RESEARCH REPORT SERIES no. 70-2011

LEATHER DRYING TRIAL
A COMPARATIVE STUDY TO EVALUATE DIFFERENT TREATMENT AND DRYING TECHNIQUES FOR WET, ARCHAEOLOGICAL LEATHER

ARCHAEOLOGICAL CONSERVATION REPORT

Angela Karsten and Karla Graham

INTERVENTION
AND ANALYSIS

ENGLISH HERITAGE

This report has been prepared for use on the internet and the images within it have been down-sampled to optimise downloading and printing speeds.

Please note that as a result of this down-sampling the images are not of the highest quality and some of the fine detail may be lost. Any person wishing to obtain a high resolution copy of this report should refer to the ordering information on the following page.

Research Report Series 70-2011

LEATHER DRYING TRIAL
A comparative study to evaluate different treatment and drying techniques for wet, archaeological leather

Angela Karsten and Karla Graham

ISSN 2046-9799 (Print)
ISSN 2046-9802 (Online)

SUMMARY

The aim of this study was to compare and evaluate different treatment and drying techniques for wet archaeological leather; using parameters such as shrinkage, flexibility, appearance, time, and costs.

The results show that a pre-treatment with EDTA results in higher shrinkage and increased flexibility. All impregnation and drying methods worked well and are equally suitable for individual and large scale treatment. There are however some minor differences with regards to shrinkage, flexibility and time according to the impregnation or drying technique. This study has shown that there are valid alternatives to the otherwise commonly used technique of vacuum freeze drying when treating wet archaeological leather.

ACKNOWLEDGEMENTS

We would like to thank Dean Sully (UCL) for donating the leather used in this study and Maarit Hirvilammi (Turun Museokeskus, Finland) and Paul Simpson (Isle of Wight Council Museum Service) for sharing their experience of non-vacuum freeze drying. We are grateful to the members of the leather working group for the many fruitful discussions held over the course of this experiment. The members of the working group are: Helen Ganiaris (Museum of London), Liz Goodman (Museum of London and London Archaeology), Jackie Keily (Museum of London), Quita Mould (Barbican Research Associate), Jane Sidell (English Heritage), Kelly Domoney (former EH and MoL intern), and Dean Sully (UCL).

ARCHIVE LOCATION

English Heritage, Fort Cumberland, Portsmouth

DATE OF RESEARCH

2009-2010

CONTACT DETAILS

English Heritage, Fort Cumberland, Fort Cumberland Road, Portsmouth, PO4 9LD
Angela Middleton (neé Karsten), 02392 856787, Angela.Middleton@english-heritage.org.uk
Karla Graham, 02392 856786, Karla.Graham@english-heritage.org.uk

CONTENTS

1 INTRODUCTION 1
2 BACKGROUND 1
3 METHODOLOGY 2
3.1 Sample material and condition 4
3.2 Recording before conservation 4
3.2.1 Photography 4
3.2.2 Drawing 4
3.2.3 Dimensions 5
3.2.4 Flexibility 5
3.2.5 Condition score 6
3.2.6 Object sheets 7
3.2.7 X-radiography 8
3.3 The trial 8
3.3.1 Pre-treatment 8
3.3.2 Impregnation 10
3.3.3 Drying 10
3.3.4 Climate Readings 13
3.4 Recording after conservation 13
4 RESULTS 13
4.1 Shrinkage 13
4.1.2 Evaluation of overall shrinkage 14
4.1.3 Evaluation of shrinkage by conservation method 14
4.1.4 Discussion of shrinkage evaluation 17
4.2 Flexibility 17
4.2.1 Evaluation of overall flexibility 17
4.2.2 Evaluation of flexibility by treatment method 18
4.2.3 Evaluation of flexibility by drying method 18
4.2.4 Discussion of flexibility evaluation 18
4.3 Condition Score 21
4.3.1 Evaluation of overall condition score 21
4.3.2 Evaluation of condition score by treatment 22
4.3.3 Evaluation of condition score by drying method 25
4.4 Evaluation of appearance 25
4.5 Evaluation of treatment time 26
4.6 Evaluation of equipment and materials needed 26
4.7 Evaluation of climate readings 27

4.7.1 Air drying 27
4.7.2 Non-vacuum freeze drying 28
4.7.3 Controlled air drying 29
4.8 Packing of the conserved leather 30
5 ANALYSIS 31
5.1 Methodology 31
5.2 Scanning Electron Microscopy (SEM) 31
5.2.1 Results of SEM examination 32
6 DISCUSSION 33
7 CONCLUSIONS 34
BIBLIOGRAPHY 35
APPENDIX 2: Example of object recording sheet 39
APPENDIX 3: SEM images 41

1 INTRODUCTION

The Leather Drying Trial is an English Heritage (EH) research project examining the effect of different treatment and drying techniques on waterlogged archaeological leather. It aims to provide up to date comparative data on the efficacy and costings of the most commonly used remedial conservation methods for waterlogged archaeological leather using parameters such as shrinkage, flexibility, appearance, time, effort and equipment. This will enable EH to provide best practice advice to internal and external groups and the Archaeological Conservation profession. The project meets the EH Research Framework SHAPE number 14171.110: Experimental Research: Sharpening the tools: Developing new techniques of analysis and understanding.

The origins of this project were twofold:

1. A research interest in testing the efficacy of vacuum freeze drying versus non-vacuum freeze drying to contribute to the new English Heritage publication: *Waterlogged organic artefacts – Guidelines on their recovery, analysis and conservation* (Karsten, Graham, Jones, Mould and Walton Rogers 2012). These guidelines are a revision and expansion of the former Leather Guidelines (Edwards and Mould 1995).

2. Arising from discussions about approaches to the conservation of leather in the London region between the University College of London (UCL) Institute of Archaeology, Museum of London and EH Archaeological Conservators and Regional Science Advisors. The issue raised was that there was a large backlog of un-conserved waterlogged archaeological leather in the London region. The cost of vacuum freeze-drying was cited as the factor preventing the conservation of this leather.

This report covers trials undertaken by the authors at Fort Cumberland, English Heritage between March and April 2009. Additional leather trials have also been undertaken by UCL MA Conservation student Kelly Domoney whilst on internship at the Museum of London between April and September 2009 and will be reported on elsewhere (Karsten, Graham, Goodman, Ganiaris and Domoney 2012).

2 BACKGROUND

Leather from archaeological sites in the UK is most likely to come from anaerobic waterlogged deposits where little or no oxygen is present. In the burial environment, the tannins contained within the leather can be washed out or degrade to leave a vulnerable, weak material that comprises mainly water and minerals taken up from the soil with very little of the original organic structure remaining.

The aim of remedial conservation[1] is to remove all the water so that the leather is stable in ambient environmental conditions[2] to facilitate further study and to enable deposition at an appropriate repository. The remedial conservation must replace the water (which is supporting the leather) with an inert substance which will support and bulk out the degraded structure, and allow it to retain its flexibility. Over the years many different methods have been used to conserve archaeological waterlogged leather including the use of different impregnation materials (Glycerol, Polyethylene glycol, dressings) and drying techniques (controlled air drying, vacuum freeze drying, non-vacuum freeze drying and solvent drying).

Currently, the most common technique used is a pre-treatment of either Glycerol or Polyethylene glycol (PEG) in water followed by vacuum freeze drying.

The initial costs of purchasing a freeze dryer, the maintenance and running costs or lack of access to a freeze dryer mean that only a limited number of commercial archaeological conservation laboratories and museums are able to offer vacuum freeze drying of leather as a service. The vacuum freeze drying of waterlogged archaeological leather is however often perceived by archaeological contractors as expensive and cited, along with access to facilities, as reasons for not conserving the leather. While other drying methods exist, the lack of comparative data seems to result in reluctance by both conservators and archaeological contractors to use these alternative methods.

Backlogs of un-conserved leather present a number of problems:

- Waterlogged leather is prone to the growth of mould and bacteria that can break down the leather and pose a health hazard.
- It may not be possible to complete the analysis and reporting of the leather by the Finds Specialist as some details of decoration, construction and features for species identification may not become visible until the leather is in a dry condition.
- The leather cannot be deposited at the appropriate repository (museum) therefore the archaeological excavating unit must take on the expense of cold storage and curation responsibilities (monitoring and changing of water to prevent biological activity).

3 METHODOLOGY

The aim of this study was to evaluate and compare different treatment and drying methods using a variety of parameters.

---

[1] Treatments used to stabilise an object for handling and storage
[2] The MGC recommend 18°C (10-25°C) and 55% Relative Humidity (dedicated organic collection, ± 5%) (MGC 1992)

The materials Polyethylene glycol (PEG) and Glycerol are commonly used in the conservation of waterlogged archaeological leather and were chosen as the impregnation medium at a concentration of 20% for three days. To evaluate the effect of the complexing agent Disodium Ethylenediaminetetra acetic acid (Na_2EDTA) on leather, half the samples were pre-treated with a 5% solution for two hours. Some samples did not receive any treatment and were dried from the wet state.

Four drying methods were chosen for this study: air drying, controlled air drying using saturated salt solutions, vacuum freeze drying and non-vacuum freeze drying (Table 1).

Table 1: Overview of treatment and drying techniques

Treatment	Number of samples in each category
No impregnation	14
5% EDTA	15
20% Glycerol	15
20% PEG400	15
5% EDTA 20% Glycerol	15
5% EDTA 20% PEG400	15

Drying Method	Number of samples in each category
Air drying	23
Controlled air drying	15
Vacuum freeze drying	26
Non-vacuum freeze drying	23

Each drying scenario, apart from the vacuum freeze dryer, was equipped with a data logger to record temperature and humidity during the drying period (Gemini Tinytag).

The following parameters were chosen to compare the various treatments: shrinkage, flexibility, appearance, time, effort and equipment needed (*see* 3.2 for a description of some of these parameters). Furthermore a condition score, originally developed by Suenson-Taylor and Sully (1997) was employed to record the condition of each piece before and after treatment.

Sample selection was random, with the exception for the vacuum freeze drying method for the leather labelled T (*see* 3.1 Sample material and condition). Samples were labelled using the already existing labels on the bags (*eg* NE1).

3.1 Sample material and condition

The leather was donated by Dean Sully, lecturer in Conservation at UCL. It was collected from a single site by UCL in 2003 from discarded material on the spoil heap of an excavation in Novgorod, an urban site in North West Russia. The leather had been used by UCL conservation students as part of their training in animal species identification. UCL had no further use for this material and it was ideal study material for this trial.

All 89 bags of leather comprised off cuts and fragments. Pieces were stored individually in water filled re-sealable polythene bags in a fridge. Some bags contained more than one piece of leather. The leather comes from three different locations on the excavation, which is indicated by the codes NE, NF and T (Table 2). During a brief visual examination it became evident that all the leather from area T was much more friable and fragmented than the leather from the other two areas. Furthermore some leather had developed mould (white spots). Some items did not have a grain surface and just seemed to consist of the corium. The leather was cleaned using running water and brushes and did not require any further washing.

Table 2: Leather samples according to the area

Area	Sample numbers
NE	1 to 15
NF	1 to 67
T	1 to 7

3.2 Recording before conservation

Recording before conservation fulfils several aims: it creates the primary record of the artefact as found, before any interventive treatment takes place and it can aid identification in case labels get lost or become indecipherable.

3.2.1 Photography

All pieces were photographed on a grid background, with a scale and a Kodak colour chart (Fig 1).

3.2.2 Drawing

Each piece was drawn and annotated on permatrace using a pencil. Where possible the leather was unfolded to illustrate the full size (Fig 2).

3.2.3 Dimensions

Thickness and length measurements were taken with a pair of callipers. If the piece allowed it, two measurements were taken (*eg* length and width) as well as thickness. The location where dimensions were taken on the fragments was recorded on the drawing (Fig 2).

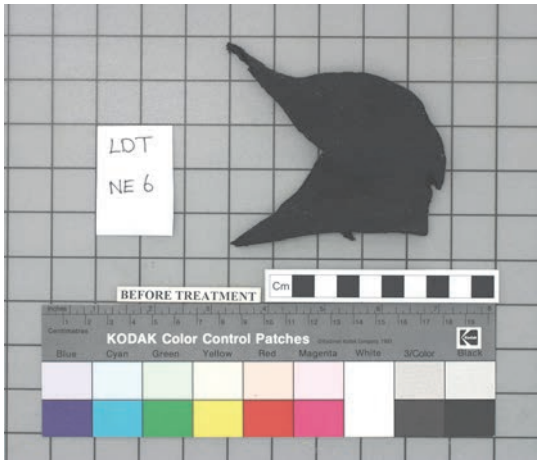


Fig1: Leather NE6 before conservation.

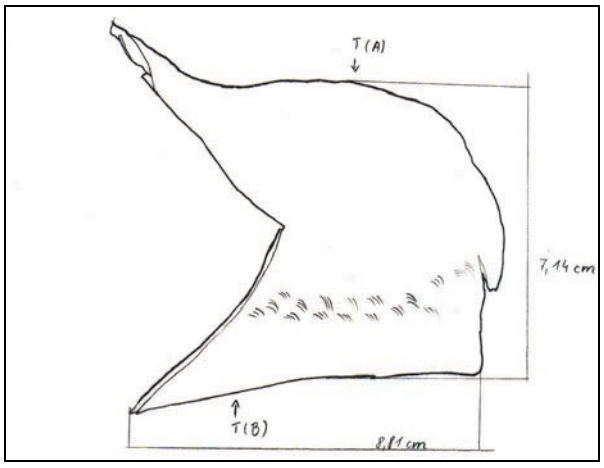


Fig 2: Leather NE6 before conservation with measurements marked on the drawing. T indicates where thickness measurements were taken.

3.2.4 Flexibility

In order to establish the flexibility before and after treatment, a flexibility test was devised[3]. For this study flexibility is defined as: the degree in change of movement when leather is suspended over an edge.

Each piece of leather was secured to a metallic cabinet by suspending the leather over the edge of the cabinet and placing a magnet on top of the leather. The degree it bent down was read on a protractor that was placed behind the cabinet. A value of -1 to -90° was recorded (Fig 3).

If the leather did not move at all or pointed upwards, the value 0 was assigned, as no change in movement took place (Fig 4). If the leather had some creases or cracks, that predetermined its flexibility or folding ability, *Not Applicable* (NA) was assigned (Fig 5).

[3] Initially it was planned to carry out a tear test. Given the limited number of leather samples and the irregular size of each sample, this method was disregarded and a flexibility test devised.

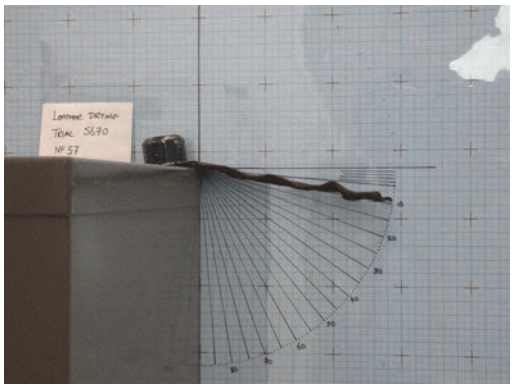


Fig 3: Leather NF57, -10° flexibility.

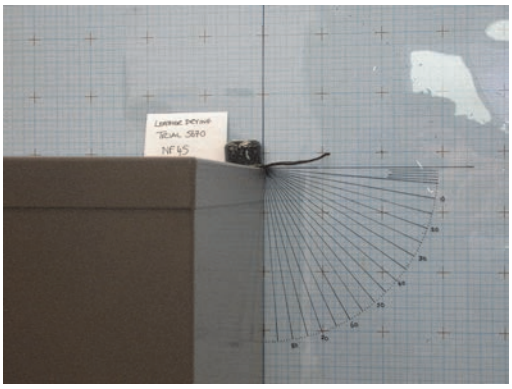


Fig 4: Leather NF45, 0° flexibility, as no change occurred.

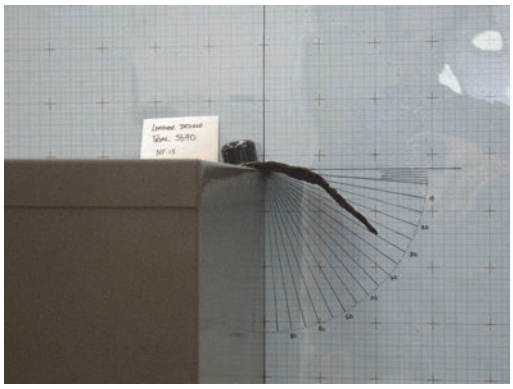


Fig 5: Leather NF15, NA, as the crack in the leather (right) predetermined the leather to bend down.

3.2.5 Condition score

The following categories were evaluated in the condition score (Tables 3 and 4 and Suenson-Taylor and Sully 1997): pre-burial damage, cohesivity, friability, flexibility. Points 1 to 4 were awarded in each category, apart from flexibility, which was only judged as unacceptable (1 point) or acceptable (2 points). The points were added up to give the overall condition score for each piece. The highest score possible, which is equivalent to the best condition, is 14 points. The lowest score is 4 points.

When one sample consisted of more than 1 fragment an average judgement for all fragments of the same sample number was made.

3.2.6 Object sheets

An object sheet was designed for each sample that summarised all the information collected during the trial. *See* Appendix 1 for an example of an object sheet.

Table 3: Condition Score Criteria from Suenson-Taylor and Sully 1997

Pre-burial damage: Assess the amount of use wear damage in relation to object type.	1 wear damage extensive or over whole area	2 wear damage over greater part	3 isolated areas of damage, not extensive	4 object intact, no wear damage
Cohesivity: Consider the integrity of the object as a whole. Look at vulnerable areas liable to loss. Bear in mind nature and shape of object.	1 many fragments readily detached during handling	2 several fragments readily detached during handling	3 minor areas of vulnerable fragments	4 leather intact, no vulnerable fragments
Friability: Assess condition of fibre network and grain surface. Where grain surface is no longer present, define condition of the remaining surface	1 fibres easily detached during handling, resulting in total loss of surface	2 greater part of surface and exposed edges liable to fibre loss	3 few areas of surface liable to loss of fibres	4 surface intact, no loss of fibres
Flexibility: Flexibility must be appropriate to the object, if flexible not so weak as to be damaging to the object. If inflexible not so brittle as to allow damage to occur during handling.	1 unacceptable: weak or stiff	2 acceptable: appropriate flexibility		

Table 4: Recording template from Suenson-Taylor and Sully 1997

Waterlogged Leather Condition Score							
Description			Pre-Treatment Condition				
Number	Description	No. of frags.	Pre-burial damage	Cohesivity	Friability	Flexibility	Pre-treatment score

Continued

Post-Treatment Condition				
	Cohesivity	Friability	Flexibility	Post-treatment score

3.2.7 X-radiography

One piece, a shoe fragment with nails, was X-rayed to get a better idea of the extent and condition of the metal fittings (Fig 6).

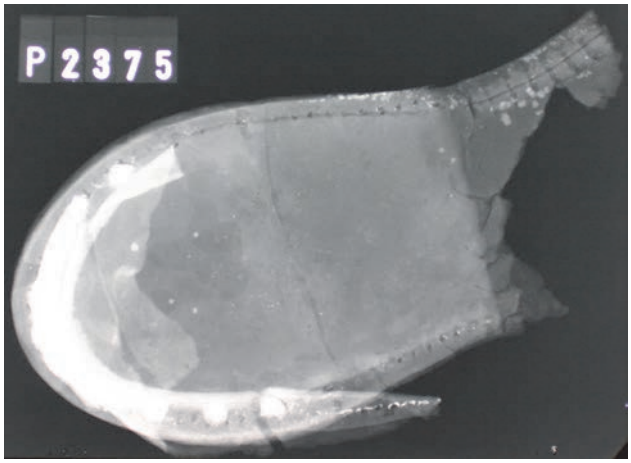


Fig 6: X-radiography of leather NF2.

3.3 The trial

3.3.1 Pre-treatment

A variety of chemicals have been used on waterlogged leather in the past to improve its appearance or flexibility. This study focused on the use of EDTA only, as it seems to be the material most widely used. Other chemicals used include solvents or acids.

A literature review confirmed that EDTA was commonly used in the past (Table 5). Often the reason for an EDTA treatment is not given. Informal discussions with several conservators did however reveal that it is used for one or more of the following reasons:

- To lighten up the colour of the leather.
- To produce a more natural looking artefact.
- To produce a more flexible artefact.
- When contamination with metal corrosion products has taken place from nearby objects or metal fittings of the same object.

Why EDTA is used

The mineral content of wet archaeological leather is sometimes considered to be a problem, which can result in iron staining and brittleness. Sequestering agents are used to

reduce the mineral content, which is also thought to prevent future problems in the oxidation of iron compounds especially during storage.

Table 5: Literature review of EDTA treatment

Reference	% EDTA	pH	Time	Rinse
Elmer 1980	10%			
Ganiaris *et al* 1982	5% Na_2EDTA		2 hours	24 hours
v. Dienst 1985	Na_2EDTA	2		
Wouters 1986	2%		24 hours	
Jenssen 1987	Commonly used			
Singley 1988	5%	4–6	2–3 hours	
Hamilton 2000	3–5%		2–3 hours	Until removed
Hovmand and Jones 2001	5% Na_2EDTA	4.5	4 days	Until conductivity reading settled
Peacock 2001	0.1M Na_2EDTA		5 hours	1 week
Godfrey *et al* 2002	5%		7 days	
Rodgers 2004	3–10%		Up to several hours per day, repeatedly	

How EDTA is used

Several sequestering agents are available; EDTA seems to be more commonly used than others. Not all publications state which type of EDTA is used; *eg* Disodium EDTA (Na_2EDTA) or Calcium disodium EDTA ($Na_2CaEDTA$). The use of Na_2EDTA is considered suitable, as the 5% solution produces a safe pH range of 3–6 for leather.

Issues

Sequestering agents such as Na_2EDTA, remove minerals from the leather. It is not clear, whether these minerals form part of the leather structure and should remain inside the leather or have leached into the leather from the burial environment and form a contaminant. Hovmand and Jones (2001) and Ganiaris *et al* (1982) have all studied the use of EDTA.

No data seems to be available to quantify the mineral content and the threshold above which it is likely to cause problems in the future due to oxidation activity or hydrolysis.

5% Na_2EDTA for two hours followed by 48 hours rinse in running tap water was included in this study as a pre-treatment to evaluate the effect on leather (with regards to shrinkage, flexibility and appearance). It was furthermore hoped that these effects can be studied using FTIR analysis. The pH of the 5%Na_2EDTA solution in deionised water (w/v) was 4.36 when the treatment began and 4.35 after two hours.

3.3.2 Impregnation

A vast variety of bulking and dressing agents have been used on waterlogged leather in the past. It is widely accepted that some impregnation has to take place before drying is attempted. The most commonly used materials today are aqueous solutions of Polyethylene glycol (PEG) and Glycerol. Concentrations and impregnation times vary and some places use a combination of both materials.

A 20% solution of PEG400 (weight/volume) and 20% Glycerol (volume/volume) was chosen as the bulking agent for this study. Impregnation time at room temperature was 3 days. The solution was stored in black polyethylene boxes away from direct sunlight and it was not agitated. The leather together with a Tyvek® label was placed inside an open mesh bag to allow for good impregnation.

3.3.3 Drying

All drying methods aim to carefully remove the water contained within the leather. Different methods can be used to achieve this:

- *Air drying*. The leather is simply allowed to dry at ambient conditions. This process can be slowed down by covering the leather with a piece of plastic.
- *Controlled air drying*. Specialist equipment or saturated salt solutions can be used to manipulate and control the environment around the leather to achieve a very controlled and slow drying environment. The relative humidity is incrementally reduced down to approx 55% RH, at which the leather is considered dry.
- *Solvent drying*. Here, the leather is placed in successive solvent-water mixtures with increasing amounts of solvents. The water in the leather is replaced with a liquid of lower surface tension. Once the leather has been immersed in 100% solvent the leather is slowly air dried.
- *Non-vacuum freeze drying*. This drying method relies on the process of *sublimation*: frozen water within the leather is transformed from the solid ice state directly to the gas state. Without going through the liquid water state eliminates surface tension. This can be carried out in a domestic chest freezer.
- *Vacuum freeze drying*. The same principle as for freeze drying applies, but the method is carried out in a vacuum freeze drying chamber. The vacuum speeds the process up by directing the sublimed water to the condenser, where it collects once again as ice.

The drying of waterlogged material even after impregnation is the most crucial part during the treatment of waterlogged organic materials. The final shape and appearance of the artefact is determined during this stage.

All leather was dried as found, for example folded pieces were not laid out flat nor weighted down. The weight of each piece was recorded every day throughout the trial. The end point was established when one or more of the following parameters were noted:

- The leather felt and looked dry.
- Two constant weights were measured.
- All ice crystals had disappeared.

Air drying

Slow air drying at ambient conditions was carried out on a polyethylene foam (Jiffy Foam®) lined tray with a polythene cover loosely draped on top (Fig 7). The tray was placed away from direct sunlight.

Controlled air drying

The use of saturated salt solutions for the conditioning of showcases is widely reported (Aastrup 1987; Aastrup and Hovin Stub 1990; Crehan 1991 a; Crehan 1991 b; Piechota 1992). Their use enables the accurate conditioning of enclosed environments which can be used for the slow drying of sensitive materials.

Controlled air drying was carried out inside a Perspex humidity chamber with the saturated salt solution placed at the bottom of the chamber and the leather above it on a grid (Fig 8). Three different solutions were used separately, each creating a specific relative humidity inside the chamber:

- Barium chloride – 90% RH
- Potassium iodide – 70% RH
- Magnesium nitrate – 55% RH

The solutions were changed after two days to slowly lower the humidity in increments. The leather was to be left in the humidity chamber for 1 week after the solution had been changed to Magnesium nitrate.

Fig 7: Slow air drying of leather.

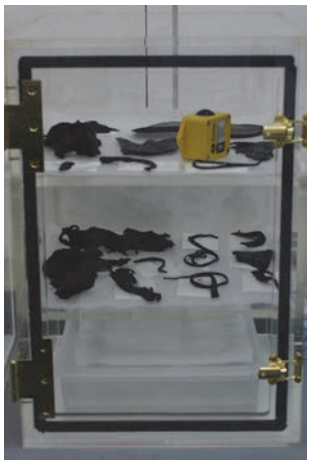


Fig 8: Controlled air drying of leather.

Fig 9: Non-vacuum freeze drying in the chest freezer.

Fig 10: Vacuum freeze dryer.

Non-vacuum freeze drying

Non-vacuum freeze drying was undertaken in a domestic chest freezer with the addition of silica gel and a fan (Fig 9). The leather was placed on thin plastazote foam inside open mesh baskets, which were stacked on top of each other. The baskets were put between the fan and the preconditioned silica gel (4.2kg split between the baskets), to allow for a gentle flow of cold air over the leather towards the silica gel. The chest freezer also contained 3 sealed sample buckets not connected to the trial.

Vacuum freeze drying

Vacuum freeze drying was carried out in a Birchover Instruments Ltd. Machine (75cm Diameter x 200cm long Chamber and 15 litre condenser) (Fig 10). The leather was pre-frozen in a domestic chest freezer for two days and then placed on acid free tissue lined trays inside the otherwise empty freeze drying chamber.

As all the leather from region T was found to be more friable than the leather from the other two regions NE and NF it was decided to deviate from the random sample selection in this case and vacuum freeze dry all the leather from region T. Vacuum freeze drying is the method the authors were most experienced in and it was felt that this method placed less risk on the very fragile leather.

3.3.4 Climate Readings

Gemini Tiny Tag data loggers were used during air drying, controlled air drying and non-vacuum freeze drying in order to record environmental parameters during the drying time.

3.4 Recording after conservation

The recording was repeated (as undertaken pre-conservation): photography, drawing, flexibility, dimensions and condition scoring (with the exclusion of the pre-burial category). To ensure consistency and allow direct comparisons, all measurements and photographs were taken at the same points and orientations.

4 RESULTS

4.1 Shrinkage

Leather, which chiefly consists of collagen, mainly survives due to waterlogging. During burial the collagen protein swells in water. The structural integrity of the collagen chain is lost, when hydronium ions (H_3O^+) in the water break bonds within the collagen chain. The final result is that protein turns into a gelatine colloidal solution (Florian 2006). This means that leather can be found in a structurally weakened state of preservation, and contains varying amounts of water.

During treatment the free water within the leather is removed. This results in some shrinkage. The behaviour of leather during conservation with regards to shrinkage is also influenced by the animal species, where on the animal the leather came from, tanning method and treatment during use, burial environment, length of burial and finally the

conservation treatment itself. A successful conservation treatment tries to limit the shrinkage and aims at retaining the dimensions of the leather object as found.

4.1.2 Evaluation of overall shrinkage

Out of 89 samples in total, 84 could be analysed with regards to shrinkage[4]. Only the length measurements were taken into account for the analysis of the shrinkage values. The overall shrinkage value is 7.3% (Fig 11). The standard deviation is 6.4.

Given the overall shrinkage results it can be concluded that 95% of all measurable samples shrank, 2.5% swelled and 2.5% experienced no dimensional change.

It is widely accepted that leather will experience some shrinkage during treatment. The mean shrinkage of 7.3% is acceptable. The high standard deviation means that there is a wide range of shrinkage values and some too high. This however is not surprising, given the variables in this studies and also taking into account that some treatment were trialled that would not normally be used as a conservation treatment (such as EDTA only or no impregnation). In reality, a more defined treatment designed for the individual condition of each object would overcome these high shrinkage values. As will become clear further down, the shrinkage values show some trends per treatment category.

4.1.3 Evaluation of shrinkage by conservation method

A total of 24 treatment categories were looked at (Table 6). Most categories contained 3–5 samples; two categories did however only contain 1 sample. This has to be borne in mind when interpreting the shrinkage values.

It becomes evident that all samples that received the 5% EDTA treatment only resulted in the highest shrinkage values, regardless of the drying method. This is not surprising, as it is widely accepted that EDTA removes minerals (and possibly other material) from the leather. In doing so, it opens up the fibre network, which results in leather that can contract more (*see* 3.3.1) (Hovmand and Jones 2001).

This effect however seems to be counteracted by the subsequent addition of either PEG or Glycerol. So even if certain minerals are removed by EDTA, the addition of a bulking agent fills the fibre network and prevents the leather from increased shrinkage.

[4] The following pieces with no grain surface (*see* 3.1 *Sample material and condition*) were not suitable for shrinkage measurements: NE3, NF33, NF48-NF50.

Table 6: Shrinkage values per treatment. The number of leather samples in each category is given in parenthesis.

Conservation Method	Average Shrinkage (%)	Average per drying method	Standard Deviation	Conservation Method	Average Shrinkage (%)	Average per impregnation method	Standard Deviation
20% Glycerol/ AD (4)	2.17	On average	3.7	20% Glycerol/ AD (4)	2.17	On average all	1.5
20% PEG 400/ AD (4)	3.17	all air dried		20% Glycerol/ CAD (2)	3.55	20% Glycerol	
5% EDTA/ AD (4)	10.99	samples shrank		20% Glycerol/ NVFD (5)	4.20	impregnated samples	
5% EDTA 20% Glycerol/ AD (3)	3.21	by 5.7%.		20% Glycerol/ VFD (3)	5.76	shrank by 3.9%	
5% EDTA 20% PEG 400/ AD (3)	5.26			20% PEG 400/ AD (4)	3.17	On average all	2.4
No impregnation/ AD (4)	9.49			20%PEG 400/ CAD (3)	4.83	20% PEG 400	
20% Glycerol/ CAD (2)	3.55	On average	7.6	20% PEG 400/ NVFD (3)	8.86	impregnated	
20% PEG 400/ CAD (3)	4.83	all controlled		20% PEG 400/ VFD (4)	6.50	samples shrank by	
5% EDTA/ CAD (3)	22.03	air dried		5% EDTA/ AD (4)	10.99	On average all	5.3
5% EDTA 20% Glycerol/ CAD (3)	3.49	samples shrank		5% EDTA/ CAD (3)	22.03	5% EDTA	
5% EDTA 20% PEG 400/ CAD (3)	4.73	by 8.8%		5% EDTA/ NVFD (4)	13.50	impregnated samples	
No impregnation/ CAD (1)	14.1			5% EDTA/ VFD (4)	10.49	samples shrank by	
20% Glycerol/ NVFD (5)	4.2	On average	3.5	5% EDTA 20% Glycerol/ AD (3)	3.21	On average all	0.9
20% PEG 400/ NVFD (3)	8.86	all non vacuum		5% EDTA 20% Glycerol/ CAD (3)	3.49	5% EDTA 20% Glycerol	
5% EDTA/ NVFD (4)	13.5	freeze dried		5% EDTA 20% Glycerol/ NVFD (3)	5.18	impregnated samples	
5% EDTA 20% Glycerol/ NVFD (3)	5.18	samples shrank		5% EDTA 20% Glycerol/ VFD (4)	4.27	samples shrank by	
5% EDTA 20% PEG 400/ NVFD (3)	5.00	by 7.5%		5%EDTA 20% PEG 400/ AD (3)	5.26	On average all	2.0
No impregnation/ NVFD (4)	8.32			5%EDTA 20% PEG 400/ CAD (3)	4.73	5%EDTA 20% PEG 400	
20% Glycerol/VFD (3)	5.76	On average	2.3	5%EDTA 20% PEG 400/ NVFD (3)	5.00	impregnated samples	
20% PEG 400/ VFD (4)	6.50	all vacuum		5%EDTA 20% PEG 400/ VFD (5)	8.95	samples shrank by	
5% EDTA/ VFD (4)	10.49	freeze dried		No impregnation/ AD (4)	9.49	On average all	2.6
5% EDTA 20% Glycerol/ VFD (4)	4.27	samples shrank		No impregnation/ CAD (1)	14.10	No impregnation	
5% EDTA 20% PEG 400/ VFD (5)	8.95	by 7.5%		No impregnation/ NVFD (4)	8.32	impregnated samples	
No impregnation/ VFD (5)	8.90			No impregnation/ VFD (5)	8.90	samples shrank by	

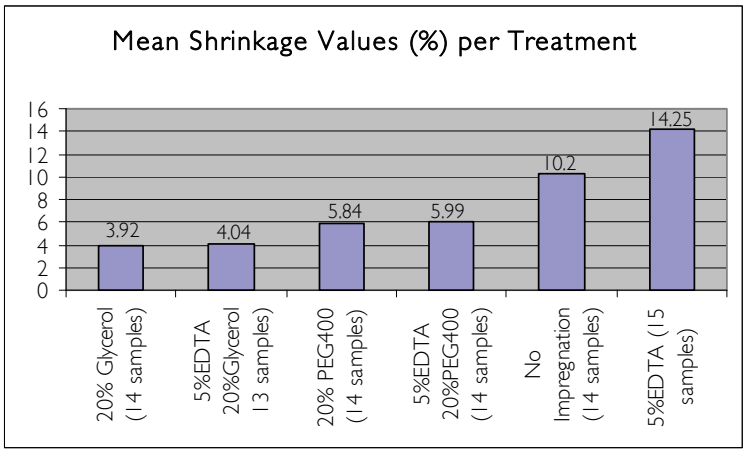


Fig 11: Mean shrinkage values (%) by treatment.

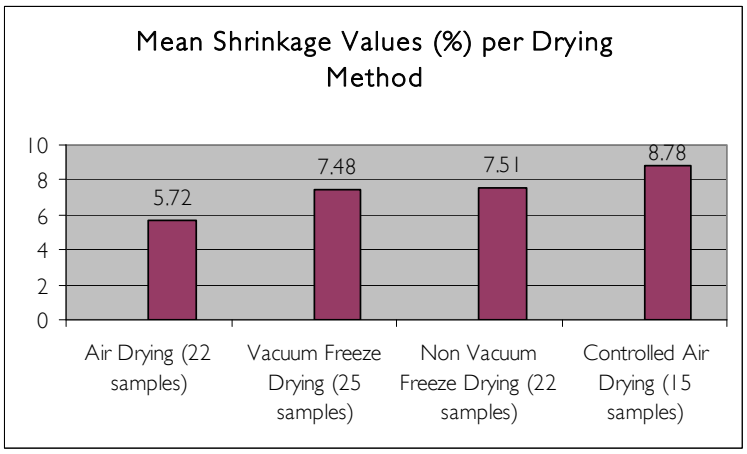


Fig 12: Mean shrinkage values (%) per drying method.

The second highest shrinkage was caused by "no impregnation". Again, this can be expected. As decayed leather has experienced some material loss and loss of structural integrity, water retains the shape of the leather. Once the water is removed, without the addition of a bulking agent the leather fibres will contract and the whole object shrinks.

The smallest shrinkage was achieved by 20% Glycerol impregnation (Fig 11).

When focussing on the drying methods, it can be concluded that the smallest shrinkage values were achieved by air drying and the largest by controlled air drying (Fig 12). The relatively high shrinkage value for vacuum freeze drying may have been caused by the fact that the very degraded and fragile leather from region T was dried using this method.

4.1.4 Discussion of shrinkage evaluation

During this trial a large number of dimensional measurements were taken, in order to gain some insight into the behaviour of leather during different treatments. Whilst the usefulness of shrinkage evaluations has been called into question in the past (Ibbs 1990), it was nevertheless deemed necessary for this experimental trial to quantify differences.

As outlined above, archaeological leather does already come with a number of variables, which all influence the shrinkage during treatment. The treatment and drying method itself furthermore alter the dimensions of leather. Leather does change in all three dimensions. Unlike wood, that has 3 clearly defined growth directions, which all behave differently with regards to shrinkage, the same is not true for leather.

This trial confirmed that taking two-dimensional measurements on an object that changes three-dimensionally is quite controversial. In addition, there is the possibility of inaccuracy when taking the measurements. This is especially true for the very small pieces, where a loss of just one millimetre in one direction can result in a very high overall shrinkage. Interesting was however, that the shrinkage results did show some trends, which could easily be explained by the treatment that the leather received (*see* 4.1.3 and Table 6).

4.2 Flexibility

4.2.1 Evaluation of overall flexibility

Flexibility was measured using two methods:

1. A standalone flexibility exercise which involved suspending each piece of leather over an edge and measuring the change in movement (*see* Figs 3 to 5).
2. Within the condition score system evaluating the flexibility of each sample in terms of appropriateness to the object i.e. either 'unacceptable: weak or stiff' or 'acceptable: appropriate flexibility' (*see* Table 3).

For method 1 the results were analysed by considering both the percentage of items increasing, decreasing or not changing in flexibility (Figs 13 to 16) and; the average loss in degrees of flexibility for each treatment and drying method (Tables 7 and 8).

Overall, the flexibility changed in 32% (method 1) and 38% (method 2) of the samples from before to after conservation. Where flexibility was empirically measured (method 1) only decreases in flexibility were recorded whereas the more subjective method 2 resulted in both increases and decreases in flexibility being recorded.

4.2.2 Evaluation of flexibility by treatment method

Method 1: No samples increased in flexibility according to method 1(Fig 13 and Table 7). Looking at the percentages of items categorised as decreasing or not changing in flexibility, the lowest percentage of items decreasing in flexibility occurred with EDTA alone (although nearly 50% of the EDTA items were classed as not applicable). The PEG resulted in the greatest percentage of items decreasing in flexibility. Looking at the actual degrees of loss, the EDTA and Glycerol treatment produced the lowest loss in flexibility (14.7 degree loss; see Table 7). The PEG and no impregnation treatments resulted in the greatest losses in flexibility (PEG: 24.5 degree loss and no impregnation: 25.5 degree loss; Table 7).

Method 2: All the samples that increased in flexibility were treated with Glycerol, EDTA or, EDTA and Glycerol (Fig 14). The treatments that resulted in the greatest loss of flexibility either received no impregnation or were treated with PEG.

4.2.3 Evaluation of flexibility by drying method

Method 1: A decrease in flexibility resulted from all drying methods (Fig 15) and the average decrease ranged from 9.8 degrees for air drying to 30.6 degrees for controlled air drying (Table 8).

Method 2: Vacuum freeze drying was the only method that did not result in any increases in flexibility (Fig 16). Non vacuum freeze drying performed marginally better than the two air drying methods.

4.2.4 Discussion of flexibility evaluation

Both flexibility evaluation methods have a drawback. Method 1 tried to overcome the subjective nature of method 2 by assigning a real value to the flexibility of the leather. This is only partly practical. The leather samples all have a different size and geometry. And even when the natural variables that leather brings with itself are not taken into account, method 1 has some clear disadvantages. The length of the leather and the way it is placed on the cabinet will influence to what degree it can bend over the edge. Therefore this method is not replicable. As Tables 7 and 8 show; the degree of variation within each category is high (*see* standard deviations).

Method 2, even though being subjective, takes a lot of parameters into account that are important to the evaluator. So rather than just deciding whether the leather is appropriately flexible, the evaluator will decide whether the flexibility is appropriate for this object.

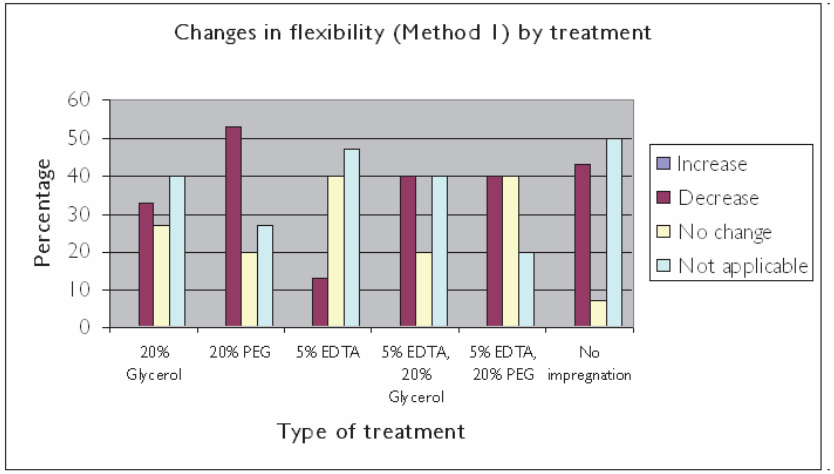


Fig 13: Changes in flexibility (Method 1) by treatment method.

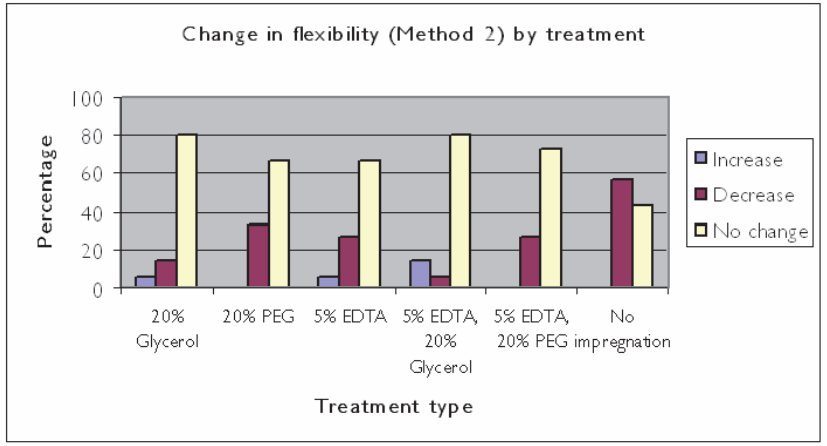


Fig 14: Changes in flexibility (Method 2) by treatment method.

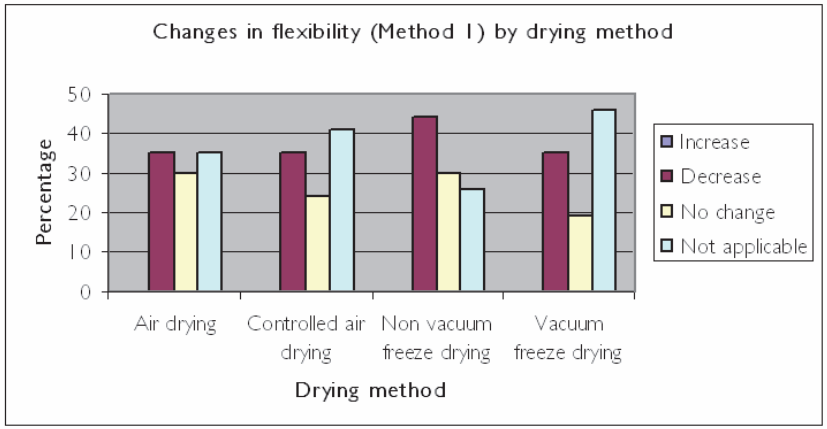


Fig 15: Changes in flexibility (Method 1) by drying method.

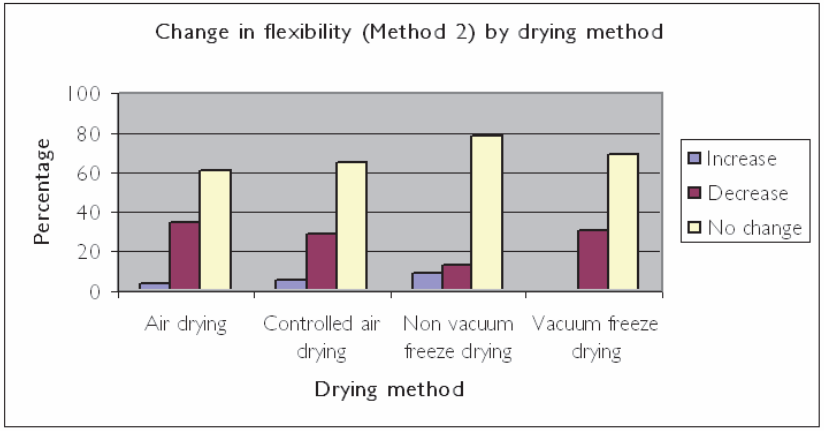


Fig 16: Changes in flexibility (Method 2) by drying method

Table 7: Results of method 1 flexibility test by treatment.

Treatment	Drying method	No. items tested.[5]	Average decrease in degrees of flexibility[6]	Standard deviation	Average decrease in degrees of flexibility by treatment	Standard deviation
20%Glycerol	Air Drying	2 (2)	3.33	5.7	16.8	22.3
	Controlled Air Drying	1 (1)	(0)			
	Non vacuum freeze drying	5	22.5	25.8		
	Vacuum Freeze Drying	1 (3)	(40)			
20%PEG400	Air Drying	2 (2)	18.0	11.3	24.5	24.8
	Controlled Air Drying	2 (1)	13.5	19.1		
	Non vacuum freeze drying	4	30.2	31.9		
	Vacuum freeze drying	3 (1)	24.8	25.0		
5% EDTA	Air Drying	3 (1)	0	0	20.3	37.9
	Controlled air drying	1 (2)	(90)			
	Non Vacuum Freeze Drying	1 (3)	(0)			
	Vacuum freeze drying	3 (1)	24.1	41.8		
5%EDTA 20%Glycerol	Air Drying	2 (1)	10.0	14.1	14.7	19.3
	Controlled Air Drying	2 (2)	5.0	7.1		
	Non Vacuum Freeze Drying	2 (1)	2.5	3.5		
	Vacuum freeze drying	3 (2)	28	24.9		
5%EDTA 20%PEG400	Air drying	4	10.0	11.5	18.0	19.7
	Controlled air drying	2 (1)	28.3	27.5		
	Non vacuum freeze drying	3	23.3	22.5		
	Vacuum freeze drying	3 (2)	13.0	22.5		
no impregnation	Air Drying	2 (2)	25.7	13.1	25.5	19.5
	Controlled air drying	2	47.0	4.2		
	Controlled Air Drying	1	(50)			
	Non vacuum freeze drying	2 (2)	1.5	2.1		
	Vacuum Freeze Drying	1 (1)	(30)			

[5] Number in parentheses represents the number of items that were assigned as not applicable for the method 1 flexibility test.

[6] Where a number is in parentheses it is not an average: there was only one item available or suitable for the method 1 flexibility test.

Table 8: Results of method 1 flexibility test by drying method

Drying	Treatment	No. items tested[5]	Average decrease in degrees of flexibility[6]	Standard Deviation	Average decrease in degrees of flexibility by drying method	Standard Deviation
Air Drying	20%Glycerol	2 (2)	3.3	5.7	9.8	11.6
	20%PEG 400	2 (2)	18.0	11.3		
	5% EDTA	3 (1)	0	0		
	5%EDTA 20%Glycerol	2 (1)	10.0	14.1		
	5%EDTA 20%PEG400	4	10.0	11.5		
	no impregnation	2 (2)	25.75	13.1		
Controlled Air Drying	20%Glycerol	1 (1)	(0)		30.6	29.7
	20%PEG 400	2 (1)	13.5	19.1		
	5% EDTA	1 (2)	(90)			
	5%EDTA 20%Glycerol	2 (1)	5.0	7.1		
	5%EDTA 20%PEG400	2 (2)	28.3	27.5		
	no impregnation	2	47.0	4.2.0		
Non vacuum freeze drying	20%Glycerol	5	22.5	25.8	19.7	25
	20%PEG 400	4	30.3	31.9		
	5% EDTA	1 (3)	(0)			
	5%EDTA 20%Glycerol	2 (1)	2.5	3.5		
	5%EDTA 20%PEG400	3	35.0	14.1		
	no impregnation	2 (2)	1.5	2.1		
Vacuum freeze Drying	20%Glycerol	1 (3)	(40)		24.5	24.4
	20%PEG 400	3 (1)	24.8	25.0		
	5% EDTA	3 (1)	24.2	41.8		
	5%EDTA 20%Glycerol	3 (2)	28.0	24.9		
	5%EDTA 20%PEG400	3 (2)	13.0	22.5		
	no impregnation	1 (3)	(30)			

4.3 Condition Score

4.3.1 Evaluation of overall condition score

As an initial evaluation the difference between the condition score before conservation and the condition score after conservation was calculated to evaluate if the score increased, decreased or remained unchanged. Pre-burial damage was excluded a0 this factor was used to consider what treatment methodology to use.

Tables Overall, 43% of the condition scores increased, 25% decreased and 32% remained unchanged. The change of condition score ranged from a loss of 1 to 3 points to a gain of

1 to 4 points with the average loss in condition 1 point and the average gain in condition 1 to 2 points (Table 9).

Table 9: Changes in condition score points

Change in condition score	Number of items
-1	16
-2	4
-3	2
No change	29
1	14
2	20
3	2
4	2

Where did the changes in condition scoring occur?

- Increases in value occurred mainly from improvements in the cohesivity and friability values
- Decreases in value occurred mainly in the flexibility value.
- Items from site T decreased in condition score across all three categories.

Overall, based on the condition score, the best treatment is 5% EDTA and 20% Glycerol followed by controlled air drying or non vacuum freeze drying.

4.3.2 Evaluation of condition score by treatment

The best performing treatment for improved condition was 5% EDTA and 20% Glycerol where 64% of the condition scores increased (Fig 17) and the highest average increase in condition score occurred (1.13 increase in score; Table 10). The worst performing treatment was no impregnation where 40% of the condition scores decreased (Fig 17) and the highest average loss in condition score occurred (-0.28 loss in score; Table 10).

Table 10: Changes in condition score by treatment

Treatment	Drying method	Average change in score	Standard deviation	Average per treatment	Standard deviation
20%Glycerol	Air Drying (4)	0	0.81	0.26	1.1
	Controlled Air Drying (2)	0	0		
	Non Vacuum Freeze Drying (5)	0.8	1.3		
	Vacuum Freeze Drying (4)	0	1.41		
20%PEG 400	Air Drying (4)	0.75	0.96	0.6	1.4
	Controlled Air Drying (3)	1	1		
	Non Vacuum Freeze Drying (4)	1	1.15		
	Vacuum Freeze Drying (4)	-0.25	2.22		
5% EDTA	Air Drying (4)	1	1.82	0.66	1.4
	Controlled Air Drying (3)	0	1.73		
	Non Vacuum Freeze Drying (4)	1	1.41		
	Vacuum Freeze Drying (4)	0.5	1		
5%EDTAl 20%Glycerol	Air Drying (3)	1	1.73	1.13	1.7
	Controlled Air Drying (4)	1.5	1.91		
	Non Vacuum Freeze Drying (3)	2.3	1.53		
	Vacuum Freeze Drying (5)	0.2	1.48		
5%EDTA 20%PEG 400	Air Drying (4)	-0.5	0.58	0.13	1.24
	Controlled Air Drying (3)	0.66	0.58		
	Non Vacuum Freeze Drying (3)	-0.66	0.58		
	Vacuum Freeze Drying (5)	0.8	1.79		
No impregnation	Air Drying (4)	-0.5	1.29	-0.28	1.44
	Controlled Air Drying (2)	1	0		
	Non Vacuum Freeze Drying (4)	0.25	1.26		
	Vacuum Freeze Drying (4)	-1.25	1.7		

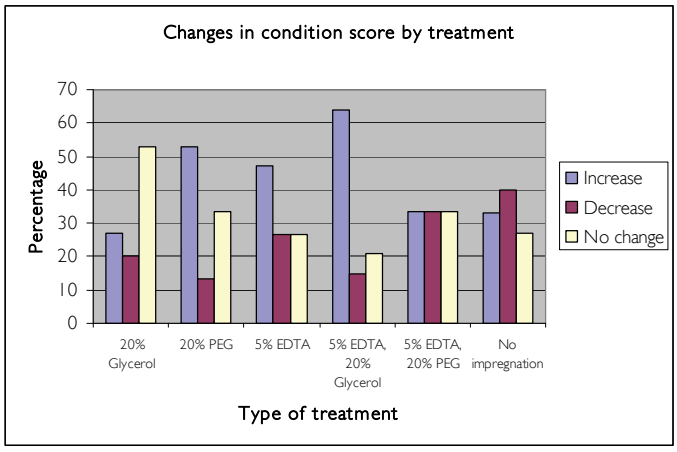


Fig17: Changes in condition score by treatment type.

Table 11: Changes in condition score by drying method

Drying Method	Treatment	Average change in score	Standard deviation	Average per drying method	Standard deviation
Air Drying	20%Glycerol (4)	0	0.82	0.26	1.3
	20%PEG 400 (4)	0.75	0.96		
	5% EDTA (4)	1	1.82		
	5%EDTA 20%Glycerol (3)	1	1.73		
	5%EDTA 20%PEG400 (4)	-0.5	0.57		
	no impregnation (4)	-0.5	1.29		
Controlled Air Drying	20%Glycerol (2)	0	0	0.76	1.2
	20%PEG 400 (3)	1	1		
	5% EDTA (3)	0	1.73		
	5%EDTA 20%Glycerol (4)	1.5	1.9		
	5%EDTA 20%PEG400 (3)	0.66	0.57		
	no impregnation (2)	1	0		
Non Vacuum Freeze Drying	20%Glycerol (5)	0.8	1.3	0.78	1.38
	20%PEG 400 (4)	1	1.15		
	5% EDTA (4)	1	1.41		
	5%EDTA 20%Glycerol (3)	2.33	1.52		
	5%EDTA 20%PEG400 (3)	-0.66	0.57		
	no impregnation (4)	0.25	1.26		
Vacuum Freeze Drying	20%Glycerol (4)	0	1.41	0.03	1.61
	20%PEG 400 (4)	-0.25	2.21		
	5% EDTA (4)	0.5	1		
	5%EDTA 20%Glycerol (5)	0.2	1.48		
	5%EDTA 20%PEG400 (5)	0.8	1.78		
	no impregnation (4)	- 1.25	1.7		

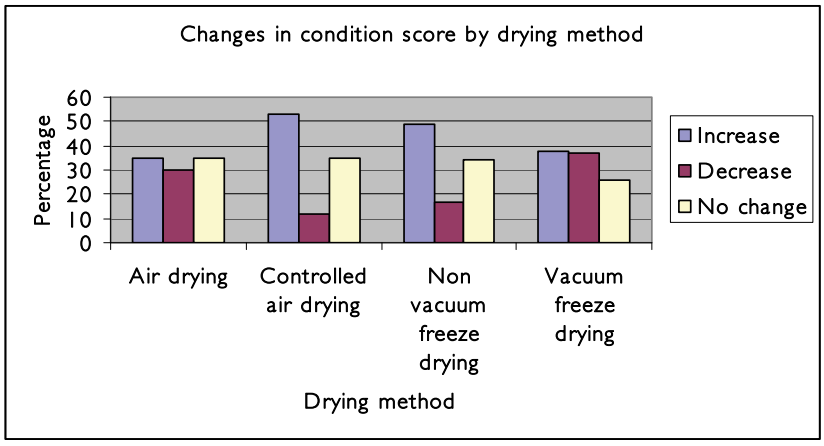


Fig 18: Changes in condition score by drying method.

4.3.3 Evaluation of condition score by drying method

The controlled air drying and non vacuum freeze drying methods both performed well with approximately half of the items increasing in condition score and the highest average increases in condition score (0.76 and 0.78 increase in score respectively; Table 11). A third of the items dried by air drying and vacuum freeze drying also increased in condition.

Vacuum freeze drying resulted in the highest percentage of items decreasing in condition score (37%; Fig 18) and lowest average increase in condition score (0.03 increase in score; Table 11) although, the selection of all the poor condition T site items for freeze drying may account for the low score. Controlled air drying resulted in the lowest percentage of items decreasing in condition score (12%; Fig 18).

4.4 Evaluation of appearance

All leather looked acceptable after treatment and was of a natural brown colour. Some items seem to have a slight red-brown tinge (Figs 19 and 20). These were mainly those having undergone Na_2EDTA pre-treatment. As colour was not recorded in a standard way before treatment, it is not clear to what extent this colour was already present in the wet, untreated leather.

Fig 19 Leather NE 2 (5%EDTA, vacuum freeze drying) appears to be slightly orange following the EDTA treatment.

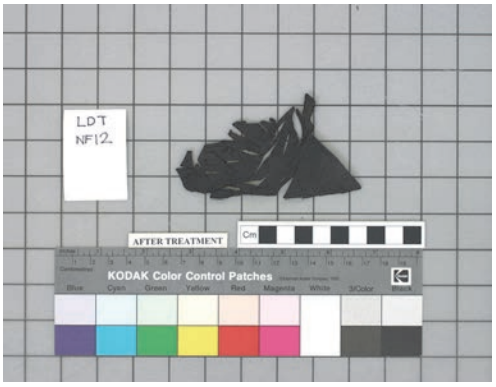


Fig 20: Leather NF 12 (no impregnation, controlled air drying) appears in a uniformly brown colour.

Leather that was dried in the vacuum freeze dryer appeared to be more dry and brittle immediately after treatment compared to the leather from the other drying set ups. The leather did however relax and acclimatise after 2 days in the laboratory environment and did not look different to the other leathers.

Surface features, when present, were preserved well. An examination by fellow conservators, curators and leather specialist confirmed the overall satisfying appearance of the leather.

4.5 Evaluation of treatment time

Since the pre-treatment and impregnation time was the same for all sample batches, only the drying time differed.

Vacuum freeze drying was the fastest method, closely followed by air drying. Non-vacuum freeze drying took longest, whilst controlled air drying was only a day shorter (Fig 21).

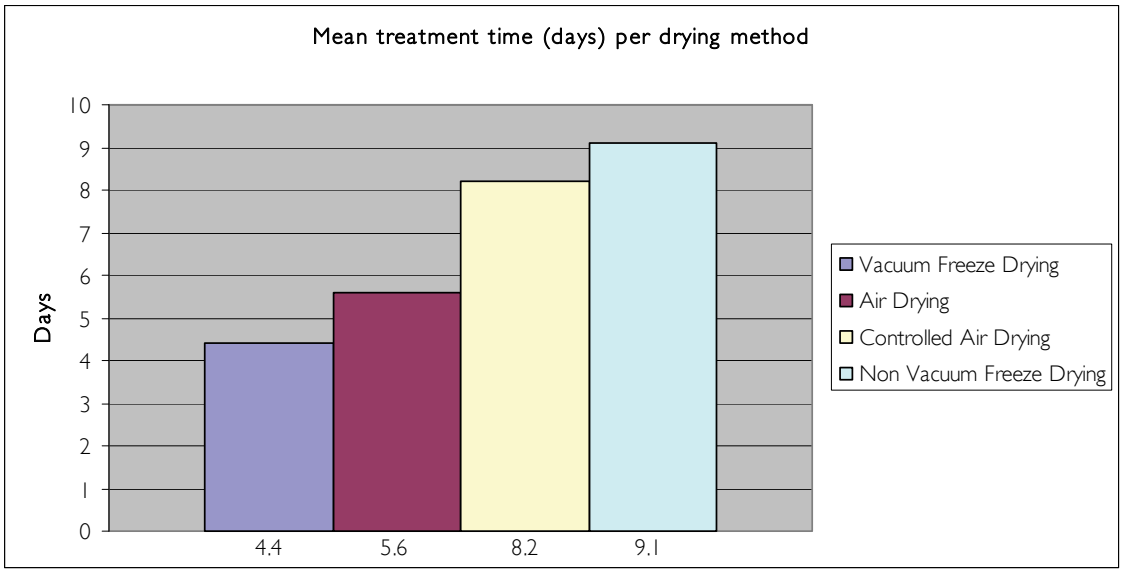


Figure 21: Mean treatment time (days) per drying method.

4.6 Evaluation of equipment and materials needed

The method that required the least amount of equipment and minimal set up was air drying. All that was needed was a tray, some foam and a polythene sheet (Table 12).

Non-vacuum freeze drying was also quite easy to carry out with only access to a domestic chest freezer required. Baskets that can be stacked on top of each other help to make use of the available space, but a tray would work just as well. This method also works without the addition of silica gel and the fan.

Vacuum freeze drying requires a freeze drying machine or access to one. When choosing this as the standard treatment method, if it is to be undertaken in-house, the initial purchase, running and service costs have to be borne in mind. Additional equipment includes only trays. If vacuum freeze drying is undertaken externally, costs will include transportation of the leather to the institution and freeze drying service charges.

Table 12: Overview of material and equipment required for each drying method

Air Drying	tray foam polythene sheet
Non-vacuum freeze drying	domestic chest freezer baskets foam (silica gel, netting bags, fan)
Vacuum freeze drying	vacuum freeze drying machine trays acid free tissue
Controlled air drying	climate chamber or well sealed box container for saturated salt solution semi-permeable membrane saturated salt solutions shelves inside the chamber hygrometer

Controlled air drying depends on a well sealed climate chamber or well sealed box that holds a container with the saturated salt solution and all the leather to be dried. Shelves or stackable baskets make best use of all the available space. A number of different salt solutions are required to lower the humidity in increments. A simple hygrometer helps to monitor the humidity on a daily basis. A fan ensures good airflow inside the chamber[7].

4.7 Evaluation of climate readings

4.7.1 Air drying

A total of 134 readings were taken between 16th March to 27th March 2009 and a summary of the readings can be found in Table 13. They show that temperature and humidity largely follow the daily fluctuations experienced in the laboratory (Fig 22). After four days the humidity drops to approximately 62% RH and moisture loss seems to slow down (vertical line on the graph).

The very deep troughs in the humidity graph correlate with the polythene sheet being removed to weigh the leather (some are marked with arrows on the graph, Fig 22).

[7] No fan was used in this trial.

Table 13: Summary of climate reading for the air drying method

Air drying		
Property	Humidity	Temperature
Logging Started	16/03/2009 12:01:14	16/03/2009 12:01:14
Logging Ended	27/03/2009 14:02:00	27/03/2009 14:02:00
Logging Duration	11 days	11 days
Interval	2 hours	2 hours
Number of Readings	134	134
Logging Mode	Minutes Mode	Minutes Mode
Minimum Reading	38.8 %RH	11.1 °C
Maximum Reading	97.1 %RH	22.6 °C
Average Reading	65.2 %RH	14.3 °C
Mean Kinetic Temperature		14.6 °C

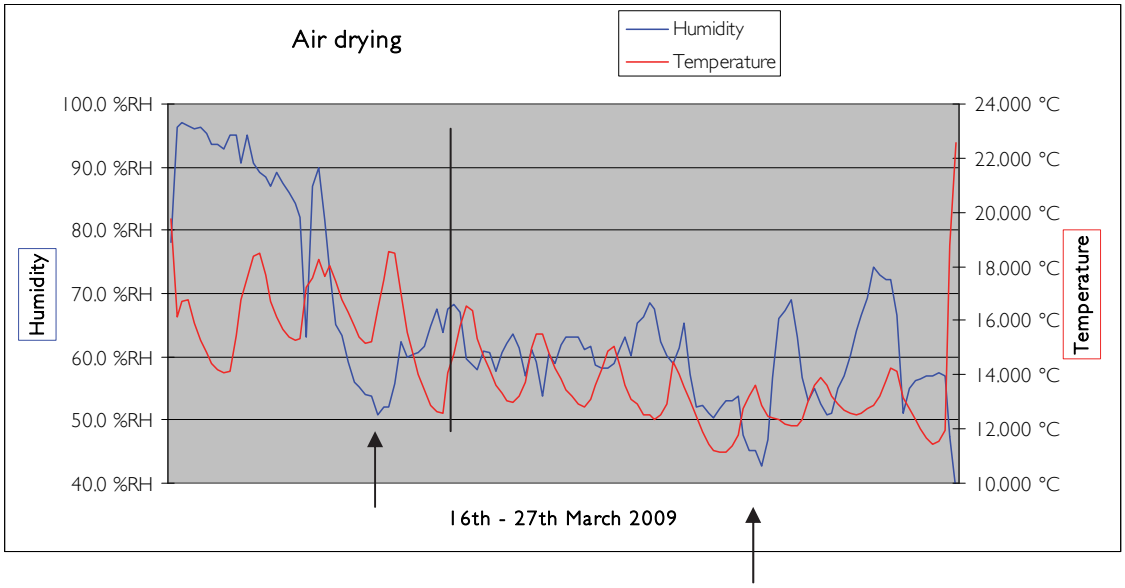


Fig 22: Temperature and humidity readings for the air drying method. The arrows indicate low points in RH where the sheeting was removed to weigh the leather. The vertical line marks 4 days after which the moisture loss seems to slow down.

4.7.2 Non-vacuum freeze drying

A total of 167 readings were taken between 16th and 30th March 2009 and a summary of the readings can be found in Table 14. Conditions inside the chest freezer are very stable and only fluctuate when the lid is opened to weigh the leather, which correlates with high peaks on the graph (Fig 23).

Table 14: Summary of climate reading for the non-vacuum freeze drying method

Non-Vacuum freeze drying		
Property	Humidity	Temperature
Logging Started	16/03/2009 13:02	16/03/2009 13:02
Logging Ended	30/03/2009 09:02	30/03/2009 09:02
Logging Duration	13.85 days	13.85 days
Interval	2 hours	2 hours
Number of Readings	167	167
Logging Mode	Minutes Mode	Minutes Mode
Minimum Reading	50.2 %RH	-26.0 °C
Maximum Reading	55.2 %RH	-24.3 °C
Average Reading	51.3 %RH	-25.0 °C
Mean Kinetic Temperature		-25.0 °C

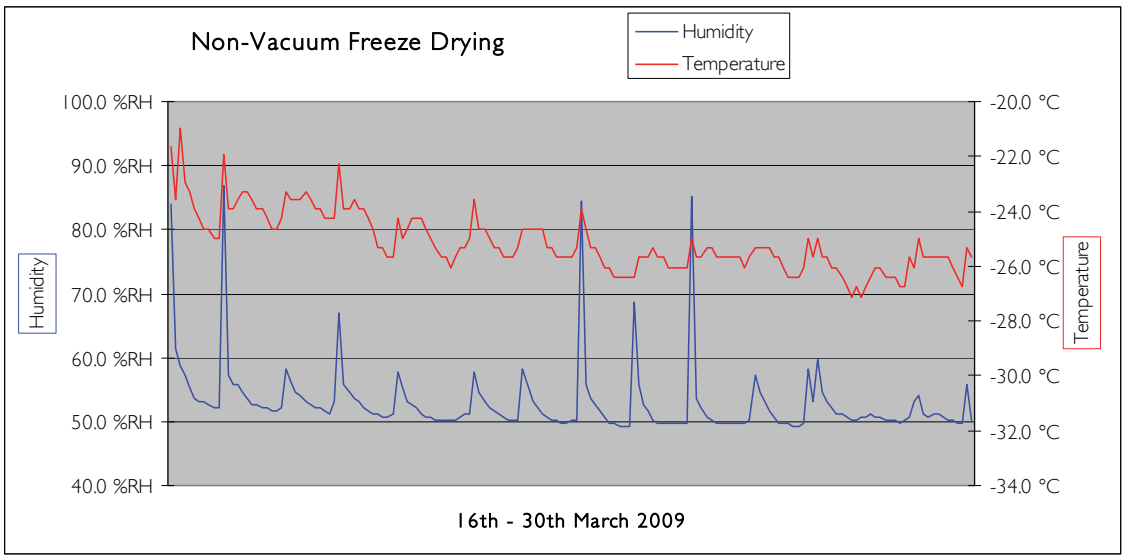


Fig 23: Temperature and humidity readings for the non-vacuum freeze drying method.

4.7.3 Controlled air drying

A total of 1331 readings were taken between 16th and 30th March 2009 and a summary of the readings can be found in Table 15. It was very difficult to create the desired humidity within the chamber and ideally the graph should have displayed three distinguishable, sloping steps. Even though the saturated salt solutions were changed every second day, it became clear that the humidity only started to fall once a considerable amount of leather had been removed from the chamber (Fig 24).

The strong troughs on the humidity graph (Fig 24) correlate with the chamber door being opened to weigh the leather.

Table 15: Summary of climate reading for the controlled air drying method

Humidity Chamber		
Property	Humidity	Temperature
Logging Started	16/03/2009 13:00:52	16/03/2009 13:00:52
Logging Ended	30/03/2009 09:31:00	30/03/2009 09:31:00
Logging Duration	13.85 days	13.85 days
Interval	15 minutes	15 minutes
Number of Readings	1331	1331
Logging Mode	Minutes Mode	Minutes Mode
Minimum Reading	42.6 %RH	13.0 °C
Maximum Reading	98.3 %RH	22.8 °C
Average Reading	80.9 %RH	17.6 °C
Mean Kinetic Temperature		18.0 °C

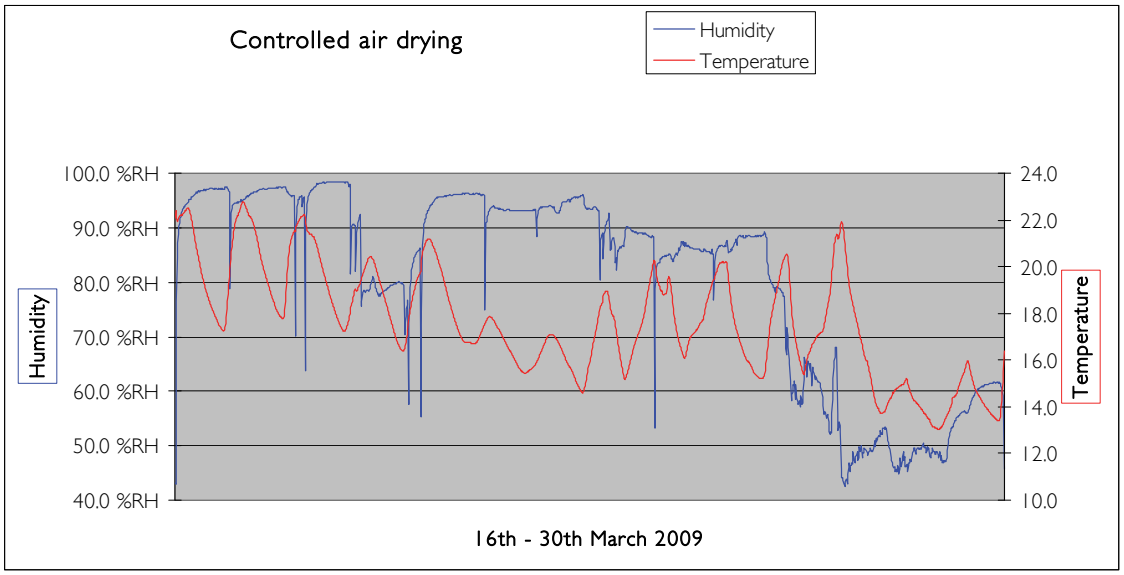


Fig 24: Temperature and humidity readings for the controlled air drying method.

4.8 Packing of the conserved leather

The treated leather was packed in perforated re-sealable polythene bags on a support of 'jiffy' polyethylene foam, which was wrapped in acid free tissue. The bags are stored in archival cardboard boxes.

5 ANALYSIS

5.1 Methodology

Two types of analysis were undertaken as part of the trial with specific aims:

1. Scanning Electron Microscopy (SEM) aimed to look at the differences in the fibre structure of leather according to three variables: different treatment, different drying methods and, at different stages of the treatment. Essentially, it aimed to see the differences in the leather structure between wet and dry fibres and between PEG and Glycerol impregnated leather.

2. Fourier-transform infrared spectroscopy (FTIR) analysis aimed to examine the changes in the leather as a result of the different treatment and drying methods and long term storage. The results of the FTIR analysis will form part of a separate report.

5.2 Scanning Electron Microscopy (SEM)

To take images of the wet samples, the Environmental SEM in the Institute of Archaeology, UCL was utilised with the assistance of Kevin Reeves and Kelly Domoney. Normally, dry samples are carbon or gold coated and imaged under vacuum. If biological and wet samples are placed under vacuum the water vapour from the material interferes with the electron beam and the samples dry out. Biological and wet samples must therefore be left uncoated and not placed under total vacuum. The UCL environmental SEM also has a cryo-stage that can reduce the temperature of the mount stage to 0–1°C.

A day was spent on the UCL environmental SEM and whilst some images were taken, there were issues with the sample drying during the process of mounting, de-gassing and specimen beam interaction. The main issue was balancing the required environmental parameters within the chamber (to maintain the samples in a wet state) and image quality. Since the cryo-stage is rarely used on the UCL SEM it was decided that there was not sufficient time and expertise with wet material to achieve optimum conditions and image quality. A decision was therefore taken to undertake SEM imaging of the leather *after* conservation and in the dry state at Fort Cumberland. The aim of this was to examine and compare the leather structure of different treatments and one sample of the following treatment categories was examined using the SEM (Table 16).

Table 16: Leather samples selected for SEM examination

Leather sample	Treatment method	Drying method
NF 58	20% Glycerol	Vacuum Freeze Drying
NF 19	20% Glycerol	Air Drying
T 4	20% PEG400	Vacuum Freeze Drying
NF34	20% PEG400	Air Drying
NE 9	no impregnation	non Vacuum Freeze Drying
NF 3	no impregnation	Air Drying
NF12	no impregnation	Controlled Air Drying
NF 13	no impregnation	Vacuum Freeze Drying

5.2.1 Results of SEM examination

For a detailed description of each sample, *see* Appendix 3. When interpreting the image results it has to be borne in mind that no direct comparison to the wet sample was possible. The original condition of the leather will also have an impact on what it looks like after treatment. For example leather sample T4 looks much more 'chaotic' than all the other samples (Fig 25). As discussed earlier, all the T leather was in a poorer condition than NF and NE leathers (*see* 3.1) and this is reflected in the SEM images.

Some differences were apparent with the main difference being between the drying methods applied. The methods involving freezing (*eg* freeze drying with vacuum and without vacuum) resulted in a leather displaying an open fibre structure (Fig 26). The air dried leathers (Fig 27) appear more compact.

The spaces between the fibres in the wet or impregnated sample are filled with either water, PEG or Glycerol. During freezing, the fibre structure is locked in place by the ice[8]. When the frozen leather dries, the ice sublimes. This retains the spaces between the fibres, resulting in a more open fibre structure (Fig 26). During air drying, where the leather is dried from the wet state, the water evaporates. The surface tension exerted by the evaporating water pulls the leather fibres together, resulting in a more compact fibre structure (Fig 27).

These findings are further supported by the flexibility results (*see* 4.2) where the drying methods that involved freezing results in better flexibility after treatment.

There were no visual differences between leather that had been PEG or Glycerol treated or, received no impregnation. This suggests that on a visual level the main factor influencing the fibre structure is the drying rather than the impregnation method.

8 Freezing takes place at low temperatures very quickly, which results in the formation of small ice crystals. The increase in volume can normally be neglected.

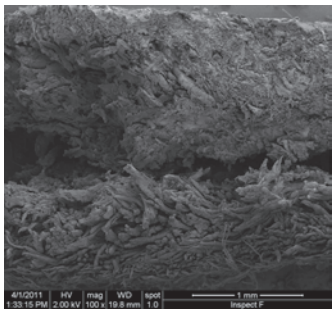


Fig 25: Leather sample T 4, displaying a chaotic fibre structure.

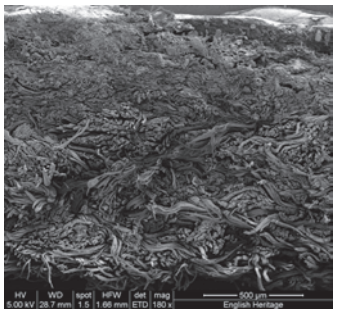


Fig 26: Leather sample NE 9 (no impregnation followed by non vacuum freeze drying), displaying a uniformly open fibre structure.

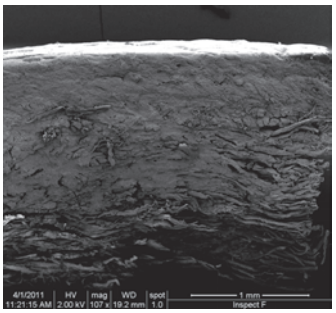


Fig 27: Leather sample NF 3 (no impregnation followed by air drying), displaying a compact fibre structure.

6 DISCUSSION

All the pre-treatment and impregnation methods worked well. Preparation time was minimal and all methods are equally suitable for bulk or individual treatment.

The only point to consider is the use of Na_2EDTA as a standard treatment: it not only prolongs the overall treatment time but, the required wash afterwards uses quite a lot of water thereby adding to the overall treatment time and costs. In some cases, such as when the leather has iron fittings or staining, it may be acceptable to use EDTA.

Air drying and non-vacuum freeze drying worked surprisingly well, with the only caveat that non-vacuum freeze drying required a little more effort in terms of set up. The silica gel required reconditioning and in this trial it was placed inside custom made nylon net bags. A simpler set up with the silica gel in open trays would have saved some time. On reflection though, this method would work equally well without the silica gel and the fan. Drying may take a little longer in this case. Overall non-vacuum freeze drying and air drying could be sped up by gently manipulating the shape of the leather, as the formulation of ice crystal in creases prolonged the drying process.

Vacuum freeze drying also worked well. The only reservation would be that drying seemed to be very rapid compared to air drying and non-vacuum freeze drying, which was reflected in the very dry and lighter appearance of the leather. This effect was however temporary.

Controlled air drying did not work very well in this trial. It proved extremely difficult to establish the required humidity and the Magnesium nitrate solution did not saturate. As a result drying at elevated humidity was prolonged. This caused some of the leather to develop white spots. On reflection the following areas of improvement can be identified:

- Use a larger humidity chamber.
- Use the correct amount of saturated salt solution for that size of humidity chamber[9].
- Aid circulation by open shelves or baskets.
- Use a fan to further aid circulation.

The extensive use of analytical methods was justified in this trial. During standard conservation treatment it is however unlikely to employ all those methods. When evaluating leather before and after conservation, the conservator or finds specialist takes a whole range of parameters into account. Rather than asking whether the appearance or flexibility are satisfactory, the question is more whether appearance and flexibility are appropriate for this type of object. A leather garment is expected to be soft and flexible to provide comfort during use. On the other hand, a leather sole is stiff to provide support and protection for the wearer.

So even by looking at various parameters to judge a certain conservation treatment, it is important to bear in mind, that conservators and finds specialist will use their own, almost subjective evaluation and no parameter is ever looked at in isolation.

7 CONCLUSIONS

The leather drying trial resulted in a vast amount of data. The analysis and interpretation of which took longer than anticipated. However, some very good conclusions can be drawn from the experiments.

Although 20% Glycerol impregnation resulted in slightly less shrinkage compared to 20% PEG, glycerol is more hygroscopic than PEG, which is an important consideration for future storage or display. As can be expected, the 'No Impregnation' samples resulted in rather high shrinkage values and for that reason, an impregnation should always be carried out.

A variation of the methods used here to suit individual objects is possible. The trial indicated that with the exception of controlled air drying, all techniques are suitable for both large scale and individual treatment. Controlled air drying was the most labour intensive method and needs improving. Non-vacuum freeze drying worked very well. This process could be sped up by gently manipulating the shape of the leather. Freeze drying was a very rapid method of drying and the leather felt rather dry and brittle when it first came out of the freeze drier. Air drying worked very well and when carried out with care and caution this could be a very valid alternative compared to vacuum freeze drying.

9 This seems to be quite difficult, as the literature is not clear about how much volume of salt solution is needed per unit of showcase/ humidity chamber.

Even though the use of an environmental SEM was not successful in this study, this is still a valuable method to examine fibre structure before treatment.

The method of choice depends on a variety of parameters, such as: time, budget, availability of equipment, experience of staff and complexity of the object. An informed decision has to be made on a case to case basis and the lack of access to a vacuum freeze drier should not be a factor limiting the conservation of leather.

Further research could focus on the mineral content in waterlogged archaeological leather to establish whether there are certain minerals that can be classified as damaging for leather or whether there is a threshold above which the mineral content becomes problematic. A repeat of this trial would be useful if the same sized leather samples ideally from one hide could be used. Sample provision might be difficult though in this case.

BIBLIOGRAPHY

Aastrup, E E 1987 'Is it worth-while re-looking at salt solutions as buffers for humidity control of showcases?', *in* K Grimstad and J Hill (eds) *Preprints 8th Triennial Meeting ICOM Committee for Conservation, Sydney, Australia, 6-11 September 1987*. Los Angeles: The Getty Conservation Institute for the ICOM Committee for Conservation, 853–858

Aastrup, E E and Hovin Stub, K E 1990 'Saturated salt solution for humidity control of showcases – Conditions for a successful system', *in* K Grimstad (ed) *Preprints 9th Triennial Meeting ICOM Committee for Conservation, Dresden, German Democratic Republic, 26-31 August 1990*. Los Angeles: ICOM Committee for Conservation, 577–582

Crehan, J 1991a 'Controlling relative humidity with saturated calcium nitrate solutions'. *Western Association for Art Conservation (WAAC) Newsletter* 13 (1), 17–18

Crehan, J 1991b 'Update and feedback: Controlling humidity with saturated calcium nitrate solutions'. *Western Association for Art Conservation (WAAC) Newsletter* 13 (2), 11–12

Dienst van, E 1985 'Some remarks on the conservation of wet archaeological leather'. *Studies in Conservation* 30, 86–92

Edwards, G and Mould, Q 1995 *Guidelines for the care of waterlogged archaeological leather*. Scientific and Technical Publications Guidelines No 4. London: English Heritage

Elmer, J T 1980 'Die Gefriertrocknung von Nassleder-Bodenfunden aus dem Bereich der Archaeologie', *in Konservering og restaurering af laeder, skind og pergament*. Kopenhagen: Konservatorenskolen det Kongelige Danske Kunstakademi, 212–225

Florian, M 2006 'The mechanisms of deterioration in leather' *in* M Kite and R Thomson (eds) *Conservation of Leather and Related Material*. London: Butterworth-Heinemann, 36–57

Ganiaris, H, Keene, S and Starling, K 1982 'A comparison of some treatments for excavated leather'. *The Conservator* 6, 12–23

Godfrey, I, Kasi, K and Richards, V 2002 'Iron removal from waterlogged leather and rope recovered from shipwreck sites', *in* P Hoffmann, J A Spriggs, T Grant, C Cook and A Recht (eds) *Proceedings of the 8th ICOM Group on Wet Organic Archaeological Materials Conference. Stockholm 2001*. Bremerhaven: ICOM-CC WOAM Working Group, 439–470

Hamilton, D 2000 'Conservation of cultural materials from underwater sites. Science and technology in historic preservation', *in* R A Williamson and P R Nickens (eds) *Advances in Archaeological and Museum Science*. Volume 4. New York: Springer, 216–217

Hovmand, I and Jones, J 2001 'Experimental work on the mineral content of archaeological leather', *in* B Wills (ed) *Leather Wet and Dry. Current treatments in the conservation of waterlogged and desiccated archaeological leather*. London: Archetype Publications, 27–36

Ibbs, B 1990 'Shrinkage calculations'. *Conservation News* 41, 7

Jenssen, V 1987 'Conservation of wet organic artefacts excluding wood', *in* C Pearson (ed) *Conservation of Marine Archaeological Objects*. London: Butterworth, 122–163

Karsten, A, Graham, K, Jones, J, Mould, Q, Walton Rogers, P 2012 *Waterlogged Organic Artefacts: Guidelines on their Recovery, Analysis and Conservation.* Swindon: English Heritage

Karsten, A, Graham, K, Goodman, L, Ganiaris, H and Domoney, K 2012 'A comparative study of various impregnation and drying methods for waterlogged archaeological leather', *in* K Straetkvern and E Williams (eds) *Proceedings of the 11th ICOM-CC Group on Wet Organic Archaeological Materials Conference.* Greenville 2010. USA: ICOM-CC Working Group on WOAM, 595–610

Museums and Galleries Commission 1992 *Standards in the Museum Care of Archaeological Collections.* London: Museum and Galleries Commission

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*. London: Archetype, 11–26

Piechota, D 1992 'Humidity control in cases: Buffered silica gel versus saturated salt solutions'. *Western Association for Art Conservation (WAAC) Newsletter* 15 (I), 19–21

Rodgers, B A 2004 *The Archaeologist's Manual for Conservation. A guide to non-toxic minimal intervention artefact stabilization*. New York: Kluwer Academic

Singley, K 1988 *The Conservation of Archaeological Artefacts form Freshwater Environments*. Michigan: Lake Michigan Maritime Museum

Suenson-Taylor, K and Sully, D 1997 'The use of condition score to determine glycerol concentration in the treatment of waterlogged archaeological leather. An experimental solution', *in* P Hoffmann, T Grant, J A Spriggs and T Daley (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, *York 1996* Bremerhaven: ICOM-CC Working Group on WOAM, 157–172

Wouters, J 1986 'A comparative investigation of methods for consolidation of wet archaeological leather. Application of freeze-drying to PEG impregnated leather', *in P B* Hallebeek (ed) *Symposium on Ethnographic and Waterlogged Leather*: Amsterdam: ICOM 1986, 61–69

APPENDIX 1: EQUIPMENT AND MATERIALS

Equipment

Freeze Drier

Chamber 680, 15 litre condenser	Birchover Instruments Ltd. 83 Bearton Green, Hitchin Herts SG5 1UG
Humidity chambers (bespoke)	Key2 Plastics Ltd, Unit C4, Hazelton Interchange Horndean PO8 9JU
Chest freezer 156 x 60cm	Bosch economic froster
Temperature and humidity data logger	Gemini Data Loggers (UK) Ltd. Scientific House,Terminus Road, Chichester, West Sussex, PO19 8UJ www.geminidataloggers.com

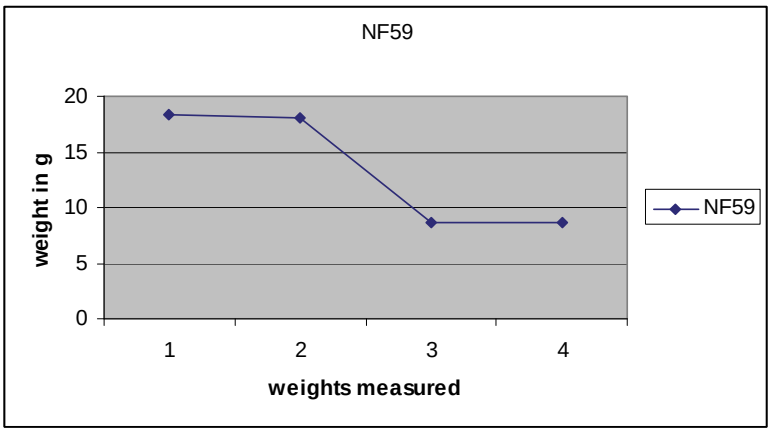
Chemicals

Barium chloride
Disodium EDTA (Na_2EDTA)
Glycerol
Magnesium nitrate
Polyethylene Glycol (PEG)
Potassium iodide

Materials

Acid free tissue paper
Polyethylene Foam (Jiffy foam®)
Tyvek® label
Zip Lock Bags
Archival Cardboard Boxes

APPENDIX 2: EXAMPLE OF OBJECT RECORDING SHEET

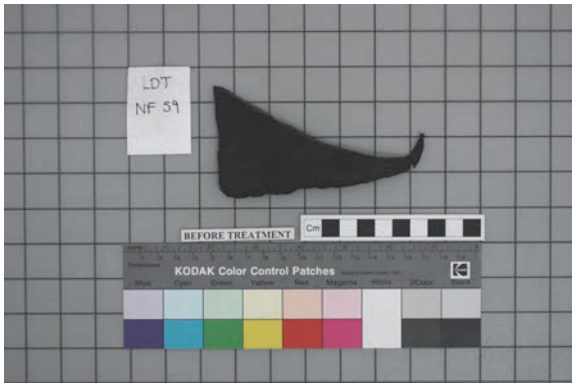
NF 59					
Description before conservation	good condition, thick piece, cut at angle: tapering towards flesh side, 1 through hole, some cracks				
Condition Score before conservation	Cohesivity	Friability	Flexibility	TOTAL	
	3	3	1	7	
Flexibility before conservation	0°				
Treatment	5% EDTA 20% PEG 400 Vacuum Freeze Drying				
Treatment time	Pre-treat	Impregnation	Freezing	Drying	Total
(days)	EDTA: 2hrs Rinse: 2	3	1	1	7
Drying Curve					
Condition Score after conservation	Cohesivity	Friability	Flexibility	TOTAL	
	4	4	1	9	
Flexibility after conservation	0°				

Dimensions	Before Conservation	After Conservation	Shrinkage %	Overall
Length	11.57cm	11.09cm	4.1	4.1%
Thickness	(A) 4.8mm (B) 5.3mm	(A) 4.6mm (B) 4.4mm	(A) 4.1 (B) 16.9	10.5%

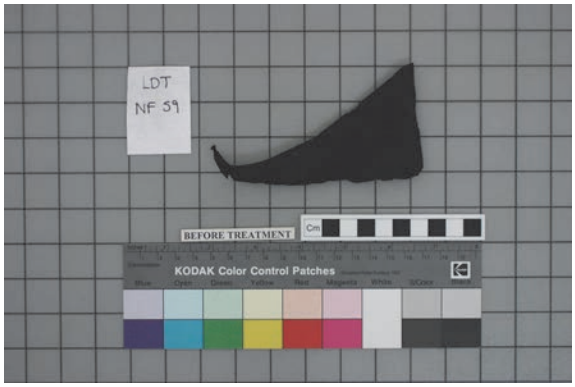
Analysis	FTIR √	SEM

Example of object recording sheet continued

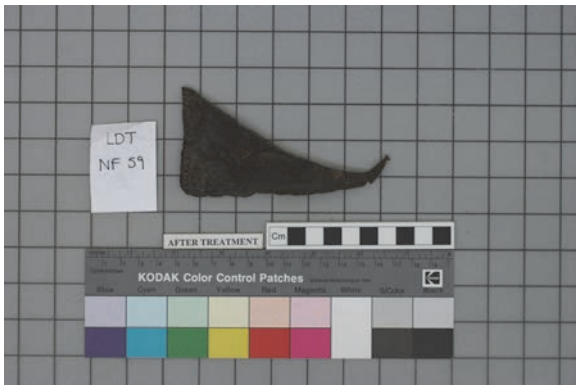
IMAGES



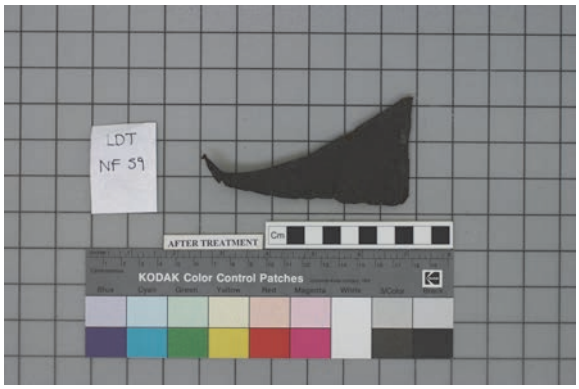
before conservation



before conservation

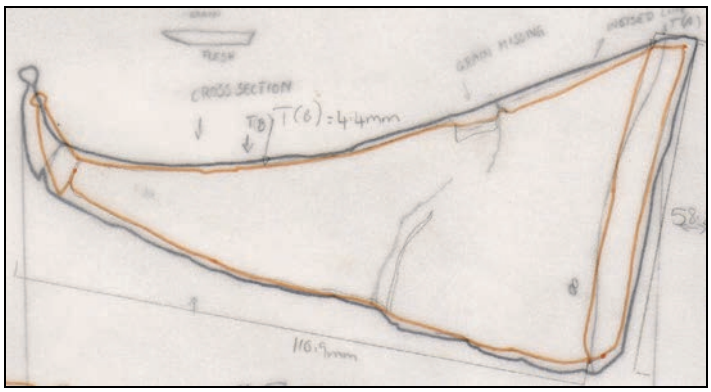


after conservation



after conservation

DRAWINGS

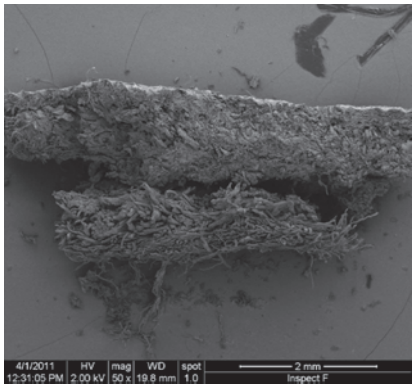
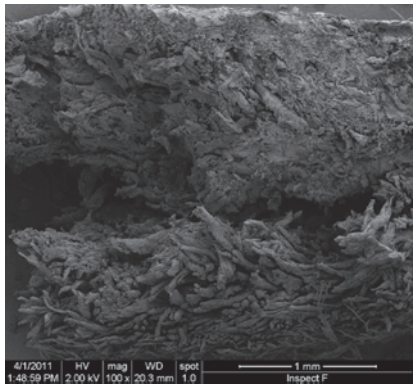
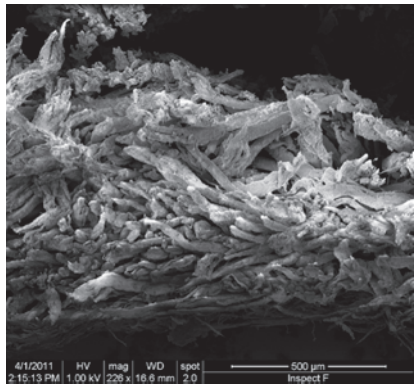
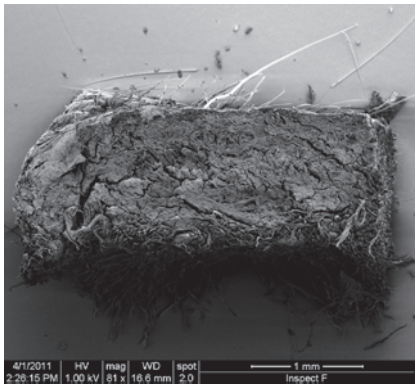
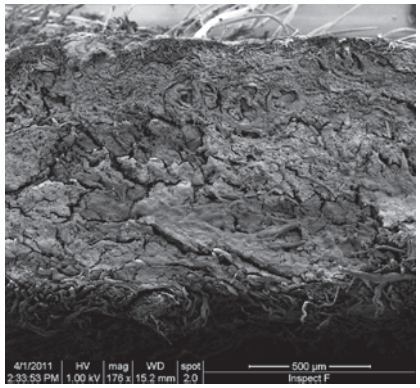
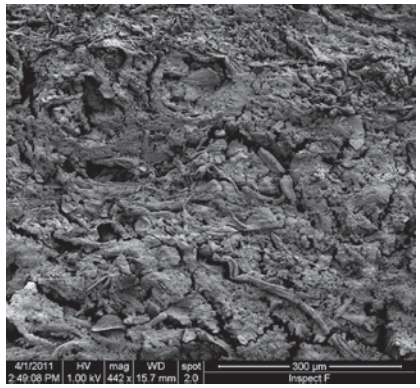


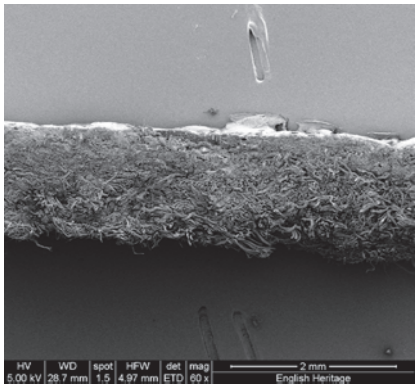
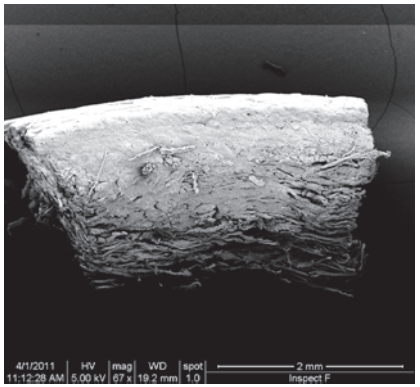
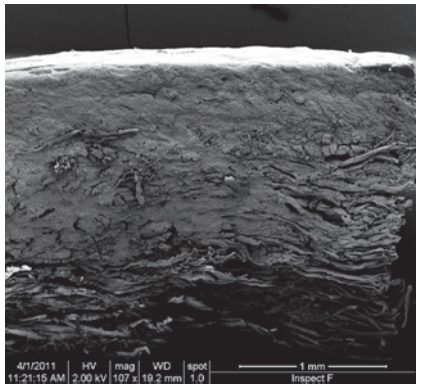
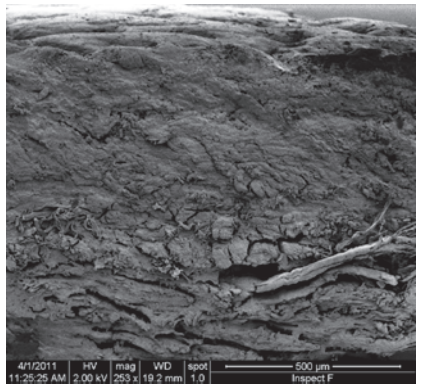
before conservation

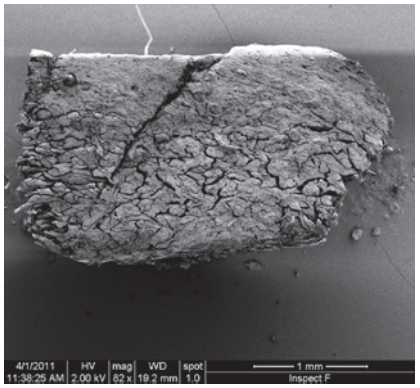
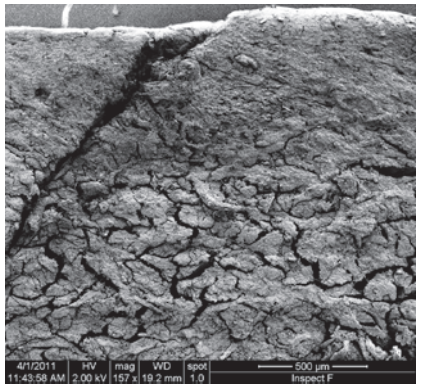
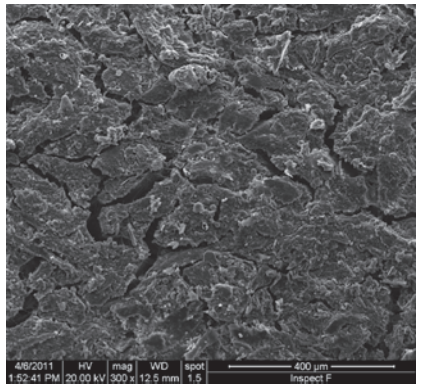
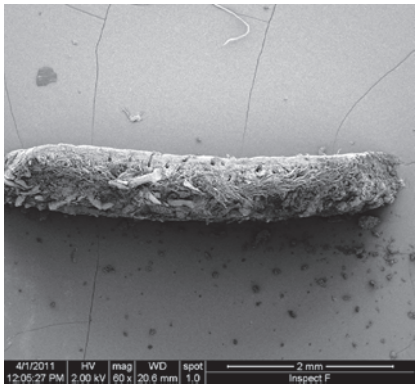
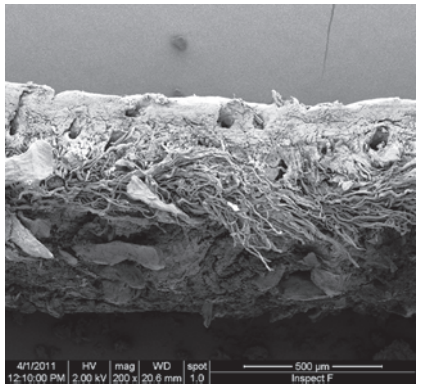
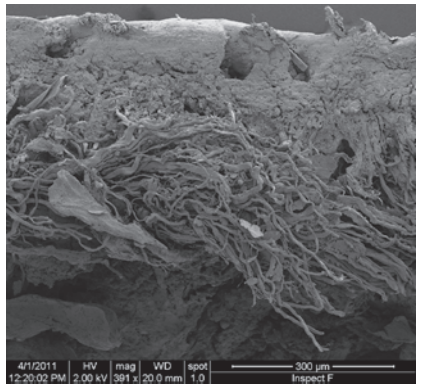
after conservation

APPENDIX 3: SEM IMAGES

Object No/ Treatment	Image Overview	Image x150 magnification	Image x300 magnification	Description
NF 58 / Glycerol Vacuum Freeze Dried				- Clear distinction between grain and corium - open fibre structure (intact)
NF 19/ Glycerol Air Dried				- Clear distinction between grain and corium - partially open structure between fibre bundles (more towards corium) (intact)

Object No/ Treatment	Image Overview	Image x150 magnification	Image x300 magnification	Description
T 4/ PEG Vacuum Freeze Dried				- no clear distinction between grain and corium - "chaotic" open fibre structure (fragmented fibre structure)
NF 34/ PEG Air Dried				- no clear distinction between grain and corium (probably only little corium present) - partially open structure between fibre bundles (intact)

Object No/ Treatment	Image Overview	Image x150 magnification	Image x300 magnification	Description
NE 9/ No impregnation Non Vacuum Freeze Dried				- no clear distinction between grain and corium - uniformly open fibre structure (intact)
NF 3/ No impregnation Air Dried				- no clear distinction between grain and corium (although there is a little difference) - partially open structure between fibre bundles (laminated, esp. towards corium) (intact)

Object No/ Treatment	Image Overview	Image x150 magnification	Image x300 magnification	Description
NF 12/ No impregnation Controlled Air Dried				- clear distinction between grain and corium - open structure between fibre bundles (intact)
NF 13/ No impregnation Vacuum Freeze Dried				- clear distinction between grain and corium - open structure between fibres and fibre bundles (intact)

ENGLISH HERITAGE RESEARCH AND THE HISTORIC ENVIRONMENT

English Heritage undertakes and commissions research into the historic environment, and the issues that affect its condition and survival, in order to provide the understanding necessary for informed policy and decision making, for the protection and sustainable management of the resource, and to promote the widest access, appreciation and enjoyment of our heritage. Much of this work is conceived and implemented in the context of the National Heritage Protection Plan. For more information on the NHPP please go to http://www.english-heritage.org.uk/professional/protection/national-heritage-protection-plan/.

The Heritage Protection Department provides English Heritage with this capacity in the fields of building history, archaeology, archaeological science, imaging and visualisation, landscape history, and remote sensing. It brings together four teams with complementary investigative, analytical and technical skills to provide integrated applied research expertise across the range of the historic environment. These are:

* Intervention and Analysis (including Archaeology Projects, Archives, Environmental Studies, Archaeological Conservation and Technology, and Scientific Dating)
* Assessment (including Archaeological and Architectural Investigation, the Blue Plaques Team and the Survey of London)
* Imaging and Visualisation (including Technical Survey, Graphics and Photography)
* Remote Sensing (including Mapping, Photogrammetry and Geophysics)

The Heritage Protection Department undertakes a wide range of investigative and analytical projects, and provides quality assurance and management support for externally-commissioned research. We aim for innovative work of the highest quality which will set agendas and standards for the historic environment sector. In support of this, and to build capacity and promote best practice in the sector, we also publish guidance and provide advice and training. We support community engagement and build this in to our projects and programmes wherever possible.

We make the results of our work available through the Research Report Series, and through journal publications and monographs. Our newsletter *Research News*, which appears twice a year, aims to keep our partners within and outside English Heritage up-to-date with our projects and activities.

A full list of Research Reports, with abstracts and information on how to obtain copies, may be found on www.english-heritage.org.uk/researchreports

For further information visit www.english-heritage.org.uk

ENGLISH HERITAGE

ISSN 2046-9799 (Print)
ISSN 2046-9802 (Online)