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SEM-EDX analysis of paper, leather and metal lock from an 18th century church book

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Abstract
In this article paper, leather from book cover and metal lock from an 18th century church book were studied. The book was printed during the time of Mihai Constantin Șuțu, with the blessing of the Metropolitan of Moldova, Iacov Stamati. The analytical method used to study the components and the methods of obtaining all the important parts was the non-destructive technique SEM-EDX. The results regarding the used paper showed typical intermeshed cellulose fibers. In the case of leather, due to its advanced state of degradation, it was impossible to determine the type of animal from which the skin was used. The elemental analyses (EDX) of the metal lock indicated that it was made of brass. The results of the study of 18th century parts of the book, gave important information about the way of paper manufacture, the conservation state of the cover and the way that the metal lock was made and the safe way to clean it in the restoration and conservation process.

Keywords: church book, 18th century, paper, leather, metal lock, SEM-EDX, non-destructive analysis.

1. INTRODUCTION

Studies on objects of historical and cultural value involve the use of various analytical techniques to obtain information about the chemical composition and the state of conservation. In order to assess the level of deterioration, in general, it is necessary to take samples, but this is hardly acceptable due to the fact that the objects are unique, expensive and with inestimable historical or cultural value. In present is recommended to use analysis that respects some characteristics. According to Janssens et al. (2000) [1] and Faubel et al. (2007) [2] the ideal technique to analyze objects of this nature should be: non-destructive even contact-free, fast, universal, versatile, sensitive and multi-elemental.

The results of these studies are used to increase the level of knowledge regarding the historical context, the technologies available and the materials that were used, information that can be useful to choose the most appropriate technique of conservation and restoration.

Books and documents transmit from one generation to another cultural legacy, scientific, political, economic and historical information. In present, the main problem of the books, parchment, paper and other old documents is the method of preservation. Physicochemical properties of the materials that were used or environmental factors such as temperature, humidity, pollution and others tend to fast forward the degradation process [3].

In Romania, the first printed books were supported by Church and state and represented the support for development of the cultural identity. In the 16 and 17 century few numbers of

titles were the recorded, but this had changed during the 18th century. The Romanian Church had supported and sponsored the printing of a high number of worship and prayer books.

One of the printing houses in Romania activated in Transylvania, Blaj and was opened in the middle of the 18th century [4].

In this article paper, cover and lock from an 18th century church book are studied. This book is printed during the time of Mihai Constantin Șuțu, with the blessing of the Metropolitan of Moldova, Iacov Stamati.

Physicochemical analysis was provided by Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-Ray Spectroscopy (SEM-EDX), one of the most used surface analytical techniques. It represents a non-destructive technique, normally used in the field of art and cultural heritage investigations [5-8], because can provide complete results without damaging the samples. The SEM micrographs have a high resolution and are obtained by scanning the surface of the sample with a high-focused electron beam. The X-ray fluorescence spectroscopy methods are used to determine qualitative and quantitative elemental concentrations. The qualitative results become more precise if the element is heavier. Another important feature of SEM-EDX is represented by its capacity of creating an elemental map of element distribution that is very useful for the study of pigments [9].

The non-destructive analyses are used to obtain information about the physical state and chemical composition. At the end, the results can be used to identify the historical background and to choose the procedures that can be used for the restoration and conservation of the artifact.

One of the most important constituents of a book is the paper that since its invention had become an important part of our lives. Paper, mainly, is made of cellulose that gives the property of resistance in time. Cellulose can be obtained from wood (up to 10000 linked monomers) or cotton (up to 15000) and it is susceptible to biodegradation [3].

Paper manufacture started in China, were they made paper for toilet purpose, for bags to preserve the tea and for printing money from hemp, mulberry and old rags. The technique of manufacturing paper mainly remains the same from the 13th century up to the 18th century [7]. To upgrade the quality of the paper, between Middle Ages and half of 19th century, was used a paste made of fibers of linen, hemp or cotton with water, pressed into a sheet and dried. After 1680, in Holland was developed the Hollander beater, the pasting time was reduced, but the final product had decreased in quality due to the shorter fibers that were used [3].

Leather is a mainly based collagen material that during the earlier periods was used preferential to bind the books as book covers. According to Mannina and Lombardo (2013) [10], before the creation of the art work, the leather is tanned. Depending of the subject, the leather can be decorated with silver or gold leaf, can be gilded with gilt or color varnish, and also can be stamped with woodblocks. The leather, commonly, comes from small mammals like sheep, goats and calves and depending on the region or historical factors, the time of manufacture took many months. Normally, the particular characteristics can be used to identify the species by carry out SEM analysis. A brief description of how the leather was prepared can be found in [11]. For the bookbinding, usually the leather was tanned, either by vegetable tanning or by metal tanning agents that were introduced after the middle of 19th century. Besides a beautiful color from lighter to darker shades of brown and red, tanning role was also to transform the skin into long lasting leather. At the end to improve the flexibility and impermeability, were used waxes or/and oils. But with all these steps of preparation, leather is also prone to alteration and degradation, putting in risk the documents inside, because it is very sensitive to environmental factors. To apply the best procedure of restoration, first a characterization of leather status needs to be done [11].

The history of metals is linked to the technological skills of the past society. Due to the property of shining and slow corrosion rate, gold and silver were used preferentially before 3000 B.C. Around 2000 B.C. was also used copper. Due to the fact that is easy to work with it, iron was used in different combinations with other elements. Also common was brass and rarely used was lead. The alloys are a combination of different metals in different percentage, used mainly to reduce the overall cost.

The church books usually had silver or gold binding that gave splendor in a church and also was suggesting the financial prosperity of the temple.

Regarding the metal lock, the SEM-EDX analysis can reveal the elemental composition and the metal working technique [12].

2. EXPERIMENTAL

The aim of this paper is to present the first results of an experimental study in which scanning electron microscopy coupled with an energy dispersive detector (SEM-EDX) was used to analyze the structure and the composition of paper, leather from the book cover and lock of an 18th century print. The studied parts of the book were provided by courtesy of Old Book Collection from the Museum of History, Culture, Christian Spirituality from the Lower Danube, Galati, Romania.

This study was focused on close observation of the objects, as well as the qualitative and quantitative of the materials that were used to make them.

Book description and sample collection

The studied book is a church book at the second edition, printed during the time of Mihai Constantin Șuțu, with the blessing of the Metropolitan of Moldova, Iacov Stamati. It is printed in Romanian language, with Cyrillic characters. The texts are written mainly in red and black inks, in two-size characters, with 34 or 25 lines respectively to the page, framed with typographical flowers. The paper is handmade with visible water lines arranged vertically. The cover is made of reddish-brown leather, vegetal tanned. The observed features are a cross in the middle framed by a floral border and floral ornaments at the four corners. The reverse features are a central golden floral pattern framed by a floral border.

Figure 1. Church book, metal lock, paper and cover material samples

To avoid damaging the integrity of the book, the sampling of the paper and leather was performed by the specialist from the Museum of History, Culture, Christian Spirituality from the Lower Danube, Galati, during the preliminary restoration procedures. The metal lock was also removed as a preliminary step of restoration (Figure 1).

As can be observed in Figure 1, all the analyzed parts of the book had suffered mechanical strain, oxidation, material loss, foxing and traces of dirt. Foxing is a biological alteration, being represented by a random circular or irregular stain, in yellow-brown-red color

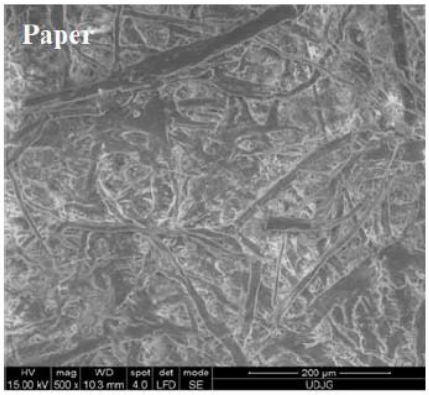
that migrates to vicinities. Foxing had generated much debate over the years, but some studies have fund fungal growth or bacteria in the area affected by this alteration, especially *Bacillus* [6].

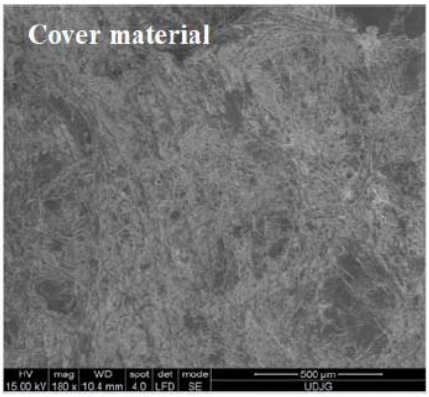
Method of analysis

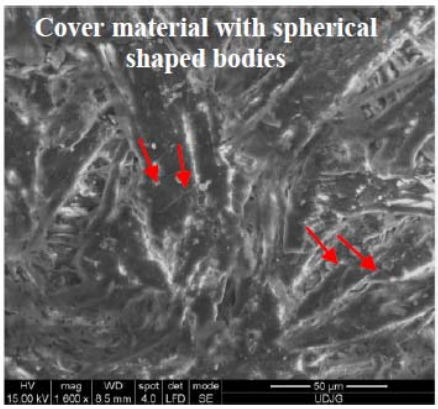
The experimental part of this paper was performed in the Electron Microscopy Laboratory, from the "Dunarea de Jos" University of Galati. The scanning electron microscope Model Quanta 200 (Philips FEI Company) was described in detail in other paper [8].

3. RESULTS AND DISCUSSION

The paper used in that period could have various provenances that can usually be seen in the watermarks. The scanning electron microscope that can be seen in Figure 2 (Paper) is used in this study for the investigation of the surface morphology of cellulosic fibers from the paper and their conservation state.







Elem	Wt %	At %	K-Ratio	Z	A	F
C K	39.18	47.74	0.1699	1.0192	0.4253	1.0004
N K	13.19	13.78	0.0235	1.0091	0.1765	1.0007
O K	34.38	31.45	0.0815	1.0000	0.2371	1.0001
NaK	6.81	4.33	0.0336	0.9335	0.5285	1.0003
MgK	0.13	0.08	0.0008	0.9563	0.6273	1.0005
AlK	0.16	0.09	0.0011	0.9243	0.7583	1.0010
SiK	0.23	0.12	0.0019	0.9442	0.8535	1.0017
P K	0.80	0.38	0.0067	0.9121	0.9169	1.0025
S K	1.63	0.74	0.0146	0.9363	0.9541	1.0021
ClK	0.36	0.15	0.0032	0.8962	0.9726	1.0030
K K	0.41	0.15	0.0038	0.8991	1.0016	1.0076
CaK	2.71	0.99	0.0250	0.9179	1.0071	1.0000
Total	100.00	100.00				

Figure 2. SEM micrographs of paper and cover material and SEM-EDX elemental analysis of the spherical shaped bodies

The micrographs of the paper presented intermeshed cellulose fibers, some flat, some with convolutions and others torn or eroded, presenting nodes with a large variety in dimensions characteristics for different vegetal materials. Also are presented impurities or fillers. The surface roughness is influenced by the manufacture type, or by the filler type and content. This characteristic can be compared with the paper samples presented by [3] where it was indicated 1700 and 1800 as the fabrication year.

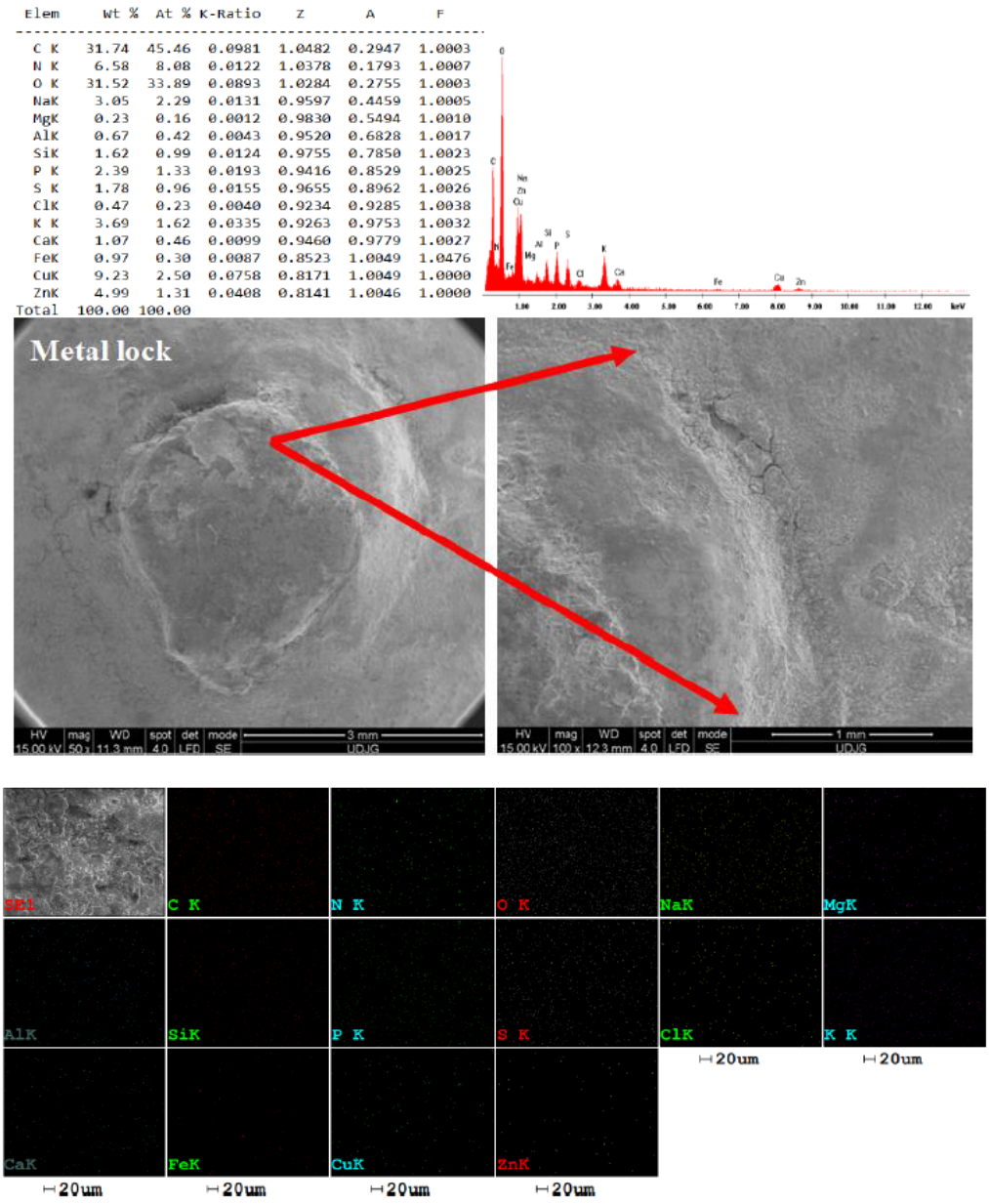


Figure 3. SEM micrograph of the metal lock and SEM-EDX elemental map of the metal lock

From the SEM micrograph in Figure 2 (cover), it can be observed that the leather is in an advanced state of deterioration. In this case, it was impossible to observe on the leather surface the hair-follicles distribution and their pattern. As a consequence, it was impossible to figure out the animal from which the leather originated. Between the fibers of the cover were found spherical shaped bodies. At EDX (Figure 2) analysis the results indicated an organic entity that can represent eggs from different types of insects.

According to the EDX analysis as presented in Figure 3, used for both elemental identifications and composition, the results obtained on metallic lock indicated the presence of an alloy of Cu (9.23 %) and Zn (4.99 %), and traces of Fe, K, Ca, Al etc. Usually, in items made of brass can be found high amounts of cooper, followed by Zn, as a second important part of the alloy. As known, brass, is very common in ecclesiastical metalwork because is easy to process but tend to oxidize in time.

4. CONCLUSIONS

The study consists in SEM-EDX analysis on paper, leather from book cover and metal lock of a Church book from 18th century. The book came from the Old Book Collection from the Museum of History, Culture, Christian Spirituality from the Lower Danube, Galati, Romania.

From the paper SEM micrographs typical intermeshed cellulose fibers can be observed, some being flat, some having convolutions and others presenting nodes, with a large variety of dimensions characteristics for different vegetal materials.

The advance state of degradation of the cover leather, made impossible the identification of the animal from which the leather was originated. The SEM-EDX analysis highlighted the presence of some type of insect eggs.

As the X-ray fluorescence analysis highlights, the metal lock was made of brass.

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