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A MULTI-ANALYTICAL INVESTIGATION OF AN IRANIAN LITHOGRAPHY BOOK FROM THE QAJAR PERIOD

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Abstract

The lithography books of Iran, despite their historical importance, have received relatively little attention. This study aims to comprehensively examine an Iranian lithography book from the Qajar period titled Hayat al-Qolub, to identify its materials. The paper pulp, sizing, inks and leather of the bookbinding were analyzed through various methods, including staining tests for identifying paper pulp, light microscopy, FTIR, Raman spectroscopy, Micro-spectrophotometry, multi-band imaging, SEM-EDS and LC-MS. The findings suggest that the book was made of rag paper composed of linen and cotton fibers, while animal glue and gypsum were used for paper sizing and filling, respectively. Carbon black was used as black printing ink and cochineal was used for red ink. The leather cover of the book was made of goat skin that was tanned with gallotannins and unhaired with lime. Evidence of the use of liming in the unhairing process was also observed in this leather. This research enhances our understanding of paper and bookmaking techniques of the Qajar period in Iran.

Keywords*: Iranian lithography book; Qajar period; Bookbinding; Paper; Leather; Material analysis*

Introduction

The Qajar period, which lasted from the late 18th century to the early 20th century, was a time of significant political and cultural change in Iran. During this period, Iranian society experienced a range of transformations, including the introduction of new technologies, the expansion of trade and the emergence of new artistic and literary traditions. One of these developments was the spread of lithographic books. Iranian lithographic books from the Qajar period are valuable cultural artifacts that provide insight into Iran's history, literature and art. The lithographic printing technology was introduced to Iran in the early 19th century [1, 2] and books produced during this period are of particular interest as they represent a critical shift in Iranian printing history, marking the transition from traditional manuscript production to modern book publishing.

Despite the rich art and history of this region, the study of Iranian historical artifacts has been limited. Few published reports have focused on Iranian historical books and those that exist have primarily concentrated on illuminated and painted manuscripts, mainly devoted to identifying pigments and inks [3-8]. However, the investigation of lithographically printed books, despite their importance and prevalence during the Qajar period, has received less attention. This lack of technical information regarding this type of historical artifact remains a significant issue.

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However, the study of these artifacts is not without challenges, as historical books are often fragile, rare and delicate objects that require specialized handling and conservation techniques. Moreover, the analysis of historical books requires non-invasive and non-destructive approaches to safeguard their integrity. To address these challenges, analytical methods have been developed to study the properties and composition of historical books. Analytical techniques are crucial for determining the materials used in the creation of historical books, including inks, pigments and paper, as well as for assessing their state of preservation.

Various analytical methods have significantly enhanced the study of historical books and facilitated the identification of various aspects of their production and preservation. Microscopic methods, such as scanning electron microscopy (SEM) and optical microscopy, are essential for identifying the components of paper and assessing its microstructure [9-11]. Spectroscopy techniques, including different atomic and molecular spectroscopic methods, enable the determination of the composition of materials used in book production, such as paper, ink and pigments [3, 12-19]. These techniques can also be used to identify any degradation or deterioration in the materials used in the production of the book [3, 20-22]. Chromatographic techniques are other powerful tools used for the analysis of historical books [23, 24]. This method is particularly useful in identifying organic materials such as dyes and pigments or tanning material of leather bookbinding.

Spectral imaging is also a commonly used technique for the study of historical books. This technique includes various methods, such as multi-band and hyperspectral imaging, that enable the visualization of hidden features, including texts and images that have been obscured by subsequent overwriting or deterioration [25, 26]. Additionally, these techniques are widely used in identifying dyes and inks used in historical paper works [3, 27, 28], as well as examining paper damage [20, 29].

In light of this, this study aims to examine an important historical Iranian lithographic printing book. Specifically, the study aims to identify the materials used in the creation of the book, including the leather cover, paper and ink. To achieve this objective, a multi-analytical approach will be utilized, which includes techniques such as microscopic examination, FTIR spectroscopy, Raman spectroscopy, LCMS, microspectrophotometry, SEM-EDS and multi-band imaging.

Experimental part

Sample introduction

This paper presents a case study that specifically examines the second volume of Hayat al-Qulub, which was authored by Allamah Muhammad Baqir Al-Majlisi. Al-Majlisi was a well-known Shi`ah traditionist who died in 1110 AH/1699 CE. This volume is part of a private collection in Tabriz, Iran and contains biographical information on prophets and imams, with a special emphasis on Prophet Muhammad, making it a valuable source on early Islamic history [30, 31].

The bookbinding is made of leather and features cartouches (Toranj) binder ornaments, while black strips are used as page margins. The book's main text is printed in black ink, while annotations and markings are inked in red. The book was published in Dhu Hijjah,1241 AH [1826 July CE], during the reign of Fath-Ali Shah [Rule 1797-1834 CE], marking the beginning years of the Qajar dynasty. The book also contains annotations, particularly in the beginning pages, indicating that it was endowed about 8 years after its publication, on 23 Shawwal of 1249 AH [1834 March 5 CE] (Fig. 1).

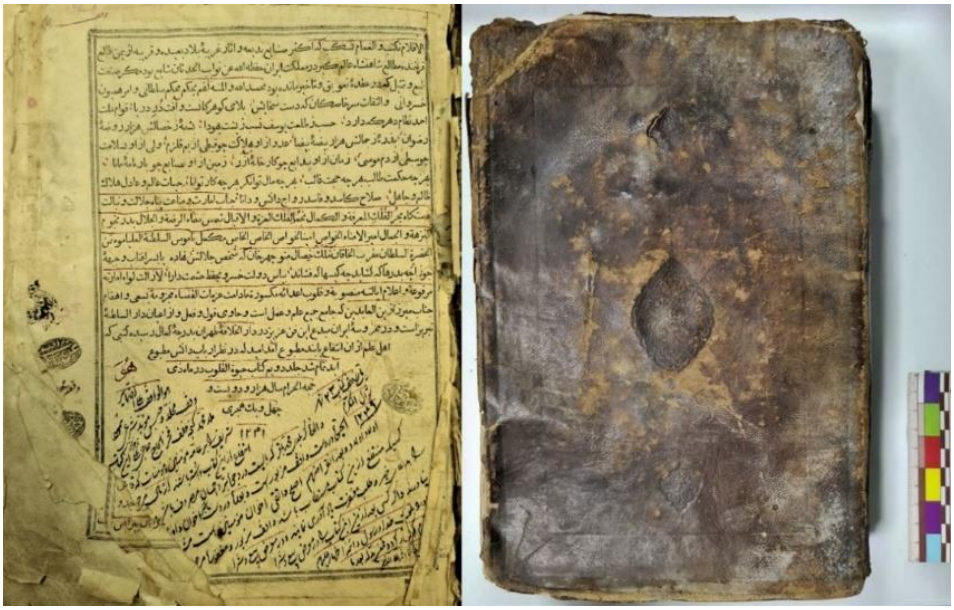

Fig. 1. The historical lithography book titled "Hayat al-Qulub" from the early Qajar period is studied. The leather binding of the book is shown on the right with some decorations. On the left, one of the first pages of the book is displayed, which indicates the date of publication in 1241 AH [1826 July CE] and an annotation about its dedication in 1249 AH [1834 March 5 CE].

Materials and Methods

Micro-slide preparation and staining

Staining tests and microscopic examination were employed to identify the type of paper pulp. A 2×2mm paper sample was heated in a test tube with 2 cc of distilled water inside a hot water bath. For better separation of fibers, a 10% sodium hydroxide solution was added and reheated in a hot water bath for a duration of 20 minutes. Neutralization of sodium hydroxide was done using 0.1% HCl acid, followed by rinsing the sample 5 times to remove the HCl and NaOH residues. The fibers were separated into four samples on a laboratory slide and three of the samples were treated with Graff C, Herzberg and Selleger reagents, respectively. Additionally, a sample was stained with methyl blue. The reagents were prepared in accordance with the guidelines specified by the Tappi T 401 standard [32]. Subsequently, the prepared slides were examined using an Olympus BX51 polarizing light microscope at 200x magnification.

Scanning Electron Microscopy (SEM)

The study involved the careful selection of torn paper fragments measuring less than 1.0mm^2. The investigation of mineral elements and micromorphology was conducted using a Scanning electron microscopy/energy-dispersive X-ray spectrometry. The SEM examination was performed using a TESCAN MIRA3 FESEM, utilizing a 15keV acceleration voltage. Prior to the examination, a thin layer of gold was applied to the samples.

FTIR Spectroscopy

This research utilized the KBr pellets for FTIR spectroscopy. The process involved extracting tannins from leather and sizing from paper, filtering and drying them to prepare KBr pellets. Tannins were obtained from fibers of the reticular layer of leather by utilizing a 1:1 solution of acetone and water. The extraction process involved adding 1.0mL of the solution per 10 mg of fiber and agitating the samples on a shaker in a closed vessel at the typical temperature

found in a laboratory setting for 48h [33-35]. Following extraction, the solution underwent filtration, centrifugation and removal of the solvent.

To extract sizing, 2 × 2mm of paper was heated with 2 cc of distilled water, in a hot water bath. The same sample was used for identifying paper pulp and sizing. The water obtained from the first stage of the microslide preparation was utilized to identify the sizing. After centrifugation, the extract was separated and the solvent evaporated. The remaining material was used for FTIR spectroscopy. FTIR spectra were collected by employing a JASCO 680-plus FT-IR spectrometer. A total of 32 scans were performed with a resolution of $4cm^{-1}$, encompassing the range between 400-$4000cm^{-1}$. Before each analysis, an air spectrum was recorded as background.

LC-MS

In order to extract red ink, a small amount of paper fibers that were inked were heated in a water bath. This process took place in a test tube containing 1.0mL of a methanol-DMF solution in a 1:1 ratio (Merck, Germany). The test tube was then heated in a boiling water bath for 30 minutes. The resulting extract was used for liquid chromatography-mass spectrometry. The LC-MS analysis was conducted using a Waters Alliance 2695 HPLC - micromass Quattro micro-API mass spectrometer system. Detection was achieved through an MS/MS ion trap detector with an electrospray ionization ion source that operated in both positive and negative ion modes. Separation was done on an Atlantis T3-C18 3µ, 2.1×100mm column, which was kept at a constant temperature of 35°C. The mobile phase consisted of a mixture of aqueous acetonitrile with 0.1% formic acid (A) and H_2O with 0.1% formic acid (B). A gradient elution technique was utilized following the outlined profile in Table 1, which also involved a re-equilibration step. The injection volume was 5µL and the flow rate was maintained at 0.2mL/min. MS detection was performed with the following ESI operational parameters: a drying gas flow rate of 200L/h, a drying gas temperature of 300°C and a capillary high voltage of 3kV.

Table 1. The system of gradients employed in the LC-MS analysis

Time (min)	Mobile phase solvents		Flow rate (mL/min^{-1})
	A (%)	B (%)	
0	10	90	0.2
1	10	90	0.2
7	60	40	0.2
11	60	40	0.2
12	10	90	0.2
15	10	90	0.2

Micro-Spectrophotometry

The micro-spectrophotometer used for this study was the Abs-Tra-001 model (Technooran Co, Iran). This device was specifically designed for microspectrophotometry, where measurements are taken in the visible to near-infrared range and at microscopic scales. To ensure accurate readings, polytetrafluoroethylene (PTFE) was utilized as a reference material. The signals captured by the device were obtained using a 40x objective lens, with a wavelength range of 450-700nm. Each spectrum was recorded for a period of 30 seconds, achieved through 12 scans with an integration time of 2.5 seconds per scan. In order to account for any variations, three spectra were documented from different points within each ink, namely black and red. The results were then averaged to obtain a representative spectrum.

Multi-band Imaging

The photographs were obtained by a Nikon D750 camera that had its UV/IR blocking filter removed to enhance the sensibility of CMOS sensor (approximately 350-1100nm).

The lens on this camera is a Nikon AF Nikkor 50mm f/1.8D. The camera was used in manual mode. Two electronic xenon flashlights (Youngenu NY660) were positioned at 45° to

light up the samples and an X-rite color checker was utilized as a spectral reference for image correction and comparison with references.

Technical images, such as Ultraviolet-Reflected (UVR), Infrared photography (IR), Visible-Reflected (VIS) and UV-induced Luminescence (UVL), were captured in RAW at the maximum resolution (24MP: 6016×4016) by the filters listed in Table 2. The RAW images captured by the camera were transformed into 16-bit TIF format using Adobe Photoshop. Following that, post-processing and calibration procedures were carried out in accordance with the methods described by *D. Kushel* [36] and *A. Cosentino* [37]. False-color ultraviolet (UV-FC) and infrared (IR-FC) images were created by combining UVR and IR with VIS images, respectively, using the technique proposed by *J. Dyer et al.* [38].

Table 2. Overview of light sources and filters utilized for each imaging method

MBI Methods	Filter(s) placed in front of sources	Filter(s) placed in front of the lens	Range under investigation
VIS	2 ×Youngenu NY660 Xenon flashlights, equipped with a softbox (without a filter).	Baader UV/IR Cut	420–680nm
UVL	+2 × Hoya U-360	Baader GUV/IR Cut	420–680nm
IR	2×Youngenu NY660 Xenon flashlights, equipped with a softbox (without a filter).	Schott RG830	830–1100nm
UVR	+2×Hoya U-360	Baader U-Venus	350–380nm

Results and discussion

Paper

Figure 2 displays microscopic images of paper pulp fibers influenced by the reagents Selleger, Herzberg and Graff C. Morphological analysis of these fibers reveals the presence of cross-bands in some fibers and a ribbon-like, twisting shape in others. These features are typically associated with linen and cotton fibers [39, 40], which occur simultaneously in the pulp used to make this paper, reinforcing the use of recycled textiles in its production. All three reagents induced a reddening of the fiber color, with the color observed in the Graff C test indicating low lignin content commonly found in rag paper pulp. Similar reddening, related to rag paper pulp, was observed in the stains for Herzberg and Selleger, as detected in the study samples [32]. Therefore, it is likely that the raw material for producing these papers is recycled cotton or linen textiles that have been dyed.

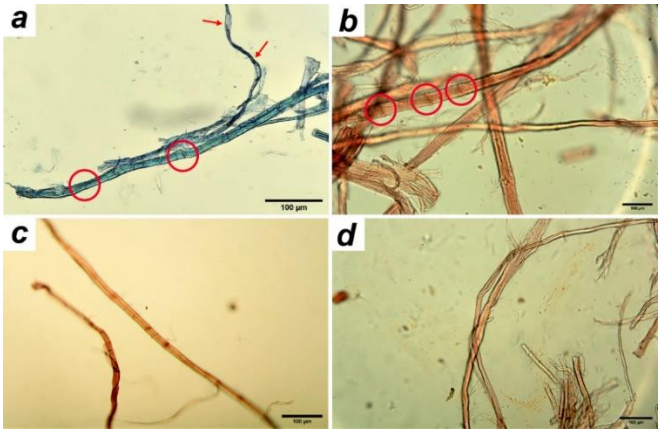

Fig. 2. a) Stained fibers of paper pulp indicate the presence of nodes in some fibers and ribbon-like shapes in others, which are characteristics of linen and cotton fibers, respectively. The red appearance results from fibers stained with Selleger (b), Herzberg (c) and Graff C (d), which are characteristic of rag papers

Figure 3a presents an SEM micrograph depicting a mass of mineral material detected amidst the paper fibers. This mass is deemed to be associated with the paper filler while also featuring fungal spores, indicative of fungal activity on the paper. Table 3 showcases the EDS analysis of this mass, which appeared in various regions of the paper samples. The analysis revealed that the filler primarily comprises approximately 59% calcium and 16% sulfur, indicating the possible use of gypsum in papermaking. Traditionally, gypsum has been one of the most commonly employed materials as a paper filler, primarily because of its inexpensiveness. Nonetheless, its application is constrained by its low solubility in water, usually resulting in 2 to 4 grams of gypsum dissolving during papermaking [41]. The limited solubility may account for the occurrence of gypsum masses in different areas of the paper, leading to its accumulation amidst the paper fibers due to its inadequate solubility.

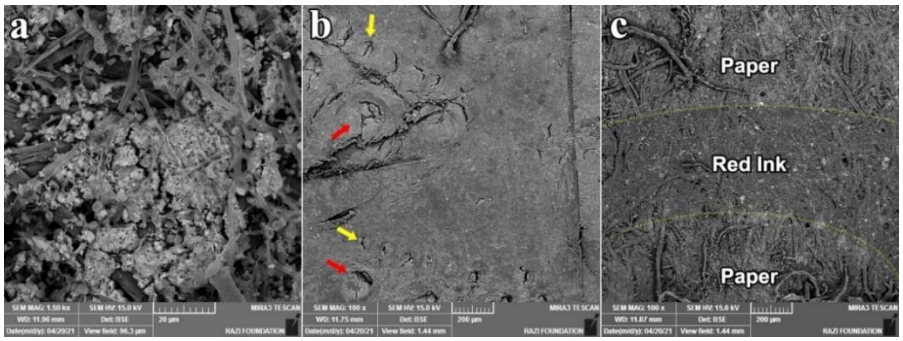

Fig. 3. SEM micrographs of different parts of the book:
(a) A cluster of a substance was observed in various parts of the paper and is likely related to a paper filler.
(b) The hair follicle pattern on the surface of the bookbinding leather shows the arrangement of follicle pits of goat skin with large (red arrow) and small (yellow arrow) pits.
(c) The identified section where the red ink passed, which, according to the darker tonality in the BSE-SEM image, contains lighter elements compared to paper

The FTIR spectrum of paper sizing, presented in figure 4, indicates the use of animal glue.

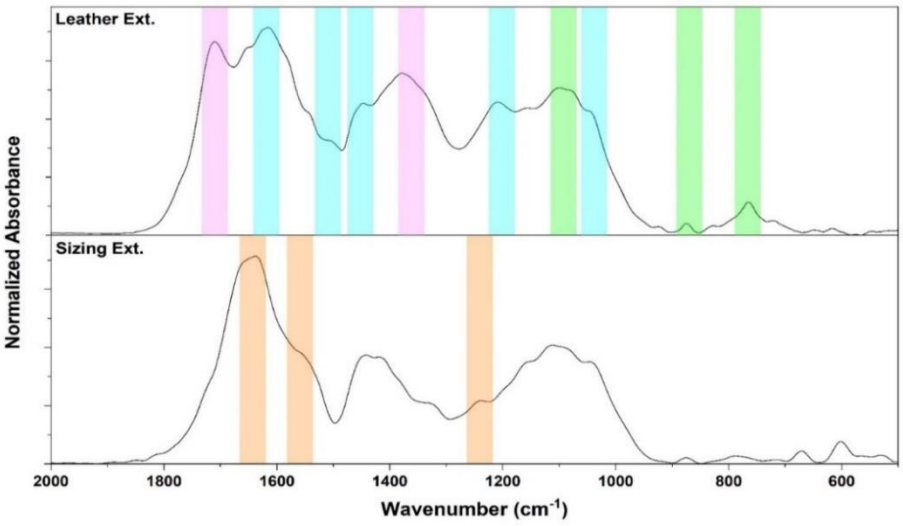

Fig. 4. FTIR spectra of extracts of the leather bookbinding (top) and paper sizing (bottom). The blue, pink and green highlights in the leather extract spectrum represent tannins, hydrolyzable tannins and gallotannins, respectively. The orange highlights in the paper sizing extract are the protein indices, namely amide I, II and III vibrations, which are at about 1640, 1540 and 123 cm^{-1}, respectively

The spectrum exhibits various bands attributable to different functional groups. The intense band observed at approximately 1640cm^{-1} is associated with the amide I band, which results from the stretching vibrations of the C=O group found in proteins present in animal glue. The band at around 1550cm^{-1} represents the amide II, which is linked to the bending vibrations of the N-H group. Additionally, a band observed at about 1235cm^{-1} is linked to the amide III bands, arising from the deformation of the N-H and C-N groups in the protein. The band observed at 1450cm^{-1} indicates the aliphatic groups in animal glue and is related to the CH_2 bending vibrations [42-44].

Leather

Figure 3b illustrates an SEM micrograph that depicts the leather surface utilized for bookbinding. The arrangement of hair follicles is clearly evident in this figure. Examination of the follicles revealed that they are arranged sequentially in a series of large and small pits. It can be stated that, on average, three small pits are situated above each large pit. This is a distinctive feature of goat skin [45]. The leather obtained from goat skin, known as "Timaj", offers superior quality for leather book covers in traditional Iranian bookbinding and is one of the most commonly used types of leather in Iranian historical works.

Furthermore, a thorough EDS analysis was performed on the grain and corium layer of the leather and the findings are detailed in Table 3. The EDS findings indicate that calcium (Ca) is the predominant element in the corium layer. This suggests the probable use of lime in the leather-making process. Lime, as a calcium-based material, has been one of the most commonly used compounds in unhairing in traditional Iranian leather-making [46]. However, the significant percentage of sulfur in the corium layer suggests the possibility of mineral substances such as gypsum penetrating into the leather. Nevertheless, the evaluation of the ratio of these two elements in the corium and grain layers, with values of 3.7 and 2.9, respectively, indicates the greater concentration of calcium in the corium layer compared to surface deposits of leather. Hence, the excess amount of calcium can be linked to the substances employed in the leather production process, further supporting the probability of utilizing liming.

Figure 4 presents the FTIR spectrum obtained from extracts of corium fibers, which were analyzed to determine the tannins type used in the tanning process. The spectral data indicates the tannin structure, as evidenced by bands observed at specific wavenumbers. The band at 1506cm^{-1} relates to the skeletal vibration of aromatic rings. The bands at 1606 and 1445cm^{-1} correspond to the stretching vibration of aromatic rings, while those at 1205 and 1035cm^{-1} correspond to the C-O stretching vibration. Additionally, the presence of hydrolyzable tannins is supported by the vibrations of free gallic acid's C=O stretching bonds at 1711cm^{-1} and OH deformation bands and the C-O-C stretching at about 1332cm^{-1}. The dominance of gallotannins in the corium layer of leather is confirmed by the absorption bands recorded at 1075cm^{-1} (ν symmetric, C-O-C aryl phenolic ester), 763cm^{-1} (breathing vibration, sugar ring) and 872cm^{-1} (C-C) [34, 47, 48].

Inks

Figure 5 presents the micro-Raman spectrum of black ink. The spectrum shows two clear peaks around 1335 and 1590cm^{-1}, indicating vibrations related to carbon-carbon bonds. These vibrations are known to identify carbon-based inks that were primarily produced from soot in Iranian manuscripts [3, 49]. Typically, four types of carbon-based inks were utilized in Iran, namely carbon, carbo-tannate-alum, peacock and starch, with carbon ink being the most widespread. While soot was the chief constituent of all these inks, carbo-tannate-alum and peacock inks contained alum and vitriol, respectively. The identification of aluminum, potassium and sulfur for the first ink and iron and sulfur for the second ink allows for the detection of these two inks [49]. However, the results from the EDS analysis presented in Table 3 indicate the lack of these elements in the inks. Therefore, the ink type is presumed to be carbon black. It must be acknowledged that it is not feasible to differentiate between this ink and starch ink solely based

on these outcomes. Nevertheless, the historical usage of Iranian ink implies the unlikelihood of starch ink being utilized.

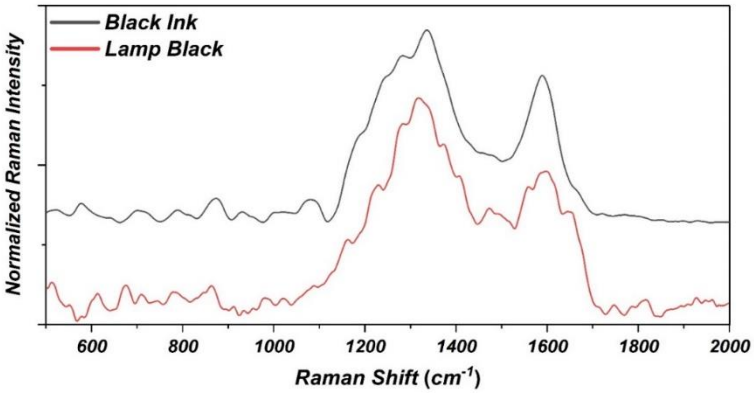

Fig. 5. Comparison between Raman spectra of black ink in the lithographic book under investigation and a reference sample of lamp black reveals their striking resemblance. The bands at wavenumbers of approximately 1590 and 1330 cm^{-1} confirms the utilization of carbon black as the ink in this particular book

In Figure 3c, the BSE-SEM image displays the writing lines in red ink, which appear darker in tonality compared to the non-inked areas, indicating the presence of light elements in the ink. This suggests the possible use of organic pigment as red ink. Analysis of the elements present in the inked and non-inked areas using EDS does not reveal any indicator element representing mineral pigments. While various red dyes were utilized in Iranian artifacts, madder and cochineal were commonly used as organic red dyes [50]. Madder is derived from the root of plants belonging to the Rubiaceae family, such as Gallium and Rubia species [51] and has been commonly found in Iranian artifacts. Rubia tinctorum, also called Persian Madder, is the most widely utilized species in Iran. Cochineal, which is obtained from the female insect of the same name, is another significant red dye. These dyes were used for fabric dyeing, paintings and manuscripts [3, 50, 52]. Previous studies have shown that red pigments from insects have higher amounts of phosphorus compared to those from plants [53]. This is also observed in the EDS results of this ink, supporting the possibility of using insect-based dyes.

Table 3. SEM-EDS analysis of various components of the studied book, including leather, paper and red ink, presented based on weight percentage (w%).

Elt.	Grain layer of leather	Corium layer of leather	Blank paper	Red Ink	Paper filler
Na	5.89	2.54	-	-	-
Mg	6.19	2.97	6.96	10.90	2.46
Al	11.33	2.33	9.08	12.30	4.15
Si	22.58	0.64	19.82	22.97	4.15
P	-	0.00	4.54	8.35	2.38
S	8.53	23.52	14.07	11.60	16.59
Cl	3.93	4.24	4.54	5.34	2.38
K	8.69	6.99	6.05	5.80	4.21
Ca	25.15	47.46	26.63	14.85	61.49
Cr	0.45	1.27	-	-	-
Mn	-	-	0.61	1.16	0.42
Fe	5.89	2.12	5.30	3.25	0.57
Cu	1.36	5.93	2.42	3.48	1.20
Tot.	100	100	100	100	100

Figure 6 indicates the multi-band images of the red ink. In the IR-FC and UV-FC images, the appearance of orange and green, respectively, is a characteristic feature of cochineal. Furthermore, the multi-band imaging demonstrates that the ink appears bright, dark and red in UVR, IR and UVL images, respectively. These findings are consistent with the known properties of cochineal described in Cosentino's work [54]. Specifically, insect-based red dyes like cochineal typically exhibit dark green fluorescence in UV-FC, which distinguishes them from red plant dyes like madder. Additionally, the appearance of orange in the IR-FC image aligns with previous reports that madder, cochineal and lac display yellow, orange and red colors, respectively, in the IR-FC image [3, 50, 54]. This observation further supports the conclusion that cochineal dye was utilized as the red ink in this lithography book.

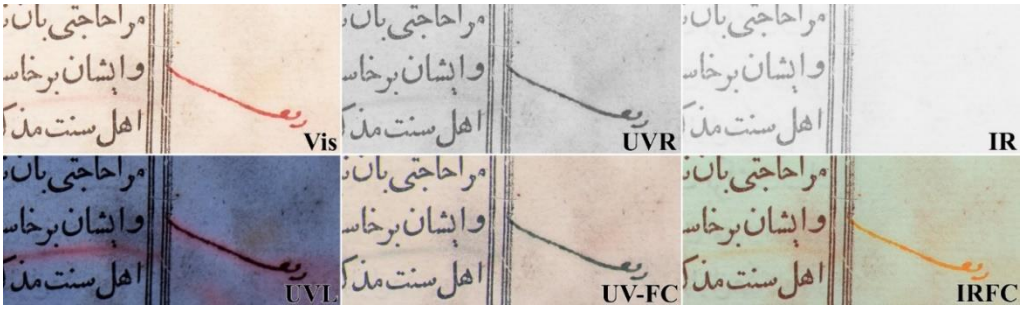

Fig. 6. The multi-band images of the inks used in the book; The appearance of the red ink as dark, bright, red, gree and orange in UVR, IR, UVL, UV-FC and IRFC images, respectively, indicate the characteristics of the cochineal. Additionally, the black ink appears black in all images, indicating the characteristic of carbon black.

Figure 7 displays the reflectance spectra of the inks used in the book. The reflectance spectrum of black ink is flat with high absorption in the visible range, a characteristic typical of carbon black.

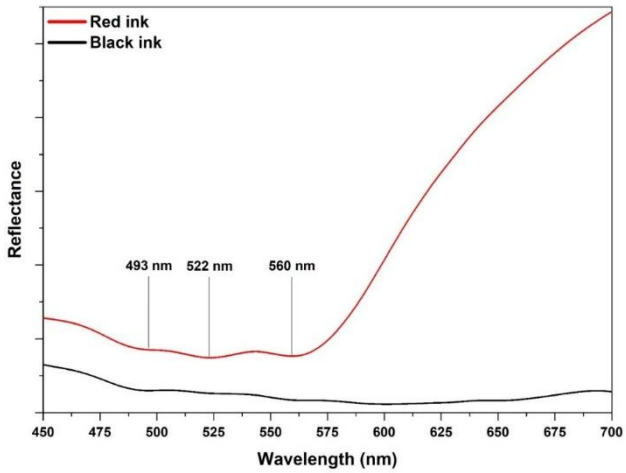

Fig. 7. Reflectance spectra of black and red inks in the visible range;
high absorption of black ink and its flat spectrum in the visible range,
as well as absorption bands of the red ink at around 522 and 560 with a shoulder at 493nm,
indicate the use of carbon black and cochineal, respectively

In contrast, the reflectance spectrum of red ink shows significant reflection bands. In Iranian works, commonly employed organic red pigments include madder and also cochineal [50]. In reflectance visible spectra, $n \rightarrow \pi^*$ sub-bands of these dyes are typically identified within

the ranges of 540-545 and 510-515nm (for madder) and 550-565 and 520-525nm (for cochineal) [55, 56]. However, it is important to note that these bands may vary in historical artworks. Within the reflectance spectrum of the red ink, two sub-bands can be observed at approximately 522 and 560nm, accompanied by a shoulder at 493nm. As stated by *B. Fonseca et al.* [55], the positioning of these bands suggests the presence of cochineal, which supports the results obtained from other analytical techniques.

Figure 8 displays the mass spectra of the index compounds ascertained via LC-MS analysis in red ink. Analytes with retention times of 7.586 and 9.399min are visible in the chromatogram. The corresponding mass spectra reveals the main negative ions of 491 and 229m/z, indicating the presence of carminic acid (492 Da; Rt: 7.586min) and kermesic acid (230 Da; Rt: 9.399min), respectively [57]. The identification of carminic acid and kermesic acid as pivotal compounds suggests that the red lines were inked using cochineal, a well-known red dye employed in Iranian historical artifacts [3, 50].

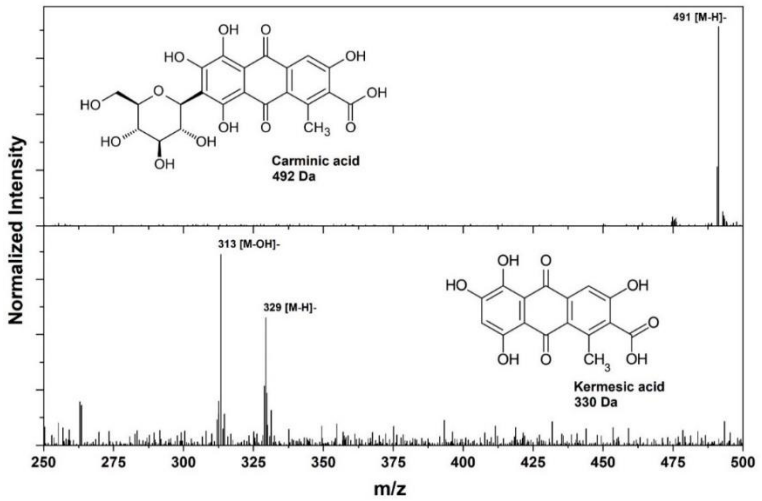

Fig. 8. The Mass spectra of the main analytes found in the red ink, including carminic acid and kermesic acid, which confirm the presence of cochineal in the ink

Conclusions

This study employed a variety of analytical techniques to examine the raw materials and inks used in a historical lithography book. The results indicate that the paper was most likely manufactured from recycled cotton or linen textiles, commonly referred to as rag paper and filled with gypsum. The sizing of the paper was identified as animal glue. Additionally, the bookbinding was constructed from goat skin, tanned using hydrolyzable tannins, with liming utilized in the unhairing process. The black ink was determined to be carbon-based, while the red ink was derived from the cochineal.

These results provide significant insights into the production techniques employed in creating historical lithography books, which can be instrumental in their preservation and restoration. Moreover, the analytical techniques employed in this study can be useful in analyzing other historical artifacts.

However, the study has some limitations that must be considered in future research. Additionally, further investigations are needed to determine the specific sources of the raw materials used in the lithography book. Despite these limitations, this study offers crucial information regarding the materials and techniques used in historical book production. The findings can inform preservation and restoration efforts for these valuable artifacts and contribute

to our understanding of historical papermaking and ink production. In conclusion, this study sheds light on the importance of investigating the historical context of these artifacts to better appreciate their significance and ensure their continued existence for generations to come.

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