

CHAPTER NINE
A Comparative Study of Extractable Lipids in the Sherds
and Surface Residual Crusts of Ceramic Vessels from Neolithic
and Roman Iron Age Settlements in the Netherlands
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Introduction: Lipid Analysis in Ceramic Studies

Pottery assemblages are a rich and durable source of information for the study of the daily behavior of people in the past. In order to assess the value of the information obtained from these assemblages, the use of the ancient vessels is an essential prerequisite. The identification of organic remains of ancient vessel contents can enable the retrieval of information about original vessel use. Since the 1970s, the study of organic residues has shown the preservation of many organic compounds in association with ceramics (Craig et al. 2000; Evershed et al. 1999; Evershed et al. 1992; Heron and Evershed 1993; McGovern et al. 1996; Mills and White 1987; Oudemans and Boon 1996; Oudemans et al. 2005; Pastorova et al. 1993; Regert and Rolando 2002; Rottländer and Schlichtherle 1979; Rottländer and Schlichtherle 1980).

The study of organic residues has focused primarily on fatty materials. Lipids are favored for organic residue studies due to their easy retrieval with solvent extraction and the continuous development of analytical techniques such as GC, GC/MS and gas chromatography isotope ratio mass spectrometry. Lipids also have obvious potential as diagnostic markers for the original vessel use due to their chemical stability (Eglinton and Logan 1991). In contrast to proteins and carbohydrates, lipids possess only a limited number of reactive sites resulting in relatively high resistance to thermal degradation during heating (Davídek et al. 1990, 169). In addition, the aliphatic nature of lipids results in low water solubility and thus enhances the immobilization of the molecular debris considered crucial to long term preservation at a molecular level (Eglinton and Logan 1991). Post-depositional exchange of lipids between residues and their surrounding soil has been shown to be very limited (Heron et al. 1991; Oudemans and Boon 1991; Oudemans, 2006).

Introduction: Types of Residues

In a few rare cases, lipids have been preserved as solidified or liquid substances in sealed vessels (Gibson and Evans 1985; Shedrinski et al. 1991), but most frequently lipids have survived in visible crusts adhering to the interior or exterior surface of a vessel (Hill and Evans 1988; Oudemans and Boon 1991; 1996; Oudemans et al. 2005; 2007; Oudemans and Erhardt 1996; Patrick et al. 1985; Regert and Rolando 2002; Rottländer and Schlichtherle 1979) or absorbed within the ceramic matrix of the vessels (Charters et al. 1995; Charters et al. 1993; Condamin et al. 1979; Dudd et al. 1998; Evershed et al. 1994; Evershed et al. 1990; Evershed et al. 1997; Gianni et al. 1990; Heron et al. 1991; Mottram et al. 1999; Passi et al. 1981; Regert et al. 1998).

The relative suitability of different types of residues for the identification of original vessel content has been discussed by a number of investigators. Although substances in sealed vessels can be in relatively good condition, their sparseness makes them less suitable for systematic study of vessel use. Absorbed lipids may occur more frequently than visible surface residues (Evershed et al. 1991), and have been claimed to be easier to identify due to their better preservation (Rottländer 1990). On the other hand, some researchers detected lipids in surface residues while none were found in the adjacent sherd (Needham and Evans 1987; Regert et al. 2001). A number of additional methodological advantages have been formulated for the study of surface residues (Oudemans and Boon 1991; Oudemans et al. in press). In short, the study of surface residues makes it possible to sample only a limited number of use phases, while absorbed residues represent the accumulated deposits of multiple use-phases in addition to possible post-firing sealing agents. Extractions of absorbed residues may also include such

Theory and Practice of Archaeological Residue Analysis

sealing agents, complicating interpretation even more. Post-firing surface sealing with organic mixtures, the 'seasoning' of the vessel, is common amongst traditional potters and is performed with a variety of materials including common foodstuffs such as milk, oil and various starch-rich foods (Rice 1987, 163-164), as well as less edible materials such as beeswax, various resins and other plant materials (Arnold 1985, 139-140; Diallo et al. 1995; Kobayashi 1994). Stern et al. (2000) confirm that fatty acids extracted from Bronze Age Canaanite amphorae show that the jars were used to hold a lipid product, but that it was impossible to distinguish single use and multiple use. An additional reason to use surface residues in cooking vessels is the relatively higher degree of thermal degradation that has likely taken place in absorbed residues. Absorbed residues have usually been exposed to more severe heating regimes (both in temperature and in time) than residues situated on the interior surface of the vessel. Although numerous quantitative studies have been performed on lipids preserved in different residue types, no quantitative comparison of lipids extracts was ever published.

Introduction: Aims

In this study the extractable lipids of different types of residues are quantitatively analyzed using corrected flame ionization detector (FID) response factors for each compound. Comparisons are made to increase our knowledge of the differences in lipid chemistry between charred and non-charred surface residues; between surface residues and the lipids absorbed in the underlying ceramic material and between charred surface residues from the Roman Iron Age and the Neolithic. In order to facilitate the comparison of the lipid profiles, three operational parameters (the saturation index, the hydrolysis index and the odd carbon number fatty acid index) are defined. The main purpose of this chapter is to address the potential variation in lipid preservation in different sample materials and to discuss the possible biomolecular origin of the extracted lipids.

Experimental: Sample Material and Treatment

Organic residues from five different prehistoric contexts in the Netherlands were studied (Table 1). The main focus of this study was a ceramic assemblage recovered from an indigenous settlement at Uitgeest-Groot Dorregeest dating back to the Roman Iron Age (Abbink 1985; 1999). Both charred and non-charred residues were chosen for analysis. Non-charred surface residues from this settlement can appear as cream-colored crusts adhering to the interior vessel wall, or as red-brown films or dripping patterns on the interior or exterior vessel wall (Table 1). Surface residues were sampled as well as the ceramic fabric of the vessel directly underneath the surface residue. In one case (sample 34-0-12 from Uitgeest-Groot Dorregeest) three

longitudinal sections of the vessel wall were sampled and lipids from the interior (S3), middle (S2) and exterior (S1) section of the vessel wall were extracted separately.

Charred surface residues of different age were collected to study the effect of burial time on the preservation of lipids. Residues from the Roman Iron Age settlements Schagen-Muggenburg (Abbink 1999; Therkorn 2004), Uitgeest-Groot Dorregeest and Uitgeesterbroekpolder 54 (Reyers 1985; Therkorn 2004) and from the Neolithic sites NO-Polder 14 (ten Anscher 2000/2001) and Hazendonk (Louwe Kooijmans 1974; 1976) were collected. All ceramic assemblages had roughly comparable burial conditions in peaty soil interspersed with sand and clay layers.

Most ceramics were washed in tap water, dried and stored in plastic bags for different lengths of time (up to 20 years). Ceramics from NO-polder 14 were treated specifically for organic residue sampling: directly after recovery from the field, pottery was wrapped in aluminum foil and stored at -20°C. Surface residues (about 5-10 mg) were scraped from the ceramics with a solvent cleaned scalpel, after removal of the upper 0.5 mm of the residue. Ceramic samples (about 2 g) were cut out of the vessel with a solvent cleaned scalpel, after removal of any surface residue and an additional 1 mm of ceramic. Samples were crushed in an agate mortar and stored in glass vials. Samples were prepared according to Evershed et al. (1990). In short, an internal standard (IS = 20 µg n-heptadecane) was added to each weighed sample, prior to extraction by solvent washing (10 ml chloroform/methanol, 2:1 v/v, 30 min ultrasonication). After centrifuging, the supernatant was dried in a round-bottomed flask by rotary evaporation at 50°C (in vacuum). A small amount (100 µl) of the solvent was added to transfer the total lipid extract (TLE) into a vial. One fifth (20 µl) of this extract was transferred into a second screw-topped vial and silylated with 25 µl N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% of trimethylchlorosilane (TMCS) and heated at 60°C for 10 min directly prior to analysis. All analytical grade solvents were distilled before use.