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The Colors in Medieval Illuminations through the Magnificent Scriptorium of Alfonso X, the Learned

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Abstract: This pioneering work studied the medieval color palette of four manuscripts produced in the scriptorium of Alfonso X, king of the Crown of Castile (r. 1252-84), including the *Songs of Holy Mary* (Cantigas de Santa Maria, in Rich Codex and Musicians' Codex), *Lapidary* (Lapidario), and *Book of Games* (Libro de los juegos). Scientific analysis based on fiber-optics reflectance spectroscopy in the visible and Raman spectroscopy showed a color palette based on lapis lazuli, indigo, azurite, vermilion, red lead, orpiment, yellow ochre, two different greens (bottle green and *vergaut*), lead white, carbon-based black, and most importantly, brazilwood pinks, reds, and purples. So, it is now the first reported use of this lake pigment in European medieval manuscript illumination. The painting technique is also discussed. The diversity of colors and techniques, with the presence of lapis lazuli, brazilwood lake pigments, purple, and gold, demonstrates Alfonso X's desire to produce sumptuous manuscripts.

Keywords: color palette; brazilwood lake pigments; *Songs of Holy Mary*; painting technique; medieval illuminated manuscripts; spectroscopic analysis; Alfonsi manuscripts; *Ajuda Songbook*

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1. Introduction

1.1. Illuminated Manuscripts Produced in the Scriptorium of Alfonso X

The intellectual action associated with Alfonso X, king of the Crown of Castile (r. 1252-84), known as the Learned, is one of the most brilliant cultural enterprises of the medieval West. This sophisticated project was articulated by specialized groups working in different fields of knowledge (history, astronomy and astrology, literature, hagiography, and law) to find and translate numerous sources (in Latin, Arabic, or Hebrew) into Castilian (old Spanish) and Galician-Portuguese, and to compose new works to serve the political and personal interests of the monarch. These works took the form of extraordinary books made by professional teams of copyists and illuminators who worked in coordination with the text's authors under the orders of the king, who played an active role in their commission and production [1–4].

This ambitious project has left us with a large number of manuscripts that, when studied together, reveal common features as they were produced in the royal scriptorium. We know these manuscripts and their textual and visual content much better today. However, many unknowns exist about their execution, especially technical aspects such as the type of materials and pigments used and the painting technique. Their study may shed some light on the production of manuscripts within an Iberian court in a highly sophisticated scriptorium. To clarify the color palette used in Alfonso's scriptorium, four manuscripts from the Royal Library of the El Escorial Monastery (Spain) have been analyzed, Figure 1; two manuscripts of the so-called *Songs of Holy Mary* (Cantigas de Santa Maria), a set of religious songs praising the Virgin Mary and depicting her miracles, the *Rich codex* (Códice Rico, T-I-1), and the *Musicians' codex* (Códice de los músicos, b-I-2); the *Lapidary* (Lapidario, h-I-15), a manuscript of scientific content that analyzes minerals and their applications in relation to the influence of the stars, and the *Book of Games* (Libro de los juegos, T-I-6), a treatise that analyzes different types of games from a social perspective.

Figure 1. Four manuscripts from the Royal Library of the El Escorial Monastery (Spain) were studied to uncover the color palette in Alfonso's scriptorium. Except for the *Book of Games*, which is dated, the other manuscripts have an approximate dating: *Rich codex*, ca. 1280–1282, *Musicians' codex*, ca. 1282–1284, *Lapidary*, ca. 1270–1275.

Besides these four Alfonsine outstanding codices, we will consider another exceptional illuminated manuscript, the *Ajuda Songbook*, an Iberian manuscript with 310 *cantigas de amor* (Provençal style male-voiced love songs) by Galician-Portuguese troubadours [5–9]. It is possible that it was created in royal or noble Iberian courts at the beginning of the 14th century or in the last decade of the 13th century. Indisputable points of contact between these Alfonsine codices and the *Ajuda Songbook* exist. Therefore, the comparative study between these manuscripts may prove relevant. To extend and complete the results, we will also compare with a group of French books of hours preserved in Portuguese collections that we have analyzed with the same methodology. In this way, we will have a broader spectrum of study.

Medieval pigments identified in Iberian medieval manuscripts are presented in Tables S1 and S2 in Supplementary material S1 [10–24]. In this Appendix, a brief introduction is also provided, and additional information can also be found in Supplementary materials S2–S4.

1.2. Establishing a Chronology through Natural Dyes in Illuminated Manuscripts—The Brazilwood Case

Concerning the contributions from our investigations on color materials within the *Ajuda Songbook*, the French-produced books of hours in Portuguese collections, and the Alfonsine manuscripts, we argue that organic colorants are one of the most promising materials for establishing a chronology, in particular the red hues: carmine, pink, and purple [20]. Among them, those obtained from brazilwood are particularly clarifying.

In medieval sources, we found descriptions of how to prepare the brazilwood lake pigments and the color ranges from pink to dark red. Most of the recipes of brazilwood describe the process of preparing a lake pigment, where the dye brazilein is extracted from the rasps of the wood with an alkaline or neutral solution and complexed with a metallic ion, usually by adding alum. This binding between the brazilein dye and the aluminum ion produces an insoluble pigment. Additives such as lead white and calcium carbonate were often added to reach the optimum precipitation pH, control the lake pigment's chemical and physical properties, and make it opaque.

Regarding carmines and roses from brazilwood, the currently accepted chronology would be from the end of the 13th century/beginning of the 14th century until the 16th century [25–28]. In this context and according to contemporary sources, the pink color produced from brazilwood is a luxury color [29].

These pigments were applied as colors using a binding media called tempera at the time. These tempera in medieval times and in medieval illuminations are based on: (1) proteins (e.g., collagen-based; glair, egg yolk); (2) polysaccharides (e.g., gum arabic, mesquite gum); and (3) mixed tempera (proteinaceous + gums). Quoting Stefanos Kroustallis, "El término latín "temperare" (...) definían el proceso de mezclar un color con su aglutinante en una disolución o emulsión acuosa y así se emplea en los tratados medievales de tecnología artística cuando se trata la preparación de los colores para la "pictura librorum" [30]". To know more, please see [31].

1.2.1. French Books of Hours in Portuguese Collections

Some of the brazilwood-based colors used in the books of hours can be reproduced using the recipes described in *the book on how to make all the color paints for illuminating books* (abbreviated as *book of all color paints*) [32,33]. Three formulations were identified in the pinks of the books of hours based on the fluorescence spectra in the visible. For this analysis, 80 emission and 80 excitation spectra were acquired in 18 brazilwood-based colors from 8 illuminated manuscripts produced between the 13th and 15th centuries. The formulations were designated BW1, 2, and 3 [33]. The color BW1 has the presence of calcium carbonate and lead white. In BW2 and BW3, calcium carbonate is accompanied by gypsum. The two colors are distinguished due to a higher proportion of gypsum in BW3. Furthermore, it was possible to compare and analytically match BW 1 and BW 3 with two recipes from the *book of all color paints* [33]. This was confirmed through their infrared spectra. To know more about these books of hours, see [33].

1.2.2. Ajuda Songbook's Pinks

Scientific analysis showed, for the light pinks in the *Ajuda Songbook*, a different formulation from that found in fifteenth-century books of hours and from all historical reconstructions of these colors prepared to date, Figure 2. In the pink color of *Ajuda Songbook*, in addition to the brazilwood lake pigment, lead white was also identified, which lightens the color, alongside calcium carbonate that is used as a filler. The binding media is based on mesquite gum [29]. These components are necessary for the stability and durability of the paint. An additive such as calcium carbonate is added in a proportion that does not alter its hue, sometimes improving color perception by increasing opacity. Furthermore, its presence improves the mechanical stability of the paint. It is interesting to note that, nowadays, it remains a filler commonly found in paint formulations, including high-quality ones such as artist pigments.

These pinks were applied to the architectural backgrounds and musical scenes, particularly in the aristocratic clothing [16]. Five shades of pink were studied from the garments used in folios 16r, 17r, 21r, 40v, and 59r, including three folios from Évora (fols. 16r, 17r, 40v) (While most of the manuscript of the *Ajuda Songbook* was found in Colégio dos Nobres in Lisbon at the beginning of the nineteenth century, a quire and loose folios were found in Biblioteca Pública de Évora, in 1842. These were then integrated into the main manuscript, but the existence of these loose folios points out to the location of the *Ajuda Songbook* in

Évora at a certain point in history [16,29]). Unlike the architectural background, the musical scenes are unfinished. Differences were found in the additives when compared to the pinks used in architecture. To better understand these "new" formulations, it was necessary to expand further the database previously built in our laboratory. So, thirteen brazilwood recipes were selected from seven Medieval treatises. From this work, the best match with the colors of the *Songbook* was a translucent rose obtained from recipes where egg white is used for extraction, and no other additives are present. The translucent rose was prepared as paint, using the same formulation from the architectural backgrounds. The correct proportions were determined through infrared spectra as translucent pink brazilwood lake pigment (0.4%), lead white (19.9%), calcium carbonate (4.9%), and mesquite gum (74.8%). For a more in-depth analysis, see [29,33,34].

An orcein-based purple was also identified on pages 1, 12, 13, 31, and 55. These complex purples are extracted from various lichen species [20]. These pages are included in the *Lineage* book, dated to the fourteenth century, and are bound with the *Ajuda Songbook*. They were used in the filigreed initials of the *Lineage* book. To know more about its identification, please see [20].

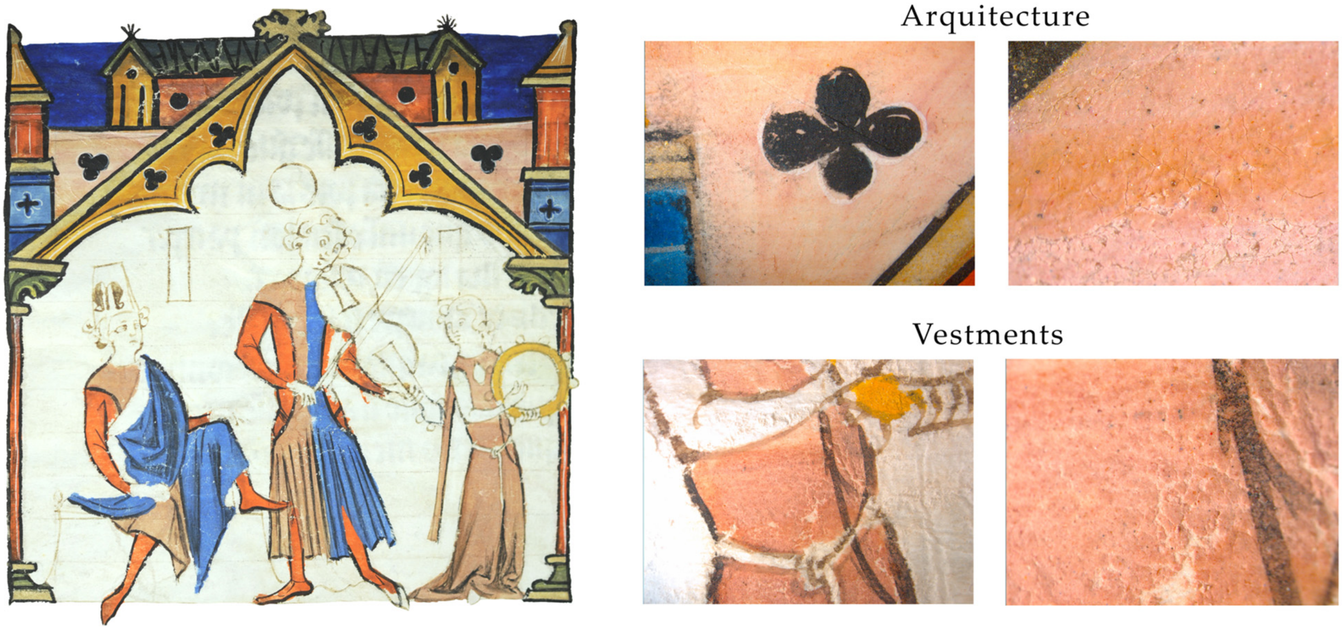

Figure 2. The pink colors in the *Ajuda Songbook* have a specific formulation. Details of these pinks in the architectural background and vestments (folio 21).

1.3. Brazilwood Trade during the Kingdom of Alfonso X

Brazilwood has been imported to Europe from Asia as *Biancaea sappan* since at least the 12th century, probably earlier, being introduced by the Islamic world into the Iberian Peninsula through the silk trade [35–37]. Its main use was possibly related to textile production. Still, the work carried out in recent years also proves its use in manuscript illuminations [16,38–40]. In the Iberian Peninsula, documentation proves the commercialization and circulation of brazilwood since the 13th century in the territories of Castile and Aragon [41]. The oldest record we currently know is a document relating to the customs duties of the Crown of Aragon, dated 1243. Even more intriguing are the privileges granted to the city of Murcia, issued on 18 May 1267 and then ratified on 28 April 1272, which express that the inhabitants of the city of Murcia can acquire and use any dye except indigo, lac dye, cochineal, and brazilwood since these were to be used only in textile production carried out in a cauldron managed by the court. However, in 1313 and 1322, a request was made to Alfonso XI to lift the ban on using these materials by the population, as was done in other places, claiming that the cauldron for royal textile production had never existed. Regardless of whether the monopoly on these dyes was effective, this information is important because it shows the use and commercialization of these colors [41]. According to Partearroyo Lacaba, the supply of brazilwood was interrupted in 1453 with the capture of Constantinople by the Turks [35]. The Portuguese resumed the commerce of the dye in 1500 in Brazil, using a different tree species, *Paubrasilia echinata* [42].

These accounts provide evidence that brazilwood was present in Iberian commerce since early medieval times and that being a luxury material [43], there was a clear wish from the Castilian crown to monopolize its production and use [41]. This can be confirmed by the consistent use of brazilwood in the analyzed manuscripts, as discussed in the Section 3 "Results and Discussion".

1.4. A Multi-Analytical Approach for the Study of Colors in Medieval Manuscripts

In a paint, there are several essential components: the colorant, the tempera, and the additives, which may have suffered degradation, depending on the history of the manuscript [34,44,45]. So, the paints of Alfonso X manuscripts were first analyzed using optical microscopy (magnifying from 7× to 80×) to understand how the final color was built up and to detect possible degradation phenomena (loss of adhesion to the support, changes in color, etc.). The complete identification of the paint requires molecular techniques such as infrared and Raman spectroscopy [34,38,46–52]. In the case of the colors of medieval illumination, we usually obtain complex signals that were decoded based on knowledge of molecular vibrations and by comparison with a database of references explicitly created for this study. It is complemented with elemental analysis using energy-dispersive X-ray fluorescence microspectrometry (microXRF) whenever possible. Using microXRF, elements are detected and semi-quantified. For paints based on organic colorants, our studies on medieval manuscripts have shown the advantage of combining microRaman spectroscopy, Fourier transform infrared microspectroscopy (microFTIR) with microspectrofluorimetry in the visible and fiber optic reflectance spectroscopy (FORS) in the UV–VIS [34].

Raman microscopy and microspectrofluorimetry, with a 1–5 µm analysis area, make it possible to selectively excite different paint components, thus simplifying the interpretation of the spectra [34]. However, these types of equipment are only available in the laboratory. Therefore, in our first on-site investigation at Escorial, it was decided to use portable instrumentation such as FORS (Fiber-Optics Reflectance Spectroscopy) and Raman, with 2 mm and 0.042–2.5 mm areas of analysis, respectively [38,49]. In future work, the complex formulations used in these colors will be explored using infrared and Raman spectra as well as fluorescence spectra in the visible [16,33,34,39].

2. Materials and Methods

2.1. Points of Analysis for the Four Alfonsine Manuscripts

The areas of analysis using portable Raman and FORS are described in Figures S25–S46 of Supplementary material S4. In the methodology used, each color was analyzed in at least three points using FORS per color hue (e.g., light blue and dark blue). This analysis was used to select the best areas to analyze via Raman, with at least one point per color. The folios were selected according to their interest and to have the widest range of colors possible, representative of each manuscript. The following folios were analyzed for each manuscript: fol. 192r and 212r for *Rich codex*; fol. 29r, 71v, 89r and 304v for *Musicians' codex*; fol. 1r, 8r, 9v, 41v, 49r, 62v, 63r, 87r, 104r, 106v, 108r, and 116v for *Lapidary*; and fol. 1r, 18r, 48r and 65r for *Book of Games*.

2.2. Preparation of Historic Paint and Ink Reconstructions

All reagents employed in this study were of analytical grade. A database of references was constructed and used for comparison to increase the confidence level for the identification of the historical paints. The paint references next described were made using 84% gum Arabic to 16% pigment in weight and applied with an nº 2 brush tool in circles of 2 cm^2 on parchment. The pigments used to prepare the reconstructions were purchased from May

& Baker LTD—Dageham England (vermilion), Kremer Pigmente—Aichstetten Germany (malachite, orpiment, bone black, and natural ultramarine blue), Zecchi Firente Italy (azurite), Aldrich—Missouri USA (indigo), PanReac—Castellan del Vallès Spain (red lead and verdigris), Casa Ferreira—Portugal (synthetic ultramarine blue), and Maimeri—Medigli MI Italy (raw sienna, sold under the name of yellow ocher).

Lead white was prepared in the laboratory at the Department of Conservation and Restoration of the NOVA School of Science—Lisbon Portugal. Lead white was synthesized using the stack process: lead plates were put into a glass container (height 15 cm, width 8 cm) with approximately 10 mL of vinegar without coming into contact with the liquid, and the container was closed. Upon formation of the white layer of corrosion—a process that typically occurs within weeks or months—the container was opened, and the lead white layer was collected. The pigment was then ground and washed three times with water. The pigments used were characterized to confirm their identity. Gum Arabic was purchased from Zecchi; the pieces were crushed to a powder, which was then dissolved in Millipore water to prepare a 20% solution.

The recipes studied related to the making of brazilwood can be divided into three colors: rose, translucent rose, and red. For more information on these recipes and typologies, consult the following work [29]. The brazilwood reference used for this work was made according to a recipe of Ms. Sloane 1754, inserted in the translucent rose typology: (1) the dye was extracted from 1g of rasps of the wood using 50 mL of egg white and left to extract for three days; (2) the extraction was filtered, and 1 g of alum was added, reaching a pH of 4.3. The paint was applied with an n° 2 brush tool in circles of 2 cm^2 on parchment.

The verdigris references were prepared using the following method: first, the verdigris was grounded and dissolved in a solution of commercial vinegar in 1:1 proportion (weight: volume); then, 1 mL of the dissolved verdigris was added to 10 mL of a solution of 20% of gelatin (collagen based), under constant stirring and heated to 40 °C. The preparation of the gelatin solution was made as follows: 2 g of leaves of alimentary grade gelatin Belbake® were weighted and cut into small pieces (<1 cm), and 10mL of Millipore water was added; the solution was stirred and heated to 40 °C until complete dissolution.

The resulting verdigris paint was applied in layers, waiting to dry between applications to a maximum of four layers.

For bottle green references, medieval recipes were considered. These advised the addition of an organic yellow to the verdigris paint to obtain green, as are examples in the recipes of the treatises *the Book of all colours paints* (pp. 216 and 220 in Strolovitch 2005) [53] and *Liber diversarum arcium* (pp. 113–115 in Clarke 2011) [54]. More treatises have been consulted, but the referred ones were studied more in-depth. The preparation of the bottle of green paints was as follows: the first part is the same as explained for the verdigris references, with the dissolution of verdigris in vinegar (1 weight: 1 volume). Then, add 1mL of the dissolved verdigris to 10 mL of a solution of 20% gelatin under constant stirring and heating at 40 °C. Finally, 2 mL of yellow weld extract is added, resulting in the bottle's green paint. The weld solution was prepared by adding 0.3 g of weld to 20 mL of Millipore water, and the solution was heated to 90° for 1 h, under constant stirring. The solution was then filtered. These bottle green paints were immediately applied on parchment in 2 cm^2 circles with a n° 2 brush. The paints were also applied in layers, waiting to dry between applications and to a maximum of four layers. The historical samples of bottle green used as part of the database for identifying the manuscripts were acquired with the same equipment and in the scope of a doctoral thesis [55].

The iron-gall ink reference was made following a 15th-century recipe found in the Archivo Histórico Provincial de Córdoba, Sección de Protocolos Notariales de Córdoba. The recipe is described elsewhere [56]. The paint was applied with a micropipette (60 μL) in squares of 2 cm^2 on filter paper.

2.3. Fiber-Optics Reflectance Spectroscopy

UV–VIS reflectance spectra were obtained with an Ocean Optics, MAYA 2000 Pro reflectance spectrophotometer equipped with single beam optical fibers and a Hamamatsu linear silicon CCD detector collecting spectra in a 200–1060 nm spectral range. The light source is an Ocean Optics HL 2000-HP halogen lamp with a 20 W output and a 360–2400 nm spectral range. Analysis was conducted with an 8 ms integration time, 15 scans, 8 box width, and 90°/90° reflection angle to the bearing surface, with a 2 mm spot. A Spectralon® white reference was used for calibration. Spectra are acquired from 350 to 800 nm and shown in reflectance (inorganic pigments) and apparent absorbance (dye-based).

2.4. Portable Raman Spectroscopy

The Metrohm Instant Mira DS Raman spectrometer (Mira DS Raman) is equipped with a 785 nm diode laser with a maximum power of 100 mW, enabling data acquisition within a spectral range of 200–2000 cm^{-1}. This equipment provides a spectral resolution of 8–10 cm^{-1}, using a laser spot of 40 µm and an area of analysis of 0.042–2.5 mm, depending on the working distance selected (adjustable in the 1–7.6 mm range). For the present work, a distance of 3 mm was preferably used, corresponding to a measuring spot diameter of approximately 1 mm. The detection technique was Orbital Raster Scan (ORS) that involves averaging the signal collected from relatively large sample areas (measuring spot) while maintaining the desired lateral resolution. All spectra were acquired with the maximum laser power and 10 scans, varying the integration time from 200 to 30,000 ms according to the target material. A minimum of three spectra were collected from the same sample to ensure data reproducibility. The spectra presented, when in the presence of a reference and not normalized, have two different y-axis, described in the figure or the caption.

When working with fragile objects, it is important to consider the energy used to analyze them, so the laser power density was calculated. The laser power density was calculated by dividing the laser power by the area of analysis. Calculations were made considering the maximum values possible, so the experimental values are generally even lower. The calculated area (circle) is 5026.55 μm^2, and the laser power is 100 mW, so the laser power density is 0.019 $mW/\mu m^2$.

3. Results and Discussion

3.1. The Molecular Palette Used to Produce the Colors of Alfonsine Manuscripts

Figure 3 presents the molecular palette used in Alfonso's manuscripts. The reds and oranges were obtained with vermilion and red lead, respectively. The pink colors are based on the brazilwood lake pigment. The main blue is prepared with lapis lazuli (natural ultramarine), followed by indigo and, more rarely, azurite. For the yellows, yellow ochre and orpiment were identified. In the greens, the bottle green, a synthetic copper proteinate, was applied in all the manuscripts, while *vergaut*, a mixture of mainly orpiment and indigo, was used in three manuscripts: *Musicians' codex*, *Lapidary*, and *Book of Games*.

The purples were obtained with a mixture of brazilwood lake pigment and a blue colorant, indigo, or natural ultramarine. Orcein purple was possibly also found in the third part of *Lapidary*. The black color was prepared using carbon-based black, and the whites were prepared with lead white. Gold is extensively used in these manuscripts.

Figure 3. The molecular color palette for the studied manuscripts of the scriptorium of Alfonso X.

3.2. Identification of Colors Based on Pigments through a Complementary Approach Using Fiber-Optics Reflectance Spectroscopy and Raman Spectroscopy

The colors were characterized using FORS and Raman spectroscopy, which allowed a better understanding of the two different color constructions present in this scriptorium: application of pure pigments, taking advantage of the support to create different hues and shades, and application of thick colors, with the use of additives and mixtures. To have an accurate characterization, the historical samples were compared to a robust database created using the references described in Section 2 "Marterials and Methods", which were thoroughly analyzed using both analytical techniques.

3.2.1. Pure Colors in the Rich Codex

Among the manuscripts analyzed, the *Rich codex* is the only one where pure colors were preferred, as previously discussed by Fernández Fernández [2,57]. In fact, the use of tonalities with various intensities on parchment is one of the distinctive features of this manuscript. In this color construction, the light/dark contrast was achieved via the illuminator using the support itself, controlling the thickness of the paints to obtain more or less concentrated hues. The preference for pure colors was observed through Raman spectroscopy, as presented in Figure 4. Vermilion and red lead were applied without additives, Figure 4a,b. The blues follow the same tendency, with lapis lazuli being used as a homogenous layer in backgrounds and frames (Figure 4c) and indigo for the architecture, vestments, frames, and in the case of Figure 4d for the depicted activity of grinding indigo itself. Azurite and orpiment were also detected in an isolated application, in folio 212r and 192r, respectively (see Figures S1 and S2, (Supplementary material S2)).

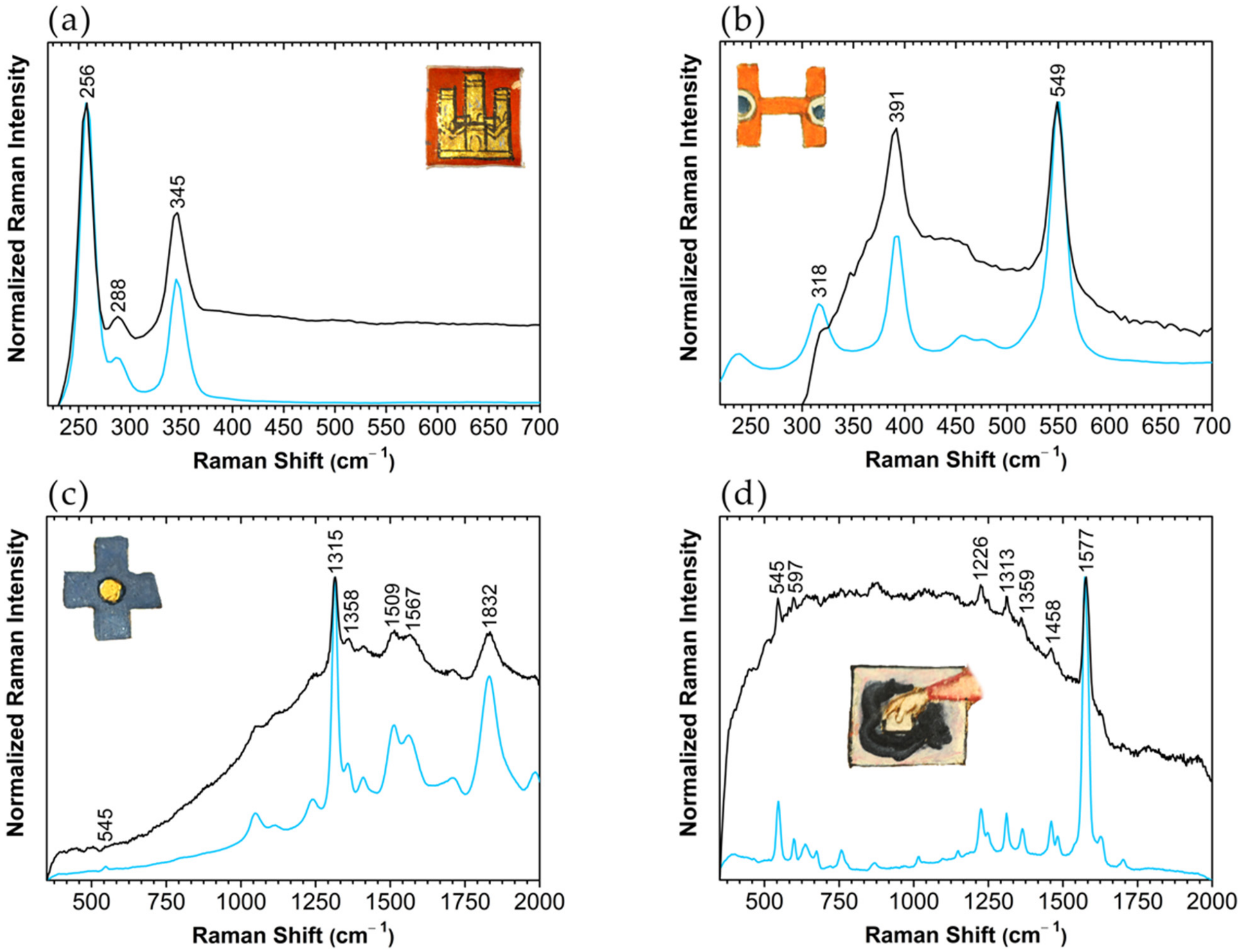

Figure 4. Raman spectra of red, orange, and blues in the *Rich codex* (black line) compared to reference spectra (blue line): (**a**) vermilion, (**b**) red lead, and (**c**) lapis lazuli applied in the background of the frame of fol.212r; (**d**) indigo paint applied to simulate the grinding of the same colorant in the illumination of fol.192r.

The only mixture paints found were purple, which will be discussed in further detail in the next section, and brown, acquired with lead white and an unidentified organic compound.

3.2.2. Colors in *Musicians' Codex*, *Lapidary* and *Book of Games*

Blues

Musicians' codex, *Lapidary*, and the *Book of Games* applied thick-layer paints with extensive use of mixtures and additives. Blue was the color that presented the highest number of variations. Lapis lazuli was the blue of choice in these manuscripts, applied as a pure pigment (Figures S3 and S4, (Supplementary material S2)) and in almost every mixture identified, Figure 5. Raman spectroscopy identified it by its characteristic bands at 545 and 1314–1316 cm^{-1}, which correspond to lazurite and fluorescence emission bands of diopside, respectively [58–61]. Lapis lazuli was mixed mainly with lead white (Figure 5a), identified by its main band at 1050 cm^{-1} ($\nu_s CO_3^{2-}$) to obtain lighter tones [62,63]. A second lighter mixture with lead white and calcium carbonate, detected by a weak band at 1086 cm^{-1} ($\nu_s CO_3^{2-}$), was identified in *Lapidary* (Figure 5b) [64]. Above these lighter mixtures, indigo was frequently applied as a thinner layer to obtain the darker shades or to form the draping of the vestments. In the Raman spectra, indigo was identified through its main band at 1575–1577 cm^{-1} (ν_sC=C, ν_sC=O) [65,66]. When observing the area of analysis, it seems to have been applied above the mixture of lapis lazuli and lead white in Figure 5c, above lead white in Figure 5d, and on top of lapis lazuli in Figure 5e.

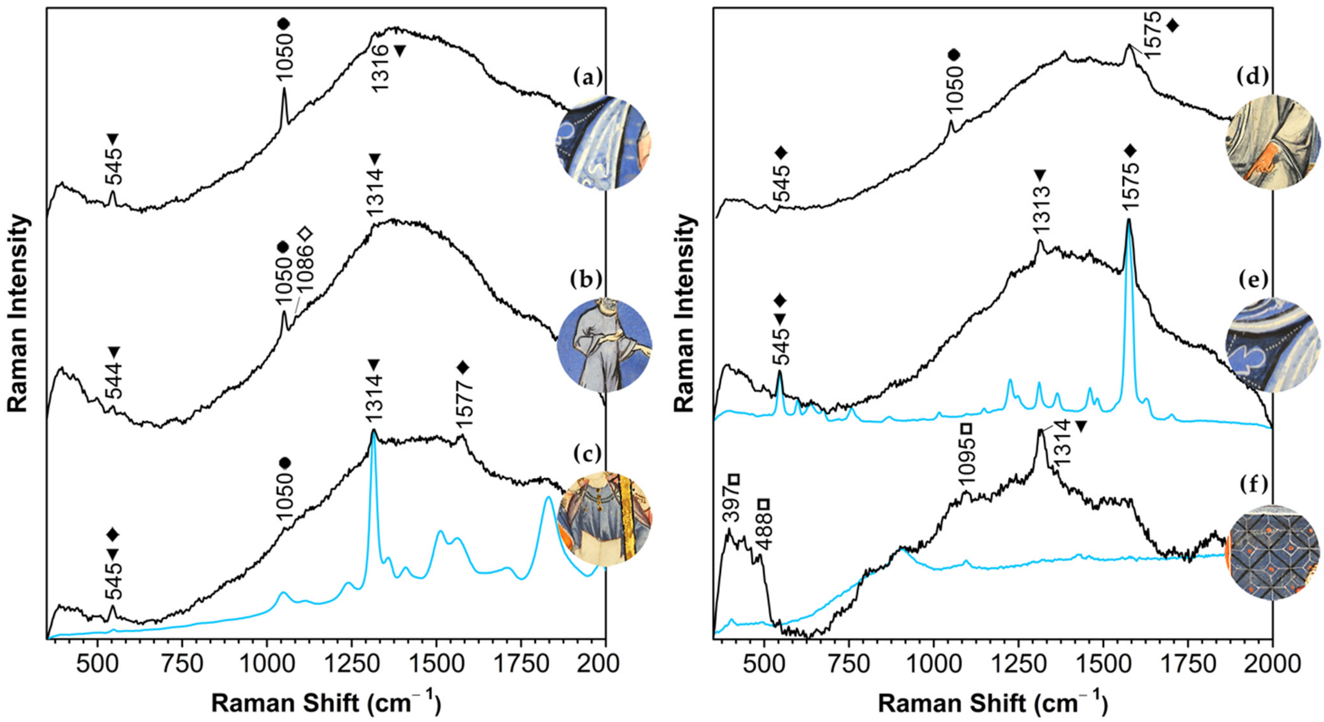

Figure 5. Raman spectra of blue colors (black line) compared with references (blue line) for (**a**) *Lapidary*, a mixture of lapis lazuli (▼) and lead white (●); (**b**) *Lapidary*, a mixture of lapis lazuli (▼), lead white (●), and calcium carbonate (◊); (**c**) *Musicians' codex*, a mixture of lapis lazuli (▼) and lead white (●) with indigo (⧫), compared with lapis lazuli reference; (**d**) *Book of Games*, indigo (⧫) applied over lead white (●); (**e**) *Lapidary*, mixture or layer of indigo (⧫) applied over lapis lazuli (▼) compared with indigo reference; (**f**) *Musicians' codex*, a mixture of lapis lazuli (▼) and azurite (☐) compared with azurite reference. Raman maximum intensity (counts) for the historical samples is between 1.7×10^4 to 3.8×10^4, and for the references: 4.5×10^4 (indigo), 5×10^4 (lapis lazuli), and 9×10^3 (azurite).

Also, a possible mixture of azurite and lapis lazuli was found in the backgrounds of the illumination in *Musicians' codex*. With the excitation laser used (λ_{exc} = 785 nm), the spectra acquired for azurite have less quality, so the bands of this pigment are more challenging to identify in a mixture. In this paint, weak bands corresponding to azurite can be found at 397 (lattice modes), 488, and 1095 cm^{-1} ($\nu_s CO_3^{2-}$) [67,68]. On a single occasion, it was possible to identify a mixture of lapis lazuli and carbon-based black, see Figure S5 (Supplementary material S2).

Reds and Oranges

As seen for the *Rich codex*, the reds and oranges are mainly applied as pure paints; for representative spectra, see Figure S6 (Supplementary material S2). Vermilion was used in the illuminations and the initials, while red lead was only used in the illuminations. Both were identified through Raman spectroscopy, vermilion by its main bands at 256 (δS-Hg-S), 287, and 345 cm^{-1} (νHg-S), and red lead by the bands at 390 (PbO_2 vibrational mode) and 548 cm^{-1}(νPb-O), Figure 6 [69–71]. The reflectance spectra of one paint area in *Lapidary* indicate the presence of vermilion, Figure 7. Due to its light color, it could be in a mixture with lead white; however, when comparing to a database of vermilion paints in a mixture with lead white, there is a shift of the inflection point to lower wavelengths, and this is not verified in the historical sample. Nonetheless, we do not have a Raman spectrum of the area to confirm.

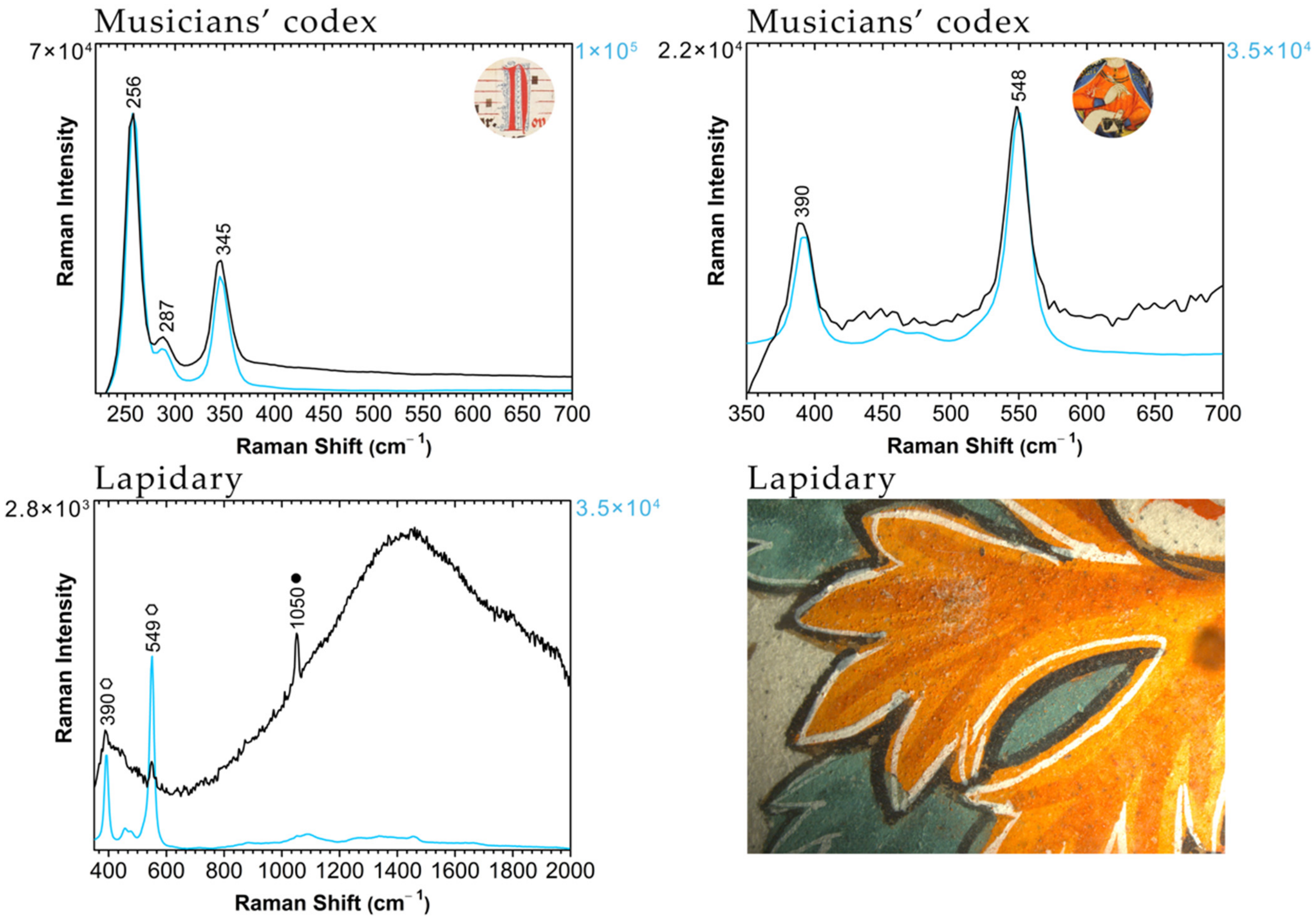

Figure 6. Raman spectra of red and orange colors (black line) compared with references (blue line) for *Musicians' codex* the vermilion used on writing is compared to a vermilion reference (**left**) and the red lead applied on vestments is compared to the red lead reference (**right**); in *Lapidary* it is possible to verify the probable influence of lead white (●) decorations in the Raman spectra of a read lead paint (○) (**left**) and respective detail of red lead paint with white lead highlights (**right**).

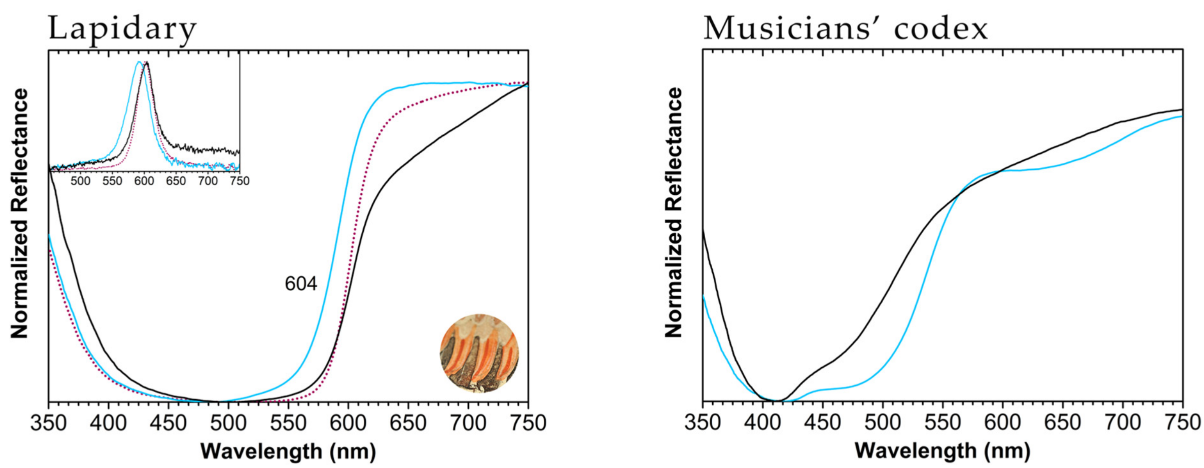

Figure 7. Reflectance spectra of red and yellow (black line) of light vermilion paint found in *Lapidary*, compared to a reference of vermilion (blue line) and a mixture of vermilion and calcium carbonate (red line) and of yellow ochre found in musical instruments and musicians' seats from *Musicians' codex* compared to yellow ochre reference.

For the red lead, on a few occasions, the Raman spectra indicate the presence of lead white, Figure 6. However, in all the areas of red lead analyzed, where this signal is present, it is possible to observe the presence of white highlights, Figure 6. So, the white lead signal might originate from those instead of a mixture of red and white lead, corroborating with the strong orange color observed.

Yellows

For the yellows, orpiment and yellow ochre were used. Nonetheless, the last pigment was only identified in one of the manuscripts, the *Musicians' codex*. In this manuscript, the reflectance spectra of the instruments and musicians' seats indicate the presence of yellow ochre, Figure 7. However, the Raman analysis of the same area indicates the presence of lead white, Figure 8. This points to a paint resulting from the mixture of yellow ochre with lead white. Orpiment, identified using Raman spectroscopy through its bands at 295 (δS-As-S), 312 (νAs-S), 355 (νAs-S), and 381 cm^{-1} (νAs-S-As), is present as a pure yellow in all the manuscripts, Figure 8c,d [69,72,73].

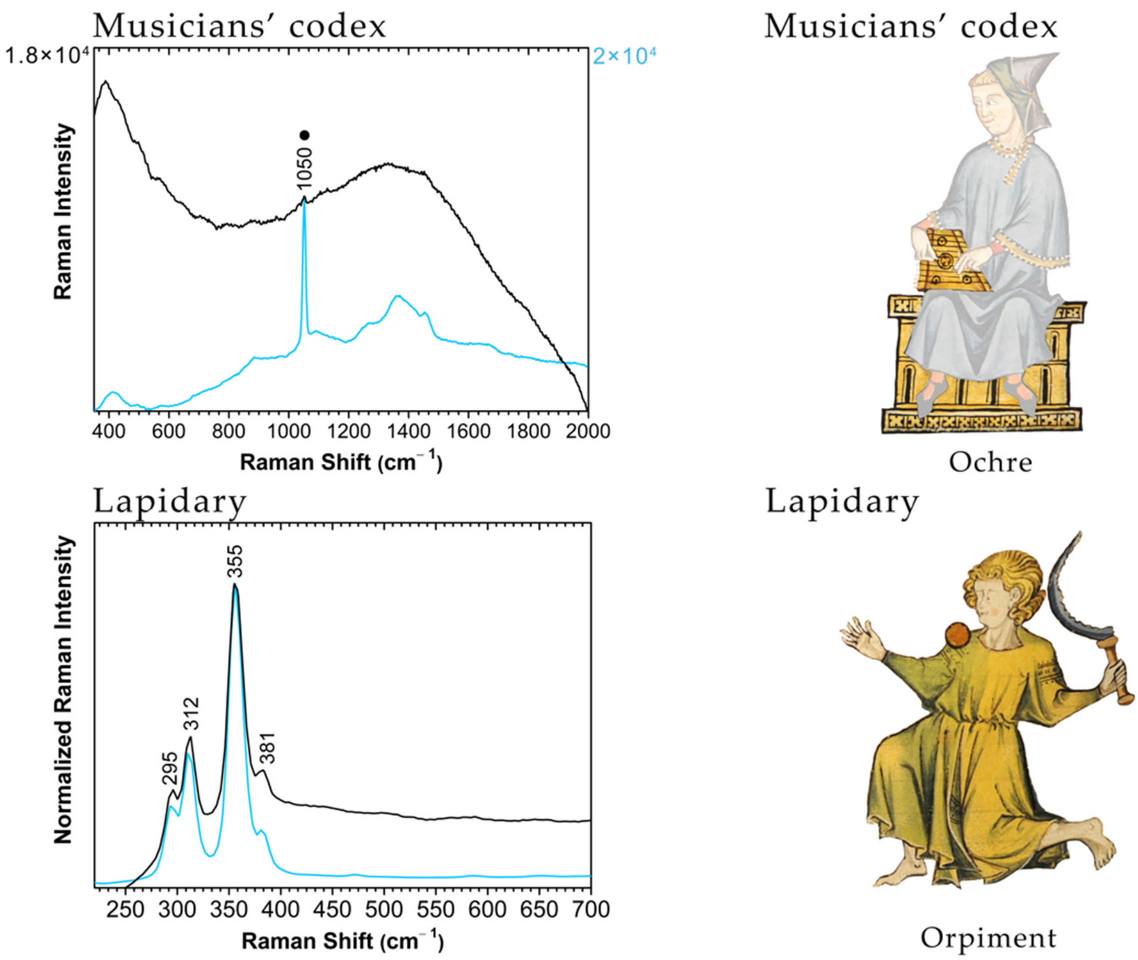

Figure 8. Raman spectra of yellow colors (black line) compared with references (blue line) for the lead white (●) in yellow paint of *Musicians' codex* (**left**) and respective detail of yellow musical instrument and musicians' seat (**right**); and for orpiment of *Lapidary* applied in the vestments, compared to an orpiment reference (**left**) and respective detail of yellow vestment found in *Lapidary* (**right**).

Greens

As shown in Figures 9 and 10, the manuscripts present two different greens: *vergaut* and bottle green. *Vergaut* was identified using Raman spectroscopy, which indicated the presence of orpiment in a mixture with indigo, Figure 9. This mixture can be found in all the manuscripts except the *Rich codex*, where bottle green is the green of election. While the orpiment and indigo are the main components found, in a few instances, the blue component can be lapis lazuli (see Figure S7a,b, Supplementary material S2). The second green, the copper proteinate, also known as bottle green, has been extensively found in manuscripts of Portuguese monastic production during the 12th and 13th centuries [45]. It was identified in all the manuscripts through FORS and comparison of the results with the spectra obtained for historical Portuguese samples, Figure 10; a more in-depth study with infrared spectroscopy is needed to confirm the identification of this synthetic copper proteinate. As in the Portuguese manuscripts, even though the bottle green's brightness and saturation have been preserved, it is detached from the support. Possibly, as in the Portuguese case, due to extensive chain scission and cross-linking of the binding media, which is confirmed by the presence of calcium oxalate [44]. In the Portuguese monastic production, we observed bottle greens with different degrees of degradation and could discuss it through a chemometrics study (pp. 86–94 in Miguel 2012) [74]. We studied various ways of preparing this bottle green, and what allowed us to achieve this type of color was using verdigris as a source of copper. A verdigris-based compound was also confirmed in a bottle green used in the Bible of the Santa Cruz Monastery (Sta. Cruz 1, 1151–1200, pp. 95–97 in Miguel 2012) [74]. This bottle green was also identified in an 11-12th century codex produced at the Fécamp Abbey (BnF Latin 5062; Coupry 1999, p. 76) [75]; for more details, see *3.2.1 Specificities of Portuguese medieval bottle green paints* in [74]. Moreover, two greens were identified in the *Book of Kells*: greens based on orpiment and indigo as well as copper-based greens. Possibly, the latter is also a bottle green paint. Doherty et al. used Raman and infrared spectroscopy to characterize these greens [49]. However, the infrared spectra were obtained in reflection mode, so essentially, calcium oxalate was identified (resulting from the degradation of the tempera).

In *Lapidary*, two different greens from the ones described previously were detected; one did not have enough Raman signal to be identified and did not correspond to bottle green through FORS and microscopic observation. The second is a mixture with calcium carbonate, identified using Raman, whereas the green component could not be determined (see Figure S7b,d, Supplementary material S2).

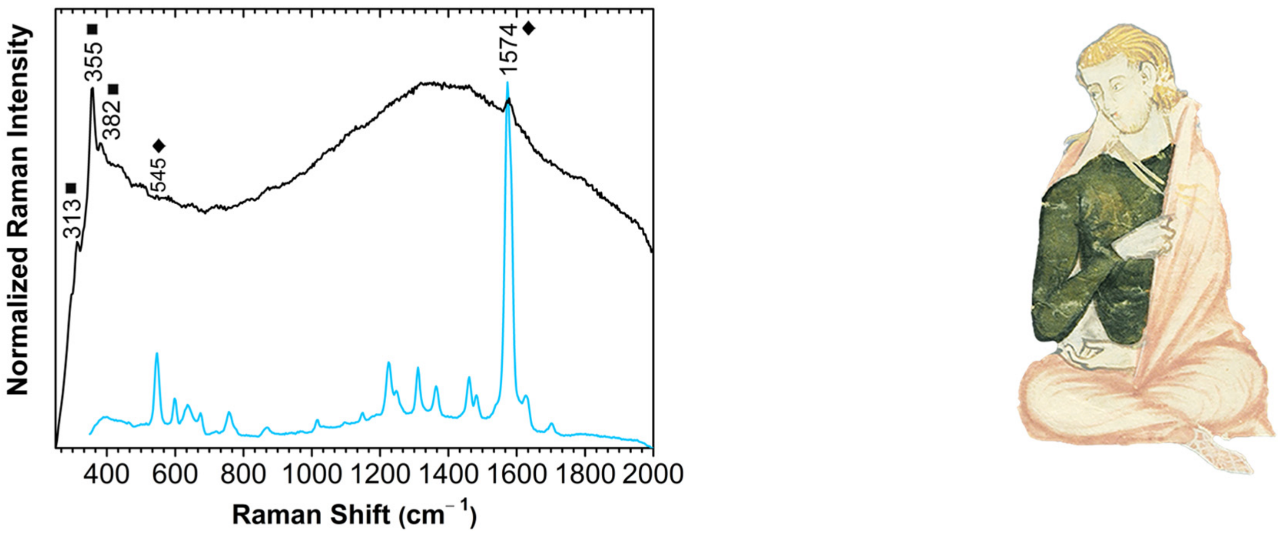

Figure 9. Raman spectrum of *vergaut* paint found in *Musicians' codex* (**left**) composed of a homogeneous mixture of orpiment (■) and indigo (♦) compared with indigo reference (blue line); and respective detail of green vestment obtained with the *vergaut* (**right**).

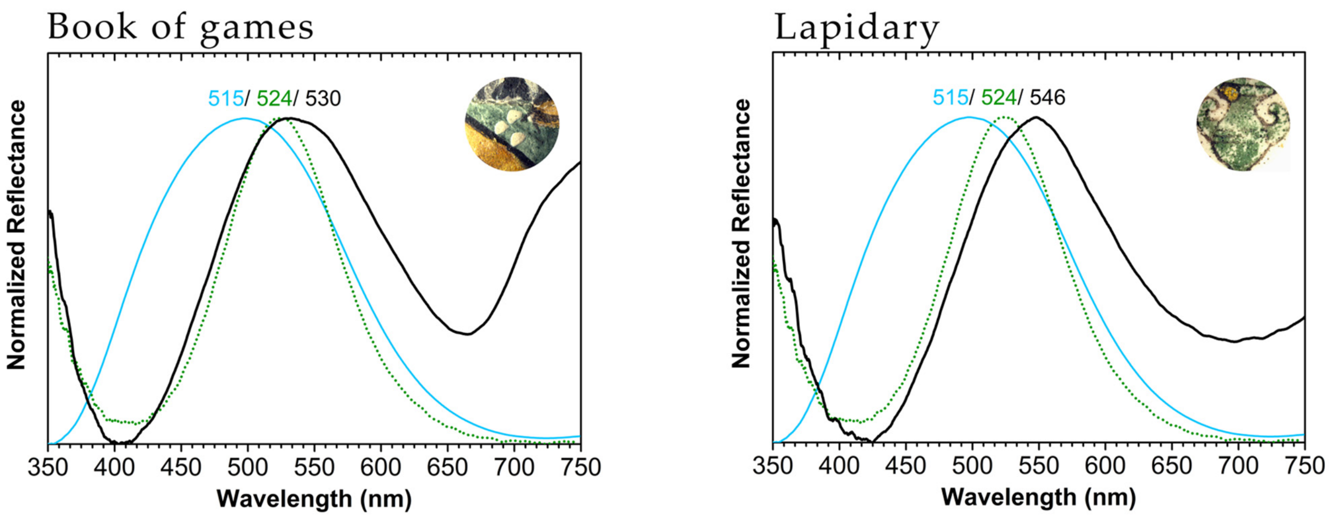

Figure 10. Bottle green in two manuscripts (black line) compared to a reference of verdigris paint (blue line) and a historical sample of bottle green found in manuscript ALC 238, also known as Alcobaça *De Avibus* (1180–1190) (green dotted line): Reflectance spectra of bottle green found in *Book of Games* and bottle green found in *Lapidary*. For more on ALC 238, see [55].

Browns, Greys, and Blacks

The browns found in *Lapidary* and *Book of Games* were obtained using a mixture of vermilion and carbon-based black, Figure 11. The bands that identify the presence of carbon are at ~1330 and ~1580 cm^{-1}; however, due to the less defined bands, it was not possible to identify which carbon-based black was used [76,77]. Carbon-based black and lead white were mixed to obtain the greys, Figure 11. Lead white and carbon-based black were also extensively used to paint elements and for the contours and highlights of the forms, respectively (see Figure S8a,c, Supplementary material S2). In *Lapidary*, black elements were also painted using iron-gall ink; see Figure S8b (Supplementary material S2).

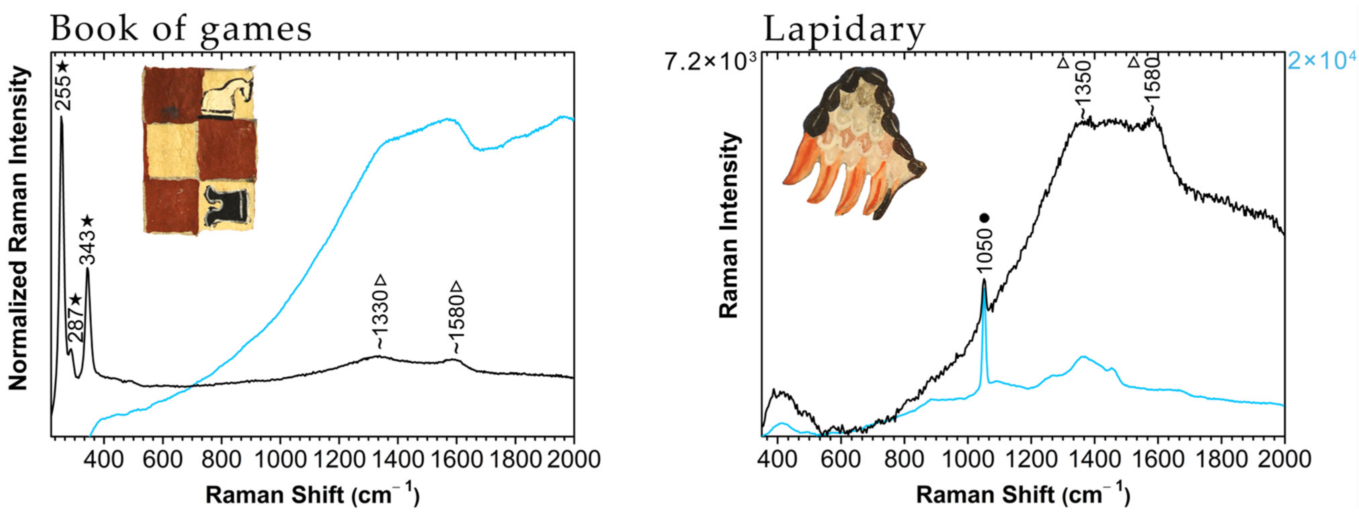

Figure 11. Raman spectra of brown and grey colors (black line) compared to reference spectra (blue line): a mixture of vermilion (★) and carbon-based black (Δ) found in *Book of Games* compared with carbon-based black reference; and a mixture of lead white (•) and carbon-based black (Δ) found in *Lapidary* compared with lead white reference.

3.3. Identification of Colors Based on Dyes through a Complementary Approach Using Fiber-Optics Reflectance Spectroscopy and Raman Spectroscopy

The pinks and purples identified in all the manuscripts have a colorant in common: brazilwood lake pigment. It was identified through its absorbance spectra, with a maximum of around 555 nm. The absorbance spectra can be very indicative of the presence of brazilein complexed with Al^{3+}; for more information, see Figure S9 (Supplementary material S2). To the authors' knowledge, the presence of brazilwood-based colors in this group of manuscripts turns them into the earliest evidence of their application in a medieval scriptorium.

The pinks in the *Rich codex* and the *Book of Games* were applied as a thin varnish-like layer without adding other components; as they were applied as a light color, it was possible to obtain good apparent absorbance spectra, Figure 12. The other manuscripts used it as a pure thick layer or within a mixture with lead white and additives. The most common mixture found was brazilwood lake pigment with lead white in the *Musicians' codex* and *Lapidary*. A less defined band characterizes the absorbance spectra of this mixture compared to the previous paints, Figure 12, while the Raman spectra allowed the identification of lead white, Figure 13. Apart from the lead white, gypsum and calcium carbonate were also found, possibly used as fillers to improve the performance of the paints, Figure 13. For representative apparent absorbance spectra of the pinks applied in the manuscripts, see Figure S10 (Supplementary material S2).

In all the manuscripts, the purple used in the illuminations was found as a mixture of brazilwood lake pigment with a blue and, in some cases, other additives. Figure 12 presents the typical apparent absorbance spectra acquired for most of the purples analyzed, which points out the presence of brazilwood by the band at 556 nm and indigo by the band at 648 nm. In the same analysis point, Raman identified indigo by the band at 1572 cm^{-1}, Figure 14. In the *Musicians' codex*, *Lapidary*, and the *Book of Games*, lead white was also identified, Figure 14. Lead white might have been added in these cases to lighten the color. In the *Musicians' codex* purple, lapis lazuli is the blue used, and indigo was not detected by the equipment. For representative apparent absorbance spectra of *Musicians' codex* and *Lapidary* see Figure S11 (Supplementary material S2). In *Lapidary*, a purple paint of higher complexity was identified, using brazilwood lake pigment, lead white, and vermilion as the base paints and a thinner layer of indigo to acquire the shades for the draping of the vestments, Figure 14.

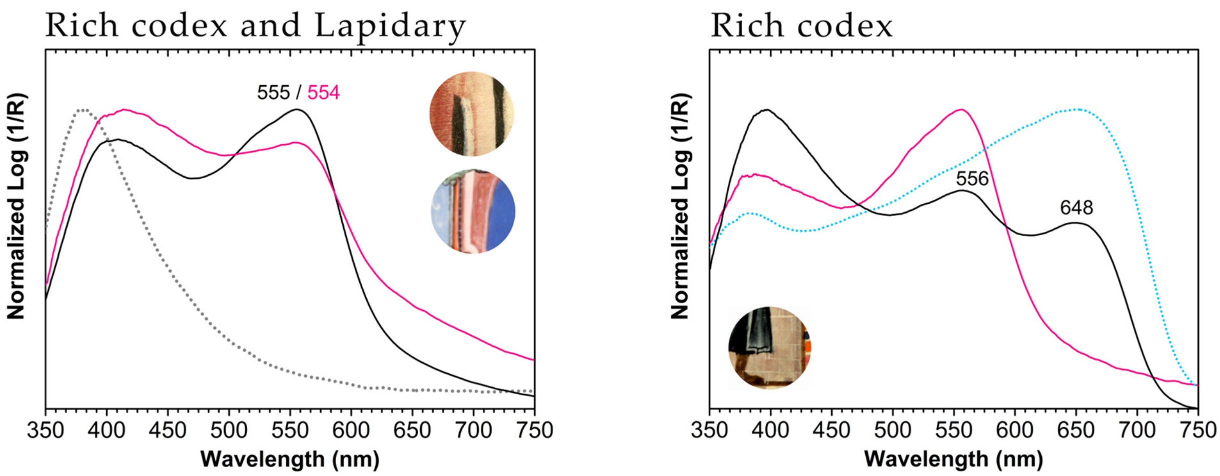

Figure 12. Pink and purple colors found in the four manuscripts compared to reference spectra (blue line): apparent absorbance spectra of pink brazilwood color in *Rich codex* (black line) and of *Lapidary* (pink line) compared to parchment spectrum (grey line); and apparent absorbance spectra of purple color in *Rich codex* compared to brazilwood (pink line) and indigo (blue line) references.

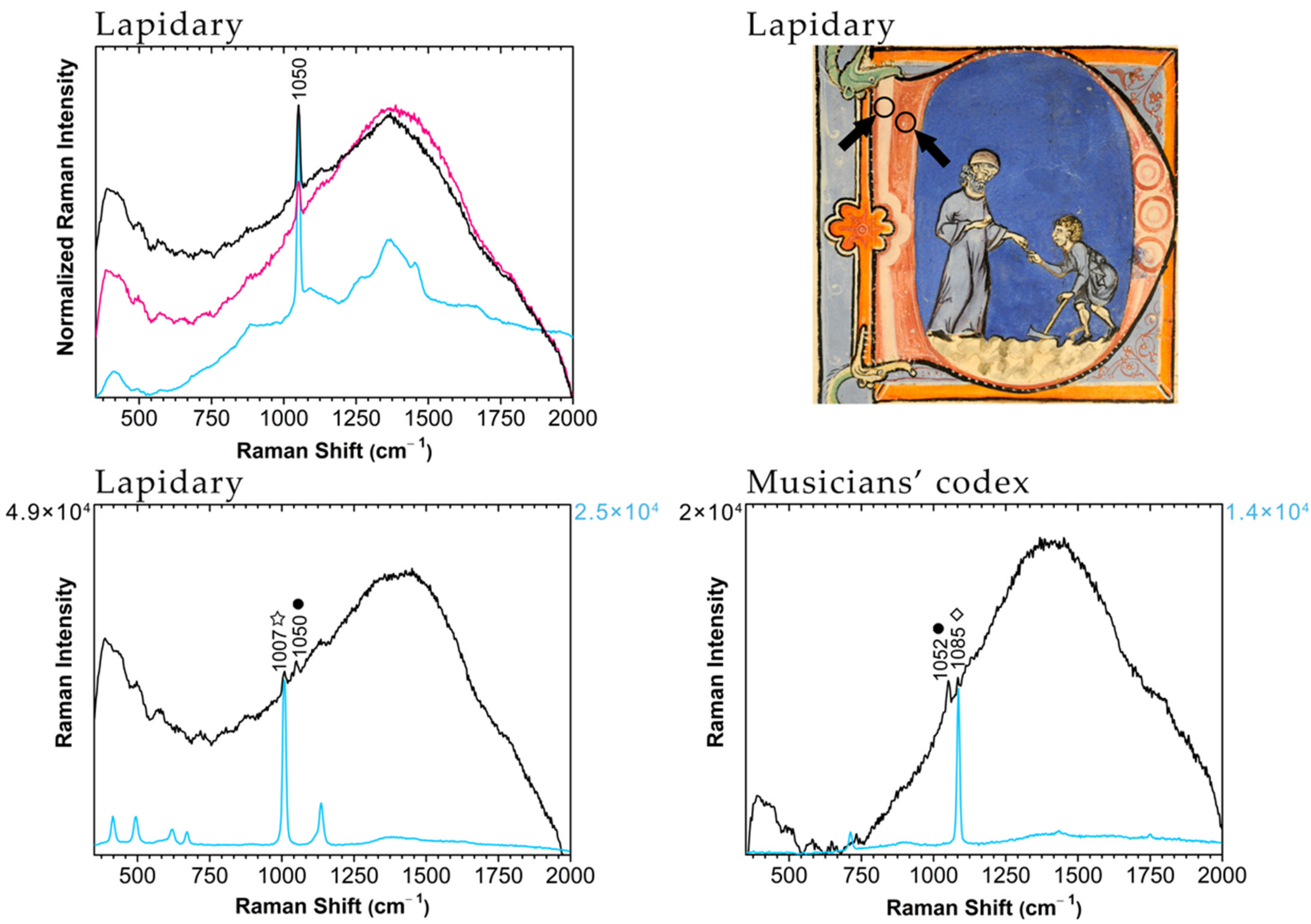

Figure 13. Raman spectra of pink colors in the four manuscripts compared to reference spectra (blue line): pink from *Lapidary* pointing out to the higher quantity of lead white in the lighter areas (black line) compared to the darker areas (pink line), and lead white reference (**top left**) and historiated initial with respective lighter and darker pink signaled (**top right**); Raman spectra of brazilwood pink with mixture of lead white and gypsum found in *Lapidary* compared to gypsum reference; and Raman spectra of brazilwood pink with a mixture of lead white and calcium carbonate found in Musicians codex, compared to calcium carbonate reference. The main Raman bands are assigned to lead white (●), gypsum (☆), and calcium carbonate (◊).

3.4. Writing Inks

The black writing inks were identified using Raman spectroscopy as iron-gall inks. Iron-gall inks, which have been used since antiquity, are prepared using a polyphenolic extract from galls, an iron salt, usually iron sulfate, and gum arabic to keep the precipitate formed in suspension.

The inks analyzed belonged to three manuscripts: the *Musicians' codex*, the *Lapidary*, and the *Book of Games*. By comparing the data, it is possible to disclose three different ink signals or typologies: INK 1, present in the *Musicians' codex* with main peaks at 1337–1339 cm^{-1}, 1394–1398 cm^{-1}, 1484–1489 cm^{-1}, and 1588 cm^{-1}; INK 2, present in fol. 29r of the *Musicians' codex* where a broad band at 1575cm^{-1} might indicate the mixture with carbon-based black; and INK 3 present in the *Lapidary* and the *Book of Games* with main peaks at 1333–1342 cm^{-1}, 1475–1480 cm^{-1}, and 1581 cm^{-1}, see Figure 15. The shifts among the main bands from inks 1 and 3 might be an indication of a different ink formulation or different degradation stages. A larger dataset is needed to draw further conclusions, as well as X-ray fluorescence analysis.

Ponce and coworkers proposed for the iron-gallate structure the following assignments: COO− and C–O stretching modes at 1315–1350 cm^{-1}, C–C ring vibrations at 1470 cm^{-1}, and the symmetrical and asymmetrical vibrations of a coordinated –COO−, to a metallic ion at circa 1430 cm^{-1} and 1579 cm^{-1} [78]. Nonetheless, because the iron-gall ink structure is yet to be disclosed, further studies are necessary to fully understand the attributions of the main iron-gall ink bands in Raman. By comparing this to the data acquired in the Alfonsi manuscripts, it is clear that the C–C ring vibrations at 1470 cm^{-1} are shifted towards higher wavenumbers (1475–1489 cm^{-1}), while the symmetrical vibrations of coordinated –COO− at 1430 cm^{-1} are shifted considerably towards lower wavenumbers (1394–1398 cm^{-1}). This might indicate a more complex structure than a simplified iron-gallate, as it has been shown in previous publications [56,79,80].

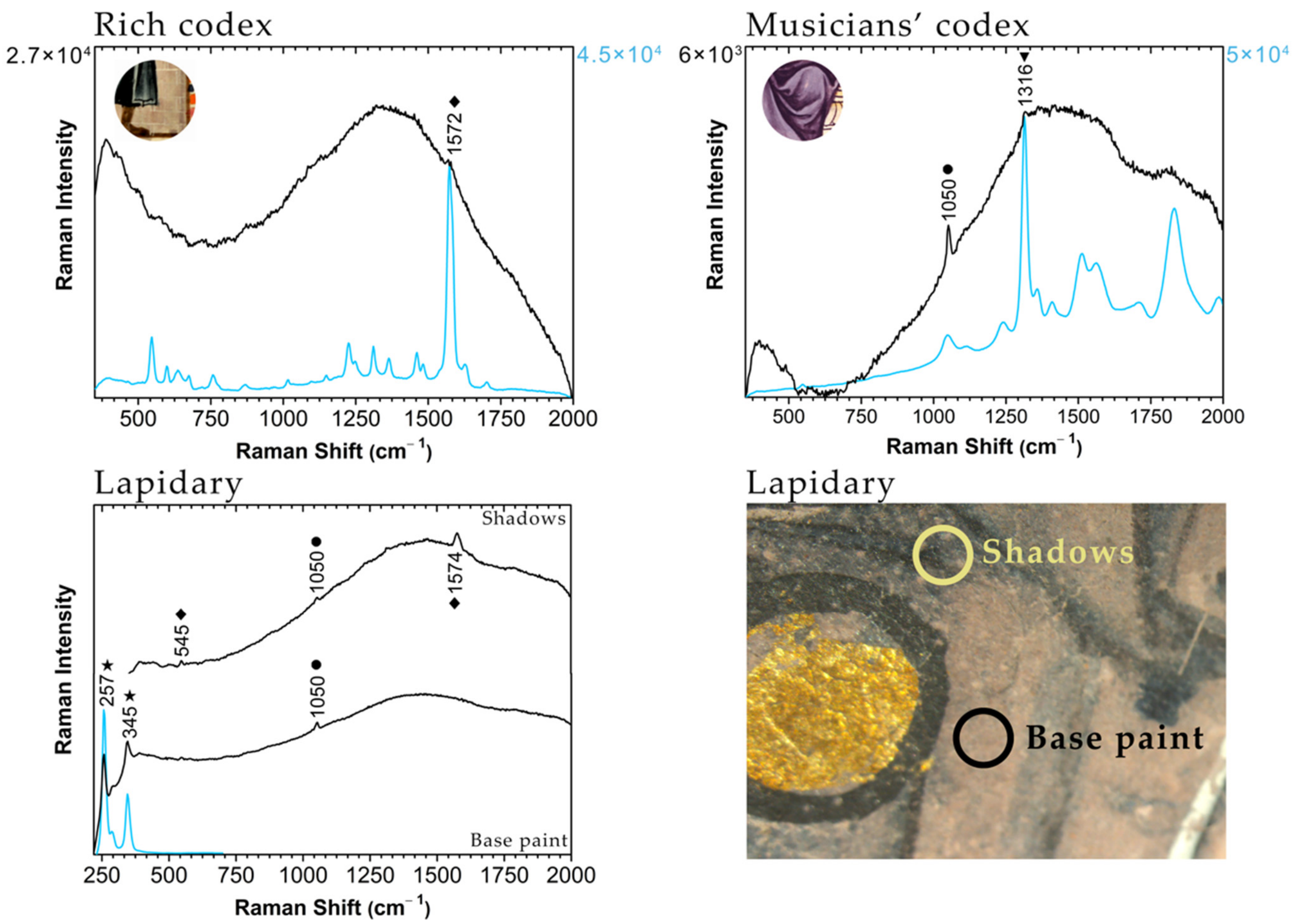

Figure 14. Purple colors based on a mixture of brazilwood lake pigment with a blue, in the four manuscripts analyzed (black line), compared to reference spectra (blue line): Raman spectra of the purple color in *Rich codex* that confirms the presence of indigo; purple found in *Musicians' codex* resulting from the mixture of brazilwood (identified using FORS), lapis lazuli and lead white compared with lapis lazuli reference; a more complex purple found in *Lapidary* obtained from the mixture of brazilwood (identified using FORS), vermilion and lead white and the application of an indigo layer (**left**), and detail of the area of analysis of this paint with base paint and shadows signaled (**right**). The main Raman bands are assigned to indigo (⧫), lapis lazuli (▼), lead white (●), and vermilion (★).

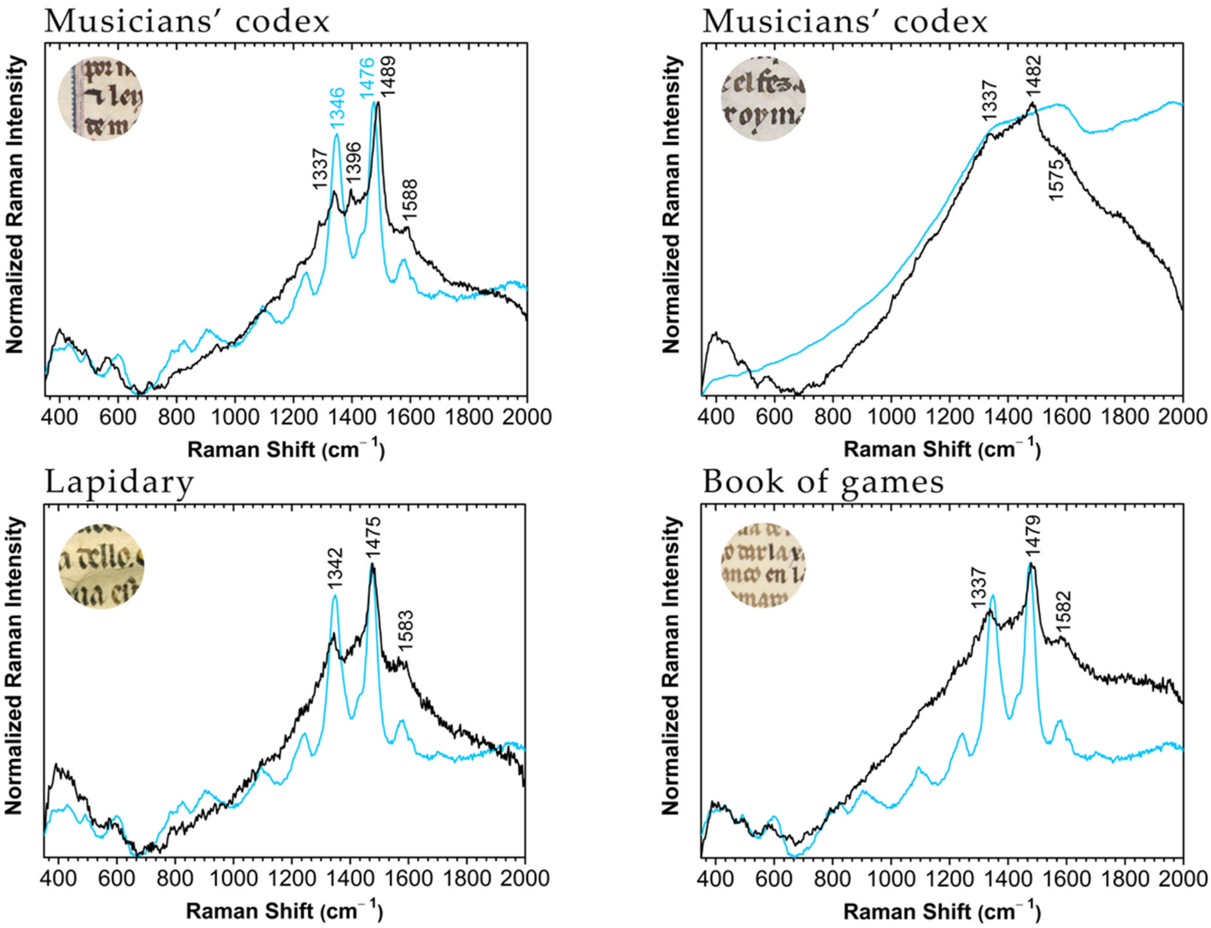

Figure 15. Raman spectra of iron-gall inks from three different ink typologies (black line) compared with references (blue line): INK 1 from the *Musicians' codex*, fol. 71v compared to iron-gall ink reference (**left**); INK 2 from fol. 29r compared to the bone black reference (**right**); INK 3 from the *Lapidary*, fol. 1r compared to iron-gall ink reference; and from *Book of Games*, fol. 18r compared to iron-gall ink reference.

3.5. Painting Technique and Comparison of Selected Materials and Techniques in Alfonso's Scriptorium and the Ajuda Songbook

3.5.1. The Main Steps to Paint a Medieval Illumination and Initial

The only medieval technical treatise in which we may find relevant information on the art of constructing an illumination is the mid-fifteenth-century *Göttingen Model Book* (hereafter, GMB). In a previous study of the Alcobaça Beatus [15], we verified that the GMB painting process was applied in its initials. This is because some decorated initials were left unfinished, allowing the reader to learn more about the precise sequence of steps used and compare them with the steps proposed in the GMB.

The GMB outlines the fundamental steps involved in the creation of ornamental illuminations, which may be summarised as follows: (1) drawing with a thin line and applying the main colors, (2) outlining, (3) shadowing, and (4) highlighting. For more details, see Figure 16 in the article of Miguélez Cavero and coworkers, "Beatus manuscripts under the microscope" [15]. A further comparison was made with the information provided by the GMB with that in the *Liber diversarum arcium*, which Mark Clarke suggests was largely written around 1300 and which offers unique and precise instructions on how to prepare color paints for illumination, describing which colors can be used to shadow or highlight [54]. Here, for example, exact instructions for the construction of the green *vergaut* can be found. The combinations of a yellow with a blue or black are described in the *Liber diversarum arcium*; under "yellow-green" and "green". For "yellow-green": "If you want to make yellow-green. Mix orpiment with black, *matiz* with orpiment". For "green": "Put orpiment and indigo or azure, makes yellow-green, *incide* with indigo tempered with vinegar or with azure such that it should be more green, *matiz* with orpiment" [54].

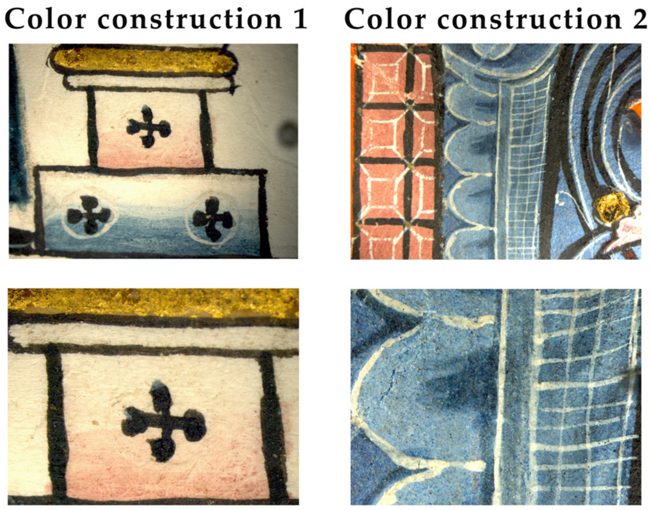

Figure 16. Details on the two different color constructions found in the scriptorium of Alfonso X. On the left are details from folio 212r of the *Rich codex*, where the paint was applied in thin layers, taking advantage of the color of the parchment support itself. On the right are details from folio 29r of *Musicians' codex*, where paints were applied in thicker layers and a mixture to obtain the lighter areas.

3.5.2. Painting Technique in Alfonsine Illumination

In the case of the Alfonsine manuscripts, we have an exceptional document, at least for the manuscripts of the *Songs of Holy Mary*, the Códice de Florencia (Florence Codex), Biblioteca Nazionale Centrale di Firenze, BR. 20. This manuscript was conceived as the second volume of the *Rich codex* and was intended to collect the poems of the book of songs devoted to the Virgin commissioned by the king from song 200 onwards. The structure of this book is the same as that of the *Rich codex*, and each song has an illuminated folio divided into six vignettes, except for the cantiga ending in number five, which has a double illuminated folio, that is, twelve vignettes, always framed by a large border with alternating floral and geometric motifs. This manuscript was left unfinished at the king's death, and its folios show different phases of the pictorial process, from the lead pencil sketches of the figures to the perfectly finished scenes. Throughout the folios, the different phases can be seen: general drawing, brown ink revision to emphasize the outline, both of the border and the architectural frame and figures, coloring of the border, application of gold, application of color in several layers, and finally the realization of the faces and hands. It is important to note that the progress is not always linear, from the first vignette to the last, but variable; it can depend on the absence of precise indications or the lack of a clear model (f. 56r, f. 99r), even sometimes the border and the composition are worked on at the same time. The use of just one color in different scenes of the folio is noticed (f. 76v).

Contrary to the Florence Codex, all the illuminations are completed in the four codexes studied. The painting technique most likely shows different illuminators, as we found diverse materials, techniques, and ways of applying colors, as discussed hereafter. For additional information, see Supplementary material S3. To shade and model, indigo blue and brazilein pinks are applied as colored varnishes; indigo blue is used to shade clothes and frames for modeling the desired shape, Figure S12 (Supplementary material S3). For *Musicians' codex*, *Lapidary*, and *Book of Games*, the colors are applied in thick layers, and there is a wide use of paints resulting from the mixture of a primary color and black or white. For example, black is mixed with vermilion to obtain brown, while white is mixed with brazilwood to obtain pink. In the *Rich codex*, colors are applied as thin layers, without mixtures, taking advantage of the parchment color, Figure 16. Both dispense the golden backgrounds characteristic of other manuscripts.

Two colors need attention: the purples and greens. Besides the purples resulting from brazilwood lake pigment and a blue (indigo or lapis lazuli), discussed in detail in Section 3.3, in the third treatise of *Lapidary*, the initials are decorated with pen-flourished motifs, possibly using an orcein purple. The fact that this colorant does not appear in the first and second treatises of the manuscript or on the other manuscripts could indicate that it may have been completed in a later chronology. Undoubtedly, this aspect could be expanded with further analysis. For the purple, in the *Rich codex*, the pink and blue were applied in layers, while in the other two manuscripts, they were used in thick layers and as mixtures.

For the greens, it was possible to identify bottle green and *vergaut* as a homogeneous mixture of orpiment and indigo. These colors will be further discussed in Section 3.5.3.

Architectural backgrounds were used in the *Rich codex*, *Musicians' codex*, *Book of Games*, and Folio 1 of *Lapidary*. Although the general organization of these architectural elements is diverse, there are similar ways of making them, as for windows and roofs, Figure 17. Different masters created these elements, each with their own style. For comparison with the architectural elements in *Ajuda Songbook*, which show great mastery in outlines, shadowing, and highlighting, see Figure 17 (right). Within the Alfonsine illumination, outlines and highlights have been applied with greater delicacy in the *Rich codex* and the *Book of Games*. In the latter, special attention was paid to creating architectural effects using thin white lines; for example, in folio 19r, Figure 17. In the *Musicians' codex*, we observe a detailed practice in folio 29r and bold applications in folio 341r, Figure S14 (Supplementary material S3).

Figure 17. Details of the architectural elements in Alfonso's manuscripts compared to the architecture of the *Ajuda Songbook*. The forms are the trilobate windows (**top**), windows (**middle**), and roofs (**bottom**).

In the *Rich codex* and *Musicians' codex*, it was possible to detect two ways of making the faces indicating the presence of at least two illuminators. In both manuscripts, one of the illuminators paints with delicate strokes of iron-gall ink over the main color; the small pupils in the eyes were made in black and sometimes outlined with indigo blue, and the detailed lips were created with orange and carmine, Figure 18 (top). For the second illuminator, the faces were always represented in three quarters; the pupil was painted in black and more prominent, the lips were obtained with just one line, and the cheeks acquired a more intense orange hue, Figure 18 (middle). For both manuscripts, the hands appear to have been created by one of the illuminators, where the lines were obtained with iron-gall ink and with the same delicacy as the faces of the first illuminator, Figure 18 (bottom).

Figure 18. Details the color construction in the faces (**top** and **middle**) and hands (**bottom**) in Alfonso's manuscripts.

In the *Book of Games*, the way of making the faces is always the same, but the hands show different practices. In the faces, the illuminator used a thick color with a pinkish hue for the cheeks and outlined the features in black. The eyes were painted white and outlined in black; the same black is used for the eyebrows, and the reliefs are shadowed, Figure 18 (top and middle); a carmine/orange color was applied to the lips and used for the cheeks. In *Lapidary*, there are two ways of making the faces; the faces are constructed like previously described for *Book of Games*, and in a second way, the only difference is that the eyes, instead of being wholly outlined, only the upper part is drawn, Figure 18 (top). For both manuscripts, a white layer was applied to the hands; however, in the *Book of Games*, two outlines were found, done with iron-gall and carbon-based black; for *Lapidary*, these were made only with carbon-based black, Figure 18 (bottom).

3.5.3. Comparison of Selected Materials and Techniques in Alfonso's Scriptorium and the *Ajuda Songbook*

Color specificities and the techniques used to create the illuminations are essential to understanding when and where these manuscripts were produced. Concerning the pigments used in the colors, there is much in common in both scriptoria, those of Afonso X and the one that made *Ajuda Songbook*. The exceptions are the colors based on mosaic gold and gold, the first only used in the *Ajuda Songbook* and the latter only in the manuscripts of Afonso X. As well as bottle green, only identified in Alfonso's scriptorium. Based on the color chronology, we can propose that the *Ajuda Songbook's* production was carried out slightly later than the manuscripts of Afonso X, given the absence of bottle green and the use of mosaic gold. Because the *Ajuda Songbook* was also produced in the context of an Iberian court (regal or nobiliary), the comparison with the same colors found in the scriptorium of Alfonso X may shed light on the production framework of these manuscripts. Considering this, even though it is possible to find parallelisms between the *Ajuda Songbook* and the Alfonsi manuscripts, pointing to a shared cultural context, the ways of preparing the paints differ. Three of the most important colors in both scriptoria will be compared and discussed: pink, blue, and green.

Pinks

When comparing the pinks found in Alfonso's scriptorium and the *Ajuda Songbook*, one aspect is visible: both use brazilein as the main dye. The *Ajuda Songbook* used lead white and calcium carbonate to produce the pinks in the walls with the trilobate windows of the architecture [16,29]. In comparison, the *Musicians' codex* and *Lapidary* use lead white in the pink colors. On the other hand, the *Rich codex* uses the parchment color and a thin layer of brazilwood paint to produce a lighter hue without additives. The formulation of the pinks found in the vestments of the *Songbook* differs substantially. Through Raman spectroscopy, calcium carbonate was shown to be extensively used in the vestments of the Ajuda Songbook, and sometimes in a mixture with gypsum. (fols. 16, 21, 33, 37, 40), Figure 19a. However, calcium carbonate was not detected as the sole additive in Alfonso's manuscripts. Although the formulations found in the Alfonsine scriptorium can have variations, such as using lead white with calcium carbonate or lead white with gypsum, there is a common trend based on the use of lead white.

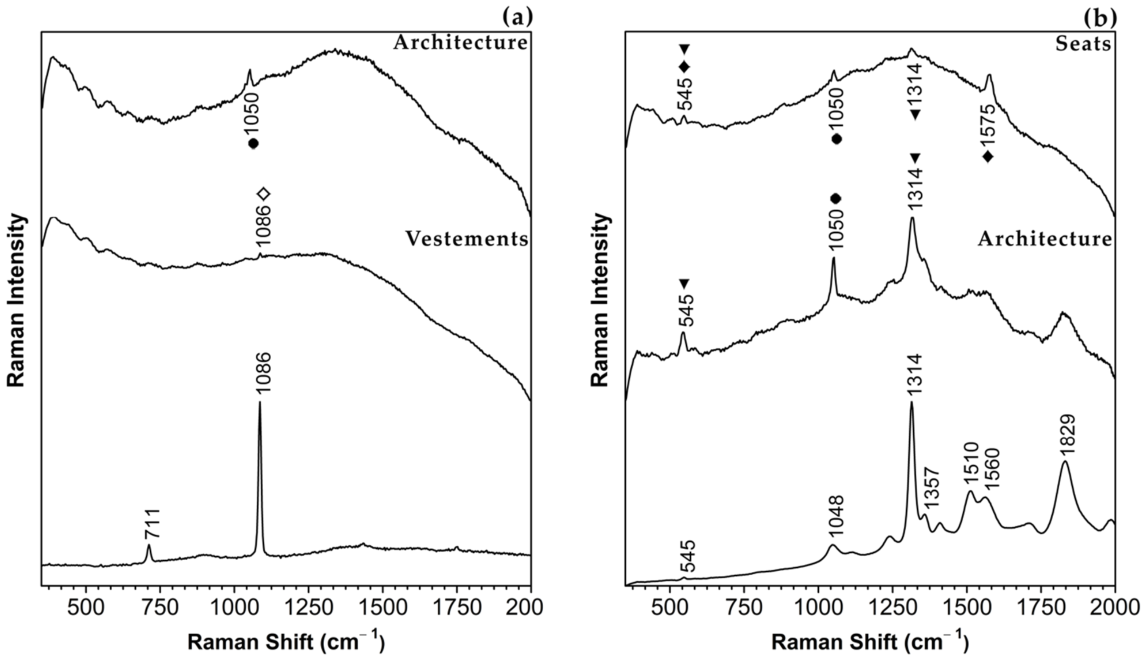

Figure 19. Raman spectra from the (**a**) pinks of the architectures and vestments and from the (**b**) blues of the seat and architecture in the *Ajuda Songbook*. Both colors show the use of additives such as lead white and calcium carbonate to control the lighter tones and the application of indigo for the shades. The main bands detected are assigned to lapis lazuli (▼), indigo (⧫), lead white (●), and calcium carbonate (◊).

Blues

Analyzing the blues of the *Ajuda Songbook* and the Alfonsi manuscripts, it is possible to observe four common formulations: (1) the blue skies composed of pure lapis lazuli, a luxury color; (2) a lapis-lazuli/lead white mixture, applied in several elements of the Alfonsi manuscripts and the towers of the architecture in the *Ajuda Songbook*, Figure 19b; (3) a lapis-lazuli, lead white and calcium carbonate mixture, only found in *Lapidary* and the vestments of the *Songbook*; (4) the shading of the lapis-lazuli/lead white mixture with thin layers of indigo, exclusively found in the draping of the textile covering the seat of the noble's in the *Ajuda Songbook*, Figure 19b. This color construction is one of the most common blues in the Alfonsi manuscripts. Nonetheless, the Alfonsi manuscripts present a wider range of mixtures and layered paints, adding to the ones shown, compared to the *Ajuda Songbook*.

Greens

Finally, bottle green was possibly used for the greens, similar to that found in Portuguese monastic production of the 12th and 13th centuries [14,15,45], indicating its earlier chronology compared to the *Ajuda Songbook*. The other green color, *vergaut,* was detected as a homogeneous mixture of orpiment and indigo. The construction of this color is different from that of the *Ajuda Songbook*, where orpiment is layered onto blue or black, Figure S13 (Supplementary material S3). For example, in the acanthus leaves that decorate the column capitals, the illuminator shades and heightens by meticulously applying orpiment over the blue/black undertone in a delicate matiz.

4. Conclusions

The identification of brazilwood pinks and reds in the manuscripts of the scriptorium of Alfonso X attests to its first use in works of art in Europe. The existence of documentary sources that indicate that the monarch wanted to control the brazilwood supply shows the relevance of this color in the territories of Castile and Aragon.

One of the reasons that led this interdisciplinary team to study the scriptorium of Alfonso X is related to the *Ajuda Songbook* [48]. At the time, it was the first reported use of brazilwood lake pigments in medieval manuscript illuminations. Based on the combined information gathered using infrared spectroscopy and molecular fluorescence spectra, we could reproduce the complete formulations of the pink colors, where besides brazilwood lake pigment, we quantified the tempera as mesquite gum and the additives such as lead white and calcium carbonate [29]. We could also differentiate the brazilwood pigment lakes used in the *Songbook* from the colors in books of hours, produced in the 15th c. in France or Flanders [38]. However, we have yet to determine the formulation of the brazilwood lake pigments in Alfonso's scriptorium. Considering that brazilwood-based colors are described in the literature as unstable [81], this information could allow us to understand further its composition and how best to preserve these colors. However, it is important to add that based on our reconstructions of medieval pinks that compare well with what was found in books of hours, we can state that the pinks in these manuscripts can be considered in very good condition [38].

Another important color is the green *vergaut*. In the *Ajuda Songbook*, *vergaut* is prepared by applying orpiment over blue or black. In the manuscripts of Alfonso X, it is used as a homogeneous mixture of blue and yellow. So, the same *vergaut*, but different ways of creating it. Besides, in Alfonso's four manuscripts, bottle green is possibly still used, which points to an earlier chronology by comparison with its use in French and Portuguese monastic scriptoria [44,45,75]. Adding to this, the absence of mosaic gold and the use of orpiment in Alfonso's manuscripts reinforces a later dating for the *Ajuda Songbook*. These data support the argument put forward by scholars of medieval literature that the *Songbook* dates to the end of the thirteenth or beginning of the fourteenth century. We could possibly narrow these dating based on Stirnemann's discussion of two citoles and two viola players (fols. 21, 37, 40v, and 55v) wearing surcoats that are cut into strips at the bottom, revealing their legs. This type of garment was fashionable throughout Europe during the last decades of the thirteenth and early fourteenth centuries [82].

Also noteworthy is the use of purple in Alfonso X manuscripts, in a mixture of brazilwood and blue (indigo or lapis lazuli). This color is absent in the illuminations of the *Ajuda Songbook*. Purple was an essential color in antiquity, related to power and religion, and its use would carry an enormous symbolic meaning. Another purple was identified in the *Songbook* and in the *Lapidary*, orcein purple, probably applied in a later chronology [22,23,48].

It is also striking how the color of the parchment is explored in the *Rich codex*. It reminds us of the illuminations of Portuguese monastic scriptoria, produced between the 12th and 13th centuries, where the color of the parchment was enhanced by the use of varnish, possibly simulating the brightness of gold; this color may be associated with the *pallidus* of Roman antiquity [6,24]. In the manuscripts of Alfonso X, gold is extensively used, again stating this legacy's importance.

Overall, the diversity of colors, accentuated by the presence of lapis lazuli blue, brazilwood pink, purple, and gold, demonstrates the luxuriousness of the color palette, and the manuscripts produced are sumptuous and magnificent. Mosaic gold, orpiment, and bottle green proved to be relevant colors to discuss the different chronologies in which the *Ajuda Songbook* and Alfonso X manuscripts were created. The similarities found attest to a common cultural environment and the sharing of knowledge; nonetheless, further research on these manuscripts is needed to gain a better understanding of book production at this time and to preserve them for future generations.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/heritage7010014/s1, Table S1—Studies made in medieval illuminated manuscripts produced in the Iberian Peninsula, with a description of the date, name or theme of the manuscript and its origin, colorants found divided by applied pure or in the mixture, techniques used to characterize them and respective reference; Table S2—Studies made in medieval illuminated manuscripts produced in the Iberian Peninsula, with a description of the date, name or theme of the manuscript and its origin, colorants found divided by applied pure or in the mixture, techniques used to characterize them and respective reference; Figure S1: Reflectance and Raman spectra of azurite found in folio 212r of the *Rich codex* (black), compared with an azurite reference (blue). This blue color was identified in a restricted area, being not the main blue. While the reflectance spectrum indicates the presence of azurite, with Raman spectroscopy, its identification is less straightforward as the spectrum is affected by fluorescence, with only two characteristic bands being identified at 401 and 488 cm^{-1}; Figure S2: Raman spectra of orpiment found in folio 192r of *Rich codex* (black), compared with orpiment reference (blue). This pigment was applied pure only in this manuscript, in the detail of a paint bottle; Figure S3: Spectra of lapis lazuli applied pure (black) compared with references (blue). Reflectance (a, b) and Raman (c, d) spectra of lapis lazuli in the *Rich codex* and *Musicians' codex*, respectively. Lapis Lazuli was applied as a pure pigment mostly in backgrounds; Figure S4: Spectra of lapis lazuli applied pure (black) compared with references (blue): Reflectance (a, b) and Raman (c, d) spectra of lapis lazuli in *Lapidary* and *Book of Games*, respectively. Lapis Lazuli was applied as a pure pigment mostly in backgrounds; Figure S5: Raman spectrum of a mixture of lapis lazuli and carbon-based black in *Musicians' codex* (black) compared with the bone black reference (blue); Figure S6: Spectra of red and orange paints (black), representative of the pigments found in the four manuscripts, compared with references (blue). Reflectance spectra and first derivative indicating (in the inset) vermilion (a) and red lead (b) in *Lapidary*. There is a close match between the historical paints and the references. This identification is confirmed with Raman analysis, where vermilion (c) is identified by its characteristic bands at 257, 289, and 345 cm^{-1} and red lead (d) by its characteristic bands at 390 and 549 cm^{-1}; Figure S7: The spectra of two distinct greens in *Musicians' codex* (a, c) and *Lapidary* (b, d). Reflectance spectra indicate (a) the characteristic spectrum of indigo and (b) the presence of a green, probably of cuprous nature. The Raman spectrum in (c) corroborates the presence of indigo, identifying also lapis lazuli. There was no signal in Raman spectroscopy for the green in *Lapidary*; however, in a similar paint of the same manuscript, it was possible to identify lead white in a mixture with the green. The main Raman bands are assigned to lapis lazuli (▼), indigo (⧫), and white lead (●). *Vergaut* and bottle green are discussed in the main text; Figure S8: Raman spectra of white and black in particular objects (black) compared with references (blue) for (a) *Rich codex*, lead white paint found in the white lion of folio 192r; (b) *Lapidary*, black paint used to paint a bird of folio 49r, that corresponds to iron-gall ink; (c) *Lapidary*, carbon-based black used to paints scorpion in folio 63r; and (d) *Lapidary*, blue found in little stone, resulting from the mixture of lapis lazuli and lead white. The main Raman bands detected are assigned to lapis lazuli (▼) and white lead (●); Table S3: Details of the elements presented in the previous analysis (Figure S8), from left to right: the white lion of the *Rich codex*, the bird, the scorpion, and the stone of *Lapidary*, in folios 49r, 63r and 87r; Figure S9: Apparent absorbance spectra of a) red dyes as pigments lakes, such as madder (blue) and lac dye (pointed); and b) dragons' blood (blue), a dye that is frequently described in medieval treatises as being used in illuminations compared to brazilwood (black);Figure S10: Apparent absorbance spectra of brazilwood pinks (black) in the manuscripts, compared with references (blue): (a) *Rich codex*, (b) *Book of Games*, (c) *Musicians' codex* and d) *Lapidary*. In *Lapidary*, the spectra are shifted, which can be indicative of the presence of additives such as lead white (black), calcium carbonate (pink), and gypsum (green); Figure S11: Apparent absorbance spectra of purple colors were found in the vestments of a) *Musicians' codex* and b) *Lapidary*. Both examples indicate the presence of brazilwood lake pigments, whose bands are shifted. The bands at 639 and 649 nm can represent the presence of indigo in the mixture, found in most purple mixtures and confirmed using Raman spectroscopy; Figure S12: Details of pink (top), blue (middle), and purple (bottom) vestments found in Alfonso's manuscripts. The difference in application is clear between the *Rich codex* and the *Musicians' codex* and *Lapidary*. Even though *Book of Games* is also different from the *Rich codex* in terms of style and various aspects of the pictorial technique, it was possible to see some similarities in the construction of colors, like the pinks and blues. In these, the illuminator took advantage of the parchment or white support for the brighter tones; Figure S13: Details of green *vergaut* resulting from a homogeneous mixture found in the frames and vestments of *Musicians' codex*, compared to the color construction of the *vergaut* found in *Ajuda Songbook*, obtained through layering of orpiment above three other colorants; Figure S14: Details of the architecture found in folio 29r and 341r of *Musicians' codex* illustrating the difference between the detailed motifs of the first and the coarser application on the second; Figure S15: Details of stairs found in division 6 of the illumination in folio 32v of the *Rich codex*; Figure S16: Details of (a) colors found in the frames of folio 212r and (b) golden castle and purple lion found in the interception of frames of folio 192r; Figure S17: Details of patterns found in the blue backgrounds of folio 29r in a, b, and c, in folio 140v in d, and folio 305v; Figure S18: Details of orange applied in the (a) initial of folio 29r and in the (b) the vestments and architecture of folio 341r. Red paint is used to control the shades and contour the shapes; Figure S19: Illumination with the bottle green serpent of folio 8r, where is visible the control over the thickness of the green and the application of the light pink for the movement; Figure S20: Details of drollery found in the left margin of folio 8r, with a scene composed of a dragon, a man, and a lion; Figure S21: Details of violet and blue stones found in the historiated initials of folio 87r; Figure S22: Details of everyday objects, accessories, and manners, represented in folio 18r; Figure S23: Details of colors in an advanced state of degradation: loss of adhesion of the green and layers of preparation, degradation of red lead, and possible damage by water; Figure S24: Details of greens applied in the architecture, vestments accessories of folios 1r, 18r, 48r, and 65r; Figure S25: *Rich codex*, folio 192r, Royal Library of Monastery of El Escorial; Figure S26: *Rich codex*, folio 212r, Royal Library of Monastery of El Escorial; Figure S27: *Musicians' codex*, folio 29r, Royal Library of Monastery of El Escorial; Figure S28: *Musicians' codex*, folio 71v, Royal Library of Monastery of El Escorial; Figure S29: *Musicians' codex*, folio 89r, Royal Library of Monastery of El Escorial; Figure S30: *Musicians' codex*, folio 304v, Royal Library of Monastery of El Escorial; Figure S31: *Lapidary*, folio 1r, Royal Library of Monastery of El Escorial; Figure S32: *Lapidary*, folio 8r, Royal Library of Monastery of El Escorial; Figure S33: *Lapidary*, folio 9v, Royal Library of Monastery of El Escorial; Figure S34: *Lapidary*, folio 41v, Royal Library of Monastery of El Escorial; Figure S35: *Lapidary*, folio 49r, Royal Library of Monastery of El Escorial; Figure S36: *Lapidary*, folio 62v, Royal Library of Monastery of El Escorial; Figure S37: *Lapidary*, folio 63r, Royal Library of Monastery of El Escorial; Figure S38: *Lapidary*, folio 87r, Royal Library of Monastery of El Escorial; Figure S39: *Lapidary*, folio 104r, Royal Library of Monastery of El Escorial; Figure S40: *Lapidary*, folio 106v, Royal Library of Monastery of El Escorial; Figure S41: *Lapidary*, folio 108r, Royal Library of Monastery of El Escorial; Figure S42: *Lapidary*, folio 116v, Royal Library of Monastery of El Escorial; Figure S43: *Book of chess, dices and tables*, folio 1r, Royal Library of Monastery of El Escorial; Figure S44: *Book of chess, dices and tables*, folio 18r, Royal Library of Monastery of El Escorial; Figure S45: *Book of chess, dices and* *tables*, folio 48r, Royal Library of Monastery of El Escorial; Figure S46: *Book of chess, dices and tables*, folio 65r, Royal Library of Monastery of El Escorial.

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References

1. Fernández Fernández, L. El Scriptorium Alfonsí: Coordenadas de Estudio. In *Alfonso X el Sabio: Cronista y Protagonista de su Tiempo*; Fidalgo, E., Ed.; Cilengua: San Millán de la Cogolla, Spain, 2020; Volume 1, pp. 89–114. ISBN 8418088070.
2. Fernández Fernández, L. De Escriptos e Libros: Los Manuscritos de Alfonso X. In *Alfonso X. El Universo Político y Cultural de un Reinado*; Otín, M.J.L., Igual, D., Gómez, Ó.L., Eds.; Universidad de Castilla la Mancha: Toledo, Spain, 2023; *in press*.
3. Kennedy, K. *Alfonso X of Castile-León: Royal Patronage, Self-Promotion and Manuscripts in Thirteenth-Century Spain*; Amsterdam University Press: Amsterdam, The Netherlands, 2019; Volume 1, ISBN 9789048541386.
4. Bango, I. *Alfonso X El Sabio*; Región de Murcia: Murcia, Spain, 2009; ISBN 9788475645223.
5. Lopes, G.V. *Cantigas Medievais Galego-Portuguesas: Corpus Integral Profano*; Biblioteca Nacional: Lisbon, Portugal, 2017; Volume I and II, ISBN 9789725655894, 9789725655900.
6. Galvez, M. *Songbook: How Lyrics Became Poetry in Medieval Europe*; The University of Chicago Press: Chicago, IL, USA, 2015; ISBN 9780226280516.
7. Ramos, M.A. O Cancioneiro Da Ajuda, Confecção e Escrita. 2 Vols. Ph.D. Thesis, Faculty of Letters, University of Lisbon, Lisbon, Portugal, 2008.
8. Vasconcelos, C.M. *Cancioneiro Da Ajuda*; Niemeyer, M., Ed.; Imprensa Nacional—Casa da Moeda: Lisbon, Portugal, 1990; Volume I and II, ISBN 9789722704779.
9. Tavani, G. *Trovadores e Jograis: Introdução à Poesia Medieval Galego-Portuguesa*; Editorial Caminho: Lisbon, Portugal, 2002.
10. Aceto, M.; Calà, E.; Fenoglio, G.; Labate, M.; Denoël, C.; Operti, L.; Agostino, A. New Evidence of Non-Traditional Egyptian Blue Manufacture in the 6th Century Ashburnham Pentateuch. *J. Archaeol. Sci. Rep.* **2020**, *33*, 102487. [CrossRef]
11. Magkanas, G.; Bagán, H.; Sistach, M.C.; García, J.F. Illuminated Manuscript Analysis Methodology Using MA-XRF and NMF: Application on the Liber Feudorum Maior. *Microchem. J.* **2021**, *165*, 106112. [CrossRef]
12. Miguel, C.; Claro, A.; Gonçalves, A.P.; Muralha, V.S.F.; Melo, M.J. A Study on Red Lead Degradation in a Medieval Manuscript Lorvão Apocalypse (1189). *J. Raman Spectrosc.* **2009**, *40*, 1966–1973. [CrossRef]
13. Melo, M.J.; Miranda, M.A.; Miguel, C.; Castro, R.; Claro, A.; Lemos, A.; Muralha, V.S.; Lopes, J.A.; Gonçalves, A.P. The Colour of Medieval Portuguese Illumination: An Interdisciplinary Approach. *Rev. História Arte* **2011**, *1*, 153–173.
14. Muralha, V.S.F.; Miguel, C.; Melo, M.J. Micro-Raman Study of Medieval Cistercian 12–13th Century Manuscripts: Santa Maria de Alcobaça, Portugal. *J. Raman Spectrosc.* **2012**, *43*, 1737–1746. [CrossRef]
15. Miguélez Cavero, A.; Melo, M.J.; Miranda, M.A.; Castro, R.; Casanova, C. Beatus Manuscripts under the Microscope: The Alcobaça Beatus and the Iberian Cistercian Tradition Revisited. *J. Mediev. Iber. Stud.* **2016**, *8*, 217–251. [CrossRef]
16. Nabais, P.; Castro, R.; Lopes, G.V.; Sousa, L.C.; Melo, M.J. Singing with Light: An Interdisciplinary Study on the Medieval Ajuda Songbook. *J. Mediev. Iber. Stud.* **2016**, *8*, 283–312. [CrossRef]

17. Barreira, C.F.; Melo, M.J.; Araújo, R.; Casanova, C. Through the Eyes of Science and Art: A Fourteenth-Century Winter Breviary from Alcobaça Scriptorium. *J. Mediev. Iber. Stud.* **2016**, *8*, 252–282. [CrossRef]
18. Edwards, H.G.M.; Farwell, D.W.; Perez, F.R.; Villar, S.J. Raman Microscopy of a Mediaeval Spanish Cantoral. *Appl. Spectrosc.* **1999**, *53*, 1436–1439. [CrossRef]
19. Edwards, H.G.M.; Farwell, D.W.; Perez, F.R.; Garcia, J.M. Mediaeval Cantorals in the Valladolid Biblioteca: FT-Raman Spectroscopic Study. *Analyst* **2001**, *126*, 383–388. [CrossRef]
20. Melo, M.J.; Nabais, P.; Guimarães, M.; Araújo, R.; Castro, R.; Oliveira, M.C.; Whitworth, I. Organic Dyes in Illuminated Manuscripts: A Unique Cultural and Historic Record. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2016**, *374*, 20160050. [CrossRef] [PubMed]
21. Tibúrcio, C.; Valadas, S.; Cardoso, A.; Candeias, A.; Barreira, C.; Miguel, C. On the Use of EDXRF and UV–Vis FORS to Unveil the Production of Two Illuminated Manuscripts from the Fifteenth Century Portuguese Royal Court. *Microchem. J.* **2020**, *153*, 104455. [CrossRef]
22. Duran, A.; López-Montes, A.; Castaing, J.; Espejo, T. Analysis of a Royal 15th Century Illuminated Parchment Using a Portable XRF–XRD System and Micro-Invasive Techniques. *J. Archaeol. Sci.* **2014**, *45*, 52–58. [CrossRef]
23. Espejo Arias, T.; Lazarova Stoytcheva, I.; Campillo García, D.; Durán Benito, A.; Jiménez de Haro, A. Caracterización Material y Proceso de Conservación de La Colección de Documentos Árabes Manuscritos Del Archivo Histórico Provincial de Granada. *Al-Qanṭara* **2011**, *32*, 519–532. [CrossRef]
24. Moura, L.; Melo, M.J.; Casanova, C.; Claro, A. A Study on Portuguese Manuscript Illumination: The Charter of Vila Flor. (Flower Town), 1512. *J. Cult. Herit.* **2007**, *8*, 299–306. [CrossRef]
25. Pastoureau, M. *Jésus Chez Le Teinturier: Couleurs et Teintures Dans L'occident Médiéval*; Le Léopard d'or: Paris, France, 2000; ISBN 9782863771501.
26. Daveri, A.; Doherty, B.; Moretti, P.; Grazia, C.; Romani, A.; Fiorin, E.; Brunetti, B.G.; Vagnini, M. An Uncovered XIII Century Icon: Particular Use of Organic Pigments and Gilding Techniques Highlighted by Analytical Methods. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2015**, *135*, 398–404. [CrossRef] [PubMed]
27. Edwards, H.G.M.; Farwell, D.W.; Newton, E.M.; Rull Perez, F.; Jorge Villar, S. Raman Spectroscopic Studies of a 13th Century Polychrome Statue: Identification of a "forgotten" Pigment. *J. Raman Spectrosc.* **2000**, *31*, 407–413. [CrossRef]
28. Karapanagiotis, I.; Daniilia, S.; Tsakalof, A.; Chryssoulakis, Y. Identification of Red Natural Dyes in Post-Byzantine Icons by HPLC. *J. Liq. Chromatogr. Relat. Technol.* **2005**, *28*, 739–749. [CrossRef]
29. Vieira, M.; Nabais, P.; Hidalgo, R.J.D.; Melo, M.J.; Pozzi, F. The Only Surviving Medieval Codex of Galician-Portuguese Secular Poetry: Tracing History through Luxury Pink Colors. *Herit. Sci.* **2023**, *11*, 37. [CrossRef]
30. Kroustallis, S. Quomodo Decoratur Pictura Librorum, Materiales y Técnicas de La Iluminación Medieval. *Anu. Estud. Mediev.* **2011**, *41*, 775–802. [CrossRef]
31. Kroustallis, S. Binding Media in Medieval Manuscript Illumination: A Source of Research. *Rev. História Arte* **2011**, *1*, 113–125. Available online: https://revistadehistoriadaarte.files.wordpress.com/2011/09/art08.pdf (accessed on 1 September 2023).
32. Melo, M.J.; Castro, R.; Nabais, P.; Vitorino, T. The Book on How to Make All the Colour Paints for Illuminating Books: Unravelling a Portuguese Hebrew Illuminators' Manual. *Herit. Sci.* **2018**, *6*, 44. [CrossRef]
33. Nabais, P.; Melo, M.J.; Lopes, J.A.; Vieira, M.; Castro, R.; Romani, A. Organic Colorants Based on Lac Dye and Brazilwood as Markers for a Chronology and Geography of Medieval Scriptoria: A Chemometrics Approach. *Herit. Sci.* **2021**, *9*, 32. [CrossRef]
34. Melo, M.J.; Nabais, P.; Vieira, M.; Araújo, R.; Otero, V.; Lopes, J.; Martín, L. Between Past and Future: Advanced Studies of Ancient Colours to Safeguard Cultural Heritage and New Sustainable Applications. *Dye Pigment.* **2022**, *208*, 110815. [CrossRef]
35. Partearroyo Lacaba, C. Estudio Histórico-Artístico de Los Tejidos de al-Andalus y Afines. *Bienes Cult.—Tejidos Hisp.* **2005**, *5*, 37–74.
36. Cardon, D. *Natural Dyes: Sources, Tradition, Technology and Science*; Archetype: London, UK, 2007; ISBN 9781904982005.
37. Bechtold, T.; Mussak, R. *Handbook of Natural Colorants*; Bechtold, T., Mussak, R., Eds.; Wiley: Hoboken, NJ, USA, 2009; ISBN 9780470511992.
38. Melo, M.J.; Otero, V.; Vitorino, T.; Araújo, R.; Muralha, V.S.F.; Lemos, A.; Picollo, M. A Spectroscopic Study of Brazilwood Paints in Medieval Books of Hours. *Appl. Spectrosc.* **2014**, *68*, 434–443. [CrossRef] [PubMed]
39. Roger, P.; Villela-Petit, I.; Vandroy, S. Les Laques de Brésil Dans l'enluminure Médiévale. *Stud. Conserv.* **2003**, *48*, 155–170. [CrossRef]
40. Vitorino, T.; Melo, M.J.; Carlyle, L.; Otero, V. New Insights into Brazilwood Lake Pigments Manufacture through the Use of Historically Accurate Reconstructions. *Stud. Conserv.* **2016**, *61*, 255–273. [CrossRef]
41. Fernández Fernández, L.; Melo, M.J.; Vieira, M. Pigmentos Para Un Rey: El Rosa de "palo Brasil" En La Paleta Cromática de Los Manuscritos de Alfonso X. In *El Libro Manuscrito Medieval: Del Pergamino al Metadato*; Editorial Dykinson: Madrid, Spain, 2023; *in press*.
42. Jansen, P. *Dyes and Tannins 3: Plant Resources of Tropical Africa*; Jansen, P., Cardon, D., Eds.; PROTA Foundation: Wageningen, The Netherlands, 2005; Volume 3, ISBN 9789057821592.
43. Dunlop, L.J.V. The Use of Colour in Parisian Manuscript Illumination c.1320–c.1420 with Special Reference to the Availability of Pigments and Their Commerce at That Period. Ph.D. Thesis, Faculty of Arts, University of Manchester, Manchester, UK, 1988.

44. Melo, M.J.; Nabais, P.; Araújo, R.; Vitorino, T. The Conservation of Medieval Manuscript Illuminations: A Chemical Perspective. *Phys. Sci. Rev.* **2019**, *4*, 20180017. [CrossRef]
45. Melo, M.J.; Castro, R.; Miranda, A. Colour in Medieval Portuguese Manuscripts: Between Beauty and Meaning. In *Science and Art: The Painted Surface*; Sgamellotti, A., Brunetti, B.G., Miliani, C., Eds.; Royal Society of Chemistry: London, UK, 2014; ISBN 9781849738187.
46. Coupry, C. A La Recherche des Pigments. *Rev. História Arte* **2011**, *1*, 127–136. Available online: https://revistadehistoriadaarte.files.wordpress.com/2011/09/art09.pdf (accessed on 5 September 2023).
47. Knipe, P.; Eremin, K.; Walton, M.; Babini, A.; Rayner, G. Materials and Techniques of Islamic Manuscripts. *Herit. Sci.* **2018**, *6*, 55. [CrossRef]
48. Orna, M. *March of the Pigments: Color History, Science and Impact*, 1st ed.; Royal Society of Chemistry: London, UK, 2022; Volume 1, ISBN 9781839163159.
49. Doherty, B.; Daveri, A.; Clementi, C.; Romani, A.; Bioletti, S.; Brunetti, B.; Sgamellotti, A.; Miliani, C. The Book of Kells: A Non-Invasive MOLAB Investigation by Complementary Spectroscopic Techniques. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2013**, *115*, 330–336. [CrossRef] [PubMed]
50. Ricciardi, P.; Pallipurath, A.; Rose, K. "It's Not Easy Being Green": A Spectroscopic Study of Green Pigments Used in Illuminated Manuscripts. *Anal. Methods* **2013**, *5*, 3819–3824. [CrossRef]
51. Panayotova, S.; Ricciardi, P. *Manuscripts in the Making: Art & Science*; Panayotova, S., Ricciardi, P., Eds.; Harvey Miller Publishers: London, UK, 2017; Volume I and II, ISBN 9781909400108, 9781912554133.
52. Salvadó, N.; Butí, S.; Cotte, M.; Cinque, G.; Pradell, T. Shades of Green in 15th Century Paintings: Combined Microanalysis of the Materials Using Synchrotron Radiation XRD, FTIR and XRF. *Appl. Phys. A Mater. Sci. Process.* **2013**, *111*, 47–57. [CrossRef]
53. Melo, M.J.; Castro, R. The "Book on How to Make Colours"—O Livro de Como Se Fazem as Cores das Tintas Todas—Medieval Colours for Practitioners. Available online: https://www.dcr.fct.unl.pt/sites/www.dcr.fct.unl.pt/files/ArquivoDigital/como%20fazer%20as%20cores%20cap%20livro/LKSK_full%20pdf.pdf (accessed on 24 October 2023).
54. Clarke, M. *Medieval Painters' Materials and Techniques: The Montpellier Liber Diversarum Arcium*; Archetype Publications: London, UK, 2011; ISBN 9781904982647.
55. Rita de Castro Sousa, O. The Book of Birds in Portuguese Scriptoria: Preservation and Access. Ph.D. Thesis, NOVA School of Science and Technology, Lisbon, Portugal, 2016.
56. Díaz Hidalgo, R.J.; Córdoba, R.; Nabais, P.; Silva, V.; Melo, M.J.; Pina, F.; Teixeira, N.; Freitas, V. New Insights into Iron-Gall Inks through the Use of Historically Accurate Reconstructions. *Herit. Sci.* **2018**, *6*, 63. [CrossRef]
57. Fernández Fernández, L.; Ruiz García, E. Quasi Liber et Pictura—Estudio Codicológico Del Ms. T-I-1 de La RBME. In *Alfonso X El Sabio (1221–1284)—Las Cantigas de Santa María—Códice Rico, Ms.T-I-1 Real Biblioteca del Monasterio de San Lorenzo de El Escorial*; Fernández Fernández, L., Ruiz Souza, J.C., Eds.; Testimonio Editorial—Patrimonio Nacional: Madrid, Spain, 2011; Volume 2, ISBN 9788495767899.
58. Osticioli, I.; Mendes, N.F.C.; Nevin, A.; Gil, F.P.S.C.; Becucci, M.; Castellucci, E. Analysis of Natural and Artificial Ultramarine Blue Pigments Using Laser Induced Breakdown and Pulsed Raman Spectroscopy, Statistical Analysis and Light Microscopy. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2009**, *73*, 525–531. [CrossRef] [PubMed]
59. Schmidt, C.M.; Walton, M.S.; Trentelman, K. Characterization of Lapis Lazuli Pigments Using a Multitechnique Analytical Approach: Implications for Identification and Geological Provenancing. *Anal. Chem.* **2009**, *81*, 8513–8518. [CrossRef] [PubMed]
60. Spoto, S.E.; Paladini, G.; Caridi, F.; Crupi, V.; D'amico, S.; Majolino, D.; Venuti, V. Multi-Technique Diagnostic Analysis of Plasters and Mortars from the Church of the Annunciation (Tortorici, Sicily). *Materials* **2022**, *15*, 958. [CrossRef]
61. Ganio, M.; Pouyet, E.S.; Webb, S.M.; Schmidt Patterson, C.M.; Walton, M.S. From Lapis Lazuli to Ultramarine Blue: Investigating Cennino Cennini's Recipe Using Sulfur K-Edge XANES. *Pure Appl. Chem.* **2018**, *90*, 463–475. [CrossRef]
62. Smith, G.D.; Clark, R.J.H. The Role of H_2S in Pigment Blackening. *J. Cult. Herit.* **2002**, *3*, 101–105. [CrossRef]
63. Ciofini, D.; Agresti, J.; Mencaglia, A.A.; Siano, S.; Osticioli, I. Temperature Sensing during Raman Spectroscopy of Lead White Films in Different Purity Grades and Boundary Conditions. *Sens. Actuators B Chem.* **2020**, *325*, 128958. [CrossRef]
64. Sun, J.; Wu, Z.; Cheng, H.; Zhang, Z.; Frost, R.L. A Raman Spectroscopic Comparison of Calcite and Dolomite. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2014**, *117*, 158–162. [CrossRef] [PubMed]
65. Tatsch, E.; Schrader, B. Near-Infrared Fourier Transform Raman Spectroscopy of Indigoids. *J. Raman Spectrosc.* **1995**, *26*, 467–473. [CrossRef]
66. Amat, A.; Rosi, F.; Miliani, C.; Sgamellotti, A.; Fantacci, S. Theoretical and Experimental Investigation on the Spectroscopic Properties of Indigo Dye. *J. Mol. Struct.* **2011**, *993*, 43–51. [CrossRef]
67. Frost, R.L.; Martens, W.N.; Rintoul, L.; Mahmutagic, E.; Kloprogge, J.T. Raman Spectroscopic Study of Azurite and Malachite at 298 and 77 K. *J. Raman Spectrosc.* **2002**, *33*, 252–259. [CrossRef]
68. Mattei, E.; de Vivo, G.; De Santis, A.; Gaetani, C.; Pelosi, C.; Santamaria, U. Raman Spectroscopic Analysis of Azurite Blackening. *J. Raman Spectrosc.* **2008**, *39*, 302–306. [CrossRef]
69. Frost, R.L.; Martens, W.N.; Kloprogge, J.T. Raman Spectroscopic Study of Cinnabar (HgS), Realgar (As_4S_4), and Orpiment (As_2S_3) at 298 and 77K. *Neues Jahrb. Mineral.—Monatshefte* **2002**, *10*, 469–480. [CrossRef]
70. Frost, R.L.; Bahfenne, S.; Keeffe, E.C. Raman Spectroscopic Study of the Mineral Gerstleyite $Na_2(Sb,As)_8S_{13}\cdot 2H_2O$ and Comparison with Some Heavy-Metal Sulfides. *J. Raman Spectrosc.* **2010**, *41*, 1779–1783. [CrossRef]

71. Edwards, H.G.M.; Farwell, D.W.; Newton, E.M.; Rull Perez, F. Minium; FT-Raman Non-Destructive Analysis Applied to an Historical Controversy. *Analyst* **1999**, *124*, 1323–1326. [CrossRef]
72. Forneris, R. The Infrared and Raman Spectra of Realgar and Orpiment. *Am. Miner.* **1969**, *54*, 1062–1074.
73. Cheng, H.; Zhou, Y.; Frost, R.L. Structure Comparison of Orpiment and Realgar by Raman Spectroscopy. *Spectrosc. Lett.* **2017**, *50*, 23–29. [CrossRef]
74. Miguel, C.A.P. Le Vert et Le Rouge: A Study on the Materials, Techniques and Meaning of the Green and Red Colours in Medieval Portuguese Illuminations. Ph.D. Thesis, NOVA School of Science and Technology, Lisbon, Portugal, 2012.
75. Coupry, C. Les Pigments Utilisés Por l'enluminure à Fécamp Aus XIe et XIIe Siècles. In *Manuscrits et Enluminures Dans le Monde Normand (Xe–XVe Siècles)*; Bouet, P., Dosdat, M., Eds.; Presses Universitaires de Caen: Caen, France, 1999; pp. 69–79, ISBN 2841330877.
76. Jorio, A.; Saito, R. Raman Spectroscopy for Carbon Nanotube Applications. *J. Appl. Phys.* **2021**, *129*, 021102. [CrossRef]
77. Tomasini, E.P.; Halac, E.B.; Reinoso, M.; Di Liscia, E.J.; Maier, M.S. Micro-Raman Spectroscopy of Carbon-Based Black Pigments. In Proceedings of the Journal of Raman Spectroscopy; John Wiley and Sons Ltd.: Hoboken, NJ, USA, 2012; Volume 43, pp. 1671–1675.
78. Ponce, A.; Brostoff, L.B.; Gibbons, S.K.; Zavalij, P.; Viragh, C.; Hooper, J.; Alnemrat, S.; Gaskell, K.J.; Eichhorn, B. Elucidation of the Fe(III) Gallate Structure in Historical Iron Gall Ink. *Anal. Chem.* **2016**, *88*, 5152–5158. [CrossRef] [PubMed]
79. Díaz Hidalgo, R.J.; Córdoba, R.; Grigoryan, H.; Vieira, M.; Melo, M.J.; Nabais, P.; Otero, V.; Teixeira, N.; Fani, S.; Al-Abbady, H. The Making of Black Inks in an Arabic Treatise by Al-Qalalūsī Dated from the 13th c.: Reproduction and Characterisation of Iron-Gall Ink Recipes. *Herit. Sci.* **2023**, *11*, 7. [CrossRef]
80. Espina, A.; Cañamares, M.V.; Jurašeková, Z.; Sanchez-Cortes, S. Analysis of Iron Complexes of Tannic Acid and Other Related Polyphenols as Revealed by Spectroscopic Techniques: Implications in the Identification and Characterization of Iron Gall Inks in Historical Manuscripts. *ACS Omega* **2022**, *7*, 27937–27949. [CrossRef]
81. Kirby, J.; Saunders, D.; Spring, M. Proscribed Pigments in Northern European Renaissance Paintings and the Case of Paris Red. *Stud. Conserv.* **2006**, *51*, 236–243. [CrossRef]
82. Stirnemann, P. La Décoration Du Chansonnier d'Ajuda. In *À Volta do Cancioneiro da Ajuda: Actas do Colóquio "Cancioneiro da Ajuda (1904–2004)"*; Ramos, M.A., Amado, T., Eds.; Imprensa Nacional—Casa da Moeda S.A.: Lisboa, Portugal, 2016; ISBN 9789722724470.