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MULTI - ANALYTIC STUDY OF ORIENTAL MANUSCRIPTS IN BOSNIA AND HERZEGOVINA DATING FROM THE 15TH - 19TH CENTURY

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Abstract

The objective of this study was the analysis of materials used in five Oriental manuscripts from Bosnia and Herzegovina dating from the 15th - 19th century. The manuscripts were examined using various analytical techniques ranging from a series of preliminary tests (visual inspection, microchemical tests, thin layer chromatography (TLC), acidity status, UV fluorescence) to Fourier-transform infrared (FTIR) spectroscopy, X-ray fluorescence (XRF), optical and scanning electron microscopy (SEM-EDS). The obtained results showed that the manuscripts were made using paper, ink and pigments derived mainly from natural sources. The paper was made from either flax fibers or the combination of flax and hemp fibres and was often sized with egg white and alum to improve its quality. Both carbon black and iron-gall inks were used for the main text, whereas vermillion was chosen only for red ink. This research provides a valuable insight into the production techniques used in Oriental manuscripts from Bosnia and Herzegovina during that period. It also represents a template approach for manuscript characterisation and science-based paper conservation.

Keywords*: Oriental manuscripts; Bosnia and Herzegovina; Spectroscopy: Microscopy; Micro-chemical tests*

Introduction

Given that Bosnia and Herzegovina (B&H) was historically an integral part of the Ottoman Empire for many centuries, it is not surprising that a significant portion of Oriental manuscripts there are of Ottoman origin. The National and University Library in Sarajevo, as an institution of material and spiritual culture, had a very important role on the development of the Islamic culture and civilization in the Balkans [1]. Along with Gazi Husrev-bey's library, the National and University Library in Sarajevo today holds some of the most important treasures of Ottoman manuscripts in B&H and in the region [2]. The manuscript collection of the Oriental institute in Sarajevo had included 5,263 manuscripts and represented one of the richest collections of Ottoman manuscripts in the Balkans before the Institute was torched to the ground and the manuscripts and other documents turned into ashes during the 1992 - 1996 war [3]. The manuscripts in libraries across B&H cover a wide range of subjects, including Islamic religious texts, literature, ethics, linguistics, history and science. They were written in Arabic, Persian, Turkish and Bosnian languages reflecting the diversity of Islamic cultures that once existed in the

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Balkans [2]. The reconstruction of some unique manuscripts and archival documents lost in the war is a difficult but crucial task today [1]. The manuscripts used in this study include Qur'anic transcriptions, books of poetry, and works on law and theology. All of them share some characteristics with oriental and Islamic manuscripts. *N.K.-Özgörüş et al*. [4] outlined the process of creating Islamic manuscripts, as a subgroup of Oriental manuscripts. The process often involves a number of artisans, including a calligrapher, illuminator, papermaker, bookbinder and others. After a high-quality paper was selected, which was often made from rags of flax and hemp, it was occasionally colored by dipping or brushing with a variety of natural or artificial chemicals (henna, freesia, cochineal etc.). Paper manufacturers also employed surface-sizing materials to create smooth writing surfaces. Various ingredients were used, but in most cases, egg white or starch was mixed with alum. The paper was left to dry for two to three months, sometimes longer. The folios were polished by stone or glass tools when they had dried properly. The writing process itself could take years. Finally, the folios were combined, bound with end bands and given a cardboard and leather bookbinding.

Conservators are well aware that modern materials used for book making could have serious detrimental effects if used for book preservation purposes. Because of the nature of old materials and the original process of manuscript creation, the conservation and restoration of Oriental manuscripts is a specialized topic within the field of conservation and restoration of written heritage. Oriental manuscripts are typically written using water-soluble ink, in contrast to books and manuscripts created in the West [5]. For the most part, preventive conservation techniques are used to preserve written materials and this is also true for Oriental manuscripts. Nevertheless, interventional conservation and restoration is often inevitable but also more successful when grounded on scientific evidence. In 2017 the Gazi Husrev-bey Library started a project to inspect and clean over 10000 manuscripts. Stains from glue, traces from previous conservation or restoration interventions, water solubility of ink, torn or missing pages, dry or cracked covers were the most common types of damage found in a large number of those manuscripts [6].

Science and technology are crucial to the field of cultural heritage conservation because they help with diagnostics, the characterization of the materials that make up the „cultural object", the creation of new conservation techniques and the creation of the ideal environmental settings for the preventive conservation of cultural heritage. There is no doubt that non-destructive techniques could offer a strong potential to addresss issues related to the identification of molecular or elemental constituents in the materials that comprise works of art, monuments, historical structures, archaeological objects and ancient papers. Science based knowledge is not only necessary in order to document deterioration factors and constitutive materials of manuscripts, it is also essential to know how to implement a coherent preservation program [7].

Evidently, Oriental manuscripts represent a specific challenge in conservation practice and it is therefore of utmost importance to provide deeper scientific understanding in order to develop adequate and effective preservation measures. For that reason, this study aimed to characterise five Oriental manuscripts from B&H that date from the 15^{th} – 19^{th} century and provide some of the first scientific analysis that will be useful in the future preservation work.

Descriptions of the manuscripts

The present study aims to identify materials used in writing and illumination of five manuscripts ranging from the 15^{th} to the 19^{th} century that are currently housed in Mesudija Library, B&H. The list of the manuscripts is presented in Table 1 along with a description. The description includes the manuscript's content, date and provenance and, lastly, its key characteristics. All manuscripts are written in Arabic script and two of them (M3 and M4) in Turkish language. The origin of all manuscripts is unknown. Each of them has previously

undergone conservation and restoration processes, with varying degrees of success. However, the condition of all manuscripts requires further preservation measures.

Table 1. Descriptions of the manuscripts

Code no.	Name of manuscript	Autor/ Amanuensis	Dating	Content	Photography
M1	**Kitabu sadri sheri'ati**	Unknown/ Unknown	15th c.	The manuscript discusses theological themes as well as topics from the field of Islamic law, i.e., Sharia. The text is written in Ta'lik script.	
M2	**Muṣḥaf**	/Unknown	18th c.	Mushaf is a written copy of the Qur'an. The text is written in Nasḫ script.	
M3	**Tefsir of Ebu Suud**	Abu's-Su'ūd Aḥmad b. Muḥammad al-ʿImādī/ Unknown	18th c.	This manuscript is the first volume of works that deals with the interpretation of the Qur'an (up to the 52nd verse of Surah Ibrahim). The manuscript is written in Turkish, using Nasḫ script.	
M4	**Eṭ-Ṭarîḳatü'l-Muḥammediyye ve's-sîretü'l-Aḥmediyye**	Birgivî Mehmed Efendi'nin (died 1157/)/ Unknown	18th c.	This is a well-known work about religion, morality and mysticism, which deals with topics such as the principles of religious life in accordance with the Qur'an and the Sunnah.	
M5	**Collection of ghazals**	Unknown/Sheikh Ali ibn Salih Muhammed	19th c.	This is a collection of gazelles, i.e., verses in Divan poetry that deals with the themes of love, beauty and joy. The gazelles are written in black non-water-soluble ink on prepared paper. The primary text is outlined by margins. On the outside, there are written remarks and explanations of the gazelles.	

Experimental part

Materials and methods

Microchemical tests

Qualitative microchemical test of lignin, starch, proteins and alum ($Al_2(SO_4)_3 \cdot 18H_2O$) in the paper support were performed using phloroglucinol solution [8], iodide-potassium iodide solution [9], 0.2% ninhydrin solution and aluminon reagent respectively [10]. In the case of positive reaction, the development of colour was observed with a Dino-Lite microscope.

Acidity status

The acidity status of the paper specimens was determined by a modified method as is described by *A. Haskovic and S. Ibragic* [11].

Paper support and sizing materials

The visual inspection of the manuscripts was performed under UV light (254 and 366 nm) and daylight. Previous conservation interventions, possible traces of biodegradation and otherwise caused damage were carefully examined and noted.

The fibre analysis was carried out using the same samples prepared for pH measurements and for further disintegration processes by following the TAPPI 401 om-88 method [8]. To accentuate morphological features of the fibres, Herzberg and Graff C reagents were prepared according to the TAPPI T 401 standard test method [8]. The microscopic analysis was performed using an Olympus DP 12 light microscope under the x10 magnification.

The preparation (sizing) of the paper support was analysed using TLC method. The qualitative test for proteins was developed by *S. Gocan* [12] and adapted to paper specimens by *A. Haskovic and S. Ibragic* [11]. The aforementioned procedure was used in this study.

The paper support of the manuscripts was analysed by FTIR analysis with an Alpha BRUKER Optics (Germany) FTIR device in ATR (Attenuated Total Reflectance) scanning mode, with a diamond crystal, in the range of wave numbers from 400 to 4000cm^{-1} and a resolution of 4cm^{-1}. The FTIR spectrum of each sample represents the average result of 24 recordings. The obtained FTIR spectra were analysed using OPUS software (BRUKER, Germany). The surface of the paper was polished by placing the diamond crystal of the device itself on the surface, non-invasively and non-destructively.

Ink analysis

The ink analysis was performed using SEM-EDS and XRF analyses. The SEM-EDS of the samples were performed with an JEOL JSM 6460LV scanning electron microscope, with Oxford Instruments INCA X-sight LN2 EDS spectrometer. Before this examination, the samples were sputtered with gold in order to ensure the appropriate conductivity of the samples necessary for this analysis. Surface sputtering (with gold) was carried out in the device BAL-TEC, SCD 005 Sputter Coater. The XRF analysis was performed using a portable XRF spectrometer (Olympus, Vanta, C Series).

Results and discussion

Paper support and preparation

Inspection under UV and visible light

During the initial phase of the study all manuscripts were examined under visible and UV light. The manuscript pages display a distinctive shine brought on by burnishing. All materials have become darker with time due to age and deposits of dirt and dust. The text was written using black ink, while the details (M2, M4 and M5 manuscripts) and margins (M3 and M5 manuscripts) were written in red ink. In the case of M2 and M3 manuscripts, some sentences or phrases were written in red ink, in addition to some details and margins. The black ink in the case of M2, M3 and M4 proved to be water soluble. Increasing humidity has caused the ink's dissolution, leaving behind stains on manuscripts M3 and M4. With the exception of manuscript M3, red ink is much more water-resistant in the case of all manuscripts. Watermarks were found on multiple pages of manuscripts M2 and M4. The three crescent-shaped, „lune" marks are visible at the manuscript M2. This kind of watermark is common in Islamic manuscripts. It is most likely an Italian paper that was exported throughout the Ottoman Empire [13]. The watermark „IMC" can be seen on the first page and numerous other pages of manuscript M4, which is typical for paper manufacturers that operated from the 17th to the 19th century. These have been discovered in papers used throughout the Ottoman Empire [14]. The anchor watermark and the six-pointed star above the anchor were also discovered at this manuscript which are characteristic of the Italian

paper producers from the 16th and 17th century. They can also be found in Ottoman manuscripts from that time.

Fig. 1. a) and b) Manuscript pages inspected under UV light, c) 'bull's eye' foxing present in M4 sample

The visible-light studies revealed various types of deterioration, as well as traces of previous conservation interventions.

The manuscripts were then examined with a UV lamp. All manuscripts, with the exception of manuscript M4, lacked the characteristic fluorescence indicating the absence of microorganisms. Only one page of manuscript M4 had foxing. It was identified as a form of foxing called „bull's eye" based on the colour and shape of the spots. The „bull's eye" is distinguished by its dark nucleus and unique concentric circles [15, 16]. The oxidation of the paper is thought to constitute the source of foxing. Metals from the ink moved and spread in the paper. In the polluted air, copper and iron (II) sulfides were formed around stains and catalysed the oxidation of cellulose.

Manuscript M4 was in poor condition, which was confirmed by the existence of other types of damage and deterioration, such as moisture stains and dark colour of the paper.

The reaction between cellulose and oxygen results in paper oxidation, which can be catalyzed by metal decomposition. It is important that a humid environment can trigger physico-chemical changes in paper, while the increase in water content promotes oxidation of the paper and the appearance of foxing. It is believed that foxing can occur as a result of interaction between arid and humid regions of the paper, periodic evaporation of water from the paper and microclimate changes during manuscript storage. However, it has been demonstrated that UV fluorescence strength weakens over time and that foxing will not fluoresce in its advanced stages. As a result, searching with UV fluorescence is no longer regarded as a reliable approach [17]. Some of the observed spots did not fluoresce under UV light, so they are considered to be in the late stages of deterioration.

Microchemical tests and acidity status

Preliminary tests were conducted to determine the presence of lignin, starch, proteins and alum - all common ingredients in the papers or in the sizing mixtures. Sizing as a process served to make the paper more hydrophobic and thus more durable [18, 19]. The Oriental approach in paper preparation relied on sizing mixtures usually prepared in form of a paste from starch of different kinds of grains, although fish glue was also in use. Pastes were cooked in water or in an infusion of absinthe, colocynth roots, or aloe to ensure good protection against worms. Sometimes alum with sour milk was used before sizing as an extra precaution against moisture. While most papers were carefully burnished, some were finished with the egg-white or gum tragacanth applied with a brush. Also, Ottoman manuscripts appear to have a substantial amount of coating layers, which gives them a glossy and creamy appearance [20].

Based on the obtained results, it was determined that the paper pulp was not made of ground wood or other lignified fibres. Papers that contain lignin are more prone to photo-oxidation, which is a critical factor of papers' discoloration [21]. Even though starch is a common ingredient in sizing materials, it was not detected in any of the manuscripts. It is rational to presume that this material was avoided in order to prevent the rapid deterioration of the paper.

Proteins, on the other hand, were found in manuscripts M1, M4 and M5 while alum was found in M3 and M4.

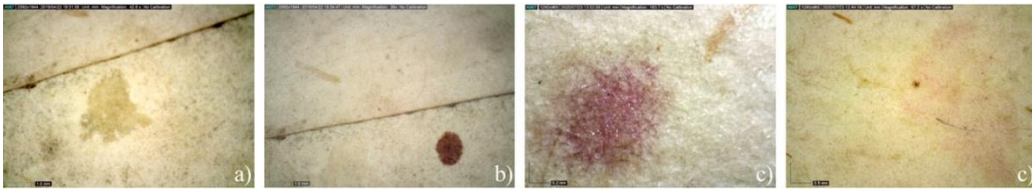


Fig. 2. Images of microchemical tests obtained with a DinoLite microscope: a) negative lignin test with fluoroglucinol, sample M3, b) negative iodine test for starch, sample M1 c) positive ninhydrin test for proteins, sample M4 and d) positive aluminon test for alum, sample M4

In the majority of the investigated manuscripts, the pH value of the papers was around neutral values ranging from 6.4 to 7.4, except for manuscript M3, which had an acidic pH value.

The acidity status and consequently, the stability of the papers and visual appearance, is not only determined by the cellulose content but also, based on the content of other compounds (e.g., lignin, hemicellulose), fillings and additives such as components used for sizing. Alum is considered the main cause of the degradation through both hydrolytic and redox processes. It can facilitate redox degradation of cellulose by initiating hydrolytic reactions that yield adversely acting H_3O^+ ions or through Al^{3+} ions. Further on, hydrolytic processes involving alum may result in the formation of sulfuric acid [22]. The acidity status and the degradation of paper is influenced by a range of other factors that can act simultaneously or independently such as the type of ink used, environmental conditions, air pollutants, biological metabolites and storage conditions [23].

Table 2. Spot tests and acidity status of the manuscripts

Sample ID	Lignin	Starch	Protein	Alum	pH value
M1	-	-	+	-	7.4
M2	-	-	-	-	7.2
M3	-	-	-	+	4.4
M4	-	-	+	+	7.0
M5	-	-	+	-	6.4

Thin layer chromatography method

Thin layer chromatography was used for qualitative analysis. However, it is a destructive method and was therefore limited to two manuscripts: M1 and M2. Using TLC method, sizing materials of the selected manuscripts were tested for the presence of proteins. The reference sizing mixtures were prepared from egg-white or egg-white with alum to check for possible interferences. Based on Rf values it was concluded that the papers of both manuscripts were sized with a mixture containing egg-white. The below Figure represents the results of the TLC method used for the sample of M1 manuscript.

FTIR analysis of M3 and M4 manuscript

The samples (regions) designated as „degraded paper" and „non-degraded paper" of manuscripts M3 and M4 (Figures 4a and 4b), were subjected to FTIR analysis in order to supplement the preliminary findings based on micro-chemical testing. Based on the acquired spectra, degradation processes in the regions of „degraded paper" were recorded (Fig. 5 and Fig. 6). These regions of the manuscript M3 were also investigated by SEM-EDS analyses (Fig. 7 – 13).

On the spectrum „non-degraded" of manuscript M3 (Fig. 5), a maximum at 1507 cm^{-1} was identified. This maximum represents the indication of the lignin existence. The presence of this compound indicates the application of an old technology in wood processing (modern processes use chemically treated wood pulp in order to be removed lignin).

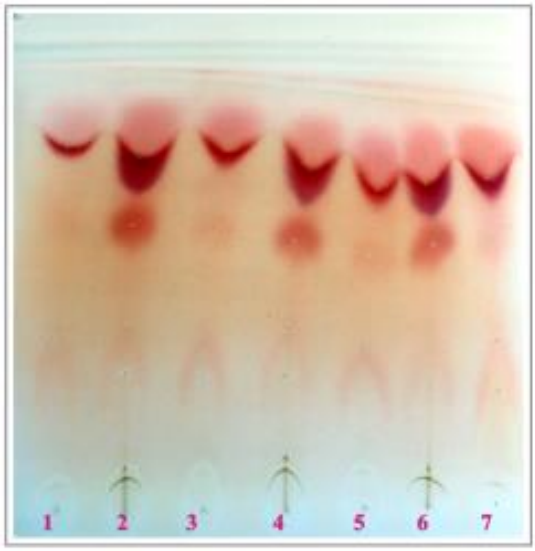


Fig. 3. TLC chromatogram of different sizing mixtures, manuscript M1: 1) egg-white, 2) sample, 3) egg-white and alum, 4) sample, 5) egg white and alum, 6) sample, 7) egg white

Fig. 4. Measuring spots: a) manuscript M3: 1 - non-degraded paper, 2 - red ink, 3 - black ink, 4 - degraded paper; b) manuscript M4: 5 - non-degraded paper

The maximum of the weak intensity, wave numbers 1400 and 874 cm^{-1}, indicate the presence of calcium carbonate, most likely used as a filler during the processing of the paper pulp.

According to literature data [24], maximum at 1375, 1335 and 1316 cm^{-1} can be used for evaluating the crystallinity of cellulose in papers. Namely, the crystallinity of cellulose decreases due to degradation processes (eg. hydrolysis). The presence of these maximum can serve as indicator considering the quality and condition state of the paper. In the case of amorphous cellulose, the maximum at 1375 cm^{-1} is less intense than in the case of crystalline cellulose. Also, in the case of crystalline cellulose, two separate peaks at 1335 and 1316 cm^{-1} are clearly visible, while with amorphous cellulose these peaks merge into one.

The cellulose absorption maximum is clearly expressed in the region 1200-900cm^{-1} (C-O-C and C-OH bonds). The peak characteristic for β-glucosidic bonds is observed at 1103cm^{-1} (basic chemical bonds between the monomer units of the D-glucose of the cellulose molecule). The broad peak at 3400-3200 cm^{-1} exists due to hydrogen bonds between -OH groups and this presents the indication of a stable crystalline structure of cellulose. The maximum of the OH group at 1636 cm^{-1} rises from „scissor“ vibrations.

In figure 5a the mentioned phenomena are clearly observed: a very weak intensity of the maximum at 1375 cm^{-1} and one intense, after merging, at the wave number 1320cm^{-1} in the degraded part of the paper (blue spectrum).

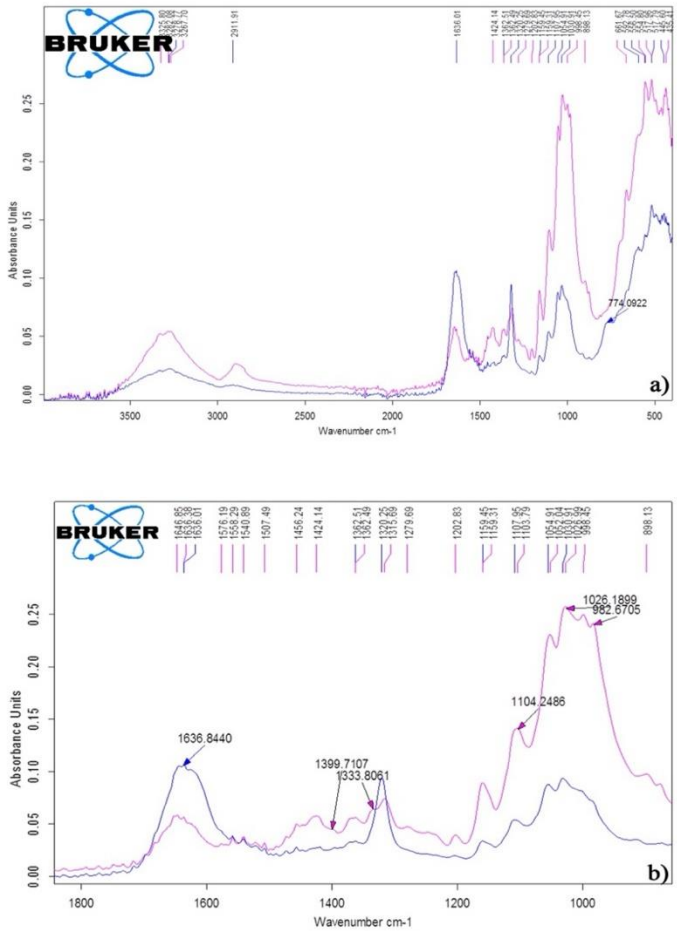


Fig. 5. FTIR spectra of: a) „degraded paper" (blue) and „non-degraded" paper (pink) of the manuscript M3 in the region between 4000 – 400cm^{-1}; b) 1750 – 850cm^{-1}

This fact confirms the thesis that the presence of amorphous cellulose is dominant in the degraded part of the paper. In the region 3400-3200cm^{-1} a weaker intensity is observed on the FTIR spectrum of sample M3 (blue spectrum), the fact which indicates a lower degree of hydrogen bonding of OH groups in cellulose molecule presenting the indicator of a weak stability of the cellulose structure. At the same time, a stronger intensity of free -OH groups are observed in the region around 1636 cm^{-1} compared to the spectrum of the non-degraded part of the paper (pink spectrum). Additionally, there is a much weaker intensity of the characteristic maximum of β-glucosidic bonds (1108cm^{-1}). This is the consequence of hydrolytic degradation processes. Hydrolytic processes are often the results of pH changes of the environment due to actions of aggressive substances (eg. acids) or microbiological contamination [25].

Based on the comparative analysis of the FTIR spectra of „non-degraded" parts of M4 and M3 papers (Fig. 6), a good overlap could be identified indicating a very similar composition of these two papers. A higher resolution of the maximum, wave numbers 1337 and 1315cm^{-1} , indicates a serious degree of cellulose crystallinity in the case of M4 paper at the analysed site. As in the case of the M3 paper, the maximum is also present around the region 1550cm^{-1}, which indicates possible presence of amide bonds of the protein.

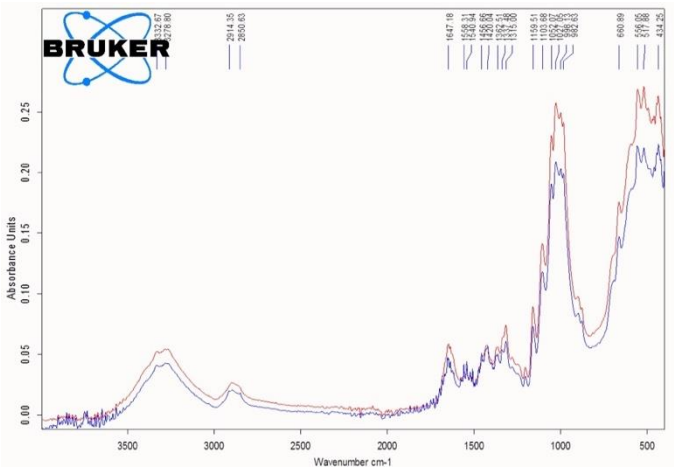


Fig. 6. Overlay of two FTIR spectra of „non-degraded" paper of manuscripts M3 (red) and M4 (blue)

Fibres

Using optical microscopy analysis and the Herzberg and Graff C reagents, the morphological properties of the fibres were identified. It is well known that chemical constitution and structure of fibres are influenced by the dyeing reagent [26], while the tenacity of fibres colour is determined by the type and degree of the fibre processing [27]. The type of fibre samples in the case of the analysed manuscripts was identified by using reference fibres of known origin as well as based on the information from the relevant literature [28, 29]. According to the obtained results (Fig. 7a-f), it is most likely that M5 was made only from flex while the fibres of the manuscripts M1 - M4 were made from the mixture of flax and hemp fibres used in various proportions. Flax and hemp are remarkably similar, barely distinguishable in the form of fibres. The flax fibre cells were described based on [30, 31] investigation. They are long, transparent, cylindrical tubes that might be smooth or striated lengthwise. The width of these fibres varies as well as their length. There are swellings or nodes at numerous points and the fibres show characteristic transverse marks. A lumen or canal passes through the centre of each fibre cell. The lumen is small but well-defined and regular in size. Hemp is cylindrical and has joints, cracks, swellings and other surface peculiarities. The cells' ends are blunt and the middle channel, or lumen, is wider than in flax.

Hemp paper was utilized because of the strength and endurance of its fibres, but it lacked fine and silky fibres seen in linen. Identification of the paper composition, considering the structure and chemical nature, is critical for further conservation treatment.

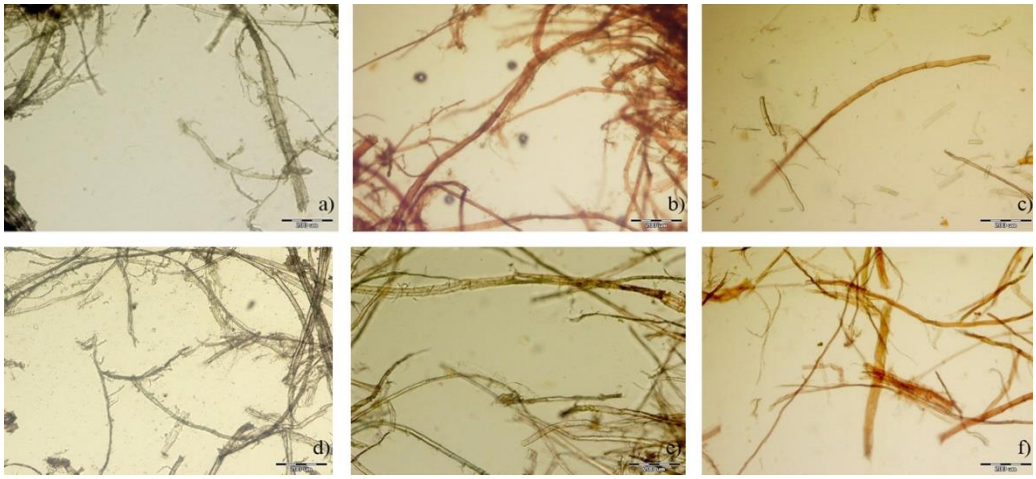


Fig. 7. Microscopic images of fibres with / without staining reagents (10x): a) M2 (hemp and flax), b) M4 (hemp and flax), c) M5 (flax), d) and e) M1 (flax and hemp), f) M3 (flax and hemp)

Ink analysis

The black and red inks of the manuscripts M1, M2 were investigated by XRF analysis. Ink of the M3 manuscript was analysed by SEM-EDS.

Inks featured in the Arabic recipes can be divided in four categories: carbon (soot) inks, iron-gall (tannin) inks, mixed (compound) inks and incomplete inks. Inks that are incomplete were prepared without a binding agent and metallic salts, whereas the mixed inks contain ingredients used traditionally in both: carbon and iron-gall inks (carbon base and tanning agents). The main ingredient of carbon ink is soot obtained by combustion of a variety of plant substances. The soot was traditionally suspended in a gum arabic, honey and water. This mixture is not a permanent compound and could be quite easily washed off. Iron-gall ink was made by mixing pulverized or fermented gallnuts, vitriol and gum arabic [20]. Iron gall ink, in chemical terms, was formed by complexation of Fe^{2+} with gallic acid obtained from tannins extracted from gall nuts [21].

XRF analysis of the manuscripts M1 and M2

The XRF elemental analysis (supplementary Table 1), or more specifically, the increased concentrations of Hg and S, reveals that the red ink in manuscripts M1 and M2 is based on vermillion. The black ink of those two manuscripts differed. It can be presumed that M1 was written using iron gall ink because the Fe concentrations in the ink are higher than those in the paper support. A different sort of black ink, most likely carbon black ink, was used in M2 given the close Fe concentrations in the ink and the paper.

SEM/EDS analyses of the M3 manuscript

Manuscript M3 is chosen for SEM/EDS analyses based on the fact that previous analyses proved the black ink in the case of M2, M3 and M4 manuscripts as water soluble substance. Increasing humidity caused the dissolution of this ink leaving behind stains. Compared to the other manuscripts, the red ink of manuscript M3 was less water resistant. It made this manuscript a good candidate for more deteriorations and for a detailed analysis.

M3 manuscript / Region of red ink (Fig. 4, area 2)

Backscattering Electron Image (BEI) of this area is given at 30x magnification, Fig. 8 The analysed surface contains heavier / lighter elements that can be visually observed. Heavier elements give an illuminated tone of the analysed photo area. Confirmation of this recording method was given through the elemental surface analysis (EDS), (Fig. 9 and Table 3).

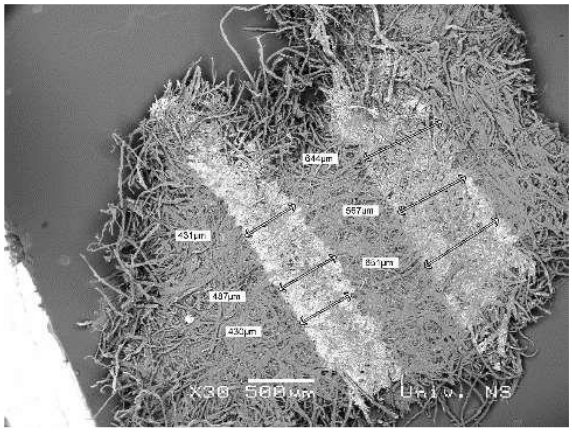


Fig. 8. SEM/BEI photo of the region of M3 manuscript, magnification 30x

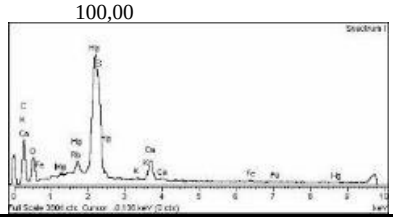
Based on the elemental analysis of the spectrum 1 from the illuminated area, which corresponds to the ink of the analyzed region (red line), (Fig. 9 and Table 3), could be concluded that vermilion pigment (known as cinnabar, HgS) was used for the red ink manufacture. Based on the presence of Ca, C and O in both (spectra 1 and 2) it can be concluded that calcium carbonate was used as the filler for paper making. The elements Al, K, Mg and Fe indicate the use of natural alum, $KAl(SO_4)\cdot 12H_2O$, with admixtures of Mg and Fe sulfate. The SEM image of this area at 1,000x magnification shows the width of the cellulose fibers of manuscript paper M3 (Fig. 10), ranging from 5.56 to 10.2 µm.

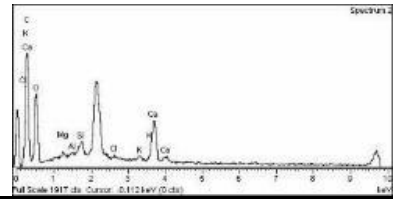
M3 manuscript/Region of black ink (Fig. 4, area 3)

BEI mode analysis of the black ink of the manuscript M3 is given in figure 11. Lighter/darker areas are identified on this photo as in the case of the red ink. The lighter tonality corresponds to black ink that contains heavier elements. The width of this area is from 514 to 439µm. The darker area (core of the photo), width from 595 to 438µm, corresponds to the paper composition. Elementary surface analysis based on EDS method is given in figure 12 and in Table 4.

Table 3. Elemental analysis of the regions 1 and 2, manuscript M3

	Spectrum 1 (red line)		Spectrum 2 (paper)	
Element	**Mas.%**	**Atom.%**	**Mas.%**	**Atom.%**
C	48,98	69,44	53,69	62,12
O	23,95	25,49	41,42	35,98
Mg	0,35	0,24	0,32	0,18
Al	/	/	0,21	0,11
Si	/	/	0,53	0,26
S	3,17	1,68	/*	/*
Cl	/	/	0,20	0,08
K	0,23	0,10	0,30	0,11
Ca	2,58	1,10	3,34	1,16
Fe	0,39	0,12	/*	/*
Rb	0,82	0,16	/	/
Hg	19,53	1,66	/	/
Total	100,00			





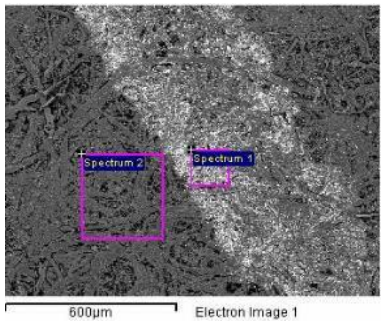


Fig. 9. SEM analysis of the region of manuscript M3 with two spectra (1and 2)

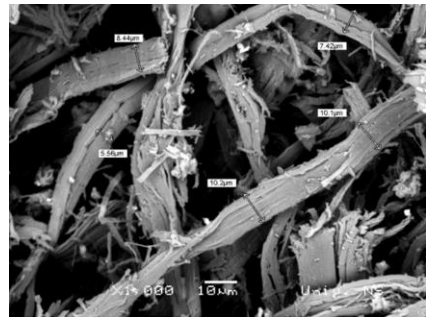


Fig. 10. SEM photo, red area of M3 sample 1,000x

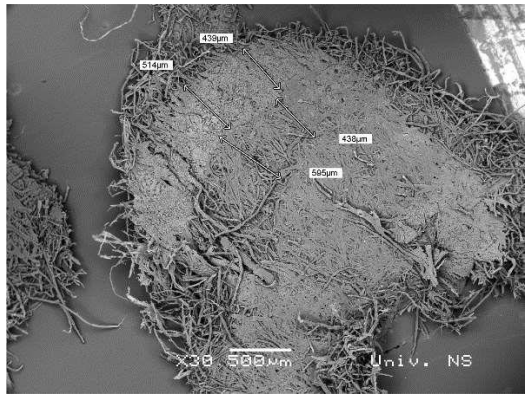
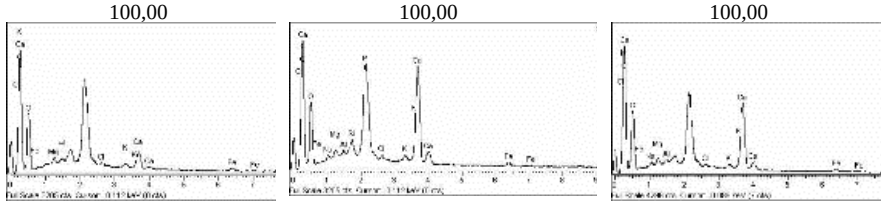


Fig. 11. SEM/BEI photo of black area, M3 manuscript

Based on the increased content of Fe in Spectrum 2 (Table 4), whose area corresponds to black ink, it can be concluded that it is a Fe gallotannin ink.

Table 4. Elemental (EDS) analysis of the black ink sample

Elements	Spectrum 1 (paper) Mass %	Spectrum 2 (black ink) Mass %	Spektar 3 (paper) Mass %
C	57,88	52,96	55,17
O	39,03	37,48	37,83
Na	/	0,34	0,29
Mg	0,46	0,43	0,41
Al	0,29	0,25	0,19
Si	*	0,60	*
S	*	*	*
Cl	0,19	0,21	0,22
K	0,34	0,40	0,32
Ca	1,38	6,69	5,07
Fe	0,43	0,65	0,52
Total	100,00	100,00	100,00



** the presence of S and Si, which was not quantified, was detected on the spectrum*

As in the case of the previous sample (red ink), Table 3, the identified elements indicate the presence of calcium carbonate (filler) and natural alum.

The SEM photo (Figs. 12 and 13), indicates the width of the cellulose fibres in the black area of the manuscript M3. These dimensions range from 9.84 to 12.5µm.

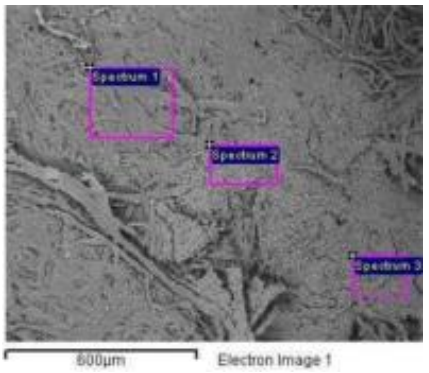


Fig. 12. SEM photo with three spectra, M3 manuscript

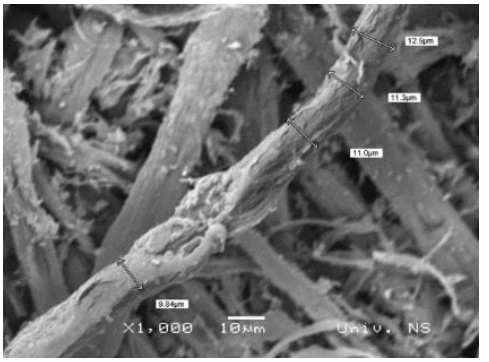


Fig. 13. SEM photo of black area, M3 manuscript

Conclusions

This study analysed five Oriental manuscripts from Bosnia and Herzegovina dating from the 15th – 19th century in order to characterise the materials and techniques during their creation process but also to subsequently facilitate science-based conservation practice. The approach was based on the selection of analytical methods that would help determine the origin of the paper fibres, the acidity status, the composition of sizing materials and the type of ink. Non-destructive methods were prioritised and used wherever possible.

Visual inspection and UV fluorescence were used to assess the condition of the manuscripts, to detect possible previous treatments and to look for signs of biodegradation. The pH of the paper in the majority of the manuscripts under investigation was around neutral levels, which reflects the stability and visual appearance of the paper. The results show that lignified wood was not used to make the paper pulp for the manuscripts. The paper was found to be made of flax or a blend of flax and hemp based on microchemical analyses. Sizing as a process enhances the paper's stability and serves as a protective layer. An interesting finding was that starch was not used in any of the manuscripts as an ingredient for the sizing mixture, however proteins and/or alum were detected in all manuscripts except for M2. In all manuscripts the presence of proteins was evaluated using microchemical tests and then confirmed by TLC (M1 and M2) or FTIR (M3 and M4). The FTIR analysis was further on useful to describe the paper stability based on cellulose, which was amorphous in M3 and more crystallic in M4. Finally, in three manuscripts the type of ink was determined using XRF or SEM-EDS. Red ink was found to be vermilion, whereas the calligraphers used carbon black or even iron-gall ink, which is less common in oriental manuscripts.

For the first time, this study allows the identification of characteristic signatures of ingredients and production techniques of Oriental manuscripts with unknown origin from Bosnia and Herzegovina (15th - 19th century). Based on the obtained results, each of the manuscripts under investigation received a customized conservation procedure.

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