



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Nonlinear Least-squares Fitting for PIXE Spectra

¹A. Tchanchane, ²M.A Benamar, ³A. Azbouche, ⁴N. Benouali and ³S. Tobbeche

¹University of El Aïn, El Aïn, United Arab Emirates

²Faculté des Sciences, Université de Blida, Blida, Algeria

³Centre de Recherche Nucléaire d'Alger 02, Boulevard Frantz Fanon, B.P. 399 Alger-Gare, Algiers, Algeria

⁴Centre de Recherche Nucléaire de Draria, Draria, Algeria

Abstract: An interactive computer program for the analysis of PIXE (Particle Induced X-ray Emission) spectra was described in this study. The fitting procedure consists of computing a function $Y(I, a)$ which approximates the experimental data at each channel I . a is a set of fitting parameters (energy and resolution calibration, X-rays intensities, absorption and background). The parameters of fit were determined by using a nonlinear least-squares fitting based on the Marquardt's algorithm. The program takes into account of low energy tail and escape peaks. The program was employed for the analysis of PIXE spectra of geological and biological samples. The peak areas determined by this program are compared to those obtained with AXIL code

Key words: PIXE spectra, least-squares fitting, microanalysis

INTRODUCTION

A reliable computer program that gives an accurate determination of the peak area of characteristic X-rays is of major importance for PIXE analysis. Knowing the expected X-ray yield of an element in a sample, the peak area is converted to elemental concentration. Therefore, a good estimation of the peak area is very crucial for the trace element analysis. PIXE spectra are complicated because of the existence of following effects:

- Interference between L and K lines of heavy and light elements respectively and between K_{α} and K_{β} lines of neighboring elements;
- Distortion of the lower side of the peak from the pure gaussian shape due to incomplete charge collection;
- Pile-up peaks due to high counting rates;
- Various physical sources contribute to the background;
- X-rays absorption into the sample and in filters and Si(Li) detector;
- Radiative Auger transitions.

This study deals with the description of a computer program that was developed to perform PIXE spectra analysis. The modeling method and the performance of the program were also described.

DESCRIPTION OF THE MATHEMATICAL MODEL

Several approaches of PIXE spectra fitting and peak modeling are described in the literature^[1-9]. In this program, the model function $Y(I)$ at channel I is defined as the superposition of an analytical function $B(I)$ that accounts for the background and a second term which accounts for all the element lines that may be present in the spectrum.

$$Y(I) = B(I) + \sum_{l=1}^{NE} P_l \sum_{k=1}^{NL_l} R_{k,l} \cdot Abs(E_{k,l}) \cdot [G_{k,l}(I) + Tail_{k,l}(I) + Esc_{k,l}(I)] \quad (1)$$

Where, NE and NL_l are the number of elements in the sample and the number of lines of element l , respectively. P_l is a free parameter corresponding to the area of the element l . $R_{k,l}$ is the relative intensity of K_{th} line of element l . Its's correct $Abs(E_{k,l})$ is a function depending on x-ray energy which corrects x-rays attenuation in the different absorbers. The absorption function at energy E_l corresponding to channel I is expressed as:

$$Abs(E_l) = Ab(E_l) \cdot Ab_f(E_l) \quad (2)$$

$Ab(E_l)$ describes the x-ray absorption into the Si(Li) detector and the filters. It is estimated by using the mass attenuation coefficients from the compilation of data of

McMaster *et al.*^[10]. $Ab_s(E_i)$ represents the sample self-absorption which is approximated by:

$$Ab_s(E_i) = \frac{1 - \exp(-b_1 E_i^{b_2})}{b_1 E_i^{b_2}} \quad (3)$$

where, b_1, b_2 are parameters.

$G_{k,1}(I)$ is an ideal gaussian representing the K_{th} line of the element l . $Tail_{k,1}(I)$ and $Esc_{k,1}(I)$ describe the low energy asymmetry and the escape peaks, respectively.

Background model: The background model is expressed as the sum of three components. It is given by the following formula:

$$B(I) = BPol(I) + BExp(I) + BRem(I) \quad (4)$$

$$BPol(I) = \sum_{j=1}^{NB1} a_{1,j} \cdot (I - I_0)^{j-1} \quad (5)$$

$$BExp(I) = a_{2,1} \cdot \exp \sum_{j=2}^{NB2} a_{2,j} \cdot (I - I_0)^{j-1} \quad (6)$$

$$BRem(I) = a_{3,1} \cdot Abs(E_i) \cdot \exp \sum_{j=2}^{NB3} a_{3,j} \cdot (I - I_e)^{j-1} \quad (7)$$

Where, I_0 is a fixed reference channel and I_e is the channel corresponding to the incident energy E_e transferred by incident proton to free electron. E_e is approximated by:

$$E_e = \frac{4m_e}{m_p} E_p \quad (8)$$

Where, m_e, m_p are the mass of electron and proton, respectively and E_p is the incident energy. NB1, NB2 and NB3 are constants.

The third term in the Eq. 4 accounts for the secondary electron bremsstrahlung background whereas the first two terms account for the other types of background, i.e. the Compton scattering and the proton bremsstrahlung background.

Gaussian shape: The ideal gaussian function $G_{k,1}(I)$ is expressed by:

$$G_{k,1}(I) = \frac{1}{2\pi\sigma_{k,1}} \cdot \exp\left(-\frac{I - C_1 - C_2 E_{k,1}}{2\sigma_{k,1}^2}\right) \quad (9)$$

Where, $\sigma_{k,1}^2 = \frac{1}{5,544} \Delta^2$ and $\Delta = C_3 + C_4 E_{k,1}$. Δ depicts the Full Width at Half Maximum (FWHM). C_1 and C_2 are the parameters of the linear energy calibration. C_1, C_2, C_3 and C_4 are handled as free parameters but varied under some constraints. They are included in the nonlinear gaussian model in order to achieve the energy calibration and the energy dependence of FWHM.

Low energy tail: A low energy tail is added to the pure gaussian. It takes into account the asymmetry of the lower side of the peak. In some cases, this tail may be neglected since more than 95% of the detected pulses are contained in a gaussian peak. However, when a weak peak is superposed to the tail of an intense neighboring peak, the relative area can be over or under estimated. In the program, we have used the method described by Marager *et al.*^[11]. The tail function $Tail_{k,1}(I)$ is given by:

$$Tail_{k,1}(I) = (4 + E_{k,1}) \cdot \exp(4(I - C_1 - C_2 E_{k,1})) \cdot \exp\left(\frac{-4(I - C_1 - C_2 E_{k,1})^2}{2\sigma_{k,1}^2}\right) \quad (10)$$

$$Tail_{k,1} = 0 \text{ if } I > C_1 + C_2 E_{k,1} \quad (11)$$

Escape peaks: The escape peaks are included in the program. They are treated as pure gaussians. The inclusion of the escape peaks tends to correct the Si- K_{α} secondary X-rays escaping from the sensitive volume of the crystal during the photon absorption. Their relative intensities are estimated by Clayton^[4]:

$$I_{esc} = 0.226(1 - 0.0141 E_{k,1}^{2.86} \cdot \log(1 + \frac{1}{0.0141 E_{k,1}^{2.86}})) \quad (12)$$

The energy of the escape peak is related to the energy $E_{k,1}$ of its parent element by:

$$E_{k,1}^{esc} = E_{k,1} - 1.739 \quad (\text{In ke V}) \quad (13)$$

1.739 keV is the Si- K_{α} energy.

The FWHM of the escape peak is chosen to be the same as for a characteristic X-ray peak at the energy $E_{k,1}^{esc}$.

NONLINEAR LEAST-SQUARES FIT

The experimental data are fitted by using the least-squares method. The parameters in the Eq. 1 are determined by minimizing the χ^2 function. The χ^2 function is defined as follows:

$$\chi^2(a, I) = \sum_{i=1}^{NC} \frac{(Y(a, I) - Y_i)^2}{Y_i} + f_c(C_1, \dots, C_4, b_1, b_2) \quad (14)$$

Where, $Y(I)$ is the model function, Y_i is the yield at channel I and NC is the number of channels in the spectrum. f_c is the constraint function and a is a set of fitting parameters (Table 1). We have based the nonlinear fitting on Marquardt's algorithm^[12] which combines both the linearisation of χ^2 function and the use of the gradient search in order to assure the convergence.

Table 1: List of fitting parameters (NP)

$a_{1,1}, \dots, a_{1,NB1}$	Polynomial background parameters
$a_{2,1}, \dots, a_{2,NB2}$	Exponential background parameters
$a_{3,1}, \dots, a_{3,NB3}$	Bremstrahlung parameters
C_1, \dots, C_4	Energy and resolution calibration parameters
b_1, b_2	Sample absorption parameters
P_1, \dots, P_{NE}	Element areas

Table 2: Comparison of K_{α} peak areas obtained with AXIL code and our program for a prawn sample PIXE spectrum

Elements	Peak area	
	AXIL code	This program
Fe	194	186
Cu	336	357
Zn	1344	1310
As	134	145
Se	17	24
Br	717	689
Rb	156	183
Sr	368	360

THE COMPUTER PROGRAM

The program is designed for a fast interactive operator control during off-line PIXE spectra analysis. The experimental data, the modeled spectrum and the modeled background may be visualized on a graphic terminal. The program is flexible and easy to use. All the input data are stored in one sequential file. The flow chart of the program is depicted on the Fig. 1. An additional option is included in the program which allows the determination of the background prior to the fitting. In this case, the background is modeled using a non polynomial approximation^[13] and stripped off from the original spectrum before its fitting. We have found this option very useful for fitting large region, small peaks and complex spectrum. The peak areas which are evaluated in the fitting process are converted to element concentrations using a separate program.

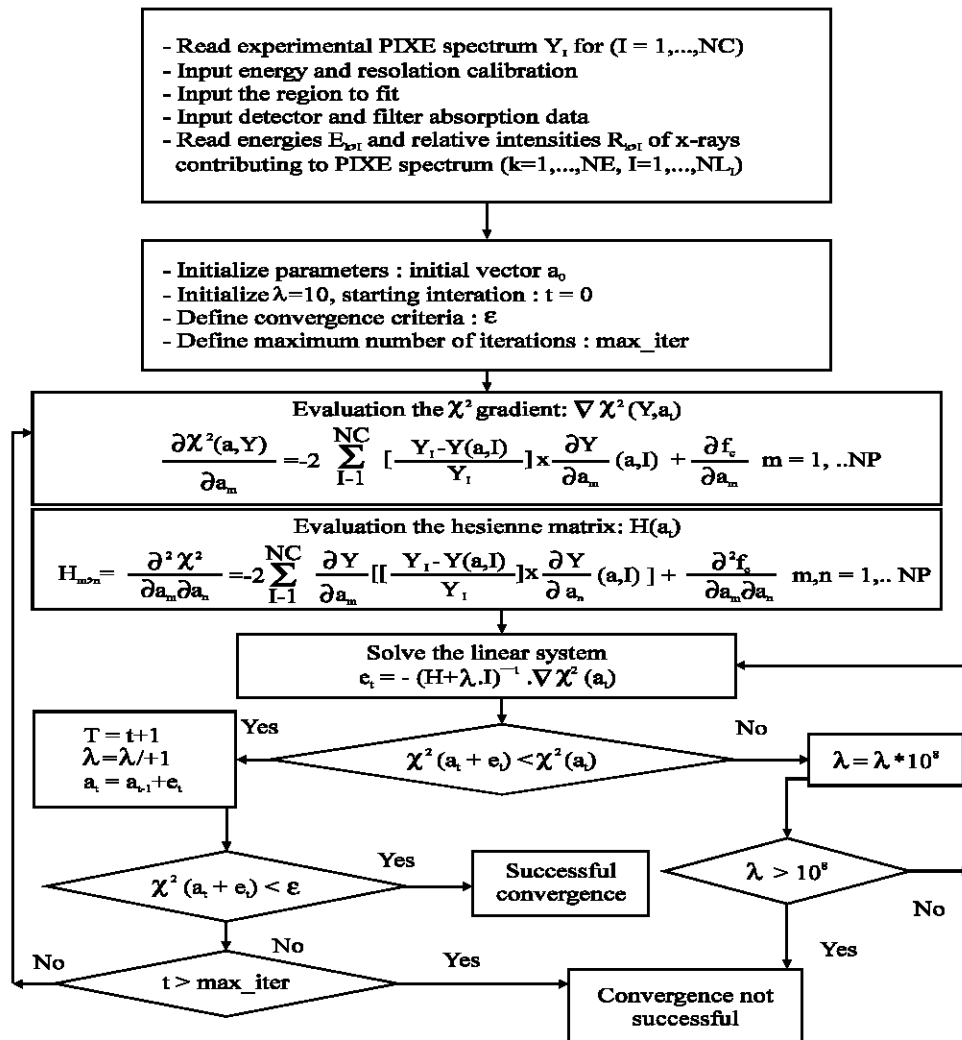


Fig. 1: Flow chart of the computer program

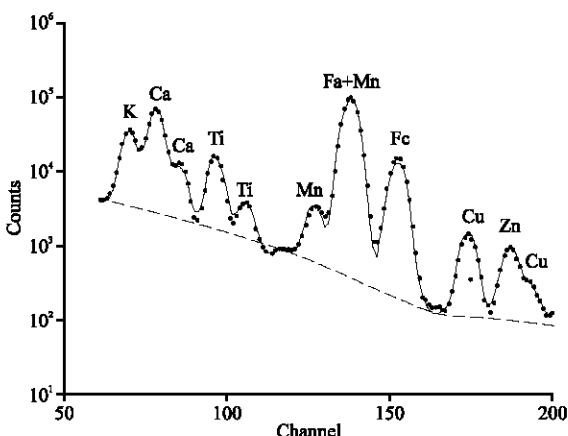


Fig. 2: Fits to the soil PIXE spectrum. Dots: experimental data, solid line: modeled spectrum, dashed line: modeled background

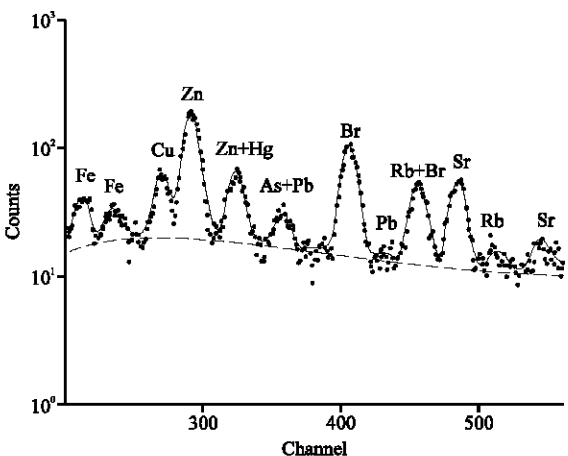


Fig. 3: Fits to the prawn PIXE spectrum. Dots: experimental data, solid line: modeled spectrum, dashed line: modeled background

APPLICATION

The computer program used to analyze PIXE spectra of geological and biological samples. The spectra were measured using 2.5 MeV protons of 10 nA beam current delivered by 3.75 MV Van de Graaff accelerator at Algiers. Two examples of fitted spectra are shown in Fig. 2 ($\chi^2 = 16$) and 3 ($\chi^2 = 15$)^[4]. The experimental spectrum is well reproduced by the fit and a good estimation of the background is noted (Fig. 2). The same spectrum was also analyzed by using AXIL code^[2]. The fit is obtained with ($\chi^2 = 1.2$). In Table 2, we compare the K_{α} peak areas of different elements evaluated with our program and AXIL code^[2]. One can notice that the values of peak areas are very similar. The observed deviations are due mainly to the statistical errors.

CONCLUSIONS

The described computer program is widely used in the laboratory to perform PIXE spectra analysis. The inclusion of escape peaks and the low energy tail leads to a more accurate evaluation of peak areas. The peak areas determined by this program are similar to those obtained with AXIL code. The program will be improved by the treatment of pile-up peaks stemming from high counting rates.

REFERENCES

1. Kaufmann, H.C., K.R. Akselsson and W.J. Courtney, 1977. REX: A computer program for PIXE analysis. Nucl. Instr. Meth., 142: 251-257.
2. Van Espen, P., H. Nullens and F. Adams, 1977. A method for the accurate description of the full-energy peaks in nonlinear least-squares analysis of X-ray spectra. Nucl. Instr. Meth., 145: 579-582.
3. Johansson, G.I., 1982. Modification of the HEX program for fast automatic resolution of PIXE spectra. X-Ray spectrom., 11: 194-2000.
4. Clayton, E., 1983. BATTY83: A computer program for thick target PIXE analysis. Nucl. Instr. Meth. Phys. Res., 218: 221-224.
5. Maxwell, J.A., R.G. Leigh, J.L. Campbell and H. Paul, 1984. Least-squares fitting of PIXE spectra with a digital filter treatment of the continuum. Nucl. Instr. Meth., B3: 301-304.
6. Maenhaut, W. and J. Vandenhaut, 1986. Accurate analytic fitting of PIXE spectra. Bull. Soc. Chim. Belg., 95: 407-418.
7. Bombelka, E., W. Koenig, F.W. Richter and V. Watjen, 1987. Linear least-squares analysis of PIXE spectra. Nucl. Instr. Meth., B22: 21-28.
8. Clayton, E., P. Duerden and D. Cohen, 1987. A discussion of PIXAN and PIXANPC: The AAEC PIXE analysis computer packages. Ibid, pp: 64-67.
9. Duffy, C.P., S.Z. Rogers and T.M. Benjamin, 1987. The Los Alamos PIXE Data Reduction Software. Ibid, pp: 91-95.
10. McMaster, W.H., N.K. Del Grande, J.H. Mallet and J.H. Hubbell, 1969-1970. Compilation of X-ray cross sections. University of California, Lawrence Livermore Laboratory Report, UCRL-50174.
11. Marageter, E., W. Wegscheider and K. Muller, 1984. A novel method for nonlinear least-squares analysis of energy-dispersive X-ray spectra. Nucl. Instr. Meth., B1: 137-145.

12. Marquardt, D.W., 1963. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Indust. Applied Math.*, 11: 431-441.
13. Kajfosz, J. and W.M. Kwiatek, 1987. Nonpolynomial approximation of background in X-ray spectra. *Nucl. Instr. Meth.*, B22: 78-81.
14. Benamar, M.A., I. Toumert, S. Tobbeche, A. Tchanchane and A. Chalabi, 1999. Assessment of the state of pollution by heavy metals in the surficial sediments of Algiers Bay. *Applied Rad. Isot.*, 50: 975-980.