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Towards a sharpest interpretation of analytical results by assessing the uncertainty of PIXE/RBS data at the AGLAE facility

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ABSTRACT

The advances in object analysis and data processing are a real asset in science and in particular in the cultural heritage field. However, results interpretations depend on the reliability of the information obtained on the archaeological material studied. At the AGLAE facility, a specific methodology using the theory of analysis of variance (ANOVA) was followed in order to calculate the uncertainty of the PIXE and the RBS analyses due to the machine and to the data processing. Repeatability and reproducibility of measurements are studied on three PIXE standards and one RBS standard and the corresponding uncertainties are developed. Then results of RBS analyses on cultural heritage objects are presented to illustrate the discussion.

1. Introduction

For more than 25 years in Le Louvre premises, non-invasive study of cultural heritage materials by ion beam analysis (IBA) at the AGLAE facility gives precious information on their provenance, manufacturing process or conservation state, which are essential issues in archaeology [1–4]. Directly applied in air on objects presenting various sizes, shapes and conservation states, PIXE (Particle Induced X-ray Emission), PIGE (Particle Induced Gamma-ray Emission), RBS (Rutherford Backscattering Spectroscopy) and IBIL (Ion Induced Iono-Luminescence) are IBA signals that can be simultaneously measured at the AGLAE facility [5,6]. Systematic imaging of such complementary information can be made from tens of μm^2 up to several cm^2 area size [5,7–9].

Scientific results presented in lectures or publications should permanently be accompanied with the corresponding uncertainty. In the cultural heritage field, this uncertainty of experimental data can be significant, as objects are most of the time heterogeneous, rough, porous, etc. [9]. However, appraising these values is of great importance as it allows a discussion on the reliability of the results and of the interpretations made from the experiments.

The uncertainty of experimental data can be divided in two parts: one concerns the object itself (area representation, potential sample collection and preparation) and the other one concerns the analysis (uncertainty due to the instrument and data processing). If the former can be appraised by the users, the latter is of great importance for the AGLAE operators in order to assess the energy stability of the beam and to offer the best experimental conditions to the users. Moreover, the *New AGLAE* project (grant ANR-10-EQPX-22) aims at automating the accelerator and improving the stabilization of the beam in energy and position. The new beamline will be operational in 2017 and the uncertainty of the measurements is expected to decrease enabling sharpest data interpretations.

However, determining uncertainties is not always easy to reach. For many experiments, two or more analyses are made for each sample or object, or even for each area of an object, in order to present an average result of the experiment. As for each measurement an uncertainty can be calculated from all factors described above, then how will be calculated the uncertainty of the average result for the entire experiment or the entire object? And how this calculation will help assessing the instrument stability and the data processing reliability?

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In order to reach this aim for PIXE and RBS analyses at the AGLAE facility, repeatability and reproducibility methodologies were performed on three reference glasses and on a gold-layered standard, usually reserved to respectively calibrate PIXE and RBS spectra.

2. Methods

2.1. The AGLAE set-up

Experiments were performed at the AGLAE facility at atmospheric pressure with an external beam composed of protons particles at 3 MeV. The beam was 30 µm in size with 0.3 µC and 0.7 µC integrated charge for each run respectively on PIXE and RBS standards.

The beamline nozzle ends with a 100 nm thick Si_3N_4 window, representing the interface with the atmosphere, and the target was placed at a work distance of 2 mm.

PIXE spectra were collected with one SDD Low Energy X-ray (LE) detector and two SDD High Energy X-ray (HE) detectors, positioned respectively at 45° and 50° relative to the beam axis [5]. The LE detector, which had no filter, enabled the detection of light elements thanks to a helium flow whereas each one of the HE detectors was covered by a 50 µm thick aluminum filter. In order to obtain the average concentration of each element for the standards, PIXE measurements consisted in one cartography of $500 \times 500\ \mu m^2$ on their surface, and one sum spectrum is extracted from each map. The targets presented here are three of the four Corning archaeological reference glasses which chemistry is well known [10]: glass A, B and D.

RBS measurements were performed with a detector collecting backscattered protons set at 130° with respect to the incident beam (Fig. 1a). The housing of the detector is placed under vacuum and, as for the nozzle, is terminated by a 100 nm thick Si_3N_4 window. The target is a multi-layered standard composed by a superficial 1.6-µm-thick layer of gold applied on a SiO_2 substrate with in between a 10-nm-thick adhesive chrome layer (Fig. 1b).

2.2. Data processing for PIXE and RBS analyses

Particle Induced X-ray Emission (PIXE) analysis is based on the X-ray emission after the atomic interactions between incident charged particles and electrons present in the target. PIXE data were processed using the GUPIXWIN calculation engine [11] coupled to the in-house TRAUPIXE software [9]. The composition of the target obtained from the LE and the HE detectors can be combined by using the iron as the pivot element, which means that it must be present in both spectra. The quantitative composition of the analyzed materials is obtained for matrix and trace elements and, to perform these calculations, the target is assumed to be thick and homogeneous. For the results presented here, only elements quantified as above the detection limit were considered.

The Rutherford Backscattering Spectroscopy is based on the elastic collision between incident charged particles and nucleus of atoms present in the analyzed target [12]. RBS data were processed using the SIMNRA software V6.05. This program aims at simulating RBS spectra (Fig. 2) and comparing them to the experimental ones in order to assess the composition and the thickness of the different layers of the sample analyzed [13]. To simulate a spectrum, once the experimental set-up is defined (see above), the target is described as a succession of layers specifying, for each layer, its thickness and the relative atomic concentration of elements. The value of the thickness is given in Thin Film Unit (TFU), corresponding to 10^{15} atoms cm^{-2}. As for Au $1{\cdot}10^{15}$ - atoms cm^{-2} corresponds to 0.1694 nm, the thickness of a 100%-Au layer of in the metric system is expressed from the thickness in TFU by [12,14]:

$$e_{nm} = e_{TFU} \times 0.1694 \quad (1)$$

The aspect of the RBS spectra can be altered by multiple factors, two of them will be discussed here: the porosity of the layers, and the roughness of the surface.

To simulate the first factor, the elements of the underlying layer can be added in the porous layer, which will reduce the relative concentration of the elements of the layer. Indeed the porosity of a layer will induce a decrease of the intensity of the peaks coming from the elements present in this layer.

Concerning the second factor, the back edge of the peak of the elements present in the rough layer in the experimental spectrum will not be vertical as the theory would plot it. A specific option is present in the SIMNRA software to simulate its effect on the spectrum: a full width at half maximum (FWHM) can be defined in TFU for the considered layer to determine the width and shape of the thickness distribution (SIMNRA assumes a Gamma distribution of layer thicknesses, resembling a Gaussian distribution visible on the spectra) [15,16]. When the simulated spectrum with a defined standard derivation is considered as the closest representation of the experimental spectrum, the uncertainty due to the roughness can be calculated as follow [15,16]:

$$\sigma = \mathrm{FWHM}/2.35 \quad (2)$$

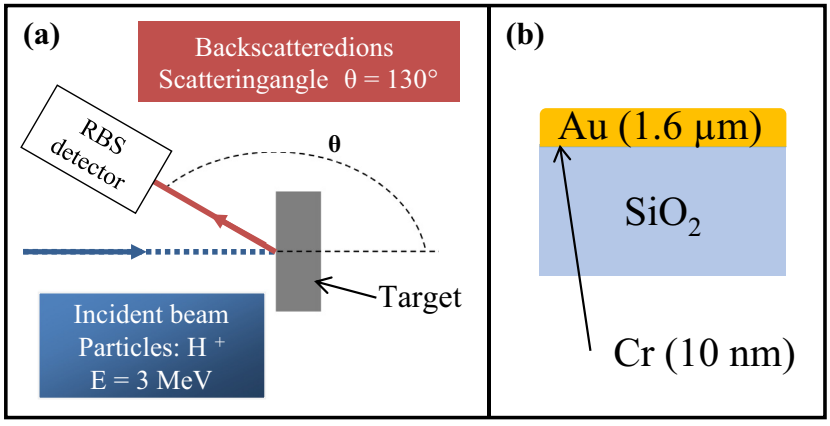

Fig. 1. (a) AGLAE set-up for RBS analyses; (b) description of the standard used as a target to estimate the uncertainty of RBS analyses due to the instrument and to the data processing.

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