Multi-analytical Study of the Paint Layers Used in Authentication of Icon from XIXth Century

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This paper presents a physico - chemical study of the paint layers of "Saint Nicholas" icon, which comes from a private collection in Romania. The icon has artistic characteristics of the Russian icons, the Post-Byzantine style, and is an expression of the painted art in the Orthodox Church. Significant information about the icon painting technique, the materials used and about the period in which the icon was made, were found using new analytical techniques. The aim of this study is to gather useful information about the icon to make a suitable conservation and restoration treatment of the artifact. For the analysis of the icon's materials (preparation layer, paint layer and varnish), Optical Microscopy (OM), scanning electron microscopy connected with X-ray spectrometry (SEM-EDX) and Fourier transformed infrared spectrophotometry (μ-FTIR), were used. It was concluded that the paint layer is made of tempera (pigment with egg-based emulsion), painted over silver leaf, over which olifa varnish was used. Based on the style of the painting and on its conservation state, it is presumed that it was painted in the XIXth century. The corroboration between the analytic data, highlighted different details of the painting process and of the used materials. Thus, mineral pigments, colored earths, silver leaf and paper stripes under the gesso were identified.

Keywords: panel painting icon, wood species identification, OM, SEM-EDX, μ-FTIR

Icons are both religious and aesthetic paintings: especially after the end of iconoclasm, they were understood to manifest the unique "presence" of the figure depicted by means of a "likeness" to that figure through carefully maintained canons of representation [1].

The subject of this study was the icon of Saint Nicholas, comes from a private collection in Tecuci, Romania. It is painted in Russian style of icons with a reduced color palette, on silver leaf and linden wooden panel. According to the characteristics of the technique and materials used by the painter, the icon can be considered to have been painted in the nineteenth century. The painting was applied on a wooden panel with two crossbeams on which a layer of cardboard was attached. On these the ground was added, in which various models have been tooled (with small chisels of various shapes) after it had been drawn. After finishing the tooling, the silver leaf was attached, the painting was made and finally, the background and parts of the Saints cloak was covered with yellow varnish to resemble gold [2].

The icon (fig. 1) illustrates Saint Nicholas, centered, holding the Gospel in his left hand and blessing with his right hand. Close to the head of the saints two medallions were depicted: one, to the right, representing Jesus Christ and one, to the left, representing the Virgin Mary. The scene is firstly framed by an engraved embroidery and then by the canonical red border. Also, the Saint's halo and halo have various patterns sculpted in the ground. The entire front of the icon is covered with silver leaf except for the Saint's face and a stole on his shoulders. From a chromatic

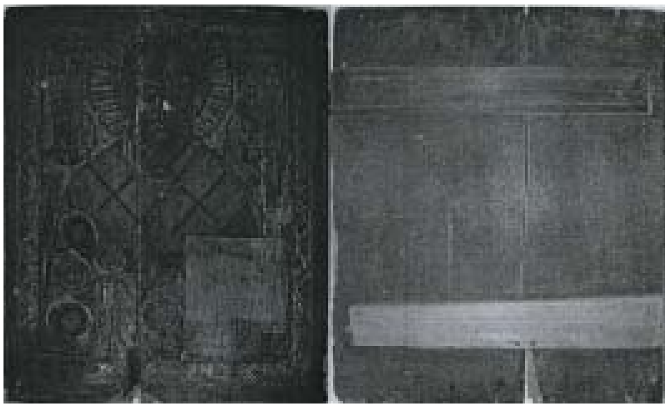

Fig. 1. "Saint Nicholas" icon: front and back sides

point of view, the icon belongs to the Russian iconography with just a small range of natural pigments having been used, like yellow and red ochres, and carbon black. The icon panel is made of two main plates and a secondary narrower one, stuck together with rabbit skin glue and fixed with two parallel dovetail crossbeams. One of the original cross-pieces has been replaced with a copy made of a different type of wood which was nailed to the back [2].

Regarding the painting itself, when the background was made with metallic leaves, the lines of the halos, faces, and figures were incised in the gesso since a normal drawing would be lost under the gold or silver layer. In the XVIIth century in particular, incised lines were often used to outline folds of clothing where darker colors of the first

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paint layers would occlude the sketch. This practice became more frequent with the use of thicker and less transparent paints in the XVIII[th] and XIX[th] centuries [3]. Both organic pigments (even blood on certain areas of very old icons) and inorganic pigments were used, often with egg yolk as a binding medium. Pigments were often mixed three or more together, even if only in small amounts [4].

Prior to the conservation treatment, the painting was extensively documented by means of non-invasive methods, including photography in visible light. The Optical Microscopy (OM) and anatomical wood identification catalogues were used to micro-analyze the wood specie and to establish that is *Tilia cordata Mill*, which is the most used wood specie in Eastern Europe for panel painting [2, 5]. Under the OM the surface of the paint layer was analyzed. The red pigment from the border shows signs of charring, a series of longitudinal cracks, varnish and adherent dirt. An enhanced image of the used paper, made with cloth fibers can be observed. The stratigraphic images are showing very thin layers of pigment and ground [6-8]. The painting technique consists of wood, cardboard paper, ground, pigment with egg yolk, silver leaf and varnish. With SEM-EDX and FTIR analysis, the pigments, fillers and lakes were identified [9-11]. The red paint from the borders is a mixture of red lead and red ochre. The face of the Saint was painted in ochre and lead white. The black stripes are made of carbon black.

The analyses of the varnish show that it is the original Russian olifa. The presence of blue fibers in the paper sample indicates a XIX[th] century paper and therefore we can assess that the icon belongs to the beginning of this century.

Experimental part

The modern analytical techniques used are optical and scanning electron microscopy and FTIR spectroscopy.

The surface microstructures have been studied using a light microscope Zeiss Imager a1M, which is attached to a camera AXIOCAM and specialized software, at magnifications of 50X-500X. All the images were analysed in reflected light.

To highlight the elemental composition and arrangement of microstructures on the samples, was used a scanning electron microscopy, SEM model VEGA II LSH, produced by TESCAN Czech Republic, coupled with an EDX detector type QUANTAX QX2, manufactured by BRUKER/ ROENTEC Germany. The microscope, entirely controlled by computer, has an electron gun with a tungsten filament and can obtain a resolution of 3nm at 30kV and a zoom range from 30X to 1,000,000X in the "resolution" mode, the acceleration tension ranging from 200 V to 30 kV and the scanning speed from 200 ns to 10 ms per pixel. Its working pressure is lower than $1x10^{-2}$ Pa. The image obtained may consist of secondary (SE) or back-scattered (BSE) electrons. The technology used, together with the visualization of the micro-photogram, allows image rendering with the location of the atoms on the surface under analysis and based on the X-ray spectrum one can determine the elements composing a certain micro-structure, or a selected area (in gravimetric or molar percents) and evaluate variations in the composition. The micrographs were enhanced between 300X and 1000X, and were analyzed in *BSE* and *SE*. The cross-sections were embedded in resin, cut, polished and coated with carbon, and the simple samples were mounted on a carbon strip.

The FT-IR spectra were recorded with a FT-IR spectrophotometer (TENSOR 27) coupled with a HIPERYON 1000 microscope, both made in Germany. They allowed an analysis of the powder samples, by reflection. The software used was OPUS/VIDEO, for interactive video data collection. The detector was of the MCT type, cooled with liquid nitrogen (-196°C). The spectral analysis domain was 600-4000cm^{-1} and the measured are ranged from 20 to 250μm, the microscope having a 10X lens. The software recorded the spectrum after 32X scanning process and the structural components were selected based on a repository of spectra.

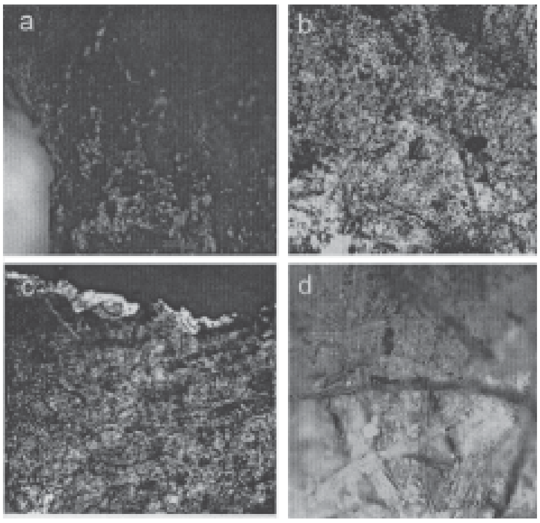


Fig. 2. Microscopic images of the painting surface: a) red pigment sample, b) face sample, c) background sample, d) cardboard paper. The images were enhanced by 200X and take in reflective light.

Results and discussions

Microscopic examination

The microscopic images of the painting layer depicted various craquelures, age related micro-fissures, adherent dirt and a very thin layer of varnish.

The red pigmented sample was taken from the lower part of the icon, where the wood is slightly burned (fig. 2a). The microscopic magnification revealed a charred surface of the varnish. The second sample (fig. 2b), taken from the gap on the Saint's face shows a light coloured pigment layer with a darkened varnish. The adherent dirt is also present on the surface as black and opaque clusters. The background image reveals the silver leaf covered with a yellow varnish to look like gold (fig. 2c). The last image depicts the cardboard paper used under the ground: the paper has a dark blue-grey color and a coarse texture (fig. 2d) [12, 13].

The stratigraphy of the different areas of the painting show a very thin layer of color 47μ over the ground layers of around 760μ. The cardboard paper has 29μ thickness (fig. 3a) and the silver leaf has almost 10μ thickness. The ground layer was not evenly applied on the entire surface of the icon, and particles different in size and texture are making the composition inhomogeneous (fig. 3b). The lack of cardboard paper in the face pigment or in the background sample suggest (fig. 3c) that strips of it were added only on the borders of the icon [13].

SEM-EDX analysis

The samples used under electron microscope were mounted on a Carbone strip and analyzed with the SEM-EDX to establish their elemental composition. In this regard, micrographs were took at magnifications of 500X, 700X and 1000X in BSE (figs.4 - 6).

In all the SEM micrographs the colour layer is very even, only detachments and craquelures are visible. The micro

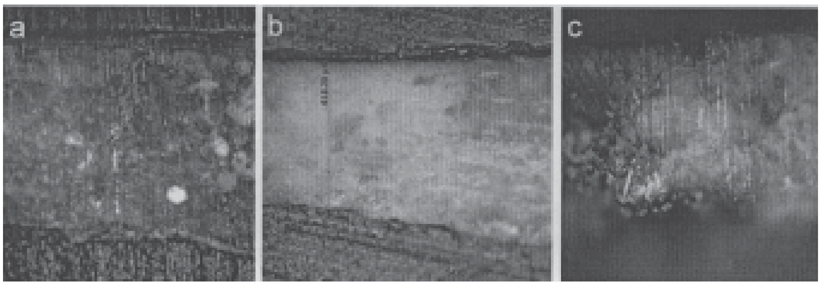


Fig. 3. Painting stratigraphy: a) edge sample with red pigment, b) face sample with white pigment, c) background sample, at 400X

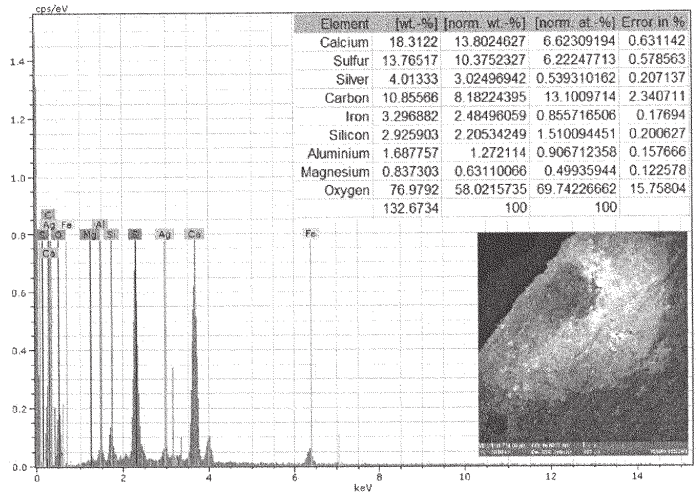


Fig. 4. EDX spectrum and SEM micrograph for the edge sample, 1000X

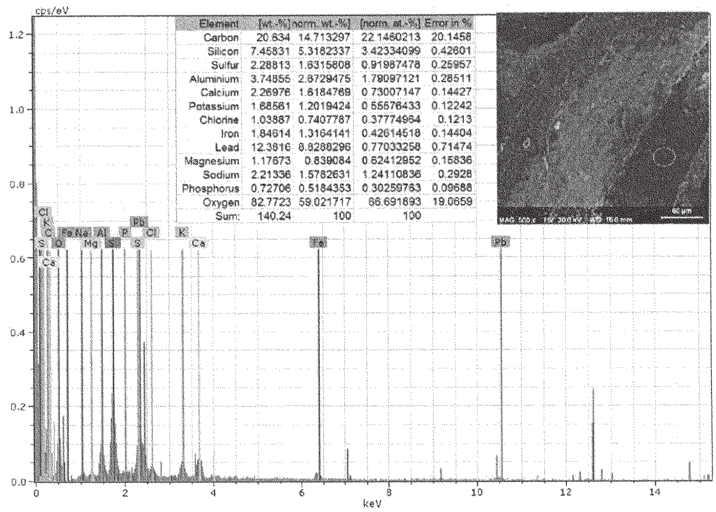


Fig. 5. EDX spectrum and SEM micrograph for the face sample, 500X

fissures that are deeper suggest that the paint layer is thicker (fig. 4 – edge and face sample).

The elemental composition identified by the EDX analysis (figs. 4 - 6), shows a rich quantity of Pb and Fe, with traces of Ca, S and other elements (Si, Al, Cl, Mg, Na, K) characteristic for the natural earth pigments (ochres) and for the gesso ground layer. Lead is a very toxic metal which is highly used in pigments from ancient times, due the beautiful colour hue and resistance in time of the pigments [14]. Minium, Pb_3O_4, also known as red lead, is a bright orange red pigment that was widely used in the Middle Ages for the decoration of manuscripts and for paintings. As well as the vermilion, it is a very intense and stable pigment. Because of the Pb content, it has a tendency to darken in time due to the presence of S. Other than minium, the red pigment has in its composition Iron Oxide (Fe_2O_3) too (fig. 4). This is marked by the presence of Iron and the high quantity of Oxygen. The presence of Aluminum, Silicon, Magnesium, Sodium and Potassium are earth impurities, elements specific for natural earth pigments. The Calcium and the Sulfur are characteristic to the gypsum ground layer [15].

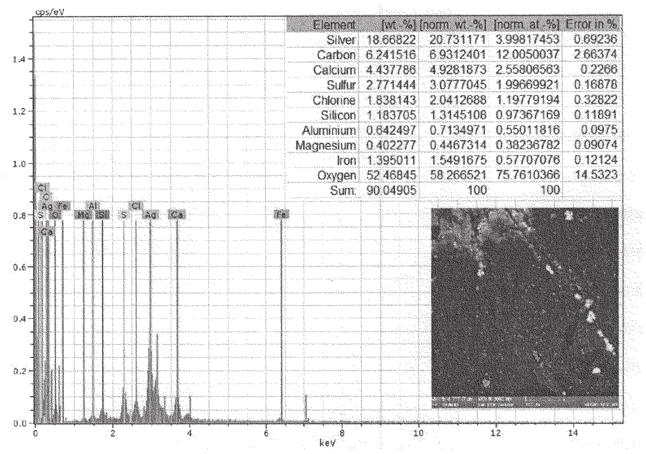
The second EDX spectrum of the face layer sample, depicts specific elements for the lead white pigment, which was intensely used since Middle Age [16]. The other elements as Ca and S are from the gypsum, and Si, Al, K, and O are elements found in natural mineral pigments, but in many cases kaolin was put into the mixture of lead white [17 - 19].

The EDX spectrum for the background sample shows a high quantity of Al. In the XVIIth century the silver leaf started to have in its composition tin, making in more malleable for gilding art objects. Although the silver leaf was preferred for panel paintings in East Europe, in some cases the tin leaf was used with gold leaf on top or colored varnish to imitate gold [20].

μ-FTIR spectrometry

To complement the results of the SEM-EDX analysis, the FTIR spectrometry was used. In this regard some new samples of 1mm^2 were taken from the same places as previous.

Taking into consideration the whole aspect of the icon, and the FTIR analysis of the varnish, it is safe to say that it is olifa, the traditional varnish of Russian icons, made from



Element	[wt.-%]	[norm. wt.-%]	[norm. at.-%]	Error in %
Silver	18.66822	20.731171	3.99817453	0.69236
Carbon	6.241516	6.9312401	12.0050037	2.66374
Calcium	4.437786	4.9281873	2.55806563	0.2266
Sulfur	2.771444	3.0777045	1.99669921	0.16878
Chlorine	1.838143	2.0412688	1.19779194	0.32822
Silicon	1.183705	1.3145108	0.97367169	0.11891
Aluminium	0.642497	0.7134971	0.55011816	0.0975
Magnesium	0.402277	0.4467314	0.38236782	0.09074
Iron	1.395011	1.5491675	0.57707076	0.12124
Oxygen	52.46845	58.266521	75.7610366	14.5323
Sum:	90.04905	100	100	

Fig. 6. EDX spectrum and SEM micrograph for the background sample, 700X.

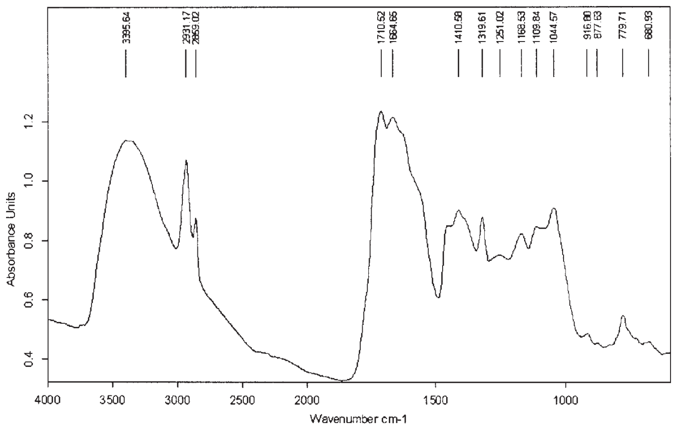


Fig. 7. μ-FTIR spectrum of the background sample

boiled linseed oil. In this regards, the FTIR spectra (fig. 7) contain peak values as 2931cm^{-1}, 2859cm^{-1} and 1710cm^{-1} which are characteristic of an aged oily varnish [17]. It is based on boiled linseed oil with the addition of a few grams of cobalt acetate 3% (in use for Russian paintings since the 18th century) or 7–8% litharge [3, 17]. The treatise of Dionysos from Fourna [21] mentions another recipe used in the monastic workshops at Mount Athos: the linseed oil was "boiled" and vegetable resin, such as dammar, mastic, or sandarac was added.

Conclusions

The corroboration between various analysis techniques helped uncover great information about the Saint Nicholas panel painting. Although it is customary for the iconographers to not write their name or year of the painting, in nowadays the authentication process of an art object goes far away enough to establish at least the century when it was made. Together with the archeometric characteristics revealed by the chemical and physical analysis made on different samples form the art object, the final answer is quite close.

The icon Saint Nicholas, is a beautiful Orthodox artwork painted in the XIXth century, in the Russian style of Post-Byzantine icons.

The SEM-EDX analysis concluded that the pigments used were minium, red ochre, yellow ochre, lead white and carbon black, and that in the background of the icon, silver leaf was used.

The μ-FTIR analysis concluded that the yellow varnish added on top of the in leaf, is olifa, the Russian traditional varnish.

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