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Characterization of Zahari Zograph's nave wall paintings in the church "The nativity of the virgin" of Rila Monastery (Bulgaria) by vibrational spectroscopy and SEM–EDX analysis

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ABSTRACT

An analytical study on the nave mural paintings of the church "The Nativity of the Virgin" of Rila monastery, Bulgaria, painted by Zahari Zograph was carried out. Vibrational spectroscopy was applied to identify the pigments and organic materials used in the mural paintings. To complement the spectral information, elemental composition of the samples was determined by SEM-EDX. The data showed that smalt with carbohydrate binder was applied for the blue background, green colour was executed by green earths and red-orange colour – by red lead. Azurite is the pigment used to paint the blue colour of the saints' hoods. The mordant for gilding was prepared of drying oil, resin and siccative metal oxides as evidenced by SEM-EDX, ATR-FTIR and pyrolysis GC-MS analysis. The use of azurite is related to Zahari Zograph's works as it was not found in any of the previously studied murals in the church painted by other artists.

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Rila Monastery; pigments; vibrational spectroscopy; SEM–EDX; pyrolysis GC-MS

Statement of significance

As national historical monument and UNESCO World Heritage Site, Rila Monastery, Bulgaria, is of great cultural, artistic and religious value. Its architecture and fine arts are characteristic example of the Bulgarian National Revival (eighteenth–nineteenth centuries). The main monastery church "The Nativity of the Virgin" presents mural paintings by some of the most prominent zographs (religious artists) of the time – Dimitar Zograph, Zahari Zograph, Kostadin Valyov and Ivan Obrazopisov. Analytical study of the wall paintings on different parts of the church, executed in different time periods and by different artists, would reveal the used materials and potentially define the evolution of their technique over time. The current contribution is focusing on the pigments used by Zahari Zograph in the nave murals.

Introduction

Rila Monastery is the largest Eastern Orthodox monastery in Bulgaria. It is located on the slopes of Rila, the highest Balkan Peninsula Mountain, 70 miles south of Sofia (Geolocation coordinates: 42°08′00″N 23° 20′25″E). The monastery was founded by the first Bulgarian hermit St. John of Rila (876–946) (Ivanov 1917). He was highly venerated and honoured through the centuries as Patron of the Bulgarian old capital Tarnovo, Patron of the Bulgarian People, the Light of the town of Sredets, etc. (Dinekov, 1995). His life, monastic work and multiple translations of his relicts lead to an exceptionally developed cult in the old Slavic literature (tenth–nineteenth century) and partly in the Byzantine literature (Malchev 2005).

The existence of the monastery is mentioned for the first time in a written source by John Scylitzes, Byzantine writer and Governor of Sredets in twelfth century, who wrote the extended Life of St. John of Rila between 1173 and 1180 in Greek, and stated within that the hermit blessed the construction of the monastery (Ivanov 1935). The monastery has played a central role in the spiritual and social life of mediaeval Bulgaria – a guardian of the tradition in education and culture, a symbol of the Bulgarian spirit and Christianity. According to history researchers (Anchev 1983; Radkova 2000) under Ottoman rule (1400–1878) the monastery influenced the development of the culture and the arts of all Christian nations within the Ottoman Empire. After the Liberation of Bulgaria (1878) the influence of Rila

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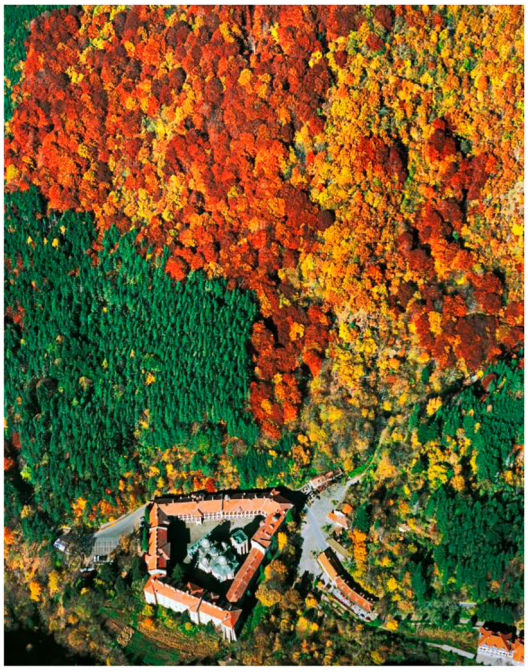
Monastery on the social life gradually decreased, but it remained important religious seat, with a considerable wealth in lands. After 1944 as result of the imposition of the Communist Regime the religious activities in the monastery were suppressed and the monastery was turned into a museum. In 1976, the Rila Monastery was given the status of a historical and architectural reserve, and in 1983 was declared a UNESCO World Heritage Site (UNESCO 1983). In 1991, the status of the monastery was restored by virtue of a special Decree of the Council of Ministers.

The Rila Monastery has a unique architecture. The complex of cultural, dwelling and farming buildings is surrounded by a 24-meter fortified stone wall of irregular pentagon shape (Figure 1(a)) (Hristov, Stojkov, and Mijatev 1959; Koeva 2003). The inner monastery yard presents an impressive view of arches and colonnades, covered wooden stairs and carved verandas of monastic cells (Figure 1(b)). The Hreliov's tower



(a)

(b)

Figure 1. (a) View of Rila Monastery from air (Ivanov 2010); (b) view of the inner monastery yard with the main church "The Nativity of the Virgin" and Hreliov's tower (Ivanov 2010).

(build in 1334–1335 by the local feudal lord Hrelio) and the main church "The Nativity of the Virgin" (build in 1834–1837) raise in the centre of the yard (Figure 1(b)). The monastery was severely damaged by fire in 1833 and the complex was rebuilt between 1834 and 1862. Its architecture and fine arts are characteristic example of the Bulgarian National Revival (eighteenth–nineteenth centuries) (Hristov, Stojkov, and Mijatev 1959; Koeva 2003; Prashkov, Bakalova, and Boyagjiev 1990). The main monastery church "The Nativity of the Virgin" was painted by some of the most prominent zographs (religious artists) of the time – Dimitar Zograph, Zahari Zograph, Kostadin Valyov and Ivan Obrazopisov (Kuyumdzhiev, 2015). Their works were treated as a standard for style and technology by many other painters until the end of nineteenth century. The technological characteristics of the mural paintings in the church "The Nativity of the Virgin" testify the advanced knowledge and artistry of the Bulgarian Revival monastery builders and painters.

While the work of Bulgarian Revival zographs is well studied from artistic point of view, analytical research on the painting materials that they have used is limited up to date. Some reports concerning materials found in the early Bulgarian Orthodox iconography are available in the literature (Sakellariou et al. 2010; Zorba et al. 2002, 2007). However, the distant time period of the studied monuments (tenth–twelfth century) presents a different technological context. Thus aiming to expand the knowledge on the painting materials and technology characteristic to the Bulgarian National Revival, we have focussed our efforts on studying the murals in Rila Monastery by analytical methods. Initial micro chemical analysis was carried out on pigments from the chapel "Assumption of St John of Rila" of the main monastery church in 2010 (Tapanov 2010). More recently, the mural paintings in the altar area of the church painted by Ivan Obrazopisov and Kostadin Valyov in 1841–1842 year were investigated by combined FTIR, XRF, HR-TEM and XRD methods (Stamboliyska et al. 2015). In both cases, the pigments found in the murals comprised in calcite, gypsum, yellow ochre, green earths, sienna, vermilion, smalt, red lead, massicot and Schweinfurt green (Stamboliyska et al. 2015; Tapanov 2010). Except for the blue paint, egg was used as organic binder (Stamboliyska et al. 2015; Tapanov 2010).

Many of the mural paintings in the church nave are made by Zahari Zograph. They stand out with impressive virtuosity and sense of monumentality, without extensive details (Figure 2(a–d)). Zahari Zograph painted with exquisite easiness and expression which makes his murals clearly distinguishable from those of the other artists.

The murals were painted in 1844, succeeding those of chapel "Assumption of St John of Rila" and the central altar. Herein we present the results from a

Figure 2. (a–d) Some of the nave scenes painted by Zahari Zograph in the main monastery church "The Nativity of the Virgin".

spectroscopic Raman and ATR-FTIR investigation on the pigments and organic materials used by Zahari Zograph in the nave murals. ATR-FTIR and Raman spectroscopies provide molecular and structural information for both organic and inorganic materials in a fast way without any sample preparation steps. Due to different selection rules in FTIR and Raman spectroscopy, the two spectroscopic techniques complement each other which make them very suitable for the study of artworks (Ali and Edwards 2014; Bitossi et al. 2005; Burgio and Clark, 2001; Castro et al. 2007; Daher et al. 2010; Derrick, Stulik, and Landry 1999). The elemental composition of the samples was determined by SEM–EDX analysis. Important details on the organic material composition were obtained by pyrolysis gas chromatography-mass spectrometry (pyGC-MS).

Materials and methods

In order to get information on the main pigments and organic matter used in the nave scenes painted by Zahari Zograph, five representative samples were collected from the murals and studied by laboratory spectral analysis. The characteristic colour shades of the paint samples are shown in Figure 3: orange–red (P1), blue (P2), deep blue (P3) and green (P4). For identification of the mordant used for gilding, one sample (P5) was collected from the halo of the saint.

These samples were compared with reference pigments purchased from Kremer Pigmente (Germany): red lead – K42500, very fine grind smalt – K10010, natural azurite – K10200, Bohemian green earth – K40810, calcite – K58720, colophony extra light – K60300, mastic from Chios, Greece – K60050 and

Figure 3. Diagram showing the characteristic colour shades of the samples collected for analysis.

dammar from Sumatra – K60000. Laboratory prepared reference samples were also used as reference materials in the study – aged dried egg (3-year-old) and starch paste glue. The mordant identification was supported by analysis of a naturally aged drying oil collected from the altar area of the church.

The ATR-FTIR spectra were measured in the middle IR region (600–4000 cm^{-1}) on Bruker Tensor 27 FT spectrometer equipped with a diamond crystal ATR accessory. The sample was directly deposited on top of the crystal and pressed in order to ensure a good contact with the ATR crystal. The spectra of the samples were referenced to the air spectrum, acquired by accumulating 64 scans at resolution of 2 cm^{-1}.

Raman measurements were carried out using the Raman microscope alpha 300R (WiTec GmbH, Ulm, Germany) equipped with a solid-state laser operating at 532 nm. The spectra were collected in the wavenumber range 100–4000 cm^{-1} with an integration time of 0.5 s and by accumulation of 200 scans for every sample. The laser beam was focused with 20× Zeiss and 50× Olympus objective lens. The laser power on the surface was varied from 0.3 to 10 mW.

SEM–EDX analysis of the samples was performed with TESCAN SEM/FIB LYRA I XMU instrument equipped with BRUKER Quantax 200 EDS detector. The samples were studied as powders. Prior the analysis the surface of the samples was carbon coated. Primary and secondary elements identified in the samples are provided in Table 1, the exact elements content is given in the Supplementary material. C and O concentration are not considered quantitatively taking into account the bias due to carbon coating and possible contamination during sample handling.

Pyrolyses were carried out with a Pyroprobe 5000 platinum-heated filament pyrolyzer (CDS Analytical, Inc, US) interfaced to a GC7890A (Agilent Technologies, US) gas chromatograph coupled with a MSD (Mass selective Detector) 5975C inert XL EI/CI. All samples were dissolved in chloroform prior to analysis and the solutions were applied. The solvent was evaporated at 80°C and the samples were pyrolyzed at 700°C for 10 s. The Py-GC interface and the injector were at 250°C. The injector was in the split mode (split ratio 1:5 for aged drying oil, 1:3 for mordant P5 and 1:20 for the rest). A 30 m × 0.25 mm i.d. open tubular column (film thickness: 0.25 µm) HP-5MS (unpolar) (Agilent Technologies, US) was used. The column was programmed from 50 to 280°C at 12°C min^{-1} with an initial isothermal period of 2 min. Helium gas flow was set at 1 ml min^{-1}. The mass spectra (1 scan s^{-1}) were recorded under electron impact ionization at 70 eV electron energy, in the range from 15 to 600 m/z.

Results and discussion

The walls of the church were built by mixed technology from crushed stones of local origin and red bricks bound by mortar made of lime and sand (Hristov,

Table 1. Elemental composition, identified components and characteristic ATR-FTIR and Raman frequencies of the studied samples.

Sample ID	Elemental composition[a]	Identified components	IR bands (cm^{-1})	Raman bands (cm^{-1})
P1	Pb, Zn, Fe, Ca, Si	Red lead (Pb_3O_4)		550(vs), 477(w), 456(w), 390(s), 314(s), 226(s) (cf. Figure 4(b))
		Calcite ($CaCO_3$)	1795(w), 1396(vs), 873(s), 714(m) (cf. Figure 4(a))	
		Lead carbonate ($PbCO_3$)	1396(vs), 683(m) (cf. Figure 4(a))	
		Binder	2970(w), 2925(w), 2850(w), 1740(vw), 1640(w) (cf. Figure 4(a))	
P2	Si, K, Fe, Ca, As, Zn, Co, S, Ni	Smalt ($CoO{\cdot}nSiO_2$)	1003(vs), 778(m), 603(m) (cf. Figure 5(a))	462(m) (cf. Figure 5(b))
		Calcite ($CaCO_3$)	871(m) (cf. Figure 5(a))	
		Carbohydrate glue	3292(w), 2980(w), 2923(w), 2850(w), 1619(w), 1418(m), 1150(m), 1086(s), 1003(vs) (cf. Figure 5(a))	
P3	Cu, Mg, S, Ca, Si, Fe	Azurite ($2CuCO_3{\cdot}Cu(OH)_2$)	3420(m), 1463(s), 1403(vs), 948(s), 833(s), 816(s), 769(m) (cf. Figure 6(a))	3427(m), 1575(m), 1425(m), 1093(m), 933(w), 825(w), 760(m), 394(vs), 241(m), 173(w) (cf. Figure 6(b))
		Gypsum ($CaSO_4.2H_2O$)	~3600(w), 3420(m), 1620(m), 1116(s), 1091(s) (cf. Figure 6(a))	
P4	Na, S, K, Ca, Mg, Zn, Fe, Si	Green earths ($K[(Al^{iii}, Fe^{iii})(Fe^{ii},Mg^{ii})], (AlSi_3,Si_4)O_{10}(OH)_2$)	974(m), 671(m) (cf. Figure 7(a))	
		Calcite ($CaCO_3$)	1410(s), 871(s), 711(s) (cf. Figure 7(a))	1082(s), 269(m) (cf. Figure 7(b))
		Gypsum ($CaSO_4.2H_2O$)	3532(w), 3398(w), 1618(m), 1114(m) (cf. Figure 7(a))	
		Carbon black (Amorphous C)		1584(m), 1343(m) (cf. Figure 7(b))
P5	S, Na, Ca, K, Mg, Zn, Pb	Carboxylates	2917(s), 2850(s), 1560(vs), 1456(s), 969(w), 717(m) (cf. Figure 8(a))	
		Triglycerides	1730(sh) (cf. Figure 8(a))	
		Triterpene resin	3304(m), 1708(m), 1161(m), 1124(m), 1093(m), 1045(m) (cf. Figure 8(a))	
		Calcite ($CaCO_3$)	1410(s), 872(w) (cf. Figure 8(a))	
P6	Naturally aged drying oil	Triglycerides	2958(m), 2929(m), 2874(m), 2858(m), 1725(vs), 1451(s), 1451(s), 1387(s), 1241(s), 1145(vs), 1066(s), 965(w), 751(w), 702(w) (cf. Figure 8(b))	

[a]Elements are given in decreasing amount (content in at. % is provided in the Supplementary material).

Stojkov, and Mijatev 1959; Koeva 2003). The dome, the vaults and the arches are built exclusively from bricks bound by lime mortar. The plaster covering the walls is applied in two layers. The adhesion between them is excellent which reveals sophisticated technology and execution. The plaster, most probably, was applied repeatedly on separate areas of the wall from top to bottom with a second plaster layer being laid on the wet surface of the first layer. This technology guarantees an excellent adhesion between the plaster layers and the wall. The first plaster layer is approximately 15–20 mm thick and made of lime, sand, brick powder and plant fibres, while the next layer is only 6–9 mm thick and made of fresh lime, powdered old (carbonized) lime and plant fibres.

Visual observation of the murals painted by Zahari Zograph did not show any separate "giornate" (day's work) or traces of incised drawing on the fresh plaster which suggested that most probably the murals are executed on dry plaster.

The preparatory drawing is freely executed with yellow ochre (Figure S1, Supplementary material). In many areas, there is an underlayer of ochre or grey pigment which has caused serious problems over time (Figure S2, Supplementary material). A consistent technological sequence was followed in the painting of the murals – first application of monochromatic paint layers, then painting of the shadows by dark tones and finally adding lighter tones and highlights to create the illusion of three-dimensionality.

The pigments and organic matter used in the murals were identified by combining the SEM–EDX data on the elemental composition with structural information obtained by vibrational spectroscopy (ATR-FTIR and Raman). Used together ATR-FTIR and Raman spectroscopy allow more precise characterization of the highly heterogeneous painting materials. Micro-Raman spectroscopy has advantage in the detection of heavy metal oxides and hydroxides, while FTIR spectroscopy is better suited for identification of oxides and hydroxides of light elements within earth pigments and other mixed painting materials (Zorba et al. 2007). In the current study, ATR-FTIR was used to obtain fast information on the composition of the bulk samples including organic matter and fluorescent materials such as silicates whose identification is hampered by Raman measurements, while the high special resolution and broader spectral range of the micro-Raman spectroscopy enabled reliable identification of the pigments dispersed in small particles within the paint matrix. In the characterization of the organic mordant for gilding, where spectroscopic and elemental data were not enough to determine unambiguously the material composition, the analysis was extended by pyGC-MS methods.

P1 – orange–red colour

The SEM–EDX analysis of sample P1 from the orange–red paint showed predominant amount of Pb, along with smaller amounts of Zn, Fe, Ca and Si (Table 1). Pb content in the sample pointed out to the use of red lead as pigment. Initial spectroscopic study of the bulk sample by ATR-FTIR provided information only of calcite and organic matter content (Figure 4(a)), therefore the red lead presence was confirmed by further micro-Raman measurements at 532 nm excitation wavelength. The resulting Raman spectrum showed bands at 550, 477, 390, 314 and 226 cm^{-1} (Figure 4(b)).

Lead pigment is prone to chemical degradation under the impact of atmospheric conditions, light,

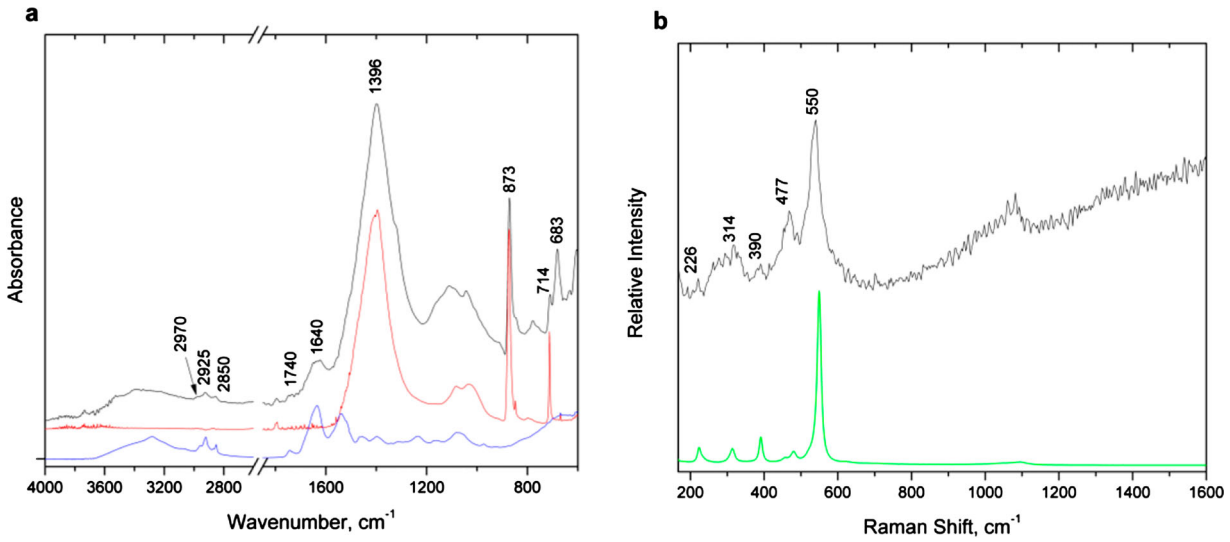


Figure 4. (a) ATR-FTIR spectrum of the orange–red sample P1 showing characteristic bands of calcite, lead carbonate and organic binder (in black); reference calcite (in red) and aged dried egg (in blue); (b) μRaman spectrum of a red grain in P1 showing characteristic bands of red lead (in black); reference red lead (in green); Raman excitation 532 nm; laser power 1 mW; 50× magnification.

contact with sulphur containing compounds and other factors (Coccato, Moens, and Vandenabeele 2017). In the present case, the preservation state of the paint layer should be regarded as stable – no blackening of the pigment was observed and the micro-Raman measurements of sample P1 did not detected any characteristic bands for plattnerite PbO_2 or galena PbS. On the other hand, a white alteration product $PbCO_3$ was revealed by the ATR-IR spectrum of the sample where the main characteristic band for calcite is low-frequency shifted and a weaker band at 683 cm^{-1} is visible (Figure 4(a), Table 1). The formation of $PbCO_3$ in the studied murals is attributed to atmospheric pollutants exposure as found for other historical monuments (Aze et al. 2008; Daniilia and Minopoulou 2009; Gutman et al. 2014).

It is documented that binder, especially proteinaceous media, has beneficial role for the preservation of red lead paints due to its protecting properties to light and humidity (Aze et al. 2008). Although not conclusive, the weak bands in the region 3000–2800 cm^{-1} (corresponding to C–H stretching vibrations) accompanied by a very weak band around 1740 cm^{-1} (for lipid carbonyl vibrations) and a weak broader band around 1640 cm^{-1} (for protein amide vibrations), infer the possible presence of egg binder in the red–orange paint (Figure 4(a)).

The orange–red frames in chapel "Assumption of St John of Rila" and the central altar of the church were also painted by red lead (Stamboliyska et al. 2015; Tapanov 2010). In these parts of the church red lead was used for execution of red garments as well, whereas pink zones in the saints' background contained vermilion (Stamboliyska et al. 2015; Tapanov 2010).

P2 – blue colour from the background

In contrast to the scenes in the central altar of the church and chapel "Assumption of St John of Rila", where the background has three zones of pink, yellow and green colour and the sky is decorated by gilded stars, the scenes painted by Zahari Zograph depict a background of rich green meadows and blue sky without star decoration (Figures 2(a–d), 3).

The elemental composition of sample P2 from the blue sky, found by SEM–EDX analysis, is typical for a cobalt glass (smalt): Si, K, Fe, Ca, As, Zn, Co, S and Ni (Table 1). Smalt was widely used as pigment between the sixteenth and eighteenth centuries due to its low cost and strong blue colour (Roy 1993). It was obtained by doping K-rich glass with Co ores of different geographic origins. Depending on the natural content of the silica and the cobalt ores, additional elements such as Al, Fe, Ni, Bi and As, are always detected in historic smalts (Robinet et al., 2013). In accordance with the SEM–EDX analysis, the ATR-IR spectrum of P2 showed strong absorptions at 1003, 778 and 603 cm^{-1} (Figure 5(a), matching the positions of reference smalt pigment. For comparison purpose, the reference smalt was also studied by SEM–EDX and showed a similar elemental composition (data are provided in Supplementary material).

Smalt is known to degrade in combination with an oil binder causing fading and yellowing of the colour (Cerasuolo 2017; Coccato, Moens, and Vandenabeele 2017). Glue or gum binder was considered as more appropriate for blue pigments than egg because the latter make the hue veer towards green (Cerasuolo 2017). Indeed, several absorptions in the ATR-FTIR spectrum of the pale blue paint (Figure 5(a)) can be ascribed to a

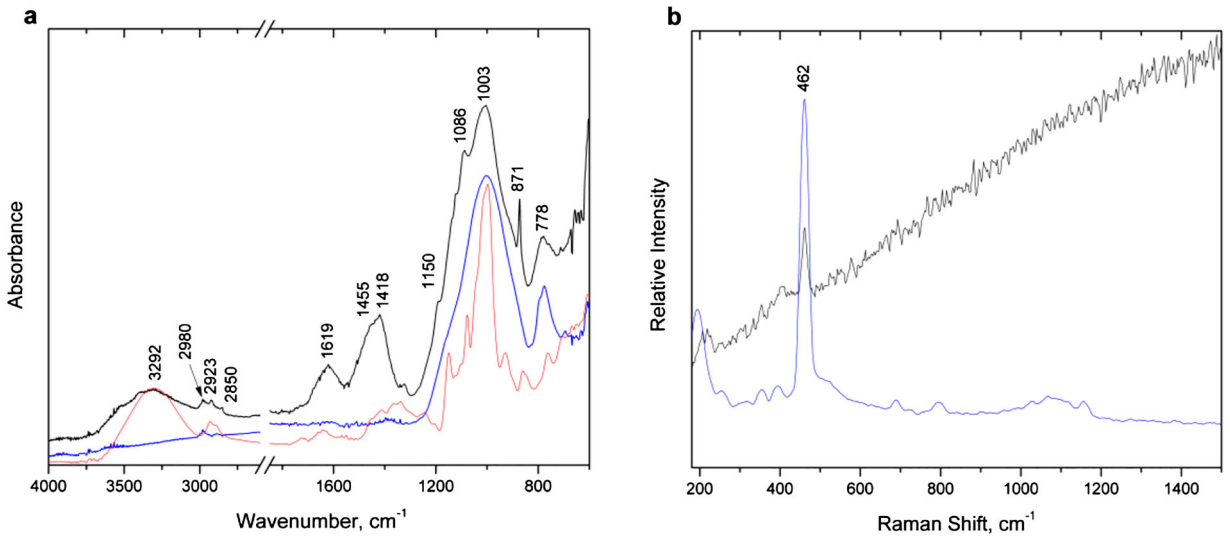


Figure 5. (a) ATR-FTIR spectrum of the blue sample P2 from the background showing characteristic bands of calcite, smalt and carbohydrate glue (in black); reference smalt (in blue) and carbohydrate glue (in red); (b) μRaman spectrum of a blue grain in P2 showing characteristic bands of smalt (in black); reference smalt (in blue); Raman excitation 532 nm; laser power 1 mW; 50× magnification.

carbohydrate binder: 3292 cm^{-1} (O–H str.); 2980, 2923, 2850 cm^{-1} (C–H str.); 1619 cm^{-1} (O–H bend.); 1418 cm^{-1} (C–H bend.); 1150, 1086, 1003 cm^{-1} (C–O str. vibrations).

Comparison with a laboratory prepared reference sample of starch paste glue gave a good coincidence with the absorption bands observed in the ATR spectrum of P2, ascertaining the presence of carbohydrate binder, most probably based on starch (Figure 5(a)).

Micro-Raman analysis of selected blue coloured grain (Figure 5(b)) showed a single band at 462 cm^{-1} due to Si–O vibrations.

The results show that smalt with a carbohydrate glue was consistently used for execution of the blue sky by the different artists in the church "The Nativity of the Virgin". However, some differences exist in the painting techniques applied by Zahari Zograph and the other zographs. In the central altar and chapel "Assumption of St John of Rila", where Dimitar Zograph, Kostadin Valyov and Ivan Obrazopisov have worked, the pigment is applied in a dense paste-like layer on top of a black underlayer at the final stage of the painting (Stamboliyska et al. 2015; Tapanov 2010). Zahari Zograph has painted the blue sky directly onto the white plaster at some earlier stage of the painting (Figure S3, Supplementary material).

P3 – deep blue colour from the garments

In the earlier painted murals of the church blue colour was encountered only in the background, within the blue zone depicting the sky. In the scenes of Zahari Zograph on the other hand, there is a second blue pigment (P3), which was used to paint the blue hoods of the saints. It was identified as azurite (Figures 6), a basic copper carbonate ($2CuCO_3{\cdot}Cu(OH)_2$, naturally occurring mineral). SEM–EDX analysis detected Cu as primary metal element and Mg, S, Ca, Si and Fe as secondary elements (Table 1). The ATR-FTIR spectrum of the P3 is characterized by a series of bands at 3420, 1463, 1403, 948, 816 and 769 cm^{-1} (Figure 6 (a)), for azurite and some peaks for gypsum (Table 1). Azurite identification was supported by micro-Raman measurements on the blue grains in the sample which showed numerous bands at 3427, 1575, 1425, 1093, 933, 826, 760, 394 and 241 cm^{-1} (Figure 6(b)). Azurite was an important blue pigment in European paintings throughout the middle Ages and Renaissance because of its texture and surface quality (Thompson 1956).

P4 – green colour

In the studied nave mural, green colour is used to execute the landscape motives of the background as well as green garments. The microscopic observation of sample P4 revealed a highly heterogeneous mixture of white, green and black particles. The following elements were found by SEM–EDX analysis Na, S, K, Ca, Mg, Zn, Fe and Si (Table 1). The presence of these elements is indication for green earth pigment. Natural earth pigments contain varying amounts of iron oxides or other colour component and white pigments (alumino-silicate as kaolinite or illite, quartz and calcium compounds as calcite, anhydrite, gypsum or dolomite). Green earths are abundant in nature and have been widely used from antiquity to modern times. Mineralogically, the green earths are clayey micas, and their main colouring agents are celadonite, glauconite and sometimes smectites, chlorites and serpentines (Ospitali et al. 2008). The use of green earths in Orthodox Church decoration was recognized at different locations of Balkan Peninsula (Cheilakou, Troullinos, and Koui 2014; Damjanović et al. 2015;

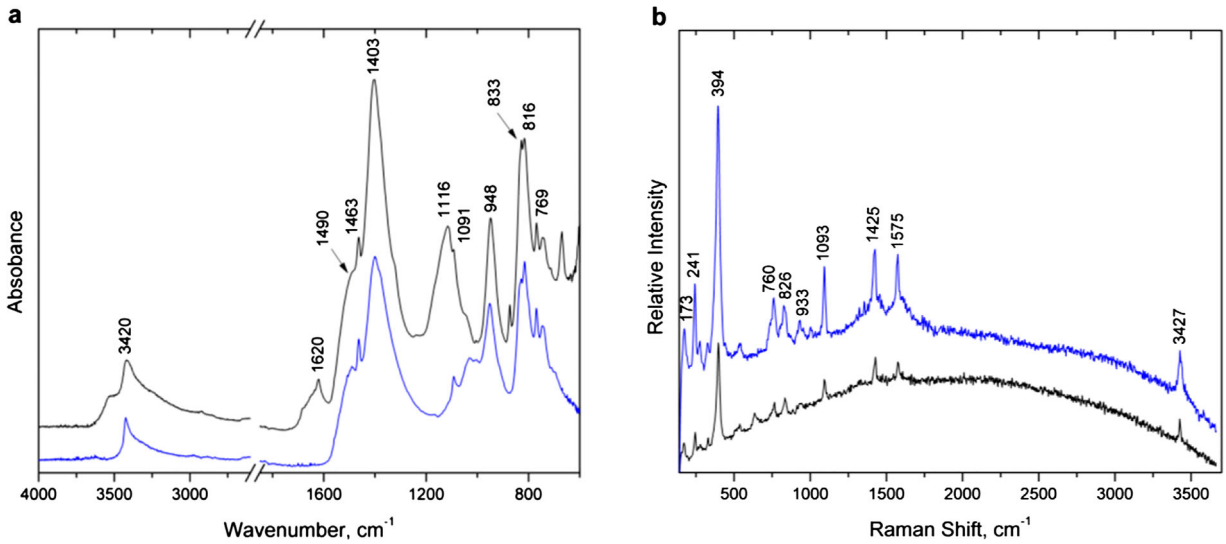


Figure 6. (a) ATR-FTIR spectrum of the deep blue sample P3 from the garments showing characteristic bands of azurite and gypsum (in black); reference azurite (in blue); (b) μRaman spectrum of a blue grain in P3 showing characteristic bands of azurite (in black); reference azurite (in blue); Raman excitation 532 nm; laser power 1 mW; 20× magnification.

Holclajtner-Antunović et al. 2016; Sister Daniilia et al. 2002). Most of the bands visible in the ATR-FTIR spectrum of P4 are related to gypsum – 3532, 3398, 1618 cm^{-1}, and calcite – 1410, 871 and 711 cm^{-1} (Figure 7(a)). However, characteristic bands for green earths could also be distinguished at 974 and 671 cm^{-1}. Their positions correspond to Si–O stretching vibrations of glauconite (Ospitali et al. 2008). As it could be seen in Figure 7(a), the gauconite-containing commercial pigment Bohemian green earth from Kremer (mineralogical content reported by Ospitali et al. 2008), shows absorbance bands at the same positions.

The micro-Raman measurement of green grains could not provide spectrum due to strong fluorescence, while the white area in the sample gave evidence of the calcium carbonate content by detecting bands at 1082 and 269 cm^{-1}. The black particles produced Raman absorptions at 1584 and 1343 cm^{-1} corresponding to carbon black.

Noteworthy, no evidences were found for the presence of a second green pigment, while in the central altar of the church a synthetic green copper pigment was detected in the garments of the saints – Schweinfurt green (Stamboliyska et al. 2015).

The ATR-FTIR spectra of the four studied paint samples contained more or less visible bands around 3600, 3420, 1620 and 1120 cm^{-1}, that can be assigned to gypsum ($CaSO_4{\cdot}2H_2O$) – a common degradation product in wall paintings. SEM–EDX analysis also signified for sulphur content (Table 1). Formation of gypsum should have been promoted by exposure of the murals to humidity and SO_2 pollutants. Alternatively, the band at 1620 cm^{-1} can be interpreted as evidence of another common degradation product – metal oxalates. Careful examination of the ATR-FTIR spectra of samples P1–P4 revealed that in all cases the main calcite band has a shoulder at app. 1320 cm^{-1}, leading to the conclusion that calcium oxalate might also be present in the paint layer as a result of binder degradation.

P5 – mordant in the gilded saints' haloes

Sample P5 was obtained from an area where the gold leaf of the halo was detached and it is expected to contain mainly organic matter coming from the mordant used for gilding. According to the SEM–EDX analysis the elemental composition of the mordant consisted of S, Na, Ca, K, Mg, Zn and Pb (Table 1). Based on BSE imaging and subsequent SEM–EDX analysis in point several small particles of Pb-contaning material were identified within the sample (data shown in Supplementary material).

The bands observed in the ATR-FTIR spectrum of sample P5 (Figure 8) supported the predominant organic content – strong absorptions for alkyl C–H stretching vibrations in the region 2950–2830 cm^{-1}, very strong bands at 1560, 1456 cm^{-1} and bands of moderate intensity at 1708 cm^{-1} and below 1300 cm^{-1}. Calcite bands are also visible at 1410 and 872 cm^{-1}, but with lower intensity.

The band at 1560 cm^{-1}, which is the strongest in the whole spectrum, evidenced the presence of large amount of carboxylates which might be metal salts of fatty acids (fatty acid soaps) (Lluveras-Tenorio et al. 2012; Otero et al. 2014; Sotiropoulou, Papliaka, and Vaccari 2016), resin metal salts (resinates) (Conti et al. 2014) and beeswax metal salts (wax soaps) (Cuní et al. 2012). Noteworthy, the carbonyl band appeared at 1708 cm^{-1} with a shoulder around 1730 cm^{-1}. While the shoulder is positioned at the typical frequency for nonhydrolyzed triglycerides,

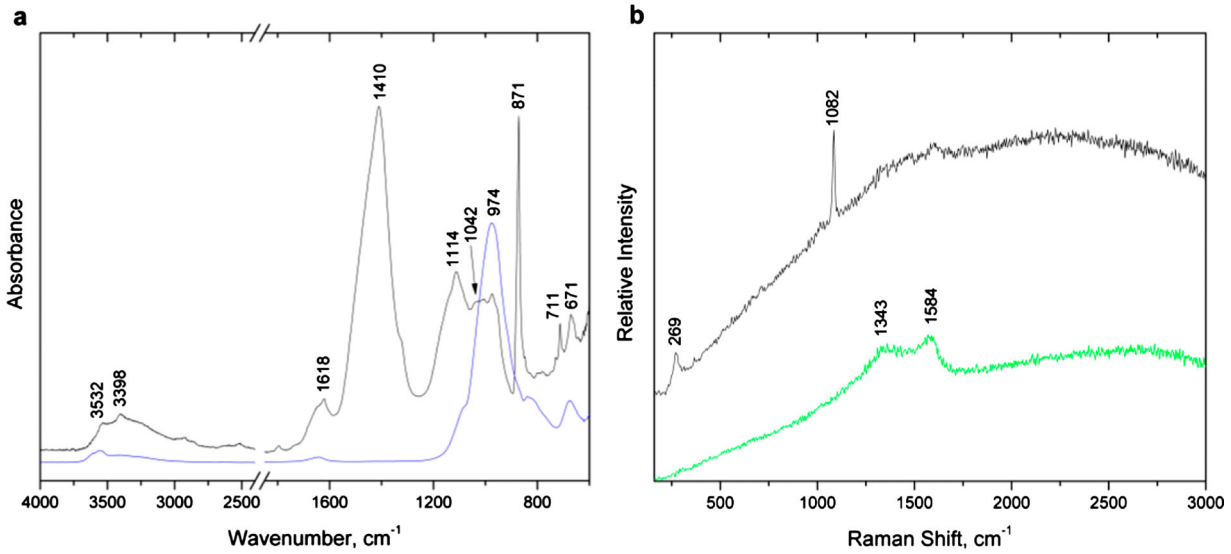


Figure 7. (a) ATR-FTIR spectrum of the green sample P4 showing characteristic bands of green earths, calcite and gypsum (in black); reference green earth (in blue); (b) μRaman spectra of P4 showing characteristic bands of calcite (in black) and carbon black (in green); Raman excitation 532 nm; laser power 5 mW; 20× magnification.

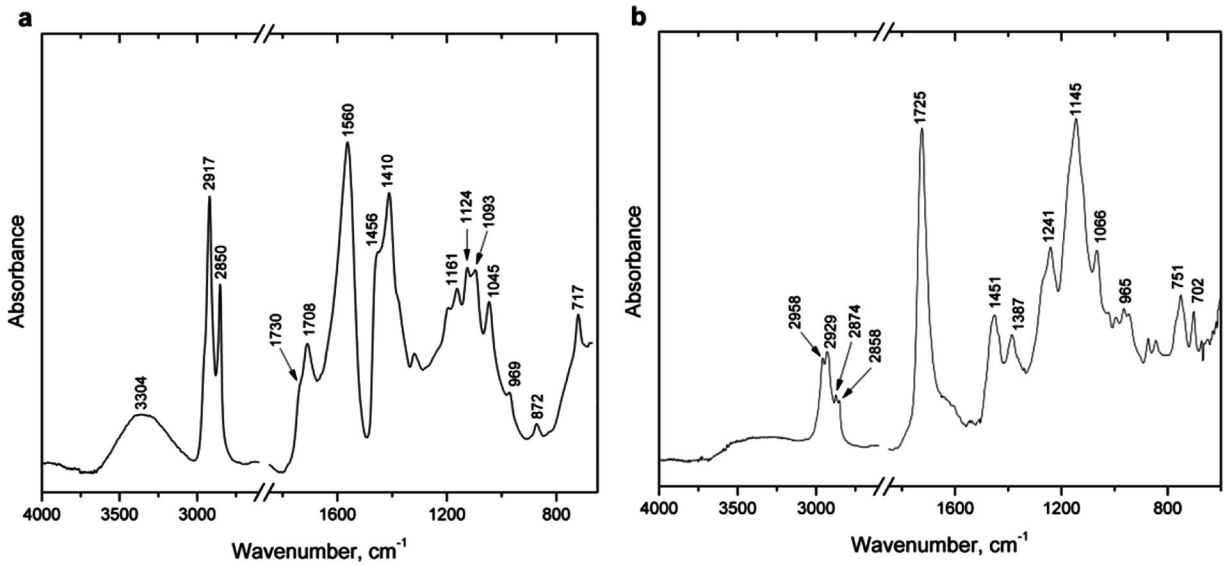


Figure 8. (a) ATR-FTIR spectrum of the mordant sample P5 showing characteristic bands of carboxylates and resin; (b) ATR-FTIR spectrum of naturally aged drying oil P6 showing characteristic peaks of polymerized triglycerides.

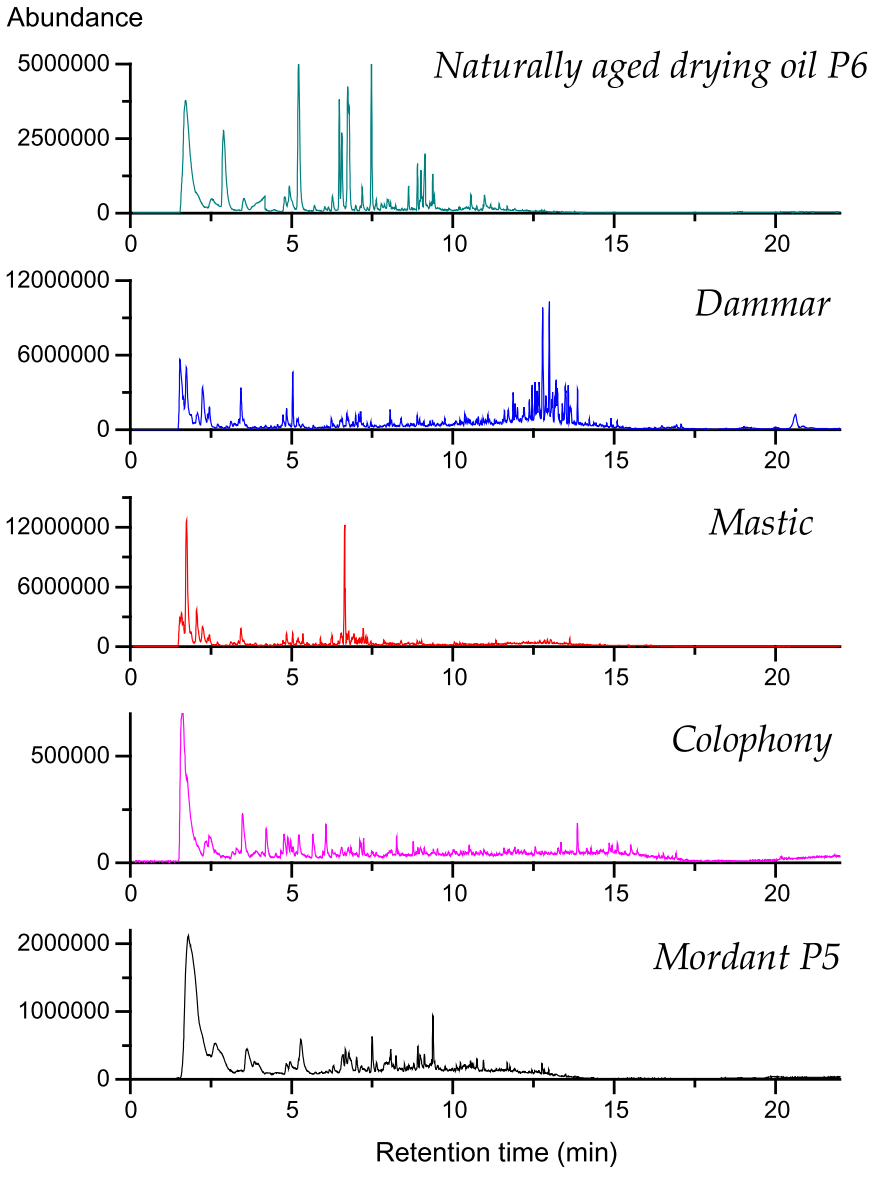


Figure 9. GC chromatograms of colophony, mastic, dammar, mordant for gilding P5 and naturally aged drying oil P6.

Table 2. Pyrolysis GC-MS analysis of reference terpene resins colophony, mastic and dammar, aged drying oil P6 and gold leaf adhesive P5.

Colophony		Mastic		Dammar		Naturally aged oil P6		Gold leaf adhesive P5	
R_t (min)	M/z	R_t (min)	M/z	R_t (min)	M/z	R_t (min)	M/z	R_t (min)	M/z
1.620	44	1.526	44	1.546	44	1.721	56	1.801	44
2.440	78	1.587	56	1.739	68	2.526	78	2.660	78
2.331	80	1.746	68	2.233	82	2.892	100	3.610	92
3.160	98	2.057	84	2.398	78	3.159	92	4.824	106
3.288	96	2.398	78	2.453	80	4.172	86	4.994	106
3.477	92	2.453	80	3.428	92	4.793	106	5.287	104
4.086	108	3.428	92	4.732	126	4.933	87	6.299	120
4.208	110	4.842	106	4.842	06	5.222	104	6.567	30
4.769	106	5.031	124	5.037	122	5.708	120	6.774	118
4.970	108	5.348	138	6.232	120	6.025	118	7.018	112
5.232	104	5.897	138	6.591	126	6.140	120	7.177	134
5.659	136	6.488	120	6.719	118	6.268	120	7.500	116
6.067	36	6.646	136	6.902	134	6.482	142	8.914	130
6.262	20	6.677	138	6.988	120	6.555	104	9.120	144
6.762	118	6.933	136	7.146	134	6.738	118	9.389	128
6.841	122	7.225	136	7.463	116	7.189	118	10.243	162
7.152	134			8.048	132	7.628	132	10.337	142
7.231	136			8.895	130	7.481	116	10.748	142
7.475	116			9.371	128	7.969	132	10.950	142
8.261	48			9.749	162	8.231	142	11.693	196
8.767	146			10.370	144	8.627	144	11.772	198
9.115	30			11.084	160	8.902	130	12.766	206
10.504	144			11.602	160	9.011	128	12.839	212
10.968	142			11.864	158	9.145	144	12.973	206
12.552	170			11.998	06	9.383	128	13.491	202
13.857	184			12.205	156	10.559	132		
15.521	96			12.461	206	10.986	166		
				12.546	206	11.437	144		
				12.784	206				
				12.991	206				
				13.192	204				
				13.253	202				
				13.394	204				
				13.668	202				
				13.863	202				
				14.229	200				
				15.100	206				

the main band is significantly shifted which might be due to free fatty acid released from the interaction of triglycerides with metal ions (Katsibiri and Boon 2004; Katsibiri and Howe 2010; van der Weerd, van Loon, and Boon 2005) or the presence of other components such as triterpene resin (Russo and Avino 2012). The medium intensity bands between 1250 and 900 cm^{-1} provide additional indication for the possible presence of a resin, as the typical ATR spectra of metal carboxylates show only bands of smaller intensity in this region. On the other hand, the intensities of C–O and C–OH stretching bands of resins observed in the latter region markedly increase with aging (Dietemann et al. 2009; Scalarone, Lazzari, and Chiantore 2002).

The carbonyl band is significantly less intensive than that of carboxylates which show that the triglycerides from original oil are largely hydrolyzed and transformed to metal carboxylates. The interaction with different kind of metal salts, different coordination states of the carboxylic acid around the metal atom and the nature of the carboxylic acid lead to variations in the frequencies observed for carboxylates (Hermans et al. 2015; Higgitt, Spring, and Saunders 2003; Otero et al. 2014). Significant broadening of the carboxylate band, as it is observed with the peak at 1560 cm^{-1} of the studied sample, is associated with amorphous state of the metal soaps (Hermans et al. 2015).

In order to clarify further the composition of the mordant, the sample was analyses by pyGC-MS. This method enables rapid characterization of natural resins using sub-mg samples, without chemical pre-treatment. Commercial colophony, mastic and dammar resin were analysed at the same experimental conditions in order to identify the specific diagnostic fragments for each resin. As a reference of naturally aged drying oil, we have used a sample collected from other part of the church, which was previously analysed by ATR-FTIR and showed the typical absorption bands of pure drying oil (sample P6, Figure 8(b)). All four references showed specific chromatographic pattern (Figure 9).

The mordant sample P6 (sample oil) showed some fragments corresponding to adamantane fragments (12.7–13 min, M/z 206) which are specific for the reference dammar (Table 2 and Supplementary material) and were observed in previous Py-GC-MS studies too (Chiavari et al. 1995). The aged oil did not show any specific signals, corresponding to any of the resins.

It was assumed therefore that the mordant used to adhere the gold leaf to the wall was prepared from drying oil mixed with dammar and Pb-siccative.

Conclusions

Our spectral studies indicated the presence of red lead, green earths and two blue pigments – smalt and azurite. Carbon black and calcite were also detected in the samples, as well as some alteration products such as lead carbonate, gypsum and calcium oxalate. The presence of organic binder in the paint suggested that most probably the murals are executed by the traditional egg tempera technique on dry plaster. The blue smalt-based paint of the background was applied mixed with a carbohydrate binder, most probably based on starch. The mordant used to adhere the gold leaf of the haloes showed composition of drying oil, resin and siccative metal oxides.

The pigments used in the painting are of relatively limited number, predominantly minerals of natural origin. A specific feature related to Zahari Zograph's works is the use of azurite, which was not found in any of the murals in the main monastery church "The Nativity of the Virgin" painted earlier by the other artists. Zahari Zograph introduced an innovative approach both in the style and in the painting technique of the murals. The obtained results provide useful basis for comparison with the murals in the church "The Nativity of the Virgin", executed in other periods.

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