Iron Age Fur Skin Tanning – a Sustainable Practice?

René Larsen[1], Anne Lisbeth Schmidt[2, 5], Martin N. Mortensen[3], Yvonne Shashoua[3], Dorte Vestergaard Poulsen Sommer[1], Jane Richter[4]

[1] Fonden Bevaring Sjælland, Videncenter for Bevaring af Kulturarven, Vasebækvej 30D, 4600 Køge, Denmark
[2] National Museum of Denmark, Conservation and Restoration, I.C. Modewegsvej 1, Brede, 2800 Kgs. Lyngby, Denmark
[3] National Museum of Denmark, Environmental Archaeology and Materials Science, I.C. Modewegsvej 1, Brede, 2800 Kgs. Lyngby, Denmark
[4] Royal Danish Academy, Conservation, Esplanaden 34, 1263 Copenhagen K, Denmark
[5] Corresponding Author (anne.lisbeth.schmidt@natmus.dk)

ABSTRACT

Tanning is among the most polluting industries in the world. Industrial-produced hides and skins are fully or pre-tanned with highly polluting chromium salts. The purpose of the study was to gain new knowledge about Iron Age tanning methods to clarify whether sustainable tanning methods can be developed based on this. Fur skin capes, uncovered in Jutland bogs, from Baunsø Mose (20-220 AD), Borremose I (365-116 BC), Huldremose I (1-174 AD) and Vindum Mose (386-203 BC) were analysed by Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR), Gas Chromatography-Mass Spectrometry (GC-MS) and morphological assessment of the skin fibres to identify tanning substances and material condition. Analyses were supplemented with source studies of previous visual assessment of the capes and measured shrinkage temperature of leather and skins excavated from bogs. Our results show that only the samples from Baunsø Mose, Borremose I and Huldremose I contain vegetable tannins. Furthermore, Baunsø Mose contains cow fat and Borremose I, Huldremose I and Vindum sheep fat. All contain indications of the presence of aluminum and iron compounds. The samples are decomposed to varying extents. Remnants from conservation were detected on Huldremose I, Baunsø Mose and Vindum Mose.

ARTICLE HISTORY
Received
13 October 2023;
Accepted
6 September 2024

KEYWORDS
Bog Find; Fur Skin; Vegetable Tannins; ATR-FTIR; GC-MS; Fibre Morphological Analyses.

Introduction

From ancient times until the 19th century, the tanning of hides and skins for leather and furs was mainly based on vegetable tanning substances extracted from local deciduous and coniferous trees, i.e., bark, wood, fruits, leaves, etc. Tanning methods involving smoke and fatty substances and tawing with alum were also used to preserve hides and skins (Reed 1972, 86-117). From 1830 to 1850, new fast methods transformed the European tanning industry, using overseas vegetable tannins, chemicals and modern techniques. However, the resulting leather had a shorter lifetime. At the beginning of the 20th century, tanning with chromium salts once again revolutionized the tanning industry in general (Aabye 1955, 97-98). Combined with the use of biocides, synthetic dyes, aluminum salts, etc., the tanning industry today poses a severe environmental burden for many countries especially in the Third World by exploiting the natural mineral resources and polluting the delicate environment. Worldwide, the disposal of toxic used waste products forms a significant challenge to societies and governments (e.g., described by Dixit et al. 2015; Sivaram and Barik 2019; Syed et al. 2010).

The current project aims to gain information from ancient but well-preserved fur capes from Jutland bogs, dated to the Danish Early Iron Age (500 BC-400 AD). The purpose is to investigate the original tanning methods that were possibly sustainable in utilizing local resources and producing minimum toxic waste. The project addresses the following UN Sustainable Development Goals: sustainable management of water (6), sustainable industrialization (9), responsible production (12), sustainable use of the oceans (14) and strengthening sustainable development (17) (United Nations). We intend to influence today's tanning industry towards sustainable production. By analysing

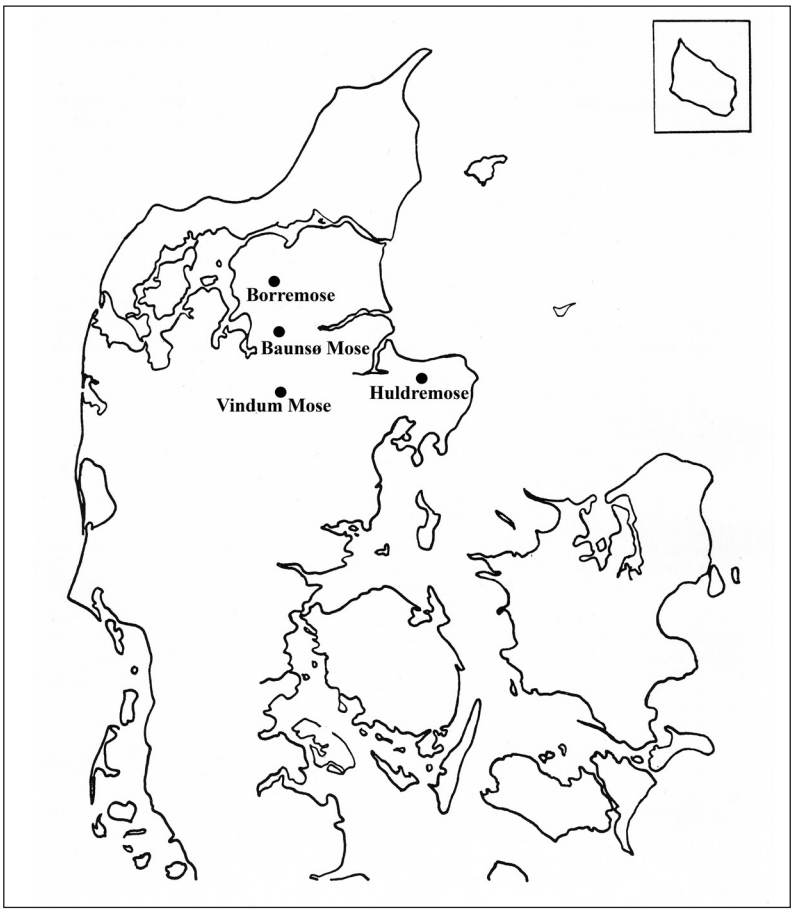

Figure 1. The four sites in Jutland, where the studied skin capes, dating from the Danish Early Iron Age (500 BC-400 AD), were recovered. After Hald 1980, p. 14.

samples from cohesive fur garments and fur fragments around 2000 years old from the collections of the National Museum of Denmark, we expect to identify for the first time, which tanning methods and tanning agents were used using Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR), Gas Chromatography-Mass Spectrometry (GC-MS) and morphological analyses of the skin fibres. The aim was to establish whether and, if so, which vegetable tannins are present. Can fatty and mineral substances perhaps used for tanning be identified? In addition, we aimed to estimate the extent of tanning and to assess the state of preservation in relation to long term stability and conservation strategies.

Materials

In Denmark, in the 19th and 20th centuries until 1953, numerous finds of well-preserved human bodies, some of them with garments and accessories of textile, de-haired skin or fur, were uncovered in bogs in connection to cutting peat for fuel. Most bog finds date from the Danish Early Iron Age. The finds were often excavated on the Jutland peninsula (Mannering et al. 2010, 262). The bog finds are described in numerous publications (e.g., Asingh and Lynnerup 2007, 290-301; Broholm and Hald 1940, 146; Ebbesen 2009; Fischer 2000, 105-125; Glob 1966, 52-83; Hald 1980; Jensen 2003, 176-185, 323-327; Munksgaard 1974, 126-128, 138-139; van der Sanden 1996; Thorvildsen 1952).

The National Museum of Denmark stores numerous skin and fur items from the bogs. In this study, we took one small sample of dermal skin from each of four garments for the above-mentioned analyses. Three samples were from fur capes: Baunsø Mose (D11103b), sample size ~4,5 x 7 mm, Borremose I (C26450), sample size ~2,5 x 4,4 mm, and Huldremose I (C3471), sample size ~3,6 x 8,7 mm. The fourth sample was a fur fragment from a cape or a wrapping skin from Vindum Mose (C5030), sample size ~6,8 x 15 mm.

All fur objects were found associated with bog bodies. See Figure 1 for the geographical location of the bog finds. The items are shown in Figure 2. The three capes (D11103b, C26450, C3471) had previously been identified for animal species by means of Mass Spectrometry of Peptide Sequence (MS-PS)

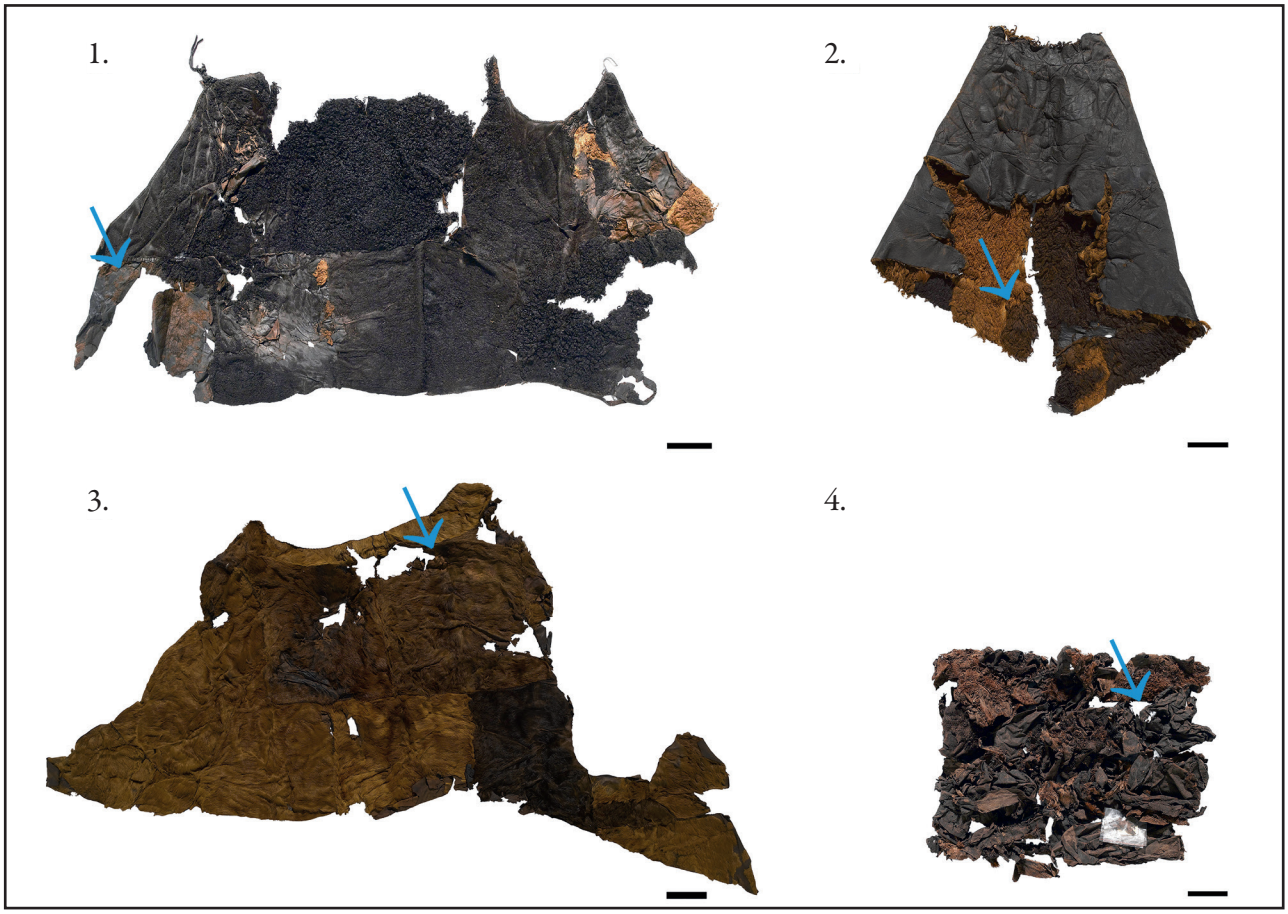

Figure 2. The four studied skin capes and fragments from the Danish Early Iron Age (500 BC-400 AD): 1) Baunsø Mose, 2) Borremose I, 3) Huldremose I and 4) Vindum Mose. The arrows indicate where the samples were taken. Bars = 10 cm (Photos: the National Museum of Denmark, Roberto Fortuna).

(Brandt et al. 2014), while the fragment (C5030) was identified through hair microscopy in transmitted light (internal notes at the National Museum of Denmark, publication in progress). Table 1 provides a survey of the analysed items. The skin samples have been buried in peat for approximately two millennia, which may have affected their properties and composition.

Analytical Methods

All analyses were performed starting with the non-destructive ATR-FTIR analysis, after which approx. 0.2 mg of fibres were used for the fibre morphological analysis and the remaining part of the sample for the GC-MS analysis.

Condition Assessment

Depending on colour, physical condition, etc., visual examination by naked eye and light microscopy may give some coarse information on the state of condition, material type and animal origin.

Method

The condition assessment of the archaeological fur skin was carried out as a visual examination and careful handling by hand by trained conservators. The flexibility of the skin, the cohesiveness of the fur layer to the skin and the tendency to shed hair or grain surface were assessed. Additionally, the possible presence of insect debris and fungal growth was noted.

Provenance Inventory no.	Object	Unearthed	14C dating	Species	Object dimensions (cm)
Huldremose I, Nimtofte, Djurs Nørre, Randers C3471	Asymmetrical inner fur cape	1879	350-41 BC[1]	Sheep[2]	Height 80 width 150
Borremose I, Aars, Aars, Aalborg C26450	Symmetrical fur cape	1946	365-116 BC[1]	Sheep[2]	Height 90 width 158
Baunsø Mose, Roum, Rinds, Viborg D11103b	Symmetrical fur cape	1927	20-220 AD[1]	Cattle[2]	Height 89 width 194
Vindum Mose Vindum, Middelsom, Viborg C5030	Fur fragments	1883	386-203 BC[1]	Sheep[3]	Not measurable

[1] ^{14}C dating (Mannering et al. 2010)
[2] Species identification (Brandt et al. 2014)
[3] Species identification (internal notes at the National Museum of Denmark)

Table 1. Survey of analysed items.

Analysis of Shrinkage Temperature Data

The use of the shrinkage temperature (Ts) as a criterion for whether skins are tanned or not tanned by burial in bogs has been subject to discussions (Thomson 2007; Ogilvie 2019, 74). To clarify this, we have analysed Ts data from previous measurements of the capes from Baunsø and Borremose I and the literature. Table 2 provides an overview.

Method

The method, used as a measure of the quality and hydrothermal stability of leather and skin, has proven also to be a fine measure of the degree of deterioration of these materials (Larsen et al. 1993, 151-155; Larsen 2000, 90-97. Upon degradation, the Ts and the shrinkage activity decreases. Untanned mammal skin has a shrinkage temperature of around 65 °C, new dehaired skin and parchment 55-60°C, new vegetable tanned leather 70-90°C and heavily degraded material may have a Ts below room temperature (Larsen et al. 1993, 151-152).

The shrinkage is a process taking place over several temperature intervals of increasing and decreasing activity. The start of the main interval, where the largest number of fibres shrink, is defined as the Ts. The measurement is performed by soaking the skin or leather fibres and heat them in the water, normally at a rate of 2°C/minute. However, the measurements of Borremose I and Huldremose I were performed using a Mettler Hot-Stage with a temperature rate of 3°C/minute (modified after Young 1990). The other samples were measured using a Mettler Hot Stage with a temperature rate of 2°C/minute according to Larsen et al. (1993, 151-152).

Fibre Morphological Analysis

Fibre morphological studies are widely used to identify the extent of degradation of skin and leather and have been used in several studies of historical parchment (Badea et al. 2012; Bell et al. 2018; Kern et al. 2018; Larsen et al. 2012; Mühlen Axelsson et al. 2012; Mühlen Axelsson et al. 2014; Mühlen Axelsson et al. 2017; Sommer et al. 2017) and more recently also in studies of vegetable tanned and non-vegetable tanned archaeological skins (Warming et al. 2020). The method is based on the observation of the morphology of separated corium

Item	Inventory number and object type	Ts (+/- 2 °C) and year of measurement	Vegetable Tannins
Borremose I	C26450, Cape	42,8 °C / 1995 (internal notes)	Yes
Huldremose I	C3471, Cape	48,2 °C / 2007 (internal notes)	Yes
Vindum Mose	C5030, Cape	31,0 °C / 2013 (Sommer et al., 2013)	No
Vester Torsted	Cape	42,5°C / 2013 (Sommer et al., 2013)	?
Baunegaard 1	Weapon shield	31,5 °C / 2019 (Warming et al., 2020)	No
Baunegaard 2	"	40,1 °C / 2019 (Warming et al., 2020)	No
Birka rim	"	36,9 °C / 2019 (Warming et al., 2020)	Yes
Birka facing	"	32,9 °C / 2019 (Warming et al., 2020)	Yes
Borremose 1*	"	- 2019 (Warming et al., 2020)	Yes
Borremose 2	"	47,2 °C / 2019 (Warming et al., 2020)	Yes
Borremose 3	"	51,1 °C / 2019 (Warming et al., 2020)	Yes
Borremose 4	"	50,8 °C / 2019 (Warming et al., 2020)	Yes
Tira 3	"	55,0 °C / 2019 (Warming et al., 2020)	No
Tira 5	"	55,3 °C / 2019 (Warming et al., 2020)	No
Tira 6	"	40,8 °C / 2019 (Warming et al., 2020)	No
Grauballe Man 1	Bog body	51,6 °C / 2005 (Larsen and Poulsen, 2007, 84)	Yes
Grauballe Man 2	Bog Body	56,8 °C / 2005 (Larsen and Poulsen, 2007, 84)	Yes

* Ts was not measurable due to severe degradation of the fibres.

Table 2. Shrinkage temperatures previously measured on tanned and untanned skins.

fibres in fully hydrated condition in excess water at ambient temperature. By uptake of the water, the fibres may transform into a range of morphological types in the form due to, e.g., swelling, shrinking, fragmentation and dissolution into a gelatinous substance, depending on the state of their condition.

Method

A 0.2 mg corium sample was taken out by careful scratching with the tip of a scalpel. The sample was placed on an object glass and covered completely with water and left to soak till the fibres were completely saturated with water (no fibres float on the water surface). Then the fibres were separated carefully using two preparation needles and covered with a cover glass. The fibres were assessed on 10-15 representative microscopical images recorded in transmitted light at x100 to x400 magnification.

The state of degradation is determined by judgement of the degree of the coherence of the fibre network, the degree of fragmentation and the type and extent of morphologies present that can be attributed to deterioration. Based on this, the samples can be roughly classified within the following five damage categories and assigned a score of between 1 and 5, with a condition between two of the categories assigned the value 0.5:

1. None or insignificant damage: Fibre network coherent, fibres intact and few fragments.
2. Slight damage: Less coherent fibre network with some fibres or part of fibres shrunken and more fragments.
3. Damage: fibre network poorly coherent and more fragmented with few intact fibres and/or part of fibres. Majority of fibres and fragments are shrunken, partly gelatinised and containing, to a minor part, frayed and/or uncoiled forms, flat, pearls on a string flat, and butterflies.
4. Severe damage: Minority of fibres intact and very little remaining of fibre network. Most fibres and fragments are shrunken and gelatinised to vari-

ous degrees as well as in the form of the morphologies mentioned in 3 and may appear as individual free and/or in bundles "glued" together.

5. Complete damage: Fibre network is completely fragmented, disconnected and/or in smaller bundles, normally in a high to completely gelatinised condition. In some cases, the fragmentation is complete with a lower degree of gelatinisation due to crosslinking caused by oxidative reactions.

ATR-FTIR Analysis

FTIR spectroscopy has been widely used to study the chemical structure and degradation of proteins and skins showing that changes in chemical structure may be attributed both to applied surface treatments and the surrounding environment (e.g., Haris and Chapman 1995; Jackson and Mantsch 1995; Kong and Yu 2007; Usoltsev et al. 2019).

The method was used in studies of the deterioration of parchment, vegetable tanned leather and other collagen-based materials (Badea et al. 2008; Boyatzis et al. 2016; Carsote et al. 2012; Derrick 1991; Odlyha et al. 2009; Plavan et al. 2010; Rowe et al. 2018; Sommer et al. 2017; Vandrucci et al. 2020; Vyskocilová et al. 2019; Warming et al. 2020) and to identify lipids in the form of fats and oils (Che Man and Mirghan 2001; Guillen et al. 2003; Nina Naquiah et al. 2017; Portaccio et al. 2023; Rohman and Che Man 2010; Safar et al. 1994; Tatulian 2019; Van de Voort and Sedman 2000).

Furthermore, the method has also been used to identify vegetable tannins in cultural heritage leather and skin materials (Carsote et al. 2012; Falcao and Araujo 2014; 2018; Ricci et al. 2015; Warming et al. 2020) as well as aluminum and iron compounds (ChemicalBook spectra base; Farahmandjou et al. 2020; Veneranda et al. 2018; Wiley spectra base).

Method

The samples were analysed on a Perkin-Elmer Frontier FTIR spectrometer fitted with a Universal ATR accessory with a diamond internal reflection element and adjustable pressure. Pressure was adjusted manually to maximise energy absorbance and minimize noise. All samples were analysed using 20 scans in the spectral range 4000-650 cm^{-1} with a resolution of 4 cm^{-1}. Five spectra were run for each sample and an average produced.

Analysis of the Spectra

FTIR spectra of skin and especially tanned skin are characterized by intensely overlapping bands that confuse interpretation. These can be resolved by calculating the second derivative of the spectrum (Baldassarre et al. 2015; Cameron and Moffatt 1987; Dong et al. 1995; Susi and Byler 1988; Usoltsev et al. 2019). One of the main advantages of the analysis of the second derivative is that it can be performed objectively without an arbitrary choice of deconvolution parameters (Usoltsev et al. 2019). Moreover, the maxima of overlapping bands are shifted compared with the true maxima, the effect of which can also be corrected by using the second derivative. The calculation of the second order derivative and other data processing such as baseline correction, peak search, normalization etc. were performed using OPUS/IR, FTIR Spectroscopy Software Package version 8 from Bruker.

The calculation of the second derivative was performed to identify key markers for collagen (Vindum Mose), vegetable tannins (Baunsø Mose, Borremose I and Huldremose I), animal fats, aluminum compounds and iron compounds (all four samples).

To evaluate the condition of the collagen, the position and intensity of the following bands of were recorded. The major amide I band (AI), found between 1680 and 1610 cm^{-1}, is mainly associated with the C=O stretching vibration related to the protein backbone and is sensitive to protein conformations (Vadrucci et al. 2020). The major amide II band (AII) found between 1540 and 1500 cm^{-1} associated with the N-H bending vibration and from the C-N stretching vibration, depending on the conformation adopted by the peptide (Jackson and Mantsch 1995; Tatulian 2019). The relative intensities and shifts of these two bands provide information on the protein denaturation. Thus, the intensity of the AI band decreases significantly relative to the AII band due to hydrolysis of the collagen while changes in the original positions of the AI and AII main FTIR peaks ($\Delta\nu$) indicates gelatinization (Derrick 1991; Odlyha et al. 2009; Plavan et al. 2010; Vadrucci et al. 2020;

Vyskocilová et al. 2019). Oxidation of the amino acid residues and the polypeptide chain results in the formation of carbonyl compounds absorbing in the 1700-1750 cm^{-1} region. Thus, increase of the band at about 1720 cm^{-1}, is related to oxidation of side chain groups, and the relative extent can be calculated as the proportion of the band intensities, AI/1720 (Vadrucci et al. 2020).

GC-MS Analysis

Various analytical procedures are widely applied in museum contexts and involve GC-MS. These often aim at characterizing organic chemical constituents in museum objects from paintings to ethnographica (e.g., Mills and White 1999). In the present study, the method using the following protocol was applied.

Method

Three extractions were carried out on each sample. The first one was with dichloromethane (DCM) to isolate nonpolar substances. The second extraction used a mixture of water and acetone to isolate more polar components. In the third extraction, methanol with sulfuric acid was used to methylate by transesterification and to extract. The extracts were derivatised and analysed by GC-MS

Samples from Baunsø Mose, Borremose I, Huldremose I and Vindum Mose were placed in a 2 mL GC vial which was then filled with dichloromethane (DCM) and placed in an ultrasonic bath for ca. 4 hours and then left to settle overnight. The clear solvent was isolated in a new GC vial and evaporated to dryness under a gentle stream of nitrogen. The extraction was repeated with a mixture of acetone and water (50/50) in an ultrasonic bath for 4 hours and left overnight after which the solvent was isolated and evaporated under a stream of nitrogen gas.

The two condensates were silylated by adding 10 µl internal standard (0,62 mg/ml deuteropalmitate CAS 39756-30-4 d31 in MTBE (methyl tert-butyl ether)) and 70 µl anhydrous pyridine. The contents of the vials were mixed thoroughly until everything was dissolved. 70 µl N, O-Bis(trimethylsilyl)trifluoro-acetamide with trimethylchlorosilane (BSTFA+TMCS) was added, mixed and left with a tight lid on a heating block at 70°C for 60 minutes. After cooling the liquid was evaporated to dryness under a gentle stream of nitrogen. The condensate was re-dissolved in 0,5 ml n-hexane using ultrasonic bath and whirl mixer and centrifugated for 5 minutes at 5000 rpm to clear the solvent, which was then isolated in a new GC vial and analysed on GC-MS.

The skin sample that has been extracted twice was dried under a stream of nitrogen. Then 10 µl intern standard (0.56 mg/ml deuteropalmitic acid) and 0.5 ml methanol were added. After whirly mixing for a minute, 25 µl 96% sulfuric acid was added. The vial was left on a heating block at 70°C for 2 hours. The solution was extracted with 3x500 µl hexane and then isolated in a new GC vial after the two phases have settled. The hexane was evaporated under a stream of nitrogen and the condensate re-dissolved in an appropriate aliquot of hexane and analysed on GC-MS.

The GC-MS instrument was a Bruker SCION 456GC-TQMS equipped with a Restek Rtx-5 capillary column (30 m, 0.25 mm ID, 0.25 µm) programmed for a 1 ml min^{-1} helium flow. 1 µl sample was applied on the PTV (Programmed Temperature Vaporization) injector, which was held at 64°C for 0.50 min, raised to 315°C at 200°C min^{-1} and held at that temperature for 40 min. The split ratio was 10 the first 0.5 min and then switched to 5. The GC oven temperature was held at 64°C for 0.5 min, then raised to 190°C at 10 °C min^{-1} and then to 315°C at 4°C min^{-1} and held at that temperature for 15 min. The EI (electron ionisation) source temperature in the mass spectrometer was 250°C and the ionisation potential was -70 eV. The mass spectrometer was operated in the full scan mode from m/z 45 to m/z 800. Peaks were identified using the NIST 2.0 MS database.

Results and Discussion

Condition Assessment

The visual inspection indicated that the Baunsø Mose, Borremose I and Huldremose I capes were in good condition: cohesive and not fragmented, and without pest or fungi infestations. The Baunsø Mose and Borremose I capes had no evident traces of daily wear, while the Huldremose I cape contained 24 patches of furred sheep skin, sewn with coarse stitching to the original worn garment. Regarding

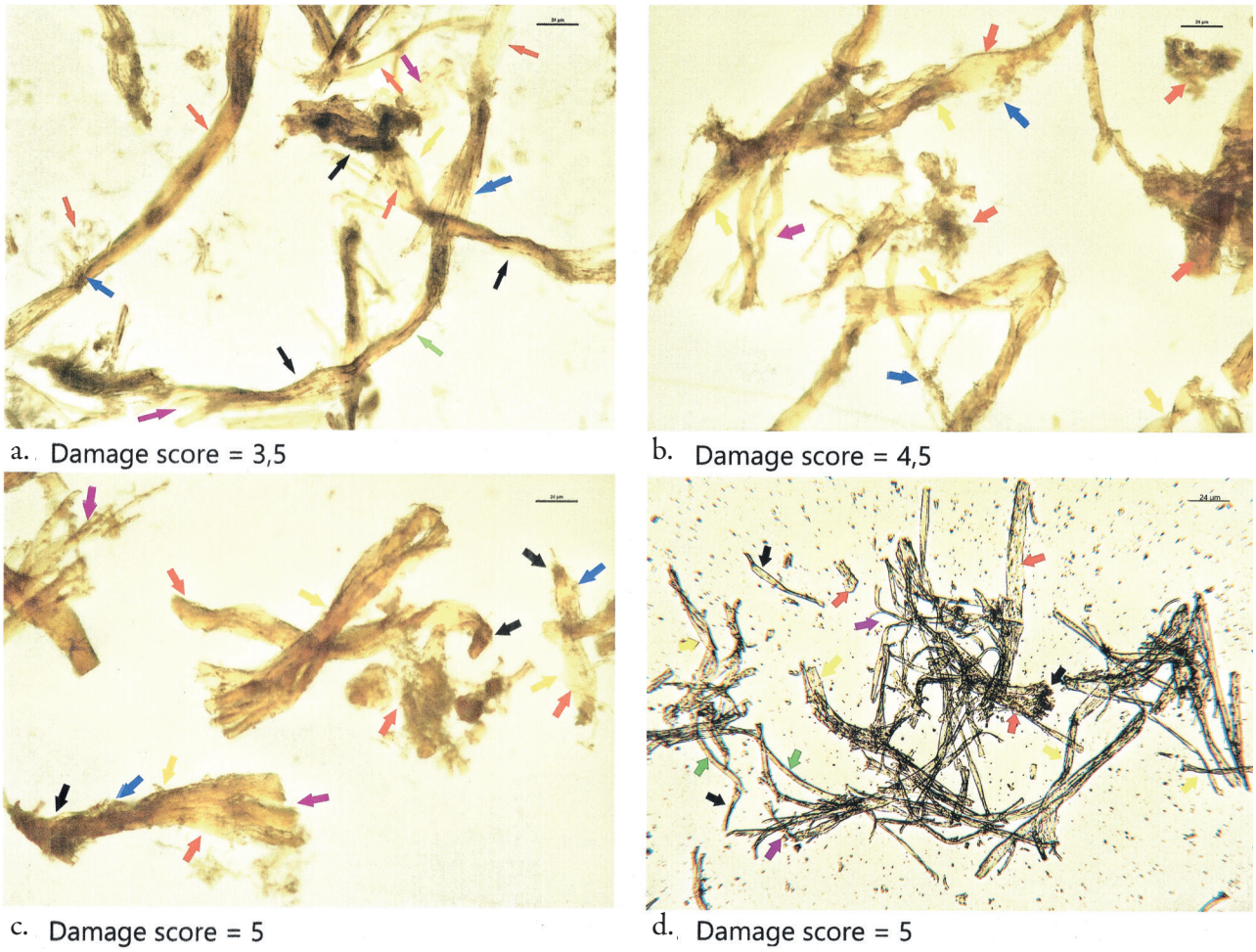

Figure 3. Examples of fibre samples in different degree of deterioration: a.- c. New vegetable tanned leathers deteriorated by hydrolysis and oxidation. d. Historical parchment deteriorated by hot storage condition. Morphological types: Intact → Shrunken → Frayed → Split → Pearls on a string → Butterfly → Gelatinised → (Photos: a-c Bevaring Sjælland, René Larsen and d Kunstakademiets Konservatorskole, Kathleen Mühlen Axelsson).

wear and tear, assessing the Vindum Mose fragments was impossible.

Analysis of Shrinkage Temperature Data

Table 2 shows Ts measured Early Iron Age leathers and skins excavated from bogs. It should be mentioned that the samples from the Grauballe Man were taken from the stomach skin. This bog body was tanned with oak bark extraction in water for 18 months in the years 1953-1954 (Strehle 2007, 43).

As seen, the highest Ts values were measured on samples of Grauballe Man and Tira, the latter of which the fibre morphological analysis and IR spectrum did not show any signs of vegetable tannins (Warming et al. 2020, 188 and 195). Furthermore, there are more than 10°C difference between some of Baunegaard and Tira subsamples.

To test the difference vegetable tannins vs. no vegetable tannins, the data was analysed using a paired samples t-test to test the null hypothesis (H_0) that the population mean of the difference between paired observations equals = 0. The analysis resulted in a probability $p = 0{,}8807$ at a 95% confidence interval and a difference in mean of 0.900. It should be noticed that the accuracy of the method is +/- 2°C. Thus, there is most likely no difference between the Ts values of the samples containing vegetable tannins and those containing none.

Fibre Morphological Analysis

Figure 3 shows comparable examples of fibres from three recently vegetable tanned leathers, aged by

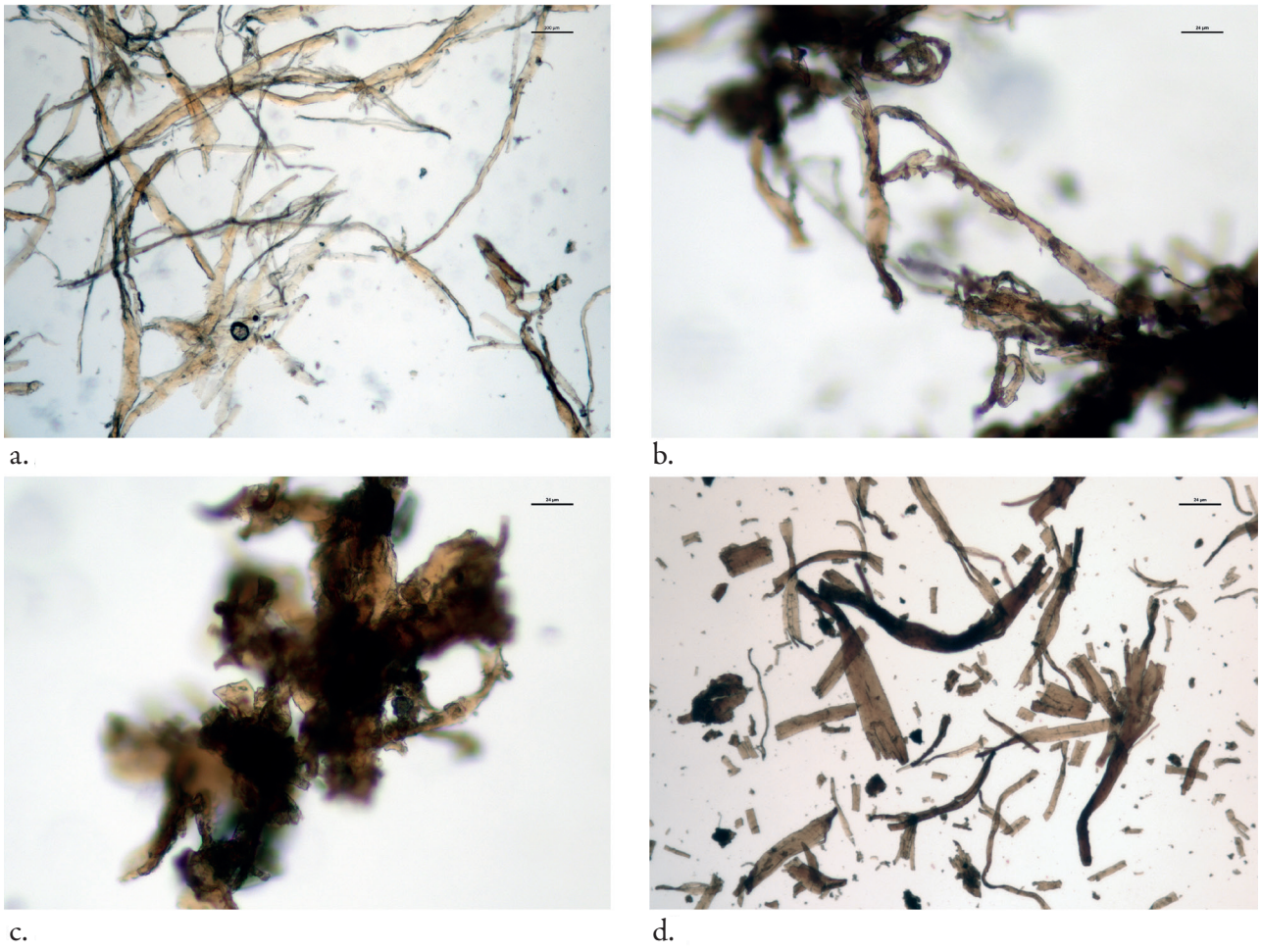

Figure 4. Fibre samples from: a) Baunsø Mose, damage score 3.5, b) Borremose I, damage score 4, c) Huldremose I, damage score 4.5 and d) Vindum Mose, damage score 5 (Photos: Bevaring Sjælland, René Larsen).

accelerated aging (Larsen 2022; Larsen et al. 2021, 6) and a parchment from the Middle East dating from the 17th to 18th century deteriorated by storage in a dry hot environment causing oxidative cleavage as well as crosslinking of the collagen (Mühlen Axelsson et al. 2012, 130). The fibre samples are very similar to samples of the four garments with concerning the degree of deterioration and fibre appearance (Figure 4).

Figure 3.a shows a fibre network with low degree of coherence and high degree of shrunken fibres (wavy and zig zag pattern) and some fibres in process of uncoiling as well as many small fragments. Some fibre parts are blurred due to gelatinising (damage score 3.5). The fibre network in Figure 3.b has a very low coherence with several larger fragments. Fibres and fragments are all gelatinised to various degree and appears in various morphological forms (damage score 4.5). In Figure 3.c, the fibre network is almost completely fragmented and appear mostly as bundles of various morphologies and a randomly shaped gelatinised substance (damage score 5). In Figure 3.d., the fibre network is also completely fragmented appearing in forms of morphologies. Most of the fragments are gelatinised. Though, a few have intact areas and only partly gelatinised (damage score 5).

The Baunsø Mose sample (Figure 4.a) is characterized by relatively long, slightly coherent yellowish-brown fibres, some of which split into smaller fibre units, typical for vegetable-tanned fibres. Some of the long fibres also have preserved intact areas. However, most of the fibres are clearly deformed with clear signs of shrinkage (wave and zig zag structures and pointed ends) also typical of tanned fibres. A partial gelatinization has caused the underlying microfibre structure to blur. Some flat gel like, fragments; typical of decomposed untanned material,

indicates lack of tanning. Overall, the sample can be characterized as lighter and incompletely tanned and close to severely damaged.

The Borremose I sample (Figure 4.b) contains bundles of fibre fragments, some with signs of a slight split of the fibres, shrinkage appearing as a wavy structure with a hint of cross-striation. This, together with the faint yellow-brown colour, indicates that the fibres are tanned. In addition, some fragments have morphological structures in the form of pearls on a string, flat and only a few areas of relative intact structure, all characteristics of degraded untanned skin and parchment. The coherence of the fibre structure is most likely due to gelatinised fibres sticking together. Thus, the sample can be characterized as slightly incompletely tanned and heavily damaged.

The fibre structure of the Huldremose I sample (Figure 4.c) can only be separated in small bundles of fragments 'glued' together due to gelatinisation. Thus, the split of the fibre fragments into smaller units, as seen by tanned fibres, are not observable due to dissolution of the fibre structure. The bundles seem to consist of randomly shaped fragments, butterflies and some zig zag structured shrunken fragments. Together with the many butterflies and slightly yellow-brown colour of the visible fibre remains, as observed also by severely degraded vegetable tanned leathers (Figure 3.c), this indicates the presence of tannins. Thus, sample can be described as tanned and severely close to completely damaged.

The fibres of the Vindum Mose sample (Figure 4.d) are completely degraded and consist of small randomly shaped fragments and longer fragments in the form of partly unfolded flat, pearls on a string and shrunken structures. All are in an advanced state of gelatinisation and without signs of split into smaller fibre units. The morphological characteristics are typical for skin not tanned with vegetable tannins. The many very randomly formed fragments indicate great stiffness in the fibres (Bartoletti et al. 2017, 267-269; Larsen 2007, 18-20). The skin can be described as possibly untanned with a completely damaged fibre structure.

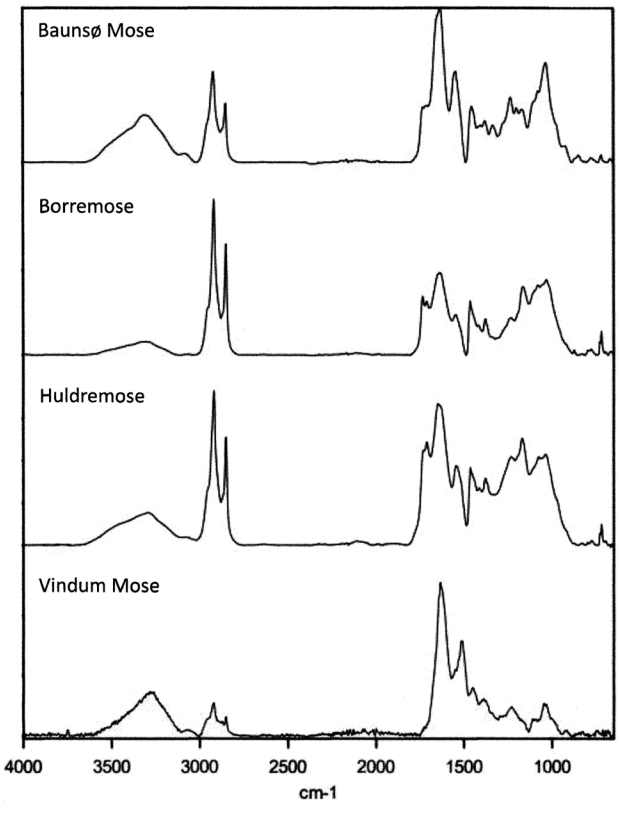

Figure 5. ATR-FTIR absorption spectra of the four cape samples.

ATR-FTIR Spectroscopy

The absorption spectra of the four samples are shown in Figure 5. The spectra profiles of Baunsø Mose, Borremose I and Huldremose I show the presence of vegetable tannins, whereas Vindum Mose only shows the typical collagen profile and no additional treatments. Previous analyses of archaeological finds of leather weapon shields also revealed both vegetable tanned skins of which one was a find from Borremose (Warming et al. 2020) as well as non-vegetable tanned skins.

Table 3 shows the observed key marker bands for Baunsø Mose, Borremose I and Huldremose I together with 15 published marker bands for historical leathers (Falcao and Araujo 2014, 7; 2018, 16) and 11 markers bands of the weapon shield from Borremose (Warming et al. 2020, 196). All three hides contain both condensed and hydrolysable tannins. The distribution of key markers suggests that Borremose I and Huldremose I may contain the same tanning material used for tanning of the Borremose weapon shield. The deviations in the Baunsø Mose spectrum (Figure 5) may be due to differences in the tanning source, type and/or the presence of other substances, e.g., from conservation. The missing bands may be due to overlapping and/or changes in the spectrum profile due to deterioration.

Vegetable tannins[1]	Historical leathers[2]	Borremose Weapon shield[3]	Borremose I	Baunsø Mose	Huldremose I
Compounds present in all classes of tannins					
1615-1606	1612-1611		1612	1611	1612
1518-1507	1518-1514	1518	1517	1517	1515
1452-1446	1448-1447	1454	1453	1450	1453
1211-1196	1207-1203	1200	1206	1201	1201
1043-1030	1040-1032	1035	1032	1030	1030
Condensed tannins					
1288-1282	1287-1283	1280	1288	1286	1281
1162-1155	1157	1166	1162	1156	1158
1116-1110	1114	1118	1114	1109	1113
976	979-976	972	973	973	976
844-842	842	841	837	835	841
Hydrolysable tannins					
1731-1704	1708-1704	1710	1710	1710	1710
1325-1317	1326-1319	1325	1319	1321	1321
Gallo tannins					
1088-1082	1097-1092		1082	1092	1097
872-870	874-870	874	875	875	875
763-758	765-760		761	766	764

[1] Falcao and Araujo 2018, 16; [2] Falcao and Araujo 2014, 505; [3] Warming et al. 2020, 196.

Table 3. Marker bands (cm-1) for Baunsø Mose, Borremose I and Huldremose I with literature values for vegetable tannins, historical leathers and the archaeological leathers.

Table 4 shows the marker band for Vindum Mose compared to references of collagen I and parchment from the literature including the untanned samples from the weapon shield finds (Warming et al. 2020). It is interesting that the best match of Vindum Mose is with 11 marker bands of the 11 bands of the collagen from Boyatzis et al. (2016, 4).

With respect to the presence of fat, the analysis is based on the detailed study of Nina Naquiah et al. (2017) as the analysis and peak identification of their published spectra resulted in a representative number of key markers for pure cow body fat (26) and pure lamb body fat (22) (Table 5). As seen in Table 5, there is convincing agreement between the 24 markers for Baunsø Mose and that of cow fat from Nina Naquiah et al. (2017), seven of these differs specific from lamb fat and those of the three other furs. Borremose I has 20 out the 22 markers of lamb fat and Huldremose I 19 of lamb and one matching cow fat and Vindum Mose has all 22 matching lamb fat and 3 matching cow fat. Borremose I and Vindum Mose has all 10 of the specific bands which differs from cow fat and Huldremose I 9 of these. As mentioned above, the missing bands may be due to deterioration and masking by bands from other compounds in the skins.

Regarding the possible presence of, e.g., brain lipids, Portaccio et al. (2023, 535) reports 12 major peaks, of which three are found in all four samples. The additional number of peaks found was Baunsø Mose (3), Borremose I, Vindum Mose (7), and

				Weaponshields			
Collagen[1]	Newparch-ment[1]	Collagen I[2]	Newparch-ment[2]	Baunegård Surface[2]	Baunegård inner core[2]	Tira S2[2]	Vindum Mose
3321	3302	3305	3292	3293	3290	3289	3292
3072	3072	3076	3073	3073	3073	3073	3072
2958	2926	2931	2926	2928	2931	2931	2936
1644	1640	1631	1631	1631	1632	1632	1645
1545	1538	1548	1538	1535	1536	1523	1546
1454	1448	1452	1448	1449	1449	1449	1450
1405	1408	1405	1405	1402	1402	1406	1407
1340	1334	1339	1335	1334	1336	1335	1337
1241	1230	1238	1235	1233	1235	1233	1237
1082	1084	1082	1081	1080	1081	1082	1082
1032	1031	1032	1031	1031	1031	1031	1034

[1] Boyatzis et al. 2016, 4; [2] Warming et al. 2020, 194.

Table 4. Marker bands in cm-1 for Vindum Mose with literature references for new collagen, new parchment, and untanned skins from archaeological weapon shields.

Huldremose I (6). Four of the brain lipid peaks has no match. Moreover, eight of the brain lipid peaks matches the average position of the peaks of the main lipid components of human cells reported by Portaccio et al. (2023, 534).

There are peaks possibly originating from aluminum (ChemicalBook spectra base) and iron compounds (ChemicalBook spectra base; Veneranda et al. 2018, 71, 73; Wiley spectra base) and mixtures of these (Farahmandjou et al. 2020, 3427-3428) in the spectra of all four samples that do not coincide with the marker peaks for collagen, vegetable tannins and fat. Regarding aluminum tops, the following were found: Baunsø Mose (12), Borremose I (9), Huldremose I (7) and Vindum Mose I (7), which in all cases partially match both aluminum hydroxide and aluminum sulphate. The number of peaks in the spectra of all four samples that may be linked to α-FeOOH, β-FeOOH and γ-FeOOH are: Baunsø Mose (3), Borremose I (6), Huldremose I (5) and Vindum Mose I (6).

The results of the analysis of the deterioration of collagen in the four samples in Figure 6 and Table 6 were based on the ratio between the major amide I (AI) and amide II (AII) bands (AI/AII), the ratio between the amide I band and the carbonyl band at around 1720 cm-1 (AI/1720) as well as the distance between the amide I and amide II bands (Δν). The calculated values show that all samples are degraded to varying degrees from hydrolysis and oxidation, which have led to gelatinisation.

The order of increasing degree of hydrolysis (AI/AII) is 1) Baunsø Mose 2), Huldremose I, 3) Borremose I and 4) Vindum Mose. With respect side chain oxidation (1720 AI) the order is almost the opposite 1) Vindum Mose, 2) Borremose I, 3) Baunsø Mose and 4) Huldremose I. When it comes to the degree of gelatinisation (Δν), the resulting damage caused by the hydrolysis and oxidation is significantly higher for Vindum Mose compared to the three other samples and for Huldremose I it is significantly higher than those of Baunsø Mose and Borremose I. The high AI/AII and Δν values for Vindum Mose may reflect the skin was not tanned, which means that the collagen easily uncoils, fragments and gelatinises in a way typical for deteriorated parchment. However, further studies are needed to reveal if a lower degree of other tannage, e.g., smoke, lipid or aluminum, lead to the same degree and type of deterioration.

Pure cow body fat	Baunsø Mose	Pure lamb body fat	Borremose I	Huldremose I	Vindum Mose	Bovine brainlipids
3000		3002			3005	
2931	2930	2930	2930	2928	2927	
2914	2917	2914	2917	2917	2918	
2868	2872		2872	2872	2870	
1750	1754					
		1739	1739	1739	1737	1742*
		1734	1733	1732	1729	
1705	1704					
		1660	1659	1660	1661	
1654	1655					1652
						1545
1467	1460	1464	1463	1463	1465	1466*
1424	1424	1424	1421	1424	1424	
1417	1417	1410	1409	1410	1411	
		1380	1377	1382	1377	1381*
1375	1372					
1350	1350				1348	
1309	1309	1306	1310	1311	1312	
		1244	1243	1243	1243	
						1234
1238	1238					
		1170	1170	1172	1169	1174
1160	1161	1160	1161	1162	1160	
1118	1118				1119	
1102	1102	1100	1101	1103	1103	
						1084*
1069	1069					
		1060	1061	1060	1058	1064*
1028	1030	1128	1029	1029	1027	
1020	1019	1020			1017	
980	980	980	984	984	986	
						971*
965						
960	961	960	957	954	961	
940	936	940	940		940	
		927	927		929	
884	885			883	885	
	820		820	818	817	822*
726	729					
	719		720		723	720*

Table 5. Marker bands (cm-1) for Baunsø Mose, Borremose I, Huldremose I and Vindum Mose with literature references for pure cow fat, pure lamb fat and bovine brain lipids.

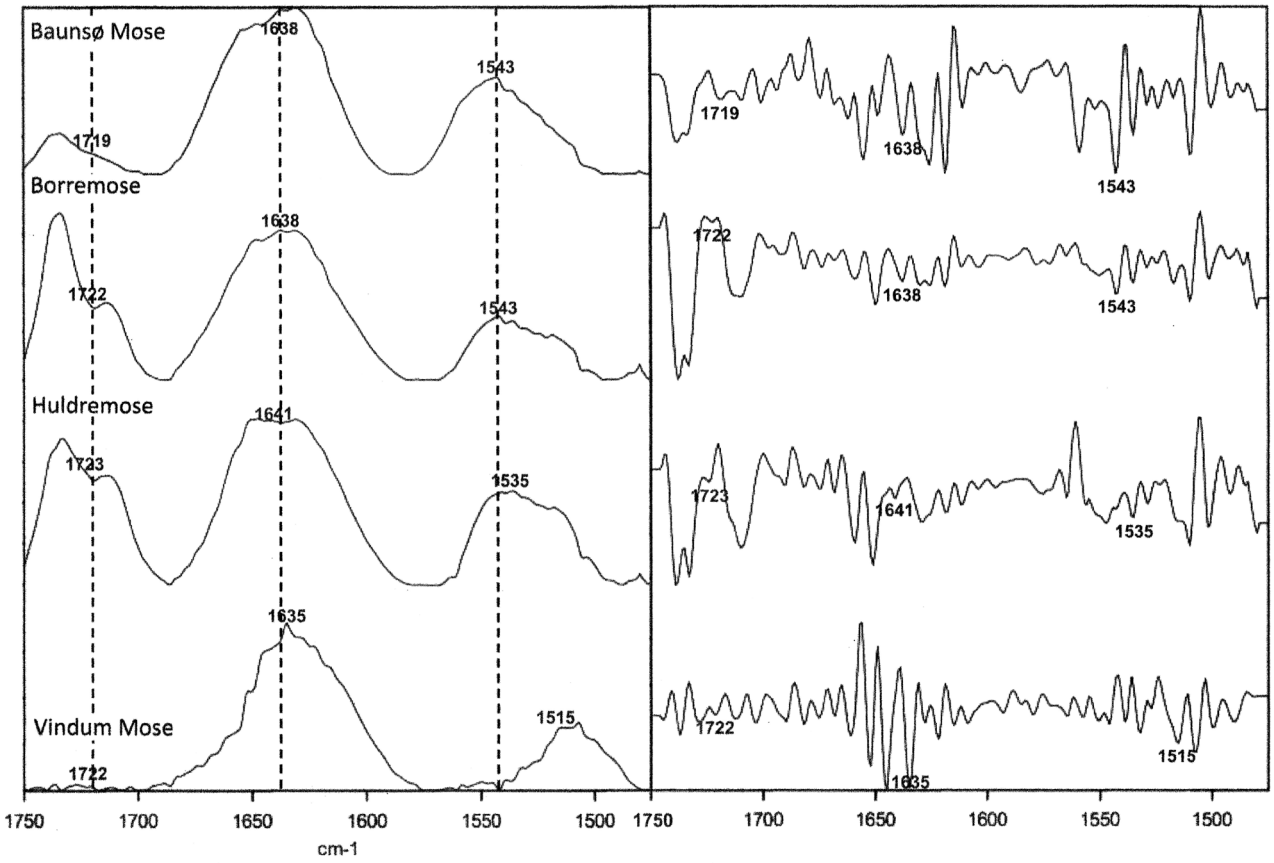

Figure 6. Absorption spectra (left) and the second derivative of these (right) in the wave number region 1775-1450 cm-1.

	Baunsø Mose	Borremose I	Huldremose I	Vindum Mose	
Measured values					**Band type**
AI (~1660) cm^{-1}	1638	1638	1641	1635	Amide I, νC=O
(ABS)	(0,048)	(0,039)	(0,049)	(0,016)	
AII (~1540) cm^{-1}	1543	1543	1535	1515	Amide II, νN-H,
(ABS)	(0,029)	(0,016)	(0,026)	(0,006)	δC=O
~1720 cm^{-1}	1719	1722	1723	1722	Carbonyl, νC=O
(ABS)	(0,034)	(0,024)	(0,037)	(0,006)	
Calculated values					**Damage type**
AI/ AII	1,66	2,44	1,88	2,67	Hydrolysis
1720/ AI	0,71	0,62	0,75	0,38	Side chain oxidation
Δν (AI-AII) cm^{-1}	95	95	106	120	Gelatinisation

Table 6. Results of the analysis of collagen deterioration based on ATR-FTIR. Data are wave numbers in cm^{-1} and absorption intensity (ABS) without unit of measure.

GC-MS Analysis

Figure 7 shows the total ion count (TIC) chromatogram (top) and a plot of *m/z* 117 (bottom) to highlight fatty acids of Huldremose I. It is seen that glycerol, a phthalate, DDT, cholesterol as well as a range of fatty acids both saturated and unsaturated were detected. The three extracts analysed from Huldremose I, indicated that this sample contained saturated and unsaturated fatty acids, glycerol, cholesterol, DDT and a phthalate. Since no hydrolysis is involved in the first extraction, the fatty acids detected are present as free fatty acids on the sample rather than as glycerides. The glycerol detected could be a product of hydrolysed (degraded) triglycerides on the sample and/or the result of a conservation treatment with glycerol, which has been common practice in leather conservation (Thorvildsen 1935-1953, Part 1, 101, 139. Part 2, 149).

The detected cholesterol is a natural constituent in animal fat which could have been added to the skin or it could be natural fat in the skin itself. A phthalate was detected in all samples which is normal since phthalates are everywhere in our environment and hence also in the samples. DDT was detected as well in Huldremose I. This is the likely result of pest control treatment of the skins or of contact with other DDT treated objects (Schmidt 2001).

In addition to a phthalate, fatty acids and cholesterol were detected in Borremose I. Baunsø Mose also contained phthalates, cholesterol and fatty acids as well as DDT, borate, glycerol and azelaic acid. The glycerol seems to be present both as glycerol and as glycerol derivatives (diethers) which

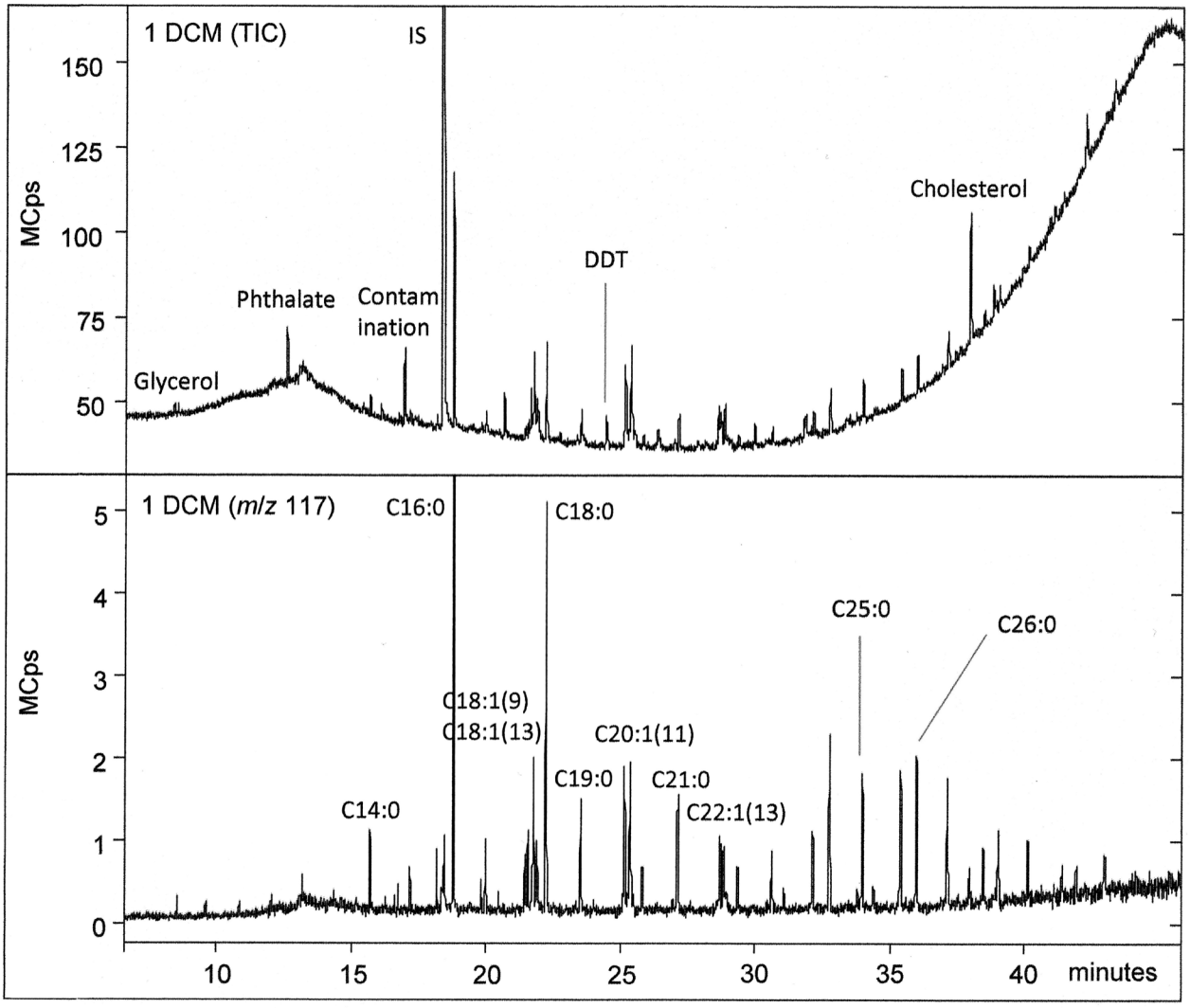

Figure 7. Partial chromatogram by GC-MS for dichloromethane (DCM) extract of Huldremose showing total ion count (top) and a plot of m/z 117 to highlight fatty acids. IS: internal standard, CX:Y: fatty acid with X carbon and Y double bonds, DDT: p,p'-dichlorodiphenyltrichloromethylmethane.

Sample	Dichloromethane (DCM)	Acetone/H2O	MeOH/H2SO4
Baunsø Mose	C14:0, C16:0, C18:1, C18:0, C19:0, C21:0, C25:0, C26:0 Glycerol (and dimers) Azelaic acid Cholesterol Phthalate DDT	C16:0, C18:0 Glycerol (and dimers) Azelaic acid Phthalate DDT Borate	C16:0, C18:1, C18:0 Azelaic acid Phthalate
Borremose I	C14:0, C16:0, C18:1, C18:0, C19:0, C20:1, C21:0, C22:1, C25:0, C26:0 Cholesterol Phthalate	C16:0	C14:0, C16:0, C18:0
Huldremose I	C14:0, C16:0, C18:1, C18:0, C19:0, C20:1, C21:0, C22:1, C25:0, C26:0 Glycerol Cholesterol Phthalate DDT	C16:0 Glycerol	C14:0, C16:0, C18:1, C18:0
Vindum Mose	C14:0, C16:0, C18:0, C20:0, C22:0 Cholesterol (intense) β-sitosterol Phthalate	C16:0 Glycerol Borate	C16:0, C18:0

Table 7. Components identified in extracts by GC-MS.

could be an indication that it has been added to the skin in significant quantities as a conservation treatment. DDT is an insecticide and borates are known biocides which must be why it was added to Baunsø Mose (Peacock 2001, 14 note 1). Azelaic acid is known to form from drying oils (e.g., linseed oil) in paintings (Mills and White 1999). Conservation of Baunsø Mose with such an oil could have led to the identified azelaic acid. Vindum Mose contained fatty acids, a large cholesterol peak, a phthalate, glycerol, borate and β-sitosterol. The latter is a plant sterol, which indicates that a plant oil has been in contact with the skin at some point. Table 7 shows the components identified in extracts by GC-MS.

Summary Discussion

The previously measured Ts of the Baunsø Mose and Borremose I capes and the examined Ts values from the literature clearly show that the Ts is not useful as a criterion for determining the type and degree of tanning of archaeological hides, but rather as a valuable measure of the degree of degradation in combination with the fibre morphological analysis. On the other hand, ATR-FTIR and fibre morphological analysis are obvious techniques for determining vegetable tanning substances in leather and fur. Thus, the results of this and the previous study by Warming et al. (2020) revealed the presence of both vegetable tanned and non-vegetable tanned skins which raises the question of whether full vegetable tannage or tannage by organic components are taking place in the bogs, as the latter would be visible in the FTIR spectra. The effects of bog environment on human skin have been investigated with respect to its ability to preserve bog bodies. Painter (1991, 123-142) points towards a specific component of sphagnum moss (Spaghnan) with tanning and sequestering properties. However, later studies of skin from several bog bodies have not been able to detect this component in the skin samples (Stankiewicz et al. 1997, 1889), nor has it been possible to verify its presence in Sphagnum moss (Ballance et al. 2007, 104-115).

The interesting results of the fat analysis based on FTIR key marker bands are supported by the

visual identification of the animal type based on the hair typology as well as the cholesterol and the fatty acids found by the GC-MS analysis. This indicates that the four samples may primarily contain their original fats, and that no other fat may have been applied during the manufacture of the skins. However, a distinction between lipid from different tissues of the animal (Christie 2024), e.g., from the brain (Poitelon et al. 2020, 3) or the liver (Kinsella 1970, 605), can be made by GC-MS and is an obvious topic for further studies. The results on the lipids and the possible presence of aluminum and iron compounds, as indicated in the ATR-FTIR spectra, also calls for an extended study including also smoke compounds as potential tanning agents. The presence of aluminum and iron compounds can be verified by X-ray diffraction (Farahmandjou et al. 2020, 3426-3427; Veneranda et al. 2018, 73-76). Key markers in the ATR-FTIR spectra can finally be determined by comparative analysis of experimental skins and leathers with and without addition of the metals.

The result of the condition assessment of the Vindum Mose fragments agrees with the results of the fibre morphology and IR analyses. On the other hand, the latter results do not agree with the condition assessments of Baunsø Mose, Borremose I and Huldremose I. These were all judged to be in good condition, showing that it can be difficult to judge the condition of the fibre network layer and to differentiate between different degrees of degradation by the naked eye and simple handling. An explanation for this is that the epidermis, which contains the hair layer and is mainly composed of the protein keratin, is more resistant to degradation compared to the corium layer.

The relatively high Ts of Borremose I (42,8°C) and Huldremose I (48,2°C) is probably due to shrinkage of fragments which emphasizes the importance of also using the fibre morphology examination in the damage assessment. With respect to Borremose I and Huldremose I, the epidermis probably ensures the cohesion of the capes, while the corium layer of the Baunsø Mose cape still has some cohesion.

In relation to the condition of the capes and their conservation it should be emphasised that research on degraded historical parchment and leather objects has shown that gelatinisation may take place

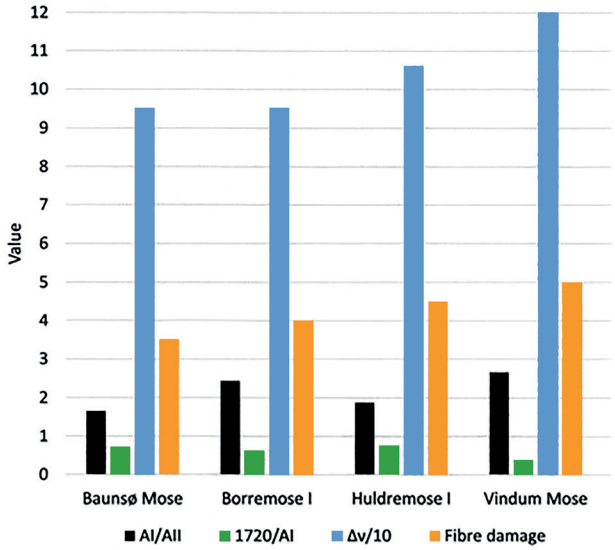

Figure 8. Results of the analysis of collagen deterioration based on ATR-FTIR and fibre analysis. Note that Δν is divided by 10 to obtain a comparable order of magnitude.

when these are exposed to water or alcohol (Derrick 1991; Larsen et al. 2012, 66; Bell et al. 2018) and not least that the degradation can occur spontaneously at room temperature and a low relative humidity (Larsen et al. 2002, 59-60; 2012, 64).

Finally, our results indicates that fibre morphological and ATR-FTIR analysis are complementary in determining the degree and type of damage. The fibre morphology visualise the total chemical modification detected by the ATR-FTIR analysis as illustrated in Figure 8. Despite the small numbers of samples, a strongly significant correlation is found between the fibre damage scores (FDS), assigned in the fibre assessment and the sum of the calculated values based on IR data (Σ_{IR} = AI/AII +1720/AI + Δν/10) representing the total degradation (Figure 9). This constitute a hypothetical relationship that should be verified in a larger study.

Interpretation of the Tanning Methods and Their Sustainability

Our results indicate that the skins have been washed and stretched after skinning, after which the flesh side has been scraped free of muscle remnants, subcutaneous connective tissue and subcutaneous fat (Harris 2012, 12-13; Rahme 1991, 46-51). From here, if the tanning has taken place before burial in the bogs, the treatment of Baunsø Mose,

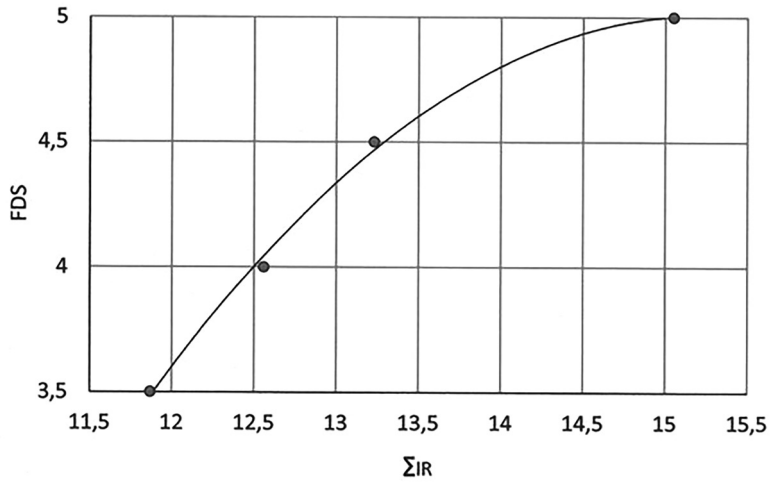

Figure 9. The fibre damage score (FDS) versus the sum of the calculated data from the IR (∑IR). The hypothetical relation follows the quadratic equation FDS = -0,1355*(∑IR)2 + 4,1267*∑IR - 26,406, with a correlation coefficient of R^2 = 0,9973.

Borremose I and Huldremose I differ from Vindum Mose. The first three were probably tanned by rubbing a decoction of locally available bark or other vegetable resources into the flesh side of the wet hide in a stretched state, which facilitates the penetration of the tanning solution into the hide (Harris 2012, 13-14; Rahme 1991, 75). The fibre structure of the skins may have been loosened before they were completely dry, to avoid the fibres sticking together and the skins becoming stiff and inflexible. Skins which are not completely dry are easier to soften manually or with a tool that pulls fixed fibres apart. In the case of Vindum Mose, the scraped hide was probably left stretched until it was halfway dry, after which it was softened manually in the same manner as described above. For both methods, enough of the original fats are left in the skins and distributed more evenly in the skin during the manual treatment. This ensures that the fibres are sufficiently isolated from each other and friction during their movement is avoided.

Assuming that no metal salt or smoke have been used in the production of the capes, the obtained results show that the tanning have been performed using raw materials which are part of the cycle of nature, and therefore has not harmed the surrounding environment. However, a contemporary large-scale production based on bark or other plant parts from slow-growing trees is not sustainable. This requires the use of cultivated fast-growing plants that contain only hydrolysable tannins to also achieve a long-lasting product.

With respect to long term stability, our analyses show that the fibre structure of the four samples range from severely to completely degraded. However, the degree of degradation must be judged in relation to the use of the capes before the burial in the bogs, the long storage time therein and the subsequent storage in the museum. In addition, three of the capes are tanned with condensed tanning substances, which have a strong degrading effect on the collagen structure, even under normal storage conditions (Hulme et al. 1905, 17-27; Innes 1933, 725; Larsen 1995, 69-78; 2000, 94-95).

In summary, the obtained results provide a solid basis for further and more detailed studies and raise, among other questions, the following: Why are some skins found in bogs vegetable tanned and others not? Is it due to differences in the bog environments? Or is it simply because some of the skins were treated with vegetable tannins and others not before burial, and the intended purpose determined the type of leather and fur produced? In this connection, it must be mentioned that Baunsø, Borremose I and Huldremose I were garments (capes), while Vindum Mose possibly had another function, e.g., as a simple body wrapping. This brings us back to the question: Does vegetable tanning occur naturally on skins buried in bogs? It is important to clarify these questions, as well as whether other tanning materials have been used in the production of leather and skins. Moreover, the condition of the examined furs and previously examined leathers and skins from weapon shields calls for studies of the long-term stability of skins tanned with methods assumed to be equivalent to Iron Age methods.

Conclusion

The garments from Baunsø Mose, Borremose I and Huldremose I appeared to be well-preserved by visual inspection, while Vindum Mose was highly fragmented. However, the ATR-FTIR, and the fibre morphological analyses results indicate serious deterioration of the four objects. Baunsø Mose has a damage score of 3.5, Borremose I of 4, Huldremose I of 4.5 and Vindum Mose of 5 (completely damaged). The ATR-FTIR key marker bands show that vegetable tannins are present in relatively slight amounts in the samples from Baunsø Mose, Borremose I and Huldremose I. In contrast, the Vindum Mose sample does not contain vegetable tannins. The tannins are condensed and hydrolysable indicating that tanning based on local plant sources, which was part of nature's cycle, was a well-known procedure during the Iron Age. However, the presence of condensed tannins in the three vegetable tanned capes, is a negative factor with respect to the long-term durability of the products. Moreover, ATR-FTIR key marker bands also indicate that the four samples may primarily contain their original fats. Thus, Baunsø Mose contains fat of calf/cow and Borremose I, Huldremose I and Vindum Mose that of lamb/sheep. However, more detailed analyses are needed to determine the presence of other possibly tanning compounds, such as compounds from smoke, lipids with a high content of unsaturated fatty acids, as indicated by the GC-MS analysis, and non-sustainable compounds from aluminum and iron, as indicated by the ATR-FTIR analysis.

Acknowledgement

The National Museum is thanked for giving us access to the samples for this study and the Krogagerfonden for funding laboratory analyses.

Declaration of Interest Statement

The authors have no competing interest to declare.

References

Aabye, J.S., 1955. *Garverbogen*. København: Teknologisk Instituts Forlag.

Asingh, P. and Lynnerup, N., eds. 2007. *Grauballe Man – An Iron Age Bog Body Revisited*. Jutland Archaeological Society Publications vol. 49. Højbjerg: Aarhus University Press.

Badea, E., Miu, L., Budrugeac, P., Giurginca, M., Mašić, A., Badea, N. and Della Gatta, G., 2008. Study of deterioration of historical parchments by various thermal analysis techniques complemented by SEM, FTIR, UV–Vis–NIR and unilateral NMR investigations. *Journal of Thermal Analysis and Calorimetry* 91(1), 17-27.

Badea, E., Poulsen Sommer, D.V., Mühlen Axelsson, K., Larsen, R., Kurysheva, A., Miu, L. and Della Gatta, G., 2012. Damage ranking of historic parchment: from microscopic studies of fibre structure to collagen denaturation assessment by micro-DSC. *e-preservation science* 9, 97-109. https://www.morana-rtd.com/e-preservationscience/2012/Badea-31-12-2012.pdf

Ballance, S., Børsheim, K. Y., Inngjerdingen, K., Paulsen, B.S. and Christensen, B.E., 2007. A reexamination and partial characterisation of polysaccharides released by mild acid hydrolysis from the chlorite-treated leaves of Sphagnum papillosum. *Carbohydrate Polymers* 67(1), 104-115. https://doi.org/https://doi.org/10.1016/j.carbpol.2006.04.020

Baldassarre, M., Li, C., Eremina, N., Goormaghtigh, E. and Barth, A., 2015. Simultaneous fitting of absorption spectra and their second derivatives for an improved analysis of protein infrared spectra. *Molecules* 20, 12599-12622. https://doi.org/10.3390/molecules200712599

Bartoletti, A., Odlyha, M., Hudziak, S., Mühlen Axelsson, M., de Groot, J. and Bozec, L., 2017. Visibilia ex invisibilibus: seeing at the nanoscale for improved preservation of parchment. *Insight-Non-Destructive Testing and Condition Monitoring* 59(5), 267-269. https://doi.org/10.1784/insi.2017.59.5.265

Bell, N., Larsen, R., Patten, K., Sommer, D.V.P., Drakopoulos, M. and Wess, T., 2018. Assessing the condition of the Domesday Books from the visual to the molecular. *Heritage Science* 6(1), 50. https://doi.org/10.1186/s40494-018-0215-0

Boyatzis, S.C., Velivasaki, G., Malea, E., 2016. A study of the deterioration of aged parchment marked with laboratory iron gall inks using FTIR-ATR spectroscopy and micro hot table. *Heritage Science* 4(1), 1-17. https://doi.org/10.1186/s40494-016-0083-4

Brandt, L.Ø., Schmidt, A.L., Mannering, U., Sarret, M., Kelstrup, K., Olsen, J.V. and Cappellini, E., 2014. Species Identification of Archaeological Skin Objects from Danish Bogs: Comparison between Mass-Spectrometry-Based Peptide Sequencing and Microscopy-Based Methods. *PLoS ONE* 9(9), 1-10. https://doi.org/10.1371/journal.pone.0106875

Broholm, H.C. and Hald, M., 1940. *Costumes of the Bronze Age in Denmark.* Copenhagen: Nyt Nordisk Forlag.

Cameron, D. and Moffatt, D., 1987. A generalized approach to derivative spectroscopy. *Applied Spectroscopy* 41, 539-544.

Carsote, C., Miu, L., Petroviciu, I., Creanga, D.M., Giurginca, M. and Vetter, W., 2012. Scientifc investigation of leather in ethnographical objects by molecular spectroscopy and MHT. *Leather and Footwear Journal* 12(3), 183-192.

Che Man, Y.B. and Mirghan, M.E.S., 2001. Detection of Lard Mixed with Body Fats of Chicken, Lamb and Cow by Fourier Transform Infrared Spectroscopy. *Journal of the American Oil Chemists' Society* 78(7), 753-761. https://doi.org/10.1007/s11746-001-0338-4

ChemicalBook. https://chemicalbook.com

Christie, W.W., 2024. The Lipid Compositions of Animal Tissues. *The Lipid Web*. https://www.lipidmaps.org/resources/lipidweb/lipidweb_html/lipids/basics/comp-animal/index.htm

Derrick, M., 1991. Evaluation of the State of Degradation of Dead Sea Scroll Samples using FTIR Spectroscopy. *The American Institute for Conservation*. http://aic.stanford.edu/sg/bpg/annual/v10/bp10-06.html

Dixit, S., Yadav, A., Dwivedi, P.D. and Das, M., 2015. Toxic hazards of leather industry and technologies to combat threat: a review. *Journal of Cleaner Production* 87, 39-49. https://doi.org/10.1016/j.jclepro.2014.10.017

Dong, A., Huang, P., Caughey, B. and Caughey, W., 1995. Infrared analysis of ligand and oxidation-induced conformational changes in hemoglobins and myoglobins. *Archives of Biochemistry and Biophysics* 316(2), 893-898. https://doi.org/10.1006/abbi.1995.1120

Ebbesen, K., 2009. En skinddragt fra Møgelmose i Jelling. *Aarbøger for nordisk Oldkyndighed og Historie* 2006, 37-51.

Falcao, L. and Araujo, M.E.M., 2014. Application of ATR-FTIR spectroscopy to the analysis of tannins in historic leathers: the case study of the upholstery from the 19th century Portuguese Royal Train. *Vibrational Spectroscopy* 74, 1-10. https://doi.org/10.1016/j.vibspec.2014.08.001

Falcao, L. and Araujo, M.E.M., 2018. Vegetable tannins used in the manufacture of historic leathers. *Molecules* 23(5), 1-20. https://doi.org/10.3390/molecules23051081

Farahmandjou, M., Khodadadi, A. and Yaghobi, M., 2020. Low Concentration Iron-Doped Alumina (Fe/Al2O3) Nanoparticles Using Co-Precipitation Method. *Journal of Superconductivity and Novel Magnetism* 33(1), 3425-3432. https://doi.org/10.1007/s10948-020-05569-0

Fischer, C., 2000. *Tollundmanden. Gaven til guderne. Mosefund fra Danmarks forhistorie*. Silkeborg: Hovedland.

Glob, P.V., 1966. *Mosefolket. Jernalderens Mennesker bevaret i 2000 År.* København: Gyldendal.

Guillen, M.D., Ruiz, N., Cabo, R., Chirinos and Pascual, G., 2003. Characterization of Sacha Inchi (Plukenetia volubilis L.) oil by FTIR spectroscopy and 1 H NMR. comparison with linseed oil. *Journal of American Oil Chemists' Society* 80, 755-762. https://doi.org/10.1007/s11746-003-0768-z

Hald, M., 1980. *Ancient Danish Textiles from Bogs and Burials*. Archaeological-Historical Series Vol. XXI. Copenhagen: Publications of the National Museum.

Haris, P.I. and Chapman, D., 1995. The conformational analysis of peptides using fourier transform IR spectroscopy. *Biopolymers* 37, 251-263. https://doi.org/10.1002/bip.360370404

Harris, S., 2012. Hide-working with dry scrape technique using stone and bone tools. *Archaeological Leather Group Newsletter* 36, 12-14. www.archleathgrp.org.uk

Hulme, E.W., Parker, J.G., Seymour-Jones, A., Davenport, C. and Willamson, F.J., 1905. *Leather for Libraries*. The Library Supply Co London. Leopold Classic Library. Monee, USA, 2023, 1-87. www.leopoldclassiclibrary.com

Innes, R.F., 1933. The Deterioration of Vegetable-Tanned Leather on Storage. V. *Journal of the International Society of Leather Trades Chemists* XVII, 725-754.

Jackson, M. and Mantsch, H.H., 1995. The use and misuse of FTIR spectroscopy in the determination of protein structure. *Critical Reviews in Biochemistry and Molecular Biology* 30, 95-120. https://doi.org/10.3109/10409239509085140

Jensen, J., 2003. *Danmarks Oldtid. Ældre Jernalder 500 f.Kr.-400 e.Kr*. København: Gyldendal.

Kern, M.S., Pataki-Hundt, A., Wouters, J. and Kirby, D.P., 2018. Accelerated Ageing of Parchment: Investigation of a Photo Catalysed, Low-Heat Approach. *Restaurator* 39(1), 33-69. https://doi.org/10.1515/res-2017-0013

Kinsella, J.E., 1970. Liver Lipids of Lactating Bovine: Fatty Acid Composition. *Journal of Dairy Science* vol. 53, no. 5, 604-606. https://www.journalofdairyscience.org/article/S0022-0302(70)86263-4/pdf

Kong, J. and Yu, S., 2007. Fourier Transform Infrared Spectroscopic Analysis of Protein Secondary Structures. *Acta Biochimica et Biophysica Sinica* 39(8), 549-559. https://doi.org/10.1111/j.1745-7270.2007.00320.x

Larsen, R., 1995. *Fundamental aspects of the deterioration of vegetable tanned leathers*, Ph.D. Thesis, University of Copenhagen. Copenhagen: The Royal Danish Academy of Fine Arts, School of Conservation, 18-20 and 105-110.

Larsen, R., 2000. Experiments and Observations in the Study of Environmental Impact on Historical Vegetable Tanned Leathers. *Thermochimica Acta*, 365. Special issue on Cultural Heritage and Environmental Implications, 85-99.

Larsen, R., 2007. Introduction to damage and damage assessment of parchment. *In*: *Improved damage assessment of parchment (IDAP). Assessment, data collection and sharing of knowledge*. European Commission, Research Report no. 18, European Communities, Belgium, 17-21.

Larsen, R., 2022. Report on the Analysis of Sulphur Free Calf Leather for Bookbinding. *News*. Online Community for the American Institute for Conservation and Foundation for Advancement in Conservation. https://community.culturalheritage.org/blogs/ren-larsen/2022/06/09/report-on-sulphur-free-calf-leather

Larsen, R. and Poulsen, D.V., 2007. Analysis of the Skin. *In*: Asingh, P. and Lynnerup, N., eds. *Grauballe Man – An Iron Age Bog Body Revisited*. Jutland Archaeological Society Publications vol. 49. Højbjerg: Aarhus University Press, 85-91.

Larsen, R., Poulsen, D.V. and Vest, M., 2002. The Hydrothermal Stability (shrinkage activity) of parchment measured by the micro hot table method (MHT). *In*: R. Larsen, ed. *Micro Analysis of Parchment*. London: Archetype Publications Ltd., 55-62.

Larsen, R., Siegel, S. and Themmen, E.R., 2021. Preliminary Report on the Development of a Sulphur Free Full Vegetable Tanned Archival Calf Leather. *Leather and Related Materials Working Group Newsletter* 10 (June), 6-7.

Larsen, R., Sommer, D.V.P., Mühlen Axelsson, K. and Frank, S.K., 2012. Transformation of Collagen into Gelatine in Historical Leather and Parchment Caused by Natural Deterioration and Moist Treatment. *In*: C. Bonnot-Diconne, C. Dignard and J. Göpfrich, eds. *ICOM-CC Leather and Related Materials Workings Group*. *Postprints of the 10th Interim Meeting*. Offenbach: Deutsches Ledermuseum Schuhmuseum, 61-68.

Larsen, R., Vest, M. and Nielsen, K., 1993. Determination of hydrothermal stability (shrinkage temperature) of historical leathers by the micro hot table technique. *Journal of the Society of Leather Technologists and Chemists* 77, 151-156.

Mannering, U., Possnert, G., Heinemeier, J. and Gleba, M., 2010. Dating Danish textiles and skins from bog by means of ^{14}C AMS. *Journal of Archaeological Science* 37(2), 261-268.

Mills, J. and White, R., 1999. *Organic Chemistry of Museum Objects* (2nd ed.). New York: Routledge. https://doi.org/10.4324/9780080513355).

Mühlen Axelsson, K., Larsen, R. and Sommer, D.V.P., 2012. Dimensional studies of specific microscopic fibre structures in deteriorated parchment before and during shrinkage. *Journal of Cultural Heritage* 13(2), 128-136. https://doi.org/10.1016/j.culher.2011.08.001

Mühlen Axelsson, K., Larsen, R., Sommer, D.V.P. and Melin, R., 2014. Degradation of collagen in parchment under the influence of heat-induced oxidation: Preliminary study of changes at macroscopic, microscopic and molecular levels. *Studies in Conservation* 61(1), 46-57. https://doi.org/10.1179/2047058414Y.0000000140

Mühlen Axelsson, K., Larsen, R., Sommer, D.V.P. and Melin, R., 2017. Establishing the relation between degradation mechanisms and fibre morphology at microscopic level in order to improve damage diagnosis for parchments – A preliminary study. *In*: J. Bridgland, ed. *ICOM-CC 18th Triennial Conference Preprints*, Copenhagen, 4-8 September 2017, art. 0507. Paris: International Council of Museums. https://www.researchgate.net/publication/319649401_Establishing_the_relation_between_degradation_mechanisms_and_fibre_morphology_at_microscopic_level_in_order_to_improve_damage_diagnosis_for_parchments_-_A_preliminary_study

Munksgaard, E., 1974. *Oldtidsdragter*. København: Nationalmuseet.

Nina Naquiah, A.N., Marikkar, J.M.N., Mirghani, M.E.S., Nurrulhidayah, A.F. and Yanty, N.A.M., 2017. Differentiation of Fractionated Components of Lard from Other Animal Fats Using Different Analytical Techniques. *Sains Malaysiana* 46(2), 209-216. http://dx.doi.org/10.17576/jsm-2017-4602-04

Odlyha, M., Theodorakopoulos, C., de Groot, J., Bozec, L. and Horton, M., 2009. Fourier Transform Infra-Red Spectroscopy (ATR/FTIR) and Scanning Probe Microscopy of Parchment. *e-Preservation Science* 6, 138-144. ISSN: 1581-9280 web edition.

Ogilvie, T., 2019. Conserving Bog Bodies: The Key Questions. *Journal of Wetland Archaeology* 19(1–2), 67-88. https://doi.org/10.1080/14732971.2020.1826196

Painter, T.J., 1991. Lindow man, Tolllund man and other peat-bog bodies: The preservative and antimicrobial action of Spagnan, a reactive glycuronoglycan with tanning and sequestering properties. Review paper. *Carbohydrate Polymers* 15, 123-142. https://doi.org/10.1016/0144-8617(91)90028-B

Peacock, E., 2001. Water-degraded Archaeological Leather: An Overview of Treatments Used at Vitenskapsmuseum (Trondheim). *In*: B. Wills, ed. *Leather Wet and Dry. Current treatments in the Conservation of Waterlogged and Desiccated Archaeological Leather*, 12-25. London: Archetype Publications.

Plavan, V., Giurginca, M., Budrugeac, P., Vilsan, M. and Miu, L., 2010. Evaluation of the physico-chemical characteristics of leather samples of some historical objects from Kiev. *Revistade Chimie* 61(7), 627-631.

Poitelon, Y., Kopec, A.M. and Belin, S., 2020. Myelin Fat Facts: An Overview of Lipids and Fatty Acid Metabolism. *Cells* 9(4), 2-17. https://doi.org/10.3390/cells9040812

Portaccio, M., Faramarzi, B. and Lepore, M., 2023. Probing Biochemical Differences in Lipid Components of Human Cells by Means of ATR-FTIR Spectroscopy. *Biophysica* 3, 524-538. https://doi.org/10.3390/biophysica3030035

Rahme, L., 1991. *Skinn och beredning med traditionella metoder*. Stockholm: LTs Förlag.

Reed, R., 1972. *Ancient Skins Parchments and Leather*. London and New York: Seminar Press.

Ricci, A., Olejar, K.J, Parpinello, G.P., Kilmartin, P.A and Versari, A., 2015. Application of fourier transform infrared (FTIR) spectroscopy in the characterization of tannins. *Applied Spectroscopy Reviews* 50(5), 407-442. https://doi.org/10.1080/05704928.2014.1000461

Rohman, A. and Che Man, Y.B., 2010. FTIR spectroscopy combined with chemometrics for analysis of lard in the mixtures with body fats of lamb, cow and chicken. *International Food Research Journal* 17, 519-526. https://doi.org/10.1080/19476331003774639

Rowe, S., Ravaioli, F., Tully, C. and Narvey, M., 2018. Conservation and Analysis on a Shoestring: Displaying Gut Parkas at the Polar Museum, Cambridge. *Journal of Conservation and Museum Studies* 16(1), 1-11. https://doi.org/10.5334/jcms.157

Safar, M.D., Bertrand, P., Robert, M.F. and Devaux Genot, C., 1994. Characterization of edible oils, butters and margarines by fourier transform infrared spectroscopy with attenuated total reflectance. *Journal of American Oil Chemists' Society* 71, 371-377. https://doi.org/10.1007/BF02540516

Schmidt, O., 2001. Insecticide Contamination at the National Museum of Denmark: A Case Study. *Collection Forum* 16(1-2), 92-95.

Sivaram, N.M. and Barik, D., 2019. Chapter 5 – Toxic Waste from Leather Industries. *In*: *Energy from Toxic Organic Waste for Heat and Power Generation.* Woodhead Publishing Series in Energy, 55-67. https://doi.org/10.1016/B978-0-08-102528-4.00005-5

Sommer, D.V.P., Botfeldt, K., Gelting, U. and Hovmand, I., 2013. The state of preservation of two skins from Danish peat bogs – an investigation of archaeological waterlogged skin from the peat bogs Vindum Mose and Vester Torsted Mose examined using four types of analysis. *Proceedings of the 12th ICOM-CC Group of Wet Organic Archaeological Materials Conference*. Istanbul 2013. Printed in Canada by Lulu.com, 342-349.

Sommer, D., Mühlen Axelsson, K., Collins, M., Fiddyment, S., Bredal-Jørgensen, J., Simonsen, K.P., Lauridsen, C. and Larsen, R., 2017. Multiple Microanalyses of a Sample from the Vinland Map. *Archaeometry* 2(59), 287-301. https://doi.org/10.1111/arcm.12249

Stankiewicz, B.A., Hutchins, J.C., Thomson, R., Briggs, D.E. and Evershed, R.P., 1997. Assessment of bog-body tissue preservation by pyrolysis-gas chromatography/mass spectrometry. *Rapid Commun Mass Spectrom* 11(17), 1884-1890. https://doi.org/10.1002/(sici)1097-0231(199711)11:17<1884::Aid-rcm62>3.0.Co;2-5

Strehle, H. 2007. The Conservation of Grauballe Man. *In*: P. Asingh and N. Lynnerup, eds. *Grauballe Man – An Iron Age Bog Body Revisited*. Jutland Archaeological Society Publications vol. 49. Højbjerg: Aarhus University Press, 33-50.

Susi, H. and Byler, M., 1988. Protein structure by Fourier Transform Infrared Spectroscopy: second derivative spectra. *Biochemical and Biophysical Research Communications* 115(1), 391-397. https://doi.org/10.1016/0006-291X(83)91016-1

Syed, M., Saleem, T., Shuja-ur-Rehman, Iqbal, M.A., Javed, F., Khan, M.B.S. and Sadiq, K., 2010. Effects of Leather Industry on Health and Recommendations for Improving the Situation in Pakistan. *Archives of Environmental & Occupational Health* 65(3), 163-172. https://doi.org/10.1080/19338241003730895

Tatulian, S.A., 2019. FTIR analysis of proteins and protein-membrane interactions. *In*: J.H. Kleinschmidt, ed. *Lipid-Protein Interactions: Methods and Protocols*. New York: Springer New York, 281-325. https://doi.org/10.1007/978-1-4939-9512-7_13

Thomson, R., 2007. Chapter 5: Leather. In: E. May and M. Jones (eds) *Conservation Science*, 92-120. Cambridge: Royal Society of Chemistry. https://doi.org/10.1039/9781847557629-00092.

Thorvildsen, E., 1952. Menneskeofringer i oldtiden. Jernalderligene fra Borremose i Himmerland. *KUML*, 32-48.

Thorvildsen, K., n.d. Konserveringsnoter 1935-1952. Danish National Museum in Brede, Conservation Archive.

United Nations. Department of Economic and Social Affairs. Sustainable Development. *The 17 Goals*. https://sdgs.un.org/goals.

Usoltsev, D., Sitnikova, V., Kajava, A. and Uspenskaya, M., 2019. Systematic FTIR Spectroscopy Study of the Secondary Structure Changes in Human Serum Albumin under Various Denaturation Conditions. *Biomolecules* 9, 359. https://doi.org/10.3390/biom9080359

Vadrucci, M., De Bellis, G., Mazzuca, C., Mercuri, F., Borgognoni, F., Schifano, E., Uccelletti, D. and Cicero, C., 2020. Effects of the Ionizing Radiation Disinfection Treatment on Historical Leather. *Frontiers in Materials* 7(21), 1-9. https://doi.org/10.3389/fmats.2020.00021

van der Sanden, W., 1996. *Through nature to eternity. The bog bodies of northwest Europe.* Amsterdam: Batavian Lion International.

Van de Voort, F.R. and Sedman, J., 2000. FTIR Spectroscopy: The new generation of oil analysis methodologies. *INFORM* 11, 614-620.

Veneranda, M., Aramendia, J., Bellot-Gurlet, L., Colomban, P., Castro, K., Madariaga, J.M., 2018. FTIR spectroscopic semi-quantification of iron phases: A new method to evaluate the protection ability index (PAI) of archaeological artefacts corrosion systems. *Corrosion Science* 133, 68-77. https://doi.org/10.1016/j.corsci.2018.01.016

Vyskocilová, G., Ebersbach, M., Kopecká, R., Prokeš, L. and Príhoda, J., 2019. Model study of the leather degradation by oxidation and hydrolysis. *Heritage Science* 7, 26. https://doi.org/10.1186/s40494-019-0269-7

Warming, R.F., Larsen, R., Sommer D.V.P., Ørsted Brandt, L. and Jensen, X.P., 2020. Shields and hide – On the use of hide in Germanic shields of the Iron Age and Viking Age. *Bericht der Römisch-Germanischen Kommission* 97, 155-225. https://doi.org/10.11588/berrgk.2016.0.76641

Wiley spectra base. https://spectrabase.com

Young, G., 1990. Microscopical hydrothermal stability measurements of skin and semi-tanned leather. *Preprints of the ICOM Committee for Conservation, 9th triennial Dresden 1990*, 626-630. Los Angeles: ICOM.