



	Co and Cu k edge XANES in ceramic pigments from glazes, lustres and porcelains of Portuguese origin from the 16th to the 18th century.	Experiment number: HG-118
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Report:

An important set of minute fragments of blue and white glazes from the National Palace of Sintra, lustres from the Fronteira Palace in Lisbon, Faïence from the Vila Viçosa Palace and porcelains belonging to the Vila Viçosa Palace and to the Santa Clara Monastery in Coimbra, previously characterized by laboratory techniques (XRD, μ -PIXE, μ -Raman, μ -XRF, Optical Microscopy and VP-SEM) [1-3] were irradiated at beamline BM25A.

The glazes display a silica-lime-alkali glass with the addition of low melting point metals and chromophores based on Co and Cu for the blue colouring. In lustres the colourless glaze has a lead-alkali silicate composition and a copper-rich lustre overlay. From Coimbra and Vila Viçosa the blue and white porcelains have Co as the colouring agent in the blue inlays.

The purpose of this experiment was to achieve a comparison between manufacturing techniques, pigments used, conservation status and origin of the pieces through the speciation of Co and Cu in the different historical fragments using XANES.

A total of 39 fragments of the different materials with 1-3 mm² were characterized as well as a set of 11 model compounds (including metals), in the range of the *K* absorption edges of cobalt (7.709 keV) and copper (8.979 keV). X-ray Fluorescence (energy dispersive spectrometry) spectra were collected at the same time for all samples.

The clarification of the role of Cu and Co in glazes and lustres through the speciation of fuser metals and colourants in ancient tile glazes and glasses is still in discussion. The local structure and bonding situation of copper and cobalt and the comparison with XANES spectra from model compounds is currently being performed and will suggest the structural role of additives currently under debate as integrated in the crystalline

colouring phases. A comparison is also in process with results already obtained from different types of glasses and with results from other studies [3-6].

Figure 1 illustrates spectra collected from samples compared to model compounds; a) represents spectra from Santa Clara monastery porcelains (SCP 2 and SCP6) and Co compounds with different coordination environments to model for the ions in the glaze, namely cobalt silicate (Co_2SiO_4); cobalt aluminate (CoAl_2O_4); cobalt (metal), cobalt (II) oxide (CoO) and cobaltite, a cobalt arsenate (CoAsS); b) illustrate spectra from model compounds for the XANES study of lusters from tile glazes from the Fronteira Palace in Lisbon and Cu compounds with different coordination environments, namely reference samples copper(II) oxide (CuO), copper(I) oxide (Cu_2O) and the metallic copper.

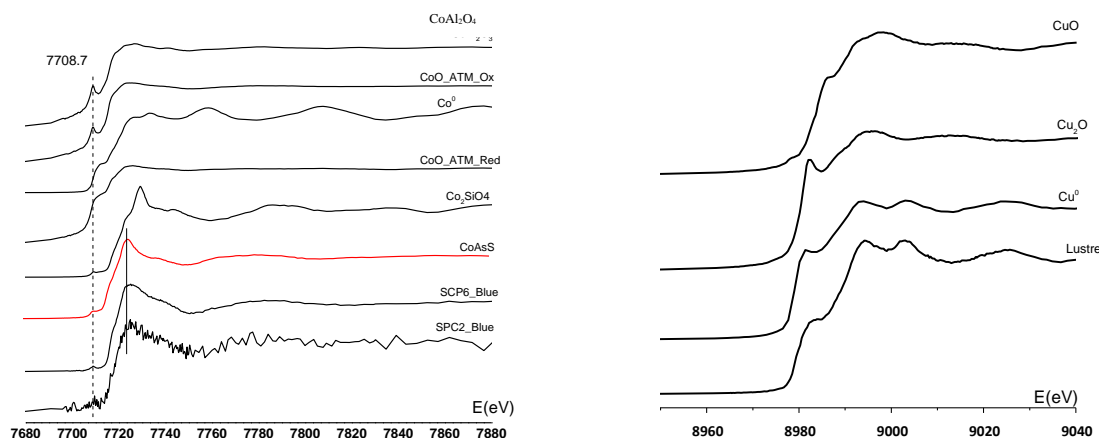


Figure 1 – a) Co K edge XANES spectra from the Porcelains and model compounds; b) Co K edge XANES spectra from tile glazes and model compounds.

Theoretical modelling of spectra the FEFF code [7] and comparison with the experimental results is currently under interpretation.

Taking profit from this experimental campaign an assessment was done on the possible use of XANES and SRXRF in a few samples from the Fogo Volcano in Cape Verde Archipelago that resulted in the inclusion of these chemical analysis results in a publication in the meantime available [8].

References:

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