Molecular studies of organic residues preserved in ancient vessels

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Chapter 3

Molecular Characterisation of Solid Organic Residues by Curie-Point Pyrolysis Gas Chromatography/Mass Spectrometry

In this Chapter analytical pyrolysis techniques are shown to be suitable for molecular characterisation of solid organic residues because of their capacity to non-selectively identify a wide range of compounds. No sample preparation other then grinding was needed and the analysis was performed on very small samples (20-30 μg). Curie-point pyrolysis mass spectrometry was used to rapidly characterise residues and chemical characteristics of the residues were compared using multivariate techniques. Curie-point pyrolysis gas chromatography/mass spectrometry study of four representative residues resulted in detailed identification of preserved compounds. Many bioorganic moieties including fatty acids and characteristic markers for proteins and polysaccharides were detected in residues situated on the inside of vessels. Since no indications could be found for severe post-depositional changes in chemical composition, it is concluded that the composition of the residues is a reflection of the original vessel contents. The refractory nature of the chars is proposed to be the primary cause for the high degree of preservation. Other classes of compounds like polynuclear aromatic hydrocarbons were detected in residues preserved on the exterior of the vessels, and were interpreted as originating from smoke condensates from open cooking fires. A regular alkane/alkene pattern found in many residues and in the ceramic material of the vessel itself, is interpreted as the pyrolysis product of an aliphatic network that was formed from foods under high temperature conditions during cooking. Soil samples and experimentally charred modern foodstuffs were analysed alongside the residues for comparison on a molecular level.

Modified after:
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*, 20, 197-227.

1. Introduction

Amorphous organic (food) remains on pottery from archaeological sites have been noted and studied chemically by archaeologists since the end of the last century (see for references Rottländer & Schlichtherle 1980). These early studies remained incidental and limited to special cases such as wine and beer residues, charred bread and ointments. No systematic approach was ever undertaken tunill the early seventies when more detailed archaeological questions could be addressed due to improvements in analytical instrumentation. The application of analytical chemistry to the study of organic residues on pottery has, since then, expanded and is concentrated mainly on fatty substances soluble in organic solvents (Morgan *et al.* 1973; Condamin *et al.* 1979; Rottländer & Schlichtherle 1979; Rottländer & Blume 1980; Rottländer & Schlichtherle 1983; Morgan *et al.* 1984; Patrick *et al.* 1985; Hill & Evans 1988, 1989). The samples are prepared by selective chemical methods that focus on the analysis of only a specific part of the original material. An additional challenge is the limited sample size of most archaeological residues. The use of Curie-point pyrolysis in combination with gas chromatographic and/or mass spectrometric techniques helps to overcome these problems because a very small sample (20-30 μg) can be analysed directly in its solid state without any preparation apart from grinding. An advantage of these techniques is their capacity to analyse a complex mixture of compounds almost without discriminating effects (although the conversion of the sample into analysable volatiles is not quantitative). Although the complications concerning archaeological interpretation are not resolved directly by using CuPyMS and CuPyGC/MS, the comparison of very different samples with one another on a molecular level is facilitated. Organic residues, pottery fragments and soil samples can all be analysed and compared to get more detailed information about the presence of different compounds.

The archaeological importance of chemical studies of amorphous residues on pottery lies in the discovery of information on the natural resources used by people in prehistoric times and on the techniques applied to prepare food, dyes, oils and paints. Such studies may also reveal information about the actual use of pottery and as such become an important factor in the determination of the relationship between form, function (actual use) and the production technology of pottery.

Chapter 1 summarises many of the changes archaeological materials may have undergone. The residues can be seen as the remainder of a series of formation processes such as: processes in prehistoric times (including heating, cooking, charring, storing or transportation); processes after use (post-depositional processes including microbial degradation, contamination with soil or leaching of original compounds into the surrounding soil); and finally post-excavational changes and handling by archaeologists (including washing, scrubbing, and contamination with greasy fingers, ink, glue or dust).

The main purpose of the work presented in this chapter is to find out whether CuPyMS and CuPyGC/MS can be applied successfully to study organic compounds hidden in, or grafted on, solid amorphous residues preserved on pottery from archaeological contexts. The success of these studies for archaeological purposes depends on the range of organic compounds that can still be detected, the possibilities to detect differences in chemical composition between the

samples, and the extent to which the origin of the different compounds can be traced back to prehistoric times.

2. Experimental

2.1. Samples and sample treatment

The material studied was found in a settlement from the Late Iron Age and Roman period. The indigenous settlement was situated on the edge of a sandy creek deposit bordered by a peat swamp at Uitgeest-Groot Dorregeest (Woltering 1982, 1983). The shards were found in three different sediments: peat, a sandy creek deposit and in organic rich clay fillings (e.g. filled up water wells from the Roman period or filled up natural creek).
The organic residues, situated on different pots, were of different colour and appearance (Table 1). The residues were mostly charred, dark brown or black crusts (on the inside of pots), but some were white or cream coloured and of flaky substance (on the inside) or red brown and deposited in streaks (on the inside or outside) or pitch black and smooth (on the outside). Samples were taken from morphologically different types of pottery (see also Chapter 2, Fig. 2). These 'types' are based on morphological variables (like diameter and height) as measured and registered by Abbink (1999) and summarised in Appendix 1. All the shards had been washed with tap water and dried prior to sampling. Microscopic examination of the residues with a scanning electron microscope (Oudemans unpublished results) up to a magnification of 500 times, showed a broad variation in visual structure between the samples. Cross sections of each residue were studied to determine the homogeneity of the residues and to make sure only one

Table 1: Experimental and archaeological samples for GC/MS analysis

Nr [a]	Sample [a]	Description [a]	Sediment [b]	Vessel [a] type	Location on Vessel [a]
-	Experiment 1	Flour, protein and fat heated for 5 min at 100 °C	-	-	-
-	Experiment 2	Flour, protein and fat heated for 125 min at 250 °C	-	-	-
26	34-0-30	Brown, 0.2 cm	Humic Clay	IIb	Interior
31	35-7-28	Cream coloured, <0.1 cm	Sand	Shard	Interior
8	14-6-4.4	Brown/black, 0.2 cm	Sand	Shard	Interior
11	18-3-2.b	Black, 0.2 cm	Humic Clay	Ib	Exterior
-	Ceramic from 14-6-4.4	Grey ceramic material	Sand	Shard	-

[a] For find number residue appearance, vessel type and residue position see Appendix 1.
[b] Sediment: the soil type in which the vessel was found.

layer was sampled (see also Appendix 1). The residues presented here show no visible division in layers so it is assumed that they represent one of the last uses of the vessel. The samples were scraped from the pottery with a solvent cleaned scalpel.
To prevent contamination with organic soil material, the top layer (0.5 mm) of the residue was first removed before the actual sample was taken. Thirty-three samples were analysed by pyrolysis mass spectrometry and twenty-eight by pyrolysis gas chromatography. Four archaeological residue-samples were selected for further pyrolysis gas chromatography/mass spectrometry analysis (Table 1, Figure 1).
The ceramic material (from shard 14-6-4.4) was also sampled and analysed. The sample was taken after removal of the residue and 1 mm of the pottery wall (to prevent mixing with the residue). Soil samples were analysed for comparison. These samples were kept in a dry state for about a year previous to analysis.
Controlled cooking experiments were performed to get information about the chemical composition of different charred materials. Samples were taken from mixtures of fresh foodstuffs (e.g. flour, bovine serum albumin, and plant margarine) that had been heated for 5 min at 100 °C and 125 min at 250 °C respectively in a glass vial on an electric burner.
Sample preparation for all samples was limited to grinding about 100 μg of each sample in a small glass mortar and pestle and subsequently making a suspension of the ground sample in about 50 μl ultra pure water (Millipore Q® grade).

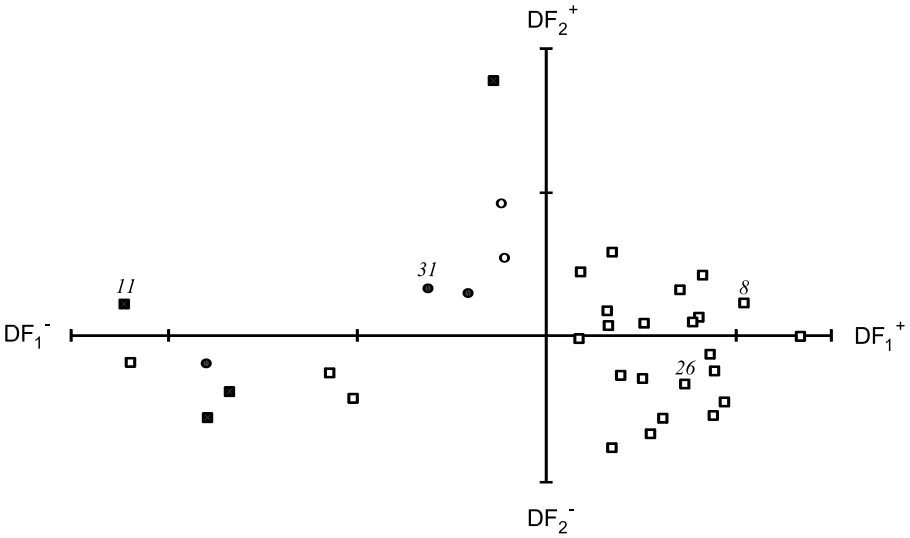


Figure 1: Comparison of chemical composition of 33 archaeological residues after CuPyMS.
Discriminant map of DF_1 versus DF_2 of residue samples (33) from interior and exterior of vessels with four sample selected for further analysis by CuPyGC/MS indicated with numbers (see also Table 1). The Euclidian distance between two sample-points represents the relative difference in chemical composition (e.g. a small Euclidian distance expresses relative similarity between two samples where as a bigger distance indicates a larger difference in chemical composition). Chars on vessel interior (□); black residues on vessel exterior (■); red-brown residues (○); and cream-coloured residues (●).

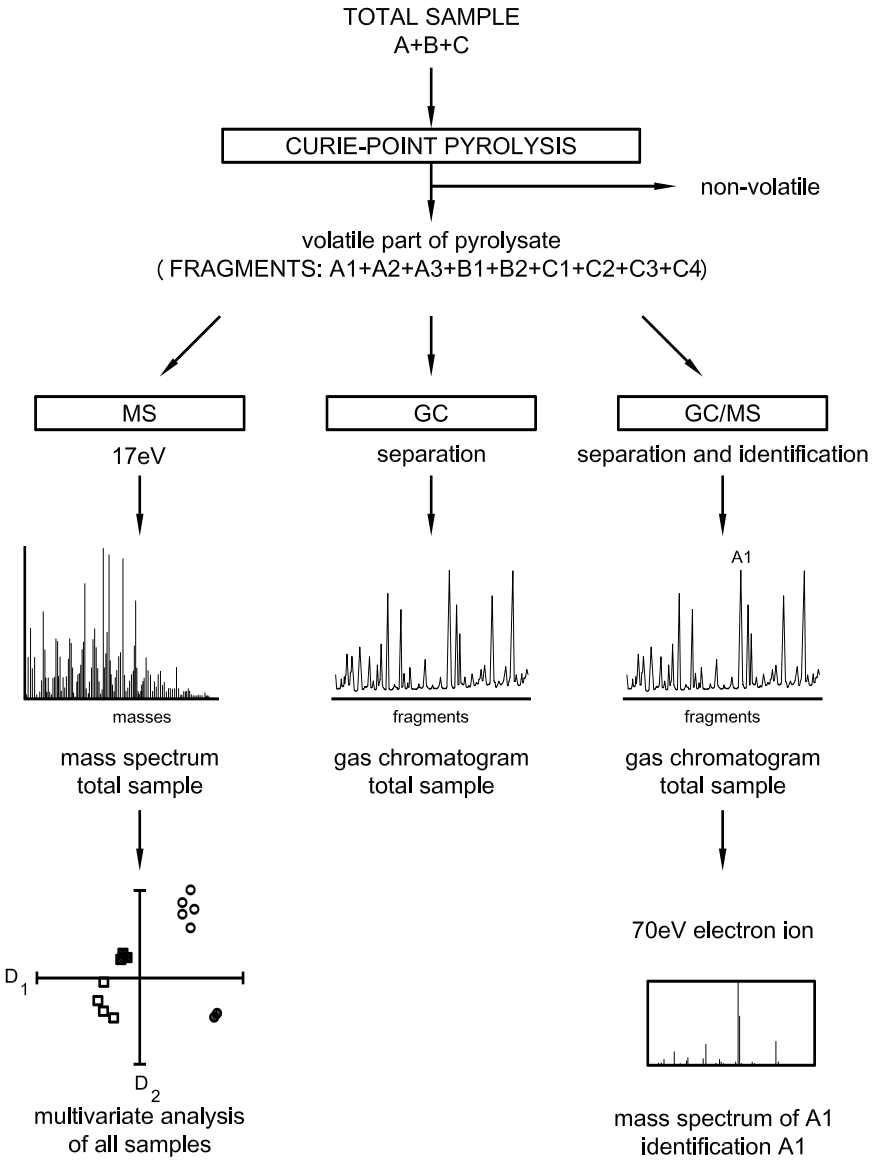


Figure 2: Analytical techniques
Different analytical techniques applied in this study for the characterisation of organic residues. The total sample is fragmented (into A1, A2, B1, B2 etc) using Curie-point pyrolysis after which analysis can be done 1) using MS giving average spectra used for for multivariate analysis, 2) using GC to separate compounds or 3) using GC/MS to separate all compounds and identify each individual compound by its individual spectrum (for instance the mass spectrum of A1)

2.2. Analytical methods and instrumentation

Figure 2 shows an overview of the analytical methods - Curie-point pyrolysis mass spectrometry (CuPyMS), Curie-point gas chromatography (CuPyGC) and Curie-point gas chromatography/mass spectrometry (CuPyGC/MS) - used in this study. Pyrolysis was used in this approach to volatilise absorbed compounds by evaporation and to pyrolyse the organic macromolecular matrix (char) into more volatile fractions, which could then be analysed by MS, GC and GC/MS.

The Curie-point Pyrolysis was carried out in the (FOM 3-LX) pyrolysis unit, designed and produced by the FOM in Amsterdam for the analysis of complex organic materials and most recently described by Boon (1987). About 10 µl of the sample suspension is applied onto a ferromagnetic wire, the sample is dried in vacuo and the analytical probe is placed in a glass liner. This glass lined analytical probe is placed in a heated pyrolysis chamber (180 °C) equipped with a high frequency coil. In CuPyGC analyses this chamber is flushed with helium while CuPyMS takes place in vacuo. The ferromagnetic wire is inductively heated within 0.1 s to its Curie-point in vacuo (PyMS) and up to 2 s in a helium atmosphere (PyGC). The thermal energy is transferred from the wire to the sample that evaporates and pyrolyses. The volatile products are either swept to the beginning of the capillary column by a carrier gas (in CuPyGC and CuPyGC/MS) or expand into an expansion chamber (in CuPyMS) for further analysis.

Pyrolysis mass spectrometry is used for rapid characterisation of complete samples. CuPyMS was carried out on the FOMautoPyMS (Boon *et al.* 1994) which has the capacity to rapidly analyse large numbers of samples and blanks. The pyrolysis chamber and the expansion chamber were heated to 160 °C and 200 °C respectively. The pyrolysis temperature was 610 °C and the total pyrolysis time 1.0 s. To minimise the fragmentation of the pyrolysis products low voltage electron impact ionisation (EI) of 17 eV was used. The mass range used was mass number m/z 23 - 240 and the scan speed was 10 scans/s with a 20 s total data acquisition time. All samples were analysed in triplicate and the CuPyMS spectra shown (Fig. 3) are averaged spectra over the total pyrolysis period. This kind of 'fingerprinting' analysis is very suitable for comparative studies of samples using multivariate analysis, but does not give much information about the nature of the individual components in the spectra because the spectra are cumulative. Multivariate analysis was performed using the FOMpyroMAP package for CuPyMS data (Windig *et al.* 1982; Hoogerbrugge *et al.* 1983; Boon 1992). Pyrolysis gas chromatography and pyrolysis gas chromatography/mass spectrometry are used to further identify the mixture of the pyrolysate by separation and identification of the different compounds involved.

The Curie-point pyrolysis gas chromatography was performed with a Carlo Erba 4200 gas chromatograph equipped with a Flame Ionisation Detector (FID). The column used was a 50 m CP Sil 5 CB fused silica capillary column (ID 0.32 mm, film thickness 1.2 µm). Both injector and detector were kept at 280 °C. The GC oven was kept at 30 °C during pyrolysis and was subsequently programmed to 300 °C at 6 °C/min. The data were recorded with a Nelson 760 interface and an Olivetti M28 PC loaded with Model 2600 Chromatography Software from Nelson Analytical.

Curie-point pyrolysis gas chromatography/mass spectrometry was done on a Packard 438-S gas chromatograph and a JEOL DX-303 double focussing mass spectrometer equipped with the

JEOL data system DA-5000. CuPyGC/MS was done under the same chromatographic conditions and on the same column as the PyGC work. The GC-column ended directly into the ion source of the mass spectrometer. Compounds were ionised at 70 eV electron impact voltage, and the acceleration voltage was 3 kV. Scan speed of the MS was 1 scan/sec over a mass range of m/z 20-1000. Mass calibration was carried out using PFK. In both CuPyGC and CuPyGC/MS helium was used as the carrier gas.

3. Results and Discussion

3.1. Survey with CuPyMS and CuPyGC/MS

The results of the CuPyMS analyses of the total set of 33 residue samples (see also Fig. 3) show clear qualitative differences in the chemical composition of residues. With the use of discriminant analysis, it was possible to quantify these relative differences. Figure 1 shows the total data set in a discriminant map (DF_1 versus DF_2). The distance between two samples represents the relative difference in chemical composition between the samples. The samples on the right side (mainly determined by the DF_1^+) show protein characteristics and free fatty acid, while samples on the far left side of the map (mainly determined by the DF_1^-) show many markers for polynuclear aromatic hydrocarbons (PAHs), alkanes and alkenes. A less clearly defined group of samples is present in the centre. The DF_2^+ axis expresses mainly markers for sulphur-containing compounds. The results of a CuPyGC survey of 28 of these samples confirm this classification. Four samples were selected for more detailed analysis of individual compounds with CuPyGC/MS (Table 1).

3.2. Identification of individual compounds with CuPyGC/MS

The CuPyGC/MS data of four organic residues from the inside and outside of different pots are shown in Figure 4. Many of the peaks in the CuPyGC data could be identified from their mass spectra (Table 2, see end of this Chapter) and many of these compounds could be assigned to bioorganic origins. However, a number of peaks have remained unidentified as can been seen in Table 2 where they are listed together with their characteristic mass peaks. In this section the main compound classes will be discussed.

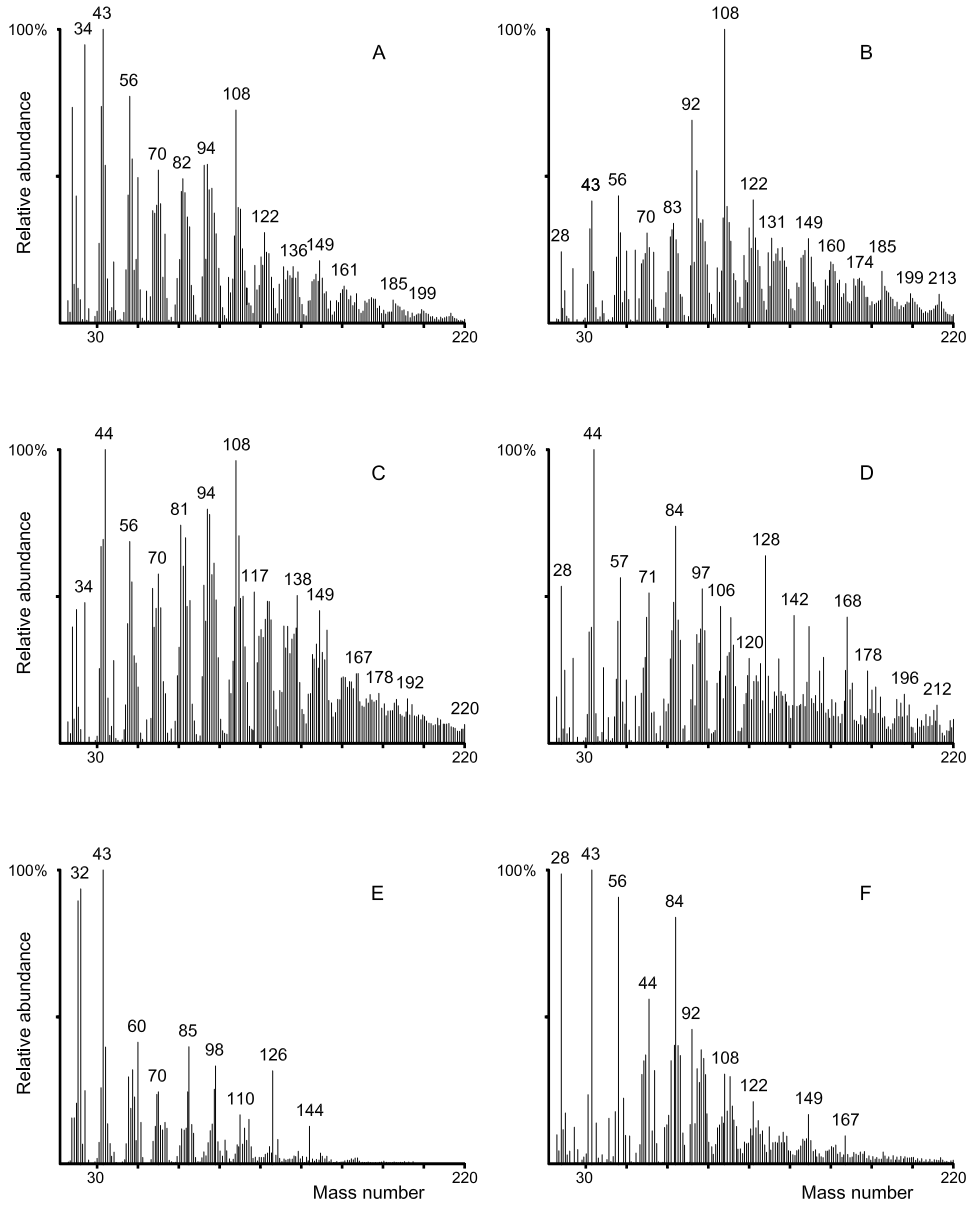


Figure 3: Mass spectra obtained with pyrolysis mass spectrometry (CuPyMS) under 17 eV (EI).
Spectra of archaeological residues and experimentally charred modern food mixtures. A = charred residue 34-0-30; B = charred residue 14-6-4.4; C = cream coloured residue 35-7-28; D = black soot residue 18-3-2.b from the exterior vessel wall; E = Experiment 1 - flour, albumin and plant margarine heated for 5 min at 100 °C; F = Experiment 2 – flour, albumin and plant margarine heated for 125 min at 250 °C.

Residues on the outside of the pottery

The CuPyGC/MS results of a black residue (sample 18-3-2.b, Fig. 4d) occurring on the outside of a small pot, show many polynuclear aromatic hydrocarbons like naphthalenes, phenanthrenes and their methylated isomers. Since these compounds were also found in the pyrolysates of low temperature pyrolysis (358 °C), they are not pyrolysis products but the result of desorption of volatile compounds from the sample. Since these PAHs are common in smoke condensates of wood fires (Medalia *et al.* 1983), these residues are probably the result of cooking on an open fire. It is notable in this context that the PAHs only occur in residues situated on the outside of the pottery. The alkane/alkene pattern detected in this sample will be explained later.

Residues on the inside of the pottery

Three residues situated on the inside of pots were sampled (samples 34-0-30, 35-7-28 and 14-6-4.4) and the CuPyGC/MS data (Fig. 4a, b, and c) show three compound classes of bioorganic significance: protein remains, remains of polysaccharides, remains of lipids (free fatty acids and fatty amides as well as an alkane/alkene pattern) which are discussed below.

Protein remains of vegetable or animal origin: The CuPyGC/MS results of samples 34-0-30, 35-7-28 and 14-6-4.4 show some specific fragments indicative of charred proteins. Pyrrole, indole, methylindole, toluene, phenol, and cresol detected with CuPyGC/MS are interpreted as 'protein' indicators because these compounds are commonly found in pyrolysates of proteins. As such they are indicative of hydroxyproline, tryptophan, phenylalanine and tyrosine (Meuzelaar *et al.* 1982, 109). Some of the pyrolysis products indicative of adjacent pairs of aliphatic amino acids in intact proteins described by Boon and De Leeuw (1987) and Smith and co-workers (1988) and of the 3,6-piperazinediones described by Munson and Fetterolf (1987) as pyrolysis products of proteins, could be detected in one of our samples. So far it can be tentatively suggested that, although the charring of the food has probably caused severe denaturation of the original peptide chain, the individual amino acid characteristics appear to be preserved in the 'char'. The details of this preservation process are not clear at this time. It is suggested here that a radical reaction (Fig. 6) causes the specific amino acid side chains to be linked chemically to (or to get 'embedded' in) the forming char. About two thousand years later, flash pyrolysis releases these characteristics again. Protein markers occur mostly in samples in combination with free fatty acids and polysaccharide markers. In samples 35-7-28 (Fig. 3c and 4c), however, they occur only in combination with inorganic compounds i.e. carbonates (evidenced by m/z 44 and 28 from CO_2 in the CuPyMS spectrum).

Remains of polysaccharides: In the past it has been stated by archaeological chemists (Rottländer & Schlichtherle 1983) that polysaccharides are unlikely to survive charring because their natural structure is destroyed at temperatures around 190 °C. However, the work of other researchers (Julien *et al.* 1991; Pastorova *et al.* 1993), has shown that low temperature chars of cellulose still retain 'sugar' characteristics. Sugar markers (i.e. methylfuran and dimethylfuran) were detected in charred samples 34-0-30 and 14-6-4.4 but are absent from non-charred sample 35-7-28. These markers are rather unspecific and cannot give any indication of the original type of polysaccharides. The possibility of an archaeological origin is shown by the fact that charring experiments with modern food also render these markers in Curie-point pyrolysates. Apparently

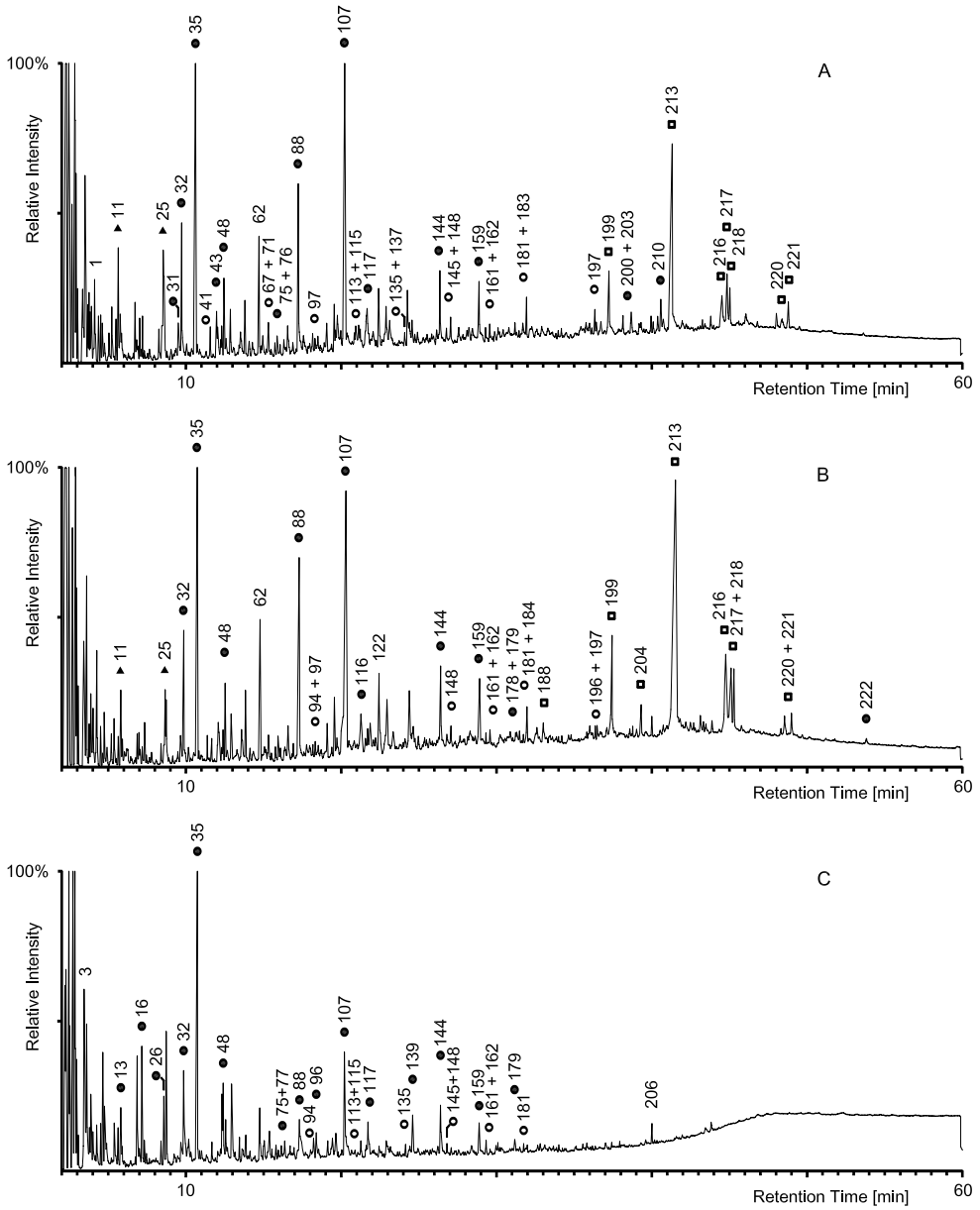
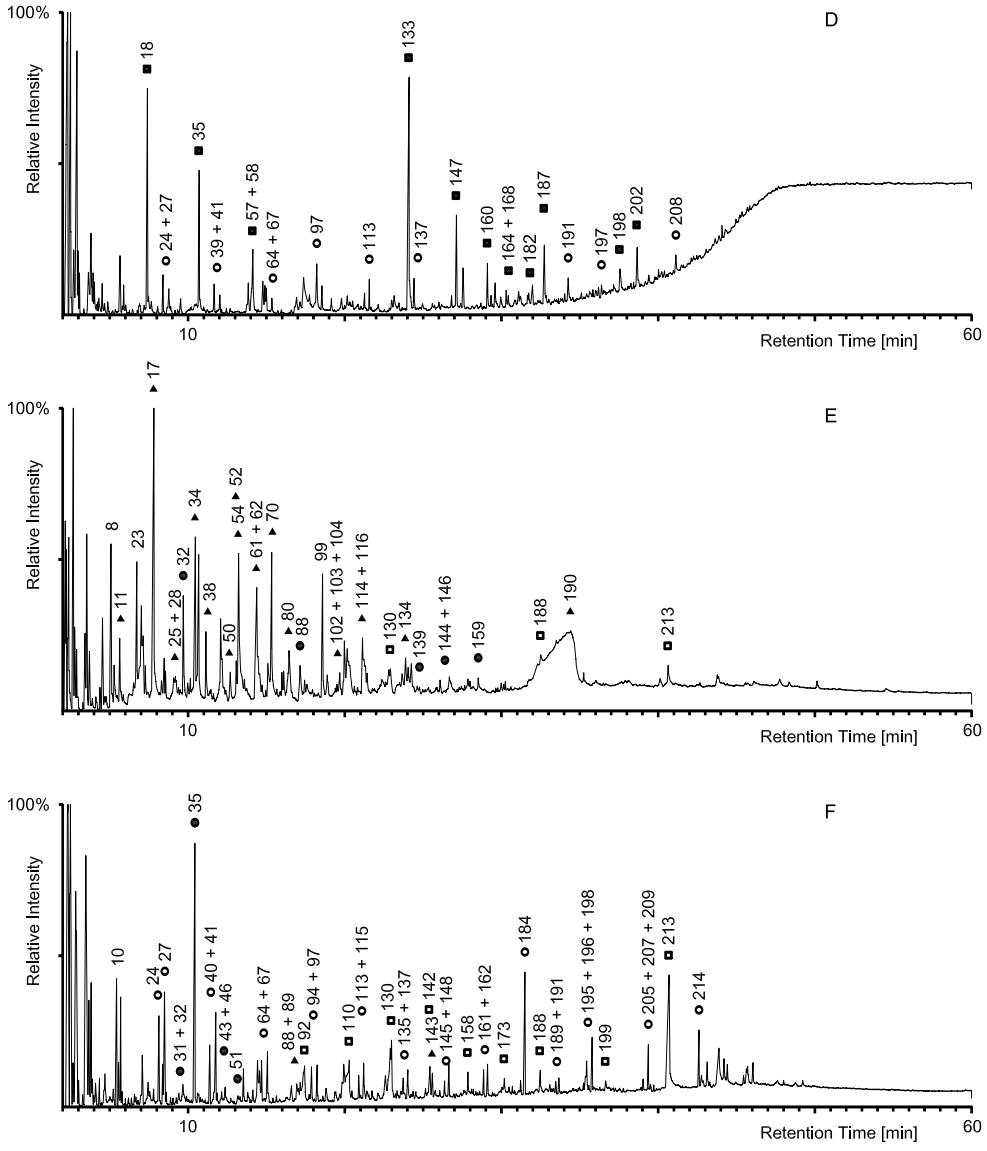


Figure 4 (see also facing page): CuPyGC/MS results of residues and experimentally heated modern foods. Identified peaks are indicated by number (Table 2). Characteristic compound classes are explained in the legend on facing page. A = Charred residue 34-0-30 contains free fatty acids and markers for proteins and polysaccharides; B = Charred residue 14-6-4.4 contains free fatty acids and markers for proteins and polysaccharides; C = Cream coloured residue 35-7-28 mainly shows protein markers; D = Black soot residue 18-3-2.b contains mainly PAHs from smoke condensates; E = Flour, albumin and plant margarine heated for 5 min at 100 °C; F: heated for 125 min at 250 °C.



Characteristic compounds

- Proteins markers
- Polysaccharide marker
- Fatty acids
- Alkanes / Alkenes
- Polynuclear Aromatic Hydrocarbons

some polysaccharide characteristics remain preserved in low temperature chars (possibly in the form of dehydrated oligosaccharides and melanoidins). Increasing the temperature during charring will reduce the recognisability of the remaining products. No simple assumptions can be made since it is not clear whether the polysaccharide markers originate from charred foods or from oligosaccharides that have impregnated the residues from the surrounding soil. Theoretically, water-soluble saccharides derived from plants or bacterial cell walls could have impregnated the archaeological residue material. Pyrolysis studies of peat samples from the Assendelver Polders (a peat comparable in age) showed a broad range of sugars from polysaccharides (Moers 1989, 89). However, the majority of the sugars in these peats are derived from the remains of vascular plants and occur in the form of water insoluble biopolymers. Such biopolymers would not have impregnated the archaeological residues. The absence of sugar markers from non-charred sample 35-7-28 and soot residue 18-3-2.b does suggest an origin in the charring of polysaccharides originating from the vessel content.

Remains of lipids - Free fatty acids and fatty amides: A number of straight chain saturated fatty acids (C11, C12, C14, C15, C16, C17 and C18:0), one mono-unsaturated fatty acid (C18:1) and three fatty amides (C16:0, C18:0 and C18:1) were detected in samples 34-0-30 and 14-6-4.4. Since free fatty acids also occur in the CuPyGC analyses of low temperature pyrolysis (358 °C), it is clear that these compounds evaporate from the sample. It should be noted that free fatty acids and fatty amides are often observed in combination with protein markers and sometimes with markers for polysaccharides (Fig. 4a and b). The presence of free fatty acids in residues on pottery and in the ceramic of the ancient pottery itself, has been proven numerous times by other researchers who isolated the fatty acids (and sometimes salts of fatty acids) using various extraction methods (see for references also Rottländer & Schlichtherle 1980; Evershed *et al.* 1992). Though the presence of free fatty acid is commonly accepted to be the result of hydrolysis of vegetable or animal fats after deposition (Den Dooren de Jong 1961), the distribution found in some of the organic residues in the pots may have been caused by additional biodegradation processes obscuring the original lipid signature. The identification of original foodstuffs based on the relative distribution of intact lipids (e.i. mono-, di- or triglycerols and sterols) in archaeological samples is a more promising process. Although neither mono, di- nor triglycerides could be detected with the pyrolysis techniques utilised in this study, their presence was confirmed through lipid extraction and presented in Chapter 5 (Oudemans & Boon in press). The fatty amides are most likely produced by heating fatty acids with amines to a temperature of 200 °C (Davídek *et al.* 1990, 183). It is not clear whether this formation happened during the preparation of food in Roman times or during the pyrolysis phase of the analysis.

Remains of lipids - Alkene/alkane pattern: In pyrolysates of many samples, a regular pattern of n-alk-1-enes and n-alkanes ranging from C6 to C18 was detected. These homologous series of alkenes and alkanes occur in residues on the interior of vessels (e.g. samples 34-0-30, 35-7-28 and 14-6-4.4), the exterior of vessels (e.g. sample 18-3-2.b), in experimental chars, and in samples of the ceramic material itself. In the residue-samples they occur in combination with other compounds like fatty acids or protein markers (Table 3). These straight chain alkane/alkene patterns have been reported before in the pyrolysates of the cuticles of modern and fossil plants (Nip *et al.* 1986), of the rootlets of Ericaceae and ericaceae peat (van Smeerdijk & Boon 1987), and in pyrolysates of coals from an early phase of coal diagenesis (Tromp *et al.*

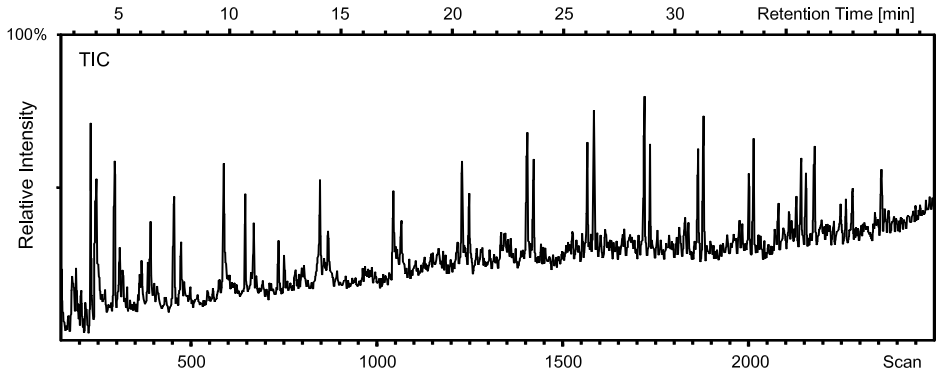


Figure 5: Alkane/Alkene pattern in CyPyGC/MS profile of a sample of archaeological ceramic material. The total ion current of the ceramic material of the archaeological shard 14-6-4.4 shows a clear pattern of alkanes and alkenes ranging from C6 to C18.

1988, 241). The pattern was interpreted as the pyrolysate of a highly aliphatic biopolymer thought to be present in the cuticles of plants and claimed to be very resistant to biodegradation. The same pattern can be found when polyethylene is pyrolysed. The most important difference with the pattern observed in our samples is the chain length distribution. The occurrence of this pattern in the pyrolysates of prehistoric (food) residues may be caused by pyrolysis of an aliphatic network created by radical polymerisation in the residues and in the wall of the pot under high temperature conditions during cooking. This aliphatic network is likely to be formed from food components. The mechanism of formation of alkene/alkane patterns during pyrolysis is not entirely clear, but Hartgers and co-workers (1995) have suggested a mechanism which explains the formation of the alkenes and alkanes as product of H-radical transfer with primary and secondary alkyl radicals that were created during pyrolysis of silicon-bound hydrocarbons. It is plausible that a similar mechanism is at work during pyrolysis of the aliphatic material described above. According to this model, pyrolysis of long chain aliphatic components that are bound to some larger structure will result in homologous series of alkenes and alkanes leading up to the C number of the longest chain minus one. Shedrinski (1991) reported on the formation of a similar alkene/alkane patterns from PyMS data of salts of fatty acids. This origin might play a role in some of the prehistoric residue samples. However, charring experiments (e.g. sample 1 and 2) show the same alkene/alkane pattern after pyrolysis (Fig. 4f), and as such support the possible origin of the aliphatic compounds. The presence of fats seems a pre-requisite since charring experiments with only water, flour and albumin do not give this alkene/alkane pattern.

Ceramic material

The ceramic from several shards was analysed by CuPyGC and the results show a pattern of straight chain n-alk-1-enes and n-alkanes ranging up to C18. In the ceramic samples these compounds form the majority of the organic fraction (Fig. 5 shows the TIC of the

CuPyGC/MS analysis of a ceramic sample from vessel 14-6-4.4). It is possible that the higher temperature reached in the wall of the pot during cooking and charring lead to the formation of aliphatic network polymers from lipids that were absorbed in the shard when the pot was in use. This seems to be the only organic material present in any significant amount.

Heating experiments

Experimental heating and charring of modern foods was performed (e.g. Experiments 1 and 2) to obtain more information about the changes in composition of different materials before and after charring (Fig. 4e and 4f). The results obtained with CuPyMS and CuPyGC/MS confirmed the fact that many characteristics of polysaccharides and proteins and fatty acids can still be found in the experimentally carbonised materials. The results from these heating experiments show many of the components that are also detected in the archaeological material.

Soil samples

Dried peat samples from the site have been analysed and show the type of pattern (polysaccharide markers, lignin markers and high molecular weight lipid markers) which are typical for peat samples in the west of the Netherlands (van Smeerdijk & Boon 1987). Though the total pyrolysis product profile from the peat samples is very different from those of the archaeological samples, it cannot be excluded that the surrounding soil matrix partly determines the remaining chemical composition of the residues. Contamination with soil particles and ground water or specific degradation processes could have an effect on the chemistry of the residues. It is therefore useful to determine the relationship between the chemical composition of the analysed residues and the type of sediment around the shards. As shown in Chapter 2, a study of this relationship by CuPyMS failed to show a direct correlation (Oudemans & Boon 1996). Also, the large difference in composition between soil, charred residue, and ceramic material suggests that exchange of soil components is very limited in the archaeological site at Uitgeest – Groot Dorregeest.

Table 3: Presence of different compound classes in reported samples.

Nr	Sample Type	Proteins	PS	FFA	FA	A/A network	PAH	Location on Vessel	Sediment
-	Experiment 1	+	+	+	-	-	-		
-	Experiment 2	+	+	+	-	+	-		
26	34-0-30	+	+	+	+	+	-	Interior	Humic Clay
31	35-7-28	+	-	-	-	+	-	Interior	Sand
8	14-6-4.4	+	+	+	+	+	-	Interior	Sand
11	18-3-2.b	-	-	-	-	+	+	Exterior	Humic Clay
-	Ceramic 14-6-4.4	-	-	-	-	+	-		Sand

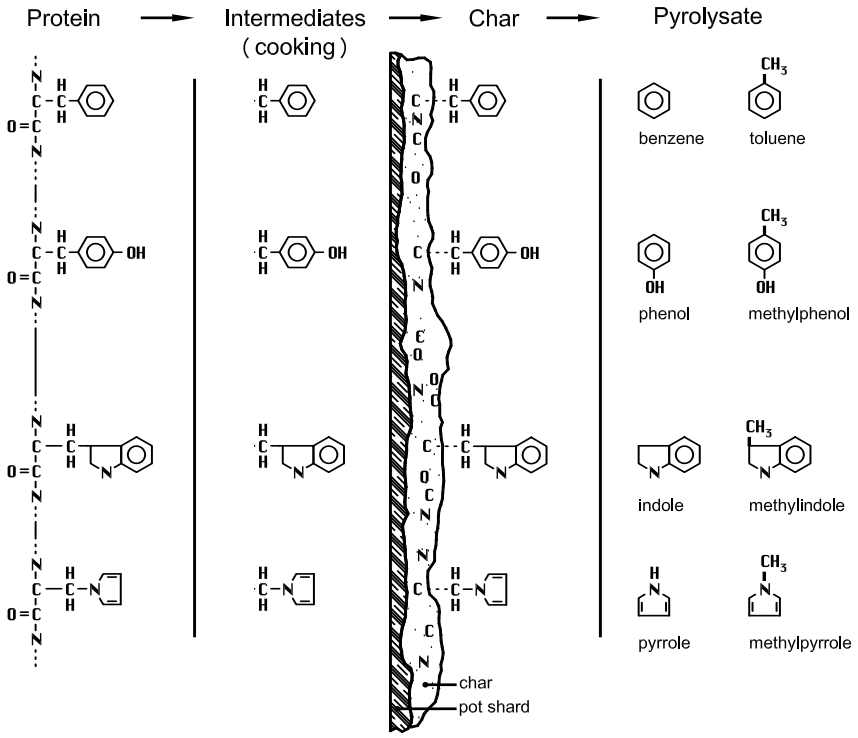


Figure 6: Suggested mechanism for the preservation of protein characteristics in charred residues.

Contaminating materials

In pyrolysates of many samples, markers for plasticisers (*m/z* 149, 167) were found (Fig. c and 3d). These markers probably originate from the plastic bags in which the pottery was kept for over a year prior to analysis.

3.3. Chemical data as evidence for vessel use in prehistoric times

The CuPyMS and CuPyGC/MS results show clear differences in the chemical composition of the residues (Table 3). The chemical composition of samples scraped from vessels cannot provide direct information about original use because the sample is the result of a series of formation processes that took place in time, such as processes in prehistory (cooking, mixing, storing, cleaning of pots), post-depositional processes (biodegradation, impregnation of soil or ground water, leaching), and post-excavational processes (excavation and handling by archaeologists and restauration people). Yet information about prehistoric use of the pottery

can be deduced from the chemical results after careful consideration is given to the influence of the formation processes on the chemical composition of the residues:

Handling by archaeologists

Excavation and handling of pottery can result in contamination of the samples, with for example plasticisers from packaging materials. It is also possible that other cases of contamination took place during washing, drying and handling (contamination with dust, paper from drying of the pottery on newspaper and fats from archaeologists' hands). When dealing with archaeological materials it is preferable to freeze (-20 °C) the samples within 24 hours after excavation to prevent any additional bacterial degradation or fungal growth. Unfortunately, the material reported here was not treated with such caution. Despite this drawback, the degree of detectable contamination is very limited. This is most likely due to the refractory nature of the charred materials and the encapsulation of indicative compounds in the macromolecular structure of the char. It is however, not unthinkable that working with washed shards means that some soft and/or soluble materials were removed during washing of the shards and therefore never studied.

Biodegradation

Biodegradation on and in the ground has a strong selective effect on preservation of different biological materials. Fresh foods especially are vulnerable to biological attack, as the digestibility of foods goes hand in hand with sensitivity to biodegradation. Only rarely will the remains of food preparation or 'home-chemistry' be preserved as a residue on broken pottery. Very specific circumstances like an anaerobic climate, aridity, extremely low temperatures, charring, carbonisation or the presence of preserving chemicals (like waxes, resins, tannins, acids, alkali's, metal oxides or salt) are needed to preserve foods in an archaeological context (Gilbert & Mielke 1985, 2). The residues that archaeologists find on pottery should therefore not be seen as representing all uses of pottery but rather as rare cases that have survived for a specific reason. The residues represented here are mostly the result of charring (with the exception of three light coloured residues such as sample 35-7-28). Charring is known to reduce the microbial degradation (and possibly also the impregnability for water) in such a way that many traces of bioorganic compounds are still present. The chemical composition of the residues therefore clearly represents processes that took place in prehistoric times.

Processes in prehistory

Many processes in prehistory will have had an obscuring effect on the evidence of the last usage. For instance the use of a vessel for different functions could complicate the interpretation of the results. Visual inspection of the chars under the scanning electron microscope showed the absence of layers in the residues (Oudemans unpublished results). For the indigenous settlement in Uitgeest-Groot Dorregeest one can thus assume that people did not cook or prepare food in 'dirty' pots. The residues are considered to represent the last use of the pot. The cooking temperature also has its effect on the chemical composition of the residue. Although the charring has a positive effect on the preservation of the residue, the denaturation

has a negative effect on the possibilities for identification of the original material. The heating temperature and heating time play a role in the chemical composition of the final residue (see also Chapter 6). Mixing of materials is something one has to take for granted in most food preparation and 'home-chemistry'. The position of the residue on the pot also determines the chemical composition of the residue that one might find. Black residues on the outside of vessels have distinctively different chemical composition from those on the inside. For the determination of the original use of a vessel, it is important to shown that differences in chemical composition are correlated to archaeological variables such as pot morphology (Oudemans & Boon 1996). More work on the identification of the bioorganic origin of the solid surface residues is presented in Chapters 4, 5 and 6.

4. Conclusions

Pyrolysis mass spectrometric techniques are useful for the chemical characterisation of organic residues on archaeological pottery. The use of CuPyMS, CuPyGC and CuPyGC/MS has resulted in the detection of many bioorganic moieties in the charred and non-charred residues including characteristic markers for proteins and polysaccharides and other compounds like fatty acids, polynuclear aromatic hydrocarbons and aliphatic polymers.
The existence of clear differences in chemical composition between the residues has been demonstrated. The chemical composition of the residues depends on whether residues are situated on the exterior or the interior vessel wall, and on whether they are charred or not.
The chemical characteristics of peat samples from the surrounding matrix are in no way similar to the results from the residues. No indications were found to assume that the chemical difference between residues is the result of post-depositional influences. It is therefore inferred that the chemical composition of these solid organic residues is a reflection of the original use in the indigenous settlement in Uitgeest-Groot Dorregeest.

Table 2 - Identified pyrolysis products in CyPyGC/MS results

Nr.	M^+	RT	Name	Samples						Origin
				Exp 1	Exp 2	26 char	31 beige	8 char	11 soot	
1	70	3'34	methyl-2-butene	-	-	x	x	-	-	
2	66	3'43	cyclopentadiene + CS2	x	x	x	x	-	x	
3	72	3'55	2-methylpropanal	x	-	-	x	-	-	Pro
4	68	3'60	cyclopentene	-	x	-	-	-	x	
5	55	4'02	cyanoethane	-	-	x	x	x	-	Pro
6	86	4'19	? *m/z* 43, 41, 71, 42, 69, 84	-	-	x	-	x	-	
7	84	4'19	2-methyl-2-pentene	-	-	x	-	x	-	
8	86	4'21	2,3-butanedione	x	-	-	-	-	-	Ps
9	72	4'40	2-butanone	x	x	x	x	x	x	
10	84	4'46	hexene	-	x	x	x	-	x	
11	82	4'53	methylfuran	x	x	x	-	x	-	Ps
12	86	4'58	hexane	-	x	x	x	-	x	
13	69	5'08	2-methylcyanopropane	-	-	-	x	-	-	Pro
15	86	5'58	3-methylbutanal	x	x	x	x	-	x	Pro
16	74	6'07	propanol	x	-	-	-	-	-	Ps
17	69	6'13	cyanobutane	-	-	-	x	-	-	Pro
		6'15	2-methylbutanal	-	x	x	x	-	x	
18	78	6'20	benzene	-	x	x	x	x	x	
19	84	6'29	2-methyl-1-buten-3-one	x	-	-	-	-	-	
20	80	6'34	cyclohexadiene	-	x	-	-	-	-	
21	82	6'57	cyclohexene	-	x	-	-	-	-	
22	100	7'00	pentane-2,3-dione	x	-	-	-	-	-	Ps
23	44	7'01	acetaldehyde	x	x	x	-	x	-	
24	98	7'23	heptene	-	x	x	x	-	x	A
25	96	7'38	2,5-dimethylfuran	x	x	x	-	x	-	Ps
26	83	7'40	2-methylcyanobutane	-	-	-	x	-	-	pro
27	100	7'43	heptane	-	x	x	-	-	x	A
28	96	7'45	? *m/z* 43, 41, 39, 27, 68	x	-	-	x	-	-	
29	80	8'14	pyrimidine or pyridazine	x	-	-	-	-	-	Pro
30		8'30	2-methylpentanal	-	-	x	-	-	x	
31	79	8'50	pyridine	-	x	x	-	-	-	Pro
32	67	9'00	(1H)-pyrrole	x	x	-	x	x	-	Pro
33	84	9'12	? *m/z* 43, 84, 55, 27, 58	x	-	-	-	-	-	
34	102	9'31	methylpyruvate	x	-	-	-	-	-	Ps
35	92	9'37	toluene	x	x	x	x	x	x	
36	84	9'54	pentenone	-	x	-	-	-	-	
37	98	9'57	methylthiophene/pentenone	-	-	-	x	-	-	
38	84	10'01	(2H)-furan-3-one	x	-	-	-	-	-	Ps
39	112	10'36	octene	-	x	x	x	-	x	A
		10'36	trialkylfuran ?	-	-	x	-	-	-	
40	110	10'37	dimethylhexadiene	-	-	x	-	-	-	A

M^+ = Molecular weight of the molecular ion. RT = Relative GC retention time. Samples as in Table 1
? *m/z* = unknown compound with characteristic main peaks (given according to relative abundance)
Origin of the compound: Ps = Polysaccharides; Pro = Proteins; FA = Fatty acids; PAH = Polynuclear Aromatic Hydrocarbons; A = Aliphatic hydrocarbons (alkanes/alkenes) and Cont = Contaminant.

Table 2 - Identified pyrolysis products in CyPyGC/MS results

Nr.	M^+	RT	Name	Samples						Origin
				Exp 1	Exp 2	26 char	31 beige	8 char	11 soot	
41	114	11'01	octane	-	x	x	x	-	x	A
42	112	11'07	? *m/z* 112, 83, 70, 55	-	x	-	-	-	-	
43	93	11'07	2-methylpyridine	-	x	x	-	-	-	Pro
44		11'15	? *m/z* 82, 39, 94, 54, 53	x	-	-	-	-	-	
45		11'20	? *m/z* 57, 41, 29, 55, 39	-	-	-	x	-	-	A
46	97	11'23	? *m/z* 112,83,70,55	-	x	-	x	-	-	
47	96	11'24	2-furaldehyde	x	-	-	-	-	-	Ps
48	81	11'37	2 of 3-methyl-(1H)pyrrole	-	-	x	x	x	-	Pro
49		11'38	benzylalcohol + ? *m/z* 110, 81, 67, 54	-	x	-	-	-	-	
50	72	11'50	methyltetrahydrofuran-3-one	x	-	-	-	-	-	Ps
51	81	12'00	2 of 3-methylpyrrole	-	x	x	x	x	-	Pro
52	116	12'14	acetyloxypropane-2-one	x	-	-	-	-	-	Ps
53		12'22	? *m/z* 43, 70, 55, 57, 56	-	-	-	x	-	-	
54	98	12'24	2-hydroxymethylfuran	x	-	-	-	-	-	Ps
55		12'36	? *m/z* 60, 98, 43, 41, 97	x	-	-	-	-	-	
56	94	12'39	? *m/z* 60, 41, 54, 43, 94	-	x	-	-	-	-	
57	106	12'47	ethyl-benzene	x	x	x	x	x	x	
58	106	12'58	dimethylbenzene (p or m-xylene)	-	-	-	-	-	x	
59	106	13'04	dimethylbenzene (p or m-xylene)	-	x	x	x	-	x	
60	114	13'27	2-heptanone	-	x	-	-	-	-	
61	95	13'32	(5H)-furan-2-one	x	-	-	-	-	-	Ps
62	104	13'43	vinylbenzene	x	x	x	x	x	x	
63	106	13'54	dimethylbenzene (o-xylene)	-	x	x	-	-	x	
64	126	13'59	1-nonene	-	x	-	x	-	x	A
65	110	14'02	2-acetylfuran	x	-	-	-	-	-	Ps
66	102	14'08	pentanoic acid C5:0	-	x	-	-	-	-	FA
67	128	14'23	nonane	-	x	x	-	-	x	A
		14'24	dimethylpyrrole	-	-	x	-	-	-	
68	98	14'25	2,5-dihydro-5-methylfuran (ß-ang. lact.)	x	-	-	-	-	-	Ps
69		14'29	? *m/z* 80, 95, 94, 53, 107	-	-	-	x	-	-	
70	98	14'32	2,3-dihydro-5-methylfuran (α-ang. lact.)	x	-	-	-	-	-	Ps
71		14'35	alkylketone + dimethylpyrrole	-	-	x	-	-	-	
72		14'38	? *m/z* 94, 95, 83, 109, 28	-	-	-	x	-	-	
73	126	14'45	? *m/z* 126, 97, 56, 55	-	x	-	-	-	-	Ps?
74	124	14'49	? *m/z* 54, 60, 41, 95, 124	-	x	-	-	-	-	
75	95	14'52	dimethylpyrrole	-	-	x	x	-	-	Pro
76	107	14'56	2,4-dimethylpyridine	-	-	x	-	-	-	Pro
77	95	15'12	1H-ethylpyrrole	-	-	-	x	-	-	Pro
78	130	15'19	4-hydroxymethyltetrahydropyran-3-one	x	-	-	-	-	-	Ps
79	130	15'24	2,3-dihydroxyhex-1-en-4-one	x	-	-	-	-	-	Ps
80	110	15'45	5-methyl-2-furaldehyde	x	-	-	-	-	-	Ps

M^+ = Molecular weight of the molecular ion. RT = Relative GC retention time. Samples as in Table 1
? *m/z* = unknown compound with characteristic main peaks (given according to relative abundance)
Origin of the compound: Ps = Polysaccharides; Pro = Proteins; FA = Fatty acids; PAH = Polynuclear Aromatic Hydrocarbons; A = Aliphatic hydrocarbons (alkanes/alkenes) and Cont = Contaminant.

Table 2 - Identified pyrolysis products in CyPyGC/MS results

Nr.	M^+	RT	Name	Samples						Origin
				Exp 1	Exp 2	26 char	31 beige	8 char	11 soot	
81	120	15'54	propylbenzene	-	x	x	-	-	x	
82		16'00	? *m/z* 82,41, 28, 55, 57, 83	-	x	-	-	-	-	
83	120	16'07	alkyl(C3)benzene	-	-	-	-	-	x	
84	103	16'21	cyanobenzene	-	x	-	x	-	-	
85	103	16'23	pyridine derivative ?	-	-	-	x	-	-	
86	113	16'27	? *m/z* 85, 57, 41, 100	-	x	-	-	-	-	
87	144	16'28	? *m/z* 111, 101, 126, 43, 43, 144	x	-	-	-	-	-	
88	94	16'38	phenol	x	x	x	x	x	-	
89		16'45	C3-benzene 4-hydro dihydropyranone	-	x	-	-	-	-	Ps
90		16'50	4-hydroxy-5,6-dihydro-(2H)-pyran-2-one	x	-	-	-	-	-	Ps
91		17'04	? *m/z* 94, 93, 73, 109	-	-	x	-	-	-	
92	116	17'05	hexanoic acid C6:0	-	x	-	-	-	-	FA
93	120	17'14	ethylmethylbenzene	-	-	x	-	x	x	
94	140	17'15	1-decene	-	x	-	x	x	-	A
95		17'28	108, 107, 57, 41, 70, 94, 121	-	-	x	-	-	-	
96	109	17'30	2,3,5-trimethylpyrrole	-	-	-	x	-	-	Pro
97	142	17'37	decane	-	x	x	-	x	x	A
98		17'44	? *m/z* 57, 41, 29	-	-	x	-	-	-	
99	112	17'54	2-hydroxy-3-methylcyclopentene-1-one	x	-	-	-	-	-	
100	118	18'11	alkyl(C3)benzene	-	-	-	-	x	-	
101	120	18'18	alkyl(C3)benzene	x	-	-	-	-	x	Pro
102	108	18'58	methylphenol (o-cresol)	x	-	x	x	x	-	
103	128	19'07	? *m/z* 128, 43, 57, 85	x	-	-	-	-	-	Ps
104	134	19'12	butylbenzene	-	-	-	-	-	x	
105	120	19'17	? *m/z* 81, 82, 39, 54, 97	x	-	-	-	-	-	
106	134	10'32	methylpropylbenzene	-	-	-	-	-	x	
107	108	19'35	methylfenol (p/m-cresol)	x	x	x	x	x	-	
108		19'46	? *m/z* 68, 107, 108, 110, 69	-	x	-	-	-	-	
109	134	19'55	alkyl(C4)benzene	-	-	-	-	-	x	
110	130	19'59	heptanoic acid C7:0	-	x	-	-	-	-	FA
111	134	20'05	alkyl(C4)benzene	-	-	-	-	-	x	
112	154	20'07	C11-alkene	-	-	-	x	-	-	A
113	154	20'21	undecene	-	x	x	x	-	x	A
114	126	20'36	3-dihydro-2-methyl-(4H)-pyran-4-one	x	-	-	-	-	-	Ps
115	156	20'41	undecane	-	x	x	x	-	x	A
116		20'46	? *m/z* 99, 59, 56, 28, 72	x	-	-	-	x	-	
117	117	20'52	benzylcyanide	x	x	x	x	-	-	Pro
118		21'01	? *m/z* 200, 154, 69, 57	-	x	-	-	-	-	
119	134	21'06	alkyl(C5)benzene	-	-	-	-	-	x	
120		21'08	? *m/z* 42, 70, 113, 41	-	-	x	-	x	-	

M^+ = Molecular weight of the molecular ion. RT = Relative GC retention time. Samples as in Table 1
? *m/z* = unknown compound with characteristic main peaks (given according to relative abundance)
Origin of the compound: Ps = Polysaccharides; Pro = Proteins; FA = Fatty acids; PAH = Polynuclear Aromatic Hydrocarbons; A = Aliphatic hydrocarbons (alkanes/alkenes) and Cont = Contaminant.

Table 2 - Identified pyrolysis products in CyPyGC/MS results

Nr.	M^+	RT	Name	Samples						Origin
				Exp 1	Exp 2	26 char	31 beige	8 char	11 soot	
121	152	21'13	? *m/z* 132, 117, 82, 54	-	x	-	-	-	-	A
122	122	21'42	dimethylfenol	-	x	x	-	x	-	
123		21'51	? *m/z* 44, 43, 144, 101, 125	x	-	-	-	-	-	
124		22'01	? *m/z* 70, 113, 43, 42, 130, 115	-	-	x	-	-	-	
125		22'12	? *m/z* 43, 41, 69, 107, 70, 57, 85	x	-	-	-	-	-	
126	148	22'13	pentylbenzene	-	x	-	-	-	-	
127	122	22'14	ethylphenol	-	-	x	x	x	-	
128		22'26	? *m/z* 113, 43, 41, 50, 100, 85, 69	-	x	-	-	-	-	
129	148	22'32	1-methyl-4-isobutylbenzene	-	-	-	-	-	x	
130	144	22'37	octanoic acid C8:0	x	x	-	-	-	-	FA
131	156	22'52	decanone	-	x	-	-	-	-	
132		22'54	? *m/z* 41, 98, 99, 28, 58, 70	x	-	-	-	-	-	
133	133	23'04	naphthalene	-	-	-	-	-	x	PAH
134	144	23'13	1,4:3,6-anhydro-a-D-glucopyranose	x	-	-	-	-	-	Ps
135	168	23'15	1-dodecene	-	x	x	x	-	-	A
136	136	23'22	? *m/z* 73, 71, 43, 97, 44, 29, 55, 57	x	-	-	-	-	-	
	120	23'22	phenylacetaldehyde	-	-	x	-	-	-	Pro
137	170	23'33	n-dodecane	-	x	x	-	-	x	A
138		23'36	? *m/z* 71, 69, 73, 97, 56, 44, 41, 29	x	-	-	-	-	-	
139	131	23'45	phenyl cyanopropane	x	-	-	x	-	-	Pro
140	146	23'54	dimethylbenzofuran	-	x	-	-	-	-	
141	134	23'57	analine derivative	-	-	-	x	-	-	
142	158	25'12	nonanoic acid C9:0	-	x	-	-	-	-	FA
143	162	25'19	butylbenzaldehyde	-	x	-	-	-	-	Ps
144	117	25'47	indole	x	-	x	x	x	-	Pro
145	182	25'59	1-tridecene	-	x	x	x	-	-	A
146		26'02	1,4-dideoxy-D-glycero-hex-1-enopyrano-3-ulose	x	-	-	-	-	-	Ps
147	142	26'13	2-methylnaphthalene	x	-	-	-	-	-	PAH
148	184	26'17	tridecane	-	x	x	-	x	x	A
149	150	26'18	vinylmethoxyphenol	x	-	-	-	-	-	
150	210	26'33	5(2-dimethyl-ethyl)pyrrolidino-3,6 piperazinedione	-	-	-	x	-	-	Pro
151	142	26'40	1-methylnaphthalene	-	x	-	-	-	x	PAH
152	210	27'00	5(1-methyl-propyl)pyrrolidino-3,6 piperazinedione	-	-	-	x	-	-	Pro
153		27'05	unknown	x	-	-	-	-	-	
154	160	27'06	trimethylbenzimidazol ?	-	-	-	-	x	-	
155	134	27'07	alkyl(C5)benzene	-	-	-	-	x	-	
156		27'18	? *m/z* 55, 98, 69, 60, 138, 153, 195	x	-	-	-	-	-	Pro
157		27'40	? *m/z* 55, 98, 69, 60, 138, 153, 195	x	-	-	-	-	-	Pro

M^+ = Molecular weight of the molecular ion. RT = Relative GC retention time. Samples as in Table 1
? *m/z* = unknown compound with characteristic main peaks (given according to relative abundance)
Origin of the compound: Ps = Polysaccharides; Pro = Proteins; FA = Fatty acids; PAH = Polynuclear Aromatic Hydrocarbons; A = Aliphatic hydrocarbons (alkanes/alkenes) and Cont = Contaminant.

Table 2 - Identified pyrolysis products in CyPyGC/MS results

Nr	M^+	RT	Name	Samples						Origin
				Exp 1	Exp 2	26 char	31 beige	8 char	11 soot	
158	172	27'43	decanoic acid C10:0	-	x	-	-	-	-	FA
159	131	28'10	2-methylindole	x	-	x	x	x	-	Pro
160	154	28'15	vinylnaphthalene	-	-	-	-	-	x	PAH
161	196	28'33	tetradecene	-	x	x	x	x	-	A
162	198	28'48	tetradecane	-	x	x	x	x	x	A
163	156	28'50	ethylnaphthalene	-	-	-	-	-	x	PAH
164	156	29'10	1,3-dimethylnaphthalene	-	-	-	-	-	x	PAH
165		29'10	? *m/z* 127, 57, 43, 147, 116	-	x	-	-	-	-	
166		29'19	? *m/z* 139, 43, 41, 69, 81, 99	x	-	-	-	-	-	
167	209	29'28	? *m/z* 138, 55, 69, 98, 166, 180, 209	x	-	-	-	-	-	Pro
168	156	29'31	dimethylnaphthalene	-	-	-	-	-	x	PAH
169	156	29'38	dimethylnaphthalene	-	-	-	-	-	x	PAH
170	147	29'54	(1H)-isoindole-1,3-(2H)-dione	x	-	-	-	-	-	Pro?
171	260	29'56	? *m/z* 55, 124, 98, 69, 166	x	-	-	-	-	-	Pro
172	156	30'01	2,6-dimethylnaphthalene	-	-	-	-	-	x	PAH
173	186	30'03	undecaneoic acid C11:0	-	x	x	-	-	-	FA
174		30'12	? *m/z* 82, 67, 83, 81, 57, 95	-	x	-	-	x	-	
175	154	30'14	biphenyl	-	-	-	-	-	x	PAH
176	190	30'23	octylbenzene	-	x	-	-	-	x	
177	147	30'30	2,3-dihydro-4-methylindole	-	-	-	-	x	-	Pro
178	145	30'45	dimethylindole	-	-	-	x	x	-	Pro
179	147	30'46	1,3-dihydro, 3-methylindole	-	-	-	x	x	-	Pro
180	168	30'50	methylbiphenyl	-	-	-	-	-	x	PAH
181	210	30'57	pentadecene	-	x	x	x	x	x	A
182	168	31'05	methylbiphenyl	-	-	-	-	-	x	PAH
183	154	31'05	? aromatic hydrocarbon	-	-	-	-	-	x	PAH
184	212	31'13	pentadecane	-	x	x	-	x	x	A
185	203	31'13	? *m/z*129, 116, 130, 101, 103	x	-	-	-	-	-	
186	210	31'33	? *m/z* 210, 144, 141, 83, 55	-	x	-	-	-	-	A
187	168	31'50	dibenzofuran	-	-	-	-	-	x	PAH
188	224	32'16	hexadecene	-	x	-	-	-	-	A
189	200	32'21	dodecanoic acid C12:0	x	x	-	-	x	-	FA
190	162	33'17	1,6-anhydroglucose	x	-	-	-	-	-	Ps
191	226	33'27	hexadecane	-	x	x	-	-	x	A
192	236	35'01	heptadecadiene	-	-	-	x	-	-	A
193	238	35'02	heptadecene	-	x	-	x	-	-	A
194	222	35'05	? *m/z* 138, 123, 157, 57, 165, 180	x	-	-	-	-	-	
195	238	35'11	heptadecene	-	x	-	-	-	-	A
196	238	35'16	heptadecene	-	x	-	-	x	-	A
197	240	35'36	heptadecane	-	x	x	-	x	x	A
198	180	36'42	(9H)-fluoren-9-one	-	-	-	-	-	x	PAH

M^+ = Molecular weight of the molecular ion. RT = Relative GC retention time. Samples as in Table 1
? *m/z* = unknown compound with characteristic main peaks (given according to relative abundance)
Origin of the compound: Ps = Polysaccharides; Pro = Proteins; FA = Fatty acids; PAH = Polynuclear Aromatic Hydrocarbons; A = Aliphatic hydrocarbons (alkanes/alkenes) and Cont = Contaminant.

Table 2 - Identified pyrolysis products in CyPyGC/MS results

Nr.	M^+	RT	Name	Samples						Origin
				Exp 1	Exp 2	26 char	31 beige	8 char	11 soot	
199	228	36'39	tetradecanoic acid C14:0	-	x	x	-	x	-	FA
200	196	37'31	5(1-methyl-ethyl)pyrrolidino-3,6 piperazinedione (cis) derivative	-	-	x	-	-	-	Pro
201	254	37'38	alkane	-	x	-	-	-	x	A
202	178	37'43	phenanthrene	-	-	-	-	-	x	PAH
203	196	38'08	5(1-methyl-ethyl)pyrrolidino-3,6 piperazinedione (trans) derivative	-	-	x	-	-	-	Pro
204	242	38'40	pentadecanoic acid C15:0	-	-	-	-	x	-	FA
205	254	38'55	alkyl ketone ?	-	x	-	-	-	-	A
206	237	39'09	? *m/z* 97, 43, 110, 57, 42,124	-	x	x	x	x	x	
208	254	39'24	heptadecan-2-one	-	x	-	-	-	-	
209	268	39'37	nonadecane	-	x	-	-	-	-	A
210	194	39'48	5(1-methyl-ethyl)pyrrolidino-3,6 piperazinedione (cis) derivative	-	-	x	-	-	-	Pro
211	194	40'03	5(1-methyl-ethyl)pyrrolidino-3,6 piperazinedione (trans) derivative	-	-	x	-	-	-	Pro
212	149	40'13	phthalate	-	-	x	-	-	-	Cont
213	256	42'14	hexadecanoic acid C16:0	-	x	x	-	x	-	FA
214		42'37	? *m/z* 122, 136, 69, 164	-	x	x	-	-	-	
215		42'58	? *m/z* 43, 57, 97, 41, 56	-	-	x	-	-	-	
216	282	43'53	octadecenoic acid C18:1	-	-	x	-	x	-	FA
217	284	44'20	octadecanoic acid C18:0	-	-	x	-	x	-	FA
218	255	44'22	hexadecanoic acid amide	-	-	x	-	x	-	
219		47'12	? *m/z* 125, 244, 91, 153, 70	-	-	x	-	-	-	
220	281	47'47	octadecenoic acetamide	-	-	x	-	x	-	
221	283	48'23	octadecanoic acetamide	-	-	x	-	x	-	
222	309	53'16	pyrrolidine derivative	-	-	-	-	x	-	Pro

M^+ = Molecular weight of the molecular ion. RT = Relative GC retention time. Samples as in Table 1
? *m/z* = unknown compound with characteristic main peaks (given according to relative abundance)
Origin of the compound: Ps = Polysaccharides; Pro = Proteins; FA = Fatty acids; PAH = Polynuclear Aromatic Hydrocarbons; A = Aliphatic hydrocarbons (alkanes/alkenes) and Cont = Contaminant.