MATRIX ABSORPTION CORRECTION OF MEDIUM THICK TARGETS IN XRF

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ABSTRACT

This paper deals with the matrix absorption and enhancement effects of thick targets in energy dispersive X–ray fluorescence analysis. Two kinds of absorption correction methods are studied especially for medium thick targets (5—10 mg/cm^2). For analysis of hair samples, both the measurement of absorption correction coefficients and the determination of sensitivity factors using an addition method are introduced. Quantitative analysis of medial thick samples is established. The relative deviation between different methods for most of the elements is found to be less than 5 %.

Keywords: X–ray fluorescence Matrix effect Nuclear analysis

1 INTRODUCTION

In recent years, energy dispersive X–ray fluorescence analysis (XRF) has been increasingly used as a powerful, rapid and non–destructive method for studies in biology, medicine, material science and environmental protection[1–3].

Most of the experiments were done with thin targets. In this case, the evaluation of the elemental concentration is simple, but the target preparation is not always easy, it should meet some requirements, such as uniformity, mass thickness, elemental loss and so on. Moreover, there are some samples that can not be prepared as thin targets. So, sample matrix effects should be considered.

Matrix effects include both absorption and enhancement. Generally, matrix absorption is ten or hundred times higher than matrix enhancement[4]. In actual analysis, matrix absorption correction is mainly considered and matrix enhancement correction is neglected. This paper deals with the matrix absorption effect of medium thick targets and discusses two kinds of absorption correction methods for the analysis of hair samples.

2 SPECIMEN MATRIX THICKNESS

In quantitative analysis, when the radiation intensity on the surface of the specimen is I_0 and the mass thickness of the specimen is m, the fluorescence intensity

I_i of a particular line of element i can be expressed as follows:

$$I_i = (\theta/4\pi)\times I_0\times\gamma\times(1-1/J)\times w\times f\times\varepsilon\times m_i\times T \tag{1}$$

$$T = \{1-\exp[-(\mu_E+\mu_i)m]\}/[(\mu_E+\mu_i)m] \tag{2}$$

where T is matrix absorption correction coefficient; μ_E, μ_i mass absorption coefficients of the matrix for the exciting radiation energy E and for the characteristic X–ray of element i, respectively; when the incidence angle ϕ and exit angle ψ are not 90°, the expressions should be $\mu_E\csc\phi$ and $\mu_i\csc\psi$; θ solid angle; τ photoelectric mass absorption coefficient for the exciting radiation; J absorption jump ratio; w fluorescence yield; ε X–ray detection efficiency; f branch ratio.

When $(\mu_E+\mu_i)m\leqslant 0.1$, absorption loss of characteristic X–ray intensity is less than 5%. These samples can be treated as thin targets[5]. There are some samples, such as biological fluids, concentrated liquids, serum, saliva, that can be prepared as thin targets by chemical methods. The matrix absorption effects of thin targets can be neglected.

When $(\mu_E+\mu_i)m\geqslant 5$, samples are infinite thick. In formula (2), $\exp[-(\mu_E+\mu_i)m]$ can be neglected, thus $T\approx 1/(\mu_E+\mu_i)m$. In such cases, the sample mass thickness is called saturated mass thickness. There are some samples such as soil and silt that can be pressed to pellets and measured. Also some samples, such as forensic samples, semiconductors, archaeological samples and alloy materials, that do not need any preparation and can be measured directly.

In actual analyses, some biological samples, such as human hair and orchard leaves, need to be ashed and prepared. Then $(\mu_E+\mu_i)m$ is between 0.1 and 5. These samples are called medium thick targets and their absorption correction should be considered also.

The aim of this work is to investigate the matrix absorption correction of medium thick targets (5— 10 mg/cm^2), both the measurement of absorption correction coefficiencts and the determination of sensitivity factors by the addition method.

3 MEASUREMENT OF ABSORPTION CORRECTION COEFFICIENTS

This correction method is developed on the basis of thin targets. In thin target analysis, using an internal standard method the content C_i of element i should be expressed as follows:

$$C_i=(N_i\times C_Y)/(N_Y\times S_{i,Y}) \tag{3}$$

where C_i and C_Y are the contents of measured element i and the internal standard element Y, respectively. N_i and N_Y are the peak intensities of measured element i and internal standard element Y, respectively. $S_{i,Y}$ is the relative sensitivity factor of element i.

Considering the absorption correction for the analysis of human hair, the above equation becomes:

$$C_i = (N_i \times C_Y)/(N_Y \times S_{i,Y} \times T) \tag{4}$$

There are two kinds of methods to obtain the absorption correction factor T. One way is to get the μ_E and μ_i from data table [6] and to obtain mass m by weighing. According to equation (2), the correction factor T can be calculated.

The other way is to determine T. Take the pure metal film of measured element i as radiation material and put it on the back of the sample tightly, filter lies between them. Under following three cases, the intensities of the characteristic X–rays were measured: intensity from radiation material without sample (with filter) I_i, total intensity from radiation material and sample I_i, intensity from sample without radiation material I_s.

For these intensities, we can derive the following expressions:

$$I_i - I_s = I'_i \exp[-(\mu_E + \mu_i)m] \tag{5}$$

$$\exp[-(\mu_E + \mu_i)m] = (I_i - I_s)/I'_i \tag{6}$$

$$\mu_E + \mu_i = -\ln[(I_i - I_s)/I'_i]/m \tag{7}$$

Thus Eq. (6,7) are put into Eq.(2) to obtain T value.

4 DETERMINATION OF THE SENSITIVITY FACTOR USING ADDITION METHOD

The chemical addition method to correct the absorption effect is different from the measurement of correction coefficients and is based on actual analysis of human hair. The following step is to get the relative sensitivity factors in which the matrix absorption has been corrected.

4.1 Measurement of the relative sensitivity factors

First, the hair matrix solution is prepared by chemical methods[7]. Then, four kinds of concentration with measured elemental standard solution ($W_{i,a}$) and internal standard solution ($W_{Y,t}$) are added into the hair matrix solution. Later, the net peak areas $N_{i,t}$ of measured element i and $N_{Y,t}$ of internal standard element Y can be obtained respectively. The expression of relative sensitivity factor $S_{i,Y}$ is as follows:

$$S_{i,Y} = (N_{i,a} W_{Y,t}) / (N_{Y,i} W_{i,a}) = [(N_{i,t} - N_{i,b}) W_{Y,t}] / (N_{Y,t} W_{i,a}) \tag{8}$$

then

$$N_{i,t} = S_{i,Y}[(W_{i,a} N_{Y,t}) / W_{Y,t}] + N_{i,b} \tag{9}$$

where $N_{i,a}$, $N_{i,b}$ are net peak counts of added element i and of element i in hair matrix, respectively.

The linear fitting for four results of every element is done. As Eq.(9) shows the line slope is relative sensitivity factor. Then, change hair matrix weight n times and repeat above experiments. The *n* relative sensitivity factors for every measured element can be obtained.

4.2 The exponential fitting formula for sensitivity factors

Calcium content is high (about 1000 ppm) in human hair and individual change range is large (150—300 ppm)[8]. The absorption of calcium is larger than those of other elements in hair matrix. So, calcium effect should be considered mainly.

As shown in Fig.1, extrapolation method is used to obtain the calcium weight. Replace hair matrix weight by hair calcium weight W_{Ca}, then fit the exponential function of sensitivity factors. The coefficients of A_i and B_i can be obtained for every element. The expression of $S_{i,Y}$ is as follows:

$$S_{i,Y} = A_i \times \exp(B_i \cdot W_{\mathrm{Ca}}) \tag{10}$$

The advantage of this method is that the change of matrix weight is not only considered but also the change of calcium weight in sample consider the self-absorption weight of calcium is 100—2000 μg. Obviously, with the calcium weight change, the relative sensitivity factor curves also change, and with the atomic number increase, the curve change range decreases.

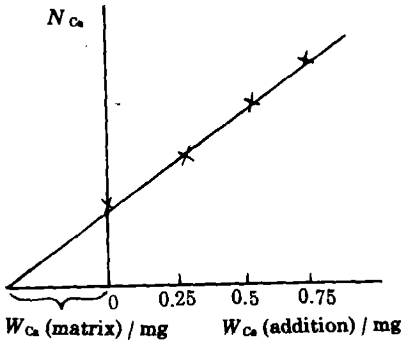

Fig.1 Obtained the calcium weight by extrapolation

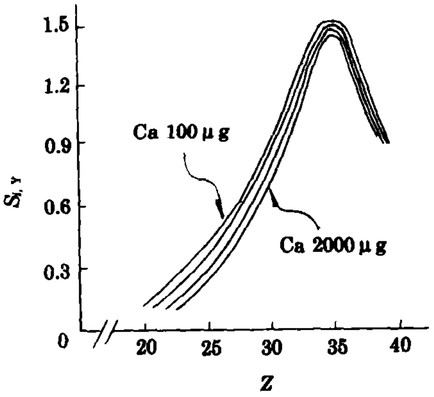

Fig.2 Relative sensitivity factor curves

4.3 Program compilation of quantity analysis

An analysis program MTXRF based on absorption correction of medium thick targets was written in Fortran and run on the PDP-11/34 computer. Since calcium weight is unknown, iterative calculation is necessary. The iteration is stopped when the calculated value agrees within a given limit 0.01 with the previous one. Besides the calcium weight, other elemental contents can be obtained by calculating $S_{i,Y}$.

5 RESULT COMPARISON

In order to compare results between two methods, the analysis of two samples was carried out using addition method and correction coefficients method including experiment and theory calculation. The results are satisfied and listed in Table 1.

From Table 1, using different correction methods, the relative deviations are found to be less than 5 % for most of elements. In first correction method, the relative sensitivity factors do not change for same samples. On the contrary in second correction method, with the change of calcium weight, the sensitivity factors for every sample are corrected ceaselessly. So the latter is most close to the actual samples, but it neglects the effects of other light atomic number elements and consumes time in iterative calculation.

Table 1

Result comparison between two methods for sensitivity factors

Element		Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Thin target		0.0937	0.140	0.284	0.376	0.517	0.689	0.790	0.929	0.624
0.6 g	Meth. (2)	0.0504	0.0984	0.230	0.295	0.435	0.587	0.694	0.794	0.631
dried hair	Meth. (1) A	—	0.102	0.222	0.304	0.430	0.603	0.707	0.851	0.605
	B	0.0518	0.104	0.226	0.309	0.438	0.616	0.724	0.871	0.622
(Ca: 524 μg)	Error/ %	1.9	2.8	1.8	2.3	0.9	2.4	2.1	4.8	2.1
0.8 g	Meth.(2)	0.0495	0.092	0.222	0.28	0.42	0.565	0.666	0.775	0.628
dried hair	Meth.(1) A	—	0.0923	0.206	0.284	0.406	0.579	0.686	0.831	0.602
	B	0.0431	0.0942	0.21	0.291	0.416	0.595	0.704	0.853	0.618
(Ca: 698 μg)	Error/ %	9.8	1.3	3.9	2.0	1.7	2.6	2.8	4.9	2.1

Meth. (1): Sensitivity factors corrected by absorption coefficients A: Experiment B: Theory
Meth. (2): Sensitivity factors obtained using addition method

Generally, while measuring the same kind of samples that content changes are not much more the former is a simple, rapid, useful and effective correction method.

REFERENCES

1 Mangelson N F, Hill M W. Nucl Instr Meth, 1981; 181:243

2 Dyson N A, Simpson A E, Dabek J T. Journal of Radioanalytical Chemistry, 1978; 46:309

3 Maenhaut W. Nucl Instr Meth, 1988; B35:388

4 Robert D G, Fred S G, Joseph M J *et al.* Anal Chem, 1973; 45(4):671

5 Rhodes J R. IEEE Trans Nucl Sci. 1974; NS—21:608

6 USAEC-UCRL—50174, (Sec.1). Compilation of X-ray cross sections. 1970; 1—24

7 Zhang Yuanxun, Wang Xuepeng, Zhi Min. XRF and PIXE applications in life science. Capri: World Scientific Publishing Co, 1990:251

8 Lyenger G V, Kollmer W E, Bowen H J M. The elemental composition of human tissues and body fluids. Weinheim:Verlag Chemie, 1978: 51