Analytical pyrolysis as a fundamental technique for the identification-characterization of Asian lacquers in Cultural Heritage objects

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Introduction

Analytical pyrolysis in **thermally assisted hydrolysis and methylation** mode, coupled with **gas chromatography and mass spectrometry (THM-GC/MS)** is currently considered the **most suitable method** for the chemical **identification-characterization of Asian lacquers** [1] such as **urushi** (from China, Japan, and Korea), **thitsi** (from Thailand, Burma, and Cambodia), and **laccol** (from North Vietnam and Taiwan). Additionally, it permits the investigation of lacquer additives such as drying oils and natural resins. In this work the potential of analytical pyrolysis as a fundamental technique applied for the identification–characterization of Asian lacquers in some Cultural Heritage objects will be presented. Additionally, particular attention has been paid to the **curing mechanism** and **light ageing process** of the less investigated **thitsi type of lacquer** in comparison to urushi.

Materials & Ageing

1 Material type selection

- **Thitsi** (Royal Forest Department of Thailand, Bangkok, Thailand)
- **Urushi** (Kremer, Germany)
- **Essential Oil** (Gurjun Balsam, Mystic Moments, Hampshire, U.K.)

2 Asian lacquer-models preparation

- Application on glass-slides as 70 µm lacquer-film of **1) thitsi pure, 2) thitsi filtered, 3) and mixed with 10 % essential oil, 4) urushi pure, 5) urushi + thitsi filtered (1:1), 6) urushi + thitsi filtered (1:4)**, and **7) urushi + thitsi filtered with 10 % essential oil (1:1)**.

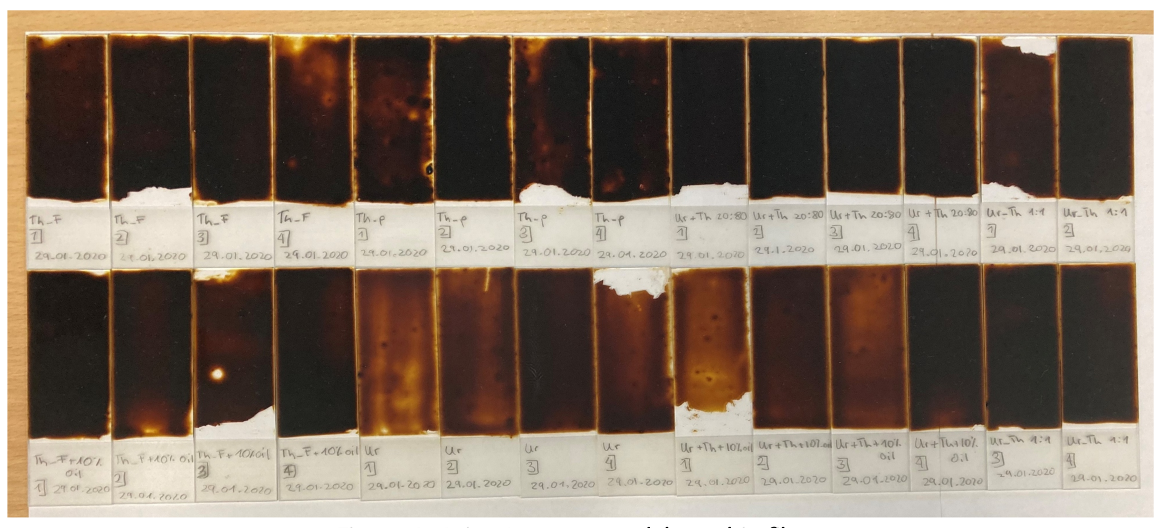


Figure 1: Asian Lacquer-models as thin films

3 Curing process

- **Curing process** in a climate chamber at 20 °C and 80 % rH:
- **Curing time:** 8 weeks except for the pure urushi, which took 1 week

4 Daylight ageing conditions

- **Daylight accelerated ageing chamber:** UVACUBE SOL 500 RF2 (Dr. Hönle, Germany) (460 W/m^2 nominal irradiance) equipped with a filter glass H1, which provides radiation with wavelengths from 320 nm, thus allowing sun-glass filtered simulation.
- **Ageing time**: 31 days.

Analytical approach

1 Assessment of chemical composition modification

Thermally Assisted Hydrolysis and Methylation of Pyrolysis - Gas Chromatagraphy / Mass Spectrometry (THM-GC/MS)

Instrument & Softwares: Pyrolyzer PY-2020id (Frontier Lab) with GCMS-QP2010 Plus (Shimadzu); column SLB-5ms (Supelco). GCMS Realtime®

Pyrolyzer conditions

Pyrolysis (Py) T 500 °C. Interface T 250 °C; injector T 280 °C. Reagent: 2 µL tetramethylammonium hydroxyde (TMAH) (25 wt% aqueous solution) (Sigma Aldrich).

GC/MS conditions

Solvent cut time 5 min, T ramp from 40 °C (2 min) to 300 °C by 6 °C/min, held for 20 minutes; He glas flow 1 mL/min; split ratio 1:50; MS interface and ion source at 280 and 200 °C, respectively; EI at 70 eV; scans from 50 to 750 m/z.

complemented to

Fourier Transform Infrared Spectroscopy (FTIR)

Instrument & Software: Lumos (Bruker), germanium crystal (Ge) (*n*= 5.7), MCT detector, (128 scans, 4cm^{-1} resolution). Opus 8®.

2 Surface morphology changes

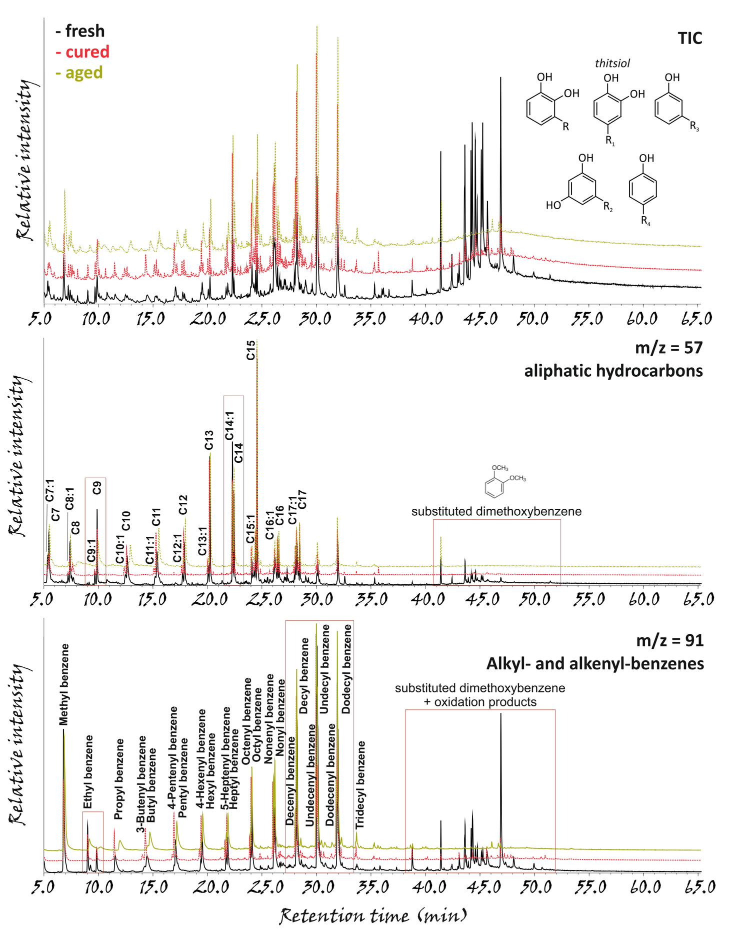
Light digital microscope/3D

Instrument & Software: Keyence VHX-6000 (RZ 100x-1000x objective - VH-Z100R) equipped with a LCD monitor and a CMOS camera (virtual pixels: 1600 (H) x 1200 (V)).

Results

THITSI

- **Digital microscopy:** formation of micro-cracks (Fig.2)
- **THM-GC/MS**: decrease of C9:1 and C9, C14:1 and C14, substituted dimethoxybenzenes, alkenyl- and ethyl benzenes, increase of dodecyl benzenes and oxidation products (Fig. 3).
- **FTIR:** decrease of monomer cathecol / unsaturated side chains, aromatic displacement, increase of quinones / aromatic ether (Fig.4).



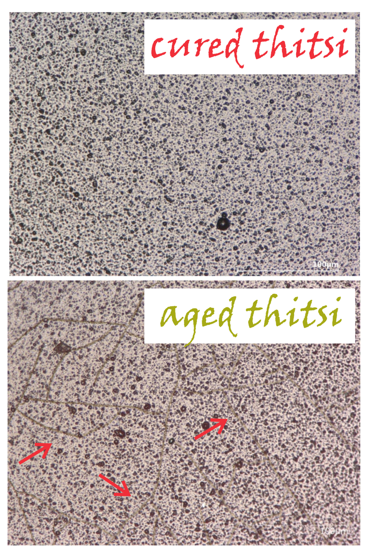


Figure 2: Comparison between photo micrographs of cured and aged thitsi. The red arrows indicate the formed micro-cracks in aged thitsi.

Figure 3: Overall pyrograms (TIC and extracted ion mass) of thitsi showing the comparison between the fresh, cured, and aged samples.

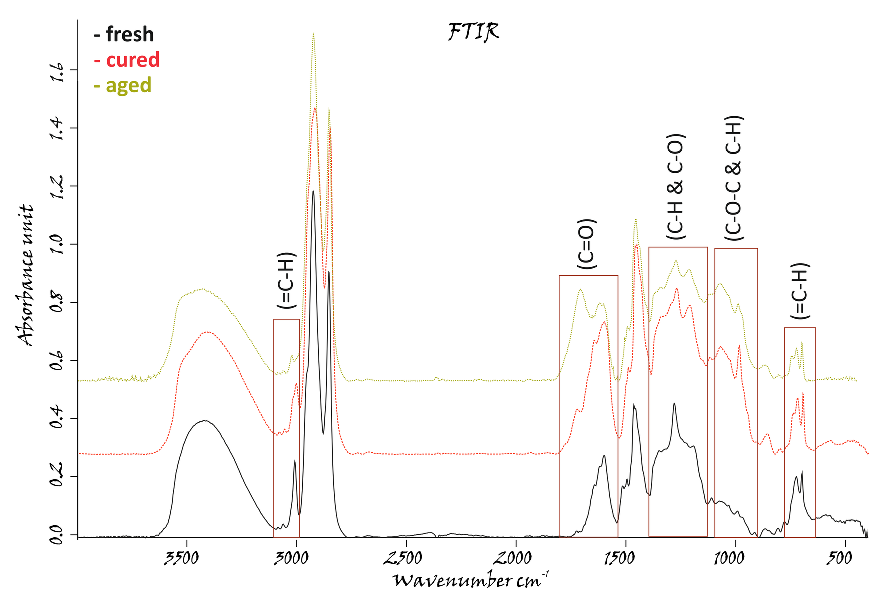


Figure 4: FTIR spectra of fresh, cured, and aged thitsi.

URUSHI

- **Digital microscopy:** no significant physical changes observed (Fig.5)
- **THM-GC/MS**: decrease of C9:1 and C9, C13:1 and C13, substituted dimethoxybenzenes, alkenyl benzenes and ethyl benzenes, increase of dodecyl benzenes and oxidation products (Fig. 6).
- **FTIR:** decrease of monomer cathecol /unsaturated side chains, increase of quinones / aromatic ether (Fig.7).

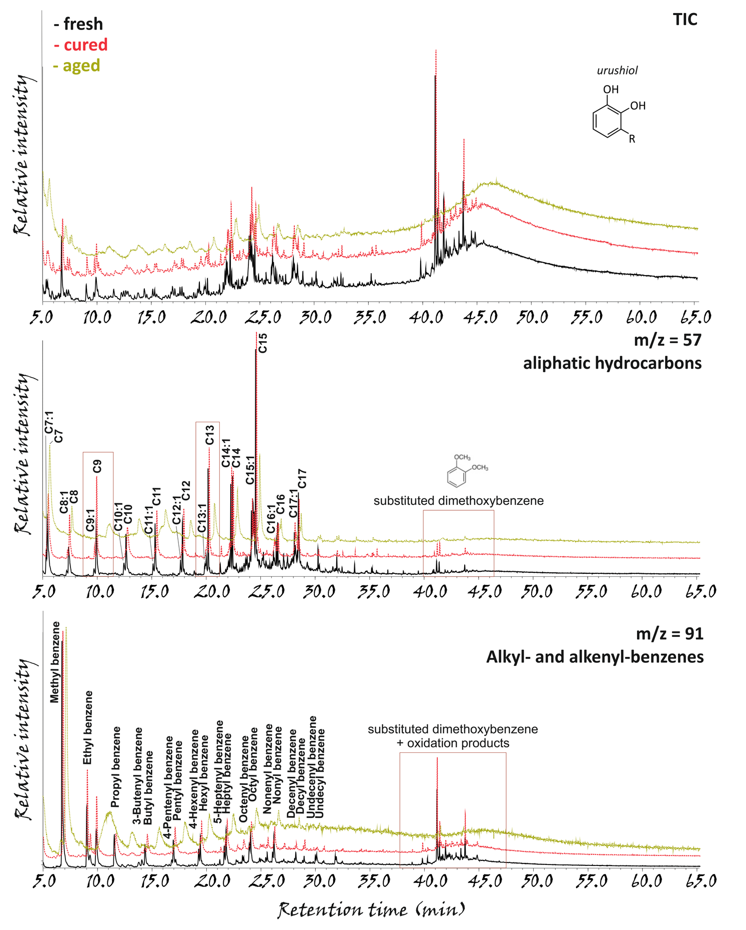


Figure 5: Comparison between optical micrographs of cured and aged urushi.

Figure 6: Overall pyrograms (TIC and extracted ion mass) of urushi showing the comparison between the fresh, cured, and aged samples.

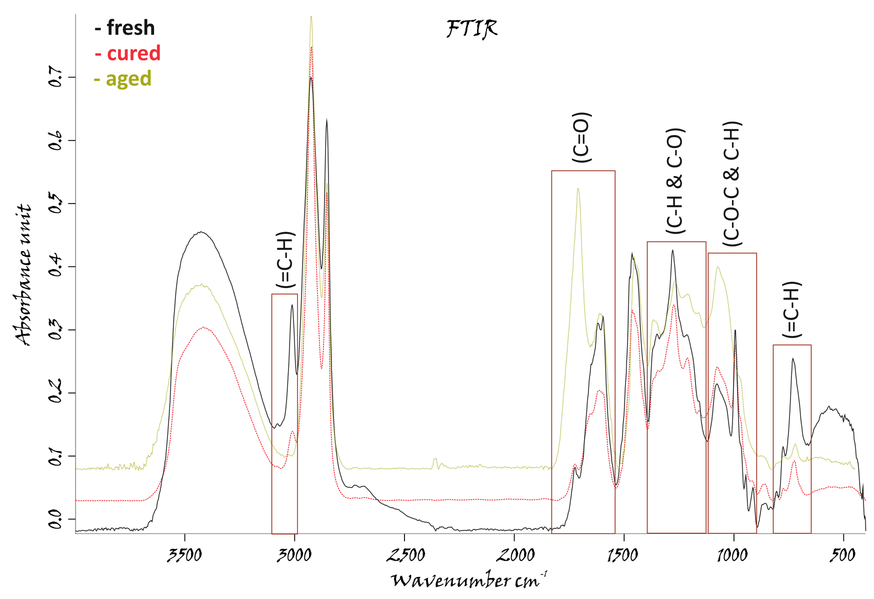
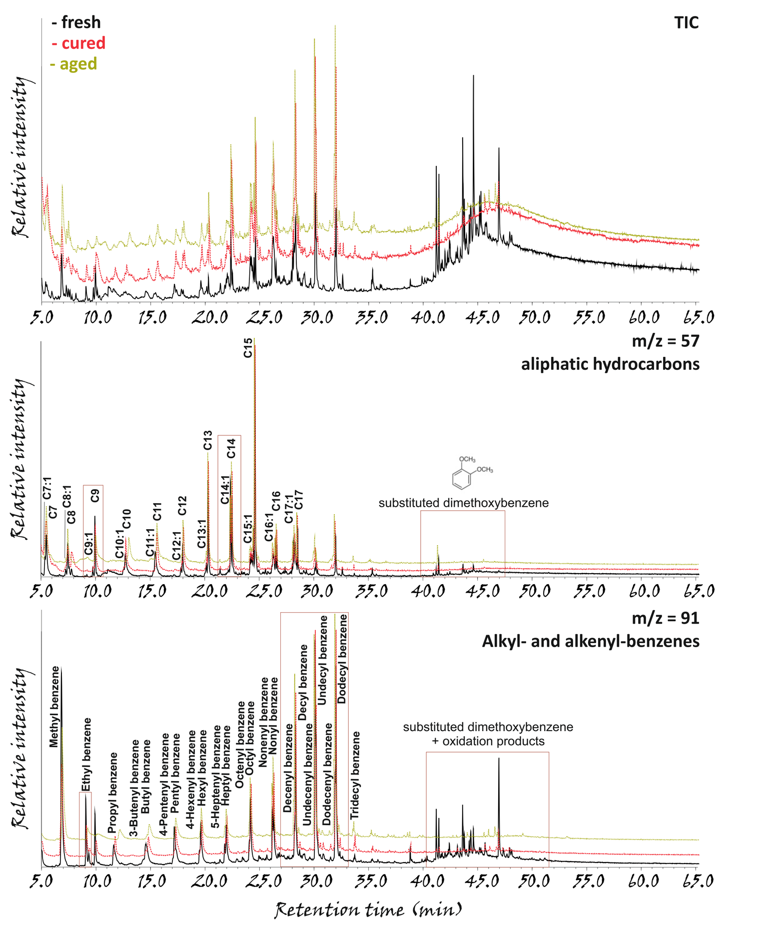


Figure 7: FTIR spectra of fresh, cured, and aged urushi.

THITSI + URUSHI

- **Digital microscopy:** slight formation of micro-cracks (Fig.8)
- **THM-GC/MS**: decrease of C9:1 and C9, C14:1 and C14, substituted dimethoxybenzenes, alkenyl- and ethyl benzenes, increase of dodecyl benzenes and oxidation products (Fig. 9).
- **FTIR:** decrease of monomer cathecol / unsaturated side chains, aromatic displacement, increase of quinones / aromatic ether (Fig.10).



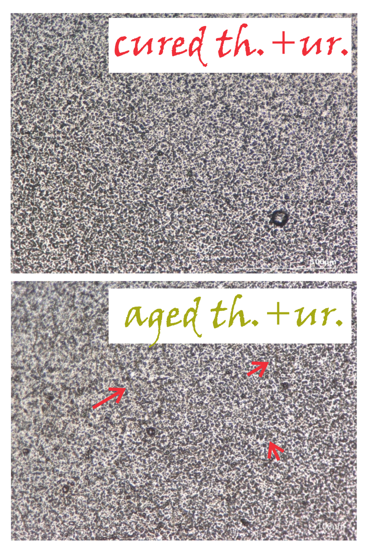


Figure 8: Comparison between photo micrographs of cured and aged thitsi + urushi. The red arrows indicate the formed micro-cracks in aged thitsi + urushi.

Figure 9: Overall pyrograms (TIC and extracted ion mass) of thitsi + urushi showing the comparison between the fresh, cured, and aged samples.

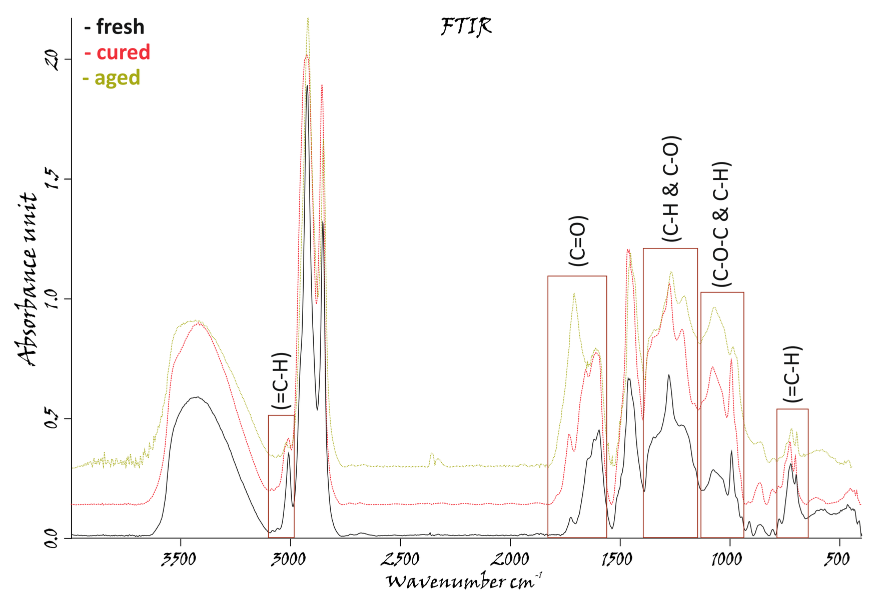


Figure 10: FTIR spectra of fresh, cured, and aged thitsi + urushi.

Conclusions & Outlook

This ongoing work demonstrated so far the chemical similarities and differences in the curing process between some Asian laquers widely found in cultural heritage objects such as thitsi and urushi, and a most rare one such as thitsi mixed with urushi.

A digital micro-optical inspection allowed to visualize the formation of fine micro-cracks after daylight ageing, which were predominant in thitsi and when mixed with urushi. The THM-GC/MS technique proved to be suitable for the detection of oxidation markers of thitsi as well as mixed with urushi, whereas the FTIR method provided useful information about the polymerization and photo-oxidation processes of the analysed lacquers.

Further research is still ongoing to better understand the exact chemical processes involved in the ageing of thitsi mixed with urushi, also including cultural heritage objects.

References

[1] Schilling M. R., Heginbotham A., van Keulen H., Szelewski M. Stud. Conserv. 2016; 61; 3–27.

Aknowledgments

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