

## Physical and chemical investigations on natural dyes

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Natural dyes have been used extensively in the past for many purposes, such as to color fibers and to produce inks, watercolors and paints, but their use declined rapidly after the discovery of synthetic colours. Nowadays we assist to a renewed interest, as natural dyes are neither toxic nor polluting.

Physical and chemical properties of selected dyes, namely red (Madder), yellow (Weld and Turmeric) and blue (Woad) colours, produced by means of traditional techniques at the Museo dei Colori Naturali (Lamoli, Italy), are objects of investigation.

In art conservation, the identification of dyes is important for historical research as well as for the selection of appropriate methods for restoration treatments. Natural organic dyes pose an interesting challenge to researchers, being their identification extremely difficult. Indeed, they enter into artifacts in very small concentrations due to their very high tinting power and the well-established techniques for their characterization are often inadequate. Moreover, in illuminations and paintings dyestuffs are laid on small areas and on delicate supports that make their recognition hard and their sampling extremely dangerous. An effective alternative resides in UV-vis reflectance spectroscopy, which permits the identification of dyes in a non-invasive way. Micro Raman spectroscopy, Scanning Electron Microscopy and Energy Dispersive X-Ray analyses complement the survey, returning compositional and morphological information, as well.

Our work is intended both to characterize the dyes through their spectral properties and to verify the applicability of laser technology for cleaning interventions on artworks where these dyestuffs are employed.

Moreover, the results support the production processes through the evaluation of the impact of different chemicals entering the production methods. The experimental methodology is described in detail in literature [1,2].

To assess the feasibility of laser cleaning procedures, dyestuffs in tempera layers are investigated

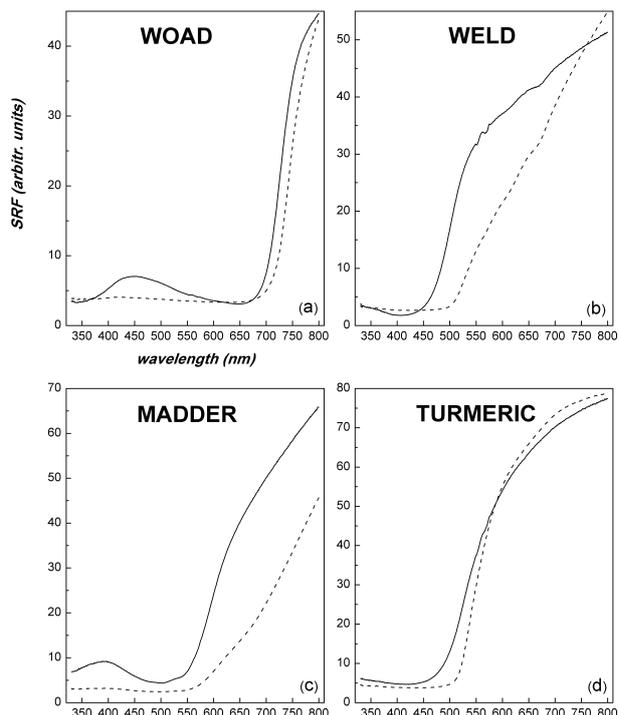


Figure 1. *SRFs* of powders (solid lines) and paintings (dashed lines) for (a) Woad, (b) Weld, (c) Madder and (d) Turmeric

before and after irradiation with an KrF excimer laser ( $\lambda = 248$  nm,  $\tau = 20$  ns)

The optical behaviour of the dyestuffs is explored by the spectral reflectance factors of both powders and painted layers. The potentiality of reflectance spectroscopy resides in its ability to discriminate among different coloured substances through their spectral and chromatic properties.

Figure 1 shows the *SRFs* plots of powders and painted layers of the investigated dyestuffs.

As evident, they are mutually well-distinguished through their spectra. Furthermore, there is evidence of reduced reflectance for each painted model with respect to the corresponding powder, mainly in the visible range,

that could be ascribed to the binding medium, to the multiple coats and to the scattering behaviours due to different morphologies. Rightward shifts of ankle wavelengths are noticeable as well and these trends are better outlined if the first derivatives of SRFs plots are compared.

In order to investigate the laser induced chromatic alterations, for each model the average colour coordinates and the degree of internal non-uniformity are previously evaluated.

The coordinated use of SEM and EDX on dyestuffs returns useful indications about chemical substances involved in the production processes. The high amount of Ca in Woad and in Turmeric arises from the calcium oxide employed as alkalizer in the former and from the gypsum fixing medium in the latter. Furthermore, the presence of P and Mg in Woad are explained in terms of the massive demand of fertilizers in growing and of chlorophyll content, respectively. Al, S and K in Weld and Madder account for the use of potassium alum as antibacterial and precipitant medium.

The Raman signals from Madder and Weld are overwhelmed by an intense fluorescence, so that the strongest bands are just visible as tiny features, whereas the weaker ones are completely obscured.

Unlike the others, Woad and Turmeric exhibit the typical features of Raman emission. Woad spectrum is characterized by the very strong doublet at 1588/1576  $\text{cm}^{-1}$  assigned to the  $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$  vibrational modes, and by the bands around 600-546 and 280-253  $\text{cm}^{-1}$ , all ascribable to Indigotin. Turmeric spectrum is dominated by bands at 1626 and 1601  $\text{cm}^{-1}$  (corresponding to the mixed  $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$  vibrational modes), at 1256  $\text{cm}^{-1}$  ( $\delta(\text{CCH})/\delta(\text{COH})$ ), at 1184  $\text{cm}^{-1}$  ( $\delta(\text{CH}_3)/\delta(\text{CCH})$ ), and at 962  $\text{cm}^{-1}$  ( $\nu(\text{C}=\text{O})/\delta(\text{COH})$ ). Even if cellulose is a common impurity in vegetal dyestuffs, no detectable occurrence is found in the spectra. Colour Damage Threshold (CDT- the fluence of a single laser pulse that induces a significant colour difference) for each model is estimated after laser irradiation. As a result of irradiation Weld, Madder and Turmeric become less vivid, whereas Woad looks more vivid; moreover, lightness of Woad and Madder increases. Every dyestuff experiences negligible alteration of hue. These behaviours are even stressed at higher fluences and number of pulses.

Each model is irradiated with an increasing pulse number,  $N$ , at fluences just lower than the respective CDT to determine the maximum value of  $N$  before damage onset, with the aim of finding out a safe irradiation procedure.

SEM analyses on the irradiated areas evidence surface smoothing that becomes increasingly se-

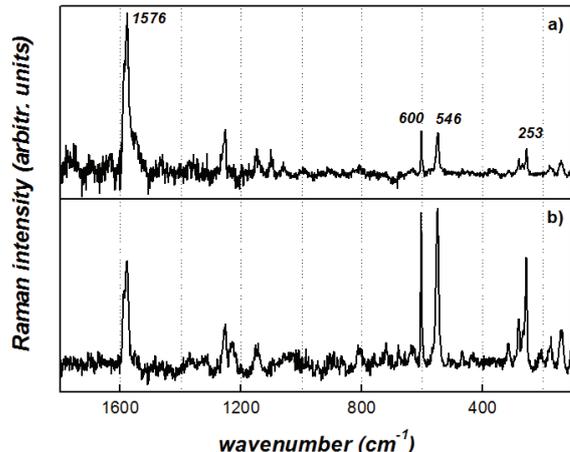


Figure 2. Raman spectra of Woad tempera (a) before and (b) after irradiation

vere at high fluences. No appreciable variations in elemental percentage ratios are detected by EDX.

Laser irradiation induces noticeable modifications in the Raman spectra of the Woad and Turmeric models. In the former it is seen as an increase in relative intensity of the bands around 600-546  $\text{cm}^{-1}$  and 280-253  $\text{cm}^{-1}$  with respect to the doublet at 1588/1576  $\text{cm}^{-1}$ . The evidence of these spectral features (Fig. 2), even for irradiations at fluences below CDT, demonstrates the onset of chemical alterations also before colour damage. In Turmeric spectrum the Raman band at 962  $\text{cm}^{-1}$  decreases its relative intensity as a consequence of laser irradiation.

In conclusion, spectral reflectance permits to discriminate dyestuffs in a non-invasive way and to monitor colour variation with the purpose of inferring the damage threshold after laser irradiation. SEM/EDX analyses and micro Raman spectroscopy allow the detection of chemical and morphological changes induced by the laser.

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## REFERENCES

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