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ORGANIC RESIDUES ANALYSIS: THE CASE OF A BEAKER FOUND IN THEBAN NECROPOLIS, EGYPT

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Abstract

Amorphous organic residues collected from a ceramic vessel from a tomb excavated in the Theban Necropolis (Egypt) were chemically investigated by an analytical procedure based on gas chromatography coupled with mass spectrometry (GC/MS). Little is known about Egyptian ceramic vessels, thus retrieving valuable information on the use of ceramics from the chemical analyses of organic residues was a key aspect of this work. The results showed that the vessel was used in connection with a number of substances such as beeswax, fat/oil and Pinaceae resin. This enabled us to draw hypotheses on the possible function of artefact in connection with mummification practices.

Keywords: *Theban Necropolis; ceramic vessel; GC/MS; Pinaceae resin; beeswax; fatty material*

Introduction

Pottery vessels are among the most frequent archaeological finds at burial, religious or domestic sites. For this reason, shedding light on the function of a vase is of fundamental importance in understanding aspects of daily life, trade or burial customs of ancient societies. However, it is quite difficult to understand the exact function of the majority of vessels. In order to retrieve such information, archaeologists normally study the site (burial, domestic or religious) where the pottery was found. They also look for similarities in documentary sources such as texts or pictures/paintings and compare or study the technological and morphological features. In fact, the choice of ceramic material, the manufacturing process and the shape were based on certain requirements. Sometimes, the object itself can provide clues, such as wear marks or kind of lip. In other cases, the ceramic vessel itself shows its function by inscriptions on its body.

Ethno-archaeology, has given a very useful contribution to this field, using a different kind of approach. It involves the study of modern societies and populations that live in contexts and cultural environments similar to ancient ones. Thus, by studying common morphological features that have similarities between ancient and modern vessels, and by analyzing the modern uses, it is possible to obtain information on the ancient functions.

Lastly, the analytical-chemical, morphological and histological criteria enable us to gain information regarding the uses and functions of the vessels [1, 2]. These criteria enable us to

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study the remains, such as amorphous residues, organic material absorbed in the ceramic matrix or as structured remains (seeds, fruits and roots) found in archaeological vessels. The chemical characterization of organic residues contained in ancient vessels is one of the most recent methods used to study how ceramics were used and is very valuable in terms of what it reveals about the artistic and manufacturing techniques of the past, and the uses of the vessel [1, 3, 4, 5, 6].

In Egyptology, the interest in the study of the pottery, unlike in other archaeological fields, has increased in relatively recent times. This is due to the fact that usually Egyptologists use other finds other than pottery to date the site and the layers. Furthermore, most Egyptian vases are not artistically significant, thus they were often put aside or simply not studied. This trend has grown and since the 1990s all archaeological missions document and study ceramic vessels. Nevertheless, the study of vessel functions is still in its early phase, and only a few typologies have been attributed to a specific function such as Bes vases, Hathor vases, or spinning bowls. There have only been a few publications on this subject [7, 8, 9, 10]. Paice [8] in particular, by studying tomb paintings reported some very interesting hypotheses on the function of vessels.

Within the framework of a study of an Egyptian tomb, M.I.D.A.N. 05 in the Theban Necropolis, investigated by an Italian Mission from the University of Pisa directed by Prof. M. Betrò [11, 12], the chemical composition of residues found in several ceramic vessels has been examined. The tomb is in Dra Abu el-Naga on the eastern side of the north hills. M.I.D.A.N.05 was built between the end of XVII dynasty (1650-1552 BC) and the beginning of XVIII dynasty (1552-1314 BC) and was used onwards until the Christian Age (2061 BC-641 AD). In particular, this paper presents the results from the chemical characterisation of organic residues found in a ceramic vessel, a beaker, from tomb M.I.D.A.N. 05. The beaker (Fig.1), which dates back to the Roman Age, has a truncated cone body, truncated cone plain foot, and semicircular everted rim [13].

Fig. 1. The ceramic vessel from which residues for GC/MS analysis were sampled.

The discovery of other small ceramic vessels with a similar shape and dimension as our beaker are reported in funerary contexts [13]. Notably, these vessels showed inscriptions (such as “resin”, “unguent”, “gum”, “natron”, “excellent oil”, “mummification preparation”, “fruits”) all relating to the contents and generally ascribable to materials and substances reported as being used in mummification practises or during religious rituals. The same beaker found in the Theban Necropolis, was discovered together with a hook, used by embalmers to remove the brain, and another beaker showing the inscription "reed marsh" [13]. In fact, in medical papyri, the extract of reed smash is reported as an ingredient in remedies for headaches, fever and for treating liver diseases [14]. All these lead us to hypothesize that the beaker contained a balm used during the mummification process, which was then left inside the tomb together with other instruments used for the same purpose and not to be used again.

By this way, the main aim was to understand the function of the vessel as well as to provide new insights into burial rites from the study of the organic residual contents found in the container. Because of the complexity of these organic residues, the analytical procedure used is based on gas chromatography coupled with mass spectrometry (GC/MS) due to its ability to obtain detailed information on the molecular composition [1].

Materials and methods

Materials

All the solvents used were Carlo Erba (Milan, Italy) pesticide analysis grade. *n*-tridecanoic acid (internal standard, IS1), *n*-hexadecane (internal standard, IS2), hydrochloric acid (HCl), potassium hydroxide (KOH) and N,O-bis(trimethyl)silyltrifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane, were purchased from Sigma-Aldrich (Milan, Italy).

Archaeological sample

The ceramic beakers still contain part of their original contents in the form of brownish-blackish solid amorphous substances. The sample (roughly 5mg) was collected with a scalpel, deposited in glass vessels and preserved before being chemically analysed.

Methods and instrumentation

The GC/MS analytical procedure [15] can be summarised as follows: a sub-sample (1-3mg) of the vessel contents was subjected to alkaline hydrolysis by adding 1mL of methanolic KOH [$KOH_{(CH3OH)}$ 10% weight/$KOH_{(H2O)}$ 10% weight = 2:3], and heating at 60°C for 3h. After hydrolysis, neutral organic components were extracted with *n*-hexane (3 x 500µL) and, after acidification with hydrochloric acid (10M; to pH 2), the acidic organic components were extracted from the hydrolysate with diethyl ether (3 x 500µL). Aliquots of both fractions were evaporated to dryness under a gentle stream of nitrogen and subjected to trimethylsilylation. This was achieved by mixing the dried aliquots with an internal standard solution (5µL of *n*-tridecanoic acid solution, $140mg\cdot g^{-1}$) and derivatised with 20µL of BSTFA (at 60°C, 30min), using 150µL *iso*-octane as the solvent. After adding 10µL of *n*-hexadecane solution ($80mg\cdot g^{-1}$) as an internal standard for the injection, 2µL of the solution were analysed by GC/MS.

The GC/MS was a Trace GC (ThermoElectron Corporation) equipped with a PTV injection port, linked to a Polaris Q (ThermoElectron Corporation) ion trap-MS detector (EI 70eV, ion source temperature 230°C, scanning *m/z* 50-650, interface temperature 280°C). The PTV injector was operated in the "constant temperature splitless with purge" mode at 280°C with a purge pressure of 100 kPa. GC separation was performed on an HP-5MS chemically bonded fused silica capillary column (Hewlett Packard; 5% phenyl 95% methylpolysiloxane, 30m x 0.25mm I.D., 0.25µm film thickness, connected to a 2m deactivated fused silica capillary pre-column, I.D. 0.32mm).

The GC conditions were as follows: initial temperature 80°C, 2min isothermal, 10°C·min^{-1} up to 200°C, 6°C·min^{-1} up to 280°C, 35min isothermal. Carrier gas: He (purity 99.9995%), constant flow 1.2mL·min^{-1}.

Results and discussion

The chromatogram (Fig. 2) obtained by GC/MS analyses of the acid fraction revealed that a mixture of Pinaceae resin and lipids was present in the beaker.

Pinaceae resin was identified from the presence of diterpenoid compounds: didehydroabietic, dehydroabietic, 7-oxo-dehydroabietic and 7-oxo-abietic acids. The lipid fraction was mainly made up of mono-(C_{12} to C_{28}, with $C_{16:0}$ and $C_{18:0}$ predominating) and di-carboxylic fatty acids, mono- and di-hydroxyacids and long chain alcohols, enabling us to determine the presence of beeswax and acyl-lipids [1, 5, 16-18, 19].

Beeswax was clearly recognized by the high abundance of palmitic acid ($C_{16:0}$) together with the presence of long-chain *n*-alcohols containing 24 to 32 carbon atoms, long-chain linear saturated monocarboxylic fatty acids containing 20 to 28 carbon atoms and, 14-hydroxyhexadecanoic and 15-hydroxyhexadecanoic acids [1, 19].

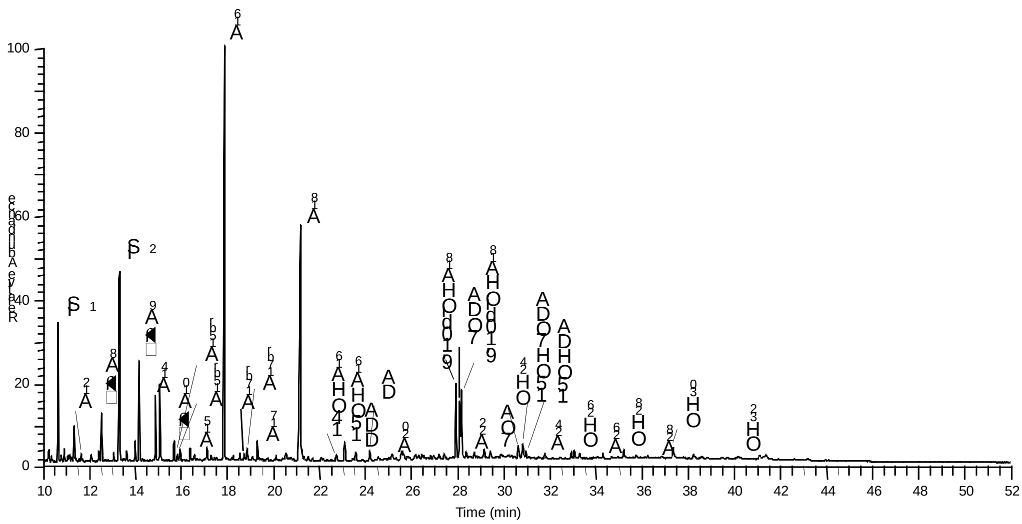

Fig. 2. TIC chromatogram of the trimethylsilylated acid fraction of the sample collected from the beaker. A_X are monocarboxylic fatty acids of chain length x; $\alpha\omega A_X$ are dicarboxylic fatty acids of chain length x OHx are *n*-alkanols of chain length x; $XOHA_X$ are hydroxy fatty acids of chain length x and with hydroxy group at position X; $9,10OHA_{18}$ are 9,10-dihydroxyoctadecanoic acids; DDA is didehydroabietic acid; DA is dehydroabietic acid; 7ODA is 7-oxo-dehydroabietic acid; 7OA is 7-oxo-abietic acid; 15OH7ODA is 15-hydroxy-7-oxo-dehydroabietic acid; 15OHDA is 15-hydroxydehydroabietic acid; IS_1 and IS_2 are the tridecanoic acid and *n*-hexadecane internal standards

Acyl-lipids were identified due to the presence of di-carboxylic fatty acids (C_8, C_9 and C_{10}), the high abundance of stearic acid ($C_{18:0}$) along with 9,10-dihydroxyoctadecanoic acids (*threo* and *erythro* isomers). Di-carboxylic fatty acids, mainly azelaic acid (C_9), and 9,10-dihydroxyoctadecanoic acids are known to be formed from the oxidation of oleic acid and therefore their presence can be correlated to the high level of oleic acid in the original acyl lipid substances [1]. The presence of linear and branched monocarboxylic fatty acids with 15 and 17 carbon atoms suggests an animal origin: these acids are known to be formed in the gut by bacteria, and cab be related to the presence of to ruminant animal fats [16, 17, 20]. However, it is not possible to rule out that a mixture with lipids of vegetable origin, such as a plant oil, was used.

Conclusions

In conclusion, the chemical characterisation based on GC/MS analysis used in this study, enabled us to reveal the nature of the residues found in the ceramic beaker from tomb M.I.D.A.N. 05 discovered in the Theban Necropolis (Egypt). The analysis showed that the organic residue recovered from the beaker was made up of Pinaceae resin, beeswax and a fatty material. This suggests that they were residues from the preparation of a balm or of an offering, confirming that the vessel was used in connection with mummification practises. The use of Pinaceae resin is documented in antiquity as a ritual balm due to its antiseptic and odoriferous properties. In the literature it is reported that the principal resin-producing Pinaceae trees were not present in Egypt and it is probable that these kinds of resins were imported from East and North Mediterranean coasts [6]. Fatty and oily substances and beeswax were identified as ingredients of mummification balms and could have been used in daily life as well as during religious ceremonies [5, 16, 17]. Information on the use of these substances during mummification practises can also be found in two papyri: the first stored in the Louvre (Pap. Louvre 5.158), and the second found in Thebes [21], a Roman copy of more ancient embalming rituals. Oils, fats and resins were used in a particular ceremony, called “the Opening of the mouth” practised after mummification. The priest used special substances called “seven canonical oils”. One of these, the Best oil of Pine (Hat(t) nt aS), was made from pine resin probably used to sprinkle on the face [22].

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