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A PROGRAM FOR QUANTITATIVE PIXE ANALYSIS OF THICK SAMPLE*

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ABSTRACT

A program for quantitative PIXE analysis of thick sample (TSPIXE) without reference material has been developed at Fudan University. Our program can be applied to the energy range of 10 keV to 10 MeV and is suitable for the analysis of all elements with $11 < Z < 92$. NBS reference materials were analyzed to provide the experimental test of TSPIXE program.

Keywords: Thick sample PIXE analysis TSPIXE

1 INTRODUCTION

In the first phase of its development (1970s) PIXE analysis was developed mainly on very thin samples. More recently (1980s) the maturing of PIXE has resulted in the ability to analyze the major, minor and trace elements in samples thick enough to stop the beam entirely. This was necessary because many sample types can not be reduced to thin films, or demanded in-situ analysis of defined portions, or must be preserved for reasons of historic value or further use of analysis. Thick sample PIXE is therefore now a very important field in PIXE analysis.

2 THEORY AND DATABASE

For a thick and homogeneous sample, the X ray yield of an element of concentration C_z is the integral of intensities reaching the detector from succesive points along the ion's range in the specimen. By integration over the proton path, the X-ray yield for the element can be expressed as:

$$Y(Z)=(\Omega_x/4\pi)[(N_{av}\omega_z b_z\varepsilon_z)/A_z]NC_z\int_{E_0}^{0}[\sigma_z(E)T_z(E)/S(E)]\mathrm{d}E \tag{1}$$

where $S(E)$ is the matrix stopping power for protons (keV · g^{-1} · cm^{-2}); $T_z(E)$ is

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the coefficient of proton attenuation; Ω_x is the X ray detector solid angle; N_{av} is Avogadro's number; N is the proton number; ω_z is the K (or L) X ray fluorescence yield; b_z is the K_a (or L_a) fraction in the K (or L) X-ray series; ε_z is the detector efficiency, A_z is the atomic mass of Zth element, C_z is the concentration by mass of Zth element, E_0 is the energy of incident proton and $\sigma_z(E)$ is ionization cross section at energy E.

In a program for quantitative PIXE analysis of thick sample (TSPIXE), the sample is divided into N_0 thin slices, the integration is replaced by the summation of X ray yields emerging from N_0 thin slices. If secondary fluorescence is neglected, the X-ray yield is given by:

$$Y(Z) = (\Omega_x / 4\pi)[NC_z \omega_z b_z \varepsilon_z (N_{av}/A_z)] \Sigma_{j-1}^{N_0} \sigma_z E(j)\, T_{zj} \triangle t \tag{2}$$

where $\triangle t$ is a real density (g/cm^2). $E(j)$ is proton energy at the jth slice, $\sigma_z[E(j)]$ is ionization cross section at energy $E(j)$ and T_{zj} is the attenuation of X rays created at the mean depth of jth slice.

Because many parameters are involved in the PIXE analysis of thick sample, such as ionization cross section, attenuation coefficients, ion energy loss, we have to choose theory and database carefully for obtaining accurate results. In TSPIXE program, we mainly choose them according to the study of J.L.Campbell *et al*[1] and Andersen and Ziegler's theory[2] was used to calculate the proton stopping powers. For the calculation of ionization cross section (ICS), the most successful model, ECPSSR theory[3] and the approach given by Cohen[4] and Benka's[5] tables of universal function were used to calculate the cross section of K and L shells. For K shells, the obtain better agreement with experiment we take the Paul's[6] analytical function s into consideration, i.e., the final cross section of K shells is equal to the cross section from ECPSSR theory multiplied by Paul's analytical function s.

$$\sigma^{\text{final}} = \sigma^{\text{ECPSSR}} \cdot s \tag{3}$$

Cohen's[7] five parameters model is used to calculate the efficiency of Si(Li) detector including filter effects. Over the energy range of 3 to 60 keV, the agreement of the model with experiment result is about ± 3 %[7]. The semiempirical approach given by Leroux and Thinh[8,9] is used to get the mass attenuation coefficients.

In TSPIXE program, the iterative method is used to calculate the concentrations relative to the internal standard and absolute concentration.

3 FRAME OF TSPIXE PROGRAM

The logical diagram of TSPIXE is shown in Fig.1. The program first get experimental conditions such as the incident energy of proton, the integrated current *etc*. According to the nature of the sample, user input how many slices (N_0) the sample is devided into, how much difference (D_0) between the results obtained from this time calculation and last time calculation in the iteration should be less than and how many times of iteration (T_0) are requested. From the output files of AXIL, a program for substracting peak areas of X-ray from spectrum, the elements of interest and their peak areas can be obtained. In the procedure of iteration, first looking the sample as one slice, the initial values (C_0) of elements of interest are obtained, then the smaple is divided into N_0 slices and calculate the concentrations of elements of interest. If the requirements of calculation are satisfied, i.e., $D_{j,j-1} < D_0$ or $T_{j,j-1} \geqslant T_0$, output the calculating results, if not, give the results of jth calculation (C_j) to C_0 and continue the calculation.

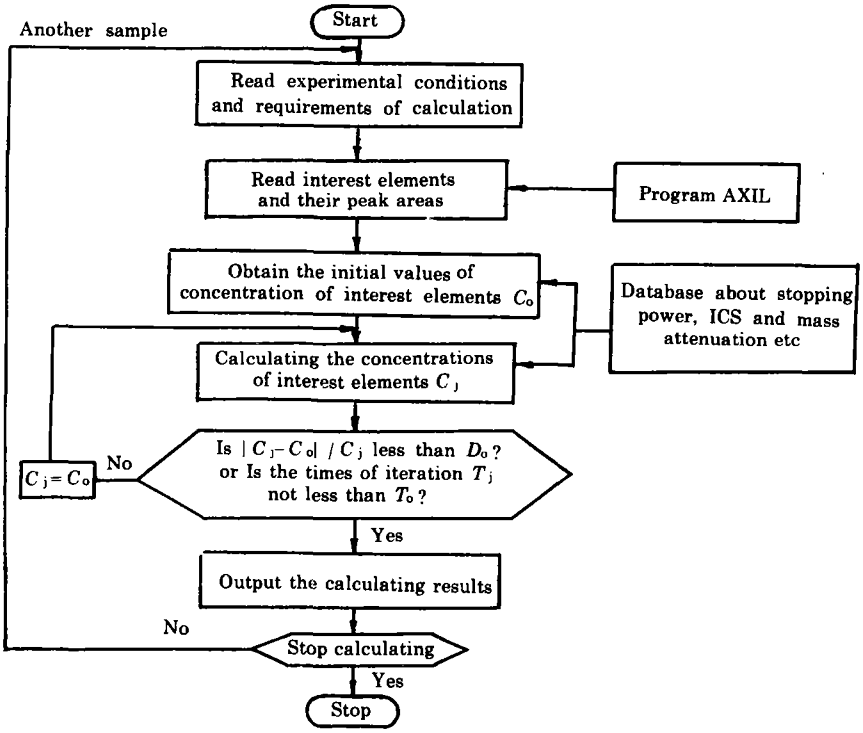

Fig.1 The logical diagram of TSPIXE

4 TEST OF TSPIXE

The program was tested using many reference materials, including biological and geological. Here the analytical result of bovine liver (NBS, SRM 1577) is presented. Firstly the liver powder was pressed into pellet (Diameter = 13.04 mm, Thickness = 0.48 mm, Density = 0.94783 g/cm^3) and then the thick sample was analyzed by μ-PIXE setup of Fudan University[10]. Using AXIL program, the peak areas of elements of interest were obtained. Finally, the absolute concentrations and relative concentrations taking sulfur as internal standard were calculated. The results are listed in Table 1. The certified values are from NBS, the absolute concentration is directly calculated from peak areas of elements of interest. The errors are obtained by formula:

$$\text{Error} = |\text{Calculated result} - \text{Certified result}| / \text{Certified result}$$

Table 1

TSPIXE analysis of SRM 1577

μg / g

	Certified from NBS	TSPIXE program			
		Absolute concentration	Error / %	Relative concentration	Error / %
P	1.11 wt %	1.073 wt %	3	1.16 wt %	5
S	0.78 wt %	0.717 wt %	8	0.78 wt %	0*
Cl	0.28 wt %	0.255 wt %	9	0.266 wt %	5
K	0.996 wt %	0.984 wt %	1	0.952 wt %	4
Ca	120	132	10	125	1
Mn	9.9	10.3	4	8.9	10
Fe	194	191	2	207	7
Cu	158	173	9	168	6
Zn	123	128	4	108	12

* Internal standard

5 CONCLUSIONS

TSPIXE has been proven to be a useful and reliable program for PIXE analysis of thick sample. The errors introduced in the program are about 10 %, but in a real experiment the overall accuracy of TSPIXE results is usually not lower than 10 %. The reason lies in the uncertainty of experiment data such as inaccuracy in detector efficiency, solid angle, integrated current, sample roughness and inhomogeneity.

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