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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:** Study of blanching of easel paintings (16th to 19th centuries) by X-ray nanotomography and nano-XRF	**Experiment number**: HG49
Beamline: ID16A-NI	**Date of experiment**: from: 6/03/2015 to: 10/03/2015	**Date of report**: 13/09/2016
Shifts: 9	**Local contact(s)**: Alexandra Joita Pacureanu (email: joitapac@esrf.fr) Remi Tucoulou Tachoueres (email: tucoulou@esrf.fr)	*Received at ESRF:*

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Report:

Introduction

This project focuses on the blanching of easel paintings, a recurring alteration that can affect the varnish layer and also the paint layer itself. The chemical and physical phenomena responsible for the whitening have not yet been identified and this is currently being investigated as PhD research work, at the C2RMF (Center for Research and Restoration of the Museums of France). Current conservation treatments are not entirely satisfactory. Understanding this alteration will therefore allow the proposal of adapted, efficient and durable conservation treatments.

Field Emission Gun Scanning Electron Microscopy observations of circa 50 non-embedded paint micro-samples revealed an highly porous structure in the altered layers with a pore size ranging from 20 nm to 4µm [1]. Nevertheless, our observations are limited to the surface or the edge of the sample and do not reflect the whole porosity distribution. Besides, the samples cannot be embedded because the pores would be filled in by the resin penetrating into the sample.

Our objective is to determine the 3D spatial distribution of the pores, their sizes, 3D morphologies and their chemical environments in order to better understand the alteration process. Analyses were performed on the nano-imaging beamline ID16A-NI using nano-holotomography in combinaison with nano-X-ray fluorescence (XRF). The use of phase contrast nanotomography was required since it enables to access a nanometric spatial resolution, and especially to distinguish regions with low and similar electron densities (pores, binder, varnish) in presence of high density compounds (pigments with iron, copper, lead, …). XRF 2D maps were collected to track possible traces of metals (potentially used as driers) and to see if their distribution is correlated with the degradation.

Experimental part

- Samples

A corpus composed of 8 paint micro-samples were analyzed by nano-holotomography and 4 samples also by nano-X-ray fluorescence (XRF) (table 1). To avoid the sample contamination by organic matter, they were pushed and blocked in quartz capillaries (figure 1, left). As they were not well fixed, they moved during the scans. So, we finally decided to stick them with the least amount of araldite glue (viscous enough to not penetrate in the whole sample). The yellow cross corresponds to the analyzed area (located on the opposite side of the glue) (figure 1, right). It is important to underline that a sample shrinking was induced by the beam and corrected using algorithm during the reconstruction process.

Sample	Nano-holotomography	Voxel size	Nano-X-ray fluorescence	Sample preparation
Lame 23 (mock-up sample)	X	50 nm		In a quartz capillary
Lame 24 (mock-up sample)				In a quartz capillary
Nattier 1	X	50 nm	X	In a quartz capillary
Crignier	X	50 nm		In a quartz capillary
Chardin	X	50 nm	X	In a quartz capillary
Van Schrieck	X	130, 50, 25 nm	X	Stick with araldite glue
Van der Bent (altered)	X		X	Stick with araldite glue
Van der Bent (after conservation treatment)	X	50 nm		Stick with araldite glue

Table 1: analyses performed and samples preparations. For nano-holotomography, the voxel size is specified.

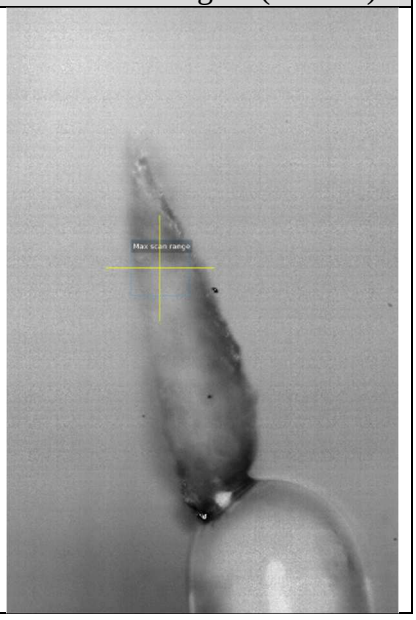
In a 200 µm quartz capillary	Stuck at the end of a capillary with araldite glue (viscous)
	

Figure 1: Sample preparation

- Experimental parameters

The samples were analyzed by magnified holotomography at the nanoscale using the experimental parameters given in table 2. Except for one, samples were imaged only with a voxel size of 50 nm because it enables a good compromise between the spatial resolution and the analyzed field of view (more than 100x100x100 μm^3) (table 1).

Energy	17 keV
Number of recorded distances	4
Exposure time	200-400 ms
Number of projection	1000-2000
Voxel size	130, 50, 25 nm

Table 2: Experimental parameters for the nano-holotomography

The XRF 2D maps were collected in the meantime (average over the beam path) with an energy of 17 keV as well, a spatial resolution of 50 nm and an exposure time of 50 ms.

Results and discussion

Three dimensional images were obtained from retrieved phase maps by tomographic reconstruction. The image processing was performed using the sofwares ImageJ and Mevislab®. A detail of a reconstructed slice of the sample "*van der Bent (altered)*" is reported in figure 2. It highlights that the pores (in red) are located in the binder (in green). The results obtained on other samples are consistant. Considering the pore size (from circa 200 nm to 4 µm), the blanching is induced by the Mie light scattering by the pores located either in the varnish or in the organic binder [1]. This results constitute a major advance toward the understanding of the alteration, since it revealed that the alteration process takes place in the organic matter.

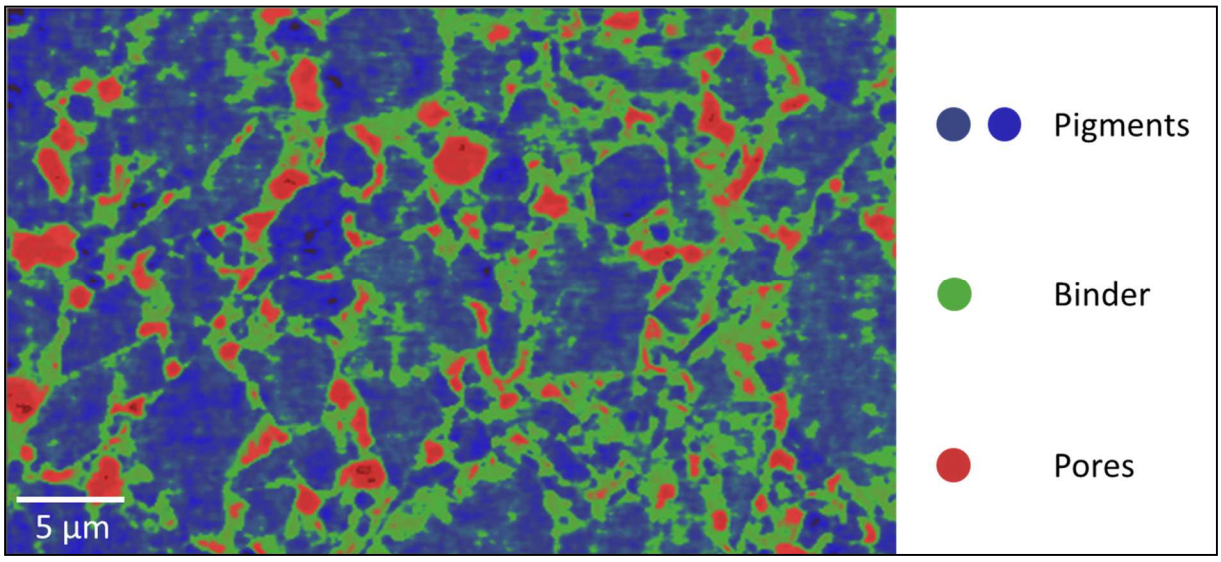


Figure 2: Detail of a reconstructed slice highlighting the presence of pores in the organic binder. Scale bar: 5µm

The analyses of the 3D images revealed that the pores are closed (not connected) and therefore hard to access from the painting surface during conservation treatments (solvents application and varnishing). Indeed, the comparative study of an altered and a conserved sample, revealed that pores are still present in the binder and that current conservation treatments are therefore not efficient to durably fill or resorb them. (figure 3).

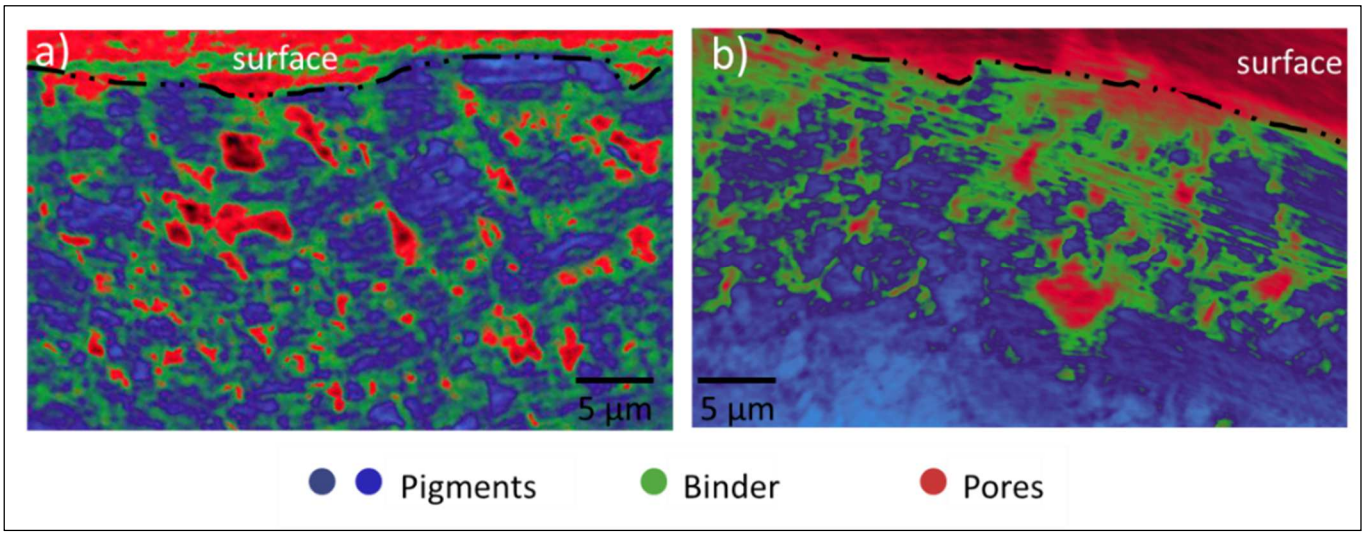


Figure 3: X-ray phase contrast nanotomography reconstructed images. a) altered; b) conserved paint micro-samples. Scale bars: 5µm.

Conclusion and perspectives

The sample 3D characterizations enables us to highligh that the pore are located in the organic matter: in the varnish or in the binder. The pore size is ranging from 200 nm to 4 µm. Concerning the 3D distribution in the layers, the pores are not connected and located throughout the layers. Moreover, the comparative study revaled that current conservation treatments are not satisfactory. These results constitute a major advance towards the understanding of the alteration and the proposal of new appropriate conservation treatments, which remains an important issue for the conservations of these paintings.

The high quality of the results obtained (more detailed in a future publication) encourages us to continue our research on conservation treatments for blanched easel paintings. More specifically, we wish to focus on the efficiency and reversibility of a new developped treatment based on a perfluoropolyether gel. We thus plan to submit a continuation of this experiment at ID16A.

References :

[1] A. Genty-Vincent *et al.*, Blanching of paint and varnish layers in easel paintings: contribution to the understanding of the alteration, Applied Physics A **121**, 779 (2015)

[2] A. Genty-Vincent *et al.*, Investigating the 3D arrangement of submicron pores in blanched easel oil paintings by X-ray phase contrast nanotomography (to be submitted)

[3] A. Genty-Vincent *et al.*, Investigating the 3D arrangement of submicron pores in blanched easel oil paintings by X-ray phase contrast nanotomography, Synchrotron radiation and neutrons in art and archaeology (SR2A), 6-8 september 2016, Chicago (oral communication)

[4] A. Genty-Vincent *et al.*, X-ray phase contrast nanotomography of porous altered easel oil paintings, ESRF User Meeting, UDM1– Nanoscience: X-ray diffraction and coherence, 8-10 february 2016, Grenoble (oral communication)