Analysis of sherd samples from Cheviot Quarry, Northumberland, for organic residues by Gas Chromatography-Mass Spectrometry.

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Sample preparation

Where present, scrapings of any adhering visible residues were taken from the interior surface the sherds. Sub-samples of the ceramic (between 0.1 and 0.3 g) were also removed to a depth of 2mm from both the exterior and interior surfaces of each sherd with a *Dremmel* electric drill fitted with a tungsten abrasive bit. The interior/exterior was determined by the sherd curvature.

These samples were extracted with three aliquots of ~3 ml DCM:MeOH (dichloromethane:methanol 2:1, v/v), with ultrasonication for 5 min. The solvent extract was transferred to a clean glass vial. The solvent was removed under a stream of nitrogen. Excess BSTFA (N, O- bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane) (*Pierce*) was added to derivatise the sample. An additional drop of DCM was added to ensure thorough mixing of sample and reagent, and the sample was left overnight. Excess derivatising agent was removed under a stream of nitrogen. The samples were diluted in DCM for analysis by GC-MS. A modern pot (previously solvent extracted) was also analysed using the same method as the samples.

Instrumental (GC-MS)

Analysis was carried out by combined gas chromatography-mass spectrometry (GC-MS) using a *Hewlett Packard* 5890 series II GC connected to a 5972 series mass selective detector. The splitless injector and interface were maintained at 300°C and 340°C respectively. Helium was the carrier gas at constant inlet pressure. The temperature of the oven was programmed from 50°C (2 min.) to 340°C (10 min.) at 10°C/min. The GC was fitted with a 15m X 0.25mm, 0.1μm OV1 phase fused silica column (*MEGA*). The column was directly inserted into the ion source where electron impact (EI) spectra were obtained at 70 eV with full scan from *m/z* 50 to 700.

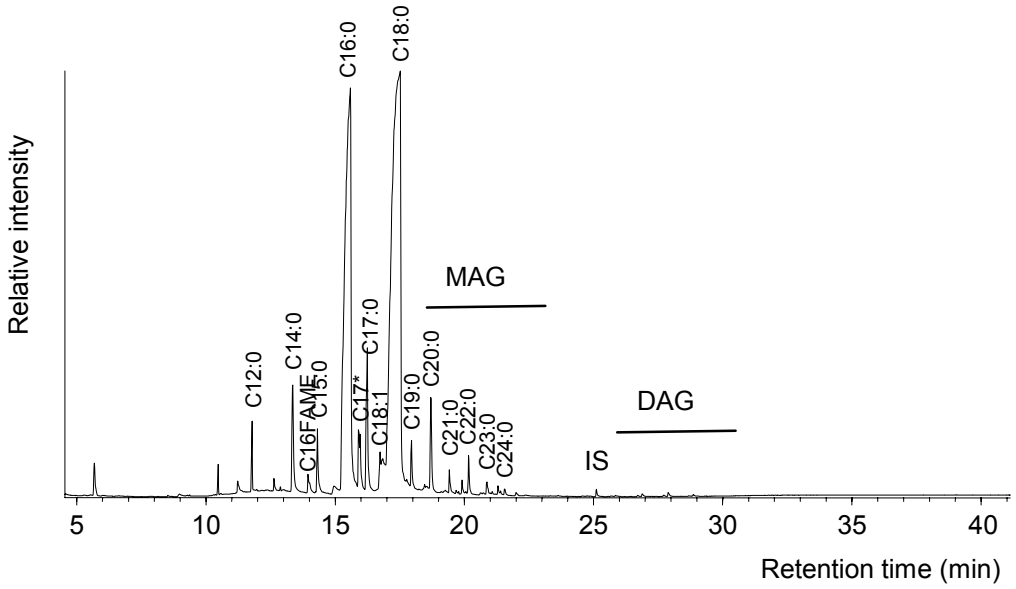
Results

The results are presented as total ion chromatograms of the BSTFA derivatized solvent extract. These show each separated component of the solvent extract as discrete peaks, the area under each peak being representative of the abundance. Extracts from the same sherd (interior, exterior and visible residue (when present)) are shown on the same page. Where identified, components have been labelled:

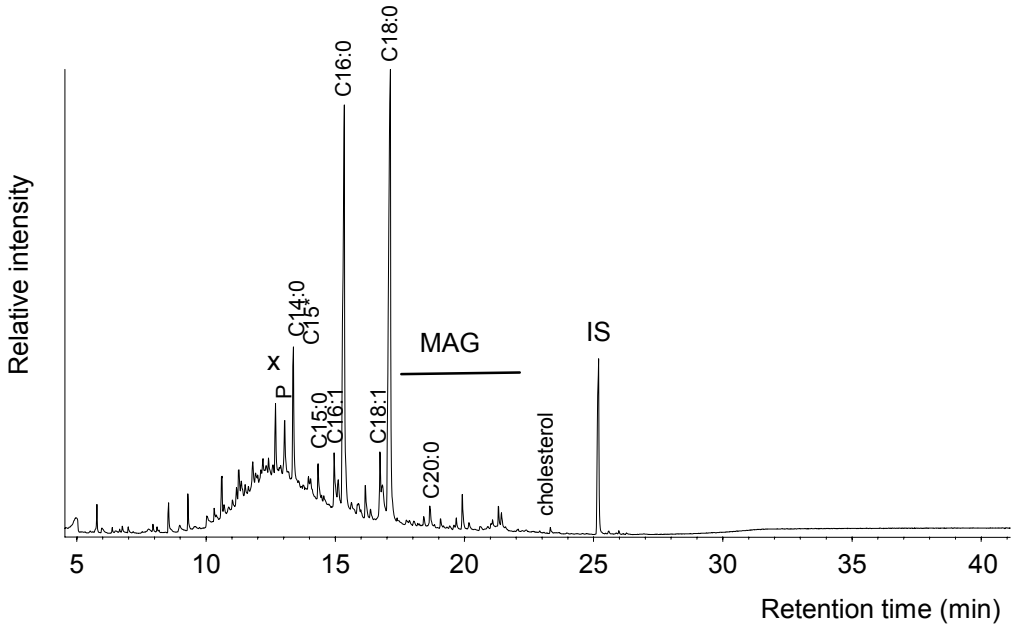
P = Phthalate plasticiser
x = analytical artefact
● = *n*-alkane
C = Fatty acid, with selected carbon numbers and degree of unsaturation, * indicated branched chain fatty acid
FAME = Fatty acid methyl ester, with selected carbon numbers
MAG = a range of monoacylglycerols
DAG = a range of diacylglycerols

For the hopanes:
1= Norhopane (C29), 2= Hopane (C30), 3= Homohopane (C31), 4= Homohopane (C31), 5= Bishomohopane (C32*), 6= Bishomohopane (C32), 7= Trishomohopane (C33*), 8= Trishomohopane (C33), *chiral at C22 so observe both isomers.

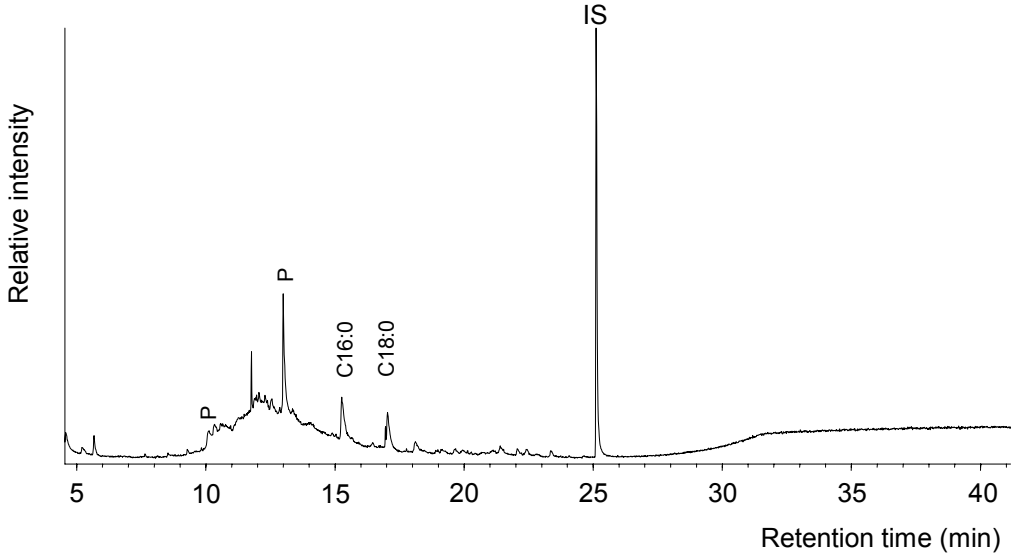
F3128I: Internal ceramic absorbed. Wood 05 pit F31 (052) [176] carinated bowl vessel No 28



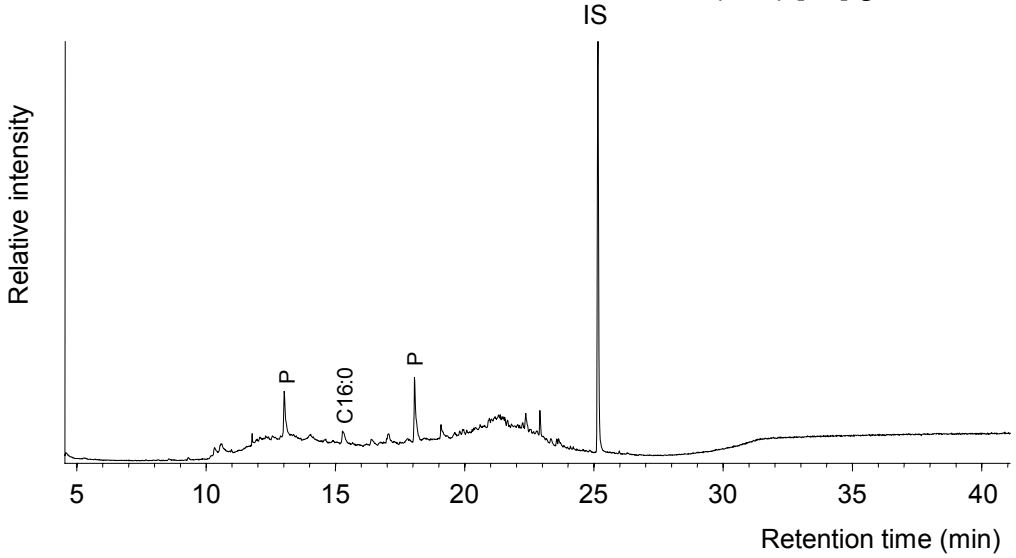
F3128E: External ceramic absorbed. Wood 05 pit F31 (052) [176] carinated bowl vessel No 28



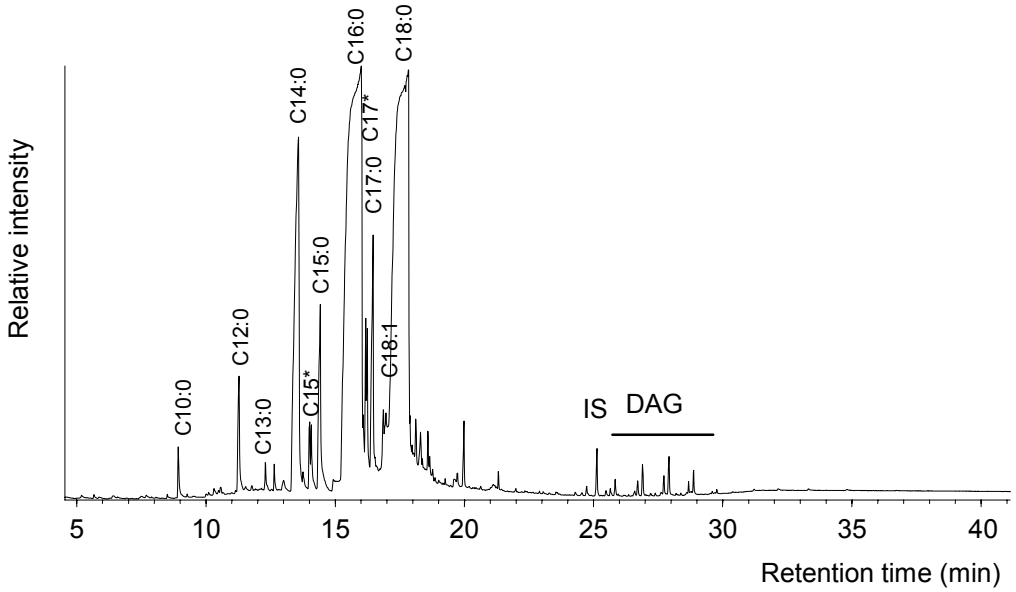
F13317I: Internal ceramic absorbed. Wood 05/2 (133) [17] grooved ware pot No 2



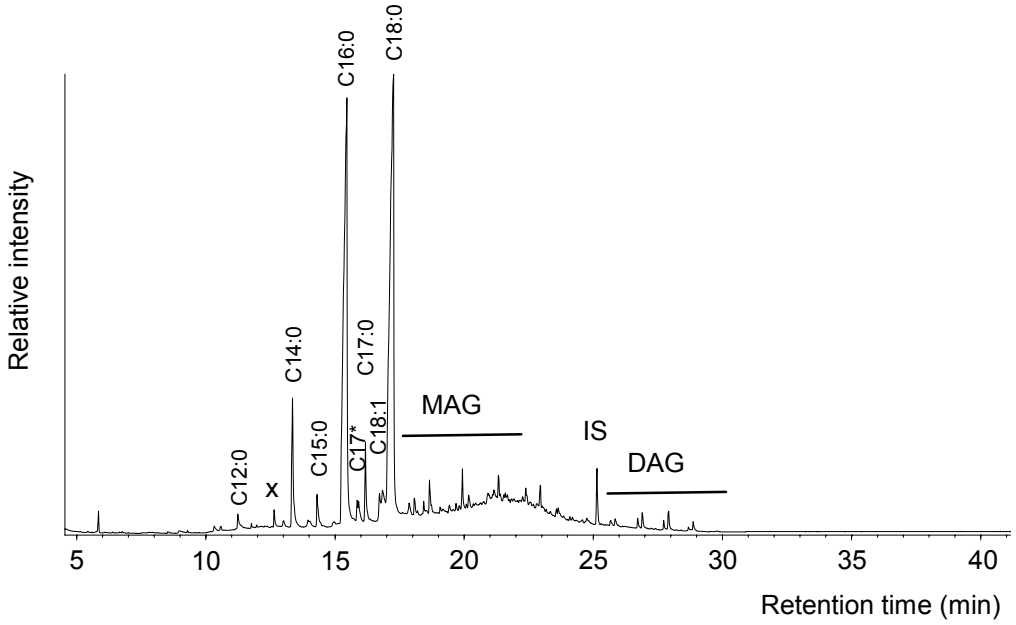
F13317E: External ceramic absorbed. Wood 05/2 (133) [17] grooved ware pot No 2



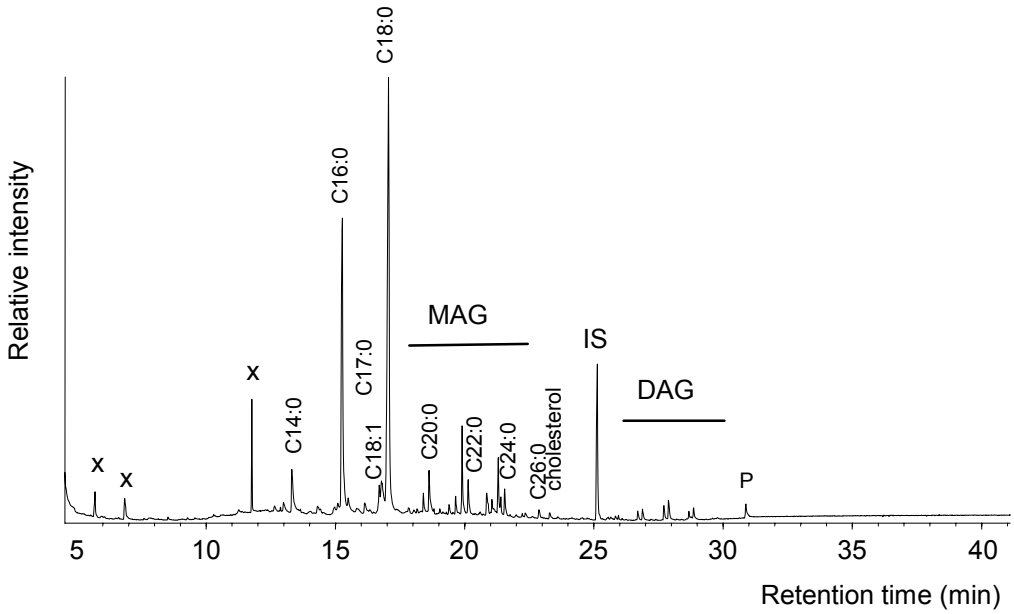
F5110I: Internal ceramic absorbed. Wood 05 F(51) [28] carinated bowl pot No 10



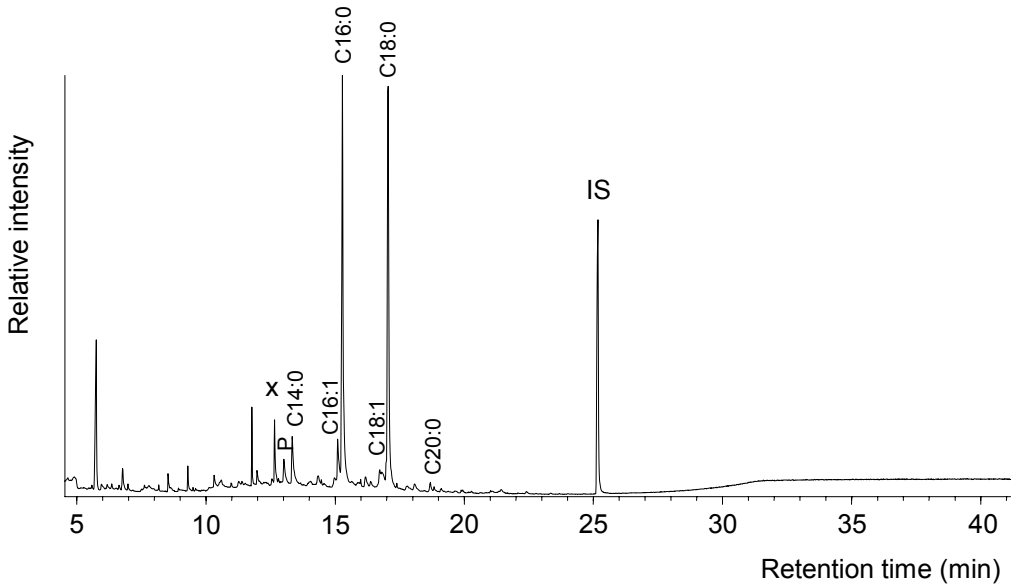
F5110E: External ceramic absorbed. Wood 05 F(51) [28] carinated bowl pot No 10



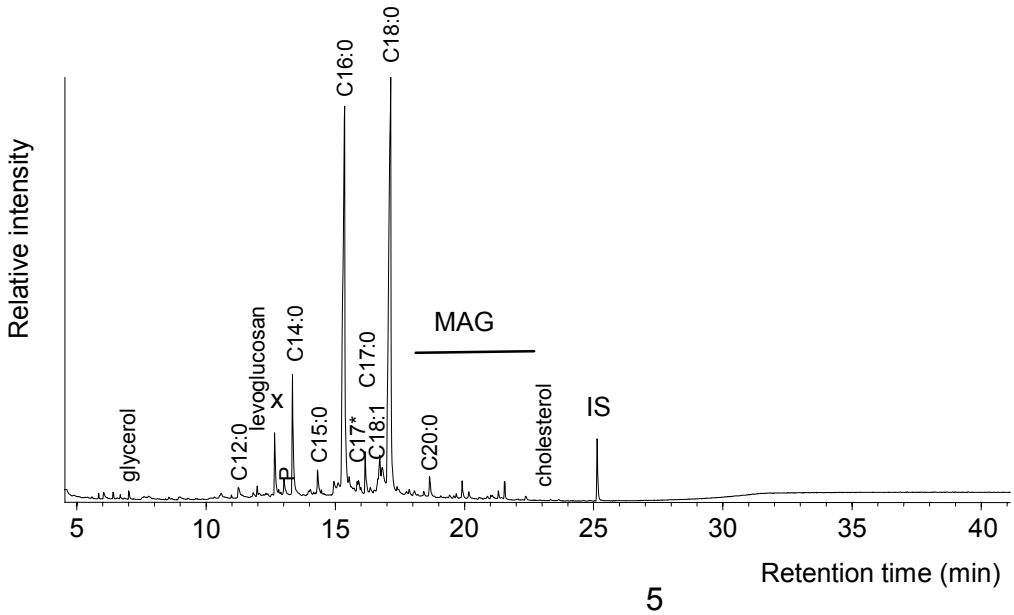
F13318I: Internal ceramic absorbed. Wood 05/2 (133) [18] grooved ware base sherd pot 2



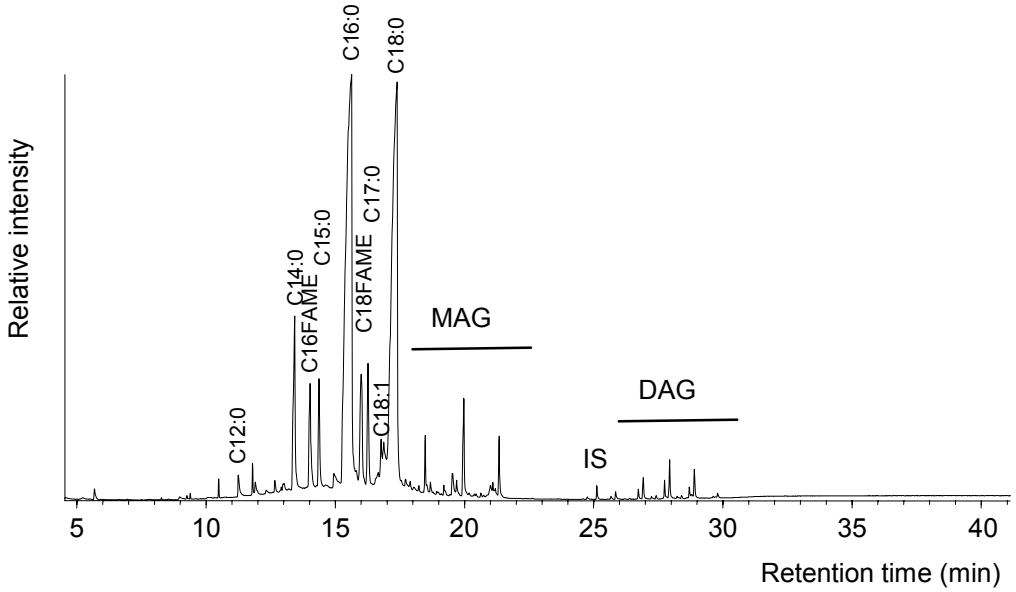
F13318E: External ceramic absorbed. Wood 05/2 (133) [18] grooved ware base sherd pot 2



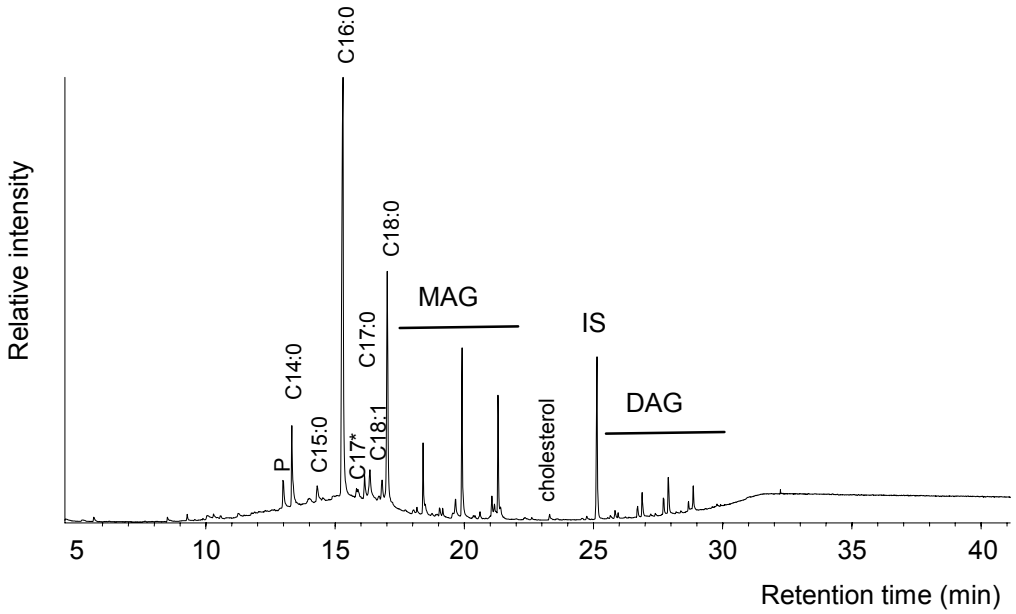
F13318V: Visible residue from interior. Wood 05/2 (133) [18] grooved ware base sherd pot 2



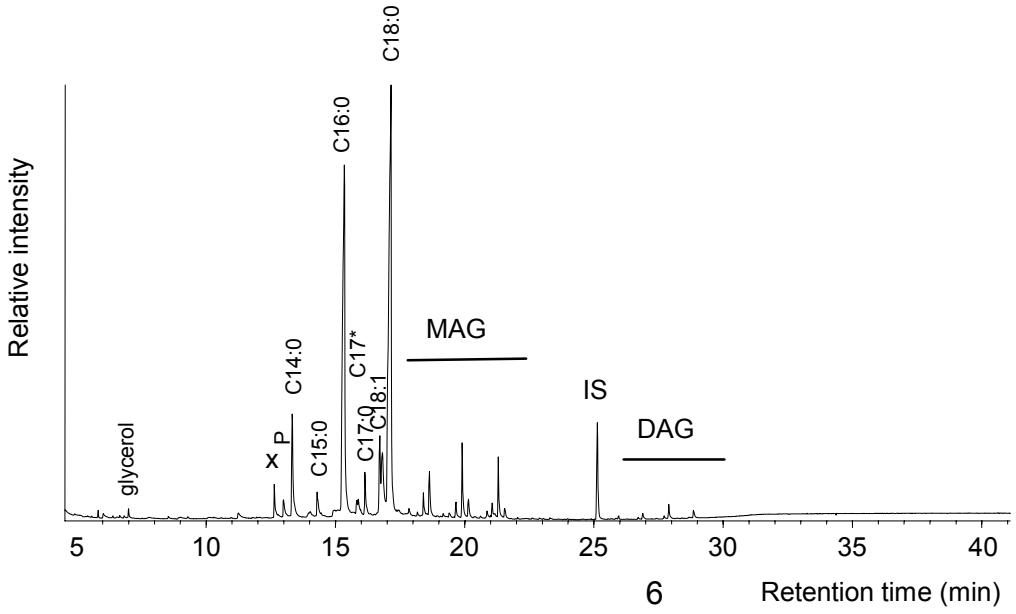
MAP1I: Internal ceramic absorbed. MAP pot 1 Rustic beaker with residue



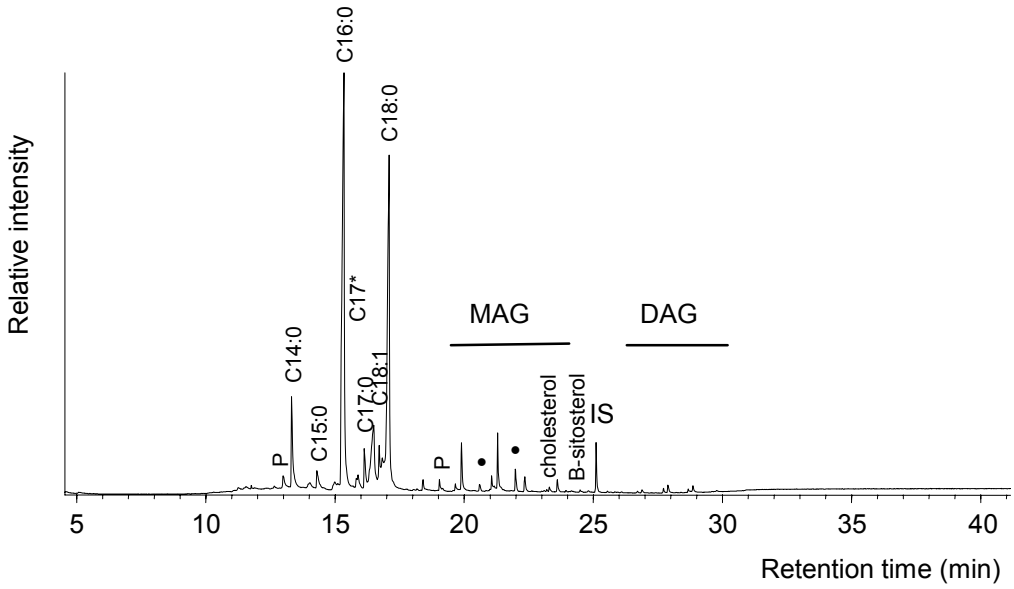
MAP1E: External ceramic absorbed. MAP pot 1 Rustic beaker with residue



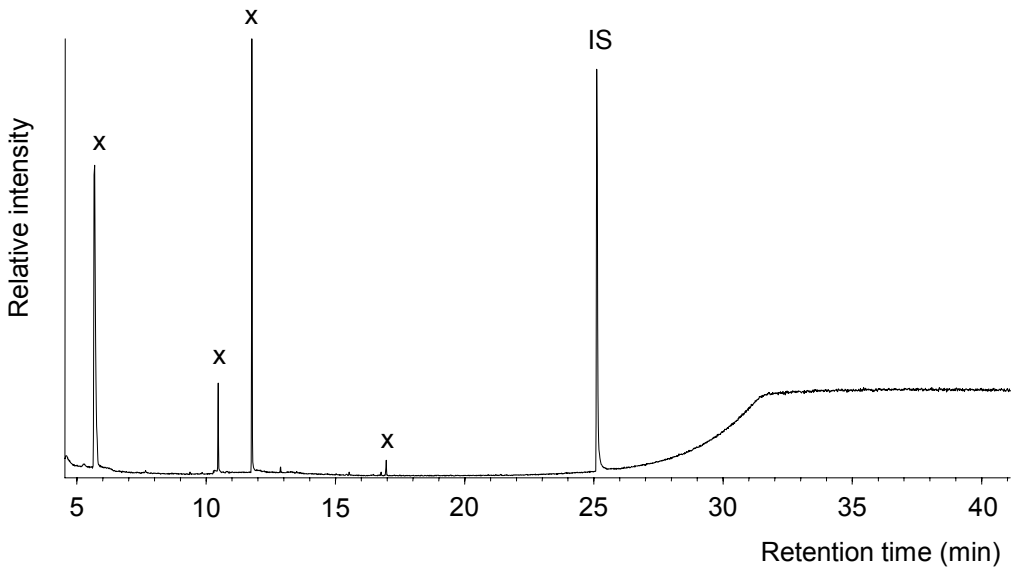
MAP1V: visible residue from interior. MAP pot 1 Rustic beaker with residue



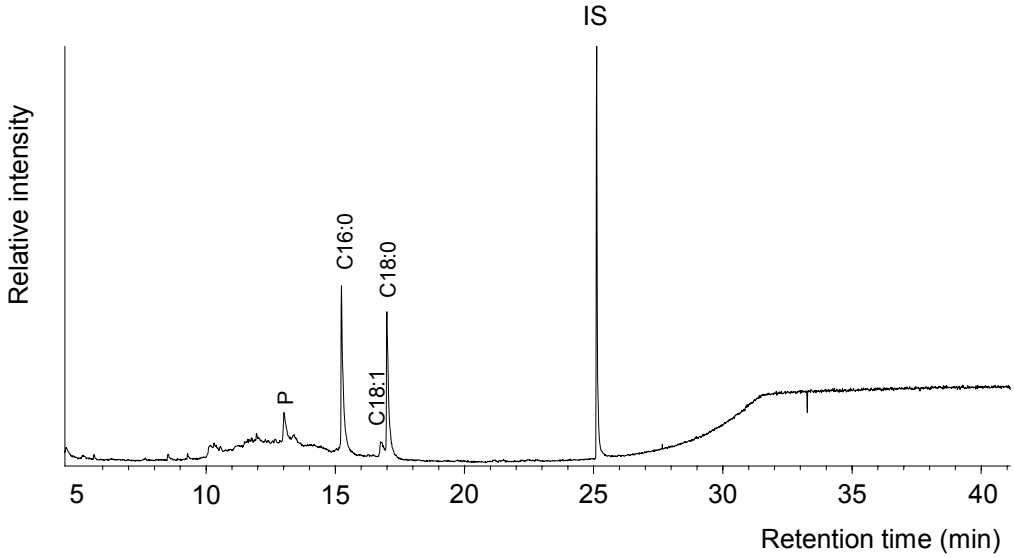
MAP204I: Internal ceramic absorbed. MAP F204 [Map1] impressed ware body sherd



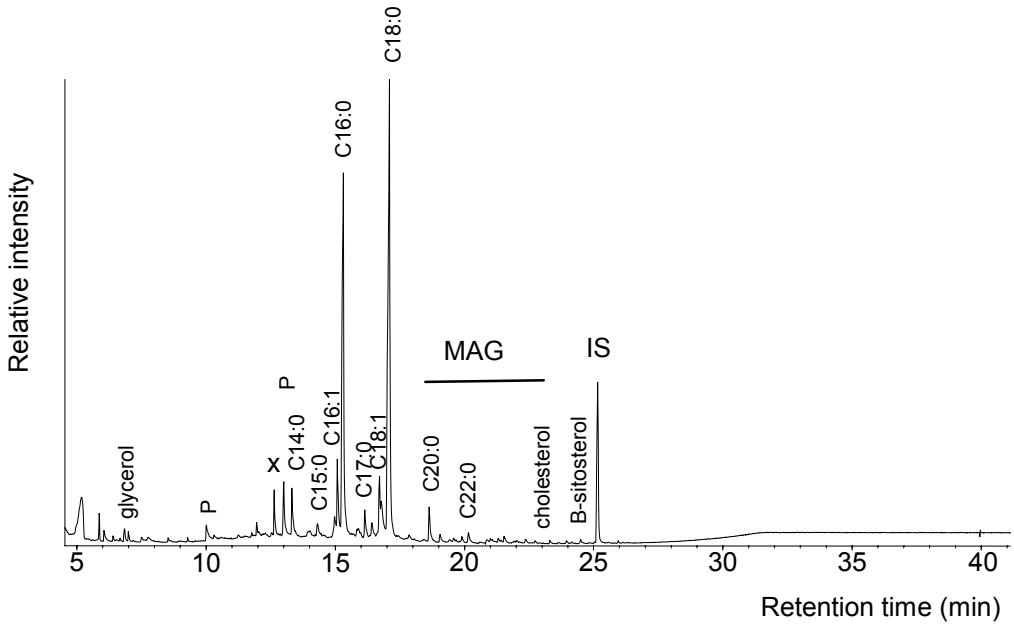
MAP204E: External ceramic absorbed. MAP F204 [Map1] impressed ware body sherd



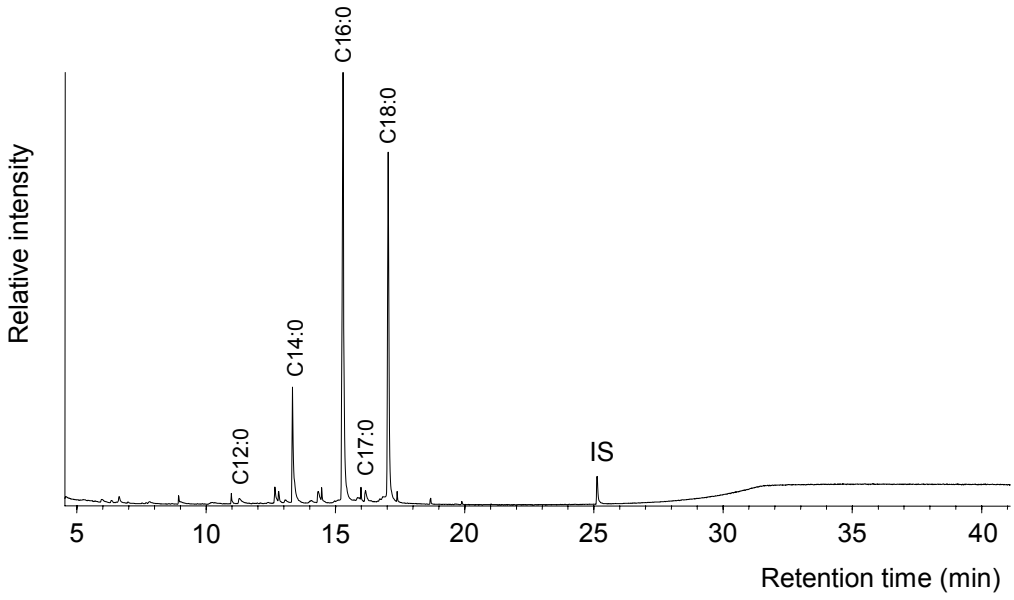
MAP2204I: Internal ceramic absorbed. MAP F204 [Map2] impressed ware body sherd



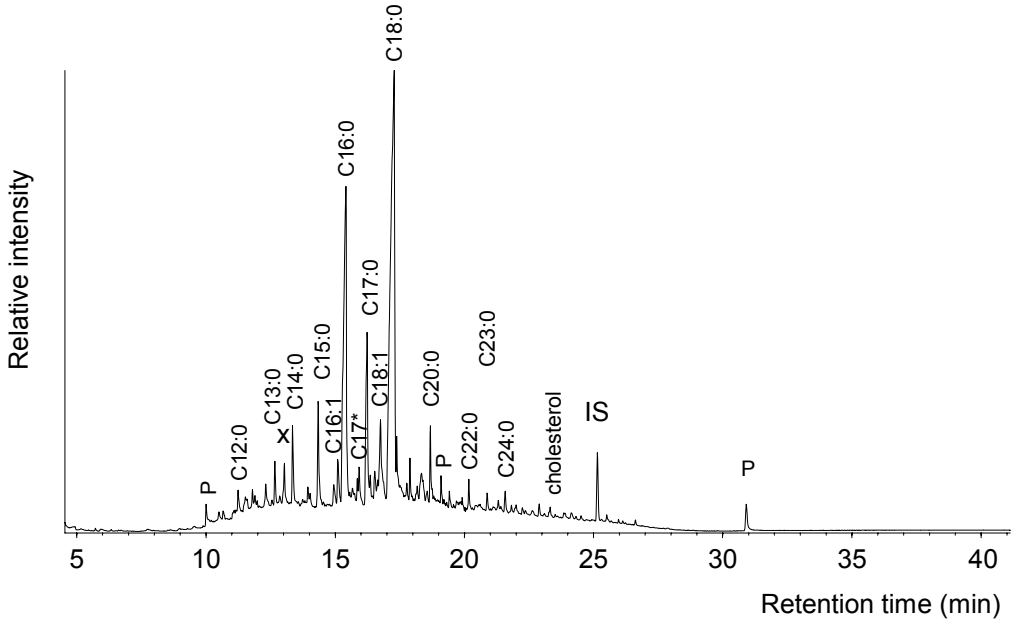
MAP2204E: External ceramic absorbed. MAP F204 [Map2] impressed ware body sherd



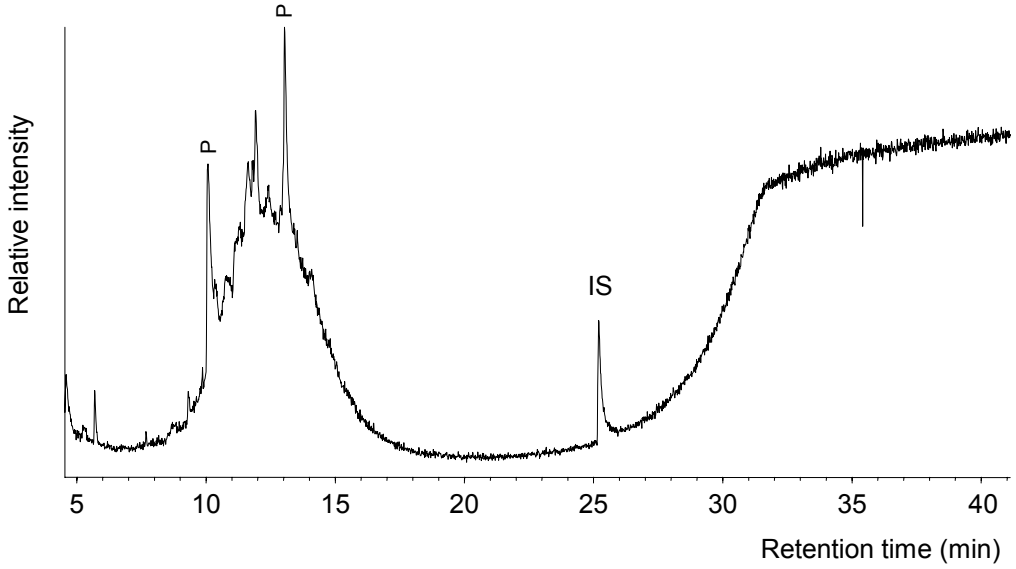
MAP2204EV: Visible residue from exterior. MAP F204 [Map2] impressed ware body sherd



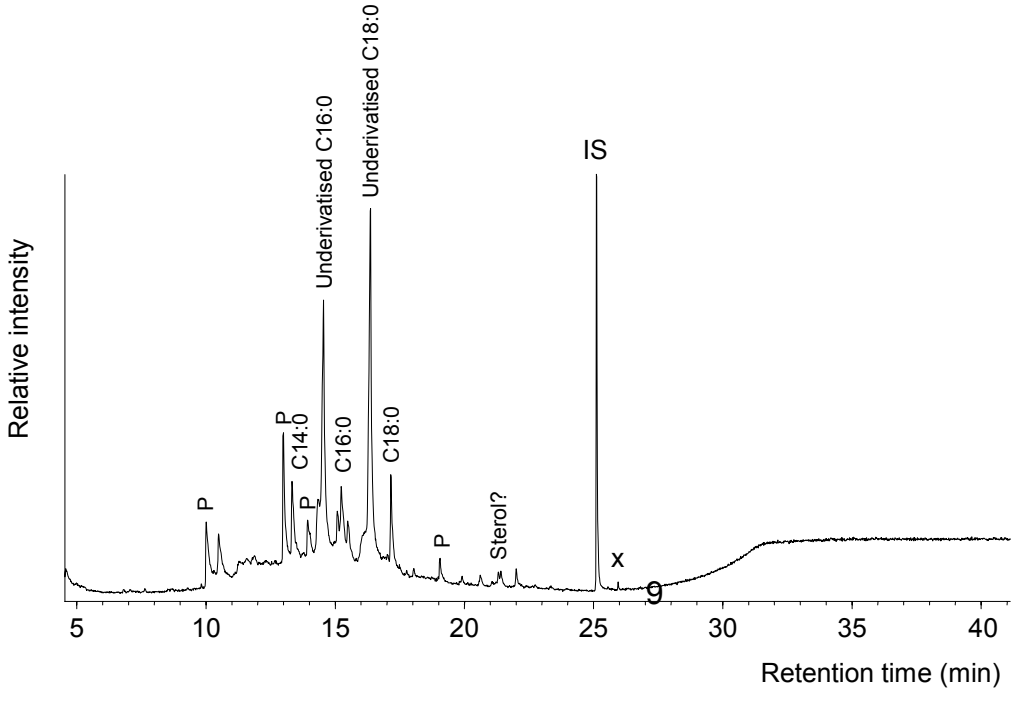
F219I: Internal ceramic absorbed. MAP Millfield Q feature No 219 large pit (central) beaker rim sherd with residue



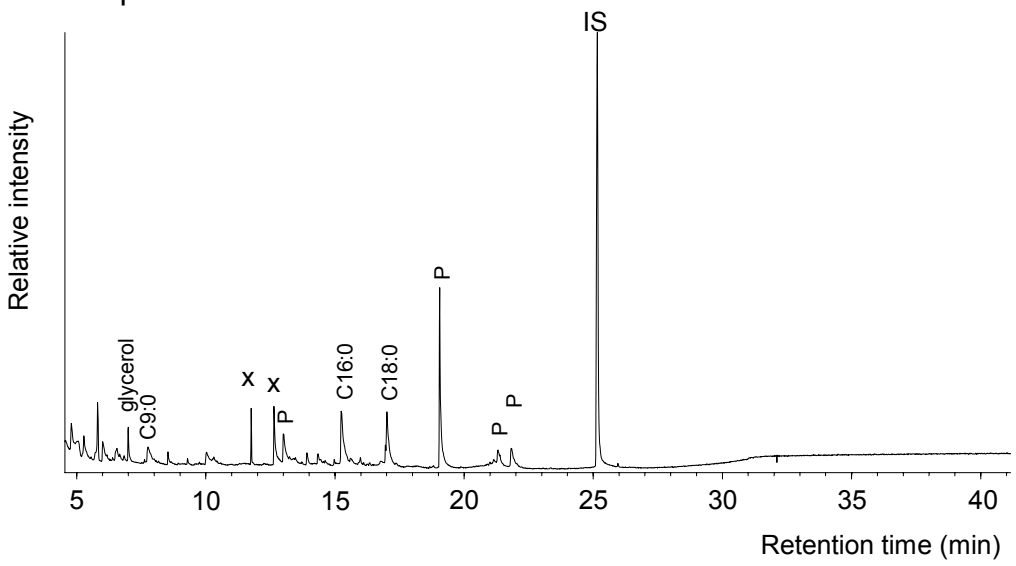
F219E: External ceramic absorbed. MAP Millfield Q feature No 219 large pit (central) beaker rim sherd with residue



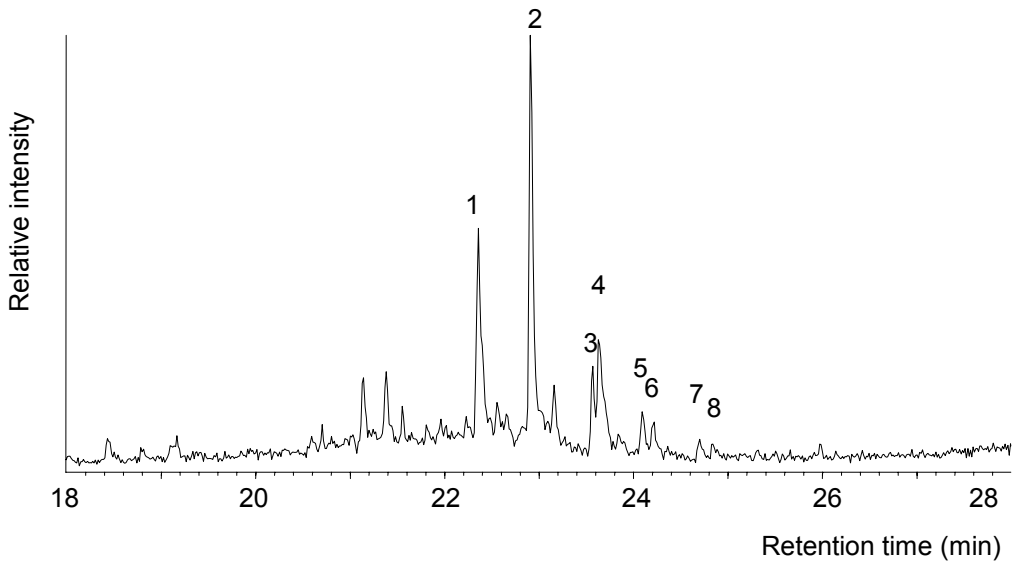
F219V: Visible residue from interior. MAP Millfield Q feature No 219 large pit (central) beaker rim sherd with residue



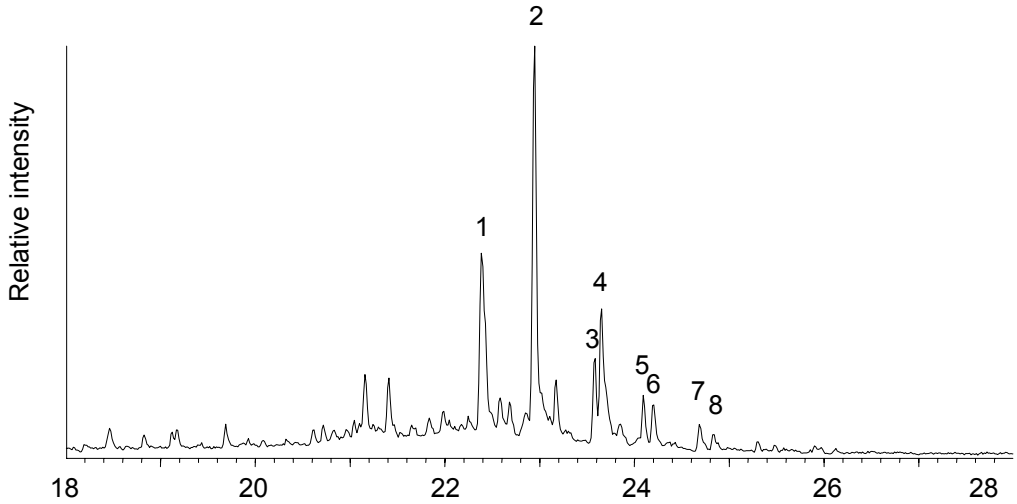
Modern pot



Partial mass chromatogram *m/z* 191 (hopanes) **F13317 external**



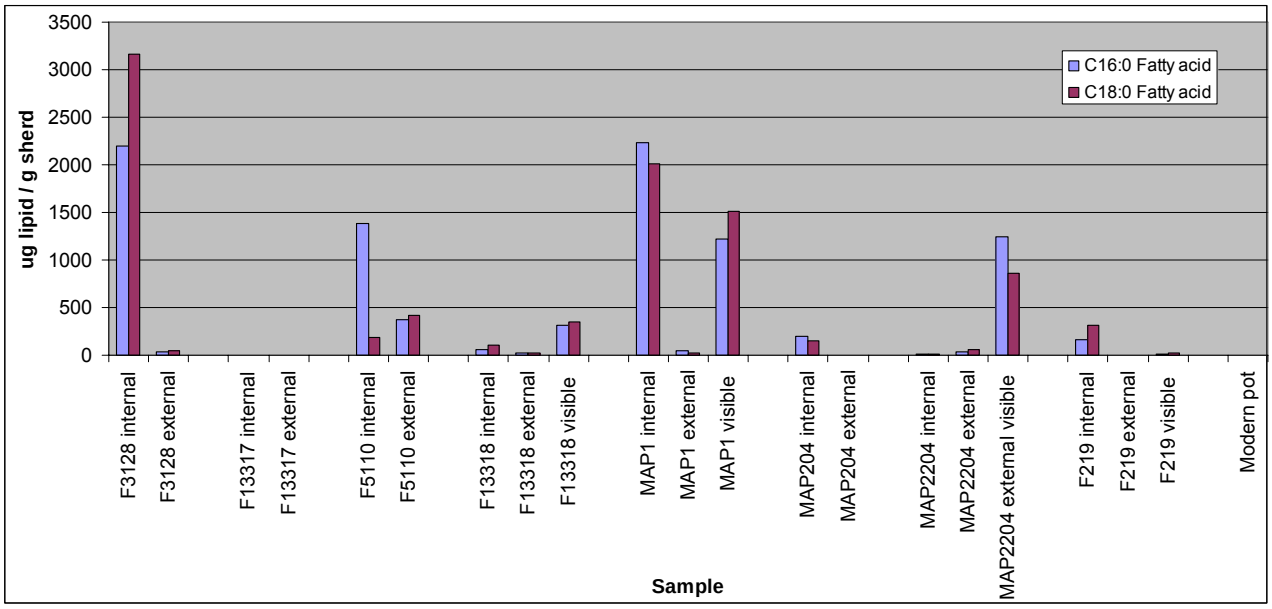
Partial mass chromatogram *m/z* 191 (hopanes) **F5110 external**



Discussion

The modern pot yielded trace levels of fatty acids, these are ubiquitous compounds and despite the precautions used to avoid contamination their presence at such low abundances is not unexpected. The modern pot also yielded glycerol, although in archaeological samples this can indicate the presence of triacylglycerols, its presence here is likely to originate from a previously run sample. Almost all the samples yield a number of compounds called phthalate plasticisers (labelled as P), these are modern synthetic compounds and are associated with leaching from plastics. In addition, a number of known analytical artefacts (labelled as x) were identified. All these components do not represent significant contamination and do not interfere with the interpretation of the extracts from the samples.

Lipids were recovered in significant abundance from all sherds except F13317. The $C_{16:0}$ and $C_{18:0}$ fatty acids were quantified (see chart below). With the exception of one sample (MAP2204) the yields from the interior were greater than those from the exterior. This would be expected if the vessels were used to contain organic material, rather than its use as decoration or waterproofing. This distribution also indicates that the lipids are indigenous to the sherds and not a result of post depositional contamination from the burial matrix, as this would be expected to contaminate both interior and exterior surfaces equally. Since the interior/exterior surfaces of each sherd was determined by curvature it may be worth re-examining sherd MAP2204 to confirm that the body curvature has not been mistaken for that due to a rim etc.



The dominant lipids extracted from the samples are fatty acids. Although the exact distributions varied, even carbon numbers were recovered across a range of C_{12} to C_{26}, with either C_{16} or C_{18} the most abundant. The unsaturated fatty acids $C_{18:1}$ and $C_{16:1}$ were also present, but at low levels which indicates degradation of the original fat/oil. There are traces of odd carbon numbered fatty acids (e.g. $C_{17:0}$) and branched fatty acids (e.g. C_{17*}) which indicates a bacterial contribution, possibly from a ruminant fat, but this may also be from bacterial degradation. A number of extracts also yielded mono-, di- and triacylglycerols. In addition, glycerol was found in some of these sherds (although this may be due to contamination). The above evidence indicates that the original content was a triacylglycerol oil or fat, which has since partially degraded to its constituent fatty acids and other components mentioned above.

Cholesterol at low abundances has been identified on a number of sherds. Fortunately the compound squalene was not identified, this is important as both cholesterol and squalene are found on human fingerprints, and although cholesterol survives over archaeological time, squalene rapidly degrades. This implies that the cholesterol is indigenous to the sherds and not a result of recent handling. Cholesterol is associated with animal fats. In addition, the sterol β-sitosterol was also recovered, this indicates a plant origin. This is potential evidence of mixing of original contents.

Levoglucosan was extracted from one extract (F13318V: Visible residue from the interior surface), this molecule is a marker for burning biomass, in particular cellulose.

A series of hopanes were extracted from the exterior of two sherds (shown as separate figures on page 10). These compounds originate from sedimentary organic matter (e.g. coals, oils, young muds) and their distribution varies with fossil fuel source/environment and maturity. No other components suggesting a fossil fuel were extracted (e.g. no alkanes, pristane or phytane) and it is unlikely that this represents bitumen, one possibility is these are from the surrounding soil matrix another could be modern contamination.

Summary

The lipid recovery was excellent, with many sherds yielding significant amounts of lipids. Generally, higher yields were recovered from the interior surfaces, indicating the lipids represent the original contents of the vessels. There is evidence of degradation, but the surviving molecules indicate that a triacylglycerol oil or fat is present. There are additional markers for both plant and animal fats. One sherd indicates the burning of cellulose, and two sherds yield a series of hopanes whose origin is still to be determined.

Recommendations

This initial assessment would recommend that organic residue analysis be carried out on a further number of sherds to identify vessel use. Samples of the surrounding matrix would also be useful to determine if the source of the hopanes is from the burial environment.

It may also be informative to extract an additional sub-sample from selected sherds and to submit this for compound specific isotopic analysis to measure the $\delta^{13}C$ values for the C_{16} and C_{18} fatty acids. This analysis has been used by other workers to identify milk and adipose fats. This analysis would need to be carried out externally, but we could prepare the samples at Bradford.