THE INVESTIGATION OF A 17TH CENTURY PARCHMENT DOCUMENT

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ABSTRACT. This study presents the investigation of a chrisov written on parchment, issued by Ștefan Lupu, the prince (voivode) of Moldavia (1659-1661), in 1660, from the collection of the National Museum of History of Romania (MNIR), in Bucharest. By using an analytical protocol based on corroboration of macroscopic and microscopic observations with the attenuated total reflection infrared spectrometry (ATR-FTIR) and X-ray fluorescence spectroscopy (XRF), information concerning parchment, inks and pigments were obtained. The Ștefan Lupu' chrisov is written on high quality goat parchment, matte, smooth, velvety, and it presents only a few manufacturing defects. ATR-FTIR analysis revealed a well-preserved structure of the collagen molecules, with a low level of hydrolytic decay. According to the XRF results, ferogallic and golden inks were used to write the Chrisov text whereas the ornaments were painted with vermilion pigment (for red color), verdigris pigment (for green color), Co-based pigment (for blue color) and fine gold powder. Both inks and pigments show a very good state of conservation.
KEY WORDS: parchment, degradation, inks, pigments, ATR-FTIR, XRF

INVESTIGAȚII ASUPRA UNUI DOCUMENT PE SUPORT DIN PERGAMENT DIN SECOLUL AL XVII-LEA

REZUMAT. Acest articol prezintă rezultatele obţinute la investigarea unui hrisov scris pe pergament, emis de Ștefan Lupu, voievodul Moldovei (1659-1661), în 1660, din colecția Muzeului Național de Istorie a României (MNIR), din Bucureşti. Prin utilizarea unui protocol analitic bazat pe coroborarea observațiilor macroscopice și microscopice cu datele obținute prin utilizarea spectroscopiei în infraroşu cu reflexie totală atenuată (ATR-FTIR) și a spectroscopiei de fluorescență cu raze X (XRF) au fost puse în evidență informații referitoare la pergament, cerneluri și pigmenți. Astfel, hrisovul lui Ștefan Lupu este scris pe pergament din piele de capră de calitate superioară, fiind mat, neted, catifelat și prezentând doar câteva defecte de fabricație. Analiza ATR-FTIR a relevat o structură bine conservată a moleculelor de colagen, cu un nivel scăzut de degradare hidrolitică. Conform rezultatelor XRF, cernelurile ferogalică și pe bază de pulbere de aur au fost utilizate pentru a scrie textul hrisovului, ornamentele fiind realizate cu pigmenți pe bază de vermilion (pentru culoarea roșie), verdigris (pentru culoarea verde), pigment pe bază de cobalt (pentru culoarea albastră) și pe bază de pulbere fină de aur. Atât cernelurile cât și pigmenții prezintă o stare de conservare foarte bună.
CUVINTE CHEIE: pergament, degradare, cerneluri, pigmenți, ATR-FTIR, XRF

L'ENQUÊTE SUR UN DOCUMENT EN PARCHEMIN DU XVIIe SIÈCLE

RÉSUMÉ. Cette étude présente l'enquête sur un chrisov écrit sur parchemin, émis par Ștefan Lupu, le prince (voievod) de Moldavie (1659-1661), en 1660, de la collection du Musée National D'histoire de la Roumanie (MNIR), à Bucarest. En utilisant un protocole analytique basé sur la corroboration d'observations macroscopiques et microscopiques avec la spectrométrie infrarouge à réflexion totale atténuée (ATR-FTIR) et la spectroscopie de fluorescence X (XRF), des informations concernant le parchemin, les encres et les pigments ont été obtenues. Le chrisov de Ștefan Lupu est écrit sur du parchemin en peau de chèvre de haute qualité, mat, lisse, velouté, et il ne présente que quelques défauts de fabrication. L'analyse ATR-FTIR a révélé une structure bien préservée des molécules de collagène, avec un faible niveau de décomposition hydrolytique. D'après les résultats de la XRF, des encres ferogalliques et dorées ont été utilisées pour écrire le texte de Chrisov tandis que les ornements ont été peints avec du vermillon (pour la couleur rouge), du pigment vert-de-gris (pour la couleur verte), du pigment à base de cobalt (pour la couleur bleue) et de la poudre d'or fine. Les encres et les pigments présentent tous deux un très bon état de conservation.
MOTS CLÉS : parchemin, dégradation, encres, pigments, ATR-FTIR, XRF

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INTRODUCTION

Historical parchment objects, such as manuscripts, documents, and maps, hold immense historical value as irreplaceable testimonies of human history. These artifacts serve as inexhaustible sources of information on both national and universal culture and civilization, allowing us to connect with the past, understanding the evolution of societies, and appreciating the cultural achievements of our ancestors. The time over which such objects maintain their ability to completely convey the intangible and tangible values decisively depends on the conditions in which they are stored or displayed and how they are restored.

Parchment, obtained by processing the animal skin, is mostly composed of collagen, the main structural protein of skin. The complex structure of collagen, which hierarchically consist of structural levels (molecules, fibrils and fibers), along with their close interconnectivity contributes to the exceptional mechanical strength and durability of parchment. However, in the case of historical parchments, the synergetic action of the environmental factors, such as temperature, humidity, light irradiation, chemical pollutants, solvents, and biological agents (fungus, bacteria, rodents, insects) results in collagen alteration over time [1-4]. Additionally, the manufacturing process can alter collagen's structure in ways that initiate its deterioration [5].

This study is dedicated to the investigation of a chrisov written on parchment, issued by Ștefan Lupu, the prince (voivode) of Moldavia (1659-1661), in 1660, from the collection of the National Museum of History of Romania (MNIR), in Bucharest. The approach used consisted on corroboration of macroscopic and microscopic observations with the information obtained by Fourier-transform infrared with attenuated total reflectance (ATR-FTIR) and X-ray fluorescence spectroscopy (XRF). Macroscopic and microscopic observations [6] provided information on animal species used for the parchment manufacture, the manufacturing defects, and indications for inks and pigments identification. The ATR-FTIR was used to identify the materials added to parchment in the manufacturing process or those formed during ageing, as well as to detect chemical changes in the molecular structure of collagen [1-4, 7], whereas the pigments and inks used for decorating and writing were identified by X-ray fluorescence (XRF) spectroscopy [2, 3, 8, 9].

METHODS

Digital Microscopy

The microscopic observations were carried out with a portable digital microscope Dino-Lite AD7013MZ with a resolution of 1.3 Megapixels and by using x50 and x150 magnifications.

Fourier-Transform Infrared Spectroscopy with Attenuated Total Reflection (FTIR-ATR)

The FTIR-ATR measurements were carried out using a portable Alpha spectrometer (Bruker Optics) equipped with a Platinum ATR module. Spectra were recorded in the 4000 – 400 cm^{-1} spectral range with a 4 cm^{-1} resolution, using 32 scans. OPUS 7.0 software was used for processing and evaluating the spectra.

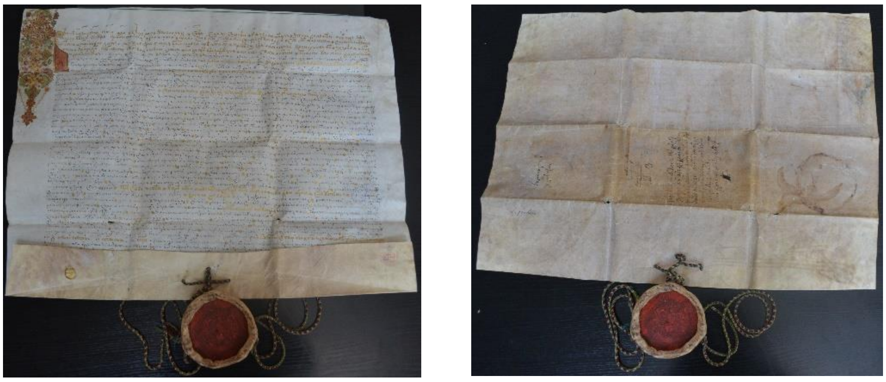
X-ray Fluorescence Spectroscopy (XRF)

The XRF measurements were carried out using an InnovX Alpha Series 6000 portable spectrometer with x-ray fluorescence with W anticathode, fitted with internal standardization and equipped with an Si PIN diode detector with U = 10-35 KV, I = 10-50 µA and < 190 eV FWHM resolution. XRF spectroscopy was used to determine the elemental composition of inks and pigments added to parchment.

RESULTS AND DISCUSSIONS

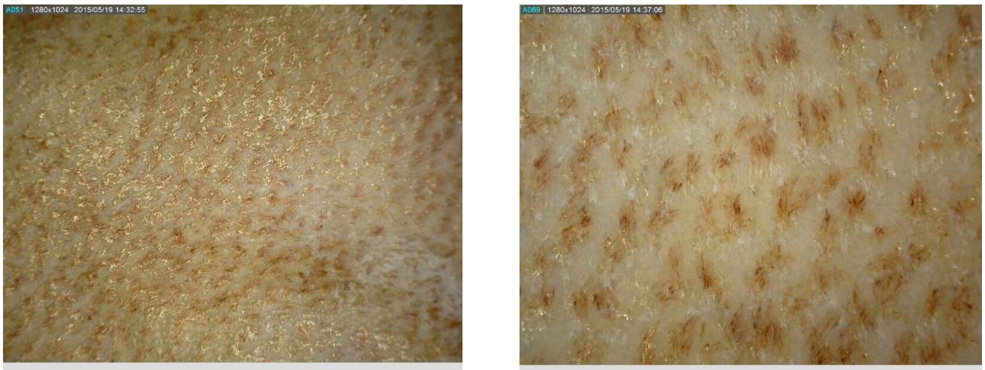
Assessment of Parchment Conservation State

The document has a regular shape (a length of 63.2 cm and a width of 63.1 cm), with a thickness of about (0.22 -0.31) mm, which may indicate the use of an old animal skin. The parchment is prepared for writing only on the *corium* side, with a matte appearance and white color. On the hair follicles side, the parchment has a granular, waxy appearance (Figure 1). The microscopic investigation of the hair follicles pattern revealed that the parchment was made of goatskin (Figure 2).



(a) (b)

Figure 1. The historical parchment document belonging to the National Museum of Romanian History: (a) front image and (b) back image



(a) (b)

Figure 2. Microscopic images: (a) 50x and (b) 150x, showing typical goat skin arrangement of hair follicles

The parchment exhibits just a few manufacturing defects, such as calcium carbonate deposits obstructing the hair follicles openings and a hole (Figure 3). Uneven calcium carbonate deposits on the surface of parchment can be attributed to the reaction between residual calcium hydroxide from the manufacturing process, which was not thoroughly washed away, allowing it to penetrate the fiber structure of the hide and hair follicle orifices, and carbon dioxide from the air. Additionally, the presence of calcium carbonate may result from the use of chalk powder during the finishing stage to bleach and degrease the parchment [2, 10]. The oval-shaped hole (Figure 3) was formed while the parchment was drying under tension on a wooden frame, whether circular or rectangular. At this stage, the still-wet hides are smoothed out by scraping with a crescent-shaped knife known as a *lunellarium* [1, 2, 10], which carries the risk of overly thinning certain areas and consequently leading to the formation of holes. Controlled, slow, and gradual drying, away from sunlight and in an environment with good air circulation, prevented contraction caused by excessive water loss, thereby ensuring the superior quality of the final product [2].

Figure 3. Manufacturing defects specific to parchment: calcium carbonate deposits in hair follicles orifices, and hole formed during drying under tension

The visual examination of the parchment document indicates a rather good conservation state. However, the document has been kept in folded form and therefore retains traces (holes and exfoliations) of this method of preservation (Figure 4). This preservation has helped to protect the written surface of the parchment, as surface degradation with the formation of oxidized fats and liquids spots has been reduced to the exposed area on the verso, which was in permanent contact with the environment (Figure 4).

Figure 4. Typical degradations of the parchment document: hole formed due to folding storage, exfoliation, oxidized fats and fat and liquids spots

Inks and Pigments Identification

The XRF spectroscopy was used to identify the inks (black and golden) and pigments (red, green, blue and golden) applied on the parchment document. Table 1 presents the chemical elements detected for each type of ink and pigment while their XRF spectra are shown in Figures 5 and 6.

Based on the XRF analysis (Table 1, Figure 5), the document was written using iron gall ink and gold-based ink [2, 3]. Iron gall ink typically consists of iron sulfate ($FeSO_4$), also known as green vitriol, galls (growths on oak trees caused by parasitic insect stings), Arabic gum, and a solvent like water, wine, or vinegar [10]. This ink was widely used in Europe from the Middle Ages through the 19th century.

The color palette of pigments applied on the parchment document includes red, green, blue and gold. By correlating XRF data (Table 1, Figure 6) with microscopic observations, the following pigments were identified: vermilion (HgS), a Cu-based pigment, a Co-based pigment, and fine gold powder. ATR-FTIR analysis of the blue area confirmed that the copper-based pigment is verdigris ($Cu(CH_3COO)_2 \bullet H_2O$). In the same area (Figure 7), calcium carbonate, calcium oxalate, and aluminosilicates were detected. The presence of calcium carbonate supports both microscopic observations and XRF results. Aluminosilicates could be from either surface dirt or fine pumice stone particles (amorphous aluminum silicate), which were used to create the parchment's velvety texture and microporous structure for ink and pigment adhesion [2] whereas calcium oxalate likely resulted from a fungal attack [11].

Table 1: XRF results for the pigments and inks

Area	Identified elements	Results
black ink	Ca, **Fe,** S, K, Pb, Cu, Zn, Sr	iron gall ink
golden ink	Ca, **Au,** S, Fe	gold-based ink
red	**Hg, S,** Ca, Au, P, K (Co, Fe, Cu, Cl)	vermilion
green	Ca, **Cu**, Au, K, P, S, Fe, Co	Cu-based pigment
blue	Ca, Hg, Au, S, Fe, K, **Co** (Cl, Cu)	Co-based pigment
golden	Ca, **Au**, P, S, Fe (Cl, Cu)	fine gold powder

Note 1. Ca and S elements are from the gypsum or chalk-based preparation layer. K comes from parchment.
Note 2. The chemical elements in brackets are present in very small quantities.

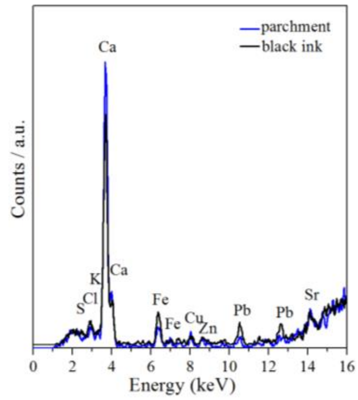


Figure 5. The XRF spectrum of the black ink as compared to that of parchment alone

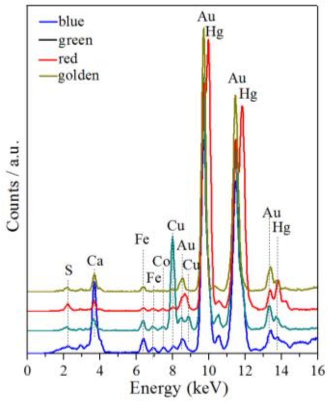


Figure 6. The XRF spectrum of the red, green, blue and golden colors

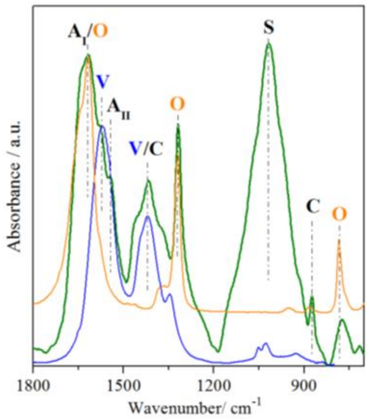


Figure 7. The ATR-FTIR spectrum of the green color (green line) as compared with those of verdigris (blue line) and calcium oxalate (orange line). Collagen absorption bands (A_I and A_{II}) as well as those attributed to verdigris (V), calcium oxalate (O), calcium carbonate (C) and aluminosilicates (S) are highlighted.

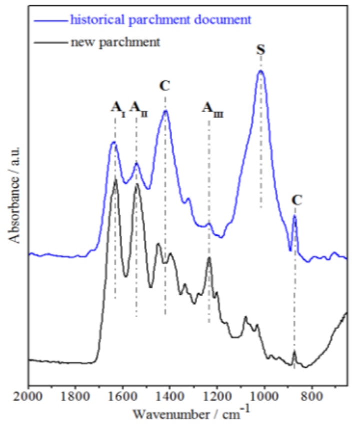


Figure 8. The ATR-FTIR spectrum of the historical parchment (blue line) as compared with that of a newly-manufactured parchment (black line). Collagen absorption bands (A_I, A_{II} and A_{III}) as well as those attributed to calcium carbonate (C) and aluminosilicates (S) are highlighted.

Molecular Alteration of Parchment

The main infrared absorption bands of collagen were used to identify the chemical modifications at molecular level. In Figure 8, the ATR-FTIR spectrum of historical parchment document is compared with the spectrum of a newly-manufactured parchment. The three specific bands of collagen, most commonly used in infrared protein studies, namely amide I, amide II, and amide III [12] are evidenced. The variation in the intensity and position of amide bands in historical parchment (Figure 8) is associated with a conformational re-arrangement of the native collagen molecules. This occurs as a result of the weakening and eventual breaking of covalent bonds within the helical chains of the collagen molecule [3].

CONCLUSIONS

In this study, optical microscopy, infrared spectroscopy in attenuated total reflection mode (ATR-FTIR), and X-ray fluorescence (XRF) spectroscopy were used to investigate a 17th-century chrisov written on parchment. The document was issued in 1660 by Ștefan Lupu, the prince (voivode) of Moldavia (1659-1661), and is part of the collection of the National Museum of History of Romania (MNIR) in Bucharest.

The chrisov, written on high-quality goat parchment, features a matte, smooth, and velvety surface. Despite traces of folding, the document is well-preserved, with the folds helping to protect the front of the parchment. Surface degradation, such as the formation of oxidized fats, is limited to the verso, which has been more exposed to environmental conditions.

ATR-FTIR analysis revealed only slight conformational changes in the native collagen molecules, attributed to the weakening and eventual breaking of covalent bonds within the helical chains of collagen.

XRF results identified the use of iron gall and gold-based inks for the text, while the ornaments were painted using vermilion (for red), verdigris (for green), a Co-based pigment (for blue), and fine gold powder. Both the inks and pigments are in excellent condition.

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