

FTIR ANALYSIS OF PAINTING MATERIALS FROM THE CHURCH SAINT PARASCHIVA, OF POIENILE IZEI, MARAMUREȘ, ROMANIA

Constantin MARUȚOIU^{1*}, Ioan BRATU²,
Alin TRIFA¹, Mariana BOTIȘ¹, Victor Constantin MARUTOIU¹

¹⁾ University Babeș-Bolyai, Faculty of Orthodox Theology, 18 Avram Iancu Square, Cluj-Napoca, Romania;

²⁾ National Institute for Research and Development of Isotopic and Molecular Technologies Cluj-Napoca, 65-103 Donath str. 400293, Cluj-Napoca, Romania

Abstract

This paper presents the research and the results of FTIR analyses on samples of immobile paintings on the wooden walls, taken from the Church Saint Paraschiva from the Village of Poienile Izei, county of Maramureș, Romania, a UNESCO World Heritage List monument. These analyses were meant to certify the type and origin of the materials used in the grounding and paint layers of the late 18th c. pictures inside this wooden church. The results obtained, revealed us that other materials had been used than expected. Results also can help in the future conservation-restoration intervention, especially in cleaning and retouching.

Keywords: mural painting; wooden church; FTIR.

Introduction

The church of Saint Paraschiva is situated in the village of Poienile Izei and lies in the very heart of Maramureș County. It was built in 1604 on a hill from the center of the village and is considered to be the most well preserved monument of the wooden architecture from Maramureș [1, 2]. The exceptional artistic qualities as well as the cultural and historical signification of the architectural ensemble, were the bases on which the church was included in 1999 on the list of the UNESCO World Heritage List, as an universal patrimony, along with the most prestigious artistic creations of the world.

The church of Saint Parascheva is built of fir, less the first row of beams from the bottom of the church and the skeleton of the tower, which are made of oak tree.

The church of Saint Paraschiva is built of fir (timbers, or a combination with European (Norway) spruce (*Picea abies*), or European (Scots) pine (*Pinus sylvestris*)) beams and is very well proportioned, managing to render a strong impression of monumentality (Fig. 1). The walls rise on a dry stone masonry and are made of manually carved with ax wide beams, being built at two levels. The nave of the church has a rectangular plan, being divided into nave, called the men's church, and narthex, called the women's church [3]. The opened exonarthex is situated on the west wing. The Altar Apse is unhooked, having a square form. Two architectural elements allow us to assume that the church was built before the fifteenth century: the Altar's apse, with four sides, and the way of jointing of the beams [4].

* Corresponding author: cmarutoiu@yahoo.com

The roof with shingle, has a double lap, and the tower that shelters the beams is set with pavilion with two arches, and not with three, as would be done later (it's an element specific for the older churches). The sharp and very splay coif lies on the short pillars of the pavilion, rising towards the sky in order to sustain the cross.

It should be noticed that on the top, right below the cross, there is a metal half-moon, which is said to have been placed there so the church wouldn't be destroyed by the Turk and Tatar invaders, during their incursions in Maramureş. Thus, the church managed to escape [5, 6].



Fig. 1. The wooden church from Poienile Izei

The immobile paintings on the wooden walls of the church were made between the years 1793-1794, as it is written on the (timbers of the nave, around the bottom of the barrel vault. From iconographical point of view, due to the artistic and cultural relations with Moldova, the painting fits the typology of the byzantine art, typical for the Orthodox Erminia [7].

The painting consists of large scenes, three or four in each register, closed in simple rectangular frames. Through its thematic and artistic qualities, but especially through the idea that stood behind its concept, it offers a repertoire of new themes, which reflects the local spirituality. The characters, few in every scene, are grouped around the main action, which has a role of symmetry axis. In their movements, we can see sometimes echoes of the Baroque style, especially in the depiction grounding of the four Evangelists, depicted lying down, with their clothing waving around their bodies. The characters wear rich costumes, depicted rendered (grounded) in volume through the shaping of the color (Fig. 2 and 3).

The stereotypical figures have their features shaped with brown over ocher color, uniformly laid, with pink cheeks. Their eyes are rendered only through a contour and the point

of light, while the chins and the noses are rendered through some lines that have nothing to do with naivety. The background of the scenes is schematic and imprecise, often being reduced to a landscape of hills (suggested through the use of two or three nuances of green), or more rarely, to architectures made of groups of houses with triangular roofs, and semicircular arches, or of churches with Baroque towers, made of over posed bulbs.



Fig. 2. The Way of the Cross, scene depicted on the northern wall of the nave.



Fig. 3. The Last Judgment, fragment, scene depicted on the northern wall of the narthex.

The decorative motives that separate the scenes are very simple, being made of concentrically nervures. The chromatic scale is enriched by nuances, such as colours and pigments similar to permanent red, brown, green Veronese, emerald green, olive, ochre, yellow, grey blue, white and black.

From technical point of view, the painting was applied as it follows. On the wooden wall of the church was applied a canvas, which played a multiple role. First of all, it consisted in a support for the painting, making the connection between the wood and the grounding. It also contributed for the smoothing of the surface of the wall, but also for the thermal isolation. The

painting applied above, seems to have been made in fat tempera and varnished with wax; that should explain the shiny and pasty aspect of the colors [7].

Yet, because the analysis with the naked eye wasn't able to relieve the precise nature of the materials that have been used both for the primer and for the color layer, the initial assumptions have to be verified with the aid of some specialized analyses [8].

Experimental data

The FTIR spectroscopy, the analytical technique that we want to use in order to find out more details, is an analytical technique based on the structure of molecules which generally offers qualitative results, but, with opportune calibrations, quantitative analyses may be done. By this technique may be analyzed the functional groups that characterize the next type of compounds: inorganic, (sulfates, carbonates, nitrates, phosphates, silicates) and organics (oxalates, other organic molecules, oils, animal glues, waxes, resins, fats) [9].

Through this method were analyzed the varnishes made with turpentine resins, the polysaccharide used as binding material in some paintings, the gelatin, the pigments. M.T. Domenech Carbo and his collaborators, managed to analyze through the FTIR spectroscopy the varnishes extracted from the surfaces of the paintings, binding materials, pigments, and inert materials from the preparation [10]. Finding the organic binding medium in a layer or in the ground of an icon, may be more difficult if the latter is present in a small quantity. In analyzing the colors used, is useful the identification of the absorption bands of the binding material that may be covered through the overlapping of the specific values of the pigment. The average value of the limit of revealing of a mixture is about 5%. The sensitivity to the compounds in small quantities may be increased in some cases through the extraction with solvents from solid samples, with the aid of some elaboration techniques on registered spectra, such as the method of the subtractive spectrum and spectral deconvolution.

Another method used is the IR microscopy associated with the FTIR spectroscopy. Exposed to some IR radiations, the molecules selectively absorb the radiation with the frequency that suits its modality of vibration. Through measuring the absorption of the IR radiation by the analyzed sample, as function of frequency, a spectrum is obtained that may be used in identifying the functional groups and, as a consequence, the structure of the compounds.

The devices used consisted of a 6100 JASCO FTIR spectrometer, an IRT-3000 microscope, and Spectral Analysis software for spectra administration. The spectrometer may be used with KBr pellet technique or in association with the IR microscope. The microscope allows collecting the spectra of some extremely small samples (several hundreds of square micrometers) [11-14].

The paintings were made by using linseed linen on the wood support used for the church construction. Fragments of red and ochre (Fig. 4 and 5) were taken from the northern part of the nave of the church, from the scene with the Unmerciful Rich and the Poor Lazarus. The green sample (Fig. 6) was taken from the south part of the nave, from the base of the scene of the Healing of the paralytic. It was also analyzed a fragment of canvas, taken from the jointing of the beams. Fragments of canvas, canvas deposition and blue were collected and analyzed, also.



Fig. 4. Red sample

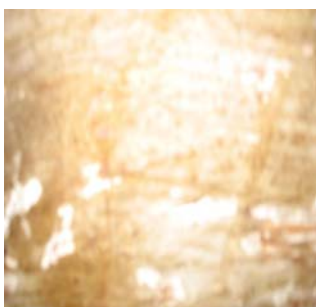


Fig. 5. Ochre sample



Fig. 6. Green sample

Results and Discussions

The spectra inserted below (Fig. 7 and 8), present the FTIR analysis applied on the samples taken from inside the church in two different wave number region, 4000-2500 and 1800-400 cm^{-1} ones, respectively.

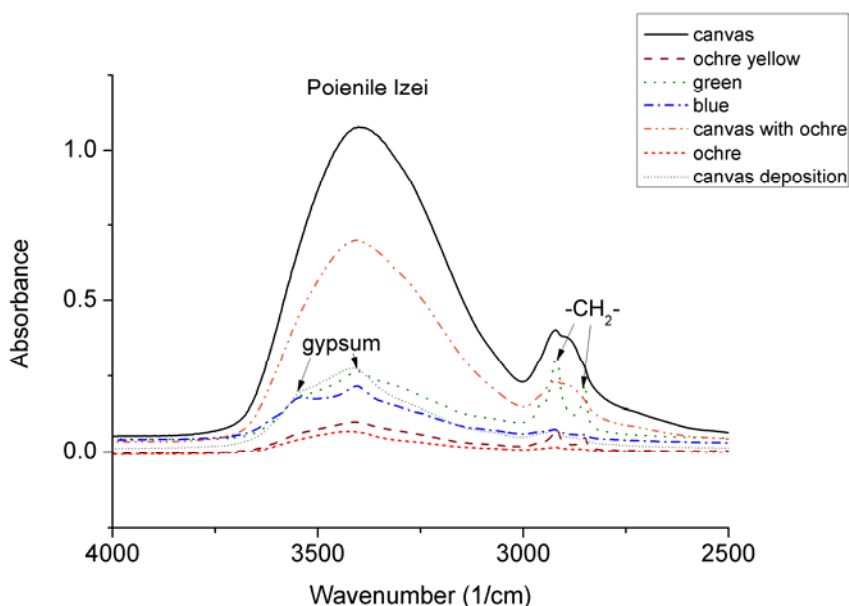


Fig. 7. The FTIR spectra of the canvas and pigments samples, 4000-2500 cm^{-1} spectral domain.

The qualitative FTIR analyses made on the samples extracted from the samples of painting have revealed the following aspects. The material used for the grounding was the lime, and gypsum, as it may be noticed in the FTIR spectra (IR absorptions at ~ 1420 and 870 cm^{-1} for lime and at 1153 and 612 and 670 cm^{-1} for gypsum, respectively). The painting was made on a composition of lime putty mixed with egg yolk (with their specific absorptions found in the $3000\text{-}2800$ and $1800\text{-}1400 \text{ cm}^{-1}$ spectral regions). The composition was applied directly on the wood, in two layers. It is interesting to notice the fact that this grounding took the shape of the wood on which it was applied, including that of the canvas between the beams.

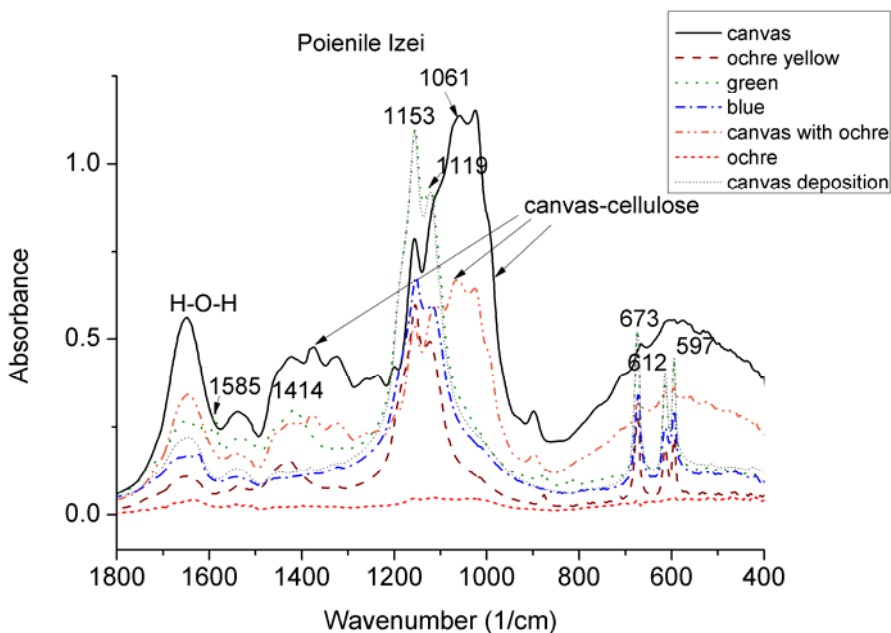


Fig. 8. The FTIR spectra of the canvas and pigments sample, 1800-400 cm^{-1} spectral domain.

The colors were mixed with egg (egg tempera) (best viewed in the ochre FTIR 3000-2800 cm^{-1} spectral region) and applied on a drawing made in situ. From the above spectra, we found out the nature of the colors used:

- the green is malachite (copper hydroxycarbonate) (the absorptions located at 1420 and 870 cm^{-1}) with some grounding;
- the blue is azurite (also known as copper hydroxycarbonate, but with different ratios between hydroxide (1640 cm^{-1}) and copper carbonate (1420 cm^{-1}); the two pigments, ochre-yellow and ochre-red (specific absorptions between 700 and 400 cm^{-1}), are cinnabar (or vermillion)
- There have also been used the following pigments in the Poienile Izei wall picture: white of lead, ochre yellow, ochre red, red cinnabar, green earth, blue azurite, iron black.
- During the restoration of the painting which took place between the years 1962-1964, there have been made some interventions and retouches. One can notice that the reparations of the grounding were made with gypsum mortar. At the same time, the painting was varnished with bee wax.

Conclusion

The analyses that have been made, and which revealed us the painting materials used at the church of Saint Paraschiva, offers us a correct perspective over the new restoration interventions that should be done. Just knowing very precisely the chemical type, structure and composition of all these materials, the future intervention could be accurate and adequate. Thus, one we will be able to avoid every potential incompatibility between the pigments and grounds, on one hand, and the solvents that will be used in the cleaning, on the other hand.

References

- [1] G. Cristea, **Maramureș, un muzeu viu în centrul Europei**, Ed. Fundației Culturale Române, București, 2000, p. 83.
- [2] I. Bârlea, **Însemnări din bisericile Maramureșului**, Ed. Atelierele Grafice SOCEC & Comp., Societate Anonimă, București, 1909, p. 252
- [3] E. Costin, **Bisericile de lemn în Maramureș**, Ed. Gutinul, Baia-Mare, 1999, p. 41.
- [4] I.D. Ștefănescu, **Arta veche a Maramureșului**, Ed. Meridiane, București, 1968, p. 82.
- [5] I. Lupaș, **Istoria bisericească a românilor ardeleni**, Ed.Arhidiecezană Sibiu, Sibiu, 1918.
- [6] S.Pascu, **Voievodatul Transilvaniei**, vol.III, Ed.Dacia, Cluj-Napoca, 1986
- [7] M. Porumb, **Bisericile de lemn din Maramureș**, Ed. Academiei Române, București, 2005.
- [8] P. Cremonese, **L'uso dei solvent nella pulitura di opera policrome**, Ed. Edifir, Firenze, 2003, p. 59.
- [9] K. Keune, *Binding medium, pigments and metal soaps characterized and localized in paint cross-section*, **PhD Dissertation** University of Amsterdam, Molart Series (11), AMOLF, Amsterdam, 2005, pp. 128-132, or **MOLART Reports**, 11, FOM Institute of Atomic and Molecular Physics. MOLART Project for Painted Art, 2005, p. 43.
- [10] M. T. Domenech Carbo, F. Bosch Reig, J.V. Gimeno Adelantado, V. Peris Martinez, *Fourier transform infrared spectroscopy and the analytical study of art for purposes of diagnosis and conservation*, **Analytica Chimica Acta**, **330**, 1996, pp. 207-215.
- [11] A. Hernanz, I. Bratu, O. F. Marutoiu, C. Marutoiu, J. M. Gavira, H. G. M. Edwards, *"Micro-Raman spectroscopic investigation of external wall paintings from St. Dumitru's Church, Suceava, Romania."* **Analytical and Bioanalytical Chemistry**, **392**, 2008, pp. 263-268 (2008).
- [12] A.Baciu, Z.Moldovan, I.Bratu, O.F.Marutoiu, I.Kacso, I.Glajar, A.Hernanz, C.Marutoiu, *Comparative Study of the Painting Materials of a Series of Orthodox Icons on Wooden and Glass Support from Transylvania*, **Current Analytical Chemistry**, **6**, 2010, pp 53-59.
- [13] S. Bruni, F.Cariati, F.Casadio, L.Toniolo, *Identification of pigments on a XV Century illuminated parchment by Raman and FTIR microspectroscopies*, **Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy**, **38**, 1999, pp.1371-1377.
- [14] 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**, 2008, pp.65-76.

Received: December 02, 2010

Accepted: February 12, 2011