Calculation of K Shell Intensity Ratios and Line Widths of Ti and some of its compounds by means of 5.96 keV energy

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Abstract. K shell intensity ratios and Line Widths of pure Ti and some of its compounds have been determined experimentally using an Ultra-LEGe detector with resolution 140 eV at 5.9 keV. The samples were excited 5.96 keV photons emitted from a 55Fe radioisotope source with 50 mCi activity. The experimental values of the K shell intensity ratios have been compared with the experimental and theoretical values available in the literature for pure Ti and line widths have been only compared with a theoretical value for pure Ti.

1. Introduction
Information experimental result regarding the K X-ray intensity ratios for different elements is important because of its extensive use in atomic, molecular and nuclear physics, properties of superconductor, semiconductor thin films, etc., and non-destructive analysis of materials using energy dispersive X-ray fluorescence (ED-XRF) techniques [1].

It is well known that X-ray emission spectra are influenced by the chemical combination of X-ray emitting atoms with different ligands. The effects of the chemical structure are not large and a theoretical interpretation of these effects has not been established completely. Therefore, chemical effects have rarely been utilized in the characterization of materials. Furthermore; the process of particle size effects, vacancy production, data analysis procedures to acquire the areas under peaks, detector efficiency, and self-absorption in the specimen have to be well controlled. On the contrary, the measured X-ray fluorescence parameters can be erratic because of the effect of these conditions [2].

A number of researchers [1, 3-10] have worked on K-shell intensity ratios for various elements, compounds and alloys with different detector types and radioactive sources but not K line widths. So this paper is aimed to determine the K Shell X-ray intensity ratios of Ti and some of compounds and K line widths. And this work is to interpret the measured results according to the chemical environment.

2. Experimental procedure
The geometry of the experimental set-up and the present experimental equipment have been described in previous study [10]. The purity of commercially obtained materials is better than 99%. Powder samples were got by purchasing from Sigma-Aldrich and Alfa Aesar company. In this experimental set-up, 5.9 keV X-ray photons emitted by an annular 50 mCi 55Fe radioactive sources were used to excite the samples. The fluorescence K X-rays from the sample were detected by a collimated Ultra-LEGe detector having an energy resolution of 140 eV at 5.96 keV. In the experimental determinations, spectral deconvolution is one of the main problems that arise when determining these parameters due to the strong peak overlapping in ED-XRF system. In the present work, a peak fitting program developed by Origin Company (Origin 7.0) was used to determine peak analysis. In the present study, Fig. 1 shows the typical K X-ray spectrum for Titanium. The experimental K, X-ray production cross-sections were acquired by the following relation:

$$\sigma_{Xi} = \frac{N_{Xi}}{I_0 G \varepsilon_{Xi}[\beta Xi]^m} [i = \alpha, \beta]$$

(1)
where \( N_{\text{xi}} \) is the measured intensity (area under the photo peak) corresponding to the \( K_i \) group of X-rays, \( I_0 \) is the intensity of the incident radiation, \( G \) is the geometric factor, \( \varepsilon_{\text{xi}} \) the detection efficiency for the \( K_i \) group of X-rays and \( \beta_{\text{xi}} \) the self-absorption correction factor for the target material, which accounts for the absorption in the target of the incident photons and the emitted characteristic X-rays.

\( m_i \) is the thickness of the target in \( \text{g/cm}^2 \).

The self-absorption correction was calculated using the equation [11]

\[
\beta = \frac{1 - \exp \left( - \frac{\mu_{\text{inc}}}{\cos \theta_1} \left( \frac{\mu_{\text{emt}}}{\cos \theta_2} \right) t \right)}{\left( \frac{\mu_{\text{inc}}}{\cos \theta_1} + \frac{\mu_{\text{emt}}}{\cos \theta_2} \right) t} \tag{2}
\]

where \( \mu_{\text{inc}} \) and \( \mu_{\text{emt}} \) are the mass attenuation coefficients [12] of incident photons and emitted characteristic X-rays, respectively; \( t \) is the thickness of the target in g cm\(^{-2}\); the angles of the incident photons and the emitted X-rays with respect to the normal of surface, \( \theta_1 \) and \( \theta_2 \), were equal to 45° and 0° in the present experimental set-up, respectively.

The product \( I_0G\varepsilon_{K_i} \), containing the terms related to the incident photon flux, geometrical factor and intrinsic absolute efficiency of the X-ray detector, was determined by collecting the \( K_\alpha \) and \( K_\beta \) X-ray spectra of samples of S, Cl, K, Ca and Ti for \(^{55}\text{Fe}\) in the same geometry using the equation

\[
I_0G\varepsilon_{K_i} = \frac{N_{K_i}}{\sigma_{K_i}\beta_{K_i}m} [i = \alpha, \beta] \tag{3}
\]

where \( N_{K_i} \) is the measured intensity (area under the photo peak) corresponding to the \( K_i \) group of X-rays, \( I_0 \) is the intensity of the incident radiation, \( G \) is the geometric factor, \( \varepsilon_{K_i} \) is the detection efficiency for the \( K_i \) group of X-rays and \( \beta_{K_i} \) is the self-absorption correction factor for the target material, which accounts for the absorption in the target of the incident photons and the emitted characteristic X-rays. \( m \) is the thickness of the target in g/cm\(^2\).

The factor \( I_0G\varepsilon_{K_i} \) was fitted as a function of energy using the following equation for \(^{55}\text{Fe}\):

\[
I_0G\varepsilon_{K_i} = A_0 + A_1E_x + A_2E_x^2 + A_3E_x^3 \tag{4}
\]
where $E_x$ is the X-ray energy and, $A_0 A_1, A_2$ and $A_3$ are constants evaluated from a fitting polynomial. The variations of the factors $I_0 G\varepsilon$ as a function of energy are shown in Fig. 2.

![Figure 2](image.png)

**Figure 2.** The variation in the factor $I_0 G\varepsilon$ as a function of the mean K X-ray energy for $^{55}$Fe radioisotope

The theoretical K X-ray production cross sections were evaluated by using the relation:

$$\sigma_{KI} = \sigma_K(E) \omega_K F_{KI}$$  \hspace{1cm} (5)

where $\sigma_K(E)$ is the K–shell photoionization cross-section of the given element for the excitation energy $E$ [13], $\omega_K$ is the K-shell fluorescence yield [14], and $F_{KI}$ is the emission rate of the fractional X-ray for K, X-rays [15].

The semi-empirical K shell fluorescence yields $\omega_K$ were measured according to the following equation:

$$\omega_K = \frac{\sum \sigma_{KI}}{\sigma_K(E)} (i = \alpha, \beta)$$  \hspace{1cm} (6)

where $\sum \sigma_{KI}$ is the total K X-ray fluorescence cross-section obtained experimentally, $\sigma_K(E)$ is the theoretical K shell photoionization cross-section of a given element for the excitation energy $E$ [13].

K shell line widths were calculated by dividing the fluorescence yield of the radiative transition rate [16] as using the formula shown below;

$$\Gamma_K = \frac{\Gamma_K(R)}{\omega_K}$$  \hspace{1cm} (7)

Where $\Gamma_K$ is the K shell line width and $\omega_K$ is K shell fluorescence yield.

Intensity ratios of K shell were determined as ratio of cross-sections of $K_\beta$ and $K_\alpha$ with using the equation illustrated below;

$$K_\beta/K_\alpha = \frac{\sigma_{K_\beta}}{\sigma_{K_\alpha}}$$  \hspace{1cm} (8)

Where $K_\beta/K_\alpha$ is K shell intensity ratio; $\sigma_{K_\alpha}$ and $\sigma_{K_\beta}$ are cross-sections belong with K shell.

3. Results and Discussion

Experimental $K_\beta/K_\alpha$ x-ray intensity ratios values for Ti and its compounds, measured for incident photon energies 5.95 keV, are presented in Table 1. Experiential K X-ray intensity ratio values have been compared with theoretical estimates based on relativistic Hartree–Fock and Hartree–Slater
theories calculated by [16,17], [18] and the other experimental values. The obtained $K_\beta/K_\alpha$ intensity ratios values are more compatible with relativistic Hartree-Fock theory’s values rather than the other one.

**Table 1. Intensity Ratios for Titanium and its compounds**

| Element     | Kβ/Kα  | Experimental | Theoretical |
|-------------|--------|--------------|-------------|
|             |        | Measured [19] [10] | [17] [16] [18] |
| Ti Powder   | 0,1049±0,0063 | 0,134 0,1282 | 0,1355 0,1137 0,1136 |
| TiCl₃       | 0,1139±0,0068 | *** *** | *** *** *** |
| TiO         | 0,1047±0,0063 | *** *** | *** *** *** |
| Ti₂O₃       | 0,1141±0,0069 | *** *** | *** *** *** |
| TiS₂        | 0,1039±0,0062 | *** *** | *** *** *** |

The values are in the agreement between present results and theoretical predictions are within the range 15-24%, 0-9%, and 0-9% respectively. According to [19] and [10], the results of present study is different between 14-23% and 11-19%, respectively. Experimental K shell line width values for Ti and its compounds, measured for incident photon energies 5,95 keV, are presented in Table 2.

**Table 2. Line Widths for Titanium and its compounds**

| Samples     | Kα Line Widths | Theoretical [14] |
|-------------|----------------|------------------|
| Ti Powder   | 0,78±0,05      | 0,94             |
| TiO         | 0,77±0,05      | ---              |
| TiCl₃       | 0,87±0,05      | ***              |
| Ti₂O₃       | 0,86±0,05      | ***              |
| TiS₂        | 0,77±0,05      | ***              |

The uncertainties in the K X-ray intensity ratios are estimated to be less than 6% and are found propagating the errors in various parameters used for the determination of the intensity ratios. The uncertainties in the parameters are listed in **Table 3**.

**Table 3. Uncertainties in the quantities used to determine the parameters**

| Quality     | Nature of uncertainty                      | Uncertainty (%) |
|-------------|-------------------------------------------|-----------------|
| N(Kᵣ) (i=α, β) | Counting statistic                        | ≤3              |
| I₀GeKᵣ     | Errors in different parameters used to evaluate factor | ≤2              |
| β           | Error in the absorption coefficients correction at incident and emitted photon energies | ≤3              |
| t           | Errors in the weight and thickness of the samples | ≤2              |

In this study, $K_\beta/K_\alpha$ intensity ratios and K line widths for Ti compounds were experimentally investigated and the conclusions are summarized in four points. First, $K_\beta/K_\alpha$ intensity ratios and K line widths vary with the change of the oxidation numbers. Second, it is known that different interatomic distances (lattice parameters) cause different interactions between the central atom and the ligand groups and these interactions can change the $K_\beta/K_\alpha$ intensity ratios K shell line widths. Third, K shell vacancies are filled by outer shell electrons and these electrons feel the effect of ligand atoms more strongly than the inner shell electrons. Fourth, the ligands bound to the central Ti atom have different electronegativity values and these differences can
change \( K_β/K_α \) intensity ratios and K shell line widths. To acquire more absolute results about chemical effects on the cross sections and intensity ratios, it is planned to extend these measurements to various elements and compounds [20].

In this work, in order to reduce the absorption, thin samples were used as the target; furthermore, an absorption correction was also performed for each sample. In order to reduce the statistical error, the spectra were collected under the \( K_α \) and \( K_β \) peaks. In the experimental determinations, spectral deconvolution is one of the main problems that arise when determining these parameters due to the strong peak overlapping in ED-XRF system. Good statistics is not enough for this purpose and a careful fitting methodology is required in order to obtain accurate values for the peak areas. Conventional fitting programs have not shown good performance, but the method of parameter optimization previously developed for X-ray fluorescence analysis. In the present work, a new peak fitting program developed by Origin Company (Origin 7.0) program was used to determine the accurate peak intensity.

The experimental values of K X-ray intensity ratios for titanium element and compounds have important role in the material, chemical sciences and industrial area.

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