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Rediscovering the Painting Technique of the 15th Century Panel Painting Depicting the Coronation of the Virgin by Michele di Matteo

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Abstract: The study concerned a diagnostic spectroscopic campaign carried out on the panel painting depicting the *Coronation of the Virgin* (first half of the 15th century) by the late-Gothic Italian painter Michele di Matteo. The main aims were the identification of the original painting materials and the characterization of the painter's artistic technique. A combined approach based on non- and micro-invasive techniques was employed. Visible and ultraviolet-induced fluorescence photography was used to select the areas of interest for spectroscopic analyses; X-ray radiography assessed the state of conservation of the support, while X-ray fluorescence and external reflection Fourier transform infrared spectroscopies allowed the chemical identification of pigments, binders, and varnishes. Attenuated total reflection infrared spectroscopy, optical microscopy, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy were used to visualize and characterize the materials in the pictorial layers. The results highlighted the presence of pigments, possibly applied with an egg binder, consistent with the period of the production of the painting, as well as modern pigments used during subsequent restorations: an *imprimitura* with lead white and a gypsum-based ground layer. Concerning the gilding, the *guazzo* technique was confirmed by identifying a red *bolo* substrate and gold leaf.

Keywords: panel painting; multi-analytical approach; XRF; ER-FTIR; ATR-FTIR; optical microscopy; electron scanning microscopy

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1. Introduction

In the field of cultural heritage, the analytical scientific approach is often used to support conservation and restoration procedures, as well as to increase the information useful for the art historical study and valorization of an artwork. This type of analysis often focuses on the identification and characterization of the different materials used to produce the artwork and their distribution in the multi-layered system present in different areas of the painting. In the case of medieval panel paintings, the stratigraphic system usually includes a ground layer (e.g., gypsum and glue), an under-drawing, overlapped paint layers, a mixture of pigments and binding media (e.g., animal glue, egg, siccative oil), and an external varnish that partially covers non-original paints or restoration materials [1–5].

The present research focuses on the analytical campaign on the panel painting from the first half of the 15th century depicting the *Coronation of the Virgin* by Michele di Matteo (Bologna, 14th century—Bologna, 1469) (Figure 1). The iconography depicts Jesus Christ placing the crown on the head of his mother sitting on the same throne. The painting is attributed to Michele di Matteo, also known as Matteo de Calcina, Michele della Fornace [6,7], or Michele di Matteo Lambertini [7,8], who was a late-Gothic painter active in Bologna from 1410 to 1469 [9]. While it is known that he was an apprentice of Giovanni da Modena [6,7], his artistic identity remains ambiguous. Consequently, conducting analytical studies of the painting techniques employed by the artist could provide valuable insights into his artistic style. The panel, which is part of a private collection, is probably the only remaining portion of a dismembered polyptych [7,10] commissioned by the *Corporazione dei Calzolari* of Bologna around 1421–1426 [6].

Figure 1. Photography in VIS light of the (**a**) front and (**b**) back of the painting *Coronation of the Virgin* (92 × 72 × 2.5 cm) by Michele di Matteo. Enlarged details of the cracks in the painting layers in correspondence with (**c**) Christ's mantle and (**d**) the golden background and halos.

The main aims of this analytical campaign were (i) the assessment of the state of preservation of the support and the pictorial layer, (ii) the characterization of both original and restoration artistic materials (e.g., pigments, lakes, binders), and (iii) the identification of the multi-layered system in order to obtain information about the painting technique (i.e., support preparation and gilding). This paper tries to provide the necessary and useful data from the first analytical campaign carried out on Michele di Matteo's painting. The results could contribute to the understanding of his painting technique, which has never been studied from a scientific point of view, and in the future, they could be a valuable reference for works by the same painter or other artists related to him. Also, the scientific investigation intends to support future restoration procedures. To these ends, a combined multi-analytical approach based on non- and micro-invasive techniques was employed to study the painting. In particular, visible photography (VIS) and visible fluorescence induced by ultraviolet radiation (UVIF) were used to select the areas of interest for the spectroscopic analyses [4,11,12]. X-ray radiography (RX) was also necessary to assess the state of conservation of the support [12–14]. X-ray fluorescence (XRF) [2,14–16] and external reflection Fourier transform infrared (ER-FTIR) [12,13,17,18] spectroscopies allowed the chemical characterization of pigments, binders, and varnishes. Considering the historical and artistic importance of the work and the painter, a micro-invasive approach, limited to a few areas of interest, was conducted. The application of attenuated total reflection infrared

(ATR-FTIR) spectroscopy, optical microscopy (OM), and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) permitted the mapping and identification of the materials in the pictorial layering, in particular the ground preparation and the gilding [1,2,17,19–22]. A limited number of fragments for micro-invasive analysis were sampled by an expert restorer, where micro-cracks or already partially detached parts were recognized. According to the literature, the above-mentioned techniques have been proven to be successful in providing information about the materials [1,3,12,14,23,24] and creating a list of possible pigments used by the artist in the different layers [25–27].

2. Experimental Section

Thirty-three representative measuring points for XRF analysis and thirty for ER-FTIR were selected (Figure 2b). Finally, to deepen the knowledge of the painting stratigraphy—both its morphology and composition—attenuated total reflection infrared (ATR-FTIR) spectroscopy, optical microscopy (OM) in visible and UV light, and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) were used to examine the paint cross-sections.

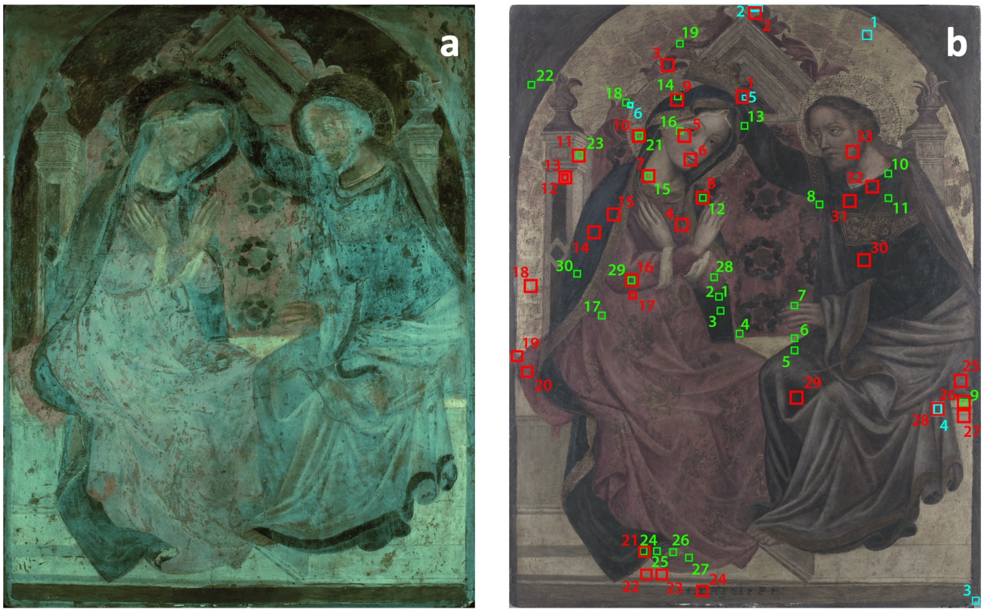

Figure 2. (**a**) UVIF image of the panel painting *Coronation of the Virgin*. (**b**) Visible image of the panel where ER-FTIR analytical spots (green squares), XRF spots (red squares) and micro-sampling areas (light blue squares) are highlighted.

The VIS and UVIF images were captured with a full-frame Nikon D600 digital camera (Minato, Tokyo, Japan) mounted with a 50 mm f.1.4 Nikkor objective (Minato, Tokyo, Japan). Visible light images (f/8 as focal ratio, ISO 100) were obtained using two softbox Godox SL-60W LEDs (T = 5600 K) (Shenzhen, Guangdong, China) to provide the required illumination. The colour profile ColorChecker®Classic X-Rite (Grand Rapids, Michigan, USA) was used for colour calibration and white balancing of the images. The UVIF images (f/8 as focal ratio, ISO 400, 15 s exposure time) were acquired by exposing the panel to two Madatec CR230B-HP UV LED lamps (365 nm UV source with a power output of approx. 3 W) (Pessano con Bornago, Italy). Adobe Photoshop CS6 graphics program was used for colour calibration, white balance, and photo post-processing. The RX investigation was carried out employing Job Corporation portable X-ray equipment PORTA 100HF. The radiographic system involves the use of an X-ray photosensitive phosphors radiographic Fujifilm Imaging Plate CR UR-1 (35.4 × 43.0 cm, resolution 50 µm) that can be scanned and digitized in real time with CR35NDT Dürr NDT (Bietigheim-Bissingen, German. The exposure parameters were 44 kV voltage intensity, 50 mA current intensity, and 6 s exposure time. The software employed for acquiring, viewing, and processing images was D-Tect 4.12.1. Eleven RX images were acquired to cover the entire painting's surface. Images were aligned, merged, and processed using Adobe Photoshop CS6 to obtain all the diagnostic information in one.

XRF analysis was carried out using ELIO, a compact, portable, and high-performance energy dispersive spectrometer produced by Bruker XGLab SRL (Milan, Italy). The X-ray source worked with an Rh anode, and the beam was collimated to a spot diameter on the sample surface of about 1.3 mm. XRF measurements were performed by fixing the tube voltage at 50 kV, the measuring time at 90 s, the tube current at 80 μA, and the acquisition channel at 2048. The data are expressed as the value of the net area counts of each element's peak (Kα) normalized to the average net area counts of the coherent scattering peak of Rh-Kα calculated on the whole dataset. Spectra were processed using ELIO 1.6.0.29 software.

An ER-FTIR spectroscopy analysis was performed using an Alpha portable FTIR spectrometer (Bruker Optics, Germany/USA-MA) equipped with an R-Alpha external reflectance module. A Globar source produces an infrared beam that is focused with a 23° incidence angle on the material surface, at a working distance of 15 mm. The beam diameter measures 5 mm. The compact optical bench comprises a SiC globar source, a RockSolid interferometer, and an uncooled DTGS detector. The reflected beam is collected with the same angle of incidence, resulting in a near-normal reflection. Spectra were collected between 7500 and 375 cm^{-1}, at the resolution of 4 cm^{-1} and with an acquisition time of 1 min. The background was acquired using a gold flat mirror. Reflection FTIR spectra were transformed to absorbance spectra by applying the Kramers-Kronig transformation (KKT). Both pseudo-absorbance and KKT spectra are exhibited in figures in the mid-IR spectral range (4000–400 cm^{-1}). Data were processed using Bruker OPUS 7.2 software.

For the stratigraphic study, six micro-samples (Figure 2b) were detached with a scalpel from different selected areas of the painting where the surface was not in an optimal state of preservation and showed cracks, or at the interface with restored areas. However, only the fragment detached from the gilding will be further discussed in Section 3.2.6, as it resulted in the most informative micro-sample. The micro-samples were then embedded in epoxy resin (Epofix Struers and Epofix Hardener with ratio 15:2) and cut in cross-sections; the sections were then polished with fine silicon carbide sandpaper (up to 8000 mesh) and observed using an Olympus BX51TF polarized light optical microscope equipped with visible (Olympus TH4–200) and UV (Olympus U-RFL-T) lights. Images at high magnification and elemental infrmation were obtained with a scanning electron microscope (FE-SEM Tescan Mira 3XMU-series, Brno, Czech Republic), set with an accelerating voltage of 15–20 kV in a low vacuum and equipped with a Bruker Quantax 200 energy-dispersive X-ray spectrometer (Billerica, MA, USA). An ATR-FTIR analysis was performed using a Thermo Scientific NICOLET iS5 spectrometer (Waltham, MA, USA) equipped with an iD7 ATR accessory and germanium crystal. All infrared spectra were recorded within the range of 4000–500 cm^{-1} with 4 cm^{-1} resolution and 32 scans. OMNIC 7.2 software package was employed for the study of spectra.

3. Results and Discussion

3.1. Preliminary Observations by Imaging Techniques

The visible image in Figure 1 shows the overall appearance and the state of conservation of the painting. The panel (92 × 72 × 2.5 cm) clearly shows the bending of the wooden support and cracks in the painting layers, along with some previous restoration treatments. Cracks were found in correspondence with Christ's mantle, the golden background and halos (Figure 1c,d), and the areas in which a loss of brightness and intensity at the level of the throne structure and the figures of Christ and the Virgin were recognizable. The UVIF image (Figure 2a) confirms the presence of an even layer of varnish, characterized by a diffuse and intense light blue-green fluorescence. Other areas, which probably were the result of retouching and over-painting, are also evidenced by a different hue of fluorescence, darker than the others, observed in correspondence with Christ's garment collar and sleeve, the Virgin's and Christ's mantles over their shoulders, Christ's face, and the central decoration of the throne seatback.

High-resolution images are provided in Supplementary Information (Figures S1–S3).

The RX investigation (Figure 3) revealed the structure of the wooden support. As visible along the left and right parts of Figure 3, the panel is made of one thick wooden plank (tentatively recognized by the restorers as poplar wood) with a vertical orientation of the fibres. The presence of cracks in the central and bottom parts (marked with green arrows in Figure 3) were highlighted, and the presence of woodworm galleries proved previous xylophagous attacks, mainly spread in the areas of the background, Christ's figure, and the Virgin's dress (marked with red arrows in Figure 3). Moreover, the presence of stucco works in various areas over the entire surface (yellow arrows in Figure 3) was revealed due to the high radiopacity of this material, which appears clearly as white areas. On the other hand, the light grey shaded areas let us suppose the presence of radio-opaque pigments on the background, composed of elements with high atomic numbers (e.g., lead white and cinnabar [14]), which have a high absorption of X-rays. Finally, X-ray radiography proved the presence of the *incamottatura,* which is a commonly employed technical practice that involves raw canvas to prepare, cover, and uniform the wooden panel. It is clearly visible in the right upper part of the painting (marked with the blue arrow in Figure 3).

Figure 3. RX of the painting where the presence of cracks (green arrows), previous xylophagous attacks (red arrows), stucco (yellow arrows), and canvas (blue arrows) are highlighted.

3.2. Non-Invasive Characterization of Painting Materials

3.2.1. Blue Pigments

The XRF analysis performed on the blue areas corresponding to the Virgin's mantle marked the presence of iron (Fe) as a major element, together with cobalt (Co), potassium (K), copper (Cu), arsenic (As), and silicon (Si) (Figure 4a). These elements suggest the presence of possibly more than one pigment: Fe could be related to Prussian blue ($Fe_2[Fe(CN)_6]^3$) [14,25,27]. The presence of this pigment is also supported by the CN stretching band around 2098 cm^{-1} [28,29], visible in the ER-FTIR pseudo-absorbance spectrum in Figure 4b. Additionally, the presence of smalt (SiO_2, K_2O, Al_2O_3, and CoO) is suggested by Co, K, As and Si XRF peaks and by the ER-FTIR bands from silicates around 1020 cm^{-1} related to the Si-O-Si antisymmetric stretching mode [4,29,30]. The presence of As is considered a good marker for the smalt pigment. This additional element may be associated with some of the cobalt ores used as raw material and related to the different processes used in pigment preparation and production [31–33]. It is worth highlighting that the presence of Prussian blue, first synthesized in 1724, is probably due to restoration, whereas smalt is a pigment coherent with the production period of the painting [27]. Beyond the pigment signals, the ER-FTIR spectrum after the KKT showed the signal of a terpenic resin as an external varnish (CH stretching at 2934, 2862 cm^{-1} and C=O stretching at 1705 cm^{-1}) [16,17,19,22,30], along with those of a proteinaceous binder (around 1660 cm^{-1} for amide I, while other bands overlapped with oxalates within the range of 1620–1315 cm^{-1}) [4,16,17,19,22], possibly a *tempera magra* in accordance with a 15th-century painting technique [2,3,20]. The low counts of Cu detected in all the analytical spots in correspondence with the mantles of the Virgin and Christ led to the hypothesis of the use of a blue Cu-based pigment, such as azurite ($2CuCO_3 \cdot Cu(OH)_2$) [5,25,27], as possibly the original underneath pigment used to paint this area [34], although it remained undetected by ER-FTIR. As for the areas in correspondence with Christ's mantle, the XRF spectra highlighted the presence of Fe as the major element, without any trace of Co, suggesting the presence of Prussian blue rather than smalt.

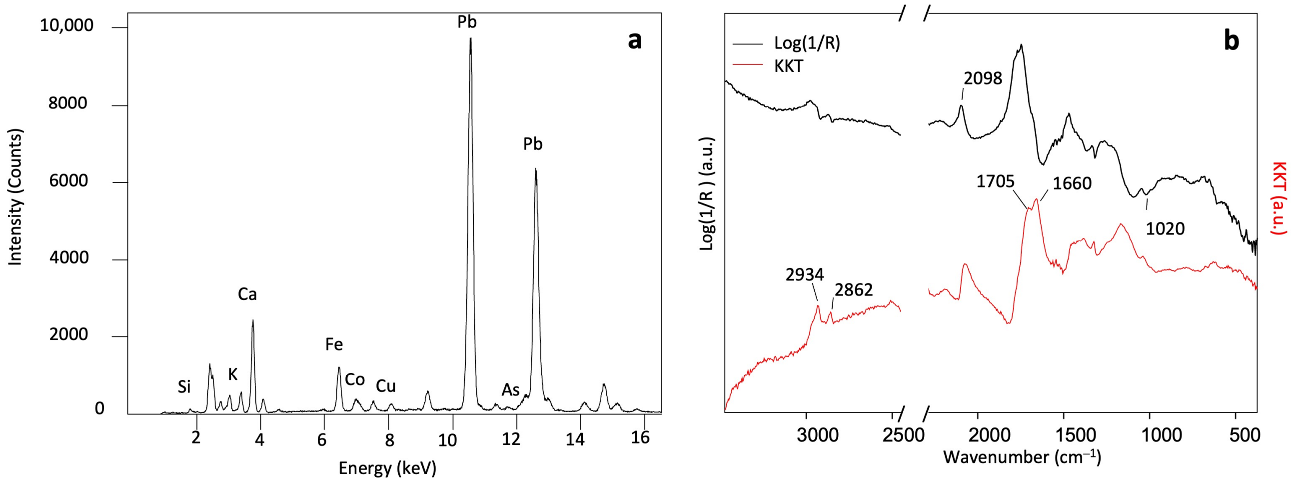

Figure 4. (**a**) XRF spectrum (spot 9 in Figure 2b, red square). (**b**) ER-FTIR pseudo-absorbance and KKT spectra (spot 14 in Figure 2b, green square) of the blue area of the Virgin's mantle over her head.

3.2.2. Green and Blue Pigments

The dark green-bluish areas corresponding to Christ's collared garment and the Virgin's dress revealed high XRF counts of Cu and Fe, together with Si. Also, for greens, a mixture of different pigments cannot be ruled out: Cu can be related to malachite ($CuCO_3 \cdot Cu(OH)^2$) or verdigris ($Cu(CH_3COO)^2 \cdot 2H_2O$) [11,25,27], the most frequent pigments used in the Middle Ages [1,11]. Fe could instead suggest a mixture with Prussian blue or green earth (hydrosilicate iron minerals) [1,14,25,27]. Unfortunately, ER-FTIR was unable to clearly detect the diagnostic features of Cu-based pigments, while the bands around 1020 cm^{-1} and 2098 cm^{-1} could reasonably support the presence of green earth and Prussian blue, respectively.

3.2.3. White Pigments

In correspondence with the whitish areas of the throne, significantly higher counts of lead (Pb), compared to the other analysis points, indicated the use of lead white ($(PbCO_3)_2 \cdot Pb(OH)_2$) [11,14,25,27]. The identification of this pigment was also confirmed by the ER-FTIR bands around 3547, 1450, and 678 cm^{-1} (Figure 5), related to the O-H bonds, $CO_3{}^{2-}$ asymmetric stretching, and in-plane bending, respectively [17,30,35]. The ubiquitous detection of Pb in any XRF spots implied the use of lead white both as *imprimitura* and white pigment to achieve light hues of colour in specific areas, as observed in the RX digital image (Figure 3). In addition, counts of Fe [11,14,25,27] along with ER-FTIR bands around

533 and 465 cm^{-1} related to the Fe-O stretching and bending bands [18,29,35] could be related to an iron-based earth pigment, possibly red ochre in low concentration.

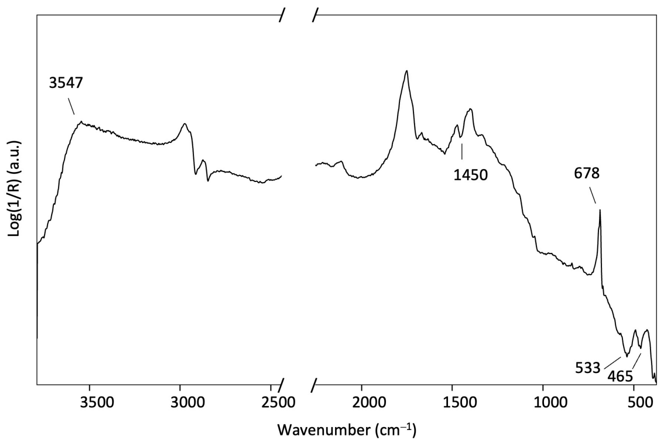

Figure 5. ER-FTIR pseudo-absorbance spectrum (spot 9 in Figure 2b, green square) of the white area of the throne structure.

3.2.4. Red Pigments

In the red areas of the Virgin's dress and pillow, mercury (Hg) and Fe were detected by XRF as the principal elements, suggesting the use of cinnabar (HgS) and red ochre (Figure 6a) [11,14,25,27]. Accordingly, ER-FTIR bands around 530 and 450 cm^{-1} related to the Fe-O bond and those of silicates between 1020 and 1030 cm^{-1} supported the use of red ochre, while cinnabar remained not visible within the working range. Moreover, a difference between the investigated red backgrounds was marked by XRF measurements: the counts of Hg are significantly higher in the pillow than in the dress, implying a greater use of cinnabar.

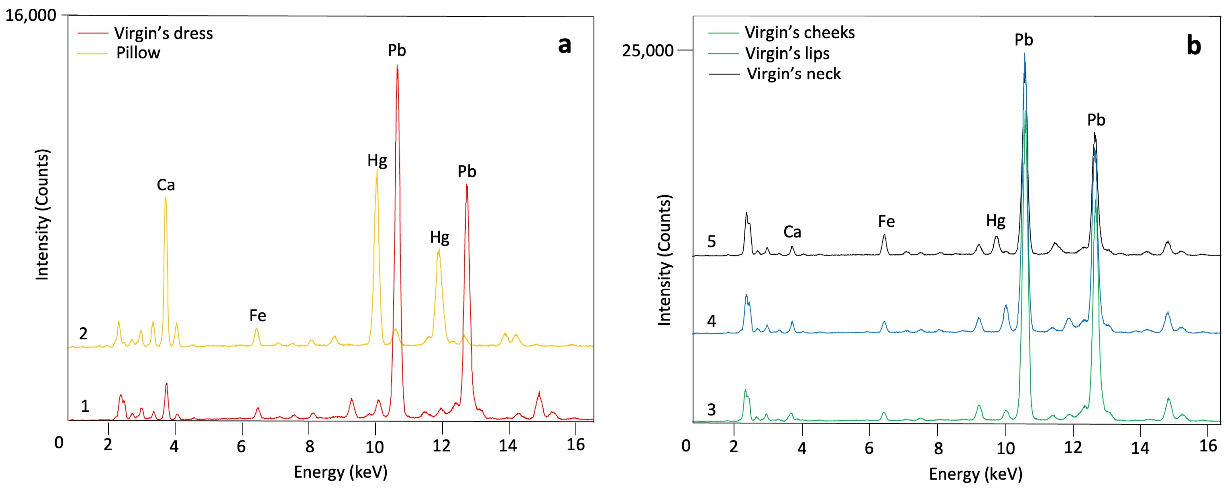

Figure 6. Comparison of XRF spectra collected (**a**) on the red areas of the (1) Virgin's dress (spot 16 in Figure 2-b, red square) and (2) pillow (spot 20 in Figure 2b, red square), and (**b**) on the flesh tone areas of the Virgin's (3) cheeks and (4) lips (spots 5 and 6 in Figure 2b, red squares) and (5) Virgin's neck (spot 7 in Figure 2b, red square).

3.2.5. Flesh Tone Pigments

The flesh tones of the Virgin's neck, cheek, and lips have similar elemental composition but different abundance of elements. In the XRF spots 5 and 6, high counts of Hg and Pb, together with the signal of Fe, suggested the use of a mixture of cinnabar, red ochre, and lead white (Figure 6b). In the same area, the ER-FTIR spectra confirmed the presence of silicates and haematite, while in the area of the Virgin's neck, lead carbonate was identified by the characteristic signals around 1440 and 680 cm^{-1} related to the O-H and C-O bonds [17,30,35]. The XRF spot 7, corresponding to the Virgin's neck, was characterized by the same elements, although higher counts of Fe than those identified in the XRF spots 5 and 6 suggested a greater amount of red ochre.

3.2.6. The Painting Technique: Ground Layer and Gilding

The execution technique of the ground layer and gilding were investigated at the microscale level thanks to the analysis with SEM-EDS and ATR-FTIR, carried out on the cross-sectioned samples from the golden background. Figure 7 highlights a structure composed of three layers: the ground layer (A), a gilding substrate or *bolo* (B), and gold leaf (C).

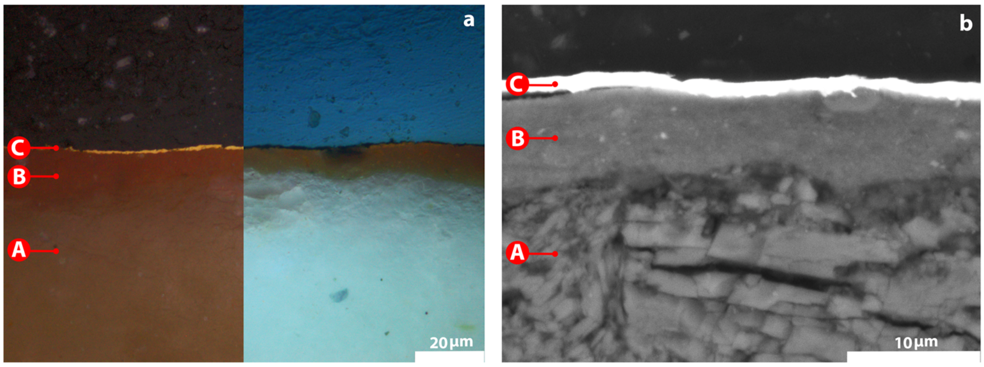

Figure 7. Cross-section of sample 2 of the area of the golden background (area 2 in Figure 2b, light blue square) observed under (**a**) the OM in VIS light (left) and UVIF (right), and (**b**) the SEM-EDS. The cross-section shows the ground layer (A), *bolo* layer (B), and gold leaf (C).

SEM-EDS analysis (Figure 8a) identified Ca and S as the main elements in the ground layer, implying the use of gypsum; while the spectrum collected in correspondence with layer B revealed high counts of aluminium (Al) and Si, which are linked to the use of clay minerals (*bolo*) such as kaolin [18] as preparation for the gold leaf. These results are consistent with the identification of gypsum by the ATR-FTIR bands around 3537 and 3390 cm^{-1}, related to the stretching modes of the O-H bonds, and around 1615, 1090 and 670 cm^{-1}, related to the stretching and bending modes of sulphate anions [4,22], along with those of proteinaceous material (commonly animal glue), appearing faintly around 1650, 1550, and 1460 cm^{-1}, related to amide I, II, and III [16,17,19,22] (Figure 8b). A ground layer of this composition is typical of traditional Italian painting of the 15th century [10].

As for the gilding preparation (layer B), ATR-FTIR bands of kaolin were detected in the range between 3695 and 3620 cm^{-1} related to the O-H stretching modes, and around 1020, 1010, and 910 cm^{-1} related to the Si-O-Si, Si-O-Al, and Al-OH stretching modes confirming the use of *bolo* for the preparation [18,29]. The external layer C corresponds to the gold leaf, characterized by a high peak of gold (Au) [11,12,14] in the SEM-EDS spectrum. This type of gilding, traditionally called *doratura a guazzo*, was made with *bolo armeno* (red clay containing oxides of Fe and Al) mixed with egg. The dry *bolo* was burnished with an agate stone, and the gold leaf was applied by means of egg white [36].

The XRF results on the different backgrounds are summarized below (Table 1). The results are supported and completed by the ER-FTIR results.

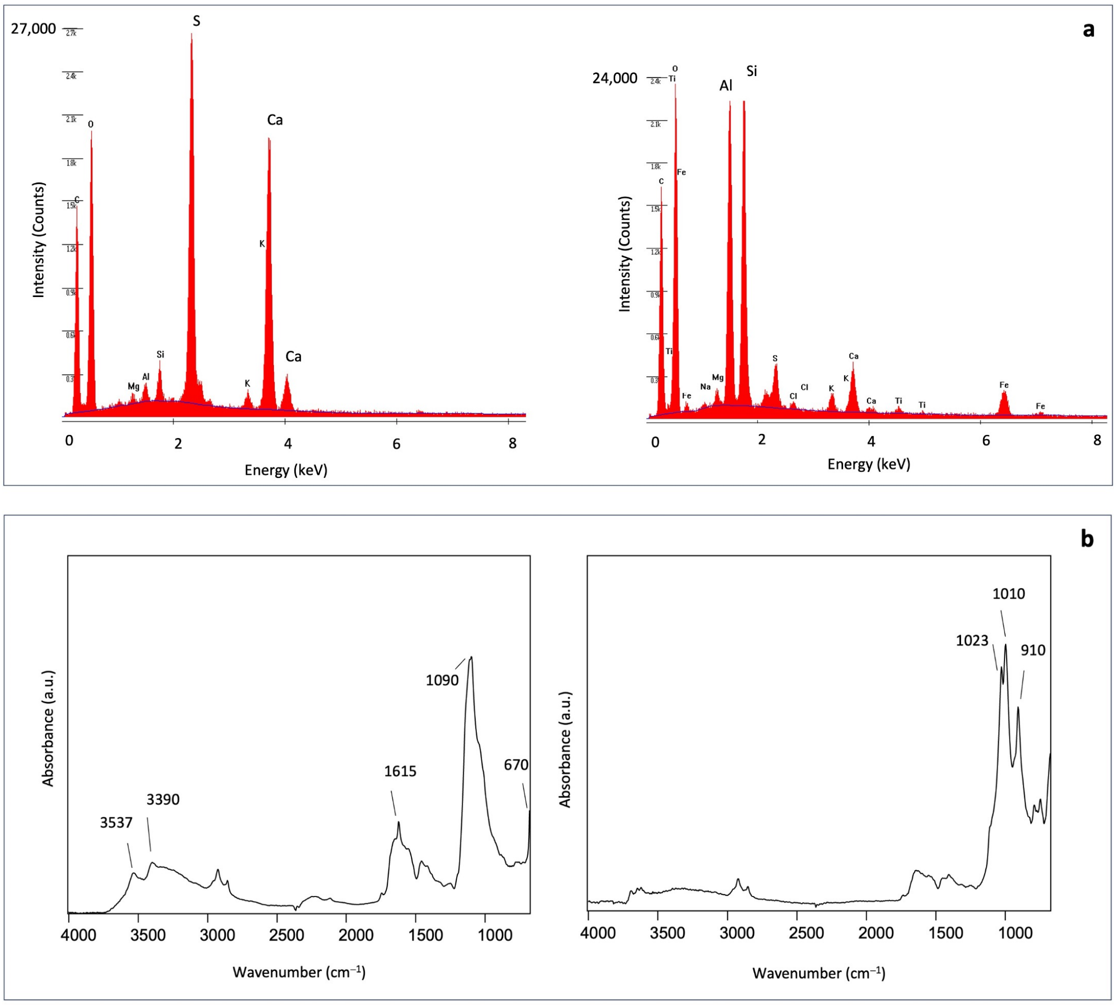

Figure 8. (**a**) SEM-EDS and (**b**) ATR-FTIR spectra acquired in correspondence of the ground layer A and gilding preparation layer B, left and right, respectively.

Table 1. Summary of the analytical results identified in the selected areas.

Investigated Area (XRF Spot)	Colour	Pigment Attribution	Marker XRF Elements	Maker FTIR Bands	References
8—Virgin's mantle over her shoulder	Blue	Prussian blue, Smalt, Blue Cu-based pigment	Fe, Co, K, As, Cu, Si	2098 cm^{-1}, 1020 cm^{-1}	[4,5,14,16,17,19, 22,25,27–30]
9—Virgin's mantle over her head	Blue	Prussian blue, Smalt, Blue Cu-based pigment	Fe, K, Co, Cu, Si, As	2098 cm^{-1}, 1020 cm^{-1}	[4,5,14,16,17,19, 22,25,27–30]
14—Virgin's mantle	Blue	Prussian blue, Blue Cu-based pigment	Fe, Cu	-	[5,14,25,27]

Table 1. *Cont.*

Investigated Area (XRF Spot)	Colour	Pigment Attribution	Marker XRF Elements	Maker FTIR Bands	References
15—Virgin's mantle	Blue	Prussian blue, Blue Cu-based pigment	Fe, Cu	-	[5,14,25,27]
25—Christ's mantle	Blue	Prussian blue, Blue Cu-based pigment	Fe, Cu	-	[5,14,25,27]
28—Christ's mantle	Blue	Prussian blue, Blue Cu-based pigment	Fe, Cu	-	[5,14,25,27]
29—Christ's mantle	Blue	Prussian blue, Blue Cu-based pigment	Fe, Cu	-	[5,14,25,27]
21—Virgin's dress	Dark Green/Blue	Green pigment based on copper, Prussian blue, Green earth	Cu, Fe, Si	1020 cm^{-1}, 2098 cm^{-1}	[4,11,14,25,27–30]
30—Christ's garment	Dark Green/Blue	Green pigment based on copper, Prussian blue, Green earth	Cu, Fe, Si	-	[11,14,25,27]
31—Christ's garment collar	Dark Green/Blue	Prussian blue, Green earth, Green pigment based on copper	Fe, Cu, Si	-	[11,14,25,27]
32—Christ's garment collar	Dark Green/Blue	Green pigment based on copper, Prussian blue, Green earth	Cu, Fe, Si	-	[11,14,25,27]
11—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	3547 cm^{-1}, 1450 cm^{-1}, 678 cm^{-1}	[11,14,17,18,25, 27,29,30,35]
12—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	-	[11,14,25,27]
13—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	-	[11,14,25,27]

Table 1. *Cont.*

Investigated Area (XRF Spot)	Colour	Pigment Attribution	Marker XRF Elements	Maker FTIR Bands	References
22—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	-	[11,14,25,27]
23—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	-	[11,14,25,27]
26—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	3547 cm^{-1}, 1450 cm^{-1}, 678 cm^{-1}	[11,14,17,18,25, 27,29,30,35]
27—Throne structure	White	Lead white, Iron-based earth	Pb, Fe	-	[11,14,25,27]
16—Virgin's dress sleeve	Red	Cinnabar, Red ochre	Hg, Fe	530 cm^{-1}, 450 cm^{-1}, 1020 cm^{1}, 1030 cm^{-1}	[4,11,14,18,25,27, 29,35]
17—Virgin's dress sleeve	Red	Cinnabar, Red ochre	Hg, Fe	-	[11,14,25,27]
19—Pillow	Red	Cinnabar, Red ochre	Hg, Fe	-	[11,14,25,27]
20—Pillow	Red	Cinnabar, Red ochre	Hg, Fe	-	[11,14,25,27]
5—Virgin's cheek	Flesh tones	Cinnabar, Lead white, Haematite	Pb, Hg, Fe	1090 cm^{-1}, 1040 cm^{-1}, 480 cm^{-1}, 540 cm^{-1}	[4,11,14,18,25,27, 29,35]
6—Virgin's lips	Flesh tones	Cinnabar, Lead white, Haematite/Red ochre	Pb, Hg, Fe	-	[11,14,25,27]
7—Virgin's neck	Flesh tones	Red ochre, Cinnabar	Pb, Fe, Hg	1440 cm^{-1}, 680 cm^{-1}	[11,14,17,25,27, 30,35]

4. Conclusions

This paper has reported and discussed the results of a diagnostic spectroscopic campaign on the painting *Coronation of the Virgin* by Michele di Matteo, dated around the first half of the 15th century. The multi-analytical diagnostic campaign based on non- and micro-invasive techniques allowed the assessment of the state of preservation and the characterization of the original painting materials used on the polychrome wooden panel, as well as the materials added during further interventions. The study of the multi-layered system from both the compositional and morphological point of view revealed the painting technique of the author. The painting showed some bending of the wooden support, cracks in the painting layers, and previous restoration interventions identified by the several retouches, over-paintings, modern pigments, and stucco works. The observed stratigraphy seems to be coherent with the traditional late-Gothic layered structure that generally includes a support, a ground layer, paint layers, and a varnish. The support is a thick wooden board covered in the upper part with canvas. The ground layer was made with gypsum and glue, and the presence of the *imprimitura* with lead white was detected by both imaging and spectroscopic techniques. For the pictorial layers, it was possible to hypothesize the presence of a selection of pigments consistent with the period of the production of the painting, as well as restoration pigments used in subsequent restorations. Cinnabar, red ochre, smalt, lead white, green earth, and green pigment based on copper were identified in red, blue, white, and green areas, possibly applied with an egg binder. Modern pigment such as Prussian blue was revealed as well. As for the gilding areas, the use of red *bolo* as a preparation for the gold leaf confirmed the use of the *guazzo* technique.

The advantages of using a multi-analytical approach proved effective in the comprehensive study of the painting. By combining and comparing the results of complementary techniques such as imaging, non-invasive spectroscopy, and micro-invasive analyses, solid and consistent outcomes were achieved. Although completing the imaging with IR reflectography could have contributed to a better localization of the pigments and a clearer distinction between retouched and original areas of the painting, the scientific investigation run so far provided necessary and useful data on the painting technique used by Michele di Matteo. These results not only contribute to the advancement of our knowledge of the painter and possibly his workshop, which have never been studied before from a scientific point of view, but can also help conservators and restorers in future restoration works and studies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage7010016/s1, Figure S1: Image of the painting in visible light; Figure S2: Image of the painting in UV light; Figure S3: X-ray radiography of the painting.

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