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Optical characterization of artist's materials in ancient paintings by spectral imaging in the VIS-IR range

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Abstract In the last few years, the non-invasive infrared reflectography (IRR) imaging technique has been improved by means of the multispectral option both in the VIS and in the NIR range in order to achieve more reliable and accurate results. Hence, the collected data can be visualised and studied both in the spatial and in the spectral domain, being processed as reflectographic images or as punctual reflectance spectra of the materials composing the painting.

This work presents the formulation and application of an easy-to-use methodology to identify and map the original artist's pigments in ancient paintings starting by a set of spectral data acquired with multispectral imaging technique in the VIS-NIR range. The preliminary results shown are obtained on a painting by Vittore Carpaccio, belonging to the collection of *Gallerie dell'Accademia* in Venice, Italy.

Keywords: Multispectral imaging, VIS-NIR, ancient paintings.

1 Introduction

1.1 Infrared reflectography

Since its introduction in the first half of the twentieth century [1], and the following work of Van Asperen de Boer [2], Infrared Reflectography

(IRR) has been increasingly employed for the analysis of ancient paintings, and becoming routinely utilized either in situ or in conservation laboratories as a major non-invasive imaging tool for the diagnostic process before any planned intervention.

This technique is based on the ability of NIR wavelengths (0.8 – 2.5 μm) to penetrate the pictorial layers – thanks to the partial transparency of most of the pigments in this spectral region – down to the preparatory ground (consisting in chalk or gypsum and glue) that is generally highly reflective, and thus allowing the detection of features beneath the paint surface, such as, for instance, the underdrawing (executed by means of a carbon black medium) that results in absorption. These differences in reflectivity also allow the detection of *pentimenti*, retouchings, paint losses, paint integrations and subsequent restorations.

The traditional reflectographic imaging method is performed in wide-band modality by irradiating the artwork with a single large band in the NIR range and by acquiring the backscattered radiation with suitable devices, and so obtaining an IR image, called reflectogram.

The capability to detect underlying features relies on the composition (materials and technique) of the investigated painting as well as on the characteristics of the employed imaging system [3].

Down the years, different NIR imaging devices have been used and implemented for IRR analyses, such as the early PbO-PbS Vidicon cameras used by Van Asperen De Boer [4], Si-based CCD cameras [5], up to the most recent scanning systems with InGaAs or PtSi detectors [6].

1.2 Multispectral imaging in the VIS-NIR range

In the last few years, the application of the multispectral imaging (already employed in geophysical remote sensing [7]) in the field of cultural heritage has improved the traditional wide-band IRR [8] [9], allowing the most effective range of wavelengths to be tailored to fit the specific case.

Multispectral imaging in the VIS-NIR is performed by irradiating the painting with a broadband source and by collecting the backscattered radiation within narrow spectral VIS-NIR bands. This spectral imaging technique allows the simultaneous collection of both spectral data and spatial information (high-resolution images), thus the result of the acquisition is a multiband stack of VIS and NIR images, which can be processed to extract the information [10]. The so-called multispectral cube (Fig. 14.1) can be analysed as a set of wavelength resolved images in NIR range (multi-NIR reflectography) or as a series of spatially resolved point reflectance spectra, one for each sampled pixel on the surface, both in the VIS and NIR range (VIS-NIR spectrometry) [6].

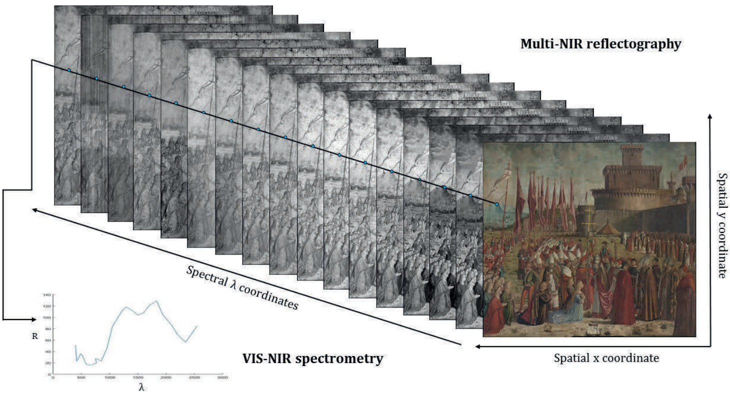

Figure 14.1: Multispectral cube.

In the multi-NIR reflectography method, the visualization of images in each band separately is useful for a manual inspection of the varied reflectance changes of particular areas. Thus, specific hidden features not visible or barely visible in wide-band modality can be detected.

The VIS-NIR spectrometry approach allows the use of the multispectral imaging for the non-invasive pixel-by-pixel qualitative recognition of similar-appearing pigments exploiting their VIS to NIR differences in diffuse reflection spectra [11].

The extraction of the reflectance spectra from the multispectral cube can be made by means of specific scripts or dedicated software. Then, in principle, a comparison between the obtained spectra and reference spectra (e.g. from punctual spectrometry techniques) helps to successfully assign each acquired spectrum to the correspondent pigment.

The identification of pigments by means of VIS-NIR spectrometry depends on the spectral range and on the spectral resolution of the device, as well as on the characteristics of the reflectance spectra of the materials under investigation. A spectral resolution in the device of about 100 nm seems to be sufficient to discriminate most of ancient pigments, which exhibit variations larger than 100 nm in the spectrum [12], otherwise, more sophisticated tools, i.e. hyperspectral devices, are necessary for pigments identification [13].

In the study of real paintings' reflectance spectra, pigments identification is not so straightforward, because the paint layering and the penetration depth of IR radiation through the layers must be taken into consideration, as these variables could lead the acquired spectra not matching the reference ones perfectly.

2 Materials and methods

2.1 The VIS-NIR multispectral scanner

The image dataset was acquired using the multispectral VIS-NIR technology, a multiband scanner available by the Iperion CH infrastructure [14].

The detection unit of the Iperion CH scanner includes a 16 channels IR module (750–2500 nm) and a 16 channels VIS module (380–780 nm), thus providing a set of 32 spatially-registered images at each acquisition. The detectors are Si (380–1000 nm) and InGaAs (1050–2500 nm) photodiodes equipped with interferential filters with a spectral width that ranges from about 20 to 30 nm for the VIS module and from 66 to 120 nm for the IR module. The image data acquired by the multiband scanner are aberration-free and hardware registered, not requiring any post-processing to be corrected or aligned.

2.2 Methodology

In this work, it is discussed a reliable and simple methodology for optical characterization of the original artists' pigments in ancient paintings, starting from the multispectral imaging in the VIS-NIR range and exploiting the dual approach of this technique.

To achieve this result, it was necessary to provide a set of reference material reflectance spectra in the same range.

The data analysis workflow is structured as follows:

1. Retrieving (and/or implementing) a spectral reference database
2. Process the spectral library for an effective comparison with the spectra extrapolated from the multispectral cube of the scanner
3. Visualization of the RGB image in the VIS range to choose the areas suitable for pigments discrimination (ROI, region of interest)
4. Material segmentation to optically discriminate the identified pigments in the image
5. Validation by means of further complementary analysis (e.g. XRF spectrometry)

Since the production of a spectral database using the same instrument employed to collect the multispectral cube is not easy and straightforward, the pipeline here developed uses reference spectra from third party database. In this paper it has been used the FORS database of CNR IFAC [15].

Different devices with different optical configurations and resolutions have been employed to record the reference spectra and the multispectral stack, and this raises the issue of the effectiveness of the comparison between the acquired data.
To overcome this problem, here it has been developed and followed a workflow to homogenize the resolution of the two instruments: the spectra retrieved from the database has been downsampled to the resolution of the multispectral scanner by averaging the reference spectra values in the bandwidth computed at full width at half maximum (FWHM) of the transmittance of each filter of the multispectral scanner:

$$\frac{1}{\lambda_f - \lambda_i} \int_{\lambda_i}^{\lambda_f} \lambda \, d\lambda$$

where λ_i and λ_f are the bandwidth limits.

The figure 14.2 shows the reference spectrum, the reflectance recorded for each scanner band, and the computed average reflectance in the bandwidth interval of each single band.

To achieve more accurate results, the transmittance curve – characteristic of each filter – could be calculated to retrieve the average reflectance data, even if this information is not always available or easy to find for online databases.

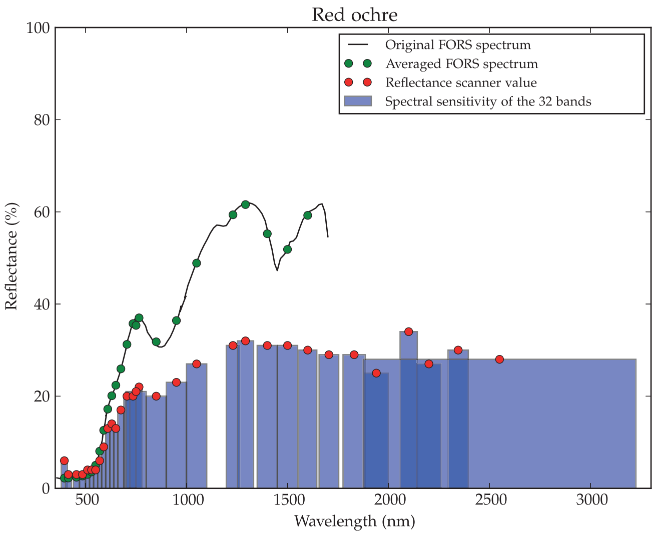

Figure 14.2: Comparison between the reference spectrum, the values recorded by the multispectral scanner (red dots) and the averaged reference values (green dots) computed in the FWHM interval of the spectral bands (blue bars).

Once the reference spectra have been processed in a single matrix, each spectrum extrapolated from the multispectral cube can be then compared with the reference from the library. For this purpose, two different algorithms commonly used in remote sensing have been implemented using Python and tested: the minimum distance and the spectral angular mapping (SAM).

The minimum distance is calculated using the following formula:

$$\frac{1}{N}\sum_{n=1}^{N}\sqrt{(x_{cube}-x_{ref})^2}$$

where N is the number of bands and x is the reflectance values of the single pixel of the band n of the hyper-spectral cube and the reference database. The SAM algorithm has been implemented referring to [16].

While for the SAM method no normalization has been necessary to achieve an effective classification, for the minimum distance method a min-max normalization of the spectra has been performed before computing the distances.

The pixel is attributed to the pigment whose reference spectra shows the lowest spectral distance and/or the lowest spectral angle.

In the end, the attribution can be eventually validated comparing the results with other data, for instance performing XRF analysis over the different areas.

Figure 14.3: RGB visible image of the selected ROI under study.

3 Results

The above methodology has been tested to identify and distinguish among four red pigments in the canvas *Incontro dei pellegrini con Papa Ciriaco* by Vittore Carpaccio. The ROI selected for pigment identi-

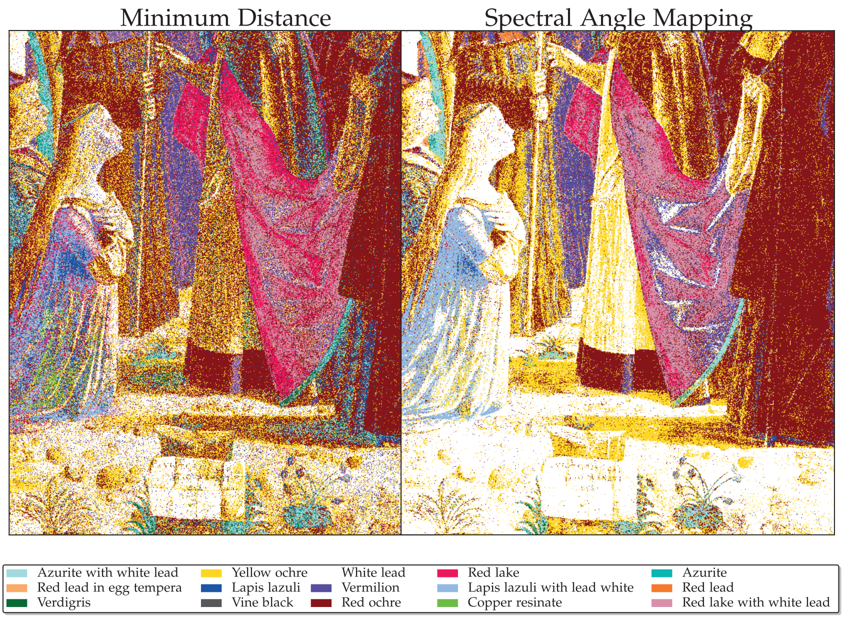

Figure 14.4: Comparison of the two classification of the pigments in the painting using the two algorithms here implemented.

fication represents the meeting of prince Ereo and princess Orsola, knelt down in sign of respect and devotion, and Pope Ciriaco, who is welcoming and baptizing the couple (Fig. 14.3). This area has been chosen because of the great variety of reds, easily distinguishable even in the RGB image.

The final output of the classification is a colour-coded image where a colour has been attributed to a pigment or a mixture of pigments (Fig. 14.4). To have an insight on the quality of the assignment, for every pixel of the image it is plotted the spectral distance and the spectral angle between the spectrum acquired from the hyperspectral cube and the reference spectrum from the database (Fig. 14.5). Low values mean a better matching between the spectra, while high values means that the attribution has been made in spite of the significant difference between the reference and the recorded spectrum.

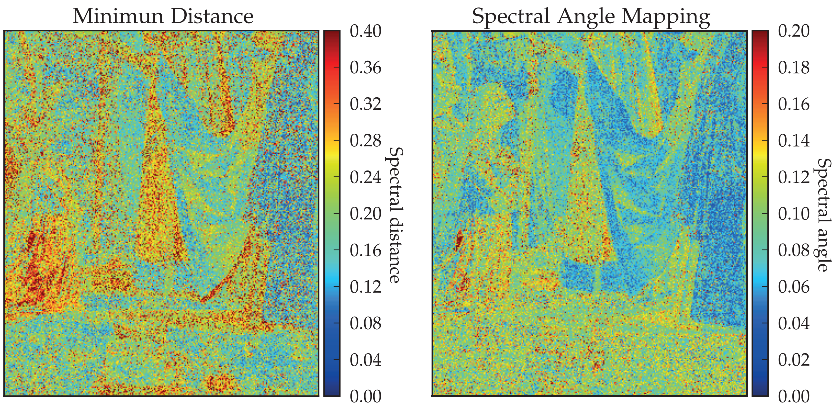

Figure 14.5: The spectral distance and the spectral angle between the reference spectrum and the sample spectrum for every pixel of the image.

4 Summary

4.1 Discussion and conclusions

A short introduction to Carpaccio's artistic technique for the pigments studied here is necessary before presenting the results. Carpaccio was renowned for his vivid and brilliant reds; indeed, red is the most outstanding colour in this painting.

Observing the VIS RGB image, red is present in virgins' dresses, in Pope, clerics and laics' choir dresses, in cardinals' *birettas* (hats) and in the flags.

In spite of the colouristic effects Carpaccio reached with red pigments, from previous studies made on other paintings it is known that his technique in red painted areas is, in fact, simple. He used to obtain the desired effect with the application of only one or two brushstrokes. In red painted layers, all the pigments commonly in use in that period were found: cinnabar, red lead, red ochre, red lake and, less extensively, realgar. Vermilion or red ochre were often used as first paint layers, over which red lake was applied as a glaze in the shadows. Red lead was mostly employed alone [17,18].

The proposed methodology allowed the identification and mapping of different pigments: the minimum distance algorithm succeed in the attribution of vermilion, red ochre and red lake, but failed in identifying red lead, while the SAM algorithm distinguished an area where this pigment is present. XRF analysis[3] on red areas confirmed the attributions.

A comparison between the results obtained by the XRF and those achieved by means of the algorithms here used suggests that spectral angle algorithm performs generally better than the minimum distance one. However, the minimum distance algorithm provides some further information: studying the spectral distance plot (Fig. 14.5), it can be observed an area in Orsola's dress where the distances between the spectra is grater and this area has been identified as a restored area where several retouches have been made. The same plot also highlights the uncertainty of the attribution of the black stripe at the end of Pope Ciriaco's cloak, here attributed to verdigris, while it is probably composed of a black pigment (visually comparing it to other dark areas in the painting).

The preliminary results presented in this work demonstrate the potentiality of the spectral imaging in the VIS-IR range for an effective characterization of the artist's materials in ancient paintings. Further work will be carried out in the framework of an interdisciplinary collaboration with the museum operators.

[3] Dr. Enrico Fiorin personal communication (2015)

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