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Multispectral Imaging and *p*-XRF for the Non-Invasive Characterization of the Anonymous Devotional Painting '*Maria Santissima delle Grazie*' from Mirabella Imbáccari (Sicily, Italy)

Antonella Privitera [1,*], Maria Francesca Alberghina [2], Elèna Privitera [3] and Salvatore Schiavone [2]

[1] Dipartimento di Scienze, Università degli Studi Roma Tre, Via Della Vasca Navale, 84, 00146 Rome, Italy
[2] S.T.Art-Test, Via Stovigliai, 88, 93015 Niscemi, CL, Italy; francesca.alberghina@gmail.com (M.F.A.); info@start-test.it (S.S.)
[3] Independent Researcher, Archivist and Art Historian, Viale Santa Panagia, 81/b, 96100 Syracuse, Italy; e.privitera9@gmail.com
* Correspondence: antonella.privitera@uniroma3.it

Abstract: This work presents the results of the in situ, non-invasive diagnostic investigations performed on the canvas oil painting depicting Madonna and Child, venerated as '*Maria Santissima delle Grazie*' by the local religious community. The work of art (72 cm × 175 cm) is located on the high altar of the main Church in Mirabella Imbáccari, near Catania (Sicily, Italy). The painter is anonymous, and the supposed dating is the late eighteenth century. Although the painting has never been studied before, it has been attributed to a Sicilian workshop in the literature, raising the doubts of the art historian who conducted this study and who hypothesized a Neapolitan manufacture. Furthermore, due to the good conservation state detected by a macroscopic examination, doubts also arose about dating. To shed light on these aspects, a technical-scientific examination proved necessary. Multispectral imaging techniques (IR Reflectography, UV-induced visible Fluorescence, X-ray) are carried out for the study of the execution technique, the identification of underlying remakes, sketch drawing and the evaluation of the conservation conditions. XRF spectrometry analysis is performed for the identification of the chemical elements constituting the pigments (inorganic chromophores). The diagnostic results allowed this research to confirm the dating suggested by the historical-stylistic knowledge and to highlight new technical peculiarities supporting the attribution to a Neapolitan workshop.

Keywords: late 18th century painting; Neapolitan workshop; oil on canvas; non-invasive characterization; pigments; optical microscopy; multispectral imaging; *p*-XRF

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1. Introduction

Southern Italy is culturally characterized by its great religious fervor, firmly connected to the representation of Saints, in the form of sculptures and paintings [1]. These represent the strong bond of man with God, and, on the other hand, they are examples of high artistic expression. However, these are not always famous artworks or of a famous artist. In fact, most of the devotional sculptures and paintings, located in churches and diocesan museums, especially in small towns, do not appear in art history books, do not have a certain identity and animate the faithfuls for centuries thanks to the halo of mystery that surrounds them. The knowledge about them is almost exclusively due to notions orally handed down and preserved by the few who are interested in the subject.

Thanks to the ever-increasing sensitivity of humanists and curators of these anonymous artworks towards applied science, scientific investigations have established themselves in making valid contributions to the disclosure of the artworks' identities, especially when the sources are silent, as in the case introduced in this paper. The object of this study is a devotional oil on canvas painting, by an unknown painter, depicting Madonna and Child, from Mirabella Imbáccari, near Catania (Sicily, Italy). The local religious community names the painting '*Maria Santissima delle Grazie*' (Our Lady of Grace), as she is the Patron Saint of this town, where the religious commemoration has been officially celebrated since 1784 every last Sunday of August [2]. The canvas is currently placed in a niche (Figure 1) made of stucco, modeled and painted in imitation marble of the Sicilian Baroque-eclectic manufacture, on the top of the main altar in the Mother Church. The latter was built between 1737 and 1749 at the behest of the lord of the town, Vincenzo Paternò Castello, fourth prince of Biscari (1685–1749). In the inventory of historical and artistic heritage of the Caltagirone diocese, the dating at the 18th century is reported for the painting, and it would have been painted inside a Sicilian workshop [3,4]. The latter information is considered incorrect by the art historian who examined the artwork in this study.

Figure 1. (**Left**): The canvas kept in the niche on the top of the main altar in the Mother Church (credits: BeWeB—Beni Ecclesiastici in web, CEI—Ufficio Nazionale per i beni culturali ecclesiastici e l'edilizia di culto). (**Right**): Religious commemoration dedicated to *Maria SS delle Grazie*, 1972 (credits: Archivio Fotografico Storico di Mirabella Imbáccari—AFSMI, author: Pino Zaccaria).

According to a local tradition, the painting was donated by the Prince of Biscari (or perhaps his son) to the community of the *Terræ* of Mirabella around 1750 [2]. However, from the various documented priestly visits at Mirabella, in 1635, 1655 and in 1682, the existence of the Our Lady of Grace cult is found even before the building of the Mother Church. However, sources refer to a "statue of Virgin Mary" (lost today), for which the wooden canopy with silver decorations for the religious procession was handmade between 1701 and 1705 [1,4]. This knowledge encourages the hypothesis that the canvas was specially commissioned for the community of Mirabella by the princes of Biscari, who were lords of this town for several generations. After all, the fifth prince of Biscari, Ignazio Paternò Castello (1719–1786), is mentioned as the best-known personality of eighteenth-century Catania and perhaps Sicilian collecting. He was able to follow the contemporary trends that manifested themselves in various Italian cities, and he was an avant-garde and philanthropist prince who guaranteed the public enjoyment of his museum, for public utility, the decorum of the city and the ease of academics and scholars [5]. As reported by Libertini G. and Guzzetta G., in 1750, the year of the Jubilee, Ignazio Paternò Castello toured Italy, stopping in Naples, Rome, Florence and other big cities, where he bought books for his library, paintings for his art gallery and ancient artifacts for his museum [6,7]. Therefore, it is not surprising that he acquired the painting during this travel with the intention of donating it to his subject people who were very devoted to the Virgin Mary cult.

Since the painting became part of the cultural heritage of Mirabella Imbáccari, it has gone through several incidents that have modified the original assembly. Two fires are known, which affected the interior part of the Mother Church: in 1850 and in 1860, the latter fire being a result of arson due to the violent clashes between the bourbon power and the new libertarian. A major earthquake followed in 1908 [2]. These catastrophic events have also destroyed the church archives, and for this reason, no historical documentation about the canvas has survived.

In this work, non-invasive, in situ scientific investigations are carried out with the aim to clarify the dating, artist or workshop attribution and to verify the conservation conditions of the inedited painting. To achieve these purposes, a well-consolidated approach based on multispectral analysis was used, which exploits the straightforward method of the UV-induced visible fluorescence (UVF) to distinguish the different materials of the surface pictorial layers [8–14] before other analysis. In fact, an oil on canvas painting is a non-homogeneous system, characterized by a stratigraphy of different materials, at its simplest: a varnish layer, one or more layers of pigments dispersed in a binder, one or more primer layers (may contain a sketch drawing), the canvas (may have tears, patches, etc.) and the frame (can be supported by glues, nails, bolts) [11,12]. In order to intentionally choose the areas to be investigated, preliminarily UVF observation and digital image acquisition provides the identification of old and recent varnishes, overpainting, integration and retouching, suggesting the original or subsequent pigments and dyes by the different fluorescence intensity and hues, typically blue-green and dark [10,15].

Multispectral imaging, for the non-destructive observation of the multi-layered structures of paintings, mostly involves the use of IR reflectography (IRR). This technique investigates the core layers of the painting by irradiating the surface with a broadband infrared source and collecting the backscattered radiation within specific spectral IR bands. Thanks to the different properties of the materials, absorbent or transparent to the infrared radiation, IRR images acquired in the NIR wideband modality allows researchers to discover the artists' working methods, in particular: the execution technique, the presence of a preparatory sketch (if it is made in IR-absorbent material such as charcoal or black pigment) and the method of sketch transposition to the canvas (engraving, dusting, free hand, etc.), *pentimenti* and retouching. Moreover, the different IR spectral response also allows researchers to discriminate pigments of different composition that are indistinguishable to the eye due to having the same hue [10,15–18].

Acquisitions of radiographic images (X-ray) integrate the information listed above, through the study of the materials discontinuity thanks to their different radiopacity to high-energy beam (~10–50 KeV) that crosses the artwork, with greater effectiveness in the identification of the underlying pictorial layers. In general, features of the deeper layers are revealed: differences in the chemical composition and trend of the brushstrokes, construction of the representation, weft, yarn and defects of the canvas, elements of the wooden frame and metal accessories, if present [15].

Finally, the qualitative elemental composition obtained by portable X-ray fluorescence (*p*-XRF) provides objective data for an improved identification of inorganic pigments [19]. In this non-invasive technique, the characteristic X-radiations emitted by the chemical elements, following the interaction with an incident X-ray beam (~10–50 KeV), allows researchers to reveal the composition of the pictorial materials used by the artist, as a function of their energies (Energy Dispersive: ED-XRF). The information comes from the surface layers of the sample, that is, from those that the secondary characteristic radiation emitted is able to pass through to reach the detector. This analysis provides useful information for the authenticity and indirect dating of the examined painting since the ages of pigments' diffusion in the art market are known.

2. Iconography Study and Stylistic Analysis of the Painting *Maria SS delle Grazie*

An iconography study reveals clues as to the likely provenance of this artwork. The mantle of the Virgin Mary is blue and symbolizes her humanity, while the robes are purple-pink, evocative of the dress worn by the Byzantine empresses, attesting to her divinity. The theme is considered by Valenti V. [2] as a re-proposition of the *Kardyiotissa* Virgin icon

(Our Lady of tenderness), however, it does not represent the act of nursing or the motion of caress.

The theme characterizing the painting *Maria Santissima delle Grazie* seems to be rather a variant of the Sacred Heart of Mary theme. The main Italian painter connected to the Eudist iconography of the Sacred Hearts is Girolamo Pompeo Batoni (1708–1787) of the Roman school [20], of which is known an oil on canvas depicting a Madonna with Child (Our Lady of tenderness, Figure 2a) preserved in the Borghese Gallery in Rome, resembling to the unknown painting from Mirabella.

(a) (b) (c) (d)

Figure 2. Some iconographic themes of Madonna with Child, painted by eighteenth-century Italian painters using the oil on canvas technique: (**a**) Madonna with Child painted in 1745 by G.P. Batoni (Galleria Borghese, Rome), (**b**) Madonna with Child and St. John the Baptist painted by S. Conca (Private Collection, credits: Pandolfini Casa d'Aste, 2017), (**c**) Madonna of the Heart painted in 1727 by S. Conca (Gerano, Rome), (**d**) *Maria SS delle Grazie*, by unknown painter (Mirabella Imbáccari, Catania).

There are also strong similarities between the canvas from Mirabella and Sebastiano Conca's paintings of the Neapolitan school [21]: a canvas depicting Madonna with Child and St. John the Baptist (private collection, Figure 2b) and a canvas located in Gerano (Rome, Figure 2c), where it is venerated as Madonna of the Heart. In particular, the canvas from Mirabella seems to be a copy of the latter, due to the remarkable correspondence with the represented symbols and motions.

In both paintings (Figure 2c,d), baby Jesus is standing on his mother's knees, offering the cross with his left hand as allusion to redemption. In this attitude, Virgin Mary becomes the Mother-Throne of her son, while with her left hand she holds the heart, offered to her son or to devotees [2]. However, while all the artworks mentioned above have a downward gaze, on the contrary, the painting from Mirabella is distinguished from its possible archetype because its gaze is gently turned towards the faithful, inviting them to perform the same motion: to give their heart to her child. To the best of the authors knowledge, this detail makes this painting a *unicum* of the eighteenth-century painting representing Madonna with Child, likely of the Neapolitan school.

The painting *Maria SS delle Grazie* seems to have no relationship with the great compositions performed by Sebastiano Conca for Roman churches or for those destinated beyond the borders of the Pontifical State. This small painting is a splendid example of that production for private destination, which was a minor but not irrelevant aspect of Sebastiano Conca, assisted by its workshop. Further scientific investigations can provide information to confirm this attribution hypothesis. In particular, some details on the executive technique may prove useful: as reported by Passeri G.B. [22], "*Neapolitan painters do not engage much in the sketch drawing, but they paint quickly with pigments and brushes*".

3. Instrumentations and Methods

The first approach to the artwork study consists in macroscopic critical observation, carried out through visual examination both in white and ultraviolet light, simple photographic documentation and optical microscopy observations in correspondence with the areas of greatest interest. Subsequently, imaging techniques are performed in order to investigate the stratigraphy of the painting and to evaluate the different materials. Finally, *p*-XRF is performed in some selected points for the identification of pigments (inorganic chromophores). Photos of some phases of the analysis are reported in Figure 3.

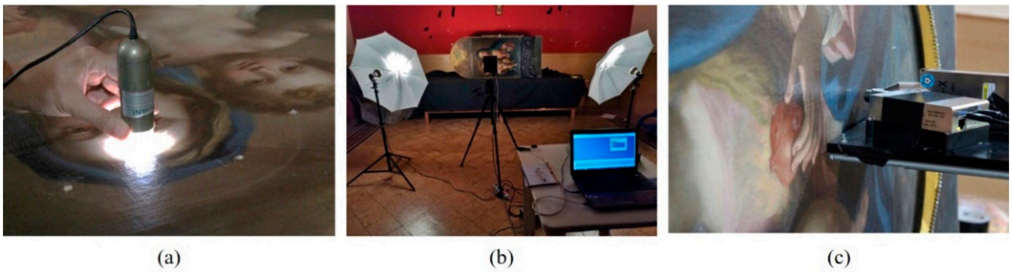


Figure 3. Photos of some phases of the of the in situ diagnostic investigations: (**a**) digital optical microscope observation; (**b**) IR Reflectography set-up; (**c**) *p*-XRF acquisition.

3.1. Digital Optical Microscopy

For the detailed observations of the pictorial surfaces and areas of interest, a portable digital microscope Dinolite (AM4113TFVW model, Dino-Lite Europe, distributor for 1321 NN Almere, The Netherlands) is used, equipped with four white light LEDs and four UV LEDs at 400 nm+ of emission. Other technical characteristics include the following: resolution 1.3 Mpixels, magnification from 10× to 50× and 200×, frame rate more than 30 fps, interface USB 2.0, sensor color CMOS, accuracy of manual calibration and measurement ±3µm.

3.2. UV-Induced Visible Fluorescence

A CCD photo sensor (MADATEC 28.2 MP multispectral system, Madatec srl, 20060 Pessano con Bornago, Italy) is used for the UV-radiation stimulated optical fluorescence acquisitions, equipped with an UV-IR cut filter in order to allow the detector to only reach the visible fluorescence radiations emitted by the examined materials. Visible fluorescence is induced by ultraviolet light sources (two filtered LED sources with emission peak centred at 365 nm, placed at 45 degrees with respect to the observed surface).

3.3. IR Reflettography

Two different devices are used for IR Reflectography acquisitions: a CCD photo sensor (MADATEC 28.2 MP multispectral system) with filters centered at 760 nm, 850 nm and 950 nm of the NIR spectrum and 1 s of exposure; a scientific photo-camera CHROMA C4-DSP series (C250ME model, by DTA srl) mounting an air cooling CCD of 6-Mpixels (3326 × 2504 points) effective (pixels with a side of 5.4 µm), equipped with a KAF8300ME sensor and eight interferential filters for selecting eight different spectral bands, with a filter centered at 1000 nm (±50 nm) and 60 s of exposure. Other technical specifications are as follows: full well capacity 25.5 ke$^-$; dark current 3.5 e$^-$/pixelsec (at −5 °C); quantum efficiency at 450, 550 and 650 nm equal to 45, 57 and 48 respectively; fill factor 100%; and Peltier cooling with ΔT = 30 °C. Two incandescent lamps for photographic use covered with umbrellas provide the homogeneous infrared radiation, absorbed, reflected or transmitted from the different materials of the painting. Channel compensation for each band is performed with certified standards with known reflectance.

3.4. Digital Radiography

An indirect digital system, which make use of an X-ray tube (Mini-X-Amptek), with a maximum voltage of 40 kV and maximum current 0.2 mA and a phosphor plate (43 cm × 35 cm) placed behind the painting, is used for the radiographic investigation. For each acquisition on limited areas, the following exposure conditions have been set: voltage 35 kV; current intensity 80 mA; integration time 18 s; X-ray tube/plate distance equal to 150 cm. No filter was applied between the X-ray tube and the investigated areas. The data were subsequently processed using a dedicated software with the application of reconstruction algorithms (hardening and softening of the image) to highlight the different structures and enhance the different density, due to the different photoabsorption.

3.5. X-ray Fluorescence

The portable XRF spectrometer used for the multi-elemental analysis of the pigments consists of the X-ray tube (Mini-X-Amptek) equipped with a Rhodium (Rh) target and operating at a maximum working voltage of 40 kV and maximum current 0.2 mA. The detection of the characteristic X-ray radiation emitted by the sample is as a function of the energy (Energy Dispersive: ED-XRF) and allowed by a Silicon Drift Detector system (X-123 SDD—Amptek) with 125–140 eV FWHM at 5.9 keV Mn Kα line Energy resolution (depending on peaking time and temperature), collimator 1 or 2 mm. The detection range of energy is from 1 keV to 40 keV, with a maximum rate of counts up to 5.6×10^5 cps. The primary beam is positioned perpendicular to the sample, while the detector is positioned at 40 degrees with respect to the primary beam. A dedicated control software allows researchers to administrate measurements and acquisitions. For the analysis of the 9 selected areas, the following measurement parameters are set in order to ensure a good spectral signal and to optimize the signal-to-noise ratio (SNR): voltage 35 kV, current 80 µA, acquisition time 50 s per area, working distance 1 cm.

4. Results and Discussion

4.1. Preliminarly Observation by Visual Analysis

The artwork measures 72 cm × 175 cm (vertically). However, from close observation, it is possible to distinguish a central rectangle of approximate 67 cm × 89 cm, which is supposed to be the original part. In this rectangle, footprints of an old frame are visible on three sides, absent at the bottom (Figure 4). This detail suggests that the original canvas has been cut or damaged in the lower part. The rest of the composition is the result of assembly on a larger canvas of the actual form. Furthermore, the reconstructed painting has been lined on the back and the frame has been renewed (Figure 4a,f).

This re-composition could be dated after the arson of 1860. Di Seri G. [4] stressed the Latin marble epigraph referred to this episode, still today located above the main portal of the church: "*Pulcrum eram, ignis me foedavit, pulcherius evenit pietatis fidelium*" (I was beautiful, the fire ruined me, I must have been more beautiful for the compassion of the faithful). This restoration intervention can be attributed to one of the Sicilian artists, authors of the other canvases acquired in the Mother Church at the end of the 19th century [2] (p. 118). On the back, removable magnets and hooks are present in some wooden rafters, useful for grappling the metal decorations (Figure 4a). In fact, some precious inserts are present on the painting (some have been removed to allow the scientific analysis): three little gold stars on the top, a gold moon on the bottom, two royal crowns on the head of baby Jesus and Virgin Mary, of which four large holes are visible (Figure 4d). Some interventions on the frame seem very recent, perhaps dating back to the 1900s. No particular signs of aging are visible to the eye on the pictorial layer and the coating varnish also looks to be in good conservation condition. Further scientific investigation can provide deeper information on this aspect and on the attribution and artist or workshop attribution.

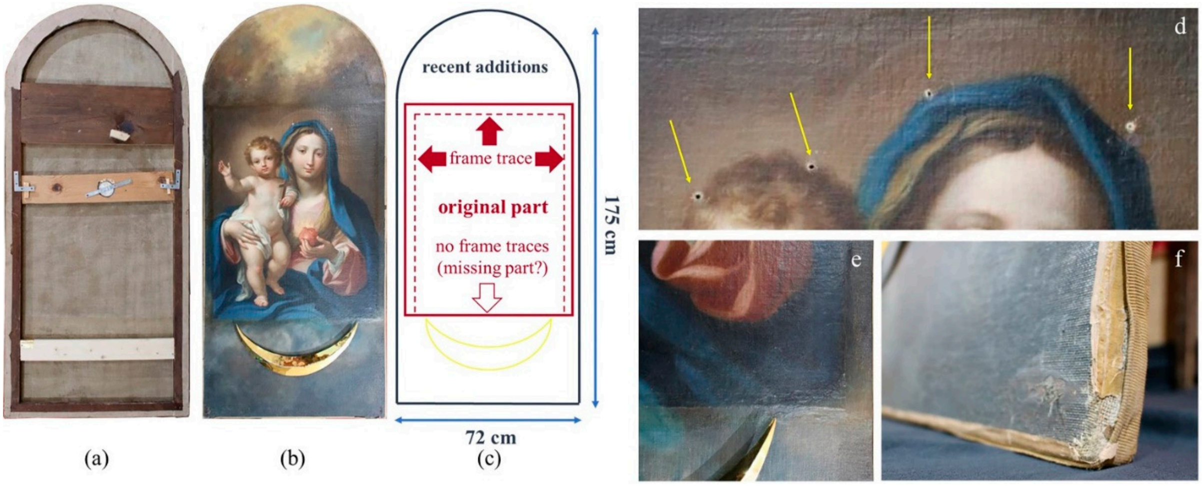


Figure 4. Size and structure of the painting: (**a**) support frame (back); (**b**) current framework of the canvas (front); (**c**) dimension of the painting and macroscopic details. Macroscopic observation: (**d**) holes detected on the heads of both subjects; (**e**) conjunction between the original and the recent support canvas; (**f**) lining canvas edge, where fabric tape and paper tape are visible.

4.2. Multispectral Imaging

The UV-induced visible fluorescence images (Figure 5a,b) show the areas of retouching and pictorial additions, represented by dark details (absence of visible fluorescence) with respect to the bluish-green spectral response of the protective varnish, the latter being typical of an aged synthetic varnish. The pictorial additions are limited to small areas, invisible to eye, corresponding to the lacunae generated by the application of jewels and gold decorations, subsequently removed for conservation purposes and to restore the original appearance of the painting, weighed down over time by an excess of jewels (Figure 5c–e). In particular, dark spots document signs of a necklace, earrings, gold Sacred Heart of Mary and the cross (Figure 5d), permanently removed.

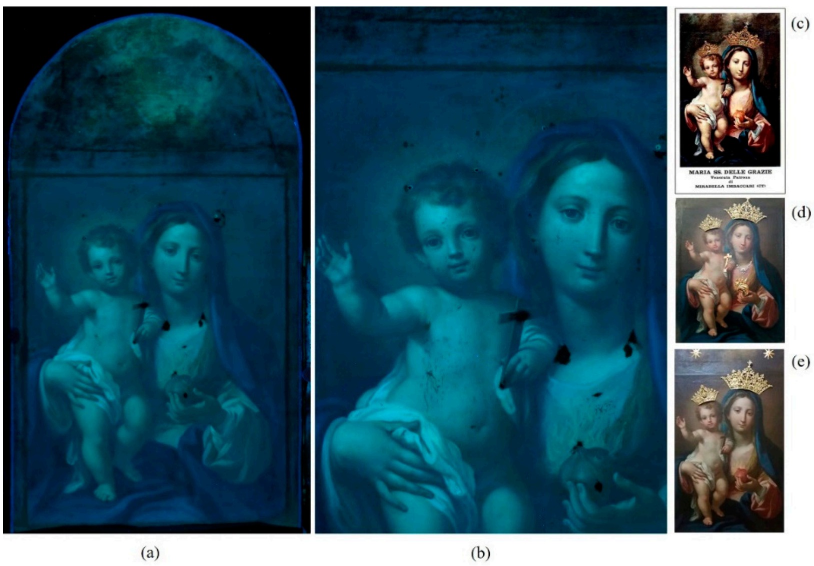


Figure 5. UV-induced visible fluorescence: (**a**,**b**) the images show the presence of pictorial additions as dark details, in correspondence of obliterated holes, and other dark details in correspondence of the old canvas perimeter; (**c**–**e**) evolution of applied gold decoration: about 1970s, 2000s and nowadays, respectively.

Moreover, the absence of UV fluorescence of the pictorial integration materials and glue allows for highlighting the retouching area along the perimeter of the rectangular canvas (original part) in correspondence with the junction with the most recent one. The non-homogeneous response of the paint in the upper part (extension canvas) compared to the rectangular part is indicative of different surface morphology, thicknesses and stratigraphy that have generated a different absorption/distribution of the varnish on the pictorial layer.

The IR reflectography investigation was mostly centred on the rectangle considered to be the original part. The wideband IR response shows a very high homogeneity and compactness of the central rectangle background, with respect to the pictorial layer of the extension canvas, as highlighted in the detailed IRR image at 1000 nm (Figure 6). The perimeter of the central rectangle affected by the pictorial retouching, performed for the aesthetic–chromatic junction of the two canvases, is clearly visible thanks to the strong IR absorption. As already observed by the UVF, spots of different material are clearly visible, if compared with the parts believed to be original, not visible by eye. These are likely recent stucco and pigments as integration materials, applied in previous restorations to hide the holes of the jewels' application. Moreover, the infrared images also highlight the traces of the original framework on the three sides of the central rectangle, absent to the bottom.

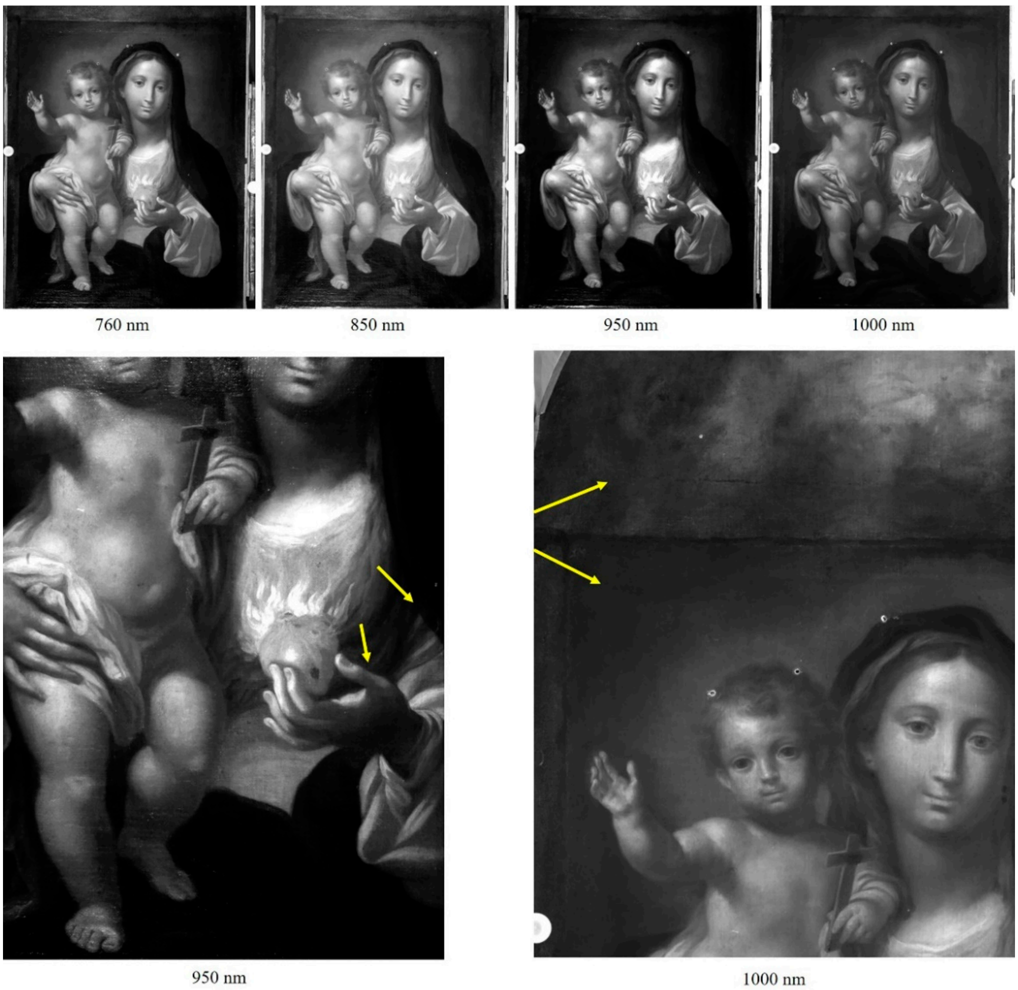


Figure 6. IR reflectography images acquired in NIR wideband modality, by using the following CCD: at 760 nm, 850 nm and 950 nm (exposure 1 s) and 1000 nm (exposure 60 s). The arrows indicate two very small repentances (detailed IRR at 950 nm) and the difference in homogeneity and compactness between the original canvas and the extension one (detailed IRR at 1000 nm).

NIR wideband acquisitions, in particular with CCD at 950 nm, also show a greater emphasis of *chiaroscuro*, where the brighter areas are characterized by a greater content of lead white, as confirmed by X-ray radiography (Figures 7 and 8a), while the shadows are to be referred to the use of brown ochres, as confirmed by XRF analysis (see the Section 4.3). In the pictorial subject, the yellow, pink and light brown halftones appear compositionally homogeneous, based on the IR reflectography response, while the absorbing IR behaviour, up to 1000 nm, of the blue painting of the mantle stands out. This evidence, in combination with the absence of significant UV-induced fluorescence [16,23,24] and the elemental composition, can recognize the blue pigment (more information on the pigments identification is reported in the Section 4.3). The observation of the IRR images revealed no traces of preparatory drawings made with absorbent IR material (charcoal, pencil or black pigment), *pentimenti* or underlying pictorial layer [16], and negligible variations are detected in two small details in correspondence with a flap of the blue mantle and on the outer contour of the left-hand thumb of the Virgin Mary (Figure 6, detailed IRR image at 950 nm). These evidences are very important from the historical-artistic point of view, because it suggests that the painter knew the subject very well and/or that the painter has performed a detailed layout traced as a brush sketch on the dark background, thus avoiding big changes during the detailed painting phase. It denotes a considerable experience and skill of the painter, so the hand of an apprentice can be excluded. Moreover, the absence of the preparatory drawing is compatible with the Neapolitan pictorial school.

The radiographic investigation, conditioned by the presence of some wooden crossbars of the frame, is performed in a large area on the bottom of the original rectangle. The result is a mosaic of two images acquired under the same experimental conditions, shown in Figure 7. From the digital processing and interpretation of the diagnostic X-ray images, it is possible to deduce some evidence: the absence of *pentimenti* or changes in the deeper layers with respect to the final layout is confirmed, and a fluid and fast *ductus* of the brushstrokes in the skin depiction (brighter areas) is observed, with curvilinear trends for the volumes' rendering. Moreover, Figure 8b highlights the craquelure characteristics typical of the pictorial layer, hardly perceptible by the eye.

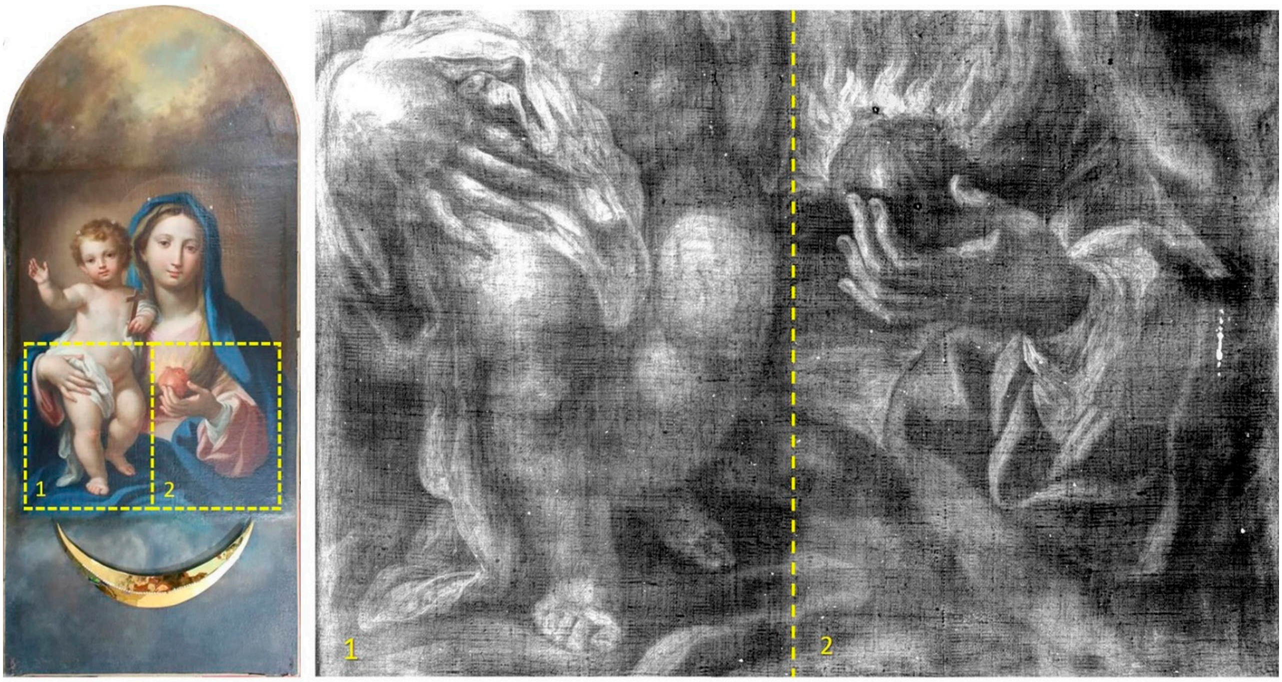


Figure 7. X-ray radiography performed on two extended area on the bottom of the painting (original part) highlighted as 1 and 2.

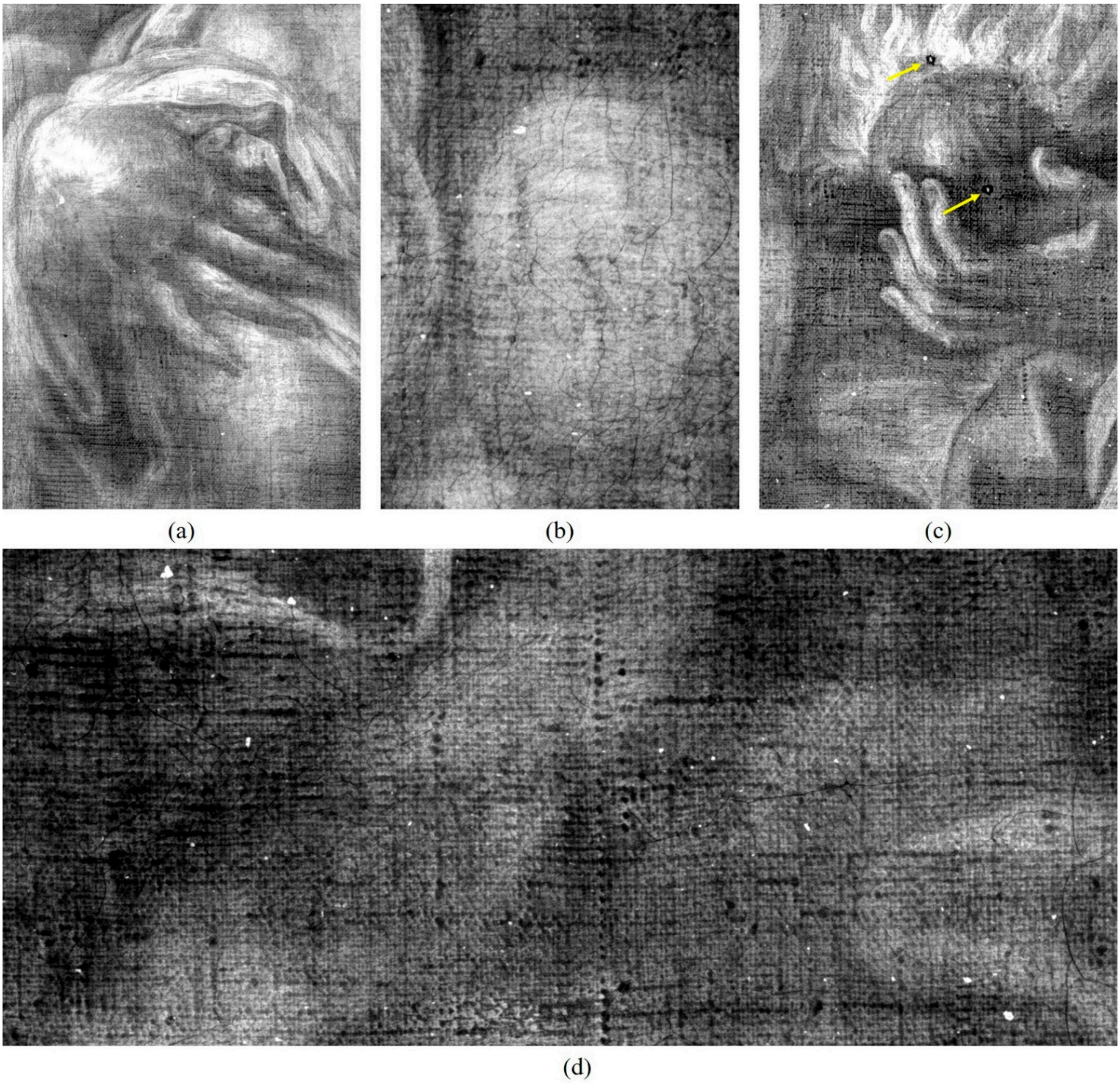


Figure 8. X-ray radiography (details): (**a**) right hand of the virgin Mary with dense brushstrokes in bright areas; (**b**) left knee of the baby Jesus with craquelure of the painting, indicating the aging; (**c**) Sacred Heart of Mary with two retouched holes; (**d**) irregular thickness, density, development of the yarn and tensioning of the canvas (original part).

The presence of two holes is detected in correspondence of the Sacred Heart of Mary, invisible to the eye because they are covered with mimetic pictorial integration (Figure 8c). The slight radiopacity of the shadow areas suggests that lead white is present in a mixture in the primer layer, instead, the high radiopacity of the brighter areas suggests that lead white is overlying to the skin tone [25]. The morphology of the central canvas, highlighted thanks to the radiopacity contrast of the primer layer, seems to be of artisanal type: in fact, the thickness, the density, the development of the yarn and the tensioning are irregular (Figure 8d), excluding an industrial origin, the latter widespread from the 19th century. The original canvas can be made of linen, hemp or cotton fibers, however, microscopic observation at magnifications over than 500× or a molecular spectroscopy technique, not performed in this work, would be necessary to determine this material [26,27].

4.3. Elemental Composition of Original Pictorial Layers

To a correct identification of the pigments, the presence of remakes or retouching on the pictorial surface have been preliminarily revealed and localized by UV fluorescence imaging. This integrated approach allows to carry out the chemical analyses only on original layers, guaranteeing the significance of the *p*-XRF results. The investigated areas, from 1 to 9 in the Figure 9, have been sampled in order to obtain compositional information on the following: skin tones (P1 and P6), yellow tones (P2 and P9), red-pink tones (P3 and P5), blue pigment (P4) and browns of the original and recent painting (P7 and P8, respectively). The selected measurement areas were previously observed at the digital optical microscope at magnification of 50×, summarized in Figure 9. The chemical analysis, reported in Table 1 and in Figure 10, allows the identification of the homogeneous and uniform presence of lead white [$(PbCO_3)_2$ $Pb(OH)_2$] according to the radiopacity level observed on X-ray images. This pigment, historically known as *biacca*, is a natural mineral pigment used since ancient times in paint for primers, thanks to its high covering power, and as pure or in mixture chromophore for pictorial layers [28]. Due to the high Pb XRF signal intensity and the widespread presence of calcium (Ca) in all the investigated areas, it is possible to assume that lead white is certainly present in the preparation or thin primer layer with some calcareous earth or calcite [29], and likely in the pictorial layer in mixture with other pigments in brighter zones (as observed in the radiographic images).

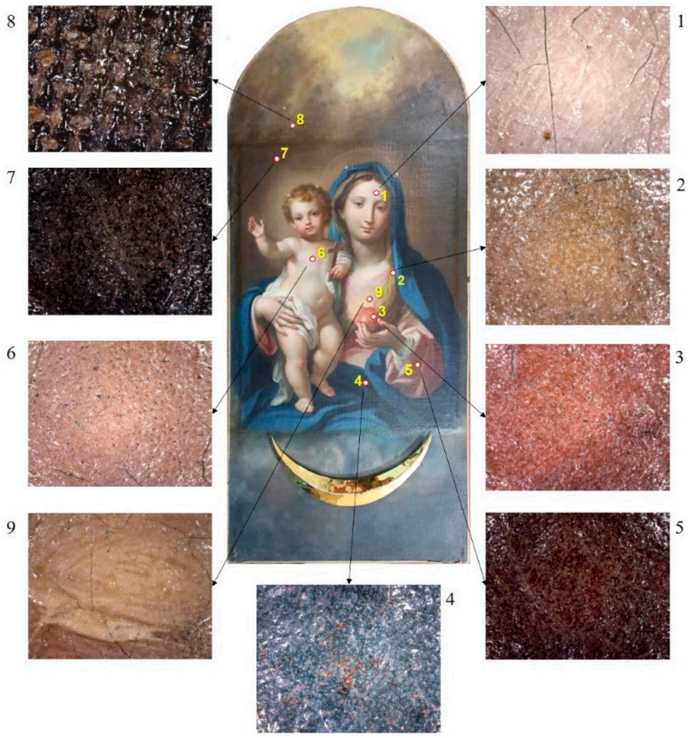


Figure 9. Digital optical microscope observation (M = 50×; image width size = 7 mm) of the representative areas, investigated by *p*-XRF for the elemental composition of original pictorial layers: skin tones (1 and 6), yellow tones (2 and 9), red-pink tones (3 and 5), blue pigment (4) and browns of the original and recent painting (7 and 8, respectively).

Table 1. Elemental composition detected in correspondence of the nine selected areas (Figure 9). The values are expressed as total collected counts ($\times 10^3$). Measurement parameter: voltage 35 kV, current 80 μA, acquisition time 50 s, working distance 1 cm. Relative XRF spectra are reported in Figure 10.

Elem.	**S**		**K**		**Ca**		**Ti**		**Mn**		**Fe**		**Cu**		**Zn**		**Sb**			**Ba**			**Hg**			**Pb**		
line	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$L\alpha$	$L\beta$	$L\gamma$	$L\alpha$	$L\beta$	$L\gamma$	$L\alpha$	$L\beta$	$L\gamma$	$L\alpha$	$L\beta$	$L\gamma$
keV	2.31	2.46	3.30	3.59	3.69	4.01	4.51	4.93	5.89	6.49	6.40	7.06	8.01	8.89	8.64	9.57	3.60	3.92	4.01	4.46	4.82	5.53	9.98	11.82	13.83	10.55	12.61	14.76
Point	total counts ($\times 10^3$)																											
1	-	-			0.51	-					0.56	0.32											0.92	0.75	-	52.54	38.33	3.75
2	-	-									5.53	1.05	0.49	-			1.36	0.36	-				0.45	0.37	-	34.52	24.45	2.68
3	4.43	3.23	0.70	-	4.83	0.89					6.31	1.27											5.52	3.24	0.49	36.68	23.27	2.59
4			0.86	-	5.62	1.04			0.46	-	14.92	2.57	0.66	-												37.12	26.93	3.02
5			1.22	-	5.43	1.03			0.51	-	8.45	1.56	0.57	-												31.09	21.59	2.42
6	-	-			1.60	0.31	0.52	-			1.34	0.44											1.08	0.70	-	40.69	28.89	2.97
7	-	-			4.16	0.77					6.65	1.28	0.42	-									0.68	0.56	-	33.04	22.30	2.47
8					2.03	0.52					5.72	1.06	0.51	-	24.39	4.25				3.26	2.30	0.79				25.70	17.77	2.13
9	-	-	0.57	-							1.13	0.44	0.55	-			1.14	0.47	-				1.77	1.26	-	51.53	37.96	3.71

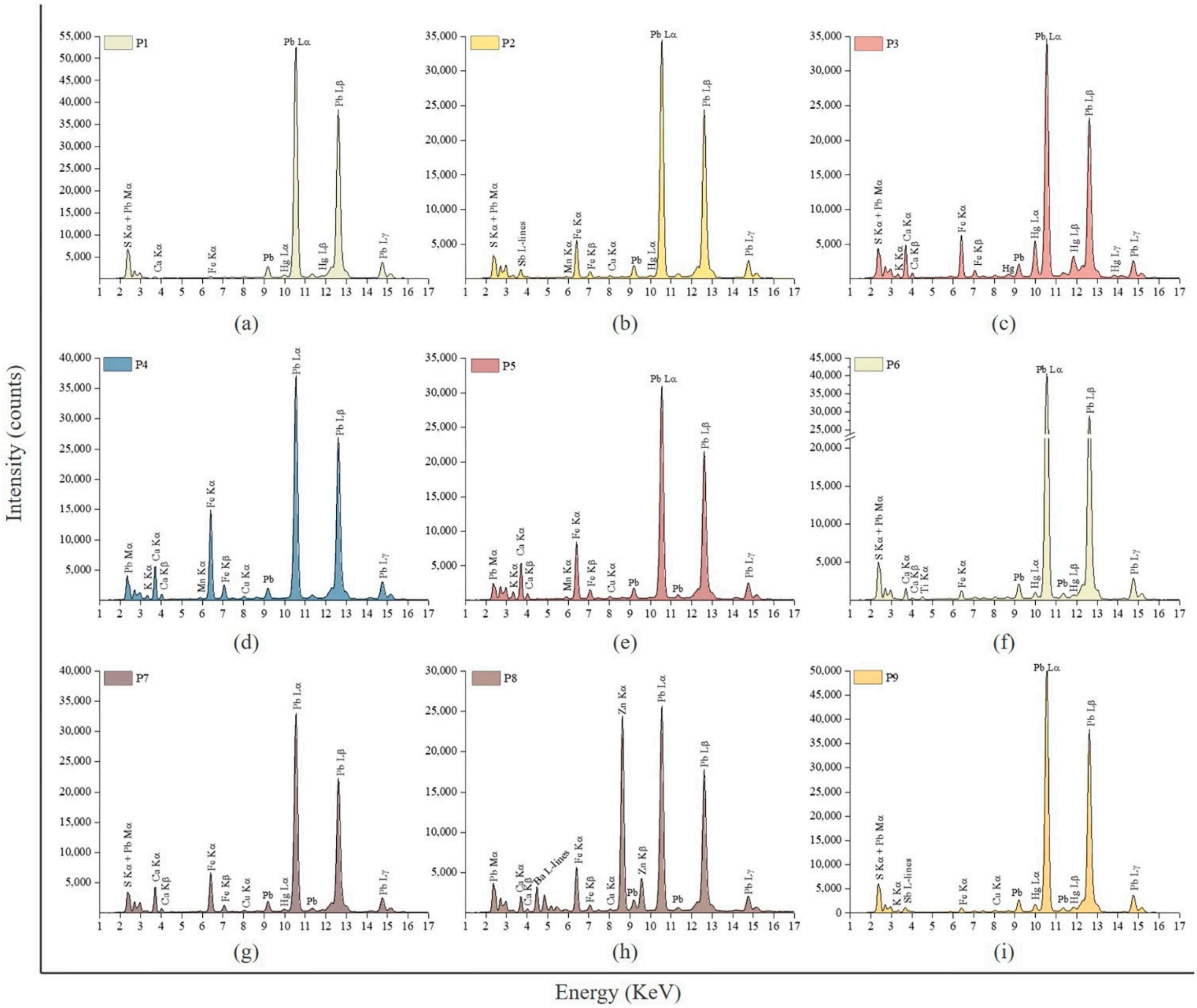
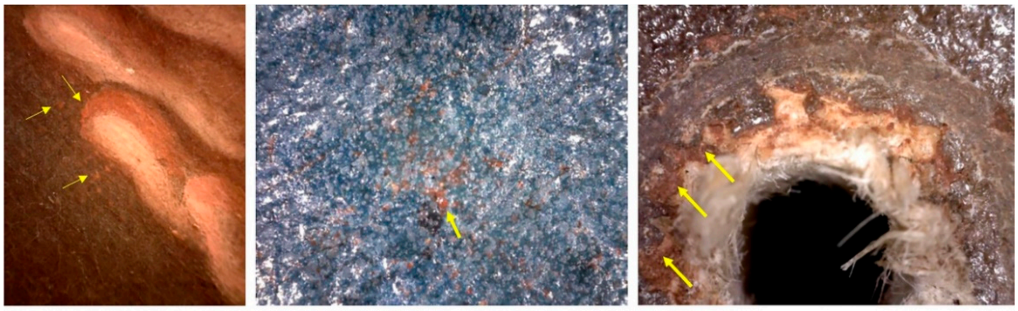


Figure 10. XRF spectra of the investigated areas: (**a**) P1 = skin tone of Virgin Mary; (**b**) P2 = headscarf yellow tone; (**c**) P3 = red heart; (**d**) P4 = blue mantle; (**e**) P5 = dark red robes; (**f**) P6 = skin tone of baby Jesus; (**g**) P7 = brown background (original part); (**h**) P8 = brown background (recent part); (**i**) P9 = yellow flame (heart) on red-pink robes.

A small amount of vermilion (HgS) is present in the mixture of the priming, together with red ochres, due to the widespread presence of Hg and Fe in the elemental composition. In fact, a reddish layer just below the painting is visible in different zones, as shown in some digital optical microscope images (Figure 11). Typically, this preliminary red thin layer guarantees a warmer tone rendering of the representation. Unfortunately, Sulphur of the vermilion cannot be uniquely distinguished in the XRF spectrum, due to the overlapping to Pb–Ma signal in the same spectral region. Moreover, vermilion is also present in small contents in the skin tones (P1 and P6) for a true-to-life rendering of redness and in abundant quantities in the correspondence of the Sacred Heart of Mary (P3), resulting in a vivid red. Vermilion is not useful for indirect dating, as it has been widely used from the East to the West, in all historical periods [28,29]. In the microscopic observations, the skin tone of the Virgin Mary appears purer and almost completely free of earth inclusions to give a pearly effect to the face, with respect to the skin tone of baby Jesus.



(a) (b) (c)

Figure 11. Macrophotography and digital optical microscope observation (M = 50×) of some details, showing a reddish layer present just below the painting: (**a**) Macro of the reddish layer left exposed at the skin contours; (**b**) OM of reddish layer left exposed under the blue painting; (**c**) OM of reddish layer visible under the painting, in correspondence of the gold crowns application holes.

The painter palette seems to be limited to a few pigments, mostly based on yellow, red and brown ochres, also mixed together to adjust the desired hue. Since there are no green tones in the investigated painting, very small quantities of copper (Cu), as well as potassium (K) and titanium (Ti), are attributable to impurities in the earth-based pigments. Ochres do not give particular indication for indirect dating, as they have been used since the prehistoric age to the present [28,29].

In correspondence to the yellow tones antimony (Sb) is present (P2 and P9), thus suggesting the addition of Naples yellow pigment, that is the lead antimoniate $Pb_3(SbO_4)_2$ or $Pb_2Sb_2O_7$. Its use dates back to ancient Egypt, however, the period of maximum diffusion of Naples yellow in the art of painting is between the 17th and 18th centuries [28]. After that, it is gradually replaced with synthetic yellow pigments.

Blue pigment is not identifiable only by XRF analysis due to the absence of the characteristic chemical elements uniquely attributable to blue chromophores. However, the absence of characteristic peaks referable to other historically used blue pigments constricts the identification to Prussian blue or to indigo. Moreover, the IR spectral response gives a clear indication: the blue painting of the mantle was found to be IR absorbent up to 1000 nm, thus strongly suggesting that it is Prussian blue, as the other blue pigments in the same spectral band are transparent to the infrared radiation [16,24]. The XRF spectrum in correspondence of the blue mantle (P4 reported in Figure 10d) is characterized by a higher presence of Fe, thus strengthening the assignment to the ferrocyanide Prussian blue, ${Fe^{3+}}_4[Fe^{2+}(CN)_6]_3 \cdot 6H_2O$. It was accidentally discovered in the early 18th century by a Berlin chemist, and it has spread in the art of painting since the second decade of the 18th century, so it is a useful marker for indirect dating [28,29].

The shadows of the *chiaroscuro* are made by the addition of *Terra d'Ombra* (raw umber), as suggested by the manganese (Mn) element detected in correspondence of the dark parts in the mantle and robe drapery (P4 and P5).

Brown background of the original part is likely made of iron-based brown (i.e., *Bruno di Marte* or Hematite), superimposed on the primer layer, hence the presence of Pb, Ca and Hg in the elemental composition detected in correspondence to P7. In the extension canvas, a similar brown is superimposed directly on to an industrial canvas (P8), since the presence of Zn and Ba suggest a lithopone-based preparation or a mixture of zinc white (ZnO) and barite ($BaSO_4$). Lithopone was synthetized for the first time in 1850, and thanks to its covering power, it was widespread on a large scale in the art of painting at the end of the 19th century [30,31].

5. Conclusions

The diagnostic campaign carried out for the first time for the non-invasive characterization of the oil on canvas painting *Maria Santissima delle Grazie* from Mirabella Imbáccari, allows for defining some aspects about the attribution, the indirect dating, its history and its conservation condition. The most important results are summarized below:

- *pentimenti*, modifications or underlying pictorial drafts are absent, as well as a preparatory drawing;
- the certainty of the execution in the subject representation, highlighted by the quick and spontaneous *ductus*, denotes a mature painter of high artistic skill;
- the author's *modus operandi* is compatible with the painters of the Neapolitan school (Sebastiano Conca and/or his workshop have been indicated as possible authors);
- the painting is made of two parts: a rectangular central part, considered the original canvas, applied on the extension canvas, which gives the present form;
- the pigments (both in painting and in preparatory layer) detected on the original part, as well as the morphological characteristics of the canvas yarn, confirm the material compatibility with the hypothesized dating to the second half of the 18th century. In particular:
    - Prussian blue gives the *terminus post quem* as it was discovered in 1704, and it spreads in the art of painting from the second decade of the 18th century;
    - Naples yellow gives the possible *terminus ante quem* as, in the art of painting, it has gradually fallen out of use since about 1850, and its period of maximum diffusion was between the 17th and 18th centuries;
- the extension canvas has morphological and compositional characteristics of an industrial canvas and can be dated from 1850; this evidence is compatible with a restoration treatment following a documented arson that affected the painting in 1860;
- the actual conservation conditions are good, despite the inappropriate interventions during the 20th century, resulting from the excessive application of jewellery and gold decorations. Some of these applications have been permanently removed, leaving irreversible holes covered by a mimetic pictorial integration.

This work once again demonstrates the success of non-invasive, in situ investigations by using multispectral imaging integrated with a portable XRF chemical analysis in the exploration of the identity of unknown artworks, thus increasing its cultural value and supporting the historical-artistic studies aimed at solving dating and attribution issues.

A systematic study of materials and manufacturing techniques, also of minor pictorial works distributed in small towns, can be fundamental to reconstruct the diffusion from the most famous centres of the models and themes invented by the most famous workshops. This would allow us to understand the success of the models, especially in the case of widespread religious subjects such as the one analysed here, giving objective indications for the analysis of fictional copies or replicas of the original subject, possibly modified over time or adapted to the needs of the local communities.

Another important issue is the knowledge of the constituent materials of the painting, useful as a preparatory support for future restoration interventions.

Finally, it is useful to underline that ecclesiastical cultural heritage is often subjected to theft and making the artworks known can prevent such criminal episodes. Otherwise, preventive diagnostic information, appropriately archived and made available for consultation, could also be decisive in identifying and authenticating artworks recovered following seizures [32].

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