Multianalytical Study on Two Wooden Icons from the Beginning of the Eighteenth Century

Evaluation of conservation state

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The old wooden icons entitled Daniel and Jeremiah prophets and Aaron and Gideon prophets, painted by an unknown artist, were realized in tempera. The chromatic of the countenance and hands is realized with brown, over it a pink-reddish color is superposed and light zones are applied in white. The composition of the painting materials obtained by Fourier Transform Infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and X-ray fluorescence (XRF) analysis is based on the following major materials: calcium carbonate, lead oxide, iron ochre and cinnabar. The fir wood samples offer information about the crystallinity and lignin to cellulose ratio changes; the lime wood samples give also details about their time degradation. The shift of the characteristic cellulose and lignin DSC peaks and the occurrence of a third peak at 468°C indicate the wood-boring beetle and fungal attack on analyzed wood sample.

Keywords: old wooden icon, painting materials, wood degrading, FTIR and XRF spectroscopy, DSC analysis

Old paintings on wooden support of Orthodox churches were made in tempera (weak or rich) or oil technique, which were subsequently varnished or not. Wood panels for paintings are first prepared by applying a layer of gypsum or chalk dust, the former being preferred because it leads to considerable smoothness, with very reduced roughness [1-6].Depending on the type of painting and its conservation state, age and value, the conservation scientist will carry out a detailed research regarding the structural parts of structural-active paint layers and supports, in order to determine the materials and to asses their conservation state. This implies, depending on the artistic technique/ painting type, the use of non-invasive methods of investigation or corroboration between interdisciplinary techniques [7-18].

The interdisciplinary study of the panel painting and identification of pigments of various old wooden icons (Albanian, Greek and Coptic ones) was already reported [19-23] together with optical and infrared and Raman microspectroscopy of polychrome wooden sculptures [24, 25]. The multianalytical techniques were also applied to the investigation of the so-called *Imperial Gates* from several old wooden churches from Transylvania, Romania [26, 27].

The aim of the paper is to investigate the constituent materials of these wooden icons in order to preserve and restore them.

Experimental part

Prophets are bust rendered, in a slight half profile, two on the panel, holding in the left hand a frontlet, (fig. 1). The characters are clothed in a tunic and cloak with a white outline.

(a) (b)

Fig. 1. Daniel and Jeremiah prophets - front side (a), and back side (b)

(a) (b)

Fig. 2. Aaron and Gideon prophets - front side (a) and back side (b)

The polychromy of the countenance and hands is realized with brown, superposed by a pink-reddish color, while light zones are applied in white. Auras have double contours incised in the underlay. The field of the pieces was carried out by applying a metal foil over a layer of red clay. The support has a circular shape with an accolade at the top. It was made of two boards placed horizontally, with a half-sunken vertical beam and marginal decoration with vegetal relief – acanthus leaves – worked with chisel. The frame is done from the thickness of the wood, and the

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marginal decor was also done from the panel thickness. Due to the precarious preservation conditions, these icons present damages both in the wooden support and the painting layer that require restoration. These wooden icons (the Prophets) are mounted in the Prophets column of the iconostasis. Both icons were made according to the old Greek school of painting. The technique used is tempera on wood. The icons are dated as being from the early eighteenth century. Both icons have Slavonic inscriptions in red and black positioned near the biblical characters shoulders: *Daniel the Prophet, Jeremiah the Prophet* and *Aaron the Prophet, Gideon the Prophet*. The icons dimensions are 71 x 63.5 x 2 cm, 68 x 62.5 x 2.5 (Daniel and Jeremiah) and 71 x 63.5 x 2 cm, 68 x 62.5 x 2.5 cm (Aaron and Gideon).

Sampling points definitions - both for XRF and FTIR spectroscopy: P1 -ornament red leafs - metallic foil; P2 - frame - Aaron face - reddish shade; P3 - inferior left side frame wood support (degraded wood); P4 - traverse - wooden side (degraded wood + wood flour); P5 - wooden support verso, superior left side (not degraded wood); P6 - yellow; P7 -yellow + red; P8 -golden aura; P9 - right side casement.

Measurements

FTIR spectra were obtained with a resolution of 4 cm^{-1} using a JASCO 6100 FTIR spectrometer in the 4000 to 400 cm^{-1} spectral domain by employing the well-known KBr pellet technique. A minimal sample quantity less that 1 mg was mixed with ~200 mg KBr and grounded in an agate mortar. Then the grounded mixture was pressed into a special evacuated die till a quasi-transparent pellet was obtained. The treatment of the FTIR spectra was performed with Spectra Analysis and Origin 8.0 software. Differential scanning calorimetry was carried out by means of a Shimadzu DSC-60 calorimeter, the ~1.5 mg of sample was heated in the range of 20-550°C with a heating rate of 10°C/min in crimped aluminum sample cell in static air atmosphere. For data collection, the Shimadzu TA-WS60 and TA60 2.1 software were employed. X-ray fluorescence measurements (non-destructive ones) were performed using an INNOV-X Alpha-6500 non-destructive portable instrument (35 kV voltage, 15 μA intensity, 3 mm filter, Be window, 2 square mm spot size and PIN Si detector). The integration time was set for 60 s, in two consecutive runs of 30 s each.

Results and discussions

FTIR spectroscopy

FTIR spectra of the samples taken from the first wooden icon represented in figure 1 are presented in figure 3, whereas figure 4 contains the FTIR spectra of painting materials employed for the wooden icon represented in figure 2.

Proposed composition based on vibrational analysis: aliphatic (2929 and 2851 cm^{-1}), carbonate (1428 and 876 cm^{-1}), lead red (520 and 489 cm^{-1}), *terra verde* - silicate (shoulder at~1032 cm^{-1}).

One can identify (for example 1200-1000 cm^{-1} spectral domain, fig. 5) lime as the wood species for P3 and P4 samples, whereas fir was employed for P5 sample.

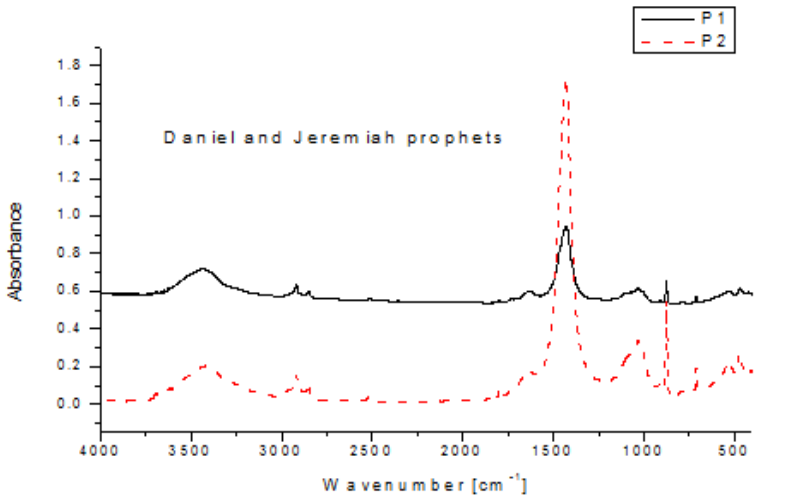

Fig. 3. P1 (solid line) and P2 (dashed line) FTIR spectra

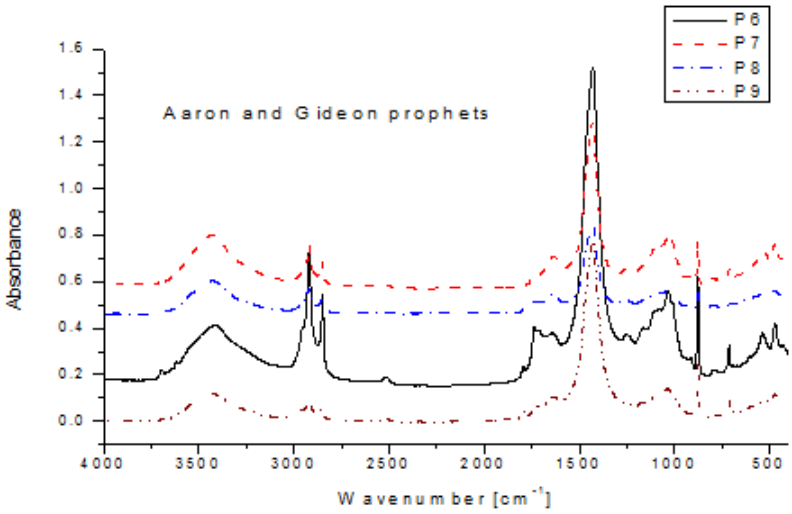

Fig. 4. FTIR spectra of P6-P9 samples

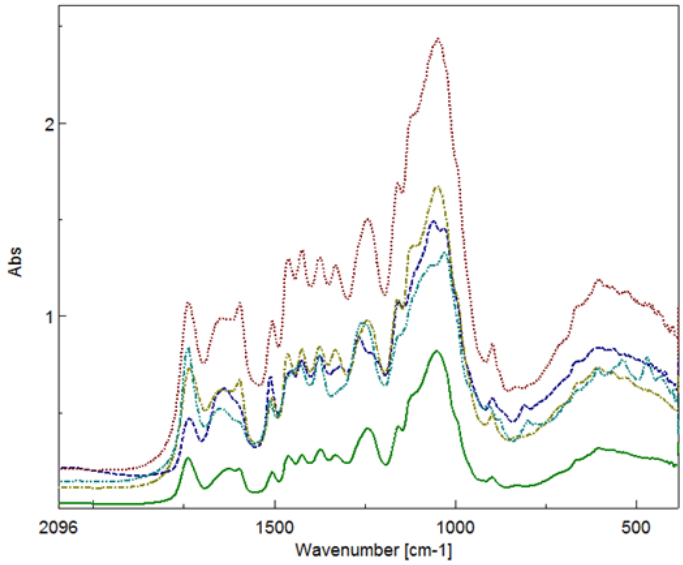

Fig. 5. Different wooden essence sample spectra: solid line-lime; dash line-fir; dot line-P3; dash-dot line-P4; dash-dot-dot line-P5

XRF spectroscopy

The results of the XRF analysis for each wooden icon are presented in tables 1 and 2.

Concentration: [mg/kg]; LOD-limit of detection; error <20%

Painting materials investigation

In what concerns the P1 – ornament red leafs-metallic foil, the XRF results are: Pb (45991), Ca (82610). Based on FTIR and XRF measurements for the painting materials one can identify the compounds in the composition of P1 and P2 samples: 2919 and 2850 cm^{-1} (aliphatic CH_2); carbonate (1429 and 876 cm^{-1}), egg yolk (ester-1735, protein-1542 cm^{-1}), 1632 cm^{-1} (protein band), 1032 cm^{-1} (silicate), Pb_3O_4 (absorption bands at~533 and 473 cm^{-1}). The proposed composition is: calcium carbonate, binder (animal glue), egg yolk, lead red.

For P2 – frame - Aaron face-reddish shade, the XRF results are: Ca (91261), Pb (31582), Hg (14804), S (46196): aliphatic (2929 and 2851 cm^{-1}), OH (3421 and 1637 cm^{-1}), protein band (1637 cm^{-1}), carbonate (1429 and 876 cm^{-1}), Pb_3O_4 (531 and 432 cm^{-1}), silicate (1033 and 798 cm^{-1}).

The proposed composition of P6 to P9 samples based on XRF and FTIR results. *Yellow halo*: As (9735), S (42998), orpiment; *Hand and face* (reddish shade): Fe (10374), Ca (25225), Hg (14804), iron oxide, vermillion, lead and calcium white; *Mitre*: Fe (33880), Ca (280728), iron oxide, and calcium white.

Consequently, the proposed composition is: calcium and lead carbonate, binder (animal glue), egg yolk, lead red, cinnabar. Two red pigments interventions were employed in order to attenuate the red color.

Table 1

XRF DATA FOR *DANIEL AND JEREMIAH* PROPHETS' WOODEN ICON

	S	Ca	Fe	Cu	Zn	As	Ag	Au	Hg	Pb
B-mitre	13062	280728	33880	40	821	870	<LOD	74	6023	3041
B-upper yellow	2888	442334	7004	27	44	26	441	12	<LOD	95
B-red-garment	13768	171191	40371	18	1182	1835	<LOD	127	16404	6759
B-Jeremiah-garment	10743	41681	11929	39	296	16615	<LOD	182	463	17481
B-parchment-background	54923	91266	3072	105	412	10438	<LOD	177	965	48304
B-hand-Jeremiah	35695	79633	3230	91	242	7542	<LOD	207	12516	33226
B-decoration-lower right	2162	5904	13637	30	535	18	1314	15	96	48
B-frame-left	1793	376337	8903	29	75	35	268	6	<LOD	84
B-Jeremiah-beard	41529	100910	2958	30	165	7176	93	139	1417	31564
C-background-yellow	17132	80036	1989	142	<LOD	13764	<LOD	376	<LOD	282

Table 2

AARON AND GIDEON PROPHETS' WOODEN ICON

	S	Ca	Fe	Cu	Zn	As	Ag	Au	Hg	Pb
A-aura	6108	283026	11340	505	107	985	747	60	3635	3806
A-upper yellow	2358	318232	10742	344	68	33	941	13	<LOD	95
A-mitre-medallion	30749	168777	4547	53	355	3426	<LOD	68	431	13223
A-reddish mitre	16323	219986	18180	87	1516	7270	<LOD	90	1334	8617
A-Aaron effigy	43045	111710	4449	<LOD	207	6633	<LOD	157	6748	29514
A-upper yellow	42998	88373	3354	140	266	9735	<LOD	254	13747	44895
Aaron red text	44319	82610	3093	122	298	10007	<LOD	207	6322	45991
Aaron-text gaps	47085	91909	3198	<LOD	230	10681	<LOD	208	2980	52199
Aaron-black text	41934	79018	3420	<LOD	422	11839	<LOD	226	991	62596
Aaron-red effigy	46197	91261	3930	<LOD	166	7298	<LOD	210	14804	31582
Aaron-hand	1604	4476	10374	<LOD	500	<LOD	1375	18	100	49
A-upper left decoration	2756	272814	10416	50	54	23	783	6	28	45
A-beard	8276	285883	13965	<LOD	122	1352	<LOD	43	331	5505
Garment	11596	220739	7440	84	619	2984	<LOD	61	379	12235

Wavenumber (cm^{-1})	Assignment
3500	O-H Valence vibrations from H_2O;
2980	$-CH_2$ valence vibrations
1740	C=O stretching of acetyl or carboxylic acid
1610-1595	C=C stretching of the aromatic ring (lignin)
1504	C=C stretching of the aromatic ring (lignin)
1465	Asymmetric bending in CH_3 (lignin)
1425	CH_2 bending (cellulose)
1335	OH in plane bending (cellulose)
1316	CH_2 wagging
1156-1162	Asymmetric bridge C-O-C stretching (cellulose)
1000	CO valence vibrations
897	Asymmetric out of plane ring stretching (cellulose)

Table 3
CHARACTERISTIC BANDS OF THE FTIR SPECTRA OF THE ICON LIME WOOD

Table 4
Cr. I. THE CRYSTALLINITY STATUS OF FIR AND LIME WOOD SAMPLES (NON DEGRADED AND DEGRADED WOODEN SUPPORTS)

Sample	P3	P4	P5	Actual fir wood	Actual lime wood
A_{1106}/A_{690}	2.40	2.57*	2.05	2.55	3.12

Legend: P3- inferior left side frame support; P4- traverse- wooden side; P5- wooden support verso, superior left side;
* Note: One can observe (see Table 4) that the crystallinity is generally higher (or similar) for actual lime wood as compared to those of the historical icon wood. This value is influenced by errors due to the fact that the corresponding bands are not well delimited, being shoulders to other pronounced or large bands. If one considers lime as the wood species, the crystallinity is lower for historical woods due to the fact that cellulose becomes more amorphous.

Table 5
LIGNIN/CELLULOSE RATIOS (L/C) TAKING INTO ACCOUNT THEIR DIFFERENT CHARACTERISTIC BANDS

Sample	P3	P4	P5	Actual fir wood	Actual lime wood
A_{1505}/A_{1738}	0.91	0.57	0.66	1.66	0.71
A_{1505}/A_{1375}	0.75	0.68	0.70	0.88	0.61
A_{1505}/A_{1158}	0.58	0.52	0.62	0.63	0.44
A_{1505}/A_{895}	1.14	1.16	1.04	1.65	1.15

Wood crystallinity and lignin/cellulose ratio determination by FTIR spectroscopy

A detailed analysis of the wooden samples' FTIR spectra is presented. The wood components (lignin, carbohydrates, cellulose, and hemicellulose) are identified by comparing with literature data [28]. A systemathic assignment of the specific bands for different wood components, based on literature data [29-31] is presented in table 3.

The estimation of the crystallinity status (Crystallinity index - Cr. I. [15]) for different wood samples, see table 4, can be obtained based on the already assigned vibrational modes that correspond to *amorphous* and *crystalline* bands, respectively.

Lignin/cellulose ratio (L/C) was determined taking into account several definitions [30] using lignin and cellulose characteristic bands intensities, respectively. The results are presented in table 5.

It can be noted that the lignin/cellulose content for historical sample is higher than for actual one due to the fact that cellulose consumption during time is more rapid than the lignin one. P3 and P4 samples are wooden destroyed samples (fungi attack probably) whereas P5 is a wooden sample quite intact, (fig. 6). The oxalate presence can be proved by comparing FTIR spectra of fungi attacked wooden samples (P3 and P4 samples) and FTIR spectrum of calcium oxalate, (fig. 6).

By comparing the (1700-1500, 1500-1300 and 1000-700 cm^{-1}) spectral regions, (fig. 6), one observe that P3 and P3 samples could contain calcium oxalates.

DSC

Wood has a complex structure being a polymeric material that consists of ligno-polysacharide amorphous matrix bonded with cellulose by polyosic chains [32-34].

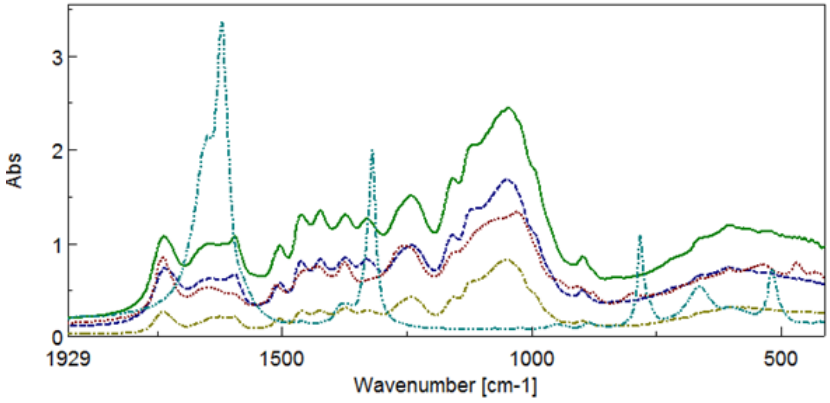

Fig. 6. FTIR spectra (1929-413 cm^{-1} spectral domain) of the icon wooden samples and of Ca oxalate: solid line - P3; dashed line - P4; dot line- P5; dash-dot line-lime standard; dash-dot-dot line -calcium oxalate.

Table 6
CHARACTERISTIC TEMPERATURES AND HEAT VALUES OF WOOD SAMPLES

	Actual lime wood	P3	P4	Actual fir wood	P5
T_{on} (°C)	280	309	275	326	315
T_p (°C)	330	334	325	346	339
T_{end} (°C)	375	363	359	398	386
Heat (J/g)	2700	2480	2780	1360	2640
T_{on} (°C)	424	410	403	444	443
T_p (°C)	441	433	429	487	494
T_{end} (°C)	447	464	443	507	513
Heat (J/g)	1510	1520	1740	1130	2710
T_{on} (°C)	-	475	454	-	-
T_p (°C)	-	480	468	-	-
Heat (J/g)	-	151	610	-	-

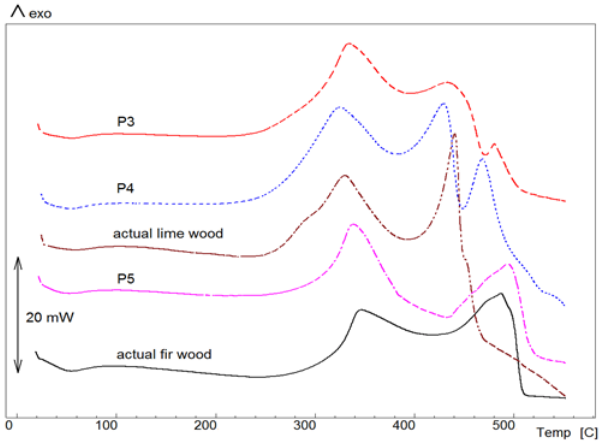

Fig. 7. DSC curves for historical wood samples as compared to actual ones.

Because of this complex structure and interactions between components of wood it is difficult to differentiate the decomposition processes corresponding to the components, such as lignin, holocellulose, hemicelluloses and pure cellulose. The decomposition data of each separated component can be found in literature [35-37]. The thermal effects are related to the changes appearing in the two components whose thermal characteristics depend on the essence and age of wood, moisture content and conservation status [34].

The thermal behavior of the samples gives information about modifications of wood components. It is known that the pure cellulose decomposes between 300-350°C; while the lignin has a high thermal stability, complete decomposition occur between 400-500°C. The characteristic temperatures are affected by age, applied treatments and wood deterioration. The wood's age causes an increase of the characteristic temperatures [26], but the degree of damage leads to their decrease, (table 6), as was observed elsewhere [37, 38].

One can observe that T_{on} for first exothermic signal increases with the wood age and decreases with the wood degradation.

In the case of sample P3, (fig. 7), the corresponding signal of lignin decomposing decreases significantly.

One can note the presence of a third peak in the DSC curves of P3 and P4 samples, more intense for P4 curve, due to the calcium salts (oxalates) decomposition [36-39] accumulated in the wood structure as a consequence of the fungal attack. The broadening of the samples' thermal signals is due to the age of the investigated samples.

Conclusions

Based on the FTIR spectroscopic and thermal analysis data, one can propose the following about the wood status of the first icon:

-the wood species are lime (for P3 and P4 samples) and fir for P5 sample;

-the crystallinity is generally higher (or similar) for actual spruce fir wood as compared to those of the historical spruce fir icon wood, confirmed also by DSC;

-the lignin/cellulose content for actual sample is higher than for historical one due to the fact that cellulose consumption during time is more rapid than the lignin one;

-fungal attack (calcium oxalate presence) was confirmed for P3 and P4 lime samples by FTIR and DSC measurements.

Regarding the employed painting materials one can specify the following compounds employed for the first wooden icon: ground-calcium carbonate + animal glue (binder); the employed pigments, specific to the respective epoque: lead red, iron red, cinnabar, orpiment and iron oxide for yellow (natural and artificial) and egg yolk as binder for painting layer.

As concerning the second wooden icon, one can assume the following composition of the painting materials: aliphatic (2929 and 2851 cm^{-1}), lead and calcium carbonate (1428 and 876 cm^{-1}), lead red (520 and 489 cm^{-1}) and silicates (~1032 cm^{-1}). Calcium carbonate was employed as ground and also as diluting agent.

The materials used for these icons suggest that these icons were painted at the end of 18th century. This fact is also sustained by the presence of zinc white.

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