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Characterization of materials in the late 15th-century animal encyclopedia at an Ottoman Library and detection of deterioration products by HPLC–DAD

Emine Torgan Güzel^{1*}, Recep Karadag^{1,2} and Nil Baydar³

Abstract

There are many manuscripts in institutions that preserve and exhibit cultural heritage such as museums, galleries, and libraries. These manuscripts are of great value because of their witnessing to the past and the historical and cultural significance they have accumulated. In addition to the organic nature and the natural aging of the paper, which is generally used as the primary carrier material in these objects, other materials used in the manuscripts are an obstacle to their preservation and reaching future generations. In this study, the 62-volume animal encyclopedia, which is known to be written in the name of animals, plants, and Islamic science at the end of the fifteenth century (1487–1501) and added to an Ottoman Library, was examined analytically. A total of 40 samples consisting of paper, ink, dye, and leather samples were analyzed using high performance liquid chromatography with a diode array detector (HPLC–DAD). After all, information on material characterization and deterioration product(s) was obtained. As a result of the analysis, vanillic acid, and its derivatives due to the natural aging of the paper and chrysophanic acid and its derivatives caused by fungi, which are the result of unfavorable environmental factors, were determined. It was concluded that the ink used in the manuscripts was iron-gall ink. In addition, it was determined that madder, weld, buckthorn, redwood, rhubarb, or dock plants were used as dyestuffs in paper and leather samples. Also, it was deduced that the leather samples were tanned with the vegetable tanning method using tannins. Since tannic acids were determined in the dyestuff analysis of three paper samples with ink, elemental analysis was performed on black ink by scanning an electron microscope with energy-dispersive X-ray spectroscopy (SEM–EDX). As a result of this analysis, the element of iron has been detected and it has been confirmed that the black ink is iron-gall ink. It is inevitable that this study will guide conservation experts in restoration and conservation studies.

Keywords Islamic manuscript, Iron-gall ink, Vegetable tanning, Deterioration, Leather, HPLC–DAD, SEM–EDX

Introduction

Regardless of the information they contain, manuscripts, which are books, papers, and documents, are tangible cultural heritage objects and reflect their era [1, 2]. The most important problem in the conservation and transfer to future generations of cultural heritage materials such as the book, paper, and leather in which the manuscripts are found, is that they are deteriorated and damaged from the moment they are produced [3]. Deterioration is any chemical and/or physical change in the state of an object.

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Physical and chemical degradation are interrelated and often occur simultaneously [4, 5]. There are many reasons for damage to manuscripts. These are production methods and techniques, materials such as ink, pigment, and dye [3, 6], storage and exhibition conditions, environmental factors, people, misgovernment, etc. [7]. Unfavorable environmental conditions are the leading factors that cause deterioration: temperature and relative humidity [3, 7, 8], light [4–8], air pollutants and biological pests such as microorganisms, insects, molds, and fungi [8]. In cases where the relative humidity is high, acid hydrolysis reactions occur and the pH value decreases accordingly. This causes the paper to become brittle. In addition, in paper or parchment manuscripts with iron-gall inks, iron ions can move to areas where there is no ink, creating additional areas for oxidation. High-temperature fluctuations and humidity cause both ink and paper to deteriorate, contributing to the exfoliation and loss of the ink layer [9]. The reactions between inks and carrier materials (paper, parchment, etc.) are strongly influenced by environmental factors, especially temperature, and relative humidity, and by sizing (an aqueous substance is prepared from materials such as starch, alum, and egg white to protect the paper from external influences such as water and moisture, to make it more durable, to look bright, to remove its roughness, and to write the ink more easily) and inorganic fillers [10].

One of the materials used in manuscripts is ink, and the oldest inks are carbon-based. These materials are easily obtained soot/smoke, coal obtained from other plant sources, and graphite obtained from nature [11]. Later, black inks obtained from ivory and bone were used. In addition to these inks, iron-gall inks used by the Late Roman Empire in the West until the nineteenth century and even the twentieth century were the primary choices for creating many manuscripts [11–16]. It is known that the expression gallotannate, which indicates iron-gall ink, was used in Pliny's book in the first century AD [11, 12, 17].

The iron-gall inks have been used throughout history as the standard writing and drawing ink, as they are more difficult to remove from the applied surface and easier to produce than carbon-based inks [16]. It has been described in the use of official records and personal letters, in diaries, map drawings [9], some paintings by artists such as Rembrandt, Guercino, and Lorrain [18], and in musical notes (J. S. Bach and Victor Hugo) [11, 12, 18–21]. These ink components contain corrosive transition metal ions and acids that have been shown to cause severe damage to the paper carrier. The use of iron-gall ink gradually declined in the nineteenth century due to the development of various synthetic inks [14, 22–24].

Another material seen in manuscripts is pigment, and the palette used in early manuscripts, Egyptian papyri, was limited. The ocr pigments, mostly obtained from iron-based soil, colored the manuscripts. After iron-based soil pigments, pigments such as Egyptian blue, Egyptian green, and cobalt blue were used in manuscripts [11]. Aceto et al. studied two Byzantine (VIth century) manuscripts in the Austrian National Library in Vienna and achieved some results. According to analyses results, they deduced that ultramarine, azurite, red lead, orpiment, red and yellow ochers, and blue and yellow colorants known as vergaut were used to give green tones [25].

Another material used as a colorant in manuscripts is dyes. Unlike pigments, dyes are organic and derived from plants, insects, fungi, etc. are obtained from structures in nature [26]. Organic natural dyes used in illumination and other manuscript decorations were applied in an aqueous solution for dyeing paper either directly or due to the use of mordant dyes. While the first semi-synthetic dyestuffs have been on the market since the last quarter of the eighteenth century [27], fully synthetic dyestuffs were introduced to the market in the second half of the nineteenth century. Until this date, dye sources of vegetable or animal origin have been used for dyeing [27, 28]. Since the natural color of the paper, dirty white, was not liked much in Islamic geography, the manuscripts were primarily applied on colored papers [22]. The dyes can generally be characterized if a sample can be obtained for chromatographic analysis [29]. While this is usually applied for textile objects containing loose threads, in principle this can be extended to manuscripts [11]. Although there are not many studies on the analysis of dyes in manuscripts, one of the studies conducted in this area revealed that the weld plant was used to color the last papers in a fifteenth century manuscript in Egypt [30]. In another study, the dyes in Moroccan manuscripts were examined. According to the analysis results, safflower dye was detected on orange-colored papers, while Safranin T, a basic dyestuff, a mixture of mono azo dyes (Ponceau RR, Fast Red AV, Crocein Orange, and Orange II) or a combination of both were determined in fuchsia-colored papers [27]. Aceto et al., on the other hand, identified indigo, madder, and Tyrian purple in dyes in two manuscripts in the Austrian National Library in Vienna [25]. Melo et al. identified Brazilwood pigment lakes and orcein purple colors in three illuminated parchment manuscripts dated to the 13th, 15th, and sixteenth centuries [31]. Hidalgo et al. investigated the iron-gall ink in medieval Iberian manuscripts using high-performance liquid chromatography-electrospray ionization-mass spectroscopy (HPLC–ESI–MS). Researchers have determined that the concentration of gallic acid in the writing

ink varies depending on the extraction method and the ink recipe [23].

The most commonly used leathers for bookbinding are obtained from calf, sheep, and goat skins [5]. Most of the leathers used in bookbinding have been tanned leather of vegetable origin since prehistoric times [32]. Tannins obtained from plants have been used for centuries in tanning peltry and leather, making the material less perishable and more waterproof [33]. The main sources of chemical degradation of leather material are UV light and air pollutants mainly SO_x and NO_x . Especially, oxidation can occur by breaking the covalent bonds between carbon and nitrogen in the collagen structure of the leather [34].

Iron-gall inks are composed of four main components: tannin, vitriol (iron or copper sulfate), water, and gum arabic [9, 13, 14, 18, 23, 35]. Vitriol has been obtained from various mines by different techniques. Therefore, ferrous sulfate can be found in the ink solution with varying proportions of many other metals such as copper, aluminum, zinc, and manganese that do not contribute to color formation [18]. The purpose of using gum arabic is to act as a binder in the dispersion of the ink in water [36]. Iron-gall inks show the infrared signature of gallo-tannins. This indicates that Fe^{3+} polygalloyl ester complexes of glucose are formed [23]. Throughout history, the quality of iron-gall inks has varied greatly depending on the quality and proportions of the ingredients. At the same time, different additives also played a large role in these changes. Examples are the use of acids to slow settling, humectants such as glycerine to slow drying, and materials such as alcohol to inhibit mold growth and prevent freezing [9].

The most well-known feature of tannin dyes is that color fastness, light and washing fastness are very good, that is, discoloration is rare. This can be a disadvantage in most cases. This disadvantage is that some gray and black colors obtained with iron mordant deteriorate over time and the color turns brown and gradually erodes the fibers to which it is attached by being fixed. Therefore, most scientists study the aging caused by iron-gall inks and dyes to preserve historical fabrics and written documents [33]. The degradation mechanism caused by the combination of a tannin substance and an iron compound was compared with the degradation caused by iron-gall ink on paper. The degradation is caused by hydrolysis from oxygen in the air catalyzed by acidic compounds and free iron ions [14, 15, 18, 36, 37]. In ink production, a complex is formed by combining tannic acid and ferrous sulfate compound (FeSO_4) before it is applied to the paper, and then the resulting black ink is applied to the paper or parchment [9, 15, 18, 37]. After the ink dries on one of these supports, it slowly oxidizes to form a complex

water-insoluble pigment that darkens from purple-gray to black [9, 18]. Iron tannate and sulfuric acid (H_2SO_4) are formed from the combination of ferrous sulfate compound and tannic acid. Also, an excess of free tannic acid and ferrous sulfate is released [37]. This is called ink corrosion [9]. Although all these obtained components are effective in the deterioration of the paper, the main reason is the released H_2SO_4 . Iron tannate can decompose into tannic acid and iron ions during degradation, which can cause hydrolysis and oxidation. The biggest reason for the deterioration of iron tannate is due to unfavorable storage conditions [37]. Iron-gall inks have a low pH due to the acidity formed by the main components iron(II) sulfate and tannic/gallic acid [14, 20, 24]. Acid-catalyzed hydrolysis, which causes low pH, causes the bonds in cellulose paper to break (decrease in the degree of polymerization) and thus the loss of fiber strength [22, 38, 39]. Components such as vinegar and urine added to change some of the ink's properties can also affect the pH of the ink. For example, the pH of a paper containing iron-gall ink can vary significantly from 2.9 to 7.1. A low pH value causes the degradation of cellulose, which is the main structural component of paper [14, 24].

Ink corrosion causes undesirable effects on paper or parchment. These include a gradual change of ink color from black to brown, discoloration, and loss of strength in paper or parchment, embrittlement, cracking or loss of fragments in ink-filled areas, and deterioration of other adjacent/close materials over time [9, 18]. In general, the accepted paper protection approach for the conservation of iron-gall ink corrosion is the so-called "calcium-phytate treatment method". In this method, paper artifacts with iron-gall ink are immersed in an aqueous suspension containing antioxidant phytate and calcium hydrogen carbonate solution [14, 40, 41].

The work of scientists and the analytical methods and techniques they use in the preservation of cultural heritage is extremely important in the decision-making process regarding the conservation approach [15]. Espina et al. studied to determine the characterization of iron-gall inks in certain manuscripts using various spectroscopic techniques such as Raman, Fourier-transformed infrared (FTIR), UV-Vis absorption, and fluorescence spectroscopy [13]. Haskovic and Ibragic used XRF and FTIR techniques for the detection of inks and pigments in manuscripts [38]. Darzi et al., on the other hand, used SEM-EDX and μ -Raman techniques to investigate the widespread use of colorants, raw materials, and color production technology in the Qur'an manuscripts of the Qajar period (1789–1925 AD), Iran. As a result of their study, they determined inorganic origin carbon black, Prussian blue, ultramarine, vermilion, and red lead pigments as colorants. In the organic structure, they

determined the anthraquinone structure in a red-colored sample. In the yellow color of another sample, they determined compounds containing saffron and lead, which are thought to be used as an agent and/or chemical drier. They also detected brass, pure gold, and gold-silver alloy as gilding ink/dye [1]. Melo et al., on the other hand, used micro spectrofluorimetry and surface-enhanced Raman spectroscopy (SERS) techniques to detect organic colorants in medieval manuscripts [43].

A wide variety of analytical methods and techniques are used to identify the elemental compositions of iron-gall inks, and the XRF technique has become the preferred analysis [15]. Most researchers [44–48], have also used the SEM–EDX method to determine the elemental chemical composition of inks on paper and parchment samples.

It is extremely important to use non-invasive, non-destructive methods and techniques to provide material characterization and other information without sampling from manuscripts [49]. Sometimes samples are separated from the main structure due to the natural aging and/or deterioration of such artifacts, and this is often referred to as self-sampling [11, 50]. Sometimes this object may owe itself to minimal sampling due to its existing bad state. Sometimes a deliberate choice may be made to take a small sample to obtain valuable information that would otherwise be inaccessible [51].

Historical background

The late fifteenth century manuscript named, Keşfü'l-beyân 'an şifâti'l-ḥayevân also known as the animal encyclopedia (Fig. 1a), probably because it is a single copy, is one of the most voluminous encyclopedias written in the Islamic world. The writer and calligrapher of this manuscript is the Alexandrian scholar Muhammad ibn 'Atiyya al-Iskenderi al-Avfi (d. 1501) [52]. The 62-volume manuscript is held in the collection of Feyzullah Efendi (d. 1703) of the Millet Manuscript Library in Istanbul.

Its most important feature is, of course, that the many volumes, each in alphabetical order, are written by a single author. It is also a rare occurrence in the Islamic manuscript tradition that the author prepared the first volume as a preface and gave detailed information about himself and his work [53]. According to the information given in the first volume, al-Avfi compiled this work between 1487 and 1501 in his own hand [52]. From the titles in the introduction, it is seen that there are sections in various fields such as Islamic sciences, poetry, botany, medicine, and philosophy. Different subjects, from plant and stone types to cloud and soil types, are also covered in the manuscript.

The author has recorded the names of nearly three thousand manuscripts, some of which he used while

preparing his work, together with their authors. He also gave place to the names and short biographies of about a thousand scholars he took lessons or chatted with throughout his life. The dimensions of this manuscripts vary between 19.7–31.3 and 29.8–32.5 cm. This manuscript contains a total of 14,493 folios and the author used 943 m² of paper while writing this work [53]. There are geometric drawings in the middle of some of the pages and he showed some of his poems and texts with drawings (Fig. 1b) [2].

Materials and methods

Historical samples

A total of 40 samples, including paper, ink, and leather, were examined from the animal encyclopedia consisting of a total of 62-volumes. The visuals and sample codes of the objects from which the samples were taken are shown in Table 1.

Chemicals

The reference pure dyestuff standards and chemicals were provided by Turkish Cultural Foundation–Cultural Heritage Preservation and Natural Dyes Laboratory (TCF-DATU) in Istanbul, Türkiye. Acetonitrile (LC grade), trifluoroacetic acid (TFA- for synthesis), methanol (LC grade), and hydrochloric acid (for analysis, fuming 37%), that used in the mobile phase and sample preparation for HPLC analysis, were purchased from Merck (Germany). All chemicals employed in this investigation were of analytical grade and were used as received unless stated otherwise. High-purity water was obtained by passing water through a Milli-Q treatment system (Millipore, Bedford, MA, the USA), and the HPLC mobile phase was prepared using Milli-Q water.

The following dyestuff standards were obtained from commercial sources and used as references: gallic acid and vanillic acid from Merck (Germany), ellagic acid from Alpha Aesar (the USA), chrysophanol/chrysophanic acid from Fluka (Germany), luteolin from Roth (Germany), apigenin, alizarin, purpurin, emodin, isorhamnetin, rhamnetin, and kaempferol from Sigma Aldrich (the USA).

High performance liquid chromatography with photodiode array detection (HPLC–DAD)

Instrumentation

Chromatographic separations were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including G1322A Degaser, G1311A Quat pump, G1329A autosampler, G13166 TCC, and G1315D Diode Array Detector. DAD detection was performed by scanning from 191 to 799 nm with a resolution of 2 nm, and the chromatographic



Fig. 1 Images from the animal encyclopedia in the Millet Manuscript Library. a- the general image of a text in the manuscript, b- geometric drawing in another text)

peaks were monitored at 255, 268, 276, 350, 491, 520, 580, and 620 nm. A Nova Pak C18 analytical column (39×150 mm, 4 μm, Part No WAT 086344, Waters) was used. An analytical column protected by a guard

column filled with the same material was used. Analytical and guard columns were maintained at 30 °C and the data station was the Agilent Chemstation. Two solvents were utilized for chromatographic separations of the

Table 1 Information and images of the analyzed samples

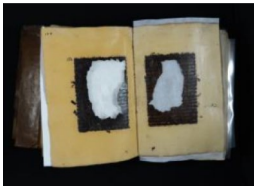















| Sample code | Sample type | Sample weight (mg) | Image of the object | Sample code | Sample type | Sample weight (mg) | Image of the object |
|-------------|-------------|--------------------|---|-------------|--|--------------------|---|
| AE-01 | Paper | 3.77 |  | AE-21 | Leather (from the inside of the cover) | 4.80 |  |
| AE-02 | Paper | 3.96 |  | AE-22 | Leather (from binding) | 12.58 |  |
| AE-03 | Paper | 4.79 |  | AE-23 | Leather (from binding) | 5.93 |  |
| AE-04 | Paper | 4.28 |  | AE-24 | Leather (from spine) | 11.53 |  |
| AE-05 | Paper | 4.32 |  | AE-25 | Leather (from spine) | 11.80 |  |
| AE-06 | Paper + ink | 8.23 |  | AE-26 | Leather (from spine) | 12.71 |  |
| AE-07 | Paper | 5.26 |  | AE-27 | Leather (from spine) | 9.94 |  |
| AE-08 | Paper | 3.64 |  | AE-28 | Paper (doublure) | 7.74 |  |

Table 1 (continued)


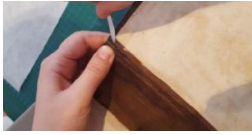



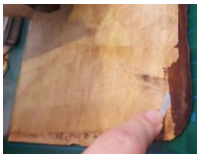














| Sample code | Sample type | Sample weight (mg) | Image of the object | Sample code | Sample type | Sample weight (mg) | Image of the object |
|-------------|------------------------|--------------------|---|-------------|----------------------|--------------------|---|
| AE-09 | Leather (from binding) | 8.13 |  | AE-29 | Paper (doublure) | 6.56 |  |
| AE-10 | Leather (from binding) | 7.41 |  | AE-30 | Paper (doublure) | 8.07 |  |
| AE-11 | Paper (doublure) | 4.65 |  | AE-31 | Paper (doublure) | 8.15 |  |
| AE-12 | Paper (doublure) | 7.58 |  | AE-32 | Leather (from spine) | 9.46 |  |
| AE-13 | leather (from binding) | 4.07 |  | AE-33 | Leather (from spine) | 7.10 |  |
| AE-14 | Leather (from binding) | 14.22 |  | AE-34 | Leather (from spine) | 4.46 |  |
| AE-15 | Leather (from binding) | 11.30 |  | AE-35 | Paper (doublure) | 7.42 |  |
| AE-16 | Paper + ink | 4.07 |  | AE-36 | Leather (from spine) | 7.62 |  |
| AE-17 | Paper + ink | 4.27 |  | AE-37 | Paper | 8.34 |  |
| AE-18 | Leather (from spine) | 5.23 |  | AE-38 | Paper (doublure) | 3.12 |  |

Table 1 (continued)




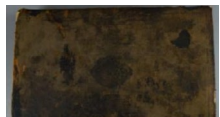
| Sample code | Sample type | Sample weight (mg) | Image of the object | Sample code | Sample type | Sample weight (mg) | Image of the object |
|-------------|----------------------|--------------------|---|-------------|------------------------|--------------------|---|
| AE-19 | Leather (from spine) | 8.63 |  | AE-39 | Leather (from spine) | 11.46 |  |
| AE-20 | Leather (from spine) | 7.65 |  | AE-40 | Leather (from binding) | 10.32 |  |

Table 2 The gradient elution program for HPLC analysis

| Time (min) | Flow rate (mL/min) | H ₂ O- 0.1% TFA (v/v) | CH ₃ CN- 0.1% TFA (v/v) |
|------------|--------------------|----------------------------------|------------------------------------|
| 0.0 | 0,5 | 95 | 5 |
| 1.0 | 0,5 | 95 | 5 |
| 20.0 | 0,5 | 70 | 30 |
| 25.0 | 0,5 | 40 | 60 |
| 28.0 | 0,5 | 40 | 60 |
| 33.0 | 0,5 | 5 | 95 |
| 35.0 | 0,5 | 5 | 95 |
| 40.0 | 0,5 | 95 | 5 |
| 45.0 | 0,5 | 95 | 5 |

hydrolyzed historical samples. Solvent A: H₂O- 0.1% TFA and solvent B: CH₃CN-0.1% TFA.

The gradient elution program used for dyestuff analysis in chromatographic separation by HPLC–DAD is shown in Table 2.

Sample preparation for dyestuff analysis

All samples were weighed separately in conical tubes before HPLC analysis (Table 1). A solution mixture of 400 mL of 37% HCl:MeOH:H₂O (2:1:1, v/v/v) was added to each of the samples in conical tubes. Each sample was then hydrolyzed in this solution mixture at 100 °C for 10 min. The same hydrolysis process was applied for all samples and no different extraction process was performed. After rapid cooling under cold running water, the solution was evaporated just to dryness in a water bath at 60–65 °C under a gentle stream of nitrogen. Each of the dry residues was then dissolved in 400 mL of MeOH:H₂O (2:1, v/v) and centrifuged at 4000 rpm for 10 min. After centrifugation, the upper clear part was taken into vials. 100 µL of the supernatant from each sample was analyzed in the HPLC [54–57].

Table 3 Retention time and absorbance maxima belong to reference dyestuff standards

| Row No | Reference dyestuff name | Retention time (min) | Absorbance maxima (nm) |
|--------|-------------------------|----------------------|-------------------------|
| 1 | alizarin | 27.199 | 251, 283, 328, 429 |
| 2 | apigenin | 25.350 | 266, 294, 337 |
| 3 | chrysophanol | 32.799 | 225, 256, 283, 317, 429 |
| 4 | ellagic acid | 16.476 | 253, 297, 367 |
| 5 | emodin | 29.859 | 223, 267, 288, 440 |
| 6 | flavone | 29.983 | 251, 295 |
| 7 | gallic acid | 3.964 | 216, 272 |
| 8 | isorhamnetin | 25.797 | 224, 233, 255, 301, 371 |
| 9 | kaempferol | 25.512 | 225, 264, 295, 323, 367 |
| 10 | luteolin | 22.442 | 217, 261, 295, 349 |
| 11 | purpurin | 28.465 | 253, 294, 455, 480, 514 |
| 12 | rhamnetin | 26.987 | 230, 257, 299, 37 |
| 13 | vanillic acid | 11.135 | 215, 261, 293 |

The dyestuff standards were not hydrolyzed and each was dissolved in 400 mL of MeOH:H₂O (2:1, v/v) and then analyzed in HPLC. Details on the retention time and UV–VIS data belonging to dyestuff standards are shown in Table 3.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX)

Instrumentation

A scanning electron microscope (SEM) with a VEGA3 model of TESCAN brand (TESCAN, Brno, Czech Republic) equipped with a backscattered electron (BSE) detector, secondary electron (SE) detector, and energy dispersive X-ray spectrometer (EDX) was used for elemental analysis of black ink samples in the manuscript. Also, a thermionic emission tungsten heated filament was used as the electron source and a Bruker brand XFlash 410-M model EDX detector (ESPRIT Compact

Esprit 1.9 software) was used for elemental analysis. With the EDX detector used, semi-quantitative results of elemental analyzes were obtained as atomic and percent by weight. Qualitative microanalysis was carried out using the ZAF method, which allows the simultaneous determination of the concentration of each element in a multi-element material and is based on the correction of the matrix effect. This method provides X-ray intensity correction, absorption correction, and fluorescence correction produced by the composition and depth of electron penetration, and the atomic number effect of each element by secondary fluorescence, respectively.

Sample preparation

For morphological analyzes performed with SEM–EDX, 10 kV energy level, and for elemental analyses 20 kV energy level and under high vacuum were studied. Paper + black ink samples were prepared by coating with Au/Pd (60/40) to obtain better SEM images and with carbon for elemental analysis. Since it will be worked under a high vacuum during the analysis, the samples were fixed on the sample holder by placing them on a carbon band that did not affect the analysis result.

Results and discussion

Visual evaluation

Evaluation of the condition of manuscripts such as paper and parchment containing iron-gall ink begins with the examination and documentation of the physical appearance of the objects. This can be done either with the naked eye or with the aid of a microscope with a different magnification scale. Situation assessment is made with the help of the created form or templates [9].

In this study, a visual evaluation was made for both ink-containing paper, ink-free papers that were used behind the front or back cover, and leather materials used for binding. Accordingly, the samples and the area where the samples are located were visually examined, and the types of deterioration in both paper and leather materials were evaluated separately. The types of deterioration detected in the examined paper objects are watering, yellowing, embrittlement, drying, and loss of parts (AE-01, AE-06, AE-07, AE-14, AE-31, AE-38). On the other hand, in the papers with black ink, ink distribution, degraded text block (AE-01, AE-02, AE-04, AE-05, AE-06, AE-07, AE-16, AE-17), and piece losses in the ink-containing area were observed (AE-01, AE-06, AE-07). The types of deterioration seen in leather materials used for binding are cracking (AE-15, AE-19, AE-24, AE-25, AE-26, AE-27, AE-32, AE-33, AE-34, AE-36, AE-39), drying, loss of flexibility, abrasion, and insect holes (AE-15, AE-21, AE-22, AE-23, AE-32, AE-33).

HPLC analysis

In this study, the HPLC method, which is a micro-destructive method, was preferred to detect both dyestuffs, tannins used in black ink or leather tanning, and degradation products for the animal encyclopedia (62 volumes), added to the Ottoman Library. The samples taken from the objects are either completely separated from the main material or samples that are about to break away. Accordingly, the dyestuffs and biological dye sources determined at the end of the HPLC analysis are shown in Table 4. In addition, it was shown that the chromatograms of selected 14 samples from the 40 samples analyzed in Fig. 2, the chromatogram belonging to detected dyestuff and degradation products in Fig. 3, and their spectra in Fig. 4.

According to the HPLC analysis results for the determination of the paper and leather main materials and the components used in ink, dye, and tanning found in these two main materials, the results in Table 4 were obtained. According to this;

- VA and/or VAd(s) were determined in the samples coded as AE-01, AE-02, AE-03, AE-05, AE-37, and AE-38. It is known that vanillic acid, one of the lignin derivative monomers, is in naturally aged papers, especially in papers containing lignin. This is because oxidation has the potential to form aromatic acids [58]. Natural aging can cause the paper to discolor and the cellulose to become more crystalline and solid. The deterioration of the color of a paper can be caused by the formation of chromophores upon aging as a result of exposure to light and volatile gases, among other things [59].
- CA and/or CAd(s) were determined in the samples coded as AE-07, AE-09, AE-12, AE-13, AE-14, AE-15, AE-16, AE-17, AE-19, AE-20, AE-21, AE-22, AE-23, AE-24, AE-25, AE-26, AE-27, AE-28, AE-29, AE-30, AE-31, AE-32, AE-33, AE-34, AE-35, AE-36, AE-37, AE-38, AE-39, and AE-40. It can be seen from here that chrysophanol and its derivatives were detected in 30 of the 40 samples analyzed. CA is an anthraquinone and its chemical name is 1,8-Dihydroxy-3-methylantraquinone. According to the authors [60–62], the 1,8-dihydroxy and 1,5,8 or 1,6,8-trihydroxy anthraquinone derivatives are the most common fungal derivatives in terrestrial fungal species. These species can be seen in many ways. Sometimes they appear in a simple form, sometimes as glycosides or as other complexes in the side chain linked by an O- or C-bond.
- The tannic acid and its derivatives were determined in almost all of the analyzed samples (except samples coded as AE-01, AE-03, AE-04, AE-05,

Table 4 The dyestuffs and other compounds detected as a result of HPLC analysis

| Sample code | *Detected dyestuffs | Biological dye sources |
|-------------|--|--|
| AE-01 | VA | – |
| AE-02 | VA, EA | Tannin-containing plant |
| AE-03 | VA | – |
| AE-04 | – | – |
| AE-05 | VA, VAd | – |
| AE-06 | GAd, EA | Tannin-containing plant |
| AE-07 | CA, CAd (×3) | – |
| AE-08 | – | – |
| AE-09 | EA, EAd (×3), CA | Tannin-containing plant |
| AE-10 | EA, EAd (×2) | Tannin-containing plant |
| AE-11 | GA, GAd, EA, EAd (×4), IRH, RH, EM | Tannin-containing plant + buckthorn (<i>Rhamnus</i> sp.) |
| AE-12 | GA, GAd (×5), EA, EAd (×7), NTC, NTCd, CA | Tannin-containing plant + redwood (<i>Caesalpinia</i> sp.) |
| AE-13 | EA, CA | Tannin-containing plant |
| AE-14 | GAd (×2), EA, EAd (×4), CA, CAd (×3) | Tannin-containing plant |
| AE-15 | GAd, EA, EAd (×6), CA | Tannin-containing plant |
| AE-16 | GA, GAd, EA, EAd (×3), CA | Tannin-containing plant |
| AE-17 | GA, GAd, EA, EAd, EM, CA | Tannin-containing plant + rhubarb (<i>Rheum</i> sp.) or dock (<i>Rumex</i> sp.) |
| AE-18 | EA, EAd (×2) | Tannin-containing plant |
| AE-19 | EA, EAd (×4), CA | Tannin-containing plant |
| AE-20 | GA, GAd, EA, EAd (×3), CA | Tannin-containing plant |
| AE-21 | GA, GAd, EA, EAd (×3), CA | Tannin-containing plant |
| AE-22 | GA, EA, CA | Tannin-containing plant |
| AE-23 | GA, EA, EAd (×3), CA | Tannin-containing plant |
| AE-24 | EA, EAd (×3), CA | Tannin-containing plant |
| AE-25 | GA, EA, EAd (×3), CA | Tannin-containing plant |
| AE-26 | EA, EAd (×3), FL, CA | Tannin-containing plant |
| AE-27 | EA, EAd (×2), CA | Tannin-containing plant |
| AE-28 | GA, GAd, EA, EAd, NTC, AL, PU, CA | Tannin-containing plant + redwood (<i>Caesalpinia</i> sp.) + madder (<i>Rubia tinctorum</i> L.) |
| AE-29 | GA, EA, EAd (×3), IRH, EM, CA | Tannin-containing plant + buckthorn (<i>Rhamnus</i> sp.) |
| AE-30 | GA, GAd, EA, EAd (×2), NTC, CA | Tannin-containing plant + redwood (<i>Caesalpinia</i> sp.) |
| AE-31 | GA, EA, EAd (×3), NTC, CA | Tannin-containing plant + redwood (<i>Caesalpinia</i> sp.) |
| AE-32 | GA, GAd, EA, EAd (×3), CA | Tannin-containing plant |
| AE-33 | GA, EA, EAd, CA | Tannin-containing plant |
| AE-34 | GA, GAd, EA, EAd (×2), KF, KFd, RH, EM, CA | Tannin-containing plant + buckthorn (<i>Rhamnus</i> sp.) |
| AE-35 | GA, GAd, EA, LU, AP, EM, CA | Tannin-containing plant + weld (<i>Reseda luteola</i> L.) + rhubarb (<i>Rheum</i> sp.) or dock (<i>Rumex</i> sp.) |
| AE-36 | GA, GAd (×2), EA, EAd, CA | Tannin-containing plant |
| AE-37 | GA, GAd, VA, VAd, EA, EAd, CA | Tannin-containing plant |
| AE-38 | GA, VA, EA, NTC, CA | Tannin-containing plant + redwood (<i>Caesalpinia</i> sp.) |
| AE-39 | GA, EA, EAd (×2), CA | Tannin-containing plant |
| AE-40 | GA, EA, EAd (×2), CA | Tannin-containing plant |

* VA: vanillic acid, VAd: vanillic acid derivative, GA: gallic acid, GAd: gallic acid derivative, EA: ellagic acid, EAd: ellagic acid derivative, CA: chrysophanic acid/chrysophanol, CAd: chrysophanic acid derivative, IRH: isorhamnetin, RH: rhamnetin, KF: kaempferol, KFd: kaempferol derivative, EM: emodin, NTC: Nowik Type C, NTCd: Nowik Type C derivative, FL: flavon, LU: luteolin, AP: apigenin, AL: alizarin, PU: purpurin

AE-07, and AE-08) (Table 4). This result shows that a plant containing tannic acid was used in the inks of the analyzed papers, and similarly, plants containing tannic acid were used in the leather tanning

process (vegetable tanning) in the leather samples. At the beginning of the plants containing tannin in dyeing are valonia oak (*Quercus ithaburensis* Decaisne), gall oak (*Quercus infectoria* Olivier), and pomegranate peel (*Punica granatum* L.) plants [63].

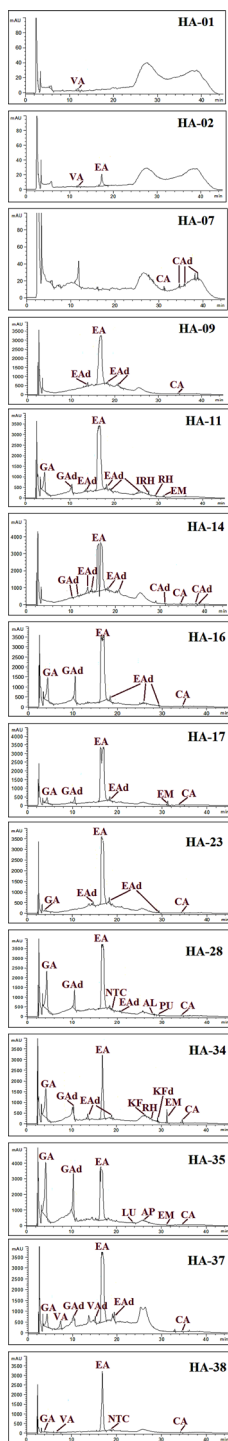


Fig. 2 The chromatograms of selected from the analyzed samples (at 255 nm)

Isorhamnetin, rhamnetin, kaempferol, and emodin dyestuffs were detected in some samples (AE-11, AE-29, AE-34). The presence of these dyestuffs indicates that dyeing is done using the fruits of the buck-

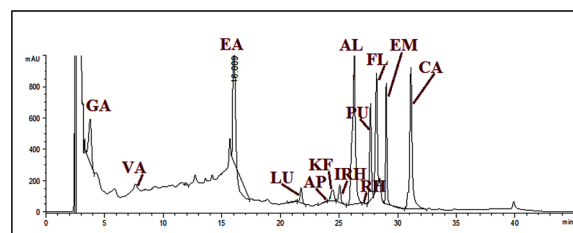


Fig. 3 Chromatogram showing detected dyestuff and degradation products (at 255 nm)

thorn plant (*Rhamnus* sp.). Buckthorn (*Rhamnus* sp.) is a plant rich in flavonoid dyestuffs. The main dyestuffs are common flavanols such as quercetin and kaempferol derivatives, as well as rhamnetin, rhamnazin, rhamnocitrin, xanthorhamnin, a 3-O-glycoside of rhamnazine [64], kaempferide and isorhamnetin [65]. It also contains anthraquinone dyes such as emodin, which is not a flavonoid [64]. The most commonly used *Rhamnus* species plants are *Rhamnus petiolaris* L. [63], *Rhamnus catharticus* L., and *Rhamnus frangula* L. [66].

Emodin was detected in the sample coded as AE-17. Emodin dyestuff is present in plants such as rhubarb (*Rheum* sp.) and dock (*Rumex* sp.). *Rumex* species plants are very rich in anthraquinone dyestuffs and the agent dyestuff is emodin. At the same time, emodin dyestuff is also present in plants of the *Rhamnus* species [66].

Luteolin and apigenin dyestuffs were determined in the sample coded as AE-35. Luteolin and apigenin dyestuffs are the two main dyestuffs of the weld (*Reseda luteola* L.) plant and it grows naturally in almost every part of Anatolia. The weld is one of the plants that has a yellow dye source and has the best fastness values. For this reason, it is often preferred in yellow dyeing. It is known that the weld was also used in Europe since prehistoric times [33, 63]. In addition to luteolin and apigenin, emodin dyestuff was also detected in the AE-35 coded sample. This result shows that the paper was dyed by being treated with two different plants (one weld and the other rhubarb dock).

NTC and NTCd(s) dyestuffs were detected in the samples coded with AE-12, AE-28, AE-30, AE-31, and AE-38. NTC and NTCd dyestuffs are seen in redwood plants. According to Nowik's research, Type C dyestuff was determined in sappanwood (*Caesalpinia sappan*), *Caesalpinia echinata*, and *Caesalpinia violacea* species [67].

Alizarin and purpurin dyestuffs were determined in the sample coded as AE-28. The presence of alizarin and purpurin dyestuffs indicates that the mad-

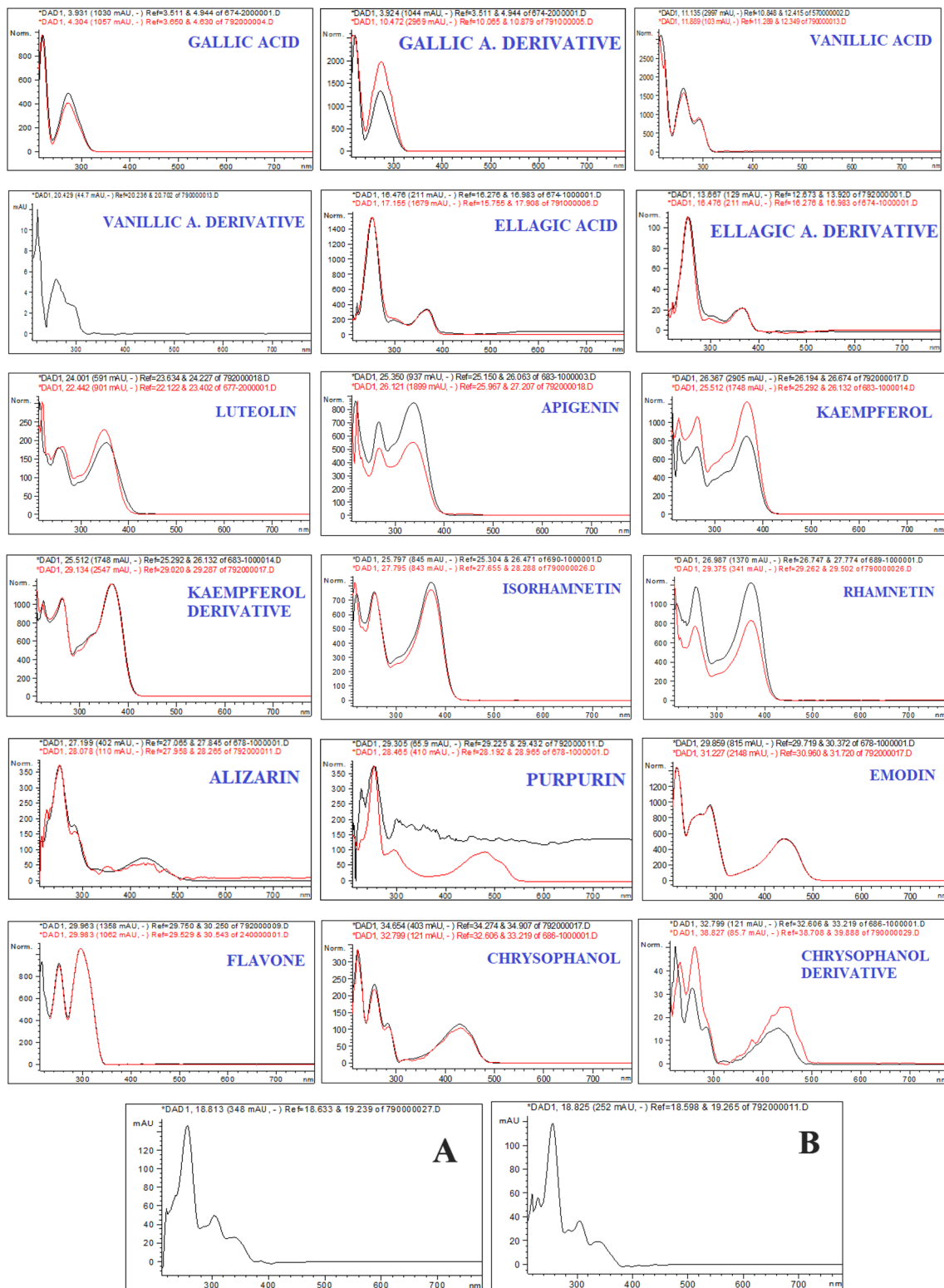


Fig. 4 The dyestuff spectra detected in the analyzed samples

der (*Rubia tinctorum* L.) plant is used. The roots of the madder (*Rubia tinctorum* L.) plant are a natural source of dye and have been used to produce the color red in many parts of the world since ancient times. The dyestuffs (dye components) in the *Rubia tinctorum* L. plant are anthraquinones, which are hydrolysis products of rubierythrin acid, which is the main dye component. The main coloring components of these anthraquinones are alizarin and purpurin. Other anthraquinones are pseudopurpurin, rubiadin, munjistin, xanthopurpurin, and other small-scale anthraquinone structures [68]. A NTC dyestuff was also determined in the sample coded as AE-28. This result shows that the sample coded with AE-28 was treated with both madder and redwood plants.

No dyestuffs or degradation products were detected in the analysis of AE-04 and AE-08 paper samples (Table 4).

In addition, in this study, it was stated that derivatives of some main components such as gallic acid, ellagic acid, vanillic acid, chrysophanol, Nowik Type C, and kaempferol were detected in most of the samples analyzed. The spectra defined as derivatives of substances belonging to these dyestuffs or degrada-

tion products are qualitatively the same as the spectra of the main components or show similarity with a slight shift (UV–Vis absorbance peaks). These components, which are qualitatively the same or similar, are expressed as "derivatives" because only the retention times are different.

SEM–EDX analysis

SEM–EDX analysis was carried out for a total of 3 samples (AE-06, AE-16, and AE-17) containing paper + black ink. The SEM images and EDX results obtained at the end of the analysis are shown in Fig. 5 and Table 5.

Three paper samples analyzed according to Fig. 5 were found to be one of the vegetable stem fibers (flax, hemp, etc.) and highly likely flax. According to the elemental analysis results, the iron element was determined in all three analyzed black inks (Table 5). Ultimately, tannic acids were determined in these inks from the dyestuff analysis results, it was confirmed that these inks were iron-gall inks.

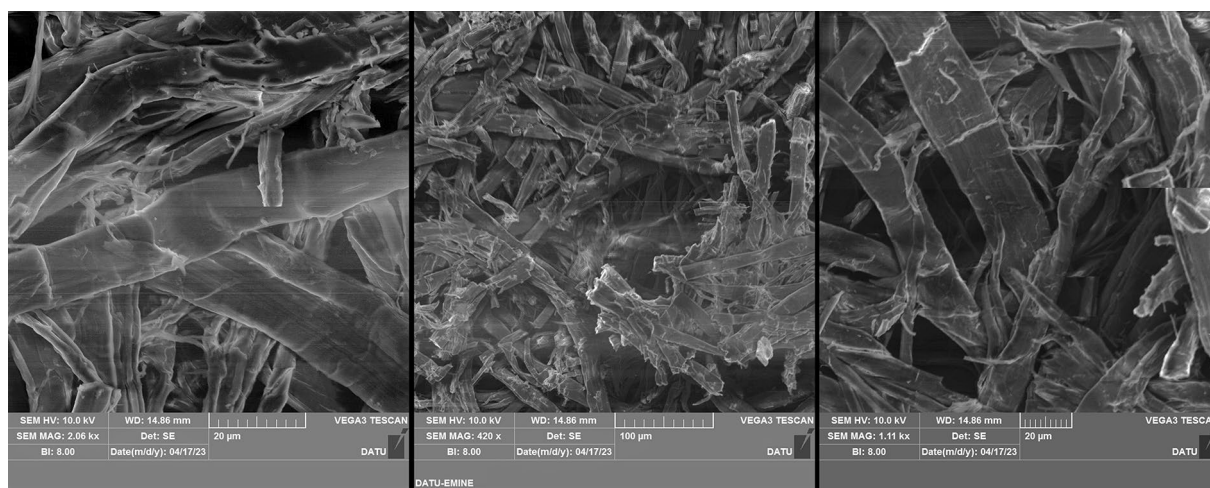


Fig. 5 SEM images of the analyzed paper samples. (AE-06, AE-16, AE17 from left to right)

Table 5 Elemental analysis results of three samples analyzed by SEM–EDX

| Sample | Identified elements and their ratio (%) | | | | | | |
|--------|---|-------|--------|--------|-------|-------|--------|
| | C (K) | O (K) | Na (K) | Al (K) | S (K) | K (K) | Fe (K) |
| AE-06 | 63.44 | 33.09 | 1.97 | 0.32 | 0.34 | 0.24 | 0.60 |
| AE-16 | 62.99 | 33.95 | 1.45 | 0.29 | 0.35 | 0.21 | 0.76 |
| AE17 | 62.87 | 34.01 | 1.53 | 0.30 | 0.30 | 0.19 | 0.80 |

Conclusion

As a result of the analysis, this study has proven that the animal encyclopedia, which was included at an Ottoman library, containing comprehensive information on the animal/living world and consisting of a total of 62 volumes, suffered from deterioration caused by unfavorable surrounding environmental conditions.

In this study, vanillic acid and its derivative(s) detected in six samples (AE-01, AE-02, AE-03, AE-05, AE-37, and AE-38) indicate that the paper naturally ages. When the objects from which these samples were taken were visually examined, it was observed that there was yellowing and drying on the paper. Many materials stored and displayed in museums are susceptible to degradation by insects, fungi, and rodents. Among these pests, especially the deterioration caused by fungi and the resulting deterioration product (chrysophanol/chrysophanic acid and its derivatives) were determined in 30 of 40 samples in our study. This result shows that most of the analyzed samples are adversely affected by the ambient conditions (especially relative humidity, temperature, pH, and airflow) where the artifact is stored or exhibited.

It has been confirmed once again thanks to this study that vegetable dye sources are used to color papers in Islamic geography. In addition to the paper, it was determined that some of the leather samples were also colored with vegetable dyes. At the same time, this study shows the best example of vegetable dyes containing tannin in the production of black ink, and these dyes are produced by combining them with the element iron. The damage given by iron-gall ink to the paper surface is quite devastating, and it has been reported in the animal encyclopedia.

Although the characterization of inks and pigments in Islamic manuscripts has aroused great interest among scholars and conservationists, limited studies indicate that sampling for the analysis of inks, pigments, dyes, papers, and leathers. Considering that the inks in the manuscripts are tanned with iron-gall inks and the leathers used in bookbinding are tanned with tannins, the characterization of these materials is of great importance in the examination of historical manuscripts and their bookbindings.

Abbreviations

| | |
|-----------------|---|
| NO _x | Nitrogen oxides |
| SO _x | Sulfur oxides |
| HPLC–DAD | High performance liquid chromatography–diode array detector |
| HPLC–ESI–MS | High performance liquid chromatography– electrospray ionization–mass detector |
| FTIR | Fourier-transformed infrared spectroscopy |
| XRF | X-ray fluorescence |
| SEM–EDX | Scanning electron microscopy–energy dispersive X-ray spectroscopy |

| | |
|----------|--|
| SERS | Surface-enhanced Raman spectroscopy |
| μ-Raman | Micro-Raman |
| UV–Vis | Ultraviolet–visible |
| TCF–DATU | Turkish Cultural Foundation–Cultural Heritage Preservation and Natural Dyes Laboratory |
| AE-01 | Animal encyclopedia-01 |
| TFA | Trifluoroacetic acid |
| MeOH | Metanol |
| VA | Vanillic acid |
| VAd | Vanillic acid derivative |
| GA | Gallic acid |
| GAd | Gallic acid derivative |
| EA | Ellagic acid |
| EAd | Ellagic acid derivative |
| CA | Chrysophanic acid/chrysophanol |
| CAd | Chrysophanic acid derivative |
| IRH | Isorhamnetin |
| RH | Rhamnetin |
| KF | Kaempferol |
| KFd | Kaempferol derivative |
| EM | Emodin |
| NTC | Nowik type C |
| NTCd | Nowik type C derivative |
| FL | Flavon |
| LU | Luteolin |
| AP | Apigenin |
| AL | Alizarin |
| PU | Purpurin |

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Author contributions

ETG: methodology, resources, writing—original draft, visualization, supervision. RK: gave high-quality suggestions, performed the analyses. NB: historical sample supply, description/historical background of the historical object. All authors reviewed the manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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References

1. Darzi M, Stern B, Edwards HGM, et al. A study of colourant uses in illuminated Islamic manuscripts from the Qājār period (1789–1925 C.E), early modern Iran. *J Archaeol Sci Reports*. 2021;39:103119.
2. Duran A, Franquelo ML, Centeno MA, et al. Forgery detection on an Arabic illuminated manuscript by micro-Raman and X-ray fluorescence spectroscopy. *J Raman Spectroscopy*. 2011;42(1):48–55.
3. Abdel-Maksoud G. Analytical techniques used for the evaluation of a 19th century quranic manuscript conditions. *Measurement*. 2011;44:1606–17.

4. Heritage Collections Council (HCC). *Damage and Decay. reCollections Caring for Collections Across Australia*. Australia: Commonwealth of Australia; 1998. p. 3–75.
5. National Park Service (NPS). Chapter 4: museum collections environment, the museum handbook Part I: museum collections, museum management program. Washington, DC: National Park Service; 2016.
6. Faubel W, Staub S, Simon R, et al. Nondestructive analysis for the investigation of decomposition phenomena of historical manuscripts and prints. *Spectrochimica Acta Part B*. 2007;62:669–76.
7. Caple C. *Preventive conservation in museums*. Oxford: Routledge, Leicester readers in museum studies; 2012. p. 37–48.
8. Hughes S. *Managing the preservation of library and archive collections in historic buildings*. London: National Preservation Office; 2002. p. 13–8.
9. International Federation of Library Associations and Institutions (IFLA). *Preservation and conservation (PAC) programme: iron-gall ink*. PAC North America. 2020. <https://www.ifla.org/iron-gall-ink/>. Accessed 6 Feb 2022.
10. Banik G. Ink corrosion: chemistry. 1998. <https://irongallink.org/ink-corrosion-chemistry.html>. Accessed 7 Jan 2022.
11. Burgio L. Pigments, dyes and inks: their analysis on manuscripts, scrolls and papyri. *Archaeol Anthropol Sci*. 2021. <https://doi.org/10.1007/s12520-021-01403-3>.
12. Burgio L, Clark RJH, Hark RR. Raman microscopy and X-ray fluorescence analysis of pigments on medieval and Renaissance Italian manuscript cuttings. *PNAS*. 2010;107(13):5726–31.
13. Espina Alba, Cañamares Maria Vega, Jurašeková Zuzana, Sanchez-Cortes Santiago. Analysis of iron complexes of tannic acid and other related polyphenols as revealed by spectroscopic techniques: implications in the identification and characterization of iron-gall inks in historical manuscripts. *ACS Omega*. 2022;7:27937–49.
14. Malešič J, Šala M, Selih VS, Kočar D. Evaluation of a method for treatment of iron-gall ink corrosion on paper. *Cellulose*. 2014;21:2925–36.
15. Rabin I. Cell death: material studies of historic inks: transition from carbon to iron-gall inks. In: Raggetti L, editor. *Traces of ink: experiences of philology and replication*. The Netherlands: Brill; 2021. p. 70–8.
16. Stijnman A. Iron-gall inks in history: ingredients and production. In: Kolar J, Strlič M, editors. *Iron-gall inks: on manufacture, characterisation, degradation and stabilisation*. Ljubljana: National and University Library; 2006. p. 25–68.
17. Edwards HGM. Analytical Raman Spectroscopy of Inks. In: *Raman Spectroscopy in Archaeology and Art History*, vol. 2. London: Royal Society of Chemistry; 2018. p. 1–15.
18. Hahn O, Malzer W, Kanngiesser B, Beckhoff B. Characterization of iron-gall inks in historical manuscripts and music compositions using X-ray fluorescence spectrometry. *X-Ray Spectrom*. 2004;33:234–9.
19. Hahn O. Analyses of iron-gall and carbon inks by means of X-ray fluorescence analysis: a non-destructive approach in the field of archaeometry and conservation science. *Restaur Int J Preserv Libr and Arch Mater*. 2010;31(1):41–64.
20. Kolar J, Strlič M, Budnar M, et al. Stabilisation of corrosive iron-gall inks. *Acta Chim Slov*. 2003;50:763–70.
21. Manca R, Burgio L, Button V, et al. Scientific analysis underpinning the multidisciplinary project “The Leman Album: an Enhanced Facsimile.” *European Phys J Plus*. 2019. <https://doi.org/10.1140/epjp/i2019-12668-0>.
22. Çakar P, Akyol E. The effects of natural dye and iron-gall ink on degradation kinetics of cellulose by accelerated ageing. *Stud Conserv*. 2022;67(6):381–8.
23. Hidalgo RJD, Córdoba R, Nabais P, et al. New insights into iron-gall inks through the use of historically accurate reconstructions. *Herit Sci*. 2018. <https://doi.org/10.1186/s40494-018-0228-8>.
24. Kolar J, Strlič M. Ageing and stabilisation of paper containing iron-gall ink. In: Kolar J, Strlič M, editors. *Iron-gall inks: on manufacture, characterisation, degradation and stabilisation*. Ljubljana: National and University Library; 2006. p. 181–94.
25. Aceto M, Agostino A, Fenoglio G, et al. First analytical evidences of precious colourants on Mediterranean illuminated manuscripts. *Spectrochim Acta Part A Mol Biomol Spectrosc*. 2012;95:235–45.
26. Degano I, Ribechini E, Modugno F, Colombini MP. Analytical methods for the characterization of organic dyes in artworks and in historical textiles. *Appl Spectrosc Rev*. 2009;44(5):363–410.
27. Desvergnès AC, Berghe IV. Dyestuff identification and significance of interleaves from Moroccan manuscripts of Dalā'il al-Khayrāt. *Stud Conserv*. 2018;63(4):236–50.
28. Cardon D. Natural dyes, our global heritage of colours. *Textile Society of America. 12th Biennial Symposium*. Lincoln-Nebraska. 2010;6–9.
29. Analytical Methods Committee. AMCTB No 101 Analysis of historical dyes on heritage objects. *Anal Methods*. 2021;13:558–62.
30. Ebeid H, Brown J, Holt Y, Singer B. A study of dyed endpapers during Islamic mediaeval times in Egypt: purpose, materials and techniques. In: Watteuw L, Hofmann C, editors. *Paper conservation: decisions and compromises*. Vienna: ICOM-CC; 2013. p. 61–5.
31. Melo MJ. History of natural dyes in the ancient Mediterranean world”. In: Bechtold T, Mussak R, editors. *Handbook of natural colorants*. Hoboken: Wiley; 2009.
32. Larsen R. Experiments and observations in the study of environmental impact on historical vegetable tanned leathers. *J Thermochimica Acta*. 2000;365:85–99.
33. Cardon D. *Natural dyes: sources, tradition, technology and science*. United Kingdom: Archetype Publications; 2007. p. 400–20.
34. Gatta GD, Badea E, Ceccarelli R, et al. Assessment of damage in old parchments by DSC and SEM. *J Therm Anal Calorim*. 2005;82(3):637–49.
35. Lee AS, Mahon PJ, Creagh DC. Raman analysis of iron-gall inks on parchment. *Vib Spectrosc*. 2006;41(2):170–5.
36. Kanngießer B, Hahn O, Wilke M, et al. Investigation of oxidation and migration processes of inorganic compounds in ink-corroded manuscripts. *Spectrochimica Acta Part B Atomic Spectrosc*. 2004;59(10–11):1511–6.
37. Hofenk de Graaff JH. Dyeing black in seventeenth-century Holland. In: Eri I, Perjes JB, Nagy KE, Bendefy MK, Kovacs PM, Sipos E, editors. *Conserving textiles studies in honour of Agnes Timar-Balazsy*. Rome: ICCROM Conservation Studies 7; 2009.
38. Strlič M, Kolar J, Žigon M, Pihlar B. Evaluation of size-exclusion chromatography and viscometry for the determination of molar masses of oxidised cellulose. *J Chromatogr A*. 1998;805(1–2):93–9.
39. Strlič M, Csefalvayová L, Kolar J, et al. Nondestructive characterisation of iron-gall ink drawings: not such a galling problem. *Talanta*. 2010;81(1–2):412–7.
40. Henniges U, Reibke R, Banik G, et al. Iron-gall ink-induced corrosion of cellulose: ageing, degradation and stabilization. Part 2: application on historic sample material. *Cellulose*. 2008;15:861–70.
41. Neevel J. Phytate: a potential conservation agent for treatment of ink corrosion caused by iron-gall inks. *Restaurator*. 1995;16:143–60.
42. Haskovic A, Ibragic S. Use of analytical methods in revealing the techniques of Ottoman calligraphers: an illuminated manuscript from the eighteenth century. *Stud Conserv*. 2022;67(5):313–26.
43. Melo MJ, Nabais P, Guimarães M, et al. Organic dyes in illuminated manuscripts: a unique cultural and historic record. *Phil Trans R Soc A*. 2016;374:20160050.
44. Bonizzoni L, Canevari C, Galli A, et al. A multidisciplinary materials characterization of a Joannes Marcus viol (16th century). *Herit Sci*. 2014;2:15. <https://doi.org/10.1186/2050-7445-2-15>.
45. Ciglanská M, Jančovičová V, Havlínová B, et al. The influence of pollutants on accelerated ageing of parchment with iron gall inks. *J Cult Herit*. 2014;15(4):373–81.
46. Nunes M, Olival F, Mitchell SG, et al. A holistic approach to understanding the iron-gall inks in the historical documents of the Portuguese Inquisition (1570–1790). *Micron*. 2023;165:103396.
47. Pereira FJ, Lopez R, Brasas M, et al. Synergism between SEM/EDX microanalysis and multivariate analysis for a suitable classification of Roman and Byzantine papyri. *Microchem J*. 2021;160:105688.
48. Zamorano GMC. The presence of iron in inks used in Valencian manuscripts from the 13th to 17th century. *Microchem J*. 2018;143:484–92.
49. Analytical Methods Committee. AMCTB No. 67. Raman spectroscopy in cultural heritage: background paper. *Anal Methods*. 2015;7:4844–7.
50. Chaplin TD, Clark RJH, Jacobs D, et al. The Gutenberg bibles: analysis of the illuminations and inks using Raman spectroscopy. *Anal Chem*. 2005;77(11):3611–22.
51. Melo MJ, Nabais P, Araújo R, Vitorino T. The conservation of medieval manuscript illuminations: a chemical perspective. *Phys Sci Rev*. 2019;4(8):20180017.

52. Kireççi MA. Ibn Atiyye el-Avfi. TDV İslam ansiklopedisi-Ek 1. İstanbul. 2016; 585–87.
53. Baydar, N. 2021 Codicological examination and conservation decisions for an encyclopaedic work consisting of 62 volumes from the fifteenth century: *Kashf al-Bayān an Sifāt al-Hayawān*. M. J. Driscoll (Eds), *Care and Conservation of Manuscripts: Care and Conservation of Manuscripts 17th: Proceedings of the Seventeenth International Seminar held at the University of Copenhagen 11th–13th April 2018*. Copenhagen: Museum Tusulanum Press. 2021; 135–147.
54. Torgan GE, Karadag R. Sustainability of organic cotton fabric dyeing with a natural dye (gallnut) and analysis by multi-technique approach. *J Nat Fibers*. 2021;18(8):1107–18.
55. Torgan Güzel E, Karadag R, Alkan R. Durability, antimicrobial activity and HPLC, analysis of dyed silk fabrics using madder and gall oak. *J Nat Fibers*. 2020;17(11):1654–67.
56. Karadag R, Torgan E. Advantages and importance of natural dyes in the restoration of textile cultural heritage. *Int J Conserv Sci*. 2016;7(Special Issue 1):315–24.
57. Karadag R, Torgan E, Taşköprü T, Yıldız Y. Characterization of dyestuffs and metals from selected 16–17-century Ottoman silk brocades by RP-HPLC-DAD and FESEM-EDX. *J Liquid Chromat Rel Tech*. 2015;38(5):591–9.
58. Shahani CJ, Harrison G. Spontaneous formation of acids in the natural aging of paper. *Stud Conserv*. 2002;47(3):189–92.
59. Van der Reyden D. Recent scientific research in paper conservation. *J Am Inst Conserv*. 1992;31(1):117–38.
60. Bick IRC, Rhee C. Anthraquinone pigments from *Phoma foveata* Foister. *Biochem J*. 1966;98:112–6.
61. Fujitake N, Suzuki T, Fukumoto M, Oji Y. Predominance of dimers over naturally occurring anthraquinones in soil. *J Nat Prod*. 1998;61:189–92.
62. Suzuki T, Fujitake N, Oji Y. Horizontal distribution of main hydroxyanthraquinones in soil. *Soil Sci Plant Nutr*. 1999;45:297–306.
63. Karadağ R. Doğal boyamacılık. Ankara:T.C. Kültür ve Turizm Bakanlığı, Geleneksel El Sanatları ve Mağazalar İşletme Müdürlüğü Yayınları; 2007. 78–89.
64. Ferreira ESB, Hulme AN, McNab H, Quye A. The natural constituents of historical textile dyes. *Royal Soc Chemistry*. 2004;33:329–36.
65. Cuoco G, Mathe C, Vieillescazes C. Liquid chromatographic analysis of flavonol compounds in green fruits of three rhamnus species used in stil de grain. *Microchem J*. 2014;115:130–7.
66. Petroviciu I, Albu F, Medvedovici A. LC/MS and LC/MS/MS based protocol for identification of dyes in historic textiles. *Microchem J*. 2010;95(2):247–54.
67. Nowik W. The possibility of differentiation and identification of red and blue 'soluble' dyewoods: determination of species used in dyeing and chemistry of their dyestuffs. London: Archetype Pub; 2001. p. 129–44.
68. Derksen GCH, Van Beek TA. *Rubia tinctorum* L. *Stud Nat Products Chem*. 2002;26:629–84.

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