

# Pigments in painting: characterization and UV laser-induced modifications

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Laser technology is greatly eligible as a safe procedure for art conservation, being both controllable and reproducible. Throughout the last decade several researches have been carried out about the interaction of laser radiation with different artistic materials (stone, marble, metals, pottery..). Studies on the laser induced effects on paintings have been accomplished, too; anyway, for cleaning interventions that prevent discoloration and surface damage, preliminary studies are mandatory on each surface of interest to determine the best laser parameters (wavelength, fluence and pulse length and number).

Our work is focused on the analyses of the effects produced by the interaction of an UV excimer laser beam onto pigments and pictorial layers. Since for the comprehension of the processes following laser irradiation, the accurate knowledge of physical and chemical properties of the artistic materials is fundamental, optical, morphological and compositional techniques were used to investigate them.

We selected some inorganic pigment powders on the strength of their historical and artistic relevance and they were bound with egg-yolk to mock painting layers on wood substrates. Powders and mocking models were studied with the aim to characterize the pigments and to quantify the chemical and physical alterations the painted surfaces experienced after irradiation with the KrF excimer laser.

Reflectance spectroscopy was used for the identification of the pigments and the monitoring of colour changes in a non-invasive way. Fibre optics reflectance spectroscopy (*FORS*) provided the spectral reflection factor (*SRF*) of each sample, which in turn returned detailed information about each kind of pigment. As an example, the different behaviour of the *SRF* of four yellow pigments is shown in figure 1. In order to monitor laser-induced chromatic changes, a contact spectrophotometer provided the colour coordinates, in accordance with the recommendations of the Commission Internationale de l'Eclairage (*CIE*). Changes in the *SRF* were interpreted in the *CIE*

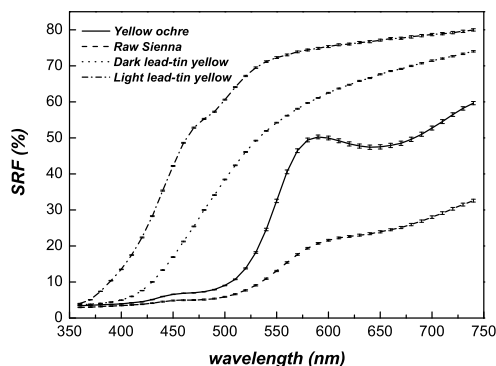


Figure 1. SRF spectra of ochre, raw Sienna, dark and light lead-tin yellow painted layers.

$L^*a^*b^*$  1976 colorimetric space, whose axes describe the differences in lightness  $\Delta L^*$ , redness-greenness  $\Delta a^*$ , and yellowness-blueness  $\Delta b^*$ , between two points, and where the Euclidean distance provides the colour differences  $\Delta E^*$ .

Morphological and elemental analyses on the painted layers, both before and after laser irradiation, were performed through a Scanning Electron Microscope (*SEM*) coupled to an Energy Dispersive X-ray (*EDX*) spectrometer. Elemental distribution was inferred to assess the actual composition of the painted layers. Indeed, usually the common name of a pigment is not enough to specify its chemical composition, but it seems to be related only to its perceived colour. The impurities conferring different colours to pigments, with the same basic composition, were detected by *EDX* analyses. Further information about chemical composition and laser induced alterations were inferred from Attenuated Total Reflection Fourier Transform Infrared (*ATR-FTIR*) spectroscopy and Raman microscopy. The experimental set-up and the methodologies used for the above analyses have been described in detail else-

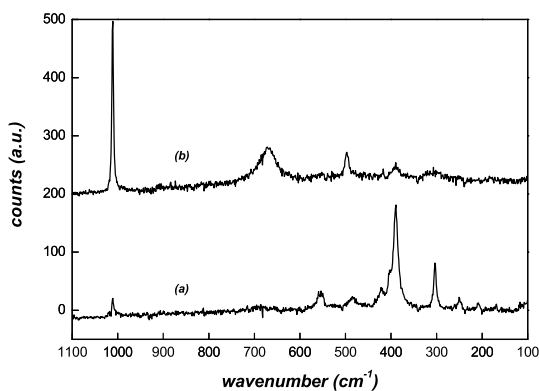


Figure 2. Ochre Raman spectra (a) before and (b) after irradiation. The peaks correspond to goethite ( $303$ ,  $389$  and  $482$   $\text{cm}^{-1}$ ), magnetite ( $667$   $\text{cm}^{-1}$ ) and gypsum ( $1010$   $\text{cm}^{-1}$ )

where [1].

The mocking models were laser irradiated in order to estimate the Colour Damage Thresholds (*CDT*), namely the fluence of a single laser pulse that induced a significant colour difference with respect to the colour coordinates before irradiation. To provide indications for a safe cleaning procedure a fluence slightly below the *CDT* was chosen and an increasing number of laser pulses was delivered on each model to establish the maximum value of pulses before damage onset. *SEM* observations indicated that at moderate fluencies, close to the *CDT*, surface morphology was almost unaltered, whereas well beyond and with many laser pulses the irradiations seemed to induce melting and reshuffling of the pictorial layer.

Chemical alterations related to chromatic changes were detected through *ATR-FTIR* and Raman spectroscopy. It was noticed that, whatever the pigment, colour alterations can be ascribable mainly to the degradation of the organic binding medium, as evident, in the *ATR-FTIR* spectra, from the altered absorption bands of the functional groups  $-\text{CH}_2-$ ,  $-\text{CH}_3$ ,  $\text{C}=\text{O}$ . This result, also reported by other authors, was confirmed by Gas Chromatography - Mass Spectrometry (*GC-MS*) analyses that showed us the occurrence of irreversible degradation of fatty acids and proteins.

Moreover, it came out that the effects on some painted layers could be partially connected also to the chemical transformations of the pigments. In particular, in the natural earths (e.g. raw Sienna and yellow ochre) the dehydration of goethite ( $\text{FeOOH}$ ), main constituent of these pigments, was markedly detected. The observed laser induced darkening was related with goethite phase

transition to hematite and/or magnetite; Raman spectra (fig. 2) on samples treated at relatively high fluences and pulse number showed the direct transformation from goethite to magnetite with no evidence of the hematite intermediate phase.

In conclusion, powders and pictorial layers of inorganic pigments in egg yolk tempera were studied to assess the effects of UV pulsed laser irradiations. Morphological and compositional analyses were carried out on the mocking models that experienced significant colour alterations. It came out that, regardless of the investigated pigment, laser induced effects on the tempera layers were undoubtedly connected to the modifications of chemical bonds in the binding medium and, in some cases, they could be also connected to the chemical transformation of the pigment. Analogous studies will be extended to some artistic widespread organic dyes.

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## REFERENCES

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