µ-XRF/µ-XRD mapping of naturally and artificially aged chrome yellow paint samples from V. Van Gogh paintings

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Lead chromate-based compounds [$PbCrO_4$, $PbCr_{1-x}S_xO_4$ and (1-y)PbCrO4·yPbO] are commonly known as chrome yellow (CY) pigments and were widely used by Vincent Van Gogh and his contemporaries. These pigments show a limited stability under light and other types of environmental factors, causing the bright yellow colour to become brownish. The most famous example of the CY darkening are the various *Sunflowers* paintings by Van Gogh. It is striking that only some Van Gogh paintings suffer from this darkening effect while others do so to a far lesser extent. Previous investigations demonstrated that the CY alteration is caused by the reduction of original Cr(VI) to Cr(III) [1][2]. The green pigment viridian ($Cr_2O_3·2H_2O$) could be identified as the alteration product that causes the darkening. This Cr(III) compound was formed in a very thin superficial layer (1 – 2 µm) in areas with high S content originating either from sulphate grains intermixed with the CY paint or sulphate-rich layers which were in contact with CY layers. Indeed, only the model paint samples containing the $PbCr_{1-x}S_xO_4$ solid solution showed a significant darkening after artificial ageing. In this work, we have performed µ-XRF/µ-XRPD experiments to verify our assumption that the CY darkening phenomenon only takes place to a significant extent in the case that the CY paint consists (largely) out of $PbCr_{1-x}S_xO_4$.

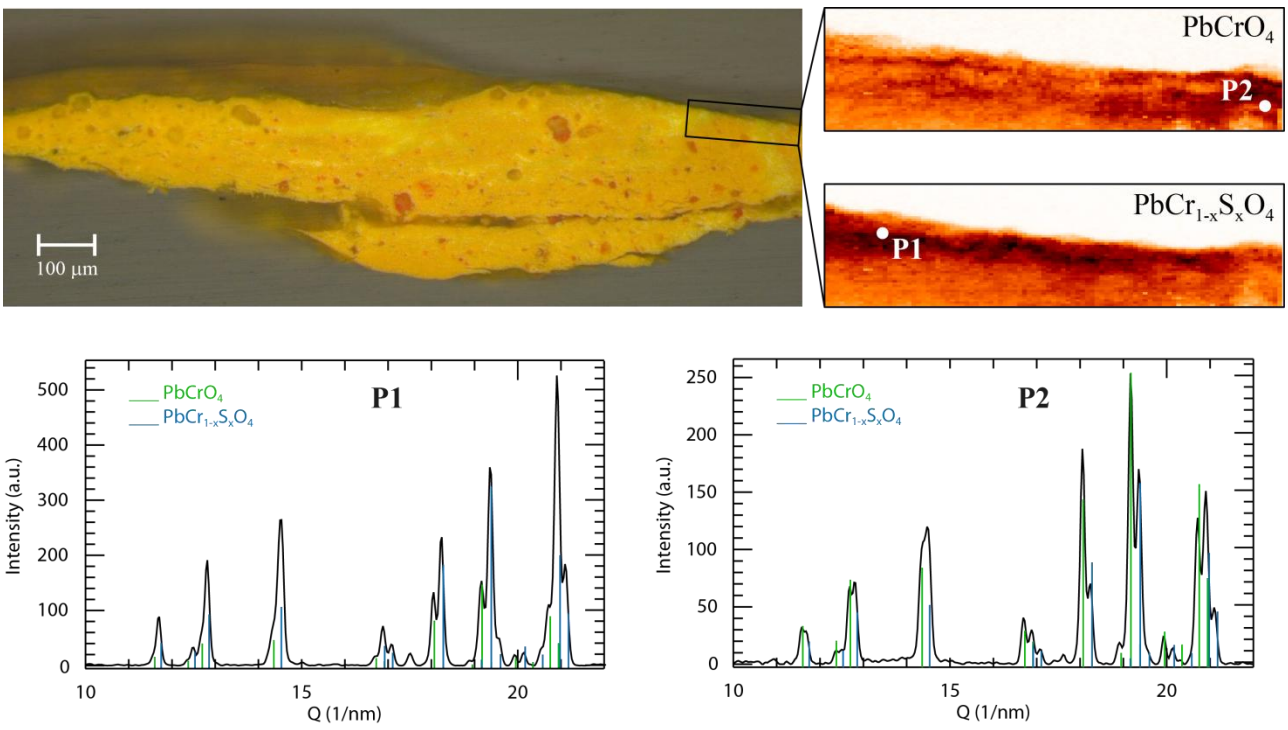

Figure 1: Visible light microscopy image and phase distribution maps of the embedded microsample F458/1 taken from the painting *Sunflowers* by V. Van Gogh (top). Integrated diffraction patterns show the simultaneous presence of monoclinic $PbCrO_4$ and monoclinic $PbCr_{1-x}S_xO_4$ (bottom) in the yellow paint layer.

Combined µ-XRF/µ-XRPD scanning experiments have been performed in the micro probe hutch of the P06 Hard X-ray micro/nano-probe beam line of the PETRAIII storage ring, using a photon energy of 18 keV. The energy was selected by means of a Si(111) double crystal monochromator. The beam was focused to 1.6 x 0.6 μm^2 (hor. x vert.) employing a Kirkpatrick-Baez mirror optic. A Keyence optical microscope equipped with a perforated mirror allowed for positioning of the

sample. Diffraction signals were recorded in transmission geometry with a 2k x 2k MarCCD area detector, with 78 x 78 μm^2 pixel size. X-ray fluorescence signals were recorded using a Si-drift detector with 50 mm^2 active area. Elemental and phase distribution maps were collected from model and real paint samples with 2 x 1 μm^2 (hor. x vert.) step size and an acquisition time of 1 sec/point. XRF spectral fitting was performed using the PyMCA software package [3] while the ensuing XRD data was analyzed with the XRDUA software [4]. Measurements were performed on aged model (9) and historic (3) samples and real paint samples (11) originating from different Van Gogh paintings.

The µ-XRPD results obtained from the embedded paint microsample from *Sunflowers* (Van Gogh Museum, Amsterdam) clearly show the presence of both monoclinic $PbCrO_4$ and the monoclinic $PbCr_{1-x}S_xO_4$ solid solution (Figure 1). The distinction between the two compounds is possible due to the high angular resolution achieved at beam line P06. Other real paint samples also showed the presence of the sulphur-rich coprecipitate, in some cases next to $PbCrO_4$ and $(1-y)PbCrO_4 \cdot yPbO$ indicating the effective use of the different CY varieties by Van Gogh [5]. These results could provide a possible explanation why only some yellow areas of a selection of Van Gogh paintings appear today darkened. The µ-XRF/µ-XRPD experiments did not show the presence of the green pigment viridian, previously identified by µ-XANES [1]. It should be noted that after the mapping experiment, some samples showed blackening caused by exposure to the X-ray beam. The degree of blackening differed from sample to sample and for some compounds this was accompanied by a decrease in crystallinity.

References

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