IJCS INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 9, Issue 1, January-March 2018: 127-136 www.ijcs.uaic.ro

USE OF SEM, FTIR, AND AMINO ACID ANALYSIS METHODS TO ASSESS THE DAMAGE OF SOME HISTORICAL LEATHER BINDINGS FROM THE XIXth CENTURY, STORED IN NATIONAL ARCHIVE, CAIRO

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Abstract

The current study aims to assess the damage of some historical leathers dating from 1806, 1848, 1880, and, respectively, 1887 A.D. Measurement of pH, infrared spectroscopy (FTIR), SEM and amino-acid composition study were undertaken, to improve our understanding of damage contained in leather. Several structural changes were observed in spectra of deteriorated leather. SEM data, however, show that corium layer are less susceptible to factors deterioration than are grain layer. The study proves that deterioration of leather results from both oxidation and hydrolysis.

Keywords*: Collagen; Leather book binding; SEM; Amino acid; Deterioration; Damage*

Introduction

Egypt has a very long history of fur and leather apparel. According to the historical literature, as early as in the primitive society (before 3000 B.C.), as evidenced by Badarian graves, the ancient Egyptian people were making clothing articles like coats, aprons and shawls with animal hides and skins [1, 2] .

In early times, ancestors processed beast hides with some simple treatments, in the same contact a fundamental property of leather is that while a raw skin is subject to rapid bacterial degradation due in the main to the action of proteolytic enzymes, leather is resistant to such microbiological attack even if it is kept wet. There are, though, a number of techniques such as salt curing, drying, solvent dehydration and acid pickling which will impart temporary preservation against bacterial attack. This resistance to decay, however, is lost if the fibres are allowed to become wet [3, 4]. Furthermore ,leather is represent a very complex material composition with a very complex and dynamic dimension constantly varying with respect to the quantity and degree of their interaction with each other and with those materials which are being stored within them [5-7].

Leather's natural degradation at all levels of structural hierarchy (from molecular to microscopic levels) can be categorized according to the cause and associated external manifestation in chemical, mechanical, and biological damage. chemical damage due to oxidation, environmental chemical pollutants like NO_x and SO_2 hydrolysis, photochemical degradation; physico-mechanical damage due to frequent stretching and shrinkage of the material that appear when fluctuations in relative humidity occur; biological damage [8].

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The investigation of these kinds of leather deteriorations is very important for museum custodians, private collectors and restorers, and involves some problems, including the achievement of some suitable preservation treatments and the restoration of the patrimonial objects. There are reviews [9-13] concerning the history of the interpretation of chemical deterioration of vegetable-tanned leathers according to which the degradation of tannin/collagen complex consists in two main processes, hydrolysis and oxidation. These reactions are influenced by, gaseous pollutants, pH etc.

So, the current study, based on SEM examination and FTIR, seeks to illustrate the morphological and structural changes of decayed leather by various degrading factors its deterioration potential in the air, which is essential for understanding the ageing of leather objects and for knowing the proper procedures to conserve them.

Materials and methods

Historical samples

Selected samples were taken from the outer covers, flaps and edges of bookbinding of the historical books (Figs.1, 2, 3 and 4). The data on historic leather used in the study is summarized in Table 1.

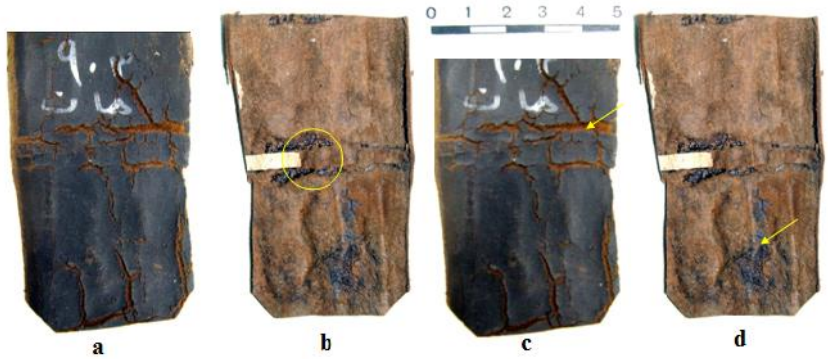

Fig. 1. Historical leather sample from 1848: a and c. Showed the deteriorated grain layer especially the cracks which penetrated in the side the corium fibres bundles; b. and d. Showed black spots in the flesh, which indicated that the leather has been exposed to uncontrolled conditions during storage in the National Archive

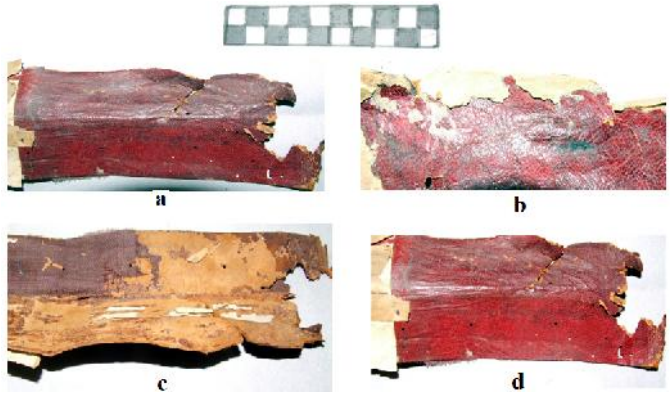

Fig. 2. Historical leather sample back to 1806: a. Leather loses its regain ability and becomes hard and brittle; b. The leather surface damaged caused by insects; c. Showed the old adhesive that covered the flesh layer; d. The arrow refer to the cracks and missing parties

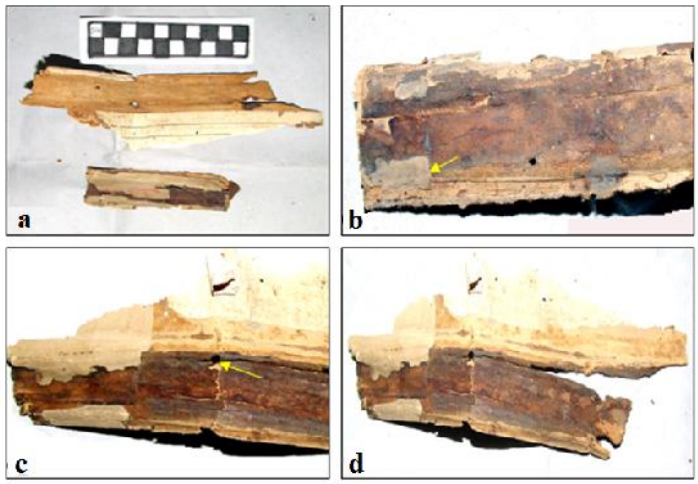

Fig. 3. Historical leather sample back to 1887 A.D.:
a. and b. Leather with some stains and dust;
c. and d. Aspects of deterioration of a bookbinding

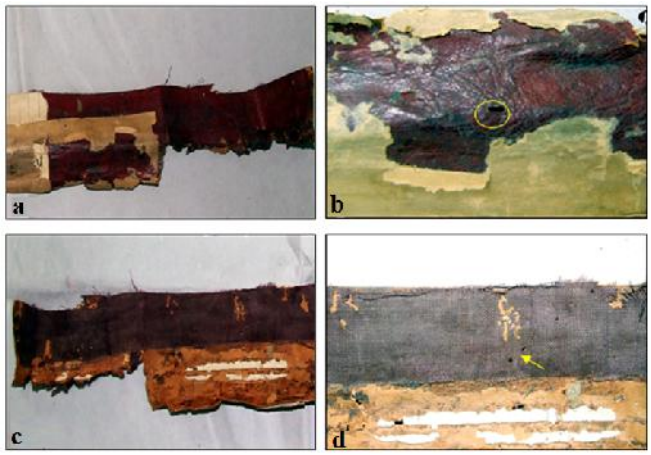

Fig. 4. Historical leather sample back to 1880 A.D.:
a. The hardness of leather sample;
b. c. and d. The leather surface damaged caused by insects.

Table 1. Data on historic leather used in the experiments.

Date	*Skin type*	*Tannage*	*Region*
1848 AD.	cattle	*Oak bark*	The castle in Cairo
1869 AD	Sheep	Myrabolam	The record of Cairo University
1845AD	*Calf*	*Acacia Arabica*	The castle in Cairo
1862AD	*Goat*	Oak bark	The castle in Cairo

pH values

1000mg of sample (grain and corium) cut into 1mm² fragments. Fragments are extracted in water for 24h at room temperature, under constant agitation in a closed polyethylene vessel. The measurements were performed directly on the aqueous extract using a pH meter (PHM62, Radiometer, Copenhagen) with a combination electrode and calibrated between pH = 3 and 7, at 28°C. To make the method available to small samples, the dilution condition of the leather

extracts (1g/50mL) differs by a factor of 2.5 from the standard procedure (2.5g/50mL). This makes the present pH readings of strong mineral acid solutions about 0.4 higher as compared to the standard procedure [14].

Scanning electron microscopy (SEM)

Specimens for this study were cut from the samples. Specimen size was 10mm diameter and it was circular in shape. These samples subjected to sputter coating (Edwards's model S 140A) of gold ions to have a conducting medium. Sputter coated samples were scanned with JEOL Model JSM-T20 SEM.

FTIR spectroscopy analysis

The IR spectra of samples were recorded by means of Nicolet380 (FTIR) spectrometer with Attenuation Total Reflection (ATR) mode with a zinc selenide crystal, in the wave length range 650-4000cm^{-1}. The IR absorbance frequencies for the samples under test were recorded with an average of 128 scans using a resolution of approximately 4cm^{-1}.

Amino acid Composition

Automatic Amino acid Analyzer AAA 400 INGOS Ltd was used to Amino acid analysis of leather bookbinding. Acid hydrolysis was carried out according to the method of Block [15, 16]. The dried grinded sample (100mg) was hydrolyzed with 6N HCl (10mL) in a sealed tube at110ºC in an oven for 24 hours. The excess of HCl was then freed from 1mL hydrolyzed under vacuum of 80ºC with occasionally addition of distilled water, then evaporated to dryness. The HCl free residue was dissolved in exact (2mL) of loading buffer (6.2M, pH = 2.2).

Results and discussion

pH

The results of pH values (Sample 1: 3.83; Sample 2: 3.30; Sample 3: 3.41; Sample 4: 3.52) show that the pH values of historical leather decreases about 5 to 6% as comparison with normal leather. Number of researchers reported that the level in the normal state of pH = 4-6 [17, 18].

The results confirmed that historical leather especially, the leather back to 1880AD could be attracted with air pollution. Chemically, Sulphuric acid in leather, originating from the adsorption of sulphur dioxide from industrial air pollution, is commonly considered as the primary agent of acidic hydrolysis in historical leathers. In sunlight, sulphur dioxide is transformed to sulphur trioxide. The sulphur trioxide is adsorbed by tannins in the leather. There it is hydrated into sulphuric acid, which dissolves in the moisture present in the leather producing active hydronium ions. These hydronium ions, in turn, break the links between the amino acids in the collagen polymer chain. It should be noted that sulphuric acid is only one part of the internal acidic environment in the leather. There are organic acids and acidic breakdown products from tannins and amino acids inherently present within the structure which add to the hydrogen ion concentration and acid hydrolysis potential [19-21].

Scanning electron microscopy (SEM)

Observation of the surface morphology of samples revealed a high degree of degradation and damage. Scanning electron microscopic (SEM) images (Figs. 5-8) show that the leather surface is extremely rough. The damage is evident in the form of scratches, large slights, holes and transverse cracking of grain layer. Figure 6 shows the destruction and random distribution of the fiber structures, erosion of the fibers, and many bores. There was total deformation of the surface morphology; besides that, the micrographs show differences in type and leather degradation patterns under this study.

Figure 6 prove that the sample N. 2 from sheep skin which have fine corium fibres interweave fairly compactly with no looseness between the grain and corium layers [22]. Furthermore, we can observe that the corium fibres exhibiting generalized thinning and erosion leading to breakdown of the grain layer which became easily fragmented. As revealed by the

SEM results in figure 7, the leather can be made of calf skin. It is generally known that calf skin have compact interweaving of the fine corium fibre bundles and the grain surface is extremely fine [23].

In contrast of such, the sample number 4 (Fig. 8) was made from goat skin, the fibre bundles of goat are relatively fine and interweave compactly at a medium angle. However, the destruction, random distribution and erosion of the fibers were spotted.

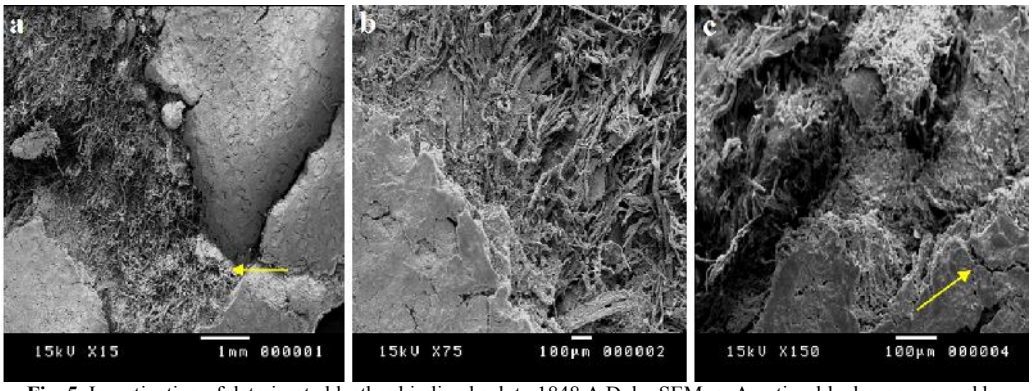

Fig. 5. Investigation of deteriorated leather binding back to 1848 A.D. by SEM: a. A noticeable damage caused by moisture, mineral residue and moldy bloom; b. Shows the damaged corium bundles; c. The arrow refer to the cracks in the grain layer

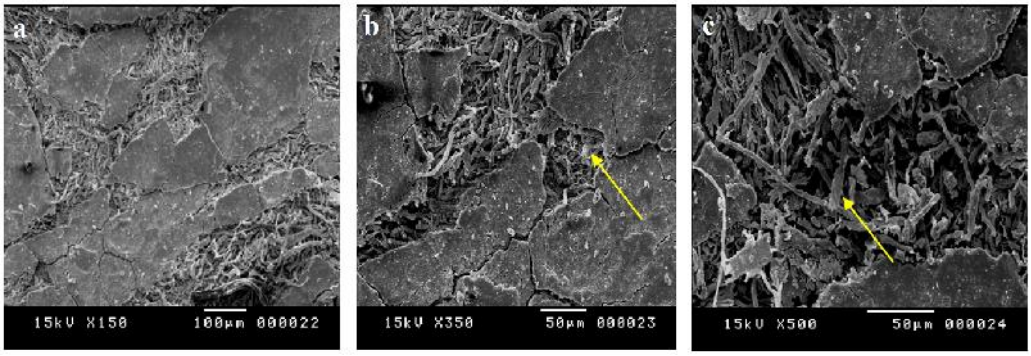

Fig. 6. Investigation of deteriorated leather binding back to 1806 A.D. by SEM: a. A noticeable destroy in grain layer; b. and c. Showed the destruction and random distribution of the fiber structures, erosion of the fibers, and many bores. There was total deformation of the surface morphology

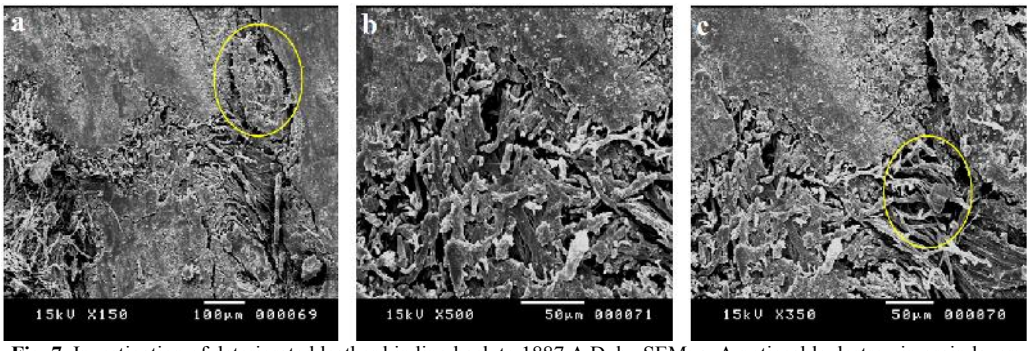

Fig. 7. Investigation of deteriorated leather binding back to 1887 A.D. by SEM: a. A noticeable destroy in grain layer; b. and c. Showed the destruction and random distribution of the fiber structures, erosion of the fibers, and many bores. There was total deformation of the surface morphology

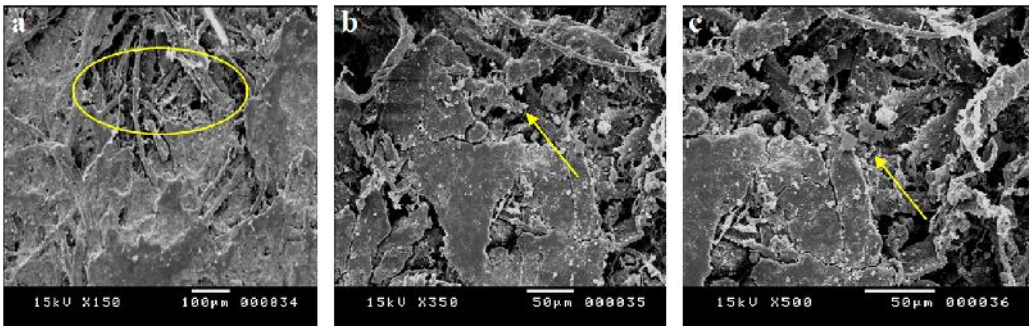

Fig. 8. SEM micrographs of weathered leather binding back to 1880 A.D.: a. Erosion troughs formed in grain layer; b. We can observe the foreign deposits may be resinous material mixed with dust inside boundless cells; c. Extremely weak decayed fibre easily fragmented

FTIR

The spectra for primary and secondary amides of ideal leather contain a strong carbonyl absorption band in the region of 1650cm^{-1}, called the amide I band. Secondary amides display an additional band near 1550cm^{-1}, called the amide II band, which is a combination of C-N and N-H vibrations. Moreover, C-H bending vibration occurring near 1450cm^{-1} has sometimes been called the amide III band. Furthermore, the relative intensities of the amide I, II and III bands in polyamides (protein, nylon, etc.) occur in a stair-step pattern. The asymmetrical and symmetrical N-H stretching vibrations occur near 3350 and 3180cm^{-1}, respectively. Hydrogen bonding may broaden the bands, giving the appearance of one band, although they are usually sharper than O-H bands. Often a stronger O-H band overlaps this region, and the N-H stretches appear as shoulders or peaks on the broader O-H band [24, 25].

When comparing IR spectra with those of modern reference spectra (Figs. 9 and 10) several changes in the spectra were noticed in deteriorated leather, it is interesting to note that here are some differences in the decrease of the relative intensity of carbonyl absorption band in the region of 1650cm^{-1} (amid I band), with corresponding amide III (1450cm^{-1}) bands in both sample (3), as well as sample (4), addition the band at 1550cm^{-1} (amide II) disappears in sample (1) and is reduced in sample (2). The results confirmed that no correlation could be observed between pH values of samples and the reduction of the band intensity at 1550cm^{-1}.

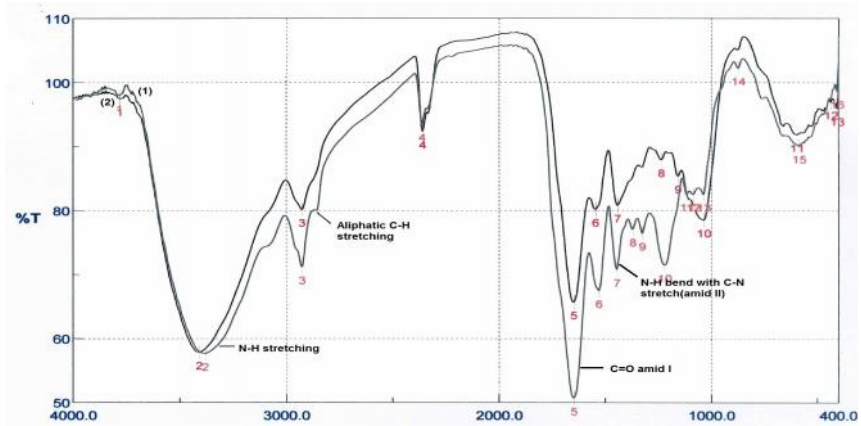

Fig. 9. Comparison of two spectra scanned in transmittance: (1) leather binding back to 1848 A.D. and (2) sample back to 1806 A.D. specimen. Bands of amid I and amid II are marked

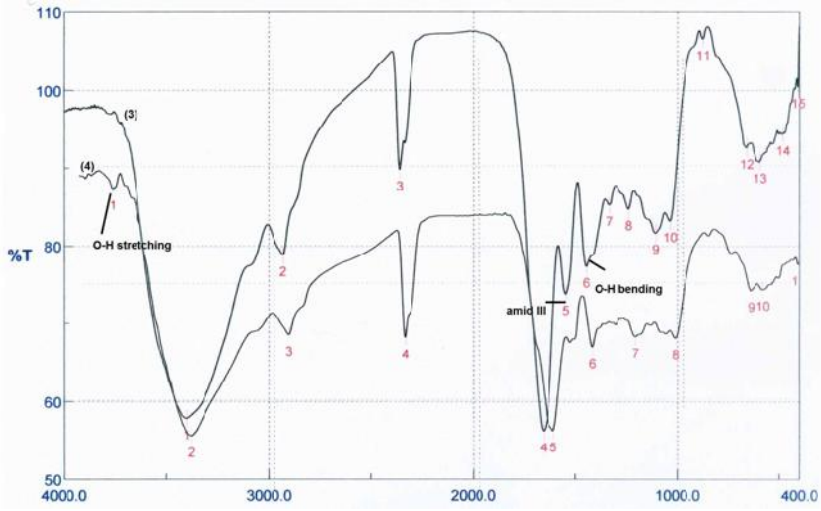

Fig. 10. Comparison of two spectra scanned in transmittance: (3) leather binding back to 1848 A.D. and (4) sample back to 1880 A.D. specimen. Bands of O-H bending & amid III are marked

Amino acid composition

It is generally known that destruction of vegetable-tanned leather results from two processes: acid hydrolysis and oxidative degradation of collagen and tannins. In oxidative degradation of collagen there is observed transformation of positively charged amino acid residues into negatively charged ones, whereas in undamaged collagen the positively charged and negatively charged amino acid residues are balanced change in this balance, including that caused by oxidative degradation of leather, leads to leather destruction [26].

The relationship B = (Arg + Hyl + Lys)/(ASP, Glu) between the amounts of basic and acidic amino acids reflects the degree of oxidation decomposition of collagen. The results of amino analysis of the leather bookbinding are illustrated in Table 2 and Figure 12.

Table 2. The concentration of amino acids in the leather bookbinding and reference sample (μg/mL)

Samples	NH_4	Glutamic	Lysine	Arginine	Aspartic
Reference	42.8393	151.25636	71.93526	191.34272	49.17012
N.1	105.24	160.89	30.67	86.84	71.21
N.4	67.0	259.0	60.44	186.0	148.53
N.2	67.04	198.66	50.60	117.11	92.21
N.3	101.3	161.43	31.58	97.42	78.8

The results confirmed that the degradation factors affect the amount of polar amino acids in the leather, primarily arginine, lysine, glutamic and aspartic amino acids. Basically, the oxidation decomposition of collagen reduced the amount of basic amino acids oxyproline and proline, whereas the amount of acidic acids increases (glutamic and aspartic) which is partly due to an increasing amount of collagen decomposition products. In the case of oxidation mechanism of collagen decomposition transformation of positively charged amino acid residues into negatively charged ones occurs. Hydrolytic decomposition of collagen gives an increase in the amount of basic amino acids due to the peptide bond breakage. The Conc (μg/mL) of lysine for reference leather was 71.9 (Table 2), whereas for historical leathers it was 30.6, 60.44, 31.58, and 60.44 for samples 1, 2, 3, and 4 respectively. Accordingly, this indicates that there was the process of oxidation destruction in collagen in the four samples; moreover, the content of acidic amino acids increased by the same value. This proves that deterioration of leather results from both oxidation and hydrolysis.

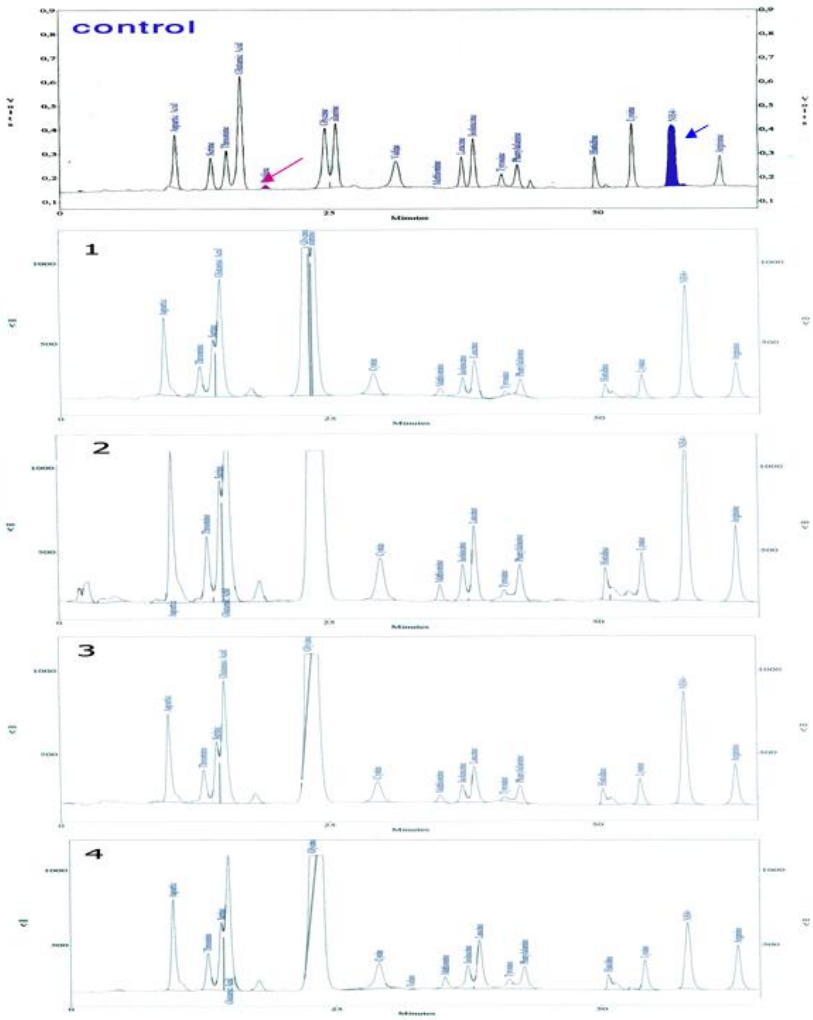

Fig. 11. Amino acids ratios of reference and deteriorated leather

Conclusion

The aim of current study was to assess the damage of the historical leather bindings, stored in National Archive, Cairo. Based on all discussed above; we would like to summarize that:

- the studied leather suffer from deterioration caused by surrounding environmental conditions;
- the pH values of historical leather decreases about 5% to 6% as comparison with normal leather;
- corium layer are less susceptible to factors deterioration than the grain layer;
- the micrographs showed differences in type and leather degradation patterns under this study;
- The amino acids analysis of leather, gave a clear indication of degradation processes, proving that the mechanism of deterioration by oxidation processes caused breaks in the backbone chain of the molecule;

– The oxidation decomposition of collagen decreases the amount of basic amino acids, whereas the amount of acidic acids increases, which is partly due to decrease amount of collagen decomposition products. Hydrolytic decomposition of collagen gives an increase in the amount of basic amino acids due to the peptide bond breakage.

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Received: Juny 12, 2017
Accepted: March 03, 2018