



HAL
open science

Mapping pigments and binders in 15th century Gothic works of art using a combination of visible and near infrared hyperspectral imaging

Laurence de Viguerie, N Oriols Pladevall, H. Lotz, V. Freni, N. Fauquet, M. Mestre, P. Walter, M. Verdaguer

► To cite this version:

Laurence de Viguerie, N Oriols Pladevall, H. Lotz, V. Freni, N. Fauquet, et al.. Mapping pigments and binders in 15th century Gothic works of art using a combination of visible and near infrared hyperspectral imaging. *Microchemical Journal*, 2020, 155, pp.104674. 10.1016/j.microc.2020.104674 . hal-02873848

HAL Id: hal-02873848

<https://hal.science/hal-02873848v1>

Submitted on 25 Jun 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Mapping pigments and binders in 15th century Gothic works of art using a combination of visible and near infrared hyperspectral imaging

L. de Viguerie¹, N. Oriols Pladevall², H. Lotz¹, V. Freni¹, N. Fauquet¹,
M. Mestre², P. Walter¹, M. Verdager³

¹ Sorbonne Université, CNRS, Laboratoire d'Archéologie Moléculaire et Structurale LAMS, Paris, France

² Laboratori Restauració i Conservació Preventiva, Museu Nacional de Art de Catalunya, Palau Nacional, Parc de Montjuïc, Barcelona

³ Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire IPCM, Paris, France

Abstract

Visible and near infrared hyperspectral imaging have allowed unprecedented analyses of two major works of art of the National Museum of Catalan Art (MNAC), 15th century Gothic altarpieces: (1) *Madonna of the 'Consellers'* (Lluís Dalmau, 1443-1445) [1], an impressive piece of Catalan painting, inspired by J. van Eyck and (2) *Princess Eudoxia exorcised in front of St. Stephen's tomb* (Vergós Group, 1495-1500) part of the altarpiece of *Sant Esteve de Granollers*.

Visible and near infrared (VNIR) hyperspectral imaging was used to highlight the artist's handling of materials in achieving light and shadow effects in the red draperies. The refinement in the modelling could be observed thanks to the distribution images of the red pigments. Short-wavelength infrared (SWIR) hyperspectral imaging revealed blackened azurite on visually altered areas of the two paintings. It is possible to map the presence of azurite below the altered layer and obtain a better understanding of the earlier appearance of the paintings. It was moreover possible to identify and map the binders used in both works of art: the use of oil in Dalmau's painting, as the earliest Catalan oil painting, is confirmed here whereas in the Vergós's painting both egg and oil may have been used in separate areas.

Keywords

Hyperspectral imaging - Binder identification – Pigment identification and mapping - Azurite darkening – 15th century Gothic Catalan altarpieces.

Highlights

- New insights on two 15th century altarpieces, major artworks of the *MNAC* (National Museum of Catalan Art, Barcelona) highlighting alterations of azurite paint and revealing the paintings' original appearance.

- Characterization of the painters' palette and technique thanks to distribution maps of pigments obtained from VNIR and SWIR hyperspectral data treatment.
- State of the art binder identification via SWIR hyperspectral imaging – mapping of egg yolk vs oil.

Introduction

Among the painters who worked in Catalonia in the 15th century are the Valencian Lluís Dalmau and the Catalan Jaume Huguet, who devoted themselves in preference to the painting of altarpieces. During this period, technological advances allow the development of new pictorial techniques, such as the purification and preparation processes of oil, introduced by the artists in their workshops to serve as drying oils and pigments' binders. In 1431, Lluís Dalmau, painter at the court of Alphonse the Magnanimous went by order of the king to Flanders, where he stayed for an indeterminate period, after which he returned to Valencia as court painter and remained there for at least five years. Ten years later, he settled in Barcelona, where he painted between 1443 and 1445 *The Madonna of the 'Consellers'* in the spirit of an 'Eyckian' painting. All historians agree that this painting illustrates the stylistic and technical evolution resulting from the Flemish influence. This painting is now known as the earliest Catalan oil painting [1]. From then on, artists became aware of the oil painting process and began to gradually use a "mixed system" with both techniques, egg and oil, as attested by notarized deeds [2].

In this context of pictorial evolution, it is of great interest to get a better understanding of the materials used by the artists. In the framework of a collaboration between the *National Museum of Catalan Art* (MNAC) and *Sorbonne Université*, we report here the hyperspectral imaging carried out on two 15th century paintings, currently on display at the MNAC: (1) *Madonna of the 'Consellers'* (Lluís Dalmau, 1443-1445) and (2) *Princess Eudoxia exorcised in front of St. Stephen tomb* (Vergós Group, 1495-1500) part of the altarpiece of *Sant Esteve de Granollers*. The Vergós family workshop follows the artistic tradition of the painters Jaume Huguet and Lluís Dalmau. The altarpiece of Sant Esteve de Granollers (1495-1500), one of the most significant works of the workshop, is of special interest because it registers the simultaneous presence of various elements, both in terms of style and technique. The aim of the analytical approach we developed is not limited to the identification of materials, but also their relationships to one another, in order to assess the various influences on the artists and the technical innovations that these works display. Samples taken from the paintings and

prepared as cross-sections had already provided a uniquely detailed insight into the stratigraphy. However, sampling provides only local information, which might be misleading and so it is useful to combine such investigations with imaging techniques which provide more representative results over a larger surface area. The past few years have seen a tremendous rise in the development of hyperspectral imaging techniques, which are imaging techniques with a sufficient number of channels to provide a complete spectrum for each pixel [3]. In the visible range, the reflectance spectrum can be used to identify pigments and colorants, particularly when they are used pure and in thick layers as is the case in illuminated manuscripts [4, 5, 6, 7]. The identification relies on comparisons with reference spectra from the literature or from a database, previously acquired from reference materials or available online such as the CNR-IFAC one (<http://fors.ifac.cnr.it/>).

In the case of easel paintings, it is more complex: different pigments are dispersed in a binder, superimposed on other layers and overlaid by a varnish [8, 9]. In the near-infrared range, the absorption spectrum exhibits harmonics and combinations of the absorption bands observed in the mid-infrared range. Hydroxyl groups and carbonates are particularly visible: gypsum, calcite and malachite are easily identified as well as different types of clays [7, 10, 11, 12]. Here again the identification is often based on comparisons with reference spectra obtained on pure materials or mock-ups. One element of great interest in this spectral range also lies in the possibility of identifying the binder: vibrations of carbonyl or amide groups, associated with organic matter (oil, egg, glue...) are visible in the 800-2500 nm range [12, 13, 14]. However absorption bands are relatively broad and may overlap, which can make the interpretation difficult in the case of mixtures and superimpositions. In the case of traditional Italian oil painting on panel, the *gesso* signal is overwhelming, often hiding most of the other paint components.

The aim of this study was thus to further evaluate the possible use of visible and near-infrared hyperspectral imaging to identify original materials, to reveal previous restorations and to characterise the painter's technique. We do not discuss the whole of the painters' palettes, but choose to focus on specific new features highlighted by the use of hyperspectral imaging.

2. Materials and method

Reference samples

Rabbit skin glue and linseed oil, cold pressed, were purchased from Laverdure (France). Azurite and madder lake were purchased from Kremer (Kremer references: 10210 and

372051), lead white from Masters Pigment (Flake White Master Pigment). Madder lake pigment is produced from Turkish madder roots following a historical recipe, mentioned in “Die Farbstoffe” by P. Schützenberger (1873), according to the provider [15]. Pigments were previously characterized to confirm their composition by means of X-ray fluorescence and visible reflectance spectroscopy in the case of madder lake [16] and X-ray diffraction for azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and lead white.

Paint reference samples were then prepared according to traditional practices:

(1) a *gesso* was first applied on a wood panel, made of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) mixed with rabbit skin glue in a 1:2 ratio. To prepare the *gesso*, the rabbit skin glue is first dissolved in distilled water (4 g dissolved in 100 mL of distilled water) while heating and stirring; once the mixture is homogeneous, gypsum is slowly added while stirring.

(2) paint (prepared with azurite / madder lake / lead white ground in different binders, specifically linseed oil and egg yolk) was then spread onto the *gesso* layer.

To prepare the paint, the pigment was first mixed with the binder and the mixture was then ground with the muller on a ground-glass slab. In the case of the paint with the egg-yolk binder, a small amount of water was added (1 mL for two egg yolks, around 30 g). The paint was prepared according to the following proportions:

Binder/ pigment	Azurite	Lead white	Madder lake
Linseed oil	57	90	50
Egg yolk	66	66	47

Table 1: Proportions of pigment in the paint preparations (in wt%), depending on the binder.

Analysed works of art

Two 15th century paintings have been analysed in their exhibition room in the MNAC: (1) *Madonna of the ‘Consellers’* (Lluís Dalmau, 1443-1445) [1] and (2) *Princess Eudoxia exorcised in front of St. Stephen tomb* (Vergós Group, 1495-1500) part of the altarpiece of *Sant Esteve de Granollers* [2].

Madonna of the ‘Consellers’ reflects, according to different studies, influences from several works of art painted by Jan Van Eyck. We do not know exactly how long Dalmau spent in Flanders, but it can be assumed that he was there before 1436 and then from 1438-1443, just before the contract for the Madonna was signed. The influence is reflected both in the composition and the colours, as well as in the use of oil as binding medium.

The altarpiece of Sant Esteve de Granollers was commissioned from Pau Vergós, who died while painting in 1495. His brother Rafael Vergós continued it. His father, Jaume Vergós II,

also collaborated. The Vergós are considered followers of the pictorial tradition of Jaume Huguet.



Figure 1: Two paintings analysed: (Left) *Madonna of the 'Consellers'* (Lluís Dalmau, 1453-1455); (right) *Princess Eudoxia exorcised in front of St. Stephen tomb* (Vergós Group, 1495-1500).

Hyperspectral analyses

Visible and near infrared hyperspectral images were acquired from selected areas of both works of art, in their exhibition room.

Visible and near infrared (VNIR) and SWIR hyperspectral camera by Specim (Oulu, Finland) were used. The camera was mounted on a rotation stage to acquire the images in push broom technique, that is by scanning the painting horizontally and acquiring full spectral information for one vertical line on the work at a time.

For the VNIR camera, the spectral range is 400 nm to 1000 nm with 212 wavelength channels (rebinned from 1200) with a spectral sampling of 2.8 nm. For the SWIR camera, the spectral range is 1000 to 2500 nm with 280 wavelength channels and a spectral sampling of 12 nm. For the SWIR camera, two optics were used: the first one (OLES30, Specim, focal length 30 mm) with a spatial sampling of approx. 1.5 mm at a camera-painting distance of 1.2 m, and the second one (OLES56, Specim, focal length 56 mm) to image smaller zones with a spatial

sampling of approximately 90 μm (distance camera-painting of 27 cm). The different acquisition parameters, camera and optics characteristics are reported in Table 2. During the investigation, diffuse illumination was provided by one 20 W halogen lamp, placed at 0.4 m away.

Table 2: Cameras and optics characteristics, with acquisition parameters (*italics*).

		VNIR (400-1000 nm)	SWIR (1000-2500 nm)	
Spatial size		1600 pixels	380 pixels	
Spectral size		1200 pixels	280 pixels	
Spectral sampling		2.8 nm	12 nm	
<i>Integration time</i>		180 ms	40 ms	
<i>Rotation frequency</i>		4 Hz	20 Hz	
<i>Rotation speed</i>		0,07 $^{\circ} \text{s}^{-1}$	0,4 $^{\circ} \text{s}^{-1}$	
Optics (Specim)	Type	OL17	OLES30	OLES56
	Focal length	17 mm	30 mm	56 mm
	<i>Distance</i>	610 mm	1.2 m	270 mm

The dedicated ENVI software (Harris Corporation, Melbourne, Florida, USA) was used for data treatment. The data was normalized with dark and bright field images using the Specim plug-in in ENVI. To check the quality of the reflectance image cube, the reflectance spectra from the white and black diffuse reflectance standards placed in the image scene were examined: in the range between 450 and 900 nm, they showed a reflectance noise level of 1.7 % for the white reference and 0.5 % for the dark reference.

The spectral angle mapper (SAM) algorithm of ENVI was used to obtain reflectance map considering only a portion of the spectral range that contained the key spectral feature/s characteristic of the material to be mapped.

Macrophotographs (Olympus OM-D E-M5 Mark II with a Olympus 60 mm macro lens) of the analysed areas were also recorded.

3. Results and discussion

Identification of the artist's palette

The two studied works of art had already been investigated by the MNAC laboratory, thanks to observations and analyses of cross sections [1,2]. In the case of *Madonna of the*

'*Consellers*', the main pigments could be identified as well as the stratigraphy of the paint layer: lead white, lead tin yellow (type I), verdigris, lapis and azurite, minium, vermilion and a red lake (of animal origin) have been identified. The results have been published in [1]. As an example the stratigraphy of dress of the Virgin Mary has been described as 1) a first layer of gesso 2) an impermeable layer of linseed oil and then 3) two layers of azurite under 4) one layer of lapis-lazuli. In the case of *Princesa Eudoxia*, we combined punctual XRF to hyperspectral imaging to confirm the observations made on cross sections. The palette is a bit more restricted without lapis nor minium: lead white, lead tin yellow (type I), verdigris, azurite, vermilion and a red lake (of animal origin), red and yellow earths.

We report in figure S1(a-j) the reflectance spectra (in visible and near infrared range) for all pigments identified. As the aim of this work is to highlight the possible benefits of hyperspectral imaging on such paintings, we detail here only few interesting results obtained thanks to this technique. A global classification approach for the hyperspectral data treatment did not prove to be appropriate, due to the complexity of the paint with mixtures and superimpositions, but also considering the size of the paintings. We thus focused on few zones in order to identify and, if possible, to map the main pigments.

Yellow and red pigments could be identified thanks to their visible reflectance spectrum, (complementary to their elemental composition). Results obtained on red pigments are detailed in the next section. In the case of the yellow zones, one of the differences between the two analysed artworks is that, while Dalmau has the ability to mimic gilding with the pigment lead-tin yellow, in the painting of the Vergós, gold leaf is still used, as well as lead tin yellow (for the pilgrim's bag for example). Lead tin yellow was identified in *Madonna of the 'Consellers'* and we can confirm its use thanks to the presence of both Pb and Sn in the XRF spectra and to the visible reflectance spectrum (figure S1h).

Thanks to the near infrared imaging (SWIR), we could confirm the use of azurite (results described in detail in the dedicated section) and lead white. Lead white is composed of a mixture of hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and cerussite (PbCO_3). We indicate in figure S2 both SWIR reflectance spectra: if cerussite does not present any characteristic feature, hydrocerussite exhibits three main bands at ca. 1440, 2310 and 2470 nm. The band at 1446 nm, attributed to the first overtone of the OH stretch, has been mainly used in the literature as the main absorption feature; Delaney *et al.* have indeed shown that they could use it to map the presence of lead white in a George Seurat's painting [17]. In our case, the use of such procedure (Spectral Angle Map on the 1435-1455 nm region) is not possible due to the strong gesso absorption, which also exhibits a hydroxyl band at ca. 1445 nm. The use of derivative

spectra (between 1421 and 1600 nm) does not show neither any interesting result. We can then consider the band at 2310 nm (combination band involving the OH fundamental stretching mode, probably with a Pb-OH bending fundamental [18]); however the maps obtained are not really meaningful as lead white is clearly present in different layers of the paintings and is used mixed with pigments in different colours.

The green pigment has been identified in [1] as verdigris, a synthetic pigment obtained by treating metallic copper with vinegar. This pigment has a high chemical variability due to the diversity of recipes used. This diversity, as well as its possible evolution over time, makes its characterization complicated. Synchrotron techniques can help in their identification on micro-samples. In the *Madonna of the 'Consellers'*, basic copper acetates, more or less hydrated, were found as well as in one of the analysed samples, compounds such as copper dioxides and copper acetates, probably alteration compounds [1]. Their characterisation by in-situ techniques is more difficult and it was not possible to conclude on the exact nature of these copper compounds. However, the results obtained are in agreement with previous observations: the XRF spectra indicate the presence of Cu and the SWIR domain can help to go further. Indeed, neither malachite nor azurite explain the spectra obtained. The SWIR spectrum of modern synthetic verdigris ($\text{Cu}(\text{CO}_2\text{CH}_3)_2, \text{H}_2\text{O}$) shows a wide range of absorption bands (Figure S1d) but the most intense ones overlap those present in gypsum (described in detail elsewhere [13]) as is the case with the intense gypsum band at about 1950 nm. The strong absorption around 1000 nm can only guide identification. To confirm these observations, it would be interesting to analyze different types of synthetic and historical verdigris to determine whether SWIR spectroscopy would allow in situ characterization of these compounds

Mapping the red pigments – effects of light and shadow

In the earlier publications on both paintings [1, 2], the red colour is suggested to be the most complex one: different layers are used to achieve modulations of light and shadow in the draperies. In *Princess Eudoxia*, two micro cross-sections from the red draperies were analysed [2]. One was taken from the purple mantle of the pilgrim, and the other one from the red garment worn by Theodosius II (the man bearing the crown). The mantle of the pilgrim is simple, without ornaments, with different gradations that mark the volumes of the drapery. The cross-section indicated the use of six red paint layers, all containing the same pigments, a mixture of red lake and lead white but differing in thickness and proportions. The other cross-section, coming from the more precious garment of Theodose II, consisted in four layers of

red paint: two layers are made of red lake and two others of vermilion, including the superficial one. In *Madonna*, one cross-section from the red dress of Santa Eulalia had indicated the superimposition of two red layers, including three red pigments: a red lake layer above one containing a mixture of vermilion and minium. These observations underlined the complexity of such colours.

In the present study, we used visible hyperspectral imaging to map the pigments' distribution on the surface and to better understand this choice of pigments and the effects of modulation in the red draperies. As an example, we discuss here the results obtained from the red pigments in the *Madonna*. The three red pigments can be easily identified thanks to their characteristic reflectance spectrum: vermilion (HgS) and minium (Pb₃O₄) display as semi-conductors an absorption edge at respectively 590 and 570 nm (Figure 2c) [16]. Minium is mainly found in a mixture with vermilion as shown by the presence of the two maxima in the derivative spectrum. The red lake (detected thanks to two small absorption bands in the 510 - 560 nm range) displays a maximum of the derivative spectrum around 605 nm. Distribution maps were calculated using SAM on the derivative data in the range 530 – 640 nm, and compared to the visible image (Figure 2a and b).

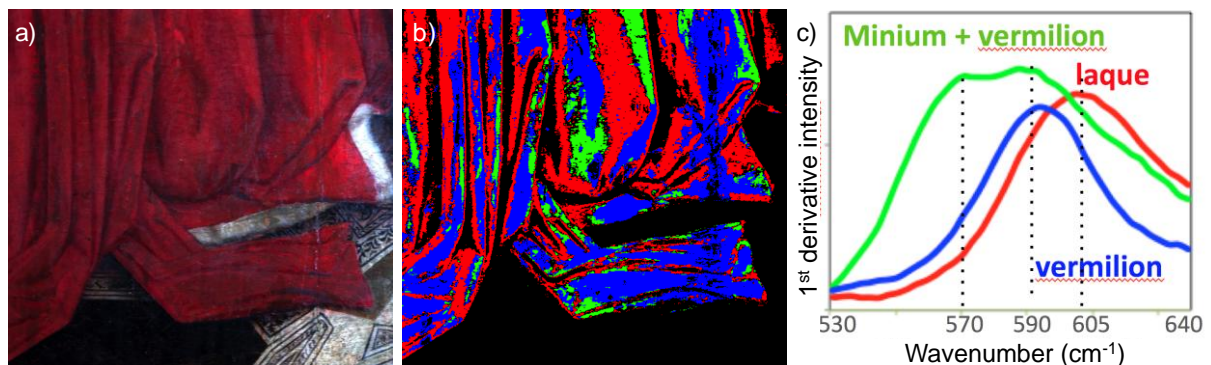


Figure 2: Analysis of the red draperies in the *Madonna*: a) visible hyperspectral image (R: 628, G: 542, B: 462 nm); b) SAM image obtained on the derivative data in the range 530-640 nm, with pre-defined endmembers shown in c).

Red lake is clearly identified in darker zones, whereas lighter areas are highlighted thanks to the use of minium combined with vermilion. The artist places the light and shadows thanks to the use of red pigments of different hues, mixed or superimposed, instead of adding white or dark pigments.

The case of azurite: highlighting degradations

Near infrared hyperspectral imaging is able to reveal the presence of azurite and to map it. Azurite (2CuCO₃.Cu(OH)₂) exhibits very characteristic spectra with three narrow absorption

features, one at 1497 nm and a doublet at 2285 and 2350 nm due to overtones and combinations of $-OH$ and $-CO_3$ vibrations [13, 19]. Therefore, a simple false colour near infrared image with red, green and blue (R, G, B) at respectively 2285, 2353, and 2319 nm, can be used to highlight the use of azurite.

In both paintings, black zones are present; such treatment on these black zones reveals the presence of azurite below the altered layer, which confirms the previous observations of degraded azurite made locally on micro cross-sections. The images obtained allow a better understanding of the original appearance of the paintings. A striking example lies in the leg of the pilgrim in *Princess Eudoxia* (figure 3 a to d) appearing today as black: his boot has been painted with carbon black, absorbing in the near-infrared region, whereas his stocking has been painted with azurite as well as the floor-tiles that now appear black. Similar azurite blackening can be observed in the decorations of the floor in the *Madonna*. The near-infrared false colour image (figure 3f) even reveals a later restoration: carbon black that must have been used to match the colour of the blackened azurite present around the damaged area.

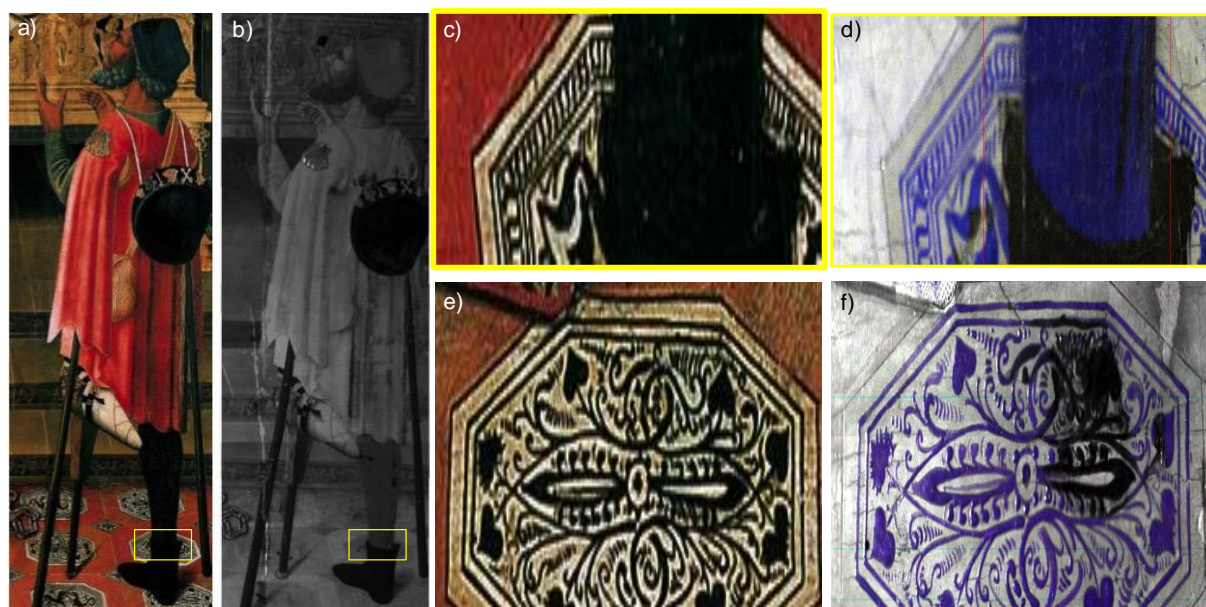


Figure 3: Analysis of black areas of *Princess Eudoxia* (a - d): a) Pilgrim in *Princess Eudoxia*, photography and corresponding SWIR image (1650 – 1750 nm). The yellow rectangle indicate the zone investigated in c) and d): c) visible hyperspectral image (R: 628, G: 542, B: 462 nm); d) SWIR hyperspectral image (R: 2285, G: 2353, B: 2319 nm). Analysis of a black area in the *Madonna*: e) visible hyperspectral image (R: 628, G: 542, B: 462 nm) f) SWIR hyperspectral image (R: 2285, G: 2353, B: 2319 nm).

No difference could be found between the spectra of degraded and non-degraded azurite, present beneath the layer of lapis of the Virgin's dress in the *Madonna*. Macro-photographs

were taken of degraded areas; surprisingly non-degraded blue pigment is still visible (figure 4). The on-going hypothesis, supported by the cross sections observations [1, 2], is that the darkening is due to dust trapped between the large grains of azurite.

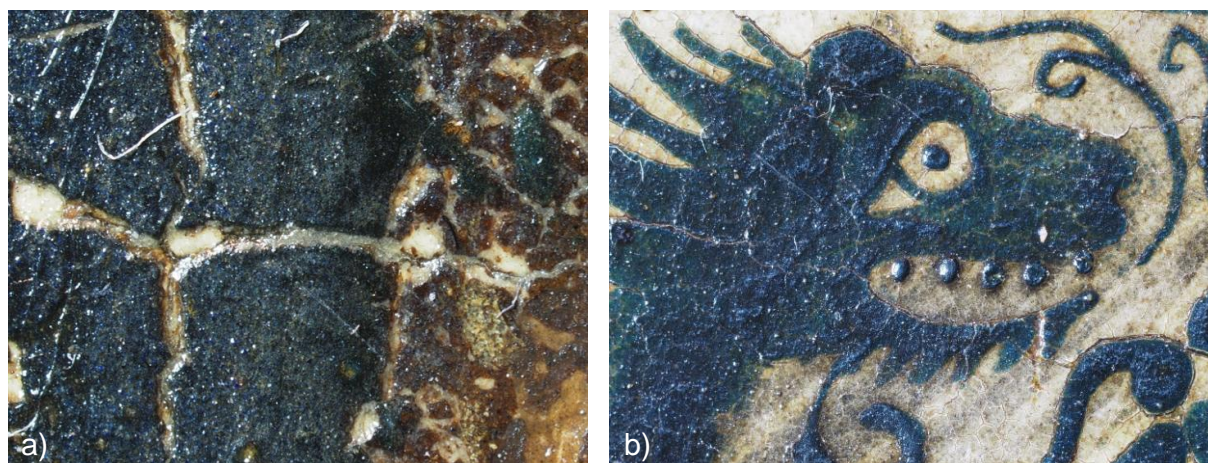


Figure 4: Macrophotographs on a) *Madonna* and b) *Princess Eudoxia*.

Binder identification

Special attention was also dedicated to binder characterisation in both works of art. *Madonna* is known to be the earliest Catalan oil painting. The painting technique of *Princess Eudoxia* is not clearly described in the literature. Oil or egg could have been used as a binder, or even both in different areas, or possibly mixed together. As observed above, the Vergós Group are considered to be followers of Jaume Huguet who painted mostly with egg tempera. However, the presence of oil in the green pigments, and the use of protein (animal glue) with azurite have also been identified in Jaume Huguet's altarpieces [20].

In-situ identification of binders is a great challenge in the field, as this is usually carried out thanks to separation methods on micro-samples taken from the painting. A previous publication of Vagnini *et al.* [21] has shown the possibility of discriminating different binders thanks to near-infrared spectroscopy. The *Washington National Gallery of Art* group then confirmed that it was possible to identify, and even map binders thanks to SWIR hyperspectral imaging [12-14]: a custom commercial camera (Surface Optics, spectral resolution of 4.4 nm) was used for the study of an early 15th century illuminated manuscript leaf on parchment painted by Lorenzo Monaco [12]. Data treatment of the results obtained on the manuscript and on mock-up samples made it possible to identify both uses of a fat-containing binder (probably egg yolk) and another one probably egg white or gum, applied selectively on different zones. The same near infrared hyperspectral camera was used to map the distribution of egg yolk and animal skin glue paint binders, in three small 15th century

panels by Cosimo Tura [13]. More recently, the same group used a custom high resolution, high sensitivity camera and proved that they are now able to differentiate oil from alkyd resin [14].

In contrast, the identification and mapping of egg yolk *vs* oil has never been carried out thanks to hyperspectral imaging, although Vagnini *et al.* proved it to be possible by near infrared Fiber Optic Reflectance Spectroscopy (FORS): with a spectral resolution of 4 cm^{-1} , they could identify the presence of drying oils in a 17th century painting [19].

To establish whether it was possible to discriminate oil from egg yolk (and glue) with our equipment (12 nm resolution in the SWIR range), when applied onto a typical *gesso* layer, mixed with different pigments, we prepared reference samples applied on a thick layer of *gesso* on a wood panel. Red madder lake, lead white and azurite were prepared with oil or egg yolk. Their SWIR spectra were compared (see Supplementary material for all spectra, Fig S3-5).

In the near infrared range, the underlying *gesso*, traditionally made of gypsum ground in rabbit skin glue, is clearly visible. The most recognisable features, originating from the gypsum, are the well-defined bands at 1446, 1490, and 1535 nm due to the first overtone OH stretch, and the combination band near 1943 nm due to the stretching and bending modes of water. This intense signal of the under-layer, makes the identification of pigments (as already seen for lead white and verdigris) but also binders more difficult.

The signal coming from the red lake reference sample is the easiest to interpret: the raw signal of red lake does not present bands that overlap those of the binders. The characteristic bands of oil, egg and glue can be assigned thanks to the previously cited literature [12-14, 19]. The most characteristic absorptions of the lipid triglycerides molecules are:

- a combination band of antisymmetric / symmetric stretching and bending of the methyl (CH_2) groups that presents itself as a doublet at 2303 nm in oil or at 2309 in egg yolk, and at 2346 nm.

It has to be noted that glue also exhibits lipid features at 2285 and 2350 nm.

- the first overtone of CH_2 stretching that occurs as a doublet at 1723 nm in oil or 1725 nm in egg yolk, and 1755 nm.

In the case of egg yolk and glue, amide bands are present at 2043 nm for glue or 2054 nm for egg yolk.

In the case of our equipment, when comparing the spectra between oil and the egg yolk binder, it appears that the lipid features are not resolved enough to allow their accurate identification

as expected. However the amide band around 2050 nm is clearly present in the case of egg yolk and not in the case of oil (as seen in figure 5c).

In the lead white sample, the same observations can be made with a supplementary limitation on the lipid features due to the presence of a band at 2310 nm broadening the one of the binder.

In the azurite sample, the carbonate doublets at 2285 and 2348 nm are visible; moreover intense bands exist at 1495 and 2033 nm, which makes an accurate interpretation tricky.

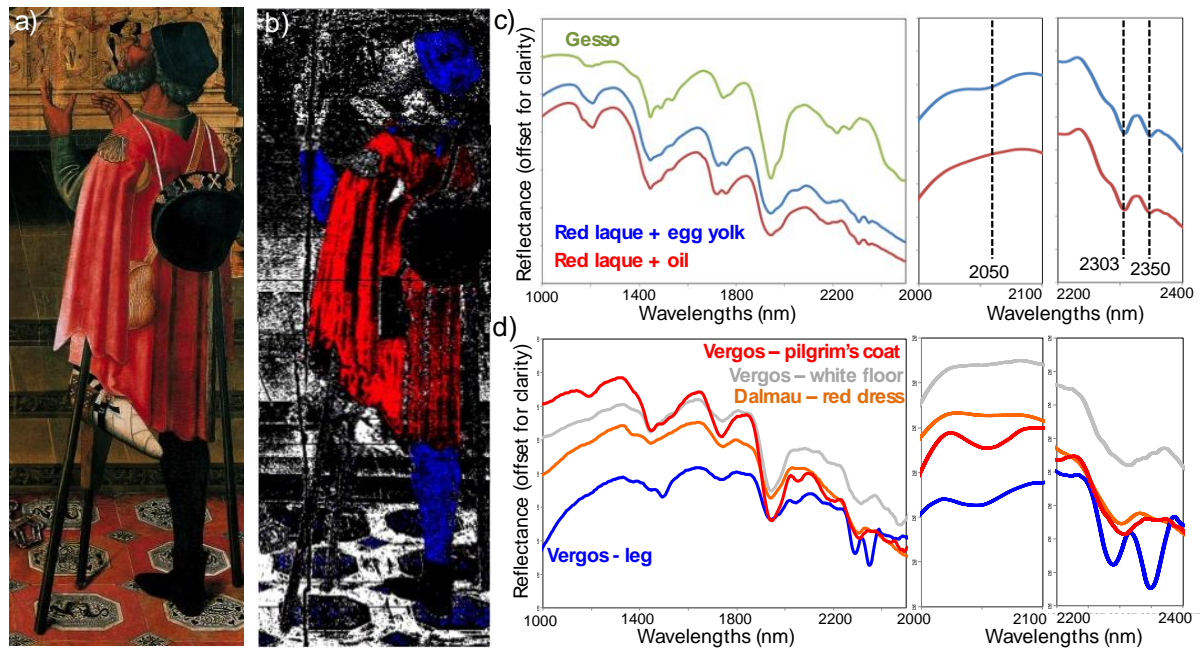


Figure 5: SWIR investigation of a selected zone in *Princess Eudoxia*: a) photograph; b) SAM performed on SWIR data from 2000 to 2100 nm, obtained with pre-defined endmembers from the reference samples: Blue: azurite, Red: red lake + egg, white: lead white + oil (a common threshold has been chosen: 0.01); c) comparison of paint references spectra; d) comparison of spectra taken from both paintings.

We thus focused on the presence of the amide band at 2054 nm to discriminate egg yolk vs. oil in the two Catalan works. As seen in figure 5d, we can confirm the use of oil in the *Madonna* painting, in agreement with the previous analyses of a few micro-cross sections via FTIR microscopy [1]. In *Princess Eudoxia*, different binders were probably used. The lipid features are seen in all colours although the band at 2347 nm is less intense particularly in the case of lead white areas, which exhibit a strong feature around 2310 nm. In contrast, the amide band is not visible in the white areas, but it can be observed in the pilgrim's red mantle indicating the probable presence of egg yolk. A distribution map was obtained using SAM from 2000 to 2100 nm on the SWIR image of the pilgrim (figure 2b). It has to be noted, that the white colour indicating the endmember "lead white + oil", can be obtained when the

pigment is not inducing any signal in the 2000-2100 range, in all areas presenting a signal of good enough intensity (the black areas, made up of carbon black, as well as the gold ones remain black in the SAM image). In the areas containing azurite, strong features overlap the binder's characteristics bands (see Supplementary Information, figure S3), and no binder identification could be achieved.

In the red areas, a possible mixture of egg and oil (emulsion binder) could also have been used but cannot be detected with the present analysis. Such a specific use of egg tempera with red lake is quite surprising, as egg tempera is more usually found in the lighter colour passages or in under layers while oil was used in richer, darker colours or in final glazes [22]: red lake pigments were more typically used with an oil medium to achieve transparency and saturation. Another explanation for the presence of proteinaceous features in the red areas could be the use of a red lake pigment prepared from dyed red wool shearings, a process that can result in the presence of protein in red lake pigment particles [23, 24, 25]. In that case, the observed proteinaceous features in the red areas would not be correlated to a specific binder, whereas the lipidic features would be due to the presence of oil. However it should be borne in mind that the reference sample was prepared using a ratio of ca. 1:1 of madder lake and egg yolk. To provide a more definite conclusion it would be thus interesting to make mixtures of different ratio in order to investigate further the relation between the amount of proteinaceous material and the intensity of the band.

Conclusion

The combination of visible and near infrared hyperspectral imaging, *per se* or combined with complementary non-invasive *in-situ* portable techniques (fluorescence spectrometry - punctual and imaging -, macrophotography, ...) can provide an in-depth understanding of the artist's techniques and intentions. In the present work, it allowed unprecedented analyses of two major 15th century works of art from the National Museum of Catalan Art (MNAC): providing new information on pigments and binders, as well as their distribution maps. Not only the whole palette of the artists could be confirmed but it was also possible to shed new light on the early Renaissance paint practices and the history of the paintings. A few results are highlighted here:

- (1) The origin of the black observed in different degraded places of the two paintings was identified as blackened azurite. It is possible to map the presence of azurite below the altered layer and to reveal the original appearance of the paintings and posterior restorations.

- (2) Distribution images of vermilion, minium and natural organic lakes, obtained from visible hyperspectral imaging on large surfaces, reveal the refinement in modelling the red draperies.
- (3) The analysis carried out with special attention devoted to the characterization of the binding medium, confirms that the *Madonna of the 'Consellers'* by Lluís Dalmau fully uses the novel oil technique, whereas a mixed technique has probably been used in the case of the Vergós panel. This information is particularly valuable at a time of technical innovation, as in the case of Barcelona's painters' workshops at the turn of the 16th century.

Important new possibilities such as the identification of binders, previously inaccessible by in situ techniques, are opening up thanks to the increasing use of the near infrared range. Broadly speaking for the investigation of easel paintings, our study allows to point out (i) the general interest of reflectance hyperspectral imaging; (ii) the usefulness of near infrared spectroscopy and the interest of combining spectroscopies in different energy ranges; (iii) the necessary conditions to fulfill to reach firm conclusions.

Imaging of large parts of the painting provides an efficient and non-destructive mean to extend the conclusions of punctual study of cross sections and to tune them (as shown here by revealing the sophisticated treatment by the painter of light and shadows on draperies).

While in the visible range, only surface pigments are detected, the near-infrared range penetrates deeper, and gives information on the chemical composition of the different layers of the material. This is a strong mean of characterization, valuable from an imaging point of view, evidencing for example, underlying drawings and compositional changes. This richness can also become a weakness, when the signals are overlapping, specially when relatively wide absorption bands are present, hiding other paint components or making their precise identification difficult: problems of spectral interpretation in the case of pigments present in different layers (here lead white) or overlaps of different signals.

Our study allows therefore to highlight common guidelines to get results on such works of art:

- in the near infrared spectral range, reference spectra obtained from pure materials and models must be acquired in the first place (see our supplementary materials) since there is a lack of reference spectra (the existing geological databases are largely incomplete for cultural heritage applications). The need of building pigments and binder's high resolution spectral databases is clear.

- with regard to data evaluation in easel paintings with complex mixtures and superimpositions, the implementation of the common procedures in this field, based on end-

members extracted in semi-automatic mode is not straightforward. It is possible to obtain characteristic images, such as distribution maps of pigments, usually over limited areas using procedures (spectral range, use of derivative data...) that have to be defined for each pigment according to its absorption's characteristics.

Acknowledgements

We thank the support from the Ile-de-France region (DIM Analytics, project IMAPAT) for the acquisition of the hyperspectral cameras, and the French State managed by the National Research Agency under the program Future Investments bearing the reference ANR-16-LCV1-0005-01 (program Labcom Lab4Art). We are grateful to Helen Glanville (LAMS) for proofreading the manuscript and improving its language. We would also like to thank Anne Michelin (CRC) for many interesting discussions on the subject as well as for the acquisition of the reference spectra of verdigris.

References

-
- [1] N. Salvadó, S. Butí, F. Ruiz Quesada, H. Emerich, T. Pradell, Mare de Déu dels Consellers, de Lluís Dalmau, Una nova tècnica per a una obra singular, *Butlletí MNAC* 9 (2008) 43-61.
- [2] Núria Prat i Grau, La tècnica d'execució pictòrica en la pintura sobre taula a Catalunya als segles XV i XVI, PhD thesis, University of Barcelona, 2015.
- [3] M. Alfeld, L. de Viguierie, Recent developments in spectroscopic imaging techniques for historical paintings - A review, *Spectrochim. Acta Part B: Atomic Spectroscopy* 136 (2017) 81-105.
- [4] L. de Viguierie, S. Rochut, M. Alfeld, Ph. Walter, S. Astier, V. Gontero, F. Boulc'h, XRF and reflectance hyperspectral imaging on a 15th century illuminated manuscript: combining imaging and quantitative analysis to understand the artist's technique, *Heritage Science* 6 :11 (2018) 6-11.
- [5] J.K. Delaney, P. Ricciardi, L.D. Glinsman, M. Facini, M. Thoury, M. Palmer, E.R. de la Rie, Use of imaging spectroscopy, fiber optic reflectance spectroscopy and X-ray fluorescence to map and identify pigments in illuminated manuscripts. *Stud. Cons.* 59:2 (2014) 91-101.
- [6] A. Mounier, G. Le Bourdon, C. Aupetit, C. Belin, C., L. Servant, S. Lazare, F. Daniel, Hyperspectral imaging, spectrofluorimetry, FORS and XRF for the non-invasive study of medieval miniatures materials. *Heritage Science* 2(1) (2014) 24.

-
- [7] C. Cucci, J.K. Delaney, M. Picollo Reflectance Hyperspectral Imaging for Investigation of Works of Art: Old Master Paintings and Illuminated Manuscripts. *Acc. Chem. Res.* 49 (2016) 2070–2079.
- [8] F. Daniel, A. Mounier, J. Pérez-Arantegui, C. Pardos, N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, K. Castro, Hyperspectral imaging applied to the analysis of Goya paintings in the Museum of Zaragoza (Spain), *Microchem. J.* 126 (2016), 113–120.
- [9] H. Liang, Advances in multispectral and hyperspectral imaging for archaeology and art conservation. *App. Phys. A* 106(2) (2012) 309–323.
- [10] R. N. Clark, Reflectance Spectra, in : T.J. Ahrens (Ed), *Rock Physics and Phase Relations, A Handbook of Physical Constants*, AGU Reference Shelf 3, 1995, pp. 178-188.
- [11] J.K. Delaney, J.G. Zeibel, M. Thoury, R. Litteton, Visible and Infrared Reflectance Imaging Spectroscopy of Paintings: Pigment Mapping and Improved Infrared Reflectography, *Proc. of SPIE* 7391 (2009) 7391031.
- [12] P. Ricciardi, J.K. Delaney, M. Facini, J.G. Zeibel, M. Picollo, S. Lomax, M. Loew, Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts, *Angew. Chem. Int. Ed.* 51 (2012) 5607 –5610.
- [13] K.A. Dooley, S. Lomax, J.G. Zeibel, C. Miliani, P. Ricciardi, A. Hoenigswald, J.K. Delaney, Mapping of egg yolk and animal skin glue paint binders in Early Renaissance paintings using near infrared reflectance imaging spectroscopy, *The Analyst* 138(17) (2013) 4838–48.
- [14] K.A. Dooley, J. Coddington, J. Krueger, D.M. Conover, M. Loew, J.K. Delaney, Standoff chemical imaging finds evidence for Jackson Pollock’s selective use of alkyd and oil binding media in a famous “drip” painting. *Anal. Methods* 9(1) (2017) 28–37.
- [15] Kremer Pigmente, Madder lake production, <https://www.kremer-pigmente.com/media/pdf/madder-lake-production.pdf>, (accessed 28 August 2019).
- [16] M. Aceto, A. Agostino, G. Fenoglio, P. Baraldi, P. Zannini, C. Hofmann, E. Gamillscheg, First analytical evidences of precious colourants on Mediterranean illuminated manuscripts, *Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy* 95 (2012) 235–245.
- [17] J.K. Delaney, D.M. Conover, K.A. Dooley, L. Glinsman, K. Janssens, M. Loew, Integrated X-ray fluorescence and diffuse visible-to-near-infrared reflectance scanner for standoff elemental and molecular spectroscopic imaging of paints and works on paper, *Heritage Science* 6 (31) (2018) 1-12.
- [18] G.R. Hunt, Spectral signatures of particulate minerals in the visible and near infrared. *Geophysics* 42 (3) (1977) 501–513.
- [19] G.R. Hunt, J.W. Salisbury, Visible and Near Infrared Spectra of Minerals and Rocks. II. Carbonates. *Modern Geology* 2 (1971) 23–30.

-
- [20] N. Salvado, T. Pradell, E. Pantos, M. Z. Papiz, J. Molera, M. Seco and M. Vendrell-Saz . Identification of copper-based green pigments in Jaume Huguet's Gothic altarpieces by Fourier transform infrared microspectroscopy and synchrotron radiation X-ray diffraction. *J. Synchrotron Rad.* 9 (2002) 215-222.
- [21] M. Vagnini, C. Miliani, L. Cartechini, P. Rocchi, B. G. Brunetti, A. Sgamellotti, FT-NIR spectroscopy for non-invasive identification of natural polymers and resins in easel paintings, *Anal. Bioanal Chem.* Chem 395 (2009) 2107–2118.
- [22] C. Higgitt, R. White, Analyses of paint media : new studies of Italian paintings of the fifteenth and sixteenth century, *Nat. Gall. Bulletin* 26 (2005) 88-97.
- [23] J. Kirby, M. Spring, C. Higgitt, The Technology of red lake pigment manufacture :study of the dyestuff substrate, *Nat. Gall. Bulletin* 26 (2005) 71-85.
- [24] J. Kirby, D. Saunders, M. Spring, Proscribed pigments in northern European renaissance paintings and the case of Paris red, in: D. Saunders, J.H. Townsend et S. Woodcock (Eds), *The Object in Context: Crossing Conservation Boundaries. Contributions to the Munich IIC Congress 28 August-1 September 2006, Londres, 2006*, pp. 236-243.
- [25] M. Spring, R. Billinge, D. Peggie and R. Morrison, The technique and materials of two paintings from fifteenth-century Cologne in the National Gallery, London, *Zeitschrift für Kunsttechnologie und Konservierung, Die Sprache des Materials* 26 :1 (2012) 88–99.