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Research Article

Using Analyses Of Scanning Electron Microscope With EDX Unit, Infrared, And X-Ray Diffraction For Proves Authenticity Printed Book.

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Abstract

The forgery of historical books is a problem. This study aimed to reduce forgery using scientific, easy, and fast methods. Different techniques were used such as scanning electron microscope (SEM) with EDX unit, Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD). Old paper of Reffa's Book was studied to achieve its authenticity compared with book printed dates is correct (Ibn Battuta) and new accelerated aging paper. The results by SEM showed that Refaa's book resembled the other book both fibers are from cotton. FTIR analysis results determined alkane and carbonyl groups, which appeared in the old paper and not appear in accelerated aging paper. In addition, there was a presence of gelatin groups due to the past manufacturing techniques. XRD analysis results showed a decrease in the degree of crystallinity and crystal size.

Keywords : *Authenticity; SEM, Accelerated Ageing Paper; FTIR; XRD.*

INTRODUCTION

Muslim Arabs learned paper making from the Chinese in the eighth century AD and then spread it in Asia and the Mediterranean region **[1]**. Paper consists of fibers from plants such as: cotton, linen or wood and some filler materials like calcium carbonate, kaolin and talc powder. The old technique could not grind fibers well **[2]** so glue (i.e. gelatin) was added to bind the ingredients together. **[3]** There are many ways to authenticate manuscripts, such as radiocarbon dating, component material analysis, and microscopic examination; especially for objects from the same time **[4]**. Previous studies illustrated that ultraviolet and infrared radiation **(UV & IR)** were used in examining forged manuscripts by revealing the hidden layers after photographing them using infrared or ultraviolet photography **[5]**. Using a scanning electron microscope provided a clear magnified image of the paper surface we can identify the type of fibers and filler materials. The big size of fibers indicates to old manufacturing method. Regarding images, it generated a current of high energy electronics from (0.5: 40) kV, so the current clashed with the sample. The sample image reflected clearly and accurately up to (10) nm. The electronic microscope features of the samples did not need much processing, except in the case of the powder sample, as the soft material was in a state of agglomeration to reduce its chemical energy. As a result, this problem can be solved by adding some acetone to the sample to reduce its energy without aggregation and picturing the structure of the sample with a clear and high magnification **[6]**, **[7]**. Fourier Transform Infrared Spectroscopy (FTIR) is considered micro-destructive analysis. **[8]** It is used to show the changes in the chemical composition of the manuscript. **FTIR** is also used to identify changes in functional groups of cellulose **[9]**. These differences helped distinguish between natural, industrial or fabricated aging. **[10]** Therefore, to prove authenticity and identify the original paper from the fake one, experimental paper samples, were made by Accelerated Ageing and then examined through an infrared analysis.

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Aging is defined as a number factor that can let to changes that occur slowly over time. National Bureau of Standards of the U.S.A (N.B.S) proved that accelerated thermal aging, at 100°C for 72 hours for cellulose, results in an effect on the mechanical properties of tensile strength and speed of collapse equivalent to 26 years. Experiments showed that raising the temperature by 5 or 10 degrees Celsius doubles the speed of the effect by a factor of 2-4% and the best temperature for accelerated aging, similar to what happens in natural aging is between 80-90°C. It is preferable to heat aging in a tightly closed oven, as any material, and the atmosphere surrounding it contains a degree of relative humidity, as the closed place retains what evaporates from the aging process. Through the decomposition products, from the aging process effect, an acidic atmosphere accelerates the aging process. **[11]**, **[12]**. There are many ways to determine the degree of crystallinity of cellulose fibers Chemical analysis and XRD. If the results were compared with standard results for fiber crystallization, this gave an indication of the degree of damage to the manuscript **[13]**. In plants with fibers (such as cotton and linen), crystallinity is equivalent to 90-100 g per 100 g, while in wood it is 60-70 g per 100 g. Measuring degree of crystallinity with XRD by calculate different between beak of crystalline cellulose (2θ200 = 22, 7°) called I200 and beak of uncrystalline cellulose called IAM (2θ = 18°) as in Segal equation. **[14]**, **[15]**, **[16]**. The manuscript, whose authenticity is to be proven, is a book of the Islamic era named ***"Al-Hawi Lilmsael Al-Nfais"***; written by (**Refaa Al-Tahtawi and Mostafa Al-Zrabi**). The book is about the Greece history and the ancient times of countries **(Fig.1)**. It is found in a special library in Upper Egypt. The importance of Rifaa al-Tahtawi lies in his being a pioneer of enlightenment in Egypt in 1801-1873 AD period, where he wrote and translated many books **[17]**.

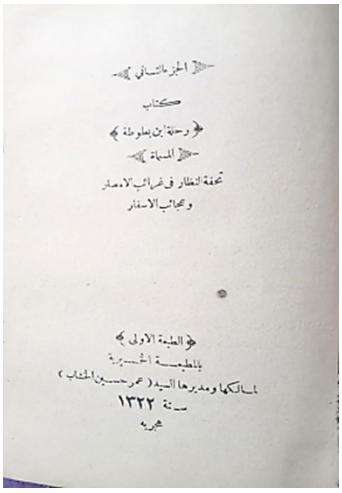
Figure 1. Reffa's book (A - cover, B - book's back C- Printing Date.



A B C

The book that the comparison will be made with has correct date and entitled: "The Journey of Ibn Battuta (Part Two) "Tuhfat al- Nozaar in the Curiosities of the Land and the Wonders of Travel," **(Fig. 2)**.

Figure 2. The Comparison Book (Ibn Battuta).



MATERIALS AND METHODS

Materials

Book which want to prove Authenticity (Reffa's book)

The book's cover is made of textile which is dyed in green colour and printed in black ink published by Dar Al Tebaa on 1254 AH -1838 AD. Book dimensions are (24 × 19 cm) of 288 pages.

The Book to be compared with (Ibn Battuta)

Book dimensions are (20 × 14 cm) of 416 pages, First Edition 1322 AH - 1904 AD, Charity Printing Press. The criteria that prompted the authors to use this book for comparison are its source. This book Inherited from ancestors.

Experimental Samples

Printing paper in 19th century in Egypt was made of cotton, so samples of cotton fibre paper, which had the same thickness, were used. The experimental papers were artificially aged for similarity to colour of the historical papers in the studied book.

Methods

SEM with EDX Unit

The scanning electron microscope was used as follows: Model Quanta 250 FEG + ED X Unit with an accelerating voltage 30 K.V. in the Egyptian General Authority for Mineral Resources in the Ministry of Petroleum. This Method used for examination and an analysis Reffa's book paper to determine the type of fibres used and analysed paper element which indicate to additives and manufacturing techniques. In addition examine paper in book of Ibn Battuta for compare the type of fibres made from.

Accelerated Ageing

A thermal oven was used which was Nabertherm – Model L N31 P in the laboratory of the Conservation Department - Faculty of Fine Arts - Minya University. This is to simulate the paper whose authenticity is to be proven by compare aged paper and Reffa's book paper.

Thermal ageing of the experimental samples was 90 ° C for 500 hours in the presence of a source of moisture and based on the scientific specifications of the measurements (TAPPI T 453) with a 90 ° pattern for 72 hours equal to 25 years old (op. cit. no. 13)

Fourier Transform Infrared Spectroscopy (FTIR)

The device used for analysis is Nicolet Nexus 750 (4000:550 wavenumber), the Central sector of conservation in Ministry of Antiquities. The Experimental sample was analyzed after every 100 hours by FTIR to discover changes of the function groups and choose the appropriate sample color compared to the Reffa's book paper.

X- Ray Diffraction (XRD)

The device used for analysis is Jsx-60PA with capper tube, 33Kv, 15 A, Wavelength λ=1.54 in Central Laboratory for Microanalysis and Nanotechnology, Minia University, Egypt. X-ray diffraction analysis was used to identify the degree of crystallinity (equation 1) (op. cit. No.16) and the size of the crystals (equation 2) (op. cit. No.17)

$$Cs = \frac{I_{200} - I_{Am.}}{I_{200}} \times 100\,(\%)$$ Cs is crystallinity degree Equation 1

$$D_{200} = \frac{K\lambda}{B.\cos\theta_{200}}$$ D_{200} is the size of crystal Equation 2

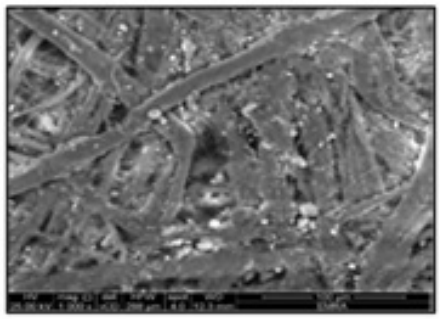
K= constant equal 0.9 λ= 0. 1542 B= wide of I200 in the half of high

RESULTS

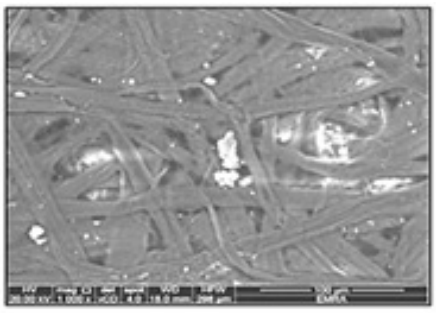
Scanning Electron Microscope (SEM) with EDX

An examination by using a scanning electron microscope proved in comparison to published standard samples **[18]**, **[19]** that the fibers used in Reffa's book are cotton fibers and the book used for comparison are from cotton fibers also. (**Fig. 3)** Through an analysis using SEM with EDX unit, the elements revealed are (C, O, Si, Al, Ca, Mg, S, Na, Cl, K, Fe,). **(Fig. 4)**

Figure 3. Fibers of (A- Reffa's book and B- Ibn Battuta book) by SEM at 1000x.

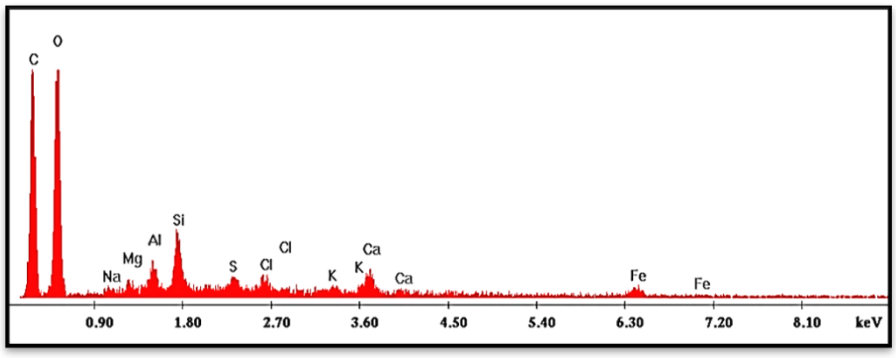


A



B

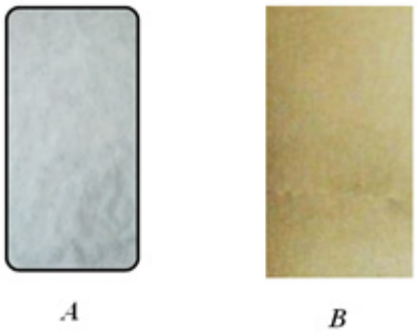
Figure 4. An Analysis by SEM with EDX unit for Reffa's book.



Accelerated Ageing

Thermal aged samples had changed in color; the closest sample of the Reffa's book paper is the sample that has been aged at 90 ° C for 500 hours **(Fig. 5)**.

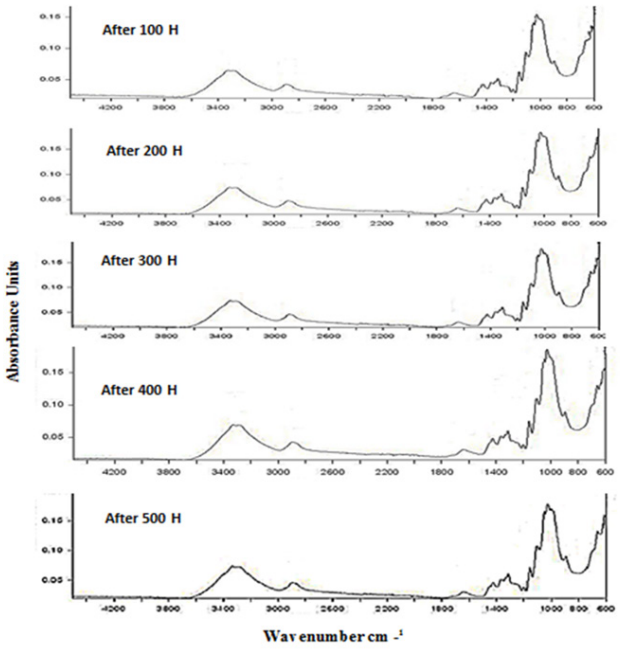
Figure 5. New Sample (A-Before and B-After 500 hrs. Aging).



Fourier Transforms Infrared Spectroscopy

An experimental accelerated aging sample is analyzed by Fourier Transform Infrared Spectroscopy (FTIR) after every (100 hours at 90°) to select the similar ones to the original manuscript **(Fig. 6)**.

Figure 6. FTIR Analysis of Five Aging Samples at (100/200/300/400/500 Hours).



There is little difference between the five samples, especially when comparing the experimental sample before and after the aging 500 hours **(Fig. 7)**. The last sample (500 hrs.) is the nearest one in color to the Reffa's book paper; therefore, it was used in the following comparisons to monitor the differences of Functional Groups Using FTIR **(Fig. 8, Table 1)**.

Figure 7. FTIR of Experimental Samples (A- Before Aging & B-After Aging 500 hrs.).

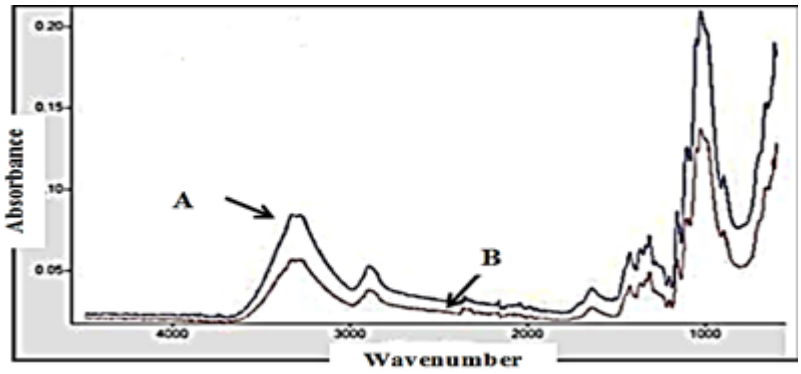
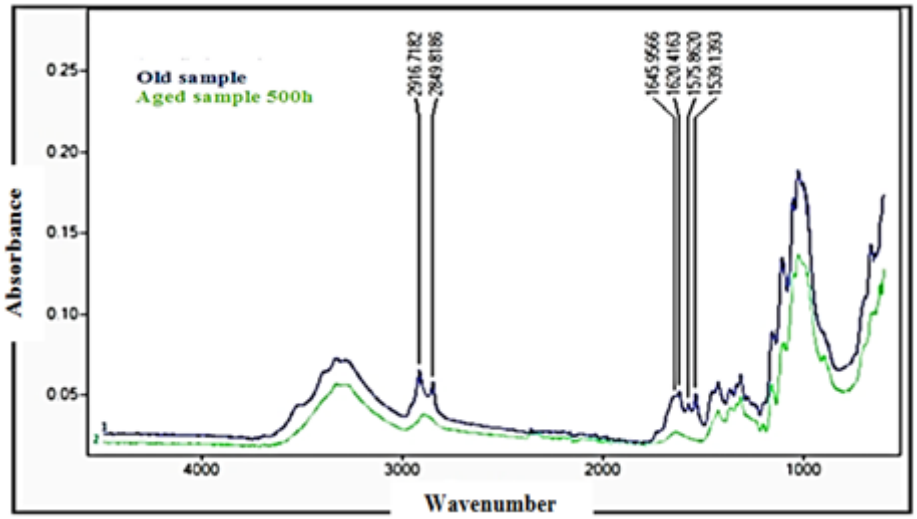


Figure 8. FTIR analysis of the Old Sample (Reffa's book) and the new Sample after Aging (500 hrs.).



C-CH3 group represented hydrocarbons. The intensity of these gelatine groups in the Reffa's book was higher than in the new sample; C-C, C-N-H and C-H. C=O is considered a component of cellulose. It was observed that the carbonyl group appeared only in the archaeological paper, because of complete drying process after losing a hydrogen atom in hydroxyl (OH) and turned to carbonyl C=O. **[20]**

Table 1. FTIR analysis to Comparison between (Reffa's book) and the new Sample (500h aging) of Paper Using (FTIR) Analysis.

Functional Groups	Reffa's book	New Sample (500 hrs.)
C-CH3	Appeared	Did not appear
C-C	Appeared	Did not appear
C-N-H	Appeared	Did not appear
C-H	Appeared	Did not appear
C=O	Appeared	Did not appear

Studying the pattern of XRD cleared crystallinity and the size of the crystals which indicate polymerization decrease according to the deterioration degree in paper of Reffa's book (Fig. 9). By calculated the Segal equation, the crystallinity degree of cellulose fibers is 85% and The size of cellulose crystal is 0. 6 nanometer = 6 Angstrom **Å**.

DISCUSSION

Using SEM investigation cleared that are both books paper have the same fibers kind (cotton) and same manufacturing technique because of the shape of surface. EDX analysis elements indicate to common compounds used in old manufacture of paper such as alum, rosin, kaolin, and calcium sulphate (gypsum). There are iron impurities, due to printing inks. The percentages of those elements were agreed with references, that there are additive materials used in the pulp 10%. The additive materials' names, according to research, are: rosin, kaolin, gypsum. **(Fig. 4) [21]**, **[22]**, **[23]**.

While the comparison between FTIR analysis of the experimental sample after aging (500 h) and the old sample (Reffa's book), the functional groups had a significant difference **Fig.8, Table 1**. A group of (C-CH3) was noticed at (2916 Cm-1). This group represented the group of hydrocarbons (alkanes), especially (methyl), which was responsible for storing energy in the old paper. This explained the speed of ignition of the old paper **[24]**. The intensity of gelatin groups (C-C) at (1620 Cm-1), (C-N-H) at (1575 Cm-1) and (C-H) at (1539, 2889 Cm-1), exists in the old sample, but not found in the experimental sample. These were due to the less developed industrial method and the manufacture treatments for the gelatine ore in the old sample which retained its density **[25]**. The carbonyl group (C= O) at (1645 Cm-1) appears only in the old sample, It is a component of cellulose, and the presence of a double bond to the carbonyl group means oxidation increased which cause old paper turned to yellow [op. cit. No.13] .

It is obvious that the amorphous cellulose decay first which increase crystalize cellulose after that the crystalized cellulosed began to decay **[26]**. So by studying XRD pattern we found decreased of amorphous cellulose (IAm) compared to crystallinity cellulose (I200) that means degradation in the paper book. After that crystallinity cellulose decreases gradually and slowly by breaking the bonds due to many factors such as physical factors including: humidity, heat, and light because of leaved the old book on the shelves for a long period of time. The minimum degree of crystallization of cotton fibers is 90% and the typical crystal dimensions of cellulose with plant fibers in space are (a, b, c) (8.01 - 8.21 - 10.35 angstroms **Å**) [op cit. No.14], [27]. The crystallization of cotton fibers for paper in Reffa's book is 85% and the size of cellulose crystal is 6 **Å** that is means decrease in cellulose crystallinity and size of cellulose crystal therefore indicating of deterioration for the archaeological paper by time and prove its authenticity.

CONCLUSIONS

SEM, FTIR and XRD are important tools to detect forgery and authenticity in the archaeological printed paper. The Scanning Electron Microscopy (SEM) examination cleared not only manufacturing development but also the kind of fibres and analysis with EDX unit attach show the elements in the paper. The SEM showed that the book whose authenticity I want to prove (Reffa's book), and the compared book (Ibn Battuta) made of cotton fibres. On the other hand, FTIR analysis results appeared functional groups in Reffa's book and didn't appeared in new Forgery sample (500 hrs. aged); such as alkenes groups and group of carbonyl which they in archaeological paper. In addition, the groups of gelatine determined in Reffa's book paper, because of the old manufacturing techniques. Finally, XRD analysis proved a decreased of crystallization degree and size of crystal; that confirms the authenticity of Refaa's book as this change needs a long period of time to happen

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