

Reflectance hyperspectral imaging for red lake pigments identification

At a glance

Red lake pigments have been documented across Europe since the Medieval period, often used within different recipes. This heterogeneity, combined with their sensitivity to light-induced degradation, poses a significant challenge in identifying them in historical painted surfaces, thus making them an interesting topic for heritage science.



Initial "D" of an illuminated manuscript from Musei Civici di Pavia, Italy.

In this application note we explore the use of reflectance hyperspectral imaging acquired with **HERA VNIR** camera as a non-invasive method for the identification of red lake pigments.

Introduction

Red lake pigments are organic colorants derived from plant or animal sources, with **cochineal red** being one of the most widely used. This pigment is extracted from insects of the cochineal species, which are found in various regions worldwide. In the past, the selection of specific materials for pigment preparation reflected the availability of resources at the time, offering valuable insights into historical artistic techniques, trade networks, and material circulation. Consequently, the study of red lake pigments contributes to a deeper understanding of past technological practices and the cultural and economic contexts in which they were used.

However, **the identification of red lake pigments is challenging** due to their complex chemical composition, variations in preparation methods, influence of painting techniques, degradation products, and processes, all of which alter their spectral characteristics once analyzed. Many studies in heritage science focused on developing advanced analytical techniques and data processing methods to improve their identification. Recently explored techniques for identifying these pigments include fiber-optic reflectance spectroscopy and hyperspectral reflectance imaging.

Measurements

Reflectance hyperspectral images have been acquired with **HERA VNIR hyperspectral camera** on mock-up paint and historical sample, using a combination of white LEDs and halogen lamps for illumination.

Mock-up paints were prepared using a mixture of Arabic gum and tin cochineal carmine pigment. Five paints with varied thicknesses were analyzed to replicate a historically painted surface. A page of an **illuminated manuscript** (Musei Civici di Pavia, Italy) was selected as historical case study to evaluate the potentiality of HERA VNIR camera for red lake pigment identification.

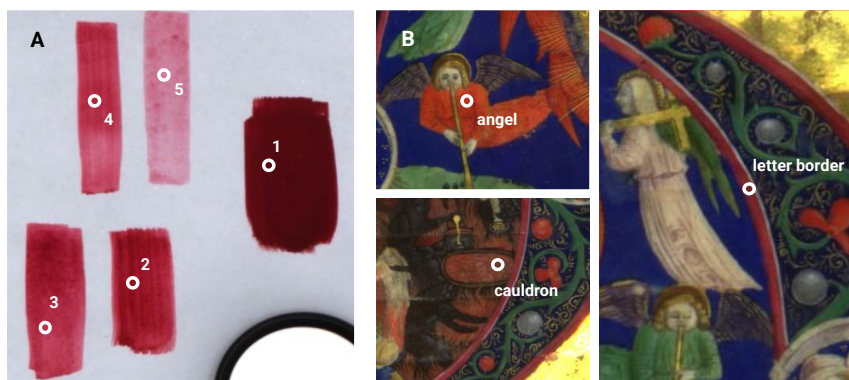


Figure 1: (A) Red cochineal pigment mock-up paints with different thicknesses (decreasing thickness from 1 to 5). (B) Zoomed areas of the letter "D" of the illuminated manuscript. White circled areas indicate the ROI for the spectral plot.

Experimental results

According to literature, the combined analysis of reflectance and first derivative spectra offers a more reliable approach for distinguishing different red lake pigments, including tin cochineal carmine pigment. Therefore, we will present this type of analysis below.

The reflectance spectra of the different mock-ups reveal resolved features only when the paint layer thickness is sufficiently thin. Considering the thinnest layer (n. 5), two inflection points are located at 521 and 556 nm, with a shoulder at lower wavelengths (480-485 nm) (Figure 2A). These inflection points become evident as peaks in the first derivative. In Figure 2B we report the limit case, i.e., the thinnest n.5 and the thickest n.1 paint layers. Only when the paint layer is sufficiently thin there are two identifiable peaks located at 500 and 536 nm, in addition to a major band at ~600 nm, observed in all samples.

Previous studies (Fonseca B. et al., 2019) have demonstrated that in case of a thick paint layer (i.e., when the sample is optically dense), the diagnostic inflection points are not visible. In these cases, the selection of another sampling area or the use of alternative analytical techniques becomes crucial.

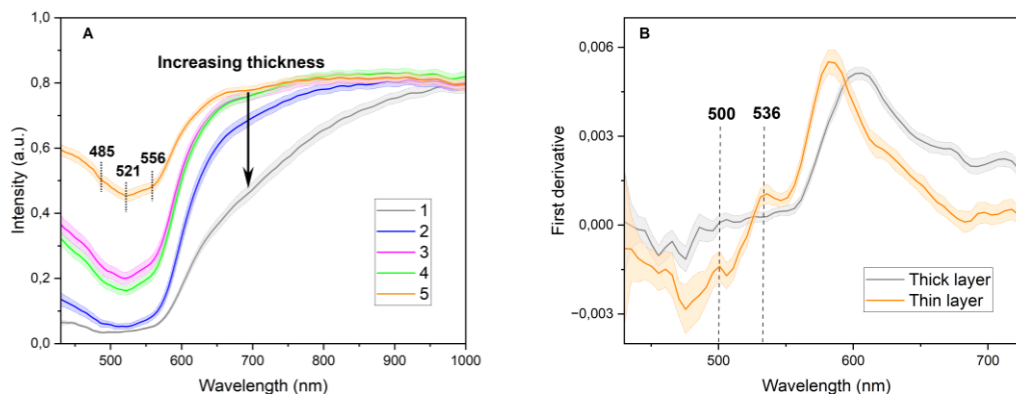


Figure 2: (A) Reflectance spectra of red cochineal mock-up sample of different thickness. (B) First derivative spectra of the thin (5) and thick (1) paint layers of red cochineal mock-ups.

Reflectance spectra and first derivative from different areas of the historical sample are reported in Figure 3. Inflection points at 486 nm and 520 nm are visible in the reflectance spectra, most prominent in the area corresponding to the angel. The diagnostic peaks can be clearly identified in the first derivative spectra, around 500 nm and 540 nm. Thanks to the combination of the reflectance and first derivative spectra and the comparison with literature (Fonseca B. et al., 2019), we can identify the pigment as cochineal-based red. The observed shift in the first derivative peaks with respect to the mock-up sample may be attributed to the use of a different cochineal red pigments or mixtures with different pigments in the painted surface.

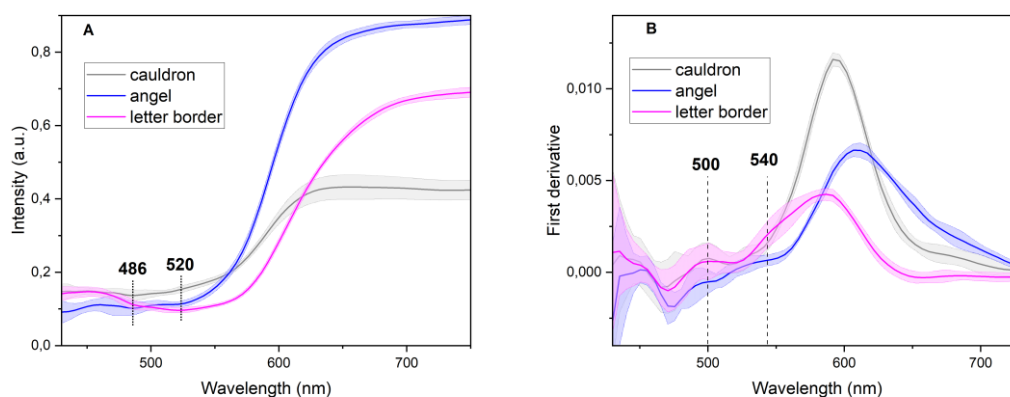


Figure 3: (A) Reflectance spectra of selected area of the illuminated manuscript sample. (B) First derivative spectra of selected area of the illuminated manuscript sample.

The first derivative spectra were used to map the distribution of the cochineal-based pigment in the illuminated manuscript. Figure 4 reports the RGB image of the illuminated manuscript and two maps based on the relative ratio of the first derivative peaks (i.e., 500/600 nm; 540/600 nm). The differences observed between the two maps indicate spectral shifts or variations in the calculated first derivative. By comparing the maps obtained with the RGB image, the 540/600 map is more effective than the 540/600 nm map in determining the distribution of red cochineal-based pigment.

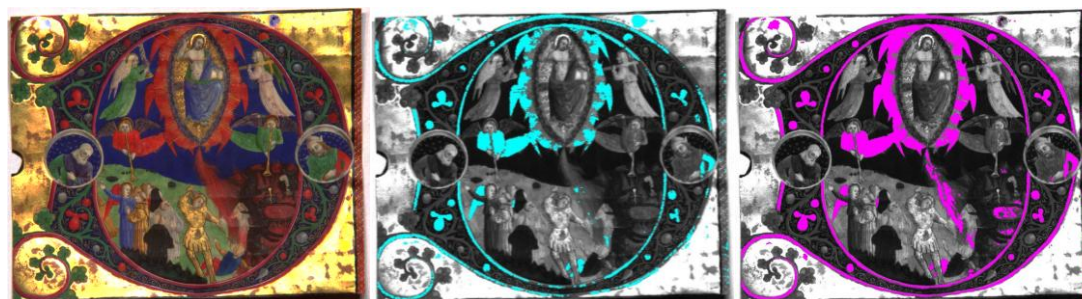


Figure 4: RGB image of the illuminated manuscript and distribution based on the combined peaks evidenced in the first derivative spectra: light blue, 500/600 nm; magenta, 540/600 nm.

References: Fonseca B. et al., (2019) Heritage Science, 7:92. <https://doi.org/10.1186/s40494-019-0335-1>