Evaluation of the Conservation State of an Wooden Icon, St Nicholas, from Transilvania (XIXth Century)

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The wooden icon of Saint Nicholas, painted in the second half of the nineteen century, comes from the southern part of Transylvania province and was investigated by XRF and FTIR spectroscopy in order to preserve and restore it. The obtained results confirmed that this icon was painted in the historical period already mentioned. Also, the aim of this paper was to assess the conservation state of the wooden support and the painting materials used for this icon.

Keywords: execution technique, wood support, paint layers conservation state, painting materials, XRF spectroscopy, FTIR spectroscopy

The intervention procedures during cultural heritage restoration can be decided after the application of physical-chemical investigation methods for the identification of paint and support materials and execution techniques [1-3]. Among others, FTIR and XRF spectroscopy are frequently employed to this purpose [4-10]. Wood analysis can be performed using FTIR spectroscopy offering information about the wood nature, crystalline-amorphous and lignin/cellulose ratios and of the conservation state (fungal attack, etc.). XRF spectroscopy, of non-destructive nature, is also helpful in the art sector for elemental identification of constitutive materials [11-13].

As a consequence of the development of the chemical industry the plastic art materials were introduced as new painting materials. These materials were also employed for painting in new churches, where icons painters adopted them. The wooden icon of Saint Nicholas, here studied, was dated back to the second half of the nineteen century. The painting was made using *tempera grassa* [14, 15]. The support was made from two lime-wood pieces attached together. Over the preparation layer, a bole layer was applied in the areas to be gilded. The paint film is made by juxtaposition of colors from dark ones to lighter ones (with fine shadows and light accents). A thin varnish layer was applied as protection coating onto the whole painted surface [16-20]. The aim of this paper was to investigate the wooden support and the painting materials employed for this icon.

Experimental part

As scientific investigation methods of the *St. Nicholas* icon, XRF and FTIR spectroscopy were used on surface of the paint and wooden frame (XRF) and also on micro-samples (FTIR).

XRF analysis was performed on 11 points from the surface of the icon, as seen in figure 1a and b. The sampling from the icon surface (fg.1) was performed taking into account the colors present both of icon and on frame. The wood icon supports Xylophage's attack. The analysis points were as follows: P.1a - blue background, P.2b – flesh tones, P.3c - St. Nicholas' halo, P.4d - red apparel, P.5e - dark brown background lower side, P.6d - metallic layer, P.7f - lower side-legs, P.8g - dark red edge, P.9h - red garment of Mother of God, P.10i - gilded area of the garment of St. Nicholas, P.11j - silver leaf on the book, P.12k – chin. For the analysis done on the frame the following numbers were used to identify the points: 1- blue; 2-colored ground; 3 - orange; 4 - gold leaf.

Fig. 1. Sampling points for Saint Nicholas icon: a – frontal side; b - frame

The sampling points for FTIR spectroscopy, given in figure 2, were noted as follows: P.1 - colored ground from previous intervention, P.2 – blue on brown (inner part of the frame), P.3 – ground (original preparation layer), P.4 – grey color - silvery (misfit intervention), P.5 - white putty (originating from previous intervention).

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Fig. 2. Sampling points on the icon:
a – frontal side; b - frame

XRF spectroscopy

X-ray fluorescence measurements (XRF) 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 seconds, in two consecutive runs of 30 seconds each.

FTIR spectroscopy

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, using KBr pellet technique for sample preparation.

Results and discussions

XRF spectroscopy

Table 1 gives the elemental data obtained from the analysis of painting materials, for the next colors: blue – Fe for iron blue and Cu for frame - azurite; red – Hg for cinnaba and Fe for red ochre; white – Pb for lead white and Zn for zinc white; ground - Ca sulfate and Ca carbonate (the places of partial restoration) for ground; yellow – As for orpiment and Pb - lead white; halo – Fe for iron oxide in the bole (appeared in the halo cracks) and Ag for silver leaf; red apparel- Hg for cinnabar; book - silver leaf and frame – gold leaf.

According to the table we can assess the presence of the following painting materials foreach sample as following: P.1a - gypsum, smalt, Prussian blue, lead white; P.2b - arsenic red, vermilon, lead white as whitening material; P.3c - iron bole, gold leaf, P.4d - vermilion; P.5e - red iron oxide; P.6d – gold leaf, bole, zinc oxide, lead white; P.7f - gypsum (ground), red ochre, zinc oxide, orpigment, vermillion, lead white; P.8g - gypsum (ground), red ochre, lead white; P.9h - gypsum (ground), vermillion; P.10i - gypsum (ground), bole, gold leaf; P.11j - gypsum (ground), bole, silver leaf; P.12k - gypsum (ground), orpigment, lead white.

The composition for the four frame samples is: 1 - gypsum (ground), azurite, smaltite, prussian blue for blue; 2 - gypsum, Prussian blue; 3 - gypsum, azurite; 4 - gypsum (ground), bole, gold leaf.

FTIR spectroscopy

In figure 3 the FTIR spectrum of icon's wood is compared with the one made for a limewood reference spectrum.

The profiles of the two spectra are similar, which shows that support icon is used to make lime wood.

Figure 3 shows comparatively the FTIR spectrum of icon's wood and of the calcium oxalate.

The oxalate presence was identified by specific absorptions at 1655, 1626, 1322 and 780 cm^{-1}.

Wood preservation state

The support suffered structural changes with irreversible effects such as convex deformation with fine longitudinal cracks arrangement. One of the major degradations presented by old wooden support isthe biological attack made by Xylophagous insects. The woodboring attack generated networks of galleries through the entire structure of the panel (which is visible to the corners and edges of the icon), which caused over the time the weakening of the mechanical strength of the support, in addition to the effects caused by fluctuations of relative humidity and temperature [21-24].

In order to determine the St Nicholas wooden icon conservation state, the crystalline indexes (defined as [25] $I_{cr}^{1} = A_{1377}/A_{669}$, $I_{cr}^{2} = A_{1109}/A_{690}$ or as $TCI = A_{1378}/A_{2925}$) and $LOI = A_{1426}/A_{895}$) were determined. Lignin to cellulose

Sample	Chemical composition (mg/kg)									
	Ca	Mn	Fe	Cu	Zn	As	Ag	Au	Hg	Pb
P.1a	48814	166	4712	156	845	9869	<LOD	<LOD	533	43012
P.2b	39273	187	3032	<LOD	472	21377	<LOD	<LOD	8106	103778
P.3c	119984	642	39913	675	261	83	<LOD	2915	461	240
P.4d	38466	240	8474	468	937	622	1251	<LOD	104735	1674
P.5e	90458	615	29775	329	5438	1294	<LOD	<LOD	1056	4843
P.6d	69215	348	63654	3337	190193	<LOD	<LOD	189	<LOD	19098
P.7f	73718	286	16148	727	34947	8033	<LOD	<LOD	5862	44838
P.8g	52358	108	9603	75	285	861	<LOD	<LOD	116	4665
P.9h	184950	216	2750	156	488	404	<LOD	<LOD	13395	1678
P.10i	149415	349	21791	5666	977	62	<LOD	2799	379	192
P.11j	156465	504	32530	119	154	138	812	<LOD	<LOD	638
P.12k	29376	228	1612	501	935	23098	<LOD	<LOD	1700	128758
1	117779	127	2471	2785	585	6186	<LOD	<LOD	404	35243
2	345861	269	11951	41	<LOD	<LOD	<LOD	<LOD	<LOD	303
3	167365	<LOD	309	1155	377	433	<LOD	<LOD	<LOD	3668
4	121070	595	38989	707	485	3327	259	1052	437	23954

Table 1
XRF DATA

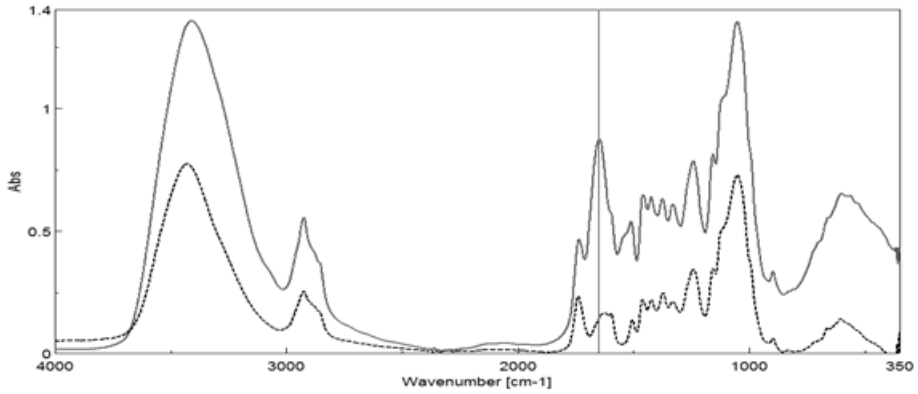

Fig. 3. FTIR spectrum of icon's wood (solid line) as compared to limewood reference spectrum (dashed line)

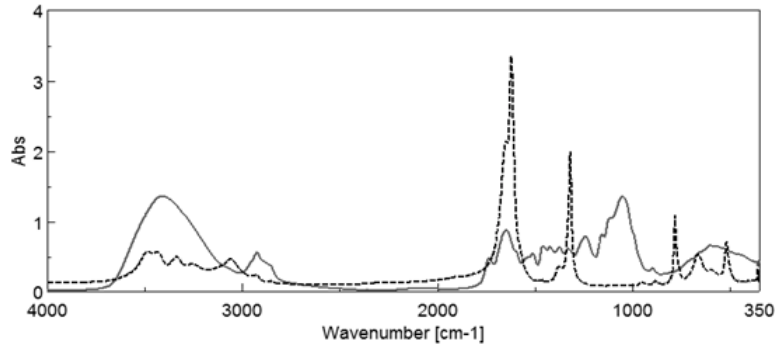

Fig. 4. FTIR spectra of icon wood (solid line) and of calcium oxalate one (dashed line)

Sample	I^1_{cr}	I^2_{cr}	TCI	LOI	$(L/C)_1$	$(L/C)_2$	$(L/C)_3$	$(L/C)_4$
Historical lime wooden support	1.67	2.29	1.39	1.16	1.14	0.65	1.58	0.85
Modern lime wood	1.21	3.11	1.25	1.71	0.71	0.44	1.15	0.61

Table 2
WOOD PRESERVATION STATE

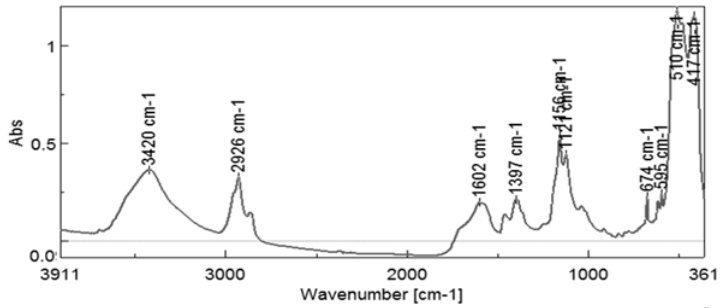

Fig. 5. FTIR spectrum of the silvered grey on yellow area of the paint

ratios, defined as [26] $(L/C)_1 = A_{1506}/A_{1738}$, $(L/C)_2 = A_{1506}/A_{1158}$ or $(L/C)_3 = A_{1506}/A_{895}$ and $(L/C)_4 = A_{1506}/A_{1377}$ were calculated for wooden samples in agreement to already established definitions. These definitions are used only as a measure of their change during time. Table 2 contains these parameters determined for historical and modern lime wood species.

If we compare LOI and I^2_{cr} ratios, the amorphous content is increased for historical wood as compared to reference of modern one. In the same time, L/C ratio is increased for historical wood as compared to reference one, due to a more rapidly consumption of cellulose as compared to lignin one.

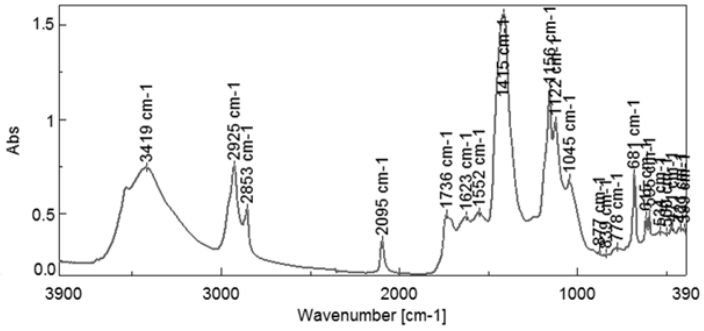

Fig. 6. FTIR spectrum of blue on brown painting material

The conservation state of the painting layer

The painting layer of the icon in study, presents superficial erosion up to the ground level, empty spots with irregular forms which appear on this edges of the paint layer, and some small visible on the bottom part of depicted image. Other forms of degradation are fissures and cracks (craquelure) generated by the t structural deformations (dilation and contraction) of the wood transmitted to the ground layers. The ground acted as a buffer layer between the ground and the paint layer, diminishing and thus relieving tensions that took place in the wood support.

Painting materials investigation

Figure 5 gives the FTIR spectrum of the silvered grey on yellow colored area from icon.

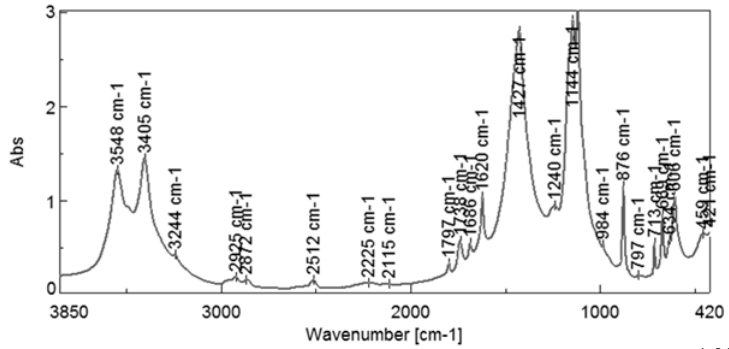

Fig. 7. FTIR spectrum of brown lute (misfit)

The composition in the upper side above the St. Nicholas' head for silvered grey over yellow colour was identified such as: gypsum (3420, 1602, 1156, 1121 and, 595 cm^{-1}), proteins (2926, 2856, 1725 and 1552 cm^{-1}), lead carbonate (1415 and 674 cm^{-1}), and zinc oxide (510 and 417 cm^{-1}) [8, 9, 16-20, 27].

FTIR spectrum of blue over brown paint area is presented in figure 6.

The composition in the blue over brown color of the frame was identified as: gypsum (3548, 3408, 1623, 1155, 1122, 615 and 595 cm^{-1}), Prussian blue (2095 cm^{-1}), lead carbonate (1415 and 681 cm^{-1}), protein egg yolk (2925, 2853, 1736 and 1552 cm^{-1}) [8, 9, 16-20, 27].

For brown lute (misfit) the FTIR spectrum is presented in figure 7.

The composition for the brown lute (misfit), on the frame border was identified as following: gypsum (3548, 3405, 1144, 634 and 608 cm^{-1}), traces of silicates (1620, 1240, 984 and 876 cm^{-1}), calcium carbonate (1427 and 713 cm^{-1}) as inert, egg yolk (2925, 2872, 1738 and 1686 cm^{-1}) [8, 9, 16-20, 27].

Conclusions

The investigations conducted on the support and paint materials of the studied icon established with certainty the type of wood species of which the support was made, and the composition of pigments in the paint layer, ground (primer) and of the binders that were used by iconographer.

Also, both methods of investigation identified Ca (gypsum/carbonate) present in the original ground layer in admixture with a binding protein (animal glue). Organic binder (egg yolk) identified in the composition of paint layer demonstrates that the iconographer used the traditional technique of painting on wood panel known as *tempera grassa*. Both methods have shown that the layer of silver gray applied over a layer of yellow (this sequence of layers is an unprofessional procedure) has in its composition zinc oxide; colored primer was identified as calcium carbonate in admixture with an iron oxide and the plaster (from a previous restoration intervention) is calcium carbonate. Blue paint (repainting empirical intervention) on the frame is made of Prussian blue, the original painting materials being azurite and smalt.

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