APPLICATIONS OF EXTERNAL PIXE TO ANCIENT EGYPTIAN ARTEFACTS

M. Moser†, I.F. Bubb, P.N. Johnston, M. El Bouanani, W.B. Stannard and R.C. Short
Department of Applied Physics, Royal Melbourne Institute of Technology, GPO Box 2476V, Melbourne, Australia
† on exchange from Technische Universität Graz, Rechbauerstraße 12, 8010 Graz, Austria

The external Proton Induced X-Ray Emission (PIXE) facility at Royal Melbourne Institute of Technology has been used to analyse ancient Egyptian glass samples, an Egyptian wall paint fragment and soil pigments. External PIXE analysis of two Egyptian glass samples enabled the partial determination of the colouring transition metals and the manufacturing technique.

1. Introduction

PIXE analysis is a widely used materials analysis technique because of its multi-elemental capability, high sensitivity, high speed and non-destructive nature [1]. The non-destructive nature of PIXE is enhanced for external PIXE and allows a wider range of analyses including (i) large items without sampling, (ii) some organic samples and samples that degrade due to ion heating, (iii) insulating materials and (iv) samples that degrade in vacuum. External PIXE is used in biological and medical analysis, aerosol analysis, earth sciences, art and archaeology, where it enables analyses of valuable or fragile specimens [2-8]. This paper describes analyses of ancient Egyptian glass samples and Egyptian wall paint as part of a wider study [9].

The external PIXE facility is described in detail elsewhere [9-11]. It uses a 0.35 mm diameter beam of 1.6 MeV protons which are extracted from the vacuum through an 8 μm gold coated Kapton foil. The beam reaches the target with an energy of 1.07 MeV after traversing 13.5 mm in air. Analysis of the spectra was carried out with the analysis package PIXAN [12].

2. Egyptian wall paint

A wall paint fragment found during the archaeological excavation of the town of Ismant el-Kharab as part of the Dakhleh Oasis Project in the western desert of Egypt was studied. It is thought to originate from a 1st century AD Roman Egyptian shrine. The aim of the study was to determine the source of the paint pigment [10]. The paint and soil pigments of similar colour from the desert surrounding the site were analysed. The paint has a high As concentration (Fig. 1) believed to come from AsO_4 [13] used for colouring the paint. The presence of sulphur

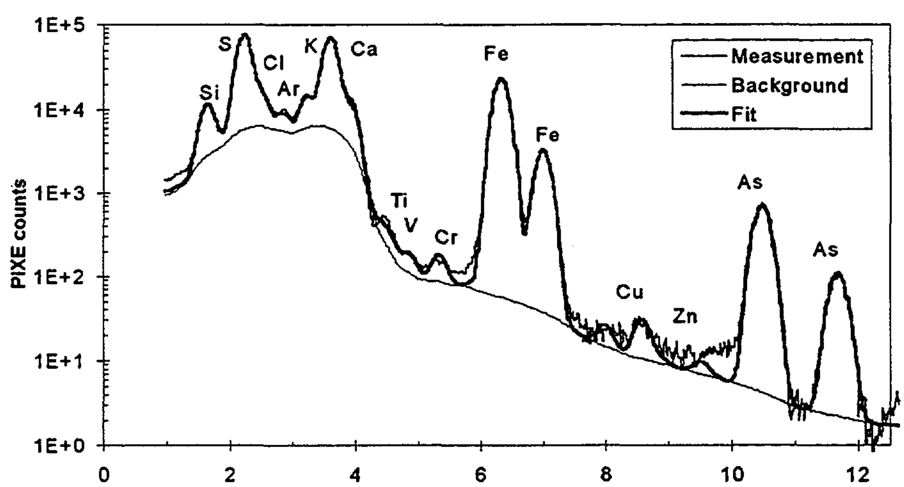

Figure 1: External PIXE spectrum from the wall paint with clearly visible As peaks.

suggests orpiment As_2S_3, which is found in yellow pigment of similar origin [2], however it was not found with XRD [9]. Exposure of the wall paint to air could allow oxidisation of orpiment to amorphous As_2O_3 and gaseous SO_2 [2]. The As in the pigment provides a means of obtaining information about the source of the pigment since As is rather unusual in soil pigments. Analysis of 17 soil pigment samples failed to show identifiable As X-ray peaks. This suggests that the origin of the colour pigment used lies outside the Dakhleh Oasis.

3. Egyptian Glass Samples

During the archaeological excavation two glass pieces, one blue and one of an unusual transparent red, were collected. Measurements were made to determine the colouring elements in the glass. PIXE analysis cannot indicate oxidation states of the metals which could be useful for identification of the colouring metal oxide. Combinations of metal oxides considerably alter the colour. An excellent review of ancient glass colouring is Newton & Davison [14].

3.1 Red Glass

During the melting of glass containing Mn and Fe an equilibrium of the different oxidation states can be found tending toward Fe^{3+} and Mn^{2+}. Fully reducing conditions result in a bright blue due to Fe^{2+} and the colourless Mn^{3+}. Oxidising conditions result in brown from Fe and purple from Mn. Intermediate conditions allow Mn to act as a decolouriser resulting in a colourless glass if the compensation of the Fe yellow due to the Mn purple is right. Imperfect conditions allow many colours such as green, yellow, pink [14]. Fig. 2 shows the spectrum from the red glass. The high concentration of Mn and Fe with the transparency of the glass suggests a decolourising of the Fe influenced by Mn. Light red colouring comes from imperfect compensation due to this decolouring effect of Mn for Fe with the high Mn concentration.

3.2. Blue Glass

The transition metals, Fe, Co and Cu are known to cause blue colouring in glass. Mn in combination with the right manufacturing conditions can cause a decolourising effect of the Fe causing a blue colour. Measurement of the Egyptian blue glass sample resulted in the spectrum in Fig. 3 showing the occurrence of all these metals. The concentration of Mn was not high enough for decolourising the glass. Co and Cu concentrations were too low to be an explicit source of the blue colouring although they are probably a contributing factor. The main source for the blue colouring is probably the high content of Fe observed in the analysis.

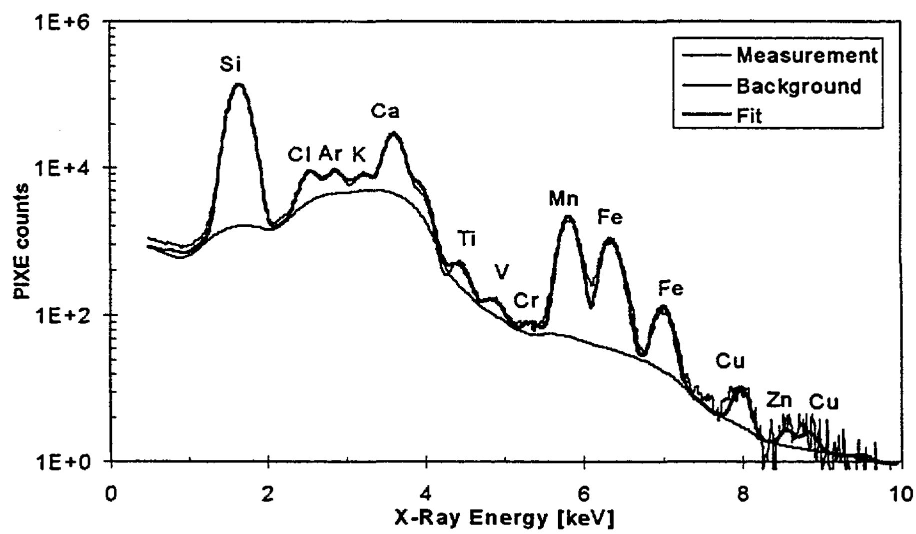

Figure 2: External PIXE spectrum of the red Egyptian glass displaying the high concentration of Mn and Fe causing the light red colour.

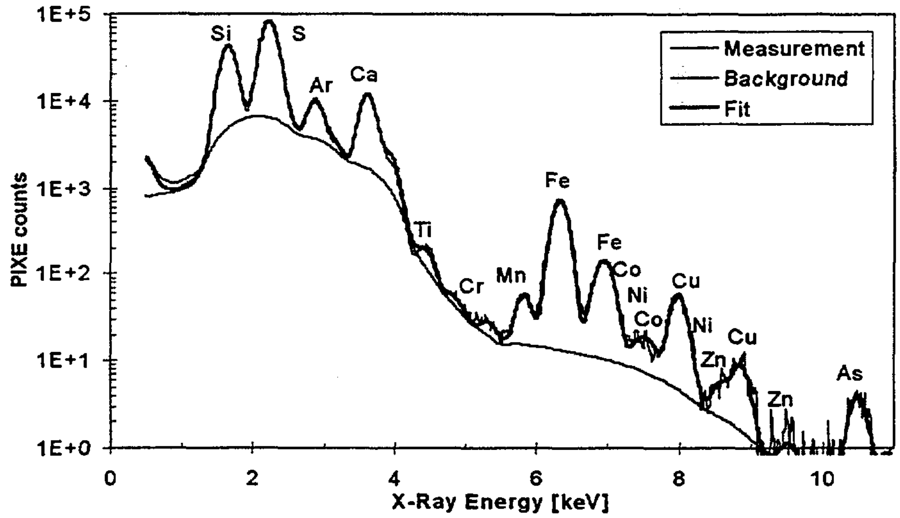

Figure 3: The high amount of Fe visible in the external PIXE spectrum of the blue Egyptian glass is the source for the blue colour of this Egyptian glass sample

5. Summary

External PIXE analysis of two Egyptian glass samples enabled the determination of the colouring transition metals showing them to be consistent with 'New Kingdom' glasses. Analysis of Egyptian wall paint and pigments from soils originating from the archaeological excavation of Ismant el-Kharab failed to uncover the origin of the paint pigment.

Acknowledgments

The authors would like to thank Alison Wain and Michelle Berry from the Museum of Victoria for supplying the samples, background knowledge and advice. MM acknowledges the support of the RMIT/TU Graz International Exchange Program.

References

[1] S.A.E. Johannson, J.L. Campbell and K.G. Malmqvist, Particle Induced X-Ray Emission Spectrometry (PIXE), John Wiley & Sons, New York 1995
[2] M. Uda, T. Tsunokami, R. Murai, K. Maeda, I. Harigai, Y. Nakayama, S. Yoshimura, T. Kikuchi, K. Sakurai and Y. Sasa, Nucl. Instr. Meth. B75 (1993) 476
[3] P. Del Carmine, F. Lucarelli, P.A. Mandò and A. Pecchioli, Nucl.Instr.Meth.B75(1993)480
[4] R. Cambria, P. Del Carmine, M. Grange, F. Lucarelli and P.A. Mandò, Nucl. Instr. Meth., B75 (1993) 488
[5] C.-M. Fou, IEEE Trans. Nucl. Sci., NS-30 No.2 (1983) 1291
[6] S. J. Stuart and C. P. Swann, Nucl. Instr. Meth. A242 (1986) 626
[7] S. R. Ryan, H. J. Fischbeck and K. Chesnut, Nucl. Instr. Meth. B10/11 (1985) 645
[8] M. Menu, Nucl. Instr. Meth. B75 (1993) 469
[9] M. Berry, Preliminary Investigation into the identification and possible provenancing of pigments from a Roman Egyptian Shrine, in manuscript, Melbourne 1997
[10] M. Moser, Thesis, Royal Melbourne Institute of Technology (unpublished), 1997.
[11] M. Moser, P.N. Johnston, I.F. Bubb, M. El Bouanani, W.B. Stannard and R.C. Short, This proceedings 'Development of an External Beam facility for PIXE at RMIT'.
[12] E. Clayton, Nucl. Instr. Meth., B22 (1987) 64
[13] K. M. Scott, American Mineralogist, 72 (1987) 178
[14] R. Newton and S. Davison, Conservation of Glass, Butterworths, London 1989.