Spectroscopy Investigation of Triptych Icon from the Borsa Church, Maramures County

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A triptych icon from the 18th century from Borsa Maramure's County, Romania was investigated by physical-chemical destructive and nondestructive methods: Fourier Transform Infrared (FTIR) spectroscopy, X-ray Fluorescence (XRF), X-Ray Diffraction and thermal analysis by Differential Scanning Calorimetry (DSC). There were identified: gypsum as ground, wooden stage (lime wood), egg yolk as binder, pigments from the painting layer (red lead, green malachite and white lead), silver foil, iron bolus and animal glue for ground. The scientific investigation of various religious objects in general, this wooden icon in the present case, is a mandatory step in the approach to conservation and restoration of cultural goods.

Keywords: lime wooden triptych, painting materials, FTIR, XRF spectroscopy, DSC analysis

The diptych (Pomelnic) is a list of names of the living and the dead which is given to the priest to be mentioned during the High Mass. In the past these diptychs were written on a plate consisting of two parts which would fold. On the left side the living persons were mentioned, on the right side the dead ones. In the orthodox churches, besides the wall paintings and icons, there were cases where the text was associated with visual representations. This is the case of the painted diptychs, mobile or fixed, painted on wood or directly to the wall in the anaphora area or behind the shrine table. Painted diptychs are common in the XIII-XIV century Christian churches [1-3].

There are several papers dedicated to the scientific investigation of different religious art or archaeological objects [3-11]. The aim of this paper was to investigate both the wooden species and painting materials employed for *Pomelnic* triptych icon (XVIII century) belonging to a wooden church of Borsa, Maramures County. This information is necessary for preservation and restoration of this wooden icon.

Fig.1. The Annunciation triptych icon

Fig.2. The inside of the triptych icon (triptych - Pomelnic)

Experimental part

Materials and methods

The triptych icon found in the Holy Archangels Michael and Gabriel church from Borsa Maramures County (XVIII century) (fig. 1) is a painted diptych which shows the Annunciation on the front side of the doors (the Virgin Mary on the left and the Archangel Gabriel on the right). The Virgin Mary is shown green dressed and kneeling with an angel above having its wings spread. The Gabriel Archangel is painted standing above a cloud, golden dressed in the upper part and red in the lower part, holding a lily in his hand. In the triangle from the upper part of the icon the Holy Spirit is painted as a pigeon on a white cloud. In central area from the interior of the triptych one can find the Pomelnic with an inscription written in Cyrillic *May the Lord mention the founders of this church* (fig. 2).

The sampling points for XRF and FTIR spectroscopy investigations are presented in figure 1. X-ray fluorescence measurements were performed using an INNOV-X Alpha-6500 portable instrument (35 kV voltage, 15 μA intensity, 3 mm filter, Be window, 2 square mm spot size and PIN Si detector). Integration time was set for 60 s, in two consecutive runs of 30 s each. FTIR spectra were registered with a resolution of 4 cm^{-1} using a JASCO 6100 FTIR spectrometer in the 4000 to 400 cm^{-1} spectral domain by employing KBr pellet technique. The spectra were processed by Spectral Analysis software. Differential scanning calorimetry (DSC) was carried out by means of a Shimadzu DSC-60 calorimeter, the sample being heated in the range of 20–550°C with a heating rate of 10°C/min in crimped aluminum sample cell. The purge gas was nitrogen purged of 60 mL/min. For data collection the Shimadzu TA-WS60 and TA60 2.1 programs were employed. The diffraction data were collected in the 2θ= 3-85° angular domain with a Bruker D8 Advance diffractometer, using Cu $K\alpha_1$ radiation (λ = 1.5406 Å) (40

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kV; 40 mA). In order to increase the resolution, a Ge 111 monochromator was used to eliminate the $K\alpha_2$ radiation. Data collection was performed at room temperature with the programs package DIFFRAC plus XRD Commander. The amorphous/crystalline ratio was calculated by using *Material Studio* software [12].

Results and discussions

Analysis of painting materials

XRF analysis

The results of XRF measurements of chemical elements identified in analysed samples are presented in table 1.

From the analysis of the data presented in this table one can conclude that the chemical elements with highest concentrations in each painting material are as follows: Ca, Fe, Cu, Pb, As and Ag. This fact shows that the painting materials employed for wooden triptych could be: gypsum, red lead (Pb_3O_4), iron bolus (Fe_2O_3), realgar (red As_2S_2), green malachite ($CuCO_3.Cu(OH)_2$), auripigment (yellow As_2S_3), white lead ($2PbCO_3.Pb(OH)_2$ silver white), silver foil, iron bolus.

FTIR spectroscopy

FTIR data support the use of gypsum as ground and white pigment, also (fig. 3). One can see that black color is given by carbon particles (lack of its specific absorption bands), gypsum (characteristic absorption peaks at 3545, 3408, 1621, 1153, 1120, 672, 613 and 596 cm^{-1}).

The figure 4 shows the existence of Ca oxalate in the wood sample.

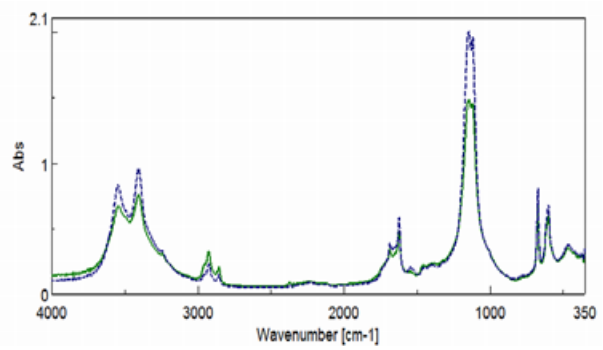

Fig. 3. FTIR spectra of painting materials: black-solid line; white-dash line

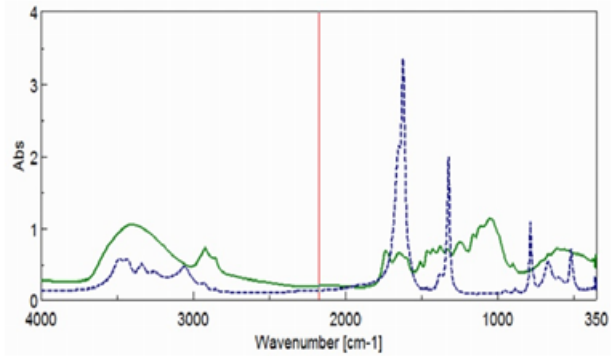

Fig. 4. FTIR spectra of wooden sample (solid line), and of Ca oxalate (dashed line), 4000-350 cm^{-1} spectral domain

Sample colour	Identified element (mg/kg)							
	Ca	Fe	Cu	As	Ag	Au	Hg	Pb
Yellow	57987	2101	71	67	1045	37	38	624
Yellow background	77888	2253	54	85	523	<LOD	36	625
Red cloth	62820	3283	89	170	690	<LOD	87	994
Green cloth	196878	3477	117	55	569	<LOD	34	580
Curtain	69796	1764	6975	113	681	<LOD	80	816
Pink	60887	2236	154	116	1210	38	71	954
Pink column	34976	721	101	5824	<LOD	<LOD	379	28446
Bright pink upper petals	77546	1899	81	62	859	29	55	635
Bright pink middle petals	80529	2052	73	83	788	22	56	664
Bright pink lower petals	84596	2197	72	92	264	<LOD	<LOD	585
Corner angel	98739	2436	74	130	490	<LOD	44	931
Back door primer	136777	768	53	74	<LOD	<LOD	<LOD	711
White paper	186226	1563	<LOD	583	<LOD	<LOD	<LOD	6414
Blue paper	232996	1734	74	557	<LOD	<LOD	<LOD	9881
Brownish -yellow paper	64789	2075	50	448	<LOD	<LOD	<LOD	5230
White paper above	203661	1658	49	1214	<LOD	<LOD	79	10274
Upper part written area	170474	1797	49	455	<LOD	<LOD	<LOD	5408

<LOD-limit of detection

Table 1
XRF DATA RESULTS

If one compares FTIR spectra, (fig. 5), based on specific absorption bands in the 3700–2700 cm^{-1} and 2000-350 cm^{-1} spectral ranges, one can decide that lime is the wooden material employed for triptych.

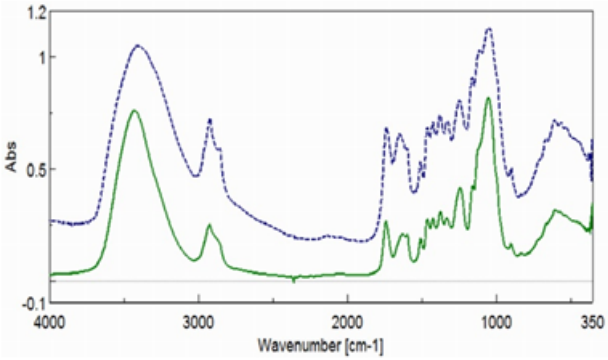

Fig. 5. FTIR spectra of wooden samples, 4000-350 cm^{-1} spectral domain (Legend: solid line-triptych wooden sample; dashed line-lime wood standard)

Analysis of wooden stage

FTIR spectroscopy

In order to determine the conservation status of the wood, the crystallinity indices, defined elsewhere[8]. $I_{cr}^{1}=A_{1377}/A_{669}$, $I_{cr}^{2}=A_{1109}/A_{690}$ or as $TCI=A_{1378}/A_{2925}$) and $LOI=A_{1426}/A_{895}$) ratios were determined, A being the characteristic absorbance. Lignin/cellulose ratios[8] were computed for wood samples. They were used only as an eye guide to follow their changes during time. Table 2 contains these parameters for icon wood and for standard lime wood.

The crystallinity decreases for historical wood as compared to modern one, see for example I^{1}_{cr} and LOI values, (table 2). Consequently, the amorphous content increases for historical wood as compared to modern wood, (table 2). The cellulose content decreased more rapidly than lignin one, *i. e.* the cellulose consumption is more rapidly that lignin one, see for example the $(L/C)_1$ and $(L/C)_2$ ratios behavior.

DSC analysis

Wood is a polymeric material consisting in two major components: lignin (18–35%) and carbohydrates (cellulose and hemicellulose) (65–75%). The thermal characteristics of wood depend on this mixture, on age and the preservation state.

Due to the complex structure and of interaction between components, it is difficult to distinguish between decomposition processes corresponding to each component. By studying the wood thermal decomposition process, the cellulose presents two exotherms at 350 and 510°C (fig. 6)[10, 13]. The majority of papers showed that lignin starts to decompose at~ 280°C, with maximum between 350 and 450°C the reaction ends between 450 and 500°C. Microorganism contribute to degradation of the wood over time by secretion of oxalic acid, the biomineralization process is favored by fungi. The calcium oxalate resulted by fungal colonization is transformed into carbonate between 400 and 550°C (peak temperature at 490°C)[10, 13].

Standard DSC wood curves present two exotherms (fig. 6), at 260 and 360°C with maximum at 330.3°C and between 400 and 500°C with maximum at 440.5°C, assigned to amorphous polysaccharides, to a natural lignin mixture and to polysaccharides decomposition, respectively. On DSC historical wood sample curve one sees a small temperature shift toward smaller values and a peak widening. Therefore, one can expect a crystallinity decreasing through time by wood degradation. One can see also, a sharp exothermic peak with maximum at 488°C, probably due to the presence of oxalates as a result of the fungal attack on the icon lime wood.

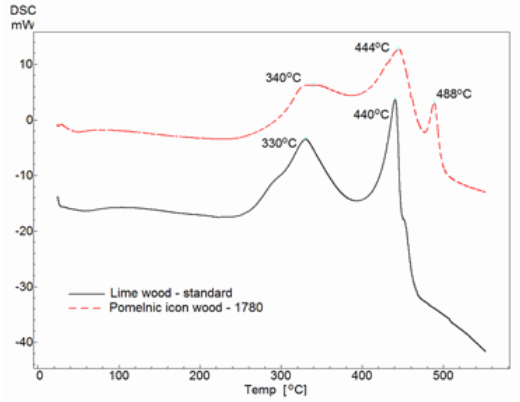

Fig. 6. DSC curves of lime wood standard (solid line) and of *Pomelnic* triptych icon wood (1780) (dashed line)

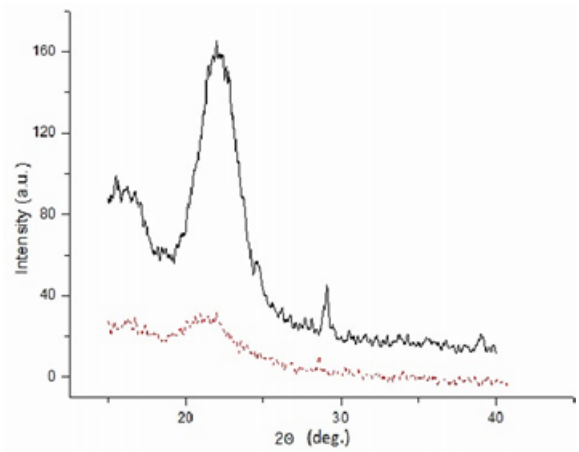

Fig. 7. X-ray powder patterns for icon and lime standard woods. Legend: solid line-lime standard wood; dash line line-Icon wood

X-Ray Diffraction

The X-ray diffraction technique is used to evaluate the degree of crystallinity of different materials. Cellulose is the only crystalline component of wood composition, the other polymers being non crystalline. The diffraction pattern is resulted from cellulose. After its deconvolution with *Material Studio* software, the crystalline index, as defined elsewhere was calculated. By comparing the X-ray powder diffraction patterns for icon wood and for lime standard,

Sample	I^{1}_{cr}	LOI	$(L/C)_1$	$(L/C)_2$
Historical wooden stage	1.18	1.91	0.78	0.58
Modern lime wood	1.21	3.11	0.71	0.44

Table 2
THE CONSERVATION STATUS OF THE WOODEN SAMPLES

(fig. 7), one can conclude[10,14-17] that the crystallinity of icon wood (32.71%) is lower than the corresponding value of lime wood standard (56.67%). Consequently, the icon wood becomes more amorphous in time

Conclusions

After scientific investigations, it was found that the employed painting materials for *Pomelnic* triptych icon, belonging to the Holy Archangels wooden church from Borsa Maramures County are: wooden stage-lime wood; gypsum as ground; egg yolk as binder; pigments-red lead (Pb_3O_4), green malachite ($CuCO_3.Cu(OH)_2$), white lead ($2PbCO_3.Pb(OH)_2$), silver white; silver foil; iron bolus; animal glue for ground. The wooden icon presents fungal attack, the oxalates being detected by FTIR spectroscopy and DSC thermal analysis. DSC and XRD analysis support the increase of the amorphous content for the icon wood as compared to the lime wood standard.

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