Analytical Methods

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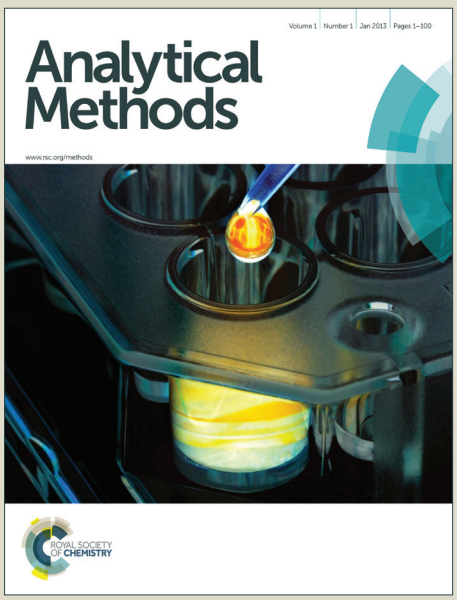

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ARTICLE

Analysis of the techniques and materials of the Coloured Paintings in the Renshou Hall in the Summer Palace

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Only few published literatures were available in the materials and techniques of the ancient Chinese construction paintings. In this paper, integrated analytical techniques were used to characterize the materials and the techniques of the coloured paintings of the Summer Palace, one of the World Cultural Heritage. The analytical techniques include X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and element analysis (EA). This is the first time to measure the content of crude protein in cultural relics by EA. By means of TGA it was possible to quantitatively determine organics and inorganics in the plaster layer. The study can be a guide for selecting restoration materials and technologies for construction paintings.

1 Introduction

The Summer Palace is located in northwest suburbs of Beijing, 15km away from downtown. It used to be an imperial residence for the emperors in the Qing dynasty (1644-1911). Being the largest and the most intact royal garden in China, it was enlisted as the World Cultural Heritage by UNESCO in 1998. As one of the important architectural buildings in the Summer Palace, the Renshou Hall(Fig.1)was the place where Empress Dowager Cixi and Emperor Guangxu met officials and foreign diplomats and conducted other duties. It was first built in 1750 AD and was rebuilt in 1886 AD. The coloured paintings in the Renshou Hall belongs to Hexi painting with the highest level, looking solemn, splendid and magnificent.

Such coloured construction paintings were greatly influenced by environment, which led to weathering such as paint loss, colour fading and gold foil ageing. According to the basic principle of keeping the historic authenticity, the original materials and techniques had better be used in conservation of antiques. Therefore, the characterization of materials and techniques of construction paintings in the Summer Palace is the most significant study for the restoration process. Although there have been many research reports on materials and techniques of wall paintings,[1,2] rock paintings,[3,4] grottoes [5] and polychrome potteries,[6-8] the reports on construction paintings are relatively few.[9] Rocco Mazzeo, et al[10] studied on the construction painting of Drum Tower in Xi'an, a wooden architecture of the Ming Dynasty, and the analytical results showed that the pigments were both original and later application of the XVIII century. As for the construction paintings of the Renshou Hall in the Summer Palace, the materials and techniques were never been comprehensively analyzed before. In the article, XRD, XRF, TGA and so on were utilized to investigate the techniques and the materials of the paint layers and the plasters of the Renshou Hall. Furthermore, it is worth to mention that EA, a micro-invasive analytical method, was first introduced in quantitative analysis of protein in construction paintings. This method was an ideal analytical technique for antiques. Due to the non-renewability of antiques, reducing the sampling volume to the minimum was actually a kind of conservation. Meanwhile, this study was the foundation for the restoration of the construction painting，which could be helpful to select the original materials and techniques as much as possible to restore the antiques as their native appearances. So that, keeping the authenticity of antiques could be well realized.

2 Experimental

2.1 Apparatus and conditions

Fig.1 The Renshou Hall in the Summer Palace.

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X-Ray fluorescence analysis was carried out using a RIX-2100 X-ray Fluorescence Spectrometer (Rigaku, Japan) with an Rh target and with the maximum power of 3KW, under the vacuum condition.

X-ray diffraction data were obtained using a D/max2400 X-ray Diffractometer (Rigaku, Japan), equipped with a Cu-Kα radiation (λ= 0.15418 nm) in the 2θ range from 5 to 70°, with a tube voltage of 40 kV and a current of 100 mA.

A STA 449C Thermo Gravimetric Analyzer (Netzsch, German) was used. The work condition was under N_2 atmosphere and with a heating rate of 10℃/min.

Element analysis was carried by a Vario EL III CHNOS Elemental Analyzer (Elementar,German) with high purity helium as the carrier gas and the working pressure of 0.2Mpa.

Micro-morphology of the samples was observed using a DMLB Biological Microscope (Leica, German) and a Stemi 2000-c Stereomicroscope (Zeiss, German).

2.2 Samples

The samples (Fig. 2) were taken from the paintings above the girder in the Renshou Hall. Sample 1# has an irregular shape, with the maximum length of 13cm and the maximum width of 4cm. On the surface, most parts are blue except a little green-and-white on the left small part. In the plaster, a great amount of fiber can be obviously seen. Sample 2# is red on the surface.

2.3 Methodologies

Cross-section. Approximate size of 0.5×0.5 cm sample was taken from the green-and-white part of Sample 1# and was embedded in the 3A glue till solidification. The consolidated sample was polished. The polished cross-section was observed by the stereomicroscope to deduce the making technique of the paintings.

Pigment analysis. The components and phases of the pigment particles were analyzed by XRF and XRD.

Fiber analysis. Ca.1cm length of fiber was used to prepare the sample by the paraffin section method.[11] The fiber section was fixed on a slide with a cover slip in order to observe the morphology using a biological microscope.

Quantitative analysis of organics and inorganics in the plaster. About 5 mg of finely grinded plaster powder were analyzed by a thermogravimetric analyzer in order to calculate the total amount of organics and inorganics.

Quantitative analysis of crude protein in the plaster. About 2 to 3 mg of finely grinded plaster powder were measured by an elemental analyzer to determine the amount of crude protein.

3 Results and discussion

3.1 Cross-section

The cross-section of sample 1# (Fig. 3) showed that the Chinese typical plaster-making technique was applied, which was "five plaster layers with one fiber layer". The total thickness of the plaster layers was about 4 mm with the fiber layer thickness of 0.2mm. The green pigment layer is right on the plaster, and then the white pigment layer is brushed on the green. The white layer has a tiny curling and flaking. Since the hemp fiber was used in the plaster layer, the wooden structure was fastened, and the tension of the plaster was enhanced so that the cracking can be prevented effectively.

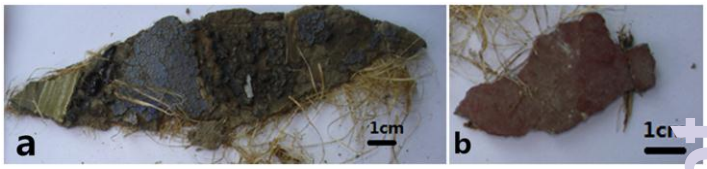

Fig.2 Painting samples above the girder of the Renshou Hall in the Summer Palace: (a) sample 1# and (b) sample 2#.

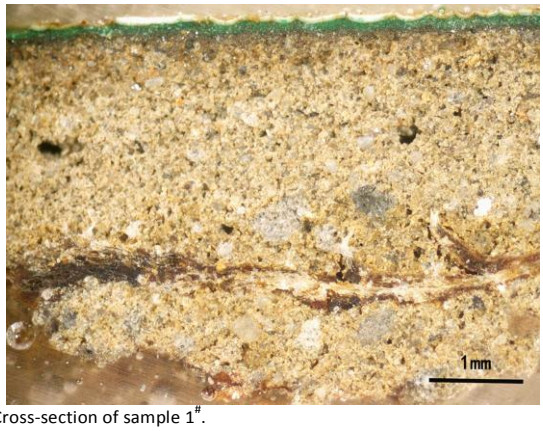

Fig.3 Cross-section of sample 1#.

3.2 Pigment analysis

The XRF results revealed (Table 1) a large amount of Fe,S,Ca,Ba,Mg,Si in the red pigment(sample 2#), S,Na,Ca,Si,Al in the blue pigment(sample 1#)and Pb,As,Cu,Ca,Si in the green-and-white pigment(sample 1#). According to the XRD analysis, the red pigment contains hematite, dolomite, barite, quartz (Fig. 4.a) and the blue pigment contains ultramarine and quartz (Fig.4.b). Consequently, the substances of red and blue should be hematite and ultramarine respectively. Hematite and ultramarine are two common pigments used in ancient paintings. For instance, it was proved that hematite existed in French polychrome sculptures[12] and Greek wall paintings in 14th century AD.[13] Additionally, ultramarine was determined in Pietro Lorenzetti's painting in Italy [14] and in a Belgian encyclopaedia in early 12th century.[15]

The XRD result (Fig. 4.c) of Green-and-white pigment illustrated that the pigment contains emerald green and lead white. Compared with the cross-section analysis, it could be seen that emerald green layer was brushed on the surface of the plaster and then lead white layer was added on the green. Furthermore, the green and white were not mixed in advance.

Green was a common colour in the Chinese cultural relics, among which malachite and atacamite were widely used while emerald green was rarely seen. Most green pigments in wall

Table 1 XRF result of pigments

Components	W/%		
	Green-and-white	Red	Blue
Na_2O	0.80	2.27	6.11
Al_2O_3	3.20	2.81	12.80
SiO_2	17.40	14.20	41.60
P_2O_5	0.26	0.27	1.33
SO_3	1.85	12.10	11.80
Cl	2.32	2.37	1.04
K_2O	1.13	0.85	2.70
CaO	10.30	11.50	7.01
Fe_2O_3	2.69	23.6	3.03
CuO	7.90	0.41	0.06
ZnO	4.91	12.9	3.38
As_2O_3	13.3	0.50	/
PbO	32.9	/	4.27
BaO	/	10.30	0.86
MgO	/	5.42	3.06
Others	1.01	0.55	0.96

paintings in Mogao Grottoes were atacamite,[16] and malachite was found in Zhongshan Caves [17]and Terra Cotta Warriors. However, emerald green was widely used in the Renshou Hall and the paintings from Jiayu Pass and other Chinese northern constructions. 15 out of 27 samples were found to use emerald green and the others was organic dye, but no malachite and atacamite. [9] Based on the report from Rocco Mazzeo,[10] emerald green was also found in the painting of the Drum Tower in Xi'an, P. R. China.

Emerald green (Cu $(CH_3COO)_2{\cdot}3Cu(AsO_2)_2$) is an artificial copper aceto-arsenite pigment, first formulated in Germany in 1814. It was widely used in China as watercolour on pith paper works and on scroll paintings since 1850s.[10] Ancient construction paintings were exposed to wind blowing, sunshine and raining, so the painting colour faded easily and should be restored every few decades. Investigation revealed that the mineral pigments, such as malachite and atacamite, were seldom used as restoration materials in construction paintings due to their relatively high price. On the opposite, the artificial materials such as emerald green and viridian were more common.

3.3 Fiber analysis

It has been showed that the transverse section of the fiber in the plaster is a polygon (Fig. 5.a) and the vertical morphology is parallel with slines (Fig. 5.b). It is identified to be the hemp fiber and distinct from the cotton fiber whose cross-section looks like cashew and vertical morphology twists naturally.[10]

3.4 Quantitative determination of organics and inorganics in the plaster

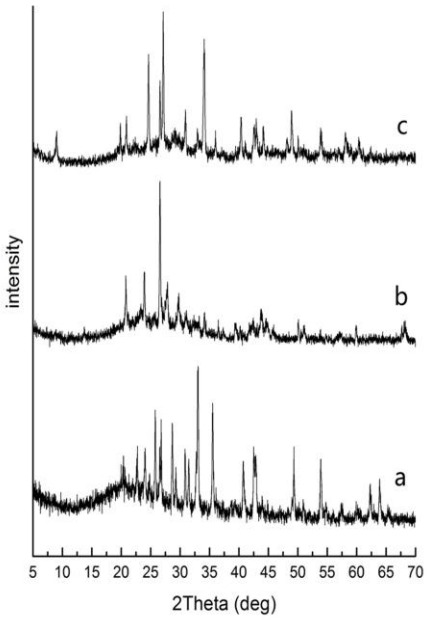

Fig.4 XRD results: red (a), blue (b) and green-and-white (c).

The thermogravimetric curve of the plaster (Fig. 6.a) showed that the sample started to lose weight at 25°C and until 150°C the weight loss was up to 2.16% due to giving off free water and absorbed water. Then the curve became steep slowly. In the range of 150 to 650°C, the weight loss reached 20.87% due to the decomposition of organics.[18] When the temperature was over 650°C, the weight of the sample kept basically constant, and the solid residues with total weight of 76.97% should be inorganics. The differential scanning calorimetry curve (DSC in Fig. 6.b) showed two obvious exothermic peaks at 375°C and 510°C, reflecting the exothermic effect of organic decomposition.

3.5 Quantitative determination of crude protein in the plaster

Blood and Flour was widely used in the plasters of Chinese official construction paintings in order to improve its cohesive force. Bull blood was also used in England and Italy paintings.[19] In addition, it was said that in Amarbayasgalant temple in Mongolia, blood was added as an adhesive in the plaster of the construction paintings. Blood et al contains protein with 16% of N element on average, and this property of protein is the significant distinction from other non-protein organics.

There are two common kinds of methods for proteinaceous determination. One is the Kjeldahl method which measures the N content by acid-alkali neutralization titration, but this method is complicated and need more samples (ca. 500mg). The other one is spectrophotometry, including Biuret method, Bradford method, Lowry method, Markwell method and so on.[20,21] Although the amount of samples used in spectrophotometry is little, these methods cannot be used to determine the protein content in the

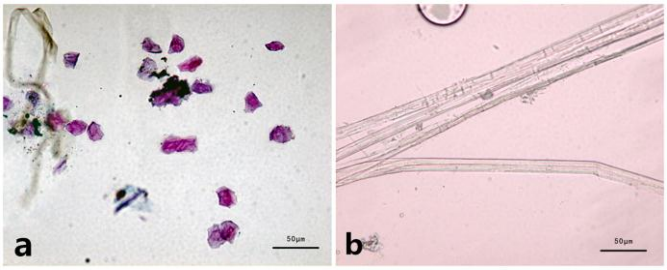

Fig.5 Cross-section of fiber: transverse section (a) and longitudinal profile (b).

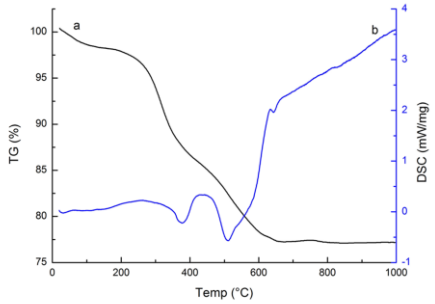

Fig. 6 TG and DSC curves of the plaster powder: TG curve (a) and DSC curve (b).

plasters of Chinese construction paintings because of the interference of Tung oil. Since the painting sample is precious and non-renewable, we first introduced the elemental analysis, a new micro-invasive analysis method for the cultural relics, to quantitative determination of protein in the plasters of construction paintings. The sampling amount is only about 2 to 3 mg, but the measurement is accuracy with the recovery of 100.15%.[22] The plaster was analyzed by this method and the results indicated that 1.05% of N, which converted into 6.56% of protein contained in the plaster.

4 Conclusions

Based on the scientific analysis of construction paintings in the Renshou Hall in the Summer Palace by XRD, XRF, TGA, optical microscope, and elemental analysis, it can be concluded that: (1) The hemp fiber is added in the plaster. (2) The pigment layers have many colours in which the blue is ultramarine, the green is emerald green, the white is lead white and the red is hematite. (3) The plaster contains 2.16% of water, 20.87% of organics and 76.97% of inorganics. (4) The total content of crude protein in the plaster is 6.56%. (5) This work not only identifies the materials of paintings but also guides the choice of the materials and the techniques in conservation and restoration of construction paintings.

Acknowledgements

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