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Case study

Multi-analytical study of the suspected binding medium residues of wall paintings excavated in Tang tomb, China

Zhenzhen Ma[a,b], Jing Yan[c], Xichen Zhao[c], Liqin Wang[a,b,*], Lu Yang[a,b]

[a] Key Laboratory of Cultural Heritage Research and Conservation (Northwest University), Ministry of Education, 710069 Xi'an, P.R. China
[b] School of Cultural Heritage, Northwest University, 710069 Xi'an, P.R. China
[c] Shaanxi Provincial Archaeology Institute, 710061 Xi'an, P.R. China

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ABSTRACT

The analysis of the organic binding media in the field of cultural relics is invariably challenging due to the micro-amount, complex ingredients and degradation problems. Black residues of suspected binding media were discovered in a tomb archaeological site of the Tang dynasty (618-907AD), one of the most prosperous time in the ancient China. In the frame of excavation campaign it is becoming a demand to analyze the precious archaeological samples to know more about the composition of these materials. In this paper, efforts were made to analyze this sample with Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC), attempting to learn the materials' consistence. This study would enrich the research of the materials of mural paintings in the Tang dynasty as well as providing a scientific basis for the future restoration.

1. Introduction and research aims

Binding medium is the substance that could combine materials by surface adhesion [1], this characteristic has been now since ancient times. Artificial stone chips covered by birch bark tar was found by archaeologists in a Paleolithic site in Italy dating about 200 thousand years ago, which was the first evidence of using binding medium by human beings [2]. Plant gum was applied for the hafting of tools in the Middle Stone Age in South Africa [3]. With the knowledge of materials and making technique improved, a variety of binding media were found and utilized, such as proteins, oils, resins and gums [4].

The earliest Chinese record concerning binding medium, "It is a necessity to make the coating layer thick", could be found in the book "Zhou Li" [5] (403BC-221BC), there was also a very vivid quotation "as close as glue" in "Shi Ji" [6] (157BC-87BC). In the ancient agronomy monumental work of "Qi Ming Yao Shu" (544AD), detailed making technique of hide glue and bone glue were described [7]. Furthermore, the geographical distribution of binders in China "There is deer glue in Yunzhong, isinglass in Wuzhong, ox glue in Donge" was also described. "These all enjoy hundreds and thousands' years of endurance", was recorded in the famous art book "Li Dai Ming Hua Ji" by Zhang Yanyuan in the Tang dynasty [8]. According to the official architectural book "Ying Zao Fa Shi" [9] (1103AD), glue (isinglass) is initially polished on the brackets, pillars and murals, which was the traditional way of making colored paintings. Judging from the above discussion, it could be concluded that the binding media, especially animal glues, have been employed in China from very early times.

Analytical techniques as FTIR [10–12], Raman [13], Gas Chromatography-Mass Spectrometry (GC-MS) [14,15], Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) [16,17] are presently used for analyzing binding media. Specifically, FTIR and Raman are suitable for the general classification rather than giving the detailed information [18,19], Py-GC/MS is now devoted more in the research of the macromolecule compounds [20,21] such as urushi lacquer. GC enjoys enormous popularity for its excellent separation efficiency and sensitivity and has already been performed in the study of various binding media [22,23].

Binding medium is undoubtedly an essential part of the wall paintings of the Tang tomb and its analysis has invariably been an attractive topic. Numerous papers concerning this study had already been published worldwide [24–26], there are also some released in China. In 1995, Li Shi made the first attempt to analyse organic binding medium with High Performance Liquid Chromatography (HPLC), illustrating that ox glue was used in wall paintings of the world-renowned Dun Huang Grottoes [27–29]. Animal glue was also applied in Kizil Grottoes [30]. Another

* Corresponding author. Key Laboratory of Cultural Heritage Research and Conservation (Northwest University), Ministry of Education, 710069 Xi'an, P.R. China. Tel.: +8613259983278.
E-mail address: wangliqin@nwu.edu.cn (Z. Ma).

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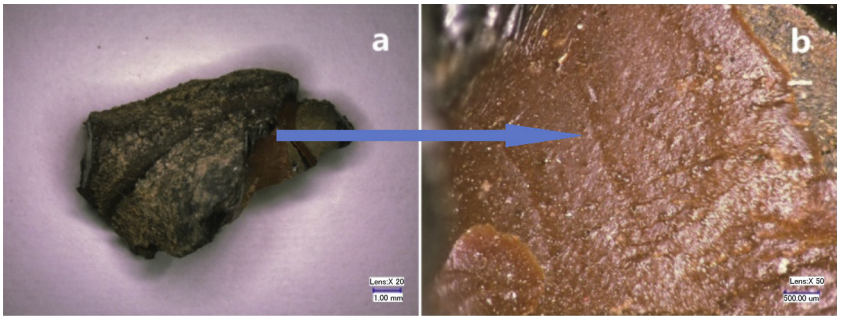

Fig. 1. Morphological Observation.

interesting study was the identification of dog collagen of the 5th century AD wall painting in the Northern China [31]. What should also be mentioned was the binding medium study of the Tang dynasty's wall paintings and that of the Da Zhao temple in Mongolia. Animal glue, peach gum, oil, natural and synthetic resins were tested to be contained [32]. However, the result might be influenced by the later intervention with peach gum and resins. In spite of the above early research, there is still a large gap in the binding medium analysis about the most delicate wall paintings in the Tang dynasty, which was one of the most prosperous period in the whole Chinese history.

In 2011, black residues (Fig. 1) were found under the bottom of the mural paintings walls in a Tang tomb excavated in Xi'an, China. The residues were light, fragile and porous. Archaeologists questioned whether they were the residues of binding media, and thus the subsequent investigation of the material composition would help to clarify this uncertainty. As a result, this study could tell archaeologists not only what it is, but could also play an essential part in the later restoration for the proper choice of cleaning solvents and consolidation materials used for the wall paintings. For this rarely found "binding media" sample, analytical methods such as FTIR and GC were proposed to perform a comprehensive scientific study about the organic composition.

2. Experimental

2.1. Sampling

The sample was black lump, a small yellowish-brown part was observed on the right side (Fig. 1a). A clearer picture was taken under 50× magnification and obviously amber films were evenly distributed (Fig. 1b), which is in the agreement with the description "the color of the binding medium is amber" in the chapter "boiling binding medium" in the Chinese ancient book "Qi Ming Yao Shu" [7].

2.2. FTIR

The FTIR analysis was performed on a Thermo Scientific Nicolet iN10 MX FT-IR imaging microscope (Thermo, USA). The sample was prepared using the classical Kbr pellet technique. Cooled detector was used under liquid nitrogen, the spectrum data was collected within the 4000 and 675 cm^{-1} wavenumber range at a spatial resolution of about 4 cm^{-1} with 16 scans.

2.3. GC

GC system (7890A, Agilent, USA) was used with FID detector. For the gas chromatographic separations, an HP-5MS fused silica capillary column (5% diphenyl-95% dimethylpolysiloxane, 30 m × 0.250 mm i.d., 0.25 μm film thickness, J&W Scientific, Agilent Technologies) coupled with a deactivated silica precolumn (10 m × 0.250 mm i.d., J&W Scientific, Agilent Technologies) was used with a quartz press fit. The parameter settings were as following: the inlet temperature was 280 °C, the carrier gas was used in the constant flow mode (He, purity 99.995%) at 1.5 mL/min, the initial temperature was kept at 100 °C for 2 min and the temperature was then increased to 280 °C at a rate of 6 °C/min, which finally kept for 10 min. The temperature of the FID detector was set at 300 °C [33].

The sample pretreatment was based on a procedure described in the literature [34], and was summarised as follows:

- preparation of the powdered sample: scratch particles from the residue and grind them into powder in the agate mortar;
- ammonia extraction of the protein: 1200 μL of 2.5moL/L ammonium hydroxide was added in the powder which was extracted for 2 hours at 60 °C, twice. The upper extraction was obtained by centrifuging prior to be dried at 60 °C;
- clean-up of the upper extraction with the C4 sorbent pipette tip;
- hydrolysis: the extraction was added into 10 mL 6 mol/L HCl before being subjected to microwave for hydrolysis;
- derivatisation: 45 μL of 0.5 μmoL/mL Nor-Leucine was added to the hydrolysate, which was evaporated to dryness under a stream of nitrogen before being subjected to derivatisation with 15 μL of N-methyl-N-(tertbutyldimethylsilyltrifluoroacetamide) (MTBSTFA) and 45 μL of pyridine (solvent). The derivatisation was performed at 60 °C for 30 min. Afterwards, 1 μL of the derivative solution was injected to be analyzed with GC-FID after 90 mins' standing.

3. Results and discussion

3.1. FTIR

The FTIR spectrum result of the sample was illustrated in Fig. 2, C-H stretching for methylene groups occurred near 2920 cm^{-1} (asymmetric) and 2850 (symmetric) cm^{-1}, these two were the widespread absorptions for the organic binding media. There was a sharp carbonyl stretching band (C=O) in 1710 cm^{-1} from the ester group, which might be induced by lipidic component in the sample. According to references, proteins were characterized by the presence of amide I and amide II bands near 1650 cm^{-1} and 1550 cm^{-1}, respectively. These two bands along with another, occasionally referred to as an amide III, found near 1450 cm^{-1}, form a consistent stair-step pattern [35]. These above mentioned features could be obviously observed from 1620 cm^{-1} to 1260 cm^{-1} in Fig. 2. The amide I band 1620 cm^{-1} arose principally from the C=O stretching vibration of the peptide group, the amide III absorption 1440 cm^{-1} was arising primarily from N–H bending and C–N stretching vibrations. But there was no amide II band probably due to the degradation of the proteins. Additionally, the presence of amide A might also be confirmed by the N–H stretching band near 3350 cm^{-1} (3442 cm^{-1} in Fig. 2), but this area was greatly

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