Cleaning of Tanned Leather: Testing with Infra Red Spectroscopy and SEM-EDAX

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Abstract

Fourier transform infra red spectroscopy and SEM-EDX were employed to analyse the alterations on the surface of tanned goat skin induced by a number of cleaning media, by investigating the molecular structure and elemental abundance correspondingly, on a set of tanned leather samples. The obtained experimental data indicate the removal of certain molecular components from the leather surface in specific cases and suggest a methodology to correlate the action of cleaning agents to the molecular conformation of leather collagen.

Keywords

vegetable tanned leather, cleaning, solvent, detergent, acid, elemental analysis, spectroscopic analysis, FTIR, SEM-EDAX

Introduction

Leather is one of the most sensitive materials used in everyday applications and art objects, subject to hard use and harsh environmental conditions. Leather cleaning techniques involve the use of various solvents, soaps and detergents, surface dry-cleaners, etc. [1, 2]. The major concern of most research work carried out on the use of these cleaning products and techniques have aimed basically at the effectiveness of cleaning procedures. However, physical/chemical interaction of the various cleaning products or

techniques with collagen, as well as with possible added compounds (due to tanning processes, etc.) is an issue that merits investigation.

Vegetable tanning is a common tanning procedure which renders, among others, elasticity to leather through a complex interaction of leather protein (collagen) with phenolic molecules present in tanning agents. Vegetable tannins, falling into the categories of condensed and hydrolysable tannins, interact with collagen basically via two possible modes: hydrogen bonding at the collagen peptide links, and "fixing" to amino and carboxylic acid groups on side chains, which is a pH-dependent process [3]. The typical mode of combination is hydrogen bonding between the hydroxyl groups of the tans (phenolic substances) and various reactive groups such as carboxyl, amine and amide groups of collagen [4].

The aim of the present study is the investigation of probable side-effects in leather structure after cleaning tests using some of the most popular cleaning materials in conservation [3, 5]. All tested samples were unused leather specimens, from vegetable-tanned goat skin. Up to date, in the majority of the cases, materials used widely for cleaning were estimated based on the resulted optical effect.

With respect to investigations in micro-structural and molecular level, the combined use of SEM (inspection in microscale), SEM-EDAX (elemental analysis of various elements on leather surface), and FTIR spectroscopy (molecular analysis of both inorganic and organic compounds, through the detection of chemical bonds in the molecules of a material) are proposed as valuable tools for the investigation into the probable side effects of cleaning. With FTIR in particular, the investigation of chemical and structural changes in the molecular level by detecting the appearance, disappearance or change of environment of chemical bonds is possible [6, 7, 8].

Experimental Section

Materials and reagents

Vegetable tanned rectangular leather samples from goat skin (approx. 2×1 cm) were used in all cases, with no further ageing.

Cleaning agents: Acetone (Fluka) was used as is; commercial ethanol (99.5% v/v was mixed with water so that final concentration was 50% v/v). Ethanol-water mixture (50:50) prepared by addition of deionized water in a quantity of commercial ethanol (95% v/v). Hydrochloric acid 3.3% w/v was prepared by addition of deionized water in a concentrated solution (Merck). White spirit (a mixture of hydrocarbons, or Stoddart's solvent, was purchased by local suppliers). Ammonia aq. solution 1% was prepared from a concentrated ammonia solution. Trichloroethane was purchased from Fluka and was used as is. Texapon N® (Sodium lauryl ether sulphate, Cognis Agrosolutions Fermentation Specialties) cleaning mixture was prepared by adding the appropriate quantity of deionized water to a final concentration 10% w/v. Vulpex® (Potassium methylcyclohexyl oleate, Picreator Enterprises Ltd.) cleaning mixture was prepared by adding the appropriate quantity of white spirit to a final proportion 1:10 v/v. Synperonic N® (nonylphenol-ethoxylate) cleaning mixture was prepared by adding the appropriate quantity of deionized water to a final concentration 10% w/v Groom stick® (Picreator Enterprises Ltd.) was used as is.

Instrumental Techniques

Infra red spectroscopy: A Perkin Elmer Spectrum GX FTIR spectrometer was used in transmission mode. PE Spectrum software was used for spectra examination and comparison. All FTIR spectra were run on powdered samples scraped directly from the leather surface, and accordingly pressed in KBr pellets with the use of a Specac apparatus. Typical spectra were run employing 20 scans and confirmed with another

spectra series (150 scans), all compensated for water (resolution in all spectra was 4 cm^{-1}). In all cases, samples from each cleaned area were comparatively analysed with samples from the closest neighbouring corresponding uncleaned area, so that spatial variations in the amounts of added compounds (tanning agent, oil, wax) are eliminated.

SEM-EDAX: A Jeol instrument (JSM-5310 with a Link Pentafet detector) was applied on graphitized leather samples. Graphitization of samples was done using a Baltec CED-030 Carbon Evaporator.

Leather Cleaning and Investigation Methodology

Two series of ten leather samples (see above) were prepared: series I aimed at SEM-EDAX investigation and series II aimed at FTIR investigation. Each sample from series I was attached on a copper foil substrate of dimensions slightly larger from those of the actual samples, using a double-sided adhesive carbon tape. The samples were accordingly graphitized and on the right half part of each, the corresponding cleaning tests were applied using a cotton tab previously immersed in the cleaning solution, except for Groom stick® which was used as a rubber directly onto the surface of leather, while leaving the left half part of the sample untreated for reference reasons. Each sample from series II was directly subjected to the cleaning testing in a similar manner: the cleaning procedure was applied to the right part while the left part was left for reference reasons. Powdered samples of leather were prepared from neighbouring spots of the treated and untreated areas of each sample using a file; these were analysed by FTIR. Through this, the effect of the cleaning procedure on the condition of leather was investigated.

Results and Discussion

Leather Cleaning

Cleaning is an irreversible conservation process and therefore, a thorough consideration should be made before any such attempt. Leather cleaning treatment should improve the aspect of an object without causing or favouring any further deterioration and without interfering to future analysis results. Removal of any deposits or stains that may have historical or ethnographic significance must be avoided. The presence of any loose parts or flaking paint layers should also be taken into consideration when a cleaning method is chosen. In general, as in any other conservation process, the principle of the minimal intervention should be followed. More specifically, care should be taken on: the chemical composition of the object (including additives), the expected nature of depositions (impurities, dirt), the state of preservation of the object and the cost of the selected cleaning method.

Cleaning treatment of leather should not chemically affect leather material, should not allow the formation of any type of products harmful to the object; further, the treatment should be capable of "effective cleaning" (i.e. remove impurities and preserve the structure of the object at the same time), should be easily inspected by specialists, and finally should be easily applied and safe for the humans involved.

In the present work, a number of cleaning agents were chosen, in a large part based on the most recent review about materials used in leather conservation [3, 5], including wet and solvent cleaners: (a) white spirit, generally used to remove excess of oil, in cases where water-based cleaning would be too risky, (b) trichloroethane a common cleaning agent for oil stains or as a solvent for resins, not as widely used as it has been in the past because of environmental concerns, (c) acetone, mostly for oil stain removal, (d) alcohol - water mixture (1:1) – used by conservators in ethnographic collections as this was found to be more effective than water or alcohol alone; detergents: (a) water-based: Texapon®, Synperonic N® - non ionic detergent added in water to improve cleaning effect (no more in use), and (b) hydrocarbon-based

(Vulpex® in white spirit) potassium methyl-cyclohexyl-oleate soap where the use of water is impractical, pH 10.5-11.5. Furthermore, acidic and alkaline media were used, even if their use is sometimes restricted: (a) hydrochloric acid (rare/no use due to catalytic effects on the hydrogen bonds of collagen; it is typically used in 2% v/w on objects with calcareous deposits, and (b) aqueous ammonia solution, as ammonia is more aggressive to dirt than water alone but is harmless to leather in low concentrations). Finally, a dry cleaner has been included: natural rubber-based surface molecular trap (Groomstick®).

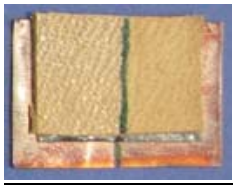
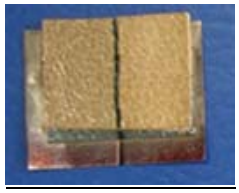
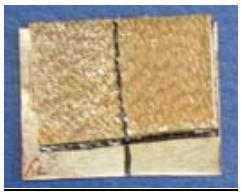
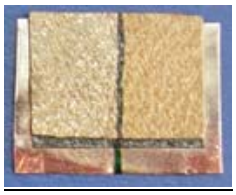
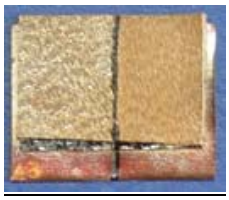
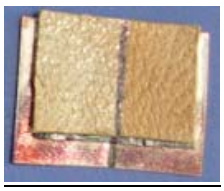
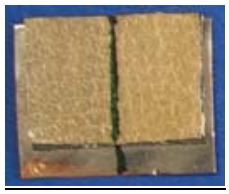
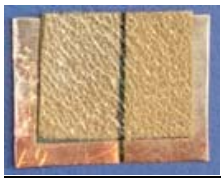
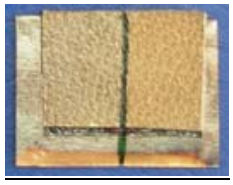
	
acetone	ethanol-water 50:50
	
hydrochloric acid 3.3%	ammonia (aq. solution 1%)
	
white spirit	trichloroethane
	
Texapon N® in water 10%	Vulpex® in white spirit 10%
	
Synperonic N® 10% in water	Groom stick®

Figure 1: Macrophotographs of tested leather samples of series I showing both treated (right) and untreated areas (left).

In the followed cleaning treatment, previously unused commercial samples of the same origin and of comparable state of preservation were partly cleaned, leaving approximately half of the surface in a non-cleaned state for comparison purposes (see experimental). Finally, both reference and treated areas were macro-photographed (Figure 1) and inspected under a stereomicroscope. Scanning electronic microscopy (SEM) has been employed for rendering high quality images of the surface of all leather samples before and after treatment. After initial examination of the samples under the stereomicroscope (10x, images not shown) investigation with SEM (50x magnification, Figure 3) showed a difference in the morphology of the surface in most cleaned areas. More specifically, the surface of samples cleaned with trichloroethane, aqueous ammonia solution, Vulpex® in white spirit and Groomstick® appeared more evenly flat, for which, one reason could be the applied pressure during treatment.

Elemental Analysis with SEM-EDAX

The surface of both treated and untreated areas of leather samples was analysed with SEM- to detect any changes in elements due to contamination or removal of certain constituents of the leather surface.

The analysis results showed significant increase of chlorine (Cl) for the hydrochloric acid - cleaned surface (Figure 2a), amounts of potassium (K) in the case of Vulpex® (Figure 2b), as well as residual quantities of sodium (Na) in the case of Texapon®. Finally, small increase of Sulphur (S), Potassium (K), Calcium (Ca) and Silicon (Si) and low amounts of Sodium (Na), Silicon (Si) and Chlorine (Cl) were detected in the case of Groomstick®. Residual quantities of cleaning agents have also been found through SEM analysis in the case of acetone, Vulpex® in white spirit and Groomstick®.

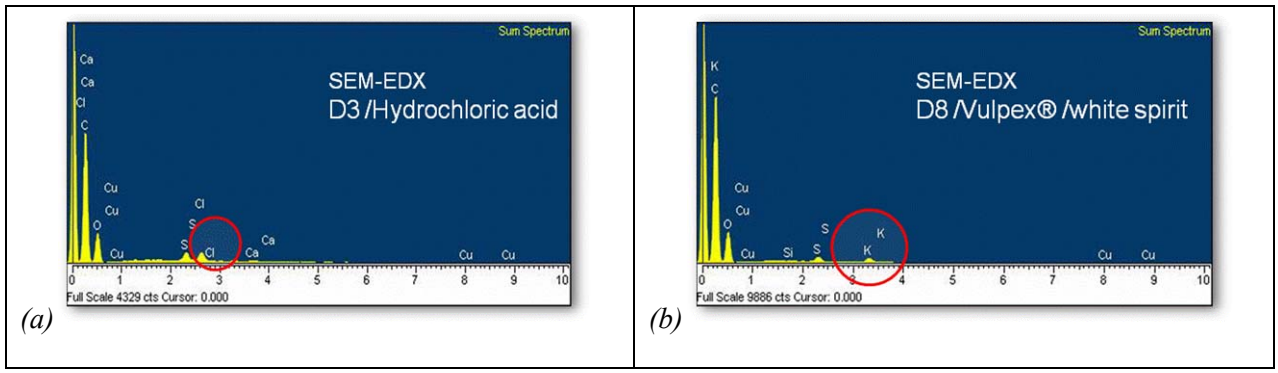


Figure 2: SEM-EDAX images from the analysis of cleaned areas of leather samples. Red circles show elements which are not present in the reference (untreated) areas: (a) treated with hydrochloric acid 3.3% and (b) treated with Vulpex® in white spirit.

Analysis with FTIR spectroscopy

Comparison of spectra

Fourier transform infra red spectroscopy (FTIR) was employed to analyse the various components of the material and the possible induced changes after treatment with cleaning agents. In an FTIR spectrum, the various bonds in the molecules of a sample are detected according to their various vibrational modes. The most important infra red absorption bands of protein materials appear due to vibrations of bonds between atoms at or near the peptide bond [9, 10, 11].

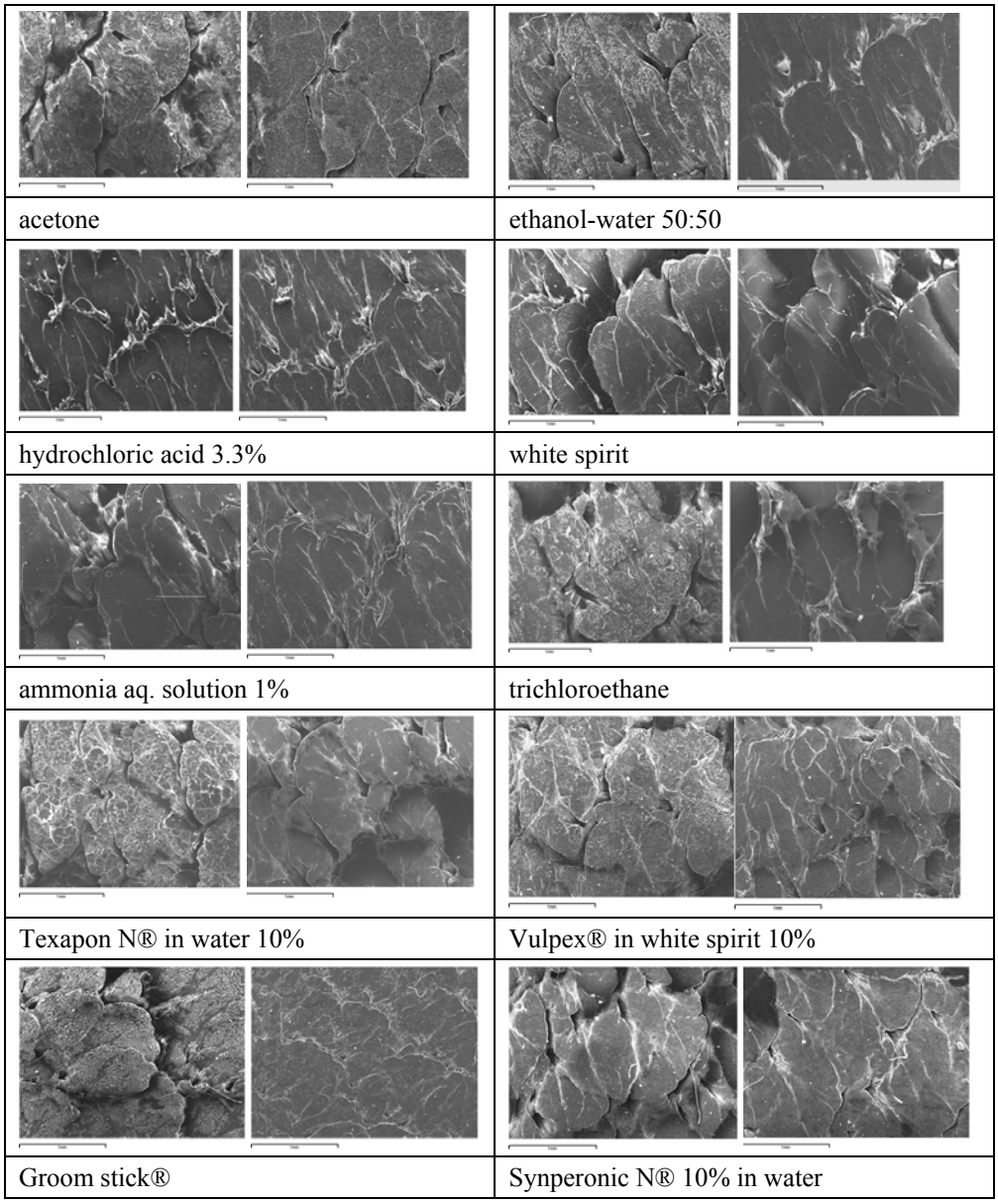


Figure 3: SEM photographs of tested leather samples. In each pair of photos, left is the reference (untreated) area and right is the cleaned area.

Powdered samples taken from leather surface of any of the tested samples showed a typical profile in FTIR (Figure 4). The protein material is detected by broad bands at 3330 cm^{-1} (due to vN-H) and 3075cm^{-1} (δNH_2 overtone) as well as at 1655, 1542, 1234 cm-1 (amide bands I, II, III, correspondingly) [13, 14]. Tanning agents also have a significant print with broad peaks at 3500-3350 cm^{-1} (vOH), at 3010 cm^{-1} (vC-H in aromatics), 1711 cm^{-1} (galloyl ester carbonyls), 1385 cm^{-1} ($\nu_{i\text{-}p}$C-OH); 1033 cm-1 link (ν_{as}C-O-C=O in tannin ester), as well as at 1735-1745 cm^{-1} (ester carbonyls possibly due to tanning). Finally, wax-like and/or oil impurities are present, as detected by their peaks at 2920 (wax), 2929 (oil,

here appearing as a shoulder) and 2853 cm^{-1} due to various modes of C-H stretch, and finally, 1457, and 1340 cm^{-1} due to bending modes of CH_2, CH_3. All detected IR peaks are summarized in table I.

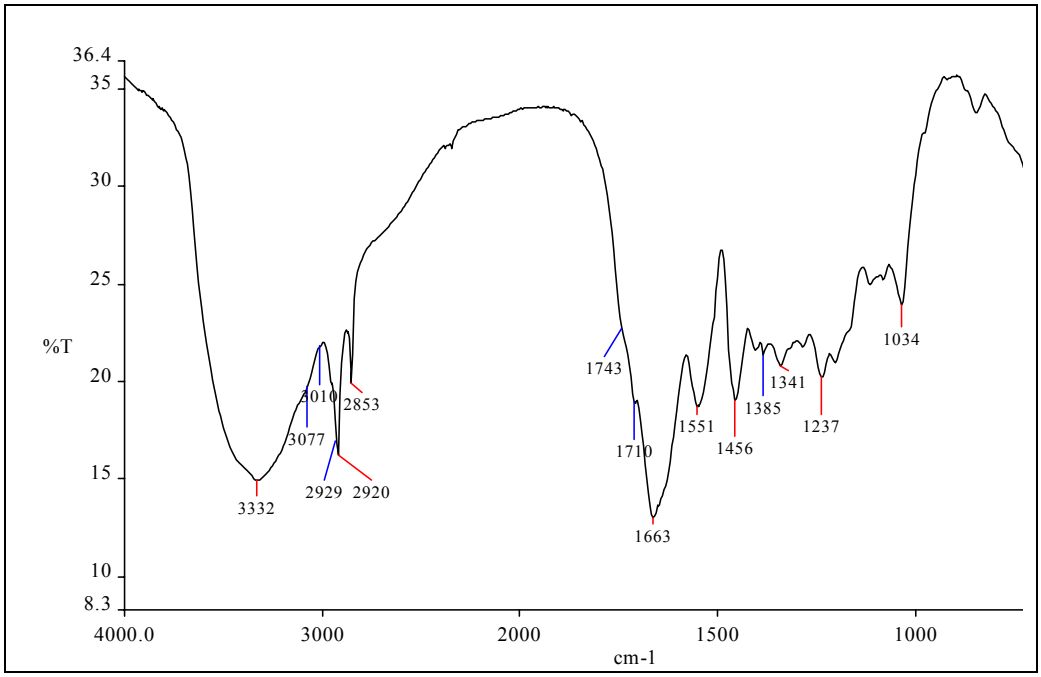


Figure 4: Infra red spectrum from an untreated area of leather sample (inset: detail of the left part of the spectrum).

All results from FTIR analysis are summarized in Table II. A discussion on two cases follows. Spectra of samples cleaned with Vulpex® in white spirit (figure 5) show significant positive peaks at 2927 and 2856 cm^{-1} (pointing down in difference spectrum, c3, see also experimental section) suggesting removal of hydrocarbon chains (basically oil-based impurities) and at 1712 due to carbonyl compounds c(possibly in tanning agents). Further inspection in the difference spectrum shows weaker peaks at 3011 cm^{-1} (vC-H in aromatic tannin ring); 1604, 1524, 1510, 1468 cm^{-1} (aromatics in tannin); 1378 cm^{-1} $\delta_{i\text{-}p}$C-O-H; 1029 cm_{-1} vC-OC (cyclic ester); all these peaks confirm the detection of tannins in the difference spectra. Moreover, peaks at 1439 cm^{-1} (δCH_2) and 723 cm^{-1} (ρCH_2) also confirm the detection of oil impurities in the difference spectrum.

These results show that this cleaning agent can selectively remove oil-based impurities, but also small amounts of the tannin-related molecules on the surface of leather. Spectra of samples cleaned with aqueous ammonia solution (figure 6) clearly show positive peaks at 1654, 1536 and 1454 cm^{-1} in the difference spectrum (c3), suggest the removal of proteinaceous material. Moreover, the shoulder at 1735 cm^{-1} suggests the removal of oil-related compounds. On the other hand, peaks at 2919, and 2852 cm^{-1} pointing up correspond to hydrocarbon-related material (wax) not affected by the cleaning process. These results suggest that aqueous ammonia removes part of the protein material together with carbonyl compounds belonging to ester-containing molecules. The same time wax is not affected as its peaks appear negative. The rest of the cases show insignificant or not detectable changes.

Table I: Assignment of basic FTIR peaks (cm^{-1}) detected in a typical leather sample containing additives	
3500-3350(br,s)	vO-H
3330(br,s)	*v*N-H
3077(sh)	δNH_2 (overtone)
3010(w)	vC-H (aromatics in tanning agent)
2958, 1851(w)	v_{as} CH_3 (oil compounds, wax)
2929(m-s)	v_{as} CH_2 (oil compounds)
2919(sh)	v_{as} CH_2 (wax)
2853(m)	v_s CH_3
1735-1745(sh)	vC=O (ester groups in tanned material)
1710 (sh)	vC=O (galloyl ester in tanning agent)
1663(s)	Amide I band of leather protein
1551(m)	Amide II band of leather protein
1457(m)	δ_s CH_2+ δ_{as} CH_3
1237(m-w)	Amide III band of leather protein
1385(w)	$\delta_{i\text{-}p}$C-OH
1340(w)	δ_s CH_3
1034(w)	v_{as}C-O-C=O

From the rest of the cases, cleaning with acetone removes both wax and oily components, while carbonyl compounds (esters) were left unaffected in the cleaned area; Groom stick® selectively removes oily material. On the other hand, Synperonic N® is capable of removing hydrocarbon chains (wax) and some proteinaceous material, while oily compounds and tanning agents remained unaffected. Finally the behaviour of trichloroethane, is still unclear, as small quantities of proteinaceous material are found to be removed.

The present work can be considered as a first approach in the study of cleaning treatments on leather. Further spectroscopic investigation regarding the possible induced changes in the distinct collagen structure [12] using FTIR techniques that have previously been applied to other proteins [15, 16, 17] is in progress.

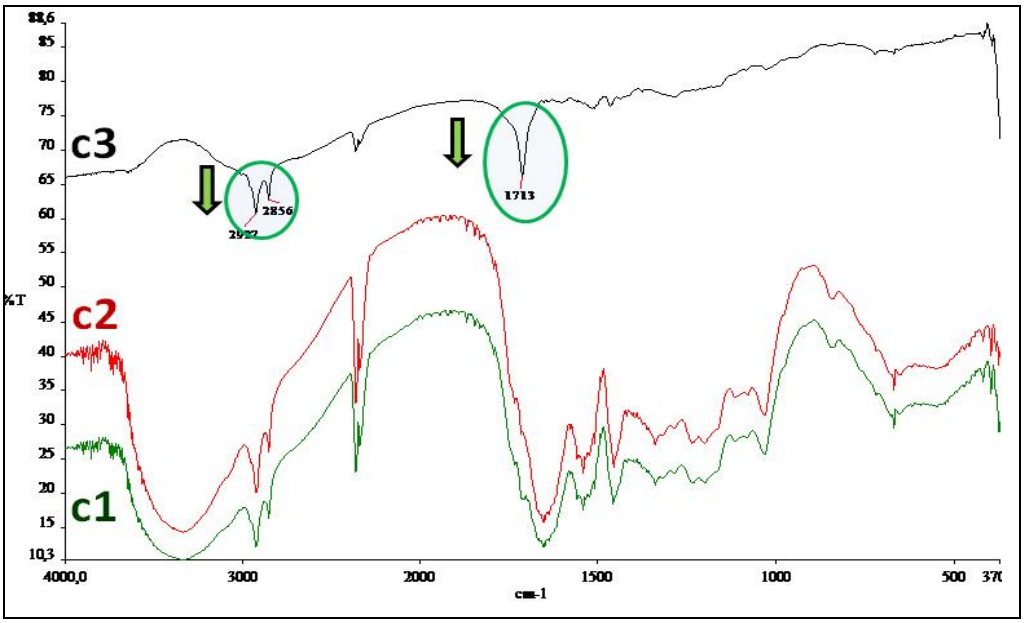


Figure 5: FTIR spectra of samples cleaned with Vulpex® in white spirit ; (a) tanned leather cleaned with Vulpex® in white spirit: FTIR spectra before (1) and after cleaning (2) and the resulting difference spectrum (3).

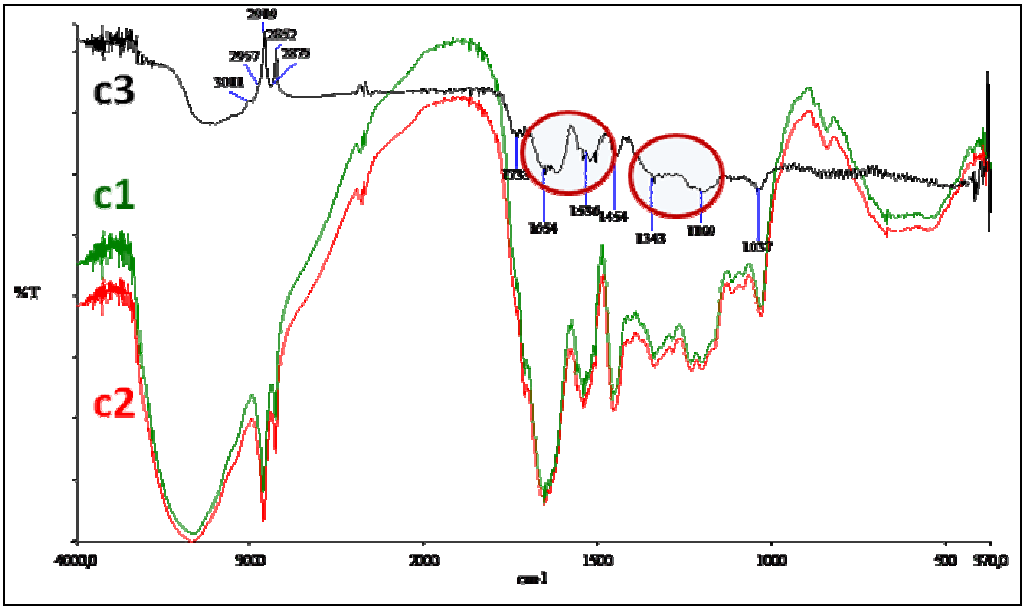


Figure 6: FTIR spectra of samples cleaned with aqueous ammonia solution. Spectra (c1) and (c2) correspond to samples before and after cleaning, while (c3) corresponds to the difference spectrum.

Table II: Results from SEM-EDAX analysis and FTIR spectra comparison of treated and untreated areas of leather samples.

Cleaning agent	Elemental analysis (SEM-EDAX)	FTIR spectra
		Remarks
acetone	Increase of C (possibly residual acetone)	Wax and oily components were removed; carbonyl compounds (esters) left in cleaned area
ethanol-water 50:50	Small increase of C (residual ethanol)	Minor changes: small quantities of carbonyl compounds and bulk proteinaceous material was removed.
hydrochloric acid 3.3%	Quantities of residual Cl	Proteinaceous material removed.
white spirit	Small increase of C	Wax was removed; carbonyl compounds (possibly tanning agents) left in cleaned area
ammonia aq. solution 1%	No significant changes	Proteinaceous material removed; hydrocarbon chains and small quantities of ester carbonyls intact in cleaned area.
trichloroethane	Small increase of C	Proteinaceous material partially removed; Wax, oily compounds and tanning agent left intact.
Texapon N® in water 10%	Small amounts of Na	Proteinaceous material removed from the surface; hydrocarbon chains (wax) left in cleaned area
Vulpex® in white spirit 10%	Increase of K	Selective removal of oily material and carbonyl compounds (possibly tanning agents).
Groom stick®	Na, Al, Cl	Selective removal of oily material.
Synperonic N® 10% in water	Small increase of C and K	Hydrocarbon chains (wax) and proteinaceous material removed; oily compounds and tanning agents remained intact.

* Difference spectra were calculated subtracting the spectrum of the treated material from that in the initial (untreated) state. According to this, positive peaks (or peaks pointing down↓ in figures 5 and 6) correspond to compounds that are removed during cleaning. Negative peaks (or peaks pointing up ↑) correspond either to intact components, or to changes inducing new features.

Conclusion

FTIR spectroscopy and SEM-EDAX were employed to investigate the alterations on the surface of tanned goat-skin induced by a number of cleaning products and techniques. FTIR spectroscopy and SEM-EDAX were employed to investigate the state of tanned leather after treatment with a number of cleaning agents. Residual amounts of chlorine, sodium and potassium were detected in the case of cleaning with hydrochloric acid, Texapon N® and Vulpex® in white spirit 10%. Infra red difference spectroscopy gave evidence for specific changes in the surface of cleaned leather samples. Moderate or small proteinaceous material was removed in the cases of ammonia aq. solution, trichloroethane, hydrochloric acid and ethanol water mixture. On the other hand, Groom stick® and Vulpex® in white spirit selectively removed oil impurities. Finally, white spirit and Synperonic N® selectively removed wax, while leaving oil impurities intact. Further work on elucidating the collagen structure and its possible induced modifications after the various cleaning treatments is in progress, which will offer a more detailed view in the effects of leather cleaning.

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