

Evaluation of On-line Derivatization Techniques Using TMAH and HMDS for the Comprehensive Analysis of *Anacardiaceae* Thermosetting Lacquer Polymers Using Pyrolysis-GC/MS and Deconvolution

Jonas Veenhoven^{1,2,3}, Steven Saverwyns², Maarten van Bommel³, Frederic Lynen¹

¹Separation Science Group, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281, 9000 Ghent, Belgium

²Laboratories Department, Royal Institute for Cultural Heritage (KIK-IRPA), Jubelpark 1, 1000 Brussels, Belgium

⁴Conservation & Restoration of Cultural Heritage Programme, University of Amsterdam, Joh. Vermeerplein 1, 1071 DV Amsterdam, Netherlands

Separation
Science
Group



INTRODUCTION

Asian lacquers are complex natural thermosetting polymers, used since prehistory to decorate and protect objects, weapons and even architecture. There are 3 predominant types, which can be harvested from different trees in Asia (Figure 1). In the context of our current research the comprehensive identification presents many challenges and obstacles, mainly because of the insolubility of the **complex polymeric matrix and stability of the chemical bonds**. Pyrolysis coupled to gas chromatography/mass spectrometry is currently the most suitable technique for analysis through thermal fragmentation of the solid lacquer polymer into gas phase molecules amenable to GC separation. However, problems that can emerge in analytical pyrolysis are related to the low volatility of acidic, alcoholic and amidic pyrolytic products, which can cause poor reproducibility, low sensitivity, bad peak shapes and memory effects, making derivatization a necessity. In a broader context of safe and effective cleaning solutions on cultural heritage objects, this contribution critically evaluates a **Thermally Assisted Hydrolysis and Methylation (THM)** method with Tetramethyl ammoniumhydroxyde (TMAH) and a silylation method after pyrolysis using hexamethyldisilazane (HMDS) reagent.

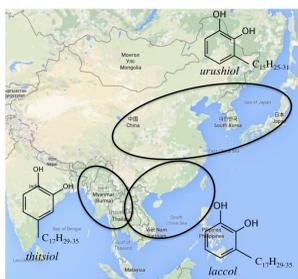


Figure 1: Geographic origin of three major types of Asian lacquer. *T. vernicifluum*, *T. succedanea* and *Melanorrhoea (Gluta) usitata* consisting respectively of main polymeric compounds of urushiol, laccol and thisiol.

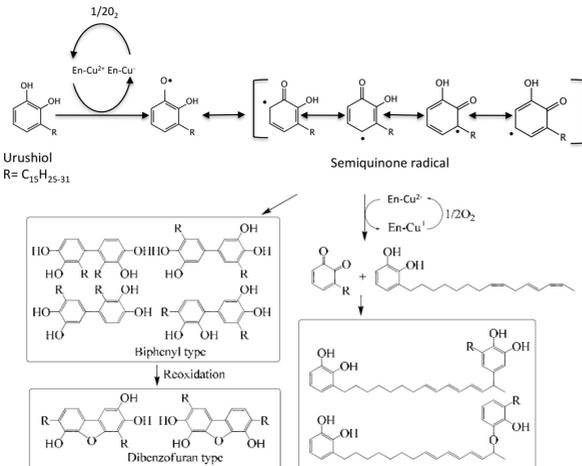
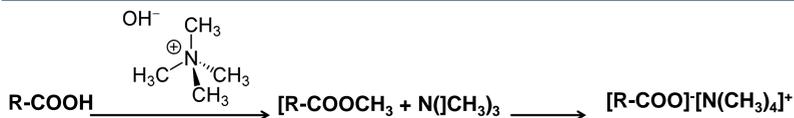
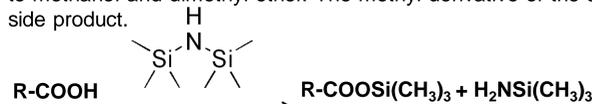


Figure 2: Polymerization mechanisms of urushiol catalyzed by laccase.

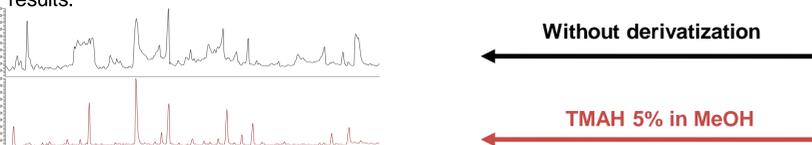
BACKGROUND



Characteristic marker molecules in Asian lacquer, produced by pyrolysis through cleavage of C-C bonds generally display large amounts of hydroxyl groups and carboxylic acid functionalities, e.g. phenols, catechols, fatty acids and acid catechols. To overcome issues during the GC/MS run such as peak broadening, memory effects and poor reproducibility, derivatization is needed to improve the analysis. The use of thermally assisted reactions with TMAH has demonstrated positive results for lacquers and related materials. As a consequence of its strong alkalinity TMAH cleaves hydrolysable bonds and deprotonates acidic groups. The excess of TMAH is thermally decomposed to methanol and dimethyl ether. The methyl derivative of the acid and trimethylamine remains as a side product.



Despite the good results with TMAH, its strong alkalinity can generate side-reactions, which might complicate the analysis, such as decarboxylation reactions, isomerisation or the formation of dehydration products. An alternative, which has already been successfully used by several laboratories is silylation after pyrolysis with HMDS, which is a relatively weak trimethylsilyl donor. After pyrolysis active hydrogen is replaced with a trimethylsilyl group (TMS). In this study both techniques are evaluated based on yield/efficiency of specific markers and reproducibility of the results.



EXPERIMENTAL

Table I: Experimental procedures

Instrumentation	Methods
EGA/PY-3030D Multi-Shot Pyrolyzer (Frontier Laboratories)	Flash pyrolysis of 80µg ground lacquer films + 3µL derivatization reagent + C13:0 IS at fixed pyrolysis temperatures (300°C → 700°C) and Ultrafast Thermal desorption (UTD) 350°C- 668°C @0.90m. 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 iso-thermal.
ISQ LT Single Quadrupole Mass Spectrometer (Thermo Scientific)	MS transfer line @ 270°C. Solvent delay @ 1.10m Ionization @ 70eV positive ion mode MS was scanned @ 29-600 amu, with a cycle time of 0.2sec.

RESULTS AND DISCUSSION

Table II: Overview of the markers

Derivatization type	Marker nr.	Marker name	RT (min)	Fragment ions (m/z)
None	1	Benzene, decyl	9.38	43, 57, 91, (218)
None	2	Benzene, dodecyl	10.96	43, 57, 91, (246)
TMAH	3	Hexadecanoic acid, methyl ester	11.20	74, 143, 227, (270)
HMDS	3a	Hexadecanoic acid, TMS derivate	11.85	74, 117, 145, (313)
TMAH	4	Octadecanoic acid, methyl ester	12.57	74, 143, 255, (298)
HMDS	4a	Octadecanoic acid, TMS derivate	13.13	74, 117, 145, (341)
TMAH	5	Methyl 8-(2,3-dimethoxyphenyl)octanoate	12.75	91, 136, 151, (294)
TMAH	6	Methyl 13-phenyl-tridecanoate	13.92	91, 104, 163, 272
HMDS	6a	13-phenyl-tridecanoate, TMS derivate	13.78	91, 179,
HMDS	7	12-phenyl-dodecanoate, TMS derivate	13.81	73, 91, 117, (333)
TMAH	8	1,2-Dimethoxy-3-pentadecylbenzene	15.34	91, 136, 151, (348)
HMDS	8a	3-pentadecylcatechol, TMS derivate	15.87	73, 179, 376, (392)
HMDS	8b	3-pentadecylcatechol, 2TMS derivate	16.23	73, 179, 450, (464)
TMAH	9	1,2-Dimethoxy-10-phenyldecylbenzene	17.19	91, 136, 152, (354)
HMDS	9a	2-(10-phenyldecyl)-phenol, TMS derivate	16.47	73, 180, 205, (382)
HMDS	9b	4-(10-phenyldecyl)-catechol, 2TMS derivate	17.98	91, 193, 267, (470)
TMAH	10	1,2-Dimethoxy-12-phenyldodecylbenzene	19.05	91, 136, 151, (382)
HMDS	10a	3-(12-phenyldodecyl)-catechol, TMS derivate	19.64	73, 91, 179, (426)

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 or HMDS for silylation of the compounds 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.

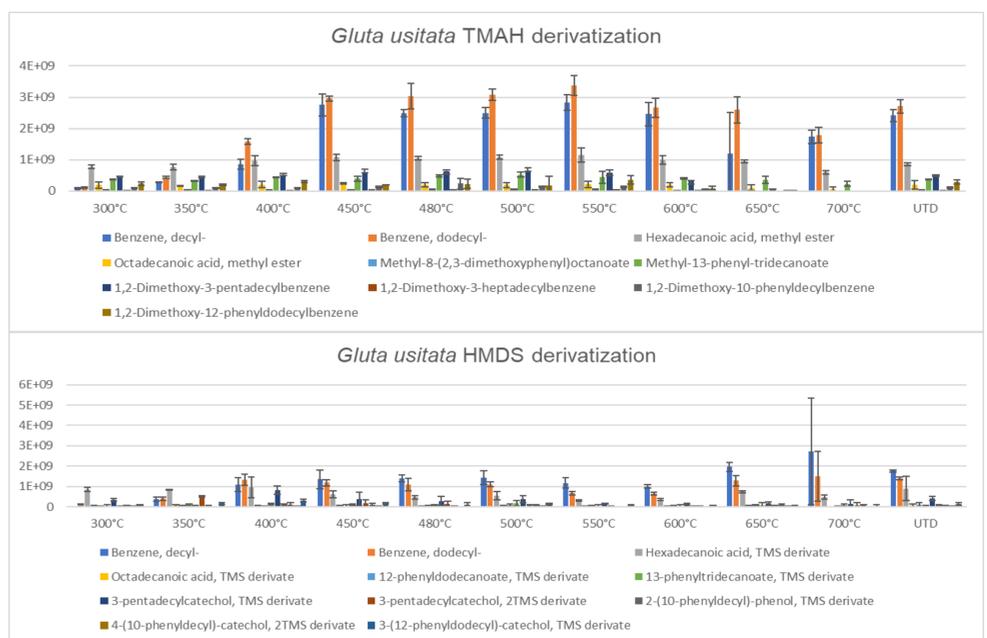


Figure 3: Plotted peak areas @ experimental pyrolysis temperatures.

Above analyses were performed in trifold. The bar graphs display the averages and error bars. Both methods show a similar pyrolysis temperature optimum between 450C-550C. However, the analyses with TMAH derivatization display a better yield. Looking at the relative standard deviation (RSD) the TMAH 5% method performs better as well with rsd's typically below 10%, for most components. For HMDS (3µL volume), this is generally 60-80%. Increasing the TMAH concentration does not affect peak areas, however reproducibility increases, with typical rsd's below 5% using TMAH 10%. The concentration of HMDS could only be increased by adding more volume, up to 5µL. This had only a minor effect on reproducibility and no effect on peak areas.

CONCLUSION

Pyrolysis temperature optimum lies between 450C-550C. The TMAH derivatization method shows generally better results in this study, both in terms of qualitative yield and in reproducibility. However, the measurements in this study were performed in trifold and larger data sets could provide a more exhaustive result. Increasing the concentration or total volume for both methods does only affect lowering the rsd's

REFERENCES

- [1] Schilling, M., Heginbotham, A., Van Keulen, H., Szelewski, M., *Beyond the basics: A systematic approach for comprehensive analysis of organic materials in Asian lacquers*, Studies in Conservation, 61:sup3, DOI: 10.1080/00393630.2016.1230978. pp. 3-27, 2016