

Determination of experimental K-shell fluorescence yield for potassium and calcium compounds

E TIRAŞOĞLU¹ and Ö SÖĞÜT^{2,*}

¹Department of Physics, Faculty of Arts and Sciences, Karadeniz Technical University, Trabzon-Turkey

²Department of Physics, Faculty of Arts and Sciences, Kahramanmaraş Sütçü İmam University, 46100 Kahramanmaraş-Turkey

*Corresponding author. E-mail: omer_sogut@yahoo.com; os4fg@yahoo.com

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Abstract. K-shell fluorescence yields were experimentally determined for potassium and calcium compounds using a Si(Li) X-ray detector system (FWHM=5.96 keV at 160 eV). The samples were excited by 5.96 keV photons produced by a ⁵⁵Fe radioisotope source. The experimental values are systematically lower than the theoretical values.

Keywords. X-ray; fluorescence yield; cross-section and chemical effects; potassium; calcium.

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1. Introduction

The K-shell fluorescence yield is the ratio of total emission of characteristic K X-ray photons to the production of primary K shell vacancies. The de-excitation of an atom with an inner K shell vacancy can proceed by either the emission of X-ray photons or the ejection of electrons (radiationless transition). These decays are assumed to be energy-independent. The fluorescence yield lies between 0 and 1. For low atomic number elements, Auger decay rate is larger than X-ray emission. For high atomic number elements, X-ray emission becomes more probable. Auger transition probability increases with decreasing binding energies of the outer shell electrons. The chemical effects are observed as differences in the X-ray and Auger transition probabilities from a given element incorporated in different chemical compounds. K-shell fluorescence yields for different elements have been investigated for many years and have been compiled by Krause [1], Bambynek *et al* [2,3] and Hubbell *et al* [4,5]. Fluorescence yield, ω_K , plays an important role in a variety of fields such as atomic, molecular and radiation physics, X-ray fluorescence analysis, cancer therapy, medical research, health physics, irradiation processes and industry [4–6]. Büyükkasap [7] investigated K-shell fluorescence yield in Cr and Ni alloys.

Table 1. K-shell fluorescence yields.

Compounds	ω_K			
	Experimental	Theoretical		
		Hubbell <i>et al</i> [5]	Krause [1]	Broll [19]
K	–	0.143	0.140	0.140
K ₄ (FeCN) ₆	0.048±0.002	–	–	–
KOH	0.036±0.002	–	–	–
K ₂ CO ₃	0.032±0.002	–	–	–
KClO ₃	0.031±0.003	–	–	–
KCl	0.029±0.002	–	–	–
K ₂ SO ₄	0.029±0.002	–	–	–
KNO ₃	0.027±0.002	–	–	–
KMnO ₄	0.027±0.002	–	–	–
KHC ₂ O ₄	0.026±0.002	–	–	–
K ₂ MnO ₄	0.024±0.002	–	–	–
K ₄ Fe(CN) ₆ ·3H ₂ O	0.023±0.001	–	–	–
KHCO ₃	0.023±0.001	–	–	–
K ₂ Cr ₂ O ₇	0.022±0.002	–	–	–
K ₂ CrO ₄	0.021±0.002	–	–	–
KIO ₃	0.019±0.001	–	–	–
KI	0.014±0.001	–	–	–
KBr	0.012±0.001	–	–	–
Ca	–	0.168	0.163	0.163
CaO	0.075±0.005	–	–	–
Ca ₃ (PO ₄) ₂	0.061±0.005	–	–	–
Ca(CH ₃ COO) ₂	0.046±0.004	–	–	–
CaSO ₄ ·2H ₂ O	0.044±0.003	–	–	–
Ca(CO ₃)	0.040±0.004	–	–	–
Ca(NO ₃) ₂ ·4H ₂ O	0.024±0.002	–	–	–
CaCl ₂ ·6H ₂ O	0.013±0.001	–	–	–

The X-ray production cross-section in Ti, V, Cr, Mn, Fe, Co, Ni and Cu molecules were studied by Sögüt *et al* [8]. K-shell fluorescence yields of atoms within $33 \leq Z \leq 53$ using 59.5 keV photons were investigated by Şimşek *et al* [9]. K-shell fluorescence yields in Br and I compounds using radioisotope XRF were examined by Sögüt *et al* [10]. Chen *et al* [11] used a Dirac–Hartree–Slater approach to list the ω_K values of elements in the range $18 \leq Z \leq 96$. Theoretical values of ω_K were obtained in the region $4 \leq Z \leq 54$ by McGuire [12,13] and Walters and Bhalla [14] using the Hartree–Fock–Slater model.

We report, in this paper, the results of K-fluorescence yields obtained for potassium and calcium compounds using a Si(Li) detector which is used to detect K X-rays. The samples were excited by 5.96 keV γ -rays emitted from (50 mCi ⁵⁵Fe filtered annular) radioisotope source. The results are compared with theoretical prediction in the literature.

2. Experimental

The experimental set-up for the annular source in the direct excitation mode used in this study is shown in figure 1. Experimental measurements were carried out for 17 potassium compounds and 7 calcium compounds: KBr, $K_2Cr_2O_7$, K_2CrO_4 , KOH, KCl, K_2SO_4 , K_2MnO_4 , K_2CO_3 , KHC_2O_4 , KNO_3 , $KMnO_4$, $KClO_3$, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_4(FeCN)_6$, $KHCO_3$, KIO_3 , KI and $CaSO_4 \cdot 2H_2O$, $Ca(CO_3)$, $Ca(CH_3COO)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $Ca_3(PO_4)_2$, CaO, $CaCl_2 \cdot 6H_2O$. Powdered samples were sieved to 400 mesh size and thickness of the prepared sample was ranging from 15 to 37 mg/cm². The samples were irradiated by 5.96 keV photons emitted from an annular 1.85 GBq ⁵⁵Fe radioactive source. The incident beam and fluorescence X-rays emitted from the target were detected and analyzed with a Si(Li) detector (FWHM=160 eV at 5.9 keV, active area = 13 mm², thickness = 3 mm and Be window thickness = 30 μm). The output from the pre-amplifier, with 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. The live time was chosen to be 2000 s for all elements. The sample was placed at 45° with respect to the direct beam and normally emitted fluorescent X-rays were detected. Figures 2 and 3 show a typical K X-ray spectrum for KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$. The K-shell fluorescence yield, ω_K was obtained according to the following equation:

$$\omega_K = \frac{\sigma_{K_i}}{\sigma_K(E)} \quad (i = \alpha, \beta), \quad (1)$$

where $\sigma_K(E)$ is the K-shell photoionization cross-section for the given element at excitation energy E , σ_{K_i} ($i = \alpha, \beta$) is the K X-ray fluorescence cross-section. In the present calculations, the values of $\sigma_K(E)$ were taken from Scofield calculations based on the Hartree–Slater potential theory [15]. The K X-ray production cross-sections σ_{K_i} ($i = \alpha, \beta$) were determined according to the following equation:

$$\sigma_{K_i} = \frac{I_{K_i}}{I_0 G \varepsilon_{K_i} \beta t}, \quad (2)$$

where I_{K_i} is the net count of the corresponding photopeak, I_0 is the intensity of exciting radiation falling on the sample, G is the geometry factor, ε_{K_i} is the detector efficiency for K_i X-rays, t is the mass thickness of the sample (g cm⁻²) and β is the self-absorption correction factor of the target material. $I_0 G \varepsilon_{K_i}$ were determined in the same geometry by the following equation:

$$I_0 G \varepsilon_{K_i} = \frac{N_{K_i}}{\sigma_{K_i} \beta_i t}, \quad (3)$$

where N_{K_i} is the number of K_α or K_β X-rays recorded under the K_α or K_β peaks. σ_{K_i} is σ_{K_α} or σ_{K_β} fluorescence cross-section. The efficiency graph of $I_0 G \varepsilon_{K_i}$ is given in figure 4. The self-absorption correction factor (β) has been calculated using the following expression obtained by assuming that the incidence angle of the fluorescence X-rays subtended the detector is approximately 90°:

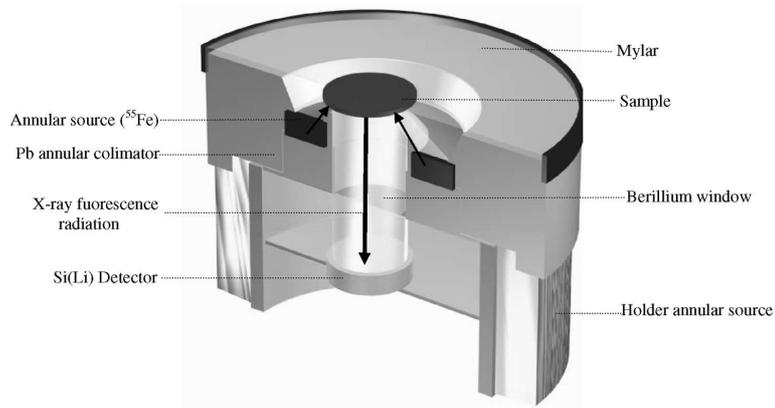


Figure 1. The experimental set-up.

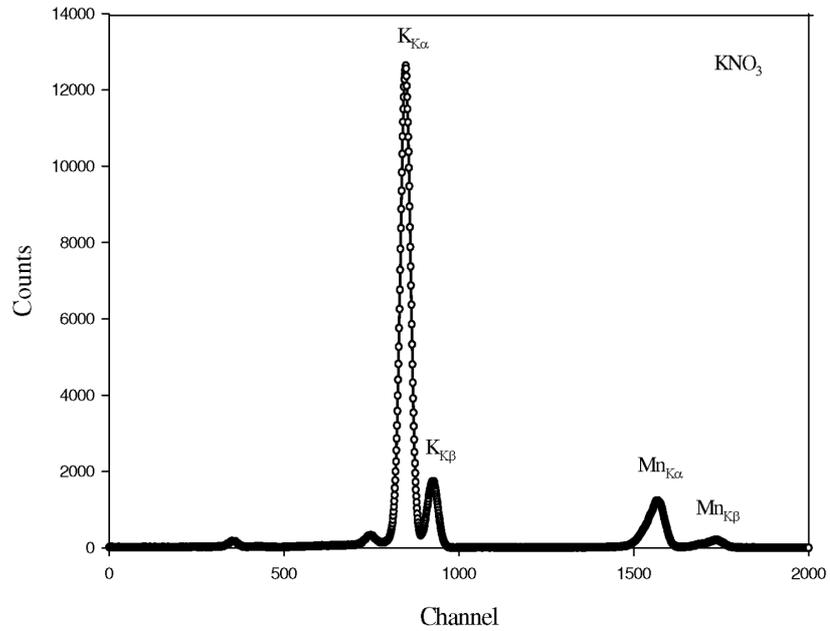


Figure 2. The typical characteristic X-ray spectrum of KNO_3 .

$$\beta = \frac{1 - \exp \left[- \left(\frac{\mu_{\text{inc}}}{\cos \phi} + \mu_{\text{emt}} \right) t \right]}{\left(\frac{\mu_{\text{inc}}}{\cos \phi} + \mu_{\text{emt}} \right) t}, \quad (4)$$

where μ_{inc} ($\text{cm}^2 \text{g}^{-1}$) and μ_{emt} ($\text{cm}^2 \text{g}^{-1}$) are the mass attenuation coefficients at the incident photon energy and fluorescence X-ray energy of the sample, respectively [16].

Experimental K-shell fluorescence yield

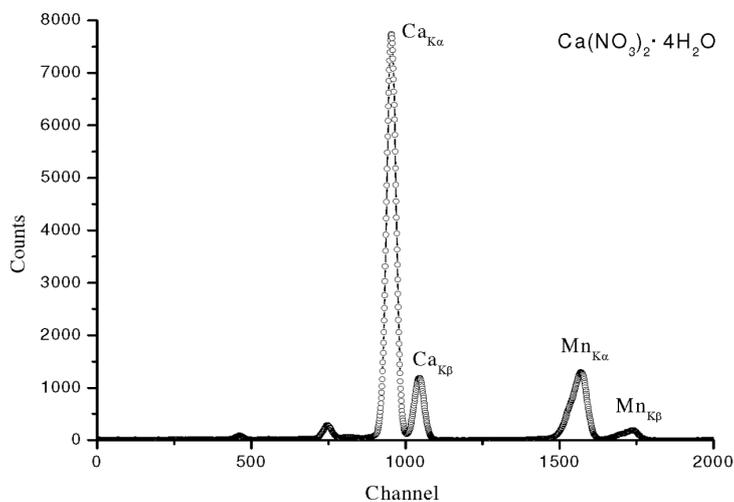


Figure 3. Typical K X-ray spectrum for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

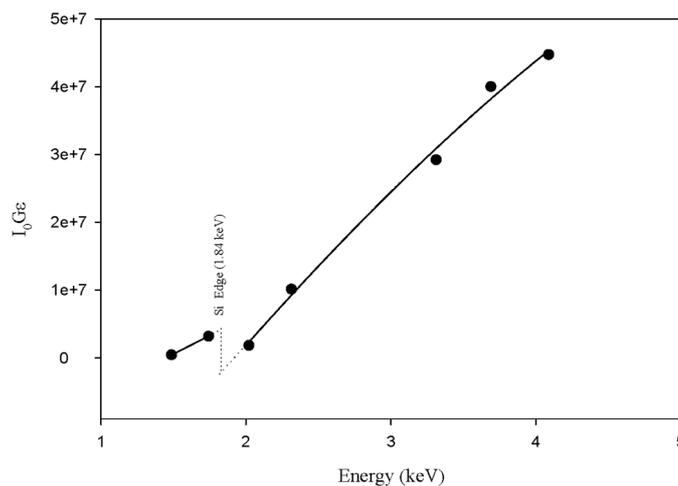


Figure 4. The efficiency graph of $I_0G\varepsilon$.

3. Results and discussion

The experimental values of fluorescence yield ω_K for potassium and calcium compounds were presented in table 1. The sources of the errors in the present measurements are due to $I_0G\varepsilon$ determination (1–2%), counting statistic for K_β and K_α (1–2%), target thickness measurements (1–2%) and self-absorption correction (2–3%). All the errors were compounded according to the classical rules of the propagation of errors and the resultant error is quoted on the measured fluorescence yields [17]. Since the emitted fluorescence X-rays consist of a large number of lines of different energies and intensities, the absorption correction coefficient is

a very sensitive function of energy. Furthermore, when a photon energy is within 1 keV from an absorption edge, the tabular fitted (μ/ρ) values could be wrong (\sim by 10%). In order to minimize these effects, the weighted mean energy instead of the energy of all the emitted fluorescent X-rays and thin samples were used. Mazalov and Treiger [18] have investigated chemical bonding effects in X-ray spectral analysis and nature of chemical effects in X-ray emission spectra and they have shown that the K X-ray emission probabilities depend on the chemical structure of different compounds of the atom.

According to the result shown in table 1, the variation of values of fluorescence yield of potassium compounds is higher than that of calcium compounds. K-shell fluorescence yield measured for calcium and potassium compounds were compared with theoretically calculated values for pure calcium and potassium. We could not make any comparison of results of calcium and potassium compounds, since these values are not available in the literature. The experimental values are lower than the theoretical values for atomic potassium and calcium. The values of the fluorescence yields of the potassium compounds differ by 25–75% from that of $K_4Fe(NC)_6$ taken as the reference compound. This difference is calculated as 66–91% with respect to Hubbell's values [5] and 64–91% with respect to Krause's [1] and Broll's values [19]. In addition, for calcium compounds, by taking CaO as a reference, the differences in the values of the fluorescence yields are found to be 19–82%. Similarly, the differences in the values of the fluorescence yields are computed as 55–92% with respect to Hubbell's values [5] and 53–92% with respect to Krause's [1] and Broll's values [19]. Since valence electrons are involved in the bonding in molecules, K X-ray transitions change according to the structure of molecules. Valence electrons participating in the formation of a chemical bond change to chemical structure of the molecules and this effect causes a change in both the electron screening and outer shell binding energies. Thus, binding energies of inner K shell electrons are strongly affected by chemical environment. The electronic configurations of K and Ca are $3p^64s^1$ and $3p^64s^2$, respectively. Electron affinities and electronegativities of the alkaline metal and alkaline earth metal are lower than those of the other elements. Especially, the electron affinity of calcium is zero while the electron affinity of potassium is 48.8 kJ/mol. In addition, while electronegativity of calcium is one, electronegativity of potassium is 0.82. For this reason, for electrons, the electronegativity of the potassium compounds is higher than that of calcium compounds. The increase in outer shell electrons increases the emission probability of K_α and K_β X-rays. K_α X-rays are produced by the transitions from L_3 subshell to K shell (called K_{α_1} ($L_3 \rightarrow K$)) and from L_2 shell to K shell (called K_{α_2} ($L_2 \rightarrow K$)). Furthermore, K_β X-rays are produced by the following transitions: K_{β_1} ($M_3 \rightarrow K$), K_{β_3} ($M_2 \rightarrow K$), K_{β_5} ($M_4 \rightarrow K$ and $M_5 \rightarrow K$) and the other transitions from the upper shells to the K shell. Since the electronic configuration of potassium and calcium are $3p^64s^1$ and $3p^64s^2$, respectively, the variations of 3p and 2p states especially change K_α and K_β X-ray emission probabilities. Therefore, the values of K-shell fluorescence yield change.

According to the results shown in table 1, K-shell fluorescence yields of K and Ca compounds depend on chemical structure. Chemical effects on the K-shell fluorescence yield for potassium compounds are larger than those of calcium compounds.

Experimental K-shell fluorescence yield

Since ^{55}Fe source (5.96 keV) stimulates L X-rays of iodine, K X-rays of potassium are enhanced in the molecules of KIO_3 and KI. But this effect is not larger than 10–15% of the total intensity. Thus, it may be concluded that K-shell fluorescence yields depend on chemical structure for the partially filled Ca and K elements.

Acknowledgements

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