Differentiation of ancient blue pigments based on three-band NIR composite images

Marina Đurić[1] , Zoran Velikić[2] , Tatjana Tripković[4],
Tijana Lazić[5] , Irena Živković[5] and Vanja Jovanović [3]

[1] Artforensics, Belgrade, Serbia
[2] Institute of Physics. Belgrade, Serbia
[3] Artlab2018, Ruma, Serbia
[4] Institute for Protection of Cultural Heritage, Belgrade, Serbia
[5] Faculty of Applied Art, Belgrade, Serbia
marina@ipb.ac.rs

Introduction

The “Virgin Mary with Christ on the throne - The prophets foretold you” was made in the traditional style of the beginning of the 18th century and is the work of an unknown painter of the Thessaloniki painting workshop.

The project Conservation and Restoration of Icons from the Collection of the Museum of Srem includes nine icons. The project represented an exceptional opportunity to perform basic multispectral analyses on all icons, and the icon representing the Virgin Mary with Christ (71 x 96 cm) was singled out as a representative example, not only because of its exceptional beauty, which is indisputable, but above all because of the devastated condition in which it was found.

After stabilization of the paint layer, when the complete paint layer became visible and accessible, multispectral imaging was performed.

Fig.1.Icon representing Virgin Mary with Christ

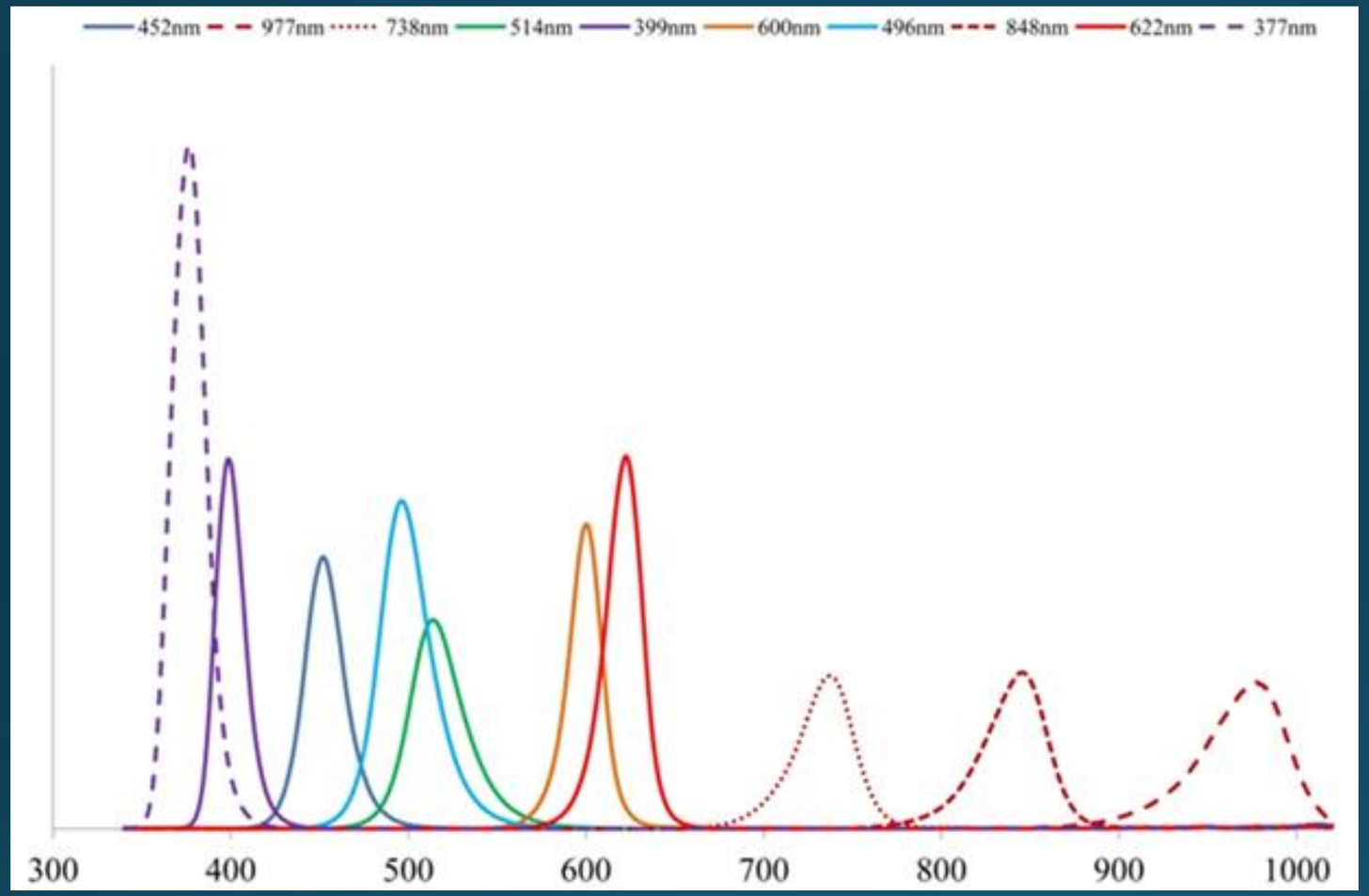


Fig. 2 Spectra of emission of LED lightsource

Multispectral imaging was performed at 10 wavelengths with a modified Cannon M100 camera.

Handmade LED light source was used and their spectral characteristics are described on Fig.2.

In addition to already established applications, these techniques provide the possibility of obtaining more detailed information about the pigments using a composite image which are obtained by combining monochrome photographs in the NIR region and transposing them into the visible region. Thus, for us, invisible characteristics and specificities become clearly visible and enable, in some cases, precise identification of pigments as well as insight into the techniques used [2]

Methods

All monochrome photos were processed using the MATLAB program in order to obtain equal level of brightness and contrast along with use of white standard and black standard through all channels. Further processing of the photographs and their spatial alignment was done using Adobe Photoshop and ImageJ.

In NIR region were captured photographs at 3 wavelengths: 730nm, 840nm and 970nm, presented on Fig.3.

Fig.3 Photograph at **NIR** a) 730nm b) 840nm c) 970nm

Composite image is obtained by transposing three NIR channels, 970nm 840nm, 730nm into RGB, respectively.

Transposing NIR channel to RGB, differences among pigments which appear similar in visible domain are become more noticeable, as underdrawings too, regarding that the wavelength of the radiation penetrates deeper layers.

In the presented NIR - RGB composite image in Fig.4, underdrawings can be seen in the lower part of the icon, showing the under mantle with pleats,

Fig.4 NIR-RGB composite image

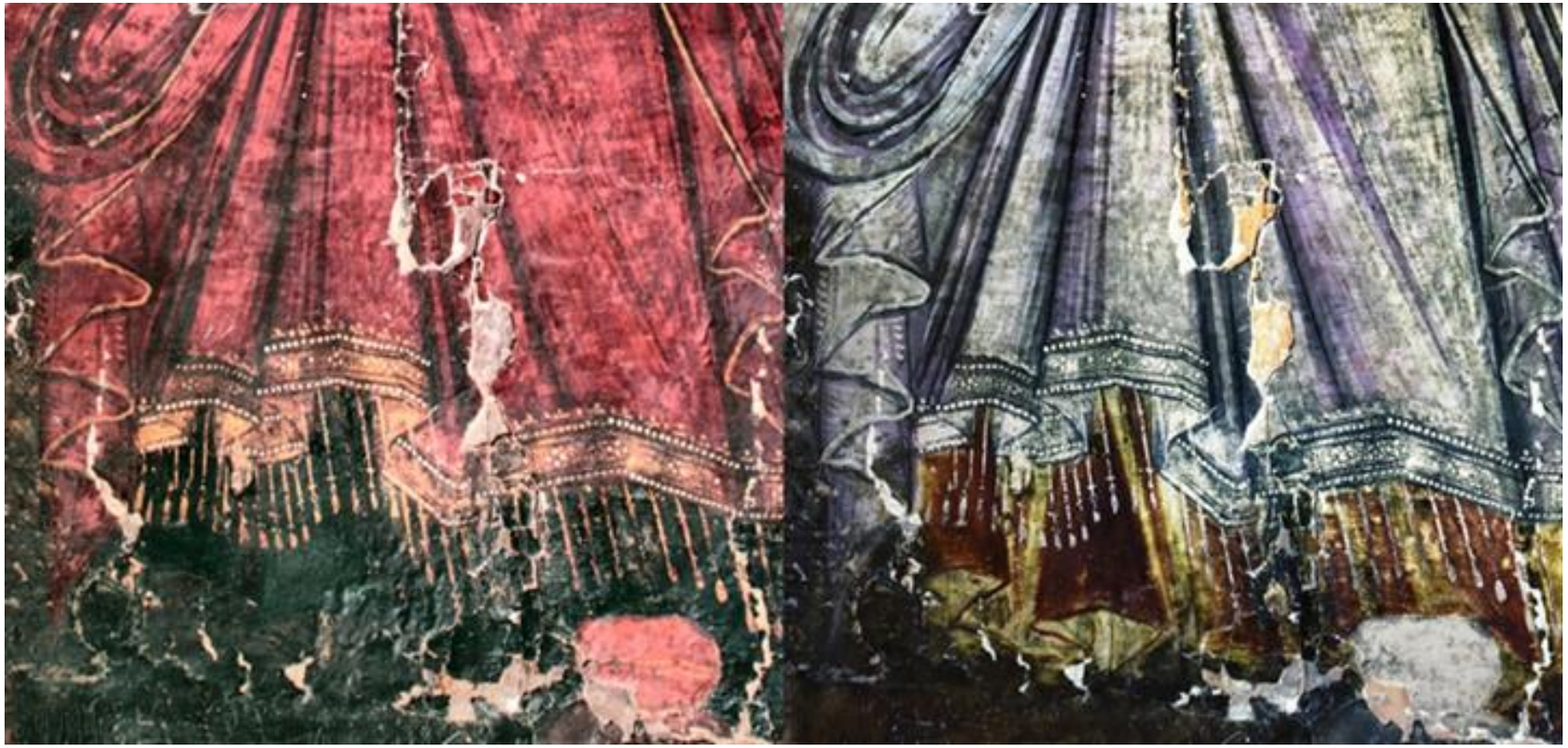


Fig.5 Detail of VIS and NIR-RGB composite image

Detail from lower part of icon present on VIS and NIR-RGB composite photographs (Fig.5) discover existence of under mantle painted with two different pigments. That is seen in the composite image in yellow and brown. Considering that the painting of the icon representing the Virgin Mary is canonized, and that the lower mantle is always painted blue, we can assume that two different blue pigments were used. The composite image also reveals two different red pigments in the drawing of the upper mantle showing in white and purple color.

Regarding the multispectral images of samples of historical pigments (Kremer Pigments) and their NIR to RGB composite images obtained in the same way as composite image of icon (Fig.6), and compare to reflectance spectra especially blue pigments [6], we could conclude that the pleats from under mantle was painted with azurite pigment, which appear in brown color on NIR-RGB composite image, and indigo for inner area of under mantle, which appear in light yellow brownish color on NIR-RGB composite image

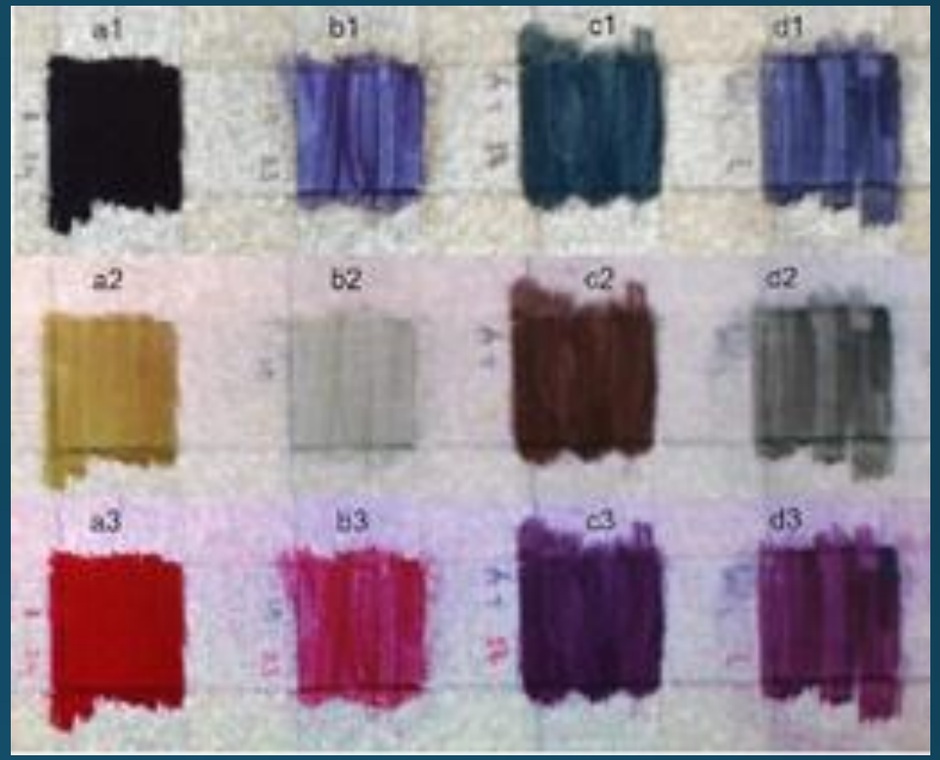


Fig.7 Samples of blue pigments:

a-indigo; **b**- cobalt blue; **c**-azurite; **d**- smalt

1-VIS; **2**-NIR-RGB; **3**-FC

This conclusion was also proven by examining the traditionally composite false color image (FC) obtained by a different combination of channels. Usually, FC are trichromatic digital images obtained using an infrared, red and green bands.

In this image the area of indigo pigment is red, and area of azurite is dark blue violet, which is consistent with the corresponding false color images of the samples.

Fig.6 False color (FC)

To confirm the assumptions about the pigments on this icon, the XRF analysis was done in selected points presented on Fig 7.

A Thermo Scientific Niton XL3t analyser was used for non-destructive elemental analysis directly on the analysed painting surface

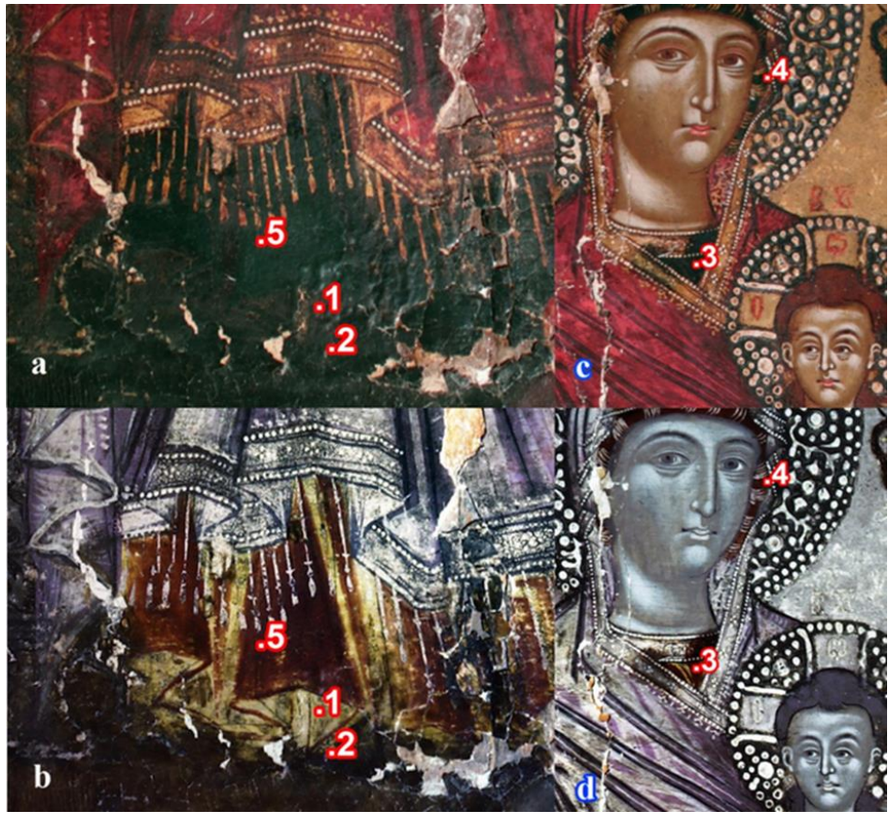
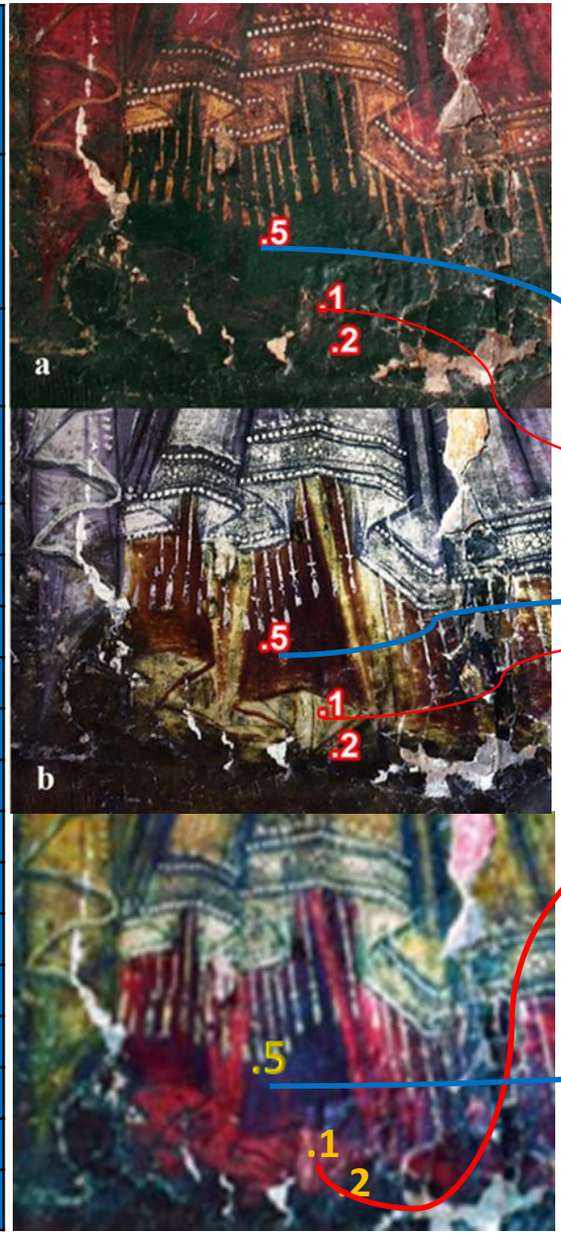


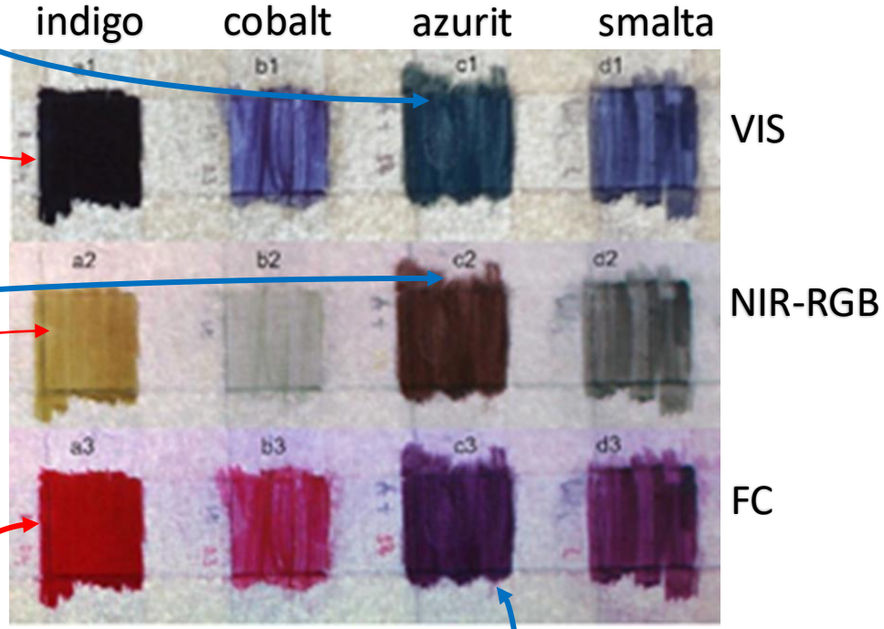
Fig.7 Details of icon with selected points: a) VIS b) NIR-RGB c) VIS d) NIR-RGB

Position No	1	2	3	4	5
Reading No	1099	1100	1101	1106	1108
Units	%	%	%	%	%
Bal	81,65	82,27	80,98	81,56	81,95
Si	6,45	5,99	6,71	4,55	5,35
Ca	5,50	5,30	3,56	2,91	2,88
S	3,41	2,86	2,08	3,14	2,04
Cu	0,29	0,79	3,56	4,17	4,47
As	0,59	0,12	0,36	0,28	0,26
Pb	0,34	0,64	1,92	1,17	1,51
Cl	0,59	1,20	0,19	0,24	0,73
K	0,36	0,16	0,55	0,23	0,29
P	0,17	0,04	0,08	0,64	0,12
Al	0,14	0,19	0,10	0,20	0,08
Fe	0,10	0,22	0,17	0,86	0,16
Ti	0,05	0,05	0,03	0,01	0,02
Zn	0,05	0,20	0,03	0,02	0,03
Hg	0,01	0,00	0,02	0,02	0,01

Table 1. XRF analysis result

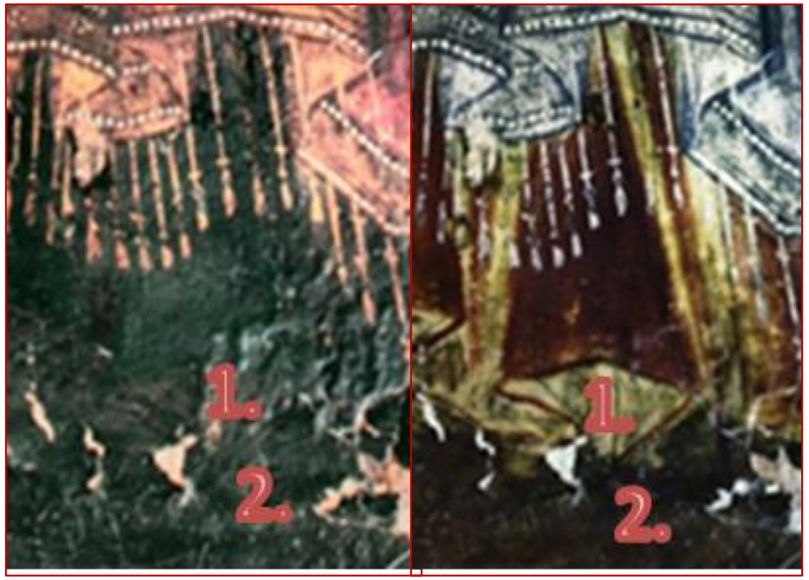
Position No	1	2	5
Reading No	1099	1100	1108
Units	%	%	%
Bal	81,65	82,27	81,95
Si	6,45	5,99	5,35
Ca	5,50	5,30	2,88
S	3,41	2,86	2,04
Cu	0,29	0,79	4,47
As	0,59	0,12	0,26
Pb	0,34	0,64	1,51
Cl	0,59	1,20	0,73
K	0,36	0,16	0,29
P	0,17	0,04	0,12
Al	0,14	0,19	0,08
Fe	0,10	0,22	0,16
Ti	0,05	0,05	0,02
Zn	0,05	0,20	0,03
Hg	0,01	0,00	0,01





Analyses

- Regarding the concentration of Cu in point **3, 4, 5** we could confirm that used pigment was **azurite**, and with addition of lead white for paint area of light blue color.
- The use of indigo could not be directly confirmed by this analysis, but neither in points **1 nor 2** were key elements detected for the identification of other blue pigments that could have been used in the early 18th century. The only blue pigment that could be used in that time and that would appear as yellow in a NIR-RGB composite image is **indigo.**



- Although the analysis showed the same results in points 1 and 2, based on the images in VIS and NIR-RGB we can conclude that in the very bottom area, in point **2**, a different pigment was used, or indigo was in the layer below. That part was the subject of earlier restorations and retouches, which made a more precise analysis impossible.

- Beside this, the pigments with which the upper mantle was painted were subject of previous XRF analyses [1], and it has proven two red pigments: cinnabar and earth red pigment, which is also in accordance to NIR -RGB composite image.

Conclusion

The optical properties of materials are unique and represent a reliable factor in the identification of pigments. This research has shown the potential of using imaging techniques and spectroscopic techniques in the analysis of easel paintings. By further improving their application, it is possible to obtain more and more information in a simple and economically accessible way.

Composite photographs obtained by transposing monochromatic photographs at 3 wavelengths in the NIR region into the visible region, NIR to RGB composite, provide the opportunity to “see” in the NIR, i.e. to make spectral specificities from the NIR region more clearly visible. This has proven successful especially for blue and red pigments. In addition, the existence of underdrawings and layers below the surface can be more clearly seen. These NIR -RGB composite images are a more efficient tool than the traditionally used false color composite images, which use mostly the integral NIR region in combination with the VIS and thus lose some information, especially at wavelengths above 900nm, where most cameras are less sensitive.

It is necessary to examine and classify appropriate composite images in accordance with the spectroscopic characteristics for selection and rough identification of pigments.

References

1.Marko Božović, Vanja Jovanović, Svetlana Subašić Conservation of a devastated wooden icon from 18 century - the importance of digital radiography when choosing and performing treatment **2025** Građa 37 187-202

2.Miquel Angel Herrero-Cortell, Marta Raïch, Paola Artoni, Isidro Puig Multi-band technical imaging in the research of the execution of paintings. The case study of the portrait of Carlos IV, by Francisco de Goya 2018 Ge-conservacion 1(14):5-15

3.Alice Dal Fovoa, Sara Mattanaa, Alessandra Ramat, Patrizia Riitano , Riccardo Cicchi, Raffaella Fontanaa Insights into the stratigraphy and palette of a painting by Pietro Lorenzetti through non-invasive methods **2023** Journal of Cultural Heritage 61, 91-99

4.Nikolaidou, N.V.; Asvestas, A.; Kaminari, A.A.; Panou, T.; Sampatakos, A.; Anagnostopoulos, D.F.; Alexopoulou, A.G.; Mastrotheodoros, G.P. Seeking the Unseen: A Multimodal Non-Invasive Investigation of a Post-Byzantine Overpainted Icon. Heritage **2025**, 8, 377. https://doi.org/10.3390/heritage8090377

5.Gajić-Kvaščev, M.; Klisurić, O.; Andrić, V.; Ridolfi, S.; Nikolić, O.; Pavlović, V.; Korolija Crkvenjakov, D. Anatomy of the Painting: The Study of the Serbian Orthodox 2.4. Icon from the Turn of the Seventeenth to the Eighteenth Century. Coatings **2024**, 14, 854. doi.org/10.3390/coatings14070854

6.Hayem-Ghez, A., Ravaud, E., Boust, C., Bastian, G., Menu, M., and Brodie-Linder, N.: Characterizing pigments with hyperspectral imaging variable false-color composites 2015, Applied Physics A: Materials Science doi:10.1007/s00339-015-9458-8

7.Amura, A.; Aldini, A.;Pagnotta, S.; Salerno, E.; Tonazzini, A.; Triolo, P. Analysis of Diagnostic Images of Artworks and Feature Extraction: Design of a Methodology. J. Imaging **2021**, 7, 53. https://doi.org/10.3390/jimaging7030053

8.Delaney, J. K., Walmsley, E., et al.,"Multispectral imaging ofpaintings in the infrared to detect and map blue pigments",Sackler NAS ColloquiumScientific examin ation of Art: Modern techniques in conservation and analysis; Proceedings of theNational Academy of sciences (2005)

9.Delaney, J. K., Zeibel, J. G., et al., "Visible and infrared reflectance imaging spectroscopy of paintings: pigment mapping and improved infrared reflectography", SPIE (2009)

10.Louisa M. Smieska • Ruth Mullett • Laurent Ferri • Arthur R. Woll
Trace elements in natural azurite pigments found in illuminated manuscript leaves investigated by synchrotron x-ray fluorescence and diffraction mapping Appl. Phys. A (2017) 123:484 DOI 10.1007/s00339-017-1093-0

11.Aguilar-Téllez, D.M., Ruvalcaba-Sil, J.L., Claes, P. et al. False Color and Infrared Imaging for the Identification of Pigments in Paintings. MRS Online Proceedings Library 1618, 3–15 (2014). https://doi.org/10.1557/opl.2014.451

Thank you for attention!