



J. Serb. Chem. Soc. 80 (6) 805–817 (2015)
JSCS–4760

Journal of
the Serbian
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 27–526.62:7.023.1–037.1+
547.97–035.67:543.4+543.424.2

Original scientific paper

Spectroscopic investigation of two Serbian icons painted on canvas

LJILJANA DAMJANOVIĆ^{1*}, OLGICA MARJANOVIĆ¹,
MILICA MARIĆ STOJANOVIĆ², VELIBOR ANDRIĆ³ and UBAVKA B. MIOČ¹

¹University of Belgrade-Faculty of Physical Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia, ²National Museum Belgrade, Trg Republike 1a, 11000 Belgrade, Serbia and

³University of Belgrade-Vinča Institute of Nuclear Sciences, P. O. Box 522, 11000 Belgrade, Serbia

(Received 22 July, revised 6 October, accepted 8 October 2014)

Abstract: A multianalytical study of two Serbian icons, “The Virgin and Child” and “St. Petka”, painted on canvas by unknown authors was performed in order to identify the materials used as pigments, binders and the ground layer. The investigated icons belong to the Museum of the Serbian Orthodox Church in Belgrade. Samples, collected from different parts of the icons, were analysed by: optical microscopy (OM), energy dispersive X-Ray fluorescence (EDXRF), Fourier transform infrared (FTIR) and micro-Raman spectroscopy. The obtained results revealed the presence of the following pigments: Prussian Blue, ultramarine, Green Earth, iron oxides, Lead White and Zinc White. Linseed oil was used as the binder. The materials used for the ground layers were gypsum, calcite, baryte and Lead White. The gilded surface of the icon “The Virgin and Child” was made of gold. The gilded surface on the frame of this icon was made of imitation of gold, *i.e.*, Schlagmetal, since EDXRF spectroscopy showed the presence of copper and zinc, while gold was not detected. Based on the style and the consideration of an art historian, as well as on the obtained results for the corresponding pigments and binder, both icons were most probably made at the end of 19th or the beginning of the 20th century.

Keywords: pigments; EDXRF; FTIR spectroscopy; micro-Raman spectroscopy.

INTRODUCTION

Preservation of cultural heritage is traditionally a task for conservators, restorers and art historians. Scientific investigation of cultural heritage started at the beginning of 20th century.¹ Nowadays, the application of different analytical methods is essential for the identification of the materials of which artworks are made and of the techniques employed by the artists. These analyses aid art histo-

* Corresponding author. E-mail: ljiljana@ffh.bg.ac.rs
doi: 10.2298/JSC140722099D

rians to better understand the history of an object since many of the choices made by the artist were influenced by the current state of technology, economics, politics and many other factors.² They provide important information not only for the determination of the provenience and authenticity of works of art, but also can help conservators and restorers to choose the most appropriate procedure for restoration, conservation and display.³

Scientific investigation of paintings or icons is a demanding task due to the small amounts of the samples, usually in the micro or sub-micro range (when available), and the presence of different organic and inorganic compounds in the sample. In order to obtain complete characterization of these complex mixtures, the application of different analytical techniques is required.⁴ When possible, samples are taken from damaged regions or from the edges of the painting, and they should be representative of the area under study. The technological procedure followed by painters and iconographers usually means that the ground layer is applied first to prepare the surface of a canvas or a panel, followed by application of a painting layer, which is a mixture of pigments and binding media and their composition gives the colour quality. Finally, varnish, which is mainly based on natural resins, is applied as a protective coating but also for particular visual effects.⁵ Pigments can be organic or inorganic compounds and chronological use of most pigments is known today.^{6,7} Hence, identification of pigments enables indirect dating of painted art objects.

In this work, a multianalytical study of two icons, "The Virgin and Child" (dimensions: 57 cm×90 cm) and "St. Petka" (dimensions: 55 cm×69 cm), painted on canvas by unknown authors was performed. The investigated icons are the property of the Museum of the Serbian Orthodox Church in Belgrade. Art historians classified the icons "The Virgin and Child" and "St. Petka" as Serbian icons made under the influence of West European baroque. The investigated icons represent two iconographic types: one depicts the Virgin Hodegetria, which is an often used motive, while other shows an individual Saint. Based on the style and art historian considerations, both icons were most probably made at the end of the 19th or the beginning of the 20th century. The icons were brought for restoration at the Academy of the Serbian Orthodox Church for Art and Conservation and a scientific investigation was performed during the restoration procedure. The aim of this study was to identify the materials used as pigments, binders and the ground layer on two icons by application of the physicochemical methods optical microscopy (OM), energy dispersive X-Ray fluorescence (EDXRF), Fourier transform infrared (FTIR) and micro-Raman spectroscopy. The obtained results contributed to the selection of an appropriate restoration procedure.

It is important to note that icons are usually studied from the historical, theological, iconographic and stylistic point of view. Only in the past decade was the materials aspect of icons considered.⁸ Therefore, the results of this study

together with art historical research will contribute to a better understanding of the painting techniques of Serbian icons.

EXPERIMENTAL

Samples

Samples were collected during the restoration procedure. Paint chips, approximately 1 mm² or even smaller, were removed by a clean and sharp scalpel from the edges of existing damaged regions on the icons (Fig. 1). All samples contained small pieces of ground layer attached to the paint layer. A description of all the investigated samples and used analytical techniques are given in Table I.



Fig. 1. Icons painted on canvas: A) “The Virgin and Child” and B) “St. Petka”. Samples were taken from the marked areas.

TABLE I. Description of investigated samples and used analytical methods

Icon	Sample ID	Description	Analytical methods
A The Virgin and Child	A1	Virgin’s mantle, Blue	OM, EDXRF, FTIR
	A2	Gilded area on the icon	OM, EDXRF, FTIR
	A3	Gilded area on the frame	OM, EDXRF, FTIR
B St. Petka	B1	Grass, Green	OM, EDXRF, FTIR
	B2	St. Petka’s mantle, Blue–Brownish	OM, EDXRF, FTIR, μ Raman
	B3	Sky, Light Blue	OM, EDXRF, FTIR

Analytical methods

Optical microscopy provides information about the sequence and the thickness of the layers in the paint chips samples and allows a preliminary characterisation of the materials in the paint layer and the ground layer. Cross sections of investigated samples were recorded by an Olympus BX51M optical microscope equipped with an Olympus U-RFL-T UV lamp and U-MWUS3 and U-MWBS3 filters.

EDXRF spectroscopy is an often used method for non-destructive analysis of cultural heritage objects. It is a fast and reliable analytical technique that provides information about the elemental chemical composition. Due to the penetrative nature of X-rays, characteristic fluorescence radiation is recorded not only from the surface paint layers, but also from the covered layers including even the ground layer. In this work, qualitative EDXRF spectroscopy measurements were performed on an EDXRF spectrometer with a Canberra Si(Li) semiconductor detector and MCA analyzer S35+. MicroSAMPO software was used for the spectra acquisition and measurement time was 800 s for all the samples. For the excitation, an annular radioisotope source ^{109}Cd (manufactured by Isotope Products) with nominal activity of 740 MBq was used.

FTIR spectroscopy was used in order to reveal the molecular composition of organic and inorganic compounds in the investigated samples. FTIR spectra of all samples were recorded on a Nicolet 6700 spectrophotometer, using the KBr pellets technique in the wavenumber range from 4000 to 400 cm^{-1} .

Micro-Raman spectroscopy as non-destructive and micro-probe method is very convenient for investigation of samples from painted objects. Micro-Raman spectra were recorded on a DXR Raman Microscope (Thermo Scientific). The 532 nm line of a diode-pumped solid-state high brightness laser was used as the exciting radiation and the power of illumination at the sample surface was 0.5 mW. Collection of the scattered light was made through an Olympus microscope with infinity-corrected confocal optics, 25 μm pinhole aperture, standard working distance objective 50 \times , and grating of 900 lines mm^{-1} . The acquisition time was 10 s, with 10 scans. The laser spot diameter on the sample was 1 μm . Thermo Scientific OMNIC software was used for spectra collection and manipulation.

RESULTS AND DISCUSSION

Icon A: "The Virgin and Child"

Representative optical micrographs of samples taken from the icon "The Virgin and Child" are shown in Fig. 2. The obtained optical micrographs, which are diversely coloured and show a multilayered structure, will be discussed later combined with the results of the EDXRF and FTIR spectroscopic analyses.

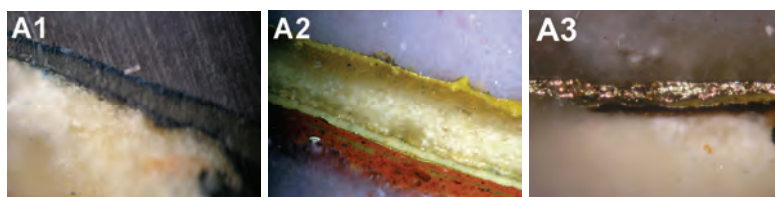


Fig. 2. Representative optical micrographs of samples taken from the icon "The Virgin and Child"; magnification 200 \times .

Samples of paint chips taken from the icon "The Virgin and Child" (Table I) were investigated by qualitative EDXRF spectroscopic analysis on both sides: the side with the surface paint layer and the side with the ground layer. The results obtained by EDXRF spectroscopy measurements are given in Table II.

TABLE II. Results obtained by EDXRF spectroscopy of samples taken from the icons “The Virgin and Child” (A) and “St. Petka” (B)

Sample ID	Detected elements
A1	Ca, Fe, Pb, Sr
A2	Ca, Fe, Cu, Zn, Pb, Au
A3	Ca, Fe, Cu, Zn
B1	Ca, Ba, Fe, Zn, Pb, Sr
B2	Ca, Ba, Fe, Zn, Pb, Sr
B3	Ca, Ba, Fe, Zn, Pb, Sr

EDXRF spectroscopy is an elemental analysis and the results obtained by this method could be inconclusive. Therefore, it was important to combine this method with other techniques for the identification of the compounds present in the investigated samples. The results obtained by FTIR spectroscopy for the samples taken from the icon “The Virgin and Child” are shown in Fig. 3. The investigated samples were mixtures of inorganic and organic compounds, which resulted in a broadening of the FTIR adsorption bands due to the overlapping of different vibrational modes.

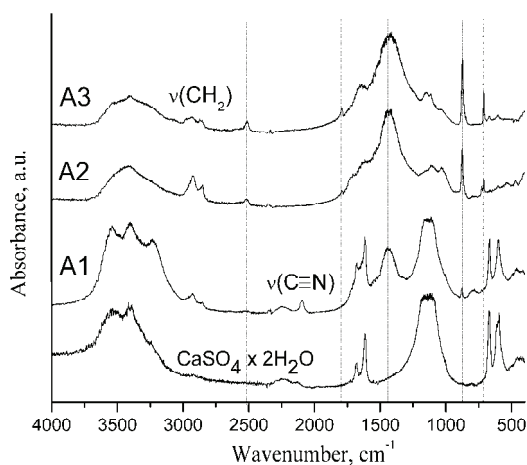


Fig. 3. FTIR spectra of samples taken from the icon “The Virgin and Child” and reference spectrum of gypsum; vertical lines represent the positions of the characteristic bands of calcite.

In the case of the blue sample, A1, the characteristic band in the FTIR spectrum, Fig. 3, at 2094 cm^{-1} was assigned to the $\nu(\text{C}\equiv\text{N})$ stretching vibration, which is highly specific for the pigment Prussian Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.⁹ This result combined with the presence of Fe determined by EDXRF spectroscopy (Table II) confirmed that Prussian Blue was used as the blue pigment. FTIR spectrum of sample A1 (Fig. 3) showed bands at 1143 , 670 and 600 cm^{-1} , which were attributed to the stretching modes of the sulphate group, $\nu(\text{SO}_4^{2-})$, while the bands at 3545 , 3405 , 1686 , 1617 cm^{-1} were attributed to OH^- stretching and bending vibrations.¹⁰ These bands originate from gypsum, dehydrated calcium

sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), as can be seen by comparison of FTIR spectra of sample A1 and gypsum (Fig. 3). Gypsum was traditionally used for the ground layer of icons^{11–13} and it was often naturally occurring mixed with celestine, strontium sulphate (SrSO_4), which explains the presence of Sr detected by EDXRF spectroscopy. The bands around $1450\text{--}1400\text{ cm}^{-1}$ originate from the vibrational mode of the carbonate group $\nu(\text{CO}_3^{2-})$.¹⁴ Weak bands at 2514 , 1796 , 873 and 713 cm^{-1} in the FTIR spectrum of sample A1 (Fig. 3) together with a broad band at 1430 cm^{-1} confirmed the presence of calcite (CaCO_3).¹⁰ The EDXRF spectra of the ground and paint layer of sample A1 are shown in Fig. 4. The intensity of the peak for Ca in the EDXRF spectra of sample A1 was higher for the ground layer than for the paint layer. Therefore, the ground layer was made of gypsum and calcite. Since Pb was detected by EDXRF spectroscopy, the carbonate bands in the FTIR spectrum of sample A1 could also originate from Lead White, basic lead carbonate ($2\text{PbCO}_2 \cdot \text{Pb}(\text{OH})_2$). The intensities of the peaks originating from Pb in the EDXRF spectra were higher for the side with the paint layer than for the side with the ground layer (Fig. 4). This finding indicates that Lead White was used as the pigment to obtain an appropriate hue of blue, which is in accordance with the presence of white grains in the blue paint layer of sample A1, observed in the optical micrographs (Fig. 2).

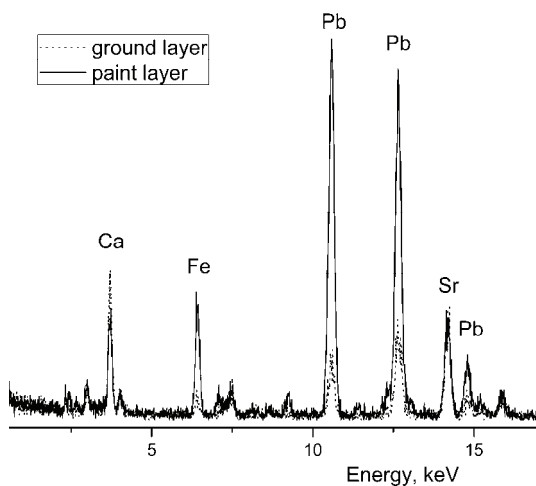


Fig. 4. EDXRF spectra of the ground layer and paint layer of sample A1.

In all the FTIR spectra, characteristic bands originating from CH_2 and CH_3 stretching vibrations appeared at 2925 and 2850 cm^{-1} , revealing the presence of organic matter¹⁵ that originates from a binder, but the particular compound could not be unambiguously determined based solely on this finding. Considering the detected pigments and style of the icon, most probably linseed oil was used.

In the cross section of sample A2, taken from the gilded area of the icon, several different layers could be seen (Fig. 2). The multilayered structure indicates that gilding was performed on several occasions.

There are two well-known gilding procedures: water gilding and oil gilding.^{5,16} Gold is usually applied in a form of thin leaves for decorative purposes on different materials. For water gilding, the ground layer was traditionally made of Red Earth pigment - Red Ochre (often called Red Bole). Application of gold on Red Ochre (composed of Fe_2O_3 , clay and silica) results in warmer colours.^{5,16} The red–orange ground layer could be seen on the cross section of sample A2 (Fig. 2). The EDXRF spectrum of the red–orange ground layer of sample A2 is shown in Fig. 5.

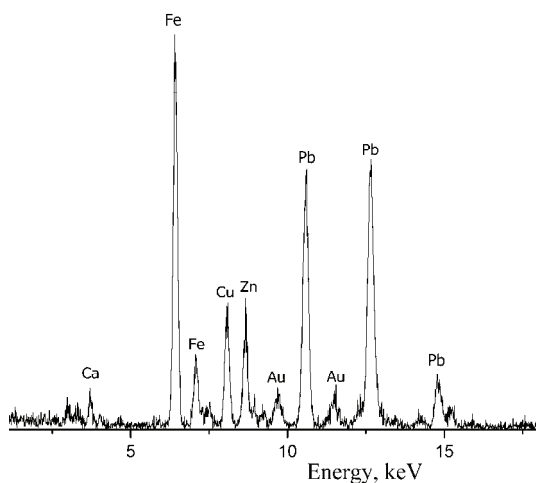


Fig. 5. EDXRF spectra of the ground layer of sample A2.

The high intensity of the Fe peaks in the EDXRF spectrum of the ground layer (Fig. 5) and the characteristic bands at 1107 and 1030 cm^{-1} in the FTIR spectrum of sample A2 (Fig. 3), originating from Si–O stretching vibrations of aluminosilicates,¹⁴ confirm the presence of the earth pigment ochre. In the case of ochres, the colouring agent is some non-clay pigment, *e.g.*, iron oxides.⁵ Depending on the iron oxide as well as on size of the grains, the ochres have different colours. In this particular case, careful examination of the optical micrograph (Fig. 2) revealed the presence of red and yellow pigment grains, which led to the conclusion that the Red Ochre was mixed with Yellow Ochre ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or FeOOH , clay and silica),¹⁷ often called Yellow Bole, for obtaining a particular visual effect. As can be seen in Fig. 5, the presence of Au was confirmed by EDXRF spectroscopy. The optical micrograph of sample A2 (Fig. 2) revealed the presence of three thin layers of gold. The first thin layer of gold was originally applied on a mixture of Red and Yellow Ochre. During previous restoration procedures, additional ground layer and gold layer were added twice on the same area.

EDXRF spectroscopy also showed the presence of Ca, Zn and Pb in this sample. The FTIR spectrum of sample A2 (Fig. 3) confirmed the presence of calcite by the presence of characteristic bands. However, a broad band at 1430 cm^{-1} attributed to vibrational mode of carbonate group $\nu(\text{CO}_3^{2-})$ could be the result of overlapping of signals originating from both calcite and Lead White. Moreover, the fluorescence of Zinc White was detected under UV light in the layer between the gold leaf applied on the mixture of Red and Yellow Bole and the next gold leaf. These findings indicate that the additional two ground layers were made of Lead White, Zinc White (ZnO) and calcite.

In addition, Cu was identified in the sample A2 by EDXRF spectroscopy. An alloy made of gold and copper is often used for gilding.¹⁶ Amount of gold in the alloy is usually higher than 70 %. The relative intensities of the Cu and Au signals did not correspond to the expected values in the case of a gold and copper alloy, showing a higher amount of Cu (Fig. 5). The optical micrographs revealed the presence of blue pigment grains in the top ground layer. Therefore, copper in the investigated sample could originate from an alloy with gold used for gilding as well as from a copper-based blue pigment in the top ground layer.

The EDXRF spectra of the surface layer and ground layer of sample A3 are shown in Fig. 6. Cu and Zn were detected in the surface layer of sample A3, but not Au. An alloy of Cu and Zn in which the amount of Cu is 80 % or higher is known as Schlagmetal. It has the visual effect of gold and is used for gilding. The relative intensities of the Cu and Zn peaks in the EDXRF spectrum confirmed that Schlagmetal was used for the surface gilding layer on the frame.

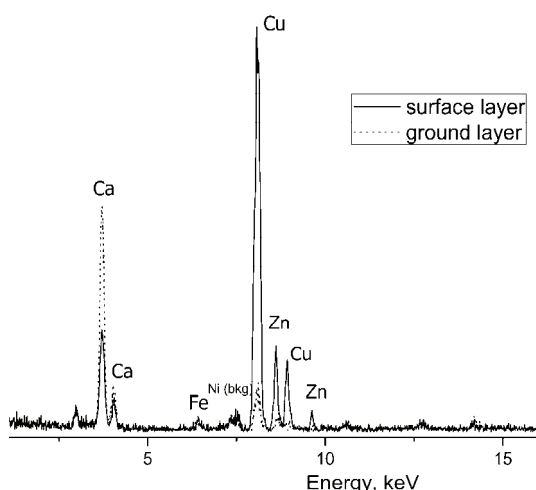


Fig. 6. EDXRF spectra of the ground layer and surface layer of sample A3; bkg – background signal.

On the cross section of sample A3 (Fig. 2), a yellow layer below the gilding could be seen. Iron present in sample A3 (Fig. 6) and the bands in the FTIR

spectrum at 1111 and 1030 cm^{-1} , originating from Si–O stretching vibrations (Fig. 3), indicate the presence of the Yellow Earth pigment – Yellow Ochre. The presence of calcite, identified in the FTIR spectrum of sample A3 (Fig. 3), indicated that a mixture of calcite and Yellow Bole was used as the ground layer for the gilding on the frame.

Icon B: “St. Petka”

Representative optical micrographs and fluorescence photographs under UV light of samples taken from the icon “St. Petka” are shown in Fig. 7.

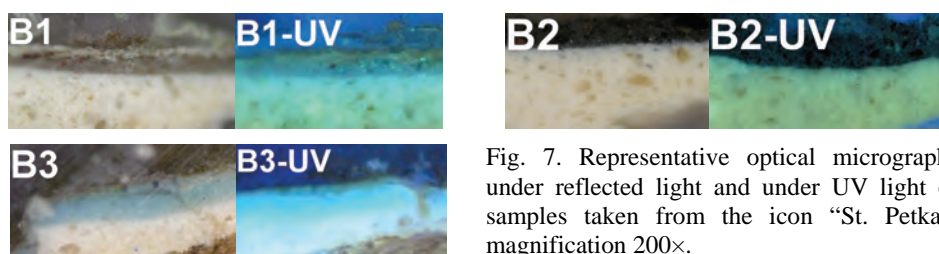


Fig. 7. Representative optical micrographs under reflected light and under UV light of samples taken from the icon “St. Petka”; magnification 200 \times .

The fluorescence photographs of the green B1 and blue B3 samples (Table I), presented in Fig. 7, show the intensive fluorescence of white pigment in the paint layer. The fluorescence was more intense for sample B3 compared to sample B1, Fig. 7, revealing that the blue paint layer of sample B3 contained a higher amount of white pigment than the green paint layer of sample B1.

EDXRF spectroscopy analysis showed for all three samples the presence of the same elements, regardless of the sample colour (see Table II). The EDXRF spectra of the paint layers of samples B1, B2 and B3 are shown in Fig. 8. The peak originating from Zn had the highest intensity in all three EDXRF spectra.

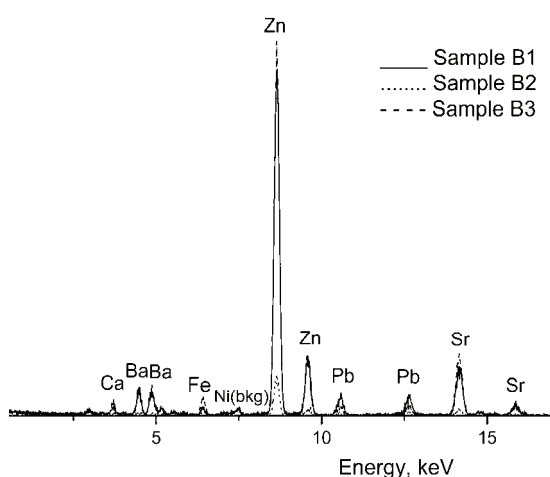


Fig. 8. EDXRF spectra of the paint layers of samples B1, B2 and B3; bkg – background signal.

The fluorescence detected under UV light in combination with the Zn identified in paint layer by EDXRF spectroscopy confirmed the use of Zinc White as the white pigment to achieve a particular hue. Application of ZnO as a white pigment started in the first half of the 19th century⁷ and by the end of the 19th century, it was considered the best quality white pigment.

The FTIR spectra of the investigated samples taken from the icon “St. Petka” are shown in Fig. 9. The bands at 1174, 1120, 1077, 643 and 608 cm⁻¹ in FTIR spectra of all three samples originated from barium sulphate (BaSO₄).¹⁸ This is in agreement with the Ba detected in the EDXRF spectra. The presence of Sr, identified by EDXRF spectroscopy, indicated that natural baryte ore was used for the ground layer.¹¹

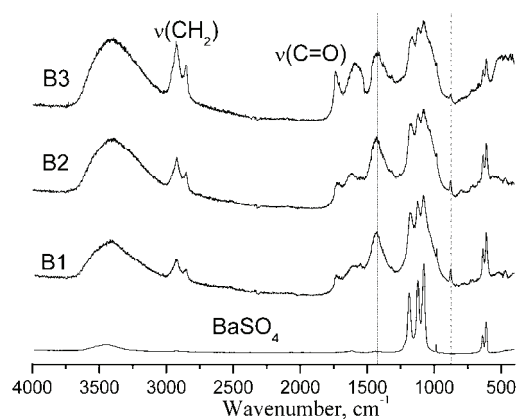


Fig. 9. FTIR spectra of samples taken from the icon “St. Petka” and the reference spectrum of barium sulphate; vertical lines represent the positions of the characteristic bands of calcite.

A broad, medium intensity band of $\nu(\text{CO}_3^{2-})$ was detected at 1430 cm⁻¹. Since Ca and Pb are present in all three samples, both calcite and Lead White could contribute to this band.

Ground layer appeared as a single, thick and consistent layer in all the investigated samples. As no fluorescence was detected in the ground layer, it can be concluded that ZnO was used as a pigment, while baryte, Lead White and calcite were used for the ground layer.

Iron detected in the paint layer of sample B1 was the only indication of which pigment was used for the green colour. Most probably it was the pigment Green Earth, the colour of which originates from the specific ratio of divalent and trivalent iron incorporated in the structure of the clay minerals glauconite and celadonite.^{5,7} FTIR bands characteristic for Si–O stretching vibrations, between 1200–900 cm⁻¹,¹⁹ were detected as a shoulder at about 990 cm⁻¹ probably due to overlapping with the bands of barium sulphate. In addition, the employed EDXRF experimental setup cannot analyse elements such as Si, Al, Na and Mg. However, green pigments, other than Green Earth, contain some of the following elements: Co, Cu or Cr, but none of them were detected in the sample B1.

In the case of sample B2 and B3, EDXRF and FTIR spectroscopic analyses did not give conclusive answers about the used pigments. For this reason, micro-Raman spectroscopic analysis was performed. For sample B2 blue pigments Prussian Blue and ultramarine ($\text{Na}_{8-10}[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_{2-4}$) were identified in the paint layer by characteristic Raman shifts,²⁰ as can be seen in Fig. 10.

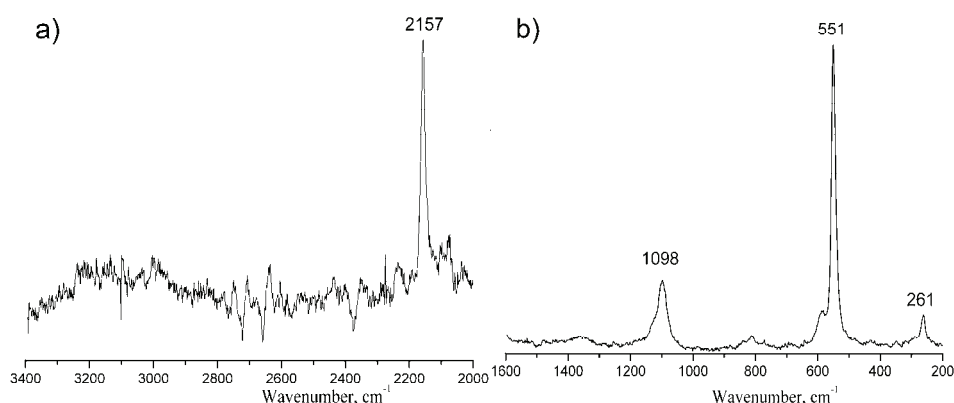


Fig. 10. Raman spectra of the blue pigments in the paint layer of sample B2: a) Prussian Blue and b) ultramarine.

Sample B3 showed intensive fluorescence during micro-Raman analysis and no definite answer about the used blue pigment was obtained. Considering presence of Fe detected in this sample by EDXRF spectroscopy, most probably Prussian Blue was used as the blue pigment.

In all FTIR spectra, characteristic bands originating from CH_2 and CH_3 stretching vibrations appeared at 2925 and 2850 cm^{-1} and carbonyl ($\text{C}=\text{O}$) stretching vibrations at 1740 cm^{-1} were present, confirming the use of linseed oil as binder.¹⁵

CONCLUSIONS

Two Serbian icons painted on canvas, “The Virgin and Child” and “St. Petka”, by unknown authors were investigated by optical microscopy, EDXRF, FTIR and micro-Raman spectroscopy. The following pigments were identified: Prussian Blue, ultramarine, Green Earth, iron oxides, Lead White and Zinc White. The binder on both icons was linseed oil. The ground layers were made of gypsum, Lead White, calcite and baryte. The gilded surface of the icon “The Virgin and Child” was made of gold, while the gilded surface on the frame of this icon was made of imitation of gold, *i.e.*, Schlagmetal, since EDXRF spectroscopy showed the presence of copper and zinc, while gold was not detected.

The materials identified as pigments, binders and ground layer in both investigated icons were widely in use during the 19th century and at the beginning of

the 20th century. This finding confirms the initial assumption of the ages of these icon made by art historians and restorers.

Acknowledgments. The authors gratefully acknowledge the financial support provided by Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of Project No. 177021. The authors would like to thank Dr Danica Bajuk-Bogdanović for performing the micro-Raman spectroscopy experiments and the art historian Mrs. Radmila Petronijević, curator of the Museum of the Serbian Orthodox Church in Belgrade, for useful discussions.

ИЗВОД

СПЕКТРОСКОПСКО ИСПИТИВАЊЕ ДВЕ СРПСКЕ ИКОНЕ СЛИКАНЕ НА ПЛАТНУ

ЉИЉАНА ДАМЈАНОВИЋ¹, ОЛГИЦА МАРЈАНОВИЋ¹, МИЛИЦА МАРИЋ СТОЈАНОВИЋ², ВЕЛИБОР АНДРИЋ³
и УБАВКА МИОЧ¹

¹Универзитет у Београду – Факултет за физичку хемију, Сивуленски брџи 12–16, 11000 Београд,

²Народни музеј, Три Републике 1а, 11000 Београд и ³Универзитет у Београду – Институт за нуклеарне науке “Винча”, б. бр. 522, 11000 Београд

Мултианалитичко испитивање две српске иконе сликане на платну (Богородица са Христом и Света Петка) које су радови непознатих аутора извршено је са циљем да се идентификују материјали коришћени као пигменти, везива и подлога. Испитиване иконе су власништво Музеја Српске православне цркве у Београду. Узорци, узети са различитих делова икона, су анализирани: оптичком микроскопијом, енергетски дисперзивном рендгенском флуоресцентном анализом, инфрацрвеном спектроскопијом са Фурије трансформацијом и микро-Раманском спектроскопијом. Идентификовани су следећи пигменти: пруско плаво, ултрамарин, зелена земља, оксиди гвожђа, олово бело и цинк бело. Ланено уље је коришћено као везиво. Материјали коришћени за подлогу су гипс, калцит, барит и олово бело. Позлаћене површине иконе Богородица са Христом су рађене од злата, док је за позлату рама исте иконе коришћена имитација злата тзв. шлаг-метал јер су EDXRF спектроскопијом идентификовани бакар и цинк, док злато није детектовано. Стил израде икона има карактеристике западно-европског барока. Идентификовани пигменти и везиво одговарају онима који су били у широкој употреби у XIX веку и почетком XX века.

(Примљено 22 јула, ревидирано 6. октобра, прихваћено 8. октобра 2014)

REFERENCES

1. F. Casadio, L. Toniolo, *J. Cult. Herit.* **2** (2001) 71
2. W. S. Taft Jr., J. W. Mayer, *The Science of Paintings*, Springer, New York, 2000
3. S. Daniilia, D. Bikiaris, L. Burgio, P. Gavala, R. J. H. Clark, Y. Chrysoulakis, *J. Raman Spectrosc.* **33** (2002) 807
4. M. T. Doménech-Carbó, M. J. Casas-Catalán, A. Doménech-Carbó, R. Mateo-Castro, J. V. Gimeno-Adelantado, F. Bosch-Reig, *Fresenius J. Anal. Chem.* **369** (2001) 571
5. D. Hradil, T. Grygar, J. Hradilova, P. Bezdička, *Appl. Clay Sci.* **22** (2003) 223
6. N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments*, Butterworth-Heinemann as an imprint of Elsevier, Waltham, MA, 2008
7. R. J. H. Clark, *C. R. Chim.* **5** (2002) 7
8. S. Sotiropoulou, S. Daniilia, *Acc. Chem. Res.* **43** (2010) 877

9. M. Ortega-Avilés, P. Vandenabeele, D. Tenorio, G. Murillo, M. Jiménez-Reyes, N. Gutiérrez, *Anal. Chim. Acta* **550** (2005) 164
10. E. Pavlidou, M. Arapi, T. Zorba, M. Anastasiou, N. Civici, F. Stamati, K. M. Paraskevopoulos, *Appl. Phys., A* **83** (2006) 709
11. D. Korolija-Crkvenjakov, V. Andrić, M. Marić-Stojanović, M. Gajić-Kvašček, J. Gulan, N. Marković, *The Iconostasis of the Krušedol Monastery Church*, The Gallery of Matica srpska, Novi Sad and Vinča Institute of Nuclear Sciences, Belgrade, 2012
12. I. C. A. Sandu, S. Bracci, I. Sandu, M. Lobefaro, *Micros. Res. Tech.* **72** (2009) 755
13. L. Burgio, R. J. H. Clark, K. Theodoraki, *Spectrochim. Acta, A* **59** (2003) 2371
14. S. Akyuz, T. Akyuz, G. Emre, A. Gules, S. Basaran, *Spectrochim. Acta, A* **89** (2012) 74
15. M. R. Derrick, D. Stulik, J. M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles, CA, 1999
16. I. Crina Anca Sandu, M. Helena de Sá, M. Costa Pereira, *Surf. Interface Anal.* **43** (2011) 1134
17. D. Bikiaris, S. Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, A. P. Moutsatsou, *Spectrochim. Acta, A* **56** (1999) 3
18. R. A. Nyquist, R. O. Kagel, *Infrared spectra of inorganic compounds*, Academic Press, New York, 1971
19. M. F. La Russa, S. Ruffolo, C. M. Belifore, V. Comite, A. Casoli, M. Berzoli, G. Nava, *Appl. Phys., A* **144** (2014) 733
20. I. M. Bell, R. J. H. Clark, P. J. Gibbs, *Spectrochim. Acta, A* **53** (1993) 2159.