

# UV fluorescence of the binders used in the gilding on medieval wall paintings

## *UV Fluorescence of the Binding Media Used in Gilding of Mediaeval Mural Paintings*

Aurélie Mounier \*, Laure Dayet \*, Floréal Daniel \* and Colette Belin \*\*

**Summary :** The paintings in the chapel of the former abbey house in Moissac were examined in situ under UV lighting. The presence of yellow fluorescences on the halos of certain figures has been shown to be an indicator of the existence of an old gilding. Fluorescences of this type, characteristic of an organic binder, have already been observed in other sites where traces of gilding are also present. A study by spectrofluorimetry shows that the fluorescence spectra of the two chemical types of binders most commonly used in the gilding technique are different. To get closer to the state of deterioration of old binders, a study of the evolution of fluorescence after accelerated aging was also carried out.

**Abstract:** *Paintings of the vault of the old abbey home of Moissac were examined using a UV source. The presence of yellow fluorescence on the halos figures is an indicator of the presence of historical gilding. Fluorescence of this type, characteristic of an organic binder, was already observed in other sites where traces of gilding are also present. A spectrofluorimetric study shows that the fluorescence spectra of the two chemical types of binders most usually used in the technique of gilding are different. To better understand the condition of aged binders, a study of the fluorescence evolution following accelerated aging was also carried out.*

**Key words:** UV fluorescences, lipid and protein binders, gilding, medieval wall paintings.

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## 1. INTRODUCTION

It is wrong to consider medieval decor, and in particular mural painting, one of its most characteristic expressions, as an austere art and entirely subject to the rigor of fresco technique. In the Romanesque period, the paintings were enhanced with metallic decorations and glass inlays to give more volume and relief and add color, reflections and shine. We

Today, most of the time, these decorations have been lost and only the layer underlying the metal sheet remains visible, the one which allowed the metal to adhere. This is why the study of gilding processes is particularly interesting from a historical point of view, because of the criteria not only aesthetic but also symbolic and prestige which are at the origin of the realization of the gilded decorations. Recently in many sites paintings dated to the xi<sup>e</sup> to the xiv<sup>e</sup> century, traces of old gilding (gold,

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silver or tin) were brought to light (Mounier *et al.*, 2009a). They are generally located in areas with a strong symbolic charge: on the halos of important figures (evangelists, Christ, musician angels). This is the case with the paintings in the chapel of the former abbey house of Moissac (Tarn-et-Garonne). They are also found on secondary decorative motifs: the stars which dot the backdrop of the decorations (south apse of the Saint-Nicolas church in Nogaro, Gers) or the florets and fleur-de-lys on the portal of the Saint-Etienne cathedral in Cahors (Lot) (Czerniak *et al.*, 2007).

On the same painting, various gilding techniques can coexist. We find the description in ancient treatises (Pliny the Elder (1<sup>er</sup> century), Théophile (12<sup>e</sup> century), Cennino Cennini (14<sup>e</sup> century), Watin, (18<sup>e</sup> century), etc.). On reading these "technical manuals" we see that from antiquity to the 18<sup>e</sup> century, the methods of application of metallic decorations have undergone few modifications. There are two main techniques which have variations and which will be considered here:

- *Gilding in tempera*. To make the metal sheet adhere, it requires the use of an organic binder such as protein glue (skin glue, nerve glue, bone glue, etc.) or gum arabic.

- *The gilding with the mixture*. It requires the use of a lipid binder of the linseed oil type, associated with white lead, for example, for its siccative power. The physico-chemical analyzes carried out show that the mixing technique is the most common (Katsibiri, 2004; Toniolo *et al.*, 1998, Bonaduce, 2006).

The metal decorations thus affixed dry, using an organic binder, exhibit greater fragility and less good conservation. Only a few traces of these metallic decorations often remain because their method of application makes them sensitive to the many factors of degradation, in particular environmental factors, to which they have been subjected over the centuries. Most often, only the residues of organic binders which served to adhere the metal foil remain. It is by their detection that it is possible for us today to locate the location of an old gilding. It is, for example, thanks to the yellow fluorescence caused by illumination under a UV lamp (fig. 1) that traces of gilding have recently been discovered in certain murals in southwestern France (Mounier

*et al.*, 2009a).

Regarding metals, gold, tin, silver have been used (Nadolny, 2006). Pewter appears to be the most economical and can be used under gold or coated with a yellow varnish to imitate gold. The choice of tin instead of silver is explained by its better conservation qualities (Mounier *et al.*, 2009b).



Figure 1: (See color plate) Yellow fluorescence obtained under UV thanks to a multispectral camera on the halo of one of the characters in the wall paintings of the vault of the chapel of the old abbey dwelling of Moissac (12<sup>e</sup> century Tarn-et-Garonne). The bluish appearance of the image corresponds to the reflection of ultraviolet light by the support and not to fluorescence.

Figure 1: (See color plate) Yellow fluorescence obtained under UV with a multispectral camera on the halo of one of the characters on the mural paintings of the chapel vault of the ancient abbey home in Moissac (12<sup>th</sup> c., Tarn-et-Garonne). The bluish aspect of the image corresponds to the ultraviolet light reflexion by the support and not to a fluorescence.

From a chemical point of view, the binders used in painting are therefore of four types: protein, lipid, polysaccharide, or a mixture of lipids / proteins. The most widely used in gilding are the first two: protein binders, such as bone glue or nerve glue, more particularly made up of collagen molecules and derivatives of this protein. Other types of protein glues exist, in particular casein or egg white; Lipid binders, drying oils are triglycerides, that is to say esters of glycerol (a triple alcohol) and fatty acids (long carbon chain acids) (Masschelein-Kleiner, 1992; Perego, 2005).

Analyzes made on samples of linseed oil show that the fresh oil produces a weak fluorescence signal, with a maximum wavelength close to 470- 480 nm (De la Rie, 1982b; Chrystoulakis, 1989). As it dries, the fluorescence intensity tends to increase when the oil is placed in the dark or heated to 100 ° C, and the maximum wavelength becomes greater than 500 nm (De la Rie, 1982b; Mallégo *et al.*, 2001). The emission wavelength of proteins seems to always be less than

470 nm (Larson *et al.*, 1991; Nevin *et al.*, 2006; Nevin *et al.*, 2007). Aged egg yolk (prepared in 1937) has a higher fluorescence maximum, centered around 580 nm (Larson *et al.*, 1991). The changes observed in the maximum wavelength after different drying times (3 months, 4 months or 1 year) are not very marked (Nevin and Anglos, 2006; Nevin *et al.*, 2006; Nevin *et al.*, 2007). The work carried out in this area is recent (Thoury *et al.*, 2007; Nevin *et al.*, 2008). They deal with the consequences of chemical alterations in binders on fluorescence emission. The results allow, for example, to identify varnishes used in restoration by comparing the UV fluorescence spectrum with that of known and artificially aged varnishes (Thoury *et al.*, 2007). Another study was carried out in order to differentiate between the protein binders used in painting (egg, egg white and egg yolk, milk and casein) as well as collagen-based glues (rabbit skin, bone, parchment and fish paste [Nevin *et al.*, 2008]).

In light of the results already published and by comparison with our experience on the exam *in situ* metal decorations in medieval wall paintings, it seemed interesting to conduct a study, the objectives of which are essentially methodological, about the fluorescence of the different chemical families of binders used in gilding techniques and the influence artificial aging on their fluorescence properties in order to answer the following questions:

Can we by UV observation *in situ*, to find formerly golden areas thanks to the residual binder? Can the color of fluorescence give us unambiguous information about the gilding technique used?

The identification and analysis of gilding on a painting provides important information. For the art historian, it allows the different elements of iconography to be hierarchized. For the restorer, knowledge of the nature of the materials used (gold or silver leaf, glued with linseed oil, wax or animal glue) guides his choices in the treatments and products to be applied for the preservation of these decorations.

## 2. EXPERIMENTAL

### Samples

Samples of pure binders were deposited in the form of films (on glass slides). Table 1 summarizes all the samples studied (a choice of nine types of binders among the most used in medieval times for the production of gilding).

The pure binders were purchased commercially. Bone glue (bone glue in beads), nerve glue (nerve glue in grains), casein, crude arabic gum and walnut oil were supplied by the company Okhra (Roussillon).

	Binders	$\lambda$ max (bibliography) in nm	Our benchmark binders and supplier	$\lambda$ max (nm) measured
Lipids	Linseed oil	540 (Chryssoulakis <i>et al.</i> , 1989; Larson <i>et al.</i> , 1991)	Lefranc et Bourgeois clarified linseed oil	545
	Egg yolk		Nut oil Okhra 555	526
Protein	Egg white	420-440 (Nevin <i>et al.</i> , 2006; 2007; 2008)	Egg white	433
	Protein glues	400-475 (Chryssoulakis <i>et al.</i> , 1989; Nevin <i>et al.</i> , 2006; 2007; 2008)	Bone glue Okhra Okhra grain nerve glue	435 436
	Casein	435 (Larson <i>et al.</i> , 1991; Nevin <i>et al.</i> , 2006)	Casein Okhra	456
Carbohydrates	Gum arabic	451 (Larson <i>et al.</i> , 1991)	Gum arabic Okhra	439

Table 1: Maximum wavelength given by the fluorimetry analyzes on the pure binders. It is observed that the maximum emission wavelength for lipids is greater than 500 nm and for proteins, less than 450 nm.

Table 1: Maximum wavelength given by fluorimetric analyzes on pure binders. It is noted that the maximum emission wavelength for the lipids is higher than 500 nm and for the proteins lower than 450 nm.

Linseed oil (clarified linseed oil) comes from the company Lefranc et Bourgeois (Le Mans).

A first series of films was left to dry. The “drying” of the oils corresponds to crosslinking and takes more time than protein binders, which is why they were left to age naturally for two years. Four series of pure binders on a glass slide were prepared. Accelerated aging of these binders was carried out according to two different protocols (thermohygro-metric [V1] or under UV [V2]) which will be described later. Unaged samples are coded V0.

## Methods

### UV fluorescence

The experimental study of the fluorescence of organic binders as a function of their chemical nature and their state of degradation is carried out using a laboratory spectrofluorimeter SPEX Fluorolog, model 212 which consists of a xenon arc source, of 450W, giving continuous polychromatic radiation, of a double monochromator made up of flat arrays for excitation, of a sample holder compartment, of a second double monochromator with arrays for emission, of a photomultiplier. The chosen acquisition parameters are as follows: angle of

22.5 ° between the incident beam and the detector; 366 nm exciter, constant excitation flux mode. The slit width is 2.2 mm, which corresponds to a pass band of 4 nm, for a step of 0.5 nm and an integration time of 0.5 seconds. A corrective function has been applied to the spectra obtained, which makes it possible to overcome the constraints linked to the instrumentation. The calibration is carried out with a fluorescent substance (Rhodamine).

The choice of operating conditions was determined by the need to compare the information obtained by other means of examining the fluorescence of the binders:

- the examination *in situ* produced using an ARTIST (Art Innovation) multispectral camera ( $\lambda = 365$  nm). The UV source is a mercury lamp with UV irradiation between 3000 and 90,000  $\mu\text{W} / \text{cm}^2$  which depends on the working distance.

- a UV source mounted on an optical microscope allowing the examination of samples and, in particular, their stratigraphic section. The Exfo X-Cite series 120PC source is a mercury lamp. The excitation filter selects a UV band from 360 to 370nm and another filter with a wavelength less than 400nm eliminates the light emitted by the sample.

For implementation, various parameters must be taken into account and must be as close as possible to compare and explain the results:

- at)  $\lambda$  excitation: The UV source ( $\lambda = 365$  nm) used *in situ* in combination with the multispectral camera is comparable to that of the spectrofluorimeter (362-366 nm) and to that coupled to an optical microscope (360-370 nm).

- b) Zone analyzed: it varies enormously from one device to another: 0.8 x 2 mm for the spectrofluorimeter; ~ 50  $\text{cm}^2$

for the multispectral camera and of the order of the micrometer under the microscope. The analysis area must be considered because depending on the method used, we do not work on the same scale. For the use of the data will be taken into account

ration the wavelength at maximum intensity ( $\lambda_{\text{max}}$ ) and the colour. The  $\lambda_{\text{max}}$ , is a quantifiable trait very often used to compare fluorescence spectra with each other.

The wavelengths corresponding to the maximum intensity were determined for each binder, as well as the corresponding color domain (Tables 1 and 2).

### Artificial aging

1- The thermo-hygro-metric aging of the samples (on glass slides) was carried out in a climatic chamber (Vötsch VC 4018). The protocol used includes eight-hour cycles that include four 90-minute phases, with 30-minute rises and falls between each cycle according to a protocol used for accelerated pigment aging (Aze, 2005). The different phases and the temperature and relative humidity conditions followed in this protocol are as follows:

	L *	a*	b *
<b>Lipids</b>			
Linseed oil	93.2	29.7	28.1
Nut oil	88.5	37.2	7.5
Egg yolk	85.9	44.0	60.3
Mixed			
Whole egg	51.4	- 0.2	- 55.0
<b>Protein</b>			
Egg white	50.7	- 30.7	- 65.8
Bone glue	62.8	- 37.9	- 56.8
Nerve glue	57.8	- 2.5	- 62.7
Casein	48.6	- 1.3	- 45.5

Table 2: Chromatic coordinates determined from the UV fluorescence spectrum of the various pure binders.

Table 2: Given chromatics coordinates from the UV fluorescence spectrum of the various pure binders.

- a phase of high humidity: temperature (T) of 18 ° C and relative humidity (RH) of 85%

- a low temperature phase: T = -10 ° C, RH = 0%

- a dry heat phase: T = 40 ° C, RH = 25%

- a humid heat phase: T = 30 ° C, RH = 60% This eight-hour cycle was repeated 90 times for a total duration of four weeks.

2- Artificial aging by exposure to UV radiations was carried out in an enclosure which allows the samples to be irradiated with UV B of wavelength 313 nm and maintains them at a constant temperature of 45 ° C ( QUV Accelerated Weathering Tester). The source irradiance is 0.71 W / m<sup>2</sup> when the samples are located at the distance of 4.5 cm. The UV exposure lasted for a total of 400 hours, or about 17 days.

### 3. RESULTS

#### $\lambda_{max}$ fluorescence emission from binders before aging

Certain limitations of the method must be taken into account. Some pigments are fluorescence inhibitors (ochres, in particular), others on the contrary provide additional fluorescence. This is why it is difficult to work on mixtures. The fluorescence of the support must also be taken into account. Comparison of the fluorescence of the binders on glass slides and on limestone shows that the same results are not observed.

Limestone has its own fluorescence emission (pink violet) which varies according to its water content. It can be thought that the fluorescence of the support has an influence on the final emitted fluorescence observed.

According to the bibliography cited above, dry oils have a  $\lambda_{max}$  > 500 nm, proteins and carbohydrates have a  $\lambda$  < 450 nm, which is confirmed by our results (table 1) obtained on protein glues, gum arabic and dry oils. We also conducted our study on eggs. The part richest in lipids (egg yolk) has a  $\lambda_{max}$  > 500 nm, the richest in protein (egg white) is less than 450 nm.

Two groups among the unaged binders stand out (Table 1):

- Protein binders (casein, glues and egg white), gum arabic and walnut oil fluoresce in blue-purple, with a wavelength between 430 and 456 nm. The whole egg can also be placed in this group, with a maximum emission wavelength of 423 nm, in the violet range.

- Linseed oil and egg yolk have a  $\lambda_{max}$  greater than 500 nm, ie in the green and green-yellow range.

The fluorescence emission of egg yolk is known to be due to the presence of the aromatic amino acids of proteins, phospholipids and derivatives. Proteins contain three amino acids that contribute to UV fluorescence: tyrosine, phenylalanine and tryptophane. The observation of the fluorescence emission of the egg yolk excited at 436 nm shows, for example, a fluorescence maximum between 520 and 570 nm (Gaspard *et al.*, 2008). In our study, the egg yolk excited at 366 nm shows a maximum fluorescence emission centered at 555 nm, which goes in the same direction as the bibliography (figure 2). These results are consistent with what we find in the literature, especially for proteins, except however for egg yolk (Castillejo *et al.*, 2002). However, we have found that for the latter, the thickness of the film has an influence on the relative intensity of the different bands of the spectrum. Further study would be needed to better understand the differences between our results and those presented in previous studies.

Fluorimetry is therefore a reliable means of discriminating between the major families of binders. Proteins and lipids do not have the same fluorescence emission spectrum shape and their maximum wavelengths are different.

#### Emission spectrum match fluorescence in chromatic coordinates

Insofar as we seek to demonstrate color variations, a \* b \* chromaticity diagrams were produced for all the binders. The advantage

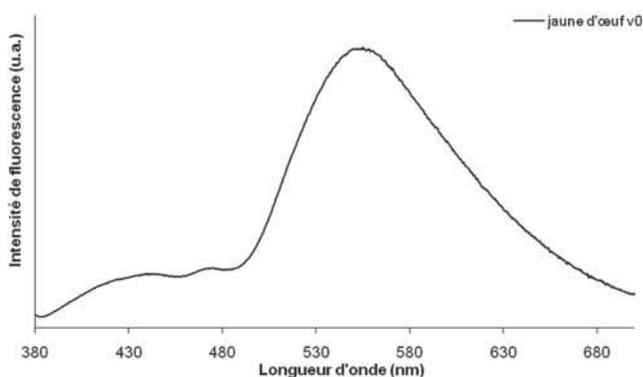


Figure 2: Fluorescence emission spectrum of egg yolk before aging. The maximum fluorescence is centered around 555 nm.

Figure 2: Fluorescence spectrum emission of the egg yolk before aging. The maximum fluorescence is about 555 nm.

of these diagrams is to take into account the entire spectrum<sup>1</sup>. They seem more appropriate than the wavelength to define what we see visually and can give the chromatic range of fluorescence. Within these diagrams, samples are distinguished by a positive (yellow) or negative (blue)  $b^*$  value, with  $a^*$  always being negative (green).

If we transpose the fluorescence emission spectra into  $L^* a^* b^*$  chromatic coordinates, two main families can be distinguished: oils (in the yellow-green quarter) and proteins (in the green-blue quarter) (figure 3).

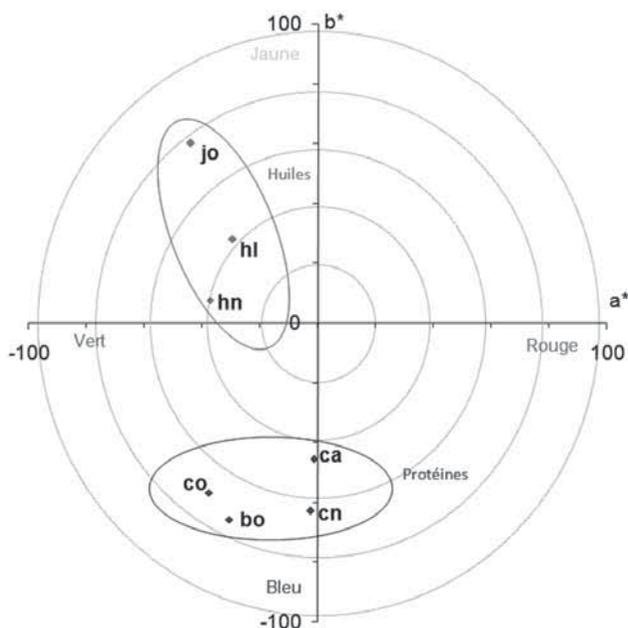


Figure 3: (See color plate) Chromaticity diagram of the maximum wavelengths of the different binders studied. The oils (jo: egg yolk; hl: linseed oil; hn: walnut oil) fluoresce with a  $\lambda$  max in yellow-green. Proteins (ca: casein; cn: nerve glue; co: bone glue; bo: egg white) with a  $\lambda$  max in the blue.

Figure 3: (See color plate) Chromaticity diagram of maxima wavelengths of the various studied binders. The oils (jo: egg yolk; hl: linseed oil; hn: walnut oil) give a fluorescence with a  $\lambda$  max in yellow-green. The proteins (ca: casein; cn: nerve glue; co: bone glue; bo: egg white) with a  $\lambda$  max in blue.

1. The fluorescence spectrum data has been reported in the logi-spectra processing sky of a Minolta CS-S1W spectrophotometer, which from the entire spectrum provides the corresponding chromatic coordinates ( $L^*$ ,  $a^*$ ,  $b^*$  or Xxy).

## Influence of aging on the emission and fluorescence color of binders

Overall, aging has very little effects for glues and arabic gum,  $\lambda_{\max}$  not varying by more than 20 nm (Table 3). For white of egg, egg and casein, there is a shift in the maximum wavelength towards the long wavelengths and a widening of the emission band for certain aging protocols. For all these binders, the maximum wavelength is always less than 500 nm, and included in the purplish blue to blue-green ranges.

Light aging has the greatest effect on maximum wavelength shift as well as color (Table 4). Thermo-hygrometric aging seems to have little effect.  $L^*$  has not been taken into account because it depends on the thickness of the adhesive film. This was not constant and uniform between the test pieces. The chromatic coordinates  $a^*$  and  $b^*$  are in relation with the color of the fluorescence emission observed (thus with the data of the image). It is these parameters that we have chosen to exploit. The general trend shows a shift in chromatic coordinates after aging. Bone glue appears to be less susceptible to these types of aging. Casein is the protein that undergoes the most evolution.

	Not aged (V0)	Aged T, HR (V1)	Aged light (V2)
Lipids			
Linseed oil	545	-	-
Nut oil	526	-	-
Egg yolk	555	-	-
Protein			
Egg white	433	434	470
Bone glue	435	450	459
Nerve glue	436	434	451
Casein	456	496	469
Carbohydrates			
Macaw gum goat	439	450	-

Table 3: Maximum fluorescence wavelengths of fresh binders (V0) on a glass slide. Maximum emission wavelengths of binders on aged glass slide (V1: Thermo-hygrometric aging; V2: UV aging).

Table 3: Maximum wavelength fluorescence of the pure binders (V0) on glass slide. Maximum emission wavelength of binders on glass slide aged (V1: Hygro-thermal aging; V2: UV light aging).

	V0			V1 (Vacc Temp)			V2 (Vacc Light)		
	L *	a*	b *	L *	a*	b *	L *	a*	b *
Bone glue	62.8	- 37.9	- 56.8	61.7	- 36.5	- 58.3	67.0	- 38.4	- 49.5
Glue nerves	57.8	- 2.5	- 62.7	61.6	- 6.6	- 57.6	68.5	- 18.4	- 48.6
Casein	48.6	- 1.3	- 45.5	84.2	35.9	20.0	77.8	- 35.3	- 32.4

Table 4: Chromatic coordinates determined from the UV fluorescence spectrum of three control proteins (bone glue, nerve glue and casein), aged by temperature and relative humidity and in light.

Table 4: Chromatics coordinates determined from the UV fluorescence spectrum of three proteins (bone glue, nerve glue and casein) references, aged by temperature and relative humidity and by UV light.

It seems that the aging protocols, and therefore the environmental factors that are varied, more or less favor the fluorescence of one or the other of the fluorescent compounds. The influence of film thickness should not be overlooked either.<sup>2</sup>

No significant effect of thermal aging was observed on the maximum wavelength of fluorescence emission from proteins, except perhaps a slight shift when they were subjected to light aging (figure 5).

As regards the oils, according to the bibliography, one expects modifications which have, moreover, been observed by FTIR (with the disappearance of the CH bands, which corresponds to a crosslinking<sup>3</sup>). Artificial aging should cause the maximum wavelength to shift to higher values (bathochrome effect).

### Observation of the degradation of binders by infrared spectrometry

For all the binders, fresh and aged, infrared absorption spectra were recorded, in order to study the degradation of the binders.

On the spectra of the glues in particular, one observes changes on the bands towards  $3290\text{--}3270\text{ cm}^{-1}$  ( $\nu$  NH), and those around  $1540\text{--}1530\text{ cm}^{-1}$  ( $\delta$  NH and  $\nu$  CN). These bands are characteristic of collagen. The shift of these bands seems to indicate a further denaturation of the collagen and its derivatives, in particular a disorganization of their structure (Rabotyagova *et al.*, 2008; Wisniewski *et al.*, 2007).

Regarding linseed oil, we note changes on the bands around  $2950\text{--}2850\text{ cm}^{-1}$  ( $\nu$  CH) and around  $1750\text{--}1720\text{ cm}^{-1}$  ( $\nu$  C = O). The decrease in intensity of

2. Data not taken into account in this study

3. Phenomenon of oxidation of unsaturated fatty acids in a drying oil leading to the formation of a three-dimensional network.

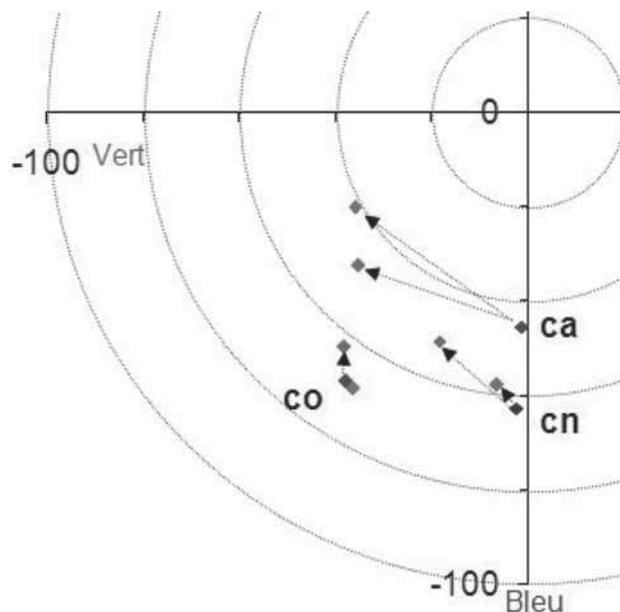


Figure 4: (See color plate) Chromatic diagram showing the evolution of the maximum wavelength after aging. There is a slight shift in the maximum wavelengths of proteins (ca: casein; cn: nerve glue; co: bone glue) from blue to green (bathochrome effect). This is even more marked with aging in the light.

Figure 4: (See color plate) Chromatic diagram showing the maximum wavelength evolution after aging. We notice a weak displacement of the proteins maxima wavelength (ca: casein; cn: nerve glue; co: bone glue) blue towards the green (bathochrome effect). This is even more outstanding with the light aging.

vibration bands  $\nu$  CH correlated with the shift of the vibration band  $\nu$  C = O of  $1740\text{ cm}^{-1}$  approximately at  $1720\text{ cm}^{-1}$ .

(Figure 6) shows us that significant oxidation phenomena have occurred, with no doubt the appearance of new carbonyl groups (C = O) and a gradual disappearance of ester bonds (Mallégol *et al.*, 2000).

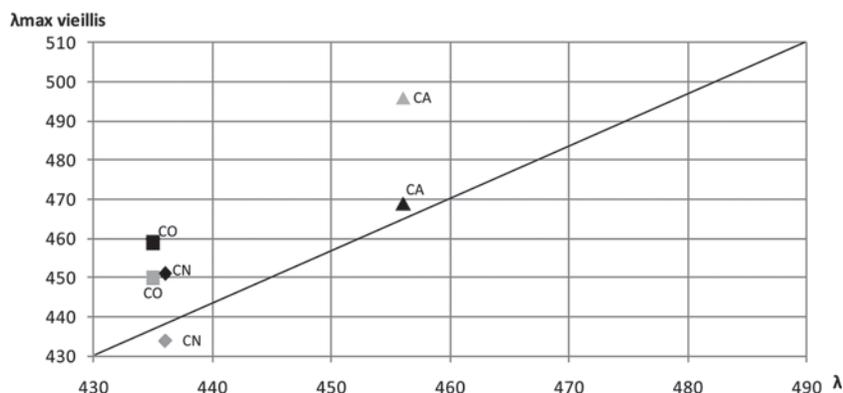


Figure 5: Graph showing the influence of accelerated aging (thermal in light gray and light in black) on the maximum wavelength of three protein binders (nerve glue: CN; bone glue: CO and casein: IT). Above the diagonal, the maximum wavelength increases after aging.

Figure 5: Graphic representing the accelerated aging influence (thermal in light gray and with the light in black) on the maximum wavelength of three protein binders (nerve glue: CN; bone glue: CO and casein: CA). Above the diagonal, the maximum wavelength increases after the aging.

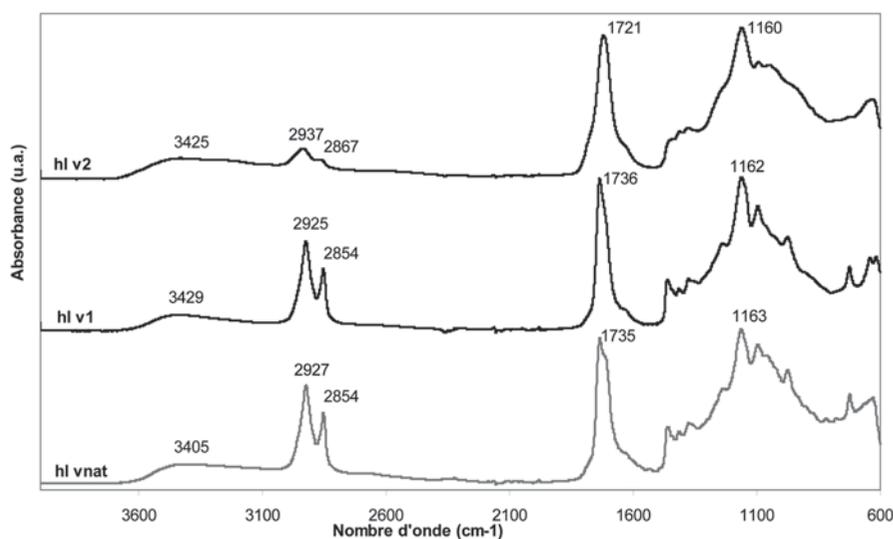


Figure 6: Infrared spectra of linseed oil, reference sample (v0) and aged samples (v1, v2). There are changes to the bands (ν CH) around 2950-2850 cm<sup>-1</sup>

and around 1750-1720 cm<sup>-1</sup> (ν C = O). The decrease in intensity of ν CH correlated with the shift of the vibration band ν C = O of 1740 cm<sup>-1</sup> approx. 1720 cm<sup>-1</sup> indicate oxidation phenomena.

Figure 6: Infrared spectra of the linseed oil, reference sample (v0) and aged samples (v1, v2). We notice modifications on the bands (ν C-H) towards 2950-2850 cm<sup>-1</sup> and towards 1750-1720 cm<sup>-1</sup> (ν C = O). The intensity decrease of ν C-H correlated with the vibration band gap ν C = O of about 1740 cm<sup>-1</sup> to 1720 cm<sup>-1</sup> indicate oxidation phenomena.

#### 4. CONCLUSION

Observation under UV makes it possible, in certain cases, to locate the zones where a metallic decoration, today disappeared or altered, could exist. Fluorescence is specific to the chemical family of the binder which is itself characteristic of the technique. This was verified by spectrofluorimetry. The exam *in situ* Using a multispectral camera, observations under an optical microscope and under UV of stratigraphic sections and analysis by spectrofluorimetry therefore provide complementary information to each other and point in the same direction. After aging, the binders see their maximum wavelength increase. For oil, light aging accelerates the oxidation process and has the greatest effect.

Longer aging can be considered in order to deepen the study of fluorescence and the degradation of binders, especially for oils. The study of mixtures (oil + white lead) is in progress in order to know the effects of siccatives on fluorescence. The association of binders with different pigments (red ochre, cinnabar, azurite) is also an avenue to be exploited since it is assumed that the pigment has a non-negligible role in the flora observed. The study of UV fluorescence of fresh binders and aged binders allowed us to determine groups of binders, taking into account the maximum wavelength on the one hand, and the chromatic coordinates  $a^*$  and  $b^*$  of somewhere else. Both allow fluorescence variations to be observed in a simple and efficient manner. Chromaticity diagrams,

maximum waveform to compare the chromatic domains of fluorescence (blue-green for proteins, egg and gum arabic  $\lambda < 500$  nm; green-yellow for oils  $\lambda > 520$  nm).

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