Micro-Raman Analysis of two 17th century Old-Slavonic Manuscripts

Irena Nastova[1], Orhideja Grupče[1], Biljana Minčeva-Šukarova[1], Violeta Martinovska[2] and Zorica Jakovlevska-Spirovska[2]

[1]Institute of Chemistry, Ss Cyril & Methodius University, PO Box 162, Skopje, Republic of Macedonia
[2]National and University Library "St. Kliment Ohridski", Bul. Goce Delčev, 6, 1000 Skopje, Republic of Macedonia

INTRODUCTION

Pigments and inks in two manuscripts, *Struga Four Gospels* (17th century) and *Zrze Four Gospels* (16th/17th century) kept in the National and University Library "Sv. Kliment Ohridski" in Skopje, Republic of Macedonia, were analyzed in this study. The manuscripts are written on paper, in old-Slavonic language, with old Cyrillic alphabet. Both books gospels begin with the ornament, followed by the gilded floral letter.

Struga Four Gospels

Zrze Four Gospels

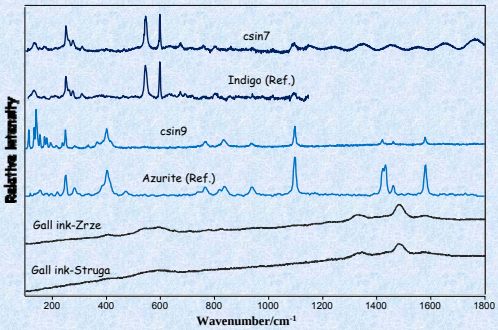
EXPERIMENTAL

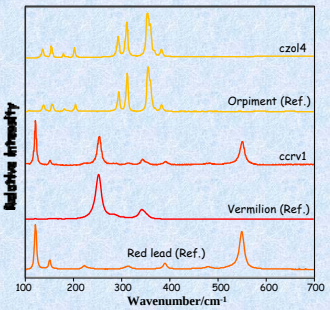
Raman spectroscopy: Micro-Raman spectrometer LabRam 300 (Horiba Jobin-Yvon) equipped with a He-Ne laser (632.8 nm) operating with 6 mW at the sample was used for all *in situ* analysis. The spectral resolution was 3-4 cm^{-1}. To avoid any damage to the manuscript, laser power was attenuated (D=0.3, D=0.6, D=1, D=2). The laser diameter on the sample was between 1 and 2 μm.

SEM-EDX: Pigments were examined in field emission scanning electron microscopy (FE-SEM-Zeiss Supra 50VP) attached with Energy Dispersive X-ray Spectrometer (EDX-Oxford INCA). The analysis was carried out on the surfaces without coating.

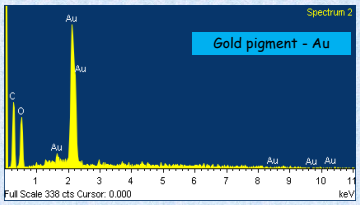
RESULTS

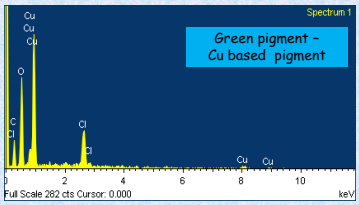
Raman spectra of few identified pigments/inks in the two manuscripts





SEM-EDX results for gold and green pigments from Struga Four Gospels





CONCLUSION

➢ ***Ornaments***: Zrze book color palette consists of red, blue, brown and gold paint while palette in Struga manuscript is richer with additional green and yellow paints.
- The differences were observed in the used red pigment. In Struga book only vermilion (HgS) was used to achieve the red color, while in Zrze book mixture of vermilion and red lead (Pb_3O_4) was used.
-The presence of pure gold applied for gilding in both book was confirmed using SEM-EDX. Gold was applied above orpiment used as under-layer (glue) in Struga book while in Zrze book no under-layer was detected; it was applied directly on the paper.
➢ ***Inks***: The text in Zrze book is written in four colored inks: black-brown, blue, red and brown-purple inks while in Struga book the inks are black, blue and red. Gall ink was identified as black-brown ink in both books, while azurite and indigo was used as blue ink. As in the ornaments, in Struga book, vermilion was used as red ink, while in Zrze book the mixture of vermilion and red lead was used. The fourth ink in Zrze book, brown-purple one, did not give Raman spectrum and its identification is still in progress.
➢ Although both manuscripts are roughly from the same period and use similar pigments, the analysis showed that the scribes have made personal preferences for the colors in the illuminations and text.

Pigments and inks identified in *Struga* and *Zrze books*

Color	*Struga Four Gospels* (17th century)	*Zrze Four Gospels* (16th-17th century)
Yellow	Orpiment	n/a
Red	Vermilion	Vermilion+Red Lead
Blue	Indigo, Azurite	Indigo, Azurite
Green	Organo-Cu complex	n/a
Brown	Gall ink	Vermilion+Red Lead+?
Gold	Gold	Gold
Inks		
Black/ Brown	Gall ink	Gall ink
Red	Vermilion	Vermilion+Red lead
Blue	Indigo, Azurite	Indigo, Azurite
Brown purple	n/a	?

XXII Congress of Chemists and Technologists of Macedonia, Ohrid, 5th - 8th September 2012