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Preliminary results of the analysis of the organic residues in amphorae from the alpine *castrum* at Loppio- S. Andrea (Trentino, Italy)

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During the archaeological excavations at the castrum Loppio-Sant'Andrea (Trentino, Italy), 1041 transport amphora sherds were collected. The amphora types recorded are quite numerous and indicate a provision of foodstuffs from different regions of the Mediterranean. The chronological range runs from the mid fifth century to the end of the seventh century AD. A selected sample of 10 amphorae belonging to the Types Keay LII, spatheion, LR1, LR2, LR4 and Samos Cistern Type have been analysed using GC-MS (gas chromatography-mass spectrometry) in order to characterize the organic residues absorbed in the ceramic material and to shed light on the transported (and/or stored) foodstuff.

Keywords: Late Antiquity, Trade, Amphorae, Organic Residues analysis, gas chromatography-mass spectrometry

Introduction (BM)

The archaeology section of the Civic Museum Foundation of Rovereto has been carrying out archaeological research since the year 1990s on the island of Sant'Andrea in the Provincial Natural Reserve "*Lago di Loppio*" (Lake Loppio), about 7 km north-east of Lake Garda (Trentino, Italy) (fig. 1a). The island, which once rose impressively from the green expanse of water, is now a small hump on the edge of a vast marshy basin. In fact, in the 1950s the lake was drained as part of the construction work on the Adige-Garda tunnel and shortly after it became a swamp. With its 112 hectares, the area has a very rich, varied environmental tapestry, which gives it great environmental value, and today it is one of the largest nature reserves in the Autonomous Province of Trento.

The archaeological excavations, begun in 1998 and completed in 2017, brought to light a multi-layered archeological site with finds ranging from the Prehistoric period to Late Antiquity, the Middle Ages and right through to the First World War. In particular, remains of buildings of a fortified settlement (*castrum*) dating back to the 5^{th}-8^{th} century AD have been unearthed on the northeast side and at the southern edge of the island (Sectors A, B, E) along with parts of the original wall which ringed the built-up area on its north-eastern and western flanks (fig. 1b and 2)[1]. In the upper area (Sectors C and C1) the investigations concentrated on the ruins of the Romanesque church of Sant'Andrea (12^{th}-17^{th} century) and on an adjacent building going back to the Late Medieval period[2].

[1] MAURINA 2016.
[2] MAURINA, POSTINGER 2020.

Fig. 1. Location of Loppio and picture of the site on the island of S. Andrea in the Provincial Natural Reserve of Lake Loppio from drone (by A. Dardani).

The *castrum*, probably built in the second half /end of the 5^{th} century, went through at least two phases of settlement: a Byzantine phase (second half of the 5^{th} century - first half of the 6^{th} century) and a Lombard phase (second half of the 6^{th} century- beginning of the 8^{th} century). In the stratigraphic deposits excavated into the buildings hundreds of objects related to domestic life, craftwork and farming were found. Particularly significant are the fittings connected to the arming and clothing of soldiers: these show the military function of the settle- ment, sited in a highly strategic position on the route between the Adige Valley and the Lake Garda. The find of objects relating to the female sphere and an infant buried in an amphora indicate that the soldiers had their families with them.

Fig. 2. Topographic plan of the site (by L. Prezzi and C. Bona).

During the excavation of the archaeological contexts a large number of fragments of ceramic vessels have been found. The majority (6783 potsherds) are related to coarse/cooking ware, while 1041 pieces are amphora sherds. The former was normally used in food preparation, while the latter was used for commercial transport of liquid and semi-liquid goods. Apart from the unique case of an almost entire vessel, they are sporadic fragments, in most cases bodysherds and occasionally diagnostic parts as rims, handles or bases. Nevertheless, many bodysherds, thanks to the particular treatment of the surface, have permitted the typological identification of the finds and in other cases the production area has been established thanks to the characteristics of the fabrics. Anyway, about the 30% of the finds remained without identification.

The amphora sherds are related to relatively few amphora types, but they indicate a provision of products from different regions of the Mediterranean. Their chronological range runs from the mid 5th century to the end of the 7th century AD. As for the provenience of the vessels, the samples have been previously analyzed in thin section to determine petrological characteristics and help to clarify the origin of the fabrics[3]. The evidence of Italian production seems to be very scarce (less than 4% of the total amount of fragments) and is represented by a single amphora form, the Keay LII type, made in Calabria and eastern Sicily near the strait of Messina. While 27% of the finds remained completely unidentified, most amphora sherds can be traced to two great Mediterranean areas of production: the eastern Aegean (54%) and north Africa (15%), showing a clear prevalence of Oriental vessels. From the first area come a series of the so-called Late Roman Amphora 1-4 and the Samos Cistern type, mostly produced in Asia Minor and the Greek islands of the Aegean, apart from the Late Roman Amphora 4, also known as “Gaza type”, made in the Syria-Palestine region. From North Africa (today Tunisia) come the small, tapered vessels called *spatheia* and the very large cylindrical amphora known as Keay LXII.

The information obtained from the study of the amphorae from St. Andrea also prove that this settlement was part of a long-distance exchange circuit, that was supplied by seaborne commerce. Actually, the transport amphorae should reach Loppio from the coastal trade centers of the North Adriatic Sea, exploiting a commercial network that was already fully active during the Roman period and was based on the road system and especially on the inland waterways of Northern Italy. It probably means that the site of Loppio should have played an important role from a strategic and military point of view. In particular, the presence of certain typologies, as *spatheia* and *Samos Cistern Type*, whose association is ment to connote the most important political and military centers of the Byzantine Empire, probably indicate a direct relationship with the supply system (the *annona*) managed by the State, as revealed by data collected in other late antique fortified settlements, as, for instance, the site of S. Antonino di Perti and the *castra* of Friuli and Slovenia[4]. In the case of Loppio it is worth while noting that the presence of these vessels seems partially related to a period in which the *castrum* had probably fallen in the hands of the Longobards. This evidence seems to argue for the hypothesis of a continuity of importation of amphora-borne commodities after the Longobard invasion in the most important strategic sites, despite the changes occurred in the political and military sphere.

Considering the relevance of the site, a military settlement with a strategic position dating to a crucial period of history, and with such a high number of fragments of pottery that was in daily use by the inhabitants of the *castrum*, a research project concerning the analysis of the organic residues absorbed in amphorae and coarse/cooking wares was started, in order to investigate through scientific methods the social and economic aspects of nutrition in relation to changes in diet during the transition from Late Antiquity to the Early Middle Ages. Beside the Fondazione Museo Civico di Rovereto, the Institute of Classical Archaeology, the Core Facility BioSupraMol and the Institute of Chemistry and Biochemistry of the Freie Universität Berlin are involved in this project, using GC-MS (gas chromatography-mass spectrometry).

The GC-MS analyses of the amphorae content (SP, AS, LP)

In this paper we discuss some preliminary results of the GC-MS analyses[5] of the amorphous organic residues preserved by absorption in the pores of the ceramic material of selected long-distance transport containers. The first step of the research in- volved the analysis of 10 fragments of amphorae and one amphora wall reused as a lid.

[3] Capelli, Piazza, Cabella 2016.
[4] Arthur 1998: 175; Villa 1998: 286-287; Murialdo 2001: 302; Sagui 2002: 15-16; Modrijan, Milavec 2011: 158; Maurina 2016: 394-395.
[5] Heron, Evershed 1993; Evershed 2008; Roffet-Salque 2017.

In recent decades, the morpho-typological and epigraphic approaches, in particular concerning the content attribution to Roman Amphorae[6], have been enriched by the application of chemical methods for the identification of the content of the transport containers[7] and the significance of ORA (organic residues analysis) techniques in the identification of amphorae-born commodities has been developed[8]. Did a specific amphora type always correspond to the same content and, if so, do we register changes according to chronological and regional variation? In general, the content of several Late Antique containers remains poorly understood[9], and they are likely to have carried a variety of foodstuffs. Therefore, it seems to be appropriate to consider the story of each single container as part of the complex supply system, even more if we consider the peculiarity of the archaeological and historical context, i.e. the economics of supplying a military Late Antique settlement in the alpine region.

Drawing on the limited sample size of this targeted investigation we do not aim to answer these complex questions, i.e. to assess a robust relationship between form and function, but to contribute to the discussion by providing scientific proxies in terms of chemical fatty acids profiles for the selected containers.

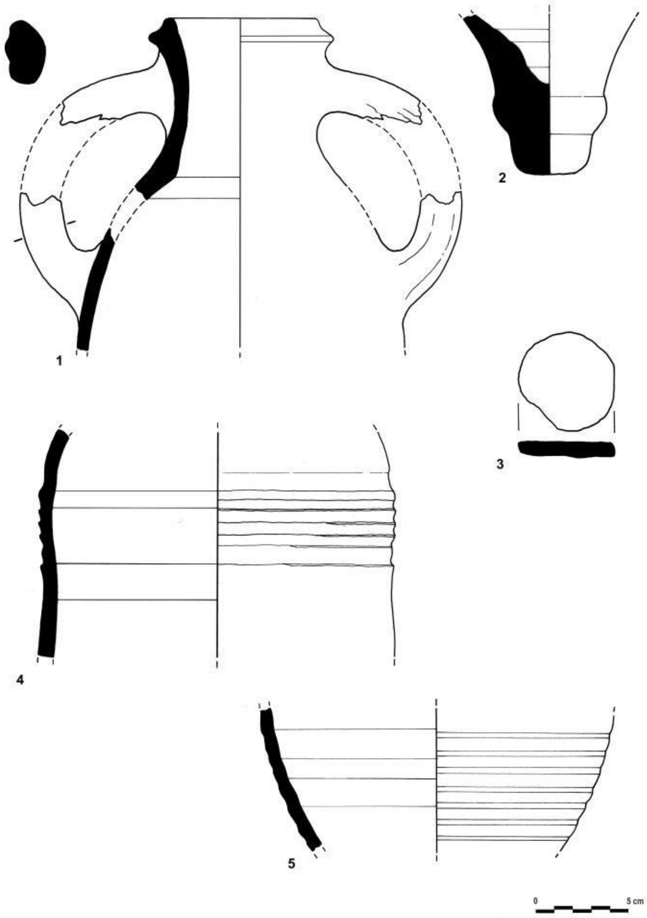

Fig. 3. Drawings of discussed amphorae samples.

Materials and Methods (AS, SP, LP)

Ten (10) samples belonging to the Amphorae Types Keay LII, Keay LXII, *spatheion*, LR1, LR2, LR4 and Samos Cistern Type found in the site have been selected for the chemical analysis of the organic residues (fig. 3)[10] using GC-MS.

Sherds were first surface-cleaned using freshly cleaned and oil-free scalpels as well as a stream of nitrogen 5.0. After grinding the sherds by hand in a marble mortar, the powdered samples were extracted using the

[6] MARTIN-KILCHER 2011.
[7] FORMENTI *et al*. 1978; GARNIER 2007; PECCI *et al*. 2010; GARNIER *et al*. 2011; GARNIER 2015; WOODWORTH *et al*. 2015; CARVER *et al*. 2019.
[8] BERNAL 2015.
[9] WOODWORTH *et al*. 2015.
[10] The amphorae were previously cleaned and washed for documentation purposes and typological study and then stored in the Archaeological Laboratory at the Civic Museum Foundation of Rovereto. Therefore, the material does'nt offer the best requirements for the preservation of organic residues. However, also analyses conducted on cleaned potsherds from museum collections have provided excellent results, showing that there was no significant difference in residue recovery rates from newly excavated sherds and those stored in museums (DUNNE *et al*. 2017, 33).

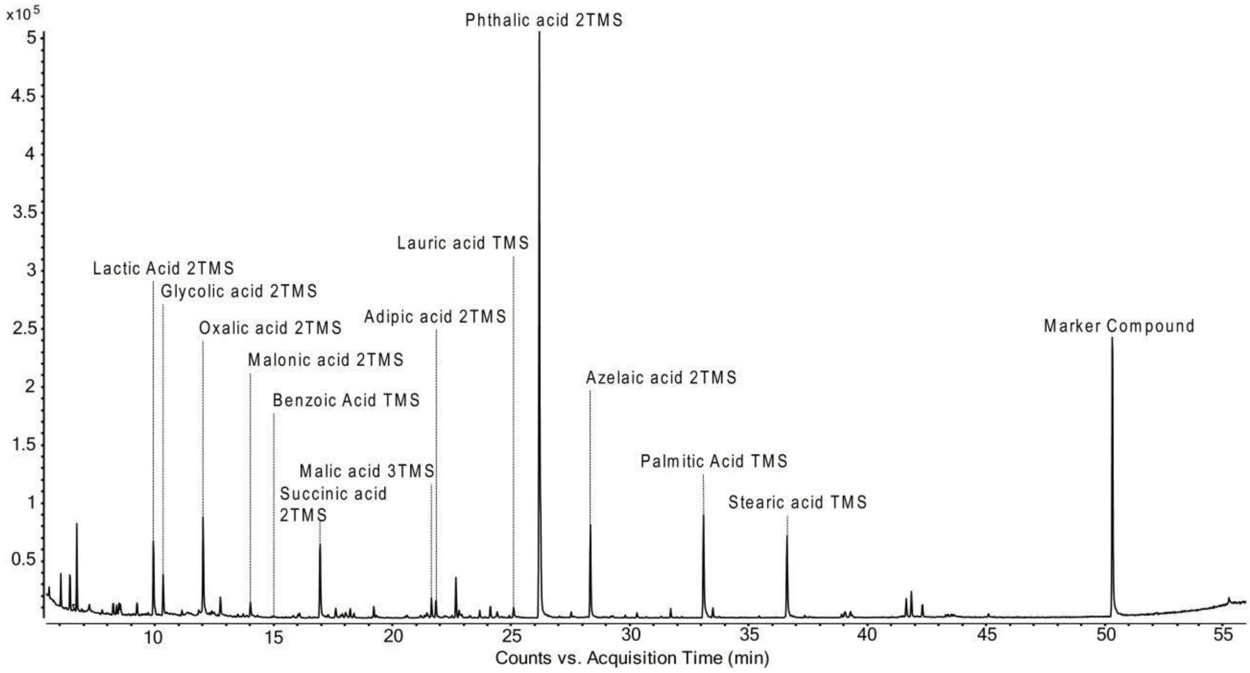

Fig. 4. GC-MS chromatograms of the sample belonging to Keay LII Amphora (sample Nr. 28456).

methods for oil and wine markers analogous to the methodology described by Pecci *et al*.[11], including the derivatization with BSTFA before analysis by GC-MS. The GC-MS method described in the literature was customized for an Agilent G1969A GC-MS system equipped with a DB-5MS GC column (30m x 0.25mm, Agilent Technologies), including a temperature programme similar to the literature (1 min at 50°C, then a ramp of 5°C/min, 10min at 300°C) utilizing added Dotriocontan as an internal standard to control retention time, peak shape and sensitivity of the GC-MS. All compounds found were then compared to the retention times and mass spectra of standards produced from pure compounds derivatised using BSTFA. A compound was only considered as detected when at least two significant peaks reflecting the abundances in the respective measurement of the standard were found and the peak was higher than a factor of 7 above the respective noise level.
The chosen methods are suitable, on the one hand, for the analysis of wine markers and other small organic acids as well as small to medium amounts of fatty acids; on the other hand, the extraction protocol for lipids enhances the chance to detect sterols, long-chain fatty acids and alkanes, specific markers for animal or plant origin and are also relevant for resins and waxes.

Results (SP, AS, LP)

The form Keay LII (sample nr. 28456; fig. 3.1) is a flat-based amphora produced in southern Calabria and in eastern Sicily between the IV and the VII c. AD, which very likely carried wine from the *Bruttium*[12]. As suggested by the presence of lactic acid, glycolic acid, malonic, succinic, fumaric and malic acid, the GC-MS analysis give hints on the hypothesis that this container transported wine (fig. 4). Probably due to preservation issues, the previous washing of the sherds (see Materials and Methods) and/or the used basic extraction method not being ideal for the compound, tartaric acid, a typical marker for wine and, in lower concentrations, derived from other fruit or microbial degradation of lignin and similar[13], could not be detected[14]. Nevertheless, the controversial origin and not unequivocal interpretation of the listed preserved acidic markers of fermentation did

[11] PECCI *et al*. 2013a, 2013b, 2013c.
[12] ARTHUR 1989; BONIFAY, PIERI 1995; NOYÉ 2000.
[13] DRIEU *et al*. 2020.
[14] GARNIEr 2007; WOODWORTH *et al*. 2015; GARNIER 2015.

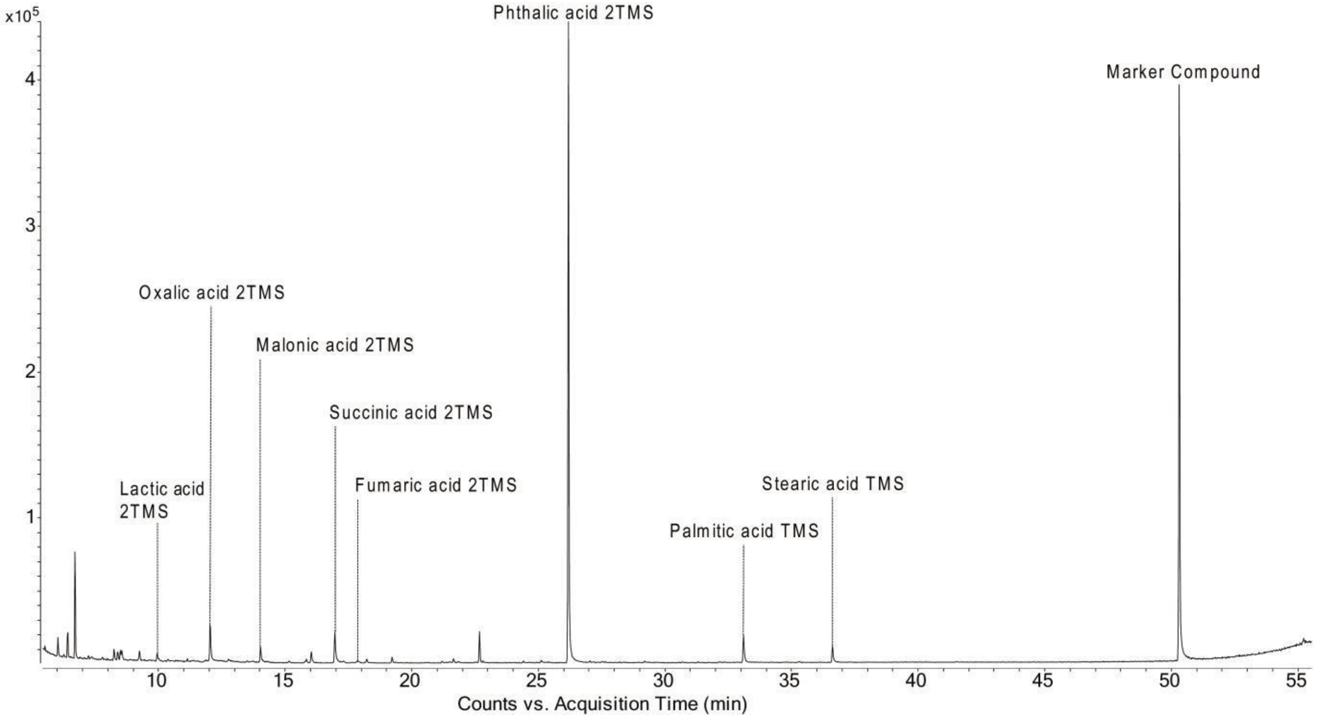

Fig. 5. GC-MS chromatograms of the sample belonging to Keay LXIIa Amphora (sample Nr. 28056).

not provide an irrefutable chemical evidence for wine[15] but increase the probability that the amphora was used for wine transportation.

The analysis of one base of Keay LXII (sample nr. 28056; fig. 3.2) shows similar results to the sample belonging to the Keay LII Amphora Type It is a large cylindrical amphora, produced for several centres in modern Tunisia during the VI and the beginning of the VII c. AD, that has been considered an oil container[16], although wine or *salsamenta* have been also hypothesized[17]. The analysis shows the presence of lactic, oxalic, malonic, succinic and fumaric acid, which may suggest fermented products (fruits or wine?) as the probable source of the identified compounds (fig. 5). The example from Loppio belongs to the variant Keay LXIIa[18], a transport container probably related to the *annona* supply system of Byzantine military settlements[19]. Previous analyses of two Keay LXIIa amphorae from La Palud dating to VI c. AD[20] show olive oil markers. One of the two amphorae has been pitched/coated with resin, probably suggesting a low-quality olive oil or the reuse of the container for other products more compatible with resin.

Three North African *spatheia* were selected for the analysis: the sample nr. 17624, a small *spatheion* dating to the VI-VII c. AD, shows the presence of tartaric acid among other wine markers, probably indicating wine as content (fig. 6). The chromatograms of other two samples (nr. 17482 and 25388), one of which belongs to a so-called "miniaturistic" *spatheion*[21], show identical peaks to the Keay LII amphora, where some wine markers are present and tartaric acid has not been preserved. The presence of lactic, glycolic, malonic, succinic, fumaric and malic acids can also be linked to the transport of fruits, as has been also suggested for the *spatheia* (figs. 7-8). Several hypotheses have been advanced, relating these small containers to the transport and trade of

[15] Drieu *et al.* 2020.
[16] Keay 1984.
[17] Albore-Livadie 1985; Ben Lazreg *et al*. 1995; Bonifay, Pieri 1995; Opait 1998; Murialdo 2001; Bonifay 2003, 2005 and 2007.
[18] Maurina 2016.
[19] Murialdo 2001.
[20] Bonifay, Garnier 2007
[21] Murialdo 2001, Tav. 14.170-174.

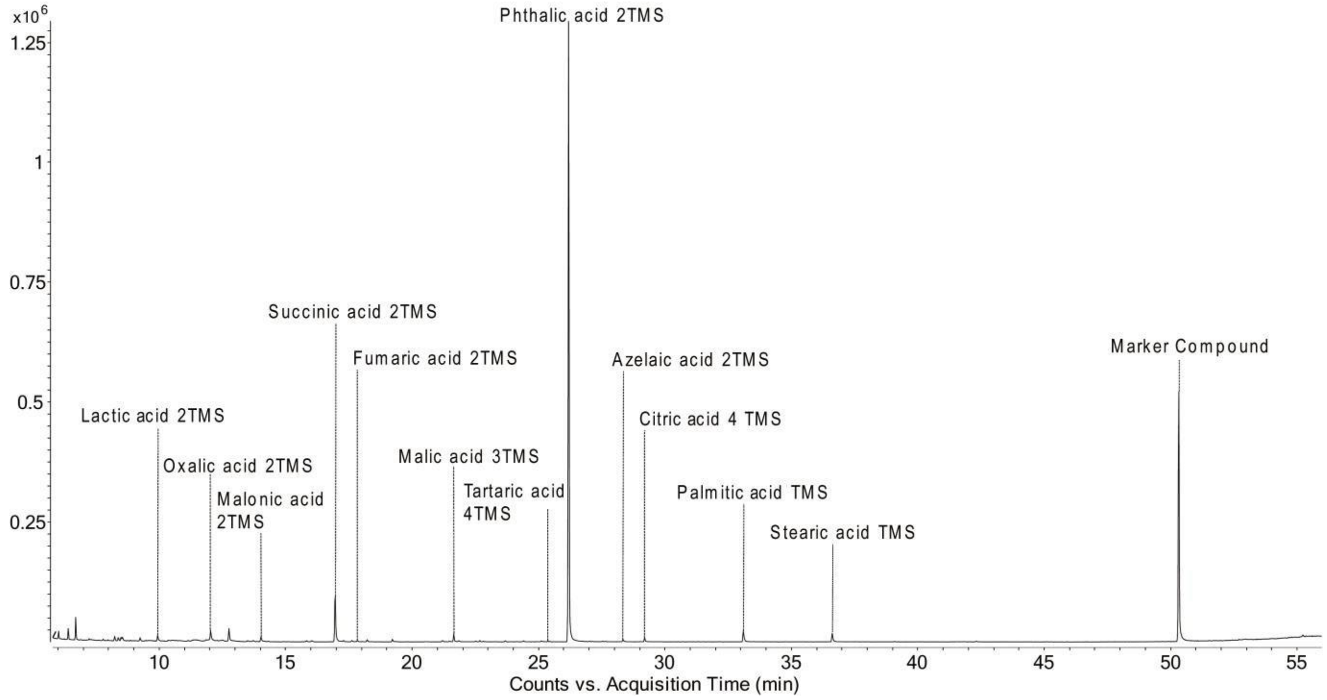

Fig. 6. GC-MS chromatograms of the sample belonging to Spatheion (sample Nr. 17624).

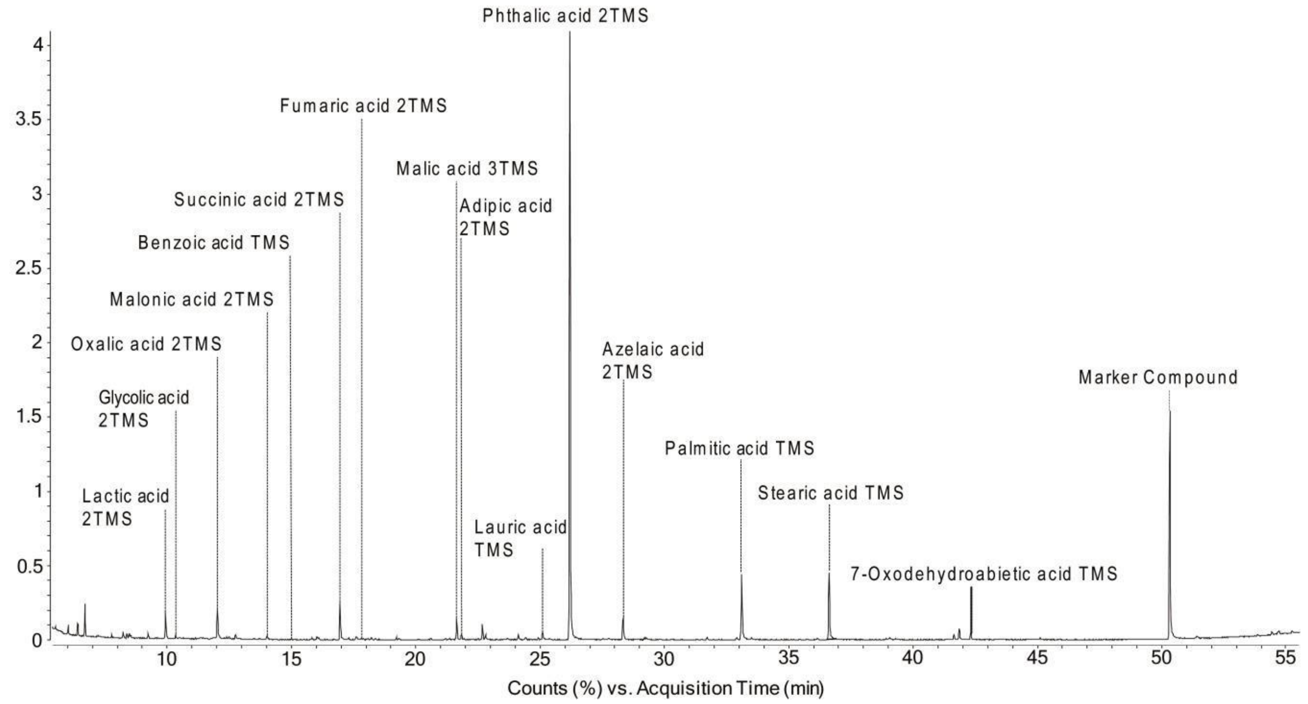

Fig. 7. GC-MS chromatograms of the sample belonging to Spatheion (sample Nr. 17482).

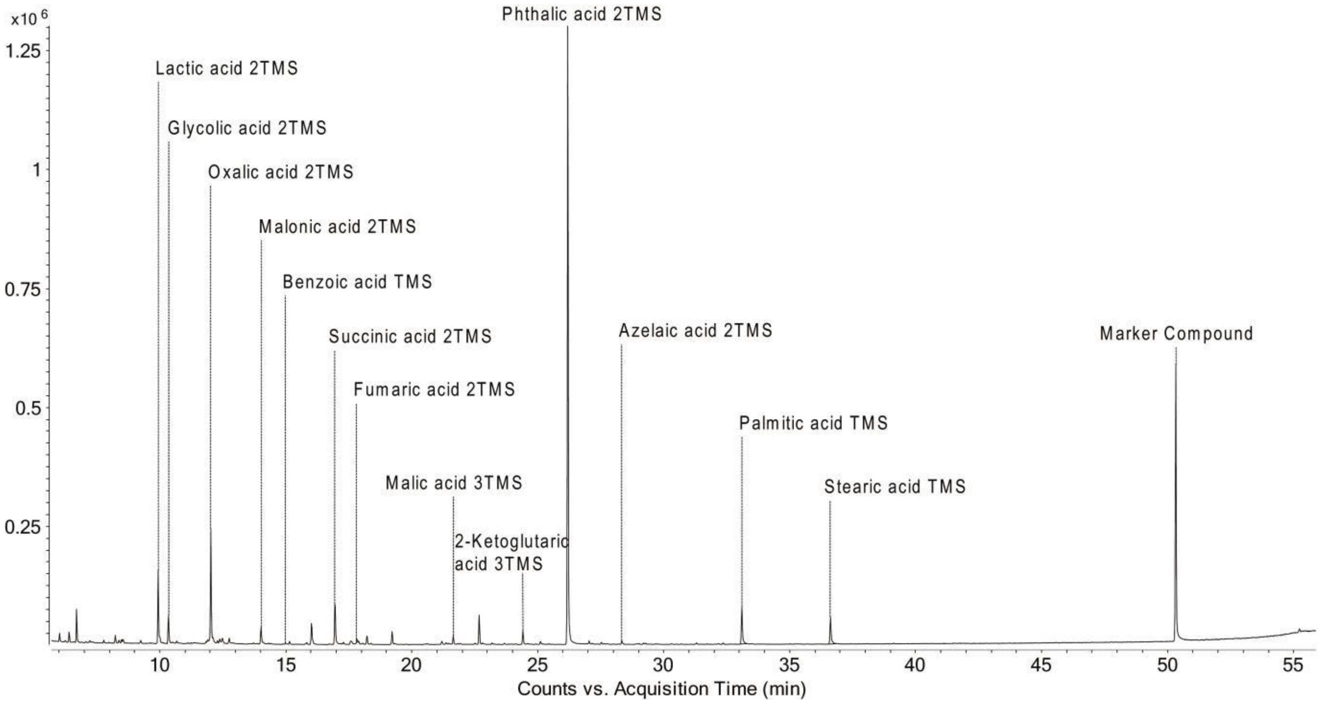

Fig. 8. GC-MS chromatograms of the sample belonging to Spatheion (sample Nr. 25388).

olives and dried fruits[22], olive oil and honey[23], oils and balsams[24], wine[25] and *salsamenta*[26] and pepper and spices[27]. GC-MS analyses of *spatheia* from Classe show vegetable oils, particularly castor oil, as content[28]. We must probably assume that these are multifunctional transport containers.

An *operculum* (lid) (nr. 24182; fig. 3.3) obtained by cutting an African amphora shows no preservation of clear markers. Fruits or wine (?) could be one source of the detected compounds (lactic, oxalic, malonic, succinic, fumaric, malic, adipic acids). Even though lauric, azelaic, palmitic and stearic acid could suggest a multiple function of the *operculum* probably also for covering oil containers (fig. 9).

Samples belonging to the Eastern Mediterranean amphora form LR1 (nr. 25416-17), a very common Byzantine transport container for wine and/or oil[29], show the presence of stearic and palmitic acids together with azelaic acid, the latter usually derived from oxidation processes of triacyl glycerides of original lipids/oxidation of unsaturated fatty acids and detected as such in relation to olive oil in experimental work on replica lamps[30], suggesting a plant oil as possible content (fig. 10). To confirm this hypothesis, analysis of the separated compounds by IR-MS would provide higher certainty. Nevertheless, malonic, succinic and malic acid were detected, which are fermentation by-products. This could indicate a poor preservation of other wine markers like fumaric and tartaric acid, and a general insufficient preservation of lipids in the sample, so that it is not possible to characterise the content with certainty.

The LR2 (samples nr. 25951 and 25594) is an eastern Mediterranean amphora, whose kilns have been found in the Argolid and which was probably also produced in the northern Aegean and on the west shores of the Black Sea and very likely carried wine[31]. The analysis of this type shows some questionable fermentation

[22] KEAY 1984.
[23] SAGUÍ 2002.
[24] CARIGNANI 1989; ARENA *et al*. 2001.
[25] BONIFAY 2004: 129.
[26] MURIALDO 2001; DUVAL *et al*. 2002; BONIFAY 2003; BONIFAY 2005.
[27] MURIALDO 2001.
[28] PECCI *et al*. 2010.
[29] PIERI 2005.
[30] COPLEY *et al*. 2005.
[31] PIERI 2005.

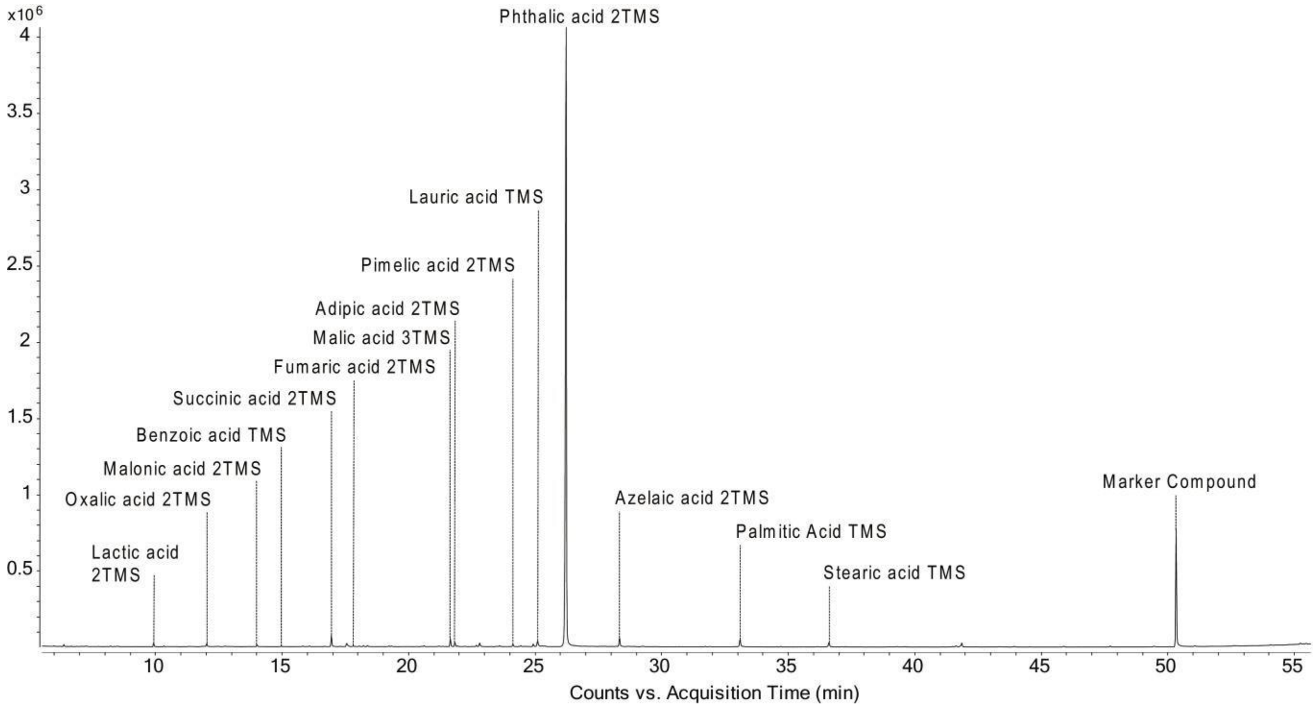

Fig. 9. GC-MS chromatograms of the sample belonging to Operculum (sample Nr. 24182).

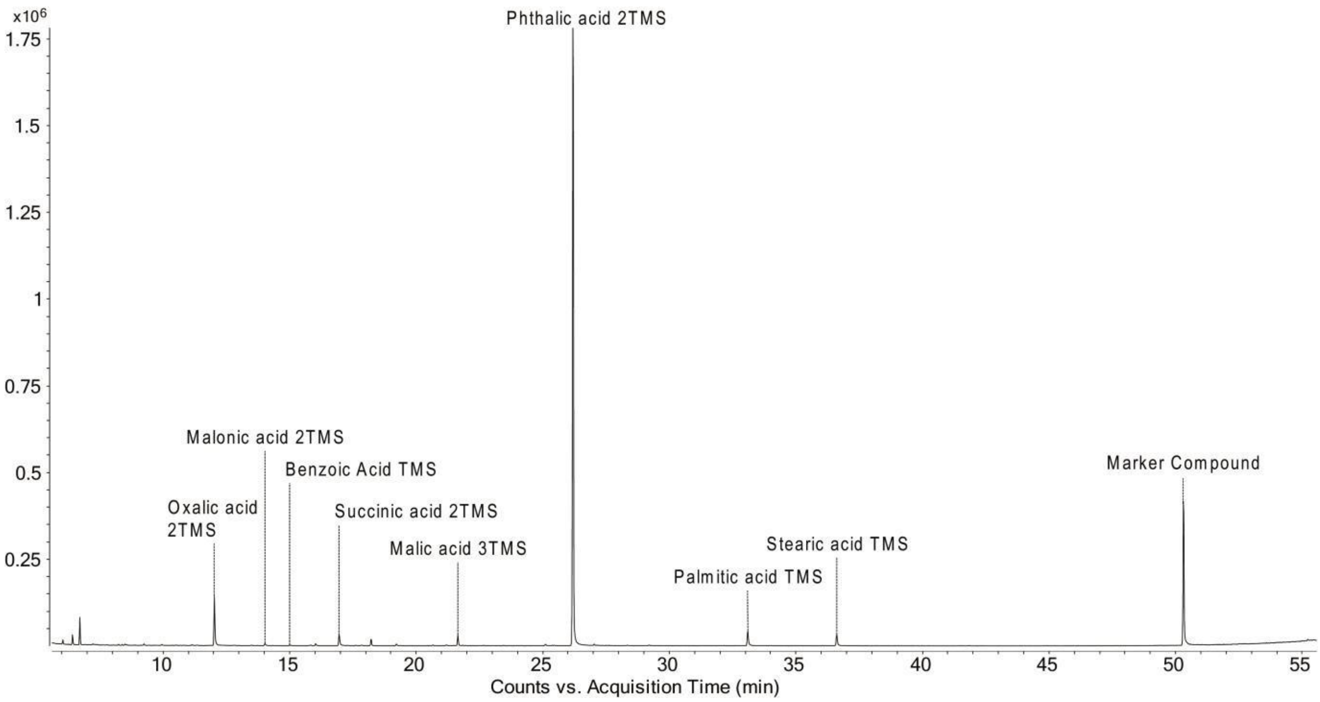

Fig. 10. GC-MS chromatograms of the sample belonging to LR1 (sample Nr. 25416-17).

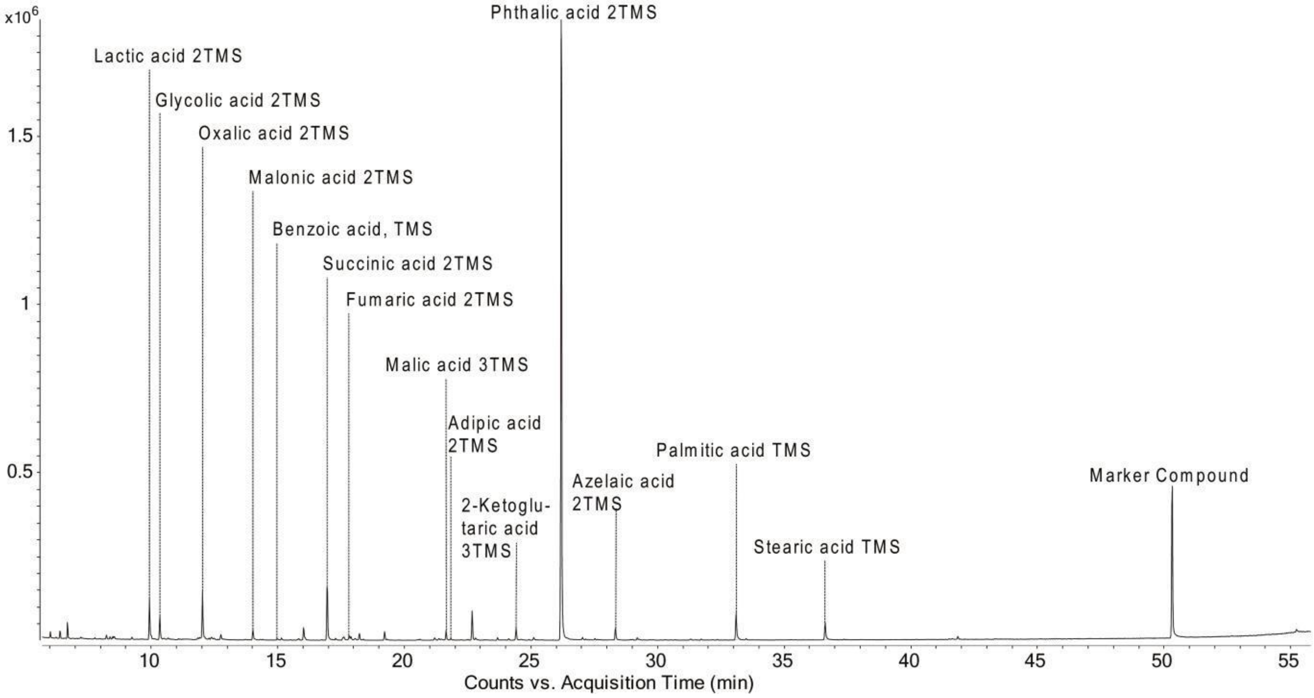

Fig. 11. GC-MS chromatograms of the sample belonging to LR2 (sample Nr. 25951).

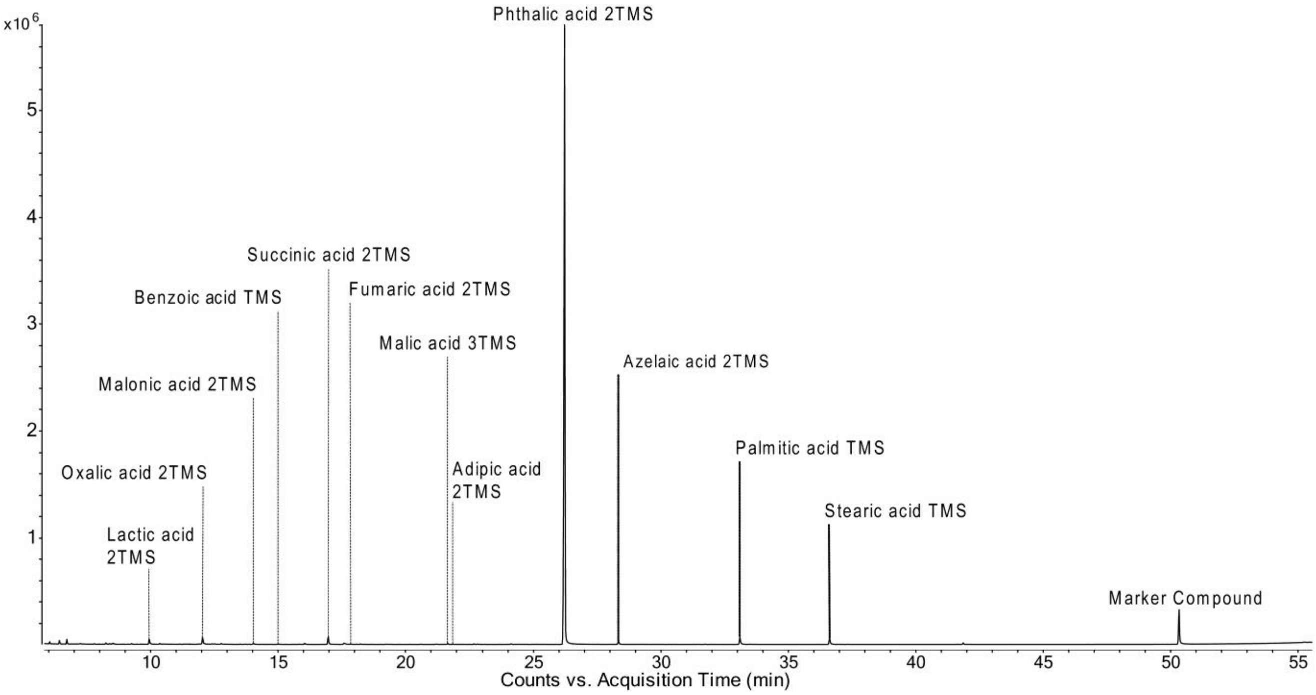

Fig. 12. GC-MS chromatograms of the sample belonging to LR2 (sample Nr. 25594).

markers and no specific wine markers like tartaric acid (figs. 11-12). LR2 Amphorae from Gortyna (Crete) show markers of wine and oil[32]. Wine markers together with castor oil have been identified in LR2 Amphorae from Hepaestia (Lemnos)[33].

[32] PECCI *et al.* 2010.

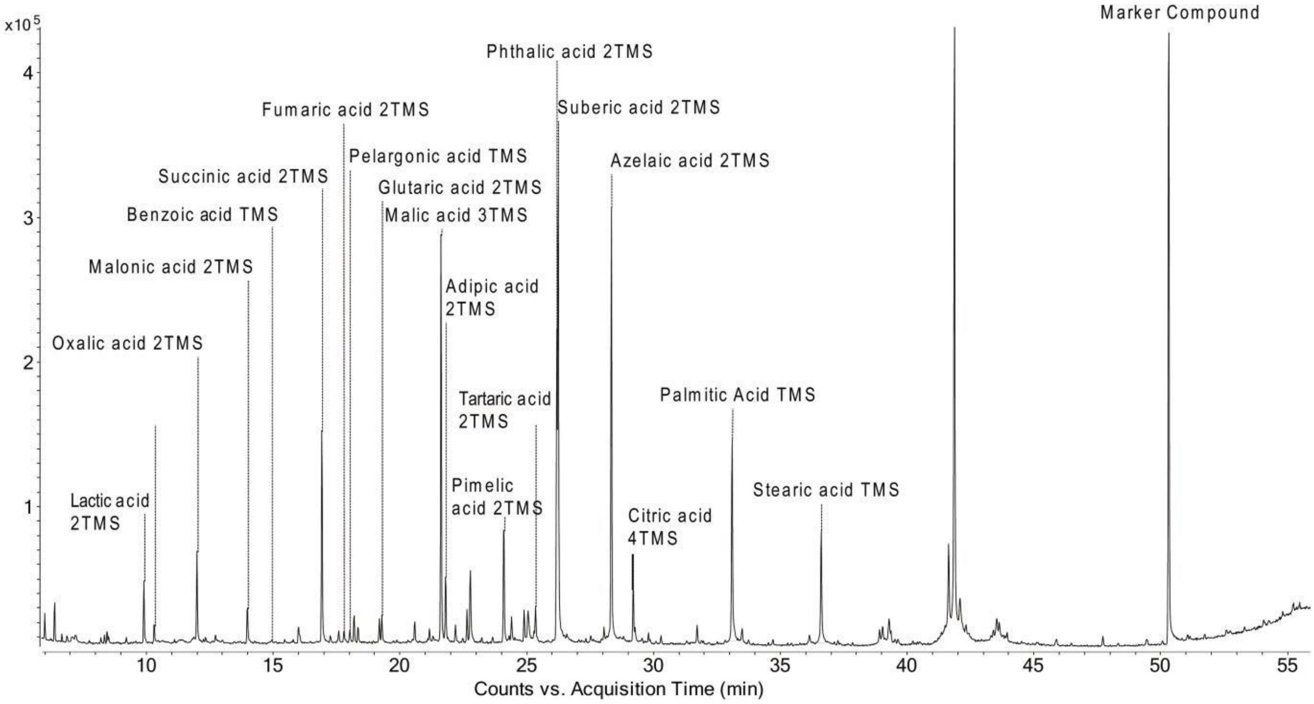

Fig. 13. GC-MS chromatograms of the sample belonging to LR4 (sample Nr. 17593).

Discrete possible wine markers (i.e. tartaric, fumaric, glutaric, malic acid: fig. 6) are found in the LR4 (sample nr. 17593; fig. 3.4), an eastern amphora produced in southern Palestine, also known as "Gaza Amphora" (fig. 13). The results confirm the transport of wine from this region[34]; or at least suggest that this LR4 amphora found at Loppio had possibly contained wine at some point of its life cycle.

The Samos Cistern Type (sample nr. 18400; fig. 3.5) is a late amphora type, produced between VI and VII c. AD probably in the region of Samos[35] or in the lower Meander valley[36]. The origin of the amphora suggests wine as content[37]. The analysis of this container shows a not very clear figure of preserved markers: wine / fermentation markers like lactic, glycolic, malonic, succinic acids are present. Nevertheless, it shows myristic, lauric and pelargonic acids in association with palmitic and stearic acid, which can be interpreted as plant (oil) lipids, probably related to the re-use of the container (fig. 14).

The results of the GC-MS analyses are resumed in Table 1 listing the analysed samples and the corresponding detected compounds. figs. 4-11 display the chromatograms of the samples in the same order as Table 1.

[33] CAMPOREALE *et al.* 2009.
[34] PIERI 2005.
[35] ARTHUR 1990.
[36] PIERI 2005.
[37] ARENA *et al*. 2001; PIERI 2005.

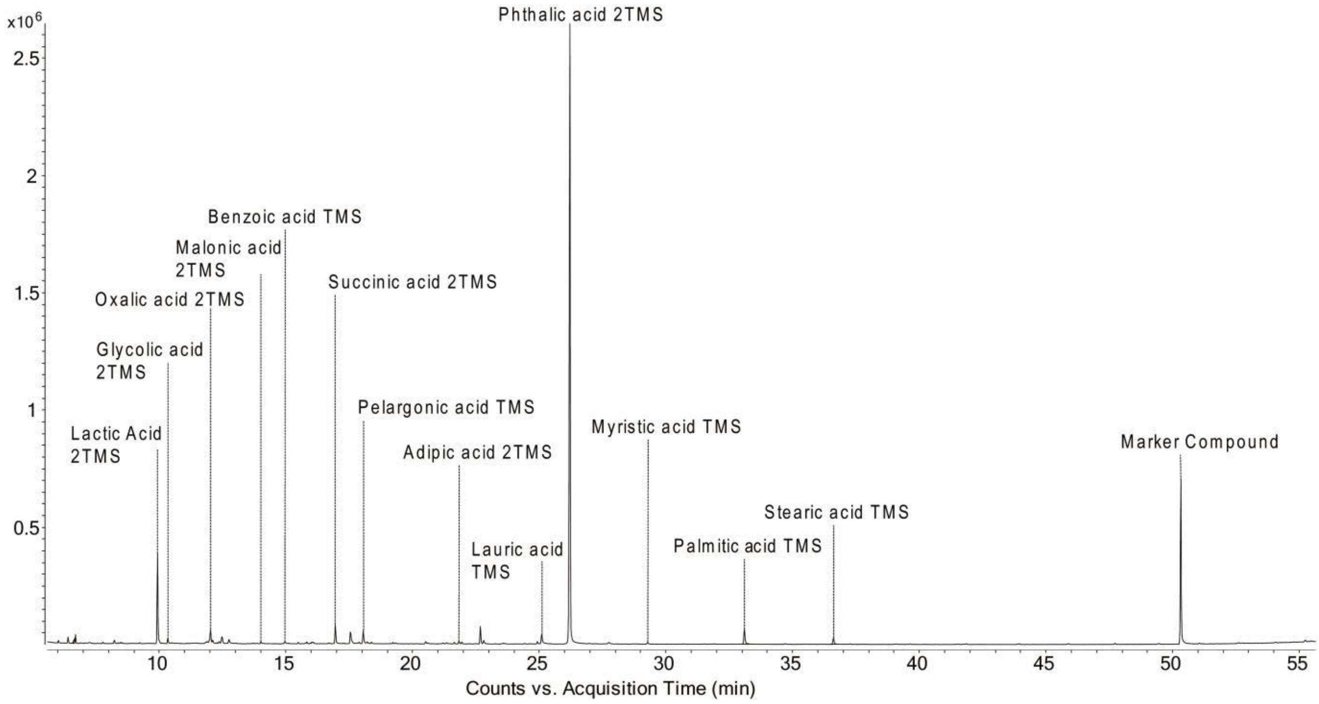

Fig. 14. GC-MS chromatograms of the sample belonging to Samos Cistern Type Amphorae (sample Nr. 18400R).

Amphorae Typology	Keay LII (sample Nr. 28456)	Keay LXIIa (sample Nr. 28056)	Spatheion (sample Nr. 17624)	Spatheion (sample Nr. 17482)	Spatheion (sample Nr. 25388)	Operculum (sample Nr. 24182)	LR1 (sample Nr. 25416-17)	LR2 (sample Nr. 25951)	LR2 (sample Nr. 25594)	LR4 (sample Nr. 17593)	Samos Cistern Type (sample Nr. 18400R)
compound, confirmed by measurement of standard (after derivatisation with BSTFA, with GC-MS)	Lactic acid	Lactic acid	Lactic acid	Lactic acid	Lactic acid	Lactic acid	Oxalic acid	Lactic acid	Lactic acid	Lactic acid	Lactic acid
	Glycolic acid	Oxalic acid	Oxalic acid	Glycolic acid	Glycolic acid	Oxalic acid	Malonic acid	Glycolic acid	Oxalic acid	Glycolic acid	Glycolic acid
	Oxalic acid	Malonic acid	Malonic acid	Oxalic acid	Oxalic acid	Malonic acid	Fumaric acid	Oxalic acid	Malonic acid	Oxalic acid	Oxalic acid
	Malonic acid	Succinic acid	Succinic acid	Malonic acid	Malonic acid	Succinic acid	Succinic acid	Malonic acid	Succinic acid	Malonic acid	Malonic acid
	Succinic acid	Fumaric acid	Fumaric acid	Succinic acid	Succinic acid	Fumaric acid	Malic acid	Succinic acid	Fumaric acid	Succinic acid	Succinic acid
	Fumaric acid	Azelaic acid	Malic acid	Fumaric acid	Fumaric acid	Malic acid	Azelaic acid	Fumaric acid	Malic acid	Fumaric acid	Pelargonic acid
	Malic acid	Palmitic acid	Tartaric acid	Lauric acid	Malic acid	Adipic acid	Palmitic acid	Malic acid	Adipic acid	Pelargonic acid	Adipic acid
	Adipic acid		Citric acid	Azelaic acid	Azelaic acid	Lauric acid	Stearic acid	Adipic acid	Azelaic acid	Glutaric acid	Lauric acid
	Lauric acid		Azelaic acid	Palmitic acid	Palmitic acid	Azelaic acid	Benzoic acid	Azelaic acid	Palmitic acid	Malic acid	Myristic acid
	Azelaic acid		Palmitic acid	Stearic acid	Stearic acid	Palmitic acid		Palmitic acid	Stearic acid	Adipic acid	Palmitic acid
	Palmitic acid		Stearic acid	Benzoic acid	Benzoic acid	Stearic acid		Stearic acid	Benzoic acid	Tartaric acid	Stearic acid
	Stearic acid					Benzoic acid		Benzoic acid		Azelaic acid	Benzoic acid
	Benzoic acid									Palmitic acid	
										Stearic acid	
										Benzoic acid	
Probable source of compounds	Wine/fruits?	Wine/fruits?	Wine?	Wine/fruits?/Plant oil?	Wine/fruits?/Plant oil?	Wine/fruits?/Plant oil ?	Wine/fruits?/Plant oil?	Wine/fruits?	Wine/fruits?	Wine/fruits?	Wine?/Plant oil?

Table 1. Overview of the results of the GC-MS analyses. All compounds have been detected as their corresponding TMS derivatives.

Discussion (SP, AS)

Degradation and bad preservation of high water-soluble wine markers seem to affect the results in this context. Interestingly, we have generally abundant markers of fermentation processes, e.g. lactic, glycolic, oxalic, malonic, succinic, fumaric, malic, benzoic acid very likely indicating fruits fermentation or wine as content and/or microbial degradation of plants and fungi[38] in all samples. In association with the markers of fermentation we also see hints for plant oil, like azelaic acid a dicarboxylic acid, which might be a decomposition product of unsaturated fatty acids[39]; pelargonic acid; lauric acid; palmitic and stearic acid. However, in absence of a TAGs profile it is not possible to assess the origin of the detected compounds.

In fact, in the case of one African *spatheion* and of a sample of LR4 amphora it was possible to presume wine as content because of the presence of discrete wine markers. No syringic acid, a debated, but important marker of red grapes/wine[40], has been detected in the samples. The results concerning the other analysed *spatheia* leave open the hypothesis of fruits (or other fermented products?) as transported goods, because of the absence of further possible wine markers like tartaric acid, probably due to preservation issues. The same results emerge from the analyses of the samples belonging to the amphorae Types Keay LII, Keay LXII.

The LR1 sample shows probably a general insufficient preservation of organic residues, while the Samos Cistern Type shows fermentation markers or microbial degradation together with some oil markers that may also be put in relation to the reuse of the container. The *operculum* shows no preservation of specific markers; as a matter of fact, it has been obtained by cutting an African amphora and thus most probably reused.

In general, biomarkers characteristic for plant oils are saturated (C16:0 and C18:0) and unsaturated fatty acids (e.g. C18:1 and C18:2), hydroxy fatty acids, dicarboxylic acids[41]. However, the general bad preservation of unsaturated fatty acids in archaeological contexts, i.e. over archaeological time scales, is to be considered. This could suggest that the detected saturated dicarboxylic acids, i.e. azelaic acid, derive from breakdown of oleic acid/degradation of original lipids[42]. Moreover, the strong similarity of the compounds profile of the most diffused plant oils poses serious problems of detectability and distinction of different sources of plant oils. Some specific fatty acids, e.g. ricinoleic acid for castor oil[43] and long-chain saturated fatty acids associated with phytosterols for ben oil[44], have been identified and discussed in literature in relation to the determination of specific plant oils.

Garnier *et al.* (2003) and Pecci *et al.* (2013b) developed specific protocols for the wine extraction, adopting an experimental approach. Nevertheless, the clear identification of wine using ORA is still controversial, partly because of bad preservation state of wine and other grape derivative residues, and there is at this stage still little consensus on the interpretation of discrete wine markers, like succinic, lactic, malic, fumaric, gallic, acetic, citric, syringic and (more abundantly) tartaric acid, in archaeological pottery[45].

Recently has been pointed out that these compounds, i.e. short chain carboxylic and phenolic compounds, that are highly soluble and for this reason probably not likely to survive over archaeological timescales, are ubiquitous in nature, can derive from natural biodegradation and have different origins in the environment and are not specific for grapes or other fruits[46]. Drieu et al. 2021 consider the detection of tartaric acid alone an insufficient evidence of wine, as it may be present in other fruits, and developed quantitative criteria, i.e. the comparison between the increase of tartaric acid in correspondence with the decrease of malic acid, in order to facilitate a more robust identification of wine in ar-

[38] DRIEU *et al*. 2020.
[39] COPLEY *et al*. 2005.
[40] GUASCH-JANE *et al*. 2004; PECCI 2013b, Fig. 6; DRIEU *et al*. 2020.
[41] HERON *et al*. 1991.
[42] COPLEY *et al*. 2005.
[43] PECCI *et al*. 2010 and COPLEY *et al.* 2005.
[44] DODINET *et al*. 2015.
[45] WOODWORTH *et al*. 2015; GARNIER, VALAMOTI 2016; CARVER *et al*. 2019; DRIEU *et al*. 2020.
[46] DRIEU *et al*. 2020.

chaeological amphorae samples. Two *spatheia* type 3 and two Keay LXIIa amphorae analysed by Drieu et al. 2021 show the presence of tartaric acid but it could not be inequivocally assigned to wine according to this criterion[47].

Nevertheless, combining the evidence of the fatty acids profile with the historical and archaeological information on amphorae content, i.e. if supported by epigraphy and landuse data from the amphorae production regions, we take into account the possibility that the discussed acidic markers of fermentation are worthy to be critically discussed as probably indicative for fruits or wine, as it has been shown in other studies[48].

Unfortunately, if visible encrustations or even adhesion of soil to the often pre-cleaned sherds are lacking, alternative methods like e.g. analysis of aDNA or proteomic approaches are doomed to fail and comparison with the markers present in the soil cannot be made, if the ORA project design doesn't allow sampling to be conducted concomitantly to the excavation.

The study of the quantification of the mobilization of goods and trade networks according to the content of a specific amphora type, i.e. linking a specific typology to a single content over time, is strongly affected by these issues. Reuse/secondary use/recycling are further critical issues in the interpretation of ORA-based results[49] and the eventuality that each container had had its own "biography" of multiple use[50], being not representative for the whole population of the same type, has to be considered.

Conclusions (BM, SP)

The evidence of amphorae indicates that the *castrum* of Loppio was part of a long-distance exchange circuit supplied by seaborne commerce that proves the importance of the site as a strategic settlement. In particular, the association of certain types as *spatheia* and Samos Cistern Type, frequent in the most important political and military centers of the Byzantine Empire, seems to prove a direct relationship with the *Annona*, i.e. the supply system managed by the State. The presence of these vessels in the site of Loppio also in the 7th century suggests a continuity of importation of amphora-borne commodities also after the Lombard conquest, despite the changes occurred in the political and military sphere.

The typological study suggests the predominance of wine containers in this context and it seems to be confirmed by chemical data. This evidence is likely to be related to the military nature of the settlement. Nevertheless, this study has still a strong preliminary character and is not based on a quantitative approach in the identification of the chemical markers of wine as recently indicated by Drieu *et al*. 2021. The implementation of the sample size and the adoption of quantitative criteria will allow in the future to contribute more substantially to the discussion of the content and function of Late Antique containers from military contexts like Loppio.

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[47] DRIEU *et al*. 2021, Supporting Information, Table S3.
[48] RAGEOT *et al*. 2019.
[49] PENA 2007; PECCI *et al*. 2017.
[50] ZANINI 2010.

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