Theory and Practice of Archaeological Residue Analysis

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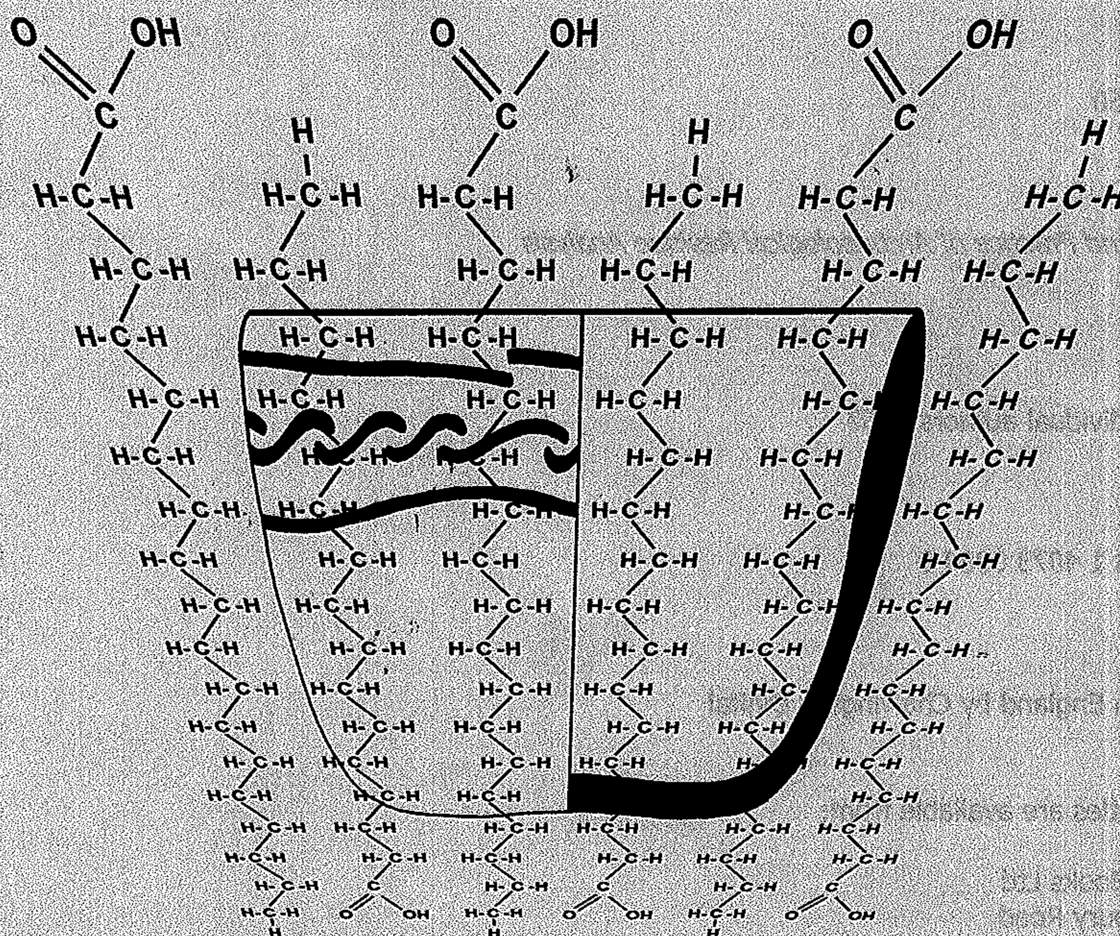

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CHAPTER SEVEN
Fatty Acid Analysis of Archaeological Residues: Procedures and Possibilities
M.E. Malainey

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Archaeological food residues extracted from areas of fat accumulation in artifacts can be characterized on the basis of relative fatty acid composition. Compositions of ancient residues are compared to experimental residues subjected to periods of oven storage, which simulates the effects of oxidative decomposition over time. Levels of medium and very long chain saturated fatty acids, C18:0 and C18:1 isomers indicate the fat content of the material of origin and probable presence of animal or plant material. This technique performs well in blind tests of decomposed residues of previously unknown foods and identification criteria remain valid over time.

Gas chromatography is an effective and efficient method of examining fatty acids in the form of methyl ester derivatives. Instruments are widely available and relatively inexpensive to obtain and operate. Gas chromatography has long been used to determine the fatty acid composition of archaeological residues. While absolute identifications are not possible, a wide range of archaeological residues can be rapidly categorized. Fatty acid compositions of cooking residues change over time; but these variations can be modeled. In particular, decreases in the relative amounts of C18:1 isomers in decomposing residues strongly correlate with logarithmic curves; the functions can then be used to extrapolate further change. Better than expected preservation of monounsaturated and, occasionally, polyunsaturated fatty acids is observed in the cooking residues of certain plant and plant and meat combinations, likely due to the presence of antioxidants.

With careful selection of archaeological samples for residue analysis, good preservation of residues is possible. The effects of microbes found in parkland, prairie and forest soils appear to be mediated by the reduced availability of oxygen in a burial environment. With a reference collection of decomposed foodstuffs from the region, one can establish possible origins of the residues and eliminate others. If desired, other methods of analysis can be employed to provide more precise identifications by confirming the fatty acid identifications and targeting molecules that can serve as biomarkers.

Previous Research

The major constituents of fats and oils are fatty acids that usually occur in nature as triacylglycerides, consisting of three fatty acids attached to a glycerol molecule by ester-linkages. Their insolubility in water and relative abundance compared to other classes of lipids, such as sterols and waxes, make fatty acids suitable for residue analysis. Since employed by Condamin et al. (1976), gas chromatography has been used extensively to analyze the fatty acid component of archaeological residues (cf. Chapter 5).

The composition of uncooked plants and animals provides important baseline information, but it is not possible to compare modern uncooked plants and animals with highly degraded archaeological residues of prepared foodstuffs. Unsaturated fatty acids, which are found widely in fish and plants, decompose more readily than saturated fatty acids, sterols or waxes. In the course of decomposition, simple addition reactions might occur changing double into single bonds (Solomons 1980), or peroxidation might lead to the formation of a variety of volatile and non-volatile products which continue to degrade (Frankel 1991). Peroxidation occurs most readily in polyunsaturated fatty acids.

Attempts have been made to identify archaeological residues using criteria that discriminate uncooked foods (Marchbanks 1989; Skibo 1992; Loy 1994). Marchbanks' (1989) percent of saturated fatty acids (%S) criteria has been applied to residues from a variety of materials including pottery, stone tools and burned rocks (Marchbanks 1989; Marchbanks and Quigg 1990; Collins et al. 1990). Skibo (1992, 89) could not apply the %S technique and used two ratios of fatty acids: C18:0/C16:0 and C18:1/C16:0. He reported that it was

possible to link the uncooked foods with residues extracted from modern cooking pots used to prepare one type of food. However, the ratios could not identify food mixtures. The utility of these ratios did not extend to residues extracted from archaeological potsherds because the ratios of the major fatty acids in the residue changed with decomposition (Skibo 1992, 97). Loy (1994) proposed the use of a Saturation Index (SI), determined by the ratio:

$$SI = 1 - \left[\frac{(C18:1 + C18:2)}{C12:0 + C14:0 + C16:0 + C18:0)}\right]$$

He admitted that the poorly understood decompositional changes to the suite of fatty acids make it difficult to develop criteria for distinguishing animal and plant fatty acid profiles in archaeological residues. The major drawback of the distinguishing ratios proposed by Marchbanks (1989), Skibo (1992) and Loy (1994) is they have never been empirically tested. The proposed ratios are based on criteria that discriminate food classes on the basis of their original fatty acid composition. The resistance of these criteria to the effects of decompositional changes has not been demonstrated. Skibo (1992) found that his fatty acid ratio criteria could not be used to identify highly decomposed archaeological samples.

In order to identify a fatty acid ratio unaffected by degradation processes, Patrick et al. (1985) simulated the long-term decomposition of one sample and monitored the resulting changes. An experimental cooking residue of seal was prepared and degraded in order to identify a stable fatty acid ratio. Patrick et al. (1985) found that the ratio of two C18:1 isomers, oleic and vaccenic acid, did not change with decomposition and this fatty acid ratio was used to identify an archaeological vessel residue as seal. While the fatty acid composition of uncooked foods must be known, Patrick et al. (1985) showed that the effects of cooking and decomposition over long periods of time on the fatty acids must also be understood.

Development of the Identification Criteria

As the first stage in developing the identification criteria, fatty acid compositions of more than 130 uncooked native food plants and animals from Western Canada were determined using gas chromatography (Malainey 1997; Malainey et al. 1999a). When the fatty acid compositions of modern food plants and animals were subject to cluster and principal component analyses, the resultant groupings generally corresponded to divisions that exist in nature (Table 1). Clear differences in the fatty acid composition of large mammal fat, large herbivore meat, fish, plant roots, greens and berries/seeds/nuts were detected, but the fatty acid composition of meat from medium-sized mammals resembled berries/seeds/nuts.

Cluster A	Subcluster			
	I	II	III	IV
Type	Mammal fat and marrow	Large herbivore meat	Fish	Fish
C16:0	19.90	19.39	16.07	14.10
C18:0	7.06	20.35	3.87	2.78
C18:1	56.77	35.79	18.28	31.96
C18:2	7.01	8.93	2.91	4.04
C18:3	0.68	2.61	4.39	3.83
VLCS	0.16	0.32	0.23	0.15
VLCU	0.77	4.29	39.92	24.11

Cluster B	Subcluster					
	V	VI	VII	VIII	IX	X
Type	Berries and nuts	Mixed	Seeds and berries	Roots	Seeds	Mixed
C16:0	3.75	12.06	7.48	19.98	7.52	10.33
C18:0	1.47	2.36	2.58	2.59	3.55	2.43
C18:1	51.14	35.29	29.12	6.55	10.02	15.62
C18:2	41.44	35.83	54.69	48.74	64.14	39.24
C18:3	1.05	3.66	1.51	7.24	5.49	19.77
VLCS	0.76	4.46	2.98	8.50	5.19	3.73
VLCU	0.25	2.70	1.00	2.23	0.99	2.65

Cluster C	Subcluster				
	XI	XII	XIII	XIV	XV
Type	Greens	Berries	Roots	Greens	Roots
C16:0	18.71	3.47	22.68	24.19	18.71
C18:0	2.48	1.34	3.15	3.66	5.94
C18:1	5.03	14.95	12.12	4.05	3.34
C18:2	18.82	29.08	26.24	16.15	15.61
C18:3	35.08	39.75	9.64	17.88	3.42
VLCS	6.77	9.10	15.32	18.68	43.36
VLCU	1.13	0.95	2.06	0.72	1.10

Table 1 (this and previous page): Summary of average fatty acid compositions of modern food groups generated by hierarchical cluster analysis. VLCS = very long chain (C20, C22 and C24) saturated fatty acids, VLCU = very long chain (C20, C22 and C24) unsaturated fatty acids.

Samples in cluster A, the large mammal and fish cluster had elevated levels of C16:0 and C18:1 (Table 1). Divisions within this cluster stemmed from the very high level of C18:1 isomers in fat, high levels of C18:0 in bison and deer meat and high levels of very long chain unsaturated fatty acids (VLCU) in fish. Differences in the fatty acid composition of plant roots, greens and berries/seeds/nuts reflect the amounts of C18:2 and C18:3ω3 present. The berry, seed, nut and small mammal meat samples appearing in cluster B have very high levels of C18:2, ranging from 35% to 64% (Table 1). Samples in subclusters V, VI and VII have levels of C18:1 isomers from 29% to 51%. Plant roots, plant greens and some berries appear in cluster C. All cluster C samples have moderately high levels of C18:2; except for the berries in subcluster XII, levels of C16:0 are also elevated. Higher levels of C18:3ω3 and/or very long chain saturated fatty acids (VLCS) are also common except in the roots which form subcluster XV.

The effects of cooking and degradation over time on fatty acid compositions were also examined. Nineteen modern residues of plants and animals from the plains, parkland and forests of Western Canada were prepared by cooking samples of meats, fish and plants, alone or combined, in replica vessels over an open fire (Malainey 1997; Malainey et al. 1999b). After four days at room temperature, the vessels were broken and a set of sherds analyzed to determine changes after a short term of decomposition. A second set of sherds remained at room temperature for 80 days, and then placed in an oven at 75°C for a period of 30 days in order to simulate the processes of long term decomposition. The relative percentages were calculated on the basis of the ten fatty acids that were regularly found in Precontact period vessel residues from Western Canada: C12:0, C14:0, C15:0, C16:0, C16:1, C17:0, C18:0, C18:1ω9, C18:1ω11 and C18:2. Observed changes in fatty acid composition of the experimental cooking residues enabled the development of a method for identifying the archaeological residues (Table 2).

It was determined that levels of medium chain fatty acids (the sum of C12:0, C14:0 and C15:0), C18:0 and C18:1 isomers in the sample could be used to distinguish degraded experimental cooking residues (Malainey 1997; Malainey et al. 1999b). These fatty acids are suitable for the identification criteria because saturated fatty acids are stable and monounsaturated fatty acids degrade very slowly as compared to polyunsaturated fatty acids (deMan 1992). Furthermore, when principal component analysis is applied to the total relative fatty acid composition, the groupings generated by multivariate analysis strongly coincide with identifications made under the criteria (Malainey et al. 1999c, Figure 10). Higher levels of medium chain fatty acids, combined with low levels of C18:0 and C18:1 isomers, were detected in the decomposed experimental residues of plants, such as roots, greens and most berries. High levels of C18:0 indicated the presence of large herbivores. Moderate levels of C18:1 isomers, with low levels of C18:0, indicated the presence of either fish or foods similar in composition to corn. High levels of C18:1 isomers with low levels of C18:0 were found in residues of beaver or foods of similar fatty acid composition. The criteria for identifying six types of residues were established experimentally; the seventh type, plant with large herbivore, was inferred (Table 2).

These criteria were applied to residues extracted from more than 200 pottery cooking vessels from 18 plains, parkland and southern boreal forest sites in Western Canada (Malainey 1997; Malainey et al. 1999c; 2001b). The identifications were consistent with the evidence from faunal and tool assemblages for each site. Settlement and subsistence patterns proposed for Aboriginal hunter-gatherer peoples who occupied the area prior to European contact were also supported (Malainey et al. 2001b).

Identification	Medium chain	C18:0	C18:1 isomers
Large herbivore	≤ 15%	≥ 27.5%	≤ 15%
Large herbivore with plant or Bone marrow	Low	≥ 25%	15% ≤ *X* ≤ 25%
Plant with large herbivore	≥ 15%	≥ 25%	No data
Beaver	Low	Low	≥ 25%
Fish or Corn	Low	≤ 25%	15% ≤ *X* ≤ 27.5%
Fish or Corn with plant	≥ 15%	≤ 25%	15% ≤ *X* ≤ 27.5%
Plant (except corn)	≥ 10%	≤ 27.5%	≤ 15%

Table 2: Criteria for the identification of archaeological residues based on the decomposition patterns of experimental cooking residues prepared in pottery vessels.

Work has continued to expand, refine and test the identification criteria (Malainey et al. 2000a; 2000b; 2000c; 2001a; Quigg et al. 2001). The reference collection now includes several food plants and animals from the Southern Great Plains. The validity of applying the criteria to cooking residues extracted from burned rocks used for stone boiling and grilling foods has been demonstrated (Quigg et al. 2001, 290-294). This enabled the study of Late Archaic subsistence patterns at the Lino site in South Texas, despite the virtual absence of vertebral faunal and burned macrobotanical remains (Quigg et al. 2001, 295-301). Comparisons of residue identifications with faunal, macrobotanical and other cultural remains recovered from other sites in Texas, New Mexico, Wyoming and Arizona, dating from the Late Paleoindian-Early Archaic to the Late Prehistoric Periods, strongly supports the soundness of applying the technique to burned rocks (Malainey 2004).

The identification criteria for archaeological residues in Table 2 were based on foodstuffs exclusively from the plains, parkland and southern boreal forest of Western Canada. In order to make the identifications more applicable to materials from the Central and Southern Great Plains and adjacent regions, data from the analysis of food plants and animals from these regions were incorporated into these criteria.

The identification of residues with high levels of C18:0 as 'Large herbivore' was found to be valid throughout the Great Plains and adjacent areas. The flesh of deer, bison, cow and moose produce these residues. Levels of C18:0 were found to increase as animals became fat-depleted over winter (Perrin 2002). Levels of C18:1 isomers in large herbivore residues were found to be a reliable indicator of the degree of meat fattiness. Very lean meat had the lowest levels of C18:1 isomers and highest C18:0; relative amounts of C18:0 were somewhat lower in fat meat. Conversely, high levels of C18:0 combined with elevated levels of C18:1 isomers was found in meat with higher levels of fat, such as in well-marbled cuts. In addition to large herbivore meat, the decomposed cooking residues of javelina meat (*Tayassu tajacu*) and tropical oils from plants such as sotol (*Dasylirion wheeleri*) are also known to have high levels of C18:0. They must be considered as potential sources of the residue if it is possible that they could have been utilized. The decomposed cooking residues of yucca root produce residues with elevated levels of medium chain fatty acids and C18:0. Under the criteria, they would be identified as 'Plant with large herbivore'.

The original category 'Plant' was renamed 'Low fat content plant' to more accurately reflect the types of foods known to fall under this category. Plant roots, greens and berries from Western Canada produced residues with high levels of medium chain fatty acids. Further south, jicama tuber (*Pachyrhizus erosus*), onion bulbs, yopan leaves (*Ilex vomitoria*), buffalo gourd (*Cucurbita foetidissima*) and biscuit root (*Lomatium* species) produce similar residues. The levels of C18:1 isomers in the decomposed cooking residues of fleshy fruit of prickly pear (*Opuntia engelmannii*) and Spanish dagger (*Yucca treculeana*) is slightly higher; these are referred to as 'Medium-low fat plants'.

The original category 'Fish or Corn' is now referred to as 'Medium fat content foods'. In addition to fish and corn, the decomposed cooking residues of mesquite beans (*Prosopis glandulosa*), cholla (*Opuntia* species), certain snails (*Rabdotus* species), box terrapin (*Terrapene* species), and the fat-depleted meat of late winter elk (*Cervus elaphus*) produce similar residues. Medium fat content food residues of plants were found to often have elevated levels of medium chain fatty acids or very long chain saturated fatty acids.

In Western Canada, the decomposed cooking residues of fatty meat of medium-size mammals, such as beaver (*Castor canadensis*) was found to have levels of C18:1 isomers in excess of 25% with much lower levels of C18:0 and medium-chain fatty acids. The rendered fat of mammals such as bear, known as bear grease or bear oil, had even higher levels of C18:1 isomers. In the Central and Southern Plains and adjacent regions, a wide variety of seeds and nuts are available and were exploited by humans in the past. Levels of C18:1 isomers in the decomposed cooking residues of some of these foods far exceeded 25%. The original category 'Beaver' has been subdivided to better reflect these findings. From lower to highest levels of C18:1 isomers, the divisions are 'Moderate-high', 'High', 'Very high' and 'Extremely high fat content foods'. The fatty meat of beaver and the seeds of Texas ebony (*Pithecellobium ebano*) are examples of moderate-high fat content foods. Olive oil, mescal seeds (*Agave perryi*) and bear meat are examples of high or very high fat content foods. Fresh bear (*Ursus americanus*) grease and the decomposed cooking residue of piñon (*Pinus edulis*) are examples of extremely high fat content foods. Again, the residues of plant origin are more likely to have elevated levels of medium chain fatty acids or very long chain saturated fatty acids.

In general, elevated levels of C18:0 are associated with the presence of large herbivores, but javalina and tropical seed oils must be considered as possible sources if they were locally available. The relative amount of C18:1 isomers in the residue indicate the fat content of the material of origin. Medium and very long chain saturates facilitate the discrimination between foods of plant origin and those of animal origin. It must be understood that the identifications given do not necessarily mean that those particular foods were actually prepared because different foods of similar fatty acid composition and lipid content will produce similar residues. It is possible only to say that the material of origin for the residue was similar in composition to the foods indicated.

Testing the Validity of Identification Criteria

Fatty acids decompose over time; this is the biggest criticism levied against their use as a means of identifying archaeological residues. While the fact they degrade is indisputable, clear decomposition trends emerged through the study of oven stored experimental cooking residues and led to the development of the identification criteria outlined in Table 2 (Malainey 1997; Malainey et al. 1999b). The next task undertaken was to test the validity of the criteria and the degree to which fatty acid degradation in cooking residues is predictable. This research was of particular importance to assessing criterion that included C18:1 isomers, as these monounsaturated fatty acids continue to slowly degrade over time. Over long periods of time, levels of C18:1 isomers continue to drop and relative amount of the other fatty acids in the residue increase. The goal was to determine how well decomposing cooking residues from different parts of a vessel conform to the various criteria and at what point are they no longer applicable. The possible effect of burial environment, in particular, microbial action in different types of soil, was also investigated.

In order to assess the validity of the criteria, fatty acid decomposition patterns of cooking residues were traced over extended periods of oven or soil storage. A variety of foods were boiled in clay cylinders after which the cylinders were cut into tiles. In one set of experiments, these tiles were stored at 75°C. Samples were taken periodically over a 68 day period and changes in the relative fatty acid composition were monitored. In another set of experiments, clay tiles were buried in soils from the plains, parkland and southern boreal forest of Manitoba stored at room temperature. Samples were taken periodically over a period of ten months. The relative fatty acid composition of the residue extracted from buried tiles was compared to that of controls after ten months, one month of oven storage and two months of oven storage.

Experimental Procedures

Residues were prepared by cooking foods in clay cylinders (approximately 15 cm outside diameter x 15 cm tall) made of medium coarse raku clay and fired in an annealing oven. The cylinders were placed inside glass beakers after which about 100 g of each food type and one liter distilled water was added. This was brought to the boil over a hot plate. The total cooking time was approximately 2 hours, 1.5 hours at a simmer. After cooling at least one hour, the clay cylinder was removed and allowed to dry and stored at room temperature. The cylinder was cut into tiles of approximately 2.5 cm square and labeled. Tiles from the two highest, the two center and the two bottom rows were designated 'upper', 'middle' and 'lower', respectively.

After being subjected to the designated periods of oven, soil and room temperature storage, lipids were extracted from the tiles using a variation of the method developed by Folch et al. (1957). Possible surface contaminants were removed by grinding exterior surfaces off with a Dremel tool fitted with a silicon carbide bit. The sample was crushed with a hammer mortar and pestle and extracted twice in 40 ml chloroform-methanol (2:1, v/v) using ultrasonication (2 x 10 min). Solids were removed by filtering the solvent mixture into a separatory funnel. The lipid/solvent filtrate was washed with 22 ml of ultrapure water. Once separation into two phases was complete, the lower chloroform-lipid phase was transferred to a round-bottomed flask and the chloroform removed by rotary evaporation. Any remaining water

was removed by evaporation with 2 ml benzene and 2 ml chloroform-methanol (2:1, v/v) was used to transfer the dry total lipid extract into a screw-top glass vial with a Teflon-lined cap. The vial was flushed with nitrogen and stored at -20°C.

Depending on its apparent concentration, 100-600 µl of total lipid extract (TLE) solution was placed in a screw-top test tube and dried in a heating block under nitrogen after which 1 ml of a 0.01 mg/ml solution of C21:0 (heneicosanoic acid) was added as an internal standard. Fatty acid methyl esters (FAMEs) were prepared by treating the dry lipid and internal standard with 6 ml of 0.5 N anhydrous hydrochloric acid in methanol (60 min at 65-70°C). Fatty acids that occur in the sample as di- or triacylglycerides are detached from the glycerol molecule (saponification) and converted to methyl esters. After cooling to room temperature, 4 ml of ultrapure water was added and the FAMEs were recovered with 3 ml petroleum ether and transferred into a vial. Solvents were removed by heat under nitrogen, the FAMEs dissolved in 75 µl iso-octane and transferred into a GC vial with a conical glass insert.

Analysis was performed on a Hewlett-Packard 5890 gas chromatograph fitted with a flame ionization detector connected to a personal computer. Samples were separated using a DB-23 fused silica capillary column (30 m x 0.25 mm I.D.; J&W Scientific; Folsom, CA). An autosampler injected a 1-2 µl sample using a split injection system with the ratio set between 1:20 and 1:80, depending on sample concentration. Hydrogen was used as the carrier gas at a linear velocity of 40 cm/sec. Column temperature was programmed from 155°C to 215°C at 2°C/min; lower and upper temperatures were held for 4 and 5 minutes, respectively. Chromatogram peaks were integrated using ChromPerfect software and identified through comparisons with known compounds (NuCheck Prep; Elysian, MN). Solvents and chemicals were checked for purity by running a blank sample. Traces of contamination were subtracted from sample chromatograms. Relative percentage composition was calculated by dividing the integrated peak area of each fatty acid by the total area of fatty acids present. Using this protocol, fatty acids are detectable to the nanogram (10^{-9} g) level.

Oven Storage of Cooking Residues

For samples undergoing oven storage only, fatty acid compositions of residues extracted from the upper, middle and lower portions of the clay cylinder were determined at the beginning of the oven storage experiment (time 0). Nine other tiles from each portion were placed in an oven at 75°C. For the first 20 days, one tile from each portion was sampled every four days; they were then sampled every 12 days until the end of the experiment after 68 days.

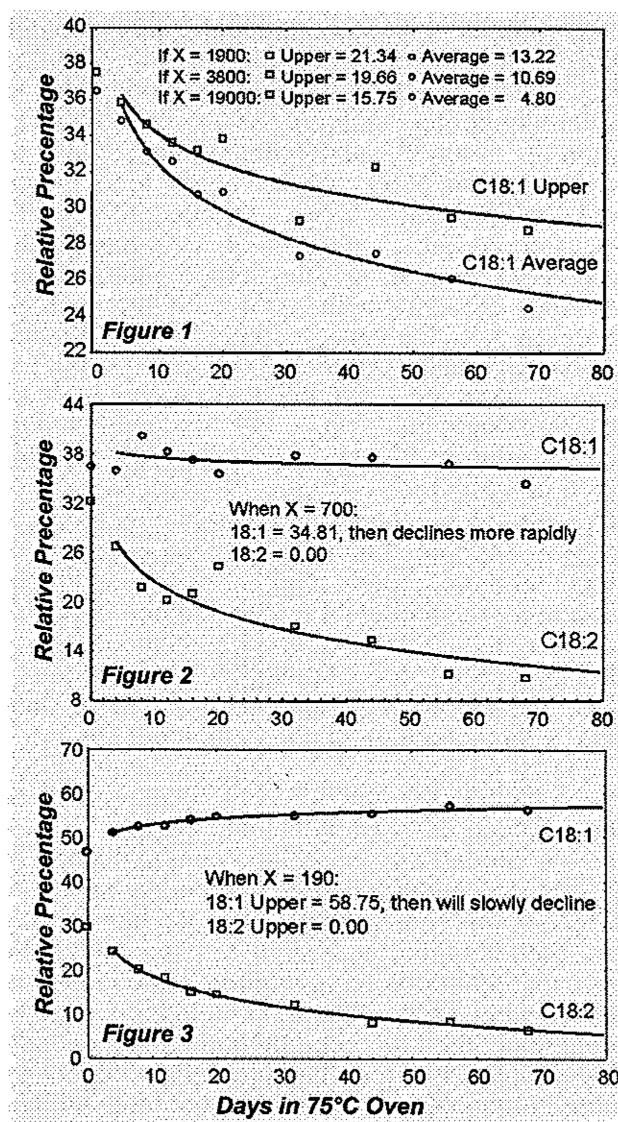

Figure 1: Plot of changes in relative amounts of C18:1 isomers in the cooking residue of smoked trout after 68 days oven storage. The logarithmic decay curve for residues from the upper portion of the clay cylinder is C18:1 isomers = 39.67 - 5.59*log10(x) + e. The overall average for residues from all areas is C18:1 Average = 40.82 - 8.412*log10(x) + e.

Figure 2: Plot of changes in amounts of C18:1 isomers and C18:2 in the cooking residue of deer and Spanish dagger after 68 days oven storage. The logarithmic decay curve for relative amounts of C18:1 isomers in residues from the upper portion of the clay cylinder is C18:1 Upper = 38.95 - 1.46*log10(x) + e. Levels of C18:2 in residues from the same area is C18:2 Upper = 34.57 - 12.15*log10(x) + e.

Figure 3 (previous page): Plot of changes in amounts of C18:1 isomers and C18:2 in the cooking residue of mescal seeds after 68 days oven storage. The logarithmic decay curve for relative amounts of C18:1 isomers in the residues from the upper portion of the clay cylinder is C18:1 Upper = 48.22 + 4.62*log10(x) + e. Levels of C18:2 in residues from the same area is C18:2 Upper = 33.12 - 14.54*log10(x) + e.

Oven storage is widely used by food scientists to accelerate oxidative decomposition of fatty acids. It has been shown that the rate of oxidative degradation doubles with every 10°C increase in temperature (Labuza 1971). One day of storage at 65°C is the equivalent of one month of storage at room temperature (Malcomson et al. 1994). At 75°C, the rate of oxidative degradation is 192 times faster than at a site with an average yearly temperature of 0°C. Oven storage at 75°C for 68 days produces oxidative degradation approximating 36.3 years at 0°C and 1900 days (5.2 years) of oven storage would simulate approximately 1000 years of oxidative degradation at 0°C. To understand the effects of the loss of monounsaturated fatty acids, relative percentages of C18:1 isomers and, where relevant, C18:2, in the residues were plotted from 'time 0' to 'day 68'. Graphs for smoked trout, the combination of deer meat and Spanish dagger fruit, and mescal, fitted with logarithmic decay curves are presented in Figures 1, 2 and 3.

Smoked trout (107 g) was cut into pieces of 10-15 g and placed inside a clay cylinder that was itself set in a glass beaker. One liter of distilled water was added and the contents were brought to the boil on a hot plate and allowed to simmer. The total cooking time was two hours. The clay cylinder was removed after the broth cooled and stored at room temperature for approximately six months. Small amounts of polyunsaturated fatty acids were still detectable in the residue at time 0 and after four days of oven storage. These were omitted prior to the calculation of the relative fatty acid composition to make time 0 and day 4 compositions comparable with the rest of the data set. At time 0, C18:1 isomer levels in residues from the upper, middle and lower portions of the clay cylinder ranged from 35.5% to 37.50% (Figure 1). Despite initial similarities, relative fatty acid compositions of the residues quickly diverged. After 68 days of oven storage, the level of C18:1 isomers from the upper portion was 28%, compared to 24% for the cylinder average.

According to the identification criteria, decomposed cooking residues of freshwater fish have C18:1 isomer levels between 15% and 27.5%. Using the logarithmic decay curves in Figure 1 to predict the amounts of C18:1 isomers, only residues from the upper portion can be correctly identified for extended periods of time. If oven storage continued for 1900 and 3800 days (10.4 years), approximating 1000 and 2000 years oxidative degradation at 0°C, C18:1 isomer levels of 19.66% and 21.34% will occur in residues from the upper portion. The relative percentage of C18:1 isomers in smoked trout residues from the upper portion would conform to the identification criteria until 25,600 days oven storage, approximating almost 13,500 years oxidative decomposition at 0°C. The identification criteria can not be successfully applied using average C18:1 isomer levels for the cylinder after a mere 1167 days oven storage, simulating just over 600 years oxidative decomposition.

Similar results were observed in the decomposed residues of another freshwater fish, pickerel. After 1900 days of oven storage, the level of C18:1 isomers is predicted to be 23.95%; after 3800 days, it would be 22.05%. After 19,000 days of oven storage, approximating 10,000 years oxidative decomposition, C18:1 isomer levels would still conform to the identification criteria for fish. Cooking residues with the highest levels of C18:1 isomers most often occur in the upper portion; although residues from the lower portion can sometimes be equally well or better preserved. Average levels of C18:1 isomers drop below 15% after less than 3000 years of oxidative decomposition.

Another cooking residue was prepared by combining the meat of a larger herbivore, 110 g deer, with 70 g chopped Spanish dagger fruit, which alone produces a medium-low fat content residue. Changes in the levels of C18:1 isomers and C18:2 in the residues extracted from the upper portion of the clay cylinder are presented in Figure 2. A notable feature of this residue is that amounts of C18:2 were maintained at levels over 10% after 68 days oven storage. By using logarithmic decay curves, C18:2 is predicted to completely disappear only after 700 days of oven storage. The relative amounts of C18:1 isomers in the residue changed only slightly over 68 days of decomposition. It is predicted that after 700 days of oven storage, the relative amount of C18:1 isomers in the residue will exceed 34%. Once C18:2 is completely lost, it is possible that the relative amounts of C18:1 isomers may decline more rapidly.

For the preparation of another residue, 33 g mescal seeds were ground and prepared as described above. Levels of C18:1 isomers and C18:2 observed in the cooking residue over 68 days of oven decomposition are shown in Figure 3. At time 0, levels of C18:2 isomers formed 30% of the relative fatty acid composition of the residue from the upper portion of the clay cylinder; after 68 days of oven storage, it dropped to 6%. With the loss of this polyunsaturated fatty acid, the relative amount of C18:1 isomers increased from about 46% to 56%. Levels of C18:2 are predicted to reach zero after 190 days oven storage; at that time, C18:1 isomers will form almost 59% of the relative fatty acid composition of the residue

and the relative amount of C18:1 isomers will begin to decline. The maintenance of C18:2 after an extended period of oven storage was also observed in the cooking residue of Texas ebony seeds, a moderate-high fat content plant. After ten months of storage at room temperature and two months of oven storage, levels of C18:2 remained at about 4% and C18:1 isomers formed more than 30% of the relative fatty acid composition of the residue.

Clearly the upper portion of the vessels in which foods were prepared (the boil line) should be targeted for residue analysis. Initial levels of C18:1 isomers are the highest, and the rate of decomposition the slowest, in residues recovered from this region. Where present, C18:2 can be preserved in the upper portion of clay cylinders exposed to extended periods of oven storage, possibly several hundred days in the case of the deer and Spanish dagger residue. Residues from the middle and lower portions are more likely to have lower levels of monounsaturated fatty acids. Fatty acid compositions of these residues conform to the identification criteria for a shorter period of oxidative degradation, the equivalent of several hundred to a few thousand years.

Soil Storage of Cooking Residues

Average air temperature in the plains and parkland of Western Canada ranges from 1.5 to 5.0°C (Hare and Hay 1979). During the winter the frost penetrates deep into the soil. The harsh winter conditions in Manitoba made an outdoor experiment impractical as microbial activity would drop significantly. In order to accelerate the effects of microbial decomposition, the storage was conducted at room temperature. Very dark gray sandy loam was collected from an uncultivated grassland environment on a terrace of the Pembina Hills Escarpment in southern Manitoba (Michalyna et al. 1988). Chernozemic parkland soil was collected from an aspen-oak grove on the grounds of a University of Manitoba Research Station south of the City of Winnipeg (Michalyna et al. 1975). Sandy forest soil was collected from the southern boreal forest near Nopiming Provincial Park in east-central Manitoba. While a professional survey has not been conducted in this particular area, the soil has the characteristics of a well-drained Minimal Podzol developed on fine sand and is quite acidic (Smith and Ehrlich 1967).

A 5 cm thick basal layer of soil was placed in clear plastic storage containers with lids and a capacity of 11.4 l. Seven clay tiles measuring about 2.5 cm square of one type of residue were laid in a single layer on the soil; at least 5 cm apart. The tiles were covered with a second 5 cm thick layer of soil. Tiles from the upper portion of the clay cylinder were placed in parkland soil; tiles from the middle portion of the clay cylinder were placed in prairie grassland soil; tiles from the lower portion of the clay cylinder were placed in the sandy forest soil. For each type of soil, residues containing lower amounts of fat were placed in one container; residues containing higher amount of fat were placed in a separate container. The containers were closed with their lids so that the soil remained moist. Three tiles of each type of residue remained exposed to the atmosphere at room temperature to serve as controls.

One tile of each residue type was collected from each type of soil after 60, 120, 180 and 240 days. At that time, 100 ml of water was sprinkled evenly on the surface to maintain soil dampness. Over the course of the storage experiment, insect life was observed and seeds in soil sprouted. After 300 days, the three remaining tiles were removed from the soil and the three control tiles were collected. Residues from one tile stored in each type of soil and one control tile were selected to show the effects of 10 months of storage. The remaining soil-stored and control tiles were immediately placed in an oven at 75°C. One tile stored in each type of soil and control tiles from the upper, middle and lower cylinders for each type of residue were stored for one month; another set underwent two months of oven storage. This was to simulate the effects of long-term decomposition on a residue modified by burial in different types of soil.

The residue for bison, a large herbivore, was prepared by boiling 112 g of meat as described above. Tiles from the upper portion of the clay cylinder, which included the area of fat accumulation, were placed in parkland soil. Compared to other areas of the clay cylinder, levels of C18:1 isomers were highest in these residues. Levels of C18:1 isomers in residues buried in parkland soil for ten months prior to one and two months of oven storage were higher than those in residues extracted from unburied control tiles (Figure 4). After a month of oven storage, C18:1 isomers formed about 48% of the total fatty acid composition of the residues; whereas the level of C18:1 isomers was only 40% in the residue extracted from the control. Similarly, after two months of oven storage C18:1 isomers represented 39% of the total fatty acid composition of the residue extracted from the tile buried in parkland soil for 10 months compared to 35% in the control. While the difference is less profound after two months of oven storage, storage in parkland soil for ten months appears to have enhanced the preservation of these monounsaturated fatty acids.

Tiles from the middle part of the clay cylinder with bison cooking residue were stored in prairie grassland soil for ten months. Residues extracted from these tiles were compared to those from unburied controls. Levels of C18:1 isomers in residues from the tiles that were buried were higher than the controls. At about 38%, levels of C18:1 isomers are virtually identical in residues from buried tiles after one and two months of oven storage. This is higher than the C18:1 isomer levels

observed in both control sherds, which were an unexpectedly low 26% after one month oven storage and about 32% after two months oven storage. Levels of C18:2 are somewhat higher in this residue which depresses the relative amount of C18:1 isomers. The exact placement on the clay cylinder may have added to the variation as the middle portion of the cylinder, as with the other sections, was cut into upper and lower rows.

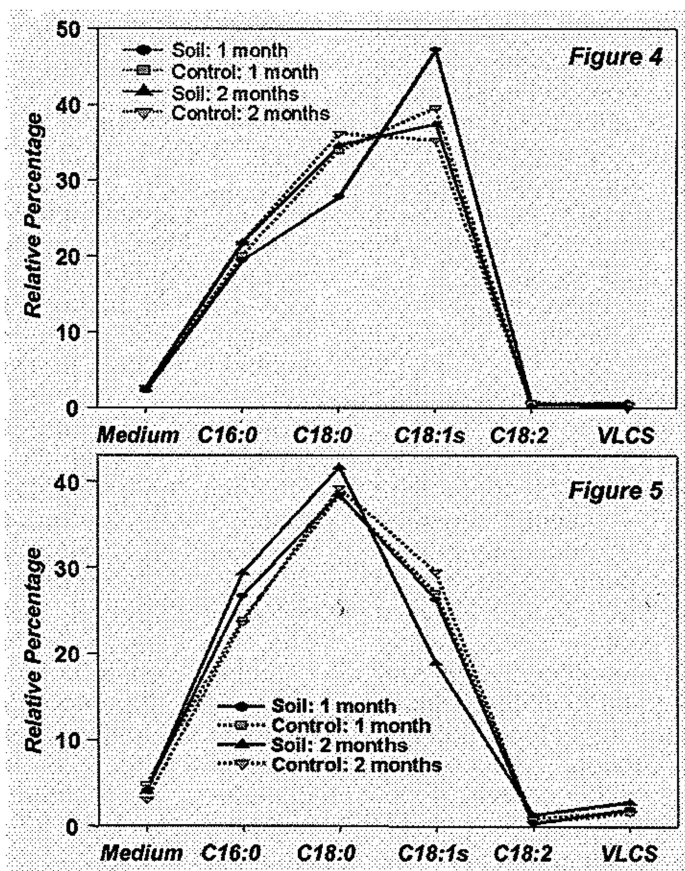

Figure 4 (top): Relative fatty acid compositions of bison cooking residues from the upper portion of the clay cylinder stored in parkland soil compared to controls after one and two months of oven storage at 75°C. VLCS = very long chain (C20, C22 and C24) saturated fatty acids.

Figure 5 (bottom): Relative fatty acid compositions of bison cooking residues from the middle portion of the clay cylinder stored in prairie soil compared to controls after one and two months of oven storage at 75°C. VLCS = very long chain (C20, C22 and C24) saturated fatty acids.

Tiles from the lowest portion of the bison residue clay cylinder were buried in forest soil and residues extracted were compared to controls (Figure 5). After one month of oven storage, levels of C18:1 isomers in residues extracted from both the control and the tile buried in forest soil were almost identical, about 29% and 29.5%, respectively. Levels of C18:1 isomers in residues extracted from tiles after two months of oven storage diverged widely. At about 30%, the level in the control exceeded all others; the amount in the residue from the buried tile was unexpectedly low, about 19%. Again, it is possible that the exact placements of the tiles on the clay cylinder may have played a role in these results.

Overall, microbial activity in parkland, prairie grassland and forest soil does not appear to adversely affect C18:1 isomer preservation in bison cooking residues. After oven storage, the degree of preservation in residues extracted from tiles buried for ten months is often equal to or better than in unburied controls. The exact placement of the tile on the clay cylinder may account for some of the variation observed.

A residue of pike was prepared by boiling 200 g of fish as described above on two consecutive days. The preservation of C18:1 isomers in the cooking residue of the pike, a freshwater fish, were similar in that the levels in residues buried in the different types of soil were generally equal to or higher than amounts in residues from unburied control tiles. After ten months of oven storage, levels of C18:1 isomers in the residue extracted from the tile buried in parkland soil exceeded 40%; the amount measured in the residue from the control tile was 33% (Figure 6). The same level of C18:1 isomers (33%) was found in the control tile after two months of oven storage; residue from the tile buried in parkland soil was only slightly lower, 31%. Levels of C18:1 isomers in residues extracted from tiles buried in forest soil were virtually identical to that of controls after both ten-months and two-months oven storage (Figure 7). A greater range of variation was observed in the levels of C16:1; it was higher in the buried tile after ten months and higher in the control after two months oven storage.

One notable exception to the pattern of equal or better preservation of C18:1 isomers was in the cooking residue of Texas ebony seeds. It was prepared by boiling 95 g of seeds that were ground immediately prior to cooking in the manner described above. Tiles from the lowest portion of the clay cylinder were stored in forest soil. The relative fatty acid compositions of residues extracted from these tiles are presented in Figure 8. After ten months of storage in soil, C18:1 levels in the residue from the buried tile was about 40%; in the unburied control, C18:1 isomer levels exceeded 50%. After two months of oven storage, levels of C18:1 isomers in the control were about 45%; in the residue from the tile buried in forest soil, levels were about 29%. The differences in preservation are so profound that further investigation is required to find an explanation for the variation.

In most residues, ten months of burial in any type of soil produced little or no difference in the preservation of C18:1 isomers. It is possible that in some cases, the burial environment was protective in that the residues were less susceptible to oxidative degradation. This could be verified experimentally by burying tiles with exactly the same degrees of residue accumulation in the different soils and comparing them to unburied controls.

Sample Selection and Handling Guidelines

Ideally, archaeological samples for fatty acid analysis should be selected in the field. To prevent the introduction of contaminants, samples should only be handled with clean tools and gloved hands. It is preferable to examine unwashed artifacts, but it is possible to extract lipid residues from samples washed in clean water. In all cases, samples should be selected from the area of fat accumulation. With pottery, the area of fat accumulation varies with how the vessel was used (Charters et al. 1995). On the Northern Plains, where most vessels were cooking pots used for boiling, sherds from the neck or shoulder area are most suitable. Vessel morphology, paste characteristics, decoration and use-alterations, such as the location of soot and carbonized residues, provide clues as to the function of a vessel if it is not known (Henrickson and McDonald 1983; Hally 1983; Smith 1983; Skibo 1992).

With thermally altered rock, it is important to identify rocks, if possible which surfaces of those rocks, are most likely to have absorbed food residues. It is also necessary to assess in which rock would residues be best preserved. Burned rock features and cooking pits are widely distributed in the archaeological record in several parts of the United States (Ellis 1997). On the basis of ethnographic research, a variety of foods were likely prepared in pits using hot rocks as heat reservoirs.

Wandsnider (1997) reported that differences in food preparation relate to fat, protein and carbohydrate content. Foods prepared in the ovens may have been dry-roasted or water may have been added so that the food was steamed. The construction of earth ovens in terms of the physical arrangement of hot rocks, insulating material, and the food within ovens is also known to have varied (Ellis 1997). On the Northern Plains, there is ethnographic evidence that some pits were lined with hide and served as receptacles for stone boiling; some of the pits in the Southern Plains may have served similar functions (Quigg et al. 2001). Features resembling platforms or beds of burned rock may have been heated then used to broil, sear or parch foods (Ellis 1997). If rocks were exposed to secondary heating after the introduction of food residues, changes in the fatty acid decomposition due to thermal degradation may lead to erroneous identifications.

In the case of earth ovens, there is ethnographic evidence that insulating material served to absorb fat and other cooking juices lost by roasted animals (Wandsnider 1997). Thick layers of insulation between the food and the heat source would prevent residues from reaching the rocks. In this case, soil from the pit wall at the apparent food layer should be targeted and a natural control from the same depth below the surface should also be collected so that the soil lipids can be assessed.

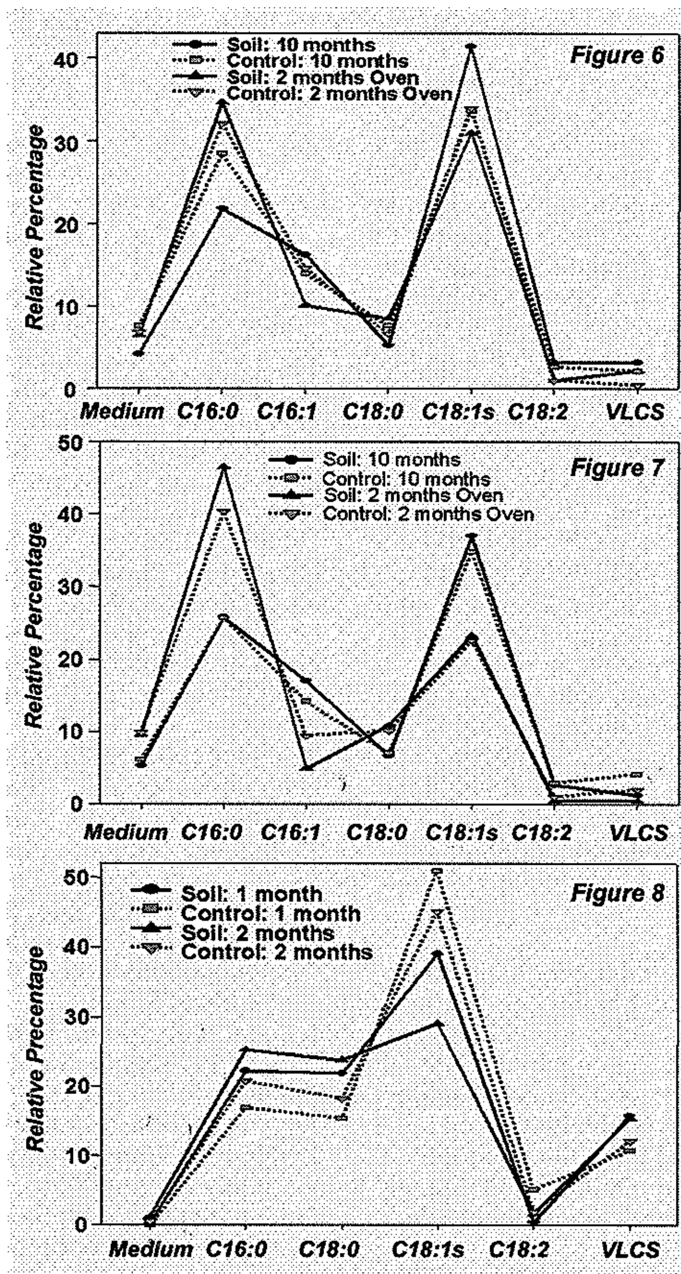

Figure 6 (top): Relative fatty acid compositions of pike cooking residues from the upper portion of the clay cylinder stored in parkland soil compared to controls after ten months and after two months of oven storage at 75°C. VLCS = very long chain (C20, C22 and C24) saturated fatty acids.

Figure 7 (middle): Relative fatty acid compositions of pike cooking residues from the lower portion of the clay cylinder stored in forest soil compared to controls after ten months and after two months of oven storage at 75°C. VLCS = very long chain (C20, C22 and C24) saturated fatty acids.

Figure 8 (bottom): Relative fatty acid compositions of Texas ebony cooking residues from the lower portion of the clay cylinder stored in forest soil compared to controls after one and two months of oven storage at 75°C. VLCS = very long chain (C20, C22 and C24) saturated fatty acids.

Conclusion

Fatty acid analysis is a relatively rapid, inexpensive and accessible method for obtaining a characterization of an archaeological residue. It is especially valuable when dealing with the material remains of cultures from periods for which there is no written history, such as those in North America prior to European contact. In these situations, a wide range of plant and animal foods may have been utilized. Under these circumstances, general characterizations of residues from many vessels may be far more beneficial than proving that a specific food was prepared in a certain vessel.

While fatty acid analysis alone cannot prove that a particular food was cooked, it is useful for showing that certain types of foods were not. This is particularly useful for delineating high fat content foods, low fat content foods and large herbivore products. It provides an independent line of evidence that can should used with other types of information, from artifact recoveries, faunal and archaeobotanical remains and other types of residue analyses, to paint a more complete picture of the activities of the site inhabitants. If desired or necessary, the total lipid extract can undergo further analyses, such as the identification of biomarkers or establishing stable isotope ratios of carbon and nitrogen (Barnard et al. 2007), which will refine the residue identification.

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