STUDIA UBB CHEMIA, LXII, 3, 2017 (p. 157-164) (RECOMMENDED CITATION) DOI:10.24193/subbchem.2017.3.12

In memory of prof. dr. Simion Gocan

THE ANALYSIS OF CONSTITUENT MATERIALS OF THE NAOS DOORS BELONGING TO THE WOODEN CHURCH FROM PETRINDU, SALAJ COUNTY

IOAN BRATU^a^{*}, CONSTANTIN MARUTOIU^b^{*}, DANA POSTOLACHE^c, CLAUDIU TANASELIA^d, OLIVIA FLORENA NEMEŞ^b

ABSTRACT In order to preserve and restore the door that separate the Naos and Pronaos belonging to the wooden church of Petrindu, Salaj County, the scientific expertise (with FTIR, XRF spectroscopy and restoring) of the wooden stage and of the painting materials (ground, pigments) was performed. FTIR spectroscopy offers information about the wooden stage whereas XRF and FTIR spectroscopic methods were employed for structural painting materials characterization. These structural data can be correlated with the artistic, theological and historical analysis of this religious patrimony object. After obtaining information about wooden stage and the painting materials, the door was restored.

Keywods: wooden church, painting materials, XRF and FTIR spectroscopy

INTRODUCTION

The forested landscape of Salaj County contained various types of wood species. This made possible for the people to settle in those areas and to acquire the materials to build their homes and churches. The first

^a National Institute for R&D of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

Corresponding author ibratu@itim-cj.ro

^b Babeş-Bolyai University, Faculty of Orthodox Theology, Cluj-Napoca, Romania

^c University of Craiova, Faculty of Orthodox Theology, Romania

^d INCDO-INOE 2000 Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania

I. BRATU, C. MARUTOIU, D. POSTOLACHE, C. TANASELIA, O. F. NEMEŞ

documentary attestation of these localities dates from 1219 [1]. The Tartar and Ottoman invasions resulted in the disappearance of many wooden churches. More were destroyed by Christians like General Bucow (1760 – 1762) or by natural calamities. These adversities did not discourage the inhabitants who raised new churches replacing the destroyed ones. This is also the story of the Petrindu wooden church, Salaj County. The church was built in the Eighteen century, and in 1965 was moved to the "Romulus Vuia" National Ethnographic Park from Cluj-Napoca [2, 3].

The identification of pigments, binders, varnishes or other materials employed in manuscripts, ceramics and other artefacts were recognized for long time as important in understanding our cuttural heritage. The topic is an art-science border subject, being studied intensively by art historians, art curators and scientists involed in preservation and restoration belonging to those museums. Many techniques were employed for this purpose, among them several are specific for the chemical elemens present in pigments, for the molecular groups. One speeks on the electronic microscopy (SEM), X-ray fluorescence (XRF), gas and liquid chromatography coupled with mass-spectrometry, Raman and IR spectroscopy, etc. [4, 5]. Petrindu wooden church has a door separating the narthex and nave (Fig.1). This is a less common occurance in the wooden church architecture [3, 6].

Several Imperial Gates from various wooden churches and other religious objects were already investigated [7-10]. The aim of the paper is the scientific investigation of the painting materials and of the conservation state of the wooden backing (stand) of the gates that separate the Naos from Pronaos and belonging to the wooden church from Petrindu.





Figure 1. The door that separate the Naos and Pronaos belonging to the wooden church from Petrindu: a) before restoration b) after restoration

THE ANALYSIS OF CONSTITUENT MATERIALS OF THE NAOS DOORS BELONGING ...

RESULTS AND DISCUSSION

XRF spectroscopic results

Based on the XRF data analysis presented in Table 1, one can propose the following composition of the painting materials employed: red door-Pb, Hg, As; yellow-As, Cu; red cloths-Fe, As; black-Fe, As; red frame-Pb=Hg> As; green- Cu, As; aura-As; green Dimitrie clothes-As, Fe.

	1		r	r	r	
Sample (door)	Fe mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Hg mg/kg	Pb mg/kg
Red door Nave-Narthex (Left)	357	<lod a</lod 	68	4104	16871	16871
Green (Left)	1324	19583	789	11865	227	227
Yellow clothing (Left)	1226	<lod a</lod 	63	11041	<lod a</lod 	<lod a</lod
White face (Left)	253	<lod a</lod 	84	112	170	170
Red clothing (Left)	5852	76	97	9273	192	192
Black (Left)	1165	<lod a</lod 	289	4689	76	76
Red casing (Left)	1420	<lod a</lod 	1394	13603	73689	73689
Green (Right)	1571	21379	<lod a</lod 	13709	201	201
Red (Right)	739	<lod a</lod 	85	6963	31255	31255
White (Right)	504	<lod a</lod 	<lod a</lod 	137	302	302
Black (Right)	1389	32	<lod a</lod 	232	343	343
Aura (Right)	976	<lod a</lod 	<lod a</lod 	5099	25	25
Red Saint George (Right)	1215	<lod a</lod 	72	4560	21668	21668
Green clothing Dimitrie (Right)	1813	<lod a</lod 	<lod a</lod 	9417	23	23
Red casing (Right)	1023	<lod a</lod 	75	5033	22678	22678

^aLOD limit of detection <20%

I. BRATU, C. MARUTOIU, D. POSTOLACHE, C. TANASELIA, O. F. NEMEŞ

FTIR spectroscopy results

FTIR data obtained for the painting and of the wooden materials are presented in the Figures 2-3.

The significance of the painting materials is given in Table 1.

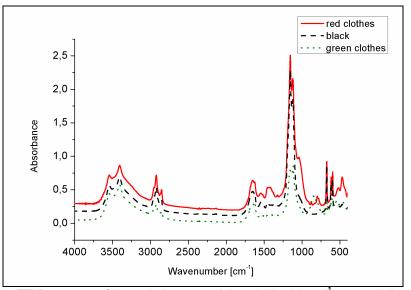
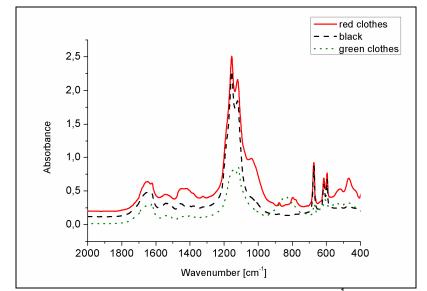
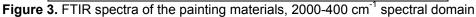


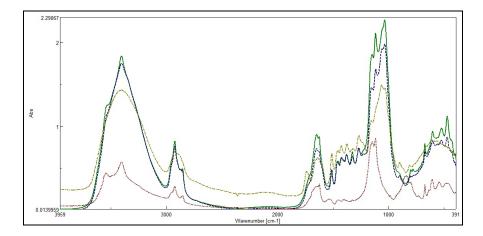
Figure 2. FTIR spectra of the painting materials, 4000-400 cm⁻¹ spectral domain

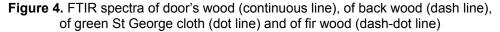




THE ANALYSIS OF CONSTITUENT MATERIALS OF THE NAOS DOORS BELONGING ...

Composition, deduced from FTIR spectra analysis: red lead (470 and 517 cm⁻¹), gypsum (3543, 3406, 1623, 1422, 1155, 1120, 644 and 595 cm⁻¹), traces of carbonate (~1422 and 877 cm⁻¹), aliphatics (2953 cm⁻¹-methyl, 2924 and 2854 cm⁻¹- methylene), proteins (1648, 1541, 1323 cm⁻¹), carbon black. Fig. 4 presents FTIR spectra of different wooden stages.





One can conclude that fir wood was employed for these doors. A report of the wood conservation state is presented in Table 2.

Sample	I cr	TCI	(L/C) ₁	(L/C) ₃
Nave / narthex wood	0.83	0.81	1.53	1.11
Back side wood	0.99	0.87	1.80	1.19
Modern fir wood	1.03	1.32	1.47	1.19

Table 2. Wood conservation state

The crystallinity decreases for historical wood as compared to modern one (see for example the l¹cr and TCI factors in Table 2). The

cellulose content decreased in time as compared to lignin one if we compare the $(L/C)_1$ si $(L/C)_3$ ratios. If we see the background wood, its crystallinity decreased more rapidly in time (see the I^1 cr and TCI ratios), whereas the $(L/C)_1$ increased in time due to a more rapid cellulose consumption than the lignin one.

The wooden assembly after restoration

The wooden assembly after restoration is presented in **Figure 1b**. The methodological approach was established and implemented in conformity with the scientific conservation-restoration principles, original technique, and state of conservation and the results of preliminary research, which was constituted by a set of interventions: gap filling of the support, consolidation of the paintings' layers, removal of dirt deposits, chromatic integration and final coating.

CONCLUSIONS

N-P doors are made from fir wood and the following painting materials were employed: red-red lead, Cinnabar, iron red and red arsenic; yellow-orpiment; black-iron arsenic; green-copper, calcium carbonate, gypsum, proteins.

The conservation-restoration methodology rendered the aesthetic unity of the painted wooden doors; the interventions were based on the minimum intervention principle as well as the interventions on the interior mural paintings (*distemper paint*) of the wooden church. By consolidation interventions, the cohesion of the painting layers with all its qualities were recovered, respectively the elasticity and flatness parameters. The original aesthetic imagery was recovered by the interventions of dirt deposits removal and the image disruptions caused by the extended lacunae and erosions were altered by means of chromatic retouching of the erosions.

EXPERIMENTAL SECTION

The door that separated the two chambers is made from two wooden pieces anchored by the wall using hinges (Fig. 2). The doors are painted by Dimitri Ispas from Gilau and each door is divided in two scenes, each portraying a saint. The door to the right measures 146 by 41.5 cm and portrays Saint George and Saint Dimitrie. The door to the left measures 146 by 40 cm and portrays Saint Martyr Nestor and Saint Martyr Lup. The painting was executed in Tempera on wood.

THE ANALYSIS OF CONSTITUENT MATERIALS OF THE NAOS DOORS BELONGING ...

X-ray fluorescence measurements were performed *in situ* using an INNOV-X Alpha-6500 portable instrument (35 kV voltage, 15 μ A intensity, 3 mm filter, Be window, 2 square mm spot size and PIN Si detector). Integration time was set to 60 seconds, in two consecutive runs of 30 seconds each. FTIR measurements were done with a JASCO 6100 spectrometer in the 4000 to 400 cm⁻¹ spectral range with a resolution of 4 cm⁻¹ employing the KBr pellet technique.

Wood preservation status

In order to determine the preservation status of the Imperial Gates' wood, several indexes are defined [11]: $I_{cr}^{1}=A_{1377}/A_{669}$, or as TCI= A_{1378}/A_{2925} (Total Crystallinity Index) and LOI= A_{1426}/A_{895}) (Lateral Order Index), A being the absorbance at maximum for each absorption band. The lignin/cellulose ratios, defined as [12] (L/C)₁= A_{1506}/A_{1738} and (L/C)₃= A_{1506}/A_{895} were calculated for wooden samples in agreement to these definitions. They can be used only as a measure of their evolution in time.

For an optimal methodological approach of the restoration of the wooden painted doors, consolidation and cleaning preliminary tests were done. Consequently, the consolidation of the painted layer was done using the aqueous solution of fish glue, in a very poor concentration, which rendered best the cohesion of the painting layers. The removal of dirt deposits was done by the use of tested solvent mixtures and mechanically with a surgical scalpel, both on the verso and recto of the doors. Chromatic attenuation of the erosions and lacunae was done using *rittocco* and *velatura techniques* with water-based colours. In the end, the whole painted surface was coated by a protective thin layer, which also has an important aesthetic role in controlling the glossiness of the painting.

DISCLOSURE

I. Bratu and C. Marutoiu are co-first authors

ACKNOWLEDGMENTS

Thanks are due to UEFISCDI for financial supporting on PN II-PT-PCCA-2013-4-1882 project I. BRATU, C. MARUTOIU, D. POSTOLACHE, C. TANASELIA, O. F. NEMEŞ

REFERENCES

- 1. Nicolae lorga, *Istoria bisericii românești și a vieții religioase a românilor*, vol. I, cap. III, "Cele d'intaiu biserici romanesti", Tipografia "Neamul Românesc", Vălenii-de-Munte, **1908**.
- 2. Ioana Cristache-Panait, Bisericile de lemn din Sălaj". *Buletinul Monumentelor Istorice* **1971**, *1*, 31.
- 3. Leontin Ghergariu, Meșterii construcțiilor monumentale de lemn din Sălaj". Anuarul Muzeului Etnografic al Transilvaniei, editia **1971-1973**: 255-273, Cluj.
- 4. L. Burgio, R.J.H. Clark,, L. Sheldon, G.D. Smith, *Analytical Chem*istry **2005**, 77, 1261.
- 5. Andreotti, L. Bonaduce, M.P. Colombini, G. Gautier, F Modugno, E Ribechini, *Analytical Chemistry*, **2006**, *78*, 4490.
- Ioan Godea, Ioana Cristache-Panait, Monumente istorice bisericesti din Eparhia Oradei, judetele Bihor, Salaj si Satu-Mare. Bisericile de lemn, Ed. Episcopiei Ortodoxe Romane a Oradei, Oradea, 1978
- 7. Măruţoiu, I. Bratu, L.Troşan, C. Neamtu, V.C. Măruţoiu, D. Pop, C.Tănăselia, S. Garabagiu, *Spectrochim Acta A, Molecular and Biomolecular Spectroscopy*, **2016**, *152*, 311.
- 8. Măruțoiu, I. Bratu, A.M. Budu, Gh. Şanta, O. F. Măruțoiu, C. Neamțu, C. Tănăselia, I. Kacso, I. C. A. Sandu, *Revista de Chimie*, **2015**, *66* (7) 992.
- Măruţoiu, L. Troşan, V-D. Toader, Z. Moldovan, Al. I. Turza, C. Tănăselia and I. Bratu, Studia UBB Chemia., 2013, 58 (4), 161.
- 10. Hernanz, I. Bratu, O.F. Măruţoiu, C. Măruţoiu, J. M. Gavira-Vallejo, H.C.M. Edwards, *Analytical and Bioanalytical Chem*istry, **2008**, 392, 1-2. 263.
- 11. M. Popescu, Y. Sakara, M. C. Popescu, A. Osaka and C. Vasile, *e-Preservation Science*, **2005**, *2*, 19.
- 12. C.M., Popescu, M.C Popescu, C Vasile, International Journal of Biological Macromolecules, **2011**, *48*(4), p.667.