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Article

Anatomy of the Painting: The Study of the Serbian Orthodox Icon from the Turn of the Seventeenth to the Eighteenth Century

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Abstract: The paper presents the results of the multi-analytical study of the painting on a panel from the icon collection of the Gallery of Matica srpska museum in Novi Sad, Serbia. It is part of the research aiming to set the methodology for the museum's database on artistic materials and techniques present in the collection. Computer tomography (CT) scanning was used to understand the structure of the wooden panel support. Ultraviolet (UV) and infrared (IC) imaging, as well as visible (VIS) macro photography, were used to study the paint layer, both the original part and restoration treatments, as well as the coat of varnish. Energy dispersive X-ray fluorescence (EDXRF) and Fourier-transform infrared (FTIR) spectroscopy revealed the pigments, binders, and metal leaf, defining the artistic technique. Optical microscopy (OM) and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) were used to disclose the stratigraphy and composition of layers in the artwork. The multi-analytical approach confirmed that protein-based binder, gilding, silver leaf, and traditional pigments were used. The data gathered from this research are important for studying the artistic materials and techniques in icon production and defining the methodology setting for the museum collection's databases as the reference material.

Keywords: work of art; anatomy; material characterization; painting techniques; multi-analytical

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1. Introduction

Old religious paintings are a valuable part of cultural heritage. They bear multiple meanings and embody diverse material information. Conserving the materials of an artwork is necessary to ensure the transition of non-material artistic and historic messages to the future.

The first step in the conservation process is a thorough understanding of all the components of the painting. In traditional art technology, the components are the panel support, preparatory, paint, and protective layers. Each layer is a complex structure made of organic and non-organic materials, fillers, binders, and coatings, crafted and mixed following traditional recipes [1]. Different artists and craftsmen could have worked on the same object during its life, and today, they are substituted by conservators-restorers and scientists [2]. Using various analytical techniques and combining results with expertise in art history and conservation, it is possible to reveal the painting's anatomy and understand its original appearance and cultural context. Among many available analytical techniques, preference is given to non-invasive [3–5] and can be used with portable or easily accessible instruments [6,7]. When possible, the sample analysis can provide more exact information, especially about stratigraphy, material distribution, and painting techniques.

The paper reports a multi-analytical study of the icon representing St. Theodore Tyron and St. George. The icon is dated 1700, just after the last Great Migration of Serbs, an important moment in national history followed by significant modernization of society and art [8]. After the fall of the Serbian medieval state, Serbs continued to live with different cultures and religious systems, the Ottoman Empire and the Habsburg monarchy of the time. Elite models of medieval icons were far away, but traditional values guaranteed the Orthodox character of the icons. The zograf painters, many of them monks, held tightly to the older tradition of Eastern Orthodox iconography.

The study is part of the project of creating a database of materials used in icon production, a pioneer project in Serbia, led by the museum—the Gallery of Matica srpska from Novi Sad—and the Vinča Institute of Nuclear Sciences from Belgrade. Existing stylistic studies of Serbian icon painting were only fragmentary followed by the material analysis, necessary for the full understanding of the transformation of Serbian medieval culture. Moreover, original artistic material is the first-grade source of information for attribution efforts, particularly because many icon painters remained anonymous. Therefore, once collected in a database, information about the materials and artistic techniques comprising all the parts of the artwork opens the possibility for further studies. The database was designed to store analytical results of the material characterization for each analyzed work of art. Custom-made for the Gallery of Matica srpska museum, this database offers storage, overview, and comparison of the analytical results. Besides the analytical results, historical data and data about artistic techniques and conservation activities are available for each work of art. Gathering data in well-structured databases offers the possibility for comparison-based provenance studies and attribution.

A variety of analytical techniques were used to study the object, including visible (VIS) and macrophotography (MACRO), ultraviolet luminescence (UV) photography, infrared reflectography (IRR), infrared false color (IRFC) photography, and computer tomography (CT), as well as spectroscopic techniques such as energy dispersive X-ray fluorescence (EDXRF) and Fourier-transform infrared (FTIR) spectroscopy. These non-invasive and non-destructive methods allowed for in-depth examination of the object. Furthermore, to gain a detailed understanding of the paint layers' stratigraphy, which is measured in micrometers rather than millimeters, samples had to be taken and analyzed using optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS)—SEM-EDS. Gathered analytical data led to the identification of the materials used and deeper insight into the painting techniques of the non-attributed icon from the turn of the seventeenth to the eighteenth century.

2. Materials and Methods

2.1. The Artifact of the Study

The object suitable for the study was the late 17th-century icon representing St. Theodore Tyron and St. George from the Gallery of Matica srpska collection in Novi Sad, Serbia. The icon shown in Figure 1a was painted on a thick wooden support by an unknown zograf painter from the south Balkans in the spirit of late Byzantine painting [9].

The holy warrior Saint George was the greatest protector of soldiers and the great martyr Saint Theodore Tyron—of recruits, of those who go off to war for the first time, and because of that are in great trials, physically, morally, and in life. The church model they both hold represents the Church, which sprung on the fields of sacrifice and death for their faith. Their heavenly reward is in the form of two golden crowns in Christ's hands, as his bust is seen in the upper segment of the icon, separated by a series of connected cloudlets. This part of the icon expresses an echo of the new times and baroque reflection, attributing the sense of a time.

Figure 1. St. Theodore Tyron and St. George, tempera on panel, around 1700, dim. 95.5 × 65 cm. Collection of the Gallery of Matica srpska, inv. No. GMS/U 6334: (**a**) front side, (**b**) reverse side.

The wooden support consists of three boards glued together, as shown in Figure 1b. The width of the boards are 25.5 cm, 23.5 cm, and 16 cm, respectively, from right to left. The thickness of the panel varies from 2 to 3 cm. The wooden support is convex, with a maximum deformation of 4 cm. Two horizontal wooden inlet bars are positioned from the back (Figure 1b). They are not original but are the result of the restoration. New inlet bars follow the convex deformation of the wooden support. The joints of the boards are strengthened with dovetail keys, with four keys for each joint (Figure 1b). According to the old conservation practice, the wood was impregnated with wax resin consolidant.

The canvas is visible on the icon's damaged edges. It has been glued to the board and then covered by a preparatory layer, which is thick and uniformly cracked over the surface.

The preparatory drawing is visible as incised lines (Figure 2), defining the main contours of the composition, the figure, and the draperies. Figure 2a shows the incised drawing, with diagonal lines in a pale red area that guide the rays of light, which are well visible in ranking light. The traditional building of volumes is visible in the blue area (Figure 2a, the sleeve) with the middle base tone, dark lines that define the folds, and two lighter tones (pale blue and white) as light accents.

Gilding covers the background of the scene. The gold leaves were applied to the orange bole layer and burnished. The silver leaves were applied to the saints' figures, giving an idea of the armory on chests and legs. The decoration and shadows of the armory are painted with a greenish-brownish glaze over a silver leaf, similar to the gold crown in Figure 2a.

The paint layer is thick and compact. The flesh and draperies are painted in a byzantine manner, with a layer of base color and highlights in lighter tones (Figure 2). The palette is simple, including blue, green, red, brown, black, and white. Yellow color is dominantly given by gold. The gilding is abraded in the central zone. The paint layer is scratched on the surface, and the eyes and mouth of St. Theodore Tyron are scraped and later retouched (Figure 2b). In the 1963 well-documented restoration, the icon was cleaned of dirt, old fillings, retouches, and over-paintings. In the 2014 restoration, new retouching with watercolors and protective varnish were applied.

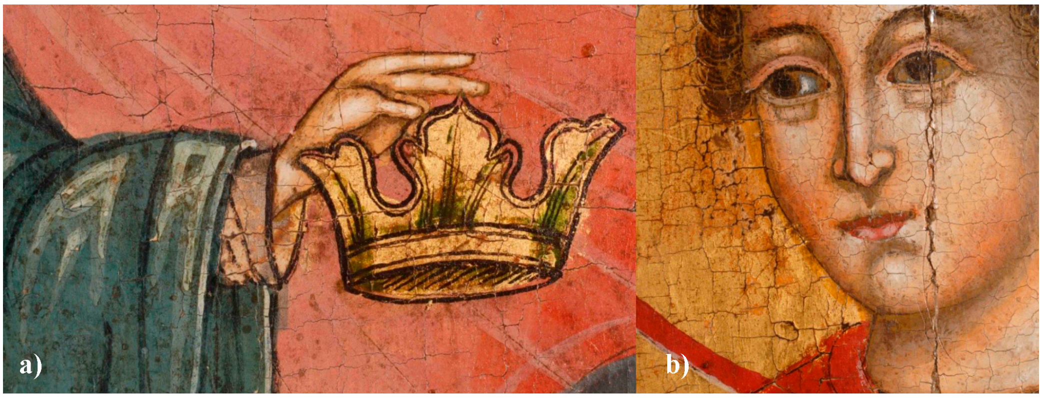

Figure 2. MACRO photograph.(**a**) Detail of the icon with visible incised drawing (in the diagonal white lines) and the traditional manner of painting draperies (blue sleeve with middle blue tone, dark lines for the folds, and two lighter hues for the light accents). (**b**) Detail featuring the face of St. Theodore Tyron, with the traditional building of volumes over the dark underpainting, left visible in the shade (as in the area under the nose).

2.2. Analytical Techniques

Imaging techniques have been used to examine the characteristics of different strata of the painted layer. Moreover, those techniques indicated areas of homogeneities/heterogeneities in the icon surface, thus helping choose the most informative regions for spectroscopic analyses and suitable ones for sampling. The icon was observed under the light of the wood lamps as the source of UV light (Figure 3a). The non-original painted areas, seen as darker zones, were marked, thus ensuring the examination of original materials only. The MICRO IR 20 reflectography camera (wavelength 400–1100 nm, 12.5 mm f1.3 lens, and VIS and IR80 filters, EIS, Rome, Italy) was used to obtain the IRR image shown in Figure 3b. The IRR and VIS images were combined using Adobe Photoshop software (version 10.0, CS3) to obtain the IRFC one, as presented in Figure 3c. At the same time, IRFC results are reported as the specific color of the painted layer for the selected icon [10,11].

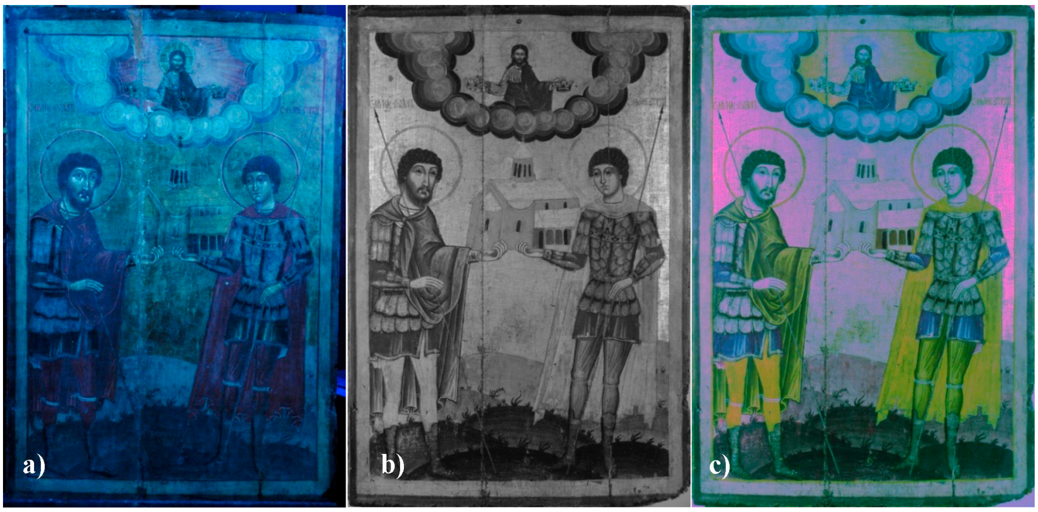

Figure 3. (**a**) UV luminescence, (**b**) IRR, (**c**) IRFC photographs.

The EDXRF and rFTIR measurements were used to determine the pigments and binders used. Spectrometric analyses were performed in situ using non-destructive analytical procedures on the spots that provide the most information about the pigment's composition. The measuring points on the icon's surface were selected to be uniformly colored and as big and flat as possible, ensuring they were suitable for both EDXRF and rFTIR measurements and sampling.

The EDXRF spectroscopy measurements were performed using a milli-beam EDXRF spectrometer with a side-window X-ray tube (Oxford instruments-OXFORD Instruments, Scotts Valley, CA, USA, Rh anode, max. voltage 50 kV, max. current 1 mA, air-cooled). The excitation beam was collimated to a spot size of approximately 2 mm on the object's surface using a layered structure pinhole collimator. The spectrometer was equipped with a Si-PIN detector (X-123, AMPTEK Inc-AMPTEK, Inc., Bedford, MA, USA, with 6 mm^2/500 μm, resolution 160 eV at Mn Kα line, 12.5 μm thick Be window, and 1.5″ extension) which was positioned at 45° to the incident beam axis. Adding the two laser pointers ensured precise, reproducible alignment of the excitation beam and visualization of the measured spot. The experimental setup, X-ray tube voltage of 40 kV, current of 800 μA, non-filtered excitation X-rays, and measurement time of 60 s were kept constant for all measurements. The spectra were acquired using ADMCA software (version 1.0.0.16, AMPTEK Inc.).

The Bruker Optics ALPHA-R (Bruker Optik GmbH, Ettlingen, Germany) portable infrared spectrophotometer was used to collect the FTIR spectra. This spectrometer features a Globar Mid-IR source, a modified Michelson all-spatial interferometer (RockSolidTM), and a DLaTGS detector (Bruker Optik GmbH trademarks TM). The spectra were collected at room temperature using an external reflection module with optics (22°/22°). The size of the analyzed spot is about 4 mm in diameter. The analysis was performed between 400 and 4000 cm^{-1}, averaging 64 scans at a resolution of 4 cm^{-1}. The recorded spectra were evaluated using the OPUS software package (version 7.0, Build 7.0).

This study performed multislice computer tomography (MSCT) on the artifact object of study using the Siemens Somatom Sensation Cardiac 64 MSCT with a gantry aperture diameter of 80 cm. The acquisition was performed using the chest protocol setting with the following parameters: 120 kV tube voltage, slice thickness of 0.6 mm, pitch factor of 1.0 mm, field of view (FOV) of 280 mm, matrix of 512 × 512, spatial resolution of 0.87 mm, and scan time of 12.05 s. Image reconstruction kernel B70f, very sharp, was used, followed by multi-planar (MPR) and volume rendering (VRT) post-processing techniques. Besides the precise 3D imaging of the artifact structure, the measure of Hounsfield units (HU) made differentiating the materials based on their attenuation coefficients possible.

Three samples were taken close to the existing damage to the paint layer. They were embedded in resin for microscopic investigation using a mixture of epoxy resin (Epoxy resin L) and hardener (Hardener EPH 161) in a 4:1.5 ratio (R&G Faserverbundwerkstoffe GmbH, Waldenbuch, Germany). Before overflowing, the samples were positioned for cross-section observation, observing manipulation with a BRESCIANI ARGO S3 microscope (Bresciani Srl, Milan, Italy). After a curing time for this epoxy mixture of 24 h, the samples were polished. The cross-sections were examined under an optical OLYMPUS BX 51M microscope (Olympus Corporation, Shinjuku, Tokyo, Japan) using dark-field normal light at magnifications up to 200×.

Before the SEM-EDS investigation, samples were sputter coated with gold (Bal-Tec SCD 005, BAL-TEC in now Leica Biosystems, Barrington, IL, USA) using current 30 mA during 100 s, at a distance of 50 mm for conductivity purposes. SEM images were collected on a JEOL JSM-6390 device from Electron Optics Laboratory Co., Ltd., Tokyo, Japan (applied voltage 20 kV at the working distance of approximately 10 mm). The morphological characteristics of the pigment grains were observed using the backscattered electrons (BSE) and the secondary electrons (SE). EDS measurements were carried out on the Oxford INCA X sight detector (Oxford Instruments NanoAnalysis&Asylum Research, High Wycombe, UK).

3. Results and Discussion

The results give insight into the structure and composition of the icon's original elements: panel support, preparatory, and paint layers. The protective varnish layer is not original due to previous restorations.

3.1. Panel Support

In the tradition of icon production, a wooden panel is the most common type of support. It was usually prepared by dedicated craftsmen who chose the wood, assembled boards, and executed decoration by woodcarving. Determining the type of wood and construction technique used for crafting the panel and documenting the location and extent of anomalies and degradation in the wood structure are all important for conservation strategies.

The most useful technique for the characterization of panel support was CT. The main advantage of using MSCT is the possibility of examining the object at the different levels of depth of the icon, otherwise inaccessible to view. Three-dimensional reconstruction by VRT allowed us to investigate the spatial geometry of the panel construction and morphological characteristics of the wood (ring growth, wormholes, restorer's additions) and to detect all the foreign bodies in the panel. CT investigations confirmed that the wooden support consists of three glued boards where each joint is strengthened with four dovetail keys (one is marked by a red triangle in Figure 4a). The wood grain orientation in the dovetail keys is perpendicular to panel one. This is a typical restoration solution for strengthening the split joints. The growth rings of wooden support, visible as darker and lighter bands, are easily distinguishable in the CT images presented in Figure 4a. Due to the presence of thick-walled growth rings and flaring rays along growth ring boundaries, the wood panel could be identified as linden (Tilia), as these are typical anatomical characteristics of this genus [12].

Figure 4. (**a**) A longitudinal CT section of the wooden panel showing details related to the growth rings, visible as darker and lighter bands, dovetail keys on joints (red triangle), xylophagous insects'

tunnels (red squares), and two metal nails (red ellipses). The dark rectangle in the upper half corresponds to the air between the panel and the new battens. (**b**) A transverse tomographic section of the wooden panel showing growth rings. The white pixels at the top of the section represent the lead-based pigments in the preparatory and paint layers (for more details, see Video S1 in Supplementary Materials). (**c**) A longitudinal CT image showing canvas reinforcements (red arrow) positioned on the weak points of the panel support: stripes on the board joints and a patch of canvas (blue arrow) on the wood knot in the lower half of the icon.

Moreover, the HU values of the wooden support were measured at four different points, presented in Table 1, and the average value of −441 HU was obtained. According to the in-house developed wood HU database, the wooden panel was identified as linden [13].

Table 1. Calculated HU values of wood panels.

No.	Average HU (SE)	ROI (cm^2)	Wood Thickness (cm)
1	−579.8 (9)	5.74	2.10
2	−433.8 (3)	5.65	2.22
3	−345.2 (6)	7.14	2.22
4	−405.8 (3)	6.13	2.29

CT images also show an irregular pattern of small rounded black zones (two of them marked by red squares in Figure 4a) due to the presence of air in the wooden support. These black rounded zones can be attributed to the activity of xylophagous insects, which made tunnels in the wooden part of the icon.

As mentioned, CT scanning can easily detect all metallic or metal-like elements in the panel. It was not difficult to notice two nails hidden in the wood, one in the upper and the other in the lower part of the icon (marked by red ellipses in Figure 4a). Similarly, it was also possible to effortlessly observe the areas of the icon with high atomic weighted materials due to their high X-ray attenuation. Therefore, the lead-based pigments in the preparatory and the paint layer were easily visible on CT images (Figure 4b).

CT also revealed canvas reinforcements (red arrow, Figure 4c) positioned on the weak points of the panel support: stripes on the board joints and a patch of the canvas (blue arrow, Figure 4c) on the wood knot in the lower half of the icon (Figure 4c).

3.2. Preparatory and Paint Layer

Preparatory layers consist of multiple strata, as well as the paint layer. Old painting manuals of the Eastern Orthodox church give instructions [1,14] for painters, but the old recipes could have been modified using local materials or introducing new tendencies in art production. Old painting manuals were written by the same artists who lived in other times and cultures and procured art materials depending on the time's trade routes and cultural connections. The text of archival documents can be incomplete or difficult for modern scientists to understand because of multiple old translations or even parts intentionally left unclear because of the secrets of the artistic workshop.

As confirmed by OM and SEM-EDS, the preparatory layer consists of two strata with different inert materials (Figure 5a,b). The lowest layer was made of chalk, as presented in Figures 5d and 6c, while the upper layer was a mixture of gypsum (Figure 6b,c) and lead white (Figure 5c), applied to the surface in broad strokes, as visible in Figure 4b,c.

Thirty-seven EDXRF spectra were collected along the icon surface. Positions for analysis were chosen so that the basic pigment could be identified. Analyzing the nuances of the base color revealed the mixture of pigments, aiming for a wider understanding of the painting techniques. The measuring spots are shown in Figure 7a, and the identified pigments are in Figure 7b.

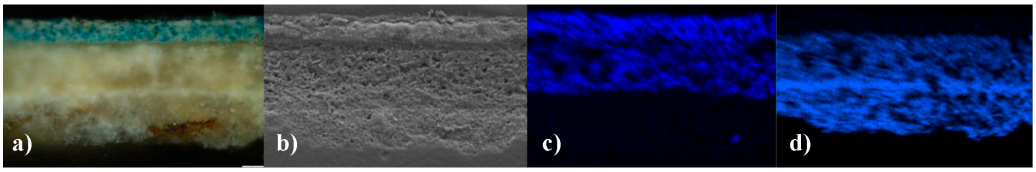

Figure 5. (**a**) OM photography of blue-colored sample (mixture of azurite and lead white). (**b**) SEM photography of the same sample. (**c**) Lead Mα1 distribution EDS map. (**d**) Calcium Kα1 distribution EDS map. More details in Supplementary Table S1.

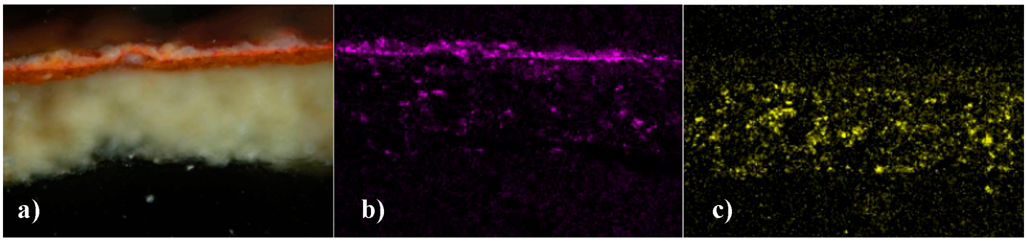

Figure 6. (**a**) OM photography of red-colored sample (mixture of minium and cinnabar). (**b**) Sulphur Kα1 distribution EDS map. (**c**) Calcium Kα1 distribution EDS map. More details in Supplementary Table S2.

(**a**)

Colour	Measuring spot number	Characteristic chemical elements*	Pigment	Mixure
White	Over the icon	Pb	Lead white	
Yellow	24	Fe	Yellow ochre	
Brown	19, 23, 25	Fe	Burnt Sienna	
Flash tone	12, 20, 22	Pb, Fe	Lead white	Red ochre
Red	7, 13, 14	Fe	Red ochre	Minium
	6, 15, 16, 30	Hg	Cinnabar	Lead-based pigments
	Each red spot	Pb	Minium	
Blue	8, 9, 33	Cu	Azurite	Lead white
Green	1, 2, 3, 38	As	Arsenic-based	Realgar or orpiment mixing with indigo
Green glaze	11, 29, 35	Cu, Fe, Ti, Sr	Copper-based	Green earth
Grey	18, 26, 27	/	Carbon black	Lead white
Silver	4, 5, 10, 31, 32, 36	Ag, Fe	Silver leaves	Red bole under gilding
Gold	17, 34, 37	Au, Fe	Gold leaves	Red bole under gilding

(**b**)

Figure 7. (**a**) The EDXRF and FTIR measuring points. (**b**) The identified pigments by EDXRF. * Only the chemical elements of interest for the identification are presented.

For blue paint clothes, azurite was mixed with lead white (Figures 5a,c, 8a, and S1). The eight different spots were analyzed in red-colored areas. The use of cinnabar, minium, and red ochre was confirmed. The bright nuance was reached by mixing cinnabar and lead-based pigments, as shown in Figures 6a and 8b. The dark red tone was achieved by mixing red ochre with minium pigment most probably (Figure 8c). One spot was analyzed in a yellow-colored area, spot 24 in Figure 7a, confirming the yellow ochre pigment (Figure 8d). The iron-based earth pigment was detected in the three analyzed spots in brown areas (spots 19, 23, and 25 in Figure 7a). The small intensity of the manganese peak indicates that burnt Sienna most probably was used instead of the umber (Figure 8e) [15]. Four points were selected for analysis on the green (dark nuance) parts in the bottom part of the icon. The use of arsenic-based pigment (realgar or orpiment) was detected (Figure S2). The same areas in the IRFC image (Figure 3c) have a reddish tone, which leads to the conclusion that arsenic-based pigment was mixed with indigo to reach a green tone, which was confirmed by FTIR (Figure S3). Mixing yellow and blue was a widespread practice for obtaining green coloration [16].

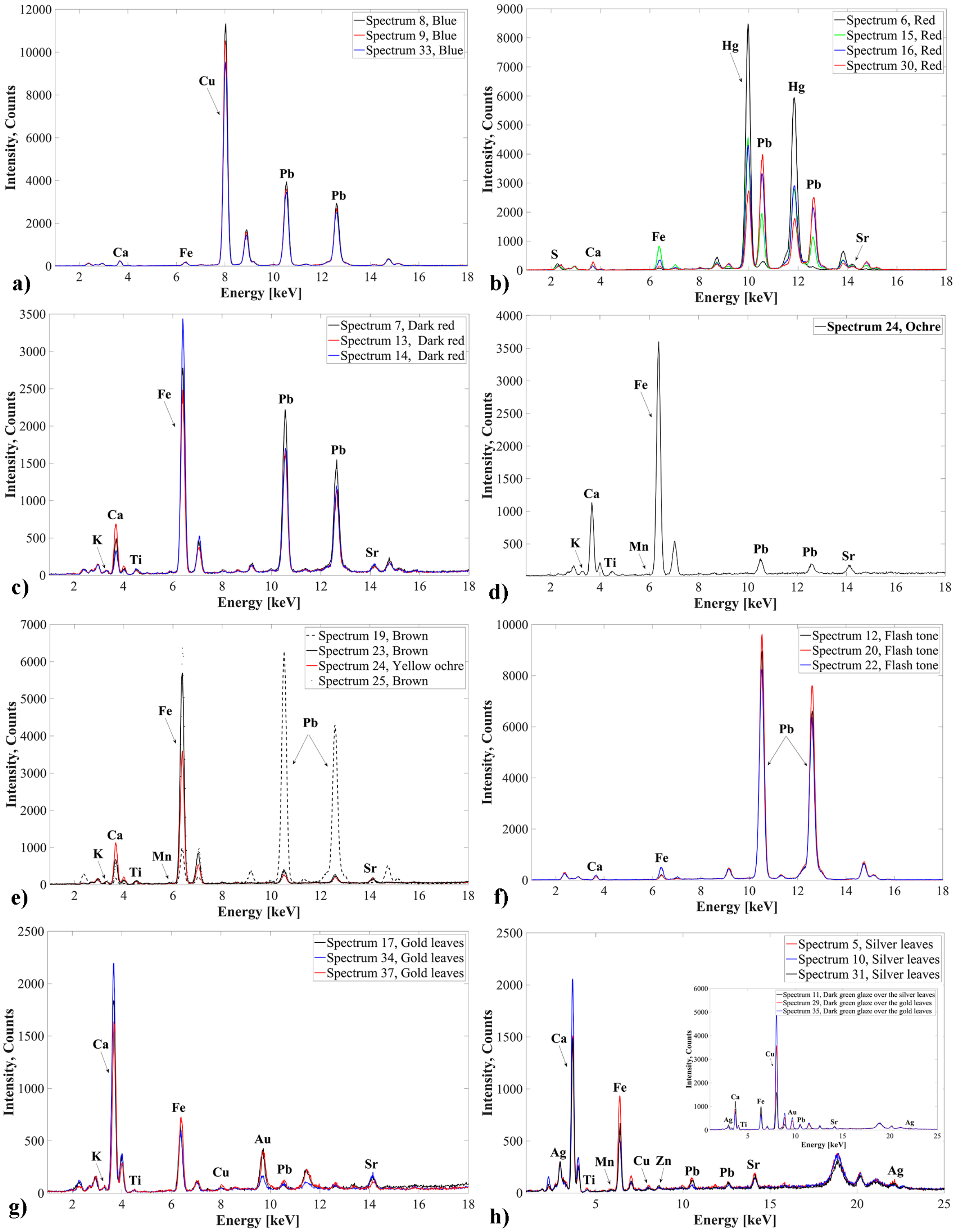

Figure 8. EDXRF spectra collected alongside the icon's paint layer onto (**a**) blue, (**b**) red, (**c**) dark red, (**d**) ochre, (**e**) brown, (**f**) flash tones, (**g**) gilded and (**h**) silver areas.

The flesh (faces, necks, and hands) was painted using the traditional method: a mixture of lead white, cinnabar, yellow, and red ochre was applied over the brown underpainting (burnt Sienna identification presented in Figure 8e, spectrum 19). Highlights were executed in pure lead white, in accordance with medieval practice, as shown in Figure 8f. Gold and silver leaf were applied over the orange bole as a gilding underlayer (Figures 2b and 8g,h). The green glaze was laid over the gold and silver leaf to create the impression of volume and shade, using copper-based green pigment, most probably mixed with green earth (Figures 2a and 8h, small figure). Cloudlets surrounding Christ in the upper part of the scene were painted in grey in three layers with gradually lighter hues, combining carbon black and lead white (Figure 9).

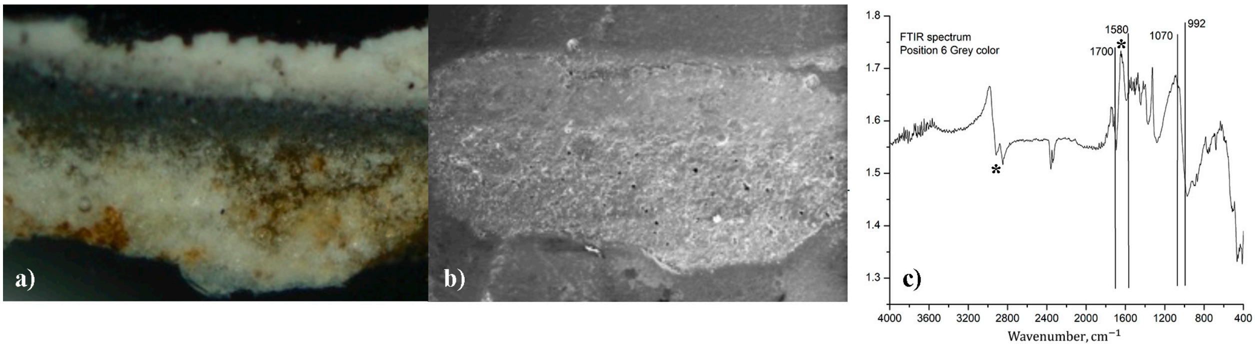

Figure 9. (**a**) OM photography of grey-colored sample. (**b**) SEM photography of the same sample (more details in Supplementary Table S3). (**c**) FTIR spectrum with the lines corresponding to carbon black pigment and egg tempera most probably (* marker).

The binding media of the paint layer is protein [17,18] (most probably egg, as confirmed by FTIR, with line doublet around 2850 cm^{-1} and 2920 cm^{-1} and a single line around 1730 cm^{-1} (Figure 9c) [19]. This traditional binder was commonly used in post-Byzantine icon painting. The visible brush strokes and the technique for creating flesh tones are consistent with the FTIR results.

4. Conclusions

The multi-analytical study of the icon has unveiled aspects of its structure and material composition, i.e., the anatomy of the artwork. The paper meticulously details the creation process, starting from the panel support and progressing to the preparatory and paint layers, including gilding.

The panel support was made traditionally. Both the original panel structure and conservators' interventions were detected. While some of these are visible, CT scanning provides much more detailed information: wood grain, internal damage by woodworms, depth of holes in the panel made for inserting dovetails, spaces between the wooden parts, cracks in the panel, as well as the type of wood (linden).

The board was prepared for the painting by spreading the preparation into two layers. The first is made of chalk, and the second is of gypsum and lead white. Lead white in the preparation's final layer contributed to the surface's luminosity, which is ready to be painted.

The icon's gilded background is a testament to traditional water gilding on red bole, while the saints' figures are adorned with silver leaf, offering a glimpse into the armory on chests and legs. The paint layer, executed in egg tempera, features a rich pigment palette that includes lead white, yellow, red, and brown ochre, green earth, copper-based green, azurite, indigo, arsenic-based pigment (likely orpiment, as cited in old painting manuals), minium, cinnabar, and carbon black. The gold and silver leaf were glazed with green glaze, adding a touch of opulence to the icon.

The artistic technique of the icon St. Theodore Tyron and St. George from the turn of the seventeenth to the eighteenth century can be defined as deeply rooted in tradition. The stylistic innovations noted by art historians, such as the separation of the Earth and Heaven in the lower and upper part of the icon, can be attributed to the influences brought to traditional icon painting in the 18th century by the Baroque stylistic period. The techniques and methodology gained the most relevant information, revealing the artifact's anatomy, which is suitable for database formation and future comparative studies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings14070854/s1, Video S1: Icon CT; Table S1: Elemental analysis maps, EDS sum spectrum and concentration of the elements detected in blue-colored sample; Table S2: Elemental analysis maps, EDS sum spectrum and concentration of the elements detected in red-colored sample; Table S3: Elemental analysis maps, EDS sum spectrum, and concentration of the elements detected in grey-colored sample; Figure S1: rFTIR spectra collected alongside the blue parts of icon's paint layer; Figure S2: EDXRF spectra collected alongside the green parts of icon's paint layer; Figure S3: rFTIR spectra collected alongside the green parts of icon's paint layer.

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