Application Of PIXE And PIGE Under Incident Variable Ion Beam Angle To Several Fields Of Archaeometry

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ABSTRACT

For several years, the specific features of PIXE and PIGE made them very attractive in the field of archaeometry. Among them, the non-destructivity is one of the most appreciated. The possibility to work under atmospheric pressure is also important because of the very different shapes and sizes of the artefacts concerned. However, these ion beam techniques suffer from the same disadvantage: the information coming from X-rays or gamma-rays produced at different places along the charged particle path is integrated. That prevents to take into account the possible element concentration gradients due to multi-layered systems or diffusion processes.

The present paper shows several applications of PIXE and PIGE applied under variable incident ion beam angle. PIGE has been mainly used for studying ancient glass items or glass windows in order to detect or evaluate the glass corrosion process. The examples given for PIGE are dealing with Roman and Merovingian glass objects and cathedral glass windows, PIXE applications concern studies for resolving multilayered structure of easel paintings. The set-up allowing to perform the measurements should be very stable, the rotation axis should pass through the beam axis and the detector should follow the sample movement.

Keywords: PIXE, PIGE, gradient, variable, incident, angle

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1. INTRODUCTION

A real problem is encountered by applying PIXE and PIGE, two methods very appreciated in the field of archaeometry [1, 3]. It is the fact that for one incident energy and under fixed incidence, it is not possible to distinguish between spectroscopic information coming from different depths in a multi-layered sample. This paper shows three typical examples chosen among many others where, by tilting the sample, it is possible to give some answer to the problem mentioned above.

2. EXPERIMENTAL SET-UP

FIGURE 1. Schematic experimental set-up and principle of the variable incident beam angle. As an example, the range of 2.5 MeV protons in glass is about 60 \( \mu \text{m} \).
The experimental in-air PIXE-PIGE set up of the IPNAS in Liège has been described elsewhere [4-5] but its main specific feature is the possibility to rotate the sample around an axis passing through the beam path (FIGURE 1). This sample holder is specially designed to allow the X-ray detector to follow the sample movement. It is quite important in the case of PIXE measurements where X-rays are partially absorbed by the sample material itself. That absorption depends on the depth where the X-rays or γ-rays are produced, therefore it depends also on the angle between the beam direction and the detector axis. It is the reason why, in order to reduce the number of parameter concerned, one keeps that angle constant. For PIGE, this problem is negligible because of the weak absorption of the gamma rays by thicknesses corresponding to the range of 2-3 MeV charged particles in the material considered. The particle beam is monitored by counting the charged particles back-scattered by a gold layer (50 nm) deposited on a polycarbonate backing which interrupts the beam at a 2Hz frequency.

2. THE VARIABLE INCIDENT ANGLE METHOD: PRINCIPLE

The principle of the method is the same for both PIXE and PIGE. It consists in a rotation of the sample around an axis passing through the beam path. This condition was checked by rotating the sample and observing that the beam spot didn’t move. Figure 1 shows the case of a simplified sample composed of two layers. By rotating the sample, one changes the relative path length in the two layers leading to an enhancement of the signal corresponding to the superficial one and reducing the signal corresponding to the inner one. As we will see further, the phenomenon is easier to handle in PIGE than in PIXE because of the weaker absorption of γ-rays comparing to X-rays. Therefore, the results obtained by PIXE will be less quantitative than by PIGE.

2. RESULTS AND DISCUSSION

2. Determination of the depth reached by the silver yellow on a stained glass window (PIXE)

Gold aspect in stained glass windows has been generally obtained by annealing transparent glass onto which silver nitrate mixed with clay or ochre has been painted. The result is a gold-colored zone due to a thin layer of silver oxide at some distance from the surface. It is interesting to know that distance because silver yellow is often considered as a protective layer against the corrosion process. On FIGURE 2, by comparing the theoretical evolution of the AgKα X-ray detected in function of the incident angle with the experimental values, one can estimate the distance mentioned above as about 1.5 µm. The theoretical values have been calculated by using different fundamental parameters as the stopping power in glass, the X-ray absorption coefficient, and the X-ray production cross-section.

FIGURE 2. Determination of the depth reached by the silver yellow stain in the glass window.
4.2. Determination of the stratigraphy present on a Byzantine icon

An icon belonging to the Treasure House of the Liège Cathedral has been investigated. Among the different pigments identified by normal incident beam, a red one was particularly difficult to explain. In this red area, we found several elements corresponding to the pigment (= lake, containing Al, Si, Ca and Fe), three elements indicating the presence of a metallic layer (Au, Ag and Cu) and also Zn. The presence of the last element is very surprising because white zinc appears only from the end of eighteen century [7]. The FIGURE 3 shows the results obtained by tilting the sample. The evolution of the signal relating to Fe, Au and Zn allows proposing the stratigraphy reported on the graph. FeKα line is continuously increasing which proves its position in first place really at the surface. AuLβi increases first, but from 55° its behaviour changes and a decreasing takes place. That is due to the fact that around 55° tilting the proton beam leaves progressively deepest side of the metallic layer. The choice of AuLβi is due to the interference between AuLα and ZnKβ. Then, one can propose the second place for this layer just under the red lake. For Zn, the constant decreasing of the ZnKα intensity indicates the third position for this element under red lake and gold-silver alloy. An attempt to explain the presence of a metallic layer (foil or metal powder + binder) under the red lake could be the use of the “mordant” or “sgraffito” gilding technique for embellishing the Jesus’ robe by imitating gold embroidery [8].

The reason of the zinc presence in the pictorial layer should be then found elsewhere. This icon was restored by Mr. J. van de Even (Brussels) in 1935. From the content of a letter sent by Mr van de Veken to J. Puraye [9], it has been possible to resolve the problem of the zinc present everywhere on the pictorial layer. Originally, the latter was applied on a parchment, which was then glued on a cedar backing. As the wood was dramatically worsened mainly by woodworms, it was decided to transpose the pictorial layer on a new backing. First, the icon was stuck on several paper foils with a glue likely to be easily dissolved later. It was then obtained a rigid structure (pigments + parchment + paper) allowing the next operation which consist in removing mechanically the deteriorated wood. A new backing was prepared by covering a wood panel surface with gesso, which is composed of rabbit skin glue (RSG), zinc white and gypsum. The pictorial layer was then laid to the new panel and the paper removed by dissolving the glue from the topside. It is then clear that the origin of Zn has to be found in the gesso composition.

FIGURE 3. Evolution of the Fe, Au and Zn X-ray intensities in function of the proton beam incident angle.
4.3. Analysis of weathering glasses (PIGE).

As the ancient glass object corrosion is generally due to the leaching of Na when the glass surface is in contact with water. It is then interesting to measure the Na concentration gradient within the first 50 µm of the glass thickness.

The cross section of the reaction $^{23}$Na(p, p'γ)$^{23}$Na is strong and well-known [6] between 1 to 4 MeV. As the γ-rays produced (0.44 and 1.63 MeV) are not so much absorbed, it is possible to measure the Na concentration gradient up to 30-90 µm by using PIGE under variable incident angle. The FIGURE 4 shows an example of scanning obtained with 4 different incident angles φ₀=0, φ₁, φ₂, φ₃. Assuming that the proton range in glass is constant, each result $S_i$ (i = 0 to 3) contains information about the depth reached perpendicularly to the sample surface. Knowing the stopping power of the protons in glass and the integrated cross section of the nuclear reaction, by a simple matrix inversion it is possible to obtain the Na concentrations in each zones. Let us note that the resolution of the technique depends strongly on the number and the choice of the different incident angles.

2. CONCLUSIONS

The method described in this work has the great advantage of its non-destructivity aspect. Some surface effect arises when the incident angle is beyond 70°. However, if the qualitative information is relatively accessible, the quantitative one strongly depends of the knowledge of several parameters as: reaction and X-ray production cross-sections, composition of medium, binders, glass... in major elements which determine the charged particle stopping.
power and the X-rays absorption coefficients. The writing of specific computing programs allowing to take into account a maximum of these data will be the best improvement in the future.

ACKNOWLEDGMENTS.
We are indebted to the Institut Universitaire des Sciences Nucléaires and the French Belgian Community (ARC) for their financial support.

REFERENCES