Studies in organic archaeometry V1: chemical analysis of organic material found in traces on an Neolithic terracotta idol statuette excavated in lower Austria

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Abstract
In an Early Neolithic settlement found in Lower Austria and excavated by the Prehistoric Department, Museum of Natural History, Vienna, pieces of broken terracotta figurines were found, all of them belonging to male and female statuettes (the latter being considered as so-called idols). Traces of an organic material found on one of them were analyzed at the Vienna University of Technology. By means of GC-MS and ensuing chemometric data analysis this organic material could be identified as birch bark pitch, a material frequently used for many purposes in prehistoric Europe.

Keywords: Archaeometry, early Neolithic terracotta figurines, GC-MS analysis, chemometrics, birch bark pitch

Introduction
In 1989 a prehistoric settlement was excavated by the Prehistoric Department, Museum of Natural History, Vienna, at Brunn am Gebirge, a Lower Austrian village situated some 100 m south of the border of Vienna. Within this Early Neolithic site (\(^{14}\)C dating: ca. 5650-5100 B.C. \(^{3,4}\)) fragments of a male and of some female terracotta statuettes were found, the best preserved of which being the female figurine to be discussed here, named Venus from Brunn am Gebirge according to the modern village at this site.

As shown in Figures 1 and 2 this idol statuette (consisting of seven fragments, total preserved length: 14.2 cm) shows grooves in the lower part of its body which were still filled with an unknown dark material. This organic material had to be identified with the intention to enable archaeologists a tentative interpretation of its prehistoric function.
Some archaeological remarks

1) Regarding the dating
The statuette was found on site IIb of the Early Neolithic’s settlement of Brunn am Gebirge, Wolfholz in pit 167. The whole settlement consists – after the last excavations in 1999 - of six different sites, on which a total of about 64 longhouses could be excavated or prospected. As shown by radiocarbon dating, site IIb is the second oldest one within the chronological sequence of the different sites, thus belonging to the formative period of Linear Ceramics Culture.

2) Regarding the cultural context
One of the roots of this culture may be the late Starčevo Culture (known from sites in southern Hungary). In settlements of Körös (eastern Hungary) and Starčevo Culture such figurines are common. It should be remarked that the statuette studied here, showing a reconstructed height of more than 25 cm, is the biggest ever observed within the Linear Ceramics Culture.

3) Regarding the function of this /of such statuettes
The prehistoric function of such figurines can only be assumed in a very speculative way. Although such figurines could also be simply interpreted as toy puppets, the idea to consider them as idols, i.e. as religious objects, became prevailing in Early Neolithic’s archaeology.

Experimental Section

Since first studies undertaken on tiny samples soon showed that the dark material in question was practically entirely organic, there was some probability to assume that it might be pitch prepared by pyrolysis of birch bark.
Indeed birch bark pitch seems to have been a real “multifunctional“ substance in prehistoric times\textsuperscript{5}: it is known to have been frequently used for a variety of purposes, e.g., as coating of pottery \textsuperscript{6,7}, as „glue“ for ancient repair work\textsuperscript{8}, as adhesive used to fix weapons (e.g. flintstone arrowheads) to their handles\textsuperscript{9} or shafts\textsuperscript{10,11} and even as a gift offered in ancient rites\textsuperscript{12}.

So the major target of our studies was to show whether or not the material in question could be identified as birch bark pitch.

**Method of analysis**

A variety of methods are described in literature\textsuperscript{13} to identify such materials as birch bark pitch. The method used for the present studies was published by us earlier\textsuperscript{1,1}, consisting mainly in a comparison of the material in question with laboratory-made “model pitches“ by means of GC-MS and ensuing chemometric studies of the data thus obtained.

In an abbreviated way our analytical sequence can be described as follows: in order to get rid of most of the atypical components all the model pitches as well as the archaeological samples were Kugelrohr-distilled (bulb-to-bulb distilled) under reduced pressure (ca. 300°C, 22-26 mbar), yielding a viscous oil which contained most of the significant terpene fraction. Upon purification by solid phase extraction this oil was subdued to GC-MS examination, while the data thus obtained were used for a chemometric evaluation by multivariate data analysis\textsuperscript{14}.

**Results of these examinations**

It was shown already by gas chromatography that the material in question is a pitch, prepared in prehistoric times from wood or bark taken from the family of *betulaceae* (trees related to the birch).

The next step within the analytical sequence, i.e., the attribution of this material to the birch (*betula*) was achieved by chemometrics as illustrated by the following plots: these compare model pitches prepared from various other trees with the sample taken from the Venus statuette (marked by x).

Each sample was characterized by the relative concentrations of 50 measured substances being mainly triterpenes. Principal component analysis (PCA)\textsuperscript{14} of these data projects the 50-dimensional data space onto a plane resulting in a scatter plot containing a point for each sample; samples with similar concentration profiles are located close together (Figure 3). The model pitches form partly overlapping clusters according to their origin. The sample from the *Venus from Brunn am Gebirge* is located within the cluster formed by birch samples (*betula*). PCA does not consider the known group memberships of the model pitches and the clusters are found solely from the concentration data.

Another method to project points in a high-dimensional space is partial least-squares discriminant mapping (PLS)\textsuperscript{15}. This approach utilizes the class memberships of the model
pitches and results in a scatter plot with an enhanced separation of the different families of trees. Figure 4 shows almost no overlap of the families and the sample from the *Venus from Brunn am Gebirge* is clearly located within the cluster formed by birch samples (*betula*).

Linear discriminant analysis (LDA) optimizes the separation of given classes of objects and is therefore often used in multivariate classification problems. Figure 5 shows a scatter plot separating the samples produced from birches and the samples from other tree families. The archaeological sample can be definitely assigned to the birch trees.

**Figure 3.** Principal component analysis indicates that the archaeological sample (x) belongs to the *betula* group.

**Figure 4.** Partial least-squares discriminant mapping clearly indicates that the archaeological sample (x) belongs to the *betula* group.
Figure 5. Linear discriminant analysis separates birch trees from other trees: the archaeological sample (x) can be definitely assigned to the *betula* group.

Summary and tentative interpretation

It could be shown that the dark organic material taken from the grooves of the Neolithic terracotta statuette called *Venus from Brunn am Gebirge* is birch bark pitch, produced in prehistoric times by pyrolysis of birch bark.

The analytical result thus obtained is therefore consistent with many other finds in prehistoric Europe, adding one more example to the list of practical applications of this polyfunctional material.

The fact that birch bark pitch was found on the figurine suggests that an additional – now lost - material was glued to parts of its surface. A reasonable suggestion what this additional material could have been is somewhat facilitated by the location of the grooves into which the pitch was mounted (see Figure 6).

Figure 6. Drawings of the statuette from right hand side, front, and back. Rests of the glue in black.
Considering that the decayed material which originally was glued to the figurine might have been of textile nature and taking into account that all the incised lines bearing pitch are found round the hip and the belly of the statuette the following interpretation seems to be conceivable: With some probability the grooves were incised with the intention to allow a better fixation of the birch bark pitch, which might have been applied as an adhesive used to glue some sort of dressing around the hip of the statuette.

At any rate these findings should encourage archaeologist who are excavating such statuettes to study them closely for similar traces of organic agglutinants.

References and remarks

1. Our earlier papers in this ARKIVOC series:

2. We express our thanks to our former co-workers E.W.H. Hayek (former Ph.D. student) and his supervisor U. Jordis (both: Vienna University of Technology) for their contributions to the topic.

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