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The Use of Numerical Calculation in the Analysis of Standardless Thick Target PIXE*

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In this paper the numerical calculation is used to correct the characteristic K-X ray intensities measured in the analysis of thick target PIXE for the following matrix effects: the slowing down of protons, the absorption of characteristic X-rays, and the enhancement of X-ray induced X-ray emission in the sample. The efficiency calibrations for PIXE analysis system are made by means of the Monte Carlo technique in order to do standardless analysis. Based on this, the PIXE analysis on some self-made standard thick specimens is made. The results are in full agreement with the known values of contents.

1. INTRODUCTION

In proton induced X-ray emission (PIXE) analysis, the incident proton energy is about a few MeV. If thickness of a specimen is no smaller than the proton range in the specimen, then this specimen should not be regarded as thin target. In this case it is necessary to correct the cross section of the X-ray emission induced by protons and the effects of various enhancements and attenuations. This paper presents several types of corrections of matrix effects in the analysis of thick target PIXE by numerical calculation.

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2. PRINCIPLE

When the proton beam with a few MeV penetrates the thick specimen, the proton energy will decrease continuously with the increase of depth, and the cross section of X-ray emission induced by the proton will also decrease. At the same time, the X-rays induced by protons in the thick specimen attenuate because of the absorption effect, which results in the attenuation of the total X-ray intensity. This is the first type of correction to be considered. Next, if some element which is heavier than the element to be measured exists in the specimen, the characteristic X-rays of this heavier element can induce the characteristic X-rays of the element to be measured. This is the second type of correction. Besides, the proton beam hitting the specimen also induces a lot of secondary electrons from the inside of the specimen, and they are able to generate vacancy in atomic internal shell of the element to be measured, that results in the enhancement of the characteristic X-ray. This is the third type of correction. The enhancement effect due to bremsstrahlungs from charged particles (protons, secondary electrons etc.) is quite small [1] in most cases, and this type of correction will be neglected.

In order to show the foregoing corrections quantitatively, we make the following assumptions:

(1) The specimens are homogeneous.

(2) The linear scale of the target is large enough to neglect all the edge effects.

(3) The correction of the proton energy attenuation is conducted only for the range of above 250 keV, and the effects of proton lower than this energy will be neglected. Under the above assumed conditions, we divide equally the effective target thickness t into many layers (e.g. 50 layers), as shown in Fig.1. We first consider all the corrections in every thin layer and then make corrections of the entire thick target.

2.1 The First Type of Correction

Let E_0 be the initial proton energy and E_p^{50} the final proton energy, so the weight factor of characteristic K-X ray induced by a proton of energy changing from E_0 to E_p^{50} in the thick target is:

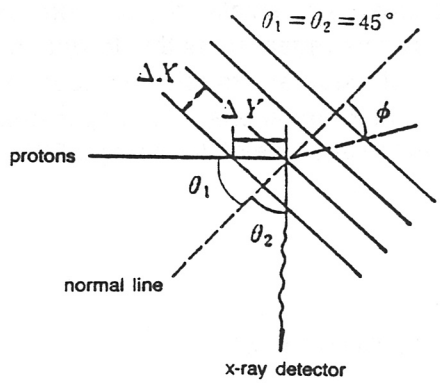

FIGURE 1 The scheme of dividing the specimen into layers.

$$W_1 = \alpha T,$$

$$\alpha = \sum_{i=1}^{50} \sigma_{x_K}(E_p^i, Z_T)\exp[-\mu i \Delta y]. \quad (1)$$

where T is the number of atoms of the element to be measured per cm^2 in each layer of the thick target, $\sigma_{x_K}(E_p^i, Z_T)$ is the K-X ray production cross section of the element with atomic number Z_T, induced by a proton with energy E_p^i in the i-th layer. μ is the mass absorption coefficient for the characteristic X-ray in the specimen matrix, $\Delta Y = \Delta X/\cos\theta$, and ΔX is the thickness per layer ($\Delta X = t/50$). According to Ref.[2], there is a relation as follows:

$$\sigma_{x_K}(E_p^i, Z_T) = (E_p^i/E_0)^{q(E_0,Z_T)}\sigma_{x_K}(E_0, Z_T), \quad (2)$$

The analytical form of $q(E_0,Z_T)$ in the equation is quite complicated. For simplicity, we use the following approximate expression:

$$q(E_0, Z_T) \approx a \lg\left[\frac{Z_T}{\sqrt{50E_0(\mathrm{MeV})}}\right],$$

where coefficient a is determined according to different Z_T value for different layer. On the basis of the expression of stopping power [2] combined with the consideration of dividing thick target into layers, we have the following expression for E_p^i

$$E_p^i = E_0\left[1 - \frac{i\Delta Y}{R(E_0)}\right]^{1/1.7},$$

where $R(E_0)$ is the average range of proton with initial energy E_0. In addition, σ_{xk} (E_0,Z_T) in Eq.(2) is the K-X ray production cross section of proton with energy E_0, and it can be expressed as:

$$\sigma_{x_K}(E_0, Z_T) = \sigma_I(E_0, Z_T)\omega f,$$

where $\sigma_I(E_0,Z_T)$ is the cross section of atomic ionization caused by proton, ω and f are the fluorescence yield and the branching ratio of K-X ray of the element to be measured, respectively. In the case of K-shell ionization, the empirical formula [3] of σ_I is as follows:

$$\sigma_I(E_0, Z_T) = \frac{1}{\mu_K^2}\exp\left[\sum_{n=0}^{5} b_n\left(\ln\frac{E_0}{\lambda\mu_K}\right)^n\right], \quad (3)$$

where λ is the ratio of incident particle mass to electron mass, (for proton, $\lambda = 1836$), and μ_K is the K-shell binding energy of target atom.

Therefore, after the numerical calculation for each layer, we can get the weight factor W_1 of the produced specific characteristic X-ray when a single proton passes through 1--50 layers.

2.2 The Second Type of Correction

Because of the isotropic distribution of the characteristic X-rays induced by protons in the matrix elements, the K-X rays of the measured element caused by K-X

rays of heavier matrix elements coming from various directions in the matrix need to be corrected. The weight factor for this type of correction due to a single photon in 1--50 layers can be expressed as:

$$W_2 = \gamma T$$

$$\gamma = \frac{1}{2}\omega_M \omega f\left(1-\frac{1}{J}\right) M\sigma^p \sum_{k=1}^{50} \exp[-\mu_M^i K \Delta Y] \sum_{\substack{l=1 \\ l\neq K}}^{50} \sigma_M(E_p^l) F(k, l). \tag{4}$$

where $F(k, l)$ is the relative attenuation factor of the intensity for the X-ray produced at l-th layer when travelling from l-th layer to k-th layer (k is not equal to l), σ^p the photo-electron cross section of the measured element caused by characteristic K-X ray of the matrix element, σ_M (E_p^l) the cross section of the matrix atomic ionization caused by the incident proton in the l-th layer, μ_M the mass absorption coefficient of the K-X ray of measured element for matrix, J the jump ratio of the absorption coefficient of the measured element and ω_M the fluorescence yield of K-X ray of matrix element.

The correction $\sigma_M(E_p^l)$ is similar to the consideration of the first type of correction, and can be characterized by using the corresponding expression (2), (3), and etc. $F(k,l)$ is given by the following equation according to its physical meaning:

$$F(k, l) = \frac{2}{\pi}\int_0^{\pi/2} (\cos^2\phi) \exp[-\mu_M^M \Delta X |l-k| / \cos\phi] d\phi,$$

where ϕ is the angle between the out-going X-ray and the normal line of the target, μ_M^M is the mass absorption coefficient of the matrix element to its characteristic X-rays. Because it is hard to get analytical form of the above integral, we carry out its numerical solution by Simpson's rule. From this, we can get the enhancement weight factor W_2 of the characteristic K-X ray of measured element, induced by the characteristic K-X ray of matrix element for a single proton.

TABLE 1

The values of W_p and W_F of some elements in oxygen and iron matrix.

Element to be detected	$W_p(10^{-11})$	$W_F(10^{-11})$	$W_p(10^{-11})$	$W_F(10^{-11})$
	oxygen matrix		iron matrix	
K	228.42	0	114.56	1.500
Ca	255.50	0	130.47	3.247
Cr	397.72	0	380.00	148.21
Co	361.37	0	306.00	0
Ni	332.91	0	240.43	0
Cu	283.77	0	176.76	0
Zn	236.32	0	146.03	0
As	112.69	0	89.12	0

2.3 The Third Type of Correction

In specimen the proton beam can induce a great number of secondary electrons whose energy distribution shows a continuous spectrum. Let T_m represent a maximum energy transferred from a proton with energy E_P(MeV) to a free electron, then T_m is approximately equal to $2 \times 10^{-3}E_P$ [4]. In the case of protons inducing secondary electrons in the specimen, all the production cross sections of secondary electrons are quite large when the electron energy increases from a lower value to T_m. But when the energy exceeds T_m, the cross section drops quickly and at $3T_m$ it is four orders lower than that at T_m. Thus the incident protons with lower energy (e.g. about 2 MeV) induce the overwhelming majority of the low energy secondary electrons in the specimen. The fluorescence enhancement effects caused by these secondary electrons are all very small for the great majority of the measured elements. For example, in the production cross section of characteristic X-ray, the contribution of secondary electron is at most 5%, when proton energy is around 2000 times the K-edge of the measured element, and this type of contribution decreases [5] correspondingly with the decrease of proton energy. Therefore, in the range of elements analyzed in this work and the experimental condition with proton energy of 2.3 MeV, this correction is negligible. However, if the incident particle energy increases, or the measured elements are the light elements with very low energy (~ 1 KeV) characteristic X-rays, the secondary electron enhancement effects must be considered.

2.4 The Emission and Detection Probability W_4 of the Characteristic X-Ray

Suppose that the characteristic X-rays from the thick specimen are collimated before they arrive at the Si(Li) detector, i.e. the edge effect of the detector can be neglected. Under this condition, we can determine the probability W_5 of the characteristic X-ray arriving at the surface of the detector, and the detection probability W_6

TABLE 2

The results of standardless PIXE analysis of some contract specimens.

Sample Number	Elements	Known relative contents (%)	Measured relative contents (%)
101	Zn	99.09	99.16±1.98
	Ca	0.49	0.51±0.05
	Sn	0.42	0.33±0.04
102	Zn	99.14	99.21±1.49
	Ca	0.12	0.14±0.02
	Sn	0.74	0.65±0.06
103	Sn	95.98	96.81±1.94
	Ca	4.02	3.19±0.41
104	Sn	97.28	97.05±1.94
	Ca	2.72	2.95±0.30

[6] by the Monto Carlo method. Hence the total emission and detection probability W_4 is

$$W_4 = W_5 \cdot W_6 \tag{5}$$

Once the W_5 and W_6 are known, the PIXE analysis without standard can be made.

2.5 The Expression of Concentration

Using the weight factors introduced above and probability W_4, we can correct the intensity of the measured characteristic K-X ray for matrix enhancement effects and give the results of the standardless PIXE analysis for the thick specimen. In the multielement matrix, the relative content of certain element in the thick specimen can be expressed as:

$$C(n) = \frac{A(n)I(n)\dfrac{1}{W_4(n)}\displaystyle\sum_{i=1}^{m}\left[\frac{C_m(i)}{\alpha(n,i)+\gamma(n,i)}\right]}{\displaystyle\sum_{k=1}^{N}A(k)I(k)\frac{1}{W_4(k)}\sum_{i=1}^{m}\left[\frac{C_m(i)}{\alpha(k,i)+\gamma(k,i)}\right]},$$

where $A(n)$ is the atomic weight of the n-th element, $I(n)$ the K-X ray intensity of the measured n-th element, $W_4(n)$ the emission and detection probability of K-X ray of the n-th element, $\alpha(n,i)$ and $\gamma(n,i)$ are the values of α and γ of the measured n-th element under the effect of the i-th matrix element (see (1) and (4)), respectively, $C_m(i)$ is the relative content of the i-th matrix element, m the number of the matrix elements and N the number of the measured elements.

3. EXPERIMENT

In order to examine the reliability of the above numerical calculation method, some thick targets were prepared as standards for comparison. The technique for the target preparation was as follows: The zinc powder, calcium oxide, tin oxide and a little boric acid, all of spectroscopic-grade, were mixed according to the predetermined ratio, then ground into homogeneous mixture and pressed into disc thick target with 13 mm in diameter and about 1 mm in thickness by a hydraulic press. The pressure was 10 ton.

The experiment of PIXE analysis was performed on the PIXE facility of the Institute of High Energy Physics in Beijing. The proton beam energy is 2.3 MeV and the diameter of the beam cross section is 1.9 mm. The area and energy resolution of the Si(Li) detector are 80 mm^2 and 178 eV at 5.9 KeV X-ray respectively. In the PIXE experiment of the above specimens, characteristic X-ray energy spectra were obtained with Si(Li) spectrometer and analyzed by AXIL01 program to get the measured corresponding spectrum intensities. Then, we corrected the intensities by the above numerical calculations, including the efficiency correction by probability value W_4. Hence, we could get the content of each element corresponding to the measured spectrum.

4. RESULTS

Suppose W_p is the detection probability of the characteristic X-ray, which is induced by the incident protons in the thick specimen, including the first type correction, W_F is the detection probability of X-ray, which is induced by matrix element X-rays, including the second type correction. The values of W_p and W_F of some elements in oxygen and iron matrix are listed in Table 1 as an example. The relative contents of the measured element are all 0.42%. The values of W_p in the table are in agreement with the results in Ref.[7].

The experimental results for a number of thick targets as comparing standards are listed in Table 2. It can be seen from this table that the corrected results of the PIXE analysis are in good agreement with the known values of contents. The contrast specimens used in this investigation belong to simpler system of thick specimen. The foregoing method of numerical calculation will be applied to the more complicated system of thick specimen in the future work.

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