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Professor Candin Liteanu on his 100th anniversary

COMPLEX INVESTIGATION OF COMPONENT MATERIALS OF TRIPTYCH ICON "MOTHER OF GOD" FROM THE PATRIMONY OF ETHNOGRAPHIC MUSEUM OF TRANSYLVANIA

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A triptych icon from the 18th century from Moeciu de Sus village, Braşov County, Roumania was investigated by physical-chemical destructive methods: Fourier Transform Infrared (FTIR) and Electron Impact Mass Spectrometric Techniques (EI-MS), as well as thermal analysis by Differential Scanning Calorimetry (DSC). There were identified: gypsum as ground, pigments from the painting layer (white, red and blue), binder (egg yolk for painting layer) and animal glue for ground and as varnish conifer resin. The triptych wooden support is lime (as being identified by FTIR and DSC techniques). The icon oldness was confirmed by the presence of Prussian blue, by the increasing of wood lignin/cellulose ratio and of the amorphous content of cellulose structure.

INTRODUCTION

The icon is the spiritual treasure of the Orthodox Church. It is a valuable document for restoring the artistic environment of the past, most icons deriving directly from the mural painting.

In sobriety of its asceticism the icon doesn't represent, but it confesses presence. The icon has created a religious phenomenon, specific to icons cult, which is essentially a manifestation of religious feeling, of expressing emotion and religious experience to the divinity present in icons.

Testimonies of faith and piety of Christianity, the icons were (treasured) conserved sacredly from ancient times until today showing steadfastness of the Church. Worship the holy icons of the Redemer, the Virgin, the Angels and Saints is a basic teaching of the Orthodox Church.

The investigation of painting materials employed for wooden icons was performed by different analytic techniques such as: FTIR and Raman spectroscopy, X-ray diffraction, X-ray fluorescence and thermal analysis. [1, 2]

The "Triptych" icon on wood originates from Moeciu de Sus village, Braşov County and it was

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purchased by the Ethnographic Museum of Transylvania from Cluj-Napoca city. The item registered with no. 3406 comes from the end of the 18th century and it is painted using tempera paint on an unprepared with primer wooden support. [3]

Central icon has dimensions of 32.2 x 22.5 cm thick wood panel 1.4 cm and doors dimensions of 26.3 x 10.7 cm and about 0.5 cm thick, cut in the form of shrine doors painted just outside and hanged to central icon with metal hinges.

Central icon depicting the "Mother of God" held on her left arm, with a vase with flowers (three lilies) and a tall candlestick with three candles on lateral sides, see Fig. 1. Doors that close the central scene are painted on the external side with several scenes grouped into three registers. At the top are represented the two archangels, one of them holds a cross in his hand and the other raised his sword and globe to mark "XC". In the middle are painted four Martyrs and Saints and in the lower register appear two military saints on horseback.

The support of icon in made from a single piece of wood, carved with decorative elements on the front panel like a frame. The wood is easily deformed showing rippling zones and has deposits of dirt adhering both front and back, some being strongly adherent, others being superficial. The wood is cracked in two areas (10 cm and 5.5 cm) and on the lower edge of the decorative elements.

The pictorial layer is scaled off and present losses, the varnish layer became brown over time, modifying the entire chromatic range. Hanging system is missing but there is a trace of nail metallic upper edge of the panel.

Triptych doors painted on the front present the same damages as the pictorial layer from the front panel. The wood has a slight deformation, cracks in wood fiber (8 cm) to the right door of the triptych and missing hinges on both doors. Inside the door is unpainted perhaps this area was used for writing commemoration.

The purpose of this article is to identify painting materials (pigments, binders, varnishes, etc.) and the base materials used for making this whole triptych, which is of great importance in understanding our cultural heritage. The items studied are the border art – science and show more interest to art historians, curators, conservation specialists and scientists.

RESULTS AND DISCUSSION

Small quantities of samples for investigations were collected from different sites of the Triptych Icon and were analyzed by using several techniques as is mentioned in Table 1.

FTIR analysis of painting materials

The proposed composition, see Fig. 2 is as follows: gypsum (~3483 and 3395 cm^{-1}, the intense absorptions at ~1620, 1161 and 1104 cm^{-1} and the doublet at ~670 cm^{-1}, see ref. [4], binder (egg yolk, aliphatic bands 3000-2700 cm^{-1}, protein Amide I and Amide II bands at ~1640 and 1560 cm^{-1}, respectively [1]; conifer resin ~aliphatic frequencies between 3000-2800 cm^{-1} ; Prussian blue (band at 2090 cm^{-1}), present also in white sample; lead minium (specific absorptions at 470 and 530 cm^{-1}).

Fig. 1 – Triptych wooden icon status: a) closed form and b) open form.

Table 1

Samples for analysis

Sample	Area of analytical sampling	Sample type	Quantity (mg)	Analysis
1	Left icon, left corners; right icon horse	gypsum	6	FTIR
2	Central icon left arcade	gypsum	4	FTIR
3	Central icon wooden ornaments	resin	5	EI-MS
4	Behind of sideway icons	resin	7	EI–MS
5	Sleeve and hand of Holy Mother	binder	4	EI-MS
6	Clothes and hands of Saints, middle register of left icon	binder	4	EI-MS
7	Left sleeve of Holy Mother, bottom part of Jesus' garment; St.George's horse	red pigment	5	FTIR
8	Right and left corner of central icon; St. George's cloak	blue pigment	5	FTIR
9	Jesus cloak and vase of central icon; white horse right sideway icon	white pigment	5	FTIR
10	Edge of the left side icon	wood	40	FTIR, DSC

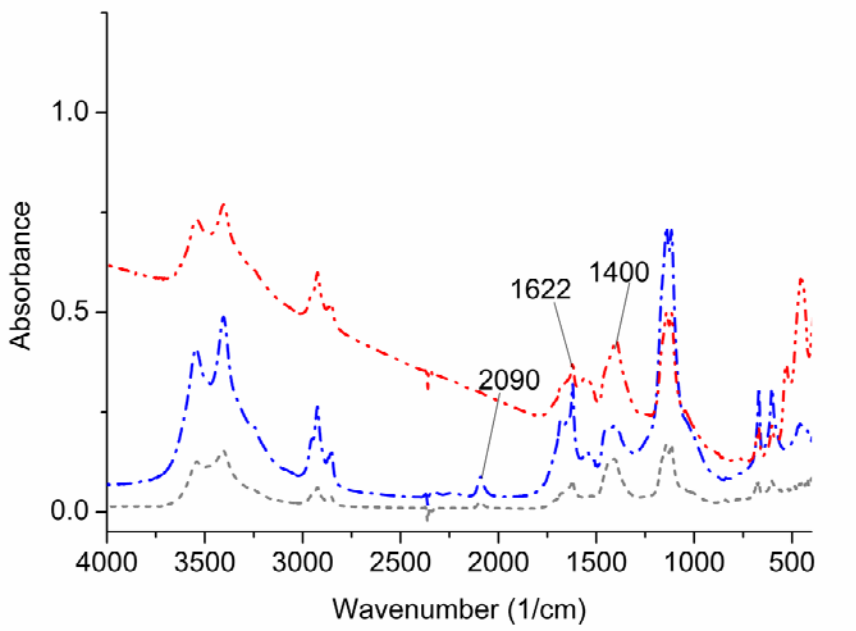

Fig. 2 – FTIR spectra of wooden icon painting materials: dash dot dot line – red painting material; dash-dot line – blue painting material; dash line – white painting material.

Identification based on FTIR spectroscopy of the wooden support and of its "health" state.

The 3406 icon does not contain the wooden essence in its catalog. Based on comparative analysis of FTIR spectra (see Fig. 3) one can assume that wooden support is of lime essence.

If the wooden support is lime, L/C ratios (see Table 1) are higher for icon wood than for lime wood, the wood cellulose is destroyed faster in time than lignin; I_{cr} (the crystallinity index) is lower for icon wood than for lime wood, the cellulose becomes more amorphous in time.

Differential Scanning Calorimetry

The two exotherms observed in the DSC analysis of lime wood at 330 and 440°C, see Fig. 4, and were assigned to amorphous polysaccharides and to mixtures of lignin and polysaccharides, respectively.[5]

One notes a lignin/cellulose ratio increasing for icon wood as compared to lime wood employed as standard and a smaller increase of characteristic temperatures both for cellulose and lignin[6] and peaks broadening also – an indication that during time the wood becomes more amorphous.[7]

Electron Impact Mass Spectrometry (EI-MS)

The sample was examined in details by Mass Spectrometry. The conditions are described in Experimental section. The obtained data revealed that this wooden icon contains natural resins. A characteristic mass spectrum is shown in Fig. 5.

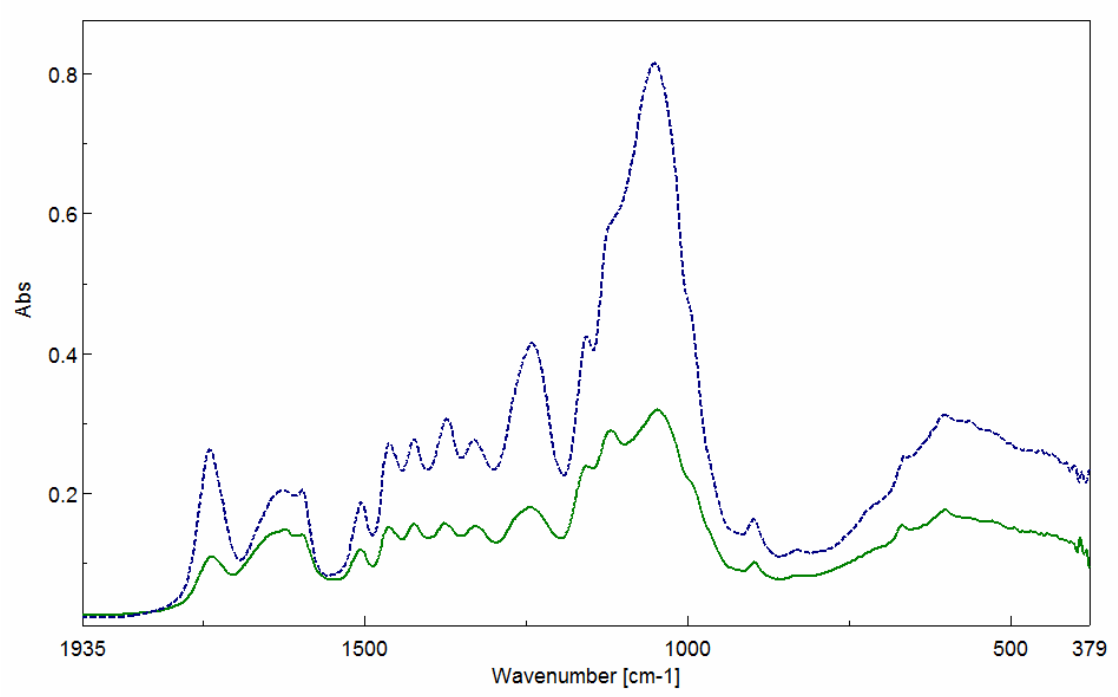

Fig. 3 – FTIR spectra of wooden samples: line 3406 wooden sample; dashed line – lime wood.

Table 1

"Health" status of wooden samples

Sample	I^1_{cr}	I^2_{cr}	TCI	$(L/C)_1$	$(L/C)_2$	$(L/C)_3$
3406	1.02	2.40	1.17	1.10	0.50	1.19
Modern lime	1.20	3.05	1.22	0.70	0.44	1.15

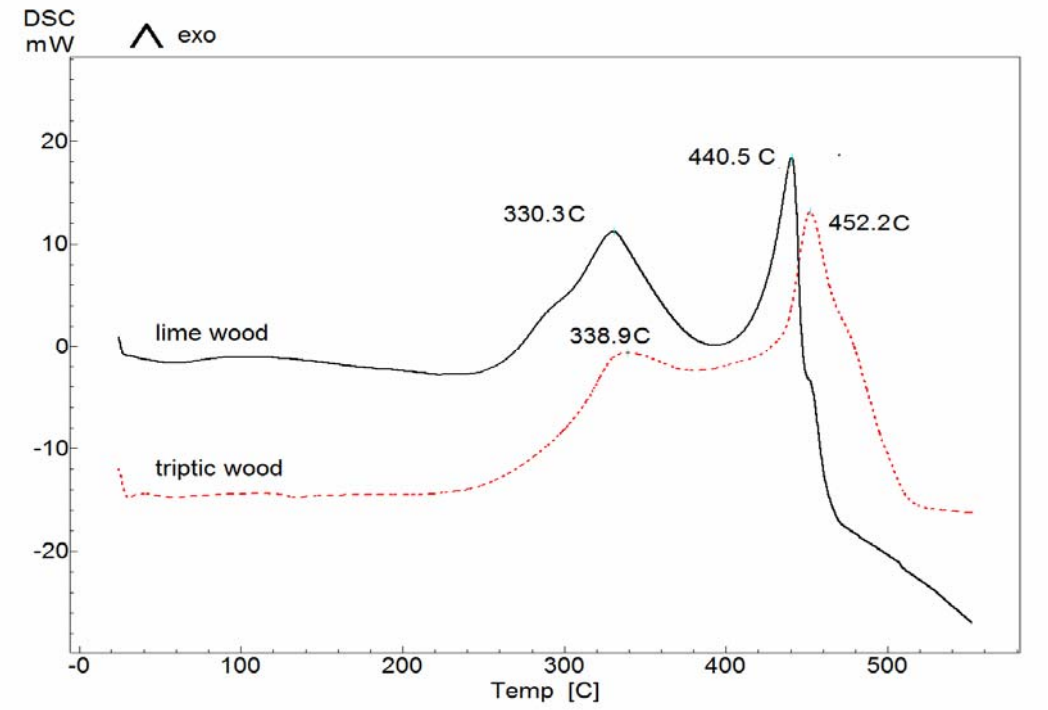

Fig. 4 – DSC curves of: icon wood (dash line) and lime wood (solid line).

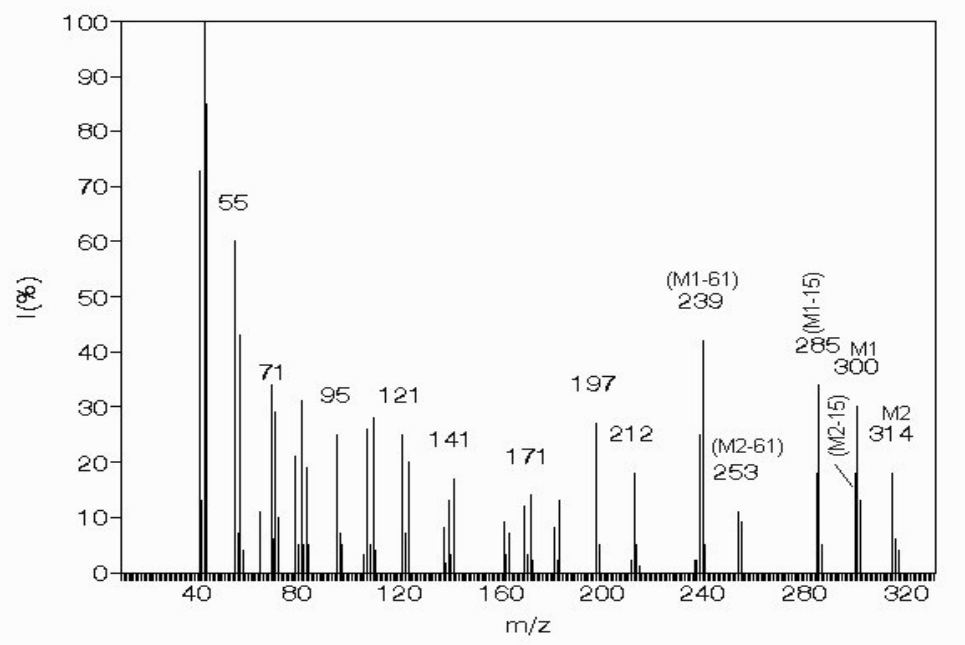

Fig. 5 – The EI Mass Spectrum obtained from 3406 triptych icon by direct introduction of the sample. The temperature of sample (at mass spectrum moment) was 180 ^{0}C.

Table 2

Identified compounds by EI-MS characteristic ions

Code	Compound	M	Characteristic ions	Observations
3406	*Dehidroabietic acid* *7-Oxo-dehidroabietic acid*	300 314	285, 239, 137 299, 253	Natural resin Natural resin

The mass spectrometric data analysis (see Table 2) leads to identification of two compounds originating from natural resins:

1) *Dehidroabietic acid* with molecular weight M_1 = 300. Other characteristic ions of the compounds are:

- m/z 285 (M_1-15), produced by elimination of the radical CH_3;

- m/z 239 (M1-15-46), produced from (M_1-15) of the group HCOOH.

2) *7-Oxo-dehidroabietic acid* with molecular mass M_2 = 314 and characteristic ions: the fragments m/z=299 and m/z 253 produced from molecular ion M2 (314) in a similar mode as *Dehidroabietic acid* by successive elimination of the group CH_3 and HCOOH respectively. The characteristic ions for every compound are confirmed by comparison of mass spectra with data base mass spectra and by interpretation by molecular fragmentation by electron impact[8] shown in Table 2.

Both compounds are considered biomarkers for natural resins as result from the papers reported in last period. [9]

EXPERIMENTAL

The samples of mg mass value were taken from the triptych wooden icon as is indicated in Table 1.

FTIR measurements were performed 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.[10, 11] In order to determine the wooden "health" status, the crystallinity indexes (defined as $I_{cr}^1=A_{1377}/A_{669}$, $I_{cr}^2=A_{1109}/A_{690}$ or as $TCI=A_{1378}/A_{2925}$) and lignin to cellulose ratios, defined as $(L/C)_1=A_{1506}/A_{1158}$, $(L/C)_2=A_{1506}/A_{1158}$ or $(L/C)_3=A_{895}/A_{1426}$ were calculated for wooden samples in agreement to already established definitions. [7] These definitions are used only as a measure of their change during time.

The measurements of wood samples were done with a DSC60 Shimadzu differential scanning, in the 20-550°C temperature range in air atmosphere, with a heating speed of 10°C/min.

The differential scanning calorimetry (DSC) experiments were carried out on a Shimadzu DSC-60 differential scanning calorimeter (Shimadzu Corporation, Japan) and Shimadzu TAWS60 and TA60 2.1 software were employed for data acquisition and analysis. No hermetic crimped aluminum pans, in which 1-2 mg of sample was accurately weighed, were used to perform the experiments. The samples were heated from room temperature up to 550°C in air atmosphere, with a heating rate of 10°C/min.

EI-MS measurements were performed at 70 eV on Electron Impact Mass Spectrometer of type MAT 311 having direct

introduction sample system; mass spectra were obtained in full scan mode, in the mass range 25-650 Daltons. The sample temperature was raised from 25^0C to 350^0C.

CONCLUSIONS

Wooden support: lime with a lower cellulose content (its consumption is faster in time than lignin one) as compared to lime standard and an increase of the amorphous content.

Painting materials: gypsum (white), Prussian blue (blue), lead minium (red), binder (egg yolk), ground (gypsum and animal glue) and conifer resin (varnish).

REFERENCES

1. D. Conde, F. Pacheco, I.C.A. Sandu, S. Campos, N. Leal and M.P. Colombini, *Conservar Património,* **2010**, *12*, 3-16.
2. S. Daniilia, D. Lucia Burgio, P. Gavala, R. J. H. Clark and Y. Chryssoulakis, *J. Raman Spectrosc.,* **2002***, 33*, 807-814.
3. I. Istudor, "Noțiuni de chimia picturii", Ed. ACS – colecția științific, edition III, București, 2011.
4. H. Moenke, "Mineralspektren", Akad. Verlag, Berlin, 1962, Tables 4.43 and 4.44.
5. S.I. Tsujiyama and A. Miyamori, *Thermochim. Acta,* **2000**, *351*, 177-181.
6. I. C. A. Sandu, M. Brebu, C. Luca, I. Sandu and C. Vasile, *Polym. Degrad. Stabil.*, **2003**, *80*, 83-91.
7. C. M. Popescu, Y. Sakara, M. C. Popescu, A. Osaka and C. Vasile, *e-PreservationScience,* **2005**, *2*, 19-29.
8. Z. Moldovan, C. Maldonado and J. M. Bayona, *Rapid. Commun. Mass Spectrom.*, **1997**, *11*, 1077-1082.
9. M. Regert, J. Langlois, E. Laval, A. S. Le Ho and S. Pages-Camagna, *Anal. Chim. Acta,* **2006**, *577*, 140-152.
10. A. Baciu, Z. Moldovan, I. Bratu, O. F. Marutoiu, I. Kacsó, I. Glajar, A. Hernanz and C. Marutoiu, *Curr. Anal. Chem*. **2010,** *6*, 53-59.
11. C. Marutoiu, S. P. Grapini, A. Baciu, M. Miclaus, V. C. Marutoiu, I. Kacso, S. Dreve and I. Bratu, *J. Spectrosc.*, **2013**, http://dx.doi.org/10.1155/2013/957456.