

Article

Revealing Artists' Collaboration in a 14th Century Manuscript by Non-Invasive Analyses

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Abstract: In the last decades, the working methods of late medieval illuminators have been widely discussed by art historians and codicologists. Non-invasive analyses are able to characterise the painting methods of illuminators as well as investigate artistic collaborations among them. The aim of this study was to characterise the painting palettes and techniques of different artists who illuminated two leaves from an early fourteenth century manuscript. The analyses were carried out with non-invasive and portable techniques such as Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometry, Fiber Optics Reflectance Spectroscopy (FORS) and Raman spectroscopy. The paper highlights the differences among three rich and varied palettes and examines the pigments ultramarine, azurite, verdigris, earths, orpiment, red lead, vermillion, lead white, yellow lake, indigo, brazilwood and lac, used independently or in mixtures. We have demonstrated the effectiveness of non-invasive analyses as a tool to differentiate hands of artists who have worked on the same page. Furthermore, the comparison with analyses carried out on leaves attributed to the workshop of Pacino di Bonaguida allows to investigate in-depth the production of the main illuminators active in Florence at the dawn of the Renaissance.

Keywords: illuminated manuscript; azurite; ultramarine; orpiment; vergaut; vermillion; lac; FORS; XRF; Raman spectroscopy



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






































1. Introduction

The role of non-invasive analysis as an indispensable tool in research on illuminated manuscripts is no longer in question [1]. The analytical approaches currently used are mainly oriented to the discussion of case studies (e.g., pigments palette of a manuscript) and identification of specific categories of pigments and binders. The close collaboration between heritage scientists, art historians and codicologists has often allowed to reconstruct the entire creative process from the artists' original invention through their choice of materials to the finished illuminated page [2]. The scientific analyses are crucial to characterise the painting palette of an artist or a workshop. Some illuminators employed a single palette throughout their careers while others varied considerably in their pigment choice, also depending on the patron. In some cases, the identification of unexpected pigments on the illuminated page can reveal the collaboration among different artists sometimes not easily characterised by stylistic analysis alone.

In the present work, a multi-analytical approach, based on non-invasive spectroscopic methods, has been adopted to investigate artistic collaboration, painting palettes and techniques in a manuscript from the early fourteenth century.

We combined non-invasive and portable techniques such as Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometry, Fiber Optics Reflectance Spectroscopy (FORS) and Raman spectroscopy for the investigation of the illuminated manuscript Gradual “D” from “Badia a Settimo” abbey in Florence. Its illuminations are considered the product of a collaboration between a group of artists close to the workshop of Pacino di Bonaguida, who started the work, the Master of the Codex of Saint George and the Maestro Daddesco, who completed the series of illuminations in the volume. This paper focuses on two illuminated leaves, folios 8r and 18r, which have been widely discussed by art historians. The aim is to verify if the art-historical attribution to different artists is corroborated by the discovery of different painting palettes and techniques. The pigment palettes of the various artists have been determined earlier through the analysis of seven illuminations of Gradual “D”: two certainly attributed to artists close to Pacino di Bonaguida (ff. 23r, 191r), three to the Maestro Daddesco (ff. 91v, 116r, 216v) and two to Master of the Codex of Saint George (ff. 108v, 133r). The palettes were then compared with those identified on ff. 8r and 18r, as shown in Table 1. Furthermore, the results of the analyses on these leaves, attributed to followers of Pacino di Bonaguida and to the Maestro Daddesco, can be compared with analyses carried out on a series of leaves attributed to the workshop of Pacino di Bonaguida, allowing to study in-depth the production of the main workshops active in Florence at the dawn of the Renaissance.

Table 1. The palettes of folios 8r and 18r compared with those of Master of the Codex of Saint George (MG), the Maestro Daddesco (MD) and “Pacinesque” artists (PA).

	MG	MD	PA 23r	PA 191r	Borders 8r, 18r	“P” Initial 8r	“I” Initial 18r
Red lead (<i>minium</i>)							
Vermillion							
Vermillion + lead white							
Brazilwood light							
Brazilwood dark							
Lac							
Yellow lake							
Ultramarine							
Azurite							
Azurite + ultramarine							
Azurite + yellow lake							
Ultramarine + yellow lake							
Verdigris							
Vergaut							
Green earth							
Brownish earth							
Indigo							
Carbon black							
Lead white							
Mosaic gold							

2. Materials and Methods

2.1. The Illuminated Manuscript Gradual “D”

The Gradual made for Badia a Settimo, composed of four volumes (A, B, C, D), is now kept in Rome, in the church of S. Bernardo alle Terme. When the first studies on the liturgical book appeared, starting from the 1970s, it was at the Basilica of S. Croce in Gerusalemme, in Rome, where it was preserved until about a decade ago. It is a splendid liturgical series of choir books, containing the chants for the Mass, and it was produced during the first half of the fourteenth centuries for the Cistercians abbey of Badia a Settimo near Florence, in Tuscany. Manuscript D (590 mm × 400 mm) contains the Sanctoral, the Proper of the saints, and it is the most interesting among the four volumes, because it shows a vast illustrative program, painted by different artists. The manuscript has been dated by its scribe, Vincenzo Monocolo, to 1315 and it has been the subject of several studies [3,4], mainly dedicated to the identification of the different illuminators who worked on this volume, which shows the richest variety of styles. However, the date of the illuminations, which were carried out by different artists, is uncertain and widely discussed. Manuscript D consists of 296 parchment leaves, copied in *littera textualis rotunda* and illuminated with 59 large initials and marginal decorations, painted in tempera at the beginning of the most important festivities. Among them, there are 43 historiated initials and 16 letters decorated only with foliage. Moreover, the manuscript contains numerous pen-flourished initials, drawn in blue and red ink. The Sanctoral displays a richly varied iconographic program, a sort of Gothic picture gallery on parchment, illuminated by three important workshops active in Florence in the first half of the 14th century: artists close to the workshop of Pacino di Bonaguida, and two anonymous illuminators known as Maestro Daddesco and Master of the Codex of Saint George. The incipit, on folio 8r, is especially interesting: the initial “P” (*Puer natus est*) with the Nativity is attributed to an artist close to the workshop of Pacino di Bonaguida, but the border shows a decoration similar in style to those of the Maestro Daddesco. The same can be said of folio 18r: the initial “I” (*In medio ecclesiae*) appears to be decorated by the workshop of Pacino, while the figure of Saint John the Evangelist, inserted next to the letter, and the border decoration have been attributed to the Maestro Daddesco.

2.2. Analytical Techniques

2.2.1. Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF)

The spectrometer consists of an X-ray tube (Amptek Mini-X, Amptek Inc., Bedford, UK) with an anode target of rhodium and a beryllium window of thickness 127 µm and was powered with an accelerating potential difference of 38 kV and an electronic current of 80 µA. The detector is a Peltier-cooled silicon drift with amplifier and integrated multichannel analyser (Amptek 123-SDD), providing for any detected X-ray photon a current pulse with amplitude proportional to the energy of the photon. The detector has a surface area of 25 mm², a thickness of 500 µm, and a beryllium window of thickness 12.5 µm. The distance of the sample is 3.5 cm from the sensitive area of the detector and 3 cm from the generator anode. The measured area is about 14 mm². The energy resolution is 140 eV, full width half maximum (FWHM) of the manganese K α line at 5.9 keV. The X-ray beam collimation was 1 mm, and the acquisition time was 300 s. The spectra were analysed with Pymca 5.5.5.

2.2.2. Fiber Optics Reflectance Spectroscopy (FORS)

Fiber Optics Reflectance spectroscopy was performed with an AvaSpec spectrophotometer (Avantes, Apeldoorn, The Netherlands) equipped with an Avantes HL-2000 FHSA halogen lamp. The spectrometer uses a diffraction grating of 300 lines/mm, blazed at 500 nm, which allows to cover the spectral range from 300 nm to 1100 nm, and a CCD linear sensor (2048 pixels). The spectral resolution is 0.8 nm. We illuminated and collected the light at 90° with respect to the surface with a reflection probe constituted by 7 optical fibers, 200 µm core, 6 for illuminating and 1 for collecting the diffuse light (FCR-7UV200-2,

Avantes). The read fiber has a N.A. of 0.22 and is located at 1 mm from the surface. The reflectance spectra were collected from 380 to 1000 nm. In some cases, the reflectance spectra were converted in apparent absorbance through the equation: $A = \log(1/R)$. Smoothing with Savitzky-Golay procedure with a 2nd degree polynomial order and 55 points window was applied to all spectra.

2.2.3. Raman spectroscopy

The Raman spectra were acquired by using a portable Raman spectrometer (B&W Tek, Newark, NJ, USA) composed by a GaAlAs diode laser emitting at 785 nm (the laser spot diameter at focal plane is 85 μm) and a Peltier cooled CCD detector to collect the dispersed light (Exemplar Plus LS, B&W Tek) with wavelength range of 190–1100 nm. The acquired spectral range was $\approx 97\text{--}2000\text{ cm}^{-1}$ with 3 cm^{-1} of resolution. An integration time of about 30 s times and 10 scans were applied to optimize the signal-to-noise ratio.

2.2.4. Microphotography

A portable digital microscope (AM7915MZT-Edge, Dino-lite, Almere, The Netherlands) was used to acquire images at 10–220 \times magnification. The integrated polarizing filter and flexible LED Control (FLC) were used to image reflective surfaces such as gold leaf.

3. Results

This section presents the results on selected pigments of ff. 8r and 18r considered as useful to differentiate a palette from another one. The complete XRF analysis of these pigments is shown in Table S1 of the Supplementary Materials. The analysis of writing supports is also provided.

3.1. Parchment

Codicological and XRF analyses have suggested the presence of a parchment support. The two parchments leaves are characterised by the presence of sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), iron (Fe), copper (Cu), lead (Pb) and strontium (Sr) in points 1 of f. 8r and 1 of f. 18r (Figure 1a,b). The occurrence of Ca is generally referred both to the lime bath used for the dehairing of the skin and to the chalk employed for drawing out any remaining grease and whitening the parchment [5]. However, the presence of S and Sr in relation to Ca may indicate the presence of celestine (SrSO_4), a mineral usually found associated to the gypsum, also used for whitening the parchment [6]. In addition, S is a constituent of the proteinaceous structures of animal skin, i.e., cysteine ([7] and references therein). Cl and K contents are likely related to the potassium chloride bath applied to avoid the putrefaction of the skins. It has been demonstrated that potassium chlorides were used mainly in the coastal regions or wherever sea salt was cheap and available in large quantities. The salting was applied immediately after the skinning of the animal, to preserve the skins before the calcination step [8]. Fe, Cu and Pb could be considered as contaminants from both the washing operations and the use of several tools for parchment manufacturing. Si and Ti, only identified in 18r, can probably be ascribed to the smoothing processes performed by means of pumice, applied as a paste, or as dry powder or stone [5].

3.2. Ultramarine and Azurite

Since ancient times, natural ultramarine has been obtained by grinding and purifying the semi-precious stone lapis lazuli (from the Latin *lapis*, stone, and *lazalus*, a latinized form of the Persian word for blue) [9]. Lapis lazuli is generically classified as a metamorphic rock, even if this definition could not be considered exhaustive, due to the complexity of mechanisms involved in its genesis [10]. Its blue colour is essentially due to the mineral called lazurite; in addition to lazurite, lapis lazuli is composed of several minerals whose presence and relative quantity varies according to the deposits of origin. In the Middle Ages, it arrived in Venice by sea, from the mines of the Badakhshan region in Afghanistan,

as reported by Marco Polo in 1271 [11]. Since this blue was imported from the Levant, it was called “ultramarine” [12]. Up to the twelfth-thirteenth centuries people painted with lapis lazuli that was simply ground and washed; later more complicated purifications were carried out, which consist in mixing the ground stone with oils, resins, and waxes to form a malleable paste. The mixture was then treated with an ash lye solution, so that the finely divided ultramarine spread into the liquid, while the impurities remained incorporated in the waxy mass [9]. Some natural impurities still seem to remain in the pigment even in the most careful extraction, and these could allow to distinguish the natural ultramarine from the synthetic one and, in case of the natural material, the provenance. Angelici et al. [13] have demonstrated the effectiveness of X-ray fluorescence for lapis lazuli provenance studies. In the present work we characterised with ED-XRF the blue ultramarine (Figure 2a) in points 2 and 3 of f. 8r (Figure 1a). The following elements, detected in the pigment, are appropriate for the natural ultramarine:

- aluminium (Al), silicon (Si) and sulphur (S) that are expected in lazurite ($\text{Na}_3\text{Ca}(\text{Si}_3\text{Al}_3)\text{O}_{12}\text{S}$) [14];
- potassium (K), likely contained in the ash lye solution of KOH used during the extraction process and/or in several mineral phases that can occur within the lapis lazuli stone [15];
- iron (Fe) and calcium (Ca) contained into the minerals pyrite (FeS_2) and diopside ($\text{CaMgSi}_2\text{O}_6$), the mostly commonly associated to the lapis lazuli [13].



Figure 1. By permission of the Library of S. Bernardo alle Terme (Roma). Points of XRF and FORS analyses of ff. (a) 8r and (b) 18r. The red rectangle shows the break between the artist close to the workshop of Pacino di Bonaguida (point 9) and the Maestro Daddesco (point 11). The complete XRF analysis is provided in Table S1 of Supplementary Materials.

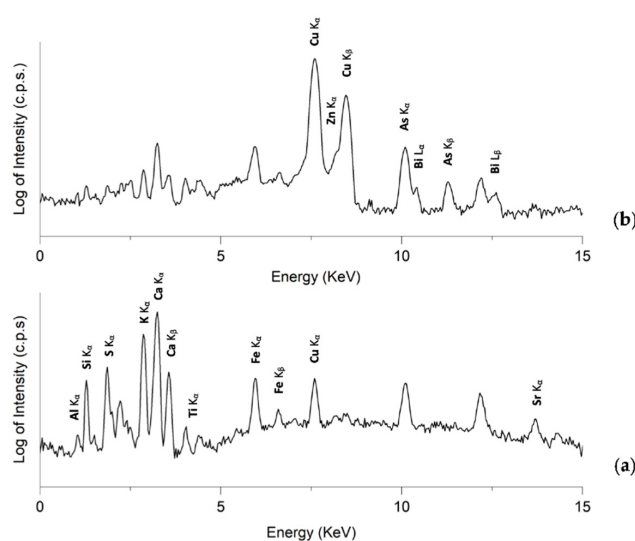


Figure 2. XRF spectra of ultramarine (a) in point 3 of 8r and azurite (b) in point 2 of 18r.

The further presence of copper (Cu) has been interpreted as a trace element of the pyrite while the strontium (Sr) and titanium (Ti) are from the diopside. In particular, the trace elements of the pyrite may be a good indicator of the Afghanistan provenance of the lapis lazuli [13].

The identification of ultramarine blue was confirmed also by the detection of its characteristic peaks at 255 and 540 cm^{−1} in the Raman spectrum [16] (Figure 3).

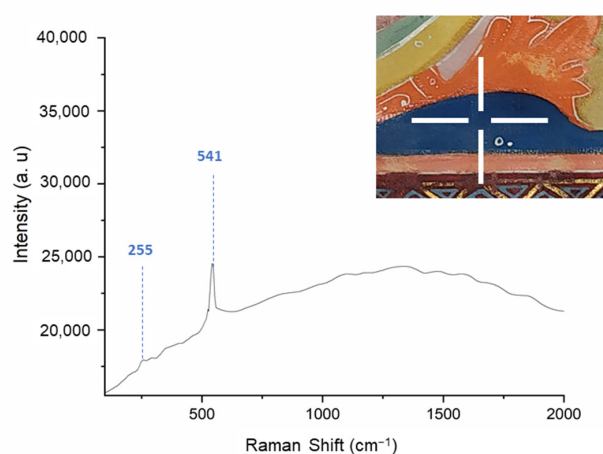


Figure 3. Raman spectrum of the blue background of the initial “P” (displayed inside the white cross). The peaks of ultramarine are reported in blue colour.

The results obtained from the scientific analyses of illuminated manuscripts refute the traditional thesis that ultramarine blue was rarely used before the fourteenth century (due to the high cost of the precious stone) [17] and show that it was even widely employed in secondary decoration (pen-flourished initials, rubrics, paragraph signs, etc.) of texts that are not exclusively liturgical.

However, a less expensive alternative to the lapis lazuli was azurite, known also as Azzurro di Alemagna, obtained from the grinding and purification of the homonym mineral composed of basic copper carbonate (Cu₃(CO₃)₂(OH)₂) [18] whose deposits were located mainly in Hungary, France, and Germany (hence the medieval name) [19]. In addition to a high amount of Cu, the XRF analysis found zinc (Zn), arsenic (As) and bismuth (Bi) (Figure 2b) in points 4 of f. 8r and 2, 3, 4, 5, 6, 7 of f. 18r (Figure 1a,b). Zn may be present in small crystals of smithsonite (Zn(CO₃)) known to naturally occur with azurite

ores [20]. Bi and As are contained into the mineral mixite $(\text{BiCu}_6(\text{OH})_6(\text{AsO}_4)_3(\text{H}_2\text{O})_3)$ which has been first identified by Berrie et al. [21] in the azurite used by Giotto and recently in azurite from illuminated manuscripts [22–24]. These findings support the idea that trace minerals in azurite can be retained after the pigment purification, and they could provide important information regarding the possible sources of the azurite employed. However, discovering the possible sources for mixite will require further research on the geology and history of mining in Europe.

The azurite and ultramarine can be distinguished on the basis of the maximum absorbance which is c. 600 nm for ultramarine and 640 nm for azurite in their respective FORS spectra; moreover, the azurite has a typical low reflectance in the red and NIR region, where ultramarine shows an increase in reflectance [25].

Occasionally the two pigments were combined together in points 5 (8r) and 8 (18r) (Figure 1a,b). Illuminators would have employed azurite to reduce the cost of materials by mixing it with the expensive ultramarine or simply to obtain different hues. The FORS spectrum (Figure 4) shows the absorption band at 620 nm which could well indicate a mixture of azurite and ultramarine. Moreover, the shoulder near to 715 nm and the moderate increase in reflectance between 700 and 950 nm can be indicative of a combination use of azurite and ultramarine. Delaney et al., on the basis of experiments carried out on modern samples [20], defined this particular spectral behaviour of FORS as typical of a layering of ultramarine over azurite. However, it is not straightforward to establish the presence of a layering without sampling it. In the blue robe the shift of the typical reflectance maxima peaks of ultramarine and azurite from c. 466 nm to 480 nm may be due to the presence of basic carbonate of lead [26], also known as lead white, as suggested by Pb XRF counts. An unusual combination of pigments azurite and ultramarine mixed with egg glair may have led to the flaking paint blue areas in the initial “I” of 18r. Glair cannot be characterised with the techniques used for this work. We suppose its presence only by a visual examination of the surface degradation. Indeed, previous studies have demonstrated that if applied in larger quantities, the glair becomes too dry and brittle over time and could cause the paint to flake off [27].

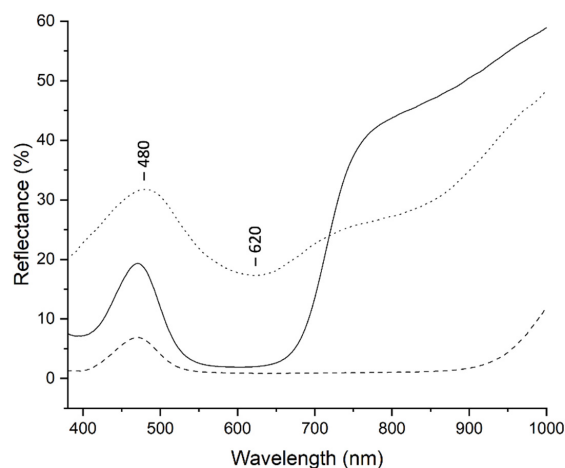


Figure 4. FORS spectra of azurite (dashed line) in point 2 of 18r, ultramarine (solid line) in point 3 of 8r, and ultramarine combined with azurite and lead white (dotted line) in point 5 of 8r.

3.3. Verdigris

In points 6 (8r) and 9, 10 (18r) a copper-based pigment has been identified as verdigris (Figure 1a,b). The characterisation of the verdigris is not straightforward with the employed techniques. XRF analysis generally only attests to the presence of copper (Cu). Ancient treatises describe different recipes for the preparation of verdigris formed as a result of the corrosion of copper when exposed to air, moisture and acid [28]. In the Middle Ages, verdigris was made by treating copper with vinegar; in some instances, plates of brass

instead of copper have been used [29] and this could explain the additional XRF counts corresponding to Zn in point 6 (8r) and 9, 10 (18r). The FORS spectrum shows an absorbance maximum at c. 725 nm and a shift towards longer wavelengths in the reflectance maximum. The typical reflectance maximum of verdigris at c. 500 nm undergoes to 40 nm shift probably due to the addition of lead white [30,31] (Figure 5a). Even though verdigris was especially volatile in proximity to lead-containing pigments, it was a common practice to combine the two pigments [27]. The microphotograph shows the deterioration of the painted surface in the green area as a result of the instability and corrosive properties of verdigris [32] (Figure 5a).

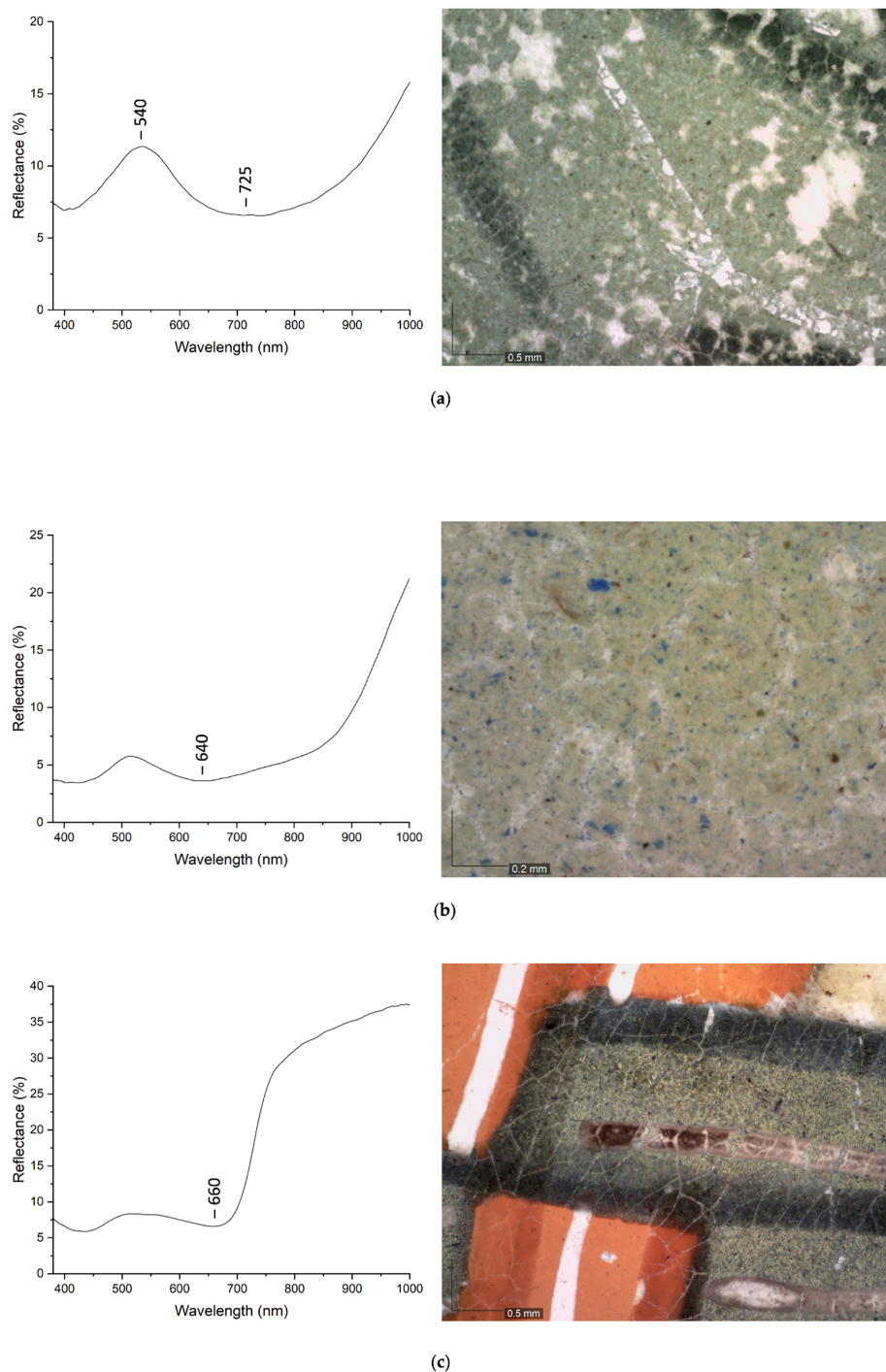


Figure 5. FORS spectra and their relative microphotographs of verdigris (a) in point 9 of 18r, azurite and yellow mixture (b) in point 12 of 18r, and vergaut (c) in point 14 of 18r.

3.4. Azurite and Yellow Mixture

In points 7, 8 (8r) and 11, 12, 13 (18r), we have characterised a mixture of blue, white and yellow pigments (Figure 1a,b). The XRF analysis is consistent with the presence of azurite (Cu, Zn, As, Bi) and lead white (Pb). The FORS spectrum shows the absorbance maximum at 640 nm typical of azurite while the broad band absorbance between 400–420 nm, the general shape of the curve and the rise in reflectance between the red and NIR region suggest the presence of a yellow pigment [25,33], likely organic, not identifiable with XRF (Figure 5b). The microphotograph shows the blue particles of mineral azurite immersed in a yellowish paint (Figure 5b). The azurite mixture appears to have been the preferred way to obtain bright green hues for Florentine illuminators between the fourteenth and fifteenth centuries, as shown by the results of analysis carried out on Florentine cuttings and manuscripts [34].

3.5. Vergaut

A mixture of indigo and orpiment, named vergaut in *De coloribus et artibus Romanorum*, has been found in point 14 (18r) (Figure 1b). Indigo is an organic colourant identified by the absorbance maximum at 660 nm in the FORS spectrum [25] (Figure 5c). The presence of the orpiment pigment, obtained by grinding the homonym mineral composed of arsenic sulphide (As_2S_3) [35], was suggested by As and S XRF counts. The mixture was validated by Raman spectroscopy through the detection of 252, 544, 1575 and 1584 cm^{-1} peaks, attributed to the indigo and, also by 136, 153, 180, 203, 292, 309, 355 and 383 cm^{-1} peaks relative to the orpiment [36] (Figure 6). The microphotograph shows bright yellow particles of orpiment mixed with the dark blue of indigo (Figure 5c). To the best of our knowledge, vergaut is frequent in Western manuscripts of the early Middle Ages, in particular in Anglo-Saxon illuminations [37–40], but evidence is also found in a French manuscript of c. 1505 [41], in the Missal of Cardinal Angelo Acciaiuoli illuminated in Florence between 1402–1405 [42], and in the illumination of the Ascension (c. 1340) from the Laudario of S. Agnese [43].

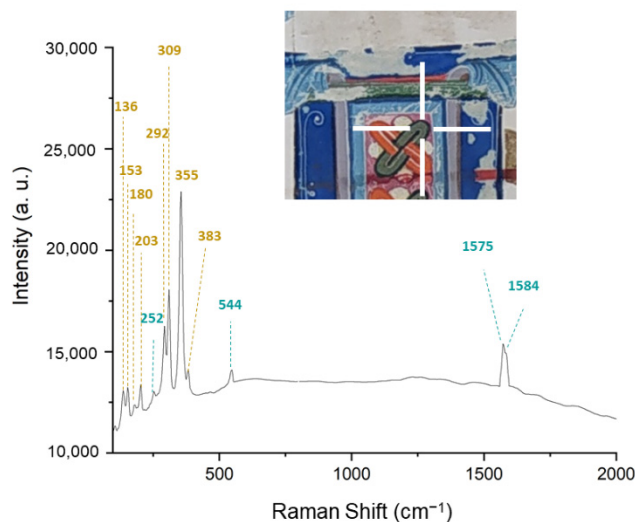


Figure 6. Raman spectrum of a green decorative element in the frame of the initial “P” (displayed inside the white cross). The peaks of orpiment are reported in yellow colour, those of indigo are indicated with a green colour.

3.6. Earth Pigments

Earth pigments might be divided into two groups according to their colour agents. The group of clay pigments includes green earths ($\text{K}[(\text{Al}, \text{Fe}^{3+}), (\text{Fe}^{2+}, \text{Mg})] (\text{AlSi}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) which mainly owe their colour to the specific ratio of divalent and trivalent iron in the structure of minerals glauconite and celadonite [44]. FORS spectrum suggest the presence of

green earth in point 9 (8r) (Figure 1a) showing the absorption maximum near to 740 nm [25,45], reflectance maxima at 555 nm and a shoulder near to 485 nm [46,47] (Figure 7). A red earth, likely the clay named ‘Armenian bole’, was employed as part of the preparatory layer for the gold leaf. We hypothesized the presence of two different preparatory layers realized with the assiso technique which involves the use of gypsum [48]. Moreover, in point 10 (8r), the light pink hue of the preparatory layer was probably due to a smaller amount of earth and a larger one of lead than the points 11 (8r) and 15 (18r) (see Table S1 of Supplementary Materials). The different hues of the two layers are visible in Figure 8a,b.

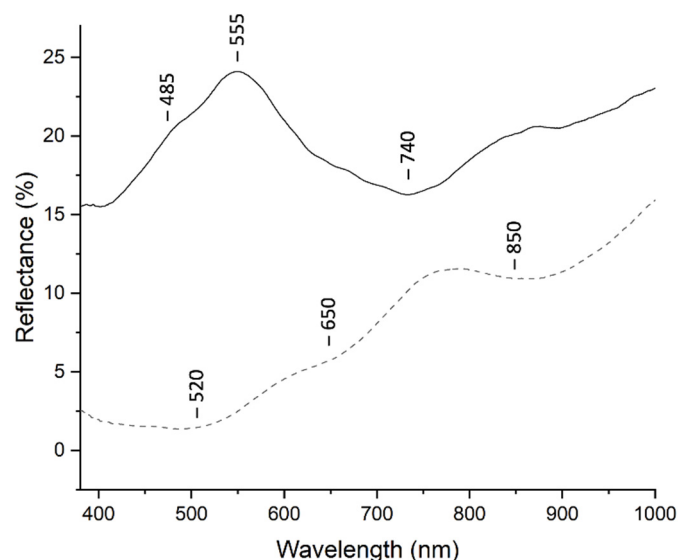


Figure 7. FORS spectra of green earth (solid line) in point 9 of 8r and brownish earth (dotted line) in point 12 of 8r.



Figure 8. Images of 8r showing (a) angel in the marginal decoration; (b) Virgin Mary in the initial “P”.

The non-clay pigments group owe their colour to the presence of different iron oxyhydroxides and oxides, mainly goethite and hematite; sometimes the colour is brownish due to manganese oxides [44]. A brownish earth pigment has been identified in point 12 (8r) and 17 (18r) as revealed by the typical shape of the FORS spectrum (Figure 7). The spectral features (absorption bands at 880, 650, 520 nm) are consistent with the presence of the hematite Fe-oxide mineral (Fe_2O_3) [49].

3.7. Vermillion

The non-invasive analyses sometimes help to distinguish the mineral cinnabar from its synthetic analogue, vermillion, on the presence of natural impurities, not found however

in these illuminations. Vermilion is a sulphide of mercury resulted from roasting mercury and sulphur. The production of vermillion is well established by the fourteenth century, but Theophilus included the recipe as early as twelfth century in his *Diversarum artium Schedula*. XRF found counts of S and Hg in point 13 (8r) of the red cheek of the Virgin Mary. On the contrary, as suggested also by Figure 8a,b, in the angel of the border this detail has an orange hue assimilable to that of red lead (minium), as confirmed by the absence of similar counts of S and Hg and the presence of XRF counts of Pb in points 14 (8r) and 16 (18r) (see Table S1 of the Supplementary Materials).

A mixture of vermillion (252, 286, 343 cm^{-1}) and lead white (1050 cm^{-1}) was used in the frame of the initial “P” and has been characterised by Raman spectroscopy [36] (Figure 9).

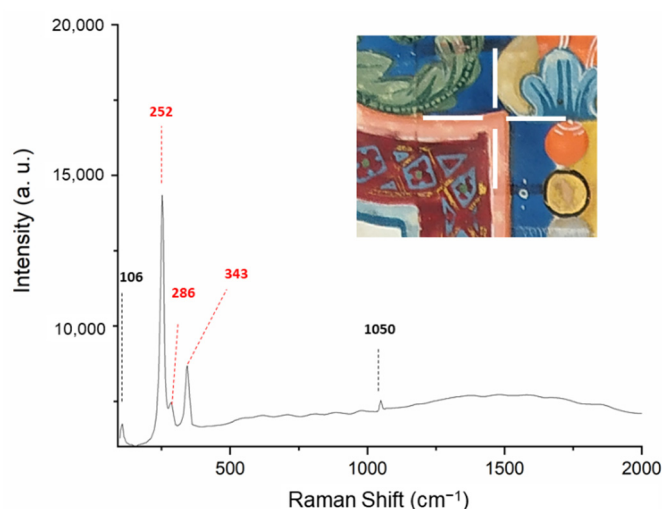


Figure 9. Raman spectra of the red frame of the initial “P” (displayed inside the white cross). The peaks of lead white are reported in black colour, those of vermillion are indicated with a red colour.

3.8. Organic Pink Pigments

Brazilwood is a redwood derived until the sixteenth century from the Asian sappanwood (*Caesalpinia sappan*). The discovery of South America revealed new trees similar to sappanwood with dyeing proprieties as well [50]. The new redwood started to be imported to Europe and partially replaced the Asian sappanwood. Brazilwood dye could be extracted from its natural plant source and precipitated in solution with an inorganic salt. The acid or basic solution determines the hue of the pigment and the additives added during the manufacture influence its opacity [50,51]. The analyses of manuscript D have suggested different preparation methods of the brazilwood which gave rise to different hues of the colourant. In points 15 (8r) and 18, 19 (18r) the light pink is characterised by XRF counts of Pb likely related to the lead white added in the initial extraction phase. On the contrary, the dark pink of point 16 (8r) and 20, 21 (18r) is characterised by S and Ca likely related to the gypsum employed in the filtration process [50]. Higher amounts of P and K were found only in point 16 (8r). All FORS spectra are characterised by a single absorption band centered to 560 nm typical of brazilwood [25] (Figure 10). The FORS spectra are similar in shape, maxima, and inflection point, despite the different recipes used to produce the pigments and the diverse hues of colours obtained.

A red insect-based dye has been identified in point 17 (8r) (Figure 1a). It is presumably lac, a resinous secretion from scale insects of the family Coccoidea. The presence of this pigment is rare since, to the best of our knowledge, lac dye has so far only been identified in Islamic [52] and Christian Portuguese [53] manuscripts with micro-invasive and non-invasive techniques. Based on the FORS spectra provided by Vieira et al. 2019 [52], we can suppose the presence of lac in 8r, suggested by two absorbance maxima at 530 nm and 568 nm due to the anthraquinone chromophore (Figure 10).

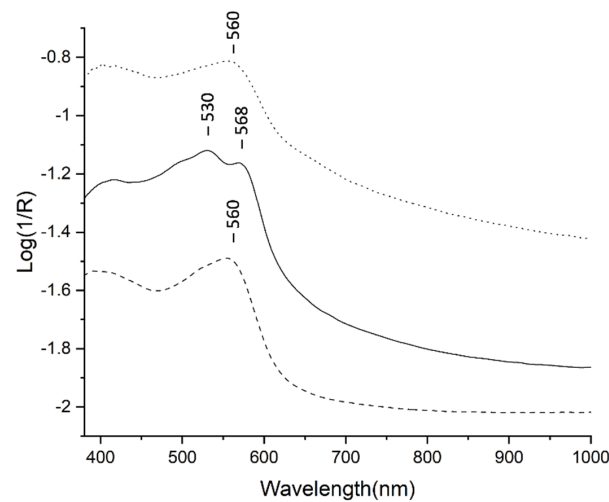


Figure 10. FORS spectra of light pink brazilwood (dotted line) in point 15 of 8r, dark pink brazilwood (dashed line) in point 16 of 8r, and lac (solid line) in point 17 of 8r.

4. Discussion

4.1. Identification of the Illuminators' Palettes

The palettes described in the borders of ff. 8r and 18r are close to each other (brazilwood light, azurite and azurite mixed with yellow lake); in a similar way, those in the two initials appear to be homogenous (brazilwood light and dark, azurite mixed with ultramarine, verdigris and brownish earth). The two palettes were then compared with those identified on seven illuminations of Gradual “D”: two attributed to artists close to Pacino di Bonaguida (ff. 23r, 191r), three to the Maestro Daddesco (ff. 91v, 116r, 216v) and two to Master of the Codex of Saint George (ff. 108v, 133r). The comparison is summarized in Table 1.

The palettes in the borders of ff. 18r and 8r are close to that employed by the Maestro Daddesco in ff. 91v, 116r, 216v, except for the use of pure azurite. The use of pure azurite exclusively in the borders could be indicative of a transition phase represented by the two leaves, in which the Maestro Daddesco intervened to complete the work that had been started by Pacino’s follower. The use of azurite therefore may have occurred when the Maestro Daddesco had not yet purchased the ultramarine, that he would then have used in the rest of the manuscript.

In the initial “I” (18r) the specific presence of flaking blue paint and vergaut indicates an artist similar to that so-called “Pacinesque” artist identified on f. 23r. In turn, the vermillion, lac, ultramarine, and green earth found in the “P” (8r) are the same used by a second “Pacinesque” illuminator on f. 191r. This discussion appears to be consistent with scholarly literature which has identified to at least fourteen distinct personalities close to Pacino in various illuminated manuscripts [54].

The analyses carried out on f. 18r have allowed to identify the break between the two artists (Figure 1b). The letter “I”, the superior foliage decoration and a part of the inferior were attributed to an artist close to Pacino; the figure of Saint John the Evangelist next to the letter and the remaining border to the Maestro Daddesco.

4.2. The Workshop of Pacino di Bonaguida in Manuscripts

We compared our analyses with those carried out with similar techniques on leaves from the Laudario of Sant’Agnese and on a series of panels painted by the workshop of Pacino di Bonaguida [20,43,54]. The main observations are listed below:

- The use of a mixture of yellow orpiment and blue indigo (vergaut) appears both in the illumination of the Ascension from the Laudario and in the “I” of 18r from the Gradual “D”. Paterson et al. [43] attributed the use of the vergaut exclusively to the panel paintings of Pacino, so the vergaut found in the Ascension is considered as an

unintentional inclusion, perhaps a contamination from the panel painter's palette. The "Pacinesque" illuminator of the "I" seems to behave just like the painter Pacino. The vergaut and the blue paint, the latter flaked off perhaps due to the addition of egg glair, could be unusual materials deriving from a panel painter's palette rather than a manuscript's one. These findings possibly provide an evidence of the proximity of manuscript and panel painting activities in the work of the illuminator of the "I".

- The use of an insect dye not clearly specified in several leaves from the Laudario could be the same used by the illuminator of the "P".
- The dotted halo shown in the image under magnification (Figure 8b) is identifiable as a characteristic of a "Pacinesque" style in the illuminations of Gradual "D" as well as in those from the Laudario.
- When comparing the approaches to painting the flesh tones across Pacino's works on panel paintings and illuminated manuscripts, it was highlighted that works dated or dateable to c. 1300–1320s do not include a green earth ground whereas those dated or dateable to c. 1330 onwards do apply a green earth ground [54]. The absence of a ground of green earth in the flesh painting of "P" initial of the Gradual could support the dating of the illumination to c. 1300–1320 s.

5. Conclusions

The characterisation of the artist's palette can be crucial to differentiate pictorial methods in collaborative illuminations. We have demonstrated the effectiveness of non-invasive analyses in the identification of painting palettes and techniques as a tool to differentiate the hands of artists who have worked together on the same page. The use of complementary techniques such as XRF, FORS and Raman spectroscopy allowed us to characterise the palette of the Maestro Daddesco in the borders of ff. 8r and 18r, and two different "Pacinesque" artists, identified respectively in the two initials "P" and "I". Limitations in the study of some pigments (e.g., verdigris and mixtures) were also outlined. The use of microscopy combined with spectroscopic techniques was especially helpful in the identification of green mixtures. The comparison with analyses carried out on illuminations attributed to the workshop of Pacino di Bonaguida enabled us to contribute to the discussion on the several followers of one of the most prolific workshops in the early fourteenth century. The study has demonstrated that integrating the results gathered from art-historical and from materials analyses provides a more comprehensive knowledge of the illuminators and their methods of work. Future research will focus on the other three volumes of the same Gradual, illuminated by the Maestro Daddesco, who completed the liturgical series without the collaboration of other workshops.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11070771/s1>, Table S1: XRF analysis of points shown in Figure 1a,b.

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