15 ORGANIC RESIDUES IN POTTERY

ARCHAEOLOGICAL BIOMARKERS

Although the first papers discussing organic residues appeared in scientific journals in the 1960s, and their number grew intensively in the 1980s, only in the past 10 or so years has the analysis of organic residues in pottery become a discipline widely present in archaeology (Barnard & Eerkens 2007). In the meantime, numerous analyses and experiments have been done on pottery, aimed at identifying traces of archaeological biomarkers, or substances occurring in organic residues that provide information relating to past human activities (Evershed 2008: 897).

Organic residues have been found at nearly all archaeological sites: some as visible evidence of human activities (such as bones, charcoal, wood, carbonized seeds, pigments) or as less visible substances such as plant and animal fats and oils, resins and waxes, but majority of them as invisible substances 'hidden' in the form of archaeological biomarkers, such as lipids and proteins (Miloglav & Balen 2013).

All organic residues present at archaeological sites are of biological origin, and they can be analysed through a combination of various methods. One of the most frequently-used methods of analysing the molecular structures of organic residues is gas chromatography-mass spectrometry (GC-MS). The application of this method in the analysis of archaeological pottery has made it possible to decompose, and analyse in detail, molecular components of the biological material. Thus far, analyses have shown that organic matter absorbed in the walls of pottery vessels, as a product of the processing of plant and animal fats, has been preserved in as many as 80% of the vessels that had been used for cooking and food preparation (Evershed 2008: 904). Information obtained through this analysis enables us to provide answers to questions relating to the vessel's function, the local and regional economy, and technological choices and changes.

There are several forms in which organic residues can persist on or in pottery:

1 – as the original content of the vessel found *in situ*. This is the form in which organic residues are most rarely found preserved in archaeological contexts;

2 – as residues visible on the interior and/or exterior of the vessel. Such marks provide direct and visible evidence of the use of cooking vessels. The exterior surface often displays soot marks, while the interior contains carbonized residues; both are consequences of the vessel's exposure to fire. Visible organic residues on pottery can also be used for radiocarbon dating. However, there is an increased chance of contamination of such samples, given that those residues have been exposed directly to external environmental factors and activities in connection with irregular storage after their recovery. Radiocarbon analysis of pottery sherds for the purpose of their dating is possible thanks to lipids preserved in the pottery. Using preparative capillary gas chromatography (PCGC), sherds containing a sufficient quantity of lipids, or fatty acids (animal fats), absorbed in their walls, are singled out. For adequate samples that can be subjected to radiocarbon dating using the accelerator mass spectrometry (AMS) method, a minimum quantity of carbon (200 μg) in the sample is sufficient. This method of radiocarbon analysis offers rather successful dating of pottery, that is, of the time it was last used (Stott et al. 2003);

3 – as invisible organic residue absorbed in pottery walls. This is the most frequent form of 'survival' of organic residues which can be found in pottery, and there are several factors that contribute to this.

The first of these factors is the vessel's use – the method and duration of its use, its physical properties, the environment in which it was deposited and its treatment after it was recovered (Heron & Evershed 1993). Experiments done on pottery have shown that proteins lose their properties and decay as soon as several months after they are deposited in the ground. Lipids are much more resistant to environmental factors: they are hydrophobic and less prone to structural modifications, and thus they can persist in high concentrations in a pottery sherd over several millennia. However, the risk of contamination is higher for lipids than proteins, both during and after an archaeological excavation. Contamination can be caused by irregular storage of pottery in plastic bags, by gluing, washing, and even by frequent inspection of pottery material. For example, traces of cholesterol can originate from animals (animal fats), but they are also present on the surface of human skin.

Squalene, which has been found on several analysed samples, is also present both in the human body and in plants and animals, and it is considered to be the main indicator of contemporary 'human traces'. This polyunsaturated liquid hydrocarbon can be found in small quantities all over the human body, it is released over the skin, and it decomposes very quickly. In the plant kingdom, this lipid is present in very small amounts – for example, in wheat-germ oil. The presence of both these compounds in pottery, in certain proportions, is considered to be indicative of modern-day contamination of pottery material through handling (Evershed 1993).

Plasticizers also cause degradation of lipids, and hence they are a frequent cause of contamination of archaeological material, which is regularly stored in plastic bags. Although pottery washing has no impact on the contamination of lipids, their concentration drops significantly through washing, which brings the results of analysis into question. This is especially true of removing the soil and barely-visible organic residues from the external and internal surfaces of sherds. Therefore, it is advisable not to wash, glue, or label those pottery sherds which will be sent for analysis, and the sample should be sent, if possible, together with the soil in which it was located. Considering everything said above, and with a view to preserving organic residues as much as possible, and eliminating possible contamination, this type of analysis should be planned for in advance and incorporated into the excavation process (Miloglav & Balen 2013).

The most frequent organic residues absorbed in vessel walls are animal fats, characterized by a high proportion of free fatty acids, especially palmitic (C16) and stearic (C18) acid. These fatty acids can easily be isolated and analysed, and they can be found in vessels that had been used for preparation and storage of food. Analyses have shown that they are mostly found in the vessel itself, rather than in the environment, or in the soil in which the vessel was deposited (Craig 2002; Copley et al. 2003). However, contamination with lipids through their migration from the soil in which the vessel was deposited is highly likely (Evershed 1993: 87) (*Fig. 73, p. 136*).

In cases in which samples of soil are not available, it is very important to compare and analyse the external and internal sides of the sherd (Stern et al. 2000). This is what occurs regularly when samples of material, recovered in previous excavations and then kept in museum collections, are sent for analysis. By analysing both the external and internal sides of the sherd, we can exclude contamination caused by its long deposition in the ground, by the vessel's handling during and after archaeological investigation, and its inadequate storage (*Fig. 74 p. 137*). Such contamination is usually present on both sides in the same concentration, while archaeologically-significant organic residues are present on one side only (Steele 2011).

The analysis of organic residues in pottery, those very good indicators of archaeological biomarkers, will be interpreted more accurately if compared with other analyses that provide evidence of human activities in the same locality. Those include analyses of plant and animal species present at the site, analysis of pottery assemblage which will enable us to establish links between vessels' shapes and their utilitarian functions, analysis of abrasive and non-abrasive processes affecting the vessel, and the context of its deposition (Miloglav & Balen 2013).

All such traces are present on pottery vessels, and they can be identified and analysed easily, as discussed in chapter 8. Therefore, information obtained through a GC-MS analysis should not be interpreted in isolation.

As for any other analysis, the applied method of sampling plays an important role in the interpretation of the results obtained. If samples consist of sherds that cannot be identified from either a functional or a stratigraphic point of view (originating from settlements or from grave units, for example), the results of analysis will be unusable. In order to avoid such occurrences, sampling should be prudent and planned, and suitable for the research question that has been posed.

The concentration of lipids in various parts of the vessel (orifice, body, base) plays a big role in the identification of the vessel's function, since the accumulation of lipids in specific parts of the vessel can suggest its function (e.g. boiling or baking) (Charters & Evershed 1995). A number of experiments have been done to that effect, and they included analyses of original parts of vessels and their replicas (Charters et al. 1997). It has been demonstrated that, in those vessels which were used for heating water and cooking food, the highest concentration of lipids can be found at their orifices. This is a result of the flotation of lipids released from food, which accumulate at the water surface and evaporate towards the orifice. Another reason is temperature, which is lower at the vessel's orifice (around 100 °C), and the degradation of lipids is not as strong as at the bottom (where the temperature can be as high as 800 °C). Furthermore, experiments have shown that lipid residues can be identified after just one cooking. With each new heating, their concentration increases, especially on the vessel's body and orifice. For these reasons, if samples are taken from different parts of the vessels, from vessels of diverse functional shapes, discovered in various depositional contexts, and if they are representative, it will be possible to obtain data which can be interpreted, through comparative and combined analyses, in the context of the analytical question or problem posed.

RESULTS OF POTTERY ANALYSIS USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

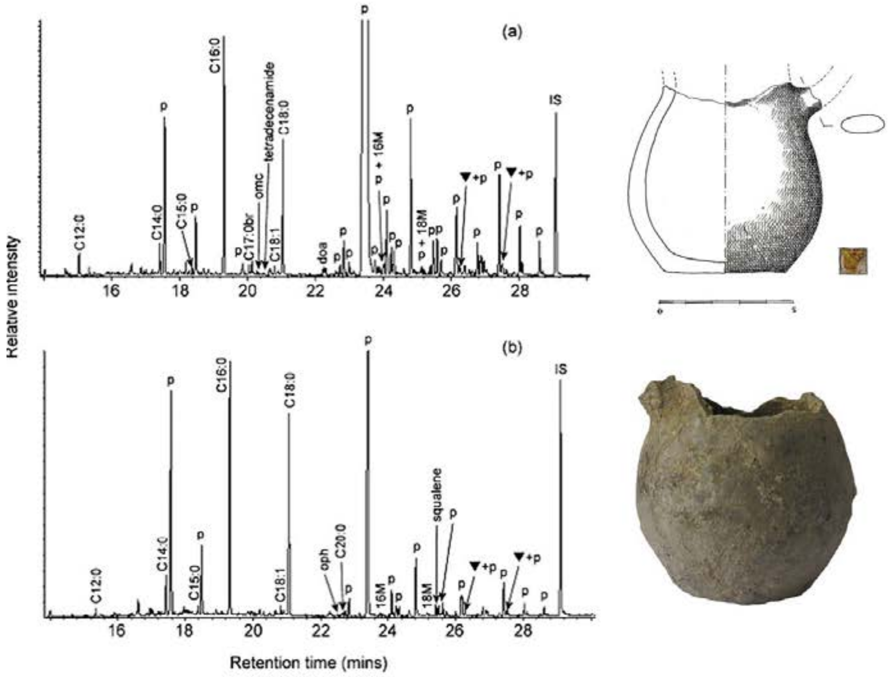
The GC-MS method was used to analyse a total of 10 pottery samples: 8 from the site of Ervenica and 2 from the site at Damića Gradina *(Fig. 75).* The analyses were done at the Division of Archaeological, Geographical and Environmental Sciences of the University of Bradford. The samples were taken from various parts of vessels (base, body, orifice), from vessels of various functional shapes (pot, bowl, cup, strainer), and from sherds of diverse surface treatment (polished and burnished sherds, and those treated with barbotine).

The questions raised included the technological aspect of the vessels' production, or possible differences in the technology of production of vessels intended to be used for cooking over a fire,

Fig. 75 – Types of vessels the analysed samples belong to. Labels refer to the designation of the sample, not the type of the vessel

and those which would not be used for thermal processing of food, and the type of food that had been prepared/cooked/stored in vessels of specific shapes. The data have been interpreted together with the results of the archaeobotanic and osteological analyses, typology of pottery shapes, the vessels' depositional contexts, and the analysis of the clay and tempers (XRD and mineralogical-petrographic analysis). In order to exclude any contamination caused by the environment in which the vessels were deposed, and by their post-recovery handling, both surfaces of the sherds were analysed (Steele 2011; Miloglav & Balen 2013: 13, Fig. 1).

All the samples analysed were contaminated by plasticizers to a certain extent, as a result of their storage in plastic bags. The majority of sherds analysed also contained cholesterol and squalene – consequences of their handling. The lipid concentration was insufficient for additional analysis of stable isotopes using gas chromatography-combustion-isotope ratio mass spectrom-



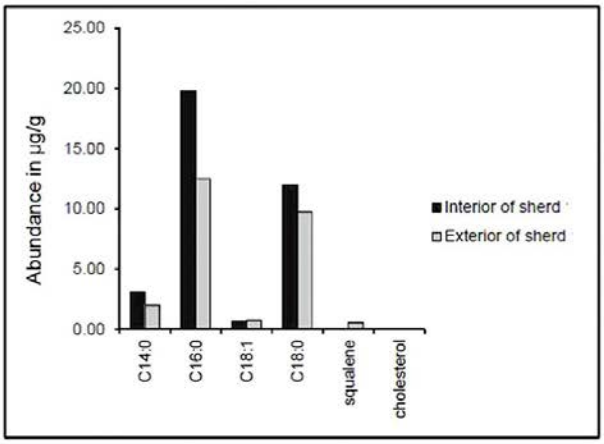


Fig. 76 – Chromatogram showing substances extracted from pottery sherd ER 1 and the chart showing the abundances of the main fatty acids, squalene and cholesterol

etry (GC-C-IRMS), which could have provided more precise information on the origin of animal or plant species (Steele 2011). This analysis allows more precise identification and distinction between ruminant (cattle, goat, sheep) and non-ruminant fats, and especially dairy products, which are otherwise difficult to distinguish from animal fats due to the lack of unique biomarkers for milk (Dudd et al. 1999; Craig 2002; Evershed 2008).

All the samples contained high amounts of C16:0 and C18:0 fatty acids, resulting from the degradation of animal fats (Steele 2011). More precise distinction of animal fats could be achieved for two functional types, the shallow bowl (ER 3) and strainer (DG 1), while possible traces of dairy fats have also been recorded on the sample that belongs to the functional shape of the cup. Degraded fats were present on both surfaces of the sherd which belonged to a cup (ER 1), although they were less present on the external surface than on the internal. According to the data interpretation (Steele 2011), the original residues of animal fats were located in the vessel's

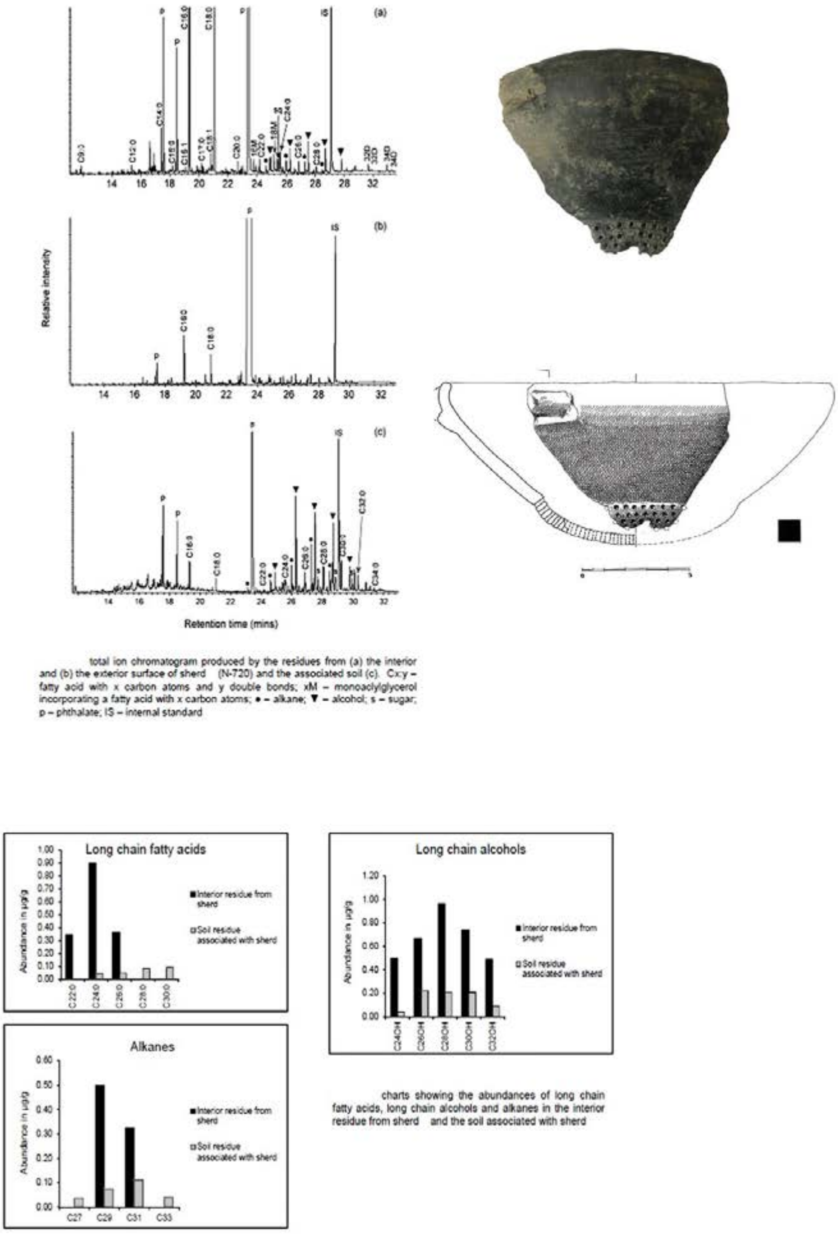


Fig. 77 – Chromatogram and charts showing substances extracted from pottery sherd DG 1 and the associated soil sample

interior, while the traces discovered on the external side were probably the consequence of spillage of the vessel's contents. In addition, these residues could be residues of ruminant fats or dairy fats (*Fig. 76*).

Although interpreting residues of dairy fats without additional analysis of stable isotopes is an ungratifying task, other analyses performed suggest that this functional shape can easily be described as a vessel used for drinking milk. Based on the parameters analysed, this type of vessel (cup – type C 1a) was not used for preparing food over a fire, since no traces that would indicate this have been found on any of the sherds analysed. Furthermore, according to the analysed animal remains, the economy of the Vučedol settlement at Ervenica was based on animal herding, primarily on raising cattle (65.24%), pigs (25.00%) and goats/sheep (4.88%), which is characteristic of the Aeneolithic period in general. Thanks precisely to GC-MS analysis, nowadays we know that dairy products were already in use in the Early Neolithic (Craig 2002; Copley et al. 2003; Craig et al. 2005; Evershed et al. 2008; Dunne et al. 2012; Isaksson & Halgren 2012; Salque et al. 2013), so it is probable that dairy products made up part of the dietary habits of the Vučedol population, too.

Ruminant fats have also been found in the interior of the strainer of type E 1a (DG 1 – *Fig. 77*), as the original content of the vessel (Steele 2011). A strainer that belongs to a different typological shape (DG 2 – type E 2a) also contained traces of lipids in its interior; these were decayed residues of fats or oils which could not be identified more precisely due to too low a concentration of lipids. Prehistoric strainers are usually interpreted as vessels used in the preparation of cheese, while some interpretations also associate them with the production of honey (Regert et al. 2001: 567; Elster & Renfrew 2003). Given that neither of the two analysed sherds revealed any traces of wax, but only traces of ruminant fats, or more generally animal fats, and bearing in mind the economy of the Vučedol population, it is likely that both strainers were used in the production of cheese. Recent analyses of some sherds from Poland have demonstrated that similar strainers were used in the production of cheese 7000 years ago, and that they played a major role in the production of dairy products with reduced lactose content (Salque et al. 2013).

A sample taken from a low vessel with thick walls (type A 1a) contained by far the greatest quantity of fatty acids (most probably ruminant fats) in its interior, while no traces of lipids have been recorded on its exterior (ER 3 – *Fig. 75*). Given its very thick walls (up to as much as 19 mm), lack of height (up to a maximum of 6.50 cm), very large orifice radius (up to 11.50 cm) and traces of soot and oxidation stains on its surface, this bowl was used for the thermal processing of food.

A technological aspect has been identified on analysed sherds originating from three vessels, which contained traces of beeswax on both internal and external sides of the samples (ER 4 – type A 4c; ER 5 – type A 2a; ER 8 – type C 1a). On one sample, traces of degraded wax were present only on its internal surface (ER 2 – type D 1a). Recording wax on pottery sherds is not new, although it may be rare, but the presence of wax has been confirmed on pottery sherds from a period as early as the Neolithic (Heron et al. 1994; Regert et al. 2001; Copley et al. 2005; Mayyas et al. 2010). It is known that honey was collected by some of the earliest prehistoric communities, and used in medicine, the arts, rituals and cosmetics, as a food supplement and for the preparation of drinks (Needham & Evans 1987; Garnier et al. 2002). The results of a recent study of a 6500-year-old human mandible from Slovenia have shown that it is the earliest known evidence of a therapeutic-palliative dental filling made of beeswax (Bernardini et al. 2012).

On pottery, beeswax is found either on its own or in combination with other natural materials, or animal and plant oils. It was used primarily to fill pores in the pottery and make it impermeable (Schiffer et al. 1994; Charters et al. 1997; Regert et al. 2001; Ogrinc et al. 2014). In chapters 5 and 6, various options of post-firing surface treatment are discussed whose goal was to decrease the vessel's permeability and improve its strength. Wax is a hard substance, insoluble in water. In can be found in both plants and animals; and, as an element of protective coverage, it can be found in plant leaves, animal furs and feathers. Natural waxes are softer, and they melt at lower temperatures (above 45°C), unlike fats and oils. The best known animal wax is beeswax, which melts at a temperature of around 65°C. In the case of the Ervenica samples, this was probably some kind of waterproofing agent, added to the pottery to fill its pores, since traces of wax have been found on both the internal and external sides of the vessel (Stern 2011). Some analyses indicate that the wax was probably applied to pottery vessels after firing, while the ceramics were still hot. Thus the wax would melt and enter the walls of the porous pottery, blocking small holes in the structure of the clay paste. Such creation of an impermeable layer would prevent liquids from escaping the vessel.

In an attempt to uncover the role of wax in pottery, an experiment was performed in which wax was heated over a vessel. The wax melted at a temperature of 60-65°C, the vessel was then taken off the fire, until the wax consolidated as a thin coat/filter over the vessel. Then the vessel was placed over a fire, so that the wax came in direct contact with the fire. The wax lost its colour and become a brown-black tar-like mass which adhered to the vessel. The procedure resulted in a black shine and softness of the vessel, similar to the polishing effect (Heron et al. 1994). Analyses and experiments have shown that, when fats and wax were found together, as a rule the wax had been applied to the vessel before the animal fats (Charters & Evershed 1995).

Although the number of samples analysed is low, certain pottery shapes can be linked to specific functions of vessels. Traces of wax recorded on analysed sherds can be interpreted within the framework of their techno-functional characteristics, given that wax has been found on vessels of different shapes: two different types of bowls, a cup and a jug. Wax is associated not with a specific type of vessel, but rather with a specific use of the vessel (Miloglav & Balen 2016). None of the vessel types analysed displayed any traces of having been placed over a fire, so they were used for consumption and/or serving food which was dry, liquid or semi-liquid, and was not thermally processed. Based on the context in which they have been found and the archaeobotanic analysis of bowls of type A 4 (ER 4 – *Fig. 75*), this shape was the most numerous in a pit in which the largest quantity of cereals has been found; this could suggest that such vessels could have been used for waste disposal, where they were deposited together with used foodstuffs.

The shallow bowl (ER 3) was used for thermal processing of food, as was one sample of pot of type B 1a which contained traces of fatty acids only in its interior (ER 7 – *Fig. 75*). According to all the indicators, the strainer was used for the preparation of cheese, while a sherd from a bowl on a cross-shaped foot (ER 6) was unfortunately contaminated with plasticizers to such a high degree that it has not provided any relevant lipid residues that would be archaeologically relevant.