Chapter 1

General Introduction

This introduction defines organic residue analysis and its importance as supplier of independent information about the actual use of ceramic vessels in the context of functional ceramic studies in archaeology. The main challenges of organic residue analysis lie in the area of sample selection, analytical protocol and the archaeological interpretation of the chemical information obtained. The approach chosen in this thesis is illustrated below by a description of the rationale of the work presented here.

1. Organic residue analysis in ceramic studies

1.1. A functional perspective towards ceramics in archaeology

Pottery assemblages are frequently studied by archaeologists in search of information about a variety of different aspects of past societies, such as socio-economic developments, the organisation of production and trade, and the mechanisms of cultural interaction. Ceramic containers form an optimal source material for archaeological studies because they were used in daily activities, were commonly produced locally (reflecting local values and needs), had a relatively limited use-life, and are frequently preserved well in archaeological context.

In order to make behavioural inferences from the shattered remains of a once thriving community, a clear understanding of the function or use of the original vessel is essential (Hally 1983; Henrickson 1990). The archaeological information stored in any assemblage of artifacts can only be interpreted fully if the actual use of the objects is known. Both the kind of questions that may be addressed (Hally 1986) and the quality and specificity of the archaeological inferences (Skibo 1992, 4-5) would be improved if an accurate assessment could be made of the original vessel use.

1.2. Intended vessel function versus actual vessel use

In spite of this clear rationale, the identification of vessel usage is one of the most difficult problems for those studying archaeological ceramics. It is therefore not surprising that vessel use has received surprisingly little attention among archaeologists until the late 1980's (Van der Leeuw & Pritchard 1984; Henrickson 1990). In the last three decades the systematic investigation of the original function of vessels within assemblages has come to be recognised as an informative strategy for archaeologists interested in learning about a wide range of domestic activities within ancient settlements (Henrickson 1990).

Most archaeological methods to identify vessel function are directed at the study of "intended vessel function" – the job (or range of jobs) the potter had in mind when making the vessel. Such studies are based on the assumption that morphology as well as other physical and technological attributes of pottery can be optimised to suit a particular range of uses (Erickson & Stickel 1973, 356) or are constrained by the intended use context (Braun 1983). The research strategy is primarily aimed at uncovering specific characteristics of vessel morphology and technology that identify functional vessel categories. However, the relationships between morphology, technology and use are not uniform and specifiable but complex and variable, and their study commonly produces only very general use categories (Howard 1981, Table 1.1; Rice 1990) or local ethnographic classifications (Henrickson & McDonald 1983). Although the comparison of cross-cultural data shows that some relationships are almost universally upheld (Henrickson & McDonald 1983; Varien & Mills 1997), many of the predicted relationships between form, technology and function have been found to be somewhat equivocal (Plog 1980, 60-62). In addition, a growing number of archaeological (Woods 1986; Mills 1999; Sinopoli

1999) and ethnoarchaeological studies (Aronson *et al.* 1994; Arnold 2000) provide evidence that a variety of factors including environmental and social factors determine the processes of pottery manufacture and use. One illustrative example of the complex nature of the relationships between vessel form, technology and use, is the study of optimal characteristics for cooking pots. Cooking vessels are generally expected to make efficient use of heat for cooking. It has become generally accepted that cooking vessels have certain forms (rounded rather than angular contours) to avoid thermal damage and permit greater exposure of the vessel base; are relatively thin walled to conduct heat better and prevent thermal stress inside the vessel wall; and are course textured, porous, and tempered with materials that have low coefficients of thermal expansion (burned shell, crushed potsherd) to accommodate thermal stress (Rye 1976; Henrickson & McDonald 1983; Rice 1987, 237). Contrary to these general rules a wide range of shapes have been recorded in cooking pots in the past and present (Rice 1987, 239). The study of the archaeological material from Britain shows many flat based cooking vessels and a majority of vessels have sandy fabrics, thus contradicting the theories concerning thermal shock resistance properties of pottery (Woods 1986). A study of factors influencing Kalinga users in their choice of cooking pots, illustrates that although technical arguments (differences in strength and weight of the vessels) play a role, kinship and social affiliation of consumers strongly influence their choice of cooking vessels (Longacre & Stark 1992; Aronson *et al.* 1994).

On the other hand, studies directed at the "actual vessel use" – the way vessels were put to task by the user - avoid trying to untangle these complex relationships and can give independent information about the original utilitarian role of the vessels. The traditional archaeological approach of inferring actual vessel use through the study of recovery context, is usually limited in scope by the small quantities of vessels recovered in their original use-context (Orton *et al.* 1993, 28-30). The most direct and detailed way to identify "actual vessel use" is through the study of "use alterations" – traces of use found in and on the ceramic material. Although the importance of the study of use-wear traces in functional studies of artifacts such as stone tools (Semenov 1964, 6) and ceramics (Matson 1965, 204-208) was already formulated in the mid 1960's, the term 'use-alterations' was only introduced in ceramic studies in the 1980's (Hally 1983).

1.3. The use - alteration perspective

Following Hally (1983), Skibo (1992, 42-45) defined 'use-alterations' as any chemical or physical change that occurs to the surface or substance of ceramics as a result of use, and identified four types of alterations: i) attrition or wear of the ceramic; ii) discolouration of the clay also called fire clouding; iii) soot depositions and iv) organic residues (adhering to either exterior or interior vessel wall or absorbed into the ceramic).

Use-wear of the vessel can be the result of use (stirring or scraping of the content, salt erosion or thermal spalling). Careful study of such phenomena can give indications of the original use (Bray 1982; Hally 1983; Henrickson & McDonald 1983; Hally 1986; Skibo 1992; Beck *et al.* 2002). However, a number of non-use phenomena can also cause these attritions and confusion

must be avoided by comparison of neighbouring shards with different wear patterns and detailed study of old and fresh break surfaces.

Colour changes of the clay caused by changes in the oxidative state of iron in the clay (also called fire-clouding) and soot deposition have been used as indications of cooking over an open fire (Hally, 1983) or for the type of cooking technique employed (Hally 1983; Henrickson 1990; Skibo 1992, 42-49; Kobayashi 1994; Skibo & Blinman 1999; Arthur 2002). Skibo showed that the presence of a light coloured patch on the bottom of the vessel indicates that the vessel was placed in the fire, while vessels with an entirely black bottom were hung over a fire. The study of these discolourations can only be performed successfully on whole vessels and must be employed carefully in order to prevent confusion with accidental secondary heating of vessels after their discard.

The chemical characterisation of organic remains found in direct association with vessels, is one of the more recently developed methods in the functional study of ceramics. Although first applied in the 1920's and 30's (see Rottländer & Schlichtherle 1980 for references), organic residue analysis has only been widely used since the 1980's (and Heron & Evershed 1993 for references; see Evershed *et al.* 1999) as a result of improvements in micro-analytical instrumentation and an increasing interest in functional aspects of archaeological ceramic assemblages.

1.4. Aims

This study is aimed at the molecular characterisation of the organic residues preserved in an assemblage of ceramic vessels originating from an indigenous settlement dating from the Iron Age and Roman period at Uitgeest – Groot Dorregeest in the Netherlands in order to better infer the way the vessels were originally used (see Appendix 1 for a more complete desciptions of the ceramics and resideus studied).

Naturally, the study of small amounts of complex organic materials preserved in the ground for thousands of years creates many analytical and methodologically challenges. The main research questions concern the following topics:

- The selection of samples: What organic residue samples best represent the original vessel use? What residues have the best preservation potential?

- Analytical protocol: What combination of analytical techniques will supply the most useful information or give the most complete answers?

- The interpretation of chemical evidence in terms of archaeological context: To what extent can the original vessel contents be identified? How can the questions of original vessel usage be addressed?

2. Choice of sample material

In the study of organic residues, much research is aimed at absorbed residues – organic matter absorbed into the actual ceramic fabric of the vessel. These studies involve the identification of extractable compounds such as lipids and waxes (Heron *et al.* 1994; Evershed *et al.* 1995; Evershed *et al.* 1999); resinous materials and wood pitches (McGovern *et al.* 1996; Eerkens 2002) and proteinaceous materials (Evershed & Tuross 1996; Buckley *et al.* 1999; Craig & Collins 2000; Craig *et al.* 2000; Craig & Collins 2002; Craig *et al.* 2005). All these studies use selective techniques to extract the absorbed organics from the ceramic material of the vessel.

An alternative approach is the analysis of surface residues - solid organic matter preserved as crusts or films adhering to the interior or exterior surface of ceramic vessels. Although the chemical characterisation of these solid surface residues is analytically complicated by the complexity of the material and limited sample size, there are various methodological arguments for the study of surface residues.

Firstly, archaeologists frequently have no prior knowledge of the actual nature of the original material involved. Choosing the appropriate extraction method is complicated by this lack of knowledge and the extracted sample may not be representative for the residue under study. The overall chemical composition of organic residues needs to be investigated prior to the application of extraction techniques.

Secondly, the study of surface residues makes it possible to sample only one layer of material. Microscopic examination of cross-sections helps to prevent the incorporation of multiple use-phases in one sample. Absorbed residues are a combined deposit of multiple use-phases, possibly including primary and secondary use remnants. Mixing of different use-phases in one extraction may hinder the interpretation of chemical results. Extractions of absorbed residues may also include post-firing sealing products complicating results even more.

A final strong argument for the study of surface residues is the fact that absorbed residues have usually been exposed to a more severe thermal regime (both in time and in temperature) than residues situated on the interior surface of the vessel. Although heating plays an important role in the preservation of surface residues (through charring or condensation), thermal degradation also causes the loss of many distinct chemical characteristics of organic remains (Pastorova *et al.* 1993; Boon *et al.* 1994; Pastorova *et al.* 1994; Braadbaart 2004; Braadbaart *et al.* 2004a; Braadbaart *et al.* 2004b; Oudemans *et al.* in press-b). Extended exposure of foods to temperatures above 300 ºC makes identification of biomolecular markers of the original foodstuffs increasingly difficult (Oudemans *et al.* in press-b).

The work presented here is focussed on the study of these solid surface residues (although chapter 5 deals with extractable lipids). The ceramic assemblage from which the samples were taken is illustrated in Appendix 1.

3. A combined spectroscopic approach

The study of small amounts of complex mixtures of degraded organic materials creates many analytical challenges. Although this thesis reflects more then a decennium of developments in organic residue analysis in archaeology, the two basic analytical approaches to obtain chemical information about such materials have not changed (see also Appendix 3). Characteristics of the sample as a whole can be determined and cumulative results obtained that give information on the level of the 'total sample'. These techniques produce chemical 'fingerprints' used for classification of residues or for comparison with reference materials. Alternatively, residues can be separated into fractions each of which can be analysed separately in detail on a molecular level. However, each separation step requires additional sample.

In this study a combined spectroscopic approach is chosen. Looking at the organic residues with different analytical techniques will lead to a multi-faceted picture of a complex mixture of solid and extractable compounds and will illustrate the possibilities and limitations of organic residue analysis in the study of ceramic vessel use to its fullest potential.

3.1. Overall composition - destructive and non-destructive techniques

Elementary and isotopic characterisation of complete samples is obtained by using a destructive technique based on the gas chromatographic analysis of the combustion gas of a small amount of sample. carbon, hydrogen and nitrogen (CHN) elementary composition indicates what fraction of the sample is organic and suggests the chemical composition of the material. The C/N ratio indicates the protein fraction in the material and the C/H ratio illustrates the degree of saturation and condensation of the material. This technique was successfully applied to determine what percentage of the total organic carbon present in ground ceramic material could be released using different preparation steps (Craig *et al.* 2004).

Bulk stable isotope ratio analysis (SIA) of stable nitrogen and carbon isotopes ^{15}N/^{14}N and ^{13}C/^{12}C, gives information on what animals, fish or plants may have been used to form the residue (Morton & Schwarcz 2004). However, mixing of foodstuffs often limits the applicability of this technique in organic residue analysis, although it is a usefull tecnique in the study of human remains, bones, dental material and indentifyable plant remains. Compounds-specific isotope analysis of individual lipids or amino acids using gas chromatography – isotope ratio mass spectrometry (GC-IRMS) has resulted in very interesting identifications of the origin of particular biomarkers (see Section 3.2).

Chemical characterisation of complete samples can also be obtained through the application of non-destructive spectroscopic techniques such as Fourier transform Infrared (FTIR) spectroscopy or solid-state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy.

FTIR is based on the light absorption characteristics of various chemical compounds in a material. Each type of chemical bond or functional group absorbs light of a particular wavelength (or range of wavelengths). The presence or absence of absorption peaks typical for

particular bond types or functional groups provides information of the presence or absence of certain compound classes and the ratio of organic - inorganic material in a given residue. FTIR is a rapid analytical technique ideal for the initial classification of organic residues (Colombini *et al.* 2003; Regert *et al.* 2003). FTIR microscopy has the added advantage that solid organic residues can be analysed by pressing them between two crystals in a diamond anvil cell. General determination of the nature of the samples can be made through comparison with reference materials. FTIR can rarely be used for detailed identification of complex mixtures because increasing complexity of the analysed sample results in decreasing resolution and a loss of identification potential (Hill & Evans 1988, 1989). In addition, FTIR is insensitive to compounds present in smaller quantities (< 5%), and is limited in its capacity to distinguish between samples containing different proportions of similar compounds.

Solid-state ^{13}C NMR spectroscopy has been designed to study the carbon functional group distribution in complex solid organic materials in medicine, biochemistry and geochemistry, and has recently been applied in the field of organic residues analysis (Oudemans *et al.* 1992; Sherriff *et al.* 1995). The identification of carbon functional groups is based on the electronic environment and magnetic susceptibility of the ^{13}C atoms. Each type of carbon bond contributes to a specific chemical shift that can be measured (in ppm) relative to a standard compound. The relative amounts of saturated C-C bonds, unsaturated C=C bonds and C-H bonds provides additional information on the degree of condensation of the organic residue. Although solid-state ^{13}C NMR spectroscopy has the analytical advantage that it provides quantitative results, and is less sensitive to sample inhomogeneity then FTIR, it also requires a much larger sample (10 - 100 mg).

In this thesis CHN analysis is applied for the identification of the overall organic fraction of the material (Chapter 5 and 6), while FTIR and solid-state ^{13}C NMR spectroscopy are combined to quantify the relationship between solid and extractable compounds in the residues and to give information about the organic functional groups present in the residues (Chapter 6).

3.2. Molecular characteristics - extractable & non-extractable compounds

In order to obtain identification of individual compounds present in mixed organic materials, a separation or fragmentation step is often required. Certain compound classes, such as lipids, terpenoids, waxes, hydrocarbons and alcohols can be extracted from a complex mixture with organic solvents. These extractable compounds can be separated and identified using gas chromatography (GC) and gas chromatography mass spectrometry (GCMS) after appropriate derivatisation or preparative separation.

Compounds-specific isotope analysis of individual lipids or amino acids using gas chromatography – isotope ratio mass spectrometry (GC-IRMS) in one of the most recent instrumental innovations that has resulted in very interesting identifications of the origin of particular biomarkers (Fogel & Tuross 2003). GC-IRMS was first applied in organic residue when Evershed and co-workers showed that the δ ^{13}C values of the alkanes and ketones preserved in early medieval vessels were consistent with those of fresh wild-type Brassica vegetables as were grown in Britain in the medieval period (Evershed *et al.* 1994). It was also

shown that the δ ^{13}C values of individual fatty acids in medieval oil lamps originated from ruminant animals such as sheep and cattle, while those in 'dripping dishes' placed under roasting spits were consistent with those from monogastric animals such as pigs (Evershed *et al.* 1997b; Mottram *et al.* 1999). Further studies confirmed the use of milk in late Neolithic settlements in Switzerland (Spangenberg *et al.* 2006), the Scottish Atlantic coast in the Iron Age (Craig *et al.* 2005) and Saxon Britain (Dudd & Evershed 1998). Proof of processing of palm fruits in Egyptian Nubia in antiquity was shown by detection of palm fruit lipids in ceramic vessels from Qasr Ibrim (Copley *et al.* 2001) and cooking of maize was shown in absorbed organic residues from a variety of Mississippi Valley potsherds (Reber & Evershed 2004b, a). The application of compound specific isotope ratio analysis is definitely one of the more promising new analytical techniques within organic residue analysis and has the potential to give extended insight in the origin of many organic compounds. A recent study of a two absorbed archaeological milk residues, showed that the δ ^{13}C values of free and bound C16:0 and C18:0 fatty acids were independent of whether they were released by solvent extraction, alkaline hydrolysis or catalytic hydropyrolysis (Craig *et al.* 2004). This conclusion confirmed that the stable carbon isotope values of extractable lipids can accurately represent the values of the overall C16:0 and C18:0 fatty acid isotope ratios. The only important limitation to compound-specific isotope analysis is that it is limited to the comparison of organic compounds with significant differences in δ ^{13}C or δ ^{15}N values. In spite of its great potential, GC-IRMS falls outside of the scope of this thesis. Obtaining detailed molecular information on the chemical composition of the remaining solid, non-extractable, chemically bound or condensed macromolecular fraction of the residue is much more complicated. The remaining compounds may include (partially degraded) proteins and complex sugars, melanoidins, condensed cyclic hydrocarbons and cross-linked drying oils. This solid fraction can only be studied after a fragmentation step. The fragmentation can involve either a chemical fragmentation procedure such as acid treatment, or a controlled thermal fragmentation step such as pyrolysis.

Proteins and complex sugars (such as gums) are most easily analysed after they have converted to their individual monosaccharides or amino acids. Sugars can be derivatised and analysed using GC (Kharbade & Joshi 1995) while amino acids composition is usually determined using high-performance liquid chromatography (HPLC) (Evershed & Tuross 1996; Oudemans *et al.* 1996; Buckley *et al.* 1999). The main limitation of these techniques is the loss of identifying information during the fragmentation process. For instance, the identification of (partly degraded) proteins from their amino acid composition is difficult because many proteins have comparable amino acid compositions. Specific protein markers have recently been shown to be identifiable using immunological techniques after a mild fragmentation and extraction procedures (Craig & Collins 2000; Craig *et al.* 2000; Craig & Collins 2002; Craig *et al.* 2005).

Alternatively, condensed materials such as (partially degraded) proteins, melanoidins, caramelised sugars, cross-linked drying oils and partially carbonised materials may be fragmented using thermal fragmentation. Analytical pyrolysis techniques such as Curie-point pyrolysis mass spectrometry (CuPyMS) or Curie-point pyrolysis gas chromatography/mass spectrometry (CuPyGCMS), and Direct Temperature-resolved Mass Spectrometry (DTMS) use a form of controlled heating in an oxygen-free environment. The added thermal energy causes

the macromolecular compounds to split (along the weakest bond in the chain) into fragments specific to the original molecule.

In this study extractable lipids were analysed using GC and GCMS (Chapter 5) in order to compare the results of various kinds of absorbed residues and surface residues. Various analytical pyrolysis techniques (Chapter 2 and 3) and DTMS (Chapter 4 and Appendix 1) were used to obtain detailed molecular information about the solid organic fraction of the residues.

4. Interpretation in an archaeological context

4.1. Definition of goals

The final archaeological value of the work presented in this thesis, depends on i) the range of organic compounds that can be detected, ii) the possibility of detecting differences in chemical composition between residues and iii) the extent to which the origin of the different compounds can be traced back to prehistoric times.

4.2. Transformation processes

Although the range of organic compounds that can still be detected and the possibility t of detecting differences in chemical composition between residues are primarily a matter of analytical protocol, the ability to infer the use of particular biomaterials in prehistoric times through organic residue analysis, is to a large extent determined by a correct understanding of the transformation processes that influence the chemical composition of the remaining residues.

Transformation processes are summarised in Figure 1 and include processes in the original prehistoric context or "systemic context", the so called C_1-transforms (cultural transforms), and processes in the post-depositional context, or "archaeological context", including N-transforms (natural transforms) as well as the C_2-transforms (cultural transforms) that can take place during and after excavation (Schiffer 1972, 1983). Each of the transformation processes creates a change in the chemical composition of the original organic materials. Some of these chemical changes will complicate recognition of the original materials due to degradation of specific chemical characteristics (degradation processes), while other chemical changes will enhance the preservation of such typical chemical characteristics of the original materials (preservation processes).

4.3. Post-firing treatment

The habit of treating ceramic containers after firing but prior to use (for the purpose of surface sealing or enhancing appearance), has frequently been described in ethnographic and ethnoarchaeological studies. Post-firing treatment with mixtures of organic components is common among traditional potters and is performed with a variety of materials including common foodstuffs such as milk and various starch-rich foods (see references in Rice 1987, 163-164), as well as less edible materials such as beeswax, bitumen, various resins and other plant materials (Arnold 1985, 139-140; Kobayashi 1994; Diallo *et al.* 1995). Most commonly the treatment involves the application of an organic liquid or paste to the pots while they are still hot from firing. Post-firing treatment can result in the formation of residues that may well be interpreted as part of a use residue, although non-edible sealing materials such as plant gums or resins are more easily distinguished from foodstuffs prepared in ceramics. Depending on the sealing material and technique, it is likely that organic components are both absorbed into the ceramic of the vessel and deposited onto the interior (or exterior) of the vessel. Although the thermal regime of cooking vessels may well result in a relatively complete thermal degradation of the original sealing material after a few hours of cooking, both residues extracted from ceramic and residues scraped from the surface of the vessel may well be contaminated with sealing materials. However, microscopic investigation of the surface residues can help prevent mixing of different layers. Extraction technique will never be able to distinguish between post-firing treatments and use residues (if similar materials are used). In short, post-firing treatments with common foodstuffs would be extremely difficult to distinguish from use residues in cooking vessels.

4.4. Food and non-food preparation

Preparation of non-food materials (e.g. glues, dyes, paints, lamp oils, medicines) as well as foodstuffs in ceramic vessels may involve two important chemical processes: mixing without heating and cooking or heating.

Mixing has both preserving and degrading effects. It obscures the original biomolecular characteristics of an organic material making it harder to identify its origin, but it also creates possibilities for the formation of new resistant compounds (for instance melanoidins are formed when proteins and sugars are heated together).

Cooking and heating result in an even more extreme combination of chemical effects. Heating of organic liquids in a ceramic vessel will certainly lead to preservation processes such as impregnation of organics into the ceramic material of the vessel and the formation of chars on the surface of the vessel. On the other hand, possible loss of water-soluble compounds and the thermal degradation that may take place also result in the loss of specific biomolecular characteristics. Charring is one of the most important formation processes that results in preservation of solid organic residues on ceramic vessels. However, the chemical changes that take place during charring are complex and can obscure a lot of the original markers. In order to understand the chemical changes during char formation, heating experiments were

performed with modern foodstuffs. In Chapters 3, 4 and 6 such experimental chars were studied alongside the archaeological residues.
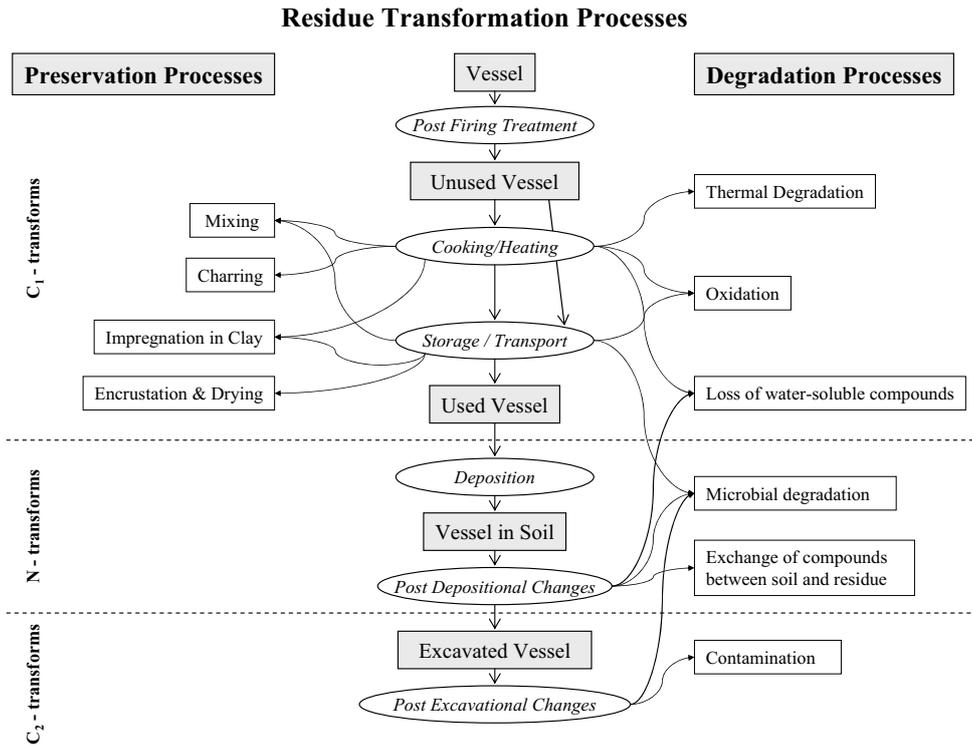
Residue Transformation Processes

Preservation Processes	Vessel	Degradation Processes

Post Firing Treatment

Unused Vessel

C₁ - transforms

Mixing

Charring

Impregnation in Clay

Encrustation & Drying

Cooking/Heating

Storage / Transport

Used Vessel

Thermal Degradation

Oxidation

Loss of water-soluble compounds

N - transforms

Deposition

Vessel in Soil

Post Depositional Changes

Microbial degradation

Exchange of compounds between soil and residue

C₂ - transforms

Excavated Vessel

Post Excavational Changes

Contamination

Figure 1: Residue Transformation Processes.
Transformation processes include processes in the original prehistoric context or systemic context C_1-tranforms (cultural transforms), and processes in the post-depositional context or archaeological context including N-transforms (natural transforms) as well as C_2-transforms (cultural transforms) that can take place during and after excavation. Each of the transformation processes creates changes in the chemical composition of the original organic materials in the vessels. Some of these changes cause the degradation of specific chemical characteristics (degradation processes), while other chemical changes will enhance their preservation (preservation processes).

4.5. Storage and transport

Using ceramic vessels for serving, storage or transport of organic materials (whether it is foods or non-foods) may leave residues behind. Liquids especially may be absorbed into the ceramic of the vessels, although sealing materials may have been used to prevent this effect in long-term storage or transport vessels. Examples of recognisable archaeological residues of such liquids are plentiful and include mostly residues of wines or other fermented beverages (Gerhardt *et al.*

1990; McGovern *et al.* 1996; McGovern *et al.* 2004), oils (Condamin *et al.* 1979; Shedrinski *et al.* 1991) and medicines (Gibson & Evans 1985). Storage or transport of solid materials is much less likely to leave residues behind, and may only be indicated by the presence of encrustations or absorbed residues that show no chemical signs of thermal degradation, but show signs of severe oxidation due to long-term exposure to oxygen.

4.6. Post – depositional changes

After a ceramic vessel has been discarded, a number of degradation processes are expected to influence the chemical composition of the organic residues: loss of water-soluble compounds, microbial degradation and the exchange of organic compounds between the residue and soil that surrounds it.

Deposition in (or on) the soil may cause further loss of water-soluble compounds due to the presence of rain or ground water.

Microbial degradation is an important degradation process to take into account. Many studies have already been directed at the microbial degradation of lipid characteristics in buried fats and bog bodies (Den Dooren de Jong 1961; Morgan *et al.* 1973; Morgan *et al.* 1984; Morgan & Titus 1985; Evershed 1991, 1992), and some experimental studies have assessed the microbial lipid contribution to degraded fats and oils in absorbed residues (Dudd *et al.* 1998). Charred residues are obviously less susceptible to microbial degradation due to the partial denaturation of the organic materials during charring (Chapter 5).

Exchange of compounds between residue and soil is a clear possibility that has been questioned by others before. Remarkably, no evidence of significant impregnation of soil compounds into the residues has been found as of today (Heron *et al.* 1991; Evershed & Tuross 1996; Oudemans & Boon 1991, 1996). However, it has always remained unclear what was lost during deposition - no evidence can be found for what is no longer present. Careful consideration must be given at all times to compounds that could originate from soils. Comparison with experimentally prepared residues must be made in order to consider missing compounds, that might have been lost during burial. Only further further experimentation may help solve this issue in the future. In this thesis soil samples were analysed alongside the archaeological residues in Chapter 2 and 3, in order to make sure analytical pyrolysis could distinguish between soil samples and residues.

4.7. Post – excavational changes

Post-excavational contamination occurs regularly in archaeological samples. Especially significant are contaminations with human skin fats from the hands of archaeologists and the compounds originating from packaging and cleaning agents. Additional microbial degradation or fungal growth may well take place after excavation. In this study growth of microorganisms and fungi was prevented by dry or cold storage and microscopic inspection of residues prior to sampling.

4.8. Final Composition

How and to what extent transformations take place is partially determined by cultural phenomena specific to the given culture, and partially the result of chemical processes. Optimally, this thesis will lead to a better understanding of the chemical processes that play a role in the preservation and degradation of biomolecular characteristics. The remaining variation in chemical characteristics can then be understood and interpreted as resulting from variation in prehistoric behaviour (for instance in the use of ceramic vessels or the choice of foodstuffs cooked in the vessels). Which chemical processes may turn out to play the most significant role in the preservation or degradation of solid organic residues will be described throughout this thesis.

5. Rationale of the Thesis

A wide range of different complementary analytical techniques was used to explore the molecular characteristics of the solid organic residues that have survived the test of time and to identify the processes that may have played a role in their preservation and degradation. Each Chapter of this thesis discusses the application of one or more of these techniques and addresses one or more of the research questions described in section 1.4.

Chapter 2 explores the analytical possibilities of Curie-point pyrolysis mass spectrometry (CuPyMS) as a tool to distinguish between solid organic residues and their surrounding soil. Subsequently, the question is addressed whether the chemical evidence is sufficient to distinguish between different residues, and whether these chemical differences are correlated to the type of vessel in which they were preserved. Multivariate analytical techniques are used for the comparison of chemical CuPyMS 'fingerprints'.

Chapter 3 focuses on the more detailed identification of compounds preserved in solid surface residues. Curie-point pyrolysis gas chromatography/mass spectrometry (CuPyGCMS) is used for its capacity to non-selectively identify a wide range of compounds. Soil samples and experimentally charred modern foodstuffs were analysed alongside the ancient residues for comparison on a molecular level.

In Chapter 4 direct temperature-resolved mass spectrometry (DTMS) is combined with multivariate techniques to group the residues. Their characteristics are subsequently compared to the chemical properties of experimentally charred modern foodstuffs in order to facilitate the determination of the biomolecular origin of the various kinds of residues.

In order to explore all possibilities, extractable lipids from both the surface residues and the directly adjacent ceramic vessel wall are analysed quantitatively in Chapter 5. The methodological argument to study surface residues rather then lipids extracted from the ceramic

fabric of the vessel is tested by comparing lipids from different types of residues and from residues from different periods.

The great challenge in the studies of solid organic residues remains the ability to gain a detailed understanding of the nature of the solid condensed phase and the mechanisms of its formation. In Chapter 6 solid-state ^{13}C magnetic resonance spectroscopy and Fourier transform infrared spectroscopy using a diamond anvil cell, are applied to quantify the relationship between solid and extractable compounds in the residues, to give information about the organic functional groups present, and to give an insight into the degree of condensation of the chars. In addition, the application of these solid-state techniques is used to verify earlier results obtained in analytical pyrolysis studies and to clarify the relationship between the (already thermally degraded) charred residues and the controlled heating fragmentation taking place during analytical pyrolysis and direct temperature-resolved mass spectrometry.

Chapter 7 summrises and reviews the results presented in earlier chapters and discusses some areas for further study.

6. Publication list

This thesis is based on papers published between 1991 and 2006. Although a part of this work is based on data published prior to 2001 (Chapter 2 and 3), this thesis not only contains additional recent publications (Chapters 4, 5, 6, and Appendix 1), but also presents an overall synthesis of the results of the combined spectroscopic study of solid organic residues found in association with ceramic vessels from prehistory and the Roman period (Chapter 1 and 7). The thesis is based on the following publications:

Chapter 1

Section 1, 2 and 4: T.F.M. Oudemans, J.J. Boon & R.E. Botto in press-a, 'FTIR and solid-state ^{13}C CP/MAS NMR spectroscopy of charred and non-charred solid organic residues preserved in Roman Iron Age vessels from the Netherlands', *Archaeometry*.
Section 3: T.F.M. Oudemans & D. Erhardt 1996, 'Organic residue analysis in ceramic studies: implications for conservation treatment and collections management', *Archaeological conservation and its consequences*, A. Roy & P. Smith (eds.), The International Institute for Conservation of Historic and Artistic Works, London, Copenhagen, 137-142.

Chapter 2

T.F.M. Oudemans & J.J. Boon 1996, 'Traces of ancient vessel use: investigating prehistoric usage of four pot types by organic residue analysis using pyrolysis mass spectrometry', *Analecta Praehistorica Leidensia*, vol. 26, 221-234.

Chapter 3

T.F.M. Oudemans & J.J. Boon 1991, 'Molecular archaeology: analysis of charred (food) remains from prehistoric pottery by pyrolysis-gas chromatography/mass spectrometry', *Journal of Analytical and Applied Pyrolysis*, vol. 20, 197-227.

Chapter 4

T.F.M. Oudemans, G.B. Eijkel & J.J. Boon in press-b, 'Identifying biomolecular origins of solid organic residues preserved on Iron Age Pottery using DTMS and MVA', *Journal of Archaeological Science*.

Chapter 5

T.F.M. Oudemans & J.J. Boon in press, 'A comparative study of extractable lipids in the shards and surface residual crusts of ceramic vessels from Neolithic and Roman Iron Age settlements in the Netherlands', in H. Barnard & J. Eerkens (eds.), *Theory and Practice of Archaeological Residue Analysis*, British Archaeological Reports International Series, Archaeopress, Oxford.

Chapter 6

T.F.M. Oudemans, J.J. Boon, & R.E. Botto in press-a, 'FTIR and solid-state ^{13}C CP/MAS NMR spectroscopy of charred and non-charred solid organic residues preserved in Roman Iron Age vessels from the Netherlands', *Archaeometry*.

Appendix 1

T.F.M. Oudemans, unpublished results

Appendix 2

T.F.M. Oudemans, G.B. Eijkel & J.J. Boon 2005, 'DTMS and DTMS/MS study of solid organic residues preserved on ancient vessels', *Proceedings of the 33rd International Symposium on Archaeometry, 22-26 April 2002, Amsterdam*, H. Kars & E. Burke (eds.), Vrije Universiteit, Amsterdam, 501-505.

Appendix 3

T.F.M. Oudemans & D. Erhardt 1996, 'Organic residue analysis in ceramic studies: implications for conservation treatment and collections management', *Archaeological conservation and its consequences*, A. Roy & P. Smith (eds.), The International Institute for Conservation of Historic and Artistic Works, London, Copenhagen, 137-142.