Report on EC 53

SIMULTANEOUS TIME-RESOLVED X-RAY DIFFRACTION AND ELECTROCHEMICAL STUDIES ON CULTURAL HERITAGE ALLOYS

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Introduction

This was the first test of a novel electrochemical cell (eCell) designed for time resolved spectro-electrochemistry of real metal surfaces such as those encountered on cultural heritage artefacts. Here, the objective was to evaluate XMaS combined with the Mar CCD camera for the study of corrosion passivation and removal, and the application of protective coatings. We were able to collect over 600 images in various time sequences, including the conversion of complex copper chlorides to cuprite (relevant to the conservation of artefacts recovered from a marine environment, such as the bronze cannon of the Mary Rose), the removal of silver tarnish, and the application of a lead carbonyl coating as a protective surface for lead artefacts. All of this data was collected in parallel with the electrochemical data from eCell, and all these processes yielded useful data which will result in at least three publications in refereed journals.

The use of the Mar Camera

The Mar CCD camera, used as a detector in reflection mode allows out of plane diffraction to be collected over a reasonable angle. This is extremely important, as whilst the surfaces we look at present tend to give powder-like diffraction patterns, the rings contain structure. Changes of orientation of surface species produce changes in spectra collected in a single plane (e.g. with RAPID 2 at Daresbury), and these cannot be distinguished from changes in surface concentration without the 2-D data. We also achieved much higher sensitivity, especially for silver tarnish, than we have previously achieved.

In our configuration, the camera plane intersects the diffraction cones at an angle to produce elliptical rings. It was completely impossible to process any of our data with FIT2D as it could not cope either with the eccentricity, or the fact that the beam centre was well off the picture.

As a result we have successfully developed a new code MARPROJECT. With this we can take any camera plane with its axis between 0 and 68 degrees to the beam, and reproject the image into 2Θ - γ space (where γ is the out-of-plane diffraction angle). The rings are therefore reprojected into straight bars. This makes integration of part or all of the image to form a spectrum a trivial exercise, and the peak intensity is easy to correct for the original length of the elliptical arc, for example. Other benefits have been that simple image rotation will correct for small amounts of axial misalignment in the camera, and we will in future have close to real time generation of spectra from images in a much simpler way than “CAKE”. (Time to load and reproject an 8MB image is around 2 seconds including display time on a typical notebook PC).

The immediate future

We are developing essential background removal routines for MARPROJECT so that the inevitable scattering which accompanies the analysis of a sample under ~100μm of fluid can be corrected.. Some peak ID and camera centring routines are being added as well as d-space reprojection.
We had some minor synchronization problems between our (moving) working electrode and the camera timing, which will be corrected in future runs by using a camera trigger pulse issued by our cell control software.

Having looked at what are essentially reference materials, for future work, we plan to move on to the examination of bronze alloys, including a set of 2000 year old corroded bronze coins.

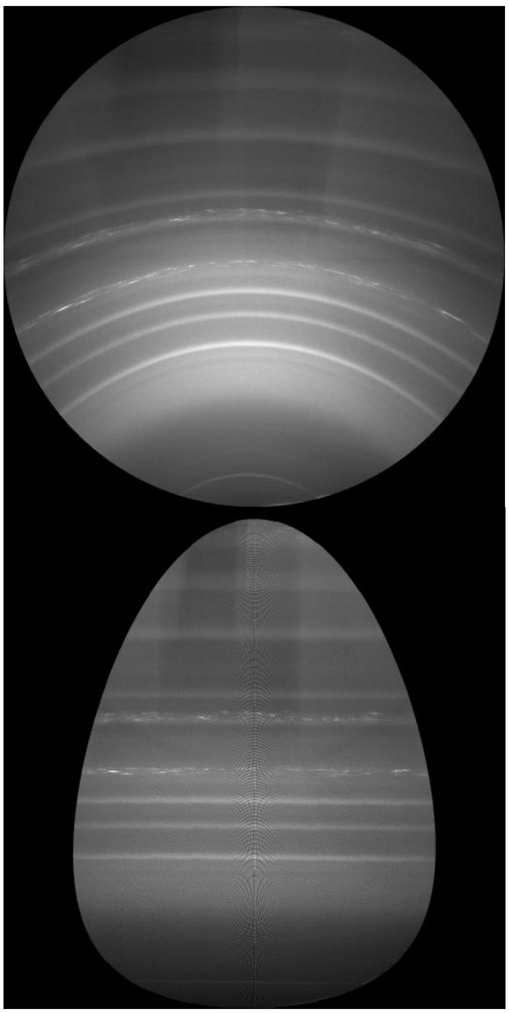

Fig 1: Image from the Mar CCD camera and its reprojection using MARPROJECT (reprojected image has been rotated by 1.5 degrees to correct for camera misalignment.)

Preliminary Publications

2 poster and 1 oral presentations on this work were given at the XMaS users meeting (University of Warwick) May 2006, and 2 posters were presented at the International Workshop on Non-destructive Testing of Museum Objects, Cyprus, May 2006