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A Multi-Analytical Study of a 17th-Century Wallachian Icon Depicting the "Mother of God with Child"

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Abstract: As part of a detailed investigation project focused on the painting materials and technical features used in Wallachia during the 17th and 18th century, the imperial icon "Mother of God with Child" from the Orthodox Church of the "Annunciation" in Râmnicu Vâlcea, Romania, was investigated before the restoration intervention. A minimally invasive multi-analytical approach consisting of high-resolution digital radiography, hyperspectral imaging, UV fluorescence imaging, portable X-ray fluorescence, and Fourier transform infrared spectroscopy was used. The results emphasized several key features, such as: the structure of the wooden panel, the nature of pigments and of the painting technique frequently used at that time, and various defects of the pictorial layer including traces of previous restoration works, most probably made at the end of the 18th century.

Keywords: imperial icon; Brancovan art; digital radiography; UV fluorescence; hyperspectral imaging; XRF; FTIR; heritage science

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1. Introduction

The production of icons has a longstanding and vibrant tradition within the Romanian cultural space. Icon production flourished especially in the Principalities of Moldavia and Wallachia, as well as in Transylvania, under the influence of both Eastern (Byzantine-style) and Western artistic traditions [1,2]. The great majority of the icons were painted in monastic centers, using the characteristic Byzantine iconography approved by the Orthodox Church. The icons were painted on wooden panels, following the egg tempera technique and were typically decorated with gold leaves on the background [3–6].

Except for some minor regional interpretations, all icons were painted following the strict Byzantine tradition [7]. In general, the chromatic palette of these icons relies heavily on red and yellow ochres, a characteristic which emphasizes the warm atmosphere given by the gold background. In contrast, blue and green pigments are less frequently found. The use of a golden background was the most common option, although variations of this practice were found (especially in small monastic workshops) due to the poor access to quality painting materials [8,9].

It should be regarded that icon painting has a well-established, centuries-old tradition only in regions closely associated with the Byzantine Empire (such as modern-day Greece, Serbia, Turkey, Bulgaria, and Macedonia). In contrast, within the cultural space of Wallachia and Moldavia, the production of icons should be regarded as more of a peripheral phenomenon [2]. In these regions, icon painting techniques were primarily transmitted through oral tradition. For centuries, this knowledge was passed down from master to apprentice inside small monasteries [3–6]. Notebooks containing technical recommendations were rare, and those available consisted mostly of sketches with iconographic solutions and a few minor instructions [10]. Furthermore, the first translation of "The Painter's manual" of Dionysius of Fourna in an archaic Romanian with many Greek influences was made only at the beginning of 19th century by Macarie Archimandrite from Căldărușani Monastery [7].

The oldest preserved icons from Wallachia date back to the 14th century [8,11]. It is important to note that religious art in Eastern Orthodox Christian regions after the Byzantine Empire's fall in 1453 is referred to as "post-Byzantine". In the 20th century, marked by the decline of the Ottoman Empire and the modernist revival of tradition and national style in architecture and arts, this term was replaced by "Neo-Byzantine" (also referred to as Byzantine Revival) [12].

Although many of the existing Wallachian icons are well preserved, still a considerable number among these valuable artworks require urgent restoration interventions. Over time, due to shifting aesthetic preferences and changes in meaning and significance to various local communities, some of the icons were being repainted or encased in silver or gilded silver [13]. This practice ensured preservation of the original painting by masking large parts of the pictorial layer, while deliberately accepting small damages produced by the fixing intervention, such as marks from the nails. For this reason, periodic restoration works represent good opportunities for an in-depth investigation of the actual conservation state of the icons, a mandatory procedure before any practical intervention.

According to the Eastern Christianity tradition, an *iconostasis* is the wall which separates the nave from the sanctuary and is usually made of carved wood (rarely by stone or plaster) [14]. Developed in the early period of the Byzantine Empire from the *templon*, the *iconostasis* was initially more modest in size, but by the 12th century already, wood replaced stone and the *iconostasis* grew in height, developing a strict rule of registers imposed by certain stages of the Christ Revelation, a certain iconographic system which is closely connected with the Sacrament of the Eucharist [5,15–18].

In most cases, the *iconostasis* has 45 icons placed on four registers. The first register features a central depiction of the Virgin Mary and is marked by the representation of the Prophets from the Old Testament announcing the coming of the Messiah. In the second register, the central part displays the image of Christ Pantocrator (*Χριστὸς Παντοκράτωρ*), with Virgin Mary and John the Baptist on either side. This second register also includes representations of the Twelve Apostles. The third register is composed from the Great Feasts in the Eastern Orthodox Church (typically twelve). The scene representing the Last Supper, a symbolic moment of the Eucharist (Holy Communion), is positioned at the center of this register. This key scene resumes the role of the *iconostasis* [19]. The last register, the fourth one, placed at the bottom (at eye level), is split between the Imperial Doors in the center and the Deacon's Doors on the sides.

The name "Imperial" derives from the Byzantine Empire (Eastern Roman Empire) history in which the Emperor was allowed to enter the altar specifically through these center doors. The icons within this last register, also known as Imperial icons, are typically larger in size. On the left side of the Imperial doors is depicted Virgin Mary as Mother of God, while on the right side is depicted Christ Pantocrator. Typically, the other icons of this register depict the patron saint of the church, the archangels or other significant saint or feast.

The Orthodox Church of the "Annunciation" in Râmnicu Vâlcea, Romania, serves as a prime example of post-Byzantine church architecture and Byzantine art [20]. Inside, its *iconostasis* features an Imperial icon depicting the "Mother of God with Child", completely restored during 2018.

The church was founded by the Romanian voivode Mircea Ciobanu (Mircea the Shepard, b. ?–d. 1559) at the beginning of the 15th century as a brick masonry building.

In the first Church *Diptychs* established between 1824 and 1828, the founder is considered Mihnea cel Rău (Mihnea the Wrongdoer/Mean/Evil; b. 1462–d. 1510) who ruled between 1508 and 1509 [20]. Burned during the Ottoman–Habsburg wars (1739), the church was built a second time in 1747. Since then, the building has been restored several times, preserving its original plan and style.

Together with the church, the artworks within underwent restoration as well. One of the objects that underwent changes in this phase is the Imperial icon "Mother of God with Child" from the *iconostasis* of the Church, as an object replete with artistic and historical worth. The combination of the circumstances of production and restoration qualified this particular object as an excellent candidate for a detailed study on a post-Byzantine icon, representative of the Brancovan art (end of the 17th century–beginning of the 18th century) [4,21]. The term refers to the art made during the rule of Constantin Brancoveanu (b. 1654–d. 1714). It is a hybridization which consisted of replacing the austere style with a more decorated style, inspired by the Baroque movement which was happening in Transylvania—a peripheral Western art influence [8,11,22].

The 2018 restoration of the icon consisted in various operations: prophylactic consolidations, mechanical removal of wax, removal of carbonized matter, grouting of gaps in the pictorial layer, removal of adherent deposits and aged varnish, chromatic integration of interventions on the support, integration with removable water base colors of new and used putties and the applications of a dammar varnish, cleaning and preservation of the silver encasement. All of these treatments were performed in the Saint Ierarch Calinic of Cernica Conservation and Restoration Center of the Valcea Holy Archiepiscopate, during 2018, and only after a comprehensive physio-chemical investigation.

Given the historical, artistic, and religious value of the imperial icon "Mother of God with Child", the main aim of this study was to obtain detailed information on the employed materials and painting technique, technical features, and overall state of conservation of the icon (at that time), such information being crucial for an adequate restoration of the icon. This study was designed to offer a case study about the potential of non-invasive imaging techniques to achieve useful information about the technical features of painted artwork, offering a viable alternative to traditional, sample-intensive approaches. The employed imaging techniques included high-resolution digital radiography, hyperspectral imaging, and UV fluorescence. For an in-depth characterization of the painting materials, elemental (portable X-ray fluorescence—XRF) and molecular spectroscopic techniques (attenuated total reflectance-Fourier transform infrared spectroscopy—ATR-FTIR) were subsequently used, after collecting a minimum set of representative microsamples. The obtained results are presented and discussed for the first time in this paper.

2. Materials and Methods

2.1. The Icon

The imperial icon "Mother of God with Child" (Figure 1) is canonically located on the left side of the *iconostasis*, near the central entrance in the altar apse [18]. The representation of "Mother of God with Child" is depicted in the Hodighitria type ("*Οδηγήτρια*" meaning—"She who points the Way"), a characteristic iconographic representation very common among the Byzantine painters that were active before 1453 AD [9], in which the Mother of God holds the Christ Child with her left hand while pointing towards Him with her right.

The icon, 84.5 × 64.5 cm, is painted on a 1.8 cm thick wooden panel with a limited color palette, mainly red, yellow, and bluish-green. Except for the portraits of Virgin Mary, Christ Child, archangels Michael and Gabriel, the front side of the icon was encased in a silver cover (most commonly named *riza* or *oklad*—Slavonic meaning "revetment"), most probably at the request of an anonymous local boyar—a member of the highest rank of the feudal nobility in the Principalities of Moldavia and Wallachia.

Figure 1. Image of the icon "Mother of God with Child" before (**a**,**b**), and after restoration (**c**,**d**). Images (**a**,**d**) reproduce the initial and the actual, respectively, restored silver encased. Sampling areas are highlighted in image (**b**).

In the icon, Christ Child is presented in a frontal posture, traditionally dressed in bluish-green chiton (Greek *χιτων*—tunic) and draped in a golden himation (ancient Greek *ιματιον*—mantle). The Virgin is painted wearing a bluish dress and wrapped in a red mantle of which folds are painted in black according to the tradition of Byzantine iconography. Moreover, following the recommendations of Byzantine "*erminia*" [16,17], the archangels Michael and Gabriel, placed on the superior register of the icon, have their faces turned to the Mary and the Child.

An interesting feature is given by the Slavonic inscription located at the left of Virgin Mary's head (Figure 1b,c) that reads Eleusa, (not Hodighitria as expected), which is a direct transliteration from the Greek word "*Ἐλεούσα*" (meaning—"That who shows tenderness/mercy"). Compared to the Hodighitria iconographic representation, the Eleusa iconographic type is characterized by the touching cheeks of Mother and Child.

Concerning the Slavonic lettering, this orthographic system was in use in local administration and the local Church until the second half of the 19th century, a time when a completely Latin alphabet became the new official orthography both in Moldavia (1860) and in Wallachia (1863) [23]. This information therefore places the production of the icon before the second half of the 19th century. Furthermore, the use of the Eleusa inscription on the icon instead of Hodighitria suggests that the icon was most probably painted in the second half of the 17th century, a period when the iconographic styles were not yet well defined [9]. At that time, icons were copied from older ones, and often the writing was done by someone who wrote beautifully but without knowing the meaning or what he was writing [24–26], which accounts for the prevalence of writing errors in inscriptions. Another argument which sustains the painting of the icon within the second half of the 17th century would be the dramatic event marked by the destruction of the church by the Turkish invasion in 1739 [20], an event mentioned in the inscription located on the bottom side of the icon (Figures 1b,c and 2).

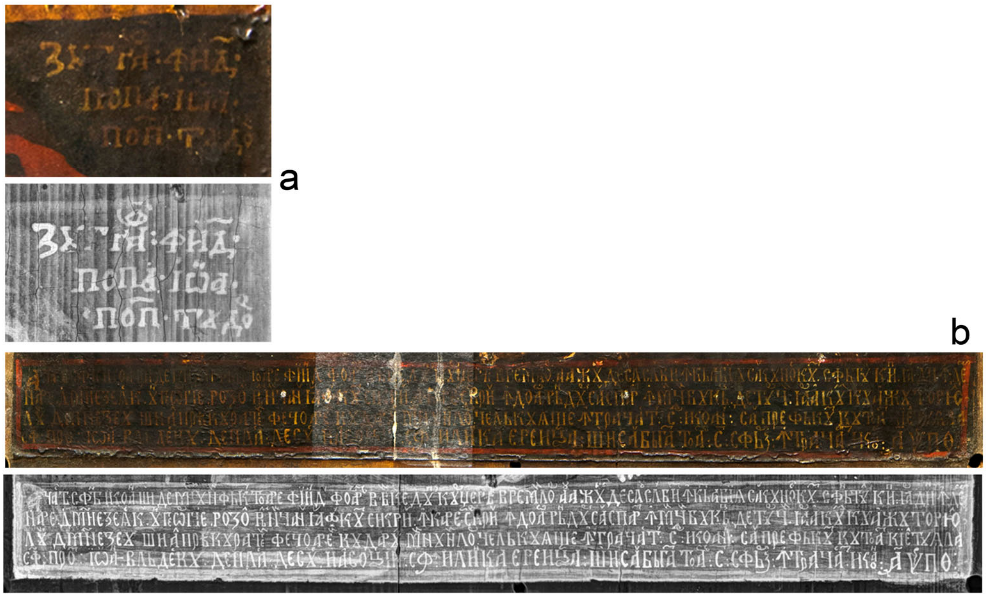

Figure 2. The photographic (upper) and radiographic (lower) images of the inscriptions attesting the names of painters (**a**) and details regarding the 1789 restoration (**b**).

Most likely, the icon was originally painted in an unknown workshop, most probably in Wallachia, without any indication of the year. According to the Slavonic inscription on the center right side of the icon (Figure 2a), the icon was originally painted by Popa Iosif and Popa Teodor. In 1789, according to the inscription on the bottom side, the icon was repaired by Gheorghe Rozol Râmnicean on the demand of the priest Ioan Vlădescu and his wife, Ilinca, for 200 Austrian zwanzigers (Figure 2b), currency used in Wallachia and Moldova until the beginning of the 19th century.

Transliterated into the current Romanian lettering, the text is (double slash marks the end of row):

Acea^{s}tă sfâ^{n}t^{ă} icoa^{nă} și de mi^{n}un^{i} făc^{ă}toare fiind foar^{te} veche du^{pă} cu^{r}gere^{a} vremilo^{r} a aju^{ns} de s-au sl^{ă}bi^{t} încât nu s-au cuno^{s}cu^{t} sfâ^{n}tu^{l} chi^{p}. Si di^{n} înde^{m} // nare d(u)mnezeia^{s}c^{ă}, un Gheo^{r}ghe Rozo^{l} Ră^{m}n^{i}cean i-au f^{ă}cu^{t} sicri^{u}; în care scri^{u} în doa^{o} râ^{n}du^{ri} s-a^{u} spar^{t} în m^{i}c^{i} bucă^{ti} de tu^{r}c^{i}. Ia^{r} acu^{m}, cu ajutoriu^{l} // lu^{i} D(u)mnezeu și a^{l} Preacurate^{i} Fecioare, cu dar(ul) m^{i}nun^{i}lo^{r} ce lăcuiaște într-acea^{s}t^{ă} s^{f} icoan^{ă} s-au prefăcu^{t} cu toa^{tă} chie^{l}tuiala // sf<ințitului> Preot Ioa^{n} Vlăde^{s}cu de pla^{s}(a) de su^{s}; i a^{r} soț^{ia} Sf<inţiei Sale este> Ili^{n}ca Ereița și s-a^{u} băga^{t} toa(te) 200 sfanți într-acea^{stă} ic(oană) 1789.

which, translated into English, means:

This holy icon and of working wonders being very old after the ages they've become weak so they did not know the holy face // And from the exhortation of God, a Gheorghe Rozol Rămnicean made him a casket that casket twice were broken into small pieces by Turks. And now, with the help of God and the Blessed Virgin, with the gift of miracles that dwells in this holy icon (the icon) was repaired with all the spending // of the holy priest Ioan Vladescu from the upper parish; and the wife of his Holiness is Ilinca Ereita, and all 200 schvantz have been put into this holy icon 1789.

The restoration of the icon in 1789, likely in response to the destruction of the Church of the "Annunciation" in Râmnicu Vâlcea in 1739, suggests that the icon's origins date to the late 17th or early 18th century. However, without radiocarbon dating, the exact age of the icon remains uncertain.

2.2. High-Resolution Digital Radiography

High-resolution digital radiography images of the icon were obtained with an ISOVOLT Mobile 160 M1 complex computerized radiography station from Waygate Technologies (Ahrensburg, Germany). The system was operated with the following experimental conditions: 100 kV energy, 5 mA current intensity, 30 s exposure time. The distance between the instrument and radiographic detector was of 100 cm. A 35 µm scanning resolution was used, resulting in 4 partial images of 10,142 × 12,327 pixels further processed with Rhythm Review software (v.5.1.) produced by Waygate Technologies and installed on a CRxVision Computed Radiography (CR) tabletop Scanner (Ahrensburg, Germany). The final X-ray image of the entire icon (Figure 3a) was obtained in Adobe Photoshop CS 6 v.13.0.1.

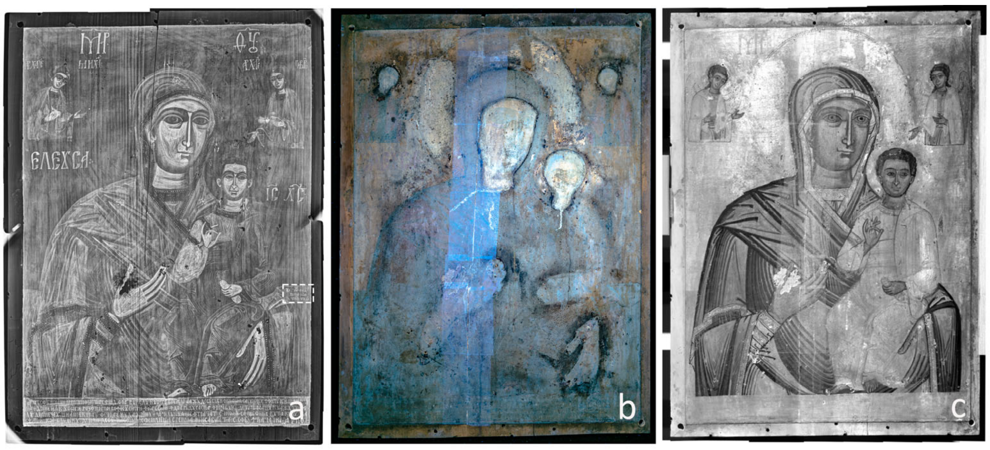

Figure 3. The digital radiography (**a**), UV fluorescence image (**b**) and 2000 nm SWIR image (**c**) of the "Mother of God with Child" icon before restoration.

2.3. Spectral Imaging—From UV Fluorescence to SWIR Hyperspectral Imaging

Hyperspectral images of the entire surface of the icon were registered using a portable and non-invasive HySpex SWIR-384 system produced by Norsk Elektro Optikk A.S. (Oslo, Norway). The camera features a state-of-the-art Mercury Cadmium Telluride (MCT) detector and is equipped with a cryogenic cooling system which ensures a constant temperature at 147 K. These characteristics enable low background noise, high dynamic range, and optimal signal-to-noise level at a maximum speed of 450 fps. For data acquisition, a 30 cm working distance close-up lens was used in order to provide the best available resolution. The system records simultaneously 288 different spectral bands in the interval 950–2500 nm, with a spectral sampling of 5.45 nm. Because the field of view (FOV) covers only 16 degrees (corresponding approximately to 8.4 cm), 12 recordings were performed in a push-broom technique, by scanning the icon in a vertical position at a fixed distance of 30 cm controlled by a laser telemeter, with the camera being mounted on a motorized *x*-*y* axis translation stage. During the investigation, which was recorded in a controlled environment, diffuse illumination was provided by two custom lamps provided by the manufacturer. Focusing the illumination to a line overlapping the camera FOV, the lamps are charged with a 12V DC power supply are equipped with T3 halogen incandescent light bulbs R7S, 12V, 150 watts, providing a proper excitation source in the range covered by the hyperspectral camera detector, and providing a light output of 2500 lumens. Radiometric calibration of data was carried out using the Hyspex RAD software (v.3.1.), thus converting the digital number (DN) in at-sensor absolute radiance values (W/sr·nm·m^2) by using a scaling factor included in the header file. Conversion of the radiance to Apparent Reflectance was made using the QUAC module, which at that time was the simplest and fastest option available, since ENVI can identify the range of the detector in the SWIR region. Data processing was carried out in ENVI (v.5.3.).

UV fluorescence images were acquired in a dark ambient without visible radiation, using a Nikon Coolpix P900 digital camera (Tokyo, Japan). The lightning source was provided by a handheld UV lamp from Karl Deutsch (Wuppertal, Germany), with a maximum peak at 365 nm and an intensity of 60 W/m^2 at a 400 mm distance. To achieve even illumination across the surface, longer exposure times were employed. Since UV fluorescence is a phenomena observable in the visible spectrum no additional filters were required [27–29].

2.4. X-ray Fluorescence

XRF measurements were performed using a portable, hand-held energy-dispersive instrument TRACER III-SD from Bruker (Billerica, MA, USA) provided with an Rh-anode X-ray tube and a 10 mm^2 X-Flash Silicon Drift Detector (SDD) with a typical resolution of 145 eV at 100,000 cps (Mn Kα line). All measurements were performed on microsamples with the following experimental conditions: 10.60 μA current intensity, 40 kV tube voltage, no filtering, air atmosphere, 60 s analysis time. Elemental identification was possible by using the standard Bayesian deconvolution with the ARTAX software (v.7.4.) and data post-processing was performed with Microsoft Office Excel 2016. For samples comprising the whole stratification (samples S5 and S7 only), XRF measurements were carried both on the top paint layer and on the back of the sample by turning around each sample on the examination window.

2.5. Fourier Transform Infrared Spectroscopy

FTIR analysis was carried in attenuated total reflection (ATR) mode on microsamples, using a Perkin Elmer SpectrumTwo FTIR spectrometer (Waltham, MA, USA) equipped with a Pike Technologies GladiATR accessory (monolithic diamond crystal, 3 mm diameter) (Fitchburg, WI, USA). Spectra were collected at 4 cm^{-1} resolution, in the 4000–400 cm^{-1} mid-infrared region, using 16 scans. All spectra shown in this paper were baseline corrected (automatic baseline correction was carried out in Spectrum 10). Spectra analysis was done in Essential FTIR Spectroscopy Software Toolbox (v.3.50). For samples comprising the full stratigraphy (samples S5 and S7 only), measurements were carried out both on the top paint layer and on the back of the sample (ground layer).

3. Results and Discussion

3.1. Imaging Documentation

The high-resolution digital radiography of the icon before restoration is reproduced in Figure 3a. Due to its high level of detail, the final radiography illustrates a multitude of features which are impossible to highlight in optical photography. In addition to the texture of the wood, which is well emphasized, the radiography shows two non-contiguous vertical fissures of the wooden panel, small holes in the superior and inferior part of the icon, or the presence of wooden knots. It is worth mentioning the absence of xylophagous insects' galleries or other traces of fungal attack, which testifies a good conservation state of the wooden panel, in spite of the icon age being estimated to more than 200 years. The fact that during its entire age the icon was encased in silver could be an explanation of the overall good state of conservation.

Other significant characteristics displayed in the X-ray images include: the presence of a very discrete yet dense *craquelure* network on the upper right quadrant of the image [30], as well as the existence of a low absorbing area located near the right hand of the Virgin (Figure 3a), an area where the pictorial layer is lacking as both images reproduced in Figure 4 confirm.

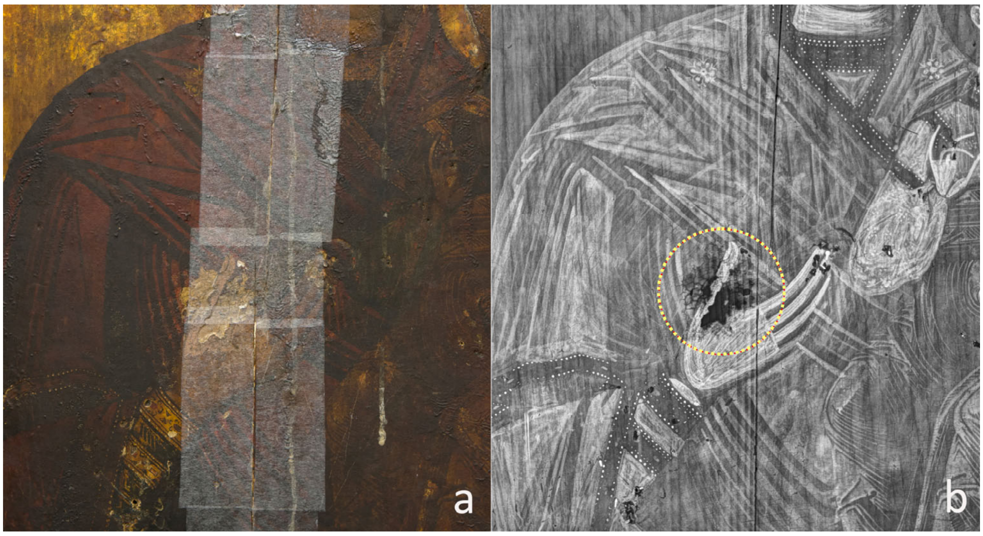

Figure 4. Detail from the "Mother of God with Child" icon: visible color image (**a**), digital radiography (**b**).

The radiographic image accurately reproduces the inscription that attests the names of the initial painters of the icon (Figure 2a). It also faithfully captures the inscription regarding the restoration work performed by Gheorghe Rozol Râmnicean in 1789 (Figure 2b). Other technical details concerning the depiction of the portraits and hands of the Virgin Mary and Christ as Child, as well as the two Archangels and the inscriptions with Slavonic lettering can be easily observed in the radiographic images. The most plausible explanation of this finding concerns the use of lead rich pigments such as lead white or red lead (minium), given the high absorption capacity of lead for X-rays. For the red painting areas, minium could have been used as the final layer for modeling ("lights") [31]. Due to its rich orange shade, minium was frequently applied on top of a vermilion layer [3,6]. The possible presence of both minium and vermilion are further discussed within the section *Painting materials*.

Complementary to radiography, the UV fluorescence and IR imaging are highly relevant in characterizing the top layers and the underlayers of a painting [32]. The UV fluorescence examination revealed on the whole surface of the paint layer the presence of an uneven, aged, and deteriorated layer of varnish which emits a bluish fluorescence (Figure 3b). A second protective coating, preliminary presumed to be shellac due to its characteristic reddish hue, is displayed only on the area that corresponds to the metal golden leaf. This particular layer, which in the visible spectrum appears to be dark reddish-brown, is orange fluorescent under the UV radiation (Figure 5b).

Due to the poor quality of the used varnish and its uneven application on the surface of the icon, the effect generated by the contraction of this coating can be easily seen in the form of an unpleasant wrinkle effect (Figure 6a). Most probably, after applying this later protective coating, the icon was not completely left to dry, leading to the effect of leakage.

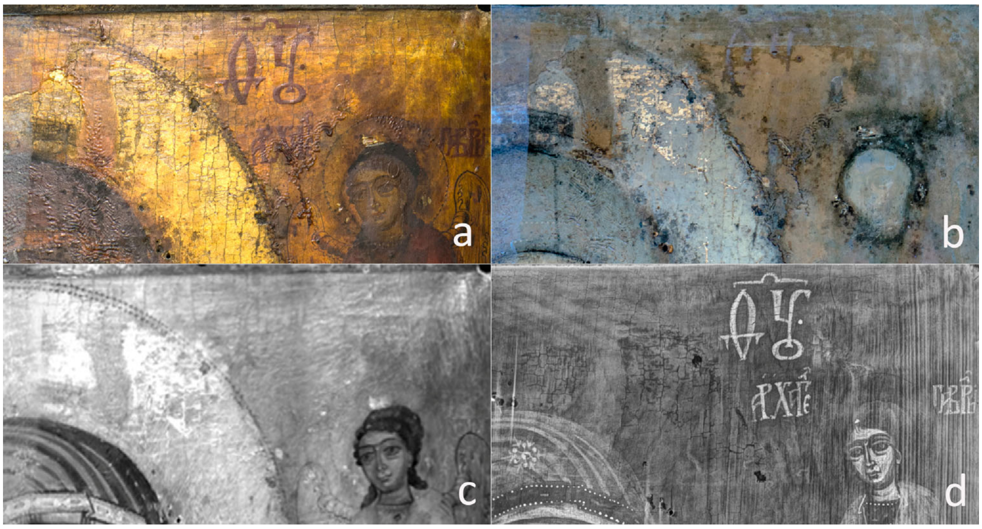

Figure 5. Detail of the upper right corner of the icon: visible color image (**a**), UV fluorescence mode (**b**), SWIR infrared 2000 nm (**c**), and digital radiography (**d**). The UV fluorescence outlines the presence of a highly fluorescent coating exclusively on the portrait of the angel. In the radiography, the strong reflection displayed as light tone, corresponding to a lead-based pigment, is emphasized on the inscription.

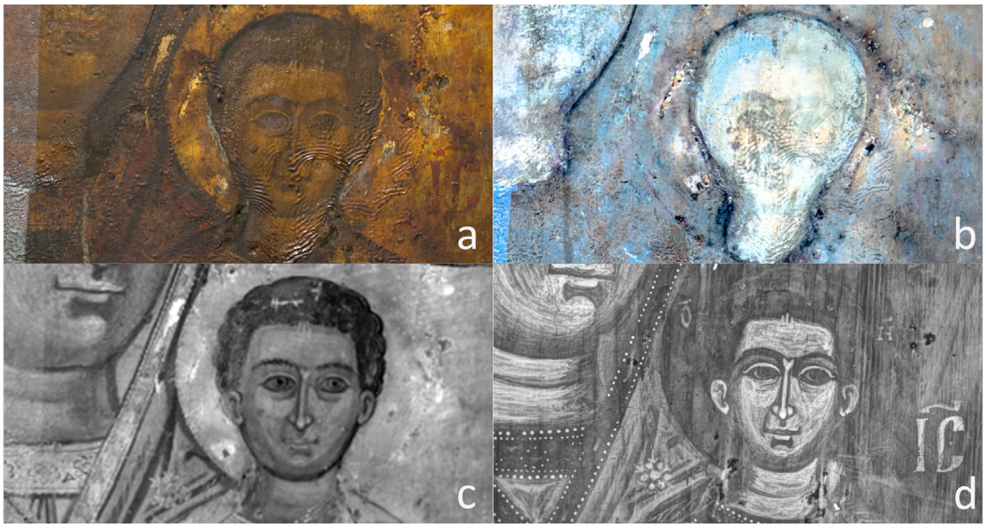

Figure 6. The portrait of Christ Child (detail): visible color image, (**a**) UV fluorescence image (**b**), far infrared 2000 nm (**c**), and digital radiography (**d**). In the visible color image, the wrinkles effect produced by the thickness of the varnish layer is clearly highlighted. The UV image displays a high fluorescence coating, clearly visible on the face of Christ Child. The border lines and the anchor points of the silver encasement are depicted in dark tones in the IR image. The radiography highlights the detailed modeling of the carnation layer made with a strong reflected lead-based pigment.

Another important feature highlighted in the UV examination was the presence of a highly fluorescent coating that is located exclusively on the faces and hands of the represented saints. Taking into context the presence of the anchor holes, it can be stated that these painted areas corresponded to the cut-outs in the silver encasement (Figure 1a,c). These high fluorescent areas also feature the effect of leakage, meaning that the icon was exposed in a vertical position (vertical plane) during the application of essential oils and aromatic substances, a common practice in the Orthodox Church. Moreover, taking into consideration the ritual and the practice from the Orthodox Church, this layer can be inferred as chrism (a consecrated oil used in Eastern Orthodox Church in the administration of certain sacraments and ecclesiastical functions)—a hypothesis that must be confirmed by spectroscopic analysis.

Another subject area clearly highlighted by the high absorption of UV radiation is the presence of adherent deposits, mainly observed at the boundary between the painted areas, still visible in the cut-outs, and the silver encasement, which corresponds to the Virgin Mary, Christ Child, and the two Archangels (Figure 3b). The most likely explanation is the accumulation of black carbon sourced over time from the candles burnt inside the church and gathered at the interface between the visible paint layer and the silver encasement during the repeated cleaning actions.

While analyzing all 288 available spectral bands from the SWIR hyperspectral cube, four relevant wavelengths were extracted and compared with the other spectral imaging modes: 954, 1600, 2000, and 2400 nm. All of these narrow bands emphasized the materials, which have strong absorption of IR radiation (Figures 5c and 6c), more precisely the dark pigment used for contour lines, most probably an earth type pigment (iron oxide) possibly mixed with carbon black [33]. The artistic quality of these lines, which correspond to the Byzantine tradition of volume representation using thick superimposed opaque layers of color generating a highly decorative aspect, is highly remarkable. Since in the Byzantine tradition of painting the preliminary sketch or drawing was made using thin incisions or yellow ochre, no strong absorption signal from a carbon-black ink or pigment was noticed on the surface, not even in the case of the written inscriptions. The hypothesis on the use of ochres for the contour lines is further discussed in Section 3.2.2.

3.2. Painting Materials

For the elemental and molecular characterization of the employed painting materials, seven microsamples were extracted from damaged areas of the icon (see Figure 1b). Sampling areas are described in Table 1. Only two samples (S5 and S7) comprise the whole stratification, while the rest of the samples are not sections but rather small fragments extracted with a scalpel from the top paint layer. The most important information concerning the nature of the employed painting materials as obtained by combined XRF and FTIR analyses are summarized in Table 1. The data registered on the ground layers (backside of samples S5 and S7), and on the pigmented areas (top paint layer of all investigated samples) are discussed in the following subsections.

Table 1. Synthetic results of the physico-chemical analyses obtained on the investigated samples.

Sample	Area Description	Typology	XRF Data [1]	FTIR Identification
S1	Red (Virgin's robe)	Painting layer	**Fe**, **Ca**, Cu, Ti, Mn (Zn, Sr, Si, Pb, Hg, S)	Natural ochre (kaolinite, calcite, quartz, iron oxides), protein binder, metal soaps
S2	Golden metallic foil (Virgin's robe)	Gold foil	**Fe**, **Ca**, Cu, Zn, Ti, Mn (Au, Cr, Si, Sr, Hg)	Iron oxides, tree resin
S3	Golden metallic foil (Angel's areole—left)	Gold foil	**Ca**, **Fe**, **Au**, Cu, Ti, Mn (Cr, Sr, Zn, Si, Hg)	Anhydrite, protein binder
S4	Dark brown (background)	Varnish	**Pb**, **Zn**, Cu, Fe, Ca, Mn (Ti, Hg, Cr, Si)	Tree resin, natural ochre (kaolinite, quartz, iron oxides), metal soaps
S5	Green (Childs' robe)	Painting layer	**Cu**, **Pb**, **Fe**, **Ca**, As, Zn, Ti, Sr (Mn, Si, Cr, Hg, S)	Natural ochre (kaolinite, calcite, quartz, iron oxides), protein binder, tree resin, metal soaps, copper carbonate (azurite)?
		Ground layer	**Cu**, **Ca**, **Pb**, Fe, As, Sr, S (Ti, Zn, Mn, Hg, Cr)	Anhydrite, protein binder
S6	Carnation (Virgin's hand)	Painting layer	**Pb**, **Fe**, Ca, Hg, Cu (Mn, Ti, Bi, Cr, Si)	Lead white, natural ochre (kaolinite, quartz, iron oxides), protein binder, metal soaps

Table 1. *Cont.*

Sample	Area Description	Typology	XRF Data [1]	FTIR Identification
S7	Contour line (Virgin's hand)	Painting layer	**Fe**, **Ca**, Hg, Sr, Cu (Pb, Mn, Ti, Zn, As, Cr, Si)	Natural ochre (kaolinite, quartz, iron oxides), protein binder, tree resin, metal soaps
		Ground layer	**Ca**, Fe, Sr, Cu, S (Ti, Mn, Hg, Pb, Cr, Zn)	Anhydrite, protein binder

[1] Elements are listed in decreasing order of abundance. With bold—major elements, regular—minor elements, in brackets—trace elements.

3.2.1. Ground Layer

According to the Table 1 data, FTIR spectra registered on the ground layer (Figure 7a) showed the presence of anhydrite ($CaSO_4$), the anhydrous form of calcium sulfate, identified based on the antisymmetric stretching (ν_3) and bending (ν_4) vibrations of the sulfate anion ($SO_4{}^{-2}$) observed at 1095 cm^{-1} (broad peak) and 700 to 500 cm^{-1} (sharp peaks), respectively [34]. As highlighted in previous studies [35], the antisymmetric stretching $\nu_3(SO_4)$ appears distorted and slightly shifted to lower wavenumbers in ATR registered spectra, as in this case. The splitting of the ν_4 mode into three well-resolved bands at 672, 609, and 592 cm^{-1} can be used to differentiate anhydrite from gypsum ($CaSO_4 \cdot 2H_2O$) in which the ν_4 vibration is observed as a doublet with peaks at 663 and 598 cm^{-1}. Another distinguishing factor between these two Ca-sulfate minerals is the absence of water molecules in the crystal structure of anhydrite. In gypsum-based ground layers, water vibrations are typically observed in the 3550–3400 cm^{-1} region (O–H stretching) and around 1629 and 1690 cm^{-1} (O–H bending) [34].

The existence of a calcium-based compound within the ground layers was confirmed by XRF analysis, based on the intense Ca-K lines registered. Minor amounts of Sr and Fe were also registered for these same areas. The presence of Sr can be linked to the presence of small amounts of celestine ($SrSO_4$) [36] or other natural sulfates that frequently accompany calcium minerals [37]. The presence of Fe within the ground layer could be linked with the addition of an ochre pigment, inferring the use of a pigmented ground. However, according to the existing literature in the field [38], pigmented grounds rarely appear in post-Byzantine icons and in the absence of any stratigraphic analysis, this hypothesis needs further investigation. More likely, the iron content comes from the upper Fe-rich painting layer.

Concerning the ground layer binding media, the shape and intensities of the bands observed at 2920 cm^{-1} and 2850 cm^{-1}, assigned to the antisymmetric and symmetric stretching vibrations of the CH_2 group, are a clear indicator for the presence of an organic binder (Figure 7a). The protein bands amide I (C=O stretching) at approx. 1652 cm^{-1} and amide II (N–H bending and N–C stretching) at approx. 1544 cm^{-1}, in conjunction with the band at 1455 cm^{-1} (C–H bending), infer the presence of a proteinaceous material in this layer [39,40]. Low amounts of calcium oxalates may also be present as inferred by the weak but very characteristic peak at 1320 cm^{-1} (C–O stretching vibration) [39]. The shoulder band around 1705 cm^{-1} could be linked with the presence of ketones, products of fat degradation [40]. All these findings point towards the use of a *gesso grosso* ground layer consisting of anhydrite mixed with a protein-based adhesive such as animal glue [38].

Similar results were reported on several Greek icons ranging from the 14th to the 19th century [36,39] as well as on several 19th century Russian–Lipovan icons [41]. Within Romania's region, studies carried so far on icons coming from workshops in Walachia and Transylvania [1,42–44] have highlighted a preference for gypsum-based ground layers, chalk (calcium carbonate) and lead white ground layers being less frequently found. Previous investigations carried out on an 18th century wooden *iconostasis* [45] coming from the same region (Vâlcea County, southern Romania) as the icon analyzed in this study have highlighted the use of a ground layer based on calcium sulfate in varying proportions of gypsum and anhydrite. These findings could indicate a preference of craftsmen from this region for these types of ground layers.

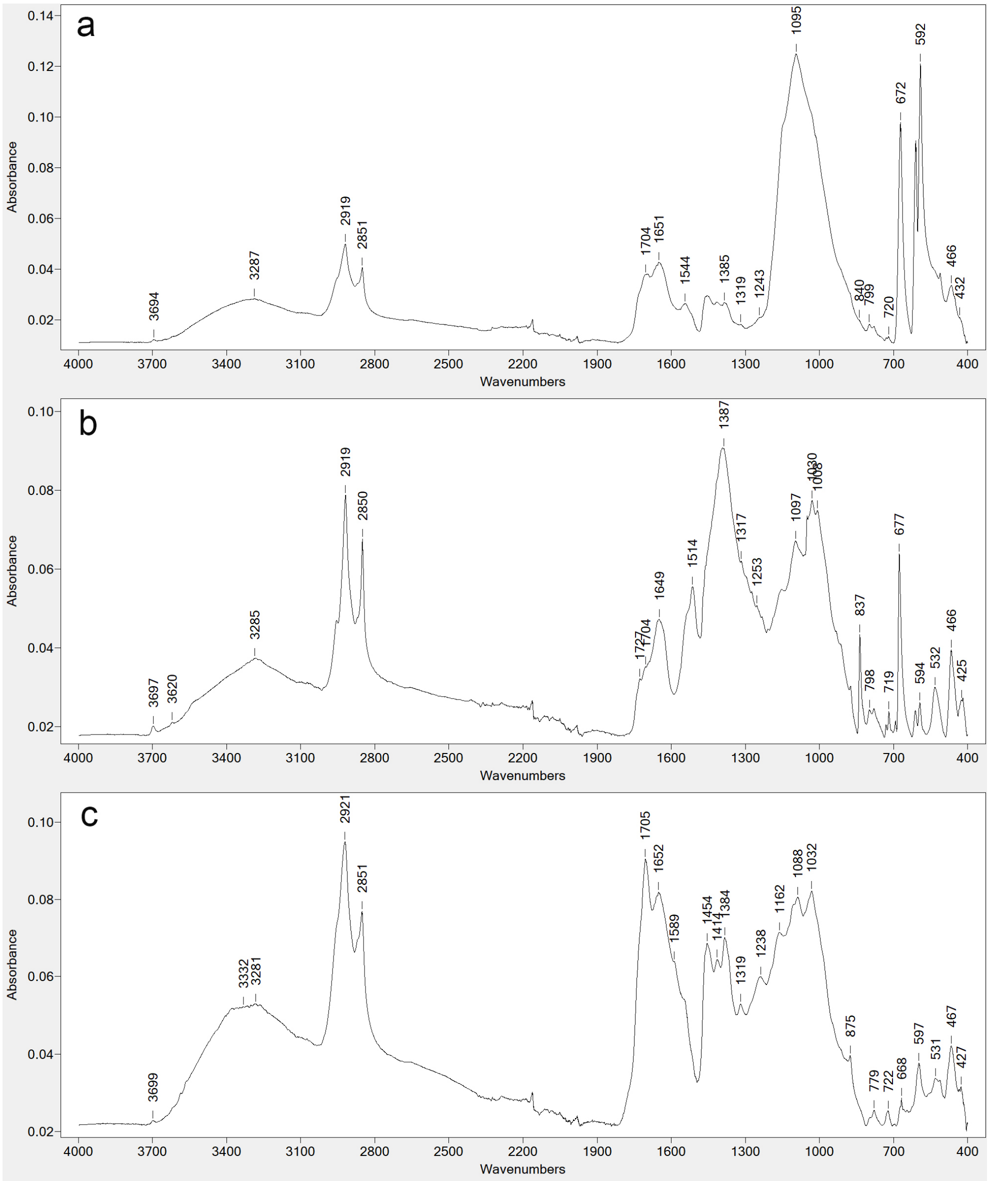

Figure 7. FTIR spectra registered on the ground layer of sample S7 (**a**), and on the paint layers of sample S6—carnation (**b**) and sample S5—green area (**c**).

3.2.2. Pigmenting Layers

In terms of pigments, as mentioned before, a relatively narrow color palette was used. As inferred from the XRF analysis, a Fe-based material like an ochre seems to have been used for the Virgin's robe (sample S1), intense Fe lines being registered for this area (Figure 8a). This hypothesis is confirmed by FTIR analysis, characteristic absorptions for red ochres [46] rich in kaolinite (aluminosilicates) being registered at 3694 and 3615 cm^{-1} (OH stretching modes), 1030 cm^{-1} (Si–O stretching) and 915 cm^{-1} (Al–OH bending), this last peak appearing as shoulder band. Low amounts of quartz (frequently found in association with kaolinite) were identified by the doublet observed at 798 and 780 cm^{-1} (Si–O stretching), along with calcium carbonate identified via the characteristic vibration modes of the carbonate ion observed at 872 cm^{-1} (asymmetric bending, ν_2) and 712 cm^{-1} (symmetric bending, ν_4). Iron oxide present as hematite was found via the diagnostic bands at 530 and 465 cm^{-1} (Fe–O lattice modes), confirming the use of a red ochre [46]. Small amounts of Cu, Ti, and Mn, also detected, can be linked to various types of accessory and clay minerals and/or impurities typically present within the iron oxide compound [46,47].

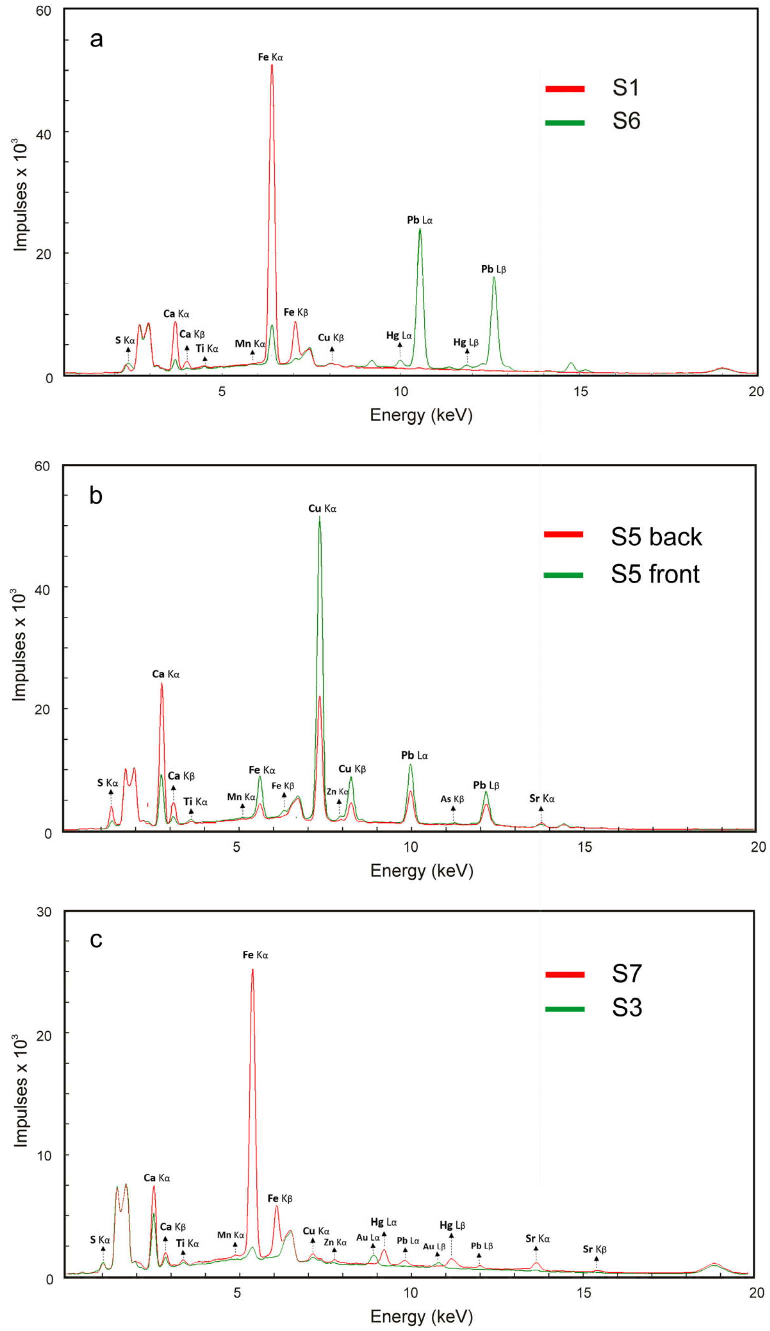

Figure 8. Representative XRF spectra registered on some of the investigated samples: red painting area (sample S1) and flesh tone (sample S6) (**a**); green painting area (sample S5) and ground layer (**b**), shadowed area (sample S7) and gold foil (sample S3) (**c**).

For the Virgin's robe (sample S1), the use of other traditional red pigments such as red lead and vermillion can be excluded, XRF data indicating the presence of Pb and Hg only in trace amounts. However, the use of vermillion in other areas of the painting is highly possible, as inferred by the ubiquitous presence of Hg within all samples investigated. The presence of Hg in minor amounts within some of samples investigated (S6—flesh tone, S7—contour line) could be linked with the use of small amounts of vermillion in order to obtain the desired hue, while in all other cases, the trace amounts of Hg registered can be linked with an obvious contamination of the areas with mercury-rich particles.

For the flesh tones (sample S6), a mixture of lead white—$2PbCO_3 \cdot Pb(OH)_2$ and iron oxides was most probably used as suggested by the intense Pb and Fe lines recorded (Figure 8a). Traditional manuals of Byzantine painting [16,17] specify the use of lead white mixed with red or yellow ochre along with small amounts of red bolus, to create flesh mid-tones (*σάρκα*—flesh). A small amount of vermilion (HgS) may also have been used, as the Hg XRF L line at 9.98 keV suggests. The XRF data are sustained by registered FTIR spectra (Figure 7b) which show intense carbonate stretching vibrations at approx. 1392, 837, and 677 cm^{-1}, all of them characteristic of lead white. The absence of the OH stretching vibration at 3535 cm^{-1} characteristics for hydrocerussite along with the presence of the 837 cm^{-1} peak can be correlated with the content of neutral lead carbonate (cerussite) in lead white. For the shadowed areas/contour lines (sample S7), a natural earth pigment (rich in iron oxides) mixed with a little vermilion may have been used as inferred by XRF data.

For the green pigmented area investigated (sample S5), intense Cu, Pb, Fe, and Ca lines were registered (Figure 8b). Zn, Ti, and Sr were also detected as minor elements. Arsenic's presence is suggested by a minor peak at 11.72 keV, which corresponds to the As $K\beta$ line [48]. However, the As $K\alpha$ peak at 10.54 keV is not visible due to its overlap with the Pb $L\alpha$ peak at 10.55 keV. This complex elemental signature infers several possibilities.

The combination of Cu and As could suggest the presence of emerald green, a copper acetoarsenite—$3Cu\ (AsO_2)_2 \cdot Cu\ (CH_3COO)_2$ of brilliant green hue introduced at the beginning of the 19th century [31]. The presence of emerald green would therefore imply that a more recent overpainting was done (after the 1789 restoration), a situation that would also explain the presence of Zn—possibly related to the use of zinc white (ZnO). However, this scenario can be excluded as the As $K\beta$ line is very low and the atomic ratio of Cu:As characteristic of emerald green is not observed in this case [49].

Another more plausible scenario that can explain the complex elemental signature registered for the green-pigmented area implies the use of a copper-based green pigment (such as verdigris—$Cu(CH_3COO)_2 \cdot H_2O$ or malachite—$Cu_2CO_3(OH)_2$) mixed with an iron-rich earth, lead white, and small amounts of orpiment. Although the use of such mixtures for obtaining green tones has been previously documented in several 17th–18th century Russian icons [50], the hypothesis on the presence of orpiment (As_2S_3), a historical pigment often encountered on Byzantine icons [36,39], needs further investigations with complementary analytical techniques (the infrared vibrations of sulfides occurs at low wavenumbers, in the far infrared region, below the spectral range of our FTIR spectrometer).

Out of the suppositions made by the XRF analysis, FTIR confirmed the use of a natural earth pigment rich in iron oxides that would sustain the presence of green earth. Generally described as a complex mixture of clay minerals containing celadonite or glauconite [46], along several other minerals such as quartz, feldspar, montmorillonite, illite, kaolinite, and iron oxides, green earth was one of the most frequently used green pigments in Byzantine and Orthodox Greek and Russian art [51].

Concerning the presence of a copper-based pigment, inferred via XRF, both malachite and verdigris have characteristic vibrations within the mid-IR region [52]. A clear identification of the green copper-based pigment was not possible, though, due to the complexity of the fingerprint region and the strong overlapping absorptions given by the presence of the other components. However, between the two suspected copper-based pigments, the use of malachite could also explain the presence of Zn and As, both of these elements being known to accompany Cu-based minerals such as azurite and malachite in the form of accessory minerals, frequently in the form of adamite [$Zn_2(AsO_4)(OH)$] and olivenite [$Cu_2(AsO_4)(OH)$] [49]. Another hypothesis could be the use of an artificial Cu/Zn-based green pigment (i.e., brass-based), as such pigments were rather commonly employed in post-Byzantine Greek icons [49].

The high intensity of the Ca lines registered for this sample (S5) is due to the *gesso* ground layer based on anhydrite, as highlighted by FTIR. This information can also be easily inferred from the XRF data. As shown in Figure 8b, the Ca Kα and Kβ lines are significantly more intense on the back side of the sample (ground layer over paint layer) compared to the front side (corresponding to the top paint surface—paint layer over ground). Moreover, another indicator that sustains this stratigraphy is given by the attenuation of the Pb lines in the case of the XRF spectra registered on the back side of the S5 sample (the ground layer based on anhydrite is acting as a filter, attenuating the emerging X-rays).

In line with Byzantine painting tradition, gold leaf was identified [16,17], as indicated by the Au XRF lines, best seen in sample S3 (see Figure 8c). The gold leaf may have been applied over a red or yellow bole layer (frequently used as a metal-leaf adhesive), intense Fe lines being observed on the gilded areas [53]. The use of a colored bole layer is not uncommon [16,17,54], warmer effects being believed to be obtained by using colored substrates underneath a thin metallic leaf. However, this theory surrounding the correlation between the substrate color and the gilded surface appearance has been recently disputed, and more likely attributed to the historical development of gilding and polychromy technologies [55]. The presence of only small traces of gold observed in the case of sample S2 could be explained by a massive degradation of the gold leaf, or it could reflect the extremely thin nature of the commonly employed gold leaves (usually around 1 μm thick).

In terms of binding media, the use of a protein-rich binder could be inferred in most of the analyzed paint samples via the amide I and amide II bands (observed at approx. 1650 cm^{-1} and 1540 cm^{-1}, respectively), along the broad peak observed at approx. 3280 cm^{-1} (N–H stretching). Although an exact identification of the proteinaceous binder is not possible by FTIR analysis alone, most probably an egg-based binder was used given the fact that egg tempera is considered the traditional technique of icon painting [15–17].

The presence of a tree resin was confirmed in most of the analyzed samples based on the characteristic bands observed at 2924, 2853 cm^{-1} (C–H stretching vibrations), 1705 cm^{-1} (C=O stretch), and 1238 cm^{-1} (C–O vibration of the ester bond), typical for lipidic/terpenic materials [39]. This finding is in accordance with the UV fluorescence imaging data.

Various types of metal carboxylates were found as highlighted by the characteristic spectral features observed in some of the registered spectra. The peak around 1516 cm^{-1} can be ascribed to lead soaps [56] while the peak at 1320 cm^{-1} is characteristic for calcium oxalates [45] that typically also display a sharp peak within the 1620–1580 cm^{-1} region, this last one overlapping in this case with the amide I band. Zinc carboxylates, related to the presence of a zinc based compound (possible use of zinc white), may also be present as inferred via the sharp peak at 1539 cm^{-1} (zinc palmitate) (Figure 7b,c) and the peak at 1454 cm^{-1} (zinc oleate) [56]. Although the zinc oleate absorption at 1454 cm^{-1} overlaps with the C–H bend absorption given by the protein binder, the sharp peak suggests that zinc soaps are present as well. Moreover, as in aged paint systems, the amide bands are typically characterized by broad and poorly defined spectral features. The hypothesis on the presence of a zinc-based compound is also sustained by registered XRF data that highlighted high concentration of Zn on sample S4, extracted from the dark brown background of the icon. The presence of copper soaps can also be inferred by the shoulder band observed at 1588 cm^{-1} [56].

4. Conclusions

In addition to their visible religious importance, post-Byzantine Orthodox icons should be recognized as valuable artifacts that play a pivotal role in the ongoing development and evolution of artistic styles. These specific artworks reflect the influences of the sociocultural context in which they were crafted [2,7], and serve as a testament to the enduring legacy of regional icon workshops where artists have persisted in practicing centuries-old traditions [57]. Such an example is the 17th-century Wallachian icon depicting the "Mother of God with Child" from the Orthodox Church of the "Annunciation" in Râmnicu Vâlcea, Romania. With the aim to document the painting materials and techniques and, secondly, to plan an optimal restoration procedure, the icon was investigated before restoration using a minimally invasive multi-analytical approach.

The employed imaging methodology, that included high-resolution digital radiography, hyperspectral imaging, and UV fluorescence imaging, was able to assess the structure of the wooden panel support, and highlight various defects present at the level of the pictorial layer, including previous restoration works made at the end of 18th century. Combined XRF and ATR-FTIR spectroscopic analysis, carried out on targeted microsamples, allowed a detailed characterization of the employed painting materials. A relatively narrow color palate based on lead white, red ochre, vermilion, green earth, and a copper-based green pigment was identified. The use of zinc- and arsenic-based compounds could also be inferred, along with the use of several pigment mixtures. In accordance with Byzantine tradition, the use of the egg tempera technique was identified. The ground layer was found to be based on anhydrite mixed with a protein binder, which, correlated with previous findings, may indicate a preference of craftsmen from this region for these types of preparatory layers.

Despite their rich symbolism and intricate craftsmanship, there is a lack of interdisciplinary, systematic studies on Wallachian icons to date. The findings of this collaborative research, which involved restoration experts and heritage scientists, adds contributions to the understanding of the painting materials and technical characteristics employed in Wallachia during the 17th and 18th centuries.

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