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A Multi-Method Analysis of a Color Painting on Ancient Architecture from Anyuan Temple in Chengde, China

Juan Li * and Rong Zhao *

School of Cultural Heritage, Northwest University, Xi'an 710217, China
* Correspondence: lijuanlijuan2024@sina.com (J.L.); rzhao23@163.com (R.Z.)

Abstract: Anyuan Temple, constructed in the 29th year of the Qing Dynasty (1764), serves as a repository of numerous Sanskrit inscriptions and Hexi color paintings from the Qing era. Among its collections, the green Tara Buddha statue, exquisitely carved from wood, is recognized as a national first-class cultural relic. This edifice is instrumental in advancing our comprehension of painting artistry in royal temples. The current research focused on the pigments and binders utilized in the color paintings within Anyuan Temple, located in Chengde. An investigative process entailed collecting four samples from the paintings adorning the temple's beams. These samples underwent comprehensive analysis using a variety of techniques, such as Scanning Electron Microscopy and Energy-Dispersive Spectrometry (EDS), Micro Raman Spectroscopy (m-RS), and X-ray Diffraction (XRD). The examination revealed that the paintings comprised pigments of lead white, cinnabar, malachite, and azurite, corresponding to the colors white, red, green, and blue, respectively. The enduring stability and aesthetic appeal of these pigments suggest their suitability for use in future conservation efforts. Additionally, Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS) analysis identified animal glue as the binding agent in the wood component paintings. These insights are pivotal for the forthcoming restoration endeavors of Anyuan Temple, offering essential guidance in selecting the appropriate materials for restoration.

Keywords: Anyuan Temple; color painting; pigments; binder

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1. Introduction

Anyuan Temple, also known as "Yili Temple" or "Jinding Temple" and colloquially referred to as "Fangting" due to the square configuration of its main hall, Pudu Hall, is situated on the eastern bank of the Wulie River in northeast Hebei Province (Figure 1a). This temple, a Gelugpa Tibetan Buddhist establishment, was constructed in the 29th year of the Qianlong reign of the Qing Dynasty (1764). Its shape is modeled after the Guerza Temple on the River Ili in Xinjiang. After the completion of Anyuan Temple, the leaders of the Mongol departments of Erut came to Rehe for a gathering every summer. This temple was the second lama temple built outside the Summer Resort by Emperor Qianlong after the Puning Temple in the process of pacifying Junggar. It houses an extensive collection of Qing Dynasty Sanskrit inscriptions and Hexi color paintings. Pudu Hall, serving as the primary hall, is particularly notable for its preservation of numerous Qing Dynasty color paintings (Figure 1b,c). The historical significance of these paintings in Anyuan Temple primarily stems from their uniqueness. The temple symbolizes the commemoration of the Dashdawa tribe of the Erute Mongols, who resisted the Amur Qashqana rebellion, relocated their troops, and upheld ethnic unity. It represents a spiritual sanctuary constructed by the Qing Dynasty to honor the religious beliefs of the Dashdawa tribe. Furthermore, Anyuan Temple exemplifies a typical Buddhist temple that melds Han and Tibetan influences, mirroring the religious beliefs and customs of the Mongolian people during the Qianlong period of the Qing Dynasty. In December 1994, UNESCO designated Anyuan Temple as a World Cultural Heritage site. Anyuan Temple is of great significance to the study of Tibetan Buddhism and provides historians with important historical support.

Figure 1. (**a**) The location of Anyuan Temple, situated in Chengde County, Hebei Province; (**b**) Pudu Hall; (**c**) Hexi color paintings.

Pudu Hall depicts (Figure 1c) the highest level of color painting in ancient Chinese paintings and is often used in palaces and temples of higher rank. The decoration of ancient architectural color paintings can cover the defects of wood grain and prevent wood from being eroded by adverse environments. From about 770 BC to 476 BC, people used pigments to make simple drawings on wood; the development of ancient architectural color paintings reached its peak during the Ming and Qing dynasties of China. Ancient architectural color paintings from this period were complicated and had a strict hierarchy, such as "Hexi" color painting. This is the highest grade of color painting, mostly painted on palace buildings or buildings associated with the royal family. Color painting involved three distinct components: a pigment layer, a ground layer, and wooden elements. The mortar used in these paintings typically consisted of brick ash, lime water, fiber, blood, and tung oil.

Color painting is an important component of ancient Chinese architecture. Studying these paintings aids in understanding their materials and craftsmanship [1], thereby informing improved protection and restoration methods [2]. As a component of ancient Chinese royal architecture, Anyuan Temple features a variety of colorful paintings with rigorous production techniques, exhibiting distinct ethnic and historical characteristics. These paintings possess immense artistic and research value. However, over 200 years of natural aging and maintenance neglect have led to extensive damage, including peeling, pollution, warping, cracking, and hollowing [3,4]. This deterioration is increasingly severe, making the protection and repair of these paintings urgent.

The primary task in the color painting protection project at Anyuan Temple involves studying the materials used in these paintings. These materials principally consist of pigments and binders. Pigments, which impart color, are crucial to color painting research. Binders strengthen the bond between the pigments and the ground layers [2,5–7]. Historically, mineral pigments were predominantly used, being favored for their varied colors, accessibility, diverse types, and stable physical and chemical properties. Common mineral pigments include cinnabar [8,9], lead red [10], iron oxide [11], carbon black [12,13], ultramarine [14], lead white [15], and azurite. Binders [16] also play a vital role in securing pigments to mortar surfaces. Water-soluble binders like fish glue and bone glue are used with hydrophilic pigments [17]. For oil-based pigments, options include castor oil, flaxseed oil, and tung oil [18]. Emulsion pigments often incorporate chicken eggs and proteins. These binders can be used individually or in combinations of two or three types.

The aim of this study is to explore the pigments and binder layers used in the architectural paintings in Anyuan Temple. Employing various scientific analysis techniques, such as Energy-Dispersive Spectrometry (EDS) [19], X-Ray Diffraction (XRD), Micro Raman Spectroscopy (m-RS) [20], and Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS), this study analyzes painting samples from Anyuan Temple. The goal is to deepen our understanding of the temple's official paintings from the Qing Dynasty and provide valuable insights for future restoration efforts.

2. Materials and Methods

2.1. Materials

Samples were collected from the peeled paint on the eastern beam of the second floor of Anyuan Temple. To preserve as much of the painting's integrity as possible, a small number of samples were collected from four areas (Figure 2). Firstly, the pigment particles were observed using a polarized light microscope. This was followed by elemental analysis with EDS. The composition and structure of the pigments were then identified using m-RS and FTIR spectrometers. Py-GC/MS was employed to characterize the organic binder in the pigment samples.

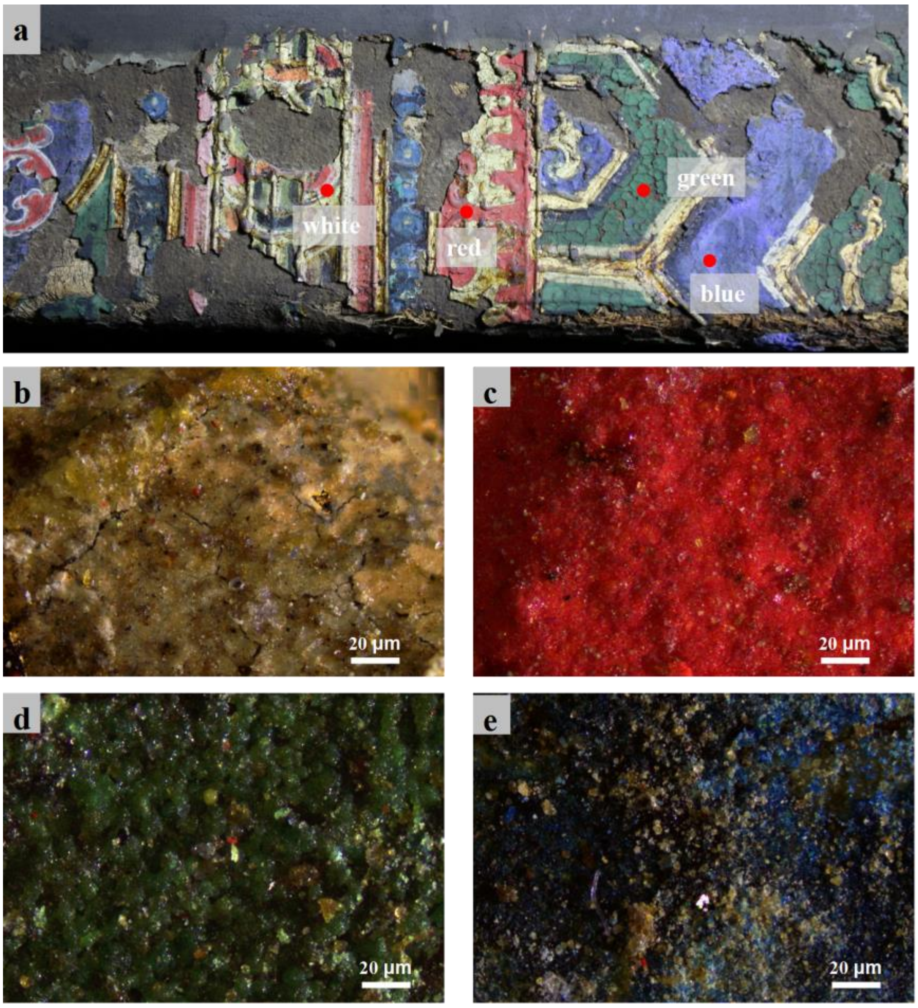


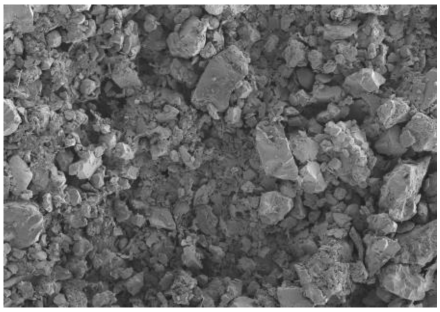
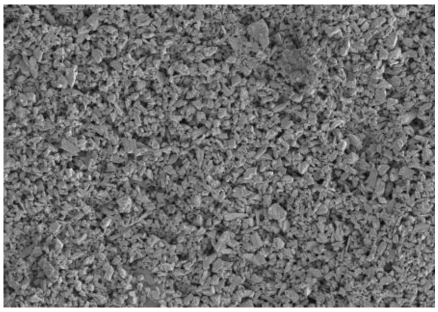
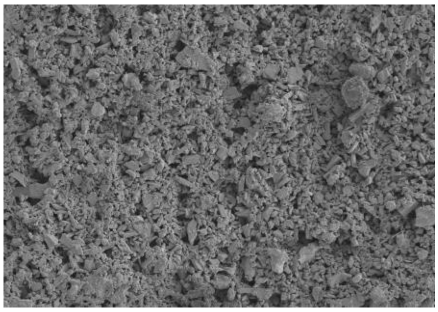
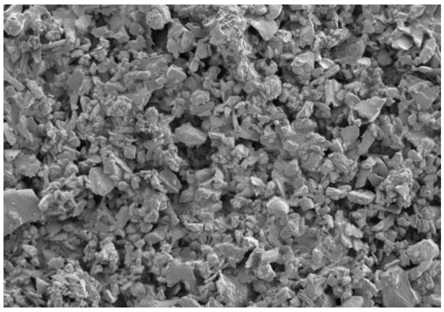
Figure 2. (**a**) Four pigment samples collected from the color painting on the beam: (**b**) white, (**c**) red, (**d**) green, and (**e**) blue pigments, as labeled with red dots. All samples were observed under 20× magnifications.

2.2. Methods

2.2.1. Energy Dispersive Spectrometry (EDS)

Elemental analyses were conducted using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (Tokyo, Japan) with a high-performance silicon drift detector and X-ray tube (Rh target); the test range was 11NA–92U. Calibration was conducted using two elements, copper and aluminum, as standard samples. The surface of the sample was coated with gold (HITACHI SU3500). The results are shown in Table 1.

Table 1. Elements and SEM of pigment particles, as detected by EDS.

Sample	Color	Elements	SEM (×500)
1	White	Pb (60.9%), Ca (16.2%), Fe (8.3%), Si (5.0%), K (4.3%)	
2	Red	Pb (53.5%), Hg (28.2%), Ca (5.0%), K (3.6%), Si (2.8%)	
3	Green	Cu (82.5%), Si (7.1%), Ca (3.8%), Pb (1.97%), Fe (1.87%)	
4	Blue	Cu (81.8%), Si (7.4%), Ca (3.7%), Pb (1.87%), K (1.8%)	

2.2.2. Micro Raman Spectroscopy (m-RS)

Micro Raman spectra were recorded using a LabRAM HR Evolution Raman microscope (Wotton-under-Edger Renishaw, UK). It was equipped with an 1800-groove/mm grating and a coupled m-RS charge detector. The excitation wavelength was 532 nm. An objective lens was used to observe the pigment over a collection range of 100–2000 wavenumbers (cm^{-1}), with a laser power of 1–2 mW; each sample was tested 3 times for 1.5 min.

2.2.3. X-ray Diffraction Meter

A Rigaku Corporation Smart Lab 9 high-resolution X-ray diffractometer was used. The testing conditions included a Cu Kα ray (λ = 1.54056 A), a 2θ range of 20°–80°, an acceleration voltage of 45 kV, a tube current of 200 mA, and a scanning speed of 5°/min.

2.2.4. Pyrolysis–Gas Chromatography–Mass Spectrometry (Py-GC/MS)

Approximately 50 µg of the pigment sample was placed into a thermal pyrolysis reactor with a pre-treatment of 3 µL of 20% *w*/*w* tetramethylammonium hydroxide (TMAH). The sample was then left to stand for 1 h in the automatic sampler before pyrolysis at 600 °C. Post-pyrolysis, the resulting products were identified using GC-MS. The Py-GC/MS setup, consisting of two parts, included a Frontier Labs EGA/PY-3030D (Koriyama, Japan) for pyrolysis and a Shimadzu QP2010 Ultra (Kyoto, Japan) with an SLB-5MS chromatography column (5% diphenyl-95% dimethylsiloxane) for GC/MS.

The initial temperature of the oven containing the column was set to 50 °C, and this was held for 5 min. The temperature was then increased at a rate of 3 °C/min to a final temperature of 292 °C, which was held for 3 min. The pre-column pressure, the flow rate, and the separation ratio were set at 15.4 kPa, 0.6 mL/min, and 1:100, respectively, and the ionization voltage, scan rate, and mass-to-charge ratio of the mass spectrometer were set at 70 eV, 0.5 s, and 50 to 750, respectively.

3. Results and Discussion

3.1. Analysis of Pigments

3.1.1. White Pigment Analysis

The EDS analysis of the white pigment reveals its primary components as Pb, Fe, Ca, and Si, among others. Figure 3 illustrates the analysis and testing results of the white pigment, which includes Raman spectroscopy (Figure 3a) and XRD (Figure 3b). Based on these results, we hypothesize that the white pigment is lead white, a pigment prevalently used by ancient artists and those in the 20th century. Lead white is composed of lead carbonate ($PbCO_3$) and basic lead carbonate ($2PbCO_3 \bullet Pb(OH)_2$) in varying proportions. Its physical properties, notably its stability and resistance to discoloration over time, have made it a favored choice among oil painting masters and craftsmen from ancient times to today [21]. The Raman spectra of the white sample (Figure 3b) show characteristic peaks at 167 cm^{-1}, 417 cm^{-1}, and 1052 cm^{-1} [4]. These peaks align with the standard Raman spectra of lead white, where the 1052 cm^{-1} peak represents a completely symmetrical vibration, and the 417 cm^{-1} peak corresponds to the vibration of the Pb-O bond [22–25]. The XRD analysis reveals that the sample's diffraction peaks at 24.6° and 36.1° are highly consistent with the lead carbonate standard. However, the presence of Si on the surface dust of the sample led to the appearance of SiO_2 features in the XRD results. These findings collectively suggest that the white pigment used in the color paintings of Anyuan Temple is lead white.

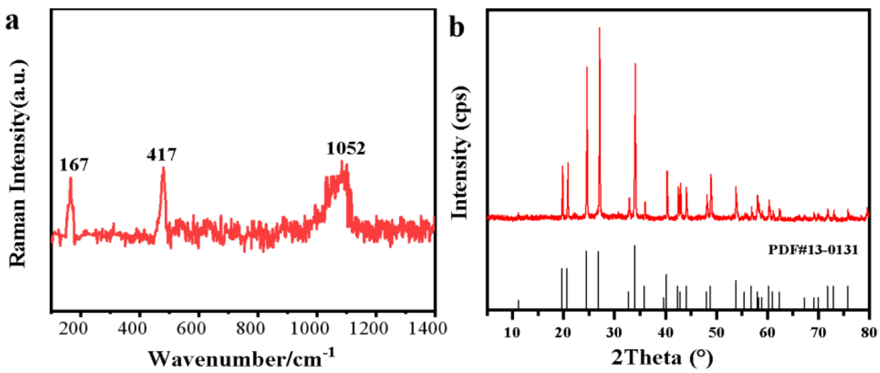


Figure 3. Raman spectra (**a**) and X-ray diffraction spectra (**b**) of the white pigments (The black line is a standard PDF card, obtained from the Jade software, and the red line is the test result).

3.1.2. Red Pigment Analysis

Red pigment is a common color in ancient Chinese architectural paintings, typically used either alone or in combination. The EDS analysis of the red pigment from this study sample revealed the presence of Pb, Hg, Ca, K, and Si. Based on the relevant literature, we hypothesize that the red pigment is likely cinnabar or lead, both commonly used in ancient Chinese architectural paintings. The presence of Ca and Si might be attributable to impurities like dust on the pigment layer's surface. To further verify the pigment's properties, SEM, Raman spectra, and XRD analyses were conducted on the red sample, as presented in Figure 4. The Raman spectra and XRD results in Figure 4 confirm cinnabar's presence, aligning with the EDS findings. Specifically, the Raman spectra of sample 4a exhibit characteristic bands at 254 cm^{-1}, 285 cm^{-1}, and 349 cm^{-1} [19,26,27], which match cinnabar's characteristic bands [28]. The XRD analysis of the sample in Figure 4b correlates with the standard HgS card, showing pronounced peaks at angles of 26.5°, 28.2°, and 31.2° [29], confirming the presence of HgS.

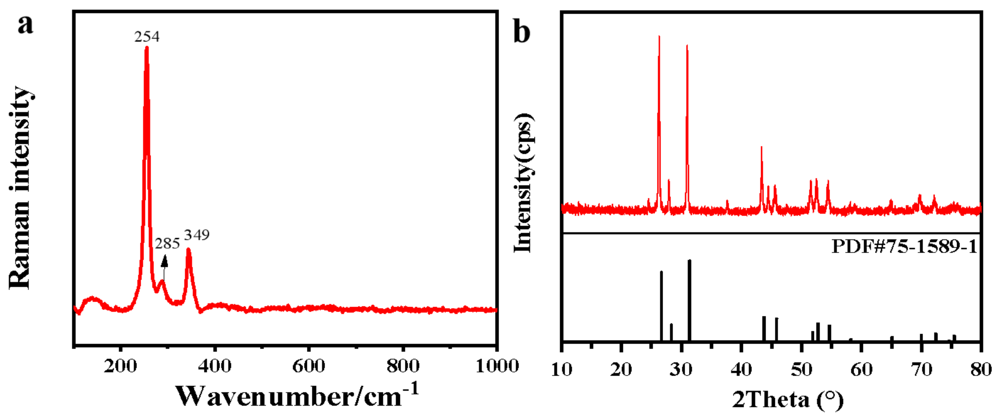


Figure 4. (**a**) Raman spectra for red pigments; (**b**) X-ray diffraction spectra of red pigments.

3.1.3. Green Pigment Analysis

Green symbolizes vitality and is prevalent in ancient Chinese architectural paintings. It not only adds brightness to colorful paintings but also, when combined with blue, enhances the depth of visual effects, particularly on eaves. Key green pigments include malachite ($CuCO_3$•$Cu(OH)_2$), atacamite ($Cu(OH)_3Cl$), and Paris green ($Cu(CH_3COO)_2$•$3Cu(AsO_2)_2$). Malachite, known for its bright hue and high cost, is extensively used in royal architectural paintings. Our EDS analysis of the green pigment in the Anyuan Temple painting revealed primary components of Cu, Si, Ca, Pb, and Fe. This composition suggests the pigment could be either malachite or Paris green. The Raman spectrum of the pigment exhibits distinct peaks at 153 cm^{-1}, 180 cm^{-1}, 218 cm^{-1}, 270 cm^{-1}, 356 cm^{-1}, 435 cm^{-1}, and 555 cm^{-1} [22,30], aligning with malachite's standard spectrum. Additionally, the XRD diffraction peaks of the sample at 31.3°, 24.1°, 17.6°, and 14.8° align with malachite (Figure 5b). Furthermore, Raman peaks at 1100 and 1440 cm^{-1}, characteristic of the blue pigment lapis lazuli, were observed. This finding, coupled with the polarized photo in Figure 2, indicates a mixture of malachite and lapis lazuli in the sample. This mixture corroborates the historical use of combined pigments to achieve a profound visual impact in color painting.

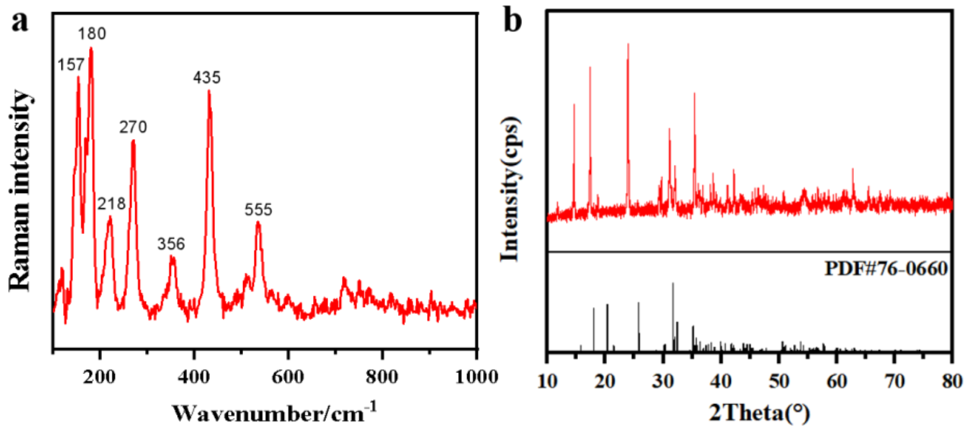


Figure 5. (**a**) Raman spectra of green pigments; (**b**) X-ray diffraction spectra of green pigments (The black line is a standard PDF card, obtained from the Jade software, and the red line is the test result).

3.1.4. Blue Pigment Analysis

We conducted a comprehensive analysis of the blue areas in the selected samples using EDS, Scanning Electron Microscopy, Raman spectroscopy, and XRD. These analyses collectively indicate that the blue pigment is azurite ($2CuCO_3{\cdot}Cu(OH)_2$). Specifically, the EDS results show that Cu is the predominant metal element in the pigment. Raman spectroscopy reveals characteristic peaks at 253, 403, and 766 cm^{-1}, aligning with the Raman spectrum of lapis lazuli. Notably, the pigment's Raman spectrum, as shown in Figure 6a, exhibits a distinct peak at 1094 cm^{-1}, attributable to the symmetric stretching of the C-O bonds [4]. Further, the XRD results, as illustrated in Figure 6b, display diffraction peaks at 17.5°, 24.2°, and 35.3°. These peaks demonstrate a high degree of consistency with the standard card of lapis lazuli, confirming the identification of the pigment. Based on these findings, we conclude that the blue pigment in the analyzed samples is indeed lapis lazuli. Historically, lapis lazuli was extensively used as a blue pigment, as evidenced in various art forms such as cave paintings in Dunhuang (Northwest China), murals from the Tang and Song dynasties, architectural paintings from the Ming and Qing dynasties, and Japanese murals. Additionally, azurite served as a primary blue pigment in medieval and Renaissance European paintings.

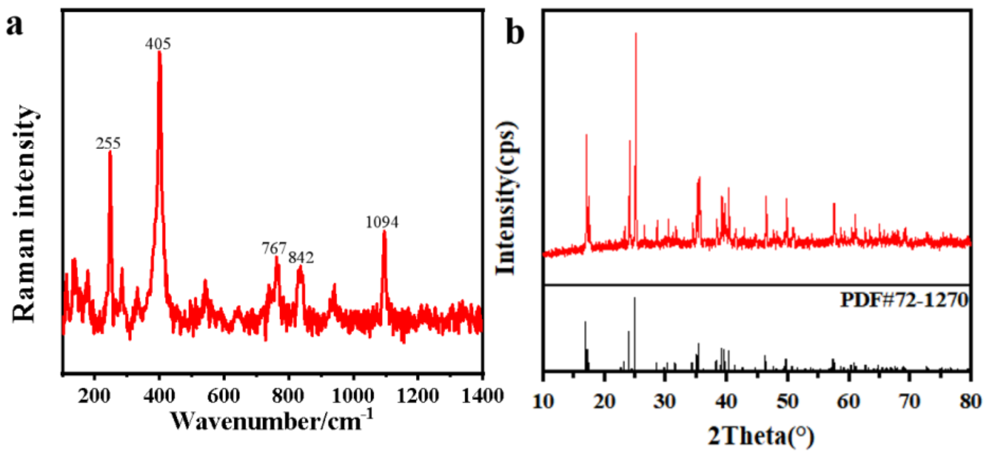


Figure 6. (**a**) Raman spectra of blue pigments; (**b**) X-ray diffraction spectra of blue pigments (The black line is a standard PDF card, obtained from the Jade software, and the red line is the test result).

3.2. Analysis of Binder

In the context of ancient architectural painting, both mineral and organic pigments present challenges in direct application. To address this, the pigments were typically applied to wooden components for prolonged retention. Ancient artisans employed binders to enhance pigment adhesion and prevent detachment during the painting process, making the analysis of these binders critical. Py-GC/MS analysis [31] was conducted on the experimental samples (as shown in Figure 6). Owing to the implementation of methylation techniques, most characteristic by-products are identified as their methylated derivatives. The corresponding peak indices are shown in Figure 7. The pyrolysis outcomes reveal a plethora of protein-specific pyrolysis products, such as 1H Pyrrole, 1-methyl (peak 1), Glycine (glue and egg white) (peak 3), Alanine (peak 4), Valine (peak 5), and metal ester (peak 7). These findings suggest the presence of protein-based binders in the samples, as supported by previous research [32,33]. The relatively low concentration of these substances can be attributed to natural aging. Concurrently, the detection of proteins (peak 8) and specific cleavage products of bone glue, such as the marker for fish glue [28], suggests that glue proteins might have been used as binders in these samples.

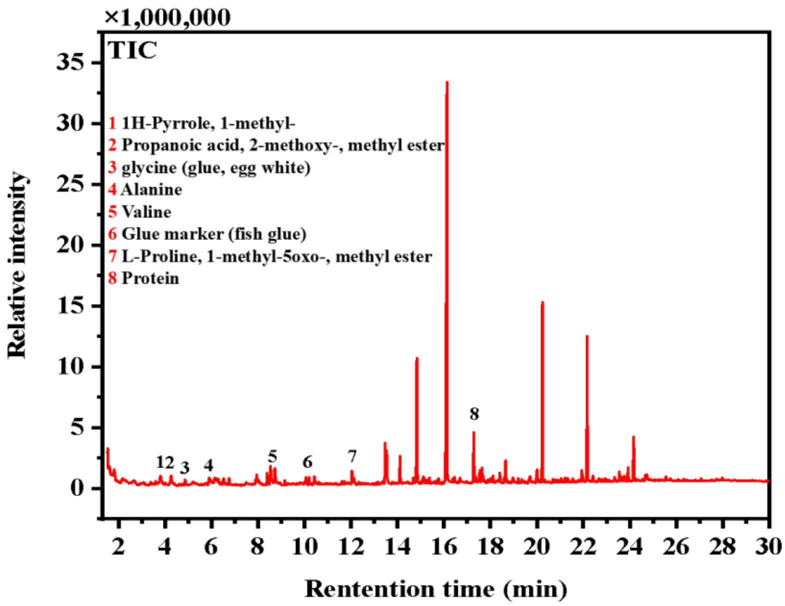


Figure 7. Binder chromatography of red samples.

The analysis of fatty acid concentration in the sample, obtained through Py-GC/MS, is depicted in Figure 8. This figure shows carboxylic acids with varying carbon numbers (n). The sample contains both monocarboxylic and dicarboxylic acids, characteristic pyrolysis products of drying oils. Figure 8 illustrates the relative concentration of fatty acids in the red sample, highlighting the presence of drying oil components (monocarboxylic and dicarboxylic acids). Drying oils exhibit stable chemical properties, with varying concentrations of palmitic and stearic acids. Consequently, the ratio of palmitic to stearic acid (P/S ratio) serves as an indicator to differentiate between the different types of drying oils. In this sample, the P/S ratio is 0.96. While P/S values for each drying oil slightly vary in the literature, with and without color, they generally fall within an acceptable error range. The P/S values are typically 0.9–1.1 for mature tung oil, 1.3–1.6 for raw tung oil, 1.2–1.5 for flax oil, 1.6–1.8 for poppy oil, and 1.8–2.0 for walnut oil [34]. Based on these values, it is inferred that the pigment layer contains mature tung oil. The presence of mature tung oil in the sample is likely a result of the historical production techniques employed in ancient Chinese architectural painting [4]. The correlation between the presence of mature tung oil and the painting process suggests that an oil layer was applied to the ground before the foundation was laid [6,18,35]. This application aimed to smoothen the surface and enhance adhesion to the foundation. Hence, the detection of mature tung oil in the sample can be reasonably attributed to the permeation from its underlying layer.

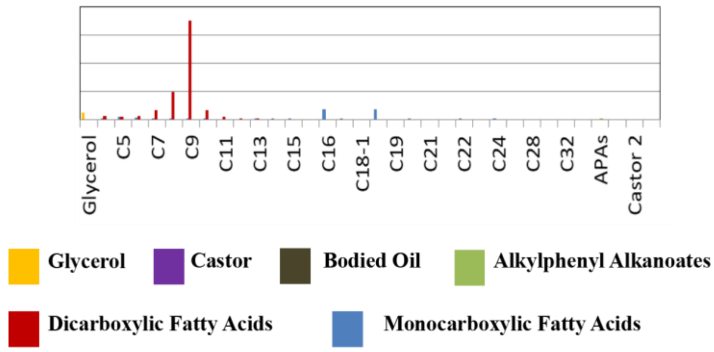


Figure 8. Relative concentrations of fatty acids of samples.

4. Conclusions

An examination of representative painting samples from Anyuan Temple suggests that the temple's architectural color paintings are characterized by their well-preserved state, exquisite craftsmanship, and vibrant hues. The analysis deployed PLM, EDS, m-RS, and XRD techniques to investigate the crossbeam paintings in Anyuan Temple. This analysis revealed the use of specific pigments: cinnabar for red, lead white for white, lapis lazuli for blue, and malachite for green. The ceiling oil paintings also employed these pigments, showcasing a similar color palette of white, red, blue, and green. Notably, all pigments identified in this study are inorganic mineral pigments.

Further, Py-GC/MS was utilized, identifying animal glue as the binder in the pigment layers of the examined samples. The detection of both raw and cooked tung oil suggests possible infiltration from the plaster material used in the temple's construction.

This comprehensive inspection and analysis of the pigment layers and binder in Anyuan Temple provide crucial data for the selection of appropriate materials for future restoration efforts. Moreover, the findings offer valuable insights for the restoration of ancient buildings related to the royal heritage of the Qing Dynasty in China, particularly those featuring painted surfaces.

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