Study on the Semi-Quantitative Analysis of Electron Probe Micro-Analysis for JEOL

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1. Introduction

The electron probe micro-analyzer (EPMA) is widely applied to analyze the chemical compositions of unknown materials, especially for irradiated nuclear fuels [1].

To know materials of unknown specimens, qualitative analyses, line analyses, mappings, and quantitative analyses are carried out by using the standard specimen with the EPMA machine through calculating the K-raw(%).

But, when quantitative analyses is done without the standard specimen, semi-quantitative analyses are performed by adapting the mathematical method of probability and statistics designed and supplied by the JEOL.

Therefore, in this paper, the adapted probability and statistics supplied by the JEOL is studied to investigate results. Also, the results displayed by the machine and by calculations for elements Zr (z=40) and Ti (z=22) are compared together to prove them.

2. Experimental & Results

2.1 specimen

The used specimen is standard specimen including elements Zr (z=40) having 100.0 wt.% and Ti (z=22) having 100.0 wt.%, but those are considered and treated unknown specimens as shown in Fig. 1.

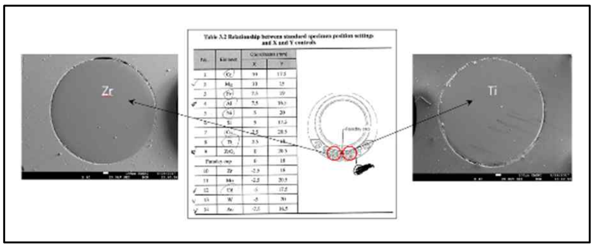


Fig. 1. The specimen of Zr(z=40) and Ti(z=22).

2.2 Electron probe micro-analyzer (EPMA)[2]

EPMA was carried out using a state of the art shielded JEOL JXA-8230 model specially shielded and modified to permit the analysis of irradiated nuclear fuels shown in Fig. 2. This equipment has 4 WDXs (Wave Dispersive Spectrometers) to analyze elements from Boron to Uranium, and an additional function of SEM (Scanning Electron Microscope).

2.3 K-raw(%)

The K-raw(%) is calculated by using following equation (1).

$$\mathrm{K-raw}(\%) = \frac{X-ray\ Intensity_{UNK_{net}}}{X-ray\ Intensity_{STD_{net}}} \times 100 \quad (1)$$

,where
X-ray Intensity : counts per beam current in cps/uA,
net : net count in cps,
UNK : unknown specimen,
STD : standard specimen.

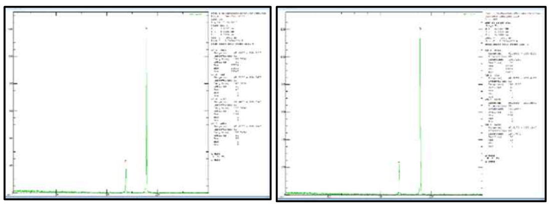
Fig. 2. The appearance of the EPMA at hot lab. in IMEF.

2.4 Qualitative analysis

To analyze the constituents of the specimen composed of the Ti and Zr, the qualitative analyses were performed under the following conditions respectively.

- HT (kV) & beam current (A) : 20.0/2.0E-08
- CH-1(LIF), CH-3(PETH)

The results of qualitative analyses were shown in Fig. 3.



(a) (b)

Fig. 3. Results of qualitative analysis for (a) Ti (z=22, LIFH) and (b) Zr (z=40, PETH).

2.5 Semi-qualitative analysis

To analyze the constituents of the specimens composed of the Zr and Ti respectively, the semi-qualitative analyses were performed under the following conditions.

- HT (kV) & beam current (A) : 20.0/2.0E-08
- CH-1(Ti, LIF/Cal_STD)
- CH-3(Zr, PETH/Cal_STD)

The test results are shown in Tab. 1.

Table 1 : The test results of semi-quantitative analysis for Ti and Zr elements

Element	Ti			Zr		
Frequency	1st	2nd	3rd	1st	2nd	3rd
Peak(mm)	191.249	191.245	191.245	194.568	194.564	194.554
Net(cps)	1818	1831.9	1794.4	5148	5124.8	5044.5
Bg-(cps)	4.4	4.4	3.6	33.2	30.6	30.8
Bg+(cps)	4.4	4.8	4.8	18.2	22.8	19.6
S.D.(%)	0.74	0.74	0.75	0.44	0.44	0.45
D.L.(ppm)	531	544	522	436	445	434
K-raw(%)	102.941	103.987	102.269	98.958	98.691	97.467
Curr.(A) :	9.93E-09	9.90E-09	9.86E-09	9.99E-09	9.97E-09	9.93E-09
Intensity (cps/uA)	1.83E+05	1.85E+05	1.82E+05	5.16E+05	5.14E+05	5.08E+05
Remarks	0115QNT			0113QNT		

2.6 Coefficients Semi-qualitative analysis for crystals

Coefficients for crystals supplied by the JEOL are calculated by an equation (2) and listed in Tab. 2.

$$\ln(I) = a + b \times Z + c \times Z^2 + d \times Z^3 \quad (2)$$

,where I = cps/100pA, Z= ln(z), z = atomic number

Table 2 : The coefficients for crystals supplied by the JEOL and calculated results

Elememt	Ti	Zr	Remarks
Channel	CH-1	CH-3	
Crystal	LIF/ka	PETH/La	
z	22	40	Atomic No.
a	3.158543	-1.97409	
b	-69.6945	-53.0312	
c	41.93018	27.82146	
d	-6.27946	-3.52669	
ln(Z)	3.091042	3.688879	
ln(I)	2.899297	3.958137	
cps/100pA	18.16137	52.35967	
CA(cps/uA)	181613.7	523596.7	Calculated
ME(cps/uA)	177331.8	497069.8	Measured
Difference	4281.1	26528.6	= CA-ME

2.7 Probability and statistics

If the population is known to normal, the sampling distribution of $\bar{X}$ will follow a normal distribution exactly, no matter how small the size of the samples [3]. So the confidence interval for μ is calculated by an equation (3).

$$\bar{x} - z\alpha/_2 \frac{\sigma}{\sqrt{n}} < \mu < \bar{x} + z\alpha/_2 \frac{\sigma}{\sqrt{n}} \quad (3)$$

, where

$$Z = \frac{\bar{X}-\mu}{\sigma/\sqrt{n}}, \; P\left(-z\alpha/_2 < Z < z\alpha/_2\right) = 1 - \alpha$$

From above equation (3), when the confidence interval, $(1-\alpha)100\%$, of the difference between calculated and measured X-ray intensities(cps/uA) is within 68.27%, 95.45%, and 97.33%, then Z-values are 1, 2, and 3 respectively.

2.8 Calculation by adapting the probability and statistics

According to clause 2.7, confidence interval and probability of it were calculated by equation (4) and the whole results are shown in table 3.

$$\mathrm{CI(Confidence\ Interval)} = \left(Z_{value} - \frac{\sigma_{UNK}}{100}\right),$$
$$\mathrm{PCI(Prob.\ of\ it)} = P(Z < CI) - P(Z > -CI), \quad (4)$$
$$K - raw(\%) = K - raw\ (\%) - 1 \times PCI$$

Table 3 : Final results for the elements of Zr and Ti

Element	Ti			Zr		
Frequency	1st	2nd	3rd	1st	2nd	3rd
Intensity_unk (cps/uA)	1.83E+05	1.85E+05	1.82E+05	5.16E+05	5.14E+05	5.08E+05
Intensity_Table_Zr (cps/uA)	177331.8	177331.8	177331.8	497073.8	497073.8	497073.8
K-raw(%)-1	1.0328	1.0434	1.0262	1.0372	1.0344	1.0216
Confidence Interval	2.9926	2.9926	2.9925	1.9956	1.9956	1.9955
Probability of Confidence Interval	0.9972	0.9972	0.9972	0.9540	0.9540	0.9540
Probability of Difference	0.9764	0.9764	0.9764	0.9493	0.9493	0.9493
Z-value	3	3	3	2	2	2
K-raw(%)	102.99%	104.04%	102.33%	98.95%	98.68%	97.46%

2.9 Summary and discussion

The K-raw(%) values are almost same between Table 1 and Table 3, so the K-raw(%) in Table 1 is calculated by program developed by JEOL considering the confidence interval with difference between calculated and measured X-ray intensity(cps/uA) for each elements such as Ti and Zr. Therefore, in case of testing the quantitative analysis for unknown specimen without standard specimens, it must be considered that the analysis results are carried out by the semi-quantitative analysis.

3. Conclusions

Throughout the comparative results of the semi-quantitative analyses between produced from the machine and calculated from calculations, the following items were investigated and concluded.

(1) The results, i.e. population, produced by the machine are seemed to have the normal distribution, $N(\mu, \sigma^2)$, on the basis of probability and statistics.

(2) To know the K-raw(%), the X-ray intensity of the standard specimen is needed but it does not have. In this case, to obtained the calculated X-ray intensity of CAL_STD spectrometer, the equation (2) is applied theoretically.

(3) The theoretical calculated value is included the errors, i.e. the uncertainty, because of the difference between the calculated and the measured X-ray intensity.

(4) The final K-raw(%) could be calculated by using the equation (4) by considering the confidence interval with understanding the meaning of the difference. It is very related to the confidence interval, $(1-\alpha)100\%$,

to the calculated X-ray intensity, and the difference is divided by the calculated X-ray intensity, then the ratio is obtained, so the Z-values is selected as follows.

1) Difference < 1σ(68.27%), z=1

2) 1σ< Difference < 2σ(95.45%), z=2

3) 2σ< Difference < 3σ(97.33%), z=3

REFERENCES

[1] S. Bremier et al., "Electron probe microanalysis of a METHPHIX UPuZr metallic alloy fuel irradiated to 7.0 at.% burn-up", Journal of Nuclear Materials 480 p.109 (2016).

[2] Y.S Choo et al., "The Development of Dismantling Machine for Capsule and HANARO fuel bundle Irradiated at HANARO", KAERI/TR-1078/98, KAERI (1998).

[3] R.Walpole et al., "Probability and Statistics for Engineers and Scientists", third edition, ISBN 0-02424170-9 (1985).