

Non-destructive identification possibilities of prehistoric hafting adhesives with DHS-GC×GC-TOFMS

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- Prehistoric men used adhesive to mount a stone tool into a handle, these adhesives tend to preserve on the stone surface
- Chemical analysis of those adhesives help our understanding of technological processes and the utilisation of natural resources
- The standard chemical analysis is highly destructive and not compatible with archaeological preservation
- We developed a non-destructive analysis of the residues on the stone tool surface by capturing the volatile compounds (VOCs)



Database

15 different adhesives, divided over 4 classes have been measured with automated dynamic headspace coupled to a GC×GC-TOFMS



Tar



Resin



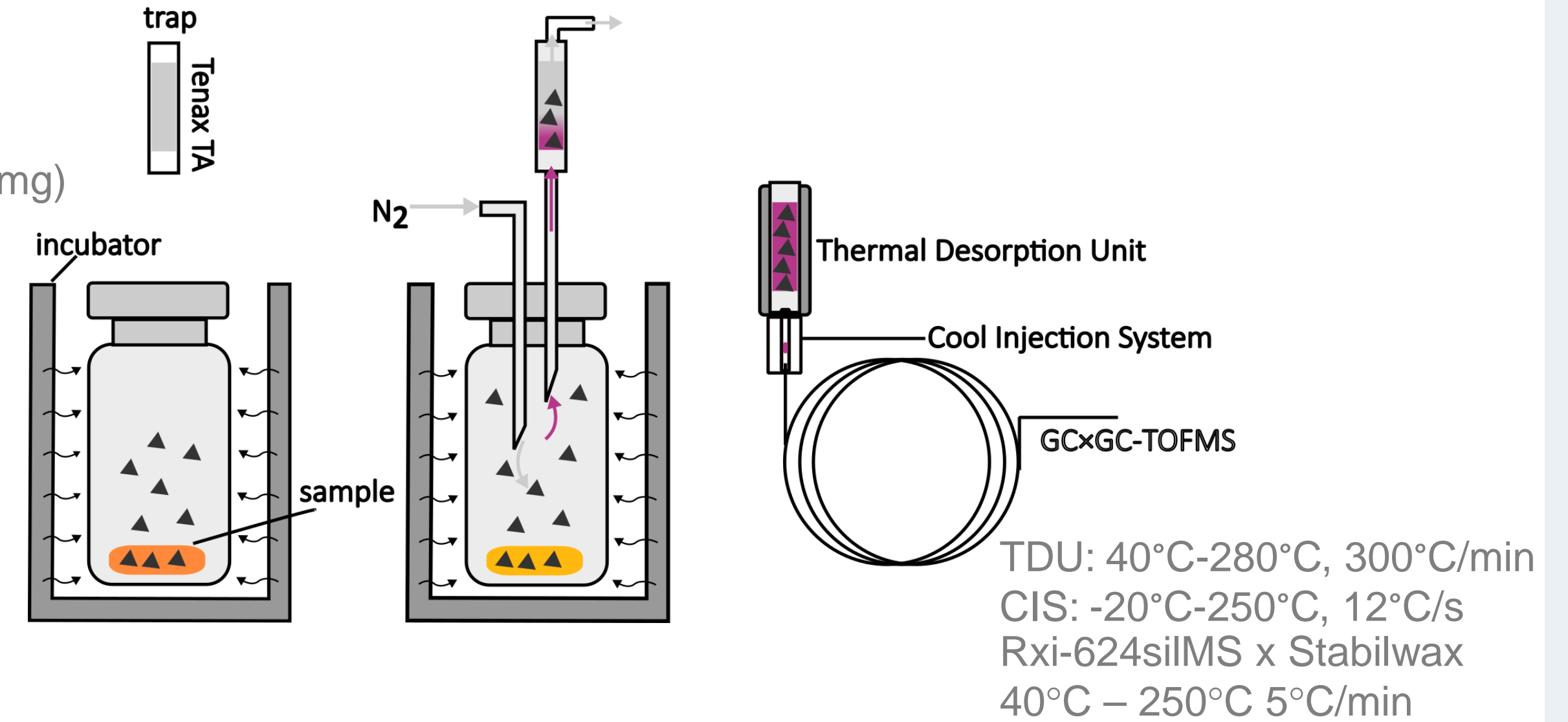
AG



Wax

Sample: 5 mg (AG 10 mg)
Incubation T: 50°C
Incubation t: 20 min
F purge: 22.5 mL/min
Vol purge: 450 mL
Trap T: 30°C
Needle T: 120°C

1 INCUBATION 2 EXTRACTION 3 DESORPTION



Case study

6 stone tools (samples 408 – 413) were artificially degraded and analysed with a manual DHS setup, the trap was afterwards inserted in the GC×GC-TOFMS



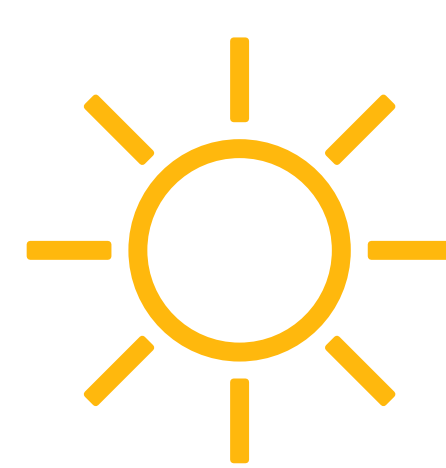
412 & 413



408 & 409



410 & 411

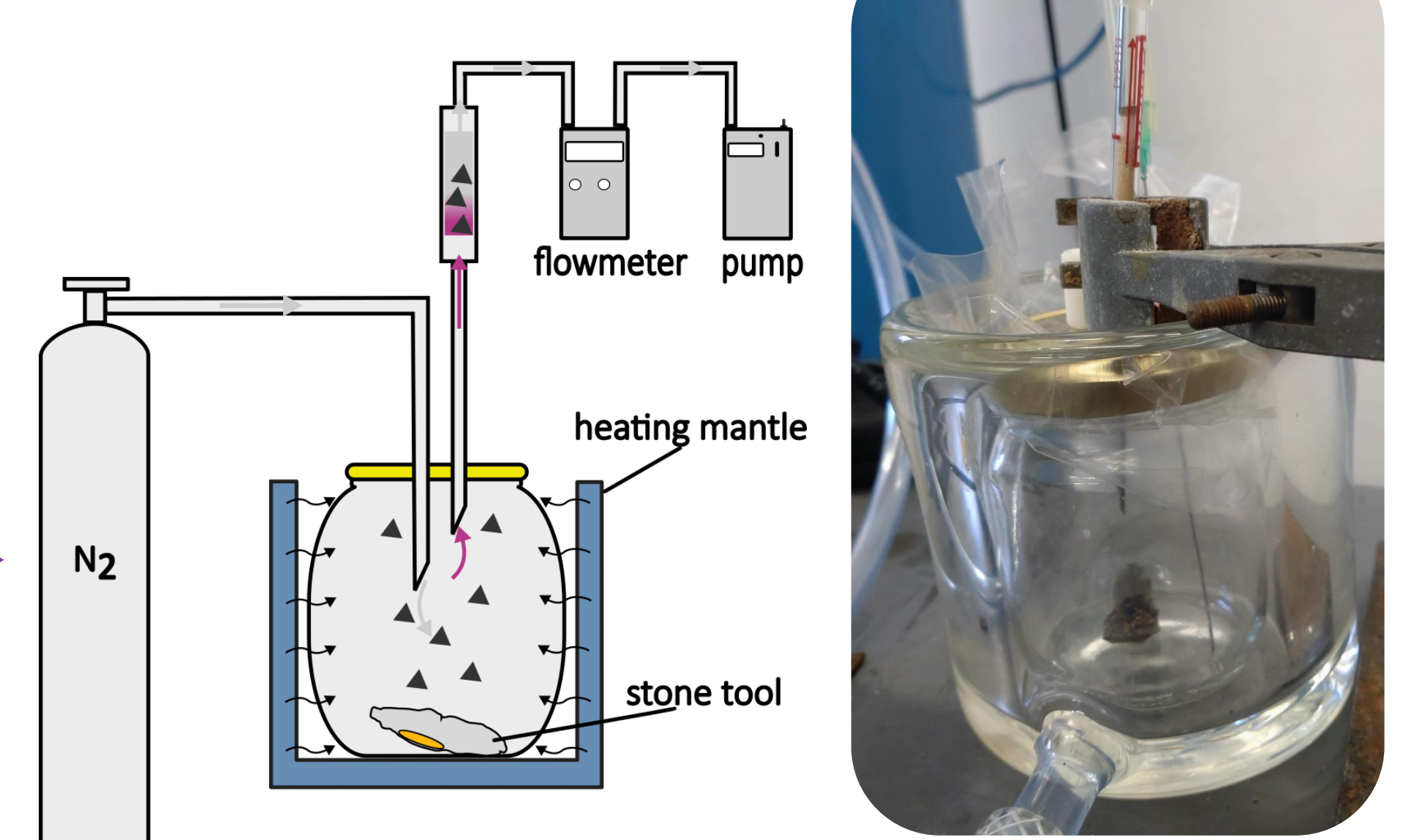


UVA & UVB

[M. Michel & V. Rots, 2022]

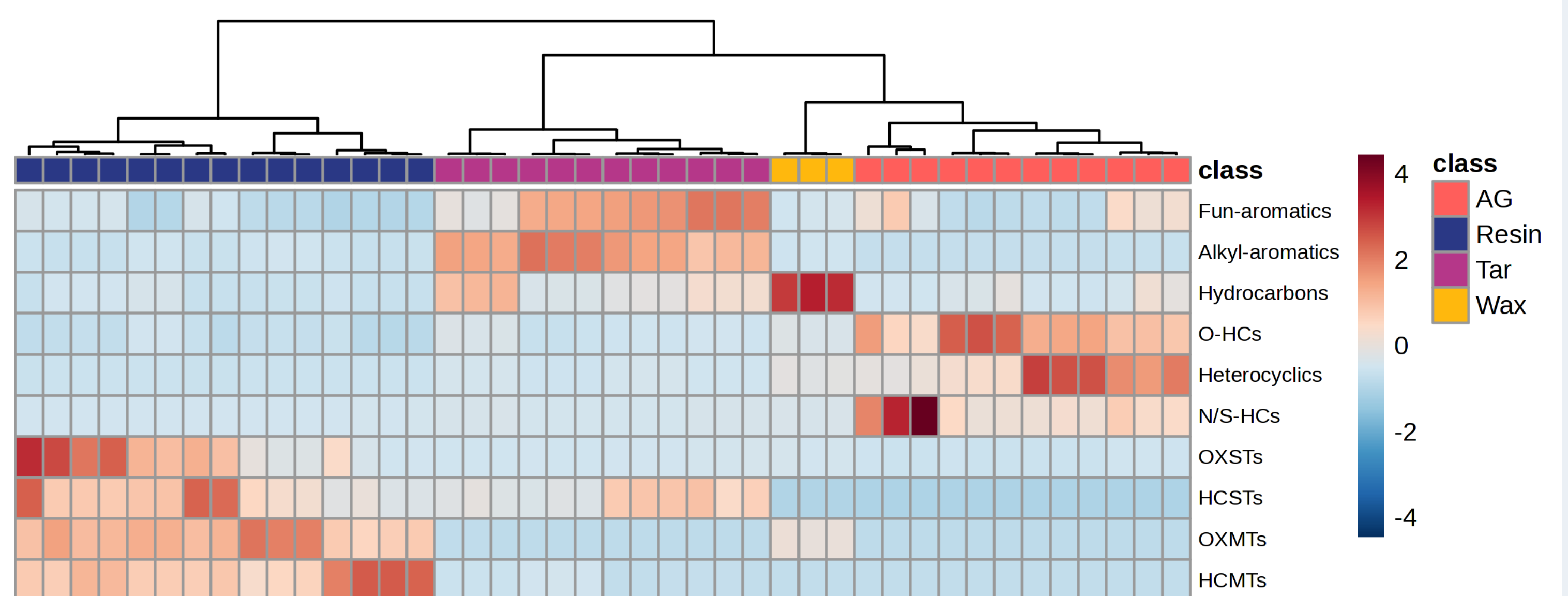
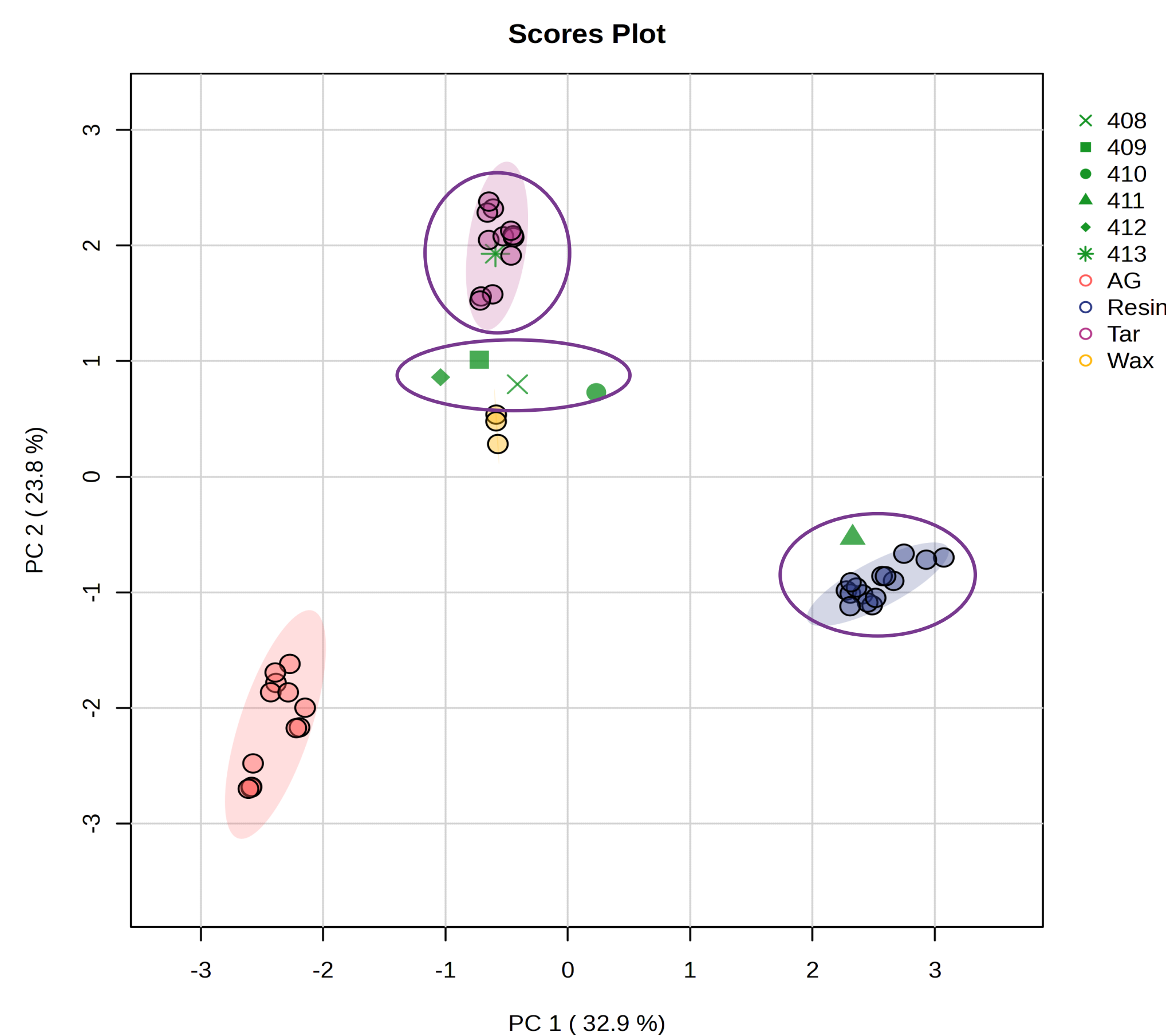
Incubation T: 50°C
Incubation t: 30 min
F purge: 80 mL/min
Vol purge: 12600 mL

2 EXTRACTION



The analytes were divided over 9 chemical classes and the total area was used for unsupervised multivariate analysis

Hierarchical clustering creates 4 clusters representing the 4 adhesive classes



Out of the 6 experimental samples 2 are placed in proximity of their corresponding adhesive class; a resin and a tar

The others could not be identified due to severe degradation resulting in loss of VOCs and less distinctive chemical groups

Despite the degradation, the experimental samples are plotted close to the adhesives and the sampling did not influence the VOC profile

- Non-destructive identification of prehistoric adhesives with DHS in combination with untargeted statistics is investigated
- The different sampling methods has little influence on the VOC profile → database is robust and useful for identification
- Degradation has more influence on the VOC profile → supervised statistics and machine learning might improve identification abilities

