Optimisation of pyrolysis temperature for chromatographic analysis of natural resins

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European Lacquer in Context

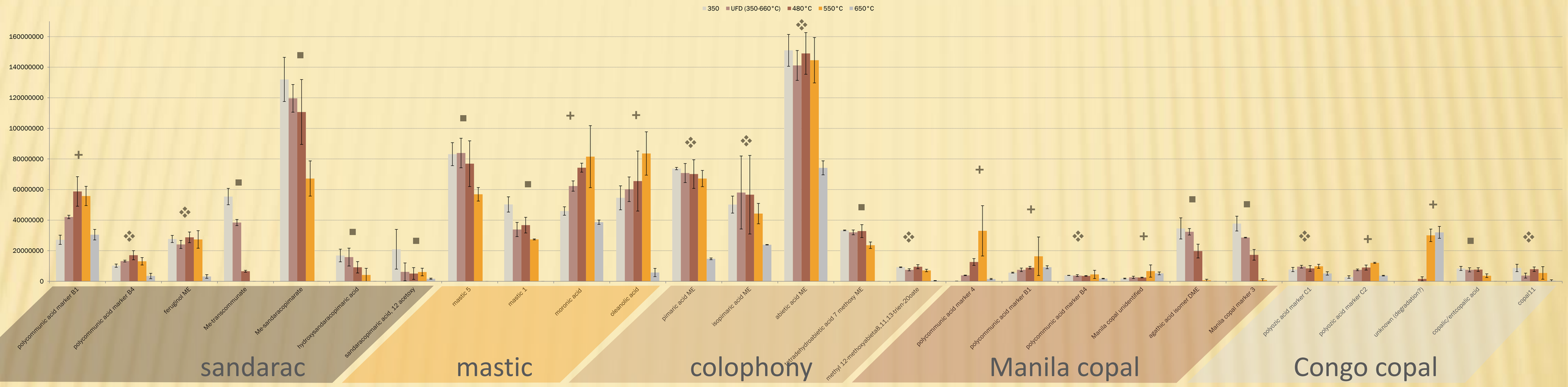
ELinC

Introduction

Oriental lacquer came into vogue in Europe starting from the 16th century. Its immense popularity stimulated craftsmen to imitate these luxury items, using their own familiar materials and techniques. European lacquers are complex, multi-layered coatings, mainly composed of various natural resins. The **European Lacquer in Context** project focuses on the historical, chemical, physical and technological study of European lacquers*. During this project, historical objects are analyzed and European lacquer is reconstructed following historical recipes and studied after artificial aging. Gas chromatography/mass spectrometry with thermally-assisted hydrolysis and methylation (THM-GC/MS) was chosen as primary method for the analysis of the pure basic materials, lacquer reconstructions and historical lacquered items. During this study, **pyrolysis temperature** was optimized for gathering of maximal information on the compounds present in five terpenoid plant resins, all important ingredients for European lacquer: **sandarac, mastic, colophony, Manila copal and Congo copal**.

Methods

For each resin, five temperature programs were tested: four fixed temperatures (**350°C, 480°C, 550°C, 650°C**) and one ultrafast thermal desorption (**UFD; 350-660°C**). In the latter, the sample falls into the oven at 350°C, and is consequently heated to 660°C within one minute. The idea of this method is that easily volatilized compounds can escape the oven before possibly being destroyed at high temperatures. When temperatures rise, more compounds are set free and gathered on the cool column. It was therefore expected, in theory, that this temperature program should be the best compromise between a fixed low or high temperature, while degradation products of compounds released at low temperatures are avoided. Each resin-temperature combination was repeated three times.



Results and discussion

From the results, it is clear that pyrolysis at fixed temperature of 650°C is not desirable. Many of the selected markers are not or less visible with pyrolysis at this temperature. 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 (❖) performs well at all remaining temperature programs (UFD, 350, 480, 550°C). Differences between them are minimal. A **second group** of markers (▪) 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 performs also very well for these molecules. 480°C is a less performing option, but can be esteemed acceptable.

A **third group** comprises molecules that tend to be more present when high temperatures are applied (+). 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 overall lower signal strength than when 480°C pyrolysis temperature was applied. Some molecules may not be formed because their precursors left the oven earlier, or other side reactions may take place.

Conclusions

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

Belgian Science Policy Office
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Acknowledgements

The authors acknowledge the institutions for facilitating access to their resin collections and/or for providing resin reference samples: Botanic Garden Meise (Viviane Leyman), Museum for Middle Africa Tervuren (Hans Beeckman), Hochschule für Bildende Künste of Dresden (Annegret Fuhrman).

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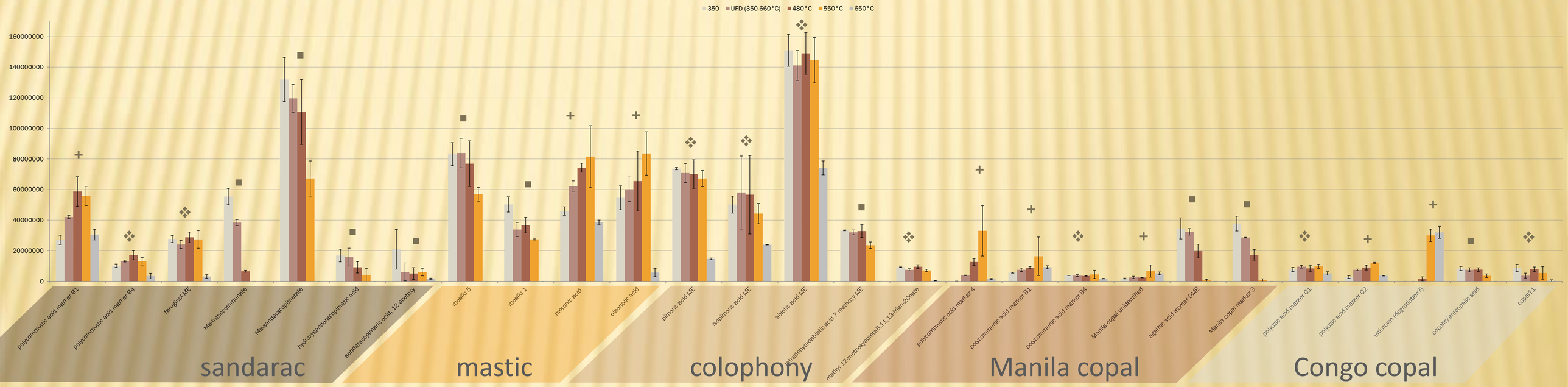

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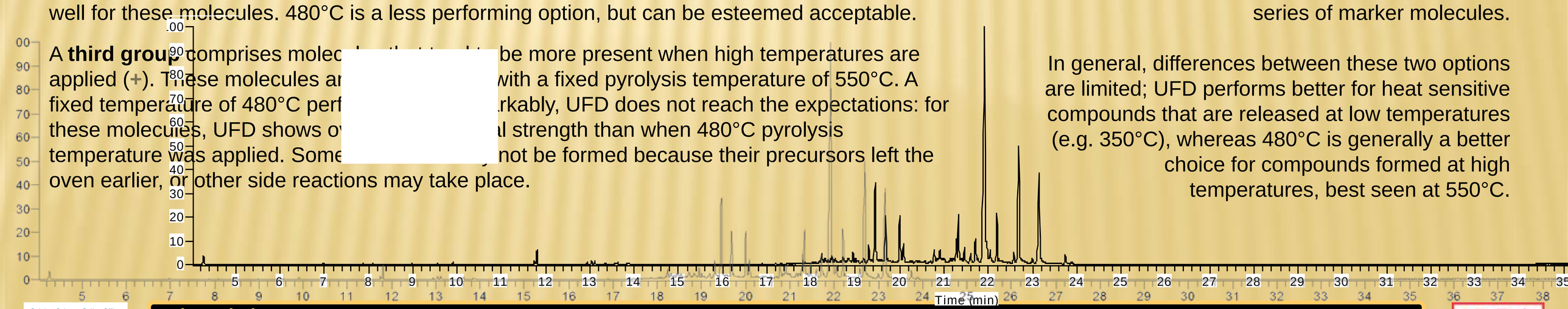

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