

Analysis of artist's palette on a 16th century wood panel painting by portable and laboratory Raman instruments



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ABSTRACT

Non-destructive analysis of the artist's palette of ancient wooden panel paintings is a difficult task and studies are rare. Here we compare different methods of analysis of a wooden panel painting, dated to the early sixteenth century, mainly by Raman and infrared spectroscopies. Raman spectra were recorded on collected/sampled micrometric fragments using portable Raman instruments with laser excitation lines at 532 and 785 nm and transportable Raman instruments at 532, 633 and 785 nm; a fixed 1064 nm Raman spectrometer was also used. Infrared analyses were performed in Attenuated Total Reflection (ATR-FTIR) mode. Using the portable instrument, the Raman spectra evidenced white lead, calcite and vermilion only. Raman spectra recorded by transportable and fixed instruments enabled the identification of most of the artist's palette: (i) white lead, calcite, gypsum and cerussite for white colour; (ii) vermilion, red lead, litharge, haematite for red; (iii) azurite, indigo and lapis lazuli for blue. IR spectra gave information on the organic binding media. XRF analysis on a brown pigment suggested a heterogeneous mixture of a red pigment (such as haematite and/or minium) and a green one as malachite. GC-MS analysis allowed identifying terpenic resin in the composition of the outer protective layer.

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1. Introduction

Pigments and binders identification in paintings is very important to document the history, provenance, dating and artist's palette. Preferred analytical techniques are those preserving the integrity of the sampled material, or much better the *in situ*, non-invasive techniques, and recording spectra of small volumes (not more than a few (tenths) μm^3) of organic and inorganic materials. In recent years, the use of Raman and infrared vibrational spectroscopies for the non-destructive characterization of art objects [1–7] has become dominant, especially with the rapid development of portable spectrometers for on-site measurements [8–12]. The varnish covering, however, makes the direct recording of the pigments signature and stratigraphy difficult for most of the paintings.

On site Raman micro-spectroscopy has proved its efficiency for more than 10 years in the study of different artworks [13,14]. Analysis of ancient wood panel paintings is however very limited:

to our knowledge, only two medieval painted artefacts, a 14th century wood panel painting and a sculpture, have been comprehensively studied [15,16], but not using vibrational spectroscopy. Samples from 16th century Perugino paintings [17] and 15th century ceiling panels [18] have been analysed using FT-IR in combination with elemental analysis (SEM-EDX). Very recently similar works has been made for 14th and 16th century panels, namely using alternative techniques (XRF, NMR, XPS) [19–21]. Comprehensive analysis with vibrational spectroscopies was only conducted on 17th century paintings [22] and more recent paintings have been studied by wide spectral range hyperspectral imaging [23]. Fluorescence generally overcomes the Raman signal recorded on ancient paintings, because of the use of solvents and glues. Collecting spectra requires the analysis of many samples, their preparation in order to find fluorescence-free spots and the testing of different excitation laser lines. Studies on icons [24,25] are more numerous, the different painting technique making the measuring conditions more convenient.

We will consider here a painting on a flat wood panel. The artwork probably was an altarpiece (Fig. S1, Supplementary materials): the only information available is the stylistic dating by Blanc Monique, a Middle Ages specialist, who placed it at the beginning of 16th century, just when canvas paintings began to

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become more popular than wood panels paintings. The artwork was originally composed of three parts – now incomplete – and probably represented the *Lamentation on the Dead Christ*: the Christ's body lies in the arms of the Virgin Mary and is accompanied by two unidentified figures. In the upper left part of the board an angel is visible, while on the right only the wings of another figure can be seen.

Our objective was to evaluate the use of Raman spectroscopy using portable, transportable and fixed instruments for the non-destructive identification of the ingredients employed in the realization of a wooden panel painting in order to collect information about the artist's palette. Due to the very limited number of Raman studies on ancient wood panel paintings, we try here to establish the methodology on a wood panel belonging to a private collection, the owner giving the permission to recover small scales fallen down and to collect a few samples. The experience gained should permit further studies on artefacts with known pedigree, especially to document the stratigraphy. The infrared absorption spectroscopy (FT-IR) was used as a complementary technique to detect and classify the organic substances. Additional analyses like X-ray fluorescence (XRF) and gas-chromatography coupled with mass spectroscopy (GC-MS) have been carried out to get more information about the protective layer, to determine if some kind of resin is present.

2. Experimental

The painting consists of two wooden panels, but only the right one was selected for analysis (1.55 m × 0.26 m, thickness ~2.5 cm, Fig. S1, Supplementary materials).

2.1. Mobile Raman spectroscopy

Investigation with mobile Raman instruments was made using HE785 and HE532 instruments (Horiba Scientific Jobin-Yvon,

Longjumeaux, France), equipped with a matrix charge-coupled device (CCD) detector cooled by Peltier effect at 200 K. A 785 nm 300 mW OEM laser (Process Instruments Inc., Salt Lake City, USA) and a 532 nm 100 mW Ventus (Laser Quantum, Cheshire, UK) were coupled to the above designed spectrometer, as well as with 785 and 532 nm remote SuperHead[®] optical heads equipped with selected high quality edge filters. The 785 nm Superhead[®] is equipped with a camera to select the exact point for the measurement. A 100x Nikon and a 100x IR optimized Olympus long working distance objectives were used. This equipment has very high sensitivity but medium resolution (~4 cm⁻¹); it can be easily transported as the components are independent and connected by cables or removable optical fibers. A black textile was used to protect the operators' eyes and to decrease the background level. The equipment was installed on a worktable in order to have the SuperHead[®] turned down and to be able to adjust manually the distance of the artwork with a XYZ micrometre stage. Note that the spectral window measured with portable instrument ranges from 80 to 3200 cm⁻¹. Furthermore, because the decrease of the CCD sensitivity above 2000 cm⁻¹ for the 785 nm excitation, corresponding band intensities are strongly decreased.

The remote SuperHead[®] was positioned using a horizontal or vertical XYZ stage with controlled micrometric displacement. Due to the strong fluorescence, no good Raman spectrum was obtained. Consequently, millimetre-sized samples that had fallen from the artefact or gently taken *via* scalpel were put in a groove, carved in a metal support (no preparation is made), in order to examine the section from the top without any preparation. Samples of various colours were taken from different parts of the painting: the blue of the sky, the dark and light blue of the Virgin veil, the white and the red of the skin of Christ and the brown of the Christ robe. At least 4 different samples for each colour have been studied. Each of them has been measured on different spots with different instruments (about one hundred Raman spectra). The most representative are presented.

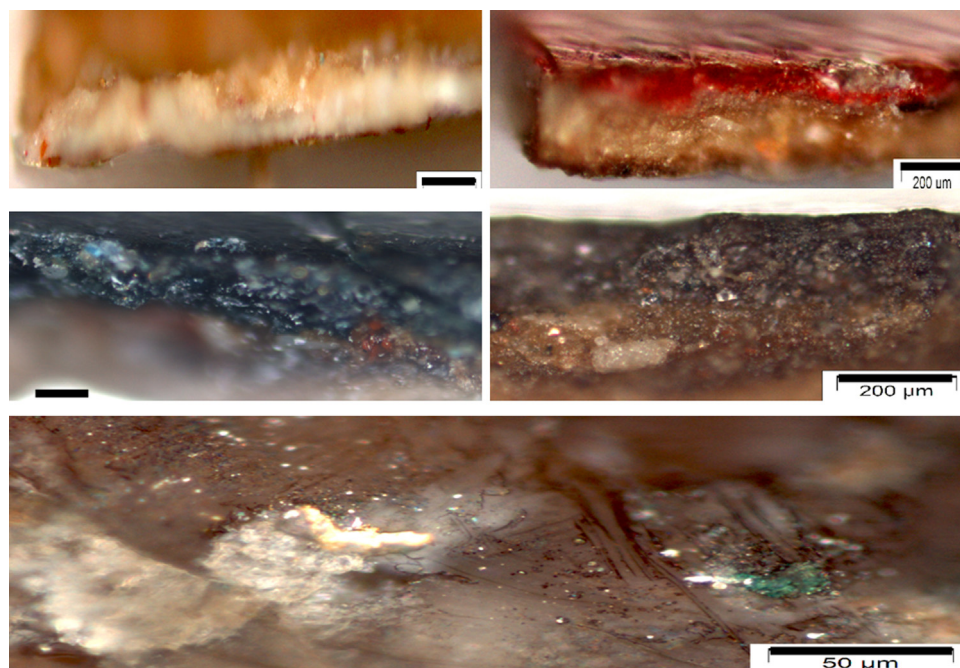


Fig. 1. Optical microscope images of the section of some fragments recovered from the right wood panel: white and red sample (top), dark blue and brown sample (centre); detail of the brown sample section where a green mineral compound seems present (bottom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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