AMERICAN UNIVERSITY OF BEIRUT

# ORGANIC RESIDUE ANALYSIS OF BEIRUT AMPHORAE BY CHEMICAL ANALYTICAL TECHNIQUES

by

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# AN ABSTRACT OF THE THESIS OF

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Amphorae are transport containers that were used during antiquity for long-distance, seaborne trade. While the general types of goods transported in this group of vessels has been established, the original content of specific classes of amphorae is still poorly understood. In order to improve our understanding of inter-regional economics during antiquity, the determination of what goods were being traded to where (i.e. the original content of amphorae) is necessary.

Chromatographic methods, most notably that of Gas Chromatography (GC) coupled with Mass Spectrometry (MS), allow for the molecular-level identification of complex organic samples and are the analytical methods of choice in organic residue analysis. Current GC/MS methodologies have proven successful in analyzing organic residue absorbed in the bodies of ceramic vessels. The initial process involves testing for tartaric acid as an indicator of wine (as well as other carboxylic acids specific to grape and/or fermented products). It is generally believed that the "Beirut amphora" contained wine, the purpose of this project is to attempt to establish this empirically.

CONTENTS

Appendix

# FIGURES

# TABLES

# CHAPTER 1

# INTRODUCTION

Until the rather recent introduction of analytic chemistry techniques in the analysis of amphorae, direct evidence for the contents of amphorae has been sparse, primarily limited to the association of amphorae in areas with archaeological features that evidence the manufacture of a particular good (e.g. wine or oil presses) and a few instances in which amphorae were recovered with identifiable remnants of their contents, almost exclusively in maritime contexts (e.g. the Ulu Burun).[1] The contents of amphorae from various geographic areas during the Classical period has been primarily based on a combination of literary and epigraphic sources.

The purpose of this thesis is to investigate samples of Beirut "main series" amphorae dating between the 1st and 4th c. AD by chemical analytical techniques in order to determine the primary contents of this amphora form and, if possible, gain additional insight into the use and reuse patterns of locally manufactured amphorae in their home market. To approach this subject matter, it is first useful to review what is known from the classical corpus, found primarily in the Roman authors such as Pliny and Columella, as to the practices of amphora use both with respect to common contents and amphora lining practices. This review will help establish what the nature of probable contents and linings that will aid characterization by the employed analytical techniques. After having reviewed the classical literary material, the results of previous analytical studies of amphorae will be reviewed. Previous studies give illustrate the various analytical techniques that have been used to characterize absorbed residue in amphorae as well as indicating the current level of research. Finally, the characterization technique for the Beirut samples are outlined and the samples analyzed.

[1] Pulak 1998.

# CHAPTER 2

# CLASSICAL CORPUS AND COMMON AMPHORA CONTENTS

## 2.1 Resin and Its Products

Much of the evidence of amphorae with respect to wine and oil (see Chapters 2.2 and 2.4) in the classical corpus is made with concern to the pre-storage preparation of the vessel interior. It is useful to first review resin, its products, as well as other plant exudates used for preparing ceramic vessels for the storage of a particular good as well as its use in wine production and preservation. Resins represent the compounds from the terpenoid family, which includes more than 23,000 different organic compounds, and serve as plant exudates, protecting a damaged plant from "excess water loss and invasion of microorganisms."[1] As such, terpenoids are secondary products of plants; that is, they are not involved in plant metabolism but rather have specific functions and are generally present in small quantities.[2]

### *2.1.1 Sources of Resin*

Resin (*resina*) is derived primarily from conifers.[3] In the eastern Mediterranean, Meiggs argues that pines would have been the principal producers of resin, the most common being the coastal pine (*Pinus halepensis* or *brutis*) and the mountain pine (*Pinus laricio* or *nigra*).[4] The Syrian Fir (*Abies cilicica*) is native to Syria-Palestine and Turkey and shares the cedar's (*Cedrus libani*) preference for moderately high altitudes (1200 m to 2000 m). The degree to which *A. cilicica* was common in the Levant during antiquity and how frequently it may have been utilized as a source of resin is not known. The use

[1] Pollard and Heron 1996, 240.

[2] Pollard et al. 2006, 153.

[3] Meiggs 1982, 468.

[4] Meiggs 1982, 469.

of cedar (*C. libani*) as a resin source (especially for the production of pitch) is mentioned once by Pliny but its use as a resin source in antiquity is debated.[5]

The primary non-coniferous resin producing species native to the eastern Mediterranean are members of the *Pistacia* genus. *P. atlantica* (also erroneously referred to as *P. terebinthus*) enjoys a wide geographical distribution–from the Canary Islands and north Africa east to Egypt, the whole of the Near East and extending as far as the Transcaucasia and Afghanistan to the north and north-east, respectively.[6] *P. lentiscus* produces a more liquid resin and is particularly associated with the island of Chios where the product is referred to as mastic and remains the only place where mastic is currently produced.[7]

Recent studies have shown that *Pistacia* resin had been traded since at least the Late Bronze Age for aromatic and medicinal purposes. The Egyptian name for a particular type of incense, 'sntr', previously identified as myrrh, has been determined instead to be *Pistacia* sp. resin.[8] The contents aboard the 13th century B.C. Ulu Burun wreck included a significant amount of *Pistacia* resin, transported as a commodity itself in Canaanite jars.[9] The resin of *Pistacia* was used by the Romans as well—Pliny the Elder comments upon its use as, amongst others, a sealant, although the use of Pistacia resin as an amphora sealant is rarely observed in analytical studies.[10]

### *2.1.2 Extraction of Resin and Production of Pitch*

The words used to describe heated resin products (e.g. pitch, rosin, tar) and even the term "resin" itself have been used in various and, at times, seemingly interchangeable capacities.[11] This problem of terminology is not new; in Latin *pix* is frequently used to de-

[5]Pliny Nat. 14.25.7; Serpico and White 2000a, 431.

[6]Meiggs 1982, 469; Mills and White 1977, 38. Concerning the misidentification of members of the *Pistacia* genus, see Serpico 2000.

[7]Dioscorides 70 from Meiggs 1982, 469; Serpico 2000, 434.

[8]Serpico and White 2000b.

[9]Stern et al. 2008. The probable destination of the Ulu Burun ship was the Aegean, although the use of *Pistacia* resin during the Late Bronze Age in the Aegean is not well understood.

[10]Pliny *NH 14.25.20;* Heron and Pollard 1988, 435.

[11]Serpico 2000, 450.

scribe both the liquid exudate extracted from resiniferous plants and that which has been processed by exposure to heat. To prevent terminological confusion, "resin" is herein used to refer to the raw viscous liquid exudate from resiniferous plants representing a complex mixture principally composed of water, volatile terpenes (referred to as "turpentines") and higher, non-volatile terpenes. Rosin is a solid at room temperature and is derived by heating resin to a moderate temperature, resulting in the loss of the water and volatile constituents.[12] Pliny describes that resin may be harvested by tapping a resiniferous tree by means of cutting incisions in the bark near the tree's base and collecting the exuded resin.[13] Theophrastus reports that this technique is used for extracting resin from conifers.[14] This practice has been documented to be still used for commercial mastic production on Chios.[15]

Pitch, an intermediary product between unprocessed resin and solid rosin, is dark in color and highly viscous at room temperature. Pitch is produced by pyrolysis (destructive distillation) by which resin or the resiniferous source material is heated to high temperature (approximately 350 °C) in an open-air environment.[16] Increasing the length of time the material is exposed to distillation temperature results in a thicker and more aromatic pitch.[17] Theophrastus describes that resiniferous logs are arranged in a pile with an open space in the center on sloped ground. Once the pile is constructed, it is covered with earth to control the temperature of the fire and set alight. The pitch flows from the fire (by virtue of the pile having been constructed on sloped ground) and is collected. This technique is said to be used by the Macedonians and Syrians.[18] Pliny also describes the same technique and notes that the pitch that flows first from the fire is

[12]Serpico 2000, 450. Concerning the boiling points of principal pine resin constituents, see Loewen 2005.

[13]Pliny *NH* 16.23.57.

[14]Theophrastus 9.2.

[15]Serpico 2000, 434.

[16]Serpico 2000, 450; Heron and Pollard 1988, 433.

[17]Heron and Pollard 1988, 433.

[18]Theophrastus 9.3.

lighter in color and lower in viscosity than that which is recovered later.[19]

Pliny states that in Europe tar (*pix liquida*) is extracted from a tree called the torch-pine (*taeda*) by heating the felled tree in an oven and is used for the coating of the tackle of ships, among other uses.[20] The liquid that is first extracted "flows like water through a pipe" and is called Cedar juice (*cedrium*) in Syria.[21] The liquid that follows is thicker and is used to produce pitch (*picem*).[22] This liquid is collected into cauldrons and is thickened by the addition of vinegar and is known as Bruttian pitch.[23] It is only useful for dolia and vasae, differing from other pitches by its viscosity, reddish color and greasy nature, but is also used to flavor wine after having been dried and pulverized.[24] "Distilled pitch" (*stillaticia*) is produced by the addition of water to the above and gentle boiling and then strained off.[25] On extracting from trees which produce pitch, an opening is made in the tree on the side facing the sun by removing the bark (not incision), establishing an exposure of, at most, two feet.[26] This process is repeated elsewhere on the tree when the previous opening ceases to produce liquid. Subsequently, the tree is felled and the timber burnt. According to Pliny, in Syria terebinth is treated in the same fashion, as is the larch in Macedonia.[27]

## 2.2 The Relationship of Resin Products and Wine

Considerations on the different kinds of wine and their relative quality features frequently in the works of the classical corpus. For instance and of particular interest, Pliny notes the wines from Beirut, Tripoli and Tyre to be held in esteem, although cat-

[19]Pliny *NH* 16.21-22.
[20]Pliny *NH* 16.21.52.
[21]Pliny *NH* 16.21.52.
[22]Pliny *NH* 16.22.53.
[23]Pliny *NH* 16.22.53.
[24]Pliny *NH* 16.22.53.
[25]Pliny *NH* 16.22.54.
[26]Pliny *NH* 16.23.57.
[27]Pliny *NH* 12.23.58-59.

egorized below some of the famous wines of Asia Minor, such as those of Chios and Lesbos.[28] The manner in which wine is made, stored and transported, however, appears to have been of considerably less interest as references to such matters are significantly less frequent.

Of the sparse commentary upon amphorae and their contents, wine is the good most commonly mentioned by authors in the Classical corpus. The most lengthy extant accounts are given by Pliny and Columella. The primary concern of both authors is that of preservation, accomplished by the application of pitch to the interior of the storage vessel. Columella states that vessels for the storage of wine should be treated with pitch (*picanda*) 40 days before being filled with wine and that the process is necessary for preserving the wine stored within.[29] Pliny reckons the appropriate time for conditioning the vessels is immediately after the rising of the Dog-star.[30] Wine jars should never be filled to capacity and a layer of must (*defruto*) mixed with certain herbs should be applied to the surface of the wine.[31]

Vessels which stand above ground (*quae supra terram consistunt*), i.e. as opposed to those which have been sunk into the ground as semi-permanent installations, have their interiors lined with pitch by means of heating the vessel inverted over a fire until it is hot enough that it cannot be touched by hand before the pitch is introduced and the vessel rolled on its side in order to fully coat the interior and then inverted to reclaim the excess pitch.[32] Columella states that 25 Roman pounds of pitch was sufficient to line one and a half cullei (30 amphorae).[33]

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[28]Pliny *NH* 14.9.

[29]Columella *Rust.* 12.18.5; 12.28.3, respectively.

[30]Pliny *NH* 14.27. The rising of the Dog-star occurs during mid-August.

[31]Pliny *NH* 14.27.

[32]Columella *Rust.* 12.18.6. Columella instructs that vessels sunken into the ground should be heated with burning torches until the pitch (applied during a previous use of the vessel) has collected at the bottom of the vessel and then spread to coat the vessel walls with a wooden ladle and iron scraper then wiped with a brush. After which, new heated pitch is added to the vessel and distributed with a new ladle and broom. Columella *Rust.* 12.18.5-6.

[33]Columella Rust. 12.18.7. "Sunt autem satis sesquicullearibus doliis picis durae pondo vicenaquina." Provided that one Roman pound equals approximately 325 grams, approximately 0.25 kg of pitch would be used for the lining of each vessel. Heron and Pollard 1988, 434. Heron and Pollard's calculation of

Cato likewise comments that jars (*vasa*) and vats (*dolia*) for storing wine should be pitched before preparing the vintage.[34] Unlike Columella, Cato specifies resin (*resinam*) may be added to the maceration during the fermentation process. The resin should be ground to a powder and suspended in the maceration by means of a basket and periodically agitated in order to aid the resin's dissolving in the wine.[35] This application of resin appears to be for the purpose of flavoring or improving the quality of the resulting product as much as for the of preservation as it is mentioned by Pliny along with marble dust and boiled must as optional additives that embolden smooth wines.[36] Pliny does warn, however, that even if a wine is flavored with resin the pitching of its storing vessel is still necessary.[37]

### 2.3 Pitch as Preservative and Flavorant of Wine

Columella instructs the introduction of pitch during the cooking down of wine lees to serve as a preservative. Specifically, he advocates the use of liquid Nemeturican pitch (*picis liquidae Nemeturicae*) and terebinth resin (*resinae terebinthinae*).[38] Another method of must preservation involves the combination of liquid Nemeturican pitch that has been treated with lye-ash (*cineris lixiviae*) and a high quality pitch, Bruttian pitch is suggested as a high quality pitch.[39] Sea-water is added to the combination of pitches and the mixture is boiled until reduced to a third of its original volume.[40] Nemeturican pitch could also be used without amalgamation with another type of pitch but first, in order that

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0.4 kg appears to owe to an incorrect attribution of equivalence between Roman and modern (international avoirdupois) pounds.

[34]Cato *Agr.* 23.2, 25.1.

[35]Cato *Agr.* 23.2. The suggested quantity of resin is 3 Roman pounds to a culleus of maceration, equating to approximately 33 grams per amphora.

[36]Pliny *NH* 14.24.

[37]Pliny *NH* 14.24.

[38]Columella *Rust.* 12.20.3. The provenance of Nemeturican pitch is in the Ligurian Alps in north-west Italy, see Columella 12.24.1.

[39]The Bruttians lived in the south of Italy. Dionysius of Halicarnassus identifies Bruttian pitch as being a product of pines (*Antiq.* 20.5), while Pliny misidentifies it as coming from spruce (*picea*) (*NH* 14.127). Concerning the misidentification of *picea*, see Meiggs 1982, 422.

[40]Columella *Rust.* 12.22.

it be rendered fit for preserving wine, had to be boiled with sea water. Afterward, once the pitch had separated from the water, the pitch could be separated, dried and added to wine after completion of the second fermentation.[41]

Pitch could also be added during the wine fermentation process to serve as a post-production preservative. Columella instructs that the people called the Allobroges, a people that inhabited modern Savoy, use a type of pitch called "bark-pitch" (*pix corticata*). This pitch dries hard and must be ground to powder. The pitch may be introduced as powder and mixed into the maceration after fermentation has ceased the second time but not more than 14 days before the termination of fermentation.[42]Pliny notes that pitch (*picis*) may be added to wine during the first fermentation so that the pitch's scent and aspects of its piquant flavor may be conferred to the wine.[43] The "raw flower of resin" (*crudo flore resinae*) is noted as a more effective means of achieving the same result.[44] In either case, the additive serves to enliven a wine that is dull in character or, alternatively, to temper a wine that is too harsh and, according to Pliny, is a practice common with wines made in northern Italy.[45] Of plants that produce resin, Pliny notes the finest is produced by the terebinth (*terebinthi*), especially from the regions of Cyprus and Syria, followed by that of the lentisk, or gum mastic (*lentisci*).[46] Pliny continues to list several other resins of lower quality from Arabia and Palestine.[47] The most highly esteemed pitch is from the Brutti; pitch obtained from the Spanish pine is poor in quality, bitter and dry.[48]

Pliny relays a statement that Chian mastich exudes from the lentisk "like a sort of gum" (*cummium modo*) and that, in the same way as frankincense may be amalga-

[41]Columella *Rust.* 12.24.1-3. The ratio specified is two cyathi of pitch to 48 sextarii of maceration, or approximately 1:374.

[42]Columella *Rust.* 12.23.1-2. Columella specifies the pitch/maceration ratio as a sextarius and half an ounce to 55 sextarii, or approximately 1:55.

[43]Pliny *NH* 14.25.124

[44]Pliny *NH* 12.25.124. Apparently, flower of resin is resin secreted by a tree as found on its bark and is also referred to as 'white resin' (*resinae albae*), Pliny *NH* 16.22.55.

[45]Pliny *NH* 12.25.124. Specifically, in Liguria and the areas around the river Po.

[46]Pliny *NH* 12.25.125. Identified as *Pistacia terebinthus* and *Pistacia lentiscus*, respectively.

[47]Pliny *NH* 14.25.

[48]Pliny *NH* 14.25

mated with other less precious resins to increase its weight, it is adulterated with resin (*adulteratur ut tura resina*).[49]

## 2.4 Olive Oil

Like that of wine, concerning olive oil and storage vessels, the focus of the classical authors is primarily concerned on proper preparation of the vessel's interior. While vessels used for the storage of wine were frequently treated with pitch for preservation purposes, Columella states that vessels (*vasa*) for the purpose of storing olives (and implicitly olive oil as well) should be new and not treated with pitch (*sine pice praeparantur*).[50] The vessels, however, still require an internal conditioning in order that the oil, in which the olives are immersed, is not absorbed by the ceramic itself. Columella advocates that the vessels be treated in the same manner as olive-casks (*olivariae metretae*), that is, soaked with liquid gum (*liquida gummi*) and dried.[51] Cato recommends a similar practice for the preparation of new oil jars. The jars (*dolia*) should first be filled with amurca, the watery liquid by-product of olive oil pressing, for 7 days before being decanted and allowed to dry.[52] Gum (*cummim*) should be soaked in water for a day and on the following day diluted (*dilutio*), presumably by the introduction of additional water.[53] Cato states that the jar should then be heated, but to a lower temperature than if it were to be pitched– it is sufficient that it be only warm. Once the jar is to temperature, the gum should be introduced and applied.[54] Cato's method is uncontradicted by Pliny who briefly summarizes it, although without the reference to gum.[55] Cato states that four Roman pounds of

[49]Pliny *NH* 12.36.

[50]Columella *Rust.* 12.49.11.

[51]Columella *Rust.* 12.49.11.

[52]On the identity of amurca, see Varro *R.* 1.55.7, 1.64.1; Pliny *NH* 15.3.9.

[53]Cato *Agr.* 69. Commentary on gum in the classical corpus is exceedingly sparse, Pliny notes that it is produced by acacia, almond, cherry, plum trees, grape vines, sometimes in olive trees, elm, juniper and sarcocolla (*Penaea sarcocolla*). Pliny *NH* 13.20.

[54]Cato *Agr.* 69.

[55]Pliny *NH* 15.8.

gum (approximately 1.3 kg) is sufficient to treat a 50 amphora-capacity dolium.[56]

[56]Cato *Agr.* 69.

# CHAPTER 3

# ORGANIC RESIDUE ANALYSIS OF CERAMICS

## 3.1 Organic Residue Identification

The idea of the "archaeological biomarker concept" was first articulated by R. P. Evershed in 1993.[1] The "archaeological biomarker concept" is defined as "those substances occurring in organic residues that provide information relating to human activity in the past."[2] With respect to organic residue analysis, the general definition of the "archaeological biomarker concept" as providing information "relating to human activity in the past" includes not only the identification of the original faunal or floral source of the residue but also includes the processes by which it was manipulated by previous human activity.[3] The utility of applying chromatographic techniques in archaeological inquires relies, in part, upon the reliable association of the organic compounds identified from archaeological ceramics with their respective plant or animal sources. The "archaeological biomarker concept," in its simplest, relies matching organic compounds, "chemical fingerprints," to "the compounds and mixtures known to exist in extant organisms likely to have been exploited in the past."[4] For instance, triterpenoid compounds encountered in ceramics from the Mediterranean are specific to the genera *Pistacia* and *Boswellia* and tartaric acid is highly specific to grapes and grape products.

[1] Evershed 1993.

[2] Evershed 2008b, 897.

[3] e.g. Colombini et al. 2005b in which GC/MS analysis of the resinous coatings coatings of Roman and Egyptian amphorae indicated differences in production techniques.

[4] Evershed 2008b, 898.

## 3.2 Techniques of Organic Residue Analysis of Amphorae

Amphorae have been the focus of a number of studies utilizing analytical separation techniques. As a ceramic class, amphorae were the subjects of several studies during the early application of organic characterization techniques with archaeological ceramics; Condamin, Formenti and Rothschilde-Boros being amongst the first to analyze specimens in an attempt to identify their contents and the presence of internal organic linings.[5] After this initial period of interest and until very recently, organic characterization studies of amphorae received relatively little interest as a proportion of total organic characterization studies of archaeological ceramics. Recent published work on amphorae as a subject matter in particular and as a subject for the application of new analytical methodologies indicate a resurgence of interest in the use of amphorae.

A number of different chemical analytical techniques have been utilized in analyzing amphora content and linings, including chemical spot tests and spectroscopic techniques (e.g. Fourier transform infrared spectroscopy (FTIR)), as well as chromatographic techniques coupled with spectroscopy, including Gas Chromatography/Mass Spectronomy (GC/MS) and High Performance Liquid Chromatography/Mass Spectronomy (HPLC/MS). Chemical spot tests, while benefiting from simple sample preparation, have proven problematic because of false positives.[6] Additionally, the low concentration of organic substances absorbed into a ceramic matrix indicates that methods with exceptionally low detection limits be employed (e.g. GC/MS and HPLC/MS). FTIR has proven a reliable technique for characterizing resinous linings in amphorae but is less well suited for non-resinous absorbed organics than combined separation and characterization techniques (i.e. GC/MS and HPLC/MS) due to lower degree of sensitivity to trace residues as well as less specificity in characterization. Despite these limitations, FTIR has been demonstrated to be a useful preliminary technique for organic analysis. Short sample preparation time and low cost of analysis permits a greater number of samples to receive at least preliminary

[5] Condamin et al. 1976; Condamin and Formenti 1978; Formenti et al. 1978; Rothschild-Boros 1981, .

[6] Stern et al. 2008, 2210; Boulton and Heron 2000.

analysis as compared to GC/MS or HPLC/MS. [7]

### 3.3 Previous Amphora Studies

Early residue analysis studies were primarily concerned with testing the potential for utilizing developed chemical analytical techniques in archaeological contexts.[8] Potential pitfalls specific to archaeological samples had to be evaluated. Low concentration of extant organics within the ceramics; the degree to which absorbed organics migrate out of the ceramics matrix during deposition (e.g. leeching due to water exposure) or, alternatively, the potential for lipid migration into the ceramic from the depositional environment; and the effects of diagenesis on the molecular composition of the absorbed organics were substantive concerns that required experimental inquiries. In fact, many of these still require additional experimental inquiry today. For these reasons, the nature of the samples (e.g. ceramic form and fabric) were sometimes not reported and, with respect to archaeological contextual information, rarely if ever. For example, in Rothschilde-Boros' pilot application (Rothschild-Boros 1981) of High Performance Liquid Chromatography (HPLC) analysis, one of the vessels is of an unknown type while the other two are identified with a vernacular "type."[9] Similarly, Condamin et al. 1976 successfully identified fatty acids in samples from a Dressel 20 and attributed them to olive oil, apparently on the basis of the vessel's form having been identified as a oil amphora, despite the fact that some of the identified fatty acids (pentadecanoic acid and heptadecanoic acid, specifically) are incompatible with an identification of olive oil.[10] Considering that no research at that time had been conducted on the potential of depositional lipid intrusion into a ceramic matrix, the conclusion that these lipids, based upon their relative concentrations, were the result of external contamination is reasonable enough.

[7] Concerning the use of FTIR for lining characterization, see Font et al. 2007; concerning the disadvantages of FTIR, see Stern et al. 2008 and Boulton and Heron 2000.

[8] For a table summary of previous residue analysis studies of amphorae, see Appendix A.

[9] See Appendix A for a summary of the study.

[10] For a brief account on the possible heterogeneity of use of Dressel 20 amphorae, see Salvini et al. 2007.

With a greater understanding today of specific complications in the application of organic analysis in archaeological contexts, as well as a developing body of experimental data and improvements in analytical equipment itself, the quality of organic residue identification studies has considerably improved as well. However, amphora residue analysis studies remain constrained in two general aspects. Firstly, the occasional tendency to exclude typological form information as well as archaeological contextual data remains present. Sometimes the vessel is identified by region only or by a 'vernacular' form name. Most often form drawings are not included. The reason for this is primarily twofold. Many of the analyses are conducted by chemists who are not archaeologists (and as such are not familiar with ceramic typologies and contextual data). Also, most of the subsequent publications are made in scientific journals in which page limits restrain the amount of data that may be expressed, the archaeological data being the less immediately relevant. The second aspect is that chemical analytical amphora studies tend to focus on a very small number of samples. The signification amount of time required for sample preparation for organic analysis as well as the significant expense of external laboratory analysis has traditionally limited analysis to either vessels of particular interest or small assemblages. Recent studies involving relatively high number of samples indicate, however, the beginning of change in this trend, due in part to an increased interest in the application of scientific techniques in archaeology, especially in Europe.[11]

These comments are are not intended to represent criticism of previous or current scholarship but reflect an inherent complication in the larger purpose of amphora analysis. With the exception of special vessels in which its particular content is of interest, the study of amphorae in general (i.e. distribution, provenancing, content analysis) serves to reconstruct regional and interregional trade in antiquity and, in doing so, regional and interregional economics. The problem lies in that much of the dynamics of use (i.e. content) of amphorae is still poorly understood. Homogeneity of content within a single form during a single period is still considered to be generally the case, although some

[11] Gregg 2009, Chapter 7. Concerning the difference in the level of development of the archaeological sciences in North America and Europe, see Gregg 2009, Chapter 7.3.

recent research indicate exceptions to this rule.[12] The more complicated and far less well understood matter is that of secondary use. Virginia Grace likened amphorae to the 'gasoline cans' of antiquity–in that, after their primary use, they were often used for secondary purposes, including, but not limited to, storage or transport.[13]

### 3.4 Secondary Use of Amphorae

Before considering evidence of potential reuse of amphorae from previous analytical studies and archaeological research, the way in which an amphora, in general, may have been reused requires definition. J. Peña's work on Roman pottery includes a classification system for ceramic reuse which will be used herein.[14] Peña divides reuse into 3 classes. Type A involves the reuse of a vessel for "an application similar to the vessel's prime-use application without any physical modification to it."[15] Type B reuse is defined like Type A but for a different application. Type C reuse involves physical modification of the vessel for an application different from its original prime-use application.[16] With respect to amphorae, reuse would be considered Type A if the vessel were reused as a packaging container for a good, without respect to whether the type of good (e.g. wine, oil or garum) were the same or different to that of the vessel's prime-use.[17] However, for the vessel's use to be considered Type A, Peña requires that the qualification of "packaging" be maintained in its reuse life cycle. That is, "packaging" is defined not simply as involving storage or local transfer but for "distribution over some distance" (i.e. regional or interregional trade).[18] In instances in which a vessel were subsequently used for storage or for local trade, this type of use pattern is considered as utilizing a different 'application' from prime-use and, as such, is classified as Type B.

[12] e.g. Pecci and Cau Ontiveros 2010.

[13] Grace 1979.

[14] Peña 2007

[15] Peña 2007, 10.

[16] Peña 2007, 10.

[17] Peña 2007, 63.

[18] Peña 2007, 63.

The reasoning behind this distinction is the significance from a "behavioral" perspective.[19] Presumably, Type A reuse would involve a relatively large number of vessels, systematically collected, filled with content and transported some distance at which time a transfer of ownership/possession of the contents (and, most likely, the vessels as well) would take place.[20] Peña is, in essence, defining Type A reuse as large-scale commerce. In contrast, Type B reuse is argued to more likely have involved a limited number of vessels that may not have undergone a change in ownership/possession and, as such, had a greater potential for having been subsequently used in an *ad hoc* or adventitious capacity.[21]

Finally, Type C reuse would involve the physical modification of an amphora for another purpose. An example that readily comes to mind is the removal of the shoulder and neck for use as a burial urn. It should be noted, however, that physical modification of an amphora is not exclusively a property of Type C reuse. Apertures were sometimes made in amphora for the purpose of removing primary content. From finds, Bonifay indicates several different ways in which amphorae were modified for accessing content including using cutting or chipping to make large apertures in the upper body (Fig. 3.1), removal of a portion of the base to create a hole (Fig. 3.2) or the chipping or drilling of small diameter holes in the body or neck (Fig. 3.3).[22]

Having defined secondary use, the determination that an amphora had been subject to reuse (be it Type A or Type B) remains problematic. Apart from exceptional depositional circumstances in which either residual content or *tituli picti* has survived, content determination, either primary or secondary, relies upon absorbed organic analysis. If for a given amphora type, assuming that its principal content be known, an identification of a content inconsistent with the known primary content would indicate either a primary

[19]Peña 2007, 63.

[20]Peña 2007, 63-64.

[21]Peña 2007, 64.

[22]It should be noted that the Beirut parallel in 3.2 is from an incomplete vessel and it is possible that, while sharing a similarity in base hole modification with the Hammamet I example, may have been the result of modification for a different use (e.g. funnel) and thus an example of Type C reuse.

use for an irregular content or a secondary use. Differentiation between the two would be dependent upon a statistical review of other analyses (i.e. does this content determination occur frequently and, if so, is there a correlation between such instances?), information from the archaeological contextual data. The problem lies in the degree to which primary content for a given amphora type was homogeneous.

Multiple use would also be indicated in specimens in which multiple content types were detected (e.g. wine and oil) or by "incompatible" or "inappropriate" contemporaneous combination of content and lining. The later has most commonly been the case for a possible secondary use of an amphora. Olive oil has been traditionally considered incompatible with resinous lining as, it has been argued, that a resinous lining would result in rancidification of oil.[23] In instances in which both resin and oil were detected, it has been generally considered to be indicative that the vessel had been the subject of multiple uses of different contents.[24] However, with the increasing number of occurrences of either resinous linings in amphora forms strongly associated with oil or the co-occurrence of both resin and oil within a single amphora, the question has been raised if perhaps our consideration of amphora lining practices may require reconsideration.[25]

Figure 3.1: Two African I amphorae with large apertures cut into the upper body, presumably for the removal of garum. Source: Bonifay 2004, 469.

[23]Heron and Pollard 1988, 430.

[24]e.g. Salvini et al. 2007, 747.

[25]Pecci and Cau Ontiveros 2010. Examples of co-occurrence include Dorrego et al. 2004 (Haltern 70), Salvini et al. 2007 (Dressel 20), Romanus et al. 2009 (LRA 1). For additional examples, see Pecci and Cau Ontiveros 2010.

Figure 3.2: Hammamet I and Beirut 4 (BEY045.1242.x1) amphora bases modified with a hole. Source: Bonifay 2004, 469; author, respectively.

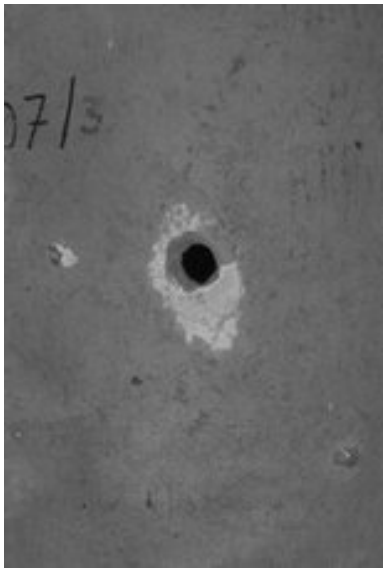

Figure 3.3: Close up of Hammamet I Amphora with Small Diameter Holes. Source: Bonifay 2004, 469.

# CHAPTER 4

# BIOMARKERS OF COMMON AMPHORA CONTENTS

## 4.1 Biomarkers

There are a considerable number of goods—liquid and solid, comestible and non-comestible—are known to have been transported in amphorae. The following section examines the organic compounds, "biomarkers," specific to the particular goods most likely transported or stored in the "main series" amphorae from Beirut—that is, wine or olive oil. The nature of organic substances used to line amphorae to prevent content loss is also examined.

### *4.1.1 Wine*

Wine residue has been the focus of more analytical investigations than other organic materials associated with amphorae. A wide range of analytical techniques have been applied in detecting wine residue—e.g. Feigl Spot and Folin-Ciocalteu testing, IR spectroscopy, FTIR and multiple types of chromatography (including Thin Layer Chromatography, GC/MS, HPLC/MS). The use of combined separation and characterization techniques (such as GC/MS and HPLC/GS) has received preference over other techniques due to the small amount of extractable residue available for analysis and, generally, greater specificity and reliability in compound identification, especially when sample compounds have been subject to diagenetic degradation or contamination.[1] While a wide variety of analytical methodologies have been applied, the biomarkers that have been commonly used to identify wine are fewer, primarily, tartaric acid, syringic acid and polyphenols.

Tartaric acid is a characteristic marker of grapes and wine as it occurs rarely

[1] Guasch-Jané et al. 2004, 1672; Pollard et al. 2006, 149.

in other plants in significant amounts (Fig. 4.1).[2] While the specificity of tartaric acid to grapes and grape products makes it a good biomarker for wine, tartaric acid is water soluble and it has been suggested that it may leach out of deposited ceramics if there is significant water exposure in the depositional environment.[3] Despite concerns over leeching, tartaric acid remains the primary biomarker of interest for wine identification.

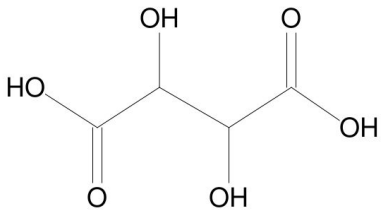


Figure 4.1: Molecular Structure of Tartaric Acid

Some recent studies have concentrated on testing for syringic acid as a biomarker for wine.[4] Unlike tartaric acid, the detectable presence of syringic acid is less affected by depositional exposure to water and has been experimentally detected in samples that tested negative for tartaric acid.[5] Malvidin (malvidin-3-glucoside) is the primary pigment (anthocyanin) of red grapes and, as such, is a relatively specific biomarker for red wine.[6] Either by natural degradation processes or by alkaline fusion in a laboratory setting, malvidin releases syringic acid which may be analyzed by a variety of techniques, most commonly GC/MS or HPLC/MS. Stern, et al. 2008 recently published the first study comparing detection of both tartaric acid and syringic acid by GC/MS and HPLC/MS (as well as the Feigl Spot test and FTIR for tartaric acid) in known samples.[7] Both GC/MS and HPLC/MS outperformed the other techniques in determining the presence of tartaric acid (in fact, the Feigl Spot test and FTIR were unable to make a positive determination

[2]Guasch-Jané et al. 2004, 1672; McGovern 1997, 84; Stern et al. 2008, 2189.

[3]Singleton 1996, 68.

[4]e.g. McGovern et al. (2009); Guasch-Jané et al. (2004); Singleton 1996.

[5]Stern et al. 2008.

[6]Singleton 1996, 70.

[7]Stern et al. 2008.

for tartaric acid in any of the test samples), HPLC/MS appears to have demonstrated a lower detection threshold for syringic acid in analyzed standards.[8]

The analysis of samples for specific types of polyphenols (e.g. flavonols) is another method of detecting wine residue that has only recently been investigated.[9] Polyphenols are members of a large group of organic compounds that frequently occur in the plant kingdom, including compounds such as tannins, flavonoids and anthrocyanic compounds (which includes malvidin).[10] Polyphenols are complex organic compounds and are susceptible to chemical change over time into more stable compounds (either by degradation into simpler compounds or polymerization).[11] GC/MS has been used to analyze amphorae residue for the resulting compounds, using modern grape and wine samples to establish characteristic compounds.[12] The initial studies have shown promise in this type of analysis as it reveals a significant amount of information about the organic makeup of a particular sample. Additional studies are necessary, however, to establish that the presence of particular polyphenols is specific to wine and not attributable to other organic sources.[13]

Recently Alessandra Pecci in conjunction with the University of Siena have developed an extraction technique for carboxylic acids that focuses on specific carboxylic acids as biomarker indicators of wine. In addition to tartaric acid, considered a highly specific biomarker for grape products, other secondary biomarkers for grapes and fermentation are taken into consideration as indicators of wine. Malic acid is another of the main organic acids found in grapes. Malic acid has a number of different botanical sources,

[8]The study reasserts the determination by Bolton and Heron that Feigl Spot testing is an unreliable technique for wine residue analysis. Boulton and Heron 2000. It should also be noted that while syringic acid was identified in standards and modern wine soaked sherds, syringic acid was not detected in any of the archaeological material analyzed.

[9]e.g. Garnier et al. 2003; Romanus et al. 2009.

[10]Garnier et al. 2003.

[11]In fact, initial degradation of some polyphenolic compounds appears to occur only months or years after the fermentation process. However, the compounds that result from the initial degradation are very stable, see Garnier et al. 2003, 156.

[12]Garnier et al. 2003.

[13]Romanus et al. 2009, 907ff.

including apples and currants. While considerably less specific on the whole than that of tartaric acid, wine contains a relatively large amount of malic acid, varying between 1-6.5 g/l.[14] In addition to grape biomarkers, other compounds produced by fermentation processes during vinification may also provide supportive evidence that a vessel contained wine.[15] Propanoic acid (lactic acid) is produced during malolactic fermentation by which a portion of the malic acid content is converted to propanoic acid by lactic acid bacteria.[16] Succinic acid (1-4-butanedioic acid) is also produced by bacterial action during fermentation; the average concentration of succinic acid in wine is 1 g/l.[17] Similarly, fumaric acid and acetic acid are also produced during fermentation.

### *4.1.2 Oils and Fats*

Vegetal oils and animal fats are complex mixtures of several different classes of lipids and are composed almost exclusively of triacyglycerols, with a minor portion comprised of free fatty acids, mono- and di- glycerides.[18] Triacyglycerols and unsaturated fatty acids are especially prone to degradation in the depositional environment, most commonly by bacterial action. Both vegetal oils and animal fats are primarily composed of the same types of lipids and attempts to differentiate the two in archaeological contexts have focused on the differing relative abundance and distribution of specific fatty acids.[19] Determination of a plant or animal origin can prove difficult due to the degradation of triacylglycerols (as well as hydrolysis).[20] Some more recent studies have focused testing for specific sterols that are unambiguous biomarkers for plants or animals.[21]

The analysis of lipids is complicated by processes of diagenetic degradation, the

[14]Ribereau-Gayon et al. 2000, 5.

[15]Pecci and Cau Ontiveros 2010.

[16]Ribereau-Gayon et al. 2000, 8.

[17]Ribereau-Gayon et al. 2000, 6.

[18]Holčapek et al. 2005, 1315.

[19]Stern et al. 2000.

[20]Pollard et al. 2006, 151ff. The ratio of the fatty acids may also be affected by exposure to water in the depositional environment, as some fatty acids exhibit significantly greater water solubility.

[21]Pollard et al. 2006, 152; Kimpe et al. 2004.

change of an organic compound into less molecularly complex compounds, due to the age and environmental conditions (e.g. heat or microbial action).[22] Archaeological pottery is especially sensitive to contamination with respect to lipids because of the ubiquity of lipids in organisms in the natural environment, as well as contamination during excavation and post-excavation treatment. Lipid analysis needs also take into consideration potential post-depositional contamination, such as oil from handling during excavation or post-excavation processing (Fig. 4.2). [23] To attempt to control for potential contaminates in

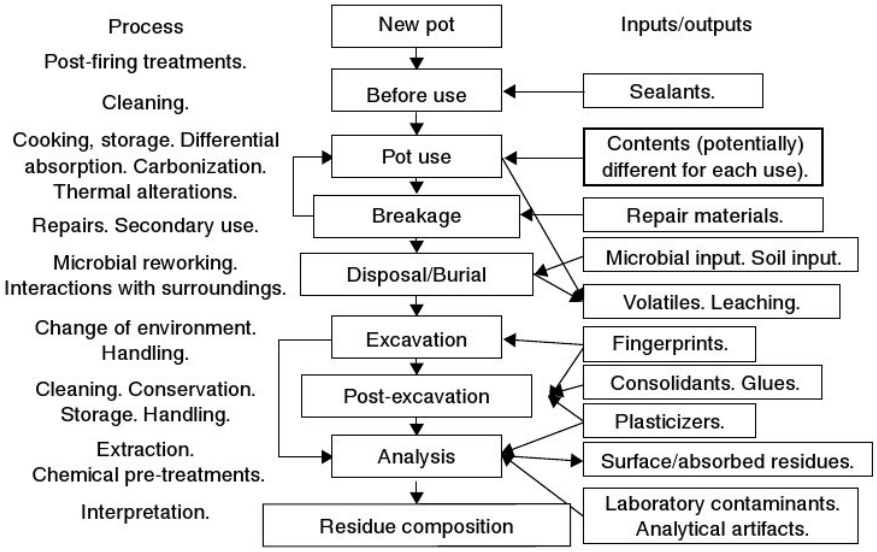


Figure 4.2: Possible transformation processes of residues in pottery from manufacture to post-excavation treatments. Source: Pollard, et al. 2007, 150.

already excavated and processed ceramics, certain protocols for lipid analysis have been suggested, including taking samples from multiple layers of a sherd, as first suggested by Rothschild-Boros in 1981.[24]

[22]Romanus et al. 2009, 909.

[23]Pollard et al. 2006, 152; Evershed 2008b.

[24]Rothschild-Boros 1981; Passi et al. 1981. Other suggested procedures for controlling for depositional contamination are described in Heron et al. 1991; Condamin et al. 1976.

### *4.1.3 Resins*

Resins represent the compounds from the terpenoid family, which includes more than 23,000 different organic compounds, and serve as plant exudates, protecting a damaged plant from "excess water loss and invasion of microorganisms."[25] Terpenoids are secondary products of plants; that is, they are not involved in plant metabolism but rather have specific functions and are generally present in small quantities.[26] Terpenoids, unlike some other organic compounds, are relatively stable and are preserved well in archaeological contexts. Two types of terpenoids are encountered in the context of amphora analysis: diterpenoids and triterpenoids. Diterpenoids are produced by members of the *Pinaceae* family, as well as by some members of *Fabaceae*.[27] In the Mediterranean, the source of diterpenoids is from the genus *Pinus*, of which there are several indigenous and introduced species. Dehydroabietic acid is the primary biomarker for diterpenes (i.e. coniferous resins and resin products). While 7-oxo-dehydroabietic acid is indicative of high temperature treatment (i.e. pyrolitic distillation) of diterpene resin.[28]

The other main group of terpenoids encountered in archaeological contexts in the Mediterranean region is triterpenoids. With respect to the Mediterranean region, triterpenoids are associated with members of the genus *Pistacia*, as well as members of the genera *Commiphora* (myrrh) and *Boswellia* (frankincense), native to the Arabian Peninsula. Myrrh and frankincense have been used since Pharaonic Egypt for their aromatic and medicinal qualities.[29] Recent studies have shown that *Pistacia* resin (alternatively referred to as 'terebinth' or 'mastic') has also been traded since at least the Late Bronze Age for aromatic and medicinal purposes. The Egyptian name for a particular type of incense, 'sntr', previously identified as myrrh, has been determined instead to be *Pistacia*

[25]Pollard and Heron 1996, 240.

[26]Pollard et al. 2006, 153.

[27]Mills and White 1977, 9. Diterpenoid-producing members of *Fabaceae* are limited to several genera of tropical trees (sub-family *Caesalpinioideae*) and can be excluded as a possible source of diterpenoids in Mediterranean amphorae.

[28]Colombini et al. 2005a.

[29]Serpico 2000.

sp. resin.[30] The contents aboard the 13th century B.C. Ulu Burun wreck included a significant amount of *Pistacia* resin, transported as a commodity itself in Canaanite jars.[31] The *Pistacia* resin was used by the Romans as well—Pliny the Elder comments upon its use as a sealant.[32] Diterpenoids and triterpenoids can be differentiated by chemical analysis. Likewise, the biological source of triterpenoids can be differentiated at the genus-level, although species-level differentiation has not been possible.[33]

## 4.2 Residue Capture and Retention in Ceramic Matrices

The ability to detect absorbed residues in archaeological ceramics is dependent upon sufficient residuality of biomarker compounds within the ceramic matrix to permit identification by the employed analytical technique. The capture and retention of organic compounds within ceramic matrices are affected by complex mechanisms, not all of which are fully understood.[34] The general categories that affect the presence and identifiability of organic compounds in transport ware include absorption proclivity and capacity of the specific ceramic, retention of the absorbed compound while in the depositional environment and the affect of the depositional environment on the molecular compounds themselves.[35]

The effect of absorption capacity of a ceramic is a factor of its porosity. Porosity is governed multiple factors including the quality, or fineness, of the clay used, the type and amount of temper, and other production techniques (e.g. wheel thrown products having a more dense grain structure than that which was hand-formed). Permeability is, in turn, affected by porosity but also by surface treatments either by manual manipulation

[30] Serpico and White 2000b.

[31] Stern et al. 2008. The probable destination of the Ulu Burun ship was the Aegean, although the use of *Pistacia* resin during the Late Bronze Age in the Aegean is not well understood.

[32] Pliny *NH 14.25.20.*

[33] Stern et al. 2008.

[34] Charters et al. 1993, 218.

[35] Additional factors that are specific to specific types of wares, e.g. thermal degradation of lipids due to repeated use in cooking ware, is not considered here. Evershed 2008a, 27.

of the ceramic surface (polishing, slipping, etc.) or by the application of non-ceramic materials (e.g. resin linings) or by the introduction of compounds to saturate the ceramic matrix itself.

Investigations by Evershed have indicated that the minimum lipid concentration level (total lipid extract) for reliable identification by GC/MS is approximately 5 μg $g^{-1}$; concentrations below that level may be due to contamination, i.e. the intrusion of lipids in the depositional environment.[36] In his experience, Evershed indicates the mean lipid content of archaeological ceramics to be c. 100 μg $g^{-1}$, while the highest reported (17.8 mg $g^{-1}$) was in a sherd of a Late Christian period lamp from Qsar Ibrim, Egypt.[37] Several studies have been conducted to establish ceramic capacity for lipid absorption. One study using replica cooking jars in which lamb was boiled multiple times established a mean lipid concentration of 21.8 mg $g^{-1}$in the analyzed rim samples.[38] Another approach, using the same vessels, but soaked in olive oil, established a maximum concentration of 13.5 mg $g^{-1}$.[39] An experiment in which cabbage (*Brassica*) leaves were boiled in modern replica vessels produced a mean lipid concentration of 262 μg $g^{-1}$ in the rim samples after 10 uses.[40] Analysis of an ethnographic vessel that had been used to cook pork once per year for 40 years indicated a maximum concentration of c. 5.4 mg $g^{-1}$.[41]

Little in the way of quantitative experimental studies on ceramic capacity for biomarkers associated with wine (e.g. tartaric and syringic acids) are available. One experimental study was conducted by Romanus to evaluate the absorption of wine and olive oil in pitched and unpitched storage vessels.[42] The experimental vessels were composed of ophiolite and tempered with quartz and crushed ceramics to imitate the fabric of local/regional Sagalassos amphorae.[43] Commercial pine pitch was applied to the pitched

[36]Evershed 2008a, 28.

[37]Evershed 2008a; Copley et al. 2005, 28, respectively.

[38]Evershed 2008a, 28.

[39]Evershed 2008a, 28.

[40]Charters et al. 1997.

[41]Evershed 2008a, 28.

[42]Romanus 2008.

[43]Romanus 2008, 83.

category of vessels and allowed to dry for 45 days. Wine and olive oil were introduced into the vessels and allowed to sit in a well-ventilated environment for 45 days, at the conclusion of which the vessels were visibly dry.[44] Experimental results indicated that pitch permeation (based on the identification of retene) was primarily evidenced within 3 mm of the ceramic surface.[45] In unpitched vessels, wine (based on the identification of gallic acid) permeated throughout the matrix; while in pitched vessels, gallic acid concentrations were detected within 3.5 mm of the ceramic surface and were higher than that of unpitched vessels. This counter-intuitive outcome appears to have occurred as a result of the use of the Folin Ciocalteu reaction as a means of wine identification. Vessels applied with pitch, but not exposed to wine or any other compounds, indicated polyphenols by the Folin Ciocalteu reaction, caused by phenolic structures in the pitch as confirmed by GC/MS.[46] It is for this reason that unambiguous analytical methodologies, such as GC or HPLC, are preferred over chemical 'spot' tests in archaeological applications.[47]

While current data suggests that the primary pathway for lipid depletion from ceramics is due to diagenetic processes, the water solubility of tartaric and syringic acids render them susceptible to leaching from the ceramic matrix due to exposure to water. Tartaric acid is highly soluble in water, approximately 1400 g/l at 20C, while syringic acid is considerably less so, approximately 5.8 g/l at 25C.[48] It has been suggested that the significant solubility of tartaric acid would make sufficient residual levels for detection unlikely in ceramics that had been exposed to water in the depositional environment.[49] When exposed to calcium tartaric acid forms calcium tartrate, which is only soluble at 0.3 g/l, and should improve retention in ceramics, although even this level of solubility may be too great for long term retention in archaeological ceramics.[50] Sources for calcium

[44]Romanus 2008, 84.

[45]Romanus 2008, 85.

[46]Romanus 2008, 88.

[47]Stern et al. 2008, 2201;Boulton and Heron 2000, 601.

[48]Singleton 1996, 68; www.chemblink.com/products/530-57-4.htm.

[49]Singleton 1996, 68.

[50]Singleton 1996, 68.

could be from treatment of the wine with limestone, a practice mentioned by Pliny or from groundwater that has filtered through calcareous deposits.[51] The ceramic material itself is also a possible vector for calcium exposure. Stern et al. observed by FTIR examination spectra associated with calcium tartrate in modern, wine treated ceramic samples that had not been buried.[52] Stern postulated that this may be a result of aging processes, i.e. "related to rates of oxidation, temperature and the precipitation of phenolic substances present in grape derivatives."[53] However, it is possible that this conversion was also effected by the presence of calcium compounds within the ceramic.[54]

Syringic acid, derived from maldivin and responsible for the color of red wine, occurs in modern, young red wine samples at approximately 200 mg/ l, although older wines may have levels five times greater.[55] Maldivin polymerizes with aging, rendering it insoluble in water and aiding its preservation, increasing the likelihood of retention in archaeological ceramic samples.[56] Maldivin, whether polymerized or not, is partially converted to syringic acid by alkaline fusion (as previously discussed).

[51]Concerning conversion of tartaric acid to calcium tartrate as an effect of the depositional environment, see McGovern 1997;Boulton and Heron 2000, 601; Singleton 1996, 68.

[52]Stern et al. 2008, 2196ff

[53]Stern et al. 2008, 2197

[54]Singleton 1996, 68. For an example of high levels of calcium compounds in amphorae, seeMaggetti 2001.

[55]Stern et al. 2008, 2189; Singleton 1996, 70.

[56]Stern et al. 2008, 2189;Guasch-Jané et al. 2004, 1673; Singleton 1996, 69ff.

# CHAPTER 5

# APPLICATION OF GC/MS AND HPLC/MS IN ANALYSIS OF SPECIFIC BEIRUT AMPHORAE: TECHNIQUE AND METHODOLOGY

## 5.1 Applied Methodologies

Initially, it was planned that two techniques be applied to analyze the samples– one technique utilizing HPLC/MS and another utilizing GC/MS. The HPLC/MS technique is specific to wine biomarkers, having been developed by Maria Rosa Guasch-Jané to test for tartaric and syringic acids in Egyptian New Kingdom wine storage jars.[1] Unfortunately, due to delays caused by equipment failure, the application of the HPLC/MS technique had to be abandoned. Instead, the GC/MS technique described in 5.1.2 was used for the analysis of all samples in this project.

### *5.1.1 Pre-Sampling and Ceramic Preparation*

For ceramic samples that were taken from either reconstructed vessels or very large sherds, a portion of the ceramic body ('pre-sample') was cut from the vessel using a rotary drill with a diamond-coated cut-off blade. The cut-off blade was cleaned with a solution of dichloromethane/methanol (2:1 v/v) before each pre-sample to prevent cross-contamination. Pre-samples were subsequently wrapped in aluminum foil and stored in labeled paper envelopes.

To prepare the ceramic sherds for analysis, the ceramic needed to be pulverized. Sample pulverization, as well as the analytical preparation of samples, was conducted in a clean environment in a laboratory in the Department of Chemistry. Latex gloves were worn during all sample preparation steps. The sherds were surface cleaned to approxi-

[1] Guasch-Jané et al. 2004.

mately 0.25 mm using a rotary tool equipped with a tungsten carbide abrasive bit.[2] The abrasive bit was cleaned by washing three times in a solution of chloroform/methanol (2:1 v/v) before surface cleaning and before sample harvesting. A powdered sample of approximately 1.5 g was then taken from the cleaned area of the sherd onto sterile aluminum foil to a depth of approximately 3 mm with the rotary tool set to 'low' (approximately 12 000 RPM) in order to prevent thermal degradation of absorbed lipids.

### *5.1.2 GC Method*

The GC/MS method was based upon that developed at the University of Siena and is employed by Alessandra Pecci at the Equip de Recerca Arqueològica i Arqueomètrica de la Universitat de Barcelona (ERAAUB).[3] The method, as it was to be applied to this research project, is composed of two parts: one technique for lipid extraction and a second for extraction of carboxylic acids which include wine biomarkers.

#### 5.1.2.1 Chemical Supplies

All chemical reagents used in this study, with the exception of deionized water, are analytical grade and were obtained from Sigma-Aldrich. Deionized water was supplied by the KAS CRSL's Barnstead/Thermolyne Nanopure lab water system.

#### 5.1.2.2 Lipid Extraction

For the lipid extraction, 1 gram of pulverized ceramic is extracted 3 times with 3 ml of chloroform/methanol (2:1 v/v), vortexed for 2 minutes and sonicated at 70C for 40 minutes. After sonication, the liquid fraction is centrifuged at 4300 RCF. After centrifugation, the liquid fraction is then again separated from any remaining ceramic material and dried using a nitrogen evaporator.

[2]The bit used was a Dremel Model 9901 Tungsten Carbide Cutter.

[3]Pecci et al. forthcoming.

#### 5.1.2.3 Carboxylic Extraction

For the carboxylic acid extraction, 500 mg of pulverized ceramic was extracted with 3 ml of potassium hydroxide in deionized water (1M) and sonicated for 90 minutes at 70C. After sonication, the liquid fraction was centrifuged at 4300 RCF. After centrifugation, the liquid fraction was then separated from the settled ceramic material. Syringe filters were utilized to remove any remaining ceramic material. To prepare for post-centrifugation filtering, the liquid fraction was acidified with hydrocloric acid (16M) to a pH of approximately 4. The liquid fraction was then filtered into a clean vial and acidified again to a pH of approximately 2. Ethyl acetate (3 ml) was added and vortexed for 1.5 minutes. The supernatant was removed to a new vial and dried using a nitrogen evaporator. The ethyl acetate extraction was conducted 3 times per sample.

#### 5.1.2.4 Internal Standard

Immediately prior to testing, 5 µl of octacosane (at a concentration of 1 mg/ml in hexane) was added to each sample.

#### 5.1.2.5 Derivatization

Samples were then derivatized by adding 25 µl of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA). After the addition of the derivatizing agent, the sample was vortexed for approximately 30 seconds in order to maximize contact between the BSTFA and the dried sample material. After vortexing, the samples were heated at approximately 70C for 60 minutes.

#### 5.1.2.6 GC/MS Conditions

After derivatization, 1 µl of sample was manually injected. Analyses were performed on a ThermoScientific Trace GC Ultra equipped with a DSQ II mass spectrometer. The column used was a Restek TR-5MS. The mass range was scanned from m/z 40-650.

Electric ionization was at 70 eV. The temperature program was as follows: initial isothermal hold for 1 minute at 50C, 50-330C at 5C/min, 3 minute hold at 330C.

#### 5.1.2.7 Analysis

Characterization of the analyte constituents separated by the chromatographic analysis was conducted by two means. In the case of tartaric and syringic acids, standards were prepared from analytical grade tartaric acid and syringic acid obtained from Sigma Aldrich. Identification of tartaric and syringic acids in archaeological samples were made by comparison of the mass spectra of the archaeological samples and standards.

Compounds other than tartaric and syringic acids were identified by the use of the chromatograph's Xcalibur software against the NIST 05 spectral database. Characterization of the identified compounds was assisted by a spectral database of compounds identified in archaeological samples developed by Vassar College (New York, U.S.), Middleditch's "Analytical Artifacts" (for characterization of contamination constituents) and literature review.

### *5.1.3 HPLC Method*

Guasch-Jane et al. developed a method employing HPLC/MS/MS for the purpose of identifying both visible and absorbed wine residue in trace amounts.[4] The method targeted tartaric acid as the identifying biomarker of wine (secondarily, syringic acid for differentiation between red and white wine). The authors examined samples of Egyptian storage jars (dating between the 1st and 18th Dynasties). As previously mentioned, the HPLC/MS method developed by Guasch-Jane was originally intended to be used in conjunction with the GC/MS technique (described below). Extenuating circumstances ultimately did not permit the inclusion of this technique in the current study. Method testing on the CRSL's Agilent 1100 Quaternary Pump HPLC was only conducted with detection of tartaric acid standards before work was terminated. The methodology is in-

[4]Guasch-Jané et al. 2004.

cluded herein as it is subsequently referenced.

Standards of tartaric acid and syringic acid prepared. A solution of L-tartaric acid is prepared at a concentration of 100mg/L in water. A solution of syringic acid is prepared at a concentration of 100mg/L in methanol/water (20:80 v/v). The working solution of 100 µg/l is prepared by diluting the respective standards with 0.1% formic acid in water/acetonitrile (90:10 v/v).

A sample of 500 mg of ceramic is extracted as explained in Chapter 5.1.1. The sample is extracted with a solution of 0.1% formic acid in water/methanol (80:20 v/v, 5 ml) in ultrasound bath (heated at 70 °C for 90 minutes). After extraction, the sample is centrifuged for 15 minutes at 4300 RCF. 4.The supernatant is decanted and reduced to 1/10 of original volume by placing under a stream of nitrogen. The sample is filtered using a PTFE 0.45 µm filter. Alkaline fusion is performed by adding 0.2 g of KOH and heated for 5 minutes (following previous literature).[5] The sample is acidified using HCl (1 M). Liquid-liquid extraction is performed three times using 3ml ethyl acetate.

The article utilized an Agilent 1100 Liquid Chromatograph equipped with a quaternary pump. A Waters Atlantis C18 column (2.1 × 150 mm i.d., 5 µm) was used at ambient temperature. The mass spectrometer was a PE Sciex API 3000 triple quadrupole MS/MS system equipped with a Turbo ion spray source operating in negative-ion mode for monitoring ions of deprotonated molecules [M – H]-. The injected volume of sample is 15 µL. A constant flow rate of 200 µL/min is used with two elution solvents: 0.1% formic acid in water (Solvent A) and acetonitrile (Solvent B). The gradient is isocratic until minute 5 with 100% of solvent A; at minute 10 solvents are A/B (80:20) and a second isocratic step is performed from minute 15 to 30 with solvents A/B (50:50).

## 5.2 Samples

The analysis of the excavated material from the Beirut excavations revealed that Beirut (including its environs) was a manufacturing center for amphorae, beginning dur-

[5] i.e. Singleton 1996; Zugla and Kiss 1987.

ing the Classical period (c. 150 B.C.) and continuing until the mid-7th c. A.D.[6] Extensive work, including the development of a linear typology, has been conducted by Dr. Paul Reynolds.[7]

During the 1st to 3rd c. A.D., Beirut produced three amphora types: the main series of "Beirut amphora," a small "carrot" amphora and a large type bearing simularities to the Dressel 14.[8] The "carrot" amphora, on the basis of the large rim diameter and small internal volume, is believed to have carried fruits, possibly dates (Fig. 5.1).[9] The large type of amphora, which is attested only during the 1st to 3rd c. A.D. is believed to have been used for either olive oil or a fish product (e.g. *garum*) (Fig. 5.2).[10]

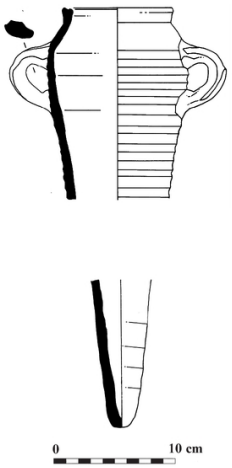


Figure 5.1: Beirut "carrot" amphora. Source: Reynolds 2008, 77.

The main series "Beirut amphora" is believed to have been used for the storage and transport of wine, a good known to have been produced in the area of Beirut during the Imperial period, although olive oil may be a possibility as well.[11] Pliny commented

[6]Reynolds 1998b. Concerning the provenance analysis of Beirut ceramics, see Roumie et al. 2004, 2006.

[7]Reynolds 1998a,b, 2003, 2005, 2008, 2010; Reynolds et al. 2010For an overview of the development of the Beirut amphora series, see Reynolds 1998b, Appendix 1.

[8]Reynolds 2008, 76.

[9]Roumie et al. 2004, 197; Reynolds 2008, 76.

[10]Reynolds 2003, 123; Reynolds 2008, 76.

[11]Reynolds 2008, 76; Reynolds 2003, 122; Reynolds 2010, 5.

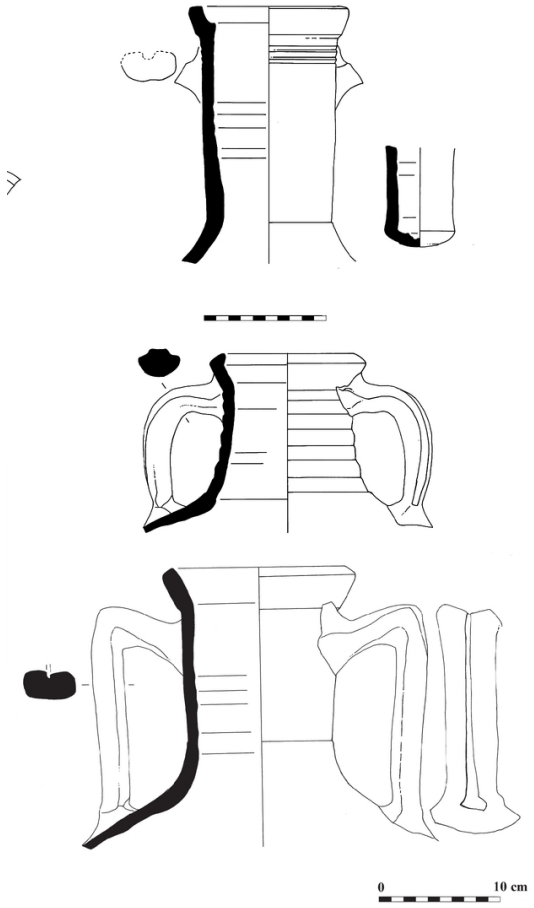


Figure 5.2: AM-72 variants. Source: Reynolds 2008, 77.

upon the relatively high quality of wine produced in the area of Beirut.[12] Although not verified by chemical analysis, visible red residue has been noted on one Beirut 2 (i.e. main series) amphora, recovered from a deposit dated to the mid-1st c. A.D., and has been tentatively identified as wine (Fig. 5.3).[13]

Samples for analysis were selected from Beirut "main series" amphorae dating between the 1st and 4th c. AD, corresponding to Beirut amphora forms 1, 1A, 2, 3, 4 and 5 (Figs. 5.4-5.7). Information concerning individual samples and context data is given in 'Sample Analysis' (Chapter 6).

[12]Pliny *NH 14.74-75*.

[13]Paul Reynolds, pers. comm.

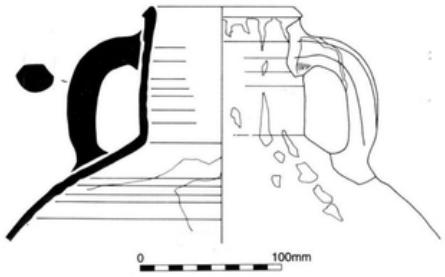


Figure 5.3: Beirut 2 amphora with visible residue “drips.” Source: Reynolds 1998b, 85.

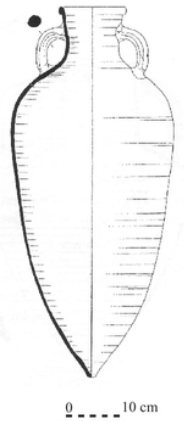


Figure 5.4: Beirut 1A. Source: Reynolds 2010, 101.

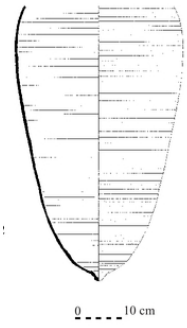


Figure 5.5: Beirut 2. Source: Reynolds 2010, 101.

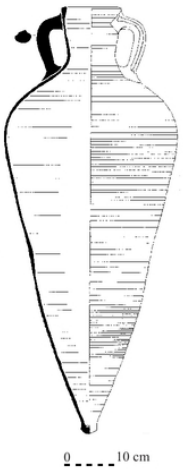


Figure 5.6: Beirut 3. Source: Reynolds 2010, 101.

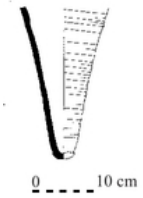


Figure 5.7: Beirut 4 base. Source: Reynolds 2010, 101.

# CHAPTER 6

# SAMPLE ANALYSIS

Samples were extracted using the carboxylic acid extraction technique and analyzed under the GC/MS conditions enumerated in Chapter 5.1.2. The sample identification (ID#) refers to the internal reference number of the ceramic sample maintained in the author's database. Photographs of the sherds may be found in Appendix B. Numbers in parentheses after chemical compounds refer to the label number in the corresponding GC/MS chromatograms. Context data and dating were obtained from the Pottery Database.[1]

***Sample 003***

Sample 003 (ID# 189) was obtained from sherd BEY006.11603.171. The sample was obtained from a Beirut amphora in heavy local fabric and was taken from the amphora's base (Fig. B.1). Context 11603 is dated to between 125 and 150 AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.1 and 6.2) indicated acetic acid (2), malonic acid (5), benzoic acid (6) and malic acid (10). A small peak was discernible at minute 24.22–the retention time corresponding to tartaric acid. Selected Ion Monitoring (SIM) was utilized in an attempt to disambiguate the mass spectra of the peak. Positive identification of tartaric acid, however, was not determined. A peak was also observed at minute 39.82–the retention time corresponding to dehydroabietic acid. Probably due to the low analyte concentration in the sample, a low probability score for identification of dehydroabietic acid was provided by mass spectral analysis even after utilizing SIM. Propanoic acid (1), succinic acid (7) and azelaic acid (15) were

[1]The data in the Pottery Database was developed by Dr. Paul Reynolds during his work with the ceramic material excavated by the Anglo-Lebanese excavations in Beirut. Concerning details of the excavations, see Reynolds 2003.

also identified in the sample but were determined to result from sample contamination. Phthalic acid (14), a plasticizer contaminate, was also identified.

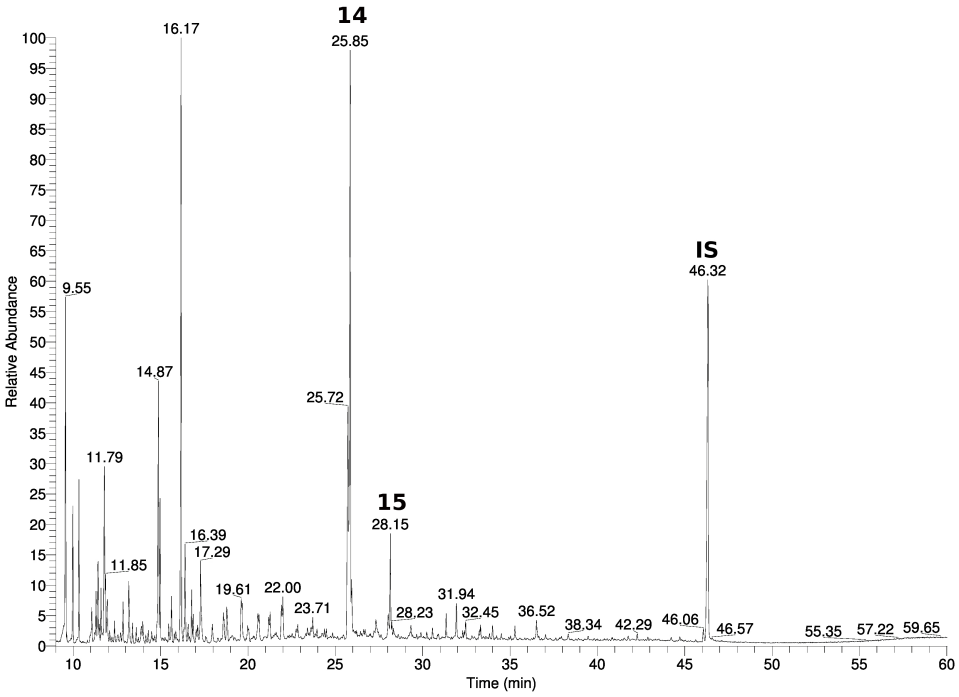


Figure 6.1: TIC Chromatogram of Sample 003

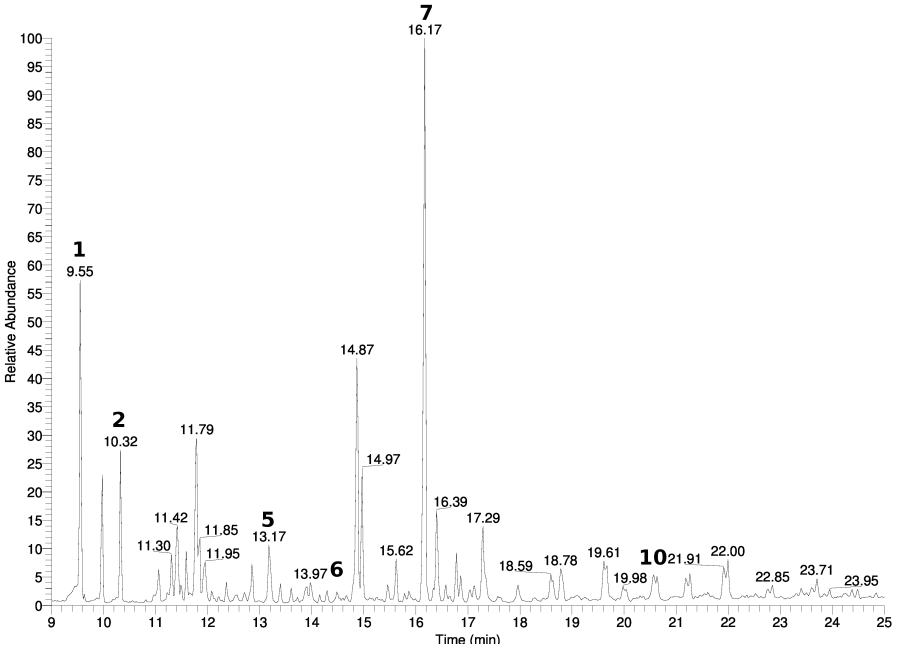


Figure 6.2: Partial TIC Chromatogram of Sample 003, minutes 9-25

***Sample 004***

Sample 004 (ID# 118) was taken from sherd BEY006.12237.x2 (Fig. B.2).[2] The sample was obtained from a Beirut 2 amphora in local reduced fabric and was taken from the amphora's base. Sherd BEY006.12237.x2 possessed visible white mineral deposits, consistent with the fact that Context 12237 is a cistern deposit ('Pat's Cistern'). Context 12237 is dated to the mid-1st c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.3 and 6.4) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8), and malic acid (10). Tartaric acid (13) was identified by both NIST mass spectral database analysis and comparison against mass spectra obtained from the tartaric acid standard (Figs. 6.5 and 6.7). Propanoic acid (1), succinic acid (7), azelaic acid (15) and phthalic acid (14) were also observed and determined to result from sample contamination.

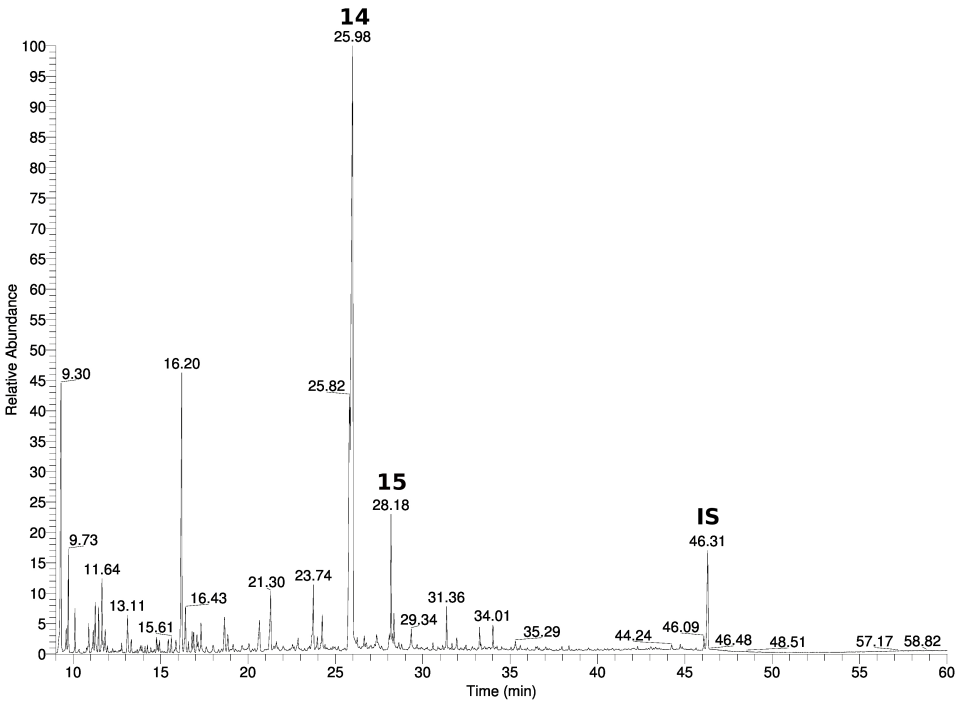


Figure 6.3: TIC Chromatogram of Sample 004

[2]It should be noted that the 'x' designation in a sherd number indicates that the sherd was either not cataloged in the Pottery Database or that the sherd could not be positively identified with a cataloged sherd (most commonly due to no extant sherd identification number on the ceramic itself).

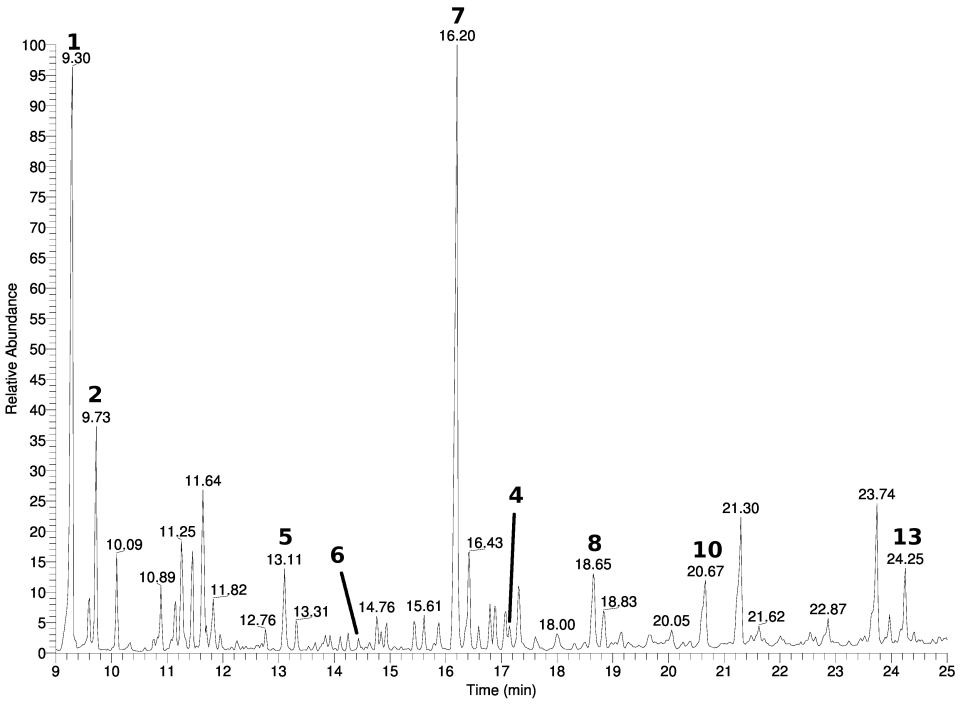


Figure 6.4: Partial TIC Chromatogram of Sample 004, minutes 9-25

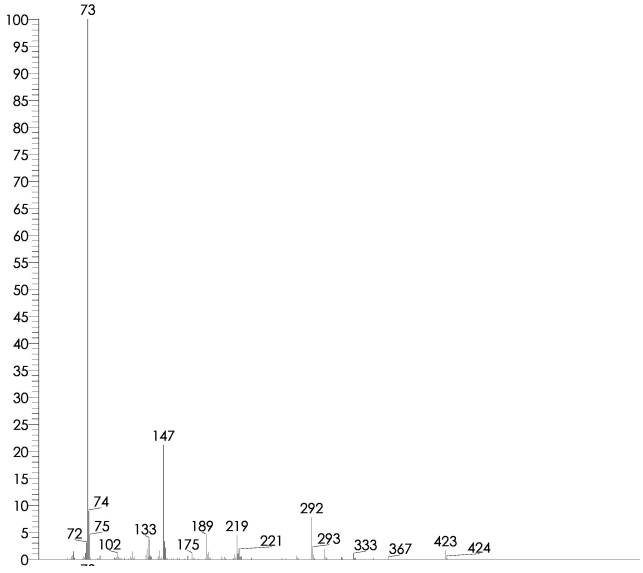


Figure 6.5: Mass Spectra of Tartaric Acid from Sample 004

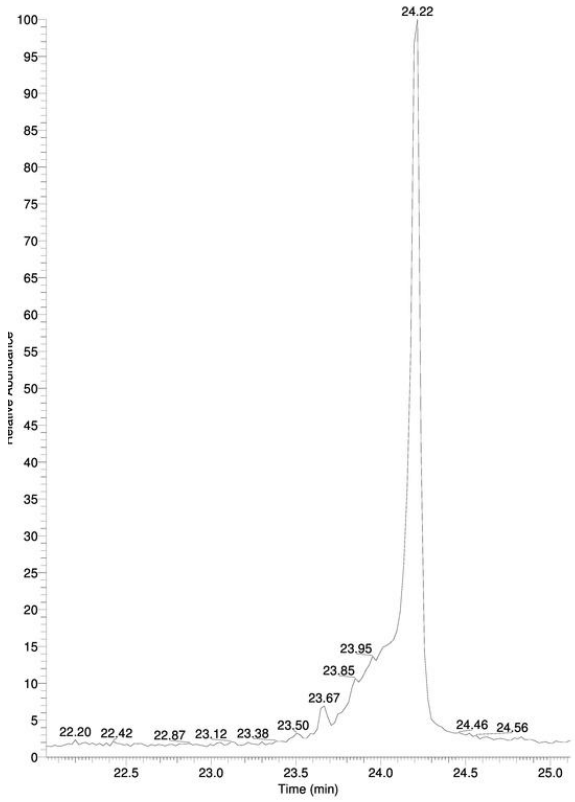


Figure 6.6: Partial TIC Chromatogram of Tartaric Acid Standard, minutes 22-25

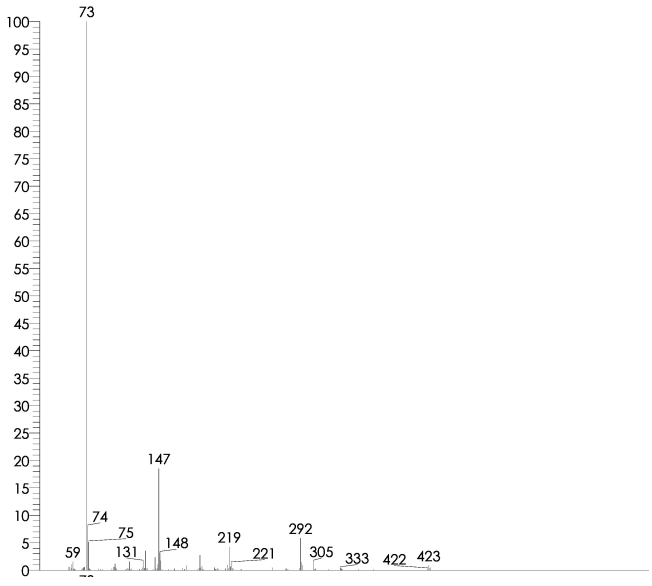


Figure 6.7: Mass Spectra of Tartaric Acid Standard

***Sample 006***

Sample 006 (ID# 107) was taken from sherd BEY006.5051.458 (Fig. B.3). The sherd is a Beirut 4 in local fabric; the sample was taken approximately 15 cm above the lower terminus of the base. Context 5051 is dated to the 3rd c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.8 and 6.9) indicated acetic acid (2), malonic acid (5), benzoic acid (6), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Dehydroabietic acid was also not identified in the sample. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

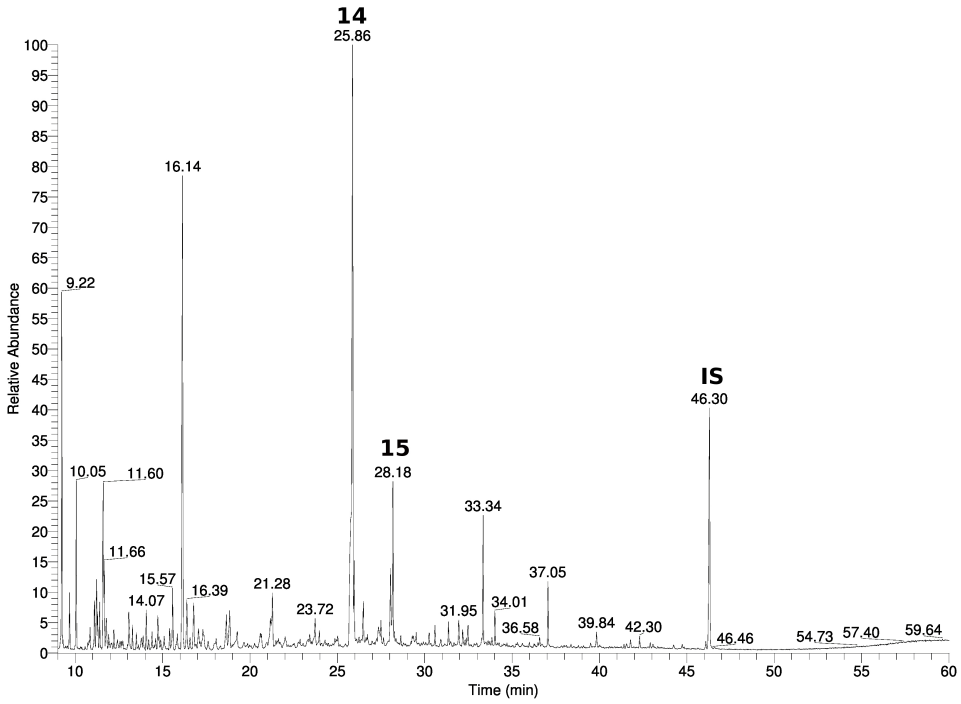


Figure 6.8: TIC Chromatogram of Sample 006

***Sample 007***

Sample 007 (ID# 117) was taken from sherd BEY006.12237.x1 (Fig. B.4). The sherd is a Beirut 2 in local fabric; the sample was taken approximately 10 cm above the

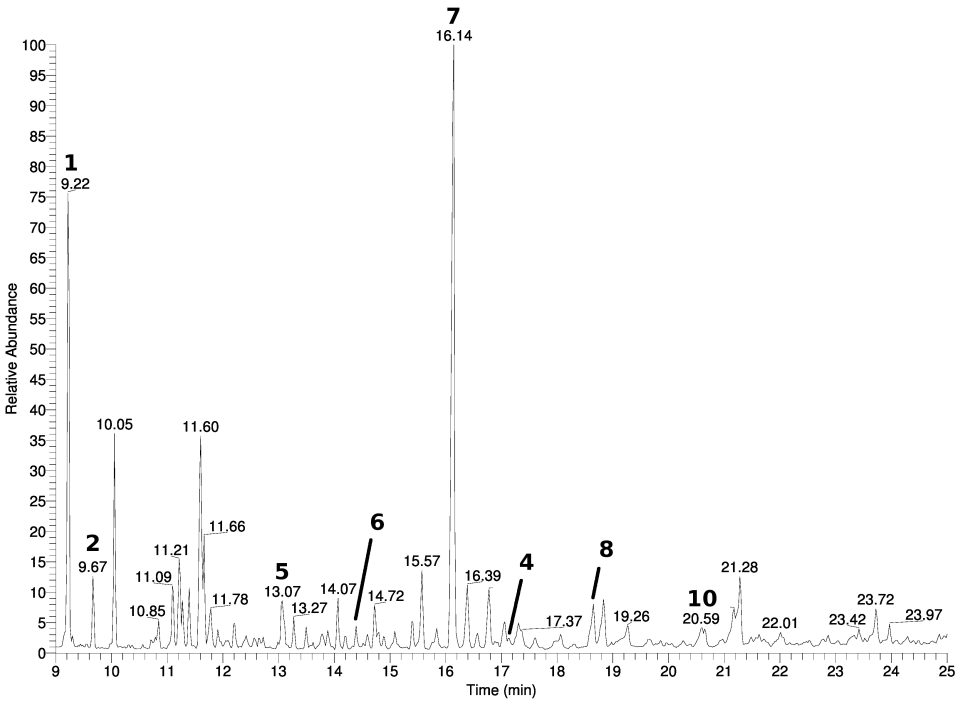


Figure 6.9: Partial TIC Chromatogram of Sample 006, minutes 9-25

lower base terminus. Unlike Sample 004, also from Context 12237, no mineral deposits were visible on the sherd. Context 12237 is dated to the mid-1st c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.10 and 6.11) indicated acetic acid (2), malonic acid (5), fumaric acid (4), glutaric acid (8) and malic acid (10). No peak associated with the retention time of tartaric acid was observed either in the TIC or by using SIM. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

***Sample 008***

Sample 008 (ID# 104) was taken from sherd BEY006.5051.549 (Fig. B.5). The sherd is a Beirut 3 in local fabric; the sample was taken from the amphora's base. As previously mentioned, Context 5051 is dated to the 3rd c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.12 and 6.13). Analysis of the sample demonstrated low residual levels of relevant biomarkers. Acetic acid (2) and

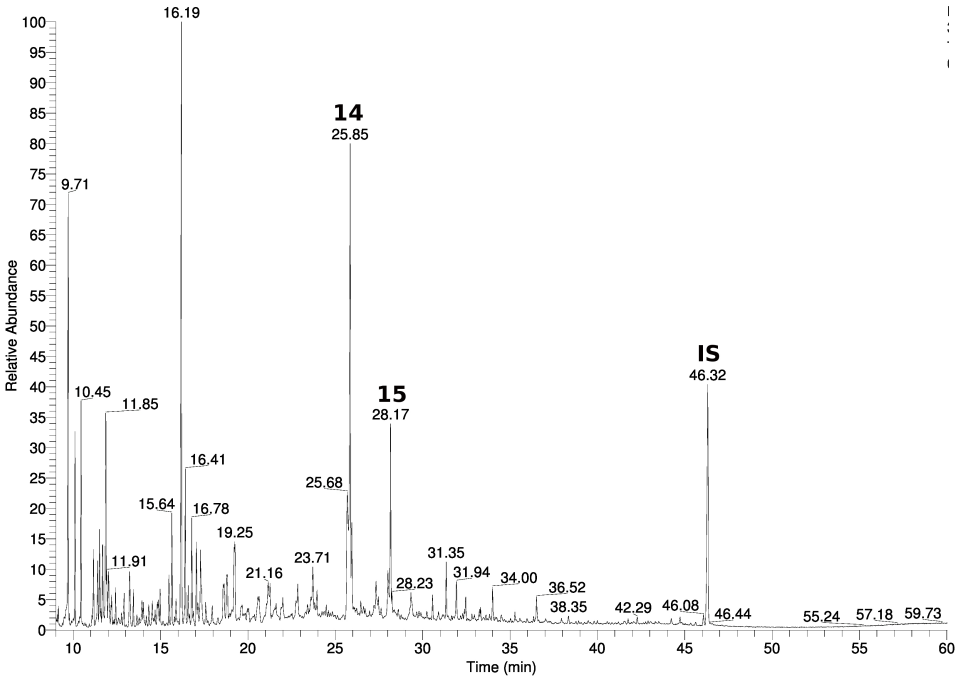


Figure 6.10: TIC Chromatogram of Sample 007

fumaric acid (4) were identified. Malic acid (10) was could not be identified in the sample. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

***Sample 009***

Sample 009 (ID# 115) was taken from sherd BEY006.12389.79 (Fig. B.6). The sherd is a Beirut 1A in local fabric; the sample was taken from the amphora's base. Context 12389 is dated to 1st c. BC with some intrusive material from the 4th/5th c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.14 and 6.15) indicated acetic acid (2), malonic acid (5), benzoic acid (6), glutaric acid (8) and malic acid (10). Tartaric acid (13) was identified in the sample. Dehydroabietic acid (18) was identified at minute 39.82. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

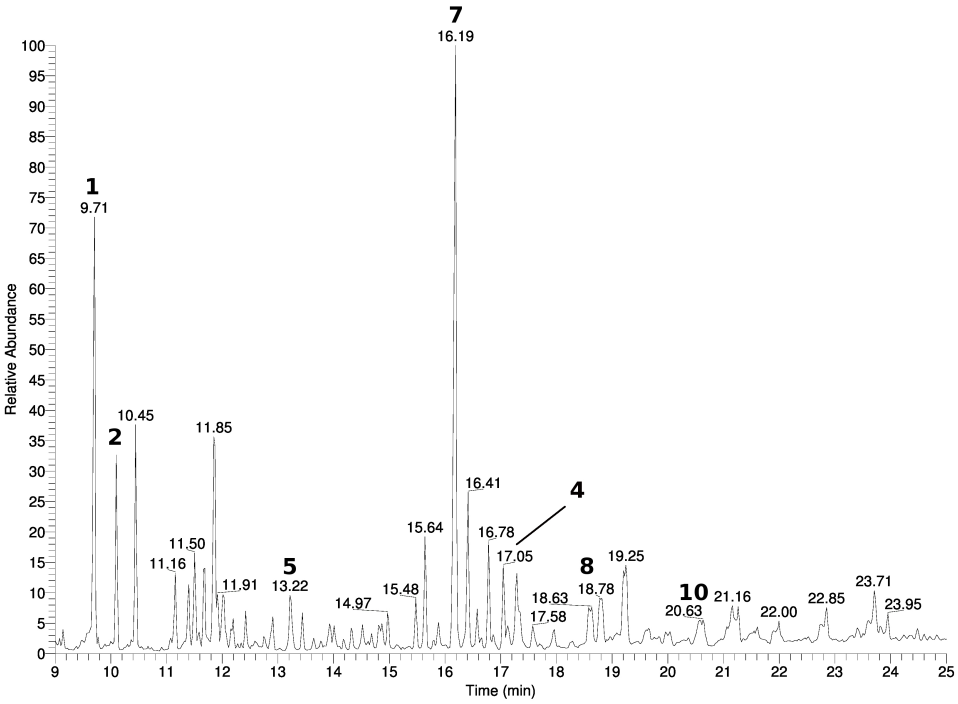


Figure 6.11: Partial TIC Chromatogram of Sample 007, minutes 9-25

***Sample 010***

Sample 010 (ID# 109) was obtained from sherd BEY006.5051.463 (Fig. B.7). The sherd is a Beirut in local fabric; the sample was taken from the amphora's base. A moderate degree of calcareous concretion was observed on the surface of the sherd. As previously stated, Context 5051 is dated to the 3rd c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.16 and 6.17). Analysis of the sample demonstrated low residual levels of relevant biomarkers. Acetic acid (2) and malic acid (10) were identified. Propanoic acid (1), succinic acid (7) and azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

***Sample 011***

Sample 011 (ID# 112) was obtained from sherd BEY006.12233.139 (Fig. B.8). The sherd is a Beirut 1 in heavy local fabric. Calcareous and yellow mineral deposits

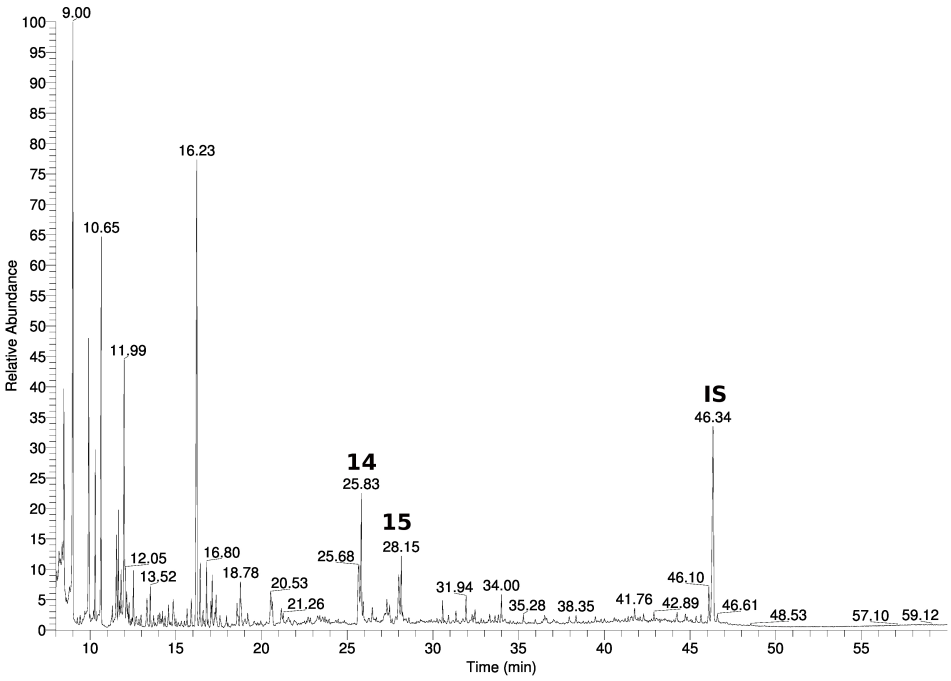


Figure 6.12: TIC Chromatogram of Sample 008

were observed on the surface of the sherd. The sample was taken from the amphora's base. Context 12233 is dated to between 75 and 50 BC and described in the Pottery Database as pit fill.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.18 and 6.19) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid (13) was identified in the sample. Dehydroabietic acid (not labeled on chromatogram) was identified at minute 39.82. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. An error in injection of the internal standard is believed to be responsible for the low relative intensity of the internal standard (IS) relative to other analytes in the chromatogram. An issue with standard injection was observed for all samples in the sample batch containing Samples 011-017.

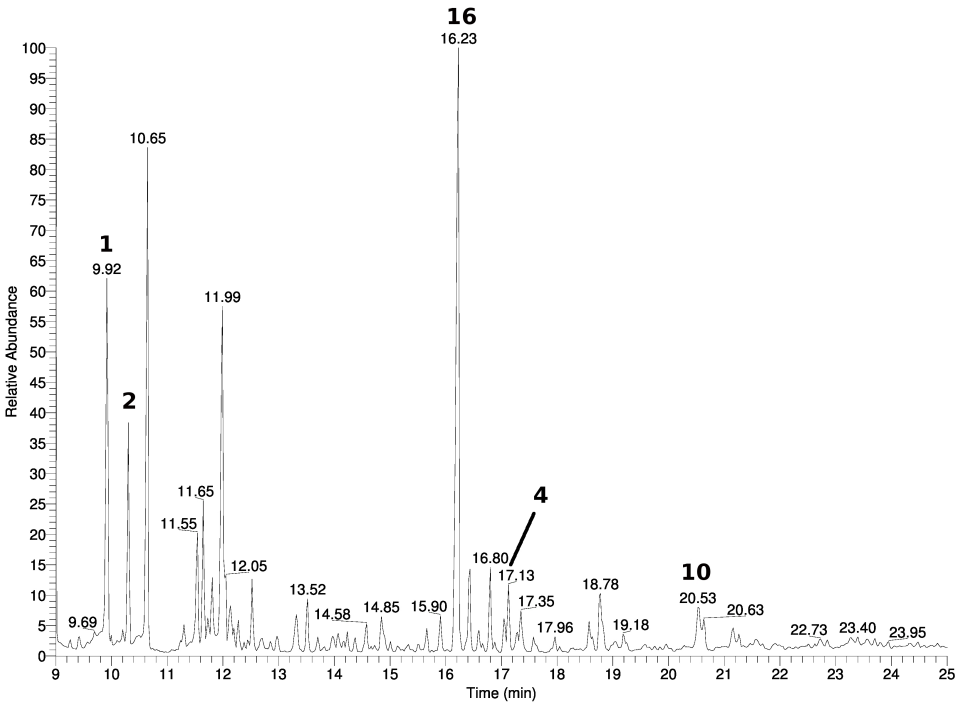


Figure 6.13: Partial TIC Chromatogram of Sample 008, minutes 9-25

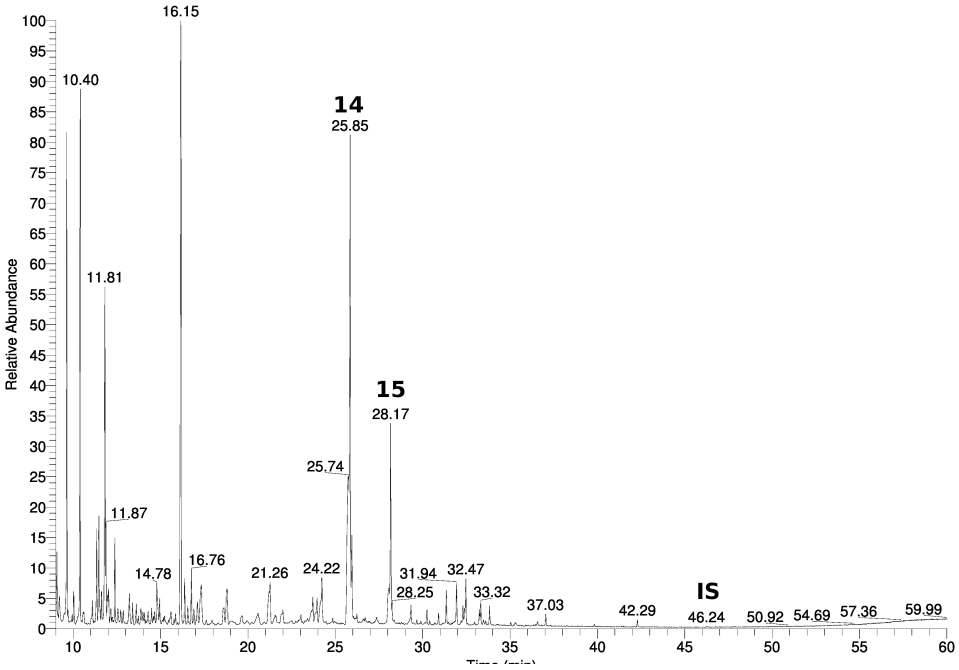


Figure 6.18: TIC Chromatogram of Sample 011

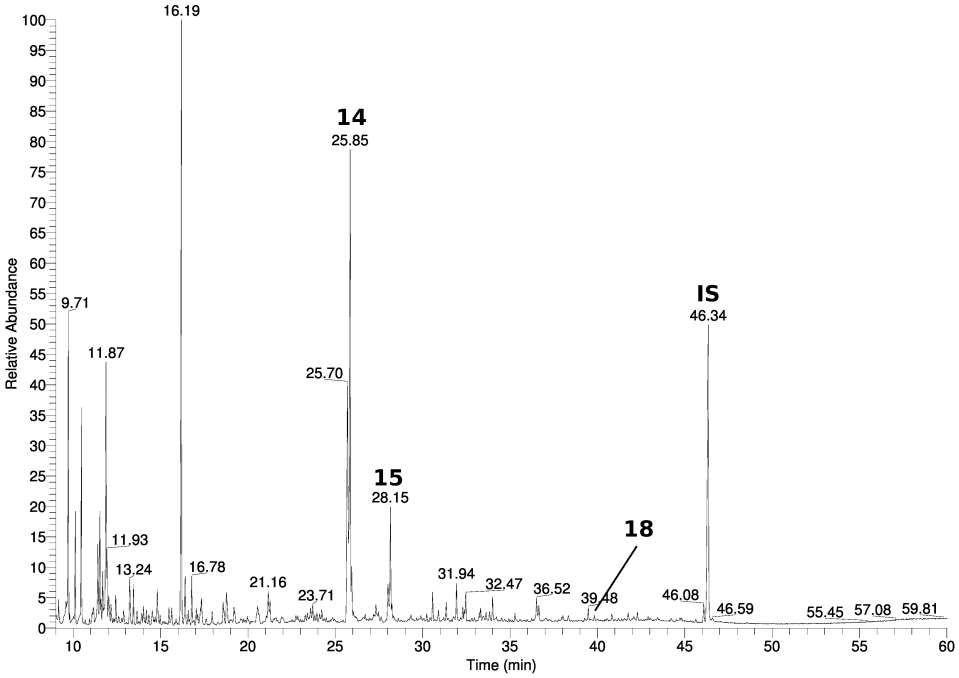


Figure 6.14: TIC Chromatogram of Sample 009

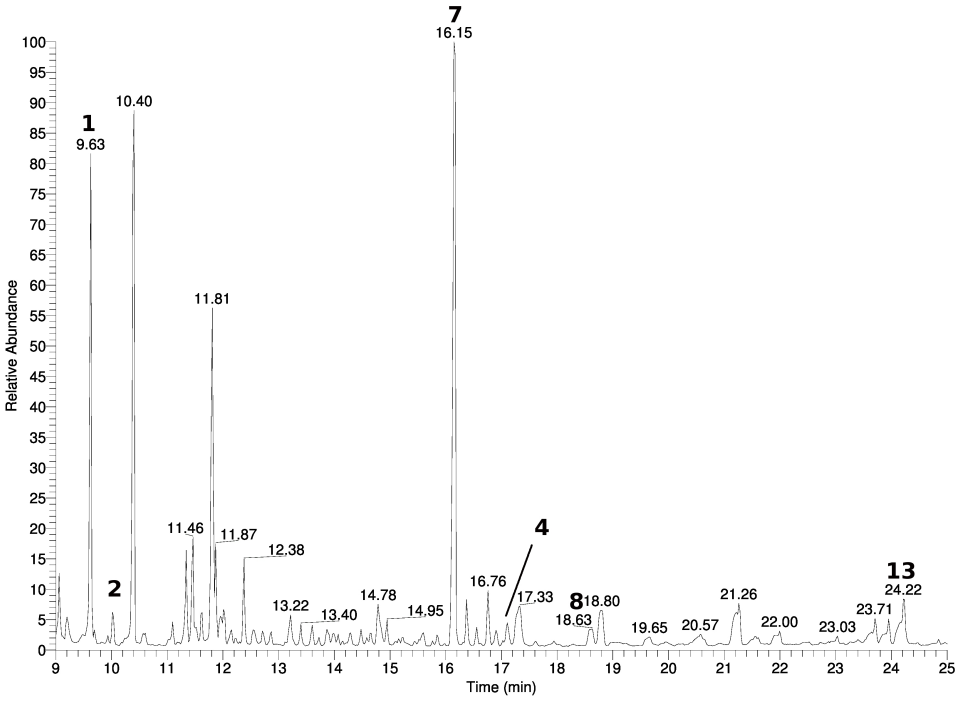


Figure 6.19: Partial TIC Chromatogram of Sample 011, minutes 9-25

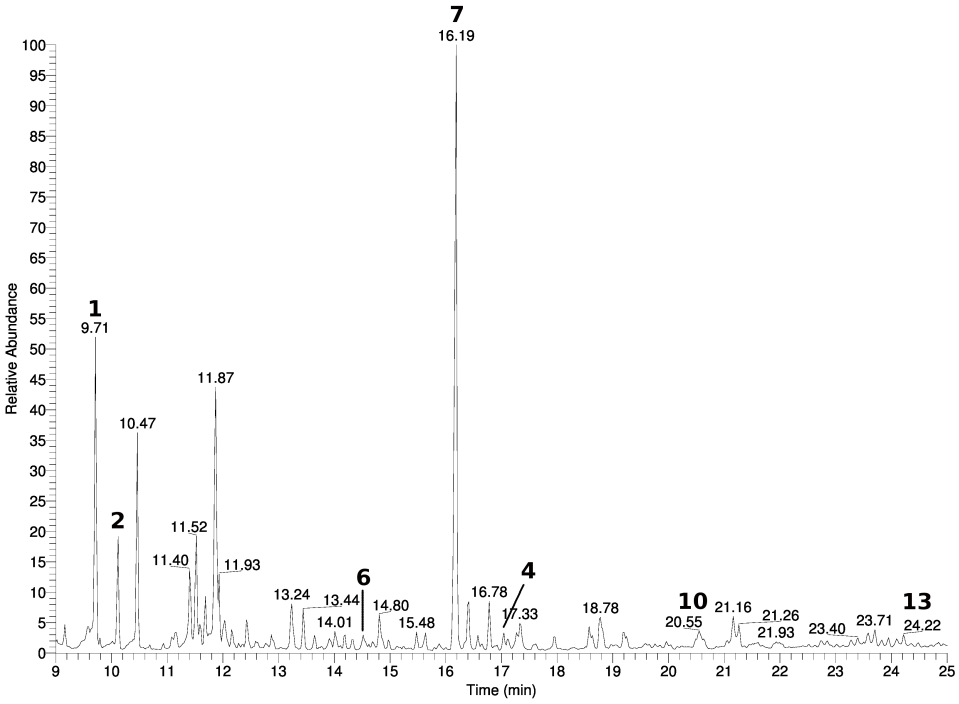


Figure 6.15: Partial TIC Chromatogram of Sample 009, minutes 9-25

***Sample 012***

Sample 012 (ID# 113) was obtained from sherd BEY006.12233.138 (Fig. B.9). Like Sample 011, the sherd is a Beirut 1 in heavy local fabric. Unlike Sample 011, no mineral deposits were observed on the surface of the sherd. The sample was taken from the amphora's base. As noted above, Context 12233 is dated to between 75 and 50 BC and described in the Pottery Database as pit fill.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.20 and 6.21) indicated acetic acid (2), fumaric acid (4), and malic acid (10). Tartaric acid (13) was identified in the sample. Dehydroabietic acid was not identified. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. As mentioned above, an error with the internal standard injection was experienced with this sample.

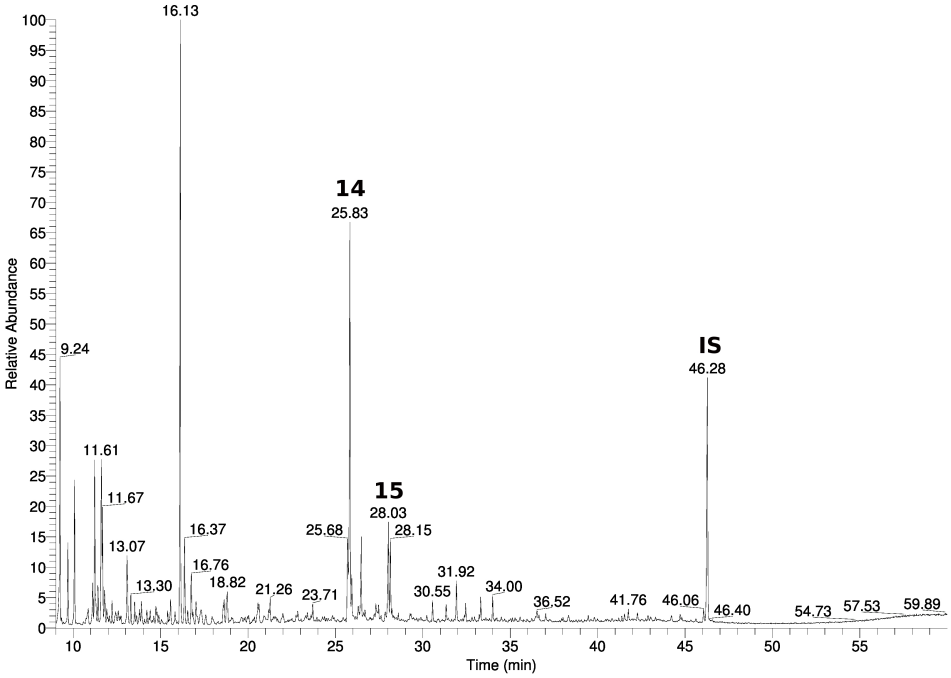


Figure 6.16: TIC Chromatogram of Sample 010

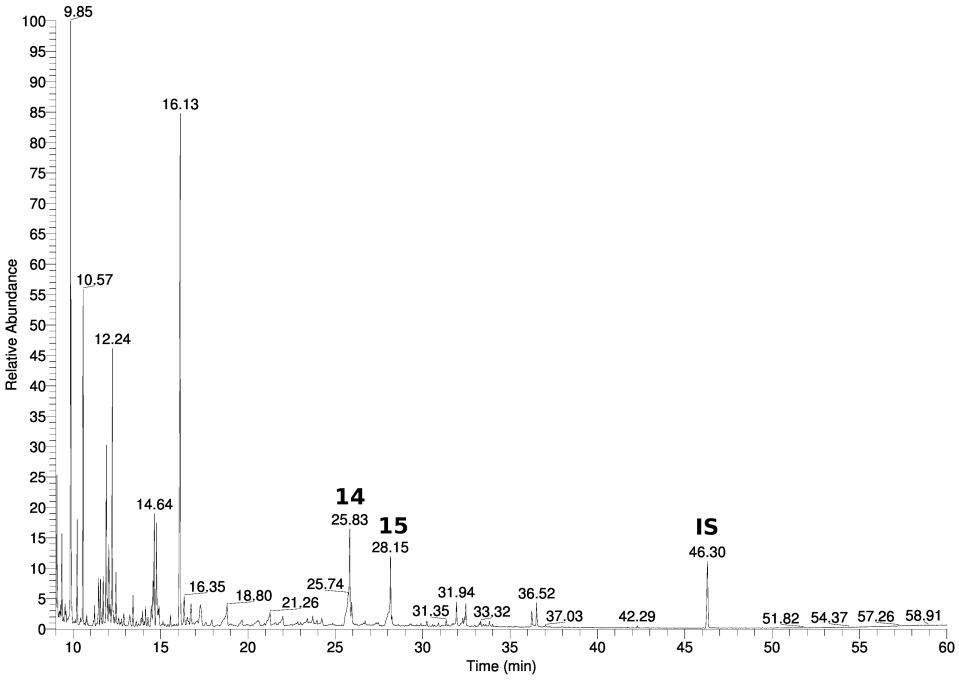


Figure 6.20: TIC Chromatogram of Sample 012

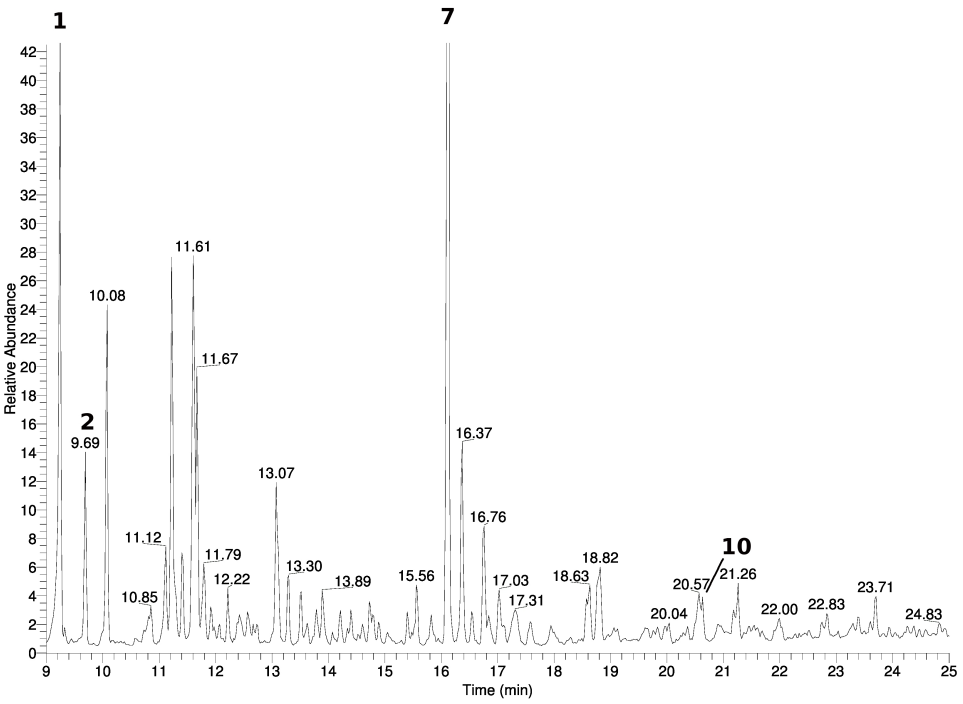


Figure 6.17: Partial TIC Chromatogram of Sample 010, minutes 9-25

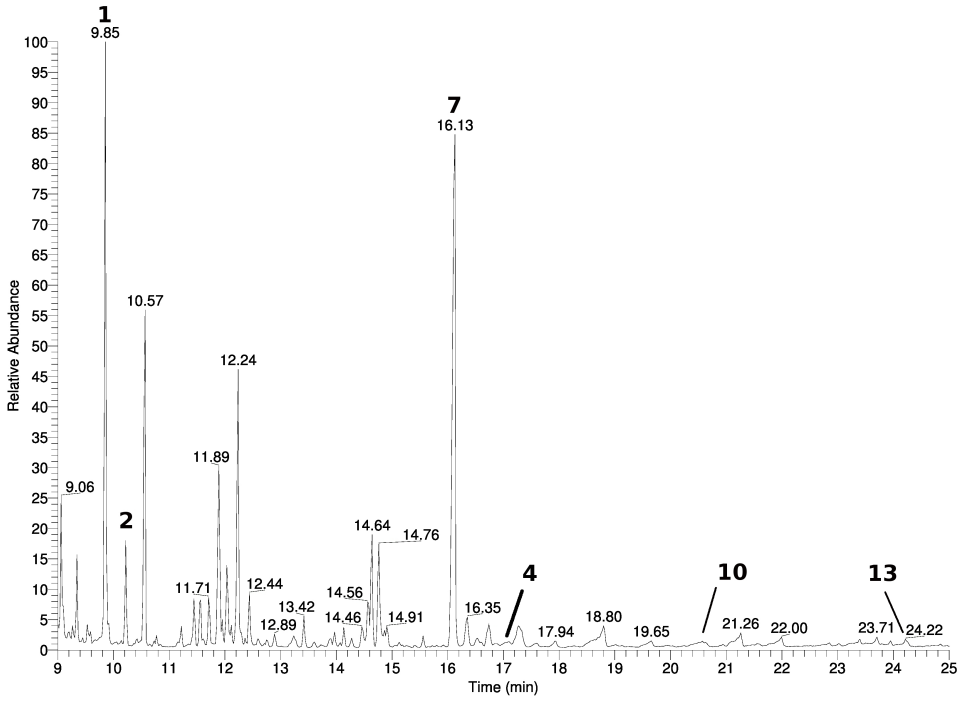


Figure 6.21: Partial TIC Chromatogram of Sample 012, minutes 9-25

***Sample 013***

Sample 013 (ID# 116) was obtained from sherd BEY006.12389.80 (Fig. B.10). The sherd is a Beirut 1A; the sample was taken from the amphora's base. Sample 013 is from the same context as Sample 009, that is, a 1st c. BC deposit with 4th/5th c. AD intrusive material.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.22 and 6.23) indicated acetic acid (2), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). No peak associated with tartaric acid was identified. Dehydroabietic acid was not identified. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. As mentioned above, an error with the internal standard injection was experienced with this sample.

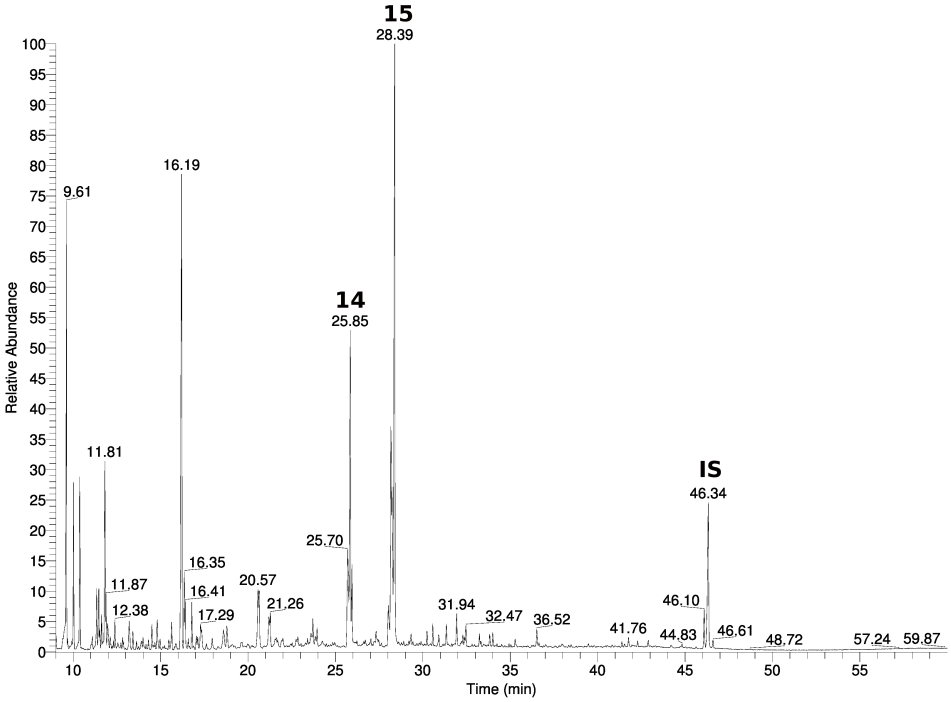


Figure 6.22: TIC Chromatogram of Sample 013

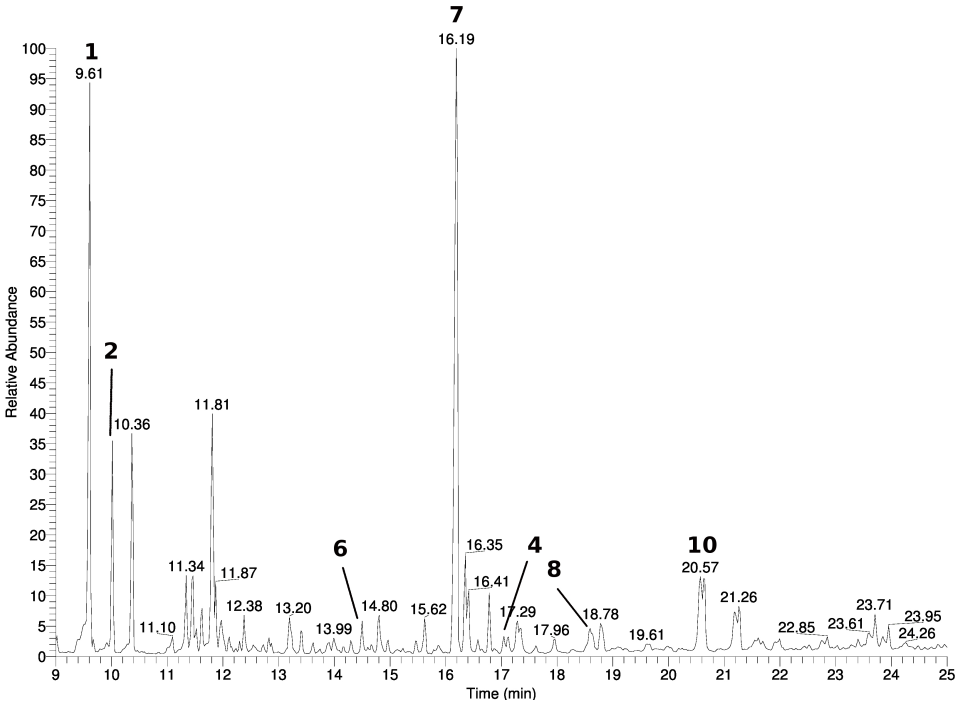


Figure 6.23: Partial TIC Chromatogram of Sample 013, minutes 9-25

***Sample 014***

Sample 014 (ID# 119) was obtained from sherd BEY006.12237.x3 (Fig. B.11). The sherd is a Beirut 2 in reduced local fabric; the sample was taken from the amphora's base. Mineral deposits were observed on the sherd's surface. Sample 014 is from the same context as Samples 004 and 007, that is, Context 12237, a mid-1st c. AD cistern deposit.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.24 and 6.25) indicated acetic acid (2), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Dehydroabietic acid was identified at minute 39.82. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. As mentioned above, an error with the internal standard injection was experienced with this sample.

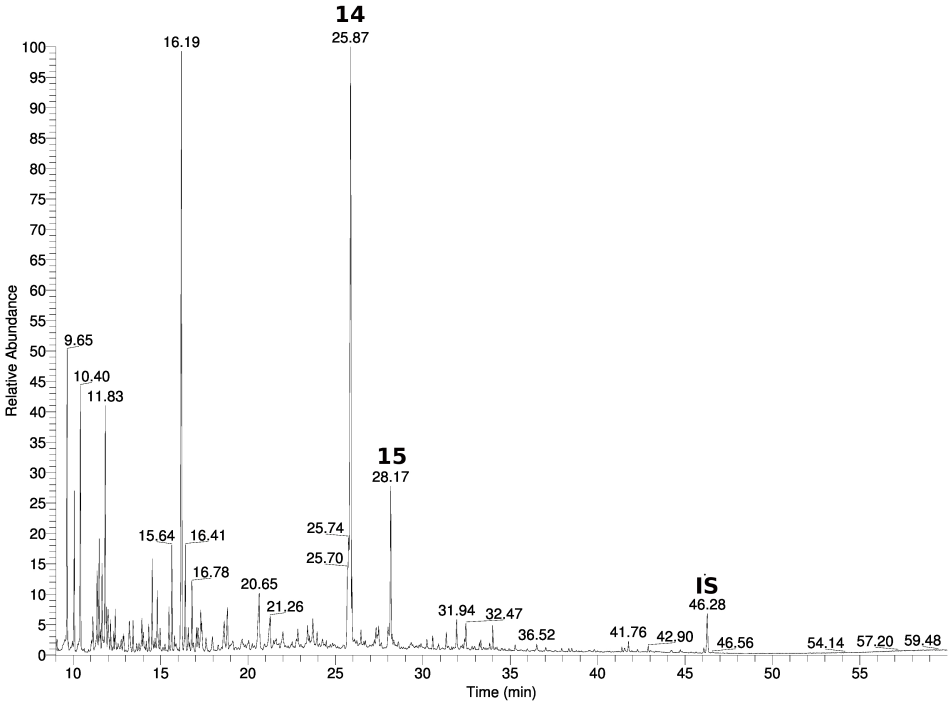


Figure 6.24: TIC Chromatogram of Sample 014

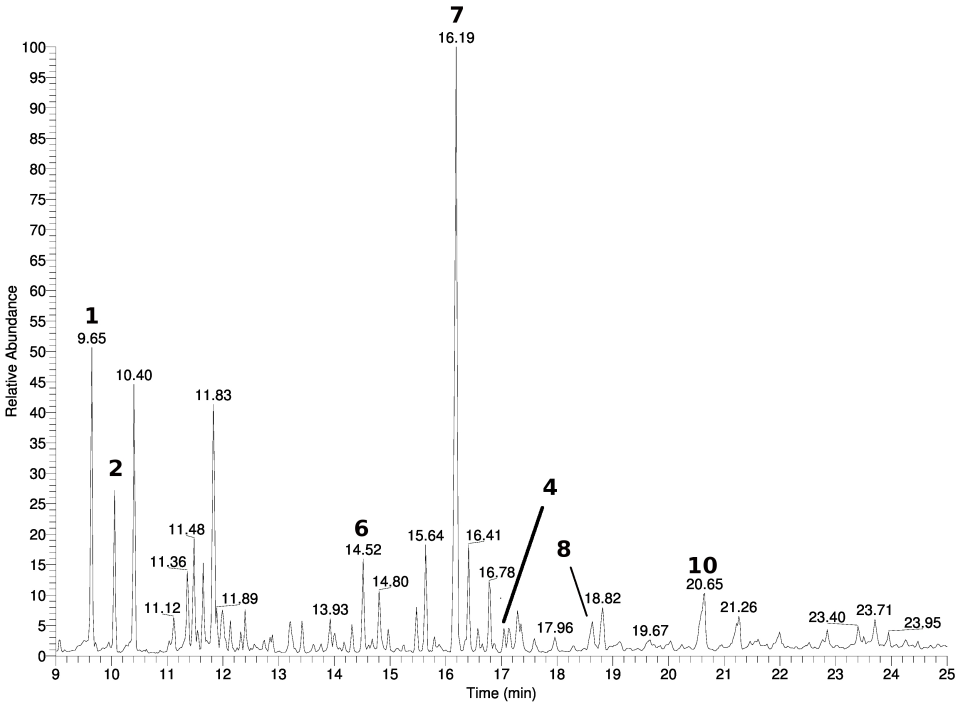


Figure 6.25: Partial TIC Chromatogram of Sample 014, minutes 9-25

***Sample 015***

Sample 015 (ID# 123) was obtained from sherd BEY045.1381.19 (Fig. B.12). While initially believed to be from a Beirut 4 in reduced local fabric, Dr. Paul Reynolds has suggested that it may instead be an AM-14, a North Lebanese amphora form related to the Beirut amphora "main series."[3] Macroscopic differentiation of the AM-14 fabric from the Beirut fabric is difficult, relying primarily on the size of quartz inclusions.[4] As this sample has not been positively identified with respect to form, it has been excluded as a Beirut amphora sample.

The sample was taken from the amphora's base. A significant amount of mortar was observed on the sherd's surface. Dr. Paul Reynolds' comments in the Pottery Database indicated that residue (possibly charcoal) was present on the interior of the vessel; however, no visible residue was observed when sherd was retrieved from collections and the sample harvested for analysis. Context 1381 is dated to the early 3rd c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.26 and 6.27) indicated low residuality in the sample. Glutaric acid (8) was identified; however, none of the other biomarkers for wine could be positively identified. Peaks corresponding to the retention time for several compounds, including tartaric acid, were observed; however, close elution of other compounds, combined with apparent low residual levels of analytes of interest, precluded identification. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. As mentioned above, an error with the internal standard injection was experienced with this sample.

Due to the small size of the sherd and the hardness of the ceramic fabric, only 250 mg of ceramic powder could be harvested for analysis. This may have contributed to the apparent low residuality of biomarkers. Another ceramic sample was subsequently taken from a larger adjoining sherd and analyzed as Sample 022.

[3]Paul Reynolds, pers. comm.

[4]Paul Reynolds, pers. comm.

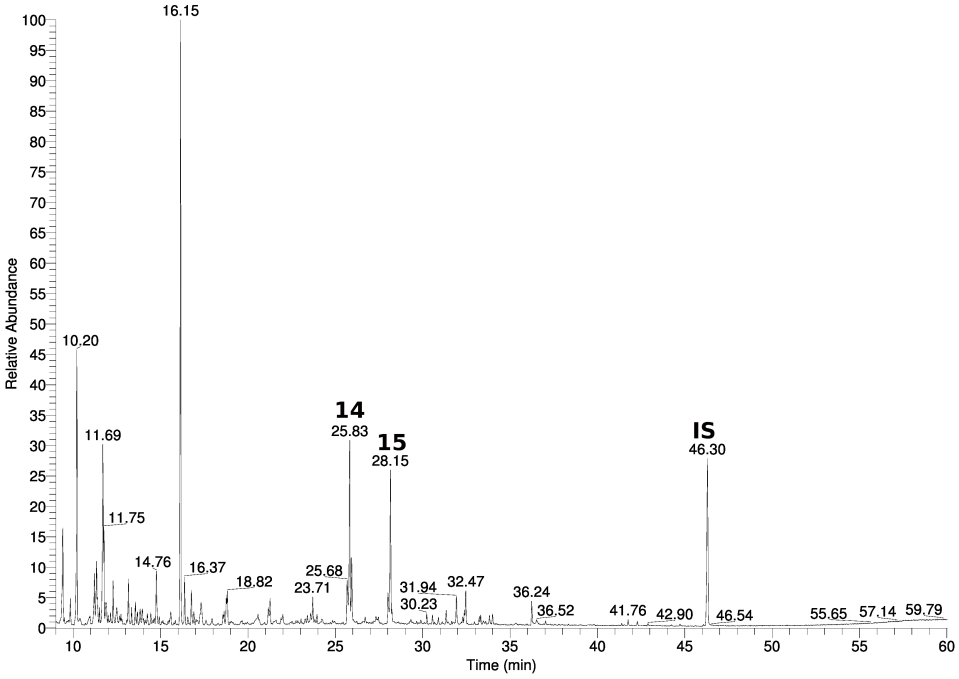


Figure 6.26: TIC Chromatogram of Sample 015

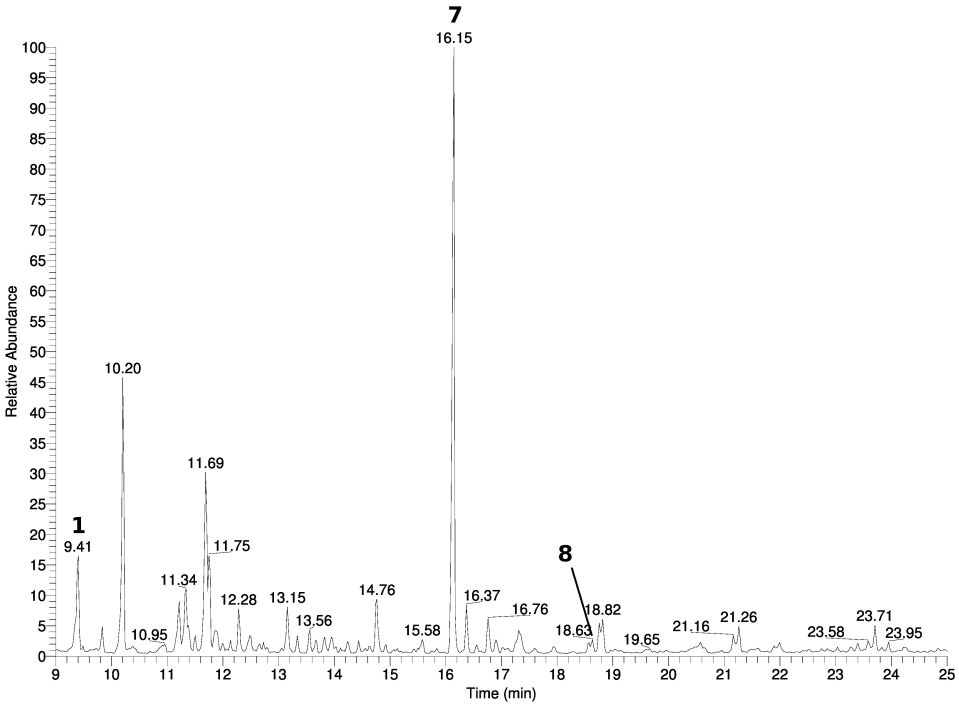


Figure 6.27: Partial TIC Chromatogram of Sample 015, minutes 9-25

***Sample 016***

Sample 016 (ID# 190) was obtained from sherd BEY006.11629.93 (Fig. B.13). The sherd is a Beirut 3 in reduced local fabric. The sample was taken from the amphora's base. Context 11629 is dated to between 125 and 150 AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.28 and 6.29) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. As mentioned above, an error with the internal standard injection was experienced with this sample.

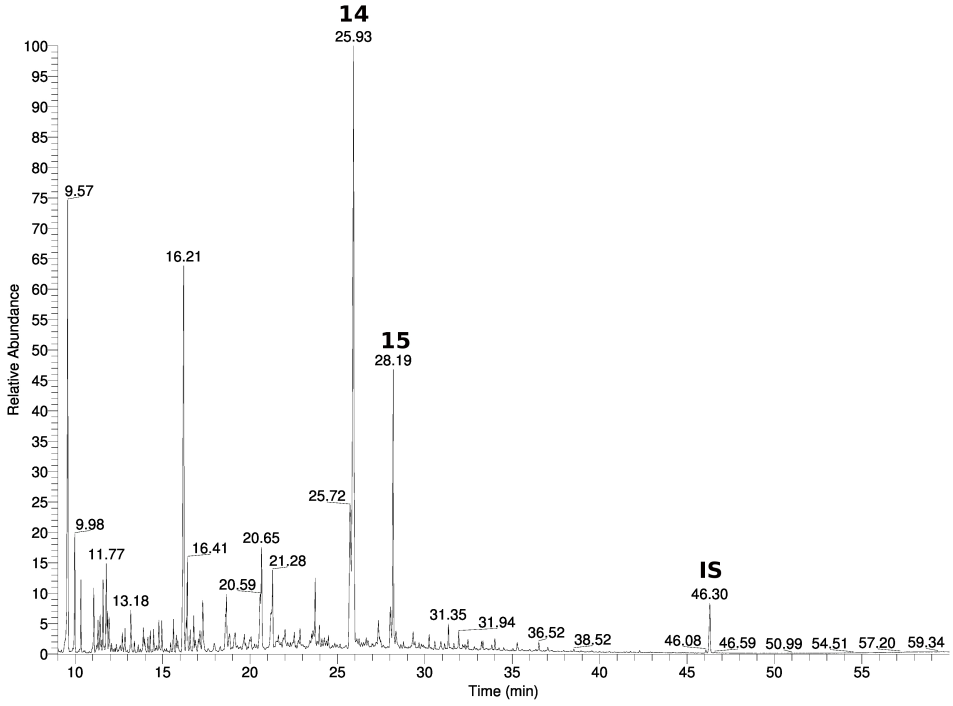


Figure 6.28: TIC Chromatogram of Sample 016

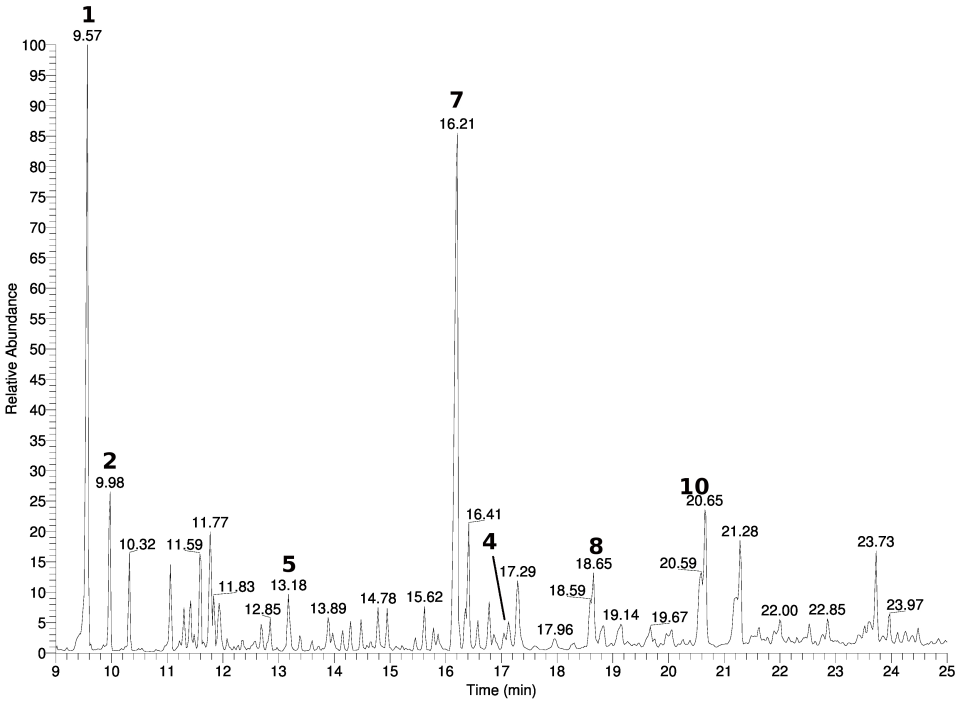


Figure 6.29: Partial TIC Chromatogram of Sample 016, minutes 9-25

***Sample 017***

Sample 017 (ID# 079) was obtained from sherd BEY006.12539.1 (Fig. B.14). The sherd is a Beirut 3 in rough local fabric. The sample was taken from the lower wall/base of the amphora. Context 12539 is dated to the late 1st c. AD with 6th c. AD intrusive material.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.30 and 6.31) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid (13) was identified in the sample. Dehydroabietic acid (18) was identified. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample. As mentioned above, an error with the internal standard injection was experienced with this sample.

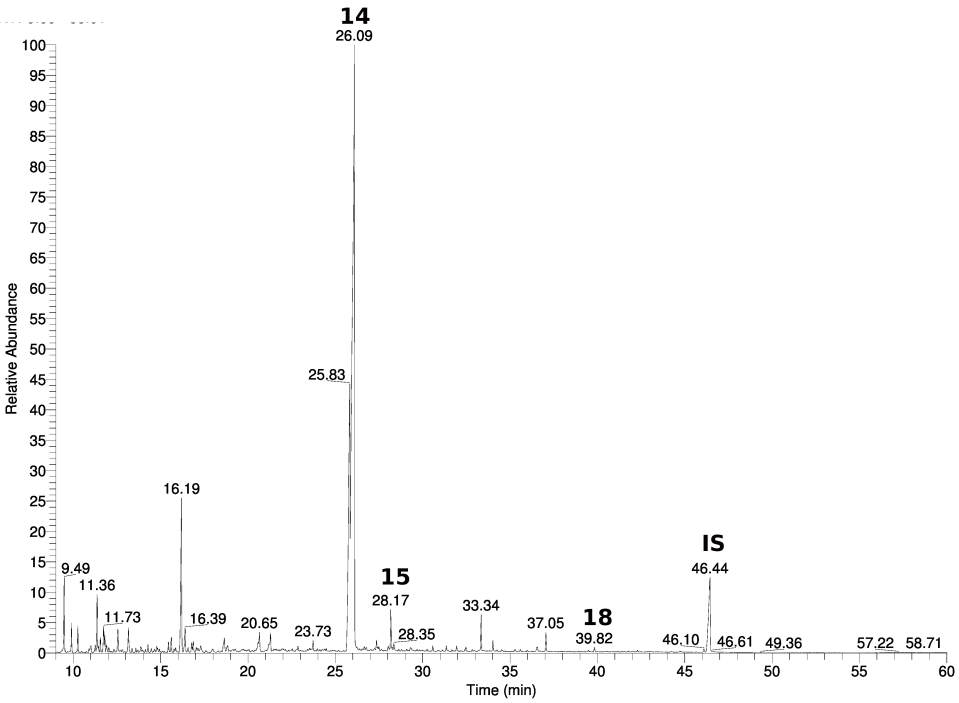


Figure 6.30: TIC Chromatogram of Sample 017

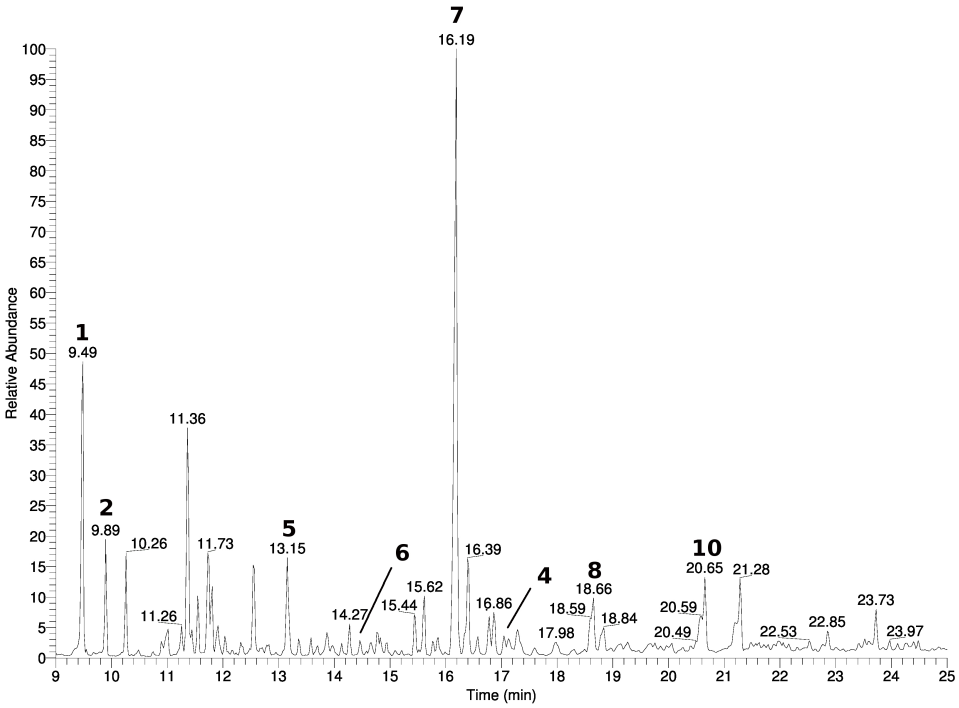


Figure 6.31: Partial TIC Chromatogram of Sample 017, minutes 9-25

***Sample 018***

Sample 018 (ID# 168) was obtained from sherd BEY006.12239.15 (Fig. B.15). The sherd is a Beirut 2 in local fabric. The sample was taken from the amphora's base. Context 12239 contained material dated to the 3rd/2nd c. BC, late 1st c. BC and 1st c. AD. The context was described as secondary drain fill.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.32 and 6.33) indicated malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Dehydroabietic acid (18) was also identified in the sample. Propanoic acid (1), a high level of succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

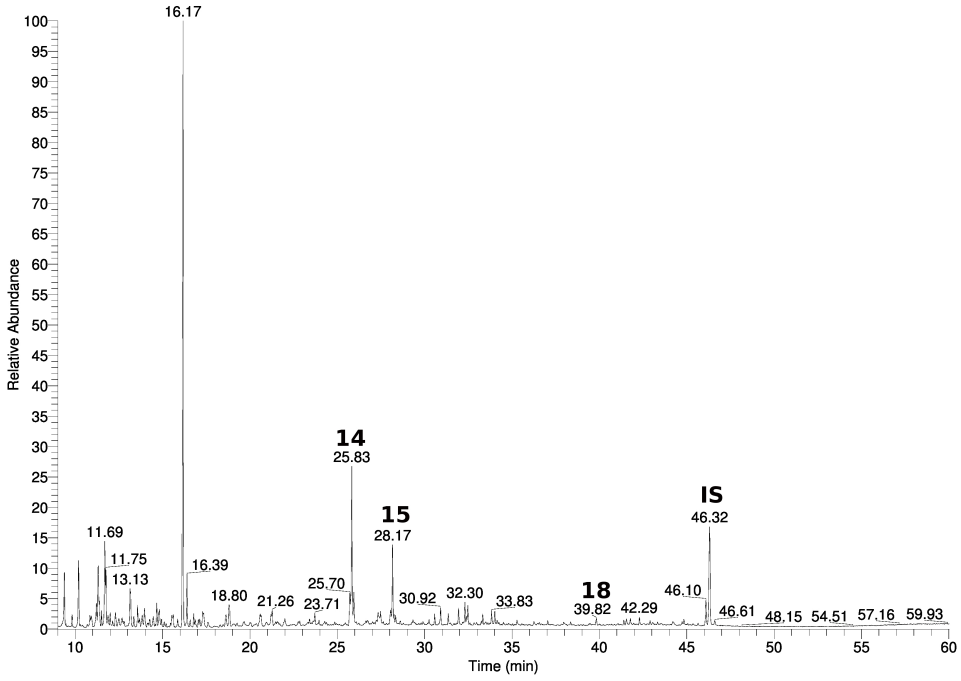


Figure 6.32: TIC Chromatogram of Sample 018

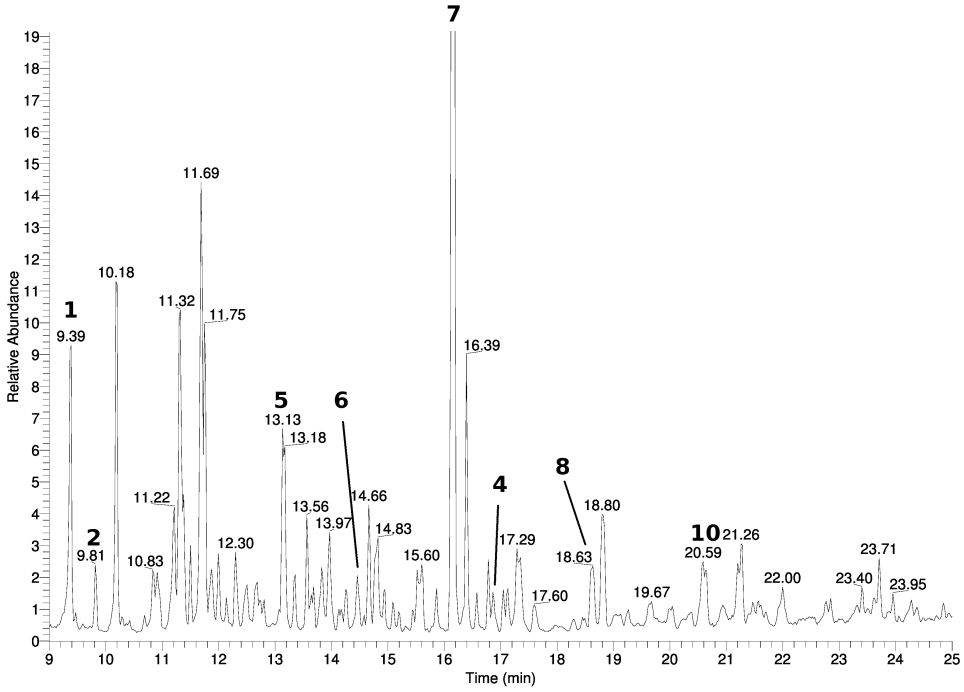


Figure 6.33: Partial TIC Chromatogram of Sample 018, minutes 9-25

***Sample 019***

Sample 019 (ID# 192) was obtained from sherd BEY045.1242.x1 (Fig. B.16). The sherd is a Beirut 3 or 4 amphora, the base of which had been drilled through (Fig. 3.2). The sample was taken from the amphora's base. Context 1242 is dated to the 3rd c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.34 and 6.35) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

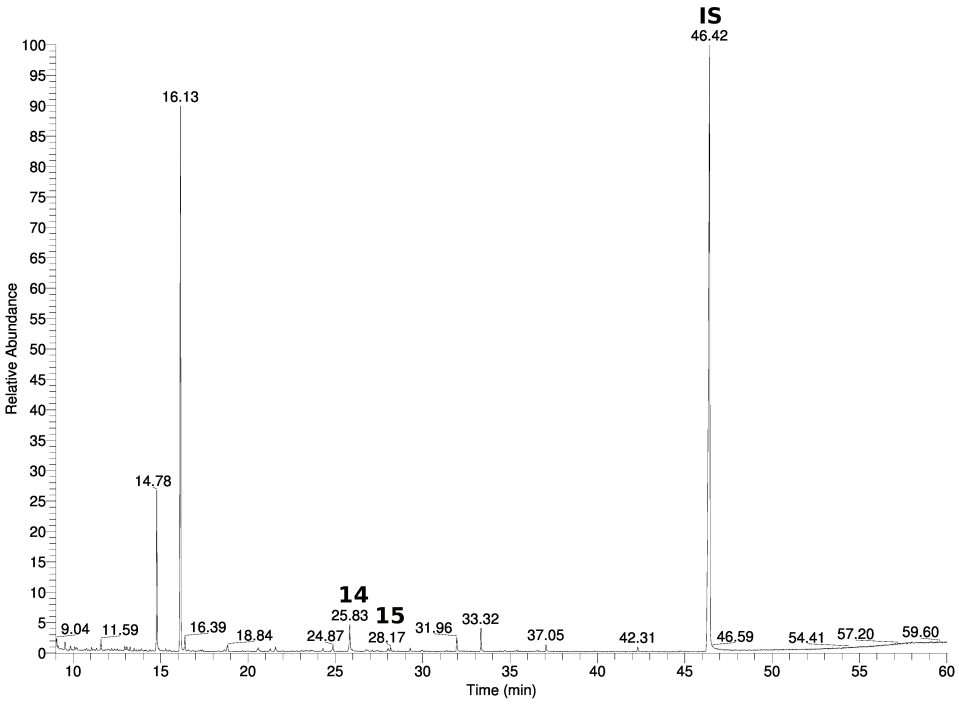


Figure 6.34: TIC Chromatogram of Sample 019

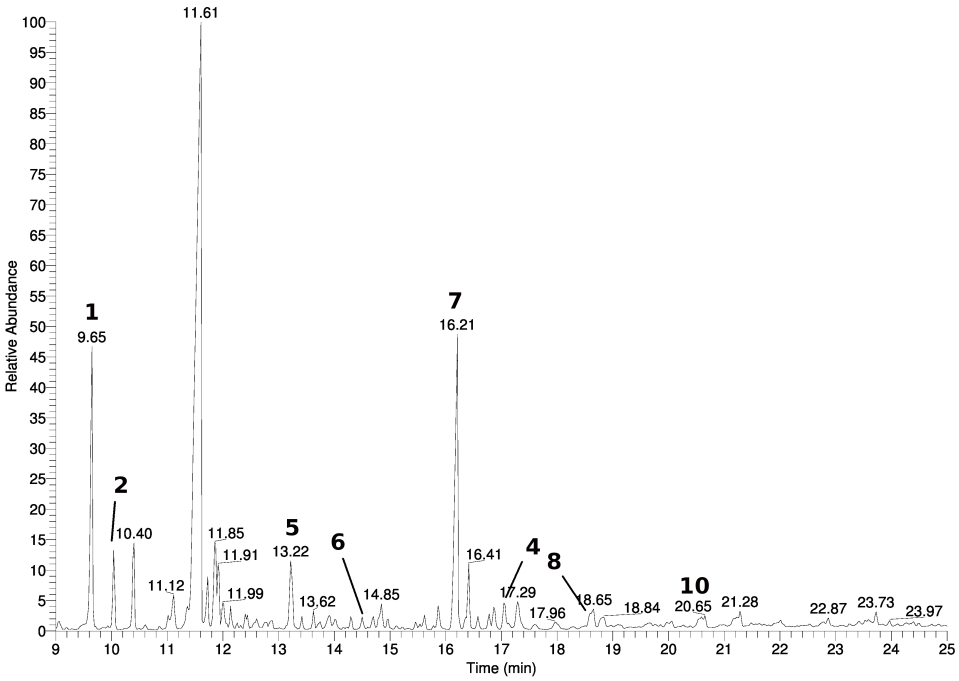


Figure 6.35: Partial TIC Chromatogram of Sample 019, minutes 9-25

***Sample 020***

Sample 020 (ID# 194) was obtained from sherd BEY006.11603.x1 (Fig. B.17). The sherd is a Beirut 3 in local fabric. A hole had been drilled through the center of the base, similar to BEY045.1242.x1. The sample was taken from the amphora's base. Context 11603 is dated to between 125 and 150 AD.

GC/MS analysis of the carboxylic acid extraction (figs. 6.36 and 6.37) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

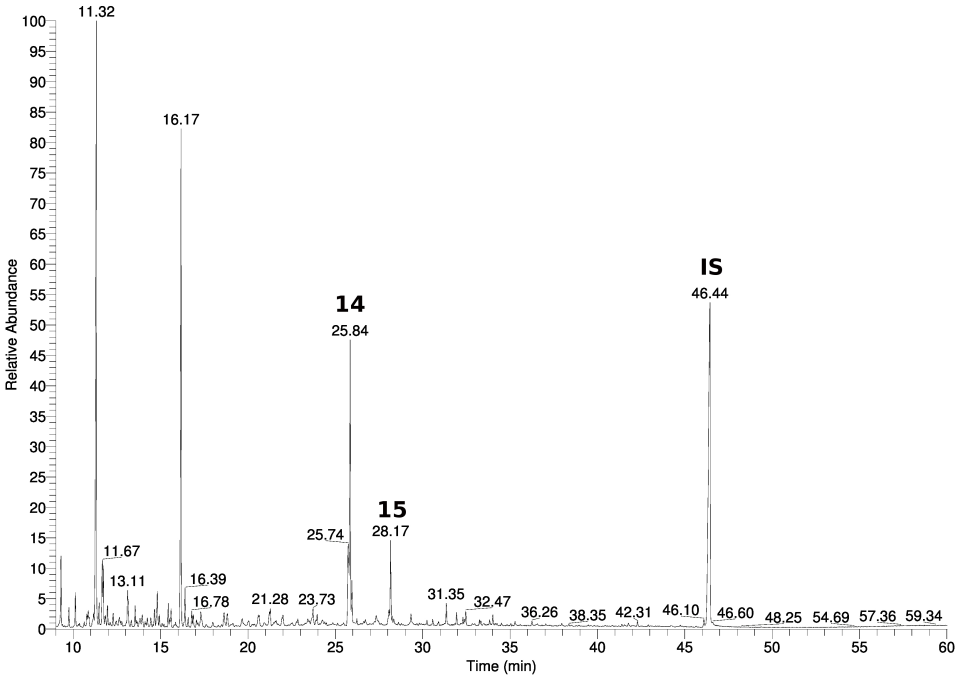


Figure 6.36: TIC Chromatogram of Sample 020

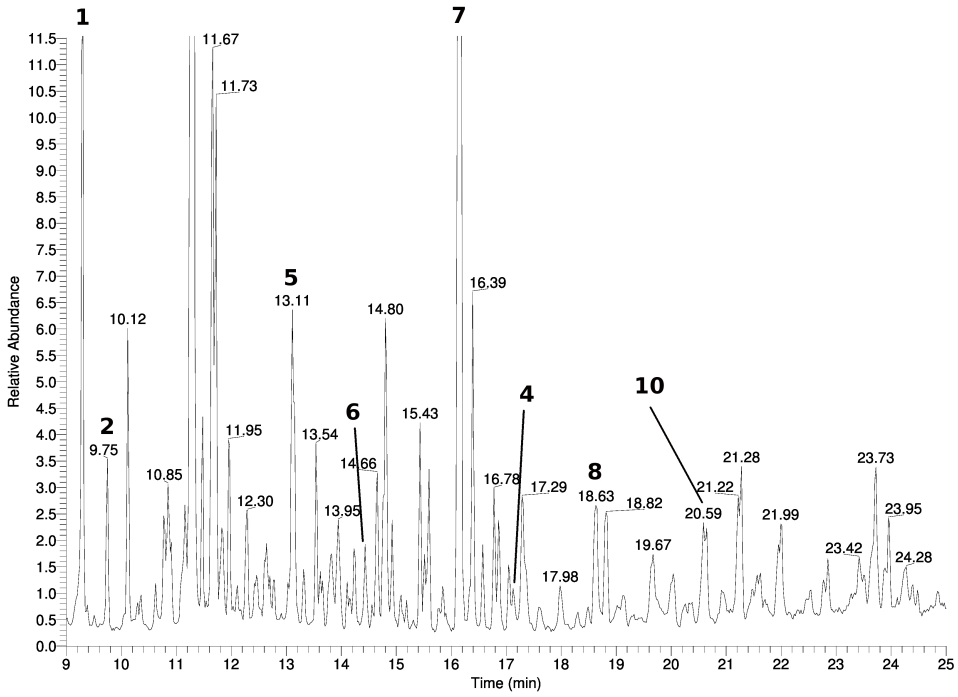


Figure 6.37: Partial TIC Chromatogram of Sample 020, minutes 9-25

***Sample 022***

Sample 022 (ID# 202) was obtain from BEY045.1381.19 (Fig. B.12). Concerning the identification of the amphora form, see Sample 015. The sample was taken from the amphora's base. Context 1381 is dated to the early 3rd c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.38 and 6.39) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

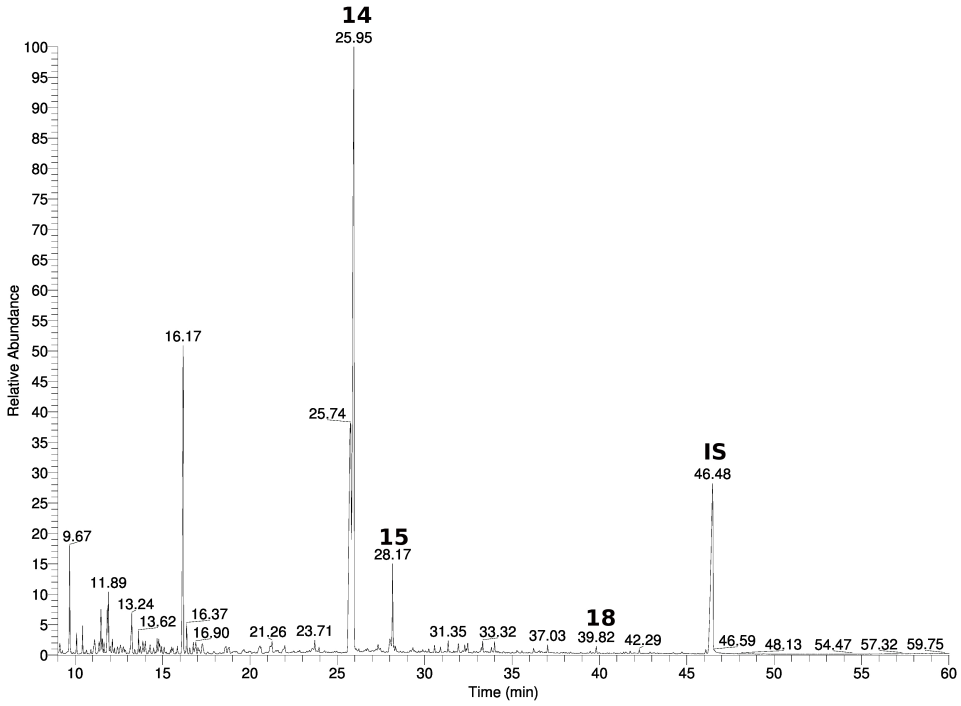


Figure 6.38: TIC Chromatogram of Sample 022

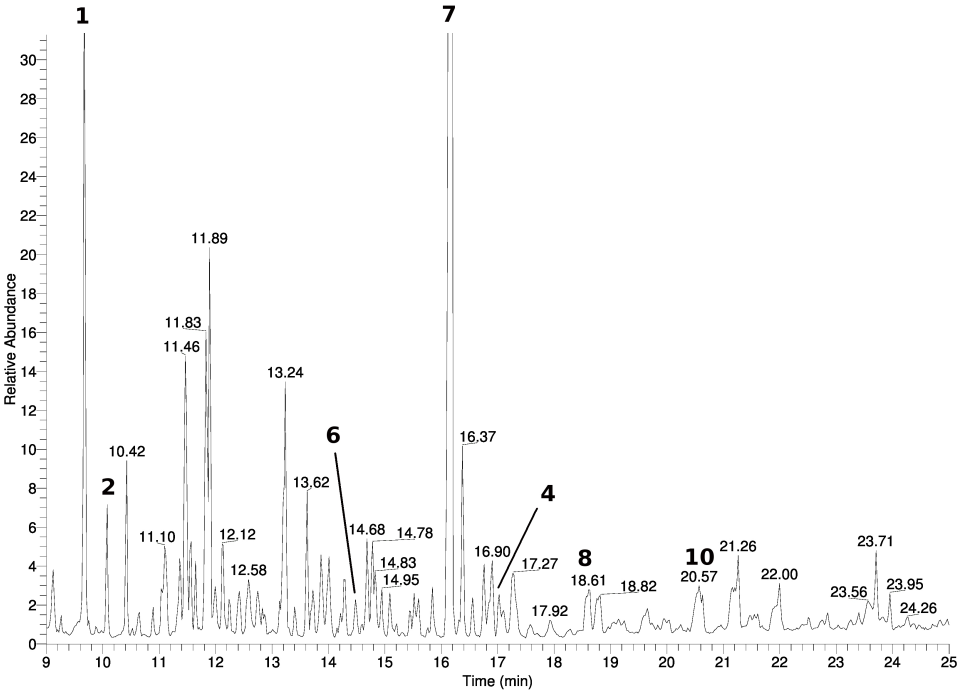


Figure 6.39: Partial TIC Chromatogram of Sample 022, minutes 9-25

***Sample 023***

Sample 023 (ID# 038) was obtained from sherd BEY006.8333.21 (Fig. B.18). The sherd is a Beirut 1 in local fabric. Notes in the Pottery Database indicate that the base toe had been pierced or drilled through. Context 8333 is dated to the early 1st c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.40 and 6.41) indicated acetic acid (2) and a poorly resolved peak identified as malonic acid (5). Malonic acid, fumaric acid and benzoic acid could not be positively identified after mass spectral analysis using SIM. The low probability is probably due to extremely low residual levels of the respective compounds. Tartaric acid was not identified in the sample. Dehydroabietic acid was identified at minute 39.82. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

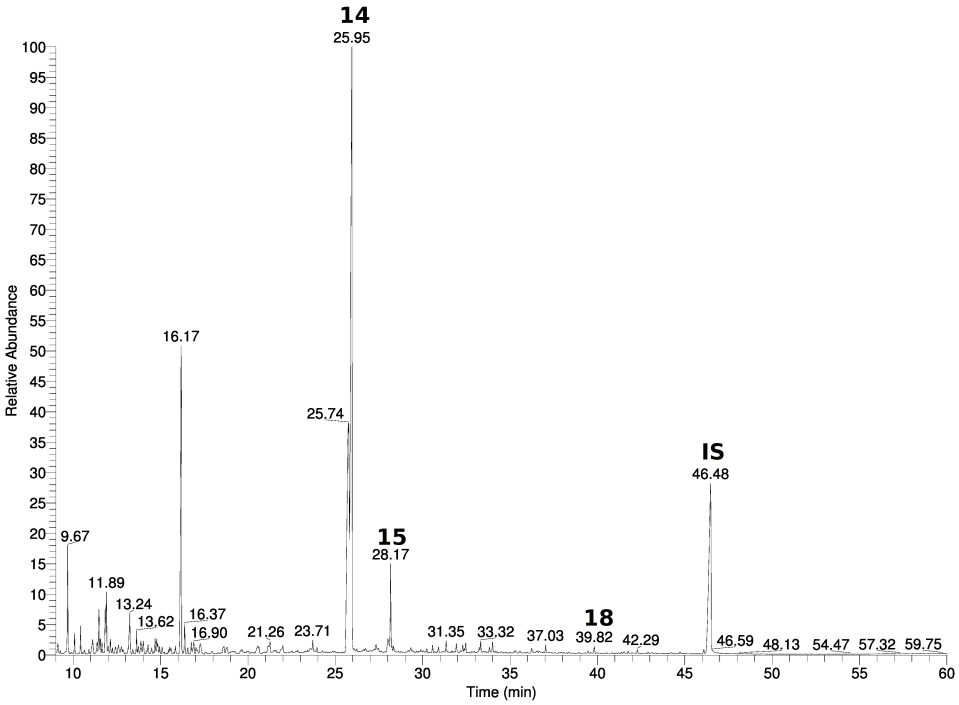


Figure 6.40: TIC Chromatogram of Sample 023

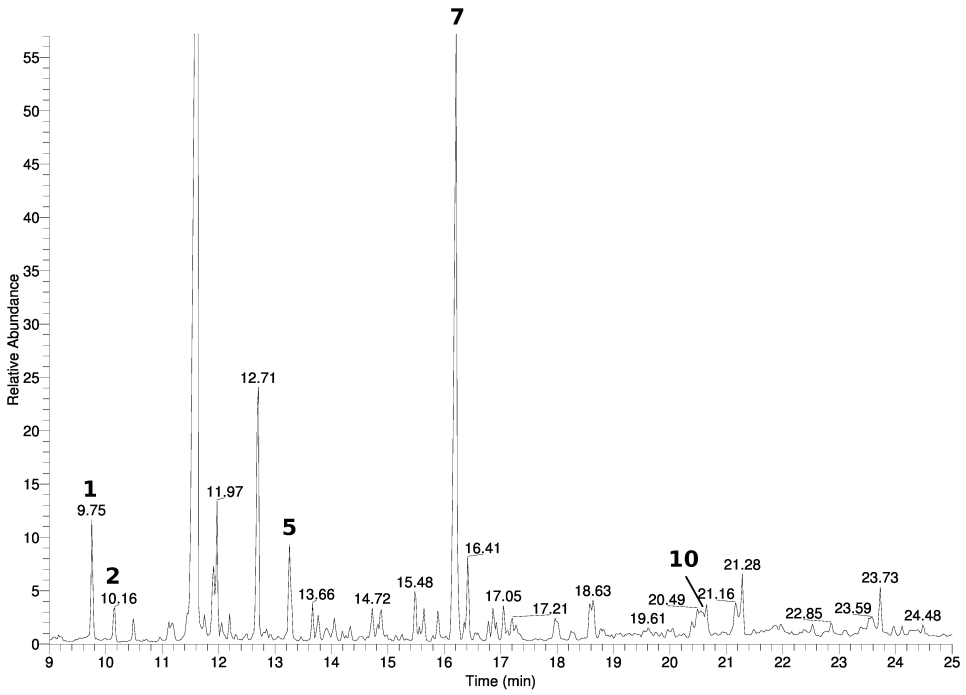


Figure 6.41: Partial TIC Chromatogram, minutes 9-25

***Sample 024***

Sample 024 (ID# 081) was obtained from sherd BEY006.10082.6 (Fig. B.19). The sherd is a Beirut 3 in local fabric. The toe of the base appeared to have been drilled through. Context 10082 is dated to the late 1st c. AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.42 and 6.43) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid was not identified in the sample. Dehydroabietic acid (18) was identified. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

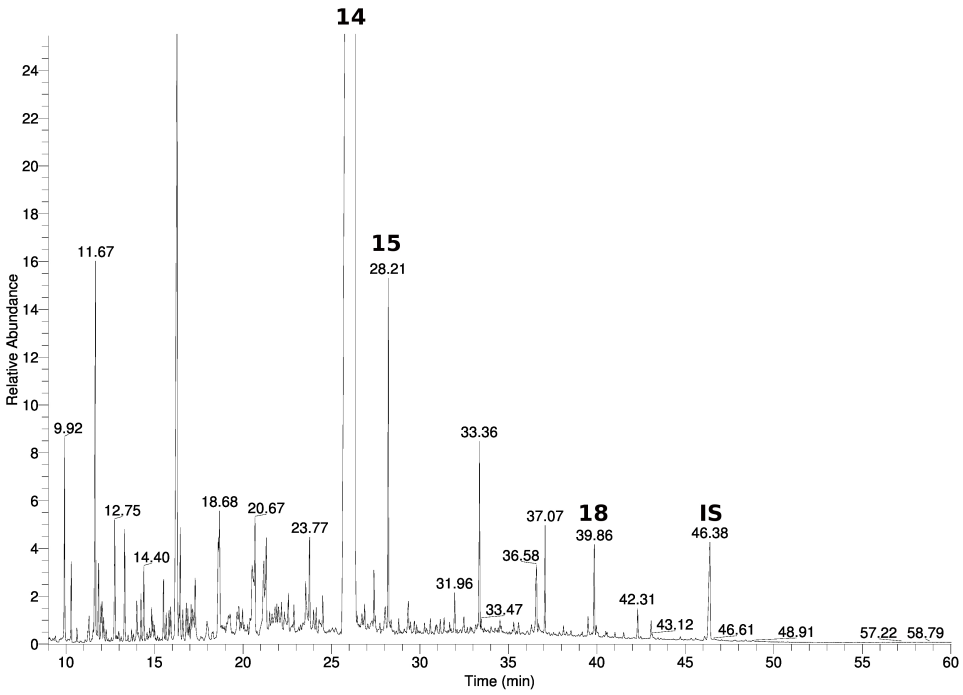


Figure 6.42: TIC Chromatogram of Sample 024

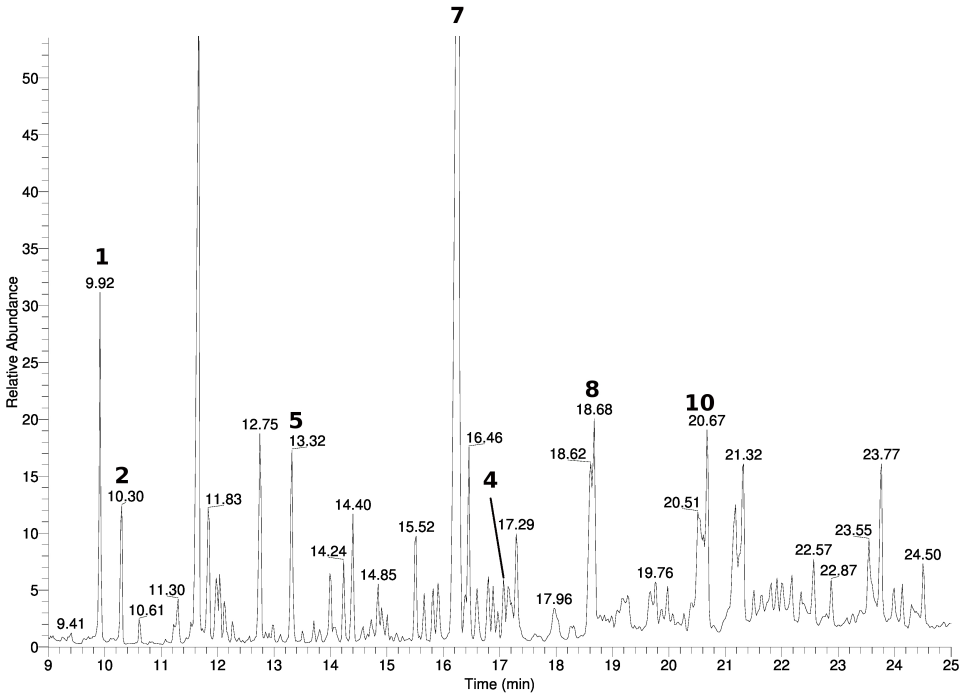


Figure 6.43: Partial TIC Chromatogram of Sample 024, minutes 9-25

***Sample 026***

Sample 026 (ID# 203) was obtained from sherd BEY006.9429.201 (Fig. B.20). The sherd is a Beirut 5 in local fabric. The sample was taken from the amphora's base. Context 9429 is dated to c. 375 AD.

GC/MS analysis of the carboxylic acid extraction (Figs. 6.44 and 6.45) indicated acetic acid (2), malonic acid (5), benzoic acid (6), fumaric acid (4), glutaric acid (8) and malic acid (10). Tartaric acid (13) was identified in the sample. Dehydroabietic acid was identified at minute 39.82. Propanoic acid (1), succinic acid (7), azelaic acid (15) were identified in the sample and were determined to result from contamination. The plasticizer contaminate, phthalic acid (14), was also identified in the sample.

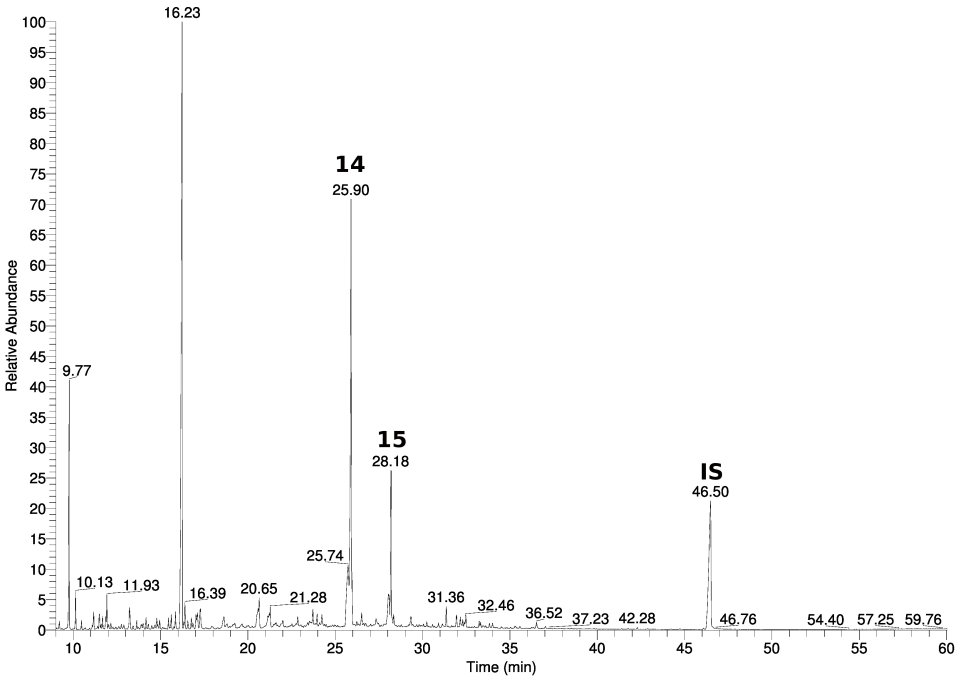


Figure 6.44: TIC Chromatogram of Sample 026

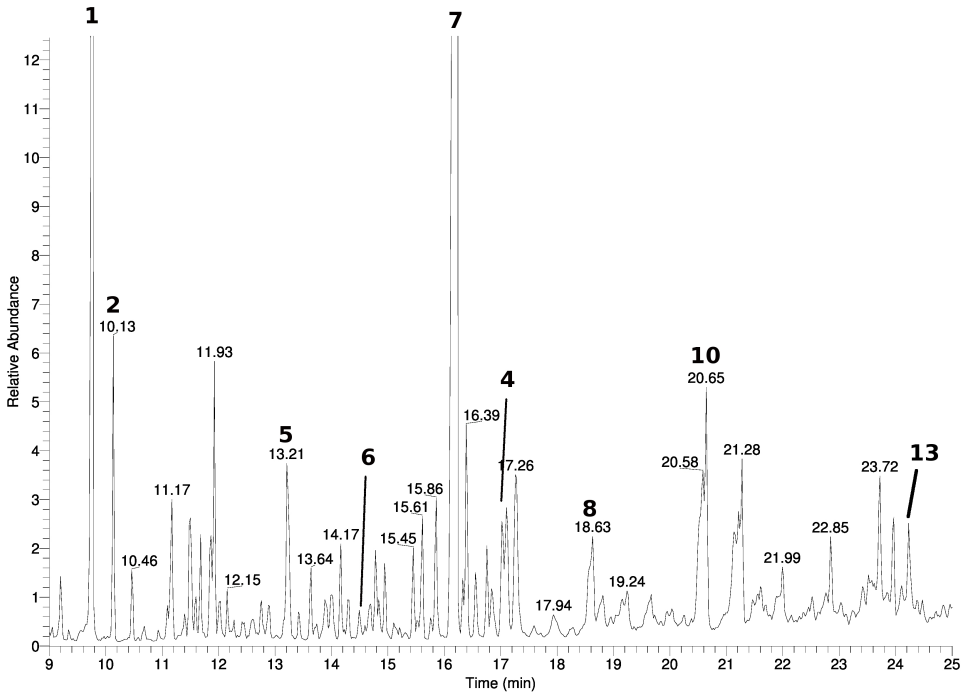


Figure 6.45: Partial TIC Chromatogram of Sample 026

# CHAPTER 7

# RESULTS AND DISCUSSION

## 7.1 Results of Analysis

In total, 19 samples from different Beirut "main series" amphorae dating between the 1st and 4th c. AD were analyzed for wine biomarkers.[1] Of the 19 samples, tartaric acid was positively identified in 6 samples (Table 7.1). The samples corresponded to vessels in Beirut amphora forms 1, 1A, 2, 3 and 5. Other biomarkers for grapes/grape products and fermentation markers co-occurred in samples in which tartaric acid was detected. These other biomarkers also appeared in many samples in which tartaric acid was not detected. However, due to the lack of specificity of these compounds in and of themselves, they should not be considered primary evidence for wine content but do suggest that other samples analyzed may possibly have contained wine. In all but one sample (Sample 026), residue levels of tartaric acid were extremely low compared to the relative abundance of other carboxylic acid biomarkers, as was anticipated by both the nature of tartaric acid (its extremely high solubility in water) and the extensive exposure of the ceramic material to water primarily during deposition and but also during post-excavation handling (sherd washing). It may be worthwhile re-analyzing samples that had complex secondary biomarker makeup but in which no tartaric acid was detected after further optimization of the technique has been accomplished as there may be residual tartaric acid levels of which were below the level of detection as the technique was configured. While wine cannot be established as the sole content of Beirut "main series" amphorae, current data indicates that wine was a content in the "main series" amphora forms between the 1st and 4th c. AD.

[1]NB: one vessel, BEY045.1381.19, was analyzed twice as Samples 022 and 015 due to initial difficulty extracting the requisite quantity of ceramic material for analysis. As previously discussed under 'Sample 015', concerns about the provenance of this sample has required that it be excluded from the Beirut amphora samples.

Table 7.1: Table of Sample Analysis Results

| Sample ID# | Sherd # | Form | Tartaric Acid |
|---|---|---|---|
| 003 | BEY006.11603.171 | Beirut | No |
| 004 | BEY006.12237.x2 | Beirut 2 | Yes |
| 006 | BEY006.5051.458 | Beirut 4 | No |
| 007 | BEY006.12237.x1 | Beirut 2 | No |
| 008 | BEY006.5051.549 | Beirut 3 | No |
| 009 | BEY006.12389.79 | Beirut 1A | Yes |
| 010 | BEY006.5051.463 | Beirut | No |
| 011 | BEY006.12233.139 | Beirut 1 | Yes |
| 012 | BEY006.12233.138 | Beirut 1 | Yes |
| 013 | BEY006.12389.80 | Beirut 1A | No |
| 014 | BEY006.12237.x3 | Beirut 2 | No |
| 016 | BEY006.11629.93 | Beirut 3 | No |
| 017 | BEY006.12539.1 | Beirut 3 | Yes |
| 018 | BEY006.12239.15 | Beirut 2 | No |
| 019 | BEY045.1242.x1 | Beirut 3/4 | No |
| 020 | BEY006.11603.x1 | Beirut 3 | No |
| 023 | BEY006.8333.21 | Beirut 1 | No |
| 024 | BEY006.10082.6 | Beirut 3 | No |
| 026 | BEY006.9429.201 | Beirut 5 | Yes |

Syringic acid was not detected in any of the samples. This compound was considered as a biomarker for red wine although, in general, it is less specific than tartaric acid as a biomarker of wine itself. Although Guasch-Jané's HPLC/MS technique successfully identified syringic acid in visible residue samples, identification of syringic acid has not been replicated neither in absorbed residue studies using Guasch-Jané's technique nor in GC/MS analyses. Because syringic acid standard was available as a supply for the HPLC technique that ultimately could not be applied during the course of this project, syringic acid detection was attempted in the samples analyzed. At the current stage of research, it is indeterminate as to the reason that syringic acid was not detected in any samples. It is both possible that the samples may not have originally contained syringic acid (i.e. white wine) and/or that other processes, such as low residuality due to leeching or diagenetic effects, resulted in insufficiently extant amounts for identification.

## 7.2 Further Work

The original scope of this analysis was to analyze both the potential lipid content of the vessels as well as that of wine biomarkers. However, due to time constraints and ceramic separation complications, lipid analysis could not be completed during this project. To date the understanding of patterns of amphora use and reuse remains poorly understood. The analysis of the samples for lipid content would improve the understanding of the Beirut amphora's use in its local market by determining if Beirut amphorae were also used for containing olive oil. Additionally, eight of the samples indicated dehydroabietic acid, the principal biomarker for pitch/resin.[2] Extraction of dehydroabietic acid by the lipid extraction technique is significantly more effective than that used for carboxylic acid and would permit a better analysis of lining practices of Beirut amphorae. Analysis of the lipid extracts would also be of use to determine if 7-oxo-dehydroabietic acid were present, which would be indicate of pyrolitic distillation of the resin.

[2]Specifically, Samples 006, 009, 010, 014, 017, 018, 023 and 024.

# APPENDIX A

# TABLE SUMMARIZING PREVIOUS AMPHORA STUDIES

| Study | Year | Amphora(e) Type/Provenance | Date | Primary Identified Biomarkers | Content/Lining Determination | Technique |
|---|---|---|---|---|---|---|
| Rothschild-Boros 1981 | 1981 | 1. unknown<br>2. "Gaza rilled"<br>3. North African white-slipped | 1. N/S<br>2. N/S<br>3. N/S | 1. none<br>2. linoleic acid, arachidic acid<br>3. N/S | 1. undetermined<br>2. olive oil, sesame oil<br>3. resin (?), oil (?) | TLC/HPLC |
| Condamin et al. 1976 | 1976 | Dressel 20 | 1st c. A.D. | fatty acids | olive oil[1] | GC/MS |
| Passi et al. 1981 | 1981 | 1. "Micaceous jar" (Anatolia)<br>2. Late Roman type 4 (Gaza)<br>3. white-slipped "Africano Grande" | 425-250 A.D. | vegetal oil markers (esp. linoleic acid)<br>3. as above, also arachidic acid | 1. olive oil<br>2. olive oil<br>3. olive oil (?), sesame oil (?) | TLC/HPLC |

[1] determination of type was made by context

| | | | | | | |
|---|---|---|---|---|---|---|
| Kimpe et al. 2004 | 2004 | local (Sagalassos) | 1st-6th c. A.D. | palmitic acid, stearic acid, oleic acid, MAG, DAG, TAG | vegetable and/or animal products | PF/GC GC/MS HPLC/MS |
| Stern et al. (2003) | 2003 | Canaanite storage jar | c. 1364-1347 B.C. | triterpenoids | resin (*Pistacia* sp.) | GC/MS |
| Colombini et al. 2005b | 2005 | 1. N/S (Pisa) 2. Peacock and Williams class 52 (Fayum, Egypt) | 1. 4th c. B.C. - 2nd c. A.D. 2. 3rd/2nd c. B.C. | diterpenoids | pine pitch (*Pinaceae*) (lining) | DE/MS GC/MS |
| Guasch-Jané et al. (2006) | 2006 | Egyptian | 14th c. B.C. | tartaric acid | wine | LC/MS/MS |
| Dorrego et al. (2004) | 2004 | Haltern 70 (Spain) | 1st c. A.D. | C16-C18 fatty acids, triterpenoids | linseed or olive oil mixed with resin (*Pistacia* sp.) (lining) | HPTLC GC/MS |
| Guasch-Jané et al. (2004) | 2004 | Egyptian | Dynasties I-XVIII | tartaric acid, syringic acid | wine | HPLC/MS/MS |

| | | | | | | |
|---|---|---|---|---|---|---|
| Stern et al. (2008) | 2008 | Canaanite storage jars | Late Bronze Age | triterpenoids | resin (*Pistacia* sp.) | HPLC/MS/MS<br>GC/MS<br>FTIR<br>Feigl Spot |
| Stern et al. 2000 | 2000 | Canaanite storage jars | Late Bronze Age | C10-C24 fatty acids | oil | GC/MS |
| Colombini et al. 2005b | 2005 | various (Pisa, Italy and Fayum, Egypt | ~4th c. B.C. - 1st c. A.D. | diterpenoids | pine pitch (*Pinaceae*) (lining) | DE/MS<br>GC/MS |

| | | | | | | |
|---|---|---|---|---|---|---|
| Heron and Pollard 1988 | 1989 | 1. Rhodian<br>2. Dressel 2-4<br>3. Polichet 47<br>4. Camulodunum 185<br>5. Dressel 30<br>6. Dressel 2-4<br>7. Camulodunum 189<br>8. Africana 2A | 1. 1st c. A.D.<br>2. 1st c. A.D.<br>3. 1st/2nd c. A.D.<br>4. 1st/early 2nd c. A.D.<br>5. 1st/early 2nd c. A.D.<br>6. 1st/early 2nd c. A.D.<br>7. late 1st/early 2nd c. A.D.<br>8. un-known | diterpenoids | pitch, probably pine (*Pinaceae*) (lining) | GC/MS |

| | | | | | | |
|---|---|---|---|---|---|---|
| Romanus et al. 2009 | 2009 | 1. LRA 1<br>2. LRA 3<br>3. LRA 4<br>4. local fabric 4 (Sagalassos)<br>5. Imitation Agora M334<br>6. unknown | Byzantine period | 1. FAME, diterpenes<br>2. FAME, polyphenols, diterpenes<br>3. none<br>4. polyphenols (one sample), diterpenes, FAME<br>5. FAME, diterpenes<br>6. FAME (one sample), diterpenes (one sample) | 1. oil, resin<br>2. oil, wine, resin<br>3. none<br>4. wine (one sample, oil, resin<br>5. oil, resin<br>6. oil, resin (one sample) | GC/MS |
| Salvini et al. 2007 | 2007 | Dressel 20 | | diterpenes, fatty acids | oil, resin | GC/MS<br>ESI/MS |
| Ribechini et al. 2008 | 2008 | Roman amphora (Liguria, Italy) | 2nd-4th c. A.D. | diterpenes | resin (contents) | DE/MS |
| Garnier et al. 2003 | 2003 | 1. Dressel 1 (Madrague de Giens wreck)<br>2. Haltern 70 (Port-Vendres II wreck) | 1. 70–60 B.C.<br>2. 41-54 A.D. | 1. polyphenols, diterpenes<br>2. polyphenols, diterpenes | 1. wine<br>2. defrutum | Py/GC/MS |

| | | | | | | |
|---|---|---|---|---|---|---|
| Beck and Borromco 1990 | 1990 | Rhodian amphora (Kyrenia wreck) | 4th c. B.C. | diterpenes | resin (lining) | GC/MS |
| Linke et al. 2008 | 2008 | “amphoriskos” (Ephesos) | 5th-7th c. A.D. | diterpenes | resin (lining) | GC/MS |
| Formenti et al. 1978 | 1978 | Dressel 1 (Madrague de Giens wreck) | 70-60 B.C. | tartaric acid | wine | GC/MS |
| Condamin and Formenti 1978 | 1978 | unknown | unknown | tartaric acid, diterpenes | wine, resin (lining) | GC/MS |
| Petit-Domínguez et al. 2003 | 2003 | R1 Phoenician | 5th c. B.C. | tannins (associated with grape products) | wine | Folin-Denis Reagent |
| Font et al. 2007 | 2007 | 1. S-51<br>2. S-55<br>3. Iberian | 1st c. B.C. - 1st c. A.D. | diterpenes | pitch (lining) | FTIR GC/MS |

# APPENDIX B

## CERAMIC SAMPLE PHOTOGRAPHS


Figure B.1: Sample 003
(BEY006.11603.171)


Figure B.2: Sample 004
(BEY006.12237.x2)

Figure B.3: Sample 006
(BEY006.5051.458)

Figure B.4: Sample 007
(BEY006.12237.x1)


Figure B.5: Sample 008
(BEY006.5051.549)


Figure B.6: Sample 009
(BEY006.12389.79)


Figure B.7: Sample 010
(BEY006.5051.463)


Figure B.8: Sample 011
(BEY006.12233.139)


Figure B.9: Sample 012
(BEY006.12233.138)


Figure B.10: Sample 013
(BEY006.12389.80)


Figure B.11: Sample 014
(BEY006.12237.x3)


Figure B.12: Samples 015 and 022
(BEY045.1381.19)


Figure B.13: Sample 016
(BEY006.11629.93)

Figure B.14: Sample 017
(BEY006.12539.1)


Figure B.15: Sample 018
(BEY006.12239.15)


Figure B.16: Sample 019
(BEY045.1242.x1)


Figure B.17: Sample 020
(BEY006.11603.x1)

Figure B.18: Sample 023
(BEY006.8333.21)

Figure B.19: Sample 024
(BEY006.10082.6)


Figure B.20: Sample 026
(BEY006.9429.201)

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