Nuclear Instruments and Methods in Physics Research B 269 (2011) 2999–3005

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

IBA techniques: Examples of useful combinations for the characterisation of cultural heritage materials

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ARTICLE INFO

Article history:
Available online 22 April 2011

Keywords:
Ion beam analysis
Cultural heritage
RBS
PIXE
PIGE
Silver
Bone
Coins

ABSTRACT

For many years, ion beam analysis techniques have successfully been used to the study of cultural heritage objects. The chemical composition of work art is usually determined by PIXE, but in many cases, RBS and/or PIGE can provide useful complementary information. RBS gives information about the depth distribution and concentration in light elements, such as carbon and oxygen. In the past years, the experimental facilities at the AGLAE (Accélérateur Grand Louvre d'Analyse Élémentaire) accelerator has been progressively developed in order to apply simultaneously PIXE, PIGE and RBS under optimal conditions using an external beam. This combination is now routinely used for point analyses or mappings. In this contribution, we present several examples of applications: manufacturing technology of lustre-decorated ceramics and silver plating, control of altered or restored surfaces, and quantification of organic phase in painting and bone. The final conclusion is that the association of PIXE with RBS is very attractive for the investigation of cultural heritage objects, in particular of materials containing both mineral and organic components or possessing a multilayered structure. The first results of the production of monochromatic X-rays for radiography purposes by PIXE are also presented.

1. Introduction

It is now well known that ion beam analysis is a valuable investigation technique for the analysis of objects of the cultural heritage [1]. PIXE has been successfully applied to the determination of the origin of gems [2], obsidian [3] or prehistoric pigments [4] as well as to the analysis of paintings [5] and metals [6–8].

However, PIXE has some limitations, namely the lack of depth information or the low sensitivity to light elements. For these reasons, the external beam of AGLAE (Accélérateur Grand Louvre d'Analyse Élémentaire) has been continuously modified to enable the use of RBS at atmospheric pressure [9]. The facility has more recently been improved in order to perform PIXE and RBS simultaneously [10]. Through this combination, the number of detected elements is increased and depth distribution information provided. This combination, which gave already original results on patination [11] or on Renaissance paintings [12,13], is now routinely used and applied systematically whatever the nature and the structure of the object under investigation.

In the first part of this contribution, different cases, where PIXE and RBS are particularly complementary, will be presented. In the case of layer-structured materials (e.g. intentional coating of metals, such as gilding and silvering), the analysis can provide technological information about the manufacture of the objects, while for altered surfaces, the PIXE–RBS combination is essential for an accurate quantification of the elements. In addition, the implementation of RBS with PIXE provides data for light element quantification. It will be also shown how the information on light elements and particularly on carbon and oxygen, which are present in organic compounds such as varnish, binder, protective product and in biomaterials such as bone, is useful.

In a second part, preliminary results on X-radiography performed using monoenergetic X-rays produced by proton bombardment of a metal target, will be discussed.

2. The PIXE–RBS combination

2.1. The experimental setup

In the past years, two different approaches were developed for the nozzle design of the AGLAE external beam line [10].

A first setup was based on separated and mechanically independent components: a beam extraction nozzle with a 100 nm thick Si_3N_4 window, two Si(Li) X-ray detectors, one surface barrier (SB) detector mounted in a small chamber under vacuum separated by a 100 nm thick Si_3N_4 window, one HP-Ge detector and a dose

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doi:10.1016/j.nimb.2011.04.059

detector using a PIN diode Peltier cooled detector for measuring the Si X-rays emitted by the exit window.

A second, more elegant, setup was then developed by integrating the SB detector in the exit nozzle in order to reduce the size of the previous set-up and improve the beam monitoring. The integrated annular SB detector, placed at of 170°, was used for both the RBS measurement and the dose monitoring. This compact system was mainly utilised for the simultaneous PIXE and RBS using 6 MeV $^4He^{2+}$-ions [14].

Presently, an upgraded version of the first arrangement is mainly used (Fig. 1). Three main modifications have been introduced:

(1) The vacuum inside the nozzle has been improved by adding a small turbo-pump on the back of the beam extractor. A better vacuum reduces the carbon deposition on the Si_3N_4 membrane and the quality (shape and size) of the beam is improved.
(2) The RBS detector is mechanically interdependent of the nozzle allowing more accurate and easier adjustments preserving the alignments. The RBS detector is now permanently mounted for all the experiments.
(3) The dose monitoring is still based on the principle of the detection of the Si K-line emitted by the Si_3N_4 exit window but the design was improved by using a weightless system. This system consists of an X123-SDD detector (area: 7 mm^2, crystal thickness: 450 μm, Be window thickness: 25 μm), a preamplifier, a digital processor, and a power supply. The installed version has the detector and the preamplifier removed from the electronics box and connected with a 9-in. flexible cable. The detector is mounted in air, in a housing mechanically connected to the beamline. The tightness between the vacuum of the beamline and the atmospheric pressure is guaranteed by a 125 μm Be membrane. The SDD detector covers a wide range of counting rate and so, the dose measurement is reliable independent of the particle flux.

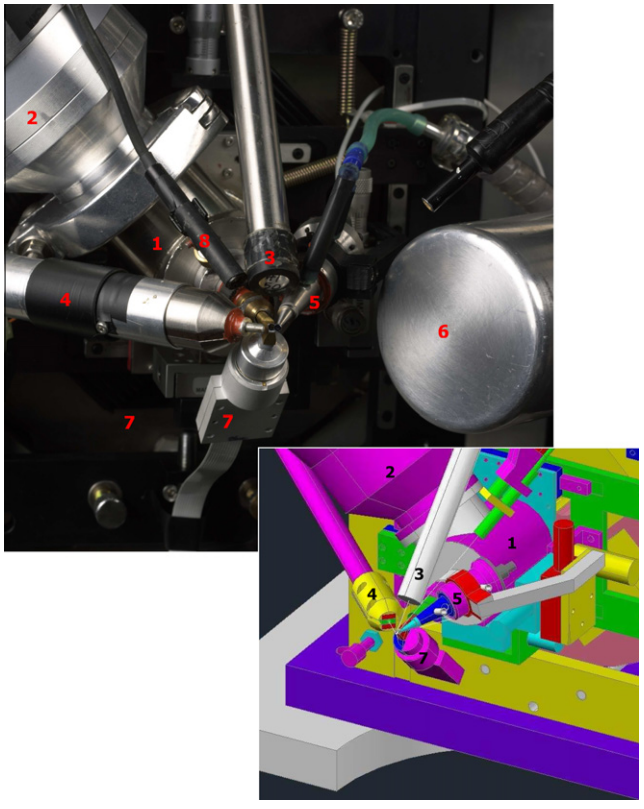

Fig. 1. External beam set-up used for simultaneous PIXE–RBS–PIGE. (1) Beam extraction nozzle with a Si_3N_4 window; (2) turbo-pump; (3) high energy Si(Li) X-ray detector equipped with a 6-μm Be window, solid angle 100 mSr; (4) low energy Si(Li) X-ray detector equipped with a deflection magnet, 0.25-μm BN window, He flux, solid angle 10 msr; (5) RBS detector; (6) gamma detector; (7) dose detector: SDD Peltier cooled detector; (8) camera for positioning.

This recent configuration, now routinely used, gives access to complementary information by the simultaneous detection of X-rays, gamma-rays and backscattered particles. The same arrangement is also utilised for elemental mappings [15].

2.2. Examples

2.2.1. Intentional surface modification: metal decoration

Noble metal layers have often been used in the past to decorate objects made of materials of lesser value (base metal, ceramics, glass, wood, plaster, etc.). The most widespread technique used metal foils but, in the particular case of lustre-decorated ceramics, the metal is in nanoparticles form included in the glaze. The iridescent and metallic appearance of lustre-decorated ceramics originates in this thin layer of silver or copper nanoparticles.

During the past 10 years, considerable efforts have been made to investigate the chemical and physical structures and the optical properties of lustre-decorated ceramics. IBA has been applied to examine the fabrication technology. For instance, studies have been carried out on Middle-East, Spanish and Italian productions [16–18]. The combination of PIXE and RBS has highlighted the differences or similarities among the various productions. The evolution of the lustre-decorated ceramic technology has been elucidated by detailed observation of the composition and the thickness of the copper and/or silver nano-particles film as well as of the composition of the glaze layer and that of the ceramic body. The typical metallic layers are between 50 and 300 nm thick with various concentrations of copper and silver depending on the colour and the production workshop. The metallic layer can directly be found on the surface of ceramics such as, for example, Hispano-Moresque lustres dated before the beginning of the 16th century, but a glaze layer of 100 nm above the metallic nanoparticles can be observed for earlier Islamic and the Italian majolica productions. All these data were obtained by performing two successive experiments, using 3 MeV H^+ for the terra cotta characterisation and 3 MeV He^{2+} for the glaze and metal layers study. A detailed summary report on the IBA contribution to the knowledge of the lustre-decorated ceramics is in progress.

Another useful application field of IBA is the study of the plating manufacturing processes. Gilding has extensively been studied [19] but the silvering processes are less known. The discovery of a large hoard of coins of the 16th century [20] containing several counterfeit coins offered an opportunity to examine their manufacturing technology and more specifically, to investigate the formation of the silver plating layer on their surface. A 3 MeV proton beam was used for RBS and PIXE. RBS was applied to the determination of the plating layer thickness while PIXE was found to be necessary for the determination of the elemental composition of the layer and that of the copper substrate. Two main types of silvering methods were brought to light. Silvering containing mercury was observed for 14 counterfeit coins among which 11 were imitations of the coat of arms of Johann August von der Pfalz-Veldenz (1598–1611, Count palatine of *Veldenz-Lützelstein*, Upper Rhine circle, Holy Roman Empire). The thickness of the layer was between 1 and 2 μm and the composition 50–60 wt.% Hg, and 50–40 wt.% Ag depending on the coin (Fig. 2). This composition