ESRF	**Experiment title:** Characterization of the lead-white based ground types of Van Gogh's paintings by micro-X-ray diffraction	**Experiment number**: EC-598
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Purpose

Our research project is focused on the lead white based grounds of Van Gogh's paintings.

It is known from his letters and examination of his paintings that Van Gogh used both canvas he primed himself and commercially primed canvas. Later on, his main suppliers of commercially primed canvas were Père Tanguy and Tasset et L'Hôte. From August 1888 until July 1890, he often used commercially primed canvas sold in rolls by Tasset et l'Hôte. These rolls of primed canvas from Tasset et L'Hôte show a characteristic asymmetric threadcount.

The aim of this research was to find characteristic criteria of the grounds to determine whether different paintings were painted on canvas from the same supplier, or even from the same roll of canvas.

This experiment has two main objectives for the batch of samples investigated:

1- To identify the mineral phases in each ground layer to characterize grounds from different suppliers

2- To quantify the ratio between the two mineral phases constituting lead white pigments (hydrocerussite and cerussite) in the different ground layers, to investigate if this could be a criterion to distinguish the different rolls obtained from Tasset et L'Hôte. New insights on this aspect have already been brought by the computer assisted automatic threadcounting research still in progress (Johnson *et al*, 2009)[1]. Matches obtained by the chemical approach will be tested against matches obtained by the method based on canvas threadcounting.

The requirement of a micrometric probe to study such samples and of an excellent source brightness made SR-XRD the key method to reach our objectives.

[1] C. Richard Johnson, Jr., E. Hendriks, P. Noble, and M. Franken, "Advances in Computer-Assisted Canvas Examination: Thread counting algorithms", in *37th Annual Meeting of the American Institute for Conservation of Historic and Artistic Works, Paintings Specialty Group Postprints* 21 (2009), pp. 25-33.

Experiments

The commercially primed lead-white based grounds of 28 Van Gogh paintings dated between November 1885 and July 1890, and of a Toulouse-Lautrec painting from 1887, were investigated by performing X-ray fluorescence (XRF) and X-ray diffraction (XRD) measurements on paint cross-sections.

21 of these paintings are assumed to have been painted on commercially primed canvas from Tasset et L'Hôte, which was confirmed by the canvas threadcount, but would have been cut from four different rolls according to the computer based automatic threadcounting method. Three paintings have commercially primed canvas from Rey et Perrot, shown by the stamp at the back of the canvas. One painting has the type of ground typically found in Van Gogh paintings in the early period of Nuenen. The 4 remaining paintings present diverse grounds and no information about the supplier is known.

The SR-based experiment was conducted on 32 samples, consisting of micrometric multilayered fragments embedded in resin and polished, resulting in cross-sections showing the different layers (ground and painting layers). Preliminary investigation of the samples was performed by SEM-EDX to identify the different layers and the main chemical elements (Figure 1a). The samples have one or two ground layer(s) with a thickness ranging from 15 to 100µm. Three standards in the form of powder (silicon (Si), hydrocerussite ($2PbCO_3$, $Pb(OH)_2$) and cerussite ($PbCO_3$)) were also analysed for calibration purposes.

The SR-XRD experiment was performed in transmission at 28 KeV. An additional fluorescence detector was placed to simultaneously collect information about the atomic composition. For each sample, a 2D map of about 100 x 60 μm^2 (ver x hor) was carried out with a pixel size of 2 x 5 μm^2 and a dwell time of about 10 seconds /pixel.

After extraction of the data from the diffraction image with Fit2D, the PyMCA software was used to process it. With this software, the XRF data can be displayed as element distribution maps of the samples. Figure 1b shows an example for sample 10536, mapping the distribution of lead (red), calcium (green) and cobalt (blue) in the sample. This enables us to differentiate between the different layers and to select the corresponding pixels to extract average XRD patterns for each layer. XRD patterns were further treated with EVA software to identify the main phases present. FullProf_Suite software was used to investigate quantitatively the ratio between the mineral phases in an attempt to perform Rietveld refinement.

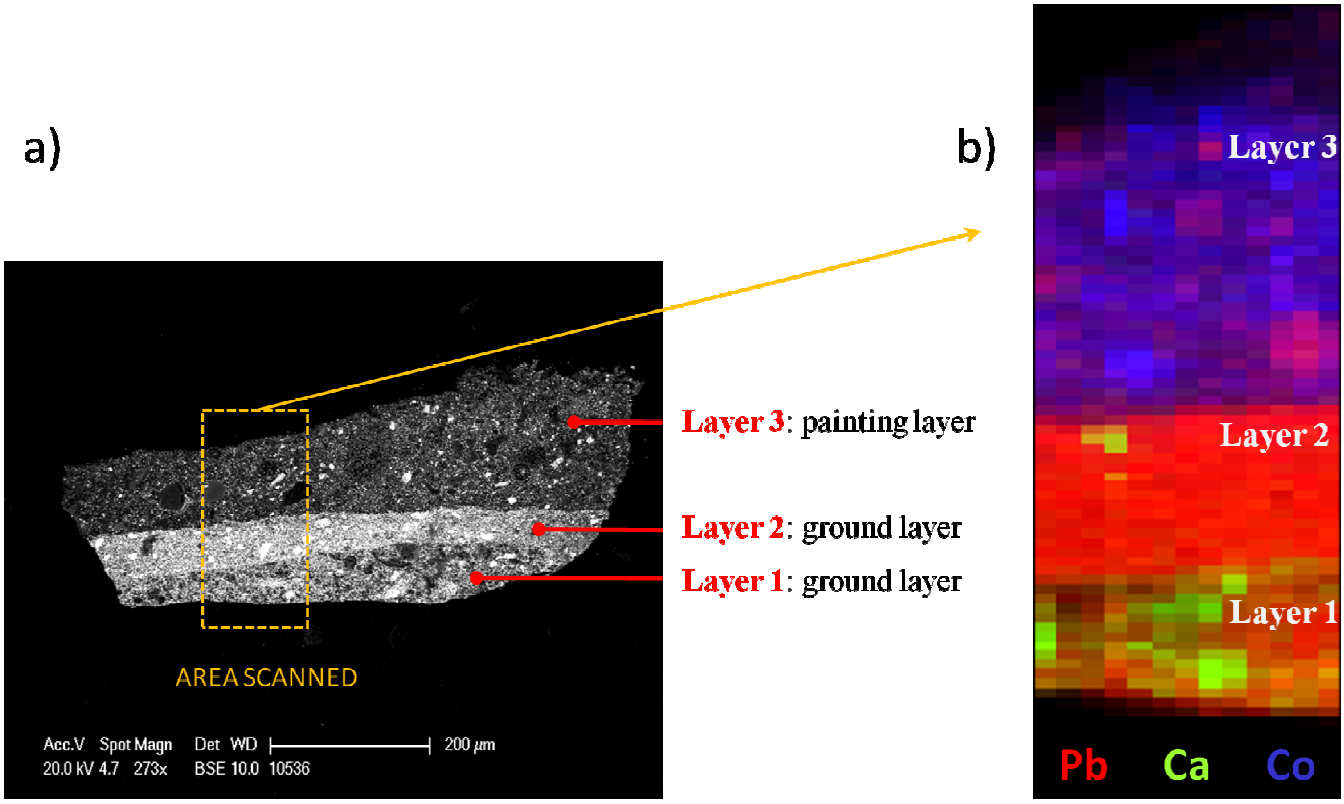

Figure 1: (a) SEM image of sample 10536, showing the 3 layers: the 2 ground layers (layer 1 and layer 2) from the commercially primed canvas, and the painting layer applied by Van Gogh on top (layer 3). Main chemical elements detect by SEM-EDX are lead and calcium for layer 1; lead for layer 2 and cobalt and zinc for layer 3. Orange dashed rectangle indicates the area scanned by SR-XRF and SR-XRD at ID18F. **(b)** RGB map (82 x 13 pixels) corresponding to the area scanned on sample 10536: red indicates the distribution of lead (Pb), green the distribution of calcium (Ca) and blue the distribution of cobalt (Co). This allows distinguishing clearly the 3 layers in the 2D map.

First results

The first objective was successfully reached. Major phases, more commonly hydrocerussite, cerussite, calcite, barite and wurtzite, could be identified in the different ground layers. Figure 2 shows the XRD pattern obtained for layer 1 of sample 10536. In this case, the five mineral phases were identified. Some variation in the major mineral phases present were found between the different grounds investigated, which provides some insights to characterize grounds from different suppliers. However, minor phases could not be yet identified, due to the significant number of peaks of major phases present in this type of samples. This latter issue is still under investigation.

We are still working on quantifying the ratio between hydrocerussite and cerussite. Observation of the XRD patterns seems to indicate there are some differences between the ratio of those two phases in the different samples. Hovewer, the microstructural effects, anisotropic broadening of the profiles and preferred orientation make it really difficult to perform satisfactory Rietveld refinement. For future experiments, it would be probably appropriate to use a more suitable standard to perform Rietveld refinement, such as NAC ($Na_2Ca_3Al_2F_{14}$). Moreover, this type of samples with heterogeneous size of particles should be investigated with a beam size of 5 x 2 μm^2 as it was performed, but also with a slightly larger beam size to evaluate better the microstructural effects of grain size.

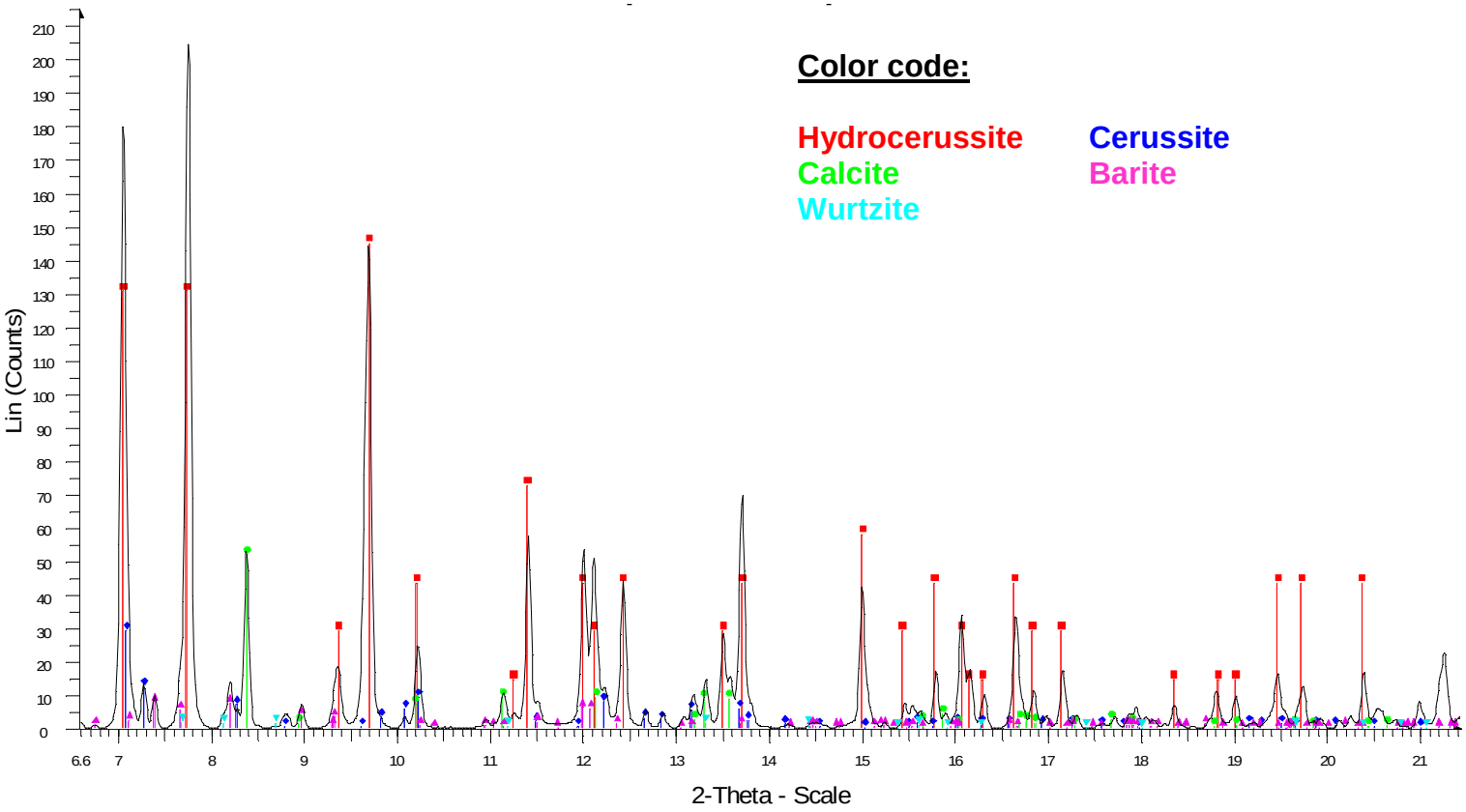

Figure 2: XRD pattern of layer 1 of sample 10536, showing the presence of 5 main mineral phases : hydrocerussite (red), cerussite (dark blue), calcite (green), barite (pink) and wurtzite (turquoise blue).