CHAPTER 3

THEORY

Neutron Activation Analysis [17-25]

When a stable isotope (nuclide) undergoes a nuclear reaction, it becomes a radioactive element. This radioisotope will decay naturally, and the activity will decrease exponentially with time according to the individual isotope. The period of time taken for the activity to decrease by one-half is known as the half-life ($T_{\frac{1}{2}}$). From the decay scheme which indicates the modes of decay of a radionuclide and its half-life, the element of interest will be identified clearly, and from the net counts under a photopeak (photopeak area) the amount (quantity) of the element will be known. The equations concerned in NAA are

$$N_t = N_o e^{-\lambda t} \qquad \text{...............(1)}$$

$$A_t = A_o e^{-\lambda t} \qquad \text{...............(2)}$$

where N_t and N_o are the number of radionuclide atoms at the time t and 0, respectively

A_t and A_o are the activity of the radionuclide at the time t and 0, respectively

λ is the decay constant ($\lambda = 0.693/T_{\frac{1}{2}}$)

When a sample is irradiated in a neutron flux (ϕ , neutrons per square centimeter per second), the atoms will undergo a nuclear reaction at the reaction rate of $N\sigma\phi$ atoms per second and become the radionuclide. These radionuclides will decay naturally at the exponential rate, so that, for the time (T) of irradiation in the neutron flux, the sample activity will become

$$\text{Activity} = \lambda N = N\sigma\phi\,(1- e^{-\lambda T}) \quad \text{........(3)}$$

where σ is the microscopic neutron absorption cross-section, cm^2/atom.

When the irradiation time is infinity for any constant neutron flux, the activity will become constant or saturate as

$$\text{for } T\rightarrow \infty, \quad \text{Saturated Activity} = N\sigma\phi \quad \text{.........(4)}$$

and at the decay time (t) after irradiation is completed, the activity in the case of the equation (3) will be

$$\text{Activity} = N\sigma\phi\,(1 - e^{-\lambda T})\,e^{-\lambda t} \quad \text{.........(5)}$$

or in the case of equation (4),

$$\text{Activity} = N\sigma\phi\,e^{-\lambda t} \quad \text{.........(6)}$$

After acquiring the data from the scaler or printed tape, the net photopeak area will be determined by the Covell's method, which is the method of determining the net photopeak area of spectrum especially for the interested peak as illustrated in Fig. 4.

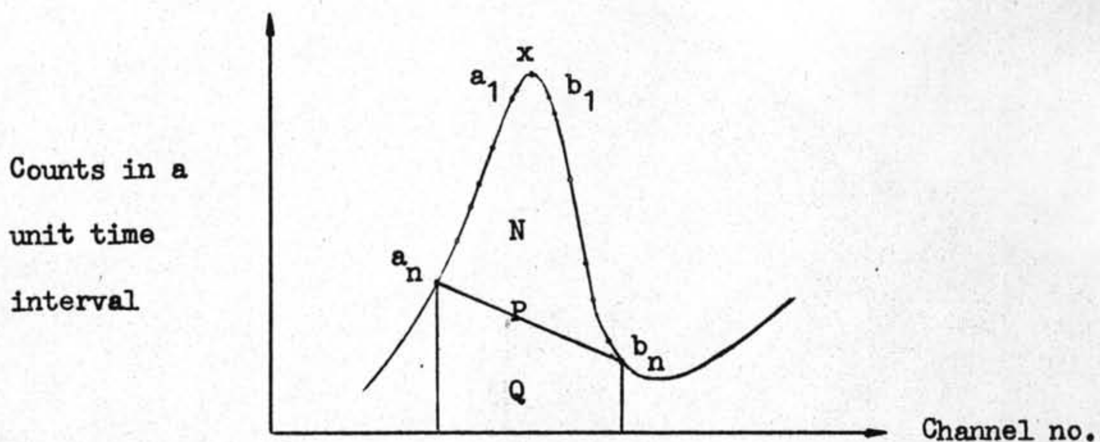


Fig. 4. The figure shows the Covell's method of determining the net photopeak area from the interested peak.

From Fig. 4., we can see that

the net photopeak area = total photopeak area − the trapezoid area under that peak

or $$N = P - Q$$

This relation can be expressed in a mathematical formula as

$$N = x + \sum_{1}^{n} a_i + \sum_{1}^{n} b_i - n(a_n + b_n)$$

where N is the net photopeak area, and x is the apex of the peak

P is the total peak area (total count under the peak)

Q is the trapezoid area under that peak

a_1 to a_n , b_1 to b_n are the number of counts in each channel

After the net photopeak area of the sample and the standards are determined and converted to the condition of $t = 0$, the comparison between them will be done to find the amount of the interested nuclide in sample.

X-ray Fluorescence Analysis[26-31]

In X-ray analysis the equation that is usually used is

$$E = h\nu = \frac{hc}{\lambda}$$

This equation shows the relation between energy and wavelength of any radiation. The primary X-ray sources used in exciting the specimen usually are isotopic annular sources (Pm^{147}/Al, Cd^{109}, Am^{241}, Pu^{238}, Co^{57}, etc.) and X-ray tube sources (Cr, Mo, Ag, Rh, W, etc. as anode material). For isotopic annular sources, the exciting radiation may be continuous radiation or discrete radiation which are usually due to the element required to analyse. For X-ray tube source, the white or continuous radiation from the tube will have the distribution expressed in terms of Kramer's formula as

$$I(\lambda)d\lambda = KZi\left[\frac{\lambda}{\lambda_{min}} - 1\right]\frac{1}{\lambda^2}\, d\lambda \qquad .....(7)$$

From this equation it will be seen that the intensity distribution is a linear function of the X-ray tube current (i) and the atomic number (Z) of the X-ray tube anode material, and λ_{min} is the minimum wavelength of the spectrum in Angstrom that can be calculated from

$$\lambda_{min} = \frac{hc}{V_o} = \frac{12.4}{V_o}$$

where V_o is the operating voltage of the X-ray tube, in kV. By differentiating the equation (7), the maximum intensity can be obtained as $\lambda_{max} = 2\lambda_{min}$.

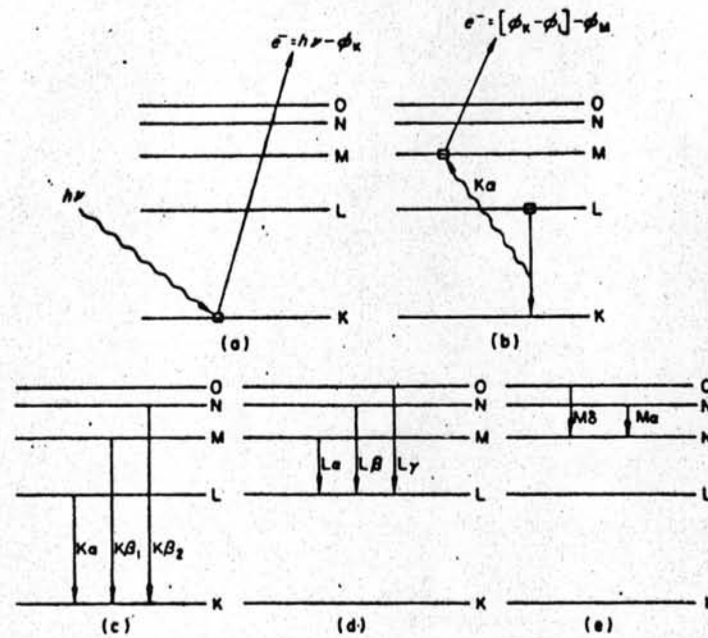


Fig. 5[26] The origin of characteristic radiation

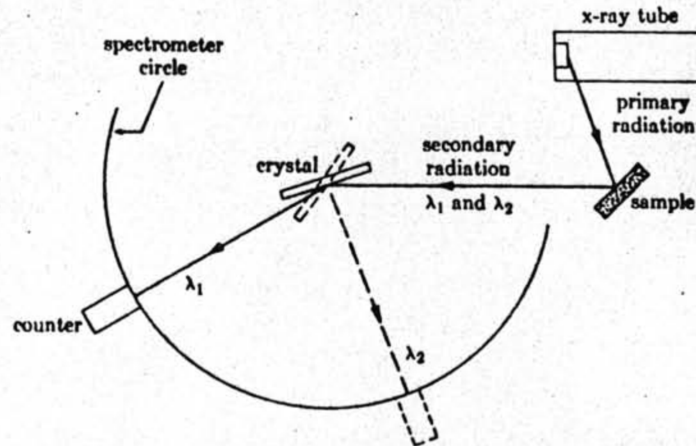
The origin of characteristic radiations can be described by using the model illustrated in Fig. 5. When a K-level electron is removed by a radiation (primary X-ray radiation) resulting the atom in an excited state, the atom can return to the ground state by two de-excitation processes. In the first process an electron from one of the upper levels jumps to the excited level and transfers its excess energy out as a characteristic radiation. The second process has initial stage similar to the first, but the produced radiation will be absorbed by an electron in one of the upper electron shells and the result is the emitting of electron called Auger electron instead of the characteristic radiation. This precess known as the Auger process can lead to the production of two (or more) vacancies in the upper levels.

The quantity of radiation from a certain level will be dependent upon the relative efficiency of the two opposing de-excitation processes involved. This relative efficiency is usually expressed in terms of the fluorescent yield (ω), defined as the number (n) of X-ray photons emitted within a given series, divided by the total number (N) of vacancies f med in the associated level, each with the same time increment. A sample of fluorescent yield for the K-series is

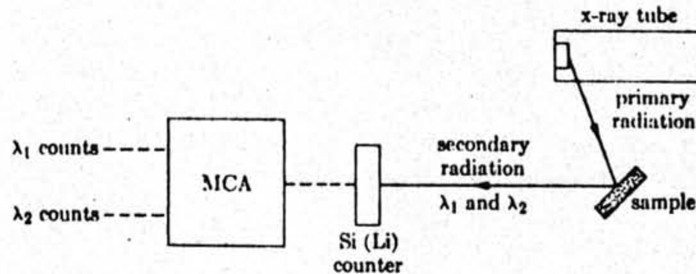
$$\omega = \frac{\Sigma(n)_K}{N_K} = \frac{n(K_{\alpha 1}) + n(K_{\alpha 2}) + n(K_{\beta 1}) + \ldots.}{N_K}$$

and the fraction of vacancies filled via the Auger process is always one minus the fluorescent yield. This fluorescent yield will decrease markedly with decrease of atomic number of the element.

Since the analytical X-ray region lies between 0.2-20 Angstrom, because the wavelengths shorter than a few tenths of an Angstrom are difficult to excite and even more difficult to disperse or separate, and the wavelengths in excess of 20 Angstrom arise mainly from outer orbit transitions and are less useful for element characterization. So, both crystal and energy dispersive spectrometer system are designed to give optimum performance over this range. The WDX is generally best towards a long wave end of this analytical range and the EDX is more useful for the measurement of shorter wavelengths. The systems of the X-ray fluorescence spectrometers between the wavelength-dispersive spectrometer and the energy-dispersive spectrometer are illustrated in Fig. 6.



(a) Wavelength-dispersive spectrometer



(b) Energy-dispersive spectrometer

Fig. 6. X-ray fluorescence spectrometers. In this example, elements 1 and 2 in the sample emit characteristic wavelengths λ_1 and λ_2. These wavelengths are separately measured by crystal diffraction in (a) or by pulse-height analysis in (b), where MCA = multichannel analyzer.

The resolution or the ability of the system to separate lines (or energy) of EDX and WDX system can be compared as:

- in EDX system, the resolution (Γ) is related to the radiation energy (E) so that for Si(Li) detector.

$$\Gamma = (K_1 + K_2E)^{\frac{1}{2}}$$

where K_1 is dependent only on the noise component of the system

K_2 is related to the true statistical fluctuation of the Si(Li) diode.

This resolution of Si(Li) detector can be improved with increasing of radiation energy (or decreasing of wavelength)

- in WDX system, the resolution $(\frac{d\theta}{d\lambda})$ can be derived by differentiation θ with respect to λ in the Bragg's law, so that

$$\frac{d\theta}{d\lambda} = \frac{n}{2d} \cdot \frac{1}{\cos\theta}$$

This resolution can improved with decreasing the 2d value of the analysing crystal, or with the increase in n (order of reflection).

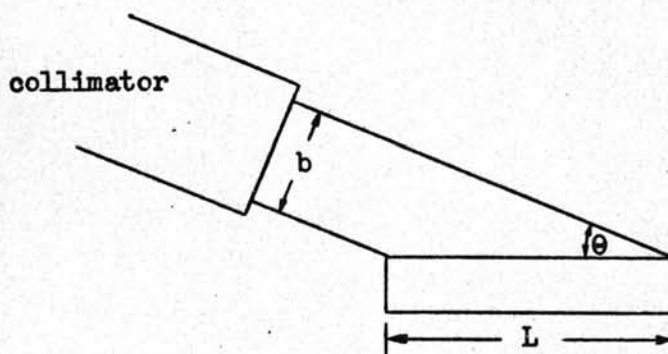


Fig. 7. The optimum length of crystal analyzer.
When the goniometer is set at an angle below this value (θ), the crystal can no longer intercept the whole of the incident beam.

The upper limit of the spectrometer is normally fixed by the angle at which further movement of the detector system is prevented by the presence of the sample chamber, depending upon the particular spectrometer design, generally around 145° (2θ).

The lower limit is set by the angle at which the analysing crystal no longer intercepts the majority of the incident radiation and depends upon the Length (L) of the analysing crystal and the width (B) of the incident beam, generally around 22.2° to 36.4° (2θ), see Fig. 7.

TABLE 1.

Sources of error in X-ray fluorescence spectrometry

RANDOM ERRORS	Counting Statistics (dependant only on time)	
	Generator and X-ray tube stability ($\sim 0.1\%$)	
	Equipment errors ($< 0.05\%$)	
SYSTEMATIC ERRORS	Sample errors	Absorption (100%)
		Enhancement (10%)
		Particle effects (100%)
		Chemical state (5%)
	Equipment errors ($< 0.05\%$)	

The errors usually encounter in practice in X-ray fluorescence analysis are systematic errors, random errors and human errors. The sources of these errors are shown in Table 1. Among these errors, the systematic errors have most effects in resulting errors in analysis. In the systematic errors, the errors except the equipment errors are called matrix effects. This matrix effects is classified into two categories:

1) Elemental interactions:

a) Absorption

b) Enhancement

2) Physical effects:

a) Particle size and surface effects

b) Effects due to chemical state

These effects are described clearly in many experiments and researches, and showed the methods to eliminate these effects too. Some of these methods will be presented here.

1. Standard Addition method.

In this method the amount of the required element is calculated from

$$X = \frac{\frac{I_x}{I_{x'+y}}\, y}{1 - \left(\frac{I_x}{I_{x'+y}}\right) D}$$

where X is the amount of the required element

I_x is the intensity of the unknown specimen

$I_{x'+y}$ is the intensity of the unknown specimen, thoroughly mixed after adding the standard weight y

y is the weight of the standard added to the unknown specimen, it should be added as little as possible

D is the dilution factor,

$$D = \frac{\text{Specimen weight}}{\text{Specimen weight + standard weight}}$$

2. Dilution method.

In this method the content of the required element in the unknown specimen is calculated from

$$\frac{C_x}{C_s} = \frac{I_s - I'_s}{I_x - I'_x}$$

where I_x is the required element intensity in the specimen

I'_x is the required element intensity in the specimen after adding the inert material such as SiO_2, boric acid, etc.

I_s and I'_s are similar to I_x and I'_x , respectively, but only for the standard or reference specimen

C_x is the concentration of the required element in the specimen

C_s is the concentration of the required element in the standard or reference

3. Interanl Standard method

In this method, the additional material having the atomic number close to the required element will be added into the specimen and the standard equally, and the required amount of the interesting material can be calculated from the empirical formula as

$$X = ADF_s \quad \frac{I_{xx}}{I_{xa}}$$

where I_{sa} is the intensity of the additional element in the standard after adding W_a

I_{sx} is the intensity of the required element after adding W_a to the standard

I_{xx} is the intensity of the required element in the sample after adding W_a

I_{xa} is the intensity of the additional element in the sample after adding W_a

W_a is the additional material weight

W_x is the sample or specimen weight

A is the concentration of additional element in % ,

$$A = \left(\frac{W_a}{W_a + W_x}\right) 100 ,$$

D is the dilution factor,

$$D = \frac{W_x + W_a}{W_x} ,$$

F_s is the intensity correction factor of the standard,

$$F = \frac{I_{sa}}{I_{sx}}$$

These methods using in elimination the matrix effects have the limitation in the conditions that the specimen or sample used in the analysis have to be used in the powder form only.