ESRF	**Experiment title:** HR-XRD characterization of lead white pigments present in paintworks of the Italian Renaissance	**Experiment number**: HG56
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Report:

This project was a continuation of the HG35 experiment that was led at the ID22 HR-XRD beamline of the ESRF in December 2014. It focused on a set of 10-15 micro-samples collected on several masterpieces of the Italian Renaissance, conserved at the Louvre Museum. The was to gather information on the composition and microstructure of the lead white pigment used in paintings of this period, using Rietveld analysis (Fullprof software).

Lead white is an omnipresent pigment in easel paintings of the Renaissance[1]. It was extensively used by painters, not only in the ground layers but also mixed with other colors in the paint layers. Lead white is composed of two mineral phases[2] (cerussite $PbCO_3$ and hydrocerussite $2PbCO_3.Pb(OH)_2$). The antique synthesis process of this pigment is known through historical treatises, but many interrogations remain as for the various qualities that were proposed at very different prices to painters by the manufactures. Historical sources reveal that after the synthesis, several post-synthesis treatments could be used in order to obtain a material of high quality[3]. Recent work by our group indicate that the use of those treatments had an effect on two main characteristics of the constitutive phases of lead white : the phases proportions, and the morphologies of the pigment crystallites[4].

The HG56 proposal aimed at detecting the possible use of those treatments in the past, by assessing those two parameters that can be considered as markers of the pigment quality.

The results previously obtained at ID22 have demonstrated the adequacy of the analytical method here proposed. Despite the small size of the samples, high quality diffraction patterns were recorded in very satisfactory times of data collection, leading to the following observations:

- Samples collected in the same layer of a same painting have very homogeneous compositions;

- The aspect of the crystallites (needle-like for cerussite, platelets for hydrocerussite) appears as expected.

The HG56 experiment focused on a corpus of 20 micro-samples (between 70 and 100 µm) collected on paintings from the Louvre Museum by Masters of the Italian Renaissance (Leonardo, Raphaelo, Botticelli, Mantegna…). A paiting sample is composed of a stratigraphy of several paint layers. For this experiment, each sample was carefully selected in order to be composed of a "simple" stratigraphy (not more than 3 layers, including the preparation layer) and to comprise only one of layer containing lead white (analyzed by SEM-EDX). An example of a classic painting stratigraphy can be seen in Figure 1 (left).

The samples were sealed into 300 or 400 µm (diameter) glass capillaries, as shown on Figure 1 (right), and placed on the spinner in front of the beam (beamsize = 1x1 mm²). With such a beamsize, each sample was globally analyzed.

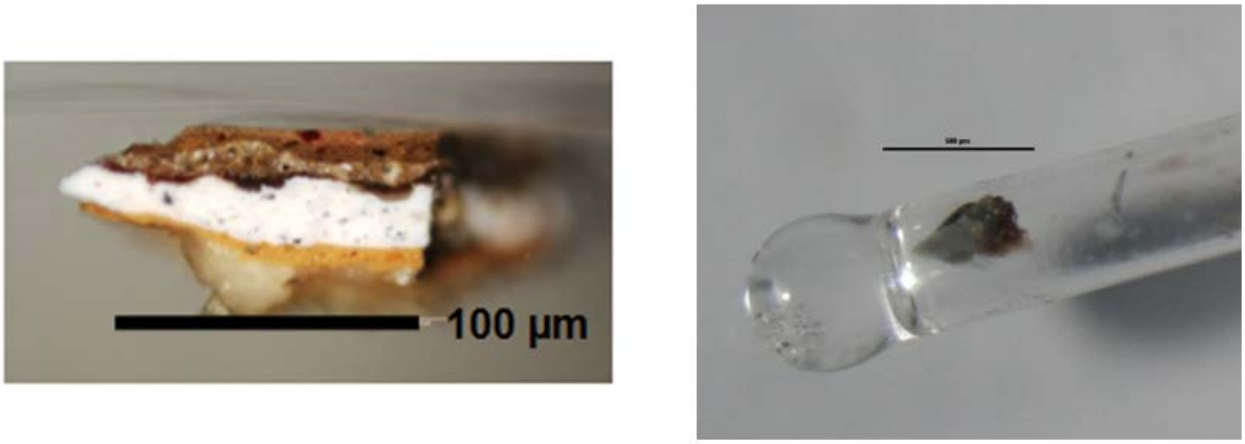

Figure 1 : Painting µ-sample with lead white layer visible (left) – same µ-sample sealed into a glass capillary at ID22 (right)

The versatily selected wavelength was λ = 0.35420088 Å, based on the previous measurements performed on this material at ID22, permitting the obtention of a good compromise to render a good peak resolution, and a sufficient data collection.
Each recording was constituted by an accumulation of successive diffractograms, on an angular range [2°,20°(2θ)]. Analysis times extended from 1 to 4 hours, according to the amount of diffracting matter contained in the capillary (that is to say, the size of the sample). Figure 2 presents an example of a diffractogram obtained during the experiment, after Fullprof treatment. A total of 38 painting samples was analyzed at ID22, which was much more than the envisionned scope of the experiment.

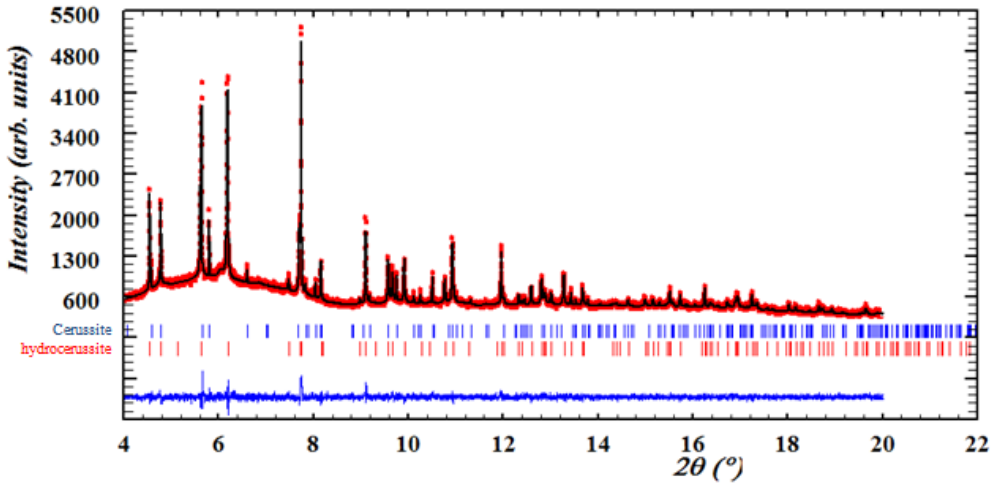

Figure 2 : Diffractogram obtained on a painting µ-sample at ID22, with only the two main crystalline phases cerussite and hydrocerussite present

Results

1. Phases ratios

The phases percentages were systematically quantified by Rietveld analysis. A preliminary tryout was led on a synthesis sample with a HC:C ratio of 50:50 (w%) : this ratio was estimated after refinement to 50.2:49.8 (w%) which indicates a satisfactory precision of the measurements.

We observed strong variations of the ratio between the different samples. It is a convincing indication in favor of the idea that different qualities of pigment could be used according to the pictorial result seeked by the artists. It is worth noticing, like in the previous HG35 experiment, that plumbonacrite, a phase sometimes associated in degraded leadwhite was never detected.

Some crystaline phases ratios obtained on several samples are given in Table 1.

Sample	% C	% HC
Scolaio di Giovanni (1370-1434)	32	68
Master of 1333 (c. 1325-135)	0	100
Fra Angelico (1395-1455)	22	78
Uccello (1397-1475)	55	45
Giovanni da Camerino Boccati (1420-1480)	55	45
Mantegna (c.1431-1506)	35	65
Botticelli (1444/45-1510)	67	33
Botticelli (1444/45-1510)	20	80
Leonardo da Vinci (1452-1519)	12	88
Leonardo da Vinci (1452-1519)	34	66
Leonardo da Vinci (1452-1519)	35	65
Lotto (1480-1557)	23	77
Lotto (1480-1557)	34	66
Raffaello (1483-1520)	20	80
Raffaello (1483-1520)	33	67
Raffaello (1483-1520)	33	67
Bronzino (1503-1572)	24	76
Parmigianino (1503-1540)	39	71
Parmigianino (1503-1540)	53	47

Table 1 : Crystalline phases % (in weight) for cerussite (C), hydrocerussite (HC), $CaCO_3$ and SiO_2 values can be considered with error ±2%

We will focus in this report on some interesting informations gained using the quantification of crystalline phases.

a) Samples with HC:C > 50:50 (w%)
For most samples, the phases ratio HC:C was found > 50:50 (w%). This result was connected to experiments performed in our lab aiming at reproducing the antique synthesis process of lead white (corossion of metallic lead in the presence of acetic acid vapour). It appears that in typical corrosion conditions, the product obtained is composed mainly of hydrocerussite. This result is consistent with what was observed at ID22: the HC:C > 50:50 (w%) could be considered as the “classical” ratio for antique lead white.

b) Samples with HC:C < 50:50 (w%).
For few samples, the HC:C ratio was found to be inverted, that is to say that cerussite was the main constitutive phase. This result is interesting because it can be connected to a post-synthesis treatment frequently applied by paint manufacturers or painters of the Renaissance: the grinding or washing of lead white in vinegar. This well-known process, often praised in historical treatises has been reconstructed in the lab. It appears that it induces the formation of cerussite, according to the reaction :

$$2Pb(CO_3).Pb(OH)_2 + 2CH_3COOH \rightarrow 2\ CH_3COO^- + 3\ Pb^{2+} + 2\ CO_3^{2-} \rightarrow 2\ PbCO_3 + Pb^{2+} + 2\ CH_3COOH^-$$

The acidic treatment leads to the dissolution of the hydrocerussite, followed by a cerussite recristallization.

In other words, the observation of HC:C < 50:50 (w%) ratios could constitute a marker of an old treatment used during the synthesis of lead white at the Renaissance. We suspect that this process was used to get rid of uncorroded metallic impurities present in the pigment (in that case, it would have been used to "save" a badly synthetized pigment).

c) Master of 1333

This painting is interesting as it is the only artwork stemming from a distinct time period and geographical location (France, 14th c.) that was analyzed during this experiment. It exhibits a HC:C ratio of 100:0 (w%). It seems very unlikely that such a ratio could result from a raw synthesis. We rather suspect that it results from the use of another post-synthesis treatment, namely the heating of the pigment in water, which would induce the reaction :

$$3PbCO_3 + H_2O \rightarrow 2Pb(CO_3).Pb(OH)_2 + CO_2$$

Interestingly, the only other painting in which a comparable ratio was also stemming from the same period and location. It was analyzed at the ID21 beamline of the ESRF, in µ-XRD mapping. Those two results could bring some very interesting results regarding the precise nature of a lead pigment used during the French Middle-ages, described in historical sources, but so far not precisely identified.

2. Crystallites modelization

As described in the HG35 report, when the quantity of diffracting matter was sufficent (sample size > 90 µm), very high quality diffraction patterns were obtained. In this case, Rietveld refinement allowed us to propose a modelization of the crystallites. As in our previous ID22 experiment, the assesment of the hydrocerussite crystallites dimensions was possible, which is impossible with classical methods used in cultural heritage research such as SEM observation, as the crystallites are often at the nanometric scale. Results recently obtained at the C2RMF have connected the crystallites morphologies to optical properties of the pigment such as covering power, and diffusion, but also to fluorescence features.

Conclusion and perspectives

The results obtained during the HG56 experiment could have a significant impact on the assesment of the pigment qualities sold to painters in the past. Connecting them with the field of art history and authentification attemps is thus very promising.

The results gathered during the HG35 experiment were presented in a first publication[4]. After the HG56 experiment, a second publication is being written.

The high quality of the results obtained encourages us to continue our research on the characterization of this pigment using SR-XRD. More specifically, we wish to combine results obtained various XRD configuration, such as µ-XRD at the ID21 beamline.

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