

Traces of Ancient Vessel Use: Investigating Prehistoric Usage of four Pot Types by Organic Residue Analysis using Pyrolysis Mass Spectrometry

In this study, Curie-point Pyrolysis Mass Spectrometry (CuPyMS) was used for the characterisation of solid organic residues situated on vessels of different shapes and sizes, found in an indigenous settlement from the Roman period at Uitgeest-Groot Dorregeest. The analysis of very small samples produced 'fingerprints' which reflect the chemical composition of the residues. Soil samples of the surrounding sediment were analyzed to check for contamination, but no indications could be found for severe post-depositional degradation or contamination of residues with soil components. The chemical composition of the residues was correlated to the size and form of the vessels using Discriminant Analysis in combination with Complete Link Cluster Analysis. This correlation reflects a distinction in original use between vessels of different forms and sizes. The presence of 'marker' compounds for fatty acids, proteins, smoke condensates and charred polysaccharides detected in the residues, gives information about the possible original use of the various types of vessels.

1. Introduction

1.1 FUNCTIONAL CLASSIFICATION OF POTTERY, THE USE-ALTERATION PERSPECTIVE

Pottery is a find-category frequently studied by archaeologists in search of information about different aspects of past societies, such as, social organisation, the organisation of trade and exchange, demography and subsistence. In spite of the long-standing tradition of ceramic studies in archaeology, it has always remained difficult to assign functions to ancient vessels. The understanding of how pottery was used is however essential to all studies that deduce information from pottery assemblages. The archaeological information stored in any assemblage of artefacts can only be interpreted fully if the actual use of the objects is known (Skibo 1992, 4).

Archaeological methods to identify vessel function are either directed to the function intended by the potter, or to the actual use of a vessel. The study of intended vessel functions is based on the assumption that the form, size and composition of pottery and, to a certain extent, its decoration, are constrained by the intended context and conditions of use (Braun 1973). The main difficulty of this

approach is the interpretation of observed morphological and technological variation in terms of function (Rice 1987, 207-232). The relationships between form, function and production technology are complex and variable. The study of intended vessel functions is therefore limited in detail and resolving power and will usually result in a general framework of possible functions (Rice 1990).

Studies directed to the actual use of vessels, on the other hand, can give independent information about the utilitarian role of a vessel. The traditional archaeological approach, the study of recovery context, is usually limited in resolution and open to multiple interpretations. The most direct and detailed way to analyze vessel use is through traces found in and on the ceramics. Hally (1983) was the first to use the term 'use-alterations' for modifications to the ceramic caused by use of the vessel. More recently, other researchers (Henrickson 1990; Skibo 1992, 42-49) have described various types of modifications including: the effects of firing such as, soot deposition and discoloration due to differences in oxidative state (*i.e.* oxygen discoloration); attrition or 'use-wear' of ceramic vessels (*e.g.* scratches, dents, chipping); and organic residues present in the vessels. Although each of these types of alterations can give information about vessel use, it must be kept in mind, that none will give information about the complete range of possible vessel uses within a society, but rather, on vessels of a selective range of daily applications.

1.2 ORGANIC RESIDUE ANALYSIS TO STUDY VESSEL USE

Studies of organic residues found in association with ancient pottery have mainly been directed to the identification of extractable compounds such as lipids and resinous materials (see bibliographies in Evershed *et al.* 1992; Heron/Evershed 1993; Rottländer/Schlichterle 1980). Both visible surface residues and compounds absorbed in the ceramic of the vessel wall are potentially useful sample material for systematic research of vessel use within ceramic complexes. In the literature some disagreement exists concerning the suitability of the different materials. Absorbed residues are probably more universally present

(Evershed 1993) and are claimed to be more protected against degradation and contamination with soil compounds (Rottländer 1990). Their analysis is, however, limited to specific classes of extractable compounds, such as lipids or resinous materials, and the results are harder to interpret because the compounds are probably accumulated in the ceramic over a longer period of vessel use. Surface residues, on the other hand, are less common but have recently been shown (Oudemans *et al.* in press) to contain a better preserved complex lipids profile. In addition, surface residues are probably the result of the last, or one of the last, phases of vessel use. In theory, this increases the likelihood of identification of the original vessel contents. Finally, solid surface residues can be studied for many classes of non-extractable compounds such as proteins and polysaccharides. Since the chemical composition of the total residues is unknown prior to analysis, solvent extracts, as obtained in the study of absorbed residues, may not be considered representative for this composition without further study.

The knowledge of complex solid biomaterials is, however, constantly increasing due to the application of new analytical techniques, such as analytical pyrolysis mass spectrometry (Boon 1992). Curie-point Pyrolysis Mass Spectrometry (CuPyMS) has been shown to be a suitable analytical technique for the study of charred natural products (Pastorova *et al.* 1993a, 1993b) and for the study of archaeological surface residues (Oudemans/Boon 1991). The advantage of this technique is the capacity to analyze a complex mixture of compounds in one single analysis. Mixtures of soluble compounds and solid materials can be analyzed.

In this paper, a series of solid organic residues from an indigenous settlement from the Roman period at Uitgeest-Groot Dorregeest was analyzed with CuPyMS to characterise their chemical composition. The mass spectra were compared using multivariate analytical techniques, resulting in clusters of chemically similar residues. The clusters were subsequently correlated to the size and form of the vessel. The hypothesis is tested (Abbink 1985, in prep), that variation in form and size of vessels represents a variation in intended use of the pottery.

2. Experimental

2.1 SAMPLES AND SAMPLE TREATMENT

The pottery studied was recovered from an indigenous settlement from the Roman period (*c.* 0-300 AD) at Uitgeest-Groot Dorregeest in the Netherlands (Woltering 1982, 1983). The settlement was situated on the remains of a coastal barrier and a sandy Dunkirk I creek deposit. During the Roman period, the settlement was bordered on SE and SW by a low lying, eutrophic peat deposit and cut

off on NW and NE by a fresh water gully running in an old course of the salt water creek. In the settlement a number of incomplete three-isled houseplans and about twenty filled-up water wells, dated to the Roman period, could be detected (Abbink 1985).

The choice of the sample material for CuPyMS analysis was based on three criteria: burial context, vessel morphology and presence of different types of surface residues (Abbink in prep). The pottery was found in three different types of burial contexts: in sandy creek deposits, in highly organic clay deposits (*i.e.* filled-up prehistoric wells or ditch fills) and in peat deposits (tab. 1). Different morphological vessel types were distinguished in the studied ceramic complex based on several size and form characteristics (Abbink in prep). Four types of vessels were selected for this study (fig. 1) of which type II represents the largest number in terms of quantity of recovered sherds. Vessel types I, III and IV were much less abundant. The sample set used in this study, contained various different types of surface residues. Most of the residues were dark brown, carbonized thick (> 1 mm) crusts situated on the interior of vessels. Although these chars occurred in all four different vessel types, they were very rare in vessels from type IV. A few cream coloured, flaky, crusts of medium thickness (*c.* 1 mm), occurred on the inside of vessels. These residues were most frequently found on vessels of type IV.

Very rarely, smooth red brown, thin (< 1 mm) residues were discovered all over the interior of vessels or situated as streaks or dripping traces on the exterior of vessels. The patterns on the exterior of vessel 8-1 were probably the result of purposeful decoration with a thick liquid. A fourth kind of residues, of pitch black colour and smooth, thin (< 1 mm) appearance could be found on the exterior of several vessels. These black residues were most frequently found on vessels of type I. The selected sample set consist of 17 sherds from complete vessels of all four types, and 10 sherds which were too small to allow identification of the original vessel type. These sherds were included because they contained well preserved residues.

All sherds had previously been washed with tap water. The residue samples were scraped from the ceramic surface with a scalpel (cleaned with Dichloromethane), after removal of the outermost 0.5 mm of the residue. In addition to the residue samples, two samples of the most organic sediments present in the site (P₁ and P₂) were analyzed in order to check for exchange of compounds from the sediment. About 100 µg of each sample was ground with a small glass mortar and pestle. Subsequently a suspension was made by addition of about 50 µl ultra pure water (Millipore Q-grade).

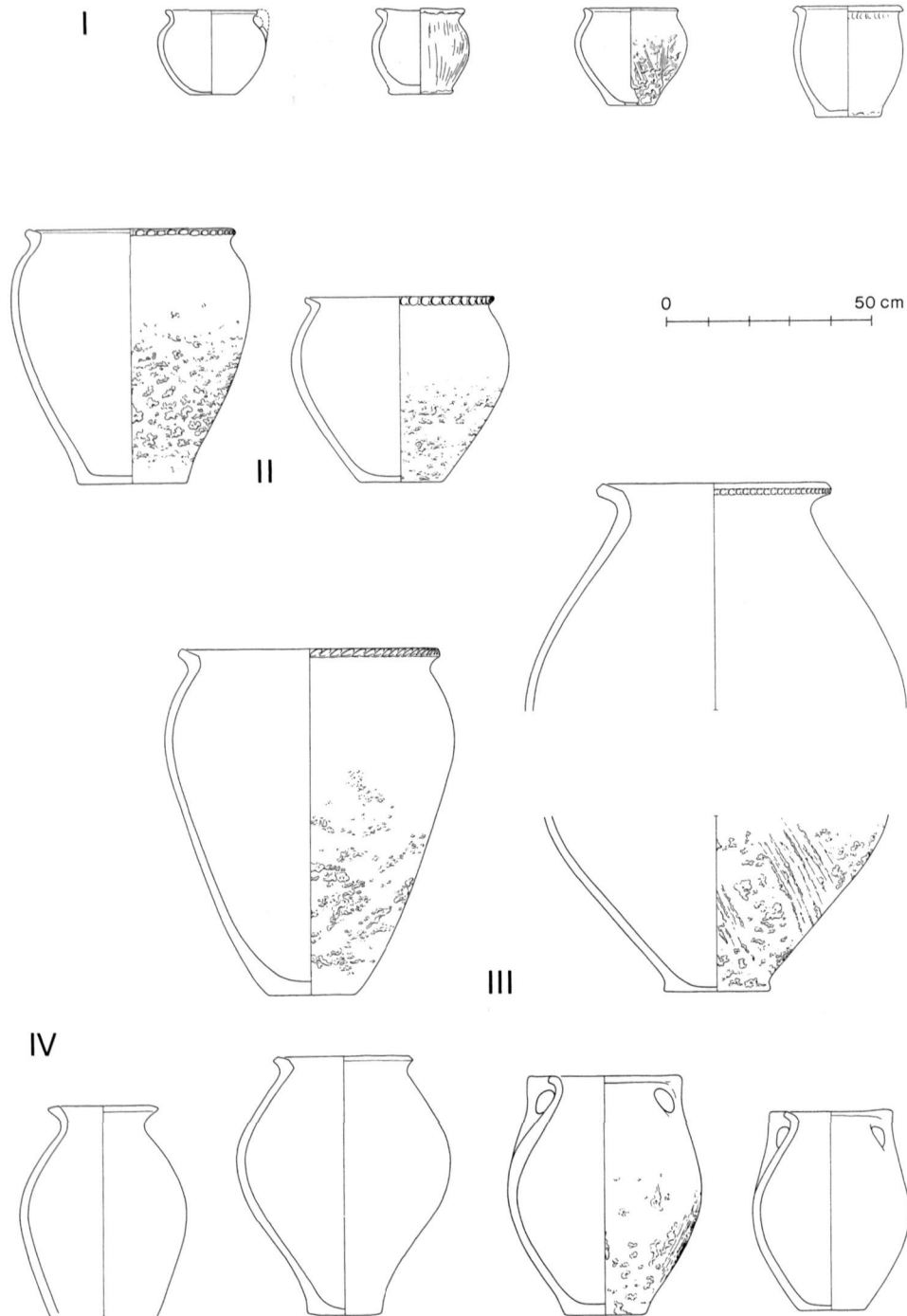


Figure 1. Morphological vessel types from Uitgeest-Groot Dorregeest (Abbink, in prep). The typology is based on form and size variables such as Greatest Diameter (GD), Rim Diameter (RD), and Distance from Rim to Greatest Diameter (DRG). Type I: small, three partite, wide mouthed vessels ($GD/RD < 1.5$, $GD < 170$ mm and $GD/DRG > 2.4$); Type II: medium sized, three partite, wide mouthed vessels ($GD/RD < 1.5$, $GD \geq 180$ mm, $GD < 340$ mm and $GD/DRG > 2.4$); Type III: large, three partite, wide mouthed vessels ($GD/RD < 1.5$, $GD > 350$ mm and $GD/DRG > 2.9$); Type IV: Jar-like, three partite, narrow mouthed vessels ($GD/RD \geq 1.5$ but $GD/RD < 2.1$ and $GD/DRG < 2.4$). Drawings by J. Hulst, State Service for Archaeological Investigations in the Netherlands (ROB).

Table 1. Residue samples and soil samples

- ^a Find number: the first number indicates the number of the excavation pit, the letters indicate multiple samples from one vessel.
- ^b Residue appearance: Brown, dark brown, thick (> 1 mm), charred crust on interior of the vessel; Black, smooth, thin (< 1 mm) black residue on exterior of the vessel; Red brown, smooth, thin (< 1 mm), red brown residue situated on interior (smooth layer) or exterior (often in streaks or dripping traces) of vessel; Cream coloured: white yellow, brittle crust of medium thickness (ca. 1 mm) on interior of vessel.
- ^c Position of the residue on the vessel: In, Interior; Ex, Exterior of the vessel.
- ^d Vessel Type: the morphological vessel type (Abbink in prep).
- ^e Sediment: the soil type in which the vessel was found.
- ^f P₁ and P₂ are peat samples from the excavation found in respectively pit 16 and pit 34.

number	find number ^a	residue ^b	position ^c	vessel type ^d	sediment ^e
1	7-7	brown	In	II	organic clay
2	8-1	red brown	Ex	III	organic clay
3	8-2	brown	In	III	organic clay
4	8-5	cream coloured	In	I	organic clay
5	14-6-4.2	brown	In	-	sandy
6	14-6-4.3a	brown	In	I	sandy
7	14-6-4.3b	black	Ex	I	sandy
8	14-6-4.4	brown	In	-	sandy
9	14-6-4.5	brown	In	-	sandy
10	18-3-3.2a	brown	In	I	organic clay
11	18-3-3.2b	black	Ex	I	organic clay
12	18.7	brown	In	II	organic clay
13	19.7-90.2a	brown	In	II	organic clay
14	19.7-90.2b	brown	In	II	organic clay
15	20-4	brown	In	II	sandy
16	20-4-157	brown	In	-	sandy
17	20-4-12-3	brown	In	II	organic clay
18	31-4a	brown	In	I	organic clay
19	31-4b	black	Ex	I	organic clay
20	32-6-18	brown	In	-	peat
21	33-5-2a	brown	In	-	peat
22	33-5-2b	brown	In	-	peat
23	33-8-2a	brown	In	-	peat
24	33-8-2b	brown	In	-	peat
25	34-0-12	brown	In	-	organic clay
26	34-0-30(=34-12)	brown	In	II	organic clay
27	34-7-62	red brown	In	II	organic clay
28	34-7-95.b	black	Ex	I	organic clay
29	34-11-3	brown	In	II	organic clay
30	35-5-120	brown	In	II	sandy
31	35-7-28	cream coloured	In	-	sandy
32	35-20	cream coloured	In	IV	sandy
33	35-21	brown	In	II	sandy
34	peat ₁ ^f	peat			pit 16
35	peat ₂ ^f	peat			pit 34

2.2 INSTRUMENTAL

The analyses were performed in triplicate on a fully automated Curie-point pyrolysis mass spectrometer, the FOM-autoPYMS, built at AMOLF in the mid seventies and described in its latest version by Boon *et al.* (1984). Pyrolysis is a thermal fragmentation of large, non-volatile

molecules in an inert atmosphere. The smaller, more volatile fragments formed during this rapid heating process are representative of the original (macro) molecules. Curie-point pyrolysis is accomplished by inductive heating of a ferromagnetic wire coated with the sample material. The thermal energy thus transferred to the sample is used for

desorption or pyrolysis of the molecules. The desorbed molecules and pyrolysis fragments are subsequently ionised and transported to the mass spectrometer where they are separated according to mass. The instrumental conditions were: heating for 0.1 s at a rate of 5000°C/s up to a Curie-point temperature of 610°C, the total heating time was 1.0 s. The pyrolysis chamber was set at 180°C, the ionisation current was 16 eV and the total mass range measured was m/z 20–240 at a scan speed of 10 scans/s with a total number of averaged spectra of 200. The results are visualised in a Mass Spectrum in which the intensity of each mass is plotted on a scale of 1 to 100% relative to the most abundant mass. Mass Spectra (fig. 2) can therefore be seen as a chemical ‘fingerprints’ of the total organic chemical composition of the sample.

2.3 MULTIVARIATE ANALYSIS

In order to facilitate the comparison of mass spectra, a data reduction technique called Discriminant Analysis (DA) was applied. The statistical package used was a modified version of the ARTHUR multivariate analysis package (Hoogerbrugge *et al.* 1983). A number of Discriminant Functions (DFs) were calculated, which express the main similarities and dissimilarities between groups of samples. The DFs are linear recombinations of highly correlated masses. The number of DFs needed to explain the total variance in a set of samples depends on the diversity of the samples and the complexity of the material studied. The total variance in a set of samples can be seen as a summation of variance introduced by systematic changes in sampling or analytical procedure (I_w = within group variance), and variance between the groups of replicate analyses of samples (I_B = between group variance). The Fisher ratio (F) of a given DF, defined as $F = I_B/I_w$, expresses the amount of variance relevant to group separation explained by that DF. The characteristic variance of a sample set is here defined as the sum of the Fisher ratios of all the DFs. Using these Fisher ratio's, a selection of DFs can be made that are most relevant to group separation. Two-dimensional representations of the discriminant space (discriminant maps of two relevant DFs) can be made (figs 3, 4), showing the samples plotted around an origin, which represents the calculated ‘average spectrum’. The relative difference in chemical composition between two samples is expressed by the Euclidean distance between two sample points in the map (*e.g.* samples close together are more similar to one another than samples further apart).

In order to outline groups of chemically similar samples, Complete Link Cluster Analysis (CLCA) was employed. Since not all DFs have the same explanatory power, each dimension is weighted prior to cluster analysis. The weighting factor k_i is defined as the percentage of the

characteristic variance explained by the given DF_{*i*}. The weighted Euclidean distance D between sample points x_1 and x_2 is defined as:

$$D_{(x_1, x_2)}^2 = \sum_{i=1}^n k_i (x_{1i} - x_{2i})^2 \quad (1)$$

in which i symbolises the dimension or DF and k_i is a weighting factor for dimension i and x_{1i} and x_{2i} are the values for x_1 and x_2 in the dimension i . CLCA was applied to the weighted Euclidean distance between the samples in the discriminant dimensions considered relevant to group separation. The similarity value S between object x_1 and object x_2 is defined as:

$$S_{(x_1, x_2)} = 1 - \frac{D_{(x_1, x_2)}}{\max D_{(x_m, x_n)}} \quad (2)$$

in which $\max D_{(x_m, x_n)}$ represents the maximal weighted Euclidean distance between two points within the set of sample points. Clusters of samples with high similarity values can thus be formulated.

In order to explain the chemical differences between the clusters in terms of molecular composition, the sets of correlated masses which define the dimensions of the discriminant space are subsequently chemically interpreted in terms of classes of bio-organic compounds (figs 3, 4).

3. Results and Discussion

3.1 SOIL SAMPLES VERSUS ARCHAEOLOGICAL RESIDUES

In order to compare the archaeological residues to the surrounding soil in which they were buried for many centuries, the CuPyMS mass spectra of residues and soil samples were included in a DA of the total sample set. A discriminant map of the discriminant functions DF₁ and DF₂, respectively expressing 41.9% and 28.6% of the characteristic variance (fig. 3), visualises a clear distinction between these two groups of samples. The soil samples are primarily characterised by mass peaks in the DF₁⁻ spectrum, whereas most of the organic residues on the vessels are characterised by the DF₁⁺. The residue samples are further characterised and divided by masses in the DF₂ dimension (not shown in fig. 3).

The spectrum representing the DF₁⁻ space contains markers for the bio-organic compound classes lignins, polysaccharides and fatty acids (see tab. 2: Soil). These chemical characteristics are quite typical for pyrolysates of peat samples and are consistent with data presented by others (Boon *et al.* 1986; Bracewell *et al.* 1980). The absence of lignin and intact polysaccharide markers in pyrolysates of archaeological residues on pottery has already been shown before in Pyrolysis GC/MS studies

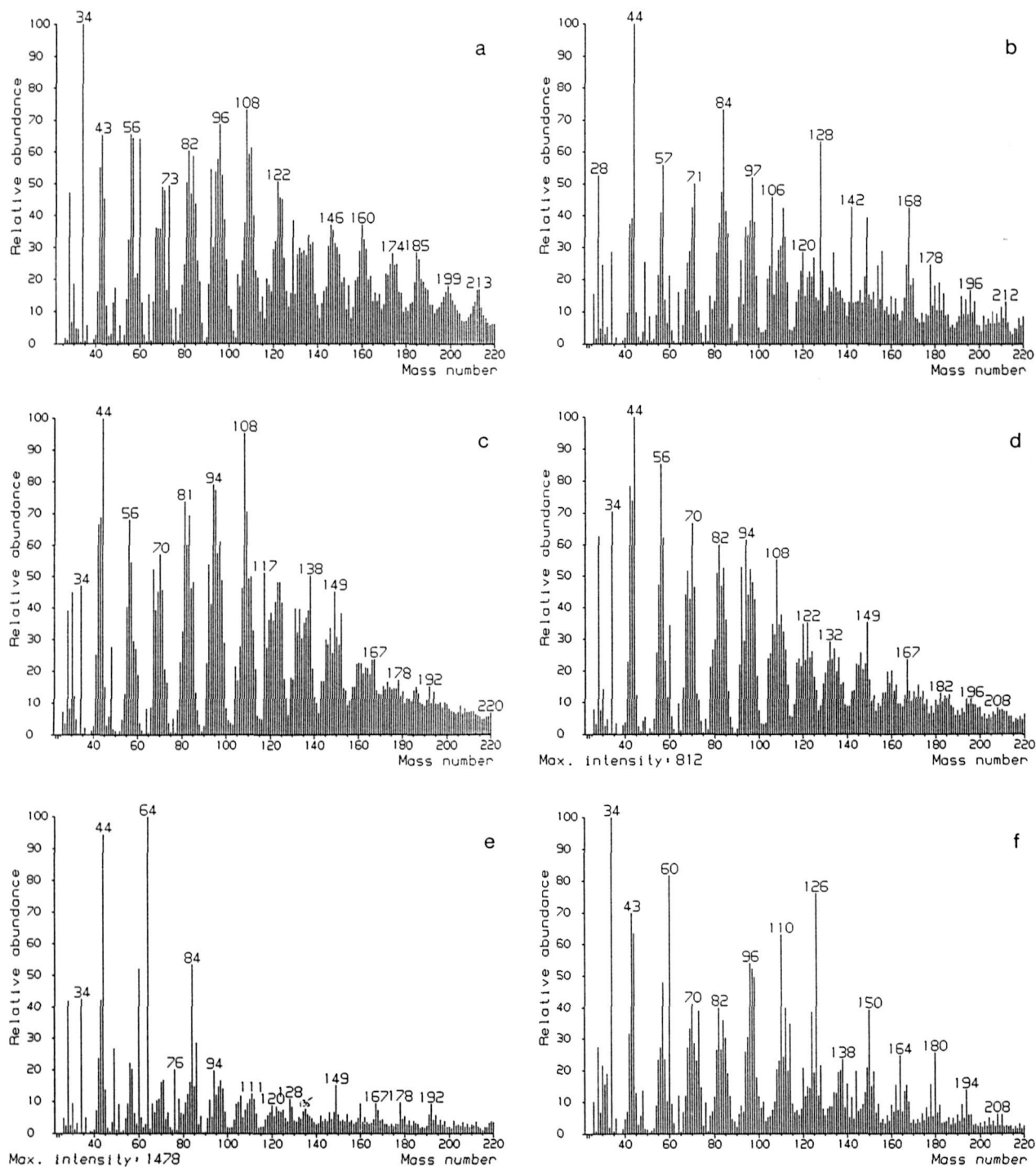


Figure 2. Mass Spectra of five archaeological residues and a peat sample. The intensity of each mass is plotted relative to the most abundant mass. Letters A through E indicate clusters of chemically similar residues (see Results and Discussion). A: sample 12 (18-70), a typical dark brown char from vessel type II; B: sample 11 (18-3-2.b), a black soot from the exterior of a vessel of type I; C: sample 31 (35-7-28), a cream coloured residue; D: sample 18 (31-4.a), a typical char from vessel type I; E: sample 28 (34-7-95.b), a black soot contaminated with Elementary Sulphur; and F: sample 34 (P₁), a peat sample from pit 16.

(Oudemans/ Boon 1991). Although polysaccharides have probably been an important component of prehistoric foods, intact polysaccharides have obviously not survived the extreme conditions during cooking or burial in the ground. Lignins originate from the 'woody' parts of plants, and are not likely to be a significant constituent of foods. Fatty acids are a different matter altogether, because they are at all times an important component of human foods. The quantity of fatty acids in the peats must, however, be much larger so they appear in the DF_1^- side of the spectrum. The archaeological residues are distinctly different in chemical composition (figs 2, 3) and are primarily typified by fragments indicative of proteins, charred polysaccharides and elementary sulphur (see also tab. 2).

Exchange of any significant quantity of compounds between archaeological residues and organic soils, such as P_1 and P_2 , has obviously not taken place, which is in agreement with a study on the exchange of soil lipids by Heron *et al.* (1991). It is therefore not likely that remains of soil, stuck to the surface of ceramics, will ever be mistaken for residues of the original vessel contents. In addition, no correlation could be found between the chemical composition of residues and the type of sediment in which they were preserved. In Figure 3 samples recovered from different sediment types were situated in various quadrants of the map. In conclusion, it can be stated that the chemical classification of the residues based on CuPyMS data is, therefore, a reflection of the original vessel contents and not an artefact of post-depositional changes in chemical composition of residues during burial.

3.2 CHEMICAL COMPOSITION OF ARCHAEOLOGICAL RESIDUES

After removal of the soil samples from the data set, a second discriminant analysis was performed to 'zoom in' on the chemical characteristics of the various residue samples (fig. 4). Although nineteen DFs were defined to explain the total variance in the data set, only the first three (explaining respectively 44.0%, 16.8% and 13.3% of the characteristic variance) were considered representative of the chemical composition of the residue material. The additional DFs represented minor variations in chemical composition due to fluctuations in analytical circumstances or presence of inorganic components. The second DF was not considered suitable for mapping, because it represents merely the presence or absence of contaminating phthalate esters (indicated by fragments m/z 149 and 167), that could be identified as originating from plasticisers. These contaminations probably take place in contact with plastic bags in which ceramics are often stored after excavation. The DF_2 is therefore not relevant to the chemical composition of the original residue.

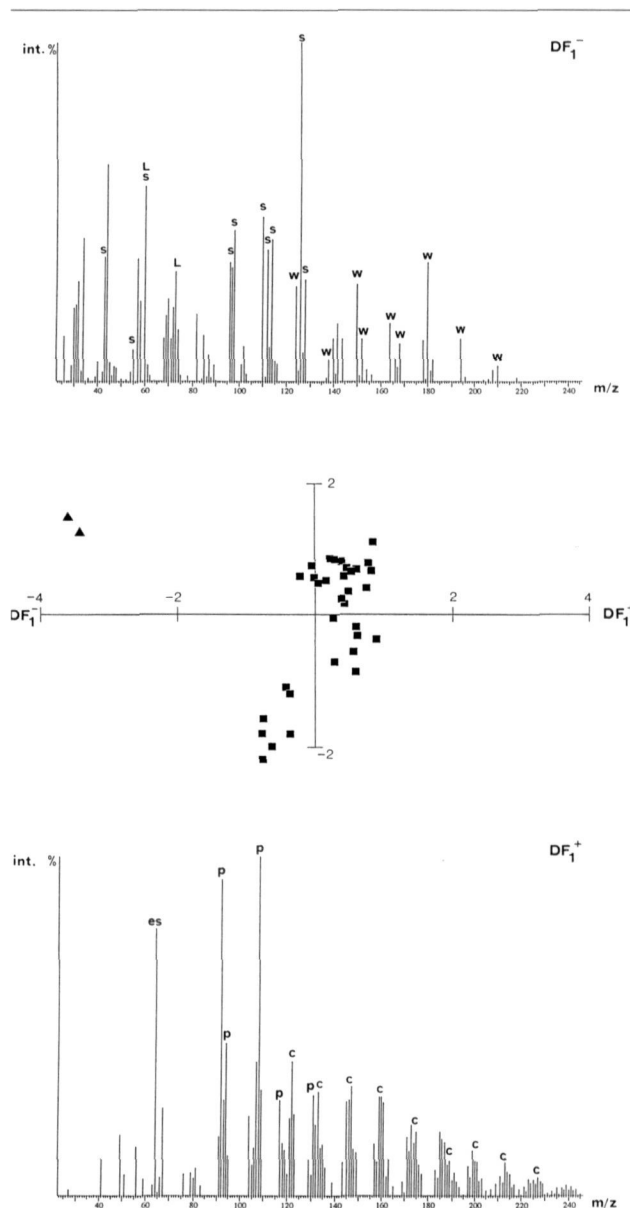


Figure 3. Discriminant map comparing Residues and Soil samples. Residues (black squares) and soil samples (black triangles) are plotted according to their similarities and dissimilarities in chemical composition. Triplicates are plotted as one average point. Markers for lignin's (W), polysaccharides (S), fatty acids (L), Proteins (P), Charred Polysaccharides (C) and Elementary Sulphur (ES) are indicated in the Spectra for the DF_1^+ and DF_1^- directions.

The weighted CLCA of the distances in the first three dimensions, indicated the existence of 5 clusters A through E (fig. 4). Clusters B and D are situated in the same direction on the map (fig. 4), and are characterised by the same masses in the given dimensions DF_1 and DF_3 . The

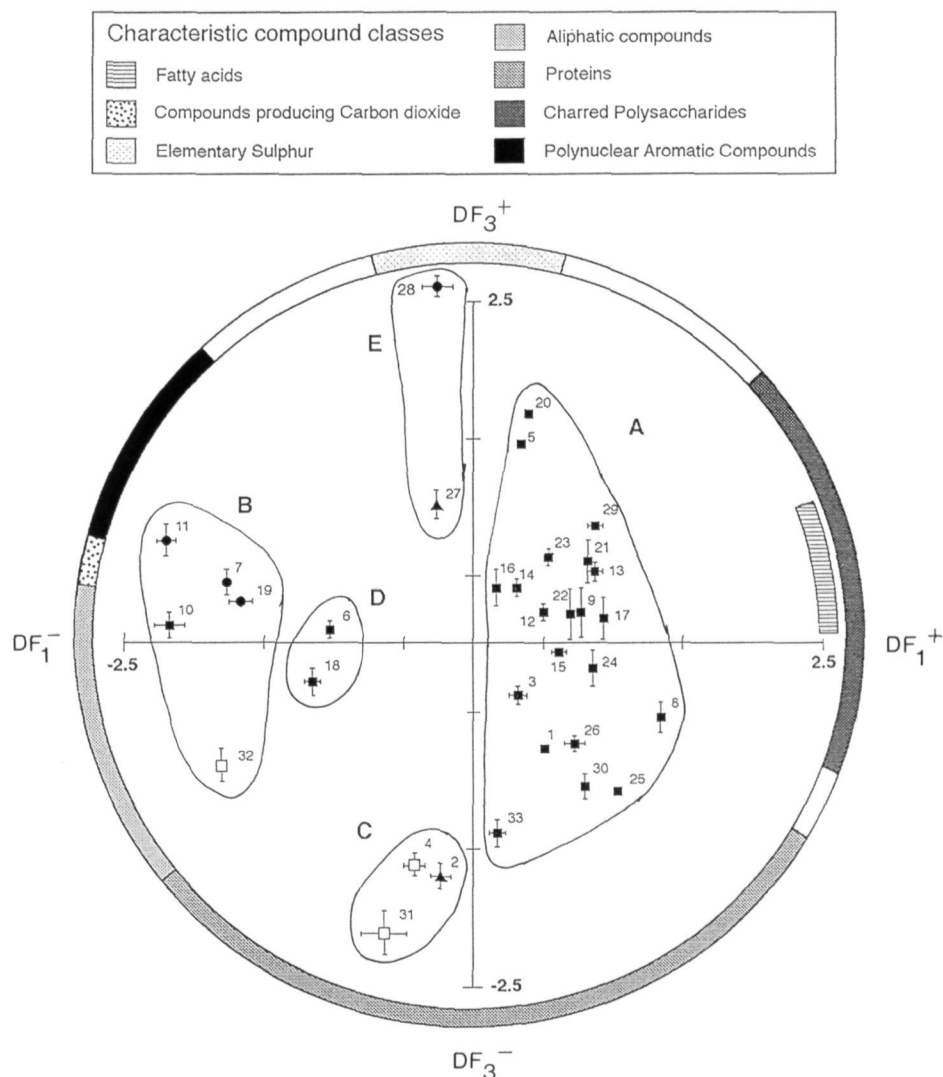


Figure 4. Discriminant map with clusters of residues (A through E) and their chemical characteristics. Triplicate measurements are indicated by standard deviation error bars. The relative difference in chemical composition is expressed by the distance between two sample points. Indicated are: brown chars (black squares); black soot residues on exterior of vessels (black dots); red brown residues (black triangles); and cream coloured residues (white squares). The shadings in the circle indicate the compound classes indicative for various directions in the discriminant map.

calculated relative similarity values give a measure for the relative chemical similarity between samples in the clusters (tab. 2). The typical chemical characteristics of the clusters can be interpreted as indicators or markers for certain compound classes (tab. 2). Features that appear in all samples will, however, not be shown as typical characteristics for either of the clusters. For the absolute chemical composition of the residues, the original mass spectra must be considered as well (fig. 2).

Cluster A consists of chars containing charred polysaccharides. The combination of markers m/z 110, 146, 147, 160, 161, 162, 174, 175, 188 and 189, is typical for polysaccharides heated under inert circumstances at temperatures over 250°C (Pastorova *et al.* 1993a, 1993b). The experiments described by Pastorova and co-workers were designed to resemble charring processes in ceramic

vessels. During the cooking of a thick liquid, high temperatures caused by restricted circulation could cause burning and eventually charring against the heated wall and bottom of the vessel. Some of the residues in cluster A contain additional characteristics, such as a strong protein influence (*i.e.* samples 1, 3, 25, 26, 30, 33) or the presence of fatty acids in relatively large quantities (*i.e.* samples 9, 13, 17, 22).

Clusters B and D consist of residues containing aliphatic compounds and/or Polynuclear Aromatic Compounds (PACs) and their methyl and ethyl derivatives. The black samples on the exterior of vessels (samples 11, 7, 9) are characterised by the presence of PACs and compounds which release CO_2 . A detailed identification of these compounds by Pyrolysis Gas Chromatography Mass Spectrometry (PyGCMS) has led to the interpretation of the

Table 2. Clusters of residues and their typical composites.

^a cluster: the cluster A through E. Soil samples are also indicated as a separate unit.

^b Sample numbers: number as indicated in Table 1.

^c Markers: typical pyrolysis markers for certain compound classes expressed in m/z .

^d Relative Similarity Values: similarity in chemical compositions of the samples within a cluster relative to the maximal variation between the two most different samples (see formula 2).

^e Compound Classes: chemical compound classes represented by the typical markers. References: 1: Pastorova *et al.* (1993 a); 2: Waller (1972); 3: Meuzelaar *et al.* (1982), 109; Munson/Fetterolf (1987); 4: Medalia *et al.* (1983); 5: Meuzelaar *et al.* (1982), 6-18, 115-149; 6: Boon *et al.* (1986); Van der Heiden *et al.* (1990).

C ^a	Sample ^b	Markers ^c	S ^d	Compound classes ^e
A	1, 3, 5, 8, 9, 12, 13, 14, 15, 16, 17, 20, 21, 22, 23, 24, 25, 26, 29, 30, 33	146, 147, 160, 161, 174, 175, 188, 189. 60, 73, 101, 115, 129. 92, 94, 117, 131, 154. 32, 34, 60, 64, 96, 128, 160, 192, 224, 226, 256, 258	0.62	charred polysaccharides (1) fatty acids (2) proteins (3) elementary sulphur
B/D	6, 7, 10, 11, 18, 19, 32	78, 91, 92, 105. 128, 142, 156, 170, 178, 192 44 55, 56, 57, 69, 70, 83, 84, 85, 97, 98, 99	0.78 0.93	phenols PAC's (4) CO ₂ aliphatic compounds
C	2, 4, 31	92, 94, 117, 131, 154	0.81	proteins
E	27, 28	32, 34, 60, 64, 96, 128, 160, 192, 224, 226, 256, 258	0.76	elementary sulphur
Soil	P ₁ , P ₂	43, 55, 60, 72, 96, 98, 110, 112 114, 126, 128 124, 138, 150, 152, 164, 168, 210, 180, 184, 194 60, 73, 101, 115, 129		polysaccharides (5) lignin's (6) fatty acids

residues as smoke condensates or 'soot' from cooking over wood fires (Oudemans/Boon 1991). In addition, we find several chars and a white residue in the clusters B and D. These residues belong to this cluster due to the presence of markers for aliphatic compounds (not due to the presence of any PACs). The aliphatic compounds are most likely pyrolysis products of some kind of aliphatic polymeric structure formed from lipids under high temperatures. This is shown to be possible by the presence of similar aliphatic markers in pyrolysates of experimentally obtained chars of recent food stuffs (Oudemans/Boon 1991). This aliphatic product may be formed by heating of oils in the vessel in order to make it more water proof. However, the obvious absence of any intact fatty acids is, in this context, rather strange. One would expect to find remainders of free fatty acids in the residues as well. Sample 32 is different in appearance as well as in chemical composition: it contains some protein markers in addition to the aliphatic compounds mentioned earlier. The origin of this residue

may be found in a combination of water proofing and the use of the vessel for storage or processing of proteinaceous materials.

Cluster C contains protein rich residues of different appearance. Although these different samples seem difficult to compare, their clustering indicates similarity in chemical composition. The mass spectra (fig. 2) show a clear pattern of protein fragments and even include some markers for intact dipeptides such as m/z 154 (Munson/Fetterolf 1987). It is not clear, whether these three residues are of a similar origin. The absence of fatty acids and charred polysaccharides from the mass spectra, does however suggest a vessel contents of primarily proteinaceous material. These residues show a relatively well preserved protein pattern, which suggests a lack of heating. The cream coloured residues 4 and 31 are situated on the interior of vessels may have been formed during storage or processing of protein-rich materials. Dairy products seem to be excluded because no significant quantities of fatty acids are present. The red

Table 3. Summary of possible origins of residues per type vessel.

^a Vessel Type as indicated in figure 1.^b Residue appearance: as indicated in table 1.^c Number: indicates the number of samples.^d Clusters as indicated in table 2 and figure 4.

Vessel ^a	Residue ^b	n ^c	C ^d	Origin	Possible vessel use
Type I	Char, interior	3	B/D	heated lipids	water proofing?
	Black, exterior	3	B/D	soot	cooking on wood fires
	Black, exterior	1	E	contamination	cooking on wood fires
	Cream coloured, interior	1	C	protein	proteinaceous material?
Type II	Char, interior	10	A	starch	starch-rich food
	Red brown, interior	1	E	contamination	proteinaceous material?
Type III	Red brown, exterior	1	C	protein	proteinaceous material?
Type IV	Cream coloured, interior	1	D	protein	proteinaceous material?

brown sample 2 is situated on the exterior of a vessel and may be a protein mixed with an inorganic pigment used for decorative purposes. The presence of a similar redbrown residue (though contaminated with elementary sulphur) sample 27 on the inside of a vessel, suggests that this material may be prepared in a ceramic vessel, causing a smooth residue all over the interior of the vessel.

Cluster E is a cluster with sulphur containing residues. The markers *m/z* 32, 34, 64, 128, 160, 192 and 256 indicate the presence of elementary sulphur (S₈). Elementary sulphur is quite rare in nature and the origin of the material is not clear. It is possible that the clay used for the production of these specific vessels contained S₈. Since the two samples (27 and 28) involved were both very thin, clay particles could have been scraped from the surface of the vessel and mixed with the sample. Elementary sulphur may also be produced by bacteria during degradation of biological compounds.

Additional results concerning the exact nature of these solid residues and their possible origin will be published in a Temperature resolved Pyrolysis Mass Spectrometric study of these materials (Oudemans/ Boon in prep).

3.3 CORRELATION WITH POT TYPE

When the morphological pot types are plotted in this map (fig. 5), it becomes obvious that there is a correlation between the chemical composition of the residue and the original size and form of the vessel on which the residue was found (tab. 3). Vessels of different size and form were therefore obviously used for different daily uses.

Although there is no complete overlap between vessel type and chemical properties of the residues, careful interpretations can be made about possible vessel usage of different vessel types.

Vessel Type II:

The majority of the residues on these vessels are found in cluster A. The origin of these residues can probably be found in the preparation of grains or porridge or other starch-rich stews. In some cases protein-rich material such as meat, fish or pulses may have been added, while in other instances fats may have enriched the mixture. Samples 27 belongs to cluster E because it contains markers for elementary sulphur. This sample is of quite a different nature and may be the result of the preparation or storage of a protein rich material (see for explanation above).

Vessel Type I:

The origin of the charred residues in this type of vessels is not completely clear. The CuPyMS data indicate that they are evidently quite different in composition from those in vessels of type II. The absence of charred polysaccharides, protein markers or fatty acids as typical features, is significant. These residues may have been formed during activities other than food preparation. A possible origin may be found in a post-firing water proofing of the vessels by heating of oil in the vessels. The high temperatures may cause cross linking of the lipids. Interesting in this case is also the frequent presence of soot on the outside of these vessels. One residue (sample 4) is clearly different and belongs to cluster C, which suggests occasional variation in use.

Vessel Type III and IV:

Due to the absence of multiple samples of these vessel types, no conclusions can be drawn on the usage of these vessel types as a whole. The MS data of the two samples that were analyzed did, however, present interesting evidence explained earlier.

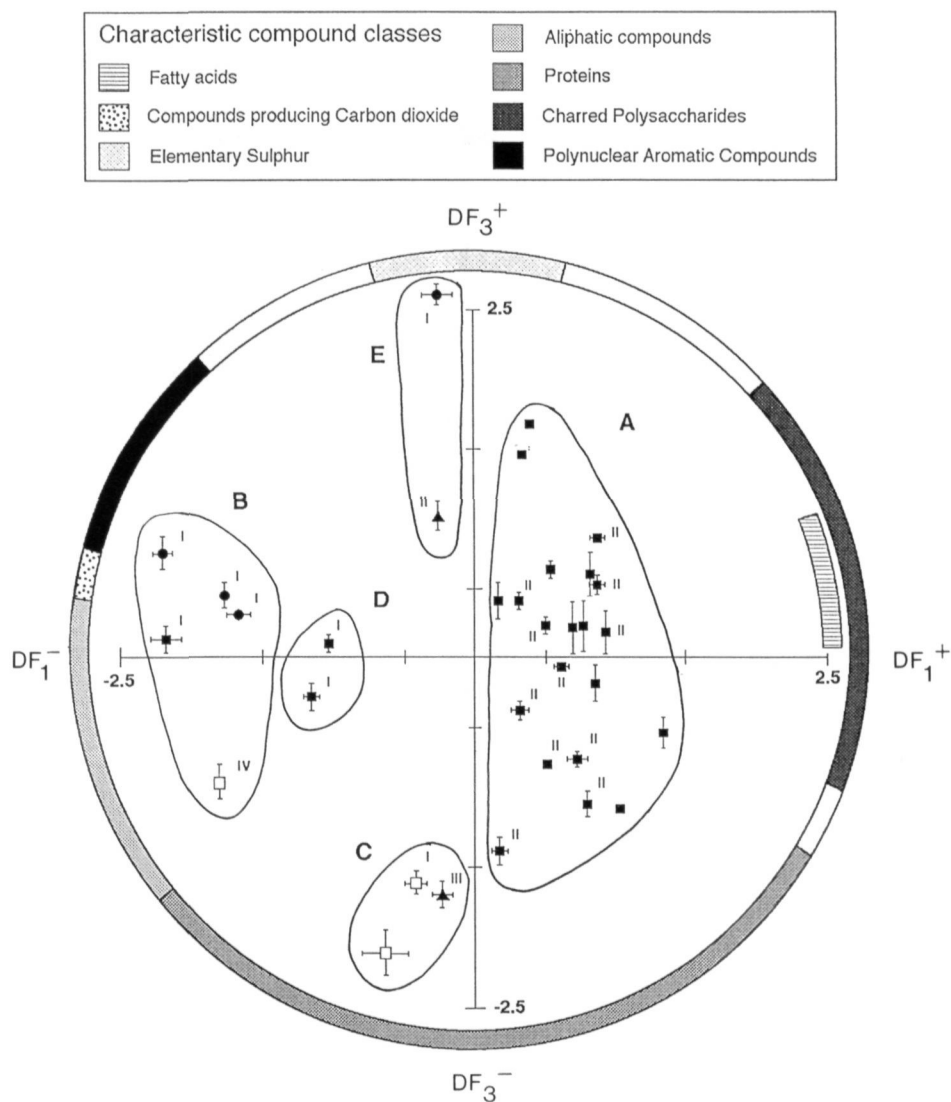


Figure 5. Correlation between vessel types and chemical composition of the residues. The vessel types are indicated I through IV. Sherds of which the vessel type could not be identified are indicated without type number. Clusters of residues (A through E) were derived from the chemical characteristics as expressed in the CuPyMS spectra (see fig. 4).

More work should be done on larger numbers of complete vessels, in order to confirm the vessel uses here suggested and check their statistical significance. However, even when the origin of samples cannot be understood completely, it can still be concluded that vessels from type I and II were used in a different way. This supports the original hypothesis that the variation in pot morphology had an utilitarian meaning in the indigenous settlement in Uitgeest-Groot Dorregeest.

4. Conclusions

This paper presents the first systematic study to correlate the chemical composition of solid organic surface residues to the form and size of vessels in which they were

preserved. It has been shown that CuPyMS, in combination with multivariate analytical techniques, is a useful method to systematically and rapidly analyze and categorise solid organic residues found on ancient vessels. The chosen analytical strategy presents not only a measure for similarity or dissimilarity in chemical composition of the samples, facilitating as such an objective classification of the residues, but also highlights the chemical components typical for the various clusters. The chemical classification was shown to be a reflection of the original vessel use, and not an artefact of post-depositional changes in chemical composition of the residues.

Results from the CuPyMS studies give clear evidence to conclude that a correlation does indeed exist between the

chemical composition of the surface residues studied and the morphological vessel type of the vessel in which they were found. Vessels of different sizes and forms were, therefore, used for a different daily use within the indigenous settlement from the Roman period at Uitgeest-Groot Dorregeest. These results support the usefulness of a morphological vessel classification as a basis for functional studies within this ceramic complex.

The significance of organic residue analysis within archaeological ceramic studies is, however, not limited to testing existing theories concerning the relation between form and function of pottery, but also lies in the detailed information about daily use of vessels that cannot be obtained by any other method.

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