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On the Hierarchical Use of Colourants in a 15th Century *Book of Hours*

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Abstract: An illuminated *Book of Hours* (in use in Chalon-sur-Saône) currently owned by the Museo Civico di Arte Antica and displayed in the prestigious Palazzo Madama in Torino (Italy) was investigated by means of optical microscopy, fibre optic reflectance spectroscopy, fibre optic molecular fluorimetry, X-ray fluorescence spectrometry and Raman spectroscopy. The aim of the scientific survey was to expand the knowledge of the manuscript itself and on the materials and techniques employed by Antoine the Lonhy, the versatile itinerant artist who decorated the book in the 15th century. The focus was to reveal the original colourants and to investigate the pigments used in rough retouches which were visible in some of the miniatures. The investigation was carried out in situ by portable instruments according to a non-invasive analytical sequence previously developed. It was evident that the use of different pigments by the master was ruled, at least partially, by a hierarchical scheme in which more precious materials were linked to the most important characters or details in the painted scene.

Keywords: non-invasive techniques; FORS; XRF; illuminated manuscripts; brazilwood; colourants; Antoine de Lonhy; Torino

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1. Introduction

The identification of the palette is among the various tasks of the scientific examination of an illuminated manuscript. Techniques and materials for illumination are reported, in principle, in some ancient manuals [1,2] which sometimes use colloquial names which may not be reliable descriptors of the substances actually employed. The combined contribution of researchers from the fields of natural sciences and humanities has shed light on this topic and now the set of the most relevant inorganic colourants employed in illumination is known [1–5]. Nevertheless, the materials used to decorate a specific codex may not be accurately recognised even by an expert eye, since different colourants may yield similar hues, they can be mixed to obtain a particular colour or applied in multilayers and the original colour can be modified and obscured by weathering [6,7]. Therefore, instrumental investigation still plays a crucial role in the recognition of the materials that were actually employed.

The characterisation of the palette gives useful information for conservation and also aids the selection of the proper conditions for preserving or exhibiting these fragile artworks. The determination of the original colourants within a manuscript may confirm or reject its authenticity [8] or may suggest a date for its production, since the period in which different colourants were in use is known. Moreover, a particular set of colourants, along with the compositions of the material employed, may lead to the identification of scriptoria and workshops or to the recognition of the intervention of different hands upon a series of codices or within a single manuscript. More generally, the knowledge of the materials employed expands the information available on a specific book, on the artists who decorated it and on the institutional or private clients for which the book was produced [9–12].

The choice of colourants used to decorate the various features is of particular interest to art historians: precious pigments may be chosen for the most important details, while more conventional materials might be used for less important details [1]. A hierarchy of colourants, following the market values of the materials, can reveal the schemes pursued by the artist in the representation of the various features. A commodity-related evaluation of the colourants used in a manuscript can be highly informative about its intrinsic value. These aspects usually receive very little attention in art historical studies.

With the aim of highlighting this specific topic, in this work we identified the colourants and evaluated the overall palette employed on a 15th century *Book of Hours* (in use in Chalon-sur-Saône) finely illuminated by the Burgundian painter Antoine de Lonhy.

Lonhy was a fascinating figure who was an itinerant artist active from circa 1446 to 1490 in Burgundy, Languedoc, Catalonia and in the Duchy of Savoy. His activity is presently documented by a large variety of artworks, including paintings on wood, frescoes, miniatures, cartoons for stained glass and embroidery [13–15]. A *Book of Hours* was a Christian devotional book with prayers to be said at certain times throughout the day. The small (17.2 × 11.7 cm) book investigated in this work consists of eighty-one pages of vellum with ten large arch-topped miniatures (Table 1) and decorated initials.

Table 1. The subjects of the miniatures.

Folio	Subject
1r	*Annunciation* (Figure 1a)
15r	*Visitation* (Figure 1b)
24r	*Nativity* (Figure 1c)
28v	*Angel announcing the Nativity to the shepherds* (Figure 1d)
31v	*Adoration of the Magi* (Figure 1e)
36v	*Holy Family in the run to Egypt* (Figure 1f)
42r	*God the Father and Jesus crowning the Virgin* (Figure 1g)
46r	*Crucifixion*, with the Virgin and St. John the Evangelist (Figure 1h)
49v	*Pentecost* (Figure 1i)
71v	*Burial service* (Figure 1j)

A rich naturalistic decoration, with acanthus, fruits and flowers, borders each page (Figure 1a).

The manuscript was made approximately between 1446 and 1449 in Burgundy, during the initial period of Lonhy's activity, but besides this, very little information was available about the manuscript until 1966, when it appeared in the catalogue of an auction house. A description of what is known about the book and its history, as well as an exhaustive review of the publications dealing with the versatile activity of Antoine de Lonhy has been produced by Saroni [16]. The manuscript has been owned by the Museo Civico di Arte Antica—MCAA—in Torino (Italy) since 2002 and it is currently displayed in the prestigious Palazzo Madama, home of MCAA, with the signature Inv. n. 399. The museum's collection includes some other artworks of the artist, who is strongly linked to Torino itself and to the surrounding region (Piedmont). The book is in fact an important element for documenting the figure of Antoine de Lonhy in his early years of activity.

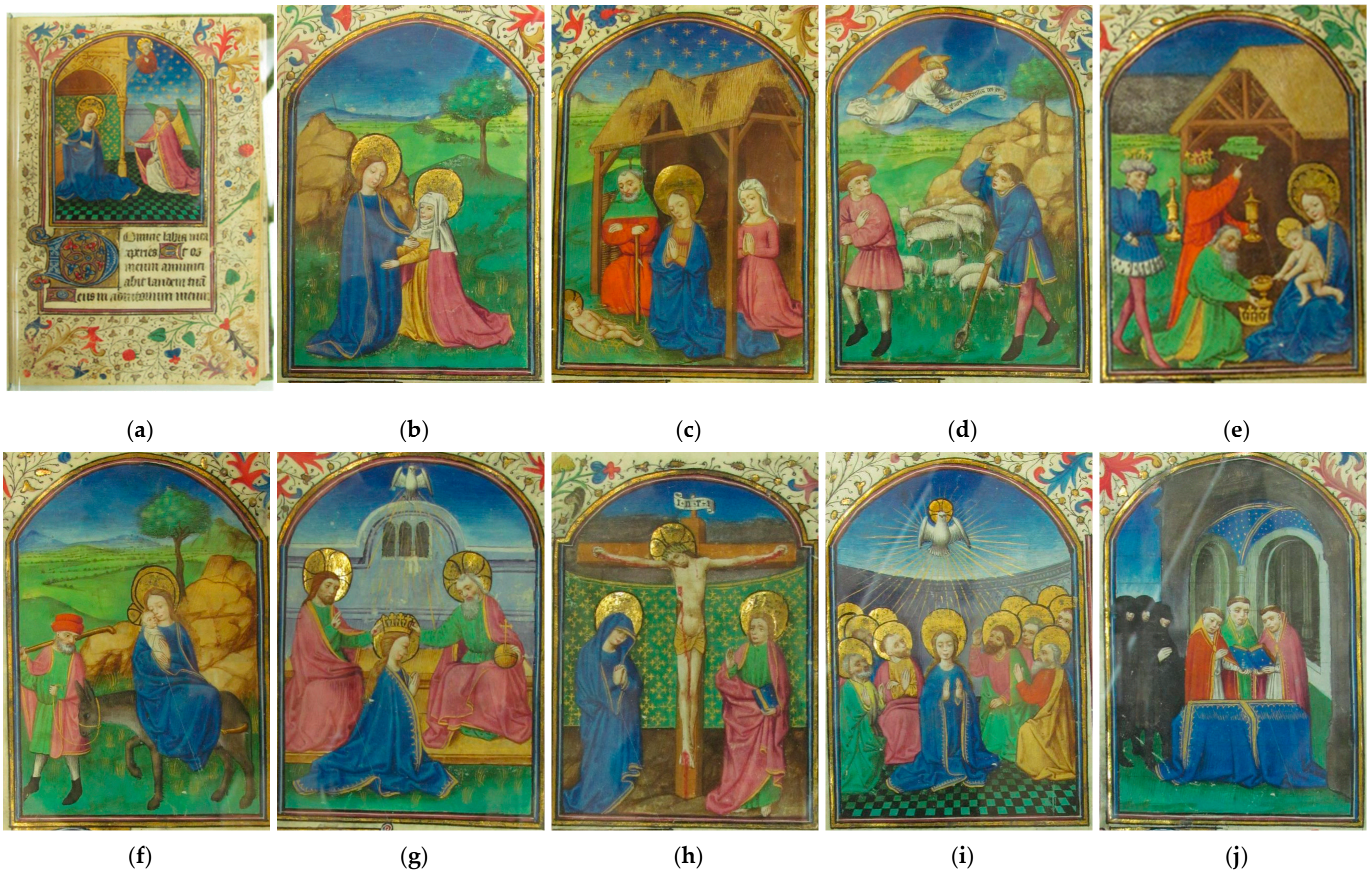


Figure 1. (**a**) f. 1r, *Annunciation*. The main characteristics of the book (illuminated capital letters, rich four-side naturalistic decorations, arch topped miniatures) are shown. (**b**) f. 15r, *Visitation*. (**c**) f. 24r, *Nativity*. (**d**) f. 28v, *Angel announcing the Nativity to the shepherds*. (**e**) f. 31v, *Adoration of the Magi*. (**f**) f. 36v, *Holy Family in the run to Egypt*. (**g**) f. 42r, *God the Father and Jesus crowning the Virgin*. (**h**) f. 46r, *Crucifixion*, with the Virgin and St. John the Evangelist. (**i**) f. 49v, *Pentecost*. (**j**) f. 71v, *Burial service*.

Evidence of some conservation treatments and inpainting are present, although the exact extension and the date of these treatments are unknown: the original bookbinding was removed, the cover was substituted and some parts are missing whereas some pages have been added. Additionally, the sequence of the devotional texts has probably been modified. Rough retouches are evident on three miniatures and the presence of other, less evident, interventions in the upper part of most of the other miniatures was suggested by experts who examined the manuscript before its acquisition by the Museum.

As requested by the curator of the Museum's collection, non-invasive techniques were selected for investigating the colourants: optical microscopy (OM), fibre optic reflectance spectroscopy (FORS), fibre optic molecular fluorimetry (FOMF), X-ray fluorescence spectrometry (XRF) and micro-Raman spectroscopy (micro-Raman). Portable instrumentations were used in order to keep the precious manuscript in the Museum during the scientific investigation. Apart from identifying the original colourants, the investigation was extended to some evident retouches in order to suggest a possible date for the interventions on the miniatures.

The results from these analyses show that the palette used by the artist was rich and variegated and it is therefore a perfect candidate to testify how painters of manuscripts exploited different colourants to express their art in the 15th century, with intrinsic meaning beyond the mere colour.

2. Materials and Methods

2.1. Digital Optical Microscopy

A Dino-Lite (Naarden, The Netherlands) AM413TL-FVW model optical microscope was employed to record digital images from the parchment. The microscope allows magnification in the range 20–90×.

2.2. XRF

XRF measurements were performed with an EDXRF Thermo (Waltham, MA, USA) NITON spectrometer XL3T-900 GOLDD model, equipped with a Ag tube (max. 50 kV, 100 µA, 2 W), a large area SDD detector and an energy resolution of about 136 eV at 5.9 keV. The analysed spot had an average diameter of 3 or 8 mm and was focused by a CCD camera, with a working distance of 2 mm. The total time of analysis was 240 s. The instrument was held in position with a moving stage allowing micrometric shifts, in order to reach the desired probe-to-sample distance; the stage was laid on a tripod. The obtained spectra were processed with the commercial software bAxil, derived by the academic software QXAS from IAEA.

2.3. FORS

The FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source with a wavelength range of 360–2500 nm; the detector and light source were connected with fibre optic cables to an Avantes FCR-7UV200-2-1,5 × 100 reflection probe. In this configuration, light is sent and retrieved with a unique fibre bundle positioned at 45° from the surface normal, in order not to include specular reflectance. The spectral range of the detector was 200–1160 nm; depending on the features of the monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2.4 nm calculated as FWHM. The diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the spectral range investigated. The investigated area on the sample had a 1 mm diameter. In all measurements the distance between the probe and the sample was kept constant at 2 mm, corresponding to the focal length; the probe was inserted into a small aluminium block. To visualise the investigated area on the sample, the block contained a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The system was managed with AvaSoft v. 8 dedicated software running under Windows 7.

2.4. FOMF

An Ocean Optics (Dunedin, FL, USA) Jaz model spectrophotometer was employed to measure the molecular fluorescence spectra. The instrument was equipped with a 365 nm Jaz-LED internal light source and an Avantes FCR-7UV200-2-1,5 × 100 reflection probe used to drive excitation light on the sample and to recover emitted light. The spectrophotometer was working in the range 191–886 nm; according to the features of the monochromator (200 µm slit width) and the detector (2048 elements), the spectral resolution available was 7.6 nm calculated as FWHM. The investigated area on the sample was 1 mm in diameter. In all measurements the distance between the probe and the sample was kept constant at 1.2 mm, corresponding to the focal length; the probe was inserted into a small aluminium block in order to exclude contributions from external light. To visualise the investigated area on the sample, the block contained a USB endoscope. Instrumental parameters were as follows: 3 s integration time, 3 scans for a total acquisition time of 9 s for every spectrum. The system was managed with SpectraSuite software running under Windows 7.

2.5. Micro-Raman

Raman analysis was performed with a portable system assembled by Horiba Jobin-Yvon (Villeneuve d'Ascq, France). The system is composed of a microHR spectrometer with a spectral resolution of 5 cm^{-1}; a CCD Synapse detector; a ModularHead analytical probe containing a video camera for visualisation of samples, a notch filter for elimination of Rayleigh radiation and a microscope objective (20×, 50× or 80×); a tripod to support the analytical probe, equipped with an XYZ stage with micrometric movements to allow accurate focusing; an Ar 532 nm and a He-Ne 632 nm lasers; optic fibres to carry laser radiation on the sample and Raman radiation to the spectrometer. The system is managed with LabSpec 5 dedicated software running under Windows XP.

2.6. Preparation of Standard Paints

In order to identify the colourants present in the manuscript under study, a spectral database was built by measuring FORS and micro-Raman spectra of reference paint samples applied on parchment. These were prepared in our laboratory by employing pictorial materials according to the indications contained in medieval treatises [1,2,4]. In consideration of the painting techniques mostly used by ancient illuminators, two binders were used to disperse pigments and lakes: egg white tempera and gum Arabic.

2.7. Analytical Workflow

In order to optimise the workflow, we employed an analytical protocol which had been developed previously [17]. A preliminary inspection of the painted areas under high magnification optical microscopy (up to 80×) was undertaken in order to highlight their micro-texture and to select the most significant spots for instrumental analysis. The chosen analytical techniques were employed sequentially, following the investigation protocol. Firstly, a large number of spots were investigated by FORS. This allowed areas to be identified with similar reflectance spectra, which can be attributed to the presence of the same materials. In several cases, the comparison of the obtained spectra with those collected in the spectral database (see Section 2.6), along with indications from literature [18,19], allowed for the colourants employed to be determined directly.

A second survey was performed with FOMF, which enabled some of the identifications obtained by means of FORS to be confirmed.

XRF spectrometry was then employed to obtain in-depth information on the underlying layers of paint and the selective identification of the colourants through the detection of key elements that can be linked to one specific pigment. XRF is of particular interest in identifying metal pigments and white/black colourants; in addition, this technique can yield information concerning the provenance of raw materials [20]. With only a few exceptions, organic dyes cannot be identified with this technique.

Lastly, Raman spectroscopy was employed to reveal the identity of those colourants that were still unknown and to confirm the presence of the pigments that had been identified by the other—less selective—techniques.

3. Results

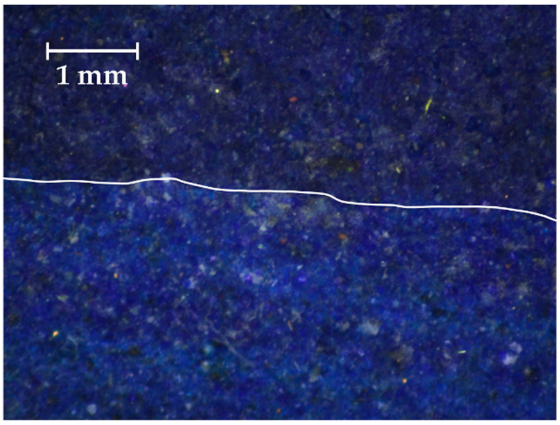
The palette used by the miniaturist is described in the following paragraphs. In addition to the identification of colourants, the discussion will focus on the choice of the colourants in the pictorial scene.

3.1. Black Pigments

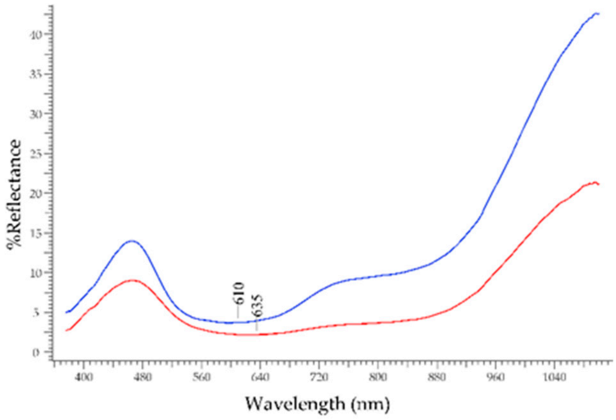
Most of the black areas in the illuminations consist of small details such as floor-tiles (ff. 1r and 49v, Figure 1a,i) or shoes (ff. 28v and 36v, Figure 1d,f), which were painted next to green areas. The spectral features shown by FORS analysis revealed the presence of a carbon-based pigment, but these areas also yielded intense signals from copper and zinc when analysed by XRF. This suggested the presence of a copper green pigment spread under the black one (see later).

3.2. Blue Pigments

Two main blue pigments were identified in the miniatures, i.e., azurite and ultramarine blue, according to their characteristic absorption bands at 640 and 600 nm, respectively. Two different cases were recognised in the spectra from the blue areas of the *Book of Hours*, each associated to a different blue hue. An exemplary case is reported in Figure 2a: the Virgin's mantle on f. 1r shows bright and dark blue hues employed to paint the drapery.



(**a**)



(**b**)

Figure 2. (**a**) Micro-photography (80×) of the mantle of the Virgin on folio 1r. The presence of different blue shades is made more evident by the white border line. (**b**) Selected FORS spectra representative of the different blue shades. The blue line represents spectra collected from darker blue areas within the miniatures and points to the presence of ultramarine, the red line represents spectra collected from lighter blue areas within the miniatures and of the blue areas in the decorations on page borders and capital letters and points to the presence of azurite.

The two different hues revealed by the FORS spectra can be related to the use of different pigments: the spectra from the brighter areas show a broad absorption band centred at about 635–640 nm, thus pointing to the presence of azurite, whereas the band centred at about 610–615 nm in the darker areas suggests the use of ultramarine blue (Figure 2b).

The presence of both pigments, and specifically of ultramarine blue applied over the azurite layer for darkening the colour in the miniatures, was confirmed by micro-Raman by focusing the analysis on grains of the two pigments. This was also was the case for the blue skies, for which the FORS spectra suggested the presence of azurite in the brighter areas and the use of ultramarine blue to darken the colour. The bathochromic shift of the absorption band for ultramarine blue (610–615 nm in place of the expected 600 nm) can be justified by considering the application of this pigment as a thin layer on top of the underlying azurite layer and therefore the final spectrum contained contributions from both pigments. This feature was verified with mock-ups prepared in the laboratory.

The blue decorations on the page borders instead gave FORS spectra that could be attributed to the presence of azurite alone, both in the lighter and darker areas: here the brightness of the colour was adjusted by mixing azurite with a white pigment.

All the XRF spectra collected from the dark and bright areas in the miniatures and from the blue decorations on the page borders showed intense copper signals, as well as signals of barium and zinc; these latter elements were indicated in the literature as possible impurities of natural azurite [11,21], since their presence can be related to the geo-chemical processes of formation of the deposits. A fairly linear relationship between the counts of copper and barium and between those of copper and zinc emerged (Figure 3) and seems to confirm the use of natural azurite throughout the manuscript. More evidence of the natural origin of azurite, as suggested by Aru et al. [22], could be the presence of iron oxides: we did not identify such accessory phases, but the counts of iron in the XRF spectra of the blue areas were on average 4 times higher than in the spectra of parchment.

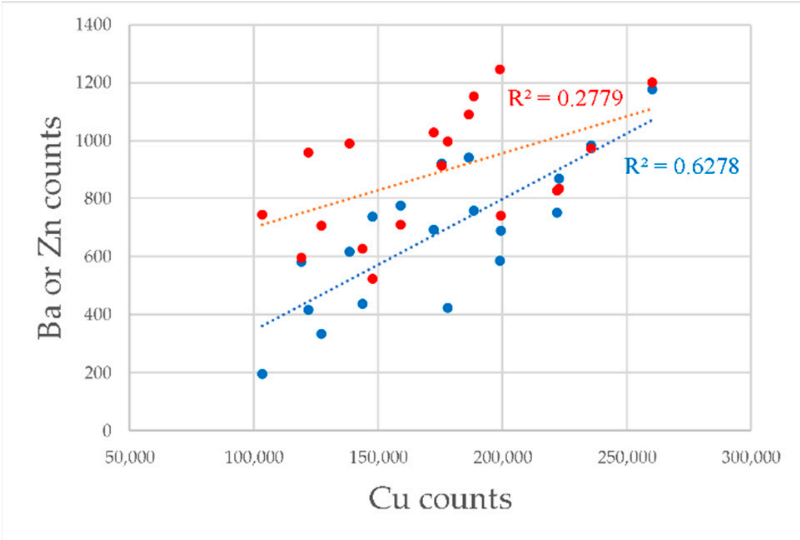


Figure 3. Bivariate plot for XRF signals of copper (K_α line, 8.05 keV) vs. barium (red dots, L_α line, 4.47 keV) and zinc (blue dots, K_α line, 8.64 keV) recorded from blue areas in the miniatures. Regression lines with coefficients R are indicated.

The results obtained by XRF on those areas where ultramarine blue was present deserve some discussion. Portable XRF instruments, that do not operate under vacuum, are generally not able to detect weak XRF signals from light elements such as sodium, aluminium and silicon, which are the main constituents of lazurite—$Na_3Ca(Al_3Si_3O_{12})S$—i.e., the blue mineral that gives the pigment its rich colour. The intensity of the calcium signals from the dark blue areas did not significantly differ from those obtained from the parchment, where this element is present due to the alkaline treatments with calcium hydroxide that occurred in the production procedures. Signals from sulphur, which is present in the structure of ultramarine blue, were detected from the dark blue areas, but this element cannot be considered as a selective marker for this pigment because it can be present in parchment itself; moreover, it is difficult to separate the S K_α line at 2.31 keV from the Pb M_α line at 2.34 keV and lead is usually present as lead white to tune the blue colour. Nevertheless, the XRF spectra recorded in dark blue areas, in which FORS and spectra Raman indicated the presence of ultramarine in the superficial layer of the miniature, differed from those recorded from the bright areas of pure azurite because of the systematic presence of high signals of potassium. No further indication could be derived from the other analytical techniques employed; therefore, possible explanations for the presence of this element in the ultramarine layers could be related to the phenomenon of vicariance between the sodium ions present in lazurite and the potassium ions present in the environment of formation of the rock (similar to that occurring in pyroxenes between Mg^{2+} and Mg-vicariant ions [23]), or to the processes adopted for the purification of the pigment (that employed potash according to Cennini [4]) or even to the possible addition of extenders to the precious pigment. Ultimately, the presence of potassium can be considered a potential elemental marker for ultramarine blue in cases where Al, Si and S cannot be clearly detected.

3.3. Brown Pigments

The brown colour was mainly used to depict architectural features, such as the inside of the huts on ff. 24r and 31v (Figure 1c,e). In all cases, the pigments used were iron oxides or iron-rich red earths, according to the features of the FORS spectra and to the dominant presence of iron evidenced by XRF. It was not possible to obtain a better identification by means of Raman spectroscopy. Some of these pigments, however, were probably related to later retouches (see Section 3.11 for further details).

3.4. Green Pigments

All the reflectance spectra of the green hues were bell-shaped in the visible region of the spectrum, with a reflectance maximum in the range 520–575 nm. The absorption band in these spectra systematically occurred at ca. 750 nm (Figure 4a), which is not fully compatible with the feature of verdigris (720 nm) nor with that of malachite (800 nm) [24].

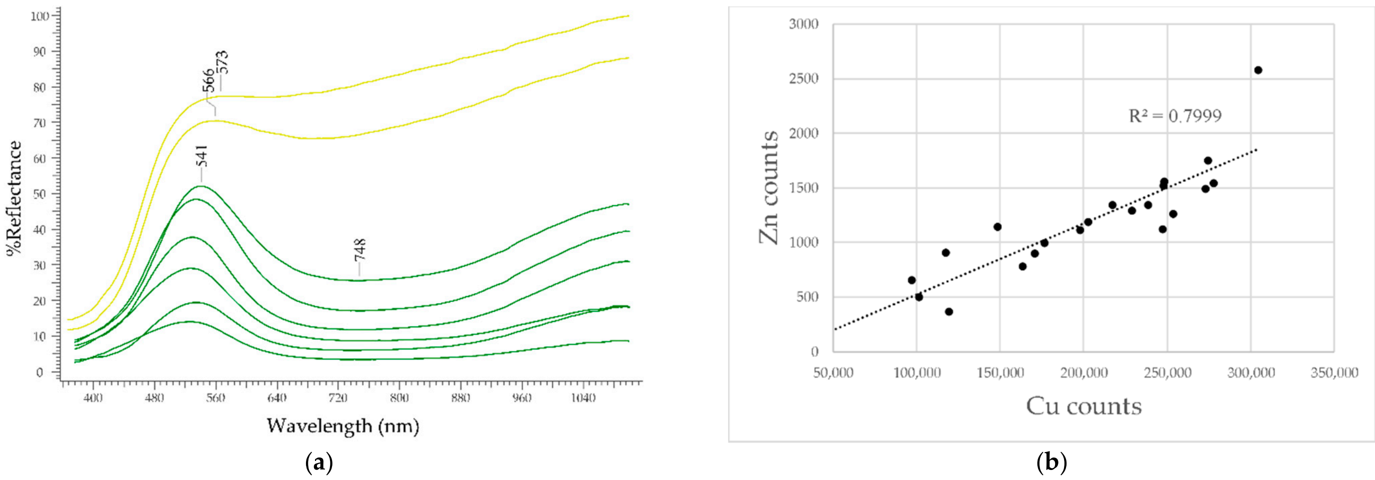


Figure 4. (**a**) selected FORS spectra representative of the different green shades. The green lines are spectra collected from green areas within the miniatures, the top yellow-green lines are spectra collected from yellow-green areas within the miniatures. (**b**) Bivariate plot for XRF signals of copper (K_α line, 8.05 keV) vs. zinc (K_α line, 8.64 keV) recorded from green areas in the miniatures; the regression line with coefficient R is indicated.

The XRF analysis detected strong copper signals, as well as weak zinc signals, that showed a linear trend when plotted on a graph (Figure 4b). Zinc ores are described as being contaminants of copper ores [21], therefore this relationship would suggest the use of a natural copper compound.

Unfortunately, with the configuration used, the micro-Raman equipment did not allow us to gain molecular information from the green pigment present and so the actual nature of the pigment remained unknown. A consideration of the features of the FORS spectra and a comparison with those obtained on other coeval *Book of Hours* manuscripts produced in the same area [25,26] suggest the use of a copper sulphate, such as brochantite or antlerite, as the green pigments. To support this tentative identification, the presence of S was suggested by the XRF spectrum, though again, as in the case of ultramarine blue, it could not be definitely confirmed due to the proximity of the S K_α line at 2.31 keV with the Pb M_α line at 2.34 keV.

The spectral range of the reflected light (see the two top spectra in Figure 4a with reflection maxima shifted towards NIR) determines the different shades (green to yellow-green) observed among the painted green areas. These shades were obtained by mixing a green and a yellow pigment, as was evident from observations of the green areas under the optical microscope (Figure 5).

In such yellow-green areas, significant tin and lead signals were also detected. Moreover, an evident correlation emerged among the XRF signals for tin and lead (not shown), and this strongly suggests the use of lead-tin yellow to brighten the colour. The presence of lead-tin yellow type I which was also used as pure yellow pigment (see Section 3.9), was also confirmed by micro-Raman analysis. The use of lead-tin yellow to modify the tonality of green pigments has already been noted in other works [25,26].

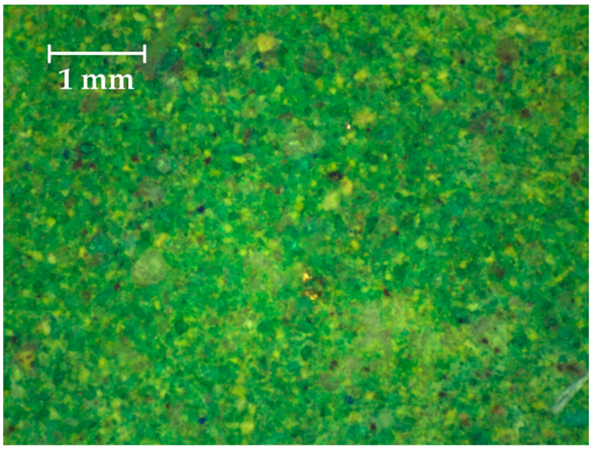


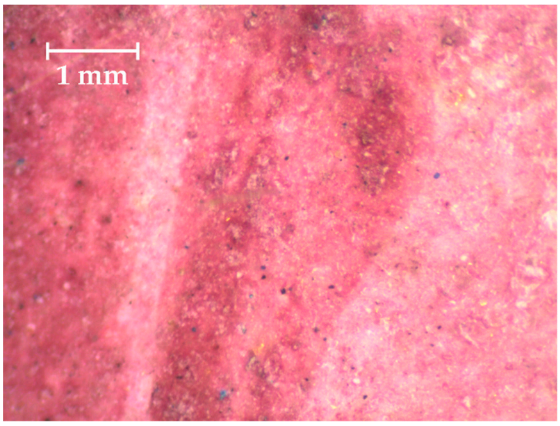
Figure 5. Micro-photography (80×) of yellow-green meadows in the background of Saint Elisabeth and the Virgin on f. 15r (*Visitation*, Figure 1b): green and yellow particles are clearly visible.

3.5. Grey Pigments

Grey horizontal bands are present at ff. 31v (Figure 1f) and 46r (Figure 1h) in the top part. At f. 71v (Figure 1j) the vaults are rendered in grey too. In all cases, silver was used as evidenced by the XRF analysis. As will be discussed in paragraph 3.11, it seems that this was a later intervention and was therefore not due to Antoine de Lonhy.

3.6. Pink/Purple/Violet Colourants

Hues ranging from pink to violet are used extensively throughout the miniatures. They were employed for painting the garments worn by anonymous shepherds as well as the rich mantles of God the Father and Christ. The observation under high magnification of areas painted in pink allowed the use of a mixture of blue and red pigments to be excluded as a potential explanation for obtaining this hue (Figure 6a). Instead, the presence of a pink colourant was also observed. Sporadically, the presence of blue and/or white particles was also evident, thus indicating the use of a blue pigment to tune the final hue towards violet and of a white pigment to brighten the colour.



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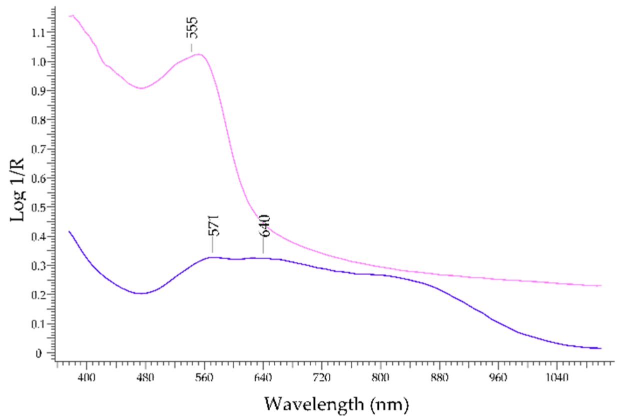


(**b**)

Figure 6. (**a**) Image under 80× magnification of a pink area. (**b**) FORS spectrum in Log(1/R) coordinates of a pink area (pink line, namely the coat of the Angel on the right side at f. 1r, Figure 1a) and of a violet area (violet line, the sky on top at f. 42r, Figure 1g).

The numerous FORS spectra collected from the pink areas showed rather homogeneous spectral features. In particular, they were characterised by an inflexion point in the range 595–600 nm, an absorption band centred at 555 nm and a reflection maximum in the range 475–500 nm (Figure 6b; spectra are shown in Log(1/R) coordinates to better appreciate the absorption features). These features, when compared with the spectra obtained from our reference palette and according to the indications given by Melo et al. [25] and by Roger et al. [27], point to the presence of brasilwood lake, a colourant obtained by adsorbing dyes extracted from the wood of various species of *Caesalpinia* trees on alum, chalk, lead white or gypsum. The identification was confirmed by the FOMF analysis that yielded emission bands at 604 and 625 (data not reported). Brasilwood was in use throughout the Middle Ages. It was mentioned by Cennini [4] with regards to improving the colour of ultramarine blue. It was also used by 15th century Parisian miniature painters [27] who preferred it to insect dyes and madder. In the present case, brasilwood was also used on a layer of azurite to obtain a violet-purple tone, such as in the wall behind the angel at f. 1r (Figure 1a) or in the wall and in the background at f. 42r (Figure 1g), or to highlight red areas, such as in the orange at f. 24r (Figure 1c).

XRF detected intense signals from lead in purple areas. This could be related both to the presence of lead white used to brighten the colour and to its use as the inorganic substrate for the organic dye to prepare the lake pigment. Weak signals of copper (and of barium), detected in a few of the analysed spots imply that the blue grains that were sporadically observed under 80× magnification are those of azurite, which is coherent with their absorption features detected at 571 and 640 nm in the violet spectrum shown in Figure 6b. However, it was not possible to obtain micro-Raman signals from the purple pigment due to the strong fluorescence that obscured the weak Raman signals (if any).

3.7. Red Pigments

Spectra recorded by FORS on red areas showed the typical sigmoid shape that characterises the reflectance spectra of warm hues within the visible region. For these hues, the wavelength associated to the point of inflection in the reflectance spectrum may be indicative of a specific pigment [24], though this spectral feature could shift depending on the concentration of the pigment or if an achromatic colourant is added. With regards to the FORS spectra recorded on red areas of the *Book of Hours* (both miniatures and floral decorations on page borders), two main groups of spectra were observed. These two groups can be clearly distinguished by the different position of the inflection point of the sigmoid-shaped portion of the spectra (Figure 7). In one group, this feature was observed at 600 nm, whereas in the other group it occurred at a significantly lower wavelength (565 nm).

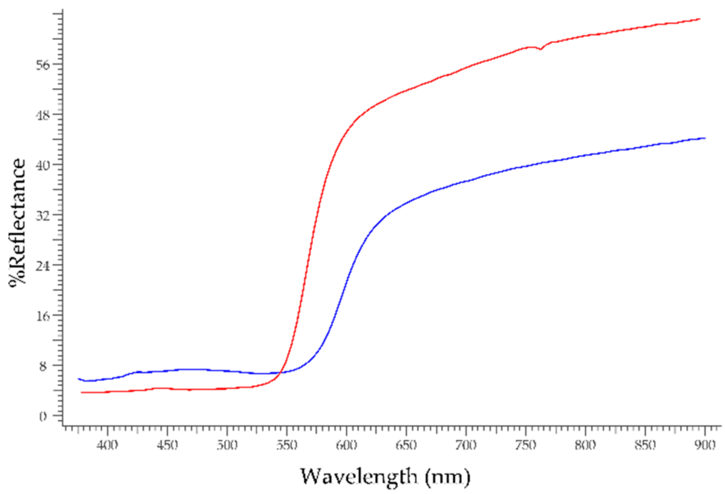


Figure 7. Selected FORS spectra representative of the two groups of spectra collected from red areas. Red line: spectrum obtained from the red vest of one of the Magi in the miniature on f. 31v (Figure 1e); blue line: spectrum obtained from the red acanthus on the upper part of f. 1v. The inflection points suggest the presence of red lead in the miniature and vermilion in the decoration on page borders.

These results suggested that two different pigments were used for reds: cinnabar or vermillion (HgS; it is not possible to distinguish between the natural and the synthetic version) and minium or red lead (Pb_3O_4), respectively. Both XRF and micro-Raman analysis confirmed the presence of these pigments. In fact, the XRF analysis revealed intense Pb signals in those areas in which the FORS analysis suggested the presence of red lead; moreover, the micro-Raman spectra of this pigment (with characteristic signals at 120, 150 and 550 cm^{-1}) were recorded from red particles in the same spots. The presence of cinnabar/vermillion was confirmed both by the occurrence of mercury, detected via XRF, and by the characteristic micro-Raman spectrum, i.e., a strong band at 254 cm^{-1} with a weak shoulder at 280 cm^{-1} and a less intense band at 340 cm^{-1}.

No red lead was detected in the decorations on the page borders and in the red letters throughout the written text, where only vermillion was used to paint red. This is consistent with a procedure involving another artisan with a different palette who decorated these parts of the manuscript. The hypothesis of a different artist working at the page borders, a less important part of the decoration, is more than reasonable if we consider that usually the decoration of a manuscript was more of a group work, in which the most important artist devoted himself to the most important aspects, namely the main miniatures.

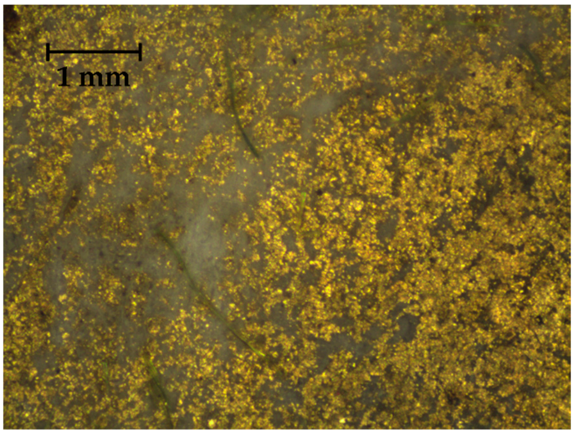
3.8. White Pigments

The white pigment employed throughout the manuscript was identified as lead white. In fact, the micro-Raman spectra of the white particles showed the sharp band at 1049 cm^{-1} that characterises this pigment, whereas XRF data resulted in very high lead signals that emerged in most of the XRF spectra collected from the manuscript. This suggests that lead white was used, by itself or mixed with other pigments, as a primer under the illuminations. The most relevant exceptions are the areas painted with gold or mosaic gold, in which very weak signals of lead were detected.

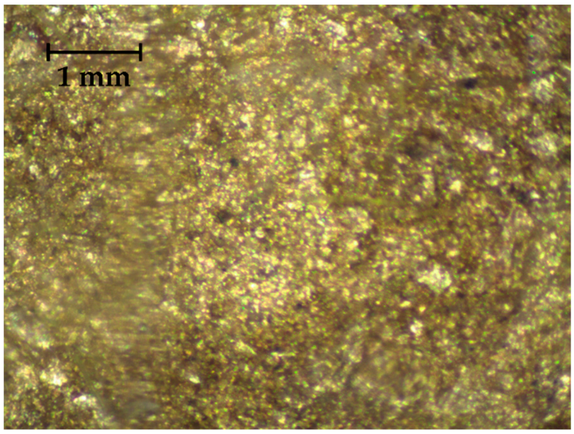
3.9. Yellow and Yellow-Brown Pigments

The set of FORS spectra collected throughout the manuscript were mainly characterised by sigmoid-shaped spectra with points of inflection within 480 and 560 nm. According to this feature, four different yellow colourants could be hypothesised after the FORS survey and the use of the other techniques allowed us to confidently identify the following yellow pigments.

1. In one instance, e.g., in the spectrum recorded from the apostle's yellow tunic in the miniature representing the *Pentecost* on f. 49v (Figure 1i), the inflexion point was at ca. 480 nm. In this case, the comparison with the spectra collected from the reference palette indicates the presence of either lead-tin yellow type I or orpiment. The presence of lead-tin yellow was also suggested by the intense signals of these two elements in XRF spectra and finally confirmed by micro-Raman analysis, which also assessed the crystalline structure of the compound as type I [28].
2. As with other yellow-brown hues, the FORS spectra and XRF analysis suggested the presence of yellow ochre or other iron-based pigments, according to the minimum at ca. 890 nm, an inflection point at ca. 570 nm, the typical shoulder at 450 nm and the identification of iron by XRF. High fluorescence prevented obtaining Raman spectra. These features were shown, for example, on the inner part of the aedicule on f. 1r (Figure 1a), as well as the Cross and the ground of the Golgotha in the *Crucifixion* on f. 46r (Figure 1h).
3. Other yellow areas, appearing darker with respect to those mentioned above, showed glittering particles on a dark-yellow background when observed under 80× magnification. The texture of these particles showed a coarser grain size (Figure 8).



(**a**)



(**b**)

Figure 8. (**a**) Micro-photography (80×) of the golden architecture on f. 1r. (**b**) Micro-photography (80×) of the glittering details on the rock painted in the picture background on f. 15r (Figure 1b).

The FORS spectrum showed an inflexion point at ca. 530 nm, which is consistent with the feature of mosaic gold (also called purpurin–SnS_2) [24], a well-known substitute for gold which is typical of medieval miniature painting. XRF analysis confirmed the presence of tin and sulphur, as did the micro-Raman analysis that yielded spectra showing a very intense peak at 321 cm^{-1} (Figure 9).

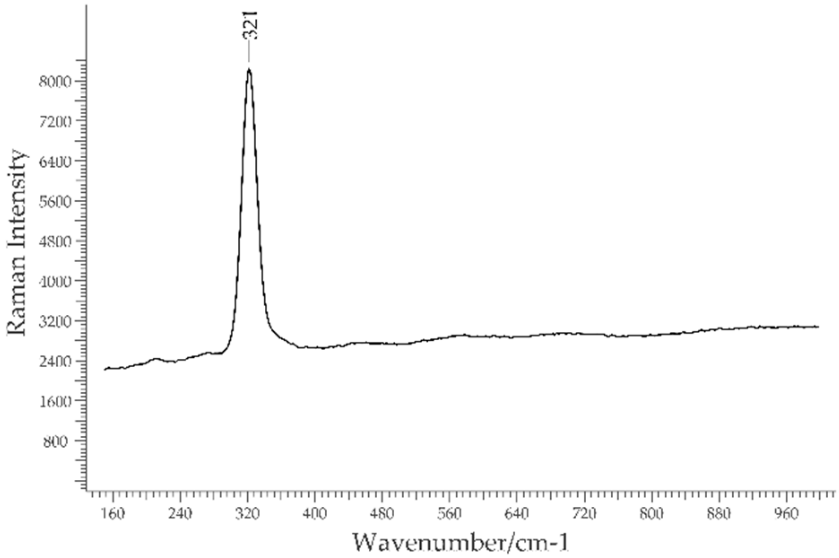


Figure 9. Raman spectrum obtained from brown-yellow areas revealing tin sulphide.

The Raman spectra of Sn(IV) sulphide reported in the literature [29] shows an intense signal at slightly lower frequency (313 cm^{-1}), therefore one can assume that different recipes could yield different molecular structures that may give slightly different Raman responses.

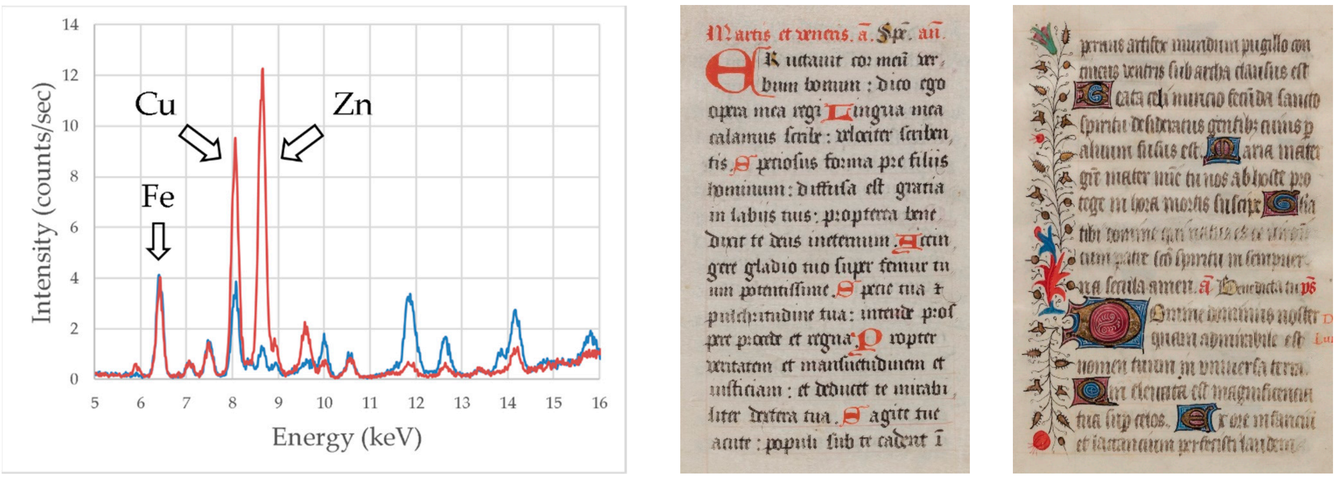
4. Finally, finer glittering particles were identified by XRF as gold; these areas also yielded a FORS spectrum with the typical inflexion point of gold at ca. 505 nm [24]. Powdered gold was used here, in the same way as other pigments, mixed with a medium and spread as a thin film with a brush; since the "ready to use" pigments were generally kept in shells, this technique is referred to as "shell gold", to distinguish it from the gold leaf technique, in which a very thin leaf of gold adheres on the vellum by means of an adhesive [30].

In the page borders decorations, the large yellowish leaves were obtained by spreading a thin layer of shell gold.

Gold was also employed for the haloes, executed using the gold leaf technique. In these areas XRF analysis also revealed calcium, sulphur and weak signals of copper and iron, in addition to gold. These traces of copper and iron are possibly related to impurities in the gold leaf while the high XRF signals from calcium and sulphur, significantly higher than those obtained from the unpainted parchment, indicate the use of gypsum in the typical *asiso* ground for gold, used in the Middle Ages starting from the 13th century [30].

3.10. Black Ink

The black ink used for writing all through the manuscript was composed of iron-gall ink, as revealed by the characteristic FORS spectrum with the reflectance level raising in the NIR [31]. The metal composition of ink is homogeneous in all the pages, being rich in iron and copper; at f. 9r a different ink, richer in copper and zinc, was highlighted (XRF spectra in Figure 10a), giving material evidence to the hypothesis of a later insertion for this folio, as suggested by the different style in the writing (Figure 10b,c).



(**a**) (**b**) (**c**)

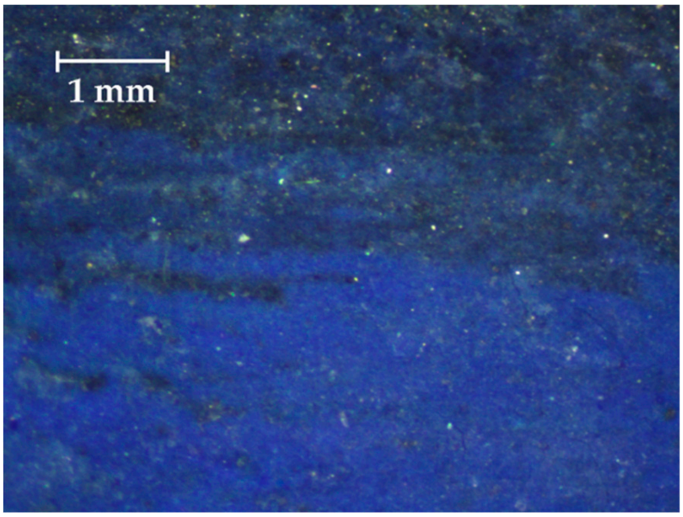
Figure 10. (**a**) XRF spectra of the black inks at f. 9r (red line) and at f. 42r. (blue line). (**b**) Black ink at f. 9r (later addition). (**c**) Black ink at f. 3r (original).

3.11. Retouches

Many of the (more or less evident) retouches are in the upper part of the miniatures, where the analysis detected, in some cases, the presence of pigments that differed from the original ones. The miniature on f. 31v (Figure 11a) appeared coarsely retouched: a large grey band was apparently added on the original picture, and it was apparent that the sky could have been completely repainted.

Inspection under high magnification supported these hypotheses, since the texture of the blue pigments was completely different from that observed in the original parts (Figure 11b), with blue particles of sub-micrometric size. Micro-Raman signals obtained in these areas are reported in Figure 12 and revealed the presence of phthalocyanine blue, a synthetic pigment available since 1935 (bands at 490, 596, 682, 747, 950, 1140, 1207, 1335, 1443, 1523 and 1569 cm^{-1}). Signals of lazurite (bands at 263, 550 and 1092 cm^{-1}), possibly pertinent to the original layers, were also detected.

(a)



(b)

Figure 11. (**a**) Miniature on f. 31v. Retouches in the upper part of the picture and in the hut are visible. (**b**) Micro-photography (80×) of the blue sky close to the grey retouch.

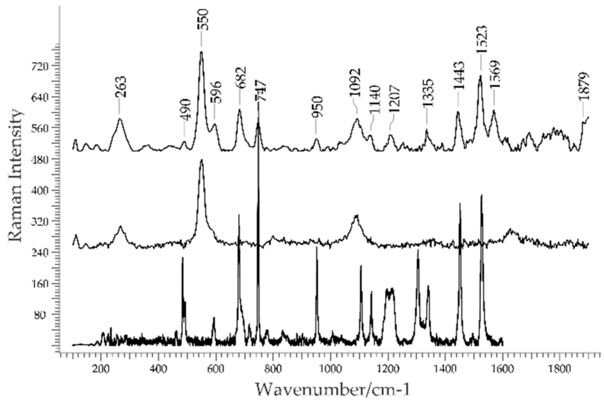
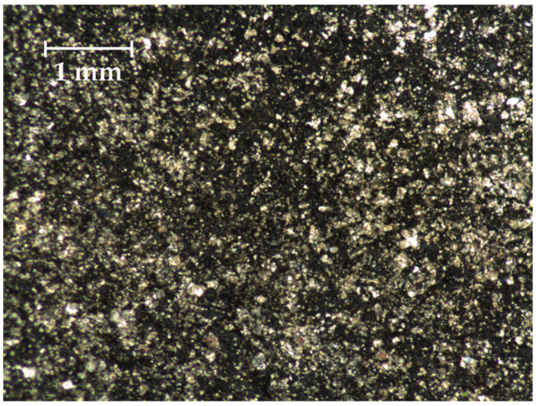


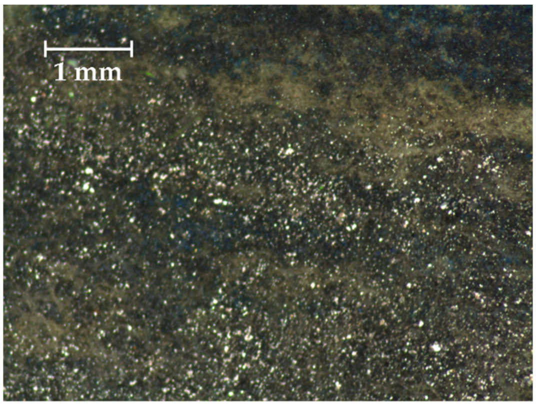
Figure 12. Raman signals recorded from the blue sky on folio 31v (**top**), from natural ultramarine spread on parchment with gum Arabic (**middle**) and from phthalocyanine blue spread on parchment with gum Arabic (**bottom**).

On examination, the grey band was attributed, via XRF, to a layer of powdered silver. Besides silver signals, XRF revealed here the presence of titanium, which points to the use of another modern pigment, i.e., titanium white (TiO_2). The lack of any micro-Raman signals from this compound, which is a strong Raman scatterer, suggests that titanium white was used to mask the underlying picture prior to the laying of silver powder which was presently darkened by weathering.

A similar rough intervention is visible on f. 46r (Figure 1h), where a grey band was added to the lower part of the sky; here again, a possible intervention on the sky itself was suggested. However, despite the various macroscopic similarities between the two restoration interventions on ff. 31v and 46r, instrumental investigation did not give us any incontrovertible evidence that they were carried out at the same time by the same restorer. In fact, glittering silver particles observed in the grey band under the microscope on f. 31v appeared significantly coarser than those observed on f. 46r (Figure 13).



(**a**)



(**b**)

Figure 13. (**a**) Micro-photography (40×) of the grey bands on f. 31v. (**b**) Micro-photography (40×) of the grey bands on f. 46r. Different dimensions of the silver particles are evident.

XRF confirmed that silver was employed in both interventions, but it did not show the presence of titanium on f. 46r, thus pointing to a different silvering technique. With regards to the blue pigments, the Raman investigation carried out on f. 46r indicated the presence of ultramarine blue, whereas the presence of phthalocyanine blue found on f. 31v was not detected; also, the FORS spectra pointed to the presence of azurite and ultramarine, i.e., the same pigments originally employed by Antoine de Lonhy. Moreover, under the microscope the sky of the miniature on f. 46r presents a micro-texture resembling that of other original parts painted with the same pigments. These results suggest that the restorer who painted the silvered band around the Cross on f. 46r spared the sky above it.

A peculiar case is the dark vaults above the main characters in the funerary scene at f. 71v (Figure 1j). Here, the morphology of the silver particles and the absence of titanium seems similar to those employed in retouches on f. 46r. However, the XRF analysis revealed the presence of gold, indicating the original presence of a golden architecture, possibly similar to that still visible in the miniature on f. 1r (Figure 1a) but covered at a later date with silver that now appears darkened.

The analysis of the sky also did not highlight any proof of retouched areas, suggesting that the sky here was spared by the restorer. The same holds for other miniatures: no clues of the use of modern materials emerged after the evaluation of micro-textural and compositional characteristics, revealing the sole presence of blue pigments that are fully comparable, from a compositional and morphological point of view, with the original ones.

Retouches on browns at ff. 24r and 31v (Figure 1c,e) are clearly visible to the naked eye. FORS spectra from the dark brown interior part of huts yielded evidence of iron oxide pigments, similar to those obtained from other brown untouched areas present in other folios. The XRF analysis of the repainted areas, however, showed lower iron signals with respect to the original iron oxide pigments; moreover, in all the retouched areas, signals of chromium and cobalt, very similar in intensity, were detected, whereas in the original brown pigments these elements were undetectable. These data strongly suggest that ff. 24r and 31v were modified by the same hand; unfortunately, a strong fluorescence band prevented the collection of micro-Raman signals which could have better elucidated the nature of the brown pigment.

4. Discussion

As highlighted by the results of the scientific investigation, the palette used by Antoine de Lonhy for this *Book of Hours* is rich and variegate (Table 2). The results also show how the different colourants were used in the decoration of the book, which may give further information and allow a comparison with the palette from the coeval manuscripts.

Table 2. The palette identified in the decoration of the *Book of Hours*.

Colour	Colourants
Black	carbon pigment
Blue	ultramarine blue azurite phthalocyanine blue [1]
Brown	iron oxides
	iron earths [1]
Green	brochantite
Grey	Silver [1]
Pink	brasilwood
Red	cinnabar
	red lead
Violet	brasilwood/azurite
White	lead white
Yellow	gold leaf shell gold mosaic gold lead-tin yellow type I yellow ochre

[1] possibly related to retouches.

4.1. The Hierarchical Use of Colourants

It emerges that—for blues, reds and yellows—different colourants were used for the same hue, and some kind of hierarchical scheme can be highlighted for the miniatures painted by Antoine de Lonhy. We are not talking here about the hierarchy of *colours*, an aspect on which there is a very wide coverage [32,33], but rather the hierarchy of the *colourants* inside the different colours. To investigate this topic, we can start from the commercial aspects discussed by S. Nash [34] in her study on the proofs of payment for artistic materials supplied to the court of the Dukes of Burgundy from the 14th to 15th centuries, which are now conserved in the Archives Départementales de la Côte-d'Or in Dijon (France).

4.1.1. The Use of Blues

In the Middle Ages the blue pigments were among the most expensive colourants. This is well known for ultramarine blue, due to the difficulty of supplying the stone lapis lazuli—from which ultramarine blue was prepared—from Afghanistan. Nevertheless, the best-quality azurite was also far more expensive than nearly all other colourants [34] (p. 130), including organic blue pigments such as indigo and woad. Therefore, it is interesting to understand how the artists managed the hierarchy of the blue pigments. There was a wide difference in price between ultramarine blue and azurite. Nash [34] (pp. 125–130) reported a cost of 128 FRF/lb for *fin azur d'Acre*, a term associated by the author to ultramarine blue, while *azur d'Alemaigne* (azurite from Germany) ranged between 1 and 20 FRF/lb. Delamare [35] (p. 132) estimated that in the Renaissance, the cost of ultramarine blue was up to 400–500 times that of azurite. The study by Kubersky-Piredda on the trade of colourants in Florence during Renaissance [36] reported a price ranging between 500 and 16.800 *soldi/libbra* for ultramarine blue and between 40 and 400 *soldi/libbra* for azurite.

However, in the miniatures of the *Book of Hours* it seems that Antoine de Lonhy used the two blue pigments in chromatic combination rather than as alternatives. In the mantle of the Virgin at f. 1r (Figure 1a), for example, he used azurite as the base and ultramarine blue for highlighting. The same holds true for the skies present in all the miniatures.

Therefore, we may suggest that the artist used the blue pigments according to their *tone* rather than their *price*.

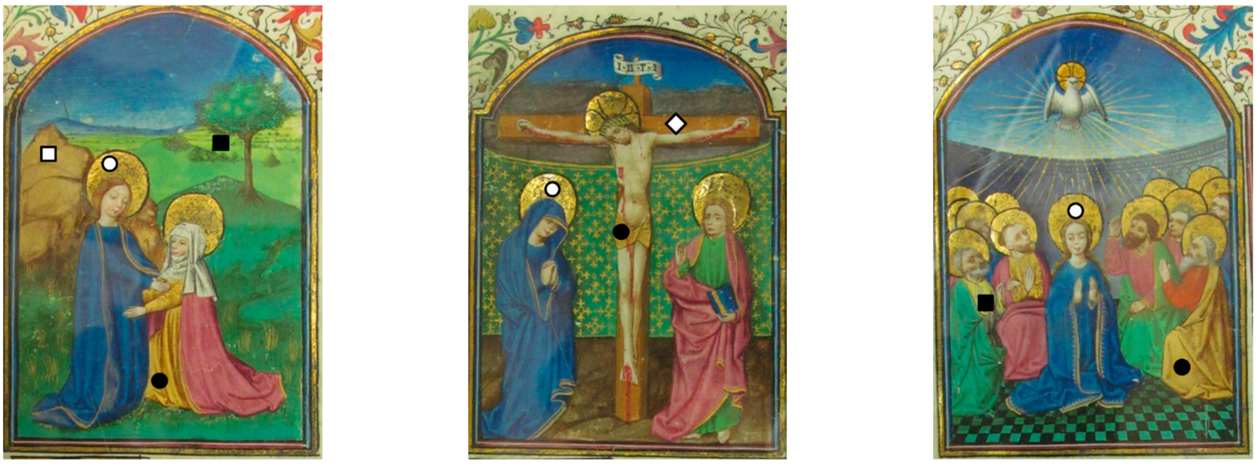
4.1.2. The Use of Reds

Although the contextual presence of vermillion and red lead in a medieval manuscript is not surprising at all, the use of these two pigments within the *Book of Hours* deserves some discussion. The difference in price is well documented; Nash [34] (pp. 143–146) reports that vermillion was sold for about four times the price of red lead.

The hierarchy followed by the author for red pigments is somewhat different than that for the blues. Red lead was used throughout the miniatures, where it was the main red pigment employed, while vermillion was then applied over the red lead to darken the hue and to heighten the red mantles of some characters, in a way similar to the combination of azurite and ultramarine blue. However, a more hierarchical use is apparent in the depiction of the blood of Jesus trickling from his hands and chest in the *Crucifixion* (f. 46r, Figure 1h), for which Antoine de Lonhy reserved the more precious vermillion.

4.1.3. The Use of Yellows

The choice of yellow pigments is perhaps the most remarkable from the hierarchical point of view. Antoine de Lonhy used five different pigments for this colour: shell gold, gold leaf, mosaic gold, lead-tin yellow type I and yellow ochre. Examples are reported in Figure 14.



(**a**) (**b**) (**c**)

Figure 14. Examples of use of yellow pigments in the *Book of Hours*. □: mosaic gold; ■: lead-tin yellow type I; ○: gold leaf; ●: shell gold; ◇: yellow ochre. (**a**) f. 15r, *Visitation*. (**b**) f. 46r, *Crucifixion*. (**c**) f. 49v, *Pentecost*.

Shell gold was of course the most expensive of the set. It was used by Antoine de Lonhy to paint various details in the miniatures, such as the bench that holds Christ and God the Father in the miniature depicting the *Coronation of the Virgin* on f. 42r (Figure 1g), as well as the garments of some characters: examples are Saint Elisabeth's tunic on f. 15r and the tunic of the apostle sitting on the right hand of the Virgin as well as the mantle of the apostle on the right part of the picture in the miniature depicting the *Pentecost* on f. 49r. Apparently, the painter chose the precious shell gold here in order to stress the relevance of the characters who deserve the most precious materials.

Lead-tin yellow type I or *giallolino* was considered quite valuable: its cost could be double that of orpiment [34] (pp. 151–152) and was much more than the various types of yellow ochres. Despite this, in the *Book of Hours* lead-tin yellow was used mostly in a mixture with a green copper pigment (see Section 3.4) to modify its tonality but rarely as pure yellow pigment, perhaps only for the coat of an apostle, probably St. Peter, praying in the left part of the miniature in the *Pentecost* on f. 49v. The fact that this pigment was reserved for this specific apostle would suggest an intentional use somehow linked to the identity of the character. In fact, St. Peter is an important apostle because it was to him that Christ entrusted the keys of heaven.

It is difficult to estimate the ranking of mosaic gold. Nash [34] does not report information for this synthetic pigment. A reference [37] can be found in a *Taxa*, i.e., a price list, issued in 1568 in the town of Liegnitz (Silesia, Poland) in which *Aurum musicum* (mosaic gold) is cited among the most expensive *Colores* or materials for painting, with a price 6 times that of *Aurum pigmentum* (orpiment), 12 times that of *Bley gelb* (lead-tin yellow or massicot) and 12 times that of *Ocker gelb* (yellow ochre). N. Turner, in her commentary study on Johannes Alcherius [38], suggested that mosaic gold, rather than being used by illuminators as an inexpensive substitute for gold leaf and shell gold, could have been used alongside them to expand the range of golden hues. In the *Book of Hours* considered here, mosaic gold was used to paint secondary subjects such as the rocks in the background on ff. 15r and 28v (Figure 1b,d), or the straw roof of the hut of the Nativity in the illuminations on ff. 24r and 31v (Figure 1c,e). Only one instance was found where shell gold had been used instead of the less precious mosaic gold, i.e., the rocks in the background of the illumination depicting the Virgin and the infant Jesus in the run to Egypt (f. 36v, Figure 1f), in order to highlight these details.

Last in ranking were the yellow ochres, which are by far the cheapest pigments in the lists reported by Nash [34] (pp. 155–157). Examples of their use are the inner part of the aedicule on f. 1r (Figure 1a) and the Cross and the ground of the Golgotha in the *Crucifixion* on f. 46r (Figure 1h).

4.2. Comparison with Other Works

There are few diagnostic works in which the hierarchy of colourants is discussed from the analytical point of view. Clark [9] cited the medieval practice of using the most valuable colourants, with particular reference to blue pigments, for the most important subjects inside a painting, but gave no specific information on the items analysed.

Bruni et al. [39] studied the decoration of a 15th century parchment folio kept at Archivio di Stato in Milan, originally commissioned by Francesco Sforza. The work is attributed to the Italian artist Michelino dei Molinari. The hierarchy of the colourants used by the artist was similar to that used by Antoine de Lonhy in the case of red pigments: the Child's vest, the tongue of a green dragon and the red initial capital letters in the text were painted with vermilion, whereas a red flower below the dragons was obtained by a mixture of red lead and vermilion. However, it was different in the case of blue pigments, since ultramarine blue and azurite were used separately for features with different symbolic value: the former was used for the mantle of the Virgin Mary and the Sforza's *Biscione* (the symbol of the Sforza dynasty), while the latter was used only for the initial capital letters in the text.

On the other hand, Bersani et al. [40], in a study on the ms. Pal. 212 (Biblioteca Palatina in Parma, Italy), a *Book of Hours* with 14th century miniatures produced in Bruxelles, found an unusual hierarchy of blue pigments, with azurite used in the central painting to realise the mantle of the Virgin Mary, one of the most important subjects of all illuminated books and lazurite used for the decoration of the frame, a feature undoubtedly less important. The authors attributed this unusual choice to the unavailability of lazurite for the artist who decorated the central painting. In the end, therefore, the choices of the artists follow their decorative schemes, but they are related to the availability of materials.

Of course, the hierarchical use of colourants can be found in other types of paintings. In the study by Edwards et al. [41] on the wall paintings of the Church of SS Cosmo and Damian in Basconcillos del Tozo (Castille y Léon, Spain), the authors highlighted the selective use of the precious cinnabar for the most important biblical figures.

4.3. Comparison with Coeval Manuscripts

It is interesting to note that a relatively similar palette was characterised by Melo et al. [25] in their analysis of three French 15th century *Book of Hours* presently in the Palacio Nacional de Mafra (Portugal). This information may support art historians in interpreting the context of production for these manuscripts and to (possibly) link other artworks to the production of Antoine de Lonhy.

5. Conclusions

The present work represents the first step towards the disclosure of materials and techniques employed by Antoine de Lonhy in the course of his artistic activity and it integrates the studies on style and iconography already carried out about the work of this versatile medieval artist. Further to this, the instrumental inspection of the untouched parts of the miniatures allowed us to recognise the colourants originally used by the master, and to highlight the criteria that he used for selecting a specific pigment. This choice appears not merely bound to technical or aesthetic reasons, since specific pigments were selected for specific parts in the miniatures. In particular, a hierarchical scheme is identifiable for yellows and partially for reds, while in the case of blues the colourant choice seems to be led by difference instances. Of course, the hierarchy of the colourants within this work offers only a partial view of what the *modus operandi* of the artist was.

The shine of gold is that of mosaic gold, while shell gold was used to paint objects and details that are somehow connected to characters whose sacredness required the use of the finest materials. As a whole, four different yellow colourants were hierarchically employed within the miniatures.

Vermilion was used to paint the stray of acanthus, strawberries and flowers in decorations on page borders (possibly by an associate of de Lonhy), while in the miniatures its use was reserved to the blood of Jesus Christ, in order to emphasise the sanctity of this detail, while less valuable red lead was used to obtain reds throughout the miniatures.

Another peculiarity concerns the use of lead-tin yellow; this pigment was largely used in all the miniatures to tune green colours. Only in one case was it used by itself, i.e., to paint the vest of the old apostle, probably St. Peter, praying in the left part of the miniature on f. 49v. It is possible that this specific use is linked to the identity of this important character.

The overall analytical results indicated that the palette used to paint the decorations bordering each page differs substantially from that used in the miniatures.

It is known that the painter who executed the miniatures generally did not work on other decorations on the page, but this investigation has also pointed out that different pigments could be used in the different stages of the decoration of the manuscript.

All in all, the palette chosen by the artist for the decoration of the ten miniatures, including the precious colourants such as gold, lapis lazuli and cinnabar, indicates the importance and credit of this work.

The investigation also gave information on the materials used for retouches. In particular, phthalocyanine blue, in use since 1935, and titanium white, also introduced during the 20th century, were found in the illumination on f. 31v, thus setting a *post quem* terminus for some of the coarse interventions clearly visible in the manuscript. Moreover, the presence of different materials would exclude, as suggested by autoptic inspection of the book, that the retouches could have been performed by the same hand.

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