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Author(s): Steele, Valerie J.

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**RESERVE THIS SPACE**

## **Organic residues in archaeology – the highs and lows of recent research**

**Val Steele<sup>1,2</sup>**

**<sup>1</sup>Department of Conservation and Scientific Research, The British  
Museum, Great Russell Street, London, UK, WC1B 3DG**

**<sup>2</sup>Current address: Department of Archaeological Science, University  
of Bradford, Richmond Road, Bradford, UK, BD7 1DP. E-mail:  
v.j.steele1@bradford.ac.uk**

### **Abstract**

The analysis of organic residues from archaeological materials has become increasingly important to our understanding of ancient diet, trade and technology. Residues from diverse contexts have been retrieved and analysed from the remains of food, medicine and cosmetics to hafting material on stone arrowheads, pitch and tar from shipwrecks, and ancient manure from soils. Research has brought many advances in our understanding of archaeological, organic residues over the past two decades. Some have enabled very specific and detailed interpretations of materials preserved in the archaeological record. However there are still areas where we know very little, like the mechanisms at work during the formation and preservation of residues, and areas where each advance produces more questions rather than answers, as in the identification of degraded fats. This chapter will discuss some of the significant achievements in the field over the past decade and the ongoing challenges for research in this area.

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## **Introduction**

This chapter represents a personal view from the perspective of ten years' involvement in the field of organic residue research in archaeology and as such is not intended to be an exhaustive review article. Comprehensive reviews of the field are available in the literature and present a more detailed view of the research published in the last 10 years (1-5). In particular this chapter does not address advances in the field of ancient DNA research as applied to archaeological residues as this is a separate field outside the scope of this review (1). It will deal with some of the challenges facing research, including questions which are fundamental to our understanding of how organic residues behave in an archaeological context and others which arise directly from current and previous research.

It will then summarize some of the significant research carried out in recent years and, looking forward, the many possibilities which are opening up through the application of new analytical techniques from other areas of research. This 'cross-fertilization' between science and archaeology has been, and will continue to be, key to advancing the field of organic residue research and to applying the results from laboratory analysis in ways which are truly relevant to archaeology in the field.

### **What are organic residues in an archaeological context?**

Organic residues encompass a vast range of amorphous materials from diverse natural sources and associated with a wide variety of artefacts. They include residues of foods and other materials in pottery, residues left on stone tools during use, substances used in mummification, residues left in plaster floors by human activities, pastes and glues used in the construction of artworks and other artefacts, binders used to apply colour to paintings and statues, organic colourants used on textiles, organic material preserved in the mineral matrix of bone, and even the remains of ancient manures found in soils (3). Their analysis can inform us about trade, technology, diet, medicine, cosmetics, arts, crafts, farming practices, how people organized their houses and how they prepared their dead for burial (3, 6-8).

For organic material to survive over archaeological time it must be relatively resistant to degradation or burial conditions must be exceptionally favourable to its preservation. Lipids (fatty and waxy materials, bituminous substances, resins etc) are the most commonly occurring materials in archaeological residues as they are relatively insoluble in water and resistant to degradation (3, 9). In the past it was considered that proteins, starches and sugars would not survive over archaeological time (9). However more recent

research has found that, in some circumstances, these too can survive hundreds, perhaps thousands, of years (10-13).

Wet chemistry methods were the only analytical tools available to early analysts of archaeological residues (14-16). These require very large samples and in many cases are not sufficiently diagnostic to fully characterize the types of degraded samples found in archaeological contexts. From the 1970s onwards instrumental methods of analysis became increasingly available (17), and today instrumental chromatography (gas or liquid), more recently combined with mass spectrometry, has been the most widely used method. Other methods used to characterize ancient organic residues include various spectroscopies (infrared (FT-IR), Raman, nuclear magnetic resonance (NMR), ultraviolet (UV) etc.), scanning electron microscopy (SEM) for imaging and elemental analysis by energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray fluorescence (XRF), and high magnification light microscopy. Since the discovery that the fractionation of stable isotopes can provide a new dimension to residue research, isotope ratio mass spectrometry (IRMS) has also become part of the residue analysts tool kit (18). Over the past 15 years the use of chromatography (gas or liquid) combined with combustion-isotope ratio mass spectrometry (eg GC-C-IRMS) to measure the carbon isotopic signatures of individual fatty acids and amino acids has also become relatively routine (3, 11, 19).

## **Challenges facing organic residue research**

There are many questions and challenges in the field of organic residue research. Some of these are outlined below with the object of highlighting some of the more interesting and relevant questions and encouraging debate about and research into some of these issues.

### **Residue formation and preservation**

Some fundamental questions about how residues form and how they survive over archaeological time remain unanswered. For example absorbed residues in ceramics are present within the voids or pores in the ceramic fabric and this provides at least partial protection from degradation and dissolution (3, 4, 6, 8, 9). In soils organic compounds are adsorbed onto the surfaces of clay particles (20, 21) and it is not unreasonable to theorize that a similar process may take place between organic materials and ceramic fabrics (3, 4, 6, 22). Similar processes may be at work in partially-carbonized visible residues found in cooking pots where residues are encapsulated in a protective, organic matrix (3,

6). However little work has been done in this area and very little is known about the effect of different ceramic fabrics on the formation and preservation of residues. It is probable that the chemistry of a pottery fabric, including the presence of metal ions such as iron and copper within the clay, will affect the formation and preservation of residues. There is evidence for this in the formation of ketones in heated fats when metal oxides are present in the ceramic fabric (23, 24). Formation and preservation of residues may also be affected by the physical nature of the ceramic (coarseness, degree of firing etc). Evidence from soil science suggests that the size of the voids in ceramics may affect the preservation of residues by limiting the size of microorganisms that can access material within the pores (20).

Similarly there is much to be learned about how residues accumulate in ceramics. Is the residue which remains in a ceramic vessel indicative of the first use of that vessel, the last use of the vessel or an accumulation over the whole lifetime of the vessel, and how much organic material can a particular ceramic accumulate? Some experimental work has been done (4), but the answer to this question is still unclear. This is in part because it is very difficult to replicate the sustained use of a cooking pot, for example, over many years. Analysis of ethnographic pottery, where an accurate use-history is available for each vessel, could provide insights into some of these questions but such studies are rare and often remain unpublished (4, 25).

The effects of degradation on the chemical composition of organic materials during their use and subsequent burial is reasonably well understood (3, 4, 6, 8, 26-30). However, the increasing importance of isotopic analysis of various types of materials raises the question of whether isotopic values are stable under burial conditions. Two studies in the late 1990s measuring the carbon isotopic values ( $\delta^{13}\text{C}$ ) of stearic and palmitic acids before and after simulated burial in oxic and anoxic environments showed that, under these conditions, isotopic values remained robust (4, 7, 31). It has also been shown that the changes in hydrogen isotopic values ( $\delta\text{D}$ ) of individual fatty acids caused by cooking followed by burial for 16 months are significantly less than the natural variation in  $\delta\text{D}$  of fatty acids from a range of animal fats (32). However analysis of experimental cooking residues produced by boiling a range of foods in replica vessels, found that the bulk nitrogen and carbon isotopic values were not preserved during burial (33). More investigation would help to provide a better understanding of the processes affecting isotopic values of materials over archaeological time.

Another area where more research would be advantageous concerns conditions at archaeological sites and how these affect the preservation of organic residues. Organic materials, including amorphous organic residues, are well preserved in water-logged burial environments and at some, but not all, very dry sites (3, 4, 26, 34-43). By contrast organic material is very poorly preserved at sites where the water table is constantly rising and falling creating

cycles of wet and dry conditions (3). Exactly how site conditions affect the preservation of organic residues has yet to be investigated in detail. It is a potentially important question as the ability to assess whether food residues are likely to be preserved in pottery vessels from a particular site, in advance of a project, would allow decisions about the feasibility of residue analysis to be made at an early stage. However, soils are very variable in their chemistry, water content, and texture, all of which may affect the survival of organic residues buried in them. Local climatic conditions, in particular temperature, may also play a part in the destruction or survival of organic residues. It is rare to be offered soil samples from a site when analysing organic residues but the availability of soil would allow basic measurements of texture and pH to be recorded. The state of water-logging at sites is generally published in site reports and is often available for interrogation. A compilation of information from published residue analysis projects could begin to provide a basic understanding of some of these issues. The incorporation of research into future projects could also build up a significant amount of data on this question which would enhance the understanding of how organic residues behave under different burial conditions.

### **Contamination**

In seeking to characterize organic material from the past analysts are faced with the problem of trying to identify traces of significant compounds within an environment full of similar compounds of modern origin. Despite this little has been published about contamination and organic residues.

Over the lifetime of an organic residue there are several possible sources of contamination. The most obvious is the burial environment but it can prove extremely difficult to quantify exactly what soil or groundwater has contributed to an organic residue. In the one published study, Heron et al. (44) analysed pottery residues and organic material from adjacent soil and concluded that differences in type, distribution and abundances of organic compounds in the soil and the pottery were too significant for the soil to be the source of the residue in vessels.

By contrast, a recent pilot project on unwashed sherds from a north African site which had been cyclically wet and dry since its abandonment about 4,500 years ago, discovered no residues of archaeological interest in the pottery (45). Instead, organic compounds which are typical of modern, urban waste water were identified (45-48). It is possible that, in this case, the degradation and dissolution of any original residues in the pottery by the constant wet and dry cycles in the burial environment allowed the ingress of organic material from the ground water during the wetter cycles.

During post-excavation handling and storage the possibilities for contamination multiply rapidly and are even less well understood. However, there have been no published studies designed to measure how much material might be absorbed by ceramics, for example, during handling, washing and storage. Compounds from sun screens and insect repellants as well as insecticides have been identified in pottery residues (49, 50). When these are recently synthesized or isolated compounds, they can quickly be identified as modern and excluded from consideration but, when they are compounds which might have been present in the ancient world, distinguishing the modern from the archaeological can be challenging.

Plasticizers from plastic storage materials are easily identified as they are very distinctive and have no ancient equivalent (6, 51). However plastics contain a wide range of compounds which have the potential to migrate into material stored in close proximity, some of which are also found in ancient materials (52-54). Some plastics exude fatty acids (53, 55) which are the biomarker compounds for degraded fats (3, 6, 8) but fatty acids are also shed from the surface of human skin and will be deposited on any artifact which is handled (6, 56). Human skin lipids and other animal fats also contain the sterol cholesterol, used as an indicator of animal origin in degraded fats, which can sometimes be deposited on surfaces by contact with hands (6, 56, 57). Skin also excretes the compound squalene which degrades rapidly (57) and it is usually considered that, if cholesterol and squalene occur together, any lipid residues present may be due to handling (6). However squalene is also present in olive and other plant oils, sometimes in large abundances (58), and is not always present in skin (57). Skin lipids in fact appear to be very variable (59) and skin may also carry compounds from food, cosmetics, topical medicines and any other materials handled (57).

As a result, fatty material present at very low abundances may not be archaeological, and could be background contamination. In addition background levels of many contaminants are present in dust and air (60, 61) and may be a source of contamination in the laboratory. One study found low, but quantifiable, abundances of fatty acids in previously Soxhlet extracted pottery (62), suggesting that background levels of fatty acids are between 3 and 13  $\mu\text{g/g}$ , and Evershed (4) suggests that levels of residues below 5  $\mu\text{g/g}$  should be considered as background.

The preparation and analysis of method blanks can identify and quantify contamination introduced in the laboratory, while the analysis of soil samples, when available, can provide a picture of potential contamination from the burial environment. In the case of pottery residues, drilling samples from both sides of a pottery sherd can provide an assessment of any contamination present as residues of archaeological interest will usually be present on only one surface of a sherd (most often the interior), while contamination will accumulate on both surfaces. An awareness of the problem of distinguishing contamination from

residues of archaeological interest, and a basic knowledge of potential contaminants, is also advantageous when seeking to interpret the results of residue analysis.

### **Identification of fatty material**

One of the most challenging questions facing organic residue researchers at the present time is the secure identification of fatty material from the past. Fat residues include the remains of meat, oily fish, dairy products and vegetable oils, and their identification is particularly relevant to questions relating to diet and food culture but also to trade, technology, arts and crafts, and the use of specific features within ancient structures. They are found primarily in pottery but can also be present in hearths, floors, plaster surfaces, on stone tools, in works of art etc.

Degraded fats are usually composed primarily of palmitic (C<sub>16:0</sub>) and stearic (C<sub>18:0</sub>) acids regardless of the original source of the fat. This is due to the processes of degradation and dissolution that occur during burial and, in some cases, alteration of the fats during the lifetime of the vessel, for example during cooking. These processes tend to deplete diagnostic biomarker compounds that are characteristic of particular fats (3-5, 63-67) preventing the unique identification of degraded fatty material.

Work by Evershed's group in Bristol during the 1990s established that it was possible to distinguish different degraded fats by measuring the carbon stable isotope ratios, expressed as  $\delta^{13}\text{C}$  values, of C<sub>16:0</sub> and C<sub>18:0</sub> (3, 32, 64, 66). Modern reference fats fall within well-defined areas on a scatter plot of  $\delta^{13}\text{C}_{18:0}$  against  $\delta^{13}\text{C}_{16:0}$ , reflecting the different metabolic processes by which different organisms synthesize these two acids (5, 32, 68). Results can also be plotted as  $\Delta^{13}\text{C}$  vs  $\delta^{13}\text{C}_{16:0}$  (where  $\Delta^{13}\text{C} = \delta^{13}\text{C}_{18:0} - \delta^{13}\text{C}_{16:0}$ ), a method which eliminates minor local variations in isotopic values by using  $\Delta^{13}\text{C}$ , while still incorporating the variations in  $\delta^{13}\text{C}_{16:0}$  produced by the presence of marine fats or C<sub>4</sub> plants (67). Isotopic analysis has proved to be a very powerful tool for identifying individual fats, in particular dairy fats, even within mixtures. However, as more archaeological residues and modern reference fats are analysed, it is becoming clear that this may not be a universal solution to the question of identifying fats. Analysis of modern, reference horse fats from Kazakhstan showed almost complete overlap in carbon isotopic values between dairy and adipose fats (32, 69). Measurements of C<sub>3</sub> plant oil isotopic signatures show them to lie either on the mixing line between ruminant and non-ruminant adipose fats (70) or in the same range as cattle adipose fats (68). This is not typically a problem in pre-historic northern Europe, where the presence of plant oils is unlikely, but will be significant in the interpretation of results from the Mediterranean. There is also some evidence that occasionally deer adipose fat shows carbon isotopic



signatures where  $\Delta^{13}\text{C}$  is lower than  $-3.3\text{‰}$  (5, 71), an offset value generally used to define milk fats. The effect of cooking on the carbon isotopic values of individual fatty acids in milk was also considered by Spangenberg et al. (68) who measured variations of up to  $4\text{‰}$  between heated and unheated milk, an effect which varied with species.

Continuing research in this area is steadily increasing understanding of the strengths and weaknesses of compound specific carbon stable isotope analysis and providing solutions to some of the problems encountered (5, 32). The measurement of hydrogen isotopic values, while technically challenging, may provide a new level of discrimination in the identification of archaeological fats, already showing success in distinguishing horse milk and adipose fats (5, 32). Nevertheless, the interpretation of isotopic data from residues should always be carried out with full reference to the results of molecular analysis and to faunal and other evidence from the site. It is unlikely that it will ever be sufficient to examine isotopic data alone for the identification of fats.

### **Detecting alcoholic drinks**

The question of how to detect alcoholic drinks in archaeological residues continues to be one of the most debated areas in organic residue analysis (3, 72). There is no consensus among researchers on what unique biomarker compounds might survive over archaeological time to indicate the presence of a fermented beverage. The difficulty arises because alcoholic drinks consist mostly of water and water-soluble compounds such as sugars and alcohols which either leave no trace or disappear very rapidly in the burial environment. The main question then becomes which of the minor components of wine or beer might survive over archaeological time and be unique to only one type of fermented drink.

Tartaric and syringic acid have been suggested as suitable biomarker compounds for wine in archaeological residues (73-77). Syringic acid is derived from malvidin and is only found in significant abundances in red wine, increasing with the age of the wine – no other plant contains significant amounts (72, 76). Syringic acid can polymerize and this may contribute to its survival in archaeological residues (72). Tartaric acid is abundant in all grapes, and is strongly adsorbed onto silicates in pottery by hydrogen bonding, facilitating its survival (72). Tartaric acid itself is water soluble but its salts are far less soluble and may survive over archaeological time (72, 76). Both tartaric acid and syringic acid have been identified in visible and absorbed organic residues from pottery using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS-MS) (73, 78, 79) and in modern pottery soaked in wine (72). However tartaric acid is present in other plant species, sometimes at much higher abundances than in grapes (80), although in many cases these other plants would not have been used in the same contexts as wine. In addition the

presence of tartaric acid would only indicate the presence of grapes and does not provide any information about fermentation (77, 80). These problems have led researchers to question its use as a biomarker for wine. More recently analysis of modern wine and archaeological residues using GC-MS has identified not just tartaric acid, but a range of other organic acids including succinic, malic, fumaric and citric which may together provide a better indication of the presence of wine in organic residues (81).

Other approaches for detecting the presence of wine in organic residues are also being explored. Garnier et al. (82) used in situ tetramethylammonium hydroxide treatment followed by thermal hydrolysis and methylation-gas chromatography-mass spectrometry (THM-GC-MS) to look for phenolic compounds in modern wines, archaeological grape pips and two samples of Roman wine present as visible residues within amphorae. Phenolic compounds were detected in the ancient wines but some of the same compounds are also present in lignin and more research will be needed to determine whether any of the phenolic compounds identified prove to be unique biomarkers for wine. Polyphenols were identified in absorbed residues by Romanus et al. (83) using the Folin-Ciocalteu colorimetric reaction. This method has the disadvantage of requiring 1g of drilled sample from a sherd (a large sample for this type of analysis) and there is potential for false positives due to a reaction with reduced iron. This method detects the presence or absence of polyphenols but does not provide a detailed analysis of the compounds present.

Much of the analysis of wine residues has been carried out on exceptionally well preserved residues that were already known to be derived from wine, and these methods remain untested on more typical archaeological residues.

Beer and other fermented beverages present similar problems. Beer forms a deposit known as “beerstone” on standing which is primarily composed of calcium oxalate (77). Calcium oxalate has been identified in beer containers using a Fiegl spot test but it is also abundant in some plants, notably rhubarb and spinach (77). More recent work by Issakson et al. (84) has suggested that ergosterol might be used as a biomarker for fermentation as it is produced in large quantities by fungi including yeasts causing fermentation. This would only identify the use of a vessel or feature for fermentation and it is impossible to determine whether this happened in the course of bread-making or beer brewing as yeast would be active in both cases (84). The fact that fungi are present everywhere in the environment, including soil, raises some questions about the unique identification of fermentation using ergosterol as the sole biomarker (84). In addition the use of ergosterol in many modern skin preparations should be noted, particularly in the light of the contamination issues raised above (84). Microscopic analysis of visible beer residues has also been used to identify the cereals used to produce beer, and also identified malting and fermentation from the morphology of starch grains within the residue (85).

Experimental work incorporating the use of traditional brewing and fermentation procedures, the use of modern reconstructed ceramic vessels and simulated burial and/or degradation experiments would be invaluable in attempting to detect the remains of fermented beverages in organic residues. In addition, continuing work on the analysis of DNA for identifying wine or grape residues and yeasts (86, 87) may also provide answers questions about detecting ancient fermented beverages.

### **New developments in organic residue analysis**

An increasing number of new methods and approaches are being tested which will shape the field of organic residue analysis in the future and may provide answers to the some of the questions posed above.

#### **New methods in the analysis of organic residues**

There are a number of techniques in use in other areas of science which show great promise as tools for the analysis of organic residues. In particular, advances in the fields of proteomics and lipidomics have potential applications to the analysis of archaeological organic materials.

##### *New mass spectrometric techniques*

Several new techniques which involve the introduction of samples directly into a mass spectrometer are proving fruitful in the analysis of some organic materials from the past. The application of direct analysis in real time-mass spectrometry (DART-MS) to the fast screening of samples for organic residues is discussed in detail elsewhere in this volume. As a method involving no/minimal sample preparation and allowing non-destructive analysis of suitable samples, it is clear that there are many potential applications in archaeological and cultural heritage situations (88-90). It may become invaluable for the screening of large numbers of samples, allowing more time to be spent on the preparation and analysis of those which contain organic material. Ionisation of the organics within the sample without the need for a vacuum presents the possibility of a whole new set of applications for direct mass spectrometry. Within the wider scientific community DART-MS is already being combined with separation techniques such as thin layer chromatography (TLC), gas chromatography (GC), HPLC and tandem mass spectroscopy (91-95) and these techniques all have the potential to find applications in the analysis of archaeological organic residues.

The use of matrix-assisted laser desorption ionization-mass spectrometry (MALDI-MS) or more specifically MALDI-time of flight mass spectrometry (MALDI-TOF) has become routine in the analysis of large molecules such as lipids, proteins, carbohydrates and nucleic acids (96-101). It has been applied more recently to the analysis of proteins in ancient bones (102, 103) and eggshells (104), where it allows the identification of species, and has been used to analyse proteinaceous and lipid binders in works of art and wall plasters (105-108). It has been used to analyze proteinaceous glue from a wooden building (109), to study the photo-degradation of terpenoid varnishes (110), and to assess the condition and penetration of polyethylene glycol in preserved ships (111). There are also potential applications to pottery residues (112) and in the analysis of proteins from dental enamel (113, 114). A variation of MALDI-TOF, graphite-assisted laser desorption ionisation mass spectrometry (GALDI-TOF) has also been tested in the analysis of aged triterpenoid resins in varnishes (115). It seems probable that more applications will be published over the next few years.

Desorption electrospray ionization-mass spectrometry (DESI-MS) has also been used to analyse proteins from experimental residues applied to stone tools and archaeological pottery with a view to applying it to archaeological residues (116). DESI-MS, like DART-MS, allows the analysis of organic material with little or no sample preparation at ambient conditions (116). It has the capacity to detect and identify large molecules and, apart from proteins, has the potential to analyse triacylglycerols in fatty material, allowing the identification of fats without the need for isotopic analysis.

The development of gas chromatography-thermal conversion-isotope ratio mass spectrometry (GC-TC-IRMS) for the compound specific analysis of hydrogen isotopes has been cited above in connection with the discrimination of animal fats (p8). It appears likely that other applications of hydrogen compound specific isotope analysis will be forthcoming.

#### *New chromatographic techniques*

Although GC-MS is probably the technique most often associated with the analysis of ancient organic residues, the potential of liquid chromatography (LC) and HPLC with mass spectrometry or tandem mass spectrometry should not be overlooked. LC and HPLC have been used to identify caffeine and theobromine from chocolate residues (117-120), organic colourants on fabrics (121-126) and in Cretan icons (127), and used to examine the degradation of dyed and natural wool and silk fibres by measuring the concentrations of their degradation products (128). It is the method of choice for examining organic colourants which are often not suitable for GC-MS analysis. As described above, HPLC-MS-MS has successfully been used to detect tartaric and syringic acids in the

search for wine residues, and this particular application highlights the use of tandem mass spectrometric techniques to isolate particular target compounds from a complex sample. However the use of tandem mass spectrometric techniques seems limited for the present, possibly due to the difficulties of method development.

In the wider scientific community there has also been a rapid growth in the use of multiple tandem techniques, for example combining GC with HPLC and MS, and the use of two dimensional GC-GC-MS. These can also be combined with methods such as FT-IR or Raman spectroscopy. Few applications in organic residue research have been seen so far but may in future provide yet more powerful methodologies for interrogating archaeological residues.

### **The application of established methods to new situations**

The application of established methods to new types of residue and the use of multiple techniques to characterize a single residue both offer exciting new possibilities.

#### *Plant microfossils*

The extraction and analysis of starch grains and phytoliths from organic residues is not new. These plant microfossils have been used extensively to examine residues from stone tools (129-133), shell tools (134), sediments (135-137), grinding stones (138), and dental calculus (139, 140). The presence of starch grains and phytoliths has also been used to identify maize and beans in pottery residues from North America (141, 142) and of a range of plant foods in residues from ceramic and stone artefacts from Bolivia (143). However the full potential of this type of analysis when applied to visible residues from pottery is only just beginning to be explored and presents a unique opportunity to identify the past culinary use of specific plants.

This approach has rarely been applied to cooking residues in northern Europe (144). Phytoliths form at a much reduced rate in plants growing in temperate conditions compared with those grown in tropical or arid regions, and until recently it was unclear whether phytoliths would still be present in residues from northern Europe (145). However, a recent study found both starch grains and phytoliths in carbonized residues from Late Mesolithic Ertebølle and Early Neolithic Funnel Beaker pottery from Neustadt in northern Germany (145). The analysis of starch grains revealed very few cereals, even in the Neolithic samples, supporting the archaeological evidence that the introduction of cereal crops was slow in this area (145). Wild resources continued to be exploited across the transition to agriculture, predominantly acorns but also sweet flag,

sedge, meadowsweet, reeds, hazelnuts and bracken (145). Phytolith analysis revealed other plant material usually considered invisible in organic residues, including plants which would have been used as flavourings (146).

#### *Residues from unexpected sources*

Over the past decade residues have been detected on and in artefacts where their survival was unexpected. The retrieval of residues from stone tools, originally regarded with some skepticism, is now well established as legitimate research (147-157). Residues of archaeological interest have also been extracted from pottery assemblages after long-term storage in museums (50), and pottery which has been washed (50).

Since 2009 two separate and independent studies on material from different countries have identified both absorbed and visible residues from soft stone cooking pots (158, 159). The study of 5<sup>th</sup> to 13<sup>th</sup> century chlorite vessels from Merv in Turkmenistan also used modern, chlorite cooking pots to investigate the structure of the stone itself, how it behaves when heated and how this could facilitate the preservation of absorbed residues (158).

The detection of partially carbonized residues from the hoard of Iron Age copper alloy and iron cauldrons found in a field near Chiseldon, Wiltshire, U.K. was unexpected (160-162). The fact that the cauldrons had been lifted in blocks and micro-excavated in the Conservation Department at the British Museum allowed areas different to the surrounding soil or metal corrosion products to be identified by the excavators (160-162). These turned out to be remarkably well-preserved, partially carbonized food residues, probably owing their good preservation to an interaction with the iron and copper corrosion products formed on the metal surfaces (20, 163).

#### *The use of multiple techniques in residue research*

There are an increasing number of papers illustrating the application of multiple techniques to a single question. Sometimes these projects employ the use of a screening method followed by more detailed analysis of selected samples. Others use multiple methods to provide a fuller picture of the nature of the residue(s) under examination, particularly where the residue has inorganic components.

In food residues the use of GC-MS followed by isotopic analysis is routine (3, 32), sometimes combined with phytolith and starch grain analysis of visible food residues (145, 164). The use of different chromatographic methods to analyse the same material is also becoming more routine, particularly in the area of dyes and paints where organic colourants may be mixed with different

binding materials (165, 166). Where inorganic colourants are also present, a combination of chromatographic and other techniques such as XRF, XRD, SEM, SEM-EDX, Raman and FT-IR can provide a complete characterization of the paints, dyes or other materials being analysed (28, 122, 167-169). This approach has also proved successful in the analysis of vessel contents suspected of being paints, inks, medicines or cosmetics (168, 170, 171). For a round robin analysis of a 17<sup>th</sup> century ointment, recreated to an authentic recipe, 11 laboratories used 10 different methods to analyse a sample of the ointment (172). The methods used included FT-IR, Raman and micro-Raman spectroscopies, surface enhanced Raman scattering (SERS), GC-MS, pyrolysis-GC-MS, solid phase micro extraction-GC-MS (SPME-GC-MS), HPLC-MS and XRF. No laboratory employed all of these methods and no laboratory completely characterized the ointment, although many identified the majority of components. This illustrates the importance of considering multiple techniques when analyzing very complex residues from the past.

### **The future of organic residue analysis**

The application of new techniques and the discovery that organic residues have the capacity to survive in unexpected circumstances are opening up increased opportunities for residue analysis. However to take full advantage of these new opportunities carefully planned, rigorously executed research is necessary that combines best practice from both science and archaeology.

All new research projects should be designed to answer one or more questions of archaeological or scientific significance. These questions will determine how the material is sampled, what methods will be used and what data is collected to give the answers required. Much time, effort and money can be wasted by not establishing the aims and objectives of a project at the planning stage.

Careful consideration should be given to how the material is sampled. The sampling strategy should be designed to answer the archaeological or scientific question and should also aim to be statistically significant (173, 174). Sampling is always a compromise between what is ideal and what is possible but careful use of the samples available can maximize the relevance of the data obtained.

Analytical methods should be appropriate to the types of samples and the information expected from the analysis. All methods have strengths and limitations and it is important to know what these are in order to decide which methodologies will provide the best results. It is also useful to know the limitations of the data produced by any analytical method so that complementary analysis can be included in the project design if necessary. Data analysis should be carried out either by, or in close collaboration with, an analyst with experience in the techniques being used.

Data interpretation must always be carried out with due reference to historical and geographical context. Some knowledge of contamination issues, including possible modern contaminants and their sources, is essential in data interpretation. This will avoid obvious mistakes in identifying a residue as a material which was not available in the historical period and/or geographical area where the residue originated. Other data from the same or similar archaeological sites, such as faunal analyses, environmental data etc., is also helpful when interpreting residue analysis data.

In designing new projects which incorporate these features, close collaboration is necessary between archaeologists and scientists. This collaboration will be the key to excellent research in the future. Ideally organic residue research should involve archaeologists who have some knowledge of science and scientific method and scientists who have a basic understanding of archaeology. With increasingly complex analytical techniques finding applications in the study of organic residues more communication will be required between scientist and archaeologist in the future.

So much is still unknown about how our ancestors lived, worked, sourced and cooked their food and buried their dead that there is ample scope for more research for many years to come. Well designed, well executed organic residue analysis projects, incorporating the best from archeology and science, have an important part to play in this quest to understand the past.

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