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High energy PIXE: A tool to characterize multi-layer thick samples

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ABSTRACT

High energy PIXE is a useful and non-destructive tool to characterize multi-layer thick samples such as cultural heritage objects. In a previous work, we demonstrated the possibility to perform quantitative analysis of simple multi-layer samples using high energy PIXE, without any assumption on their composition. In this work an in-depth study of the parameters involved in the method previously published is proposed. Its extension to more complex samples with a repeated layer is also presented. Experiments have been performed at the ARRONAX cyclotron using 68 MeV protons. The thicknesses and sequences of a multi-layer sample including two different layers of the same element have been determined. Performances and limits of this method are presented and discussed.

1. Introduction

Analysis of cultural heritage objects is a very active application field for the PIXE method [1–3], especially thanks to its ability to determine their elemental composition in a non-destructive way. In many cases, those objects consist of a stack of many layers (paintings, coins...) with sometimes several layers made of the same element. Differential PIXE [4], using low energy beam, was developed in order to provide depth concentration profile, composition and ordering of the layers. The principle of this technique relies on the comparison between PIXE spectra recorded at different beam energies [5] (e.g from 1 to 4 MeV) or at different incident angles [6]. Complementary information about the target is obtained for each measurement due to the strong variation of the ionization cross sections, at low energy, within the target. It is, therefore, possible to use a de-convolution algorithm to extract the contribution of each layer. Differential PIXE has been used to study multi-layer samples [7] with a thickness up to tens of microns [8].

High-energy PIXE (HEPIXE) is suitable to perform non destructive analysis of thick samples, in normal air, due to the high penetration range of energetic light ions in matter and their ability to excite the energetic K X-rays. HEPIXE has already been used in the field of cultural heritage [9–11] and especially for the characterization of ancient paintings with several superposed layers [12]. Metallic archeological objects can be also investigated without removing the patina layer present on their surface. The investigated thicknesses in those works were between few dozens and few hundred of micrometers. But in this case, contrary to the usual differential PIXE method, ionization cross sections change smoothly with the energy and incident angle variation. However, HEPIXE analysis using $\frac{K_\alpha}{K_\beta}$ (or $\frac{K_\alpha}{L_\alpha}, \frac{L_\alpha}{L_\beta}$) ratio provides qualitative information about the thicknesses and the sequences of several layers but assumptions on the sample composition is required [12]. In a recent work [13], we demonstrate the possibility to perform quantitative analysis of simple multi-layer samples without any assumption on their composition. This method, based on the relative variation of $\frac{K_\alpha}{K_\beta}$ (or $\frac{K_\alpha}{L_\alpha}, \frac{L_\beta}{K_\alpha}$) when the sample is rotated, had given good results for patterns of different pure material foils. But in more realistic applications, there might be some repetition of a layer inside the samples. The present work aims at studying samples with repeteated layers based also on the relative variation of $\frac{K_\alpha}{K_\beta}$ (or $\frac{K_\alpha}{L_\alpha}, \frac{L_\beta}{K_\alpha}$) ratio. This study is an extension of the previous method [13] and it is a step further to develop an acurate quantitative method in order to analyze cultural heritage samples later on. Firstly the experimental setup is described. Secondly, the key parameters of the method such as the self attenuation and the impact of the layer placed in front of the emitting one are described. Finally, the extension of the previous method [13] to the analysis of a multi-layer sample with a repeated layer is presented.

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2. Experimental procedure

2.1. Experimental set-up

High energy experiments were carried out at ARRONAX cyclotron [14] using 68 MeV protons. The beam diameter on the sample was in the range of 1 cm. The X-rays are detected by a High Purity Germanium (HPGe) detector. The distance between the sample and the detector is 25 cm. The sample holder can be rotated with respect to the incident beam in order to change the angle between the sample and the detector, with a precision of 0.01°. An ionization chamber is used in order to monitor the number of particles penetrating the samples. The ionization chamber current is measured by a high precision commercial electrometer (MULTIDOS-PTW). Prior to the samples irradiations, the ionization chamber is calibrated using a faraday cup. During the experiments, the beam intensity is kept around 100 pA and the irradiations last about 15 min. The high energy PIXE platform is described in more details in [15].

2.2. Studied samples

The composition and the thickness of the samples prepared for this work are listed in Table 1. The samples are composed by a stack of several pure material foils. Those foils are provided by GoodFellow and their dimensions are 25 × 25 mm^2. The Al-Ti sample is used to study the linearity of $\Delta\mu \cdot d$ (see Section 3.2) involved in the determination of the layers thicknesses. The Ti-Ag_1-Au-Ag_2 is prepared as a multi-layer sample with a repeated layer in order to perform the associated analysis. References samples for each elements are also irradiated using the same experimental configuration as the Ti-Ag_1-Au-Ag_2 irradiation. Those reference samples are used to reduce the experimental errors (such as detection efficiency) on the quantification of the layers thicknesses.

The thicknesses of the foils presented in Table 1 are given by GoodFellow. Acurate values obtained using a scanned and a high precision scale for the Ti of Ti-Ag_1-Au-Ag_2 are presented in Table 4.

2.3. Multi-layer analysis method

The analysis method [13] is based on the relative variation of $\frac{K_\alpha}{K_\beta}$ (or $\frac{K_\alpha}{L_\alpha}, \frac{L_\beta}{K_\alpha}$) ratio ($K_\alpha$ is the number of detected K_α X-rays), named $\frac{\Delta R}{R}$, as a function of the angle between the target and the detector, $\theta = 0$ when the detector axis is normal to the sample, i.e their surfaces are parallel. This relative variation is given by:

$$\frac{\Delta R}{R} = \frac{R(\theta_1) - R(\theta_2)}{R(\theta_1)} = 1 - f_{\text{self}} \cdot \frac{e\left(\frac{\Delta\mu \cdot d}{\cos(\theta_2)}\right)}{e\left(\frac{\Delta\mu \cdot d}{\cos(\theta_1)}\right)}, \tag{1}$$

where $\Delta\mu = \mu_{K_\beta} - \mu_{K_\alpha}$ with μ the attenuation coefficient [16] of the layers placed in front of the emitting one, d is X-rays path in this layer and f_{self} is given by the equation:

$$f_{\text{self}} = \frac{\left(\frac{1-e^{\left(\frac{-\mu'_\alpha \cdot d'}{\cos(\theta_2)}\right)}}{1-e^{\left(\frac{-\mu'_\beta \cdot d'}{\cos(\theta_2)}\right)}}\right)}{\left(\frac{1-e^{\left(\frac{-\mu'_\alpha \cdot d'}{\cos(\theta_1)}\right)}}{1-e^{\left(\frac{-\mu'_\beta \cdot d'}{\cos(\theta_1)}\right)}}\right)}, \tag{2}$$

where μ' is the attenuation coefficient of the emitting layer and d' the X-rays path inside it. The function f_{self} represents the ratio of the $\frac{K_\alpha}{K_\beta}$ attenuation in the emitter layer itself, in other words the self attenuation. The impact of this factor is presented in the next section.

When f_{self} is negligible, we can extract from Eq. (1):

$$\Delta\mu \cdot d = \frac{1}{\frac{1}{\cos(\theta_2)} - \frac{1}{\cos(\theta_1)}} \cdot ln\left(1 - \frac{\Delta R}{R}\right). \tag{3}$$

$\Delta\mu \cdot d$ contains the attenuation of the effective layer located between the emitting one and the detector (the effective layer has the same effect on the X-ray attenuation than real layers). Using the photoelectric mass attenuation coefficient (far from the shell edge), $\frac{\mu}{\rho}$ given in [17] and Eq. (3) we can calculate the attenuation of K_α lines (or $K_\beta, L_\alpha, L_\beta$) M_{K_α}

$$M_{K_\alpha} = \sum_{i=0}^{n} e^{(-\mu^i_\alpha \cdot d^i)} = e^{-\Delta\mu \cdot d \cdot \left(\frac{\frac{1}{(E_{K_\alpha})^{7/2}}}{\frac{1}{(E_{K_\beta})^{7/2}} - \frac{1}{(E_{K_\alpha})^{7/2}}}\right)}, \tag{4}$$

where n is the number of layers placed in front of the emitting one and E the energy of the considered X-ray. The detected number of K_α X-rays (or $K_\beta, L_\alpha, L_\beta$), $N^{layer}_{K_\alpha}$, can then be corrected from this attenuation. Therefore we can determine the thickness of a layer, e_{layer}

$$e_{layer} = -\frac{1}{\mu'_\alpha} \cdot ln\left(1 - \frac{N^{layer}_{K_\alpha}}{N^{Standard}_{K_\alpha} \cdot M_{K_\alpha}}\right), \tag{5}$$

where $N^{Standard}_{K_\alpha}$ is the X-ray intensity of a standard sample irradiated in the same condition.

To determine the sequence of a multi-layer sample, $\Delta\mu \cdot d$ can't be used because of its dependency on the energy of the X-rays. Using the definition of $\frac{\mu}{\rho}$ given in [17], we can calculate a new term $(\Delta\mu \cdot d)'$ defined by Eq. (6).

$$(\Delta\mu \cdot d)' = \frac{1}{\frac{1}{E^{7/2}_{K_\beta}} - \frac{1}{E^{7/2}_{K_\alpha}}} \cdot \frac{1}{\frac{1}{\cos(\theta_2)} - \frac{1}{\cos(\theta_1)}} \cdot ln\left(1 - \frac{\Delta R}{R}\right) \tag{6}$$

$(\Delta\mu \cdot d)'$ is also equal to: $\rho \cdot d \cdot Z^5 \cdot \frac{N_a}{A}$, where E is the energy of the considered X-ray, N_A is the Avogadro constant and Z, A, ρ, d are the effective atomic number, mass number, density and thickness of the layers placed in front of the emitting one. The comparison between $(\Delta\mu \cdot d)'$ values for each detected elements allows to determine the sequences of the layers (demonstrated in [13]).

3. Robustness of the method

In this section, the main parameters (described in the previous section) of the analysis method are studied.

3.1. Self attenuation

The relative variation of R, $\frac{\Delta R}{R}$, is function of the self attenuation and of the attenuation inside the layers placed above the emitting one. In order to use $\frac{\Delta R}{R}$ to determine the thickness and the position of the emitting layer, the self attenuation factor has to be small

Table 1
Composition of the irradiated samples for this study. The value in the parenthesis is the thickness of the given pure foil.

Sample name	Composition
Al-Ti	Al(20 μm)/Ti(10 μm)
Ti-Ag_1-Au-Ag_2	Ti(10 μm)/Ag(10 μm)/Au(10 μm)/Ag(25 μm)
Ti_{ref}	Ti(10 μm)
Ag_{ref}	Ag(10 μm)
Au_{ref}	Au(10 μm)