Article

Investigation on the Painting Materials and Profile Structures Used in Ancient Chinese Folk Architectural Paintings by Multiple Analytical Methods

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Abstract: In order to understand the painting materials and profile structures used in the creation of Chinese ancient folk architectural paintings, the architectural paintings of the Bell and Drum Tower at Fushan Temple in Shaanxi Province of China was investigated. In this study, optical microscopy, Fourier transform infrared spectroscopy (FTIR), micro-Raman spectroscopy, scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS), and chemical experimental methods were used. The profile structures, and the elemental and chemical compositions of the pigments and binders in the ground layer of the 12 samples were determined. Results showed that the painting profile structures in both towers comprised of pigment layer, underpainting layer and ground layer, where no starch was found in the chalk ground layer. The pigment layer mainly comprised of iron oxide red, chalk, lapis lazuli, carbon black, green earth, and a dark green pigment that is formed by a combination of carbon black and green earth. To-date, the use of green earth pigment in Chinese architectural paintings was not found in Chinese related academic literature; hence, this study marked the first identification of green earth being used in the architectural paintings. Tung oil, commonly used in Chinese architectural paintings as a binder for pigment, was also identified in the samples. Results from this study will serve as an important reference for better scientific investigation methods on ancient Chinese folk painting materials.

Keywords: ancient folk architectural paintings; pigments; binders; profile structures; FTIR spectroscopy; micro-Raman spectroscopy; SEM-EDS

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1. Introduction

Ancient Chinese architectural paintings, commonly used to decorate the surfaces of building columns, beams, walls and other structural elements, consist mainly of pigment and ground layer. These paintings are important features of ancient Chinese architecture, with great historical, cultural, and artistic value [1]. However, due to natural degradation over time, the paintings on the building faced deterioration problems such as flaking, peeling, and fading of the pigment layer and ground layer, thereby leading to the gradual loss of cultural and artistic heritage [2]. Many types of ancient Chinese architectural paintings are still in existence and are widely distributed, but to-date, limited studies can be found on the proper evaluation methodology for the original production processes of ancient Chinese architectural painting. In particular, previous studies mostly focused on the study of ancient Chinese official architectural paintings, such as the Cining Palace paintings [3], the Xi'an Drum Tower paintings [2], and the Foguang Temple paintings [4]. The study of ancient folk architectural paintings, on the other hand, has rarely been discussed. Thus, there is an urgent need to understand the painting profile and material composition before conservation works can be carried out properly. The Shaanxi Fushan temple is, by far, one of the few remaining folk temples in China that was first established in the Tang dynasty and has witnessed thousands of years of ancient Chinese civilization. Hence, to

better understand the painting profile structures and materials used in the production of the ancient Chinese folk architectural paintings, the architectural paintings of the Fushan Temple was selected as a representative case due to its long historical background.

Located in Heyang county of Shaanxi Province, the ancient architectural complex of Fushan temple is the fourth batch of cultural relics protection unit listed in the Shaanxi Province (Figure 1). Based on historical records, the building complex was first established in the Tang dynasty, and had undergone several major constructions between the Ming and Qing dynasties. Last recorded repair and construction works, involving the existing Bell and Drum Towers and the additions of new ancillary structures (Sanqing pavilion, Praying pavilion, Earth pavilion and Wall of Blessing) took place in 1882 AD. Due to natural weathering over time, the architectural paintings on the Drum and Bell Towers faced severe deterioration problems, such as flaking, peeling, and discoloration, subsequently leading to exposure and gradual decay of the wooden components. As the Bell and Drum Towers are the last remaining group of original buildings left within the complex, the decision was made to select samples with the most severe damage condition from different parts of the Bell and Drum Tower for investigation and analysis.

Figure 1. (a) the location of Fushan Temple in Weinan, Shaanxi Province, China; (b) the entrance of Fushan Temple; (c) the Drum tower; (d) the Bell tower.

In recent years, micro-Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS), and other analytical techniques have been used widely to investigate the composition, morphology, and microstructure of various painted artworks [5–8]. Raman spectroscopy has been used to analyze a wide range of pigment compositions in artwork because it is non-destructive and can potentially characterize mineral materials [9,10]. For example, Proietti et al. [11] used Raman spectroscopy to identify the composition and pigments in Nubian mural painting layer, and confirmed the presence of pigments such as hematite,

gypsum, and atacamite. The materials of mural paintings from Liao dynasty in Xuanhua, China, were also identified by micro-Raman spectroscopy and indicated that the pigments of plaster, hematite ultramarine, and carbon were applied [6].

Similar to micro-Raman spectroscopy, FTIR spectroscopy can be used for qualitative analyses of artwork materials and since it complements the results obtained by Raman spectroscopy, FTIR spectroscopy is also considered as an important method for the detection of organic materials with polar molecules [12,13]. Cheilakou et al. [7], for example, identified the presence of organic binders in various types of pigments in addition to cinnabar, ochre, and celadonite, used in the Byzantine wall paintings by Fourier transform infrared spectroscopy, and confirmed that the binders were protein-based substances by analyzing their infrared spectral absorption peaks. Moretti et al. [12] also used FTIR spectroscopy to determine the composition of Argentinean murals and confirmed the presence of gypsum and drying oil.

SEM-EDS and optical microscopy are particularly useful for observing the microscopic morphology and structure of painted artwork materials [14,15]. For example, in the case of the fresco sections in an Andean church, Tomasini et al. [16] determined the morphological characteristics of the layers and the elemental composition using optical microscopy and SEM-EDS, and confirmed that the sequence of the fresco's sections began with the pigment layer lining the surface, followed by white ground layer applied above the adobe wall. In the study conducted by Demir et al. [14], the painting techniques were also analyzed by optical microscopy and SEM-EDS, and the results indicated that the paintings were composed of a fine plaster and a thin paint layer over the plaster layer.

In this paper, profile structures of the samples from various parts of the Drum Tower and Bell Tower were analyzed using optical microscopy. Elemental and chemical compositions of the pigments, binders, and ground layer in the paintings were also qualitatively analyzed using micro-Raman spectroscopy, FTIR spectroscopy, and EDS. As noted in two important ancient Chinese building construction manuals, namely the Song dynasty “*Yingzao fashi*” [17] and the Qing dynasty “*Gongcheng Zuofa Zeli*” [18], starch (such as flour) was commonly used as one of the ingredients for the ground layer of architectural paintings. Hence, iodine staining tests were applied to the samples to determine whether starch was present in the ground layer of the paintings. Finally, based on the results obtained from the above tests, scientific methods on the selection of materials and techniques for the future restoration of ancient Chinese architectural paintings were proposed.

2. Methods and Experimental Design

2.1. Samples and Dyeing Experiments

Twelve samples were carefully extracted from the severely damaged portions of the Bell and Drum Towers' columns, beams and Queti (a beam-supporting brace structure). Based on the “Principles for the Conservation of Heritage Sites in China” [19], tiny fragments from the painting layers with severe deterioration or flaking condition were gently scrapped with a scalpel so as to reduce the damage done towards the historic decorations. The fragments were then placed in sample bags and sealed for subsequent laboratory tests and analysis. Details of the 12 samples are listed in Table 1 and Figure 2.

Figure 2. The Sampling position: (a) the Drum tower; (b) the Bell tower.

Table 1. Details of samples collected from the Bell and Drum Towers.

Sampling Location		Drum Tower (DT)				
Sampling number	DT-01	DT-02	DT-03	DT-04	DT-05	DT-06
Sampling colour	Red	White	Black	Blue	Green	Dark green
Sampling position	Beam (West)	Beam (West)	Beam (North)	Beam (West)	Queti (South)	Wooden column (West)
Sampling location		Bell Tower (BT)				
Sampling number	BT-01	BT-02	BT-03	BT-04	BT-05	BT-06
Sampling colour	Red	White	Black	Blue	Green	Dark green
Sampling position	Beam (West)	Beam (North)	Beam (North)	Beam (West)	Queti (East)	Wooden column (East)

Curing process was required to facilitate observations and stratigraphy analysis of the paint samples' profiles. In the first step, epoxy resin and curing solution were prepared at a ratio of 2.5:1 and poured into a 4 cm × 4 cm × 4 cm mold. After rapid stirring for 3 min until no white flocculent was visible, a portion of each sample was placed in the mold for approximately 12 h to allow the resin to fully cure. Next, a slicer was used to obtain cured sample sections with a thickness of approximately 0.5 mm, which were then sanded with sand papers and cleaned with alcohol.

To obtain accurate analysis of the type of binding medium used in the colored paintings, it was necessary to extract the binding material out from the samples. Hence, a portion of red samples, the most heavily flaked and with a larger sample size, was placed in a test tube, before adding 20% petroleum ether. Extraction involved placing the treated samples in an oscillator at room temperature for 1 h. The mixture was then separated by centrifugation and the supernatant was aspirated and placed in a test tube [20].

It was noted in the Qing building construction manual [18] that starch was one of the ingredients used in the preparation of the ground layer. Hence, in order to determine the presence of starch in the ground layers, only samples DT-02 and BT-02 (typically contained higher concentration of the white pigments) were selected for the iodine staining test. Each sample was extracted after grinding with a calcium chloride solution (Mass Fraction: 80%), where the calcium ion complexed with the hydroxyl group of the starch and allowed the starch to dissolve fully. The samples were placed on slides, before placing two to three drops of iodine into the samples. After leaving the iodine-stained samples for 5 min, the samples were observed under a microscope to detect discoloration [21].

2.2. Experimental Equipment

2.2.1. Optical Microscope and SEM-EDS

The SGO-PH80 optical microscope (ShenShi GuangGu Optical Instrument Ltd., Shenzhen, China) was used to observe the cross-sections of the solidified samples, equipped with an SGO-KK204 camera (ShenShi GuangGu Optical Instrument Ltd., Shenzhen, China). The product model of SEM-EDS was a Carl Zeiss EVO 10 (Jena, Germany) equipped with an Oxford X-act EDS (Oxford Instruments Ltd., Oxford, UK) that detected chemical elements from 4Be to 94Pu. The working distance was set to 9.88 mm and an acceleration voltage of 15 kV was used. Conductive sheet connection was applied and the magnification range was adjusted between 7 and 800 K. The sample was prepared as a solid block for SEM-EDS, with gold sprayed on the surface before analysis.

2.2.2. Micro-Raman Microscopy and FTIR Spectroscopy

Micro-Raman spectra was acquired using Thermo Fisher DXR2xi Raman imaging microscope (Waltham, MA, USA). The colored region of the sample surface was observed

using a magnification of 50× objective. Laser was excited at a wavelength 532 nm. With exposure time and scanning times set to 2 s and 30 times, respectively, the recorded wave number range was adjusted from 50 to 3500 cm^{-1} .

As the Micro-Raman analysis results obtained for the red samples showed signs of fluorescence hindrance, FTIR spectroscopy was used to further support the Raman analyses. The infrared spectrometer used in this test was a Thermo Fisher Nicolet iS50 (Waltham, MA, USA) equipped with an attenuated total reflection accessory for detection within the spectral range from 650 to 4000 cm^{-1} . The attenuated total reflection (ATR) crystal type is monocrystalline diamond and the background was scanned 32 times before detection. OMSNIC software (version 8.2) was used for substance querying and baseline adjustment of the assay results. The Micro-Raman and FTIR spectra were analyzed and processed with Origin 2019 software.

3. Results and Discussion

3.1. Painting Profile Structures Analysis

A better understanding on the stratigraphy and sequential application of the Bell and Drum Towers' architectural paintings was established from the microscopic section images of the painted samples (Figure 3). The profile structures of the red samples (DT-01 and BT-01) consisted of two layers, an outer layer of red pigment and an inner layer of red and white crystalline particles interspersed within the ground layer. The white samples (DT-02 and BT-02), on the other hand, were found to have three different layers, namely an outermost white pigment layer, a blue pigment layer in the middle and a mixture of red and white crystals particles forming the ground layer. As the thickness of the white and blue pigment layers turned out to be comparable (approximately 20 μm each), the blue layer can be viewed as a form of underpainting layer for the surface white layer. The underpainting layer was mainly used to provide a transparent, coordinated base for the pigment layer. According to the painting content, the color of underpainting layer was commonly red, gray or blue, and the samples of DT-02 and BT-02 was blue mainly due to dominant color of the area in blue. In addition, the ground layer, consisting a mixture of red and white crystals particles, was mainly used as a substrate for the underpainting layer. Similar to the function of canvas, the ground layer can also indirectly serve as a protective coating for the building components. Likewise, in the case of the white samples, black (DT-03 and BT-03), blue (DT-04 and BT-04) and green samples (DT-05 and BT-05) also exhibited three layers—an outmost pigment layer, a red underpainting layer (mainly due to the dominant red color) and a ground layer of scattered red and white crystal particles.

The layering structure of the Drum Tower's dark green sample (DT-06) was similar to that of the green, blue, and black samples. However, the dark green sample of the Bell Tower (BT-06) was distinctly different from the Drum Tower's, because it contained six layers in total, where the outermost layer was the dark green pigment layer, followed by a second red underpainting layer and the third ground layer of scattered red and white crystal particles that were similar to the above samples. From the fourth to the innermost layers, the profile structure was identical with the upper three layers, namely a light green pigment layer, a yellow underpainting layer and a ground layer of white crystal particles. Thus, the above results suggested that the dark green portions of the Bell Tower might have been repainted at least once at a later period.

In general, the above analysis demonstrated the presence of red and white crystalline particles in the ground layer of all samples, with the exception of the dark green sample. By cross-referencing with historical records and the ancient Chinese building construction manuals, the features identified in this study are relatively similar to the architectural painting methodology of the Qing dynasty, where the red pigment was first applied as the underpainting layer for the columns, beams, and the brace structure (Queti), followed by the application of other pigments to the structural members of the building.

Figure 3. Microscopic section images of the painted samples.

3.2. Materials Used in Architectural Paintings

3.2.1. Pigments

Red Pigment

Iron oxide red (Fe_2O_3), mainly derived from the processing of hematite [22], was found to present in the two red samples (DT-01 and BT-01). The results obtained by EDS analysis showed that the two red samples mainly comprised of C, O, S, Ca, and Fe, with trace amounts of Na, Al, and Si (Figure 4a), thereby suggesting that the red color could be due to the presence of iron oxides. Additionally, the infrared absorption spectra obtained for the two samples contained characteristic peaks at 671 and 1109 cm^{-1} (Figure 4b). The above results corresponding to the characteristic peak of iron oxide at 671 cm^{-1} that was attributed to the Fe–O stretching vibration [23]. These analyses above confirmed that the pigment in the two red samples was iron oxide red, similar to the studies of pigments in the Dunhuang frescoes, painted sculptures in the Han dynasty tombs and architectural paintings of the Foguang Temple [4]. In addition, the two samples' characteristic peaks obtained at 711 , 870 , 1391 , and 1793 cm^{-1} were in good agreement with the calcium carbonate characteristic peaks in the infrared spectrum, where the peak at 711 cm^{-1} was attributed to the C–O in-plane bending vibration; the peak at 870 cm^{-1} was due to the CO_3^{2-} out-of-plane bending vibration; the peak at 1793 cm^{-1} was the result of C–O symmetric stretching vibration, and the peak at 1391 cm^{-1} was caused by the C–O antisymmetric stretching vibration [24]. The presence of a trace amount of calcium carbonate could be due to previous application during repainting for color adjustment purpose or could be due to particle infiltration from the ground layer.

Figure 4. (a) Elemental analysis by SEM-EDS and (b) Infrared spectra by FTIR spectroscopy for the red samples (DT-01 and BT-01).

White Pigment

Chalk, comprised mainly of CaCO_3 , also known as Baishan clay, was found to be present in the two white samples (DT-02 and BT-02). The EDS results for the white samples are shown in Figure 5a. DT-02 sample mainly composed of C, O, Ba, Ca, and S, with small amounts of Mg and Si, while C, O, Ba, Ca, S, Si, and trace amounts of Al were mainly found in BT-02. According to the elemental composition, it was estimated that Calcium or Barium salts was used in the white pigment. Further investigation into the chemical compositions of the two white samples revealed the Raman characteristic peaks at 179, 304, and 1098 cm^{-1} , and were generally in good agreement with the characteristic peaks of chalk (CaCO_3) [15,25] (Figure 5b). The peak at 1098 cm^{-1} was due to the C–O symmetric stretching vibration in the sample while the peak at 304 cm^{-1} arise from the stretching vibration due to the relative motion between CO_3^{2-} [24]. The above findings confirmed that the white pigment was chalk and that the presence of elements such as Al, Si, Ba, Mg, and S for both samples could have been due to contaminants adhering to the surface.

Figure 5. (a) Elemental analysis by SEM-EDS and (b) Raman spectra for the white samples (DT-02 and BT-02).

Black Pigment

Carbon black was found to be present in the two black samples (DT-03 and BT-03), generally produced from the burning of plants or animals [26]. Figure 6a presents the main constituent elements of the two black pigments. DT-03 sample consisted of C, O, Ca and small amounts of Mg, Al, Si, P, and S while BT-03 sample contained C, O, Ca, Si and trace amounts of Al and Na. From the results of elemental composition, it can be assumed that carbon or compounds of aluminum and magnesium was used in the black samples. Furthermore, the Raman spectra of the two black samples contained characteristic peaks at 1343 and 1604 cm^{-1} , which matched well with the peaks for carbon black (Figure 6b), confirmed that both samples contained carbon black [27]. Further, the absence of a characteristic peak at 960 cm^{-1} in the Raman spectra suggested that carbon black was not produced by the burning of animal fat or bone [28]. The presence of elements such as Mg, Al, Si, P, and S might be due to contaminants on the surfaces of the samples, while the high O and Ca contents might be caused by the movement of particles from the ground layer and external environment contaminants.

Blue Pigment

Lapis lazuli, one of the oldest blue pigments, was found in the two blue samples (DT-04 and BT-04) [11]. The results obtained by EDS analysis showed that the two blue samples mainly comprised of S, Ca, O, and trace amounts of Al and Si (Figure 7a). From the results

of the elemental composition, the blue pigments of DT-04 and BT-04 were estimated to be Calcium or Aluminum sulfate or Silicate. Additionally, the Raman characteristic peaks of the two samples at 256, 549, 803, and 1097 cm^{-1} , corresponded with the characteristic peaks of lapis lazuli [29] (Figure 7b). These peaks of the samples were due to the S^{3-} deformation vibration, the Si–O–Si bending vibration, the Al–O symmetric stretching vibration, and the SO_4^{2-} antisymmetric stretching vibration [30]. The above results confirmed that both blue samples comprised of lapis lazuli, the same pigment commonly found in the architectural paintings of the Ming dynasty Xi'an drum tower and the Qing dynasty Linxi Pavilion in the Cining Palace [2,3]. However, by cross-referencing with the elemental results of a lapis lazuli sample from the Longxing Temple Buddha statue in Qingzhou, Shandong province [31], a higher count of O and Ca contents were noted in our samples. This could be due to the migration of particles from the ground layer or from external contaminants.

Figure 6. (a) Elemental analysis by SEM-EDS and (b) Raman spectra for the black samples (DT-03 and BT-03).

Figure 7. (a) Elemental analysis by SEM-EDS and (b) Raman spectra for the blue samples (DT-04 and BT-04).

Green Pigment

Green earth, derived from iron silicate-rich sedimentary rocks [32], was found to be present in the two green samples (DT-05 and BT-05). The EDS results for the green samples are shown in Figure 8a. DT-05 sample consisted mainly of Ca, C, O, Fe, and trace amounts

of Si, Na, and Al. In the case of BT-05, high levels of Mg in addition to C, O, Ca, and Fe were observed, while no significant amount of Si, Na, and Al were detected, probably due to their low contents. According to the elemental composition's results, it was estimated that Iron salts were used in the green pigment. Furthermore, the characteristic peaks of the green samples at 142, 393, 516, 638, and 838 cm^{-1} , were in line with the characteristic peaks at 145, 399, 510, 636, and 820 cm^{-1} for green earth [33] (Figure 8b). The peak at 142 cm^{-1} was due to Fe–O stretching vibrations while the peak at 393 cm^{-1} was the result of Al–O stretching vibrations; the peak at 516 cm^{-1} was caused by the Si–O–Fe stretching vibrations whilst the peaks at 638 cm^{-1} and at 838 cm^{-1} were due to Si–O stretching vibrations and Si–O–Al stretching vibrations, respectively. Thereby confirming that the green pigment used in the architectural paintings on the Bell and Drum Towers was green earth. By comparing with the green pigments in the mural paintings on the Eastern Han tomb at Haotan in Dingbian county of Shaanxi province, the absence of potassium in our samples was presumably due to the presence of sodium instead of potassium [34].

To-date, limited literature was found on the use of green earth in ancient Chinese architectural paintings. Hence, we still do not have a clear standing why green earth was seldom mentioned in the studies relating to ancient Chinese architectural paintings. One possible speculation could be that malachite and atacamite were found to be more brightly-colored than the green earth pigment, thus making these alternatives possibly more favorable from the application and aesthetic point of view.

Figure 8. (a) Elemental analysis by SEM-EDS and (b) Raman spectra for the green samples (DT-05 and BT-05).

Dark Green Pigment

Figure 9a presents the main constituent elements of the two dark green samples (DT-06 and BT-06). DT-06 sample consisted of C, O, Mg, Ca, and trace amounts of Fe and Si. BT-06 contained similar constituent elements to DT-06, but with lesser amounts of Fe and Mg. Furthermore, the Raman spectra for the two samples contained characteristic peaks at 144, 838, and 1008 cm^{-1} , which matched well with the characteristic peaks of green earth in the Raman spectrum. Moreover, the characteristic peaks at 1340 and 1536 cm^{-1} were in good agreement with those of carbon black, thus confirming the presence of both green earth and carbon black pigments in the dark green samples (Figure 9b). Carbon black was probably used to tone down the brightness and color of the green pigment. The mixing of multiple pigments to adjust the color tone and brightness was also found in other studies of architectural paintings, for instance, the blue pigment in the architectural painting of Linxi Pavilion in Cining Palace was found to be a mixture of azurite, lapis lazuli, and smalt; whilst the red pigment in the architectural painting on the Foguang Temple was created by the mixing of lead red and cinnabar [3,4].

Figure 9. (a) Elemental analysis by SEM-EDS and (b) Raman spectra for the dark green samples (DT-06 and BT-06).

3.2.2. Binding Media

Results of the FTIR spectroscopy of binders in two red samples were compared with the standard spectra of binding media for animal glue, Tung oil, and egg glue (Figure 10). IR spectroscopy characteristic peaks obtained at 1456, 1075, 2854, and 2918 cm⁻¹ for the two binders matched well with the three binding media's standard spectra. The peak at 1456 cm⁻¹ was the result of deformation vibration for CH₂/CH₃ in lipids; the peak at 1075 cm⁻¹ was due to the swing deformation vibration for CH₃; and the peaks at 2854 and 2918 cm⁻¹ were the result of symmetric and antisymmetric stretching vibration for CH₂, respectively. However, further examination revealed that the two binders contained characteristic features similar to that of Tung oil where significant vibrational peaks were observed at 725, 1032, and 2958, which are assigned to the CH₂ in-plane bending vibration, the C–O stretching vibration, and the CH₃ antisymmetric stretching vibration, respectively. Animal glue and egg glue, on the contrary, will not produce significant vibrational peaks at these wave numbers. Thus, the above results confirmed that Tung oil was used as the binding medium in the architectural paintings on the Bell and Drum Towers.

Figure 10. Infrared spectra obtained for binding media samples compared with those for animal glue, egg glue, and Tung oil.

Tung oil was a plant-based binding medium that was commonly used since ancient times. Its main chemical component fatty acid was obtained by pressing the seed from the

nut of the Tung tree. This production process was recorded in ancient literature such as “*Qimin yaoshu*” and “*Jilei bian*”. During the Song dynasty, the Tung oil refinement process became more sophisticated and its usage was then at its peak. In addition, Tung oil dries quickly and has good resistance to high temperatures and corrosion, as well as water. These properties are due to the presence of triple conjugated double bonds in the main component of Tung oil comprising of the tungstic acid molecule, which allows the oil to readily oxidize and polymerize in the air to form a flexible and solid Tung oil film that blocks moisture movement, resists bio-deterioration by fungi and other micro-organisms, and prevents mold and mildew. Therefore, Tung oil was widely used in architectural paintings, such as in the case of the Ming dynasty drum tower in Xi’an, Shaanxi Province [2].

3.2.3. Ground Layer

As the ground layers of the white, blue, and dark green samples (DT-02, DT-04, DT-06, BT-02, BT-04, and BT-06) are more intact, hence they were selected for EDS and Raman spectroscopy analysis. Elemental results from the EDS analysis were summarized in Table 2. The ground layers of the above six samples composed mainly of C, O, and Ca, with the exception of the dark green samples (DT-06 and BT-06) containing a small amount of Mg. The Raman characteristic peaks obtained for the six samples were similar with the chalk reference curve (Figure 11), where the characteristic peaks at 179, 304, and 1098 cm^{-1} were generally in agreement with the characteristic peaks of chalk (CaCO_3) [25]. With the presence of the C–O symmetric stretching vibration at 1098 cm^{-1} and the relative motion vibration between CO_3^{2-} at 304 cm^{-1} [24], the above findings further confirmed that the ground layer was chalk, and that further investigation of the dark green samples was required due to the presence of small amounts of Mg. Although chalk was found from the above results, which seemingly suggested the use of the Qing building construction manual’s traditional technique for the ground layer, subsequent iodine staining test results showed no discoloration was observed in the samples (Figure 12). Additionally, the IR spectra of the samples were similar to those of the calcium chloride extract, where no C–O–H bending vibration, C–O and C–H stretching vibration were found for starch at 1090 cm^{-1} , 1130 cm^{-1} , and 2850 to 2920 cm^{-1} , respectively (Figure 13). Thus, it was confirmed that starch was not found in the ground layers of the samples and the techniques used for the preparation of the ground layer in this study was different from the method used in the Qing building construction manual.

Figure 11. Raman spectra obtained for ground layer materials.

Table 2. Elemental compositions of the ground layer samples.

(wt.%) Sample	Element								
	C	O	Ca	Si	Mg	Na	Al	K	
DT-02	14.04	47.96	38.01	0.00	0.00	0.00	0.00	0.00	
DT-04	20.53	42.74	34.51	0.00	0.97	1.24	0.00	0.00	
DT-06	14.43	47.42	25.10	0.00	13.06	0.00	0.00	0.00	
BT-02	16.76	47.47	35.04	0.00	0.74	0.00	0.00	0.00	
BT-04	12.83	44.72	42.46	0.00	0.00	0.00	0.00	0.00	
BT-06	9.94	31.50	46.42	0.00	10.32	1.82	0.00	0.00

Figure 12. Micro-images obtained for the extracts of ground layer: (a) before iodine test; (b) after iodine test. **Figure 13.** FTIR spectra obtained for DT-02 and BT-02.

4. Conclusions

In this study, painting profile structures, pigments, ground layers, and binding media of ancient Chinese folk architectural paintings on the Bell and Drum tower were investigated by multiple analytical methods.

Firstly, the results by optical microscopy revealed that all the architectural paintings profile comprised of pigment layers, underpainting layers and ground layers. The ground layer was found to be mainly composed of a mixture of red and white crystals particles, with the exception of the dark green sample from Bell tower that contained signs of repainting at least once at a later period. Additionally, the white crystal particles of ground layers were confirmed to be chalk, without the addition of starch.

Secondly, micro-Raman spectroscopy results showed that the pigments used in the architectural paintings of the Bell and Drum tower was iron oxide red, carbon black, lapis lazuli, chalk, green earth and dark green pigment, where the dark green pigment consisted of a mixture of carbon black and green earth. In addition, this study marks the first identification of green earth being used as a pigment in ancient Chinese folk architectural paintings. Finally, the FTIR spectra obtained from the binding media confirmed that the binding medium used in the architectural paintings of the Bell Tower and Drum Tower was Tung oil.

The findings in this study not only deepened our knowledge on ancient Chinese architectural paintings, but also highlighted the urgent need for more detailed research into ancient Chinese folk architectural pigments and binding media so as to provide more informed advice on future protection and repair works.

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