5. Methods

The methods used during this study fell into three groups. The first included methods used to extract and identify organic residues from archaeological pottery, while the second comprised methods used to examine the pottery itself. A third line of investigation involved calculations to determine the approximate volume of typical RLWm ware vessels.

5.1 Residue analysis

5.1.i Background

5.1.i.a Survival of residues

The first attempt at the analysis of the contents of ancient pottery vessels was published in 1933 by Johannes Grüss (Pollard & Heron, 2008, 383). Grüss used wet chemistry techniques to analyse the burnt material still present in cooking vessels, concluding that these visible residues were formed from the burning of milk fats (Pollard & Heron, 2008, 383). The survival of any visible residues, either as the contents of whole vessels or as residues on the surfaces of sherds, is relatively rare (Evershed, 2008a and b). Two visible residues were examined during this study and one analysed during a previous study was re-examined.

Although visible residues are rare, unglazed pottery contains a network of pores into which the contents of the vessel can be absorbed during vessel use, and

which provides a semi-protected environment where organic material can survive over archaeological time (Evershed, 1993; Heron & Evershed, 1993; Dudd *et al*., 1998; Evershed *et al*., 1999; Heron *et al*., 1999; Evershed *et al*., 2001; Evershed, 2008a and b). Not only do the pores in ceramics provide a degree of protection from microbial activity and the action of water, sunlight and chemicals in the burial environment, but the clay minerals in the pottery matrix also provide a large surface area onto which residues may be adsorbed (Heron & Evershed, 1993; Evershed, 1993; Evershed *et al*., 1999; Craig & Collins, 2000; Evershed *et al*., 2001; Ashman & Puri, 2002; Evershed, 2008a and b).

The first reported analysis of absorbed residues from unglazed ancient pottery was the identification of olive oil in amphorae of unspecified date and a gallo-roman lamp (Condamin *et al*., 1976). Over the past thirty years the techniques of analysing absorbed pottery residues have developed significantly and this type of analysis can now provide valuable information about how ancient vessels were used and what they contained (Evershed *et al*., 2001).

Despite the partially protected environment within the pores of archaeological ceramics, residues are still subject to the effects of degradation due to microbial attack and the action of water, air, chemicals in the burial environment (Heron & Evershed, 1993; Evershed, 2008a and b). Post excavation handling and storage can also affect the survival of residues. Some molecules are more resistant to degradation than others with the result that some classes of compound are preferentially preserved in archaeological residues. Proteins for example are very easily denatured or destroyed and are rarely seen in pottery

residues (Logan & Collins, 1991; Evershed, 1993; Evershed & Tuross, 1996; Craig & Collins, 2000; Craig *et al*., 2000). Simple carbohydrates are soluble in water and are easily lost in the burial environment (Eglinton & Logan, 1991; Evershed, 1993). Because they are relatively resistant to degradation and relatively insoluble in water, lipids – the compounds which make up fats and oils, waxes, resins and fossil fuels – are the most likely to survive (Evershed et al., 1990; Eglinton & Logan, 1991; Logan & Collins, 1991; Evershed, 1993; Heron & Evershed, 1993; Evershed *et al*., 1999; Evershed *et al*., 2001; Evershed *et al*., 2002; Evershed, 2008b). Consequently the analysis of organic residues in pottery is essentially (although not exclusively) the analysis of lipid residues, and methods appropriate to the detection and identification of lipids are those most frequently used in the analysis of residues in ancient ceramics. Lipids themselves may also be considerably altered by degradation during vessel use, burial and post-excavation handling. This is discussed further below (p106-108) and specific examples are given in chapter 7.

5.1.i.b Analytical techniques

The absorbed residues from the interior and exterior surfaces of 73 sherds were examined by gas chromatography (GC) (table 5.1a). Lipid analysts were very involved in the initial stages of the development of gas chromatography and it is highly suited to the separation and detection of small, non-polar, volatile compounds such as lipids (Christie, 1989, 3). Christie (1989, 85) describes GC as the technique of choice when analysing mixtures of fatty acids and Evershed (2001) records that it "…..provides a very powerful means of separating the

complex mixtures of lipids commonly encountered in archaeological materials". One of its major advantages in archaeological analyses is the high sensitivity that can be achieved. Modern systems can detect a few micrograms (μg) of a compound and the most sensitive systems can measure a few picograms (pg) (Christie, 1989, 3; Grob, 2004). In archaeological materials this means that, although the technique is destructive, only very small samples are needed to carry out an analysis. Gas chromatography also allows the separation (with a suitable column) of molecules which are similar both physically and chemically (Grob, 2004; Pollard *et al*., 2007, 142). It is also relatively cheap, easy to use, fast (Christie, 1989, 3; Grob, 2004) and can produce quantitative as well as qualitative results (Christie, 1989, 61-62; Braithwaite & Smith, 1996, 165; Evershed *et al*., 2001; Pollard *et al*., 2007, 145). Gas chromatography is also a versatile technique which can be adapted to the analysis of a wide range of compounds by the use of columns with different stationary phases, temperature programming of the GC oven and derivatisation of samples (Evershed, 1992b; Braithwaite & Smith, 1996, 165; Evershed *et al*., 2001; Grob, 2004).

The major disadvantage is that GC can only analyse compounds which are both volatile and thermally stable – only about 20% of all known compounds – although derivatisation of samples prior to analysis can extend the range of possible analytes considerably (Evershed, 1992b; Braithwaite & Smith, 1996, 165; Masucci & Caldwell, 2004; Pollard *et al*., 2007, 142). Derivatisation can be used to alter or replace polar functional groups allowing polar compounds to be analysed by GC. The two most commonly used methods in archaeological analyses are methylation and silylation where polar groups are replaced with a

methyl or a trimethylsilyl (TMS) group as shown in figure 5.1.

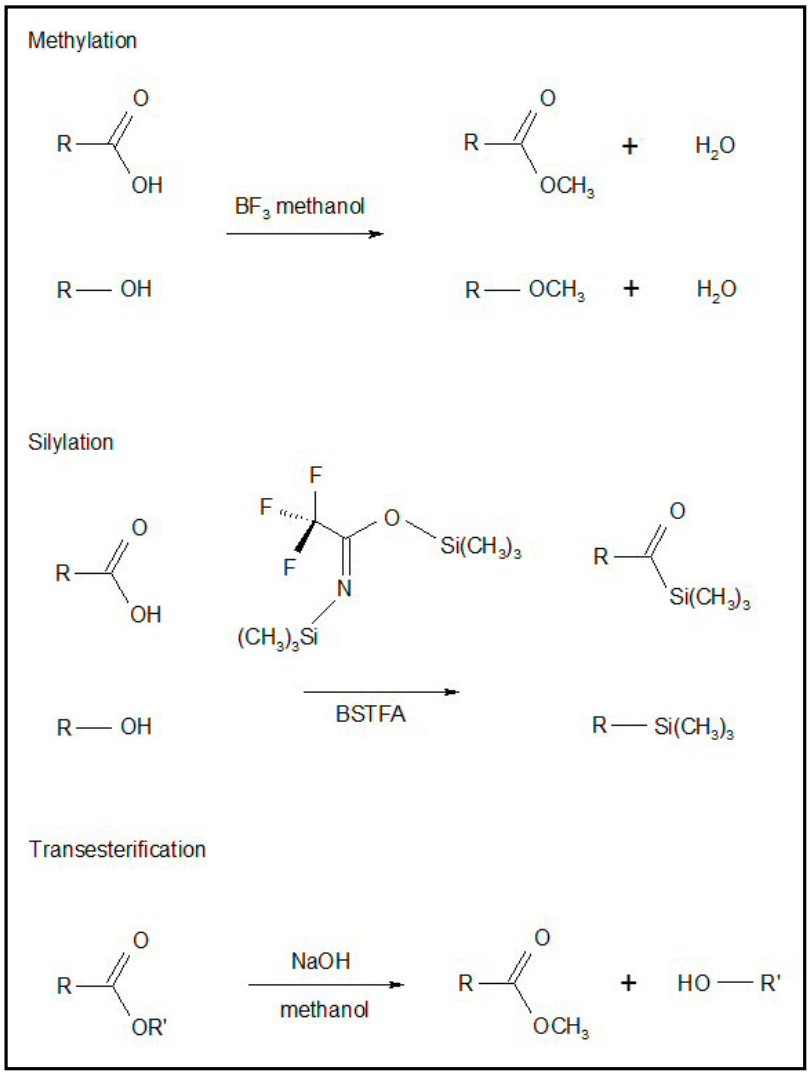


Figure 5.1: Chemical reactions involved in methylation, silylation and transesterification.

Gas chromatography is a separation technique and, although it is sometimes possible to identify compounds solely from a chromatogram by matching the retention times of standards with those of peaks in the sample, this does not give reliably unique identifications (Christie, 1989; Pollard *et al*., 2007). In order to characterise residues fully, some samples in this study were selected for further preparative treatment and analysis by gas chromatography-mass

spectrometry (GC-MS), the selection being carried out on the basis of the GC results (table 5.1a). Christie describes GC-MS as "…one of the most powerful tools in the hands of lipid analysts" (Christie, 1989, 161), and Pollard *et al*. (2007, 174) as "the "gold standard" for the identification of organic samples". Evershed *et al*. (2001) go so far as to say that "GC/MS is vital to biomarker investigations of archaeological materials". The combination of gas chromatography with mass spectrometry allows not only the separation of the compounds in a complex mixture but the identification of those compounds from their characteristic mass spectra (Evershed, 1992b; Braithwaite & Smith, 1996, 165; Evershed *et al*., 2001; Masucci & Caldwell, 2004). The technique is capable of analysing volatile, thermally stable compounds with molecular weights of 50-700 amu (Braithwaite & Smith, 1996, 165; Pollard *et al*., 2007, 142, 175).

The main limitation of GC and GC-MS methods is their inability to analyse compounds with are not both thermally stable and volatile. Over archaeological time it is quite possible that volatile compounds have evaporated and low molecular weight compounds, which are more soluble in water than larger molecules, may be dissolved by water in the soil during burial and by post-excavation washing. It is therefore possible that residues not susceptible to analysis by GC may be present in archaeological samples and these require a different analytical method.

High performance liquid chromatography (HPLC) by contrast can analyse compounds provided they are soluble in a suitable solvent (Meyer, 1994, 2-3;

Pollard *et al*., 2007, 146). This includes many organic and ionic inorganic compounds (Meyer, 1994, 2-3). However HPLC, even HPLC coupled with a mass spectrometer, has not often been used in archaeology (Heron & Evershed, 1993). This is mainly due to the difficulty of analysing samples which may contain mixtures of many different groups of unknown compounds. HPLC columns are usually highly specific and each column is designed for analysing one particular group of compounds (Meyer, 1994, 218-219; Rizzi, 1998; Hanai, 1999, 31-56). To get a complete analysis of an unknown sample therefore requires either repeated runs of the same sample with several different columns or the development of analytical techniques which involve preparative chromatography to separate the different groups of compounds within the sample (Nicolaou, pers. comm.). A technique which is promising is HPLC combined with tandem mass spectrometry (HPLC-MS-MS) which can be used to detect very small quantities of particular compounds by tuning the mass spectrometer arrangement to detect only the molecular ion and stable daughter ions of the compound(s) under investigation. This allows analysts to search for and identify a specific target molecule, even in the presence of large concentrations of other compounds.

HPLC-MS and HPLC-MS-MS can be used successfully in archaeology where the desire is not to characterise a sample completely but to search for a particular substance by identifying one or more of its unique biomarkers in a residue. For example the theory that particular Mayan vessels were used for making a chocolate drink was confirmed by the identification of theobromine and caffeine in residues from the vessels using HPLC-MS (Hurst *et al*., 2002).

To investigate the possibility that some RLWm ware vessels had been used for the storage or transport of wine HPLC-MS-MS was carried out on a small group of samples to try and identify the presence of tartaric acid (table 5.1a and b). Grapes contain significant quantities of tartaric acid which is otherwise rare in nature (McGovern & Michel, 1996; Singleton, 1996; Guasch-Jané *et al*., 2004; Stern *et al*., 2008). Tartaric acid is also present in grape-based wines and the detection of tartaric acid is considered indicative of the presence of wine in ancient residues (McGovern & Michel, 1996; Guasch-Jané *et al*., 2004; Pollard *et al*., 2007, 149; Stern *et al*., 2008). In addition to tartaric acid red wines contain syringic acid and this can be used to distinguish white and red wines in residues (McGovern & Michel, 1996; Guasch-Jané *et al*., 2004; Pollard *et al*., 2007, 149; Stern *et al*., 2008). However in this case the aim was to establish the presence or absence of wine in these RLWm ware vessels and the extraction and analysis for syringic acid was not attempted.

For this study eighteen samples were selected from those already analysed by GC or GC-MS, some of which contained lipid residues and others which did not. A further consideration was the amount of sherd remaining as new samples had to be drilled for this analysis. Fourteen of these samples, one a visible residue, had been analysed during previous studies (table 5.1b).

Another limitation of GC-MS as a technique for the analysis of archaeological residues is the difficulty of distinguishing fats and oils from different sources. Degradation and dissolution of fatty material can significantly alter the ratios of fatty acids contained in fat or oil making an identification of the original residue

impossible using GC-MS alone (Evershed, 1993; Heron & Evershed, 1993; Mottram *et al*., 1999; Copley *et al*., 2003; Spangenberg *et al*., 2006; Evershed, 2008a and b). In order to retrieve more information about the original materials processed or stored in pottery vessels, further analysis is required.

Compound specific stable isotope analysis can be used to determine the source material of degraded fatty residues (Evershed *et al*., 1994; Evershed *et al*., 1997; Mottram *et al*., 1999; Meier-Augenstein, 2002; Copley *et al*., 2005d; Craig *et al*., 2005; Spangenberg *et al*., 2006; Craig *et al*., 2007; Evershed, 2008a and b). Individual compounds within any fat or oil are formed by different metabolic pathways in different organisms and each metabolic pathway will produce a distinctive fractionation of carbon stable isotopes in the final product. Measuring the ratio of carbon stable isotopes, the $\delta^{13}C$ value, of individual fatty acids, most usually palmitic acid ($C_{16:0}$) and stearic acid ($C_{18:0}$), can distinguish between fatty acids from different original materials eg ruminant milk fat and ruminant adipose fat (Evershed *et al*., 1997a; Dudd & Evershed, 1998; Evershed *et al*., 1999; Mottram *et al*., 1999; Evershed *et al*., 2001; Evershed *et al*., 2002; Copley *et al*., 2003; Copley *et al*., 2005a-d; Spangenberg *et al*., 2006). This ratio appears to be unaffected by degradation processes and can be used to distinguish the origins of archaeological fats and oils (Evershed *et al*., 1997a; Evershed, 2008). For this study thirteen archaeological samples, three visible residues and ten absorbed residues, were prepared and sent to the NERC stable isotope facility at the Centre for Environment and Hydrology at Lancaster University for GC-C-IRMS (table 5.1a). Four absorbed and one

visible residue had already been examined by GC/GC-MS during a previous study. Ten modern plant oils were also sent for analysis (p135ff).

In addition to the absorbed residues, three visible residues were also available for analysis, one analysed by GC-MS during a previous study (Steele, 2004, 74-79; Steele *et al*., 2007) and two analysed for the first time during this study. The two visible residues analysed during this study were examined by GC-MS, saponification followed by GC-MS and GC-C-IRMS. The third visible residue was further examined by GC-C-IRMS and also by Fourier Transform infra-red spectroscopy (FT-IR). FT-IR has the advantage when examining visible residues that no sample preparation is required, so the sample remains unaltered (Heron & Evershed, 1993). The absorption bands detected by FT-IR are produced by the absorption of energy at a unique frequency by a particular molecular group resulting in peaks in an IR spectrum which give information on the chemical bonds present in a sample (Pollard *et al*., 2007, 77-79). This means that different compounds may produce similar IR spectra due to their similar chemical groups (Pollard *et al*., 2007, 78-79). In the complex mixtures which constitute most archaeological residues this can make the identification of the actual molecules present very difficult (Heron & Evershed, 1993; Pollard *et al*., 2007, 79). For this study the one examination of a visible residue was carried out to see what information can be obtained by FT-IR analysis and whether this might be a useful technique for further study.

5.1.i.c The use of biomarkers for identification of residues

The chemical analysis of pottery residues yields information about the molecules present in residues. However this in itself does not give a definitive identification of the original source material. This further step relies on the comparison of the compounds present in a residue with contemporary plant or animal products (Evershed, 1993; Heron & Evershed, 1993; Pollard *et al*., 2007, 148-149; Evershed, 2008a and b). The identification of molecules or groups of molecules characteristic of both ancient residues and modern materials allows the original source of the residue to be characterised. These characteristic molecules are known as biomarkers.

Biomarker compounds are those in which the basic structure, or skeleton, of the molecule remains recognisable even after extensive degradation (Evershed *et al*., 1999; Killops & Killops, 2005, 135; Peters *et al*., 2005, 3; Evershed, 2008b) – a "chemical fossil" (Evershed *et al*., 1999; Killops & Killops, 2005, 135). These molecules must also be common and abundant but occur in one specific material or group of materials (Peters *et al*., 2005, 3; Pollard *et al*., 2007, 148).

A single molecule may be considered a biomarker – for example the occurrence of ricinoleic acid in large concentrations only in castor oil makes this acid an effective indicator of the presence of castor oil (Gunstone, 2004, 3). More commonly, groups of compounds, sometimes in a distinctive pattern of abundances, form biomarkers for a particular product. For example degraded beeswax exhibits a characteristic distribution of odd carbon numbered *n*-

alkanes, even carbon numbered long chain alcohols and wax esters (Mills & White, 1999, 49-50; Serpico & White, 2000b; Evershed *et al*., 2001). Biomarkers can be general, as in the identification of a degraded fat or oil from the presence of fatty acids. They may be more specific biomarkers for example the terpenoids present in resins or the detection of leafy vegetables in cooking residues from the presence of *n*-nonacosane, nonacosan-15-one and nonacosan-15-ol (Evershed *et al*., 1991; Charters *et al*., 1997).

Biomarkers were used in the course of this study to identify the source material of both absorbed and visible residues.

5.1.ii Contamination

In extracting and analysing archaeological residues a primary concern is not to introduce contamination during sample preparation and analysis. To avoid this, nitrile gloves were worn at all times and all glassware and tools were triple washed in dichloromethane (DCM) before use and between samples. When drilling sherds the drill bit was sonicated in DCM for 5 minutes between samples to ensure that all traces of sherd powder from the previous sample were removed. All solvents were Analysis grade or HPLC grade as appropriate.

A control sample was prepared and analysed with each batch of archaeological samples to allow any contamination introduced in the laboratory to be identified. These control samples were prepared from modern, unused flower pot which had been Soxhlet extracted for 24 hours using DCM:methanol (93:7 v/v) to

remove solvent soluble lipids. Method blanks were also used during more extended sample preparation, for example in saponification and methylation procedures.

5.1.iii GC and GC-MS analysis

All pottery samples and visible residues were subjected to solvent extraction and the resulting residues analysed using GC and/or GC-MS. Before any sample preparation was carried out all sherds were examined using a x10 hand lens and a general description recorded. Photographs were also taken of the interior and exterior surfaces of each sherd and of any other features of interest, such as pot marks, which were present.

5.1.iii.a Sample preparation

To extract lipid residues from the pottery fabric a 2mm thick layer was separately ground from the interior and exterior surface of each sherd using an electric drill (*Dremel*) with an abrasive tungsten bit. A small number of sherds were coated in a white deposit (fig. 5.2). If no sherd surface was visible, this deposit was removed with the drill prior to grinding the sample. Many of the sherds had been excavated from sites where the underlying geology is limestone indicating that these deposits are calcium carbonate precipitated from water during burial. Samples of the deposit also effervesced with cold 2M hydrochloric acid – a classic test for calcium carbonate (Cook & Kirk, 1991, 19;

Bishop *et al*., 2001, 65). A few of these deposits were examined by GC and contained no organic matter.

Interior and exterior surfaces of each sherd were sampled separately as an additional control in the absence of soil samples from any of the sites. Residue only present on the interior surface of a vessel will reflect the actual contents of that vessel, while contamination from the burial environment is more likely to be present on the exterior surface (Stern *et al*., 2000) or equally on both surfaces. Contamination from post-excavation handling of sherds is usually present on both surfaces.

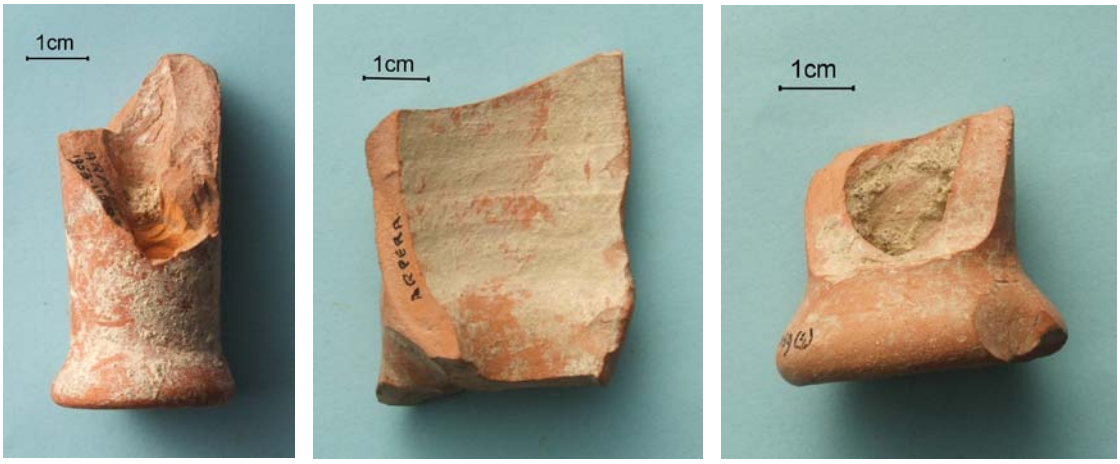


Figure 5.2: Three sherds exhibiting a white deposit – from the left Arpera sherd 3, Arpera sherd 5 and Hala Sultan Tekke sherd 7.

Approximately 0.1g of sherd powder was accurately weighed into a clean glass vial. The powder was then sonicated for 5 minutes with three aliquots of approximately 1ml DCM:methanol (2:1 v/v). The samples were centrifuged at 2000 rpm for 5 minutes and the supernatant pipetted off into a clean vial. The

three extracts were combined and the resulting sample was evaporated to dryness under a gentle stream of dry nitrogen over low heat. Samples were stored in the refrigerator at 4°C until analysed by GC or GC-MS.

Visible residues were prepared by carefully removing a small portion of the residue using a clean scalpel. This was placed in a clean vial and the sample extracted as above.

After initial analysis by GC some samples were re-extracted and the extracted residues were saponified (table 5.1a). During saponification an alkali is used to hydrolyse complex lipids such as triacylglycerols and wax esters which contain ester bonds (fig. 5.3). Hydrolysis breaks these ester bonds releasing the component fatty acids and other compounds allowing them to be identified by GC-MS (McMurry, 2000, 867-868; Dudd *et al*., 1998; Regert *et al*., 2003). Samples which contain large amounts of polymerised lipids such as dried oils or fats are also broken down, releasing individual fatty acids which can then be identified (Regert *et al*., 2003). Saponification was carried out by adding 3ml 0.5M sodium hydroxide (NaOH) to each extracted sample and heating in a closed vial at 70°C for 2 hours. After cooling the non-saponifiable fraction was extracted if required. This fraction contains the non-polar compounds that are not soluble in aqueous alkali and includes sterols, hydrocarbons and long chain alcohols. Each sample was sonicated with 3ml hexane for 5 minutes, and left to stand. As hexane is not miscible with aqueous solutions it forms a separate layer which can be pipetted off into a clean vial. This process was repeated twice more, combining the non-saponifiable extracts. The sample was then

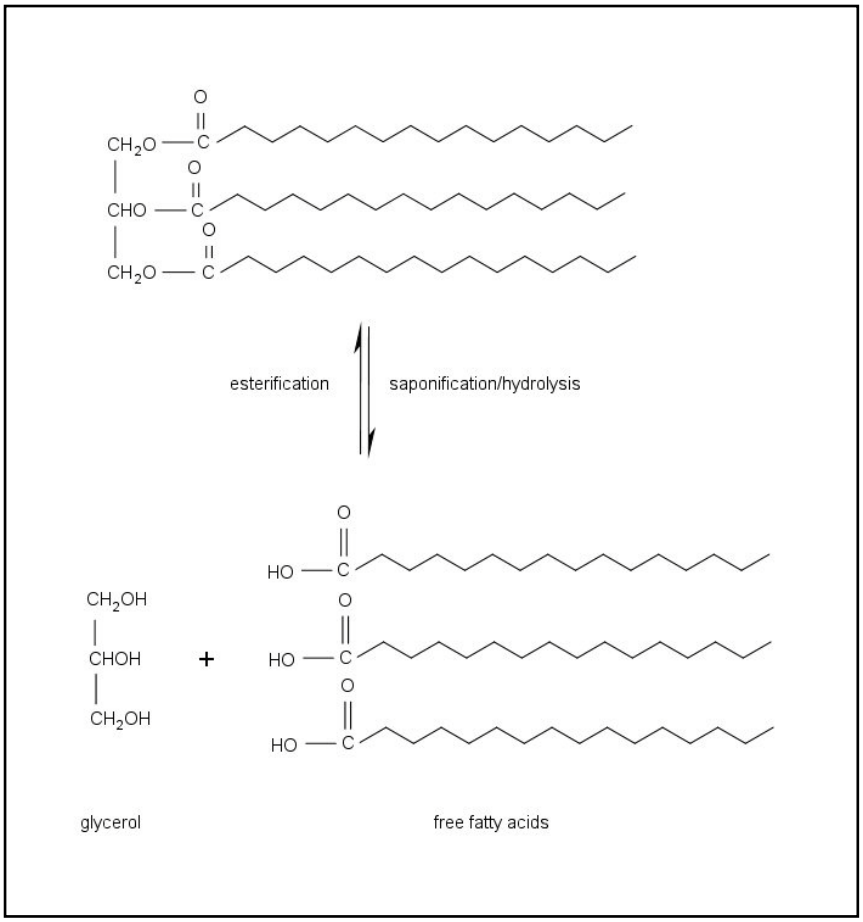


Figure 5.3: Process of saponification of triacylglycerol, in this example tripalmitin, to glycerol and free palmitic acid.

acidified with concentrated hydrochloric acid (HCl) to complete the saponification reaction and extracted with three aliquots of 3ml hexane using the method above. All samples were evaporated to dryness under a stream of nitrogen over gentle heat and stored in a refrigerator at 4°C.

Before analysis by GC or GC-MS all samples were derivatised with an excess of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethyl-chlorosilane (TMCS). They were heated gently for 30 minutes to facilitate the derivatisation reaction. Excess BSTFA was removed prior to analysis by

evaporating under nitrogen. This process produces trimethylsilyl (TMS) derivatives by replacing polar hydrogen with a TMS group (fig. 5.1).

Selected samples which did not produce any residues following solvent extraction were treated using alkaline extraction (table 5.1a). There is some evidence that lipids absorbed in pottery may form insoluble polymers which can be broken down by saponification into soluble compounds which can then be analysed by GC-MS (Oudemans & Boon, 1991; Regert *et al*., 1998; Mills & White, 1999, 35-41).

Either the previously extracted sherd powder or a freshly ground sample was used for this analysis. Approximately 0.1g of sherd powder was accurately weighed into a clean Hach tube. 1.5ml of 0.5M aqueous methanolic NaOH (methanol:water 9:1 v/v) was added, the tube sealed and heated for 90 minutes at 70°C. After cooling the samples were extracted with 3 aliquots of 3ml hexane to remove any non-saponifiable compounds. The extracts were combined in clean vials and the hexane removed by evaporating under nitrogen with gentle heat. These non-saponifiable extracts were stored in the refrigerator at 4°C for separate analysis. The samples were then acidified using approximately 1ml 1M hydrochloric acid and extracted, dried and stored as for the non-saponifiable extracts. All samples were derivatised with BSTFA before analysis by GC and GC-MS.

5.1.iii.b Chromatographic methods

Before all GC analyses a measured amount of an internal standard, C_{34} *n*-alkane, was added to each sample to allow quantification of the results.

Gas chromatography was carried out on a *Hewlett Packard 6890* gas chromatograph fitted with a split-splitless detector and a flame ionisation detector (FID). Hydrogen was used as a carrier gas and maintained at a constant flow rate. The split ratio was maintained at 5:1. The injector was maintained at 300°C. The following fused silica capillary columns were used during the course of this study – 15m *MEGA*, inside diameter of 0.25mm, coated with 0.1µm of OV1 liquid phase; 15m *Varian*, inside diameter of 0.32mm and 0.25µm CP-SIL 5CB 100% dimethylpolysiloxane coating; 30m *Zebron ZB-5*, inside diameter of 0.25mm and a 0.1µm coating of 5% phenyl/95% dimethylpolysiloxane liquid phase. These columns are all quite similar in their chromatographic performance, the main difference between them being in altered retention times. Compounds eluted in the same order on all columns. Performance was optimised at the start of each day's work.

For all analyses the FID was maintained at 350°C with an hydrogen flow of 30ml/minute and an air flow of 400ml/minute. For trimethylsilylated archaeological samples the oven programme was as follows: initial temperature 50°C for 2 minutes, 50°C to 340°C at 10° per minute, 10 minute hold. For samples containing triacylglycerols or wax esters the final hold time was extended to 20 minutes.

Individual peaks were identified by using one of three methods.

- By analysing the same sample using GC-MS and matching the peaks
- By cross-matching peaks with those in another sample which had already been identified by GC-MS
- By matching the peaks with standards run using the same derivatisation process, column and temperature programme. This was only applied to some methylated samples where stearic and palmitic acids needed to be identified and GC-MS was not available.

Unfortunately, during the final stages of the project, the lack of a suitable column for the GC resulted in very poor chromatography and some analyses were too poor to provide any information about the sample except whether lipids were present or not (see p173).

5.1.iii.c Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry was performed on a *Hewlett Packard 5890* series II GC connected to a *5972* series mass selective detector. The splitless injector and interface were maintained at 340°C. Helium was used as the carrier gas. Several fused silica columns were in use during the period of this study. They included a *Varian-WCOT* 15m x 0.25mm with a 0.25µm CP-SIL 5CB dimethylpolysiloxane coating, a *Varian-WCOT* 15m x 0.32mm with 0.25µm of DP-SIL 5CB dimethylpolysiloxane coating, *Supelco-WCOT* 15m x

0.25mm Equity 5 with 0.25µm of 5% phenyl/95%dimethylpolysiloxane coating, and a *Zebron* ZB-5 30m x 0.25mm with 0.1µm of 5% phenyl/95% dimethylpolysiloxane coating. The oven was programmed to start at 50°C for 2 minutes, rising to 340°C at 10° per minute with a 10 minute at 340°C. For samples containing triacylglycerols the final hold was increased to 20 minutes. The column was inserted directly into the ion source of the mass spectrometer where electron impact ionisation occurred at 70eV. Spectra were obtained with a full scan from *m/z* 50 to 700.

During the final stages of the study an equipment failure resulted in GC-MS facilities being unavailable at Bradford. A limited selection of the residues most critical to the completion of the project were taken to the British Museum where the Department of Scientific Research had offered access to GC-MS facilities for a short period of time. These analyses were carried out using an Agilent 6890 GC attached to an Agilent 5973 mass selective detector. Injection was splitless with the injector at 250°C. Carrier gas was helium at a total flow rate of 64.2ml/min. The GC column was a 30m x 0.25mm Agilent HP-5MS with 0.25µm of (5% phenyl)-methylpolysiloxane stationary phase. The oven was programmed for 2 minutes at 50°C, rise of 10° per minute to 325°C and 10 minutes isothermal hold. The column was inserted directly into the mass spectrometer and spectra were obtained with a full scan from *m/z* 50 to 700.

Mass spectra were identified by comparison with a library (NIST NBS75K), other collections of mass spectra (*eg*. www.lipidlibrary.co.uk) or published papers. In some cases interpretation was carried out from first principles.

5.1.iii.d Quantification and errors

Quantification of residues was carried out using GC chromatograms by measuring peak areas. The area under a peak is proportional to the amount of compound present and adding a known weight of standard allows quantification by comparing the area of the standard peak with the areas of unknown peaks (Pollard *et al*., 2007, 145). Peak areas were measured by manual integration in the Agilent Chemstation data analysis software. The unknown concentration could then be calculated by using the equation:

$$wt_u = \frac{wt_{IS} \times A_u}{A_{IS} \times wt_p} \mu g/g$$

where wt_u is the unknown weight, wt_{IS} is the weight of the internal standard added, A_u is the area of the unknown peak, A_{IS} is the area of the internal standard peak and wt_p is the weight of pottery powder extracted.

Errors in the quantifications were estimated by adding the percentage errors accrued at different stages of the process of preparing and adding the internal standard, weighing the pottery powder before extraction and measuring the peak areas (Pollard *et al*., 2007, 310-312). The main errors in the preparation and addition of the internal standard were in weighing the standard, in measuring the volume of solvent in which it was dissolved and in measuring the volume of internal standard added.

Errors in the peak areas were estimated by measuring the areas of two separate peaks, one large and one small, ten times and calculating the standard deviations of the measurements. The error was then taken to be two standard deviations as 95% of values will lie within ±2s (Pollard *et al*., 2007, 310-312). The total percentage error in quantifying a peak was estimated to be ±9%.

5.1.iv HPLC-MS-MS analysis

5.1.iv.a Sample preparation

Sherd powder was drilled from the interior surface of each sherd as above (p109). Approximately 0.1g was weighed into a clean vial. Approximately 5ml 0.1% formic acid in methanol:water (20:80 v/v) was added to each sample. This was then sonicated for three minutes and centrifuged (2000 rpm, 5 minutes). The extract was pipetted off into a clean vial and reduced to about 20% of the original volume under a stream of dry nitrogen over gentle heat. Samples were stored in refrigerator at 4°C until analysis by HPLC-MS-MS. All solvents and mobile phases were of HPLC grade.

5.1.iv.b HPLC-MS-MS analysis

This analysis was based on the methods described by Guasch-Jané *et al*. (2004) and was linked to a larger study of material from the LBA Ulu Burun shipwreck (Tellefson, 2005; Stern *et al*., 2008).

Analyses were performed on a *Waters Alliance 2695* HPLC connected to a *Micromass Quatro Ultima* triple quad mass spectrometer. The HPLC was programmed with a flow rate of 0.2ml/min and an injection volume of 15µl. Two solvents were used as the mobile phase. Solvent A consisted of 0.1% formic acid in deionised water and solvent B was 100% acetonitrile. The HPLC was programmed with a solvent gradient as follows: five minutes isocratic solvent A at 100%; 10 minutes A/B 80/20 mixture; 15 minutes A/B 50/50. A five minute wash using 100% solvent A was added after each run to avoid any cross-contamination of samples within the column. The column was a *Phenomenex Synergi 4u fusion-RP 80-A* operating in reverse phase at a pressure of 63-73 bar.

The mass spectrometer used electrospray ionisation and was operating in negative ion mode. Conditions were optimised using repeated injections of standard solutions at 1µg/ml and were as follows: capillary voltage 2.44-2.52kV, collision energy 15V, source temperature 100°C, desolvation temperature 360°C, cone voltage 99V. The mass spectrometer was set up to scan for the molecular ion of L-tartaric acid at *m/z* 149 and a stable daughter ion at *m/z* 87, scanning 3458 scans in 30 minutes. The limit of detection (LOD) was determined by running standard solutions of decreasing concentration. For this analysis the LOD was 0.01µg/ml.

5.1.v Compound specific stable isotope analysis

5.1.v.a Sample preparation

For compound specific stable isotope analysis absorbed residues were extracted as described above (p109-110) with the exception that the target weight for sherd powder used was between 0.2g and 0.5g. This limited the number of samples which could be analysed but produced a higher yield of residue giving a more accurate analysis (Stott, 2005, pers. comm.). For visible residues, a pin-head sized piece of the residue was used. Some samples were then saponified and methylated; others were subjected to methylation only (fig. 5.3). Which samples were saponified was determined by the results of GC-MS analysis.

An initial batch of ten samples was prepared using method A. The dry extracted residue or sample of visible residue was saponified by heating with 4ml 5% methanolic NaOH in a sealed tube for 2 hours at 70°C. After cooling the non-saponifiable fractions were then extracted with 3 aliquots 2ml hexane, evaporated to dryness and stored for future analysis as described above. The samples were then acidified with 6M HCl and the saponified fraction extracted as described above (p110-112). The saponified extracts, together with those extracts not saponified, were methylated by adding approximately 2ml 14% boron trifluoride-methanol complex (BF_3) to each sample and heating in a closed vial for 1 hour at 70°C. After cooling the fatty acid methyl esters (FAMES) were extracted with 3 aliquots 2ml hexane and evaporated to dryness.

A sample was taken for GC/GC-MS analysis to check the methylation procedure and produce a GC chromatogram for sending with the samples. 100µl DCM was added to each sample and shaken gently to ensure the FAMEs had dissolved. A 20µl portion was then extracted to use for GC/GC-MS. Both portions of the samples were blown to dryness and stored in a freezer at -20°C until used for analysis.

When fatty acids are methylated a carbon atom of unknown $\delta^{13}C$ value is added to each molecule and a correction has to be made for this. To work out this correction for the first batch of samples, FAMEs of palmitic and stearic acid standards were prepared and sent with the samples for analysis by GC-C-IRMS. The carbon stable isotope values of multiple samples of the unmethylated standards were measured by bulk stable isotope analysis. The correction required can then be calculated and the applied to each sample by using the equation:

$$\partial^{13}C_{FA} = \frac{((n+1)(\partial^{13}C_{FAME})) - \partial^{13}C_{BF_3\ MeOH}}{n}$$

where $\delta^{13}C_{FA}$ is the corrected value for the fatty acid, *n* is the number of carbon atoms in the fatty acid chain, $\delta^{13}C_{FAME}$ is the value for the free fatty acid and $\delta^{13}C_{BF3MeOH}$ is the correction factor for the carbon added during derivatisation (Woodbury *et al*., 1998 citing Jones *et al*., 1991; Copley *et al*., 2005).

Method A produced samples which contained a white powder, probably sodium hydroxide residue from the saponification. After some consultation with the analyst a less vigorous method (method B) was developed for archaeological

samples (Stott, 2006, pers. comm.) and all further archaeological samples were prepared using this method. Concern was also raised about transesterification taking place during saponification resulting in the production of methyl esters. The process is shown in figure 5.1 and the results had been observed after saponification both during a previous study (Steele, 2004, figs. 55, 77) and during the course of this study (Chapter 7, p233-234). If significant amounts of methyl esters are produced this will introduce carbon atoms of unknown and unquantifiable $\delta^{13}C$ value into some FAME molecules, potentially affecting the measured $\delta^{13}C$ values. After consultation with several researchers using this technique, method B was also adapted to take account of this problem (Berstan, 2006, pers. comm.; Bull, 2006, pers. comm.).

The procedure for method B was essentially the same as that for method A, the main differences being in the concentration and composition of the reagents, the quantities used and the time of heating. Saponification was carried out using 0.5M aqueous methanolic (1:9 v/v) NaOH (Berstan, 2006, pers. comm.; Bull, 2006, pers. comm.; Stott, 2006, pers. comm.). Heating was carried out for one hour only (Stott, 2006, pers. comm.). Acidification was carried out with 2ml 0.5M HCl. Extraction was performed with hexane as above. Methylation was carried out using about six drops BF_3 and heating for 20 minutes. After heating, a few drops of deionised water was added to quench the reaction (Stott, 2006, pers. comm.). Extraction of methyl esters was carried out using hexane as above.

The correction for modern carbon added during methylation was carried out by analysing a sample of the BF_3 methanol complex with the samples. This is a more accurate way of measuring the correction required than that described in method A. This can then be incorporated into the equation above to correct each sample.

5.1.v.b GC-C-IRMS analysis

GC-C-IRMS analyses were carried out at the *NERC* Stable Isotope Facility at the Centre for Environment and Hydrology at Lancaster University. Analyses were carried out using an *Agilent 6980* GC connected to a GV Instruments Isoprime mass spectrometer via a platinum/copper oxide combustion furnace. The GC was fitted with a 50m, 0.32mm inside diameter column with 0.25µm coating of CP-WAX52 (carbowax equivalent). Helium was used as the carrier gas. The GC oven was programmed as follows: 50°C isothermal for 5 minutes, 50° - 170°C at 10°/min, 170° - 300°C at 3°/min, 300° - 320°C at 15°/min, isothermal at 320°C for 15 minutes. The furnace was heated to 850°C with an interface temperature of 300°C. Post combustion water was removed by a water permeable nafion membrane.

Six pulses of carbon dioxide of known isotopic composition were fed into the ion source from a reference gas injector box during each run. A methyl ester standard of $C_{16:0}$ and $C_{18:0}$, of known isotopic value, was run prior to each batch of analyses to ensure that the combustion furnace and instrument were

functioning correctly. The standard deviation of the standard fatty acid methyl ester mixture was better than or equal to 0.3‰ for all analyses.

5.1.vi Fourier Transform Infra-Red Spectroscopy

One visible residue from a previous study was examined using FT-IR. No sample preparation was required. The analysis was carried out on a *Digilab UMA400* IR microscope operating in the contact APR mode. Spectra were recorded in transmittance mode and results converted to absorbance *vs* wavelength plot using the Digilab software.

5.2 Pottery Analysis

Although the main focus of this study was the contents of RLWm ware vessels, selected examination of the pottery fabric was carried out. This ware was widely imitated during the LBA and local wares from sites in Turkey and Cyprus can appear very similar. Examples of this are shown in figure 5.4 which shows one RLWm ware sherd and two sherds of similar appearance but with different chemistry and mineralogy from Boğazköy in Turkey. It was therefore important to confirm as far as possible that all the samples identified as RLWm ware were part of that fabric group.

Some samples used in this study had already been examined using thin section analysis and neutron activation analysis (NAA) (Schubert & Kozal, 2007, Knappett *et al*., 2005). The thin sections from the study by Knappett *et al*.

(2005) were available for further examination and permission was also given to use the raw NAA data from the same study (Knappett *et al*., 2005: Kilikoglou, 2007, pers. comm.). Both were re-examined during the course of this study.

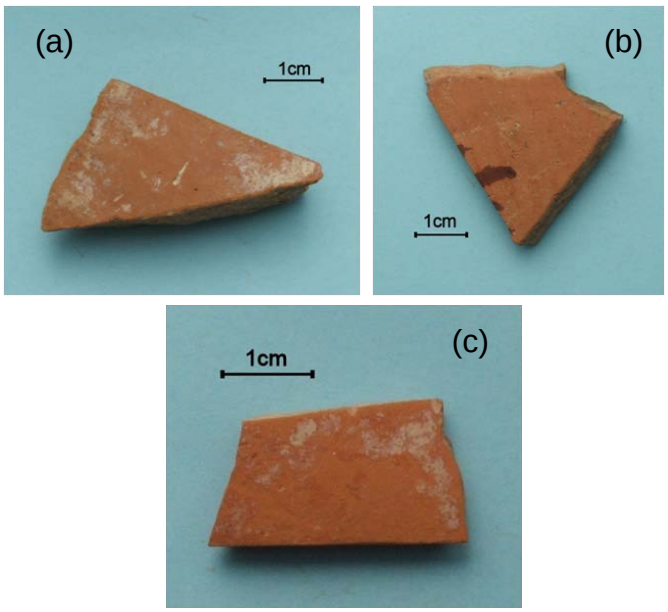


Figure 5.4: Examples of local and RLWm ware sherds from Boğazköy. (a) and (b) show samples of two local fabrics (sherds 35 and 37) while (c) is a classic RLWm ware (sherd 16).

A petrographic microscope was used to re-examine the thin sections available in both plane polarized light and between crossed polarizers. The purpose of this examination was not a full fabric description as this had already been carried out (Knappett *et al*., 2005). However very few photographs are available of RLWm ware in thin section and one aim was to become familiar with the petrographic features exhibited by this ware. A further aim was to look for any features not reported by Knappett *et al*. (2005) and record them photographically for future reference.

Thin section analysis of pottery using petrographic techniques allows identification of mineral and other inclusions and gives information on their size, distribution, shape and orientation within the ceramic matrix (Rice, 1987, 376-382). It also provides information about the coarseness of ceramic fabrics, the nature, shape and distribution of voids within the fabric, the degree of firing and some information about the clay minerals that make up the ground mass (Rice, 1987, 382, 379). It can also reveal the presence of slips, glazes, paints and surface treatments (Rice, 1987, 382) and may even provide information on the manufacturing process as revealed by the shape and alignment of voids and inclusions (Rice, 1987, 380).

NAA analysis measures the concentrations of trace elements within a ceramic sample, thus creating a “chemical fingerprint” of each sherd analysed (Pollard *et al*., 2007, 123; Pollard & Heron, 2008, 50-51). However, with the possibility of measuring up to 40 – 50 elements simultaneously (Pollard *et al*., 2007, 132), the data sets created by this type of analysis are large and require further manipulation to provide information about the ceramics under examination. The NAA data on sherds from this study were re-analysed using both scatter plots, which compare two elements, and principal component analysis which allows the variation in multiple elements to be analysed simultaneously.

Principal component analysis is a useful tool for processing large data sets as it reduces the variation in a large group of variables to a much smaller number of variables while retaining as much of the original information as possible (Shennan, 1997, 265-267, 297-298; Baxter, 2001). It is one way of extracting

information from large data sets which are not otherwise amenable to straightforward interpretations (Shennan, 1997, 297). This further analysis also allowed results from the study by Schubert and Kozal (2007) to be compared with the results of Knappett *et al.* (2005).

As not all samples had undergone elemental analysis a few sherds were examined using laser ablation inductively coupled plasma induction-mass spectrometry (LA-ICP-MS). This was designed to identify any sherds which were potentially different to the bulk of RLWm ware. RLWm ware fabric is remarkably consistent in both its elemental composition and mineralogy (see chapter 2, section 2.3.iii). However it is also clear that the ware was widely imitated in the Late Bronze Age (Eriksson, 1993, 157-159; Knappett *et al*., 2005). Some of the samples examined for residues during this study had not been analysed by either NAA or thin section analysis therefore a few of these were submitted to elemental analysis by LA-ICP-MS. One sherd in particular, the only sherd from Myrtou-*Pigadhes*, appeared different to classic RLWm ware on visual examination. It was felt important to check whether this sherd actually came from an RLWm ware vessel, especially as little is known about its exact provenance (chapter 4, p77-78).

ICP-MS measures the concentrations of up to 70 elements within a sample (Pollard *et al.* 2007, 199) and is a fully quantitative technique (Pollard *et al.* 2007, 205-207). However it requires a liquid sample and dissolving ceramic requires digestion in hydrofluoric acid (Pollard *et al*., 2007, 196-197, 337-338) which was beyond the scope of this study. Laser ablation allows the analysis of

solid samples although this means that only semi-quantitative data can be collected (Pollard *et al.* 2007, 197-199). However LA-ICP-MS can be used to establish differences or similarities between samples run on the same day. By combining unknown sherds with those already identified as classic RLWm fabric by other methods any significantly different samples can be identified.

Tables 5.1a and b summarise the analytical procedures carried out on all samples.

5.2.i Re-examination of thin sections

Examination was carried out on a *Nikon Optiphot2* binocular petrographic microscope using both plane polarized light and crossed polarizers. Photographs were captured using an *E-REC Electronics EPS-145CF* camera and *Fire-i* software version 3.5.0.1.

5.2.ii Neutron Activation Analysis Data Manipulation

Neutron Activation Analysis had been carried out on 95 samples of RLWm ware and related wares from seven sites across the eastern Mediterranean (Knappett *et al*., 2005). Thirty eight of these were analysed for residues during this study and 40 had been examined during a previous study (Steele, 2004). The concentrations of 22 elements – Sm, Lu, U, Yb, As, Sb, Ca, Na, K, La, Ce, Th, Cr, Hf, Cs, Tb, Sc, Rb, Fe, Ta, Co and Eu – were measured.

Firstly the data from all seven sites was combined to give a comprehensive view of the elemental composition of RLWm ware as a whole rather than examining its characteristics site by site as in the original study (Knappett *et al*., 2005). This data was then re-examined using *Microsoft Excel 2002 SP3* to create scatter plots of pairs of elements and *SPSS 13.0* to produce a synthesis of the data by principal component analysis. For the principal component analysis only six elements were used in each of the two analyses. Many of the 22 elements measured showed very little variation as revealed by their very low standard deviations. Omitting these elements from the analysis still retains the majority of the information about variability in the samples but reduces the data handled by excluding from the data set results which show very little variation. However the first attempt at this selection process included elements like sodium and calcium which are not considered reliable indicators of ceramic variability due to their potential alteration in the burial environment (Jones, 1986, 33-38; Pollard & Heron, 2008, 126-129). The elements included in the final analysis were therefore the elements with the highest variability as determined by their variance which are also considered reliable in the analysis of pottery fabrics (Jones, 1986, 33-38).

5.2.iii Laser Ablation Inductively Coupled Plasma-Mass Spectrometry

Eleven sherds were analysed: five already identified by NAA and thin section analysis as classic RLWm ware and six which had been identified by archaeologists as RLWm ware but had not been subject to elemental analysis.

5.2.iii.a Sample preparation

Very little sample preparation was required. A fresh surface is required for LA-ICP-MS to measure the elemental composition of the actual fabric rather than any surface contamination. This was achieved either by using an area recently drilled for residue extraction or by breaking off a small piece of the sherd for analysis using a pair of pliers.

5.2.iii.b LA-ICP-MS analysis

The ICP-MS was a *Thermo PlasmaQuad 3* linked to a *Microprobe II Nd:YAG* UV (266nm) laser ablation system. The laser ablation was set to raster across the sample in a continuous mode with a spacing of 120µm. The laser was used at 75% energy (3MJ) at a scan speed of 30µms^{-1} with a spot size of 50µm and a depth of 5µm. Two standards (NIST611 and NIST613) were run at the beginning and end of the analysis to check the calibration. Seventy one elements were measured (Li, Be, B, Na, Mg, Al, Si, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Td, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U). The results were processed using *SPSS 13.0* to produce a principal component analysis of the data to distinguish any differences or similarities between already identified RLWm ware sherds and the other samples.

5.3 Estimation of vessel volumes

The size of a vessel often has a direct bearing on the type of contents stored or traded in that vessel. Small vessels are used for precious commodities supplied in small amounts while staple food stuffs might be transported or stored in much larger quantities. Some general information on the type of commodities might have been transported in RLWm ware vessels could therefore be obtained by examining the capacities of some of those vessels. The three most common forms of RLWm ware vessels – the spindle bottle, the pilgrim flask and the arm-shaped vessel – vary quite considerably in their dimensions (Eriksson, 1993, Catalogue). In addition only one record could be found of volumetric measurements on RLWm ware vessels. In this case the volumes of an unspecified number of vessels from Kalavasos had been measured. Specific results for very large pilgrim flasks from one tomb (5.5 litres) are recorded with other vessels being characterised as smaller than this (South & Steel, 2007).

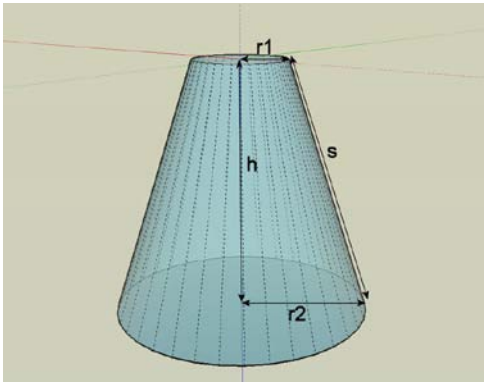
No access could be gained to complete vessels in order to measure their volumes so a method of estimating the capacities of vessels from scale drawings and photographs was adopted to calculate the volume of a few of each type of vessel (Ericson & Stickel, 1973; Rice, 1987, 220-221; Senior & Birnie III, 1995). This, while not very accurate, did allow an approximate measure of the capacities of each form of RLWm ware vessels to be established (Ericson & Stickel, 1973; Rice, 1987, 220-221; Senior & Birnie III, 1995).

For these estimations a spindle bottle was treated as a conical frustum with an inverted spherical segment on top, a pilgrim flask as two spherical segments joined together and an arm-shaped vessel as a conical frustum. Measurements were taken from scale drawings in Eriksson (1993) and South and Steel (2007) along with a photograph of a spindle bottle in the Royal Albert Memorial Museum in Exeter during a previous study (Steele, 2004, figs. 2, 5). South and Steel (2007) had recorded their drawings as being at a scale of 1:4 and this was accepted as accurate. Eriksson (1993) recorded no scale for any diagrams but her catalogue contains measurements for many of the examples depicted. Unfortunately some of these drawings did not exhibit the same scale in all dimensions and had to be dismissed as inaccurate, but some did relate accurately to the measurements supplied in the catalogue and the examples used were selected from these. The example from Exeter was measured before photographs were taken and any further measurements required were calculated by measuring the photograph and scaling accordingly.

The equations used for the volume calculations were taken from Råde and Westergren (1988). There is some disagreement between different sources on how to calculate the volume of a spherical section which is further complicated by the different labelling systems used to describe radii, heights, angles etc. (Ericson & Stickel, 1973; Rice, 1987, 221; Råde & Westergren, 1988, 52). For this exercise the Råde and Westergren equation was used.

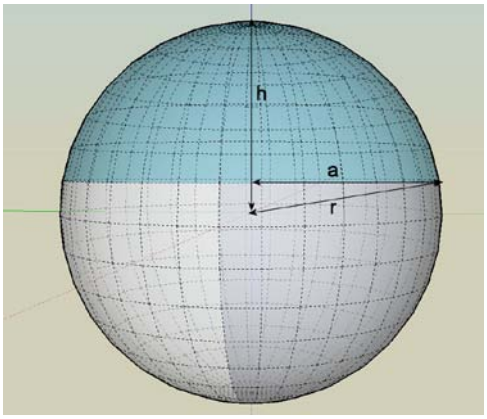
Conical frustum:

$$V = \frac{\pi h}{3}(r_1^{\,2} + r_1 r_2 + r_2^{\,2})$$



Spherical segment:

$$V = \frac{\pi}{3}h^2(2r - h) \quad \text{or} \quad V = \frac{\pi}{3}ha^2$$



Site	Sherd number	GC	GC-MS	Saponification + further GC-MS	Residue identified	Alkaline extraction of extracted residue + GC	HPLC-MS-MS	GC-C-IRMS	Thin sections available for re-examination	NAA data re-examined	LA-ICP-MS
Arpera, Cyprus	1	Y	N	N	N	N	N	N	N	N	N
	2	Y	I&E	N	I&E(tr)	N	N	N	N	N	N
	3	Y	I	N	I	Y	N	N	N	N	N
	4	Y	Y	N	I	N	N	N	N	N	N
	5	Y	N	N	N	N	N	N	N	N	N
	6	Y	I	N	I	N	N	N	N	N	N
	7	Y	I	N	I	N	N	N	N	N	Y
	8	Y	I&E	N	E	N	N	N	N	N	N
	9	Y	N	N	E	N	N	N	N	N	Y
	10	Y	I	N	N	N	N	N	N	N	Y
Bogazköy, Turkey	11	Y	N	N	N	N	N	N	Y	Y	N
	12	Y	N	N	N	N	N	N	Y	Y	N
	15	Y	N	N	I	N	I	N	Y	Y	N
	16	Y	N	N	I	N	N	N	Y	Y	N
	18	Y	N	N	N	N	I	N	Y	Y	N
	20	Y	N	N	N	N	I	N	Y	Y	N
	21	Y	N	N	I&E	N	N	I	Y	Y	N
	22	Y	N	N	N	N	N	N	Y	Y	N
	23	Y	N	N	I	N	N	N	Y	Y	N
	24	Y	N	N	E	N	N	N	Y	Y	N
	25	Y	N	N	I(tr)	N	N	N	Y	Y	N
	26	Y	N	N	I	N	N	N	Y	Y	N
	28	Y	I	I	I	N	N	I	Y	Y	N
	29	Y	I	I	I	N	N	I	Y	Y	N
	32*	Y	N	N	I	N	N	N	N	Y	N
	33*	Y	N	N	N	N	N	N	N	Y	N
	34*	Y	I	I	I	N	N	I	N	Y	N
	35*	Y	N	N	N	N	N	N	N	Y	N
	36*	Y	N	N	I	N	N	N	N	Y	N
	37*	Y	N	N	I	N	N	N	N	Y	N
	38*	Y	I	N	I	N	N	N	N	Y	N
	39*	Y	I	N	I	N	N	N	N	Y	N
	40*	Y	N	N	I	N	N	N	N	Y	N
	41	Y	N	N	N	N	N	N	N	Y	N
	42$	N	N	N	N	N	N	N	N	Y	N
Dhenia, Cyprus	1	Y	I	N	I	I&E	N	N	N	N	Y
Enkomi, Cyprus	1	Y	I	N	N	N	N	N	N	N	N
	2	Y	N	N	E	N	N	N	N	N	N
Hala Sultan Tekke, Cyprus	1	Y	I	N	N	N	N	N	Y	Y	N
	2	Y	I	N	I	N	N	N	Y	Y	Y
	3	Y	I	N	I	N	N	N	Y	Y	N
	4	Y	I	N	I	N	N	N	Y	Y	N
	5	Y	I	N	I	N	N	N	Y	Y	N
	6	Y	I	N	I	N	N	N	Y	Y	N
	7	Y	N	N	US	I&E	N	N	N	N	N
	8	Y	N	N	US	I&E	N	N	N	N	N
	9	Y	I	N	I	I&E	N	N	N	N	N
	10	Y	N	N	US	I&E	N	N	N	N	Y
	11	Y	I	N	I	I&E	N	N	N	N	N
	12	Y	N	N	US	I&E	N	N	N	N	N
	13	Y	N	N	US	I&E	N	N	N	N	N
Kalavassos, Cyprus	1	Y	I	N	N	N	N	N	Y	Y	N
	2	Y	I	N	N	N	N	N	Y	Y	N
	3	Y	E	N	E	N	N	N	Y	Y	Y
	4	Y	I	N	I	N	N	N	Y	Y	N
	5	Y	N	N	N	N	N	N	Y	Y	N
	6	Y	I	N	N	N	N	N	Y	Y	N
	7	Y	I	N	N	N	N	N	Y	Y	N
	8	Y	I	N	I	N	N	I	Y	Y	N
	9*	Y	E	N	N	N	N	N	Y	Y	N
	10	Y	N	N	N	N	N	N	Y	Y	N
Kazaphani, Cyprus	4	Y	I	N	I&E(tr)	N	N	N	Y	Y	N
	5	Y	N	N	I	N	N	N	Y	Y	N
	6	Y	I	N	N	N	N	N	Y	Y	N
	7	Y	N	N	E	N	N	N	Y	Y	N
	10*	Y	I	N	I	N	N	N	Y	Y	N
Kouklia, Cyprus	2$	N	N	N	N	N	N	N	Y	Y	N
	3	Y	N	N	N	N	N	N	Y	Y	N
	5	Y	N	N	N	N	N	N	Y	Y	N
Kuşakli, Turkey	1	Y	I	N	I	N	N	N	N	Y#	N
	2	Y	N	N	I	N	N	N	N	Y#	N
	3	Y	I	N	I	N	N	N	N	Y#	N
	4*	Y	I	N	I	N	N	N	N	N	N
Myrtou-*Pigadhes* , Cyprus	1	Y	I&E	N	N	N	N	N	N	N	Y
Tel-Tweini, Syria	1	Y	I	N	I	N	N	N	N	N	N

Table 5.1a: Details of analyses carried out on all sherds during this study. Y – analysis carried out; N – analysis not carried out; I – interior surface; E – exterior surface; tr – trace; US – results unusable due to equipment failure; * - not RLWm ware; $ - sherd too small to analyse for residues; # - analysis carried out by Schubert and Kozal (2007) and results compared with this study.

Site	Sherd number	Residue detected during previous study	GC-MS	GC-C-IRMS	HPLC-MS-MS	Thin section available for re-examination	NAA data re-examined	LA-ICP-MS
Bogazköy, Turkey	1	(E)	N	I	N	Y	Y	N
	2	E	N	N	I	Y	Y	N
	3	I	N	N	N	Y	Y	N
	4	I	N	N	N	Y	Y	N
	5	I	N	N	N	Y	Y	N
	6	I	N	N	I	Y	Y	Y
	7	I	N	N	N	Y	Y	N
	8	N	N	N	N	Y	Y	N
	9	N	N	N	I	Y	Y	N
	10	I	N	N	N	Y	Y	N
	13	I	N	N	N	Y	Y	N
	14	N	N	N	N	Y	Y	N
	17	I	N	N	I	Y	Y	N
	19	E	N	N	N	Y	Y	N
	27	N	N	N	I	Y	Y	N
	30	I	N	N	N	Y	Y	N
Kazaphani, Cyprus	1	N	N	N	I	Y	Y	N
	2	I	N	N	I	Y	Y	Y
	3	E	N	N	N	Y	Y	N
	8	N	N	N	N	Y	Y	N
	9	N	N	N	N	Y	Y	N
Kilise Teppe, Turkey	36	N	N	N	N	Y	Y	N
	37	N	N	N	N	Y	Y	N
	43	N	N	N	I	Y	Y	N
	44	NA	N	N	N	Y	Y	N
	201	N	N	N	I	Y	Y	N
	202	N	N	N	N	Y	N	N
	203	N	N	N	I	Y	N	N
	204	N	N	N	I	Y	Y	N
	205	I	I	I	N	Y	Y	N
	206	I	I	I	N	Y	N	N
	207	NA	N	N	N	Y	N	N
	208	N	N	N	N	Y	N	N
	5501	I	N	N	I	Y	Y	N
Kouklia, Cyprus	1	I	I	N	I	Y	Y	Y
	4	I	N	N	N	Y	Y	N
	6	I	I	I	N	Y	Y	N
Saqqara, Egypt	2	I	N	I	N	Y	Y	N
	3	I	N	N	N	Y	Y	N
	4	I	N	N	N	Y	Y	N
	5	I	N	N	N	Y	Y	N

Table 5.1b: Details of further analyses carried out on sherds examined during previous studies (Steele, 2004; Knappett *et al*., 2005). Y – analysis carried out; N – analysis not carried out; NA – not available for residue analysis; I – interior surface; E – exterior surface.