MS91.P05

Acta Cryst. (2011) A**67,** C764

Studies of archaeologicals 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 ($CuCO_3 \cdot Cu(OH)_2$).

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

MS91.P06

Acta Cryst. (2011) A**67,** 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 Cu^{1+}. As this ion does not exhibit absorption bands in the visible range the presence of small (<10%) amounts of 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 Fe$_2$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 Fe$^{2+.}$ This ion is in a tetrahedral site and the ratio Fe^{2+}/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]. 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 Fe^{2+}/Fe^{3+} and the complex Fe^{3+}S^{2-} would have an effect on the blackish slabs [2].

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Keywords: AS, glass, Archaeometry

MS91.P07

Acta Cryst. (2011) A**67,** 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 Cu^{2+} ions dispersed in the glassy matrix and to other chromophorous ions, such as cobalt, while copper, mainly present as Cu^{1+} ion, is not chromophorous. In addition, quantification of Cu^{1+} and Cu^{2+} ions in the analysed samples demonstrated that, when 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 presence of metallic copper, and to cuprite in the orange tesserae. These phases are responsible for both the colour and opacity of the samples. In this context, in addition to the redox conditions in kilns, the relationships between the precipitation of the above phases and differing amounts of copper and lead in the samples were also discussed.

Lastly, the similarity of the present results with those already reported in the literature indicates routine glass production processes, notwithstanding their different age and provenance.

Keywords: archaeometry. XAS, glass

MS91.P08

Acta Cryst. (2011) A**67,** C765

Using 2D detectors for x-ray imaging

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The unique properties of newer generation solid state 2D detectors - like the combination of high dynamic range, low background and high spatial resolution with no point spread broadening - offer the possibility for new imaging applications.

In this contribution we will show examples of non-destructive X-ray imaging applications with a PIXcel^{3D} detector that is based on the Medipix2 technology. Examples include imaging techniques based on transmission geometry, Bragg diffraction (X-ray topography) and non-coherent scattering effects. These imaging applications allow to combine traditional X-ray analysis with micro-structural investigations of the samples and the correlation with macroscopic material properties. Examples of organic samples and semiconductor materials will be shown.

Keywords: imaging

MS92.P01

Acta Cryst. (2011) A**67,** C765

Macromolecular crystallization: robotics, procedures and Innovations

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At the time of crystallization experiments the structure of a macromolecule is not known and hence an optimum strategy cannot be established. At the LMB, scientists can undertake initial experiments using a wide variety of conditions and robust automated procedures [1]. The procedures are straightforward, enabling LMB scientists to operate independently. We are continuously developing methods, like the Pi sampling [2] and devices to increase the chance of crystallization and crystal optimization. There are now different MRC crystallization plates that can be used on commercially available robots [3]. Also, we have created screens like MORPHEUS [4] to complete the formulation of commercial kits.

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Keywords: macromolecular crystallization, screen, automation

MS92.P02

Acta Cryst. (2011) A**67,** C765

Utilization of desiccant for enhancing protein crystallization

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The vapor diffusion (hanging or sitting drop) technique is widely used in protein crystallization screens. In conventional vapor diffusion crystallization screens the concentration of protein usually increases from $0.5C_p$ (C_p: the initial protein concentration before mixing with the reservoir solution) to ~C_p. This limited concentration range reduces the probability of the solution being in the nucleation zone. If the protein concentration range is increased, we may expect to see a higher crystallization success rate.

Based on the above consideration, we proposed a new method to increase the concentration range in protein crystallization by using desiccant instead of the reservoir solution in the vapor diffusion technique[1]. Fig. 1 illustrates the difference in the arrangement of crystallization cells between the conventional and modified vapor diffusion methods.

Thirteen proteins were tested using the modified and conventional sitting drop methods. It was found that the improvement by using the modified method is strikingly significant. With consideration of the following features we recommend this modified method for practical protein crystallization screens. (1) Conditions under which drops remain clear in the conventional vapor diffusion method may yield crystals in the modified method. (2) The modified method can produce crystals from solutions with lower initial protein concentrations, which consumes less protein. It is always very difficult to produce protein samples at concentrations sufficient for crystallization trials. Using the modified method, we did not need to worry as much about the concentration of the protein during sample preparation. (3) The involved modification is very simple and efficient and can be applied without the need for large changes to the standard vapor diffusion protocol. The modification can also be integrated into automated systems. (4) Finally, the modified method reduces the cost of screening because no reservoir solution is necessary.

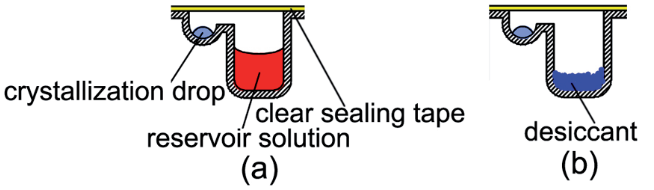

Figure 1. Schematic illustration of the difference in the arrangement of crystallization cells between the conventional and modified vapor diffusion methods. (a) The arrangement of crystallization cells in the conventional vapor diffusion method (sitting drop method). (b) The arrangement of crystallization cells in the modified vapor diffusion method[1].

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Keywords: protein, crystallization, methodology

MS92.P03

Acta Cryst. (2011) A**67,** C765-C766

Fields and crystals: what can we learn about quality?

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