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LEAST-SQUARES FITS OF FUNDAMENTAL PARAMETERS FOR X-RAY ANALYSES AS A FUNCTION OF Z ($10 \leq Z \leq 93$)

A. ZARARSIZ*, H. DEMIREL*, E. AYGUN**

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ABSTRACT

In order to make elemental analyses with X-ray fluorescence technique without standard elements, all of the fundamental parameters (Edge energy, Characteristic energy, Fluorescence yield, Jump factor, Transition probability and so on) corresponding to each element have to be known. In this study, the fundamental paramters of elements for which $10 \leq Z \leq 93$ have been fitted to polynomials with the best determination coefficients (r^2). The results are in good agreement with a previous work for which $11 \leq Z \leq 83$, and we extend the upper range of Z from Z=83 to Z=93 with better determination coefficients in the fitting process.

INTRODUCTION

Numerical values of fundamental parameters have central importance in XRF analyses of elements without standards. The fundamental parameters of an element are the edge energy (E_{edge}), the characteristic energy (E_{char}), the fluorescence yield (w_i), the jump factor ($1-1/r_i$), the transition probability (p_i) and so on.

In this study the fundamental parameters of elements for which $10 < Z < 93$, are fitted to polinomials which are functions of the atomic number Z. The fitted polinomials are so determined that to give the best values for the determination coefficient (r^2). Our results are compared with the results of previous works (Poehn et al., 1985, Fink et al., 1966) and the range of Z is extended 11 elements beyond their range.

THE SHIRAIWA AND FUJINO EQUATION

The elemental weight fraction of samples are determined by making use of the Shiraiwa and Fujino (1966) equation in computarized calculation of concentrations. The equation reads;

* Ankara Nuclear Research and Training Center
** University of Ankara, Faculty of Science, Physics Department.

$$I_{i,s}=qQ_iC_i \quad \frac{\mu_i(E_o)}{\mu_s(E_o)+A\mu_s(E_i)}\left[1+\tfrac{1}{2}Q_jC_j \ \frac{\mu_j(E_o)}{\mu_i(E_o)} \ L_o \ \frac{\mu_i(E_j)}{\mu_s(E_j)}\right] \qquad (1)$$

where

$$L_o = \frac{\text{Ln}\ [1+\mu_s(E_o)\,/\,\sin\psi_1\mu_s(E_j)]}{[\mu_s(E_o)\,/\sin\psi_1\mu_s(E_1)]} + \frac{\text{Ln}\,[1+\mu_s(E_i)\,/\sin\psi_2\mu_s(E_j)]}{[\mu_s(E_i)\,/\,\sin\psi_1\mu_2(E_j)]}$$

and

$$Q_j = (1 - 1\,/\,r_j)\ w_jf_j$$

In order to save the computer memory location, the fundamental parameters appearing in the eq. (1), are expressed as function of the atomic number Z. in the previous works done by Poehn et al. and Fink et al., the fundamental parameters are fitted to different order of polinomials in Z. In those studies values of the determination coefficient (r^2) for their polinomials are subject for discussions as it is commented in the conclusion and the range of the atomic number Z is not as broad as it is in this work. We enlarged the range of Z as $10 \leqq Z \leqq 93$ and selected the polinomials for which r^2 has the best values.

LEAST SQUARES FITS OF FUNDAMENTAL PARAMETERS OF ELEMENTS

Any fundamental parameter F(Z) of elements is expressed as a function of its atomic number Z as the following

$$F(Z) = \sum_{n=o}^{N} A_nZ^n \qquad (2)$$

where A_n is the regression coefficient. The regression coefficients in the eq. (2) can be determined by the method of least squares. A computer program, (BASICA-REG) is prepared to determine the coefficients of the polinomials up to the order of $n=N=7$. Concequently A_n values are determined by the computer programme.

For the case of edge energies; E_K, E_{LI}, E_{LII}, E_{LIII} and E_{MIV} values are taken from Bearden (1967), and fitted to the polinomials which give the best determination coefficients. The range of the edge energy is 0.6 KeV.$\leqq$Ecrit $\leqq$ 116 KeV. and the corresponding range of the atomic number is $10 \leqq Z \leqq 93$. The fitted values of the regression coefficients are listed in the Table 1. And the fitted curves of the critical energy as a function of Z are given the Fig. 1 and 2.

Table 1. Fit Parameters of Edge Energies

E/A_n	A_0	A_1	A_2	A_3	A_4	A_5	Z
K	-0.288	3.165E-2	7.041F-3	1.412F-6	7.607E-9	7.607E-9	10-93
L_I	1.096	-8.920E-2	2.834E-3	2.169E-5	-4.070E-7	2.733E-9	27-97
L_{II}	0.978	-6.698E-2	1.500E-3	4.932E-5	-6.872E-7	3.794E-9	27.92
L_{III}	;.995	-6.531E-2	1.092E-3	5.802E-5	-7.856E-7	3.657E-9	27.92
M_v	-5.259	0.220	-2.290E-3	-1.321E-5	3.542E-7	-3.35;E-10	45.92

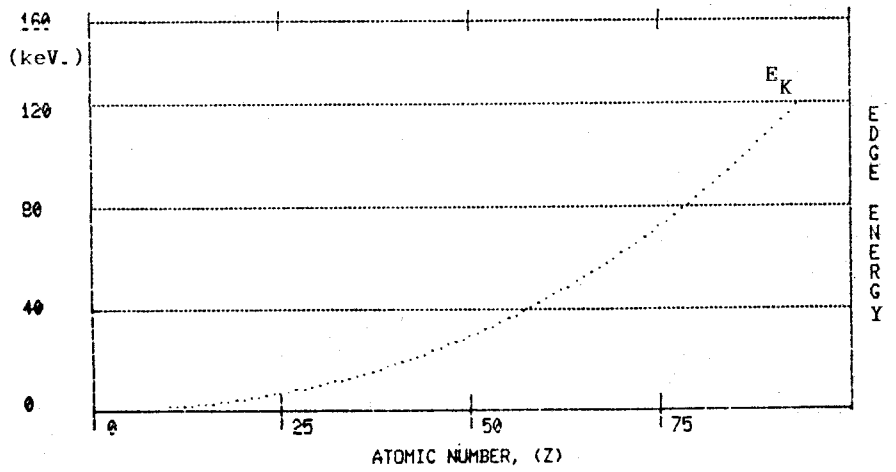

FIG. 1. LSF Edge energy, E_K

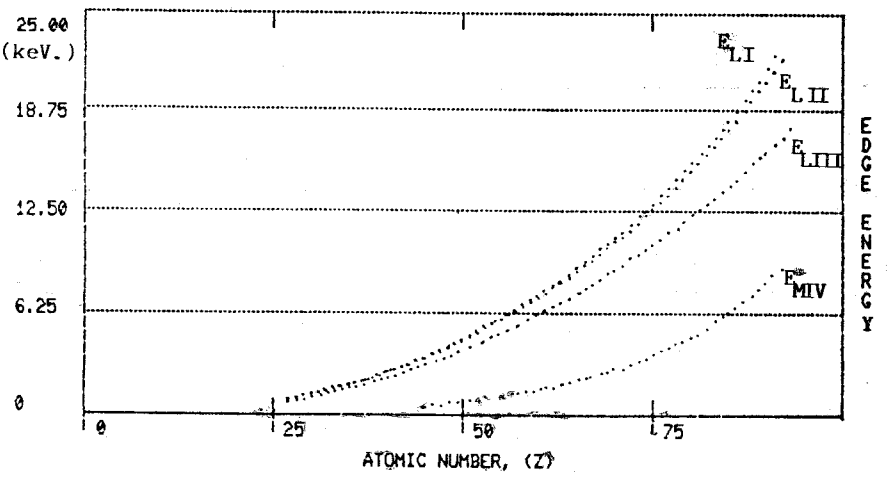

FIG. 2. LSFs of Edge energies, E_{LI}, E_{LII}, E_{LIII}, E_{LMIV}

For the case of the characteristic energies, values of $E_{K\alpha}$ and $E_{L\alpha}$ are calculated from the following equations:

$$E_{K\alpha} = \frac{2E_{K\alpha 1} + E_{K\alpha 2}}{3} \tag{3a}$$

and

$$E_{L\alpha} = \frac{9E_{L\alpha 1} + E_{L\alpha 2}}{10} \tag{3b}$$

for each element separately. Values of the quantities on the right hand side of the eq. (3) are taken from Bertin (1975). The numerical values found from this calculation is fitted to the best fit polinomial which is a function of the atomic number Z. The fitted values of the regression coefficients are given in the Table 2. And the fitted curve of the characteristic energy as a function of Z is given in the Fig. 3 for $E_{K\alpha}$ and $E_{L\alpha}$ separately.

Table 2. Fit Parameters of Characteristic K_α and L_α Radiations.

E/A_n	A_0	A_1	A_2	A_3	A_4	Z
K	0.220	−4.898E-2	1.604E-2	−3.266E-5	3.985E-7	10–90
L111	−0.577	3.109E-2	2.384E-4	1.872E-5	−7.416E-8	30.92

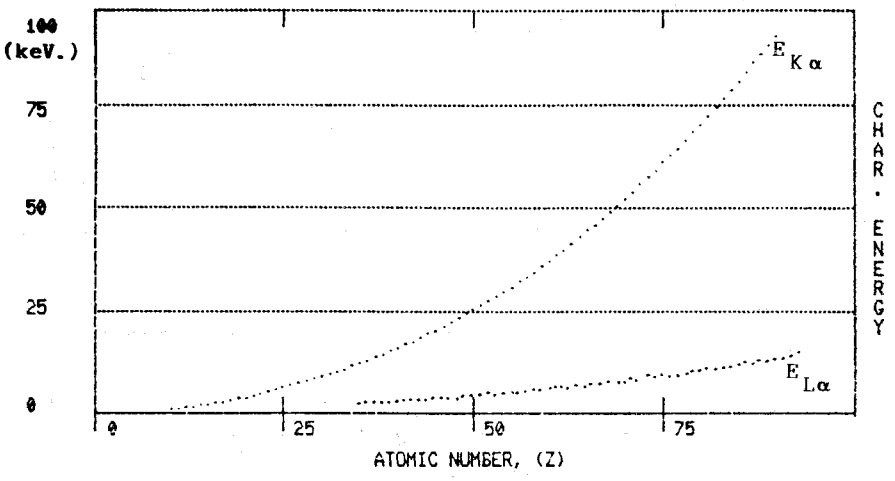

FIG. 3. LSFs of Characteristic K_α and L_α energies

For the case of the jump factor, the fluorescence yield and the transition probability, the experimental values of McMaster et al. (1969), Bambynek et al. (1972), Schreiber and Wims (1982) are used respectively in these calculations. The corresponding fitted values of the regression coefficients are given in the Tables 3–5. The plots of the jump factor and the fluorescence yield are given in the Figs. 4 and 5 respectively.

Table 3. Fit parameters for jump Factor

J/A_n	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	Z
K	1.051	-1.251-E2	1.485E-4	1.411E-5	-6.046E-7	2.858E-9	2.247E-10	-3.065E-12	15–48
L111	4.463	-0.349	1.042E-2	-1.174E-4	1.635F-7	-5.929E-9	2.590E-10	-1.839E-12	35.70

Table 4. Fit Parameters of Fluorescence Yields wK and wL

W/A_n	A_0	A_1	A_2	A_3	A_4	A_5	Z
K	0.293	-6.416E-2	4.296E-3	-7.954E-5	4.770E-7	—	10–50
L_{III}	0.148	-8.184E-3	8.361E-5	1.586E-6	-8.156E-9	-4.276E-11	30–90

Table 5. Fit Parameters of Transition Probabilities, PK

P_K/A_n	A_0	A_1	A_2	A_3	A_4	A_5	Z
I	-1.224	0.132	-4.372E-3	5.205E-5	—	—	20–32
II	-3.557E-2	0.729E-3	-1.382E-4	1.020F-5	-1.864E-7	7.384E-10	33–44
III	-0.247	1.245E-2	1.190E-4	-6 334F-6	6.432E-8	-1.913E-10	55–85

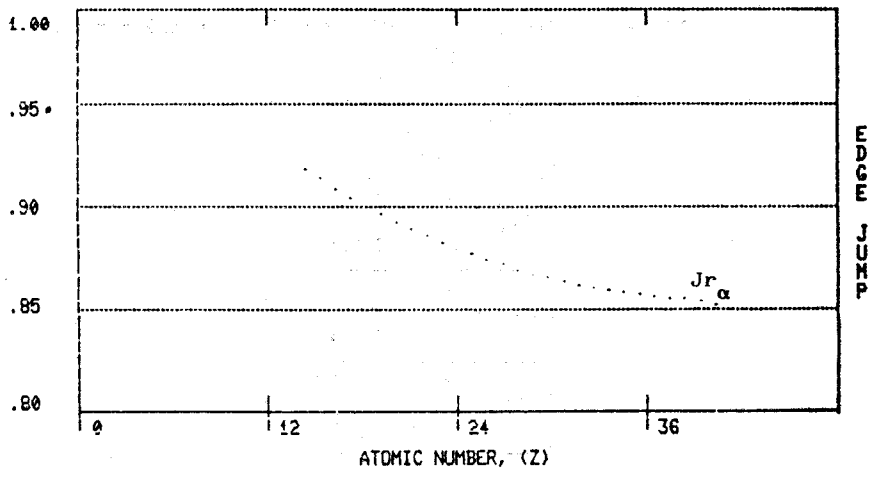

FIG. 4. LSF of J Jump factor

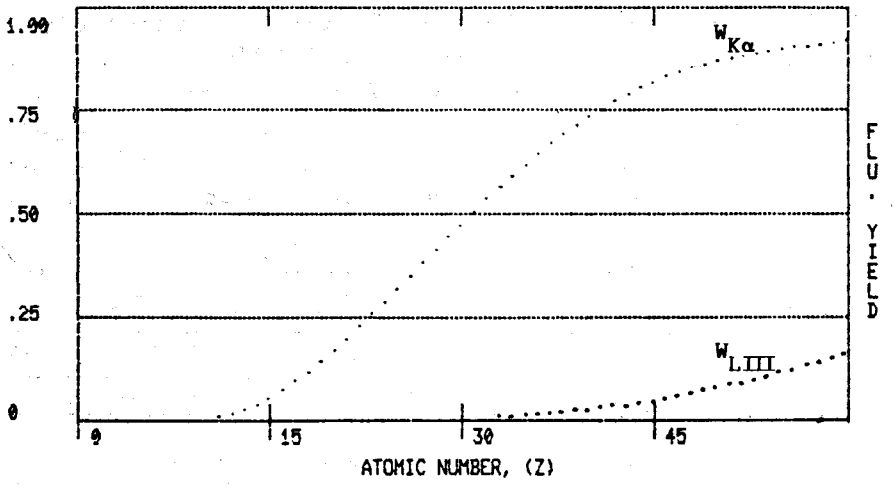

FIG. 5. LSFs of wK and wLIII fluorescence yield

CONCLUSION

Least-square fits of fundamental parameters are very beneficial in XRF analyses of elements without standards. The determination coefficients of the provious works done by Poehn et al. and Fink et al. range $0.985 \leqq r^2 \leqq .998$, while the values of r^2 for this work are almost ideal. Our values for r^2 are tabulated in the Table 6. The range of Z we

Table 6. The Determination Coefficient of Fundamental Parameters

F_{edge}	E_K	1.000
	E_{LI}	1.000
	E_{LII}	1.000
	E_{LIII}	1.000
	E_{MIV}	1.000
E_{char}	$E_{K\alpha}$	1.000
	$E_{L\alpha}$	1.000
(1–1 / r)	K	1.000
	L111	0.994
W	K	1.000
	L111	1.000
P	KI	1.000
	KII	0.998
	KIII	0.997

used is $10 \leqq Z \leqq 93$, which covers almost all the elements with which one may perform tubular or radioisotope excitations in XRF analyses.

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