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# Identification of pigments used in a Qajar manuscript from Iran by using atomic and molecular spectroscopy and technical photography methods

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## Abstract

The present study aimed to identify pigments used in writing and decorating a Qur'an manuscript related to the early years of the Qajar era, a royal dynasty ruling over Iran from 1789 to 1925. The pigments were analysed using  $\mu$ -XRF, SEM-EDS, Raman, and FTIR spectroscopy. Also, various technical photography methods were used to study the pigments including visible-reflected (VIS), infrared photography (IR), ultraviolet-reflected (UVR), and ultraviolet-induced visible luminescence (UVL) along with infrared false color (IRFC) and ultraviolet false color (UVFC) methods. Carbon black, red lead, and indigo were identified as black ink, orange, and blue pigments, respectively. A mixture of red lead and vermilion was also detected in the red/orange ink. White lead and calcite were also used as additives in blue color. A cochineal-based pigment was also used as red ink in some parts of the manuscript. However, the evaluation of golden color showed two types pigments of gold and brass alloys in different parts of the manuscript. Copper carboxylate was identified as the product of the destruction of this pigment. According to the results of the study, technical photography methods along with spectroscopic methods are a good tool to examine manuscripts and identify included pigments and reduce the amount of possible error and the need for destructive sampling.

**Keywords:** Qajar manuscript, Pigments, Technical photography,  $\mu$ -XRF, SEM-EDS, Raman, FTIR

## Introduction

Pigment identification is one of the most important goals in the scientific study of historical objects [1]. In general, recognizing color is important from several aspects, including the historical understanding of an art work, understanding the processes of its destruction and even the development of conservation methods, as well as solving the problems of dating and attribution to the creator of the work [2–4]. Also, recognizing the elements in a work of art or history provides the first acceptable clues for comprehending the origin of raw materials and the used process [5]. Aesthetic, stylistic, and archived

assessments are usually somewhat responsive [6]. However, in many cases, extracting information about pigment identification requires laboratory methods and tools to understand the structural nature of pigments, with the help of which we can talk about the origin and authenticity of the works confidently [7].

Generally, several methods such as X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD) analysis, Raman spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, particle induced X-ray emission (PIXE) spectroscopy, scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) and polarized light microscopy (PLM) have been used to identify pigments [2, 3, 8–14]. Non-destructive X-ray analysis methods have been widely used to study historical pigments. This method is popular as a result of its relatively

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lower cost in addition to its non-destructive properties in its simultaneous application allowing to study the mineralogy and chemical properties of the samples [3]. XRF provides potential information about the constituent elements of pigments in various materials [15]. This method has long been used to identify historical manuscript illustrations pigments and oil paintings [4, 6, 16]. In addition to with XRF, SEM–EDS is another efficient method for the analysis of artistic and historical pigments, which allows the simultaneous study of microstructure and chemical properties in addition to needing for amount of sample and cost-effectiveness [3]. SEM–EDS is also used to study the degradation of metal-based pigments [17]. Moreover, it is used to determine the initial composition of pigments and metal or organic inks used in writing and decorating historical manuscripts [18, 19]. Along with all these analytical tools, some researchers have used different methods of multispectral or hyperspectral imaging to identify pigment [20, 21]. Although this way of analysis is somewhat limited, it can provide useful information for analyser on a large scale in a short time and at low cost [22]. Among such methods are infrared photography (IR), ultraviolet reflected (UVR), ultraviolet luminescence (UVL), ultraviolet false color (UVFC), infrared false color (IRFC) methods, which are used to identify pigments, coatings, variations, and underdrawings in studying historical artifacts, especially paintings [22–28]. However, there are many studies using combined pigment detection methods that certainly provided more reliable results and presented other researchers comprehensive understanding of the nature of an object regarding the limited access to the sample [9]. Accordingly, as mentioned, the identification of pigments not only provides significant information in the field of art history, but also provides the basis for identifying their degradation processes to provide optimal treatment solutions and allow the recognition of the originality of the work.

There are several reports to identify pigments in Persian historical manuscripts, especially related to the Qajar period (1789–1925). The reports show the most identified colorants are mineral-based pigment. Red lead [29], vermilion [8, 29], ultramarine [29], Prussian blue [29], orpiment, verdigris, lead white, barium sulfate, emerald green, lead chromate, viridian pigments [30] and carbon black and iron-gall inks [8, 29, 30] have been identified in many Qajar manuscripts. Cochineal, indigo and saffron are also common organic-based pigments in these manuscripts [29]. Moreover, lead-containing compounds are usually identified as a thickening agent and/or chemical drier along with other pigments, especially organic pigments such as indigo or saffron [29, 30]. Pure gold, brass, as imitation gold, and sometimes gold-silver alloys were also used to gild the manuscripts [29–31].

Therefore, this study is also aimed to identify the pigments used in writing and decorating the pages of a manuscript using  $\mu$ -XRF, SEM–EDS, Raman and FTIR spectroscopy along with technical photography methods. This is a manuscript of the Holy Quran related to the early Qajar era, dated 1210 AH (1795–1796 AD). The identification of the constituents of the today's work reveals new windows of science and technology of the artists of the past.

## Materials and methods

### Sample preparation

The work studied in this research is a manuscript dated 1210 AH (1795–1796 AD), based on a stamp in Abdu-Ahsan-Ibn-Ali's name (Fig. 1b), related to the first years of Qajar dynasty in Iran [32]. This manuscript belongs to a family collection in Kashan city (In Isfahan province, Iran), which was transferred to the conservation laboratory of Tabriz Islamic Art University for conservation work. The main part of the text was written using black ink. Moreover, parts of the text were written by light red ink and red/orange ink. The edges of the pages are also decorated with blue, black, golden and orange strips as a margin. Golden color changed to green in only a few pages, indicating pigment degradation and the possibility of using two types of golden color. Golden pigments without and with green corrosion products were named golden I and II, respectively (Fig. 1). Sampling for SEM–EDS,  $\mu$ -XRF and Raman spectroscopy was performed with the paper support in dimensions of 1mm<sup>2</sup>, using a scalpel. Removal of sediments and contaminants of surface was performed by mechanical method and the samples for FTIR spectroscopy were prepared in powder form by surface cutting method using a scalpel, under a stereo microscope. All samples were kept in standard laboratory conditions until experimental analysis.

### Polarized Light microscopy

An optical microscope Olympus BX51 M was used, and photomicrographs were recorded with a digital canon camera. The Blue sample was embedded in an epoxy resin support, then cross-sectioned and polished using silicon carbide card with successive grids from 100, 400, 800, to 1200. This polished cross-section was examined under reflective cross-polarized light at 1000 $\times$  magnification. Immersion oil was also used to increase the optical resolving power of the microscope. The surface of other pigments was examined with a 10 $\times$  objective, without preparation.

### SEM–EDS

Field emission gun-scanning electron microscopy (FEG-SEM) analysis was done by a TESCAN MIRA3 FEG-SEM



model (Tescan, Czech Republic) with energy-dispersive X-ray spectroscopy (EDS) and primary electron beam energy 15 keV (in central laboratory, University of Tabriz). EDS analysis was performed on black inks, light red ink and blue pigment to identify light elements. The samples were analysed without coating to assess the possibility of the presence of gold. Elements were identified using NIST DTSA-II Lorentz software and spectra were processed using OriginPro 2021 software.

#### FTIR Spectroscopy

The blue and golden II pigments along with paper were analysed by a Fourier transformed infrared spectrometer. Blue pigment was analysed to identify different compounds in the pigment mixture and golden II pigment to identify its green corrosion products. FTIR analysis was carried out using a 680Plus FTIR spectrometer (Jasco Inc., Japan) with KBr pellets (in central laboratory, Tabriz Islamic Art University). All spectra, including samples and backgrounds, were collected at room temperature in the range of  $400\text{--}4000\text{ cm}^{-1}$  with a resolution of  $2\text{ cm}^{-1}$  and 64 numbers of scan. The background spectrum was collected before each sample spectrum. Omnic 9 (ThermoFisher Scientific Inc., USA) and OriginPro 2021 software were used to analyse the spectra.

#### $\mu$ -XRF spectroscopy

XRF analysis was used to identify the major elements of black ink, light red ink, orange, red/orange and golden pigments along with paper. An Unisantis 104 X-ray micro fluorescence spectrometer was used for XRF experiments (in central laboratory, Art University of Isfahan). 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 inks and pigments, except for the golden pigments, were recorded at room temperature using a HORIBA Jobin Yvon Raman spectrometer with 532 nm (green), 638 nm (red) and 785 nm (red) lasers (in Physics Department Laboratory, Humboldt-University of Berlin). Data was collected with both a 1200gr/mm and an 1800gr/mm grating, with 60 accumulations of 10 s for light red ink and 10 accumulations of 10 s for other pigments. Raman spectra were recorded with excitation of 532 nm for light red ink and 785 nm laser for other pigments with a resolution of  $2\text{ cm}^{-1}$ . All reference spectra are from Pigments

Checker v.5, a free spectra database of pigments from cultural heritage science open source (CHSOS) [33].

### Technical photography

All images were captured by the modified camera Nikon D750 after removal of the inbuilt UV-IR blocking filter, in order to exploit the full sensitivity of the CMOS sensor (ca. 350–1100 nm). 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 flashlight placed at 45 degrees angle to the subject were used as illuminate sources and an X-rite color checker was used as a spectral reference to correct images and compare with reference samples.

Technical photography images, include Visible-Reflected (VIS), Infrared photography (IR), Ultraviolet-Reflected (UVR), and Ultraviolet-induced Visible Luminescence (UVL), were recorded in RAW format and highest resolution (24 megapixel: 6016 × 4016) using the filters described in Table 1. Raw images obtained from the camera were converted into 16bit TIF format in Adobe Photoshop software. Post-processing and calibration procedures were performed according to Kushel method [34] and Cosentino recommendations [35]. False-color infrared (IRFC) and false-color ultraviolet (UVFC) images were obtained by combining VIS with IR and UVR images, respectively, based on the method proposed by Dyer et al. [36].

## Results and discussion

### Atomic and molecular spectroscopy

#### Black ink

SEM-EDS and  $\mu$ -XRF spectroscopy were used to investigate the elemental composition of black ink used in the margin tabulation and the main text. Although according to ancient ink-making recipes, there were different types of inks, carbon black and Iron-gall ink have been normally two widely used types of inks in different historical era of Iran. They are sometimes used in combination and the amount of iron in the

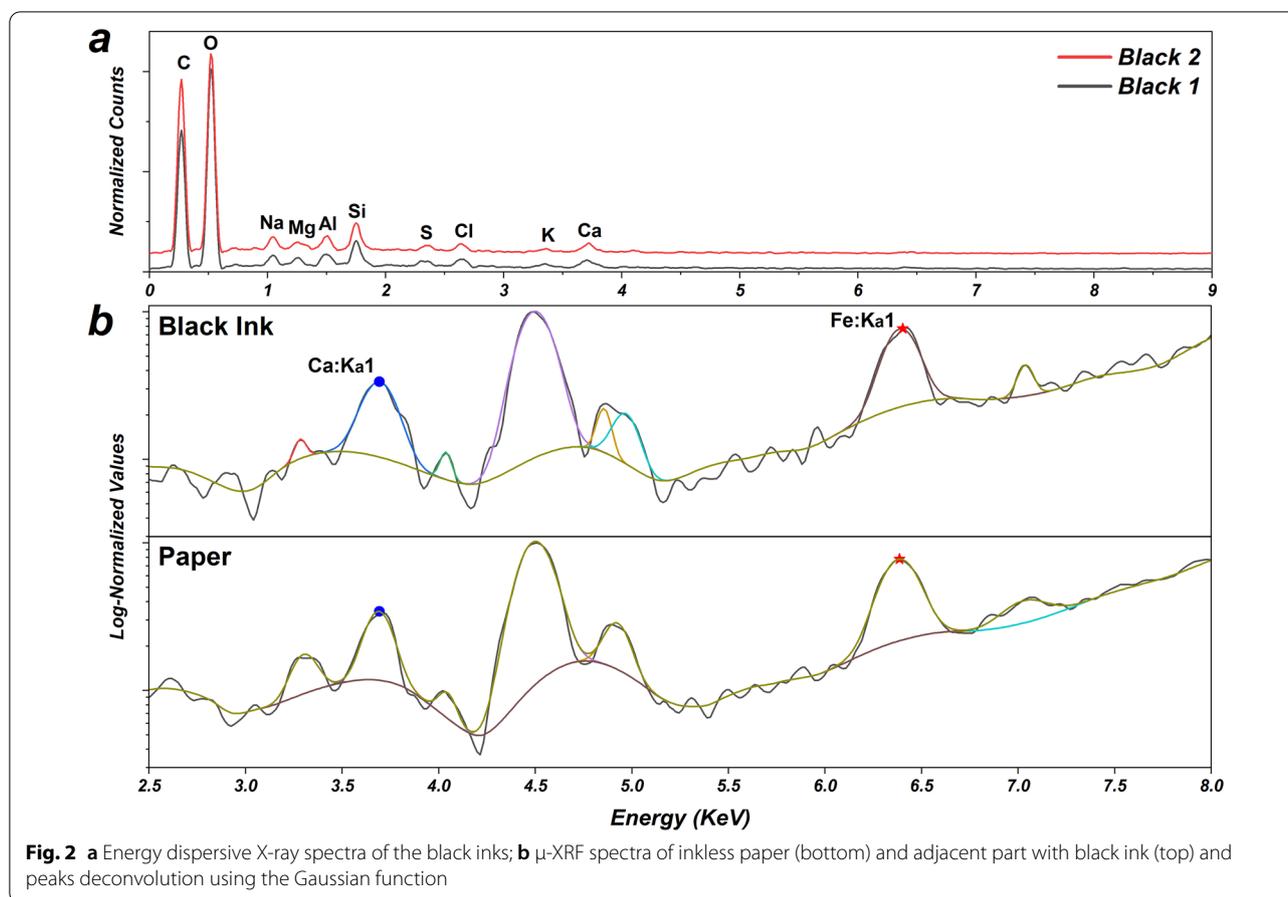
compound can be considered as a criterion for determining the type of ink [37]. A qualitative evaluation of the index elements in the pigment composition using SEM-EDS is presented in Fig. 2a. Spectra of black inks represent no significant element other than carbon, which indicates the possibility of using an iron gall ink in writing this manuscript is negligible. However, a very small amount of iron is observed in the range of 6.4 keV corresponding to its  $K\alpha$  line.

Figure 2b shows the  $\mu$ -XRF spectra related to the parts of the paper with and without ink for investigation of the presence of iron as an indicator of the possibility of using iron-gall ink. The peak intensity ratio of iron to calcium was used to qualitatively evaluate the difference between the content of iron in the ink compared to paper. In fact, the higher ratio of iron to calcium in the ink can be considered a criterion for expressing the presence of more iron in the ink. For this purpose, peak deconvolution is performed on these spectra and the characteristics of iron and calcium peaks ( $K\alpha$  line) are presented in Table 2. The  $I_{Fe}/I_{Ca}$  ratio is 2.339 and 2.468 in ink and paper, respectively. In other words, the iron/calcium ratio did not increase in the inked area, rather slightly decreased. This indicates the absence of iron in the ink. Hence, the ink type cannot be considered as iron gall.

Figure 3 shows the Raman spectrum of black ink. Raman spectroscopy is generally a good tool to study the pigments and distinguish the carbon black from iron-gall ink. According to previous studies, carbon black is can be normally recognized by two index bands of about  $1335\text{ cm}^{-1}$  and  $1585\text{ cm}^{-1}$ . The iron-gall ink, has an index and a sharp peak of about  $1480\text{ cm}^{-1}$  [38–41]. Based on the spectra of sample, carbon black and Iron-gall inks [33] in Fig. 3, only two wide peaks of about  $1585\text{ cm}^{-1}$  and  $1335\text{ cm}^{-1}$  can be seen in the ink of this manuscript, therefore, due to the absence of an indicator band of about  $1480\text{ cm}^{-1}$ , carbon black should be considered as the type of this ink.

**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 camera	Range investigated
Visible-reflected imaging (VIS)	2 × Youngenu NY660 Xenon flashlight, each mounted with soft box (without filter)	Baader UV/IR Cut	420–680 nm
Ultraviolet-induced visible Luminescence imaging (UVL)	+ 2 × Hoya U-360	Baader GUV/IR Cut	420–680 nm
Infrared imaging (IR)	2 × Youngenu NY660 Xenon flashlight, each mounted with soft box (without filter)	Schott RG830	830–1100 nm
Ultraviolet-reflected imaging (UVR)	+ 2 × Hoya U-360	Baader U-Venus	350–380 nm



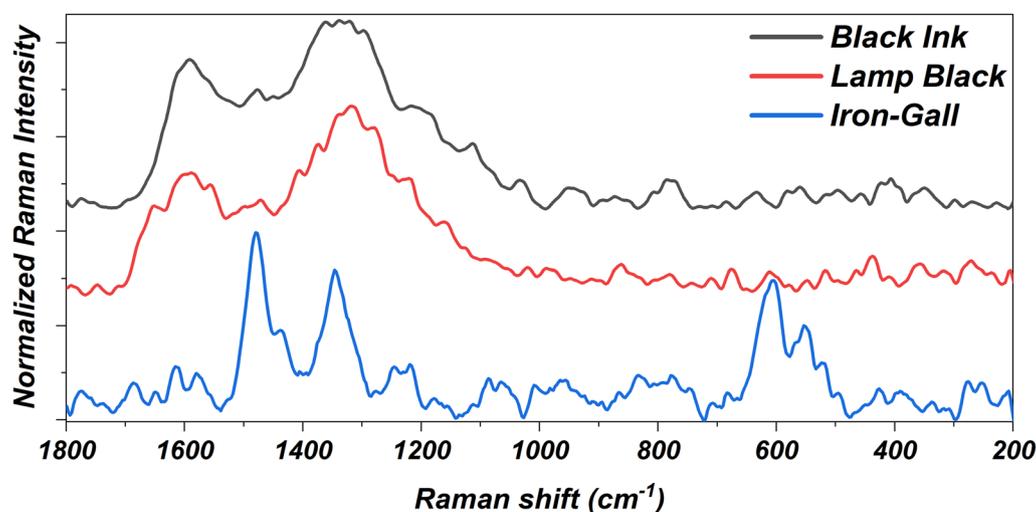
**Table 2** Characteristics of  $\mu$ -XRF deconvoluted peaks related to Fe-K $\alpha$  and calcium for ink and paper

Sample	Element	Peak Type	Area	Center	Height	FWHM	$I_{\text{Fe}}/I_{\text{Ca}}$
Paper	Ca: Ka	Gaussian	0.03896	3.6888	0.22694	0.16129	2.468
	Fe: Ka	Gaussian	0.13555	6.38509	0.56015	0.22733	
Black Ink	Ca: Ka	Gaussian	0.04965	3.69192	0.23261	0.20051	2.339
	Fe: Ka	Gaussian	0.11654	6.39177	0.54406	0.20124	

### Red and red/orange pigments

The two orange and red/orange pigments are seen in the margins of all the pages of the book and parts of the text, respectively (Fig. 4a, b). The  $\mu$ -XRF spectrum evaluation of orange pigment can be seen in Fig. 4c. In evaluating the spectrum of this pigment, significant indicative peaks of about 10.54 keV and 12.61 keV related to the Pb-L $\alpha$  and Pb-L $\beta$ , respectively, representing the use of lead-based pigment. The presence of a lead-based pigment was validated by Raman spectroscopy through the detection of 226, 315, 392 and 550  $\text{cm}^{-1}$  peaks, attributed to the red lead [42] (Fig. 4e). Red lead ( $\text{Pb}_3\text{O}_4$ ) is a popular and widely used pigment in red/orange color. It has been

widely used in Iranian art and paintings [43]. In this manuscript, it was used to draw the strips of paper margins. A red/orange pigment was also used in some parts of the text, for which the  $\mu$ -XRF spectrum of is represented in Fig. 4d. In this pigment, lead is the dominant and indicator element representing the use of a lead-based pigment in this sample. However, the deconvolution of the curve in this sample indicates the presence of minor peaks in 9.9 keV and 11.8 keV related to the Hg-L $\alpha$  and Hg-L $\beta$ , respectively. This indicates the possibility of using a mercury-based pigment, such as vermilion (mercury sulfide), in combination with lead-based red pigment or the presence of Hg as an impurity in the paint. The Raman



**Fig. 3** Raman spectra of the black ink used in the studied manuscript along with carbon black and iron-gall inks, collected with 785 nm laser excitation

spectrum of pigment is presented in Fig. 4e close to the red lead and vermilion as reference [33]. In this pigment, the mixture of red lead and vermilion was validated by Raman spectroscopy through the detection of 230, 315, 392 and 550  $\text{cm}^{-1}$  peaks, attributed to the red lead and, also by 255, 287 and 346  $\text{cm}^{-1}$  peaks relative to the vermilion [42]. Microscopic examination of red/orange pigment with cross-polarized light also shows the mixture of two types red pigments (Fig. 4b).

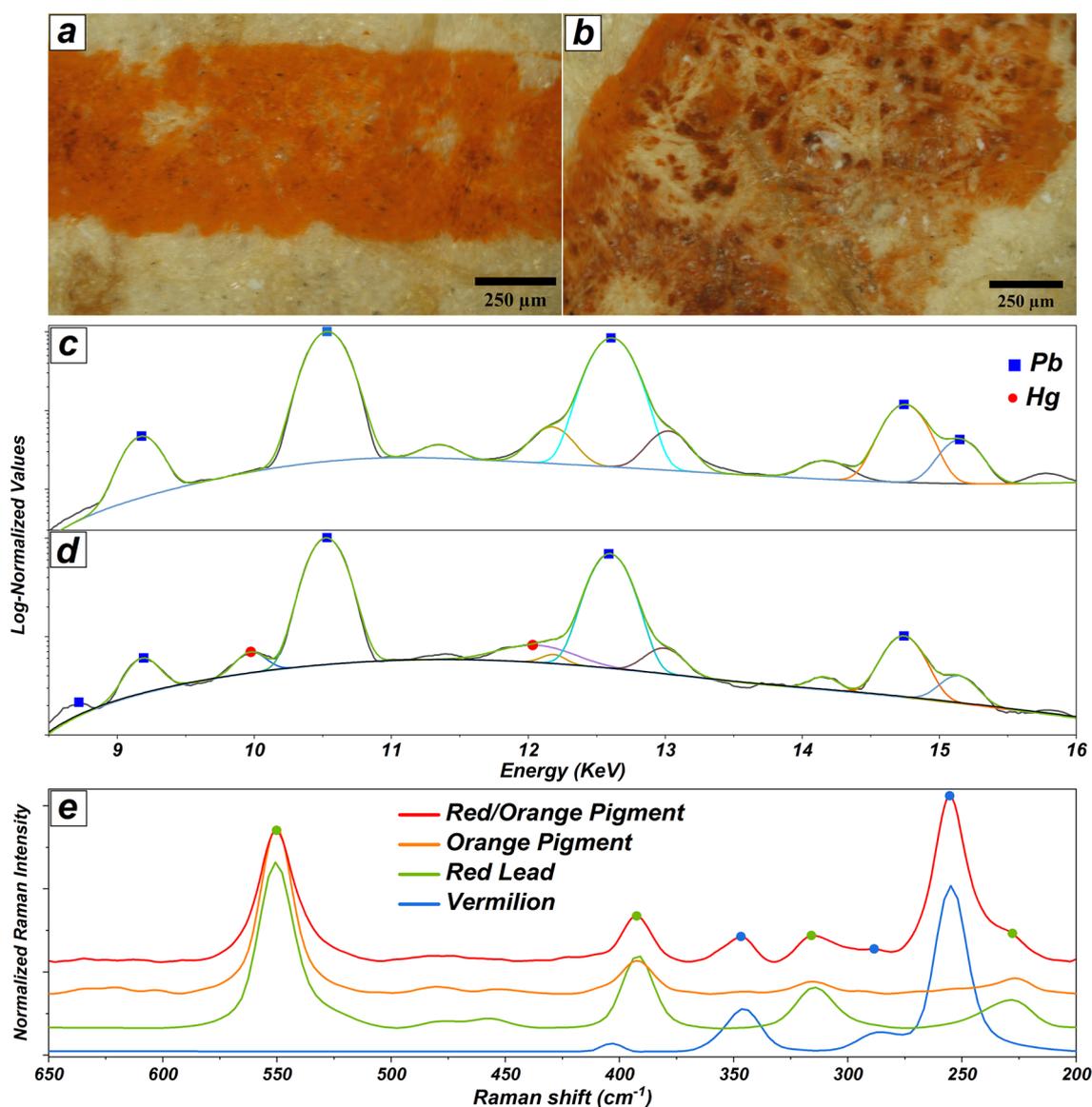
Of course, using the combination of red lead and vermilion was common in the past centuries owing to the relatively high price of vermilion [44]. Hence, adding vermilion to red lead to improve its color properties for writing in this manuscript, is not unexpected.

In addition to the red/orange pigments, a light red ink can also be seen in some parts of the manuscript. However, examination of the  $\mu$ -XRF spectrum represent no significant elemental difference compared to the background paper (Fig. 5b). In general, according to historical Persian treatises, the pigments of cinnabar, iron oxide, realgar, red lead and cochineal have been the main red pigments used in Persian miniature and painting [45]. Failure to identify the indicator element in excess of the paper elements suggest the use of an organic dyes in this ink. Moreover, analysis of this sample was performed using SEM-EDS analysis as shown in Fig. 5a representing no significant elements related to mineral pigments, which indicates the organic nature of the dyeing agent of this sample. However, there is a clear difference between the spectrum of this dye and other spectra in 2.01 keV for the P-K $\alpha$ , which is not observed in other samples. Previous studies indicated that the presence of phosphorus in

red pigments is generally due to the animal source in the dye extraction [46]. Since phosphorus is an important element in the metabolic processes of insects, it is usually found in greater amounts in pigments derived from insects rather than in plants [46]. The main red dyes derived from scale insect include cochineal, kermes and lac dye. Raman spectrum acquired from this pigment at 532 nm excitation exhibit indicator signals at 1643, 1476, 1316, 1220 and 1104  $\text{cm}^{-1}$ , which match the main Raman bands of cochineal-based pigments (Fig. 5c) [47].

#### Blue pigment

A blue strip is used in the margins of all pages. Microscopic examination with cross-polarized light shows the combination of two pigments of white and blue in this section (Fig. 6a), which seems to be more blue in the edges of this strip. A single layer of a mixture of blue and white pigments can also be seen in the cross-section with 1000 $\times$  magnification (Fig. 6b). The elements of this pigment were identified using SEM-EDS. Examination of the EDS spectrum in Fig. 6c shows a significant peak around 2.34 keV, related to the Pb-M $\alpha$ . The high amount of lead in this sample is probably related to the white lead, which is used to dilute the blue pigment. White lead is one of the most important pigments used in painting and decoration of Iranian manuscripts and it is commonly used along with other pigments to improve their properties [10, 48, 49]. Considering the absence of another element representing a mineral blue pigment, the possibility of using an organic pigment in combination with white lead is not unexpected. Examination of historical Iranian treatises also shows that the use of indigo with white lead

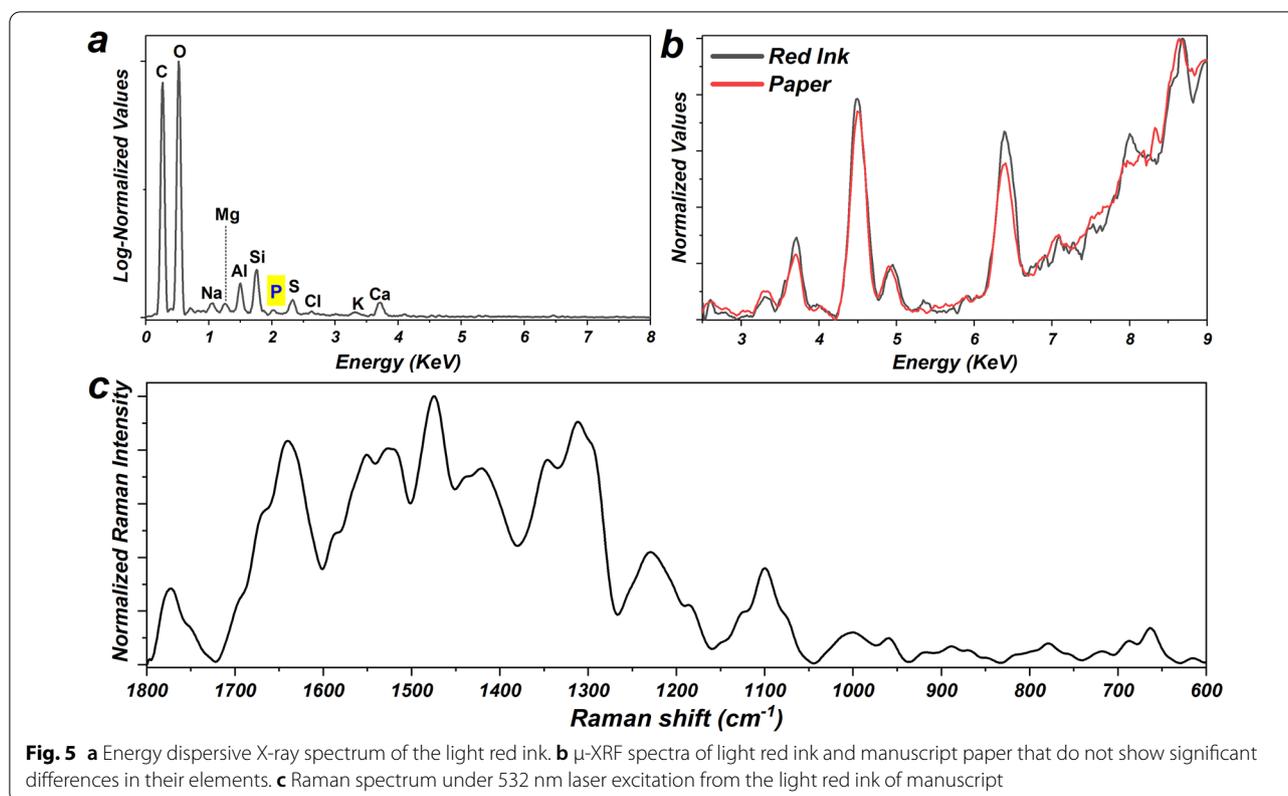


**Fig. 4** Reflective cross-polarized light microscopic image of the orange strip at the margins of the papers (a) and red/orange pigment (b), indicating a mixture of two types pigment;  $\mu$ -XRF spectra of orange (c) and red/orange (d) pigments with peak deconvolution based on the Gaussian function in the range 8–16 keV; (e): Raman spectra of the orange and red/orange pigments of manuscript with red lead and vermilion, collected with 785 nm laser excitation, showing the presence of red lead in orange and a mixture of red lead and vermilion in red/orange pigment

was very common in decorating Iranian historical manuscripts [50]. White lead was normally added to the indigo pigment to brighten and substantiate [51], and their combination was reported in various studies [52–54].

Figure 7 shows the FTIR spectrum of the blue sample. The reference spectra of white lead and calcite are also presented for comparison. In this spectrum, the absorption band of about 1411 cm<sup>-1</sup> is associated with the carbonate vibrations. This vibration for white lead

and calcite was reported at 1405 cm<sup>-1</sup> and 1440 cm<sup>-1</sup>, respectively [2]. Based on the spectra in Fig. 7, the main difference between calcite and white lead in the absorption band at 683 cm<sup>-1</sup> was associated with carbonate vibrations [55]. Vibration at 3540 cm<sup>-1</sup> is observed at the white lead spectrum, which is not seen in calcite. In contrast, carbonate vibrations in calcite have two significant absorption bands in 712 cm<sup>-1</sup> and 873 cm<sup>-1</sup> [56, 57]. Therefore, the range of 650 to 900 cm<sup>-1</sup> can

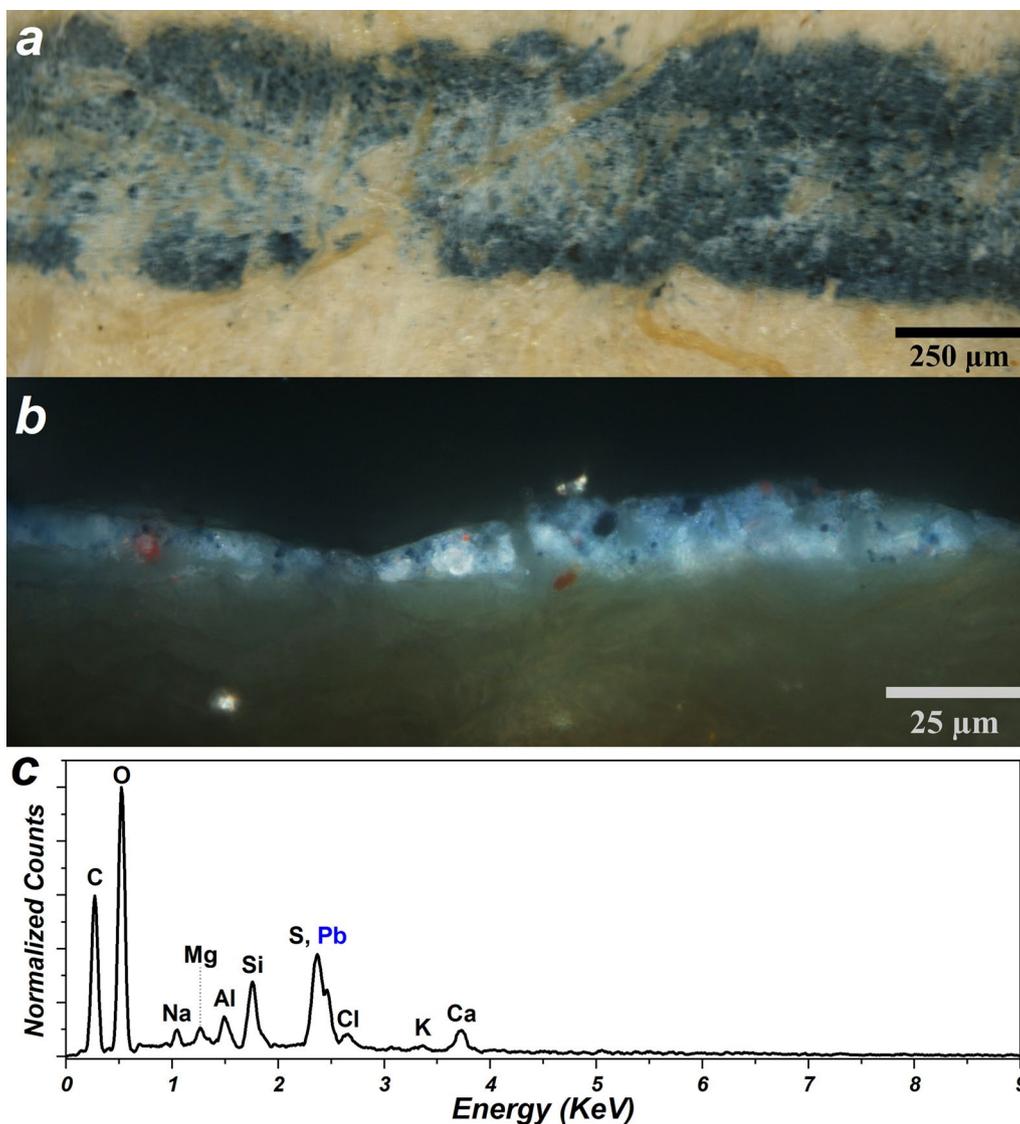


be considered appropriate for the separation of calcite and white lead using FTIR spectroscopy. Evaluation of the blue sample spectrum in Fig. 7a shows two absorption bands of 683  $\text{cm}^{-1}$  and 3540  $\text{cm}^{-1}$  of white lead. The absorption bands of 712  $\text{cm}^{-1}$  and 873  $\text{cm}^{-1}$  are also visible, which are characteristics of calcite. Furthermore, another index absorption band of the calcium carbonate is around 2512  $\text{cm}^{-1}$  [58], which is not seen in white lead. Therefore, the second derivative was examined in the range of 2450 to 2600  $\text{cm}^{-1}$  (Fig. 7b) to investigate the weak peaks, according to which the absorption band 2512  $\text{cm}^{-1}$  can be observed in calcite and blue sample. In addition, the paper spectrum does not show the vibrations of the calcite structure, and hence the origin of the calcite is related to the blue pigment. Therefore, it seems that in this sample white lead along with calcium carbonate was also used to correct the blue color characteristics. The presence of amount of calcium in the sample can also be observed in SEM-EDS spectrum (Fig. 6c).

Moreover, in deconvoluted FTIR spectrum of blue in the range 1560–1670  $\text{cm}^{-1}$  (Fig. 7c), the absorption bands of 1630  $\text{cm}^{-1}$  are also seen corresponding to the stretching vibrations of C=O and bending vibration N–H, the absorption bands of 1613 and 1589  $\text{cm}^{-1}$  corresponding to stretching vibrations of C–C ring and also the absorption

bands of 1075  $\text{cm}^{-1}$  corresponding to the stretching vibrations of C–C and bending vibration of C–C and N–H, which are structural characteristics of indigo pigments [59, 60].

To more accurately identify the indigo pigments, Raman spectroscopy was used with a focus on the blue dots. The sample spectrum is presented in Fig. 8 close to the indigo as a reference [33]. The most significant signal observed at about 1577  $\text{cm}^{-1}$  is associated with the stretching vibrations of the dual bands C=C and C=O and also band of N–H in the indigo ring structure. The rocking vibrations of the N–H groups are found at about 1221  $\text{cm}^{-1}$  and the stretching vibrations of CC ring and the asymmetric rocking vibrations of CH are observed at about 1312  $\text{cm}^{-1}$  indicating the indigo structure. In addition to these vibrations, the signals of 1367  $\text{cm}^{-1}$  (rocking NH, stretching CN and rocking in phase CH), 862  $\text{cm}^{-1}$  (in-plane C–C, C–N and N–H), 596  $\text{cm}^{-1}$  (in-plane C–H, C–C and N–H), 544  $\text{cm}^{-1}$  (C–H and in-plane C–C) and 254  $\text{cm}^{-1}$  (twisting vibrations of C–N, C–H and C–C) are also associated with the vibrations of the indigo pigment structure based on the previous studies [59–61]. Furthermore, a peak at about 1095  $\text{cm}^{-1}$  was observed in the sample spectrum related to the vibrations of carbonate in the



**Fig. 6** Reflective cross-polarized light microscopic image of the surface (a) and cross section (b) of blue strip at the margins of the papers indicating a mixture of blue and white pigments. c Energy dispersive X-ray spectrum of the blue pigment

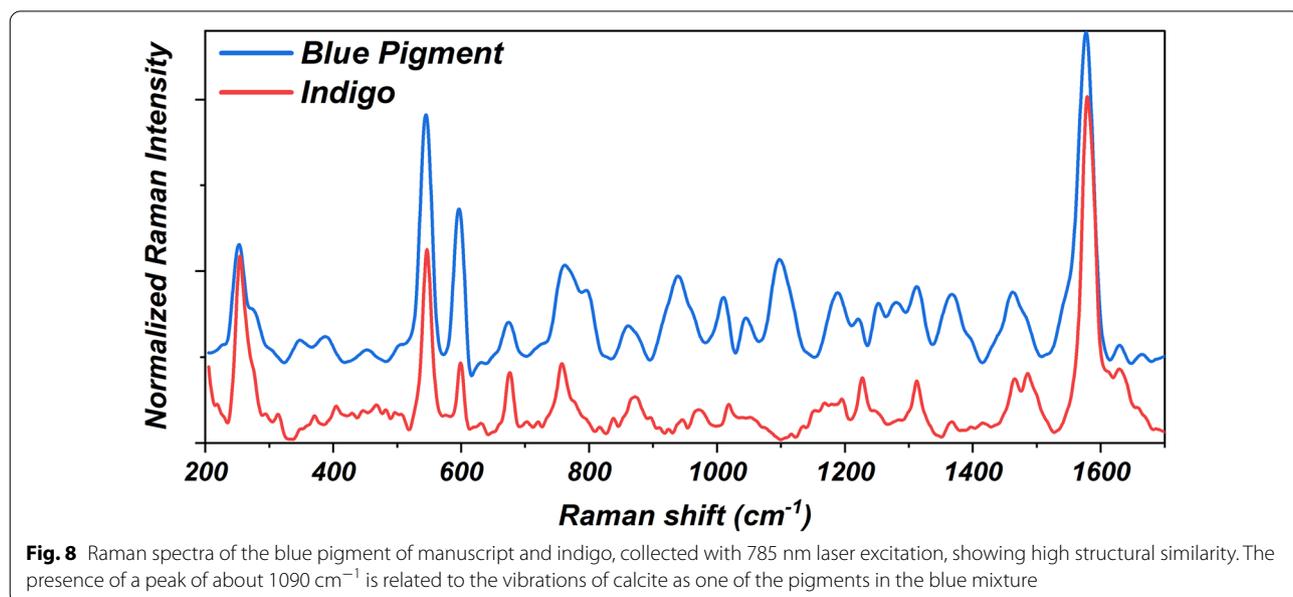
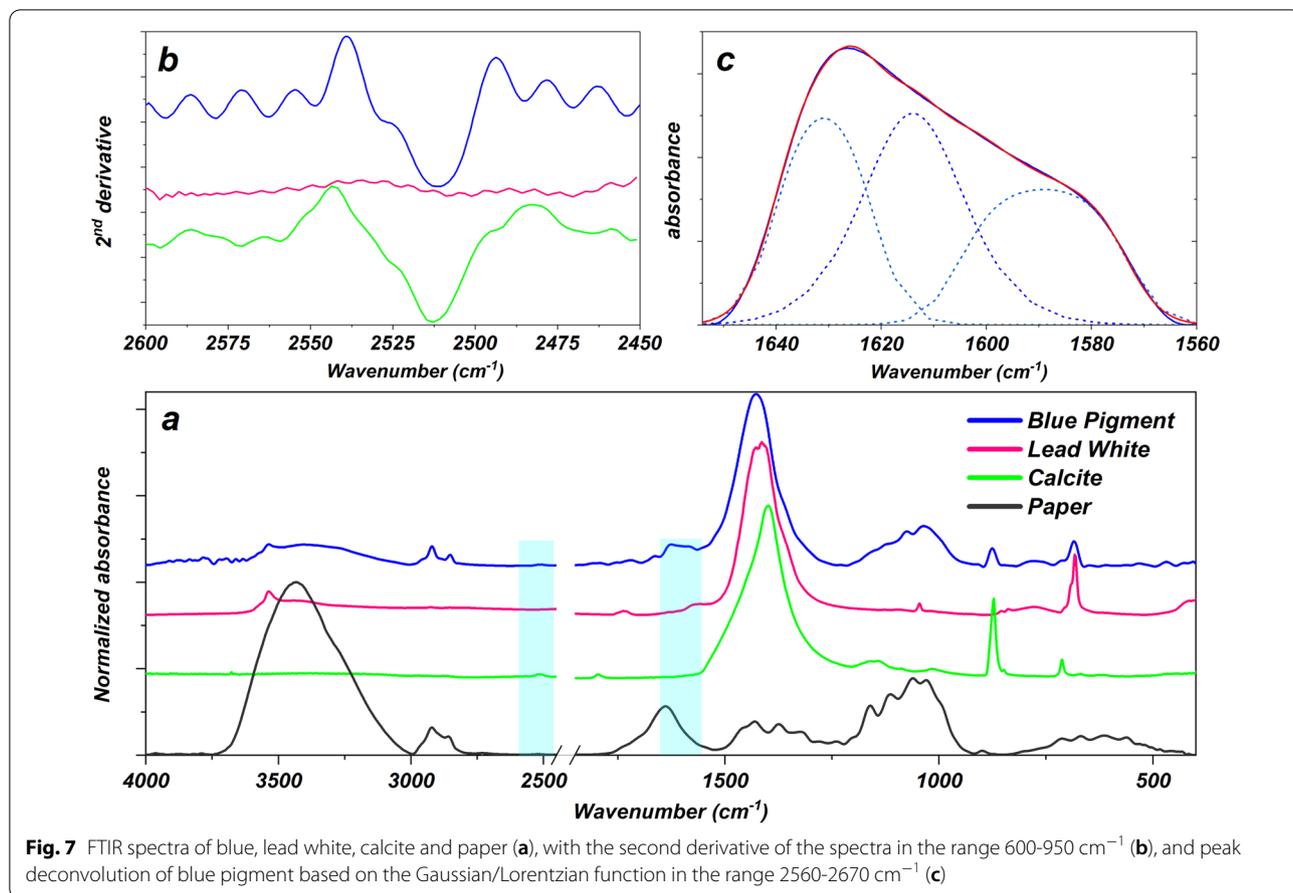
calcite structure [62], the presence of which in the blue mixture was also detected in FTIR spectroscopy.

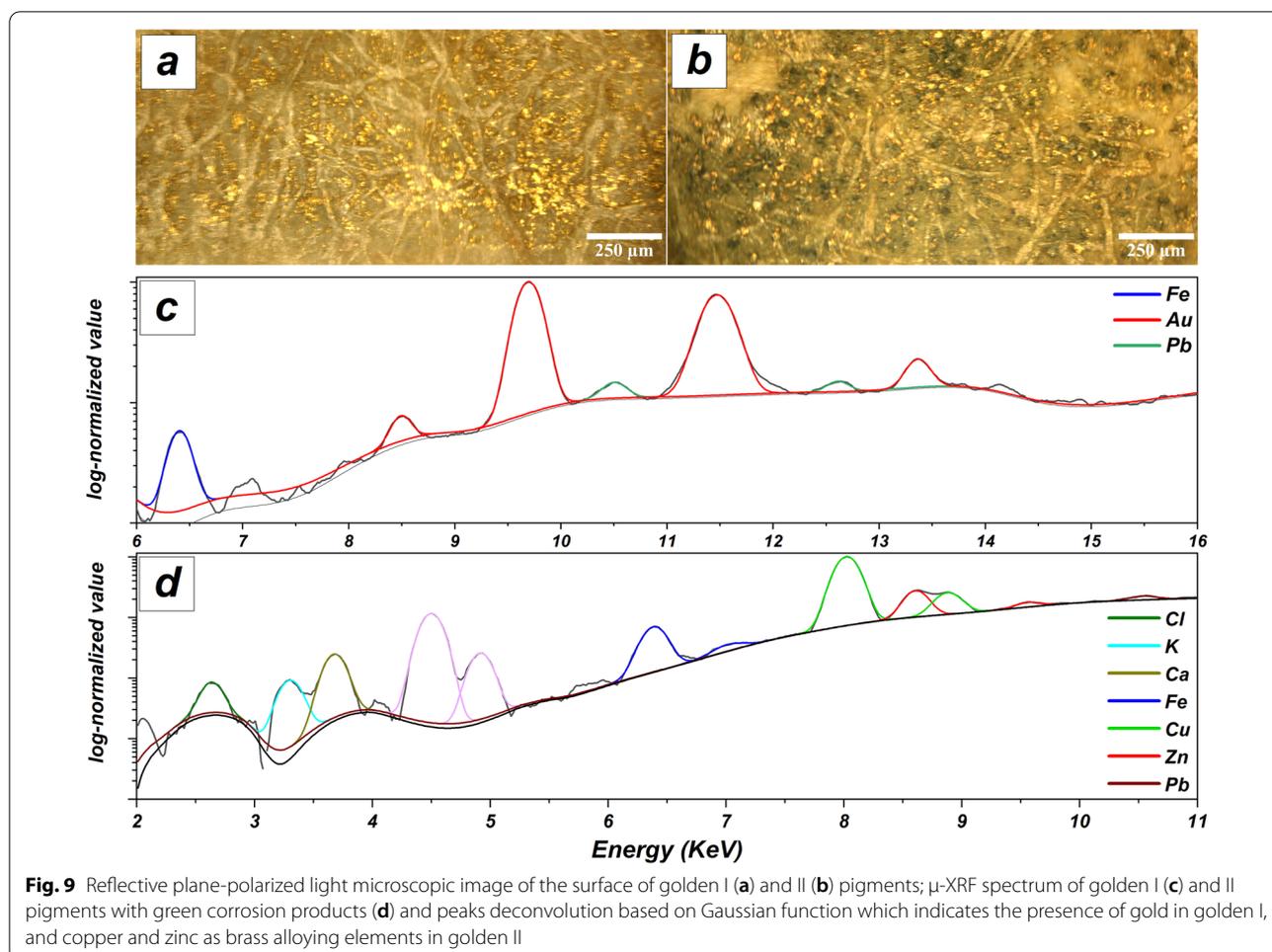
#### Golden pigments

The golden pigment is used as a strip in the margin of all pages and the sign of the verses. However, on some pages, this pigment indicates green damage raising the possibility of using two different types of golden in this manuscript (Fig. 9a, b).  $\mu$ -XRF analysis was used to identify golden I pigment, pigment without corrosion. The  $\mu$ -XRF spectrum of this sample can be seen in Fig. 9c. Examination of the  $\mu$ -XRF spectrum of this sample shows the presence of the gold element. In

other words, gold was used in this manuscript in the parts without green corrosion in golden pigments representing the value and importance of the manuscript for its makers. Gold is one of the main colors of the palette of Iranian artists in the past centuries, which is generally used in powder form and sometimes in the form of sheets. Its formation process making and usage has been often mentioned in historical Persian treatises [63].

Figure 9d shows the  $\mu$ -XRF spectrum of golden II sample related to green corrosion products at some pages. This spectrum shows two peaks in the range of 8.04 and 8.91 keV, respectively associated with the





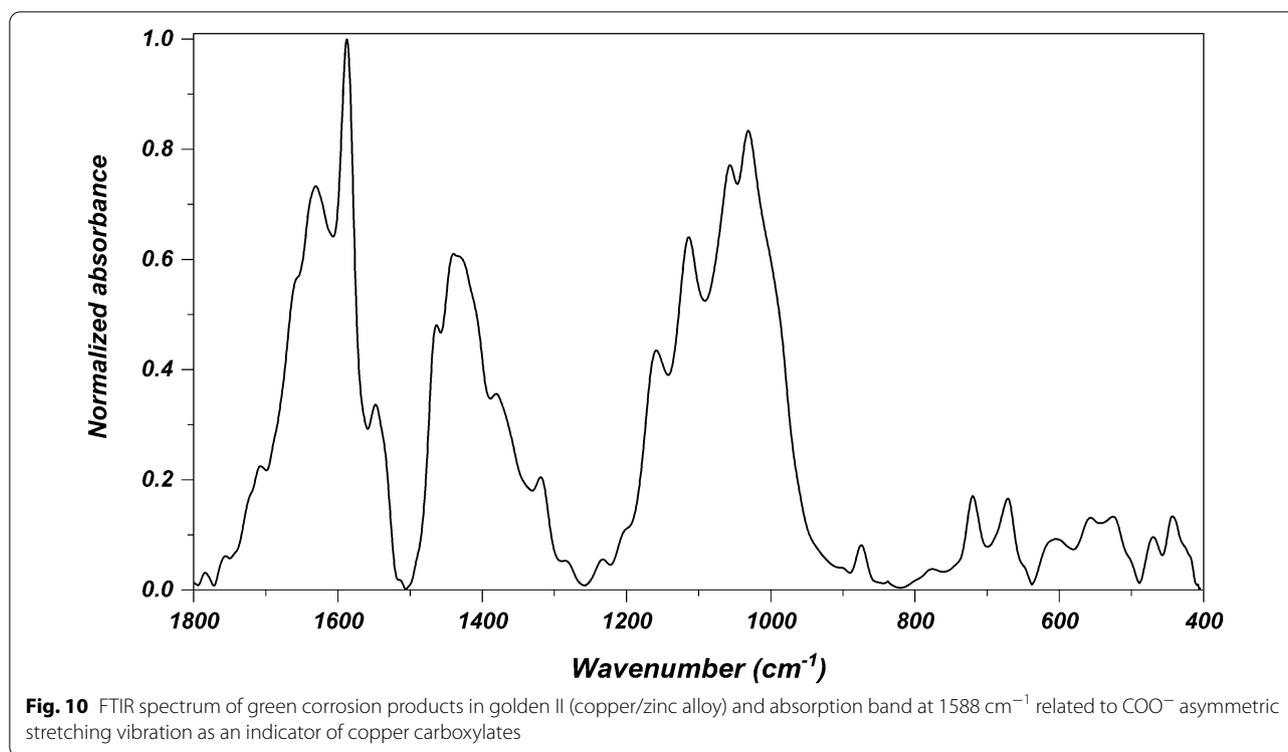
Cu-K $\alpha$  and Cu-K $\beta$ . Moreover, the Zn-K $\alpha$  and Zn-K $\beta$  are also visible in 8.6 and 9.5 keV. The presence of two elements of copper and zinc in golden II indicates the use of brass alloy, which was used as an imitation of gold in the decoration of some Qajar manuscripts [30, 31].

The nature of green corrosion products was investigated using FTIR spectroscopy on the parts containing brass alloy. Examination of the FTIR spectrum of this corrosion product shows a specific peak in the range of 1588  $\text{cm}^{-1}$  related to asymmetric stretching vibration of  $\text{COO}^-$  (Fig. 10). This peak along with adsorption band of 1462  $\text{cm}^{-1}$  of symmetric stretching vibration  $\text{COO}^-$  is one of the distinguishing features of copper carboxylates. Moreover, this spectrum shows a peak at 1548  $\text{cm}^{-1}$ , which is assigned to zinc carboxylates [64]. It can be stated that two types of golden pigments were used in this manuscript, one with a combination of gold metal (I) and the other with an alloy of copper and zinc or brass (II). In other words, the accumulation of green corrosion products in the form of copper carboxylates can be

found in some plates containing copper-zinc alloy similar to previous reports [31]. In the FTIR spectrum of corrosion products, other absorption bands at 1031 (C–O–C glucopyranose ring stretching vibration), 1056 (cellulose vibration C–O), 1113 (C–O stretching vibration of cellulose), 1158 (stretching vibration of the glycosidic oxygen bridge), 874  $\text{cm}^{-1}$  (C–O–C stretching of glucosidic bond) indicate the presence of cellulose fibers of paper [32, 65].

#### Technical photography

Technical photography is a good way to complete the process of detecting a variety of dyeing agents. It provides significant benefits to researchers as a result of not need for sampling and analysis of a large area. Figure 11 presents the results of technical photography of the samples based on the different methods, for which the respective observations are summarized in Table 3. Although Cosentino's observations do not prefer a multispectral imaging method (UVR, UVL, IRR, IRE, IRFC, UVFC) compared to the separation of black pigments



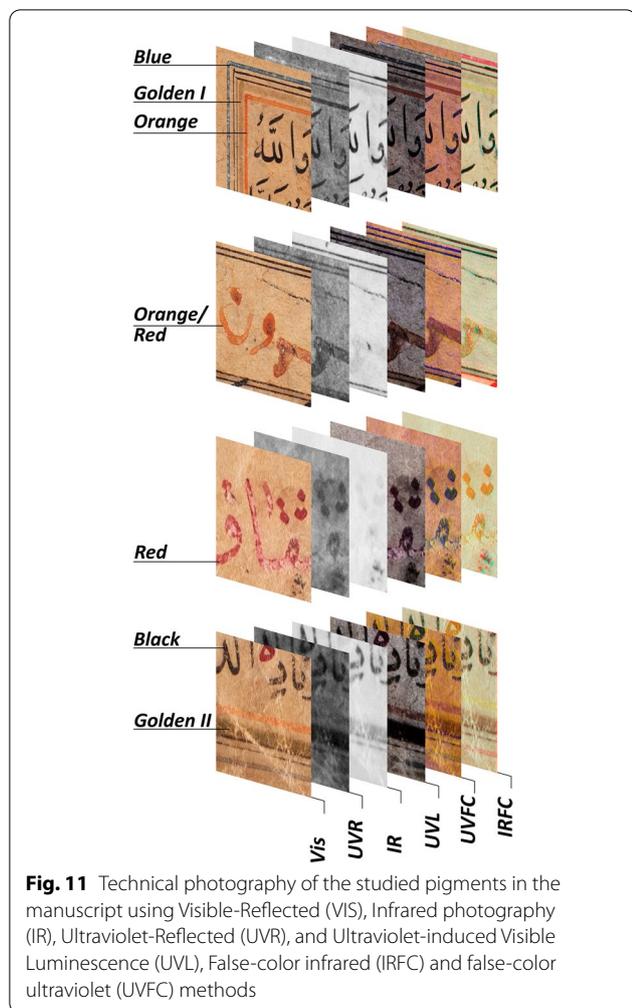
[22], according to Zekrgoo studies, the IRFC method can be used to separate black inks [37]. This investigation shows that carbon black ink is seen in black in the IRFC method. While iron-gall ink in this method create a bright red color. Therefore, the ink used in the studied manuscript creating a black color in the IRFC should be carbon black.

The orange strip and red/orange at the words in the text showed no fluorescence. These pigments also had low absorption in infrared and strong absorption in ultra-violet. According to previous reports, some dyes may be eliminated in these results from the list of possibilities including plant-based dyes, insect-based dyes, and red ochre pigment. IRFC results also limit the options to red lead, vermilion, and cadmium red, although lead red is more possible owing to the yellow color created in this method [22, 25, 66]. Finally, since these pigments appeared in dark red in UVFC processing, it is likely that the considered pigment is red lead [27]. In red/orange pigment, in addition to dark red, a number of deep violet dots are observed. These violet dots in the UVFC could indicate the presence of vermilion in the pigment mixture [67], which was also confirmed by spectroscopic methods.

Examination of the bright red ink used in the text indicated the possibility of using an organic dye of insect origin. Since plant-derived pigments such as alizarin and

insect-derived pigments (Cochineal, kermes and lac) have low fluorescence [30], the UVL method can be a good way to initially distinguish reds. Although the UVL method is used to separate the alizarin from other red pigments/dyes, it makes the interpretation difficult owing to the fluorescence of the paper [35]. Despite the very close fluorescence of alizarin compared to insect-derived dyes, which can also be altered by the effect of paper sizes [27], the results of other spectroscopy imaging should be considered. IRFC processing results for this red also showed an orange hue confirming the possibility of alizarin or pigments of insect origin [22]. This pigment also appeared in green in the UVFC processing results, which will be probably cochineal according to the UVL and IR results [22]. Technical photography makes it possible to identify parts with the same spectral characteristics on all pages. Also in technical imaging, the painted parts do not show the same feature compared to the surrounding areas. In other words, there is no halo around the written or colored parts. This can indicate a proper density and no excessive penetration of pigment into the paper.

Observations of ultraviolet absorption in blue indicate its combined state because the absorption at the outer edges of the strip with the center is very different. The results obtained in the IRFC and UVFC, which are seen in red and blue, respectively, indicate the use of indigo blue in this pigment [66]. However, the



**Fig. 11** Technical photography of the studied pigments in the manuscript using Visible-Reflected (VIS), Infrared photography (IR), Ultraviolet-Reflected (UVR), and Ultraviolet-induced Visible Luminescence (UVL), False-color infrared (IRFC) and false-color ultraviolet (UVFC) methods

identification of this mixed pigments requires the completion of the results by other methods, which contain white lead and calcite based on the results of atomic and molecular spectroscopy.

As shown in Fig. 11, the importance of using technical photography techniques in golden pigments lies in the

feasibility of distinguishing different types of these pigments where two types of gold and brass were used based on elemental analysis. The reflective ultraviolet results show a significant difference in the absorption of golden II compared to gold pigments. Of course, despite the difference in UV absorption, more distinguishable results are expected to have in UVFC, but due to the color halo of the paper, separation is not easily possible. Although there is no precise concentration on the use of technical photography to identify and separate metal-based pigments, especially gold and brass, it can be stated that this method can be used as a preliminary study in some cases where metal corrosion is observed.

### Conclusion

The present study deals with the identification of the inks and pigments used in a manuscript related to the early Qajar era in Iran using  $\mu$ -XRF, SEM-EDS, FTIR, Raman and technical photography. The results of this study showed that carbon black was used for writing revealing that technical photography can also be used to identify the black inks used in historical manuscripts, in addition to molecular and atomic spectroscopy methods.

Red lead is also used as a red/orange pigment in the tabulation strips of the work. In the sections where red lead is utilized in the writing, an amount of vermilion mixed with it have been used. Cochineal pigment has also been used as a red ink in writing of the manuscript parts. Evaluation of this dye using SEM-EDS showed that phosphorus can be considered as a benchmark element for the primary detection of pigments of insect origin.

According to the results, the blue pigment used in this manuscript is indigo. According to the data obtained from FTIR spectroscopy, white lead and calcite were used as additives in this pigment. This study showed that FTIR makes it possible to identify and separate carbonate compounds such as white lead and calcite. However, the

**Table 3** Results of technical photography along with identified index elements based on atomic spectroscopy methods

Color	Main elements	Technical photography observations						Result
		VIS	UVR	IR	UVL	UVFC	IRFC	
Black ink	C	Black	Dark	Dark	None	Black	Black	Carbon black
Orange	Pb	Orange	Dark	Bright	None	Dark red	Yellow	Red lead
Orange/red	Pb + Hg	Orange /red	Dark	Bright	None	Red-brown	Yellow-orange	Red lead + Vermilion
Red	P	Red	Dark	Bright	Dark red	Green-Blue	Orange	Cochinal dye
Blue	Pb	Blue	Dark	Bright	None	Blue	Red	Indigo + lead white and calcite
Golden I	Au	Golden	Dark	Bright	Gray	Purple	Brown	Gold
Golden II	Cu, Zn	Golden	Darker	Dark	Black	Brown	Brown	Brass/copper carboxylate

evaluation of golden pigment showed that two different types of golden pigment were used, including gold and brass, in the decoration of this manuscript. Generally, the parts containing brass, were associated with the formation of copper corrosion products of the carboxylate type.

The use of these two types of golden pigments indicates the transition era from the Safavid era, when gold was generally used as a mold pigment, to the Qajar era, when the use of brass alloy was expanded instead gold. This can also indicate that this manuscript was written by two different authors.

Technical photography showed that the penetration of pigments and inks in the paper was low, which occurred due to the proper paper sizing process or the proper concentration of colorants. In general, the research results indicate the proper performance of molecular and atomic spectroscopy along with technical photography methods to identify pigments on the historical manuscripts. This study shows that technical photography has a good performance in the initial identification of various pigments, especially pigments of organic origin, which are generally more difficult to identify in the study of historical artifacts. It also seems that this technique can be used in the initial identification of gold and corroded brass. However, it is necessary to expand the databases of technical photography and multispectral imaging of different pigments, especially for the mixture of pigments.

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#### Authors' contributions

AK designed the work process and analysed and interpreted the data. SAG and BJB participated in experiments. All authors discussed the results and contributed to the final manuscript. All authors read and approved the final manuscript.

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#### Availability of data and materials

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#### Declarations

#### Competing interests

The authors declare that they have no competing interests.

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