-while to activate a sample for a period of time greater than a few half-lives of the radioisotope of major interest. Longer activations are, in fact, undesirable, as they result in generation of more longer-lived interfering activities. With short-lived activities, irradiation times are then quite short, resulting in a short overall analysis time.

Decay after irradiation.

After conclusion of the irradiation, prior to counting, each induced activity then decays according to its particular half-life.

$$A_t = A_0 \exp(-0.693 t_d / t_{1/2}) \quad \dots\dots\dots(2.3)$$

where t_d = decay time after conclusion of the irradiation.

2.2 Comparative Technique. (1, 2, 3)

Rather than relying on literature values of isotopic abundances, atomic weights and cross-sections, or precise knowledge of the neutron flux or irradiation time, a comparison method is used. A sample containing an accurately known weight of the element of interest is irradiated at the same time as the unknown sample, under identical conditions, and is then counted identically. Then, by merely correcting the counting rate of one to the same decay time as the other, the two counting rates are in the same proportion as the weights of the element present in the two, one of which is known.

The quantity of a selected trace element in the sample matrix is calculated by the simple equation:

$$m_x = \frac{C_x}{C_s} * m_s \quad \dots\dots\dots(2.4)$$

where m_x = weight of unknown element.

m_s = weight of standard element.

C_x = count rate of unknown element.

C_s = count rate of standard element.

We see that the activity of the sample does not depend on ϕ or σ or the efficiency of the counter, but depends on the weight of the sample.

It is essential to compare the sample and reference-standard in the same type of container and should both be at the same volume in order to have identical counting geometries.

2.3 Interfering Reactions. (2).

The effects of interfering nuclear reactions depend on the composition of the constituents of the sample. The reactions induced in the sample constituents which yields the same nuclides as the principal activation reaction.

Interference may proceed either directly or through an activation reaction followed by beta decay of the primary activation product.

The thermal neutron activation, the principal sources of interference with (n, γ) reaction in an element of atomic number Z are fast neutron induced (n, p) and (n, α) reactions in elements having atomic number $Z + 1$ and $Z + 2$ respectively.

The extent to which the fast neutron induced reactions interfere with thermal neutron activation analysis depends on the relative concentrations of the target nuclides in the sample, the ratio of their cross-sections and the ratio of the fast to thermal neutron fluxes.

The interfering reactions will be important only if the trace element is very low concentration, because the effective fluxes and cross-section for fast neutron reactions are usually much less than those for thermal neutrons.

In most cases more than one radioactive species is generated, in detectable amounts, by activation of the sample.