Raman Spectroscopy of Medieval Manuscripts in Bulgarian National Library – Preliminary Results

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Abstract. This paper presents the initial stages for preparation of a digital catalog (library), including analytical information gathered by using portable Raman spectroscopy instrument for the study of medieval parchment manuscripts from the repository of the Bulgarian National Library" Saints Cyril and Methodius".

Keywords: Raman Spectroscopy, Parchment, Manuscript, Palimpsest, XRF.

1 Introduction

Raman spectroscopy is a powerful tool in the analysis and conservation of written heritage. It offers a non-invasive and non-destructive method for the analysis of materials used in historical documents and codices, which is essential for their proper conservation and scientific study. The characteristic spectral bands specific to the molecular or crystal structure of the material can be used to create a database that allows for the comparative study of various aspects based on quantitative and qualitative identification. The analytical data obtained provide information about both the parchment itself and the inks and pigments used. It provides information about the structure of organic compounds or inorganic substances with a crystal lattice, which allows for their qualitative identification. Combining the method with X-ray fluorescence (XRF) or other non-invasive techniques allows for additional determination of the concentrations of chemical elements in the studied material (Rigante et al., 2025). This is particularly useful for identifying numerous inorganic pigments used in colored inks or for coloring miniatures in medieval manuscripts. The study of medieval written monuments using Raman spectroscopy is carried out in several directions. These are mainly analyses related to the type and structure of inks and pigments (Nastova et al., 2011, 2015; Cappa et al., 2019; Retko et al., 2024), as well as the method of making the parchment or the degree of its damage as a result of the influence of various environmental factors (Schütz et al., 2013; Malea et al., 2024).

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Material analysis with Raman spectroscopy, on the one hand, allows the selection of the most appropriate methodology for the restoration and conservation of the manuscript, and on the other, provides valuable information which helps to determine the written monument's dating and geographical region of origin and use. The possibility of applying the Raman method *in situ* is also important for the study of cultural monuments, and has several advantages over the laboratory study: 1) valuable manuscripts are examined on site - without disturbing their usual storage environment; 2) the measurement of parameters is performed non-invasively and does not interfere with the integrity of the manuscript; 3) the parameters are taken within seconds, which allows particularly fragile and valuable monuments to be examined within a very short timespan; 4) the mobile Raman instrument allows for the collection of data from a number of manuscripts in one session, and compile a database for comparative research.

Earlier material analysis *in situ* of manuscripts in Bulgaria is carried out in 2011 and 2017, mainly within the framework of the project "The Enigma of the Sinaitic Glagolitic Tradition", funded by the Austrian Science Fund (Brenner et al., 2019) and involving a team of experts from the interuniversity Center of Image and Material Analysis (CIMA) – Vienna. Previous experience of manuscript material analysis in Bulgaria is implemented for the study of manuscript indexed as NBKM 17 (Dobrejshov's Gospel) (Vulkova, 2009) and Cod.d.gr.212 from the Center for Slavic-Byzantine Studies "Prof. Ivan Duychev" (Haralampiev, 2013) only in laboratory setting. The current study is performed under the project КП-60-Н06/9, "Interdisciplinary methods and tools for the study of manuscripts", funded by the Bulgarian Science Fund (BSF). The manuscript analysis is carried out with a specially purchased portable Raman spectrometer Optosky ATR3000 (Fig. 1), with a fiber Raman probe, allowing for a greater precision of the measurement, and adjustable exciting laser radiation power, adapted to the objectives of manuscript study. This paper presents results from preliminary work on digital database creation, containing analytical information on the type and condition of parchment manuscripts from the repository of the Bulgarian National Library "St. St. Cyril and Methodius".

Fig.1. Portable Raman spectrometer Optosky ATR3000.

2 Exposition of the Investigation

The analysis of the manuscripts was carried out *in situ* at the Bulgarian National Library "St. St. Cyril and Methodius", using portable devices. The Raman spectra were recorded using an OPTOSKY ATR3000 Raman spectrometer with a wavelength of the exciting laser radiation of 785 nm, a highly sensitive CCD detector cooled to -10°C, a spectral range from 120 to 2700 cm^{-1} with a resolution of 5 cm^{-1}, and the ability to adjust the power of the exciting radiation between 50 and 500 mW. To avoid possible damage to the manuscripts, initially all points selected for study were analyzed at a minimum laser power of 50 mW, after which the power was increased to 100 or 150 mW. It was found that depending on the type of irradiated material (parchment without inscriptions, ink from the letters, or pigment from the miniatures), spectra of different quality are obtained at different power settings.

The portable XRF (pXRF) instrument used for comparative purposes in this study was a Bruker Titan S1 spectrometer (Center of Archaeometry with Laboratory of Conservation and Restoration – Sofia University) equipped with a Fast Silicon Drift Detector (SDD) cooled by Peltier elements and a resolution of the order of 160 eV FWHM at 6 keV. The excitation source of this instrument was a Rh target X-ray tube, 4W, 40 kV, with a spot size of 3 mm^2 and a five-position automatic filter change. The duration of each measurement was 90 seconds in the geoexploration mode, which allowed determining for each element heavier than sodium if it was present in the material.

3 Results and Discussion

Five medieval manuscripts from the National Library's collection were analyzed using the Raman spectrometer. Additionally, the pXRF analysis was also applied to three of the codices at the same spots. These are manuscript No. 17 – Dobreishovo Gospel from the beginning of the 13^{th} century, manuscript No. 880 – Dragotin Menaion and Apostle from the 12^{th}-13^{th} centuries, and manuscript No. 1378. In this section of the article we present the main results of the study and material analysis of Dragotin Apostle (codex No. NBKM 880), a palimpsest manuscript from the late 12^{th} - early 13^{th} century, kept at the National Library of the Republic of Bulgaria. It contains text in Cyrillic and Greek, hidden under the Cyrillic upper layer. A fragment of the Greek text is identified as 11^{th} century Octoechos, and the Cyrillic palimpsest folios (48 in number) contain an Old Bulgarian 12^{th} c. menaion (Christova-Shomova, 2018). The codex is partially studied in 2011 within the framework of the project "The Enigma of the Sinaitic Glagolitic Tradition", funded by the Austrian Science Fund. Manuscript NBKM 880 is of particular interest to us, as it includes two separate palimpsest parts with heterogenous provenance, written in Greek and Cyrillic. This suggests that the monument contains two works, the parchment folios of which, inks, and pigments were made at different times or using different techniques. The previous study of this manuscript (Christova-Shomova, 2018) analyzed the parchment and the inks of the Cyrillic palimpsest part (from f.95 to f.159) – combining the various results of the complementary analyses performed by XRF and rFTIR. Our study focuses on the specific characteristics of

Greek palimpsest folios in comparison to the Cyrillic ones. In this preliminary study we are mainly interested in the parchment measurements, taken by both instruments – Optosky Raman spectrometer and Bruker Titan S1 XRF. Our ultimate goal is to identify measurement parameters, which will serve to specify manuscript region of origin and, possibly, dating.

The measurements are taken from folio No. 34 (Greek palimpsest) and folios 95, 101, 105, and 159 (Cyrillic palimpsest). A description of several of the sampled points is given in Table 1, where the concentrations of some of the determined chemical elements in mass percent or parts per million (ppm) are also indicated.

Table 1. Elemental composition of several samples from manuscript No. 880.

Index	Example	Al, %	Si, %	P, %	S, %	Cl, %	K, %
34v/2	Parchment	1.08±0.07	2.35±0.06	0.50±0.02	1.14±0.02	1.16±0.02	0.84±0.01
34r/1	Black ink	0.29±0.05	0.69±0.04	0.32±0.02	0.47±0.01	0.39±0.02	0.49±0.01
34r/4	Red pigment	0.90±0.06	2.17±0.06	0.40±0.02	2.01±0.035	0.75±0.02	0.80±0.01
95v/1	Pale letter from the palimpsest	1.36±0.07	2.84±0.07	0.57±0.02	1.32±0.02	1.64±0.03	1.08±0.01
95r/1	Parchment	0.41±0.05	0.95±0.04	0.27±0.02	0.55±0.01	0.58±0.02	0.43±0.01
95r/2	Black ink	0.15±0.03	0.25±0.03	0.21±0.01	0.23±0.01	0.18±0.02	0.30±0.01
101r/1	Pale letter from the palimpsest	0.52±0.05	1.23±0.06	0.37±0.02	0.72±0.02	1.65±0.03	0.66±0.01
105r/1	Red pigment	0.30±0.04	0.61±0.04	0.40±0.02	0.58±0.02	0.36±0.02	0.54±0.01
159v/1	Parchment	0.75±0.06	1.30±0.05	0.75±0.02	0.74±0.02	2.07±0.03	0.79±0.01

Table 2. Continued.

Index	Ca, %	Mn, ppm	Fe, %	Cu, ppm	Zn, ppm	As, ppm	Sr, ppm	Pb, ppm
34v/2	5.67±0.03	458±39	0.24±0.01	21±3	28±3	126±9	77±6	448±17
34r/1	6.46±0.03	213±30	0.18±0.01	14±3	13±3	23±5	67±5	81±10
34r/4	5.27±0.02	339±37	0.63±0.01	14±3	39±3	226±12	53±5	597±20
95v/1	2.31±0.02	478±39	0.26±0.01	23±3	41±3	14±4	55±5	65±9
95r/1	1.32±0.02	189±27	< 0.001	12±3	21±2	5±4	22±4	35±8
95r/2	0.29±0.01	273±23	0.07±0.01	14±3	19±3	6±6	10±3	65±11
101r/1	1.16±0.01	318±33	0.03±0.00	14±3	26±3	< 1	26±4	15±7
105r/1	0.76±0.01	170±25	0.08±0.01	19±6	47±5	167±19	17±3	369±28
159v/1	1.94±0.02	390±35	0.07±0.01	23±4	26±3	21±6	45±5	93±11

The higher concentrations of the elements listed in Table 1 – the Greek palimpsest parchment (sample 34v/2) compared to that with Cyrillic text (samples 95r/1 and 159v/1, respectively) are notable. The increase often exceeds 100%, and for elements such as calcium, arsenic, and lead, it can reach 3 to 25 times higher concentrations for the parchment from fol. 34. Considering that the folios are part of a written monument with a common binding stored under the same conditions over the centuries, these significant differences in the elemental composition can be attributed to the different method of processing the leather into parchment suitable for writing. The indicated differences in the concentration of chemical elements can also be attributed to the additional scratching of the palimpsest folios to prepare the surface for the *scriptio superior*. It is possible that the technology for erasing the older text resulted in a significant "cleansing" of the parchment sheets from residues of mineral substances used for the initial treatment of the leather.

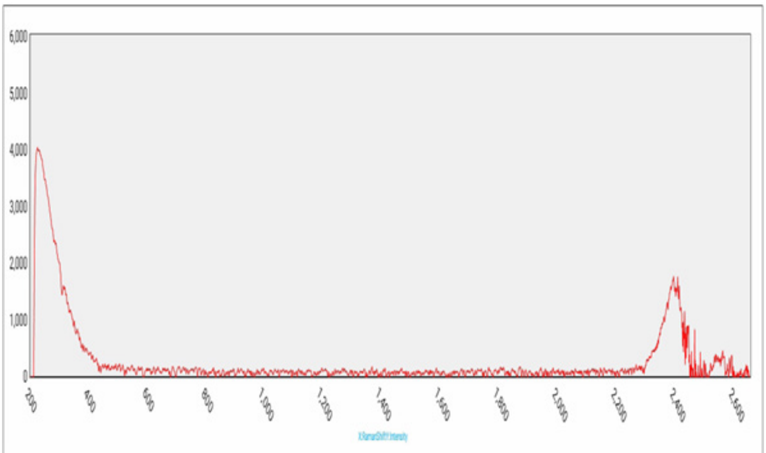

Fig. 2. Raman spectrum of Codex 880, fol. 34v.

The differences in the chemical elements concentration between fol. 34 and folios 95, 101, 105, and 159, determined by XRF analysis, are also corroborated by the spectra obtained using the Raman technique. Figures 2, 3, and 4 exhibit the spectral images of the parchment from folios 34, 95, and 159. In all three spectra, an intense band seqience around 290-300 cm^{-1} is observed, which can be attributed to the organic compound dimethyl sulfide. It is usually of biogenic origin (Barletta & Roe, 2011), and in this case, it may be a product of the processing of collagen by certain types of bacteria.

Regarding the rest of the spectral region between 400 and 2600 cm^{-1}, differences are observed for the three spectra. The band around 900 cm^{-1} in the obtained Raman spectrum of the parchment from fol. 159 can be attributed to valence bonds in the proline and glycine molecules, which are part of the collagen structure (Malea et al., 2024). In this spectrum, a weakly marked band of the carbonate ion at 1080 cm^{-1} can also be seen.

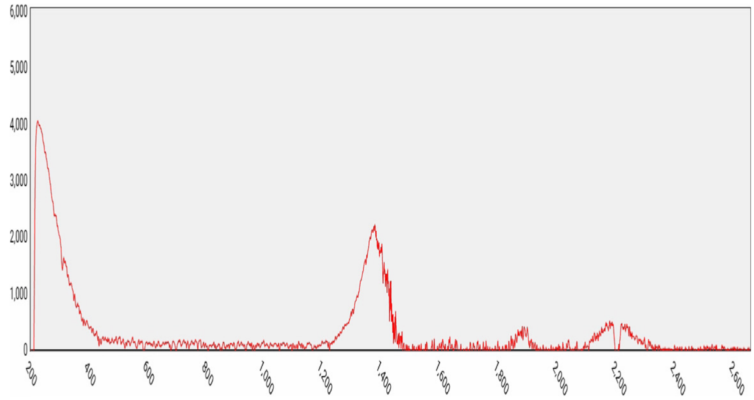

Fig. 3. Raman spectum of Codex 880, fol. 95r.

The series of Raman bands between 1200 and 1450 cm^{-1} in the spectrum of fol. 95 correspond to the so called *stretching vibrations* in the lysine molecule, the Amide III complex (a series of bands associated mainly with the structure of collagen), or to deformation vibrations in the NH_3 molecule. These bands, although less intense, are also observed in the spectrum of the other folios of the Cyrillic palimpsest – fol. 159, but not in the parchment with Greek palimpsest – fol. 34. The latter differs from the other two – it exhibits intense bands around 2400 cm^{-1}, which is characteristic of the *stretching vibrations* in the hydroxyl and carboxyl groups of organic compounds.

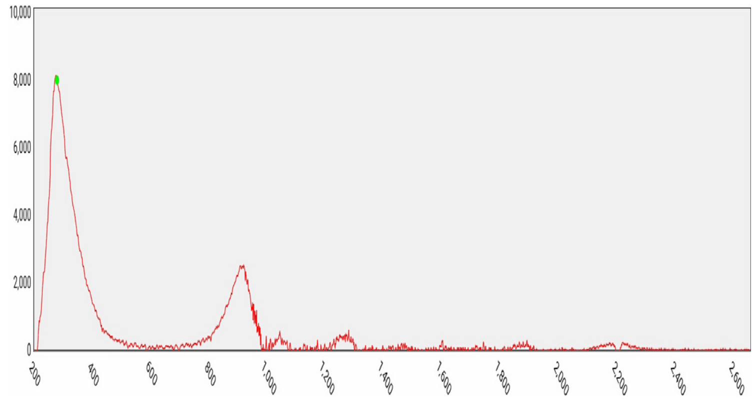

Fig. 4. Raman spectrum of Codex 880, fol. 159r.

The discussed differences in the structure of several parchment folios from the two studied medieval texts, give reason to believe that Raman spectrometry would be suitable for classifying parchment-written monuments based on differences in the technology of their production.

4 Conclusions

This paper presented a case study of Raman spectroscopy implementation for identification of differences between two types of parchment in the Greek and Cyrillic palimpsest-parts of codex NBKM880, where Raman spectroscopy precisely identified their nature as well as their composition, specific to the molecular or crystal structure of the material. The characteristic spectral bands, obtained through this technology, can further be used to create a digital database that allows for the comparative study of various aspects of the medieval manuscript heritage, based on quantitative and qualitative analytical data.

As a result it can be concluded, that Raman technology for manuscript analyses provides reliable and accurate data which can yield new and verifiable hypotheses based on the comprehensive information about the physical and chemical properties of each individual manuscript, the history of its treatment, the origin of materials it is made of. The application of new non-invasive methods of analysis as a methodology for comprehensive study of the material body of parchment manuscripts contributes to their more precise historical, codicological and linguistic research and helps for their reliable digitalization, conservation and restoration.

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References

Barletta, R. E., & Roe, C. H. (2011). Differential Raman cross section of dimethyl sulfide. *Journal of Raman Spectroscopy, 42*, 117–121. https://doi.org/10.1002/jrs.2749

Brenner, S., & Miklas, H. (2019). Multispectral imaging of degraded manuscripts in the Ivan Vazov National Library in Plovdiv. *Godišnik na Narodna biblioteka „Ivan Vazov" (2014–2018)* [*Yearbook of the Ivan Vazov National Library (2014–2018)*], 32–48.

Cappa, F., & Schreiner, M. (2019). Raman spectroscopy for the material analysis of medieval manuscripts. In *Nanotechnologies and nanomaterials for diagnostic, conservation and restoration of cultural heritage*.

Christova-Shomova, I. (2018). *Dragotin minej. Bulgarski rukopis ot nachaloto na XII vek* [*The Dragotin Menaion: Bulgarian manuscript from the beginning of the 12th century*]. University Press "St. Kliment Ohridski".

Haralampiev, N. (2013). *Dissertation abstract: Tehnika i tehnologija na ukrasata vav vizantijskite pergamentni rukopisi. Tehnologichen analiz na izborno evangelie Cod. D. Gr. 212 ot CSVP "Prof. Ivan Dujchev"* [*Technique and technology of decoration in Byzantine parchment manuscripts. Technological analysis of the selected Gospel Cod. D. Gr. 212 from CSVP "Prof. Ivan Duychev"*]. https://digital.libsu.uni-sofia.bg/bg/v/3034

Malea, E., Boyatzis, S. C., Karlis, D., Boghosian, S., & Zervos, S. (2024). The complementary use of Raman, ATR-FTIR spectroscopy, and chemometrics for investigating the deterioration of artificially aged parchment. *Journal of Raman Spectroscopy, 0*, 1–15. https://doi.org/10.1002/jrs.6755

Nastova, I., Grupče, O., Minčeva-Šukarova, B., & Kostadinovska, M. (2015). Spectroscopic analysis of pigments and inks in manuscripts. III. Old-Slavonic manuscripts with multicolored rubication. *Vibrational Spectroscopy, 78*, 39–48. http://dx.doi.org/10.1016/j.vibspec.2015.03.005

Nastova, I., Grupče, O., Minčeva-Šukarova, B., Kostadinovska, M., Turan, S., Yaygingol, M., Ozcatal, M., Martinovska, V., & Jakovlevska-Spirovska, Z. (2011). Micro-Raman spectroscopic analysis of inks and pigments in illuminated medieval Old-Slavonic manuscripts. *Journal of Raman Spectroscopy, 43*, 1729–1736. https://doi.org/10.1002/jrs.4084

Retko, K., Legan, L., Kosel, J., & Ropret, P. (2024). Identification of iron gall inks, logwood inks, and their mixtures using Raman spectroscopy, supplemented by reflection and transmission infrared spectroscopy. *Heritage Science, 12*, 212–231. https://doi.org/10.1186/s40494-024-01323-0

Rigante, C. L., Calvano, C. D., Ventura, G., & Cataldi, T. R. I. (2025). Look but don't touch: Non-invasive chemical analysis of organic paint binders – A review. *Analytica Chimica Acta, 1335*, 343251. https://doi.org/10.1016/j.aca.2024.343251

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