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Full Length Research Paper

X-ray spectroscopic evaluation of zinc at different applied pressure

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***K* X-ray fluorescence cross-sections** of **zinc (Zn) in linear region and infinite mass thickness region are measured using Si(Li) detector at photon excitation energy of 59.5 keV. Besides, this study has investigated the effect of experimental fluorescence cross-sections on relation between two different mass thickness of the sample with different applied pressures. Harmony between linear and infinitive (critical) mass thickness region and applied pressure on sample has direct effect on experimental *K*α and *K*β X-ray peaks. Experimental results were compared with various theoretical values in literature.**

Key words: Sample prepare, pressure effect, X-ray fluorescence spectroscopy.

INTRODUCTION

Information regarding the experimental values of *K* X-ray fluorescence cross sections for different elements at various photoionization energies is important because of its wide use in atomic, molecular and radiation physics and in the non-destructive elemental analysis of materials using energy dispersive X-ray fluorescence system (Singh et al., 1990). Precise knowledge of photon cross sections is important because of their usefulness in various fields such as radiation protection, crystallography, medical diagnosis and electron probe micro-analysis. Numerous experiments have been carried out to measure the X-ray fluorescence crosssections at various energies in different elements (Durak et al., 1998; Pious et al., 1992; Tang et al., 1999). But there is rare experiments related with hydraulic pressure effect on mass thickness at X-ray fluorescence spectroscopy studies. Earlier on, İçelli and Erzeneoğlu (2002) measured the intensity ratio $K\beta/K\alpha$ as a function of hydraulic pressure on mass thickness of powder sample used for compressing the pallets. It is known that X-ray fluorescence intensity is proportional with both mass absorption coefficients and mass thickness. In this state, it is expected that *K* Xray fluorescence intensity is connected with mass thickness because mass absorption coefficients is constant for a given X-ray photon energy, that is, hydraulic pressure on powder sample may change mass thickness. There are a few studies to strengthing our findings. For instance; Zagorodniy (2003) have experimentally studied physical-mechanical characteristics of powder irradiators on the fluorescence intensity of elemental analytical lines. Zagorodniy (2003) has utilized constant pressure for pelletized sample at present experiment. As a result, the parameters (particle size, powder bulk density, packing density and applied pressure on sample) were found having great effect on the fluorescence intensity of powder materials. Separately, Zagorodniy (2003) have researched effect of surface roughness of powder sample (μm) at different pressures (kN) and have showed that with increase in pressure and decrease in particle-size, the value of roughness decreases from 5-6 μm (at 5 kN and particle size 100 μm) to 1 to 2 μm. Mzyk et al. (2002) have researched on grain size effect in X-ray fluorescence analysis of pelletized samples.

In this study, the dry materials have been pelletized under a constant pressure of 200 kN cm^2 (Mzyk et al., 2002). Abdel-Rahman et al. (2000) have investigated the effect of the sample thickness on measured values of the mass attenuation coefficients of Perspex, bakelite, paraffin, Al, Cu, Pb and Hg at different energies. So, range linear-infinitive (critical) of absorber thickness or thickness effect on measured values of the $K\alpha$ and $K\beta$ X-ray peak intensity has been expected. In addition to these studies, our reference study is Togel (1961). Variation according to different pressure and particle size of Zn $K\alpha$ intensity (k counts/min) have been studied by Togel (1961) for both different pressures at range 0 to 20 (ton/$inch^2$) and different particle size at range

30 to 300 μm. In his study, Togel (1961) concluded that for a given briqueting pressure, the smaller the particle size, the higher is analyte-line intensity. For a given particle size, the higher the briqueting pressure, the higher is the analyte-line intensity. The use of a binder or diluents accentuates the decreased intensity with increased particle size, and reduces the effects of pressure in overcoming this decrease.

This study is important in view of what to appeal if pressure effect is affected on palletizing sample in X-ray fluorescence spectroscopy studies.

This paper also investigates the effects on measurement of *K* X-ray fluorescence cross sections at different mass thickness (K-X-ray fluorescence cross-section do not depend on mass thickness at all, directly) in which linear and infinite mass thickness region preferentially choose and applied different pressures on sample. There are direct effects on the experimental results of the different applied pressures on the sample.

As follows, variations in packing density may cause variations in analyte-line intensity unless an internal standard is used, or unless the same weight of each specimen in the analysis is briqueted at same pressure (Eugene, 1985). For any given series of samples and standards, uniform packing density is achieved by compacting the same weight of powder at the same pressure for each specimen (Eugene, 1985), so, packing density is affected from different pressures. Besides, the most serious difficulties with powders arise from particle size effect. The spectral-line intensity of a specified element in a powder depends on the particle size (Eugene, 1985).

Prior to being packed into cells or briqueted, the powder should be grounded to 400-mesh. In order to decrease particle size effect, powder samples of Zn in our present study have been sieved (400-mesh) describing the number of holes per inch squares. Generally, particle-size effects substantially disappear at 400-mesh, but this standardization may be demolished for the different applied pressures on sample. If the particle size affects the analyte-line intensity, then all samples must have the same average particle size. But particle-size effects are minimized to one or more methods having briqueting at high pressure (Eugene, 1985).

From this point of view, particle size may be affected by the different applied pressure on sample. That is to say, particle-size is not same for each pressure. Particle-size effect is expected to affect from effective mass thickness, especially, linear and infinitive (critical) mass thickness. This study wants to constitute a curve from spectral line intensity measured from sample as a function of mass thickness at each pressure and determine linear and infinite region with the help of this curve. The curve has three regions. For thin samples, attenuation of incident primary and emergent secondary spectral-line radiation is small. The curve is linear, and intensity is simply proportional to thickness. For samples of intermediate thickness, attenuation of both primary and secondary X-rays increases with depth. The longer-wavelength components of the primary beam are absorbed preferentially, so that as the beam penetrates progressively deeper, it becomes both weaker and of shorter effective wavelength. The emergent secondary spectral X-rays continue to increase in intensity with thickness, but at a decreasing rate. At infinitive (critical) thickness, secondary X-rays are excited at depths from which they cannot emerge to the surface. Further increase in thickness results in no further increase in intensity. In powders consisting of more than one element, the absorption coefficient of the film is different for the spectral line of each element. Thus, infinitive (critical) thickness is different for each spectral line. To determine linear and infinite (critical) mass thickness, the researchers have choosen range 0.057-0.184 g/cm^2 for Zn samples having 12 different thicknesses. From this curve, linear and infinitive (critical) thickness 0.099 and 0184 g/cm^2, respectively were determined.

MATERIALS AND METHODS

The experimental arrangement and geometry used in the present measurements are shown in Figure 1. It consists of a 3.7 × 109 Bq (100 mCi) 241 Am annular source, which essentially emits monoenergtical (59.5 keV)_ rays. The intensities of fluorescent X-rays were measured using collimated Si(Li) detector (FWHM of 160 eV at 5.96 keV) with an active area of 12.5 mm^2, sensitive crystal depth of 3 mm, and Be window of 0.0255 mm thickness coupled to a 1024 multichannel analyzer in which the data were collected. The spectra from Zn were collected for a period of 1800 s. In order to decrease particle size effect spectroscopically, pure powder targets of Zn (99.9%) have been sieved (400-mesh) describing the number of holes per inch squares. The mass thickness of these powders being 0.099 and 0.184 g/cm^2 have been determined by gravimetric method, that is samples not yet subjected to the press (powdered form). Each of these samples is studied as a function of the applied pressure on sample in the range from 4.06×105 to 28.5×105 MPa via the measurement of Zn *K* α or Zn *K* β line intensity. The powder samples of Zn were mixed for 15 min and compressed into pellets for 10 s at ranging from 4.06×105 to 28.5×105 MPa pressure using a manual hydraulic press. During the intensity measurements, the pellets were removed from the press, and the applied pressure was zero. Targets had an area of 707 mm^2. The target-source distance was set to 13 mm, which was determined by measuring *K* X-ray intensities at different distances. A typical *K* X-ray spectrum of Zn is shown in Figure 2. The weighted averages of *K* α or *K* β energies of Zn are 8.631 keV and 9.572 keV, respectively.

Data analysis

Theoretical method

We know that pressure, mass thickness, packing density and particle size, etc. arising from experimental apparatus have not been taking into consideration at theoretical calculations. But we have calculated theoretical values to various authors as seen in Table 2 in order to compare with experimental values.

The theoretical *K* X-ray fluorescence cross-sections have been calculated using the following equations:

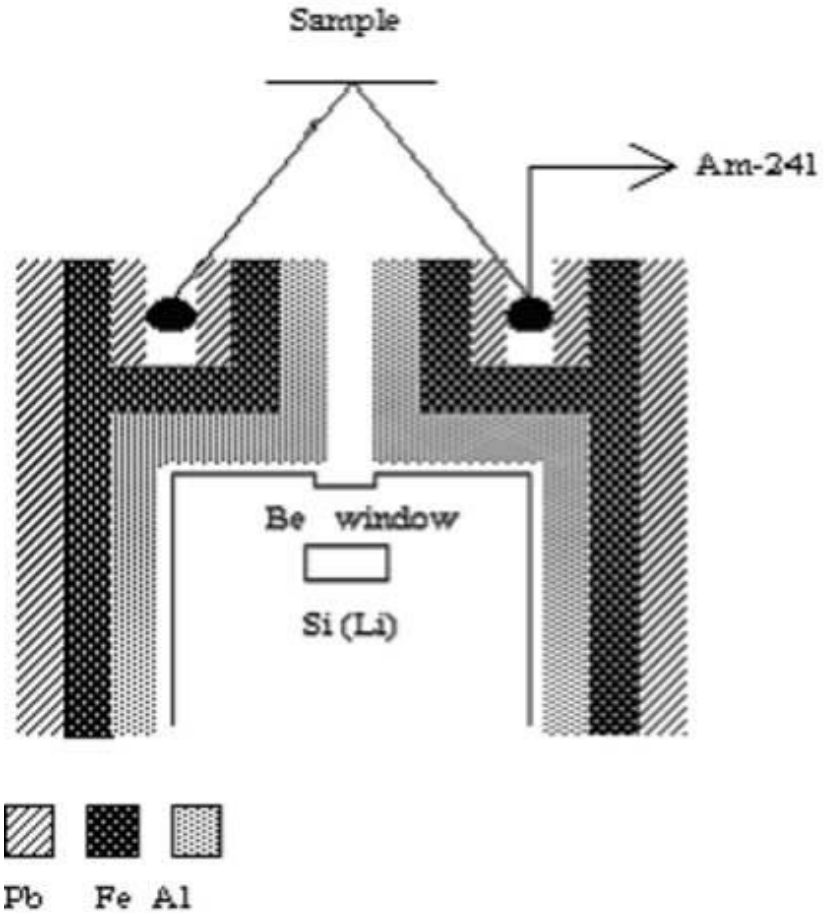

Figure 1. Schematic diagram of the experimental arrangement.

$$\sigma_{K\alpha} = \sigma_K(E)\omega_K F_{K\alpha}$$
$$\sigma_{K_\beta} = \sigma_K(E)\omega_K F_{K_\beta} \quad (1)$$

where $\sigma_K(E)$, K -shell photoionization cross-section for the given element at excitation energy (E); ω_K, K -shell fluorescence yield; $F_{K\alpha}$ and $F_{K\beta}$, fractional X-ray emission rates for K α; K β X-rays are defined as:

$$F_{K\alpha} = (1+\frac{I_{K_\beta}}{I_{K_\alpha}})^{-1} \qquad F_{K\beta} = (1+\frac{I_{K_\alpha}}{I_{K_\beta}})^{-1} \quad (2)$$

where $I_{K\beta}$ / $I_{K\alpha}$, K β to K α X-ray intensity ratio.

In the present calculations, the value of σ_K (E) was taken from Scofield (1973) based on Hartree-Slater potential theory and the values of ω_K were taken from Tables of Krause (1979) and Walters and Bhalla (1971). The values of $I_{K\beta}$ / $I_{K\alpha}$ intensity ratios were taken from Scofield (1974a), Scofield (1974b), Marques et al. (2001) and Kotzé and Mingay (1988).

Experimental method

The experimental K X-ray fluorescence cross-sections of Zn for the different pressures and the two samples (of different starting mass thicknesses) have been measured using the equation:

$$\sigma_{Ki} = \frac{N_{Ki}}{I_0 G \varepsilon_{Ki} T_{Ki} m} \qquad (i = \alpha, \beta) \quad (3)$$

where N_{Ki}, number of counts per unit time under K_i X-ray peak of the given element; I_0, intensity of exciting radiation; G, geometrical factors; ε_{Ki}, efficiency of the detector for the characteristic X-rays; m, mass thickness in g/cm^2 of the sample for linear and infinitive section; T_{Ki} is the target self-absorption correction factor for both the incident and emitted radiations.

I_0 $G\varepsilon_{Ki}$ values in present experimental set-up were determined in a separate experiment by collecting the K_α X-ray cross sections from standard samples of Ti, Mn, Co and Cu as emitting fluorescence X-rays in the energy range 4.5-11.7 keV irradiated in the same geometry and emitted fluorescence X-rays were counted. $I_0 G\varepsilon_{Ki}$ value for the present set-up was determined by following the relationship:

$$I_0 G \varepsilon_{Ki} = \frac{N_{Ki}}{\sigma_{Ki} T_{Ki} m}, \quad (4)$$

where N_{Ki} is the net number of counts under the corresponding photo peak. Theoretical σ_{Ki} values were calculated using Equation 1.

The self-absorption correction factor T_{Ki} have been calculated for both $K\alpha$ and $K\beta$ separately by using the following expression (Garg et al.,1992):

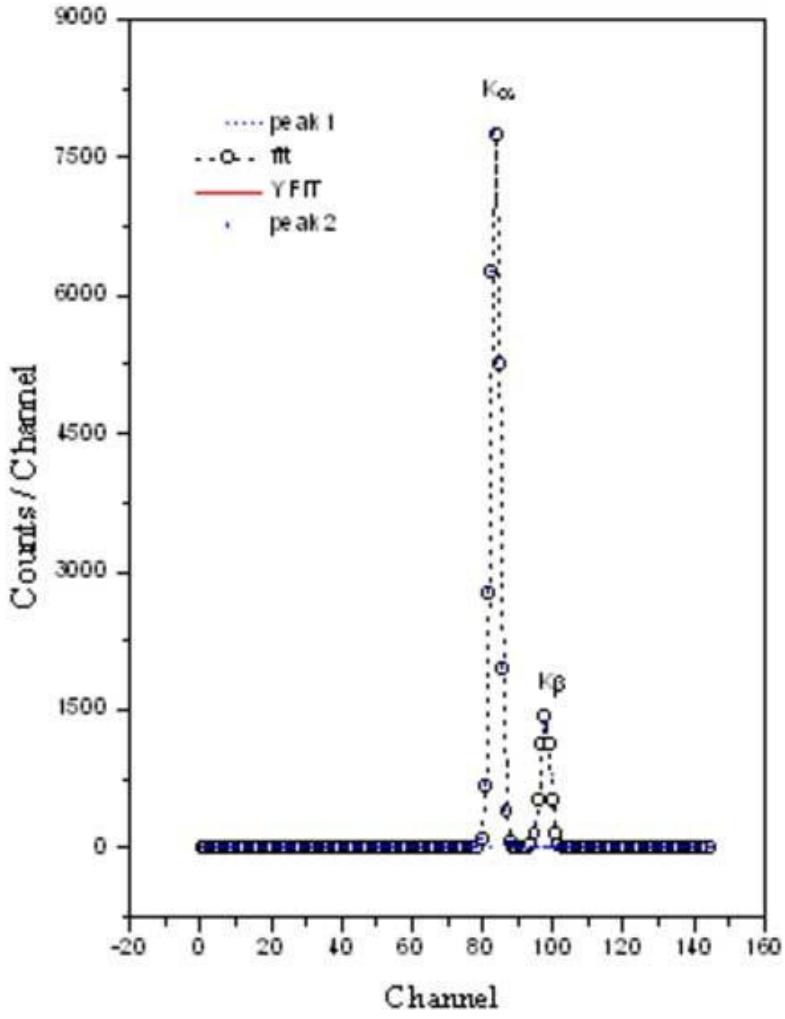

Figure 2. Representative spectrum of K X-rays of Zn excited 59.5 keV γ-rays from Am^{241} at 28.5×10^5 MPa pressure.

$$T_{Ki} = \frac{1-\exp[-(\mu_{inc}\csc\theta_1 + \mu_{emt}\csc\theta_2)m]}{(\mu_{inc}\csc\theta_1 + \mu_{emt}\csc\theta_2)m} \quad (5)$$

where μ_{inc} (cm^2 g^{-1}) and μ_{emt} (cm^2 g^{-1}), sample mass attenuation coefficients which are quoted by Hubbell and Seltzer (1995) whose tables have been softwared by Gerward et al. (2001) for the incident (59.5 keV) and emitted energies (*K* X-ray energies of Zn), respectively; θ_1, angle between the incident X-ray and the sample surface; θ_2 takes off angle (in all the cases we have $\theta_2 = 90^o$). Here θ_1, has been calculated as 69° by using the expression of Zararsız and Aygün (1989).

RESULTS AND DISCUSSION

The experimental results are listed in Table 1. Subsequently, according to various authors, theoretical calculations are listed in Table 2. In examining Table 1, the present experimental $\sigma_{K\alpha}$ X-ray fluorescence cross-sections in linear region (t=0.099 g/cm^2) are more in agreement with theoretical values than values in infinite (critical) region. But, $\sigma_{K\beta}$ X-ray fluorescence cross-sections in infinitive region (t=0.184 g/cm^2) are more in agreement with theoretical than values in linear region. This state may be attributed that counting statistics of the data under $K\beta$ peaks is poorer than $K\alpha$ peaks. Table 1 can be evaluated as an important result that *K* X-ray fluorescence cross-sections decreased with increase in the different pressures applied on the sample for two mass thickness values. As mentioned in introduction section, It is known that X-ray fluorescence intensity is proportional with both mass absorption coefficients and mass thickness.

In this state, It is expected that *K* X-ray fluorescence intensity is connected with mass thickness because mass absorption coefficients is constant for given X-ray photon energy. That is, hydraulic pressure on powder sample may change mass thickness and is an associate point

Table 1. Experimental $K\alpha$ and $K\beta$ X-ray fluorescence cross-sections (barns).

Pressure (MPa $10^{5)}$	$^{\sigma}K\alpha$		$^{\sigma}K\beta$	
	T=0.09 [g/cm^2]	T=0.184 (g/cm^2)	T=0.099 (g/cm^2)	T=0.184 (g/cm^2)
4.06	56.7±2.9	49.6±2.4	10.4±0.55	9.31±0.49
8.13	54.6±2.8	49.2±2.4	9.92±0.53	9.12±0.47
12.2	54.3±2.8	48.9±2.4	9.85±0.52	9.00±0.47
16.3	54.1±2.7	48.2±2.3	9.65±0.51	8.89±0.46
20.3	53.6±2.7	47.6±2.1	9.44±0.49	8.77±0.45
24.4	53.3±2.7	46.7±2.1	9.39±0.49	8.58±0.44
28.5	52.3±2.6	46.3±2.0	9.17±0.47	8.54±0.43

Table 2. Theoretical $K\alpha$ and $K\beta$ X-ray fluorescence cross-sections (barns).

$\sigma K\alpha$	63.4[a]	62.4[b]	62.7[c]	62.6[d]	67.0[e]	66.0[f]	66.3[g]	66.3[h]
$\sigma K\beta$	7.874[a]	8.81[b]	8.56[c]	8.59[d]	8.32[e]	9.32[f]	9.00[g]	9.091[h]

a, values calculated using krausel (1979) for ωk, scofield (1974a) for $FK\ \alpha, \beta$; B, values calculated using krause (1979) for ωk scofield (1974b) for $FK\ \alpha, \beta$; c, values calculated using krause (1979) for ωk, Kotzé (1988) for $FK\ \alpha, \beta$; *d,* values calculated using krause (1979) for ωk, Marques (2001) for $FK\ \alpha,\beta$; e,values calculated using walters (1971) for ωk, scofield (1974a) for $FK\ \alpha,\beta$; *f,* values calculated using walters (1971) for ωk, scofield (1974b) for $FK\ \alpha,\beta$; *g,* values calculated using krause (1979) for ωk, Kotzé (1988) for $FK\ \alpha,\beta$; *h,* values calculated using walters (1971) for ωk, Marques (2001) for $FK\ \alpha,\beta$.

that *K* X-ray fluorescence cross-sections decreased with increasing pressure and increasing mass thickness. It is interpreted that applying manual hydraulic press changes mass thickness as seen in Table 1. Dependence to pressure may be interpreted as decrease of mass thickness with applying pressure. For a given briqueting pressure, the smaller the mass thickness, the higher is the spectral –line intensity. For a given mass thickness, the higher the briqueting pressure, the smaller the spectral-line intensity. Also, it is known that chemical state can slightly influence the intensity of both $K\alpha$ and $K\beta$ X-ray peaks. In the case of Zn powder pressed into tablet, one can expect such chemical effect because of surface oxidation of Zn powder grains. Oxidation effects probably increase with pressure by oxidation reaction with air in pores.

The errors in the evaluation of the area under the $K\alpha$ X-ray peaks 2% and that for the $K\beta$ X-ray peaks is 4%, in the determination of the mass thickness of sample is 1.24%, in the counting statistics is 1.06% and in the efficiency is 4.3%.

Conclusion

From the findings of this study, it can be concluded that there are important factors to be taken into account in X-ray fluorescence spectroscopy studies; two different mass thickness of the sample and different pressures applied on the sample. *K* X-ray fluorescence cross-sections have been affected from change of effective mass density of samples. Besides, *K* X-ray fluorescence cross-sections have been influenced from granularity at different pressure applied on sample for the same mass thickness. Present study concludes that applied pressure factor on sample must be taken into consideration to obtain sensitive values in X-ray fluorescence spectroscopy studies. The effect employed in our present work is confirmed to that described by previous authors (İçelli and Erzeneoğlu, 2002; Zagorodniy, 2003; Togel, 1961). In X-ray fluorescence spectroscopy studies, sample composition has been affected from different pressures applied on sample expected to have effect on sample composition of mass density. Mass density for particularly different mass thickness might influence the fluorescence events. Probably the effect shown with experimental measurement is due to the consequent increase of effective mass density of the sample and effect of granularity on the fluorescence through-put. The suspect is that two quantities; mass density and self absorption (Equation 3) are insufficiently under control under the pressure conditions. But to constant mass density and self-absorption in different pressures on sample is not possible under experiment. So, pressure effect may be added as correction multiple to Equation 3.

As a result, it is predicted that apart from serving as a pressure indicator, pressure-induced changes in the powder samples may have other important applications in quantitative and qualitative analysis of sample, mineral exploration, geological dating, etc. Further experimental

studies on applied pressure effect on sample will be useful to confirm, understand and interpret the observed differences between the measured and calculated cross sections for different elements, in various mass thicknesses and different meshes describing the number of holes per inch squares. As a result, the results and compression discussed are current for only Zn.

Also in future, thinking and planing measurement using a wavelength dispersive X-ray fluorescence spectroscopy for different elements will be necessary so that further information could be received on the effects of pressure for high-resolution experiments.

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