INVESTIGATION OF SOME 17th LEATHER FRAGMENTS FROM SUCEVITA MONASTERY

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Rezumat: *Lucrarea prezintă cele mai importante analize fizice şi chimice efectuate pe pielea a două strane din secolul XVI-XVII, aflate în Muzeul Mănăstirii Sucevița. Investigațiile fizice au arătat că meşteşugarii au folosit piele de bovină (cornute), tanată vegetal, în timp ce analiza compoziției a relevat starea precară de conservare a pielii. Deshidratarea, pierderea elasticității, murdăria datorată rolului pe care-l au, pierderile de materie, ruperea sunt printre cele mai frecvente tipuri de degradări.*

Conservation state of pieces

The pieces, preserved in the main exhibition of Sucevita Monastery Museum, require an immediate intervention, because of their advanced state of deterioration state.

Photo1.Ensemble Analog/Sucevita

Photo2. Ensemble Analog/Sucevita

The leather covering the book's support (the mobile part) has 70% losses of material at the lower part (be ringed), and an advanced level of degradation:

dewatering, dirt and dust deposit (wax, smoke, fats), gren leather surface peeling, holes caused by boring insects, discolorations, grazes especially on selvages, absence of some clamping elements.

The leather that covers the plane wood surface under the mobile part of the Lectern is extremely fragile and brittle due to advanced dewatering of leather. Besides, it is rendered on about 30 cm, presents dirt and dust deposit, discolorations, numerous grazes, holes of boring insects, losses of material and of many clamping wood elements.

Physical investigations

From preliminary physical investigation at macroscopic and microscopic level, the analyzed leather has the aspect of bovine, more likely vegetable tanned in the technique used at that time. The typical aspect of the gren surface bovine leather was observed (in a slightly altered form due to damages), examination being made by comparing the stereomicroscopic images of the sample with a reference. (Photos 2, 3)

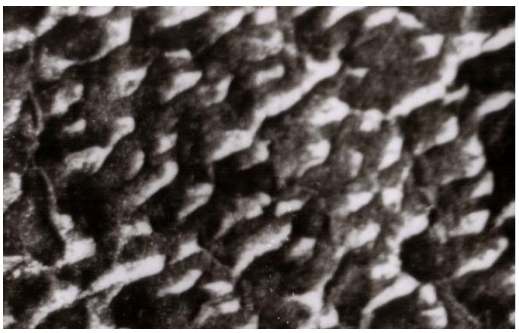

Photo 2. Sample bovine leather

Photo 3. Sample Lectern leather

The vegetable tanning was the prevalent technique used until chrome-tanning technique appeared in 1835. From both the aspect, color and the quality of leather and by considering the techniques used at that time it could be supposed that the leather was vegetable tanned. More detailed studies are need in order to identify the type of substance used for tanning, the respective results and methodology being the subject of a future presentation.

Chemical investigation of the adhesive

The results of chemical investigation (made by FTIR spectroscopy) for the adhesive used for the leather attachment to wood holder comes to support the idea that protein based glue was used. This was observed according to the signals after subtraction of calcium carbonate spectrum (Fig 1and Fig. 2). This was need due to band overlapping in the 1400 cm^{-1} region. However, even if the typical protein bands (≈1660; 1550; 1460 cm^{-1}) could be distinguished, it is difficult to attribute them to protein glue, as the same spectra is also typical for protein in leather.

On the spectra obtained, it could be also observed that no bands characteristic for vegetable glue (starch or other similar) are present.

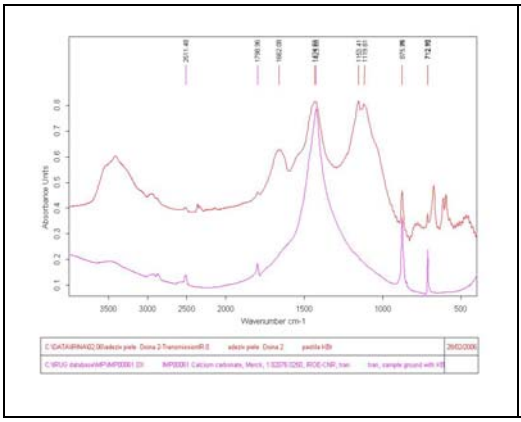

Fig. 1. Spectra corresponding to calcium carbonate

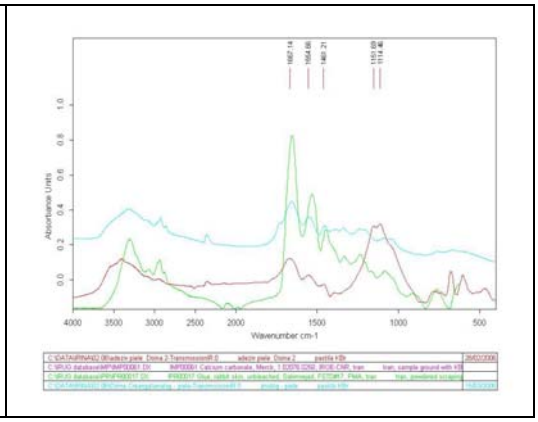

Fig. 2. Spectra of glue used for attaching the leather to wood.

Analysis were performed by is Fourier Transformed Infrared Spectroscopy (FTIR), transmitting mode, samples being mixed with KBr and analyzed in pellets. Results are obtained by interpreting the infrared spectrum acquired. This technique is limited at the compounds with characteristic bands in Mid-IR area (4000/400 cm -1). This does not exclude the presence of other compounds, under the detection limit of the method, or the presence of some compounds that do not positive rejoin in mentioned area. Samples are usually analyzed with complementary techniques in order to obtain a certain result but in this case no other technique was available.

Chemical investigation for composition

The chemical investigations were performed in order to obtain information on the type and quality of tanning and the conservation state of the Lectern's leather.

Chemical investigations were made by direct estimations in standard terms. In order to determine the conservation state of the piece according to leather composition, the results are displayed by comparison with two new, model prepared vegetable-tanned (chestnut tree and quebracho).

Results are displayed in the table below:

No.	Characteristics	Sample 1	Sample 2	Sample 3
1	Humidity	12,76	14,06	14,77
2.	Leaching substance	5,07-5,81*	12,24-14,24*	9,71-11,39*
3.	Total ashes	5,40-6,57	1,62-2,20	0,92-11,39
4	Insoluble ashes	0,92-1,12	1,14-1,55	0,44-0,58
5.	Dermal substance	49,23-59,91	50,3-68,25	53,11-70,33
6.	Total soluble substance	12,53-15,25	2,07-2,81	2,18-2,89

7	Mineral soluble substance	4,48-5,45	0,48-0,65	0,48-0,64
8	Organic soluble substance	8,05-9,8	1,59-2,16	1,70-2,25
9	Tanning substance	19,49	21,78	21,49
10	Tanning parameter	39,59	43,30	40,46
11	pH of aqueous extract	6,3	5,3	5,0
12	Shrinkage temperature	66ºC	84ºC	76ºC

*The values of ashes, nitrogen, dermal substance, and total soluble substance, mineral and organic soluble substance are reported to the leather free of humidity and leaching substance, and those for leaching substance to the leather free of humidity

Sample 1 – fragments from Lectern's leather from Sucevița
Sample 2 – new bovine leather quebracho-tanned
Sample 3 – new bovine leather chestnut tree-tanned

According to the data presented, the following observation could be made:

- the leather sample has a relative suitable content in dermal substance, which proves a few dermal substance losses, the collagen fiber having a rather good conservation state;
- the low level of the leather's content in fat leaching substance is good correspondence with the restorer's observations, the leather being very dry;
- comparing with the new hides, the low level of the shrinkage temperature prove the degradation and detaining of the Lectern's leather';
- the values of the soluble substance and those of pH denote an increase in susceptibility of the ancient leather to a new fungus attack, in auspicious conditions of humidity and temperature, which could be also confirmed by biological investigation.

Biological investigation

In the case of the Lectern preserved in Sucevita Monastery Museum the biological investigations were aimed to distinguish the material susceptibility at molds and the identification of the fungal types that grew there.

The leather has no an active fungal attack but, because of it's stiffness, the low of extractive fats and because the slightly acid pH, it can be supposed that these characteristics occurred after fungal surface attack in the past.

The fungal growth on the objects in a museum is caused by airborne fungi conidia – the hyphae may penetrate the porous substrate but do not digest their way into it. They may utilize sugars commonly used as fillers or free amino acids left by the tanning process between the collagen fibers. The fungi are only utilizing the amino acids freed by the bacterial degradation of the collagen, being often associated with badly degraded wet leather. The collagen may also have become soluble due to a chemically or physically deteriorating environment. There are a few fungi that can

break down the collagen – these are usually related to the tanning process during which the soaked raw hide is stored wet before tanning for long periods.

The attack of microorganisms varies depending on whether the skins were tanned or not. Bacteria under conditions of high humidity attack untanned skins. Tanned leathers are not readily subject to bacterial attack, but are degraded by fungi. Usually, after tanning, leather has a pH of about 3 to 5, which is more suitable for fungal growth, who require usually an optimal pH between 4 and 6. Vegetable-tanned leathers are more susceptible to fungal growth than chrome-tanned types because they contain some amount of glycosides.

Fungi that attack tanned leather often belong to lipolytic species and utilize the fats present in leather as a source of carbon. In this case the proteins are not directly affected, but can be damaged by organic acids released as a metabolic end products and the artifact becomes stained and stiff. The principal effects of microbial deterioration on proteic materials are the presence of different stained spots, loss in tensile strength, and, if the proteins are attacked, hydrolysis of the leather appears.

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