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Multi-analytical study on the wall paintings of Kurilo monastery "St. Ivan Rilski", Bulgaria

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

This contribution describes the results obtained from the characterisation of wall paint materials from Kurilo Monastery "St. Ivan Rilski", Bulgaria. Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy (RS), Scanning Electron Microscopy coupled with Energy Dispersive X–ray Spectroscopy (SEM-EDS) and X-Ray Powder Diffraction (XRD) were used for the inorganic content determination. Organic materials in the paint samples were analysed based on Attenuated Total Reflectance (ATR) IR spectra. Via these complementary techniques and by the help of our spectral database, containing local reference materials, we were able to identify the mineral pigments and organic binders in the paint samples.

Key words: Kurilo monastery; pigments; Raman; ATR-IR; SEM-EDX; XRD

INTRODUCTION

Kurilo monastery is situated on the slopes of the Balkan Mountains, 15 km northwest of Sofia. It is one of the monasteries that have remained from the monastic network called "Mala Sveta Gora" (Holy Mount of Sofia) surrounding the city. Founded in the Middle Ages, it was several times destroyed and rebuilt [1,2].

The present monastery church was built in the end of the 16th century and painted in 1596. The restoration and wall painting of the monastery is related to the work of the Bulgarian missionary and enlightener Saint Pimen Zografski [3,4]. Inspired by the idea to awake and strengthen the Bulgarian national consciousness, he has left his solitary confinement at Mount Athos and returned to his homeland to start a broad activity of restoration, building and painting of more than 300 churches and monasteries. Having learnt the icon painting in his youth, Saint Pimen Zografski taught dozens of painters who later became his disciples in the noble work of Bulgarian spirit revival. In this way Saint Pimen Zografski established the first painting school in Bulgarian lands. It accommodated not only painters, but also writers of religious books, teaching the future priests. Regrettably nowadays the enormous contribution of this great Bulgarian cleric is nearly forgotten. Many of the preserved churches are abandoned in bad condition and need urgent restoration.

There are only limited research on the painting techniques, technology and materials used by the school of Saint Pimen Zografski so far. Therefore a systematic and comprehensive study is necessary in order to identify the color palette – specific pigments, binders and painting techniques in the different churches associated with the school.

The present study is reporting on the pigments and binders used in the wall paintings of Kurilo monastery church (Fig. 1) and will contribute to the characterization of post-Byzantine wall painting in the end of the 16th and the beginning of the 17th century, as well as to acknowledge the great work of St. Pimen Zografski.

Molecular and structural information on the mineral pigments and organic materials is provided by combined Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy (RS), Scanning Electron Microscopy coupled with Energy Dispersive X–ray Spectroscopy (SEM-EDS) and X-Ray Powder Diffraction (XRD) methods. FTIR and Raman spectroscopies are widely employed in the identification of art and archaeological materials [5-10]. For the complete characterization of the objects, the spectral analysis was complemented with other analytical techniques, such as Scanning Electron Microscopy coupled with Energy Dispersive X–ray

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Spectroscopy (SEM-EDS) and X-Ray Powder Diffraction (XRD).

EXPERIMENTAL

Representative samples were collected from the mural paintings as shown in Figure 2. A brief description of the samples is given in Table 1.

The ATR-FTIR spectra were measured on a Brucker Tensor 27 FT spectrometer by direct deposition on a diamond ATR crystal, by 64 scans at resolution of 2 cm^{-1} in the middle IR region (600-4000 cm^{-1}).

The Raman spectra were obtained using a LabRAM HR Visible (Horiba Jobin- Yvon) Raman spectrometer. The spectra were collected in the wavenumber range 100 - 4000 cm^{-1} with an integration time of 0.5s and by accumulation of 200 scans for every sample. An objective X50 was used both to focus the incident laser beam onto the sample surface into a spot with a diameter about 2μm and to collect the scattered light. The used excitation was He-Ne 633 nm laser line. The laser power on the surface was varied from 0.3 to 10 mW.

Scanning electron microscopy (SEM) of the samples were conducted on JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) in regimes of secondary electron image (SEI) and Backscattered Electron contrast (BEC). The accelerating voltage was 20 kV, I ~65 mA and the pressure was of the order of 10-4 Pa.

Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. Phase identification was performed with the Diffracplus EVA using ICDD-PDF2 Database.

RESULTS AND DISCUSSION

Pigments identification

The identification of painting materials is considerably facilitated by the use of an appropriate spectral database, especially when spectra from real samples are provided along with the reference materials. For this purpose, we have supported the spectral analysis by comparison with FTIR and Raman spectra from our recently developed spectral database of art and archaeological materials [11]. The database provides information on a number of pigments and dyes, adhesives, oils, resins, gums, bulk components, fillers, mixed materials, as well as archaeological and art work samples [11].

Table 1 shows the identified pigments in the different samples. Selected ATR-FTIR and Raman spectra are illustrated below in Figures 3-6. SEM-EDX and XRD analysis of selected samples are provided in the Supplementary materials.

a b c

Fig. 1(a-c). Some of the scenes on the wall paintings in the Kurilo monastery church: Kiss of Judas (a); Saint Malahya (b); and the Last Supper (c).
For references to color in this figure, the reader is referred to the web version of this article.

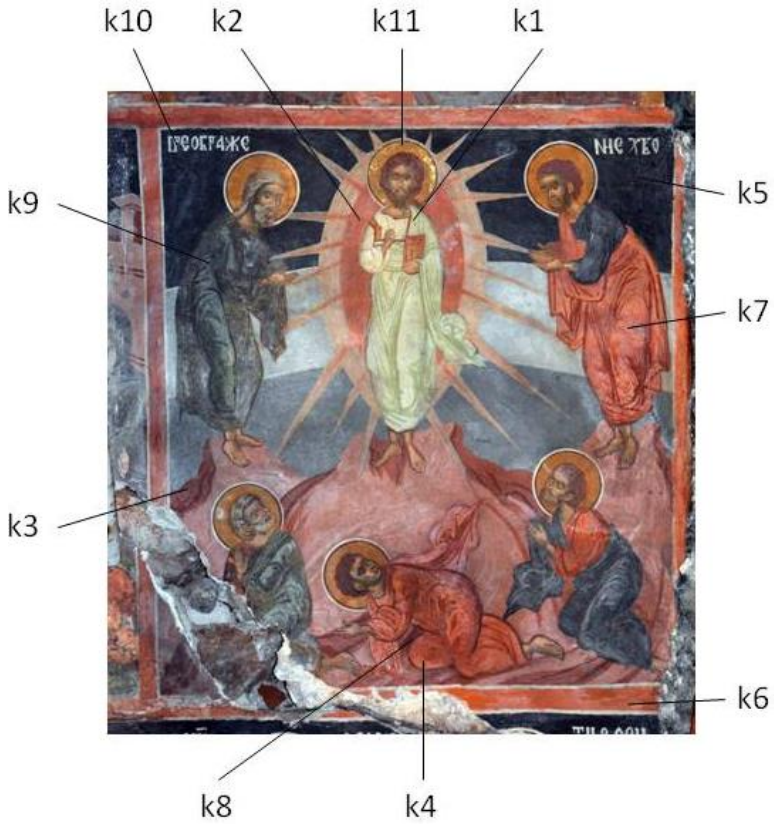

Fig. 2. . Diagram showing the locations of the samples collected for analysis

Table 1. List of studied samples, elemental analysis and identified pigments

Sample ID	Color	Elemental analysis (EDX)	Pigments
K1	green	Mg, Al, Si, S, K, Ca, Fe	celadonite, goethite, calcite, gypsum
K2	red	Na, Mg, Al, Si, S, K, Ca, Fe, Hg	cinnabar, calcite, gypsum
K3	brown	Mg, Al, Si, S, K, Ca, Fe, Cu, Pb	goethite, plumbojarosite, calcite, dolomite, quartz
K4	red	Mg, Al, Si, S, K, Ca, Fe, Hg	cinnabar, calcite, hematite, gypsum, kaolinite
K5	black	Na, Mg, Al, Si, S, K, Ca, Ti	carbon black, calcite, monohydrocalcite, weddellite, whewellite, quartz
K6	yellow orange	Mg, Al, Si, S, K, Ca, Fe, Zn, Pb	goethite, hematite, massicot, calcite, bassanite
K7	red	Mg, Al, Si, S, K, Ca, Ti, Fe, Pb, Hg	cinnabar, calcite, gypsum, kaolinite, muscovite
K8	brown	Na, Mg, Al, Si, S, Cl, K, Ca, Cr, Fe, Ni	hematite, calcite, gypsum, quartz, talc, halloysite
K9	green	Mg, Al, Si, K, Ca, Ti, Fe	celadonite, calcite, quartz
K10	white	Mg, Al, Si, K, Ca, Fe, Pb	calcite, gypsum, quartz
K11	Gold lead adhesive	Mg, Al, Si, S, K, Ca, Fe, Pb	drying oil mixed with Pb-containg drier and colophony

Red pigments used in the wall paintings are red ochre, cinnabar and red lead. Hg was detected by the EDX analysis in all the red samples. In accordance with this, XRD analysis showed the presence of cinnabar in the three samples, along with hematite in sample K4 and silicate minerals in samples K4 and K7 (Table 1, Figs 1S and 2S in Supplementary materials). Identification of cinnabar was supported by Raman spectroscopy – the pigment gave characteristic peaks at 346, 288

and 256 cm^{-1} matching with those of the reference cinnabar (Fig. 3). In sample K7 red lead is also present as evidenced by the elemental analysis.

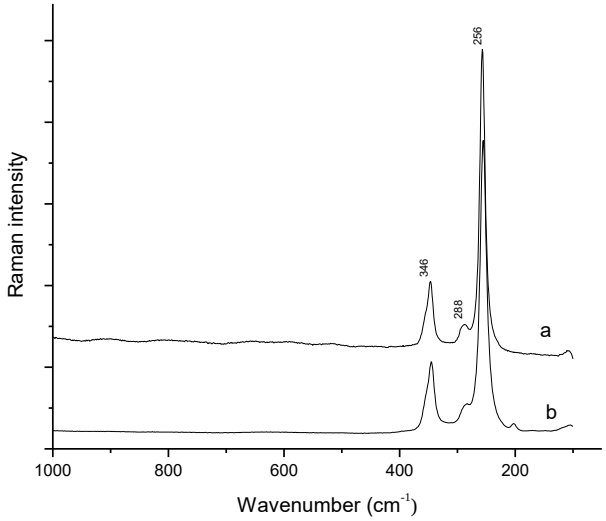

Fig. 3. Raman spectra of sample K2 (a) and reference cinnabar (b); 633 nm excitation, wavenumber range 100-4000 cm^{-1}.-

The green colors are achieved by the use of green earth containing the green mineral celadonite, a hydrated silicate of iron and magnesium, as can be seen by the EDX and XRD analysis of samples K1 and K9. In addition, K1 contains goethite. Both samples gave strong fluorescence which did not allow characterization by Raman spectroscopy, but ATR-IR measurements provided good coincidence with reference green earths (Fig. 4).

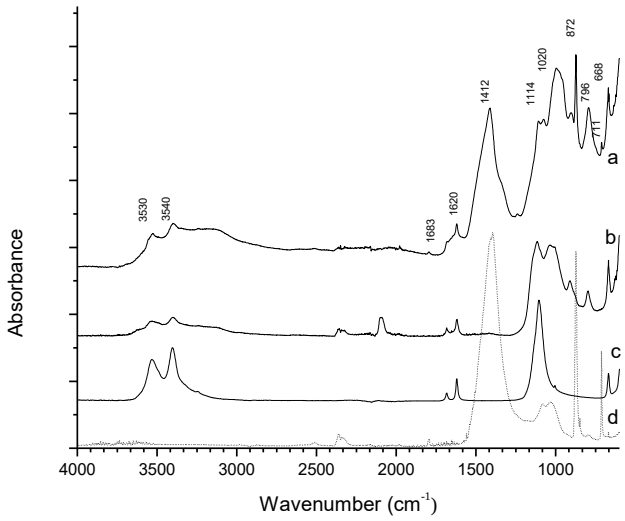

Fig. 4. ATR-IR spectra of sample K1 (a), reference green earth (b), reference gypsum (c), reference calcite (d); wavenumber range 600-4000 cm^{-1}.

Brown color pigments were identified as natural ochres by the simultenous presence of minerals goethite, plumbojarosite (in sample K3), hematite (in sample K8) and silicate minerals (in both samples) evidenced by the XRD and ATR-IR analysis. The ATR-IR spectra of K3 along with reference goethite and calcite are presented in Fig. 5. Characteristic absorption peaks of goethite are well seen at 896 and 796 cm^{-1}.

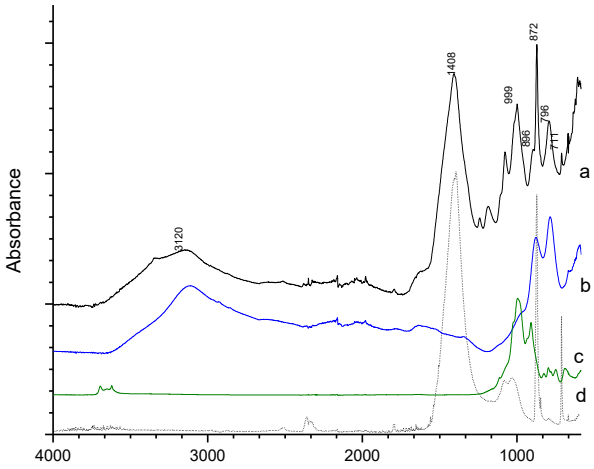

Fig. 5. ATR-IR spectra of sample K3 (a), reference goethite (b), reference kaolinite (c) and reference calcite (d); wavenumber range 600-4000 cm^{-1}.

Yellow color sample showed more complex composition. The presence of yellow ochre was conferred by XRD identification of goethite and hematite and characteristic absorption of silicate minerals revealed by the ATR-IR spectrum. In addition, the elemental analysis showed Pb content, supported by XRD identification of massicot (Fig. 3S in Suppl. material). Evidently the painter has applied a mixture of yellow ochre and massicot in order to achieve the desired color hue.

The black color pigment showed two broad peaks around 1600 and 1360 cm^{-1} in the Raman spectrum as characteristic for carbon based pigments. The XRD analysis showed the presence of calcite, monohydrocalcite, weddellite, whewellite and quartz. The ATR spectrum of the sample gave a good match with those of reference bister pigment, beech wood soot (Fig. 6). This pigment has been made by carbonizing beech wood and it produces a dark greyish brown color rather than true black. However considering the black color of sample K5, it was concluded that the painter has used a mixture of soot pigments.

Calcite and white lead are the pigments used for the white areas. The EDX analysis of sample K10 showed Mg, Al, Si, K, Ca, Fe and Pb content (Fig. 4S in Suppl. material).

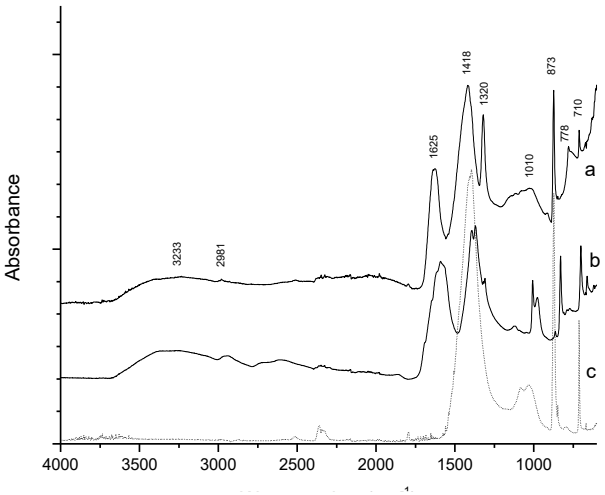

Fig. 6. ATR-IR spectra of sample K5 (a), reference bister (b) and reference calcite (c); wavenumber range 600-4000 cm^{-1}.

Identification of organic materials

Paint binder was identified by the ATR-IR spectra of samples K4 and K6 as egg. In the region 3000-2800 cm^{-1} three bands of weak intensity appeared accompanied by a very weak band around 1740 cm^{-1} (attributed to lipid carbonyl vibrations) and a weak broader band around 1640 cm^{-1} (attributed to protein amide vibrations).

The ATR spectrum of the gold leaf adhesive material (sample K11) provided several strong bands for calcite - at 1412, 873, 711 cm^{-1}, along with less intensive bands in the region 3000-2800 cm^{-1} and around 1730 and 1680 cm^{-1} (Fig. 5). According to the SEM-EDX analysis the elemental composition of the adhesive material consisted of C, O, Mg, Al, Si, S, K, Ca, Fe, Pb.

In order to identify the organic content, the sample was extracted with chloroform solvent. The concentrated extract provided an ATR-FTIR spectrum (Fig. 5b) which shows a close resemblance to a sample of drying oil obtained from the Church "The Nativity of the Virgin" of Rila monastery and reference colophony resin. The absorptions in the region 2950-2830 cm^{-1} are characteristic for C-H stretching vibrations. Several strong bands were found between 1800 1nd 1700 cm^{-1}. The first of them, at 1727 is assigned to the carbonyl stretching vibration of drying oil, while the other should be attributed to the resin. The position of the shoulder at 1695 is indication that the resin is from the diterpene type, presumably colophony. The presence of Pb in the sample is evidence that the drying of oil was induced by the Pb siccative. Therefore, it was concluded that the adhesive material was made by a mixture of drying oil and diterpene resin with Pb siccative.

The chemical composition of adhesive material is discussed recently in the other studies on the gilding technique in post-Byzantine wall paintings [12, 13]. The authors have found that the gold leaf was adhered to the paintings by means of a mordant containing linseed oil with a lead-based dryer and an earth pigment or clay.

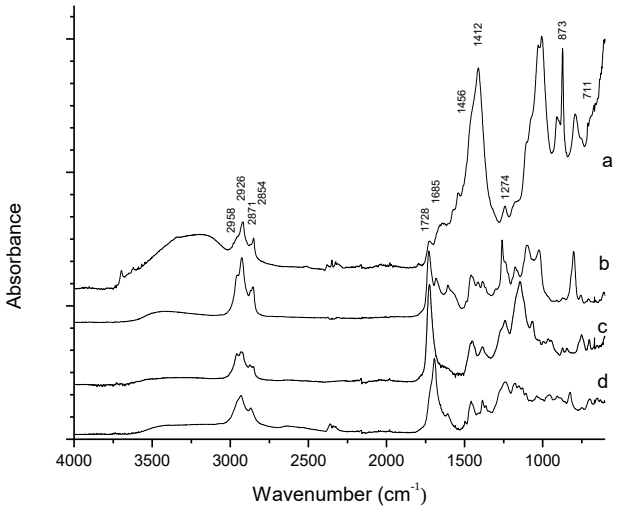

Fig. 7. ATR-IR spectra of sample K11 (a), chloroform extract of sample K11 (b); drying oil from Rila monastery (c), reference colophony (rosin) (d); wavenumber range 600-4000 cm^{-1}.

CONCLUSION

Combined IR, XRF, HR-TEM and XRD analysis showed that the colour palette comprises in natural pigments and synthetic pigments. Green earths containing celadonite and goethite were used as green pigments. Red colored paint samples showed cinnabar, red ochre and red lead content. Yellow and brown colors are based on natural ochre pigments. Calcite and lead white were present in white paint. Extraction by various organic solvents and ATR-IR spectral analysis enabled the identification of adhesive material as made by a mixture of drying oil and diterpene resin with Pb siccative. The desirable color hues were produced by applying mixtures of several pigments. In all cases, egg was used as organic binder. The provided useful information on the pigments, organic binders and fillers indicate that the technique of egg tempera painting was employed.

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Electronic Supplementary Data available here

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КОМБИНИРАНО АНАЛИТИЧНО ИЗСЛЕДВАНЕ НА СТЕНОПИСИТЕ ОТ КУРИЛСКИЯ МАНАСТИР "СВ. ИВАН РИЛСКИ"

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(Резюме)

Това изследване представя резултатите, получени при охарактеризирането на художествените материали, използвани за изографисването на Курилския манастир "Св. Иван Рилски", България. За определяне на неорганичните пигменти бяха използвани инфрачервена спектроскопия (FTIR), Раманова спектроскопия, сканираща електронна микроскопия (SEM-EDS) и рентгенова прахова дифракция (XRD). Органичните материали в пробите бяха анализирани въз основа на отражателни инфрачервени спектри (ATR). Чрез тези допълващи се техники и с помощта на нашата спектрална база данни, съдържаща местни референтни материали, ние успяхме да идентифицираме минералните пигменти и органичните свързващи вещества в пробите.