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The analysis of European lacquer: optimization of thermochemolysis temperature of natural resins

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Abstract In order to optimize chromatographic analysis of European lacquer, thermochemolysis temperature was evaluated for the analysis of natural resins. Five main ingredients of lacquer were studied: sandarac, mastic, colophony, Manila copal and Congo copal. For each, five temperature programs were tested: four fixed temperatures (350, 480, 550, 650 °C) and one *ultrafast thermal desorption* (UFD), in which the temperature rises from 350 to 660 °C in 1 min. In total, the integrated signals of 27 molecules, partially characterizing the five resins, were monitored to compare the different methods. A compromise between detection of compounds released at low temperatures and compounds formed at high temperatures was searched. 650 °C is too high for both groups, 350 °C is best for the first, and 550 °C for the second. Fixed temperatures of 480 °C or UFD proved to be a consensus in order to detect most marker molecules. UFD was slightly better for the molecules released at low temperatures, while 480 °C showed best compounds formed at high temperatures.

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1 Introduction

Oriental lacquers are natural polymers produced from the exudates of three species from the *Anacardiaceae* family growing in different regions of Asia [1–3]. They are the object of a long tradition of craftsmanship, admired for their durability and gloss. With the rise in overseas trade in the seventeenth century, oriental lacquerware arrived on a more regular basis in Europe. It was scarce, valuable and not well understood. The impact of its arrival was considerable and long-lasting: loved for their exclusivity and beauty, these glossy luxury objects came into vogue and brought a new, exotic taste to the Old World [4]. Soon, local production of furniture and small objects was inspired by the success of imported oriental lacquer. Lacking the raw materials and the technology of the East, European craftsman imitated Asian lacquer using materials and skills familiar to them. The flourishing worldwide trade brought them a wide range of possible ingredients to choose from, including mastic, sandarac, shellac, amber, copals, gum elemi and benzoin. It is remarkable how close the imitations can resemble their oriental examples in gloss and smoothness. A new tradition was born, gradually more independent from the East [5].

European lacquers are complex, multilayered coatings, mainly composed of various natural resins. Depending on the recipes, oils, gums, pigments and other ingredients can be added. Unlike Asian lacquer, different resins were usually combined to achieve the best coating properties, such as gloss, color, applicability, hardness and flexibility [6, 7]. Hard resins such as copal and sandarac could for

example be mixed with gum elemi as plasticizer [7]. If resins in themselves are complex in constitution, European lacquers are even more. A wide range of different molecules is expected to be present, including terpenoids, fatty acids, alcohols and hydrocarbons. Moreover, the polylabdanoid matrix in many of them as well as compositional evolution during preparation and aging (oxidation, polymerization, cleavage reactions, partial volatilization…) can make them hard to dissolve in standard solvents, making the analysis of European lacquer challenging.

In order to know more about the technology and ingredients used, subsequent lacquer layers have to be sampled and analyzed separately, at the same time minimizing the damage to the object. This results in many samples of very limited size. For these small samples of diverse constitution, thermochemolysis–gas chromatography–mass spectrometry, also called thermally assisted hydrolysis and methylation gas chromatography–mass spectrometry (THM–GC/MS), was chosen as the main technique, efficiently returning a maximum of information on the different ingredients with the use of only very limited sample amount. THM–GC/MS is today one of the most important techniques to analyze resinous materials in general [8–20], and it is a powerful method to analyze European lacquer as well [21, 22].

Prior to gas chromatography, thermochemolysis transforms the sample to less polar, alkylated and smaller molecular weight products. Since the introduction of pyrolysis GC–MS with in situ derivatization, tetramethylammonium hydroxide (TMAH) has been a preferred alkylation reagent for the analysis of natural resins [14]. Methylation of acidic and hydroxylic groups in combination with transesterification of esters and cleavage reactions can take place [20, 23]. Thermochemolysis has been applied in many setups, with different alkylation reagents and at different temperatures; all three factors may have important influence on the cleavage and methylation obtained. The choice for TMAH during this project has been motivated by the maximal interchange of results and findings with other institutes.

When optimizing the thermochemolysis for the ingredients present in European lacquers, it is the aim to obtain a chromatogram that is most characteristic for the used materials, so that most can be known about how the lacquer was made. Molecules have to be cleaved and methylated to enable analysis, but more extensive fragmentation or modification hampers the interpretation and are therefore to be avoided. Unwanted side reactions, including isomerization, dehydration of hydroxyl groups and nitrogen incorporation, have been frequently observed in thermochemolysis with TMAH as alkylation reagent, with solvent type, excess of TMAH and temperature being identified as influencing factors [15, 20, 24–30]. Water as solvent for the TMAH is suggested to perform better than methanol, but limited solubility of resins and a long drying time are important counter arguments [27, 28, 31]. Excess of TMAH favors side reactions by increasing both alkalinity and availability of reactive nitrogen groups in the reaction [27–29]. More clearly, however, high thermochemolysis temperature has been proven to enhance the occurrence of unwanted side products [15, 20, 26, 27].

Therefore, a main focus point in the method optimization for European lacquer was the choice of the temperature program to be used for hydrolysis and methylation of the resin sample in presence of TMAH. For resinous materials in general, an optimized temperature is not agreed upon. Temperatures of 600–650 °C or higher have been reported frequently [10–13, 18, 25, 32–34]. Also a double-shot method combining a lower temperature thermal desorption at 250 or 300 °C, followed by high-temperature pyrolysis (600 or 610 °C) has been used successfully by some authors [8, 19, 35]; 550 °C is also applied for varnish and lacquer analysis [3, 9, 36]. For the study of amber, thermochemolysis temperatures up to 650 °C are applied [18, 37], but after optimization study by Anderson [15], 480 °C is frequently preferred, sometimes completed with an additional analysis at 300 °C to avoid destruction of the polylabdanoid matrix [14, 16, 17, 38, 39]. Steadily increasing temperatures have been used rarely (200–700 °C) [22].

The aim of this study is to determine an optimal thermochemolysis temperature for five terpenoid natural resins, all important ingredients in the production of seventeenth-, eighteenth- and nineteenth-century European lacquer: sandarac, mastic, colophony, Manila copal and Congo copal. While terpenoids exhibit enormous structural diversity and chemical complexity, they are all united by a common biosynthetic origin [40]. They can be subdivided into mono-, sesqui-, di- and triterpenes, depending on the number of five carbon building blocks (isopentenyl diphosphate and dimethylallyl diphosphate) which were involved during biosynthesis. Mono- and sesquiterpenes are usually volatile [40]. They can have important influence during the production and application of the lacquer, but, due to their volatile nature, they are unlikely to survive aging in detectable amounts [13]. Therefore, in this study focus is given to the detection of diterpenes (as present in sandarac, colophony, Manila copal and Congo copal) and triterpenes (as present in mastic) and their polymers.

The five selected resins were analyzed at five different temperature programs. For four programs, a fixed oven temperature was chosen: 350, 480, 550 and 650 °C. The fifth program, called ultrafast thermal desorption (UFD), consisted of a rising temperature, climbing from 350 to 660 °C in 1 min.

2 Materials and techniques

2.1 Reference materials

Since contamination and misidentification easily happen with resins [13, 41–46], resin samples from historical, non-commercial origin were chosen. All five have been harvested at least 100 years ago, and were stored as lumps, in closed jars, in dark environment at least in recent history. Although they unavoidably underwent natural aging during their long storage, they were not submitted to the harsh conditions that resinous materials can suffer from when applied as lacquer in thin layers and exposed to light, oxygen and humidity. The sandarac and mastic samples date from the eighteenth century, conserved in the well-studied Vigani's cabinet in Cambridge Queens' College (resp. resins "Sandaracha" A/26 and "Mastiche" A/11 [47, 48]). The colophony and Manila copal were provided by Botanic Garden Meise (resp. "*Pinus taeda* L." BR-CBC-02205 originally from the collection of Ambroise Delacre, pharmacist at Brussels, ca. 1880 and "Resina Copal Manilla" BR-CBC01525, originally from the collection of Carl von Martius (1794-1868)); Congo copal was provided by the Royal Museum for Middle Africa in Tervuren ("*Copaifera demeusei*" 202 100/30).

2.2 Preparation of samples for thermochemolysis-GC/MS

Several grains of each sample were ground, and a small amount of 200–400 µg was transferred to a glass vial. 80–160 µl 2.5 wt% TMAH in methanol solution (tetramethylammonium hydroxide 25 wt% in methanol, Sigma-Aldrich, and absolute methanol for HPLC analysis, Acros Organics, 99.99%) was added, relative to the weight of the sample. This solution also contained 100 ng/µl heptadecanoic acid (Sigma-Aldrich, >98%) and 5 ng/µl anthracene (Sigma-Aldrich) in solution, both as internal standard. The first internal standard was meant as a stable measure for inserted quantity, while the second was added as a control for successful methylation. The content of the vial was well mixed to homogenize, and 2 µl was transferred to the stainless steel pyrolysis cup (Eco-cup LF, Frontier Lab) with auto-Rx glass fiber disk. For the fixed temperatures, the cup was pyrolyzed at given temperatures for 0.2 min and left in the oven when chromatographical analysis started. For ultrafast desorption, the cup was heated for 1 min, and ejected a few seconds later, before chromatographical analysis was started. In order to minimize variability of the sample constitution or concentration, one solution of a resin was used for all analyses.

Efforts were taken to minimize the time span between preparation of the mixture with TMAH and the last analysis of the resin, because a long contact period of the sample with the alkaline TMAH can be considered as disadvantageous for certain molecules [29]. The series of five temperatures for a resin was analyzed three times, adding up to 15 analyses per resin.[1] It resulted in a time span of 19 h on average, and less than 6 h for the first series. The authors believe that with this setup of three repeated series, the influence of contact time on the conclusions is minimized or detected if significant. Five days after the experiment, a subset of *Guibourtia* was reanalyzed to assess the influence of the TMAH contact time. The data did not suggest a significant influence of TMAH contact time on the markers studied here. Not to extend the period of analysis more than necessarily, blanks were only run before and after the analysis of a resin–TMAH mixture. These blanks did not show peaks related to the markers studied here. Also general experience with the equipment learns that as long as the system is not thoroughly overloaded, natural resin peaks in general and the markers studied here in particular, do not show up in blanks in significant amounts to be comparable with the signals reported for this experiment.

2.3 Instrumentation online thermochemolysis-GC/MS

Thermochemolysis was carried out in a Frontier Lab Multi-Shot Pyrolyzer (3030D), in a helium atmosphere, fed with an autoshot sampler AS-1020ET. The interface and the injector of the chromatographic system were kept at 300 °C, but the analytical column was directly coupled to the pyrolyzer via a custom-made split device (split ratio 20), minimizing dead volume and improving the signal.[2] For the chromatographic separations, a TraceGC gas chromatograph (Thermo), hyphenated with a PolarisQ ion trap mass spectrometer (Thermo), was used. Separations were accomplished on a SLB-5 ms capillary column (Supelco, 20 m × 0.18 mm i.d. × 0.18 µm film thickness) applying following temperature program: initially, the oven temperature was maintained at 35 °C for 1 min after pyrolysis. Next, a 10 °C/min gradient was applied until 240 °C. Finally, the column was heated to a temperature of 315 °C at a rate of 6 °C/min; this temperature was maintained for 5 min. Carrier gas was helium at a constant flow of 0.9 mL/min. The MS transfer line temperature was kept at 290 °C. Ionization was carried out in the ion volume of the ion trap mass spectrometer under the standard EI

[1] Due to one failed analysis, only two measurements for the combination 480 °C—mastic could be used.

[2] Kindly provided by Henk van Keulen, Rijksdienst Cultureel Erfgoed (RCE), Amsterdam, the Netherlands.

positive mode at 70 eV. The scan range was 35–650 amu, with a cycle time of 0.59 s.

2.4 Data treatment of pyrograms

Integrated signal of selected markers in the pyrograms was calculated with the AMDIS software (*Automated Mass spectral Deconvolution and Identification System*, v.2.70). AMDIS computes the *integrated signal* value as the area under the component after deconvolution [49]. Deconvolution prior to integration avoids taking into account signal from background and adjacent peaks. Kováts retention indices were calculated by AMDIS, based on the separation of a C7–C30 alkanes mixture (Supelco C7–C30 saturated alkanes standard 1000 µg/ml in hexane). Retention indices higher than 3000 could not be determined. Mass spectral identification was performed using the NIST 11 Mass Spectral Library, using spectra provided by other institutions (via shared libraries of RAdICAL/ESCAPE and Users' Group for Mass Spectrometry and Chromatography MaSC) and published reference data.

Signal strength depends on the sample amount which was pyrolized. Data can be corrected with normalization to correct for possible inaccuracy during sample transfer, making data more consistent. A good normalization measure is present in every measurement and varies according the pyrolized amount. It is important for the conclusions of this study that the measure does not depend on the temperature program used. Three different normalizations were considered for the data presented here: the internal standards anthracene, heptadecanoic acid and the total sum of peaks. Unfortunately, none of these met the criteria. Anthracene's signal strength was stable over the different temperature programs, but showed an unexpected high variability (21% average relative standard deviation). This variability was not reflected in fluctuations in general signal strength or heptadecanoic acid methyl ester. Therefore, the important and unexplained fluctuations observed in the anthracene signal are not a correct measure for the pyrolysed amount. The heptadecanoic acid methyl ester signal is more stable (9% average relative standard deviation) and may be considered as a possible measure for the pyrolysed amount. However, important degradation was observed at higher temperatures. Temperature dependency was also observed for the total sum of peaks. It was decided not to normalize the pyrograms. Therefore, both instrumental deviations and possible inaccuracy during sample transfer contribute to the errors observed between repeated measurements.

3 Results and discussion

Molecules produced during thermochemolysis depend on the compounds present in the sample. They can be part of a polymerized labdanoid network or trapped in it. Some will be released at low temperatures; others are only formed at high temperatures, or they may be destroyed or altered at higher temperatures. Therefore, it is expected that marker compounds react differently on different temperature programs.

For each resin, a set of peaks was selected to compare their integrated signal through the different temperature programs. During selection, attention was paid to choose markers that did not tend to present any overloading or overlap. Table 1 summarizes the total of 27 molecules selected, most of them were (partially) known markers [4, 8–10, 25, 42, 45, 47, 50]. One is an unidentified peak that appears when Congo copal is submitted to high temperature; it was selected for this characteristic. A THM–GC/MS chromatogram of each resin at 480 °C is given in Fig. 1, with the position of markers indicated. The mean and standard deviation of three measurements for all selected molecules are shown in Fig. 2.

Some pyrolysates are not characteristic for only one resin. Both sandarac and Manila copal contain a polycommunic acid polymer; the free diterpenes in sandarac mainly consist of sandaracopimaric acid, while agathic acid and related compounds are predominant in Manila copal. This similarity results in some common peaks [8, 10, 19, 25, 45]. The polycommunic acid markers' properties regarding pyrolysis temperature may differ, being present in a structure that is chemically not identical. Therefore, polycommunic acid markers "b1" and "b4" are followed separately for both resins. These markers were named by Van den Berg [19], with structures suggested there and in studies on class 1 amber [16, 39, 51].

In the ultrafast thermal desorption (UFD) heating program, the sample falls into the oven at 350 °C, and is consequently heated to 660 °C within 1 min. The idea of this method is that easily volatilized compounds can escape and condense on the cool column before possibly being destroyed at high temperatures. When temperature rises, more compounds are set free and gathered on the column. It was therefore expected, in theory, that this temperature program should be the best compromise between a fixed low and high temperature, as a possible alternative for double-shot analysis. Double-shot analysis, in which a low-temperature thermal desorption followed by high-temperature pyrolysis on the same sample but in two chromatographic runs, has the advantage over normal single-shot analysis that easily volatilized compounds and compounds formed at high temperatures are both detected, in separate runs. With this clear distinction, high-temperature degradation products of compounds released at low temperatures are avoided. Major drawback of this method, at least with the autosampler equipment used in this experiment, is that TMAH, volatilized in the first step, cannot be added again for the second—if not added manually again. Recovering

Table 1 Overview of resin samples used and the markers selected of each

Resin (current plant name)	Marker number	Markers	Retention Index (retention time)	Retention Index (Van Keulen 2015 [9])	Characteristic EI fragment ions (m/z)
Sandarac (*Tetraclinis articulata* (Vahl) Mast.)	1	Poly communic marker b1	1601 (14.52)	1614	161-177-236
	2	Poly communic marker b4	1758 (16.29)	1774	173-188-248
	3	Ferruginol methoxy	2239 (20.93)	2246	189-285-300
	4	Trans-communic acid methyl ester	2257 (21.09)	–	105-121-241-316
	5	Sandaracopimaric acid methyl ester	2265 (21.15)	2300	121-181-257-316
	6	Methyl-hydroxy sandaracopimaric acid	2413 (22.45)	2414	121-346
	7	Sandaracopimaric acid, 12 acetoxy	2511 (23.3)	2507	121-299-314
Mastic (*Pistacia lentiscus* L.)	8	Mastic compound 5	– (32.04)	–	219
	9	Mastic component	– (32.27)	–	203-219-262
	10	Moronic acid ME	– (32.96)	3505	189-249-468
	11	Oleanolic acid ME	– (33.17)	3588	203-262-468
Colophony (*Pinus taeda* L.)	12	Pimaric acid ME	2244 (20.97)	–	121-257-316
	13	Isopimaric acid ME	2307 (21.53)	–	241-257-316
	14	Abietic acid ME	2397 (22.31)	–	241-256-316
	15	Tetradehydroabietic acid 7 methoxy ME	2451 (22.79)	–	227-267-342
	16	Methyl 12-methoxyabieta8,11,13-trien-20oate	2488 (23.13)	–	269-344
Manila copal (*Agathis dammara* (Lamb.) Rich. & A.Rich.)	17	Marker 4	1593 (14.44)	–	145-160-188-220
	18	Poly communic marker b1	1598 (14.50)	1614	161-177-236
	19	Poly communic marker b4	1756 (16.26)	1774	173-188-248
	20	16.17-bisnordehydroabietic acid ME	2163 (20.26)	–	211-271
	21	Agathic acid isomer DME1	2445 (22.74)	–	189
	22	Agathic acid isomer DME2	2498 (23.21)	–	121-175-201-288
Congo copal (*Guibourtia demeusei* (Harms) J.Leonard)	23	Poly ozic marker C1	1637 (14.93)	1678	161-177-236
	24	Poly ozic marker C2	1733 (16.01)	–	173-189-248
	25	Copal unknown	2141 (20.04)	–	107-177-305
	26	Copalic/entcopalic acid	2315 (21.56)	2330	81-244-303
	27	“copal 11”	2395 (22.26)	–	223-305-318

Retention index (completed with published values by van Keulen) and retention time are given, as well as main fragment ions

the cup and manually adding TMAH is time-consuming and also bears the risk of losing the sample. With the UFD method, the pyrolysis step is placed only seconds after the first thermal desorption and gas chromatography is combined in one run again. This is a faster option, in which some TMAH could possibly still be available during pyrolysis as well.

From the results, it is clear that pyrolysis at fixed temperature of 650 °C is not desirable. Many of the selected markers are less clearly defined with pyrolysis at this temperature, or are completely absent. Only marker 25, an unidentified component formed at high temperatures in Congo copal, possibly a side product, is best detected at 650 °C. This temperature program will be left out in the further discussion.

When comparing the intensity of a peak at the remaining temperature programs, three groups can be discerned. A first group of markers (2, 3, 7, 12, 13, 14, 16, 18, 19, 23, 27, indicated with ° in Fig. 2) performs well at all temperature programs (UFD, 350, 480, 550 °C). Differences between them are not statistically significant. A second group of markers (4, 5, 6, 8, 9, 15, 21, 22, 26, indicated with * in

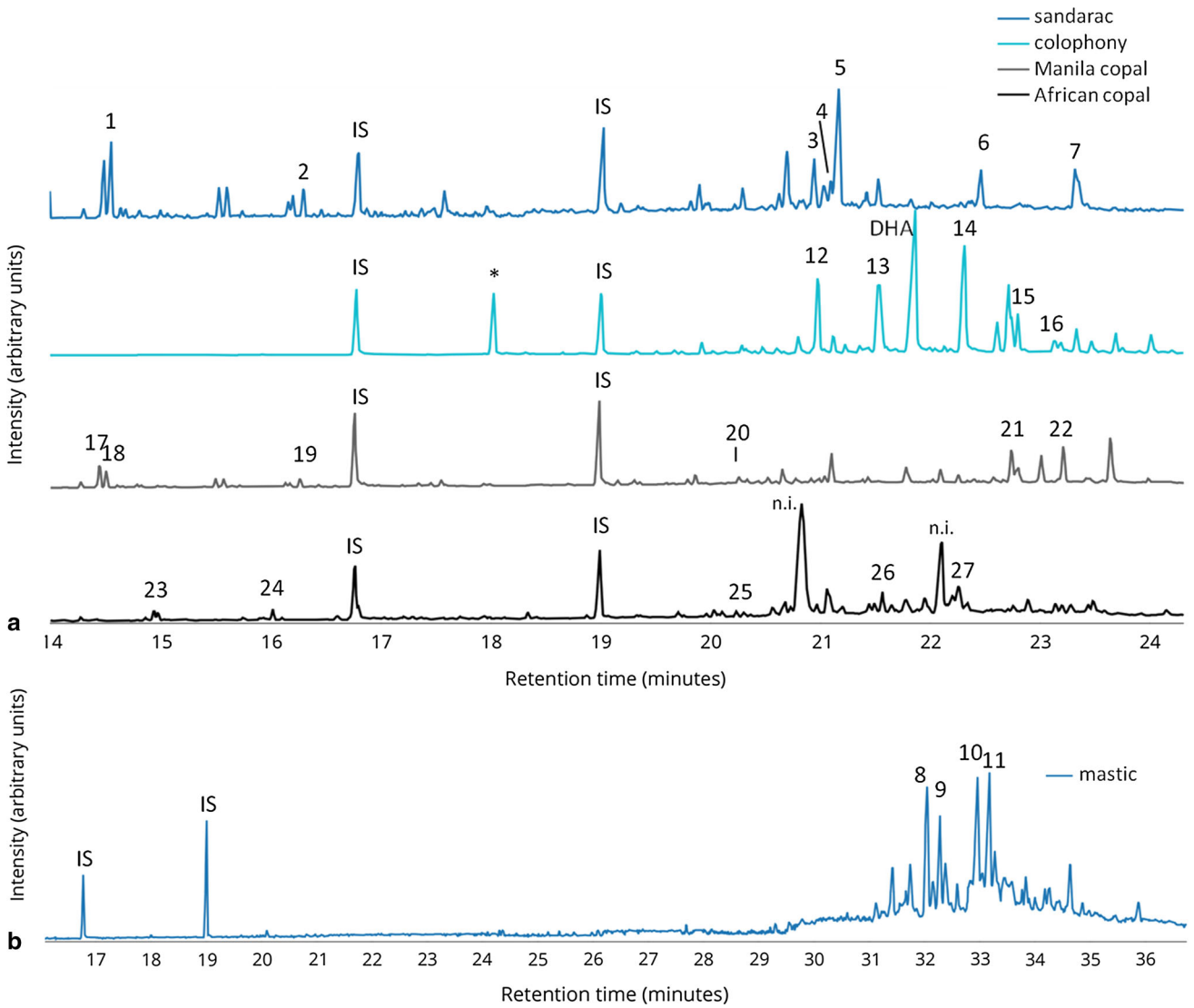

Fig. 1 Total ion count (TIC) of gas chromatogram of sandarac, colophony, Manila copal and Congo copal (**a** diterpenoid region) and mastic (**b** triterpenoid region), pyrolyzed at 480 °C. *Selected markers* are indicated. *IS* internal standard, *DHA* dehydro abietic acid methyl ester; *n.i.* not identified; *hexadecanoic acid methyl ester (contamination)

Fig. 2) shows a slight or important trend in favor of low temperatures; these tend to decrease in intensity or disappear at high temperatures. For these molecules, a temperature of 350 °C is preferable. As expected, UFD also performs very well for these molecules. It seems that those molecules are indeed condensed on the column before higher temperature could destroy them. Pyrolysis at 480 °C is a less performing option, but can be considered acceptable.

A third group comprises molecules that slightly or explicitly tend to be more present when high temperatures are applied (1, 10, 11, 17, 20, 24, 25, indicated with + in Fig. 2). These molecules are best detected with a fixed pyrolysis temperature of 550 °C. A fixed temperature of 480 °C performs well. Remarkably, UFD does not reach the expectations for these molecules: UFD shows an overall lower integrated signal than when 480 °C pyrolysis temperature was applied. Several explanations could be valid and may enforce each other. Possibly, the rise in temperature is so steep that some molecules are still present in the pyrolysis oven and get partially destroyed when the temperature of 660 °C is reached. However, some limited tests with an adapted UFD, that rise in 1 min to only 550 °C, keeping this temperature for another minute, did not perform better. Some molecules may not be formed because their precursors left the oven earlier, or other side reactions may have taken place. The TMAH, abundantly present at the start of the temperature rise, might be volatilized and evacuated together with the first compounds formed,

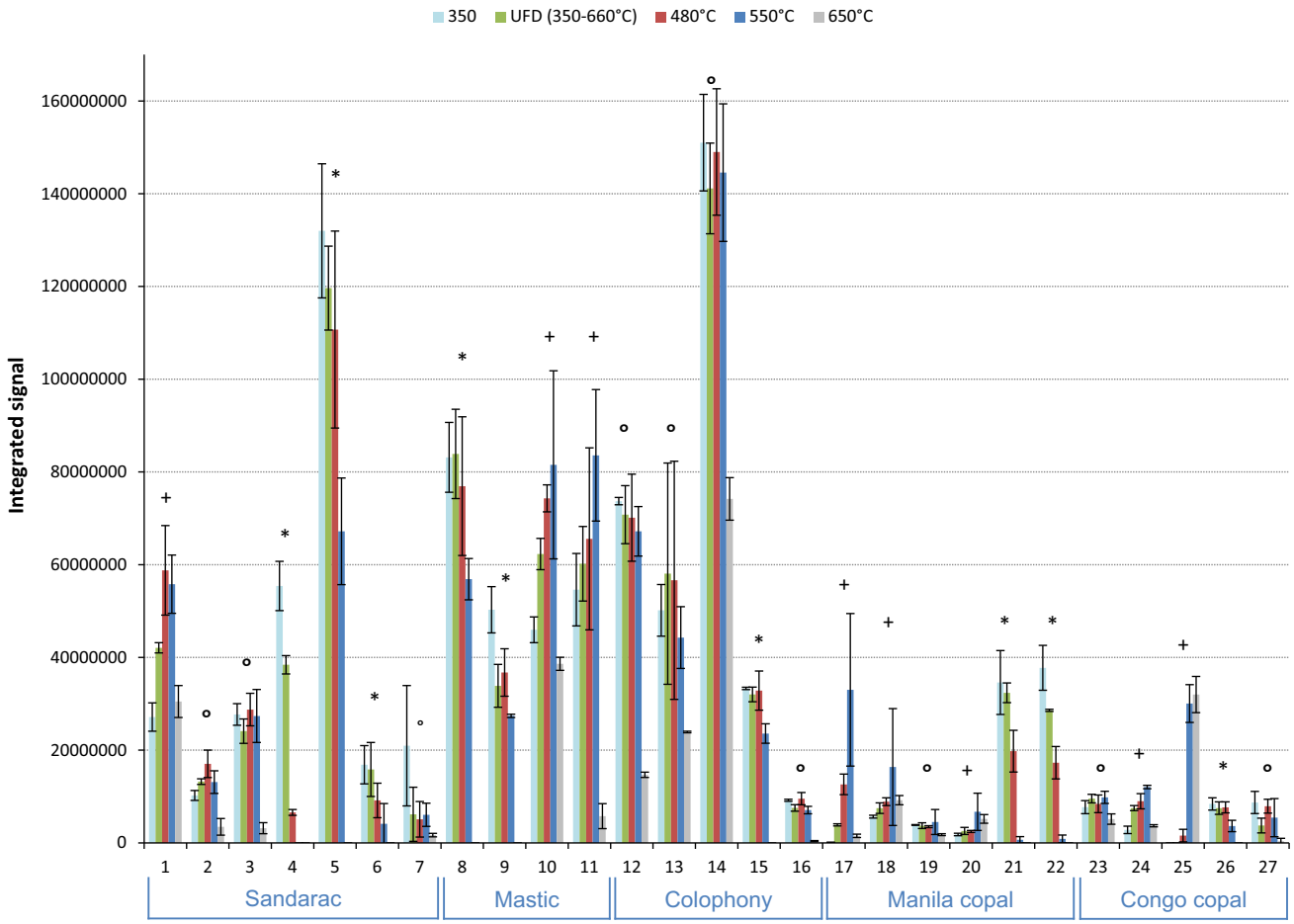

Fig. 2 Mean and standard deviation of integrated signal of selected markers for temperature programs 350 °C, UFD (350–660 °C), 480, 550 and 650 °C. Marker numbers are specified in Table 1. Based on their behavior, markers can be divided into three groups, indicated with °, * and + (discussion below). *Error flags* of one standard deviation

being absent for the compounds formed at higher temperatures.

The analysis of all results shows that both 480 °C and UFD are valuable pyrolysis temperature programs, returning a significant signal for a whole range of marker molecules. In general, differences between these two options are limited; UFD performs better for heat-sensitive compounds that are released at low temperatures (e.g., 350 °C), whereas 480 °C is generally a better choice for compounds formed at high temperatures, best seen at 550 °C.

Another argument to take into account is variability: it would be an important asset if a temperature program yields a more consistent and therefore more repeatable signal. However, *repeated measures ANOVA* could not reveal any significant difference between relative standard deviations grouped by temperature treatment, because variation within one temperature program was too large.

4 Conclusion

The experiment illustrates the important influence of thermochemolysis temperature on the integrated signal of several resin markers. The optimal temperature depends on the molecules of interest. However, fixed temperatures of 550 and 650 °C are not ideal as consensus temperature to detect most markers. 350 °C could be considered, but a fixed temperature of 480 °C or UFD gives best results in detecting the whole series of marker molecules.

Temperature optimization was only performed on resins, not on mixtures or aged lacquer. Indeed, due to more complex interaction with other resins, pigments, oils and gums, responses of the markers to the different thermochemolysis temperatures may change. Some first analyses of real-object samples of European lacquer pyrolized at a temperature of 480 °C and with UFD [52] seem to suggest successful analysis, but more are needed to confirm the results of this study.

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References

1. J.C. Frade, M.I. Ribeiro, J. Graça, J. Rodrigues, Anal. Bioanal. Chem. **395**, 2167 (2009)
2. T. Honda, R. Lu, N. Kitano, Y. Kamiya, T. Miyakoshi, J. Appl. Polym. Sci. **118**, 897 (2010)
3. A. Heginbotham, M.R. Schilling, in *East Asian Lacquer: Material Culture, Science and Conservation*, ed. by S. Rivers, R. Faulkner, B. Pretzel (Archetype Publications, London, 2011), pp. 92–106
4. J. Koller, K. Walch, U. Baumer, in *Japanische Und Europäische Lackarbeiten: Rezeption, Adaption, Restaurierung/Japanese and European Lacquerware: Adoption, Adaptation, Conservation*, ed. by M. Kühlenthal (Bayerisches Landesamt für Denkmalpflege, Munich, 2000), pp. 537–559
5. M. Kopplin, *European Lacquer* (Selected Works from the Museum Für Lackkunst Münster. Himler, Munich, 2010), pp. 11–21
6. V. Cattersel, L. Decq, C. Indekeu, E. Van Binnebeke, D. Steyaert, W. Fremout, S. Saverwyns, in *Furniture Finishes*, ed. by M.V. Dias (Stichting Ebenist, Amsterdam, 2015), pp. 56–62
7. M. Webb, *Lacquer: Technology and Conservation: A Comprehensive Guide to the Technology and Conservation of Asian and European Lacquer* (Butterworth-Heinemann, Oxford, 2000), pp. 99–116
8. K.J. van den Berg, J. van der Horst, J.J. Boon, in Preprints ICOM Committee ICOM for Conservation 12th Triennial Meeting, Lyon, France, 29 Aug–3 September 1999, vol. II (James & James, London, Lyon, 1999), pp. 855–861
9. H. van Keulen, in *Furniture Finishes*, ed. by M.V. Dias (Stichting Ebenist, Amsterdam, 2015), pp. 134–141
10. J. Romero-Noguera, I. Martín-Sánchez, M.T. Doménech-Carbó, L. Osete-Cortina, M.M. López-Miras, F. Bolívar-Galiano, Int. Biodeterior. Biodegradation **90**, 99 (2014)
11. M. Regert, T. Devise, A.-S. Le Hô, A. Rougeulle, Archaeometry **50**, 668 (2008)
12. A.-S. Le Hô, M. Regert, O. Marescot, C. Duhamel, J. Langlois, T. Miyakoshi, C. Genty, M. Sablier, Anal. Chim. Acta **710**, 9 (2012)
13. I.D. van der Werf, K.J. van den Berg, S. Schmitt, J.J. Boon, Stud. Conserv. **45**, 1 (2000)
14. J. Poulin, K. Helwig, Org. Geochem. **44**, 37 (2012)
15. K.B. Anderson, R.E. Winans, Anal. Chem. **63**, 2901 (1991)
16. K.B. Anderson, R.E. Winans, R.E. Botto, Org. Geochem. **18**, 829 (1992)
17. P.S. Bray, K.B. Anderson, Geochem. Trans. **9**, 3 (2008)
18. M. Havelcová, V. Machovič, M. Linhartová, L. Lapčák, A. Přichystal, Z. Dvořák, Microchem. J. **128**, 153 (2016)
19. K. J. van den Berg, J. Ossebaar, H. van Keulen, in Proceedings of Art 2002, 7th International Conference on Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, 2–6 June 2002, Antwerp, Belgium, ed. by R. Van Grieken, K. Janssens, L. Van't Dack, G. Meersman (Antwerp, Belgium, 2002)
20. F. Shadkami, R. Helleur, J. Anal. Appl. Pyrolysis **89**, 2 (2010)
21. A.-S. Le Hô, C. Daher, L. Bellot-Gurlet, V. Yannick, J. Bleton, B. Myrtho, D. Léa, J. Langlois, C. Paris, M.-A. Paulin, F.-C. Anne, A. Jacquin, in ICOM-CC Conference Paper (2014)
22. A. Heginbotham, H. Khanjian, R. Rivenc, M. Schilling, in 15th Triennial Conference New Delhi, 22–26 September 2008: Preprints, ICOM Committee for Conservation (Allied Publishers, New Delhi, 2008), pp. 608–616
23. J.W. de Leeuw, M. Baas, J. Anal. Appl. Pyrolysis **26**, 175 (1993)
24. S. Watts, E.R. de la Rie, Stud. Conserv. **47**, 257 (2002)
25. D. Scalarone, M. Lazzari, O. Chiantore, J. Anal. Appl. Pyrolysis **68–69**, 115–136 (2003)
26. K. Sutherland, J. Chromatogr. A **1149**, 30 (2007)
27. A. Piccirillo, D. Scalarone, O. Chiantore, J. Anal. Appl. Pyrolysis **74**, 33 (2005)
28. J.D.J. van den Berg, J.J. Boon, J. Anal. Appl. Pyrolysis **61**, 45 (2001)
29. D. Jun-Kai, J. Wei, Z. Tian-Zhi, S. Ming, Y. Xiao-Guang, F. Chui-Chang, J. Anal. Appl. Pyrolysis **42**, 1 (1997)
30. I. Pastorova, K.J. van den Berg, J.J. Boon, J.W. Verhoeven, J. Anal. Appl. Pyrolysis **43**, 41 (1997)
31. J.M. Challinor, J. Anal. Appl. Pyrolysis **61**, 3 (2001)
32. C. Riedo, D. Scalarone, O. Chiantore, Anal. Bioanal. Chem. **401**, 1761 (2011)
33. D. Scalarone, M. Lazzari, O. Chiantore, J. Anal. Appl. Pyrolysis **64**, 345 (2002)
34. M.T. Doménech-Carbó, J. de la Cruz-Cañizares, L. Osete-Cortina, A. Doménech-Carbó, H. David, Int. J. Mass Spectrom. **284**, 81 (2009)
35. S. Prati, S. Smith, G. Chiavari, Chromatographia **59**, 227 (2004)
36. S. Saverwyns, M. Vermeulen, E. Van Binnebeke, E Preserv. Sci. **11**, 64 (2014)
37. I.D. van der Werf, D. Fico, G.E. De Benedetto, L. Sabbatini, Microchem. J. **125**, 85 (2016)
38. K.B. Anderson, R.E. Botto, Org. Geochem. **20**, 1027 (1993)
39. K.B. Anderson, Geochem. Trans. **7**, 2 (2006)
40. J.H. Langenheim, *Plant Resins: Chemistry, Evolution, Ecology, and Ethnobotany* (Timber Press, Portland, 2003)
41. R.J. Stacey, C.R. Cartwright, C. McEwan, Archaeometry **48**, 323 (2006)
42. J. Koller, U. Baumer, E. Schmid, D. Grosser, *Baroque and Rococo Lacquers* (Bayerischen Landesamtes für Denkmalpflege, Munich, 1997), pp. 379–394
43. F. Piozzi, S. Passannanti, M. Paternostro, G. Nasini, Phytochemistry **13**, 2231 (1974)
44. U. Baumer, P. Dietemann, Anal. Bioanal. Chem. **397**, 1363 (2010)
45. J.S. Mills, R. White, Stud. Conserv. **22**, 12 (1977)
46. G. Nasini, F. Piozzi, Phytochemistry **20**, 514 (1981)
47. G. Steigenberger, The Vigani Cabinet—Analysis of Historical Resinous Materials by Gas Chromatography—Mass Spectrometry and Infrared Spectroscopy—Ph.D. Dissertation (the Department of Mathematics and Natural Sciences at the Technical University Dresden, 2013)
48. G. Steigenberger, C. Herm, Anal. Bioanal. Chem. **401**, 1771 (2011)
49. (n.d.) Changes in AMDIS. http://chemdata.nist.gov/mass-spc/amdis/changes.html. Accessed 17 June 2016
50. G. Chiavari, S. Montalbani, V. Otero, Rapid Commun. Mass Spec. **22**, 3711 (2008)
51. K.B. Anderson, W. Bray, Archaeometry **48**, 633 (2006)
52. V. Cattersel, L. Decq, C. Indekeu, W. Fremout, S. Saverwyns, White European Lacquers—a case study. Poster presentation at Conference Verband der Restauratoren, Würzburg (2015)