EUROPEAN SYNCHROTRON RADIATION FACILITY

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# 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**.

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- 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:** Analysis of composition, microstructure and ageing of lead white pigments in Goya's paintings using HR synchrotron diffraction | **Experiment number**: HG35 |
| --- | --- | --- |
| **Beamline**: ID22 | **Date of experiment**: from: 04/12/14 to: 06/12/14 | **Date of report**: |
| **Shifts:** 6 | **Local contact(s)**: A. Fitch, Y. Wattier | *Received at ESRF:* |

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## Report:

The main objective of the project was to investigate the composition and microstructure of the lead white pigment found in those samples. Indeed, lead white is a pigment omnipresent in most easel paintings from the Renaissance to the 20$^{th}$ century, not only in the preparation (or ground) layers, but also mixed with other colors in the paint layers[1]. Lead white is composed of two main mineral phases[2] (cerussite $PbCO_3$ and hydrocerussite $2PbCO_3.Pb(OH)_2$), sometimes associated with plumbonacrite ($Pb_5O(OH)_2(CO_3)_3$). The phase proportions vary according to the manufacture processes and the post-synthesis treatments paint manufacturers used[3].

The projected aimed at taking a next step towards an in-depth analysis of the lead white pigment. SR-XRD coupled with semi-quantitative Rietveld analysis (Fullprof software) appeared as a well adapted technique to achieve two main goals :

- Quantification of the 3 lead carbonate varieties and observation of minor phases (extenders like $CaCO_3$, $BaSO_4$ and $SiO_2$).
- Modelization of the crystallites according to their respective habitus (expectedly needles for cerussite, platelets for hydrocerussite).

Those two parameters are precious hints for determining the fabrication process of the pigment, but could also yield conclusions regarding the artist's preferences in terms of composition, quality and microstructure. According to our study led in parallel on re-created pigments, these parameters have indeed a very significant effect towards optical properties.

The HG35 experiment focused on a corpus of ~20 micro-samples (between 70 and 100 µm) collected on masterpieces from the Louvre Museum. The project was originally focused on works painted only by Goya (18-19$^{th}$ century), but considering the sucess of the first measurements, we extended it to other painters, thus broadening the scope of our research at the ESRF. 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 that at least one its layers contained 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).

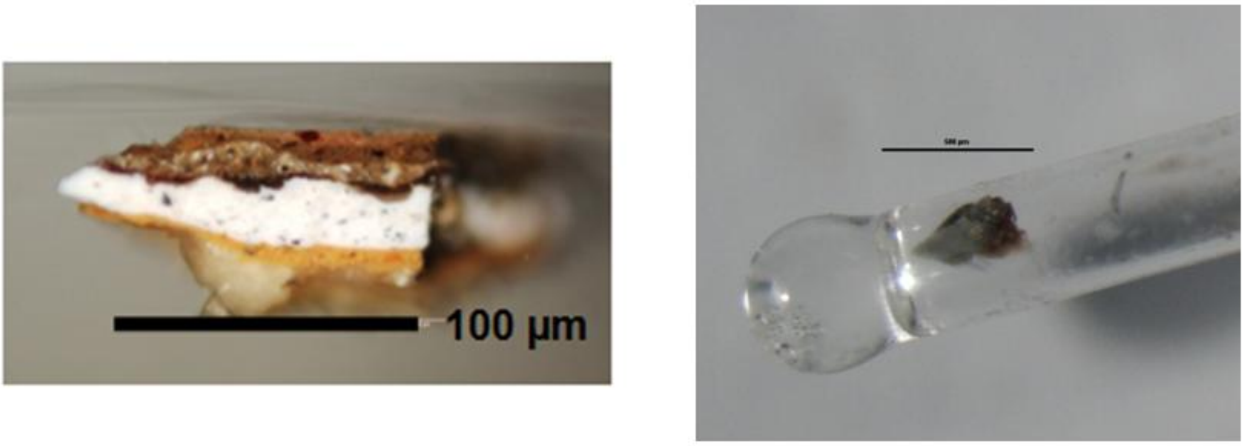


*Figure 1 : Painting µ-sample with lead white layer visible (left) – same µ-sample sealed into a glass capillary at ID22 (right)*

The versatily of the ID22 HR-XRD beamline allowed us to select a wavelength of $\lambda$ = 0.35420088 Å. This wavelength was chosen after preliminaries tryouts : it permited the obtention of a good compromise to render a good peak resolution, and a sufficient data collection.
Beam size was 1x1 mm². This surface allowed a global analysis of the entirety of each sample, once they were correctly aligned with the beam. Each recording was constituted by an accumulation of successive diffractograms, on an angular range [2°,30°(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 : while data were collected up to 30°(2θ), it appeared that limiting the angular range to [2°,20°(2θ)] was sufficient to obtain refinements of good quality. A total of 15 painting samples was analyzed at ID22, which was within the envisionned scope of the experiment.

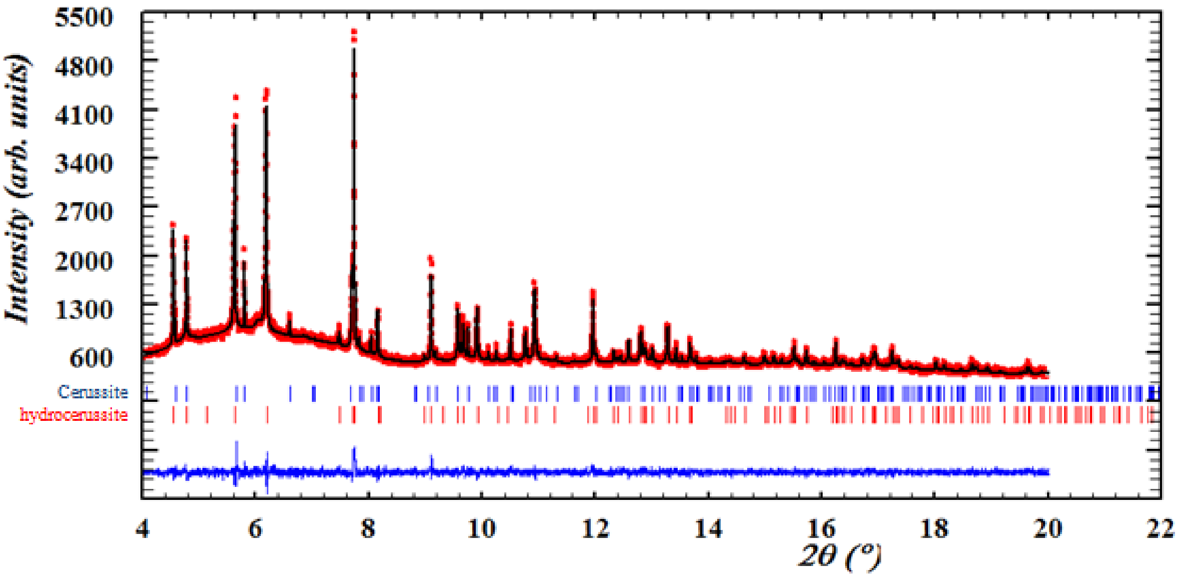


*Figure 2 : Diffractogram obtained on a painting µ-sample at ID22, with only the two main crystalline phases cerussite and hydrocerussite present*

# 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 (wt%) : this ratio was estimated after refinement to 49.7/50.3 (wt%) which indicates a satisfactory precision of the measurements.

The firt observation was that two samples collected on the same pictorial layer of a painting but at different positions exhibited very homogeneous compositions : we obtained concentrations for the two lead carbonates phases of ~70% for cerussite (**C**) and ~30% for hydrocerussite (**HC**) on two pictorial fragments collected on the painting *The Virgin and Child with St. Anne (1503-1519)* by Leonardo da Vinci, as seen in Table 1. This result demonstrated the adequacy of the analytical method used. Locations of the two samples (**a** and **b**) are presented on the picture on the right.

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 that plumbonacrite was never detected.

As expected, several minor phases were detected and quantified. The most common was $CaCO_3$, a crystalline phase known to have been frequently employed as an extender of lead white in paintings since the Middle Ages. It is known through historical treatises that the presence of this extender was a marker of a pigment of lesser quality. While its detection is easy by SEM-EDX or XRF, its quantification is a supplementary clue to a fine characterization of the pigment value. During our experiment, calcite was detected and quantified in samples collected on paintings by Giotto, Tintoretto, Grünwald, Goya and Van Gogh. Starting from the end of the 18$^{th}$ century, additionnal extenders to lead white were proposed. Thus, $SiO_2$ was found present (sometimes in addition to $CaCO_3$) in paintings by Goya and Van Gogh.

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

| **Sample** | **% C** | **% HC** | **% $CaCO_3$** | **% $SiO_2$** |
|---|---|---|---|---|
| Giotto | 11.7 | 62.1 | 26.2 | 0 |
| Botticelli | 76.4 | 23.6 | 0 | 0 |
| Tintoretto | 12.6 | 72.5 | 14.9 | 0 |
| Grünwald | 38.8 | 61.2 | 0 | 0 |
| Leonardo 1 | 11.4 | 88.6 | 0 | 0 |
| Leonardo 2-a | 68.1 | 29.8 | 2.1 | 0 |
| Leonardo 2-b | 70.8 | 28.1 | 1.1 | 0 |
| Goya 1-a | 11.7 | 79.8 | 0 | 8.5 |
| Goya 1-b | 18.8 | 81.2 | 0 | 0 |
| Goya 2 | 78.8 | 4.1 | 17.1 | 0 |
| Goya 3 | 74.4 | 3.2 | 22.4 | 0 |
| Monet 1-a | 6.7 | 74.2 | 19.1 | 0 |
| Monet 1-b | 10.6 | 78.2 | 11.2 | 0 |
| Monet 1-c | 10.0 | 90.0 | 0 | 0 |
| Van Gogh | 8.8 | 23.0 | 4.4 | 63.8 |

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

The study of some of those ratios imediatly provides us with very interesting results. We will focus in this report on three significative informations obtained on three painters representative of distinct periods of time.

### a) Leonardo da Vinci

The first result bears on the two samples (2-a and 2-b) collected on the *The Virgin and Child with St. Anne* by Leonardo da Vinci (1452-1519). As said in the first part of this report, the fact that the phases proportions are equivalent validates the experimental method. Moreover, it is surprising that in this painting, the cerussite percentages are superior to the hydrocerussite ones. Indeed, during the manufacturing of lead white, while the formation of basic lead carbonate is expected, cerussite is often considered as a byproduct, forming only when carbonatation is allowed to proceed too far. A high percentage of cerussite could mean a pigment of low quality, forming a less satisfactory paint. However, experiments curently led at the C2RMF could invalidate this claim, as cerussite seems to present some interesting optical properties when mixed with an organic binder in a painting film.

### b) Goya

The two samples (Goya 1-a) and (Goya 1-b) were interesting as they originated from a single one. Sample (Goya 1-a**)** is only composed of the preparation layer of the painting, while sample (Goya 1-b**)** is only constituted by the painting layers. It is most of the time impossible to split a painting sample in such a clean way : in this case it allowed us to study separately the pigment used by Goya (1746-1828) at two different stages of his work. The results obtained are highly interesting, as they show that two different pigments were used by the painter for his ground layer and his pictorial layer. Indeed, the pigment employed in the preparation contains $SiO_2$, an extender often mixed with lead white. The presence of such an extender tends to give a pigment of lower quality, and as a result, of lower price than pure lead white. Its use in the preparation is consistent with the utilization a painter could have of his materials : the preparation layer is deep in the painting stratigraphy, and a poor quality pigment would remain unnoticed. On the contrary, using a good pigment in the upper layers of the painting could permit the obtention of optical effects of quality, such as nice hues when mixed with other colors (as it is often the case with lead white). This result highlights the discrepancy in pigment quality that could exist within the same painting.

### c) Monet

Three samples coming from the same painting by Monet (1840-1926) were analyzed during our experiment. However, the three of them are representative of three distinct stages of the painting evolution. The first one (Monet –a) has been collected on the original preparation, applied by Monet on his canvas. The second one (Monet –b) comes from an enlargement of the canevas, probably performed by the painter himself. Finally, the sample (Monet –c) was selected as it comes from a transposition coating, suspected not to be of origin.
Examining the results, it appears that the enlargment was realized with a different pigment than the original preparation (phases proportions vary with ~5%). Thus, we gather precise informations on the painting practice chronology of Monet during the making of his painting. Finally, it appears that the transposition was achieved with yet another quality of lead white. Indeed, while Monet used a pigment mixed with $CaCO_3$, the coating used does not contain calcite : despite its more vulgar utilization, it is composed of a pigment of better quality.

Those three results highlight the large scope of questions that can be answered by having a precise estimation of the crystalline phases that constitute the pigment of interest. As strong variations can be observed on a same painting from one paint layer to another, it shows that a global XRD analysis (such as in 2D-detection mode) is not fully satisfactory. This is especially true for lead white, as preferential orientations of hydrocerussite platelets are likely to happen within the paint layers, making it difficult to obtain precise percentages, as we observed with laboratoty-based XRD.

## 2. Crystallites modelization

When the quantity of diffracting matter was sufficent (sample size > 90 µm), very high quality diffraction patterns were obtained. Those data combined with Rietveld refinement allowed us to propose a modelization of the crystallites. In this preliminary report, we will focus on the hydrocerussite phase. The space group of this phase is R-3m. We present here the average dimensions of the crystallite in three directions of the reciprocal space in Table 2.

| **Sample** | **l (Å)** | | |
|---|---|---|---|
| | **(300)** | **(110)** | **(006)** |
| Leonardo 1 | 2200 | 2950 | 850 |
| Goya 1-a | 6660 | 14700 | 2090 |
| Goya 1-b | 6120 | 6650 | 1730 |
| Monet -a | 4980 | 10000 | 1250 |
| Monet -b | 5380 | 10120 | 1570 |
| Monet -c | 6800 | 12340 | 1340 |
| Van Gogh | 6790 | 13000 | 2470 |

*Table 2 : Dimensions of the hydrocerussite cristallites for 3 directions of the reciprocal space*

When examining those results, we can see that the experiment permits the assesment of the hydrocerussite crystallites dimensions. This is a very interesting result, as lead white particles are closely aggregated in paint films, making their SEM observation impossible : gaining an access to their morphologies and shapes with precision is unprecedented. Considering that these two parameters seem to constitute the main quality marker for the pigment, the decisive contribution of SR-XRD to the study of painting samples micro-structure is here demonstrated. Studies are curently underway at the C2RMF to connect those parameters to optical properties of the pigment such as covering power, brilliance, diffusion.

## Conclusion and perspectives

The results obtained during the HG35 experiment and presented in this report illustrate the high diversity of questions that can be answered using SR-XRD. Those results 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.

This experiment allowed us to get an overview of the use of lead white in Europe, for a time period ranging between the end of the Middle-ages and the $20^{th}$ century. The high quality of the results obtained (more detailed in a future publication) encourages us to continue our research on the characterization of this pigment using SR-XRD. More specifically, we wish to focus on a new corpus of samples, coming from a precise period of time, at a precise location (the Italian Renaissance). We thus plan to submit a continuation of this experiment at ID22.

## References

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[2]E. Welcomme, P. Walter, P. Bleuet, J.-L. Hodeau, E. Dooryhée, P. Martinetto, M. Menu, Classification of lead white pigments using synchrotron radiation micro X-ray diffraction, App. Phys. A, 2007, vol. 89, p. 825-832.

[3]M. Stols-Witlox, 'The heaviest and the whitest': lead white quality in north western European documentary sources, 1400-1900 *in* Studying Old Master Paintings, (Archetype ed. London), 2011, p. 284-294.