Cumhuriyet Science Journal
CSJ

e-ISSN: 2587-246X
ISSN: 2587-2680

Cumhuriyet Sci. J., Vol.40-1(2019) 117-124

Investigation on L_i ($i = l$, β, and γ)–to-L_α X-ray Intensity Ratios of Tl in Thallium Compounds

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Received: 19.12.2018; Accepted: 10.01.2019

http://dx.doi.org/10.17776/csj.499424

Abstract. The L_i ($i = l$, β, and γ)–to-L_α X-ray intensity ratios of Tl in some thallium compounds were measured by EDXRF spectrometer. These compounds were excited by 59.5 keV gamma-rays from a ^{241}Am annular radioactive source. L X-rays emitted by the compounds were counted using an Ultra-LEGe detector with a resolution of 150 eV at 5.9 keV. L_i–to-L_α X-ray intensity ratios of Tl in these compounds are compared with that of the pure Tl calculated theoretically. While the values of L_l/L_α and L_γ/L_α intensity ratios are compatible with the theoretically calculated value, the values of L_β/L_α intensity ratios have differences.

Keywords: Thallium, intensity ratio, EDXRF, chemical effect, multiple ionization effect.

Talyum Bileşiklerindeki Tl L_i/L_α ($i = l$, β ve γ) X-ışını Şiddet Oranlarının Araştırılması

Özet. Bazı talyum bileşiklerindeki talyumun L_i/L_α ($i = l$, β and γ) X-ışını şiddet oranları EDXRF spektrometresi yardımıyla ölçüldü. Bu bileşikler ^{241}Am halka radyoaktif kaynağından yayımlanan 59.5 keV enerjili gama ışınları ile uyarıldı. Bileşiklerden yayımlanan L X-ışınları rezülasyonu 5.9 keV'ta 150 eV olan Ultra-LEGe dedektör ile sayıldı. Bu bileşiklerdeki talyumun L_i/L_α X-ışını şiddet oranları saf talyum için teorik olarak hesaplanan değer ile karşılaştırıldı. L_l/L_α ve L_γ/L_α değerleri teorik olarak hesaplanan değer ile uyumlu iken, L_β/L_α X-ışını şiddet oranı değerleri farklılıklara sahiptir.

Anahtar Kelimeler: Talyum, şiddet oranı, EDXRF, kimyasal etki, çoklu iyonizasyon etkisi.

1. INTRODUCTION

Thallium is a soft and ductile heavy metal found in the sulphide ores of heavy metals such as lead, copper and zinc, and in coal. The burning of fossil fuels, oil refining, metal smelting and some industrial operations will cause the thallium to accumulate in soil and water. The increase in the amount of thallium will cause it to be taken by plants and livestock. Thallium is a non-essential metal present in low concentrations in human tissues and is a highly toxic element. Thallium has been once used in medical treatment such as ringworm of the scalp, tuberculosis, venereal diseases and malaria, and used as a rodenticide against rats and squirrels, and used as an insecticide. Besides, thallium is used in the electrical and electronics industries, scintillation counters, low-temperature thermometers, mixed crystals for infrared instruments and laser

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equipment and etc. Radioactive isotopes of thallium are used in physics for measurement of exact time periods, in industry for measuring the thickness of material, and in medicine for scintigraphy of heart, liver, thyroid and testes, and for the diagnosis of melanoma [1, 2].

Increasing the complexity of materials used in industrial and scientific applications has increased the importance of physical and chemical analysis of these materials. For this purpose, ED-XRF method has been successfully used for qualitative and quantitative analysis of element compounds in a sample [3]. Besides, the correct determination of the atomic parameters of the elements such as fluorescence cross-section, intensity ratios and fluorescence yield using ED-XRF method is particularly important in atomic, molecular and radiation physics, in medical physics. The fluorescence parameters of the K, L and M shells of the elements are used in scientific researches especially in nuclear power plants, radiation protection, storage of radioactive materials, space studies etc. Moreover, a comparison of the fluorescence parameters with theoretical estimates provides a check on the validity of various physical parameters in the evaluation of theoretical estimation [4]. When looked at the literature, the L X-ray intensity ratios of the samples have been studied by a number of researchers using different detectors and sources [5-19].

The aim of this study is to investigate the L_i ($i = l$, β, and γ)–to-L_α X-ray intensity ratios of Tl in thallium compounds occurred with different ligands, and interpret the differences between the experimental values of these compounds and the theoretical value of the pure thallium.

2. EXPERIMENTAL PROCEDURE

The measurement geometry between detector, radioactive source and sample are shown in Figure 1. Thallium compounds were obtained commercially and their purities were better than 99%. The compounds were exposed to 59.5 keV photons emitted by an annular 50 mCi ^{241}Am radioactive source. The fluorescence L X-rays from each compound were detected by an Ultra-LEGe detector having a thickness of 5 mm and energy resolution 150 eV at 5.96 keV. The output from the preamplifier, with a pulse pile-up rejection capability, was fed to a multi-channel analyzer interfaced with a personal computer provided with suitable software for data acquisition and peak analysis. For determining peak intensity, the X-ray spectra were analyzed with the use of the Origin program. The L X-ray spectra of Tl for Tl_2SO_4 are shown in Figure 2.

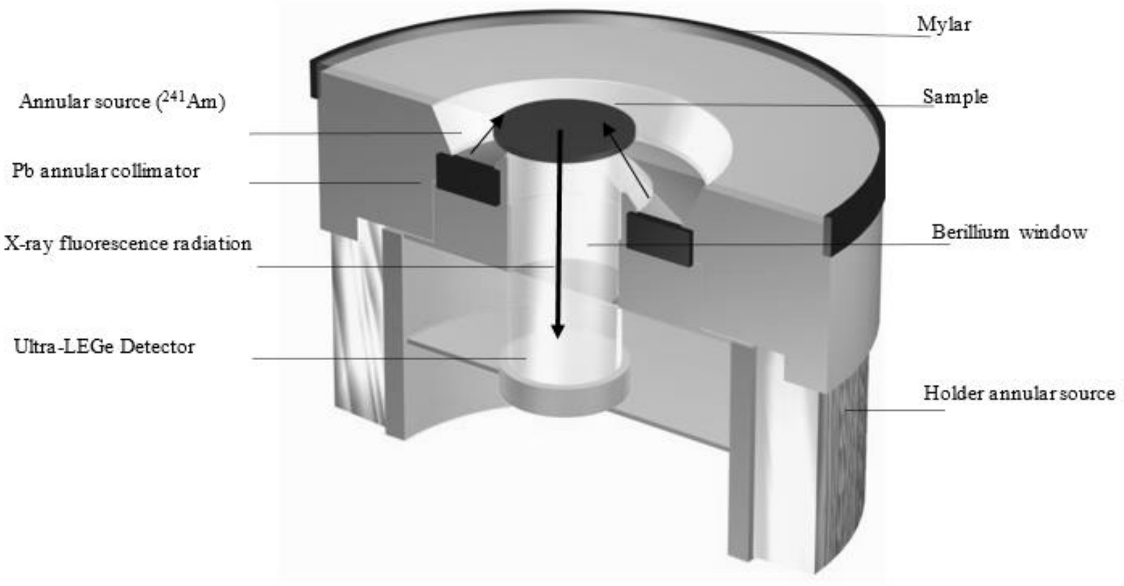

Figure 1. The measurement geometry.

The experimental L_i (i = l, β, and γ)–to-L_α X-ray intensity ratios were evaluated using the following equation [7]:

$$\frac{I_{L_i}}{I_{L_\alpha}} = \frac{N_{L_i}}{N_{L_\alpha}} \frac{\beta_{L_\alpha}}{\beta_{L_i}} \frac{\varepsilon_{L_\alpha}}{\varepsilon_{L_i}} \qquad (1)$$

where N_{L_i} and N_{L_α} are the ratios of the counting rates under the L_i and L_α peaks; β_{L_α} and β_{L_i} are the ratios of self-absorption correction factors of the target that accounts for the absorption of incident photons and emitted L X-ray photons; and ε_{L_α} and ε_{L_i} represent the ratios of the detector efficiency values for L_α and L_i X-rays, respectively.

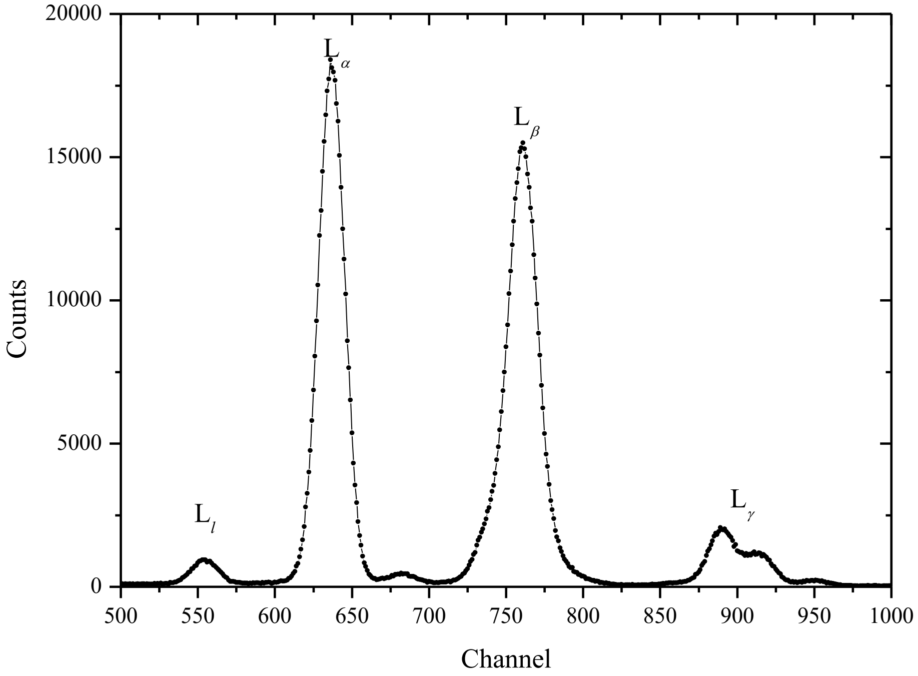

Figure 2. The K X-ray spectra of Tl in Tl_2SO_4

The self-absorption correction was calculated as below:

$$\beta_{K_X} = \frac{1-\exp\{[-(\mu_{inc}\csc\theta_1 + \mu_{emt}\csc\theta_2)t]\}}{(\mu_{inc}\csc\theta_1 + \mu_{emt}\csc\theta_2)t} \qquad (2)$$

where μ_{inc} and μ_{emt} are the mass attenuation of incident photons and emitted characteristic X-rays, respectively [20]; the angles of incident photons and emitted X-rays with respect to the sample surface, θ_1 and θ_2, were equal to 45^0 and 90^0, respectively. t is the target thickness in g/cm^2.

The product $I_0G\varepsilon$ that contains the incident photon flux, a geometrical factor and absolute efficiency of the X-ray detector, was determined for this study by collecting K_α and K_β X-ray spectra of samples of Cr, Fe, Zn, As, Se, Sr, Zr, Ru, and Cd in the same geometry using the equation:

$$I_0 G\varepsilon_{K_x} = \frac{N_{K_x}}{\sigma_{K_x}\beta_{K_x} m_i} \qquad (x=\alpha \text{ and } \beta) \qquad (3)$$

where the terms N_{K_x} and β_{K_x} are the same meaning in Eq. (1). m_i is the elemental concentration (g/cm^2). σ_{K_x} X-ray production cross-section was calculated using the following equation [7]:

$$\sigma_{K_x} = \sigma_K(E)\omega_K F_{K_x} \qquad (4)$$

where $\sigma_K(E)$ is the K-shell photoionization cross-section of the given element for the excitation energy E [21], ω_K is the K-shell fluorescence yield [22], and F_{K_x} is the emission rate of the fractional X-ray for K_α and K_β X-rays [23].

The factor $I_0 G\varepsilon_{K_x}$ was fitted as a function of energy using the polynomials:

$$I_0 G\varepsilon_{K_x} = A_0 + A_1 E_i + A_2 E_i^2 + A_3 E_i^3 \qquad \text{(1st part)} \qquad (5)$$

$$I_0 G\varepsilon_{K_x} = B_0 + B_1 E_i + B_2 E_i^2 \qquad \text{(2nd part)} \qquad (6)$$

where E_i is the K_α or K_β X-ray energy. The variation $I_0 G\varepsilon_{K_x}$ as a function of the K X-ray energy is shown in Figure 3. The Equations 5 and 6 correspond to the left-hand side and right-hand side of Figure 3, respectively.

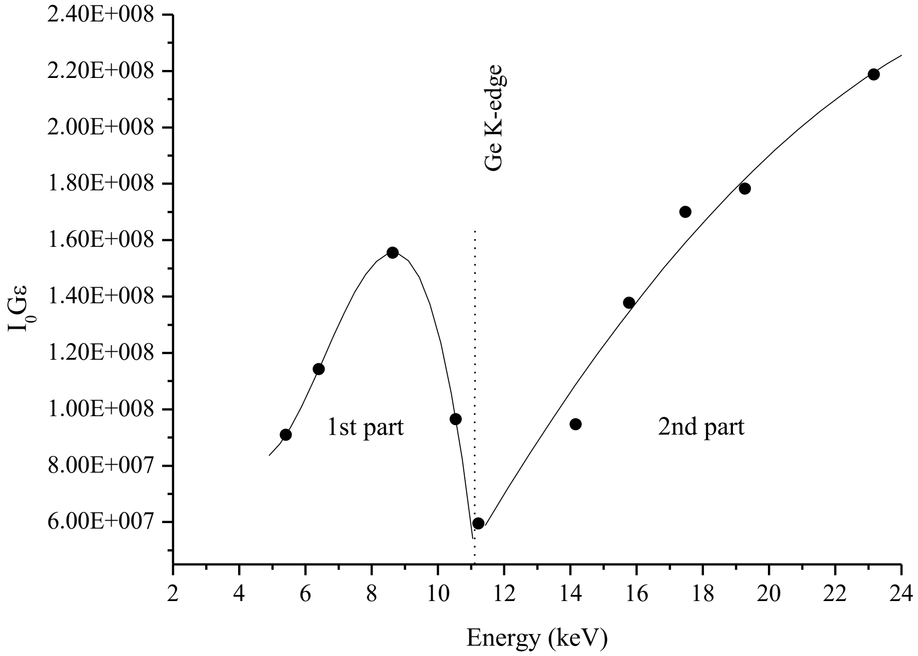

Figure 3. The variation of $I_0G\varepsilon$ as a function of K X-ray energy.

The theoretical L-shell X-ray intensity ratios L_i/L_α were determined using the following equation:

$$\frac{I_{Li}}{I_{L\alpha}} = \frac{\sigma_{Li}}{\sigma_{L\alpha}} \qquad (i = l, \beta \text{ and } \gamma) \qquad (7)$$

where σ_{Ll}, $\sigma_{L\alpha}$, $\sigma_{L\beta}$ and $\sigma_{L\gamma}$ are the production cross-sections calculated theoretically using the following equations [7]:

$$\sigma_{L\ell} = \left[\sigma_{L1}^{P}\left(f_{12}f_{23}+f_{13}\right)+\sigma_{L2}^{P}f_{23}+\sigma_{L3}^{P}\right]\omega_3 F_{3l} \tag{8}$$

$$\sigma_{L\alpha} = \left[\sigma_{L1}^{P}\left(f_{12}f_{23}+f_{13}\right)+\sigma_{L2}^{P}f_{23}+\sigma_{L3}^{P}\right]\omega_3 F_{3\alpha} \tag{9}$$

$$\sigma_{L\beta} = \sigma_{L1}^{P}\omega_1 F_{1\beta} + \left[\left(\sigma_{L1}^{P}f_{12}\right)+\sigma_{L2}^{P}\right]\omega_2 F_{2\beta} + \left[\sigma_{L1}^{P}\left(f_{12}f_{23}+f_{13}\right)+\sigma_{L2}^{P}f_{23}+\sigma_{L3}^{P}\right] \omega_3 F_{3\beta} \tag{10}$$

$$\sigma_{L\gamma} = \sigma_{L1}^{P}\omega_1 F_{1\gamma_{2,3}} + \left[\left(\sigma_{L1}^{P}f_{12}\right)+\sigma_{L2}^{P}\right]\omega_2 F_{2\gamma_1} \tag{11}$$

where σ_{Li}^{P} (i=1,2,3) is the sub-shell photoionization cross-section of the given elements at 59.5 keV [21]. ωi (i=1,2,3) is the L sub-shell fluorescence yield and fij (i≠j=1,2,3) is the Coster- Kronig transition probability [22]. F_{ny} ($F_{3\alpha}$, F_{3l} etc.) is the fraction of the L X-rays originating from the L_n (n = 1, 2 and 3) transition that contributes to Ly (y = l, α, β and γ) peak [23].

3. RESULTS AND DISCUSSION

The experimental results for the L_i ($i = l$, β, and γ)–to-L_α X-ray intensity ratios of Tl in thallium compounds are presented in Table 1. The overall error in the present measurement is estimated to be 6%. This error is the quadrature sum of the uncertainties in the different parameters used to evaluate the K-shell fluorescence parameters, i.e. target thickness (2%), the evaluation of the peak area (3%), the detector efficiency $I_0G\varepsilon K_x$ (3%) and the absorption correction factor (3%).

Table 1. The experimental $I_{Li}/I_{L\alpha}$ (i=l, β and γ) intensity ratio values.

Compounds	IL_l/IL_α		IL_β/IL_α		IL_γ/IL_α	
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
Tl_2CO_3	0.0508±0.0028	0.0518	1.2842±0.0719	1.0914	0.1699±0.0095	0.1802
Tl_2SO_4	0.0512±0.0029		1.3000±0.0728		0.1710±0.0096	
Tl_2O_3	0.0517±0.0029		1.2424±0.0696		0.1748±0.0098	
TlCl	0.0532±0.0030		1.2677±0.0710		0.1810±0.0101	
TlI	0.0518±0.0029		1.2651±0.0708		0.1873±0.0105	
$TlNO_3$	0.0511±0.0029		1.3024±0.0729		0.1743±0.0098	
Tl_2O	0.0497±0.0028		1.1472±0.0642		0.1727±0.0097	

The experimental values of the Li ($i = l$, β, and γ)–to-L_α X-ray intensity ratios of Tl in thallium compounds were compared with the theoretically calculated value of pure thallium. While the values of L_l/L_α and L_γ/L_α intensity ratios are good agreement with the theoretically calculated value of pure Tl within the experimental error, the values of L_β/L_α X-ray intensity ratios have differences. One of the reasons of the differences is the chemical effect. It is well known that the chemical effects on the energy levels and electronic transitions of the atom in a molecule can be interpreted according to the change in characteristic X-ray intensity released from the atom. The individual characteristics of the molecular structures (polarity, valence, the electronegativity of atoms, coordination number, bond type, etc.) significantly affect the positions of atomic lines.

The addition of an atom to chemical bond will result in a significant change in the electron density, particularly in the electron density of the valence. Electron density decreases or increases in the molecule, crystal or complex depending on the type of binding with the adjacent atom. In addition, the inner shell energies are strongly dependent on the change in the electron density of the atom [24]. Removal of a valence electron of the atom in the bond formation will change both the density and the shielding of the valence electrons. A reduction in the shielding effect will be observed and the remaining electrons will bind more tightly to the atom. Thus, a shift will be observed in the binding energies of the inner shell electrons. The change in these binding energies will increase with the increase in the number of valance electrons involved in the bond formation [25]. This will cause changes in X-ray peak shape and intensity. The valence states of thallium consist of 6s and 6p electrons. These electrons determine the chemical properties of the elements. L_β and L_γ transitions may be most affected by chemical effects. Because these transitions take place from the shells close to the valence shell.

Another reason for the difference between experimental and theoretical values of L_β/L_α X-ray intensity ratios may be the effect of electron removal from the shells above the L shell. Multiple ionization processes occur as a result of collisions of energetic particles with atoms or ions, or by reorganization of atomic shells after the an initial inner-shell vacancy has been filled [26]. For ionized atoms, very different configurations are possible depending on the number of electrons extracted from the different shell or subshell [27]. Multiple ionization of atoms can be a source of observed deviations. Because the additional ionizations generated on the worked shell can change the possibilities of Auger, Coster-Kronig, Super Coster-Kronig and radiative transition probabilities [28]. In the case of multi-ionized atoms, the shielding of the inner shell electrons is changed, so that the electrons' bonding energy also changes. This changes the life time of situations, and the X-ray peak shape and peak intensity are modified. The change in peak intensity and peak shape is strongly associated with non-radiative transitions. The non-radiative transitions for Tl were presented by Cooper [29]. These transitions may be affected by the reorganization process of the atomic shells. Consequently, the L X-ray intensity ratios can be affected. Therefore, the observed deviations on the L shell fluorescence parameters may also arise from the multiple ionization effect.

Acknowledgments

The present work was carried out in the Atomic and Nuclear Physics Laboratory of the Physics Department in Karadeniz Technical University.

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