ASMAT GVAZAVA
Korneli Kekelidze Georgian
National Centre of Manudcripts,
Georgia
agvazava@manucript.ge

რევაზ კლდიაშვილი
Korneli Kekelidze Georgian
National Centre of Manudcripts,
Georgia
rezo.kldiashvili@yahoo.com

APPLICATION OF MODERN RESEARCH METHODS IN BOOK CONSERVATION-RESTORATION (STUDY OF THE 14TH CENTURY MANUSCRIPT [Q-1263] WITH XRF EDX 3600B) AND THE RESULTS OF IT)

The cultural significance of writing materials, particularly parchment and paper, in human history is immense. Manuscripts, printed books, and archival materials serve as crucial repositories of recorded history. In the digital era, conservation-restoration plays a pivotal role in material preservation, requiring specialist intervention. Various methods, including conservation, restoration, and prevention, contribute to heritage care. Modern research strategies, especially those involving interdisciplinary collaboration, offer more informative insights than visual studies alone.

Collaboration between the Scientific Laboratory of Conservation-Restoration at the Kekelidze National Center of Georgian Manuscripts and the “Republican Center for Diagnostics and Processing of Gemology and Mineral Substances Research” of the Technical University of Georgia is highlighted. Such studies are essential for the maintenance of material cultural heritage, involving conservation, chemistry, and biology laboratories. The complementarity of knowledge leads to new discoveries.

The paper emphasizes the importance of studying chemical effects on units due to environmental conditions and the processes employed by restorers to maintain or restore damaged units. This involves visual inspections, laboratory studies, and collaboration between modern research methods and restoration techniques. Microscopic studies of inorganic or organic elements in manuscripts provide crucial information about material production, aging, and deterioration causes. Critical observation of micrometric objects and structures reveals surprising insights, emphasizing the importance of understanding chemical components' origins for accurate conclusions.

DISCUSSION ON MATERIAL CULTURAL HERITAGE RESEARCH AND PARCHMENT ANALYSIS:

When delving into material cultural heritage research, particularly concerning historical monuments or written heritage, choosing a research method is challenging due to the need for a broad range of indicators without causing harm to the unit. For manuscripts, restrictions often prevent direct movement or removal of parts, making non-invasive methods crucial. The Conservation-Restoration Scientific Laboratory of the Kekelidze National Center for Manuscripts in Georgia emphasizes the integration of modern research methods in conservation-restoration.

An initial study on Georgian manuscripts focused on ink structure, utilizing scanning electron microscopy, probe microscopy, and force microscopy. Expanding this research, the team examined samples from various eras, including 14th-century etrat, 18th-century Hebrew manuscript paper, and 19th-century manuscript paper and cover fabric. The analysis aimed to understand the material characteristics of each era, comparing written source information with actual circumstances affected by time, environmental conditions, and material properties.

Before delving into research specifics, the paper briefly reviews the technology behind etrat-making. Understanding parchment properties is crucial for analyzing its status and damage. Mammalian skin, comprising epidermis, dermis, and subcutaneous tissue, exhibits collagen-rich dermis, keratin-rich epidermis, and fat-rich subcutaneous tissue. The research correlates directly with the material-making process, allowing the identification of chemical elements introduced during manufacturing or influenced by environmental factors over centuries.

Raw animal skin for parchment contains water, protein, fat, mineral salts, and other substances. Proteins include elastin, collagen, keratin, and non-structural proteins. While the basic structure is consistent, geographical or economic variations led different cultures to employ diverse minerals or solutions in the preparation process. Historical records and preserved recipes reveal cultural-specific techniques, contributing to the diversity of materials in manuscripts. The interplay between unique recipes, storage conditions, and the passage of time results in varying degrees and foci of damage in handwritten books and documents.

This comprehensive approach to material cultural heritage research highlights the importance of considering historical, geographical, and cultural contexts in analyzing and preserving valuable artifacts.

X-RAY FLUORESCENCE (XRF) SPECTROSCOPY ANALYSIS OF ETRATE COMPOSITION:

Etrate, primarily composed of collagen, undergoes a multi-step production process using animal skin, resulting in a product that reaches the skin layer. Processed parchment contains various compounds from the same leather (lipids, waxes, peptides) and production processes (salts and minerals such as Al, Si, Mg, K, S, etc.). These compounds leave traces that often create a challenging connection with the structure, making it difficult to identify their origin. Historical sources indicate the use of alkaline salts, such as lime and sodium chloride (NaCl), for etrate treatment. Post the 4th century, the removal of hair involved soaking animal skin in a calcium hydroxide solution, and calcium-based compounds were used to smoothen the surface, enhancing text writing.

The minerals determining writing material quality can become points of damage over time. The presence of potentially harmful mineral compounds in parchment materials can be challenging to assess due to the difficulty in determining the nature, origin, and dispersion of minerals in the organic matrix. This complexity may lead to false conclusions, highlighting the need for various research techniques in manuscript material analysis.

The choice of a specific device for cultural heritage object analysis depends on factors such as result accuracy, characteristic size, measurement location, and the necessity for non-invasive and safe procedures. In this study, the X-ray fluorescence analyzer (XRF EDX 3600B) was chosen for its non-invasive, non-contact, and non-destructive capabilities. The standard methodology (Khs. M. No. 1.G-18) was employed, using the EDX for Mineral and its Alloys - ORE (ores) and Soil (soil) program (ORE).

X-ray fluorescence spectroscopy is a powerful method for characterizing inorganic materials. While XRF can detect individual elements in inorganic materials, it does not detect the main elements (C, H) in organic materials. To overcome this limitation, energy dispersive X-ray spectroscopy (EDX) was incorporated into the study.

The analysis focused on a palimpsest specimen of the etrate (coded Q-1263) at the National Manuscript Center. Despite challenges such as non-portability and the need to bring manuscripts to the site, XRF EDX 3600B provided valuable insights into the chemical composition of etrate. This approach allows researchers to understand the historical production of etrate and the factors influencing its preservation or degradation over time.

It should also be noted that the research process is complicated by the fact that the analyzer (XRF EDX 3600B) is not a transportable technique and therefore it is necessary to bring the manuscripts to the site, in addition, EDX requires placing the samples in a vacuum chamber, which is against the principle of non-invasiveness, that is why taking samples from the manuscripts Minor details were removed only from areas that would not damage or change the authentic appearance of the original.

The analysis was carried out at the National Manuscript Center on a palimpsest specimen of the etratus coded Q-1263, which consists of 7 kefis, the text being executed in Nuskhur dates from the fourteenth century, and the etirat is of a much earlier period, a sample from the scroll was taken from the most damaged part of the first kefim totaling 2x3 mm. size

Research shows that along with organic material, the main chemical elements are silicon (Si), calcium (Ca), aluminum (Al), sulfur (S), sometimes more than one percent, and magnesium (Mg) in relatively small amounts (in the form of tenths of percent). Potassium (K), sodium (Na), iron (Fe), zinc (Zn), copper (Cu),

ნიმუშის დასახელება	ეტრატი (127)	ტესტირების დრო	200(s)	
კვების წყარო		სამუშაო პროგრამა	ORE	
ძაბვა	9(KV)	პროცესი	Admin	
დენი	150(μA)	ტესტირების თარიღი	1/24/2023 1:12:13 PM	
ელემენტი	ინტენსივობა	შემადგენლობა %		
Mg(%)	15.905	0.7263		
Al(%)	3.295	0.1118		
Si(%)	1008.04	2.3576		
P(%)	31.595	0.1360		
S(%)	57.73	0.7681		
K(%)	158.91786	0.4358		
Ca(%)	617.24	1.5971		
Ti(%)	4.40545	0.0884		
V(%)	1.62647	0.0000		
Cr(%)	0.91446	0.0087		
Mn(%)	2.34726	0.0937		
Fe(%)	29.4565	0.0000		

even smaller amounts of chromium (Cr), titanium (Ti), manganese (Mn), zirconium (Zr) and nickel (Ni).

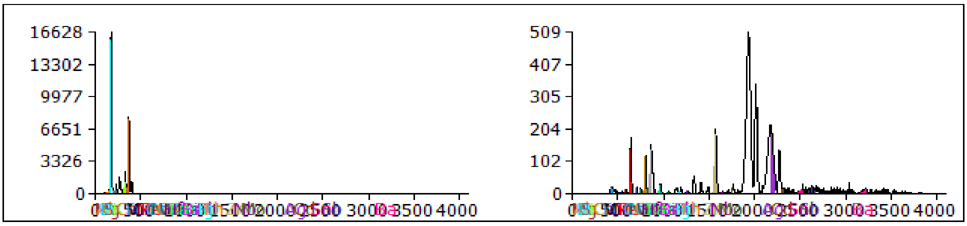
RESULTS OF XRF EDX 3600B ANALYSIS ON MANUSCRIPT ETHRATE (Q-1263):

The study of manuscripts, particularly at a microscopic scale, provides intriguing insights into the production of ethrate. In the case of ethrate, the research becomes more fascinating due to the historical recipes documented in ancient texts and foreign studies that detail the solutions used in the production of various parchment types. Different cultures introduced unique recipes, resulting in diverse materials. This discussion focuses on Ethiopian-made ethrate, which exhibits morphological features distinguishing it from Western or Jewish parchment and bearing some resemblance to Georgian ethrate.

While specific written sources on the use of lime in the initial stage of parchment processing in Georgia are not available, historical practices indicate the active use of lime, acidified milk, and various aqueous solutions in the leather tanning process. Fur and skin removal involved mechanical processes, such as stretching lame skin on a frame and scraping it with a pumice stone and sharp metal. Similarly, the Ethiopian production process did not include a lime bath or various chemical treatments. The leather underwent peeling on both sides after being stretched over a frame. The final step involved washing and cleaning both sides using knives, pumice stones, calcite, other stones, and herbal soaps until achieving a smooth, white surface resembling paper. The phytolacca plant served as a soap in this process, and sometimes castor oil was added to the phytolacca extract to enhance the surface's shine and increase parchment resistance to microorganisms.

The XRF EDX 3600B analysis was conducted on a palimpsest specimen of ethrate (coded Q-1263) at the National Manuscript Center. The results indicate the presence of various chemical elements, including silicon (Si), calcium (Ca), aluminum (Al), sulfur (S), magnesium (Mg), potassium (K), sodium (Na), iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), titanium (Ti), manganese (Mn), zirconium (Zr), and nickel (Ni). These findings contribute to a comprehensive understanding of the chemical composition of ethrate, shedding light on the historical production processes and factors influencing its preservation or degradation over time. The absence of lime and chemical treatments in both the Georgian and Ethiopian processes highlights the uniqueness of their parchment-making techniques, enriching our knowledge of cultural practices in manuscript production.

The chemical elements identified as a result of our research give us a certain idea about the processing and pollution centers of Georgian-speaking Palemsist etrate. The research showed that in the sample of etrate taken, together with the main chemical elements, there are: silicon (2.04%), calcium (1.59%), aluminum (0.11%), phosphorus (0.13%), sulfur (0.76%), magnesium (0.0.45%).), potassium (0.0.43%), zinc (0.084%), copper (0.028%), chromium (0.027%), titanium (0.08%), manganese (0.03%), zirconium (0.034%) and nickel (0.012%))



SPECTRAL IMAGE ANALYSIS OF MANUSCRIPT ETHRATE (Q-1263) WITH XRF EDX 3600B ANALYZER:

The examination of the Georgian ethrate manuscript (Q-1263) using the XRF EDX 3600B analyzer has provided valuable insights into its chemical composition. The spectral image reveals the presence of various chemical elements, including silicon (Si), calcium (Ca), aluminum (Al), sulfur (S), magnesium (Mg), potassium (K), sodium (Na), iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), titanium (Ti), manganese (Mn), zirconium (Zr), and nickel (Ni). These elements contribute to understanding the material's composition and offer clues about the historical processes involved in its creation.

Drawing a parallel between the Georgian and Ethiopian ethrate-making processes, a reference to an Ethiopian manuscript (Crypt.AET.7, 17th century) analyzed at the ICRCPAL Chemistry Laboratory for Conservation and Restoration is made. This Ethiopian manuscript displayed a yellow compound, identified as a mixture of saponins and castor oil, on its surface. Microscopic analysis revealed spherical micro-objects containing phosphorus (P), magnesium (Mg), calcium (Ca), and potassium (K), identified as spherulites, indicators of insect excretion. These spherulites, along with bilobate phytoliths associated with herbaceous plants, suggested the use of herbivorous animal waste, particularly animal manure, in the parchment production process.

In the Georgian ethrate case, the research material was obtained from a somewhat polluted sample. Considering the possibility of parallels with the Ethiopian process, the presence of spherulites on the Georgian ethrate's surface, indicated by phosphorus (P), magnesium (Mg), calcium (Ca), and potassium (K), raises the intriguing possibility of incorporating herbivorous animal waste in the leather processing. The identification of insect excrement during pre-restoration research further supports this hypothesis, aligning with the practices observed in Ethiopian parchment production.

This shared aspect between Georgian and Ethiopian ethrate production not only enriches our understanding of historical parchment-making techniques but also highlights the cultural and ecological considerations in these processes. The examination of spectral images serves as a valuable tool in uncovering such intricate details and drawing connections between seemingly distinct cultural practices.

HYPOTHESES REGARDING PHYTOLITHS, INK COMPOSITION, AND FURTHER RESEARCH:

The conclusion drawn from the analysis of phytoliths raises an alternative hypothesis suggesting that their presence might be attributed to ink made from burning herbaceous plants. However, studies have dismissed this notion, indicating that the carbon content in the ink of the Q-1263 ethrate does not originate from the burning of native weeds. Instead, the ink used in this Georgian manuscript is identified as iron-gallic ink, characterized by a mixture of plant extract and soluble iron.

Carbon ink, considered the oldest black ink type, is ruled out through a combined study of reflectography and X-ray fluorescence. Modern research methods, particularly Raman spectroscopy, sensitive to carbon pigments, provide unequivocal answers about ink composition. Iron-gallic ink, with two characteristic phases, proves to be the ink type employed in creating the text of the 14th-century Georgian manuscript. Its initial black color, akin to carbon ink, transforms over time due to oxidation, resulting in a yellowish-greenish haze around the text and a dark brown color for the ink itself.

While visual observation can often discern differences between carbon and iron-gallic ink, comprehensive laboratory studies are essential for precise conclusions. The current research, focused on one manuscript, acknowledges its limitations in providing a complete understanding of writing material production, causes of damage, and methods to mitigate aging processes. Generalizing findings from a single manuscript necessitates more extensive studies, involving larger portions of manuscripts to draw definitive conclusions.

The challenges associated with laboratory studies of cultural heritage monuments, including restrictions on sample collection, are acknowledged. Despite these obstacles, the ongoing efforts are seen as a slow but determined progression toward enriching knowledge about manuscript production, comparing laboratory findings with historical sources, and engaging in discussions from a historical perspective.

This study, though preliminary, lays the groundwork for future, more extensive examinations that can contribute to a deeper understanding of manuscript conservation, restoration, and historical production processes. It reflects the commitment to unraveling the mysteries of cultural heritage through a combination of historical, codicological, and laboratory studies.

REFERENCES

Zina Cohen, Composition Analysis of Writing Materials in Cairo Genizah Documents. Cambridge Genizah Studies, vol. 15; BRILL, LEIDEN | BOSTON 2019, pp. 36-52.

American Paper and Pulp Association. The Dictionary of Paper, including pulp, paperboard, paper properties and related papermaking terms. 3rded. New-York. 1965.

Hunter, Dard. Papermaking. The History and Technique of and Ancient Craft. Dover publications, New-York 1943 (1970).

Stutermeister, Edwin. The Story of Papermaking. R.R. Bowker Company, New-York, 1954.

Érica Mendes dos Santos, Lucas Malvezzi de Macedo, Louise Lacalendola Tundisi, Janaína Artem Ataide, Gisele Anne Camargo, Rita C. Alves, Maria Beatriz P.P. Oliveira, Priscila Gava Mazzola. *„The Journal of Materials Research and Technology"*, ELSEVIER, Volume 9, Issue 4, July–August 2020, pp. 9412-9421.

T. Kikutani. In Encyclopedia of Materials: Science and Technology, "Polymer Fibers: Formation and Structure", ELSEVIER, 2001.