Analytical Letters

ISSN: 0003-2719 (Print) 1532-236X (Online) Journal homepage: https://www.tandfonline.com/loi/lanl20

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To cite this article: D. Neme#, C. Măru#oiu, I. Bratu, C. Neam#u, I. Kacso, O.F. Nemes & I. Udrea (2020): Characterization of the Paint Used by Dumitru Ispas in the Wooden Straja Church, Cluj County, Romania, Analytical Letters, DOI: 10.1080/00032719.2020.1749649

To link to this article: https://doi.org/10.1080/00032719.2020.1749649

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ANALYTICAL LETTERS
https://doi.org/10.1080/00032719.2020.1749649

SPECTROSCOPY

Characterization of the Paint Used by Dumitru Ispas in the Wooden Straja Church, Cluj County, Romania

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ABSTRACT
The wooden Straja Church represents an interesting historical monument from Transylvania that still retains the original popular religious paintings with various degrees of degradation. This paper aims to present the scientific investigation results about the materials and methods used by the painter and his son for both restoration and conservation purposes, and also to enrich the knowledge regarding the work of this author in particular and Transylvanian historical religious art in general. The investigations were performed by means of X-ray fluorescence (XRF) spectroscopy, destructive and nondestructive Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC).

ARTICLE HISTORY
Received 8 November 2019
Accepted 27 March 2020

KEYWORDS
Differential scanning calorimetry (DSC); Fourier transform infrared (FTIR) spectroscopy; painting materials; wooden church; X-ray fluorescence (XRF)

Introduction

Straja is a village documented since 1219 (Gnezted) that hosts an interesting historical monument, the Church of the Archangels Michael and Gabriel (Figure 1), built at the beginning of nineteenth century. The church is built from fir wood placed on an oak base that is composed of the altar, nave and narthex. The entrance is located on the south side and is protected by a porch. The bell tower rises above the narthex which was added later and that is not decorated. The roof is covered with fir shingles. The semicircular altar differentiates and personalizes this monument, enhancing its architectural value. The interior still retains the popular mural painting. The arrangement of religious scenes respects the traditional post-Byzantine standards.

The mural painting was executed by the painter Dumitru Ispas from Gilau with his son Ştefan. The work of the painter Dumitru Ispas was always signed. There is an inscription in the altar written in Romanian with Cyrillic characters on which is provided the date of painting (1806), the names of the painters, Dumitru Ispas and Stefan Ispas, as well as the names of various important members of the community, including the priest, the curator, and other leaders (Cristache-Panait 1980; Vătăşianu 1982; Toşa 1982; Porumb 1982).

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Supplemental data for this article is available online at https://doi.org/10.1080/00032719.2020.1749649.

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Figure 1. Photograph of the wooden Straja Church, Cluj County, Romania.

The investigation of the materials employed by other artists from this geographical area to paint the icons and the interiors of the churches have been carried out using X-ray fluorescence (XRF) spectroscopy, destructive and nondestructive Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) in order to characterize these significant works of religious art (Neamtu et al. 2018; Nemes et al. 2018; Măruīoiu et al. 2016, 2017, 2018; Bratu et al. 2017; Lee et al. 2018; van der Werf et al. 2008).

Experimental

The investigation of the fresco painting layer from the Holy Archangels Michael and Gabriel church from Straja Village, Cluj County was carried out using nondestructive (XRF and FTIR reflectance) and destructive (FTIR absorption spectroscopy and DSC differential calorimetry) spectroscopic methods.

The nondestructive analyzes were performed on the scenes from the altar shown in Figure 2 and on the wall that divides the altar and nave (e.g., the altarpiece) displayed in Figure 3. The destructive analyzes were performed on materials that had peeled off or had fallen off of the layers.

Nondestructive FTIR spectroscopy

FTIR reflectance spectroscopy was performed using a tripod mounted Bruker Alpha II instrument equipped with a contactless forward-looking reflection unit designed for the analysis of paintings. The spectral domain was from 400 to 4000 cm^{-1} with a resolution equal to 2 cm^{-1} using the OPUS/IR software in Windows 10.

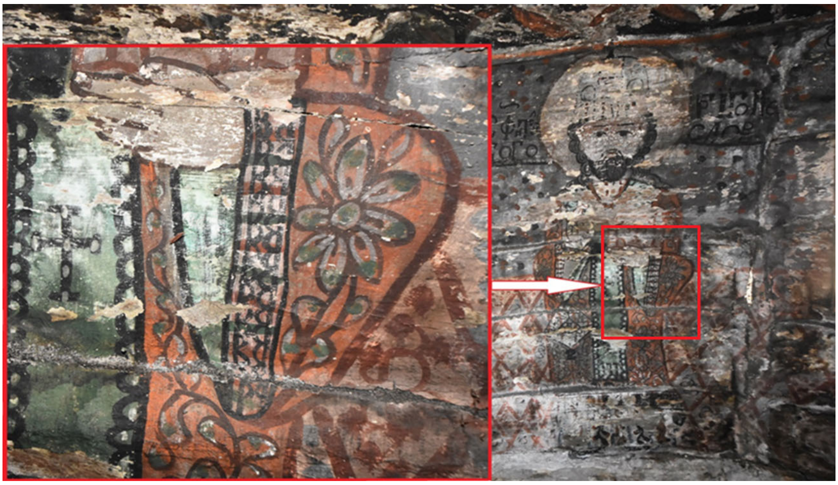

Figure 2. Photograph from the altar of the wooden Straja Church, Cluj County, Romania.

Figure 3. Photograph of the altarpiece of the wooden Straja Church, Cluj County, Romania.

Nondestructive XRF analyses

Nondestructive energy dispersive X-ray fluorescence elemental analyses (XRF) were performed by the use of a handheld model S1 Titan series Bruker spectrometer equipped with a silicon diode PIN detector (SiPIN) and a rhodium target X-ray tube that operating with a maximum voltage of 50 kV. The measurements were performed for 30 seconds with the device located adjacent to the painting surface.

Destructive FTIR absorption spectroscopy

The FTIR absorption destructive technique was employed using samples that had peeled off and fallen from the surface. These measurements were performed by the use of a Jasco 6100 FTIR spectrometer across the 4000 to 400 cm^{-1} spectral domain with a resolution of 4 cm^{-1}. The samples were prepared by use of the KBr pellet technique.

Table 1. XRF results for the paint samples. The concentrations are reported as percentages (%).

Sample	Red	Red-orange	Green	Aura	Blue	White
Element						
Calcium Ca	12.64	8.89	6.02	14.79	18.57	7.37
Iron Fe	**6.97**	0.16	0.28	0.17	**0.42**	0.14
Lead Pb	0.09	**3.67**				**5.62**
Arsenic As		0.46	0.03	**0.39**		0.75
Strontium Sr			0.03		0.25	
Copper Cu	0.03		**12.79**			
Tin Sn		0.15				0.26
Potassium K	1.89	2.12		1.32		2.20
Manganese Mn	0.03			0.05		

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC-60 instrument. The sample was heated from 20 to 550 °C using a 10 °C min^{-1} scanning rate into an aluminum cell in the ambient atmosphere. The Shimadzu TA-WS60 and TA60 2.1 software programs were employed for data collection and analysis. The calorimeter was calibrated by the use of zinc and indium reference standards.

Results and discussion

XRF spectroscopy

The XRF investigations were employed to identify the nature of the inorganic painting pigments. The results for each of the measurements are displayed in Table 1.

The XRF spectrum of the red sample shows that the employed pigment is red iron as shown in Supplemental Figure S1. The XRF spectrum of the red-orange colored sample demonstrates that the pigment present is lead red as shown in Supplemental Figure S2. The XRF spectrum of the green color indicates the used pigment is malachite as shown in Supplemental Figure S3.

The XRF spectrum of the aura sample shows the employed pigment is orpiment as shown in Supplemental Figure S4. The XRF spectrum of the blue material demonstrates that the used pigment is Prussian blue as shown in Supplemental Figure S5. The XRF spectrum of the white color shows the pigment present is white lead (e.g., lead carbonate) as shown in Supplemental Figure S6.

FTIR reflection spectroscopy

The FTIR reflectance nondestructive analysis of dark red pigment is shown in Figure 4. The specific absorption values with the maxima in provided in cm^{-1} were identified along with the responsible functional groups. The peaks at 3425, 626, and 572 cm^{-1} are due to gypsum; 2936 and the 2850 cm^{-1} shoulder are from CH_2 groups attributed to linseed oil; 2136 cm^{-1} are induced by traces of Prussian blue; 1676 cm^{-1} are caused by cholesterol as a degradation product of egg yolk; 1543 and 1330 cm^{-1} due to egg yolk proteins; 1446 and 703 cm^{-1} by calcium carbonate; and 485 cm^{-1} from iron oxide.

The FTIR reflectance analysis of red-orange pigment is shown in Figure 5. The specific absorption peaks with maxima in cm^{-1} were identified at 3487 and 615 cm^{-1} to be

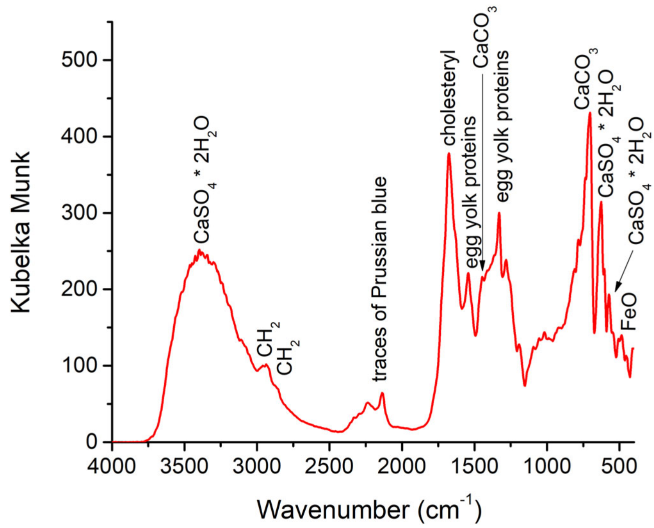

Figure 4. FTIR reflectance spectrum of dark red pigment.

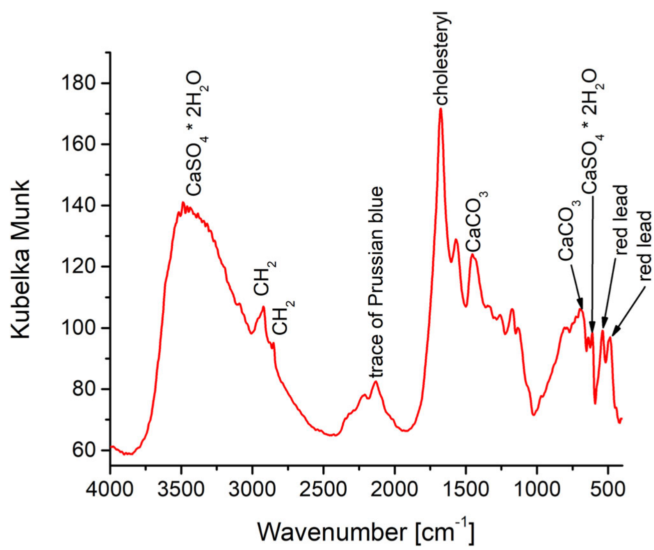

Figure 5. FTIR reflectance spectrum of red-orange pigment.

due to gypsum; 2822 and 2853 cm^{-1} by CH_2 groups attributed to linseed oil; 1677 cm^{-1} from cholesterol as a degradation product of egg yolk; 1454 and 698 cm^{-1} due to calcium carbonate; and 538 and 486 cm^{-1} produced by red lead.

The red pigment was superimposed upon the blue pigment which explains why Prussian blue was identified in the red pigment.

FTIR absorption spectroscopy

The assignments of the infrared bands were made (Colthup, Daly, and Wiberley 1990) by comparing the spectrum of the green pigment from the paintings with the spectrum

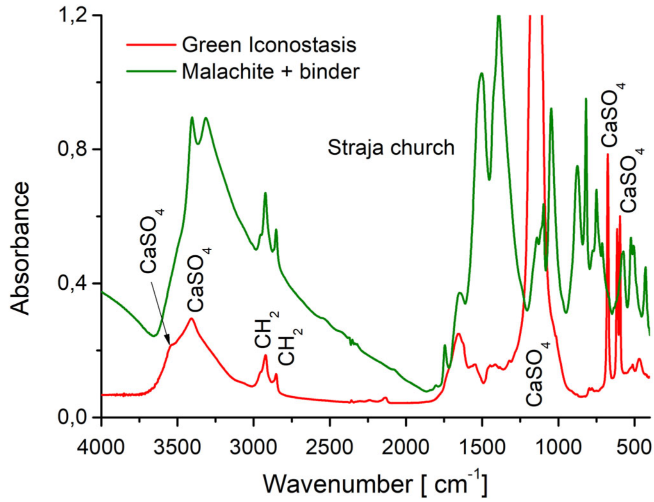

Figure 6. FTIR absorption spectrum of malachite in comparison to a green iconostasis pigment sample.

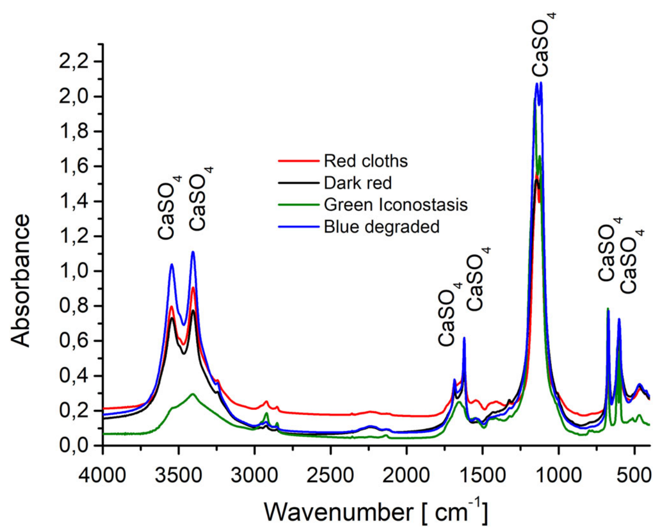

Figure 7. FTIR absorption spectra for the painting materials employed in the wooden Straja Church.

of malachite as shown in Figure 6. The FTIR absorption spectrum of the altarpiece green sample compared to malachite shows the following relevant bands at 3400 cm^{-1}, 1629 cm^{-1}, 1100 to 900 cm^{-1}, and 700 to 500 cm^{-1} due to gypsum; 3000 to 2800 cm^{-1} caused by CH_2 groups from the binder; and 1600 to 1200 cm^{-1} due to the malachite.

Figure 7 presents FTIR the absorption spectra of various painting materials collected from the walls of the wooden church. The destructive FTIR spectra obtained upon the hemp canvas are shown in Figures 8 and 9. The most important results from the FTIR spectral analysis involves the CH_2 group absorptions across the 3000 to 2800 cm^{-1} spectral region shown in Figure 9. These results demonstrate that the canvas from the church altarpiece is composed of hemp.

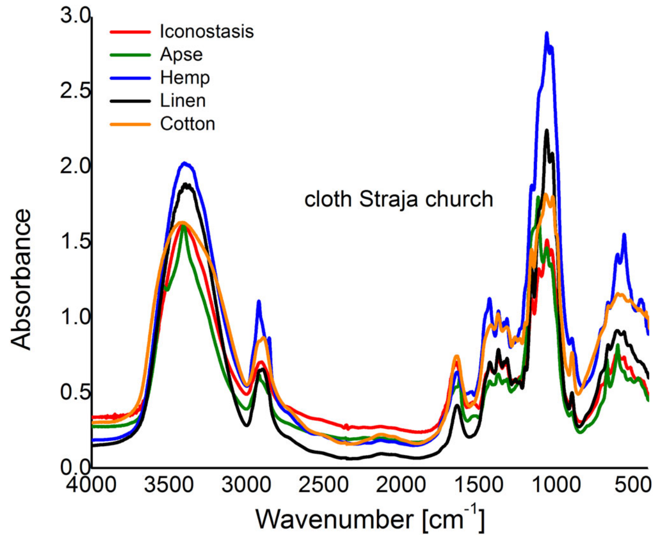

Figure 8. FTIR absorption spectra of the altarpiece canvas across the entire spectral region from 4000 to 500 cm^{-1}.

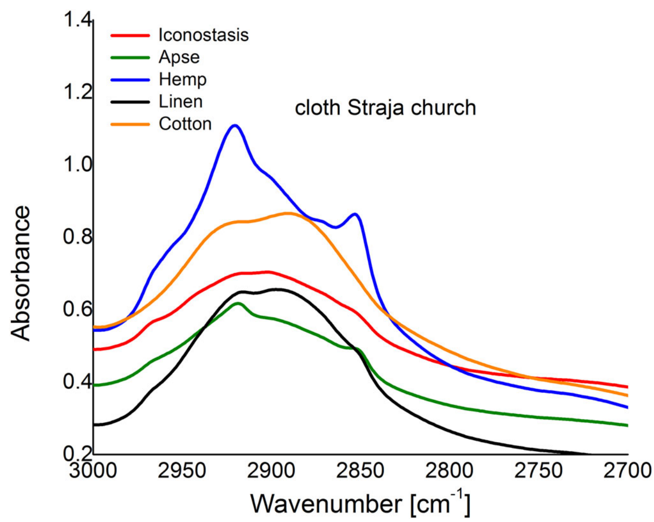

Figure 9. FTIR absorption spectra of the altarpiece canvas across the spectral region from 3000 to 2700 cm^{-1}.

DSC calorimetry

The differential scanning calorimetry (DSC) profile of the analyzed canvas is shown in Figure 10. The thermal analysis was performed using controlled heating and demonstrated a sharp endothermic peak between 120 and 145 °C with onset temperature of 125.2 °C, a peak temperature at 135.7 °C, and enthalpy of fusion (ΔH) equal to -95.58 J g^{-1} due to the loss of absorbed water (Ouajai and Shanks 2005).

Two broad exothermic peaks are present from 270 to 395 °C and from 400 to 480 °C. The first band is caused by the depolymerization of hemicellulose from 320 to 340 °C,

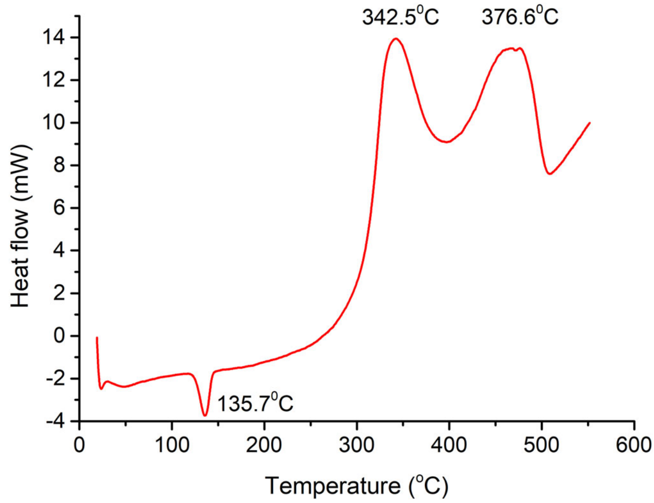

Figure 10. Differential scanning calorimetry profile of the historical canvas from the church altarpiece across the temperature range from 20 to 550 °C using a 10 °C/min heating rate in the ambient air atmosphere that was identified as being composed of hemp cloth.

cellulose from 350 to 370 °C and the degradation of lignin from 310 to 390 °C (Stevulova et al. 2014). The second peak is induced by the oxidative degradation of residues (Stevulova et al. 2017). The identified thermal events are in good agreement with properties of hemp that have been reported in the literature (Le Troedec et al. 2008, Kabir et al. 2013).

Conclusions

In the period between the end of the eighteenth century and the beginning of the nineteenth century when the painter Dumitru Ispas created the studied work of art, the number of available pigments was relatively small that included red iron, red lead, red mercury, orpiment (yellow), malachite (green), chalk white (calcium carbonate), lead white and Prussian blue. These well-known painters also mixed these pigments in order to produced additional colors or shades.

In order to produce the painting at the wooden Straja Church, the artist applied a thin layer of primer on the walls that was composed of gypsum and animal glue. The religious scenes were subsequently painted on this surface according to the Christian dogma. The fresco was prepared using the fresco-secco technique in which the pigments require a binding medium such as eggs (tempera).

The painter employed the tempera-grassa technique which involved the mixing of the egg yolk with the pigment along with a small amount of linseed oil for fluidization. He employed Prussian blue, lead red, iron red, calcium carbonate, malachite, orpiment, and lead white for the pigments. A hemp canvas was used for the altarpiece and was bound with animal glue at the joints of the beams. Additional areas were analyzed, and the obtained results were consistent throughout the artwork.

Funding

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI—UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0812/53PCCDI, within PNCDI III.

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