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INVESTIGATION INTO THE PRESERVATION OF LIPIDS IN POTTERY SAMPLES FROM TELL HALULA (SYRIA) USING THE ACIDIFIED METHANOL EXTRACTION AND GC-MS

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Los porcentajes de preservación de los análisis de residuos orgánicos en la producción cerámica más antigua del Próximo Oriente caen por debajo del 15%. Dados estos hechos, los objetivos de esta pequeña investigación se centran en realizar un test piloto que evalúe la validez de la extracción en metanol acidificado en muestras de un yacimiento Pre-Halaf (Tell Halula).

Palabras clave: Extracción en metanol acidificado, Tell Halula, Análisis de residuos orgánicos, Pre-Halaf.

Preservation ratios on organic residue analysis studies on the oldest pottery of the Middle East fall below 15%. Given these percentages, the aims of this small research are to conduct a pilot test that evaluates the appropriateness of the acid extraction on samples from a Pre-Halaf site (Tell Halula).

Keywords: Acidified methanol extraction, Tell Halula, Organic Residue Analysis, Pre-Halaf.

INTRODUCTION, AIMS AND OBJECTIVES

Tell Halula is a site located on the Syrian Euphrates valley. It conceals a settlement with a wide chronology that goes from the first phases of the pre-ceramic Neolithic (PPNB) to the ceramic periods (Halaf), in which the consolidation of the first agro-pastoral communities can be studied. Tell Halula is, therefore, a key site to understand the birth and development of the first uses of pottery in Neolithic societies (Molist/Vicente 2013) (Fig. 1).

One of the main methodological approaches to understand pottery use in prehistory is organic residue analysis. Although this technique has been established and practiced since the 90' (Evershed 1993) organic residue analysis has only been recently applied on pottery from the Middle East (Barnard *et al.* 2011, Evershed *et al.* 2008, Gregg *et al.* 2009, Gregg/Brettell/Stern 2007, Gregg/Slater 2010, Thissen *et al.* 2010). Such phenomenon is due to the low preservation that organic matter presents in arid zones such as Syria and Iraq. Research applying the standard Chloroform/Methanol extraction (Evershed/Heron/Goad 1990) has not been able to recover any significant quantities of lipids in 88% of the samples (Evershed *et al.* 2008) or in 97.5% of the samples (Gregg/Slater 2010). Given this limitation, up to 300 samples would be needed to obtain a statistically significant result of 30 detected residues. Because that the Chloroform/Methanol extraction usually needs 2g of pottery, a researcher must be willing to lose 540g of ar-

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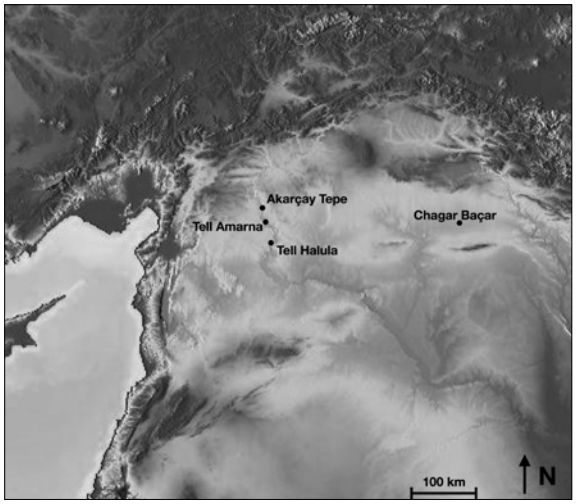

Figure 1. The location of Tell Halula relative to other relevant sites such as Akarçay Tepe, Tell Amarna and Chagar Baçar. Source: http://grupsderecerca.uab.cat/sappo/es/content/tell-halula.

chaeological material and cover the costs of an analysis 5 times more expensive than in other more humid and cold climates. These limitations motivated the development of new extraction methods with the objective to improve the lipid yields and, therefore, the number of positive results in samples from the Middle East.

To date, three new strategies have been published. The first one, the Microwave-assisted solvent extraction, modifies the standard extraction by using a microwave accelerated reaction system and 5g of sample. It has been able to improve the preservation rate up to 52% of positive results (Gregg/Slater 2010). The second one, an acid-base extraction, was initially used in the Mediterranean (Regert *et al.* 1998) and has also been applied with good results in Middle Eastern samples (Mayyas *et al.* 2013). The third one, the Acidified methanol extraction, only uses 1g of sample (Correa-Ascencio/Evershed 2014). The results of this last technique have not been published yet on pottery from the Middle East but its results in other areas of the planet seem promising. In Mesoamerica, where the preservation rate was around 2% with the Chloroform/Methanol extraction, 94% is achieved with Acidified Methanol (Correa-Ascencio/Evershed 2014). In the British Neolithic, the rate goes from 86% to 100% (Correa-Ascencio/Evershed 2014) and in the Canadian Palaeolithic the recovery rate reaches 82% (Taché/Craig 2015). This new technique has also been used to minimise to 0.1g the amount needed in samples with good preservation such as Jōmon pottery (Papakosta *et al.* 2015).

Therefore, given that the first pottery productions in the Near East have a significantly high archaeological value; it is necessary to test the Acidified Methanol extraction on them to evaluate the recovery rates and the result's interpretability.

MATERIALS AND METHODS

10 samples from sectors 1, 7 and 14 in the Pre-Halaf layers of Tell Halula were analysed. To account for possible morphological, technical and functional differences that could explain the presence of different residues, 6 rims and 4 bases were selected. 90% of the samples could be classified as *coarse ware* because of the presence of vegetal inclusions. Only sample 9, which presented significant mineral temper, could be classified as *fine ware* (Faura 2013). 30% of the samples presented a wall thickness between 0.8 and 1.1cm, 40% were between 1.1 and 1.29cm and 30% were between 1.3

Sample ID	TLE (µg/g)	Free Fatty Acid Range	Dicarboxylic acids	Other
1	16.7	C12:0, C14:0-C18:0, C16:1, C18:1, C18:2	Nonanedioic acid	
2	3.5	C15:0, C16:0, C18:0, C16:1, C18:1		
3	26.7	C15:0, C16:0, C18:0		
4	4.8	C15:0, C16:0, C18:0, C16:1, C18:1		
5	37.4	C12:0-C18:0	Nonanedioic acid	Citric acid
6	11.9	C12:0, C15:0, C16:0, C18:0, C16:1, C18:1		
7	17.7	C12:0, C14:0-C18:0, C16:1, C18:1		
8	24.7	C12:0, C14:0-C16:0, C18:0 C16:1	Nonanedioic acid	
9	31.7	C12:0, C14:0-C22:0, C16:1, C18:1	Nonanedioic acid	
10	12.4	C7:0-C12:0, C15:0, C16:0, C18:0	Nonanedioic acid	Monoterpenoid (Champhor)

Figure 2. Total Lipid Extracs of each sample with the relevant molecules detected.

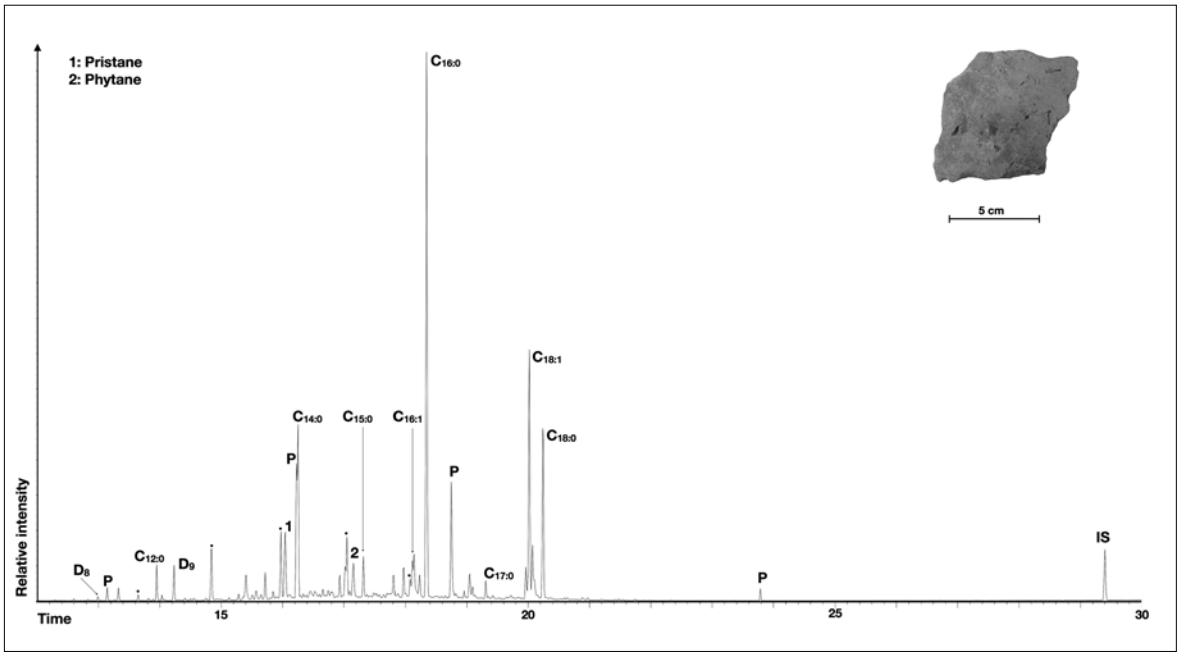

Figure 3. Chromatogram of sample 7. Cxx:x = fatty acids with its chain length and its degree of unsaturation. DX = Dicarboxilic acids and its chain length. • = alkanes, P = phthalate plasticiser, IS = Internal Standard (tetratriacontane).

and 1.5cm. The presence (40%) and absence (60%) of slip was also noted. The samples had been fired under an atmosphere with an irregular input of oxygen, which created areas with both oxidised and reduced colours. Two samples were completely oxidised and one (sample 6) seemed to be slightly overcooked. Finally, a broad density estimate of the material was calculated by weighing the samples and dividing it by its dimensions (surface times the thickness). Following these calculations, 30% of the sherds had a density between 1 to 1.3 g/cm^3, 40% were between 1.31 and 1.5 g/cm^3 and finally 30% of the samples were denser than 1.51 g/cm^3. The extractions of residues were performed on 1g of pottery from the inner wall of the vases. The outside surfaces, which present higher probability of contamination (Heron *et al.* 1993), were removed before drilling. 4ml of methanol were added to the sample and the mixture was ultrasonicated for 15 minutes and acidified with 0.8ml of concentrated sulphuric acid. The result was heated at 70ºC for 4 hours and then left to cool. Lipids were extracted 3 times by adding 2 ml of hexane, mixing under a vortex, leaving the sample to partition and extracting the hexane layer. The extracts were left on copper turnings overnight and then dried under a gentle stream of nitrogen. Finally, the samples were re-suspended in hexane and transferred to inlet vials, which had been prepared with 10µg of n-tetratriacontane as the internal standard.

Samples were analysed with a 7890A Agilient Technologies Gas Chromatograph (GC) and a 5975C Agilient Technologies Mass Spectrometer with a triple axis detector and Electric Ionisation (EI). Injection was done in splitless mode at a temperature of 300ºC and the analyses were performed on an Agilient HP-5MS 30m x 0.25mm x 0.25µm fused silica column with helium as the carrier gas. Oven temperature was set for an initial 2 minutes isothermal period at 50ºC. Afterwards, it ascended at 10ºC min^{-1} until it reached a maximum of 350ºC. Temperature, then, was held constant for the remaining 10 minutes of the analysis. The resultant eluted compounds were identified using its mass spectra and compared with a reference database (NIST 2.0).

Quantification of the samples was performed by calculating the peak area of each molecule and comparing it to the peak area of n-tetratriacontane, which corresponded to a known amount of 10µg. Nevertheless, this method of quantification does not to account for losses during the extraction process. For this reason, an extra sample composed of the main molecules found in organic residues (C16:0 and C18:0) with a known quantity of 100µg was run and quantified alongside the archaeological samples. The error detected in this sample has been used to correct the total lipid extract (TLE) values.

RESULTS

The Total Lipid Extracts (TLE) of each sample along with the presence of the most significant detected molecules

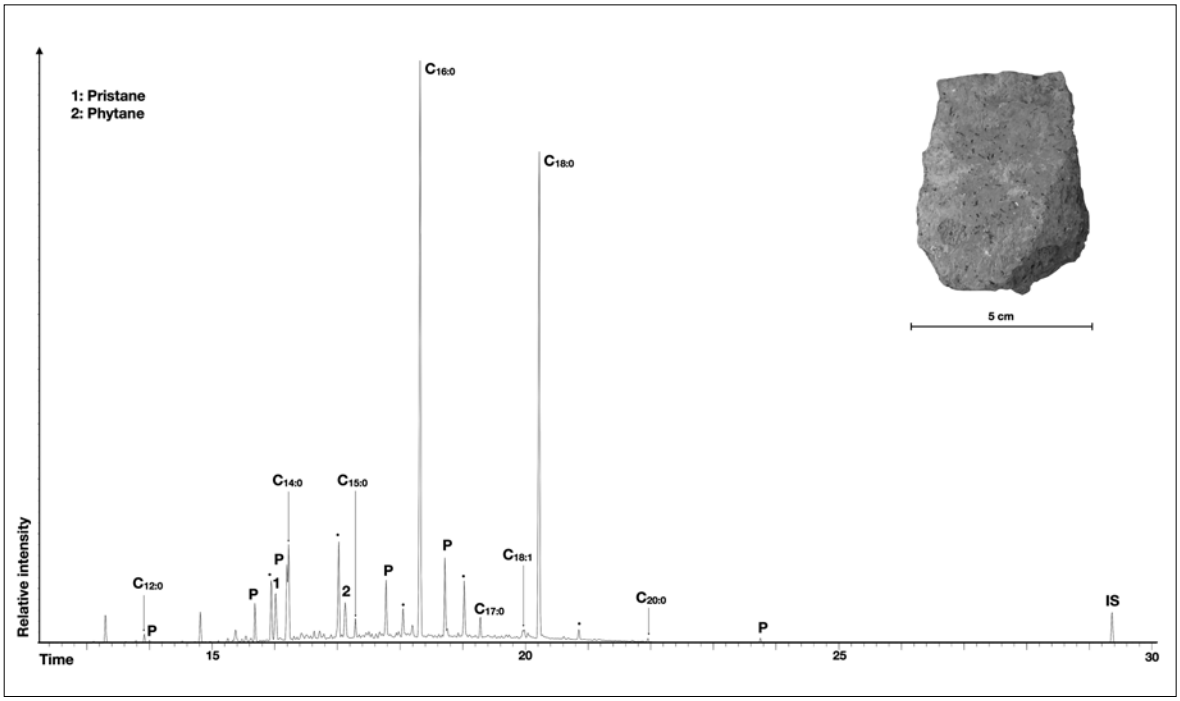

Figure 4. Chromatogram of sample 1. Follows the same annotation criteria as figure 3.

is presented in figure 2 (Fig. 2). The preservation rate has been calculated using a 5µg/g threshold (Craig *et al.*, 2011) and it is reported as a percentage of the total.

Therefore, taking data from figure 2 into account, the preservation rate in samples from Tell Halula has reached 80%. Furthermore, Figures 3 and 4 present chromatograms which show profiles presented in the literature as characteristic of animal fats and plant residues (Copley *et al.* 2001, Copley *et al.* 2003, Dunne *et al.* 2012).

Although not all samples have provided lipid patterns as clear as the ones presented, the detection of a pair of singular molecules should also be considered. In sample 5, the comparison of the mass spectra with the reference database has allowed the detection of Citric acid (Fig. 5).

Citric acid is one of the main modern acidifiers and a significant compound in citrus fruits such as lemons or oranges. Its presence in a residue in which the fatty acid profile does not point to an animal origin could point at the possibility that the vessel had contained a plant product. Nevertheless, this compound has only been detected once and not in a significantly high quantity, therefore, it is difficult to provide a meaningful archaeological interpretation for it. Citric acid has been previously detected in archaeological residues (Eerkens 2005, Manzano *et al.* 2015). Therefore, its appearance can be used as an indicator that these types of molecule can also be recovered under the acidified methanol extraction.

In sample 10, a molecule eluting at minute 8.83 with the mass spectra presented in figure 5 was identified as Camphor, a specific monoterpenoid. This molecule is also highly used nowadays in products for alimentation, medical and religious purposes.

Nevertheless, also in this case, Camphor has also only been found once in a vessel whose fatty acid profile does not point at an animal origin. The high volatility of the molecule and the absence of other terpenoids suggest its origin might not be archaeological. However, its detection indicates that it can also be extracted by the acidified methanol technique (Fig. 6).

Finally, the presence of significant quantities of lipids has allowed comparing the TLE with different vessel characteristics (Fig.7). Figure 7 compares the amount of residue with sherd shape, firing atmosphere, presence of slip as a surface treatment, density and thickness.

As shown in the graphs, some minor differences on lipid quantities exist depending on the characteristics of the sherd. Bases seem to yield slightly less lipids than rims and pottery with slip also tends to present better preservation. Other differences are not acute enough to affect the presence of organic residues in the vessel.

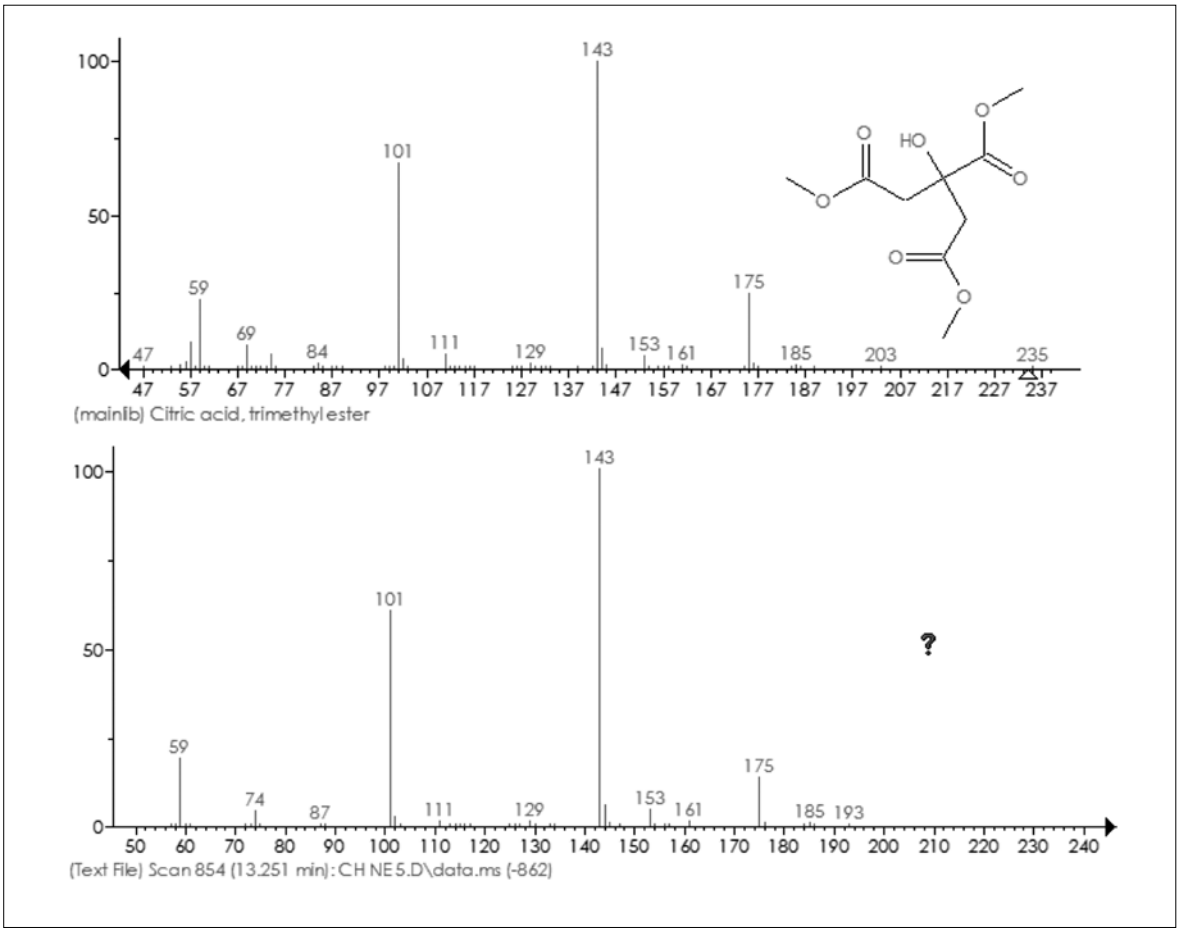

Figure 5. Comparison of mass spectra for Citric Acid. Top: Spectra from methylated Citric acid as presented in the NIST database. Bottom: Spectra from Rt: 13.24 min in Sample 5.

DISCUSSION

Taking the objectives of this research into account, several questions can be specifically answered: Is the Acidified Methanol extraction more effective in samples from the Near East?

The use of the Acidified Methanol extraction has clearly achieved similar results to those published in the literature (Correa-Ascencio/Evershed 2014, Papakosta *et al.* 2015, Taché/Craig 2015). More precisely, complex molecules such as triacylglycerols, long-chain ketones and wax esters do not seem to have survived in this case. The absence of such compounds could be due to the important degradation activity (hydrolysis) of the sulphuric acid, which is used during the extraction. This could be an important limitation in other preservation environments, where the amount of complex molecules is significant. Nevertheless, more arid and aggressive soils such as the ones in the Near East would hardly preserve these molecules (Gregg/Slater 2010). Therefore, although this is a clear limitation of the method, its negative consequences can be avoided in the case of the Near East.

When evaluating which quantity of lipids is sufficient to attempt any archaeological interpretation, researchers have used different thresholds such as 5µg/g (eg: Craig *et al.* 2011, Evershed *et al.* 2008) 10µg/g (Craig *et al.* 2005) and 20µg/g (Baeten *et al.* 2013). The use of the lowest cap is considered a standard practice since minor contamination from soils and modern compounds must be considered. The 5µg/g limit is the most commonly used in the literature (ex: Copley *et al.* 2005; Craig *et al.* 2011, Dudd/Evershed/Gibson 1999, Evershed *et al.* 2008). Nevertheless, since the acidified extraction increases the quantity of lipids recovered, it is also possible that lipids that can be classified as contamination also increase. Therefore, to add an extra layer of certainty to the interpretation of the results, the 10µg/g limit was also considered. The number of samples with TLE's above these thresholds is 80% for the Pre-Halaf layers at Tell Halula whereas the Microwave-assisted approach reached 52% (Gregg/Slater 2010) and the Chloroform/Methanol extraction detected significant quantities of lipids in 12-20% of the samples in studies from other chronologically similar sites in the Middle East (Evershed *et al*. 2008, Thissen *et al*. 2010).

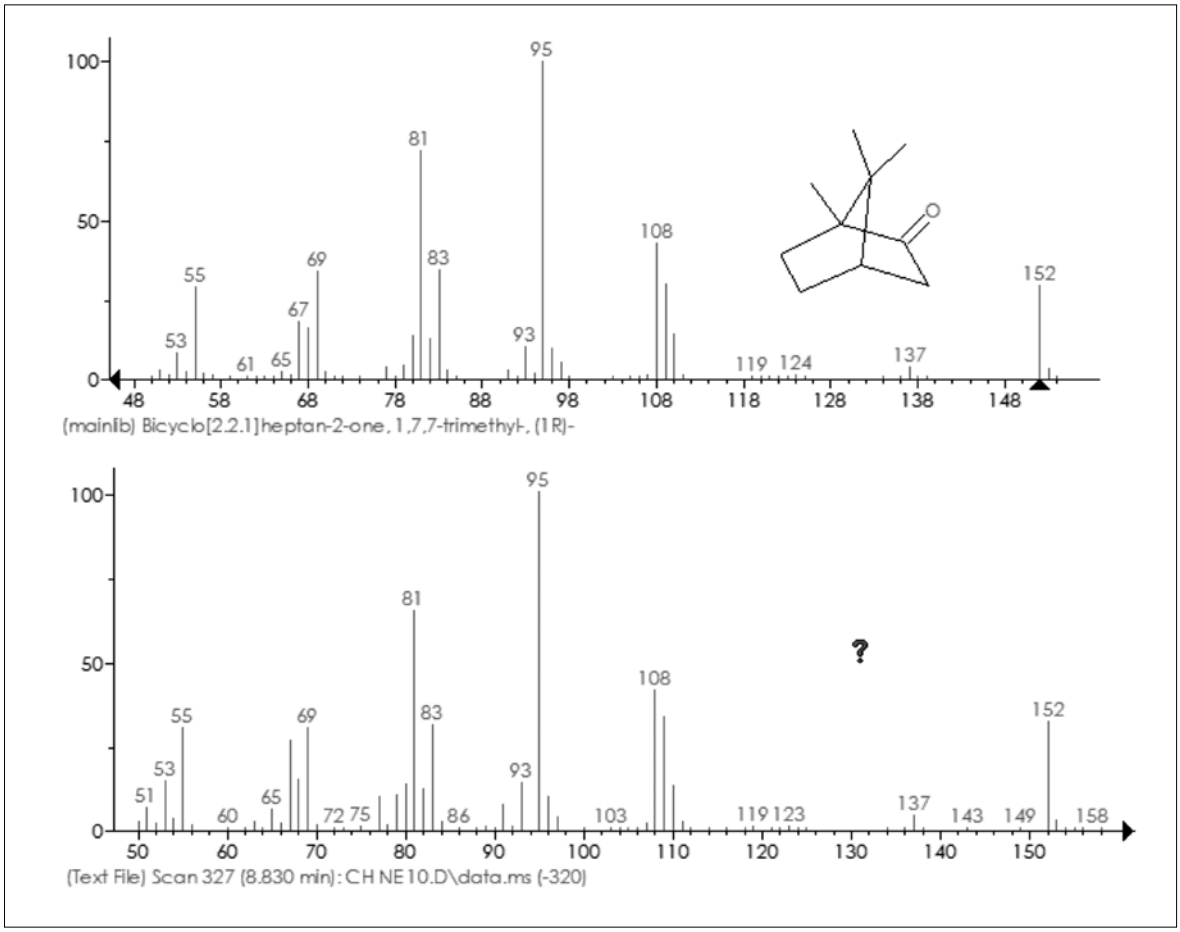

Figure 6. Comparison of mass spectra for Camphor. Top: Spectra from methylated Camphor as presented in the NIST database. Bottom: Spectra from Rt: 8.8 min in Sample 10.

As shown, the Acidified Methanol extraction has been effective in 8 out of 10 samples for both thresholds, which presents a clear improvement of the lipid yields when compared to the other practiced methods. Although the aggressiveness of the acid extraction is considerably higher than other extraction methods and some information could be lost, the overall result is a gain in the amount of chemical information that could be further interpreted by the archaeologist.

Which products did the analysed vessels use to contain? Although lipid quantities have been improved, not all the detected residues could be clearly characterised. Three main factors have caused interpretation problems. First, the management of the sherds once they are excavated normally involves the use of plastic bags and direct contact with the human skin. Plastic bags contain highly volatile compounds such as phthalic acids. These molecules are easily incorporated in the clay matrix when the sherd is introduced in the box and, when performing the analysis, create noise and sometimes hide possible relevant ancient molecules. Phthalic acids have been widely found in the samples from Tell Halula. Its high abundance is also caused by a second factor. The fact that these samples were excavated in 1993 implies that the sherds were removed from a closed and stable environment under earth and placed in a new environment with changes in light, temperature and humidity. After 22 years in storage, an important part of the residue could have been lost and plastics had a lot of time to enter the clay matrix. Finally, although lipids are not leached in water, the more time the sample stays under earth, the higher the chances the residue degrades and disappears. In consequence, the fact that these samples come from the oldest pottery productions in the Middle East also adds more uncertainty onto whether the original residue would survive in a state that allows its identification.

In consequence, the fact that the Acidified Methanol extraction has been able to find significant quantities of lipids in 80% of the samples it is a clear example of the potential of this new technique. Nevertheless, interpretation of the residue origin could be a more difficult task. In terms of the identification of the residues, sam-

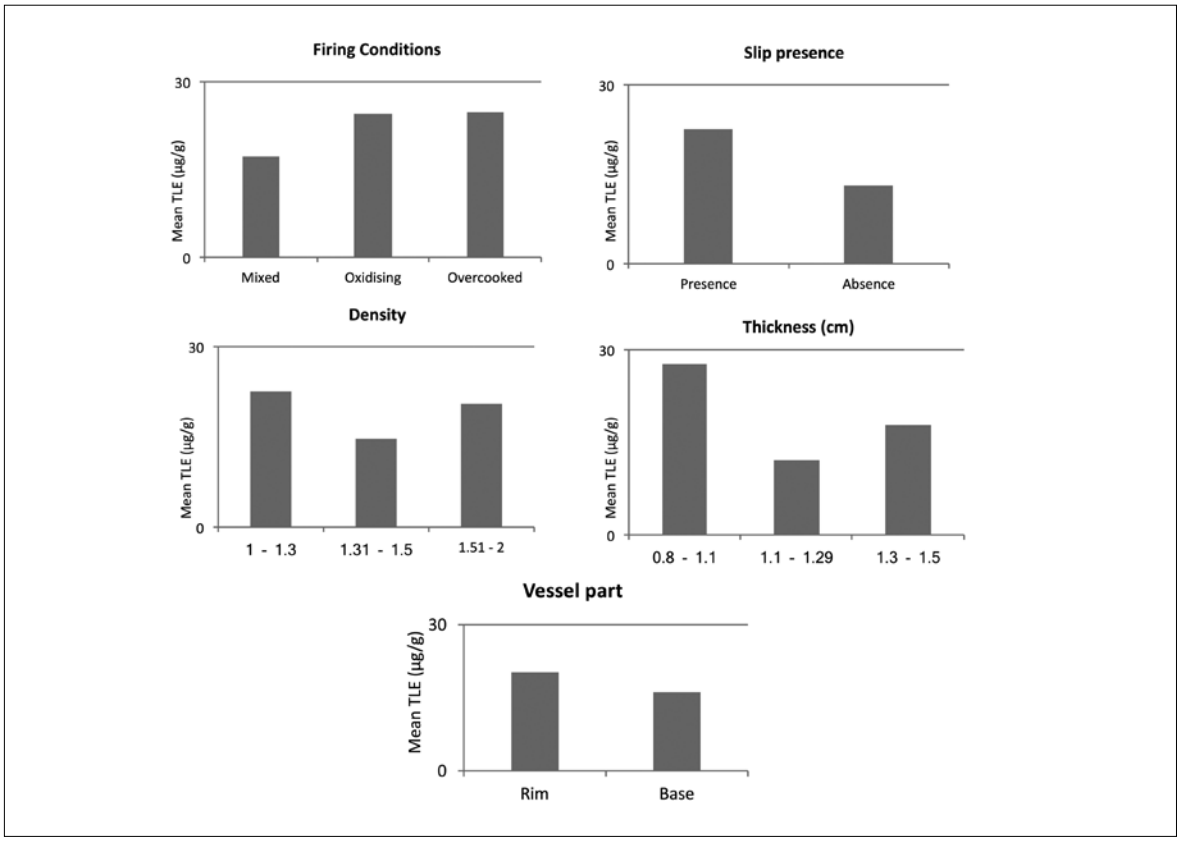

Figure 7. Bar diagrams showing the mean total lipid extract (TLE) compared related to firing conditions, slip presence, density, thickness and the vessel part.

ples 7 and 9 present a clear abundance of $C_{16:0}$ and $C_{18:0}$ which suggest the presence of animal fat. These molecules could be further analysed by gas chromatography coupled to combustion and isotope ratio mass spectrometry (GC-C-IRMS). This analytical technique provides the stable light isotopic ratios of the carbon atoms in the $C_{16:0}$ and $C_{18:0}$ molecules, which can be used to differentiate between ruminant and non-ruminant animals, terrestrial and marine fats, and milk and adipose fat.

Furthermore, sample 1 presents a clearly different profile with $C_{18:1}$ being more abundant than $C_{18:0}$ and $C_{16:0}$ being the dominant peak. When this profile is complemented with a slight increase in the abundance of *n*-alkanes and the detection of nonanedioic acid, the residue can be cautiously interpreted as probably originating from a plant product. Therefore, the isotopic study of the main fatty acids would allow the differentiation between C_3 and C_4 plants.

Sample 5 presents a lipid profile that should also be commented. The detection of citric acid could suggest the presence of some type of fruit. Nevertheless, critics such as lemons or oranges were not introduced into the Near East until more recent chronologies. Moreover, previous research on fruits (Copley *et al.*, 2001) suggest that its chemical profile contains a dominant presence of $C_{12:0}$, a molecule that is only present in small amounts in sample 5. Nevertheless, the low quantities of $C_{18:0}$ related to $C_{16:0}$ suggest that the residue does not have an animal origin. Following this line of thought, a plant origin should not be discarded but it is also possible that Citric acid was somehow incorporated into the sample from the surrounding soil or by the excavators. Although laboratory blanks indicate that no contamination comes from the treatment process, more samples with the same profile should be found before Citric acid can be interpreted with no uncertainty as an ancient molecule.

The detection of terpenoids has been associated with resins (Pollard *et al.*, 2007, 153). The presence of Camphor in sample 10 hints at the possibility that this type of product might have been present during transformation processes that also involved ceramics. Nevertheless, although monoterpenoids are specific of plants, because of its low molecular weight and volatility, they are not often found in archaeological vessels (Pollard *et al.*, 2007, 153), therefore, a possible contamination from modern organic matter should not be discarded. Terpenoids should be detected in more samples from

the site before any firm archaeological interpretation can be made in this matter.

Sample 10 also presents a clearly different profile. It is the only sample that presents significant abundances of mid chain fatty acids ($C_{6:0}$ to $C_{12:0}$). Such molecules have been interpreted in the literature to naturally come from ruminant milk lipids. Nevertheless, the quantity of $C_{18:0}$ in the sample is not high enough to strongly support this hypothesis. Analysis through GC-C-IRMS would be able to provide a clear answer to this possible identification. Nonetheless, the strength of the extraction practiced in the samples could have broken larger molecules into mid chain fatty acids. Therefore, it would be advisable to practice other softer extractions such as the microwave-assisted chloroform/methanol technique before concluding that these mid chain fatty acids genuinely originating from an ancient product.

CONCLUSIONS

As suggested by previous research (Correa-Ascencio/Evershed 2014, Papakosta *et al.* 2015, Taché/Craig 2015) the acidified methanol extraction has improved lipid preservation rates. Data from Tell Halula, where 80% of the samples presented TLE's above 10µg/g, suggest that ceramic archaeological samples from low lipid recovery environments might provide relevant archaeological information when using the Acidified Methanol extraction. Nevertheless, the aggressiveness of the procedure carries several limitations such as the destruction of complex molecules. In consequence, comparison with results from other "softer" extraction techniques should still be practiced until the acidified extraction and its consequences are better understood.

The possible differences in use between fine and coarse ware (Faura 2013) might be investigated under this technique, thus opening the possibility to new studies that connect the *chaîne operatorie* with the active life of the artefact.

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