ANALYSIS OF ORGANIC RESIDUES AND ARTEFACTS IN ARCHAEOLOGICAL FINDINGS BY MASS SPECTROMETRY

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Introduction:

Archaeological samples present a challenging task - to determine presence of an unknown organic material thereby confirming its use by the people of the examined culture. Mass spectrometry is a valuable tool in this context, due to its identification power, mainly in tandem MS approach. Low concentration of analytes is usually present and certain level of degradation can be expected as well. Invasiveness of the technique must be reduced to preserve items of cultural value while sampling has to be done in a way that does not contaminate the sample. Therefore, close cooperation of archaeologists with analytical chemists is desirable. In the presented study, soil from excavated ceramic vessels and surface of metal jewelry were examined by various MS techniques with emphasis on organic residues detection and identification.

Ceramic vessels:

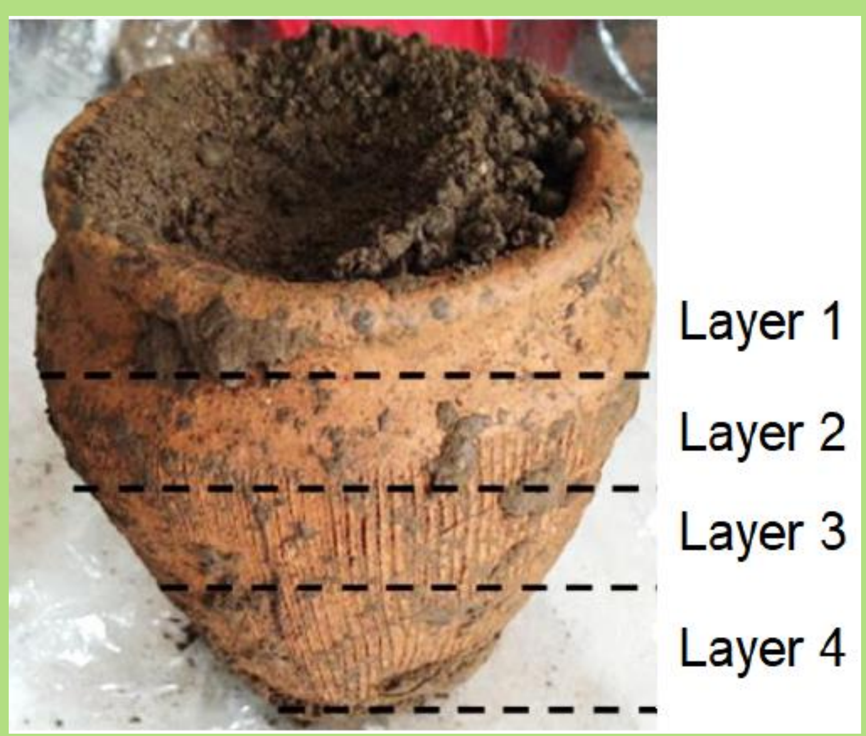

Fig. 1. Soil from excavated ceramic vessels was divided into several layers (4 in the picture above) and analysed separately. The first (top) layer was considered a blank as the concentrations of the analytes are expected to rise towards the bottom of the vessel.

Miliacin as a marker of millet:

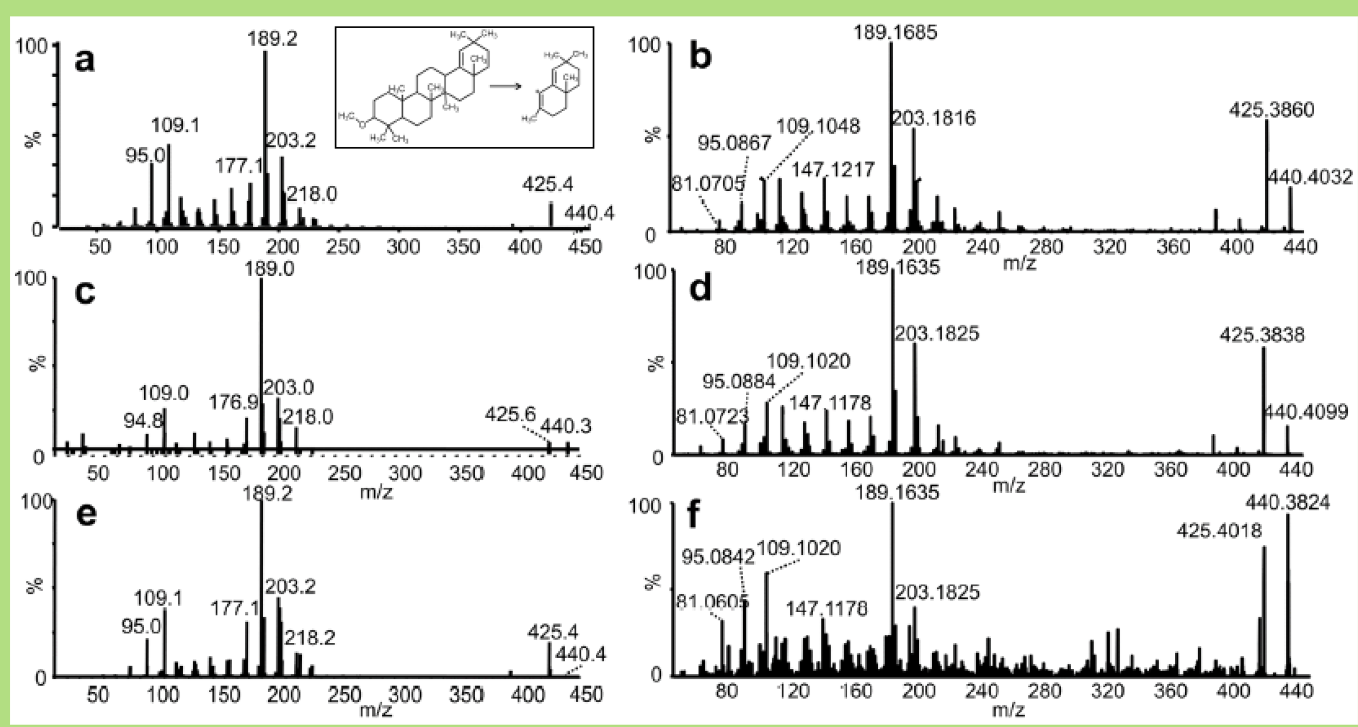

Fig. 2. MS/MS spectra of miliacin standard (a: GC/MS, b: ASAP-MS), compound identified as miliacin in recent broomcorn millet (c: GC/MS, d: ASAP-MS) and unknown compounds from a ceramic vessel (e: GC/MS and f: ASAP-MS). Proposed fragmentation scheme in inset of a. [1]

Triacylglycerols as markers of dairy products:

Most significant markers in S-plots (m/z)	Differences in Da between adjacent signals (explanation)	Elemental composition	Difference from theoretical mass (mDa)	Carbon number:double bond number
673.5123	-	37:2	$C_{40}H_{73}O_5K$	5.0
687.5341	14.0218	38:2	$C_{41}H_{75}O_5K$	-1.1
701.5410	14.0069	39:2	$C_{42}H_{77}O_5K$	7.6
715.5629	14.0219	40:2	$C_{43}H_{79}O_5K$	1.4

Fig. 3. Markers of triacylglycerols (in the form of potassium adducts) were found in the soil in certain excavated vessels using MALDI-MS. Data were processed using Orthogonal Projection to Latent Structures - Discriminant Analysis (OPLSDA). Corresponding signals were found in a study done by G. Piccariello where they were assigned to milk fat [2]. Subsequent ELISA tests confirmed presence of bovine beta-lactoglobulin.

S-shaped-end ring jewels:

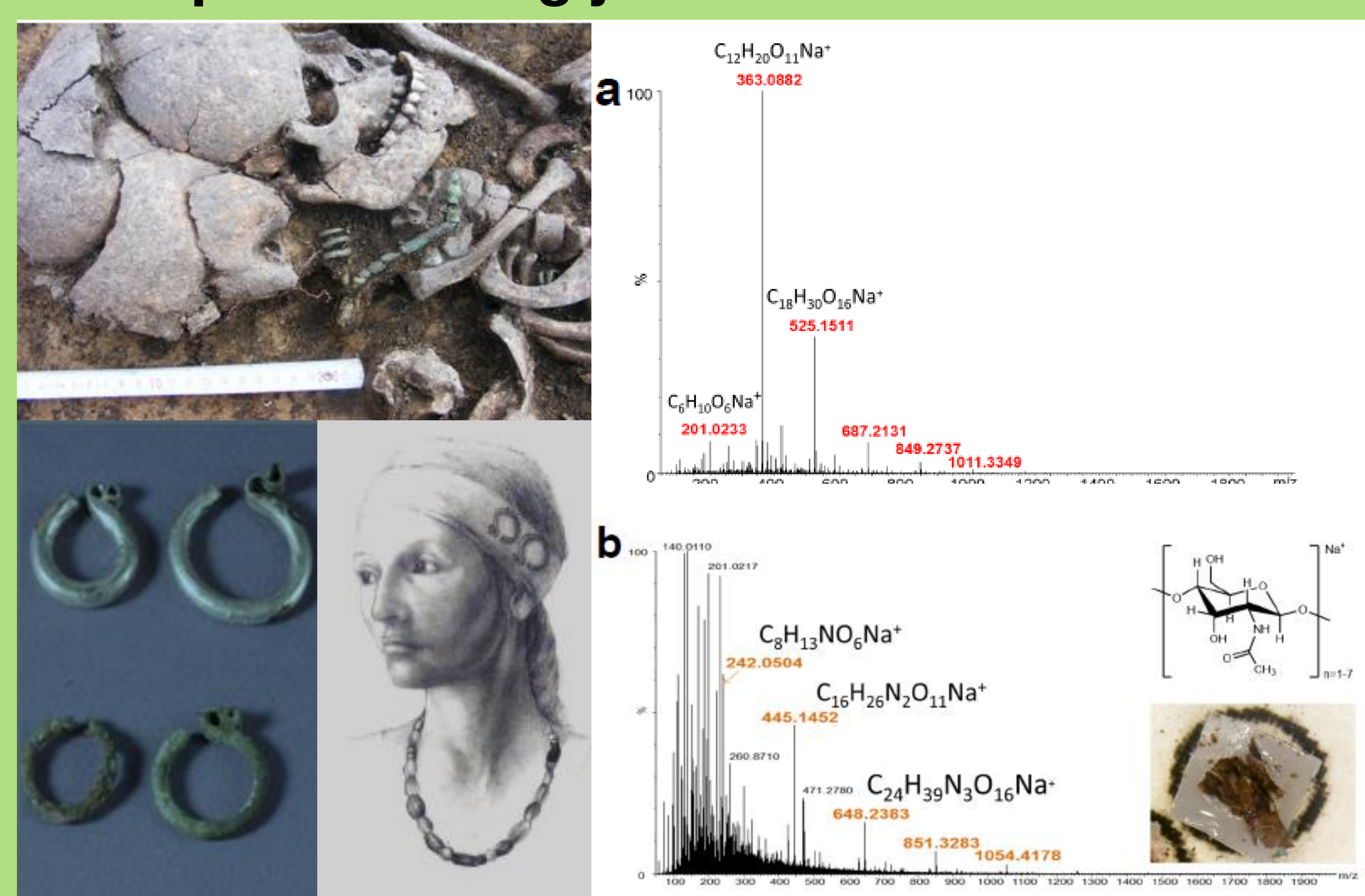

Fig. 5. S-shaped-end ring jewels are found in graves next to skulls of the buried. They could have been worn directly in hair or attached to the clothing. MALDI-MS analysis revealed presence of saccharidic units in several findings (MS spectrum **a**) - the signal could be assigned to plant fiber materials (e.g. linen, hemp, nettle, bramble). These signals were found curled fibrous microstructures as well as on the metallic surface of the eylet of the jewel. In other findings (MS spectrum **b**), N-acetyl glucosamine chains were detected. These molecules could originate from chitin - the main component of insect cuticule. This can indicate presence of corpseeating bugs. In the insets of **b**, N-acetyl glucosamine structure and photo of the measured sample on the MALDI plate are shown.

A "sun cross" artifact:

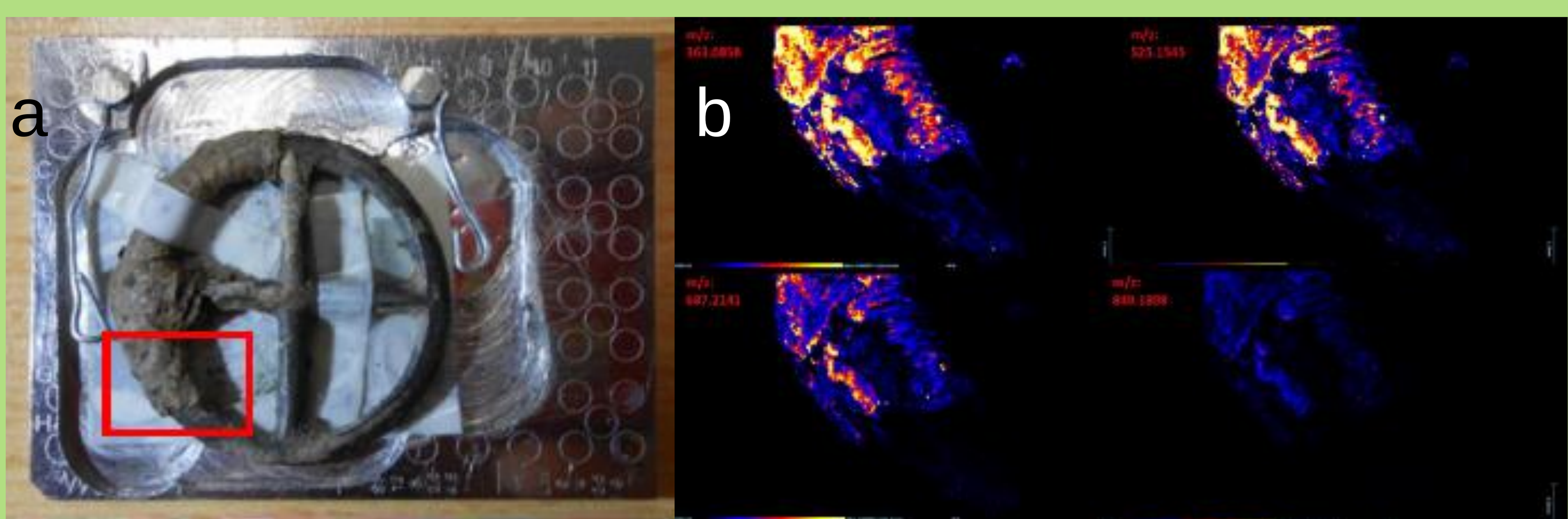

Fig. 4. "Sun crosses" (named after their assumed connection to the solar-related prehistoric religions) represent relatively common design of metallic findings dating from Eneolithic to Iron Age. One of the excavated sun crosses (**a**) was covered by a crust of organic material. Part of the item (highlighted in red in **a**) was measured by MALDI-MS/MS in imaging mode using a modified (milled) MALDI plate. Signals corresponding to subsequent losses of hexose units were observed with intensity lowering towards higher masses. Combined with the fact that the surface resembles a textile-like structure, also in this case the crust was likely formed from a processed plant material covering (or attached to) the sun-cross.

Conclusion:

Analyses of ceramic vessels belonging to the Moravian Corded Ware culture by GC-MS and ASAP-MS evidence that broomcorn millet was used in Central Europe already in Eneolith. This is the earliest evidence of millet usage in this area. Both techniques are suitable for analysis of miliacin as a marker of broomcorn millet. Besides, diary products were detected by MALDI-MS in soil content of aforementioned excavated vessels (based on specific triacylglycerole signals). Furthermore, laser desorption-ionization mass spectrometry and imaging mass spectrometry prove to be useful tools for analysis of organic residues deposited on ancient jewels, where residues of plant fibres (polysaccharides) and chitin (N-acetylglucosamine) were detected and identified. With the use of MALDI imaging, a biological residue on another metallic finding - a "sun cross" artifact - was examined. Signals of saccharides were observed in the part of the item covered by the organic crust.

References

Kučera, L. et al., Anthropol. Sci, submitted.; Picariello G., et al., Eur. J. Lipid Sci. Technol. 109 (2007) 511.

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