# The PIXE technique applied to an old painting

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An external beam facility for PIXE analysis has been installed in the Laboratório de Análise de Materiais por Feixes Iônicos-LAMFI of the Institute of Physics of the University of São Paulo. This setup is being used for non-destructive 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 [1,2]. In addition most art and archeological objects are too large to be placed in an evacuated analysis chamber. The above facility was applied to a painting from the beginning of last century with interesting results [2].

In this experiment a 2.4 MeV proton beam was passed through a 7.5 μm thick Kapton exit foil and 30 mm air path and reached the samples with a final energy of approximately 1.8 MeV. For X-ray detection a portable AMPTEC XR-100CR (Si-PIN) (FWHM 220eV@MnKα) mounted on a water-cooled support was used. This detector was placed about 10-15 mm from the target at an angle of 135 degrees related to the incident beam. To avoid the entrance of scattered beam into the detector a mylar absorber of 12 μm was place in front of the detector.

Typical beam currents used to analyze the painting were about 2 nA to keep dead time and pile-up low and to prevent any damage to the painting. The acquisition time was set to around 600 seconds for each point. The presence of Ar X-rays worsened the detection limits for the K-lines of Cl and K. However the X-ray peak from Ar can be used for normalization. The beam spot in the painting is approximately 2 mm of diameter.

Presented here is the analysis of a painting, probably from the 17th century by an unknown artist. The painting technique is oil on canvas whose theme is a Calvary scene. The painting (figure 1) presents the varnish cover oxidized and has been selectively cleaned and repainted. To identify chemical elements present in the painting, twelve spots were selected with and without varnish. The analyzed pigments were analyzed in the following colors: blue (spots 18 and 20), yellow (14, 17), red (6, 16), brown (0, 5), white (7, 15, 27) and a cream (30).

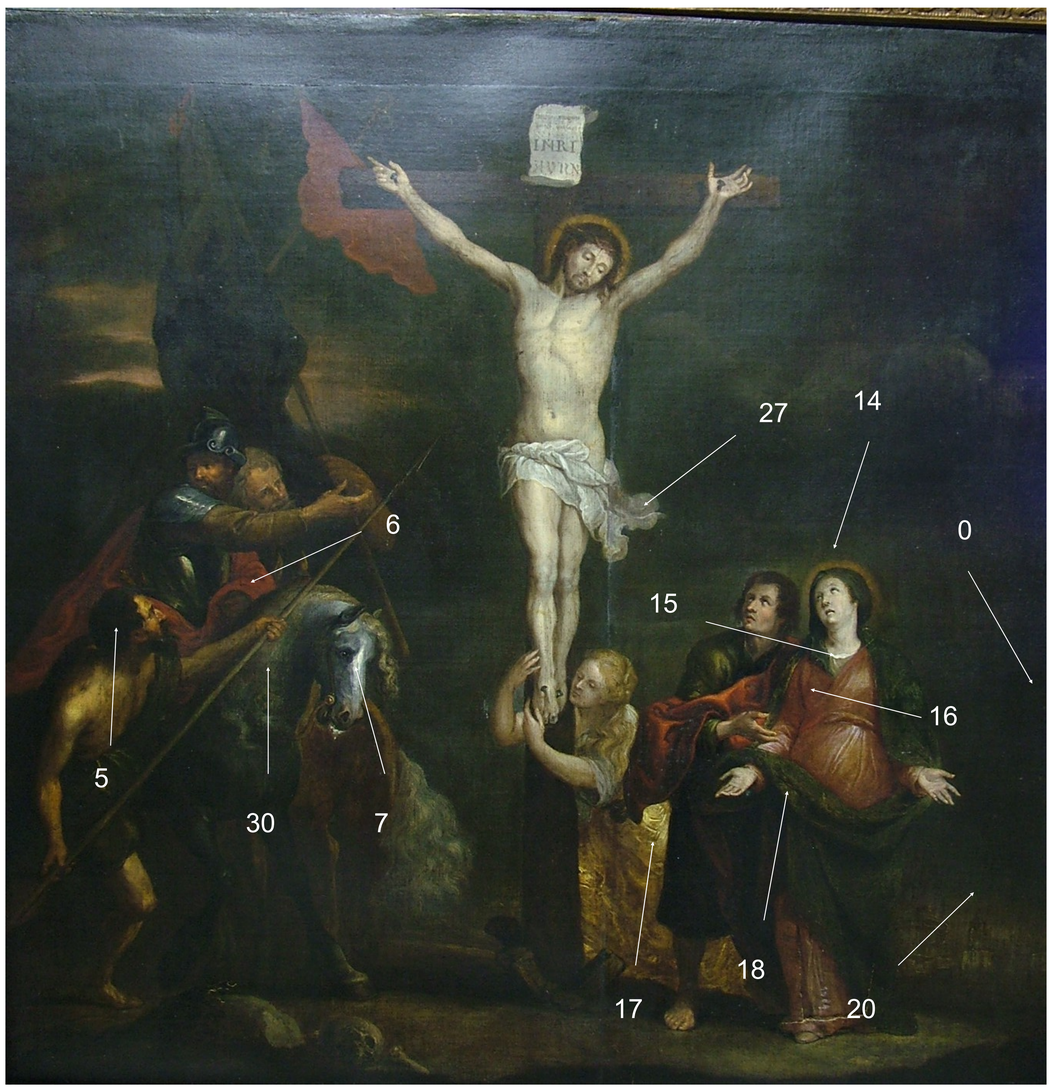


Figure 1 – A picture of the painting with the analyzed point marks.

## Results

PIXE spectra of selected spots are presented in figure 2. The table 1 presents the element concentration ratios relative to Ar. Elements such as Si, S, Cl, K, Ca, Fe and Pb were detected in almost all spots analyzed as can be seen in polar plots of some of the colors in figure 3. UV photography was applied in order to examine the repainted and cleaned parts of the painting. Lead is the principal element in the white pigment (spots 7 and 15) except for the repainted point 27 and 30. On the point 27 Ti was also observed, which suggests that the Ti-white pigment was used in the restauration process, while Ca is the most intense element seen. The point 30 was cleaned and probably caused the removel of varnish and white pignment layers. On the other hand, the Zn element (used in the Zn-white) was not observed in these points. Ba appears in white color pigments (7,15,27). Fe, Mn and Cu are principal elements forming the brown color (0,30). Hg appears in spots 6 and 27, and Sn only in spot 17. Small quantity of Co is present in spots 18 and 27.

In a recent measurement, not yet analyzed, a gamma detector was included in the setup to search for Na element in blue pigment. Na is present in blue ultramarine (XI to XIX century)[3], an expensive pigment used mainly on the mantle of Christ or Virgin.

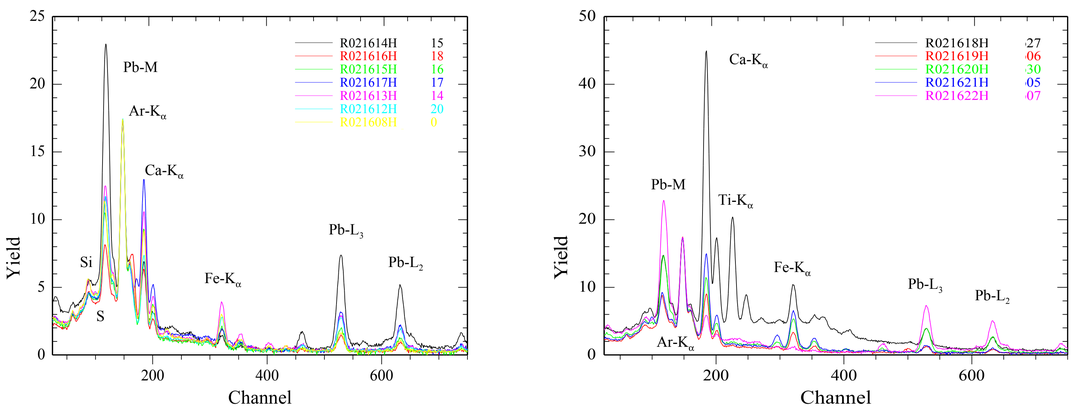


Figure 3 – Polar plots of the observed trace elements in the blue, red and yellow colors of the analyzed points in the painting.




Figure 2 – Comparison of the PIXE spectra of some of the analyzed points on the painting.

| | | Si | S | Cl | K | Ca | Ti | Cr | Mn | Fe | Co | Cu | Zn | Sn | Ba | Hg | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | Virgin's cloth | 14,5 | 26,2 | 4,89 | 6,13 | 49,7 | | 0,82 | 1,64 | 7,98 | | | | | | | 170 |
| 6 | Soldier's mantle | 5,49 | 30,8 | 5,13 | 5,23 | 45,2 | | 0,41 | 1,19 | 22,0 | | | 1,96 | | 0,93 | 28,3 | 70,7 |
| 5 | Man's hair | 9,95 | 18,1 | 5,71 | 6,30 | 130 | | | 12,4 | 83,5 | | 1,48 | | | | | 91,0 |
| 15 | Virgin's collar-cloth | 13,1 | 25,8 | 10,6 | 3,03 | 24,6 | | | | 3,88 | | | | | 6,28 | | 2608 |
| 30 | Horse-hair | 10,7 | 18,8 | 10,0 | 3,56 | 74,2 | 0,67 | | 4,05 | 57,5 | | 2,35 | | | | | 705 |
| 7 | Horse's head | 3,25 | 32,0 | 13,1 | | 15,6 | | | | 1,77 | | | | | 6,29 | | 2449 |
| 27 | Christus' cloth | | 27,8 | 14,5 | 3,15 | 1078 | 304 | 5,92 | | 170 | 6,86 | 11,1 | | | 6,29 | 30,2 | 606 |
| 18 | Virgin's mantle | 15,5 | 9,63 | 2,96 | 21,1 | 20,5 | | | | 6,42 | 2,49 | | | | | | 89,4 |
| 20 | Sky | 14,1 | 14,5 | 5,03 | 3,41 | 28,5 | | | | 16,1 | | | | | | | 351 |
| 17 | Magdalen cloth | 5,28 | 11,5 | 8,17 | 3,63 | 94,0 | | | 0,88 | 6,13 | | | | 35,4 | | | 468 |
| 14 | Virgin's aureole | 15,1 | 21,3 | 11,0 | 8,05 | 65,1 | 0,65 | | 1,06 | 30,6 | | 3,24 | 1,75 | | | | 394 |
| 0 | Near border | 18,5 | 39,0 | 10,3 | 11,7 | 45,4 | 1,68 | | 0,84 | 16,9 | | 1,39 | 2,04 | | | | 113 |

Table 1 – Concentration ratios relative to Ar of principal elements observed.

## Conclusion

PIXE can be used for elemental composition analysis of a painting. The measurements were done non-destructively with no observed damage. Qualitative analysis shows that the composition pigments in the painting are composed of different elements which permit to link, for example, the pigments with the painter or to help the identification of the time when the picture was painted. Quantitative analysis are difficult due to the unknown thickness of varnish and paint layers present in this painting.

The observed absence of Zn (used in white pigment since 1834) and Ti (1918– ) in the paint pigment indicates that the painting could be an old one, while Mn in brown pigment could be associated with the van Dyck's brown (XVI– ), and the presence of Sn in yellow color to the yellow of lead and tin ( –1750) [3] .

References

1 M.A. Rizzutto et al., Nucl. Instr. and Meth. In Phys. Res. B240 549-653, 2005.

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3 A.J. Cruz, in http://ciarte.no.sapo.pt/material/pigmento/pig_cor.html, accessed at Augst 8th, 2006.