

THE WALL PAINTINGS IN THE RUSSIAN CHURCH ST.
NICHOLAS IN SOFIA: A TECHNOLOGICAL STUDY BY
INTEGRATED ANALYTICAL APPROACH

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Abstract

For the first time, wall paintings of 20th century Russian artists in Bulgaria were analysed by means of complementary analytical methods. Representative samples collected from the Russian church St. Nicholas in Sofia, decorated by the famous Russian artists Vasily Perminov, Michail Maletski and Nikolay Shelehov during different periods of time, were examined by means of micro-Raman spectroscopy, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and X-Ray fluorescence (XRF). The results of the study reveal that colourful palette was achieved by using various pigment mixtures of traditional and modern synthetic pigment as titanium white, barium white, calcite, chrome green, green earth, hematite, ultramarine, madder lake, carbon black, vermilion, Naples yellow. The analysis of the paint binders allow to conclude that Maletski and Shelehov have used egg tempera as painting technique, while Perminov has worked in two painting techniques – oil and egg tempera.

Key words: Russian church, pigments, binder IR, Raman, XRF

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Introduction. The liberation of Bulgaria in 1878 marks the beginning of a new stage in the development of Orthodox architecture and art in Bulgaria. Many prominent Russian artists were also involved in the construction and decoration of the new churches. Their ecclesiastical wall paintings influenced the works of numerous Bulgarian artists in that period and have significant place in the art history of the country [^{1,2}].

An example for a church in Bulgaria entirely painted by Russian artists and their students for nearly a century is the church of St. Nicholas in Sofia, known as the Russian church. Initially the interior was decorated with wall paintings in 1911–1912 by the Russian artist Vasily Perminov and his team. The second stage of wall painting decoration dates from 1945–1946, when the south chapel was reconstructed after the bombardment during World War II. This part of the church was painted by another Russian artist, Michail Maletski. In 1954 the crypt of the church was embellished with wall paintings by Nikolay Shelehov, also a Russian artist. The fourth and final stage of the wall paintings dates back from 1996, when the antechamber of the crypt was decorated [³].

Despite the importance for the art history of the country, publications on the technical features of the ecclesiastical wall paintings created by Russian artists in Bulgaria are sparse and incomplete. No comprehensive analytical study on the wall paintings of the Russian church, nor another church decorated by Russian artists, has been published in the literature so far.

The present investigation is a pilot study and aims to characterize the paint materials used by the artists at different painting stages in the Russian church and in addition – to extend the knowledge on the technical features of the ecclesiastical wall paintings of the Russian artists who have worked in Bulgaria in the 20th century.

Materials and methods. Microsamples from all the three periods of the wall paintings were taken for analysis – namely from the scene of “Congregation of Russian Saints” in the western apse painted by Vasily Perminov; the inscription to the figure of “Archangel Michael” in the southern stairway, painted by Michail Maletski; the scene of “Virgin Orans” and the scene “Mourning of Jesus Christ” in the crypt, painted by Nikolay Shelehov (Fig. 1). The samples were collected by carefully scratching the wall painting layer, however, inevitably some small amount of the ground layer might also have been introduced into the samples during the scratching.

XRF Elemental composition was determined by Shimadzu EDX-720 spectrometer. The instrument is scanning by default the elements in two groups using 15 kV in the tube for 100 s (called Na-Sc range) and 50 kV for 100 s (called Ti-U range). Operational current intensity up to 1 mA was used. The results of the XRF analysis should be regarded only as qualitative as no special preparation of the samples was undertaken. The fact that the lower layer is also interfering with the results should be taken into consideration but using the different meth-

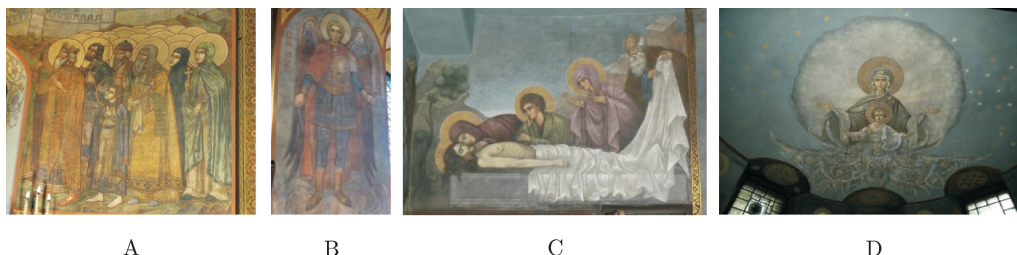


Fig. 1. Scenes where microsamples were collected: A) The scene of Congregation of Russian Saints, B) The figure of Archangel Michael, C) The scenes of Mourning of Jesus Christ, and D) Virgin Orans

ods together gave us possibility to check the obtained information and clarify it.

The Raman spectra of the samples collected from the western apse and the southern stairway were measured on a Raman microscope alpha 300R with a solid state 532 nm laser. The spectra were collected in the wavenumber range $100\text{--}4000\text{ cm}^{-1}$ with integration time of 0.5 s and accumulation of 200 scans. The laser power on the surface was varied from 0.3 to 10 mW by a laser power device. The laser beam was focused with $20\times$ Zeiss and $50\times$ Olympus objective lens. The samples collected from the crypt were studied on a Renishaw Raman spectrometer with microscope inVia Qontor with a 785 nm laser. The spectra were collected in the wavenumber range $150\text{--}3600\text{ cm}^{-1}$ with 10 accumulations of 3–5 seconds each, applying laser powers between 0.04 and 8.5 mW controlled by filters. The optical microscopy pictures were taken prior to the Raman measurements under $50\times$ magnification.

The ATR-FTIR spectra were measured in the middle IR region ($600\text{--}4000\text{ cm}^{-1}$) on Bruker Tensor 27 FT spectrometer equipped with a diamond crystal ATR accessory. The samples spectra were referenced to the air spectrum, acquired by accumulating 64 scans at resolution of 2 cm^{-1} .

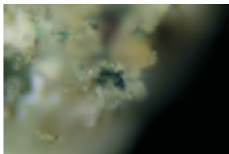
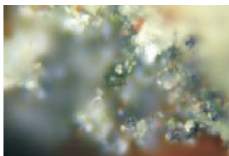
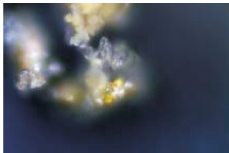
Results and discussion. The samples were analyzed by multi-technique approach, including XRF analysis for examination of the elemental composition, optical microscopy for initial examination of the paint mixtures, micro-Raman spectroscopy for molecular characterization of the pigments and IR spectroscopy for identification of the organic binders.

Examination of the collected samples by optical microscopy prior to the Raman analysis revealed that all colours were composed by a mixture of different pigments. Nevertheless, the use of a Raman microscope allowed the spectral identification of each individual component in the complex paint mixture, by focusing the laser beam onto the grains of different colours. The pigments present were identified by their characteristic Raman spectra. Table 1 summarizes the distribution of the pigments in the studied paint samples and further in the discussion they are presented colour by colour.

Pigments identification. *White.* The analysis of the white grains led to

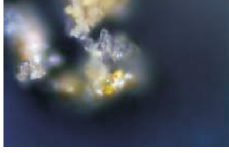
T a b l e 1

Description, elemental composition and identified components of the samples, taken from the murals presented in Fig. 1

Sample description	Element composition (XRF)	Microscopy images	Components	Identified pigments
The Virgin Orans				
White from Jesus' face	Ti, Ca, Cr, Fe, Si, K, Pb		White grains Green grains Dark green grains	Ti white Chrome green Green earth
White from the garment	Ti, Si, S, Ca, Cr, K, Mn		White grains	Ti white
Green from the garment	Si, Ca, S, Ti, Cr, Fe, K, Mn		White grains Green grains	Ti white Chrome green
Brown from the garment	Ca, Ti, Fe, Cr, S, Mn, Zn, Pb, Se		Red grains Black grains White grains	Hematite C black Ti white
The Mourning of Jesus Christ				
Blue from the sky	Ti, Si, S, Ca, Fe, K, Cr, Mn, Cu, Pb		White grains Blue grains Green grains	Ti white Ultramarine Chrome green
White from Jesus' face	Si, Ti, Ca, Cr, Fe, K, Pb, Sb, Se, Cu		White grains Yellow grains	Ti white Naples yellow

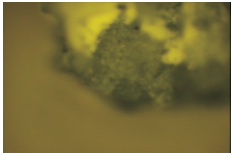
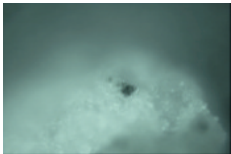
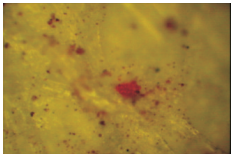
T a b l e 1

Continued

Sample description	Element composition (XRF)	Microscopy images	Components	Identified pigments
White from the garment	Ti, Si, S, Ca, K, Cr, Fe		White grains	Ti white
Green from the garment	Si, S, Cr, Ti, Ca, K, Fe, Mn, Cu, Se		Green grains White grains Red grains	Chrome green Ti white Madder lake
Brown from the garment	Ca, Ti, Fe, Pb, Co		Red grains Black grains White grains White grains	Hematite C black Ti white Calcite
Figure of Archangel Michael				
Orange from the inscription	Ba, S, Fe, Ca, Ti, Cr, Pb, Zn		Black grains Red grains White grains	C black Hematite Barium white
Brown from inscription	Ba, S, Si, Fe, Ca, Ti, Cr, Pb, Zn		Black grains White grains	C black Ti white
Congregation of Russian Saints				
Black from the garment	Ca, S, Si, Fe, K, Cr, Mn, Sr		Black grains	C black

T a b l e 1

Continued

Sample description	Element composition (XRF)	Microscopy images	Components	Identified pigments
Green from the garment	Ca, Si, S, Fe, K, Cr, Ni, Mn, Cu		Green grains White grains	Green earth Calcite
Blue from the shoe	Ca, S, Si, Ba, Zn, K, Fe, Cu, Pb		Blue grains Black grains	Ultramarine C black
Red from the shoe	S, Fe, Hg, Br		Red grains	Vermilion

the identification of three different pigments: the modern synthetic titanium white and barium white as well as the traditional pigment calcite.

In all samples collected from the crypt, Ti was detected by XRF analysis and therefore it was supposed that the white grains in the pigments mixtures are titanium white (TiO_2). It is the most widely used white pigment because of its brightness and nontoxic nature. The natural form has been used as a pigment historically, but its synthetic analogue has been used far more extensively since its first production in the early twentieth century [4]. Two of the three possible polymorphs of titanium (IV) oxide (TiO_2), known as anatase and rutile, were used as white pigments in the 20th century. In the studied samples, the white grains were identified as anatase, as the characteristic bands of anatase (Fig. 2A) at 143(s), 391(m), 515(w) and 636(s) cm^{-1} are present in the Raman spectrum, while those of rutile at 446(m) and 609(m) cm^{-1} are missing [5].

In the samples collected from the southern stairway, where Ba was found by XRF analysis, the white grains were recognized as barium white. Barium white (barium sulphate BaSO_4) appeared as a pigment around 1782–1783 in its natural mineral form, but had limited use until the beginning of the 19th century. Later on both the natural and the synthetic forms became widespread [6]. As it can

be seen in Fig. 2B, the Raman spectrum of the white grains from the southern stairway have characteristic bands for barium white [5] at 453(w), 460(m), 617(w) and 988(vs) cm^{-1} .

The most traditional white pigment calcite is also present in all parts of the church (Table 1). Calcite was identified by the following bands in Raman spectrum: the strong band at 1084 cm^{-1} , weak bands at 712 cm^{-1} and middle bands at 280 cm^{-1} (Fig. 2C) [4].

Green. The colour palette comprised two green pigments of different hues. The analysed light and dark green grains were identified as chrome green and green earths, respectively.

In the samples where light green grains were observed, the element Cr was detected by XRF elemental analysis (Table 1). Chromium oxide (Cr_2O_3) and hydrated chromium oxide ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) are the only common green pigments based on chromium. Both chrome green pigments were in use from the mid-nineteenth century. Because of their permanence and lack of toxicity they have replaced other toxic green pigments [7]. Based on the Raman spectrum (Fig. 2D), where the bands at 350(w), 552(vs) and 611(w) cm^{-1} were observed, the light green pigment was recognized as chromium oxide [8].

The dark green grains were identified as green earth. Green earths have varying composition $\text{K}[(\text{Al}^{\text{III}}, \text{Fe}^{\text{III}})(\text{Fe}^{\text{II}}, \text{Mg}^{\text{II}})](\text{AlSi}_3\text{Si}_4\text{O}_{10}(\text{OH})_2)$ and are widespread natural pigments for wall painting. The green earth pigments are composed of clayey micas and iron oxides, in which the colour is conferred by the ratio of divalent and trivalent iron ions [9]. The characteristic bands for green earths [8] could be distinguished at 149(vs), 388(w), 509(w), 633(m), 684(m), 1076(vw), 1189(vw), 1271(m), 1381(m), 1437(w), 1496(s) and 1532(s) cm^{-1} (Fig. 2E). The presence of elements Fe and Si, detected by the XRF analysis, is also indication for green earth pigment.

Blue. All studied blue grains were identified as ultramarine, the finest blue known to the ancient artists. It is a complex sodium calcium aluminium silicate sulphate ($\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$) and was obtained from the precious stone lapis lazuli (lazurite). The synthetic pigment was first synthesized in the 19th century, and it was widely employed due to its cheaper price compared with the natural lapis lazuli [10]. Ultramarine blue was identified by the most characteristic very strong Raman band [4] at 548 cm^{-1} , and middle intensity band at 1096 cm^{-1} (Fig. 2F).

Red. Analysis of the red grains led to the identification of three pigments: hematite, vermilion and madder lake.

The elemental analysis of some of the samples with red pigment grains identified Fe (Table 1), indicating the presence of iron oxide (hematite) as the possible material producing the red colour. Both the synthetic form (Mars red) and natural pigments (red ochre, sienna) were used in wall paintings [11]. The presence of hematite was explicitly proved by the Raman spectra of red grains in which the characteristic bands [5] at 223(s), 244(m), 295(s), 410(s), 496(w), 611(m) cm^{-1} are

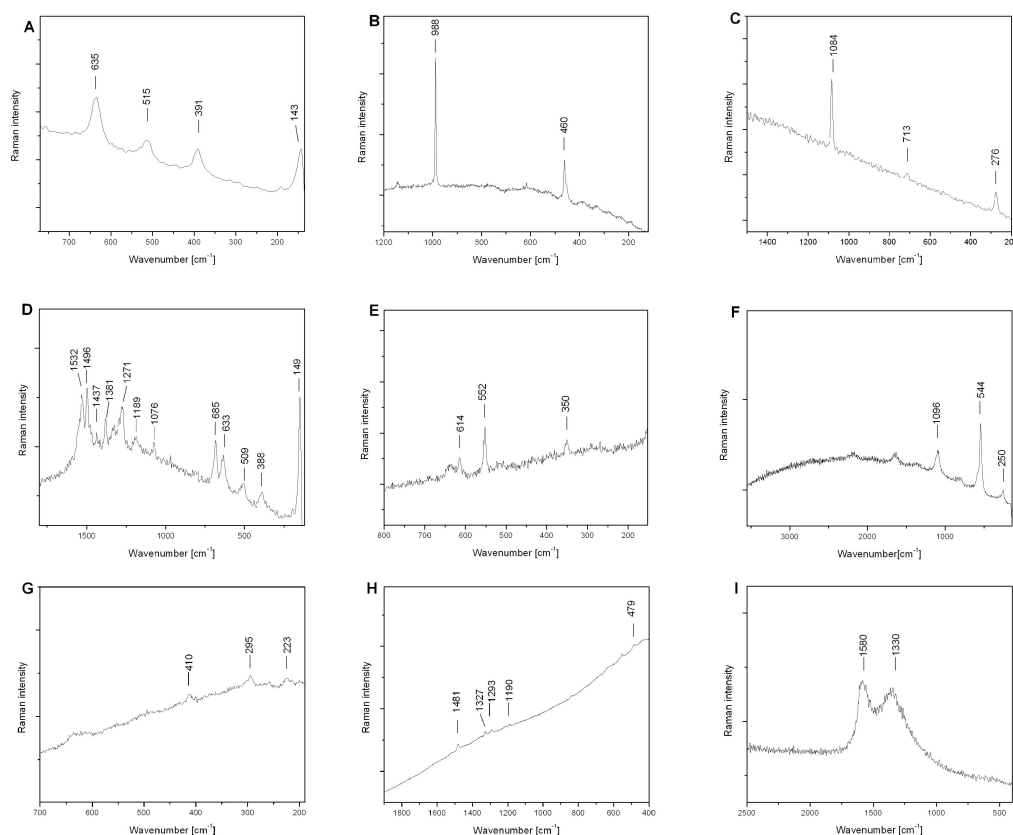


Fig. 2. Raman spectra of white, green, blue, red and black pigments identified in the wall paintings of the Russian church: A) titanium white, B) barium white, C) calcite, D) chrome green, E) green earth, F) ultramarine, G) hematite, H) madder lake, I) carbon black

observed. The absence of Si and Al in these samples excludes the use of natural ochre in this case.

The highly intense red grains in the sample from the western apse were identified as mercuric sulphide (HgS). The natural mineral cinnabar was used as a pigment since ancient times, while the synthetic form – vermilion, has been introduced in the 8th century [12]. The pigment has well-defined characteristic Raman peaks [5], but the Raman measurements in our case did not yield a spectrum. However, considering the elements Hg and S found by the XRF in the sample (Table 1) with intensive red gains, it was assumed that most probably the pigment is HgS.

The third red pigment with a wine-red hue was identified as organic dye, most likely – madder lake, which is a lake pigment made from the natural dyestuff madder, obtained from the root of the madder plant (*Rubia tinctorum*). It is one of the most stable natural pigments, known since ancient times, and its colour is due

to the colouring compounds alizarin and purpurin. The manufacturing of synthetic alizarin (PR83) has begun in 1869, soon after the synthetic production of the first organic colourants mauveine (in 1856) and fuchsine (in 1858) for dyeing textiles [13]. Madder lake was identified by its Raman bands [5] at 479(m), 1190(m), 1293(m), 1327(m), 1482(s) and 1519(w) cm^{-1} .

Black. The black grains were identified as carbon black. Carbon black was used as a pigment from very early times. Carbon black is a common name for a variety of black pigments, traditionally produced from charring materials such as charcoal, wood, bones, etc. [14]. The Raman analysis shows two broad bands that correspond to amorphous carbon, at 1580 and 1330 cm^{-1} . XRF analysis did not show phosphorus, which is characteristic for the apatite found in the black pigments of bone or ivory origin. The Raman peak of apatite at 965 cm^{-1} assigned to the symmetric stretching mode of phosphate was also not observed. It suggested that the black pigment is neither bone black nor ivory black.

Yellow. Detected by XRF analysis, the elements Pb and Sn in the composition of the yellow paint indicated the possible use of Naples yellow ($\text{Pb}_2\text{Sb}_2\text{O}_7$). Lead antimonate yellow is one of the oldest synthetic pigments. It has a very good tinting strength, drying properties and chemical stability [15]. The Raman spectrum of the yellow samples showed the characteristic very intensive band [8] of this pigment at 143 cm^{-1} , but unfortunately, the presence of Naples yellow cannot be confirmed unequivocally, since the characteristic intensive band coincides with that of titanium white, which is also present in the samples.

Binders of the paint layer. Finally, the samples were examined by ATR infrared spectroscopy in order to identify the painting techniques.

The studied samples from the south chapel, western apse and the crypt, showed absorption bands for proteins around: 3300, 1646 and 1541 cm^{-1} and lipid

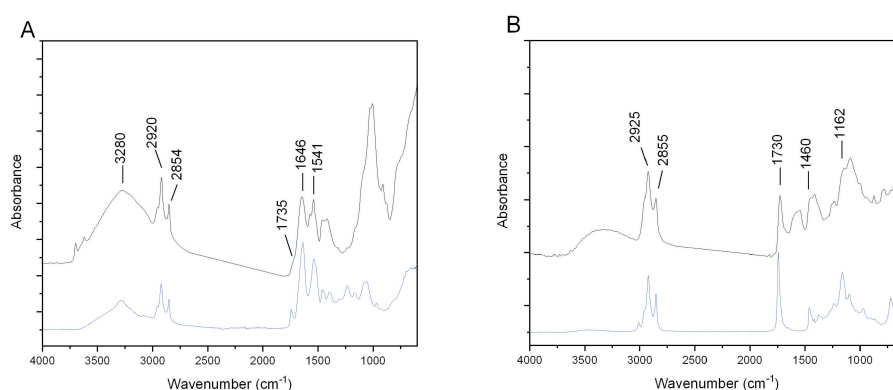


Fig. 3. A) ATR-FTIR spectrum of the sample from the south chapel (in black) compared to that of naturally aged dried egg (in blue); B) ATR-FTIR spectrum of the sample from the altar conch (in black) compared to that of naturally aged drying oil (in blue)

absorption bands located at around 1730 cm^{-1} and in the region of $2960\text{--}2850\text{ cm}^{-1}$. The simultaneous presence of protein and fat IR bands can be related to the presence of egg binder. In Fig. 3A the bands recognized as egg in the ATR-IR spectrum of a paint sample from the south chapel were compared with the bands in the spectrum of aged dried egg and gave very good matching.

Unlike the rest of the samples, the IR spectrum of the paint collected from the altar conch showed characteristic bands of polymerized triglycerides at 2925 , 2855 , 1730 and 1240 cm^{-1} , that implied the use of oil technique. The spectrum of the sample from the altar conch was compared with the IR spectrum of naturally aged drying oil in Fig. 3B and an excellent correspondence can be seen.

The results allow to conclude the following: Maletski's painting technique in the south chapel and stairway is egg tempera; Shelehov's paintings in the crypt is also egg tempera, but Perminov worked in two painting techniques: in oil (e.g. in the altar conch) and in egg tempera (e.g. in the lower part of the western apse).

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