



Characterization and identification of urushi using *in situ* pyrolysis/silylation–gas chromatography–mass spectrometry

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ABSTRACT

Analytical pyrolysis coupled with gas chromatography and mass spectrometry is a very powerful tool to analyze polymers and macromolecules. In this paper this technique was applied to the characterization of the urushi oriental lacquer (qi-lacquer in Chinese) with the aim to set up an alternative analytical method to identify the lacquer.

Urushi is mostly rich in alcoholic polar moieties, thus, a derivatization step is required, which is crucial for the detection and MS identification of all the compounds deriving from the thermal degradation. In this work hexamethyldisilazane (HMDS) was used for the first time as a derivatizing agent, thus, proving to be a valid alternative to more common methylating agents.

Adopting this *in situ* Py/silylation–GC–MS procedure, we were able to characterize urushi lacquer and identify characteristic pyrolytic profiles of silylated alkylcatechols, silylated alkylphenols, aliphatic hydrocarbons, alkylbenzenes as well as characteristic molecular biomarkers.

The method was thus used to analyze six archaeological samples from Sichuan (China) dating back from the 2nd century BC to the 12th century AD, in which the presence of urushi was suspected, and the lacquer was identified in all of them through the identification of all the characteristic pyrolytic profiles and molecular biomarkers.

The method set up is also promising to be used for the characterization of the other oriental lacquers, such as laccol and thitsi.

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1. Introduction

Urushi (qi-lacquer in Chinese) is considered as the oldest and most precious lacquer in East Asia. It has been used for thousands of years as a coating material to decorate or protect objects, because of its capacity to lend the object great and lasting brightness, toughness and water resistance. It has been and is still used on several substrates, such as wood, ceramics and metals [1].

Objects of significant cultural value coated with urushi have maintained their beautiful surfaces for over two thousand years [2]. However, depending on the conservation conditions, there may be severe degradation, for example the Qin Shi Huang's Terracotta Army. In fact, the priming layer of urushi, which is waterlogged due to the long period of time in humid soil, shrinks when the relative humidity decreases below 92%, thus, causing the paint layer to become detached [3,4].

Oriental lacquers can be extracted from three species of the same tree, belonging to the Anacardiaceae family. These varieties are native to specific areas of East Asia: *Rhus vernicifera* from China, Japan and Korea, *Rhus succedanea* from North Vietnam and Taiwan, and *Melanorrhoea usitata* from Thailand and Burma [5,6]. Urushi is extracted from *R. vernicifera*. Although these plants are native to East Asia, in the mid-16th century, East Asian lacquered objects started to generate great interest and were imported to Europe. European craftsmen started to imitate East Asian lacquers with the use of other materials, such as plant terpenoid resins, oils, proteins and inorganic pigments [7]. Today, the only way to distinguish imitations from true oriental lacquer is chemical analysis [7,8].

In order to identify oriental lacquers in artistic and archaeological samples, a reliable analytical method is thus needed, which can also be used on small samples containing mixtures of organic and inorganic materials [9,10], as is the case with samples from works of art.

The sap from the three tree species is composed of water (30%), glycoproteins (2%), plant gum (7%), laccase enzyme (1%), and a mixture of catechol derivatives (60–65%), which varies

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depending on the plant of origin [5]. The mixture contained in the sap of *R. vernicifera* is called urushiol, laccol in *R. succedanea* and thitsiol in *M. usitate*. The principal component of urushiol is 3-pentadecylcatechol and the principal component of laccol is 3-heptadecylcatechol. The aliphatic chains may be saturated or have one, two or three double bonds. The composition of thitsiol is more complicated: in addition to the typical compounds of urushiol and laccol, it also contains alkylphenylphenols and alkylphenyl-1,2-dihydroxybenzenes (alkylphenylcatechols), such as 3-(10-phenyldecyl)phenol/catechol and 3-(12-phenyldecyl)phenol/catechol [2,6,11,12].

The drying process of oriental lacquers is different from European lacquers, because of the phenolic fraction of the sap. During this process, polymerization occurs, resulting in a very resistant film, which is inert to acids, alkalis and alcohols, is stable up to 300 °C, and is insoluble in most common solvents. The structure and composition of the final polymer depends on the hardening process [12,13]. Polymerization starts, thanks to the laccase enzyme, and leads to the formation of C–C aromatic nucleus-side chain coupling bonds, C–O phenolic oxygen-side chain coupling bonds and C–C bonds between side chains. The result is a cross-linked polymer, whose structure has not yet been completely clarified [2,12].

Several techniques have been used to analyze the lacquer, such as NMR [12,14,15], FTIR [2,12,13,15], XPS [16], thermal analysis (TG/DTA–MS) [13,15,17]. These studies mainly provide information on the structure and the chemical state of the polymer, however, they are not useful for diagnostic purposes. GC–MS is used to characterize the monomeric fraction of the lacquer [11], but it cannot provide information on the polymerized fraction, which is the most abundant, and thus this method is unsatisfactory [18].

Pyrolysis techniques are the most suitable for the analysis of chemically untreatable polymeric materials, because they enable the polymeric network to be broken down into smaller molecules, which can then be more easily studied [19]: DIMS (direct inlet mass spectrometry) provides preliminary information on the type of lacquer [8]; EGA–IAMS (evolved gas analysis–ion attachment–mass spectrometry) has been used to characterize Japanese lacquers and to study the kinetics of water release during heating [20]; direct probe Li⁺ ion attachment mass spectrometry has been recently used and the results compared with those achieved with Py–GC–MS [21].

Py–GC–MS is currently the most common technique for characterizing and identifying oriental lacquers [5,8,13,18,22–25], and the most promising results have been achieved using thermally-assisted reactions with tetramethylammonium hydroxide (TMAH) as a derivatizing agent [18,22].

One of the main problems of the pyrolysis technique is, in fact, related to the low volatility of acidic, alcoholic and aminic pyrolysis products, which are not really suitable for gas chromatographic analysis, causing a rather low reproducibility of the resulting pyrograms, low sensitivity for specific compounds, and strong memory effects [19]. Moreover, the high fragmentation of natural macromolecules during pyrolysis leads to the formation of many unspecific compounds.

To overcome these problems, the sample can be pyrolyzed using a suitable reagent, which transforms polar functionalities into less polar moieties. Tetramethylammonium hydroxide (TMAH) is one

of the most commonly used reagents for the on-line methylation of acidic and alcoholic moieties. Although the tetramethylammonium hydroxide thermochemolysis (TMH) method has been extensively applied to the characterization of materials used in the creation and restoration of works of art, the strong alkalinity of TMAH may cause problems in the interpretation of pyrograms. Consequently, other derivatizing agents have been proposed, mainly in the analysis of samples collected from artistic and archaeological objects, including methylating and silylating agents [26–31].

In this work, we investigated into the Py/silylation–GC–MS characterization and identification of urushi, using hexamethyldisilazane (HMDS) as a silylating agent for use *in situ* during pyrolysis prior to GC–MS analysis.

2. Material and methods

2.1. Samples

A reference layer of urushi (from *R. Vernicifera*) was analyzed. The raw material was bought at a local producer in the northern slopes of the Qinling mountains near Xi'an (China) in 2007. The film was made in 2008. Six archaeological samples dating back to the Western Han dynasty (206 BC–24 AD) and Southern Song dynasty (1127–1279 AD) were analyzed. The samples were collected from six different objects found in the Sichuan region of China. The description of the samples is presented in Table 1.

2.2. Instrumentation and method

Analytical pyrolysis with 1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9%, Sigma–Aldrich Inc., USA) as a silylation agent for the *in situ* derivatization of pyrolysis products was applied. The instrumentation consisted of a 5150CDS Pyroprobe 5000 Series pyrolyzer connected to a gas chromatograph 6890 N (Agilent Technologies, Palo Alto, CA, USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl–95% dimethyl-polysiloxane, 30 m × 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m × 0.32 mm i.d., Agilent J&W, USA). The GC was coupled with a 5973 mass selective detector (Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer operating in electron ionization mode (EI) at 70 eV.

The pyrolysis temperature was 600 °C, which was maintained for 20 s using a platinum coil probe and quartz sample tubes. Samples in the order of 100 µg and HMDS (5 µL) were inserted into the centre of the pyrolysis quartz tube with quartz wool, and then placed in the pyrolysis coil filament. The interface temperature was 200 °C. The GC–MS injector was used in split mode, at 280 °C and 1:40 split ratio. Chromatographic oven conditions were as follows: initial temperature 32 °C, 10 min isothermal, 10 °C min^{−1}–280 °C, 2 min isothermal, 15 °C min^{−1}–300 °C, 30 min isothermal, carrier gas: He (purity 99.995%), constant flow 1.0 mL min^{−1}.

Table 1
Description of the analyzed archaeological samples from Sichuan Province (China).

Sample name	Dynasty	Object	Description
L2	Western Han (206 BC–24 AD)	Terracotta bowl	Inside red, outside black
L3	Western Han (206 BC–24 AD)	Wooden support of lacquerware	Dark red lacquer layer
L4	Southern Song (1127–1279 AD)	Buddha figure	Lacquer layer
L7	Early Western Han (2nd cent. BC)	Wooden support of lacquerware	Red with black corner
L8	Early Western Han (2nd cent. BC)	Wooden support of lacquerware	Thin lacquer layer, black with red pattern
L9	Early Western Han (2nd cent. BC)	Wooden support of lacquerware	Black layer

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