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**A Micro-Analytical Approach for Pigments Identification on Qajarid
Wooden Panels in Isfahan: Identification of Conicalcrite as a
Degradation Product of Emerald Green**

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Abstract

Decorating Iran's historical monuments often involves painting on wood, an area relatively underexplored in research. Examining the color palette utilized by artists in these works can offer valuable insights into the era's commercial, cultural, and economic milieu, while also aiding in identifying deterioration processes and proposing conservation strategies. This study seeks to determine the pigments employed in the paintings on wooden panels of the Shahsavaran House, a structure dating back to the Qajar period in Isfahan city. Utilizing micro-Raman spectroscopy and micro-XRF spectroscopy, the pigment composition of white, green, blue, yellow, and red hues was analyzed. The findings revealed a preliminary layer of white lead applied to the wood surface, followed by the painting execution. Examination of the pigments unveiled the presence of white lead, red lead, chrome yellow, and ultramarine blue. Notably, the green pigment was identified as conicalcrite, a pigment not commonly utilized, likely arising

from the degradation of emerald green. Furthermore, the presence of massicot alongside white lead in white areas suggests the degradation of white lead in an outdoor environment. The identified pigments in this artwork include lead white, lead red, and ultramarine blue, which are traditional and commonly used pigments in Iranian art-historical works. However, through the identification of chrome yellow and the potential use of emerald green, it is estimated that the paintings can be dated from the mid-19th to the mid-20th century.

Keywords: Historical pigments, Pigment identification, Iranian wood painting, Qajar painting, Pigment degradation.

1. Introduction

Identifying pigments has always been one of the most critical topics for researchers in studying historical artifacts [1]. These studies provide valuable information on the authenticity of art and historical pieces, attributing them to specific artists, their origin, approximate creation date, and insights into the color palette used by artists in historical periods. Therefore, identifying historical pigments plays a significant role in advancing art history knowledge. Furthermore, the detection of these pigments will also play a crucial role in selecting conservation approaches and identifying or predicting damages to artistic pieces [2-5].

Colors have been essential in various artifacts, including textiles, illuminated manuscripts, murals, and many other historical objects. Colors have been used on various surfaces, creating highly engaging artistic pieces, especially in decorating functional

objects. In Iranian art, colors have played a considerable role in decorating many artistic and historical objects [6]. Painting on wood is an important decorative element found in historical buildings in Iran [7, 8]. These painted wooden pieces have been extensively used on historical buildings' walls, columns, windows, doors, and ceilings. Iranian architecture knows one of these wooden elements as "*Shir-sar*." *Shir-sar* is, in fact, a decorative and functional element in Iranian historical buildings that is usually made of wood. *Shir-sar* is a canopy along the roofline of a structure, which, in addition to its beauty, prevents intense sunlight and acts as a shield for other Iranian architectural elements like sash windows (*Orosi*) against rain or snow. The intricacies in the design and various patterns on these elements have turned them into effective elements in beautifying the spaces of historical Iranian buildings.

As mentioned, one of the most significant branches of study in these artifacts is the identification of colorants used in them. However, unlike other Iranian artistic-historical pieces, such as paintings or illuminated manuscripts, the study of painting on wood, especially this type of work, has received less attention from various perspectives. This underscores the necessity for a comprehensive examination of these types of works, including identifying colorants, more prominently than ever.

Numerous studies have been conducted to identify pigments in Iranian art-historical artifacts. These studies have focused on various Iranian works, including manuscripts, wall paintings, textiles, papier-mache, and other artistic pieces. Various pigments such as paratacamite, malachite, atacamite, emerald and chrome green as green pigments [9-11], azurite, ultramarine, and indigo as blue pigments [5, 6, 10], chrome yellow, orpiment, and litharge as yellow pigments [10, 12, 13], red lead, cinnabar, cochineal and ochre as red

pigments [5, 10], along with other pigments have been identified in the history of Iranian art [12, 14-16]. However, studies on painted wooden panels in Iranian art have been limited, and an examination of a specific panel from the Qajar period in the *Zarir* Mosque in northwest Iran revealed the use of gypsum, carbon black, red lead, orpiment, and ultramarine as pigments [12].

Generally, different methods have been utilized to identify pigments and dyes in historical artifacts, including chromatography-based methods widely used for identifying organic dyes [17-19]. Various spectroscopic methods, especially X-ray-based techniques, have demonstrated efficient performance in examining mineral pigments [20-22]. Among these methods, X-ray fluorescence spectroscopy, which provides information regarding the elements present in the chemical structure of pigments, has gained popularity among researchers in this field. Additionally, multispectral and hyperspectral imaging methods have been used to investigate a wide range of historical artifacts [23], such as pigments [24-26], paintings [12, 27, 28], textiles [29], coatings [30] and manuscripts [5, 11] due to their ease of use. Molecular spectroscopic methods such as FTIR and Raman have also shown adequate performance in identifying pigments and dyes. Among the various methods, Raman spectroscopy can be considered one of the most effective approaches for identifying mineral and organic pigments [9, 20, 31]. In addition to micro-Raman, satisfactory results have been reported using a fiber optic reflectance spectrophotometer [32-35]. Nevertheless, a multi-analytical approach based on XRF and Raman spectroscopy enables the acceptable identification of pigments. Therefore, this paper aims to identify pigments used in *Shir-Sar* wood panel paintings in the *Shahsavaran* historical house in Isfahan, dating back to the Qajar period, using a spectroscopic approach based

on Raman and XRF microscopy methods.

2. Experimental

2.1. *Shahsavaran* house and samples

This research focused on analyzing five pigments found in the wooden paintings of the *Shahsavaran* historical house. The historic *Shahsavaran* house, previously called the *Yazdi-ha* house, is located along *Naqsh-e Jahan* Square, a UNESCO world heritage site, in the historical area of Isfahan, Iran. It is situated near the *Sine-Paeini Bazaar*, at *Kitabi Alley*, with the address No. 46, close to *Hakim Street* and *Abdul-Razzaq Street*.

Based on its architectural style, this house dates back to the Qajar period (1789-1925). The *Shahsavaran* House has a rectangular layout with a central courtyard. The rooms are on all four sides of the courtyard, giving the house a traditional appearance and design. The main section of the building is on the northern side. The eastern and western parts of the courtyard are likely served for daily living and overnight use. On the southern front, two rooms are on the upper level, and a basement is on the lower level. The kitchen is situated in the southeastern corner of the courtyard.

The upper part of the house's porch features wooden elements called *Shir-sar* (a kind of eaves), which still display visible painted motifs despite being covered with dust and sediment. The *Shir-sar* is a type of wooden canopy primarily used on the main facade of the building, though it may also be applied to other parts of the house for protection from rain (Figure 1). The *Shir-sar* has sturdy wooden brackets spaced about 30 cm apart. The bottom of the brackets is secured with nails around 50 cm from the ceiling beams, and the lower portion is covered with patterned boards. The *Shir-sars* are decorated with floral

motifs and have a thickness of about 10 cm at the edges. These *Shir-sars* protrude between 60 and 90 cm from the building (Figure 2a, b).

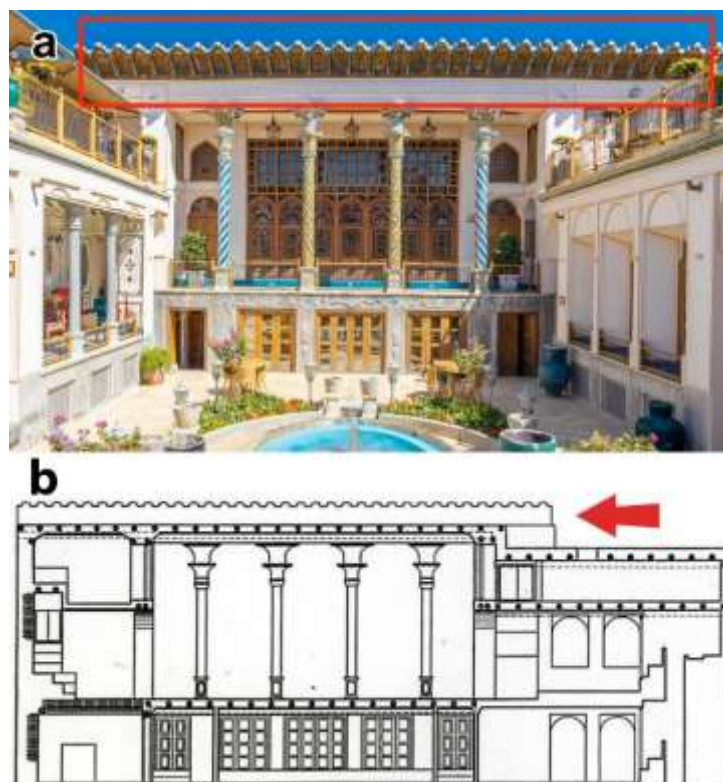


Figure 1. a: Image of the courtyard of the *Shahsavaran* house and the position of *Shir-sars*; b: The front view of the porch and the position of the *Shir-sar*

The vase motif can be seen in the center of the *Shir-sars*, which is decorated with other plant motifs and framing around it. It appears that a thin white layer was initially applied to the wood surface before the painting was executed. However, this layer has lost pigments in most areas. The study specifically examined the identification of five pigments used in these paintings: white, yellow, blue, green, and red (Figure 2c). Samples were collected that measured 2×2 mm in size and were analyzed. The samples were taken using a scalpel from areas with color spillage or broken edges of the wood panels. These specific sampling locations were chosen to minimize any damage to the appearance of the artwork.

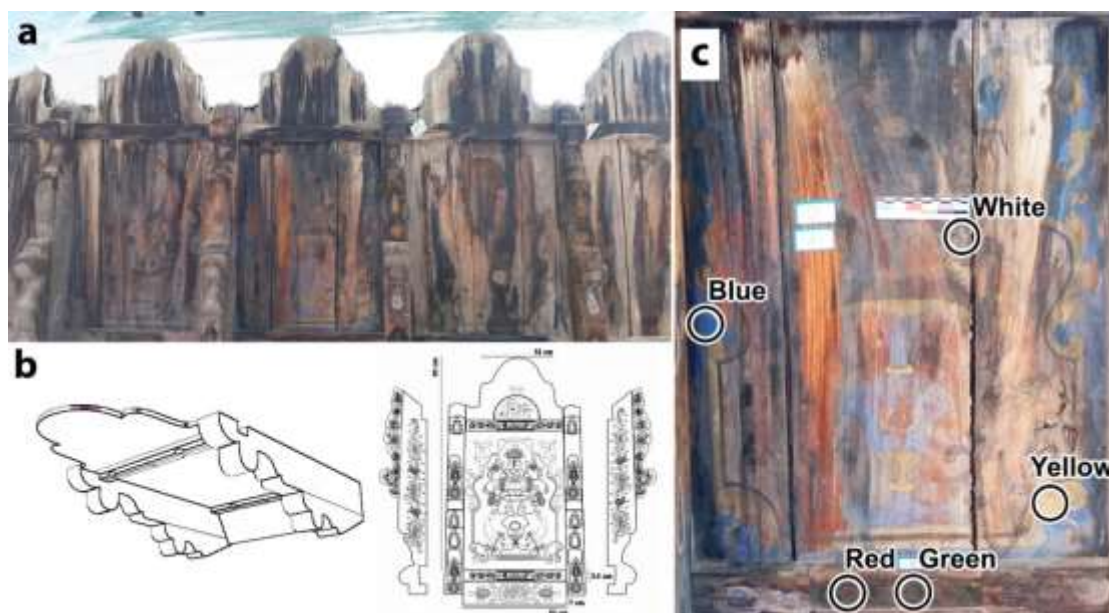


Figure 2. a: A view from the bottom of the row of *Shi-sars* with vase motifs in the center of each; b: Schematic image of *Shir-sar* and its components and dimensions; c: One of the wooden panels of *Shir-sars* and the location of the pigment samples under investigation.

2.2. XRF spectroscopy

The samples were analyzed using an XMF-104 benchtop micro-XRF device from Unisantis S.A. It was equipped with a Mo X-ray tube (5000 X-ray tube from Oxford Instruments), a Si-PIN detector (XR-100CR Peltier-cooled Si-PIN from Amptek with an energy resolution of 186 eV for ^{55}Fe at 5.9 keV), and a Kumakhov poly capillary lens operating at 35 kV and 400 μA in air. The samples were positioned on a motorized X–Y–Z stage and the signals were collected for 300 seconds.

2.3. Raman spectroscopy

The Tekram II super-resolution Raman spectrometer from Teksan Co., Iran, was utilized for Raman spectroscopy. It was equipped with two excitation lasers at 532 nm and 785 nm and used an LWD 60X objective and grating 1200 l/mm and 1800 l/mm (specifically

for green pigment) to record the spectra. The spectrum of white pigment was obtained using a 785 nm excitation laser at 50 % power for a 10-second integration. The blue pigment spectrum was recorded using 10 % laser power over 6 accumulations of 10 seconds each. Similar settings were applied to the red pigment, with 2 % laser power and 5 accumulations of 10 seconds. The yellow pigment was examined using 532 nm (2 % power, 2 accumulations of 10 seconds) and 785 nm (70 % power, 3 accumulations of 3 seconds) excitation lasers. The spectrum of the green pigment was captured using a 532 nm excitation laser, 1800 l/mm grating, and 70 % laser power over 2 acquisitions of 10 seconds each. Pigment reference spectra were prepared using the Cultural Heritage Science Open Source (CHSOS) [36] and RRUFF database.

3. Results and Discussion

In certain areas of the wooden surface, there are visible white patches, likely remnants of the primer layer paint, some of which can still be faintly seen on the wood. Furthermore, some of the motifs are white, and analysis using micro-Raman and micro-XRF revealed they have the same composition. The micro-XRF spectrum of this white pigment is depicted in Figure 3, indicating that the primary element in this pigment is lead. This suggests using white lead $[2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2]$. According to traditional Iranian pigment production recipes, lead-based white pigments known as "*Sefidab-e Sheikh*" are not limited to carbonates like cerussite $[\text{PbCO}_3]$ and hydrocerussite $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$, but also include lead chlorides such as laurionite $[\text{PbCl}(\text{OH})]$ and blixite $[\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4]$, as well as phosgenite $[(\text{PbCl})_2\text{CO}_3]$ [37]. Examination of the Raman spectrum of this pigment, shown in Figure 3, reveals the presence of the white lead index peak related to

carbonate vibrations at around 1053 cm^{-1} [15, 38]. Lead white is considered a prominent white pigment in Iranian art and has been identified in various works such as paintings [39], manuscripts [11, 15], papier mache [9], and other art pieces from different historical periods [10, 40]. Additionally, two other distinct peaks around 145 and 283 cm^{-1} are observed, attributed to massicot vibrations [41, 42]. Based on the studies of Gliozzo and Ionescu [43], massicot may be one of the degradation products of white lead, which is plausible given the exposure of these wooden panels to open-air conditions.

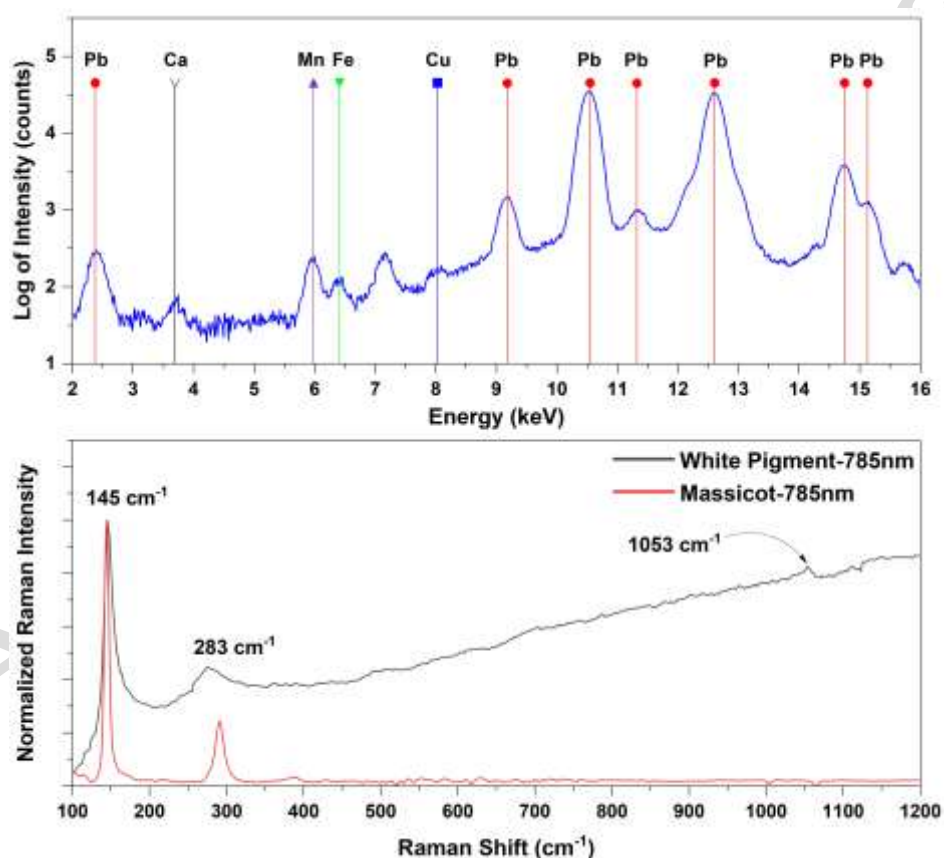


Figure 3. Top: Micro XRF spectrum of the white pigment indicating a high amount of lead. Bottom: Micro-Raman spectrum of the white pigment recorded using a 785 nm laser excitation alongside the massicot reference spectrum (CHSOS).

The blue pigment, another important pigment used in these painted panels, is used to paint the margins of these panels and the central vase motif. The analysis of this pigment

using micro-XRF in Figure 4 shows various elements, which, apart from lead, have very low values similar to the micro-XRF analysis of the white pigment. The amount of lead is likely due to the white primer layer used underneath the paint layer on the entire wood surface. However, due to limitations in identifying light elements using this XRF equipment, the XRF results are insufficient for determining the probable type of pigment. Figure 4 displays the micro-Raman spectrum of this pigment using a 785 nm laser excitation. A weak peak from the white lead structure vibrations in this spectrum is observed around 1050 cm^{-1} , related to the primer layer. Nonetheless, the characteristic peak of this pigment is observed around 548 cm^{-1} , which indicates identifying the ultramarine blue pigment [6]. This band is usually associated with the symmetric stretching vibrations S_3^- in ultramarine [44]. The variety of blue pigments in Iranian historical works is wide, but reports mainly focus on identifying ultramarine, azurite, copper sulfate, and indigo. Ultramarine should be considered the most prominent blue pigment in Iranian artifacts [6]. The presence of this pigment in the decorations and paintings of Safavid and Qajar historical buildings in Iran has been reported numerous times [6, 45, 46]. This pigment was initially obtained and used naturally, mostly extracted from the Badakhshan mines in Afghanistan, with evidence of its use found in the *Konar-Sandal* excavations dating back to the third millennium BC or the wall paintings of the *Ali Qapu* Palace during the Safavid era in Isfahan [6, 47]. However, with the synthesis of this pigment in 1787 and producing it on a larger scale in 1814, simultaneously with the Qajar period, the use of its synthetic form became widespread [48]. This pigment has also had extensive use in the wooden panel paintings in historical Iranian buildings, and in addition to the specimen studied in Isfahan, it has also been reported in wood paintings in

the *Zarir* Mosque in the northwest of Iran from the Qajar period [12].

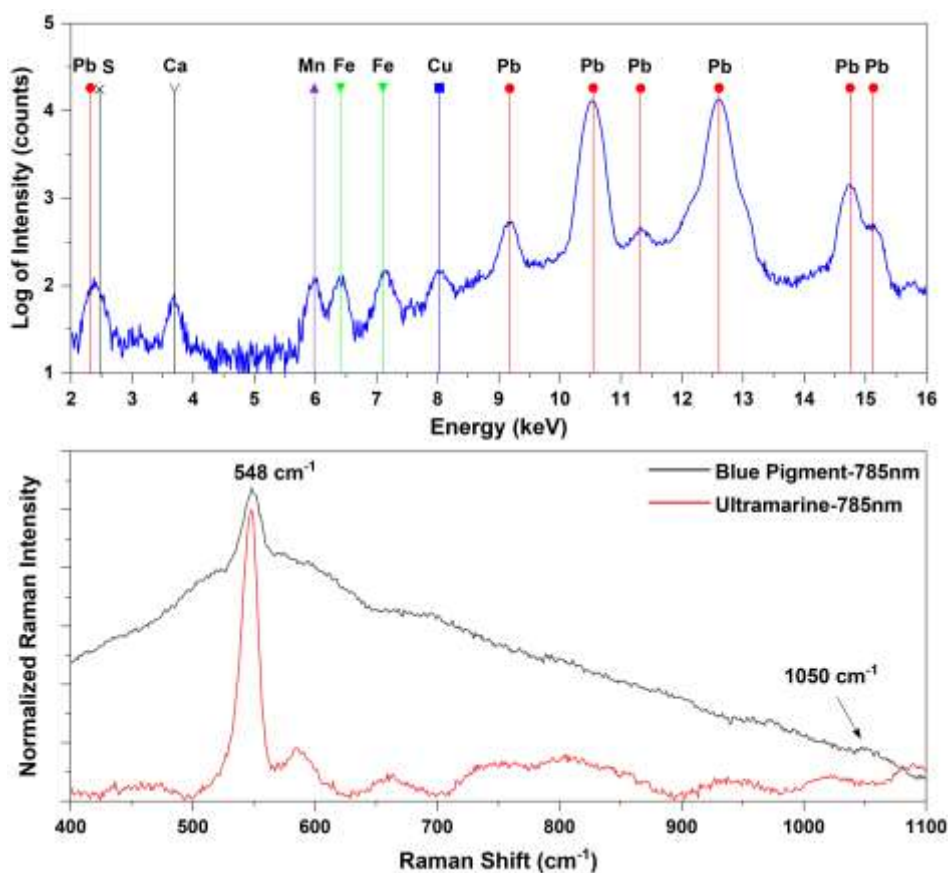


Figure 4. Top: Micro-XRF spectrum of the blue pigment showing only lead related to the primer layer accompanied by some sulfur values. Bottom: Micro-Raman spectrum of the blue pigment recorded using a 785 nm laser excitation, along with the reference spectrum of ultramarine blue (CHSOS).

The XRF spectrum of yellow pigment is presented in Figure 5. The main element in this pigment is lead, likely originating from the primer layer. However, another indicative element, chromium, has been identified in this pigment in addition to lead. The presence of these two elements indicates the possibility of using lead chromate. The Raman spectra of this pigment, recorded using two laser excitation wavelengths of 532 and 785 nm, are also presented in Figure 5. In these two wavelengths, the vibrations of lead chromate are observed at approximately 830 and 845 cm^{-1} , which are characteristic for identifying

chrome yellow (PbCrO_4). Another peak indicative of chrome yellow is also observed at approximately 350 cm^{-1} [49, 50].

After the discovery chromium in 1797 by Vauquelin and the synthesis of lead chromate in 1809, chrome yellow (PbCrO_4) entered artists' palette in the 19th century. Its commercial production began in England between 1814 and 1816 by Dr. Bollman and began a few years later in the United States and France [51]. Likely, through the expansion of trade relations between Iran and Europe during the Qajar period, chrome yellow gradually entered the palette of Iranian artists after this date. Hence, the paintings using this pigment can be dated to after 1810. This pigment has also been reported in some Iranian paintings from the Qajar period, and evidence of its use in the form of chrome green (a mixture of chrome yellow and a blue pigment) has been reported in a Qajar pen-box papier-mache [9].

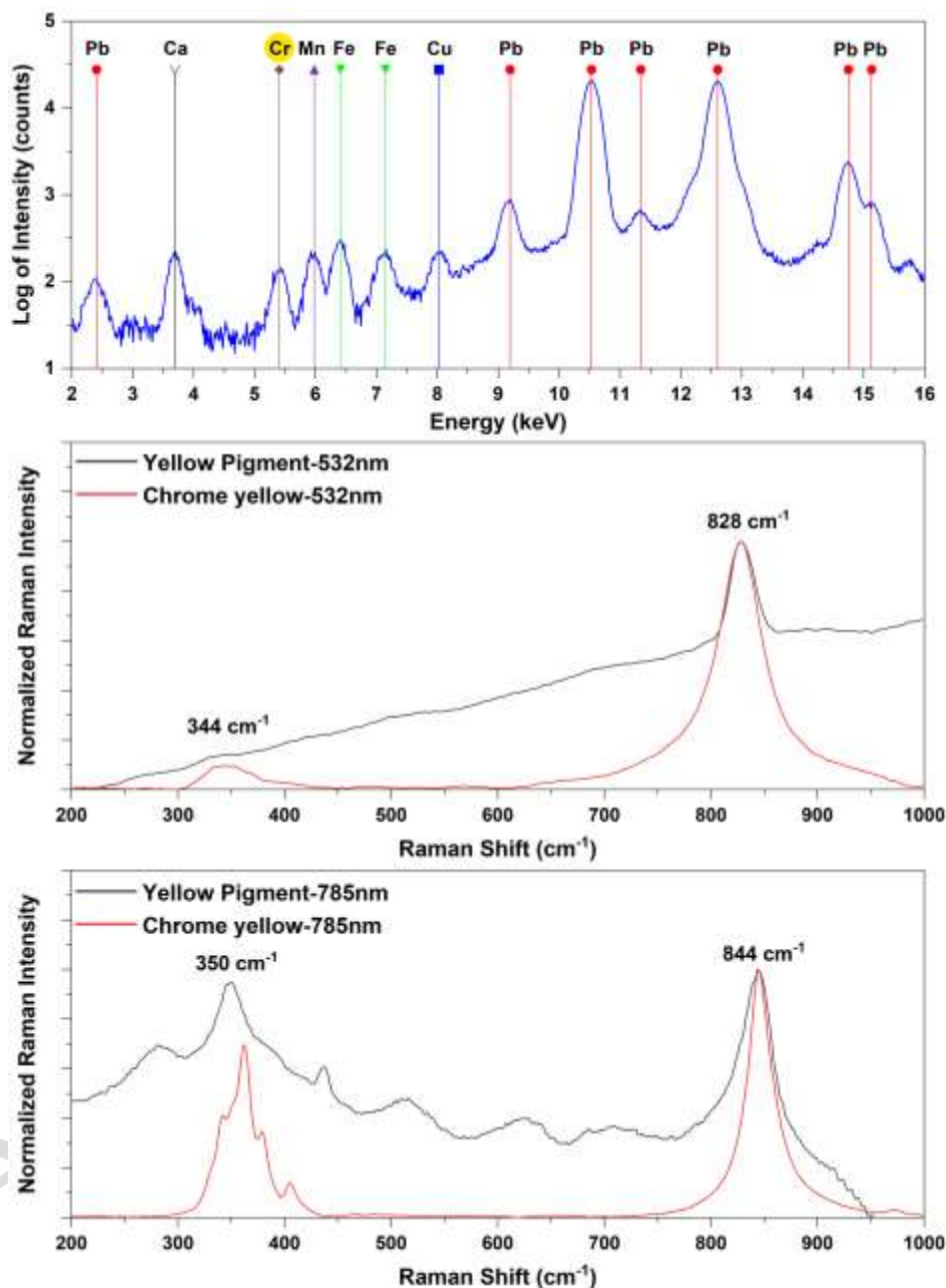


Figure 5. Top: Micro-XRF spectrum of the yellow pigment showing chromium and lead as indicative elements. Middle: Micro-Raman spectrum of the yellow pigment recorded using a 532 nm laser excitation, along with the chrome yellow reference spectrum (CHSOS); Bottom: Raman spectrum recorded with a 785 nm laser excitation.

Figure 6 shows the micro-XRF spectrum of the green pigment. Besides lead, originating from the primer layer, copper and arsenic are indicative elements in this pigment. The

presence of these two elements suggests the possible use of emerald green $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2]$. However, the Raman spectrum of emerald green, along with distinct peaks at approximately 155, 175, 220, 240, 295, 325, 370, 430, 490, 540, 685, 760, 835, and 950 cm^{-1} corresponding to the vibrations of acetate [11, 52], differs from the green pigment spectrum.

The analysis of the Raman spectrum of the sample reveals a distinct peak around 830 cm^{-1} and two additional peaks at approximately 535 and 485 cm^{-1} , which are likely attributed to conichalcite $[\text{CaCu}(\text{AsO}_4)(\text{OH})]$ [53, 54]. Although conichalcite has been reported as a green pigment in some studies based on limited evidence [55-58], it is rarely considered a common pigment. It has not been previously reported in Iranian artworks. Shen, Wang [54] have identified challenges associated with the identification of conichalcite as a pigment. Their research suggests that detecting conichalcite or other copper arsenates in green pigments containing copper and arsenic may be due to the alteration and aging of emerald green pigments. Undoubtedly, the degradation observed in these panels can be attributed to exposure to outdoor air and severe environmental factors. The instability and drastic alterations in the emerald green color are frequently observed in historical murals, including those in Iran. According to Holakoei, Karimy and Nafisi [13], lammerite $[\text{Cu}_3(\text{AsO}_4)_2]$ has been reported as another degradation product of emerald green in Persian murals dating from the mid-nineteenth to mid-twentieth century.

The synthesis of emerald green pigment by Wilhelm Sattler in 1814 in Schweinfurt, Germany, marked its introduction into artists' palettes by 1822 [59]. Therefore, the wood panels were definitely painted after this time. Analysis of Iranian historical works from the 19th and 20th centuries indicates that emerald green pigment was likely brought to Iran

in the mid-19th century. Before this, there is no evidence of its use in Iranian art. However, once it was introduced, artists were captivated by its brightness and allure, leading to its frequent incorporation in works from the latter half of the 19th century and the first half of the 20th century [10]. Therefore, the creation date of these paintings should also be considered during this period, i.e. the end of the Qajar period and the beginning of the Pahlavi period.

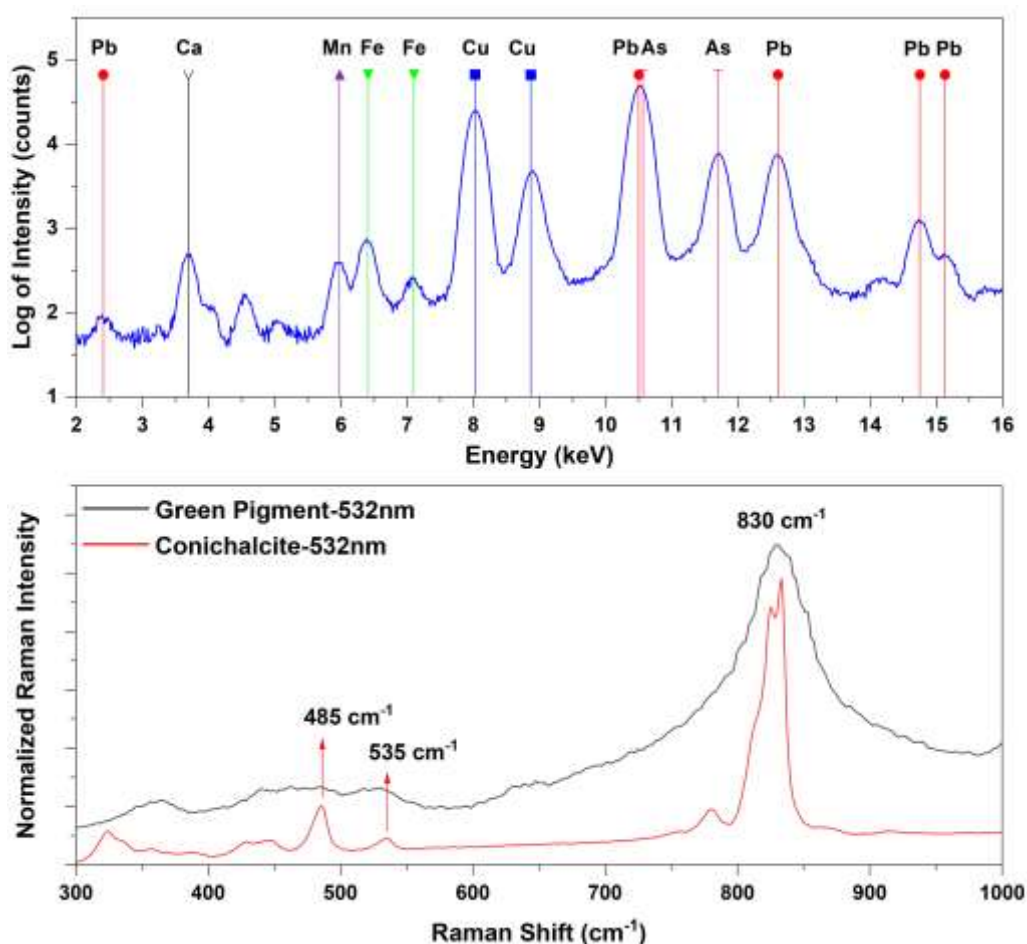


Figure 6. Top: Micro-XRF spectrum of the green pigment showing copper and arsenic as indicative elements. Bottom: Micro-Raman spectrum of the green pigment recorded using a 532 nm laser excitation alongside the conicalcrite reference spectrum (RRUFF ID: R070447).

Another pigment examined is the red pigment, the micro-XRF spectrum presented in Figure 7. As illustrated in Figure 2c, the sample position of the red pigment under study

is placed on the green color. Hence, the evaluation of the micro-XRF spectrum of this pigment also shows copper and arsenic elements, which are related to the green pigment. In addition to these two elements, the red pigment contains significant amounts of lead, indicating the possible use of lead-based pigments. The Raman spectrum analysis of this pigment also reveals a prominent band at approximately 545 cm^{-1} , characteristic of red lead (Pb_3O_4), indicating the Pb(IV)-O bond stretching [60]. Other bands corresponding to the red lead Raman spectrum are also observable at around 390, 310, 220, 150, and 120 cm^{-1} [41, 42]. Red lead is one of the most important red pigments in Iranian artworks, and its use is not limited to a specific period or type of artwork. Numerous reports have so far identified this pigment in painted wooden panels [12], manuscript illuminations [5, 10, 11], papier-mache [9] and paintings [13, 45, 46], indicating its popularity among Iranian artists.

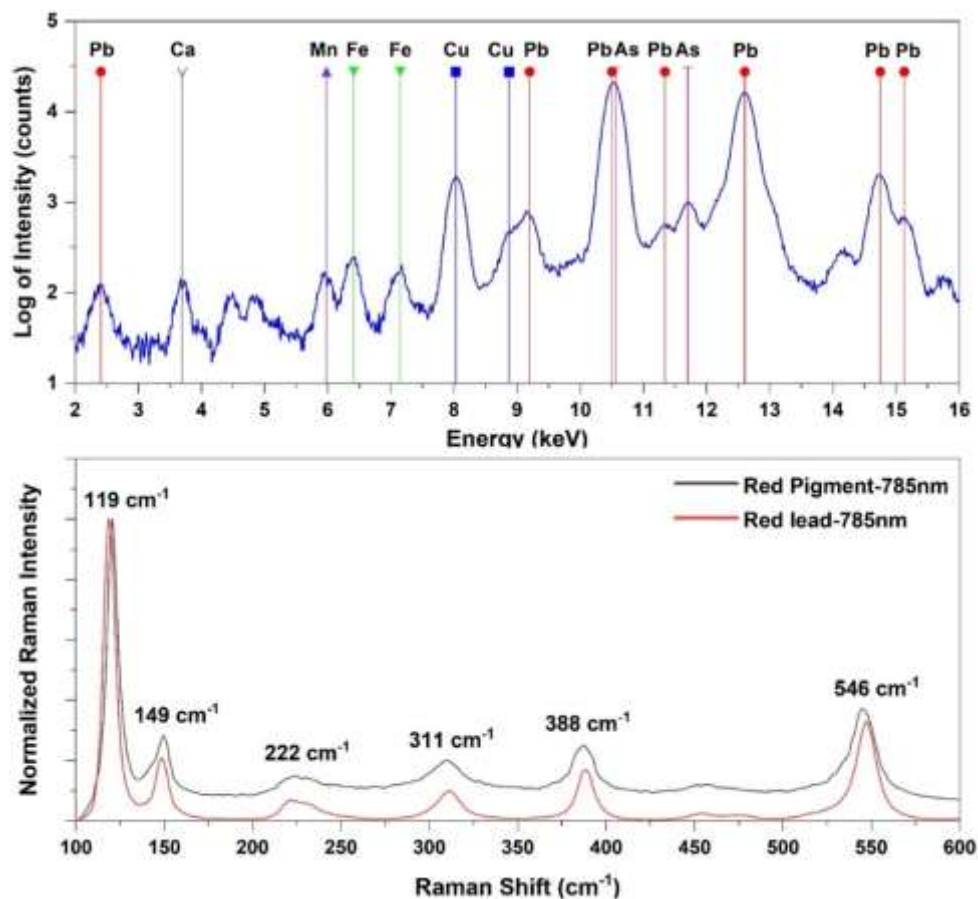


Figure 7. Top: Micro-XRF spectrum of the red pigment showing copper and arsenic elements related to the lower green pigment layer and lead. Bottom: Micro-Raman spectrum of the red pigment recorded using a 785 nm laser excitation alongside the red lead reference spectrum (CHSOS).

The Raman and X-ray fluorescence (XRF) spectroscopy results can be summarized in Table 1. This table presents the key Raman peaks and the main elements identified for different pigments. Based on the information in the table, it is possible to report using the following pigments: red lead, ultramarine blue, chrome yellow, massicot, and conicalcrite. It's worth noting that massicot and conicalcrite are degradation products of white lead and emerald green, respectively.

Table 1. Overview of Raman and XRF spectroscopy findings and identified pigments.

Sample	Main elements (XRF results)	Main Raman shifts	Pigment
White	Pb	785 nm: 145, 283 cm^{-1}	Massicot as degradation product of white lead
Blue	S	785 nm: 548 cm^{-1}	Ultramarine
Yellow	Pb, Cr	532 nm: 344, 828 cm^{-1}	Chrome yellow
		785 nm: 350, 844 cm^{-1}	
Red	Pb	785 nm: 119, 149, 222, 311, 388, 546 cm^{-1}	Red lead
Green	Cu, As	535, 830 cm^{-1}	Conicalcrite the degradation product of emerald green

4. Conclusion

The present study successfully identified pigments used in the paintings on wood panels of the historical Shahsavaran House in Isfahan. These painted panels functioned as *Shir-sar*, a traditional Iranian architectural feature typically found on the edges of roofs. The analytical techniques of micro-X-ray fluorescence (micro-XRF) and micro-Raman spectroscopy were employed to carry out this identification. The findings revealed the presence of red lead, white lead, ultramarine blue, chrome yellow, and conicalcrite in the green areas of the paintings. Conicalcrite, an uncommon pigment, is believed to have formed due to environmental exposure in open-air conditions following the degradation of emerald green. Additionally, detecting massicot alongside white lead suggests possible deterioration of the white lead pigment. The identification of chrome yellow and the potential presence of emerald green indicate that the paintings date back from the mid-nineteenth to mid-twentieth century, placing them in the second half of the Qajar period and to the beginning of the Pahlavi period. This study has not only shed light on the artists' palette used in wood painting but has also provided valuable insights into the

degradation and transformation of certain pigments. In conclusion, the results of this research significantly contribute to our understanding of the materials and techniques employed by artists working in the realm of wood painting, offering valuable information on the preservation and conservation of these historic artworks. Further discussions and research on the implications of pigment degradation and transformation in paintings are warranted to deepen our knowledge.

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