The identification of binding agent used in late Shang Dynasty turquoise-inlayed bronze objects excavated in Anyang

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ABSTRACT

The paper presents the results of the analysis of the binding media used in turquoise-inlay bronze artifacts in late Shang Dynasty, which were excavated in Anyang, Henan Province of China. Techniques applied include pyrolysis gas chromatography and mass spectrometry with thermal assisted hydrolysis and methylation (THM-Py-GC/MS), as well as GC/MS with derivatization reagent of MethPrep II. Marker compounds of urushi including methylated pentadecyl catechol and the oxidation products: 6-(2,3-dihydroxyphenyl) hexanoic acid; 7-(2,3-dihydroxyphenyl) heptanoic acid and 8-(2,3-dihydroxyphenyl) octanoic acid as their methylated forms were found, indicating Urushi (lacquer) was used as binding agents for the inlay. In addition, a series of fatty acids was detected with relative higher concentration of azelaic acid, which represents the presence of plant oil in the sample. Furthermore, a group of glue marker compounds and a series of long-chain fatty acids as well as a group of long-chain alcohols were detected in the sample.

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1. Introduction

Yin Ruin, located in the northwest suburb of Anyang City in Henan Province, the capital city of Shang Dynasty, is the only documented Shang capital site in ancient literature that is confirmed by archaeological excavations. In Yin Ruin area, a number of great archaeological findings have been discovered, which include twelve royal tombs, more than one hundred palaces and royal temples building foundations, Huanbei Shang city and Oracle cellars etc. (Institute of Archaeology, Chinese Academy of Social Sciences, 1987). Thus, due to its unique importance in archaeology, Yin Ruin was listed in the UNESCO World Heritage Sites in 2006. The Shang Dynasty tombs, located in Huan Yuan Zhuang east in Anyang, were excavated from 1992 to 2002 (Institute of Archaeology, Chinese Academy of Social Sciences, 2007). In tomb M54, many precious bronze swords, arrows, vessels, jade artifacts and ceramics were found (Fig. 1). Especially, one group of objects, namely six bow-shaped bronzes with beautiful turquoise inlay on the surface were unearthed. The turquoise was nicely cut and inlayed as a special pattern — the Tao tie pattern, which represents a mysterious monster from Chinese legend. The function of those objects is still unclear. Some researchers thought that they were used during ritual practice, while others said they were the parts of a carriage, but where and how they were used in the carriage remains unclear.

Turquoise is a hydrous phosphate of copper and aluminum, \( \text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8\cdot4\text{H}_2\text{O} \), which was highly valued and used as ornaments in ancient China due to its beautiful colour. In the last decades, many precious turquoise-inlaid artifacts were found by archaeologists from noble tombs (Hao and Hao, 2002; Guo, 2008; Ding and Zhu, 1996; Hu, 1993). The earliest ones are the turquoise Goddess (a human-sized female statue with eyes decorated with turquoises) from the Hongshan Culture (4500–2250 BC) and turquoise-inlaid jade artifacts from the Liangzhu Culture (5000–4800 BC) (Zhang, 1996; Guo, 2008). After its presentation to the public, the technique of how the turquoise inlay was made attracted the attention of the people (Archaeological Team at Danjiang Dam of Henan Province, 1980; Henan Institute of Cultural Relics and Archaeology, 2004; Shi and Cai, 2007). At the beginning, there has been a debate on whether binding agents were used for the turquoise inlay until it was realized that there were indeed binding agents between the turquoise and the substrate. The question then arose what kinds of materials were used to fix the...
inlay during the ancient time. One paper reported that the whitish residues sampled from an Eastern Zhou (770–256 BC) turquoise-inlaid bronze sword are chemically similar to shellac by using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer (SEM/EDS) techniques analysis (Cheng et al., 2008). In a more recent publication, a sword with turquoise embedded in its handle from Qiao-jayuan in northeastern Hubei Province (central China), dating back to Chu state (6th–5th BC) was studied. The binding agents to stick the turquoise on the bronze sword were identified as beeswax by using FTIR and X-Ray Diffraction (XRD) techniques (Luo et al., 2012). However, the authors suggested the samples still need to be studied with other analytical methods to see whether ingredients other than beeswax are present. Other materials such as lacquer was used as coating materials for objects and also for binding media in ancient time in China (Bonaduce et al., 2008; Wei et al., 2011). For example, a mixture of Chinese lacquer and lime milk was identified as binding agent to bond the gold foil to the bronze base unearthed at the Sanxingdui site (ca. 2800–800 BC) in southwestern China (Zeng, 2005). It will be also interesting to study the samples from different times and areas to see whether other binding agents were used to inlay turquoise.

In ancient times in China, the possible materials used as binding reagents could be drying oils, lacquer, resins and waxes etc. (Chen, 2003). Lacquer originates as the sap of lac trees and is tapped from the tree. According to the region of the tree origin, there are mainly three types of oriental lacquers — Rhus vernicifera (the phenol derivative is urushiol), Rhus succedanea (the phenol derivative is laccol) and Melanorrhoea usitata (the phenol derivative is thitsiol) (Niimura et al., 1999). These monomers are considered as the most characteristic markers to distinguish particular lacquer (Lu et al., 2006). Lacquer film is a cross-linked polymer that polymerised by laccase and it is insoluble in most solvents. Due to this fact, only a few analytical techniques are available for the scientific investigation. Pyrolysis–gas chromatography and mass spectrometry Py-GC/MS (Niimura et al., 1996, 1999; Niimura and Miyakoshi, 2006; Lu et al., 2006, 2007a, b; Kumanotani, 1995, 1998; Burmester, 1988; Frade et al., 2009) have been mostly applied. The advantage of the Py-GC/MS is that no sample preparation or pre-treatments of the specimen is necessary and only a very small amount of sample is required. However, one of the main problems of the pyrolysis technique is, when confronted to the polar compounds of acidic and alcoholic pyrolysis products, causing a rather low reproducibility of the resulting pyrograms. Moreover, the high fragmentation of natural macromolecules during pyrolysis forms many unspecific compounds. To overcome these problems, Py-GC/MS with thermal assisted hydrolysis and methylation technique were applied (Mazzeo et al., 2004; Cappitelli et al., 2002; Chiavari et al., 2001; Piccirillo et al., 2005; Le Hô et al., 2012; Schilling, 2014). Tetramethylammonium hydroxide (TMAH) is one of the most commonly used reagents for the online hydrolysis of acidic and alcoholic moieties. Py-GC/MS with thermal assisted hydrolysis and methylation (THM) reagent of TMAH were successfully used to simultaneously characterize binding media used in artifacts such as drying oil, lacquer etc. (Schilling, 2012).

The technique of gas chromatography coupled to mass spectrometry (GC/MS) was used to identify binding media of drying oil, resin and wax in artworks or archaeological objects (Cappitelli et al., 2002; Challinor, 1996; Pitthard et al., 2006; Bonaduce et al., 2009). The GC/MS analytical procedure for the analysis of lipids is based on the transesterification of fatty acids and the determination of their relative ratios to identify particular lipids, while the analytical procedure for the analysis of resinous binding media is based on the esterification of resinous acids followed by the identification of particular resins according to their resinous acid methyl esters (Pitthard et al., 2010; Colombini and Modugno, 2009; Valianou et al., 2011). Samples from archaeological context are normally very difficult due to their complex environment and long term ageing. The analyses results of archaeological samples by THM-Py-GC/MS and GC/MS techniques can complement or approve each other to provide unambiguous information. Thus in this study, techniques including THM-Py-GC/MS with in situ methylation reagent of tetramethylammonium hydroxide (TMAH) and GC/MS techniques were carried out for the identification of the binding agents used in turquoise inlaid into the bow-shape bronze artifacts from Shang Dynasty in Anyang Yin Ruin. The results are significant for archaeologist to further study and compare the materials used to inlay turquoise on bronze in different periods, and to find out the inheritance and change of the materials used in the history. The information will be also helpful for making conservation treatment strategy in the future.

2. Experimental

2.1. The samples

Fig. 2. A. The turquoise inlay bow-like bronze ware (M54-303), the yellow areas indicate where samples were taken; B. Schematic graph of M54-303 side view; C. Schematic graph of M54-303 vertical view; a) one piece of turquoise; b) an assay binding agent sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
The agents remained (Fig. 2). The samples are visually dark brownish color. Firstly, two samples (M54-203a and M54-303a) were subjected to THM-Py-GC/MS procedure for the identification of the materials respectively. Afterwards, M54-203b was analyzed by using the GC/MS technique. The GC/MS analytical procedure can be used to simultaneously identify oil, resin and wax, excluding glue, which makes the chromatogram simpler in comparison with the pyrogram. Furthermore, since the archaeological samples are very complicated, the two techniques of THM-Py-GC/MS and GC/MS may complement or support each other to provide unambiguous information.

2.2. THM-Py-GC/MS procedure

The procedure for thermally assisted hydrolysis and methylation pyrolysis (THM-Py-GC/MS) with TMAH analysis was performed as follows: about 0.2 mg of the samples were placed in a sample cup, and then 3 μL of 25% aqueous TMAH (Aldrich, USA) solution were added with a micro syringe to the sample. The cup was introduced into the pyrolyzer (furnace) by the auto sampler and pyrolyzed immediately; afterwards the temperature program of the GC/MS was started. The pyrolysis-gas chromatography/mass spectrometry measurements were carried out using a double-shot pyrolyzer PY-2010iD (Frontier Lab, Japan) attached to a gas chromatograph and mass spectrometry GC/MS-QP2010 Plus (Shimadzu, Japan). A capillary column SLB-5MS (5% diphenyl/95% dimethyl silicone) with a 0.25 mm internal diameter, 0.25 μm film thickness and 30 m length (Supelco, USA) was chosen in order to provide an adequate separation of the components. The Shimadzu GC/MS is controlled by the real time analysis software package, where peak integration and mass spectra evaluation is included.

Pyrolysis was performed at 600 °C, the pyrolyzer interface was set at 320 °C and the injector at 250 °C. The chromatographic conditions were as follows: the oven initial temperature was 40 °C.

Fig. 3. The chromatogram of sample M54-303 obtained by THM-Py-GC/MS, the compounds identified are listed in Table 1. Cn:0 — Saturated carboxylic acid with carbon number of n methyl ester; 2Cn:0 — dicarboxylic acid with carbon number of n methyl ester; C — Alkane; G — Compounds from glue; P — Compound from blood; P — Phenol; L1 — Methyl 6-(2,3-dimethoxyphenyl) hexanoate; L2 — Methyl 7-(2,3-dimethoxyphenyl) heptanoate; L3 — Methyl 8-(2,3-dimethoxyphenyl) octanoate; L4 — Methylated pentadecyl catechol.

Fig. 3b. The mass spectrum of the marker compounds of urushi sample M54-303 by THM Py-GC/MS analysis; L2: methyl 7-(2,3-dimethoxyphenyl) heptanoate; L3: methyl 9-(2,3-dimethoxyphenyl) nonanoate; L4: Methylated pentadecyl catechol.
with a gradient of 10 °C min⁻¹ to 300 °C, which was held for 20 min. The carrier gas was Helium with an inlet pressure of 15.5 kPa and 1:100 split ratio. The electronic pressure control was set to the constant flow mode. Ions were generated by electron ionization (70 eV) in the ionization chamber of the mass spectrometer. The mass spectrometer was scanned from m/z 50 to 750 (mass to charge ratio) with a cycle time of 0.5 s. EI mass spectra were acquired by total ion monitoring mode. The temperatures of the interface and the source were 280 and 200 °C, respectively. NIST 05, NIST 05s Library of Mass Spectra and Getty library for lacquer group were used for identifying the compounds (Schilling, 2014). The chromatographic conditions were the same as for Py-GC/MS analysis.

2.3. GC/MS procedure

Solid reference materials from natural resins (drying oils, waxes, resins) and original samples taken by scalpel (0.2 mg) were placed in vials with conical inserts and treated with 30 ml of a 0.2M methanolic solution of Meth-Prep II-(m-trifluoromethylphenyl)trimethylammonium hydroxide (TFTMAH) and 70 ml of a solvent mixture (methanol: toluene = 1:2 v/v). Each sealed vial was then heated to 60 °C for 1 h, cooled and centrifuged. The clear solution was transferred to a new vial and 1 μl was injected into the GC.

3. Result and discussion

3.1. The analysis results by THM-Py-GC/MS

About 0.2 mg samples taken from M54-303 and M54-203 were analyzed by THM-Py-GC/MS. The total ion chromatogram of sample M54-303 obtained is shown in Fig. 3; while the mass spectra of the three maker compounds of urushi and the oxidization products as their methylated forms are shown in Fig. 3b. The main compounds identified are listed in Table 1. AMIDS software (Schilling, 2014) was used to evaluate the data obtained by THM-Py-GC/MS. AMIDS software has the function of deconvolution, which lowers the limitation of the identification compounds. According to the program developed by Michael Schilling, the data can be classified into different groups, including hydrocarbons, fatty acids, unverified

Table 1
The compounds identified in sample M54 303 by THM-Py-GC/MS with AMMIDS software and the Getty library.

<table>
<thead>
<tr>
<th>RT</th>
<th>Name</th>
<th>Area%</th>
<th>RT</th>
<th>Name</th>
<th>Area%</th>
</tr>
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<td>4.47</td>
<td>1-Heptene</td>
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<td>22.94</td>
<td>1,2,3,4-Trimethoxybenzene</td>
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<td>5.26</td>
<td>Butanoic acid, methyl ester</td>
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<td>23.40</td>
<td>Benzoic acid, 2,3-dimethoxy- methyl ester</td>
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<td>5.74</td>
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<td>Methyl-2-aminobenzoate</td>
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<td>26.76</td>
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<td>FA-2C22 di me, birch tar</td>
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<td>53.77</td>
<td>Octacosanoic acid, methyl ester</td>
<td>0.46</td>
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compounds from glue/blood, dimethoxybenzene methyl esters, alkyl guaiacols, alkyl phenols, alkyl benzenes, alkyl phenyl ketones etc.

The chart of the anacard compounds of the sample M54-303 obtained (Table 1) through THM-Py-GC/MS is generated as in Fig. 4. It can be seen the marker compounds of urushi including homologous series of hydrocarbons and catechol with C15 maximum side chain length — pentadecyl catechol as methylated form (1,2-dimethoxy-3-pentadecylbenzene) was detected. In addition, the oxidization products of urushi including 6-(2,3-dihydroxyphenyl) hexanoic acid; 7-(2,3-dihydroxyphenyl) heptanoic acid and 8-(2,3-dihydroxyphenyl) octanoic acid as their methylated forms were identified. They are methyl 6-(2,3-dimethoxyphenyl) hexanoate; methyl 7-(2,3-dimethoxyphenyl) heptanoate and methyl 8-(2,3-dimethoxyphenyl) octanoate (indicated as blue colour in the chart). The most abundant acid catechol

![Fig. 4. The relative concentration of anacard compounds of sample M54-303 obtained by THM-Py-GC/MS analyses.](image)

![Fig. 5. The relative concentration of fatty acids of sample M54-303 obtained by THM-Py-GC/MS; Cn — carboxylic acid with carbon numbers of n.](image)
is 8-(2,3-dimethoxyphenyl) octanoate (Fig. 3). Alkyl benzenes found are propyl benzene and butyl benzene (as green colour in the chart). According to the previously published Py-GC/MS analysis, the typical pyrolysis products of urushiol are tridecane, heptene, tetradecene, methylbenzene methylphenol, heptylphenol. The identification of urushiol is also confirmed by the presence of pentadecylcatechol and heptycatechol (Niimura et al., 1996, 1999; Niimura and Miyakoshi, 2006; Lu et al., 2006, 2007a, b; Frade et al., 2009; Pitthard et al., 2010; Wei et al., 2012), the typical pyrolysis product of the urushi pentadecyl catechol (MW320), when reacted with methylation reagent to produce 1,2-dimethoxy-3-pentadecylbenzene (methylated pentadecylcatechol, MW348) (Mazzeo et al., 2004; He et al., 2009; Le Hô et al., 2012; Schilling, 2012). Hydrocarbons derived from the cleavage of C–C bonds between the side chains and C–O bonds between phenolic oxygen and side chains (Le Hô et al., 2012). From the detection of those anacard compounds, it can be concluded that urushi (lacquer) exists in the sample.

Another group of compounds detected is a series of fatty acids including monocarboxylic and dicarboxylic acids as their methyl/dimethyl esters. The relative concentration of the fatty acids detected from sample M54-303 is depicted in Fig. 5. Relative higher concentration of short chain monocarboxylic (C4–C9) and dicarboxylic acids (2C4–2C10) are observed in both of the samples (Sample M54-203 and M54-303), with palmitic acid to stearic acid (P/S) and azelaic acid to palmitic acid (A/P) value of 1.3 and 0.6 indicating the presence of plant oil in the samples. However, since relative higher concentration of long chain fatty acids (C22–C28) were found, especially the detection of long chain alcohol (RT 38.87min, 1-hexatriacontanol) indicating the existence of wax in the samples. Since wax contains palmitic acid and stearic acid as well, the value of P/S ratio can be affected by the presence of wax, and therefore cannot be used to classify the type of the oil in the sample.

The third group of compounds are from proteinacious materials such as pyrrol (m/z 67), toluene, methyl pyrrol and typical glue marker with (m/z 93, 186) (Chiavari and Galletti, 1992), phosphate, unverified glue markers nine compounds and two unverified markers for blood (see Table 1 and Fig. 3), indicating that proteinacious material present in the sample is most likely blood (Schilling, 2012).

The chromatogram of sample M54-203 obtained by THM-Py-GC/MS is depicted in Fig. 6. The compounds detected include markers from urushi, plant oil and blood, which are not listed here.

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**Fig. 6.** The chromatogram of sample M54-203 obtained by THM-Py-GC/MS. Cn:0 – Saturated carboxylic acid with carbon number of n methyl ester; C – Alkane; L1 – Methyl 6-(2,3-dimethoxyphenyl) hexanoate; L2 – Methyl 7-(2,3-dimethoxyphenyl) heptanoate; L3 – Methyl 8-(2,3-dimethoxyphenyl) octanoate; L4 – Methylated pentadecyl catechol; A1 – 1-Dotriacontanol; A2 – Clerodol; A3 – 1-Tetracontanol.

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**Fig. 7.** The chromatogram of sample M54-203 obtained by GC/MS with Meth-Prep II, C – Alkanes; Cn:0 – Saturated carboxylic acid with carbon number of n methyl ester.
due to the similarity of the results of sample M54-303. The differences are that there are relative higher amount of wax markers (long-chain alcohols) of 1-dotriacontanol (C32H64O), 1-tetracontanol (C34H70O) in sample M54-203. In order to clarify the type of wax, another analysis (M54-203b) was carried out by GC/MS with Meth-Prep II.

3.2. The analysis results by GC/MS

According to the procedure in section 2.3, GC/MS with Meth-Prep II was carried out to analyze sample M54-203b. The chromatogram of sample M54-203b obtained by GC/MS is shown in Fig. 7. According to the series of the alkanes and the fatty acids, with relative higher amount of tetracosanoic acid (C24:0) and hexacosanoic acid (C26:0), combining the results obtained by the THM-Py-GC/MS analysis (the detection of long chain alcohols), the wax used in the sample can be confirmed as beeswax (Long, 2004; Heron et al., 1994; Regert et al., 2001; Wei et al., 2012).

4. Conclusion and discussion

Binding media used for the turquoise inlay on bronze artifacts (M54-303 and M54-203) from tomb M54 in Huanyuan Zhugang site, Anyang City were characterized through techniques of thermal assisted methylation pyrolysis gas chromatography and mass spectrometry (THM-Py-GC/MS) and GC/MS. Marker compounds of urushi including methylated pentadecyl catechol, methyl 6-(2,3-dimethoxyphenyl) hexanoate; methyl 7-(2,3-dimethoxyphenyl) heptanoate and methyl 8-(2,3-dimethoxyphenyl) octanoate were found, indicating Urushi (lacquer) was used as binding agents for the inlay. In addition, a series of fatty acids were detected with relative higher concentration of azelaic acid, which represents the presence of plant oil in the sample. The earliest usage of lacquer and another analysis (M54-203b) was carried out by Meth-Prep II was performed to analyze sample M54-203b. The chromatograph of sample M54-203b obtained by GC/MS with Meth-Prep II.

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