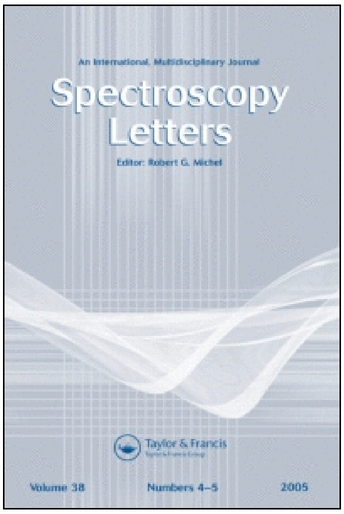

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Determination of Chemical Effect on the $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ X-Ray Intensity Ratios of 4d Transition Metals

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Determination of Chemical Effect on the $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ X-Ray Intensity Ratios of 4d Transition Metals

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ABSTRACT It is clear that detailed studies performed under identical experimental conditions are desirable to determine the effect of the chemical environment on the value of intensity ratios. To better understand this effect, we conducted measurements on $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ x-ray intensity ratios. The $K\alpha$ and $K\beta_{1,2}$ emission spectra for compounds of 4d transition metals Y, Zr, Nb, and Mo were measured using a Si(Li) solid-state detector. The samples were excited by 22.69 keV x-rays emitted from a ^{109}Cd radioisotopes source. The experimental results for pure elements are compared with the other experimental and theoretical values.

KEYWORDS 4d transition metals, ^{109}Cd source and EDXRF, chemical effect, intensity ratio

INTRODUCTION

An excited atom, after the ejection of one of its electrons from a given energy level, constitutes an unstable system. Its stability, however, can be regained by a transition of an electron from a higher level to the hole left by the ejected electron. For instance, atom excitation in level *K* may be followed by electron transition from *L, M*, etc., which in turn leaves a new hole in the energy level involved. This new hole may then be filled by an electron coming from a still higher level. Each time an electron is transferred from a higher to lower energy level the atom loses a certain amount of energy. This energy may be emitted from the atom in the form of electromagnetic radiation called characteristic or fluorescence radiation. The de-excitation phenomenon is schematically shown in Fig. 1, where the different arrows denote the allowable electron transitions from higher levels to levels *K* and *L*.

The $K\alpha$ and $K\beta$ x-rays are two main components of the *K* emission lines of an atom. However they can be easily resolved by a solid-state x-ray detectors, such as Si(Li) or intrinsic Ge detectors. Due to recent advances in solid-state detectors, numerous experimental data have been reported for

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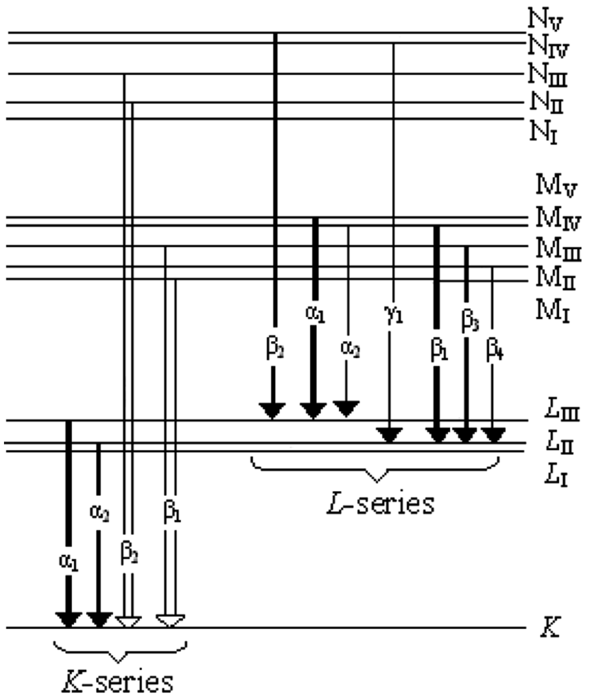

FIGURE 1 *K* and *L* series electron transitions in a heavy atom.

K x-ray emission following radioactive decays, photon irradiation and charged-particle impact.[1–10]

From past to present, several studies have been carried out to measure the dependence of $K\beta/K\alpha$ intensity ratio on the chemical state of the element and the excitation mode. Paic and Pecar[11] found that for first-row transition elements the $K\beta/K\alpha$ ratio depends on the mode of excitation. Brunner et al.[12] reported deviations up to 5% in the $K\beta/K\alpha$ values for compounds of 3d-shell elements when compared with their pure forms. Brunner et al.[12] explained their experimental results by the change in screening of 3p electrons by 3d valance electrons as well as the polarization effect. They also pointed out that the chemical effect is almost the same order of magnitude as the effect of excitation mode and both effects should be studied separately. Brunner et al.[12] derived a simple equation to predict the $K\beta/K\alpha$ intensity ratio as a function of the 3d share of the valance-charge difference. Similar results were obtained by Arndt et al.[13] and they pointed out that the difference comes from a strong shake-off process. They also pointed out that the chemical effect is almost the same order of magnitude as the effect of excitation mode and both effects should be studied separately.

Mukoyoma et al.[14] have calculated the $K\beta_2/K\alpha$ intensity ratios for chemical compounds of 4d transition elements using the simple theoretical method of Brunner et al.[12], originally developed for 3d elements. Although they obtained good agreement between theory and experiment, it was found that their model is inadequate for the metallic cases. Mukoyoma et al.[15] have calculated the electronic structures of tetraoxo complexes of 4d and 5d elements with the discrete-variational $X\alpha$ (DV-$X\alpha$) MO method. They found that for Tc compounds, the calculated values were in good agreement with the measured values. In the case of Mo *K* x-rays, the agreement theory and experiment is not as good as with Tc compounds. Yamoto et al.[16] studied the variation of the relative *K* x-ray intensity ratios for compounds involving Tc isotopes, ^{95m}Tc, ^{97m}Tc and ^{99m}Tc. They found that the chemical effect on the $K\beta/K\alpha$ ratios for 4d elements is small but the dependence of the $K\beta_2/K\alpha$ ratios on the chemical environments is appreciable.

In this study, we report the elemental analysis of different kinds of 4d materials using the energy dispersive x-ray fluorescence (EDXRF) technique. The targets have been excited with 22.69 keV photons from ^{109}Cd sources. The intensity ratios $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ are derived from the fits and critically compared with previous measurements.[17–20]

EXPERIMENTAL

For powdered samples, particle size effects have a strong influence on the quantitative analysis of infinitely thick specimens. Even for specimens of intermediate thickness, in which category the specimens analyzed in the present study fall, these effects can be significant. Therefore, in order to circumvent particle size effects all samples were grounded and sieved through a -400 mesh ($<37\,\mu$m) sieve. A 10 ton hydraulic press was used to compress the samples powder into a thin pellet of 13 mm diameter. The pellet mass was kept in the 5 to 15 mg cm^{-2} range. The Y targets (YBr_3, YCl_3, YF_3, $Y(NO_3)_3\cdot 6H_2O$, Y_2O_3, YPO_4, $Y(SO_4)_3\cdot 8H_2O$ and Y_2S_3), Zr targets ($ZrBr_4$, $ZrCl_4$, $ZrCl_4\cdot 8H_2O$, $ZrOCl_2\cdot 8H_2O$, ZrF_4, ZrH_2, ZrI_4, ZrN, $ZrO(NO_3)_2\cdot XH_2O$, $ZrSiO_4$, $ZrSi_2$, $Zr(SO_4)_2\cdot 4H_2O$ and $ZrTe_2$), Nb targets ($(NbF_5)_4$, Nb_2O_5 and $NbSi_2$), and Mo targets ($MoCl_3$, MoO_2, MoO_3, MoS_2 and $H_3[P(Mo_3O_{10})_4]$) were prepared in the form of pellets from the fine powders and were

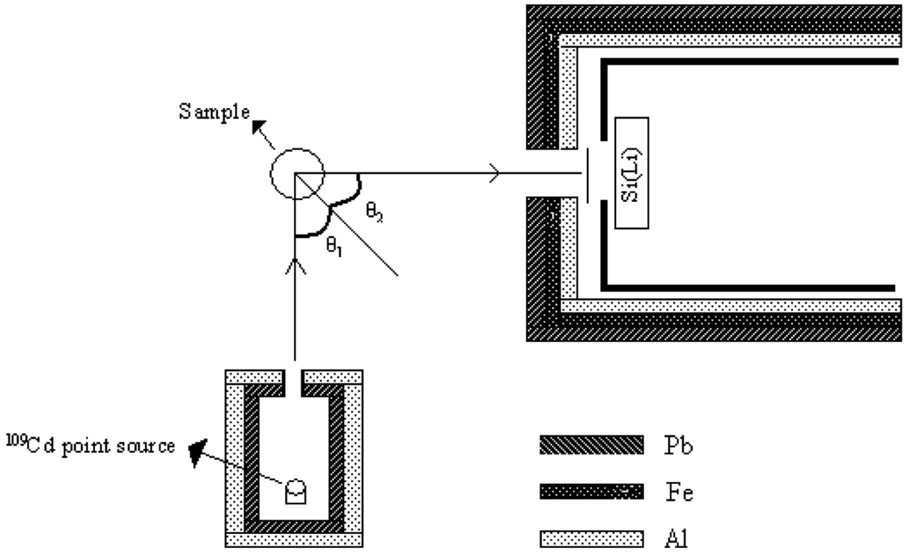

FIGURE 2 Experimental set-up.

excited with a 22.69 keV x-rays from a ^{109}Cd radioactive point source (providing 5.0×10^3 steradian^{-1} photon flux of Ag x-radiation).

A Si(Li) detector with a resolution 180 eV at 5.9 keV was used to count the characteristic *K* x-rays emitted from the samples. The experimental set-up and source-target-detector geometry used are shown in Fig. 2. A graded conical shield of Al and Pb was used between the sample and the detector to obtain a large beam of emergent radiation and to avoid the interaction of the x-rays emitted by the component elements of the radioactive capsule and detector. The detector was shielded by a graded filter of Pb, Fe and Al to obtain a thin beam of photons scattered from the target and to absorb undesirable radiation shielded the detector. The sample-detector and excitation source-sample distances were optimized to get maximum count rate in the fluorescent peaks. The sample was placed approximately at 45° to the source-place as well as to the detector-plane so that the intensity of scattered radiation could be minimized.[21] The count rate kept below 1000 counts s^{-1} in order to avoid peak broadening, energy shift, and non-linearity. The data were collected into 16384 channels of a digital spectrum analyzer DSA-1000. A typical characteristic x-ray spectrum of Mo is shown in Fig. 3. The Microcal Orgin 7.5 was used for peak resolving, background subtraction, and determination of the net peak areas of *K* x-rays. Origin$^{\text{TM}}$ (Microcal Software, Inc., Northhampton, MA, USA) is one of several software packages designed specifically for plotting and analyzing quantitative data. You will be using Origin$^{\text{TM}}$ for a variety of applications. The primary capabilities of Origin$^{\text{TM}}$ software is namely plotting and curve-fitting capabilities. The *K* x-ray spectra consist of many peaks, several of which strongly overlap. These complex spectra were analysed using non-linear least squares fitting procedure and the photo peaks assumed to consist of pure Gaussians. The experimental uncertainties were determined taking into account multiple measurements and multiple fits of each spectrum.

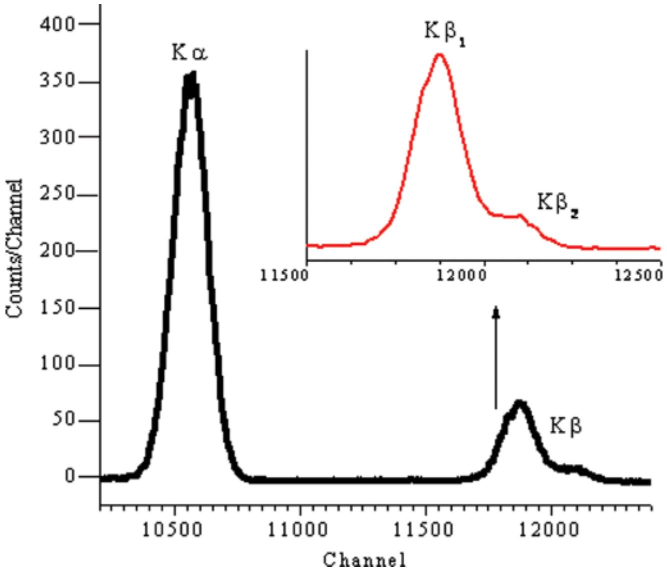

FIGURE 3 A typical *K* x-rays spectrum of the Mo target.

The $K\beta/K\alpha$ x-ray intensity ratio values have been calculated using the relation

$$\frac{I(K\beta)}{I(K\alpha)} = \frac{N(K\beta)}{N(K\alpha)}\frac{\varepsilon(K\alpha)}{\varepsilon(K\beta)}\frac{\beta(K\alpha)}{\beta(K\beta)} \tag{1}$$

where $N(K\alpha)$ and $N(K\beta)$ are the net counts under the $K\alpha$ and $K\beta$ peaks, respectively. $\beta(K\alpha)$ and $\beta(K\beta)$ are the self-absorption correction factor of the target and $\varepsilon(K\alpha)$ and $\varepsilon(K\beta)$ are the detector efficiency for $K\alpha$ and $K\beta$ rays. The values of the factors, $I_0G\varepsilon$ which contain terms related to the incident photon flux, geometrical factor, and the efficiency of the x-ray detector, were determined by collecting the $K\alpha$ and $K\beta$ x-ray spectra of Ti, As, Br, Sr, Y, Zr, and Ru with the mass thickness 0.02 to 0.17 g/cm^2 in the same geometry and were calculated using the following equation

$$I_0G\varepsilon_{Ki} = \frac{N_{Ki}}{\sigma_{Ki}\beta_{Ki}t_i} \tag{2}$$

where N_{Ki} and β_{Ki} ($i = \alpha, \beta$) have the same meaning as in Eq. (1). σ_{Ki} is x-ray fluorescence cross-section, G is a geometry factor and t is the mass of the sample in g/cm^2.

The self absorption correction factor β is calculated for both $K\alpha$ and $K\beta$ separately using the following expression

$$\beta_{Ki} = \frac{1 - \exp\{-[\mu(E_0)\sec\theta_1 + \mu_{Ki}(E)\sec\theta_2]t\}}{[\mu(E_0)\sec\theta_1 + \mu_{Ki}(E)\sec\theta_2]t} \tag{3}$$

where $\mu(E_0)$ and $\mu_{Ki}(E)$ are the total mass absorption coefficients taken from WinXCOM program, which is the Windows version of XCOM. XCOM is the electronic version of Berger and Hubbell's Tables.[22] The angles of incident photons and emitted x-rays with respect to the normal at the surface of the sample θ_1 and θ_2 were equal to 45° in the present setup.

The term σ_{Ki} represents the K x-ray fluorescence cross-sections and is given by

$$\sigma_{Ki} = \sigma_K^P w_K f_{Ki} \tag{4}$$

where σ_K^P is the K shell photo ionization cross-section,[23] w_K is the fluorescence yield[24] and f_{Ki} is fractional x-ray emission rate.[17]

RESULTS AND DISCUSSION

The accurate knowledge of the $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ intensity ratios is required for a number of practical applications of x-rays, e.g., molecular and radiation physics investigations, in non-destructive testing, elemental analysis, medical research, etc. Therefore, these ratios depend sensitively on the atomic structure. Thus they have been widely used also for critical evaluation of atomic structure model calculations. We now discuss the values of these ratios as obtained in our measurements. All K x-ray emission rates are given in Table 1.

The relevant information in a spectrum is contained in its peaks whose position and area are linked, respectively, to the photon energy and the activity of the connected radionuclide. The peak areas can also be used to determine emission probabilities. In this work, peak areas were determined after the $K\alpha$, $K\beta_1$, and $K\beta_2$ areas were separated by fitting the measured spectra with multi-Gaussian function plus polynomial backgrounds using Microcal Orgin 7.5 software program. Details of the experimental set up and data analysis have been reported earlier.[25,26]

The overall error in the present measurements is estimated to be 3 to 8%. This error is attributed to the uncertainties in different parameters used to determine the $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$, and $K\beta/K\alpha$ values; such as, $I_0G\epsilon$ product (1.0 to 2.5%), in the absorption correction factor (0.3 to 1.5%), the error in the area evaluation under the $K\alpha$, $K\beta_1$, $K\beta_2$, and $K\beta$ x-ray peak (0.5 to 3.0%) and the other systematic errors (1.0 to 2.0%).

The theory for the relativistic calculation of the atomic x-ray emission rates was developed by Scofield.[19] Results were given for the Hartree-Slater potential for transition filling vacancies in the K and L shells of a number of atoms. After this work, Scofield[17] developed a new theory. In this theory, the model used in treating the atoms is identical to that of the earlier calculation, with the exception that nuclear charge distribution of finite extend are used. In his work, the x-ray line designations indicate the following transitions:

Table 2 lists the theoretical values which were calculated by Scofield.[17,19] Addition to this, the

TABLE 1 **Ratios K x-ray Emission Rates**

$K\alpha_1$	K-L_3	$K\beta_5$	$(K$-$M_4) + (K$-$M_5)$
$K\alpha_2$	K-L_2	$k\beta_1'$	All K-M transitions
$K\alpha_3$	K-L_1	$K\beta_2$	$(K$-$N_2) + (K$-$N_3)$
$K\alpha$	All K-L transitions	$K\beta_4$	$(K$-$N_4) + (K$-$N_5)$
$K\beta_1$	K-M_3	$k\beta_2'$	K-N and all higher shells
$K\beta_3$	K-M_2	$K\beta$	K-M and all higher shells

TABLE 2 ***$K\beta/K\alpha$* X-ray Intensity Ratios of Pure Y, Zr, Nb, Mo, and their Compounds**

Element	Oxidation state	Intensity ratio	This work	Scofield[17]	Scofield[19]	Manson and Kennedy[20]	Ertuğral et al.[18]
Y	–	$K\beta_1/K\alpha$	0.2307 ± 0.010	0.22910			
		$K\beta_2/K\alpha$	0.0317 ± 0.008	0.02902			
		$K\beta_2/K\beta_1$	0.1981 ± 0.011	0.19220			
		$K\beta/K\alpha$	**0.1822 ± 0.008**	**0.16960**	–	**0.1685**	**0.1856 ± 0.009**
$Y(NO_3)_3 \cdot 6H_2O$	3	$K\beta_1/K\alpha$	0.2339 ± 0.008				
		$K\beta_2/K\alpha$	0.0325 ± 0.010				
		$K\beta_2/K\beta_1$	0.1987 ± 0.011				
		$K\beta/K\alpha$	**0.1829 ± 0.011**				
YCl_3	3	$K\beta_1/K\alpha$	0.2341 ± 0.010				
		$K\beta_2/K\alpha$	0.0329 ± 0.008				
		$K\beta_2/K\beta_1$	0.1992 ± 0.009				
		$K\beta/K\alpha$	**0.1836 ± 0.010**				
YPO_4	3	$K\beta_1/K\alpha$	0.2355 ± 0.010				
		$K\beta_2/K\alpha$	0.0333 ± 0.010				
		$K\beta_2/K\beta_1$	0.1999 ± 0.010				
		$K\beta/K\alpha$	**0.1840 ± 0.009**				
YBr_3	3	$K\beta_1/K\alpha$	0.2359 ± 0.008				
		$K\beta_2/K\alpha$	0.0341 ± 0.007				
		$K\beta_2/K\beta_1$	0.2004 ± 0.009				
		$K\beta/K\alpha$	**0.1848 ± 0.010**				
Y_2O_3	3	$K\beta_1/K\alpha$	0.2364 ± 0.011				
		$K\beta_2/K\alpha$	0.0349 ± 0.010				
		$K\beta_2/K\beta_1$	0.2008 ± 0.010				
		$K\beta/K\alpha$	**0.1856 ± 0.011**				
YF_3	3	$K\beta_1/K\alpha$	0.2371 ± 0.008				
		$K\beta_2/K\alpha$	0.0352 ± 0.009				
		$K\beta_2/K\beta_1$	0.2011 ± 0.010				
		$K\beta/K\alpha$	**0.1859 ± 0.010**				
$Y(SO_4)_3 \cdot 8H_2O$	3	$K\beta_1/K\alpha$	0.2380 ± 0.007				
		$K\beta_2/K\alpha$	0.0355 ± 0.012				
		$K\beta_2/K\beta_1$	0.2015 ± 0.010				
		$K\beta/K\alpha$	**0.1867 ± 0.011**				
Y_2S_3	3	$K\beta_1/K\alpha$	0.2385 ± 0.012				
		$K\beta_2/K\alpha$	0.0359 ± 0.009				
		$K\beta_2/K\beta_1$	0.2019 ± 0.009				
		$K\beta/K\alpha$	**0.1876 ± 0.008**				
Zr	–	$K\beta_1/K\alpha$	0.2355 ± 0.011	0.2332			
		$K\beta_2/K\alpha$	0.0340 ± 0.009	0.0313			
		$K\beta_2/K\beta_1$	0.2099 ± 0.009	0.2039			
		$K\beta/K\alpha$	**0.1877 ± 0.009**	**0.1737**	**0.1913**	**0.1725**	**0.1898 ± 0.008**
ZrN	1	$K\beta_1/K\alpha$	0.2361 ± 0.009				
		$K\beta_2/K\alpha$	0.0347 ± 0.009				
		$K\beta_2/K\beta_1$	0.2104 ± 0.010				
		$K\beta/K\alpha$	**0.1883 ± 0.011**				
$ZrOCl_2 \cdot 8H_2O$	2	$K\beta_1/K\alpha$	0.2370 ± 0.011				
		$K\beta_2/K\alpha$	0.0355 ± 0.009				
		$K\beta_2/K\beta_1$	0.2117 ± 0.010				
		$K\beta/K\alpha$	**0.1889 ± 0.011**				
ZrH_2	2	$K\beta_1/K\alpha$	0.2377 ± 0.008				
		$K\beta_2/K\alpha$	0.0359 ± 0.008				

(*Continued*)

TABLE 2 Continued

Element	Oxidation state	Intensity ratio	This work	Scofield[17]	Scofield[19]	Manson and Kennedy[20]	Ertuğral et al.[18]
		$K\beta_2/K\beta_1$	0.2119 ± 0.009				
		$K\beta/K\alpha$	**0.1897 ± 0.009**				
$ZrO(NO_3)_2 \cdot XH_2O$	2	$K\beta_1/K\alpha$	0.2406 ± 0.010				
		$K\beta_2/K\alpha$	0.0362 ± 0.007				
		$K\beta_2/K\beta_1$	0.2221 ± 0.011				
		$K\beta/K\alpha$	**0.1903 ± 0.008**				
$Zr(SO_4)_2 \cdot 4H_2O$	2	$K\beta_1/K\alpha$	0.2415 ± 0.011				
		$K\beta_2/K\alpha$	0.0364 ± 0.012				
		$K\beta_2/K\beta_1$	0.2226 ± 0.011				
		$K\beta/K\alpha$	**0.1906 ± 0.012**				
$ZrSi_2$	4	$K\beta_1/K\alpha$	0.2422 ± 0.011				
		$K\beta_2/K\alpha$	0.0371 ± 0.009				
		$K\beta_2/K\beta_1$	0.2234 ± 0.010				
		$K\beta/K\alpha$	**0.1909 ± 0.010**				
$ZrCl_4$	4	$K\beta_1/K\alpha$	0.2429 ± 0.010				
		$K\beta_2/K\alpha$	0.0377 ± 0.010				
		$K\beta_2/K\beta_1$	0.2241 ± 0.011				
		$K\beta/K\alpha$	**0.1913 ± 0.010**				
$ZrTe_2$	4	$K\beta_1/K\alpha$	0.2436 ± 0.010				
		$K\beta_2/K\alpha$	0.0388 ± 0.011				
		$K\beta_2/K\beta_1$	0.2245 ± 0.009				
		$K\beta/K\alpha$	**0.1916 ± 0.008**				
ZrF_4	4	$K\beta_1/K\alpha$	0.2439 ± 0.011				
		$K\beta_2/K\alpha$	0.0397 ± 0.010				
		$K\beta_2/K\beta_1$	0.2249 ± 0.011				
		$K\beta/K\alpha$	**0.1921 ± 0.011**				
ZrI_4	4	$K\beta_1/K\alpha$	0.2444 ± 0.008				
		$K\beta_2/K\alpha$	0.0405 ± 0.009				
		$K\beta_2/K\beta_1$	0.2254 ± 0.009				
		$K\beta/K\alpha$	**0.1927 ± 0.009**				
$ZrBr_4$	4	$K\beta_1/K\alpha$	0.2450 ± 0.011				
		$K\beta_2/K\alpha$	0.0411 ± 0.011				
		$K\beta_2/K\beta_1$	0.2261 ± 0.010				
		$K\beta/K\alpha$	**0.1929 ± 0.010**				
$ZrSiO_4$	4	$K\beta_1/K\alpha$	0.2453 ± 0.012				
		$K\beta_2/K\alpha$	0.0417 ± 0.009				
		$K\beta_2/K\beta_1$	0.2264 ± 0.008				
		$K\beta/K\alpha$	**0.1931 ± 0.009**				
$ZrCl_4 \cdot 8H_2O$	4	$K\beta_1/K\alpha$	0.2451 ± 0.011				
		$K\beta_2/K\alpha$	0.0419 ± 0.007				
		$K\beta_2/K\beta_1$	0.2266 ± 0.012				
		$K\beta/K\alpha$	**0.1933 ± 0.009**				
Nb	–	$K\beta_1/K\alpha$	0.2414 ± 0.009	0.2372			
		$K\beta_2/K\alpha$	0.0359 ± 0.010	0.0328			
		$K\beta_2/K\beta_1$	0.2166 ± 0.010	0.2102			
		$K\beta/K\alpha$	**0.1984 ± 0.010**	**0.1772**	–	**0.1759**	**0.1993 ± 0.008**
$(NbF_5)_4$	5	$K\beta_1/K\alpha$	0.2419 ± 0.010				
		$K\beta_2/K\alpha$	0.0366 ± 0.010				
		$K\beta_2/K\beta_1$	0.2171 ± 0.010				
		$K\beta/K\alpha$	0.1991 ± 0.011				

(*Continued*)

TABLE 2 Continued

Element	Oxidation state	Intensity ratio	This work	Scofield[17]	Scofield[19]	Manson and Kennedy[20]	Ertuğral et al.[18]
Nb_2O_5	5	$K\beta_1/K\alpha$	0.2425 ± 0.009				
		$K\beta_2/K\alpha$	0.0373 ± 0.011				
		$K\beta_2/K\beta_1$	0.2177 ± 0.010				
		$K\beta/K\alpha$	**0.1999 ± 0.010**				
$NbSi_2$	–	$K\beta_1/K\alpha$	0.2428 ± 0.011				
		$K\beta_2/K\alpha$	0.0379 ± 0.009				
		$K\beta_2/K\beta_1$	0.2185 ± 0.010				
		$K\beta/K\alpha$	**0.2002 ± 0.009**				
Mo	–	$K\beta_1/K\alpha$	0.2441 ± 0.011	0.2410			
		$K\beta_2/K\alpha$	0.0388 ± 0.008	0.0348			
		$K\beta_2/K\beta_1$	0.2246 ± 0.010	0.2189			
		$K\beta/K\alpha$	**0.2007 ± 0.010**	**0.1809**	**0.1981**	**0.1794**	**0.2016 ± 0.009**
$MoCl_3$	3	$K\beta_1/K\alpha$	0.2444 ± 0.009				
		$K\beta_2/K\alpha$	0.0397 ± 0.011				
		$K\beta_2/K\beta_1$	0.2251 ± 0.012				
		$K\beta/K\alpha$	**0.2015 ± 0.009**				
MoO_2	4	$K\beta_1/K\alpha$	0.2455 ± 0.011				
		$K\beta_2/K\alpha$	0.0406 ± 0.009				
		$K\beta_2/K\beta_1$	0.2259 ± 0.011				
		$K\beta/K\alpha$	**0.2022 ± 0.010**				
MoS_2	4	$K\beta_1/K\alpha$	0.2458 ± 0.008				
		$K\beta_2/K\alpha$	0.0411 ± 0.012				
		$K\beta_2/K\beta_1$	0.2263 ± 0.010				
		$K\beta/K\alpha$	**0.2029 ± 0.010**				
MoO_3	6	$K\beta_1/K\alpha$	0.2471 ± 0.011				
		$K\beta_2/K\alpha$	0.0401 ± 0.009				
		$K\beta_2/K\beta_1$	0.2274 ± 0.011				
		$K\beta/K\alpha$	**0.2036 ± 0.011**				
$H_3[P(Mo_3O_{10})_4]$	–	$K\beta_1/K\alpha$	0.2476 ± 0.009				
		$K\beta_2/K\alpha$	0.0409 ± 0.011				
		$K\beta_2/K\beta_1$	0.2278 ± 0.010				
		$K\beta/K\alpha$	**0.2040 ± 0.011**				

measured values of the $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ intensity ratios in Y, Zr, Nb and Mo and previous experimental and the other theoretical values of these ratios for pure elements and their compounds are listed in Table 2. When you look to the table, a serious difference between the $K\beta_1/K\alpha$ experimental and theoretical values can be seen. This situation is mainly because of the limited resolution of the detector. The $K\alpha_1$ and $K\alpha_2$ x-ray components appear as one line. In the most general case, chemical speciation is preferably performed via the analysis of the $K\beta_{1,3}$ or $K\beta_2$ lines. These lines, emitted after transition of valance electrons are more sensitive to the chemical environment.

As can be seen from Table 2, the $K\beta/K\alpha$ ratios of Y in all Y compounds and Zr in ZrN, $ZrOCl_2 \cdot 8H_2O$, ZrH_2, and $ZrO(NO_3)_2 \cdot XH_2O$ are in close agreement with the ratios of corresponding pure metals. The greatest increase of the $K\beta/K\alpha$ ratio has been observed for $ZrCl_4 \cdot 8H_2O$ and $H_3[P(Mo_3O_{10})_4]$. For Zr and Mo, we found a general increase of the $K\beta/K\alpha$ intensity ratios with increasing formal oxidation number and a large spread of the intensity ratios for different compounds at a fixed oxidation number. This situation is more complex because the $K\beta/K\alpha$ intensity ratio is affected by the chemical bonding type, (ionic, metallic, covalent), the individual characteristics of the structure of molecules, complexes and crystals (polarity, valency and electronegativity of atoms, co-ordination number, ionicities of covalent bond, etc.).

We found that the chemical effect on the $K\beta/K\alpha$ ratios for 4d elements is small but the dependence of the $K\beta_2/K\alpha$ ratios on the chemical environments is appreciable. This can be understood by the fact that in 4d elements the valance state consists of the 4d, 5s, and 5p electrons and the influence of the chemical state on the $K\beta_{1,3}$ (3p→1s) x-ray emission is negligible. Yamoto et al.[16] found similar results for compounds involving Tc isotopes and Mukoyoma et al.[15] found similar results theoretically for Mo and Tc compounds.

CONCLUSION

The EDXRF technique has been used to study the effect of chemical state of an element on characteristic x-ray intensity ratio. A correlation between the $K\beta/K\alpha$ intensity ratio of 4d elements and chemical state was found in this work. Excluding the values for Y and Nb, we can state that $K\beta/K\alpha$ intensity ratio increases with increasing formal oxidation number. The $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$ and $K\beta/K\alpha$ intensity ratio values were obtained in the present work and listed in Table 2 and compared with other experimental and theoretical values. As a result, we can say that the uncertainties of the measured values are too large to allow any statement about the specific dependence of the $K\beta/K\alpha$ intensity ratio on the formal oxidation number, but small enough to show significant increase in the $K\beta/K\alpha$ intensity ratio with increasing formal oxidation number.

We measured 8 different Y compounds, 13 different Zr compounds, 3 different Nb compounds, and 5 different Mo compounds. The most common radioactive sources used in the laboratories for the EDXRF techniques are ^{55}Fe ($T_{1/2} = 2.7$ years), ^{109}Cd ($T_{1/2} = 453$ days) and ^{241}Am ($T_{1/2} = 458$ years) which emit x-rays and gamma rays of different energies (27). X-rays of 22.69 keV from a 10 mCi ^{109}Cd point source have been used to ionize the target atoms and the emitted x-rays were detected by a Si(Li) detector. At this point, this work differs from other experimental results.

In general, our experimental values are qualitatively in agreement with the other experimental values. There are some differences between the results of this study and those of previous experimental work[18] because these studies were carried out in different laboratories and different systems. We were not obtained researches interested in $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$, and $K\beta/K\alpha$ intensity ratio values for Y, Zr, Nb, and Mo compounds. So we do not compare compounds $K\beta_1/K\alpha$, $K\beta_2/K\alpha$, $K\beta_2/K\beta_1$, and $K\beta/K\alpha$ intensity ratio values in literature values. Rigorous systematic experiments and theoretical calculations are urgently needed for comparison with present experimental result.

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