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Article

Decorative Coatings of the Saint Demetrius Basarabov Reliquary's Wooden Pedestal

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Abstract: This study presents the results and information revealed by in-depth physicochemical investigations carried out on an 18th-century polychrome wooden pedestal of the holy relics of Saint Demetrius Basarabov preserved at the Romanian Patriarchy of Bucharest. The preliminary stylistic observations and examinations on its present state of conservation were followed by optical microscopy, X-ray fluorescence (XRF) spectrometry, and attenuated total reflectance Fourier-transform infrared spectroscopy (FTIR-ATR) analysis performed in order to adopt an appropriate restoration treatment for bringing the artifact, as close as possible, to its original appearance as well as for dating/attributing the artifact and assessing its state of conservation. It was revealed that several interventions were subsequently undertaken on the original gilded surface consisting of a gypsum support layer with an iron oxide layer of bolus on which a silver foil or a gold foil and a natural resin on top of it as a protective layer were applied. The regilding and later restoration interventions consisted in applying, over the original, layers of a copper–zinc alloy foil (Dutch metal as an imitation of gold) with a resin layer of vernis over it. The final decision on the restoration intervention was taken based on the scientific analysis outcome. This work attempts also to highlight the importance of the interdisciplinary collaboration between researchers, conservation scientists, restorers/conservators, and curators for the preservation and valorization of the historical religious Romanian heritage artifacts, largely unknown worldwide.

Keywords: coatings; heritage; FTIR; XRF; optical microscopy; conservation; wood; gold gilding

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1. Introduction

The scientific analysis of historic monuments, cultural goods, works of art, or heritage artifacts has developed exponentially in the 21st century [1–3]. This approach is relatively new in Romania due to both the maintaining of the traditional, "conservative" manner of dealing with the conservation–restoration of art objects and the relative scarcity of technical equipment available in the museum's laboratories [4–6]. In this context, the collaboration between technical experts and art conservation professionals is very important, especially in the framework of Romanian religious heritage preservation, mostly unknown worldwide. After the fall of Constantinople in 1453, religious Byzantine art and tradition perpetuated in the Romanian, Bulgarian, and Serbian Christian territories, already previously strongly connected to the Ecumenic Patriarchy, and thus very valuable artifacts, produced by skilled Byzantine craftsmen and their disciples may be found in this Balkan zone [7].

The purpose of this work is to show how the results of infrared and X-ray spectroscopic techniques in combination with optical microscopy investigations may help to elucidate the successive decorative coatings applied as well as the conservation–restoration decision of a very precious polychrome wooden pedestal of Saint Demetrius Basarabov, the protector of the Romanian capital Bucharest and the whole country. The pedestal for the reliquary containing the Holy Relics of Saint Demetrius Basarabov was present for a while in the Patriarchal Cathedral in Bucharest (Figure 1) and is now in the course of restoration. The Holy Relics were placed with great honor on this pedestal on 13 July 1774, when Saint Demetrius the New or Basarabov became the protector of Bucharest city and the whole country [8]. The pomposity of the religious Byzantine ceremony is well emphasized in Figure 1 by the rich decorations of the iconostasis, walls, and furniture from the gold gilding technique used. The most precious materials were used to illustrate the glory of God, to create a special ambiance for the prayers, and the general appearance of the interior resembling the typical Christian churches. In the picture, the object of this research work, the holy reliquary gold gilded wooden support, may be observed, being highlighted with a red arrow.

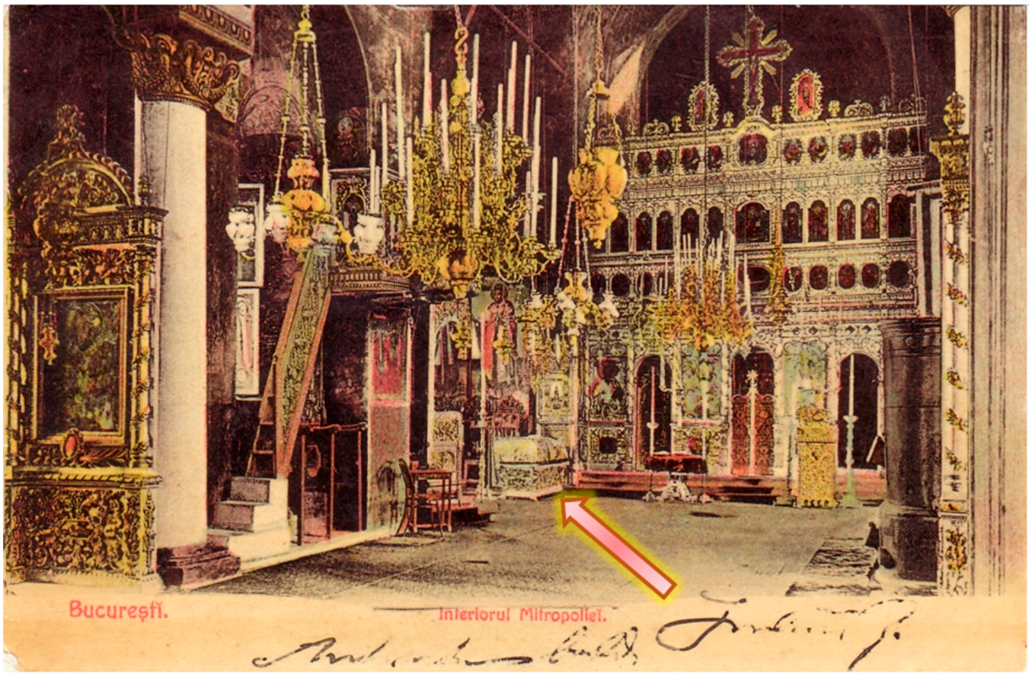


Figure 1. The interior of the Romanian Mitropoly in 1901–1905. The Brancovan-style gilded wooden pedestal of Saint Demetrius Basarabov is highlighted with a red arrow [adapted from [9] https://imagoromaniae.ro/produs/bucuresti-mitropolia-interior/].

The Christian orthodox tradition in Romania helped the country to survive troubling times in this place of intersection between Europe and Asia, between Western and Eastern cultures, and continues to be maintained today. Great Romanian rulers, now consecrated, like Stephen the Great (1457–1504), Neagoe Basarab (1512–1521), and Constantin Brancoveanu (1688–1714), of medieval and the beginning of modern times, respectively, built numerous churches and contributed to the development of art and architecture and the continuity of the Byzantine tradition in the southeastern part of Europe [10–12]. The very cultivated and rich prince Constantin Brancoveanu supported the introduction of European Renaissance elements and modernization in the 17th–18th centuries of Romanian art and architecture, both civil and religious. Brancovan art delimitates a unique blend between occidental Renaissance Baroque and oriental styles, characterized by rich sculpted elements with floral and zoomorphic decorations [13].

Accurate descriptions of art objects based on detailed physical–chemical analysis in correlation with stylistic analysis are outlined before any restoration treatments or for attribution to a certain artistic current. The surface of the art object is the first interface, offering most of the information, providing the esthetic role but also protecting it from the physical, chemical, and biological agents [14,15]. Unfortunately, in the premodern era in Romania, the religious value of an item was considered superior to its artistic value; thus, it is possible to discover precious old art pieces repainted according to the new stylistic developments as is the case of whole Brancovan iconostasis of Sirineasa village church [16]. Consequently, physical–chemical investigations are mandatory before any intervention in agreement with the most recent art conservation developments [17–19]. In the case of polychrome wood, the most frequent technical–scientific approach consists of optical microscopic stratigraphic, followed by XRF and/or SEM-EDAX and FTIR and/or FT-Raman [18,19] to identify the materials, the techniques, and the conservation condition of the investigated artifacts.

This study's main aim is to clarify the structure and composition of successive layers of coatings in order to elucidate the controversy on its restoration intervention: Should experts keep the original brancovan layer of painting or a newer layer? What solutions would be the best for removing some of the recently applied coatings during previous conservation procedures? The conclusions of this study supported the proposed restoration intervention to restore the actual coating of the wooden piece since the original one is almost entirely lost.

2. Materials and Methods

2.1. Gold Gilded Wooden Pedestal of the Saint Demetrius Basarabov Reliquary

Physical–chemical investigations were performed to elucidate the original and successive applied coatings of a XVII-century wooden pedestal for the reliquary containing the Holy Relics of Saint Demetrius Basarabov (Figure 2). The "gold gilded" wooden sculpture pedestal presents large richly carved surfaces, with relief and openwork ornaments and vegetal decoration: vine, bud, flower, and acanthus leaf. A type of approach that combines elements of the Baroque and Rococo styles with those of the Renaissance and Neoclassicism is found, reminding us of the Brancovan blend between occidental and oriental art styles with the autochthon tradition. The decoration is carved in openwork, decorated with volutes, in which the magnolia flower and the acanthus leaf alternate, having a symmetrically organized composition, completed with cherub heads located at the corners and in the central part, which follow curved paths, with high relief, typical of these styles. Both in the upper and lower parts, there are friezes with geometric decoration and neoclassical motifs.

(**a**)

(**b**)

Figure 2. *Cont.*

(c)

(d)

Figure 2. Gold gilded wooden pedestal of the Saint Demetrius Basarabov reliquary: (**a**) front view, width 170 cm; (**b**) lateral view, width 60 cm; (**c**) front view angel detail; (**d**) corner view angel head—detail (**bottom**), pedestal neoclassic decoration (**top**); the samples analyzed are marked with *1 and *2 in (**a**).

2.2. Conservation State of the Gold Gilded Wooden Pedestal of the Saint Demetrius Basarabov Reliquary

The analyzed wooden pedestal is about 250 years old and had a functional role as a cult object. As expected, its conservation state is relatively poor; as such, various degradations at the level of wooden support and of the polychromy were found and presented in detail in the Supplementary Material (Figures S1–S6). Several previous conservation interventions of overpainting/"re-gilding" are visible, identified in the following with the help of physical–chemical investigations.

2.3. Physical–Chemical Characterization of the Decorative Coatings

The stylistic analysis of the artwork, performed by the conservator, was followed by nondestructive in situ and ex situ X-ray fluorescence (XRF) measurements, respectively, optical microscopy, and a micro-ATR-FTIR spectroscopy analysis of small detached fragments.

XRF analyses were performed using a mobile Bruker X-Raman type device (XG Lab, Milano, Italy) in situ. The apparatus generated an X-ray beam by applying a voltage of 40 kV to the Rhodium-based tube, generating a current of 20 µA for a duration of 40 s. The spot on each analyzed sample had a circular profile and a diameter of 1 mm. Characteristic X-ray spectra were recorded using a Silicon Drift Detector (SDD), with each acquisition performed on 4096 channels. These parameters were kept for each of the analyzed points. XRF spectra of detached samples were taken in laboratory using a handheld X-ray Fluorescence spectrometer Tracer 5^i from Bruker Instruments (Kennewick, WA, USA). The penetrating power of the X-ray beam is up to several tens of microns, thus being a surface analysis. The simplicity of the radiation spectrum, the very short measurement time of 10–1000 s, and the possibility of measuring concentrations from p.p.m. to 100% are important advantages. The spectrometric analysis of the elemental chemical composition of the samples is calculated for the elements starting with magnesium (Mg) up to uranium (U). It has, as an excitation source, an X-ray tube with Rh anode, with the voltage used during the analyses being 6–50 kV and the current intensity being 5–500 microA. Collimation of the X-ray beam for an angle of approx. 53° in front of the control panel surface is selectable with focal spot sizes of 8 mm^2 and the Silicon Drift Detector (SDD) solid detector with an area of 40 mm^2. Analysis were employed on the detached fragments, without a filter, using the built-in both alloy and geochemical mining modes, with each analysis measurement time of 60 s (more information at https://www.bruker.com).

Optical microscopy analysis were performed in reflected light with a Nikon (Tokyo, Japan) stereomicroscope SMZ1000, and in reflected, polarized and UV fluorescent light with a Nikon optical microscope Eclipse LV-100ND. The microscopy images were acquired with a Nikon DSLR camera D90 equipped with a Nikon image capture software Camera Control Pro 2 (version 2.3.0) and a Nikon microscope imaging software NIS-Elements Basic Reserach (BR).

ATR FTIR spectra were acquired with a Bruker (Ettlingen, Germany) FTIR spectrometer Tensor 27 equipped with a micro ATR unit Helios and a single reflection diamond crystal set to absorbance mode at 4 cm^{-1} resolution and 64 scans per spectrum. The data were analyzed with Opus software (version 6.5) developed by Bruker (Ettlingen, Germany).

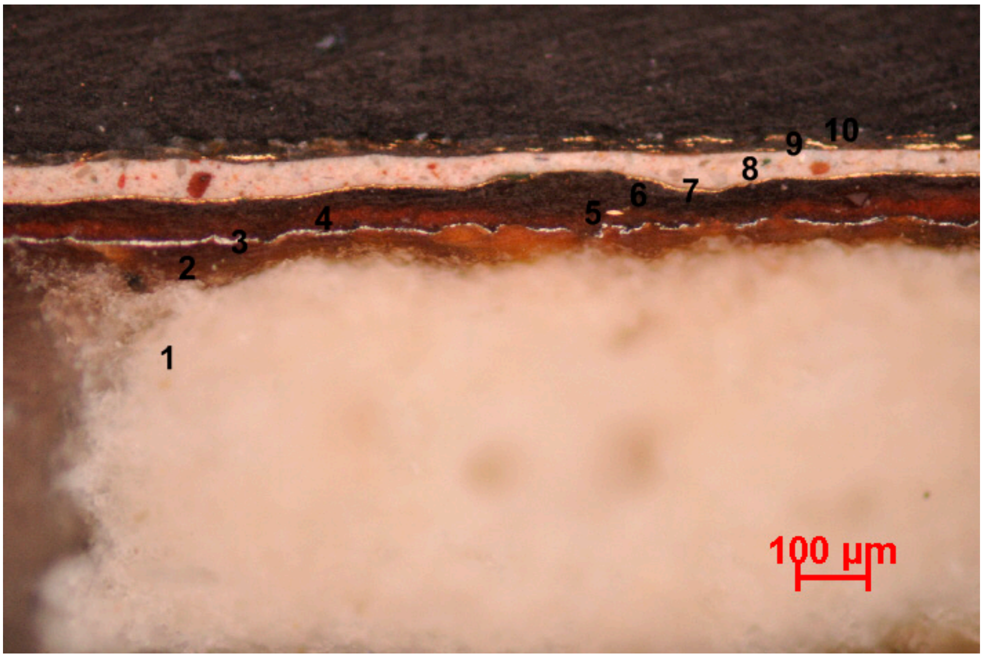
3. Results and Discussion

Physical–Chemical Characterization of the Decorative Coatings

After detailed visual inspection, two areas of decorative coatings were selected for analysis: one with presumably original silver decoration (sample 1) and one with gold foil decoration (sample 2). Figures 3–5 show the successive optical microscopy investigations of the silver "gilded" sample 1, revealing three different layers of metallic foil coatings applied on a red-iron-based preparatory bolus layer on top of the gesso support layer: the original silver foil with a natural resin varnish (fluorescent in UV) applied on it as a protective coating, and the two copper–zinc alloy foils (schlagmetal or Dutch metal foil) subsequently applied.

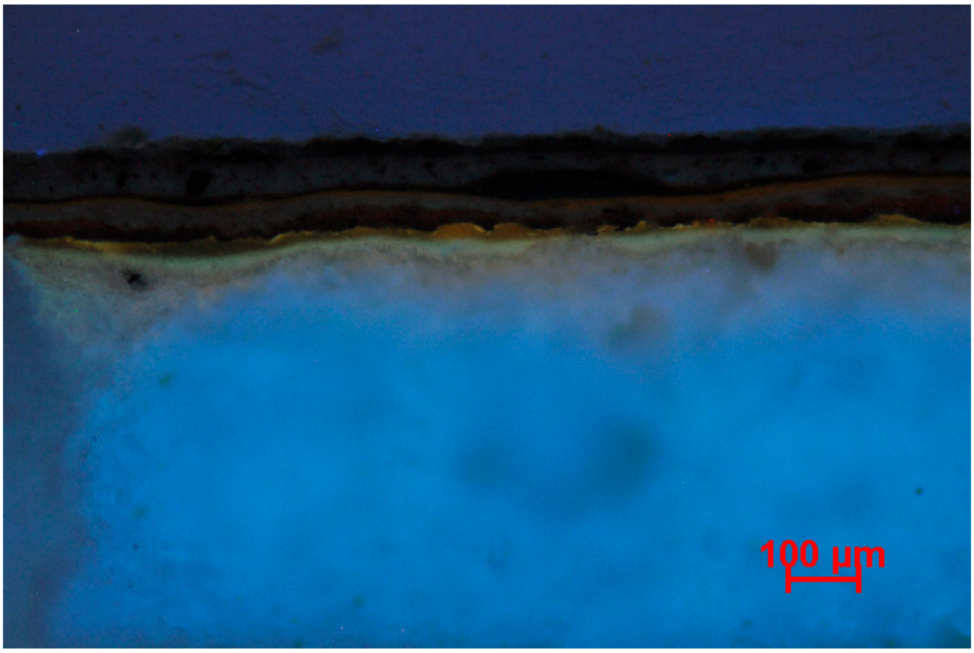
Also, another originally decorated gold sample morphology is depicted by optical microscopy analysis in Figure S7 of the Supplementary Material, revealing the typical stratigraphy of gilded wooden artifacts [15–20].

The complex decoration stratigraphy revealed by optical microscopy is confirmed by XRF (Figure 6a—gold foil and Figure 6b—silver foil) and ATR-FTIR (Figure 7) spectroscopy analysis.



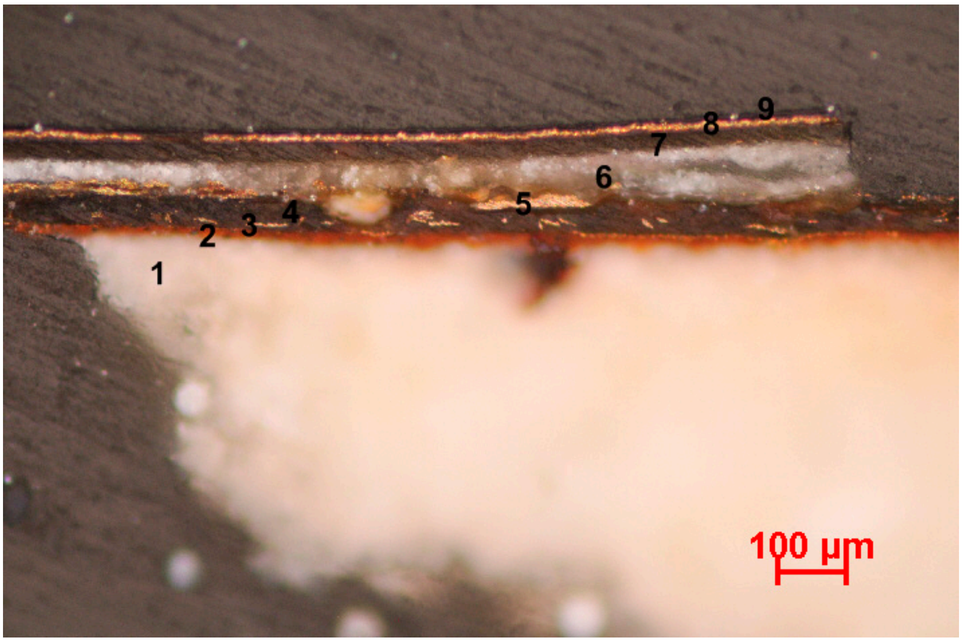
(**a**)

Figure 3. *Cont.*



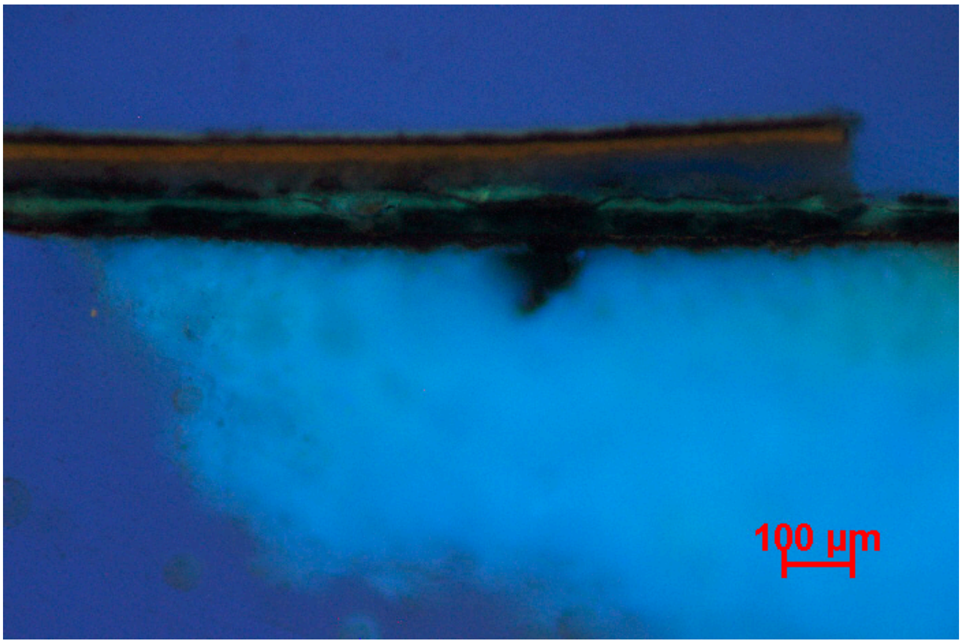
(**b**)

Figure 3. Cross-section microscopy image of sample 1: (**a**) in reflected light (200×) and (**b**) in fluorescent light with UV filter (200×). The following could be seen in the original painting layers: 1. gesso ground with glue; 2. possibly minimum red with egg tempera (fluorescent, visible in (**b**)) UVF image; 3. a silvery foil on which the subsequent layers of overpainting 1 was applied. Overpainting 1: 4. iron red ochre bole; 5. traces of gold foil (XRF); 6. varnish, natural resin (fluorescent in UV). Overpainting 2: 7. golden foil, possibly a Cu-Zn alloy foil (schlagmetal), and green corrosion products formed on the metallic surface of the foil could be seen at higher magnifications. Overpainting 3: 8. calcium carbonate chalk ground with iron ochre oxides; 9. golden foil, possibly schlagmetal (Cu-Zn alloy); 10. varnish, natural resin.



(**a**)

Figure 4. *Cont.*

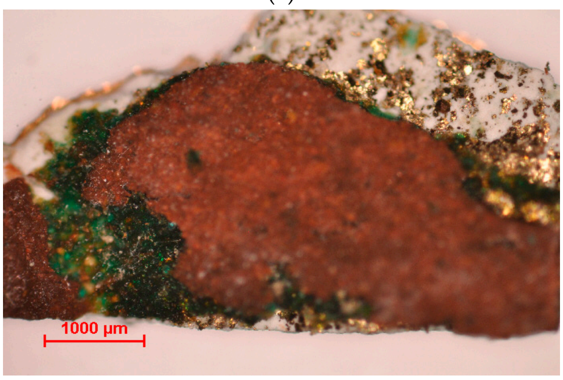


(**b**)

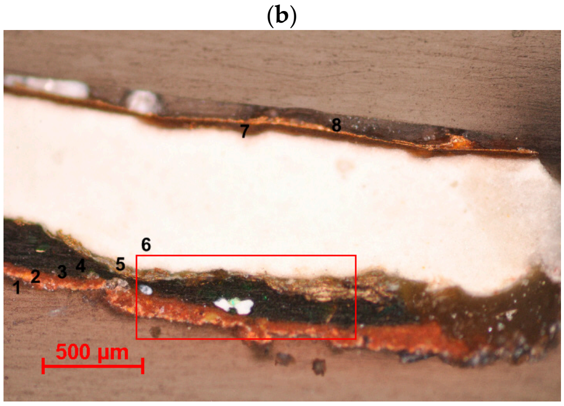
Figure 4. Cross-section microscopy image of sample 2: (**a**) in reflected light (200×) and (**b**) in fluorescent light with UV filter (200×). Original painting: 1. gesso ground with glue; 2. iron red ochre bole; 3. golden foil, possibly gold (XRF); 4. varnish, natural resin (fluorescent in UV). Overpainting 1: 5. golden foil. Overpainting 2: 6. calcium carbonate chalk ground, possibly with glue; 7. possibly a red lake (madder lake has a characteristic orange UV fluorescence); 8. golden foil, possibly a Cu-Zn alloy foil (schlagmetal); 9. varnish, natural resin.

(**a**)

(**b**)

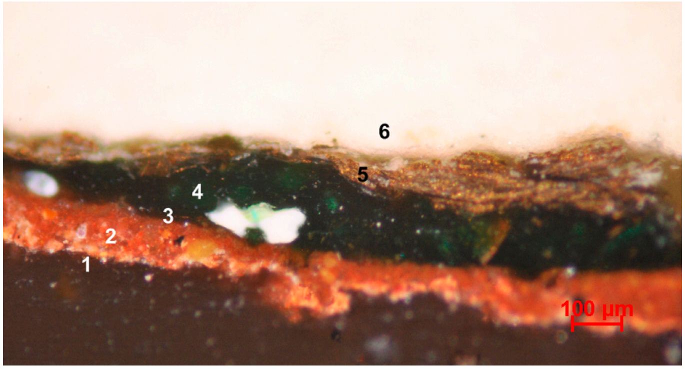


(**c**)

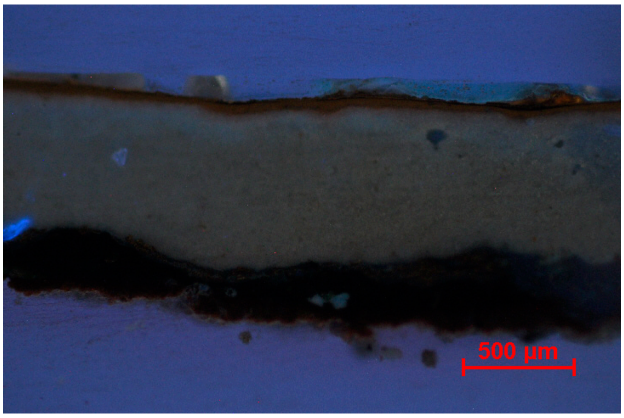


(**d**)

Figure 5. *Cont.*

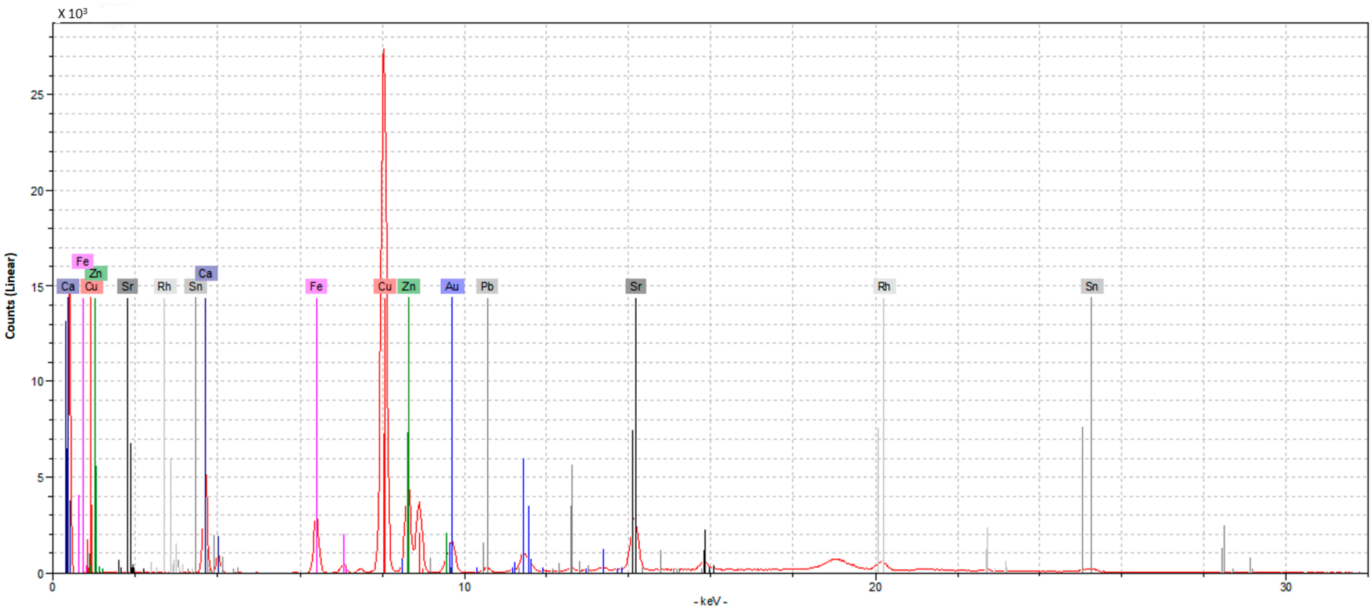


(**e**)



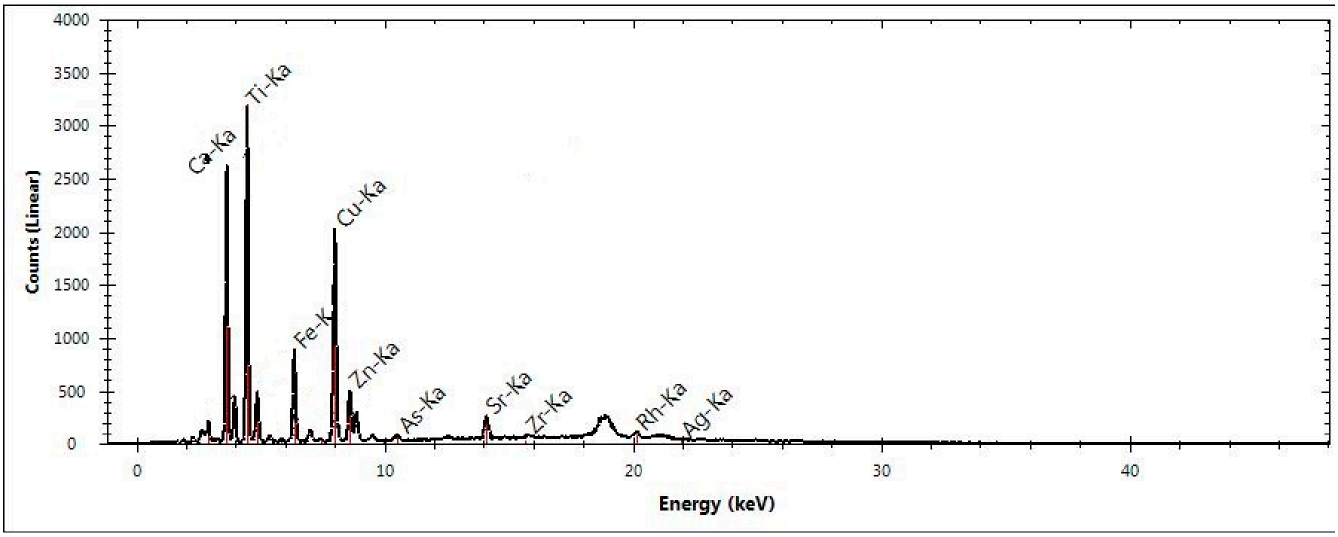
(**f**)

Figure 5. Sample 2 golden wood fragment (**b**) from which a new micro sample 3 was taken along with the optical microscopy images of sample 3 in reflected light, (**a**) face (50×) and (**c**) verso (50×), and the sample's cross-section images in polarized light, (**d**) 100× and (**e**) 200×, (**f**) fluorescence light with UV filter (100×). In the cross-section images, the different layers subsequently applied to the original painting could be observed: 1. underlay of glue, possibly directly applied on the wooden support; 2. iron red ochre bole with aqueous egg tempera; 3. traces fragments of golden foil; 4. varnish (natural resin, fluorescent in UV) with corrosion green products (possibly, malachite green—basic copper(II) carbonate hydroxide $CuCO_3 \times Cu(OH)_2$)) developed on the Cu-Zn alloy foil (5, possibly schlagmetal) applied as Overpainting 1. Overpainting 2: 6. probably, gesso ground; 7. iron ochre red bole with egg tempera; 8. schlagmetal (Cu-Zn alloy) foil.



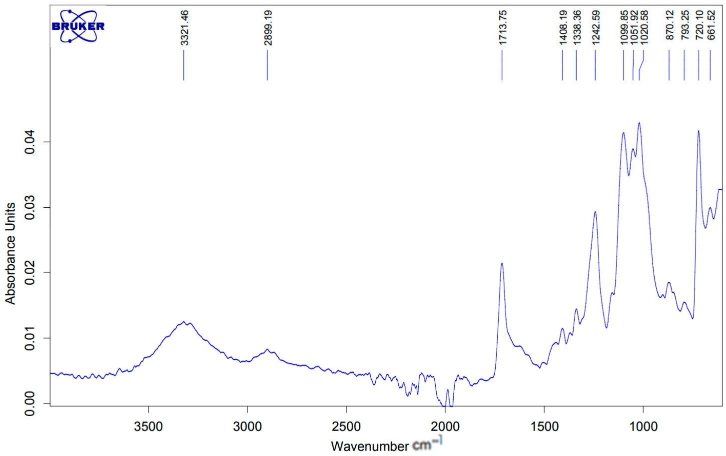
(**a**)

Figure 6. *Cont.*

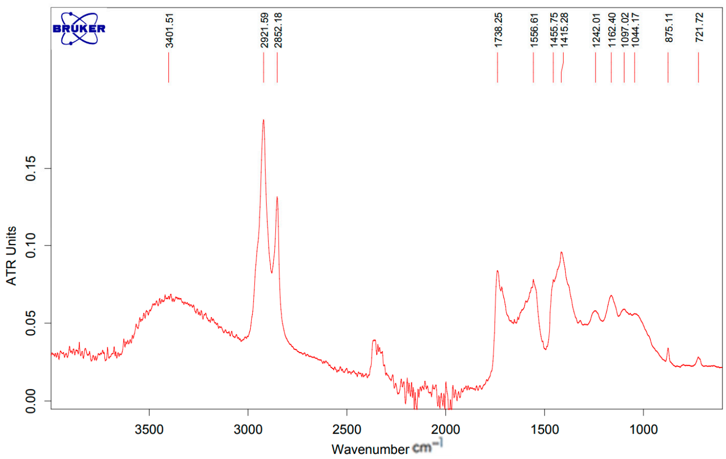


(b)

Figure 6. XRF spectra of the original (**a**) gold foil area and original silver decorated area (**b**) depicting the calcium carbonate ground composition and two successive coating layers of brass Cu-Zn-based alloys (in the Figure 6b are not given all the elements identified to increase the text legibility).



(**a**)



(**b**)

Figure 7. ATR FTIR spectra of the detached fragments showing the different organic and inorganic constituents materials identified in (**a**) sample 1 and (**b**) sample 2.

The XRF analysis confirms the existence of complex compositions with several layers of ground (calcium carbonate), bolus (iron oxides earth clay), original metallic foil (of gold and silver, respectively), and Dutch metal Cu alloy with Zn, as depicted by optical microscopy. The analysis shows low concentrations of Au and Ag, which led to the decision to keep the actual copper alloy decoration of the wooden pedestal after cleaning, consolidation, and retouching.

The identification of composition and fine structure differences using FTIR spectroscopy was demonstrated for complex multimaterial artifacts as well as for different multicomponent samples [19,20]. FTIR spectroscopy data (Figure 7) confirmed the existence of calcite as a ground layer (1415 cm^{-1}), also of the bolus preparation of ochre (1044 cm^{-1}), and animal glue (3401 cm^{-1} amide A band, 1650 cm^{-1} amide I band, 1557 cm^{-1} amide II band, 1242 cm^{-1} amide III band), respectively, with egg white (bands partially superposed with protein band of animal glue) as well as residues of wax (bands at 2921 cm^{-1}, 2852 cm^{-1}, 1738 cm^{-1}), The spectra of the constituent materials identified in the analysed samples were compared with the similar spectra from the IRUG database [21].

4. Conclusions

To obtain complete information on the materials and techniques used for producing ancient polychrome wooden art pieces with different layers of successively applied decorations, several complementary analytical methods of analysis must be performed. The classical nondestructive methods of investigation are optical microscopy, vibrational spectroscopy techniques, FTIR, and X-ray fluorescence, routinely used for the analysis of organic and inorganic constituent materials of historic and artistic works, combining molecular and elemental analysis [22–25]. Our approach revealed and emphasized the existence of original gold and silver layer decorations on a wooden relic pedestal recalling the Romanian Brancovan adaptation of Byzantine tradition and two successive copper–zinc alloy metallic coatings. The metallic coatings were applied on the ground and bolus layers as revealed by optical microscopy, XRF, and ATR/FTIR investigations. Due to poor conservation of the gold and silver foil original coatings, the intervention decision was to restore the actual coating of copper alloy Dutch metal foil. Thus, the importance of the art and science multidisciplinary collaboration for the preservation of esthetic, historic, and religious artifacts was demonstrated.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13122092/s1. Figure S1: Gaps of different depths, Figure S2. Lack of carved elements/fragments, Figure S3. The presence of the flight holes of xylophagous insects on the verso of the pieces and on the carved polychrome surfaces, Figure S4. Superficial deposits of dust and the presence of cobwebs, Figure S5. Detachments of the polychrome layer/Detachments and dislocated polychrome layer fragments, Figure S6. Gap in the polychromy layer, up to the level of the wooden support/Extensive gap areas—irreversible loss of the polychromy layer, Figure S7. Optical microscopy images of the sample 2 originally decorated with gold foil: (a) in polarized light (×50); (b) reflected light (×50); (c) ultraviolet fluorescent light (×50) (d) reflected 1ight (×50).

Author Contributions: Conceptualization, I.S. and D.F.; methodology, Z.B.; validation, D.M. and D.C.-S.; formal analysis, D.F. and V.P.; investigation, I.S., Z.B., D.M. and D.C.-S.; resources, I.B.L.; data curation, I.S.; writing—original draft preparation, I.S. and D.F.; writing—review and editing, I.S. and Z.B.; project administration, I.B.L.; funding acquisition, I.B.L. All authors have read and agreed to the published version of the manuscript.

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