Reflectance spectroscopy of natural dyes

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Physical and chemical properties of Madder, Weld, Turmeric and Woad, produced at the Museo dei Colori Naturali (Lamoli, Italy), have been investigated. The chromatic properties of powders and tempera models have been studied through the reflectance spectroscopy technique. Micro-Raman and *SEM/EDX* analyses have complemented the survey.

1 Introduction

Since prehistoric times natural dyes have been used for many purposes, but their use declined rapidly after the discovery of synthetic colours. Anyway, nowadays there is a growing interest, natural dyes being neither toxic nor polluting.

Natural organic dyes and derived lakes pose an interesting challenge to researchers since their identification is extremely difficult. Indeed, they are present in artifacts in very small concentration due to their very high tinting power.

UV-Vis reflectance spectroscopy permits the identification of dyes and pigments in a non-invasive way.

In this work the chromatic properties of some selected dyestuffs are investigated through the spectral reflectance factors. For a deeper insight, micro-Raman spectroscopy, Scanning Electron Microscopy and Energy Dispersive X-Ray analyses are used to return interesting compositional and morphological information.

2 Experimental

The analysed samples include four dye powders produced by means of traditional techniques at the Museo dei Colori Naturali (Lamoli, PU, Italy); Madder, Weld, Turmeric and Woad are used to produce egg yolk tempera models, too.

The experimental arrangement and the methodology used for spectrocolourimetric analyses have been described in detail elsewhere [1]. A fibre optics reflectance spectroscopy (*FORS*) module (Zeiss *MCS-CCD*) and a contact spectrophotometer (Minolta CM-2600d) provide the spectral reflection factor (*SRF*) and the colour coordinates of each model in the UV-Vis spectral range.

SRF spectra are interpreted in the *CIELab* 1976 [2, 3] colorimetric space, whose axes describe the attributes of lightness *L** (ranging from 0-black to 100-white), redness-greenness *a**, and yellowness-blueness *b** (both unbounded). However, our results are expressed with the *CIELab* cylindrical coordinates, where the perceptual attributes of chroma, *C**, and of hue, *h*, substitute for *a** and *b** in a constant lightness plane.

Microscopy observations are made by means of a scanning electron microscope (JEOL *JSM-*6480*LV*) equipped with an *EDX* analyzer. The Raman spectra were obtained by employing different excitation lines by means two Raman microscopes: a confocal Jobin Yvon Labram (λ = 632.8 nm) and a Renishaw inVia (λ = 442, 785 nm).

3 Results and Discussion

Different analytical techniques are employed to investigate optical and chemical properties of the dyestuffs. The combined resulting information, about elemental composition, molecular bonds and reflectance behaviour, allow the identification of every dyestuff, even when a single technique could yield ambiguity. In particular, the combined use of Raman spectroscopy and *SEM/EDX* analyses return useful indications about chemical substances and methods involved in the production processes.

Optical behaviour of 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. First derivatives of *FORS SRF*s are calculated to highlight characteristic spectral features of each investigated sample. Figure 1 shows the *SRF*s plots of powders and painted layers of every single dyestuff. The dyestuffs 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 related to different morphologies.

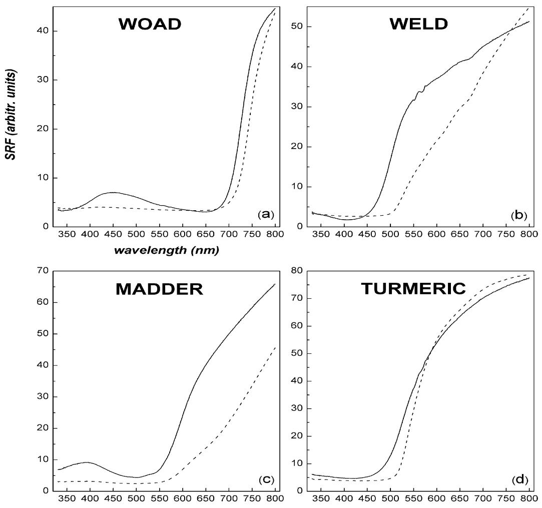

***Fig. 1** SRFs of powders (solid lines) and paintings (dashed lines).*

Rightward shifts of ankle wavelengths are noticeable as well; these trends are better outlined by the comparison of the first derivatives (Fig. 2). As a rule, peak wavelengths locate the inflection points, while the bandwidths (full width at half maximum-*FWHM*) characterize the steepness of the *SRF* curves.

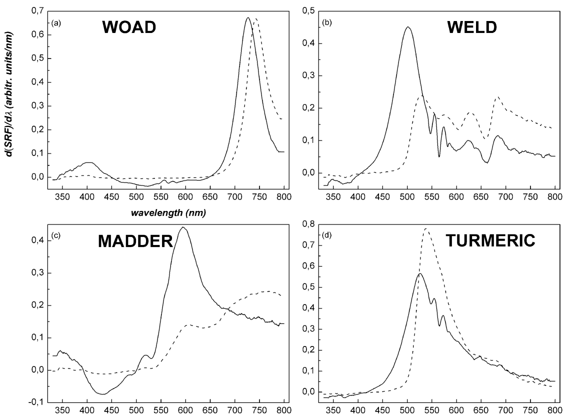

***Fig. 2** First derivatives of the SFR curves of powders (solid lines) and paintings (dashed lines).*

It's worthwhile to point out that the two yellow (Weld and Turmeric) paintings are easily discriminated through *SRF* and the derivative plots, though having almost the same hue. As a proof that in the majority of cases *SRF*s and their first derivatives qualify as able to distinguish among different colour substance, yellow inorganic pigments, investigated in our previous work [4], show fairly well different optical characteristic. Nonetheless, in case of possible ambiguous response compositional measurements do the trick.

4 Conclusions

Characterizations of Woad, Weld, Madder and Turmeric produced by means of ancient methods have been effected. Reflectance spectroscopy allowed the identification of dyestuffs in a non-invasive way. *SEM/EDX* analyses gave additional insight into production processes through the detection of the elemental constituents of the employed chemicals. Micro Raman spectroscopy completed the framework when the fluorescence was not hindering vibrational emissions.

These results are an undeniable benefit for manufacturers, since they will be able to revise their procedures to improve quality, even in terms of time stability, purity and yield.

Moreover, this research activity goes deep into the field of artwork restoration being a preliminary study in support of laser cleaning. Indeed, UV laser induced effects on natural dyestuffs are currently in progress.

References

[1] S. Acquaviva, E. D'Anna, M. L. De Giorgi, A. Della Patria, L. Pezzati, „Optical characterization of pigments by reflectance spectroscopy in support of UV laser cleaning treatments," in *Appl. Phys. A* **92**:223-227(2008)

[2] R. S. Berns, *Principles of Colour Technology,* (Wiley, New York 2000)

[3] C. Oleari, *Misurare il colore. Spettrofotometria, fotometria e colorimetria. Fisiologia e percezione,* (Hoepli, Milano 2002)

[4] S. Acquaviva, P. Baraldi, E. D'Anna, M. L. De Giorgi, A. Della Patria, L. Giotta, S. Omarini, R. Piccolo „Yellow pigments in painting: characterization and UV laser-induced modifications," in *J. Raman Spectrosc*. Doi:10.1002/jrs.2316 (2009)