Integrated Analytical Study for the Authentication of Five Russian Icons (XVI–XVII centuries)

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ABSTRACT This article presents an integrated approach for the authentication of five Russian icons through the study of their paint materials (elemental composition and stratigraphic mapping), state of conservation and artistic technique. The results of the applied analytical protocol, involving optical and scanning electron microscopy coupled with energy-dispersive X-ray spectrometry and Fourier transformed infrared spectroscopy/microspectroscopy, led to the conclusion that the five icons belong to the same group and iconographic school (from Northern Russia) and date from the end of the 16th century to the beginning of 17th century. Because of massive overpainting, the icons “suffered” a change in iconographic style and significance, and restoration treatment brought to light the original painting and its attribution. Identification of the composition of the original chromatic palette used by the iconographer, the stratigraphic mapping and the conservation state of the painting materials, along with the features of the original artistic technique, furnished key elements for the icons’ authentication. Here, we present the first experimental data concerning the identification of the authentication characteristics, being part of a large project that has as its final aim the evaluation of the effectiveness and effects of the cleaning agent on the paint layers. *Microsc. Res. Tech.* 72:755–765, 2009. © 2009 Wiley-Liss, Inc.

INTRODUCTION

After the conquest of Constantinople by the Turks in 1453, the art of the Icons testified to the continuation of Byzantine traditions in several countries: Greece, Bulgaria, Romania, Russia, Macedonia, Albania, Serbia, Croatia, etc. These religious works of art ensured the survival of “Byzantium after Byzantium” through the foundation of local schools, and contributed to the preservation of national identities of the aforementioned peoples, which shared a common faith and roots (Lobefaro, 2003; Popova et al., 2003; Sandu et al., 2005; Sendler, 2001; Taylor, 1979). Among them, Russia was one of the major producers of icons and the cities of Kiev, Novgorod, Moscow, Pskov, Palech, etc. became important iconographic centres, famous the world over.

The present research aimed to authenticate five Russian icons representing Saint Prophets, belonging to an Italian private collection. As usually happens with post-Byzantine icons, improvised “restorers” had introduced overpainting, puttying, and cleaning without taking into consideration the original materials and basic principles of conservation and restoration. Thus, the owner requested further restoration treatments, focused on the removal of the negative effects of these “mutilating” interventions, from a private laboratory in Northern Italy (Biella). The restoration work begun in June 2007, aimed to consolidate the paint layers and clean the icons, mainly by removing the overpaintings

that were hiding the original iconography and chromatic palette.

The five icons were painted on one-piece coniferous wood panels of ~68 cm × 31.8 cm, with gilded halos around the heads of each of the Saints. From a stylistic point of view, the icons were initially assigned to Northern Russia (Karelia?) and the period between the end of 16th and beginning of 17th centuries (Fig. 1). Signs of original drawing were visible in the red vest of the prophets Malachia and Samuel (Icons 2 and 3), in black color and with free-hand brushing.

Authenticating post-Byzantine and late icons is one of the trends of this collaboration, as it is a challenging and multidisciplinary activity, in which art history, iconography, chemistry, and material sciences bring their contribution to the establishment of parameters or characteristics useful for assessing the originality, uniqueness and/or authorship of the studied art-objects (Danti et al., 2008a,b; Domenech et al., 1996; Kouloumpi et al., 2007; Sandu et al., 2006a,b, 2007, 2008a,b).

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Fig. 1. The five sampled icons.

The main objective of this work is to distinguish between the original materials and those added by subsequent overpainting interventions (Casellato et al., 1995; Ganitis et al., 2004). An integrated multimethod approach using microscopy and spectroscopy is proposed and tested for authenticating these religious paintings on wooden supports (Domenech et al., 1996; Schreiner et al., 2007; Sotiropoulou et al., 2008). Pigments, mineral charges, and metallic leaves were characterized using light microscopy (OM, UV-Vis), scanning electron microscopy coupled with energy-dispersion X-ray spectroscopy (SEM-EDX) and micro-FTIR, whereas the organic components of the paint layers

(binders and varnishes) were identified by the specific fluorescence images using UV light microscopy and by Fourier transform infrared spectroscopy. By crossreferencing the results obtained from these three techniques, it was possible to make an accurate distinction between the original materials/layers of the paint in the five icons and the overpainting.

MATERIALS AND METHODS Sampling and Analytical Protocol

The nine samples of paint layers taken from the five icons (as it is shown in Table 1 and Fig. 1) covered the

TABLE 1. Description of the sampled icons

Icon no.	Title/dimensions	Description	No. of samples
1	S. Proph. Michea, 68 × 31.8 × 3.6 cm × cm × cm	Tempera, gilding layer (mecca technique), on entire wooden panel with frontal grooved background	3
2	S. Proph. Samuel, 68 × 31.5 × 3.5 cm × cm × cm	Tempera, gilding layer (mecca technique) on entire wooden panel with frontal grooved background (two overlapped icons)	2
3	S. Proph. Malachia, 68 × 32 × 3.8 cm × cm × cm	Tempera gilding layer (mecca technique) on entire wooden panel with two movable slats on the backside	1
4	S. Proph. Jezechiel, 68 × 31.8 × 3.8 cm × cm × cm	Tempera gilding layer (mecca technique) on wooden panel with frontal grooved background	1
5	S. Proph. Geremia, 68 × 31.8 × 3.5 cm × cm × cm	Tempera gilding layer (mecca technique) on wooden panel with frontal grooved background	2

TABLE 2. Taken samples and performed analyses

Icon no.	Samples ID	Area of sampling	MO (UV-Vis) on cross-section	SEM/EDX on cross-section	FTIR on samples
1	1S1	Green-brown fragment from the vest of the Prophet, with original "olifa" (varnish)	—	—	X
	1S2	Gilding layer fragment from the halo of the Saint	X	X	—
	1S3	Red-brown fragment (overpainting) from the left border of the icon	X	X	X
2	2S1	Red fragment from the vest with white original highlights	X	X	—
	2S2	Yellow-ochra fragment from the left border, treated with a cleaning agent	X	—	X
3	3S1	Fragment of flesh from the Prophet's forehead with a small area of overpainting	X	X	X
4	4S1	Dark green fragment from the vest with white highlights and original olifa	X	X	X
5	5S1	Red fragment from the vest	X	X	—
	5S2	Brown fragment from the background, left border, area of overpainting	X	X	X

entire chromatic palette and were selected with the aim of obtaining information regarding the pigments and painting technique, as well as for describing of the state of conservation of the paint in stratigraphic sequence. Table 1 summarizes the main data: titles, dimensions, short description, and number of samples taken from each icon.

With the help of a magnifying glass, the samples were taken with a scalpel from representative areas (fulfilling the condition of selective sampling of a polychrome artwork), taking into consideration lacunas, cracks, or abrasions that could facilitate sampling of the entire structure of the paint layers (Table 2). The samples are indexed as follows: the first number represents the icon's number, *S* is abbreviation for Sample, and the last number is the sample's progressive number for each icon (e.g., 1S1, 1S2, etc.). The weight of each sample varied between 0.4 and 1 mg.

After microscopic observation and photographic documentation, a microfragment was identified in each sample which was embedded in synthetic resin to obtain cross-sections representative of what had been observed. Part of the sample was preserved for spectroscopic analysis.

Optical Microscopy (OM) on Cross-Section

The cross-sections, obtained from fragments of the paint-layer samples, which were embedded in Polyester resin Mecaprex SS (Leica), were properly polished after the necessary curing time, and observed under a Nikon Eclipse E600 binocular microscope (4–40× magnification), with both visible and UV light, and then photographed with a Nikon DXM1200F digital camera.

The block of filters used for UV fluorescence was B-2A type (excitation radiation at 330–380 nm—EX, observation at 420 nm—BA).

SEM Microscopy Coupled with EDX Microanalysis

For the morphological characterization of the samples embedded as cross-sections and for EDX microanalysis, a SEM, VEGA II LSH scanning electron microscope (TESCAN, Czech Republic) coupled with an EDX, QUANTAX QX2 detector (ROENTEC, Germany) was used, working at $<1 \times 10^{-3}$ Pa vacuum pressure, a 30.00 KV voltage, varying the working distance between 11 and 20 mm (16.6 mm for EDX analysis) and the magnifying power between 78 and 1.000× in the resolution mode, with a scanning speed between 200 and 10 ms per pixel. The seven cross-sections analyzed by this method (as shown in the Table 2) were coated with a thin layer of graphite.

The qualitative and quantitative (for some cross-sections) microanalyses were done both on areas and spots (cross-bared points) on the analyzed samples.

FTIR and Micro-FTIR Spectroscopy

The FTIR analysis was done with a Perkin Elmer System 2000 spectrophotometer at 64 scans in the interval of 4000–500 cm^{-1} , in transmission mode with a diamond cell.

For confirming the presence of a green Cu-based pigment in the surface layers, two micro-FTIR analyses were preformed on two samples. A Nicolet Nexus spectrophotometer interfaced with a Continuum microscope with a MCT-A detector cooled by liquid nitrogen

was used. The spatial resolution is 30 μm , the spectra being obtained with a resolution of 4 cm^{-1} and 128 scans, in absorbance mode, in an interval between 4000 and 600 cm^{-1} , using a Thermo diamond anvil compression cell.

RESULTS

The microscopic analyses were useful for assessing the stratigraphic sequence and the morphological, chromatic, and compositional characteristics of the original paint layers versus the overpaintings and also for describing their conservation state and the extension of previous restorations. OM and SEM observation allowed comparison of the morphologic pattern of the ground layers and also the measurement of the thickness of the layers in the cross-sections. The fluorescence image of the various layers in the cross-sections observed under UV light, in some cases, indicated the presence of an oily varnish and helped also to distinguish between the original paint layer and any overpainting.

The FTIR and micro-FTIR spectroscopy correlated with EDX microanalysis allowed the identification of various mineral charges and pigments, and also the composition of the gilding layers of Icon 1. With the help of SEM-EDX analysis, distribution maps of various elements of each layer in the analyzed cross-sections were also obtained.

DISCUSSION

Painting Materials and Technique

Table 3 summarizes the main pigments, mineral charges, and other components identified in the analyzed icons, for each layer of sample stratigraphy.

The ground (white preparation layers covering the wooden support) has a variable thickness between 0.2 and 0.4 mm. It was applied over pieces of cloth that do not cover all the surface of the panels but only some areas that are more sensitive to dimensional variation, such as the upper and lower sides and the biggest knots in the wood, as showed by radiographic analysis. The thick preparation was generally applied in several layers, separated from one another in Icons 2, 3, and 4, clearly visible under microscopic observation (Fig. 2). The combined information of FTIR spectra and EDX microanalysis of the ground layers indicate the presence of dihydrated calcium sulfate (gypsum) as mineral charge, in many cases accompanied with aluminum-silicates as colored grains inside the matrix of gypsum crystals (Figs. 3 and 4). The grain size and morphology of the charge in various samples, observed at 1000 $\times$ with the backscattered electron detector (BSE), indicates analogous composition and thus homogeneous methods of preparation of the gesso grounds in the five icons (Fig. 4).

The gypsum crystals have a relatively homogeneous round-shaped granulometry, with inclusions of various dimensions and colors, containing Al and Si. The presence of these impurities (clay minerals based on Al and Si elements) corresponds to what is referred to in the literature as the use of white earths based on kaolinite in grounds and priming layers for post-Byzantine icons (Genestar and Pons, 2005; Hradil et al., 2003). The identification of gypsum (known as "levkas" in Russian

language) in the preparation of all five icons confirmed the assessment in the literature concerning the traditional use of this charge in ancient icon painting (Daniilia et al., 2002; Lobefaro, 2003; Matteini and Moles, 1989; Sandu et al., 2006a,b).

Although the paint samples have a complex composition and the corresponding FTIR spectra display many peaks, in most of the samples the identification of constituent materials was possible. A certain differentiation was done during sampling, by dividing the fragments and selecting only small quantities of preparation or paint layer. In many cases, it was not possible to remove only the varnish from the surface paint layer and therefore in the same spectrum peaks belonging to the colored layer (binder and pigment) and to the varnish were identified. The same situation was verified for FTIR analysis of colored samples of paint in which residues of preparation were detected.

The pigments are mainly of mineral origin, the chromatic palette being limited to few pigments, such as: red and yellow earths (Ochras), Cu-based pigment (Verdigris), green earth and brown earth or umber, Caput Mortum. The basic lead carbonate was used both in mixtures with other pigments in the paint layer and as pure pigment (lead white, a typical pigment for post-Byzantine icon painting) for highlights on vests and flesh, as in Icon 2 (sample 2S1) and Icon 4 (sample 4S1) (Fig. 5).

In the green layer of sample 4S1, the EDX analysis detected the presence of Cu together with Si, K, Fe, Al, and this can be an indication of a mixture of Copper pigment (Verdigris) and silicates (Green earth). In fact, the micro-FTIR and FTIR spectra (Fig. 6) of this green layer confirm the presence of Cu acetate (Verdigris) mixed with a small quantity of proteinaceous material, as the EDX microanalysis (Fig. 3) identified the presence of Ca together with Cu. An ancient painting recipe mentioned by Sendler (2001) indicates the use of calcium caseinate (or better, the curdled milk) for the preparation of the green pigment known as Verdigris (caseinate as substitute of acetate is an hypothesis to be further verified with chromatographic analysis, although the absence of P from the EDX spectrum would exclude the presence of casein—a phosphor-protein used as binder in ancient painting) (Sendler, 2001). The micro-FTIR spectrum of 4S1 green layer is similar to the spectrum obtained for the same color of sample 1S1, and this confirms the use of the same pigment or mixture of pigments for the Icons 4 and 1.

The binder present inside the ground is made of animal glue (proteinaceous material), confirmed by the FTIR spectra obtained for various samples of preparation layers (Fig. 6); identified by specific absorbance values at 1630–1680 cm^{-1} (amide band) and 1520–1560 cm^{-1} (NH_2) in conjunction with the strong peaks attributed to methylenic groups at around 2929 and 2850 cm^{-1} in the relative FTIR spectra (Adrover, 2001).

The binder inside the original paint layers is the traditional emulsion made of egg yolk, as many of the acquired FTIR spectra contain the values: 2924, 2850 cm^{-1} for CHstr (proteins), 1731–1736 cm^{-1} for CO (triglycerides), 1650–1658 cm^{-1} (CO) and 1535–1541 cm^{-1} (NH_2) for Amides I and II (Adrover, 2001; Daniilia et al., 2002; Domenech et al., 1996). The use of egg yolk was a common practice in icon painting since the 14th

TABLE 3. Results of the analyses for each layer of the samples [Color table can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Sample	Surface color of sample	Color of layers in cross-section	Mineral charge and pigments	Organic components (binders, varnishes)
1S1	Brown-green from the vest of the Saint	White (preparation)	Gypsum (FTIR)	Animal glue as binder (FTIR)
		Green-brown with residues of varnish	Gypsum, Verdigris, Silicates (Green Earth?) (FTIR)	Residues of oily varnish (olifa) (FTIR)
1S2	Gilding area from the Saint's aureole	White (preparation)	Gypsum (FTIR, SEM-EDX)	Animal glue as binder (FTIR)
		Red	Gypsum and red earths (SEM-EDX)	—
		Silver	Leaf of silver, several applications (SEM-EDX)	—
1S3	Brown-ochra from the background	White (preparation)	Gypsum with silicatic impurities (FTIR, SEM-EDX)	Animal glue as binder, residues of an oily emulsion? (FTIR)
		Yellow	Yellow ochra/earths (SEM-EDX)	—
		Red-brown	Red earths (FTIR, SEM-EDX)	Egg emulsion as binder (FTIR)
2S1	Red-yellowish fragment from the vest of the saint	White (preparation)	Gypsum (SEM-EDX)	—
		Yellow orange	Mixture of lead white and yellow—red ochra/earths (SEM-EDX)	—
		White	Lead white with kaolin impurities (SEM-EDX)	—
2S2	Ochre from the background	White (preparation)	Gypsum (FTIR)	Animal glue as binder (FTIR)
		Yellow ochre	Ochre/yellow earths (FTIR)	Egg emulsion as binder (FTIR)
3S1	Brown-ochre from the forehead of the Saint	White (preparation)	Gypsum with earthy impurities (FTIR, SEM-EDX)	Animal glue as binder (FTIR)
		Red-brown ochre	Red ochras/earths and litharge, as dessicant agent in the varnish layer (FTIR, SEM-EDX)	Egg emulsion as binder, oily varnish (olifa) (FTIR)
4S1	Green from the vest of the Saint	White (preparation)	Gypsum with silicatic impurities (FTIR, SEM-EDX)	Animal glue as binder (FTIR)
		Green	Green earth and copper pigment (Verdigris) (FTIR, SEM-EDX)	Egg emulsion as binder (FTIR)
		Brown and white (the white is a highlight on the garment)	Brown earths, lead white (FTIR, SEM-EDX)	Oily varnish (olifa) (FTIR)
5S1	Red fragment from the vest, repainting area	White (preparation)	Gypsum with silicatic impurities (SEM-EDX)	—
		Red	Red earth/ochra and silicates (SEM-EDX)	—
5S2	Brown fragment from the background, repainting area	White (preparation)	Gypsum (FTIR, SEM-EDX)	Animal glue as binder (FTIR)
		Yellow	Yellow ochra/earths (SEM-EDX)	Egg emulsion as binder, oily varnish (olifa) (FTIR)
		Brown-bluish	Lead pigment—Litharge in the olifa layers (FTIR, SEM-EDX)	—
		Grey-bluish	Brown earths (mixtures of pigments) and Litharge (FTIR, SEM-EDX)	—
		Red-brown	Brown earth/caput mortum, litharge (FTIR, SEM-EDX)	—

Fig. 2. Cross-sections showing the ground in sample 3S1 made of various layers of gesso, observed in visible and UV light ($\times 100$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 3. Element mapping in sample 4S1 analyzed by SEM-EDX. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to 15th centuries, whereas the mixed technique (“tempera grassa”: egg and linseed oil as binder) was introduced to the Russian icon after the era of Peter the Great. Considering that the spectrum of aged yolk is very similar to the one of linseed oil, it is difficult in this case to assess with extreme precision whether a yolk or an oily egg emulsion was used as the binder (Daniilia et al., 2008a,b; Ganitis et al., 2004; Sandu et al., 2008b). In this case, if small amounts of oil are present it could also be due to the penetration of “olifa” during repeated varnishing (all five icons were subject to several applications of olifa, the traditional varnish of Russian icons, made from boiled linseed oil added with a desiccant pigment or charge).

The carbonyl peaks (usually attributed to fatty fraction, esters, of binders or varnishes, Adrover, 2001) occur at $1710\text{--}1714\text{ cm}^{-1}$ for overpainting layers in samples 1S3 and 5S2 (Fig. 7), at $1733\text{--}1730\text{ cm}^{-1}$ for brown layer in sample 1S1 and at $1736\text{--}1734\text{ cm}^{-1}$ in sample 4S1. These values of absorbance can be indicative of the presence of oily medium/varnish (olifa) in overpainted areas (samples 1S3 and 5S2) and of egg yolk in the other samples.

The varnish is not present in all the samples as it was removed during previous cleaning interventions (mainly from Icon 2), but in a few cases (samples 1S1, 1S3, 4S1, 5S2) the FTIR spectra contain peak values ($2920\text{--}2928$, $2848\text{--}2855$, $1710\text{--}1720\text{ cm}^{-1}$) which are

Fig. 4. Comparison between detailed SEM photos (backscattered electrons) at 1000× of the studied ground layer for icons: (a) Icon 1, (b) Icon 2, (c) Icon 3, and (d) Icon 5.

Fig. 5. Cross-section under visible light of samples: 2S1, ×100 and 4S1, ×50 (red and green areas with highlights). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

characteristic of an aged oily varnish, and could be attributed to the traditional olifa (Daniilia et al., 2002; Ganitis et al., 2004). In layers corresponding to this oily varnish (samples 1S3, 2S1, 5S2) Pb was detected,

and its presence can be an indication of the use of a lead pigment as a dessicant for olifa (Litharge, PbO), as the traditional technique required (Lobefaro, 2003; Sandu et al., 2005; Sendler, 2001).

The painting technique seems to be the canonical one: egg tempera, paint structure made of several layers, varying in complexity from a simple stratigraphy of one layer of paint to more complex ones (Figs. 2,

Fig. 6. FTIR spectra of sample 4S1, green layer based on Verdigris and fragment of ground. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 7. FTIR spectra of overpaintings in samples 1S3 and 5S2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

5, and 8), in which more than four color layers can be present (particularly in the case of Icon 5, sample 5S2, where several layers of overpainting over the yellow one were added). The ground has a multilayer structure, characterized by the presence of three layers of “gesso sottile” (thin gesso) applied over a thick gypsum priming (“gesso grosso”), as shown by sample 3S1 (Fig. 2).

The halos of the saints were done with “mecca gilding” with various applications of silver leaf, coated with final protective layers of a resinous varnish. For Icon 1, the silver leaf identified in sample 1S2 was applied with “mecca” technique (Fig. 9), with several applications of thin leaf, interlayered with varnish, and silicate-based layers of overpainting (probably a red earth) (Daniilia et al., 2002; Lobefaro, 2003; Sandu et al., 2005, 2006b).

The icons’ original yellow background was almost entirely overpainted and this intervention was probably the cause for the change in the chromatic appearance of the paint due to darkening of the original varnish (olifa), whereas for flesh the overpaintings could be attributed to a stylistic change, known to have been developed during the second half of 17th century but which spread to the most far provinces during the 18th century (Popova et al., 2003).

This yellow background is made of an ochre-based pigment (found in samples 1S3, 2S2, 5S2) over which other applications of a red-brown color were introduced in Icons 1, 3, and 4. The FTIR and the EDX spectra, together with the relative SEM mapping for this layer in sample 5S2, indicate the presence of residues of gesso (O, 54.63%; C, 22.35%; Ca, 0.69%) and Si (10.88%), Al (5.34%), Fe (5.23%), K (0.87%); the pigment used in this case was a yellow Earth-Ochra (Fig. 10). The FTIR spectrum of sample 2S2 indicates for the same yellow-colored layer, the presence of silicatic components, identified by a broad band between 800 and 1150 cm^{-1} (Genestar and Pons, 2005).

State of Conservation

The cracks that are clearly visible in the images obtained with OM and SEM (as for the sample 3S1 in Fig. 11) indicate an ageing process of all the constituent materials of the paint.

By simple observation, the most evident paint alteration is the darkening and yellowing of the olifa

Fig. 8. Cross-section of sample 5S2 showing the overpainted area under UV-Vis light, $\times 200$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 9. “Mecca” gilding of the halo of the Saint, sample 1S2, detail of cross-section observed under UV-Vis at $\times 200$ and SEM image BSE at $\times 88$ of the same cross-section. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 10. Cross-section of sample 5S2 observed at SEM ($\times 488$, se) and the relative EDX spectrum for the yellow-ochre layer, marked with an yellow square on the SEM image. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(protective layer), that in several cases was covered by extensive overpainting (in Icons 1, 4, and 5). The overpaintings need to be removed by cleaning from Icons 1, 3, 4, and 5, whereas Icon 2 should be consolidated.

Important losses of paint layers and lacunas are localized on the external borders of the icons (Fig. 1). The samples taken from these areas showed the effect of the aforementioned interventions on the appearance

Fig. 11. Cross-sections of samples 3S1 and 1S3 observed with the light microscope under visible (a) and UV (b) light, $\times 50$ —age cracking in the paint stratification and surface residues of an oily varnish. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and color of the preparation layers. For example, in sample 1S3, the preparation has transversal fissures, penetrated by a brown material, representing a solvent that dissolved the soot allowing it to penetrate the cracks (Fig. 11).

The intense yellow fluorescence of the two central applications of preparation in sample 3S1, together with the clearly delimited layers of “gesso sottile,” indicate the ground’s technique of application: first the “gesso grosso” with a warm layer of glue over and then three thick layers of gesso sottile separated after a previous polishing of the surface by layers of animal glue (Figs. 2 and 11).

In the samples 1S2-3, 2S2, 3S1, 4S1, and 5S2, which were taken from areas of the background or gilded halos, the various forms of degradation (cracks, lacunas) allowed the penetration of the warm glue or of dissolved “olifa” from upper layers, during cleaning.

Previous Interventions of Overpainting and Cleaning

In the past, the five icons were overpainted in several areas (as can be seen in samples from Icons 1, 1S3; 3, 3S1; and 5, 5S2) and were also subject to severe interventions of cleaning (complete or partial removal of “olifa” with an aggressive cleaning agent in the case of Icons 2, 3, 4 and 5). The only icon that gave a fair indication of the original colors of the chromatic palette

was Icon 2, which preserved signs of an aggressive and disturbing cleaning and puttying intervention.

The overpainting layers at the level of the background were observed using the optical microscope. In the cross-sections of samples taken from Icons 1 and 5, the original layers were distinguished from the added ones by their sequence, morphology and UV fluorescence (such as in samples 1S3, Fig. 11 and 5S2, Fig. 8). As Figure 1 illustrates, this intervention respected the central image, and was done mainly on the borders, over the original layer of yellow ochre. This layer proved to be the original background color of all the icons, as shown in Figures 5, 8, and 11.

CONCLUSIONS

The reported analytical study led to the following conclusions:

- the five icons were made with a similar technique and comparable materials (according to the post-Byzantine icon tradition), in the style of Northern Russian schools of iconography, at the end of the 16th and beginning of the 17th centuries: several paint layers with egg yolk emulsion applied on grounds made of “gesso” and animal glue;
- the ground has a homogeneous granulometry, with relatively round-shaped grains and aluminum-silicatic inclusions of various dimensions and colors,

made up of clay minerals (white earths) and oxides; the application of “gesso” layers corresponds to the traditional sequence: “gesso grosso” as a first application and three layers of “gesso sottile,” with thin layers of animal glue in between them;

- the different appearance of the preparation layers in correspondence with the cracks and lacunas extending from the paint layer inside the “gesso” could be a result of several applications of warm oily varnish (a practice quite often encountered in the case of Russian icons) or of interventions of cleaning that resulted in the penetration of dissolved “olifa” inside the ground;
- the colored layers are applied continuously and the boundaries between one layer and another are clearly distinguishable, meaning that the traditional technique of application was respected: each layer was applied after the previous one had dried;
- the pigments are mainly of mineral origin, the chromatic palette being limited to a small number of pigments, such as: red and yellow Earths (Ochras), green and brown earth or umber/Caput Mortum, copper pigment (Verdigris) mixed with green earths, lead white;
- the pigments were mixed with a medium made of egg yolk and the varnish identified in few samples of surface paint is the traditional “olifa,” made of siccativ linseed oil and additives such as Pb oxides (known as litharge, PbO);
- each represented Saint has a gilded halo around the head, probably a later intervention of gilding with “a mecca” technique as the SEM-EDX analysis identified the presence of Silver leaf in several application with intermediate layer of organic medium;
- the microscopic analyses revealed the presence of cracks that overcross the entire structure of the pictorial layers (Icons 1, 2, 3, and 5), as a result of the ageing process that occurred over time;
- the intervention of overpainting (brownish layer) on the grooved border was confirmed for Icons 1 and 5 (samples 1S1, 1S2, 1S3, and 5S2), whereas the absence of the varnish in paint samples 1S3, 2S2, 5S1 indicates a previous cleaning of Icons 1, 2, and 5.

The multimethod approach, combining microscopic and spectroscopic techniques, was confirmed to be extremely useful for establishing the authenticity of the analyzed icons through the identification of the constitutive materials and their methods of application. In addition, the results confirmed that a careful study of materials and artistic technique/technology in a work of art can lead to better planning and execution of the restoration, by discriminating between the original and added materials, and offering a better diagnosis of their original state of conservation. The obtained information will also be the basis for the study and assessment of the effectiveness of the cleaning process to be reported in a future article.

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