2005 International Nuclear Atlantic Conference - INAC 2005
Santos, SP, Brazil, August 28 to September 2, 2005
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 85-99141-01-5

EXTERNAL BEAM PIXE ANALYSIS OF PAINTING

Paulo R. Pascholati[1], **Márcia A. Rizzutto**[1], **Marcel D.L. Barbosa**[1],
Cindy Albuquerque[1], **Graziela Neves**[2]

[1] Instituto de Física, Universidade de São Paulo – IFUSP
Rua do Matão, travessa R, 187
05389-970 - São Paulo, SP
pascholati@if.usp.br, rizzutto@if.usp.br, mbarbosa@if.usp.br,
cindy@if.usp.br

[2] Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
graziela@if.usp.br

ABSTRACT

The preservation and conservation of mankind cultural heritage has become an important issue worldwide. Non-destructive analytical techniques are suitable, for example, to analyze precious and unique objects of art and archeology. Among those techniques Particle Induced X-Ray Emission (PIXE) has good advantage to identify elemental composition present in these kinds of objects. The Laboratório de Análise de Materiais por Feixes Iônicos-LAMFI of the Institute of Physics of the University of São Paulo has been installed an external beam facility for PIXE analysis. This new setup is being used for the analysis of archeological pottery artifacts, paintings and biological tissues (teeth and bones), which are not compatible with the high vacuum of the regular PIXE target chamber. In addition most art and archeological objects are too large for the evacuated analysis chamber. Applications of this facility will be presented in the analysis of one painting of the beginning of the last century. The chemical elements identified in the painting were Ca, Ti, Cr, Cu, Fe, Zn, Pb and Ba. The PIXE measurements were done non-destructively and no visible damage was observed on the irradiated object.

1. INTRODUCTION

The preservation and conservation of our cultural heritage is an area of great interest and has become an important issue worldwide [1]. This area is multidisciplinary and necessity the interaction of different specialists in different areas of knowledge. In particular there is an increasing need for non-destructive investigations in objects of art and archaeology. In addition to the conventional analytical procedures, techniques employing nuclear instruments and methods are increasing in this field [2,3]. Techniques as XRF (X-Ray Fluorescence), PIXE (*Particle Induced X-Ray Emission)*, PIGE (*Particle Induced Gamma-Ray Emission), XRD (X-ray Diffraction)* and NMR *(Nuclear Magnetic Resonance)* are extensively applied in these fields [4,5,6]. The most straightforward and frequent application of PIXE is the determination of the elemental composition of the sample. In the case of painting the PIXE characterization can help to understand the composition and the kind of the paints used by the artists [4,7]. The detailed knowledge of the "palette" of a painter could certainly be very important and useful for artists and art historians. An example is reported here where a painting of the beginning of the last century was analyzed and some elemental compositions were obtained.

2. EXPERIMENTAL

The analyzed painting was produced by a Brazilian painter in the beginning of the last century and consists of a picture of a landscape, see Fig. 1. The painting has 460 mm length e 185 mm width on a wood support. The PIXE measurements were performed at LAMFI (Laboratório de Análise de Materiais por Feixes Iônicos), where a 1.7 MV Tandem Accelerator is installed. A 2.4 MeV proton beam, and an exit window made of a 7.5 µm thick Kapton foil was used. In the external beam PIXE setup, shown in Fig. 2, the beam is led through a carbon collimator placed inside a transparent Perspex tube [8]. To prevent electrical breakdowns the internal wall of the Perspex tube was covered with a metal net. Due to the 10 mm air path and the Kapton exit window the final beam energy which reach the painting was approximately 2.2 MeV.

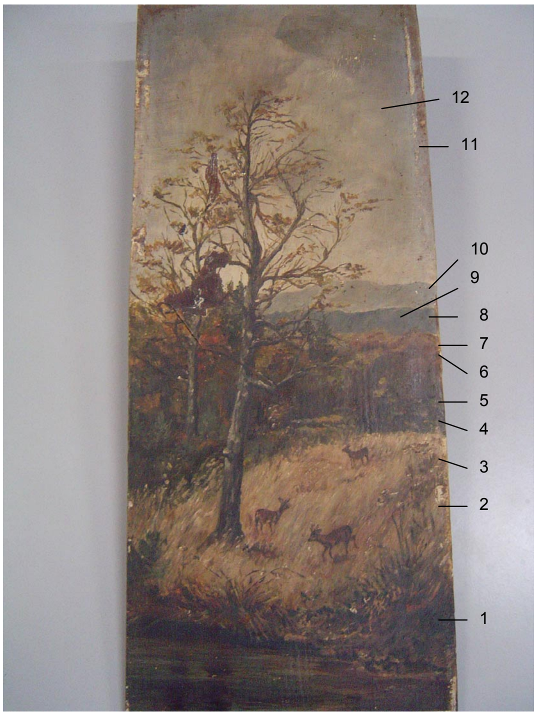

Figure 1. The analyzed painting and the points where the PIXE measurements were performed.

The X-ray detection of the elemental composition in the painting was determinate by a portable AMPTEK XR110CR (Si-PIN) detector mounted on a water-cooled Al base (FWHM 220eV for the Mn Kα line). To avoid the entrance of scattered beam into the detector a mylar absorber of 12 μm was placed in front of it. This detector was placed at about 10 mm from the target at an angle of 135 degrees related to the incident beam. Typical beam currents used to analyze the painting were about some nA to keep dead time and pile-up low and to prevent painting damage. The acquisition time was set to 1 200 seconds for each point analyzed. The presence of air argon X-rays worse somehow the detection limits for the K-lines of Cl and K. However the X-ray peak from Ar can be satisfactorily used for normalization. The intensity of the extracted beam was estimated indirectly using an Al foil inside the chamber and a Si particle detector. During the analysis part of the beam is Rutherford back scattered in the Al foil and measured in the Si detector. The Al peak spectra are normalized to known charge values. The painting was horizontally laid over at a distance of approximately 10 mm from the exit window. An Al collimator of 0.3 mm diameter limited the analyzed area and was positioned just after the external Kapton foil. The beam spot at painting is 1 mm.

Figure 2. View of the multi-use chamber with the new external beam setup installed and the X-Ray detector (XR-100CR) and the painting.

2.1. Measurements and results

PIXE measurements were made on 12 selected points 8 mm from the boarder except two (points 9 and 12) at 32 mm, one of them belongs to a damaged region (point 2). These points are indicated in Fig. 1. The PIXE spectra taken at these several points give us an idea about the elemental composition of some colors used by the author. Strong X-ray peaks of Fe, Zn and Pb are present, and Ca, Ti, Cr, Ba and Cu are also be seen with less intensity. Air Ar peak are present in all spectra with the same intensity allowing good comparison among the intensities of the other elements.

The main observations can be summarized in the following. Lead, seen by the strong Pb-L lines, was found at almost all points, except the point 2 in the painting, indicating the use of lead white. Calcium came probably from chalk or gypsum used as priming. Iron, zinc and titanium also appeared in all points, the latter except at point 2. Among X-ray spectra taken, we select three groups with three spectra each: one showing different brown gradation, another blue gradation and one relating blue, brown and a damaged white.

The PIXE spectra from brown group is shown in Fig. 3 and corresponds to select point 3(dark brown), 5(light brown) and 7(intermediated brown), see Fig. 1 for positions. The greater difference is the presence of chromium and copper in the light brown. However there are intensities differences in lead, iron and zinc. The high intensity of Pb in point 3 (light brown) is in relation to the mixture of white color.

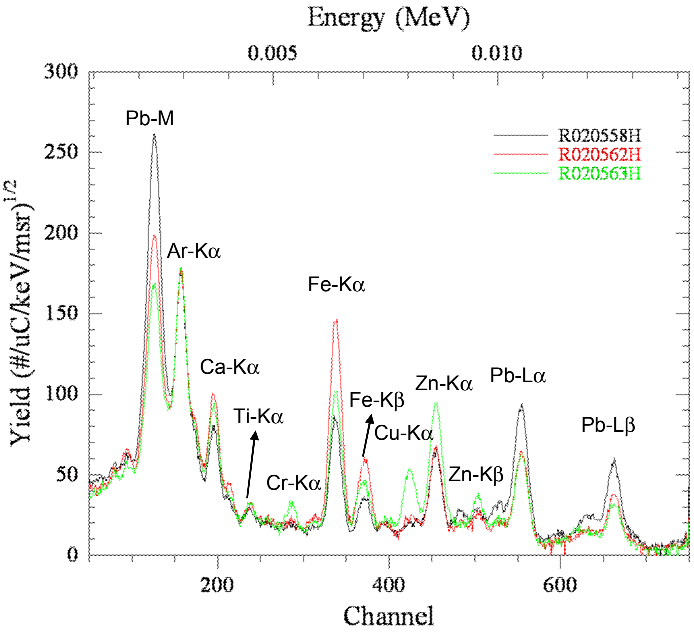

Figure 3. PIXE spectra taken at points 3(black) – dark brown, 5(green) – light brown and 7(red) – intermediate brown of different paint traces. The location of the points are indicated and numbered in Fig. 1.

All points of the blue group (10, 11 and 12) in spectra PIXE, see Fig.4, show similar intensities for Ti. At point 11 – dark blue the intensities of Zn and Pb are little more than in points 10 – mountain blue and 12 – light blue. The intensities of calcium and iron at point 12 are slightly greater than in other points.

The last group, presents in Fig. 5, show PIXE spectra from points 2 – damaged white, 7 – intermediate brown and 10 – mountain blue. The greatest intensities differences appear in the damaged white point. At it there are almost no Pb and more zinc and copper than at the other points. PIXE spectrum from damaged white is the only showing barium K-lines, probably from priming. The point of intermediate brown presents more iron than that of mountain blue and damaged white.

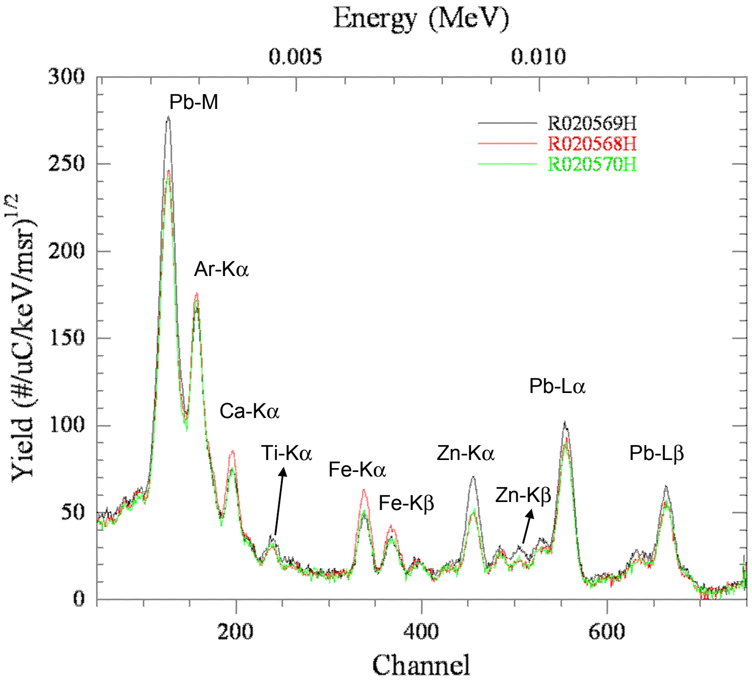

Figure 4. PIXE spectra taken at points 10(green) – mountain blue , 11(red) – dark blue and 12(black) – light blue. See Fig. 1 for location of the points.

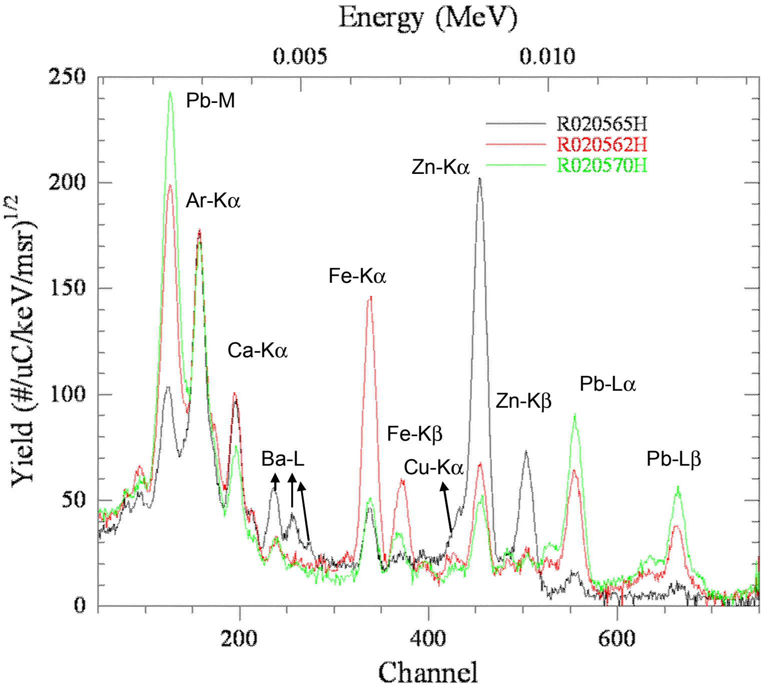

Figure 5. PIXE spectra taken at points 2(black) – damaged white, 10(green) – mountain blue and 7(red) – intermediate brown. See Fig. 1 for location of the points.

In almost all spectra the presence of titanium in a white pigment would indicate that the painting has no more than 100 years, as TiO_2 as white pigment was discovered in 1908 [9].

CONCLUSIONS

PIXE can be used to analyze the elemental composition of a painting. The measurements were done non-destructively and no visible damage was observed on the irradiated painting. Qualitative analysis shows differences of elemental composition of the paint pigments which could allow to link paintings from the same painter. Improvements are needed for better analysis, although quantitative results are difficult to obtain.

ACKNOWLEDGMENTS

M.A.R. wishes to grateful FAPESP and PRP to CNPq for financial support. We would like to thank Dra. Carmem C. Bueno from IPEN-SP for kindly providing the XR-100CR (Si-PIN) detector.

REFERENCES

1. See for example the website from *The International Centre for Conservation Roma – ICCROM*, http://www.iccrom.org .
2. A. Adriaens, G. Demortier, "COST Actions G1 and G8:Eu programs on the use of radiation in art and archeometry," *Nucl. Instr. and Meth*. **B226**, pp. 3-9 (2004).
3. T. Calligaro, J.-C. Dran, J. Salomon, Ph. Walter, "Review of accelerator gadgets for art and archaeology," *Nucl. Instr. And Meth*. **B226**, pp. 29-37 (2004).
4. C. Neelmeijer, I. Brissaud, T. Calligaro, G. Demortier, A. Hautojärvi, M. Mäder, L. Martinot, M. Scheiner, T. Tuurnata, G. Weber, "Paintings – a Challenge for XRF and PIXE Analysis," *X-Ray Spectrom*. **29**, pp. 101-110 (2000).
5. G. Demortier, PIXE, PIGE AND NMR study of the masonry of the pyramid of Cheops at Giza," *Nucl. Instr. and Meth*. **B226**, pp. 98-109 (2004).
6. M. Uda, S. Sassa, S. Yoshimura, J. Kondo, M. Nakamura, Y Ban, H. Adachi, " Yellow, red and blue pigments from ancient Egyptian palace painted walls," *Nucl. Instr. and Meth*. **B161-163**, pp. 758-761 (2000).
7. A. Denker, J. Opitz-Coutureau, "Paintings – high-energy protons detect pigments and pain-layers," *Nucl. Instr. and Meth*. **B226**, pp. 667-682 (2004).
8. M.A. Rizzutto, M.H. Tabaknics, M.D.L. Barbosa, N. Added, J.F. Curado, W.A. Santos-Júnior, "The external beam facility at the LAMFI-SP", *Proceeding of XXV Reunião de Trabalho sobre Física Nuclear no Brasil and V Latinamerican Symposium on Nuclear Physics*, Santos, Brazil, 1 to 5 September, pp. 29-30 (2003).
9. H-.P. Schramm, B. Hering, *Historische Malmaterialen und ihre Identifizierungen*, Seemann, Leipzig Germany (2000).