The contribution of Micro-Raman and FTIR spectroscopy in art history study of wall painting from the 16th century church in Republic of Macedonia

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INTRODUCTION

We report here the preliminary study towards the characterization of the traditional painting technique and materials used in the 16th century church "St. Nikola"- Monastery of Toplica in Republic of Macedonia. According to the art historians the largest part of the painting in this church has been created during the first half of 16th century, but there is also an assumption that a part of the lower zone (area marked on Fig.1) could date from the end of 14th century. The results of this analysis are to be implemented in the study of the artwork history, author attribution and problems related to the conservation restoration issues.

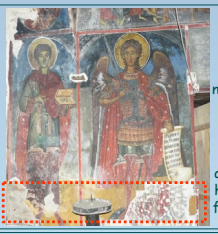


Fig. 1. Wall painting in the Western wall – nave dating from 16th century. Marked area indicates older painting, which according to art historians dates from 14 century.

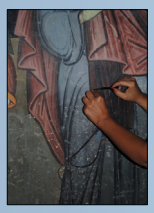
EKSPERIMENTAL

The main aim of these analyses was identification of the pigments used in the wall painting. For that purpose, total of 38 samples of pictorial layers from different murals were collected to be analyzed. The first employed technique in this study was optical microscopy which provided information about the morphology of the pigment's grains, homogeneity, optical characteristics and stratigraphy of pictorial layers. The characterisation of pigments was performed by use of micro-Raman spectroscopy and additionally by FTIR spectroscopy.

METHODOLOGY

Sampling

The samples were taken either by gently rubbing the color from the painting surface or by detaching a small piece of the wall painting in order to prepare a cross sections.



Preparing of cross sections

Cross sections of the samples were prepared by embedding selected small fragments in poly ester resin creating 1×1×1 cm modules.
In order to produce smooth surface of the cross sections all samples were polished by abrasive papers (2400 grits).
The sectioned samples were used for optical microscopy and micro-Raman measurements.

Optical microscopy

The cross sections were observed by optical microscopy using Universal micro-scope Axiplan 2000 Zeiss with magnification up to 100x, under reflection light.

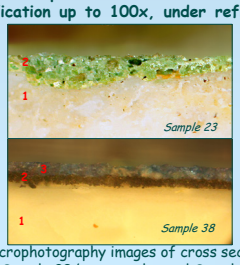


Fig.2 Microphotography images of cross sectioned samples: Sample 23/ green color and Sample 38/ blue color. Legend: 1- ground; 2, 3- pictorial layer.

Micro - Raman spectroscopy

The measurements were performed (in 100-1600 cm^{-1} range) with LabRam 300 (Horiba Jobin-Yvon) micro-Raman spectrometer equipped with two lasers: He-Ne laser operating at 633 nm (with 6 mW power on the sample) and doubled frequency Nd:YAG laser operating at 532 nm (with 4 mW power on the sample). Olympus MPlanN microscope with objectives LWD50x/10.6 mm was used for observation and analysis. All spectra were baseline corrected and filtered if needed with LabSpec software

Infrared spectroscopy

The FTIR measurement were performed using IRPrestige-21 Shimadzu FTIR spectrometer (in 400–4000 cm^{-1} range) with spectral resolution of 4 cm^{-1}. The spectra were recorded in transmittance mode with 45 scans. The technique of KBr pellets was used. For spectra manipulation IRSolution software was used.

RESULTS

Micro-Raman specroscopy

All pigments were identified according to their reference Raman spectra (dotted lines in Fig. 3) using pigment library database and by using characteristic Raman bands for the corresponding pigments.

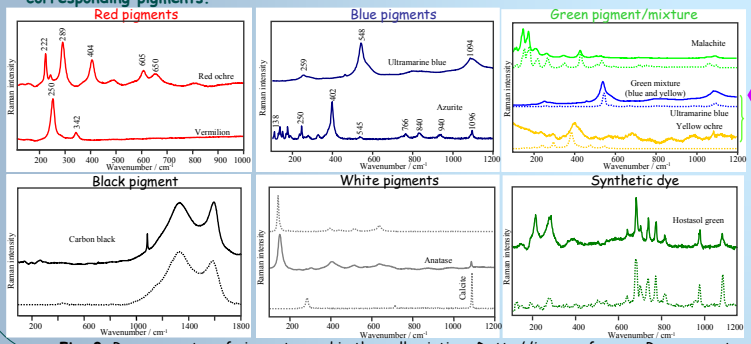
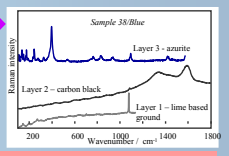


Fig. 3. Raman spectra of pigments used in the wall painting. *Dotted lines* – reference Raman spectra.

Two major points could be highlighted:

(1) Micro-Raman technique enables determination of mixture of pigments in individual layer. For *Sample 23*, the Raman spectra confirmed that the mixture of pigments: ultramarine blue and yellow ochre was used for producing green colour (see Fig.2).

(2) Characterization of each micro-metric layer highlighting the stratigraphy composition of the wall paintings. For *Sample 38* lime based ground was identified in layer 1, carbon black in layer 2 and azurite in layer 3 (see Fig. 2).



Results from the Raman analysis of pigments in the wall painting in the church "St. Nikola" suggest:

- The original artistic pallet is composed of traditional pigments, dating before 18th century, such as yellow/red ochre, vermilion, ultramarine blue, azurite, malachite, calcite and carbon black.
- The pigments were used mainly as pure/single pigments, but also in combination of pigments, producing the certain colors, specially the green ones.
- The white pigment, anatase and the synthetic dye hostasol green indicates that some restoration interventions have been performed, since they date from the 20th century.

Inrared spectroscopy

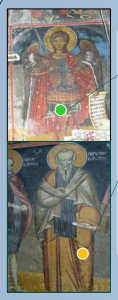
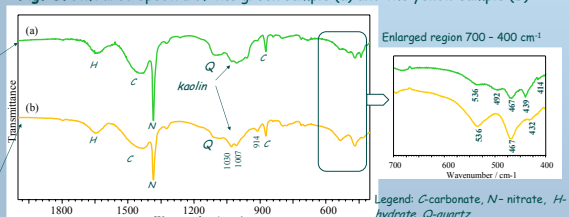


Fig. 4. Samples taken from the wall painting in the Western wall-nave (the green) and Nothern chapel (the yellow)

Fig. 5. Infrared spectra of the green sample (a) and the yellow sample (b)



Legend: C-carbonate, N- nitrate, H-hydrate, Q-quartz.

- For the yellow color: The peaks at 1030 (Si-O-Si), 1007 (Si-O-Al), 914 (Al-O-H), 536 (Si-O-Al) and 467 (Si-O) indicate the presence of kaolin and thus natural yellow earths ochre is probably applied.
- For the green color: The IR spectra confirm the use of yellow ochre in the green color, as already found in the Raman spectra.
- For salt efflorescence: The IR spectra indicates the presence nitrates and carbonates. The later may be due to the lime plaster.

CONCLUSIONS

- The optical microscopy of most of the samples revealed single pictorial surfaces, although in some samples (Northern wall – nave, *sample 38*) two pictorial layers were detected indicating re-painting.
- Micro-Raman spectroscopy demonstrated invaluable contribution to the unambiguous characterization of the pigments (Table 1), allowing examination of powdered form of the paint specimens, but also layer by layer, analyzing the pictorial sequences with the thickness of few microns (Fig. 2).
- FTIR confirmed that natural pigment yellow ochre was used, but also enabled determination of the composition of the salt efflorescence.
- The identified pigments suggest that the wall painting in the church "St. Nikola" is performed in the same period, most probably during the 16th century.
- Some of the identified materials indicate that the restoration intervention in some regions (Northern wall in the nave, Eastern wall in the narthex and North Chapel) was carried out in the past, since the synthetic materials were detected. In the Northern wall of the nave azurite (Table 1) was also detected as a re-paint layer.

Table 1. Pigments identified using micro- Raman spectroscopy.

	Western wall - nave		Northern wall nave	Eastern wall narthex	North chapel
	Lower painting	Upper painting			
Red	Vermilion Red ochre	Vermilion Red ochre	n.a.	Vermilion Red ochre	Red ochre
Yellow	Yellow ochra	Yellow ochra	n.a.	Yellow ochra	Yellow ochre
Blue	Ultramarine blue	Ultramarine blue	Azurite	Ultramarine blue	Ultramarine blue
Green	n.i.	Malahite	Mixtire: Ultramarine blue and Yellow ochra Hostasol green (20th)	Malahite	Mixtire: Ultramarine blue and Yellow ochre
White	Calcite	Calcite	n.a.	Calcite Anatase (20c)	Calcite Anatase (20c)
Black	Carbon black	Carbon black	Carbon black	Carbon black	Carbon black

n. i. - not identified; n. a. -not analyzed

References

[1] Spectral ID (3.02), Thermo Galactic (Horiba Jobin-Yvon Database of Raman Spectra).
[2] I. M. Bell, *et al., Spectrochim. Acta A*, **1997,** *53*, 2159;
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[4] D. Bikiaris, *et al., Spectrochim. Acta A*, **1999**, *56*, 3.