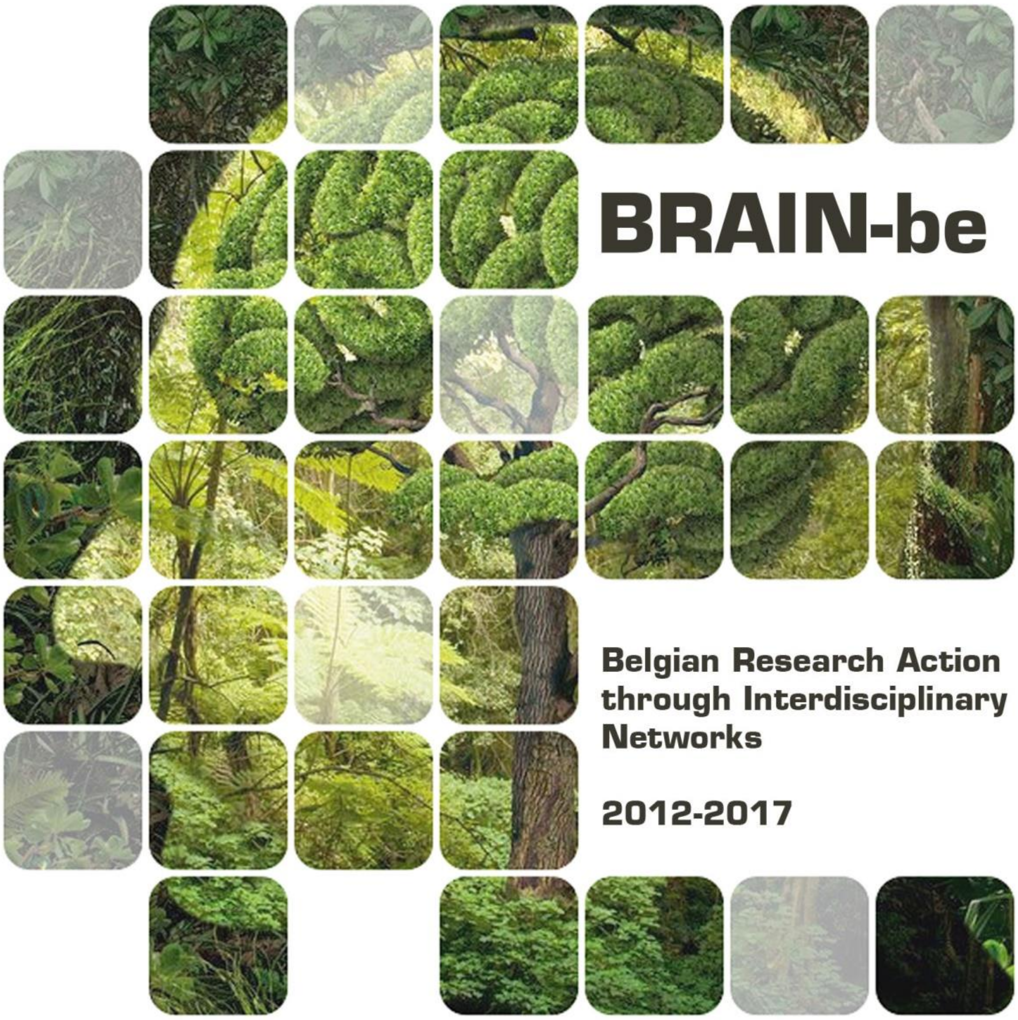

PHySICAL

Profound study of Hydrous and Solvent Interactions in Cleaning Asian Lacquer

Steven Saverwyns (Royal Institute for Cultural Heritage) – Jonas Veenhoven (Ghent University) – Delphine Mesmaeker (Royal Museums of Art and History)

Axis 3: Cultural, historical and scientific heritage

NETWORK PROJECT

PHySICAL

Profound study of Hydrous and Solvent Interactions in Cleaning Asian Lacquer

Contract - BR/175/A3/PHySICAL

FINAL REPORT

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ABSTRACT

Context

Asian lacquers, derived from the sap of indigenous trees in various parts of Asia, have been historically employed for centuries to embellish a diverse array of objects, admired for their lustrous finish and enduring durability. As these artifacts age, however, they exhibit increased sensitivity to water and solvents. Numerous such items, including those housed in the Royal Museums of Art and History (RMAH), are stored in the museum reserves, necessitating careful cleaning and conservation procedures to enable the objects to be displayed in the museum galleries. Yet, traditional cleaning methods involving water or solvents pose significant risks.

Objectives

In this project we undertook a comprehensive investigation, considering both the conservation and chemical perspectives, to establish optimal practices for cleaning aged Asian lacquers, with the primary goal of preserving selected objects from the RMAH collection.

The chemical research component aimed at refining the standard pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) method for analysing (aged) Asian lacquers. Additionally, alternative analytical approaches were explored to better characterize these lacquers. The analyses were designed to provide insights into both the composition of aged lacquer and the compounds extracted from aged Asian lacquers using a range of solvents and water, as employed during the cleaning phase.

A final objective was to inventory and reorganize the RMAH collection of Asian lacquers, ensuring their preservation for future generations.

Conclusion

During the project, a significant step was taken in the reorganisation of reserves to provide secure storage for lacquered objects, underscoring the commitment to the preservation of the objects. Within this context, a remarkable discovery unfolded during inventory and study—a unique object crafted using the dry lacquer technique. This unexpected find adds to the significance of the collection.

Chemical analyses proved necessary as a precursor to establishing a cleaning protocol; a nuanced understanding of the composition of each artefact is necessary. In the process, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was optimised towards the analyses of different compounds present in Asian lacquers, and valuable insights were provided for the compounds extracted when using water or solvents as cleaning agents for aged Asian lacquers. Additionally, the technique shed light on the metabolism of polysaccharides in Asian lacquers.

Against this backdrop, the study successfully culminated in the establishment of a comprehensive cleaning protocol applicable to Asian lacquer objects. However, given the unique nature of each object with its distinct characteristics, the importance of preliminary physico-chemical analysis before embarking on the cleaning process remains paramount for ensuring the preservation of these valuable and distinctive items. The multitude of variable parameters involved, however, makes it nearly impossible to establish a standardized protocol that would facilitate the implementation of cleaning treatments for any give lacquered object.

Keywords: Asian lacquer, cleaning, best practices, water and solvent, pyrolysis-gas chromatography-mass spectrometry, polysaccharide metabolism

1. INTRODUCTION

Asian lacquer, derived from the sap of specific endemic trees from the Anacardiaceae family, historically found in Southeast Asia, Japan, and China, serves as a versatile coating material frequently employed for decorating various substrates, including bamboo, wood, metal, leather, and ceramics (Kopplin, 2002; Langenheim, 2003; Szczepanowska and Ploeger, 2019; Webb, 2000). The historical use of lacquer can be traced back to China during the Shang dynasty (16th-11th century BC) and in Japan as early as the initial Jōmon period (8000-5000 BC) (Matsumoto, 2018).

Over the centuries, Asian lacquer has transcended geographical boundaries (Impey, 2000; Nagashima, 2011), finding its way into numerous collections, including those in the Royal Museums of Art and History (RMAH) in Brussels, encompassing both East Asian and Southeast Asian artifacts. These artifacts are primarily constructed on a wooden core and feature intricate decorations that involve not only lacquer but also a diverse array of other materials, including gold, silver, aluminium powder, mother of pearl, applied metals, and pigments (figure 1).

Figure 1. A richly decorated lacquered inro (M.1137) from the collection of the RMAH.

Regrettably, a significant portion of this collection remains off-display or is only temporarily exhibited. The exhibition of these objects and their long-term storage expose them to the risk of degradation due to factors such as light exposure, fluctuations in relative humidity, and dust deposits. From a conservation perspective, intervention is imperative, beginning with the surface cleaning, to enable their display and safeguarding the objects for future generations. It is well-documented that aged lacquer surfaces become progressively more vulnerable to water and polar solvents (Coueignoux, 2009; Han et al., 2023; Mcsharry et al., 2007; Webb, 2000). These commonly used cleaning agents for the conservation of Asian lacquers, presents complexities in the conservation treatment. This makes the cleaning of lacquer surfaces a high-risk endeavour due to the potential for damage to the original surface.

Current cleaning methods, particularly those relying on solvents, are notably deficient in a solid scientific foundation and carry the risk of potential long-term harm. Guaranteeing the preservation of Asian lacquered objects and formulating best practices for their cleaning necessitates a comprehensive assessment of cleaning procedures from multiple perspectives, including conservation, chemistry, and physical considerations. This evaluation is especially vital for objects destined for exhibition within museum environments.

The comprehensive cleaning of Asian lacquer also entails the chemical identification of the specific type of lacquer used (urushi, laccol, or thitsi, from respectively *Toxicodendron vernicifluum*, *Toxicodendron succedaneum* and *Gluta usitata*). Simultaneously, these analyses offer valuable insights into the preservation state of the lacquer objects. Asian lacquers, owing to their high inertness, pose a challenge when it comes to dissolution, often a necessary step for a thorough chemical analysis. The key lies in the application of pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC-MS), which enables the analysis of solid samples to elucidate the organic compositions of Asian lacquers (Tamburini, 2021). This procedure requires for a thorough understanding of the composition of the lacquers and their degradation products, nonetheless, meticulous evaluation and optimisation.

2. STATE OF THE ART AND OBJECTIVES

Previous studies that focused on the cleaning and identifying Asian lacquer are primarily based on urushi (from *T. vernicifluum*). Lacquers from *T. vernicifluum* are known for the high-quality urushiol-based composition, commonly used for Japanese and Chinese objects. Research on the chemical composition of Chinese and Japanese export lacquer has, however, revealed that the composition of the lacquer layers is more complex. In addition to urushi, other materials, such as Burmese thitsi lacquer *(*from *G. usitata)* and laccol lacquer *(*from *T. succedaneum)*, have been shown to be used as well (Heginbotham and Schilling, 2011; Schilling et al., 2014). To date, the most thorough published work on cleaning Asian lacquer was conducted as part of a PhD study (McSharry, 2009). In this study specific solvents were determined to be suitable for cleaning degraded urushi lacquer. The limitation of the study was that the research was restricted to only urushi lacquer. Additionally, the chemical analyses, were not conducted on the molecular level. The relation to the physico-chemical and visual changes observed by conservators were also not considered.

In similar research aimed at improving cleaning procedures for water-sensitive oil and acrylic emulsion paints, the influence of solvents was examined through the analysis of solvent extracts using e.g. GC-MS and FTIR (Erhardt et al., 2002; Shibayama et al., 1999; Sutherland, 2003). These analytical procedures were not yet applied to studies of Asian lacquer cleaning, while applying these techniques to lacquer could yield crucial information for establishing cleaning treatments, which is the focus of this study.

The primary objective of this project was to **develop enhanced cleaning strategies for common Asian lacquer formulations** by investigating the interaction of solvents with damaged Asian lacquer surfaces, considering both the conservator's and the chemist's perspectives.

The study focussed on objects from the MRAH lacquer collection, many of which are not currently on display or are only partially exhibited. Their current condition was assessed to identify observed degradation effects and determine which pieces require treatment, enabling their transition from storage to museum exhibition. Furthermore, the collection was inadequately documented, and the objects were stored under diverse climatological conditions due to the age and condition of the museum building. An additional goal was **systematic documenting** of the lacquer objects to help the museum **relocate lacquered items to a more suitable environment for preservation**.

To gain a better understanding of the composition of Asian lacquers, the **analytical methods**, primarily Py-GC-MS and LC-MS (Le Hô et al., 2012; Schilling et al., 2016; Szczepanowska and Ploeger, 2019; Tamburini, 2021; Yu et al., 2021a, 2021b), had to be **optimised**. The emphasis was on the individual study of the different chemical classes of compounds present in the lacquers and under what analysis conditions they could be best studied. Special attention was dedicated to the **metabolism of polysaccharides** in the lacquers, a field of study that has been relatively underexplored until now (Kumanotani, 1995; Lu et al., 1999a, 1999b). This step in the research is crucial for comprehending the changes in the chemical and physical properties of the cured and ultimately aged polymers.

Scientific analyses were initially conducted on artificially aged reproductions to **optimise the analytical methodology**, to comprehensively **elucidate the lacquer composition** and to **identify compounds extracted during cleaning,** or formed through the cleaning of objects. Using various analytical techniques, information about the influence of solvents at a molecular level, was extracted. This includes quantitative aspects, such as the degree of leaching of compounds from the polymeric network, as well as qualitative aspects related to the molecular identification of compounds extracted from the lacquer structure.

The analytical results were compared with visible changes on the cleaned surface for direct treatment application. Cleaning procedures were defined for specific types of Asian lacquers with minimal risk of removing the original material. This research enables predictions of cleaning effects, especially if prior knowledge of the lacquer's composition is obtained.

The assessment of the actual state of preservation of RMAH objects, coupled with a comprehensive, scientifically grounded examination of the lacquer composition and of solvent cleaning procedures for damaged Asian lacquers, eventually provided **guidelines for preventive conservation and best practices for treatment**. In a broader context, this study contributes to the global understanding of the identification, preservation, and cleaning of lacquer objects, ultimately enabling their display in a museum environment and ensuring the protection of these valuable artifacts for future generations.

3. METHODOLOGY AND SCIENTIFIC RESULTS

3.1. Summary of the methodology

The methodology followed is summarised below, with a schematic overview in figure 2. The evaluation of solvent cleaning procedures was primarily conducted on reproductions and on a depreciated lacquered object from the RMAH collection. To create representative mock-up samples, a comprehensive review of the scientific literature on Asian lacquer compositions was undertaken. This was complemented by chemical analyses of a broad selection of lacquered objects from the Asian collection of the RMAH. This approach ensures that the study's results directly apply to a chosen number of objects from the RMAH collection.

The study encompassed the three primary types of Anacard lacquers (thitsi, laccol, and urushi) to represent a wide range of lacquer compositions, considering that the cleaning procedure can vary based on the lacquer type. Various mock-up samples were prepared, including free films and one-layer samples. For practical purposes, standardised reproductions were employed in the project, with each set differing by a single ingredient. The reproduction protocol was outlined in close collaboration with Marianne Webb and researchers at the Getty Conservation institute (GCI). Additional ingredients, such as oils and pigments, were added depending on the literature survey and analysis results from the RMAH objects. While initially planned in the project proposal, the creation of full stratigraphic layer samples was ultimately not undertaken due to their intricate nature and the extended preparation time involved. Instead, an authentic depreciated lacquer object from the RMAH collection, which had already suffered from natural degradation, was utilised as a substitute. This object, a Chinese etagere composed of three levels, proved to be an ideal subject for study. The aging between the various levels differed, and significant variations were observed between the top, side and bottom of each level.

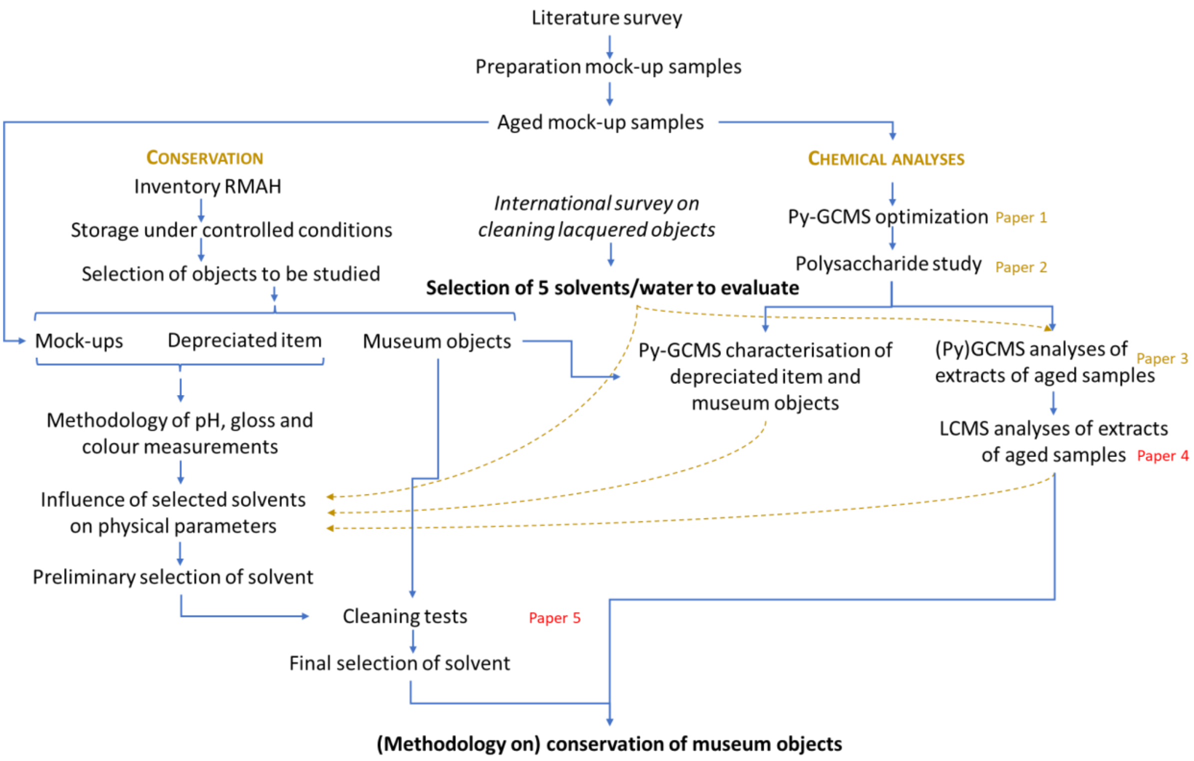


Figure 2. Schematic overview of the methodology of the PHySICAL-project.

Given that aging renders lacquers vulnerable to solvent cleaning procedures, all scientific research was conducted on aged samples. Consequently, all reproductions underwent artificial aging before assessing the cleaning procedures. The samples were subjected to light aging using Xenon light in combination with filters simulating interior daylight exposure, maintaining a constant relative humidity and temperature. After conducting the cleaning tests, the samples were subjected to a second round of artificial aging to assess the long-term effects of the cleaning on the lacquer surface.

Drawing from the scientific literature on solvent cleaning of vulnerable surfaces (not limited to lacquer surfaces but also encompassing studies on cleaning water-sensitive oil paints), and based on an international survey conducted within the PHySICAL project, promising solvents suitable for cleaning Asian lacquers were selected.

The selected solvents were evaluated on the mock-up samples and the Chinese etagere to determine their effectiveness in cleaning and to what extent they affected the appearance and physical aspects of the lacquer surface, including colour, gloss, and acidity. In conjunction with physico-chemical testing, it was determined if solvent-extractable compounds can be removed without damaging the original surface or, conversely, if they may contribute to additional degradation phenomena. Given the subjectivity of visible changes, instrumental investigations on the lacquered samples under consideration were conducted, focusing on gloss, colour, surface acidity, and micro-cracking. To accurately measure these properties, it was necessary to optimise and evaluate the available methods, especially concerning colour, gloss, and acidity of the lacquer surface. Two master students worked on these topics as part of their master's theses.

The influence of the different solvents on the lacquer surface were evaluated by analysing solvent extracts to determine if and to what extent molecular compounds or macromolecules are extracted from the lacquer surface. Achieving precise and qualitative evaluations of the extraction capabilities of the solvents necessitates the use of state-of-the-art analytical techniques.

At present, the most used technique for studying the composition of Asian lacquers is Thermally Assisted Hydrolysis and Methylation-Pyrolysis-Gas Chromatography Mass Spectrometry (THM-Py-GC-MS). This technique allows for the analysis of solid samples using minimal quantities of lacquer (<100 µg). Data processing and the identification of Asian lacquer composition can be performed semi-automatically, thanks to the research conducted at the Getty Conservation Institute (GCI) in the Recent Advances in Characterizing Asian lacquer (RAdICAL) research program. Py-GC-MS was the primary used technique for studying the composition of the lacquers from the RMAH collection and for elucidating the composition of solvent extracts. Prior knowledge of the lacquer composition is essential as cleaning procedures can be contingent on the type of lacquer used.

While Py-GC-MS was already well-established for the study of Asian lacquers, a thorough optimisation was desired for the current research. This was necessary as not only the identification of the lacquers but also the comprehensive study of degradation products was required. This involved using different pyrolysis temperatures and evaluating two derivatisation reagents (tetramethylammonium hydroxide and hexamethyldisilazane). This optimisation provided new insights into the macromolecular structure of aged lacquers. Results of this study were published in an extensive paper in the *Journal of Analytical and Applied Pyrolysis* (Veenhoven et al., 2023).

The optimisation of Py-GC-MS with in situ trimethylsylilation, using hexamethyldisilazane, also paved the way for an in-depth study of the characterisation of polysaccharides present in Asian lacquers, an understudied area. Results were published in the eminent journal *Carbohydrate Polymers* (Veenhoven et al., 2024). It was also found that the presence of polysaccharides made it possible to distinguish between distinct types of lacquer.

As GC-MS has limitations when it comes to studying larger molecules, also liquid chromatography coupled with a high resolution orbitrap mass spectrometer (LC-HRMS) was employed to identify larger molecules in the solvent extracts. The high mass resolution of HRMS allows the precise determination of molecular weight of the compounds to elucidate their elemental composition (paper forthcoming).

Simultaneously, the Asian lacquered objects in the RMAH collection were studied meticulously, including using chemical analyses, and condition reports were prepared when necessary. Based on this study, objects were selected for applying the solvent cleaning procedure to real-life samples, as opposed to mock-up samples, with extensive testing on the Chinese etagere as intermediate step. Finally, a few objects from the collection were chosen and cleaned according to established best practices using the solvents determined as effective and safe for the lacquer in the physico-chemical part of the research.

As a result, new and scientifically founded solvent cleaning procedures for aged and damaged Asian lacquers could be formulated.

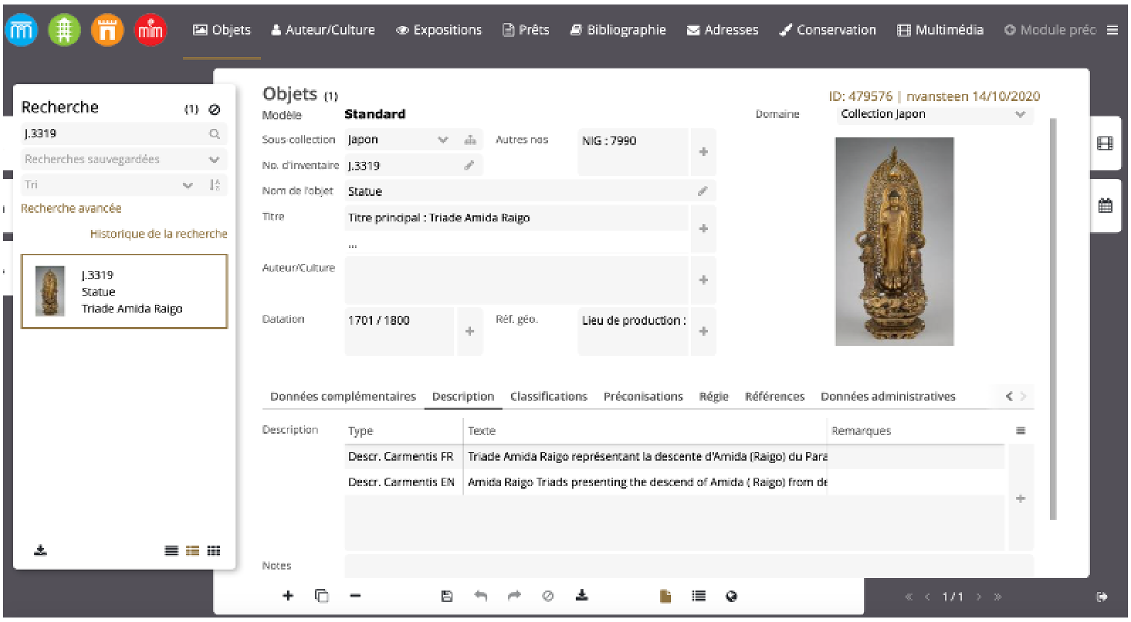
3.2. Inventory of lacquered objects in the collection of the RMAH

The collection at the RMAH of Asian lacquered objects remains undiscovered which includes only 25 items on display in the museum exhibition rooms (figure 3).

The PHySICAL project's research domain encompasses two significant departments within the RMAH collections. The first department focuses on East Asia, including China, Japan, and Korea, while the second department represents the Indian/Southeast Asian part of the continent. The majority of lacquered objects are currently stored in four different storage areas distributed across various sectors of the building. Due to past knowledge gaps and potential misunderstandings about the material, a primary goal of the inventory was to "search for the lacquer" and clearly identify these objects in the collection.

Figure 3. A selection of lacquered objects on display in the RMAH.

After thoroughly exploring both storage areas and exhibition rooms, we cross-referenced our observations with the available paper and digital inventories. Leveraging the museum's ongoing digital transition, we took the opportunity to integrate the inventory of wood lacquers into the collection management system (CMS) MuseumPlus RIA (figure 4). This presented a chance to conduct a more detailed and comprehensive inventory, improving accessibility to the collection.



Recherche: J.3319

J.3319
Statue
Triade Amida Raigo

ID: 479576 | nvansteen 14/10/2020

Modèle: Standard
Domaine: Collection Japon
Sous collection: Japon
Autres nos: NIG : 7990
No. d'inventaire: J.3319
Nom de l'objet: Statue
Titre: Titre principal : Triade Amida Raigo
...
Auteur/Culture:
Datation: 1701 / 1800
Réf. géo.: Lieu de production :

Description

Type	Texte	Remarques
Descr. Carmentis FR	Triade Amida Raigo représentant la descente d'Amida (Raigo) du Para	
Descr. Carmentis EN	Amida Raigo Triads presenting the descend of Amida (Raigo) from de	

Notes

Figure 4. Screenshot of the new MuseumPlus Ria database, with the addition of a lacquered object.

Specific thesauri related to lacquer art techniques were created and seamlessly integrated into the program, facilitating access for both the public and researchers. This collaborative effort was undertaken with eCollection, the service coordinating the digitization of the museum's collections.

MuseumPlus RIA offers the advantage of centralizing all information related to each object in one location: general details, photographic documentation, archives, movement or exhibition histories, condition reports, conservation treatment, scientific analyses, and more.

To enhance the database, the museum's photographic studio documented all lacquered works with wooden support, capturing a minimum of six photos for each piece. By cross-referencing information from prior inventories or the earlier digital inventory with on-site observations, we updated the data, leading to a more comprehensive understanding of certain objects.

In the end, we successfully identified and inventoried over 750 lacquered wooden objects, incorporating them into the inventory with some having simplified records. Each piece underwent a condition report, identifying items requiring treatment or urgent intervention. Additionally, this inventory clarified information about certain objects previously misunderstood or misinterpreted. Notably, the identification of a dry lacquer Buddha, previously cataloged as a gilded wooden Buddha, is a significant discovery, providing valuable insights into the museum's unique collection.

3.3. Storage of the lacquered objects under climatised conditions

The lacquered objects on wooden bases are housed in various areas of the museum, including exhibition rooms and storages, each subject to different conservation conditions. Two exhibition rooms (the China gallery and the Southeast Asian gallery) and four storages (Extrême-Orient EO, Schotsmans, Indonesia, and Catacombs) are involved. In optimal conditions lacquered wooden works are preserved at a temperature of 18°C (±5°C), a relative humidity of 50% (±5%), and exposure to 50 lux, excluding UV.

Since 2015, the museum has lacked standardized and systematic records of the exhibition and conservation conditions for the artworks. A new monitoring plan was under consideration at the project's inception and is expected to be operational in the coming years. To evaluate the current situation and develop a long-term preventive conservation plan, we conducted a systematic study and recording of the conservation conditions.

<u>Situation before the project</u>

Exhibition rooms

The exhibition rooms (figure 5) did not have significant issues, although obtaining a comprehensive overview was challenging due to the lack of monitoring equipment in most spaces. Only the China gallery had a thermo-hygrometer and a humidifier placed near a sensitive piece. Following the completion of the PHySICAL project, a comprehensive installation of thermo-hygrometers has taken place across the museum to systematically assess the conditions in various sectors. This initiative was overseen by the consulting bureau responsible for the feasibility study of an overarching master plan. The air conditioning challenges in the exhibition rooms are intricate, influenced by their structural design and size. Notably, the

Figure 5. An exhibition room at the RMAH with a lacquered Chinese bed on display.

China gallery has many windows, with only the main hall's windows having light-filtering blinds. However, the intermediate room's openings, where the two largest lacquer pieces of the collection are displayed, have no light filtration. As for the Southeast Asia galleries, they lack temperature and humidity readings and are windowless.

Storage rooms

- <u>The “Schotsmans” storage</u>

The "Schotsmans” storage utilized by both Asian departments, is situated on the ground floor and accessed through a poorly insulated double wooden door. The storage area features two single-glazed windows facing an interior courtyard, allowing natural light. One window is equipped with bars and a broken fan. Illumination was provided by eight operational neon lights. The China/Japan/Korea department employs 36 closed metal cabinets, with designated storage space for panels and screens. The storage accommodated diverse materials, including wood, ceramics, stone, textiles, organic materials, etc., along with significant-sized objects. Metal cabinets were in place to shield items from light exposure. Notably, this storage lacked a thermo-hygrometer or humidifier.

- <u>The “Extrême-Orient” storage (EO)</u>

Acquired by the department in 2010, this storage facility is situated in a museum wing constructed in the 1980s, positioned just below the temporary exhibition room. Located at level -1, it is shielded from exposure to natural light (figure 6). Entry is facilitated through a double wooden door, and illumination was provided by neon lights, with half of them non-functional.

Figure 6. Image of the “Extrême-Orient” storage at the start of the project.

- <u>The “Indonésie”storage</u>

This storage facility housed artworks from China, Japan, and Korea, which were originally stored in the Schotsmans storage, predominantly consisting of organic materials. Regarded as the most stable storage space, it featured an outdated and inefficient humidifier. Two-thirds of the area was furnished with repurposed metal cabinets and furniture, while the remaining section accommodated wooden transport boxes containing armors and some large objects.

- <u>The “catacombs” storage</u>

Situated in the basement, this storage area has been unattended for an extended period and poses accessibility challenges. The conservation conditions are dire, with no available records of temperature or humidity. A sign on the access door indicates microorganism contamination since January 2017, leading to restricted access. The clutter in the reserve complicates object access and inventory creation. Observations identified initial signs of microorganism growth, the presence of pests, and a suspected woodworm attack. Collaborating with the museum's pest management company, initial measures were taken. The woodworm infestation was determined to be old. New anti-pest systems (for moths and rodents) were installed, and mold samples were cultured, with findings indicating inactivity.

Setting up a preventive conservation plan

To address the various challenges in spaces housing lacquered objects, several protocols were implemented, including the installation or replacement of thermohygrometers, humidifiers, and dehumidifiers, recording and data control, replacement of defective lighting, ventilation improvement, the development of an emergency plan, etc. Concurrently, a reorganization of the reserves was initiated, expediting the grouping of objects by material sensitivity, a process initiated in 2010. The most sensitive objects were relocated to the most stable storage room.

Regular manual recording of relative humidity and temperature data offered a comprehensive climate overview in each reserve, aiding in determining the most suitable space for preserving sensitive works. The EO reserve was selected to accommodate most lacquered wooden objects due to its stable climate. In the absence of compactus shelving, additional metal cabinets and shelves were repurposed from other departments. The layout was optimized, non-functional furniture was replaced, creating extra storage space. The works were reinstalled, maximizing space and improving conditions through the installation of plastazote© film, visual documentation of each cabinet, labeling, and rearranging inro to enhance their condition and accessibility (figure 7).

Figure 7. Detail of the “Extrême-Orient” storage room (left) and top view of the storage of the numerous inro (right) after reorganisation.

In addition to transferring objects to healthier reserves, an emergency plan was initiated to disinfect objects stored in the "catacombs." Conservation-restoration students were recruited to execute the plan. The first group of five students (2018) was engaged for durations ranging from 2 to 6 weeks, and a second group (2021) of two students worked for 4 weeks (figure 8). Professional supervision was provided, and a treatment protocol was established to systematize the process and ensure proper management and object monitoring.

Figure 8. A student disinfecting objects from the ‘”catacombs” storage room prior to relocation to a healthier reserve.

The first session successfully salvaged over 750 ceramic, stone, and metal objects from the "catacombs" storage. The second session focused on treating non-lacquered wooden objects, with over 200 items removed. A quarantine period was established for each disinfection campaign to ensure the effectiveness of the treatment. After six months of surveillance, the various objects could return to their new reserves.

3.4. Selection of the lacquered objects to be further studied, cleaned and conserved

During the inventory and reorganization of the reserves, attention was given to objects eligible for an in-depth study and eventual cleaning and conservation treatment. Selection criteria included aesthetic value and suitability for exhibition in the museum. Ultimately, eight objects were chosen, as depicted in figure 9. These objects underwent detailed studies, including an analysis of their chemical composition. Following a second round of selection, four objects were retained for cleaning and conservation treatment (highlighted in red in figure 9). Additionally, one object, rediscovered in a severely damaged and non-inventoried state, was identified as a suitable test case (Chinese shelves-etagere, indicated in purple in figure 9). The following section provides a more comprehensive description of the selected objects.

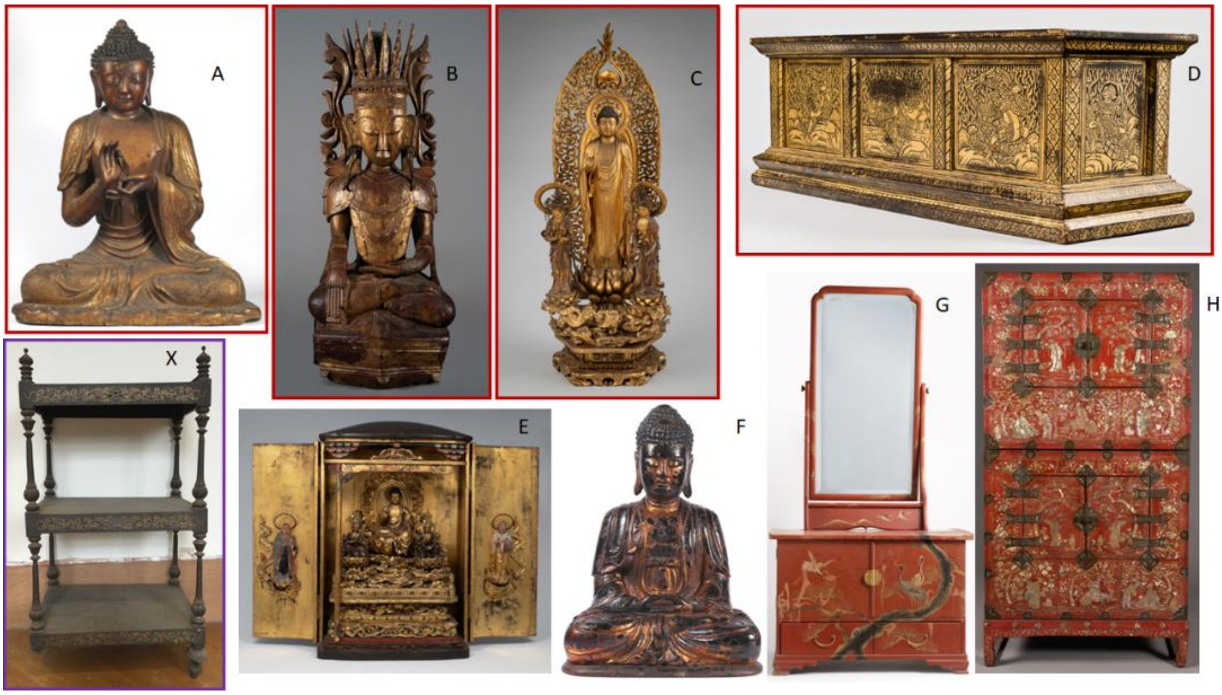


Figure 9. The meticulous selection process for lacquered objects, culminated in the identification of eight items, a number further reduced to four, highlighted in red for in-depth examination, and subsequent cleaning and conservation treatment. Additionally, a Chinese etagere, denoted by a purple outline, emerged as a noteworthy inclusion—a depreciated yet invaluable specimen from the collection of the RMAH, serving as a practical and insightful test object.

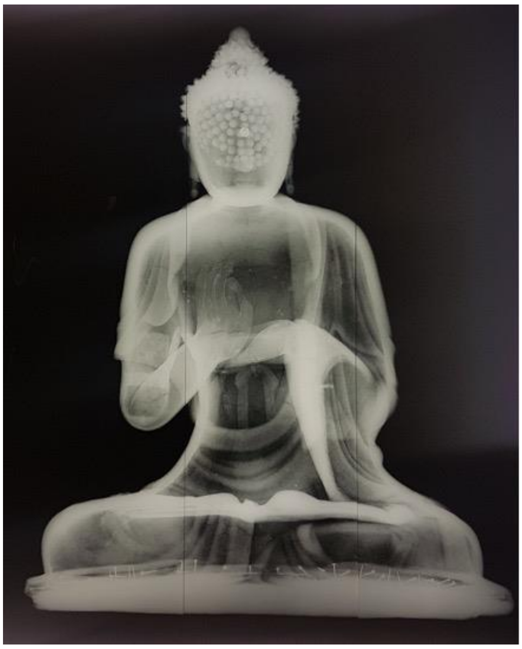
A) Buddha, China, 17th Century, inv.: EO.1706

A.1. Historical and stylistic research

This sculpture of a seated Buddha deity making the argumentation gesture entered the collections of the RMAH in 1955. Correspondence between Madame L. Rosseels (the seller) and the chief curator, Count de Borchgrave d'Altena, provide precise details about the acquisition of this large sculpture (113cm tall). Recorded in the original inventory as a “gilt lacquered wooden sculpture”, the correspondence between the chief curator and the curator Mlle. Houyoux mentions “...a sculpture in gilt lacquered wood on a thick layer of stucco. The piece is good, seemingly dating back to the late Ming period (17th century) and originating from the Verbert collection.” (Léon Verbert (1879-1941), collector of Asian art). Although the initially requested price was 20,000 francs in December 1954, it was later reduced to 18,000 francs, and the sculpture became part of the collection in 1955.

This statue is believed to represent Amitabha making the argumentation gesture (*vitarka mudra*). The right hand is vertical, palm facing forward, with the thumb and index finger touching, the left hand is inclined and slanted, palm facing inward, with the thumb and index finger touching. This gesture symbolizes Buddha’s first sermon, his initial public teaching delivered before his five ascetic companions whom he encounters in the deer park. He is seated in the lotus position (*padmasana*), his legs folded at the knees, with crossed feet soles facing upward. He is dressed in a richly adorned robe decorated with relief designs.

A.2. Technological and scientific study



Originally categorized as “gilt lacquered wood” in the initial inventory, further examination of this sculpture revealed distinctive features. Notably, its relatively light weight for a wooden sculpture of its size, challenges in sampling layers due to a thick preparation layer, and the unexpected presence of textile. Upon placing the sculpture on its back, an opening beneath the wooden base became apparent, prompting a closer investigation.

Initial observations, coupled with an examination of lacunae edges, initiated an expanded inquiry. Radiography conducted at KIK-IRPA confirmed suspicions regarding the use of the **dry lacquer technique** (夾紵 *jiazhu*) in crafting this sculpture. The dry lacquer technique involves molding a sculpture using numerous layers of cloth soaked in lacquer.

Radiographic analysis unveiled a cavity throughout the work, showcasing the thickness of the multiple layers constituting the dry lacquer. Furthermore, the examination identified the presence of nails securing the wooden panel closing the cavity.

Once the structure of the sculpture was better understood, examinations of the decorative lacquer layers were conducted. Samples were taken to prepare cross-sections and to carry out scientific analyses to understand the lacquer composition (see further paragraph 3.8). However, due to the impossibility of taking a sample containing all layers, stratigraphic sampling was carried out within and on the edge of a lacuna. This study highlighted the succession of more than 7 textiles, alternating layers of lacquer and preparation layers. Further analysis of the textile fibres by the laboratories of KIK-IRPA identified the use of jute fibres.

A.3. Condition report of the object

While the sculpture exhibits numerous fissures and cracks, it is structurally sound, showing no signs of insect infestation or micro-organism damage. Notably, several historical interventions and alterations are discernible upon close examination.

- Heavy dusting and soiling of the entire lacquered surface and the polychromy of the hair
- Lifting of the upper layers of lacquer
- Gaps and detached elements in the hair
- Lifting of all the layers of dry lacquer (preparation layers and lacquer layers)
- Lot of cracks
- Old, non-esthetic interventions
- Lacunae

B) Buddha, Burma, 20th Century, inv.: EO. 3124

B.1. Historical and stylistic research

Acquired by Mr. Jean Leroy during his extensive travels in Asia and Southeast Asia, this sculpture joined the museum's collection in 2018 as part of his generous donation. Precise information regarding the history or acquisition of this sculpture could not be found in his travel journals.

This 165 cm tall sculpture depicts Buddha seated in the *bhumisparsa virasana mudra*, the Earth Witness posture. This posture symbolizes an important moment in the life of the historical Buddha (Shakyamuni), when he called upon the Earth to bear witness to his faith and determination. In this pose, he is depicted seated with the right leg folded over the left in a lotus position, with the right hand resting on the right knee to touch the Earth. This lacquered wooden sculpture shows most of the characteristics of the Burmese sculpture: a rounded face with a broad forehead that tapers to a small chin; delicate, small, and arched eyebrows; large hand and feet, earlobes extending to the shoulders; a band encircling the hairline. Buddha is draped in a monastic robe covering his shoulders, while numerous jewels adorn his crown, wrists, and ankles.

B.2. Technological and scientific study

Sculpted in the round, the main body of this object is made from a single piece of wood. The other elements, such as the decoration on the crown, the earrings, and the hands, appear to be added elements. The obverse side is very detailed, while the reverse side has no detail at all. Some elements appear to have been modelled using a paste (?). There is a hollow part under the base, probably used to fit the sculpture onto an altar. The chemical composition of the lacquer is summarized in paragraph 3.8.

B.3. Condition report of the object

The sculpture is structurally sound, devoid of significant structural issues. However, the lacquer layer and wood exhibit several cracks, particularly noticeable in the hands. The crown displays loose elements, which have been previously affixed using grey silicone. Additional historic interventions are visible in areas such as the face, knees, crown, and chest.

The overall condition of the sculpture is characterized by a gentle creasing across the lacquer surface, and a layer of earth is observed on the back.

C. Triade, Japan, 18th century, inv. J.3319

C.1.Historical and stylistic research.

This Amida Raigo triad represents Amida descending from the Pure Land on a cloud, making the gesture of charity and that of teaching. He is accompanied by his two attendants Seishi, hands in prayer, and Kannon who usually holds the seat of the lotus for the soul of the dead. This ensemble is part of the bequest Peeters, 1957.

This finely sculpted ensemble portrays Buddha and his attendants standing on lotus flowers, themselves set upon carved clouds. The central figure representing Amida wears the monastic robe covering both shoulders, revealing a portion of the torso. His face displays all the typical features of Buddha representations: the hair depicted in tight curls (108?), with the *ushnisha* (protuberance) at the top of the skull; the *urna*, or third eye symbolized by an embedded stone; elongated earlobes; and closed eyes signifying meditation. The attendants are bodhisattva, they are wearing the monastic robe, revealing more of their torsos. Both bear a halo, a crown, and numerous metal-inlaid jewelry adorned with glass beads.

C.2. Technological and scientific study

The triad is composed of seven movables elements: the base, the Amida, the halo (surrounding the head and the body, rendered in gold to represent the divine light emanating from the being), the two acolytes: Kannon and Seishi both with movable halos. Each of the movable elements is composed of an assembly of several wooden pieces. The lotus flowers appear to be made from a central piece on which the sculpture is placed, while the petals are separately sculpted and then adhered. In some places a textile has been laid directly on the wood.

The three figures seem to be sculpted in multiple parts: the Buddha's inlaid eyes are crafted using the *gyokugan* technique. This method involves creating cavities for the eyes and placing a glass cup onto which a tissue paper or a painted representation of the eye is affixed. The first step of the investigations has been done by naked eye, sometimes with help of a microscope, revealing traces of decoration in some places (figure 10).

These observations have been completed with scientific analyses (cross sections, layer-by-layer sampling, Py-GC/MS and SEM-EDx; see paragraph 3.8).

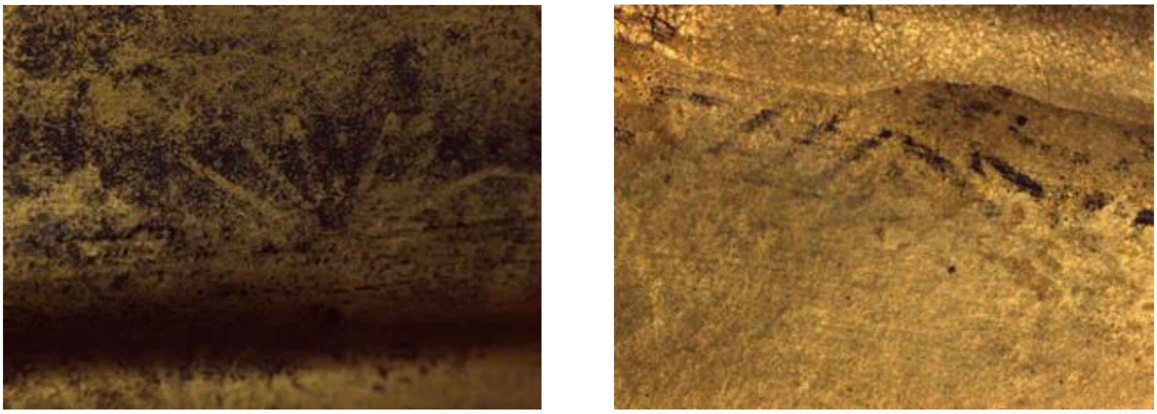


Figure 10. In some parts of the Buddha traces of decorations can be observed.

C.3. Condition report of the object

The overall conservation condition of the Amida Raigo triad is relatively good, yet it bears noticeable alterations primarily resulting from previous interventions. These interventions, including partial regilding and more invasive restoration attempts, have unfortunately caused deterioration.

Issues arising from past interventions are evident in tension-induced cracks and material ruptures caused by collages. Additionally, the incorporation of elements such as nails, screws, and metal wires has led to lifting and lacunae. Some interventions overflow, contributing to both structural and aesthetic deterioration. Accumulation of dust is observed across all elements of the sculpture, with more pronounced soiling on the metallic jewelry of the acolytes.

Notably, excessive retouches using bronzine, now completely oxidized, have resulted in a dark greenish appearance, disrupting the aesthetic coherence of the artwork.

D. Manuscript box, Thailand, 20th century, inv.: EO.3129

D.1. Historical and stylistic research.

This box is also part of the Jean Leroy donation (cf.sup.) and entered the collection in 2008. To date, no information has been found in the archives available at the RMAH. Traditionally used to store prayer books, these boxes are richly decorated using a technique that combines a black lacquer ground with gold.

D.2. Technological and scientific study

The box is a crafted assembly of wooden planks, typically teak, with some intricately moulded pieces. It comprises two main components: the body and the lid. The decorative technique employed is a traditional Thai method known as *lai rot nam*, which translates to "water-sprinkled ornament" (Bas, 2021).

In the execution of this technique, multiple layers of black lacquer are successively applied. Once the final layer is in place, a stencil is utilized to transfer the design. The artist employs a yellow soluble ink to delineate the elements intended to remain black. A concluding layer of lacquer covers the entire surface to receive the application of gold leaf. In the final step, the areas marked with yellow ink are delicately moistened using blotting paper, dissolving this layer and revealing the intricate design.

For the chemical composition reference is made to paragraph 3.8.

D.3. Condition report of the object

This manuscript box is in very good condition, except for a few losses and raised areas. The most concerning issues involve the shellac layer applied over the lacquer. This layer is oxidizing and beginning to turn yellowish, which in the long term could disturb the reading of the designs. It would be advisable to lighten or even remove this layer for better long-term conservation.

X. Chinese etagere, China, 20th century,

X.1. Historical and stylistic research.

This free-standing display furniture with three shelves and an intermediate pilaster, is richly decorated with plants and birds and appears to be a product typically crafted for export. This furniture was discovered in the attic of the museum. It was not recorded in any inventory and thus not part of the collection. However, the label placed under the first shelf informs us that this shelf originates from Foochow (Fuzhou, China) and was exhibited at the International Universal Exhibition in Liège (1905).

CHINE.

Objet : Etagère en laque
Numéro : 223.
Provenance : Foochow
Valeur : Fco 120.00
Classe : 69.

Apart from the province, the label mentions a number (223) referring to the special catalogue of the objects exhibited in the Chinese section of the Liège Exhibition. It is likely that an error occurred in the numbering because the catalogue does not mention this number in the furniture section. However, the description of N° 233 in the catalogue could very well correspond to this object: ”a fancy shelf in fawn-colored lacquer, decorated”. Apart from that, the provenance is unclear. No trace on how the object was brought to the museum could be found.

X.2. Technological and scientific study

The three shelves and intermediate pillars of this etagere are detachable, as are the legs. All elements are made of wood, and a layer of textile is observed between the support and the decoration layers. Several layers of lacquer appear to have been applied, and under the soiled layer, decorations of plants, insects, and birds van be observed. These colourful and gilded decorations are painted and in relief. More information on the lacquer composition can be found in paragraph 3.8.

X.3.Condition report of the object

The compromised state of preservation of this object can likely be attributed to the adverse storage conditions it endured over many years. Prolonged exposure to natural light has severely impacted the decorative layer, now obscured by a thick layer of dust and pigeon droppings (figure 11). Cracks at the assembly points suggest that the piece has undergone significant fluctuations in temperature and humidity.

The object has deteriorated to such an extent that it can be deemed a total loss. Given that it exhibits all the characteristics of the issues under investigation in the research project, a collective decision between the museum's management and the curator has been reached. It has been chosen as a focal point for research purposes, serving as an application context for the cleaning techniques studied within the framework of the PHySICAL research project.

Figure 11. Details of the Chinese shelves showing a thick layer of dust and the poor condition.

3.5. Preparation of the mock-up samples

Most of the study is first conducted on mock-up samples, followed by test on the Chinese etagere before tackling the cleaning and conservation of the selected objects.

Objects decorated with lacquer contain numerous layers and materials (Brunskog and Miyakoshi, 2021; Han et al., 2023; Heginbotham and Schilling, 2011; Webb et al., 2016). Typically, foundation layers consist of inorganic clay powders mixed with organic binding media (Niimura and Miyakoshi, 2000; Webb, 2000), such as Asian lacquer, proteinaceous materials, or polysaccharides (Heginbotham and Schilling, 2011; Schilling et al., 2016; Webb, 2000). In addition to this, Asian lacquer layers can be enriched with drying and essential oils to adjust their working properties and enhance the quality of the resulting film. Pigments may also be introduced to modify the colour (Han et al., 2023; Webb, 2000).

A significant number of mock-up samples were prepared using the three different lacquer types (urushi, laccol and thitsi), to which an ingredient was consistently added based on literature data and the analyses of the lacquer objects (see section 3.8) to create representative samples. A summary of the lacquer composition of the mock-ups is given in table 1. The most crucial ingredients, of course, being the Asian lacquers. Japanese lacquer from *T. vernicifluum* (urushi) was acquired from Watanabe-Shoten, Tokyo, Japan, in 2017. The raw lacquer sap was harvested and *kurome* processed in Japan. Taiwanese *T. succedaneum* (laccol) lacquer, processed using a similar technique to *kurome*, was obtained as samples of high-quality lacquer sap and came from JC Cultural Creative Service CO., LTD, Taiwan in 2017. The lacquer sap used was harvested and processed in Taiwan. Thai *G. usitata* (thitsi) lacquer was acquired from the Thailand Royal Forest Department in 2017. The raw lacquer sap had not undergone any pretreatment, which is common for *G. usitata* lacquer, unlike *T. vernicifluum* and *T. succedaneum* lacquer saps. Dry season, November-March harvest, sap is used, which has less water in its composition for high quality *G. usitata* lacquer work. The *G. usitata* lacquer sap was gathered in Mae Hong Son province, Thailand, in January 2016. All the lacquer saps were pure uncoloured reference materials, and before preparing the mock ups, the materials were verified using Py-GC-MS.

Table 1. Composition of the lacquer mock-up samples.

Formula nr.	Formula name	Composition
#1	PHy-U	Japanese (transparent) kijiro urushi, Watanabe Syoten A09
#2	PHy-UO	Chinese, processed in Japan (transparent with added linseed oil) syuai urushi, Watanabe Syoten A04
#2B	PHy-UOp	Japanese (transparent) kijiro urushi, Watanabe Syoten A09 mixed with 15% perilla oil, Kremer
#3	PHy-UOB	Chinese, processed in Japan, Japanese (black urushi with linseed oil) kuro nuritate, Watanabe Syoten A05
#3B	PHy-UOpB	Japanese (black urushi) roiro, Watanabe Syoten A10, mixed with 15% perilla oil, Kremer
#4	PHy-UOC	Chinese, processed in Japan, (transparent with linseed oil) syuai urushi, Watanabe Syoten A04, mixed with cinnabar pigment, Watanabe Syoten G03, ratio lacquer/pigment 1/3
#5	Phy-UB	Japanese (black urushi) roiro, Wtanabe Syoten A10
#6	PHy-L	Taiwanese transparent laccol, JC Cultural Creative Service CO., LTD
#7	PHy-LO	Taiwanese transparent laccol, JC Cultural Creative Service CO., LTD, mixed with 15% perilla oil, Kremer
#8	PHy-LOB	Taiwanese black laccol, JC Cultural Creative Service CO., LTD, mixed with 15% perilla oil, Kremer
#9	PHy-LOC	Taiwanese transparent laccol, JC Cultural Creative Service CO., LTD, mixed with 15% perilla oil (Kremer), and cinnabar pigment, Watanabe Syoten G02, ratio lacquer/pigment: 1/3
#10	PHy-CEL	Taiwanese black laccol, JC Cultural Creative Service CO., LTD, mixed with 15% perilla oil and 10% cedar oil, Kremer
#10B	PHy-LOCO	Taiwanese transparent laccol, JC Cultural Creative Service CO., LTD, mixed with 15% perilla oil and 10% cedar oil, Kremer
#11	PHy-T	Thai dry season thitsi, Royal Forest department
#12	PHy-TO	Thai dry season thitsi, Royal Forest department, mixed with 10% tung oil, Kremer
#13	PHy-TC	Thai dry season thitsi lacquer, Royal Forest department , mixed with cinnabar, Watanabe Syoten G03
#14	PHy-TOW	Thai dry season thitsi lacquer, Royal Forest department mixed with 5% tung oil, Kremer and 5% wood oil, Etsy

All the lacquer saps underwent an initial filtration process using Japanese Miyoshinogami filtering paper, obtained from Watanabe-Shoten, Tokyo, Japan. The lacquer was, subsequently meticulously applied to 2mm thick borosilicate glass slides using an Elcometer 3525 film applicator, obtaining single layer mock-up samples. The wet film thickness for the lacquer layers was uniformly set at 50 µm. To initiate the enzyme catalysed polymerisation, the lacquer films were polymerised in airtight polypropylene containers under controlled elevated relative humidity (RH) conditions, at 70-80% RH.

The microclimate within these containers was carefully established using Art Sorb 70% RH preconditioned silica gel for both the *T. vernicifluum* (urushi) and *T. succedaneum* (laccol) lacquer mock-ups. Silica gel M, conditioned at 80% RH, was employed for the *G. usitata* (thitsi) lacquer samples. Maintaining a stable temperature of 21 °C inside the containers, both RH and temperature were continuously monitored through calibrated LOG210 dataloggers from Dostmann electronic GmbH. The Art Sorb, Silica gel M, and data loggers were all sourced from Long Life for Art, Eichstetten, Germany. The mock-up samples were allowed to polymerise over a period of 3 months. In figure 12 a selection of the polymerised single layer mock-up samples are shown.

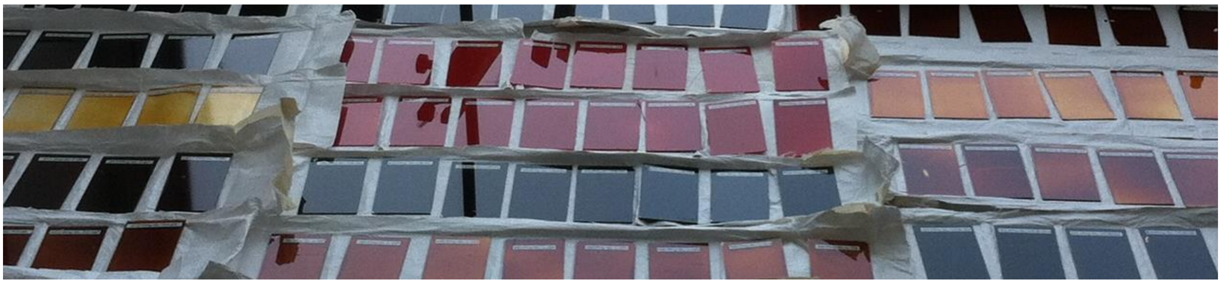


Figure 12. A selection of single layer mock-up samples of Asian lacquers prepared during the PHySICAL project.

The same procedure as for these pure lacquer samples was followed, with the addition of extra ingredients to eventually assess the role of these components in the aging processes or how these additional ingredients affect the cleaning result. In table 1 the preparation of the remaining samples is outlined. In addition to the black lacquer samples, a number of red lacquer samples were also prepared, as shown in figure 13, representing the two most common lacquer colours.

In some experiments, free film samples were used, obtained by delicately removing the single-layer samples from the borosilicate glass substrate using a razor-sharp blade of a woodworker's plane. The wet film thickness was set at 10 µm for the free film mock-ups.

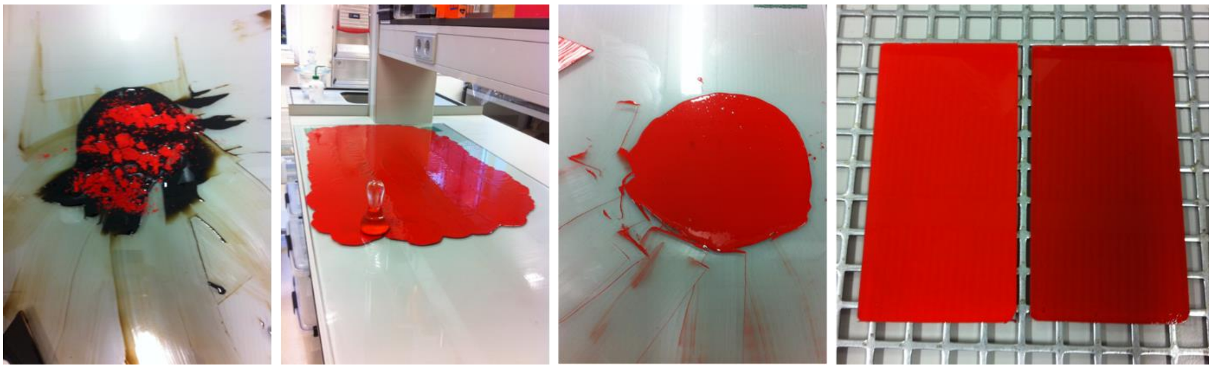


Figure 13. Preparation of a red lacquer by the addition of red vermillion.

3.6. Artificial ageing of the mock-up samples

The natural aging of the sequential layer structure of Asian lacquers is a gradual process that occurs over many years, influenced by factors such as sunlight exposure, humidity fluctuations, and other environmental conditions. To mimic these conditions artificial ageing of the mock-up samples is needed. A slightly modified version of the ageing method outlined by Han et al. (Han et al., 2020) was used to age the mock-ups. Typically, naturally aged, lacquered surfaces exhibit centuries of natural aging, and precise storage conditions are often unknown. Establishing an equivalent in years for artificial aging regimes can be challenging. To overcome this, efforts were made to 'fingerprint' the molecular degradation process of lacquers taken from naturally aged surfaces. The mock-ups underwent, stepped aging. After each step of the ageing regime the samples were monitored using Py-GC-MS until the artificial results matched naturally aged object analyses. This process resulted in the following artificial ageing regime.

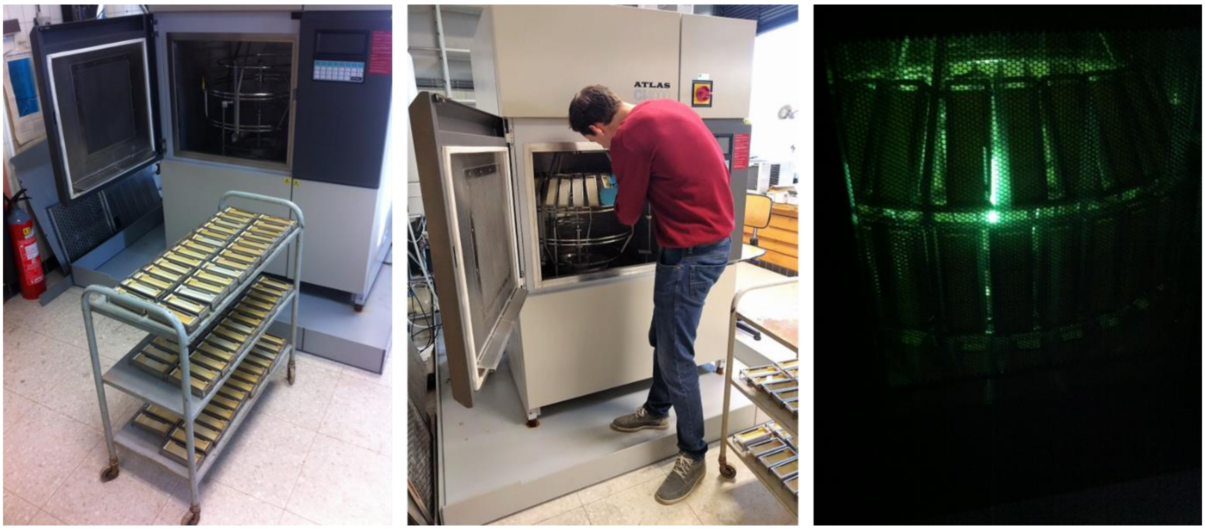


Figure 14. Filling of the Weather-Ometer, using custom-made Lego sample holders, for artificial ageing of the mock-up samples.

A Ci4000 Atlas Weather-Ometer system was employed, equipped with a water-cooled Xenon arc light source (6500W) (figure 14). The light source was operated at 0.50W/m2 and fitted with a sodium borosilicate glass inner filter (type S65) to filter out part of the UV light. To block a portion of the infrared wavelengths, a sodium lime glass with a CIRA coating outer filter (type S65) was used. This filter combination allowed for an irradiance range between 340 and 800 nm. The black panel temperature was maintained at 40 °C, the chamber temperature at 30 °C, and the relative humidity inside the chamber was kept at 65%. To control the relative humidity, a moisture nebuliser was utilised, spraying fine water droplets into the chamber, which might end up on the lacquer surfaces, causing unfavourable aging phenomena. The simulation aimed to replicate indoor aging conditions, and to protect the samples from water damage, custom-made sample holders with 2mm thick borosilicate glass slides in front of the samples were used, see figure 15. In total, the samples were subjected to 576 light hours, resulting in approximately 1039 kJ and an illuminance of around 93,000 lux.

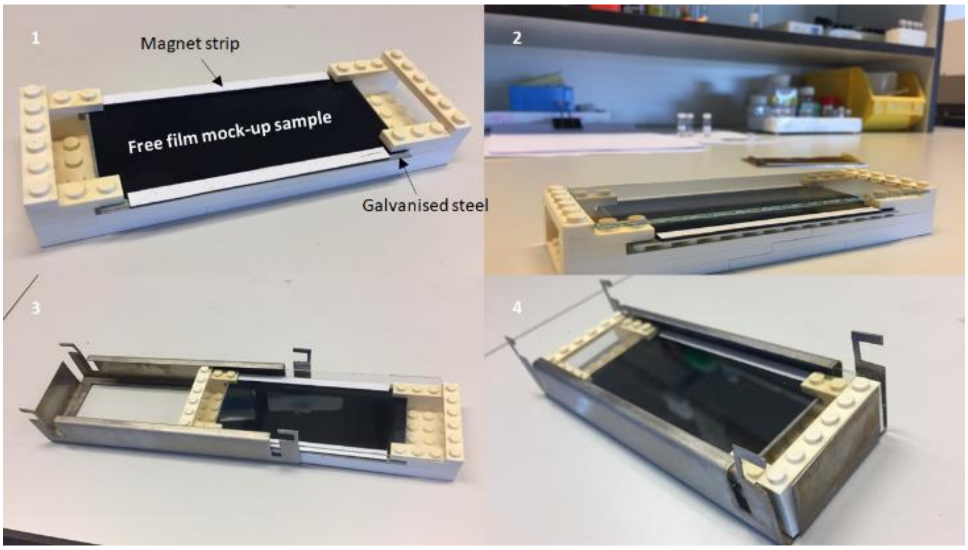


Figure 15. Custom-made Lego sample holders shielded with borosilicate glass slides to protect the samples from water damage. To place free film samples in an upright position, required for fitting the samples in the weather-Ometer ageing machine, they were placed on galvanised metal plates and fixed with magnet strips.

3.7. Optimising the analyses of Asian lacquers using Py-GC-MS

Identifying and distinguishing Asian lacquer polymers presents a formidable challenge, yet it holds significant relevance, particularly in gaining insights into polymer degradation. The knowledge on the chemical composition of the lacquer polymers, prior cleaning, was thereby shown to play an essential role for assessing the potential impact conservation treatments can have on the lacquer surfaces. To improve the characterisation of artificially aged polymers from *Gluta usitata* (thitsi), *Toxicodendron succedaneum* (laccol), and *Toxicodendron vernicifluum* (urushi), an exhaustive study using pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was conducted. We delved into the effects of pyrolysis mechanisms by using different pyrolysis temperatures. We also evaluated the application of two online derivatisation techniques to study the efficacy of the derivatisation step and to compare the obtained analytical results based on e.g. molecular selectivity, peak areas of the compounds studied and repeatability. The derivatisation methods employed included trimethylsilylation with hexamethyldisilazane (HMDS) and thermal hydrolysis and methylation with tetramethylammonium hydroxide (TMAH).

The findings revealed that a gradual increase in flash pyrolysis temperature proved valuable in distinguishing primary pyrolysis reactions from the formation of secondary products. This approach provided invaluable insights into reconstructing the polymeric structure of the lacquers based on the identified pyrolysates and peak areas obtained at specific pyrolysis temperature ranges.

We also discovered that derivatisation of polar compounds, typically having COOH and/or OH functional groups, within the samples was imperative for obtaining reliable data. While results using HMDS were somewhat inferior to the data obtained with TMAH in terms of derivatisation efficiency and overall analytical repeatability, HMDS exhibited greater selectivity toward alkenylcatechols. The selectivity towards alkenylcatechols was in particular noticeable for alkenylcatechols associated with the *T. succedaneum* (laccol) polymer and when analysing carbohydrates in samples of all polymeric types. By reducing the split flow, we significantly improved the derivatisation efficiency with HMDS. This method also allowed for better identification of resorcinol isomers in *G. usitata* (thitsi) polymers.

Detailed results of this study can be found in the publication on optimizing Py-GC-MS for Asian lacquer analyses (Veenhoven et al., 2023)

3.7.1. Asian lacquers from a chemical perspective

Asian lacquers are natural polymers, secreted as tree saps by species belonging to the Anacardiaceae family, which were historically primarily found in East Asia. These saps undergo a hardening process when exposed to air and elevated humidity conditions. The primary types of Anacardiaceae polymers are referred to as urushi, laccol, and thitsi, as mentioned before.

Lacquer saps are complex water-in-oil emulsions, comprising around 30% water, 7% polysaccharides, 2% glycoproteins, 1% enzymes, and a mixture of substituted catechols, making up 60-65% of the composition. The ratios of these components can vary both qualitatively, depending on the specific botanical source, and quantitatively, based on the timing of sap harvesting (Lu and Miyakoshi, 2015; Tamburini, 2021; Webb, 2000).

In mildly oxidised lacquer sap, dimerisation occurs through a complex oxygen oxidative mechanism, primarily catalysed by enzymes such as peroxidase, stellacyanin, and, most notably, laccase (Kumanotani, 1978; Wan et al., 2006). Stellacyanin and laccase are copper-containing enzymes that facilitate the oxidation of the hydroxyl groups within the catechols, resulting in the formation of a radical structure, which is subsequently converted to reactive semiquinone radicals (Kumanotani, 1995; Lu and Miyakoshi, 2015). These radicals can either react with each other to produce carbon-to-carbon (C-C) bonded biphenyls or attack the methylene groups in the alkenyl side chains to form covalent C-C or carbon-to-oxygen-to-carbon (C-O-C) bonds with the side chains. Enzyme-catalysed dimerisation plays a pivotal role in the formation of dimers, trimers, and oligomers in Anacardiaceae lacquer saps.

Through repeated enzymatic and autoxidative dimerisation processes, the lacquer polymer gradually becomes insoluble in organic solvents, leading to significant challenges in molecular analysis. The nature of the cross-links formed also makes it impractical to employ wet chemical pretreatments for breaking down the lacquer polymer into its individual monomers.

Upon aging by photo-degradation processes, lacquer surfaces, however, become extremely vulnerable, leading to physico-chemical alterations that modify the original properties. Visually, these alterations manifest as a loss of the lacquer's original gloss, while microcracks become visible under the microscope. These microcracks disrupt the specular reflection of light on the lacquer's surface, affecting its characteristic mirror-like appearance. These changes are attributed to the formation and efflorescence of polar and acidic degradation products. Consequently, the lacquered surface exhibits an increasing hydrophilic character as it ages. This hydrophilic character can be nicely illustrated by applying a water droplet to both a non-aged lacquer and an aged lacquer surface (figure 16). A non-aged lacquer generally exhibits a more hydrophobic character, where the surface tension of the droplet remains high, giving it a spherical shape. Due to the increased hydrophilic nature of the aged lacquer, the droplet spreads out, covering a larger surface area.

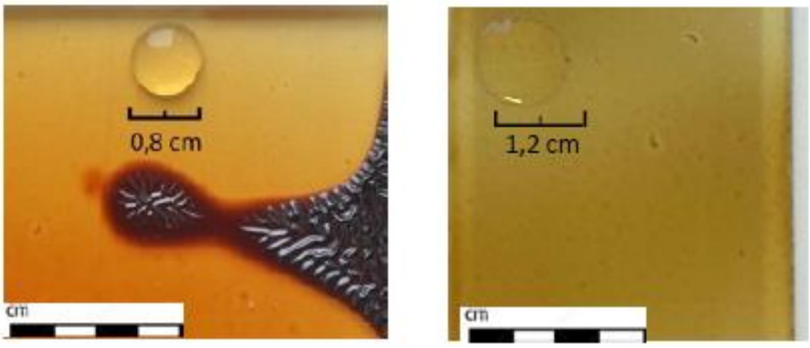


Figure 16. A water droplet in contact with a hydrophobic non-aged urushi lacquer (left) and an aged urushi lacquer (right).

3.7.2. Py-GC-MS with derivatisation

Derivatisation involves the conversion of the hydroxylic and carboxylic groups into less polar moieties, enhancing the volatility of the pyrolysates. Two widely used derivatisation methods are alkylation and trimethylsilylation (TMS). Alkylation can be achieved through thermally assisted hydrolysis and methylation (THM) with tetramethylammonium hydroxide (TMAH), which methylates the carboxylic and hydroxylic functional groups and transesterifies esters present in the sample (Decq et al., 2019; Schilling et al., 2016; van Keulen, 2009). Hexamethyldisilazane (HMDS) is a common silylation reagent used in combination with Py-GC-MS, whether offline or in situ (Fabbri et al., 2003a; Kuroda, 2000; Mattonai et al., 2016). HMDS has shown its effectiveness in combination with Py-GC-MS for the identification of Anacardiaceae lacquers (Tamburini et al., 2019, 2017, 2016, 2015a, 2015b). Compound identification is typically robust with TMS derivatives, producing distinct mass spectra.

HMDS has, however, limitations due to its weaker silylating donor capability, especially when considering the brief contact time during the online pyrolytic process. Additionally, steric hindrance issues arising from the larger size of TMS groups can negatively impact derivatisation, leading to partially derivatised pyrolysates and resulting in complex pyrograms and less repeatable measurements.

Another critical aspect in a Py-GC-MS setup is the pyrolysis temperature. For the analysis of Anacardiaceae lacquers, pyrolysis temperatures ranging from 400 to 550 °C are frequently reported and generally sufficient for polymer cleavage while maintaining monomeric specificity [(Lu et al., 2006; Ma et al., 2014a; Pitthard et al., 2010). This temperature range allows for qualitative identification and differentiation between Anacardiaceae lacquer types. Specific research inquiries may, however, necessitate the analysis of single molecules or molecular groups at their peak area optimum in a repeatable manner.

In this part of our research, we aimed to enhance the identification of the polymeric composition of light aged urushi, laccol, and thitsi polymers by systematically evaluating and optimising derivatisation procedures, pyrolytic conditions, and chromatographic parameters.

3.7.3. Py-GC-MS methodology

For a comprehensive understanding of the methodology, we refer to our published paper on this topic (Veenhoven et al., 2023), but we provide a concise overview of the main parameters here.

To simplify interpretation, we exclusively used pure lacquer mock-up samples. Film fragments of the lacquer mock-ups were carefully separated from their glass substrates using a scalpel and then placed in 1.1 mL glass vials with a 15 µL cone. Subsequently, these film fragments were ground into fine powder using a custom-made glass rod. All analyses were conducted using an EGA-PY-3030D multi-shot pyrolyser from Frontier Laboratories, coupled with a Trace 1310 gas chromatograph and an ISQ LT single quadrupole mass spectrometer, both manufactured by Thermo.

In each analysis, 80 µg of ground sample was loaded into a pyrolysis cup (Eco-Cup SF) from Frontier Laboratories. To derivatise the compounds in the sample, we employed a 3 µL solution containing reagent and an internal standard. For TMAH, a 5wt% solution in methanol was prepared, which contained 800 ng/mL tridecanoic acid, while for the HMDS reagent, 60 µg/mL tridecanoic acid was added. Reactive pyrolysis using TMAH or HMDS was performed in a helium-saturated atmosphere using single-shot, flash pyrolysis mode at fixed temperatures: 270 °C (for a single measurement on the T. *vernicifluum* polymer) and then at 300, 350, 400, 450, 480, 500, 550, 600, 650, and 700 °C. As an alternative to flash pyrolysis, we used ultrafast thermal degradation (UTD), where the temperature was ramped from 350 °C to 700 °C in 0.98 minutes (Decq et al., 2016). The interface temperature of the pyrolyser was held at 290 °C for all analyses. For each analysis a new sample was used, in other words: samples after being pyrolysed for the first time were not pyrolysed again using a subsequent higher pyrolysis temperature.

The analytical separations were conducted on a fused silica SLB-5ms capillary column from Supelco, which was 20m in length, with an inner diameter of 0.18mm and a film thickness of 0.18 µm, featuring a silphenylene polymer stationary phase. The initial GC oven temperature was set at 35 °C for 1.50 minutes, followed by a gradient increase of 60 °C per minute until 100 °C was reached. Subsequently, the temperature was ramped up to 250 °C at a rate of 14 °C per minute. Finally, the temperature was increased at a rate of 6 °C per minute to 315 °C, which was then maintained isothermally for 1.50 minutes.

In the mass spectrometer, electron ionisation was carried out at 70 eV, and the ion source was maintained at 250 °C. The mass spectrometer operated in scan mode within the m/z range of 29-600, with a cycle time of 0.2 seconds. The solvent delay was set at 1.10 minutes for THM analyses and 2.90 minutes for in situ silylation.

3.7.4. Concise summary of the results of the Py-GC-MS optimisation

Due to the intricate composition of Asian lacquers, we are unable to provide an in-depth discussion of the results detailed in our publication. Instead, we highlight a few key findings, followed by a general conclusion. For a more comprehensive understanding of the research, we encourage you to refer to the complete article.

In this study, an exploration of the behaviour of primary chemical groups generated during the pyrolysis of Asian lacquers, as a function of pyrolysis temperature (figure 17), facilitated the distinction between primary pyrolysis products and secondary thermal dehydration products. This differentiation allowed identification of the types of cross-links present in the structures of Anacardiaceae polymers. Additionally, the analysis provided evidence of the existence of an unpolymerized fraction and highlighted polymeric decomposition, particularly in the case of aging (urushi). Notably, the presence of alkylbenzenes emerged as a distinctive feature for the identification of thitsi polymers.

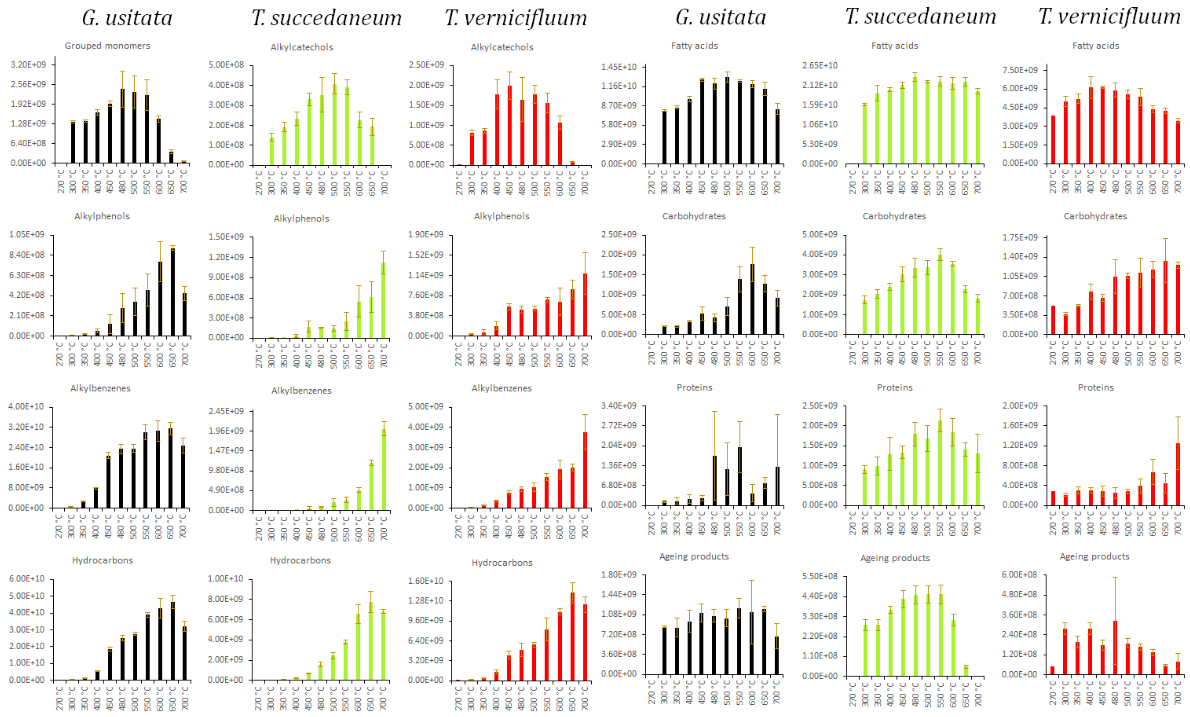


Figure 17. Integrated signal totals per molecular group resulting from THM-Py-GC-MS analyses on aged Anacardiaceae polymers.

In the aged lacquers, various degradation products were successfully identified. These products originate on the lacquer surface or within the polymeric matrix following exposure to sunlight, triggering photo-oxidation processes. This photo-oxidation leads to irreversible changes, resulting in the formation of diverse types of carboxylated compounds.

The degradation compounds were categorised into two main groups: those as "unpolymerised" or "free" compounds and those that were "trapped" within the polymeric matrix, or potentially formed covalent bonds with the polymeric structure. To release the compounds trapped in the polymeric matrix, pyrolysis of the polymer was necessary. In contrast, compounds covalently linked to the polymer required pyrolytic cleavage of the intermolecular bonds for their detection and identification.

The distribution of these various types of degradation products is summarised in figure 18.

The analysis revealed that the most significant integrated signals related to degradation products were observed in the thitsi polymer, followed by the laccol polymer, with the urushi polymer exhibiting the least photo-oxidation. In the case of urushi polymers, the identified compounds primarily consisted of unpolymerized compounds, which could be easily desorbed at very low temperatures (300-350 °C). This observation suggests that the aging of the urushi polymer predominantly occurs at the surface.

Further evidence supporting this observation comes from cross-sections of the three different aged lacquers observed under UV light. These cross-sections showed that the degradation manifested as a fine fluorescent layer in the urushi sample, while in the laccol and thitsi samples, the fluorescence was distributed throughout the samples. (figure 19).

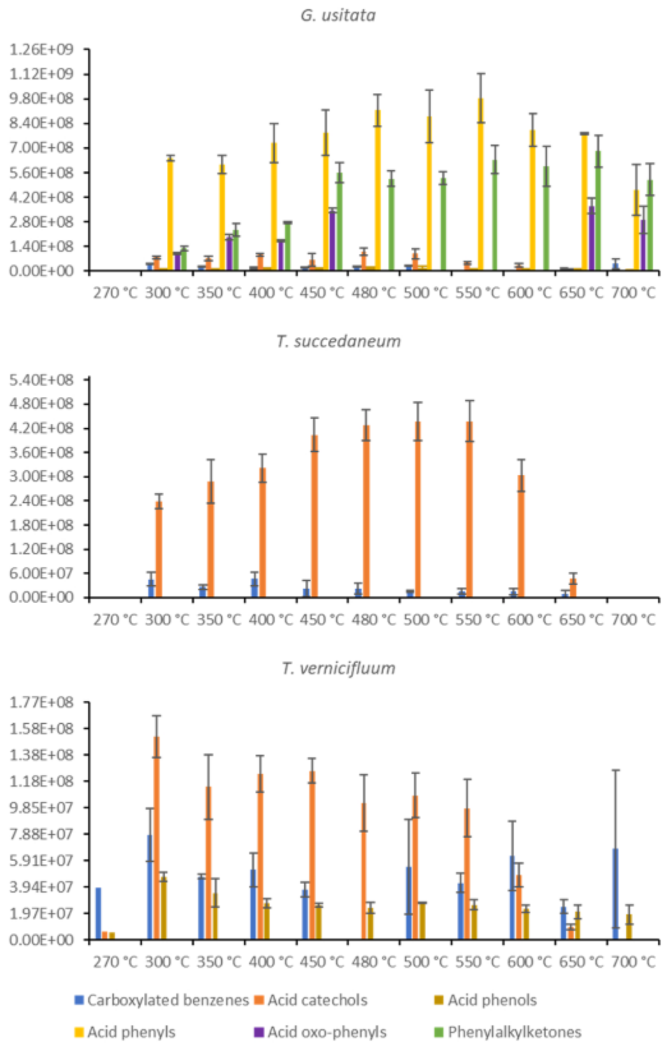


Figure 18. Distribution of degradation products in Anacardiaceae polymers.

A comparative analysis between two derivatisation reagents, namely TMAH and HMDS, to evaluate their performance, was also conducted. The objective was to qualitatively compare the derivatisation efficiency for a range of characteristic molecular classes. The results of this comparison can be seen in figure 20 and are summarised in table 2.

Findings indicated that, overall, the derivatisation efficiency using HMDS was notably lower compared to the results obtained with TMAH. This discrepancy may be attributed to the steric hindrance caused by the larger trimethylsilyl (TMS) groups formed by using HMDS. Additionally, the very brief contact time in the analytical 'flash' pyrolysis process might contribute to this difference, and it is possible that a combination of these factors plays a role.

Furthermore, the use of HMDS was detrimental for detecting degradation products that incorporate more than one derivatisable site. In general, the repeatability of the analyses was also better when using TMAH, both for characterising the aged lacquers and their degradation products.

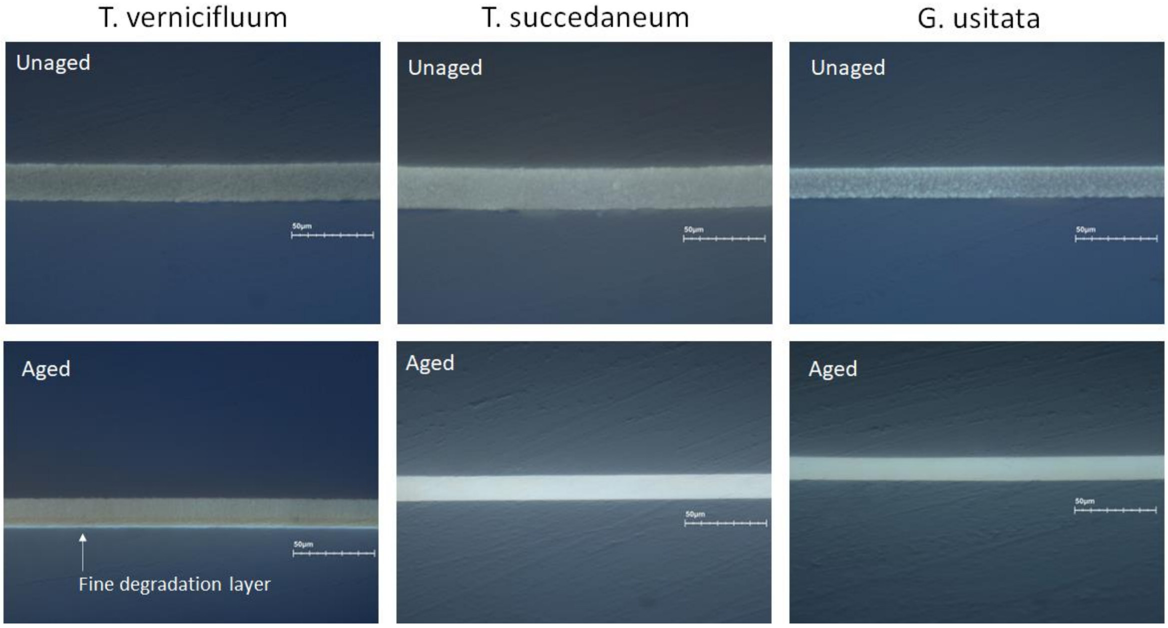


Figure 19. In the examination of single-layer samples under UV light, distinct differences between unaged and aged urushi, laccol, and thitsi lacquers are observed. Notably, an evident fine degradation layer was observed on the surface of the *T. vernicifluum* (urushi) sample. In contrast, for the two other lacquers, from *T. succedaneum* (laccol) and *G. usitata* (thitsi), the fluorescence appeared to be evenly distributed throughout the entire lacquer layer. This observation suggests that the degradation in these cases occurs not only on the surface but also within the lacquer layers.

The detection of e.g. carbohydrates with improved selectivity and sensitivity when employing in situ trimethylsilylation with HMDS, is possible. This enhancement was achieved by modifying the analysis conditions, specifically by increasing the in-situ contact time of HMDS with the lacquer sample by lowering the split flow. The extended derivatisation time allowed for a slower post-pyrolytic transfer and longer contact time with the HMDS reagent, resulting in an increased derivatisation yield, as demonstrated in figure 21.

As a consequence of these adjustments, it became possible to differentiate between urushi, laccol, and thitsi polysaccharides via in-situ silylation based on Py-GC-MS analyses. This achievement represents a novel development that, to our knowledge, had not been reported before. The improved detection of carbohydrates following silylation with HMDS prompted a more in-depth investigation into the polysaccharide characterisation. This study also involved a possible modification of the carbohydrates through polymerisation of the lacquers, and/or as a result of ageing processes. The polysaccharide modification was fully characterised and proved to be based on biochemical metabolism within Asian lacquers. Further details regarding this study can be found in section 3.9.

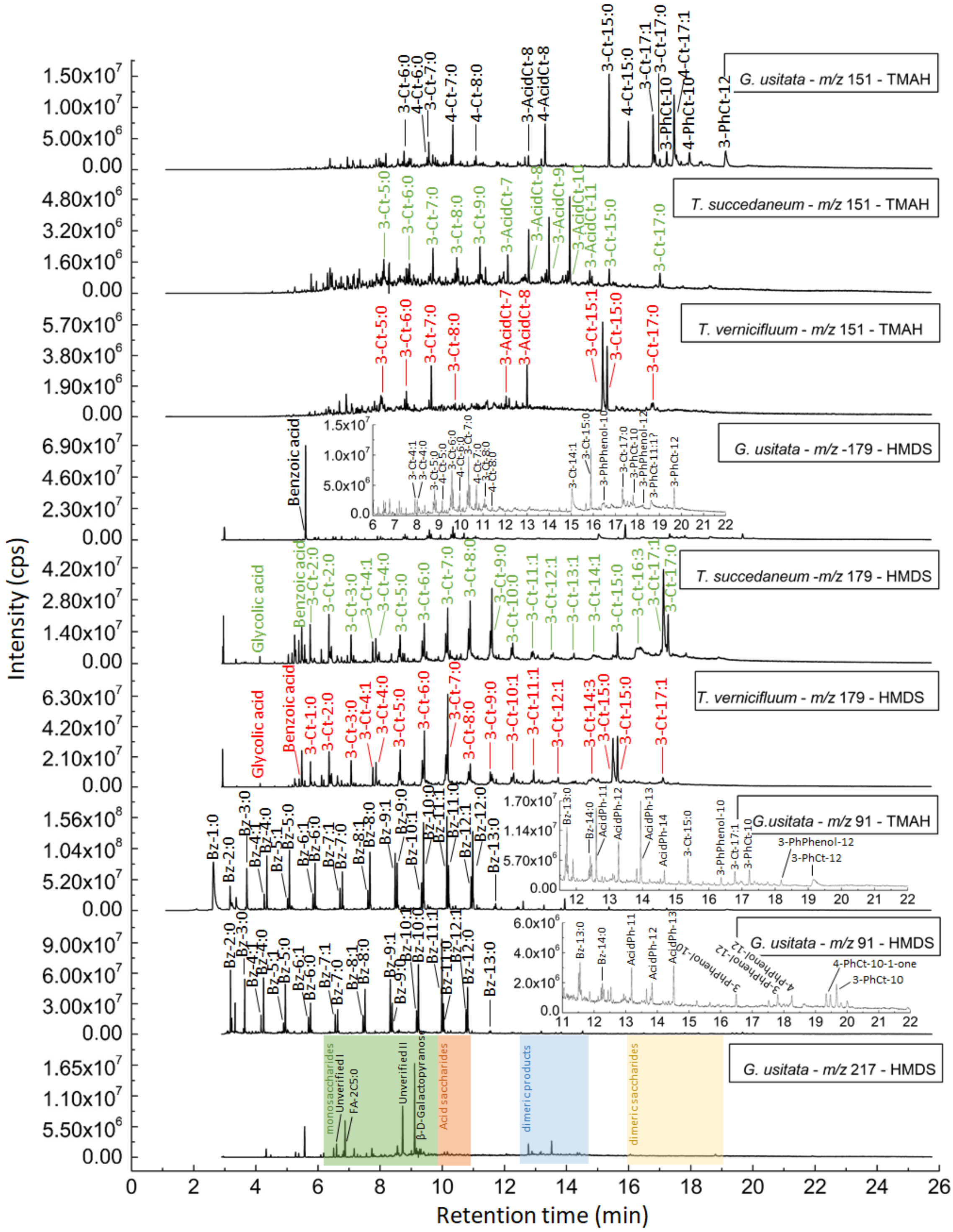


Figure 20. Extracted ion chromatograms obtained using THM(TMAH)-Py-GC-MS and TMS(HMDS)-Py-GC-MS on *G. usitata* (thitsi), *T. succedaneum* (laccol) and *T. vernicifluum* (urushi) polymers. The pyrolysis temperature was 500 °C for analyses *on G. usitata* and 550 °C for analyses on *T. succedaneum* and *T. vernicifluum* polymers. Analyses using TMAH represent completely derivatised compounds. For analyses performed using HMDS compounds are partially derivatised (single TMS groups). The peak labels correspond to the compounds listed in table 2.

Table 2. Compounds identified using THM and/or in-situ trimethylsilylation-Py-GC-MS analysis.

Molecular group	Compound name	Peak label	Molecular group	Compound name	Peak label
Alkylcatechols	Catechol	Ct	*Alkylbenzenes*	Methylbenzene	Bz-1:0
	3-methylcatechol	3-Ct-1:0		Ethylbenzene	Bz-2:0
	3-ethylcatechol	3-Ct-2:0		Propenylbenzene	Bz-3:1
	3-propylcatechol	3-Ct-3:0		Propylbenzene	Bz-3:0
	3-butenylcatechol	3-Ct-4:1		Butenylbenzene	Bz-4:1
	3-butylcatechol	3-Ct-4:0		Butylbenzene	Bz-4:0
	3-pentylcatechol	3-Ct-5:0		Pentenylbenzene	Bz-5:1
	4-pentylcatechol	4-Ct-5:0		Pentylbenzene	Bz-5:0
	3-hexylcatechol	3-Ct-6:0		Hexenylbenzene	Bz-6:1
	4-hexylcatechol	4-Ct-6:0		Hexylbenzene	Bz-6:0
	3-heptylcatechol	3-Ct-7:0		Heptenylbenzene	Bz-7:1
	4-heptylcatechol	4-Ct-7:0		Heptylbenzene	Bz-7:0
	3-nonylcatechol	3-Ct-9:0		Octenylbenzene	Bz-8:1
	3-decenylcatechol	3-Ct-10:1		Octylbenzene	Bz-8:0
	3-undecenylcatechol	3-Ct-11:1		Nonenylbenzene	Bz-9:1
	3-dodecenylcatechol	3-Ct-12:1		Nonylbenzene	Bz-9:0
	3-tridecenylcatechol	3-Ct-13:1		Decenylbenzene	Bz-10:1
	3-tetradecatrienylcatechol	3-Ct-14:3		Decylbenzene	Bz-10:0
	3-tetradecylcatechol	3-Ct-14:0		Undecenylbenzene	Bz-11:1
	3-pentadecenylcatechol	3-Ct-15:1		Undecylbenzene	Bz-11:0
	3-pentadecylcatechol	3-Ct-15:0		Dodecenylbenzene	Bz-12:1
	4-pentadecylcatechol	4-Ct-15:0		Dodecylbenzene	Bz-12:0
	3-hexadecatrienylcatechol	3-Ct-16:3		Tridecylbenzene	Bz-13:0
	3-hexadecylcatechol	3-Ct-16:0		Tetradecylbenzene	Bz-14:0
	4-hexadecylcatechol	4-Ct-16:0	*Acid catechols*	6-(1,2-dihydroxybenzene)-3-hexanoic acid	3-AcidCt-6
	3-heptadecenylcatechol	3-Ct-17:1		7-(1,2-dihydroxybenzene)-3-heptanoic acid	3-AcidCt-7
	4-heptadecenylcatechol	4-Ct-17:1		7-(1,2-dihydroxybenzene)-4-heptanoic acid	4-AcidCt-7
	3-heptadecylcatechol	3-Ct-17:0		8-(1,2-dihydroxybenzene)-3-octanoic acid	3-AcidCt-8
Alkylphenols	Phenol	Phenol		8-(1,2-dihydroxybenzene)-4-octanoic acid	4-AcidCt-8
	3-methylphenol	3-Phenol-1:0		9-(1,2-dihydroxybenzene)-3-nonanoic acid	3-AcidCt-9
	3-ethylphenol	3-Phenol-2:0		10-(1,2-dihydroxybenzene)-3-decanoic acid	3-AcidCt-10
	3-hexylphenol	3-Phenol-6:0		11-(1,2-dihydroxybenzene)-3-undecanoic acid	3-AcidCt-11
	3-octylphenol	3-Phenol-8:0	*Acid phenols*	7-(hydroxybenzene)-3-heptanoic acid	3-AcidPhenol-7
	3-nonylphenol	3-Phenol-9:0		8-(hydroxybenzene)-3-octanoic acid	3-AcidPhenol-8
	3-decylphenol	3-Phenol-10:0	*Acid phenyls*	10-phenyldecanoic acid	AcidPh-10
	3-heptadecylphenol	3-Phenol-17:0		11-phenylundecanoic acid	AcidPh-11
Phenylalkylcatechols	3-phenyldecylcatechol	3-PhCt-10		12-phenyldodecanoic acid	AcidPh-12
	4-phenyldecylcatechol	4-PhCt-10		13-phenyltridecanoic acid	AcidPh-13
	3-phenylundecenylcatechol	3-PhCt-11:1		14-phenyltetradecanoic acid	AcidPh-14
	3-phenyldodecylcatechol	3-PhCt-12	*Acid-oxo-phenyls*	8-(1,2-dihydroxybenzene)-phenyloctan-1-one	PhCt-8-1-one
	4-phenyldodecylcatechol	4-PhCt-12		10-(1,2-dihydroxybenzene)-3-phenyldecan-1-one	3-PhCt-10-1-one
Phenylalkylphenols	3-phenyldecylphenol	3-PhPhenol-10		10-(1,2-dihydroxybenzene)-4-phenyldecan-1-one	4-PhCt-10-1-one
	4-phenyldecylphenol	4-PhPhenol-10	*Carbohydrates*	Unverified carbohydrate I	Unverified I
	3-phenyldodecylphenol	3-Ph-Phenol-12		Unverified carbohydrate II	Unverfied II
	4-phenyldodecylphenol	4-Ph-Phenol-12		β-D-Galactopyranose-anhydro	β-D-Galactopyranose

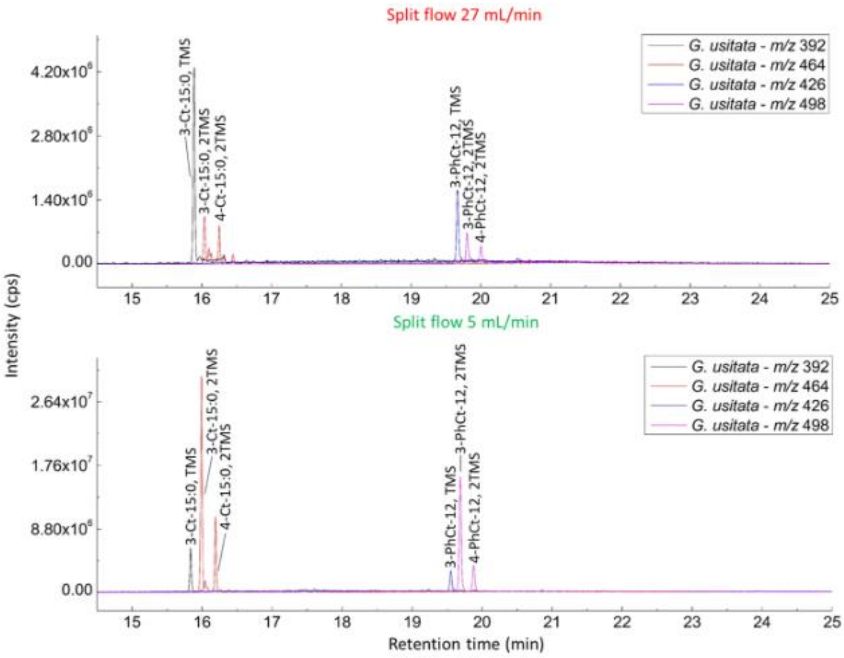


Figure 21. Extracted ion chromatograms showing HMDS derivatisation optimisation results for pentadecylcatechols (Ct-15:0) and phenyldodecylcatechols (PhCt-12) obtained from aged *G. usitata* polymeric samples. Analyses were performed using a 27mL/min split flow and using a split flow of 5mL/min.

Through this part of the study, the utility of pyrolysis temperature optimisation for monitoring specific molecules or molecular groups in the analysis of Anacardiaceae polymers was demonstrated. This optimisation has significantly improved the characterisation of the polymeric compositions. Flash pyrolytic temperature ranges were determined that enable the differentiation between primary pyrolysis reactions and secondary products that result from the primary pyrolysates. This distinction greatly enhanced the ability to identify the macromolecular matrices within the studied lacquers.

Both *G. usitata* and *T. vernicifluum* polymers were found to possess highly crosslinked matrices, necessitating pyrolysis at very high temperatures (550–650 °C) to achieve effective analysis. These matrices exhibited extensive crosslinking, primarily due to the incorporation of both the hydroxyl groups of catechols in covalent intermolecular bonds, see figure 22. Notably, the *T. vernicifluum* polymer showed signs of depolymerisation, which was determined to be an effect of aging.

The hypothesis that more cross-linking occurred in *G. usitata* and *T. vernicifluum* was investigated, and it appeared to be confirmed after a gravimetric evaluation of the pyrolysis efficiency at 550 °C. This resulted in almost complete pyrolysis of the *T. succedaneum polymer*, 98.93%, while pyrolysis was incomplete for the *G. usitata,* 87.23%, and *T. vernicifluum* polymers, 87.36%.

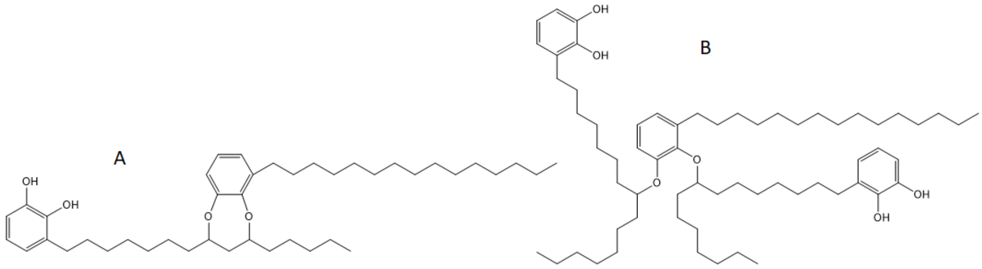


Figure 22. Exemplary saturated C-O-C cross-linked structure, incorporating both hydroxyl groups of the catechol in covalent bonds with one (see A) or two other alkylsubstituted catechols (see B).

The insights gained from these processes are expected to be valuable for future analyses of lacquer samples with unknown compositions. We recommend using fixed pyrolysis temperatures in the range of 480 to 550 °C when conducting analyses with flash pyrolysis. In cases where uncertainties persist, pyrolysis temperatures can be modified to emphasize specific compounds or processes, such as aging, polymerisation, or depolymerisation.

Furthermore, it was found that online derivatisation of Anacardiaceae polymers was invaluable in obtaining reliable, sensitive, and repeatable analyses. TMAH generally outperformed HMDS, resulting in better derivatisation efficiencies for most compounds. The effectiveness of derivatisation was, however, heavily dependent on the completeness of the pyrolysis step.

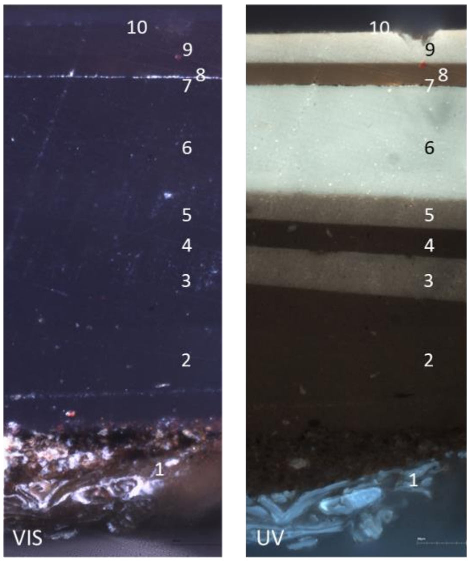
The efficiency of HMDS for the study of carbohydrates could be greatly enhanced by extending the contact time of the reagent with the sample, which holds great promise for a comprehensive investigation of polysaccharides in Asian lacquers, as discussed further in the report.

3.8. Characterisation of the composition of the selected objects

The composition of the various layers constituting the lacquerwork of each selected object was meticulously studied, primarily focusing on the organic components. For some objects, scanning electron microscopy coupled to energy dispersive X-ray analysis (SEM-EDX) was also conducted to identify the inorganic materials. Following a detailed examination of each object, which included photography using visual light and UV, see section 3.4, a sampling location was carefully chosen. Two samples, encompassing all layers, were collected: one for preparing a cross-section illustrating all layers, and a second for layer-by-layer sampling based on the cross-sectional results. The organic lacquer layers become particularly distinguishable under UV light. Under normal lighting conditions, the various layers are sometimes barely or not distinguishable from each other. Utilising a stereomicroscope with a micro-chisel under alternating visible and UV light, each layer was sampled separately to achieve the most accurate analysis possible. To visualise the substrate or structure underneath the lacquer and foundation layers some objects underwent X-Ray imaging. In figure 23 the results obtained on a Vietnamese Buddha (no part of the final selection of objects) are shown, and for the Chinese etagere these are summarized in figure 24. The results obtained for the selected objects from the collection of the RMAH are summarised in table 3.

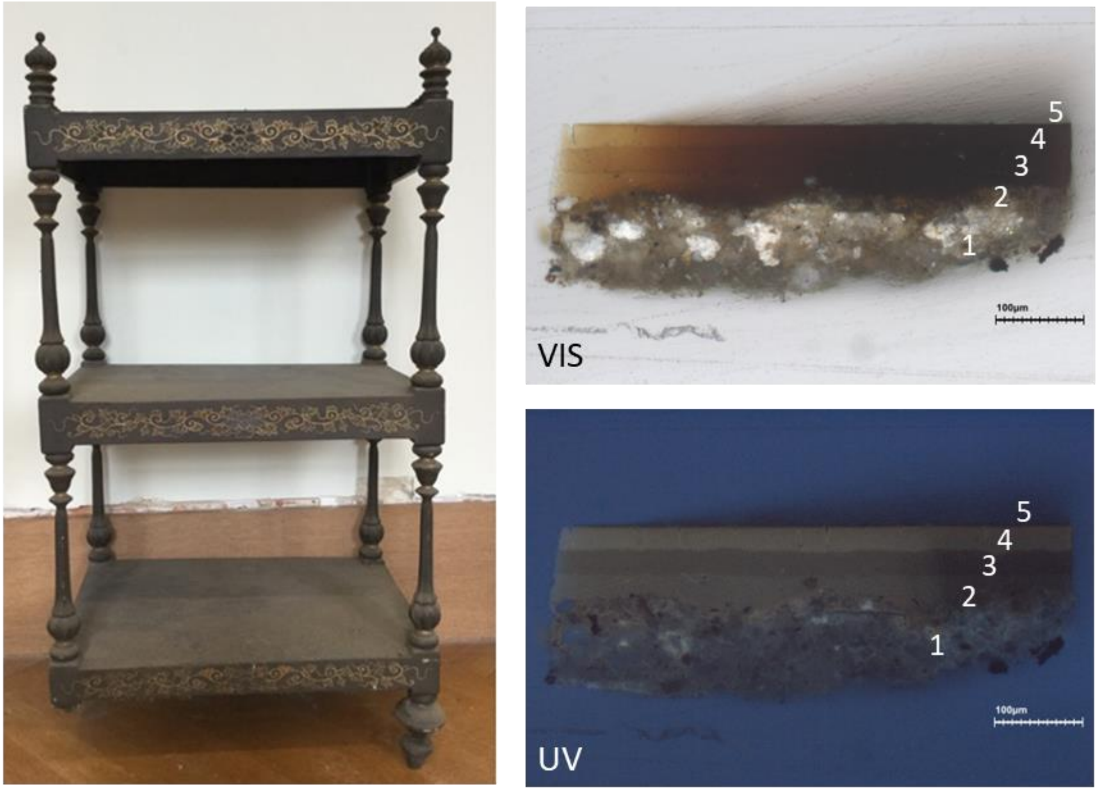
Table 3. Summary of the layer-by-layer lacquer composition identified by Py-GCMS analyses of the four selected objects and the Chinese shelves (etagere) from the collection of the RMAH.

	Chinese Buddha	Surface	Lacquer layers	Foundation	**Burmese Buddha**	Surface	Lacquer layers	Lower lacquer layers	Foundation	**Japanese triade**	Surface	Lacquer layers	Lower lacquer layers	Foundation	**Thai Manuscript box**	Surface	Lacquer layers	Foundation	**Chinese etagere**	Surface	Lacquer layers	Lower lacquer layers	Foundation
Orpiment																					x	x	
Realgar																							
Cinnabar													x										
Iron oxide								x															
Aluminium foil																							
Gold foil			x																				
Gold powder							x					x	x										
Dammar varnish																							
Wax		x																					
Shellac																x		x					
Amber resin																							
Pine resin													x			x							
Carbon black			x			x	x						x				x						
Tofu				x																			
Starch																x							
Blood																							x
Paper																							
Animal glue														x									
Jutte fibres				x																			
Wood oil													x										
Rapeseed oil			x																		x		
Unverified drying oil							x																
Perilla oil																x	x	x		x			
Tung oil			x																		x	x	x
Cashew nut shell polymer																							
Urushi (T. vernicifluum)			x	x							x	x								x	x	x	x
Laccol (T. succedaneum)																						x	x
Thitsi (G. usitata)						x	x	x				x	x				x	x					



10. Protective layer:	Dammar varnish
9. Top lacquer layer VI:	Laccol, tung oil, soot
8. Lacquer layer V:	Laccol, tung oil
7. Metal foil:	Aluminium foil, laccol, tung oil
6. Lacquer layer IV:	Laccol, tung oil, pine resin
5. Lacquer layer III:	Laccol, tung oil, amber
4. Lacquer layer II:	Cashew nutshell polymer, laccol, amber
3. Lacquer layer I:	Cashew nutshell polymer, laccol, soot
2. Foundation:	Cashew nutshell polymer, soot, drying oil
1. Wood	

Figure 23. The technical studies conducted on the objects from the collection of the RMAH starts with VIS and UV photography, occasionally combined with X-Ray imaging. Two small samples are then taken from the object. The first sample is used for preparing a cross-section to visualise the layers, using optical light microscopy. The second sample is used to sample all layers separately, which were analysed one by one using Py-GC-MS.



5. Lacquer layer IV:	Urushi, perilla oil, maybe blood
4. Lacquer layer III:	Urushi, tung oil, rapeseed oil
3. Lacquer layer II:	Urushi, tung oil, rapeseed oil, laccol
2. Lacquer layer I:	Urushi, tung oil, possibly laccol
1. Foundation layer:	Urushi, tung oil, proteinaceous material (possibly blood), possibly laccol

Figure 24. Cross-sections from samples from the Chinese etagere, together with the results of the layer-by-layer analyses by Py-GCMS of the organic compounds.

3.9. The characterisation of polysaccharides in Asian lacquers

The optimisation of the Py-GC-MS method, by using HMDS and an extended contact time achieved through a reduced split flow, revealed that compounds from polysaccharides could be sensitively detected. The analysis of aged lacquer samples provided substantial insights into this hitherto overlooked class of lacquer components. Given the detection of numerous components, the metabolism of polysaccharides in Asian lacquer could be unravelled. The results of this study have been published (Veenhoven et al., 2024), and below, highlight some key findings from the article are highlighted.

As previously mentioned, chemically, lacquer saps consist of a mixture of substituted catechols, laccase and stellacyanin enzymes, glycoproteins, and polysaccharides. The curing process of lacquer sap involves a complex oxidative polymerisation mechanism catalysed by laccase, followed by autoxidation (Lu and Miyakoshi, 2015; Oshima et al., 1985). Much of the research on lacquer curing mechanisms over the last decades has focused on these enzyme catalytic mechanisms in the phenolic fraction. The identification of polysaccharides and glycoproteins dispersed in the cross-linked polymer remains, however, an underexplored area.

It has been demonstrated that polysaccharides complex with glycoproteins to form densely packed grains (Kumanotani, 1995). This polysaccharide/proteinaceous "shield" is proposed to function as a protective barrier against oxygen, inhibiting oxidation and degradation of the catecholic polymer (Kumanotani, 1995). Preprocessing procedures of lacquer saps significantly impact the formation and distribution of the grain structure. The *kurome* technique, as it is called in Japan, is applied *to T. vernicifluum* lacquer sap, which involves stirring for several hours while gently heating the sap at approximately 45 °C. A similar technique is also used for *T. succedaneum* sap. During the treatment the sap is homogenised, the water content lowered, and ideal conditions for enzyme activity are created. (Kumanotani, 1998; Niimura and Miyakoshi, 2006; Webb, 2000). As a result of this process, the water content is typically lowered to around 3%. Simultaneously, by the reaction with environmental oxygen at elevated relative humidity (RH), enzyme-catalysed oxidation of the catechols is initiated, followed by dimerization. The grain structure is formed once the water content is lowered to 10%, and polysaccharides move from the aqueous into the oil phase, where they complex with the glycoproteins.

While studies on carbohydrates in raw lacquer sap have provided structural evidence, the results are mostly based on isolated polysaccharides from non-polymerised lacquer saps. This approach does not provide insight into the interplay between various compound groups, including polysaccharides, during polymerisation. In this part of the work, a comprehensive characterisation of the polysaccharides in cured Anacardiaceae polymers. This is crucial for understanding the changes in chemical and physical properties of the cured and, eventually, aged polymers. To the best of our knowledge, the identification of carbohydrates in both cured and light-aged lacquer has not been investigated thus far.

Artificially aged samples were used for this study. It is important to point out that the studied catabolic and anabolic modifications of carbohydrates in Asian lacquers, are typical in vivo processes taking place in living plants. It is not likely that the enzymes, required for the biochemical processes, are very active after harvesting the sap from the tree and especially in fully polymerised samples, enzymatic activity should not be considered. These processes are also not induced through the action of (UV) light. The compounds identified, using the aged samples, were also found in analyses on unaged samples. The signal intensity for carbohydrate compounds in analyses on unaged samples, however, was found to be much lower. The reason why aged samples were used, is due to the difference in the degree of crosslinking. We have already pointed out (despite the aging step) the high degree of cross linking in aged samples and the detrimental efficacy this has on pyrolysis efficiency, see section 3.7.4. The complete pyrolysis of unaged polymers is likely even more inefficient leading to e.g., the polysaccharides to remain trapped in the unpyrolysed fraction, or the carbohydrate compounds can be excessively thermally fragmented to form non informative secondary pyrolysates. To obtain improved recovery of primary carbohydrate pyrolysates aged samples were used.

The pyrolysis of polysaccharides involves a complex process encompassing both primary and secondary reactions. Primary pyrolysis occurs when glycosidic bonds between monomeric carbohydrate units are thermally cleaved, often accompanied by the elimination of a single water molecule from sugar hydroxyl groups. Secondary pyrolysis reactions manifest as primary pyrolysates are further broken down to produce furans, pyranones, cyclopentenones, hydroxybenzenes, and other small molecules through processes like retroaldolisation, eliminations, fragmentations, and rearrangements (Fabbri et al., 2003b; Fabbri and Chiavari, 2001; Mattonai et al., 2016). In this study, with a strong focus on elucidating individual monomeric units from polysaccharides, we concentrated on primary pyrolysates and parent molecules. The preservation of the carbohydrate structure, functional groups, and stereochemistry in most cases led us to prioritise these compounds.

Anhydrosugars emerged as the most abundant pyrolysis products. The carbohydrate fraction in the three lacquer types primarily consists of galactose, aligning with the polysaccharide structure after isolation from lacquer saps (Lu et al., 1999b; Lu and Yoshida, 2003; Oshima and Kumanotani, 1984). Numerous other carbohydrates and carbohydrate metabolites were identified in Anacardiaceae polymers. Validation of carbohydrate identification was achieved using standards, which were derivatised and analysed in situ through Py-GC–MS and offline derivatisation, followed by GC–MS analysis. A target compound library was made in AMDIS[1] consisting of carbohydrate parent molecules, through GC-MS analyses, and the pyrolysis products, analysed by means of Py-GC-MS. The carbohydrates detected in the lacquer samples were only identified as such when the mass spectrum and retention index (RI) showed a perfect match to the analyses on standards. This facilitated an unambiguous characterisation of carbohydrate compounds from polysaccharides in Anacardiaceae polymers, allowing to explain structural modifications via various metabolic routes and biosynthesis.

Table 4. Expected compounds derived from the various biochemical pathways.

Biochemical pathway	Label	Name	Biochemical pathway	Label	Name
I: Leloir pathway	Ia	β-D-galactose	IV: Shikimate pathway	IVf	5-Enol-pyruvylshikimic acid-3-phosphate
	Ib	α-D-galactose		IVg	Chorismic acid
	Ic	α-D-galactose-1-phosphate		IVh	Prephenic acid
	Id	α-D-galactose-1-diphosphate-uridyl		IVi	Arogenic acid
	Ie	α-D-glucose-1-diphosphate-uridyl		IVj	*p*-Hydroxyphenylpyruvic acid
	If	α-D-glucose-1-phosphate		IVk	Phenylpyruvic acid
II: Glycolysis	IIa	α-D-glucose-6-phosphate		IVl	L-tyrosine
	IIb	α-D-fructose-6-phosphate		IVm	*L*-phenylanaline
	IIc	α-D-fructose-1,6-diphosphate	V: Cinnamate pathway	Va	Cinnamic acid
	IId	Dihydroxyacetone-1-phosphate		Vb	*p*-Hydroxycinnamic acid
	IIe	Glyceraldehyde-3-phosphate		Vc	Caffeic acid
	IIf	1,3-diphosphateglyceric acid		Vd	Ferulic acid
	IIg	3-phosphoglyceric acid		Ve	5-Hydroxyferulic acid
	IIh	2-phosphoglyceric acid		Vf	Sinapic acid
	IIi	2-phosphoenolpyruvic acid		Vg	Coumaryl alcohol
	IIj	Pyruvic acid		Vh	Coniferyl alcohol
III: Pentose phosphate pathway	IIIa	D-gluconolactone-6-phosphate		Vi	Sinapyl alcohol
	IIIb	D-gluconic acid-6-phosphate		Vj	Syringaresinol
	IIIc	Ribulose-5-phosphate	VI: Uronic acid pathway	VIa	α-D-glucose-1-phosphate
	IIId	Ribose-5-phosphate		VIb	α-D-glucose-1-diphosphate-uridyl
	IIIe	Xylulose-5-phosphate		VIc	α-D-glucuronic acid-1-diphosphate-uridyl
	IIIf	Sedoheptulose-7-phosphate		VId	α-D-glucuronic acid-1-phosphate
	IIIg	Erythrose-4-phosphate		VIe	α-D-glucuronic acid
	IIIh	Erythritol-4-phosphate		Vif	L-gulonic acid
	IIIi	Erythritol	VII: Vitamin C biosynthesis	VIIa	L-gulonic acid-1,4-lactone
IV: Shikimate pathway	IVa	3-Deoxy-D-arabino-heptulosonic acid 7-phosphate		VIIb	2-Keto-L-gulonic acid
	IVb	Dehydroquinic acid		VIIc	L-ascorbic acid
	IVc	Dehydroshikimic acid	VIII: Galactose dehydrogenasis	VIIIa	β-D-galactose
	IVd	Shikimic acid		VIIIb	α-D-galactose
	IVe	Shikimic acid-3-phosphate		VIIIc	Galactonic acid-γ-lactone

In the paper we discuss the identified metabolic pathways of the carbohydrates in lacquers in detail. Comprehending the routes of biochemical modification, however, exceeds the scope of this end report, due to the complexity of the processes. The identification of various carbohydrate compounds allowed for the summarisation of the metabolism process in a scheme, as illustrated in table 4 and figure 25.

It could be concluded that the molecular composition of carbohydrates in *G. usitata*, *T. succedaneum*, and *T. vernicifluum* Anacardiaceae polymers undergoes chemical modifications through metabolism

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[1] The use of target compound libraries in the Automated Mass spectral Deconvolution and Identification System (AMDIS) allows to semi automate interpretation of GC-MS data by scanning the analytical data against the target library. The AMDIS software thereby computes a match based on retention index (RI) and mass spectrum similarity. The sofware also calculates the integrated signal value as the area of a given component after deconvolution.

and biosynthesis. Chemical transitions were linked to in vivo metabolic processes, initiating with galactose catabolism followed by a combination of glycolysis and pentose phosphate pathways. This allowed for qualitative differentiation between the three polymer types based on carbohydrate compositions. Enzymatic conversion of uronic acid polysaccharide terminals, particularly glucuronic acids, to aldonic acids was observed. The *G. usitata* polymer exhibited higher enzymatic activity, evident from the amount of phenylpropanoids formed from a minor polysaccharide content, compared to *T. vernicifluum* and *T. succedaneum* polymers, where polysaccharide concentrations are known to be much higher. Analysis of the *T. vernicifluum* polymer indicated the formation of phenylpropanoids to a lesser degree, while no phenylpropanoid compounds were identified in the *T. succedaneum* polymer. This study underscores that a comprehensive understanding of the composition of polymerised and eventually aged Anacardiaceae polymers requires consideration not only of the phenolic fraction but also of the various component groups constituting the polymeric matrices. We therefore greatly encourage future studies on the degradation of Anacardiaceae polymers to put the emphasis on the synergies between the different compounds or macromolecules in the phenolic, carbohydrate and proteinaceous fractions.

3.10. Results of the international survey on the use of water and solvents in cleaning Asian lacquers

To assist in refining the selection of aqueous solutions and solvents for the cleaning of Asian lacquers, an online questionnaire was disseminated to lacquer conservators, seeking insights into their experiences with solvents - in free form or in a mixture - and aqueous solutions, used during conservation campaigns. A total of 121 responses were received, with respondents actively engaged in professional practices, either in private or institutional/museum settings.

Key findings are summarised below:

- More than half of the respondents graduated between 2000 and 2019.

- Conservation activities varied, with 30% involving the removal of dust and accumulated dirt, 15% addressing fingerprints, 13% focused on watermarks, 17% targeted varnish removal, 9% addressed the removal of fungi and biological microorganisms, and 16% dealt with other residues.

- The use of aqueous solutions and solvents was evenly distributed at 30%. In 6% of cases, they were applied in combination with surfactants, while enzymes were used in 4% of cases. Mechanical removal was employed in 23% of all cases.

- Common aqueous solutions included demineralised water (25%) and deionised water (22%). Adjusted pH and conductivity solutions favoured a pH of 5.0

- Free-form solvent usage varied: Ethanol (25%), Shellsol D40-aliphatic mineral spirits (13%), Acetone (11%), Petroleum benzene (7%), Xylene (7%), Iso-octane (4%), Shellsol D38-aliphatic mineral spirits (4%), Ethyl acetate (4%), Cyclomethicone D5 (2%), Exxsol 80/100 (2%), Dimethyl formamide (2%), Propan-2-ol (2%), Benzyl alcohol (3%), Acetone (11%), Cyclohexane (4%), Methanol (1%), Toluene (1%), Dichloromethane (1%), Butanol (1%).

- Solvent mixtures were used by 30% of all respondents at some point in their conservation work.

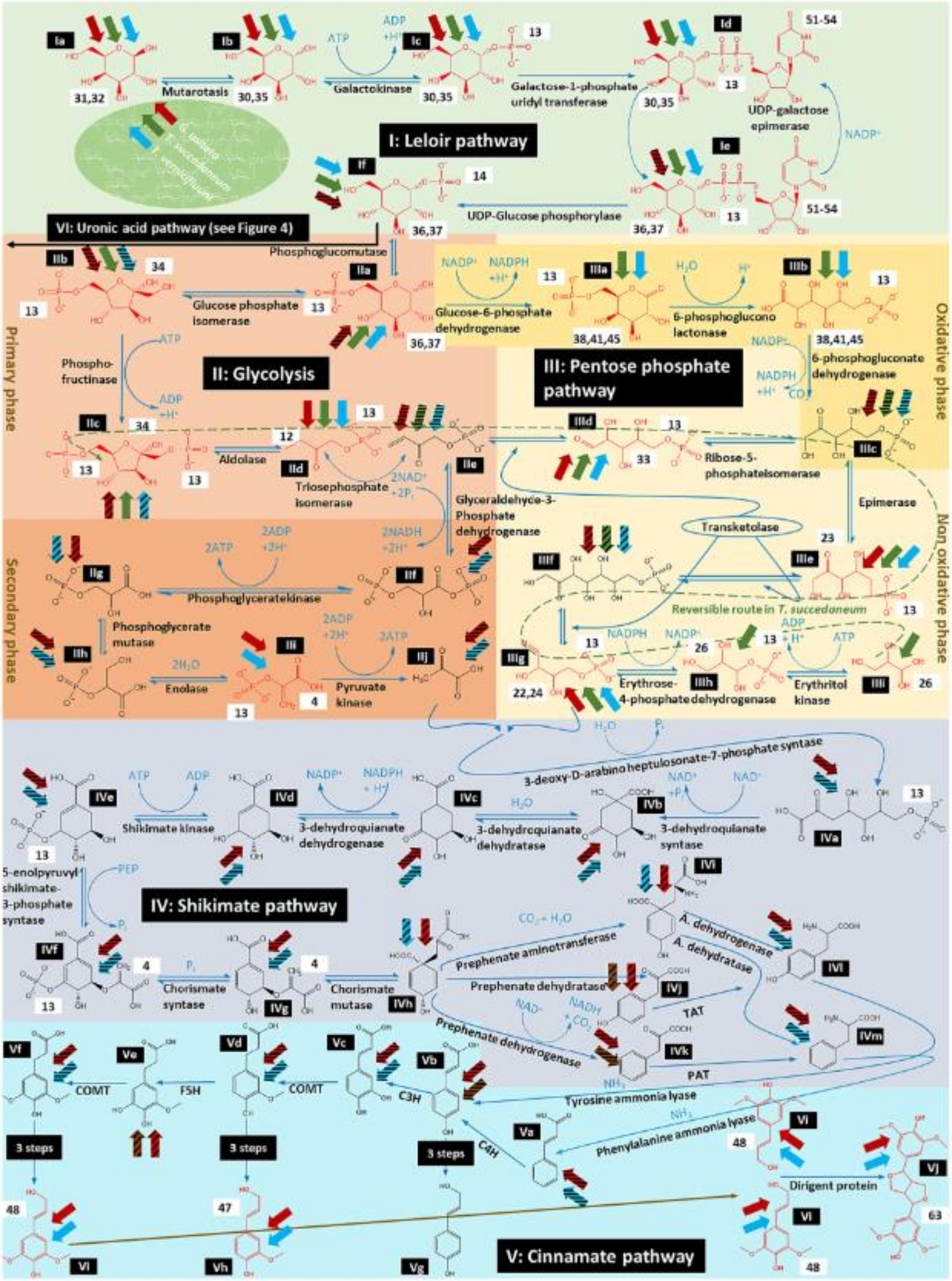

Figure 25. Carbohydrate metabolic pathways identified in Anacardiaceae polymers. The large red, green and blue arrows indicate, respectively, the *G. usitata*, *T. succedaneum* and *T. vernicifluum* polymers, which are used to specify the identification of compounds in these samples. The coloured red, green and blue arrows with black hatching indicate: not identified but likely to be formed or present. The compound labels, mentioned as roman characters, refer to the metabolite names listed in table 4. The structures shown in red depict compounds that were identified, or pyrolysates thereof. For the numerical annotations reference is made to table 1 in the paper.

3.11. Results of the cleaning tests from a conservation point of view

3.11.1. Introduction on cleaning

In her book “Conservation of Furniture”, Shayne Rivers (Rivers and Umney, 2003) defines the ideal cleaning as follows: “Cleaning is a step in any conservation-restoration treatment that aims to improve the aesthetic aspect of the artwork and prevent any future degradation”. She specifies that: “An ideal cleaning treatment would remove undesirable dirt, leave the original object material unaffected, and leave no residue behind” (Shayne Rivers, p.495). Regarding lacquers, it is crucial to underscore that the cleaning process should focus on the removal of dirt while safeguarding the degraded product itself. Simultaneously, we underscore the significance of considering both the object's aesthetic qualities and the preservation of its historical journey. This perspective encompasses an enduring comprehension of the ramifications of cleaning, acknowledging its irreversible nature within the treatment process.

The complexity of cleaning Asian lacquerware arises from a degradation process that evolves over time and is influenced by exposure to ultraviolet rays. This progression leads to elevated surface acidity and sensitivity, culminating in the development of micro-cracks, rendering the surface more hydrophilic. The increased susceptibility of the surface to elements such as water, polar solvents, and high pH levels gradually amplifies over time.

In Japan, traditional cleaning methods for lacquer artworks involve the use of pure water (Webb, 2000). This technique entails soaking a soft cloth in water and then carefully wringing it out. Subsequently, this damp cloth is wrapped around another dry cloth; both cloths are then wrung together, with the second one (less damp) being used for cleaning purposes (Matsumoto, 2005).

It is crucial to keep in mind that cleaning constitutes an irreversible step in the overall conservation process. Indeed, if pushed too far, cleaning may remove an upper layer of lacquer. The inherent characteristics of lacquer impose various constraints, and the cleaning protocol was meticulously designed with consideration for the surface's mechanical and chemical sensitivity. In our tests, we evaluated the cleaning effectiveness, removal of surface elements (decorations, pigments), alterations to the surface (such as bleaching or discoloration), application method, and ease of implementation as crucial criteria.

3.11.2. Optimisation of the physical tests to measure colour, gloss and pH of lacquered objects

The cleaning of a lacquerware with aqueous solutions or solvents aims to efficiently remove dirt with minimal impact on the lacquer layers, both chemically and visually. Cleaning can, after all, also influence the colour and gloss of the lacquer and may have an impact on the acidity (pH) of the lacquer surface. This pH tends to decrease with aging (see also the chemical studies) and can increase again after the removal of the degradation layer. The pH plays a crucial role in conservation itself. When using aqueous solutions, the pH can be adjusted to match that of the lacquer surface to enhance cleaning efficiency.

Measuring these parameters is, therefore, a necessary step in evaluating the aqueous solutions and solvents for cleaning lacquerware. The measurement of colour and gloss is performed on test samples, before and after cleaning with the different solvents, or the object itself, and although there are some limitations, this task is relatively easy to carry out. The determination of acidity is much more complex because pH measurement inherently occurs in an aqueous environment. Therefore, water must be somehow applied to the lacquer surface, and the pH measured in the aqueous extract.

Gloss and colour measurements - methodology

Colour and gloss measurements were conducted by Pierre Lesage as part of his master's thesis at the University of Liège. For a comprehensive discussion of the results, reference is made to his thesis (Lesage, 2022); a brief introduction on colour and gloss and the key findings are summarised below.

The appearance of an object is the human perception of the complex interaction between incident light on the object's surface and its optical characteristics, defined by:

a) specular reflection (first surface);

b) substrate diffusion;

c) material absorption;

d) and regular transmission (in the case of transparent or semi-transparent materials)

Incident light that is not reflected on the surface enters in the material, where it is transmitted, refracted, or absorbed. The refracted light eventually returns to the surface, leaving the object in the form of coloured diffuse reflection, dependent on the selective wavelengths that have been absorbed in the material. Thus, this part of the reflected light is responsible for the sensation of colour.

The term "gloss" describes the nature and relative importance of the mirror reflection of a surface perceived by an observer. A very smooth and shiny surface will have a high degree of gloss because its upper face reflects a significant portion of the incident light unchanged in the specular direction (i.e., at an angle equal but opposite to the incident light).

Conversely, the reflection from a rough surface will be primarily diffuse, occurring in all directions visible to the observer. It virtually lacks specular reflectance, resulting in a less shiny (more matte) appearance. Changing the surface texture, such as polishing or increasing surface roughness, does not alter the total amount of reflected light. However, it does vary the proportion of each type of reflection, provided the incident light remains exactly the same.

Therefore, if the surface exhibits more diffuse reflection (which is white - or at least the same colour as the incident light - and visible in all directions) than specular reflection, the coloured reflection from the interior of the object will be less visible (desaturated) to the observer. A high proportion of scattered white reflection can give a milky appearance and be perceived as hazy.

This implies that the sensation of "bleaching" can be entirely or at least partially induced by an increase in surface roughness. Thus, measuring the difference in gloss can be useful for comparing and evaluating the cleaning action on the lacquer.

To determine gloss, the specular reflectance of a sample is measured using a reflectometer (gloss meter) and compared to that of a standard glossy surface taken under the same experimental conditions. The resulting value, designated as gloss units (GU), is a measure of the magnitude of specular reflection compared to that of the standard surface. This value is a dimensionless number and typically ranges from 100 (high gloss) to 0 (low gloss) for non-metallic surfaces.

The international protocol recommends taking measurements at three angles. The choice of the angle depends on the measurement result obtained at the reference angle of 60°.

1. 20° Angle: Used for very glossy surfaces. Result at the reference angle higher than 70 GU.

2. 60° Angle: Used for glossy surfaces. Result at the reference angle between 10 GU and 60 GU.

3. 85° Angle: Used for matte surfaces. Result at the reference angle lower than 10 GU.

For gloss measurements, readings were taken using a micro-TRI-gloss gloss meter from BYK Gardner GmbH. This instrument allows for measurements to be taken directly at all three angles.

Colour is a much more complex sensation than gloss because it is considered to have a three-dimensional character, consisting of an attribute for brightness and two chromatic attributes called "hue" and "saturation."

- Brightness: Correlated with light reflectance, it is simultaneously an attribute of both colour and gloss. It corresponds to the total amount of light reflected by a surface and ranges from black to white.
- Hue: Refers to the colour perception attribute that allows us to judge whether a surface is red, blue, green, etc.
- Saturation: Expresses the "concentration" of colour, or more precisely, the degree of difference from grey at the same brightness.

Thus, to fully describe a colour, three coordinates and a standardised colour space are necessary. The device used for the measurements takes measurements in the CIELAB colour space. The CIELAB 1976 colour space provides L*a*b* values, where L* refers to the brightness of the sample, a* is a measure of redness (positive value) or greenness (negative value), and b* represents the degree of yellow or blue (+ b*/ - b*). The higher the values of the colour coordinates a* and b*, the more saturated the colour of the sample. If they approach zero, they indicate neutral colours, such as white, greys, and blacks. The measurements were taken using a spectrophotometer spectro2guide Pro 45/0 from BYK Gardner GmbH. This instrument allows for both absolute measurements and measurements in Delta (designating colour differences) according to a defined standard. In our case, it was decided to use the average of the measurements on an aged, uncleaned surface as the comparison standard. This standard corresponds to the origin points of the axes.

For both gloss and colour measurements, 10 readings were conducted per sample, and the average as well as the standard deviation of the average were calculated.

Methodology

For colour measurements, the device uses a circular spot size of approximately 1 cm. As some mock-up samples exhibited uneven colour, it was crucial to ensure measurements were consistently taken from the exact same spots—on the aged lacquer surface before cleaning, after cleaning, etc. This was needed to maximize the accuracy and repeatability of the measurement results. A custom-made sample holder was crafted in-house for this purpose, facilitating measurements on the precise locations on the mock-up samples (figure 26).

Gloss measurements, on the other hand, didn't require a sample holder, as the measuring area covered the full width of the mock-up samples. During investigations involving both colour and gloss on the mock-ups, a sheet of white felt served as a background for measurements.

Colour and gloss assessments were conducted on artificially aged mock-ups prior to cleaning and on the aged and cleaned mock-ups. Subsequently, the mock-ups underwent additional artificial aging to evaluate the long-term effects of cleaning. To ensure the validity of this assessment, the uncleaned aged mock-up samples were also artificially aged for a second cycle. For both the aged-cleaned-aged and twice-aged mock-up samples without cleaning, colour, and gloss measurements were conducted.

The aging method settings, as described in section 3.6, were repeated for the second cycle of artificial aging. In each series of colour and gloss investigations, 10 measurements were taken, and the averages and standard deviations were calculated.

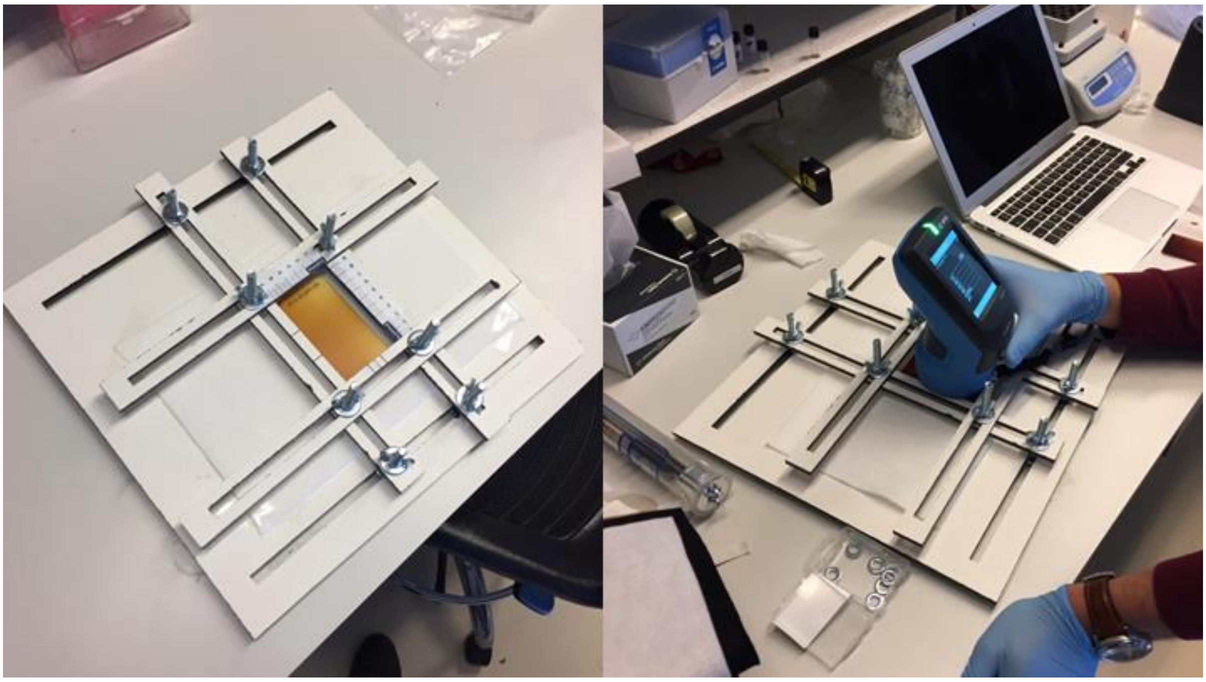

Figure 26. The procedure of performing colour measurements using a custom-made sample holder.

<u>Gloss and colour measurements - results</u>

In the case of pure urushi samples, when using the organic solvents acetone and ethanol, the gloss increases significantly after cleaning (figure 27). When using demineralised water this effect is less pronounced. For Shellsol D40 and cyclomethicone D5, there is hardly any noticeable difference. This aligns with the observation that polar organic solvents, ethanol and acetone, efficiently extract, polar aged, lacquer components, as indicated by chemical analyses (see further). The apolar solvents, Shelsoll D40 and cyclomethicone D5, remove little to nothing, and demineralised water falls somewhere in between. Water and solvents also impact the colour, generally resulting in a shift towards more yellow, warmer, tones after cleaning, except for water, where the colour becomes slightly cooler. After aging (for a second ageing cycle) the cleaned samples there is, however, another colour shift, now more towards the green hue. Bleaching is also frequently observed after cleaning.

Upon aging of the cleaned samples, it is noteworthy that the gloss decreased again, even for apolar solvents, indicating that the aging process continues. Only for cleaning with water does the gloss seem to remain preserved, at least for the pure urushi sample.

When oil is added to urushi lacquer, the observations differ. The increase in gloss is less pronounced when cleaning with polar solvents, and for demineralised water and apolar solvents, there is barely any difference observed. The decrease in gloss after reaging is also less pronounced than for pure urushi.

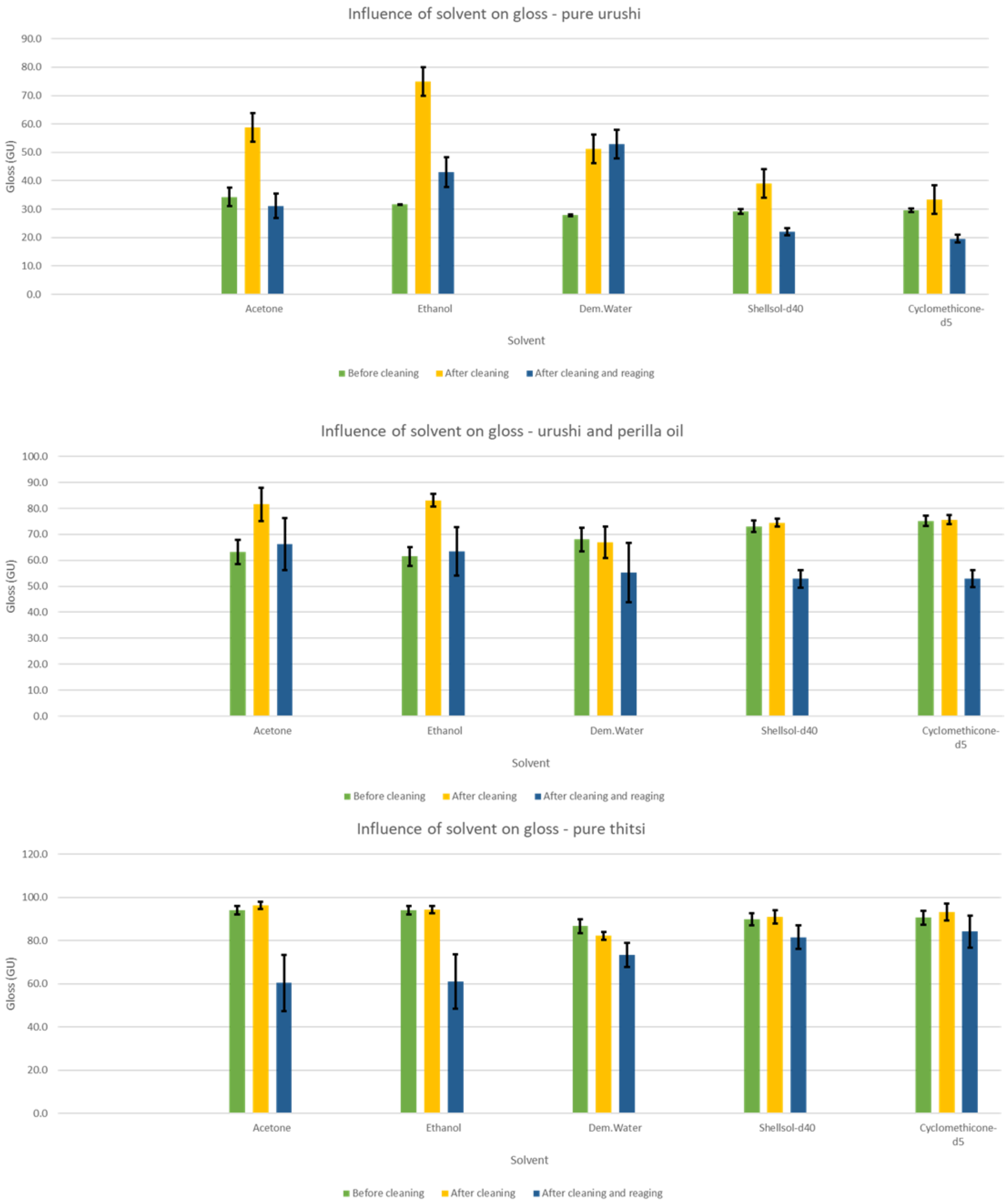

Figure 27. Influence of solvents and demineralised water on the gloss of different lacquer compositions.

For pure thitsi, the influence on gloss appears minimal (but the gloss was near to 100 GU at start) when using solvents or demineralised water. However, after aging the cleaned samples, the gloss diminishes most significantly when polar solvents were used.

The influence of solvents and demineralised water on other lacquer samples varied also depending on the lacquer composition. It was challenging to assess the impact of different components on colour and gloss during cleaning based on these experiments. However, some general observations were made. Typically, the use of polar solvents led to the strongest increase in gloss, but gloss also decreased most significantly after aging of the cleaned samples, implying that polar solvents influence the long-term aging effects after cleaning. Demineralised water usually resulted in a gloss increase, but the decrease after ageing was less pronounced than with organic solvents. The impact of apolar solvents on gloss was minimal, but they also proved inefficient in removing dirt, see section 3.11.3. Chemical analyses indicated that these apolar solvents extracted little to no products from the lacquer (see section 3.12). Due to their inefficient behaviour, apolar solvents seem less suitable for cleaning, at least based on the results of the aged mock-up samples. Polar solvents clearly had the most significant influence on the lacquer surface appearance, but after aging, their impact on aging also seemed the most substantial. Chemical analyses also showed that these solvents extracted the most lacquer components, including degradation products. Although water and polar solvents are the most efficient for cleaning, they also pose the greatest risk, especially in the long term. Demineralised water falls somewhere between polar and apolar solvents. It can remove dirt, the gloss increases slightly, and the decrease after aging is less drastic. The use of demineralised water seems to be the best solution. However, further tests on real samples are necessary, discussed in section 3.11.3.

These tests also clearly demonstrate how the composition of the lacquer can influence colour and gloss after cleaning. The exact behaviour is challenging to predict, emphasising the importance of chemical analyses for accurately determining the lacquer's composition before starting the conservation intervention.

It can be noted that the error in gloss analyses generally increases significantly for the aged samples when polar solvents were used during cleaning. This implies that the gloss is less homogeneous after surface cleaning. These polar solvents are more volatile than demineralised water, which can lead to different contact times, resulting in a less uniform surface in terms of gloss. The method of applying the solvent can also have a significant impact.

Finally, water possesses unique properties that make it generally the most effective choice for cleaning surface grime. The properties of water can be manipulated and adapted to the specific properties of the artwork to be cleaned. Indeed, the pH and conductivity, along with the composition of the aqueous solution through the addition of surfactants, chelators, or enzymes, allow the properties of the water to be tailored to those of the surface while controlling the way it is delivered to the surface, for example, by gelling it.

pH measurements – introduction

As acidic degradation products form during the aging of lacquer (see 3.12), it is expected that the acidity (or pH) of the lacquer surface will vary with the passage of time. Since Asian lacquers are complex systems with many layers, each potentially having a different composition, determining the pH of a lacquered object requires measurement. Moreover, for water-based cleaning, conservators can adjust the pH of the water according to the surface to be cleaned, which can be a determinant for the success of the cleaning treatment. This implies that pH can be accurately measured, which is no easy task considering lacquer is solid and becomes vulnerable to water damage as it ages. Yet, pH is consistently measured in aqueous extracts. In this context, wetting the surface is generally the applied methodology in the field of art conservation to obtain pH measurements as it is less invasive and destructive than sampling and measuring the pH in a water extract. Instead of adding water droplets to the surface, agarose hydrogels can be considered (Aguado-Guardiola, 2017). It should be taken into account that the hydrophilic nature of aged lacquers can cause damage, an aspect that needs to be taken into account when optimising methods for pH measurement.

pH measurements – method evaluation

In his part of the research, carried out to a large extend by Chiara Bianchi, of which the results culminate in her master’s thesis (Bianchi, 2021), five different methods for pH measurement were evaluated on artificially aged *urushi, laccol* and *thitsi* mockups (figure 28): a pH measurement procedure was implemented consisting of using a water droplet (WD), a common method used in the conservation field. Additionally, two agarose hydrogels at different percentages of gelling agent were employed, at 2.5% agarose hydrogel (AHG) 2.5%, and AHG 4%, (Aguado-Guardiola, 2017; Aguado-Guardiola et al., 2023), along with a chromatography paper-based methodology (CP) and a so-called "focused-water” (FW) system developed specifically for this research. The focused-water system was achieved with a 3mm diameter o-ring and a polypropene pipette tip cut to the same diameter size. All four alternative methods were designed to minimise either the amount of water involved in the pH measurement or the surface contact area between the water and the water-sensitive surface. The results regarding the reproducibility and reliability of the pH values obtained through series of pH measurements and by using the various methods, were correlated with microscopic evaluations of the impact of the water on the lacquer surfaces. Additionally, the usability of each method was assessed based on the resulting surface changes on the lacquer surface or the extent of halos, and the criteria for water uptake, diffusing into the lacquer layer was evaluated. This comparison aimed to identify the advantages and disadvantages associated with each method when conducting pH measurements on water-sensitive Asian lacquered surfaces.

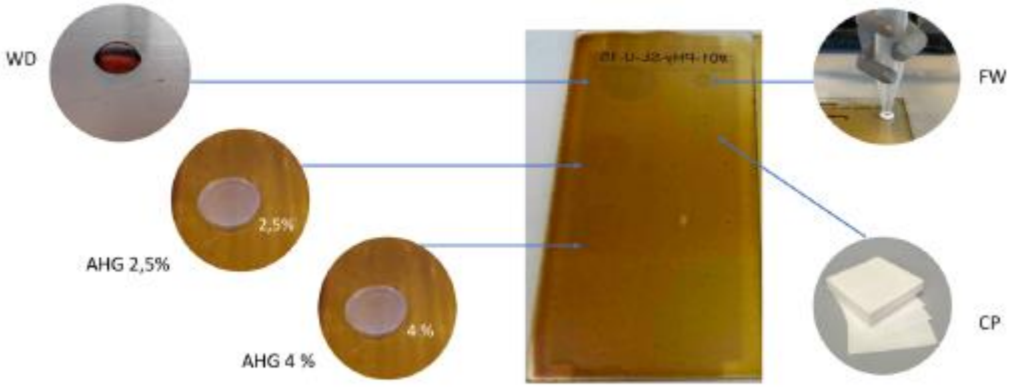

Figure 28. Five different pH measurement methodologies were tested on an aged urushi single-layer mock-up: Water droplet (WD), Focused Water (FW), 2.5% Agarose Hydrogel (AHG 2.5%), 4% Agarose Hydrogel (AHG 4%), and Chromatography paper (CP). Image taken from the Master thesis of Chiara Bianchi.

Surface pH measurements were conducted using these five different methods on one-layer mock-up samples composed of urushi, laccol, and thitsi after artificial aging. Two pH meters were employed: a handheld HORIBA LAQUAtwin® flat sensor electrode pH meter and a HANNA HI99171 pH meter equipped with a surface contact probe electrode.

For each method, pH measurements were repeated three times, targeting nearby yet distinct areas on the same mock-up. A standardised time of 2 minutes was selected for all pH measurements.

To assess the precision of each method, the relative standard deviation (% RSD) was calculated for the different methods. Figure 29 indicates that the Water Droplet (WD), Focused Water (FW), Chromatography Paper (CP), and 2.5% Agarose Hydrogel (AHG 2.5%) methods exhibit very low % RSD, consistently below 4%. Notably, the FW method shows the lowest % RSD across all tested lacquer surfaces. In contrast, Agarose Hydrogels at 4% (AHG 4%) display a higher relative standard deviation, reaching up to 6% when measuring laccol and urushi lacquer surfaces. Consequently, AHG 4% was excluded from the reliability evaluation, leaving four retained methods, WD, FW, CP, and AHG 2.5%.

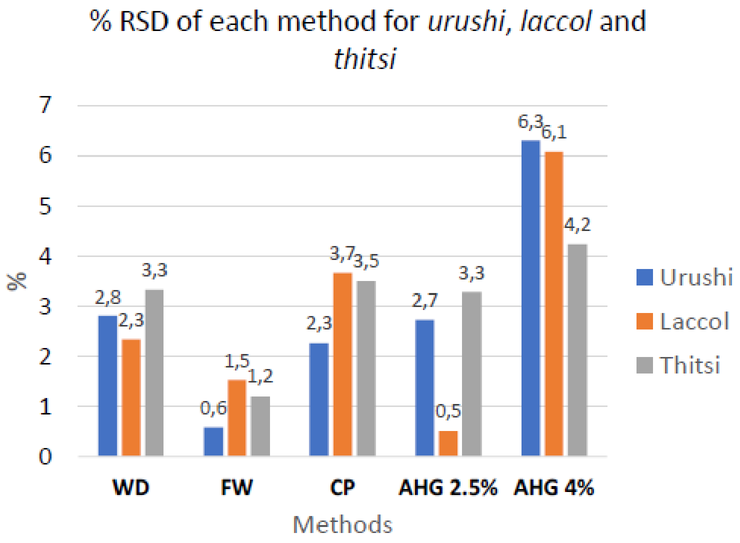

Figure 29. Precision of the five evaluated methods: water droplet (WD), focussed water (FW), chromatography paper (CP) and agarose hydrogel (AHG), resulting from pH measurements on the three lacquer types. Graph taken from the Master thesis of Chiara Bianchi.

The pH values for each aged lacquer sample from the four remaining methods were very close to each other. With the exception of the laccol sample, the methods using pure water (WD, FW) seem to yield a slightly lower pH compared to the methods in which water is confined, CP and AHG 2.5% (figure 30). All evaluated methods, however, provide reliable surface pH values for artificially aged lacquer samples. The average pH values for urushi, laccol, and thitsi are 4.4, consistent with what can be expected for aged lacquer surfaces.

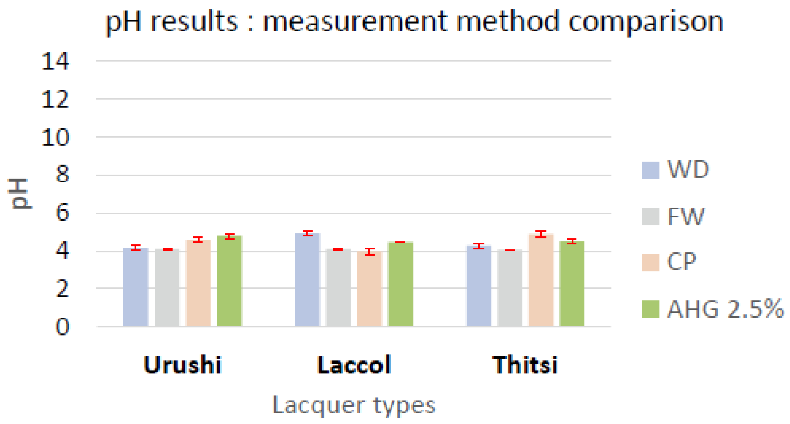

Figure 30. Measured pH values obtained with the water droplet (WD), focussed water (FW), chromatography paper (CP) and agarose hydrogel (AHG) methods on the three lacquer types. Graph taken from the Master thesis of Chiara Bianchi.

Nonetheless, since all these methods resulted in an irreversible marking of the lacquered surface, pH measurements on aged lacquers may only be deemed suitable for mock-ups intended to support scientific experiments. From the conservator/restorer perspective, the pH measurement procedure on objects with aesthetic, historical, or material value should be limited.

The challenge encountered when employing water in its free form, such as with the WD method, stems from the hydrophilic nature of the aged lacquer surface, rich in small molecules carrying carboxyl functional groups that exhibit a strong affinity for water. Upon application to the surface, water rapidly loses its surface tension, spreading seamlessly across the surface and interacting with numerous water-soluble compounds present in the lacquer.

An advantage in the current study is, however, that methods using water in its free form allow for water recovery after the pH measurements are taken, hence, allowing for chemical analysis of lacquer components extracted in the water. The drawback is that on aged lacquer samples, the water spread (halo) can be significant in the WD method, and the water droplet cannot be recovered. Using the FW method, this issue does not occur, but the lacquer must withstand the pressure associated with maintaining water in such a small area and applying this method to curved surfaces is difficult. In the CP method, water is confined to the dimensions of the paper, but on aged lacquers, a larger area can be affected due to the hydrophylic nature of the lacquer surface. The water will penetrate less into the lacquer, better reflecting the surface pH value. Using the AHG 2.5% method, the halo is limited to the size of the gel plug, which is 1 cm in diameter. Diffusion of water into the lacquer layer is most limited using the AHG method, primarily measuring the surface pH.

Aside from an evident water mark, no visible changes to the lacquer surface were discernible to the naked eye following pH measurements using various methods. However, through digital microscopy, employing a Hirox microscope the following alterations were uncovered. Examination of the untouched areas on the mock-ups revealed no microcracks on the lacquer's surface, whereas microcracks were identified on surfaces measured with the water droplet (WD), focused water (FW), and chromatography paper (CP) systems. Among these methods, pH measurements conducted with chromatography paper (CP) proved to be the least damaging, in contrast to the more impactful WD and FW methods. Our observations indicate that pH measurements with chromatography paper (CP) induce smaller cracks compared to those observed on samples measured with the WD and FW methods. No microcracks were detected in areas measured with agarose hydrogels (AHG) at 2.5%. These findings might be linked to the diffusion of water into the lacquer layer what can result in the formation of more microcracks. A potential explanation is that when water diffuses into the layer, non-uniform swelling occurs in specific areas of the lacquer layer. This inevitably induces stress within the lacquer layer, leading to the formation of microcracks. However, when water is gelled, the diffusion of water into the lacquer layer is restricted, as the release of liquid from the gel is more controlled. This limitation in water diffusion minimizes stress, as swelling in the layer is mitigated, thereby preventing the formation of microcracks on the measured surfaces. On real objects the application of the AHG method might hence be considered as the least damaging method.

Summary

It can be stated that the water droplet (WD) method is the most convenient but also the most damaging in terms of microcrack formation. The focused water (FW) method, despite being less practical, is the most repeatable and reduces the halo extent the most. Among the methods involving free liquid water, the chromatography paper (CP) method minimises microcracking and the procedure is easy for conservators to execute. The CP method, however, showed slightly higher variability in the obtained surface pH values. The agarose hydrogel at 2.5% retains the most water, by which no microcracks were observed but having a larger halo extent. Despite the advantages and disadvantages, all methods result in irreversible surface alterations, making them destructive for conservators. Instead safe pH ranges for cleaning may be defined when direct measurements on valuable objects are not possible.

pH measurements - results

The pH values, using the WD-method, obtained on unaged lacquers after a 2-minute contact closely matched the pH of the initial water droplet alone. This is attributed to the polymerised matrix of newly cured Asian lacquer, preventing extraction of water-soluble compounds during a brief surface pH measurement. The results on unaged lacquer surfaces are deemed to be solely influenced by deionised water rather than the lacquer surface. After aging, all mock-ups exhibited a clear shift towards acidity, with pH values ranging between 4.1 ± 0.1 on urushi and a maximum of 4.9 ± 0.1 on laccol. This trend indicates the lacquer's propensity to acidify during aging, irrespective of the lacquer type. The minimal difference in surface pH values between aged urushi and laccol suggests that a safe pH range for aged Asian lacquers could be identified within the pH 4-5 range.

3.11.3. Results of the cleaning tests of the Chinese etagere

While the cleaning tests on the mock-up samples provided a good initial impression of the effect of the chosen solvents and demineralized water, these samples are only an artificial approximation of reality. Before embarking on the cleaning of objects from the museum collection, it was deemed necessary to introduce an intermediate step, for which the previously described Chinese étagère was used. The same solvents were applied, along with demineralized water. Since the initial tests indicated the effectiveness of water and the pH of the lacquer surface can be quite acidic (between 4-5), water was also tested at different pH levels. The pH at various levels in the etagere was determined, and the influence on colour, gloss, efficiency of dirt removal, bleaching, and homogeneity of the lacquer surface after cleaning were evaluated, as described in the following paragraphs.

pH measurements on the Chinese etagere

The acidity of various parts of the Chinese etagere was determined using the AHG 2.5% method, as this method causes the least damage (cracking) to the lacquer objects, as discussed in the previous paragraph. This test object reflects real conservation issues such as variations in gloss and colour among different parts of the object corresponding to varying degrees of degradation, an irregular morphology likely caused by microcracks, and the presence of a soiling layer. pH measurements were conducted on three distinct areas of each of the three trays (figure 31). The selection criteria included areas with varying degrees of light exposure, different types of degradation, and one area with the presence of a soiling layer.

Figure 31. Chinese etagere, with indication of the areas where the pH measurements were conducted. Areas 1 are sites well exposed to light, while areas 2 are less exposed (bottom of the shelves). Areas 3 are exposed to light and soiled. Image taken from the Master thesis of Chiara Bianchi.

The summarised results of the pH measurements are presented in table 5. The parts exposed to light (areas 1), resulting in more photodegradation, showed the lowest pH values. An exception is area 2 of the top tray also showing a low pH value. Possibly due to its elevated position in the etagere, it might have been more exposed to light, compared to the bottom parts of the lower trays. The less exposed areas 2, display less acidity, indicated by higher pH values. These areas, better shielded from light, show less degradation, reflected also in the relative high gloss of the surfaces. Based on the pH values, however, even the less exposed areas (areas 2) have undergone photodegradation. It is noteworthy that the pH range falls between 4.0 and 4.8 for all exposed areas measured, aligning well with the pH range of aged mock-up samples and the proposed safe pH range for cleaning aged lacquers. The pH of the soiled parts (areas 3) is higher, despite exposure to light. As these surfaces are soiled the pH measurements are considered representative of the soiling layer rather than the lacquered surface.

Table 5. pH results of the different measuring spots of the Chinese etagere

Tray/spot	1	2	3
A	4.0	4.1	4.8
B	4.0	4.8	4.9
C	4.2	4.6	5.2

<u>Solvent and water cleaning tests on the Chinese etagere</u>

Tray A of the étagère (figure 31) exhibits the most degradation, primarily attributed to the higher exposure to UV radiation. Additionally, it manifests the most substantial soiling, with specific areas bearing evidence of bird droppings. The lateral sides display slight alterations and exhibit minor soiling, while the bottom is relatively better preserved, presenting a satin, glossy appearance, albeit with some minor soiling. These findings have markedly influenced the colour and gloss measurements, which must be taken into account on interpretation of the results.

Only colour and gloss measurement results of tray A are reported here to evaluate the cleaning tests. The measurements were conducted following the methodology used for the mock-ups. However, given that this object encompasses a complete stratigraphy, including support, preparation layers, lacquer layers, and decorations, the analysis method required slight adjustments. In this case, there was no need for a background (as with the white felt placed under the mock-ups), but instead, a template was crafted to ensure the repeatability of colour measurements (figure 32).

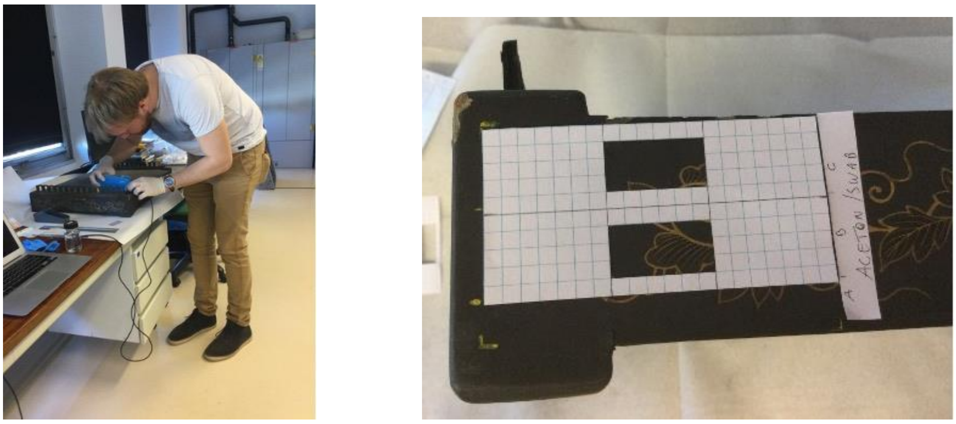

Figure 32. Gloss measurements (left) and template used for the colour measurements (right) on the Chinese etagere.

The cleaning tests performed on tray A centred on the solvents identified through the international study (acetone, ethanol, Shellsol D40, cyclomethicone D5, and demineralized water). This was complemented by a series of tests using water with adjusted pH levels (pH 3.5, pH 4, and pH 5). The choice of appropriate water was inspired by the most recent internationally conducted studies on sensitive surface cleaning methodologies.

The way in which the solvent or water is applied also has an impact on the cleaning process. Three common methods were evaluated. The first method utilized cotton swabs, representing the most commonly employed technique by the majority of conservators during their treatments. The second method incorporates the traditional Japanese practice that employs cotton textiles (see 3.11.1). The final method involves the use of Evolon® CR, a material that has been utilized in conservation for over five years. Invented by Freudenberg, the manufacturer describes the product as follows: “Endless bi-component filaments are spun, uniformly laid on a belt, then simultaneously split into microfilaments and entangled using high pressure water jets to create the final fabric. No solvents or chemical binders are used in the process” (https://evolon.freudenberg-pm.com/evolon_technology/technology, last accessed 18 November 2023).

Evolon is produced in various thicknesses. However, until recently, the main supplier in conservation product, Defner and Johannes, had only one type in their catalogue: Evolon Cr®. A thicker formula was recently added to the catalogue, but it was not available at the time of conducting the cleaning tests.

In a recent study on the use of Evolon CR as a tool for varnish removal (Vergeer et al., 2019), the advantages and disadvantages of using this microfiber for varnish removal are discussed. In the case of altered lacquers, what caught our attention was that its use allowed for a reduction in the quantity of solvent employed and minimized the mechanical action on the surface.

For the test implementation, two drops of solvents were applied using a dropper onto the selected medium for cleaning. However, this technique proved to have its limitations, particularly in the case of polar solvents where the volatility did not allow for effective cleaning. In such instances, we had to add more solvent, repeating the operation until achieving the desired cleaning effect.

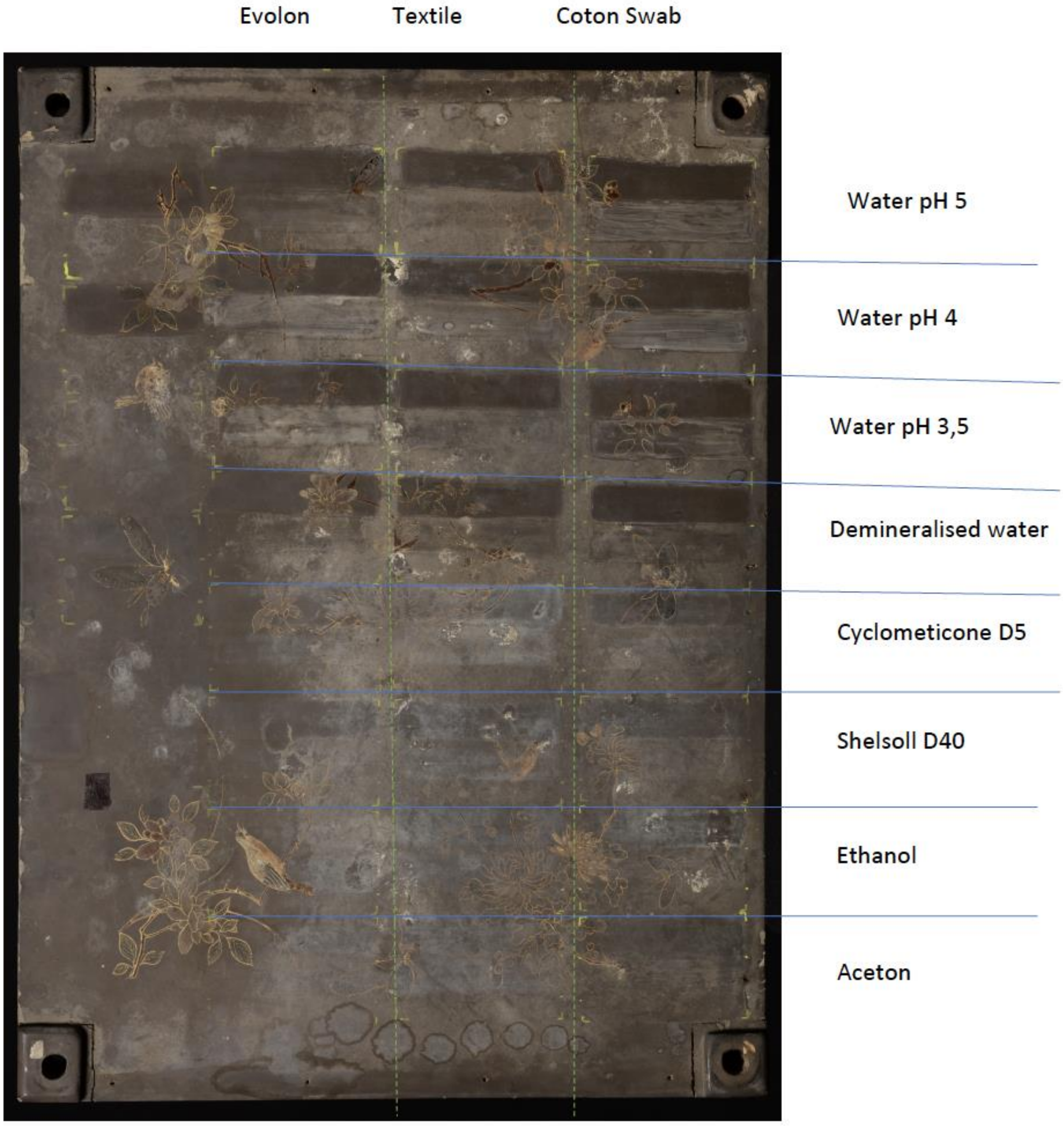

Figure 33. Overview of the results of the cleaning test on the top of tray A of the Chinese etagere.

Table 6. Summary of the cleaning test results of tray A of the Chinese etagere: influence of the solvent or water on gloss, colour, efficiency of dirt deposit removal, bleaching and homogeneity after cleaning of the lacquer surface.

	Acetone			Ethanol			Shellsol D40			Cyclomethicone D5			Water			Water pH 3.5			Water pH 4			Water pH 5		
	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon	Cotton swab	Cotton textile	Evolon
	Top																								
Gloss*	+	+	-	+	++	+	+	+	+	(+)	(+)	(-)	++++++	+++	+++	++++	+++++++	++++	++++	+++++	++	+++++	++	++++
Colour tone**	D:+	D+	D	D:+	no	D	D	no	D	D:+	L	D	D:++	D:++	D:++	D:++	D:++	D:++	D:++	D:++	D:++	D:++	D:++	D:++
Colour hue**	C :+	C:+	C:+	C:+	C:+	C	C	C:+	C	C:+	C	W	C:+	C:+	C:+	C:+	C:+	C:+	C	C:+	C+	C:+	C:+	C+
Removal of dirt deposit***	+	+	+	+	+	+	++	++	+	++	++	++	+++	+++	+++	+++	+++	++	++	+++	+++	+++	+++	++
Presence of bleaching***	++	++	++	++	++	++	+	++	++	-	++	+++	-	-	+	-	+	+	-	++	-	-	-	+
Homogenity***	--	---	---	---	--	--	--	--	--	--	---	---	+++	-	+	+	+	++	++	--	+++	+++	+++	++
	Bottom																								
Gloss*	+	++	+++	+	++	++	+	+	++++	(+)	+	++++	+++	++	+++++++	++++	+	+++++++	+++	++	++++	++	++	++++++
Colour tone**	D	D	D	D	D	D	no	no	D	no	no	D	D:++	no	D:+	D:+	(D)	D	D	D:+	D:+	D:+	D:+	D:+
Colour hue**	no	W	no	no	W	no	no	no	no	no	no	no	C:+	no	W	W	(C)	C	W	W:+	(C)	W	W:+	(W)
Removal of dirt deposit***	+	+	+	+	-	+	++	++	+	+	+	+	++	+++	++	++	++	++	+++	++	++	++	++	++
Presence of bleaching***	+	+	+	++	++	+	+	+	+	-	++	+	-	(+)	(+)	-	-	-	-	-	-	-	-	-
Homogenity***	+	+	+	+	+	+	+	+	+	--	-	-	++	-	+	+	+	++	++	++	++	++	++	++
	Side																								
Gloss*	+	+	(+)	++	+	+	+	(+)	+	++	+	(+)	+++	+	+	++	+	++	++	+	+	++	++	+
Colour tone**	D:++	no	D:+	L:+	no	D	no	L	no	no	no	no	C:+	no	no	L	no	L	D:++	no	L	D:++	no	no
Colour hue**	W:+		C:+	W:+	W	no	C	C	W	no	no	no	W	no	no	no	C	no	W:+	C:+	no	W++	no	no
Removal of dirt deposit***	++	+	+	+	+	--	+	+	+	+	+	+	+	+	++	+	+	+	+	++	+	+	+	+
Presence of bleaching***	+	no	no	+	+	+	+	+	-	-	+	+	no	no	+	-	-	-	-	-	-	-	-	-
Homogenity***	--	++	+	--	-	-	++	+	+	++	++	++	++	+	++	++	++	++	++	++	++	++	++	+

* gloss difference shown as measured GU in comparison the uncleaned surface

** difference indicated as measured LAB colour change compared to the uncleaned surface.

*** subjective observation by D. Mesmaeker, Asian lacquer conservation expert

Gloss

+=increase of 5 GU
++=increase of 10 GU
+++=increase of more than 15 GU
(+)=undere 1

Color

color tone: D= darker; L= lighter
Color hue: W= warmer, C: colder

The results obtained from the cleaning tests are shown in figure 33 for the top of tray A of the Chinese etagere, and all results obtained on tray A are summarised in table 6.

Optimal outcomes were observed with water-based cleaning methods, demonstrating superior efficacy compared to polar and non-polar solvents. The impact of these solvents on soil solubilization proved relatively limited, resulting in fewer discernible alterations in colour and gloss measurements. Moreover, the use of these solvents resulted in bleaching and yielded non-homogeneous results.

The utilization of water offers the advantage of solubilizing the soiling layer without inducing bleaching upon drying. The removal of this substantial layer of soiling brings about a significant transformation in both colour and gloss. Tests conducted with pH-adjusted water produced the most uniform results and did not lead to bleaching after drying. In her study titled "*Uber die reiningung ostasiatischer (Urushi) lack*"[2], Nanke Schellmann notes that the solubility of organic acids in water is inherently linked to their pH value. A correlation has been established between elevated pH levels and a negative effect on the observed glossiness during the cleaning of aged surfaces.

She also mentions in her thesis (Schellmann, 2003) that using water with a lower pH than that of the surface seems to yield the best results. The results of our tests on tray A do not show significant changes among the different pH scales. However, various subjective observations related to the application have led us to select the lowest pH (3.5) as the cleaning solution taking also into account the observation that Schellmann made. Whether it was the sensation during the cleaning process (more slippery feeling on the surface and less adhesion) or the observation of residues present on the cotton swabs (the cotton swabs used during cleaning with a pH of 4 showed the presence of brown residues, generally indicative of lacquer solubilization or degradation products), both factors contributed to this decision.

Innovative methods for applying water as cleaning agent tested on the Chinese etagere

Once the solvent selection was finalized, our attention shifted to the application methods. Two of the three methods employed so far exhibited certain disadvantages: residues of cotton and textile fibres lingered on the surface, adhering even to the slightest irregularities (such as decorations), necessitating substantial mechanical action to eliminate the soiling residues. Consequently, we explored cleaning techniques applied on sensitive surfaces, such as paper, acrylic paint, and tempera paint, which led us to choose three alternative application methods that have demonstrated their effectiveness in addressing issues related to sensitive surfaces. In addition to Evolon CR® (A), we tested: cellulose membrane, KSG™ silicon gel, and Nanorestore Gel® High Water Retention - HWR (formerly known as Max Dry).

Cellulose membrane (B)

Constructed from regenerated cellulose (70%), glycerin (19 to 25%), and water (6 to 11%), cellulosic membranes (Viskase© HS13 CLEAR) have been integrated into the realm of conservation and restoration for over two decades, particularly in treatments involving textile artworks (Bouzid, 2002). These membranes are designed with porosity and permeability, allowing for controlled water supply and physical ion exchange between two mediums. The membrane effectively regulates water supply,

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[2] Nanke Shellmann, *Uber die reiningung ostasiatischer (Urushi) lack*. Uncorrected manuscript as submitted to the editor of "*Handbuch der Oberflächenreinigung*"(Handbook of Surface Cleaning), P.B. Eipper(ed.) 5th/6th edition München: Verlag Müller-Straten, Confidential courtesy of the author)

facilitating the extraction of solubilized dirt (Chomienne and Beugnot, 2015). The product's inherent structure enables the use of pH-adjusted water, reducing the need for intensive mechanical cleaning.

Particle emulsion in KSG (C)

Silicone gel KSG$^{\text{TM}}$ 350-Z acts as an emulsion stabilizing polymer. It is composed of a gelling agent (cyclopentacyloxane PEG 15/lauryl polydimethylsiloxyethyl dimethicone) and cyclomethicone D5. The grafted polyether chains create a hydrophilic domain, thus enabling emulsions without the use of surfactants. Cyclomethicone D5, on the other hand, is a volatile methysiloxane. With very low polarity, it evaporates slowly and possesses a very low surface tension, making it highly penetrative. Used as a barrier solvent, it reduces the impact of water on hydrophilic surfaces (Pedersen, 2018).

Nanorestore Gel ® High water Retention- HWR (formerly known as Max dry)

Nanorestore Gel® Dry is a water-based chemical gel designed by the CSGI (Research Center for Colloids and Nanoscience) for artifact treatment. Its highly retentive network allows safe application on water-sensitive surfaces, releasing minimal liquid to the surface due to its limited interface action. These gels are initially water-loaded but can also contain polar solvents (like ethanol) or water-based nanostructured fluids from the Nanorestore Cleaning® series. Acting as a container for the cleaning agent, Nanorestore Gels® Dry effectively removes grime, dirt, and aged varnishes through solubilization or swelling/detachment of unwanted materials. Their formulation prevents rapid evaporation of the cleaning agent and uncontrolled penetration into porous materials, ensuring safer cleaning without leaving residues on treated surfaces (https://www.csgi.unifi.it/products/about.html; last accessed 18 November 2023).

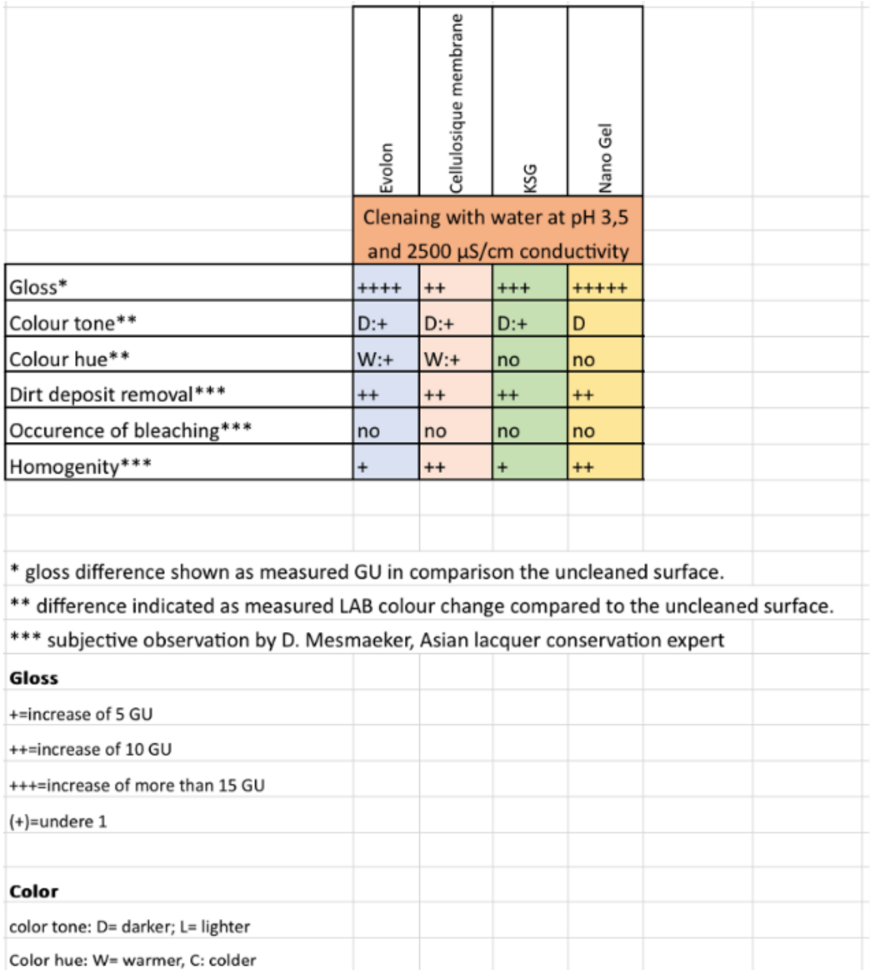
The advantages and disadvantages of these application methods have been summarised in table7.

Table 7. Summary of the advantages and disadvantages of the innovative application methods.

Method	Advantages	Disadvantages
Evolon	easy to use can be used with ajusted water exist in different thickness The evolon can be washed non toxic	mechanical action is needed to remove dirt
Cellulosique membrane	can be loaded with adjusted Water reduces mechanical action cleaning efficiency is positive can be used several times non toxic	not really easy to use on 3D difficult to use on vertical surface the membrane is not completely flexible
KSG	Can be loaded with adjusted water (max30%) can be use on each type of surfaces non toxic for human	Need the use of cyclometicone D5 as a barrier solvent silicone gel seems quite greasy when applied need several times of application the barriere solvent takes time to evaporate the cyclometicone is toxic for the environement
Nano gel	can be loaded with adjusted Water can be reused up to 5 times exist in different retention no mechanical action needed non toxic	take 12 hours to be loaded very expensive

Figure 34: Cleaning test results on tray B of the Chinese etagere using different methods of application of the water cleaning agent: A: Evolon CR®, B: cellulose membrane, C: silicone solvent KSG, D: Nanorestore gel ®.

Table 8. Summary of the influence of the method of application of water on gloss, colour, efficiency of dirt deposit removal, bleaching and homogeneity after cleaning of the lacquer surface.



	Evolon	Cellulosique membrane	KSG	Nano Gel
	Clenaing with water at pH 3,5 and 2500 µS/cm conductivity			
Gloss*	++++	++	+++	+++++
Colour tone**	D:+	D:+	D:+	D
Colour hue**	W:+	W:+	no	no
Dirt deposit removal***	++	++	++	++
Occurence of bleaching***	no	no	no	no
Homogenity***	+	++	+	++

* gloss difference shown as measured GU in comparison the uncleaned surface.

** difference indicated as measured LAB colour change compared to the uncleaned surface.

*** subjective observation by D. Mesmaeker, Asian lacquer conservation expert

Gloss

+=increase of 5 GU

++=increase of 10 GU

+++=increase of more than 15 GU

(+)=undere 1

Color

color tone: D= darker; L= lighter

Color hue: W= warmer, C: colder

The results from the cleaning tests conducted on tray B of the Chinese shelf using innovative application methods show quite encouraging outcomes. All of these methods perfectly meet the constraints associated with any cleaning treatment of an artwork. The four proposed solutions allow for the removal of surface dirt while limiting the introduction of liquid onto the micro-cracked surface (figure 34 and table 8).

In all the applied methods, a noticeable enhancement in gloss is evident, intricately associated with the removal of the dirt layer, while the object maintains its characteristic appearance of aged lacquer, which has developed a matte finish over time. No discernible removal of degradation products is observed. The impact on colours and their saturation remains fairly consistent across the various methods. Importantly, none of the tested methods result in residues or surface whitening. The most homogeneous results in lacquer appearance were achieved through the application of the cellulose membrane and nanorestore gel for cleaning.

Each of methods evaluated demonstrates effectiveness while presenting distinct advantages and disadvantages. Evolon requires mechanical action, varying in intensity based on the degree of soiling, while the use of silicone solvent KSG-Z, with its slow-evaporating barrier solvent, prolongs the treatment time and hampers the visibility of the cleaning progress. In contrast, the cellulose membrane allows clear visibility of the cleaned area and tends to preserve the surface impeccably.

In the case of this particular object (soiled Chinese etagere), it was necessary to re-wipe after each application, given the thickness of the dirt layer, which couldn't be completely absorbed by the mediums.

These four application methods have proven effective in cleaning flat lacquered surfaces. The applicability of these methods to three-dimensional object surfaces will be an intriguing area for further exploration (section 3.15).

3.12. Results on the solvent and water extractions of aged lacquer samples

In this section we discuss the chemical compositions of water and solvent extracts obtained by immersing 2 mg of aged free film samples. It is important to note that this method, although not mirroring typical cleaning interventions on lacquered objects, is considered necessary.

The extracts comprise numerous small molecules, including high-similarity structures like isomers. While individual compound concentrations may be low, their combined peak areas can be significant. Sampling small surface extracts during cleaning treatment often yields challenging mass spectra, or none at all, due to detection limit constraints. Immersion helps concentrate compounds, facilitating accurate identification and ensuring concentrations surpass detection limits.

The results offer insights into the compounds extractable during an object's cleaning treatment. Immersion extraction enhances compound identification certainty, allowing for the construction of target compound libraries in AMDIS for subsequent detection in conservation-related samplings.

GC-MS, following trimethylsilylation, and LC-HRMS with an orbitrap mass spectrometer was employed for the identification of small molecules in lacquer/solvent extracts. Additionally, EGA-MS revealed the presence of macromolecules in the extracts, while LC-HRMS elucidated their molecular weights. Characterisation of the macromolecular structures involved wet chemical pretreatments to degrade them into monomeric building blocks, subsequently analysed using GC-MS.

Due to the high complexity of Asian lacquers, the comprehensive study on solvent extracts was limited to aged pure Asian lacquers—*G. usitata*, *T. succedaneum*, and *T. vernicifluum* (thitsi, laccol, and urushi, respectively). The selection of solvents, extensively tested on Asian lacquers, was based on the international survey outcomes (section 3.10). These solvents include demineralised water, ethanol, acetone, cyclomethicone D5, and Shellsol D40, with the corresponding extracts depicted in figure 35.

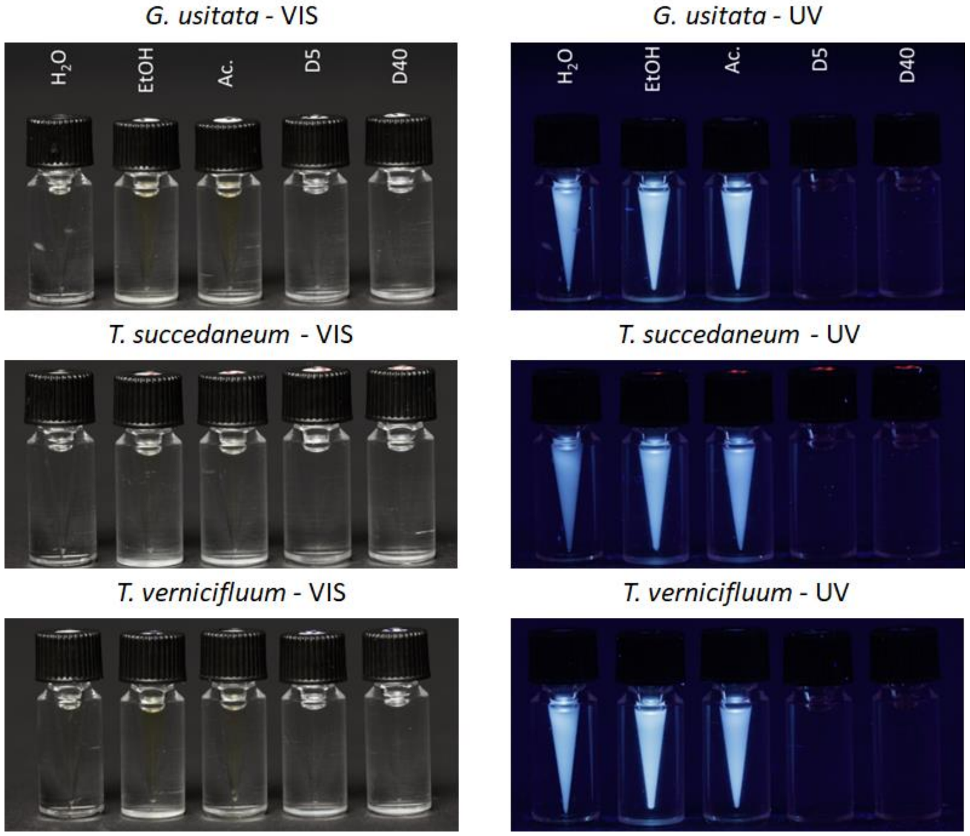


Figure 35. Asian lacquer/solvent extracts using photography under visual and UV light illumination. Using visual light, the ethanol and acetone extracts show yellowing. The yellowing occurred mostly for *G. usitata* (thitsi) *and T. vernicifluum* (urushi) samples*.* Yellowing of the water extracts was typically much less compared to the polar solvents. A similar trend is shown in the UV images, the *G. usitata* (thitsi) and *T. vernicifluum* (urushi) samples showing most fluorescence. No changes in colour or UV fluorescence were shown for cyclomethicone D5 or Shellsol D40 apolar solvents.

Sample preparation

Free film mock-ups were used. Each sample comprised 2 mg of sample to which 100 µL of solvent was added. The Asian lacquer samples, immersed in solvent, were extracted for 24 hours. The liquids, containing the extracted compounds were transferred to a clean vial. To avoid particles occurring in the extracts, the extracts were centrifuged, and the supernatant extract was transferred to a clean sample vial. For GC-MS and LC-HRMS the solvent was evaporated using a combination of vacuum and centrifugation. The samples used for EGA-MS were evaporated in a pyrolysis cup.

Evolved gas analysis-mass spectrometry (EGA-MS)

In the EGA analysis, the pyrolyser and GC-MS instrumentation were employed (see section 3.7.3). In the EGA-configuration, the pyrolyser is linked to the mass spectrometer (MS) inlet through a short deactivated narrow-bore capillary. During analysis, the furnace of the pyrolyzer undergoes a gradual ramping from 200 °C to 800 °C, while molecules in the evolved gas phase are directly transferred to the MS via a helium carrier gas flow.

EGA-MS should not be regarded as a technique for compound identification since there is no chromatographic separation prior to MS detection. Consequently, compounds cannot be individually separated in time. Additionally, due to the use of electron ionization (EI), evolved compounds undergo heavy fragmentation. The ions detected within a specific temperature range constitute a complex mixture of molecular ions and fragment ions.

Despite these limitations, the thermograms resulting from EGA-MS analyses offer a rapid overview of the sample matrix, encompassing small molecules, larger, less volatile structures, or macromolecules. These analyses prove to be a valuable asset in researching the effect of solvents when cleaning Asian lacquer surfaces. They facilitate the evaluation of sample matrices in solvent extracts and the assessment of Anacardiaceae polymeric samples both before and after solvent application.

After introducing the sample into the pyrolyser, the following temperature gradient was applied: an initial temperature of 200 °C was maintained for 1 minute. The temperature was then ramped at 70 °C/min until reaching 800 °C, which was held isothermally for 1 minute. Evolved compounds were transferred to the MS detector through a 1-meter deactivated fused silica capillary (0.10 mm i.d.). The GC oven was programmed isothermally at 300 °C, and a constant (He) capillary flow was maintained at 0.9 mL/min.

The following section provides a succinct overview of EGA-MS analyses conducted on Asian lacquer free film mock-up samples. As of November 2023, these findings remain unpublished and will form the topic of two forthcoming papers in which results will be discussed more into detail.

The scope of EGA-MS analyses included unaged free film mock-up samples, artificially aged samples, solvent extracts resulting from immersing free film samples, and analyses conducted on the free film samples after solvent immersion. The resulting thermograms are shown in figure 36. Typical ions detected were attributed to their parent molecules (see table 9).

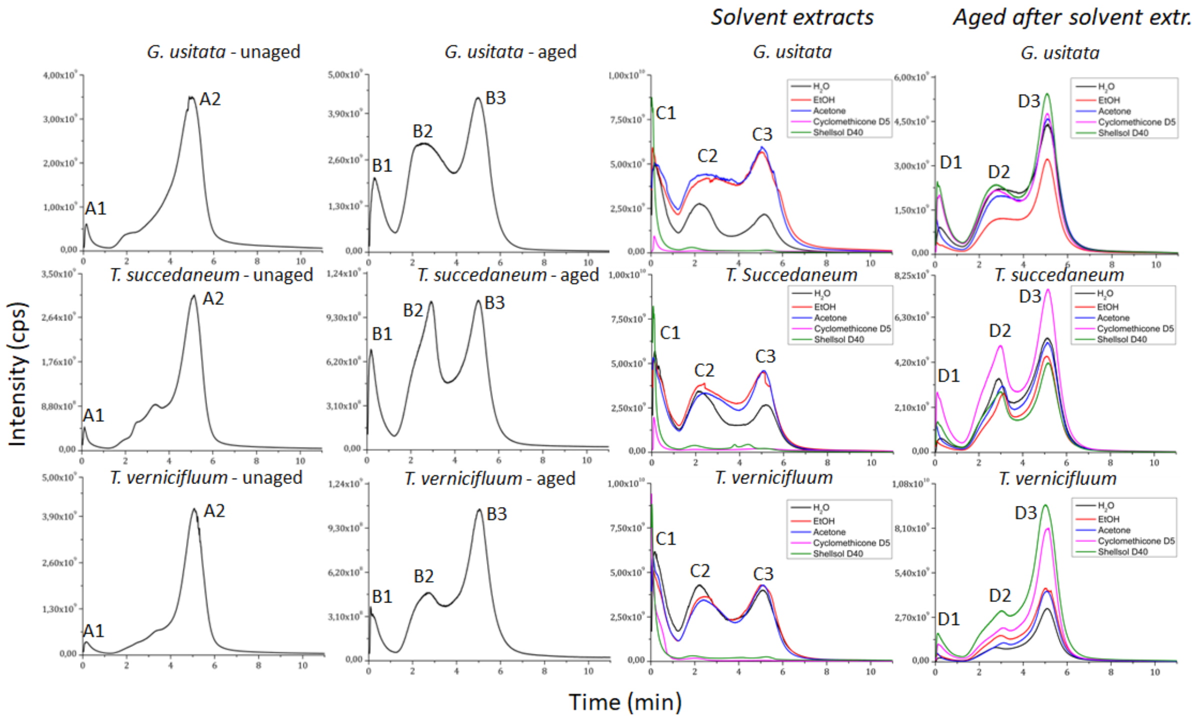


Figure 36. EGA-MS thermograms resulting from analyses of Asian lacquers: unaged, aged, solvent extracts and the aged solid samples after immersion in solvents.

While many macromolecules typically decompose below 1000 °C, Asian lacquer polymers resisted complete pyrolysis under EGA conditions. This incomplete pyrolysis was notably observed in G. usitata and T. vernicifluum polymers, as well as in T. succedaneum polymers. Consequently, sample residues persisted in the pyrolysis cups after the completion of measurements. The inefficiency of pyrolysis was further demonstrated in our Py-GC-MS optimisation study, highlighting the impact on identical samples using flash pyrolysis (see section 3.7.3).

The consideration of pyrolysis inefficiency is crucial in the data treatment of Anacardiaceae polymer analyses using EGA-MS. While EGA and flash pyrolysis are often employed in tandem, it is essential to recognize their fundamental differences. EGA involves the gradual heating of the sample from low to high pyrolysis temperatures, whereas flash pyrolysis, using the same micro furnace, exposes samples to a fixed pyrolysis temperature within milliseconds, transitioning them from ambient to pyrolysis temperature (> 450 °C). The observed incomplete pyrolysis with EGA is likely attributed to the gradual heating process, in contrast to the instantaneous temperature shock effect with flash pyrolysis. Consequently, the temperature shock effect can be deemed a prerequisite for significantly enhancing the efficient scission of intermolecular bonds in Anacardiaceae (Asian lacquer) macromolecules.

For brevity, only the primary temperature ranges will be summarized here. More detailed explanations can be found in our forthcoming article.

Unaged polymers

The results of unaged polymers show a minute fraction comprising small volatile molecules evolving at 200 °C, see A1 in figure 36. The main ions detected are *m/z* 60 and *m/z* 73, which show fragment ions of fatty acids and decomposed carbohydrates. For fatty acids the *m/z* 60 radical ion ($[(OH)_2\text{-}C{=}C]^{+\bullet}$) appears as a consequence of a McLafferty rearrangement characteristic for fatty acids that contain a minimum of 4 carbons in the main chain (Kingston et al., 1974). Similarly the *m/z* 73 shows an [C-C-CO-OH]$^+$ ion that can be attributed to the thermal desorption of fatty acids. The two ions, *m/z* 60, 73, are especially abundant in thermogram of the *T. vernicifluum* polymer. Although carbohydrates are non-volatile molecules, the compounds are prone to temperature induced decomposition at a relatively low temperature. Initial carbohydrate decomposition starts between 150 and 190°C and involves the repeated loss of water molecules (Moldoveanu, 2010). Carbohydrate decomposition other than dehydration, via water loss, should not be considered using a temperature 200 °C. All lacquer polymers show signals at *m/z* 123, [dihydroxytropylium]$^+$, corresponding to the thermal desorption of alkylcatechols (Ma et al., 2014b). Additionally, *m/z* 165 detected in the *G. usitata* thermogram was identified as a fragment ion of alkylcatechols, attributed to [butylcatechol]$^+$.

The pyrolysis temperature range (430-550 °C) is the region of EGA-MS-thermograms where cleavage of the polymers (pyrolysis) is shown, see A2 in figure 36. Mass spectra contain *m/z* 55, 67, which are characteristic for aliphatic chains, and *m/z* 91, 107 and 123, which are characteristic for *urushiol*, *laccol* and *thitsiol* moieties. Analyses on lacquer polymeric fractions demonstrate molecular ions corresponding to monomeric compounds; for *T. vernicifluum and G. usitata* (*m/z* 320) pentadecylcatechol, for *T. succedanea* (*m/z* 346) heptadecenylcatechol. *G. usitata* displays subsequently (*m/z* 354) phenyldodecylcatechol. Thermal profiles are similar for *T. vernicifluum* and *T. succedaneum*, while for *G. usitata* a less steep, slope is shown, probably relating to different types of polymeric bonds and less cross-linked matrices.

Aged polymers

In the thermal desorption temperature range (200 °C), see B1 in figure 36, all aged lacquers show dicarboxylic fatty acids with short carbon chains (*m/z* 74, *m/z* 100 and m/z 114). Results of the *G. usitata* polymer showed in combination with common fatty acid fragment ions (*m/z* 60, 73), *m/z* 138 indicative for decanedioic acid and *m/z* 152 for nonanedioic acid. The *m/z* 138, ions were absent in analyses of both *T. vernicifluum* and *T. succedaneum* polymers upon thermal desorption (200 °C). *m/z* 152 ions were only found in the thermal degradation- and pyrolysis ranges of *T. vernicifluum* and *T. succedaneum* polymers, see B2 and B3 in figure 37. This suggests their origin from oligomeric or polymeric matrices, rather than existing as free compounds, as observed in *G. usitata* polymers.

The thermal degradation range, see B2 in figure 36, shows a noticeable increase of evolved compounds compared to analyses of unaged lacquers. The thermal degradation range for *G. usitata* initiates at slightly lower temperature compared to analyses on *T. vernicifluum* and T. succedaneum polymers. The mass spectra are very similar for all lacquers in the initiatial part of the thermal degradation range and correlate to short chain dicarboxylic fatty acids. Over the complete temperature range of thermal degradation, compounds are exclusively carboxylated referring to a mixture of different degradation products. At the slope-inflection butanedioic- (*m/z* 74, *m/z* 100) and pentanedioic acids (*m/z* 114) evolve rapidly followed by dicarboxylic fatty acids with various carbon chains: for *G. usitata* up to nonanedioic acid (*m/z* 152) and for *T. vernicifluum* and *T. succedanea* until dodecanedioic acid (*m/z* 126). *G. usitata* shows *m/z* 91 and m/z 123 as well constituting from *thitsiol* oligomeric matrices or sidechain oxidised degradation products deriving from it.

The mass spectra within the pyrolysis temperature range are similar to analyses of unaged samples, with the exception of the *m/z* 115 ion, which is abundant in all lacquers, see B3 in figure 37. The m/z 115 ion might constitute from octanoic acid after pyrolytic scission at the benzylic position of 8-(2,3-dihydroxyphenyl)-octanoic acid. Compounds like this are commonly referred to as 'acid catechols', which form after oxidation of the hydrocarbon side chains of alkylcatechols.

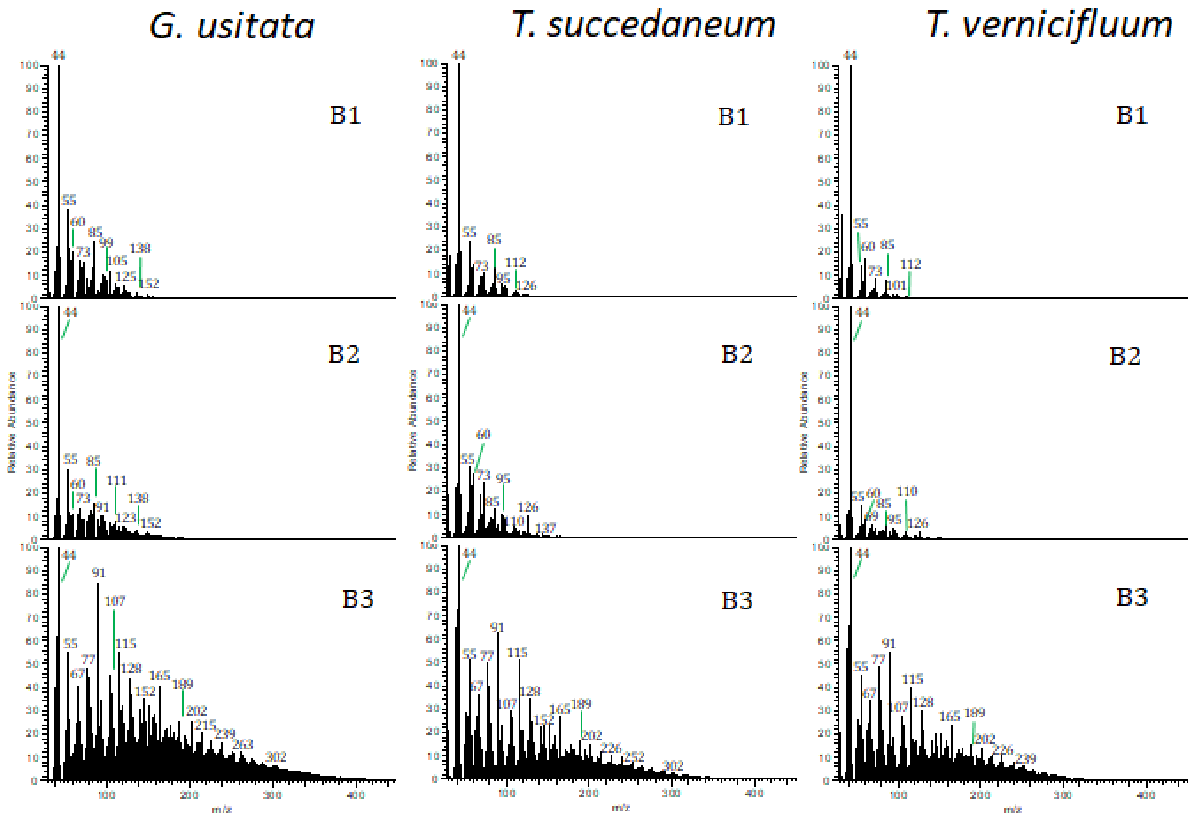
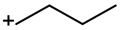
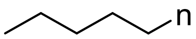
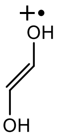
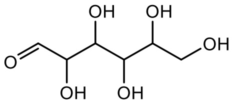
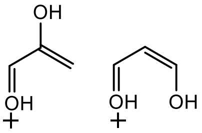
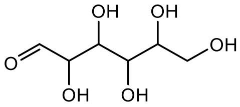
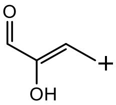
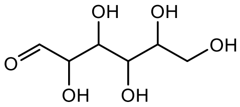
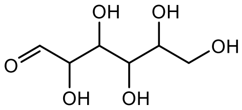
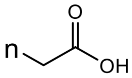
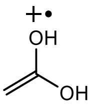
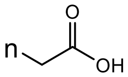
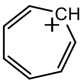
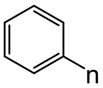
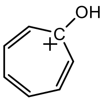
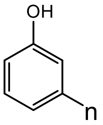


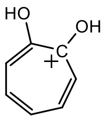
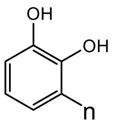
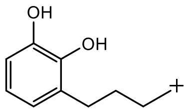
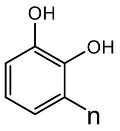
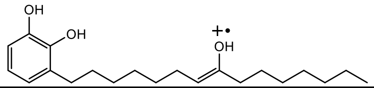
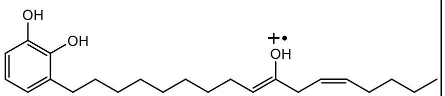
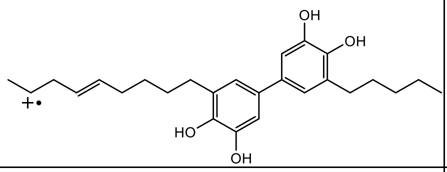
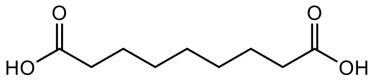
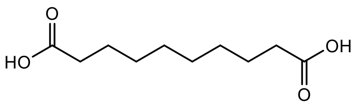
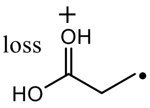
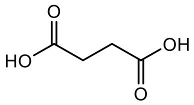
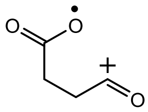
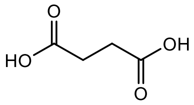
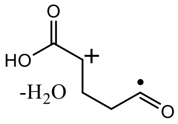
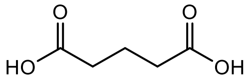
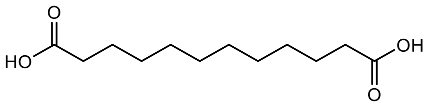
Figure 37. EGA-MS results on aged mock-up samples: averaged mass spectra for small volatile molecules (B1), evolving at 200 °C, a thermal degradation range (B2) between 230-390°C, and a pyrolysis range (B3) between 430-550 °C.

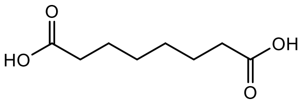
Solvent/lacquer extracts

What directly stands out from the analyses of the extracts is that water, ethanol and acetone solubilise besides small volatile molecules, which evolve at 200 °C, see C1 in figure 36, also macromolecules, see C2 and C3 in figure 36. The first temperature range in which the macromolecules are pyrolysed lies between 230 and 400 °C. These mass spectra contain mainly *m/z* 85 indicative for carbohydrates, hence, it is likely that a small polysaccharide fraction is present in the extracts. The second pyrolysis range, between 430 and 550 °C shows *m/z* 91 for alkylbenzenes, *m/z* 107 for alkylphenols and *m/z* 123 for alkylcatechols. These compounds are indicative for *thitsiol*, *laccol* and *urushiol* based matrices. We mentioned earlier the depolymerisation of urushi taking place as an effect of ageing (see Py-GC-MS optimisation section). Using EGA-MS the effect of depolymerisation seems confirmed, also for the other two lacquer types. The EGA-MS results show that the depolymerised macromolecules can be easily extracted during cleaning with polar solvents or water. Judging from the relative amounts it is clear that ethanol and acetone can extract much more macromolecules than water. The amounts of macromolecules in comparison to small molecules is also higher for ethanol and acetone compared to water. The two apolar solvents tested, cyclomethicone D5 and Shellsol D40, showed only a small fraction of small volatile molecules in the extracts, with only a negligible occurrence of macromolecules in these extracts. These solvents can be considered very safe when used on aged Asian lacquers, however, as we have explained, the apolar solvents are no effective cleaning solvents when used in a single solvent cleaning system. On the other hand, high caution should be taken into account when ethanol or acetone are used in single solvent cleaning systems as these solvents are highly effective in extracting lacquer molecular compounds, by which there can be an enhanced risk for further decay of Asian lacquers that were cleaned with these solvents.

Table 9. Summary of the EGA-MS ions.

Nr.	Name	m/z value	Structure	Molecular source
1	Butyl kation	57		 Hydrocarbons
2		60		 Carbohydrates
3		73		 Carbohydrates
4		85		 Carbohydrates
5		149	Confirmed fragmentation of galactose (unverified structure)	 Carbohydrates
6		73	Confirmed fragmentation of fatty acids (unverified structure)	 Fatty acids
7		60		 Fatty acids
8	Tropylium kation	91		 Alkylbenzenes
9	Hydroxy tropylium kation	107		 Alkylphenols

10	Dihydroxy tropylium kation	123		 Alkylcatechols
11		165	 Tentative structure	 Alkylcatechols
12		334		C-O-C linked alkylcatechol dimers
13		360		C-O-C linked alkylcatechol dimers
14		410		C-C linked alkylcatechol dimer
15		152	Confirmed fragmentation of dicarboxylic acids (unverified structure)	 Nonanedioic acid, MW 188
16		138	Confirmed fragmentation of dicarboxylic acids (unverified structure)	 Decanedioic acid, MW 202
17		74	CO_2 loss 	 Butanedioic acid, MW 118
18		100		 Butanedioic acid, MW 118
19		114	 Confirmed dehydration	 Pentanedioic acid, MW 132
20		138	Confirmed fragmentation of dicarboxylic acids (unverified structure)	 Dodecanedioic acid, MW 230

21		115	Confirmed fragmentation of dicarboxylic acids (unverified structure)	 Octanedioic acid, MW 174

Gas chromatography-mass spectrometry

Gas chromatography was initially only applied to the identification of small molecules. Based on the results we obtained on these analyses we found few inconsistencies.

The colour of the polar solvent extracts typically exhibited a yellow hue, corresponding to the presence of various light-absorbing phenolic compounds. Interestingly, the water extracts displayed less yellowing, despite maintaining a similar ratio of phenolic compounds to other non-light-absorbing compounds when compared to the other extracts. This phenomenon was particularly pronounced in laccol extracts, where the water extract appeared nearly colourless, while the ethanol and acetone extracts exhibited a slight yellow tint, see figure 35.

Gravimetric research was employed to measure the weight of laccol free film samples before and after immersion in water. The results revealed a quantitative leaching of around 20%, a finding not corroborated by the GC-MS analysis.

In order to have a better idea about the sample matrix of the extracts we used EGA-MS, see previous section. These findings indicate the extraction of not only small molecules but also depolymerized macromolecules, undetectable by GC-MS. However, the detection of these macromolecules was achieved through reversed-phase LC-HRMS. Two distinct fractions were identified using LC-HRMS—one highly polar and another of moderate polarity. Elucidation of their molecular weights revealed higher masses exceeding 2000 Da for both fractions.

To gain a deeper understanding of the macromolecules within the extracts, a preliminary screening for amino acids was conducted to assess the potential presence of glycoproteins. Hydrolysis with 6 M HCl was employed for this purpose, yielding negative results. Subsequently, hydrolysis with 1 M trifluoroacetic acid was utilized to target polysaccharides, resulting in positive findings. Notably, polysaccharides were prominently present in the water extracts, but were also detected in the ethanol and acetone extracts.

Samples for small molecule and carbohydrate analyses underwent a similar derivatization protocol prior to GC-MS analysis. Derivatization involved the addition of 60 µL BSTFA, 20 µL acetonitrile, and 10 µL of pyridine. The sample vials were then purged with N2 gas for 10 seconds, tightly sealed, and placed in an oven at 60 °C for 2 hours. Finally, 10 µL of acetonitrile containing methylstearate as an internal standard (IS) was added, resulting in a total IS concentration of 10 ng/µL.

GC-MS analyses were performed in splitless mode using an inlet temperature of 250 °C. The injection volume was 1 µL and the splitless time was 2.30 min, after which the liner was purged using a 27 mL/min split flow. Gas saver mode was enabled after 7 min, reducing the split flow to 10 mL/min. Septum purge was set at 3 mL/min. The initial GC oven temperature was 40 °C for 3.30 min, followed by a 12 °C/min gradient until 140 °C. The temperature was ramped until 200 °C at 10 °C/min. Finally, the temperature was raised 6 °C/min. until 320 °C, which was maintained for 2 min. The initial column flow was 0.66 mL/min for 3.30 min followed by a flow ramp rate of 0.019 mL/min until 0.82 mL/min.

Subsequently, the flowrate was ramped 0.037 mL/min until 1.040 mL/min and finally a 0.005 mL/min gradient was used to 1.13 mL/min. The 1.13 mL/min flowrate was maintained for 2 min.

For mass spectrometry the transfer line of the MS was set at 270 °C and ionisation was carried out in positive ion mode at 70 eV. Solvent delay was set at 6.90 min for GC-MS measurements and 2.90 min for Py-GC-MS analyses. Mass spectral information was recorded in a range of 29-600 atomic mass units (amu), with a cycle time of 0.2 s.

The small molecules identified comprised fatty acids, hydroxy fatty acids, oxo fatty acids, dicarboxylic acids, hydroxy dicarboxylic acids, oxo-dicarboxylic acids, tricarboxylic acids, poly-hydroxy-carboxylic benzenes and a few monosaccharides. The resulting peak areas are shown in figure 38. The nature of the extracts is heterogeneous, composed of high molecular weight, difficult to vaporise, macromolecules, and volatile small molecules. This heterogeneity can detrimentally affect the sample transfer from injection to condensation on the column, which is likely the reason in general why high standard deviations were observed between successive analyses. The averaged peak areas could not be used by means of absolute quantification. Therefore, averaged peak areas were used as general trends, regarding amounts extracted using various solvents.

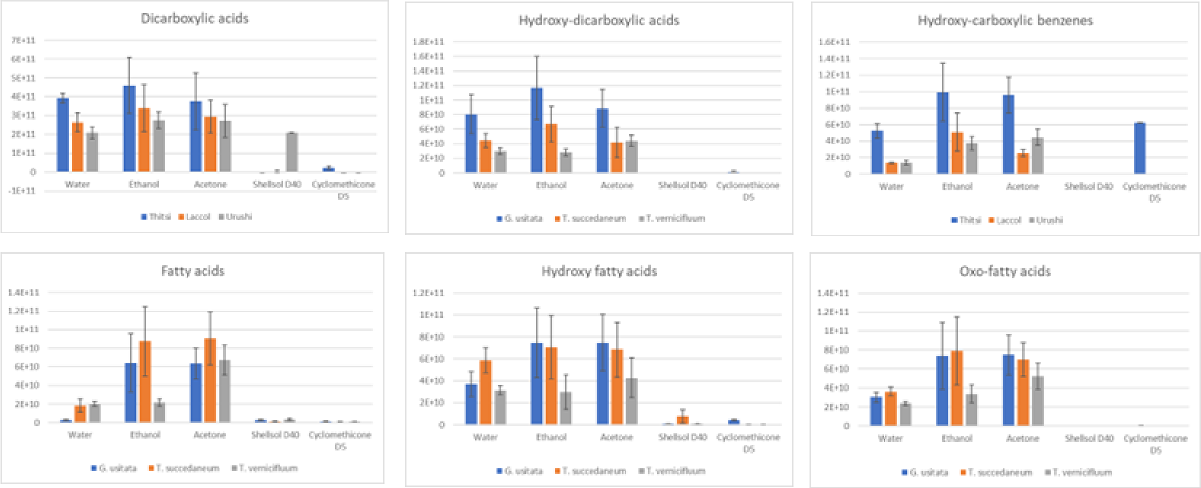


Figure 38. The summed peak areas of various compound groups in water and solvent extracts after GC-MS analysis.

Extraction with ethanol and acetone resulted in the largest peak areas for all molecular groups. The thitsi polymers showed highest sensitivity to polar solvents and water. Especially compounds with more than one carboxylic group are extracted in much higher concentrations from thitsi polymers compared to the other two lacquer types. For the laccol polymer typically fatty acids, hydroxy fatty acids and oxo-fatty acids were detected. An explanation for the higher concentration of such compounds, is found in the composition of the laccol polymer, which contains a small native oil fraction, hence, the fatty acids and its derivatives might constitute from this oil fraction. For the thitsi polymer no native oil fraction was identified. For analyses on urushi, which also contains an oil fraction, this phenomenon was not as obvious. It might be because of the degradation of the urushi polymer, taking place primarily at the first few µm of the surface. The urushi polymer might therefore not be as rigorously degraded as the laccol polymer. Although analyses of the urushi/solvent extracts showed in general smaller peak areas, the peak areas were shown to increase for dicarboxylic acids. The water extracts showed in general smaller peak areas compared to the analyses on ethanol and acetone extracts. It should however be noted that content of polysaccharides macromolecules the water extracts is much higher, especially in the laccol/water extracts. The colour of the water extracts, being less yellowish for urushi and thitsi extracts, to even completely colourless for laccol is likely caused due to the presence of polysaccharides, which do not absorb light. Carbohydrates also do not have any UV absorbance making the water extracts less fluorescent, due to higher concentration of sugars, compared to the ethanol and acetone extracts.

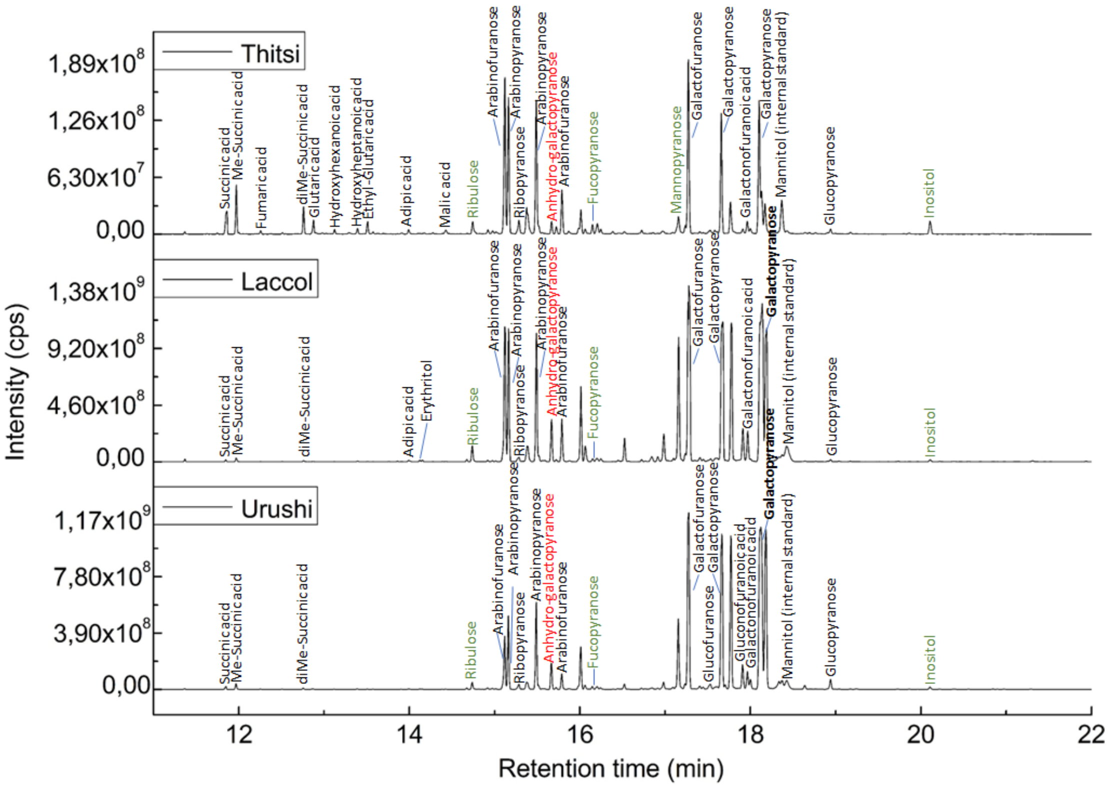


Figure 39. GC-MS-analyses resulting from hydrolysed polysaccharides in the water extracts of thistsi, laccol and urushi.

The GC-MS carbohydrate analyses proved useful for two main reasons. It allowed to fully characterise a macromolecular fraction in especially the water extracts (figure 39). Given the higher molecular weight of these structures (>2000 Da) the polysaccharides make up a large part of extract composition. The analyses also served by means of additional verification of the polysaccharide characterisation study for which we used Py-GC-MS (see section 3.9). Few compounds, shown in green colour, such as ribulose, were additionally identified, which could not be elucidated using Py-GC-MS. Their identification via the GC-MS approach further strengthens our analytical results on the Asian lacquer carbohydrate topic.

For more information on the analyses of the extracts with GCMS and LC-HRMS we refer to the forthcoming publications.

3.13. Description of the final cleaning protocol

Considering that no solvent is entirely harmless and that any cleaning action is irreversible, it is essential to bear in mind that despite the advancements in scientific research, treatment as complex as that of cleaning photo degraded lacquers involve a series of compromises. The multitude of variable parameters involved makes it nearly impossible to establish a standardized protocol that would facilitate the implementation of cleaning treatments.

However, projects such as the PHySICAL-project have contributed to complementing the framework established by previous studies. Waters with adjusted pH (and conductivity) have demonstrated their effectiveness. Their study has been extensively explored through concrete tests on mock-ups as well as on the heavily soiled Chinese etagere.

Having a concrete idea of the pH and conductivity of the surface to be cleaned is a valuable aid in establishing a cleaning protocol. Recording these measurements should be done while minimizing their impact on the surface. The selection of the cleaning product should be based on the object's composition and the presence or absence of decorative elements.

As studied during recent tests, the application method will be one of the keys in implementing the cleaning process and its final result. The methods proposed above have proven their effectiveness on flat surfaces but now need to be tested on three-dimensional objects to determine their feasibility for broader use. As cleaning techniques and their applications are continuously evolving, it seems pertinent for us to remain informed about the development of these techniques.

Finally, numerous parameters must be considered in establishing a cleaning protocol, including the material, its alterations, the pH, and the conductivity of its surface. However, as mentioned by various mentors in the profession, we emphasize the importance of coupling all these parameters with the skills and sensitivity of the restorer trained in these issues.

3.14. Cleaning and conservation of the selected objects

Following a comprehensive evaluation of the conservation state of the four selected objects detailed in this research project, conservation treatments have begun in the workshop. The majority of required structural and fixing treatments are nearing completion. As of November 2023, the conservation process for the selected objects is still ongoing. Upon completion, treatment reports related to the cleaning and conservation of these items will be provided as annexes. A concise overview of the current state of affairs is outlined below.

<u>The Burmese Buddha:</u> Previously applied silicone adhesive (grey sanitary) has been removed, and residues were mechanically cleared. Elements of the crown have been repositioned and adhered. Where necessary, fillings have been performed, with final touch-ups scheduled after cleaning.

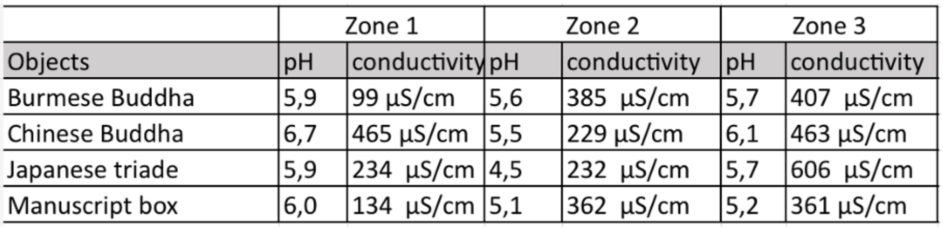
<u>The Thai box</u>: All lifted elements have been secured using the traditional Japanese technique of "*shimbari*." This method allows for a gradual repositioning of scales and their maintenance under pressure until the fixative dries.

<u>The Triad</u>: Metal jewellery and glass ornaments of the acolytes have been cleaned, uncovering the presence of included coloured pearls and glassware. Previous restorations (adhesive applications) causing tension in the halo have been dismantled, along with unnecessary metal screws and wires. New adhesives are being gradually applied, occasionally incorporating new bamboo tenons. The previous intervention on the cloud-shaped base (left side) has also been dismantled due to unstable adhesion and noticeable misalignment.

The Chinese Buddha: This sculpture displayed previous interventions causing tension and resulting in fissures, some of which were meticulously removed under a binocular microscope.

Finally, to initiate the cleaning treatments, pH (and conductivity measurements) of the various objects have been conducted and recorded in the table W below.

Table 10. pH (and conductivity) results of the four selected items from the collection of the RMAH.



	Zone 1		Zone 2		Zone 3	
Objects	pH	conductivity	pH	conductivity	pH	conductivity
Burmese Buddha	5,9	99 µS/cm	5,6	385 µS/cm	5,7	407 µS/cm
Chinese Buddha	6,7	465 µS/cm	5,5	229 µS/cm	6,1	463 µS/cm
Japanese triade	5,9	234 µS/cm	4,5	232 µS/cm	5,7	606 µS/cm
Manuscript box	6,0	134 µS/cm	5,1	362 µS/cm	5,2	361 µS/cm

These data show the complexity involved in cleaning lacquered objects due to variations in pH and conductivity within a single object.

The results obtained from the tests conducted on shelf B of the Chinese etagere have demonstrated the relevance and usefulness of adapting innovative application methods for the cleaning of sensitive surfaces such as altered lacquers. The four methods tested on shelf B have proven their relevance concerning the constraints posed by the cleaning of these types of objects.

Through the analyses on the Chinese etagere, it became apparent that all these innovative methods had the advantage of cleaning without leaving residues on the surface. Their application on three-dimensional objects will now be explored through the cleaning process of the four objects entrusted by the museum. The results of these applications will be available in the treatment reports.

3.15. General conclusion

In the realm of Asian lacquer conservation, the PHySICAL project has yielded invaluable insights and practical guidelines for cleaning aged surfaces. The Royal Museums of Art and History (RMAH) successfully documented and relocated 750 lacquered items within the museum's collection, enhancing preservation conditions. The evaluation of cleaning solvents revealed water, with adjusted pH, as the most effective method for aged lacquer surfaces.

The chemical analyses, conducted at the Royal Institute for Cultural Heritage (KIK-IRPA) and the Ghent University, particularly Py-GC-MS and LC-(orbitrap)MS, provided a nuanced understanding of lacquer composition and degradation products. Notably, a developed Py-GC-MS method unveiled improved sensitivity in analysing polysaccharides unravelling the polysaccharides mechanism in Asian lacquers —a groundbreaking achievement in Asian lacquer analysis.

In conclusion, the PHySICAL project not only advances best practices for cleaning but also offers a meticulous approach to the conservation and display of culturally significant artifacts. Its global impact extends beyond the RMAH collection, contributing to a broader understanding of Asian lacquer cleaning practices for the benefit of future generations in academia, conservation, and enthusiast communities. The project's results fortify the appreciation of these objects and ensure their enduring place in the cultural heritage tapestry.

4. DISSEMINATION AND VALORISATION

Participation to conferences:

- International conference "Nanban. Far east. Close art" 4-5 October 2019 Warsaw, Poland. Delphine Mesmaeker, Jonas Veenhoven, Nathalie Vandeperre, Maarten van Bommel, Henk van Keulen, Frederic Lynen and Steven Saverwyns. *The physical project: research protocol applied on a Japanese buddha statue* (poster presentation)
- International conference "Nanban. Far East. Close Art" 4-5 October 2019 Warsaw, Poland. Elise Andersson, Jonas Veenhoven and Paul van Duin. *Material and cross-section analysis of Japanese Namban lacquer* (oral presentation)
- 42nd International Symposium of Capillary Chromatography (ISCC), 14-18 May 2018, Riva del Garda, Italy. Jonas Veenhoven, Steven Saverwyns, Henk van Keulen, Maarten van Bommel, Michael Schilling, and Frederic Lynen, F. *Method development for the analysis of artificially light aged Asian Lacquer films using pyrolysis and thermal desorption techniques hyphenated with gas chromatography/mass spectrometry.*
- 9th meeting of the Users' Group for Mass Spectrometry and Chromatography – MaSC, Canadian Conservation Institute (CCI), 3-7 juni 2019, Ottawa, Canada. Jonas Veenhoven, Steven Saverwyns, Henk van Keulen, Maarten van Bommel and Frederic Lynen, *GCMS identification of de-polymerized leachable molecules in organic solvent extracts from unaged an artificially light aged Asian lacquer films for evaluating cleaning procedures* (oral presentation)
- 19th ICOM-CC Triennial conference Beijing, China, May 2021, Saverwyns, S., Veenhoven, J., Mesmaeker, D., Vandeperre, N., van Keulen, H., van Bommel, M., Lynen, F. *Evaluation of cleaning solvents for Asian lacquers* (poster presentation, due to Covid19-restrictions: online participation)
- 17th international symposium on hyphenated techniques in chromatography and separation technology, Ghent, Belgium. 18-20 May 2022 J. Veenhoven, S. Saverwyns, H. van Keulen, M. van Bommel, F. Lynen. *Chromatography and mass spectrometry to study cleaning effects on Asian lacquered cultural heritage objects.* (poster presentation)
- 10th meeting of the users' group for mass spectrometry and chromatography (MaSC), Bordeaux, France. 29-30 September 2022, J. Veenhoven, D. Mesmaeker, L. Decq, A. Coudray, S. Saverwyns, N. Vandeperre, H. van Keulen, M. van Bommel, F. Lynen. *Comparison of thermal hydrolysis and methylation versus in situ trimethylsilylation pyrolysis-gas chromatography-mass spectrometry applied to the analysis of Asian lacquer of a Burmese buddha sculpture* (poster presentation)
- 10th meeting of the users group for mass spectrometry and chromatography (MaSC), Bordeaux, France. 29-30 September 2022, J. Veenhoven, S. Saverwyns, H. van Keulen, M. van Bommel, F. Lynen. *Differentiation between primary and secondary pyrolysis reactions to improve the identification of Asian lacquer macromolecules.* (oral presentation)

Participation in workshops:

- Practical session with Heri Gahbler: Intensive lecture and instruction about grounding of urushi-lacquer work on different sample boards. 2 September 2017
- Practical session with Heri Gahbler: Intensive Workshop about pigments and coloured lacquer. 21 October 2017
- Workshop on *Buffer solutions, theory and kit preparation*, *Shake in Conservation,* Brussels. 3 and 4 May 2018.

- Workshop on *Soft Particles* held at the University of Antwerp, 24 Octobre 2019. This workshop was organized by *Shake in conservation* in collaboration with Defner & Johann company and Maren Dümmler, paper conservation specialist.
- Workshop on *The aqueous environment and solvents for treatments on works of art on paper application to documents, ancient art and contemporary art* by Paolo Cremonesi and Leatitia Sato. ENSAV La Cambre 4-7 November 2019.

Others:

- RMAH and KIK-IPRA partners have made an oral and poster presentation about the PHySICAL research project during the *JPI Cultural Heritage meeting* on 13 and 14 Th November 2019 hosted by the Royal Museum of Art and History.

5. PUBLICATIONS

All papers are (will be) published in peer review journals.

- Jonas Veenhoven, Steven Saverwyns, Henk van Keulen, Maarten van Bommel, Frédéric Lynen, *Polysaccharide metabolism in Anacardiaceae (Asian lacquer) cross-linked polymers elucidated using in situ trimethylsilylation pyrolysis-gas chromatography–mass spectrometry*, Carbohydrate Polymers, Volume 323, January 2024, 121373. DOI: 10.1016/j.carbpol.2023.121373

- Marine Wojcieszak, Jonas Veenhoven, Tess van den Brande, Steven Saverwyns, Frédéric Lynen, Mathieu Boudin, *Radiocarbon dating of Asian lacquers: molecular characterization and assessment of a pretreatment method prior to accelarator mass spectrometry,* Radiocarbon, November 2023, 1-20. DOI: 10.1017/RDC.2023.90

- Jonas Veenhoven, Henk van Keulen, Steven Saverwyns, Frédéric Lynen and Maarten van Bommel, *Optimising the analysis of Anacardiaceae (Asian lacquer) polymers using pyrolysis-gas chromatography-mass spectrometry*, Journal of Analytical and Applied Pyrolysis, 2023 (170), 105845. DOI: 10.1016/j.jaap.2022.105845

Three other publications are in preparation: one on the identification of the water and solvent extracts of aged Asian lacquers with (Py-)GC-MS, one on the identification of the water and solvent extracts of aged Asian lacquers with LC-(orbitrap)MS, and a final one discussing all results of cleaning and conservation of the objects (mock-ups, Chinese etagere, and selected objects from the collection of the RMAH).

Master thesis

- Bianchi, C., 2021. *pH measurement as a tool for the conservation of water-sensitive surfaces and for heritage science: The PHySICAL collection of Asian Lacquers.* École Nationale Supérieure d'Arts Visuels de La Cambre, Brussels.

- Lesage, P., 2022. *L'utilisation des solvants utilisés dans la restauration des laques asiatiques anciennes et sur l'influence de ces derniers sur brillance couplés à des analyses GCMS*. Liège Université, Liège

PhD thesis

- Veenhoven, J. 2024 (in preparation). Universiteit Gent/Universiteit van Amsterdam

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ANNEXES

Full treatment reports on the four selected objects will be provided when available. For the scientific paper references is made to the scientific journals as they were not published in open access.

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