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ART ANALYSIS

Characterization of the Paint from "The Lord's Transfiguration" Icon by Grigore Ranite

I. Bratu[a†], C. Măruţoiu[b†], D. Nemeş[b], D. Toader[c], O. F. Nemeş[b], and R. C. Suciu[a]

[a]Department of Physics of Nanostructured Systems, National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania; [b]Faculty of Orthodox Theology, Babes-Bolyai' University, Cluj-Napoca, Romania; [c]Ethnographic Museum of Transylvania, Cluj-Napoca, Romania

ABSTRACT

"The Lord's Transfiguration" icon painted by Grigore Ranite belongs to a collection of altarpiece icons from the Ethnographic Museum of Transylvania. The aim of this paper is to present the results obtained from the scientific investigations carried out to establish the materials and methods used by the painter for the accomplishment of the religious art work, both for conservation and restoration purposes, as well as to enrich the knowledge about the work of this particular author and about the Transylvanian iconography in general. The analyses were performed by means of X-ray fluorescence (XRF) spectroscopy and destructive and nondestructive Fourier transform infrared (FTIR) spectroscopy.

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KEYWORDS
Painting materials; wooden icon; X-ray fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopy

Introduction

The work of the icon and church painter Grigore Ranite (from eighteenth century) covers a large area comprised of Oltenia, Transylvania and Banat regions of Romania and also Subotica in Serbia. The surviving work of art show that this artist is one of the most talented painters from the second generation of Brancovan style school of artists and one of the most cherished painting teachers from the Romanian country of those times (Iorga 1905; Porumb 2003; Dumitran 2010).

The icon subjected to scientific investigations (dimensions $48.5 \times 32.5 \times 3.7$ cm, Figure 1) belonging to the Ethnographic Museum of Transylvania originates from Galda de Sus village, Alba county. The icon is painted in a post "Brancovan" style and it depicts the biblic theme of "The Lord's Transfiguration". According to the traditional representation, Christ is centrally represented inside a mandorla, sitting on the top of Tabor Mountain. On the sides of Christ, Moses and Elijah are depicted, representing the Law and the Prophets, both of them are Old Testament visionaries who experienced the presence of God on Sinai and Carmel. At the bottom of the painting there are three of the apostles: Peter, John and James, impressed and overwhelmed by the sight of the divine glory.

CONTACT I. Bratu ibratu@gmail.com National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat st., 400293 Cluj-Napoca, Romania.

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†I. Bratu and C. Măruţoiu provided equal contributions to the paper.

The inscription with the name of the icon, written with Cyrillic characters, appears at the top of the composition: "PREOBRAJENE" (meaning "transfiguration"). In the cruciform aura of Christ the "OωN" monogram appears ("Who he is" (Exodus 3, 13–14).) The panel is made by joining two fir-tree boards of uneven widths, with a half-burried fir beam across the back. The stepped and painted frame is made of 4 fir wood strips attached to the edges of the panel with wooden nails. The icon chromatic is composed of tones of green, red, ocher, blue, gray and gold leaf ground.

Despite the fact that Romania has a rich treasure of painted icons dating from the sixteenth century to the present, most of them are the property of the monasteries, various dioceses or private collections and their study by modern analytical methods is still in its infancy.

Different artworks have been investigated by use of spectroscopy (X- ray fluorescence - XRF, Raman, Fourier transform infrared - FTIR), chromatography and mass spectrometry, thermal analysis and X-ray diffraction (Navas et al. 2008; Manzano et al. 2009; Marcella et al. 2016, Mercedes et al. 2018; Bratu et al. 2017; Măruīoiu et al. 2017; Lee et al. 2018; Măruīoiu et al. 2018; Neamţu et al. 2018; Nemeş et al. 2018; Saverwyns, Currie, and Lamas-Delgado 2018; Bratu et al. 2019).

The study of the pigments provides information regarding the period when an icon was created, repaired or restored; all of them are important in establishing the icon school as well as the authenticity (Valianou et al. 2011).

The results of the complex analyzes of the paint from "The Lord's Transfiguration" icon by Grigore Ranite for the restoration are the object of this study.

The novelty of this work is consisting in the use of the techniques (XRF and FTIR spectroscopy) for realizing and the identification of the painting materials employed for the restoration of these wooden icons. FTIR Spectroscopy characterizes the *"tempera grasa"* technique, i.e., the employment of egg yolk and linen oil for the fluidization of the pigment.

Experimental

The wooden icon (Figure 1) was investigated by means of XRF and FTIR spectroscopic methods. FTIR analyses were performed using both destructive and nondestructive techniques.

XRF nondestructive analyses

Nondestructive X-ray fluorescence elemental analyses (XRF) were performed with a handheld Bruker spectrometer, S1 Titan series (EDXRF) configured with a Silicon diode PIN detector (SiPIN). A rhodium target X-ray tube was employed with a maximum voltage of 50 kV. All of the paint colors were analyzed 'in situ' (Cesareo et al. 2004; Franceschi et al. 2011). The measurements were performed for 30 seconds with the device positioned next to the painted surface. The measurement spot size is approximately 30 mm^2. Light elements, such as C, N, O, Na, Mg, Al, Si, S, P, and Cl cannot be determined by *in situ* analysis due to absorption by the air.

FTIR reflectance spectroscopy

FTIR reflectance spectroscopy was performed using a tripod mounted Bruker Alpha II device with a contactless forward looking reflection unit designed for painting analysis.

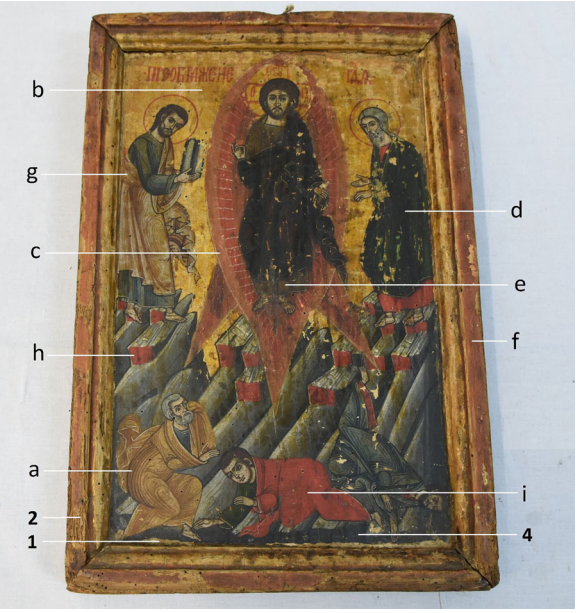

Figure 1. Sampling areas for the nondestructive and destructive analyses.

The spectral domain was from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. Instrument control and data analysis were performed by the use of the OPUS/IR software in Windows 10.

Destructive FTIR spectroscopy

The FTIR absorption destructive technique involved measurement with a Jasco FTIR spectrometer in the 4000 to 400 cm^{-1} spectral domain with a resolution of 4 cm^{-1} using 256 scans employing the KBr pellet technique.

The sampling areas for nondestructive and destructive analyzes are shown in Figure 1: sample number 1, preparation canvas; number 2, frame wood; number 3, panel wood; and number 4, lower green pigment.

Results and discussion

X-ray fluorescence elemental analyses

Compared with the FTIR analysis, which evidenced mainly the organic compounds of the painting, the XRF is useful in identifying the nature of inorganic painting pigments. The elements identified for each of the XRF measurement spots (as shown in Figure 1) are presented in Table 1.

The predominant chemical element, besides lead whose count numbers vary according to the darkness of the color, is Fe. The absence of Mn and Fe together leads to the conclusion that the pigment applied is natural or burnt yellow ocher (Križnar et al. 2008) mixed with basic earth pigment with organic black (Ca).

Table 1. Elements and their concentrations (%) for each of the XRF measurement locations a, b, c, d, e, f, g, h, and i. The locations are shown in Figure 1.

Sample Element	a	b	c	d	e	f	g	h	i
Calcium	5.19	9.05	1.39	4.14	5.93	1.53	3.29	1.82	3.89
Iron	2.97	0.26	0.36	0.30	0.23	0.24	0.31	0.57	0.62
Lead	1.00	0.07	32.98	2.03	0.16	8.00	8.34	11.18	1.07
Arsenic							1.17		
Titanium	0.16								
Strontium	0.13	0.16	0.11	0.13	0.15	0.15		0.25	0.47
Copper				2.99	3.42		0.08		
Platinum		0.08							
Gold		0.89						0.15	0.12
Tin			1.02			0.26	0.31	0.24	
Bismuth			0.15						
Silver					0.08				
Potassium							1.51		1.36
Mercury								3.69	1.79

The XRF spectrum at location a in Supplementary Figure S1 shows a mixture of red iron and red lead used together with white lead for the brown-ocher color.

The XRF spectrum at location b in Supplementary Figure S2 shows a base layer under the gold that is often used to enhance the smoothness of the surface (al Khasaweh and Elserogy 2019). Gold leaf was used for this paint.

The XRF spectrum at location c in Supplementary Figure S3 identifies lead and iron as a mixture of red iron and white lead results for the red-brown aura of Jesus.

The XRF spectrum at location d in Supplementary Figure S4 indicates that malachite was mixed with lead white in the composition of the green material for the green clothing of St. Elijah on the right side.

The XRF spectrum at location e in Supplementary Figure S5 shows malachite and traces of white lead were present for the light green–brown Jesus.

The XRF spectrum at location f in Supplementary Figure S6 demonstrates the presence of red iron, red lead and white lead in the red icon frame.

The XRF spectrum at location g in Supplementary Figure S7 shows that the brown clothing of Moses to the left contains red lead, white lead and small quantities of red iron.

The XRF spectrum at location h in Supplementary Figure S8 indicates the presence of red iron, red mercury, red lead and white lead in the red rocks.

The XRF spectrum at location i in Supplementary Figure S9 shows that the predominant element in red clothing of Apostles is Hg (Supplementary S9), which reveals that the red pigment applied is cinnabar. The K_{α} peak of sulfur, another characteristic element of this pigment (A. Križnar et al. 2008), is also observed. The small iron peaks show that the painter probably mixed cinnabar with small amount of red ocher.

The presence of lead and iron in all samples that can be attributed to the use of a lead-based paint and an earth pigment (Vagnini et al. 2018).

FTIR spectroscopy

Nondestructive spectroscopy

Red lead was identified to be present in the red paint (Figure 2).

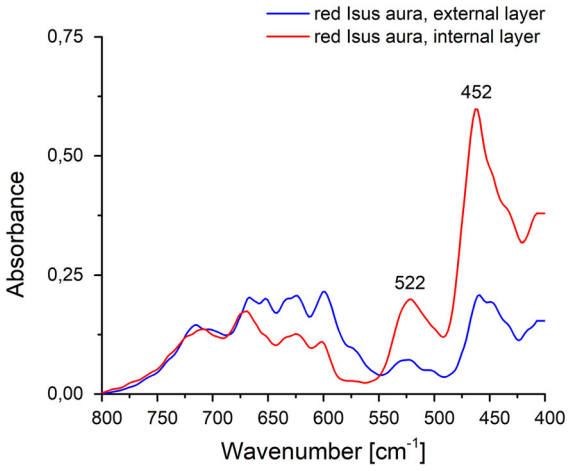

Figure 2. FTIR reflection spectra of the red paint.

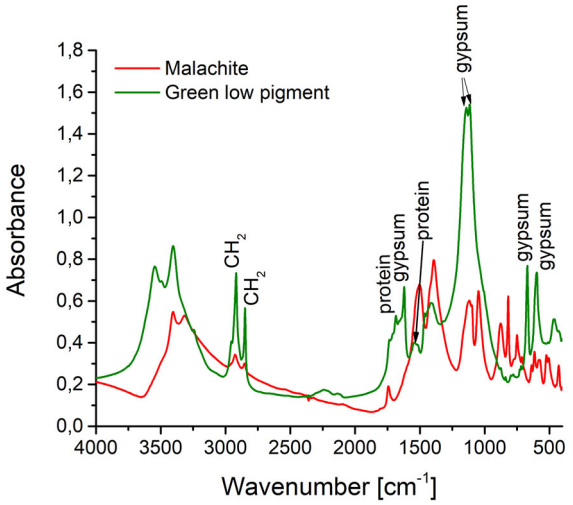

Figure 3. FTIR absorption spectrum for malachite in comparison to the lower region of the green sample.

Destructive spectroscopy

In the FTIR absorption spectra of malachite and the green sample (Figure 3), the following peaks are present: approximately 3400, 1742 as a shoulder, and 1600 to 1400 cm^{-1} due to malachite; 3000 to 2800 cm^{-1} by CH_2 groups from the linseed oil binder; 1629, 1100 to 900 and 700 to 500 cm^{-1} from gypsum; and approximately 1640 and 1540 cm^{-1} due to proteins. Cholesterol, which is a degradation product of egg yolk, was identified as a degradation product at approximately 1680 cm^{-1} as an absorption peak in the spectral massif.

Figures 4 and 5 show the FTIR spectra of the wood used to make the icon. The FTIR spectra of the icon wood panel and frame are compared with the spectra of fir and lime wood. The wood was identified to be fir based upon the specific absorption in its absorption spectral range from 1100 to 900 cm^{-1}.

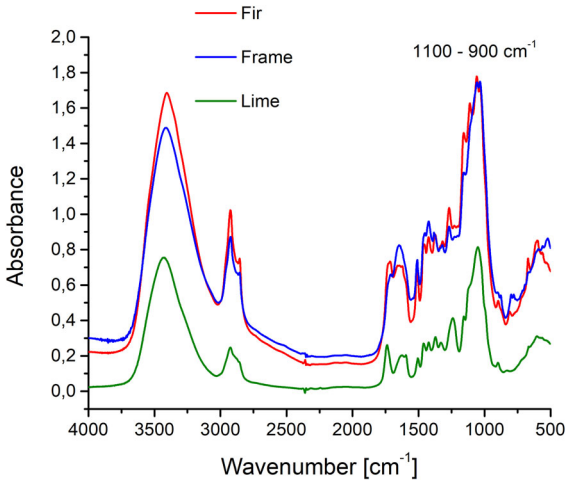

Figure 4. FTIR spectra of frame wood, fir wood, and lime wood.

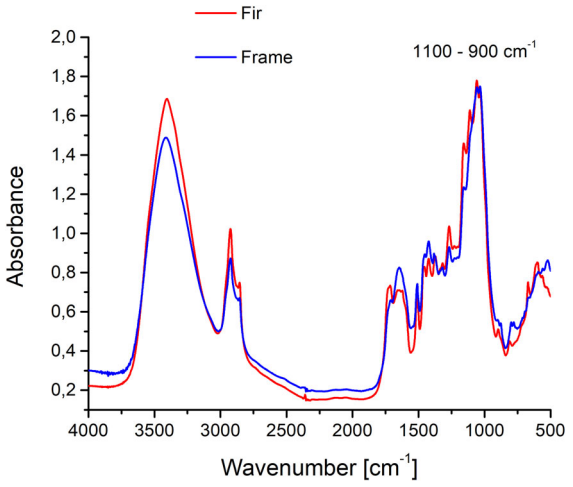

Figure 5. FTIR spectra of icon panel wood and fir wood.

These measurements demonstrate that fir was used for both the panel and the frame of the icon.

Figure 6 compares the spectrum of the canvas from the icon compared to standard spectra of hemp, cotton and linen canvases. The analysis of the specific vibrations present in the spectral region from 2900 to 2700 cm^{-1} shows that a hemp canvas was used by Grigore Ranite to manufacture the icon.

FTIR spectroscopy was employed for the identification of hemp as the textile support for the icon.

Conclusions

Following the complex reported investigations, it has been established that the icon "The Lord's Transfiguration" icon painted by Grigore Ranite was manufactured from a

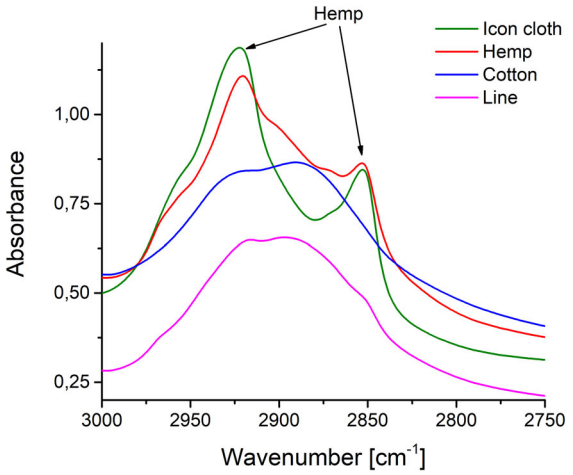

Figure 6. FTIR absorption spectra of the icon canvas, hemp, cotton and linen in the 3000 to 2700 cm^{-1} spectral region.

fir panel on which a hemp canvas was applied. The primer was composed of gypsum and animal glue. The technique employed for the paint layer was *tempera grasa* using egg yolk and linseed oil binder. The pigments used by the painter were: red iron, red lead, cinnabar, lead white, malachite and gold.

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ORCID

I. Bratu http://orcid.org/0000-0002-8575-6549

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