EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Visualizing the hidden paint layer of an important Italian Renaissance Painting with XRD phase mapping	**Experiment number**: EC764
Beamline: ID15B	**Date of experiment**: from: 20/04/2011 to: 24/04/2011	**Date of report**:
Shifts: 12	**Local contact(s)**: Veijo Honkimaki	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Introduction:

The goal of this experiment was to further test the feasibility of imaging (hidden) paint layers on real paint samples by high energy X-ray powder diffraction (HE-XRPD). A previous study showed the difficulty in imaging certain pigments (goethite, hematite, cobalt blue) in the presence of hydrocerussite due to peak overlap with strong hydrocerussite reflections [1]. Hydrocerussite is a component of lead white, a pigment frequently used as a background layer in paintings. Two dimensional XRPD measurements were performed on an icon (Figure 2a) containing various commonly used pigments on a ca. 2 cm wooden panel. Mappings were performed with and without a lead white covering layer. As a second part of this experiment stereoscopic X-ray imaging – a technique consisting of recording two projected images at two different viewing angles – was performed on a test sample (a mock-up painting (Figure 2b) was used as over painting on the previously scanned icon). The possibility for using this technique to separate pigments used in both the top (covering) layer and the bottom (original) layer was determined.

Quality of measurement/data:

The 300 x 300 μm^2 beamsize was well suited for the two dimensional scanning experiments. Due to the high-speed acquisition of the Pixium detector and the high energy (ca. 87 keV) and flux of the primary X-ray beam it was possible to achieve a scanning speed of ca 8.5 min cm^{-2} (0.4 mm step size; 0.5 seconds exposure) whilst collecting high resolution 2D XRPD patterns in transmission mode.

Status and progress of evaluation:

The two dimensional diffraction patterns were analyzed using the XRDUA software package [2]. Thanks to explorative batch fitting less abundant phases and/or phases that only make up small parts of the scan can be visualized (and identified) as illustrated in Figure 1. After identification, phase dependent distribution maps can be obtained by using batch fitting with a pre-defined model.

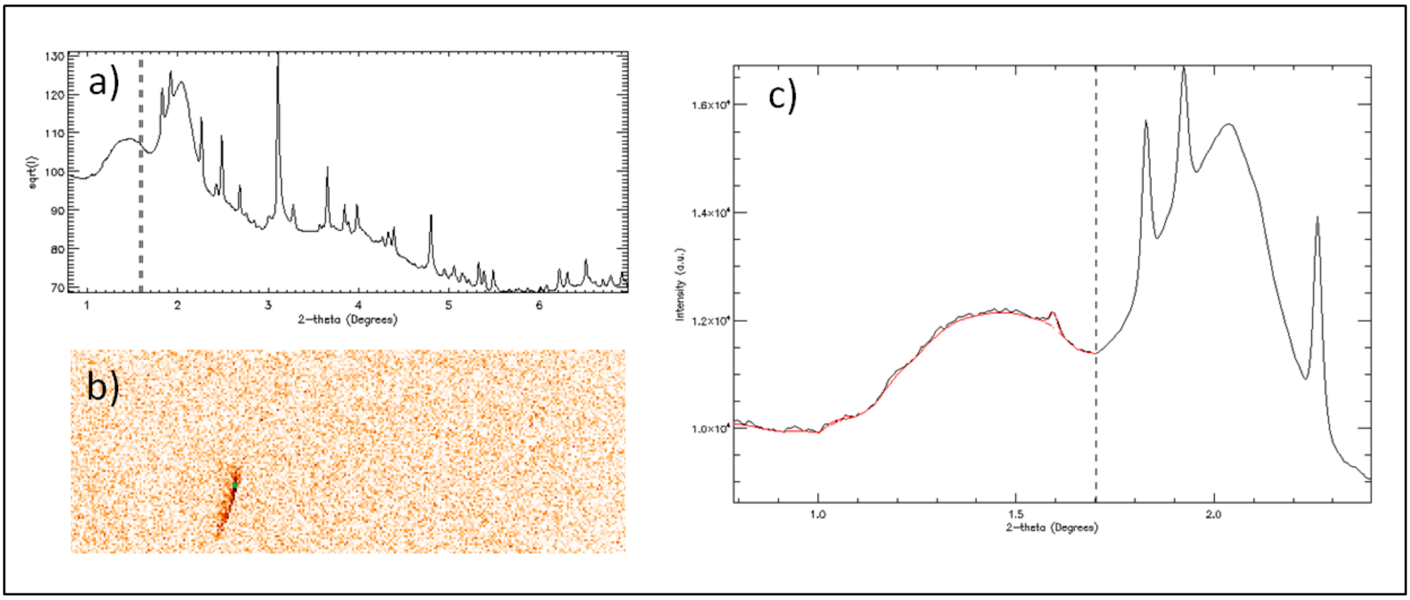

Figure 1 a) Average diffractogram of an entire scan; b) Explorative distribution map based on the region of interest between the vertical dashed lines shown in a); c) Diffractogram of the green point selected in b). As the fitted signal is the only reflection for this crystalline phase, a model is made for a limited 2θ range which can be used for batch fitting of the entire scan. The signal modeled in c) matches the most intense reflection of prussian blue.

Results:

The different pigments found in the icon and mock-up as well as the reconstructed images are given in Figure 2.

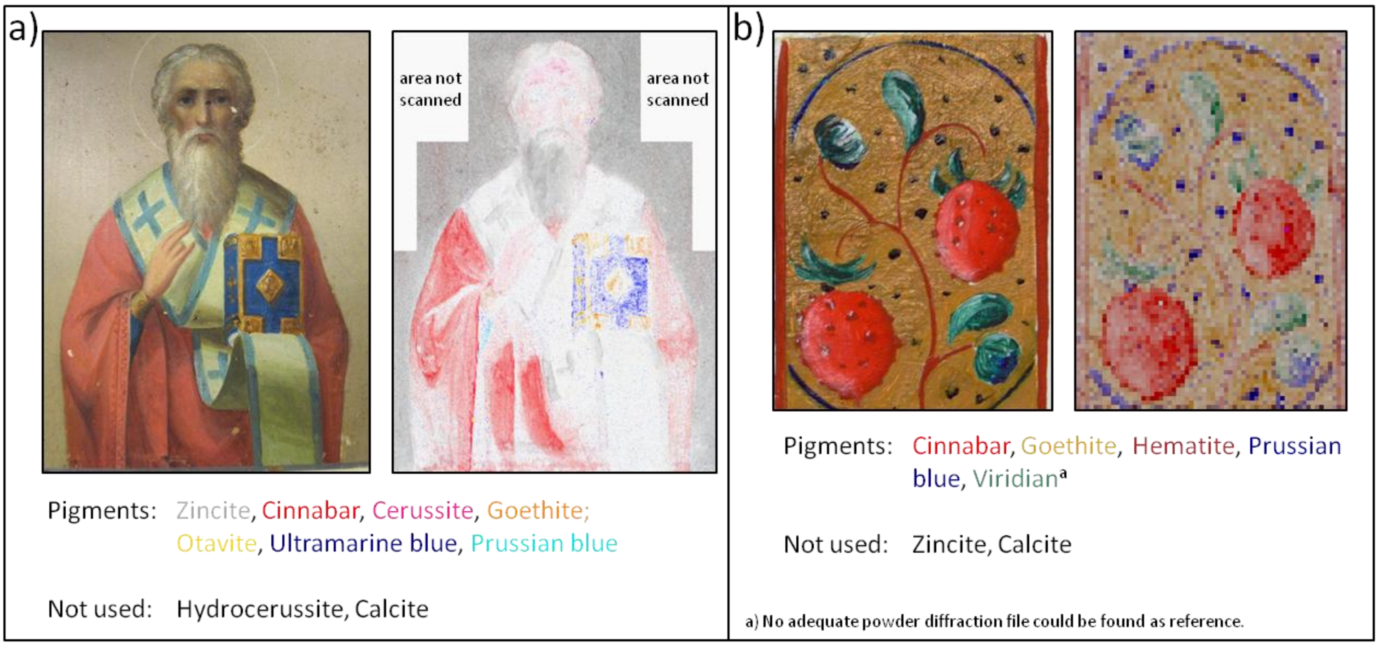

Figure 2 a) Photograph of the icon (left) and reconstructed image using the different distribution maps of the pigments shown in color (right). The distribution maps of hydrocerussite and calcite are not included in the reconstructed image. b) Photograph of the mock-up (left) used for stereoscopic X-ray imaging and reconstructed image (right). The distribution maps of zincite and calcite are not included in the reconstruction.

The high angular resolution of the XRD patterns makes it possible to visualize and identify (to a certain degree) the different phases in a complex sample. Additional phases in the icon have been visualized but identification has not (yet) been successful. Figure 3 shows the cinnabar distribution maps obtained from two different viewing angles (left and right) of the combined mock-up – icon test sample. The anaglyph image (middle) gives a clear indication that the cinnabar used in the mock-up is located at a different depth than the cinnabar used in the icon.

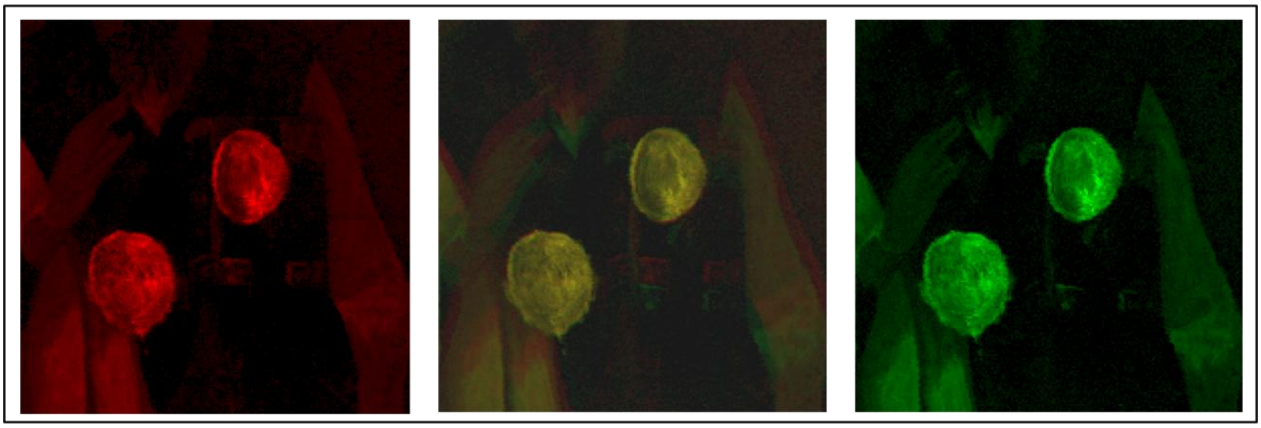

Figure 3 Cinnabar distribution maps obtained from two different viewing angles (left and right image) and the anaglyph image (middle). All images have been gamma corrected to improve visualization. The anaglyph image is obtained by overlapping the strawberries in the red and green image. It is clear that the cinnabar used in the icon shows a significant shift between the two viewing angles.

References

1 De Nolf, W., et al.; *High energy X-ray powder diffraction for the imaging of (hidden) paintings*, Journal of Analytical Atomic Spectroscopy, **2011**, 26, 910 – 916

2 De Nolf, W., Janssens K.; *Micro X-ray diffraction and fluorescence tomography for the study of multilayered automotive paints*, Surf. Interface Anal., **2010**, 42, 411 – 418