MULTI-ANALYTICAL STUDY OF THE ARCHAEOLOGICAL LEATHER DISCOVERED NEAR THE MEDIEVAL ORATEA FORTRESS

CRISTINA CARSOTE
ELENA BADEA
EUGEN S. TEODOR

REZUMAT

Recente cercetări arheologice realizate pe platoul aflat la est de cetatea medievală de la Oratea (Podu Dâmboviței, județul Argeș) au avut ca rezultat evidențierea unei poziții fortificate romane. Printre descoperiri se remarcă un fragment destul de mare din piele, aparținând primei faze de amenajare (începutul sec. II d.Chr). Descoperirea este una foarte rară, condițiile de sol și climatice adecvate prezervării obiectelor din piele fiind rareori întâlnite în România. Contactul cu atmosfera a determinat un proces rapid de deshidratare, conducând la fragmentarea materialului colagenic. Prin urmare, extragerea unor informații utile din aceste fragmente a necesitat o abordare multianalitică, primul pas constând în evaluarea stării de degradare. În acest scop au fost utilizate tehnici spectroscopice de analiză moleculară (spectroscopia în infraroșu cu reflexie totală atenuată, FTIR-ATR) și elementară (spectroscopia cu fluorescență cu raze X, XRF), microscopia de scanare cu electroni (SEM) și analiza prin micro-calorimetrie diferențială dinamică (micro-DSC).

Analiza comportamentului componentelor spectrale ale colagenului a permis detecția superficială a gelatinei, punând în evidență o pierdere aproape completă a structurii helicoidale a colagenului, în timp ce analiza micro-DSC a furnizat și o evaluare cantitativă a gradului de deteriorare a colagenului prin de-tabăcire, gelatinizare și transformare în masă amorfă. Caracteristicile morfologice și microstructura fragmentelor de piele au fost puse în evidență prin intermediul observațiilor SEM. Analiza XRF a furnizat și informații privind compoziția solului. În general, toate probele arheologice analizate prezintă o fragilitate extrem de mare și tendința de a se transforma în pulbere la uscare. Acest comportament este datorat structurii gelatino-amorfe a pielii, stabilizată doar de prezența componentelor minerale ale solului. Pentru a evita riscul pierderii acestor probe, autorii recomandă consolidarea prin încorporare de haloizit sau alte nanoargile, cât mai curând posibil după descoperire.

ABSTRACT

Recent archaeological excavations made on the plateau located east of the medieval fortress at Oratea (Podu Dâmboviţei, Argeş County) evidenced a fortified position of the Roman Age. Among other finds there is a relatively large leather fragment, belonging to the earliest phase (beginning of the second century AD). This discovery is extremely rare since suitable preservation conditions for leather are rarely meet in the specific soil and climate conditions in Romania. The contact with atmosphere induced sudden dehydration and consequent fragmentation of leather, which required a multi-analytical approach to extract useful information about its degradation condition. A combination of molecular (Fourier transform infrared spectroscopy in attenuated total refection mode, FTIR-ATR) and elemental (X-ray fluorescence, XRF) spectroscopic techniques with micro differential scanning calorimetry (micro-DSC) and scanning electron microscopy (SEM) was applied to this purpose.

FTIR-ATR analysis allowed us to detect gelatin on the samples' surface based on the collagen spectral components. Collagen extended de-tanning, gelatinisation and conversion into amorphous structures was quantified by micro-DSC. The alterations of leather microstructure and morphology were observed by high magnification SEM. XRF analysis also provided the elemental composition of soil. Overall, the archaeological samples shown extremely high fragility and the tendency to turn into powder on drying. This behaviour is due to the gelatinous-amorphous structure of leather strengthened only by the mineral components of the soil. Given the extremely high risk of loss, the authors recommend the application of a consolidation method based on halloysite and other nanoclays incorporation with utmost urgency.

CUVINTE CHEIE: piele arheologică, FTIR-ATR, micro DSC, XRF, SEM, degradare

KEYWORDS: archaeological leather, FTIR-ATR, micro DSC, XRF, SEM, decay

Introduction

Within the frame of HiLands Project[1] have been made diagnostic excavations near the Oratea Fortress (Middle Ages), on the eastern plateau, searching for a (previously unknown) Roman station of *Limes Transalutanus*, on the Rucăr-Bran Pass, at nearly 1000 m altitude. Near the precipice facing south it was revealed a palisade with no less than three different phases of development. The first phase – of interest here – is dated for the early second century AD, in the time of the Roman-Dacian wars or immediately later, controlling the only road driving to the pass. The wooden palisade had on top a roofed fighting platform, standing on several pillars, later put on fire. In one of the pit-holes of this building was found a relatively large fragment of leather,[2] about 300 sq. cm. The cold and wet environment could favour the conservation of the leather – a rare kind of discovery in Romania.[3] A second condition for this unusual preservation of leather is the depth, 85 cm below the surface. Although the object was kept in a wet package asfter the discovery, a travel in Bucharest was possible only after several weeks, and the decay was much faster than imagined, and it broken into small pieces.[4] The initial shape of the artefact – a sheet of about 20 x 15 cm, still of concave shape[5] – excludes the most usual uses of the leather within the military equipment, as shoes, belts or straps, our best guess being a cover for a shield.

As the find cannot be archaeologically studied, the surviving fragments were broght to a lab, hoping that some of the information can be recovered. The paper is describing this process.

Leather as material

The common occurrence of processed animal skins through time whether oil or fat cured skins, vegetable-tanned leather, alum-tawed leather or parchment attest to the enduring utility and desirability of animal skins as a material. A rather large variety of archaeological remains of shoes and garments, horse-gear, teints, shields, armour components, household objects, etc. made either entirely or partially from leather continue to be discovered and extracted from archaeological excavations. The most commonly leather items recovered during archaeological excavations are however shoes, tentage, waste from the processing of hides or leatherworking, and unidentifiable fragments.

As processed hide was one of the major materials in the past and it has been common practice to refer to any product made of animal hide as leather. Only vegetable-tanned leather can however be considered as true leather, since 'only vegetable tanning is capable of producing permanent and irreversible changes to the skin structure which are resistant to water.'[6] All other treatments – smoking, dressings of mineral earths, animals fats or oils – are 'pseudo-tannages' resulting in cured leathers which are not water resistant and will decay in waterlogged or damp conditions. *De facto*, the purpose of tanning is primarily to increase the hydrothermal stability of native collagen, secondarily to increase its biological inertness, and finally, to improve the utility of the hide's physical properties. Vegetable tannage with organic materials obtained from different parts of plants including woods, barks, fruits, fruit pods, seeds and leaves left to macerate in water was mostly used since the end of Neolithic[7] up to 19th century.

Leather was an everyday material used by people of all classes across the Roman empire. It was the main constituent of many essential items in both military and civilian contexts. The introduction of vegetable tanned leather and the expansion of ironworking were some of the major technological innovations of the Roman period allowing the mass production of sturdy footwear. The spread of vegetable tanning technology was almost certainly a consequence of the supply requirements of Roman imperial army. The Roman army's demand for leather was enormous. It is very likely that hides were sourced from across the empire (e.g. goatskins were probably supplied from north Africa and the eastern reaches of the empire, since there were not many goats in the north-west) but perhaps transported and tanned centrally by military owned/controlled tanneries.[8]

It has been suggested that the Quraysh tribe of southern Syria may have supplied large quantities of hides, tanned leather and/or manufactured leather goods to the Roman military in the east

---

[1] Abbreviation for Hidden Landscapes, 2018-2022, see https://hilands.net4u.ro/.

[2] For details of the archaeological report see Teodor 2022 (in this volume), especially Fig. 12, the western section of the Trench1, the G layer from the left side.

[3] There are quite few discoveries of the kind, for instance M-Kiss 2007, where many pieces of leather were partially preserved (about 150 fragments), especially late middle ages shoes, in a marshy environment. See especially the chapter related with environment conditions for leather preservation, 164-165. Note the high pH of the soil from the discovery area (table at the page 154), which is not the case here. .

[4] Note that although the leather was not directly touched by fire (being below the ground), at the time of the event it was located in a pit subjected to intense heat, which could play against its better preservation, dehydrating it.

[5] As it would have been caught under the pillar, very likely by accident.

[6] Sykes, 1991

[7] Forbes, 1957; Haslam, 1997

[8] Groenman-van Waateringe, 2007

However, it is also very probable that a proportion of the many leather items in use in Roman empire were locally made. The thick hides of cattle were an essential resource for the Roman military, while sheep hides were less valued than those of goats as they produced an inferior leather.

The tomb monument sculptures in the Roman province of Dacia Felix reveal numerous leather items such as clothing and accessories, i.e. sheepskin coats, fur hats, various belts, ribbons and straps, bags, decorated harness, saddles and saddle girths, a tympanum, suggesting the influence of Roman way of life.[9] Information on the footwear type was found in Apulum – Alba Iulia and Romula/Malva – Reșca and Sarmizegetusa (i.e., Caliga - a high boot with leather gaiters, corrigae, and sandals).[10]

The fact that leather processing and working was a local tradition is witnessed by the essential terms related to leatherworking, clothing and footwear making of both Dacian and Latin origin.[11]

It is worth mentioning that most of the archaeological leather items come from forts or *vici* –sites that were inhabited for many years, and often with more than one separate period of occupation. On these settlements, whether civilian or military, large deposits of rubbish would accumulate and often the leather could come of waste and discard.

The properties of leather are in part due to the intrinsic chemical, morphological and physical properties of collagen, a fibrous protein which is the main component of skin. Additionally, the method with which hide was processed and the species from which it originates highly influences the properties of leather. Through tanning, thermal stability and mechanical strength of hides are enhanced[12] allowing leather to well survive under extreme condition such as arid waterless area, waterlogged area, permafrost, peat bogs etc.[13] However, like any organic material, leather ages and deteriorates over time. External factors such as temperature, humidity, chemical pollutants, light, microoorganisms, unproper treatments and handling add to the ageing and deterioration processes and speed up the decay. In case of archaeological leather, the sudden change of the environmental conditions through exposure to the atmosphere could dramatically accelerate deterioration. The archaeological leather damage condition should therefore be evaluated with utmost urgency to define the optimal conservation conditions and prioritize possible conservation interventions.

In this study, we used a combination of molecular (Fourier transform infrared spectroscopy in attenuated total refection mode, FTIR-ATR)[14] and elemental (X-ray fluorescence, XRF) spectroscopic techniques with micro diferential scanning calorimetry (micro-DSC)[15] and scanning electron microscopy (SEM)[16] to assess the decay of several samples of archaeological leather discovered nearby the medieval Oratea Fortress, Romania and date from the beginning of the 2nd century A.D.

Methods

Microscopic examination

The microscopic[17] examination was carried out on both sides of the leather fragments *(*corium - the flesh side and grain – the hair side) to evaluate the surface features. It is worth mentioning that the identification of the animal species through the hair folicles specific pattern was not possible.

The microscopic observations were carried out at 50X and 200X magnification with a portable digital microscope Dino-Lite AD7013MZ, with a resolution of 1.3 Megapixels.

pH measurement

The pH[18] is a measure of hydrogen ion concentration (i.e., of the acidity or alkalinity) of water solutions. A pH value of 7 indicates that a solution is neutral; at pH lower than 7 the solution is acidic, while values higher than 7 indicates alkalinity.

Surface pH measurements on archaeological leather were performed with a Nahita model 903 benchtop pH meter equipped with a fat membrane ceramic electrode 901. Each measurement spot (1×1 cm) was damped with a

---

[9] Pop, 2013.

[10] Pop, 2013.

[11] Pop, 2013.

[12] Covington 2019, p. 195-202.

[13] Note yet that such extreme conditions are favourable for leather conservation, but they are not often recorded in Romania, and leather is a rare find.

[14] Vichi et al., 2018; Carsote et al., 2020; Proietti et al., 2020; Sebestyén et al., 2022; Vyskočilová et al., 2022.

[15] Carsote et al., 2016; Carsote and Badea, 2019; Carsote et al., 2021.

[16] Badea et al., 2019.

[17] Goffer 2007, p. 34

[18] Goffer 2007, p. 504

Fig. 1. Archaeological leather samples from the grain side (upper row) and the corium side (lower row).

droplet of water using a pipette. After 3-min extraction, the electrode was placed on the surface and the pH of the water film was measured. The pH value was obtained as the average between 3 measurements.

X-ray fluorescence (XRF)

X-ray fluorescence (XRF)[19] spectrometry is a non-destructive method widely used to determine the elemental composition of materials. In case of leather, the inorganic compounds could be identified.

XRF measurements were carried out using an Elio portable XRF spectrometer (Bruker). The system is composed of a X-ray source based on a Rh anode operating at a voltage between 10-50 kV and a current up to 200 µA for a maximal power of 4 W, and a Silicon Drift Detector with an active area of 25 mm². The source emission is collimated creating an analysis spot diameter of 1.2 mm on the sample at a working distance of 1.4 cm. Analyses were performed at 40 kV and 80 µA, with an accumulation time of 120 s.

Scanning electron microscopy (SEM)

The microstructure and the morphology of archaeological leather surface was examined by SEM using a FEI Quanta 200 microscope. Samples mounted on carbon stubs were observed at diferent locations at increasing magnification (from 1000X to 4000X). SEM observation were performed in low vacuum mode without the need of a conductive layer, at 10 keV accelerating voltage with a tungsten filament and working distance of 10 mm.

Fourier transform infrared spectroscopy in attenuated total refection mode (FTIRATR)

FTIR-ATR is a non-destructive method frequently used for the characterisation of historical and archaeological artefacts. The FTIR spectrum contains information regarding absorption in the infrared region of the functional groups within the molecules of the investigated sample. In the case of leather, the FTIR-ATR spectra provide information regarding the chemical changes which occur at the collagen molecular level (triple helix) and allow identification of materials added to leather during manufacturing or those formed during the deterioration processes.

FTIR-ATR measurements were carried out using an ALPHA FTIR (Bruker Optics, Germany) equipped with a Platinum ATR module. Spectra were recorded by co-adding of 32 scans in the range from 4000 to 400 cm^{-1} with a spectral resolution of 4 cm^{-1}. Opus 7.0 software (Bruker Optics, Germany) was used for the acquisition and processing of the spectra, while their graphic presentation was done with Origin 7.5 software.

Micro Differential Scanning Calorimetry (micro DSC)

DSC is a powerful quantitative technique which provides a measure of protein (i.e. collagen) hydrothermal stability and an indication of its long-term stability.[20] It is successfully used for damage assessment of ancient

---

[19] Goffer 2007, p. 35

[20] Miles 1993

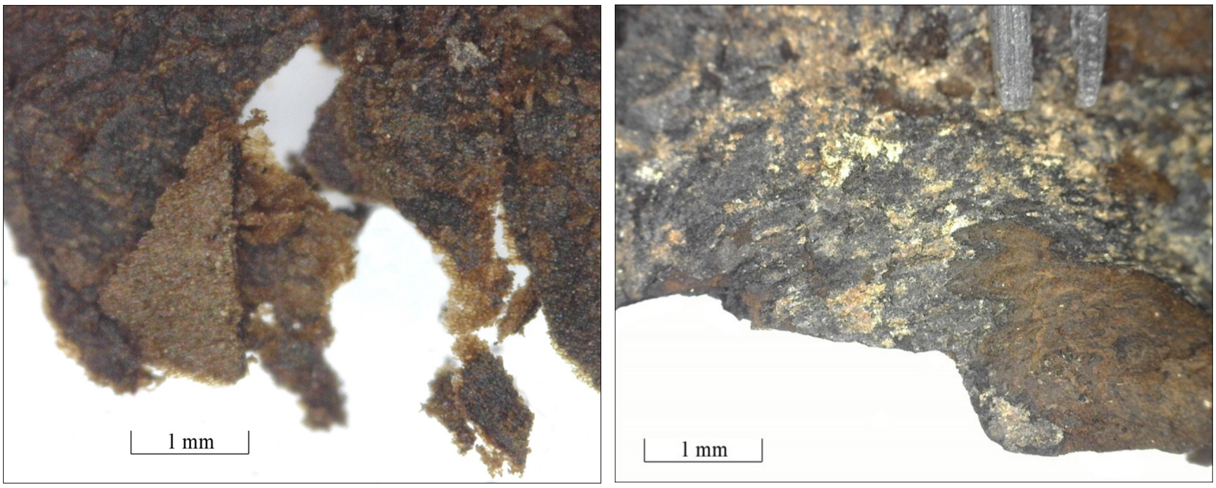

Fig. 2. Microscopic images of the archaeological leather samples
The corium side of the leather, without evidence of fibrous structures (left).
The grain side of the leather covered by a mineral crust (right)

collagen based materials (i.e. leather and parchment) based on the calorimetric parameters associate to collagen denaturation using micro-samples of only 1-2 mg.[21]

Micro DSC measurements were carried out with a high-sensitivity SETARAM Micro-DSC III calorimeter using 850 µl stainless steel (Hastelloy C) sample cells. Measurements were performed in the temperature range (5–95) ◦C at 0.5 K min^{-1} heating rate. Samples of about (2.0–5.0) mg were suspended in 0.5 M acetate buffer (pH = 5.0) directly in the measure cell and left for 2 h at 5 ◦C to assure fully hydration. At least two measurements were run for each archaeological leather sample. Experimental DSC data acquired with the SETARAM SetSoft2000 software were analysed with PeakFit 4.1 (Jandel Scientific) to obtain the specific calorimetric parameters of collagen thermal transition, while the PeakFit Gaussian algorithm was used to deconvolute the DSC multiple peaks of archaeological leather to identify the various collagen populations with different thermal stabilities.

Results and discussions

The macroscopic[22] and microscopic images of archaeological leather samples are presented in Figs. 1 and 2. The analysed leather samples of dark brown colour are stiff but brittle, with a high tendence to turn into powder, without evidence of fibrous structures. The loss of the fibre matrix cohesion makes leather very fragile and unstable. The pH values range between 6.0 and 6.3.

SEM analysis

The leather micromorphology observed by SEM (Fig. 3) shows a mineral crust (left side image) covering the leather (right side image) characterised by thin, fragile and swollen (gelatinised) fibres (indicated by the arrows) surrounded by extended melted/gelatinised areas.

XRF analysis

The elemental composition of both surface and inner layers of leather samples is reported in Table 1. In Fig. 4, the XRF spectra collected on surface and inner layers of a sample are compared. The higher Si, K, Fe and Ti concentration on the surface confirm the presence of a thin mineral layer adhering on the leather surface. Their presence in the inner leather indicate the minerals penetration in the structure and the loss of leather flexibility by a kind of cementation. The origin of Ca can be attributed to both leather composition (remains of slaked lime $Ca(OH)_2$ from the hide dehairing process) and soil composition (most probably a clay-limestone soil) (Fig. 4, Table 1 further).

---

[21] Badea et al., 2011; Carsote and Badea, 2019

[22] The both sides of the leather, corium (upper images) and grain (bottom images) are shown in Fig. 1.

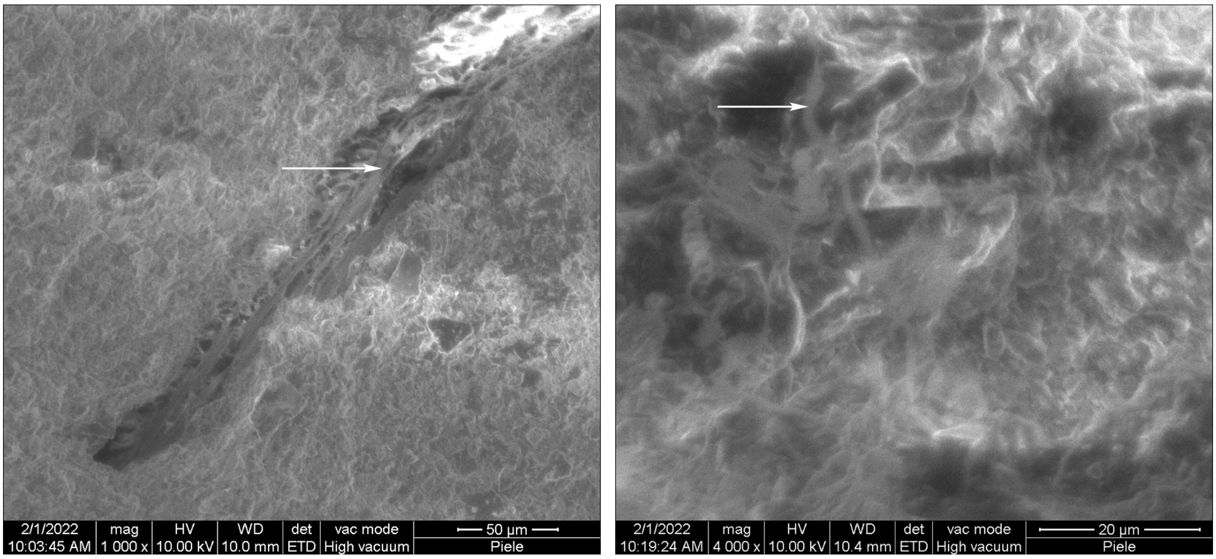

Fig. 3. SEM images of archaeological leather showing a mineral surface crust covering leather (left side, 1000X) and very thin and gelatinised fibres surrounded by extended melted/gelatinised areas (4000X).

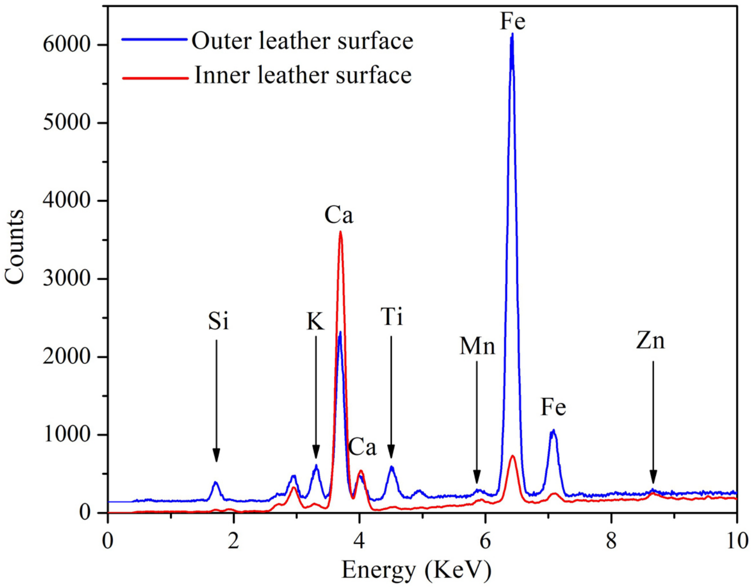

Fig. 4. XRF spectra of both outer and inner surfaces of the archaeological leather.

FTIR-ATR analysis

A FTIR-ATR spectrum collected from an archaeological leather sample is presented in Fig. 5 together with the spectrum of a new vegetable tanned leather. A leather tanned using hydrolysable-tannin was selected since the archaelogical leather presents some of the characteristic bands of hydrolysable tannins.[23] In general, collagen and tannin bands are considered for evaluating the deterioration degree in leather.[24] In fact, all main absorption bands of collagen[25], namely amide A (A_A): 3280 cm^{-1} (ν_{N-H}), amide B (A_B): 3070 cm^{-1} (δ_{NH2} overtone), amide I (A_I): 1635 cm^{-1}, amide II (A_{II}): 1541 cm^{-1} and amide III (A_{III}): 1234 cm^{-1} in the archaeological sample spectrum exhibit very low intensities compared to the same bands in the spectrum of newly manufactured leather. This cleary indicates the almost complete loss of the secondary structure of collagen and its conversion to gelatine.

---

[23] Falcão and Araújo, 2018.

[24] Vyskočilová et al., 2022; Sebestyén et al., 2022; Carsote et al., 2021.

[25] Barth, 2007.

Table 1. The elemental composition of outer (Fig. 1, upper row) and inner (Fig. 1, lower row) surfaces of the archaeological leather determined by XRF spectroscopy.

	Outer leather layer	**Inner leather layer**
Chemical element	*Concentration (%)*	*Concentration (%)*
Si	68.81	25.83
Ca	19.32	70.64
K	5.39	-
Fe	5.04	2.55
Ti	1.28	0.36
Mn	0.13	0.46
Zn	0.02	0.14

The archaeological leather spectrum also shows signals at ~2920, 2850 and 1735 cm^{-1} (ν^{a}_{C-H}, ν^{s}_{C-H} and ν^{s}_{C-O}) which are due to the waxy or fatty materials that could have been used in the manufacturing process (i.e., leather finishing) or as softening dressing (i.e., during leather lubrification). The high intensity bands at 1025, 525 and 464 cm^{-1} (ν_{Si-O}, $\delta_{Al-O-Si}$ and $\delta_{Si-O-Si}$) indicates the presence of aluminosilicates from soil (Fig. 5).

The second derivative FTIR-ATR spectrum of archaeological sample allowed us to identify a couple of the characteristic bands of hydrolysable tannins at 1708 and 1509 cm^{-1} (Fig. 6). These signals are so weak that it is difficult to identify them in the FTIR-ATR spectrum. This very weak tannin fingerprint suggests a massive de-tanning (breakdown of the interactions between collagen and tannin molecules), tannin hydrolysis (promoted by the slightly acidic soil) and their washout from leather due to the soil moisture.

The application of the second derivative analysis allowed us to better identify the amide I components and evidence the unfolding of the native left-handed triple helix and its conversion into random coil structures and gelatin. In fact, the collagen-to-gelatin conversion is supported by the lack of the amide I component at ~1650 cm^{-1} (signal assigned to the helical structure of collagen) and the presence of the amide I component at ~1628 cm^{-1} (signal assigned to gelatin).[26]

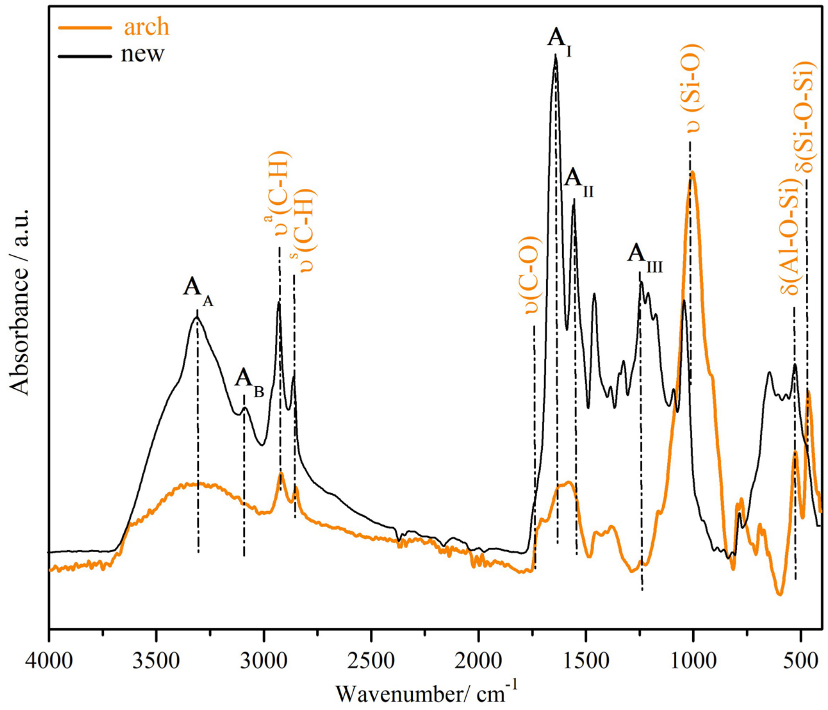

Fig. 5. FTIR-ATR spectrum of the archaeological leather sample compared with that of a new vegetable tanned leather. The amide bands of collagen (AI and AII), those assigned to the waxy or fatty substances (ν^{a}C-H, ν^{s}C-H and ν^{s}C-O), as well as the bands corresponding to the aluminosilicates (vSi-O, δAl-O-Si, δSi-O-Si) from soil are highlighted.

---

[26] Payne and Veis, 1988; Vichi et al., 2018.

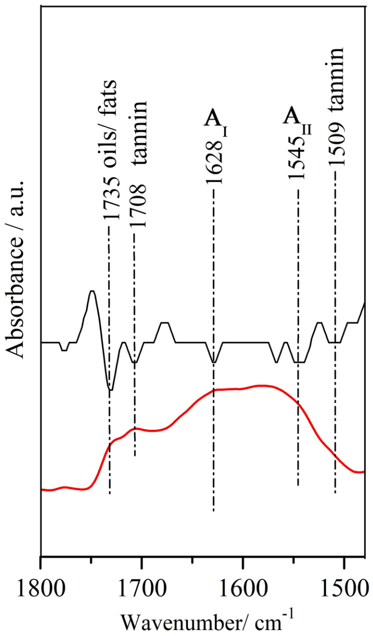

Fig. 6. FTIR-ATR spectrum of the archaeological leather sample (red line) and its second derivative in the (1800–1480) cm^{-1} region evidencing two bands typical of hydrolysable tannins (1708 and 1509 cm^{-1}) and the components at 1628 cm^{-1} and 1545 cm-1 of amide I (AI) and amide II (AII), respectively.

Micro-DSC analysis

In general, the hydrothermal stability of historical leather is evaluated by thermal microscopy, or the so called Micro Hot Table (MHT) method.[27] This method is widely used by conservators due to the low cost of the equipment and the ease of performing the measurement and interpreting the results.[28] However, in the case of archaelogical leather, whose fibre matrix is rigidized/cemented by minerals from soils, this method becomes unsuitable as reported by Vyskočilová et al.[29] We have therefore performed micro-DSC measurements to characterise the denaturation behaviour of collagen in the archaeological samples. Micro-DSC is a micro-invasive and micro-destructive technique, but has the advantage of providing a full picture of collagen condition, including damage quantification.[30] The transition of collagen macromolecules is revealed by micro-DSC as an endothermic curve at a defined temperatures, called denaturation temperature, T_{max}. This value mainly depends on the strengths of the collagen-tannin interactions.

In Fig. 7, the endotherm curve related to the denaturing process of collagen in the archaeological sample is compared to the endotherms of both damaged (historical leather)[31] and not damaged (modern vegetable-tanned leather) leathers. The endotherm of the archaeological sample is very broad and was deconvoluted as shown in Fig. 8. The correponding parameters of the different components of the broad curve are reported in Table 2. These parameters measure the stability of the collagen matrix stability (through the T_{max} and ΔH values) while at the same time provide a means to quantify the distribution of the various collagen population with distinct thermal stabilities (that is different structural stability/ integrity). In fact, the collagen-tannin bonds weaken as a result of ageing and deterioration, when collagen and tannin progressively detach until complete de-tanning. De-tanned collagen molecules denature at lower temperatures. They continue to deteriorate and form more and more thermally destabilized intermediate states that are easily converted to gelatin. This complex dynamic of deterioration was characterized and quantified by the decrease of T_{max} and variation of the percentage distribution of the various collagen populations with distinct thermal stability. Carsote and Badea[32] characterized the pattern of deterioration of a historical leather

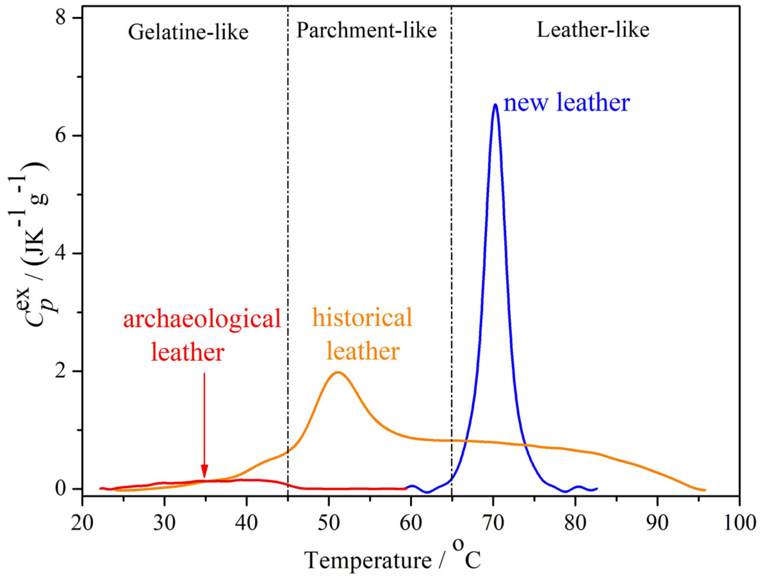

Fig. 7. Micro-DSC curve associated with thermal denaturation of collagen within archaeological leather sample compared to both damaged historical leather and modern leather tanned with hydrolysable tannin. Both historical and new leather show a net maximum of their curves, while a very broad curve was obtained for archaeological sample.

---

[27] Larsen et al., 1993; Larsen et al., 1994.

[28] Malea, 2010; Budrugeac et al., 2017; Carsote et al., 2018.

[29] Vyskočilová et al., 2022.

[30] Carsote et al., 2016.

[31] A sword hilt dated 1837, from the National Military Museum“Ferdinand I”, Bucharest.

[32] Carsote and Badea, 2019.

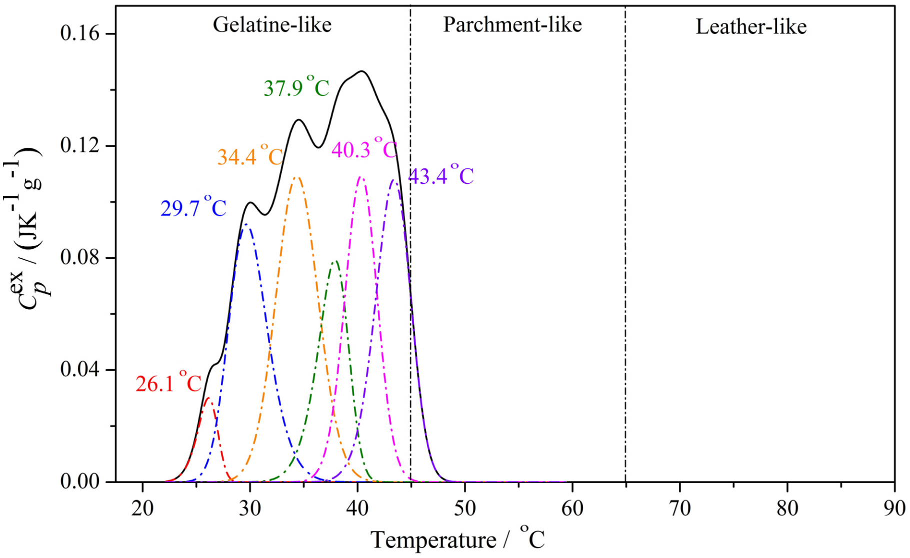

Fig. 8. Deconvolution of the archaeological leather DSC denaturation curve showing multiple denaturational transitions of collagen in the gelatine-like domain.

sample by deconvoluting its micro-DSC curve and calculating the denaturation enthalpy corresponding to the various collagen populations showing thermal transitions in the following temperature intervals:

- "Leather-like" (L) domain: 65 °C < *T* < 85 °C, where tanned collagen shows denaturation;
- "Parchment-like" (P) domain: 45 °C < *T* < 65 °C, where fully de-tanned collagen shows denaturation;
- "Gelatin-like" (G) domain: *T* ≤ 45 °C, where gelatinized collagen shows thermal transition. For all the archaeological leather samples, collagen populations shown thermal transitions in the gelatine-like domain.

The micro-DSC analysis can thus be interpreted as follows: all collagen in the archaeological leather is either in gelatinised or amorphous form. It should be mentioned that the amorphous collagen does no longer give a calorimetric signal. Actually, the very low enthalpy of denaturation of the archaeological leather is a net evidence of its amorphous structure prevalence.

Table 2. Thermal stability profiles of archaeological and modern vegetable-tanned leathers: overall denaturation enthalpy, ΔH; temperatures of denaturation, Tmax ; and percentage of each collagen population: leather-like population, parchment-like population and gelatine-like population.

Sample	ΔH / J·g^{-1}	T_{max} / °C	**Gelatine-like population**		**Parchment-like population**		**Leather-like population**	
			T / °C	%	T / °C	%	T / °C	%
New vegetable tanned leather	25.1	70.3					70.3	100
Historical leather	10.7	52.2	42.8	15	52.2	32	69.0 80.4	36 17
Archaeological leather	2.2	26-43	26.1	3.3	-	-	-	-
			29.7	19.2				
			34.3	24.7				
			37.9	13.3				
			40.3	18.0				
			43.4	20.5				

Conclusions

The analytical study and diagnosis of archaeological leather has as its primary purpose to pioritise and design its preservation and restoration, but the information that can be obtained in this way can also fall into many areas of past everyday lives such as crafts, animal resources, trade, climate, religion, preference for certain materials, including arts and fashion. In the case of archaelogical remains which has no longer an immediately recognizable form (i.e., shoes, bags, gloves, garments, harness, shield etc.), the analytical information could help to get more insight into the type of leather and its most probable use.

This work aimed to study the archaeological leather fragments discovered at Oratea, using a multi-analytical approach based on SEM, XRF, FTIR-ATR and DSC in order to provide the best insight into their deterioration. Examination of the fragments under the scanning electron microscope showed that the leather fibres are thin, fragile and gelatinised, and covered by a mineral crust. It is worth mentioning that due to leather condition, the identification of the animal species based on the hair follicle pattern observed under the microscope was not possible. The XRF results confirmed the mineral layer adhering on the leather surface, based on the identification of high Si, K, Fe and Ti concentration. The soil minerals were also detected in the inner leather structure indicated that its mechanical strengthening is due to the cementation efect. According to FTIR-ATR results, the collagen within leather is almost complete converted to gelatin suggesting a very high level of degradation. Collagen extended gelatinisation and conversion into amorphous structures was also identified by micro-DSC. Consequently, the first reccommended step should be the stabilisation and consolidation of leather fragments, preferably by applying a consolidation method based on halloysite[33] and other nanoclays incorporation.[34] A second analysis campaign will include Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)[35] and NMR analysis[36] to get more information on the tannin type and lipids content. The identification of the animal species of the skin could get insight into the animal exploitation in the area where the leather was found. Animal species identification is usually done through microscopy and, when the condition of leather no longer allows to visualize the specific pattern of hair follicules on the grain side of leather, through Zooarchaeology by Mass Spectrometry (ZooMS).[37] The latter method is based on the collagen analysis which shown to better survive archaelogical degradation then DNA. It, however, still has the drawback of being relatively labour intensive and is not yet applied to large scale.[38] Noteworthy, some limitations could appear due to the heavy damage of leather, for example the very low content of tannin may fall bellow the detection limits. Finally, the more fragmented samples could be used as study materials for MSc students in conservation science to be introduced to the theoretical background of the chemical, biological, archaeological and historical methods to be applied in order to answer materials and research questions.

References

Badea, E., Carsote, C., Habimbu, E., Sendrea, C., Lupas, M.C., and Miu, L., 2019. The effect of halloysite nanotubes dispersions on vegetable-tanned leather thermal stability, Heritage Science 7:68. https://doi.org/10.1186/s40494-019-0310-x.

Badea, E., Della Gatta, G., Usacheva, T., 2011. Effects of temperature and relative humidity on fibrillar collagen within parchment: a micro Differential Scanning Calorimetry (micro DSC) study. Polymer Degradation and Stability 97:346-53.

Baglioni, M., Poggi, G., Chelazzi, D., and Baglioni, P., 2021. Advanced Materials in Cultural Heritage Conservation. *Molecules* 26: 3967. https://doi.org/10.3390/molecules26133967

Barth, A., 2007. Infrared spectroscopy of proteins. *Biochimica et Biophysica Acta Bioenergetics* 1767: 1073–1101. https://doi.org/10.1016/j.bbabio.2007.06.004.

Brandt, L. Ø., Haase, K., and Collins, M. J., 2018. Species identification using ZooMS, with reference to the exploitation of animal resources in the medieval town of Odense, *Danish Journal of Archaeology* 7, 2: 139-153, DOI: 10.1080/21662282.2018.1468154

---

[33] Badea et al., 2019; Cavallaro et al., 2020.

[34] Baglioni et al., 2021.

[35] Sebestyén et al., 2022.

[36] Proietti et al., 2020.

[37] Brandt et al., 2018.

[38] Ebsen et al., 2019.

Budrugeac, P., Carşote, C., and Miu, L., 2017. Application of thermal analysis methods for damage assessment of leather in an old military coat belonging to History Museum of Braşov – Romania, *Journal of Thermal Analysis and Calorimetry* 127: 765-762.

Carsote, C., Badea, E., Miu, L., and Della Gatta, G., 2016. Study of the efect of tannins and animal species on the thermal stability of vegetable leather by diferential scanning calorimetry. *Journal of Thermal Analysis and Calorimetry* 124: 1255-1266. https:// doi.org/10.1007/s10973-016-5344-7

Carsote, C., Şendrea, C., Micu, M.C., Adams, A., and Badea, E., 2021. Micro-DSC, FTIR-ATR and NMR MOUSE study of the dose-dependent efects of gamma irradiation on vegetable-tanned leather: the infuence of leather thermal stability. *Radiation Physics and Chemistry* 189: 109712. https://doi.org/10.1016/j. radphyschem.2021.109712.

Carsote, C., and Badea, E., 2019. Micro diferential scanning calorimetry and Micro Hot Table method for quantifying deterioration of historical leather. *Heritage Science* 7, 48: 1-13. https://doi.org/10.1186/s40494-019-0292-8.

Carsote, C., Badea, E., Caniola, I., Paunescu, S., Lupas, M.C., Sendrea, C., and Miu, L., 2020. The Homiliary of Varlaam: scientific investigation of the leather bookbinding. *Revista de Chimie* 71, 3: 51–8. https://doi.org/10.37358/RC.20.3.7973.

Carsote, C., Kövari, L., Albu, C., Hadimbu, E., Badea, E., Miu, L., and Dumitrescu, G., 2018. Bindings of Rare Books from the collections of the Romanian Academy Library - a multidisciplinary study, *Leather and Footwear Journal* 18, 4: 307-320.

Cavallaro, G., Milioto, S., and Lazzara, G., 2020. Halloysite Nanotubes: Interfacial Properties and Applications in Cultural Heritage, *Langmuir* 36, 14: 3677-3689.

Covington, AD., 2019 Tanning chemistry: the science of leather. In: Wise W, Covington AD, editors. Cambridge: *The Royal Society of Chemistry,* 195-202.

Crone, A., Sands, R. and Skinner, T., 2007. The waterlogged wood assemblage. In: Thomas 2007b, 101-15.

Ebsen, J.A., Haase, K., Larsen, R., Poulsen Sommer, D.V., and Brandt, L. Ø., 2019. Identifying archaeological leather – discussing the potential of grain pattern analysis and zooarchaeology by mass spectrometry (ZooMS) through a case study involving medieval shoe parts from Denmark, *Journal of Cultural Heritage* 39: 21-31, https://doi.org/10.1016/j.culher.2019.04.008

Falcão, L., and Araújo, M.E.M., 2018. Vegetable tannins used in the manufacture of historic leathers. *Molecules* 23:8–10. https://doi.org/10.3390/molec ules23051081.

Forbes, RJ., 1957. Leather in Antiquity. Studies in Ancient Technology. 1st ed. Brill Publishers. Leiden: The Netherlands 5:1 −77.

Groenman-van Waateringe, W., 2007. *Leather.* In: Hanson, W. S. with Speller, K., Yeoman, P.A. and Terry, J., Elginhaugh: a Flavian Fort and its Annexe, Volume 2. London: Society for the Promotion of Roman Studies, 470-478.

Goffer, Z., 2007. Archaeological Chemistry 2nd Edition, John Wiley & Sons, INC.

Haslam, E., 1997. Vegetable tannage: Where do the tannins go?. *Journal of the society of Leather Technologists and Chemists* 81:45–51.

Larsen, R., Vest, M., and Nielsen, K., 1993. Determination of hydrothermal stability (shrinkage temperature) of historical leathers by Micro Hot Table technique. *Journal of the society of Leather Technologists and Chemists* 77: 151-156.

Larsen, R., Vest, M., and Nielsen, K., 1994. Determination of hydrothermal stability. In: Larsen R, Vest M, Kejser UB, editors. STEP Leather Project. *Evaluation of the correlation between natural and artifcial ageing of vegetable tanned leather and determination of parameters for standardization of an artifcial ageing method*. Copenhagen: Bjarnholt Repro, p. 151-164.

M-Kiss, H., 2007. Obiecte de piele, in F. Draşovean (editor), *Timişoara în amurgul evului mediu. rezultatele cercetărilor arheologice preventive din centrul istoric*, Timişoara: Mirton, 161-220.Miles, CA., 1993. *Kinetics of collagen denaturation in mammalian lens capsules studied by differential scanning calorimetry*. International Journal of Biological Macromolecules 15:265–71.

Malea, E., 2010. Assessment of physical condition of waterlogged archaeological leather. Proceedings of the *11th ICOM-CC WOAM (waterlogged Organic Archaeological Materials) Conference*, p. 571-594

Payne, K. J., and Veis, A., 1988. Fourier transform ir spectroscopy of collagen and gelatin solutions: Deconvolution of the amide I band for conformational studies. *Biopolymers* 27: 1749-1760.

Pollard, A.M., Batt, C.M., Stern, B., Young, S.M.M., 2007. Analytical chemistry in archaeology.

Cambridge University Press New York

Pop, M., 2013. *Paleology and old history of footwear in Romania*, Revista de Pielarie Incaltaminte

13(3): 235-246.

Proietti, N., Di Tullio, V., Carsote, C., and Badea, E., 2020. ^{13}C solid-state NMR complemented by ATR-FTIR and micro-DSC to study modern collagen-based material and historical leather. Magnetic Resonance in Chemistry 58: 840–859. https://doi.org/10.1002/mrc.5024.

Sebestyén, Z., Badea, E., Carsote, C., Czégény, Z., Szabó, T., Babinszki, B., and Jakab, E., 2022. Characterization of historical leather bookbindings by various thermal methods (TG/MS, Py-GC/MS, and micro-DSC) and FTIR-ATR spectroscopy, Journal of Analytical and Applied Pyrolysis 162: 105428. https://doi.org/10.1016/j.jaap.2021.105428.

Sykes, R.L., 1991. *The Principles of Tanning, in Leather its composition and changes with time*, C. Calnan and B. Haines Editors, The Leather Conservation Centre, Northampton.

Teodor, E.S., 2022. New research around the Oratea Fortress, *Cercetări Arheologice*, 29, 1 (this volume), 155-184.

Van Driel-Murray, C., 2001d. *Footwear in the North-Western Provinces of the Roman Empire*. In: Goubitz et al 2001, 337-76.

Vichi, A., Eliazyan, G., and Kazarian, S.G., 2018. Study of the degradation and conservation of historical leather book covers with Macro Attenuated Total Refection-Fourier Transform Infrared Spectroscopic Imaging. *ACS Omega* 3:7150–7157.

Vyskočilová, G., Ševčík, R., Carşote, C., and Badea, E., 2022. Burial-induced deterioration in leather: a FTIR-ATR, DSC, TG/DTG, MHT and SEM study, Heritage Science 10: 7 https://doi.org/10.1186/s40494-021-00638-6.

CRISTINA CARSOTE
Center for Research and Physical-Chemical
and Biological Investigations,
National Museum of Romanian History
criscarsote@yahoo.com

ELENA BADEA
Advanced Research for Cultural Heritage Group (ARCH Lab),
National Research & Development Institute for Textiles and Leather,
ICPI Division, Bucharest, Romania
Department of Chemistry, Faculty of Sciences,
University of Craiova, Craiova, Romania
elena.badea@edu.ucv.ro

EUGEN S. TEODOR
Institute of Archaeology, Bucharest
esteo60@yahoo.co.uk