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A NEOLITHIC SETTLEMENT ON THE DUTCH NORTH SEA COAST *c.* 3500 CAL BC

EDITED BY LEENDERT P. LOUWE KOOIJMANS
AND PETER F.B. JONGSTE

LEIDEN UNIVERSITY 2006

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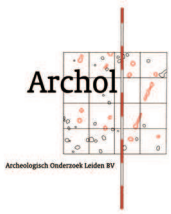

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20a Analytical report on some archaeological charred residues from Schipluiden

Jaap Boon

Residues on ceramic pottery found in Schipluiden were investigated with direct temperature resolved mass spectrometry to determine whether they contain organic constituents that can be related to food preparation. Some residues on the outside shows aromatic compounds from soot precipitation. Charred proteins were also common. There is evidence for lipids but only fatty acids remain and some compounds with a cholesterol origin indicative for an animal origin. One residue microscopically identified as a porridge shows evidence for lignocellulosic constituents from resistant plant cells of woody tissues. Compared to preserved residues from other archaeological sites, the ones from Schipluiden are poorly preserved on the molecular level and therefore hard to relate to food substances.

20a.1 Introduction

Five samples of charred remains from the Schipluiden site were submitted by Lucy Kubiak-Martens for chemical analysis. One sample is a presumed resides of porridge while others were removed from pottery sherds. The nature of the material was unknown to the analysts.

Direct Temperature resolved Mass Spectrometry was the analytical technique used. In principle, this method implies the mass spectrometric monitoring of a sample that is heated on a Pt/Rh filament. Compounds adsorbed or sequestered in the sample are evaporated before the non-volatile residue is thermally decomposed to smaller fragments. The result is a dataset that consists of mass spectra (mass range 20-1000 Dalton) collected as a function of time/temperature.

This methodology has been used for analysis of complex organic materials often in association with inorganic substances. Typical recent applications are carbonised grains and peas (Braadbaart 2004), carbonised food residues and coatings on ancient pottery (Oudemans/Boon 1996; Oudemans *et al*. 2005a, b). Recently the methodology has been applied to various archaeological objects from the Louvre (Regent/Rolando 2002). Residues on pottery have often undergone severe thermal exposure either on the exterior of the pots or as burned food residues on the interior. My laboratory has been involved in a number of studies of such residues since 1990. In a number of cases it has been possible to retrieve data on fatty components (various acylglycerols, free fatty acids, various sterols), polycyclic aromatics from soot, phenolic compounds from wood burning fires, and various heteroaromatic compounds released from weakly and strongly charred proteins and polysaccharides. The degree of preservation depends highly on the original burning and charring conditions.

The samples were analysed as received. Aliquots of about 50 microgram of the power were homogenised in ethanol in a glass micro mortar and applied to the filament probe. The instrument use was a JEOL SX102-102A tandem mass spectrometer. The MS condition were: 16 eV electron ionisation, 8kV acceleration voltage, scan range m/z 20-1000 at a rate of 1 s/scan. Data were processed in a JMA7000 data system and software.

20a.2 Results

Results are presented as mass spectra and mass chromatograms in figures 20a.1-5. A short interpretation of the data is presented here. The questions from Kubiak-Martens concern the nature of the residues observed on the pottery with a focus on proteins, fats and cereal polysaccharides. The data are summarized in table 20a.1. The lipid fractions are clearly recognizable in the data by their molecular ions and fragment ions. Only sample 9381 shows some evidence for intact acylglycerides with C16 and C18 fatty acid moieties [m/z 550 (C16/C16), 578 (C16/C18) and 604 (C18/C18)] but the relative amounts are very low compared to samples from other archaeological contexts (see for example Oudemans *et al*. 2005a, b). Sample no. 7163 shows the most prominent pattern of polycyclic aromatic hydrocarbons [m/ 128 and 142 from naphtalenes and m/z 252, 276, 302 and 326 from perylene and higher homologues].

Polysaccharides and lignocellulosic complexes have been subject to extensive studies in our group (Pastorova *et al*., 1993 and 1994, Van der Heijden *et al*.; 1993; Van der Haage *et al*. 1993). Residues from lignified matter were discovered in sample no. 7292 as m/z 85 and 114 from pentoses, m/z 144 and 126 from hexoses and lignin derived guaiacyl and syringyl markers at m/z 164 and 194. Proteins as heteropolymers with a polyamide backbone show very complex peak patterns in DTMS. Charred proteins are often rather aromatised and characterised by m/z 67, 92, 94, 107,

file number	DTMS code	material	fats/oils/resins	proteins	polysaccharides	other
no. 7292	11nov04012	charred processed cereal food	fatty acids C16:0 & C18:0 tocoferol	charred	hexosan and pentosan plus G/S lignin	reduced sulfur
no. 4084	11nov04011	charred crust on pottery	sequestered C16:0 & C18:0	charred	none	PAH soot reduced sulfur
no. 1059	11nov04013	charred crust on pottery	cholesterol, oxycholesterol phytosterols fatty acids C16:0, C18:0, C18:1, OHC18:1 cross-linked oils	charred	none	reduced sulphur (lots)
no. 7163	11nov04010	charred crust on pottery	trace of C16:0 and C18:0 FA	charred	none	PAH soot reduced sulphur
no. 9381	11nov04009	charred crust on pottery	cholesterol, oxycholesterol and phytosterols C16:0 , C18:0, C18:1 and OH-C18:1 FA Acylglycerols	charred	none	reduced sulphur

Table 20a.1 Summary of the main compounds observed in the DTMS data.

108, 117,131, 145, and 186. Studies by Oudemans *et al*. (2005a, b) and Braadbaart (2004) demonstrate the gradual loss of characteristic features at higher exposure temperatures. One feature recognized recently in charred protein reference material studies is the mass peak m/z 27 [HCN] that shows a steady increase at the higher analysis temperatures. HCN is presumably released from N-containing aromatic compounds. The presence of this feature is a sure sign of nitrogen compounds in the charred mass. Elemental analysis indeed confirmed this (Braadbaart 2004). The presence of HCN released at high temperature in the analytical profile was confirmed by mass chromatography in samples no's 9381, 7163, 4048, and 7292.

20a.3 Sample analysis description

Sample no. 7292; DTMS code 11nov04012)

The DTMS Total Ion Current trace (TIC) is relatively broad (scan 60-110) pointing to multiple polymeric fractions. There are no evaporating smaller compounds in this sample. The summation spectra in figure 20a.1 are summarised over three scan ranges (60-75 (a); 75-85(b); 85-95(c)). The range of 60-75 (a) shows peaks at 95, 96, 109, 110, 114 (pentose mass markers), 126 (hexose mass marker) pointing to partially charred polysaccharides. The peaks at 124, 150, 164, 178, 180, 194, 208 and 210 point to a partially preserved guaiacyl-syringyl lignin. These peaks have a somewhat higher intensity in the range 75-85 (b). The high relative intensity of m/z 44 from CO_2 resulting from decarboxylation points to the presence of acid groups which are usually an indication of oxidative conditions. The latter and the peak pattern demonstrate that the residue contains oxidized and thermally altered lignopolyssaccharides compared to fresh lignocellulosic plant matter. The m/z 64 (see c) is strong evidence for incorporation of reduced sulfur presumably from sulfate reduction by anaerobic bacteria. At lower scans very small amounts of the C16:0 and C18:0 fatty acids are observed and a peak at m/z 430 from tocoferols (partial spectrum not shown).

In conclusion: no evidence for preserved milk and meat fats, nor for starches. The lignopolysaccharide complex point to preserved lignocellulosic fractions from more woody plant parts. Can a possible contamination from peatified plant part of soil debris be excluded?

Sample 4084; DTMS code 11nov04011

The TIC, mass spectra and mass chromatograms are shown in figures 20a.2a-c. The TIC is rather broadened and peaks at scan 90 pointing to a highly condensed thermally resistant organic matter. A main peak in the spectrum is m/z 44 (CO_2) from decarboxylation of acids groups in the organic matter. Mass m/z 34 (H_2S) and m/z 64 (SO_2 or S_2) point to incorporation of sulfur in the organic matter. The range from 40-85 (a) shows peaks at m/z 252,276,302 from polycyclic aromatic hydrocarbons (PAH) (see also 7163 with a much stronger signature of soot) from soot deposited. There is evidence for m/z 256 and 284 from palmitic (C16) and stearic (C18) fatty acid in sequestered form, which is evidenced in the mass chromagram of m/z 129 (general fatty acid fragment ion) and m/z 284 (stearic acid molecular ion). The sample shows a complex envelope that resembles charred proteins. Further evidence for nitrogen compound

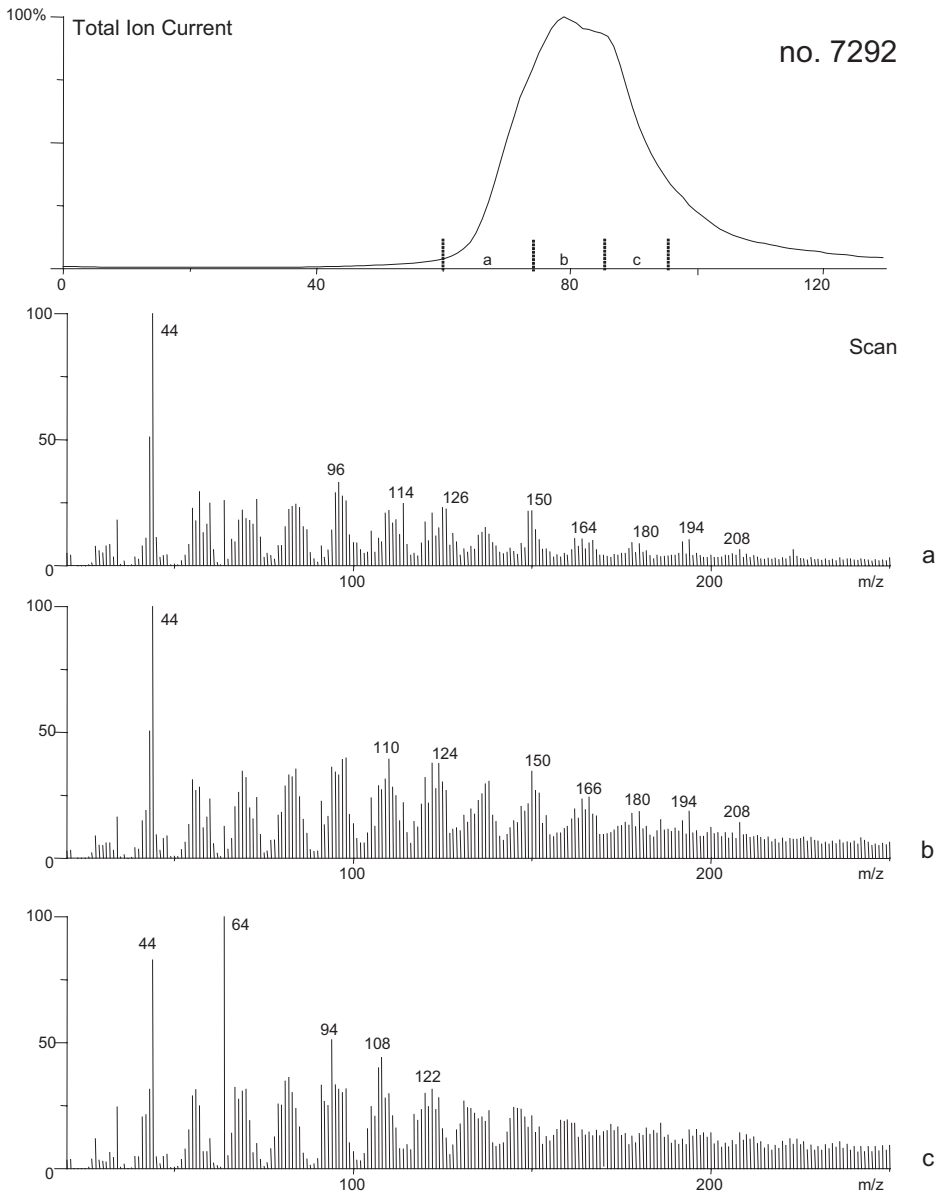

Figure 20a.1 DTMS data of Schipluiden no. 7092 charred food (?) material showing a total ion current profile and the mass spectra summarised over in the scan ranges corresponding to thermally induced dissociation events of lignocellulosic materials (scan range a, b and c). Mass spectrum a corresponds to pentose and hexose polysaccharides with some peaks for guaiacyl and syringyl lignin.

incorporation is found in the profile of m/z 27 (HCN) in figures 20a. 2a-b. The prominence of m/z 78, 91, 92, 128, 142 from alkyl benzenes and naphtalenes points to high degrees of carbonisation and condensation.

In conclusion: No evidence for starch and fats. Food source hard to give but proteins are contributing to the signature. Evidence for soot is present.

Sample 1059; DTMS code 11nov04013

The TIC, mass spectra and mass chromatograms are shown in figure 20a.3. TIC ranges from scan 55-100 pointing to a condensed residue. The mass chromatogram of significant marker peaks point to a relatively uniform dissociation of the organic matter in the sample with the exception of m/z 386 from cholesterol. Peaks m/z 129 (general marker for fatty acids) and m/z 284 from stearic acid point to sequestered fatty acids. M/z 117 (from tryptophane) and m/z 27 are evidence for proteins. Further inspection of figure 20a.3 demonstrates a rich peak pattern. The zone is interpreted as a DTMS of a charred protein possibly mixed with some plant oils. The scan range from 59-73 shows a peak pattern from dehydrated phytosterols (C27:368;

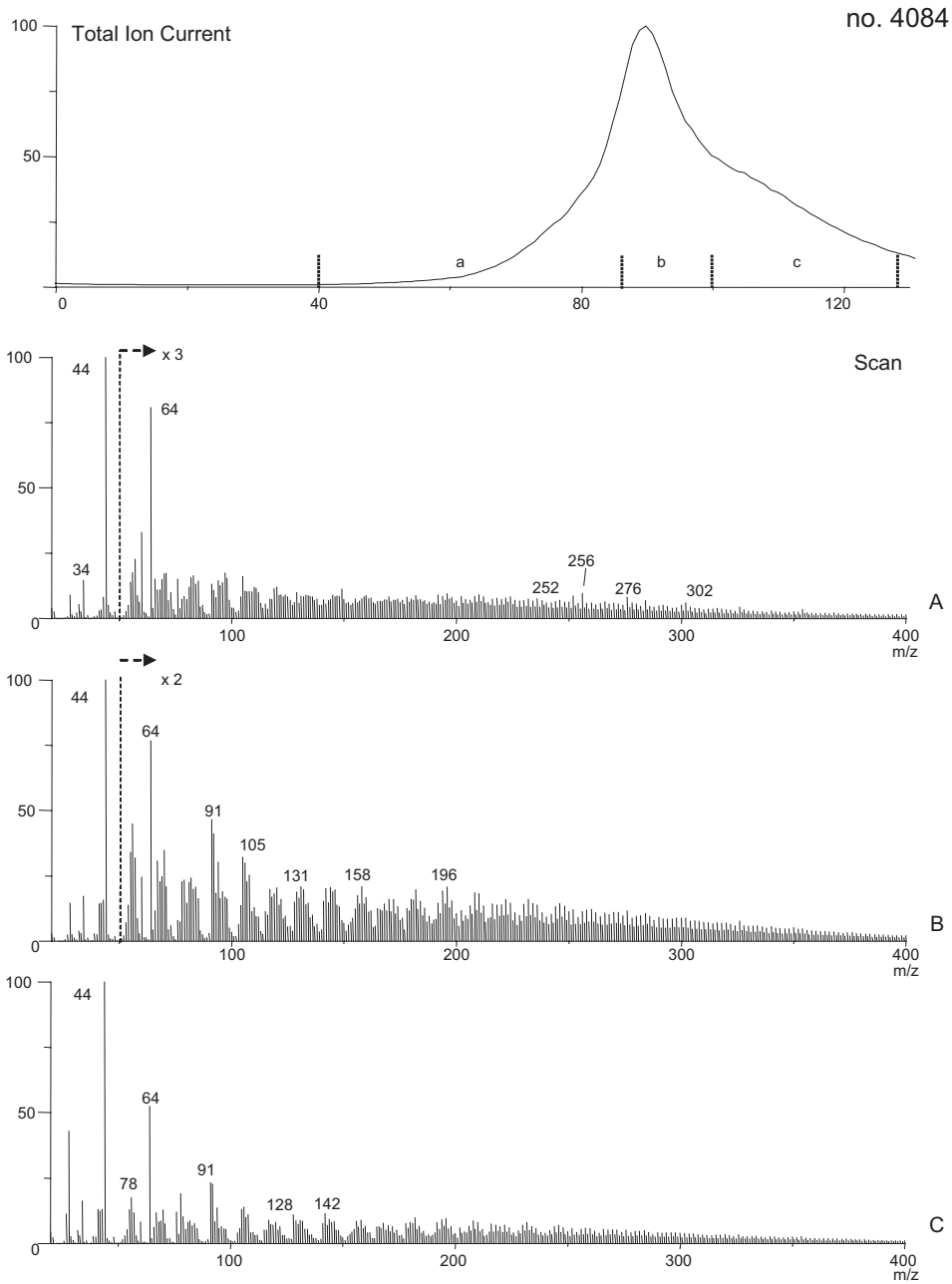

Figure 20a.2a

C28:382 and C29:396) and an oxycholesterol at m/z 400. The highest peak at m/z 386 in combination with 368 points to cholesterol. There are several peaks from fatty acids such as m/z 256 (C16:0), 264 (acylium ion of C18:1), m/z 280 (C18:2, but more likely a dehydration product of OH-C18:1) and 284 (C18:0). The fatty acid moieties in this sample shows a remarkable degree of preservation. I suspect that this is caused by the very abundant presence of reduced sulfur evidenced by m/z 34 (H_2S) and 64 (S_2) with its isotope at 66. No acyldiglycerides were observed suggesting that the fatty acids are eliminated directly from the organic matter.

In conclusion: sulfur plays a role in the preservation of the unsaturated fatty acids and sterols. The observed composition points to a plant oil source. There are no preserved diglycerides that could support a milk source for the lipids.

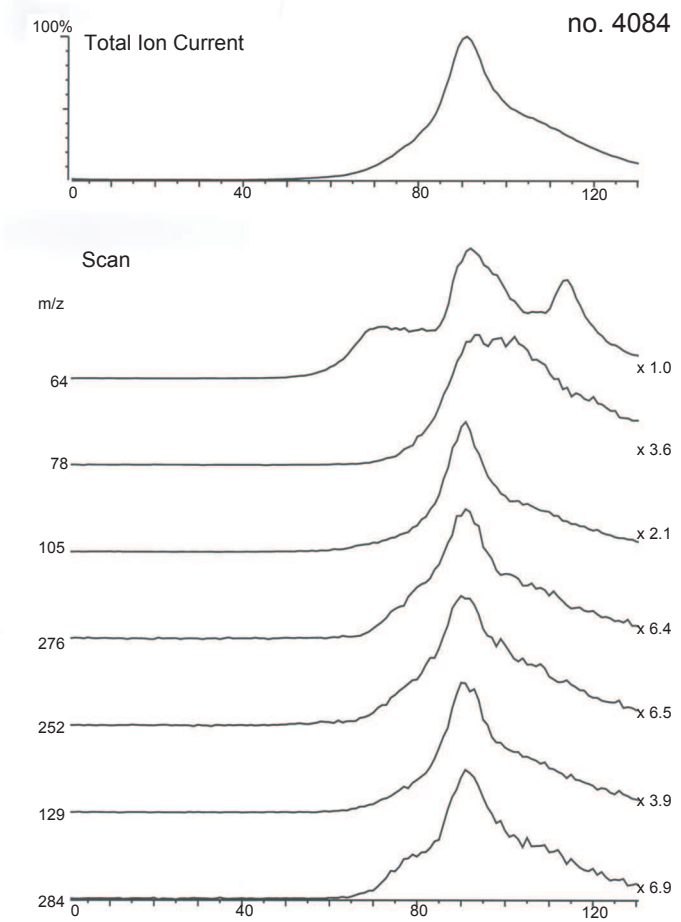

Figure 20a.2b

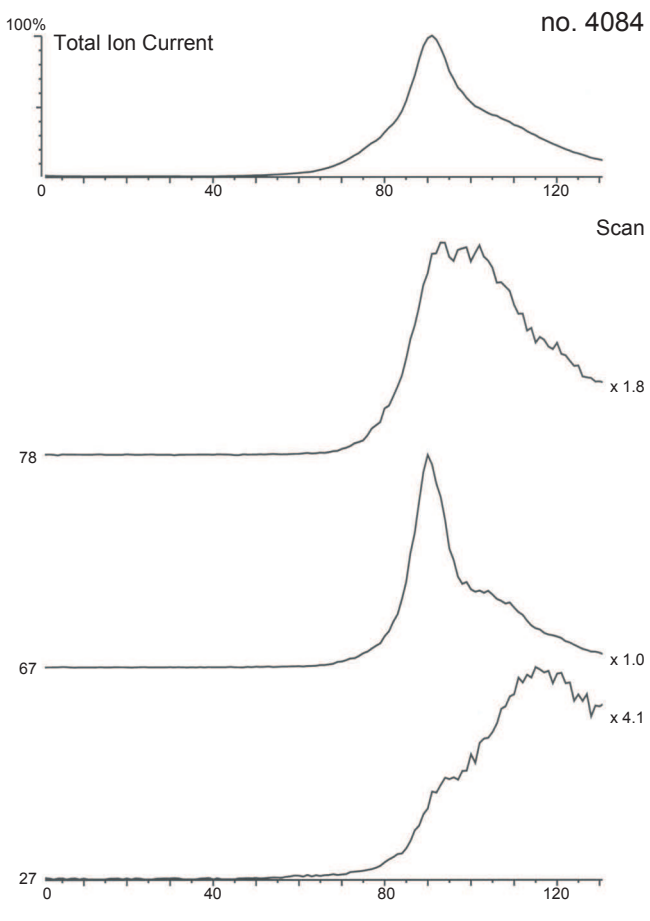

Figure 20a.2c

Figure 20a.2 DTMS data of Schipluiden no. 4084 charred material on pottery.
a Total ion current profile and the mass spectra summarised over in the scan ranges A, B and C.
b Mass chromatograms of selected single ion profiles plotted as a function of temperature showing fatty acids (m/z 129 and 284), polycyclic aromatic hydrocarbons (m/z 252 and 276) and condensed fractions (m/z 105 and 78). Mass 64 is indicative for various forms of sulfur compounds because of its multiple peak profile. The profiles are normalized to maximum intensity per channel hence the multiplication factors.
c Mass chromatograms as selected single ion profiles as a function of temperature of charred proteins (m/z 27 and 67) and condensed fractions (m/z 78).

The combination of proteins and plant oil derived compounds suggest that plant seeds might be the source of the organic matter.

Sample no. 7163; DTMS code 11nov04010
The TIC is very broad. The spectral data (20-75) suggest strongly the presence of soot by the PAH with molecular ions at m/z 252, 276, 302, 326 (see also fig. 20a.4). These compounds desorb clearly before the dissociation event from the charred protein. The thermal behaviour of m/z 64 that shows five separate elimination events is extremely peculiar and points to multiple forms of sulfur. There are some tiny amounts of sequestered C16:0 and C18:0 fatty acids.

In conclusion: no evidence for starch, but clearly evidence for charred proteins and soot.

Sample no. 9381; DTMS code 11nov04009
The DTMS data in the lower temperature range (see fig. 20a.5) shows evidence for cholesterol (m/z 386 and 368), oxycholesterol (m/z 400) and phytosterols (m/z 382 and 396). The sterols evaporate already in the scan range of

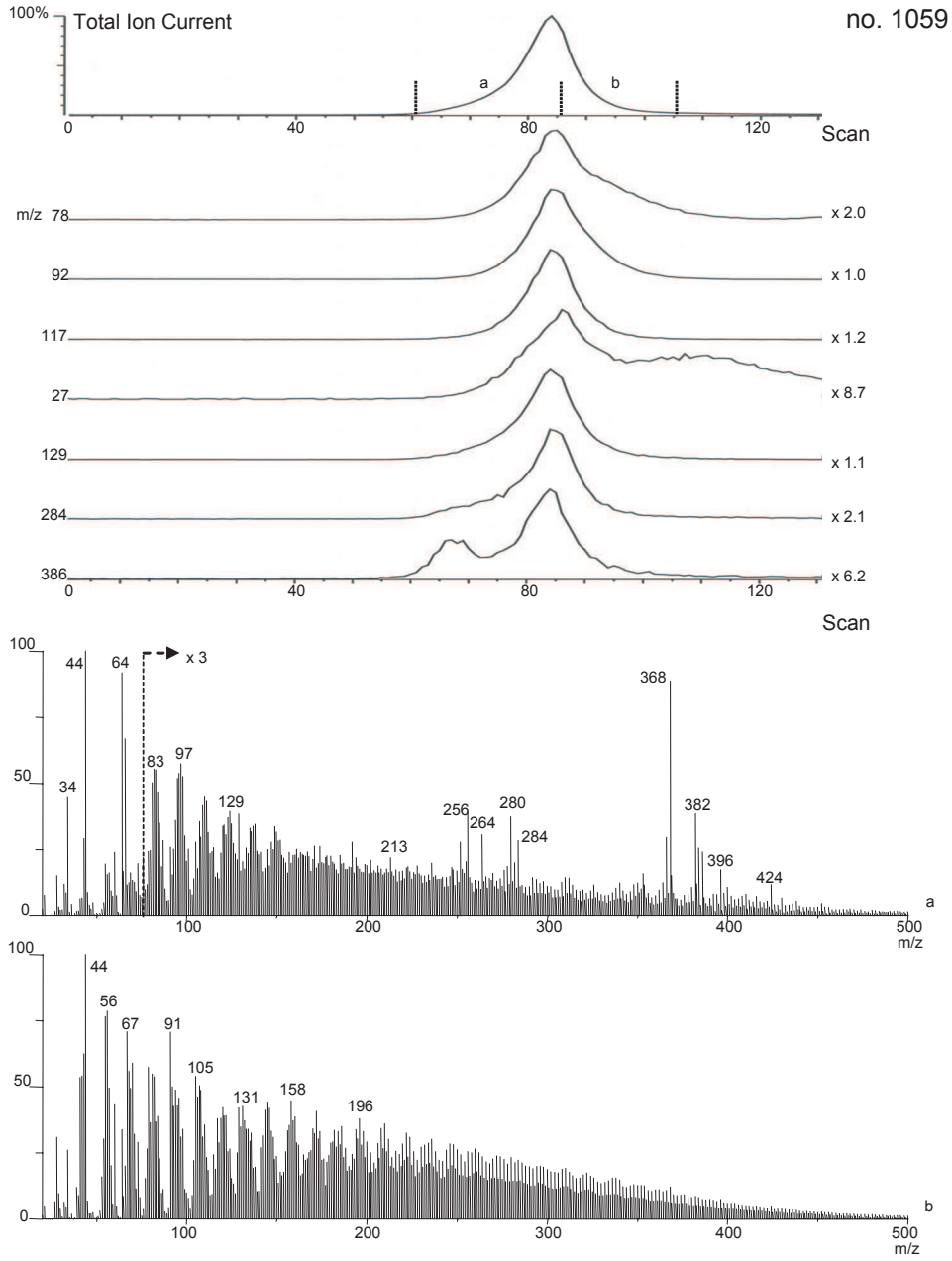

Figure 20a.3 DTMS data of Schipluiden no. 1059 charred crust on pottery showing a total ion current trace, mass chromatograms and summary spectra over scan range a and b. The mass chromatograms of selected single ion profiles plotted as a function of temperature show the profiles of appearance of cholesterol (m/z 386), fatty acids (m/z 129 and 284), charred proteins (m/z 27, 117, and 92) and condensed fractions (m/z 78). The profiles are normalized to maximum intensity per channel hence the multiplication factors.

30-40 (a) which means that they are loosely adsorbed. The fatty acids of this sample show C16:0, C18:0, C18:1 and OH-C18:1 or C18:2 but these are sequestered in the condensed organic matter part of the sample because they appear between scan 50 and 125. The distribution pattern resembles the data from sample 1059. Reduced forms of sulfur also play a role in this sample. The cross-linked material shows evidence for proteins (see fig. 20a.5) mass chromatograms of m/z 117, 67, 27 and the spectra in fig. 20a.5). In this sample some diacylglycerols from C16/C16, C16/C18:1, C16/C18 and C18/C18 are observed pointing to some preservation of the biological glycerol ester bond.

In conclusion: no evidence for carbohydrates and polysaccharides. Evidence for charred proteins in combination with saturated and a monounsaturated fatty acid. Several sterols suggest a plant oil source. The composition of the sample resembles sample 1059.

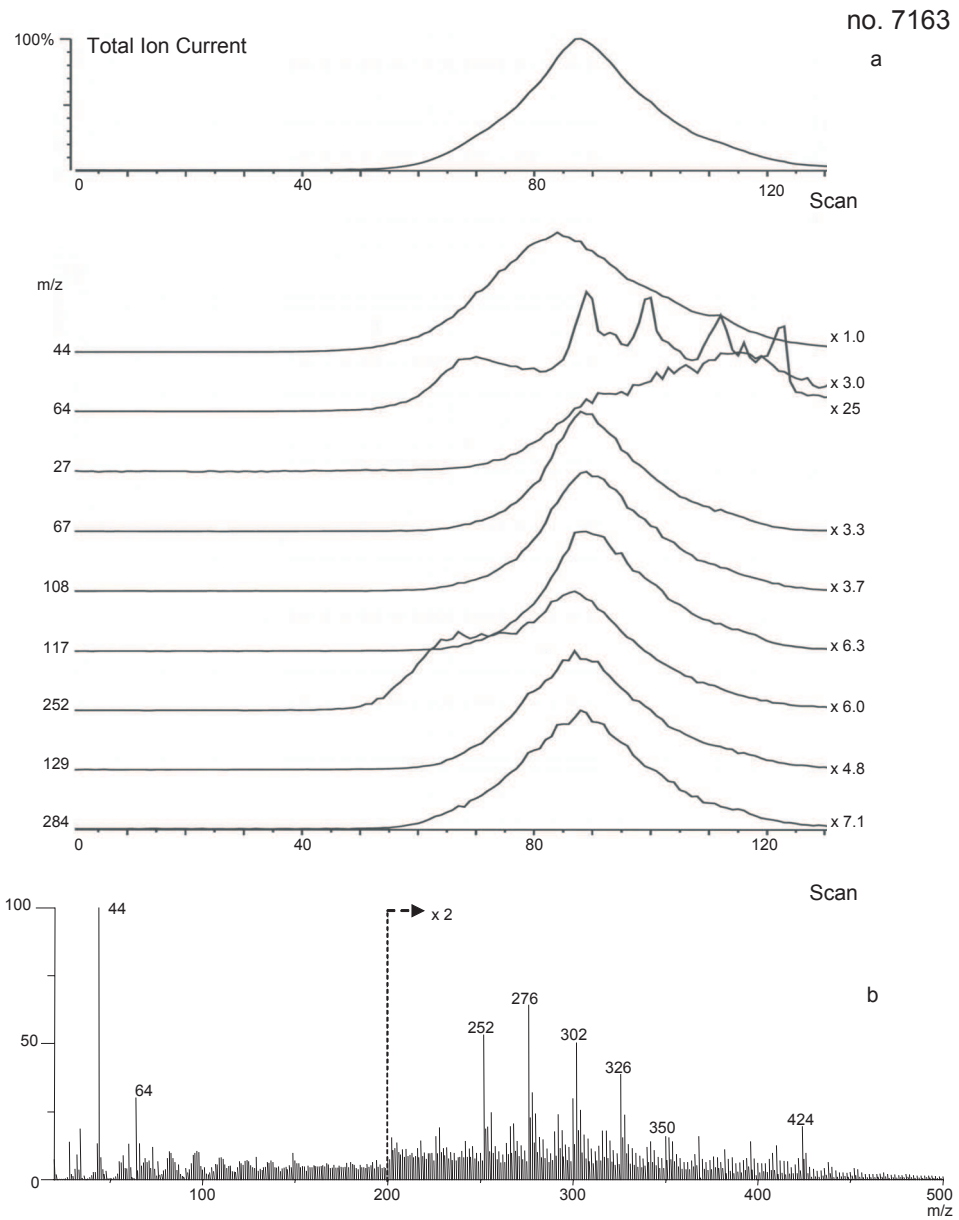

Figure 20a.4 DTMS data of Schipluiden no. 7163 charred crust on pottery showing a total ion current trace, mass chromatograms and the summary spectrum over scan range from 50-90 (b). The mass spectrum (b) shows an intense pattern of polycyclic aromatic hydrocarbons from soot. Note the peculiar multiple peak pattern of m/z 64 pointing to multiple emission events and thus forms of sulfur in the crust. The profiles are normalized to maximum intensity per channel hence the multiplication factors.

20a.4 Final remarks

I have assumed that the samples are not contaminated. The sequestered nature of many features is a kind of guarantee that no foreign materials have been introduced. Sulfur plays presumably an important role in the preservation of the unsaturated fatty acids. In contrast to other residues from the Roman Iron Age analysed earlier by Oudemans, there are very few acylglycerols preserved. Is the soil perhaps rather acidic? This is unfortunate because these compounds play an important role in the identification of animal fats and milk fats. There is no evidence for starch but sample 7292 shows preserved thermally altered lignocelluloses. It is not very likely that this sample represents porridge. The proteins were recognisable by some tracer features but their degree of charring is relatively high.

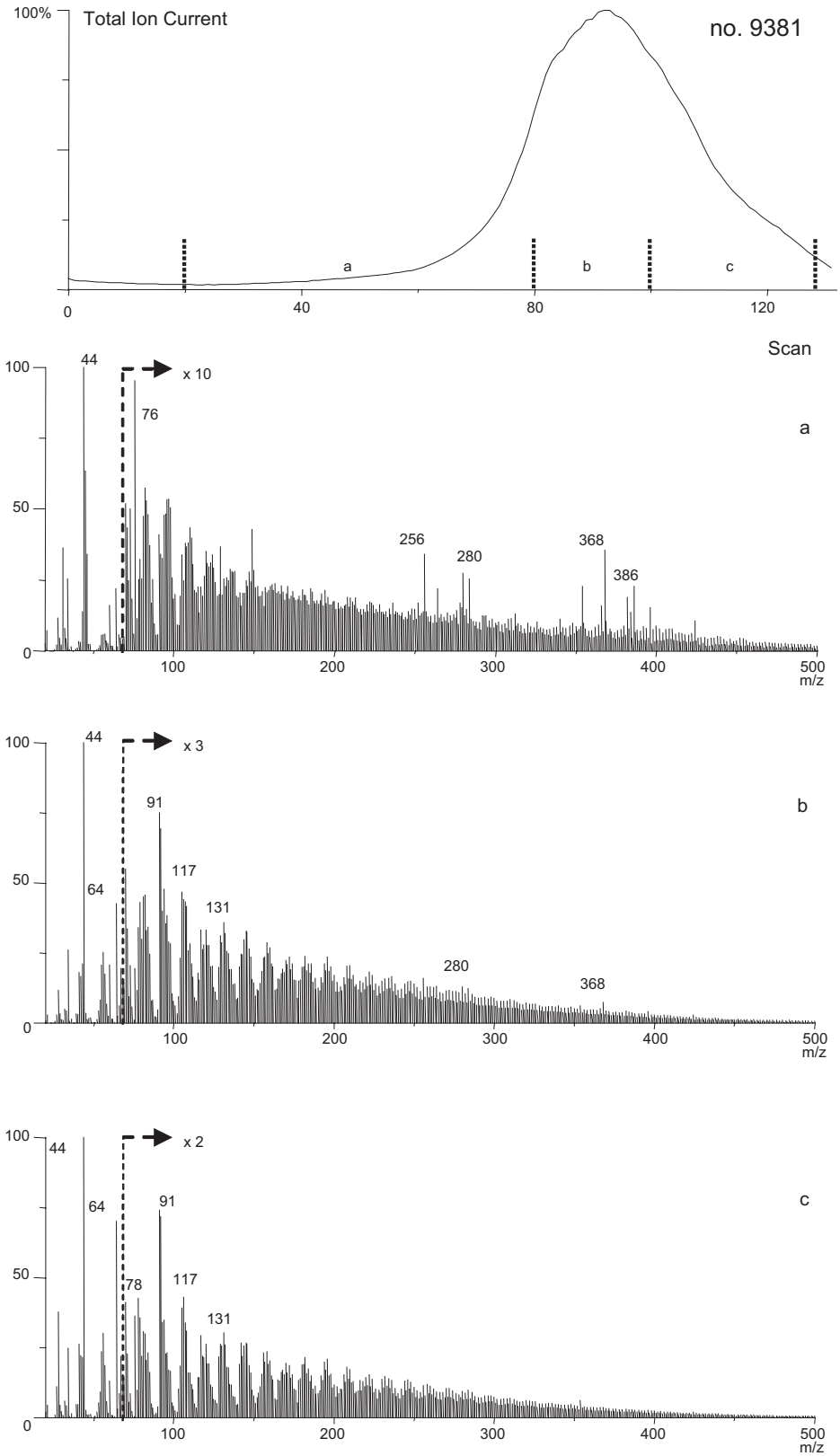

Figure 20a.5 DTMS data of Schipluiden no. 9381 charred material on pottery.
a Total ion current profile and the mass spectra summarised over in the scan ranges a, b and c.

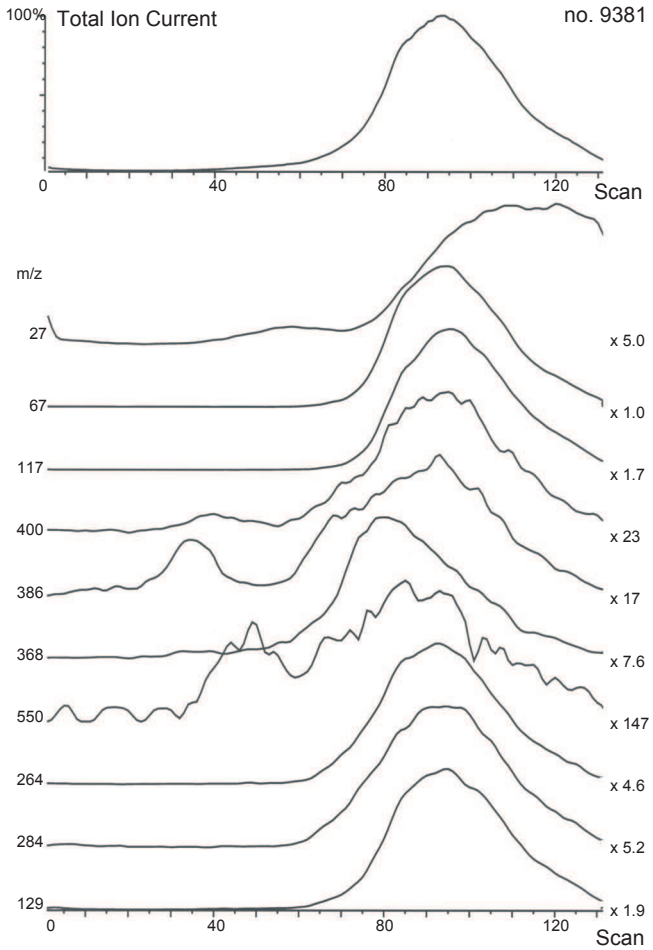

Figure 20a.5 (cont.)
b Mass chromatograms as selected single ion profiles as a function of temperature of fatty acids (m/z 129, 264, 284), diacylglycerols (m/z 550), cholesterols (m/z 368, 386 and 400), charred proteins (m/z 27 and 67) and condensed fractions (m/z 78). The profiles are normalized to maximum intensity per channel hence the multiplication factors.

References

Braadbaart, F. 2004. *Carbonisation of peas and wheat – a window into the past,* PhD thesis Leiden.

Hage, E.R.E. van der/M.M. Mulder/J.J. Boon 1993. Structural characterization of lignin polymers by temperature resolved in-source pyrolysis mass spectrometry and Curie-point pyrolysis gas chromatography/mass spectrometry, *Journal of Analytical and Applied Pyrolysis* 25, 149-183.

Heijden, E. van der/J.J. Boon 1994. A combined pyrolysis mass spectrometric and light microscopic study of peatified *Calluna* wood isolated from raised bog peat deposits, *Organic Geochemistry* 22, 903-919.

Oudemans, T.F.M/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* 26, 221-234.

Oudemans,T.F.M./G.B. Eijkel/J.J. Boon 2005a. DTMS and DTMS/MS study of solid organic residues preserved on ancient vessels. In: H.Kars/E.Burke (eds.) *The 33rd International Symposium on Archaeometry 22-26 April 2002, Vrije Universiteit Amsterdam*, Amsterdam, 501-505.

Oudemans,T.F.M./J.J. Boon/G.B. Eijkel 2005b. Identifying biomolecular origins of solid organic residues preserved on Iron Age pottery using DTMS and MVA, *Journal of Archaeological Science* (in press).

Pastorova,I./T.F.M. Oudemans/J.J. Boon 1993. Experimental polysaccharide chars and their "fingerprints" in charred archaeological food residues, *Journal of Analytical and Applied Pyrolysis*25, 63-75.

Pastorova, I./R.E. Botto/P.W. Arisz/J.J. Boon 1994. Cellulose char structure: a combined analytical Py-GC-MS, FTIR, and NMR study, *Carbohydrate Research* 262, 27-47.

Regert, M./C. Rolando 2002. Identification of archaeological adhesives using direct inlet electron ionization mass spectrometry, *Analytical Chemistry* 74, 965-975.

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