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Non-invasive imaging and spectroscopy techniques for identifying historical pigments: a case study of Iranian manuscripts from the Qajar era

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Abstract

In recent years, the expansion of non-invasive methods has been a trend in identifying historical pigments. Accordingly, this study aimed to identify the pigments used in three Iranian historical manuscripts from the Qajar era by utilizing a non-invasive and multi-analytical approach. A combination of various multi-band imaging methods, along with μ -XRF, Raman and FORS spectroscopy, were employed to identify pigments. The results revealed that emerald green, cochineal, ultramarine, orpiment, and red lead were used as pigments for green, red, blue, yellow, and orange colors on a golden leaf made of brass alloy. The study also demonstrated the mixtures of lead-barite white, lead white-ultramarine and lead white-red lead-indigo-cochineal in the white, light blue, and pink sections. While multi-band imaging was found to be a suitable tool for the primary classification of pigments, relying solely on this method without a complete pigment database is not advisable, as differences in underlying paint layers and mixed pigments can affect imaging results. Overall, the combination of imaging and spectroscopic techniques provides a reliable and non-invasive approach to identifying historical pigments and their alterations.

Keywords Non-destructive analysis, Pigment identification, Qajar manuscript, Multi-band imaging, Raman spectroscopy

Introduction

Illuminated manuscripts are highly prized examples of unique artwork, which contain many colorants. These manuscripts are of historical, structural, and scientific importance, making it essential to conduct further research on them [1]. The identification of coloring materials constitutes a significant aspect of these studies. Chemical analysis of coloring agents can provide cultural heritage specialists with essential information for selecting the appropriate conservation and restoration

methods. Furthermore, it can distinguish between original and later-added colorants while authenticating the manuscript's dating [2].

Although there are a considerable number of illuminated Iranian manuscripts, only a few studies have been carried out regarding pigment identification, highlighting the significance of investigating these valuable Iranian works. The objective of analyzing these artworks was to determine the pigments used in paper dyeing and decorations [3–8], as well as the binders [9], ink, and paper-making process [9–11]. Two approaches were employed in these studies: analyzing traditional instructions and examining various case studies. The findings of these investigations have identified a range of pigments, providing insight into the color palette utilized by artists in creating these works. Furthermore,

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these studies have facilitated a better understanding of the production process and the historical context of these artworks.

Various analytical techniques have been employed for pigment identification such as molecular spectroscopy like Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, and FORS, and X-ray-based methods like scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS), X-ray fluorescence (XRF) spectroscopy and particle-induced X-ray emission (PIXE) spectroscopy for the elemental analysis or X-ray diffraction (XRD) analysis to identify crystalline phases present in the pigments [12–17]. Chromatography methods combined with mass spectrometry are also effective tools to characterize organic coloring agents [18–20].

The selection of appropriate identification processes or techniques depends on various factors such as limitations of the method, cultural heritage condition, research questions, and possibility of sampling [2, 3, 21–25]. However, a multi-analytical approach is crucial for pigment identification [26, 27]. Furthermore, traditional methods of pigment analysis involve destructive sampling, which is not appropriate for valuable and irreplaceable artworks. Therefore, using non-invasive analytical techniques for cultural heritage studies is essential, given the limitations of sampling in such studies.

In addition to mentioned methods, scholars have used various spectral imaging techniques, like technical, multi-band, hyperspectral imaging, for pigment identification [28–32]. Although these methods have some limitations, they provide beneficial information at low cost and time consumption, specifically for pigment identification, coatings, past conservation intervention, degradation of the material, and underdrawings in historical paintings.

While imaging methods are useful in the preliminary classification of pigments, precise pigment identification requires additional analysis. To this end, simultaneous use of non-invasive imaging and spectroscopy techniques have emerged as promising alternatives for pigment identification.

This paper focuses on the innovation of identifying mixture pigments through imaging methods and understanding the artistic palette of Iranian artists, while also considering the impact of metallic substrates on imaging results in pigment identification. To achieve this, non-invasive imaging and spectroscopic methods such as μ -XRF, Raman spectroscopy, and FORS are used to examine Qajar-era Iranian manuscripts and identify the pigments used in their decoration. The research demonstrates the effectiveness of these techniques in identifying pigments within historical artworks and offers new opportunities for their preservation and investigation.

Materials and methods

Objects

The focus of this study is on manuscripts from 1334 AH (1916 AD) that relate to the final years of Iran's Qajar dynasty (1789–1925). It is possible that these manuscripts are even older than the oldest dated note in the collection. The collection comprises 40 different parts of the Qur'an, which are bound separately but together form the complete text. This collection, identified as code 10059, is held at the Borujen Museum in Chaharmahal and Bakhtiari province, Iran. To preserve and study the manuscripts, three of them, which had black leather covers and measured 22×14.5 cm, were sent to Tabriz Islamic Art University. The artist who created these manuscripts is unknown. The illuminated parts of the manuscripts were examined to identify the pigments used. The main text was written in black ink, with sura titles in red ink. The margins of the pages were decorated with blue, black, golden, and red stripes, although the golden color had faded to green in some areas due to pigment degradation. The first pages of each volume were gilded and illuminated in various colors such as golden, red, blue, white, green, black, orange, pink, light blue, and yellow. This study analyzed all pigments used in illuminated parts, with their positions shown in Fig. 1.

Multi-band imaging

All images were captured by the modified camera Nikon D750 after the removal of the inbuilt UV-IR blocking filter, in order to exploit the full sensitivity of the CMOS sensor (ca. 350–1100 nm). The camera was equipped with a Nikon AF Nikkor 50 mm f/1.8D lens. The camera was operated in fully manual mode. Two Youngenu NY660 xenon flashlights placed at 45 degrees angle to the subject were used as illuminating sources and an X-rite color checker was used as a spectral reference to correct images and compare with reference samples.

Multi-band images, including Visible-reflected (VIS), Infrared photography (IR), Ultraviolet-reflected (UVR), and Ultraviolet-induced Visible luminescence (UVL), were recorded in RAW format with the highest resolution (24 megapixels: 6016×4016) using the filters described in Table 1. Raw images obtained from the camera were converted into 16-bit TIF format in Adobe Photoshop software. Post-processing and calibration procedures were performed according to Kushel method [33] and Cosentino recommendations [34]. False-color infrared (IR-FC) and false-color ultraviolet (UV-FC) images were obtained by combining VIS with IR and UVR images, respectively, based on the method proposed by Dyer et al. [30]. Also, along with the usual methods, Ultraviolet-induced Blue luminescence imaging (UVBL) and Ultraviolet-induced Red luminescence imaging (UVRL) methods were also



Fig. 1 The first illuminated page of one volume, as well as illuminated parts of two others, from a collection of Holy Quran manuscripts dating back to the early 20th century. Studies pigments locations are marked: golden (a), orange (b), yellow (c), light blue (d), white (e), pink (f), blue (g), green (h), red (i), black (j), and blank paper (k)

Table 1 Summary of radiation sources and filters used for each imaging method

MSI technique	Filter(s) in front of radiation sources	Filter(s) in front of the camera	Range investigated
Visible-reflected imaging (VIS)	2 × Youngenu NY660 Xenon flashlight, mounted with soft box (without filter)	Baader UV/IR Cut	420–680 nm
Ultraviolet-induced Visible Luminescence imaging (UVLI)	+ 2 × Hoya U-360	Baader UV/IR Cut	420–680 nm
Ultraviolet-induced Blue Luminescence imaging (UVBL)	+ 2 × Hoya U-360	MIDOPT BP470 + Baader UV/IR Cut	425–495 nm
Ultraviolet-induced Red Luminescence imaging (UVRL)	+ 2 × Hoya U-360	MIDOPT BP635 + Baader UV/IR Cut	615–645 nm
Ultraviolet-Reflected imaging (UVR)	+ 2 × Hoya U-360	Baader U-Venus	350–380 nm
Infrared imaging (IR)	2 × Youngenu NY660 Xenon flashlight, each mounted with soft box (without filter)	Schott RG830	830–1100 nm

performed in order to check the luminescence intensity in the blue (425–495 nm) and red (615–645 nm) ranges, respectively [35].

μ-XRF spectroscopy

μ-XRF analysis was used to identify the major elements of all pigments along with the paper. An Unisantis 104

X-ray micro fluorescence spectrometer was used for XRF experiments. The excitation settings were 25 kV and 300 mA/120 s. SmartXRF software was used to identify the peaks of elements and spectra were analysed using OriginPro 2021 software.

Raman spectroscopy

Raman spectroscopy was used to identify pigments based on molecular vibrations. Raman spectra of all pigments were recorded at room temperature using a Tekram micro-Raman spectrometer (Teksan co., Iran) with a 60× LWD objective. Data were collected with a 1200 g/mm grating, with 5 accumulations of 10 s for all pigments. Raman spectra were recorded with excitation of 532 nm with a resolution of 6 cm^{-1} and power of 30 mW in the range 100–2000 cm^{-1} .

Fiber optics reflectance spectroscopy (FORS)

Fiber optics reflectance spectroscopy (FORS) was applied to the analysis of red pigment. The UV–Vis–NIR reflectance spectrum was obtained using an AvaSpec-2048 fiber optic spectrometer, an AvaLight-DHc compact deuterium-halogen light source, and a glass fiber reflection probe (Avantes Inc., Netherlands), operating in the 200–1050 nm. Spectrum was recorded with a 2 s integration time and 5 average. Fourier self-deconvolution (FSD) was also used for reducing bandwidths and resolving overlapped bands from one another. OriginPro 2021 was used for this purpose. Obtained spectrum was compared with the spectra of reference pigments. Reference spectra were from Pigments Checker v.5, a free spectra database of pigments from cultural heritage science open source (CHSOS) [36].

Results and discussion

Multi-band imaging

The analysis of three manuscripts revealed the existence of 10 distinct colors, namely blue, light blue, red, orange, pink, green, yellow, white, black, and golden. The preliminary findings of the multi-band images indicated that the same pigments were used for the same color in all three manuscripts (Fig. 2), resulting in an initial categorization for further scrutiny through analytical approaches.

The colors observed in IR-FC and UV-FC images of blue pigment were dark red and blue-green, respectively, which are typical of ultramarine pigment [37]. This indicates that the blue sections may contain ultramarine. The UVL images helped identify modified or discolored parts, as the original parts and altered parts had weak and bright blue fluorescence, respectively. The UVBL images were particularly useful in distinguishing between these two parts. The most effective imaging techniques for identifying ultramarine among various blue pigments of historical significance are UVL and UV-FC methods. These imaging methods play a crucial role in differentiating new components from the original ones, which helps

in selecting appropriate sampling positions for analytical procedures.

According to Table 2, the metal substrate affected the UVL, IR-FC, and UV-FC images of the red and orange pigments. As such, just as sizing influences spectral images [38], the metal substrate could also affect results. In the metal substrate, different fluorescence was observed in parts that turned green following corrosion. Moreover, the UVL images of the golden parts exhibit sizing effects, but not in the green portions. The IR images of the two samples show that the edges of the golden parts have turned dark, as has a portion of the golden edge in another sample. This has resulted in a darker hue in false color images, making it not debatable to identify the pigment. The peripheral parts of the paper manuscripts, with the golden portion, exhibit a significant luminescence effect, indicating possible destruction in this area. Copper alloys have been used as a substitute for pure gold in the form of thin sheets or a combination of powder and binder. Due to their metallic luster, it is difficult to identify these pigments using multi-band imaging. However, examining the destroyed parts can yield better results [3].

Presently, existing databases for spectral imaging of pigments do not cater to mixed pigments. Nonetheless, in some imaging techniques, the luminescence or absorption of one pigment may override the other [29], which can help confirm the available possibilities. The UV-FC images also portray pale blue spots within the pink parts, which can be observed as white halos, potentially indicating an irregular mixture of white pigment, presumably lead white, and dye, perhaps indigo blue. Conversely, this color also exhibits red-pink fluorescence in UVL images, which could imply the presence of madder or cochineal in the color's mixture. The UV-FC method has been reported as the most efficient way to separate cochineal from other red organic dyes like lac, kermes, and madder (when colors are not mixed) [18, 38]. The method reveals the red parts with a greenish tint, which helps in identifying cochineal. Table 2 summarizes the predictions made by various imaging methods and databases. These predictions are based on the combined results of all imaging modalities used.

Spectroscopic methods

Golden pigment

Figure 3 illustrates the μ -XRF and Raman spectra of the golden pigment. The XRF spectrum of the gilded parts indicates the presence of copper-zinc alloy in these areas. Specifically, the golden regions are composed of a brass alloy. This alloy was widely used as a cheaper alternative to gold in Iranian paintings during the Qajar era. Numerous reports highlight the importance of brass pigment in



Fig. 2 Multi-band images of the gilded part of the studied manuscripts, including visible, UVL, UVR, IR, IR-FC, UV-FC, UVBL and UVRL images

artworks of this period, including wall paintings and illuminated manuscripts [3, 39, 40].

The visual resemblance of brass to gold, along with the abundance of copper ore in Iran and the high malleability of copper-based alloys, makes it a viable and cost-effective alternative to imitating gold [41]. However, there is a lack of analytical studies on Iranian gilded manuscripts, making it difficult to confirm the extent of copper alloy pigments used as gold substitutes. Additionally, due to the well-preserved gold

gildings in many historical documents, there has been little reason to analyze them, resulting in many cases where the gold gildings have been assumed to be genuine [40]. Nevertheless, evidence suggests that the use of brass alloy increased during the Qajar period compared to the Safavid period [3, 39–42]. Further investigation into the economic and social conditions of Iran in different time periods is essential to confirm this hypothesis. Moreover, a thorough examination of various historical artifacts from diverse eras is needed to

Table 2 Results of multi-bands imaging and prediction of possible pigments

Color	Imaging method							Expectancy [3, 28, 29, 37]
	IR	UVR	UVL	UVRL *	UVBL *	UV-FC	IR-FC	
Blue	Bright	Bright	Weak: Blue	Dark	Deep Blue	Blue-Green	Deep Red	Ultramarine
Light Blue	Bright	Bright	Weak: Blue	Dark	Deep Blue	Blue-Green	Pink	Ultramarine (Mixed with a white pigment?)
Red	Bright/Gray (**on Golden area)	Dark	Dark Red/Inert (**on Golden area)	Light Red	Dark	Deep Green	Orange	Cochineal
Orange	Bright/Gray (**on Golden area)	Dark	Inert	Dark	Dark	Red Brown	Yellow/ Green (**on Golden area)	Red Lead
Pink	Bright	Bright	Red	Light Red	Light Blue	Light Blue	Light Yellow	(White: Lead White?) + Indigo + (Red: Possibly Madder or Cochineal)
Green	Dark	Dark	Inert	Dark	Dark	Dark goldenrod	Dark Blue	Malachite
Yellow	Bright	Dark	Inert	Dark	Dark	Pink	Pale Yellow	Orpiment/Yellow Ochre
White	Bright	Bright	Weak White	Light Red	Light Blue	Pale Yellow	White	Lead White
Black	Dark	Dark	Inert	Dark	Dark	Black	Black	Carbon Black
Golden	Bright	Dark	Weak Black/ Black (on Green area)	Light Red/Dark (on Green area)	Light Blue/Dark (on Green area)	Brown	Light Brown	Brass

*So far, no report has been published on the results of these two imaging methods for artistic pigments.

**So far, no report has been published on the results of multi-bands imaging of different pigments in a multilayered manner on a pigment or metal substrate such as gold, silver or brass.

ascertain whether these conditions impacted the pigment preferences of artists.

However, the degradation of brass pigment is evident in the green corrosion products observed in some parts of two manuscripts, as shown in Fig. 2. According to previous studies, these forms of corrosion products are generally known as copper carboxylates. This pigment degradation occurs due to various factors such as a binder, paper sizing, or pollutants [3, 40].

The Raman spectrum of the degraded areas of this pigment is demonstrated in Fig. 3b. The symmetric and asymmetric stretching vibrations of CH_2 are in the range of $2800\text{--}3000\text{ cm}^{-1}$, and the CH_2 rocking and C–C stretching vibrations appeared in the range of $890\text{--}920\text{ cm}^{-1}$. However, the significant vibrations of this spectrum are observed in the range of $1200\text{--}1750\text{ cm}^{-1}$ (Fig. 3c). The main characteristic Raman bands of the metal carboxylates as a degradation product are around 1470 cm^{-1} , which were accurately evaluated using the second derivative. The C–O stretching and CH_2/CH_3 bending vibrations associated with metal carboxylates were observed approximately at 1465 cm^{-1} [43, 44].

Despite the above, the high laser power may cause thermal degradation of the organic materials of these pigments, leading to the appearance of specific carbon bands similar to the studied sample at about 1580 cm^{-1}

and 1350 cm^{-1} [44]. Thus, the type of copper carboxylate cannot be determined with certainty. Nevertheless, carboxylates are the main products of brass pigment degradation and the leading cause of the green color observed.

Black ink

The XRF spectrum of the black ink indicates that it shares the same elemental composition as the paper (Fig. 4a). However, the Raman spectrum of this pigment in Fig. 4b, displays significant peaks at 1330 and 1580 cm^{-1} , which can be attributed to carbon black vibrations [45]. These results suggest that in the manuscripts used carbon-based inks, which is consistent with the multi-band imaging outcomes. Although multi-band imaging is not suitable for identifying black pigments, it can help distinguish carbon black inks from Iron gall ink, particularly in IRFC images [10, 28].

Upon analyzing traditional Persian recipes, it has been observed that Iranian works typically employ six different types of black ink, namely carbon, iron-gall, carbo-gall-vitriol, carbo-gall-alum, peacock, and starch. With the exception of starch and carbon inks, the composition of elements in the other inks varies from that of paper. Despite the similarity in Raman spectra between starch and carbon inks, the extensive usage of carbon black ink

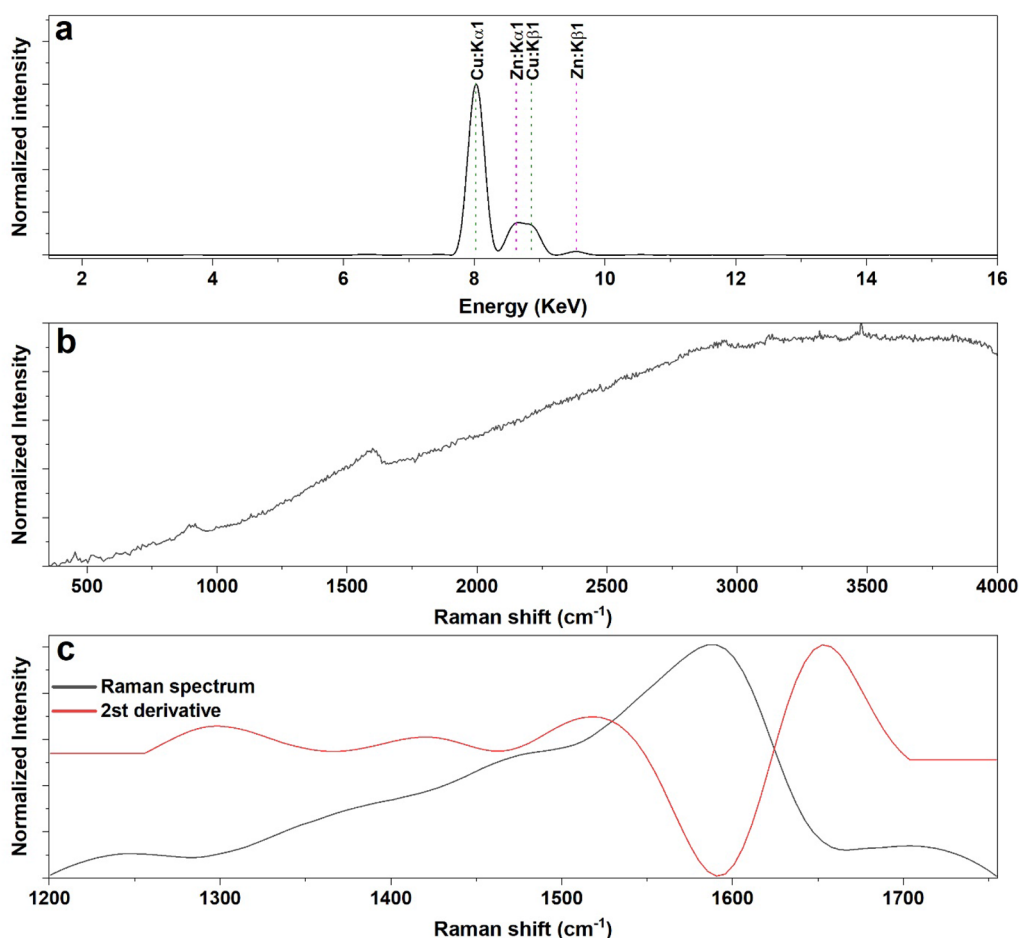


Fig. 3 **a** μ -XRF spectrum of golden parts; **b** Raman spectrum of green corrosion products of golden parts and, **c** the 1200–1750 cm^{-1} range of this spectrum after baseline correction, along with its second derivative, which indicates the metal carboxylates index band at 1465 cm^{-1}

in Persian manuscripts increases the possibility of its use in the studied manuscripts [10].

White pigment

The white pigment analysis using XRF shows a considerable amount of lead (Fig. 5a). This element is likely from the use of lead-based white pigments. However, the white pigment also contains barium, indicating the potential utilization of barite white or lithopone in this color. Therefore, it may be a combination of lead-based and barium-based white pigments.

The Raman spectrum of this white pigment reveals three characteristic peaks at 1049, 985, and 460 cm^{-1} (Fig. 5b). The ultramarine peak at 543 cm^{-1} is also observed in this sample, which is a result of the blue layer underneath the white pigment. In the white pigment spectrum, 1049 cm^{-1} is a characteristic of lead white [46], and 985 and 460 cm^{-1} are characteristic of barite white [47]. Therefore, as the μ -XRF and Raman results indicate, this color represents a mixture of lead white

and barite pigments. Multi-band imaging also identified the presence of lead white, but it is not possible to understand the mixture of this pigment with barite white without spectroscopic methods. Hence, it is evident that imaging results should be supplemented with spectroscopic techniques.

Lead white has been a widely used pigment in Iranian art for a considerable period. Historical sources and various studies have identified it as the primary white pigment and the main ingredient in historic production recipes [39]. On the other hand, barite white is a relatively new pigment in Iranian art, and its usage is not very old. Barite can be obtained naturally or artificially at a low cost, and its discovery dates back to the 16th century. However, it only gained popularity as a pigment in the early 1800s in Europe [48]. The use of this pigment in studied manuscripts indicates that they belong to the Qajar period and suggests that Europe introduced synthetic pigments or their manufacturing techniques to Iran during that era.

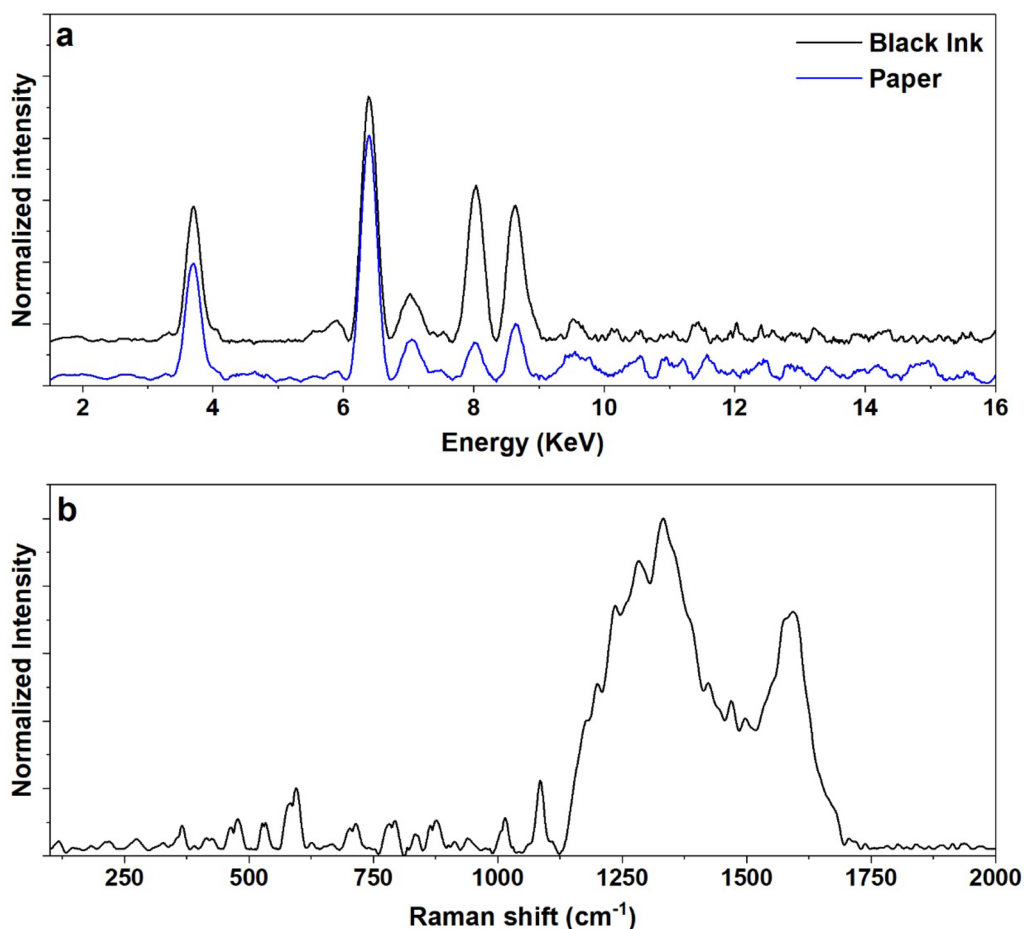


Fig. 4 **A** XRF spectra of black ink and paper exhibiting similar elements. **B** The Raman spectrum of black ink displays the distinctive bands of carbon black at 1330 and 1580 cm^{-1}

Blue pigments

The μ -XRF spectrum of the blue pigment does not reveal any indicator element (Fig. 6a). However, the Raman spectrum shows the characteristic band of ultramarine at 545 cm^{-1} , which is associated with S_3^- as the primary contributor to the blue color (Fig. 6b). Additionally, the carbonate band of calcite, an impurity in ultramarine, was observed at 1088 cm^{-1} [49]. These results suggest that ultramarine was used as a blue pigment in these manuscripts. Ultramarine is a sodium aluminosilicate that contains sulfides and sodium polysulfides, with the chemical composition $(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot m\text{SiO}_2) \cdot x\text{Na}_2\text{S}_n$. The polysulfide radicals (S_3^-) identified in the Raman spectrum are responsible for the blue color of this pigment. The μ -XRF results also indicate the presence of sulfur in this pigment. The identification of ultramarine is consistent with the predictions based on the multi-band imaging results. Thus, multi-band imaging appears to be effective in detecting ultramarine.

Ultramarine, which is a deep blue pigment found on various objects from different times and places, has been extensively studied and discussed in historical treatises [39]. Its chemical composition remained unknown until Desormes and Clement analyzed it in 1806. The pigment is derived from lapis lazuli, a mineral now known as lazurite, which gets its distinctive blue color from the Persian word *Lazaward* [49, 50]. Natural ultramarine was obtained from quarries in present-day Afghanistan and typically contains impurities like iron sulfide or pyrite [39, 49, 50]. However, μ -XRF results indicate that the blue pigment has even less iron content than paper (Fig. 6a), making synthetic ultramarine a more viable option. Although attempts to create artificial ultramarine began in 1787, it was only around 1814 that France started producing it on a larger scale [50].

Examination of the multi-band images related to the light blue pigment also reveals the presence of ultramarine mixed with another pigment (white). Investigation of the μ -XRF spectrum of the light blue pigment

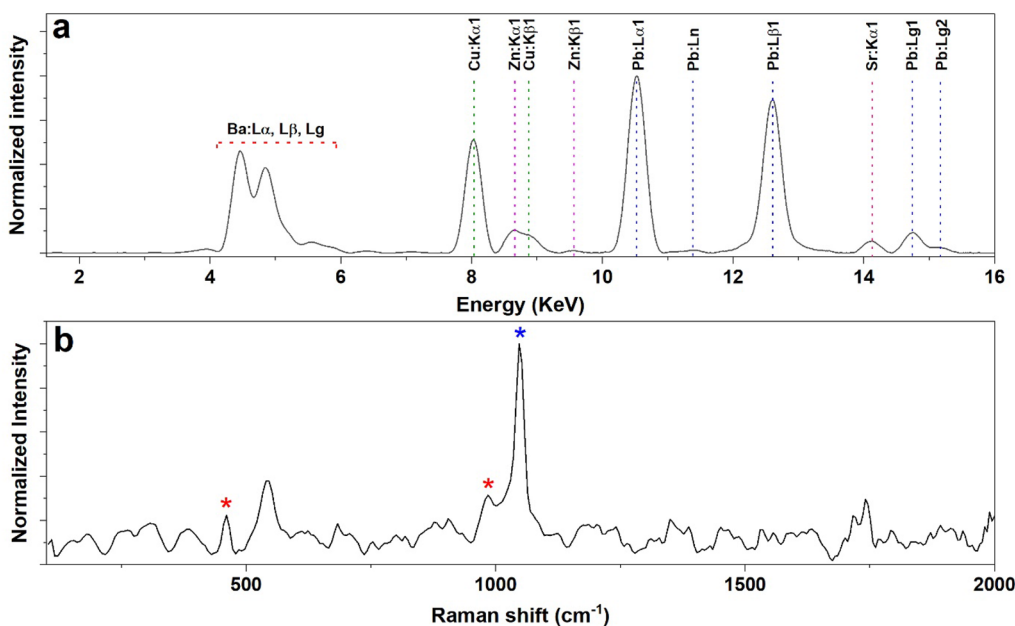


Fig. 5 a μ-XRF spectrum of the white pigment showing the presence of barium and lead. b Raman spectrum of the white pigment with indicator peaks for lead white and barite white marked with blue and red stars, respectively

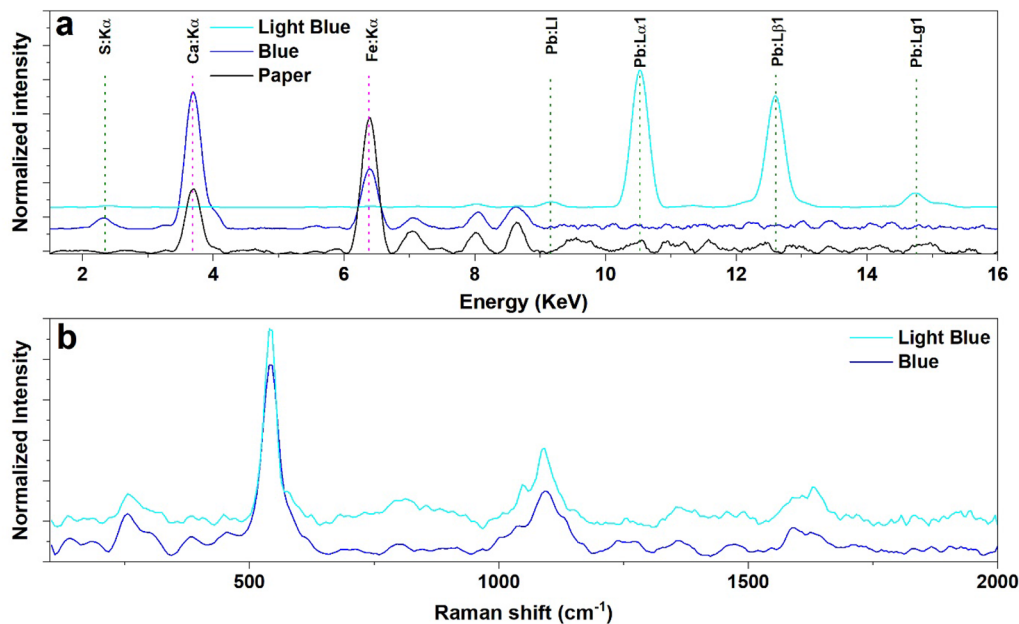


Fig. 6 a μ-XRF spectra of blue and light blue pigments, as well as the paper. b Raman spectra of blue and light blue pigments indicate the presence of ultramarine and a mixture of ultramarine and lead white, respectively

indicates significant amounts of lead, suggesting that lead white may have been used in the mixture of this pigment (Fig. 6a). The Raman spectrum of this pigment shows the vibrations of S_3^- at 545 cm^{-1} and the

vibrations of calcite at 1090 cm^{-1} (Fig. 6b). The peak around 1050 cm^{-1} , characteristic of lead white [46], is also visible in this spectrum, confirming the presence of a mixture of ultramarine and lead white in this pigment. Iranian artworks commonly use lead white as a

white pigment, and its mixture with blue pigments is frequently reported in artworks [3, 15, 51, 52].

Red pigments

Multi-band imaging revealed the possibility of using red lead in orange pigments. However, in sections with a golden substrate, the images showed distinct characteristics compared to the red lead. This was especially evident in the IR-based images, IRR and IRFC, due to the greater penetration of IR rays. Notably, the type of substrate can affect the characteristics of captured images, specifically the IR images. Examination of the μ -XRF spectrum of this pigment also displayed a high amount of lead, as expected (Fig. 7a). Additionally, the Raman spectrum of this pigment revealed the characteristic peaks of red lead at approximately 137, 277, 374, and 541 cm^{-1} (Fig. 7b) [47]. This pigment was widely used in historical Iranian artworks, and references to its use are found in many works [3, 53]. According to earlier reports, the use of red lead in Iran dates back to the Sasanian era [54]. The great popularity of red lead led to its use in combination with other pigments [3]. In the studied works, the μ -XRF spectrum of the pink pigment demonstrated a significant amount of lead as an indicator element, in addition to the orange pigment. The results of the multi-band imaging of this pigment indicated the possibility that a mixture of various white (probably lead white), blue (probably indigo), and red (probably cochineal or

madder) pigments were used. However, the Raman spectrum of the pink pigment showed characteristic peaks of red lead, similar to that of the orange pigment (Fig. 7b). In addition, a weak band corresponding to lead white was observed at 1050 cm^{-1} [46]. Furthermore, the characteristic band of indigo was seen at 1580 cm^{-1} . It is associated with the stretching vibrations of the dual bands C=C and C=O and also the band of N-H in the indigo ring structure [3, 46, 55]. Although spectroscopy does not indicate the use of organic red pigments, based on the UVL images and the observation of red luminescence in this pigment, the possibility of using organic red pigments, especially cochineal, should be considered high [18, 56]. This pigment was commonly used to dye textiles and has also been used as a pigment for painting or writing ink in historical Iranian manuscripts [3, 18].

Regarding the red pigment, the results of μ -XRF spectroscopy did not show the index elements of red mineral pigments (Fig. 7a). Only the element iron was seen in this sample, the amount of which was almost equal to that of the paper substrate. This demonstrated the possibility of using organic pigments, just as imaging techniques also showed the possibility of using cochineal. This pigment also displayed high fluorescence in Raman spectroscopy, making it impossible to record the corresponding spectrum. Therefore, FORS was used to identify this pigment. The reflectance spectrum of this sample together with the cochineal is shown in Fig. 8a. These two spectra

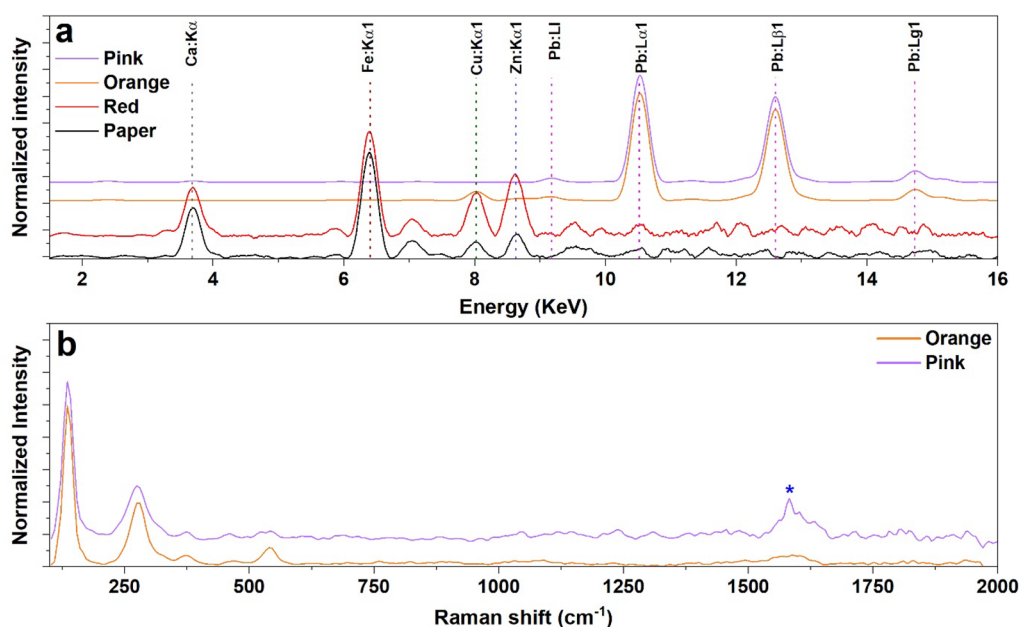


Fig. 7 **a** μ -XRF spectra of red family pigments, including red, pink, and orange, as well as paper, indicating the use of lead-based pigments in pink and orange pigments. **b** Raman spectra of orange and pink pigments providing evidence of the use of red lead and a mixture of red lead, lead white, and indigo, respectively

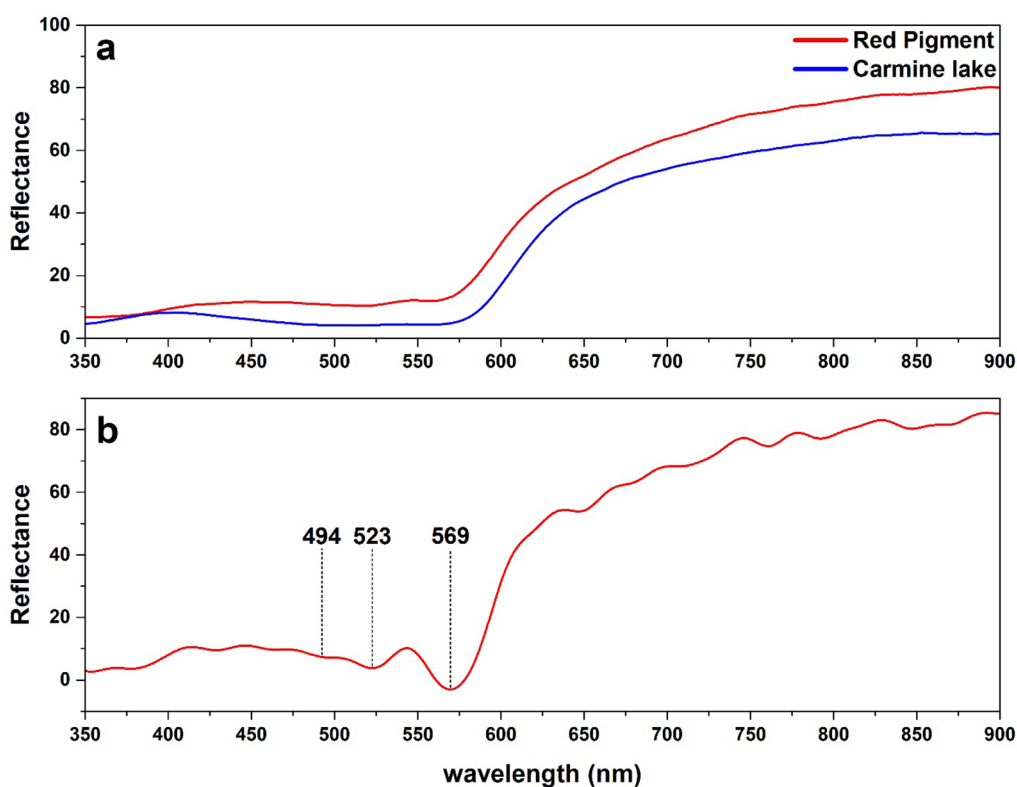


Fig. 8 **a** FORTS spectra of red pigment along with carmine lake; **b** deconvoluted FORTS spectrum of red pigment by Fourier self-deconvolution method, which shows absorption bands of cochineal dye around 494, 523 and 569 nm

displayed high similarity in the 400–900 nm range. The two most common organic red pigments in Iranian works are naturally cochineal and madder [18]. Based on the reflectance spectra of madder and cochineal pigments, the two $n \rightarrow \pi^*$ sub-bands are usually reported at 510–515 and 545–540 (for madder) and 525–520, and 550–565 nm (for cochineal) [57, 58]. However, these bands may be shifted in historical samples. Fourier self-deconvolution was used to determine the position of these bands (Fig. 8b). In the deconvoluted spectrum, two sub-bands were visible around 523 and 569 nm, and a shoulder at 494 nm. According to Fonseca et al. [57], the position of these bands is characteristic of cochineal dye, which is also consistent with the results of multi-band imaging. It appears that cochineal was extensively used as red ink in Iranian manuscripts. This is evident from the examination of another Qur'an from the Qajar period, which confirmed its use in red writing [3].

Yellow pigment

Arsenic is the main element detected in yellow pigments (Fig. 9a). Among traditional yellow pigments, the most prominent arsenic-based yellow pigment is

orpiment [59]. In Fig. 9b, the Raman spectrum of this pigment exhibits characteristic orpiment bands at approximately 145, 200, 300, and 350 cm^{-1} [60, 61], but the features captured in the multi-band images show the possibility of using orpiment or yellow ochre. In contrast, there is no evidence for the use of yellow ochre (iron oxide) in Raman and μ -XRF spectroscopy. It seems that the common methods of multi-band imaging are not able to separate some pigments, especially yellow pigments. In such cases, molecular spectroscopy is inevitable to identify the exact nature of the pigment.

Orpiment is a historical pigment that was discovered on ancient Egyptian works and paintings. It is mentioned in Greek and Roman literature. This pigment is one of the oldest yellow pigments used, and numerous pieces of evidence of its use can be seen in ancient Egyptian works [62–64]. In Iran, which has been introduced as one of the sources of orpiment [65], it has been used in many paintings and manuscripts. For example, in the study of the pigment palette of four Persian manuscripts from the 16th and 17th centuries using Raman spectroscopy, orpiment was identified as a yellow pigment in all four manuscripts [51].

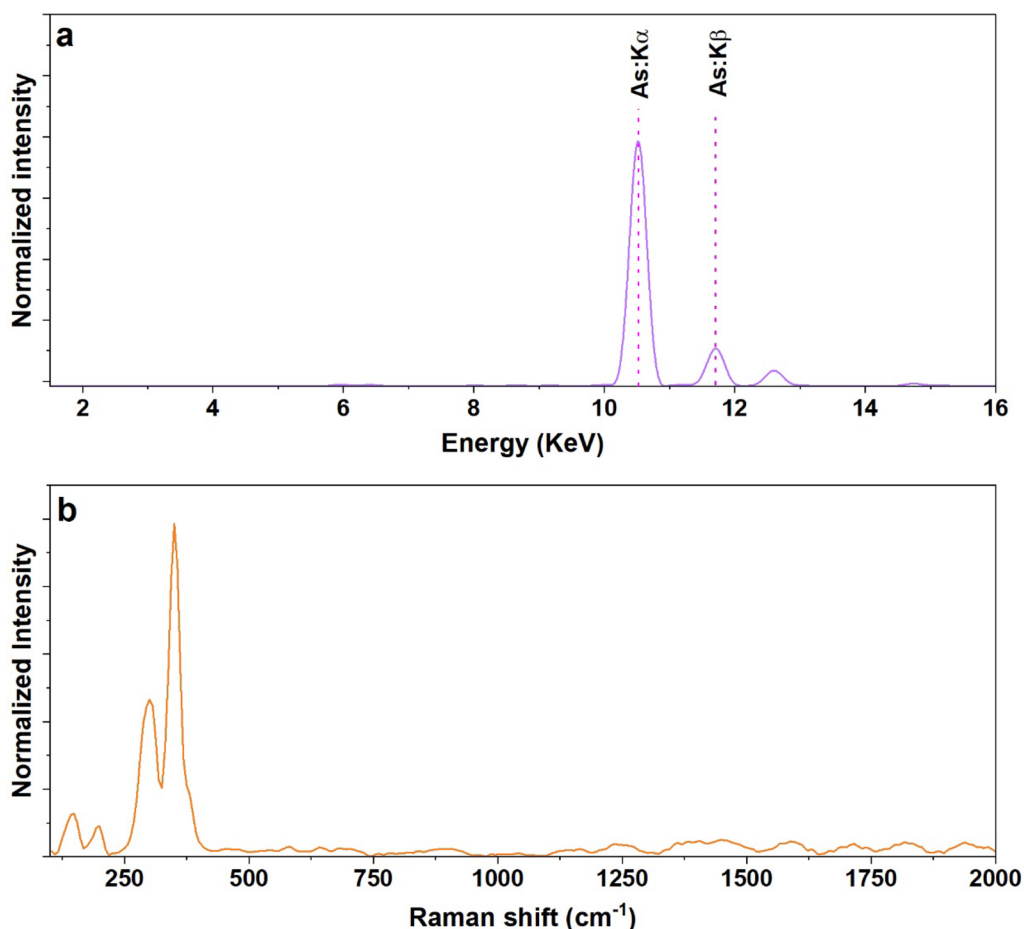


Fig. 9 **a** μ -XRF spectrum of yellow pigment indicating a significant presence of arsenic; **b** Raman spectrum of the same pigment displaying characteristic bands of Orpiment

Green pigment

The green pigment found in the two manuscripts studied contained elements of copper and arsenic (Fig. 10a). This suggests the possibility of emerald green in these parts. Examination of the Raman spectrum of this pigment in Fig. 10b shows specific bands around 154, 175, 217, 242, 295, 324, 371, 430, 491, 539, 686, 761, 836, and also 951 cm $^{-1}$ (corresponding to acetate vibrations). These bands are the identification characteristics of emerald green in Raman spectroscopy [66, 67]. Emerald green with the chemical composition $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ is a bright green synthetic pigment. This pigment was first synthesized in 1814 by Wilhelm Sattler in Schweinfurt, Germany, and quickly found its way into artists' palettes in 1822 [68]. Accordingly, the date on which these manuscripts were written will definitely be after this date. Through analysis of Iranian historical works from the 19th and 20th centuries, it has been discovered that emerald green pigment was likely introduced to Iran during the mid-19th century. Prior

to this, there were no records of this pigment being used in Iranian art. However, once it arrived, artists were drawn to its brilliance and charm, resulting in its frequent use in works from the latter half of the 19th century and first half of the 20th century [39]. This time frame aligns with the dates found in the manuscripts under examination.

The key point, however, is the similarity of the characteristics captured in multi-band imaging for most of the green pigments. Thus, based on the results of multi-band imaging, this pigment was misdiagnosed to be malachite. It is important to mention that there have been limited investigations into the characteristics of emerald green when observed through multi-band imaging. This study, however, is the first to provide a comprehensive analysis of this pigment using multi-band imaging methods. This shows the importance of expanding the multi-band imaging databases of traditional pigments.

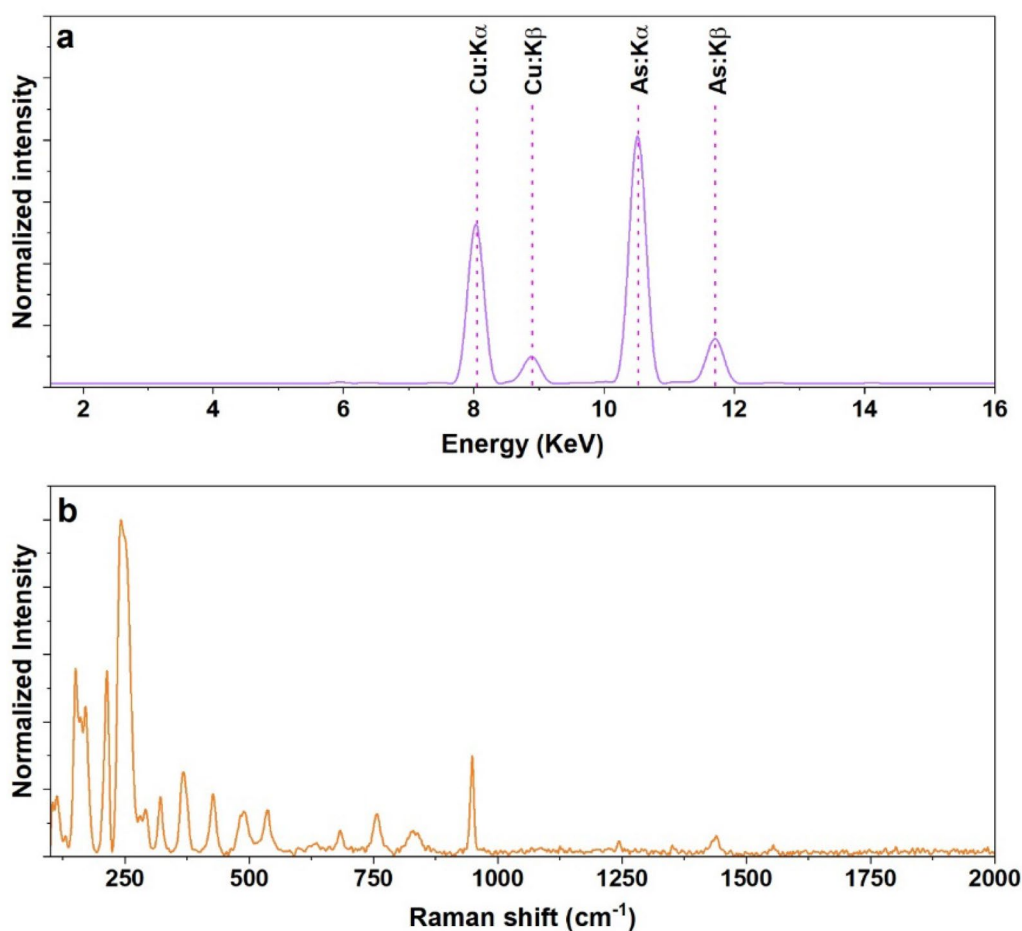


Fig. 10 **a** μ -XRF spectrum shows the presence of copper and arsenic elements in the green pigment. **b** Raman spectrum of the same pigment, highlighting the characteristic bands of emerald green pigment

Conclusions

This study aimed to identify the pigments and inks used in three Qajar-era illustrated manuscripts, each of which had distinct colors and motifs. Non-invasive analytical tools such as Raman spectroscopy, μ -XRF, FORS, and spectral imaging were employed to perform this identification. The primary classification of artwork pigments was found to be feasible through multi-band imaging. In addition, multi-band imaging offered clues regarding the nature of the pigments used in the manuscripts. However, the results obtained from μ -XRF and Raman spectroscopy were occasionally inconsistent with those from multi-band imaging due to metal substrates having an impact on the acquired images of the studied manuscripts. Therefore, it is necessary to supplement multi-band imaging with methods such as Raman spectroscopy to identify the types of pigments. Moreover, databases of multi-band imaging should be completed and updated based on the type of substrate. In addition, multi-band imaging is a valuable tool for evaluating the prior

treatment history and current condition of artwork conservation, allowing for discrimination between original and conservation areas. Specifically, the tool can identify discoloration, sizing, and metal corrosion, particularly in UVL images. Furthermore, it was observed that combined pigments were used, and multi-band imaging helped better understand the nature of these pigments.

Additional investigation obtained by using μ -XRF and Raman spectroscopy represents the use of brass sheets as a gold background, which was associated with corrosion and the formation of copper carboxylates in some parts. As expected, the black pigment used in ink and black parts of artworks is Carbon black. Examination of the white pigment indicates that lead white has been used mixed with barite. Furthermore, emerald green, cochineal (identified with FORS), ultramarine, orpiment, and red lead were used in the green, red, blue, yellow, and orange parts, respectively. The identification of emerald green, which became common in artists' palettes from the middle of the 19th century, confirms the attribution

of these works to the Qajar era. Besides to white color, the use of a mixture of pigments in pink and light blue colors was also observed. Accordingly, In the case of the pink color, evidence of the use of red lead, lead white, indigo, and probably cochineal was observed. In this regard, the results of multi-band imaging played an essential role in the identification of this color due to cochineal luminescence. The light blue pigment was also identified as a mixture of ultramarine and lead white.

These findings highlight the need for updating multi-band imaging databases for historical pigment identification, particularly for mixed pigments and with different substrates, which present challenges.

Author contributions

AK designed the work process and analyzed and interpreted the data. EMM and BJB participated in experiments. All authors discussed the results and contributed to the final manuscript. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this published article.

Declarations

Competing interests

The authors declare no competing interests.

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