PHYSICAL and CHEMICAL TECHNIQUES in CULTURAL HERITAGE

Organization: *Centro de Física Atómica* (UL), *Arquivo Nac. Torre do Tombo*, *Instituto dos Museus e Conservação*

Open Meeting, CFA-UL - June 1-2, 2011

X-Ray Spectroscopic Techniques applied to the Characterization of Pigments in Ancient Glazes: from Portuguese Tiles to Chinese Porcelains

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X-Ray Spectroscopic Techniques applied to the Characterization of Pigments in Ancient Glazes: from Portuguese Tiles to Chinese Porcelains

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The use of non destructive techniques is mandatory in the study of ancient cultural materials, thus rendering most valuable the conjugate application of various X-ray techniques, including absorption spectroscopy. The fundamentals of X-ray absorption fine-structure spectroscopy (XAFS) induced by synchrotron radiation are briefly explained with emphasis on the near-edge structure (XANES) and the extended fine structure (EXAFS) of absorption spectra.

Illustrative examples of the application of these techniques to the characterization of pigments in ancient siliceous glazes are described, starting with glazed ceramic tiles (*azulejos*) manufactured in the 17th and 18th century to exemplify the valuable complementary relationship between local and extended structure when dealing with amorphous cultural materials. The role played by various metal ions in the glaze either as network formers (Zn^{2+}) or modifiers (Pb^{2+}) and as pigmenting agents (Sb^{3+}) are considered on the basis of the XANES spectra collected in fluorescence yield mode using the instrumental set-up of beam line BM-29 at the ESRF (Grenoble/France)* . The L_3-edges of Pb plus Sb were studied as well as the *K*-edge of Zn plus Fe, the latter from the mineral pigment vivianite .

Conversely, both XANES and EXAFS spectra were collected at the Co *K*-edge by similarly irradiating the blue glaze of Chinese porcelain archaeological fragments*. Spectroscopic results confirm the expected (2+) valence state of cobalt and corroborate a mean coordination number slightly higher than four around Co^{2+} ions. In fact, Chinese porcelains have lately been the object of many compositional studies to ascertain production periods and sites; after the maritime contact started by the Portuguese navigators in the 16th century, the trade of blue-and-white porcelains to Europe was intensified along the 17th century and nowadays European museums and traders have an increased need for certifying the authenticity of such art objects.

* Financial support of the EU through the Action Access to Research Infrastructures to perform experiments at the ESRF is acknowledged, as well as the support from the Portuguese Scientific and Technologic Foundation (FCT-MCTES) - Project PTDC/HAH/69506/2006.