REPORT ON THE ANALYSES OF THE ORGANIC RESIDUES IN ARCHAEOLOGICAL SAMPLES FROM THE PROJECT “EXCAVATING THE ROMAN PEASANT”.

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ANALYSIS OF THE ORGANIC RESIDUES IN CERAMIC AND PLASTERS FROM THE PROJECT “EXCAVATING THE ROMAN PEASANT”

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1. Introduction

Porous materials absorb the liquid and semi-liquid substances that came in contact with them. In particular, almost 40 years of research have shown that through the chemical analysis of samples it is possible to try to understand the original content of ceramic vessels (Condamin et al. 1976, Evershed 2008).

This kind of analyses has an important application for the study of amphorae, and therefore of the economy in the Mediterranean area in ancient times. The early stage of chemical analyses of archaeological materials corresponded essentially to the study of amphorae content (Condamin et al. 1976, Formenti et al. 1978, Rotshild-Boros 1981, Passi et al. 1981, Heron, Pollard 1988) and in later years the study of contents has had a new impulse (Garnier 2004, 2007a, 2007b Brun 2004, Romanus et al. 2009, Pecci 2009). Still, there is still a lot of work to do. Sometimes, in fact, the analyses offer data that are consistent with those proposed by the literature, while some other times the content is similar to that one expected, although a little different. Finally, in some cases, they show new and unexpected data (Pecci et al in press.). This is why it is more and more important to establish on scientific bases the contents of the different types amphorae, in order to give consistency to the hypothesis on the goods stored and transported in them, and therefore to understand ancient economy.

The analyses carried out on some materials recovered during the Project “Excavating the Roman peasant” have the objective of clarifying if several local-regional amphorae were devoted to contain wine and to understand the food prepared in two coarse ware cooking vessels.

Residues analysis can also be performed on porous materials different from ceramics, such as plasters (Barba 1986, 2007). At La Pievina, the plaster coating of a basin was sampled, in order to try to understand the function of the basin and therefore try to identify food production markers at the site.
2. Materials and methods

Materials

Two samples (1-2) were taken from the plastered coatings of a basin. Six samples were taken from *amphorae* locally and/or regionally produced, showing a different chronology to test if changes raised in time, and in particular in Late Antiquity. Two samples were taken from import *amphorae* (one K26 and one K25 or 26) and, finally, two samples were taken from Late Roman cooking ceramic vessels (*a testo* or pan and a pot) to verify the food cooked in them (Table 1).

Table 1. Samples analysed.

<table>
<thead>
<tr>
<th>sample n.</th>
<th>sample id.</th>
<th>laboratory n.</th>
<th>part sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CN2010 -1-US 5005</td>
<td>62</td>
<td>basin us 5005</td>
</tr>
<tr>
<td>2</td>
<td>CN2010 -2 US 5005</td>
<td>63</td>
<td>basin us 5006</td>
</tr>
<tr>
<td>3</td>
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<td>64</td>
<td>amphora local-regional</td>
</tr>
<tr>
<td>4</td>
<td>inv.1010036</td>
<td>65</td>
<td>amphora local-regional</td>
</tr>
<tr>
<td>5</td>
<td>inv. 1010144</td>
<td>66</td>
<td>amphora local-regional</td>
</tr>
<tr>
<td>6</td>
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<td>7</td>
<td>US 5014</td>
<td>70</td>
<td>amphora local-regional</td>
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<td>8</td>
<td>US 5014</td>
<td>71</td>
<td>amphora local-regional</td>
</tr>
<tr>
<td>9</td>
<td>inv.1010130-US 1019</td>
<td>68</td>
<td>amphora K26</td>
</tr>
<tr>
<td>10</td>
<td>inv.1010090-US 1026</td>
<td>69</td>
<td>amphora K25 or 26</td>
</tr>
<tr>
<td>11</td>
<td>olla inv.1010180-US 1006</td>
<td>72</td>
<td>Cooking pot</td>
</tr>
<tr>
<td>12</td>
<td>testo inv.1010090-</td>
<td>73</td>
<td>Cooking pan</td>
</tr>
</tbody>
</table>

Methods

Each sample was cleaned mechanically before it was subsampled in the laboratory. No samples of the earth that was in contact with the ceramic vessels and the basin were recovered, therefore we could not have a blank sample for the analysis.

The samples were studied by the ERAAUB, using the infrastructure of the Archaeometric Laboratory of the Departament de Prehistòria, Història Antiga i Arqueologia of the Facultat de Geografia i Història (UB), where the samples were crushed, and the infrastructure of the Serveis Científico-Tècnics de la Universitat de Barcelona, where the samples were analyzed with gaschromatography – mass spectrometry (GC-MS).

The ceramic and plaster samples were analysed using the following methodology:

a. The *total lipid extract* was obtained following the procedure described by Mottram et al. (1999):
Analyses of the organic residues in ceramics and plasters from the project Excavating the Roman peasant

1g of grounded sample was extracted twice with CHCl3/MeOH (2:1 v/v, 3 ml) in sonicated bath for 40 min. at 70°C. 5 µl of a standard solution of octacosane (3 mg/ml) were added to the powder before extraction. The liquid fraction was recovered after centrifugation and dried using a gentle stream of nitrogen.

b. Half of the total lipid extract was extracted with KOH in methanol (1 M, 6 ml), leaving overnight. The day after 6 ml of water were added and acidified. CHCl₃ (2x3 ml) was added and mixed with a vortex. The extract was separated and dried using a gentle stream of nitrogen.

c. For some samples, the solid fraction of each sample was extracted with KOH (1 M, 3 ml) in a sonicated bath at 70°C for 90 min. After cooling and centrifugation, the liquid fraction was recovered and acidified. CHCl₃ (2x3 ml) was added and mixed with a vortex. The extract was separated and dried using a gentle stream of nitrogen.

d. For the identification of wine markers, the extraction with KOH was repeated with 500 mg of sample. This time 3 ml of ethyl acetate were added twice to the liquid fraction and mixed with the vortex. They were then separated and dried using a gentle stream of nitrogen.

All the extracts were derivatized adding 25 µl of N,O-bis(trimethylsilyl)triﬂuoroacetamide (BSTFA, Sigma-Aldrich) and heating at 70°C for 1h. 75 µl of hexane were added and 5 µl of a standard (dotriacontano - 1 mg/mL). For the analysis 1 µl was injected.

The analysis were performed with a chromatographer Thermo Scientiﬁc TS GC ultra, with a 30 m x 0.25 mm (i.d.) x 0.25 µm film thickness fused silica capillary column and a mass spectrometer Thermo Scientiﬁc ITQ 900 operated in electronic ionization (70 eV).

The mass range was scanned in the range of m/z 40-650. The oven temperature of the GC was kept at 50°C for 1 min, and then raised of 5°C/min until the 330°C and kept constant for 10 min.

3. Results

Samples 1-2

<table>
<thead>
<tr>
<th>sample n.</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CN2010 -1-US 5005</td>
<td>62</td>
<td>basin us 5005</td>
</tr>
<tr>
<td>2</td>
<td>CN2010 -2 US 5005</td>
<td>63</td>
<td>basin us 5006</td>
</tr>
</tbody>
</table>

In the total lipid extract of sample 2 the main picks after the standard are oleanitrile and oleammmide (Figures 1 and 2). Also in the hydrolisis of the total lipid extract oleamide is the main pick. The presence of these compounds could be due to a reaction of oleic acid in a basic environment, and could therefore be attributed to the presence of a vegetable oil in the sample.
These compounds were also identified in African *amphorae* filled with lime and/or plaster and supposed to have contained oil, that were recovered at Pompei during the “Garum Workshop project” directed by Bernal and Cottica and studied by the authors of this contribution.

In the ethyl-acetate extraction, also traces of azelaic acid are present. This compound is considered to be a by-product of the degradation of oleic acid (Dudd et al 1998).

Figure 1. Chromatogram of the total lipid extract of sample 2 (basin).
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Figure 2. Spectra of the oleanitrile in the sample (top) and in the Nist library (bottom).

Figure 3. Oleamide spectra in the sample (top) and in the Nist library (bottom).
Samples 3, 4 and 5

<table>
<thead>
<tr>
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<tr>
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<td>amphora local-regional Neck</td>
</tr>
<tr>
<td>4</td>
<td>inv.1010036</td>
<td>65</td>
<td>amphora local-regional Bottom</td>
</tr>
<tr>
<td>5</td>
<td>inv. 1010144</td>
<td>66</td>
<td>amphora local-regional Wall</td>
</tr>
</tbody>
</table>

Samples 3, 4 and 5 come from local-regional *amphorae*.

While sample 3 is not rich in residues, sample 4 shows very abundant traces of resin/pitch: dehydroabietic acid is in fact the main pick together with 7 oxodehydroabietic, and abietic acid is also present.

The abundance of resin in sample 4 could be due to the fact that the amphora was coated with a lot of pitch, and part of this pitch could have accumulate in the bottom of the amphora.

Although in sample 4 the tartaric acid, usually considered to be the marker of wine (Guash Jané et al 2004, Mc Govern 2004) is absent, there are other compounds that are present in wine, such as malonic, benzoic, vanillic, succinic, and cinnamic acids, that in sample 9 were identified together with tartaric acid. These acids, could support the archaeological hypothesis that the *amphora* contained wine. In this case, the resin could have also had the function of flavouring the wine.

Sample 5 is also rich in residues. Here, like in sample 4, although no tartaric acid was identified, other compounds that are usually found in wine are present in the ethylacetate extract (succinic, benzoic, malonic and vanillic acids). Traces of resin were identified also in this sample, while no traces of vegetables oils were present in the samples.
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Figure 4. Chromatogram of the total lipid extract of sample 4.

Figure 5. Ethyl acetate extract of sample...

**Samples 6, 7 and 8**

<table>
<thead>
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<th>laboratory n.</th>
<th>part sampled</th>
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<tbody>
<tr>
<td>6</td>
<td>US 5048</td>
<td>67</td>
<td>amphora local-regional Wall</td>
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<tr>
<td>7</td>
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<tr>
<td>8</td>
<td>US 5014</td>
<td>71</td>
<td>amphora local-regional Wall</td>
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</table>

The analysis of samples 6, 7 and 8, taken from local or regional *amphorae* show almost no residues, as the relative proportion to the standards in the total lipid extracts suggests (Figures 6 and 7). In samples 6 and 8, some traces of resin are present, possibly used to coat the *amphorae*, while in sample 7, long chain fatty acids such as C\textsubscript{20}, C\textsubscript{21}, C\textsubscript{22} and C\textsubscript{24} were identified. These compounds could be related with the presence of waxes.

Figure 6. Chromatogram of the total lipid extract of sample 7 (laboratory 70).
Sample 9 (laboratory 68)

<table>
<thead>
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<tr>
<td>9</td>
<td>inv.1010130-US 1019</td>
<td>68</td>
<td>amphora K26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
</tr>
</tbody>
</table>

The analyses of the K 26 amphora (sample 9) allowed to identify tartaric acid both in the ethylacetate extraction and in the total lipid extract. Tartaric acid is commonly considered to be the marker of wine. Besides this acid, also other compounds that are typical of wine were identified (malic, malonic, benzoic, and succinic acids).

Traces of resin are present in all the extractions of the sample.

Azelaic acid and 9,10-dihydroxyoctadecanoic acids are present in the hydrolysates. These compounds are usually considered among the markers of oil. Nevertheless, C\textsubscript{18:1} is not high and more data are needed to establish if an oil could have been contained in the amphora. If this was the case, we could suggest that the amphora was re-used, as it is possible to exclude that oil and wine were carried together.

The data obtained for this amphora are interesting, as they provide more material for the discussion on the goods that this kind of amphorae carried. They are in fact supposed to have carried wine or fish sauces; but the analysis of five K 26 recovered in the port of Classe showed castor oil residues (Pecci et al in press).

Like in the amphorae coming from Classe, this one had a resin/pitch coating.
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Figure 8. Chromatogram of the hydrolysis in ethyl acetate of sample 9.

Figure 9. Particular of the chromatogram of the hydrolysis in ethyl acetate of sample 9. The markers of wine can be observed here.

**Sample 10 (laboratory 69)**

<table>
<thead>
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<th>Laboratory n.</th>
<th>part sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>inv.1010090-US 1026</td>
<td>69</td>
<td>amphora K25 or 26</td>
</tr>
</tbody>
</table>

Sample 10, belonging to a K 25 or K 26 amphora, is very rich in pitch. Dehydroabietic acid, together with 7 - oxodehydroabietic acid are in fact very abundant in all the extracts. In the hydrolysis of the total lipid extract also the methyldehydroabietic acid, considered to be the marker of the distillation of pitch directly from the wood (Colombini et al 2005) is present (Figure.). The pitch probably due to presence of the coating of the amphora, is so abundant that it might have
prevent at least part of the residues of the content from penetrating the ceramic body. In any case, malonic, benzoic, succinic, glutaric and vanillic acids are present in the extraction for the wine markers, suggesting a wine content.

Figure 10. Chromatogram of the hydrolisis on half of the total lipid extract of sample 10.

Figure 11. Spectra of the methyl dehydroabietic acid present in the NIST library (left) and obtained with the analysis of sample 10 (right).
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Sample 11

<table>
<thead>
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<th>sample id.</th>
<th>laboratory n.</th>
<th>part sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>olla inv.1010180-US 1006</td>
<td>72</td>
<td>Cooking pot</td>
</tr>
</tbody>
</table>

Sample 11 was taken from a cooking pot. The abundance of the stearic acid together with the cholesterol present in some of the extracts, suggests the animal origin of the fats. Although no isotopic analyses were performed, the presence of branched odd fatty acids such as C_{15} and C_{17} suggest that the fat derives mainly from ruminant animals (Mottram et al 1999). These data are similar to those obtained with the analysis of Late Roman and Medieval cooking pots analysed by the authors of this contribution.
Figure 13. Chromatogram of the hydrolisis on half of the total lipid extract of sample 11.

Sample 12

<table>
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<tr>
<th>sample n.</th>
<th>sample id.</th>
<th>laboratory n.</th>
<th>part sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>testo inv 1010090-</td>
<td>73</td>
<td>Cooking testo/pan</td>
</tr>
</tbody>
</table>

Sample 12 was taken from a possible testo or pan. It has abundant residues as it is shown by the proportion with the standards that can be observed in Figure 13. Like in sample 11, the presence of cholesterol and the abundance of the stearic acid suggest the animal origin of the fats. Although no isotopic analyses were performed, the presence of branched odd fatty acids such as C_{15} and C_{17} suggest that the fat derives mainly from ruminant animals (Mottram et al. 1999).

The quantity of animal origin residues suggests that it is more likely that the vessel was a pan than a testo. Testi are in fact usually considered to have been used to cook bread or similar foodstuff (Quiros Castillo 1998, Pruno 2003). Although the analysis of some medieval testi coming from Tuscan archaeological sites have shown that some of them were possibly used to cook animal origin products or to serve them on the table (Pecci 2009), the amount of residues present in this ceramic vessel suggests an intense use for the cooking of animal fats, similar to the one usually performed in pots or pans.
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4. Conclusiones

The results of the analyses allowed to recover in formation on the use of the amphorae and the basin found at La Pievina.

Some of the amphorae showed residues that could be related with their use, such as the wine markers present in the K26 and possibly in other amphorae. In other cases no residues were identified. This could be attributed to the fact that they degraded because of the aging or the post-depositional processes, nevertheless it is also possible that these amphorae were used for the storage and transport of water and/or substances that do not leave traces that can be identified with the analyses performed.

Acknowledgments

The samples were analyzed at the Serveis Científico-Tècnics of the Universitat de Barcelona in the department of gas chromatography. This report is part of the activities of the project “Production, trade and consumption of food in Late Antiquity” (PROFOLANT), PIEF-GA-2009-235863, 7th Framework Programa, People, Marie Curie actions, IEF.
References

Pecci A., Salvini L., Cirelli E., Augenti A., c.s. Residue analysis of some Late Roman amphorae


