



Analytical characterization of lacquer objects excavated from a Chu tomb in China

Shuya Wei^{a,*}, Valentina Pintus^{a,b}, Václav Pitthard^c, Manfred Schreiner^{a,b}, Guoding Song^d

^a Institute of Natural Sciences and Technology in Arts, Academy of Fine Arts in Vienna, Austria

^b Institute of Chemical Technologies and Analytics, Analytical Chemistry Division, Vienna University of Technology, Austria

^c Conservation Science Department, Kunsthistorisches Museum, Vienna, Austria

^d Department of Scientific History and Archaeometry, Graduate University, Chinese Academy of Science, Beijing, China

ARTICLE INFO

Article history:

Received 17 December 2010

Received in revised form

17 May 2011

Accepted 24 May 2011

Keywords:

Py-GC/MS

TMAH

Tung oil

Linseed oil

Lacquer

Urushi

ABSTRACT

This work presents the results of an investigation of the lacquer objects excavated from a Chu tomb in China (Warring States, 481–221 BC). This study is engaged in the examination of the methods and the materials used for the urushi coating on the objects. X-Ray fluorescence and Scanning Electron Microscopy/Energy Dispersive Using X-Ray (SEM/EDX) analyses were applied for the pigment identification. The results show that vermilion was for the red colour, while carbon black was for the black colour. Pyrolysis gas chromatography and mass spectrometry (Py-GC/MS) was applied for the characterization of the lacquer resulting that it is based on urushi. The possibility to classify the drying oil (tung or linseed oil) present in the lacquer is highlighted and discussed in this paper. Py-GC/MS with in-situ hydrolysis and methylation reagent tetramethylammonium hydroxide (TMAH) were performed on reference materials of linseed oil and tung oil as well as on the lacquer object samples. The results show that it is possible to unambiguously identify the drying oil, in our case, linseed oil was identified to retard the rate of hardening.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

A tomb dated back to the Warring States (481–221 BC) was excavated in 1998 by the Provincial Institute of Relics and Archaeology of Henan, China. The tomb is located on a range running from north to south at Geling village, 25 km north-west of Xincai County, Henan Province of China. The tomb occupant is 'Pingye' according to the inscriptions on the bronzes and bamboo slips excavated from the tomb. He was a famous aristocrat of the Chu State, a kingdom in the Warring States Period, which was recorded in the historical literature. The tomb is very close to the 'Geling ruin city' (1330 × 1200 m²), where is most likely the principality of Pingye. The tomb pit was directly filled with the "livid sticky mud" on the lacquered wooden coffin; afterwards it was filled with normal soil. Cultivated earth is on the top layer of the tomb. The burial chamber is rectangular (25 × 23 m²). It was divided into four rooms, structured with piled timbers (the cross section is 0.5 × 0.5 m²). The tomb was robbed several times in its history, but still a number of burial articles were found. The great discoveries included: the bronze weapons, bronze chariot and horse fittings, curved ivory

objects, painted horn ornaments, tin articles and the armours, gold foils, lacquer wares and bamboo slips with inscriptions. There are a lot of chronological inscriptions on bamboo slips and bronze wares, which helps for dating the tomb (Song, 2002, 2003). The armours are made of lacquered leather for both humankind and horses. As an example, the lacquer wares fragments showing the different designed patterns with black and red colours are depicted in Fig. 1a–d. Two samples were taken from the lacquered leather fragment (labelled as GL1, Fig. 1a) and from lacquered wooden fragment (labelled as GL2, Fig. 1b). Those samples are available for this study.

The lacquer crafts in China have a long history that can be traced back to the Neolithic. Lacquers as coating materials have been used for wooden, ceramics, leather and metal objects (Niimura et al., 1996). The best quality objects are produced through a long manufacturing process in which a large number of lacquer layers, alone or mixed with other materials, are applied (Webb, 2000). Mixing lacquer with oil is a common technique that does not require so much surface polishing to obtain the lustre. A red wooden bowl was excavated in 1977 in Hemudu, Zhejiang province, from ruins that date to about 7000 years ago, which was the earliest examples of the Chinese lacquer ware (Chen et al., 1995), but there is no scientific analysis confirmation of the lacquer. The structure of the coating film of Chinese lacquer ware from different periods at the Linden-Museum, Stuttgart, Germany has

* Corresponding author. Tel.: +43 1 588168615.

E-mail address: sywei66@hotmail.com (S. Wei).

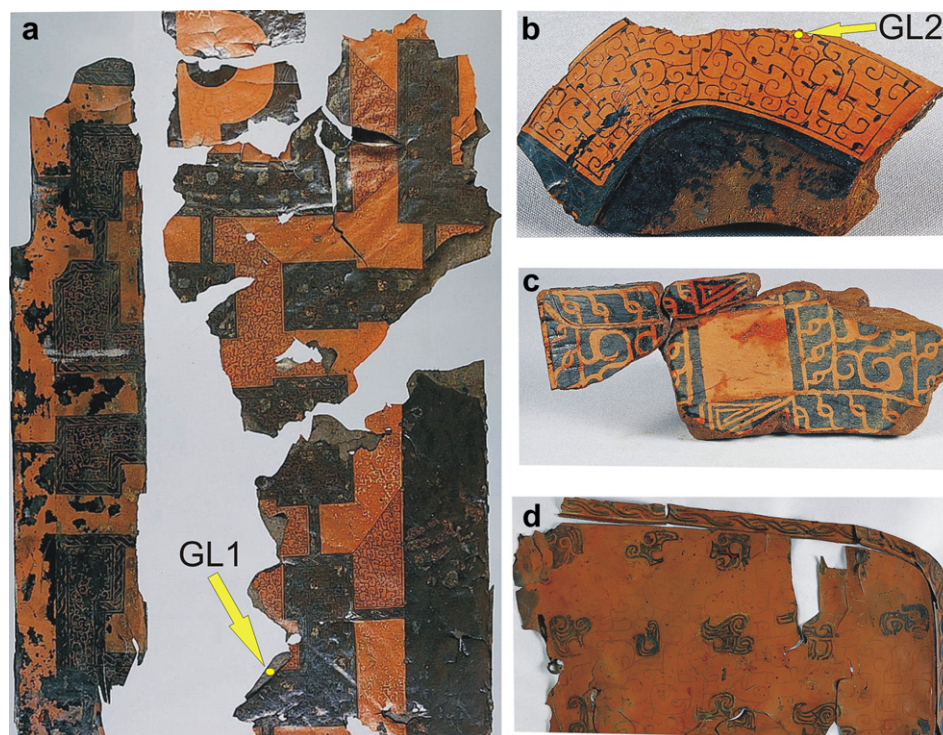


Fig. 1. Images of lacquer fragments of a) lacquered leather armour; b) wooden chariots; c) wooden chariots; d) lacquered leather armour.

been reported (Okada, 2000). Mineral pigments were found in lacquer in the past, mainly with cinnabar for red (Snyder, 1989; Chen et al., 1995), carbon for black and orpiment for yellow colours (Garner, 1963). Lacquer was used to decorate chariots, harnesses, bows and arrows from 1122 BC (Leeds, 1983). According to a Ming manuscript, lacquer was used for writing on bamboo slips. However, in the literature there is rare scientific information concerning the chemical composition of the lacquer.

Lacquer originates as the sap of lac trees and is tapped from the tree. It can be applied to a wooden object with a brush and will take a high polish after hardening. According to the region of the tree origin there are three types of oriental lacquers - *Rhus vernicifera* (the phenol derivative is urushiol), *Rhus succedanea* (the phenol derivative is laccol) and *Melanorrhoea usitate* (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 and determination of the chemical compositions of such materials. Nuclear magnetic resonance (Lambert et al., 1991), Fourier transform infrared spectroscopy (Derrick et al., 1988; Kumanotani, 1988; Jin et al., 2000; Niimura and Miyakoshi, 2006) and especially pyrolysis-gas chromatography and mass spectrometry Py-GC/MS (Niimura et al., 1996, 1999; Lu et al., 2006, 2007a, b) have been mostly applied. The advantage of the Py-GC/MS in comparison to the methods mentioned is that no sample preparation or pre-treatments of the specimen is necessary and only a very small amount of sample is required.

Raw lacquer was always modified with a drying oil to retard the rate of hardening and affected the physical properties of the film (Lu et al., 2007b). Tung oil is derived from the fruits of the tung tree, originating in Asia (Thomas, 2006). It was already known in China before Christ and used for the treatment of wooden materials (Poth, 2006 and Fonrobert, 1951). It was reported to be used in lacquers to

improve the process of a film formation (Zhang et al., 1995; Wangchareontrakul, 2000; Heginbotham and Schilling, Submitted for publication). However, linseed oil - a typical drying oil - was also reported to be added to lacquer as a solvent (Niimura et al., 1999; Lu et al., 2006). Linseed oil was the most studied drying oil due to its use in western oil paintings (Scalarone et al., 2001; Pitthard et al., 2006; Bonaduce et al., 2009) and in the Byzantine art (Valianou et al., 2011). Those two oils can be clearly identified in a fresh state by its fatty acid composition using GC/MS: tung oil contains a large amount of α -eleostearic acid (C18:3c), but no linolenic acid (C18:3); while there is no α -eleostearic acid in linseed oil (Schönemann et al., 2006). However, it is difficult to classify in the aged objects by the GC/MS whether the drying oil is linseed or tung oil due to the oxidization/polymerization of those unsaturated fatty acids (Schönemann et al., 2006). The identification of the drying oil used in the lacquer was mainly based on the detection of a series of fatty acids by direct Py-GC/MS analysis (Niimura et al., 1996; Lu et al., 2006; Pitthard et al., 2010). However, polar compounds such as fatty acids cannot be quantitatively analyzed by direct Py-GC/MS, so it is difficult to tell whether the drying oil is linseed oil or tung oil. The quantitative analysis can be improved by using thermal assisted hydrolysis and methylation (THM) (Scalarone et al., 2001; Mazzeo et al., 2004; He et al., 2007) or HMDS (Chiavari et al., 2001). A higher degree of reproducibility was achieved and the ability to differentiate between each type of drying oil using the palmitate/stearate (P/S) ratios was improved (Piccirillo et al., 2005), unfortunately, tung oil was not included in that study. The on-line derivatisation using tetramethylammonium hydroxide (TMAH), where quaternary ammonium salts of fatty acids are produced and immediately thermally decomposed into the corresponding methyl esters in a pyrolysis interface, THM is well reported in the literature (Challinor, 1996; Scalarone et al., 2001; Cappitelli et al., 2002).

In this study, tung and linseed oil were investigated by THM-Py-GC/MS using TMAH to see if it is possible to unambiguously classify

these two oils. The aim of this paper is to characterize the materials used in the lacquer excavated from the Chu tomb including the pigments, the type of lacquer, and especially the drying oil added to the lacquer, as well as to exam coating methods used on the lacquer objects. Therefore, optical microscopy and x-ray fluorescence (XRF) analysis are applied for the characterization of the pigments and the lacquer layers; a direct Py-GC/MS technique was successfully used for the chemical identification of the type of lacquer present in the objects from the Chu tomb, while for the classification of the drying oils THM-Py-GC/MS analysis was carried out.

2. Experimental

2.1. Samples

Reference materials of linseed oil and tung oil were purchased from Kremer, Germany, while Ki-urushi (raw urushi) was from the collection of Conservation Science Department, Kunsthistorisches Museum, Vienna, Austria.

Black and red lacquer archaeological samples (GL1 and GL2) from leather and wood substrates from the Chu tomb, Geling, Xincui county are available for this study (Fig. 1a and b). Firstly, the non-destructive technique XRF analysis was directly carried out on the samples of GL1 and GL2. Afterwards, each of the samples was divided into two: GL1 to (GL1a and GL1b), GL2 to (GL2a and GL2b) for cross-sections and Py-GC/MS analysis, respectively.

2.2. Natural and artificial UV ageing

Naturally and artificially aged linseed and tung oil were opportunely prepared by casting them in thin films on glass slides. Naturally aged samples were stored for five years in the laboratory at room temperature. Artificially aged samples were obtained by exposing the samples in a UV chamber UVACUBE SOL 2/400F of the company Dr. Hönle GmbH UV-Technology, Germany. The source for UV light was a 910 W/m² Xenon arc solar simulator with an incorporated H2 filter, which provides radiation with wavelengths between 295 and 800 nm. The maximum temperature on the sample was kept below 50 °C by forced air circulation.

2.3. Microscopy analysis

Microscopic studies should answer the question concerning the multilayer structure of the coating of the lacquer objects. Two small samples (GL1a and GL2a) containing the whole layered structure of the lacquer were taken from the surface in order to prepare cross-sections. Therefore, a black (GL1a) and a red (GL2a) were embedded in epoxy resin respectively, grinded and polished after curing. The microscopic investigations were carried out using polarised light in the visible range, but also UV-radiation for UV-fluorescence imaging. A microscope Axioplan 2 imaging, Carl Zeiss Micro Imaging GmbH, Germany was available therefore.

2.4. X-ray fluorescence analysis

X-ray fluorescence analysis was performed with the XRF-System COPRA¹ using the characteristics in Table 1.

Table 1
Characters used for X-ray fluorescence analysis.

| X-ray tube | Oxford XTF5010 |
|--|---|
| Anode material | Mo |
| Max. capacity | 50 W, 0.35 mA |
| Cooling | Air |
| Generator | Spellman XRM 50P50 |
| Detector | Röntec X-flash LT Drift chamber, X-benchOEM |
| Energy resolution | <170 eV |
| Cooling | Peltier cooling |
| Focusing | Polycapillary, XOS 629-01 |
| Optical system | Microscope Opto Zoom 100D |
| Max. enlargement | 10x |
| Depth of focus of the max. enlargement | 50 µm |

2.5. Scanning electron microscopy (SEM) analyses

The instrument applied for SEM/EDX analysis was a Quanta 200 MK2 of the FEI Company with an EDX detector of AMETEK, USA. The cross-sections of the black lacquer sample (GL1a) and red lacquer sample (GL2a) were analyzed.

2.6. Direct Py-GC/MS

For the direct Py-GC/MS analysis about 0.2 mg of sample was placed in a sample cup. The cup was placed on top of the pyrolyzer at near ambient temperature and then introduced into the furnace by the autosampler, 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 siloxane) 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 500 °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 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 ionisation (70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from *m/z* 50 to 750 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 and NIST 05s Library of Mass Spectra were used for identifying the compounds.

2.7. THM-Py-GC/MS procedure

The procedure for thermal 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 4 µL of 25% aqueous TMAH (Aldrich, USA) solution were added with a microsyringe to the sample. The cup was introduced into the pyrolyzer (furnace) by the autosampler and pyrolyzed immediately; afterwards the temperature program of the GC/MS was started. The parameters for pyrolyzer and GC/MS were set like in the direct Py-GC/MS procedure (see chapter 2.6).

¹ Compact Portable Roentgen Analyzer, the instrument was designed and built for non-destructive analysis of objects of art and archaeology within the EU-Project No. SMT4-CT98-2237, project coordinator: Prof. Dr. K. Janssens, University of Antwerp, Antwerp/Belgium; partners: Dr. J. Heckel and Dr. P. Klinger, Spectro, Kleve/Germany; Prof. Dr. M. Schreiner, Academy of Fine Arts, Vienna/Austria.

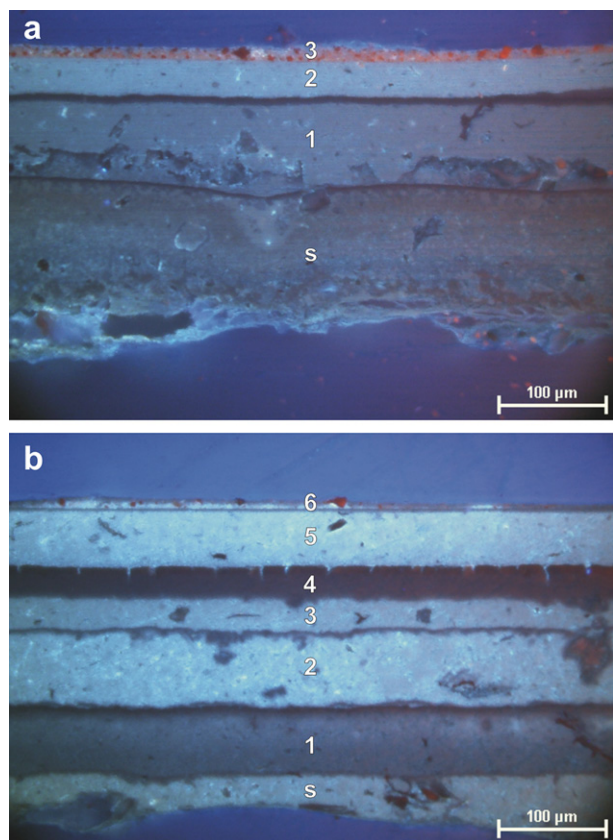


Fig. 2. The cross-sections of lacquer samples a) red lacquer fragment under reflected UV light; b) black with red pattern under reflected UV light. Note: s = substrate, numbers of 1–5 = number of the layers present. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Cross-sections of the lacquer samples and microscopy analysis

The examination of the techniques used for the urushi coating on the lacquer wares was carried out under a microscope. Two cross-sections of the lacquer samples were prepared, including a black sample with red patterns on the top from leather object

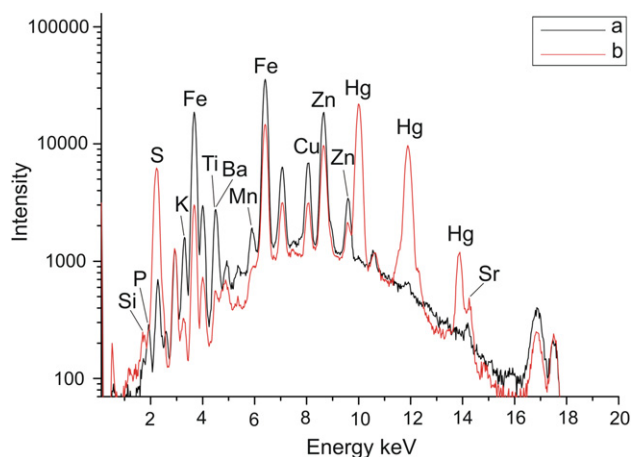


Fig. 3. XRF spectra of the lacquer sample: a black area, b-red area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

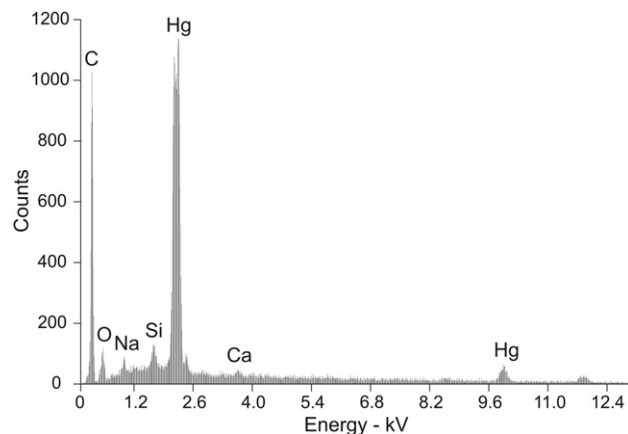


Fig. 4. SEM/EDX spectrum of sample GL2a (red).

(GL1a) and a red sample from the wooden object (GL2a). The images of the cross-sections taken under reflected light in the UV light are depicted in Fig. 2. Under UV light it is possible to distinguish an accurate stratigraphy of the samples with the complete

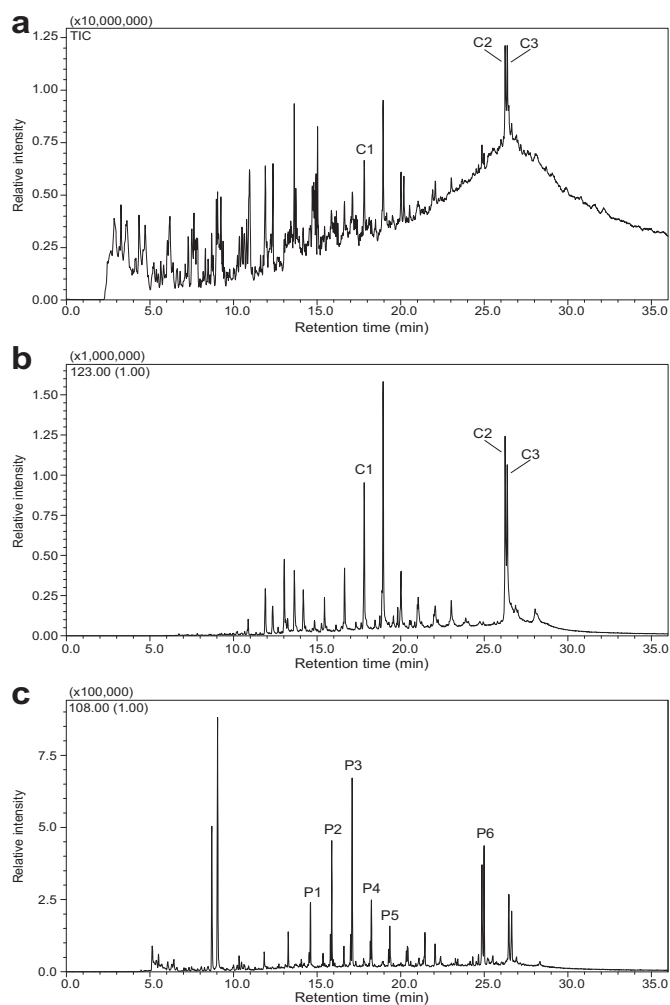


Fig. 5. Pyrograms of Ki-urushi reference standard obtained by Py-GC/MS: (a) total ion pyrogram; (b) m/z 123 extracted ion pyrogram; (c) m/z 108 extracted ion pyrogram. Note: C = catechols (C1 = 3-heptylcatechol, C2 = 3-pentadecylcatechol, C3 = 3-pentadecylcatechol); P = phenols (P1 = 3-pentylphenol, P2 = 3-hexylphenol, P3 = 3-heptylphenol, P4 = 3-octylphenol, P5 = 3-nonylphenol, P6 = 3-pentadecylphenol).

layer built-up of the lacquer, while no clear structure could be seen under reflected visible light. In fact, several layers with a similar thickness and contemporary application of the organic material were highlighted. For instance, shown in the Fig. 2a, the stratigraphy of the red lacquer on the wooden object is relatively simple: a thin red layer with a heterogeneous whitish fluorescence, in which vermilion has been mixed to lacquer, can be observed on the top (layers 3). Underneath that, two layers with a weak brownish

fluorescence (layers 1 and 2) are visible. Additionally, one layer that exhibits a yellow-brownish fluorescence (layer s) is directly on the wooden support. Contrary to that, Fig. 2b related to the cross-section of the black sample with red patterns on top revealed that six layers were applied above the leather body: layers s, 2, 3 and 5 show a similar yellowish fluorescence and layers number 1 and 4 are yellow-brownish fluorescence. Because of the homogeneous fluorescence of the organic matrix present in all layers, no mineral materials were found except on the top layer, which shows a thin paint layer with red pigment grains in order to form the pattern. Unfortunately, the identification of the black pigment seems to be difficult since no black particles or minerals were observed in black layers. However, due to the fact that carbon black is properly mixed with urushi and some components of coal such as liptinites which are from fatty and waxy parts of plants (Eastaugh et al., 2008) have strong green or yellow UV fluorescence, carbon black could be present in the lacquer matrix because of the strong yellowish fluorescence of all the layers of the black sample.

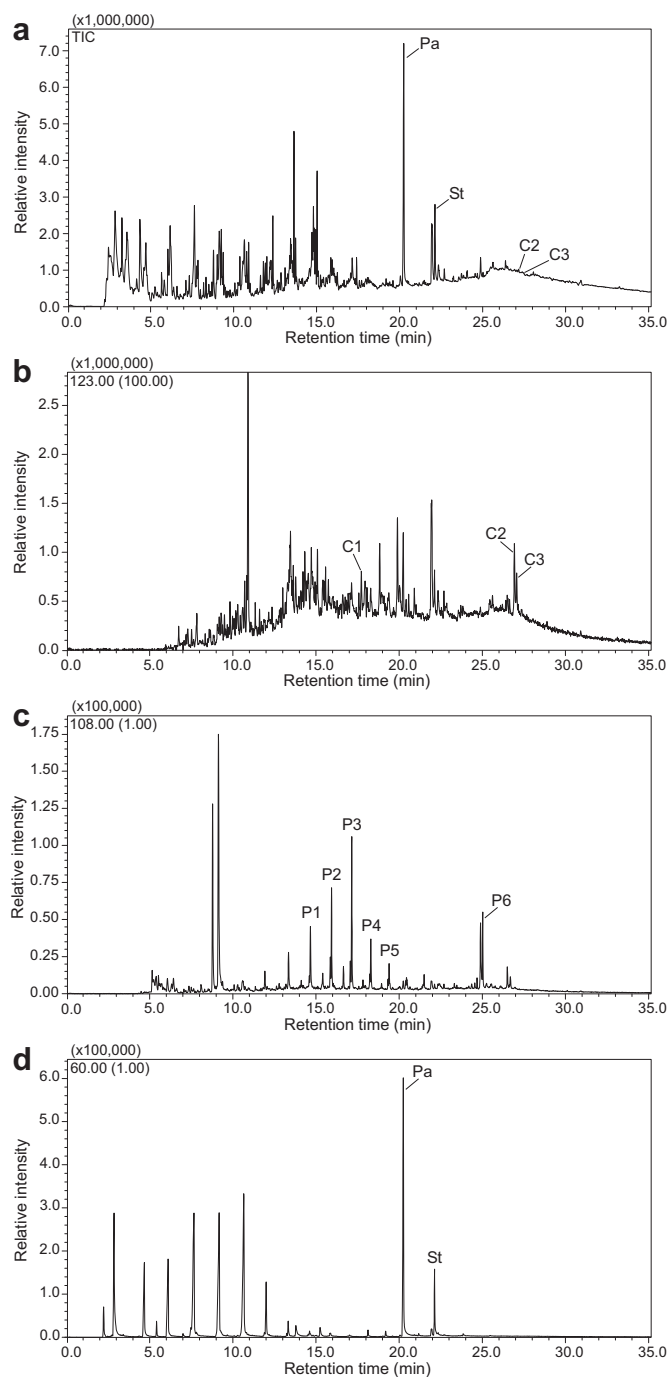


Fig. 6. Pyrograms of archaeological sample GL black 1 obtained by Py-GC/MS: (a) total ion pyrogram; (b) m/z 123 extracted ion pyrogram; (c) m/z 108 extracted ion pyrogram; (d): m/z 60 extracted ion pyrogram. Note: C = catechols (C1 = 3-heptylcatechol, C2 = 3-pentadecylcatechol, C3 = 3-pentadecylcatechol); P = phenols (P1 = 3-pentylphenol, P2 = 3-hexylphenol, P3 = 3-heptylphenol, P4 = 3-octylphenol, P5 = 3-nonylphenol, P6 = 3-pentadecylphenol); Pa = palmitic acid, St = stearic acid.

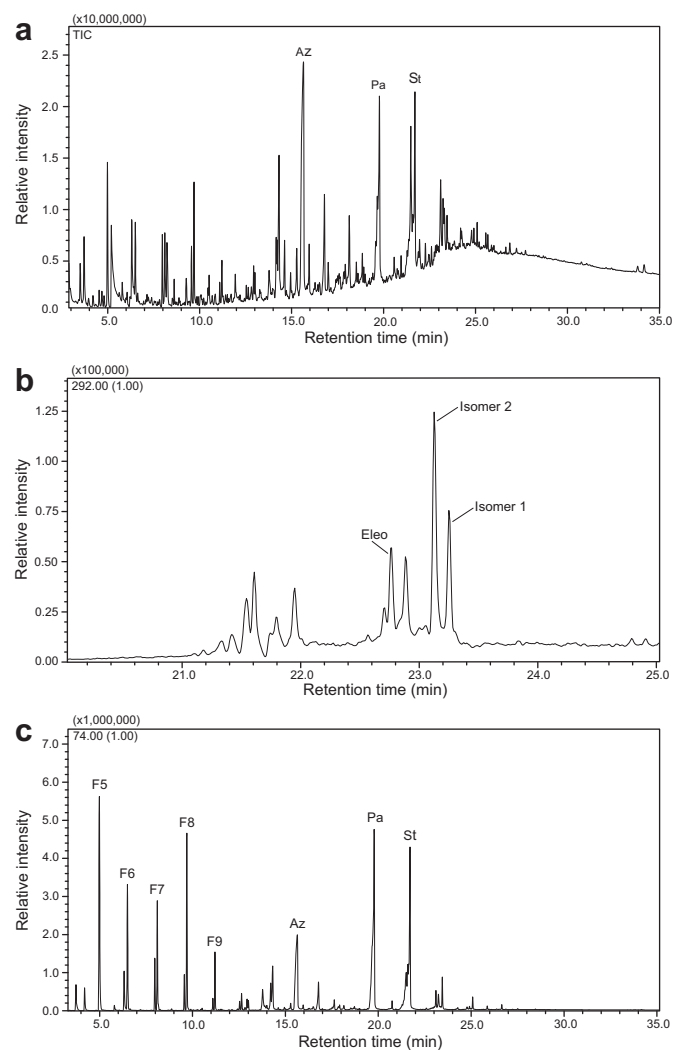


Fig. 7. Pyrograms of naturally aged tung oil reference material obtained by THM-Py-GC/MS: (a) total ion pyrogram; (b) m/z 292 extracted ion pyrogram; (c) m/z 74 extracted ion pyrogram. Note: Eleo = α -eleostearic ME, isomer 1 and isomer 2 are the two isomers of α -eleostearic acid ME; F5 = pentanoic acid ME, F6 = hexanoic acid ME, F7 = heptanoic acid ME, F8 = octanoic acid ME, F9 = nonanoic acid ME, Az = azelaic acid ME, Pa = palmitic acid ME, St = stearic acid ME; (ME - methyl ester).

3.2. X-ray fluorescence and SEM/EDX analyses

X-ray fluorescence analyses on the black and red areas have been carried out directly on the surface of the paint samples (not on the cross-section). The spectra of the samples GL black (spectrum a) and GL-red (spectrum b) are depicted in Fig. 3a and b. Spectrum a is characterized by a higher intensity of Fe, Cu, Zn, Ca, K, Ti, Ba and Mn and a lower intensity of S, P and Si. These chemical elements detected in the black sample could suggest the use of iron oxide or carbon black as a pigment, even if it is not possible to establish the use of carbon black due to the measurements in air. Spectrum b revealed a high intensity of Hg, S and Si, indicating the use of the red pigment vermilion.

In order to see whether the vermilion is artificial or natural, and whether it is possible to confirm the black pigment, SEM/EDX was applied on the cross-section of a black (GL1a) and a red layers (GL2a). The SEM/EDX results of cross-section GL1a show that minor elements of silicon, calcium, sodium were detected, apart from the main elements of mercury and sulphur. These can be correlated to minerals associated with natural vermilion (Schröcke and Weiner, 1981; Burmester, 1988). The spectrum is depicted in Fig. 4. Unfortunately, also in the cross-section sample GL2a (black), no particles could be determined in the backscattered electron image in the SEM due to the presence of urushi. However, with area analysis, only carbon could be detected in the black layer, which provides another indication for the use of carbon black as the black pigment.

3.3. Direct Py-GC/MS analysis of the reference urushi and the lacquer samples

A reference standard of Ki-urushi (raw urushi) from the *R. vernicifera* tree was analyzed by Py-GC/MS. The pyrogram obtained by Py-GC/MS is depicted in Fig. 5a. According to the previously published Py-

GC/MS analyses (Niimura et al., 1996, 1999; Niimura and Miyakoshi, 2006; Lu et al., 2006, 2007a,b; Pitthard et al., 2010), the typical pyrolysis products of the urushi are the urushiol components, 3-pentadecenylcatechol (MW 318) and 3-pentadecylcatechol (MW 320), which were identified in our samples too (C2, C3 in Fig. 5a). By using extracted ion technique, the alkylcatechols (m/z 123) and alkyl phenols (m/z 108) were detected according to their base peaks, which are shown in the extracted ion pyrogram in the Fig. 5b and c. Alongside with the pentadecylcatechols that have the longest side chains in *R. vernicifera* a peak belonging to 3-heptylcatechol was also identified. The highest relative intensity was observed for 3-heptylphenol, which is a characteristic pyrolysis fragment of the *R. vernicifera* lacquer. The alkyl phenols with the longest side chain are the pentadecylphenols. These are the products of pyrolysis of the nucleus side chain C–O coupling for the urushiol polymer (Lu et al., 2006). Since the major products of the pyrolytic fragmentation of urushi reference standard were proved experimentally, the same criteria could be applied for the interpretation of the lacquer samples from the archaeological objects.

Four analysis of the archaeological lacquer samples (samples were taken with a scalpel, which have the whole stratigraphy) from the leather and wood object from the Chu tomb were carried out by Py-GC/MS. The total ion pyrograms of the samples are identical, and therefore only one of them – of sample GL black – is presented in Fig. 6a. The pyrolysis products clearly indicate a good correspondence of the sample constituents with the reference standard of urushi (*Rhus vernicifera*). The presence of the two distinctive catechols as well as the other catechols' and phenols' profiles based on the m/z 123 and m/z 108 ions resemble the reference standard (see Fig. 6b and c). Additionally, the samples were also scanned for a possible presence of a drying oil (m/z 60). As can be seen in Fig. 4d, high amounts of short-chain fatty acids, palmitic acid and stearic acid were detected and indicate the presence of an additional drying oil in the lacquer (Chiavari et al., 1993). The oil was presumably added to

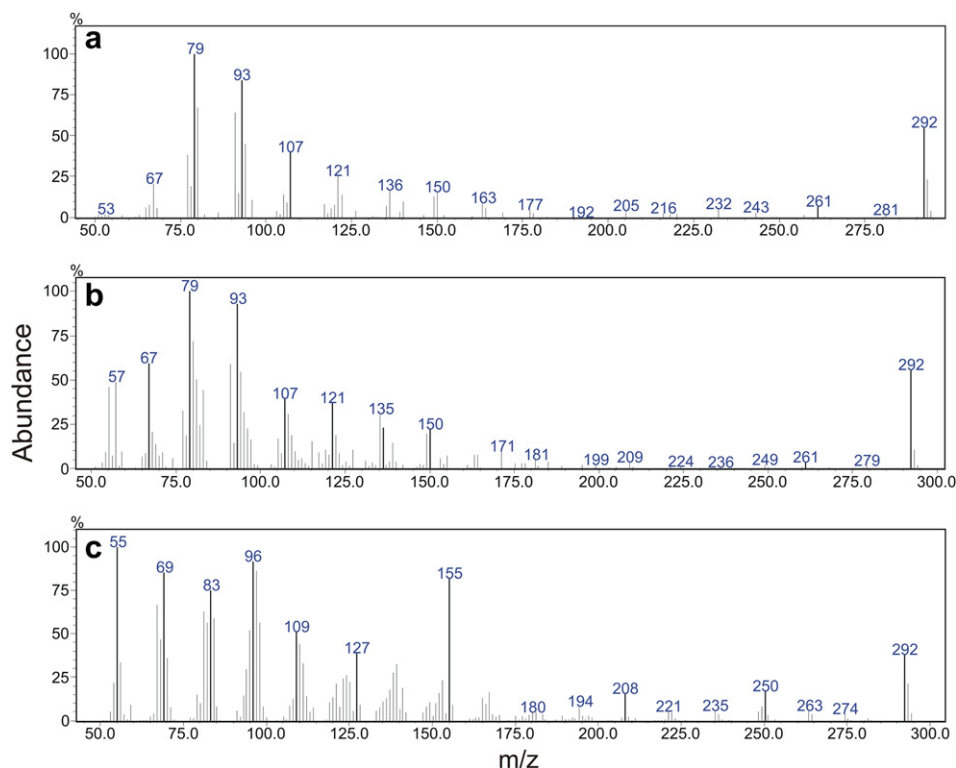


Fig. 8. The mass spectra of (a) α -eleostearic acid ME; (b) eleostearic acid ME isomer 1; (c) eleostearic acid ME isomer 2; (ME - methyl ester).

the lacquer as a solvent to retard the hardening process of the urushi lacquer and at the same time to receive a lacquer of higher lustre and elasticity (Niimura et al., 1999). As stated in the introduction, some reports claimed that tung oil was used for lacquers. However, the oil identification based only on the scanning of m/z 60 cannot give unambiguous results whether linseed or tung oil is present. It is known that the classification of oils is based on the ratio of palmitic to stearic acid (P/S) and the presence of an oxidized product of oil, such as azelaic acid. Since fatty acids are polar compounds, their quantitative analysis without any further derivatization is rather difficult. In order to see whether the oil can be clearly classified, the on-line derivatization with TMAH by Py-GC/MS analysis was performed as discussed in the next chapter.

3.4. THM-Py-GC/MS analysis

Reference materials of the tung and linseed oil films, naturally aged in the laboratory at room temperature for five years and artificially aged in the photo-ageing apparatus for two weeks have been analysed by using the THM-Py-GC/MS procedures described above. Consequently, the ratios of the methyl esters of palmitic to stearic acid and azelaic to palmitic acid (P/S and A/P ratio) were used to identify the drying oils (Mills and White, 1994). Every type of drying oil has a characteristic range of P/S ratio, and since the saturated components are stable, the ratio is considered to remain constant during the ageing making it a suitable indicator for the kind of oil present in the samples (Colombini et al., 1999).

Pyrograms of naturally aged tung and linseed oil reference materials obtained by THM-Py-GC/MS are depicted in Fig. 7a and Fig. 9a. P/S and A/P ratios were also determined for both oils. The P/S ratios for linseed oil and tung oil are around 1.2 (RSD 9%) for three replicate measurements on each oil. It can be seen that the methodology gives reproducible results. Such results are also in agreement with data found in the literature (Mills and White, 1994; Colombini et al., 1999). Azelaic acid as a characteristic marker of aged drying oils is produced during the oxidative degradation of fatty acids, and therefore, the A/P ratio is not constant with time (Mills and White, 1994). Thus those characters can not be used to differentiate those two oils due to their similar P/S of tung oil and linseed oil, as well as the inconstant A/P ratios.

Moreover, the idea to identify tung oil by the presence of α -eleostearic acid (cis, trans, trans-9, 11, 13-octadecatrienoic acid, C18:3c) seems to be not useful in a very aged sample. This triunsaturated fatty acid with a conjugated double bond system constitutes up to 86% of tung oil (Schönemann et al., 2006) and can be detected only in not very aged tung oil. During the ageing α -eleostearic acid is transformed into two isomers (isomer 1 and 2), which can be deduced from their mass spectra (M^+ at m/z of 292, see Fig. 8a–c). In order to see whether α -eleostearic acid and the isomers were still detectable in tung oil by THM-Py-GC/MS, a select ion (m/z 292) was checked in the pyrogram of tung oil obtained by the THM-Py-GC/MS analysis. It was found that in the naturally aged tung oil, α -eleostearic acid and two isomers are still detectable (see Figures 7b and 8a–c). However, they could not be detected in the extended aged tung oil samples (artificially aged for additional two weeks). So the presence of α -eleostearic acid or its isomers can only be used as an indicator of the presence of tung oil in not very aged samples.

Nevertheless, the only criterion for identifying these two oils was by using the relative intensities of short-chain acids as their esters in the ion extraction chromatogram (m/z 74), which shows a characteristic pattern. In the pyrograms (Figs. 7c and 9b) it can be seen that pentanoic acid (C5:0) has the highest intensity in tung oil (in the range of C5:0–C9:0), while the highest intensity was detected for octanoic acid (C8:0) in linseed oil. That is characteristic

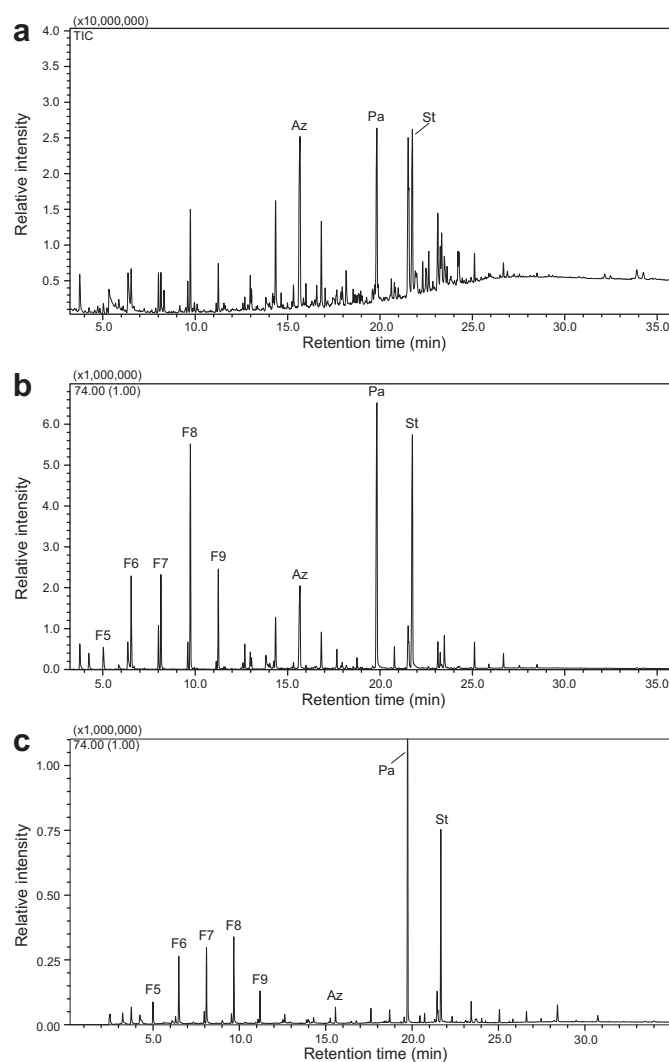


Fig. 9. Pyrograms of linseed oil and archaeological sample GL black 2 obtained by THM-Py-GC/MS: (a) total ion program of linseed oil; (b) m/z 74 extracted ion program of linseed oil; (c) m/z 74 extracted ion program of GL black (archaeological sample). Note: F5 = Pentanoic acid ME, F6 = hexanoic acid ME, F7 = Heptanoic acid ME, F8 = octanoic acid ME, F9 = nonanoic acid ME, Az = azelaic acid di-ME, Pa = palmitic acid ME, St = stearic acid ME; (ME - methyl ester).

and reproducible for both, naturally and artificially aged samples (the data of artificially aged reference samples is not presented).

The same THM-Py-GC/MS procedure was subsequently applied to the lacquer sample from the Chu tomb and it was determined that the lacquer has a P/S ratio of about 1.3, which is in the range for the assignment of either linseed or tung oil. The samples scanned with the select ion of m/z 292 indicated the presence of neither α -eleostearic nor its two isomers. However, when scanned with the select ion of m/z 74 for the presence of fatty acids methyl esters (Fig. 9c, archaeological sample) and compared with the pyrograms of the reference standards (Figs. 7c and 9b, reference samples), it was found that in the pyrogram of the lacquer object octanoic acid (C8:0) is having the highest intensity in the range of short-chain fatty acids. From the characteristics discussed above, the drying oil used in the lacquer object is most likely linseed oil.

As discussed in the paper of (Heginbotham and Schilling, submitted for publication), the availability of linseed oil is rather late in Japan, based on a historical book (Rein, 1889). In the paper of (Mazzeo et al., 2004), drying oil was found as binding media used in a Ming Dynasty monument built up in 1380 AC. It was assigned as

tung oil based on a historical book. Whether linseed oil is available or not in China in ancient times, further study is needed on more archaeological samples and historical books. Perilla (*perilla frutescens*) was stated as the dominant traditional oil used in lacquer and other varnish applications (Rein, 1889). The P/S ratio of perilla (about 4, according to our analysis) is much higher than it is for linseed oil or tung oil. As for animal fat, walnut and poppy seed oil, they have also relative higher P/S ratio (Mills and White, 1994). They can be easily distinguished from linseed or tung oil by using P/S ratio.

4. Conclusion

The lacquer objects excavated from the Warring States Chu tomb (481–221 BC) were characterized with optical microscopy, XRF, SEM and Py-GC/MS with/out TMAH reagent techniques. For the black with red pattern object in total six layers could be revealed, whereas for the red wooden object just two layers were applied on the support and an additional layer (approximately 10 μm thickness) with vermilion on top. The lacquer could be identified as urushi by Py-GC/MS analysis. The drying oil used to modify the property of the lacquer was most likely linseed oil. Especially, the possibility to unambiguously differentiate tung oil and linseed oil by THM-Py-GC/MS with in-situ TMAH methylation technique has been demonstrated and discussed. The lacquer coating films were applied with different numbers of layers and vermilion was used as red pigment. Carbon black probably was used as black pigment. A mixture of urushi and drying oil (most likely linseed oil) was used on the lacquer objects during the Warring States period. This investigation definitely will provide scientific support for the archaeologists.

References

- Bonaduce, I., Cito, M., Colombini, M.P., 2009. The development of a gas chromatographic-mass spectrometric analytical procedure for the determination of lipids, proteins and resins in the same paint micro-sample avoiding interferences from inorganic media. *J. Chromatogr. A* 1216, 5931–5939.
- Burmester, 1988. Technical Studies of Chinese lacquer, in: *Urushi*. In: Proceedings of the Urushi study group. Getty Conservation Institute, pp. 163–188.
- Cappitelli, F., Learner, T., Chiantore, O., 2002. An initial assessment of thermally assisted hydrolysis and methylation-gas chromatography/mass spectrometry for the identification of oils from dried paint films. *J. Anal. Appl. Pyrolysis* 63, 339–348.
- Chen, Y., Xie, Y., Lu, H., Zheng, Y., Jin, X., He, Y., 1995. Studies on analysis and identification of prehistoric Chinese lacquer. *Wen wu bao hu yu kao gu ke xue* 7 (2), 12–20.
- Challinor, J.M., 1996. A rapid simple pyrolysis derivatisation gas chromatography-mass spectrometry method for profiling of fatty acids in trace quantities of lipids. *J. Anal. Appl. Pyrolysis* 37, 185–197.
- Chiavari, G., Galletti, G., Lanterna, G., Mazzeo, R., 1993. The potential of pyrolysis-gas chromatography/mass spectrometry in the recognition of ancient painting media. *J. Anal. Appl. Pyrolysis* 24, 227–242.
- Chiavari, G., Fabri, D., Pratti, S., 2001. In-situ pyrolysis and silylation for analysis of lipid materials used in paint layers. *Chromatographia* 53 (5–6), 311–314.
- Colombini, M.P., Modugno, F., Giacomelli, M., Francesconi, S., 1999. Characterisation of proteinaceous binders and drying oils in wall painting samples by gas chromatography-mass spectrometry. *J. Chromatogr. A* 846, 113–124.
- Derrick, M.R., Grzywacz, C., Preusser, F., 1988. FTIR analysis of finishes on oriental style 18th century European furniture. In: *Urushi: Proceedings of the Urushi Study Group*, June 10–27, 1985, Tokyo. The Getty Conservation Institute, Los Angeles, pp. 227–234.
- Eastaugh, N., Walsh, V., Chaplin, T., Siddall, R., 2008. *Pigment Compendium. A Dictionary and Optical Microscopy of Historical Pigments*. Elsevier Ltd, Butterworth-Heinemann.
- Fonrobert, E., 1951. *Das Holzöl*. Berliner Union, Stuttgart.
- Garner, S., 1963. Technical studies of Oriental lacquer. *Stud. Conservation* 8 (3), 84–98.
- He, L., Nie, M., Chiavari, G., Mazzeo, R., 2007. Analytical characterization of binding medium used in ancient Chinese artworks by pyrolysis-gas chromatography/mass spectrometry. *Microchemical J.* 85 (2), 347–353.
- Heginbotham, A., Schilling, M. New evidence for the use of Southeast Asian raw materials in seventeenth century Japanese export lacquer. "Crossing Borders" conference proceedings. Submitted for publication.
- Jin, Ch., Sano, Ch., Kumanotani, J., 2000. A study on the degradation of urushi (oriental lacquer) by micro-FT-IR-ATR spectroscopy – strategies for the judgment of urushi in ancient cultural properties. In: Kühnenthal, M. (Ed.), *Japanese and European Lacquerware*. Bayerisches Landesamt für Denkmalpflege, München, pp. 149–160.
- Kumanotani, J., 1988. The super-durable structure of oriental lacquer films. *Polym. Materials* 59, 278–282.
- Leeds, A.B., 1983. Fundamentals of lacquering. In: *Preprints of papers presented at the eleventh annual meeting, Baltimore, Maryland, 25–29 May 1983*. American Institute for Conservation of Historic and Artistic Works, pp. 82–85.
- Lambert, J.B., Frye, J.S., Cariveau, G.W., 1991. The structure of oriental lacquer by solid state nuclear magnetic resonance spectroscopy. *Archaeometry* 33, 87–93.
- Lu, R., Kamiya, Y., Miyakoshi, T., 2006. Applied analysis of lacquer films based on pyrolysis-gas chromatography/mass spectrometry. *Talanta* 70, 370–376.
- Lu, R., Kamiya, Y., Wan, Y.Y., Honda, T., Miyakoshi, T., 2007a. Synthesis of Rhus succedanea lacquer film and analysis by pyrolysis-gas chromatography/mass spectrometry. *J. Anal. Appl. Pyrolysis* 78, 117–124.
- Lu, R., Kamiya, Y., Miyakoshi, T., 2007b. Preparation and characterisation of Melanorrhoea usitata lacquer film based on pyrolysis-gas chromatography/mass spectrometry. *J. Anal. Appl. Pyrolysis* 78, 172–179.
- Mazzeo, R., Cam, D., Chiavari, G., Fabbri, D., He, L., Prati, S., 2004. Analytical study of traditional decorative materials and techniques used in Ming Dynasty wooden architecture. The case of the Drum Tower in Xi'an, P.R. of China. *J. Cult. Heritage* 5, 273–283.
- Mills, J.S., White, R., 1994. *The Organic Chemistry of Museum Objects*. Butterworths-Heinemann, Oxford.
- Niimura, N., Miyakoshi, T., Onodera, J., Higuchi, T., 1996. Characterisation of Rhus vernicifera and Rhus succedanea lacquer films and their pyrolysis mechanisms studied using two-stage pyrolysis-gas chromatography/mass spectrometry. *J. Anal. Appl. Pyrolysis* 37, 199–209.
- Niimura, N., Miyakoshi, T., Onodera, J., Higuchi, T., 1999. Identification of ancient lacquer film using two-stage pyrolysis-gas chromatography/mass spectrometry. *Archaeometry* 41, 137–149.
- Niimura, N., Miyakoshi, T., 2006. Structural study of oriental lacquer films during the hardening process. *Talanta* 70 (1), 146–152.
- Okada, F., 2000. A study on the structure of the coating film of urushiware at the Linden Museum, Stuttgart. In: Kühnenthal, M. (Ed.), *Japanese and European Lacquerware*. Bayerisches Landesamt für Denkmalpflege, München, pp. 135–148.
- Piccirillo, A., Scaroni, D., Chiantore, O., 2005. Comparison between off-line and on-line derivatisation methods in the characterisation of siccative oils in paint media. *J. Anal. Appl. Pyrolysis* 74, 33–38.
- Pitthard, V., Griesser, M., Stanek, S., Bayerova, T., 2006. Study of complex organic binding media systems on artworks applying GC-MS analysis: selected examples from the Kunsthistorisches Museum. Vienna. *Macromol. Symp.* 238, 37–45.
- Pitthard, V., Wei, S., Miklin-Kniefacz, S., Stanek, S., Griesser, M., Schreiner, M., 2010. Scientific investigation of antique lacquers from a 17th century Japanese ornamental cabinet. *Archaeometry* 52 (6), 1044–1054.
- Poth, U., 2006. Drying oils and related products. In: *Ullmann's Encyclopedia of Industrial Chemistry*, seventh ed., vol. A9. Wiley-Verlag, Weinheim, pp. 55–71.
- Rein, J.J., 1889. *The Industries of Japan*. Hodder and Stoughton, London.
- Scaroni, D., Lazzari, M., Chiantore, O., 2001. Thermally assisted hydrolysis and methylation-pyrolysis-gas chromatography mass spectrometry of light-aged linseed oil. *J. Anal. Appl. Pyrolysis* 58–59, 503–512.
- Schröcke, H., Weiner, K.-L., 1981. *Mineralogie Berlin*.
- Schönemann, A., Frenzel, W., Unger, A., Kenndler, E., 2006. An investigation of the fatty acid composition of New and aged tung oil. *Stud. Conservation* 51, 99–110.
- Snyder, D.M., 1989. An overview of oriental lacquer: art and chemistry of the original high-tech coating. *J. Chem. Educ.* 66 (12), 977–980.
- Song, G., 2002. The excavation of Henan Xincai Pingye Jun - Cheng tomb. *Wen Wu* 8, 1–24.
- Song, G., 2003. *Xincai Geling Chu Tomb*. Daxiang publisher, Henan Province, Zhengzhou.
- Thomas, A., 2006. Fats and fatty oils. In: Matthias Bohnet, et al. (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, seventh ed., vol. A10. Wiley-Verlag Weinheim, pp. 173–243.
- Valianou, L., Wei, S., Mubarak, M.S., Farmakalidis, H., Stassinopoulos, S., Rosenberg, E., Karapanagiotis, I., 2011. Identification of organic materials in icons of the Cretan School of Iconography. *J. Archaeological Sci.* 38 (2), 246–254.
- Wangchareontrakul, S., 2000. Quality improvement of lacquer from Melanorrhoea usitata. In: Kühnenthal, M. (Ed.), *East Asian and European Lacquer Techniques*. ICOMOS Journals of the German National Committee XXXV, Munich, pp. 135–138.
- Webb, M., 2000. *Lacquer: Technology and Conservation*. Butterworth-Heinemann, Oxford.
- Zhang, W., Shan, W., Guo, S., 1995. Analysis of Chinese lacquer wares from Han Dynasty. *Wen wu bao hu yu kao gu ke xue* 7 (2), 28–36.