

# Hyper-Spectral Acquisition on Historically Accurate Reconstructions of Red Organic Lakes

Tatiana Vitorino<sup>1</sup>, Andrea Casini<sup>1</sup>, Costanza Cucci<sup>1</sup>, Maria João Melo<sup>2</sup>,  
Marcello Picollo<sup>1</sup>, and Lorenzo Stefani<sup>1</sup>

<sup>1</sup> Istituto di Fisica Applicata “Nello Carrara”  
Consiglio Nazionale delle Ricerche (IFAC-CNR), Florence, Italy  
tatianamfv@gmail.com, (a.casini, c.cucci, m.picollo,  
l.stefani)@ifac.cnr.it

<sup>2</sup> Department of Conservation and Restoration, Faculdade de Ciências e Tecnologia,  
Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal  
a1318@fct.unl.pt

**Abstract.** Our cultural heritage is constituted by irreplaceable artworks that must be known and preserved. Their study and documentation should be in principle carried out using non-invasive approaches. The technological advances in spectroscopic imaging acquisition devices made it possible to apply this methodology to such purpose. In this context, the present paper discusses a particularly challenging task within the conservation field, which is the identification of red lake pigments in artworks, applying Vis-NIR hyper-spectral imaging spectroscopy. The latter was used to characterize and discriminate between historically accurate paint reconstructions of brazilwood (vegetal) and cochineal (animal) lake pigments. The same paints were also analyzed with Fiber Optic Reflectance Spectroscopy to validate the data obtained with the imaging method. The requirements for a successful identification of these pigments are addressed, and future research is suggested in order to increase the usefulness of the technique's application.

**Keywords:** Hyper-spectral imaging • Non-invasive approach • Red lake pigments • Brazilwood • Cochineal.

## 1 Introduction

The study of the materials that are part of our cultural heritage constitutes one of the most challenging tasks within the conservation field, and it should only be carried out using non-invasive multi-analytical approaches in order to preserve the artworks' integrity. Due to the technological advances in hyper-spectral image acquisition devices, imaging-based spectroscopic techniques that combine non-invasive analytical possibilities and imaging, are now a promising tool to such purpose. Mainly used with paintings and manuscripts, they can contribute to a better understanding of the objects' construction and condition. This paper discusses these techniques as promising powerful when it comes to the particular study of red organic dyes and lake pigments.

Natural red organic dyes of both vegetable and animal origin (plants such as brazilwood, and insects such as cochineal) and their complexes have been used by artists for artworks since Antiquity [1]. These complexes, known as lake pigments, and their paints are generally composed by the colored dye and its complexing metal ion (aluminum, in most cases), the inorganic component, and the binder. Their identification in artworks is seldom successful due to the complexity of their chemical composition; the presence of different chromophores, degradation products, and other pigments; and the nature of their application. Additionally, these colors are prone to fading, leading to changes in the artworks visual appearance, which may be differently interpreted from the original intention [2].

The identification of these materials in our cultural heritage has been commonly carried out with sampling-based methods [3]. Despite promising efforts have been developed [4,5], the non-invasive techniques usually used in the identification of other classes of artists' materials are generally not adequate in this case [3]. UV-Vis-NIR Fiber Optic Reflectance Spectroscopy (FORS) could be in principle used for the identification of the organic colors since it is very sensitive to this class of pigments, and allows collecting information in a non-invasive way [3]. However, several factors can influence reflectance spectra, which may lack unique features that enables a precise identification [3,6,7]. As a result, several studies have been published, in which red dyes or lake pigments are identified but not discriminated [6,8,9,10]. Most of the times, these are only classified based on their vegetal or animal origin, without identifying the real colorant. In order to solve this challenge, the recently aroused imaging spectroscopic techniques can hopefully be used as a valuable tool for the non-invasive identification of red dyes and lake pigments, and their mapping in artworks [11].

Spectral imaging technology records simultaneously spectral and spatial information from an object in a non-contact way [12]. Initially designed for areas other than that of conservation science, the development that this method has undergone enabled its application in different fields of research, including that of cultural heritage [12]. It allows to survey the entire surface of an artwork, which means that spectra acquisition is no longer limited to visually identified points thought to be representative of the pigments and mixtures used [6,7]. In this sense, while avoiding the extrapolation of results from point analysis to the rest of the artwork, it enables to increase the representativeness of the data obtained and ensure the pigments' diversity and spatial distribution present in the object. This identification and mapping of pigments based on their spectral characteristics helps to understand how paintings and manuscripts were constructed [13]. On the other hand, the combination of reflectance spectroscopy with the advantages of digital imaging, makes this imaging technique a powerful tool for conservators who wish not only to understand the artwork but also to document it.

In this paper, we will focus on the advantages and limitations of Vis-NIR hyperspectral imaging spectroscopy (IS) in the context of the analysis of red lake pigments. In particular, IS was applied to characterize and discriminate between historically accurate paint reconstructions of brazilwood and cochineal lake pigments. FORS was also used in order to validate the data obtained with the imaging method. This was a first approach towards the development of an optimized use of non-contact optical measurement techniques to the accurate identification of dyes and red lake pigments,

and their state of conservation in artworks. This study will indeed provide useful information that will ensure access to the best documentation of works of art, enhancing their understanding and helping their long-term preservation. Moreover, the preparation of such accurate references enables the creation of a database of materials that, not only helps the interpretation of the data obtained, but can also be used to compare with case studies [14].

## 2 Experimental Design

### 2.1 Preparation of Historically Accurate Reconstructions

Brazilwood and cochineal lakes were prepared based on recipes from the 15<sup>th</sup> century documentary text *Livro de como se fazem as cores* and the Winsor & Newton 19<sup>th</sup> century archive, both valuable and representative sources of technical information of their time [15]. Reconstructions were prepared using as much as possible historically accurate methods and materials, starting from the dyes' raw materials: wood scrapings from *Caesalpinia echinata* species, and cochineal insects (*Coccus cacti*). This is essential because we can only create a useful database of reference samples that can be analytically characterized and compared with case-studies if reconstructions with as much historical accuracy as possible are performed following reliable and representative sources of technical information. This approach is important because modern materials do not represent those from the past and cannot be used to give insight into it [16].

Twelve pigments (6 brazilwood and 6 cochineal lakes), ranging from light pink and dark red to carmine and purple, were used to prepare the mock-ups. FORS and IS measurements were carried out directly on paints applied with different binders in filter paper. Each pigment was painted with three binders: egg white (or glair), gum-arabic, and polyvinyl acetate. Also, selected reconstructions of brazilwood pigments were mixed with selected cochineal pigments, in different proportions (1:1 and 1:2), and painted with gum-arabic, in order to see if the presence of other chromophores might influence the reflectance spectra obtained. All paints were prepared by grinding the pigment alone with a mortar and pestle, then grinding it with water, and then with the binder. Afterwards they were painted on filter paper sheets (29 cm x 21 cm) with a brush. Efforts were made in order to obtain homogeneous paint films with the same number of layers (2/3). Each individual paint was applied in order to cover several squares with dimensions 2 cm x 3 cm.

### 2.2 Apparatus

FORS measurements of the paints in the 350-1000 nm range were performed using the same apparatus and conditions as that described in [14].

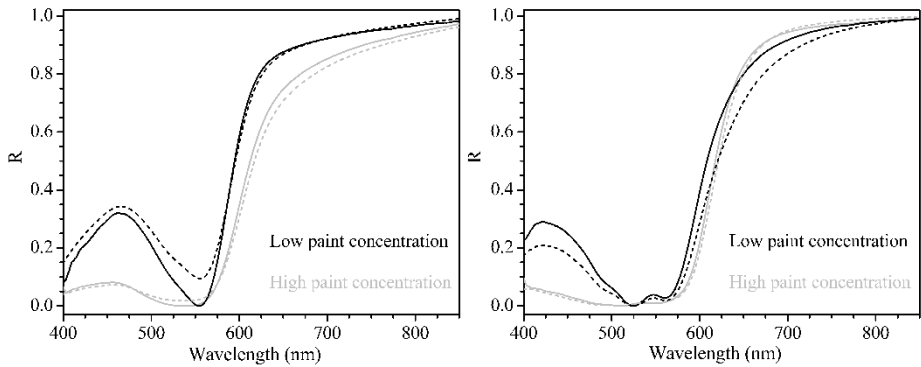
Hyper-spectral imaging spectroscopic measurements of the paints in the 400-900 nm range were performed by means of a hyper-spectral scanner designed and assembled at IFAC-CNR [17]. The system is based on a prism-grating-prism line-spectrograph ImSpectorTM V10E (SpecIm Ltd), with a 30  $\mu\text{m}$  slit. The spectrograph

is connected to a high sensitivity CCD camera (Hamamatsu ORCA-ERG). The mechanical system can scan a maximum area of about  $1 \times 1 \text{ m}^2$ , with 20 vertical line-scan stripes. The spatial sampling rate guarantees a spatial sampling of  $\sim 11$  points/mm ( $\sim 279$  ppi) and resolution better than 2 lines/mm at 50% of contrast reduction. The system's spectral sampling is about  $\sim 1.2$  nm and resolution is  $\sim 2.5$  nm at half maximum. The hyper-spectral scanner is equipped with customized software, developed at IFAC-CNR, for the management of the file-cube acquired (that contains both spatial and spectral information, and can easily reach several tens of megabytes) and the visualization and interpretation of data [17]. A certified Spectralon<sup>®</sup> standard is used as white reference for calibration. After measurements and before data treatment, calibration of the wavelength axis was performed with a holmium oxide (HO) wavelength calibration standard.

### 3 Discussion of Results

Both IS and FORS made possible to discriminate between the two natural red organic dyes of vegetable and animal origin since brazilwood and cochineal reflectance spectra display characteristic features in the visible range at optimal conditions. Pink brazilwood paints present characteristic reflectance spectra with a shoulder at 355 nm, a strong absorbance band with a small shoulder at *ca.* 520 nm and with maximum at 556 nm, and a sharp increase in reflectance around 600-615 nm into the NIR region (Fig. 1). Cochineal paints gave reflectance spectra with distinct features from those of brazilwood, this discrimination being fairly easy at optimal paint concentrations. The characteristic reflectance spectra for carmine cochineal lakes present a strong absorption band divided into two well-defined sub-bands at 525 and 562 nm, a small shoulder at  $\sim 490$  nm, and also a sharp increase in reflectance around 615-670 nm (Fig. 1). Exception to these values (not reported) was observed for the purple cochineal paint, which presents the same spectral shape but with a red shift to 535, 570 and 498 nm (two sub-bands and shoulder, respectively). The addition of brazilwood pigments to cochineal caused little changes on cochineal paints original color, and no changes in their spectra, showing that there is greater contribution to absorption from cochineal rather than from brazilwood.

Similarly to what is reported in [3], in both cases (brazilwood and cochineal) best reflectance results were obtained at low paint concentrations and for the lighter colors. In fact, when the paints were saturated or had very dark color, the absorption intensity is very high and only a strong absorbance in the visible region is observed instead of the characteristic maximum at 556 nm for brazilwood paints, or the absorption sub-bands for cochineal paints (Fig. 1). So, for the same dye it was neither the different pigment recipes nor hues that caused distinct spectra, but the way the paints were applied (i.e. to obtain an opaque layer). Thus, this lack of precise features hinders a clear identification since paints display similar reflectance characteristics.



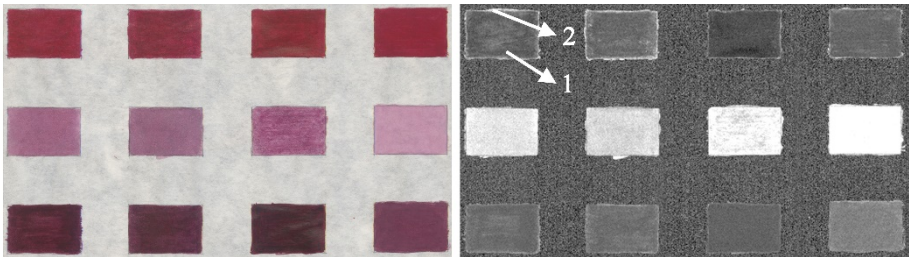
**Fig. 1.** Comparison between reflectance spectra acquired on brazilwood (left) and cochineal (right) paints with the hyper-spectral scanner (solid lines) and with FORS (dotted lines)

On the other hand, analysis of paint samples with the hyper-spectral scanner provided highly accurate RGB visible images with high quality and resolution (Fig. 2). From these imaged pictures, it was possible to select each point/pixel and extract the respective reflectance spectrum. In this work, spectra could be extracted from areas of approximately 0.36 mm x 0.36 mm, or from larger areas in order to increase the signal-to-noise ratio. Reflectance spectra reported in Fig. 1 were extracted from averaged  $\sim 22$  mm x 15 mm areas in the middle of the painted rectangles ( $\sim 30$  mm x 20 mm). In this case, spectra are of high quality. Comparing them with those acquired with FORS, shapes are very similar with regard to position of the absorption bands and to absorption intensity (Fig. 1), therefore validating the IS data. In other words, with this spatial resolution, it was proved that the results gathered with IS needed no support from the site-specific technique (FORS). The spectral resolution of IS achieved at low spatial resolution proved to be as high as the spectral resolution obtained with FORS.

To explore the technique's potentiality, in selected paint squares spectra were also extracted from sample areas with  $\sim 0.36$  mm x 0.36 mm and compared with the average spectrum (Fig. 3). This example shows not only the heterogeneity of the paint films, but also the possibility offered by the scanner to extract spectra from areas of reduced size, and the good agreement between the average spectrum and the spectra extracted from the smaller areas. However, since the sample size was reduced, the quality of the reflectance spectra acquired on the smaller areas was also diminished. This also shows the need to obtain a compromise between the desired spectral and spatial resolutions, since increasing spectral resolution requires a reduction in spatial resolution and vice versa [18].

Also, taking as reference a cochineal paint spectrum with well-defined sub-bands at 520 and 560 nm, a convexity map was obtained to show the different spectral behavior considering a parabolic fit in the range 507-537 nm. Areas where cochineal paint is less concentrated (therefore, presenting a well-defined spectrum) can be highlighted by fitting, for each pixel of the acquired hyper-spectral image, a parabolic curve to the band shape of the reflectance spectra in the 507-537 nm range, where the first absorption sub-band of cochineal is centered. The image of the painting was then

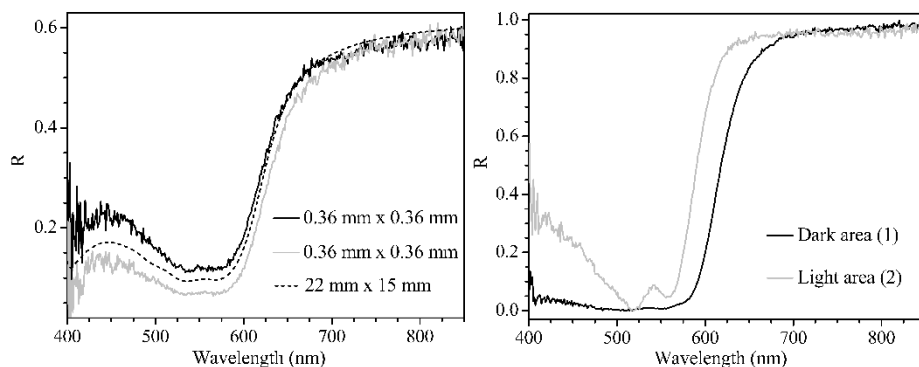
reconstructed in grey levels, with the lighter areas corresponding to the greater fit (Fig. 2). Fig. 3 shows two spectra extracted from a darker and a brighter area of the same square of paint on the concavity image (1 and 2, respectively, Fig. 2), which are clearly distinct due to the different paint's concentration. This ability to identify areas of different concentrations and to obtain spectra on areas of reduced size can be an advantage when FORS is not capable of identifying these pigments because paints are too concentrated or applied with a highly absorbing pigment. In other words, if the saturated paint film is not totally homogeneous, it will be possible to select areas where the paint is less concentrated, eventually providing additional information that may be helpful in the identification of the dye. This example is also good to show the possibility offered by IS to determine the materials' spatial distribution in an artwork. Moreover, the comparison of these elaborated maps with the RGB visible picture makes easier the interpretation of the spectroscopic data, and can greatly enrich the readability of an object.



**Fig. 2.** RGB color image of part of the filter paper sheet with cochineal paints reconstructed from the IS cube file (left), and the respective 2D map considering a parabolic fit in the 507-537 nm range (right)

## 4 Future Research

Hyper-spectral imaging spectroscopy was presented as a powerful technique in the identification of brazilwood and cochineal lake pigments, since both present characteristic reflectance spectra, as well as in expanding the information obtained from the point-measurement technique FORS. However, there are still limitations to overcome in order to improve and optimize the technique's usefulness in the study of this class of artists' materials and understanding how they were prepared and applied. For example, at the moment, emphasis still has to be put either on the imaging or on the spectral component. Also, since organic lake pigments fluoresce depending on their chemical structure and their micro-environment, the combination of reflectance with luminescence imaging spectroscopy could also be of great value [6]. Once these further developments are obtained, they will help to build the needed knowledge to use the full potential of this innovative method of investigation, thus providing the greatest benefit to the conservation field.



**Fig. 3.** Reflectance spectra extracted from areas of different size (left) and of different concentrations (right) of cochineal paints with the hyper-spectral scanner

**Acknowledgements.** Part of this work was supported by the European Cooperation in Science and Technology, COST Action TD120: Colour and Space in Cultural Heritage (COSCH, [www.cosch.info](http://www.cosch.info)). Tatiana Vitorino is sincerely grateful to the COST Action TD1201 Management Committee for approving the short-term mission COST-STSM-ECOST-STSM-TD1201-141013-036659. Also, the most honest ‘thank you’ to Vanessa Otero and Cristina Montagner for useful discussions.

## References

1. Melo, M.: History of Natural Dyes in the Ancient Mediterranean World. In: Bechtold, T., Mussak, R. (eds.) *Handbook of Natural Colorants*, pp. 3–20. John Wiley & Sons (2009)
2. Pilz, K., et al.: Van Gogh’s Copies from Saint-Rémy: Between Reminiscence, Calculation and Improvisation. In: Vellekoop, M., et al. (eds.) *Van Gogh’s Studio Practice*, Van Gogh Museum, Amsterdam; Mercatorfonds, Brussels, pp. 106–131. Yale Distributed Press, New Haven (2013)
3. Bisulca, C., et al.: UV-VIS-NIR Reflectance Spectroscopy of Red Lakes in Paintings. In: 9th International Conference on NDT of Art, Jerusalem, Israel (2008)
4. Leona, M., et al.: Nondestructive Identification of Natural and Synthetic Organic Colorants in Works of Art by Surface Enhanced Raman Scattering. *Analytical Chemistry* 83, 3990–3993 (2011)
5. Lofrumento, C., et al.: SERS Detection of Red Organic Dyes in Ag-Agar Gel. *Journal of Raman Spectroscopy* 44(1), 47–54 (2013)
6. Delaney, J.K., et al.: Visible and Infrared Imaging Spectroscopy of Picasso’s Harlequin Musician: Mapping and Identification of Artist Materials in Situ. *Applied Spectroscopy* 64(6), 584–594 (2010)
7. Ricciardi, P., et al.: Use of Imaging Spectroscopy and in situ Analytical Methods for the Characterization of the Materials and Techniques of 15th Century Illuminated Manuscripts. *JAIC* 52(1), 13–29 (2013)
8. Miliani, C., et al.: Colouring materials of pre-Columbian codices: non-invasive in situ spectroscopic analysis of the Codex Cospi. *Journal of Archaeological Science* 39, 672–679 (2012)

9. Picollo, M., et al.: Non-invasive XRF and UV-Vis-NIR Reflectance Spectroscopic Analysis of Materials Used by Beato Angelico in the Manuscript Graduale N. 558. *Revista de História da Arte, Série W* N° 1, 218–227 (2011)
10. Ricciardi, P., et al.: Use of visible and infrared reflectance and luminescence imaging spectroscopy to study illuminated manuscripts: pigment identification and visualization of under-drawings. In: Salimbeni, R., Pezzati, L. (eds.) *Proc. of SPIE*, vol. 7391, pp. 739106.1–739106.12. O3A: Optics for Arts, Architecture, and Archaeology II (2009)
11. Cucci, C., et al.: A Hyper-spectral Scanner for High Quality Image Spectroscopy: Digital Documentation and Spectroscopic Characterization of Polychrome Surfaces. In: *ART11 - 10th International Conference on Non-destructive Investigations and Microanalysis for the Diagnostics and Conservation of Cultural and Environmental Heritage* (2011)
12. Fischer, C., Kakoulli, I.: Multispectral and hyperspectral imaging technologies in conservation: Current research and potential applications. *Reviews in Conservation* 7, 3–16 (2006)
13. Picollo, M., et al.: Hyperspectral Image Spectroscopy: A 2D Approach to the Investigation of Polychrome Surfaces. *Conservation Science* (2007)
14. Melo, M., et al.: A Spectroscopic Study of Brazilwood Paints in Medieval Books of Hours. *Applied Spectroscopy* 68(4), 434–443 (2014)
15. Vitorino, T.: A Closer Look at Brazilwood and its Lake Pigments. Master thesis, Faculty of Sciences and Technology, New University of Lisbon (2012)
16. Otero, V.: Historically Accurate Reconstructions and Characterisation of Chrome Yellow Pigments. Master thesis, Faculty of Sciences and Technology, New University of Lisbon (2010)
17. Cucci, C., et al.: Open issues in hyperspectral imaging for diagnostics on paintings: when high spectral and spatial resolution turns into data redundancy. In: Salimbeni, R., Pezzati, L. (eds.) *Proc. of SPIE*, vol. 8084, pp. 80848.1–80848.10. O3A: Optics for Arts, Architecture, and Archaeology III (2011)
18. Delaney, J.K., et al.: Multispectral Imaging of Paintings in the Infrared to Detect and Map Blue Pigments. In: *Scientific Examination of Art – Modern Techniques in Conservation and Analysis*, pp. 120–136. The National Academies Press, Washington, D.C. (2005)