

Organic residue analysis in archaeological pottery. Heating markers in non-cooking vessels from Etruscan Tarquinia (Italy): a sampling problem?

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Abstract

The organic residues in the material of a series of pottery vessels from a votive deposit (3rd - 2nd century B.C.) in the excavations of the Etruscan city of Tarquinia (Italy) were analyzed by gas chromatography – mass spectrometry (GC-MS). Long-chain (31, 33 and 35 carbon atoms) ketones were initially detected in the lipid extracts of all the ceramic samples examined, irrespectively of the characteristics of the vessels in terms of shape and texture and of the possibility they had been used for cooking, recognized in several studies as the main cause of the formation of these compounds. Considering that some cases have also been reported in the literature in which the presence of these ketones seemed unexpected for a given ceramic container, it was decided to examine the possible correlation of their occurrence, for the set of vessels examined in the present work, with the sampling mode used to obtain the ceramic powder before extraction with solvents for the recovery of the organic residue. It was thus possible to demonstrate that the use of a drill for sampling, a modality not unusual in this kind of study, can give rise to the formation of these compounds in an archaeological ceramic material in which fatty acids are absorbed, particularly if it contains calcium carbonate, as demonstrated by X-ray diffraction (XRD) analysis of the examined pottery fragments.

A laboratory experiment based on a fragment of modern pottery in which palmitic and stearic acids were absorbed from a solution, and from which powder samples were then obtained both by drilling and by manual scraping of the pottery surface, allowed to validate the hypothesis above. It was therefore possible to highlight the importance of careful consideration also of the sampling phase in interpreting the results of the analysis of organic residues in archaeological pottery.

Keywords

Organic residue analysis; archaeological pottery; gas chromatography – mass spectrometry; sampling; long-chain ketones.

1. Introduction

In the last three decades, organic residue analysis has acquired an ever increasing importance as a tool to clarify the function or intended use of an archaeological artefact, or even the activity carried out in a given archaeological context. In this framework, pottery undoubtedly represents the class of archaeological materials with which organic residues are most commonly associated, even if predominantly in the form of traces of absorbed substances invisible to the naked eye.

Among such substances, lipids (including fats, waxes and resins) are considered potentially better preserved, than, for example, carbohydrates and proteins, above all thanks to their hydrophobicity, which limits losses due to percolation water and microbial attack (Evershed, 2008). However, altered chemical structures can also be observed for lipids, originating from burial conditions, as in the case of free fatty acids (*n*-alkanoic) deriving from the hydrolysis of triacylglycerols, but also linked to the original transformation of the material for its use (Evershed, 2008). This is the case, for example, of terpenes resulting from abietic acid in heating pine wood for waterproofing (Evershed et al., 1985), or of ω -(*o*-alkylphenyl)alkanoic acids formed from unsaturated fatty acids when heated above 270°C and therefore associated with the processing of products of marine animal origin or other foods containing these acids (Evershed et al. 2008a).

A peculiar group of compounds possibly attributed to the thermal transformation of lipid substances is represented by long-chain ketones, typically with an odd number of carbon atoms between 31 and 35. Although these compounds can also be found in the epicuticular waxes of higher plants, it has been shown that they can result from the pyrolysis of free fatty acids or triacylglycerols at temperatures of 300 °C or greater in the presence of a fired clay matrix (Evershed et al., 1995; Raven et al., 1997). The reaction is a condensation between two fatty acid moieties, accompanied by free radical-induced dehydration and decarboxylation. According to this reaction, a C₃₁ ketone with the

carbonyl group at position 16 (hentriacontan-16-one) is obtained from two molecules of palmitic (C_{16}) acid, a C_{33} ketone with the carbonyl group at position 16 (trtriacontan-16-one) from a molecule of palmitic and one of stearic (C_{18}) acid and a C_{35} ketone with the carbonyl group at position 18 (pentatriacontane-18-one) from two molecules of stearic acid. Laboratory experiments and analytical results on archaeological vessels have shown a characteristic 1:2:1 distribution of the three compounds, with the ketone having 33 carbon atoms being the predominant one (Evershed et al., 1995; Raven et al., 1997). Since their first observation and experimental reproduction of their formation in the laboratory, these long-chain ketones have been recurrently detected in lipid extracts of ceramic material and/or surface residues in archaeological pottery and used as markers of repeated heating of vessels during their use (see for example: Dudd et al., 1999; Evershed et al., 2008b; Salque et al., 2013; Nieuwenhuyse et al., 2015; Carrer et al., 2016; Poulain et al., 2016; Mayyas et al., 2017). It is interesting to note that, in some cases, these characteristic compounds have also been recognized in the organic residues of containers whose shape and thermal properties suggested that they could not be used for cooking (Matlova et al., 2017; Rageot et al., 2019). The hypothesis of post-firing treatment of the hot surface of vessels with animal fats for waterproofing has been advanced (Matlova et al., 2017) and experimentally reproduced (Drieu et al., 2020a) as a possible explanation of the above observation.

In this short communication, the problem of interpreting the presence of long-chain ketones in the lipid extracts of archeological pottery will be examined with reference to a set of ceramic fragments from the excavation of the so-called ‘monumental complex’ of the Etruscan city of Tarquinia, located in central Italy (province of Viterbo) near the Tyrrhenian coast. The archaeological site of Tarquinia includes, in addition to the Monterozzi necropolis with the famous painted tombs, the excavation of the ancient city on the Civita plateau with the remains of a temple, called the Ara della Regina, and of the sacred area of the “monumental complex” itself (Figure 1).

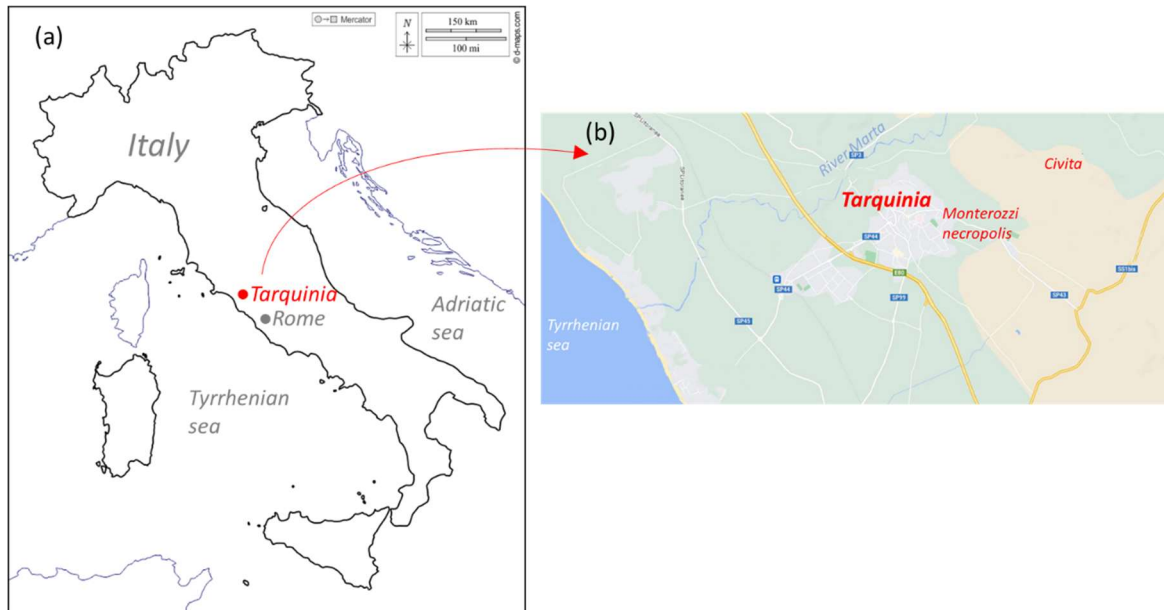


Fig. 1. (a) The location of Tarquinia in the Italian peninsula and (b) a detailed view of the relative locations of the modern city, the necropolis area, and the Civita plateau.

The origin of the settlement can be traced back to the 10th century B.C. and its continuity is documented up to the Roman and Medieval time (Bagnasco Gianni et al., 2018). The ceramic sherds examined belong to a single set of large portions of fragmentary vases, found in a votive deposit located in the upper part of a well in the north-eastern area of the excavation at the “monumental complex” and dated to the end of the 3rd – first half of the 2nd century B.C. (Bagnasco Gianni et al., 2018). Both coarse (*impasto*) and fine ceramic materials are included in the set. The lipid extracts from the sherds were analyzed by gas chromatography – mass spectrometry (GC-MS) and the communication will focus in particular on the effect on the analytical results of the sampling method adopted to obtain the ceramic powder suitable for the extraction. X-ray diffraction (XRD) was also used to evaluate the possible influence of the mineralogical composition of the ceramic material on these results. Finally, thermography was applied to monitor the local temperature of the ceramic surface during drilling sampling.

2. Materials and methods

2.1 Archaeological ceramic materials: types and discovery context

Archaeological research in Tarquinia was started in 1982 by Maria Bonghi Jovino, and now managed by Giovanna Bagnasco Gianni since, 2004. Moving from the initial 'Tarquinia Project', a Coordinated

Research Centre (C.R.C.) was created at the University of Milan in 2015: six Departments took part in it and support archaeological research from a naturalistic and I.T. perspectives, with the collaboration of colleagues from the Polytechnic University of Milan (Department of Architecture and Urban Studies). These collaborations were set to structure skills and contributions from the scientific disciplines applied to every aspect of the research. Research at the Department of Chemistry has made it possible to define the identity classification of local ceramic productions based on their chemical composition [Bruni et al., 2001] and is now developing, as a further step, the investigation of the organic residues in the vessels, in the context of which the data presented in this short communication were acquired.

The deposit where the fragmentary vases examined in the present study were found occupies the upper level of a well dug down to the water level at a depth of about 21.5 meters and had a ritual purpose (Bagnasco Gianni et al., 2018).

The nine sherds analyzed belong to vessels with different ceramic pastes, shapes and, most likely, intended use, as listed in Table 1. Four fragments came from *impasto* containers, including a basin (C977/1899) of an unusual shape with two funnels, a saucepan (C977/1277), a jug (C977/524) attributable to Iberian production of the Ampurias type, and an olla (C977/1155) very popular during the Hellenistic period in many contexts, for both funerary and everyday life use. (Figure 2). Another sherd belonged to a Phoenician-Punic amphora (C977/1950) of the Ramon Torres 7.3.1.1 type (Ramon Torres, 1995). Four other samples were instead taken from fragments of the walls of fine ware vessels.

Table 1

Ceramic samples from vases of the votive deposit of Civita di Tarquinia, analyzed for the organic residue in the present work. For each sample, the table reports a description of the corresponding vessel and the sampling mode(s) used to obtain the ceramic powder, the amount of the total lipid extract (TLE) based on the fatty acid content, the relative quantities of palmitic and stearic acids, the relative quantities of hentriacontan-16-one (K_{31}), tritriacontan-16-one (K_{33}) and pentatriacontane-18-one (K_{35}) and the ratio of palmitic acid to the sum of the three ketones, as estimated based on the corresponding chromatographic peak areas. Legend: n.d. = not detected.

Sample	Description of the vessel	Sampling mode	TLE ($\mu\text{g/g}$)	C_{16}/C_{18}	$K_{31} : K_{33} : K_{35}$	C_{16}
						$K_{31} + K_{33} + K_{35}$
C977/1899	basin, coarse ware, early 2 nd century B.C.	drilling	55	1.3	1 : 1 : 0.2	0.8
		manual scraping	48	1.2	n.d.	-
C977/1950	amphora, late 3 rd – first half 2 nd century B.C.	drilling	54	0.9	1 : 0.8 : 0.1	0.3
		manual scraping	124	1.1	n.d.	-

C977/524	Iberian (Ampurias) jug, coarse ware, early 2 nd century B.C.	drilling	290	1.3	1 : 0.6 : 0.1	4.7
C1161-7/10/10	fine ware vessel, fragment of a wall 6 th – 2 nd century B.C.	drilling	99	0.9	1 : 0.6 : 0.1	0.8
		manual scraping	186	1.1	n.d.	-
C977-21/09/10	fine ware vessel, fragment of a wall 6 th – 2 nd century B.C.	drilling	82	1.6	1 : 0.6 : 0.1	1.0
		manual scraping	199	0.9	n.d.	-
C1161-12/09/11	fine ware vessel, fragment of a wall 6 th – 2 nd century B.C.	drilling	100	1.4	1 : 0.5 : 0.2	1.6
C977-2/10/09	fine ware vessel, fragment of a wall 6 th – 2 nd century B.C.	drilling	90	1.8	1 : 0.8 : 0.1	0.6
C977/1277	pan with burning traces, coarse ware, 3 rd – 2 nd century B.C.	grinding	44	1.0	1 : 1.9 : 1	15.0
C977/1155	olla, coarse ware, late 4 th – mid 2 nd century B.C.	grinding	9	1.0	1 : 1.5 : 0.5	5.4

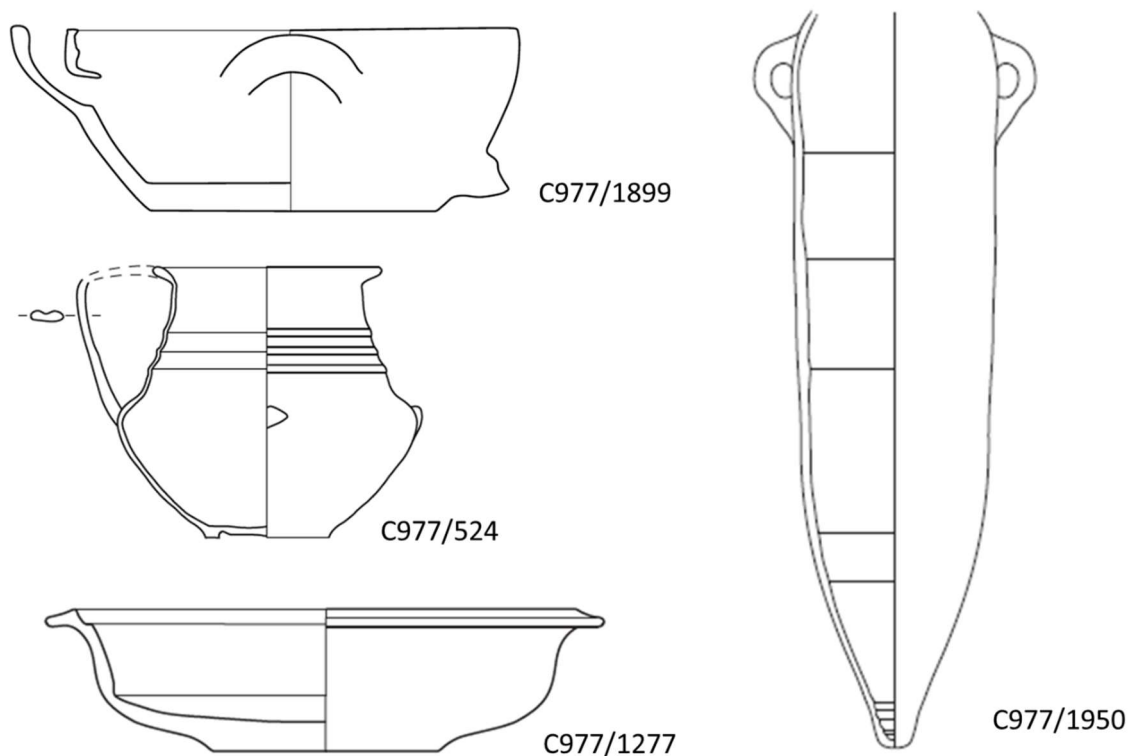


Fig. 2. Drawings of four of the nine vases of the votive deposit in the excavation of Civita di Tarquinia from which the samples analyzed in the present work were taken.

2.2 *Modern pottery replica*

A fragment of modern unglazed ceramic (Fornace Curti, Milano), weighing 28.9 g, was immersed in the minimum volume of a methanolic solution containing a quantity of a commercial mixture of palmitic acid (about 52% in weight) and stearic acid (47%) (Greenstearine 4906, Greenoleo, Italy) of about 100 µg per gram of ceramic material. After three days, the sherd has been extracted from the solution, rinsed with methanol and allowed to air dry.

2.3 *Sampling methods*

It should be noted that different sampling methods for the analysis of organic residues in archeological pottery are described in the literature. From a general point of view, all methods provide for the preventive removal of the surface layer, i.e., the ceramic part most likely contaminated by the burial environment, using a scalpel blade (as described for example in Evershed et al., 1990) or, now more frequently, a drill (e.g. a modeling drill with an abrasive bit as reported in Evershed et al., 2002).

Afterwards, in several procedures described in the literature, the sherd is ground in a mortar (see again Evershed et al., 2002), while in other cases the powder is obtained using a drill (see for example Craig et al., 2005; Rageot et al., 2019; Drieu et al., 2020a), sometimes referred to as a modeling drill and in other cases of an unspecified type. The latter approach is useful, for example, when a comparison has to be made between the internal and external surfaces of the ceramic vessel, in order to establish whether a given substance can be associated with soil contamination (e.g. in the case of tartaric acid as wine marker, as suggested by Drieu et al., 2020b) or to estimate the depth of penetration of organic substances into the ceramic wall (Drieu et al., 2020a).

In the present work, seven of the nine ceramic sherds from the votive deposit of the Civita were at first sampled using a drill equipped with a diamond tip (Table 1), after removing the surface layer with the same instrument to avoid contamination. The powder was taken from the part of the fragments corresponding to the internal face of each vessel.

After detecting a relevant quantity of ketones with 31, 33 and 35 carbon atoms in the lipid extract of all seven sherds (see Section 3.1), a subsequent experiment consisted in examining two other fragments, coming from vessels which could have reasonably been used for cooking, i.e., the saucepan and the coarse olla (Table 1). In these two cases, it was decided to obtain the ceramic powder by grinding the fragments in a mortar with pestle, after removing the surface layer by hand with the diamond tip.

Finally, as reported in Table 1, four of the first seven sherds examined were also sampled a second time, using the diamond tip by hand, on a part of the surface close to that previously sampled with the drill.

The modern ceramic sherd treated with the solution containing palmitic acid and stearic acid in mixture (Section 2.2) was sampled in three different ways: manually with the diamond tip; with a traditional drill equipped with the same tip and, finally, with a mini drill-equipped with a silicon carbide bit and operated at half speed.

2.4 Extraction of the lipid component

An amount of ceramic powder, obtained as described above, ranging from 0.5 to 1 g for each sample was extracted with chloroform/methanol 2:1 for 30 minutes in an ultrasonic bath, repeating the procedure twice. For each extraction, a volume of 1 to 2 mL of the mixed solvent was used. The extracts were recovered by centrifugation and, after being combined in a vial, they were dried under a gentle nitrogen flow.

2.5 GC-MS analysis

Prior to GC-MS analysis, tridecanoic acid was added to the extracts as an internal standard. The samples were then treated with 20 μL of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (Sigma Aldrich) under stirring at room temperature for 5 minutes. After addition of 200 μL of 2,2,4-trimethylpentane, the reaction was continued for 1 hour at 70 $^{\circ}\text{C}$, again under magnetic stirring.

GC-MS analyses were performed by a Thermo Fisher Trace 1300 GC connected to a Thermo Fisher Scientific ISQ QD single quadrupole mass spectrometer. The chromatograph was equipped with a DB-5MS capillary column (30 m \times 0.25 mm \times 0.25 μm) and the injector was operated in splitless mode. The temperature of the injector was 280 $^{\circ}\text{C}$. Helium was used as carrier gas. The temperature program of the oven was as follows: 60 $^{\circ}\text{C}$ for 1 min; 60 to 70 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$; 70 to 240 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$; 240 to 285 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$; 285 $^{\circ}\text{C}$ for 25 min. Mass spectra were acquired using electron ionization at 70 eV and obtained by scanning between m/z 50 and 100 in 0.2 s. The transfer line and the ion source were maintained at 300 $^{\circ}\text{C}$.

Peak integrations and identifications based on the comparison with mass spectra in NIST EI MS main library were performed by Thermo Xcalibur 4.0 software (Thermo Fisher Inc.).

2.6 X-ray powder diffraction

X-ray powder diffraction (XRPD) analysis was performed with a PANalytical X'PertPRO X-ray diffractometer using a Cu $K\alpha$ radiation source ($\lambda = 1.5418 \text{ \AA}$) and operated at 40 kV and 30 mA. The diffraction patterns were collected over the 5 $^{\circ}$ –65 $^{\circ}$ 2θ range at a step size of 0.02 $^{\circ}$.

2.7 Thermography

The local temperature of the ceramic surface during drilling was monitored using an AVIO TVS700 thermal camera, with 0.5 K thermal resolution at room temperature and 0.2 mm spatial resolution in the experimental conditions.

3. Results and discussion

3.1 Archaeological ceramic samples from the votive deposit of the Civita

As reported in Table 1, for all the seven ceramic vessels that were sampled by drilling, relevant amounts of hentriacontan-16-one (K_{31}), tritriacontan-16-one (K_{33}) and pentatriacontane-18-one (K_{35}) could be detected in the lipid extract by GC-MS. In this set of samples, the overall amount of the lipid extract ranged from about 50 to 300 μg per gram of ceramic material and the ratio between palmitic and stearic acid from 0.9 to 1.8 (Table 1). The ratio between the palmitic acid peak area to the sum of the three ketone peak areas was just 0.3 for the amphora C977/1950 and about 1 for the other samples, reaching a value of 4.7 only for the Iberian jug (Table 1). Figure 3a shows an example, referring to the fine ware vessel C1161-7/10/10, of the chromatograms obtained for the seven samples, where the characteristic fragments of the two most abundant fatty acids, palmitic (m/z 313) and stearic (m/z 341), and of the three ketones (m/z 255 and 267), besides that of the internal standard (m/z 271), were selected. An example of TIC chromatograms obtained for this set of samples is reported in Figure S1 (Supporting Information).

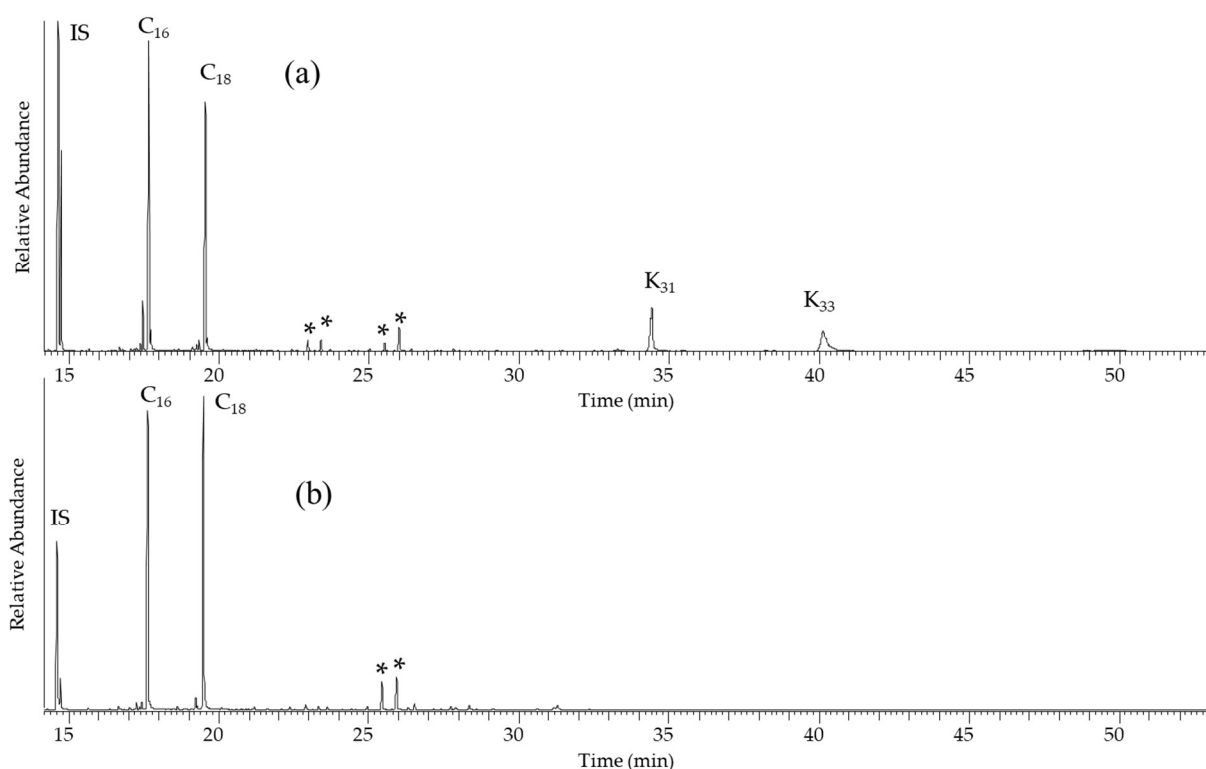


Fig. 3. Partial chromatograms (m/z 313, 341, 255, 267 and 271) of the lipid extract obtained from a sherd of the fine ware vessel C1161-7/10/10: (a) sampled by drilling; (b) sampled manually using the diamond tip. Legend: C₁₆ = palmitic acid; C₁₈ = stearic acid; K₃₁ = hentriacontan-16-one; K₃₃ = tritriacontan-16-one; K₃₅ = pentatriacontane-18-one; IS = internal standard; * = plasticizer.

It should be noted that in all cases the relative areas of the three long-chain ketones exhibited the pattern shown in Figure 3a and summarized numerically in Table 1, i.e., K₃₁ was the most abundant ketone, K₃₃ followed with an area of equal to one half and then K₃₅ was the less abundant with a peak area of about one-tenth.

The presence of a significant quantity of the asymmetric ketone K₃₃ have led to discard the hypothesis that these compounds may be associated with plant leaf waxes (Raven et al., 1997), but at the same time their possible formation as a consequence of repeated heating of the vessels during their use seemed unlikely. It should in fact be remembered that this group of objects included an amphora (C977/1950), an unusual basin with funnel openings (C977/1899) and a jug (C977/524), all containers whose intended use did not include heating and which, in any case, showed no traces of burns.

The analysis of the lipid extracts was thus performed for two more vessels from the same deposit, C977/1277 and C977/1155, which, unlike the previous ones, could actually have been used for cooking. This was particularly true for the pan C977/1277, that had also blackish traces of burning on one side. It should be remembered that the sherds from these two containers had not been sampled by drilling, but ground in a mortar as described in Section 2.3, according to the procedure suggested by Evershed et al., 2002. Interestingly, as shown in Figure 4 and reported in Table 1, the lipid extract of both samples, respectively of 44 and 9 µg/g, contained again the three ketones, but with a higher ratio of palmitic acid to their sum (15 for the pan and 5.4 for the olla) and with a pattern of the relative areas close to 1:2:1. As already mentioned in the Introduction, this is exactly the pattern reported in the literature for those cases in which the ketones derive from the heating of fatty acids in the presence of the clay matrix, both in archaeological pottery vessels and in laboratory replicas of the reaction (Evershed et al., 1995; Raven et al., 1997).

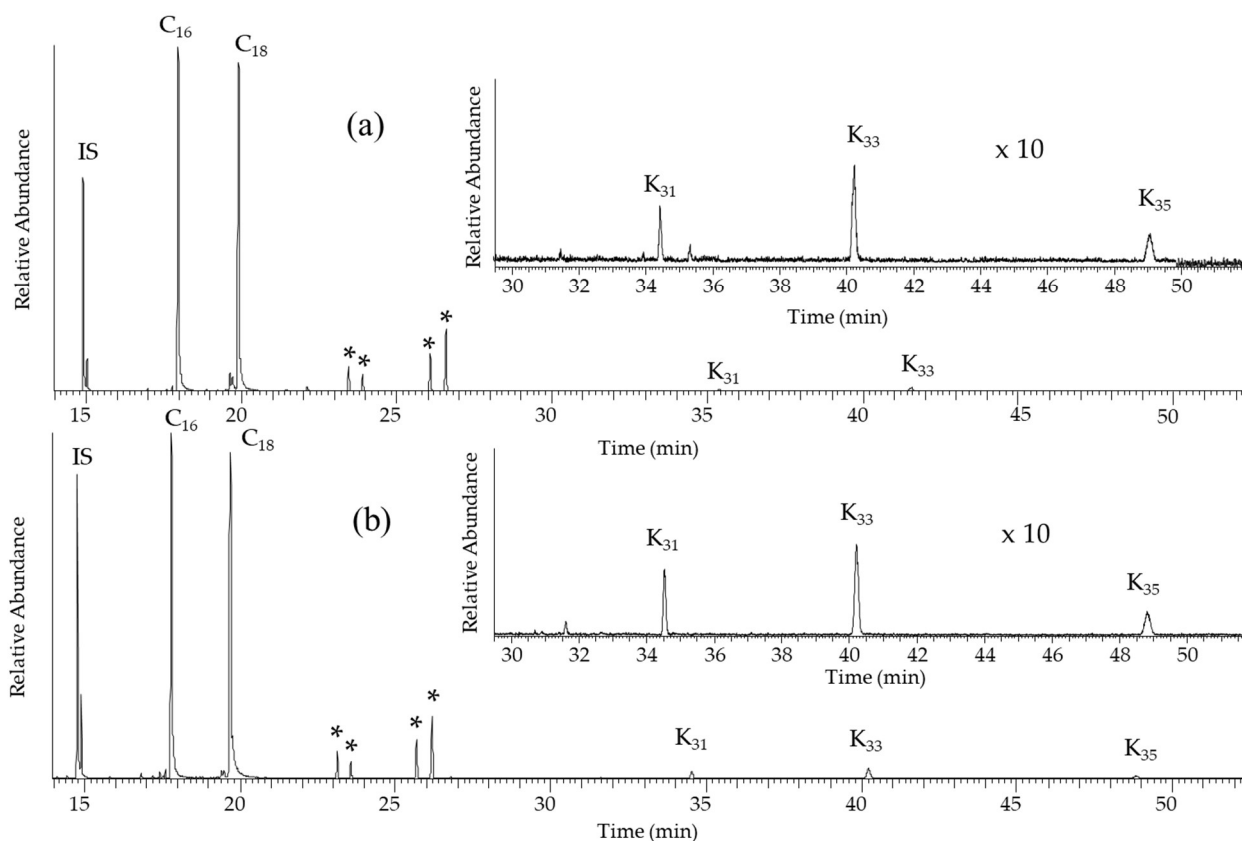


Fig. 4. Partial chromatograms (m/z 313, 341, 255, 267 and 271) of the lipid extract obtained from sherds of: (a) the pan C977/1277; (b) the olla C977/1155. The ceramic powder was obtained from both sherds by grinding them in a mortar. The inserts show the enlargements of the part of the chromatograms where the ketone peaks are found. Legend: C₁₆ = palmitic acid; C₁₈ = stearic acid; K₃₁ = hentriacontan-16-one; K₃₃ = tritriacontan-16-one; K₃₅ = pentatriacontane-18-one; IS = internal standard; * = plasticizer.

The observations described, i.e. the high relative quantity with respect to palmitic acid taken as reference and the different trend of the peak areas, have led to hypothesize that the sampling mode based on the use of a drill, an instrument that gives rise to local heating of the material, could be the cause of the presence of the long-chain ketones in the extracts of all those vessels of the votive deposit for which heating during use could be excluded.

For four of the first group of seven vessels, it was possible to make a second sampling from an area close to the one previously sampled by drilling, and this was done by scratching the pottery by hand with the diamond tip, to ensure that only the use of the drill had been removed from the experiment. The GC-MS analysis showed that the lipid extracts of these new samples did not contain the ketones (Table 1 and Figure 3b), thus demonstrating that they had been previously generated thanks to the local heating due to the use of a drill. Apparently, this condition seems to have favored the

decarboxylation of palmitic acid slightly more than that of stearic acid, yielding proportionally higher amounts of K₃₁ and K₃₃, i.e., those of the three ketones in which a C₁₆ moiety is present.

Interestingly, among these seven pottery samples, the highest relative amount of the long-chain ketones was obtained for the amphora C977/1950 and the lowest for the Ampurias jug C977/524 (Table 1), and the quantities detected for these samples did not generally correlate with the total amount of lipid extract. As it is known from the literature that the presence of calcium carbonate (or oxide) admixed with the fired clay favors the formation of the ketones (Evershed et al., 1995; Raven et al., 1997), the mineralogical composition of the seven pottery sherds was analyzed by XRPD. The diffraction patterns (Figure S2, Supporting Information) indeed showed a correlation between the amounts of ketones formed and the calcium carbonate content in the ceramic materials. In particular, calcium-containing phases were detected for all samples with the exception of the jug C977/524. Among these phases, calcium carbonate as calcite was present for most samples, and particularly abundant for the amphora C977/1950. In the case of the fine ware sherd C1161-12/09/11 diopside, gehlenite and anorthite were instead observed, presumably as a consequence of a higher firing temperature of the ceramic. For sample C977-21/09/10, lime was detected instead of calcite, from which it probably derived by decarbonation. In agreement with these mineralogical composition data, with the same sampling procedure the lowest relative quantity of the three ketones (ratio of palmitic acid to the sum of ketones equal to 4.7) was detected for the Iberian jug, in which material neither calcite nor other phases containing calcium are present. Conversely, for the Phoenician-Punic amphora calcite is the predominant phase containing calcium ions and in fact the highest relative amount of ketones has been measured (ratio value 0.3). The remaining pottery samples contain calcium carbonate (or lime) as well as phases formed upon firing of the ceramic above 900 °C, such as diopside and gehlenite, and in these cases calcite is probably of secondary origin (Heimann and Maggetti, 1981). For the latter samples, intermediate values (0.6 – 1.0) of the ratio of palmitic acid to the sum of the ketones could be determined, and a smaller quantity of ketones (corresponding to a greater ratio value of 1.6) is observed for sample C1161-12/09/11, which contains only calcium silicates but no carbonate.

The above set of experimental observations suggested that, in the samples here examined which had been obtained from the pottery vessels by drilling, the ketones with 31, 33 and 35 carbon atoms were formed during the sampling operation, and their formation was favored, as expected, for ceramic materials richer in calcium carbonate.

3.2 Modern pottery replica treated with the fatty acid solution

In order to corroborate the interpretation given for the archaeological samples, as described in Section 2.2 a fragment of unglazed modern pottery was immersed for 3 days in a solution containing comparable amounts of palmitic and stearic acids. Samples of ceramic powder were then taken from the fragment by manually scraping its surface with the diamond tip and either using a conventional drill equipped with the same tip or a modeling drill, operated at low speed and equipped with a silicon carbide bit. The first two methods are the same as previously applied to the first group of archeological sherds, while the latter method was tested because it was reported in the literature, and the intent was to verify whether it had a different effect from the point of view of the formation of the ketones compared to the use of the conventional drill.

As shown in Figure 5a, no traces of ketones were detected in the GC-MS analysis of the lipid extract of the powder taken by hand, for which the peaks due to palmitic and stearic acids were anyway well evident, for a total amount of about 60 μg per gram of ceramic material. For the sample of ceramic powder obtained with the modeling drill, it was instead possible to observe the incipient formation of K₃₁ and K₃₃ (Figure 5b). A similar result was obtained for the sample taken with the diamond tip mounted on the conventional drill, even if with lower quantities of the compounds of interest, in agreement with the fact that in the previous case it was possible to empirically appreciate a more significant local heating of the ceramic material and with the results of the thermographic analysis described below.

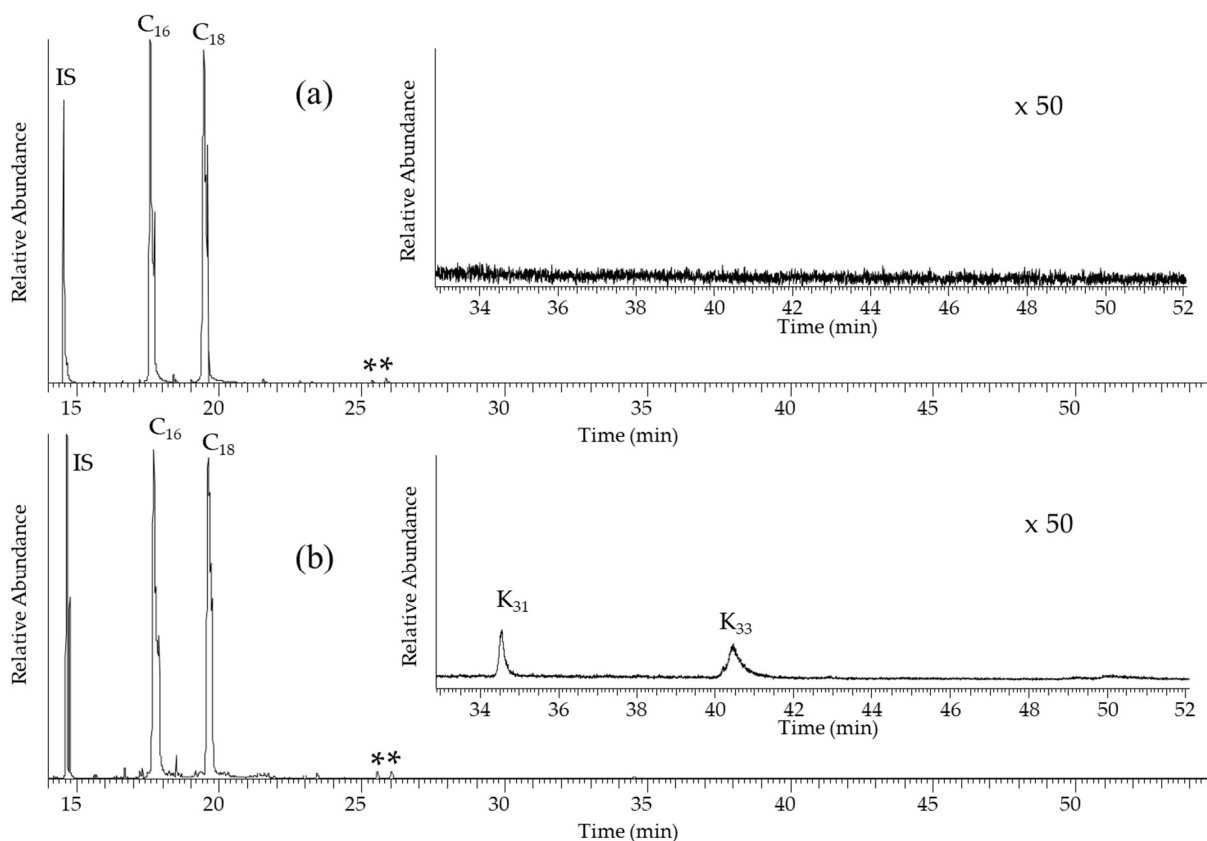


Fig. 5. Partial chromatograms (m/z 313, 341, 255, 267 and 271) of the lipid extracts from the fragment of modern pottery after immersion in a solution of palmitic and stearic acids about 1:1. For chromatogram (a), the ceramic powder was obtained by scraping the fragment manually with a diamond tip. For chromatogram (b), the powder was taken using a modeling drill with a silicon carbide tip. The inserts show the enlargements of the part of the chromatograms where the ketone peaks are located. Legend: C_{16} = palmitic acid; C_{18} = stearic acid; K_{31} = hentriacontan-16-one; K_{33} = tritriacontan-16-one; IS = internal standard; * = plasticizer.

As can be seen from the enlargement factor used in Figure 5b to highlight the ketone peaks, the quantity formed in this experiment is more limited than observed for archaeological pottery. This is not unexpected for various reasons. First, obviously the interaction with the matrix of the fatty acids absorbed from the solution in the modern ceramic material, probably only in the surface layer, was not as efficient as in the case of ancient vessels which have been in prolonged contact with lipid substances during their use. Consequently, the catalytic action of the fired clay was limited, even compared with the laboratory experiments carried out by directly mixing the ground clay fabric with the fatty acids themselves (Raven et al., 1997). Moreover, the modern ceramic material used in the present experiment, as a result of a firing temperature higher than 900 °C, did not contain calcium carbonate, but only the calcium silicate wollastonite and the aluminosilicate gehlenite (Figure S2, Supporting Information), thus further reducing the catalytic role of the matrix (Evershed et al., 1995).

Nevertheless, the experiment succeeded in demonstrating the possibility of the formation of ketones, particularly K₃₁, in the drilled ceramic material.

3.3 Thermographic estimate of local temperature during drilling

The local temperature of the ceramic surface during drilling (Figure S3, Supporting Information) was monitored by means of a high-resolution thermal camera.

The experiment was carried out on the archaeological ceramic C977/1950, drilled with the conventional drill equipped with the diamond tip or with the modeling drill with the silicon carbide bit. The highest temperature, up to 270 °C, was measured using the modeling drill, while lower values, around 50 °C, were detected using the conventional drill.

A further experiment was carried out on the modern ceramic fragment, drilled with the modeling drill with the silicon carbide tip. In this case the measured temperature reached 200 °C.

It is therefore evident that the recorded temperature differs greatly depending on the type of ceramic and drilling head. The modern pottery was in fact softer than coarse archaeological pottery, also rich in mineral inclusions, and this is another possible reason for the formation of lower amounts of ketones in the former. Furthermore, it should be highlighted that the frame acquisition rate and spatial resolution of the thermal camera may not allow recording temperature peaks higher than the above values, which therefore can be considered as average values over larger areas than those affected by the mechanical abrasion. When comparing the values recorded for the two drills, it should also be noted that the diamond tip had a diameter larger than 10 mm and could therefore partially occlude the view of the abrasion point.

4. Conclusions

The problem addressed in the present work was the abundant presence of long-chain ketones (with 31, 33 and 35 carbon atoms) in the lipid extracts of a series of archaeological pottery vessels from a votive deposit in the excavations of the Etruscan city of Tarquinia. The ceramic objects examined differed from each other in terms of shape, texture (coarse or fine) and intended use. Most of them were not suitable for cooking, nor did they show traces of burning, thus the presence of the ketones could not be associated with repeated heating of the vessels themselves. Only for two of them, a saucepan and an olla, could these compounds be related with their use, but in those cases their relative quantities, with respect to palmitic acid, were lower than in the other containers, and the areas of the corresponding chromatographic peaks followed the trend already described in the literature for long-

chain ketones resulting from prolonged heating of the vessels (Evershed et al., 1995; Raven et al., 1997). For the other pottery samples, it was demonstrated that the ketones originated from the use of a drill for sampling the ceramic powder before extraction, and their formation was particularly favored for those, among the materials examined, which contained calcium carbonate, as suggested again in the literature (Raven et al., 1997). A laboratory experiment was also conducted, based on the sampling with different methods of a fragment of modern pottery immersed for three days in a solution of palmitic and stearic acids. This experiment confirmed the onset of the formation of long-chain ketones when the ceramic powder was taken using a drill. The monitoring of the local temperature of the ceramic surface during drilling also evidenced a dependence on the specific tool used and on the physical characteristics of pottery. The use of an abrasive tip on coarse ceramic samples rich in inclusions appeared to be the situation where the highest average values could be observed, up to temperatures comparable with those reported in the literature (Evershed et al., 1995) for the formation of ketones from the condensation of long-chain carboxylic acids.

This study has highlighted that, although until now little discussed, also the first step of organic residue analysis in archaeological pottery, i.e. sampling, must be carefully considered in the interpretation of the analytical results.

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Figure captions

Fig. 1. (a) The location of Tarquinia in the Italian peninsula and (b) a detailed view of the relative locations of the modern city, the necropolis area, and the Civita plateau.

Fig. 2. Drawings of four of the nine vases of the votive deposit in the excavation of Civita di Tarquinia from which the samples analyzed in the present work were taken.

Fig. 3. Partial chromatograms (m/z 313, 341, 255, 267 and 271) of the lipid extract obtained from a sherd of the fine ware vessel C1161-7/10/10: (a) sampled by drilling; (b) sampled manually using the diamond tip. Legend: C₁₆ = palmitic acid; C₁₈ = stearic acid; K₃₁ = hentriacontan-16-one; K₃₃ = tritriacontan-16-one; K₃₅ = pentatriacontane-18-one; IS = internal standard; * = plasticizer.

Fig. 4. Partial chromatograms (m/z 313, 341, 255, 267 and 271) of the lipid extract obtained from sherds of: (a) the pan C977/1277; (b) the olla C977/1155. The ceramic powder was obtained from both sherds by grinding them in a mortar. The inserts show the enlargements of the part of the chromatograms where the ketone peaks are found. Legend: C₁₆ = palmitic acid; C₁₈ = stearic acid; K₃₁ = hentriacontan-16-one; K₃₃ = tritriacontan-16-one; K₃₅ = pentatriacontane-18-one; IS = internal standard; * = plasticizer.

Fig. 5. Partial chromatograms (m/z 313, 341, 255, 267 and 271) of the lipid extracts from the fragment of modern pottery after immersion in a solution of palmitic and stearic acids about 1:1 For chromatogram (a), the ceramic powder was obtained by scraping the fragment manually with a diamond tip. For chromatogram (b), the powder was taken using a modeling drill with a silicon carbide tip. The inserts show the enlargements of the part of the chromatograms where the ketone peaks are located. Legend: C₁₆ = palmitic acid; C₁₈ = stearic acid; K₃₁ = hentriacontan-16-one; K₃₃ = tritriacontan-16-one; IS = internal standard; * = plasticizer.