



## 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 using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now 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.

**Experiment title:**

Comparison of several twin copy panels from Bruegel with different state of degradation of mercury sulfide by micro-XANES

**Experiment number:**

EC979

<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 29/05/2012      to: 04/06/2012	<b>Date of report:</b> 11/11/2012
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Marine Cotte	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

**Marie Radepont<sup>a,b\*</sup>, Marine Cotte<sup>a,c\*</sup>, Koen Janssens<sup>b</sup>, Jana Sanyova<sup>a\*</sup>, Emeline Pouyet<sup>c\*</sup>, Willemien Anaf<sup>b\*</sup>.**

(a) LAMS, UMR 8220 CNRS, Ivry-sur-Seine, France

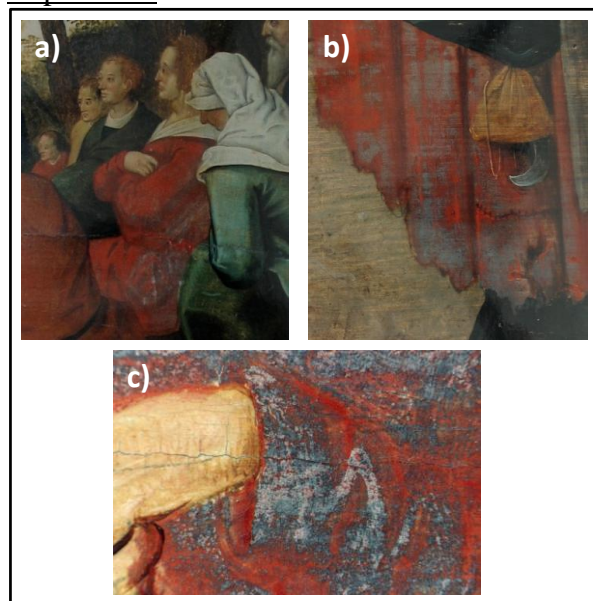
(b) University of Antwerp, Department of Chemistry, Antwerp, Belgium

(c) ESRF, Grenoble, France

(d) KIK-IRPA, Bruxelles, Belgium

**Report:**Purpose

The aim of this investigation was to study samples coming from several paintings of the 16<sup>th</sup> C. painter P. Bruegel the Younger and its workshop containing the red pigment mercury sulfide ( $\alpha$ -HgS, called vermilion for its synthetic form). In these paintings, vermilion presents degraded areas with grey crusts on its surface. The direct comparison of paint samples obtained from related artworks would give a better insight into the factors influencing the alteration of this pigment.

Experiment

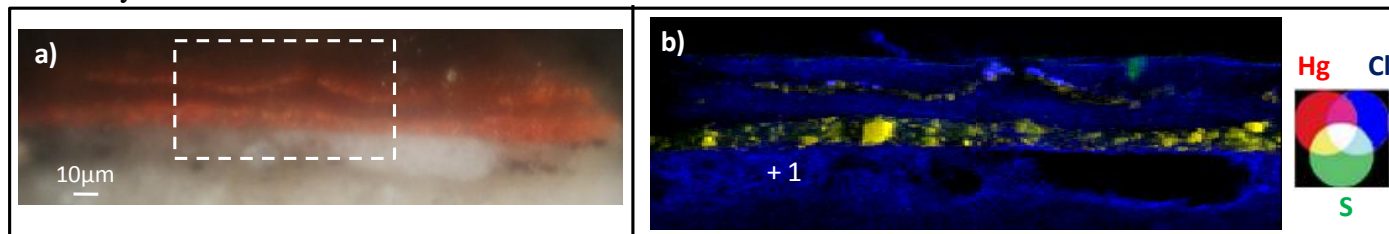
**Figure 1** Enlargements of paintings where samples were taken: **a)** “Preaching of John the Baptist; **b)** “The Village Lawyer”; **c)** “The Wedding Dance”.

Four samples were analyzed during this experiment, coming from three major paintings from P. Bruegel the Younger: “Preaching of John the Baptist” (Lier, Belgium), “The Village Lawyer” (Ghent, Belgium) and “The Wedding Dance” (Ghent, Belgium). From the first painting, two samples were taken from the red coat of a figure in the right, one in the shadow (C006) and one in a degraded area (C007). Both samples present a thick preparation layer with calcite and lead white. Above this, two superimposed layers of red mercury sulfide are visible, separated by a varnish layer. On top of them, some black crusts are present below the superficial varnish. From the second painting, one sample was taken from the red dress of the bending woman in the center (C012). From the last painting, one sample was taken from the red shirt of the man in the center (C052). (see Fig. 1)

A micrometric beam ( $0.5 \times 0.2 \mu\text{m}^2$  - hor x ver) was necessary for the study of these cross-sections composed of multiple micrometric layers. For each sample, chemical maps were acquired and XANES spectra at Cl and S K-edges were collected. After acquisition, data were analyzed using PyMCA<sup>1</sup>.

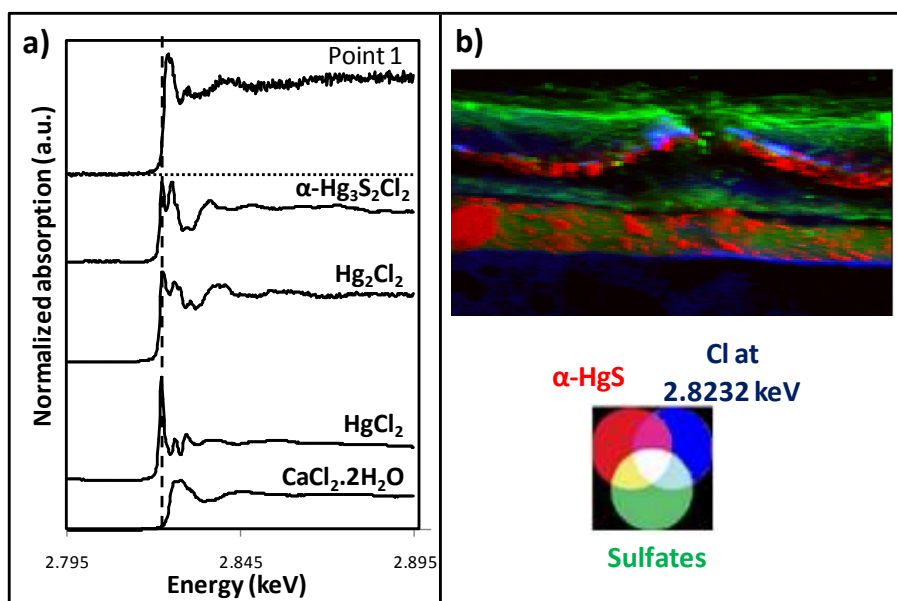
## Results

As chlorine was already proven to be involved in the alteration of red mercury sulfide<sup>2</sup>, the presence of this element was studied first by  $\mu$ -XRF. Maps acquired on the different samples at high energy (7.9 keV) showed that chlorine was present in the cross-sections and in almost all layers (preparation, pictorial) (see Cl map for sample C007 Fig. 2b). The only sample taken from a non-degraded area (C006) also showed the presence of chlorine, but the concentration of this element seemed to be homogeneous in all layers of the cross-section. For the three others samples, chlorine seemed to be present in higher concentration on top of red mercury sulfide layers.



**Figure 2** a) Visible picture of C007; b)  $\mu$ -XRF maps of the entire sample, acquired at high energy (7.9 keV), showing the combination of mercury (red), sulfur (green) and chlorine (blue).

$\mu$ -XANES spectra were acquired in different points of these samples in order to identify the chlorine species visible in XRF maps. On areas where chlorine was high concentrated (on C007, C012 and C052), a peak typical for mercury chlorine compounds with energy of maximum absorption at 2.8232 keV was present in Cl K-edge spectra. Nevertheless the absence of clear features on these spectra did not allow the identification of a specific phase. On the other areas of all samples, Cl K-edge spectra showed one peak with an energy of maximum absorption at 2.8242 keV, slightly higher than the white line of mercury chlorine references (Fig.3a).  $\mu$ -XANES spectra at S K-edge just shows the presence of red mercury sulfide (2.4716 keV) and a peak corresponding to the energy of maximum absorption for sulfates (2.4825 keV).



**Figure 3** a)  $\mu$ XANES spectrum acquired at chlorine K-edge (from 2.795 to 2.895 keV) on the point 1 (localized in Fig.2)) compared to the ones of chlorine containing references; b) Results of mapping of the dashed white rectangle in Fig.2a with one combination of three maps: sulfur at 2.4716 keV (cinnabar, red), sulfur at 2.4825 keV (sulfates, green) and chlorine at 2.8232 keV (blue).

Unfortunately, XANES spectra acquired on these four samples from Brueghel the Younger's panels did not allow a clear identification of the different chlorine containing compounds which seem to be present in the cross-sections. In these samples, chlorine seemed to be present in all layers, which could be indicating that the binder used by the painter contains this element and is then a potential source of this element which could directly degrade the red mercury sulfide pigment with the action of light.

1 V. A. Sole, E. Papillon, M. Cotte, P. Walter and J. Susini, *Spectrochim. Acta, Part B*, 2007, 62, 63–68.

2 M. Radepon, W. de Nolf, K. Janssens, G. Van der Snickt, L. Klaassen and M. Cotte, *J. Anal. At. Spectrom.*, 2011, 26, 959-968.

To have a better idea of the disposition of these compounds, maps were acquired at these two energies and at the energy of chlorine in mercury chlorine compounds (2.8232 keV). Layers of original pigment ( $\alpha$ -HgS) were visible and for C007, C012 and C052 maps acquired at 2.8232 keV showed that this type of chlorine containing compounds were present on top of pictorial layers. For C007, these chlorine phases were present above an opening presented by the higher  $\alpha$ -HgS layer, and not above the lower one (Fig.3b). A sulfate layer is visible on top of all samples, and for C007 a thin layer of sulfate is also present between the two pictorial layers (Fig.3b).

These samples are still under study in order to explain the difference between C006 (from non-degraded area) and the other samples.