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The Determination of *M* Shell Average Fluorescence Parameters From ^{70}Yb to ^{92}U and of Hg, Pb and Bi Compounds Using 5.96 keV Photons

Nuray KÜP AYLIKCI[1*], Abdelhalim KAHOUL[2,3] Volkan AYLIKCI[4], Engin TIRAŞOĞLU[5]

[1]*İskenderun Technical University University, Department of Energy Systems Engineering, Faculty of Natural Sciences and Engineering, Hatay, TURKEY*

[2]*Mohamed El Bachir El Ibrahimi University, Faculty of Sciences and Technology, Department of Materials Science, Bordj-Bou-Arreridj, ALGERİA*

[3]*University of Mohamed El Bachir El Ibrahimi, Laboratory of Materials Physics, Radiation and Nanostructures (LPMRN), Bordj-Bou-Arreridj, ALGERİA*

[4]*İskenderun Technical University, Faculty of Natural Sciences and Engineering, Department of Metallurgical and Materials Engineering, Hatay, TURKEY*

[5]*Karadeniz Technical University, Faculty of Arts and Sciences, Department of Physics, Trabzon, TURKEY*

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Abstract. In this study, the empirical average M shell fluorescence yields were calculated from ^{70}Yb to ^{92}U. These obtained values will supply more experimental data for theoretical estimations of atomic structure calculations and spectroscopic analysis which is used for material characterization. And also, chemical effects on average *M*-shell fluorescence yields for Hg, Pb, and Bi compounds were determined using *M* X-ray production cross-sections at 5.96 keV photon energy. The samples were irradiated using a 1.85 GBq ^{55}Fe radioactive source. *M* X-rays emitted by samples were counted using a multi-channel analyzer with a Ultra-LEGe detector. The measured experimental values have been compared with theoretically and empirically (only for M-shell average fluorescence yields) calculated values of pure elements.

Keywords**:** Chemical effect, *M* shell, fluorescence yields, ^{55}Fe radioactive source, Ultra-LEGe detector.

5.96 keV Enerjide Hg, Pb and Bi Elementlerine ait Bileşiklerin Ortalama M Kabuğu Floresans Verimlerinin Araştırılması ve ^{70}Yb ile ^{92}U Arasındaki Elementlerin Ortalama M Kabuğu Floresans Verimlerinin Deneysel Olarak Hesaplanması

Özet. Çalışmada ^{70}Yb elementinden ^{92}U elementine kadar olan saf elementler için ortalama M kabuğu floresans verimleri deneysel olarak hesaplanmıştır. Elde edilen veriler, teorik atomik yapı hesaplamaları için ve malzeme karakterizasyonunda kullanılan spektroskopik yöntemler için daha çok veri sağlayacaktır. Ve ayrıca, M kabuğuna ait ortalama floresans verimler Hg, Pb ve Bi elementleri içeren bileşikler için 5.96 keV'de M kabuğu X-ışını üretim tesir kesitleri kullanılarak hesaplanmıştır. Bileşikler 1.85 GBq ^{55}Fe radyoaktif kaynağı ile uyarılmıştır. Uyarılmış numuneden yayınlanan M kabuğuna ait X-ışını fotonları Ultra LEGe dedektörü ile sayılmıştır. Kimyasallardaki elementlerden elde edilen veriler literatürde yer alan ve çalışmada deneysel olarak hesaplanan değerlerle karşılaştırılmıştır.

Anahtar Kelimeler**:** Kimyasal etki, M kabuğu, Floresans verim, ^{55}Fe radyoaktif kaynağı, Ultra LEGe dedektör.

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* Corresponding author. *Email address:* *nuray.aylikci@iste.edu.tr*

1. INTRODUCTION

X-ray fluorescence spectroscopy is a non-destructive and practical analytic tool for qualitative and quantitative analysis. Also the obtained fluorescence parameters by using this practical way can be a guide for the electronic structure calculations. The theoretical estimations will be performed by using these experimental values. There are lots of studies about K and L shell X-ray production cross section both experimentally and theoretically, whereas measured *M*-shell X-ray production cross section data are scarce, due in part to the complexity associated with the *M*-shell X-ray spectrum. The number of transitions from higher shells to M-shell vacancy is much greater than for K or even L shell vacancies.

The ground state electronic configurations of Hg, Pb and Bi are known as [Xe] $4f^{14}5d^{10}6s^2$, [Xe] $4f^{14}5d^{10}6s^26p^2$ and [Xe] $4f^{14}5d^{10}6s^26p^3$, respectively. Hg element is one of the 5d elements and its valence state consists of 5d, 6s and 6p electrons. The valence state of Pb and Bi consist of 6s and 6p electrons and any changes in valence shell electronic structure will affect the nature of X-ray transitions from these levels to the inner shells. It is generally known that the produced vacancies in M shell will be filled by the electron transitions from upper shells. *M* shell is fairly close to the valance state. The interaction between the central metal and ligands come into existence in valance state and the electrons in valence states are higly affected by the chemical environment. And so, it can be comprehensible that the most affected transitions will be *M* shell X-ray emissions by the ligands more than inner shell X-ray emissions.

The effect of chemical structure of elements to the X-ray emissions (which called as chemical effect) is being studied experimentally in the last two decades and different compounds were studied to explain the changes in chemical structure by using X-ray fluorescence parameters. In the literature the intensity ratios, cross-sections and fluorescence yields of K and L X-rays were used for explaining the chemical structure effect [1-12]. This study includes important results for the determination of the changes in *M* shell electron transitions. The other key point of this study is the determination of *M* shell parameters for elements from Z=70 to 92. In the literature, *M* shell X-ray production cross-sections and fluorescence yields have been measured using the various sources (such as; ions, protons, γ-rays etc.) and detectors. *M* shell X-ray production cross sections of Ir, Pt, and Pb [13] and the elements from hafnium to thorium [14] were reported by using 0.4-2.2 MeV $^4He^+$ ions and protons of energy 0.6-4 MeV respectively. By using the impact of protons and nickel ions, M shell X-ray production cross-section of Pb was measured [15]. Also, M shell cross-sections of Hg [16], Au and Bi [17, 18] were reported where the experimental parameters were measured in different energy ranges. L X-ray production cross-sections for Zr, Nb, Mo, Ag, Cd, In, Sn and M X-ray production cross-sections for Au, Pb, Th, U [19] and for five elements in the range $81 \leq Z \leq 92$ were measured at 5.96 keV energy [20]. M shell fluorescence yields of Bi, Pb, Au, Os [21], $L_{2,3}$ and $M_{2,3}$ fluorescence yields of Cu [22], the average *M* shell fluorescence yields for Pt, Au and Pb [23], total *M* shell X-ray production cross sections and average fluorescence yields for some heavy elements [24] and $M_{4,5}$ subshells average fluorescence yields for Thorium and Uranium [25] were performed by using different experimental and theoretical methods. M shell ionization cross sections and M X-ray production cross sections were calculated within the Energy loss, Coulomb deflection, Perturbed Stationary State and Relativistic effects (ECPSSR) theory for elements with $72 \leq Z \leq 90$ for protons with 0.1-4.0 MeV energy [26].

In the present work, the *M* shell average fluorescence yields (ϖ_M) of compounds of Hg, Pb and Bi elements were measured using the *M* X-ray production cross-sections ($\sigma^x_{M\alpha\beta}$) and the results were interpreted without the oxidation number and chemical bond dependence. In addition to this, the empirical M shell fluorescence yields (ϖ_M) for elements from ^{70}Yb to ^{92}U were calculated using the reported measurements covering the period from 1955 to 2005 in the literature. This study will supply important data for theoretical estimations of electronic structure calculations.

2. MATERIALS AND METHODS

The geometry of the experimental set-up and the present experimental equipment has been described in the previous study [27]. In this work, the measurements were performed for Hg, Pb, and Bi compounds. The studied compounds were listed in Table 1 with the crystalline forms and lattice parameters in the literature [28]. The purity of commercially obtained materials was better than 99%. Powder samples were sieved using 400 mesh and the particle sizes were sufficiently small that there was no significant correction to the data.

The samples were irradiated by 5.96 keV photon emitted by an annular 1.85 GBq ^{55}Fe radioactive source. An Ultra-LEGe detector (FWHM 150 eV at 5.9 keV) was used for $M_{\alpha\beta}$ line measurement. The spectra were analyzed by using Origin Company (Origin 7.0 demo version) software program using least-square fit method.

Table 1. The studied compounds with the crystalline forms and lattice parameters in the literature.

Sample	Bond structure	Oxidation state	Lattice parameters (A^0)	Crystalline form	Binding Energies (kjmol^{-1})
$HgSO_4$	covalent	+2	a=4.815 b=6.5752 c=4.781	Orthorhombic	….
Hg_2S	covalent	+1	….	….	….
$Hg(NO_3)_2$	covalent	+2	….	….	….
$Hg(Ac)_2$	covalent	+2	….	….	….
Pb	metallic	……	a=3.265 b=3.265 c=5.387	Hexagonal	….
PbO	covalent	+2	a=5.6085 b=5.6036 c=4.9893	Orthorhombic	3520
$Pb(NO_3)_2$	covalent	+2	a=7.8594 b=7.8594 c=7.8594	Cubic	2067
PbO_2	covalent	+1	a=10.023 b=5.246 c=5.116	Orthorhombic	11217
$PbCl_2$	covalent	+2	a=7.6222 b=9.0448 c=4.5348	Orthorhombic	2229
$Pb(CH_3COO)_2.3H_2O$	covalent and ionic	+2	….	….	2247
Bi_2O_3	ionic	+3	a=b=c=10.267	Cubic	….
BiOCl	covalent and ionic	+3	a=3.891 b=3.891 c=7.369	Tetragonal	….
$Bi(NO_3)_3.5H_2O$	covalent and ionic	+3	a=8.6521 b=10.6828 c=6.5253	Triclinic	….
$Bi(C_2H_3O_2)_3$	covalent	+3	….	….	….
$Bi_2(CO_3)_3$	covalent	+3	….	….	….

3. DATA ANALYSIS

3.1. Experimental method

The experimental $M_{\alpha\beta}$ X-ray production cross sections, $\sigma^{x}_{M\alpha\beta}$ (cm^2/g) were determined by using Eq. 1.

$$\sigma^{X}_{M\alpha\beta} = \frac{N_{M^x}}{I_{\circ}G\varepsilon_{M^x}\,\beta_{M^x}\;m}, \qquad (1)$$

In this relation, $N_{M_i^x}$ is the net count per unit time under the associated elemental photo-peak, $I_{\circ}G$ is the intensity of exciting radiation falling on the sample, ε is the detector efficiency for the M X-rays of the element, m is the thickness of the target in g/cm^2 and β_M^x is the self- absorption correction. The self-absorption correction factor was evaluated by the following relation.

$$\beta_{M^x} = \frac{1-\exp\left[-\left(\dfrac{\mu_p}{\cos\theta_1}+\dfrac{\mu_e}{\cos\theta_2}\right)\right]m}{\left(\dfrac{\mu_p}{\cos\theta_1}+\dfrac{\mu_e}{\cos\theta_2}\right)m}, \qquad (2)$$

where μ_p and μ_e are the total mass absorption coefficients (from XCOM [29]) of target material at the incident photon energy and at the emitted average $M_{\alpha\beta}$ X-ray energy [30], θ_1 and θ_2 are the angles of primary and emitted radiation with respect to the sample surface.

Average M shell fluorescence yields were evaluated as the ratio of the total M shell X-ray production cross-section to the M shell photoionization cross section at 5.96 keV [31].

$$\varpi_M = \sigma^{x}_{M\alpha\beta}\big/\sigma^{P}_{M}, \qquad (3)$$

3.2. Theoretical method

In this study, $M_{\alpha\beta}$ X-ray production cross sections for the Hg, Pb, and Bi compounds were calculated at 5.96 keV using the following equations:

$$\sigma^{x}_{M4}=[\sigma_{M1}(S_{14} + S_{12}S_{24}+S_{13}S_{34} + S_{12}S_{23}S_{34})+$$
$$\sigma_{M2}(S_{24} + S_{23}S_{34})+\sigma_{M3}S_{34} + \sigma_{M4}]\omega_4 \qquad (4)$$

$$\sigma^{x}_{M5}=[\sigma_{M1}(S_{15} + S_{12}S_{25} + S_{13}S_{3} + S_{14}S_{23}f_{45} + S_{12}S_{23}S_{35} + S_{12}S_{24}f_{45} +$$
$$S_{13}S_{34}f_{45} + S_{12}S_{23}S_{34}f_{45} +\sigma_{M2}(S_{25} + S_{24}f_{45} + S_{23}S_{35} + S_{23}S_{34}f_{45}) +$$
$$\sigma_{M3}(S_{35} + S_{34}f_{45}) + \sigma_{M4}f_{45} + \sigma_{M5}]\omega_5 \qquad (5)$$

$$\sigma^{x}_{M_{4,5}} = \sum_{i=4-5}\sigma^{x}_{Mi} \qquad (6)$$

In these relations, σ_{Mi} (i=4-5) are the M shell photoionization cross section [31], ω_i (i=4-5) are the M sub-shell fluorescence yields, S_{ij} (i=1-3, j=2-5) are Super Coster-Kronig transition probabilities and f_{45} Coster-Kronig transition probabilities [32].

Theoretical M X-ray productions cross sections were determined by using following equations:

$$\sigma^{x}_{M_\alpha} = \sigma^{x}_{M5}F_{5\alpha} \qquad (7)$$

$$\sigma^{x}_{M_\beta} = \sigma^{x}_{M4}F_{4\beta} \qquad (8)$$

where F_{ij} ($F_{5\alpha}$ and $F_{4\beta}$) are the fraction of the radiative transitions of the sub-shell M_i (i= 4 and 5) contained in the jth spectral line. This fraction rates were determined by the following two equations:

$$F_{5\alpha} = \frac{\Gamma(M_5-N_6)+\Gamma(M_5-N_7)}{\Gamma_5} \qquad (9)$$

$$F_{4\beta} = \frac{\Gamma(M_4 - N_6)}{\Gamma_4} \qquad (10)$$

where Γ_i (i= 4 and 5) is total radiative width of M_i sub-shell. This values obtained radiative transition probabilities to fill a vacancy in the M_4 and M_5 sub-shells [33].

3. Calculation of empirical average M shell fluorescence yields $\overline{\omega}_M$

The available data covering the period from 1955 to 2005 was compiled for the average M-shell fluorescence yield measurements. Table 2 gives a summary of the compiled database of average M-shell fluorescence yields for elements from ^{70}Yb to ^{92}U with respect to the target atomic numbers Z. The references, the Weighted-mean values and Standard error (SE) have been also listed. The weighted means values of $\overline{\omega}_M$ for different measurement for each element have been calculated using the following formula [34]:

$$\overline{\omega}_{M\text{-}WMV} = \left(\sum_{i=1}^{N} (\Delta\overline{\omega}_i)^{-2} \right)^{-1} \sum_{i=1}^{N} \left[\overline{\omega}_i / (\Delta\overline{\omega}_i)^2 \right] \qquad (11)$$

In this equation, $\overline{\omega}_i$ is the average experimental M-shell fluorescence yield, $\Delta\overline{\omega}_i$ represents the uncertainty of the experimental values and N is the number of experimental data.

Table 2. Summary of experimental average M shell fluorescence yields $\overline{\omega}_M$ used in this work for the calculation of empirical values: Weighted-mean values and Standard deviation (SD).

Z	$\overline{\omega}_M$ (exp)	Ref.	Weighted mean value	Standard errors (SE)	Z	$\overline{\omega}_M$ (exp)	Ref.	Weighted mean value	Standard errors (SE)
^{70}Yb	0.0140±0.0011	[24]	0.0141	0.0013	^{81}Tl	0.0305±0.0022	[24]	0.0306	0.0012
	0.0117±0.0012	[35]				0.0282±0.0014	[35]		
	0.0161±0.0011	[36]				0.0335±0.0022	[36]		
						0.0332±0.0020	[20]		
^{71}Lu	0.0192±0.0013	[24]	0.0170	0.0012					
	0.0155±0.0011	[35]			^{82}Pb	0.0312±0.0023	[24]	0.0320	0.0010
	0.0154±0.0155	[36]				0.0323±0.0021	[35]		
						0.0354±0.0024	[36]		
^{72}Hf	0.0176±0.0017	[37]	0.0176	-		0.0362±0.0024	[20]		
						0.0311±0.0025	[41]		
^{73}Ta	0.0190±0.0019	[37]	0.0190	0.0001		0.0334±0.0027	[37]		
	0.0187±0.0800	[38]				0.0260±0.0050	[21]		
						0.0290±0.0020	[39]		
^{74}W	0.0188±0.0016	[24]	0.0179	0.0009		0.0320±0.0030	[42]		
	0.0208±0.0014	[35]				0.0280±0.0040	[40]		
	0.0178±0.00018	[36]							
					^{83}Bi	0.0341±0.0029	[24]	0.0359	0.0008
^{75}Re	0.0200±0.0014	[24]	0.0212	0.0014		0.0358±0.0018	[35]		
	0.0229±0.0017	[35]				0.0366±0.0032	[36]		
						0.0325±0.0600	[38]		
^{76}Os	0.0225±0.100	[38]	0.0130	0.0047		0.0370±0.0070	[43]		
	0.013±0.0030	[21]				0.0300±0.0060	[21]		
						0.0350±0.0020	[39]		
^{77}Ir	0.0276±0.0022	[37]	0.0276	-		0.0384±0.0020	[20]		
						0.0356±0.0025	[37]		
^{78}Pt	0.0285±0.0023	[37]	0.0285	-					
					^{90}Th	0.0448±0.0600	[38]	0.0506	0.0020
^{79}Au	0.0240±0.0050	[21]	0.0250	0.0007		0.0440±0.0040	[40]		
	0.0230±0.0010	[39]				0.0525±0.0036	[20]		
	0.0250±0.0040	[40]				0.0537±0.0037	[41]		
	0.0264±0.0021	[41]				0.0512±0.0035	[37]		
	0.0300±0.0024	[37]							
	0.0266±0.0016	[24]			^{92}U	0.0516±0.0040	[24]	0.0520	0.0005

	0.0242±0.0017	[35]			0.0518±0.0039	[35]
	0.0272±0.0019	[36]			0.0506±0.0041	[36]
	0.0266±0.0800	[38]			0.0510±0.0050	[40]
					0.0539±0.0037	[20]
^{80}Hg	0.0269±0.0018	[24]	0.0267	0.0007	0.0535±0.0037	[41]
	0.0258±0.0014	[35]			0.0514±0.0031	[37]
	0.0290±0.0023	[36]				
	0.0280±0.1500	[16]				

The Standard Errors is calculated from the expression:

$$SE(\overline{\omega}_M) = \sqrt{\frac{1}{N(N-1)}\sum_{i=1}^{N}(\omega_i - \overline{\omega})^2} \qquad (12)$$

where N is the number of experimental data, ω_i the experimental fluorescence yields ($\overline{\omega}_M$) and $\overline{\omega}$ is the average experimental data. The empirical average M-shell fluorescence yields of elements in the range 70≤Z≤92 have been obtained from the interpolation of the *Weighted-mean* of experimental data used a polynomial formula as follows:

$$\overline{\omega}_{M-WMV} = \sum_{n=0}^{3} b_n Z^n \qquad (13)$$

The total deviation of the Weighted-mean experimental data ($\omega(\text{data})$) from their corresponding interpolated values ($\omega(\text{emp})$) has been expressed in terms of the root-mean-square error (ε_{rms}) calculated using the expression

$$\varepsilon_{rms} = \left[\sum \frac{1}{N}\left(\frac{\omega(\text{data}) - \omega(\text{emp})}{\omega(\text{emp})}\right)^2\right]^{1/2} \qquad (14)$$

where N is the number of experimental data. The corresponding coefficient b_n, ε_{rms} and the standard deviation have been listed in Table 3. It is noted that the number of experimental data of formula (13) should be sufficient to produce a satisfactory interpolation. The M-shell fluorescence yields have been calculated using the formula (13) and given in Table 4 for all elements in the region 70≤Z≤92.

Table 3. Fitting coefficients for the calculation of empirical average M shell fluorescence yields $\overline{\omega}_M$.

Parameters	Values	Standard Deviation (SD)	ε_{rms}
b_0	2.03057±2.097	0.0032	0.126
b_1	-0.07594±0.0786		
b_2	(9.34413±9.779)E-4		
b_3	(-3.72394±4.038)E-6		

Table 4. Present empirical average M shell fluorescence yields $\overline{\omega}_M$.

Z	Empirical $\overline{\omega}_M$ (this work)	Z	Empirical $\overline{\omega}_M$ (this work)
^{70}Yb	0.01608	^{82}Pb	0.03322
^{71}Lu	0.01637	^{83}Bi	0.03542
^{72}Hf	0.01693	^{84}Po	0.03763
^{73}Ta	0.01776	^{85}At	0.03984
^{74}W	0.01883	^{86}Rn	0.04201
^{75}Re	0.02011	^{87}Fr	0.04414
^{76}Os	0.02158	^{88}Ra	0.04618
^{77}Ir	0.02322	^{89}Ac	0.04813
^{78}Pt	0.02502	^{90}Th	0.04996
^{79}Au	0.02693	^{91}Pa	0.05165
^{80}Hg	0.02896	^{92}U	0.05317
^{81}Tl	0.03106		

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4. RESULTS

M shell production cross-sections and average fluorescence yields which are measured for Hg, Pb and Bi elements in different compounds are listed as Table 5. The analysis of Table 5 shows that the measured parameters for chemical compounds are different from the elemental form of Hg, Pb and Bi. The changes of measured parameters between the elemental and chemical form of these elements are defined as the chemical effect in the literature. It is known that the outer energy levels (valence states) are responsible for the formation of any chemical compounds where some valence charge is removed (or transferred) from the atom. The transferring or removing of valence charges cause the changes in outer shell electronic distributions, electronic screening and so binding energy of valence electrons. The physical mechanism of the changes in the M shell X-ray fluorescence parameters can be explained by two different mechanism defined as charge transfer and rearrangement processes. In charge transfer process, valence electrons can move from one element to another (in ionic or metallic bonds) but the rearrangement of electrons (in covalent or metallic bonds) can occur between valence electronic states in the same atom.

Table 5. The M shell X-ray-production cross-section and average fluorescence yield values for Hg, Pb and Bi compounds.

Chemical Formula	Exp.	Theo.			ϖ_M				
	$\sigma^x_{M\alpha\beta}$	$\sigma^x_{M\alpha}$	$\sigma^x_{M\beta}$	$\sigma^x_{M\alpha\beta}$	Experimental	Calculated (in this work)	Theoretical prediction using data from		
							[44]	[45,46]	[47]
Hg	--	5.82	3.27	9.09	--	0.02896	0.0288	0.0282	0.0260
$HgSO_4$	5.90±0.30				0.0170±0.00087				
Hg_2S	6.32±0.32				0.0182±0.00092				
$Hg(NO_3)_2$	5.58±0.28				0.0161±0.00082				
$Hg(Ac)_2$	6.95±0.35				0.0201±0.00102				
Pb	11.90±0.61	6.87	4.14	11.01	0.0325±0.00165	0.03322	0.0320	0.0313	0.0292
PbO	10.10±0.51				0.0275±0.00140				
$Pb(NO_3)_2$	9.90±0.50				0.0270±0.00138				
PbO_2	10.89±0.56				0.0297±0.00151				
$PbCl_2$	7.16±0.37				0.0195±0.00099				
$Pb(CH_3COO)_2\ 3H_2O$	9.85±0.50				0.0269±0.00137				
Bi	--	7.46	4.51	11.97	--	0.03542	0.0334	0.0329	0.0310
Bi_2O_3	11.02±0.56				0.0290±0.00148				
BiOCl	8.11±0.41				0.0213±0.00109				
$Bi(NO_3)_3\ 5H_2O$	7.34±0.37				0.0193±0.00098				
$Bi(C_2H_3O_2)_3$	9.26±0.47				0.0244±0.00124				
$Bi_2(CO_3)_3$	10.78±0.55				0.0284±0.00145				

According to the crystal field theory, the central atom and the ligands interact with each other in the valence state. It is generally known that the orbital energy levels are close to each other with increasing principal quantum number which determines the energy of each electronic states. The adjacency of the outer levels for heavy metals makes these states more susceptible to the chemical effect or the changes of density of electrons. These levels are strongly affected by ligands in view of crystal field theory.

The changes of the number of outer shell electrons have a crucial effect on the related parameters in the bond formation. The measured parameters such as relative intensity, fluorescence yields and etc. will be different for pure elements and elements in different chemical compounds. Especially, the parameters related with outer shell electrons are more sensitive compared to inner shell fluorescence parameters. An increase (or decrease) of the valance electron density should cause an increasing (or decreasing) of screening on 5d 6s and 6p valance electrons for Hg and 6s, 6p valance electrons for Pb and Bi. When the screening effect is increased (or decreased), the binding energy of valance electrons is decreased (or increased). The decrease (or increase) in the binding energy of valance electrons leads to shortening (or extension) of vacancy lifetime where the probability of non-radiative processes (Auger, Coster-Kronig and super Coster-Kronig transition) will increase (or decrease). Since the total probabilities of radiative and non-radiative transitions are equal to one, the increment of non-radiative transition probability cause to the decrement of the fluorescent X-ray transition probability. Also, it is possible to say that the crystalline form of compound also affects the involvement of outer orbital in the emission of *M* X-rays when vacancy is created in a shell or a sub-shell. In addition, it is known that different bonding energies and interatomic distances depend on different interactions between central atom and ligands in chemical compounds. Therefore, electron transition probabilities of total *M* X-ray production cross-sections and average fluorescence yields, may be changed by changing lattice parameters. These effects play an important role in the *M* X-ray transitions. So it is possible to say that there is an indirect or direct chemical effect on total *M* X-rays production cross-sections and average fluorescence yields.

Table 6 shows the electronegativity values of some elements which are used for the production of chemical compounds. Different electronegativity values can change the density of electrons in the outermost levels of any atom. A change in the electronegativity around the central atom can affect the binding energies of the outermost shell electrons because the outermost electron cloud of the central atom are pulled by the ligands because of the increase of the electronegativitiy values. Therefore, this factor may cause some variations.

Table 6. Electronegativity values.

Element	Atomic number	Electronegativity
H	1	2.20
C	6	3.04
N	7	2.55
O	8	3.44
S	16	2.58
Cl	17	3.16
Hg	80	2.00
Pb	82	2.33
Bi	83	2.02
Ac	89	1.1

From the explanations written above, it can be said that the measured parameters for Hg, Pb and Bi elements in different compounds are very different from the measured and calculated parameters for elemental states (Table 5). But there is an interesting result that the changes cannot be explained by the electronegativity differences. According to Table 6 Hg, Pb, Bi and Ac elements have lower electronegativity values than that of C, N, O, S and Cl elements. If Table 5 is examined carefully, it can be expected that the measured parameters will be lower for elements which have higher electronegativity value. Ac element has lower electronegativity value than Hg and the increment of valence electrons because of the electronegativity differences will decrease the probability of M X-ray transitions and so the related parameters. But other reductions in the measured parameters for Hg compounds cannot be explained by using the electronegativity differences. The measured parameters are lower than elemental value for Hg compounds even if N, O and S elements have higher electronegativity values than Hg. The reason of this result can be explained by the atomic number. Hg, Bi and Pb are defined as bigger element in size and these elements can be polarized easily. Since the other elements have smaller size than Hg, Pb and Bi, these elements can only polarize the outer shell states of Hg, Pb and Bi. The polarized electronic states will shift to the outermost energy levels from the nucleus. And thus the decrement in energy of levels will decrease the M shell X-ray fluorescence parameters as seen in Table 5. The same observation can be possible for all Pb and Bi compounds. Also it can be said that the changes can be explained by the electronegativity differences where the atomic numbers in chemical compounds close to each other such as $Hg(Ac)_2$.

The change ratio for Bi element in Bi_2O_3 compound does not exceed the experimental error limits(6%-7%). It can be expected that O has higher electronegativity value and it polarizes Bi. The reason of this result may be the ionic character of the chemical bond for Bi_2O_3 compound having cubic crystalline structure (Table 1). The other compound $Pb(NO_3)_2$ has also cubic crystalline structure but the chemical bonding type is covalent. In covalent bond, the valence electrons are shared together in compound and Pb may be polarized easily in $Pb(NO_3)_2$ than Bi in Bi_2O_3.

In the context of this study, it is performed the calculation of empirical average M shell fluorescence yield values for elements between Z=70 and Z=92 because there is no competent data on this subject. The obtained parameters will be beneficial for the theoretical estimations of atomic structure calculations (Table 4).

The uncertainties in the measurements are estimated to be less than 6% and are found propagating the errors in various parameters used for determination of X-ray parameters. The uncertainties in these parameters are listed in Table 7.

Table 7. Uncertainties in the quantities used to determine the parameters.

Quality	Nature of uncertainty	Uncertainty (%)
N(K$_i$) (i=α, β, KLM, KMM)	Counting statistic	≤ 3
$I_0 G \varepsilon_{K_i}$	Errors in different parameters used to evaluate factor	≤ 2
β	Error in the absorption coefficients at incident and emitted photon energies	≤ 3
t	Non-uniform thickness	≤ 2

5. DISCUSSION

In this study, the average *M* shell fluorescence yields (ϖ_M) and *M* X-ray production cross-sections ($\sigma^x_{M\alpha\beta}$) for Hg, Pb, and Bi compounds were experimentally investigated. In addition to these measurements, the empirical M shell fluorescence yield values was calculated from ^{70}Yb to ^{92}U using the compiled database from 1955 to 2005 and reported in this work. It was found that the changes could be explained by the electronegativity differences where the atomic numbers closed to each other in chemical compounds. In verse, the elements which had smaller size could only polarize the bigger element in the same compound even if it had higher electronegativity value.

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