Chromatography and mass spectrometry to study cleaning effects on Asian lacquered cultural heritage objects

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Buddha at HTC, what is the catch?

Figure 1 *Buddha seated in lotus position (padmasana), hands making the gesture of teaching (dhyana mudra). Vietnam, 19th century. H. 66.5 x W 48.5 cm. Royal museums of art and history (Brussels).*

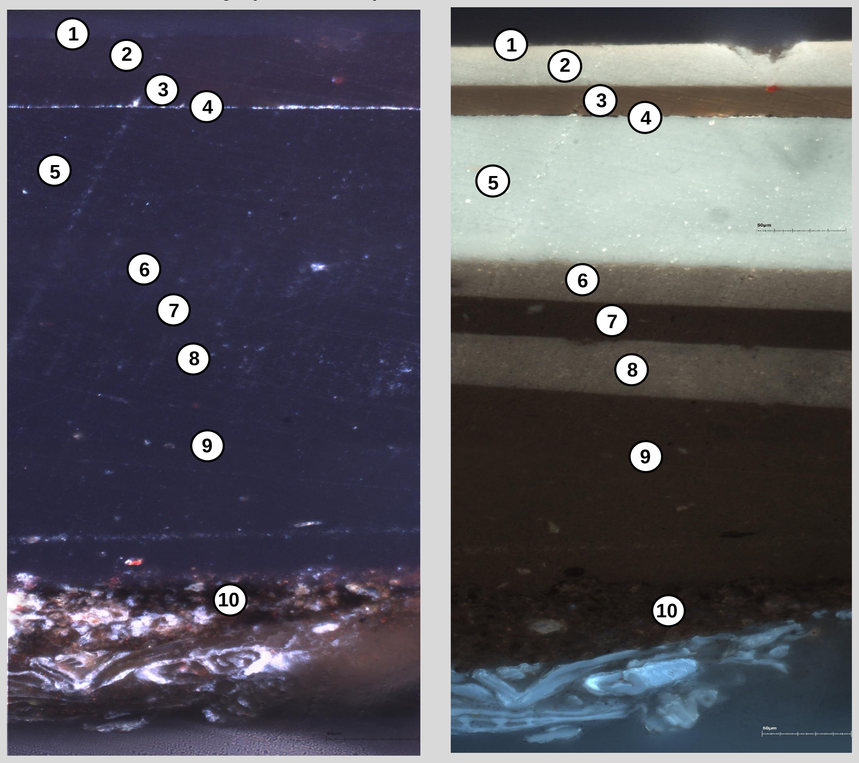

Figure 2 *Optical light microscopy images of the cross-sections from the Buddha statue under VIS and UV illumination, with layer annotations*.

Nr	Name	Result of the analytical study
1	Protective layer	Dammar varnish
2	Top lacquer layer VI	Laccol, tung oil and soot
3	Lacquer layer V	Laccol and tung oil
4	Metal foil	Aluminium foil, laccol, tung oil
5	Lacquer layer IV	Laccol, tung oil and pine resin
6	Lacquer layer III	Laccol, tung oil and amber
7	Lacquer layer II	Cashew nutshell polymer, laccol and amber
8	Lacquer layer I	Cashew nutshell polymer, laccol, amber, soot
9	Foundation	Cashew nutshell polymer, soot and a drying oil
10	Wood	Unverified

Table I Py-GC-MS results.

Acknowledgements

Our gratitude goes to Louise Decq and Alexia Coudray for their microscopy studies on the cross-sections and SEM analyses.

The molecular art of cleaning

Solvent induced leaching on artificially aged Asian lacquer mock-up samples was chemically investigated. Asian lacquers are saps exudated by trees within the Anacardiaceae family, which polymerise to highly crosslinked macromolecules. The main types; ***urushiol*, *thitsiol* and *laccol* based polymers** (referred to as **urushi, laccol and thitsi**, respectively) are studied, but with a focus on the lacquer formulation identified on a Vietnamese buddha statue. **GC-MS** was used for this purpose and **RPLC-HRMS analysis** was performed for the verification of the GC-MS results. The molecular changes observed after cleaning treatment, both in the short and long term, were thereafter evaluated on solid samples taken from the lacquer surfaces, which were analysed through **pyrolysis-GC-MS**.

Solvent induced leaching of Asian lacquer surfaces

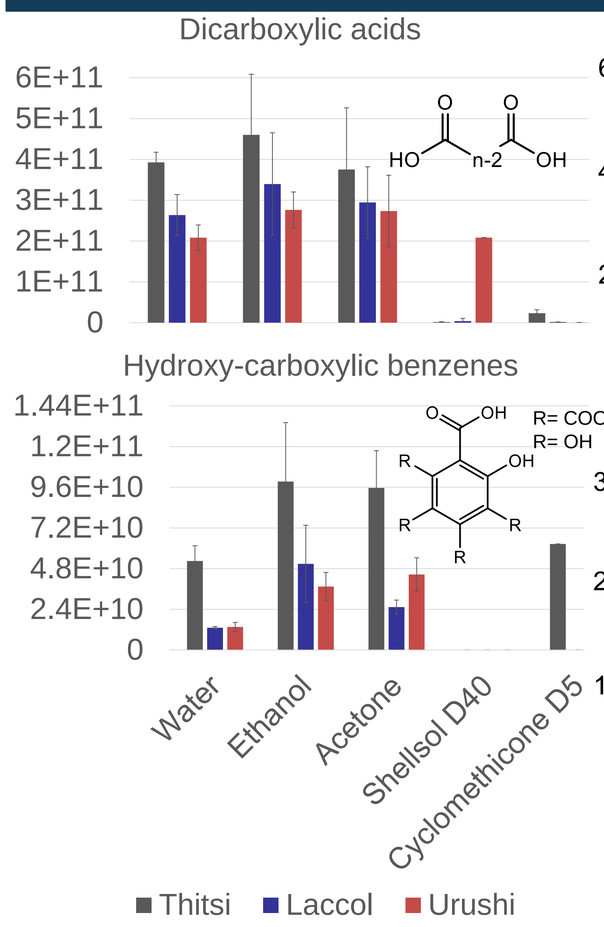

Figure 3 *Summed peak areas of all dicarboxylic acids and hydroxy-carboxylic benzenes, identified, through **GC-MS** analysis, in solvent extracts of aged Asian lacquer (laccol) mock-ups.*

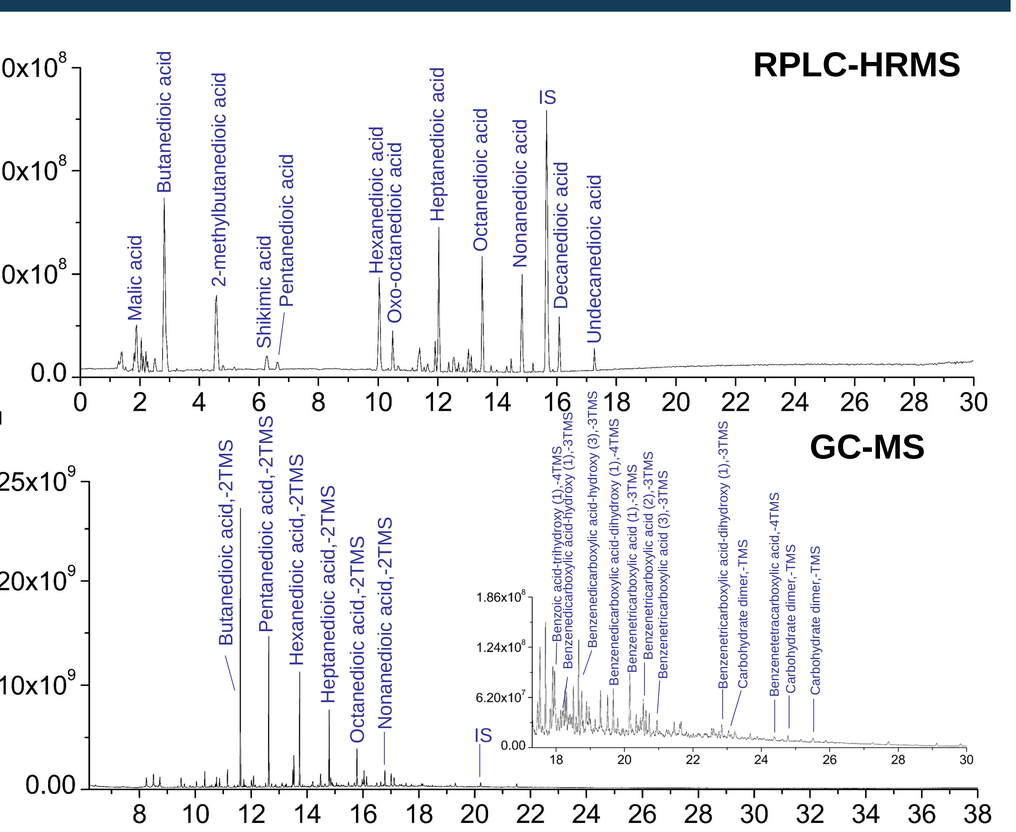

Figure 4 *Typical total ion chromatograms obtained through RPLC-HRMS and GC-MS analyses of water extracts, obtained from a **Asian lacquer (laccol) mock-up sample**. The insert shows an **EIC (m/z 147)** in which the identified hydroxy-carboxylic benzenes are annotated.*

Polar extracts, analysed using GC-MS, contain many **hydroxy-carboxylic benzenes** (shown in Figures 3 and 4). The benzene substituted compounds can comprise up to 6 carboxylic acids or hydroxylic groups, which were identified in the polar solvent extracts, using ethanol or acetone. In water extracts the maximum amount of benzene substituted carboxylic groups was 4. The **pentacarboxylic-** and **hexacorboxylic acid** compounds are likely difficult to dissolve in water. **Dicarboxylic acids** were found to be the most significant (photo-oxidation) products. The compounds were identified using both **GC-MS** and **RPLC-HRMS** and typically consist of short chain compounds, such as **butanedioic acid**. As both molecular groups contain numerous carboxylic groups, we assume that those compounds are important denominators contributing to the surface acidity and polarity of aged lacquer surfaces, in turn making the surfaces highly sensitive to potentially 'destructive' polar solvents or water.

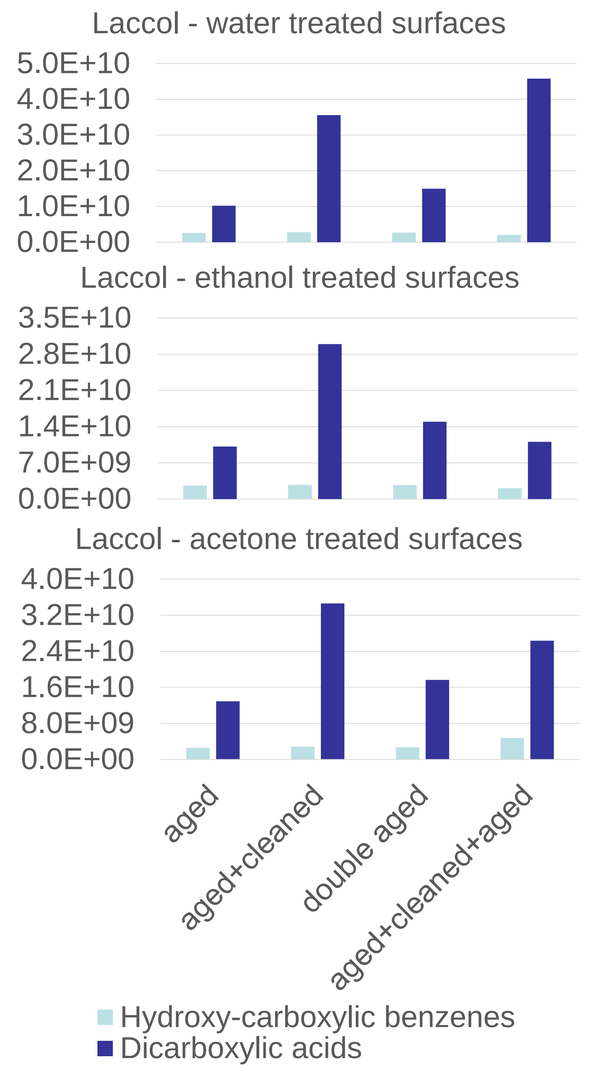

Figure 5 *summed peak areas of all dicarboxylic acids and hydroxy-carboxylic benzenes peaks identified, after sampling of the surface and analysis using **Py-GC-MS**.*

The life of buddha extended?

It is clear that Asian lacquer surfaces become extremely sensitive to polar solvents and water when photo-degraded. This makes cleaning a **high risk procedure**, especially since apolar solvents, although safe, are **very poor cleaning products** and therefore not useful. It was also shown (see Figure 5) that for al polar solvents tested an **accelerated degradation** took place succeeding the cleaning treatment. More dicarboxylic acids appeared after treatment with water, and cleaning using acetone resulted in a two-fold peak area increase for hydroxy-carboxylic benzenes. The drastic decrease of dicarboxylic acids after using ethanol could indicate the formation of other photo-oxidation products. This makes the cleaning practice of the Buddha statue complex, and might require, **tailoring polarity** of polar solvents by adding apolar solvents to them, by limiting contact times, or by using novel application strategies such as gels or compresses.