

CREATION OF A HYPER-SPECTRAL IMAGING REFERENCE DATABASE OF RED LAKE PIGMENTS

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ABSTRACT:

To ensure the best possible documentation of an artwork conservators must cover all its aspects such as the visual appearance, the material composition, and its state of conservation. Information on the materials can be gathered through non-invasive multi-analytical approaches. However, the analytical results alone may not be sufficient and can only be accurately interpreted if they are cross-referenced with records in databases of accurate reconstructions of historic materials. Such comparison not only supports a precise identification of materials, but also helps to unravel the meaning behind what is found through scientific analysis. Following this approach, the present contribution — developed in the course of a COSCH Short Term Scientific Mission — focuses on the creation of a hyper-spectral imaging reference database of historically accurate reconstructions of red lake pigments. This is an important class of artists' materials, whose identification in artworks is seldom successful. Hyper-spectral imaging extends the measurement domain of one-dimensional reflectance spectroscopy to the two-dimensional domain, constituting a very useful tool for the study and documentation of cultural heritage. To start building the database, reconstructions of cochineal and brazilwood paints were prepared with as much historical accuracy as possible and characterised with a hyper-spectral imaging device in the Vis-NIR range. The same paints were also characterised with Fibre Optic Reflectance Spectroscopy in order to validate the data obtained. This work foregrounds the importance of reference databases for conservation science, and for the exploration of the advantages and constraints of hyper-spectral imaging systems for the study of red lake pigments.

1. INTRODUCTION

1.1 Reference Database of Historically Accurate Reconstructions

The knowledge about materials and methods used in the creation of valuable artworks is essential at the time of restoring, conserving and documenting these cultural heritage objects. It allows us to unravel the artists' choices, to recognise the technology of their works, and to understand how time has impacted on the objects whose present condition is often different from the original condition. Examinations that provide such knowledge should be carried out using non-invasive analytical approaches. However, these analytical results alone may not be sufficient to identify and understand the materials under examination, and can only be accurately interpreted

if they are compared with reference data entered in databases consisting of historically accurate reconstructions.

To create a reliable database of reference samples it is fundamental to perform reconstructions with as much historical accuracy as possible. Such reconstructions must be prepared based on representative documentary sources of technical information, contemporary to the artworks under study (Carlyle and Witlox, 2005). This approach is important since modern materials do not represent those from the past and do not offer insights into the materials present in historical artworks (Otero et al. 2012). Therefore it is only possible to establish what materials were used, and how they were prepared, by examining material evidence and turning to representative written sources. Old treatises and technical handbooks

can provide essential evidence of historic materials and techniques contemporary to the artist. A comparison to accurate historic samples and references to documentary primary sources support a more precise identification of the materials (Melo et al. 2014), helping to understand what is found through scientific analysis.

1.2 Red Lake Pigments and their Identification in Artworks

Artists have been using natural red organic dyes, of both vegetable and animal origins, and their complexes since antiquity (Melo, 2009). The complexes, known as lake pigments, and their paints, are generally composed of the dye (which can be extracted in acidic, neutral or basic solutions) and its complexing metal ion (generally, aluminium), an inorganic component, and the binder. Their identification in artworks is a challenging and seldom successful task due to the complexity of their chemical composition; the frequent presence of different chromophores, degradation products and other pigments; and the nature of their application. Additionally, these colours are prone to fading, leading to undesirable changes in the artworks' visual appearance, which may be differently interpreted from the original intention (Pilz et al. 2013).

Despite earlier promising efforts (Leona et al. 2011) the techniques usually used in the identification of other classes of artists' materials are generally not adequate for the study of these materials in objects of cultural heritage (Bisulca et al. 2008). This kind of examination has been commonly carried out using invasive and destructive methods, which often require time-consuming sample preparation. UV-Vis-NIR Fibre Optic Reflectance Spectroscopy (FORS) has been applied for such a purpose (Bisulca et al. 2008), allowing the collection of information in a non-invasive way. However, several factors can influence the reflectance spectra. Unique features may be lacking to enable a precise identification (Bisulca et al., 2008; Delaney et al. 2010). As a result, several studies have been published, in which red dyes or lake pigments are identified, but not discriminated (Delaney et al. 2010; Picollo et al. 2011; Miliani et al. 2012). Most of the times, these materials are only classified based on their vegetal or animal origin, without identifying the actual colorant. The authors believe that this problem can only be solved through the creation of a reference database, and applying an effective *in situ* approach. In this context, the recently introduced imaging spectroscopic techniques can hopefully be used as a valuable tool for the non-invasive identification of red lake pigments in artworks.

1.3 Hyper-spectral Imaging

Spectral imaging technology allows the simultaneous recording of spectral and spatial information from an object in a non-invasive way (Fischer and Kakoulli, 2006; Kubik, 2007; Liang, 2012). Although initially designed for mining and geology, later developments have enabled its application to different fields of research, including material cultural heritage (Fischer and Kakoulli, 2006). Two-dimensional, imaging-based spectroscopic techniques are now promising tools for the study and

documentation of artworks, especially paintings and manuscripts. They allow the survey of the entire surface of an object. Therefore, spectra acquisition is no longer limited to visually identified points thought to be representative of the materials used (Delaney et al., 2010). In this sense, while avoiding the extrapolation of results from point analysis to the entire artwork, it enables the increase of the representativeness of the data obtained and ensures the materials' diversity and spatial distribution present in the object. This mapping of materials based on their spectral features can be an advantage since it helps to understand how cultural heritage objects were made. The combination of reflectance spectroscopy with the advantages of digital imaging, makes this technique a powerful tool for conservators who wish to understand and document artworks.

This contribution focuses on the application of Vis-NIR hyper-spectral imaging spectroscopy (IS) for the characterisation of red lake pigments. In particular, IS was applied to characterise and discriminate between historically accurate paint reconstructions of brazilwood (brazilein) and cochineal (carminic acid) lake pigments. FORS was also used to validate the imaging method and to ensure that it could be used for creating a reference database. The results obtained will be used to create a database of red lake pigments.

2. EXPERIMENTAL DESIGN

2.1 Preparation of the Historically Accurate Reconstructions

Brazilwood and cochineal lake pigments were prepared according to different 15th- (Strolovitch, 2010) and 19th-century (Clarke and Carlyle, 2005) recipes. Reconstructions were prepared using as much as possible historically accurate methods, starting from the dyes' raw materials: wood scrapings from *Caesalpinia echinata* species, and cochineal insects (*Coccus cacti*). In all recipes, aluminium in the form of alum (aluminium potassium sulphate dodecahydrate, $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) was used as complexing agent.

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. IS and FORS measurements were carried out directly on paints applied with different binders on filter paper. Each pigment was painted with different binders such as egg white (or glair), and gum-arabic. All pigments were also painted with gum-arabic and barium sulphate (BaSO_4), which is a material that has no colouring power and is generally used as an inert pigment or filler. Also, selected reconstructions of brazilwood pigments were mixed with cochineal pigments in different proportions (1:1 and 1:2), and painted with gum-arabic. Finally, some brazilwood reconstructions were mixed with vermilion (HgS , mercuric sulphide), red lead (Pb_3O_4 , minium), and white lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, basic carbonate of lead) in equal proportions (1:1), and painted with gum-arabic. All these mixtures were prepared in order to see how the presence of other chromophores,

pigments and/or fillers might influence the reflectance spectra obtained, and to build a more complete database.

All paints were prepared by first grinding the pigment(s) with a mortar and pestle, then by grinding it with water, and finally with the binder. Afterwards, the materials were painted on filter paper sheets (290 mm x 210 mm) using artists' brushes (Figure 1). The goal was to obtain homogeneous paint films containing the same number of layers (2/3). Each individual paint was applied in 20 mm x 30 mm squares.

2.2 Apparatus

FORS measurements were performed using a single-beam Zeiss (Jena, Germany) spectroanalyser, model MCS601 UV-NIR (190-1015 nm range), with a 1024-element silicon photodiode array detector. The spectral resolution was 0.8 nm/pixel. Radiation was provided by a voltage-stabilised 20W halogen lamp (module Model CLH600). Measurements were performed in the 350-1000 nm range using three fibre optic linear bundles connected with a 0°/2x45° geometry. In this configuration, the surface of the sample is illuminated by the light coming from the two bundles at 45°, while the reflected light is gathered by the bundle perpendicular to the surface. The area of analysis covered is about 2 mm in diameter. Calibration of the system was performed by means of a Spectralon® diffuse reflectance standard (99% reflectance). Three measurements were acquired on each sample, with each measurement resulting as the average of three acquisitions to increase the signal-to-noise ratio. All spectra were analysed using Aspect Plus® software from Zeiss.

Hyper-spectral imaging in the 400-900 nm range was performed using an instrument that was previously designed and assembled at IFAC-CNR (Cucci et al. 2011). The system is based on a prism-grating-prism line-spectrograph ImSpector™ V10E (SpecIm Ltd, Oulu, Finland), with a 30 µm slit. The spectrograph is connected to a high sensitivity CCD camera (Hamamatsu ORCA-ERG, Hamamatsu, Japan). The line-segment analysed is usually focused on the entrance slit of the spectrograph by means of a telecentric lens Opto-Engineering Srl (Mantova, Italy), which is normally used to limit distortion due to effects when the surface is not perfectly planar. The line-segment is illuminated by two Schott-Fostec fibre-optic line-lights equipped with focusing lenses that are fixed to the scan-head and symmetrically project their beams at 45° angles with respect to the normal direction of the imaged surface (0°/2x45° observation/illumination geometry). Light is supplied by a 3200 K 150-Watt QTH-lamp. The mechanical system, which allows movements along two orthogonal axes of a vertical plane, can scan a maximum area of about 100 cm x 100 cm using 20 vertical line-scan stripes. The system provides a spatial sampling of ~ 11 points/mm (~ 279 ppi) and a resolution better than 2 lines/mm at 50% of contrast reduction. The system's spectral sampling is about ~ 1.2 nm and resolution is ~ 2.5 nm at half maximum. The scan is carried out in the 'free-run' mode. The vertical movement runs freely at a constant speed of 1.5 mm/sec, while the acquisition of images proceeds independently at a

constant rate of 15 frames/sec. The system is calibrated with a certified Spectralon® white standard. The variations with time of the emission of the QTH lamp are compensated by means of frequent refreshing of the calibration. After conducting the measurements and before performing the data treatment, calibration of the wavelength axis is carried out with a holmium oxide (HO) wavelength calibration standard. The hyper-spectral scanner is equipped with customised software, developed at IFAC-CNR, for the management of the file-cube acquired and the visualisation and interpretation of data. The file-cube contains spatial and spectral information and can reach up to several tens of megabytes.

3. RESULTS AND DISCUSSION

3.1 Characterisation of Brazilwood and Cochineal Paints

After the analysis of the surrogate paint samples, a comparison was made between the data acquired with both instruments. This comparison showed that the data acquired with the hyper-spectral method were accurate and in very good agreement with the reflectance spectra obtained with FORS. Shapes are very similar with regard to the position of the absorption bands and to the absorption intensity. In particular, with a low spatial resolution, the spectral resolution of IS proved to be as high as the spectral resolution obtained with FORS.



Figure 1. RGB colour images of the filter paper sheets with brazilwood and cochineal paints, reconstructed from the IS cube file: a) brazilwood; b) cochineal; c) brazilwood mixed with cochineal; d) brazilwood mixed with other inorganic pigments.

Brazilwood and cochineal paints showed reflectance spectra with characteristic features in the visible range, at optimal conditions (Vitorino et al., 2014). Spectra are characterised by a strong absorbance band with a maximum at 556 nm for the pinkish brazilwood paints (Figure 2), and an absorption band with two maxima at 525 and 562 nm for the carmine cochineal colours (Figure 3). An exception to these spectral features was observed for the purple cochineal paint, which presents the same spectral shape of the carmine paints but with a red shift (Figure 3a). The purple lake recipe is the only one that has both zinc and aluminium ions acting as complexing agents, which may explain the shift in the wavelength positions. This fact demonstrates that the wavelength position of the characteristic bands can depend on many factors, including the overall molecular structure, as well as the local environment.

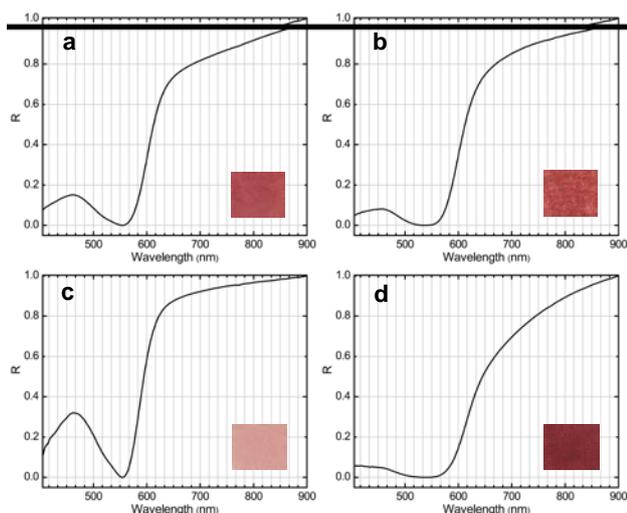


Figure 2. Reflectance spectra of gum-arabic paints of selected brazilwood lakes (a) acidic extraction + chalk; b) acidic extraction + gypsum; c) acidic extraction + chalk; d) basic extraction, without additive), extracted from the IS cube file.

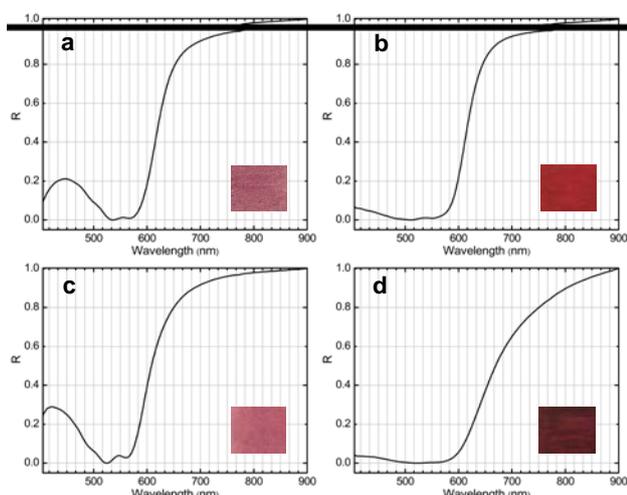


Figure 3. Reflectance spectra of gum-arabic paints of selected cochineal lakes (a) addition of zinc sulphate; b) acidic extraction + milk + sodium tetraborate; c) basic extraction + potassium hydrogen tartrate + calcium sulphate hemihydrate; d) basic extraction + potassium hydrogen tartrate + potassium bicarbonate), extracted from the IS cube file.

sulphate hemihydrate; d) basic extraction + potassium hydrogen tartrate + potassium bicarbonate), extracted from the IS cube file.

On the other hand, in both cases (brazilwood and cochineal), the way in which paints were applied (for example, to obtain an opaque layer) had an effect on the spectra obtained, which sometimes lack precise features (Bisulca et al. 2008). Better results were obtained at low paint concentrations and for the lighter colours. In fact, when the paints were saturated or had very dark colour, the absorption intensity was very high. In these cases, only a strong absorbance in the visible region was observed instead of the characteristic maximum at 556 nm for brazilwood paints (Figure 2b and 2d), or the two sub-bands for cochineal paints (Figure 3b and 3d). Thus, this lack of precise features hinders a satisfactory identification since paints display similar reflectance characteristics. This also highlights the importance of having a reference database to avoid misinterpretations and inaccurate characterisation of spectra.

The addition of barium sulphate, as filler, to both brazilwood and cochineal paints produced lighter and more opaque coatings, and the resulting spectra show very well defined absorption bands. This allows the clear observation of the spectral features, which can be difficult to identify when the lakes are used alone and the paint layers are saturated and opaque. The addition of inorganic pigments (HgS and Pb₃O₄) to brazilwood paints clearly caused a change to orange colours, and the resulting reflectance spectra present an intense s-shape absorption (Figure 4a and 4b). Also, the addition of lead white to brazilwood lakes produced spectra with a very well defined absorption band, but with the same position (Figure 4c). On the other hand, the addition of brazilwood pigments to cochineal caused little changes on cochineal paints original colour, and no changes in their spectra (Figure 4d), showing that there is greater contribution to absorption from cochineal rather than from brazilwood.

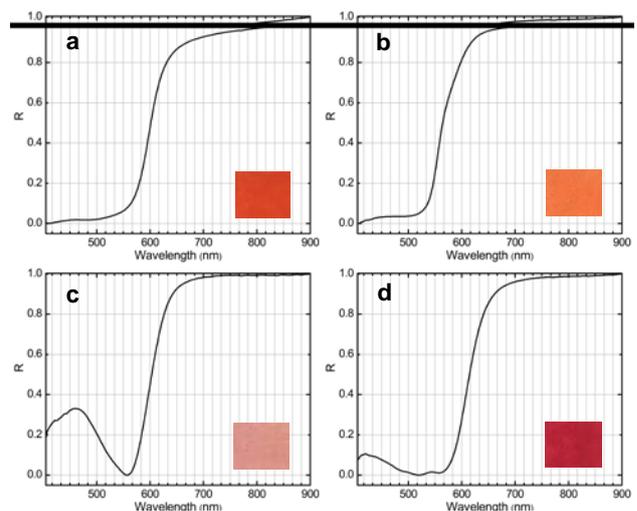


Figure 4. Reflectance spectra of brazilwood lakes mixed with vermilion (a), red lead (b) and lead white (c), and of cochineal and brazilwood lakes (1:1) (d), painted with gum-arabic, extracted from the IS cube file.

3.2 Advantages and Limitations of Hyper-spectral Imaging when Employed for the Analysis of Surrogate Paint Samples

Analysis of paint samples with IS provided highly accurate RGB visible images with high quality and resolution (Figure 1). From these images, it was possible to select each pixel and extract the respective reflectance spectrum. In this work, spectra could be extracted from very small areas (approximately 0.36 mm x 0.36 mm), or from larger areas (22 mm x 15 mm) in order to increase the signal-to-noise ratio. Reflectance spectra of high quality, extracted from these averaged 22 mm x 15 mm areas in the middle of the painted rectangles, are reported in Figures 2–4.

When spectra were extracted from sample areas with ~ 0.36 mm x 0.36 mm and compared with the average spectra, there was a good agreement between the average spectra 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 shows that, despite the possibility offered by the hyper-spectral technique to extract spectra from areas of reduced size, there is a need to obtain a compromise between the desired spectral and spatial resolutions, since increasing one of them requires a reduction in the other (Vitorino et al. 2014).

Apart from the RGB images, it was also possible to obtain convexity maps that show different spectral behaviours considering a parabolic fit in a selected wavelength range. Areas with the greatest fit are highlighted by adjusting, for each pixel of the hyper-spectral image, a parabolic curve to the shape of the reflectance spectra in the defined range. In the map reconstructed from the hyper-spectral image in grey levels, the areas that present a greater fit in that range appear lighter, while the areas with different spectral behaviour appear darker. In the present work, taking as reference a cochineal paint spectrum with well-defined sub-bands at 520 and 560 nm, a convexity map was obtained for the filter paper sheet with cochineal paints to show the spectral behaviour considering a parabolic fit in the 507-537 nm range, where the first absorption sub-band of cochineal is centred. Areas where cochineal paint is less concentrated and presents a well-defined spectrum show a greater fit and therefore are highlighted in the image reconstructed in grey levels. This possibility allows the easy identification of areas where the spectral behaviour is different (helping to determine the materials' spatial distribution) and eventually provide additional information to the accurate characterisation of the materials. Moreover, the comparison of these reconstructed maps with the RGB visible image makes easier the interpretation of the spectroscopic data and can greatly enrich the readability of an artwork.

* If a parabolic curve is well defined by a second degree polynomial, its convexity is given by the second degree coefficient of that polynomial, which is also a good estimate of the second order derivative of the curve.

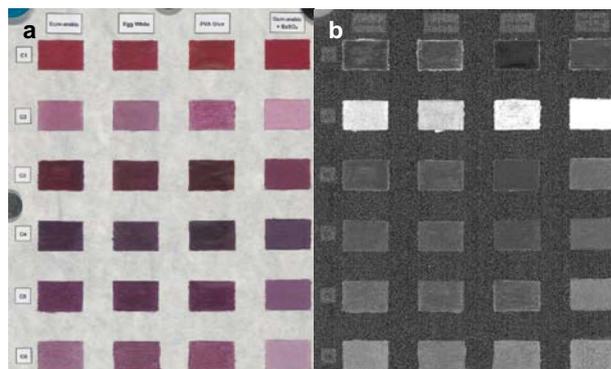


Figure 5. RGB colour image of the filter paper sheet with cochineal paints (a) and 2D map of the same sheet considering a parabolic fit in the 507-537 nm range (b), reconstructed from the IS cube file.

4. CONCLUSIONS AND FUTURE WORK

In this work, hyper-spectral imaging was presented as a promising technique for the identification of brazilwood and cochineal lakes, since both present characteristic reflectance spectra at optimal paint conditions, and which can be used to build a reference database of red lake pigments. However, there are still limitations to overcome in order to optimise the technique's usefulness in the study of this class of artists' materials and understanding how they were prepared and applied. For example, at present, the emphasis still has to be placed either on the imaging or on the spectral component since as mentioned earlier, a compromise between spectral and spatial resolution must be reached due to their inversely proportional relationship. Also, future research will include the preparation of historically accurate paint reconstructions of other red lake pigments, such as madder and lac-dye, in order to build a useful and reliable database. In the end, the further development of the technique and the preparation of a complete reference database will provide the greatest benefit to the conservation field. Red lake pigments present in artworks will be analysed using the same analytical approach and the spectra obtained will be compared with those from the database, allowing the identification and characterisation of these artists' materials.

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