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EXAMINATION OF HAFTING ADHESIVES ON PALEOLITHIC STONE TOOLS USING GC×GC-QTOFMS

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Stone tools are the most frequent artefacts found at prehistoric sites and due to the rare preservation of organic material, stone tools are one of the main sources of information to gain insight regarding prehistoric lifeways. An important debate in Paleolithic studies is whether stone tools were mounted onto an organic handle. Hafting is an invention that revolutionized stone tool use and that requires a capacity for abstract thought and planning. Knowing whether stone tools were hafted and how they were hafted allows an understanding of the cognitive and technical capabilities of their makers. Stone tools can be hafted in various ways, but adhesives from plant origin were used frequently (i.e. resins, gums or tar). Archaeological evidence indicates that these adhesives may have been used in the Paleolithic period from around 120,000 years ago, but evidence from this period is sparse. The long exposure to biochemical alteration processes limits the preservation of Paleolithic adhesives and if it occurs, quantities are so small that extraction and GC-MS characterization is challenging. Due to the fact that adhesives were mixed with various plant and animal products, including several essential oil components, their volatile organic compound (VOC) profile is extremely complex and can benefit significantly from multidimensional separation techniques. In this study, comprehensive two-dimensional gas chromatography – quadrupole time-of-flight mass spectrometry (GC×GC-QTOFMS) was used to analyze the VOCs from experimental adhesive samples and archaeological samples with the aim of determining adhesive composition. GC×GC was used to provide optimal chromatographic separation of adhesive components and visualize the chromatographic adhesive fingerprint of each sample. QTOFMS data was used in order to obtain high-resolution mass spectral data to contribute to compound identification. Further compound identifications were investigated using product ion spectra to provide more selective identifications and structural elucidation.