

THE INVESTIGATION OF PAINTING MATERIALS OF THE JESUS CHRIST ROYAL ICON

Olivia Florena NEMEȘ^{1*}, Ion SANDU^{2,3,4,5}, Constantin MĂRUȚOIU¹,
Dan NEMEȘ¹, Teofil TIA¹, Alin TRIFA¹, Dan Alexandru HORVAT⁶,
Sister Epiharhia (Vasilica Cristina NICULA)¹

¹Babes-Bolyai' University, Faculty of Orthodox Theology, N. Ivan St., 400692, Cluj-Napoca, Romania

²Academy of Romanian Scientists AOSR, 54 Splaiul Independentei St., Sect 5, 050094 Bucharest, Romania

³Alexandru Ioan Cuza University of Iasi, Interdisciplinary Research Institute – Science Department,
11 Carol I Bulevard, 700506 Iasi, Romania

⁴National Institute for Research and Development in Environmental Protection, 294 Splaiul Independentei,
Sector 6, 060031 Bucharest, Romania

⁵Romanian Inventors Forum, Sf. Petru Movila St., L11, 3-3, 700089 Iasi, Romania

⁶The Parish from the Village of Gheorgheni, Cluj County, Romania

Abstract

The royal icon of Jesus Christ belongs to the “Saint Archangels Michael and Gabriel” church from the village of Gheorgheni, Cluj County, and it dates from the beginning of the 18th century. Considering the importance, the age, and the ongoing process of restoration of this icon, research has been done to establish the composition of the painting materials. The investigations were carried out using nondestructive Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Fluorescence (XRF) measurements. The ground applied over the wood was identified as gypsum. The painting technique used was tempera grassa, and traditional pigments were used: white lead, mercury red, iron red, copper green, Prussian blue, brown iron oxide, and carbon black. Gold and silver leaves were also used, the beautiful painting being complemented by rich decorations.

Keywords: *Wooden icon; Painting materials; X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR)*

Introduction

The statement that God became man, and that man might become God represents the center of the orthodox dogmatic teaching. The icon also states this fundamental truth of faith by means of colors. This unique style of painting has been developed inside orthodox Christianity. Due to ritual practices, such artifacts have constantly been produced for more than 17 centuries. This long period of time has been divided into three subperiods: the Byzantine period (330-1453), the post-Byzantine period (1453-1830), and the modern period (after 1830). In the year 1453 was the fall of Constantinople (the capital of the Byzantine Empire) under Turkish rule, while 1830 was the year of the Greek Declaration of Independence [1, 2]. The art of religious painting continued its way according to the Byzantine style. The iconographic techniques and materials used by religious painters remain unchanged, but in a different social and political context [3-6].

* Corresponding author: olivia_nemes@yahoo.com

The royal icon of Jesus Christ (Fig. 1) belongs to the Romanian Orthodox Parish “Saints Archangels Michael and Gabriel,” from the village of Gheorgheni, Cluj County. It dates to the beginning of the 18th century.



Fig. 1. Royal icon of Jesus Christ

The icon depicts Jesus Christ in half length, flanked in the upper side by the Mother of God and Saint John the Baptist. The icon is painted on a wooden panel made by joining several boards. The panel is surrounded by a wooden frame whose upper cutout is different from the side and lower ones. There is also a golden frame inside the panel with a very thin cutout on the side and lower parts and the rope motif on the top vaulted one. The space between the exterior and interior frame that appeared at the top of the icon shows two floral ornaments in relief.

Jesus Christ is represented in the center of the icon, filling most of its space. The miter on His head is the only element that indicates that we are in front of the typology of the Great High Priest, since his vestments belong to the other very well-known iconographic type, the Master Teacher. The combination between these two typologies makes this icon an interesting and unique one. Both vestments, the red and the blue, are richly ornamented. Christ is blessing with his right hand while holding a small open Bible in his left one. On his right and left sides Mother of God and John the Baptist are being depicted, smaller in size and standing on clouds, in a praying posture.

In terms of chromatics, we are dealing with a very unitary icon, due to the use of very few colors. The blue, the yellow from the golden leaf, and the red are the three colors that cover the largest area of the icon. The analysis of the drawing and the artistic anatomy shows the same deformities specific to folk art, which can also be seen in glass icons. The line is simple, the shapes are slightly synthesized, and the artistic expression is direct and sincere. Despite its naïve nature, the drawing gives the faces an expression of calm, gentleness, mercy, and kindness. The slight clumsiness visible at an anatomic level is compensated by spontaneity and artlessness. As a perfect illustration of the complementarity between the image and the sacred text, many inscriptions may be seen in this icon. As expected and also canonic, the names of the

holy persons could not miss from the icon: IC XC next to Christ, MP QV and John next to the Mother of God and St. John the Baptist.

Letters O and N, which appear to the right and left of Christ's halo, are an expression of His aseity. Other inscriptions may also be seen in the Bible that Christ holds in His hand and on the blue background from the top of the icon.

Similar religious works of art and artifacts have been investigated using spectroscopy (XRF, Raman, and FTIR), chromatography and mass spectrometry, as well as thermal analysis [7-14]. Considering the importance, the age, and the restoration process of this icon, investigations have been carried out to establish the composition of the painting materials. The investigations were carried out using nondestructive Fourier Transform Infrared Spectroscopy (FTIR) and portable X-ray Fluorescence Spectroscopy (pXRF) investigations for each color in different points.

Experimental part

Methods

Non-destructive investigations (without taking physical samples) were carried out to analyze the pigments used to make the icon. The analyzes were performed using portable devices by bringing them close to the painting layer.

XRF spectroscopy

X-ray fluorescence elemental analysis (XRF) was performed with a portable Bruker spectrometer S1 TITAN series (EDXRF) configured with a Silicon diode PIN detector (SiPIN), Rh target X-ray tube with a maximum voltage of 50kV.

FTIR reflectance spectroscopy

FTIR reflectance spectroscopy was performed using a tripod mounted Bruker Alpha II device with a contactless forward-looking reflection unit specialized for paintings, spectral domain 400-4000 cm^{-1} , resolution 2 cm^{-1} , OPUS /IR software in Windows 10.

Results and discussion

FTIR spectroscopy

The absorption bands (Fig. 2) at 2927 and 2855 cm^{-1} - CH_2 groups; 1743 cm^{-1} ester stretching bands which by age become broader; 1720 cm^{-1} possible free fatty acids; the bands suggest the use of linseed oil [8] 2097 cm^{-1} – indicating the presence of Prussian blue; 1680 cm^{-1} – Amide I, 1549 cm^{-1} Amide II, 1472 and 1332 cm^{-1} Amide III – proteins from egg yolk [15].

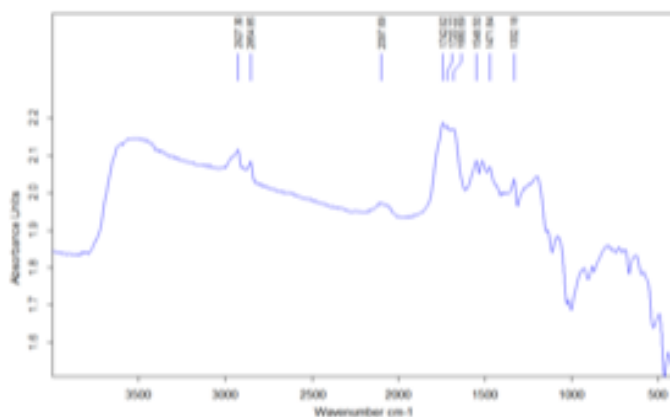


Fig. 2. FTIR spectrum for blue color – Jesus Christ's vestment (Area A)

The blue and red colors were canonically used to depict Jesus Christ’s clothing. The pigments were mixed with egg yolk and linseed oil, a technique known as *tempera grassa*.

The pair of peaks at 625 and 691cm⁻¹, together with the accompanying 1243 and 1684cm⁻¹ peaks [13, 14, 16], although slightly shifted to the left, show that the ground used was gypsum (Fig. 3).

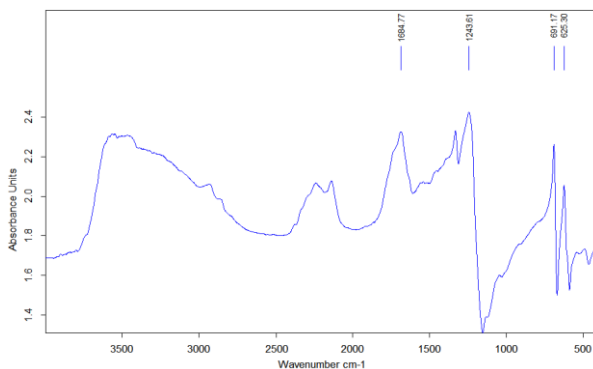


Fig. 3. FTIR spectrum for ground (Area B)

pXRF spectroscopy

The icon background was made with golden leaf: gold L lines, at 9.67, 11.5 and 13.4keV (Figs. 4 and 5).

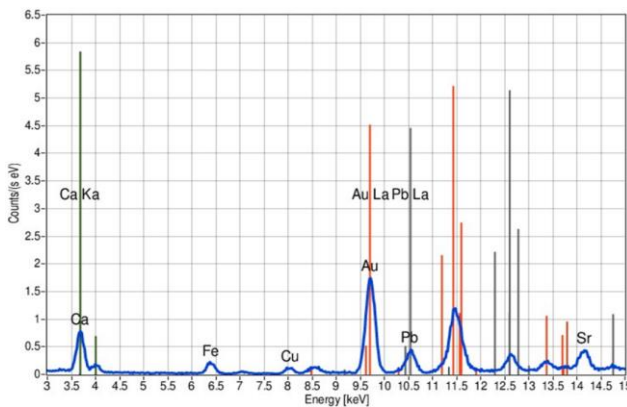


Fig. 4. Golden background upper area (Area C)

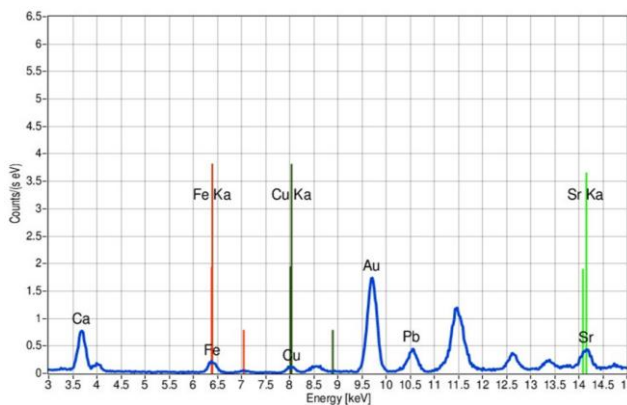


Fig. 5. Golden background upper area (Area C) – detail of trace elements

Calcium from the underneath ground layer is clearly represented (K line, at 3.7keV). Also belonging to the second layer (underneath the gold foil), lead lines are visible, suggesting a layer of white lead was applied to the calcium-based ground (L lines at 10.5, 12.6 and 14.8keV). The lead L lines are less pronounced than those from other areas measurements, suggesting an attenuating effect due to the superimposed gold leaf over the ground [17].

The iron content ($K\alpha$ and $K\beta$ lines, at 6.4 and 7.06keV) is due to the gold foil application on bolus (natural clay containing iron oxides) [18, 19]. Traces of copper ($K\alpha$ and $K\beta$ lines, at 8.04 and 8.94keV) are visible and due to the golden foil alloy (adding small quantities of copper enriches the foil color). The traces of strontium are expected because it is naturally found in calcium deposits and has a strong XRF signature, even in very low quantities (Sr $K\alpha$ line at 14.15keV). Strontium found in the ground/primer substrate takes the form of Celestine ($SrSO_4$) [18-20].

Calcium, strontium, and lead are common to all XRF spectra and will not be discussed further unless variation is due to other factors.

Traces of silver foil use are visible: $K\alpha$ and $K\beta$ lines, at 22.1 and 24.9keV (Fig. 6); the iron content originates from the bolus traditionally used to prepare the site for the foil application.

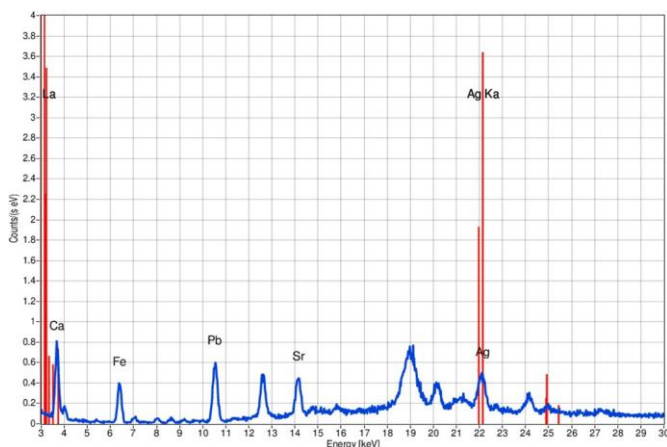


Fig. 6. Silver-white clothing edge (Area D)

Mercury red (cinnabar) was used for the red color, mercury: L lines, at 10.0, 11.8 and 13.8keV (Fig. 7). The low lead content from the ground layer preparation is similar to other colors (except for very high white lead concentration skin areas or the grey/blue clothing), suggesting that no supplemental red lead pigment was used.

The skin shade was obtained by mixing large amounts of white lead: L lines, at 10.5, 12.6 and 14.8keV (Fig. 8) with small amounts of mercury red (which diminish or disappear towards the whiter areas).

Copper green was used: $K\alpha$ and $K\beta$ lines at 8.0 and 8.9keV (Fig. 9). The green pigment experienced significant degradation and exfoliated over large areas in multiple places (Virgin Mary's clothing, Saint John's clothing, Jesus Christ's inner sleeves, icon frame), being by far the most affected pigment from the icon and showing consistent damage in all the areas it is encountered. This could be attributed to the copper-based pigment effect of generating metal soaps in oil and egg temperas [15]. Lead lines were also marked to identify the lines present in the spectrum.

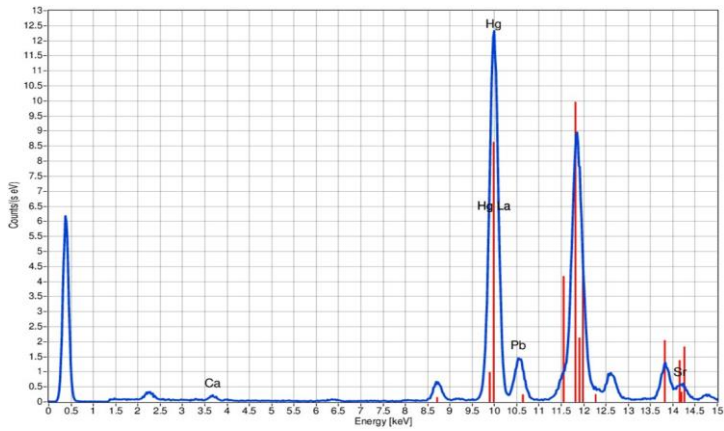


Fig. 7. Jesus Christ's red vestment (Area E)

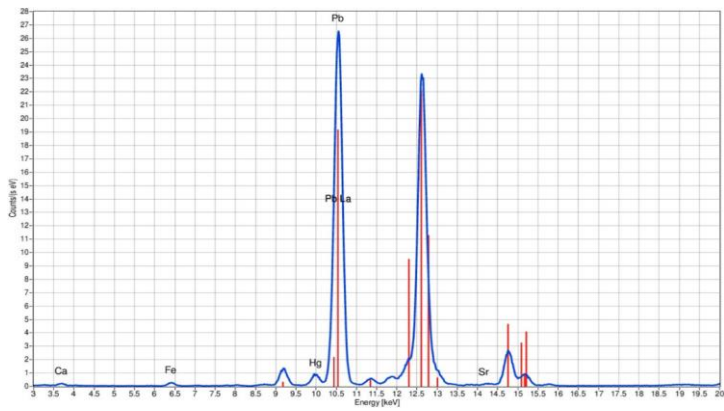


Fig. 8. Jesus Christ's carnation white (Area F)

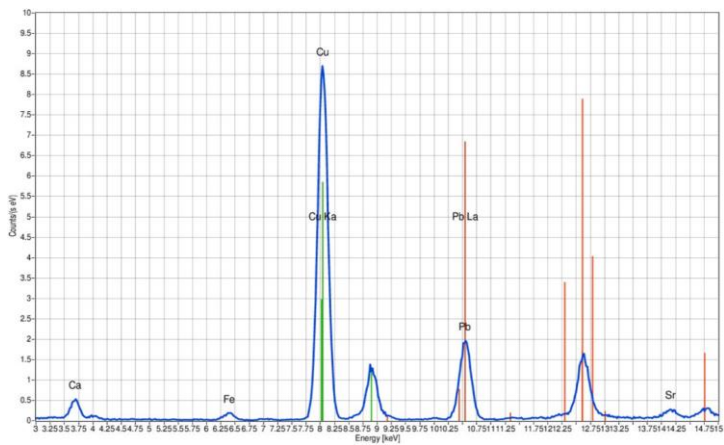


Fig. 9. Virgin's Mary green clothing (Area G)

The dark grey/blue color contains traces of Prussian blue (see FTIR spectrum, Fig. 10).

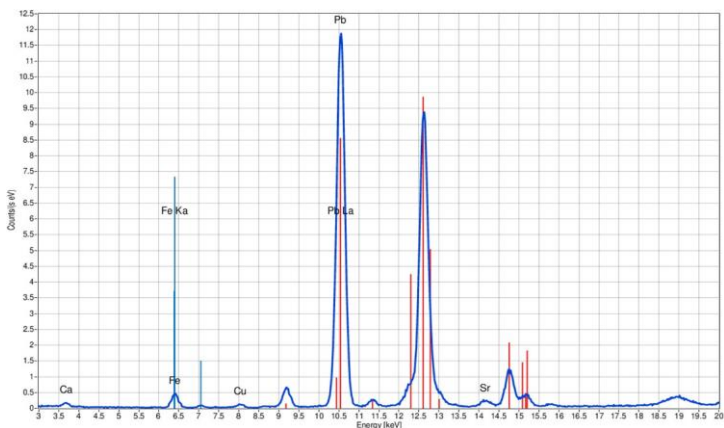


Fig. 10. Jesus Christ's dark blue vestment (Area A)

The consecutive horizontal lighter and darker hues were obtained by using different ratios of white lead and carbon black. Supporting this theory is the absence of manganese and the low iron content, suggesting that the black color used to darken the lines is probably based on a simple carbon black [19]. White lead was commonly used in Byzantine-style paintings to impart brightness [18]. The low traces of copper observed could be due to contamination from the very degraded inner sleeve green pigment above the measurement area.

Christ's dark brown beard shades were obtained by mixing simple iron oxide and mercury red with probably carbon black for darker shades [19]. The absence of manganese from the spectrum points against the usage of brown earths like umbra or sienna. The absence of manganese, cobalt, and the low iron content from the black color point against the use of more complex black pigments. The beard was painted over the carnation; therefore, a high level of lead from white lead is present (Fig. 11). The small quantity of copper could be contaminated from the large degraded green pigment areas (from both the painting and the frame), but the intentional use of a copper green pigment by the painter cannot be ruled out (cleaning of the icon could offer more insight).

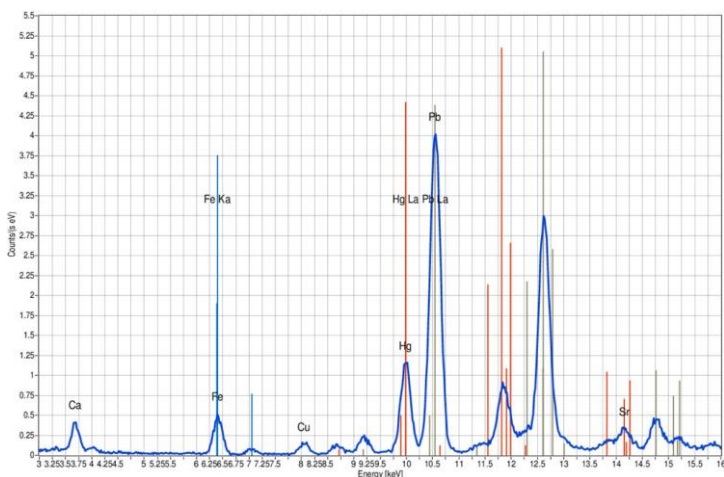


Fig. 11. Jesus Christ's beard area (Area H)

The red color was obtained using red iron oxide (Fig. 12). The calcium, strontium, and lead lines are similar to the main painting ground spectrum, and the white underlying plaster is visible in the worn-out areas of the frame. Furthermore, the existing lead line is also too weak to suggest usage of red lead pigment.

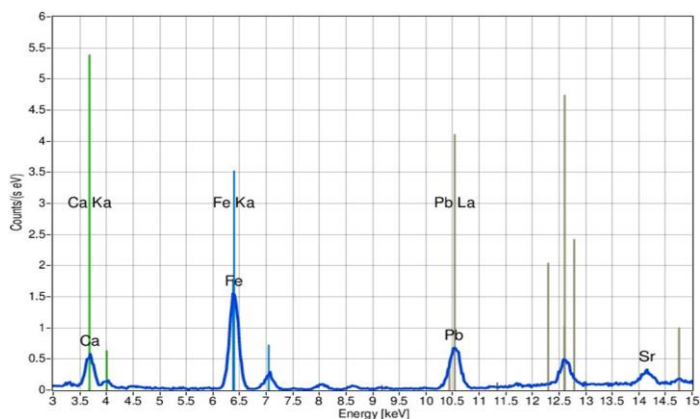


Fig. 12. Red iron exterior frame (Area I)

The common calcium/white lead combination is observed, indicating the use of white lead pigment as a primer layer applied over gypsum (Fig. 13), which was a common practice for the artists [18-20]. The small iron content could suggest the presence of impurities in the gypsum, with an effect on the perceived whiteness of the plaster (if used without additives).

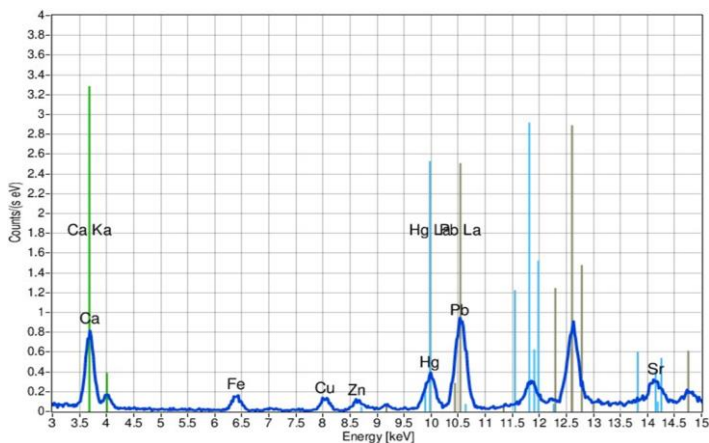


Fig. 13. Ground/plaster from the lower central exfoliated area (Area B)

Small copper traces were found throughout the spectrum, which could indicate either the presence of impurities or, more likely, contamination from the many areas where the green paint peeled off on both the painting area and large areas of the frame painted in green. The small zinc traces could suggest a white pigment, but the very low line is more likely to be attributed to mineral impurities in the plaster. The mercury content is expected because the exfoliated area that was studied is near the red clothing, leading to contamination with mercury sulfide.

Conclusions

The royal icon of Jesus Christ (fig. 1) was painted on wood with materials specific to those times. A layer of calcium-based primer (gypsum) was applied on the wooden board, and another thin layer of white lead was applied on the whole painting area and on the wooden frame before the painting process to enhance the whiteness of the primer layer [17-20]. The iron impurities could indicate the whiteness of gypsum, warranting the need of applying a supplemental white-enhancing layer.

The commonly used painting technique was *tempera grassa*, the pigments being mixed with egg yolk, oil, and water to adhere to the primer. The presence of lipid materials (linseed oil) and proteins (egg yolk) was shown by the FTIR investigations.

The pigments used were white lead, mercury red, iron red, copper green, Prussian blue, brown iron oxide, and carbon black. Gold and silver leaf were also used (applied using the common technique of preparing the primer with bolus). Despite the color palette being limited, some of the materials used were expensive, offering insight about the economic status of the community that supported the painting expenses. The use of Prussian blue dates this icon execution after the first decade of the 18th century, when the newly discovered pigment started being used across Europe.

Future investigations could be made to obtain more information about the painting. The green pigment that suffered massive degradation could be of special interest, especially as it experienced disproportionate exfoliation compared to all the other pigments and cannot be explained by mechanical erosion, being applied in multiple areas of the icon [21, 22]. The limiting factor for further investigations is using non-destructive methods, as taking material samples requires approval by the owner and is discouraged by restorers.

References

- [1] G.P. Mastrotheodoros, M. Theodosis, E. Filippaki, G. Konstantinos, K.G. Beltsios, *By the Hand of Angelos? Analytical Investigation of a Remarkable 15th Century Cretan Icon*, **Heritage**, **3**(4), 2020, pp. 1360-1372. DOI: 10.3390/heritage3040075.
- [2] P. Vokotopoulos, **Byzantine Icons**, Ekdotiki Athinon, Athens, Greece, 1995.
- [3] E. Christopoulou, N. Laskaris, T. Ganetsos, *Pigment identification of two post-bizantine icons of Theodoros Poulakis by pXRF and Raman spectroscopy: Case study*, **Scientific Culture**, **6**(2), 2020, pp. 65-72. DOI: 10.5281/zenodo.3785044.
- [4] L. Nica, V. Vasilache, A. Drob, S. Pruteanu, I. Sandu, *Preservation and Restoration of An Old Wooden Icon with Complex Carved Ornaments, in a Conservation State of Precollapse*, **Applied Sciences-Basel**, **12**(10), 2022, Article Number: 5073. DOI:10.3390/App12105073.
- [5] I.C.A. Sandu, S. Bracci, I. Sandu, M. Loberfaro, *Integrated analytical study for authentication of five Russian icons (XVII-XVIII Century)*, **Microscopy, Research and Technique**, **72**(10), 2009, pp. 755-765. DOI: 10.1002/jemt.20727.
- [6] I.C.A. Sandu, S. Bracci, I. Sandu, *Instrumental analyses used in the authentication of old paintings I. Comparison between two Icons of XIXth Century*, **Revista de Chimie**, **57**(8) 2006, pp. 796-803.
- [7] I. Bratu, C. Măruțoiu, D. Nemeș, D. Toader, O.F. Nemeș, R.C. Suciuc, *Characterization of the Paint from "The Lord's Transfiguration" Icon by Grigore Ranite*, **Analytical Letters**, **54**(1-2), 2021, pp. 204-211. DOI: 10.1080/00032719.2020.1743716.
- [8] C. Neamțu, I. Bratu, C. Măruțoiu, V.C. Măruțoiu, O.F. Nemeș, R. Comes, Ș. Bodi, Z. Buna, D. Popescu, *Component Materials, 3D Digital Restoration, and Documentation of the Imperial Gates from the Wooden Church of Voivodeni, Sălaj County, Romania*, **Applied Science**, **11**(8), 2021, Article Number: 3422. DOI: 10.3390/app11083422.

- [9] D. Nemeș, C. Măruțoiu, I. Bratu, C. Neamțu, I. Kacso, O.F. Nemeș, I. Udrea, *Characterization of the Paint Used by Dumitru Ispas in the Wooden Straja Church, Cluj County, Romania*, **Analytical Letters**, **54**(1-2), 2021, pp. 255-264. DOI: 10.1080/00032719.2020.1749649.
- [10] Z. Moldovan, I. Bratu, C. Măruțoiu, I. Kacso, L. Troșan, D. Pop-Toader, O.F. Nemeș, C. Tănăsolia, *Characterization of an Eighteenth-Century Wooden Icon from the Ethnographic Museum of Transylvania*, **Analytical Letters**, **49**(16), 2016, pp. 2597-2605. Special Issue: SI. DOI: 10.1080/00032719.2015.1121394.
- [11] R.A. Cristache, I.C.A. Sandu, A.E. Simionescu, V. Vasilache, A.M. Budu, I. Sandu, *Multianalytical study of the paint layers used in authentication of icon from XIXth century*, **Revista de Chimie**, **66**(7), 2015, pp. 1036-1039.
- [12] R.A. Cristache, I.C.A. Sandu, A.M. Budu, V. Vasilache, I. Sandu, *Multi-analytical study of an ancient icon on wooden panel*, **Revista de Chimie**, **66**(3), 2015, pp. 348-352.
- [13] I.C.A. Sandu, C. Luca, I. Sandu, V. Vasilache, M. Hayashi, *Authentication of the ancient easel paintings through materials identification from the polychrome layers - II. Analysis by means of the FT-IR spectrophotometry*, **Revista de Chimie**, **59**(4), 2008, pp. 384-387.
- [14] I.C.A. Sandu, C. Luca, I. Sandu, M. Pohontu, *Research regarding the soft wood support degradation evaluation in old paintings, using preparation layers. II. IR and FTIR Spectroscopy*, **Revista de Chimie**, **52**(7-8), 2001, pp. 409-419.
- [15] R. Mazzeo, S. Prati, M. Quaranta, E. Joseph, E. Kendix, M. Galeotti, *Attenuated total reflection micro FTIR characterisation of pigment-binder interaction in reconstructed paint films*, **Analytical and Bioanalytical Chemistry**, **392**(1-2), 2008, pp. 65-76. DOI: 10.1007/s00216-008-2126-5.
- [16] * * *, **SpectraBase**, John Wiley & Sons, Inc. (<https://spectrabase.com/>).
- [17] R. Cesareo, A. Castellano, M. Marabelli, G. Buccolieri, S. Quarta, P. Santopadre, M. Ieole, S. Ridolfi, G.E. Gigante, *Optimization of portable systems for energy dispersive X ray fluorescence analysis of paintings*, **In situ Applications of X-ray Fluorescence Techniques, Final Report of a Coordinated Research Project 2000-2003** (Editors: A. Markowicz, D. Wegrzynek and K. Will), IAEA, Vienna, 2005, pp. 158-164.
- [18] T. Gerodimos, A. Asvestas, G. Mastrotheodoros, G. Chantas, I. Liougos, A. Likas, D.F. Anagnostopoulos, *Scanning X-ray Fluorescence Data Analysis for the Identification of Byzantine Icons' Materials, Techniques, and State of Preservation: A Case Study*, **Journal of Imaging**, **8**(5), 2022, Article Number: 147. DOI: 10.3390/jimaging8050147.
- [19] E. Merkaĵ, N. Civici, *Application of a Portable XRF Spectrometer for In-Situ and Nondestructive Investigation of Pigments in Two 15th Century Icons*, **Open Journal of Applied Sciences**, **10**, 2020, pp. 305-317, DOI: 10.4236/ojapps.2020.106023.
- [20] E.G. Morales Toledo, T. Raicu, L. Falchi, E. Barisoni, M. Piccolo, F.C. Izzo, *Critical Analysis of the Materials Used by the Venetian Artist Guido Cadorin (1892–1976) during the Mid-20th Century, Using a Multi-Analytical Approach*, **Heritage**, **6**, 2023, pp. 600-627. DOI: 10.3390/heritage6010032.
- [21] P. Spiridon, I. Sandu, L. Stratulat, *The conscious deterioration and degradation of the cultural heritage*, **International Journal of Conservation Science**, **8**(1), 2017, pp. 81-88.
- [22] I. Sandu, *Modern Aspects Regarding the Conservation of Cultural Heritage Artifacts*, **International Journal of Conservation Science**, **13**(4), 2022, pp. 1187-1208.

Received: February 20, 2024

Accepted: November 14, 2024