INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 6, Issue 3, July-September 2015: 369-382 www.ijcs.uaic.ro

A "TAFSIR AL KHAZEN" MANUSCRIPT (17TH CENTURY AD). A TECHNICAL STUDY

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Abstract

This study focuses on using analytical techniques for identifying the components of the manuscript to explain its deterioration process. The "Tafsir Al Khazen" manuscript, a rare manuscript of the seventeenth century, consists of paper sheets and leather bookbinding; it had been damaged by sewage water in the courtyard of the Al-Azhar mosque. Concerning measurements, we used visual assessment, pH measurements, isolation and identification of fungi, moisture content, investigation of the surface morphology by SEM, identification of pigment binder by FTIR - ATR, chemical testing of the paper components, X-ray diffraction and EDX analysis of ink and pigments X- ray diffraction analysis (XRD) for determining paper crystallinity. The results revealed that cotton fibres may have been used as raw material in the creation of paper. Alum, gelatine have been used as a sizing in paper manuscript. Goat skin was identified as the animal skin of the bookbinding, the black ink used was carbon ink, the pigments used on the paper were silver sulphide (HgS) for red colour, gold leaf for gold colour and natural ultramarine mixed with white lead for blue colour. Aspergillus sp. and Penicillium sp. were the most dominant fungi found on the manuscript. The pH of leather was higher than in normal conditions.

Keywords: *Rosin; moisture content; SEM; amino acids; pH; fungi; crystallinity.*

Introduction

Paper materials including manuscripts, book and painting are all subject to various forms of deterioration; initially the paper may be strong and white, but in due course of time, on account of physical, chemical and biological factors, their properties undergo changes and they deteriorate and get damaged [1]. Besides natural causes like climate, light, fungi and insects, there are several man-made factors which caused damage to the paper and added materials such as ink and hand colouring with pigments or dyes. Deterioration of paper-based materials is mainly due to the degradation of cellulose caused by many factors, such as chemical attack due to acidic hydrolysis, oxidative agent, light, air pollution and biological attack and also due to the presence of microorganisms like bacteria and fungi [2]. The leather itself represents a very complex material composition. Its surroundings are, likewise, a very complex and dynamic dimension constantly varying in terms of quantity and degree of their interaction with each other [3]. Animal skins have been used since pre-historical times for the preparation of a wide variety of household articles (clothes, shoes, bags, beds and chairs, shields, etc.) and for fine art objects, particularly book bindings [4]. The most common types of damage sustained by bookbinding are caused by poor handling, poor storage methods, inappropriate display methods,

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and wear and tear from repeated use, chemical changes in the materials making up the leather objects and bookbinding leathers exposed to polluting gases. Bookbinding leather exposed to air and light exhibited a great content of sulphuric acid originating from the polluting atmosphere. Degradation induced by the absorption of airborne SO_2 is commonly known as the "red rot", which mainly affects the vegetable bookbinding leathers. Sulphur dioxide is oxidized by vegetable tannins (pyrocatechol tannins are stronger oxidizer than pyrogallol ones) to sulphur trioxide, which reacts with air humidity and forms the sulphuric acid, an aggressive leather ageing agent. Sulphuric acid breaks down the polypeptide chains to amino acids and ammonium salts. This study aims to identify the materials used in the manuscript studied, to apply the most effectiveness techniques of analysis (for determining the paper and bookbinding degradation) and to explain the mechanism of deterioration.

Materials and methods

Description of the manuscript

The manuscript of "Tafsir Al Khazen" is a complete book made of paper, with leather bookbinding measuring 56.5 × 33 cm². It was received by the venerable Prince Louaa Ayoub, formerly Dafter Dar of Egypt, Mohamed Abu El Dahab in 1193 AH. It was written in black, red and golden ink. It was listed under No 2910 in the stores of Al Azhar Al Sharif Grand Mosque. The manuscript is a book on meanings interpretation for the revelations of the Holy Koran, named "Tafsir Al Khazen".

For determining the materials used with the manuscript and for explaining the deterioration processes, a number of analytical techniques were used in this study: pH, SEM, EDAX, X-ray diffraction, FTIR [5], moisture content (amino acids, biological insulation of paper and leather to identify the fungi that may be present on the manuscript). The techniques used were selected to obtain a significant identification and to obtain the optimum amount of information concerning the materials used. The analytical techniques used were more effective in explaining the deterioration processes of the manuscript.

Visual assessment and photography

The author performed visual assessment to determine the aspects of deterioration found on the manuscript's paper and leather. This method is very effective because the causes and mechanism of deterioration can be easily identifiable [6].

Measurement of the pH

Measurement of the pH was in accordance with Tappi 509 om-02 (cold extraction, 1g of sample per70mL of water, 1h) [7, 8]. The leather was taken off mechanically, in the form of loose fibres, from as near as possible to the damaged area on the surface (grain) of the leather. The samples of the paper and the leather were cut into very small pieces. The pH was measured approximately 6 h after the suspension had been prepared. To allow the ions to migrate into the solution, we used ML1010PH, Misura Line, Romania.

Isolation and identification of fungi

Abundant superficial fungal colonies were found on the surfaces of paper and leather binding of historical manuscript during in situ observation. The isolation of fungi was performed directly in the laboratory after swabbing. The fungi were isolated by rubbing the swabs gently on culture medium of Czapek-Dox Agar/1Liter composed of 41g K_2HPO_4, 30g sucrose, 0.5g magnesium sulphate, 3.0g sodium nitrate, 0.5g potassium chloride, 0.01g Iron (II) Sulphate, 17g agar, pH = 5.5-6, at 25°C for 1–3 weeks. Inoculated Petri dishes with fungi were incubated at 25±2°C for 7 days. Resultant cultures were purified using the hyphal tip and/or a single spore technique. Fungi colonies were identified according to the method of Merck [9]. A standard plate count method was used to determine Total Fungal Count (CFU/g sample) for the paper and leather samples.

Moisture content

Measurement was carried out according to A.O.A.C 2000 [10]. About 0.77g of leather and about 0.67g of paper were weighed. Both were placed separately in Pyrex pan in oven at temperature of 105°C for 24 hours, and the sample was weighed again until the weight was stabilized and internal water content calculated according to the water content.

Investigation of the surface morphology by SEM

The Scanning Electron Microscope, Model Philips XL 30, was used for the investigation of the paper and the leather surface morphology. The fine gold coating (XL 30, Philips, 550X sputter coater) was used for coating samples.

X-ray diffraction and EDAX analysis of ink and pigments

The (black, red, blue, and gold) ink samples were analysed by X-ray diffraction using Compact X-ray Diffract meter System PW 1840 – Analytical Equipment – Philips– Eindhoven – the Netherlands (Cu Kα radiation with Ni-filter). EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n). FEI Company, Netherlands was used for EDX analysis.

Identification of pigment binder by FTIR- ATR

"Smart performer ATR" unit accessory with *Zinc Selenite FTIR spectrophotometer, Thermo Scientific Company, Nicolet 380 Special range 4000-400cm`1 was used in order to identify the binder of the ink and pigments used on the manuscript paper.*

X- ray diffraction analysis for determining the paper crystallinity

Compact X-ray Diffract meter System PW 1840 – Analytical Equipment – Philips– Eindhoven – the Netherlands (CU Ka radiation with Ni- filter) was used for determining the paper crystallinity.

The crystallinity index was calculated according to equation [11]:

$$I_{Crys} = \{(I_{002} - I_{am})/(I_{002})\} \times 100$$

where: I_{Crys}= crystallinity index, I 002 = intensity at approximately 2θ = 22.6°, I am = intensity at approximately 2θ = 19°.

And this is as good as any other approach for the relative ranking of cellulose/crystallinity [12-15].

Chemical testing of the paper components

Detection of lignin

We used the aniline sulphate solution prepared by dissolving 1g of aniline sulphate in 50cm^3 of distilled water to which one point of sulphate acid was added, as follows: one point of the previously prepared solution was placed on paper to be tested. In case of lignin, it produces yellow colour; second: detection of lignin was also done using the fluoroglycinol (2g of fluoroglycinol is dissolved in 50cm^3 of pure alcohol). Concerning the method, we used it as follows: two drops of the fluoroglycinol solution that was previously dissolved is placed and one drop of concentrated hydrochloric acid is added. The colour appears red, which indicates that lignin exists, and the red colour reflects the lignin concentration in paper.

Detection of aluminium

We used aluminon prepared by melting 0.05g of aluminon in 5cm^3 of distilled water. The method of use depends on the placement of drops of the previously prepared solution and the dark red colour that shows the existence of aluminium in the composition.

Detection of rosin

A small piece of paper is placed on a microscopic slid and one drop of saturated solution of sugar is placed on the surface. It is placed there for about 5 seconds and then the excess is removed with a piece of filter paper. One drop of concentrated sulphite acid is added to the same spot. If a brilliant red colour becomes visible, rosin is present.

Detection of gelatine

Gelatine or animal jelly can be tested with the help of Ehrlich's reagent. To prepare the reagent, 1gm p- dimethylaminobenzaldehyde is dissolved in 20 cm^3 of 1-propanol. A colourless or slightly pale yellow solution is obtained. A small piece of paper or its few fibres are taken in a micro test-tube and treated with a 6M NaOH solution. It is heated in a water bath for a few minutes and allowed to cool. 1mL of 0.01M copper sulphate solution and a few drops of hydrogen peroxide, a few drops of sulphuric acid and the reagent are used. After adding copper sulphate solution and hydrogen peroxide, foaming will emerge. When it subsides, it is placed in the boiling water bath for 5 minutes. When the hydrogen peroxide is completely decomposed, sulphuric acid is added. The tube is again cooled and a drop of sulphuric acid and the reagent is added and mixed; in the presence of gelatine a pink colour develops.

Leather bookbinding analysis by FTIR

A small amount of leather was removed by micro-scalpel and placed on spectrum. The IR spectra, in transmittance mode, the surface of a freshly prepared KBr pellet (transmittance was obtained from different areas of the specimens, using an aperture of 20-100μm in the spectral region 4000-400cm^{-1}). The resolution was 0.1cm^{-1} and the number of co-added scans was 64 for each spectrum. The spectrum of the KBr pellet was used as background. The spectra presented are baseline corrected and converted to absorbance mode.

Amino acid analysis of leather

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 [16]. The dried grinded sample (100mg) was hydrolyzed with 6N HCl (10mL) in a sealed tube at 110ºC 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

Visual assessment and Photography

The storage of the manuscript was very poor and led to advanced deterioration. We mention the following aspects of on leather bookbinding (Fig. 1A): general hardness, fungal spots, erosion of tanning material, holes caused by insects, and missing parts. The following aspects of deterioration were noticed on the manuscript paper (Fig. 1B, C and D), as well as local missing parts and local damage in the corners with multiple folds and creases, stains derived from different sources (fungi, fats dusts).

Measurement of pH

The pH of the studied paper was 5.5 This may be due to some acids that formed within the paper, or those absorbed from the environment that were neutralized before they had a chance to degrade the cellulose chains. It was stated that fibres made of cellulose chains degrade when exposed to an acidic environment in the presence of moisture. In this acid hydrolysis reaction, cellulose chains are repeatedly split into smaller fragments as long as the source of acid remains in the paper. This acid hydrolysis reaction produces more acid and the degradation accelerates [17]. It was noticed that the pH of leather was acidic, but the pH increased more than the level in the normal state of pH = 4-6 [18, 19]. The pH of the leather bookbinding ranged between 8 and 8.2. The increasing of pH may be due to alkaline accumulation in the leather, caused either by insufficient removal of alkaline residues from processing or by air-pollution like ammonia. Ammonia evolves from decaying organic materials; it is easily dissolved in water and it results in alkaline solutions. It reacts with other gases to form salts that deposit on surfaces and change local acidity [20].

Fig. 1. Number of manuscript deterioration: (A) missing parts of leather bookbinding, (B) folding of the fibres and hardness,(C) stains of dust, (D) destruction of paper edges

Isolation and identification of fungi

The results of this study revealed that the most dominant fungi on the manuscript paper (Table 1) were *Aspergillus niger* and *Aspergillus flavus*. Most dominant fungi found on leather bookbinding (Table 1) were: *Aspergillus terreus*, *Aspergillus flavus* and *Aspergillus niger.* Leather and paper are organic materials and are susceptible to numerous microbial deterioration processes, especially fungi. Fungi that attack tanned leather often belong to lipolytic species and utilize the fats present in leather as a source of carbon. Effects of microbial deterioration on protein materials are the presence of different stained spots, the loss in tensile strength and, if the proteins are attacked, the hydrolysis of leather [21]. Biological agents cause great damage to paper materials, fungi make paper soft, limp and, since the sizing is also decomposed, it becomes absorbent [22, 23].

Table 1. The most dominant fungus on paper and leather of the manuscript

Sample	Total Fungal Count (CFU/g sample)	Fungal species
Paper	3	*Aspergillus niger, Syn. A. fuscus, Van Tieghem Schumann*
	2	*Aspergillus flavuslink, Syn. A. humus*
Leather	5	*Aspergillus niger, Syn. A. fuscus, Van Tieghem Schumann*
	4	*Aspergillus flavus, link Syn. A. humus*
	32	*Aspergillus terreus, Syn. A. humus, Thom Massee*

Moisture content

The moisture content of paper and leather plays an important role in its stability. Low humidity causes paper to dry out and become brittle. On the other hand, with high moisture content, the paper becomes limp and soggy. High humidity also encourages the growth of microorganisms. There is different moisture content at any given relative humidity depending on whether the moisture was desorbed (brought into equilibrium from higher relative humidity) or adsorbed (brought into equilibrium from lower relative humidity). The curves for desorption and adsorption are not the same. This is known as the hysteresis effect [24]. The results showed that the percentage of water content of leather was 10.80, while the percentage of water content of paper was 4.58. It was noticed that the moisture of paper was very low and decreased more than the level in the normal state of moisture 8-12% [25].

Investigation of the surface morphology by SEM

It was clear by a study of the grain surface of leather bookbinding by SEM and the comparison with control goat skin (Fig. 2A-B) that the type of skin used for the bookbinding was goat skin, long used as a strong and flexible bookbinding material [26]. The leather surface was smoothed and glazed. The coarse follicles were in the form of groups. There was a wide and smooth surface between these groups. The grouping of coarse and fine follicles was easily recognized and the investigation of leather bookbinding (Fig. 2C) showed the destruction and random distribution of the fibre structures, the erosion of the fibres and many bores. There was total deformation of the surface morphology, (Fig. 3B) showing that the manuscript paper was probably made from cotton, because cotton fibres are long; the length ranges between 10 and 65 nm [27, 28]. Some contaminations (Fig. 3B) from stains and dusts were noticed on the surface of the original paper. Damages caused by physical factors (Fig. 3C) appeared in the form of bores, and the tearing of paper fibres and deformation of the paper appearance were also noted.

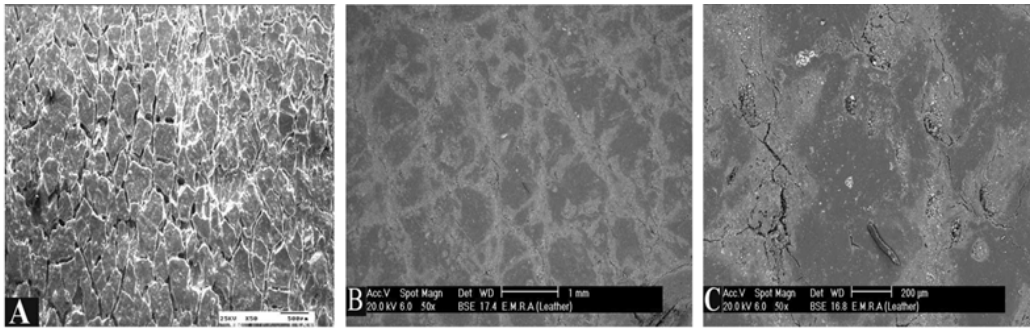

Fig. 2. Investigation of deteriorated leather by SEM & Identification of animal skin: (A) goat skin, (B) goat skin from the historical bookbinding, (C) historical bookbinding with damaged caused by factors of deterioration

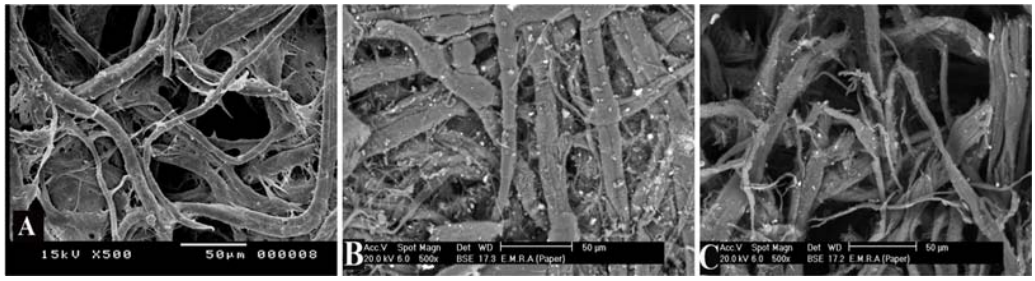

Fig. 3. Investigation of deteriorated paper by SEM (A) blank cotton paper (B) original paper manuscript; (C) the tearing of paper fibres

X-ray diffraction and EDAX analysis of ink and pigments

It was clear from the X-ray diffraction (fig.4) and the EDAX analysis (Table 2) that the gold colour was from gold shell, because it would stick to the medium used to suspend the paints. Shell gold was used to illuminate manuscripts; it is made of powdered gold suspended with gum. It was cheaper than gold leaf and could be applied with a pen. Shell gold allowed for finer detail and could be applied after the paint. The data obtained (Fig. 5 and Table 2) showed that the red colour was vermillion (formed from red mercuric sulphide obtained from cinnabar which solved in vinegar and mixed with Gum Arabic or white egg). It was clear from Fig .6 and Table 2 that the blue colour is natural ultramarine because the artificial ultramarine was not known in France in 1824. Ultramarine consisted mainly of aluminium sodium silicate with sulphur. Ultramarine is a deep blue colour and a pigment which was originally made by grinding lapis lazuli into a powder. The pigment consists primarily of zeolite-based mineral containing small amounts of polysulphides. It occurs in nature as a proximate component of lapis lazuli. Ultramarine is the most complex of the mineral pigments, a complex sulphur-containing sodium-silicate $Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$ [29] containing a blue cubic mineral called lazurite (the major component in lapis lazuli). Some chloride is often present in the crystal lattice, as in this manuscript. The blue ultramarine was mixed with basic lead carbonate. This is more commonly termed lead white, an umbrella term that encompasses a wide range of white lead-based paints, the most common being $2PbCO_3 \cdot Pb(OH)_2$. This pigment has been used widely from antiquity to the present day, although its use declined with the introduction of less toxic white pigments such as zinc white and titanium dioxide whites [30]. The black ink (Fig. 7) was made of carbon ink which was commonly made from lampblack [31, 32] or soot and a binding agent such as gum Arabic or animal jelly. The binding agent keeps the carbon particles in suspension and adhered to paper. The carbon particles do not fade over time even when exposed to sunlight or when bleached. One benefit of carbon ink is that it is not harmful to the paper. Over time, the ink is chemically stable and therefore does not threaten the strength of the paper. Despite these benefits, carbon ink is not ideal for permanence and ease of preservation. Carbon ink has a tendency to smudge in humid environments and can be washed off a surface. The best method of preserving a document written with carbon ink is to ensure it is stored in a dry environment.

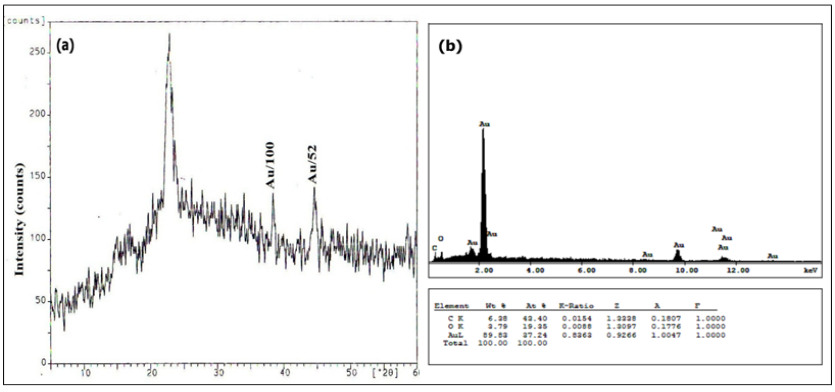

Fig. 4. X-ray diffraction pattern (a) and EDX (b) of gold colour

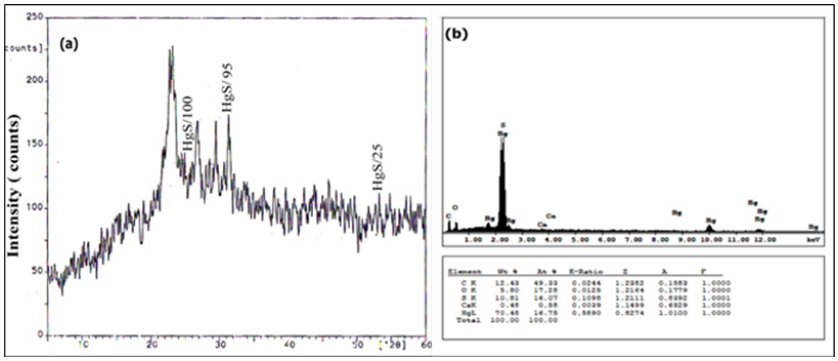

Fig. 5. X-ray diffraction pattern (a) and EDX (b) of red colour

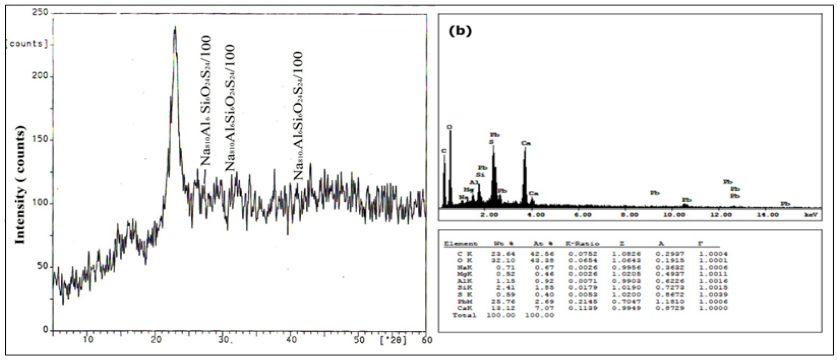

Fig. 6. X-ray diffraction pattern (a) and EDX (b) of blue colour

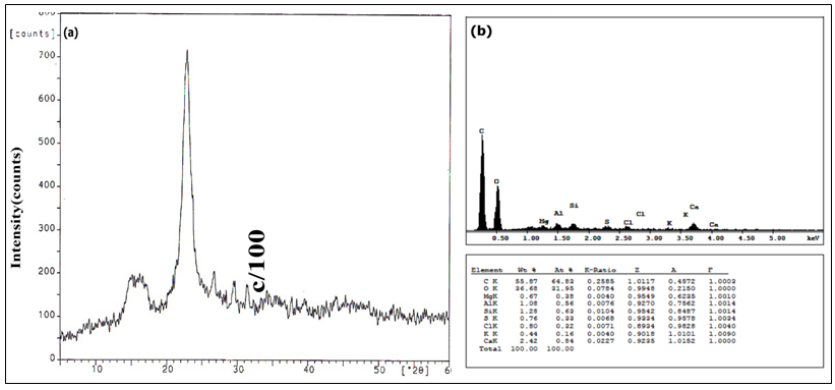

Fig. 7. X-ray diffraction pattern (a) and EDX (b) of black ink

Table. 2. EDAX analysis of ink and colourings used on paper manuscript

Colour	Element (wt %)													Total
	Na	Mg	Al	S	Hg	C	O	Ca	Au	Si	Cl	K	Pb	
Gold						6.38	3.79		89.83					100.00
Red				10.81	70.48	12.43	5.80	0.48						100.00
Blue	0.98	0.78	0.74	0.46		23.66	35.37	11.77		1.71			24.52	100.00
Back	0.83	0.87	2.17	0.88		46.35	42.01	4.21		1.07	1.04	0.56		100.00

Identification of pigment binder by FTIR- ATR

The binder used with the black ink and pigments (Fig. 8) was identified as gum Arabic after a comparison with the blank sample of pure gum Arabic (a natural polysaccharide extracted from the Acacia tree). Molecular mass averages around 580,000 of Acidic polyelectrolytec, extremely soluble in water. Gum Arabic was used by ancient Egyptians to prepare carbon-black ink. Gum Arabic has long been used as the medium in inks and water paints [33]. A number of function groups appeared: CH bending band at 1480-1300cm^{-1}, a very strong band at 1300-900cm^{-1} due to C–O and O-H stretching band at 3600 - 3200cm^{-1},O-H bending band at 1650cm-^{1}, which indicated the characteristics of polysaccharides.

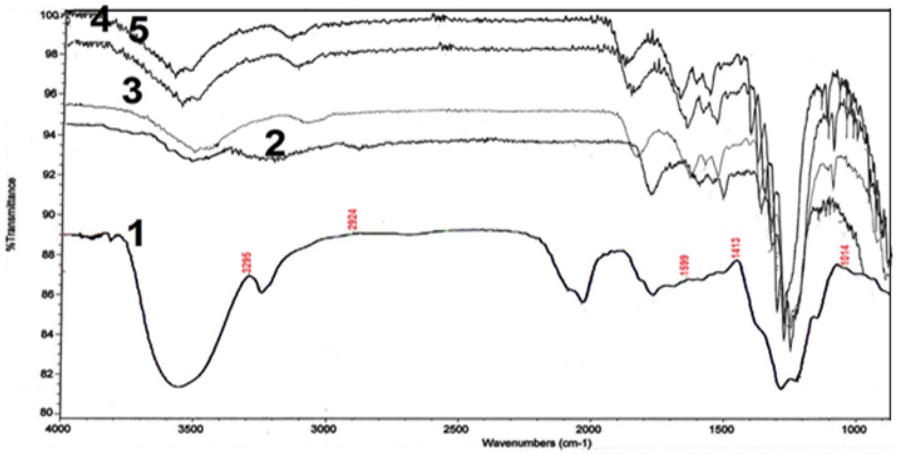

Fig. 8. FTIR analysis of gum Arabic binder used with ink and pigments:
(1) control, (2) gold colour, (3) red colour, (4) black ink, and (5) blue colour.

X- ray diffraction analysis (XRD) FOR determination of paper crystallinity

Primary methods of papermaking have ensured that paper is a material composed primarily of fibrous polysaccharide cellulose. Native crystalline cellulose is comprised of chains arranged in parallel with twofold screw symmetry along the chains due to the β-[1, 4] linkage of the D-glucose subunits.

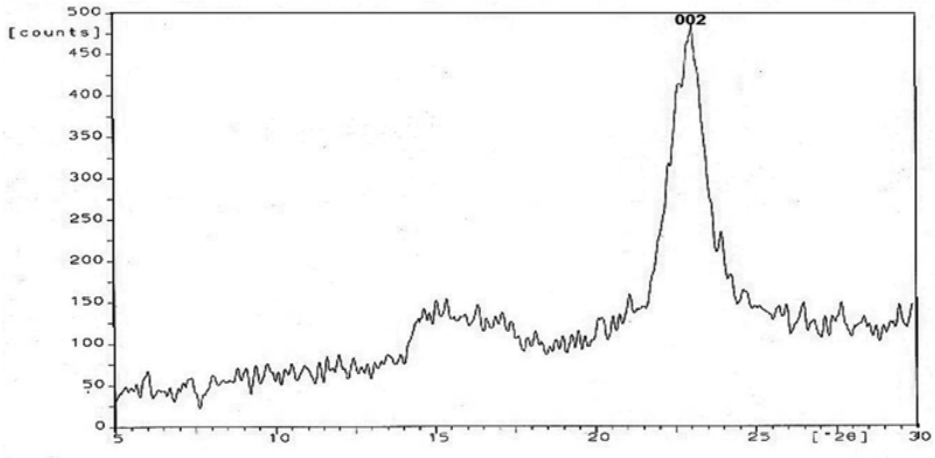

Fig. 9. X-ray diffraction pattern of paper manuscript

Two phases coexist within native cellulose type I, Iα and Iβ1. The degradation of the cellulose in the paper may be a function of processes such as acid hydrolysis or free-radical mediated oxidative process. In both cases, the scission of cellulose polymers is evident. Factors such as the presence of inks, temperature, pH, humidity and the application of cleaning techniques may be implicated in accelerating cellulose degradation; the precise method of historical degradation of cellulose is unclear. Recent studies have indicated that amorphous regions of cellulose may be more susceptible to damage than crystalline regions [34]. It was noticed from data (Fig. 9) that paper crystallinity was 76.8%. The high crystallinity value indicated the role of high RH, because paper crystallinity may increase with natural ageing if there is more water in the air [35].

Chemical testing of the paper components

Paper is, in general, a complex multi-component system consisting of a network of cellulose fibres, together with other substances, such as rosin, alum, glue, starch, dyes, pigments, gelatine and fillers, depending on the production technique employed. Early handmade papers were mainly made from cellulose fibres.

Detection of lignin

It was noticed that the paper was free of lignin. This finding argues that pure cellulose (cotton) was used in the manufacturing of the original paper. In earlier times, paper was made by hand like cottage industry. Given the increase in consumption, it became necessary to discover materials which would be available in bulk for paper making, hence the technique of refining wood by removing its lignin.

Detection of aluminium

It was noticed from testing that aluminium (aluminium sulphate) has been used as an agent to deposit rosin sizing in paper manuscript; however, it hydrolyses to from sulphuric acid [36].

Detection of rosin

Findings showed that the paper was free of rosin, which has long been used for sizing the paper; the material used consists of rosin dissolved in alkali. Alum was added afterward to precipitate compounds of aluminium and rosin which are absorbed by paper fibres.

Detection of gelatine

It was clear from the test that gelatine was used as sizing [37, 38]. The earliest use of gelatine as a sizing agent in replacement of the starch paste that was usually employed earlier in Arab papers can be traced back to the second half of the 13^{th} century. This method of sizing remained in use with no significant changes until the 18^{th} century. However, after the 16^{th} century, other additives such as alum were added to the gelatine and started to become increasingly widespread. Early papermakers saw additional advantages to gelatine, including its ability to improve strength and the abrasion and soiling resistance of paper. Gelatine is a protein obtained following the denaturation and structural degradation of collagen (the principal constituent of hard and soft connective tissue in animals) [39]. In the past, these tissues were boiled in water (nowadays chemical treatments using acids or bases are used). Gelatine is the result of the somewhat random breakage of chemical bonds in collagen to form shorter chains of amino acids. The length of these peptide chains, which affects several properties of gelatine, can vary greatly depending on the preparation method employed.

Leather bookbinding analysis by FTIR

The results in Fig. 10 showed that C-H bending at 1480 -1300cm^{-1} [40] disappeared, intensity of N-H bending stretching band at 3400 - 3200cm^{-1}increased, all the bands between 1500-1600 cm^{-1} (amid II region) [41] decreased and that new bands due to c-o stretching appeared in the region between 1056 - 1033 m^{-1}. These bands were formed as a result of heat breaking down of intermolecular hydrogen bonding; more carbonyl groups were formed as a result of further oxidation of C-H groups of protein molecules.

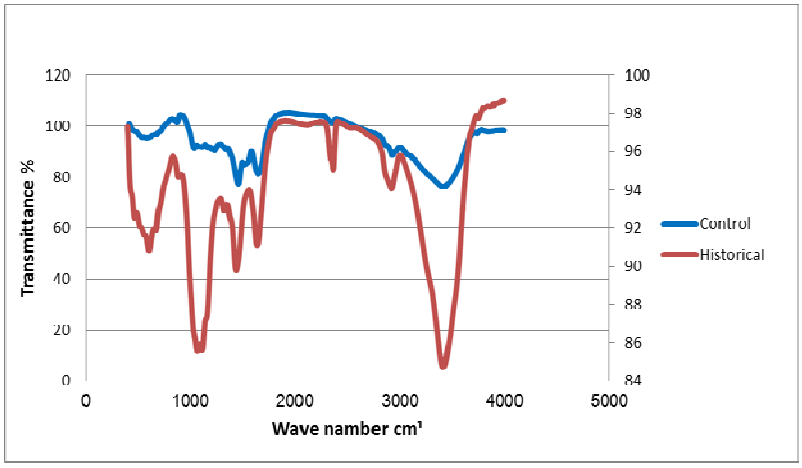

Fig.10. FTIR analysis of leather bookbinding of manuscript

Amino acid analysis of leather

The method of amino acid analysis is particularly useful to characterize the oxidative breakdown of leather corium collagen. The oxidative changes are first of all seen as low values of basic amino acids lysine, arginine and, in some cases, proline. These changes are accompanied by increasing values of acidic amino acids glutamic acid and aspartic acid, together with the formation of several breakdown products in form of amino acids, of which six have been quantified.

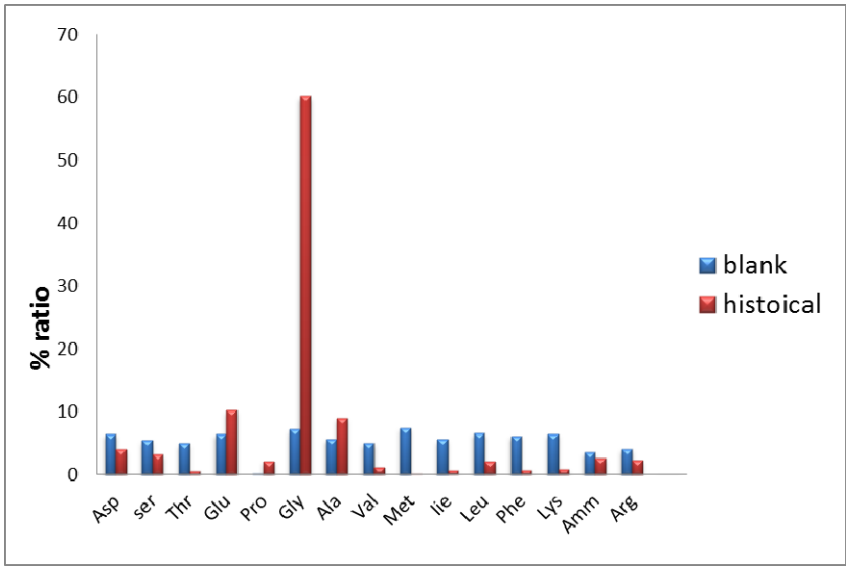

Fig. 12. Amino acids of leather bookbinding compared to blank sample

The B/A ratio = (Arg + Hyl + Lys)/(ASP, Glu) has shown to be fine measure of a verge degree of oxidation [42]. The B/A value is about 0.7 for intact hide and leather collagen and the value decreases with increasing oxidation. Thus, B/A values below 0.5 have been observed in

highly deteriorated leathers. The results of amino analysis of the leather bookbinding are illustrated in Table 3 and Fig. 12. In general, they confirmed the significant oxidative changes of the leather collage, reflected in the amino acid distribution, which follows the same patterns as the historical leather previously analyzed. The lowest values of lysine and arginine observed for the analyzed historical sample was 0.89 and 2.33 respectively. For aspartic and glutamic acid, the lowest values are 3.97 and 10.25, with respect to the B/A vary from 0.22.

Table. 3. The amino acids of the leather bookbinding manuscript and blank sample

Samples	NH_4	Glutamic	Lysine	Arginine	Aspartic
Blank	3.56	6.51	6.45	4.09	6.51
Historical sample	2.63	10.25	0.89	2.33	3.97

Conclusions

The archaeological manuscript has been investigated using different experimental techniques, visual assessment, pH measurements, isolation and identification of fungi, moisture content, investigation of the surface morphology by SEM, identification of pigment binder by FTIR- ATR, chemical testing of the paper components, X-ray diffraction and EDAX analysis of ink and pigments X- ray diffraction analysis (XRD) for determining paper crystallinity, and FTIR spectroscopy. The conclusions that can be reached from this research can be summarized as follows:

Many aspects of deterioration were noted on the surface of the paper or leather bookbinding, such as holes caused by insects, wrapping, erosion of tanning material and missing parts. The most dominant fungi were *Aspergillus terreus, Aspergillus flavus* and *Aspergillus niger.* The pH values of the paper and leather bookbinding were higher than their normal values because this manuscript was damaged by alkaline environmental conditions. Alum and gelatine have been used in the manufacture of the manuscript paper. The black ink was made of carbon, the gold colour from gold shell, the red colour from mercuric sulphide and the blue colour from ultramarine mixed with $Pb_3(CO_3)_2(OH)_2$; the binder used with black ink and pigments was gum Arabic. The original paper used as support for writing materials was made from cotton; goat skin was the animal skin used for leather bookbinding. It is worth highlighting the importance of analyzing the manuscript which we need to restore in order to determine the best methods and materials for conservation.

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Received: January, 23, 2015
Accepted: August, 21, 2015