

**MS91.P05***Acta Cryst.* (2011) A67, C764**Studies of archaeological by X ray imaging, fluorescence and diffraction**

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The X Ray Imaging (XRI), Radiography and Computed Tomography (CT), is a valuable support to X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) analysis of archeological remains from excavation. XRI gives a complete document of the object and an indication of the points of interest for XRF analysis and where to take samples for XRD. The data are useful to characterize the material composing the object, to determine its state of decay and to help to choose the best procedure for restoration and also support the work of archaeologists and restorers.

Here we present two studies of different objects. The first one is a clod containing human remains from Crustumerium, an ancient town in the North of Rome (IX sec. b. C.). The XRI allowed us to locate the ornaments of the arms and the position of the teeth; furthermore, we were able to identify points of interest for taking samples for XRD analysis and CT scan gave us a complete picture of the spatial arrangement of the ornaments inside the clod which would have been lost during micro-excavation due to their poor condition. This kind of ornament has never been seen before. Finally with XRF we identified the presence of Cu, Sn and Pb and therefore the bronze alloy.

In the second one, we used X-Ray radiography, XRF and XRD to study coins from excavation in the Palatine hill in Rome (first half of I sec. a. C.). Best results were obtained for three coins. The radiography allowed us to recognize details on corroded coins even when surface features were markedly worn. By using XRF we characterized copper alloys and by XRD we recognized corrosion products, mainly Malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ).

**Keywords:** X-ray diffraction, X-ray imaging, ancient materials

**MS91.P06***Acta Cryst.* (2011) A67, C764**Metals and colors: the case of glass slabs from late antique faragola (Italy)**

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Since Antiquity metals have been used to stain glasses. A wide range of colors was obtained by changing their valence state or site symmetry. In this contribution, a study based on X-ray Absorption Spectroscopy (XAS) is presented, aiming to identify the coloring agents in glass slabs of Late Antique age.

The samples come from the archaeological excavations performed at Faragola (Foggia, southern Italy). The investigations allowed the individuation of a richly decorated dining room (*cenatio*), dated back to the Late Antique period (fourth to sixth century AD). Three panels in *opus sectile* were placed along the central axis of the *cenatio*, surrounded by polychrome marbles and a very rare masonry *stibadium* of a semi-circular shape. The panels were made of glass slabs variously colored.

XAS analyses at the Cu-K, Fe-K and Mn-K edge were carried out at the GILDA-CRG beamline (Grenoble, ESRF) to study the link between the chemical state and local geometry around metals in red, orange, green, dark blue and blackish (deep greyish olive green) glass

slabs sampled from the panels. From the different edges several results were obtained:

**Cu-K edge** - The investigations identified both metallic (28%) and oxidized (72%, with a +1 charge) Cu phases in the red slabs. The orange samples revealed that the Cu particles were predominantly in the form of crystalline cuprous oxide (cuprite). In blue and green slabs, the predominant phase for Cu is  $\text{Cu}^{1+}$ . As this ion does not exhibit absorption bands in the visible range the presence of small (<10%) amounts of  $\text{Cu}^{2+}$  is supposed to give the color.

**Fe-K edge** - In blue and green slabs, the edge position (first inflection point of the absorption coefficient) corresponds to that of  $\text{Fe}_2\text{O}_3$ , whereas in the blackish slab the edge appears to rise at a lower energy. Considering also that the average Fe-O distance measured by EXAFS is longer for this sample we can derive that here there is a considerable presence of  $\text{Fe}^{2+}$ . This ion is in a tetrahedral site and the ratio  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is around 0.2-0.4.

The application of XAS investigation to the study of archaeological glasses fully demonstrated the power of this analytical technique for the non-destructive identification of coloring agents. The red and orange slabs are colored by metallic copper and cuprite respectively [1].  $\text{Cu}^{2+}$  should be the responsible for the light blue colours as well as for the green colours when coupled with Pb antimonates [2]. The abundance ratio of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and the complex  $\text{Fe}^{3+}\text{S}^{2-}$  would have an effect on the blackish slabs [2].

[1] A. Santagostino Barbone, E. Gliozzo, F. D'Acapito, I. Memmi, M. Turchiano, G. Volpe, *Archaeometry* **2008**, *50*, 451-473 [2] E. Gliozzo, A. Santagostino Barbone, F. D'Acapito, M. Turchiano, I. Memmi, G. Volpe, *Archaeometry* **2010**, *52*, 389-415.

**Keywords:** AS, glass, Archaeometry

**MS91.P07***Acta Cryst.* (2011) A67, C764-C765**The role of copper on colour of paleo-christian glass mosaic tesserae: an integrated study**

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The present study, carried out on coloured glass mosaic tesserae from the disrupted palaeo-Christian glass mosaic of St. Prosdocimus (Padova), which is one of the only two known in the Veneto region (Italy), reports results from XAS (X-ray Absorption Spectroscopy) and EMPA (Electron Microprobe) analyses, coupled in selected samples with X-ray Powder Diffraction (XRPD) and colorimetric analyses, aimed at clarifying how the different local structure, oxidation state and quantity of copper could influence the colour of glass tesserae.

The combined approach, involving integration of analytical results, yielded better knowledge of glass production processes in the 6th century AD and demonstrated that variations in colour are due to deliberate technical operations - particular redox conditions in kilns and the composition of glass batches - which were applied with the aim of obtaining various colours. In particular, copper imparts different colours depending on its state of oxidation.

In the case of the blue and green tesserae, the colour is due both to  $\text{Cu}^{2+}$  ions dispersed in the glassy matrix and to other chromophorous ions, such as cobalt, while copper, mainly present as  $\text{Cu}^{1+}$  ion, is not chromophorous. In addition, quantification of  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$  ions in the analysed samples demonstrated that, when  $\text{Cu}^{2+}$  is the main chromophorous ion, colour intensity is directly correlated to its content in the glass.

In the case of red and brown tesserae, colour is mainly due to the