

## ASSESSMENT OF THE PHOTO-CHEMICAL DEGRADATION OF SILVER GELATIN PHOTOGRAPH PRINT-OUT

Rasha SHAHEEN<sup>1\*</sup>, Mona FOUAD<sup>2</sup>, Osama SAQR<sup>3</sup>, Sameh REDA<sup>4</sup>, Ahmad LABEEB<sup>5</sup>

<sup>1</sup> Conservation Department, Egyptian Textile Museum, Ministry of Archaeology, 4 El-Khronfash St., Gamaleya, Cairo, 12621, Egypt

<sup>2</sup> Faculty of Archaeology, Conservation Dept., Cairo University, Street between the chateaux, Cairo, 12613, Egypt

<sup>3</sup> Faculty of Applied Arts, Photographs Dept., Helwan University, Al-Sukari Street, Giza, 12624, Egypt.

<sup>4</sup> National Institute for Measurement and Calibration, Terrsa, Haram, Giza, 12211, Egypt.

<sup>5</sup> Microwave Physics and Dielectrics Dept., National Research Centre, 33 El Buhouth St, Dokki, Cairo, 12622, Egypt

### Abstract

*Museums and libraries hold many of archives which include photographic prints. These prints are affected by the ultraviolet rays in these places, whether it is from natural or industrial sources. This paper presents the assessment of the effect of UV rays on white and black gelatin photograph prints. Experimental samples were processed. Samples were exposed to ultraviolet rays. Photochemical and mechanical degradation was assessed before and after exposure. Mechanical change was assessed by testing tensile strength, elongation, and penetration strength. Colour change were assessed by using the CIE Lab system. Scanning Electron Microscope with signal unit elemental analysis (SEM-EDX) to assess morphology of surface. XRF analysis was used to identify change in the proportion of the elements that make up the image. ATR-IR spectroscopy to recognize the change in absorption frequency bands and the functional groups in the molecular of gelatin. UV radiation have a negative effect on the image of silver gelatin photograph prints.*

**Keywords:** UV radiation; Gelatin Silver Print; Photo-chemical Reactions.

### Introduction

The most used chemical process in black-and-white photography prints is the gelatin silver process. Gelatin is used as a suspension of silver salts on a support that is either paper, glass, or flexible plastic film. The photosensitive silver salts after the printing process are stable under appropriate preservation conditions. This was an improvement over the wet process of collodion prevalent from the 1850s to the 1880s, which had to be exposed and developed immediately after exposing. The gelatin silver process was produced on a paper support by Richard Maddox in 1871 and followed by Charles Harper Bennett in 1878 with improvements to this process [1].

Silver gelatin printing paper was made commercially of the start of 1874, but it has poor quality because the emulsion carrying sensitive silver salts was directly on the uncoated paper, although coating machines to produce continuous rolls of delicate paper were in use by the middle of the 1880s, and that widespread adoption of gelatin silver printing materials did not occur until the 1890s. As the first printing papers did not contain the baretta layer, which was not adopted as a commercial process until the 1890s, for the first time in Germany starting with 1894, and then handled by Kodak by the year 1900. The silver gelatin printing process is

\* Corresponding author: rashashaheen55@yahoo.com

divided into two stages, namely (POP) and (DOP) [2]. Silver gelatin or (DOP) is a monochrome imaging process based on light sensitivity to silver halides. It is the result of a short exposure to the negative of a latent image. The image is then made permanent by processing with a photographic stabilizer, which removes the remaining photosensitive silver halides. Then the substrate goes to the water bath, which removes the fixer from the print, as with the residue of the fixer on the image, it exposes it to fading and yellowing over time. At the end, we find that the image consists of small particles of silver attached to a layer of gelatin. This gelatin image layer is only one of the four layers found in a typical gelatin silver print, which usually includes the coat, image layer, baretta and paper backing. The multilayer structure of gelatin silver printing and the sensitivity of silver imaging salts require specialized coating equipment and fine manufacturing technology to produce a stable product free of image harmful impurities [3, 4].

The paper support is the base which serves as the substrate onto the subsequent layers attached. Paper is a successful upholder of gelatin photographs for several reasons: lightweight, it is flexible, and strong to withstand wet handling and regular handling involved in the curing and fixation process. The base of the photographic paper shall be made of materials free from optical impurities, especially iron and lignin. In order to obtain a pure paper base that does not contain lignin, a paper was made from rag cotton, but after the World War I, paper started to be made from purified wood, which continues to be in use until nowadays. The second layer is the Baretta layer, which is a white opaque layer made of gelatin and barium sulfate, and it is intended to mask the paper fibres and form a smooth surface on which to place the gelatin. The third layer is the gelatin layer that holds the silver particles of the photograph in a suspended form. Gelatin has several qualities that make it an ideal photographic binder. The special characteristics are hardness, resistance to wear when drying, ability to swell and allow penetration of chemicals during the treatment process [5, 6].

When producing gelatin photo printing paper, the image layer is a transparent gelatin matrix containing photosensitive silver halides. For gelatin silver photography prints the silver salts used are a mixture of silver bromide and silver chloride. Negativity is usually exposed with a magnifier, although contact printing was popular in the early 1900s. During this process light falls on the paper, the silver halides form small spots of silver metal on their surface through a chemical reduction process. Exposure is greater in the print areas corresponding to clear portions of the negatives, which become shadows or high print density areas. In this process, the latent image is formed, which initially is an invisible image on the paper and becomes visible after the chemical treatment processes. The paper is placed in the developer, which turns the silver halide particles containing the latent image into metallic silver. The image is now visible, but the remaining unexposed silver halide must still be removed to make the image permanent. Therefore, the printed image is placed in the stopper basin, which stops development and prevents the developer from contaminating the fixture [7, 8].

## Materials and Methods

### *Samples Preparation*

Two samples gelatin silver photographs were prepared, and their dimensions were  $21 \times 15$  cm. Black and white gelatin silver paper is used FOMABROM. The production has been controlled according to the international standard ENISO 9001. Safe lighting limits was red or orange light - the photocopy paper is not sensitive to red and orange - so that the bulb used was 15W. Developer bath consisted of salts were dissolved in 750mL of water to be sure that salt is completely dissolved before adding the next salt. The dissolution was done under a temperature of  $3^{\circ}\text{C}$  for a period of 1.5 - 2 minutes, then solution was diluted in 1L of water and placed in a dark bottle. As this composition is sensible to light and only a part is used when needed, it was

placed in the display basin and covered in order to be protected from the light when not in use, as shown in Table 1.

**Table 1.** Ingredients of developer and fixer baths

Developer materials	Quantity	Fixer materials	Quantity
Agua	750mL	Agua	500mL
Metol	1g	Sodium thiosulfate	250g
Sodium sulfite, crystals	44g	Potassium metabisulfate	25g
Hydroquinone	4g		
Sodium carbonate, crystals	59g		
Potassium bromide	1g		

The stabilizer bath consists of sodium thiosulfate salt and Potassium metabisulfate salt, where it is dissolved in 1L of water, dissolving in approximately 5-10 minutes, and then placed in a dark bottle so that it is not affected by the lighting as shown in Table 1.

#### *Printing Photographs*

As negative was used from a 35mm plastic film, then put it on the magnifier and exposed the image to lighting for 15 seconds, then put it in a basin of water first, so that the gelatin absorbed the water and could be affected by the appearance. On the next stage, it was placed in the appearance basin for two minutes, then washed with running water, put it in a fixer bath for 20 minutes, washed it with running water, and leave it to dry at a room temperature (Fig. 1). Images were saved until they were used in the measurement and analysis processes in a dry and cool place under a temperature of 21°C, and at a humidity of 40 - 60%.



**Fig. 1.** The tools and materials used in the image printing process. A shows the baths. B shows crastals of developer. C shows crastals of fixer

#### *Accelerated ageing test*

Laboratory of National Institute for Standard was used for aging. Ingram Frojd has shown that exposure photograph prints for 72 h at 100° C is equal to 28 years under normal circumstances, with the fixation of humidity, but heat when used alone as a way of accelerated aging, the results were not accurate, because of aging due to heat alone does not represent changes that occur in the normal aging, so humidity be an essential part in aging [9, 10]. Samples of photograph prints were subject of accelerate aging for 15 days by using a thermal oven at 80° C and 65% humidity.

#### *Fading test*

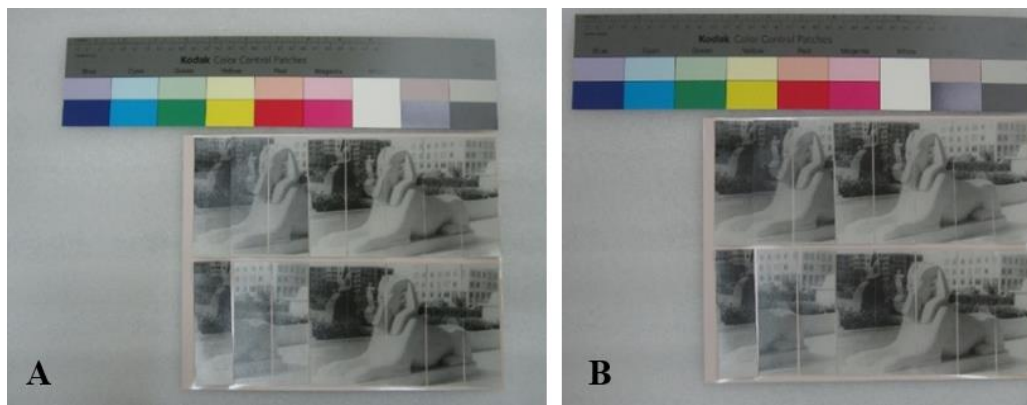
The samples were subjected to UV exposing cabinet which consists of set of 10 UV fluorescent lamps, 20W, 60cm length, three types of lamps can be installed UVA, UVB, and UVC, and/or mix of it. In our case UVA lamps only were used, at fixed distance from the samples. This cabinet was in Radiometry Department, Photometry & Radiometry Division, National Institute for Standards [11] (Fig. 2).

For accurate measurements of the irradiance levels, the exposing area was divided to three columns and three rows resulting in 9 measuring positions irradiance levels at each point

measured five times. Irradiance levels measured using UVA radiometer from UDT at the sample level of 30cm from the sources. The sample was prepared to be control without exposing to UV radiation was given the symbols SB, while the exposing samples to UV radiation was given the symbols SA (Fig. 3).



**Fig. 2.** Shows UV exposure device while placing samples inside with constant distance between the lamp and the photograph



**Fig 3.** Shows samples before and after exposing to UVA. A: before (SB), B: after (SA)

## Results and discussion

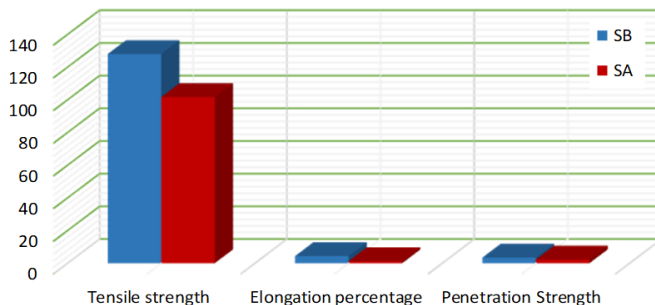
### *Tensile strength, elongation, penetration strength tests (mechanical change)*

The **tensile strength** (TS) is the maximum tensile force per unit in the sample upon rupture or refraction upon stabilization of conditions, while the **elongation force** (EF) is the tensile stress developed in the test sample at the maximum tensile force before rupture upon stabilization of conditions, however **Penetration Strength Test** (PST) is to estimate the power needed to make a breakthrough, holes or rupture in the photographic print examined the ability assessed by Newton.

Dimensions of the samples has  $10 \times 5$ cm and have been conducted measurements according to the American Standard Specifications ASTN 1682 in National Institute for Standards under the Ministry of Scientific Research [12, 13]. This examination was made on samples before and after exposing as shown in Table 3.

**Table 2.** Average results of the light fading test in mechanical properties, comparing between before and after exposing

samples	TS (N)	EF (%)	(PST), (N)
SB	128	4.392	3.45
SA	101.7	1.295	2.295
<b>Ratio degradation</b>	20.54%	70.5%	33.47%



**Fig. 4.** Comparing change values in mechanical characteristics before and after

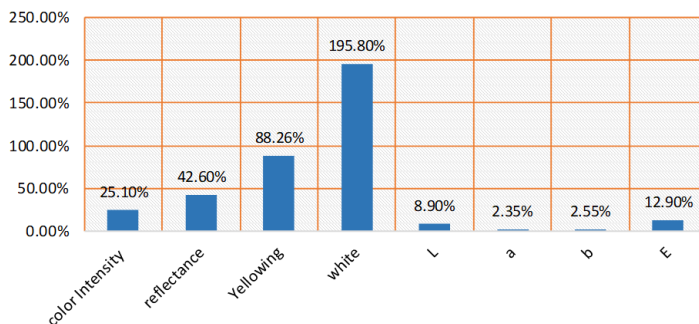
The previous table and figure show the results of mechanical properties in the samples before and after exposure to UV rays. Where the TS decreases from 128 N in samples SB to 101.7 N in samples SA. In addition to a decrease in the EF from 4.392 in the samples SB to 1.295 in the samples SA. The PST decreased from 3.45 to 2.295. This decrease is due to exposure to high-energy UV rays, which leads to a breakdown of the cellulose particles forming the paper support.

*Change in tonal qualities*

The Colour meter in National Institute for Standards was used to identify the change in tonal qualities in the samples as shown in Table 4.

**Table 3.** Average results of the tonal qualities due to light fading test, comparing between before and after exposing

Sample	Colour Intensity	Reflectance	Yellowing	White	L*	a*	b*	E*
SB	1.99	22.63	- 6.56	46.26	-0.04	- 0.14	0.58	0.60
SA	1.49	32.29	- 0.77	- 44.32	8.05	- 0.47	2.06	8.32
<b>Ratio degradation</b>	25.1%	42.6%	88.26%	195.8%	8.9%	2.35%	2.55%	12.9%



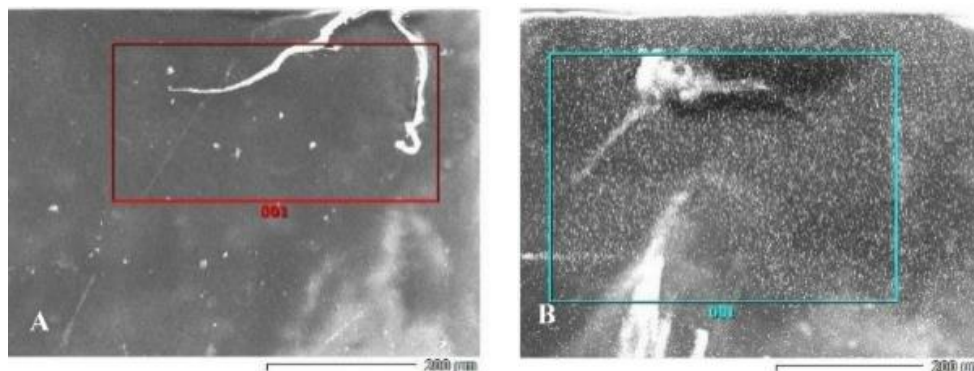
**Fig 5.** Degradation in tonal qualities

The previous figure and table show the change in the colour characteristics of the image in samples before and after exposure to UV rays, as there is a decrease in the colour intensity and the white test, and increase in the value of the reflection and yellowing test. CIE Lab system colour scale shows decreasing in  $\Delta L^*$  mean lacking black, increasing negative in  $\Delta a^*$  mean excess green, and significant increasing in  $\Delta b^*$  mean excess yellowing (Fig. 5).

### *Assess of chemical degradation aspects of gelatin silver print-out (DOP)*

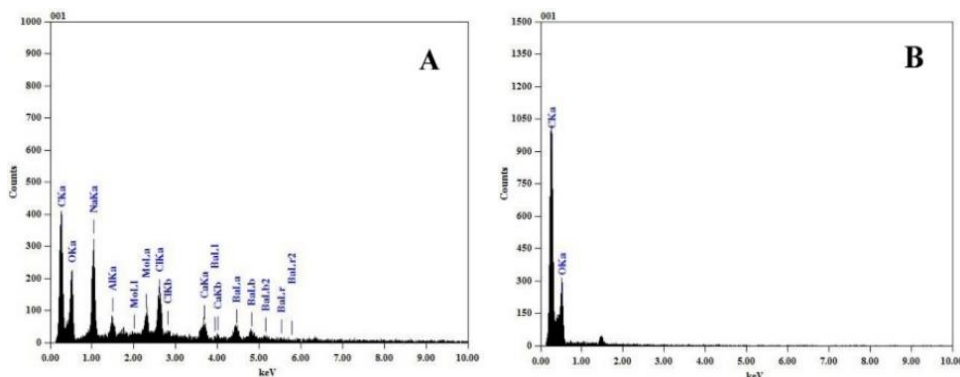
#### *SEM-EDX*

SEM-EDX in Atomic Energy Commission and Nuclear Safety Laboratory was used to identify the morphology of the image's surface. We observe the purity of the gelatin before exposure, while this purity disappears after exposure (Fig. 6).



**Fig. 6.** SEM (200 ×) of a sample of photographs after exposing to UV rays and we observe the change in the gelatin surface. A: Shows sample (SB). B: Shows sample (SA)

The previous analysis shows that the silver salts used are silver chloride. The emulsion used is gelatin. The presence of the Baryta layer due to the presence of the barium element at a rate of 6.15 sulfur at a rate of 1.05, which is the main component of the barium layer, barium sulfate. The presence of impurities of other metallic elements that exist naturally with the silver (Fig. 7).



**Fig. 7.** The EDX analysis shows the elements in the sample (SB) and (SA)

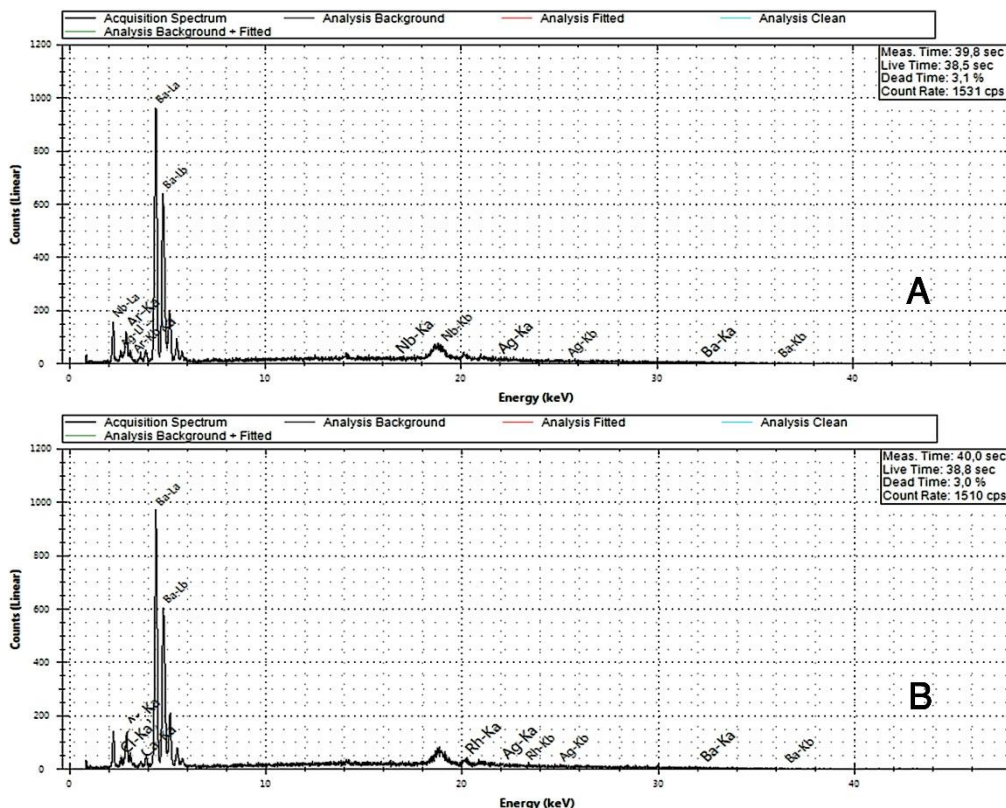
#### *XRF Analysis*

XRF analysis in Conservation Lab at Egyptian Museum was used to identify the percentage of silver element. Results shows that a significant decrease in the concentration of the silver element after exposure, where the process of oxidation of silver occurred because of exposure to high energy resulting from exposure to ultraviolet rays of high energy. Thus, the risk of the image to fade and discoloured over time as shown in Table 5 and Figure 8.



**Table 4.** XRF analysis results of the samples

Samples	Ba	Ag	Ca	Cl
A	83,51%	0,21%	1,5%	14,78%
B	88,43%	9,75%	1,73%	11,09%

**Fig. 8.** XRF spectrum result for the samples where. A: Shows sample (SB), B: Shows sample (SA)

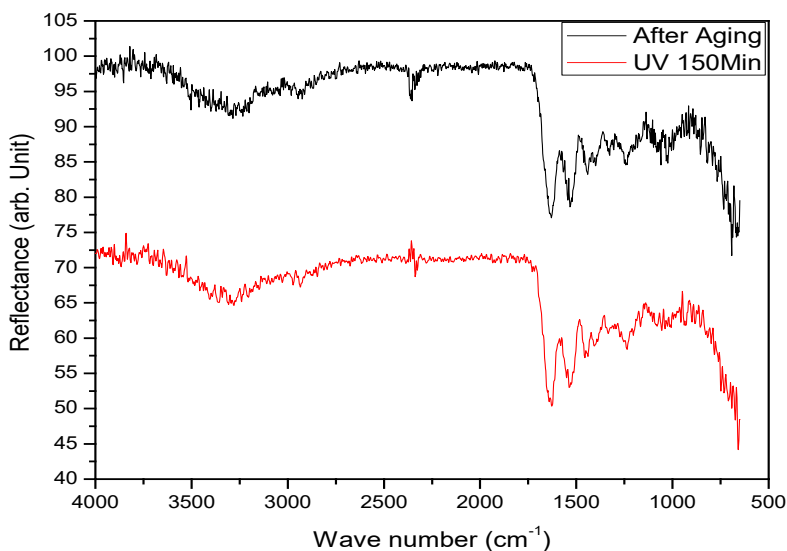
### FTIR-ATR Spectroscopy

FTIR-ATR analysis in National Research Centre was used to *identify* the change in functional groups in gelatin molecule *after exposing to UV rays* [14, 15]. The IR spectrum *before exposing* was measured in IR region  $400\text{--}4000\text{cm}^{-1}$ . The functional groups revealed in gelatin fraction and their characteristic absorption frequency bands as shown in Table 6. The gelation had been observed clearly as N-H stretching peak at  $3300\text{cm}^{-1}$  for amide group (strong) overlapped with O-H  $3200\text{cm}^{-1}$  stretching broaden peak (strong) for stretched H-bonded. The peak at  $1630\text{cm}^{-1}$  is typical for C=O stretching amide group. The peak at  $1526\text{cm}^{-1}$  represent the N-H bending which is strong due to many existences of this N-H bond in the gelatin. Moreover, it is noticed a weak N-H bend mode at  $878\text{cm}^{-1}$  but in opposite direction to previous strong  $1526\text{cm}^{-1}$  N-H bend mode due to chirality and helical structure of gelatin. The C-H bond has a bend mode vibration in plane at  $1444\text{cm}^{-1}$  while the stretching mode at  $2924\text{cm}^{-1}$ . The bending vibration has lower energy than stretching vibration as seen in C-O-H which bends at  $1396\text{cm}^{-1}$  with medium strength, whereas, the C-O stretching only at  $1232\text{cm}^{-1}$  in medium–weak strength for hydroxyl group. The C-N bond was detected at  $1323\text{cm}^{-1}$  beside a weak peak at  $1300\text{cm}^{-1}$  for O-H bending in plane. Additionally, the bond C-C-C has two medium bending peaks at

1018 and 1080 $\text{cm}^{-1}$ . Finally, gelatin is suitable *emulsion* to the silver chloride atoms in sensitive material on the photographic papers. Thus, peak at 540 $\text{cm}^{-1}$  indicate to the presence of Cl atom although it is not in the structure unit of gelatin. The two bands 1500-1700 $\text{cm}^{-1}$  and 3200-3450 $\text{cm}^{-1}$  are identification of carbonyl (C=O) or amide (CONH<sub>2</sub>) and amine groups (NH) which specify the gelatin structure as presented in the gelatin structure [16, 17]. IR spectrum from FTIR-ATR confirmed the structure of gelatin, therefore, gelatin consists of different blocks of several and single polypeptides including from 50 to 1000 amino acids in a helical structure of left-handed proline [18].

**Table 5.** Basic functional groups and their characteristic absorption frequency bands in control sample.

Functional Group	Characteristic Absorption(s) ( $\text{cm}^{-1}$ )
Alkyl C-H Stretch	2950-2850 (m or s)
Alkenyl C-H Stretch	3100-3010 (m)
Aromatic C-H Stretch	~3030 (s)
Aromatic C-H Bending	860-680 (s)
Alcohol/Phenol O-H Stretch	3550-3200 (broad, s)
Carboxylic Acid O-H Stretch	3000-2500 (broad, v)
Amine N-H Stretch	3500-3300 (m)
Aldehyde C=O Stretch	1740-1690 (s)
Ketone C=O Stretch	1750-1680 (s)
Ester C=O Stretch	1750-1735 (s)
Carboxylic Acid C=O Stretch	1780-1710 (s)
Amide C=O Stretch	1690-1630 (s)
Amide N-H Stretch	3700-3500 (m)



**Fig. 9.** The comparison of IR spectra of gelatin before and after exposure to UV beam in the UVA band

Figure 9 presents the FTIR-ATR Spectrum in the sample after exposing. The analysis revealed that the difference in gelatin before and after exposure is not significant, and this indicates the resistance of gelatin to UV radiation in the short term [19].



## Conclusions

By testing the mechanical properties of the samples, it was found that the tensile strength of the photographic sample decreases significantly after exposure to ultraviolet rays for 150 minutes, and this explains the great deterioration caused by these rays to the photographs, and the elongation ratio of the experimental samples also decreases significantly. By testing the penetration and tearing strength, it was found that it significantly decreases when the experimental sample was exposed to ultraviolet rays, which explains the breakage of the cellulose fibers in the paper used as a support for the image in addition to the breakage of the gelatin molecule due to the high energy of ultraviolet rays, which affects the physical properties of the photograph.

By testing colour properties of the sample, we found that the colour intensity decreases significantly when the experimental sample was exposed to ultraviolet rays, and the colour difference significantly increased by exposure to ultraviolet rays. We found that the value of ( $L^*$ ) was low when exposure to ultraviolet rays was low, meaning the image was exposed to fading and decreased in colour, the value of ( $a^*$ ) decreased when exposed to ultraviolet rays, i.e. the tendency of the image to be red, while for the value of ( $b^*$ ) it was very low after exposure to ultraviolet rays, indicating the lack of clarity of the image, and the reflection rate decreased significantly compared to the standard sample, and the yellowing rate of the sample increases.

By examining and analyzing with a Scanning Electron Microscope (SEM), the image in the gelatin layer was blurred as a result of exposure to ultraviolet rays, and this was evident in examining the surface of the gelatin layer, while the analysis with EDX confirmed that the disappearance of some silver-colour and metallic elements that were present in the form of impurities associated with silver halides and helps to give the image a silver colour such as helium element, H, element Sb, element Strontium Sr, and element Niobium Nb - thus reducing the percentage of silver in the image, as it was confirmed by the analysis by X-ray fluorescence (XRF).

By analyzing the ultraviolet spectrometer, it was found that the damage occurred in the form of dissociation in the double bonds and the bonds of the salts that make up the gelatin molecule, i.e. an almost noticeable breakdown in the protein structure of gelatin.

While FTIR analysis confirmed that gelatin is somewhat resistant to ultraviolet rays in the short term, the effect of long-term UV accumulation can be observed because of rearranging the molecular network of gelatin, as UV rays encourage radicals. The free gelatin molecule has a role in rearranging the molecular structure of individual gelatin molecules.

## References

- [1] \* \* \*, *Coping and Duplicating: Photographic and Digital Imaging Techniques*, **Kodak Publication M-1**, CAT No. E1527969, Sterling Publishing, 1996, pp. 20-32.
- [2] D. Stulik, A. Kaplan, **The Atlas of Analytical Signatures of Photographic Processes**, The Getty Conservation Institute, 2013, pp. 3-5.
- [3] S. Wagner, C. McCabe, B. Lemmen, **Guidelines for Exhibition Light Levels for Photographic Materials**, **9**, 2001, pp. 127-128.
- [4] A. Stucki, **Internal and External Factors Influencing the Implementation and Diffusion of the Open Innovation Models: The Case of the Postal Sector**, EPFL Scientific Publication, 2009, pp. 8-9.
- [5] B. Bernier, *Issues in Humidification and Drying of Gelatin Silver Prints*, **Photographic Materials Group of the American Institute for Conservation of Historic & Artistic Works**, **11**, 2005, pp. 6-16.

- [6] I. Frojd, *Preservation Research Related to Swedish R & D Project on Paper Preservation*, **Preservation Research and Development**, Library of Congress, 1993.
- [7] L. Stroibel, J. Compton, **Photographic Materials and Processes**, Focal Press, New York, 1986.
- [8] T.T. Schaeffer, **Effects of Light on Materials in Collections**, The Getty Conservation Institute, 2001.
- [9] S. Zervos, *Natural and Accelerated Ageing of Cellulose and Paper, A Literature Review*, **Department of Library Science and Information Systems, Faculty of Management and Economics, Technical Educational Institution of Athens**, 2010, pp. 1-42.
- [10] R.L. Feller, **Accelerated Aging: Photographic and Thermal Aspects, Research in Conservation**, The Getty Conservation Institute, 1994.
- [11] T.W.G. Solomon, C. Fryhle, S. Snyder, **Organic Chemistry**, 11<sup>th</sup> Edition, Wiley, 2014, pp. 94-95.
- [12] \* \* \*, **American Standards, ASTM E 1682-2005 Standard Guide for Modeling the Colour Metric Properties of a Visual Display Unit**, American Society for Testing Material (ASTM), 2005.
- [13] K. Okuyama, G. Wu, N. Jiravanichanun, C. Hongo, K. Noguchi, *Helical twists of collagen model peptides*, **International Journal of Biomaterials**, **84**(4), 2006, pp. 421-432.
- [14] A. Bigi, S. Panzavolta, K. Rubini, *Relationship between triple-helix content and mechanical properties of gelatin films*, **International Journal of Biomaterials**, **25**, 2004, pp. 2-3.
- [15] E.M. Masutani, C.K. Kinoshita, T.T. Tanaka, A.K.D. Ellison, B.A. Yoza, *Increasing Thermal Stability of Gelatin by UV-Induced Cross-Linking with Glucose*, **International Journal of Biomaterials**, **35**, 2014, pp. 4-6.
- [16] B. Fiske, L.S. Morenus, **Ultraviolet and Infrared Examination of Japanese Woodblock Prints: Identifying Reds and Blues**, The Book and Paper Group Annual 23, 2004, pp. 21-32.
- [17] K. Okuyama, X. Xu, M. Iguchi, K. Noguchi, *Revision of collagen molecular structure*, **Biopolymers**, **84**(2), 2006, pp. 181-191.
- [18] J. Perron, *The use of FTIR in the Study of Photographic Materials*, **Topics of Photographic Preservation**, **3**, 1989, pp. 112-122.
- [19] A. Richards, **Reflected Ultraviolet Imaging for Forensics Applications**, Santa Barbara, 2010, pp. 181-198.

---

Received: October 28, 2019

Accepted: November 30, 2020