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## Article

# Ephemeral Orchil in the Lady and the Unicorn Tapestry: Recipe, Experimentation, and Characterisation

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**Abstract:** Spectroscopic techniques were carried out to identify the dyes used on the famous mediaeval Lady and the Unicorn tapestries kept in the Cluny Museum. Among the six tapestries, *La Vue* shows a colour variation between the front, which appears blue, and the back, which appears violet, on the Lady's skirt. In the Middle Ages, it was common for the violet colour to be made with a blue dye bath (woad or indigo) followed by a red bath, which could be madder, cochineal, kermes, or orchil. Since orchil is known to be very unstable to light, its potential use in the original recipe was investigated and a study on this dye was performed. Contactless analyses (hyperspectral imaging in the visible-near-infrared range and UV fluorescence spectroscopy) were carried out on both the tapestry and mock-ups prepared following various mediaeval recipes. The investigation allowed for the identification of woad and orchil on the back of the tapestry, which was preserved from exposure to light. In addition, an ageing study elucidated colour degradation, revealing not only the different responses to light of different dyes but also the effect of specific dye preparations on light resistance. The experiments showed that the longer the maceration, the higher the light resistance of the dye. Furthermore, the red orchil colour fades faster than the woad.

**Keywords:** orchil; contactless and portable methods; light degradation; dyes; tapestry



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## 1. Introduction

The 19th century saw a renewed interest in medieval art and craftsmanship, leading to increased study of European tapestry history, especially the 14th and 15th centuries, known as the “Golden Age” of tapestry [1–4]. Numerous documents from this period provide insights into remarkable French tapestries, for instance, the Apocalypse, commissioned by the Duke of Anjou, and the Lady and the Unicorn [5,6]. While these texts focus on the chronology and the involvement of craftsmen and commissioners, they largely overlook the materials, particularly dyes, which are crucial for historical, social, and economic insights and conservation. Consequently, the analysis of these materials is essential for a comprehensive understanding of artwork.

Recent research into tapestries generally favours the use of non-contact methods for material characterisation. Mordants are detected using X-ray fluorescence (XRF) [7], while dyes are determined through fibre optic reflectance spectroscopy (FORS), hyperspectral imaging, and spectrofluorimetry in various ranges such as UV and visible (VIS) [8–12]. Near-infrared (NIR) is used to determine the type of textile [8,9,13]. However, it is sometimes necessary to take samples to validate hypotheses using methods considered invasive. These include SEM-EDS (scanning electron microscopy with energy dispersive X-ray spectroscopy) for fibre analysis [13], high-performance liquid chromatography with diode array

detection (HPLC-DAD), or mass spectrometry detection (HPLC-MS/MS) for dye identification [8,10–12,14,15] and laser-induced breakdown spectroscopy (LIBS) for mordant detection [14].

The study of the Lady and the Unicorn tapestry, using primarily spectroscopic methods, allows us to characterise both the materials used in its creation and those used during the various restoration campaigns it has undergone. These restorations, numbering twelve, span from the late 19th century to the present day [16]. Few of them provide detailed information on the interventions or the materials used; only recent restorations document and provide reports on the analyses and work carried out. For example, during the 2012 restoration campaign, the Laboratoire de Recherche des Monuments Historiques (LRMH) conducted colourimetric measurements of various sections of the tapestry of the Lady and the Unicorn [17]. That study aimed to track changes in dye appearance on both the front and back surfaces after washing the six tapestries carried out by De Wit Manufacture. Upon examination of the *La Vue* tapestry on the Lady's skirt after cleaning treatment on the recto side, a light blue hue was evident. In contrast, a significant colour difference with a Delta  $E_{2000}^* = 15.0$  in CIEL\*a\*b\* space was observed on the verso side, which was characterised by a purplish tint. This distinction was already observed and documented between 1941 and 1944 by the Atelier Bregère, who restored the tapestry in that campaign and listed all the changes it had undergone since its creation and before its intervention. In the document, it is possible to read about a colour change in the skirt of the Lady from violet to light blue because of action of air and light: «à l'origine, le coloris de cette partie du vêtement était mauve, soutenu par des ombres noires; ce coloris mauve est devenu bleu clair par l'action de l'air et la lumière» [18]. The following question then arose: what dyes and recipes were used to make the Lady's skirt? What makes up this violet colour that has now faded?

In natural dyeing, there are very few dyes that can be used to dye violet. Only shellfish purple (e.g., *Hexaplex trunculus*) and some lichens can be used to obtain a reddish-purple dye. As the use of shellfish purple is very expensive, other techniques have been developed to obtain similar violet shades [19,20]. One of these techniques involves dyeing blue and then red. All the recipes have in common that the first step is to dye with a plant containing indigoid molecules. In Europe, these plants could be woad in the Middle Ages or indigo after the 17th century [19]. The second step is to make a second bath with a red dye [21]. At the time of the Lady and the Unicorn tapestry's manufacture, plants such as madder (*Rubia tinctorum* L.) or insects such as kermes (*Kermes vermilio*), Armenian or Polish cochineal (*Porphyrophora hamelii* and *Porphyrophora polonica*), or lichen-like orchil were employed to dye in red colours [19,22]. Orchil is obtained from different families of lichens. There are sea orchils (*Roccella tinctoria*, *fuciformis* or *phycopsis*) and land orchils (*Ochrolechia parella* or *Lasallia pustulata*) [23,24]. Particular interest in this dye has developed because of its use in a large number of heritage items. It has been used since Antiquity and was rediscovered in the Middle Ages in France in the 14th century [24]. Orchil has been identified on parchments [25,26], illuminations [27,28], and textiles [29,30] from various periods. These studies are often conducted using contactless methods (FORS VIS-NIR, UV fluorimetry) and supplemented by micro-invasive analyses (Raman, MALDI, ICPMS). Furthermore, some studies focus on the nature of the lichens used based on their different chemical characteristics using destructive techniques such as Raman SERS (surface-enhanced Raman scattering) or liquid chromatography accompanied by mass spectrometry detectors (HPLC-MS/MS) [31,32]. Furthermore, light degradation experiments were performed to observe and study ageing products possibly responsible for the variation in signals collected on degraded objects under study [27,29,33].

As orchil is known for its low resistance to light compared with other dyes [20], this study aimed to identify its potential use in the original recipe for the violet used in the Lady and the Unicorn tapestry (the Lady's skirt of *La Vue*) and to deepen our understanding of the physico-chemical properties of this dye. For this reason, various mock-ups of orchil were made in the Myrobolan studio using different protocols to complete our database that comprises different dyes used in tapestry manufacture. Absorbance spectra were

then collected using a contactless methodology consisting of hyperspectral imaging in the visible-near-infrared range and UV fluorescence spectroscopy and compared with the tapestry results. Furthermore, HPLC combined with a PDA detector (photodiode array) was used on a sample collected from the tapestry. Finally, a methodology for degrading samples under natural light was set to observe the loss of colours and the influence of the fading on spectra.

## 2. Materials and Methods

### 2.1. Creation of the Colour Charts

All the samples were dyed on a canvas fabric made from wool from Belgian and French sheep (Texel and Suffolk breeds 50% + *Est à laine merinos* breeds 50%), washed in Belgium and processed (spinning, weaving, fulling) in Germany.

#### 2.1.1. Orchil

The lichen used in this study was *Lasallia Pustulata*, hand-picked in southeast France by a lichen specialist. The literature on orchil production provides varying information regarding the recipes [22,23,34,35]. The challenge was with the proportions between products, such as the ratio of lichen to ammonia solution, the percentage of ammonia in the solution, maceration time, maceration conditions, the ratio of fibre weight to be dyed to the initial weight of lichen, and the methodologies employed in dyeing.

The orchil preparation initiates with maceration in an ammonia solution. To observe the influence of maceration, the samples were dyed starting from the 17th day of maceration, with a new sample dyed every 3 days thereafter. The last sample was dyed after 87 days of maceration. Twenty-five pots were prepared, each containing 5 g of lichen powder in 100 mL of ammonia solution, composed of 1/3 ammonia at 13% concentration and 2/3 tap water at pH 5.5. The resulting solution was observed to have a pH of 11.5, which was maintained throughout the experimental procedure by adding 13% ammonia from the 38th day of the experiment. The container was opened for approximately 30 min daily to agitate the liquid.

Once the desired maceration was obtained, the contents of the pot were diluted in 500 mL of water and heated to 30 °C. The wool was introduced, and the dye bath was gradually raised to 75 °C. Once this temperature was reached, it was maintained for 1 h and 30 min. Subsequently, the sample was rinsed with clear water and naturally dried. The following day, the process was repeated on the same sample and in the same dye bath to achieve a superposition and intensify the colour. It was repeated a third time on the subsequent day to obtain a third overlay.

#### 2.1.2. Woad Blue

This study employed woad obtained from a supplier in the Tarn region of southwestern France, who produced a woad indigo pigment paste. A 5 L vat was established for sampling. The formulation comprised 200 g of woad paste, analysed to contain 12% indigotin, 150 g of fructose as the reducing agent, and approximately 80 g of lime. The vat was prepared 3 days before the dyeing process.

#### 2.1.3. Violets

To obtain the violet-dyed samples with orchil, the previously prepared woad samples were introduced, instead of the natural wool, into the dye bath containing the orchil-based solution described in Section 2.1.1. Similarly, the cochineal-, kermes-, and madder-based violet samples were dyed over the previously dyed woad samples. The ingredients used to prepare the 3 dye baths for these red dyes are listed in Table 1. These three samples were prepared by our research team in collaboration with the Myrobolan studio during a previous study of Aubusson tapestries [7].

**Table 1.** The ingredients used to prepare the 3 dye baths for cochineal, madder, and kermes on woad (for 100 g of wool).

Sample	1st Bath Dye	Mordant	2nd Bath Dye
Woad and cochineal	Woad	15 g Alum 9 g White tartar	6 g Cochineal
Woad and madder	Woad	31 g Alum 6 g White tartar	50 g Madder
Woad and kermes	Woad	20 g Alum 10 g Red tartar	71.5 g Kermes

## 2.2. *The Lady and the Unicorn Tapestry: La Vue*

The tapestry *La Vue* (Figure 1) was chosen for this study because it was the only one cited by Atelier Bregère to contain a violet hue. It features a simple composition in the form of a pyramid. In the centre, a seated Lady contemplates the unicorn on her lap, stroking it with her left hand. Her right hand holds a mirror in which the unicorn is looking. The lion carrying the coat of arms to the Lady's right seems to be watching over the scene to ensure that the Lady is not disturbed [6]. This is the smallest tapestry in the set (314 × 325 cm). The tapestry underwent numerous restorations since its purchase by the Musée de Cluny in 1881 [36]. This research study focused on a specific section of the tapestry—the Lady's skirt (as depicted in Figure 1)—because of its notable fading, making it an intriguing subject for analysis.



**Figure 1.** Photograph of *La Vue*—Tapestry the Lady and the Unicorn (314 × 325 cm) © Musée de Cluny. The dotted square indicates the area of interest in this study.

### 2.3. Spectroscopic Measurements

#### 2.3.1. Hyperspectral Imaging Spectroscopy

Spectral data from the mock-ups and the yarn sample collected on the back of the tapestry (1 cm) were acquired using a hyperspectral camera portable (SPECIM), mounted on a 1.30 m rail and operated as a line scanner to capture data. The visible-near-infrared (VNIR) CCD camera (HS-XX-V10E) employed has a spectral resolution of 2.8 nm (FWHM) and a spectral sampling of 0.7 nm, with a pixel size of  $54.7 \mu\text{m}^2$ . This camera constructed a 3-dimensional data cube (1600 pixels  $\times$  X pixels  $\times$  840 bands), where X represents the image width's pixel count, spanning wavelengths from 400 to 1000 nm. Two halogen lamps set at a  $45^\circ$  angle illuminated the samples, and analyses were conducted at a working distance of 70 cm for the mock-ups and 10 cm for the tapestry yarn, with illumination of 2200 lux. A Spectralon fluoropolymer (99% reflectance) covered the detector's entire field of view, serving as a white reference during data acquisition. Additionally, a second acquisition was conducted with the shutter closed to serve as a dark reference, aiding in quantifying electronic noise. These references were pivotal in flattening the field and converting data into reflectance factors.

The front of the tapestry and the spectral data from the degradation study were acquired using a second ultra-portable hyperspectral camera (SPECIM IQ), which covered the visible light and near-infrared (Vis-NIR) spectral range from 400 to 1000 nm, with 204 spectral bands across the entire wavelength range. The spectral resolution (FWHM) was 7 nm. The resolution of the resulting image was  $512 \times 512$  pixels. The camera was positioned on a photographic tripod, and the analyses were conducted at a working distance of approximately 40 cm under diffuse halogen lighting provided by two single lamps of 1000 W. The integration time for the analysis was 10 ms for the mock-ups and 73 ms for the tapestry analysis. A white Spectralon standard was employed for HSI data calibration. Spectra acquisition, storage, and calibration were executed using IDAQ software v.3.62. All the spectra are collected using Envi software v.5.0 and presented in the form of reflectance spectra as well as second derivatives to highlight absorbance maxima.

#### 2.3.2. LED $\mu$ -Spectrofluorimetry (LED $\mu$ SF)

Fluorescence emission spectra were captured utilising an LED $\mu$ SF, a Thorlabs spectrometer (CCS200/M) equipped with an optical fibre ( $\varnothing$  400  $\mu\text{m}$ ) and boasting a spectral range spanning from 200 to 1000 nm. A low-power LED emitting at 375 nm, filtered at 455 nm, served as the UV excitation source. The analysed area of the sample measured approximately 1–2 mm in diameter. The analysis time ranged between 1 s and 12 s. To enhance the signal-to-noise ratio, a background spectrum was recorded and subtracted from each measurement of the sample spectrum. Subsequently, spectral smoothing was applied. The LED $\mu$ SF was operated and controlled via a USB connection to a laptop, featuring a graphical interface developed with Windows Forms using Arduino IDE and MS Visual Studio Express C++ [37]. The instrument was securely mounted on a tripod with micrometric adjustment capabilities, aided by two red lasers to adjust the working distance fixed at 4 cm without any direct contact with the tapestry or the samples. The spectra were collected using Thorlabs software v.2.90.

### 2.4. High-Performance Liquid Chromatography UV–Visible (HPLC–PDA)

The chromatographic analysis was carried out on a 5 mm yarn taken from the reverse of the tapestry in the Lady's skirt. This sample was taken during the 2012 restoration campaign at the Musée de Cluny. The primary objective of characterising these samples was dual-fold. First, to identify the dyes in both the original sections and the restored areas of the tapestry. This served to document the tapestry's history and anticipate potential risks associated with dye bleeding if subjected to washing. The removal of the lining facilitated the sampling process from the back of the tapestry, focusing on areas less exposed to light. Sample selection targeted regions exhibiting a wide spectrum of colours spanning various historical periods (including medieval and subsequent restorations).

The extraction of the dyestuff was carried out using 5 mm of dyed thread in 20  $\mu\text{L}$  of MeOH (Methanol absolute—HPLC supra gradient from Biosolve)/H<sub>2</sub>O/Oxalic acid 0.2 M (99% purity from Sigma Aldrich, St. Louis, MI, USA) (8:2:1) solution, heated for 15 min at 60 °C with sonication and put into Eppendorf PP tubes before being vacuum dried for 12 h. Then, the extracted residue was dissolved in 10  $\mu\text{L}$  of dimethyl sulfoxide (DMSO for spectroscopy 99.9% from Acros organics), for a couple of minutes with sonication at 60 °C. The solution was filtered through 0.2  $\mu\text{m}$  PTFE membrane filters into a glass tube, and 10  $\mu\text{L}$  of this was injected into the chromatographic system [38–40].

The separation was carried out with an HP 1100 system from Agilen Technologies (Walbronn, Germany) consisting of vacuum degasser G1322A, quaternary pump G1311A, autosampler G1329A with thermostat G1330A, thermostated column compartment G1316A, diode array detector G7117C with 10 mm optical path length cell, and ChemStation version C.01.07.SR3 software. The resolution of the diode array detector was less than 1 nm in the range of 190–640 nm. Chromatographic separations were carried out at 30 °C using a Hypersil BDS C-18 3  $\mu\text{m}$  (100  $\times$  2.1 mm) column with guard column 10  $\times$  2.1 mm from Thermo (Runcorn, UK), with an eluent flow rate equal to 0.3 mL·min<sup>-1</sup>. The mobile phase consisted of A: water (for HPLC gradient from Fisher Scientific), B: acetonitrile (ACN gradient grade for HPLC—99.9% purity from Merck), and C: 1% solution of formic acid (FA—99% purity from Biosolve) in water. They were applied in a gradient mode as follows: A: 85%, B: 5%, C: 10%, linear gradient in 41 min to A: 30%, B: 60%, C: 10%, plus 1 min constant A: 30%, B: 60%, C: 10%, before returning to initial conditions.

### 2.5. Degradation by Natural Light

Natural degradation was achieved by placing the mock-up samples in a south-facing window for 1 month during March 2024. Temperature, relative humidity, and the number of lux received by the samples were measured twice a week around midnight (22 < T° (C°) < 36, 19 < RH (%) < 47 and 4.5 < Klux < 49, respectively). Colour and spectral measurements were taken before exposure and after 1, 2, 3, and 4 weeks using the SPECIM IQ hyper-spectral camera and the UV  $\mu$ -spectrofluorimeter (described in Sections 2.3.1 and 2.3.2, respectively) and the spectrophotometer Konica Minolta CM 2600d. The spectrophotometer was used to investigate the chromatic variations (in the CIEL\*a\*b\* space) that occurred during ageing. Measurements were conducted with an investigation area of 3 mm in diameter in SCI (specular component included) mode, using a standard illuminant of D65 and a CIE 1964 10° standard observer. The spectrophotometer registered the average of three measurements taken simultaneously. The recorded data were processed using Spectra Magic NX software v.3.31. The Delta E 2000 formula ( $\Delta E_{2000}^*$ ) was utilised to calculate the colour differences observed after degradation [41].

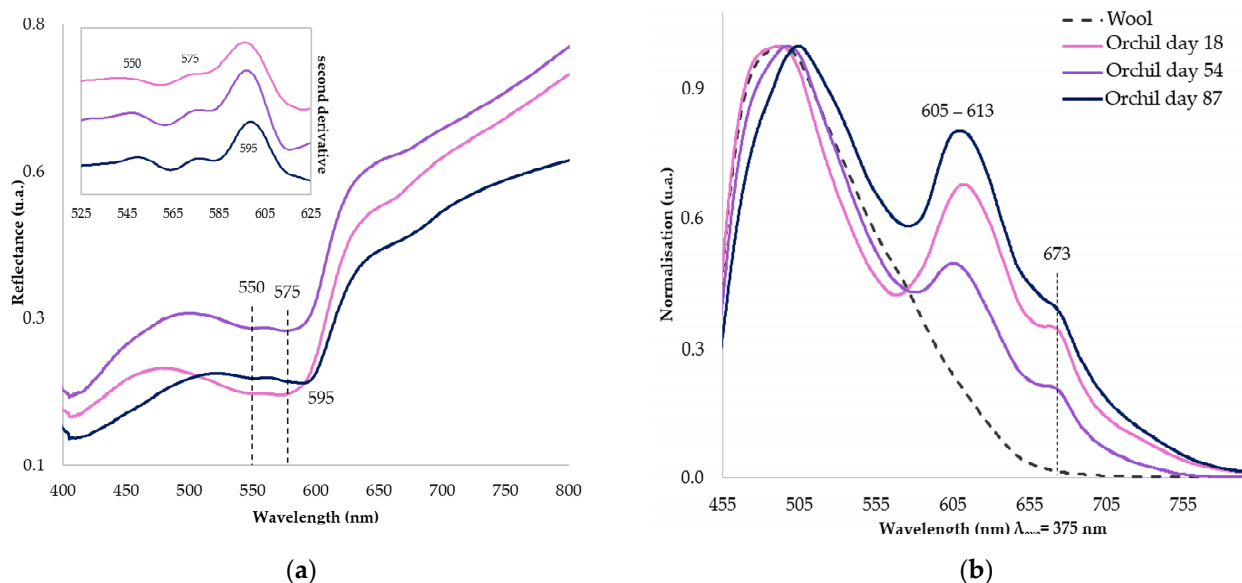
## 3. Results and Discussion

### 3.1. Characterisation of the Spectral Features of Orchil

The orchil-based samples, taken after different days of maceration, were analysed with spectroscopic methods. The achieved spectra display significant similarities. For example, Figure 2a shows the reflectance spectra of samples taken on days 18, 54, and 87 of maceration, which were selected to represent the results obtained at the beginning, middle, and end of the experiment. All three spectra show one absorbance band at around 550 nm. Another band at 575 nm is observed in the first and second samples, while it appears slightly shifted towards higher wavelengths (595 nm) on day 87 of maceration.

These absorption bands were further confirmed with a more precise visualisation through the second derivative spectra (graph at top left of Figure 2a). The first band of maxima for all samples corresponds to the value observed in the absorption spectrum (550 nm), while the second band, which is different in the absorption spectrum, appears to be split into two bands (575 and 595 nm for the three spectra). The appearance of these two bands is explained by the presence of a very broad absorption band in the reflectance spectrum. When a sample has a very broad absorption band, as in this case, it is preferable

to refer to the corresponding inflexion point, which, in this case, is at 610 nm for all the samples. These findings agreed with the data in the literature [25,27,28,42] and suggested that the rest period before the dyeing does not influence the spectroscopic signal.

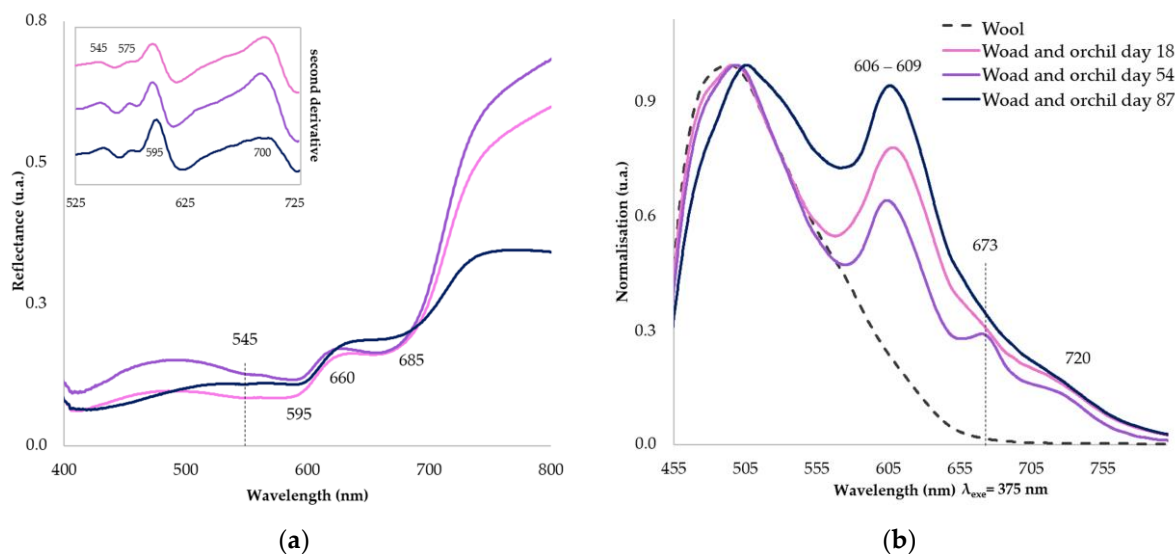


**Figure 2.** (a) Reflectance spectra of orchil samples dyed after 18, 54, and 87 days of maceration. The upper left panel shows the second derivative of these samples as a function of wavelength. (b) Fluorescence emission spectra of the same three orchil samples normalised to the natural wool signal (dotted line).

The fluorescence emission spectra of the same three samples confirmed the assumption that the maceration time has no effect on the spectroscopic signal of the samples, as shown in Figure 2b, where all spectra are normalised to the textile signal. The main emission band of orchil is observed at around 610 nm, slightly shifting from what is reported in the literature [25,28,42]. This shift towards shorter wavelengths can be explained by the hypsochromic phenomenon, which is related to the concentration of the dye in relation to the textile and the fluorescence of wool [7]. The application of the Kubelka–Munk equation might help correct the fluorescence emission spectra by cancelling the self-absorption of the dye [43,44]. However, this correction is not applicable to textiles as they are neither flat nor opaque, and homogeneity is not verifiable. In the three samples, it is also possible to observe an emission band at 673 nm, corresponding to the presence of chlorophyll, which is part of the composition of lichens [45].

Then, the samples prepared with a blue and a red dye were studied to investigate the colour violet. In the case of orchil, the same experiment as the one with the dye alone was repeated with a first woad bath. As in the first case, all samples were analysed, and the results of the reflectance spectra of 18, 54, and 87 days, shown in Figure 3a, were selected as representatives of the complete dataset. All three absorption spectra of the textiles dyed with woad and orchil show absorption bands characteristic of orchil (545 and 595 nm), together with a wide third absorption band between 660 and 685 nm, indicating the presence of indigotin, the primary colouring molecule in woad [46]. In all samples, the visualisation of the second derivative allowed for a better characterisation of this third band at 700 nm. As seen in the case of orchil, because of the presence of a broad band, it was preferable to consider the inflexion point at 710 nm. The corresponding fluorescence emission spectra (Figure 3b) showed the presence of indigoid molecules characterised by a small band around 720 nm [47–49]. The main band at around 606 nm and the shoulder at 673 nm correspond to the presence of orchil and the detection of chlorophyll, respectively.





**Figure 3.** (a) Reflectance spectra of woad and orchil samples dyed after 18, 54, and 87 days of maceration. The upper left panel shows the second derivative of these samples as a function of wavelength. (b) Fluorescence emission spectra of the same three woad and orchil samples normalised to the natural wool signal (dotted line).

In conclusion, the acquired data from the manufactured samples revealed no significant spectral changes relative to maceration time, either for the orchils alone or when dyed on woad. The 54th day sample, characterised by the two main absorption bands at 545 nm and 595 nm associated with orchil, along with the absorption band at 700 nm characteristic of indigotin, was chosen as the reference for investigating the orchil-based violet in the tapestry.

### 3.2. Orchil Degradation Study

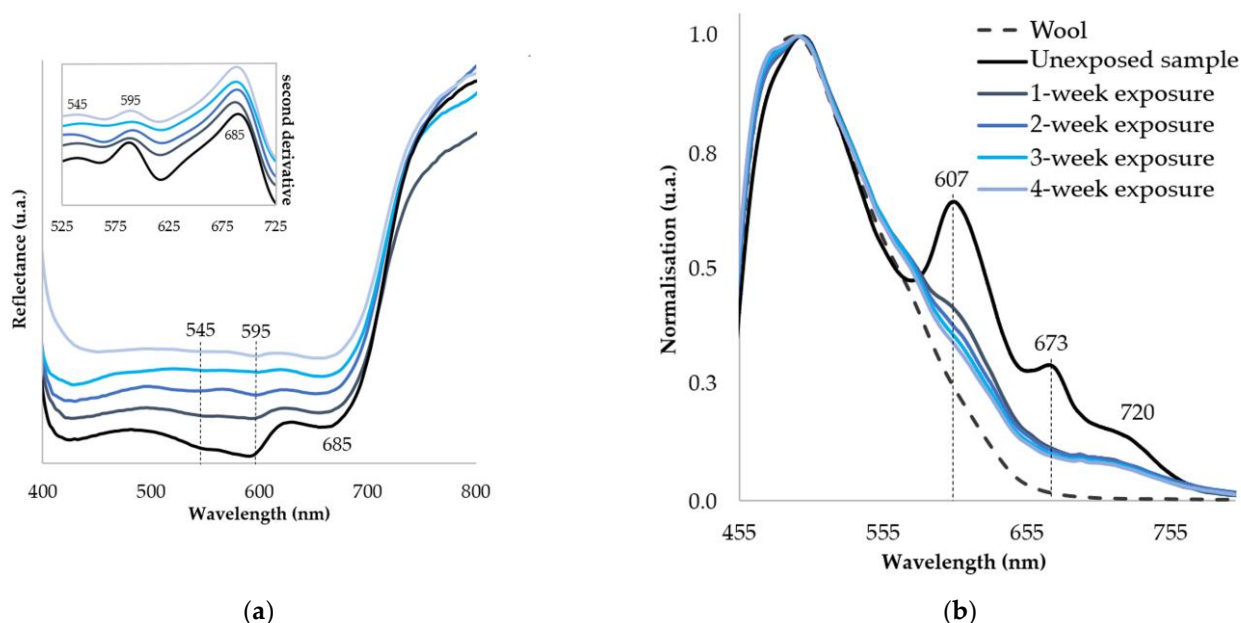
When analysing tapestries, we usually only have access to the front side exposed to light, which is often degraded. Therefore, spectral identification using databases recorded on fresh samples could be biased. The spectra of aged dyes should thus be added to the database. A natural ageing study was performed on the orchil and woad/orchil samples presented above after 18, 54, and 87 days of maceration.

The colourimetric measurements taken after 1, 2, 3, and 4 weeks of exposure for the six samples are presented in Table 2. All the  $\Delta L$ ,  $\Delta a$ , and  $\Delta b$  coordinates are available in Table S1. The orchil sample that macerated for 18 days showed a much more pronounced degradation than the other two samples. Despite the slight superiority of the delta E values of the 54-day sample throughout the exposure, the results were very close to those obtained after 87 days of maceration. This observation can suggest the presence of an optimal maceration threshold to obtain a more durable dye over time and is in agreement with the advice in the dye manuals, which tend to recommend an extended maceration period for orchil [23,34,35]. A similar trend was observed for samples dyed on woad.

**Table 2.**  $\Delta E_{2000}^*$  obtained after 1, 2, 3, and 4 weeks of exposure to light for samples of orchil dyed on natural wool and woad after 18, 54, and 87 days of maceration.

Sample	First Week	Second Week	Third Week	Fourth Week
Orchil day 18	9.9	12.5	13.5	17.2
Orchil day 54	6.4	8.3	8.6	10.4
Orchil day 87	4.6	7.3	7.6	9.6
Woad and orchil day 18	5.4	7.8	9.2	10.7
Woad and orchil day 54	5.2	8.8	8.3	9.1
Woad and orchil day 87	4.2	5.9	7.8	8.1

Figure 4a shows the absorption spectra of the woad orchil sample dyed after 54 days of maceration following exposure to light for 0, 1, 2, 3, and 4 weeks and their second derivative. A rapid and nearly complete disappearance of the absorbance band associated with orchil was noticeable after 4 weeks of exposure. Conversely, the absorption band for woad remained detectable even after 1 month of exposure. Similar observations were noted in terms of fluorescence emission (Figure 4b). The chlorophyll emission band was the first to vanish after the initial week [50], while the orchil-associated band gradually diminished over time. The woad emission band, already visible, remained unaffected by the accelerated degradation.



**Figure 4.** (a) Reflectance spectra of woad and orchil samples dyed after 54 days of maceration unexposed and exposed to the light after 1, 2, 3, and 4 weeks. The upper left panel shows the second derivative of these samples as a function of wavelength. (b) Fluorescence emission spectra of the same four samples normalised to the natural wool signal (dotted line).

When the  $\Delta E_{2000}^*$  values of the different shades of violet (Table 3) presented in this study were compared after 1 month of exposure, there was a significant difference between the violet obtained from orchil and those obtained from madder, cochineal, and kermes. These three samples showed a  $\Delta E_{2000}^*$  below the limit of distinction (less than 3) [51], in contrast to what was observed with orchil (Figure S1). The significant difference in the lightfastness of these dyes is essential information for museum curators. Knowing the materials that make up cultural artefacts and their sensitivity to light will enable curators to take better care of them during their exhibitions.

**Table 3.**  $\Delta E_{2000}^*$  obtained after one month of exposure to light for samples of orchil, cochineal, madder, and kermes dyed on woad.

Sample	1-Month $\Delta E_{2000}^*$
Woad and orchil	9.1
Woad and cochineal	1.7
Woad and madder	1.2
Woad and kermes	2.0

### 3.3. The Identification of the Violet Colour of the Tapestry “La Vue”

As previously mentioned, the *La Vue* tapestry presents an important loss of colour when comparing the area of the Lady’s skirt on the obverse and reverse sides (Figure 5).

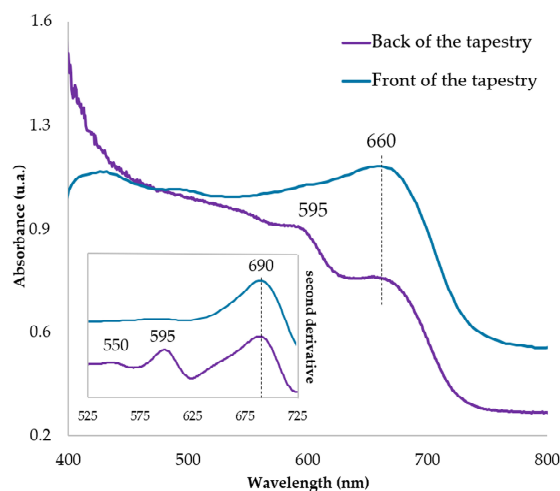
This difference was also observed spectrally, as the absorbance spectra of the obverse and reverse of the tapestry (Figure 6) exhibited two different signals. In detail, the spectrum of the reverse back of the tapestry seems to indicate the mixing of an indigoid (absorption band at around 690 nm) [46] and a red dye (at around 550 and 595 nm). The absorbance band of the red dye, around 595 nm, seems to have disappeared.



(a)

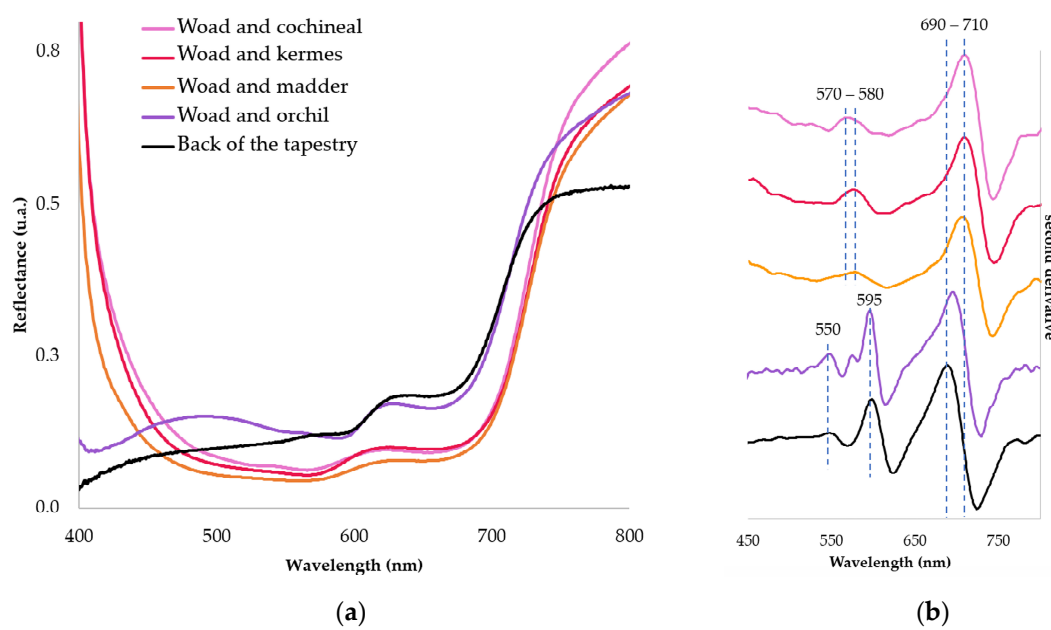
(b)

**Figure 5.** (a) Detail of the Lady's skirt on the front of the tapestry *La Vue* © Musée de Cluny. (b) Detail of the Lady's skirt on the back of the tapestry *La Vue*. The photo is from the restoration report [36].



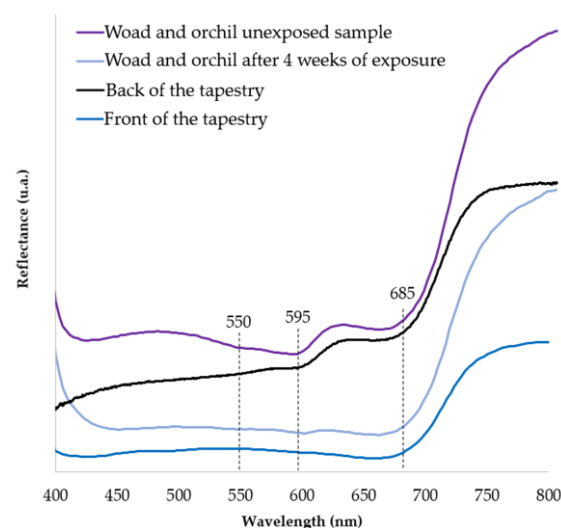
**Figure 6.** Absorbance spectra of the back and front of the tapestry. The insert panel shows the second derivative of these two zones as a function of wavelength.

The absorbance spectra of all violet dye recipes in our database were compared with the absorbance spectrum from the reverse side of the tapestry (Figure 7a). The characteristic absorption band of woad is discernible across all spectra, typically appearing around 660 nm. The comparison of the bands in the red absorption zone proved challenging because of their broad widths. Therefore, the second derivative of the spectra, shown in Figure 7b, was investigated to facilitate the comparison. This visualisation enabled the distinction among the bands present in mixtures containing cochineal, kermes, and madder, notably located at 570–580 nm and 710 nm, and those of the orchil/woad mixture and tapestry at 550 nm, 598 nm, and 690 nm. Therefore, thanks to the second derivative visualisation of the spectrum, it was possible to attribute the dyes used in the tapestry to a mixture of woad and orchil.



**Figure 7.** (a) Reflectance spectra of all the violet samples and the back of the tapestry. (b) The second derivative of the same samples.

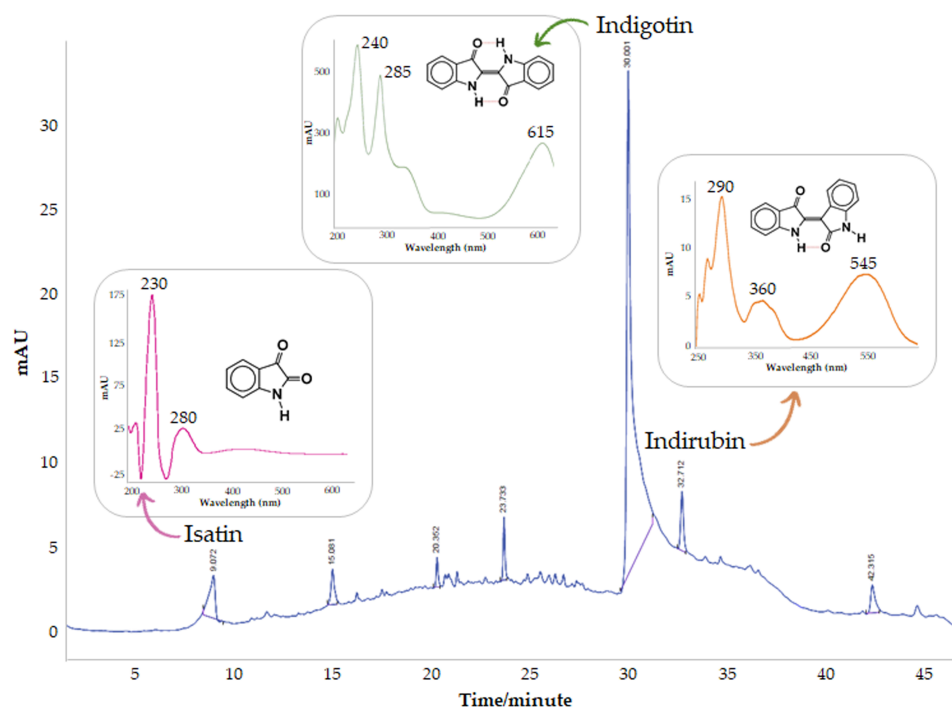
Figure 8 compares the degraded spectrum of the orchil/woad sample to the spectrum obtained on the front side of the tapestry to validate this assumption. The spectra of the orchil/woad and those of the front or back of the tapestry appeared almost in perfect agreement. As mentioned in Section 3.2, the absorption bands of orchil tend to disappear when degraded, unlike those of woad, which remain stable. This initial approach to understanding the degradation of woad/orchil dyes provides new information on the Lady of the Unicorn tapestry and confirms the importance of identifying the components and products of degradation in order to assess the current state of conservation of the object [52].



**Figure 8.** Reflectance spectra of woad and orchil samples dyed after 54 days of maceration, unexposed and exposed to the light after 4 weeks, and reflectance spectra of the front and back of the tapestry.

To complete the results, chromatographic analysis was performed on a thread collected from the back of the tapestry. The chromatogram at 485 nm depicted in Figure 9 illustrates the presence of three indigoid components. The major peak corresponds to indigotin,

observed at 30 min, with its distinctive absorbance band at 615 nm [53]. This is followed by indirubin at 32 min ( $\lambda_{\max}$  545 nm) and isatin at 9 min, identifiable by their absorption maxima at 230 and 280 nm [53,54]. It was not possible to assign the other peaks to any of the known red dye molecules, including alizarin for madder, carminic acid for cochineal, or kermesic acid for kermes [19]. Neither of the main colouring molecules in orchil, namely, hydroxyorceins or aminoorceins [20], were identified on the chromatogram. However, it is interesting to mention that many other previous studies failed to detect orchil in the sample using this technique [20,55], whereas it was identified with spectroscopic techniques, such as that on the *Bible de Théodulfe* (9th century, Puy-en-Velay, France) [56]. Most likely, the difficulty in identifying this dye is related to the advanced state of degradation of the sample studied, which may have led to the loss of the distinct features of orchil, hindering its identification.



**Figure 9.** Chromatogram of the yarn sample from the back of the Lady and the Unicorn tapestry at 485 nm.

#### 4. Conclusions

A spectroscopic examination of the Lady and the Unicorn tapestry La Vue provided valuable insights into the dyes used, shedding light on the observed colour variation between the front and back of the Lady's skirt. The method included the integration of a comprehensive set of spectroscopic data of orchil and woad/orchil on wool into the database of different dyes used in tapestry manufacture. This study identified woad and orchil on the violet skirt at the back of the tapestry, which had been preserved from light exposure. The artificial ageing study further clarified the dyes' lightfastness, revealing that longer maceration times enhance the dye's resistance to light. It was confirmed that the orchil sample on the woad exhibited significant light fragility compared with the other violet samples studied, with the red orchil colour degrading faster than the woad. The comparison of spectra from light-aged samples with those from the front of the tapestry strengthened the hypothesis of woad/orchil use. Unlike the spectroscopic methods, the chromatographic analysis of the sample taken from the back of the tapestry only identified blue dye molecules, most likely because of the advanced state of deterioration of the analyses that hindered the presence of orchil. To better understand and characterise the components present in the chromatogram in search of potential orchil degradation products,

chromatographic analyses should be performed on the degraded samples in our database. This should provide a better understanding of the mechanisms involved in the degradation of orchil and allow us to refine our analytical methods for future studies on cultural heritage objects. In this sense, the results of these contactless analyses are of great importance for the historical understanding of the tapestry. By identifying the dyes used at the time the tapestry was made, valuable information was obtained about the dyeing practices of the time and the financial resources of the commissioner, who preferred to use a fugitive dye such as orchil rather than the much more expensive shellfish purple.

This identification sheds new light on the tapestry, as the deterioration of the dyes influences our general perception of the work and can therefore affect its interpretation, as has already been demonstrated in the case of the tapestry *Verdure fine aux armes du comte de Brühl* [7]. Characterisation also provides valuable information for restorers and conservators, facilitating the conservation and restoration of the tapestry. Moreover, identifying the original colours is essential for understanding the artistic aspects, usage, and distribution of colours. It helps us comprehend the degradation phenomenon and explain it, raising awareness among conservators-restorers about this degradation. Now that the methodology has been established to detect this dye, the other five tapestries can benefit from it.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/heritage7070163/s1>, Table S1:  $\Delta L$ ,  $\Delta a$ , and  $\Delta b$  coordinates and  $\Delta E_{2000}^*$  obtained before ageing and after 1, 2, 3, and 4 weeks of exposure to light for samples of orchil dyed on natural wool and woad after 18, 54, and 87 days of maceration; Figure S1: Orchil samples and woad/orchil samples dyed after 18, 54, and 87 days of maceration, unexposed and exposed to the light after 4 weeks.

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