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A Micro-Analytical Approach for Pigments Identification on Qajarid Wooden Panels in Isfahan: Identification of Conichalcite 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 conichalcite, 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. Prog. Color Colorants Coat. 18 (2025), 73-85© Institute for Color Science and Technology.

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

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

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.

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 55Fe 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.

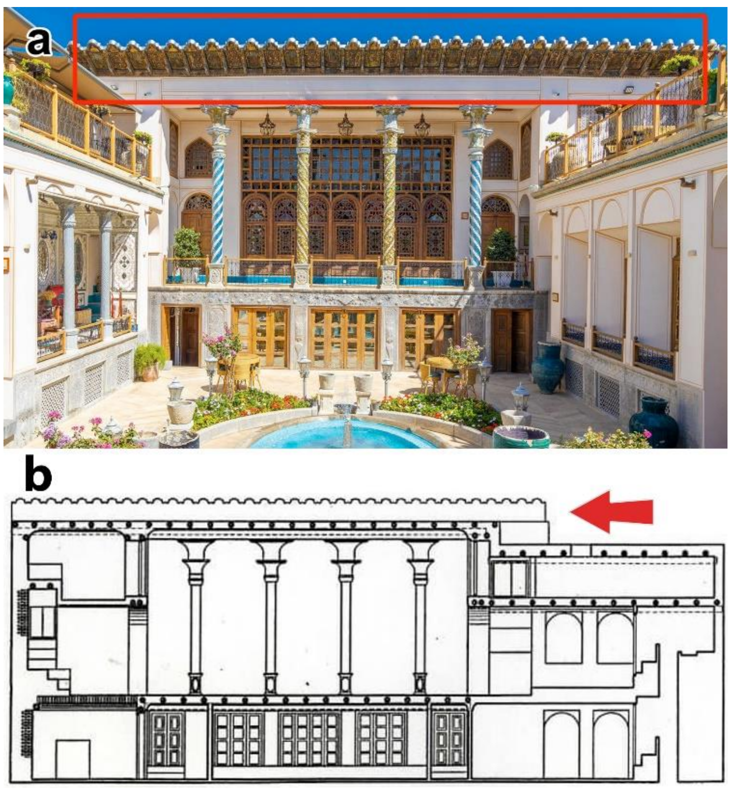

Figure 1: a) Image of the courtyard of the *Shahsavaran* house and the position of *Shir-sar*s; b) The front view of the porch and the position of the *Shir-sar.*

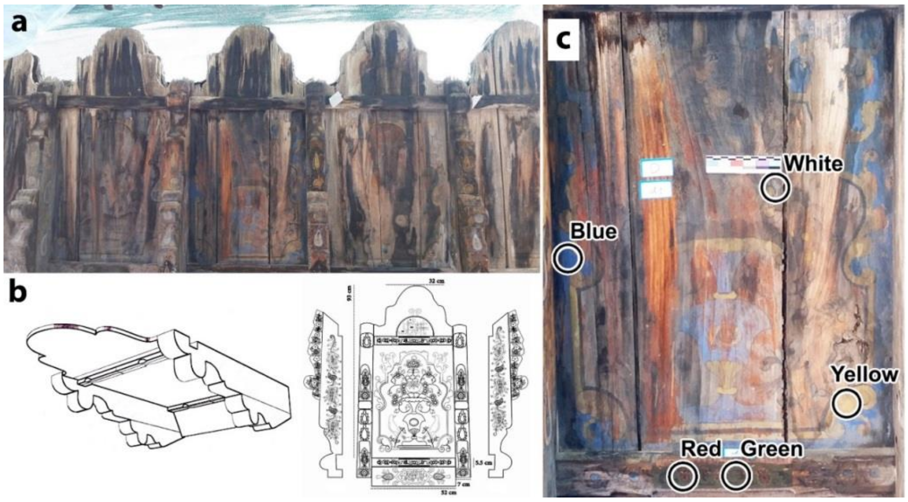

Figure 2: a) A view from the bottom of the row of *Shi-sar*s with vase motifs in the center of each; b) Schematic image of *Shir-sar* and its components and dimensions; c) One of the wooden panels of *Shir-sar*s and the location of the pigment samples under investigation.

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 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 [$2PbCO_3 \cdot Pb(OH)_2$]. According to traditional Iranian pigment production recipes, lead-based white pigments known as "*Sefidab-e Sheikh*" are not limited to carbonates like cerussite [$PbCO_3$] and hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], but also include lead chlorides such as laurionite [PbCl(OH)] and blixite [$Pb_8O_5(OH)_2Cl_4$], as well as phosgenite [$(PbCl)_2CO_3$] [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.

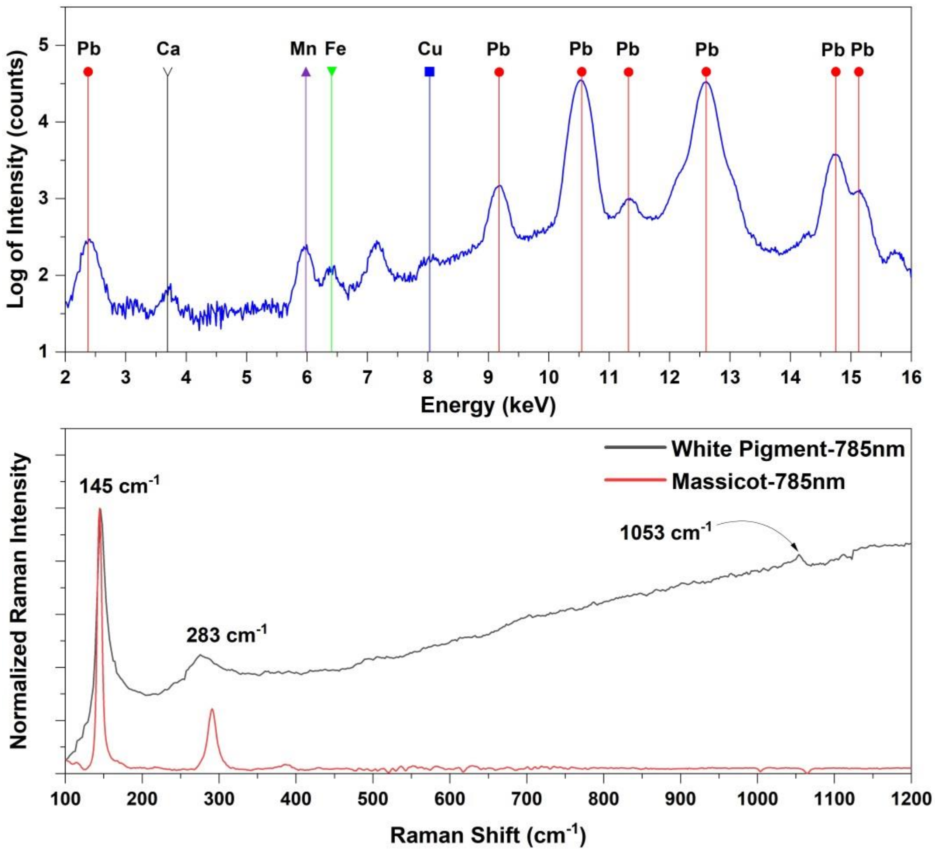

Figure 3: Top) Micro XRF spectrum of the white pigment indicating a high amount of lead; Bottom) Micro-Raman spectrum of the white pigment recorded using a 785 nm laser excitation alongside the massicot reference spectrum (CHSOS).

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].

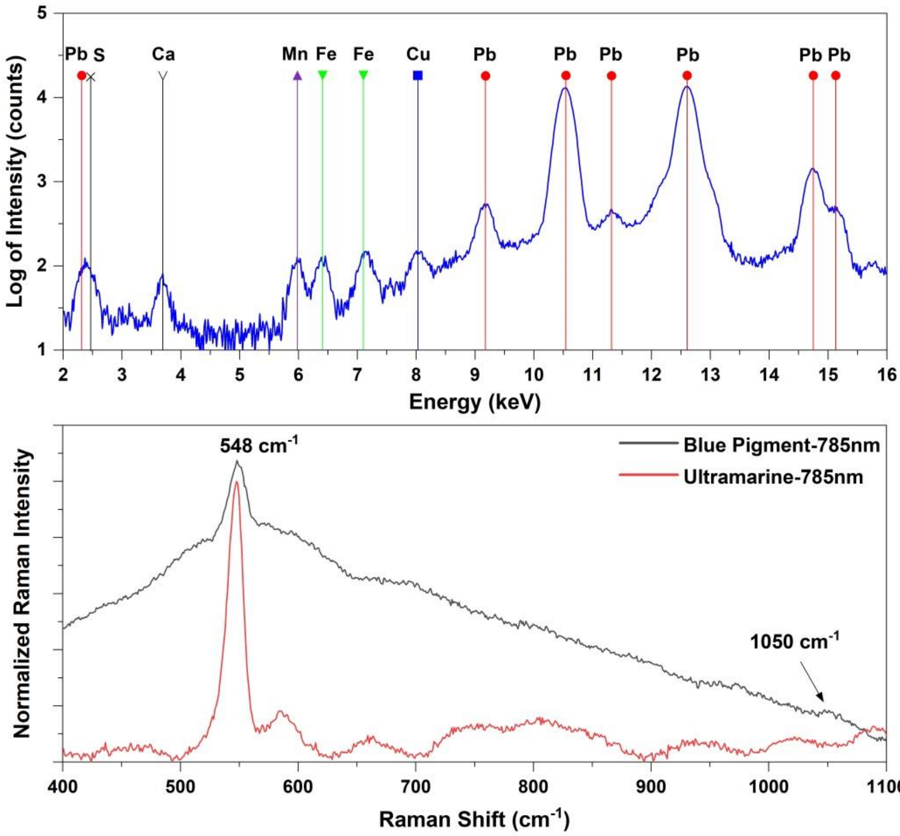

Figure 4: Top) Micro-XRF spectrum of the blue pigment showing only lead related to the primer layer accompanied by some sulfur values; Bottom) Micro-Raman spectrum of the blue pigment recorded using a 785 nm laser excitation, along with the reference spectrum of ultramarine blue (CHSOS).

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 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 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 $[Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2]$. 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.

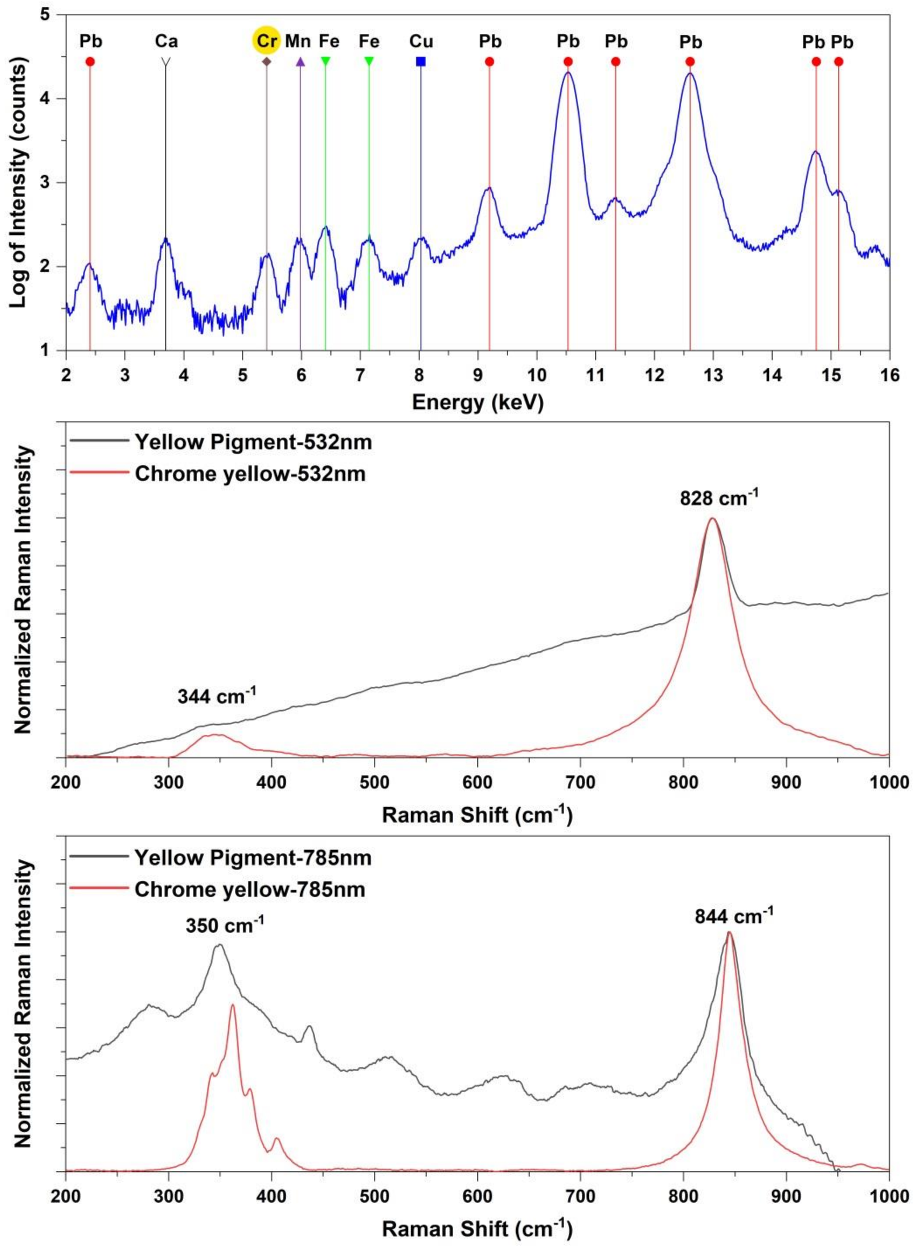

Figure 5: Top) Micro-XRF spectrum of the yellow pigment showing chromium and lead as indicative elements; Middle) Micro-Raman spectrum of the yellow pigment recorded using a 532 nm laser excitation, along with the chrome yellow reference spectrum (CHSOS); Bottom) Raman spectrum recorded with a 785 nm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

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 [$CaCu(AsO_4)(OH)$] [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 et al. [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 Holakooei, Karimy and Nafisi [13], lammerite [$Cu_3(AsO_4)_2$] 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 19^{th} and 20^{th} centuries indicates that emerald green pigment was likely brought to Iran in the mid-19^{th} 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 19^{th} century and the first half of the 20^{th} 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.

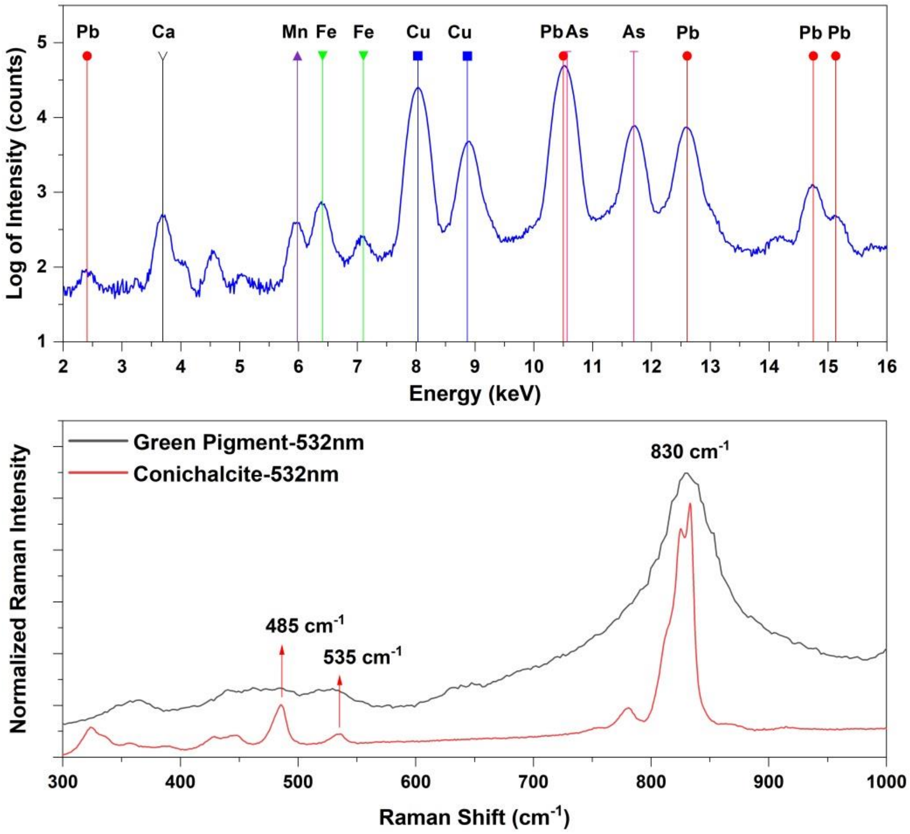

Figure 6: Top) Micro-XRF spectrum of the green pigment showing copper and arsenic as indicative elements; Bottom) Micro-Raman spectrum of the green pigment recorded using a 532 nm laser excitation alongside the conichalcite reference spectrum (RRUFF ID: R070447).

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.

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 conichalcite. It's worth noting that massicot and conichalcite 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}	Conichalcite the degradation product of emerald green

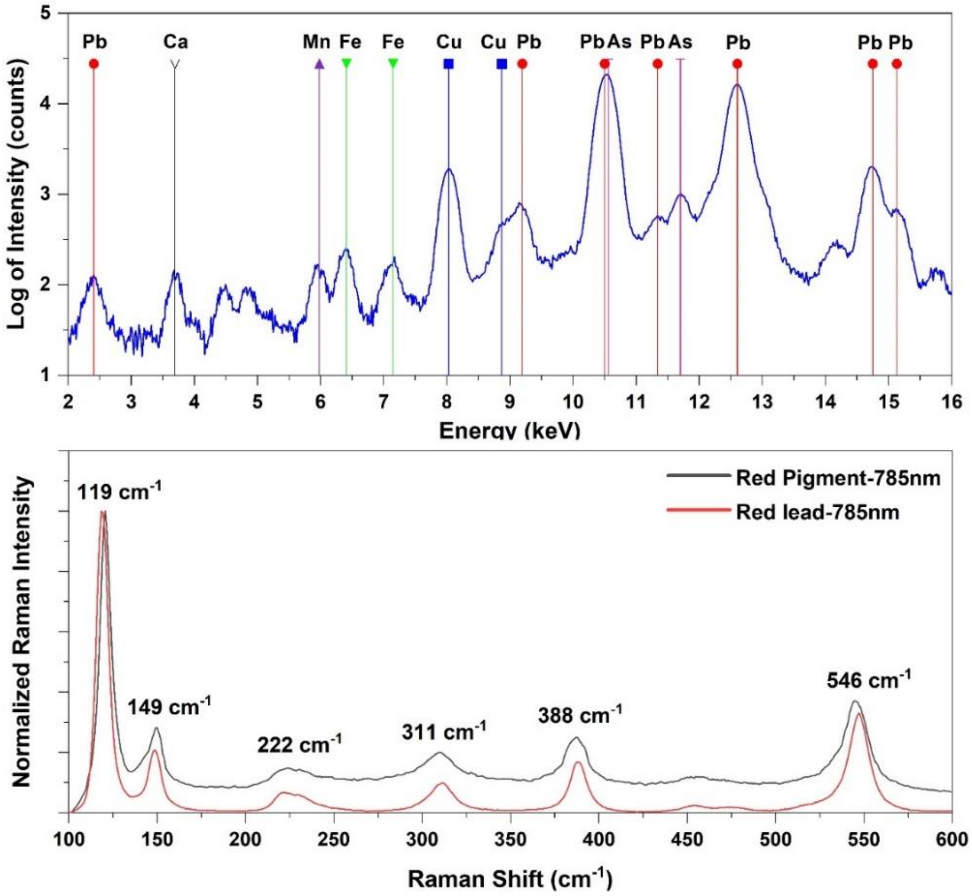

Figure 7: Top) Micro-XRF spectrum of the red pigment showing copper and arsenic elements related to the lower green pigment layer and lead; Bottom) Micro-Raman spectrum of the red pigment recorded using a 785 nm laser excitation alongside the red lead reference spectrum (CHSOS).

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 conichalcite in the green areas of the paintings. Conichalcite, 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.

5. References

1. Silva CE, Silva LP, Edwards HGMde Oliveira LFC. Diffuse reflection FTIR spectral database of dyes and pigments. Anal Bioanal Chem. 2006; 386(7):2183-91. https://doi.org/10.1007/s00216-006-0865-8.
2. Franquelo ML, Duran A, Herrera LK, Jimenez de Haro MCPerez-Rodriguez JL. Comparison between micro-Raman and micro-FTIR spectroscopy techniques for the characterization of pigments from Southern Spain Cultural Heritage. J Mol Struct. 2009; 924-926:404-12. https://doi.org/10.1016/j.molstruc. 2008.11.041.
3. Josa VG, Bertolino SR, Laguens A, Riveros JACastellano G. X-ray and scanning electron microscopy archaeometric studies of pigments from the Aguada culture, Argentina. Microchem J. 2010; 96(2):259-68. https://doi.org/10.1016/j.microc. 2010. 03.010.
4. Klockenkämper R, Von Bohlen AMoens L. Analysis of pigments and inks on oil paintings and historical manuscripts using total reflection x-ray fluorescence spectrometry. X-Ray Spect: An Inter J. 2000; 29(1):119-29. https://doi.org/10.1002/(SICI)1097-4539(200001/02)29:1%3C119.
5. Koochakzaei A, Alizadeh Gharetapeh SJelodarian Bidgoli B. Identification of pigments used in a Qajar manuscript from Iran by using atomic and molecular spectroscopy and technical photography methods. Heritage Sci. 2022; 10(1):30. https://doi.org/10. 1186/s40494-022-00665-x.
6. Koochakzaei A, Hamzavi YMousavi Sultanzadeh M. Characterization of the mural blue paintings in ornamental motif of Ali Qapu palace in Isfahan, Iran, using spectroscopic and microscopic methods (a case study). J Archaeological Sci: Rep. 2022; 45:103632. https://doi.org/10.1016/j.jasrep.2022.103632
7. Floor W. The woodworking craft and its products in Iran. Muqarnas. 2006;23:159-89. https://doi.org/10.1163/22118993_02301008
8. Ghiasian MR, Mashhadi Nooshabadi M. Ilkhanid Wood Carvings in the Mountain Villages between Kashan and Natanz. Iranian Stud. 2023; 56(2):255-75. https://doi.org/10.1017/irn.2022.72
9. Koochakzaei A, Marefat-Izadi P. Application of micro-Raman Spectroscopy for Identifying Pigments in Qajar Papier-Mache Penboxes (Qalamdan). J Color Sci Technol. 2024; 18(1): 57-66. https://dorl.net/dor/ 20.1001.1.17358779.1402.18.1.5.7
10. Knipe P, Eremin K, Walton M, Babini A, Rayner G. Materials and techniques of Islamic manuscripts. Heritage Sci. 2018; 6(1):55. https://doi.org/ 10.1186/ s40494-018-0217-y.
11. Koochakzaei A, Mobasher Maghsoud E, Jelodarian Bidgoli B. Non-invasive imaging and spectroscopy techniques for identifying historical pigments: a case study of Iranian manuscripts from the Qajar era. Heritage Sci. 2023; 11(1):157. https://doi.org/10.1186/ s40494-023-01011-5.
12. Koochakzaei A, Jelodarian Bidgoli B, Naserahari M. A Multi-Analytical Approach to Identify Colorants in the Qajar Painted Wooden Decorative False Ceilings, From Northwest Iran. Microscopy Microanal. 2024; 30(2): 401–414. https://doi.org/10.1093/mam/ozae029
13. Holakooei P, Karimy A-H, Nafisi G. Lammerite as a degradation product of emerald green: Scientific studies on a rural persian wall painting. Studies

Conservation. 2018; 63(7):391-402. https://doi.org/10.1080/00393630.2017.1419658.

14. Bruni S, Cariati F, Casadio F, Guglielmi V. Micro-Raman identification of the palette of a precious XVI century illuminated Persian codex. J Cultural Heritage. 2001; 2(4):291-6. https://doi.org/10.1016/S1296-2074(01)01131-1.
15. Muralha VSF, Burgio L, Clark RJH. Raman spectroscopy analysis of pigments on 16–17th c. Persian manuscripts. Spectrochimica Acta Part A: Mol Biomol Spect. 2012; 92:21-8. https://doi.org/10.1016/j. saa.2012.02.020.
16. Purinton N, Waiters M. A Study of the Materials Used by Medieval Persian Painters. J Am Institute Conserv. 1991; 30(2):125-44. https://doi.org/10.1179/019713691806066728.
17. Corso G, Gelzo M, Chambery A, Severino V, Maro AD, Lomoriello FS, D'Apolito O, Russo AD, Gargiulo P, Piccioli C, Arcari P. Characterization of pigments and ligands in a wall painting fragment from Liternum archaeological park (Italy). J Separation Sci. 2012; 35(21):2986-93. https://doi.org/10.1002/jssc.201200490
18. Karapanagiotis I, Minopoulou E, Valianou L, Daniilia S, Chryssoulakis Y. Investigation of the colourants used in icons of the Cretan School of iconography. Anal Chimica Acta. 2009;647(2):231-42. https://doi.org/10.1016/j.aca.2009.06.012
19. Koochakzaei A, Sarhaddi-Dadian H, Oudbashi O, Achachluei MM, Moradi H. Parthian dyed fabric discovered from Kuh-e Khwaja archaeological site, Sistan, Iran: A multi-analytical study for dye identification. J Archaeological Sci: Reports. 2023; 52:104288. https://doi.org/10.1016/j.jasrep. 2023. 104288.
20. Clark RJH, Mirabaud S. Identification of the pigments on a sixteenth century Persian book of poetry by Raman microscopy. J Raman Spect. 2006; 37(1-3):235-9. https://doi.org/10.1002/jrs.1473.
21. Haswell R, Carlyle L, Mensch KTJ. Van Gogh’s Painting Grounds: Quantitative Determination of Bulking Agents (Extenders) Using SEM/EDX. Microchimica Acta. 2006; 155(1):163-7. https://doi.org/ 10.1007/s00604-006-0536-7.
22. Chaplin TD, Clark RJH, Martinón-Torres M. A combined Raman microscopy, XRF and SEM–EDX study of three valuable objects – A large painted leather screen and two illuminated title pages in 17th century books of ordinances of the Worshipful Company of Barbers, London. J Mol Struct. 2010; 976(1):350-9. https://doi.org/10.1016/j.molstruc.2010.03.042.
23. Dyer J, Verri G, Cupitt J. Multispectral imaging in reflectance and photo-induced luminescence modes: A User Manual. London: British Museum; 2013.
24. Cosentino A. Identification of pigments by multispectral imaging; a flowchart method. Heritage Science. 2014;2(1):8. https://doi.org/10.1186/2050-7445-2-8.
25. Cosentino A. Practical notes on ultraviolet technical photography for art examination. Conservar Património. 2015; 215(21):53-62. https://doi.org/10.14568/cp2015006.
26. Koochakzaei A, Ghaffari T. Identification of traditional black Persian inks by spectroscopic and spectral imaging techniques: Presenting a flowchart method. Vibrational Spect. 2023; 127:103545. https://doi.org/10.1016/j.vibspec.2023.103545
27. Daniel F, Mounier A, Pérez-Arantegui J, Pardos C, Prieto-Taboada N, Fdez-Ortiz de Vallejuelo S, Castro K. Hyperspectral imaging applied to the analysis of Goya paintings in the Museum of Zaragoza (Spain). Microchem J. 2016; 126:113-20. https://doi.org/10.1016/j.microc.2015.11.044.
28. Grabowski B, Masarczyk W, Głomb P, Mendys A. Automatic pigment identification from hyperspectral data. J Cultural Heritage. 2018; 31:1-12. https://doi.org/10.1016/j.culher.2018.01.003.
29. Koochakzaei A, Oudbashi O. A courtly brocade belt belonging to Qajar period (1789–1925), Iran. Heritage Sc. 2023; 11(1):29. https://doi.org/10.1186/s40494-023-00875-x.
30. Koochakzaei A, Nemati Babaylou A, Jelodarian Bidgoli B. Identification of Coatings on Persian Lacquer Papier Mache Penboxes by Fourier Transform Infrared Spectroscopy and Luminescence Imaging. Heritage. 2021; 4(3):1962-9. http://dx.doi.org/10.3390/heritage4030111.
31. Edwards HGM, Villar SEJ, David AR, de Faria DLA. Nondestructive analysis of ancient Egyptian funerary relics by Raman spectroscopic techniques. Anal Chimica Acta. 2004; 503(2):223-33. https://doi.org/10.1016/j.aca.2003.10.057.
32. Aceto M, Agostino A, Fenoglio G, Idone A, Gulmini M, Picollo M, Ricciardi P, Delaney JK. Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. Anal Methods. 2014; 6(5):1488-500. https://doi.org/10.1039/C3AY41904E.
33. Bacci M, Picollo M, Trumpy G, Tsukada M, Kunzelman D. Non-invasive identification of white pigments on 20th-century oil paintings by using fiber optic reflectance spectroscopy. J Am Institute Conservation. 2007: 27-37. https://doi.org/10.1179/019713607806112413.
34. Cheilakou E, Troullinos M, Koui M. Identification of pigments on Byzantine wall paintings from Crete (14th century AD) using non-invasive Fiber Optics Diffuse Reflectance Spectroscopy (FORS). J Archaeological Sci. 2014; 41:541-55. https://doi.org/10.1016/j.jas.2013.09.020.
35. Dupuis G, Elias M, Simonot L. Pigment identification by fiber-optics diffuse reflectance spectroscopy. Appl Spect. 2002; 56(10):1329-36. https://doi.org/10.1016/j.jas.2013.09.020.
36. Cultural Heritage Science Open Source (CHSOS). Pigments Checker v.5, FREE Spectra Databases. 2019.

37. Niknejad M, Karimy A-H. Lead White or Lead Whites? Reconsideration of Methods of sefidāb-i-sorb Production in Iran. Studies Conservation. 2019; 64(1):1-9. https://doi.org/10.1080/00393630.2018.1457290
38. Bell IM, Clark RJ, Gibbs PJ. Raman spectroscopic library of natural and synthetic pigments (pre-≈ 1850 AD). Spectrochimica Acta Part A: Mol Biomol Spect. 1997; 53(12):2159-79. https://doi.org/10.1016/S1386-1425(97)00140-6
39. Roohi S, Holakooei P. Art historical and scientific controversies about four easel paintings attributed to Kamal al-Molk, the renowned nineteenth-twentieth century Persian painter. Heritage Sc. 2023; 11(1):197. https://doi.org/10.1186/s40494-023-01033-z
40. Barkeshli M. Paint Palette Used by Iranian Masters based on Persian Medieval Recipes. Restaurator International Journal for the Preservation of Library and Archival Mater. 2013; 34(2):101-33. https://doi.org/ 10.1515/res-2013-0007.
41. Benquerença M-J, Mendes NFC, Castellucci E, Gaspar VMF, Gil FPSC. Micro-Raman spectroscopy analysis of 16th century Portuguese Ferreirim Masters oil paintings. J Raman Spect. 2009; 40(12):2135-43. https://doi.org/10.1002/jrs.2383
42. Costantini I, Lottici PP, Castro K, Madariaga JM. Use of Temperature Controlled Stage Confocal Raman Microscopy to Study Phase Transition of Lead Dioxide (Plattnerite). Minerals. 2020; 10(5):468. http://dx.doi.org/10.3390/min10050468
43. Gliozzo EIonescu C. Pigments—Lead-based whites, reds, yellows and oranges and their alteration phases. Archaeol Anthropol Sci. 2021; 14(1):17. https://doi.org/10.1007/s12520-021-01407-z.
44. Osticioli I, Mendes NFC, Nevin A, Gil FPSC, Becucci M, Castellucci E. Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy. Spectrochimica Acta Part A: Mol Biomol Spect. 2009;73(3):525-31. https://doi.org/10.1016/j.saa.2008.11.028
45. Koochakzaei A, Hamzavi Y, Shojae far F. Identification of red, blue and golden pigments in Qajar Mural Painting anaclitic fire place in Goharion House in Tabriz. J Color Sci Technol. 2022; 15(4):287-99. https://dorl.net/dor/20.1001.1.17358779.1400.15.4.3.4
46. Holakooei P, Karimy A-H, Vaccaro C. A multi-analytical approach to the examination of nineteenth-century European wallpapers in Vasiq-Ansari House in Isfahan, Iran. Studies Conservation. 2014; 59(3):150-60. https://doi.org/10.1179/2047058413Y.0000000091
47. Oudbashi O, Shekofteh A, Eskandari N. Provenance of the Bronze Age lapis lazuli pieces from the Early Urban Center of Konar Sandal, Jiroft, Southern Iran. J Archaeol Sci: Rep. 2024; 55:104527. https://doi.org/10. 1016/j.jasrep.2024.104527.
48. Eastaugh N, Walsh V, Chaplin T, Siddall R. Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments. London: Routledge; 2008.
49. Monico L, Janssens K, Hendriks E, Brunetti BG, Miliani C. Raman study of different crystalline forms of $PbCrO_4$ and $PbCr1{-}xS_xO_4$ solid solutions for the noninvasive identification of chrome yellows in paintings: a focus on works by Vincent van Gogh. J Raman Spect. 2014;45(11-12):1034-45. https://doi.org/ 10.1002/jrs.4548.
50. Monico L, Janssens K, Miliani C, Brunetti BG, Vagnini M, Vanmeert F, Falkenberg G, Abakumov A, Lu Y, Tian H, Verbeeck J, Radepont M, Cotte M, Hendriks E, Geldof M, van der Loeff L, Salvant J, Menu M. Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Spectromicroscopic Methods. 3. Synthesis, Characterization, and Detection of Different Crystal Forms of the Chrome Yellow Pigment. Anal Chem. 2013; 85(2):851-9. https://doi.org/10.1021/ac302158b
51. Otero V, Carlyle L, Vilarigues M, Melo MJ. Chrome yellow in nineteenth century art: historic reconstructions of an artists' pigment. RSC Adv. 2012; 2(5):1798-805. https://doi.org/10.1039/C1RA00614B.
52. Petrova O, Pankin D, Povolotckaia A, Borisov E, Krivul'ko T, Kurganov N, Kurochkin A. Pigment palette study of the XIX century plafond painting by Raman spectroscopy. J Cultural Heritage. 2019; 37:233-7. https://doi.org/10.1016/j.culher.2018.11.010
53. Reddy BJ, Frost RL, Martens WN. Characterization of conichalcite by SEM, FTIR, Raman and electronic reflectance spectroscopy. Mineralogical Magazine. 2005; 69(2):155-67. https://doi.org/10.1180/0026461056920243.
54. Shen L, Wang C, Zhang J, Cui B, Zhu S, Mao J. Cu and As containing pigments in Zhejiang architecture polychrome paintings: a case study of degradation products of emerald green. Heritage Sci. 2023;11(1):9. https://doi.org/10.1186/s40494-022-00834-y.
55. Chen E, Zhang B, Lin Y, Meng C. Research on painting pigments and binders in Murals of traditional buildings in Zhejiang Province. Orient Mus. 2018;3:107-13.
56. Aggelakopoulou E, Sotiropoulou S, Karagiannis G. Architectural polychromy on the athenian acropolis: an in situ non-invasive analytical investigation of the colour remains. Heritage. 2022; 5(2):756-87. http://dx.doi.org/10.3390/heritage5020042
57. Svorová Pawełkowicz S, Wagner B, Kotowski J, Żukowska GZ, Gołębiowska B, Siuda R, Jokubauskas P. Antimony and nickel impurities in blue and green copper pigments. Minerals. 2021; 11: 1236. https://doi.org/10.3390/min11111236.
58. Tsatsouli K, Nikolaou E. The ancient Demetrias figurines: new insights on pigments and decoration techniques used on Hellenistic clay figurines. STAR: Sci Technol Archaeol Res. 2017; 3(2):341-57. https://doi.org/10.1080/20548923.2018.1424302

59. Herm C, Emerald green versus Scheele's green: evidence and occurrence. Proceedings of the 7th interdisciplinary ALMA conference, Bratislava, Slovakia; 2019. pp.189-202.

60. Bioletti S, Leahy R, Fields J, Meehan B, Blau W. The examination of the Book of Kells using micro-Raman spectroscopy. J Raman Spect. 2009; 40(8):1043-9. https://doi.org/10.1002/jrs.2231.

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