Pre-Protection Analysis of Unearthed Water-Saturated Lacquered Woodware – With Lacquered Woodware Unearthed from the Zeng Guo Cemetery of Guojiamiao, Hubei Province as Examples

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Abstract

Wooden lacquerware cultural relics are very characteristic cultural relics in China. Ancient wooden lacquerware excavated underground has relatively intact paint cover, but its bodies are mostly decayed, generally with a moisture content of 100-400%, and in some cases going as high as 700%. Therefore, dehydration and reinforcement of water-saturated bamboo, wood, and lacquer artifacts is the most critical step for restoration and protection. In order to protect the unearthed wooden lacquerware in a targeted manner, it is necessary to conduct a detailed pre-protection analysis of the cultural relics. In 2014 and 2015, the Hubei Provincial Institute of Cultural Relics and Archaeology worked with Jingzhou Cultural Relics Conservation Center and many other organizations to respectively carried out a more comprehensive excavation of the Caomenwan and Guojiamiao Cemeteries, and cleared more than 110 tombs. The tomb in question was inscribed on the list of China's Ten Major Archaeological Discoveries in 2014. From the tomb 186 water-saturated pieces of lacquered woodware were unearthed. Due to the biological and microbial corrosion in the buried environment, the lacquered woodware urgently needed protective dehydration. In order to better protect the cultural relics and retain as much of the original information as possible, it is necessary to analyze this batch of lacquered woodware before placing them under protection.

Introduction

The Guojiamiao Zeng Guo Cemetery is located inDongzhaohu Village, Wudian Town, Zaoyang City, Hubei Province (Figure 1). It is located between the Dahong and Tongbai Mountains, at the western end of Suizao Corridor, and on the north bank of the Gunhe River, a tributary of the Hanshui River. The cemetery stretches about 1,000 meters from north to south, and about 800 meters from east to west. Consisting of two hilly areas situated respectively in the south and the north, it is bounded by the low-lying land between the two hills, with Guojiamiao in the north and Caomenwan in the south[1]. In 2002, in order to cooperate with the construction of the Fuzhou-Yinchuan Expressway, the Hubei Provincial Institute of Cultural Relics and Archaeology and other organizations conducted rescue excavations at the Guojiamiao Cemetery and cleared 25 tombs including M21, or Zeng Boqi's Tomb. Based on the released data on the excavation, it is more evident that the cemetery is a cemetery of Zeng Guo, or the State of Zeng, dating from the late Western Zhou Dynasty to the early Spring and Autumn Period[2]. In 2014 and 2015, the Hubei Provincial Institute of Cultural Relics and Archaeology, together with Jingzhou Cultural Relics Conservation Center and other organizations, carried out a more comprehensive excavation of the Caomenwan and Guojiamiao Cemeteries and cleared more than 110 tombs. Among them, Caomenwan M1 and Guojiamiao M60 are both large-scale and high-level tombs[3-5]. More than 100 pieces of lacquered woodware were unearthed. Due to biological and microbial corrosion in the buried environment, these pieces of lacquered woodware have been sent to the Jingzhou Cultural Protection Center for protective dehydration. The current dehydration technology is mainly based on chemical filling. After dehydration, a large amount of chemical materials penetrate into the lacquered wood, which results in the

loss of some information of the lacquered wood. Therefore, it is very necessary to conduct a scientific analysis of the lacquered wood before dehydration.

The current research on saturated lacquered wood generally goes in two directions. The first is to research paint coating mainly with the techniques of ELISA, FTIR, Py-GC/MS and THM-Py-GC/MS. THM-Py-GC/MS is a typical method for investigating organic matters in lacquerware. It can provide a wide range of marking compounds to help identify catechol components and paint additives such as drying oils, natural resins, proteins, starches, and colorants. SEM-EDS, XRD, and Raman spectroscopy are commonly used methods for analyzing inorganic materials in lacquerware[6,7]. The second direction is to research the dehydration of substrates of saturated lacquered woodware, mainly focusing on the tree species, moisture content, and corrosion degree of the substrates, and various dehydration materials and methods[8,9].

With the introduction of scientific and technological means, they have played an important role in the protection and restoration of ancient lacquerware. The materials, structures and painting techniques of lacquerware from different historical periods are different. Domestic lacquerware research mainly focuses on the structure, paint composition and types of lacquerware. In order to understand the complexity of lacquerware craftsmanship and compare the materials and production processes of utensils with different functions, a comparative study is carried out on lacquerware. First, use an optical microscope to observe the topographic image of the cross-section of the paint cover. Secondly, employ the scanning electron microscope (SEM), energy spectrometer (SEM-EDS), x-ray diffractometer (XRD) and Raman microscope to study inorganic materials. Then, the organic materials are characterized with the Fourier transform infrared spectroscopy (FTIR) and pyrolysis-gas chromatography/mass spectrometry using tetramethylammonium hydroxide for thermally-assisted hydrolysis and methylation (THM-Py-GC/MS). The results of the analysis show that different materials are used to make objects with different functions.

1. Experimental Samples And Methodology

1.1 Archaeological sampling

Samples of a *dou* and a bow unearthed from Tomb M1 at Caomenwan(Figure 2).

1.2 Tree species identification

After the sample is treated properly, it is frozen, sectioned, dyed, dehydrated, glued, and sealed on a glass slide. Then the anatomical features of three sections of the timber sample are observed and photographed with the Leica DM4500P polarization microscopeat 50, 100, and 200 times, and the type and properties of the wood of the unearthed wooden cultural relic are determined with reference to the wood atlas[10,11].

1.3 Water content and loss of organic matter

After taking the sample, weigh the initial mass G0; then immediately put the test piece in a constant temperature oven with a temperature of 103±2℃ for twohours, take it out, weigh it, and make a record; then put it back into the oven to continue drying until the weight G1 weighted for the last two times remains unchanged. For the water content W, the calculation formula is W=(G0-G1)/G0×100%.

1.4 Paint cover analysis

A VHX-900 super-depth three-dimensional video microscope (Keynes, Japan) is used to obtain cross-sectional images of the sample. The lens is VH-Z20R, the illumination method is vertical illuminance, the light source is built-in, the depth of field is 34-0.44 mm, and the magnification is 20-200.

1.5 Energy-dispersive X-ray Spectroscopy (SEM-EDS) enhanced scanning electron microscope

A part of the sample is mounted in epoxy resin and polished with metallographic sandpaper #600, #1000, #1500, #2000, and #2500 and 0.5μm grinding paste. Finally, spray gold on the sample.

The backscattered electron image (BSE) of the sample is obtained by a Tescan Vega 3 XMU scanning electron microscope (Czech Republic), with an acceleration voltage of 15kv and a working distance of 15.78 mm. The elements in the sample are obtained with the 610M EDS detector of Bruker Nano Gmbh.

1.6 Raman Spectroscopy (RS)

The instrument used for Raman spectroscopy is the Almega Micro Confocal Raman Spectrometer from Thermo Nicolet Company, equipped with an Olympus BX-50 microscope and an automatic focusing platform. The laser wavelengths are 532nm and 785nm, the objective lens is 50x, and the spatial resolution is 1-2μm.

1.7 X-ray diffraction (XRD)

For XRD analysis, a diffractometer (from Smartlab Rigaku Ltd.) is used together with a Cu Kα radiation source at 200kV, with a scanning range of 45□2θ, and a scanning speed of 10°-90° 1°/min and a step length of 0.02°. The XRD data is analyzed using the JCPDF database.

1.8 Fourier transform infrared spectroscopy (FTIR)

The samples are measured by NICOLET iN10 Fourier Transform Infrared Spectrometer (Thermo Scientific Corporation). In the experiment, the acquisition mode is set to Attenuated Total Reflection (ATR), with the spectral resolution being 4 cm^{-1}, and the number of scans being 64. Each sample is scanned at 25°C, and the data acquisition system used is OMNIC. The spectral range for all the samples is 4000-650 cm^{-1}.

1.9 Pyrolysis-gas chromatography/mass spectrometry using tetramethylammonium hydroxide for thermally-assisted hydrolysis and methylation (THM-Py-GC/MS)

The pyrolysis-gas chromatography/mass spectrometry measurement is performed with a PY-3030D pyrolyzer (Frontier Laboratory, Japan) connected to a gas chromatography/mass spectrometry GC/MS-QP2010Utra (Shimadzu, Japan). The model of the chromatographic column is UA5-30M-0.25F (Frontier Lab, with the stationary phase being 5% biphenyl and 95% dimethyl diphenyl polysiloxane). The pyrolysis temperature is 600°C, the pyrolysis interface temperature 300°C, and the ejector temperature 280°C. The initial temperature is 50°C, and the gradient is 10°C/min to 280°C, maintained for 20 minutes. The carrier gas is helium, the inlet pressure is 100 kPa, and the split ratio is 1:100. The electronic pressure control is set to constant current mode. Ions are generated by electron ionization (70 eV) in the ionization chamber of the mass spectrometer. The scanning range of the mass spectrometer is m/z 50 ~ 750, and the scanning period is 0.5s. The data obtained with the THM-Py-GC/MS technique is analyzed with the AMIDS program and RIDICAL software.

The TMAH THM-Py-GC/MS analysis of the process of heat-assisted hydrolysis and methylation pyrolysis is conducted as follows: take a 0.2 mg sample and place it in the sample cup, then use a pipette to add 3 μL 25% TMAH (Sinopharm Company, China) aqueous solution, and let it stand for onehour until the sample is completely dissolved. The cup enters the pyrolyzer (furnace) through the autosampler, and is pyrolyzed immediately; subsequently, the GC/MS temperature program is started.

2. Results And Discussion

2.1 Tree species identification

The growth rings are obvious, and the material has semi-annular to annular holes. The ducts are oval and round in the cross-section of the dry timber belt, 1-5 rows wide, with thin walls and abundant intrusion. The cross-section of the latewood belt shows clustered irregular polygons. Featuring single perforation, thread thickening is occasionally seen on small ducts. The pits between the tubes are arranged alternately. The axial parenchyma is few, and the rings are tubular. In the latewood, pore clusters are often connected with the parenchyma to form intermittent chords in belts. There are few single-row rays, which are 1-9 cells in height; multi-row rays are 2-4 cells in width, and most of them 7-15 cells in height. End walls show nodular thickening, with many obvious horizontal wall pits. Ray tissues are either of Heterogeneous Type III or homogeneous, arrayed in both single and multiple rows. The pit type between the rays and the ducts are similar to intervascular pitting. The intercellular tract is absent. Based on this, it is judged as C.ovata Don of the Catalpa Scop genus, in the family of Bignoniaceae,as shown in Figure 2.

The growth rings are very obvious, with the earlywood changing abruptly to the latewood. It has ring pores, with the pores of the earlywood usually larger, and arranged continuously into obvious earlywood belts 1 to 3 pores wide. Latewood pores are smaller and arranged in rows that are usually 1-2 cells wide. It has single oval perforation and round alternate pitting. Circumferential tracheids are abundant, often mixed with parenchyma, surrounding large pores and in the area of latewood pores. The axial parenchyma is in large quantities, scattered-aggregated and separated in belts that are 1-3 cells wide and rather irregularly arranged into intermittent chords direction, or scattered in the middle. Wood fiber walls

are thick. There are many single rows of wood rays, and the wide wood rays are as wide as many cells, and sometimes divided by single rays. The ray organization has the same shape as in single and multiple rows. The type of pits between the pores and rays is notched and kidney-shaped or similar to the type of pits. Based on this, the timber can be judged to be q. ACUYISSIMA Carrof the QucercusL genus, in the family of Fagaceae Dum.

2.2 Moisture content of body and paint coating

Table 1. Test results of moisture content

Serial	Wet weight (g)	Dry weight (g)	Water content (%)	Thickness (mm)
Body of the *dou*	3.3159	0.9060	366	-
Body of the bow	1.2106	0.3237	374	-
Paint coating of the *dou*	0.5532	0.4159	33.0	0.12
Paint coating of the bow	1.7239	1.3574	27.0	0.23

According to calculations, the water content of the *dou's* body is 366%, and the water content of the bow's body 374%. Moisture content is currently an important criterion for evaluating the deterioration of water-saturated wooden cultural relics, and the moisture content here refers to the maximum moisture content of the wood in a saturated state. At present, the most commonly used classification method, developed in the 1970s, is to divide the deterioration degree of water-saturated wooden cultural relics into three grades according to the moisture content parameter: a moisture content above 400% means Degree-I Degradation; a moisture content between 185%~400%, Degree-II Degradation; a moisture content less than 185%, Degree-III degradation, in which case only the surface has degraded[12]. Therefore, these two cultural relics are moderately corroded and can be subjected to general dehydration treatment. The moisture content of the paint coating of the *dou* is 33%, and the moisture content of the paint coating of the bow is 27%. Due to the difference in the thickness, the moisture content is also different. The increase in the thickness of the paint coating will gradually reduce the moisture content. The water content of the paint coating is mainly related to the amount and exposure of hydrophilic substances in the coating, as well as to the dents on the painting coating and internal and external channels. The expansion of cavities formed by hydrophilic groups on the paint film and the formation of paint film channels will consequently increase the water content of the paint coating[13].

2.3 Study of the appearance and elements of the paint coating

The cross-sectional morphology of the painting cover is observed with a three-dimensional video microscope and a scanning electron microscope. The cross-sectional image is shown in Figure 4. It not only shows the structure of the paint coating, but also the morphological characteristics of the filler in it. As shown in Figure 4, the sample paint coating consists of three layers: a colored layer (6-10μm), a paint layer (30-50μm), and a paint base layer (60-80μm). The paint coatings of the *dou* and the bow are similar.

The EDS analysis results are shown in Table 2. C, O, Hg, and S are detected in the colored layer of the sample, which indicates that the red pigment is cinnabar (HgS). Silicon may be derived from quartz (SiO_2), which may be an impurity in pigments. The EDS results of the paint show that the main elements are C (74.5%) and O (25.5%). The EDS results of the mortar layer show that the main elements are C, O, Si, Al, Na, Mg, K, Ca, Fe, which may be quartz, aluminum, sodium, magnesium, potassium silicate, etc.

Table 2 EDS analysis

Sample	C	O	Na	Mg	Al	Si	S	K	Ca	Fe	Hg
dou	45.5	12.0	–	–	–	2.9	3.4	–	–	–	36.2
	45.4	33.7	0.4	0.4	3.5	13.5	–	1.1	1.0	1.0	–
	6.5	43.7	8.1	–	9.8	31.9	–	–	–	–	–
bow	42.8	10.7				0.6	7.7		–	–	38.2
	77.9	20.3					1.1		0.7		
	4.0	49.1			0.6	46.3					

Although the red pigments in the two samples are similar to cinnabar, the contents of mercury, sulfur, and silicon are different, which indicates the material differences between them. It can be seen from the photos of the optical microscope that the two samples have different red colors. In the case of the *dou*, the color is reddish brown, and in the case of the bow—this may be related to the purity of cinnabar. The content of silicon in the paint coating of the *dou*is higher than that of the bow. Another reason accounting for the difference in red brightness between the two pieces of lacquerware is related to the particle size of the cinnabar pigment. The smaller the grain of cinnabar, the brighter the color. The SEM images of the two pieces of lacquerware are shown in Figure 5. It can be seen that the particle size of the cinnabar used in the paint coating of the bow is slightly larger than that of the *dou*.

2.4 Raman spectroscopy and XRD analysis

Raman spectroscopy and X-ray diffraction (XRD) are used to further identify the composition of inorganic substances in the sample of the *dou*. Analysis of the results of Raman spectroscopy further confirmed that cinnabar is the red pigment. The Raman spectrum of the red pigment layer is shown in Figure 5a. The characteristic peaks of cinnabar are very strong, with peaks of 253cm^{-1}, 387 cm^{-1} and 344 cm^{-1} respectively. Cinnabar was a commonly used red pigment in ancient China. It has been found on the lacquer bowls unearthed at the Hemudu site dating to around 7000 years ago and the oracle bone inscriptions unearthed at the Yinxu site dating to around 3000 years ago. A large quantity of red lacquerware has been unearthed from the Zeng Guo Cemetery.

XRD analysis is conducted on the paint base layer of the *dou*. From the XRD pattern, we can learn that the paint base layer is mainly composed of quartz (silica), with the characteristics being 2θ20.87°, 26.61°,

36.50°, 42.45°, 45.78°, 50.14°, 54.84°, 59.97°, 67.76°, 68.23°, 75.63°, and a small amount of calcite (calcium carbonate) in 2θ29.90° and 43.55°. The addition of these inorganic substances is to improve the physical properties of the paint coating and reduce costs.

2.5 Infrared spectrum analysis

Fourier transform infrared spectroscopy (FTIR) is used as a non-destructive analytic method. Here, the sample is analyzed by FTIR point scanning. The infrared spectrum is shown in Figure 7. The spectrum shows that the peak at 3278 cm^{-1} is -OH; because the peak shape is broad, it indicates that it is multi-molecular associative water. The transmittance of this peak is 20%, which is relatively low, indicating that the paint coating contains a relatively great amount of free water. The peaks at 2920 $cm^{-1}$and 2853 cm^{-1} are due to the stretching of $-CH_2$, and at the peak of 1633.9 cm^{-1}, C=C. Because the peak shape there is wide and has burrs, it is probably affected by water molecules[9], and the light transmittance reaches 29%, which further proves that the paint film contains a relatively great amount of free water. The shoulder peak at 1423 cm^{-1} is due to the shearing of $-CH_2$ and the asymmetric phenyl shearing of $-CH_3$. The two peaks are very close and overlap each other to form a shoulder. The peak at 1670 cm^{-1} is due to the C=O bond, which indicates the presence of oil. The peak values in the region of 1300-1000 cm^{-1}, including those at 1274cm^{-1}, 1200 cm^{-1} and 1028 cm^{-1}, contributes to phenyl C-O, and its transmittance is 14%, indicating that the degradation of the paint film is relatively serious. The peak is reached at 719 cm^{-1}, which is caused by the in-plane bending of the benzene ring of the main component 1,2,3-trisubstituted benzene in the paint.

2.6 THM-Py-GC/MS analysis

Under the ultra-depth of field video microscope, the black paint cover is peeled off layer by layer with tweezers and a scalpel to obtain the six layers of the paint coating, and then take a 1mm×1mm sample of each layer to perform THM-Py-GC/MS analysis. The total ion current chromatogram of the sample is shown in Figure 9, and the corresponding thermal cracking products are shown in Table 3. Due to the addition of the methylating reagent TMAH into the sample, the carboxyl- and hydroxyl-containing substances undergo a methylation reaction and become the corresponding methyl ester and methyl ether substances. For example, catechol turns into 1,2-Dimethoxybenzene, fatty acid into fatty acid methyl ester, and glycerol into an alcohol with *n* methoxy groups (*n*=1,2,3).

The cracked products of large lacquer are found in the cracked products of all the paint layers of the black paint cover: catechols and catechol oxidation products, alkanes and alkenes, hydrocarbyl benzenes, phenols, and carboxyl benzenes. Figure 10 shows more intuitively the pyrolysis products and their relative contents in the lacquer. It can be seen that the side chain catechol with the largest number of carbon atoms is C15 (3-pentadecylcatechol), the Catechol oxide with the highest content is C8 (8-(2,3-dimethoxyphenyl) methyl octanoate), the olefin with the highest content is C14-1 (tetradecene), and the alkane with the highest content is C15 (Pentadecane). In addition, in the first to third and fourth layers of the paint cover, the short-chain catechol with the highest content is C7 (3-heptyl catechol). Based on this

it can be determined that in the lacquer used for the black paint cover there is urushiol, a kind of lacquer collected from the *Rhus vernicifera sumac* tree that grows in China, Japan and South Korea.

In addition, mono-fatty acids, di-fatty acids, and glycerol are detected in all the layers of the paint cover (Table 3), proving the addition of drying oil. Among them, C16 (palmitic acid, denoted by P) and C18 (stearic acid, denoted by S) are the saturated components of oil. The type of oil can be judged according to its mass ratio (P/S), and the P/S value of the paint cover can be seen in Table 3. The P/S values of the first to third, fourth, and fifth layers are consistent with the P/S values of perilla seed oil (2-4) and tallow tree oil (≈3). The drying oil added in the 1st to 5th layers of the paint cover is perilla seed oil or tallow tree oil. Sesamin is detected in the sixth layer of paint, which is a characteristic pyrolysis product of sesame oil, and the P/S value of the sixth layer is 1.79, which is consistent with the P/S value of sesame oil[14]. It can be judged that the drying oil added to the sixth layer of paint is sesame oil.

Pyrene is detected in all the layers of the black paint cover, so is cadalene in the first to third paint films, and juniperene in the sixth layer. These products are all thermal cracking products of oil-bituminous coal (Table 3). The *Qin Yuan Yao Lu Qin Shu*, completed approximately in the Northern Song Dynasty, writes that fine "great lacquer" can be made with "1 *jin* good raw lacquer, six *liang* sesame oil, 2 *cun* saponins, 6 *qian* soot coal, 1 *qian* lead powder, and 1 medicine terminalia fruit". In Volume 1 of *Complete Collection of the Supreme Sound* (*Tai Yin Da Quan Ji)*byYuan Junzhe of the Ming Dynasty, there is also a record about making fine lacquer by “frying high-quality raw lacquer with ash bark, iron powder, and soot coal..." Therefore, it can be inferred that soot coal was used to refine and improve the lacquer of the paint cover.

Trimethyl phosphate was also detected in the sixth layer of the paint cover, but no blood characteristic compounds or cholesterol substances are detected, and it is impossible to determine whether blood is added. The discovery of trimethyl phosphate may be due to the addition of bone ashes as a filler in the paint ash.

Table 3 Compound list

Retention time (min)	Lacquer	Peak area			
	Catechol and catechol oxides	**1st-3rd layers**	**4th layer**	**5th layer**	**6th layer**
4.611	Phthalic Ether	19272	–	204046	252643
5.2055	3-Methyl Phthalic Ether	–	–	132042	–
6.0705	3-Ethyl Phthalic Ether	–	–	217979	
6.7975	3-Propyl Phthalic Ether	–	–	62286	
8.704	3-Pentyl Phthalic Ether	23546	–	–	–
9.524	3-Hexyl Phthalic Ether	55894	–	–	–
10.324	3-Heptyl Phthalate	104860	51812	–	–
15.042	3-(8-pentadecenyl)-phthalic ether	51150	93992	79616	139390
15.19	3-pentadecyl-phthalic ether	33359	98684	110701	193098
11.887	Methyl 7-(2,3-dimethoxyphenyl)heptanoate	–	21678	–	–
12.566	Methyl 8-(2,3-dimethoxyphenyl)octanoate	23752	64228	113555	142172
	Hydrocarbons (alkanes and alkenes)				
2.5795	1-Nonene	–	–	578571	3300119
2.825	Nonane	98297	79093	433327	949973
3.4805	1-Decene	–	127617	108106	238827
3.5385	Decane	141921	–	307744	1196496
5.8325	1-Undecene	367032	260598	441636	1661699
4.2585	Undecane	189769	146614	262421	–
4.981	1-Dodecene	113724	109922	435931	1089242
5.049	Dodecane	–	33641	286656	659293
7.647	1-Tridecene	322609	272563	628083	1300466
5.9055	Tridecane	410072	288944	519164	1917548
6.711	1-Tetradecene	1352967	1212826	1784186	6116440
6.778	Tetradecane	287542	303808	380031	1258764

7.5295	1-Pentadecene	262610	160147	302438	1215570
7.647	Pentadecane	677253	658765	747634	2635393
	Hydrocarbylbenzenes				
3.2235	Propylbenzene	61311	42781	255682	622382
3.716	3-Butenylbenzene	–	–	70129	133007
3.9705	Butylbenzene	63532	–	–	335082
5.4405	Hexylbenzene	–	–	80464	228051
	Phenols				
7.8255	2-n-hexylphenol	24299	17894	38625	111927
9.0365	2-heptylphenol	67713	42930	52362	304125
14.9105	2-pentadecylphenol	37645	47682	17142	134770
	Carboxybenzenes				
4.273	Methyl benzoate	11201	51250	164367	–
7.065	Dimethyl phthalate	–	–	118276	–
7.503	Dimethyl 1,3-phthalate	–	–	32183	–
7.507	Dimethyl 1,4-phthalate	–	–	–	54691
Retention time (min)	**Lacquer**	**Peak area**			
	Mono Fatty Acids	**1st-3rd layers**	**4th layer**	**5th layer**	**6th layer**
2.183	Methyl valerate	27445	–	–	–
2.7455	Methyl 5-hexenoate	–	–	620356	–
3.0115	Methyl caproate	125362	175444	825687	1385324
3.6445	Methyl 6-heptenoate	83629	123861	791345	644800
3.7055	Methyl Enanthate	181462	302711	819091	995314
4.435	Methyl caprylate	230790	379084	812728	1162358
5.0185	Methyl 8-nonenoate	–	–	137708	–
5.2415	Methyl nonanoate	206171	341141	668986	1182828
5.0875	Methyl decanoate	–	–	188497	284683
5.942	Methyl dodecanoate	–	–	154017	418037

9.501	Methyl Myristate	103290	249448	384300	441106
10.278	Methyl Pentadecanoate	91814	232737	277192	13940434
11.024	Methyl palmitate	4668017	9544687	12219888	–
11.7305	Methyl Heptadecanate	–	95586	–	7799105
12.2405	Methyl 9-octadecenoate (methyl oleate)	790102	953922	1045275	1893928
12.411	Methyl octadecanoate (methyl stearate)	1888456	3474421	5578592	–
12.8295	Methyl 9,12-octadecadienoate	480814	375384	241601	–
13.7005	Methyl Eicosanate	181547	262187	369412	442096
16.756	Methyl tetradecanoate	–	105263	–	–
18.5355	Methyl hexadecanoate	117892	269082	–	–
20.397	Methyl octadecanoate	–	59245	–	–
9.8325	Dry oil characteristic compound 1	–	19757	–	–
	Dibasic fatty acids				
3.7745	Dimethyl Succinate	–	67895	–	–
4.38	Dimethyl glutarate	–	–	39761	–
6.2705	Dimethyl Pimelate	45500	93398	126159	–
7.163	Dimethyl suberate	194015	434952	671503	773322
8.0345	Dimethyl Azelaate	779281	1344098	1864979	2550288
8.882	Dimethyl Sebacate	51184	204393	–	–
	Glycerols				
2.7845	1,3-Dimethoxy-2-propanol	–	–	–	1955022
2.958	2,3-Dimethoxypropane-1-ol	6782	17160	199359	1796895
	Sesame oil characteristic compound				
20.3065	Sesamin	–	–	–	400843
Retention time (min)	**Soot coal**	Peak area			
		1st-3rd layers	**4th layer**	**5th layer**	**6th layer**
9.223	Cadalene	30765	–	–	–

12.1495	Pyrene	22004	34732	52487	131912
6.189	Juniperene	–	–	–	1690083
Retention time (min)	**Others**	Peak area			
		1st-3rd layers			**1st-3rd layers**
3.15	Trimethyl phosphate	–	–	–	201230

3. Conclusions

Various tools and techniques including the optical microscope, SEM-EDS, Raman spectroscopy, XRD, FTIR, and THM-Py-GC/MS are employed to study the *dou* and bow unearthed from the Guojiamiao Cemetery at Caomenwan. The materials of the bodies of the *dou* and bow are Catalpa wood and Sawtooth oak respectively. The moisture contents of the bodies of the lacquerware is at 300%, and hence the two relics are moderately corroded and can be dehydrated by the most commonly used glyoxal method in China. The three-layer structure of the paint coating are measured, including the mortar layer, the lacquer layer and the layer of mixed colored inorganic pigments. Although the red color in the two pieces of lacquerware is recognized as cinnabar, there are differences in purity and particle size. The research results not only enhance ourscientific understanding of ancient lacquer-making materials and techniques but also provide a scientific basis for protecting the lacquerware.

Declarations

Contributions

Chen Zifan has compiled the papers and produced the final manuscript. Wei Shuya and Fu Yingchun have provided some supports with experimental operation. All authors read and approved the final manuscript.

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Ethics declarations

Consent for publication

Written informed consent for publication was obtained from all participants.

Competing interests

The authors declare that they have no competing interests.

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Figures

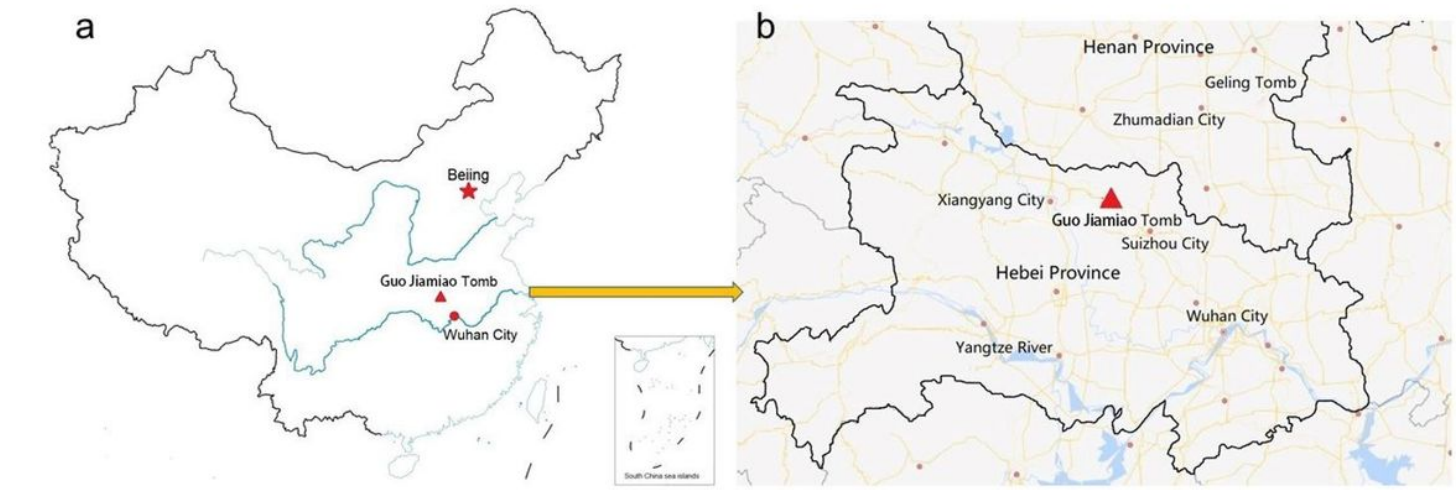


Figure 1

Location of GuojiamiaoCemetery. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Dou and bow

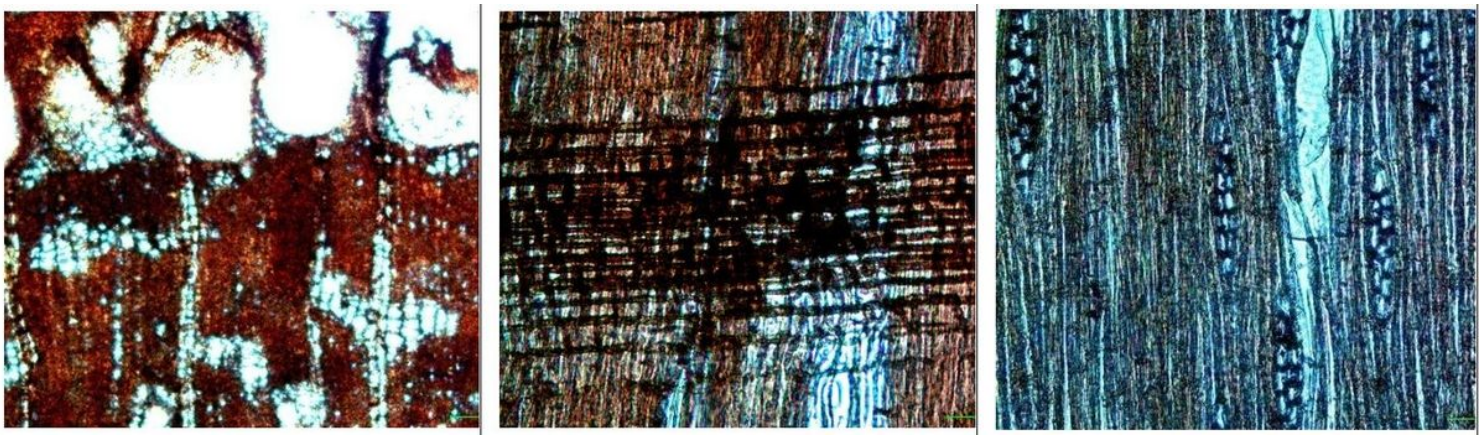


Figure 3

Dou

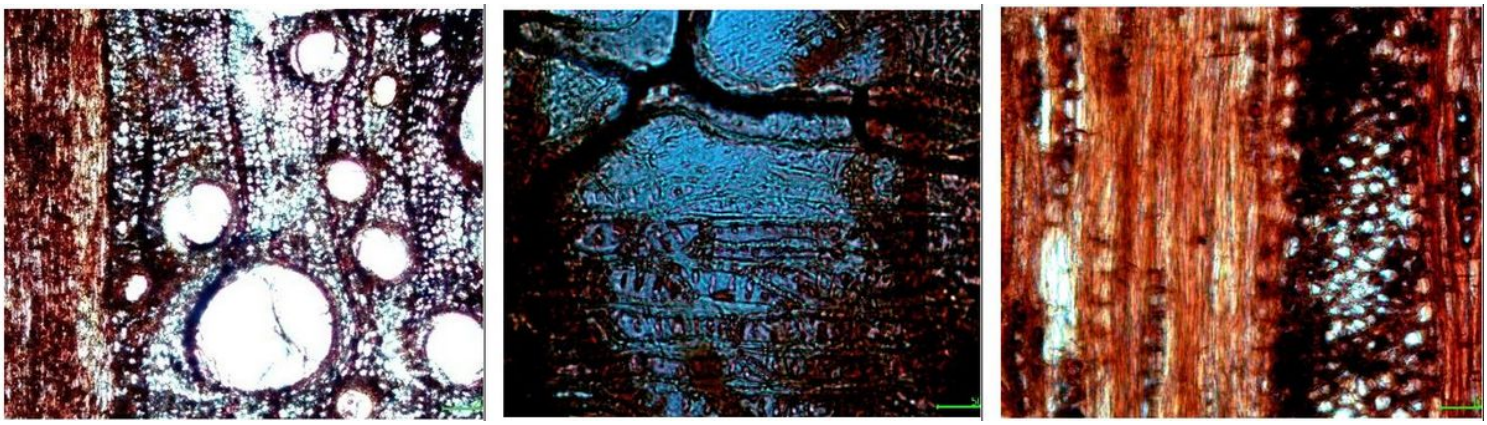
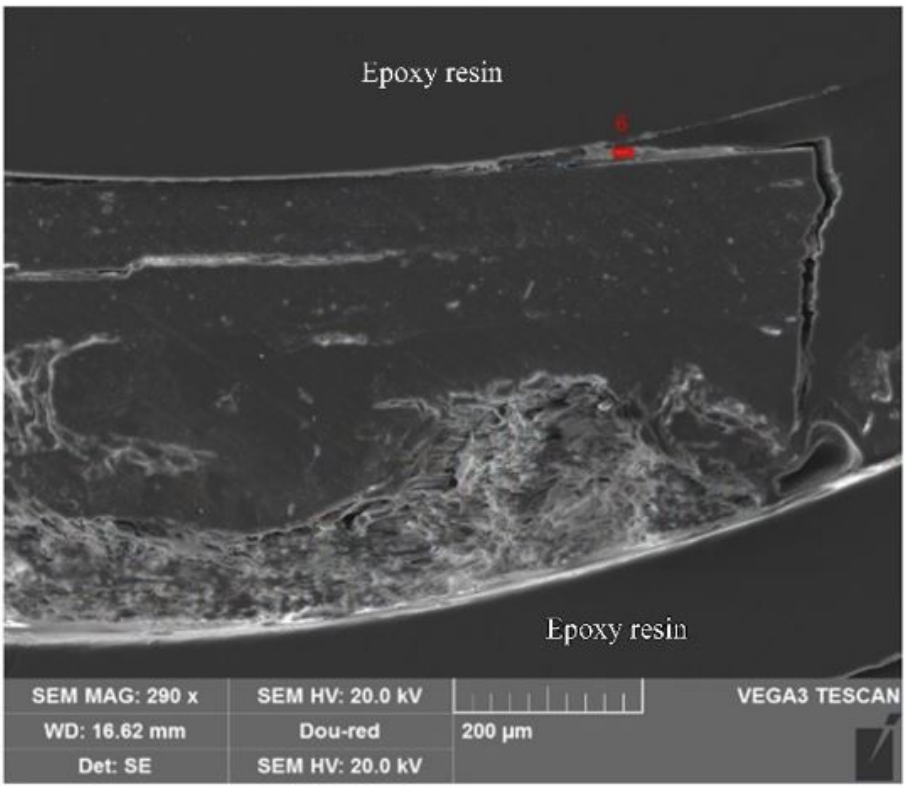


Figure 4

Bow



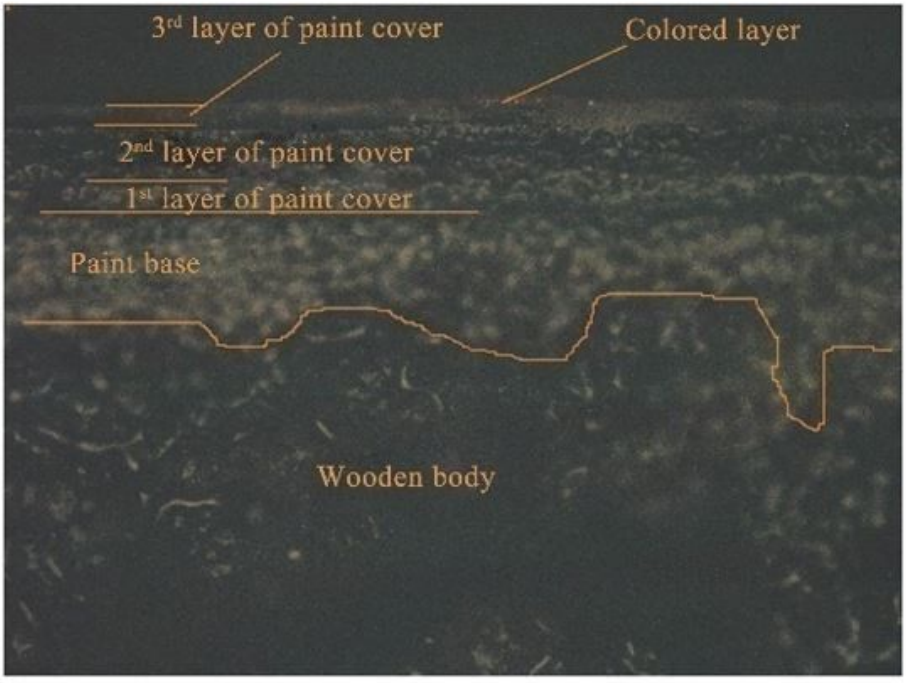


Figure 5

Cross-section of paint coating

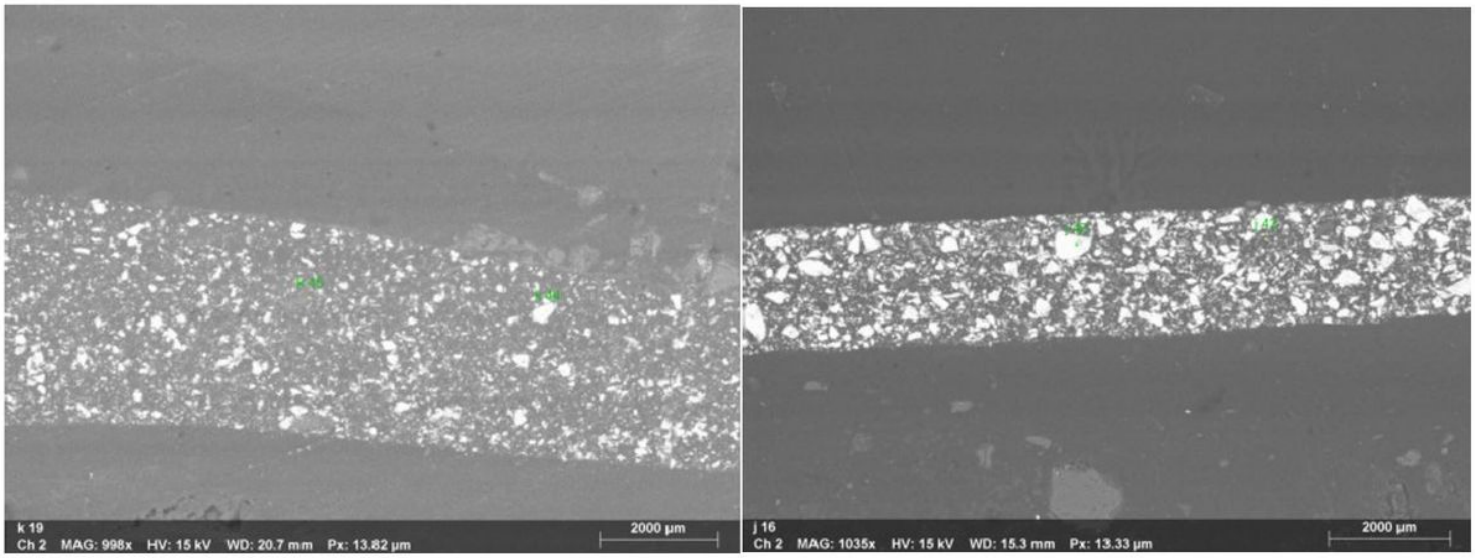


Figure 6

Cross-section of the colored layers

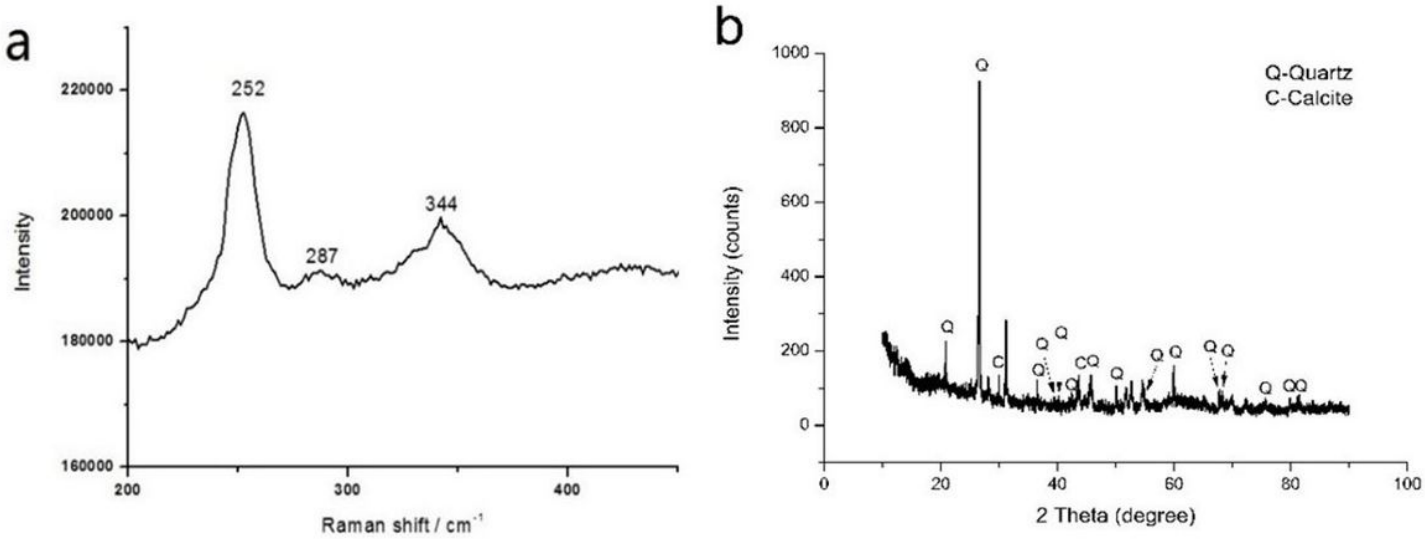


Figure 7

Ramanspectrum and XRD patterns

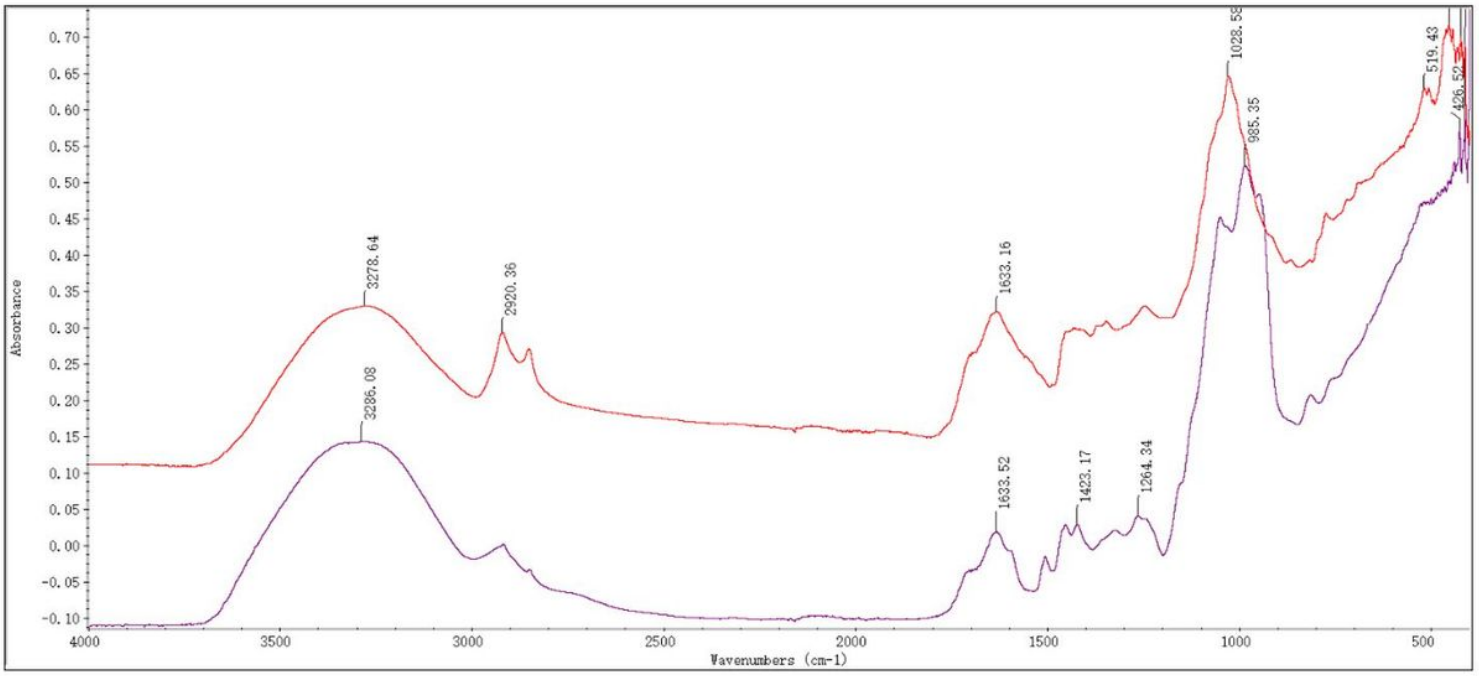


Figure 8

Infrared spectrum

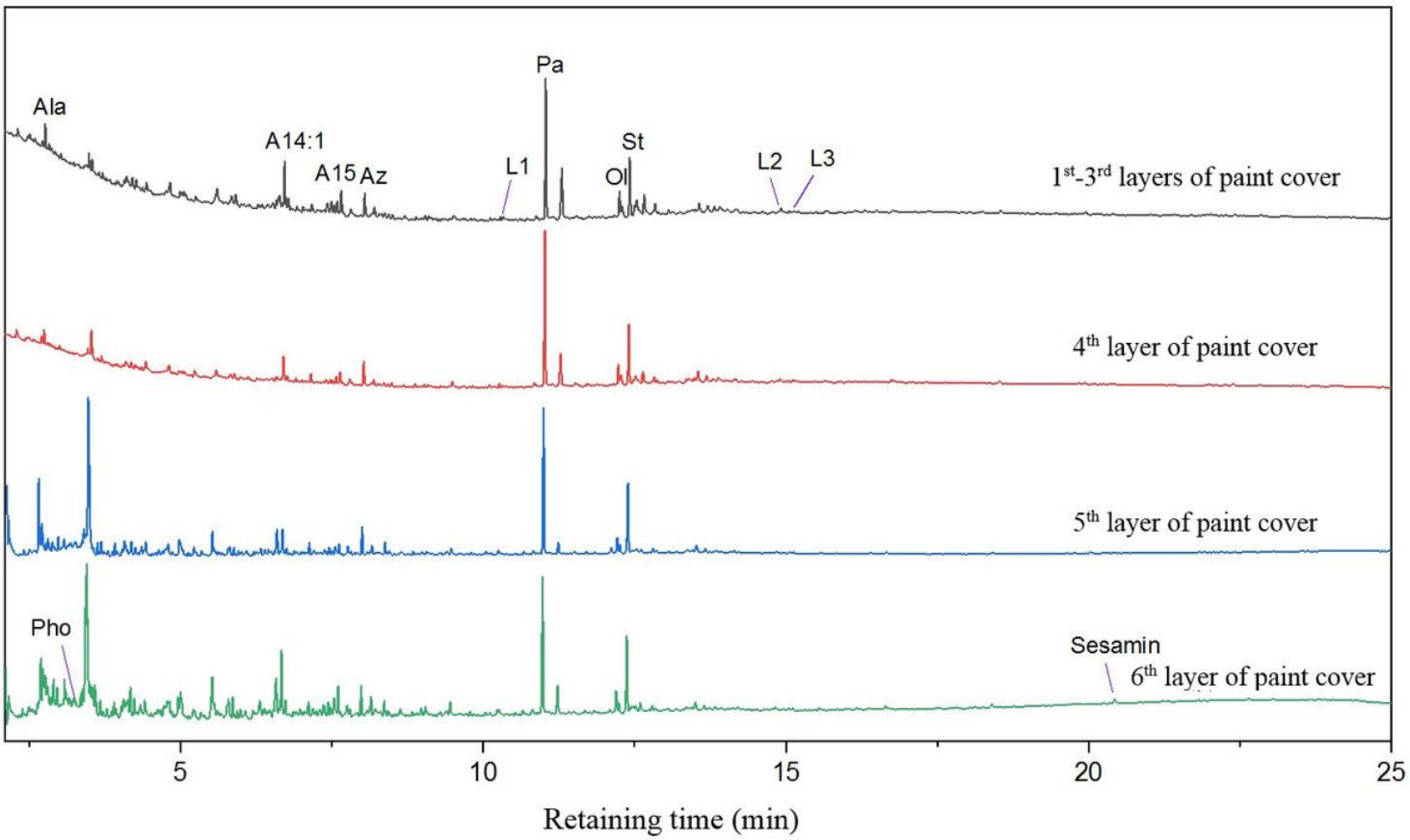


Figure 9

Total ion current chromatograms of different layers of the paint cover (Ala: methyl alanine; A14:1: 1-tetradecene; A15: pentadecane; Az: dimethyl azelate; Pa: Methyl palmitate; Ol: methyl oleate; St: methyl stearate; L1: 3-heptyl phthalate; L2: 3-pentadecenyl phthalate; L3: 3- Pentadecyl Phthalic Ether; Pho: Trimethyl Phosphate; Sesamin: Sesamin)

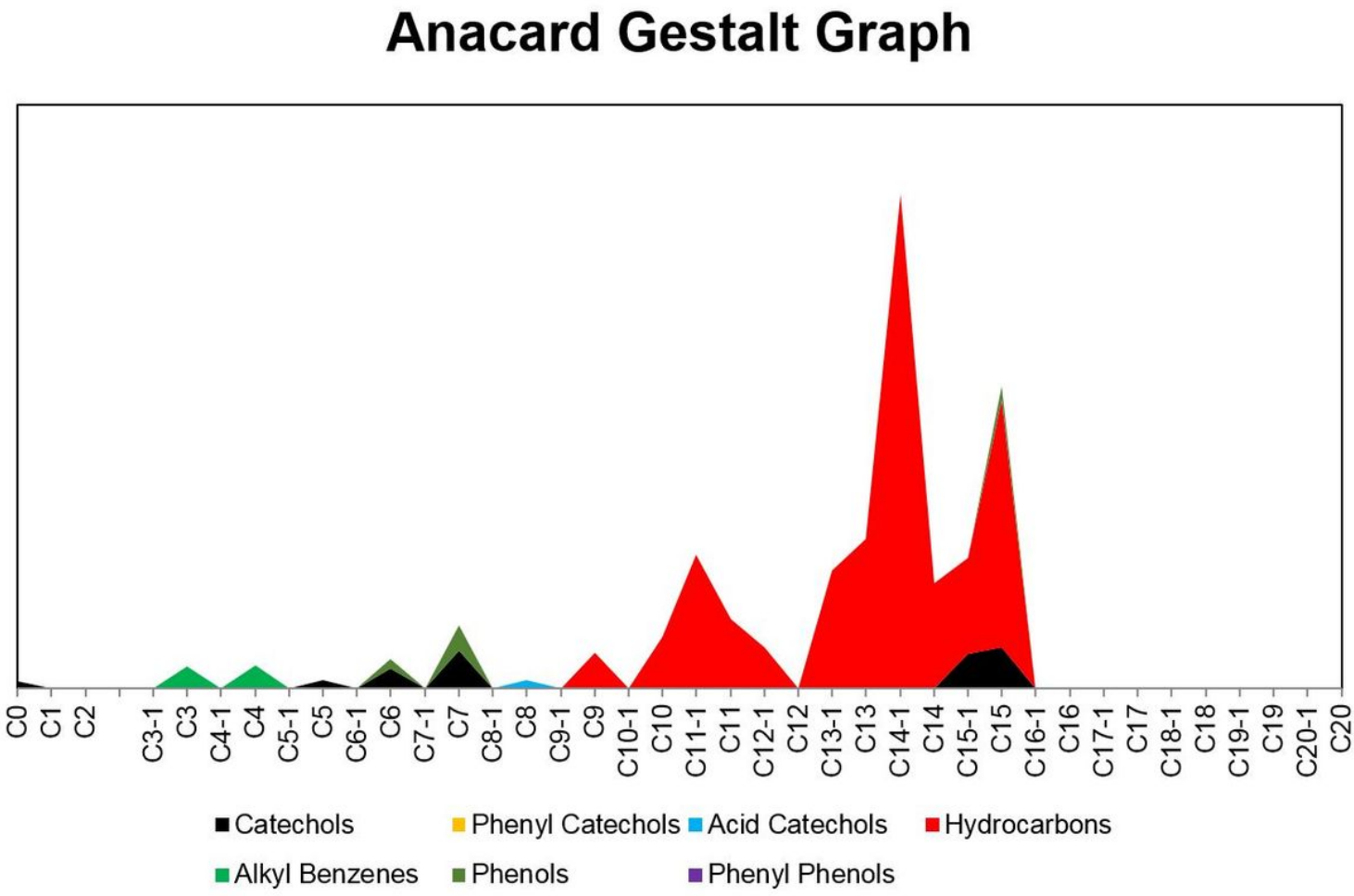


Figure 10

Cracked products of medium and large lacquer(first to third layers) in black paint cover

Supplementary Files

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- graphicalabstract.jpg