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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

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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.

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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:** Revealing the painting technique of Leonardo da Vinci in l'Adorazione dei Magi	**Experiment number**: EC801
Beamline: ID21	**Date of experiment**: from: 09/06/2011 to: 14/06/2011	**Date of report**: 27/08/2011
Shifts: 15	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

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Report:

The main goal of the experiment was to determine the painting technique used in an intriguing and important work of art: The Adoration of the Magi by Leonardo da Vinci; an unfinished early painting by Leonardo. However, as part of *The Giotto project* of the Opifico delle Pietre Dure (OPD, Florence, Italy) with the collaboration of the Getty Institute, some samples from the mural paintings in the Bardi and Peruzzi Chapels (Santa Croce, Florence, Italy) could be also added to the array of samples studied by means of SR micro imaging techniques. Figure 1 shows the masterpieces studied as part of the experiment EC 801.

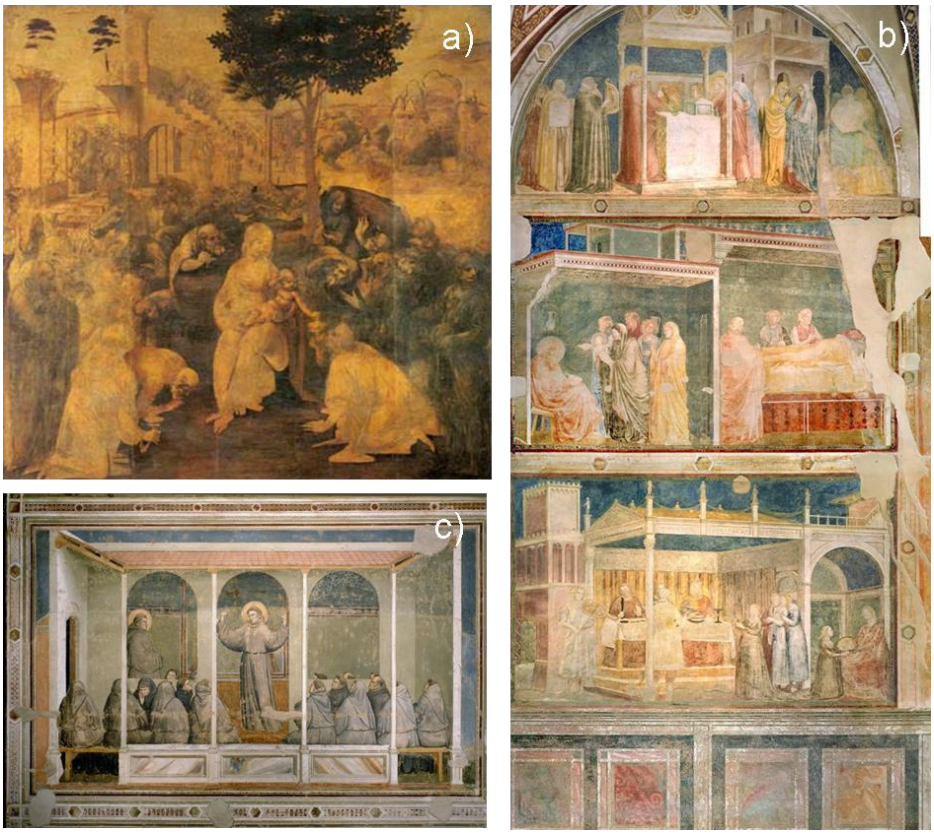

Figure1. a) The Adoration of the Magi by Leonardo da Vinci (Uffizi Gallery, Florence, Italy); b) scheme of one of the walls of the Peruzzi Chapel by Giotto (Santa Croce, Florence, Italy); c) Scene showing the *Appearance at Arles of* Sant Francesco in the Bardi Chapel by Giotto (Santa Croce, Florence, Italy).

Experimental

A Table summarising the samples studied at ID21 as part of the Experiment EC801 and the work-of-art of provenience is presented below. Preliminary results on the materials present in the sample obtained by the use of conventional techniques are also summarised in the Table.

Table 1. Samples analysed at ID21 as part of the Experiment EC801.

Painting	Number of Samples	Materials identified by conventional techniques	
		Inorganic compounds	Organic compounds
The Adoration of the Magi (Leonardo da Vinci)	4	-	Proteinaceous material
Cappella Peruzzi (Giotto)	3	Silicate, calcium carbonate, lead carbonate, calcium oxalates	Proteinaceous material /siccative oil
Cappella Bardi (Giotto)	2	-	-

Samples were already embedded in resin and cross sections were obtained to be investigated by visible and electronic microscopy. The importance of the paintings does not allow the collection of a great number of samples nor samples of a big size. Samples measure less than 1-2 mm^2 and show a variable number of layers as well as layer thickness (down to 2 μm). The absence of more samples to perform invasive analysis and the impossibility of collecting other, evidence the necessity to use powerful imaging techniques. Figure 2 show the optical microscope images of the cross-sections of the samples analysed.

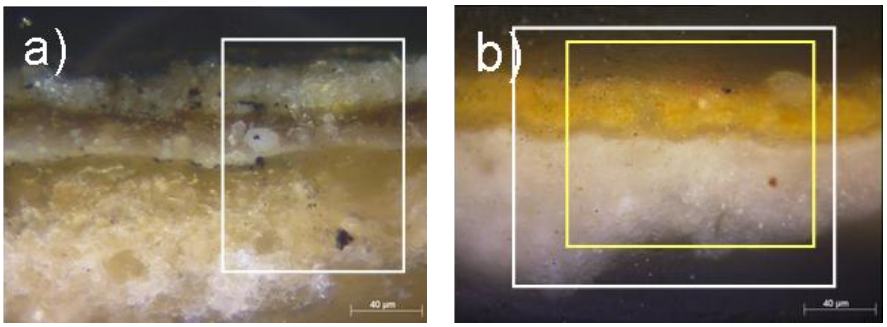

Figure 2. Optical microscope image of the cross-section of samples from a) L'Adorazione dei magi; b) from Peruzzi Chapel . Squares correspond to the areas chosen for: XRF map (yellow) and ATR-FTIR map (white).

Two sets of experiments were performed in order to completely analyze the painting cross-sections:

- SR μFTIR. very good signal was obtained with the new ATR device. The ATR resulted perfectly adapted for the study of embedded cross-sections, allowing the analysis of the cross-sections without

altering the embedded fragment and thus its build-up nor composition [i]. Moreover, synchrotron radiation characteristics permit working with a spot down to 7x7 um2 necessary to determine the distribution of painting materials layer by layer. The beam size was of 28 microns. Identification was made by comparison with reference data [ii, iii, iv, v, vi, vii, viii, ix].

• SR μXRF. An energy of 9.05keV was chosen due to the characteristics of the samples. Fluorescence was collected with a Ge detector, and spectra fitted with PyMca [x]. The spot size of SXM was 1 μm permitting the study of thin painting layers.

Mappings were performed with the two techniques on the same regions in almost all cases. Areas chosen for both the μXRF and μATR-FTIR mappings (around 10x20 μm^2) are highlighted in Figures 2.

Results

The morphological characterisation of the samples by means of the optical and scanning electronic microscopes highlighted that samples presented some similarities on their stratigraphies based on the work-of-art of provenance. XRF and ATR-FTIR mapping results are summarised below: similarities in both the elemental and molecular data obtained could be also observed between them.

L'Adorazione dei Magi (Leonardo da Vinci)

The cross-sections from l'Adorazione dei Magi samples reveal that a preparation layer was applied on the sketch, and on top of this several paint layers were applied [i]. XRF data showed that the pictorial layers are lead based layers while the preparation layer is calcium and sulfur based. Other elements identified and mapped by XRF were Al, Si, Mn, Fe and K .

As far as the organic material is concerned, bands at 3300, 3080, 2924, 2850, 1650 and 1540 cm^{-1} pointed to the presence of a proteinaceous material. The presence of oxalates in some areas and the penetration of the embedding resin that can be noticed in the spectra of the superficial layers make difficult their unequivocal interpretation. An oil medium can be identified in some spectra by the presence of the characteristic CH st and CO st bands in the regions 3000-2800 cm^{-1} and 1750-1650 cm^{-1}, respectively.

Figure 3 shows a representative micro XRF elemental maps and micro ATR-FTIR molecular maps of the samples from l'Adorazione dei Magi.

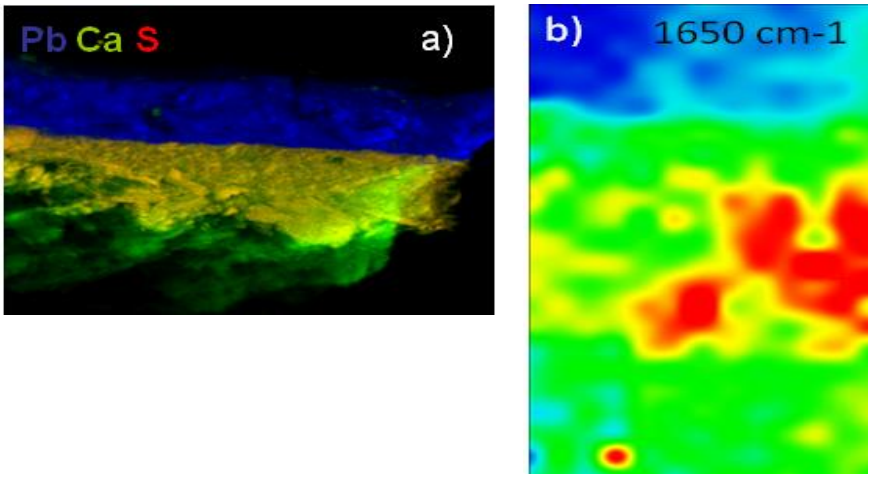

Figure 3. a) µXRF elemental map and b) µATR-FTIR molecular map of a sample from l'Adorazione dei Magi . The elements and vibrational bands mapped are indicated in the figure.

Mural paintings by Giotto: Peruzzi and Bardi Chapels

Giotto samples mainly consisted in a preparation layer with a painting layer on top. XRF and FTIR mapping on samples from Santa Croce mural paintings by Giotto showed that the preparation layer consisted in calcium carbonate mixed in almost all cases with silicates containing Fe, K and Mn. The organic materials identified in the samples were: a proteinaceous material used as binding media (in both the preparation and the paint layers), and a drying oil used in the metallic layers preparation layer. These results are in agreement with the GC/MS ones.

Conclusions

The main goal of the experiment was achieved: the elemental and molecular mapping of the samples cross-section was obtained. Both experiments gave complementary data on the samples obtaining the distribution of organic materials such as binders and varnishes from the FTIR mapping and of pigments, fillers and dryers by XRF mapping in the sample build-up.

Moreover, experiment EC801 highlighted that the FTIR end station at ID21 presents the ATR device that suits perfectly well with the characteristics of painting samples. Good quality spectra with high signal-to-noise ratio were obtained for all the samples allowing the recognition of the characteristic IR features of the materials present (both organic and inorganic). Therefore, the use of an ATR device not only simplifies a critical point such as the preparation of samples for imaging analysis but also ensures the analysis of the very same area for both elemental and molecular mapping.

Discussion of the results obtained with curators and restorers from the Opificio delle Pietre Dure (Florence, Italy), The Getty Institute (USA) and Eng. Seracini will allow integrating all the data available on L'Adorazione dei Magi and the Santa Croce Chapels in order to determine the painting technique of Leonardo da Vinci and Giotto and to establish the originality of the materials identified.

References

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