CHAPTER II
SURVEY OF LITERATURE ON X-RAY FLUORESCENCE: THEORY AND EXPERIMENT
Survey of literature on x-ray fluorescence: Theory and Experiment.

A. Interaction of photons with matter.

B. X-ray fluorescence phenomenon and K x-ray fluorescence parameters.

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   i) Theory.
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References.
A. Interaction of photons with matter.

The interaction of photons with matter leads to removal of photons from the beam of photons and produces secondary electrons. It is well known that the interaction between photons and matter depends upon their energy and the atomic number of the material.

A well-collimated beam of photons with an absorber follow an exponential law of attenuation, \( I = I_0 \exp(-\mu t) \), where \( \mu \) (cm\(^2\)/g) is the mass attenuation coefficient and \( t \) (g/cm\(^2\)) is the thickness of an absorber. This is because photons are absorbed or scattered in a single event and those photons absorbed or scattered are removed from their path in the beam while the others are transmitted in the same direction as that of the incident beam without any interaction. Since an absorber is an aggregation of individual atoms, each atom in the absorber acts individually independent of its surroundings resulting in the absorption or scattering of incident photons. Then with each atom, there associates a particular type of interaction process characterized by a cross-section. In such interaction the photon may lose all, part or no energy to the atoms, which may be termed as absorption, inelastic or elastic scattering process respectively. Each process has corresponding cross sections. Therefore total cross section for the interaction of photon by all the possible processes is the sum of these partial cross sections.

Following are the important processes through which photons, in the low energy region, interact with matter:

i. Photoelectric effect.
ii. Compton scattering.
iii. Rayleigh scattering.
iv. Thomson scattering.
v. X-ray Raman effect.
vi. Resonant Raman scattering and Resonant Raman - Compton scattering.

Although low energy photons interact with matter through all these processes, only some of them, in fact it is only the Photoelectric effect and however in a small measure and over a certain region of energy only the other inelastic processes such as Raman effect, Resonant Raman effect and Resonant Raman-Compton effect, contribute to x-ray fluorescence process. Therefore we give a brief account of only these processes as below.

**Photoelectric effect:**

The photoelectric effect is a predominant process at low energies. In this process, the incident photon of energy $h\nu$, which is greater than the binding energy $B_e$ of an electron in atomic shell, is completely absorbed by one of the inner shell electrons in an atom (usually K or L) and that electron is ejected from the atom with kinetic energy $T$, where $T$ is given by

$$T = h\nu - B_e$$  \hspace{1cm} (2.1)

The remainder of the energy appears as characteristic x-rays or Auger electrons from the filling of the vacancy in the inner shells. It may be noted that, in order to conserve the energy and momentum, a tightly bound electron in an atom absorbs the energy of incident photon. More the tightly bound, an electron in an atomic shell, more the probability of photoelectric absorption. Thus the most tightly bound electron, that is, the K-shell electrons have the greatest probability (about 80% of the total photoelectric cross section) provided that the incident photon energy is more than the K-shell binding energy. The variation of the photoelectric absorption coefficient as a function of the photon energy shows a sharp
abrupt rise in absorption as the photon's energy reaches the binding energy of an electron of a particular shell. These are called absorption edges. As the energy $h\nu$ increases beyond the K-absorption edge, which appears at a higher energy than the other edges (L, M etc.), there is a rapid decrease in the value of total photoelectric cross section. Thus the photoelectric effect is important at relatively low energies.

The total photoelectric absorption cross section for K-electrons (Heitler 1954) is given by

$$\tau_\text{K} = \Phi_e Z^4 \alpha^4 4\sqrt{2} \left( \frac{m_0 c^2}{h\nu} \right)^{7/2} \quad \text{(for } h\nu \gg m_0 c^2\text{)},$$

(2.2)

where $\Phi_e = \frac{8\pi}{3} \left( \frac{e^2}{m_0 c^2} \right)^2$ is the Thomson scattering cross section, $m_0$ is the rest mass of electron, $\alpha$ is Sommerfeld's fine structure constant and $Z$ is the atomic number of the absorber. Thus for high $Z$ elements, at low energies, the K-shell photoelectric cross section predominates.

**X-ray Raman effect:**

If the incident photon excites an electron in the atom to one of the vacant upper states and the photon is scattered out with reduced energy, the process is called Raman effect. For instance, the incident photon may lift one of the K-shell electrons to one of the vacant levels of the atom. This process can take place irrespective of the energy of incident photon, less than or greater than the K-shell binding energy. If the incident photon energy is greater than K-shell binding energy, it is referred to in literature as X-ray Raman effect.

**Resonant Raman effect:**

If the incident photon energy is close to but less than the binding
energy of the K-shell electron, a K-shell electron may be lifted to one of the unoccupied levels in the atom. In the intermediate state of the interaction the K-shell electron deexcites to reach its original place and on deexcitation it may cause excitation of an L-shell electron to one of the unoccupied levels in the atom. In the final state, there will be a vacancy in the L-shell and a photon will be scattered with reduced energy. Note that K-shell electrons are intact. This process involves K-shell electron in the intermediate state and hence is known as K-shell Resonant Raman effect. Quantum mechanically this process is distinct from the incident photon interacting directly with L-shell electron.

**Resonant Raman - Compton effect:**

If the incident photon energy is close to but less than the binding energy of the K-shell electrons, the deexcitation of K-shell electron in the intermediate state may lead to the ejection of a L-shell electron out of the atom and the photon gets scattered. In this, the final state consists of a free electron ejected from L-shell and a scattered photon with reduced energy. This may be called Resonant Raman-Compton effect. In this process the ejected electron and the scattered photon share the available energy and hence the spectra of the photon and the electron are continuous.
B. X-ray fluorescence process and K x-ray fluorescence parameters.

X-ray fluorescence and Auger process:

X-ray fluorescence is an important phenomenon in atomic and nuclear physics. When a beam of particles such as protons, electrons or a beam of photons interact with an atom, electrons in the K-, L-, shells may get ejected out of the atom, resulting in the creation of vacancies in that particular shell, provided the energy of the incident radiation is greater than the binding energy that shell electron. Thus when gamma or x-rays interact with an atom, vacancies are created by photoelectric effect. The creation of a vacancy in an atomic shell initiates a series of rearrangement processes of electrons resulting in the emission of characteristic x-rays or Auger electrons. A single vacancy created, for example, in K-shell, is filled in a very short time by an electron coming from higher shell, thus shifting the vacancy to the higher shells. This process repeats and the vacancy is shifted to higher and higher shells. The difference in the binding energy between two shells is either released in the form of characteristic K x-ray or transferred to any one of the bound electrons of higher shells like L, M, N, etc., resulting in the ejection of that electron. The former process is called x-ray fluorescence and the latter process is called Auger effect. The electron emitted in the Auger process is known as Auger electron, after Auger (1925), who was the first to identify these electrons in a cloud chamber following exposure to x-rays. Auger process is also known as radiationless transition. The fluorescence phenomenon is depicted in Fig. 2.1. The emission of fluorescence K x-rays is isotropic in nature.

It is readily seen that an atom which has emitted an Auger electron now has two vacancies, neither of which is the same as the vacancy created by the initial ionizing event. Continued Auger transitions give rise
Fig. 2.1. Schematic diagram of x-ray fluorescence phenomenon in the simplified Rutherford-Bohr model of the atom.
to emission of L, M, ...... characteristic x-rays and Auger electrons, resulting in an atom with multiple vacancies in its outer shells.

The transitions to K-shell, constitute K-series, and to L-shells constitute L-series etc. These transitions are subjected to the transition rules

\[ \Delta l = \pm 1, \quad \Delta m = 0, \pm 1, \]

where \( l \) and \( m \) are the orbital angular momentum quantum number and magnetic quantum number respectively. A diagram depicting K x-ray emission and partial energy levels of singly ionized atom is shown in Fig. 2.2.

In the L-shell of an atom, there are eight electrons grouped into three sub shells \( L_\text{i}, L_\text{ii} \) and \( L_\text{iii} \), each of which corresponds to a definite quantum state. Often intrashell transition may occur. This moves a vacancy from one subshell to another (\( L_\text{i} \) to \( L_\text{ii} \), \( L_\text{i} \) to \( L_\text{iii} \) and \( L_\text{ii} \) to \( L_\text{iii} \)). Therefore, a primary vacancy, which is initially created in \( L_\text{i} \) subshell may move to \( L_\text{ii} \) or \( L_\text{iii} \) subshell or vacancy created in \( L_\text{ii} \) subshell may move to \( L_\text{iii} \) subshell, before it is filled by an electron from a higher (M, N, ...etc.) shells. These transitions are called Coster-Kronig transitions (Coster and Kronig 1935).

**X-ray fluorescence yield and x-ray fluorescence cross-section:**

The fluorescence yield is defined as the probability that a vacancy in a given shell results in radiative transition. Then the fluorescence yield of the \( i \)th shell of an atom, \( \omega_i \), is the probability that a vacancy in that shell is filled by radiative transition. In other words, the ratio of the number of characteristic x-rays emitted to the number of primary vacancies in the atom is called the fluorescence yield. Therefore \( \omega_i \) is
Fig. 2.2. Energy level diagram for a singly ionized atom showing only K-series.
where \( n_x \) is the number of characteristic x-ray photons emitted, \( n_i \) is the number of primary vacancies in the \( i^{th} \) shell and \( n_e \) is the number of Auger electrons ejected. The probability of radiative transition is approximately proportional to \( Z^4 \). On the other hand, the Auger yield of the same shell, \( a_i \), is defined as the probability that an electron is emitted when the vacancy is filled from higher shell electron. The radiationless transition (Auger transition) probabilities vary relatively slowly with atomic number. This is predominant in low Z elements. The calculation of the \( K-, L-, ... \) shell fluorescence yield involves consideration of the relative probabilities of these two alternative processes. Compton and Allison (1935) have given full description of the fluorescence yield.

The x-ray fluorescence cross section is defined as the probability for x-ray production and is given by the product of photoelectric cross section for \( i^{th} \) shell, \( \tau_i \), and the fluorescence yield, \( \omega_i \), of the same shell,

\[
\sigma_i = \tau_i \omega_i
\]

where \( i = K, L, M, ... \). So it can be defined as the number of characteristic x-rays produced per incident radiation per atom per second.

Let \( \Gamma \) be the total width of an excited state of an atom having a vacancy in it and is related to the mean life \( \tau \) of the state by the relation:

\[
\Gamma = \frac{\hbar}{\tau}
\]
where $\Gamma$ is the sum of radiative width $\Gamma_R$, the radiationless width $\Gamma_A$, and the Coster-Kronig width $\Gamma_{CK}$, that is,

$$\Gamma = \Gamma_R + \Gamma_A + \Gamma_{CK} \tag{2.6}$$

The fluorescence yield $\omega$ is therefore given by

$$\omega = \frac{\Gamma_R}{\Gamma} \tag{2.7}$$

Thus for a sample of many atoms, the fluorescence yield of a shell or subshell is equal to the ratio of the number of characteristic x-ray photons emitted, when the vacancies in the shell or subshell are filled, to the total number of primary vacancies present in that shell or subshell. Therefore fluorescence yield of the K-shell of atom, containing two $S_{1/2}$ electrons, is then given by

$$\omega_K = \frac{I_K}{n_K} \tag{2.8}$$

where $I_K$ is the total number of characteristic K x-rays emitted from the sample and $n_K$ is the number of K-shell vacancies. The number of vacancies, $n_K$, created in the K-shell of $n_a$ number of atoms is given by

$$n_K = I_0 \tau_K n_a = \frac{I_0 \tau_K n_a}{\varepsilon_i \exp(-\mu_{iw} t_w)} \tag{2.9}$$

where $I_0$ is the number of photons incident on the target, obtained after correcting the measured intensity $I_0'$, for the efficiency of the detector, $\varepsilon_i$, and for the attenuation in the window of the detector, $\exp(-\mu_{iw} t_w)$; where $\mu_{iw}$ is the mass attenuation coefficient of incident photons in the detector's window of thickness $t_w$, $\tau_K$ is the K-shell photoelectric cross
section of the target atom at the incident photon energy and \( n_a \) is the number of atoms per square centimeter area of the target and is given by

\[
n_a = \frac{N_A t}{A}
\]

(2.10)

Here \( N_A \) (atoms per mole) is the Avogadro's number, \( t \) (g/cm\(^2\)) is the thickness of the target expressed as mass per unit area and \( A \) (g/mole) is the atomic weight of the target element. In the case of compound targets the atomic weight \( A \) should be replaced by molecular weight \( M \) of the compound. The values of \( \tau_k \) were computed, at energies of interest, from the table of Scofield (1973) using the log-log interpolation scheme given by (Cullen et al. 1989),

\[
\log \left[ \sigma (E) \right] = \log \left( \frac{\sigma \left( E_2 \right)}{\sigma \left( E_1 \right)} \right) + \log \left( \frac{\sigma \left( E_1 \right)}{\sigma \left( E_2 \right)} \right)
\]

(2.11)

where \( \sigma (E) \) is the K-shell photoelectric cross section at an energy \( E \) that lies between the two tabulated energies \( E_1 \) and \( E_2 \).

In the experimental situations, the number of characteristic x-rays emitted from the target has to be estimated properly. Therefore the number of characteristic x-rays measured has to be corrected for efficiency of the detector and for window attenuation (wherever necessary), and for the self-absorption in the target to estimate the total number of x-rays generated from the target in the forward hemisphere. Therefore to correct for self-absorption of characteristic x-rays in the target material, we used the correction factor \( \beta \). This correction factor, \( \beta \), is termed the self-absorption correction factor for the target material. However, in the present experiment, since we have employed 2\( \pi \)-
geometrical configuration, the whole target is exposed to incident radiation. Therefore, the fluorescence x-rays are produced at various sites, at various depths in the target. Taking into account the isotropic emission of K x-rays and the fact that we are measuring the intensity of all x-ray photons emerging from the target in all the forward directions, that is, emitting into a solid angle of 2π sr., we use the factor β without involving the scattering angles:

\[
\beta = \frac{1 - \exp(-\mu_i + \mu_e)t}{(\mu_i + \mu_e)t}
\]

(2.12)

where \(\mu_i\) and \(\mu_e\) are the mass attenuation coefficients of the incident and emitted K x-ray photons respectively in the target and are computed from the Tables of Hubbell and Seltzer (1995) using log-log interpolation scheme (Eqn. 2.11). In the case of a chemical compound or a mixture, the values of mass attenuation coefficients, \(\mu_i\) and \(\mu_e\), can be approximately evaluated according to the mixture rule:

\[
\mu = \mu_1w_1 + \mu_2w_2 + \mu_3w_3 + \ldots
\]

(2.13)

where \(w_1, w_2, w_3\ldots\) are the proportion by weight of the constituent elements in the compound.

So in order to estimate the total number of K x-ray photons emitted from the target as a whole, the corrected number has to be multiplied by a factor of 2, as the K x-rays are emitted isotropically (4π sr.) in the target. Therefore the total number of K x-rays emitted from the target in all directions is given by
where \( I_k \) is the measured K x-ray intensity, \( \varepsilon_x \) is the efficiency of the detector at fluorescence x-ray energy and \( \exp(-\mu_{xw} t_w) \) is the window attenuation correction factor for fluorescence x-rays; here \( \mu_{xw} \) is the mass attenuation coefficient for fluorescence K x-rays in the detector's window of thickness \( t_w \). Substituting the Eqs. 2.9 and 2.14 in Eqn. 2.8, we get,

\[
\omega_k = 2 \frac{I_k}{I_0} \left( \frac{\varepsilon_i}{\varepsilon_x} \right) \frac{\exp(-\mu_{xw} t_w)}{\exp(-\mu_{xw} t')} \frac{1}{\tau_k n_s \beta}.
\]  

(2.15)

The x-ray fluorescence cross section for K-shell of atom is given by

\[
\sigma_k = \tau_k \omega_k.
\]  

(2.16)

Substituting for \( \omega_k \) from Eqn. (2.15), we get,

\[
\sigma_k = \frac{I_k}{I_0 n_s} = 2 \frac{I_k}{I_0} \left( \frac{\varepsilon_i}{\varepsilon_x} \right) \frac{\exp(-\mu_{xw} t_w)}{\exp(-\mu_{xw} t')} \frac{1}{n_s \beta}.
\]  

(2.17)

**Ratio of level widths:**

The ratio of radiative transition width to radiationless transition width (Auger transition width) for K-shell of atom, \( \frac{\Gamma_k}{\Gamma_A} \), can be expressed, in terms of \( \omega_k \), in the form

\[
\frac{\Gamma_k}{\Gamma_A} = \frac{\omega_k}{(1 - \omega_k)}.
\]  

(2.18)

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Substituting \( \omega_K = \frac{I_K}{n_K} \), we get

\[
\frac{\Gamma_R^K}{\Gamma_A^K} = \frac{I_K}{(n_K - I_K)}
\]  

(2.19)

The values of \( I_K \) and \( n_K \) are obtained from the measured values of intensity of fluorescence x-rays and incident photons as described earlier.
C. A brief survey of theoretical and experimental methods.

Over the years many workers have published the theoretical and experimental values of K-shell fluorescence parameters. We present here the brief account of the same.

i) Theory.

Burhop (1935), a pioneer in this field, has calculated the radiative transition probability using the nonrelativistic-screened hydrogenic wave functions.

In subsequent years using unscreened hydrogenic wave functions, Geffrion and Nadeau (1959) have calculated the K-shell radiative transition probability and showed that it is proportional to the fourth power of the atomic number, that is,

$$\omega_n(K) \propto Z^4. \quad (2.17)$$

Callan (1963) computed K x-ray emission rates, semi-empirically, using the equation,

$$\omega_n(K) = \sum_n A_n Z^n. \quad (2.18)$$

Where $A_n$ are empirical coefficients for the $np \rightarrow 1s$ transitions, suitably modified for the filling of shells. His results agree fairly well with the experimental values existed at that time and also with the theoretical values.

Scofield (1969) treating electrons relativistically and taking retardation effect into considerations, computed the total radiative decay rates and the rates of emission of a number of x-ray lines for a range of...


Numerical calculations were performed using the Hartree-Fock-Slater approach with Kohn-Sham and Gaspar exchange, by Walters et al. (1971) and produced the K-shell fluorescence yields for elements covering the range Z = 4 to 54.

Kostroun et al. (1971) derived the theoretical K-shell fluorescence yields by combining Scofield's radiative widths with radiationless transition probabilities calculated from nonrelativistic hydrogenic wave functions, and found good agreement with a set of selected most reliable experimental values of ωK in the atomic range 10 ≤ Z ≤ 55.

The x-ray fluorescence cross sections for K and L x-rays of the elements in the atomic range 5 ≤ Z ≤ 101 for K-series and 12 ≤ Z ≤ 101 for L-series, in the energy range 1 to 200 keV, have been calculated by Krause et al. (1978).

Langenberg et al. (1979) have evaluated the K-shell fluorescence yields from 257 experimental values for the elements in the atomic range 3 ≤ Z ≤ 98.

Krause (1979) used relativistic Hartree-Fock values of radiative width for calculation of K-shell fluorescence yield after an extensive survey of radiative and nonradiative yields for K- and L-shells. He
tabulated the values of \( \omega_k \) for the elements in the atomic range \( 5 \leq Z \leq 110 \).

Using Dirac-Hartree-Slater potential wave function, Chen et al. (1980) have carried out the systematic relativistic calculations for K-shell Auger transitions for 25 elements with atomic number from \( Z = 18 \) to 96.

Crasemann (1984) has reviewed the theory of photon emission in energetic atomic transitions and calculations of the total width of atomic hole states. He has also outlined the consequence limitations on theoretical fluorescence yields of single vacancy states and some general principles regarding the fluorescence yields of multiple ionized systems.

Hubbell (1989) has reviewed x-ray fluorescence yield experimental and theoretical information beyond that available in earlier extensive reviews by Fink et al. (1966), Bamberjak et al. (1972) and Krause (1979). In this article, an annotated bibliography from 1978 to 1988 is also included. Tables of fitted values of K-, L- and M-shell fluorescence yields are presented.

Kodre et al. (1990) have shown that deep inner-shell electrons (holes) have pronounced independent particle character, as evidenced by the fact that simple screened hydrogen wave functions allow one to calculate the K-shell fluorescence yields and widths to accuracy of the order of 1%.

Hubbell et al. (1994) have reviewed the measured K-, L- and higher atomic shell x-ray fluorescence yield data, covering the period from 1978 to 1993, following the major previous compilations by Bamberjak et al. (1972) and Krause (1979). The bibliography of fluorescence yield measurements, analysis, fits and tables from 1978 to 1993 is presented.
Comparisons of the fluorescence yields of K-, L- and M-shells based on measurements and on theoretical models are presented. In addition, selected well-characterized measured fluorescence yields of K-, L- and M-shell results restricted to the period from 1978 to 1993 are listed. These selected measured values are fitted by least squares to polynomials in \( Z \) of the form \( \sum a_n Z^n \) and compared with theoretical and with earlier fitted values. A section on application of fluorescence yield data to computations of x-ray mass energy-absorption coefficients is also included.

Schoenfeld et al. (1996) have evaluated K-shell fluorescence yield, mean L-shell fluorescence yield, ratios of x-ray emission probabilities, ratios of emission probabilities of Auger electrons and vacancy transfer coefficients from experimental and theoretical values of the same constants collected from the literature.

**Semi-empirical fit formula for \( \omega_K \):**

A semi-empirical fitting formula for \( \omega_K \), introduced by Burhop (1955) has been established in the literature, and it is of the form

\[
\left( \frac{\omega_K}{1 - \omega_K} \right)^{1/4} = C_0 + C_1 Z^1 + C_2 Z^2 + C_3 Z^3 = \sum_{i=0}^{3} C_i Z^i. \tag{2.19}
\]

This can be rewritten as

\[
\omega_K = \frac{\left[ \sum_{i=0}^{3} C_i Z^i \right]^4}{1 + \left[ \sum_{i=0}^{3} C_i Z^i \right]^4}. \tag{2.20}
\]
Bambynek et al. (1972), in their review article (the most comprehensive and widely quoted fluorescence yield reference), have fitted their collection of "selected 'most reliable' experimental values," with the parameters, for Eqn. (2.20), above, of values:

\[
\begin{align*}
C_0 &= 0.015 \pm 0.010 \\
C_1 &= 0.0327 \pm 0.0005 \\
C_2 &= 0 \\
C_3 &= -(0.64 \pm 0.07) \times 10^{-6}.
\end{align*}
\]

In a subsequent review, Krause (1979) incorporated additional new data in a revised evaluation and presented a table of adopted values of K-shell fluorescence yields for all elements in the range 5 \( \leq Z \leq 110 \), but did not provide corresponding parametric fits.

In 1984, Bambynek presented a further revaluation of K-shell fluorescence yield incorporating about hundred new measurements subsequent to Bambynek et al. (1972) evaluation. Using a stepwise regression analysis with 119 selected \( \omega_K \) measurements, Bambynek fitted his new evaluation to the form in the Eqn. (2.20) with the parameter values:

\[
\begin{align*}
C_0 &= 0.0370 \pm 0.0052 \\
C_1 &= 0.03112 \pm 0.00044 \\
C_2 &= (5.44 \pm 0.011) \times 10^{-5} \\
C_3 &= -(1.250 \pm 0.070) \times 10^{-6}
\end{align*}
\]
ii) Experiment.

The experimental determination of K x-ray fluorescence yield, $\omega_K$, K x-ray fluorescence cross section, $\sigma_K$, and the ratio of radiative transition width to radiationless transition width (Auger transition width) for K-shell of atom, $\frac{\Gamma_K^R}{\Gamma_K^A}$, have been of great interest, because of great importance of these quantities in numerous contexts of various fields. Consequently a considerable amount of effort has been devoted to the field of x-ray fluorescence studies by many investigators. Starting from Kossel (1923) to Şimşek et al. (2002) and Özdemir et al. (2002), many researchers have adopted various methods for measuring the K x-ray fluorescence yields and K x-ray fluorescence cross-sections. In Table 2.1, we give the list of the methods employed over the years by many investigators, which vary according to ionization process, target material, detector system used and the geometry adopted in the measurements.

K x-ray fluorescence to occur, a vacancy in the K-shell is to be created. Such vacancies can be created by different means, namely, by charge particle impact, by photo ionization, and by nuclear decay process etc. The resultant fluorescence x-ray photons are detected by employing various types of detectors such as photographic plate, ionization chamber, proportional counter, NaI(Tl) crystal scintillation detector and solid-state detectors. The targets employed may be gaseous or solid or both. It is observed that the reflection geometry configurations are adopted in most of the cases. Allawadhi (1993) has reviewed all types of reflection geometries and are shown in Fig. 2.3. A few measurements in the early fifties involve variable geometry from collimated to broad beam geometry including 2x-geometry (Roos et al. 1954).

We present here a brief survey of various methods employed over
### Table 2.1. List of various methods employed for fluorescence studies.

(Ref: Bambynek et al. 1972)

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* The following abbreviations are used:

CC - Cloud Chamber. IC- Ionization Chamber. PC- Proportional Counter.
D-Double proportional counter. MW-Multiwire Proportional counter.
PHC- Photo Cathode. PPL – Photographic film or Plate, SC-Semiconductor detector.
SD- Double focusing spectrometer. SL-Lens Spectrometer and $\gamma$- 180° spectrometer.
Fig. 2.3. Schematic diagram of different geometrical set ups used for measurements of x-ray fluorescence parameters (Ref: Allawadhi 1993).
the years, by many investigators to determine the K x-ray fluorescence parameters.

In the beginning the cloud chambers, ionization chambers and photographic emulsion plates were used for the determination of fluorescence parameters.

Auger (1925) has used the cloud chamber to determine the total number of single electron tracks and calculated the fluorescence yields. By this, Auger for the first time established the existence of radiationless transitions, which are now named after him.

The K-shell fluorescence yield values of Fe, Ni, Cu, Zn, Mo and Ag have been measured by Balderston (1926). The primary radiation is monochromatized by reflection from a crystal in a Bragg spectrometer. The general conclusions of his work agree well with the values of other experiments. He has also shown that $\omega_K$ is independent of wavelength of incident radiation and increases with increasing atomic number. His numerical values, however, especially for the elements of higher atomic number, were not agreed well with the experimental values of other workers.

Using a filtered beam of primary x-rays as incident radiation, Martin (1927) has measured $\omega_K$ for Fe, Ni, Cu and Zn metals foils. The ionization chamber of semi-cylindrical shape was employed to measure the intensity of x-rays.

In 1929, Compton has devised a method to determine the K x-ray fluorescence yields of Ni, Se and Mo elements in the form of solids.
employing an ionization chamber and using the x-rays from x-ray tube to fluoresce the targets.

Haas (1933) has measured $\omega_K$ for Si, S, Cl, Ca and Cr elements in the lower atomic number region. In his experiment, the incident radiation is made monochromatic by reflection of primary x-rays from a crystal in a vacuum spectrometer. The fluorescence radiation is measured in a wedge-shaped ionization chamber. No evidence of variation of $\omega_K$ with the wavelength of incident radiation was observed.

Germain (1950) has determined the fluorescence yield of Po by using electron sensitive photographic plates soaked in a solution containing Astatine-211. From the observed number of tracks with and without Auger tracks $\omega_K$ is deduced.

The K-shell fluorescence yield of Krypton has been measured by West et al. (1950) using proportional counter.

Roos (1954, 1957) has measured the K-shell fluorescence yields of Zr, Nb, No, Rh, Pb, Ag, Cd and Sn, and Fe, Ni, Cu and Zn elements by solid angle variation method using NaI(Tl) scintillation detector. The use of NaI(Tl) scintillation detector enabled them to vary the solid angle subtended by the detector from almost $2\pi$ to effectively zero. Since the primary x-rays, which eject the K-shell electrons from the sample foil, are well collimated and the fluorescence radiation is emitted isotropically, this large change in solid angle enable them to distinguish between the primary and fluorescence radiation. From the ratio of the fluorescence to the direct primary beam (no sample) the K-shell fluorescence yield is obtained.
The K Auger yields of Yb, Po and U have been measured by Gray (1956) using magnetic beta ray spectrometer. He has also presented K Auger electron intensity ratios.

Patronis et al. (1957) have measured the K-shell fluorescence yields of Ni, Cu and Zn using proportional counter and 22 keV K x-rays from \(^{109}\)Cd source. Besides, they have measured the mean L-shell fluorescence yield of Pb.

Fink et al. (1966) have made an extensive review on experimental methods of measuring of x-ray fluorescence yield. All available experimental values of K-, L-, and M-shell fluorescence yields together with L-shell Coster-Kronig yields were summarized. They tabulated the values of \(\omega_k\) of elements ranging from Z = 6 to 93 and compared with available theoretical values.

The K-shell fluorescence yields of elements in the atomic range 13 \(\leq Z \leq 27\) have been measured by Baily et al. (1967) using gas flow counter mounted at right angles to the primary x-ray beam. The K x-rays in the target foils and gas targets are excited by monochromatic x-ray beam.

Dick and Lucas (1970) have measured the K-shell fluorescence yields for low Z elements Be, B, C, F and Mg. The primary vacancies in the K-shell are produced by an intense beam of K x-rays of Al or C targets generated by electron bombardment. The measured values of \(\omega_k\) agree quite well with the values calculated from a theoretical prediction of Wenzel.

Hribar et al. (1977) have measured the K x-ray fluorescence yield
of Xenon by using wall-less proportional counter, filled with propane and a small amount of xenon. The photoelectrons liberated from xenon atoms, by the interaction of gamma rays from $^{241}$Am and Er Kα x-rays, are detected by the proportional counter.

Espenschied et al. (1978) have determined the K-shell fluorescence yields of Cl and Br using a multi-wire proportional counter with methane and argon as counting gases.

Keith et al. (1978) have described a method to measure K-shell fluorescence yield and $K_\alpha/K_\beta$ ratios in the same experiment. The K x-ray fluorescence yield and $K_\alpha/K_\beta$ ratios of Ni have been measured.

Magnier et al. (1978) have carried out the precise measurement of K x-ray emission rate and K-shell fluorescence yield of copper using electron capture decay of $^{54}$Mn. They have employed two methods to measure the K x-ray emission rate; by means of pressurized $4\pi$-proportional counter with gas at 1.5 Mpa and by means of medium geometry-defined solid angle counter.

High precision measurements of K-Auger electron emission rate and K x-ray emission rate of several transuranium elements have been carried out by Ahmed (1979) to determine the K-shell fluorescence yields of Np, Pu, Cm, Bk, Cf and Es. The electron spectra are measured with a cooled Si(Li) spectrometer and the photon spectra are taken with Ge(Li) spectrometer.

Takiue et al. (1980) have obtained the fluorescence yields of Ag and In by measuring K Auger electron emission rates following electron capture decays of $^{109}$Cd and $^{113}$Sn. The K-Auger electrons are measured
by mixing these radionuclides with small amount of liquid scintillator, thus, allowing the K-Auger electrons to be effectively detected with a 100% efficiency while the interfering x-rays escape without detection.

Arora et al. (1981) have measured the K-shell fluorescence yields of elements in the atomic range $28 \leq Z \leq 53$ by using 59.6 keV gamma rays from $^{241}$Am of strength 100 mCi and adopting the reflection geometry.

Bhan et al. (1981) have calculated the K x-ray fluorescence cross sections for elements with $11 \leq Z \leq 69$ at three excitation energies corresponding to Mn, Ag, and Te K x-rays from $^{55}$Fe, $^{109}$Cd and $^{125}$I respectively and at 59.6 keV gamma rays from $^{241}$Am source. Measurements for ten elements in the atomic range $18 \leq Z \leq 48$ at two excitation energies from $^{109}$Cd and $^{125}$I annular radioisotopes have also been made using a Si(Li) detector spectrometer in single reflection geometry. The agreement between the measured values and the theoretical predictions is shown to be good.

The K-shell fluorescence yields of Al, Ca, V and Mn have been measured by Kuhn et al. (1981), bombarding thin solid targets of 0.5 to 4 $\mu g/cm^2$ on 6 to 10 $\mu g/cm^2$ carbon backing with relativistic electrons of 30 and 60 MeV and by simultaneous detection of the x-ray and Auger electrons by means of Si(Li) detector and an electrostatic electron spectrometer respectively.

Singh et al. (1983, 1984) have measured the K-shell fluorescence yield of Cs and As from the analysis of sum peaks observed with a high-resolution intrinsic Ge detector.

Casnati et al. (1984) have measures the K-shell fluorescence yield
of monocrystalline Germanium. The procedure involves the use of the information contained in the escape peaks, which are present in the x-ray spectra of HPGe detector. A 500 mCi $^{241}$Am source was employed in this measurement. Details of the experimental methodology, peak area evaluation and uncertainty treatments are described neatly.

Garg et al. (1985) have measured the $K_{\alpha}$ and $K_{\beta}$ x-ray fluorescence cross sections for some elements in the atomic range $20 \leq Z \leq 56$ at different excitation energies using Si(Li) detector spectrometer. Energy dependence of $K_{\alpha}$ and $K_{\beta}$ x-ray fluorescence cross sections has been shown.

Kodre et al. (1986) have made an attempt to measure the relative intensities of resonant Raman scattering and the corresponding Auger process. A multiwire proportional counter is employed to distinguish the two processes. The experiment leads to the improved method of determining the fluorescence yield. By this method, the fluorescence yield of Krypton is measured.

Al-Nasr et al. (1987) have measured the x-ray fluorescence cross-sections and yields of K-shell for the elements in the range $42 \leq Z \leq 57$ at an excitation energy of 59.54 keV from $^{241}$Am radioisotope of 20 mCi strength using a planar Ge solid-state detector of 100 mm$^2$ active area and a resolution of 179 eV at 5.895 keV. The detector is coupled to a Canberra S-80 Multi-channel analyzer interfaced with an on line microcomputer.

Brunner (1987) has measured the K-shell fluorescence yields of Si and Ge by recording the ratio of escape peak to main peak. The results are compared with Bambynek et al. and Krause tables.
The x-ray fluorescence cross sections of K-shell for six elements in the atomic range $73 \leq Z \leq 82$, at the excitation energy 121.9 keV gamma rays from $^{57}$Co radionuclide, have been measured by Saleh et al. (1987) using a planar Ge detector.

Rani et al. (1988) have measured the x-ray fluorescence cross sections of K-shell for some low Z elements Na, Mg, Al, Si, S, Cl and K using photon excitation method.

Casnati et al. (1991) have carried out the measurements of K x-ray fluorescence cross sections of Mo, Cd and Sn stimulated by the 59.6 keV photons emitted by a $^{241}$Am source. They have used planar HPGe detector and adopted the reflection geometry arrangement in the measurements.

The K-shell fluorescence yields for five elements Fe, Cu, Zn, Ge and Mo have been measured by Pious et al. (1992) using reflection geometry and employing a xenon gas filled proportional counter spectrometer. The targets are photoexcited using 59.6 keV gamma rays from $^{241}$Am radioactive source of strength 300mCi. An effective graded shielding arrangement is used to minimize the background radiation and multiple scattering. They have used elemental foils of uniform thickness and purity better than 99.5% as targets. The fluorescence spectra are recorded in a 1K multichannel analyzer.

Sole et al. (1992, 1993 & 1994), in a series of papers, reported the measurements of $P_{K\alpha K}$ from the decays of $^{58}$Co and $^{65}$Zn, and obtained the $\omega_K$ values for Fe and Cu and using windowless Si(Li) detector the $\omega_K$ values of Ca and K.
Balakrishna et al. (1994) have measured K-shell fluorescence yields for 16 elements in the atomic range $29 \leq Z \leq 92$ using a low energy HPGe photon detector by employing a reflection geometry setup. The target atoms are excited using 59.6 keV and 279.2 keV gamma rays from $^{241}$Am and $^{203}$Hg radioactive sources of strengths 20 mCi and 40 mCi respectively.

Horakeri et al. (1997 & 1998) have carried out the measurements of K-shell fluorescence yields of elements in the atomic range $62 \leq Z \leq 83$ by adopting a $2\pi$-geometrical configuration and by employing NaI(Tl) detector spectrometer coupled to 1k ORTEC multichannel analyzer. The targets used are both in elemental and in compound form, and are excited by gamma rays from $^{57}$Co and $^{51}$Cr sources of strength of the order of $10^4$Bq. The results obtained by this method are in close agreement with the experimental values obtained by adopting single and double reflection geometries.

Durak et al. (1997 & 1998) have measured K-shell fluorescence yields for Ba, Ce, Nd, Dy, Er, Yb, and the selected elements from Cs to Pb using a Ge(Li) detector by employing the reflection geometry. They have used 122 keV gamma rays from $^{57}$Co radioactive source of strength 100 mCi to excite the characteristic x-rays from the targets.

The K x-ray fluorescence cross-sections and yields of K-shell for 12 elements from Zr to Yb have been measured by Durak (1998) using 122 keV photons from $^{57}$Co radioactive source of strength 100 mCi employing Ge(Li) detector spectrometer and adopting reflection geometry. The results are compared with theoretical predictions, experimental values and semiempirical fits available in the literature.
Durak et al. (1998) have measured the x-ray fluorescence cross sections of K-shell for some elements in the range $40 \leq Z \leq 70$ using a high resolution Ge(Li) detector and adopting reflection geometry. The targets were excited by 122 keV gamma rays from $^{57}$Co source of 100 mCi strength.

Budak et al. (1999) have measured the x-ray fluorescence cross sections of K-shell for elements in the atomic range $44 \leq Z \leq 68$ at an excitation energy of 59.6 keV gamma rays from $^{241}$Am radioisotope of strength 100 mCi with a Si(Li) detector. Comparison is made between experimental results and theoretically calculated values.

Durak et al. (2001) have performed the measurements of K-shell fluorescence cross section and fluorescence yields of 14 elements in the atomic range $25 \leq Z \leq 47$ using photoionization by 59.6 keV gamma rays from $^{241}$Am radioactive source of strength 100 mCi and employing Si(Li) detector spectrometer having a resolution of 188 eV at 5.9 keV. The results are compared with theoretical, semi-empirical and other experimental values.

Yashoda et al. (2002) have determined the K x-ray fluorescence cross sections and yields of K-shell for 10 elements in the atomic range $60 \leq Z \leq 82$ at excitation energy of 661.6 keV gamma rays from $^{137}$Cs radioisotope using a well type NaI(Tl) detector spectrometer.

The K x-ray fluorescence yields for the elements in the atomic range $33 \leq Z \leq 53$ have been measured by Şimşek et al. (2002) by adopting reflection geometry. The K x-rays excited by 59.5 keV gamma rays are measured with a Ge(Li) detector. The results are compared with
theoretical predictions, experimental values and semi-empirical fitted values available in the literature.

The K x-ray fluorescence cross sections and yields for the elements from Cd to Dy have been measured by Özdemir et al. (2002) using Si(Li) detector spectrometer. The K x-rays are excited by 59.54 keV gamma rays from $^{241}$Am source of 100 mCi strength. The results are compared with theoretical predictions, experimental values and semi-empirical fitted values available in the literature.
D. Statement of the research problem.

A brief survey of photon excited fluorescence (Allawadhi et al. 1993, Hubbell et al. 1994, Durak et al. 1998) experiments clearly indicates that x-ray fluorescence (XRF) parameters are measured by employing variety of methods involving variety of detectors. Complicated experimental arrangements such as double reflection and single reflection geometries armed with sophisticated equipments and with radioactive sources of strengths of the order of $10^9$ Bq. are used to measure x-ray fluorescence parameters accurately. In the mean time x-ray fluorescence phenomenon finds application in multivarious fields starting from atomic physics, industry, agriculture, forensic science, archeology, and so on. So it may be of assistance to this increasing application of XRF phenomenon if the measurements of XRF parameters in geometries other than existing types are made. In this direction a sandwich type of geometry where the target is sandwiched between the source and the detector may be the one type, which is of frequent use in diverse fields. So the measurement of XRF parameters in such geometry would provide an assistance to check whether it produces accurate results as those obtained in reflection geometries and if successful could be adopted in laboratories of different grades. Some work, in this direction, has already been done in our laboratory (Horakeri et al. 1997 & 1998). This showed that it is possible to produce the K shell fluorescence yields of high Z materials.

In the present investigation, we propose to study the method in detail, so that it can be developed as an alternate and as a novel method of measuring not just the K x-ray fluorescence yield but other parameters such as K x-ray production cross section, radiative widths etc., for after all, they are all connected parameters. Before we embark upon the
measurements we must be sure of the method's advantages and limitations.

The important points to be considered in the measurements of XRF parameters, we thought, are
i) the intensity of fluorescence x-rays should be high and be measured accurately,
ii) the interference of unwanted radiations into the region of interest should be kept minimum, if possible should be avoided,
iii) the number of correction factors should be made minimum,
iv) the intensity of incident photons must be measured accurately, for this the radiation that enters the target and produce the fluorescence x-rays.
v) the attenuation of fluorescence x-rays in the target should be as less as possible but at the same time the production of fluorescence x-rays must be maintained to a good level.

In fact, Bambynek et al. (1972) pointed out in their most listed review article that the production of fluorescence x-rays must be predominant over their attenuation in the target. This optimum thickness depends on the atomic number of the target. If the thickness of the target is too small, the attenuation x-rays becomes negligible but x-ray production gets reduced for a given source strength. If the source strength is increased to increase the production of x-rays, this would increase the dead time loss and also increases the interferences of unwanted radiations into the region of interest. On the other hand if the thickness is large the attenuation becomes almost same as the production or if it crosses the limit, it predominates over the production. Therefore the thickness of the target that satisfies the "Bambynek criteria" is to be determined.
In fact, a thorough analysis of these points and the fact that we have moderate equipments made us to opt for this sandwiched type geometry beam - $2\pi$ geometry method. The use of $2\pi$ - geometrical configuration has the following advantages:

4. The intensity of fluorescence x-rays emitted into a solid angle of $2\pi$ steradians is quite appreciable. Thus a good number of counts can be acquired in shorter intervals of time and good counting statistics can be maintained. The total duration of the time for acquiring all the necessary data may be just a few hours or so. Because of this, any effects due to change in the stability of the equipments, peak position, background intensity and so on are less probable.

5. From 1, it is clear that sources of low strengths and shorter half-lives can be employed. So there is no necessity of shielding the source or the detector. Personnel involved can handle the source at ease without the risk of exposing themselves to the radiations. Because there is no shielding, the question of extraneous fluorescence x-rays from the shield that could interfere into the region of interest will not arise.

6. If the method could be developed as a standard method of producing accurate XRF parameters, the same could be adopted by laboratories of any grade. This can easily be adopted as class room or as laboratory experiments to study the XRF phenomenon and other related topics (such as Bohr's frequency condition, Moseley law etc.).

Thus the method would help both research and the teaching fields.

In view of these, in the present investigations, we have extended the $2\pi$ - geometrical configuration to measure the K x-ray fluorescence
parameters - K x-ray fluorescence cross-section, $\sigma_K$, and K x-ray fluorescence yield, $\omega_K$ and the ratio of radiative width to radiationless width (Auger width) of K-shell, $\frac{\Gamma_K^r}{\Gamma_K^A}$ - of medium and high Z elements employing a weak $^{57}$Co radioactive source. We present the details of our investigation and its results and conclusion in the following chapters.

A few research papers related to this investigation are submitted for publication in the International Journals.
References.


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