Recent Advances in Characterizing Asian Lacquers

LACQUER ANALYSIS REPORT

Results of examination and analysis undertaken by

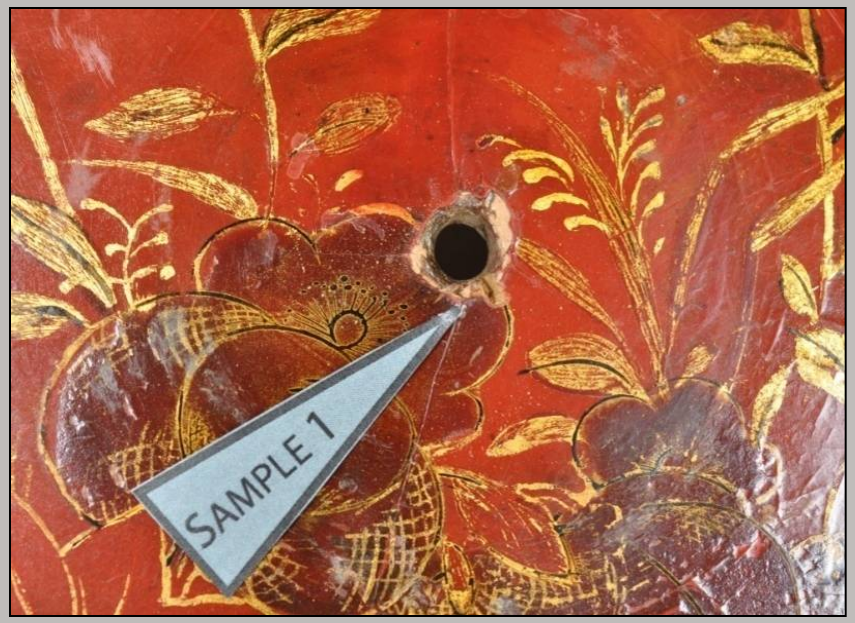
Michael Schilling, Arlen Heginbotham, Nanke Schellmann and Raina Chao

Recent Advances in Characterizing Asian Lacquers workshop

October 2012

Title: Inkstand (Encrier)

Owner: The J. Paul Getty Museum
Accession Number: 76.DI.12
Origin: French (gilt bronze mounts) and Chinese (porcelain and lacquer)
Dimensions: H: 20.3 x W: 35.6 x D: 26.7 cm
Date: Porcelain and lacquer early 18th C; mounts about 1750.
Conservators: Arlen Heginbotham, Raina Chao
Scientists: Michael Schilling, Nanke Schellmann
Sample Number: 1
Sample Location: adjacent to the mounting hole for the central inkpot.



Purpose and context for analysis:

The origin of the lacquer on this tray has been a matter of contention for many years. Currently in Museum records, it is officially listed as European 'japanning'. The purpose of this analysis was to determine, as far as possible, the region of origin of the lacquer.

EXPERIMENTAL

Cross Section Examination with Optical Microscopy and Staining Methods

Lacquer flakes were mounted in clear polyester resin for cross section examination, and polished using Micro-Mesh papers up to 12000 grit. Cross sections were examined using an optical microscope alternating between incident white light and blue light (high-pressure mercury lamp filtered through an I3 cube). After applying staining solutions to the cross sections, they were examined under both types of illumination, and photomicrographs recorded their appearance. The stains and their corresponding binding media are: Amido Black 10B (AB2) for proteins; iodine – potassium iodide (I_2KI) for starches; Sudan Black B for drying oils and lipids; Nile Blue sulfate for oils and protein.

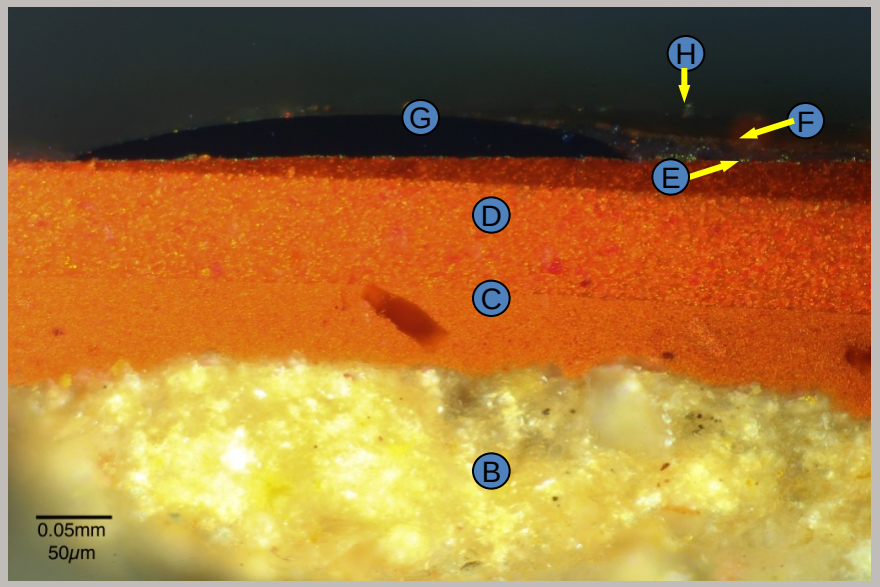
Micro-Excavation to Remove Samples from Individual Lacquer Layers

Cross section samples taken from well-preserved and representative sample sites were examined by visible light and UV microscopy. These yielded a clear understanding of the layer structure at the sample site, including the number, appearance and thickness of original and restoration layers present. Sampling for Py-GC/MS analysis was done by scraping with a micro-chisel from an area approximately 2 mm x 2 mm, 'excavating' layer-by-layer and collecting the scrapings from each layer separately. The work of excavation was conducted under a stereomicroscope using both visible light and a high-intensity UV spotlight. Cross section photomicrographs were regularly consulted as sampling progressed to aid in the identification of each layer. Scrapings of the target layer were carefully extracted and placed in the well of a single-depression microscope slide. Collection of sample material was halted when the next, underlying layer began to be exposed and posed a risk of interlayer contamination. Layers more than 20 µm in thickness could usually be sampled discretely with little or no contamination from adjacent layers.

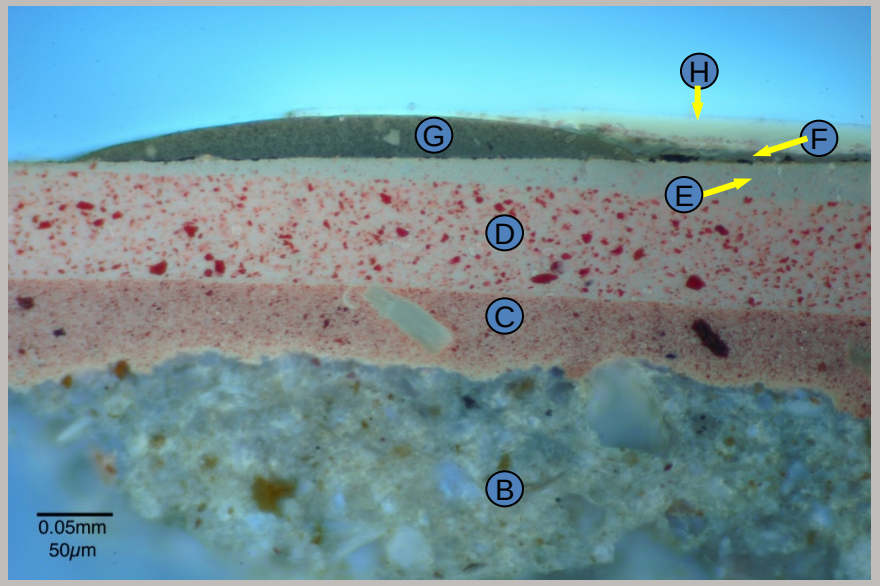
THM-Py-GC/MS of Lacquer Layer Samples

A Frontier Lab PY-2020D double-shot pyrolyzer system was used for pyrolysis. The pyrolysis interface was maintained at 320°C. The pyrolyzer was interfaced to an Agilent Technologies 5975C inert MSD/7890A gas chromatograph/mass spectrometer. A J&W DB-5MS-UI capillary column was used for separation (30 m x 0.25 mm x 0.25 µm). By attaching the column to a Frontier Vent-Free adaptor, the effective column length was 40 m. The helium carrier gas was set to 1 ml/minute. The split injector was set to 320°C with a split ratio of 50:1 and no solvent delay. The GC oven temperature program was 40°C for 2 minutes, then ramped to 320°C at 6°C /minute, followed by a 9 minute isothermal period. The MS transfer line was at 320°C, the source at 230°C, and the MS quad at 150°C. The mass spectrometer was scanned from 10-600 amu at a rate of 2.59 scans per second. The electron multiplier was set to the autotune value. Samples were placed into a 50 µl stainless steel Eco-cup fitted with an Eco-stick, and three microliters of a 25% methanolic solution of tetramethyl ammonium hydroxide (TMAH) were introduced for derivatization. After three minutes, the cup was placed into the pyrolysis interface where it was purged with helium for three minutes. Samples were pyrolyzed using a single-shot method at 550°C for 6 seconds. Marker compounds for lacquer components were identified, peak area percentage reports were generated and a final report was made using a specialized Excel worksheet from the Getty.

STRATIGRAPHY



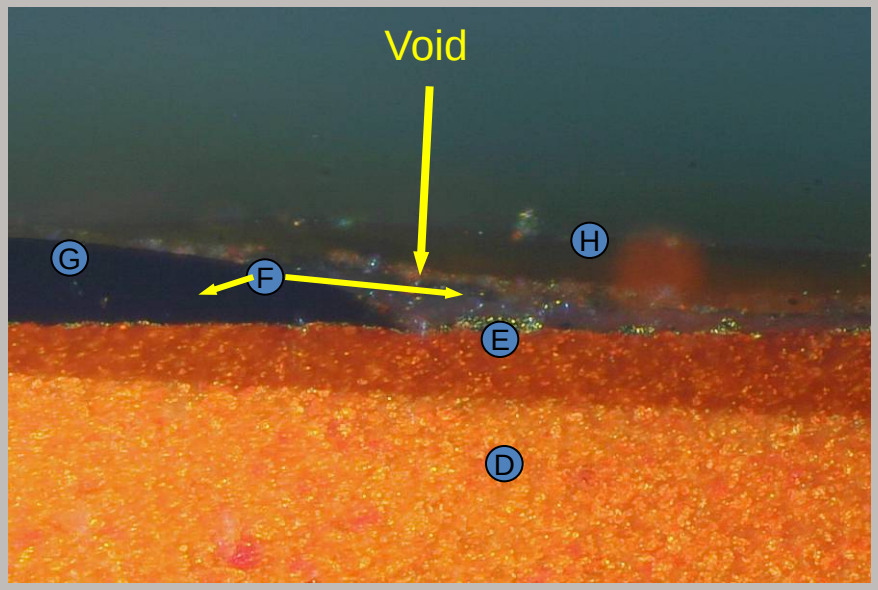
Visible Light Illumination



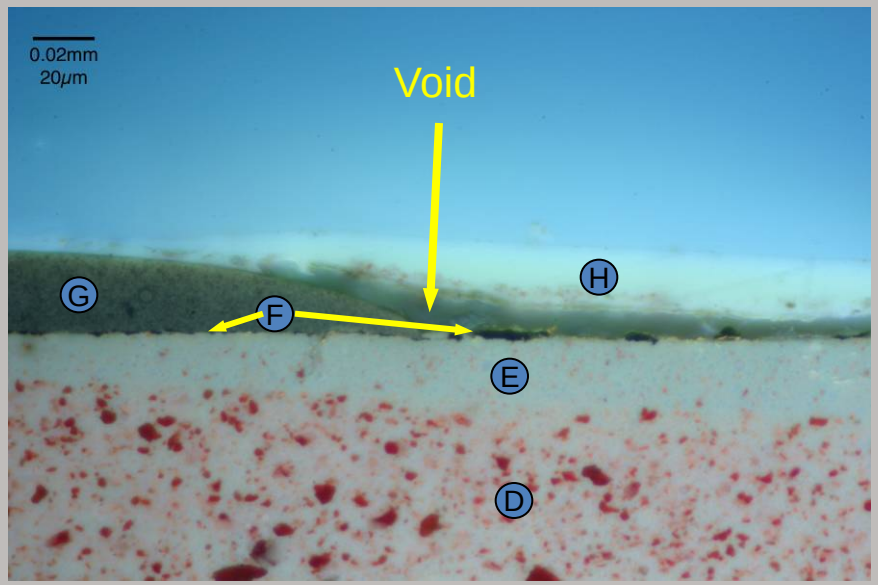
Ultra Violet Illumination

Layer	Name	Description
H	Restoration Varnish	Yellowish, brittle, fluoresces yellow/ green under UV; contains some red pigment in the lower portions.
G	Black Outline	Dark, very small particles, probably of carbon black; lacquer apparently contains copper sulfate as an additive.
F	Gold	Very interrupted; where present below the black line, it is certainly the original gold.
E	Dark Red Size	Dark, small particles, probably of hematite. Relatively sparsely pigmented. Appears to have copper sulfate added.
D	Bright Red Upper Lacquer	Brighter red, larger, coarser particles of natural ground vermillion, brighter under UV
C	Red Lower Lacquer	Duller red, very fine particles, probably of hematite, slightly darker under UV. Appears to have copper sulfate added.
B	Ground	Thick, tan, contains fibrous materials. Appears to be a clay-based ground utilizing a clay rich in rare earth elements (cerium and lanthanum in particular). China holds the largest share of the world's naturally occurring rare earth elements .
A	Wood (not visible in photo-micrograph)	Identified as *Erythrina,* spp. (Coral wood), see Wood ID Report

STRATIGRAPHY (DETAIL)



Visible Light Illumination



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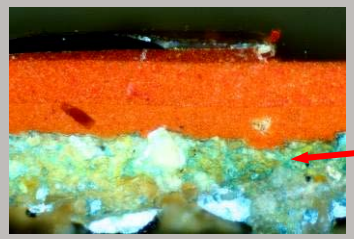
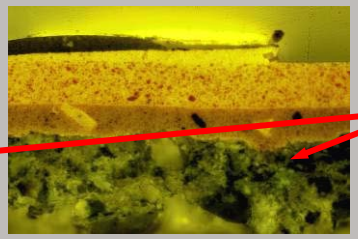
STAINING RESULTS

No Stain – visible light (VIS)

No Stain – blue light cube (I3)

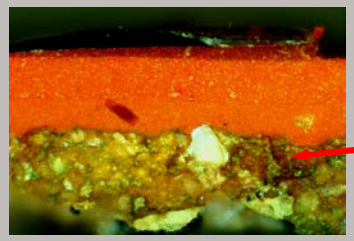


Amido Black 10B (AB2) – VIS

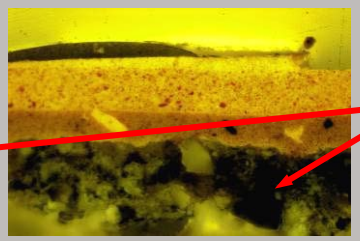


Amido Black 10B (AB2) - I3 cube

Positive staining for protein in layer B

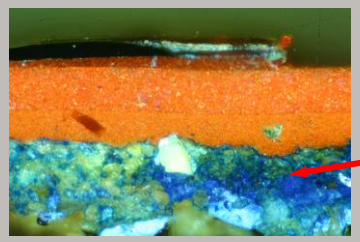


I_2KI (starch) – visible light

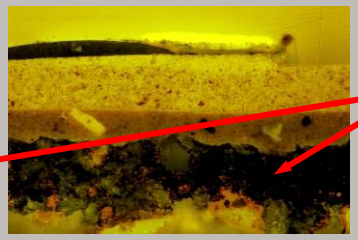


I_2KI (starch) – blue light cube (I3)

Positive staining for starch in layer B



Nile Blue sulfate (oil/protein) – VIS



Nile Blue sulfate (oil/protein) – (I3)

Positive staining for oil/protein in layer B

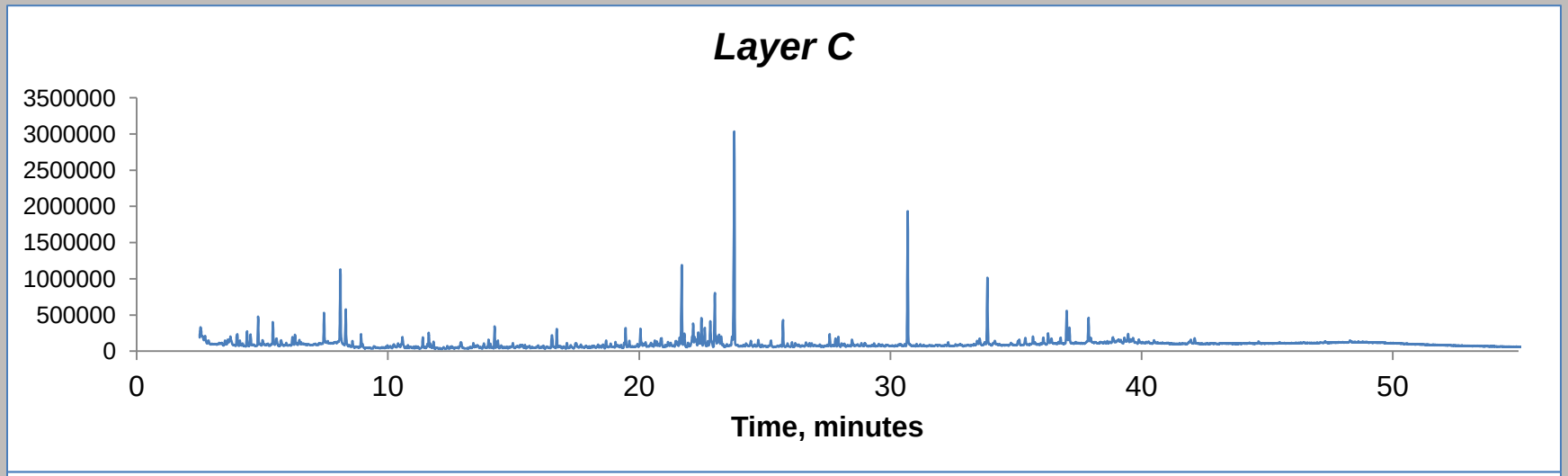
Sudan Black B (oil/lipids) – VIS

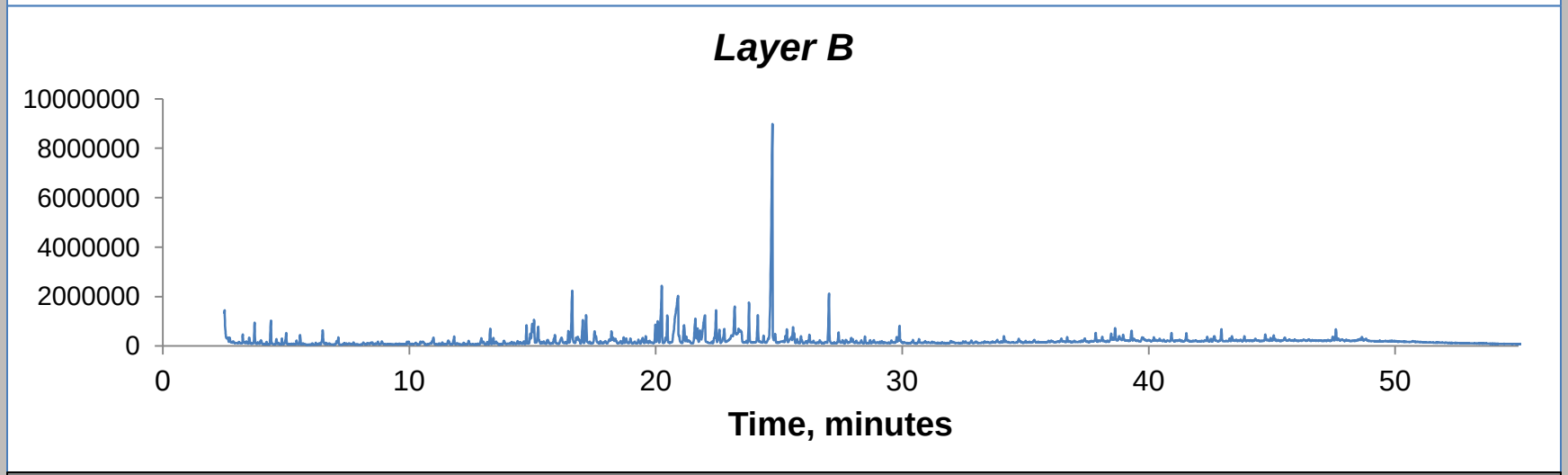
Sudan Black B (oil/lipids) – (I3)

Positive staining for oils/lipids in layer B and possibly in H

Layer	Name	Fluorescence/Staining results
H	Restoration Varnish	Before staining: bright yellow fluorescence in blue light suggests an oil-containing varnish layer. Positive staining result with Sudan Black B (black appearance in blue light): varnish layer appears to contain drying oil and/or other lipids .
G	Black Outline	Dark caramel-brown fluorescence under blue light suggests the presence of Asian lacquer (pigmented with black pigment or possibly stained black with iron compound).
F	Gold	n.a.
E	Dark Red Size	Fluorescence of binder matrix under blue light suggests a mixture of Asian lacquer with a significant amount of additive (probably oil, protein or persimmon juice).
D	Bright Red Upper Lacquer	Fluorescence of binder matrix under blue light suggests a mixture of Asian lacquer with a significant amount of additive (probably oil, protein or persimmon juice).
C	Red Lower Lacquer	Fluorescence of binder matrix under blue light suggests a mixture of Asian lacquer with a significant amount of additive (probably oil, protein or persimmon juice).
B	Ground	Positve staining results for protein (weak staining), starch (weak staining), oil/protein and oil/lipids. High oil content at the interface between layer B and C. According to the whitish-green fluorescence of the layer before staining, Asian lacquer is unlikely to be contained in layer B.
A	Wood	Not present in cross-section.

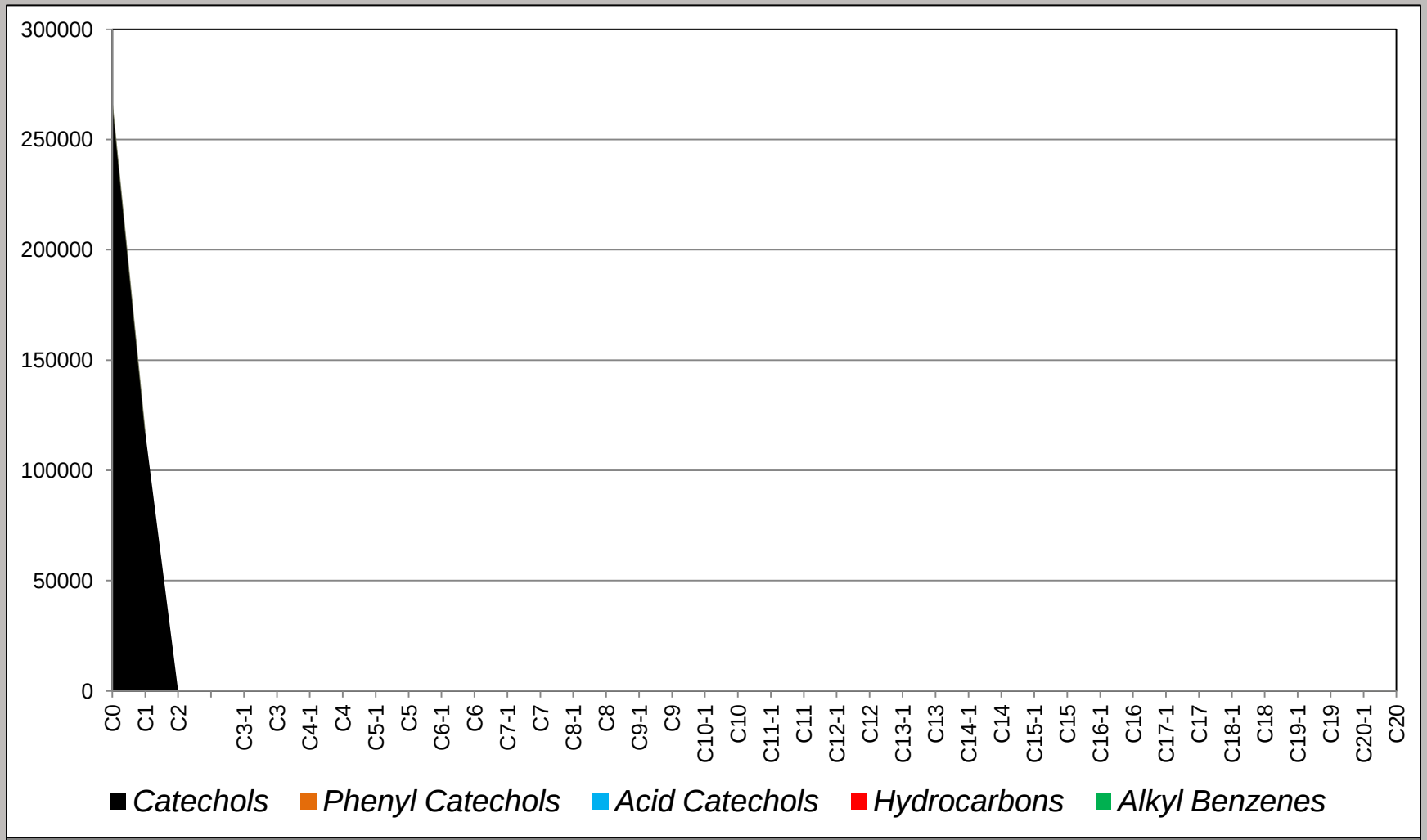
THM-Py-GC/MS TOTAL ION CHROMATOGRAMS





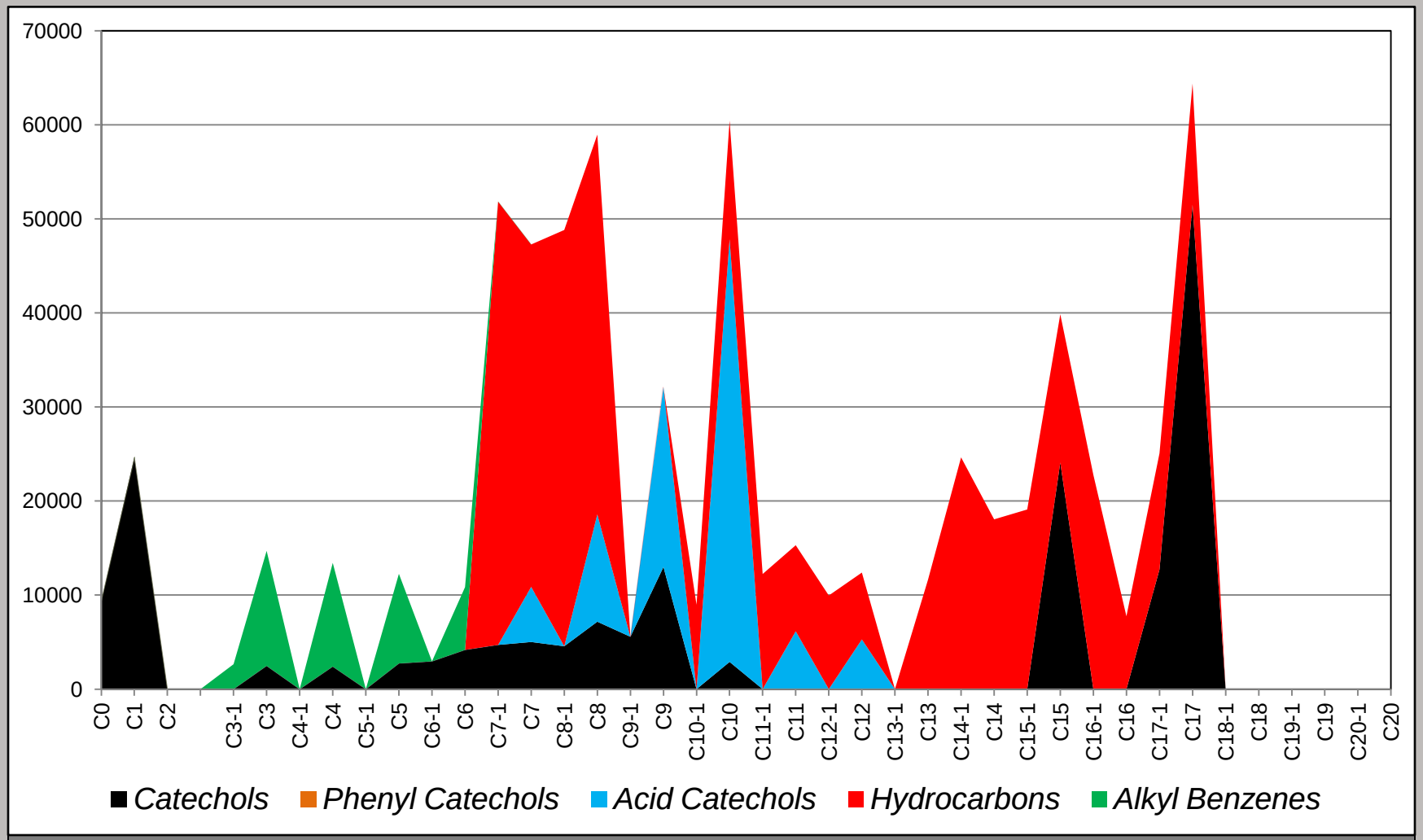
Interpretation: Sample B, the foundation layer, contains a large quantity of plant fibers. The TIC contains a large number of peaks from methylated carbohydrates, along with many late-eluting peaks that are not in the marker compound database. The vast majority of peaks in the red lower lacquer layer (sample C), are listed in the marker compound database.

GESTALT GRAPH OF ANACARD MARKERS: FOUNDATION



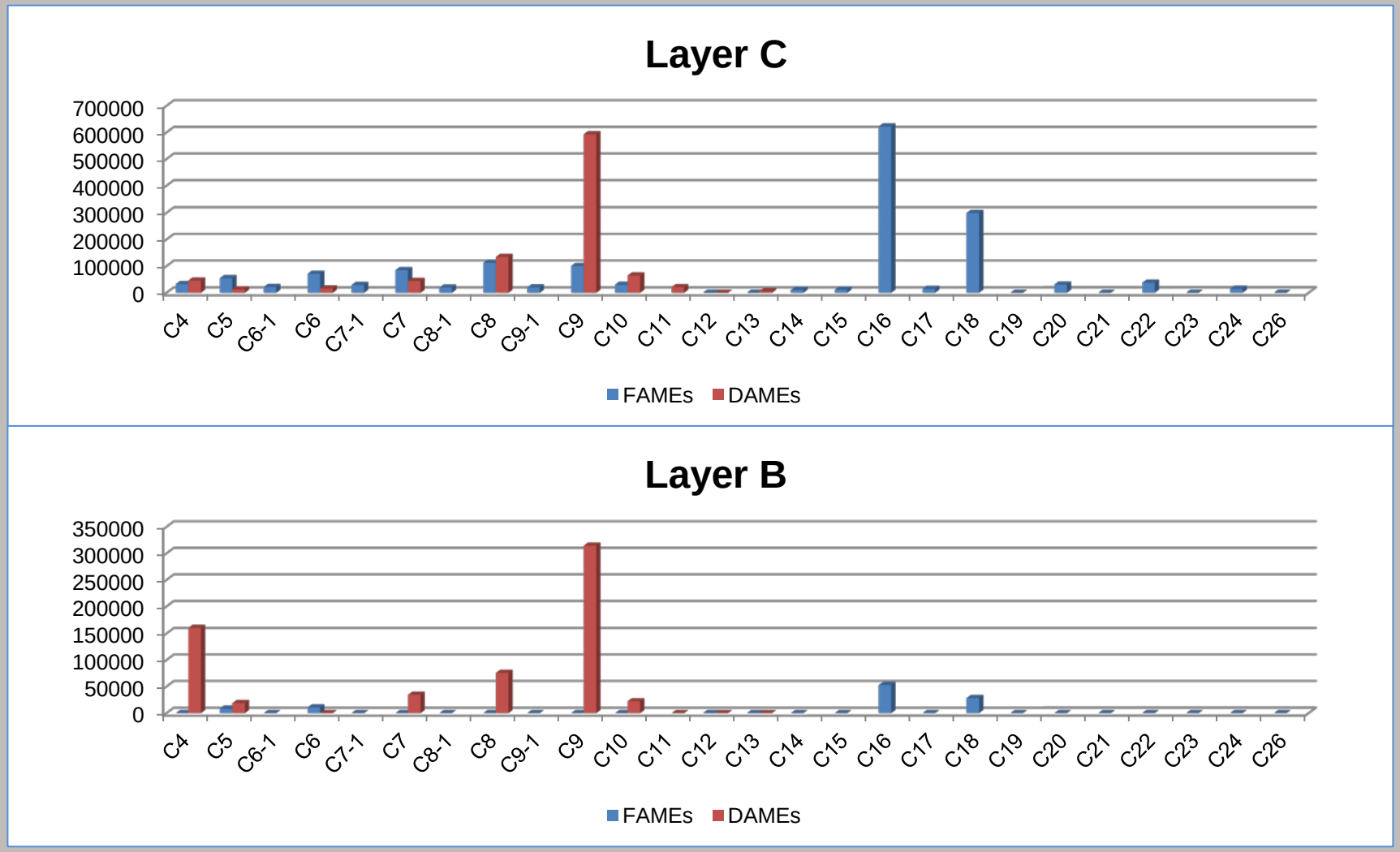
Interpretation: No Anacard markers of any kind were detected in the foundation layer (sample B). Catechol and methyl catechol may be formed by non-Anacard materials.

GESTALT GRAPH OF ANACARD MARKERS: FINISH LAYER



Interpretation: In the red lower lacquer layer (sample C), the marker compound evidence points toward laccol. A large peak for Arlenic acid, the C_{10} acid catechol, is abundant in laccol. Further confirmation for laccol comes from the presence of heptadecylcatechol and heptadecenylcatechol, and a maximum in the hydrocarbon series for heptadecane.

FATTY ACIDS FROM OILS



Interpretation: Based on the proportions of fatty acid methyl esters (FAMEs) and dicarboxylic fatty acid methyl esters (DAMEs), rapeseed oil is likely present in the red lower lacquer layer (sample C) due to the elevated levels of higher molecular weight fatty acids, although the 2.1 ratio of palmitate to stearate (P/S) is a bit lower than the typical reference data for rapeseed oil. Linseed oil is indicated in the foundation layer (sample B) based on a P/S of 1.9 and a very high A/P ratio (6.0).

RESIN MARKER COMPOUNDS

Cedar oil or pitch	Time	Layer B	Layer C
Alpha-cedrene	21.2	0	0
Beta-cedrene	21.5	0	0
Cedrol	24.9	0	14731

Gum benzoin	Time	Layer B	Layer C
Methyl cinnamate	20.2	0	0
Methyl 4-methoxybenzoate	19.9	0	5719
Benzaldehyde, 3,4-dimethoxy-	22.2	628778	6737
Benzaldehyde, 4-methoxy-	9.3	0	0
Methyl p-methoxycinnamate, cis	26.0	0	0
Methyl benzoate	13.4	20763	11177
Methyl-3,4-dimethoxybenzoate	24.3	6274168	0

Interpretation: The red lower lacquer layer (sample C) contains cedar oil or cedar pitch, and the lack of cedrene is fairly commonplace. Although the foundation layer (sample B) contains several markers of gum benzoin at high concentration, the lack of methyl cinnamate makes its presence highly unlikely. It is possible these markers come from a carbohydrate, which is abundant in the sample. No markers were detected for colophony, shellac, camphor or dipterocarpus resin.

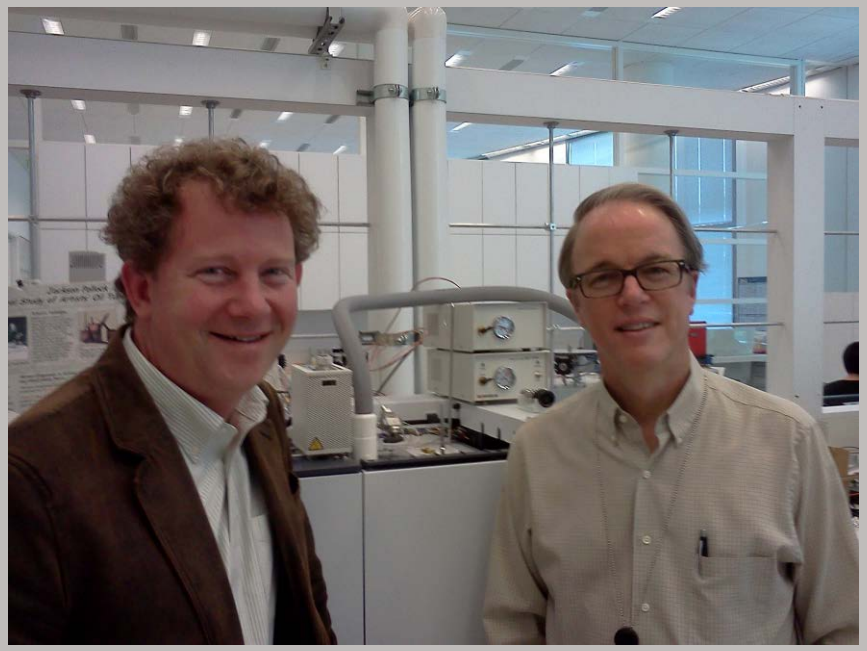
OTHER ASSORTED MARKER COMPOUNDS

Proteins	Time	Layer B	Layer C
1-Methyl pyrrole	4.3	17908	0
Pyrrole	4.5	0	10340
Possible glue markers			
Protein marker 2 (glue)?	13.1	0	4224
Protein marker 3 (glue)?	18.8	0	0
Protein marker 4 (glue)?	21.0	0	0
Protein marker 5 (glue)?	26.3	0	0
Glue marker - Mazzeo	26.6	0	7513
Possible blood markers			
Protein marker 2 (blood)?	24.0	0	30667
Protein marker 3 (blood)?	22.3	0	0

Carbohydrates	Time	Layer B	Layer C
Furfural	6.2	30975	16048
Methylated carbohydrate	20.1	342839	0
Carbo marker - Mazzeo	16.1	137634	0
Persimmon juice			
1,2,3-Trimethoxybenzene	12.6	70358	10527
1,2,4-Trimethoxybenzene	19.9	152613	68660
1,2,3,4-Tetramethoxybenzene	21.5	48002	39873
Methyl 2,3-dimethoxybenzoate	24.5	0	11246
Wood Volatiles			
Yangambin	49.8	10791	0

Interpretation: Both layers contain some type of protein, although it is unclear if it is glue, blood or both. The fibers in Layer B contributed greatly to the totals of carbohydrates, unassigned aromatic compounds and methoxybenzenes. All four markers for persimmon juice are present in Layer C, so its presence in the layer is certainly possible. Yangambin, occasionally detected in foundation layer samples, is thought to originate from the underlying wood.

CONCLUSIONS

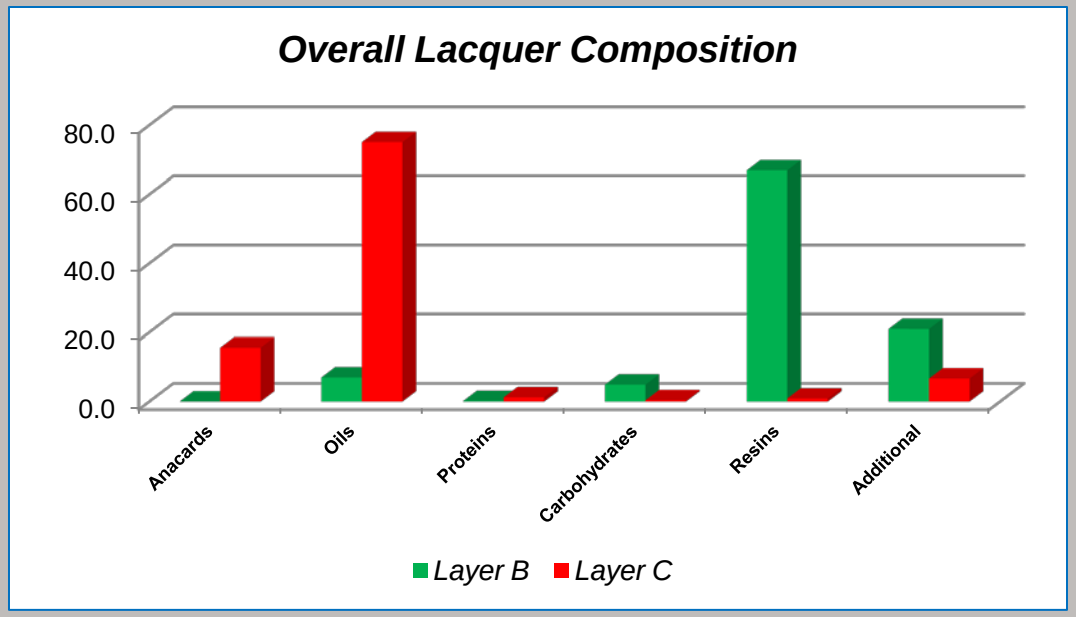


SUMMARY OF RESULTS

The finish layer contains a drying oil (such as rapeseed oil), laccol, persimmon juice, cedar oil (or cedar pitch), and a proteinaceous material.

The foundation layer contains an overwhelming amount of plant fibers, mixed with persimmon juice, a drying oil such as linseed oil, and protein.

In conclusion, although museum records list this object as European ‘japanning’, the unexpected conclusion is that the inkstand is actually decorated with Asian lacquer.



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