



DT2 a PIXE spectra simulation and fitting package

M.A. Reis^{(a)*}, P.C. Chaves^(a), L.C. Alves^(a,b), N. P. Barradas^(a,b)

(a) ITN, EN10 Sacavém, Apartado 21, 2686-953 Sacavém, PORTUGAL

(b) CFNUL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, PORTUGAL

Abstract. Recently, a new PIXE code, LibCPIXE, was produced as a variant to the old DATTPIXE package but following a normally unused approach to PIXE data handling. In LibCPIXE, in opposition to most PIXE codes, PIXE set-up yields are simulated from first principles and experimental details of the measurement and the set-up facilities. This is the approach required to merge PIXE data handling code to other IBA data handling procedures, which many times requires a knowledgeable user interacting with the computer in order to build a good model for the sample, mainly when facing complex samples. The merging of LibCPIXE and NDF (a well known code for handling RBS and other IBA methods data) showed afterwards that complex structures in the samples can also dramatically change the observed PIXE yields. A full stepwise process was then undertaken in order to produce a new PIXE data handling code that uses this approach not only to simulate the K and L alpha yields of the elements, in structured samples, but to fit the entire PIXE energy spectra. This approach is of particular importance for the new high x-ray energy and high resolution PIXE set-up being installed at ITN, for the precise interpretation of PIXE spectra from complex targets, and also as a robust basis to RYIED work discussed elsewhere in this conference. In this communication we present the fitting core for the new DT2 package and discuss its capacity.

Keywords: Bayesian inference, spectra fitting, PIXE, relative intensity variations.

INTRODUCTION

The number of computer codes available to handle PIXE data is not very large (see for instances the review by Blaauw et al [1]), still, the operational methodologies used are still less variable. In the vast majority of the cases, the starting step is a deconvolution of the spectrum assuming a list of known atomic parameters, including among which the element line ratios. This is assumed necessary to overcome the problems of peak overlapping, and be able to properly quantify main lines which overlap minor ones, a quite frequent case. Still, the work being followed, since 2002, in Lisbon, at the ITN ion beam laboratory, on single element lines relative yield dependence on ion beam energy [2-4] as well as the problems faced during the analysis of complex layered targets [5-7], call for a different approach. In the case of the DT2 package, which is an evolution of the 1992

DATTPIXE package [8], this approach was setted immediately at the development stage as DT2 is being designed to be able to tackle also Relative Yield Ion Energy Dependence, RYIED [3] data, also referred in two other communications presented at this conference [9,10]. The essence of this new approach is the use of a robust fitting core capable of dealing with the problem of heavy line overlapping without lost of control and also capable of providing reliable fitting errors reports. A methodology of “computer assisted” interactive deconvolution process was selected for the new DT2 core, and a fitting code was produced which uses known atomic parameters, namely line ratios, just as a first coarse “wild” guess, while it produces as output an extensive list of the fitted areas of the peaks as well as the corresponding list of relative intensities for each line group used.

PACKAGE DESCRIPTION

Like in the case of DATTPIXE [8] the package is structured in blocks. Still, unlike DATTPIXE which uses a BASIC v7.1 code interface, the DT2 interface is written in Python and is therefore essentially platform independent, therefore aiming at having the final code running on both Linux and Windows. The interface handles in a user friendly manner all the steps necessary for preparing several input ASCII files required by each of the clustered active codes. The fitting routine and the data quantification steps remain separate as was already the case in DATTPIXE. This option not only gives the analyser the possibility of checking the process in a step by step approach as well as it provides a versatile code and the possibility of using package blocks separately. In the remaining text of this communication we will restrict the description to the new fitting routine which was named IBIXF (for Ion Beam Induced X-rays Fitting).

THE IBIXF PROGRAM

One of the main problems associated with fitting PIXE spectra is the common presence of many overlapping lines. This problem is aggravated by the complex form of the lines as detected by Si(Li) detectors, and is much more crucial in the case of L-spectra. A second problem which sometimes limits strongly the outcomes of the fitting is pile-up. This is well known to be a problem mainly in the low energy region of the spectra where pile-up rejection units quite often fail to operate properly. The third, although not so problematic step because it refers to a usually small contribution, is related to the continuous background removal. Still, irrespectively of its nature, contributions to the spectra are handled in IBIXF in a similar way, namely by establishing a first definition of shape of the contribution for each and every spectra component and have it calculated for all the spectrum channels, in an essentially normalization free way. The correct normalizing quantity is then fitted using a simulated annealing approach followed by a Bayesian inference routine developed by Barradas [11]. Calculating the contribution of each of the components passes by a detailed definition of the shapes of all of them. In the case of the x-ray lines, the model presented by Alves in 1996 [8] was used, and the x-ray energy dependence of the model parameters was fitted using the SigmaPlot® commercial package and a series of calibration K x-ray spectra having few overlapping lines. The model assumes that the Si(Li) detector response, $F(E)$, is expressed by a sum of four components :

$$F(E) = H_g \cdot [G(E) + C(E) + S_l(E) + G_e(E)] \quad (1)$$

where H_g is the line Gaussian height which is the fitting parameter in IBIXF exclusive to each x-ray line of energy E_0

$$G(E) = \left[\sqrt{2\pi} \cdot \sigma(E_0) \right]^{-1} e^{-\left[\frac{E - E_0}{\sqrt{2} \cdot \sigma(E_0)} \right]^2}$$

is the normalized main Gaussian peak, and $\sigma(E_0)$ is the x-ray line Gaussian standard deviation, obtained as a second order polinomial function of the x-ray line energy:

$$\sigma(E_0) = \sigma_{coef} (asig + bsig * E_0 + csig * E_0^2),$$

σ_{coef} is a fitting parameter, the same for all lines in the spectra, which may or may not be allowed to vary during the fitting process according to a flag provided in the input file.

$$C(E) = \frac{Ht_{ng}(E_0)}{4} \cdot e^{\frac{E - E_0}{\beta(E_0)}} \cdot \text{erfc}[t] \cdot \text{erfc}[s] \text{ with}$$

$$Ht_{ng}(E_0) = \frac{a_1}{E_0^{a_2}} + a_3 \cdot E_0 + a_4 \cdot E_0^2 + a_5 \cdot E_0^3,$$

$$t = \frac{1}{\sqrt{2}} \cdot \left[\frac{E - E_0}{\sigma(E_0)} + \frac{\sigma(E_0)}{\beta(E_0)} \right]$$

$$ts = \frac{(c1 + c2 \cdot E_0) \cdot E_0 - E}{\sqrt{2} \cdot \sigma(E_0)} \text{ and}$$

$$\beta(E_0) = (d_1 + d_2 \cdot E_0 + d_3 \cdot E_0^2 + d_4 \cdot E_0^3) \cdot \sigma(E_0),$$

$$S_l(E) = \frac{Hsl_{ng}(E_0)}{2} \cdot \text{erfc}[s] \text{ with}$$

$$Hsl_{ng}(E_0) = \frac{b_1}{\left\{ 1 + \left(\frac{E_0}{b_2} \right)^{b_3} \right\}^{b_5}} + b_4 \text{ and}$$

$$s = \left[\frac{E - E_0}{\sqrt{2} \cdot \sigma(E_0)} \right].$$

Finally, the Gaussian escape peak is expressed as,

$$G_e(E) = R \cdot e^{-\left[\frac{E - E_e}{\sqrt{2} \cdot \sigma(E)} \right]^2}$$

where

$R = \frac{\eta(E_0)}{(1-\eta(E_0))}$ is the ratio to the main line and,

$$\eta(E_0) = k_1 \cdot \left[1 - k_2 \cdot E_0^{k_3} \ln \left(1 + \frac{1}{(k_2 \cdot E_0^{k_3})} \right) \right].$$

The parameter values adjusted to the ITN Gresham Scirus Si(Li) detector were as follows: *i) asig*, *bsig* and *csig*, 3.819e-2, 6.220e-3 and -2.295e-4, *ii) a1* to *a5*, 0.1436686, 3.610927, 1.0096680e-2, -3.015231e-3 and 2.271632e-4, *iii) c1* and *c2*, 0.686141 and 6.26161e-3, *iv) d1* to *d4*, 1.00, -2.570317e-1, 7.685280e-1 and -4.812815e-2, *v) b1* to *b5*, 3.2349e-4, 1.8638, -5.5347, 2.5044e-4 and 5.2, and *vi) k1* to *k3*, 0.03196, 0.03927 and 2.5661.

The background is composed of a non adjustable linear contribution and two bump shaped forms, which height is fitted independently while the shape is fixed by the operator by adjustment of six input parameters. Each of the two bump background curves, $B_n(i)$ was chosen ad-hoc to have a form given by the equation:

$$B_n(i) = x^{-(b \cdot x)^2} \text{ being } x = (E(i) - E_0) / E_c$$

Where i is the channel number, $E(i)$ is the x-ray energy corresponding to the channel number i and E_0 , E_c and b are the input parameters adjusted by the operator. For channels having an energy below E_0 , $B_n(i)$ is assumed constant. Each background contribution is calculated for the whole spectrum range like all individual x-ray lines, and added also in the same way as all x-ray lines.

In what concerns pile-up, a decision was made for using the recently implementation of the absolute pile-up ab-initio Wielopolski algorithm [9] and allow the shape obtained height to be slightly adjusted during the fitting process.

RESULTS AND DISCUSSION

Figure 1 shows details on the pile-up fitting of the Mo-L spectrum of a 99.99% pure Mo foil. The combination of the use of the Wielopolski algorithm and the above shaped background allows for a perfect reproduction of the uncorrected pile-up to such a detail that the small contamination of the Mo foil can be seen. It is important to notice here that a ratio of roughly 0.5/1000 is to be found between the Mo-L height and the contamination lines.

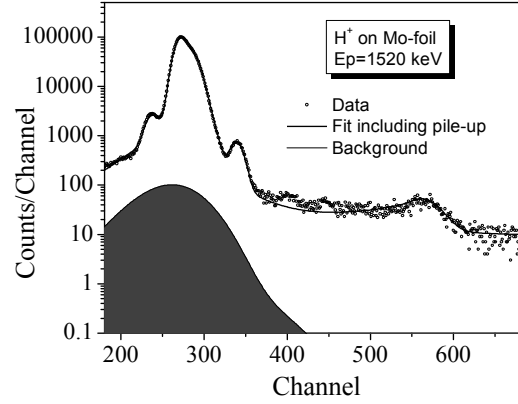


FIGURE 1. Details on the pile-up fitting of the Mo-L spectrum of a 99.99% pure Mo foil.

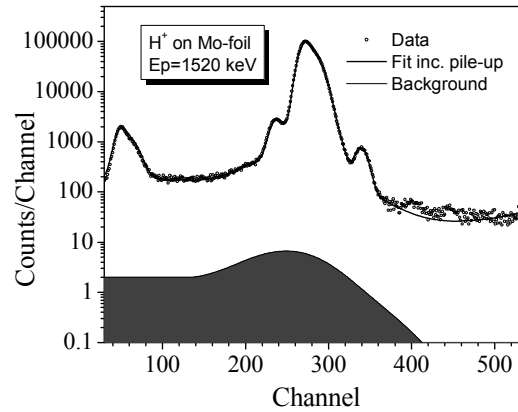


FIGURE 2. Detail of the peak tails and low energy side background of the fitting of the Mo-L spectrum of a 99.99% pure Mo foil.

In Figure 2, the details on the peak tails and background are shown for the fitting of this Mo-L spectrum. Both the escape peak and the low energy spectra are perfectly fitted, thus showing that this ad-hoc background function can be made to reproduce quite well the expected background.

In Figure 3 a spectrum of Gd-L lines from a GdDOTA complex collected with a thick Mylar x-ray absorber, is presented. GdDOTA is a chelate complex of Gadolinium used as base for contrast agents in Nuclear Resonance Imaging. In this figure, a simulated high resolution spectra, which assumes a detectors resolution 10 times better than the Si(Li) resolution is also presented, and it can be seen that the expectable advantage of such a detector are overwhelming. In

fact, the simulated high resolution spectra characteristics allowed us to use it to plot the shape of the background for this case. It can be seen that the ad-hoc function used is well tuned to deal with the background for this type of situation as in fact, were it not for the background contribution and a unexplained region would be present between the $L\alpha$ and $L\beta$ groups. In the case of this spectrum, 37 independent lines were fitted for Gd (about 17 groups can be seen in the simulated high resolution spectrum) and additional ones were required to fit a Ca contamination, responsible for the low energy “background” look of the spectrum. Many of the peak areas were determined with an error of 5% or less as is pointed out in two other communications presented also at this conference.

CONCLUSIONS

PIXE data handling software is normally based on the deconvolution of spectra assuming well defined atomic parameters, which values appear changed in spectra just due to matrix effects. Still, since 2002, the work carried out in respect to the variation of relative line intensities shows that new approaches are required. DT2 is a new software package, inspired in its predecessor DATPIXE [2] in respect to user friendly interfaces, but in a totally new approach relative to spectra fitting. We have here shown that the new IBIXF fitting core is perfectly capable of dealing with many independent lines without following into conditions of strong indetermination. So far only the interface and the IBIXF core are operational, the full package is expected to be operational in a very near future.

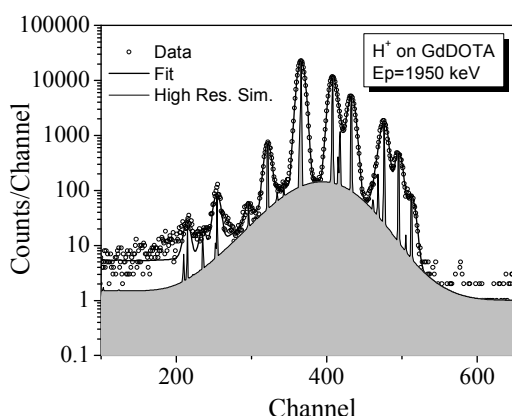


FIGURE 3. The whole region of interest used for fitting of a Gd-L spectrum from a 97.5% pure GdDOTA complex. Besides the 37 lines of Gd fitted, a Ca contamination was determined which is responsible for the low energy “background” counts seen in the spectrum.

REFERENCES

1. M. Blaauw, J.L. Campbell, S. Fazinic, m. Jaksic, I. Orlic, p. van Espen, Nuclear Instruments and Methods in Physics Research, B 189 (2002) 113-122
2. P.C. Chaves, M.A. Reis, Proceedings of the X International Conference on PIXE and its Analytical Applications, Portorož, Slovenia, June 4-8, – IJS, Ljubljana 2004 (ed. in CD-ROM).
3. M.A. Reis, P.C. Chaves, J.C. Soares, Nuclear Instruments and Methods ion Physics Research, 229 (2005) 413-424.
4. P. C. Chaves, M.A. Reis, N. P. Barradas, Matjaž Kavčič, Nuclear Instruments and Methods in Physics Research B (2007) (in press)
5. G.González Aguilar, A. Wu, M.A. Reis, A.R. Ramos, I.M. Miranda Salvado, E. Alves, M.E.V. Costa, Surface Science 600 (2006) 1780-1786
6. C. Pascual-Izarra, M.A. Reis, N.P. Barradas, Nuclear Instruments and Methods in Physics Research B 249 (2006) 780-783
7. M.A. Reis, N. P. Barradas, C. Pascual-Izarra, P.C. Chaves, A.R. Ramos, E. Alves, G. González-Aguilar, M.E.V.Costa, I. Salvado, Nuclear Instruments and Methods in Physics Research B (in press)
8. M.A. Reis, L.C. Alves, Nuclear Instruments and Methods in Physics Research B68 (1992) 300-304
9. M.A. Reis ,P.C. Chaves, A. Taborda, A. Carvalho, this conference, PI-6
10. P.C. Chaves, M.A. Reis, M. Kavčič, this conference, PI-4
11. N.P. Barradas, private communication (2006)
12. L.C.Alves, A.P.Jesus, M.A.Reis, Nuclear Instruments and Methods in Physics Research B109/110 (1996) 129-133
13. N.P. Barradas, M.A. Reis, Accurate calculation of pileup effects in PIXE spectra from first principles, X-ray Spectrometry 35 (2006) 232-237