Archaeological residues analysis applied to 5th- 4th century BC. Perfume containers (Attic lekythoi) from Kition (Cyprus)

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Abstract

This work presents the chemical analysis of organic residues extracted from archaeological samples: four completely preserved ceramic vases, discovered in a funeral context in Kition (Cyprus); Attic lekythoi, produced in Athens during the 5th and 4th centuries, exported to Kition and used in funeral rituals. The aim of our study was to determine the use and the function of these Attic vases taking part within the framework of Phoenician local customs. The invisible impregnations let by the original content in the inner sides of the ceramics have been analysed by gas chromatography-mass spectrometry (GC-MS). This analytical approach is of great archaeological significance because it helps discovering the contain and use of vases. Our study succeeds in identifying the presence of unguents in two of the vases, composed of *Styrax* and *Pinus Pinaster* and of dairy product (milk, cream, butter) and oil in the two others. We aim to discuss the use of imported vessels from Greece in a different cultural environment.

Keywords – 3-7

Chemical analysis, organic residues, Attic lekythoi, Phoenician customs, Cyprus, *Styrax*, *Pinus Pinaster*.

1. Introduction

The durability of ceramics in the archaeological record provides the archaeologist with abundant material for the study of human activities and the organic material contained in ceramics represents an essential evidence for the vessel use. Analysis and interpretation of organic residues contained in pottery are not recent, because C. Renfrew already insisted on the need for such approaches, in 1977 and the more advanced Anglo-Saxon researches highlight the necessity for such approaches to be centred on precise issues concerning human behaviour (Renfrew, 1977). Nowadays, thanks to the progress in analytical chemistry and archaeologists' interest in these approaches, we can proceed to analyze organic residues contained in ancient ceramics, and thus get acquainted with the container's content and obtain direct knowledge of their use (Garnier, 2012; Frère and Hugot, 2012; research programs ANR Perhamo and MAGI, France). Yet, our pioneer analyses applied to ceramics found in Phoenician context of the Persian period bring a new light e about the production and use of perfumes. No study of this type has been conducted on imported vessels found in Phoenician cultural environment.

The principle aim of this paper is to answer a specific archaeological question: determine the use and function of Attic vases taking part within the framework of Phoenician local customs. Samples taken from these vases has been analyzed by gas chromatography, and identified by mass spectrometry. We have carried out a study on four completely preserved ceramic vases (Attic lekythoi, produced in Athens in the 5th and 4th centuries), and discovered in funeral context in Kition (Cyprus).

2. Methods

2.1. Analyzing technique used

Samples from vases have been obtained by scratching the inside walls (samples are produced by the author Iva Chirpanlieva). These powdered samples have been analyzed by Garnier Laboratory (France): the powder has been extracted by ultrasounds by a mixture 1:1 dichloromethane/methanol (Charters *et al.*, 1995). After evaporation under a gentle flux of nitrogen, the solid extract is derivated by BSTFA in the presence of pyridine (80°C, 30 min), evaporated to dryness, and reconstituted in dichloromethane (10 µL). 1 µL was injected *splitless* at 280°C onto a 20 m × 0.18 mm internal diameter × 0.1 µm film thickness Phenomenex Zebron-5MSi of a Thermo GC Trace coupled with a DSQ II mass spectrometer. The oven temperature was held at

50°C for 8 min, then programmed to increase at 10°C/min to 350°C and then hold for 7 min, for a total run time of 45 min. The transfer line to the mass spectrometer was at 300°C, and the source of the spectrometer heated at 200°C. The range 50-800 amu is scanned at 7500 amu/s. The compounds were identified according to their mass spectrum recorded in electronic impact mode (70 eV), by comparison with the NIST and Wiley libraries and by studying the fragmentation mechanisms for butylated compounds.

The powder, already extracted, was mixed with a solution of potassium hydroxide in methanol (0.5 M, 5 mL, 80 °C, 2 h) in order to study the unsaponifiable and polymerized fraction. The reaction mixture is the cooled, neutralized by the addition or hydrochloric acid (6 M), and extracted three time by dichloromethane. The organic phases are gathered, washed by MilliQ water, and dried over magnesium sulfate. The purified saponified extract is derivated as before by BSTFA and pyridine. After evaporation to dryness, the residue is reconstituted in dichloromethane (50 µL), and analysed by GC-MS according the method described supra.

3. Data and Results

The GC-MS analysis of the lipidic and the saponified extracts reveals the presence of complex mixtures. Unfortunaltely, as the material has been stored in museum for a long time and already restored, the main markers come from synthetic and modern pollutions. However, the precise study of chromatograms allows the identification of the preserved biomarkers, and the biological materials. For each sample, an analytical record presents the chromatograms, the preserved markers identification and their interpretation[1].

3.1. Samples and results

Sample N°1: MLA 1444, T4/5, 1981, Attic black-figured lekythos, Beldam Painter, dated back to 500-450 BC., Larnaca museum, Cyprus (fig. 1; fig. 2). The vase presents a huge contamination by phtallates, mainly as octyl, decyl, and isodecyl diesters (DIDP), common plasticizers used for the production of plastic bags. Traces of odd- and even-numbered, linear and branched fatty acids are associated to cholesterol. The latter indicates an animal origin, and the large distribution (6:0 to 18:0) orientates to dairy products. The distribution of fatty acids liberated by saponification is equivalent, and confirm the presence of linear and

[1] Modern pollution by plastic tools is noticed, probably linked to the vases' restoration or their preservation. However, it doesn't hinder the analyze of the content and we disregard it in the analyze.

ramified of-numbered fatty acids. No other markers are detected in both extracts, indicating that the lekythos would have contained a dairy product, without further adjuvant.

Sample n°2: CD6294, Attic red-figured lekythos, Painter of Achilles, dated back to 440-430 BC., Nicosia museum, Cyprus (fig. 3; fig. 4). The vase is strongly contaminated by plastics (phtallates, DIPDP), and also sugars, mono- and major disaccharides. The main markers, sucrose and mycose, are considered as environmental pollutions, coming from the soil, more precisely from fungi and bacteria (Rogge et al. 2007). The fatty acids profile consists in odd- and even-numbered, linear and branched, fatty acids, with a broad range (10:0 to 18:0). Their association to cholesterol would traduce a dairy product. The absence of phytosterols, and specially sistosterol, allows to discard plant oils. The association of phenolic acid (benzoic acid, vanillic acid, 3,4,5-trimethoxyhydrocinnamic acid) could reveal traces of an aromatic vegetal substance such as a balsam. However, in the absence of specific marker, the nature of this substance could not be better specified. Also, dehydroabietic present in the both extracts reveals a resinous material from coniferous species. A very few amount of dehydroabietic methyl ester, indicates resine.

Sample n°3: MLA 1230, CS2488, Attic red-figured lekythos, dated back to 425-375 BC., Larnaca museum, Cyprus (fig. 5; fig. 6). The vase present, besides the plastic pollutions, a very large distribution of odd- and even-numbered, linear and branched fatty acids (5:0 to 17:0), associated with phytanol and cholesterol. Few amounts of campesterol, stigmasterol, and sitosterol indicates a vegetal oil.

Sample n°4: MLA 1613, 1992, T1/1, Attic black galzed patterned lekythos, *ca* 425 BC., Larnaca museum, Cyprus (fig. 7; fig. 8). Mainly shows plasticizer markers (phtallates, monoglycerides, 2,2-bis-(4-hydroxyphenyl)propane, bisoflex, etc.), but also odd- and even-numbered, linear and branched fatty acid (6:0 - 18:0), associated to cholesterol. A tiny trace of dehydroabietic acid, present as free and in methylated form, indicates a coniferous resine. A trace a p-coumaric could come from a vegetal substance like a balsam, but also plasticizers. As plastic pollutions are very important in this sample, no interpretation can be seriously proposed for this marker, in the absence of other phenolic acids. It may have contained *Pinaceae*'s resin, as well as some cinnamon acid's by-product. We can say its content is similar to the one of CS6294 vase (sample 2).

3.2. Interpretation

According the high degree of pollution from plasticizers, the interpretation of preserved biomarkers is difficult. Nevertheless, the profiles of fatty acids associated with cholesterol indicates the presence of dairy products in all four objects, as milk, butter, or cream.

Vases that may have contained one or more fats:

Sample 1 – a dairy product (milk, cream, butter).

Sample 3 – it has obviously contained a dairy product, as well as some oil whose highly oxidized traces have been detected.

Vases that may have contained one or more fats, as well as some aromatic components:

Sample 2: the vase contains dairy product stuff, some pine resin (oxidized over the time, but which has not been used as pitch, which was meant to make vases waterproof), as well as a product containing some benzoic, vanilla, cinnamon and trimethoxy hydroxycinnamic. The resin containing these four components present in this geographic area is the *Styrax* resin, more precisely the *Styrax officinalis* resin.

Sample 4 – According to the same methodology of interpretation, we can come to the conclusion that the vase has contained some non-ruminant animal's fat, pine resin and styrax resin.

3.3. Origin of the components found in sample 2 and sample 4:

Dehydroabietic acid

This is an oxidized form (previous to the formation of acid 7-oxodehydroabietic) of the Asiatic acid, typical for the resin (resin also called colophony) which exudes naturally from *Pinus pinaster* trunks, which grows around the Mediterranean sea. Usually, pine resin was used in the form of pitch (tarry resin obtained when wood is heated slowly) in order to make vases waterproof, but in this case, we speculate that the resin wasn't used in such a form, but for its olfactory properties.

Organic aromatic acids: benzoic, vanilla, cinnamon and hydroxycinnamic: the styrax is the one to contain all of these organic acids and the aromatic (in the olfactory sense of the word) present in the vase CS6294 (sample 2).

The vase (sample 4) only contains a small quantity of derived cinnamon acid, which could mean that there has been a cinnamon's addition. But in terms of geographical layout this

hypothesis isn't acceptable. We would rather think that other acids that come from *Styrax* are in amounts which are too low to have been detected.

Origins of these perfumes:

Botanical species whose extracts have been identified in the vases are proper to the Eastern Mediterranean. Maritime pine (*Pinus pinaster)* or cluster pine (Pinaceae's family) is a conifer of the *Pinaceae* family. This tree is common on the Mediterranean coasts. The *Styrax* is a plant (a winding shrub from 2 to 4m high) from the Mediterranean areas, which can be seen in its natural state in the Middle East, on the oriental Mediterranean coasts, in Cyprus, in Rhodes, in continental Greece and in Italy .

Thanks to Archaeobotany /Paleoethnobotany (identification of aromatic sources present in the surrounding area) and chemical analysis of the residues, E. Dodinet shows that these two species are used in perfume production in the East during the Bronze Age (Dodinet, 2008). It comes from an essentially resinous olfactory universe, with spicy notes from the Levant sometimes. Styrax is also present in Assyriological dictionaries. It's of interest to notice that the same species are still chosen during the Persian period.

In Greece, the analysis of some Attic lekythoi dated back to the 6th century, show that they have contained a flavoured olive oil. In a general way, myrrh, *Styrax*, iris, cardamom, rose, etc. have been used too (Touzé, 2008).

3.4. Interpretation concerning the functionality of the different components

It is possible to think that these flavoured oils have been produced in the same way perfumes are produced nowadays, which is done in a simplified way. Modern perfume is composed of head notes (the first ones to be perceived), of heart notes (we perceive them some seconds later), and a base note (we perceive it some hours later) as well as of a solvent whose function is to allow to apply and spread the perfume on the body. Perfume found in vases' samples 2 and 4 may obey to that principle, with the presence of fat, whose function was possibly to dilute the set, as well as to extract resins from the aromatic components. Pine resin used to bring the head and heart notes (woody and resin notes). Styrax's function was to add the base notes (soft, vanilla flavoured and ambergris smelling notes). Fatty substance was needed for the extraction or the fluidizing of the used resins, which are originally solids. Perfumed mixtures contained in these vases were the product of a simple technology, leading to a well formulated perfume, with a head note, a heart note and a base note on a fat base. The small

opening of the vases suggests that the perfumed balm was more or less liquid, in order to be extracted from the vase.

4. Discussion

During the Iron Age and the Persian period, production and consumption of perfumed oils were common in all the Eastern Mediterranean and there was a long-standing ancient tradition of production and use of perfumes in the Orient (Egypt, Mesopotamia, Levant and Cyprus). Researches have been focused on perfume production and their containers, rather than the matter of using them.

4.1. Perfume in Phoenician cultural context

At this point of the analysis, we must consider the fragmentary character of the documentation on the Phoenician's customs and cultural practices compared to the Egyptians' one. According to literary and epigraphic sources, myrrh (*commiphora* species) was used in Ugarit (during the Bronze Age) (*KTU* 1.41, 20; 1.87, 22; 4. 14, 2.8.15; 4. 91, 16; 6.44, 2.), attested in Phoenicia from where it reached the Greek areas and in a Cyprus sanctuary there were incensed altars with incenses *olibanum* species (Lipinski, 1995). From what Pline wrote, *olibamun* was imported by Tyrians from Southern Arabia to Greece (Pline, *Histoire naturelle* XII, 30,54). In Carthage, a fragmentary ritual proves incense was used in official worship (*CIS* I, 166 ; *KAI* 76, B. 3. 6). These sources certify the use of perfumes in sanctuaries and it is established also thanks to the presence of incense burners (*thymiateria*), and little lekythoi. The Phoenician civilization was familiar with incense's religious use for worship, and the incense burners are present in sanctuaries as well as on steles. Even so, perfumes have multiple uses in sanctuaries: they can be used during sacrifice rites, for libations, to coat worship statues in order to strengthen the sensory image of God, but also during celebrations.
In contrast, the perfume use in funeral customs is not that much known in the Phoenician world and the funeral vases' content remains the main key to understand the funeral rites. Archaeological data show that in Phoenician-Punic funeral assemblages exist perfume containers: as an example the mushroom type vases, often present in Phoenician's graves (as many in Kition as in Lebanon and Israël), they are used as perfume containers, but as well glass vases such as alabastra or small glass perfume bottles. In the area of Sidon, we also find raised vases against the graves wall that are perfume phials (Doumet, 1996). We must add to

this lot the imported perfume vases such as Egyptian alabastra. We have noticed the low amounts of Corinthian ceramics in the site of Kition and the total absence thus far of Corinthian aryballos in the graves has to be underlined, but it is mainly a question of market, as importations in the Orient come essentially from East Greece: we have two examples in Kition – an amphoriskos of the Fikellura style and a plastic vase, both designed for perfume (Chirpanlieva, 2013). Attic lekythoi also found in Phoenicians' graves must be added to this list, as here we have the proof they have been used as perfume containers. Iconographic sources are also testament to the perfume presence in the funeral rites. Perfume offering is shown on Carthage *stelae*: flasks, *thymiateria* and other incense burners (Lipinski, 1995; *CIS* I, 256; 1242; 1271; 1282; 1288 etc.).

But beyond the perfume's offering function can we understand the symbolism of these offered to the dead perfumes?

On some anthropoid sarcophagus, we find representations of the deceased person holding a flower or an alabastron. Cl. Doumet read these as symbols of immortality reflected to what we know of Egyptian world (Doumet, 1996). Let us remind that in the myth of Horus, the perfumed oil that he coats Osiris was to bring him back to life. Perfumed oil has clearly a regenerative role; we also find this idea in Egyptian funeral rites. Yet, can we admit that perfume symbolized immortality in the Phoenician cultural context? In her P.h.D. Iva Chirpanlieva have demonstrated that Œdipe's and Sphinx's scenes on the lekythos analyzed here (sample 2) was certainly symbolising the belief in immortality (Chirpanlieva, 2013). Yet this vase was possibly filled with pine and *Styrax* perfume. In this case, can we deduce that the contained perfume in this vase had the same function as the picture, that is to say provide the dead's immortality.

Perfumes have clearly a sacred vocation, but we can also observe a daily and personal use, still difficult to precise, but we have archaeological testimonies in the habitat of Tell Arqa and in Dor where was found even an Attic white-ground lekythos.

Perfumes that have filled these Attic lekythoi were most likely a local production, as components were present in the natural environment and in the oriental traditional production of perfume. These Athenian lekythoi reinstate into an offering Phoenician's system (such as the Egyptian perfume vases) and the Attic lekythos is doubtless a prestigious offering as a perfume vase.

It is not possible to know if the people of Kition imported Greek perfumes in the lekythoi because we have little in the primary context (such as shipwrecks). However, we know it's from Arabia that were imported exotic products such as spices and perfumes.

5. Conclusions

Our study allowed defining the use of Attic lekythoi in Phoenician funeral customs as containers of perfume. At least for two of the vases we could tentatively characterize the contain - pine and *Styrax* perfume. It is probably the vase itself that is imported as a luxury product reserved for perfume use. This observation is valid for the great quantity of lekythoi found all around the Levantine coast during the Persian period.

In the general context where these trade phenomenon are developed is a considerably urbanized Mediterranean, in particularly the Phoenician's sites of the Levantine coast. This urban development comes out as a new space management, a denser population on the coast; it comes with the economics opening, an increase in wealth and affluence in the Phoenician's harbors. Hence, this is about an environment characterized by customs of ostentatious consumption of luxury products in the urban centres in the Eastern Mediterranean – wine, perfumed oils, prestigious table sets, imported perfume vases (Foxhall, 2005).

In an effort to address this problem, the potential for a systematic study of a large assemblage is welcome in future research.

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Appendices

Figures

Fig. 1. Photography of the vase MLA 1444, T4/5, 1981, Attic black-figured lekythos (author Iva Chirpanlieva).

Fig. 2. Results of the analysis of vase MLA 1444, T4/5, 1981 (author Nicolas Garnier).

Fig. 3. Photography of the vase CD6294, Attic red-figured lekythos (author Iva Chirpanlieva).

Fig. 4. Results of the analysis of vase CD6294 (author Nicolas Garnier).

Fig. 5. Photography of the vase MLA 1230, CS2488, Attic red-figured lekythos (author Iva Chirpanlieva).

Fig. 6. Results of the analysis of vase MLA 1230, CS2488 (author Nicolas Garnier).

Fig. 7. Photography of the vase MLA 1613, 1992, T1/1, Attic black galzed patterned lekythos (author Iva Chirpanlieva).

Fig. 8. Results of the analysis of vase MLA 1613, 1992, T1/1 (author Nicolas Garnier).

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