Chapter-3

Measurement of K shell absorption edge jump ratio \((r_k)\) and jump factor \((J_k)\)

3.1 Introduction

In this Chapter, measurement of K shell absorption edge jump ratios \((r_k)\) and jump factors \((J_k)\) in elements Mn, Fe, Co, Cu, Zn, As and Sr using 90° reflection geometry are presented in detail. X-PIPS Si (Li) detector was used to detect the fluorescent K X-rays emitted from the target elements excited by 59.54 keV gamma-rays emitted from an \(^{241}\)Am radioactive point source.

Gamma rays, particularly having energy in the range from a few keV to a few MeV, can interact predominantly with matter through three processes, namely the photoelectric effect, Compton scattering and pair production. In the low energy region the photoelectric effect is predominant. In photoelectric interaction, if energy of incident photon is less than 0.1 MeV, photoelectric cross-section shows sharp discontinuities. Thus, the plot of photoelectric cross-section against energy looks like saw-tooth type. These discontinuities are due to absorption edges and occur when a photon impinging on an atom carries energy just above the binding energy of the electron of a specific shell/sub-shell (K, L, L\(_1\) or M etc). In this way the probability of interaction between photon and electron of a particular shell/sub-shell (K, L, L\(_1\) or M etc) increases suddenly, which results into an abrupt change in the value of photoelectric cross-section

Part of this work has been published in

across absorption edge. The cross-section corresponding to the lower energy branch of absorption edge is attributed to the photoelectric effect in the L and higher shells and the cross-section corresponding to the upper energy branch is due to the K shell and higher shells. Ratio of the values of photoelectric cross-section on higher energy and lower energy side of an edge directly gives absorption jump ratio. Similarly, absorption jump factor is associated with photoelectric absorption coefficient $\tau$ for different shells/subshells (i.e. $\tau_K$, $\tau_{LI}$, $\tau_{LII}$ ....) and is defined as the fraction of the total absorption that is associated with a given shell rather than for any other shell. For K shell, jump ratio $r_K$ is given as

$$
 r_K = \frac{\tau_K + (\tau_{Li} + \tau_{Li} + \tau_{Li}) + ....}{(\tau_{Li} + \tau_{Li} + \tau_{Li}) + (\tau_{Mi} + \tau_{Mi} + \tau_{Mi} + ...) +} \tag{3.1}
$$

Similarly, K shell absorption jump factor $J_K$ is given as

$$
 J_K = \frac{\tau_K}{\tau_K + (\tau_{Li} + \tau_{Li} + \tau_{Li}) + (\tau_{Mi} + \tau_{Mi} + \tau_{Mi} + ...) +}
$$

or $J_K = 1 - r_K^{-1}$

where $\tau_i$ is photoelectric cross-section of $i^{th}$ shell.

The survey of literature, as discussed in the previous chapter, shows that some researchers have measured the values K shell absorption edge jump ratio and jump factor for many elements with $Z \geq 40$ using different techniques viz. the gamma ray or X-ray attenuation method, Compton peak attenuation method, EDXRF technique and the bremsstrahlung transmission method. However, for low Z elements with $Z \leq 38$, experimental measurement of these parameters by using any of the above stated methods is not available in literature. Thus, in present study, the author has measured K shell absorption edge jump ratio and jump factor for Mn, Fe, Co, Cu, Zn, As and Sr elements using EDXRF technique at 59.54 keV photon energy to achieve the following
objectives:

- to provide the experimental data for K shell absorption edge jump ratio and jump factor for the elements with Z ≤40, where no experimental data is available so far.
- to check the reliability and accuracy of EDXRF technique for measuring these absorption edge parameters for low Z elements.

Details of the experimental setup and method of measurement of various parameters needed for the evaluation of K shell absorption edge jump ratio and jump factor using EDXRF technique has been discussed in following sections.

### 3.2 Details of experimental set up

Target of Mn, Fe, Co, Cu, Zn, As and Sr in the form of circular discs of 4.5 cm diameters have been irradiated with 59.54 keV gamma-rays emitted from 100 mCi $^{241}$Am source in $90^\circ$ reflection geometrical setup shown in figure 3.1. $^{241}$Am source has been procured from RITVERC Isotope products St. Petersburg, Russia. These targets were placed in Perspex target holder. Metallic targets of Fe, Cu and Zn and self-supporting targets of Mn, Co, As and Sr has been used in present investigation. Self-supporting targets has been made from their powdered stable chemical compounds MnO$_2$, CoCO$_3$, As$_2$O$_3$ and Sr$_2$CO$_3$ by using the technique described as below:

A known quantity of powdered compound was thoroughly mixed with polystyrene dissolved in benzene and was left to dry on a thin Al backing placed in a stainless steel cell of internal diameter of 4.5 cm. On drying, the target was taken out and the Al backing was carefully removed. Any residue left in the cell was treated with excess of benzene to dissolve polystyrene and was filtered using filter paper. Thus, exact amount of powdered compound and polystyrene in the target was determined. All
the targets were procured from Sigma-Aldrich and were 99.999% pure as quoted by manufacturer.

The K-shell fluorescence X-rays emitted from targets were analyzed by Canberra X-PIPS Si (Li) energy dispersive X-ray Detector (D) with an active area 8 mm$^2$ and Be window of thickness 25 μm. This detector is embedded with a collimator of width 1.1 mm. The thickness of X-PIPS Si (Li) detector chip is 500μm. The resolution of detector is <190 eV at 5.9 keV photon energy and is coupled to EG&G Ortec multichannel analyzer. Block diagram of the spectrometer is shown in figure 3.2.

$^{241}$Am radioactive point source, in addition to 59.54 keV gamma rays, also emits Neptunium (Np) L X-rays, 26 keV gamma ray and some high energy gamma rays. Energies and relative intensities of various additional gamma rays and X-rays emitted from $^{241}$Am source are listed in Table 3.1. These high energy gamma rays are not of much significance in the present measurement because of their very low intensities and small K and L shell ionization cross-sections of the target elements used in the present experiments. However great care has to be exercised to avoid the interference from Np L X-rays and 26 keV gamma rays because of their large interaction cross-sections. These were almost completely (>99.99%) filtered out from the beam of gamma rays incident on the targets by using a graded filter of Al, Fe and Pb. In present geometrical setup, source target distance is 4.5cm and target detector distance is 3.5 cm. Detector is shielded with a graded shielding of Al, Fe and Pb in such a way that it cannot see the source directly. The graded shielding was used for preferential absorption of fluorescent X-rays produced in the lead shielding. The natural background counts were recorded for equal time. This was done by removing $^{241}$Am source from its original position. This background was subtracted from the K X-ray spectrum recorded with 59.54 keV gamma rays incident upon the target. Procedure of the measurement of K shell absorption edge
D : XIPS Si (Li) Detector
T : Target
C1, C2 : Collimator(s)
G : graded absorber of Al and Fe

Fig. 3.1: Schematic diagram of $90^\circ$ reflection geometry used in present measurements.
Fig. 3.2: Schematic diagram of Si (Li) Energy Dispersive spectrometer.
Table 3.1  The energies and relative intensities of various X-rays and gamma rays lines emitted from $^{241}$Am source.

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Energy in keV</th>
<th>Relative intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12-22 Np L X-rays</td>
<td>~40</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>43</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>59.54</td>
<td>35.3</td>
</tr>
<tr>
<td>6</td>
<td>99</td>
<td>0.02</td>
</tr>
<tr>
<td>7</td>
<td>103</td>
<td>0.02</td>
</tr>
<tr>
<td>8</td>
<td>125</td>
<td>0.004</td>
</tr>
<tr>
<td>9</td>
<td>208</td>
<td>$6 \times 10^{-4}$</td>
</tr>
<tr>
<td>10</td>
<td>335</td>
<td>$8 \times 10^{-4}$</td>
</tr>
<tr>
<td>11</td>
<td>370</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>12</td>
<td>663</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>13</td>
<td>722</td>
<td>$3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
jump ratio and jump factor and associated parameters have been given in details in subsequent sections.

3.3 Measurement and determination of various parameters and factors needed for the evaluation of K shell absorption edge jump ratio and jump factor

In present measurement, K-shell jump factor, $J_K$, of an element have been derived using the relation (Ertugrul et al., 2002)

$$J_K = \frac{\sigma_{K\alpha}^X}{(\sigma_t - \sigma_{ts})\omega_K} \left( 1 + \frac{I_{K\beta}}{I_{K\alpha}} \right)$$ (3.3)

where $\sigma_{K\alpha}^X$, $\sigma_t$, and $\sigma_{ts}$ are $K_{\alpha}$ X-ray production cross-section, total atomic cross-section and total scattering cross-section at incident gamma-rays of energy 59.54 keV respectively, $\omega_K$ is K shell fluorescence yield, $I_{K\alpha}$ and $I_{K\beta}$ are the intensities of $K_{\alpha}$ and $K_{\beta}$ X-rays of elements under study. The presently measured values of $J_K$ have been further used to extract the values of jump ratios, $r_K$ in elements under study by using the relation

$$r_K = \frac{1}{1 - J_K}$$ (3.4)

Thus K-shell jump factors and jump ratio of elements Mn, Fe, Co, Cu, Zn, As and Sr has been measured by making use of measured values of the parameters $\sigma_{K\alpha}^X$, $\sigma_t$, and intensity ratio $I_{K\beta}/I_{K\alpha}$ and by using the theoretically values of scattering cross-section ($\sigma_{ts}$) and $\omega_K$. 
3.3.1 General principle of method of measurement of X-ray fluorescence cross-section using 90° reflection geometrical setup

When a photon is incident on target, depending upon the energy of incident radiations, vacancies in the different inner shells of the atoms of the target element are produced due to following processes:

1. Photo ionization with the inner shell electrons.
2. Compton Scattering from inner shell electrons.
3. Interaction of photoelectrons and Compton recoil electrons produced in the target with the inner shell electrons of the target element.
4. Inner shell vacancy transformation.

Consider an arrangement of 90° reflection geometry as shown in figure 3.3. In this figure, target (T) is irradiated with photon from source (S) and the resulting inner shell fluorescent X-ray are detected with detector (D).

Assume the target (T) is of thickness ‘t’ and is made up of large number of small elementary targets each of thickness ‘dx’ as shown in figure 3.4. The inner shell fluorescence X-ray produced in one of the elementary target ‘dx’ at a depth ‘x’ will be detected by the detector if,

a) The incident beam reaches the elementary target ‘dx’ at depth ‘x’ without any interaction.

b) After interaction with the inner shell electrons of the atoms of the elementary target ‘dx’, the inner shell fluorescent X-ray thus produced come out of the target for detection by the detector.

The number of inner shell fluorescent X-ray emitted from the target as a result of the interaction of incident photons with that of target atoms can be calculated as follow:

Let the photon beam of intensity $I_0$, which is equal to $S(\omega_k/4\pi)(\text{where } S \text{ is the source})$
strength and $\omega_i$ is solid angle subtended by source on the target), be incident upon the target at an angle $\theta_i$ with the normal to the surface of target. The intensity of photon beam reaching the element ‘dx’ will be equal to

$$I_o \exp(-\mu_i (BC))$$

This in turns comes out to be:

$$I_o \exp(-\mu_i \frac{x}{\cos \theta_i})$$

where ‘$\mu_i$’ absorption coefficient of the target material at the incident gamma/X-ray energies. The incident photon will interact with inner shell electrons and will produce inner shell fluorescent X-rays. The intensity of fluorescent X-rays thus produced will be equal to the product of following factors:

a) Intensity of photon beam reaching the elementary target ‘dx’.

b) Atoms per gram of the target element $\left( = \frac{N_a}{M} \right)$, where $N_a$ and $M$ are Avogadro’s number and molecular mass of target element.
c) Thickness of the elementary target ‘dx’.

d) X-ray production cross-section (say $\sigma^X$).

e) The correction factor for absorption of gamma-rays in source and air column, $\alpha$

The intensity $dN (E)$ of the inner shell fluorescent X-rays which comes out of the target will be given by:

$$dN (E) = (\text{number of fluorescent X-ray produced in elementary target of thickness 'dx'}) \times (\text{fraction of X-rays transmitted through the thickness 'x'})$$

This can be written as:

$$dN(E) = I_o \exp(-\mu_e \frac{x}{\cos \theta_1}) \frac{N_u}{M} \alpha \sigma^x \, dx \exp(-\mu_e \frac{x}{\cos \theta_2})$$

(3.7)

where $\mu_e$ absorption coefficient of the target material at emitted fluorescent X-ray energy.

Putting the value of $I_o$, the above expression can be written as:

$$dN(E) = \frac{S}{4\pi} \omega_1 \frac{N_u}{M} \alpha \sigma^x \, dx \exp(-(\frac{\mu_1}{\cos \theta_1} + \frac{\mu_2}{\cos \theta_2})x)$$

(3.8)

If the target is placed symmetrically, i.e. $\theta_1=\theta_2=0$(say), the number of inner shell fluorescent X-rays emitted from the target of real thickness ‘t’ is obtained by integrating expression (3.8) from 0 to t. Thus by integrating above expression, the number of inner shell fluorescent X-rays emitted is given by:

$$N(E) = \int_0^t \frac{S}{4\pi} \omega_1 \frac{N_u}{M} \alpha \sigma^x \, dx \exp(-(\frac{\mu_1 + \mu_2}{\cos \theta})x)$$

(3.9)

The number of inner shell fluorescent X-rays emitted from the target and detected by the detector (D) will be given by:

$$N(D) = N(E) \frac{\omega_2}{4\pi} \varepsilon(E)$$

(3.10)
where $\varepsilon(E)$ is the detector efficiency at the energy of emitted florescent X-rays and $\omega_2$ is the solid angle subtended by detector on target.

Expression (3.10) can be written as:

$$N(D) = S \frac{\omega_1 \omega_2}{(4\pi)^2} \frac{N}{M} \alpha \sigma_x \varepsilon(E) \frac{1 - \exp(- (\mu_t + \mu_e) t / \cos \theta)}{(\mu_t + \mu_e) / \cos \theta}$$  \hspace{1cm} (3.11)

In the expression (3.11) the term

$$\frac{1 - \exp(- (\mu_t + \mu_e) t / \cos \theta)}{(\mu_t + \mu_e) / \cos \theta}$$  \hspace{1cm} (3.12)

is known as ‘effective thickness ($t_{\text{eff}}$)’ of target i.e.

$$t_{\text{eff}} = \frac{1 - \exp(- (\mu_t + \mu_e) t / \cos \theta)}{(\mu_t + \mu_e) / \cos \theta}$$  \hspace{1cm} (3.13)

This can be re-written as:

$$t_{\text{eff}} = t \beta$$  \hspace{1cm} (3.13)

where ‘$t$’ is the thickness of target element in gm/cm$^2$, ‘$\beta$’ is known as ‘target self-absorption correction factor’ and is given as:

$$\beta = \frac{1 - \exp(- (\mu_t + \mu_e) t / \cos \theta)}{(\mu_t + \mu_e) t / \cos \theta}$$  \hspace{1cm} (3.14)

Using expression (3.14), expression (3.11) can be re-written as:

$$\sigma_x = \frac{(4\pi)^2 N(D)M}{S \alpha \omega_1 \omega_2 \varepsilon(E) N_{\epsilon} t \beta}$$  \hspace{1cm} (3.15)

From this expression, it is clear that X-ray production cross-section can be determined from the measurement of $N(D)$ and from the knowledge of other factors i.e. $S$, $\alpha$, $\omega_1$, $\omega_2$, $\varepsilon(E)$, $\frac{N_{\epsilon}}{M}$, $\beta$ and $t$. The determination of $N(D)$ along with other factors has been discussed at the relevant places, wherever needed.
3.3.1.1 Measurement of \( K_i \) X-ray production cross-section (\( \sigma_{Ki}^X \))

The intensity of \( N_{Ki} \) of the \( K_i \) (i=\( \alpha, \beta \)) shell fluorescent X-rays of target under study measured under the photo peak using energy dispersive X-ray spectrometer is given as:

\[
N_{Ki} = S\alpha \frac{\omega_i \omega_x N_a}{M} \sigma_{Ki}^X \varepsilon_{Ki} t \beta_{Ki}
\]  

(3.16)

Where \( \sigma_{Ki}^X \) is the cross-section for the production of \( K_i \) group of K X-rays at the incident gamma ray energy and other symbols have the same meaning as explained above, but for \( K_i^{th} \) group of K X-ray. 

Re-writing expression (3.16), we get

\[
\sigma_{Ki}^X = \frac{N_{Ki} M}{t \beta_{Ki}} \left[ \frac{S\alpha \omega_i \omega_x \varepsilon_{Ki} N_a}{(4\pi)^2} \right], \text{ Where } i=\alpha,\beta
\]  

(3.17)

Thus \( K_i \) X-ray production cross-section for \( K_i^{\text{th}} \) X-ray can be determined from this equation using the measured values of \( N_{Ki} \), factor \( \frac{S\alpha \omega_i \omega_x \varepsilon_{Ki} N_a}{(4\pi)^2} \) and calculated values of self-absorption correction factor (\( \beta_{Ki} \)). The measurement/determination of these quantities is discussed in the following sections.

3.3.1.2 Measurement of (\( N_{Ki} \))

The targets of elements Mn, Fe, Co, Cu, Zn, As and Sr were irradiated with 59.54 keV gamma rays and the K\( _i \) X-ray spectra were recorded in each case. Spectra of these different elements have been recorded for a time \( 3 \times 10^4 \) s and sufficient numbers of runs were taken to achieve statistical accuracy of \( \leq 1\% \) in counting rates. Spectrum of Mn, Fe and Co was not completely resolved due to limited resolution of detector. For
Fig. 3.4: Target geometry (Reflection)
these elements K$_\beta$ and K$_\alpha$ photo peaks were well separated by fitting the measured spectra with appropriate multi-Gaussian function using software programme Microcal OriginPro8.0. Typical K$_\beta$ and K$_\alpha$ spectrum of Mn, Cu and Sr target elements for 59.54 keV photon has been given in figure 3.5, 3.6 and 3.7 respectively.

### 3.3.1.3 Determination of self-absorption correction factor ($\beta_{ki}$)

The targets of elements/compounds used in the present experiments were not infinitely thin. Therefore, the absorption of incident radiation in the target before interaction and the absorption of resultant fluorescent X-rays before emission from the target has to be taken into account. The actual thickness ‘t’ is replaced by the effective thickness ‘t$_{\text{eff}}$’ of the target, where t$_{\text{eff}}$= $\beta$\textbf{t}, ‘$\beta$’ is the correction factor which takes into account the absorption of incident gamma rays and emitted X-rays inside the target and is known as self-absorption correction factor of the target as already explained in section 3.3.1. The correction factor ‘$\beta$’ is a function of the angle of incidence and emergence and absorption coefficients $\mu$$_i$ and $\mu$$_e$ of incident gamma rays and emergent X-rays in the target material.

In present case, values of self-absorption correction factor for emitted $K_i$ X-ray energies of the target elements/compounds under investigation have been calculated using following expression:

$$
\beta_{ki} = \frac{1 - \exp\left[-\left(\frac{\mu_p}{\cos \theta_1} + \frac{\mu_e}{\cos \theta_2}\right)t\right]}{\left(\frac{\mu_p}{\cos \theta_1} + \frac{\mu_e}{\cos \theta_2}\right)t}
$$

(3.18)

where $\mu$$_p$ and $\mu$$_e$ are the mass absorption coefficients of the target element at incident photon energy (59.54 keV) and emitted $K_i$ X-ray energies respectively.
As the value of $\theta_1$ and $\theta_2$ in the present experiment was taken to be $45^0$, so expression (3.18) gets simplified to

$$\beta_{ki} = \frac{1 - \exp\left(- \left(\mu_p + \mu_n\right)\sqrt{2t}\right)}{\left(\mu_p + \mu_n\right)\sqrt{2t}}$$

(3.19)

The values of absorption coefficients at desired energies needed for the evaluation of $\beta_{ki}$ have been calculated using interpolation method as explained below.

Let $E$ be the energy at which the value of absorption coefficient $\frac{\mu}{\rho}$ of particular element is to be calculated. Corresponding to two consecutive values of energies $E_1$ and $E_2$ such that $E_1 < E < E_2$, the value of absorption coefficients $\frac{\mu_1}{\rho}$ and $\frac{\mu_2}{\rho}$ were noted from the tables. Care has to be taken that the energy interval $(E_1 - E_2)$ should be as small as possible and no shell/subshell edge should present in between $E_1$ and $E_2$ for smooth variation of absorption coefficient with energy.

Obviously,

$$\frac{\mu_1}{\rho} \propto (E_1)^n$$

or

$$\frac{\mu_1}{\rho} = k(E_1)^n$$

(3.20)

$$\frac{\mu_2}{\rho} \propto (E_2)^n$$

or

$$\frac{\mu_2}{\rho} = k(E_2)^n$$

(3.21)

Where ‘$n$’ is the index to the power of energy with which absorption coefficient varies.

From relation 3.20 and 3.21 we have:

$$\frac{\mu_1}{\rho} / \frac{\mu_2}{\rho} = \left(\frac{E_1}{E_2}\right)^n$$

or

$$\log\left(\frac{\mu_1}{\rho} / \frac{\mu_2}{\rho}\right) = n \log\left(\frac{E_1}{E_2}\right)$$
Fig. 3.5: Typical fitted spectrum of Mn representing $K_{\alpha}$ and $K_{\beta}$ peaks recorded with X-PIPS Si (Li) detector irradiated with 59.54 keV photons.
Fig. 3.6: Typical spectrum of Cu representing K$_\alpha$ and K$_\beta$ peaks recorded with X-PIPS Si (Li) detector irradiated with 59.54 keV photons.
Fig. 3.7: Typical spectrum of Sr representing $K_{\alpha}$ and $K_{\beta}$ peaks recorded with X-PIPS Si (Li) detector irradiated with 59.54 keV photons.
\[
\Rightarrow n = \frac{\log\left(\frac{\mu_1}{\rho} / \frac{\mu_2}{\rho}\right)}{\log(E_1/E_2)}
\]

(3.22)

In this way the value of ‘n’ was determined. The corresponding value of absorption coefficient at desired energy E can be found from any of the following expressions:

\[
\frac{\mu}{\rho} = (E/E_1)^n \frac{\mu_1}{\rho}
\]

or

\[
\frac{\mu}{\rho} = (E/E_2)^n \frac{\mu_2}{\rho}
\]

(3.23)

This procedure of finding the absorption coefficient by determining the index to the power ‘E’ with which \(\frac{\mu}{\rho}\) varies avoided any graphical error which would have entered if it was determined from the plot of \(\frac{\mu}{\rho}\) vs. E. The selection of small interval of energies \(E_1\) and \(E_2\) justified the relation 3.20, 3.21 and 3.22 as the plot of \(\log(E)\) vs \(\log\left(\frac{\mu}{\rho}\right)\) was found to be straight line, the slope of which equals to ‘n’ especially when the energy interval was taken not to be very large.

As stated earlier, in all cases metallic foils were not available and hence in some cases, chemical compounds of the element under investigation were used. In such cases, the value of absorption coefficients for a compound, say \(A_xB_yC_z\) were calculated by the following relation:

\[
\frac{\mu}{\rho}(A_xB_yC_z) = \sum w_i \left(\frac{\mu_i}{\rho}\right)
\]

(3.24)

where \(w_i\) is the weight fraction of the \(i^{th}\) constituent element and \((\mu/\rho)_i\) is the absorption
coefficient of constituent element. This well-known mixture rule is valid with the assumption that the effects of molecular binding, the chemical and crystalline environment are negligible.

In present investigations, value of self-absorption correction factor for target elements under study has been calculated by taking the values of absorption coefficients from WinXCom (Gerward et al., 2001).

3.3.1.4 Measurement of geometrical efficiency related factor

\[
\left[ \frac{S\alpha\omega_1\omega_2e_{Ki}N_a}{(4\pi)^2} \right]
\]

Value of factor \( \frac{S\alpha\omega_1\omega_2e_{Ki}N_a}{(4\pi)^2} \) in expression (3.17) which contains the terms related to flux of 59.54 keV gamma-ray emitted from source, geometrical factor and absolute efficiency of detector has been determined in a separate experiment (Mann et al., 1991). For this purpose target elements 22\( \leq Z \leq 40 \) other than those used in main experiment having same size as the experimental targets were irradiated with gamma-ray from source. \( N_{Ki} \) is the number of X-rays falling under \( K_i \) peak emitted from the targets in this experiment and counted under the photo peak per unit time, are given by following relation:

\[
N_{Ki} = S\alpha\omega_1\omega_2\frac{N_\omega}{M}\sigma_{K_i}^X e_{K_i} t \beta_{K_i}
\]

(3.25)

Rewriting expression (3.25) we get:

\[
\frac{S\alpha\omega_1\omega_2e_{Ki}N_a}{(4\pi)^2} = \frac{N_{Ki}M}{t \beta_{K_i}\sigma_{K_i}^X}
\]

(3.26)

The theoretical values of \( \sigma_{K_i}^X \) for these target elements needed in expression (3.26) have been calculated using relation

\[
\sigma_{K_i}^X = \sigma_K^p \omega_K F_{K_i}
\]

(3.27)
where $\sigma^p_k$ is K-shell photo ionization cross-section at incident gamma-rays of energy 59.54 keV and has been taken from the tabulation of Scofield (1973), $\omega_k$ is K shell fluorescence yield and has been taken from Krause (1979), $F_{ki}$ is the fractional Ki X-ray emission rates given by Scofield (1974). The measured values of the factor $\frac{N_{ki}M}{t\beta_{ki}\sigma^X_{ki}}$ were then fitted to second-degree polynomial as a function of the $K_i$ X-ray energies of these elements. The value of this factor at energies of $K_{\alpha}$ X-ray peak needed to determine the $K_{\alpha}$ X-ray production cross-section of elements under study were then read from the plot. Values of this factor against $K_i$ X-ray energies of target elements have been given in Table 3.2.

Measured/determined values of $N_{ki}$, self absorption correction factor $\beta_{ki}$ and geometrical efficiency related factor ($\frac{S\alpha_1\alpha_2\varepsilon_{ki}N_{\alpha}}{4\pi}$) have been used in expression 3.17 to obtain the values of $K_i$ X-ray production cross-section ($\sigma^X_{ki}$). Values of $K_{\alpha}$ and $K_{\beta}$ X-ray production cross-section have been displayed in Table 3.3.

### 3.4 Measurement of intensity ratio ($I_{K\beta}/I_{K\alpha}$)

The fraction of $K_i$ ($i=\alpha$, $\beta$) X-ray radiative rates, $F_{ki}$, for elements under study have been measured using the relations

$$F_{\alpha} = \left(1 + \frac{I_{\beta}}{I_{\alpha}}\right)^{-1} \quad \text{and} \quad F_{\beta} = \left(1 + \frac{I_{\alpha}}{I_{\beta}}\right)^{-1} \quad (3.28)$$

where $I_{\alpha}$ and $I_{\beta}$ are the measured intensities of $K_{\alpha}$ and $K_{\beta}$ X-rays of elements under study respectively. The ratio $I_{K\beta}/I_{K\alpha}$ has been measured experimentally by using the relation (3.17) which can be re-written as:
Table 3.2: Values of factor \( \frac{S_a \omega_1 \omega_2 \varepsilon \alpha N_a}{(4\pi)^2} \) for Mn, Fe, Co, Cu As and Sr targets at \( K_i \) (i=\( \alpha \) and \( \beta \)) X-ray energies.

<table>
<thead>
<tr>
<th>Element</th>
<th>( K_i ) X-ray group</th>
<th>Value of factor ( \left[ \frac{S_a \omega_1 \omega_2 \varepsilon \alpha N_a}{(4\pi)^2} \right] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>( K_\alpha )</td>
<td>1.64\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>1.82\times10^7</td>
</tr>
<tr>
<td>Fe</td>
<td>( K_\alpha )</td>
<td>1.80\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>1.94\times10^7</td>
</tr>
<tr>
<td>Co</td>
<td>( K_\alpha )</td>
<td>1.97\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>2.10\times10^7</td>
</tr>
<tr>
<td>Cu</td>
<td>( K_\alpha )</td>
<td>2.17\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>2.28\times10^7</td>
</tr>
<tr>
<td>Zn</td>
<td>( K_\alpha )</td>
<td>2.25\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>2.33\times10^7</td>
</tr>
<tr>
<td>As</td>
<td>( K_\alpha )</td>
<td>2.34\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>2.27\times10^7</td>
</tr>
<tr>
<td>Sr</td>
<td>( K_\alpha )</td>
<td>1.78\times10^7</td>
</tr>
<tr>
<td></td>
<td>( K_\beta )</td>
<td>1.17\times10^7</td>
</tr>
</tbody>
</table>
\[
\frac{I_{k\beta}}{I_{k\alpha}} = \frac{N_{k\beta} \beta_{k\alpha} \varepsilon_{k\alpha}}{N_{k\alpha} \beta_{k\beta} \varepsilon_{k\beta}}
\]  

(3.29)

where \( \varepsilon_{k\alpha} \) and \( \varepsilon_{k\beta} \) are the efficiencies of detector for \( K_{\alpha} \) and \( K_{\beta} \) X-rays energy respectively, others terms have the same meaning as explained earlier in expression but for \( K_{\beta} \) X-rays. Measured values of intensity ratio \( I_{k\beta}/I_{k\alpha} \) along with theoretical values for target elements under investigation have been shown in Table 3.4.

### 3.5 Measurement of total K shell photoionization cross-section

For this, first total atomic cross-sections \( (\sigma_i) \) of incident gamma-ray in elements Mn, Fe, Co, Cu, Zn, As and Sr have been measured using narrow beam transmission method by employing the geometry as shown in Figure 3.8. Incident \( (I_0) \) and transmitted intensity \( (I) \) of gamma-rays photons without and with absorber were measured and the values of \( \sigma_i \) for elements under examination has been calculated from the relation

\[
\sigma_i = \frac{M}{N_a} \ln \left( \frac{I}{I_0} \right)
\]  

(3.30)

where ‘t’ is thickness of target element, \( M \) is atomic mass of target sample and \( N_a \) is Avogadro’s number. In present measurement, detector was properly shielded with lead and the total scatter acceptance angle was 2.97° which is <3°. Therefore for this acceptance angle, scattered radiations reaching the detector can produce a ray sum error of the order of 1.0%, which is within tolerable limit (Midgley, 2006). Measured values of total atomic cross-sections \( (\sigma_i) \) along with the calculated values have been presented in Table 3.5. Values of K shell photoionization cross-section have been deduced from the measured values of total atomic interaction cross-sections \( (\sigma_i) \) by subtracting the contribution of
Fig. 3.8: Schematic diagram of linear transmission geometry.
scattering cross-section.

3.6 Measurement of absorption edge jump factor (J_k) and jump ratio (r_k)

As already explained in section 3.3, measured values of K_\alpha X-ray production cross-section (\sigma_{K\alpha}^X), intensity ratio (I_{k\beta}/I_{k\alpha}), total atomic interaction cross-sections (\sigma_t) along with the calculated values of \omega_k given by Krause (1979) and \sigma_{\alpha\alpha} by WinXCom (Gerward et al., 2001) have been used in expression (3.3) for obtaining the values of K shell absorption edge jump factor (J_k). Value of absorption edge jump factor (J_k) so obtained has been then used in expression (3.4) to get the values of corresponding absorption edge jump ratio (r_k).

3.7 Result and Discussion

The K_i (i=\alpha,\beta) X-ray production cross-section (\sigma_{Ki}^X) of Mn, Fe, Co, Cu, Zn, As and Sr target elements has been measured by employing 90^\circ reflection geometry using expression (3.17). Measured values of K_i X-ray production cross-section have compared with theoretical values. Theoretical values of K_i (i=\alpha,\beta) X-ray production cross-section (\sigma_{Ki}^X) calculated using expression (3.27) by making use of K-shell photoionization cross-section \sigma_i^+(E) tabulated by Scofield (1973), \omega_k by Krause (1979) and the fractional K_i X-ray emission rates (F_{Ki}, i=\alpha, \beta) by Scofield (1974a). Obtained results have been depicted in Table 3.3 as well as in graphical form (figures 3.9 and 3.10). From table and figures, it has been clearly observed that the measured values were in good agreement with theoretically calculated values within experimental uncertainty.

Values of intensity ratio (I_{k\beta}/I_{k\alpha}) for aforesaid elements have been measured
using expression (3.29). Obtained values along with theoretical values of Scofield (1974a) have been presented in Table 3.4 and in Figure 3.11. A comparison shows that a fairly good agreement has been achieved between the present experimentally measured and theoretical values.

In second phase of experiment, total atomic cross-section ($\sigma_i$) of aforesaid target elements has been measured using transmission geometry. Obtained values of total atomic cross-section ($\sigma_i$) along with theoretical values calculated from WinXCom (Gerward et al., 2001) has been displayed in Table 3.5 and in graphical form (figure 3.12). A good has been achieved between experimental and theoretical values.

Finally measured values of K shell absorption edge jump factor ($J_K$) and jump ratio ($r_K$) using expressions (3.3) and (3.4) along with the calculated values (Gerward, 2001; Storm and Israel, 1970; Chantler et al., 2005) for elements Mn, Fe, Co, Cu, Zn, As and Sr as well as the values for elements Cu and Zn deduced from the experimental data of (Chantler et al., 2001; Rae et al., 2010) has been depicted in tabular form as shown in Table 3.6 and 3.7 as well as in graphical form (figures 3.13 and 3.14) respectively. It has been found that the measured values are in good agreement with theoretical calculated as well as other’s experimental values within experimental uncertainties. A fairly good agreement between measured and calculated values clearly established that the EDXRF technique used here is an accurate and reliable for determining these parameters.

The overall estimated error associated with present measurement is of the order of ~6%. A detailed breakup of the errors/uncertainties in different factors used for determination of cross-sections, intensity ratios, absorption edge jump ratios and jump factors has been given in Table 3.8.
Table 3.3: Comparison of the measured values of $\sigma_{K\alpha}^X$ and $\sigma_{K\beta}^X$ X-ray production cross-section with calculated values.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Element</th>
<th>$\sigma_{K\alpha}^X$ (b/atom)</th>
<th>Theoretical values$^a$</th>
<th>$\sigma_{K\beta}^X$ (b/atom)</th>
<th>Theoretical values$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental values</td>
<td>Theoretical values$^a$</td>
<td>Experimental values</td>
<td>Theoretical values$^a$</td>
</tr>
<tr>
<td>1.</td>
<td>Mn-25</td>
<td>18.488</td>
<td>19.168</td>
<td>2.621</td>
<td>2.661</td>
</tr>
<tr>
<td>2.</td>
<td>Fe-26</td>
<td>23.537</td>
<td>24.887</td>
<td>3.222</td>
<td>3.401</td>
</tr>
<tr>
<td>5.</td>
<td>Zn-30</td>
<td>63.121</td>
<td>62.420</td>
<td>8.743</td>
<td>8.836</td>
</tr>
<tr>
<td>7.</td>
<td>Sr-38</td>
<td>228.143</td>
<td>224.089</td>
<td>40.609</td>
<td>41.105</td>
</tr>
</tbody>
</table>

$^a$ Scofield (1973)
Table 3.4: Comparison of the measured values of intensity ratio $I_{k\beta}/I_{k\alpha}$ with calculated values.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Element</th>
<th>Intensity ratio $I_{k\alpha}/I_{k\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental values</td>
</tr>
<tr>
<td>1.</td>
<td>Mn-25</td>
<td>0.142</td>
</tr>
<tr>
<td>2.</td>
<td>Fe-26</td>
<td>0.137</td>
</tr>
<tr>
<td>3.</td>
<td>Co-27</td>
<td>0.139</td>
</tr>
<tr>
<td>4.</td>
<td>Cu-29</td>
<td>0.140</td>
</tr>
<tr>
<td>5.</td>
<td>Zn-30</td>
<td>0.139</td>
</tr>
<tr>
<td>6.</td>
<td>As-33</td>
<td>0.148</td>
</tr>
<tr>
<td>7.</td>
<td>Sr-38</td>
<td>0.178</td>
</tr>
</tbody>
</table>

$^a$ Scofield (1974$^a$)
Table 3.5: Comparison of the measured values of total atomic cross-sections ($\sigma_t$) with calculated values. Total atomic scattering cross-section ($\sigma_{ts}$) calculated from WinXCom has also been given.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Element</th>
<th>$\sigma_t$ (b/atom)</th>
<th>$\sigma_{ts}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental values</td>
<td>Theoretical values $^a$</td>
</tr>
<tr>
<td>1.</td>
<td>Mn-25</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>2.</td>
<td>Fe-26</td>
<td>111</td>
<td>114</td>
</tr>
<tr>
<td>3.</td>
<td>Co-27</td>
<td>127</td>
<td>131</td>
</tr>
<tr>
<td>4.</td>
<td>Cu-29</td>
<td>169</td>
<td>172</td>
</tr>
<tr>
<td>5.</td>
<td>Zn-30</td>
<td>201</td>
<td>195</td>
</tr>
<tr>
<td>6.</td>
<td>As-33</td>
<td>290</td>
<td>280</td>
</tr>
<tr>
<td>7.</td>
<td>Sr-38</td>
<td>485</td>
<td>478</td>
</tr>
</tbody>
</table>

$^a$WinXCom (Gerward et al., 2001) values
Table 3.6: Comparison of measured values of absorption edge jump factor ($J_k$) with calculated values.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Element</th>
<th>Absorption edge jump factor ($J_k$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>1.</td>
<td>Mn</td>
<td>0.878</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Fe</td>
<td>0.874</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Co</td>
<td>0.873</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Cu</td>
<td>0.867</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Zn</td>
<td>0.869</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>As</td>
<td>0.864</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Sr</td>
<td>0.858</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Storm and Israel (1970) values  
$^b$ WinXCom (Gerward et al., 2001) values  
$^c$ FFAST Chantler et al. (2005) values  
$^d$ Chantler et al. (2001) values  
$^e$ Rae et al. (2010) values.
Table 3.7: Comparison of measured values of absorption edge jump ratio ($r_k$) with calculated values.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Element</th>
<th>Absorption edge jump ratio ($r_k$)</th>
<th>Experimental</th>
<th>Theoretical</th>
<th>Other’s Experimental measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Mn</td>
<td></td>
<td>8.196</td>
<td>8.130&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.006&lt;sup&gt;b&lt;/sup&gt; 8.458&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2.</td>
<td>Fe</td>
<td></td>
<td>7.936</td>
<td>8.064&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.889&lt;sup&gt;b&lt;/sup&gt; 8.239&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.</td>
<td>Co</td>
<td></td>
<td>7.874</td>
<td>7.936&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.801&lt;sup&gt;b&lt;/sup&gt; 8.025&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4.</td>
<td>Cu</td>
<td></td>
<td>7.519</td>
<td>7.752&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.564&lt;sup&gt;b&lt;/sup&gt; 7.595&lt;sup&gt;c&lt;/sup&gt; 7.652&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>5.</td>
<td>Zn</td>
<td></td>
<td>7.633</td>
<td>7.692&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.547&lt;sup&gt;b&lt;/sup&gt; 7.592&lt;sup&gt;c&lt;/sup&gt; 7.103&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>6.</td>
<td>As</td>
<td></td>
<td>7.353</td>
<td>7.462&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.317&lt;sup&gt;b&lt;/sup&gt; 7.435&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>7.</td>
<td>Sr</td>
<td></td>
<td>7.042</td>
<td>6.993&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.889&lt;sup&gt;b&lt;/sup&gt; 6.865&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Storm and Israel(1970) values
<sup>b</sup> WinXCom (Gerward et al., 2001) values
<sup>c</sup> FFAST Chantler et.al (2005) values
<sup>d</sup> Chantler et.al (2001) values
<sup>e</sup> Rae et.al (2010) values.
Table 3.8: Details of the uncertainty involved in the quantities used in the measurement of X-ray production cross-section ($\sigma_{Ki}^X$), intensity ratio ($I_{K\beta}/I_{K\alpha}$) and total interaction cross-section ($\sigma_i$).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Quantity</th>
<th>Nature of uncertainty</th>
<th>% uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$N_{Ki}$ ($i=\alpha,\beta$)</td>
<td>Statistical and other possible Errors in area evaluation</td>
<td>~1%</td>
</tr>
<tr>
<td>2.</td>
<td>$\beta_{Ki}$</td>
<td>Due to error in the absorption coefficient at incident and emitted photon energies and in the measurement of target thickness</td>
<td>~3%</td>
</tr>
<tr>
<td>3.</td>
<td>$\frac{S\alpha\omega_1\omega_2\varepsilon_{Ki}N}{(4\pi)^2}$</td>
<td>Statistical, error in area evaluation, errors in absorption coefficients at incident and emitted photon energies and in the values of $\sigma_k$ and $\omega_k$ and in the measurement of target thickness</td>
<td>~5%</td>
</tr>
</tbody>
</table>
Fig. 3.9: Variation of $K_{\alpha}$ X-ray production cross-section ($\sigma_{K\alpha}^V$) as a function of atomic number (Z).
Fig. 3.10: Variation of Kβ X-ray production cross-section ($\sigma_{K\beta}^X$) as a function of atomic number (Z).
Fig. 3.11: Variation of K shell intensity ratio ($I_{k\beta}/I_{k\alpha}$) as a function of atomic number ($Z$).
Total atomic cross-section $\sigma_t$ (b/atom) as a function of atomic number (Z).

Fig. 3.12: Variation of total atomic cross-section ($\sigma_t$) as a function of atomic number (Z).
Fig. 3.13: Variation of K shell absorption edge jump factor ($J_k$) as a function of atomic number (Z).
Fig. 3.14: Variation of K shell absorption edge jump ratio ($r_k$) as a function of atomic number ($Z$).