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HORSE-HEADED SAINT CHRISTOPHER FRESCO IN THE SVIYAZHSK ASSUMPTION CATHEDRAL (16th -17th CENTURY, RUSSIA): HISTORY AND ARCHAEOMETRY

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ABSTRACT

The present paper is devoted to the study of wall paint of the late 16th - early 17th centuries with zoomorphic image of St. Christopher located at the Assumption Cathedral (which became UNESCO object in 2017) of the town-island of Sviyazhsk and is the first investigation of Russian murals of this time. The work includes archaeometry examination of wall paint with portable X-ray fluorescent spectrometer (pXRF) for the pigment's determination and by optical microscopy and scanning electron microscopy (OM-SEM) for fresco structure study with some notes of the appearance of an unusual image of the saint and history of this fresco creating. The analysis found the ancient masters used red and yellow ocher, umber, "green earth", blue smalt as colorants. The discovered cinnabar, minium, lead white, paints with chromium, titanium and nickel are evidence of restoration work of the different time. As studies have shown some regions of fresco have several painting layers indicating alterations in original image of Saint Christopher with the dog head. Results of plaster examination showed that it was made from dolomite raw material. In addition, white scurf near the cracks in the wall has been studied by X-ray diffraction (XRD). Separation of calcium and magnesium structures due to degradation process of the fresco base was revealed on the OM-SEM-pictures.

KEYWORDS: fresco base, pigments, 16th -17th centuries, OM-SEM, pXRF, dolomitic plaster, degradation process.

1. INTRODUCTION

The purpose of this study is to determine fresco bases and colored pigments that have been used by ancient Russian masters when creating the image of St. Christopher - of one fresco at the Sviyazhsk Assumption Cathedral. Results of examination by pXRF, SEM and XRD methods with some historical aspects are presented in this work.

The Cathedral of the Dormition of the Mother of God (the Assumption Cathedral) at the town-island of Sviyazhsk was constructed by a decree of Ivan IV the Terrible after the conquest of the Khanate of Kazan. This cathedral had particular politico-military and clerical-cultural importance for Christianization of the conquered territories with polyethnic population - Muslim Tatars and Finno-Ugrians pagans. It is due to unique disposition of the island in the Volga trade route, in the center of the Volga region (Valeev et al., 2016). Magnificent fresco painting which survived to our days determines special status of the Assumption Cathedral. It is Russia's only fresco painting of such a large size (1080 sq. m.) dating back to the second half of the 16th century, which survived in a full compositional cycle.

Restoration of frescoes of Svijazhsk Cathedral has been underway since 2010. Analytical investigation is usually the essential part of restoration works (Liritzis et al, 2015; Kholod et al, 2016; El-Sheikh et al., 2017). Paint composition (Vinner, 1948; Linn, 2017; Thomoson, 1956; Taft and Mayer, 2000), fresco painting technique (Linn, 2017; Kolovrat, 1969) and peculiarities of creation (Horgines et al., 2015; Thompson, 1956; Farmakovskj, 1950) are equally important because they provide information for better restoration and long-time monitoring and conservation (Mugnaini et al., 2006; Edvards and Farrel, 2008; Gil et al., 2008; Guet et al., 2015). Both destructive and non-destructive methods are used for examination of wall paintings. Polarized light optical microscopy (Samanian, 2015), electron microprobe (Westlake et al., 2012), nuclear magnetic resonance (Proietti et al., 2005), SEM-EDS, FT-IR (Samanian, 2015), X-ray diffraction (XED) (Al-Emam et al., 2015), Raman spectroscopy (Zucchiatti et al., 2004) and mass spectrometry (Nord et al., 2017) require definite amount of a sample for examination.

A lot of researchers widely use X-ray fluorescence (Liritzis and Polychroniadou, 2007; Gehad et al.,) including portable devices (Tortora et al., 2016; Čechák et al., 2001; Cesareo et al., 2004; Syta et al., 2014; Valadas et al., 2011) for determination of chemical composition of paints and fresco plaster.

2. SUBJECT OF THE RESEARCH

2.1. *Image of Saint Christopher*

St. Christopher is a martyr venerated by several Christian denominations who presumably lived in 3 A.D. (Myths of Nations of the World, 1982). Traditional depiction of Saint Christopher differs in Catholic and Orthodox traditions. In the canonical Catholic tradition Saint Christopher (Χριστόφορος in Greek, "Christ-bearer") is portrayed as a giant that carries Christ Child over a river (Fig. 1, a-c). In the Orthodox tradition there are three versions of Saint Christopher's iconography. On some icons he is represented as beautiful young man with long hair and a cross in his right arm, on other he is depicted as in the Catholic tradition (Fig. 1, d, e). In the Byzantine and post-Byzantine art the saint is portrayed with a dog head (Fig. 1, f). Most probably this image is connected with mistranslation of Latin word Cananeus (from Canaan) as canineus (canine) (Ross, 1996).

The zoomorphic appearance of St. Christopher has its Mediterranean roots. Geradot, Ctesias, Megasthenes, Pliny the Elder described in his classical work cynocephaly (κῠνοκέφᾰλοι), who lived in Libya, Ethiopia, India, Scythia. It should be noted also that Duamutef, Wepwawet, and Anubis, deities of ancient Egypt, were among the first representatives of sacred creatures with the dog head and a human body.

In Russian icon-painting tradition dog-headed image of Saint Christopher had become particularly popular from the second half of 16th century (Fig. 1, g). Fresco in the Sviyazhsk Assumption Cathedral was made in this icon-painting tradition.

2.2. *Fresco of St. Cristopher in Sviyazhsk Cathedral*

The Sviyazhsk Assumption Cathedral had been built in three years and was consecrated in 1560. All walls of the church are covered in painting which dates back to the second half of 16 - beginning of the 17 centuries. Part of frescoes was painted after Cathedral reconstruction in the 18th century on newly built areas. All paintings in the Assumption Cathedral are made in classical fresco technique on a fresh and still wet plaster. Cathedral painting is unique cultural heritage object, because it is the only wall painting of the 16 century that survived to our days in its original form. Most of Russian churches of that time was repainted in 18th -19th centuries and destroyed after the Russian Revolution of 1917.

Wall painting contains 138 narrative images. Among them there are images of warrior-saints situated on the lower tier of Cathedral's pillars. Fresco of Saint Christopher is situated on the western face of the northwest pillar (Fig. 2). The saint is depicted in military clothing lapped in a red cloak with a cross in the right hand and lowered sword in the left. Head of the saint is in the horse form with a mane resembling human hair with flying curls. The height of the fresco is 3.04 m., width is 1.62 m.

Figure 1. a - Cathedral of the Virgin Mary, 11th c., Augsburg, Germany; b - Hans Memling. 1484. Groeningemuseum, Bruges (https://muzei-mira.com/kartini_gollandia/925-svyatoy-hristofor-hans-memling.html); c – St. Christopher, fountain, 1584, Ulm; d - Fresco. Church of Christ the Pantocrator. Decani. Kosovo. Serbia. Around 1350 (http://pravicon.com/image-11134); e - Monastery of Stavronikita. Athos. 1546 (http://starove.ru/obychai/tajna-svyatogo-muchenika-hristofora-s-golovoyu-pyosej-psa); f - Byzantine Museum, Athens, 13th century (http://www.medievalists.net/2013/10/werewolves-and-the-dog-headed-saint-in-the-middle-ages/saint_christopher_cynocephalus); g - Chudov Monastery, Moscow Kremlin, 16th century (http://starove.ru/obychai/tajna-svyatogo-muchenika-hristofora-s-golovoyu-pyosej-psa).

3. METHODS OF EXAMINATION

Areas of different colors were initially examined with non-destructive method of X-ray fluorescence analysis. Sixteen test points in differently colored parts of the fresco were examined by X-ray fluorescence spectrometry using the S1-Turbo Bruker portable spectrometer equipped with a silicon drift detector working at 145 eV at 100000 pulses/sec. The measurement area is 5 mm in diameter and the acquisition time is 50 seconds. Twenty-one major, minor and trace elements were determined: CaO, MgO, Fe_2O_3, PbO, SO_3, Sb_2O_3, Al_2O_3, SiO_2, P_2O_5, K_2O, TiO_2, CuO, As_2O_3, MnO, Co_3O_4, ZnO, Cr_2O_3, NiO, ZrO_2, SrO, SnO_2.

Optical microscopy (OM) and scanning electron microscopy (SEM) were used to study painting layers and fresco plaster on finer scale. Examinations were performed with scanning electron microscope

AURIGA CrossBeam with energy-dispersive spectrometer INCA X-MAX and optical microscope system Axio Observer Z1, Axio Imager.Z2m. Ten samples with size less than 0.02 mm^3 from regions of different colors were taken for SEM analysis. Fresco base composition was determined for five samples. Fifteen elements were detected: Al, As, Ba, Ca, Cl, Co, Fe, Hg, K, Na, Mg, Pb, S, Si и Ti.

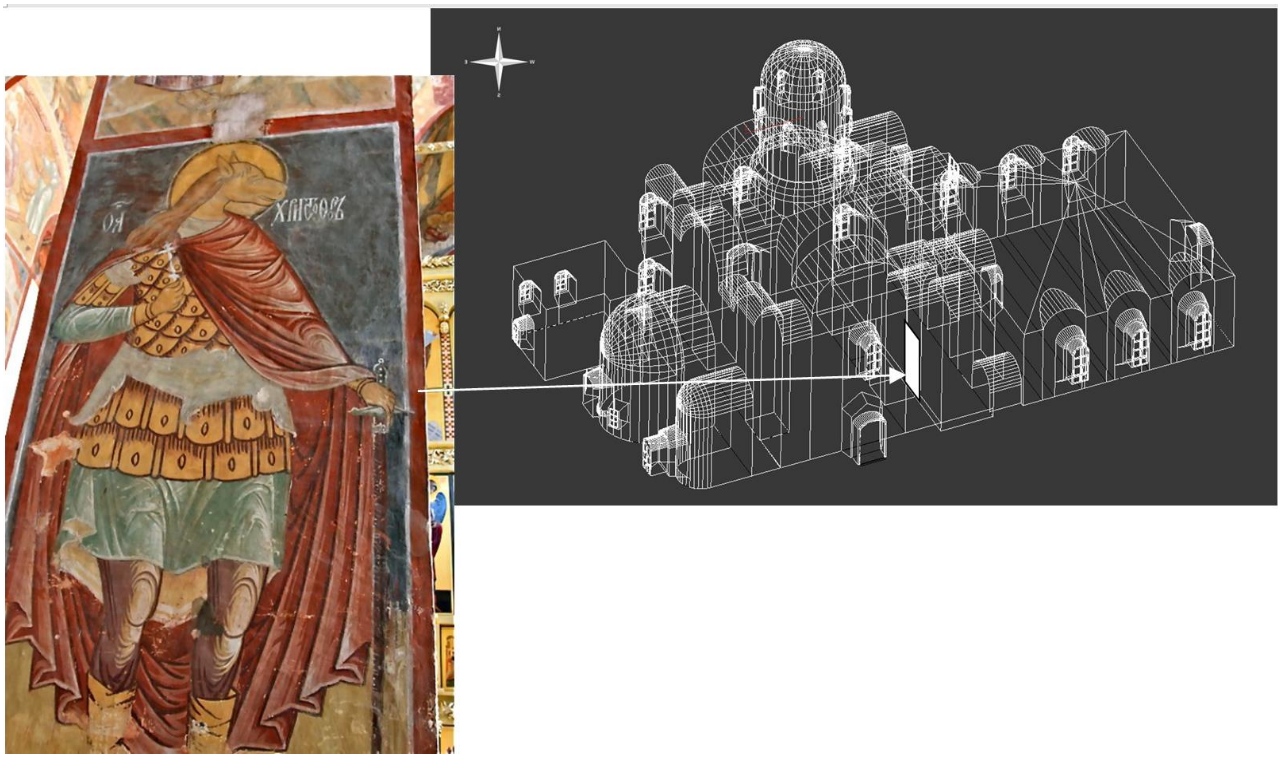


Figure 2. «Saint Christopher» fresco and its position on the plan of the Sviyazhsk Assumption Cathedral.

3.1. *Samples preparation technique*

Preliminary cleavage of samples was made in the regions of interest. Then, the cleavages were fixed to an aluminum holder using conductive carbon tape. Primary images were obtained by optical microscopy and the regions of interest coordinates were saved for further application of correlated light and electron microscopy (CLEM) method.

Then, samples were sputtered with a carbon film (25-30 nm) on a Quorum Q150T ES unit to avoid the accumulation of electric charge on the surface and obtain high-resolution micrographs. The following parameters were used for sputtering: Pulse current 50 A, pulse length 3 sec, pulse number 3, vacuum 4x10-4 mBar.

To obtain images using an electron microscope, the following modes were used: SE2 (secondary electrons) for primary visualization of the overall morphology of the enamel coating, as well as for energy dispersive X-ray analysis (20 kV, 700 pA) and InLens (high-resolution secondary electron mode), which allows visualize the inclusions and obtain the coating surface structure images with the highest resolution (15 kV, 180 pA).

The chemical composition of samples was determined by energy dispersive X-ray analysis using the INCA X-Max spectrometer (resolution 127 eV). The operating procedure for the energy dispersive spectrometer is:

- setting the optimal pulse counting mode imp / s, the dead time value (when the microscope mode is SE1, 20kV, 800pA);
- obtaining spectra from the regions of interest;
- building maps of the elements distribution for selected areas of the sample to obtain general information on the composition of the sample and the distribution of elements over the surface;
- the construction of spectra, summary tables (weight and atomic% composition), an image with sections of the spectra carried out, as well as a general spectrum.

Due to high resolution, electron microscopy allows studying small samples (less than 0.3 cm^2) with simultaneous investigation of surface and inner layers. CLEM gives an opportunity to visualize the boundary between the glass and the enamel coating.

White fluffy coating near an old restored crack was examined in course of the study by X-ray crystal analysis method. Radiographic survey of the sample was performed on diffractometer Shimadzu XRD-

7000 at Bragg angles 3-40° with 2Θ, scanning angle step – 0.02°, speed – 1°/min, tube current 20mA, voltage 30kV, emission CuKa. As a database for radiograph decoding international radiographic card file PDF-2 was used.

4. RESULTS AND DISCUSSION

The fresco painting of the Cathedral was created in the classic technique by application of paint on a wet plaster. "Day" seams of areas which were painted at one time are visible on the walls. There are also relief scratches made by a sharp tool to designate main contours of a fresco. Table 1 represents results of pXRF and SEM analysis. Peculiarities of the chemical composition of plaster and paints are described below.

4.1. *Plaster*

Plaster composition varies depending on location and time of creation of a wall painting (Elsen, 2006) and plays a key role in a quality of mural (Hussein, 2012). The main component of a fresco base was calcium hydroxide $Ca(OH)_2$ (Amadori et al., 2015). It could be mixed with sand, marble powder (Thompson, 1956; Cuni, 2016), crushed volcanic rock (Luk'yanova and Kusk, 2015) or crushed ceramics. Sometimes fresco base was also made of "mud, gypsum and lime" (Elsen, 2006).

The art of fresco painting had come to Rus' from the Byzantine Empire along with the spread of Christianity and from the XI-XII centuries Rus' craftsmen painted walls of churches and cathedrals on the territories of Kievan and Novgorod principalities. Complex technology of wall painting was transferred from master to apprentice and for the long time secrets of fresco painting were known only to the limited circle of masters and often were forgotten after death of an old master. To the XVI century craft of fresco painting achieved artistic maturity and mastery. According to Kolovrat (1969), Russian craftsmen used Italian painters' recipe for plaster production. This technology assumed at least three layers of matrix with different proportions of sand and lime (Piovesan et al., 2012).

Five samples of fresco base were examined with OM-SEM. Visual and instrumental examinations revealed that the plaster has sufficiently homogeneous structure. It consists of only one layer 100-200 mm thick and contains no traces of quartz, sand or any other filler. Analysis of the plaster composition of the Saint Christopher fresco revealed high concentrations of Ca and Mg in proportions which are similar to dolomite chemical composition. Mg / Ca proportion is 19.91-34.28% / 75.51-62.09%.

This plaster composition is unusual and non-traditional for the art of fresco painting in Russia. Usage of dolomite as a plaster for fresco paintings has been never revealed before. Russian renovators suppose that presence of Mg component does not allow obtaining high-quality plaster (Nikitin and Mel'nikova, 1994). However, in construction industry dolomite lime is considered to be more solid. During hardening of dolomite and magnesium lime water, that escapes during the carbonization of calcium hydrate $Ca(OH)_2$, partially binds with hydrating magnesium oxide MgO. Thus, humidity of walls in newly-built houses decreases; this is why dolomite lime is especially suitable for internal plaster production (Jung et al., 1952). Element mapping of the examined fragments revealed interesting peculiarity of distribution of Mg, K and Ca in two samples. Figure 3 represents mappings of samples of the orange paint of the armour (a) and the green paint of the sleeve (b). As it can be seen there is inverse correlation between K and Ca distribution. In the regions with high K concentration there is significantly lower Ca concentration in comparison with volume average. At the same time Mg component is distributed throughout the volume with noticeable decrease of concentration on the surface.

It can be possibly explained by gradual degradation occurring in the plaster. Authors examined the plaster material from the site near the renovated crack on the wall. This wall had been exposed to moisture for a long time before the renovation began. Figure 4a represents SEM images with elemental mapping. The picture captured process of spatial disaggregation of dolomite $CaMg(CO_3)_2$ into a separate magnesium part (orange color) and calcium part (blue color). The magnesium part has acicular-lamellar structure that resembles fluff. The white fluffy coating which formed on the moisturized region was examined with X-ray diffraction analysis (XRD). Figure 4b demonstrates the X-ray pattern of the sample indicating that coating consists of magnesium hexahydrite with trace amount of gypsum.

Table 1. Chemical composition of base and paints of fresco "St. Christopher" of Sviyazhsk Assumption Cathedral.

Method - sample	Point of fresco, colour	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	As_2O_3	CoO	SO_3	P_2O_5	PbO	MnO	TiO_2	
	base														
SEM-110		24,07	0,67	2,22		72,02	0,56			0,46					
SEM-126		19,91	0,93	2,7		75,51	0,41			0,54					
SEM-127		23,76	1,15	1,58		72,07	0,45			0,98					
SEM-129		34,28	0,45	2,61		62,09	0,58								
SEM-132		23,63	1,02	4,8	0,21	68,72	0,38			1,24					
	blue-gray (after restoration)														
XRF-4176	*top background*	14,10	2,89	26,40	1,17	41,90	1,44	0,60	0,88	3,14	1,52	0,66	0,06	1,21	
SEM-126	*top background*	2,32	1,38	67,11	10,8	3,64	2,72	9,32	2,66						NaO
SEM-126	smalt	2,8	1,62	66,88	10,3	3,6	2,12	10,06	2,22						0,44
	gray-brown (before restoration)														
XRF-4176	*top background*	16,00	3,94	15,90	0,69	27,60	1,23	0,66	0,41	7,78	1,21	1,49	0,04	3,67	BaO
SEM-129	*top background*	12,01	1,38	26,86	0,84	41,76	2,19	2,72	1,65	2,44		3,32			4,35
	red														
	fresco's ending														HgO
SEM-132	red (upper layer)	3,06	2,21	5,18	0,39	39,81	24,99			3,29		7,16		8,35	5,63
SEM-132	red (midle layer)	3,11	1,6	7,37		3975	25,49			0,7		13,99		8	
SEM-132	light red (bottom layer)	10,74	18,82	49,68	3,94	8,54	7,71			0,54					
	cloak														
XRF-4181	red clothes	17,70	9,56	13,40	1,28	30,00	7,99	0,62		4,93	1,47	4,20	0,08	0,57	
SEM-109	red (upper layer)	4,58	10,51	6,37	0,63	40,09	18,28					19,53			
SEM-109	pink (bottom layer)	5,94	15,64	35,57	7,66	16,11	19,02								
XRF-4182	pink strokes	16,80	6,70	8,89	0,59	36,10	8,70	0,81		3,20	1,41	6,81	0,08	0,54	
	brown														
XRF-4178	*clothes ending*	30,38	2,79	6,67	0,50	26,30	17,30	0,53		2,27	0,95	3,64	1,30	5,89	
XRF-4188	*sword*	34,36	2,01	6,54	0,43	22,80	18,30	0,66		0,60	0,74	5,46	1,30	6,06	
	armor's ending														BaO
SEM-128	1 layer, red-brown	4,98	4,85	10,59	0,31	17	55,73			1,9	0,88	1,9			1,86
SEM-128	2 layer, white	4,01	0,69	3,11		85,78	5,16								
SEM-128	3 layer, green	11,33	9,56	48,93	5,72	13	11,46								
SEM-128	4 layer, yellow	8,55	14,69	37,46	3,09	14,07	22,14								
	orange, *armor*														
SEM-110	upper layer	6,92	8,25	21,66	1,27	45,28	13,73			1,27		0,92		0,7	
SEM-110	bottom layer, yellow	9,97	15,75	36,31	3,56	8,92	24,3			1,18					
	yellow														
XRF-4186	*armor shield*	11,42	9,67	26,70	1,31	38,70	5,11			1,77	1,37	0,30	0,06	1,06	
SEM-126	*armor shield*	11,88	14,06	31,88	1,68	32,18	7,69			0,62					BaO
SEM-131	*bottom background*	7,5	6,8	15,77	1,14	55,47	5,33			2,35		2,48			3,71
XRF-4177	*nimbus*	9,75	11,80	24,30	0,89	39,10	4,88			2,87	1,41	0,60	0,04	1,99	
XRF-4179	*head*, yellow	18,23	13,20	32,10	1,28	20,20	6,27	0,23		3,62	1,05	0,88	0,12	1,76	
XRF-4180	*the point on the upper dog head*	16,65	10,10	23,30	1,17	30,60	7,69	0,24		4,58	1,31	0,85	0,12	1,78	
	beige, *cheec of head*														
SEM-130	upper layer	6,29	7,11	22,57	2,48	52,58	8,62			0,34					
SEM-130	ash	22,03		1,65	3,96	66,07				6,29					
SEM-130	bottom layer, smalt	11,19	1,74	65,29	4,58	1,94	2,47	10,42	2,12						
	green														Cr_2O_3
XRF-4187	*sleev of dress(SD)*	22,59	4,80	24,20	3,89	24,90	12,00	0,15		1,37	0,97	0,30	0,07	2,81	0,94
SEM-127	*sleev of dress*	14,53	6,91	38,78	5,73	19,12	12,15			2,22	0,56				
SEM-127	*SD*, fibers	12,54	11,77	52,39	6,44	3,22	11,82			1,28	0,54				
SEM-127	*SD*, fibers	22,87	7,92	40,54	5,17	8,45	8,54			4,65	1,52			0,36	
SEM-127	*SD*, transparent formations	19,82	4,08	19,46	4,11	31,72	4,86			12,8	3,1				
XRF-4189	*sword hilt*	17,59	7,88	30,60	3,83	19,00	12,30	0,37		1,67	0,82	4,00	0,09	0,97	
XRF-4185	**gray**, *cape under the cloak*	16,90	3,33	6,08	0,48	60,10	1,15			2,20	1,81	0,69	0,05	1,04	
	white														
XRF-4191	strokes on the sleeve	16,20	3,51	6,50	1,12	54,60	6,38	0,19		3,04	1,79	0,88	0,05	1,12	
XRF-4190	*cross*	-	1,62	2,56	-	12,30	0,71	0,27		4,02	-	4,40	0,02	19,40	
XRF-4183	*letters*	-	-	4,91	-	0,62	0,08	0,26		7,28	-	3,50	0,02	5,61	

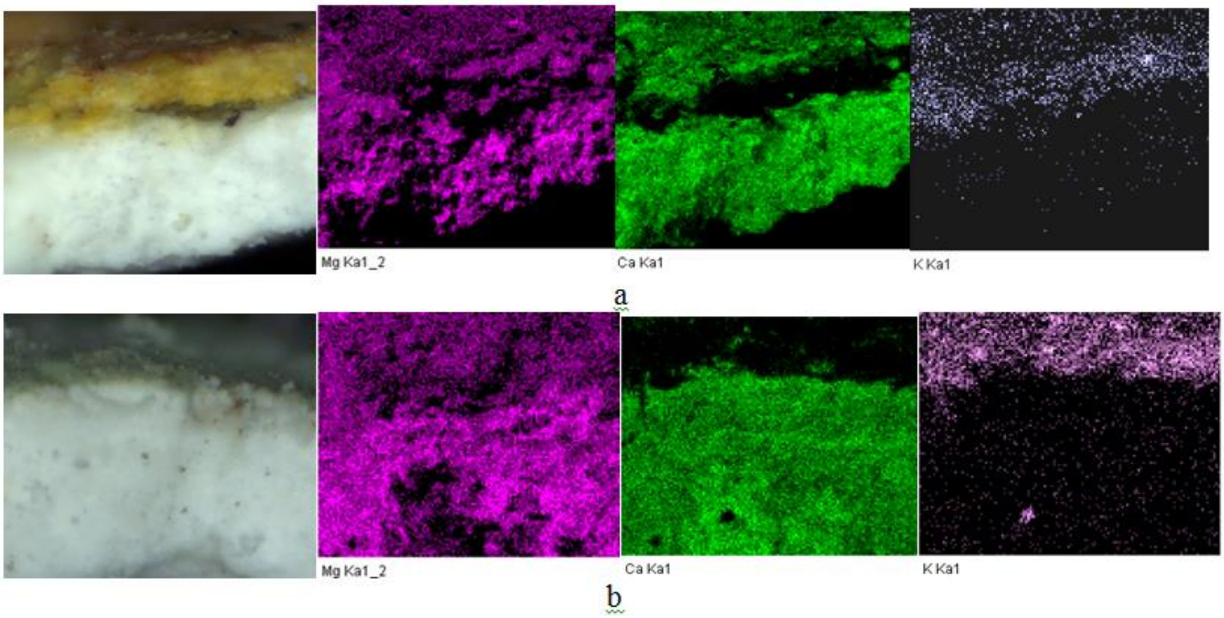


Figure 3. Mapping of Mg, Ca and K distribution for the sample; a) represents the orange pain of the armour, b) represents the green paint of the sleeve.

4.2. *Paints*

Analytical studies of mural provide valuable information to restorers about the pigments used (Gutman et al., 2016).

Gray-blue. According to XRF data cobalt is present in the paint. As it follows from OM and SEM results, cobalt glass with small trace of coal gives gray-blue background in the upper part of the fresco (Fig.5, a). Evidence of the cobalt glass usage is the chemical composition of the paint which contains Si, K, Co and As. It is unknown when cobalt was first employed in Europe for glass making, but probably the Venetian glass makers knew of its properties (Gettens and Stout, 1966). The oldest wall painting with blue smalta created between 1325 and 1453 was discovered in the Chora Church (nowadays Kariye Müzesi, Istanbul, Turkey) (Gettens and Stout, 1958), and the earliest mention of the paint belongs to Vincenzo Borghini (Grenberg, 1982). Considering that frescoes of Russian temples are insufficiently investigated, we cannot name the date of beginning of smalt usage in Russian fresco painting.

Restorers left the unrefined reference area of gray-brown color in the upper part of the fresco. Investigation of the unrestored section (Fig.5, b) revealed barium and lead oxides (BaO, PbO) that indicate later interventions.

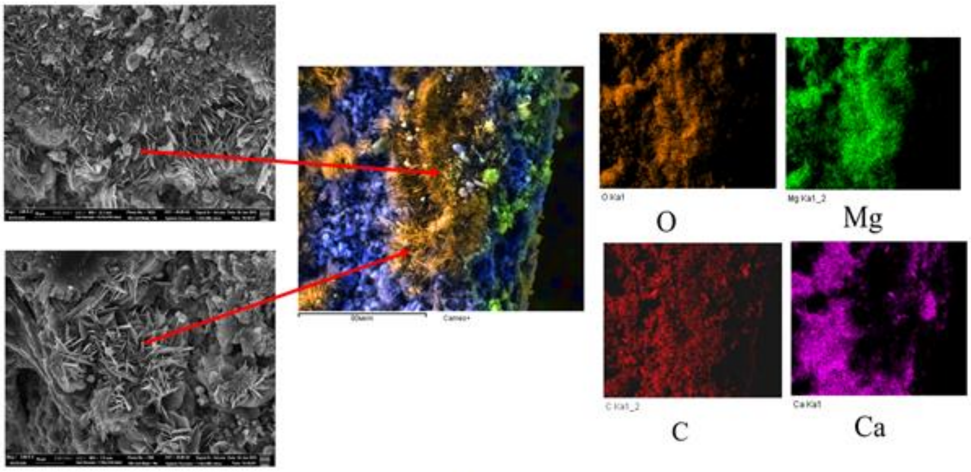
Red. There is 10 cm width red framing going along the perimeter of the fresco. Figure 5c demonstrates OM picture of the sample where three different layers which have different tones can be seen. Analysis data also revealed the difference in chemical composition of the layers. High concentrations of oxides Fe_2O_3 (24.99%), PbO (7.16%), TiO_2 (8.35%) and HgO (5.63%) are found in the scarlet layer. In the lower light-red layer Pb and Ti are absent and Hg is present only in near-surface area. These data show that minium in mixture with titanium white was used in course of first restorations works, and cinnabar was used during the second correction. Preliminary XRF analysis of the red paint of the cloak revealed Fe (Si, Al) and Pb in the quality of coloring reagents. SEM results showed that initially this region was painted in pink color (Fig.5, d), that was obtained by mixing of ocher and dolomite. This is proved by the high content of Al, Si and Fe. Red paint (50-60 μm) which is mixture of ocher, minium and calcite had been laid on atop this layer. Pink surface had been treated with potassium-rich agent before the application of the red paint.

Pink brushworks on the cloak which impart volume of the clothing were obtained by application of mixture of ocher and dolomite atop the red paint. Consequently "fresco secco" technique was used during the painting of the Cathedral along with classic technique.

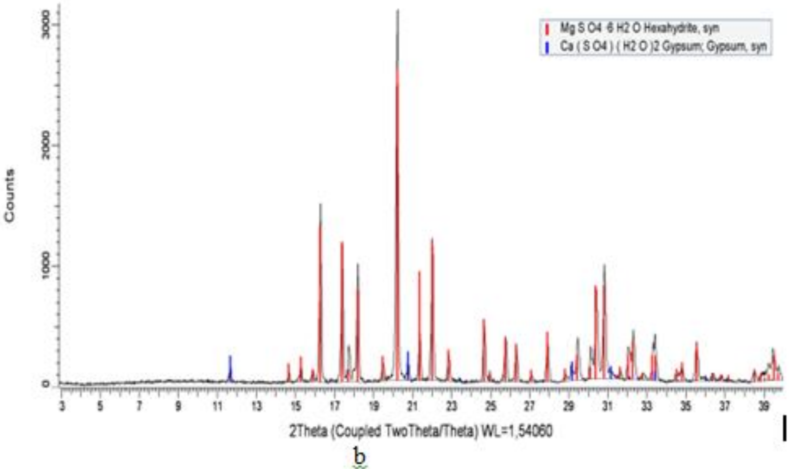
Brown. According to XRF data there are increased concentrations of iron oxides Fe_2O_3 (26.3%) and MnO (1.3%) in the brown framing of the cloak. The framing is made of umber. The sword in the left arm of Saint Christopher has almost the same composition.

Investigation of a sample from the red-brown contour of the armour revealed several layers of different colors (Fig.5, e). The upper layer of 20-30 μm depth is determined as ochre pigment with high content of Fe_2O_3 (55.73%). Underneath this layer there is a white layer of 10-15 μm depth with calcium oxide

CaO predominance (85.78%). Below the white layer there is green layer of 10-15 μm depth colored with "green earth". The bottom original layer of yellow color is made of yellow ochre and has composition that is similar to the armour paint, but differs from it by brighter dyeing and higher concentration of Fe (22.14%).



a



b

Figure 4. a - SEM- images and cartograms of O, Mg, C and Ca distributions; b – X-ray pattern of the white fluffy coating from the moisturized wall.

Orange. From the OM image it can be seen that the orange color of the armour nearby the brown-red contour of the armour plates was obtained by application of a red layer on a yellow base (Fig.5, f). In such a manner the painter imparted volume to the armour image. The yellow color is very bright and pure and obtained from ochre with high concentrations of Al (15.75%), Si (36.31%) and Fe (23.2%) in conversion to oxides. This paint is similar to the bottom layer of the red-brown contour of the armour. Thin layer of aqueous solution of dolomite limestone mixed with red ochre was applied near red contours of the armor to the yellow paint that had dried already. Small admixture of Pb and Ti indicates restoration works. Despite the similarity of chemical composition of the pink paint of the previous sample and the yellow paint of the bottom layer, OM image shows their cardinal distinction. The pink paint consists of dolomite with admixture of ochre particles, the yellow sample is dyed with bright yellow color without perceptible inclusions.

Yellow. The yellow color of the armour plates (Fig.5, g) differs from the yellow color of bottom layers of previous samples by lighter tone and composition. According to XRF and SEM data this pigment contains less iron oxide Fe_2O_3 (7.09%). It indicates that yellow ochre of different composition or origin was used. The yellow paint of the background in the lower part of the fresco (Fig.6, h) and the horse head has similar concentrations of main elements.

Beige (grey-yellow). Sample from the cheek of the horse head appeared to be double-layered (Fig.5, i). The lower layer on the plaster is similar to the grey-blue background in the upper part of the fresco and is colored by blue smalt. Upper layer of dark-brown color was obtained by addition of powdered black coal into the yellow pigment of the same composition as the yellow paint of all upper layers of the fresco. Data in Table 1 show high concentration of sulphur oxide SO_3 (6.29%) in a coal particle.

Green. According to XRF/SEM data the green paint of the sleeve contains silicon oxide SiO_2 (24.2%/38.78%), iron oxide Fe_2O_3 (12.0%/12.15%) and aluminum oxide Al_2O_3 (4.8%/6.91%) correspondingly which proves "green earth" usage. OM image shows a grainy semitransparent structure of the surface of the paint with inclusions of gray-black semitransparent fibers (Fig. 6, j). A sample of the green paint has fibrous (branchy) structure captured on the SEM image (Fig.5, k). The peculiarity of the paint is higher concentration of magnesium oxide MgO (12.54-22.87%) in comparison with calcium oxide CaO (3.22-8.45%) in the branched formations of the paint surface. At the same time grey-black fibers consist of flat ellipsoidal links and beside "base" flat elements of the green paint contain sulfur oxide SO_3 (12.84%) and phosphorus oxide P_2O_5 (3.1%). Microbiological studies did not reveal any organic elements in the paint. This is why we can consider grey-black fibers as special mineralogical structures.

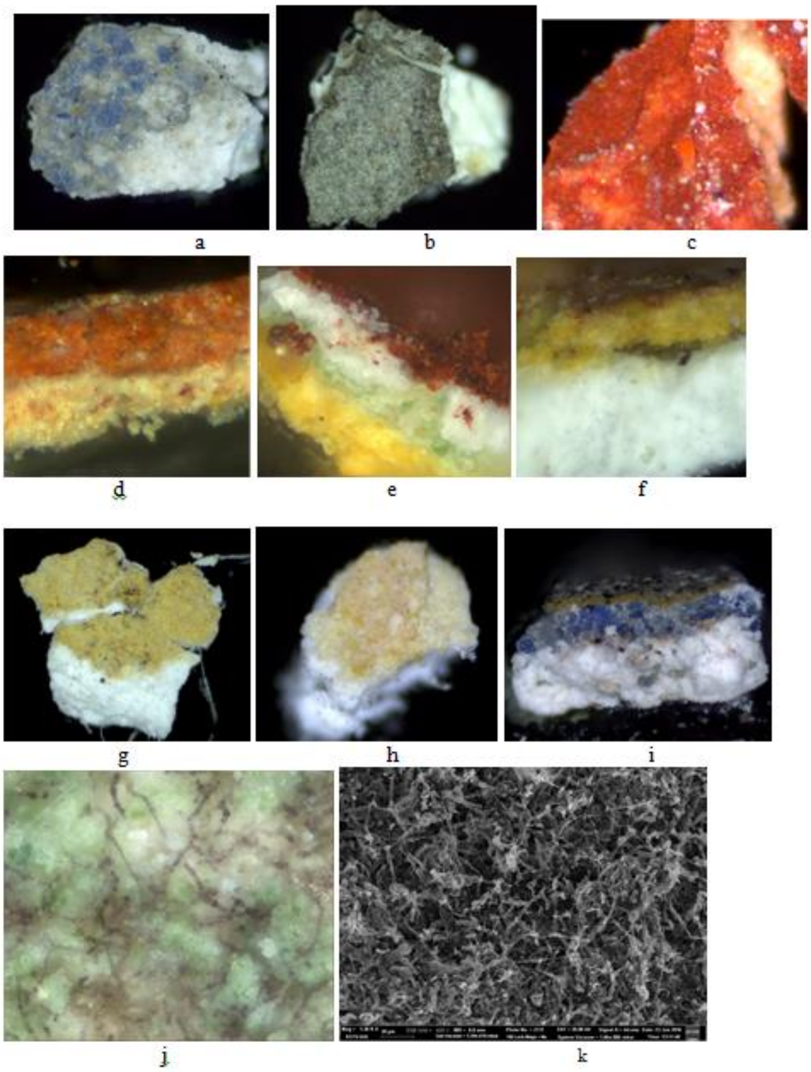


Figure 5. OM images: a –blue background (after the restoration), b – grey background (before the restoration), c – red paint of the fresco framing, d – red paint of the cloak , e – brown paint of the armour contour, f – orange paint of armor, g, h – yellow paint of the armour and background, i – dark-beige paint of the horse head green paint of the; j, k – OM and SEM image of the green (sleeves) region.

Composition of the green paint of the hilt is identical to the green paint of the clothes.

Grey. In-depth contours made by a keen object on the plaster reveal that grey element on the right shoulder under the cloak had been painted and then painted over. According to XRF data on chemical composition the paint was obtained from dolomite limestone.

White. Cross in the right hand of Saint Christopher and inscription of his name are applied over the main paints, they are of pure white color and had been repeatedly renovated, which can be seen both visually and from the chemical composition of paints. High concentrations of titan and lead testify later renovation efforts.

According to restorations data egg yolk was used as a fixing reagent during the restoration work in the 1980s. This fact can possibly explain the presence of significant concentrations of potassium and phosphorus in many paint samples. Small concentrations of Ti, Pb and Ba signify later restoration interventions, because paints based on these materials appeared much later than 16th -17th centuries (Fedoseeva, 1999). Presence of Cr in the green paint of the sleeve also suggests that restoration works were conducted.

The presence of multilayered fragments in paints of armour and head (cheeks) indicates the redrawing of the original image.

Closer examination of the saint's head revealed initial contour of the dog-head (Fig. 6) with a sharper face and two eyes. In addition, the background of the halo under the chin of a horse's head differs from the upper background of the halo in a lighter shade. Given the fact the lower layer on the cheek was of the same color as the upper background of the fresco, corresponding to the blue sky, it is possible the nimbus around the head had initially only a contour without internal coloring.

Reasons why this "corrections" of the image were made are unknown. Saint Christopher with a dog head was rather traditional image in icon painting in Russia of 16th-17th centuries. It is possible that redrawing of the head was made in the 18th century during the partial renovation which was performed to fashion the Cathedral into Russian Baroque style. At this period, the saint was portrayed in Russia with a more "noble" horse head (Chernova, 1999).

Figure 6. The contours of the original image of St. Cristopher

5. CONCLUSIONS

The data collected by the first experience of interdisciplinary investigation of Russian fresco paintings of 16-17 centuries have particular importance both as information source on history of painting development as well as knowledge database for renovators. Examination of Saint Christopher fresco at the Assumption Cathedral of the town-island of Sviyazhsk with XRF and OM_SEM methods gave opportunity to reveal a number of facts about plaster, painting materials and about the fresco itself.

The fresco was made in the classic technique on the wet plaster. Composition of the plaster differs from the classic plaster made of calcific lime. Instead, creators of the painting used dolomite powder to make the plaster. Initial base painting layers have thickness about 10-60 μm. Traditional materials are used as painting pigments: various ochers for red and yellow color, "green earth" for green color, umber for brown color. Blue cobalt glass, which has become grey-blue for several centuries, was used to create upper background of the fresco. All contours and strokes were made in "fresco secco" technique by solution of dolomite powder mixed with painting pigments. Chemical composition analysis revealed traces of restoration works made with paints which contained Pb, Ti and Ba. Cinnabar was one of the dyes that were used for renovation of the fresco's red framing.

New research data provided valuable information for art experts, renovators and historians, gave the opportunity to reveal initial image of Saint Christopher with the dog head, revealed the process of fresco base degradation at the micro level. The studies carried out are of particular importance for the correct, scientifically based restoration measures. Most likely, it was sulfur, which is part of the egg yolk, acted as a catalyst for the decomposition of the dolomite structure of the fresco base on magnesium hexahydrite and gypsum. Thus, the application of yolk was a mistake by restorers, due to the lack of knowledge of the composition of cement.

At the moment there is no possibility of a detailed study of the fresco by surface scanning with other analytical technologies to identify all the lower layers of paint and determine the original appearance of the saint. However, the identified change in the image of St. Christopher's head is fully consistent with the traditions of Russian icon painting in in 16^{th} -18^{th} centuries.

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