



	<b>Experiment title:</b> Cobalt plus copper as chromophore elements in ancient glazes: a local structure approach through the Co and Cu K-edges.	<b>Experiment number:</b>
<b>Beamline:</b>	<b>Date of experiment:</b> from: 15 <sup>th</sup> Nov 2008 to: 21 <sup>st</sup> Nov 2008	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Sakura Pascarelli	<i>Received at ESRF:</i>
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## Report:

When considering cultural materials and the conservation and restoration of cultural artifacts it's fundamental to understand surface behavior for interpretation of degradation mechanisms, crucial for choosing materials and the implementation of conservation and restoration methodologies. A relevant contribution may be provided by XAFS data that supply information on speciation and local environment of a specific element.

*Fusers* and *colorant ions* in glassy ancient materials play a decisive role in the *ageing processes* that induce the deterioration of artistic pieces (e.g. [1]). XAFS studies at the ESRF have been performed on elements such as copper, zinc, lead and antimony in ancient glassy cultural materials, providing information on the structural behaviour of the metallic elements in the silicious vitreous matrix.

The aim of the proposed experiment was to perform an X-ray absorption study on the bonding state and coordination environment of **cobalt** and **copper** in glazed faiences of Portuguese manufacture as well as in cobalt blue-and-white glazes of Chinese porcelains manufactured for the Portuguese market in 16<sup>th</sup>-17<sup>th</sup> century, ultimately contributing to evaluate authenticity and possibly dating of museum pieces and to define correct conservation and restoration strategies.

EXAFS and XANES spectra were collected at the **K-edge** from 8 chinese porcelain fragments, 6 faience fragments and 3 tile glaze fragments from the 16<sup>th</sup> to 18<sup>th</sup> century (Portuguese manufacture).

To model different coordination environments and valence states of cobalt, the following compounds were irradiated:  $\text{Co}_2\text{SiO}_4$  and the spinel phase  $\text{CoAl}_2\text{O}_4$  ( $\text{Co}^{2+}$  in octahedral coordination),  $\text{Co}_3\text{O}_4$  (also a spinel, with  $\text{Co}^{3+}$  in tetrahedral and  $\text{Co}^{2+}$  in octahedral coordination), cobaltite ( $\text{CoAsS}$ ), the commercial pigment cerulean blue ( $\text{CoSnO}_3$ ), and cobalt metal (with an *fcc* structure) used to callibrate the energy.

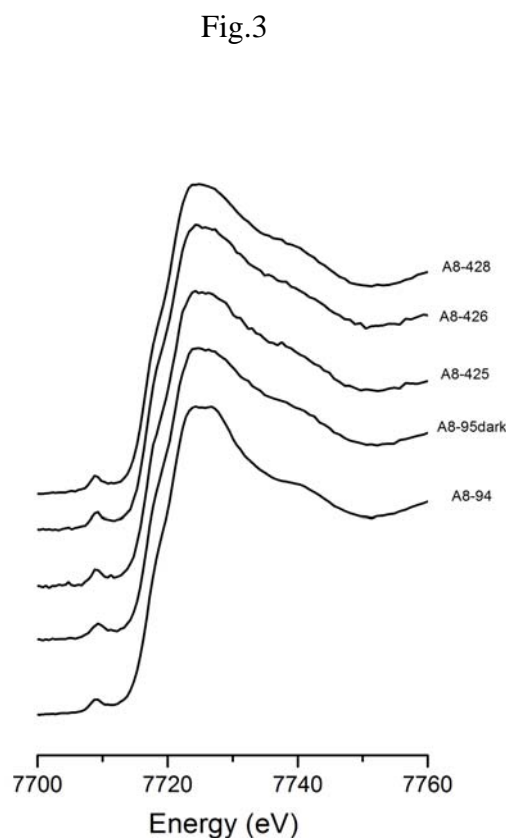
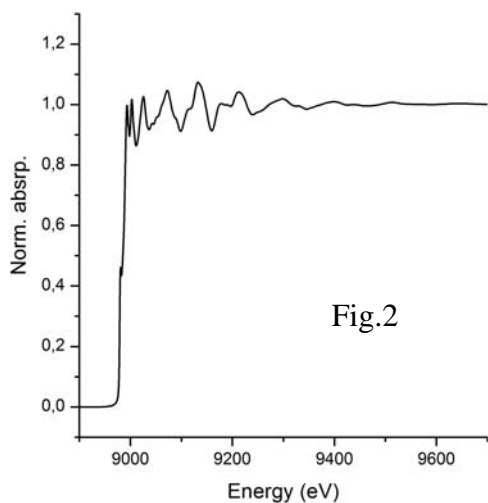
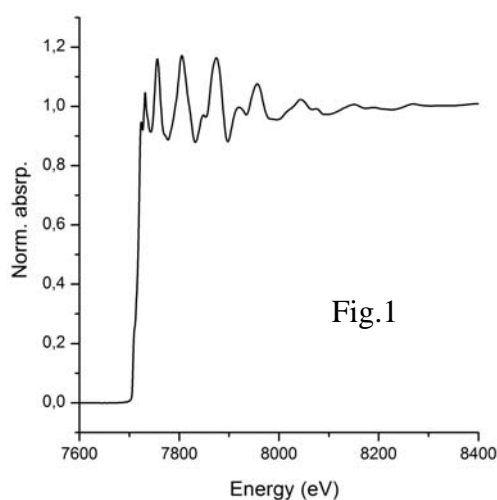
Since various copper model compounds were measured in prior experiments, only the commercial pigment Egyptian blue ( $\text{CaCuSi}_4\text{O}_{10}$ ), with copper in square coordination, was studied at the Cu K-edge.

The porcelains, faiences and tile glaze fragments were irradiated in several points and usually 4 to 5 spectra were collected at each point, depending on the quality of the collected fluorescence signal. The reference compounds were pelletized and measured in transmission mode.

A total of 71 good EXAFS spectra were collected at the Co K-edge; conversely, at the Cu K-edge, EXAFS spectra were only collected from the Egyptian blue due to the low fluorescence signal recovered from irradiated fragments.

Figs. 1 and 2 illustrate Co K-edge and Cu K-edge EXAFS spectra collected respectively from  $\text{CoAl}_2\text{O}_4$  and Egyptian blue.

Fig. 3 reproduces various Co K-edge XANES spectra obtained from 16<sup>th</sup> century Chinese blue-and-white porcelains (edge position as expected for  $\text{Co}^{2+}$ ). These XAFS data provided interesting results summarized in the abstract of a communication recently submitted for presentation at the forthcoming EMRS09 Spring Meeting [2].



A preliminary appraisal of Ce L-edge in BETESPT (bis-tri-ethyl-oxy-silyl-propyl-tetrasulphide) thin films deposited over an aluminum alloy and treated with cerium nitrate was also attempted (16 spectra).

## References

- [1] J.P. Veiga & M.O. Figueiredo (2006) Copper blue in an ancient glass bead: a XANES study. *Applied Physics A* **83** 547-550.
- [2] M.O. Figueiredo, T.P. Silva, J.P. Veiga, I. Dias (2009) Speciation state of cobalt in blue glazes: a XAFS study on XVI century Chinese blue-and-white porcelains. Submitted to symposium R, EMRS Spring Meeting.