A new method for identifying experimental and Palaeolithic hafting adhesives using GC×GC-HRTOFMS

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INTRODUCTION

Hafting adhesives can be seen as an indication of the cognitive and technical capabilities of the manufacturers and therefore play a key role in the debate on human evolution. These adhesives are mainly from plant origin (resins, gums or tar) and are often mixed with beeswax and other additives in order to make them less brittle. Archaeological evidence indicates that these adhesives were already in use in the Palaeolithic from at least 120.000 years ago. However, discoveries for this period are very rare and only become abundant from the Neolithic onwards.

The longer exposures of adhesives to taphonomic processes limits the chance of survival in the archaeological record. If adhesives are present on Palaeolithic stone tools, they appear often in such small quantities that they are challenging to identify by conventional gas chromatography - mass spectrometry (GC-MS) or even to remove them effectively from the stone tool. Moreover, the destructive nature of extraction for GC-MS analysis may damage these rare samples and may inhibit other types of analyses.

AIM

Our study aims to overcome this problem by using headspace-solid phase micro extraction (HS-SPME) for sample extraction and analysis by comprehensive two-dimensional gas chromatography − high-resolution time-of-flight mass spectrometry (GC×GC-HRTOFMS), which has the benefit of analysing the volatile organic compound (VOC)s from the substance. The method is non-destructive because the sample does not need to be removed from the stone tool surface, it does not need pre-treatment and it is not damaged by the analysis itself.

EXPERIMENTAL SETUP

- An examination of experimental compound adhesives (pine and spruce resin, acacia gum and birch tar; beeswax)

ID	Adhesive	% Resin	% Beeswax	Amount (mg)
PN	Pinus (Pinus nigra var. nigra)	100	0	5
PN+BW	Pinus (Pinus nigra var. nigra)	50	50	5
PA	Spruce (Picea abies)	100	0	5
PA + BW	Spruce (Picea abies)	50	50	5
AG	Arabic Gum	100	0	5
AG+BW	Arabic Gum	50	50	5
BI	Birch Tar	100	0	5

Table 1. Reference samples analysed by GC×GC-QTOFMS with compositions in weight %

- Blind test on experimental samples to test the reliability of the method and to determine the minimal quantity necessary for analysis.
- Analysis of in situ experimental adhesives adhering to the stone tool surface

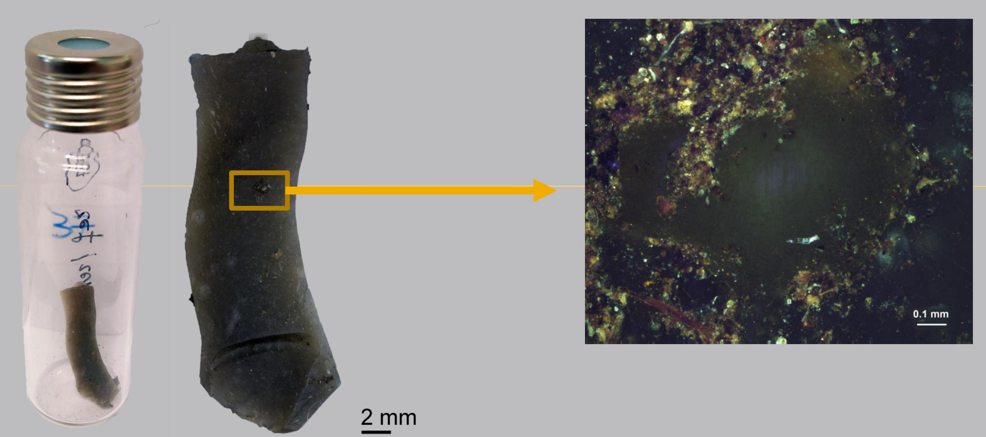

Fig. 1 Example of an in situ sample that is placed directly into a vial and contained only one drop of Picea abies resin with a surface area of 0.33 mm²

- Sample vial incubation (10 min at 50 °C) and HS-SPME exposure (DVB/CAR/PDMS fibre, 15 min at 50 °C)
- Analysis using a LECO Pegasus HRT with an Rxi-624Sil MS first dimension column and a Stabilwax second dimension column

RESULTS

Adhesive profiling

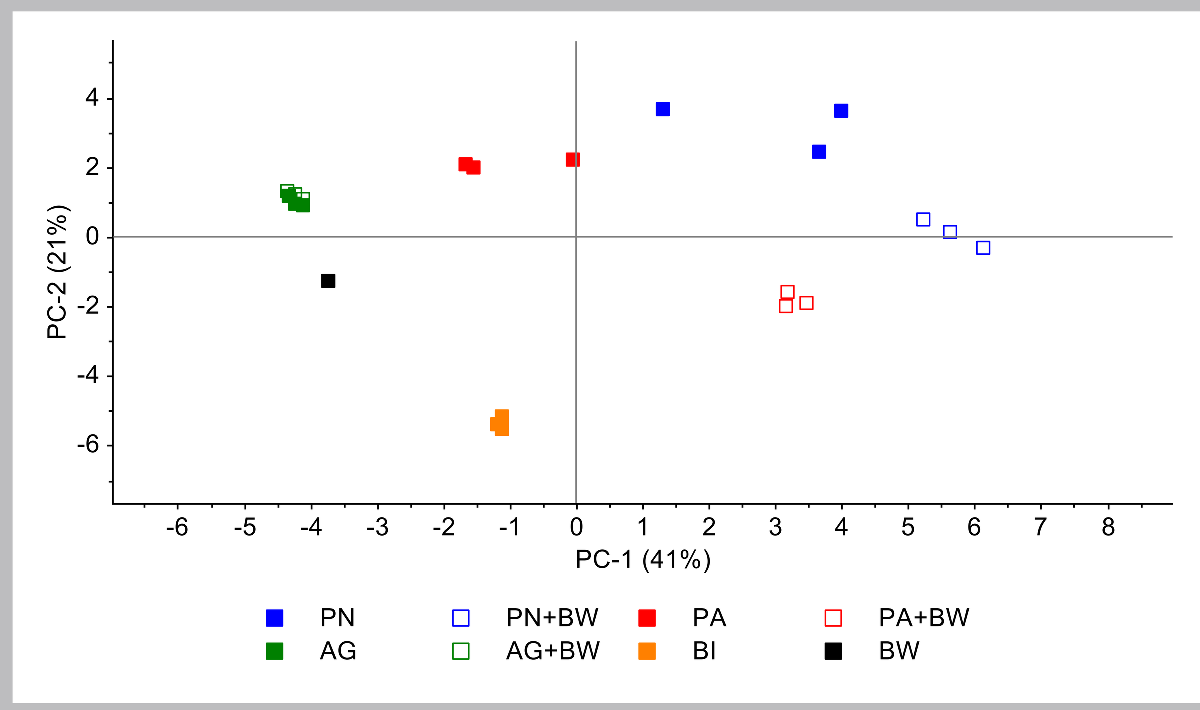

Fig. 2 PCA analysis of the reference samples : PN= Pinus nigra, PA = Picea abies, BW = Beeswax, AG = Arabic gum, BI = Birch

- Each adhesive produces a statistically relevant complex volatile signature
- The different wood resins appear to have distinct profiles
- The presence of beeswax can be identified in adhesive mixtures

Blind test

- Adhesive mixtures are correctly identified in the majority of the cases, independent of the sample size
- Detecting the addition of beeswax to the mixtures proves slightly more challenging, but it is still correct for the majority of the cases

In situ analysis

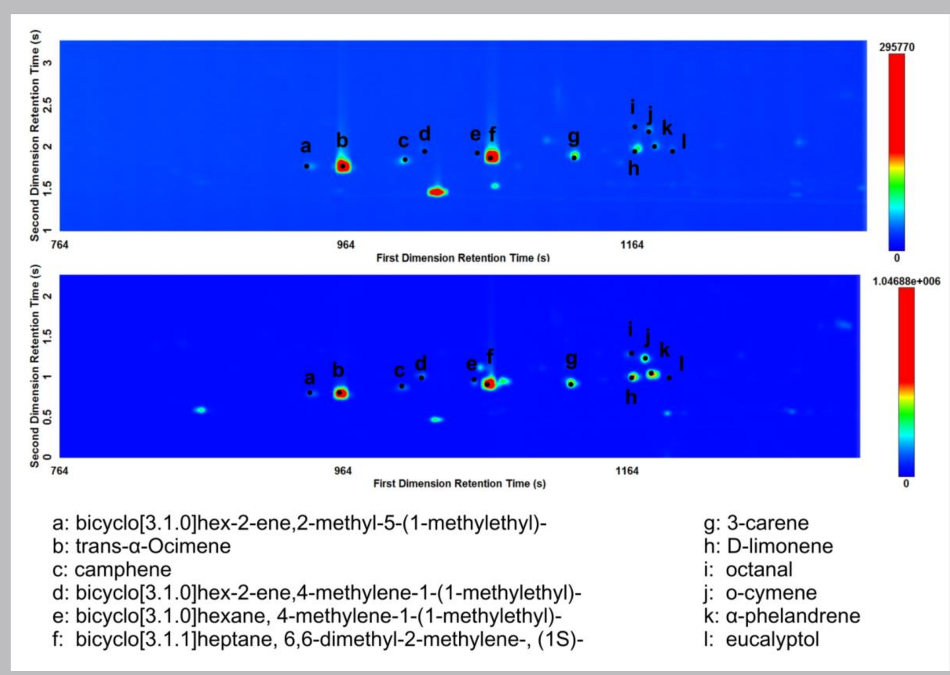

Fig. 3 Total Ion Chromatogram (TIC) comparison between in situ sample (above) and Picea abies reference sample (bottom).

- In-situ volatile characterization is possible using quantities in the milligram range

DISCUSSION & CONCLUSION

Our results show that GC×GC-HRTOFMS is a reliable method for analysing compound adhesives; even within the milligram range. Non-destructive identification of in situ adhesives is possible with the sensitivity of the method. Additionally, the VOC profile of these compound adhesives proves extremely complex and benefits significantly from multidimensional separation techniques. A statistical analysis of the GC×GC-HRTOFMS data produces distinctive profiles for each of the adhesive components. This new analytical technique thus has enormous potential for identifying Palaeolithic adhesives. Future work will focus on the analysis of altered experimental samples and on an application to archaeological adhesive samples.

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