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Characterisation of East Asian Lacquers by Laser Desorption Mass Spectroscopy (LD-MS)

Abstract

Lacquer samples from five different Chinese dynasties (Warring States period, Qin, Han, Tang and South Song) were investigated with matrix-assisted laser desorption mass spectroscopy (MALDI) and laser desorption mass spectroscopy (LD-MS). Until now reported mass spectra of original aged lacquer were acquired with the pyrolysis gas chromatography mass spectroscopy (Py-GC/MS) technique only. Both methods presented here are used for the characterisation of urushi lacquer for the first time. The evaluation of the LD mass spectra shows the distribution of 3-catechols with different side chain lengths. It can be determined whether the lacquer was made from the sap of Rhus vernicifera or from Rhus succedanea.

Qi or urushi lacquer is a water in oil type emulsion[1]. In its raw state it is partly soluble in solvents like acetone. After polymerisation however the hardened lacquer is insoluble. It can now be imagined to consist of macromolecules with very high molecular masses.

Therefore, characterisation or spectroscopical evaluation is difficult. Most of the physico-chemical methods commonly applied to gain structural information of the macromolecule have the prerequisite that the analyte is in solution. Differences in the molecular structure can be attributed to various causes: origin of the lacquer, type of the lacquer tree, pretreatment of the raw lacquer and application technique.

Infra-red spectroscopy does not restrict itself to solutions, therefore lacquer can be investigated. This is done with pulverised samples in a KBr disk or with a diamond anvil cell in a thin film with ATR (attenuated total reflection) technology. Therefore, most of the papers concerning lacquer analysis focus on this technology.

If lacquers can be distinguished by a certain method, this method has to have the ability to somehow break up the natural lacquer polymer. All methods with the need to have a solution of the analyte cannot be used, because of the insolubility of the polymerised lacquer. Pyrolysis destroys the polymer by strong heating, the determination is then carried out by gas chromatography (Py-GC). During this process the sample is constantly heated, side reactions among the already pyrolysed fragments can take place. If oxygen is present, the fragments are readily oxidised.

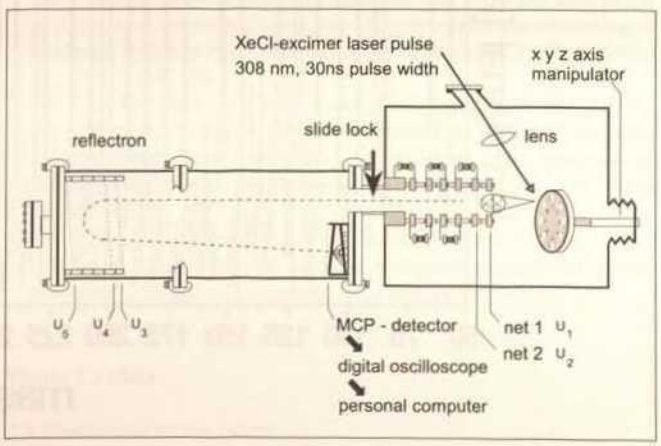
Py-GC measurements on East Asian lacquers from the Qin and Han dynasties were carried out at the Rathgen Forschungslabor by Dr. Herm in 1995. The gas chromatograph was not connected to an IR- or mass spectrometer, thus analyses were difficult to interpret.

The constituents of the qi- or urushi lacquer are presented in the contribution by Tetsuo Miyakoshi. He presents the Py-GC method coupled with a mass-spectrometer to analyse monomeric urushiol. He used a refined acetone fraction of the sap of the lac tree and analysed an ancient Japanese lacquer in a two step pyrolysis[2]. Thus he obtained fragments in the mass spectrum up to about 320 u (atomic mass unit).

MALDI (matrix assisted laser desorption and ionisation) is a new and promising method to generate mass spectra (MS) of high molecular substances, especially biomolecules and technical polymers. Ionised molecular fragments are generated by directing a laser pulse onto the sample. The sample substance is dispersed in a material which is easy to sublime (matrix) and which is supposed to take up the laser energy. In the quick evaporation process of the matrix the sample fragment ions are formed in the desorption plume. In the MALDI process fragments with a high molecular mass are formed predominantly.

For laser desorption a XeCl excimer laser LPX-100 Lambda Physik (308 nm, 30 ns pulse width) was used. The positively charged ions generated were separated by a non-commercial reflectron time-of-flight mass-spectrometer[3] (RETOF-MS, fig. 1) with a mass resolution of $m / \Delta m = 2000$. In contrast to most commercial systems, the laser desorbed ions were allowed to drift for ca. 2 cm before being extracted by a pulsed electric field. The ions were detected by dual multi-channel plates and the signal was collected by a digital oscilloscope. The spectra were then transferred to a PC for further evaluation. The delay between laser pulse and ion extraction allows one to pre-select the mass of the ions detected.

Fig. 1. Section of the laser desorption mass spectrometer



This method was tested in order to find out whether it can be used as an independent method for identifying and analysing Oriental lacquer material. Initial experiments were conducted to find the best matrix for qi-lacquer. Among the matrix materials tested 5-methoxy-salicylic acid gave the best results. Another promising matrix seems to be graphite[4]. The powdered lacquer sample was thoroughly mixed with the solid matrix in a concentration of approx. 1–2 vol.%. The matrix/sample mixture was pressed into a thin layer and onto a carrier pellet (13 mm diameter) made from KBr.

The evaluation of 137 recorded mass spectra found that the sample spectra and the matrix spectrum overlap to such an extend that a deconvolution of the lacquer spectra is not possible. With MALDI we could not obtain a spectrum that is characteristic for each sample.

Table 1. Antique lacquers investigated by LD-MS

One sample of each of the following Chinese dynasties:
Warring States period (481–221 BC)
Qin/Lintong (221–206 BC)
West Han (206 BC–8 AD)
Tang (618–907 AD)
South Song (1127–1279 AD)

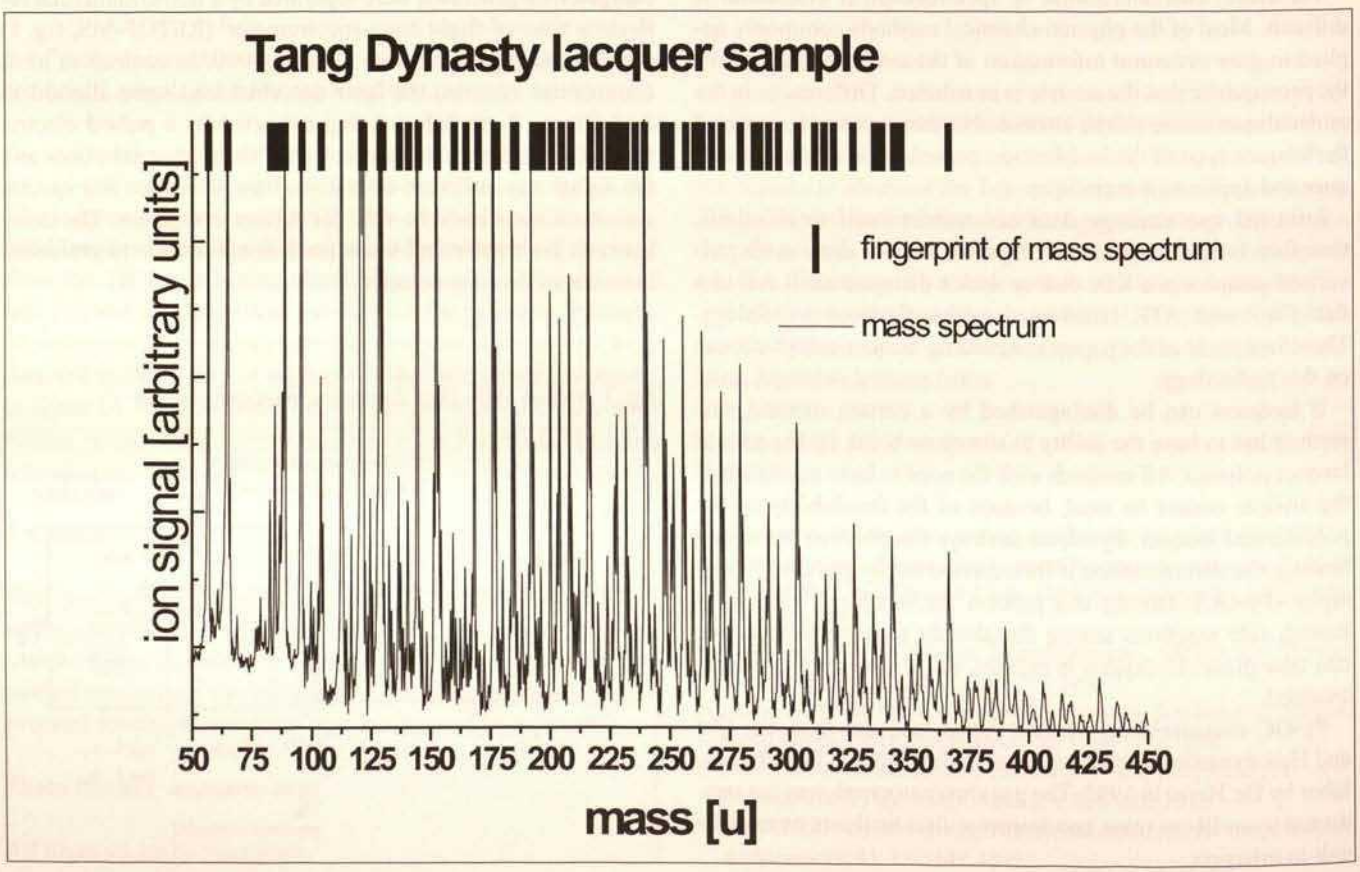
Therefore, experiments without matrix were performed, the method of analysis is then called laser desorption mass spectroscopy (LD-MS). With LD-MS it is possible to see smaller fragments of the lacquer, with MALDI larger fragments can be detected (matrix peaks have to be eliminated). However, the advantages of MALDI (fragments of higher mass, gentle desorption process, reduced thermal stress during analysis) cannot be used with LD-MS. Table 1 shows the antique lacquers which were investigated.

During the laser desorption the polymer is broken up by a strong laser pulse at a wavelength of 308 nm (UV, XeCl excimer laser). This laser pulse lasts for only 30 ns (30×10^{-9} seconds). Thermal stress of the lacquer is thus minimised. The investigation is carried out in vacuum, therefore no interaction of fragments with oxygen is possible. The mass spectrum will only show unadulterated mass peaks. In contrast to the aforementioned Py-GC the LD-MS method can be carried out within a quarter of an hour. Recorded mass spectra are summed over 100 single mass spectra to ensure a spectrum representative of the investigated sample. Figure 2 presents a LD-MS mass spectrum together with a fingerprint of the peaks of highest intensity.

The correct assignment of mass units to a molecule requires a high degree of structural assumptions. Unassigned peaks are attributed to lacquer additives and degradation products.

Mass spectra were transformed to a kind of fingerprint for easier presentation and evaluation. Figure 3 depicts the compiled results of the analysed qi-lacquer samples.

Fig. 2. LD-MS mass spectrum and fingerprint of a Tang dynasty lacquer sample



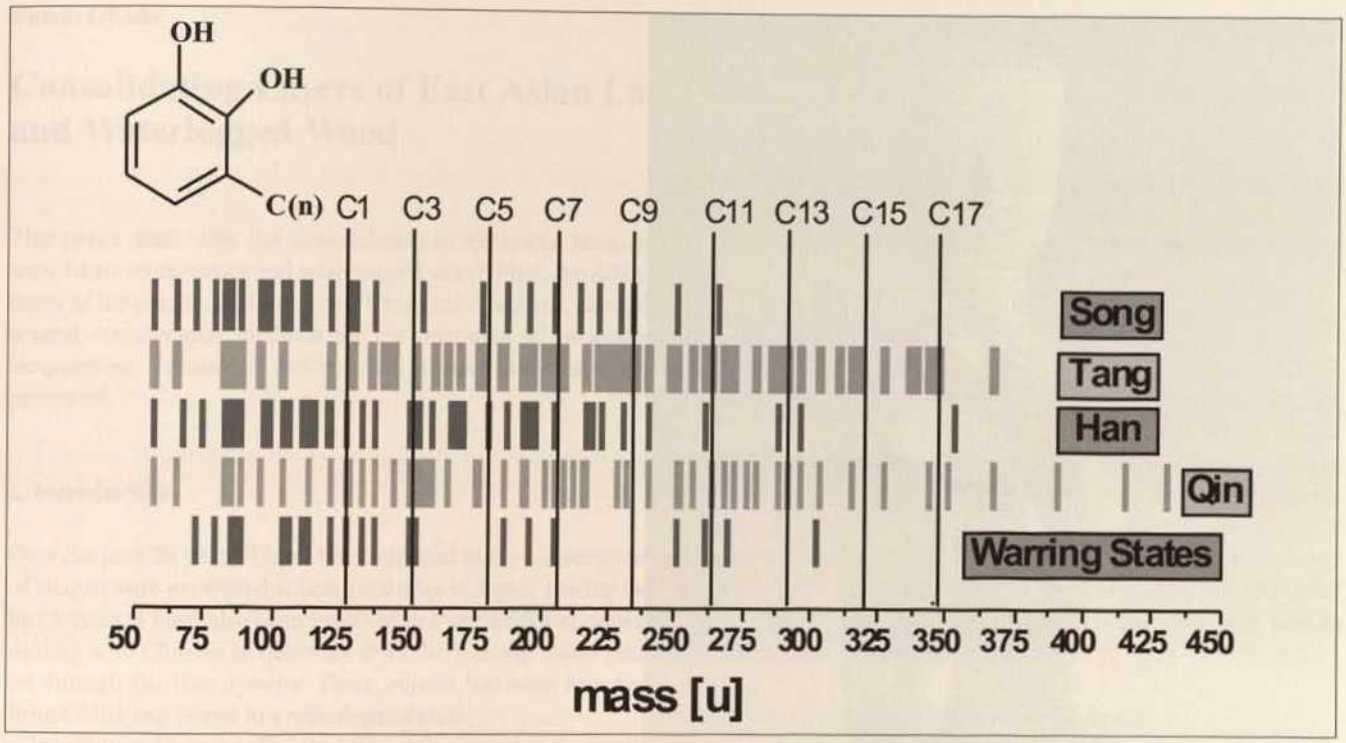


Fig. 3. Fingerprints of the laser desorption mass spectra

For all depicted spectra it can be said that fragments with shorter side chain lengths of urushiol/laccol dominate the spectra. Urushiol and laccol are a mixture of 3-alkylcatechols comprising one or more double bonds. The alkyl side chain of laccol mainly consists of 17 C-atoms ($C_{17}H_x$) whereas urushiol has side chains with 15 C-atoms ($C_{15}H_x$). Taking this into consideration one can conclude that the lacquer samples from the Warring States period, the Han and the South Song dynasty are urushiol based and thus made from *Rhus vernicifera* (Toxicodendron vernicifluum (Stokes) F. A. Barkl.). According to this LD-MS investigation the two samples from the Qin and the Tang dynasty are based on laccol which is the main component of *Rhus succedanea.*

Warring States period lacquer sample: For this sample catechols with side chain lengths of C1–C14 were detected, dominant were peaks for C7 and C11.

Qin lacquer sample: Catechols with C1–C17 were found, C6 side chains are prominent.

Han lacquer sample: Side chains with C1–C13 were evident in the mass spectrum, dominant peaks are found for C11 and C13.

Tang lacquer sample: In this sample C1–C17 side chains were found for the catechols.

Song lacquer sample: Peaks were detected in the mass spectrum for C1–C10 catechol side chains, a dominant peak was found for C7.

In order to distinguish between different East Asian lacquers one has to take into consideration the different factors during the manufacturing process: Which kind of lacquer was used concerning quality, occurrence and method of drying. Additives have to be taken into account. The spectra presented here do not allow to attribute certain patterns in the mass spectrum to a specific dynasty.

Nevertheless, it was found that the laser desorption mass spectroscopy is a technique which is quick in acquiring mass spectra of qi/urushi lacquer. The method allows to use samples without further preparation, small artefacts can be put into the sample chamber directly. Only minute samples are needed to obtain spectra of artefacts which are too large to be put into the apparatus. The evaluation of spectra allows to determine whether the lacquer is laccol or urushiol based. Further evaluation has not been undertaken yet.

LD-MS can be seen as an alternative to pyrolysis gas chromatography mass spectroscopy. The information contained in the mass spectra of both methods is similar but not identical. Therefore, the choice between both analytical techniques depends on the information one wants to obtain from using mass spectroscopy on ancient lacquers.

Notes

1 Kumanotani, Ju: 'Urushi (oriental lacquer) – a natural aesthetic durable and future promising coating', *Progress in Organic Coatings*, 26, 1995, pp. 163–195.

2 Niimura, Noriyasu/Miyakoshi, Tetsuo et al.: 'Characterization of Rhus vernicifera and Rhus succedanea lacquer films and their pyrolysis mechanisms studied using two-stage pyrolysis-gas chromatography/mass spectrometry', *Journal of Analytical and Applied Pyrolysis*, 37, pp. 199–209.

3 Rogner, Ingo/Birkett, Paul/Campbell, Eleanor E. B.: 'Hydrogenated and chlorinated fullerenes detected by "cooled" modified matrix-assisted laser desorption and ionisation mass spectroscopy (MALDI-MS)', *Mass Spectrometry and Ion Processes*, 156, 1996, pp. 103–108.

4 Zumbühl, Stefan et al.: 'A graphite-assisted laser desorption/ionization study of light-induced aging in triterpene dammar and mastic varnishes', *Analytical Chemistry*, 70, 1998, pp. 707–715.

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