# UNILATERAL NMR FOR DAMAGE ASSESSMENT OF VEGETABLE-TANNED LEATHER. CORRELATION WITH HYDROTHERMAL PROPERTIES

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Unilateral NMR has proven to be a valuable tool in the field of collagen-based cultural heritage where non-destructive analyses are highly demanded. Old leather is a collagen-based biomaterial made from animal hides chemically treated by vegetable or mineral tanning to increase chemical and physical durability and confer desired handling and working characteristics. In this study unilateral Nuclear Magnetic Resonance (NMR) combined with shrinkage temperature measurement by the Micro Hot Table (MHT) method were applied to evaluate the conformational, structural and stability changes of variously vegetable tanned leathers exposed to accelerated ageing by heating at 70 °C in controlled atmosphere at 30% relative humidity (RH) and irradiated with 4000 lx in the visible light region for 8, 16, 32 and 64 days. Longitudinal relaxation time T1 values, measured by NMR MOUSE portable equipment using a saturation recovery sequence, showed specific variations depending on both animal species and tanning agent, and ageing time. Collagen fibres' shrinkage temperature Ts values evaluated using the home made MHT equipment available at INCDTP-ICPI, Bucharest, complemented the hydrothermal information on fibre level.

Keywords: Vegetable tanned leathers, NMR-MOUSE, MHT method.

## INTRODUCTION

Historical and archaeological leather objects and artefacts are an infinite source of information of historical and cultural interest. They illustrate the evolution of social customs, habits, aesthetics and technology, but also the perpetuation of popular and religious traditions. It is vital therefore that these materials and artefacts remain well preserved. The aim of our study is to bring together non- and minimal invasive investigation techniques for collagen fibre characterisation as practiced by conservators, i.e. shrinkage activity measurement, with the current nanoscale measuring systems, i.e. unilateral NMR, to relate information at the fibre level to that at the collagen fibril level. Early detection and identification of deterioration by using qualitative tests as unilateral NMR and MHT method can highly extend the life of the objects/artefacts.

Unilateral NMR has been developed after 1990, when the first portable equipment NMR MOUSE (Mobile Universal Surface Explorer) was built (Casanova *et al.*, 2011). NMR MOUSE is a relatively small and compact device design to perform noninvasive and nondestructive analyses, highly valued in the field of cultural heritage. Objects like mummies (Rühli *et al.*, 2007), paintings (Presciutti *et al.*, 2008), frescoes (Proietti *et al.*, 2005) and parchments (Badea *et al.*, 2008; Masic *et al.*, 2012) were successfully analysed using NMR-MOUSE.

The hydrothermal stability of collagen fibres is currently evaluated by a micro-destructive diagnostic technique based on the combined use of optical microscopy and thermal analysis and called MHT method. The shrinkage temperature $T_s$ of collagen

fibres characterises the collagen fibres structural collapse and hence the loss of mechanical stability and strength. This parameter is widely used to evaluate degradation level of collagen-based historical materials.

This work concerns with the investigation of the synergetic high temperature, low RH and visible light irradiation effect on the deterioration of calf and sheep leather tanned using various vegetal tanning extracts by correlating $T_1$ (longitudinal relaxation time) and $T_s$ (shrinkage temperature) values.

## EXPERIMENTAL PART

New leather from calf and sheep hides was obtained through traditional using different tannin extracts such as mimosa bark, quebracho and chestnut wood at the National Research and Development Institute for Textile and Leather, Leather and Footwear Research Institute Division (INCDTP-ICPI), Bucharest.

A first series of leather samples were exposed to accelerated ageing treatments inside a test chamber Binder APT Line KBF-ICH, at 70°C, 30% RH and 4000 lx illuminance (visible light region) for 8, 16, 32 and 64 days. It should be mentioned that the visible light exposure corresponds to 60, 120, 250 and 500- year dose, respectively.

Unilateral NMR measurements were performed with a portable Magritek NMR MOUSE, model PM 25, at 13 Mhz frequency. Longitudinal relaxation time $T_1$ was measured using a saturation recovery sequence combined with Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. $T_1$ values were measured by directly placing the leather samples on the measurement window of the instrument.

Shrinkage temperature $T_s$ was measured with the home-made MHT equipment available at INCDT-ICPI using the procedure previously described (Badea *et al.*, 2012b). For the *Ts* evaluation a few fibres (~0.3 mg) from the corium side were immersed in demineralised water, covered with a cover glass placed inside the thermostatic cell of the hot table and heated at 2°C $min^{-1}$. Collagen fibres' shrinkage activity was recorded with the camera connected to the stereomicroscope and then visually evaluated by the operator.

## RESULTS AND DISCUSSION

### New Leather

Longitudinal relaxation time $T_1$ values for the new, untreated leather samples are presented in Figure 1, and shrinkage temperature $T_s$ values for the same samples are reported in Figure 2. It can be seen that $T_1$ values depends on both tannin type and animal species. In general, $T_1$ values were higher for the leather samples tanned with chestnut wood extract (hydrolysable tannin), while the lowest $T_1$ values were obtained for the sheep hides tanned with mimosa bark extract (condensed tannin) independently of animal species. Since $T_1$ value is a measure of the strength of water – collagen fibres bonds we may infer that water interactions with collagen fibres in leather depend on both tannin type and animal species. We can thus assert that the number of leather sites capable of strong interactions with water is determined by both the tannin chemical structure and morphological structure of collagen fibres.

Shrinkage temperatures $T_s$ showed to not depend on animal species. In addition, the chestnut tanned hides presented the highest $T_s$ values. Shrinkage measurements results

indicated higher hydrothermal stability for leathers obtained using condensed tannins, in good agreement with the data in the literature (Larsen, 2000; Cucos *et al.*, 2014).

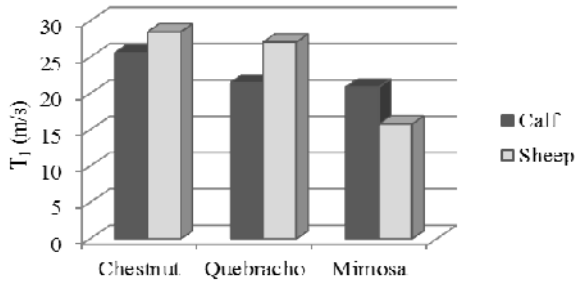


Figure 1. Longitudinal relaxation time $T_1$ values measured with NMR MOUSE for calf and sheep leather obtained using condensed (quebracho and mimosa) and hydrolysable (chestnut) tannins

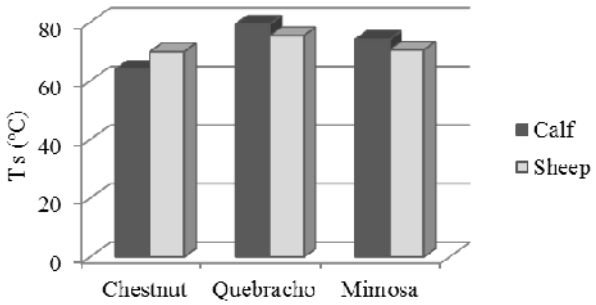


Figure 2. Shrinkage temperature $T_s$ values measured through MHT method for calf and sheep leather obtained using condensed (quebracho and mimosa) and hydrolysable (chestnut) tannins

**Accelerated Aged Leather**

The longitudinal relaxation time $T_1$ values for the accelerated aged leather samples are presented in Figs 3 and 4, while shrinkage temperature $T_s$ values for the same samples are reported in Figs. 5 and 6.

Data presented in Figures 3 and 4 indicate that the accelerated ageing treatment did not significantly influenced on $T_1$ values for calf leather (Figure 3), whereas for sheep leather a considerable decrease with ageing time was observed, especially for mimosa tanned leather (Figure 4).

As far as the hydrothermal stability is concerned we observed a progressive decrease of $T_s$ value with ageing time for both calf and sheep leathers (Figures 5 and 6). Chestnut tanned leather showed to be the less resistant, calf leather being less hydrothermally resistant than sheep leather.

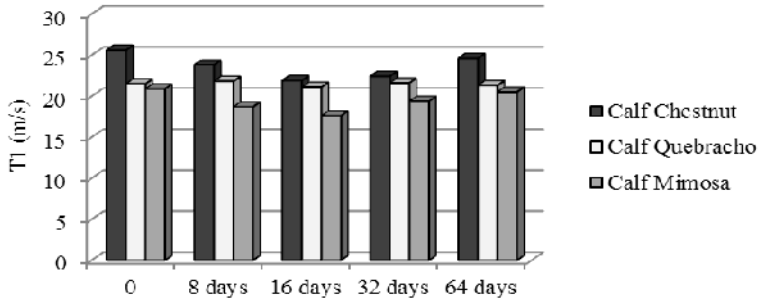


Figure 3. Variation of longitudinal relaxation time $T_1$ values measured with NMR MOUSE for calf leather obtained exposed to accelerated ageing at 70°C, 30%RH, and visible light irradiation for 8,16, 32 and 64 days

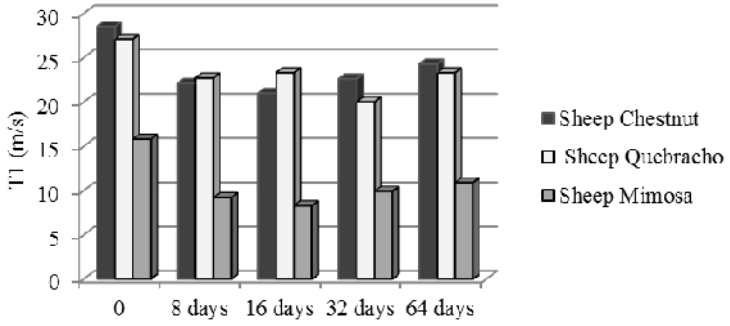


Figure 4. Variation of longitudinal relaxation time $T_1$ values measured with NMR MOUSE for sheep leather obtained exposed to accelerated ageing at 70°C, 30%RH, and visible light irradiation for 8,16, 32 and 64 days

The behavior illustrated by $T_1$ and $T_s$ values suggest that thermal destabilization of calf leather may be attributed to the progressive conformational alterations resulting in formation of collagen populations with lower hydrothermal stability without significantly affecting the collagen – water interactions. This well correlates with the deterioration pattern observed for parchment exposed to accelerated ageing at high temperature, low RH and light irradiation (Badea *et al.*, 2012a). On the contrary, for sheep leather, both the hydrothermal stability and collagen – water interactions are influenced by accelerated ageing treatments.

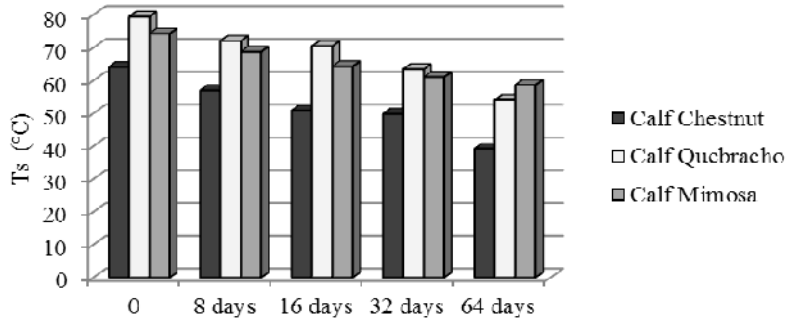


Figure 5. Variation of shrinkage temperatures $T_s$ measured through MHT for calf leather exposed to accelerated ageing at 70°C, 30%RH, and visible light irradiation for 8,16, 32 and 64 days

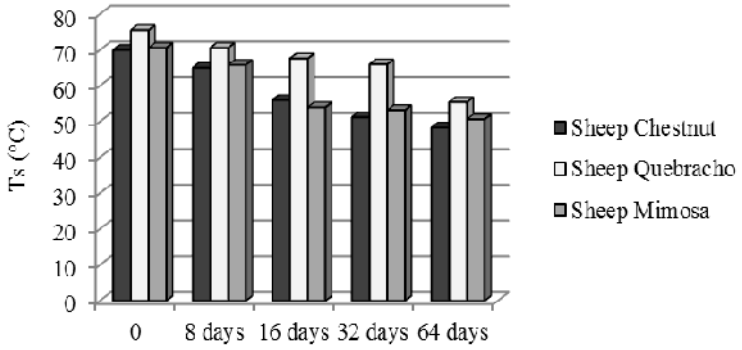


Figure 6. Variation of shrinkage temperatures $T_s$ measured through MHT for sheep leather exposed to accelerated ageing at 70°C, 30%RH, and visible light irradiation for 8,16, 32 and 64 days

## CONCLUSIONS

The synergetic effect of high temperature, low relative humidity and visible light iradiation on vegetable tanned leather from calf and sheep was investigated. The interaction between intrinsic water and collagen fibres was evalueted by measuring the longitudinal relaxation times $T_1$. Both new and accelerated aged calf and sheep leather obtained using both condensed (quebracho and mimosa) and hydrolisable (chestnut) tannins were non-invasively measured using a portable NMR MOUSE equipment. The hydrothermal stability of the samples was evaluated by measuring the shrinkage temperature $T_s$ through MHT method. In summary, the main results of our study are as follows:

- Shrinkage temperature $T_s$ significantly decreased with ageing time independently of animal species and tannin type. Chestnut tanned leathers were the most sensitive to the ageing treatment.
- $T_1$ values showed to depend on both animal species and tannin type. Moreover, sheep leather was sensitive to the ageing treatment, while calf leather does not show significant changes during accelerated ageing treatment.
- $T_1$ and $T_s$ parameters are potential indicators for characterising tannin – collagen interactions as well as for assessing conformational, structural and stability changes during ageing and deteriorating of leather.

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