

Method development for the analysis of artificially light aged Asian lacquer films using pyrolysis and thermal desorption techniques hyphenated with gas chromatography/mass spectrometry

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INTRODUCTION

The comprehensive characterization of Asian lacquers presents many challenges and obstacles, such as the limited solubility of the **complex catechol-based polymeric matrix**. The material is the tree sap that exudes from different trees from the *Anacardiaceae* family and crosslinks to a hard film, known for its long lasting durability, hardness and gloss properties. The lacquer is applied as a decorative or protective coating since the early Shang Dynasty in China (16th-11th century BC) and the initial Jōmon period in Japan (8000-5000 BC) and is still today preserved in many museum collections, for this an exemplary object is presented in **Figure 3**. Pyrolysis coupled to gas chromatography/mass spectrometry with thermal assisted hydrolysis and methylation (**THM-Py-GC/MS**), with **tetramethyl ammonium hydroxide** (TMAH) as derivatising reagent, provides the possibility for direct analysis of the solid lacquer material, not requiring dissolution prior to analysis. Moreover, minute sample amounts are needed, efficiently returning a wealth of marker compounds and at the same time minimizing the damage to the precious art object. Although limited, the required sample amount still forms a problem, and especially in the context of a broader study on the cleaning of Asian lacquers, detection limits need to be downscaled to allow the identification of biomarkers that are present in low concentration. Regarding the reduction in required sample amounts, at the same time having minor effect on analysis efficiency the optimal pyrolysis temperature is of utmost importance.

CHEMISTRY OF ANACARD LACQUERS

Predominantly 3 types of lacquer have been used for Asian lacquer making, all belonging to the *Anacardiaceae* family, hence labelled **Anacard lacquers**. Chemically the materials share an abundance of catechol derivatives with an ω-phenylalkyl chain at the 3- and 4-positions, consisting of 10 to 12 carbon atoms for *G. usitata*. The predominant alkenyl substituents for *Toxicodendron vernicifluum* and *Toxicodendron succedaneum* are C15 and C17 alkenyl chains. The curing proceeds in different steps, but is in principle a radical oxidative polymerization process, catalyzed by laccase; a copper containing enzyme, leading to the formation of C-C aromatic-nucleus-side chain coupling, C-O phenolic oxygen-side chain coupling and C-C bonds between side chains to create a polymer network.

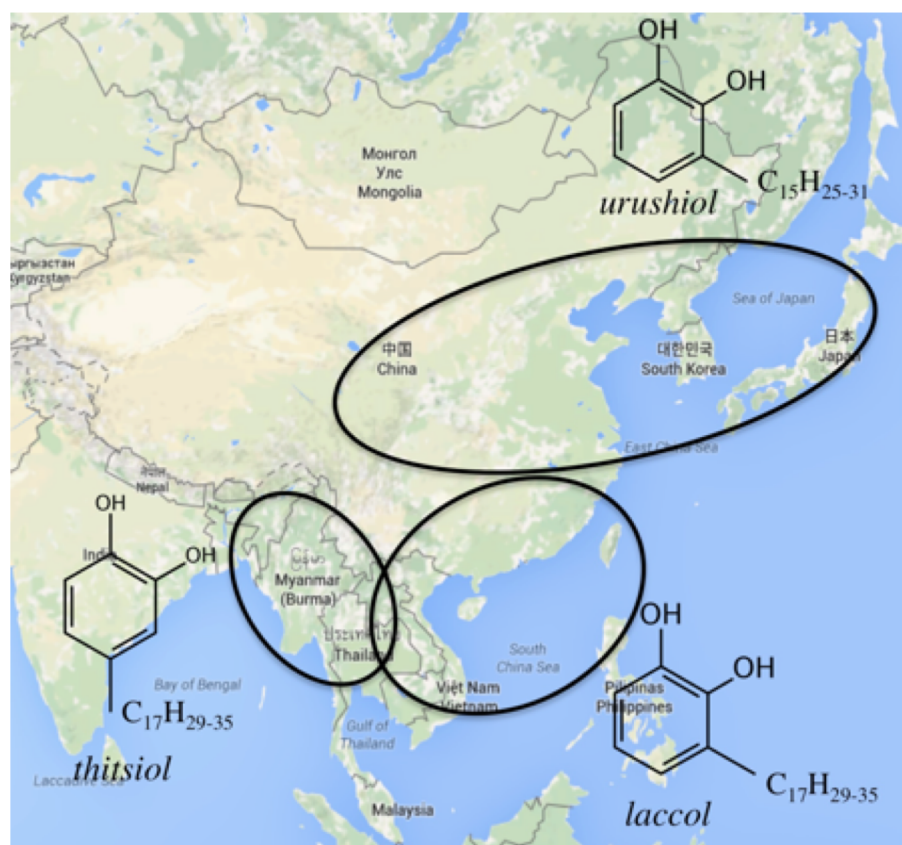


Figure 1: Geographic origin of three major types of Asian lacquer. *T. vernicifluum*, *T. succedanea* and *Melanorrhoea (Gluta) usitata* consisting respectively of main polymeric compounds of urushiol, laccol and thisiol.

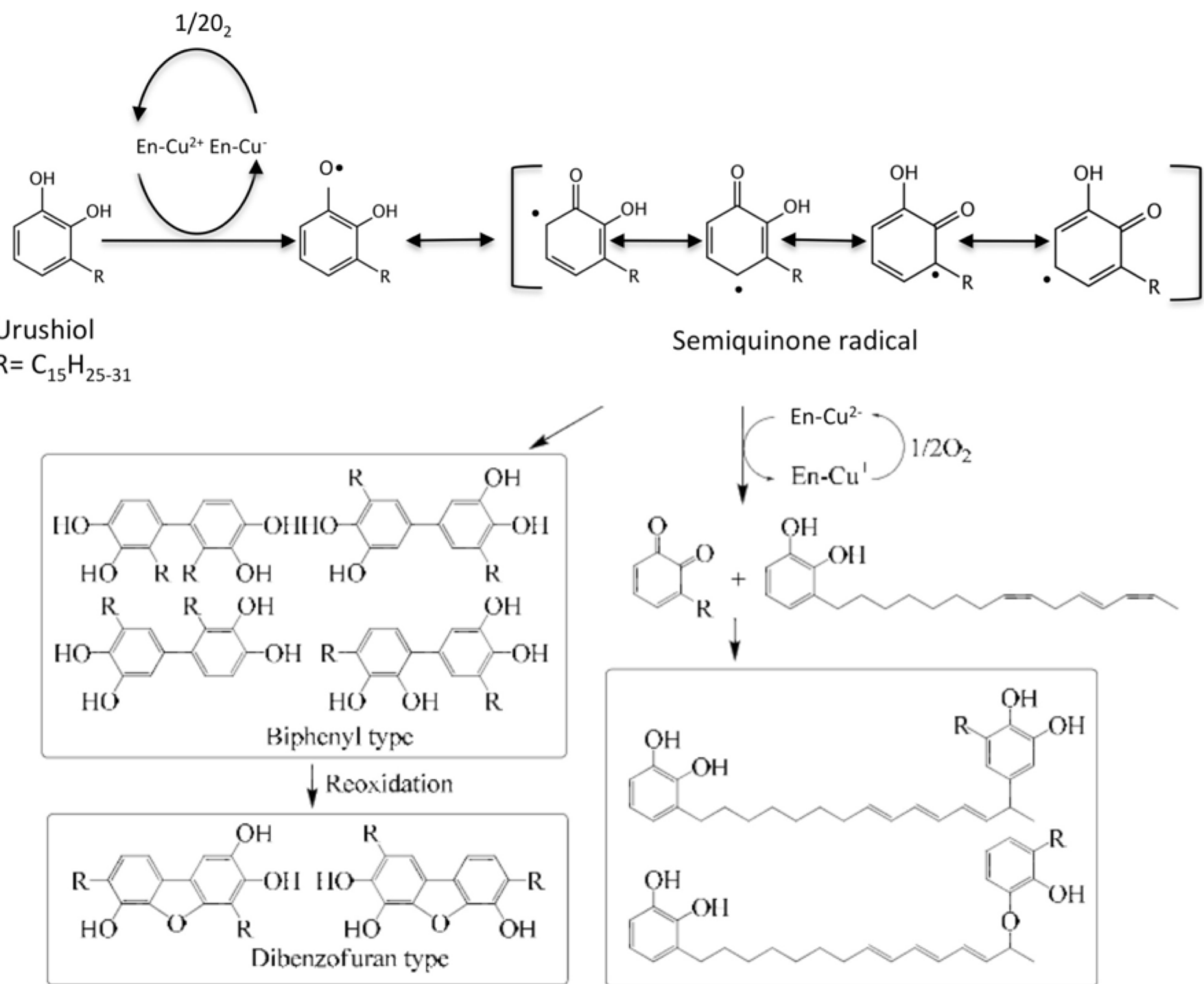


Figure 2: Polymerization mechanisms of urushiol catalyzed by laccase.

EXPERIMENTAL

Table I: Experimental procedures

Instrumentation	Methods
EGA/PY-3030D Multi-Shot Pyrolyzer (Frontier Laboratories)	Flash pyrolysis of 80µg ground lacquer films + 3µL TMAH reagent (5% in MeOH-C13:0 IS) at fixed temperatures (300°C → 700°C) @0.20min. Ultrafast Thermal desorption (UTD) 350°C- 668°C @0.90min. Interface was set at 290°C
Trace 1310 Gas Chromatograph (Thermo Scientific)	Fused silica SLB-5MS capillary column (Supelco, 20 m, 0.18 mm i.d. x 0.18µm film thickness, silphenylene polymer stationary phase) Constant carrier gas flow (He) of 0,9ml min ⁻¹ Split 1:30 (1 min) Injector temperature: 300°C GC oven: Initial 35°C (1.50 min hold), 60°C/min ramp → 100°C. 14°C/min. ramp → 250°C- 6°C/min ramp → 315°C- 1.50 min. isothermal.
ISQ LT Single Quadrupole Mass Spectrometer (Thermo Scientific)	MS transfer line @ 270°C. Solvent delay @ 1.10min. Ionization @70eV in positive ion mode MS was scanned @ 29-600 amu, with a cycle time of 0.2sec.

RESULTS AND DISCUSSION



Figure 3: Japanese Netsuke. Early 17th century. © Royal Museums of Art and History, Brussels.

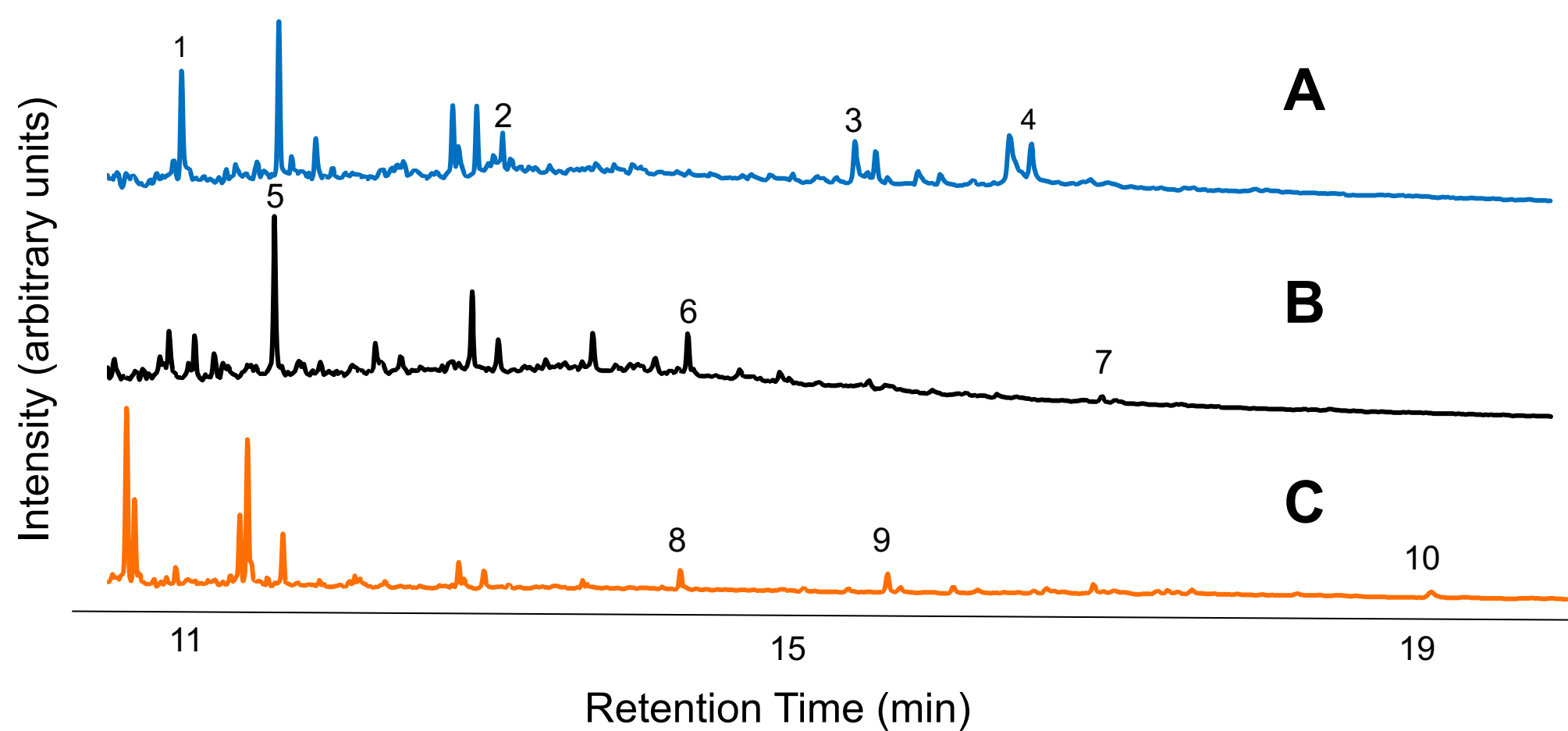


Figure 4: Total ion count (TIC) pyrograms @ UTD of (A) *T. vernicifluum*, (B) *T. succedaneum* and (C) *G. usitata*, and their associated markers.

Table II: Overview of the lacquer samples with associated Anacard markers

Lacquer type	Marker nr.	Marker name	RT (min)	Fragment ions (m/z)
<i>T. vernicifluum</i>	1	3-Heptylcatechol	10.51	29, 106, (123) 208
	2	Methyl 8-(2,3-dimethoxyphenyl)octanoate	12.73	91, (136), 151, 294
	3	3-Pentadecenylcatechol	16,24	(123), 136, 318
	4	3-Pentadecylcatechol	16.39	(123), 136, 320
<i>T. succedaneum</i>	5	1,2-Dimethoxy-3-nonylbenzene	11.13	136, 152, (264)
	6	Methyl 10-(2,3-dimethoxyphenyl)decanoate	14.01	91, 136, 151, (322)
	7	1,2-Dimethoxy-3-heptadecylbenzene	16.88	136, 151, (376)
<i>G. usitata</i>	8	Methyl 13-phenyl-tridecanoate	13.92	(91), 104, 272, 304
	9	1,2-Dimethoxy-pentadecylbenzene	15.34	91, 136, 151, (348)
	10	1,2-Dimethoxy-12-phenyldodecylbenzene	19.04	91, 136, 151, (382)

Previous research has shown the main pyrolytic pathways that lead to the formation of series of catechols, phenyl catechols, phenols and alkylbenzenes marker compounds in Anacard lacquers. For each serie, there is maximum alkyl side chain length, which can hence be related to the corresponding lacquer type. In *T. vernicifluum*, catechols and hydrocarbons with a maximum C15 side chain, C7 being as it's most abundant member is identified. C17 side chains, with C8 as the most persistent member is found in *T. succedaneum* lacquer. Likewise, phenyl catechols, phenyl phenols and alkyl benzenes are unique markers for *G. usitata*. The significant advantage of using TMAH as a methylating reagent is that it allows for the identification of series of successive marker compounds formed through aging and consequent oxidation. Methyl 8-(2,3-dimethoxyphenyl)octanoate is for example the dominant marker identified in *T. vernicifluum* and *G. usitata* lacquers. In *T. succedaneum* Methyl 10-(2,3-dimethoxyphenyl)decanoate is the most abundant member. Those markers, termed acid catechols, form, from oxidation reactions along the alkenyl side chain of the substituted catechols. Methyl 13- phenyl-tridecanoate is a representative compound of a serie of aging products that can be found in *G.usitata* lacquer, which forms from the oxidation of the unsaturated side chains of alkenyl benzenes.

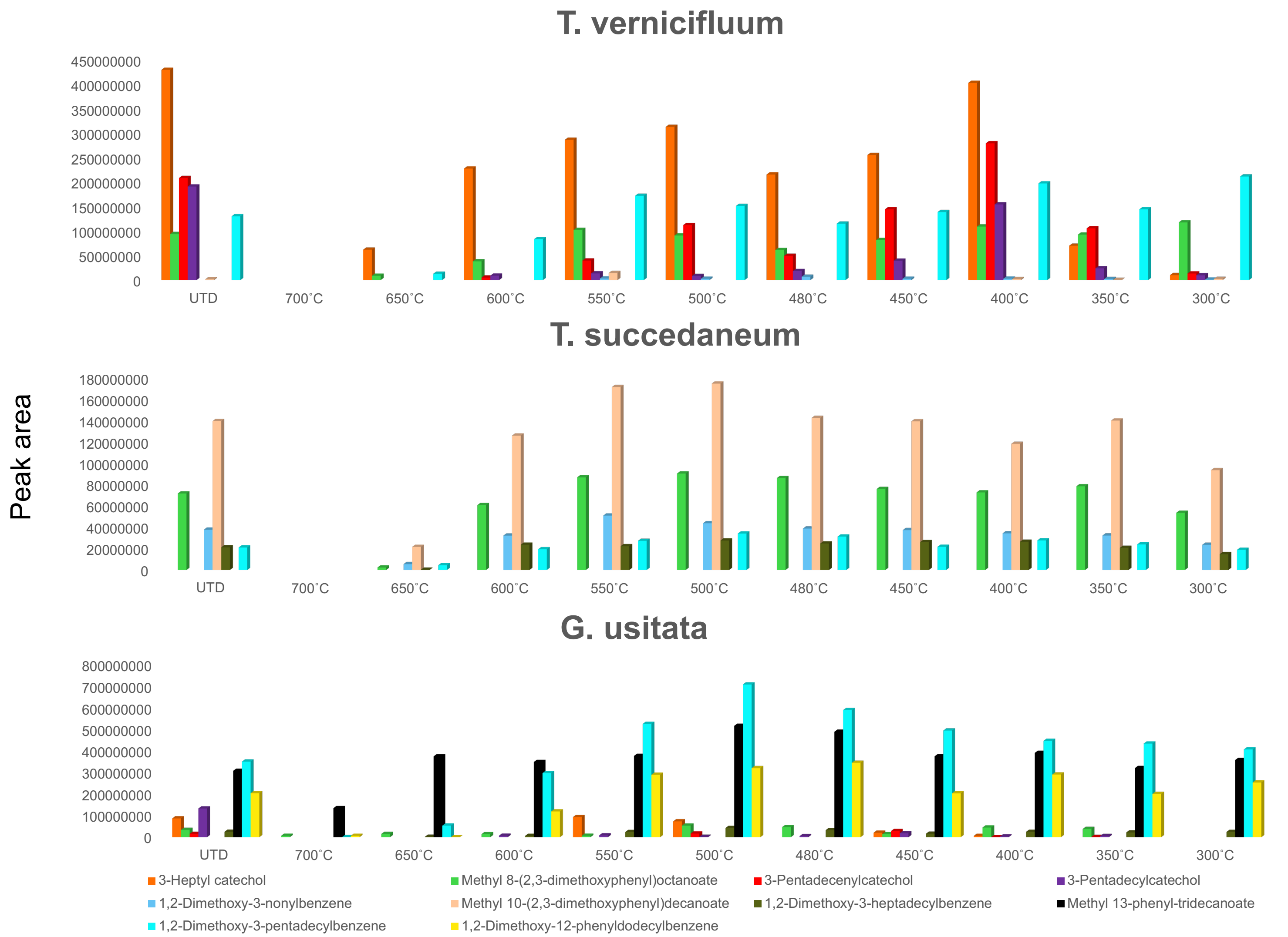


Figure 5: Plotted peak areas @ experimental pyrolysis temperatures.

Table II summarizes the different pyrolysates selected. Some of the components are present in more than one lacquer type, however their ratios differ. The pyrograms of 3 lacquer types is given in Figure 4 in which the positions of the Anacard markers are indicated. The bar graphs in Figure 5 presents the peak areas through the application of different pyrolytic conditions. In the Ultrafast Thermal Desorption (UTD) the sample drops from ambient temperature into the micro furnace, which is initially set at 350°C and is consequently heated to 668°C within 0.90min. This allows for the more volatile compounds, that might be present in a sample, to gradually escape and condense on the GC-column (set at 35°C) before they might be destroyed at high temperature(s). This method is especially efficient in samples where the ingredients are unknown. The method can be termed as an alternative to a so called double shot analysis in which a low temperature thermal desorption step is followed by high temperature pyrolysis, but in two GC runs. From the analyses it's clear that pyrolysis at temperatures below 400°C results in reduced peak areas. High pyrolysis temperature (650°C, 700°C) is also not desirable as it results in most of cases in total absence of the markers. All of the measurements show that UTD or fixed pyrolysis at 480° → 550°C in general yield satisfactory results. However, for *G. usitata* a fixed temperature of 500°C does present a significant increase in peak areas over the UTD method.

CONCLUSION

The performed analyses illustrate the importance of pyrolysis temperature on the peak areas of the Anacard markers. However, fixed temperatures above 550°C result in a decrease or total absence of peaks, causing excessive fragmentation and formation of (unwanted) pyrolytic side products. Temperatures below 400°C induced in a decrease in peak areas as an effect of incomplete polymer fragmentation. The UTD and fixed temperatures (480°C → 550°C) seemed most promising, as it evoked a significant increase in peak areas . The analyses were performed on single materials, not on mixtures, which might interact differently in turn affecting ideal pyrolytic conditions, and is subject for further study.

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