Mobile hyperspectral imaging for the non-invasive study of a mural painting in the Belves Castle (France, 15th C).

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Abstract Art History and the conservation of paintings require knowledge of the artist’s materials used, such as pigments, binders and preparatory layers. This information can also provide insight into the artist's working methods.

In recent years, research carried out mostly on paintings has proved that imaging spectroscopy techniques can be used efficiently for material identification and for mapping on artworks. The development of such in situ tools capable of examining the entire surface of a painting is of interest to the fields of history of art techniques and conservation In the context of a research project on the analytical study of the mediaeval mural painting in the Belves Castle (XV century), the potential of a new mobile system for hyperspectral imaging is explored.

The pigments identified on the Belves mural paintings correspond to “classic” materials used in medieval times (red lead, red ochre, calcite and carbon black). From the methodologic point of view, the combination of methods has shown its efficiency. HSI allows a global vision and mapping of the pigments; point methods (Raman, EDXS) complete the results of reflectance spectra data.

Keywords mobile hyperspectral imaging; Raman; EDXRF; in-situ; pigments

Received 26 June 2015; accepted 23 April 2016

1. Introduction

As regards the medieval mural paintings, the knowledge of the materials used is based on recipes, described in ancient texts, in synthesis works of ancient sources, in studies of materials and on analyses which helped to characterize them. In this last case, the quality of the information about the material nature of paintings depends on the implementation of the analytical methods, some of which allow in situ analyses, protecting the integrity of the studied artworks. However, these methods give point analysis and the quality of the results and their interpretation depends on the choice of the analyzed zone. It is thus important to have a global vision of the constituents of the whole painting beforehand. This preliminary stage can be reached by hyperspectral imaging.

In recent years, research carried out mostly on paintings has proved that imaging spectroscopy techniques can be used efficiently for material identification and for mapping on artworks. The term “hyperspectral imaging” was created in the 1980’s (MacDonald, Ustin and Schaepman 2009). It can be considered as the combination of digital imaging with reflectance spectroscopy and fibre optic reflectance spectroscopy (FORS). Spectral imaging systems provide a powerful tool for non-invasive, non-contact identification and characterization of pigments, inks, substrates and treatments of artefacts, allowing completely non-destructive analyses for research and preservation in archaeology, canvas paintings (Daniel et al. 2016), illuminations (Mounier, Denoël and Daniel 2016; Mounier and Daniel 2015; Mounier, Denoël and Daniel 2015; Mounier et al 2014), wall paintings (Liang et al. 2014). In some cases, the identification of pigments is possible by comparison of the reflectance spectra with fibre optics reflectance spectrometry (FORS) databases (Institute of Applied Physics 2011; Cosen-tino 2014). However, regarding the identification of pigments, their diverse nature and the presence of complex mixtures, the analysis of HSI results is difficult in most cases. Obviously, for interpretation, this method requires the previous creation of a reflectance spectra database of the components (pigments) of paintings. The quality of the hyperspectral data interpretation (images and spectra) depends on the quality of the database. In any case, despite algorithms for the post processing of data, HSI analysis may need confirmation by other analytical methods such as Raman Spectroscopy and X-ray fluorescence (EDXRF).

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1.1. In-situ chemical analysis by X-ray fluorescence

The development of such in situ tools capable of examining the entire surface of a painting and doing a preliminary selection of zones for further study using point analytical methods (Raman, XRF, …), is of interest to the fields of history of art techniques and conservation (Mounier et al. 2014; Liang 2011; Comelli et al. 2011; Delaney et al. 2010).

In the context of a research project on the analytical study of the mediaeval mural painting in the Belves Castle (XV century, Fig. 1), the potential of a mobile system for hyperspectral imaging (Fig. 2) is explored.

Belves is situated in the southeast of Périgord, on a rock pointing to the East. The castle is located at the end of one of the two east-west axes connecting the castle outside of the city. The murals of XV century are situated in the east room (attic) (Ricarrère 2012). By their iconography and their aesthetic qualities, the paintings, placed in the last floor of a medieval house, today transformed into an attic, represent an important example among the civil pictorial production of the end of the Middle Ages in France. The theme is the “Nine brave knights”, group of legendary and historical heroes, carriers of the chivalrous virtues for the old aristocracy of the late Middle Ages (Zuwiyya 2011) (Fig. 3a, 3b, 3c).

2. Materials and methods

2.1. Mural paintings

The paintings (15th c) represents the Nine Valiant knights, unique example in Aquitaine for the mural. This theme was mentioned first in the "Voeux du paon" by Jacques de Longuyon (before 1312) (Zuwiyya 2011). The nine heroes are presented in the order in which they would always be remembered: three pagan heroes, Hector, Alexander and Caesar; three Jewish heroes, Josué, David and Judas Maccabeus; three Christian heroes, Arthur, Charlemagne and Godfrey of Bouillon. As in fact the painting represents ten knights, probably Bertrand du Guesclin completes this group.

On the eastern wall, on both sides of the fireplace, two riders are painted in the same composition. On a false tapestry, Josué in the left (Fig. 3a), Judas Maccabeus in the right.

On the opposite wall (west wall), eight riders with weapons go to the left, accompanied with phylacteries today without text, on a grey-blue bottom feigning a brocade (Fig. 3b and c). Over the door, David followed by Hector (or Bertrand du Guesclin), then by Alexandre, Godefroy de Bouillon, Charlemagne, a non identified knight (Hector or Bertrand du Guesclin?), Caesar and Arthur.

On the Josué painting (east Wall) some samplings were done (see Table 1), in order to assess the results of HSI data and to study especially the blue-grey pigments of the tapestry as no blue pigments were employed in the paintings. On the paintings of the west wall, only HSI experiments were done.

2.2. Mobile hyperspectral system

A portable imaging system was developed for in situ high resolution, accurate colour and spectral imaging in the visible/near infrared. A VNIR hyperspectral camera is placed, vertically or horizontally, on a translation rail fixed on two photo tripod. This configuration was designed to make our system mobile allowing the in situ data acquisition. Hyperspectral remote sensors
collect image data simultaneously in hundreds of narrow, adjacent spectral bands. These measurements make it possible to derive a continuous spectrum for each image pixel. In this research, the hyperspectral CCD camera (HS-XX-V10E), developed by SPECIM (Finland) has a 1600×840 pixel resolution, a spectral resolution of 2.8 nm and a wavelength range between 400 to 1000 nm. The focal length is 23 mm. The rail allowing the horizontal displacement of the camera system measures 1.30 m and was controlled by the IDAQ software. The image was taken line by line, and the two halogen lamps moved on the translation rail at the same time as the camera, guaranteeing the reproducibility of the lighting throughout the duration of the scan. For the study of the paintings, the scan speed of 13 mm/s. The duration of a scan depends of the size of the artwork. For the Belves paintings the duration of the scan varied from 30 s to 1 min. The image corresponds to 50×100 cm of the paintings (length of our spectralon target useful length of the translation rail). The software provides data acquisition, storage and wavelength calibration. A methodological development of the technique as well as preliminary tests on reference pigments, allowed to validate the analytical parameters and to establish a database of spectra references. The painting is illuminated by two halogen lamps at 45°, 118 cm away from the wall paintings.

Calibrated diffuse reflectance targets (Spectralon, by Labsphere, US) were used to calibrate the resulting spectra. The treatment of the data cube is performed with ENVI 5.0 + IDL software.

This technique generates data which can be treated, by selecting three wavelengths, to obtain an RGB image (R = 670 nm; G = 550 nm; B = 448 nm) with a matrix of reflectance spectra (400 to 1000 nm) associated with each pixel of the image. An infrared false color (IRFC) image can be also obtained by selecting an infrared band in place of the red band, and selecting two others in the visible range for the green and blue band (R → 900 nm; G → 650 nm; B → 550 nm). The IRFC image typically distinguishes single pigments or pigments mixture of similar colour but of different composition. The comparison of the IRFC image of the reference pigments with those of the painting allows us to hypothesize about the nature of the pigments (Moon, Schilling and Thirkettle1992). Since the 1960’s, infrared reflectography is a technique used to look through the paint layers. When the longer wavelengths of infrared radiation penetrate the paint layers, the upper layers appear transparent. The degree of penetration depends on

Table 1:  SEM/EDXS and Raman analytical results on the samples of east wall paintings of Belves (the sample number corresponds à those in the fig. 3a). *The ultramarine blue is due to a recent restoration.

| N° | Reference Lab BDX | Hue  | Pigment          | SEM/EDXS        | Raman                  |
|----|-------------------|------|------------------|-----------------|------------------------|
| 1  | 15555             | black| Carbon black     | Ca, Si, Al, P, Na, Cl | Carbon black, ultramarine blue*, calcite |
| 2  | 15556             | black| Carbon black     | Ca, Si, Al, S, Cl, P, K | Carbon black |
| 3  | 15557             | red  | Red ochre        | Ca, Si, Al, Fe, S, Cl, K | Hematite, ultramarine blue*, calcite |
| 4  | 15558             | yellow| Yellow ochre     | Ca, Si, Al, Fe, S, Cl, K | Goethite, calcite |
| 5  | 15559             | black| Carbon black     | Ca, Si, Al, S, K    | Carbon black, ultramarine blue* |
the thickness of the paint, the type of pigment used, and the length of the wave of infrared radiation. The contrast of absorption of various materials reveals layers of the painting not visible to the naked eye, such as the underdrawings and changes in the paint layers. In some cases, the identification of most of the component of the paintings is done by the comparison of the reflectance spectra with FORS database which allows the pigment mapping (spatial distribution of the end members/pigments on the surface of the painting).

ENVI software compares the reflectance of the reference spectra of our database with those obtained for the mapping of pigments on the painting and can also assign a color code to each identified pigment. This allows the mapping of the distribution of the pigments over the whole image. The mapping of the pigments (classification) allows differentiating the original painting and the previous restorations or repaints.

However classifications, in most of the paintings, are not easy when reflectance spectra are very close or when light modifications of spectra due to a pigment alteration or to mixture with another pigment or a binder. In such cases, we have to introduce a tolerance of similarity between spectra. This can be done by algorithms like spectral mapping methods is Spectral Angle Mapper (SAM), one of the most commonly used. This method simply treats each spectrum as a vector in an n-dimensional scatter plot (or n-D space). The mathematical technique computes an angle (here, 0.4°) between the reference and observed spectrum. The smaller the angular separation gives the closer the match between the observed and reference spectra.

Obviously, for interpretation, this technique requires the constitution of a reference spectra database about the components (pigments) of paintings. The quality of the hyperspectral data interpretation (images and spectra) is based on that of our reference database which considers >150 organic and inorganic pigments used in medieval times and modern pigments.

However, in spite of these methodologic procedures the uncertainties about certain pigments, make necessary to confirm the pigments identification by other classical point methods such as SEM/EDXS and Raman spectrometry.

2.3. Chemical analysis by SEM-X-ray spectrometry and Raman Spectroscopy

The murals paintings of Belves Castle were the object of a previous study about the medieval “false-blue” pigments for which the perception of certain grey pigments seems bluish (Daniel, Mounier and Ricarrère 2012). Colors measurements, physico-chemical analyses (SEM/EDS, Raman) and spectro imaging were used to characterize the pigments.

Elemental analyses of the samples (without coating) were carried out by a SEM/EDXS (JEOL JSM 6460LV) with energy dispersive X-Ray spectrometry (Oxford INCA 300), with an acceleration voltage of 20 kV and a pressure of 15 Pa. The semi-quantitative analyses were performed using a method based on fundamental parameters. The analyses done on each point were obtained as the average spectra of three replicated measurements. The acquisition time for each spectrum was 60 s.

The molecular characterization was done by Raman spectroscopy by using a Raman spectrometer Renishaw RM 2000 including a Leica DMLM confocal microscope a 633 nm excitation laser and a CCD detector (Peltier cooled). The integration times as well as the spectra accumulations were set to obtain the better signal-to-noise ratio. The laser power was reduced below 1% of the nominal maximum power to avoid photodecomposition and/or chemical transformation of the analysed compounds. The interpretation of Raman results was accomplished by comparison with standard Raman spectra obtained from on-line databases such as RRUFF (Bell, Clark and Gibbs 1997).

3. Results and discussion

3.1 HSI on the west wall paintings

The recording of high resolution spectral images and non-invasive monitoring of wall paintings are particularly important to provide the means of identifying pigments and non-invasive monitoring of the conservation condition of the paintings (Matouskova, Pavelka and Svadlenkova 2013). The mobile system showed that he allowed us to acquire hyperspectral data in situ. Although mobile, the size and the weight of the set remain relatively important but its good stability and the uniform and constant lighting permit to obtain images of wide zones of murals with a good spatial and spectral resolution.

- IRFC images

As previously with photographic devices (Moon, Schilling and Thirkettle 1992), the comparison of the IRFC image of the reference pigments to those of the painting allows hypothesis about the nature of the pigments used in the painting. IRFC often allows us to hypothesize on the pigment used by comparing colors with that of the same images (RGB and IRFC) of reference pigments (Cucci et al. 2011). Red lead becomes yellow as is shown in the IRFC image obtained on the reference pigment chart. For example, the pigment that appears bright yellow is red ochre/red lead mixture (fig. 4).

On the west wall, hyperspectral imaging was done on details of the paintings and on a range of pigments commonly used in mediaeval period, such as lead white, azurite or red lead.

Classification is done using the SAM algorithm (angle 0.4) in order to obtain the spatial distribution of the pigments. The reflectance spectra in this part of the paintings are enough characteristic to allow an identification with the exception of the black areas.
which are difficult to identify because the reflectance spectrum has a relatively flat profile and low intensity.

The classification of HSI data spectra gives a mapping of the different identified pigments (Fig. 5) at each pigment correspond a colour code.

- Pigment mapping

The classification shows the distribution of pigments on the surface of the painting (Fig. 5). Red are pure red ochre (broad reflectance peaks at 615 nm and 740 nm) (Fig. 6) which corresponds to a restoration (4), the horse mane and its eye are mixtures in variable proportions of calcite and red ochre (2, 3). The corresponding reflectance spectra show indeed both ochre characteristic bands at 620 and 740 nm. The hand which holds the sword is darker and results probably from a mixture of red ochre with carbon black (1). The whites consist of calcite (6) more or less mixed with carbon black in shadow zones, what gives them a bluish aspect (5). As for the tapestry motives they consist of carbon black (8) sometimes mixed with calcite (7).

On the head of Alexandre horse (Fig. 5), red lead was identified. Red lead also known as minium, is a bright orange red pigment that was widely used in the Middle Ages for painting. It was made by roasting white lead pigment in the air; the white lead would gradually turn into an orange lead tetroxide (Pb₃O₄). White and black seem have been mixed with minium (red lead).

In a detail of the unidentified knight (Fig. 4), the red of the mantle (spectra upper) appears to be red ochre mixed with red lead.

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**Fig. 5** (left) Visible color image of the head horse detail of the painting with zones of corresponding reflectance spectra (center); (right) False color near-infrared luminescence image (550, 650, and 900 nm) and (right) the spatial distributions of the different pigments in the painting.
3.2 Analyses on samplings taken from the east wall paintings

On the east wall the mural paintings represents a knight (Josué), the palette is limited to four pigments: carbon black, calcite for the white and ochre (red and yellow) in braids and blinkers of the horse. The Raman spectra confirm the identification (Fig. 7). These results are in accordance with previous analyses realized in 2011 at the request of the restorer Cornelia Cione (R&C lab, unpublished).

Fig. 6 (left) Reflectance spectra of calcite, red ochre, red lead and carbon black reference pigments and (right) Reflectance spectra on different parts of the east wall paintings.

Fig. 7 Samples 4 (15558, red) and 5 (15559, black) of the Josué knight and their Raman spectra. Red ochre and calcite was identified on the red sample (15558) and ultramarine on the other sample.
In the grey blueish zone (background, tapestry), no blue pigment has been found. It seems to be a «false blue» composed of a mixture of black and white pigments, as we found many examples in previous studies on mural paintings in the south West of France (Daniel, Mounier and Ricarrère 2012). Colour measurements have been made on the different colours of the painting showing that grey-blueish zones of the tapestry are in fact grey as it results of a mixture of calcite and carbon black.

The tapestry and the griffon are represented in two nuances of grey which seem bluish because of a simultaneous contrasting effect due to the presence of red ochre nearby (Daniel, Mounier and Ricarrère 2012). This grey is perceived as blue because of the nearness of complementary colours. The phenomenon was described by Chevreul in 1839 (Chevreul 1839). According to his law of simultaneous colour contrast, the local tone is dependent on the colour of the surrounding objects. For any perceived colour, the brain creates a complementary tone. The eye tends to create the missing colour (the complementary) to form a neutral balance in our brain. In some of the paintings, orange elements (obtained by a mixture of yellow and red) are juxtaposed to a grey colour and this creates a bluish tone. It is certainly the reason why during a recent restoration a light retouch was made with a blue ultramarine which was identified by Raman spectrometry (table 1).

Conclusion

The mobile HSI system designed for CRP2A, is well adapted to in situ analysis of paintings. HSI allows pigment mapping in a surface and not a point analysis which increase a lot the sampling. In some cases, an identification of the pigment by this method is possible. In the case of the paintings of Belvès, previous studies by point techniques assessed only the use of red ochre in the red zones. The discovery in limited zones, by hyperspectral imaging of red lead, was later confirmed with conventional point methods. The pigments identified on the Belvès mural paintings correspond to “classic” materials used in medieval times (red lead, red ochre, calcite and carbon black). The combination of methods has shown its efficiency. HSI allows a global vision, point methods complete the results of reflectance spectra data.

From a methodological point of view, hyperspectral imaging can be applied to fragile paintings without damage, and more generally to Cultural Heritage objects for imaging and identification of materials. Others techniques give the possibility to map pigments as XRF, Raman. The advantage of HSI, compared with these others techniques, is its rapidity of scan and acquisition of data on the entire image. These techniques allow the examination of all the pigments over the whole image. The availability of a relatively quick procedure capable of examining the entire surface of a painting, or to at least guide the site selection for further study using point analytical methods (for the stratigraphic study, i.e.) is of interest to the history of art techniques and conservation fields.

Acknowledgments

This study was led within the framework of an HYPER-SPEC program research (Coord. F. Daniel) supported by the LaScArBx (Cluster of Excellence, Bordeaux archaeological sciences). Many thanks to M. François Dequeune, owner of the Belvès Castle, for his authorization to access to the paintings and facilitate their analysis.

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