Analysis of organic residues and artefacts in archaeological findings by mass spectrometry

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Abstract

Chemical analysis of organic residues and artefacts is a key part of current research in archaeology. Extensive rescue archaeological survey commonly precedes larger infrastructure constructions. During this work a lot of archaeological objects are obtained that must be inspected in short time to evaluate the relevance of findings and decide on the need for further (more detailed) research in a given locality. Appropriate analytical techniques providing reliable information on the chemical composition of archaeological findings in a timely manner are highly appreciated in this process. The modern analytical instrumentation, i.e. mass spectrometry especially in combination with multivariate statistical methods appeared to be powerful tool for that purpose.
In this communication, capability of high resolution mass spectrometry with (matrix assisted) laser desorption ionization ((MA)LDI-MS), Atmospheric Solids Analysis Probe (ASAP-MS) and gas chromatography/mass spectrometry (GC/MS) for the characterization of organic materials present in various archaeological findings in wide time range will be discussed.

GC/MS study of differences among particular soil layers in excavated vessels from the end of Eneolithic period revealed the presence of triterpenoid milliacin that occurs in broomcorn millet. Subsequent ASAP-MS experiment provided high resolution tandem mass spectra unambiguously confirming the identity of this compound (being the first utilization of ASAP-MS in archaeology). This finding of milliacin can be considered as the earliest evidence of broomcorn millet usage in Central Europe. MALDI-MS combined with Multivariate statistical approaches revealed the presence of fatty residues in some of the excavated vessels. Signals belonging to di- and triacylglycerols were found in ceramic beakers belonging to Corded Ware culture. Those results were confirmed by ELISA assay that proved the presence of cow milk or a dairy product.

Besides, LDI-MS was used for analysis of unknown fibre pieces captured in eyelet of S-shaped-end ring jewels found in proximity of female skulls in tombs. Signals of sodium

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adducts of oligosaccharide chains suggest the presence of plant material (presumably linen, hemp or nettle) used for fixation of the jewels.
Finally, LDI-MS in combination with multivariate statistics allowed estimation of the geographical origin of amber artefacts found.

Keywords: mass spectrometry, organic residues, analytical chemistry, laser desorption/ionization, gas chromatography