Fabrics and food: 25 years of scientific analysis of medieval ceramics

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SUMMARY

Scientific techniques have been extensively applied to medieval ceramics over the last 25 years, and as the techniques have developed the types of information obtained have widened. Major advances have been made in provenance studies, including a number of large-scale projects involving hundreds of sherds. Questions of ancient technology have also held the attention of scientists and ceramic specialists. In addition, the uses to which pots were put have been investigated by the analysis of food residues and other organic deposits using techniques for organic chemical analysis.

INTRODUCTION

Ceramic studies have shared in the burgeoning growth of the use of scientific methods in archaeology over the last quarter-century. Archaeological science conferences reflect the main research efforts of archaeometrists, and have continued to feature ceramics as one of the major themes which occur on all timetables. For a material scientist, ceramics offer endless fascination; their relative lack of change in structure since firing means that the original technology used to make them is still 'frozen' in the fabric, rather than being lost though corrosion or chemical decay processes. The fabric also contains a chemical 'fingerprint' of the original clay deposit from which it was fashioned.

Equally important questions about ancient technology have been pursued ('How was this pot made?'), and the use of the scanning electron microscope has done much to improve our knowledge of pottery materials and techniques at the 'micro' scale, especially the use of clay fabrics, pigments and glazes. The forming processes of pottery have also yielded to the application of radiography, including the more specialised version of Xeroradiography. The actual household uses of pots have not been neglected and there have been numbers of studies by a few research groups, using organic analysis methods on food residues found on or in the fabric of pottery sherds. These take us back to the foodstuffs originally boiled, cooked or burnt(?) in them.

This paper will look briefly at broad aspects of the application of scientific techniques to medieval ceramics over the last 25 years. General as well as more detailed descriptions of the techniques will be found in the range of books on archaeometry now available, for example Tite (1972), Pollard and Heron (1996), Lambert (1997) and Henderson (2000). A handbook has recently been published (Barclay 2000) which sets out to guide archaeologists and others through the range of information that might be sought through scientific analysis.

POTTERY DATING

Two scientific techniques can be used for the dating of pottery using physical characteristics; both depend on setting a mineral 'clock' to zero when the pottery was fired. Thermoluminescence (TL dating) of pottery was developed in a number of centres in the 1960s, including the Research Laboratory for Archaeology and the History of Art at the University of Oxford (Aitken *et al.* 1968). In outline, the technique depends upon the action of ionizing radiation on mineral grains, which frees electrons and traps them within defects in the crystal lattice. A slow build-up of energy stored in this way can be released by heating the ceramic, allowing light energy to be emitted and detected. In general terms, the more light emitted, the longer the build-up and hence time since the 'clock' was set to zero at the time of firing. Modern descriptions of the technique describe its refinements and pitfalls (Aitken 1990); its application to medieval ceramics has been relatively limited, but it remains a method

of potential. Thermoremanent magnetism of fired clays, including kiln structures as well as ceramic artefacts, involves the detection of their intensity and direction of residual magnetism, reflecting that of the earth's magnetic field at the time of firing (Aitken 1990). The dating of kilns has been its major contribution to medieval ceramics.

PROVENANCE STUDIES: TECHNIQUES AND RESULTS

Probably a majority of the applications of scientific techniques to medieval ceramics developed over the last 25 years have been in the field of provenance studies — the use of scientific analysis to determine the source of the clay (and therefore its likely place of production). Petrology (thin-section analysis) has been in use for decades; it examines visually the mineral fabric, concentrating especially on the inclusions. It is not considered in detail in this paper, but it is appropriate to emphasise that petrological and chemical analytical techniques are complements rather than rivals. Because inclusions form by definition only a minor part of the fabric, chemical analysis of the whole fabric is dominated by the chemistry of the clay matrix, derived from the clay minerals in the original deposit. Thus the two approaches examine different features of the fabric, and their combined use on a single ceramic provides a powerful combination, each providing explanations of the features in the other technique. Whereas statistical methods have been developed for summarising and comparing assemblages of pottery (Orton, this volume), rather different statistical methods, using multivariate techniques and related taxonomic methods for classification (e.g. cluster analysis) are required for the interpretation of the mass of numbers generated during a typical ceramic provenance project.

There are almost 100 naturally occurring chemical elements in nature, and even trace amounts of each are present in all inorganic materials. Routine techniques for elemental analysis can often detect about one third of these in ceramics; the rest are below their detection limit. The introduction of 'big machines' (e.g. proton accelerators) have increased the numbers of elements detected, but for reasons of cost and personnel remain restricted to a few laboratories.

Neutron activation analysis (NAA)

Of elemental analysis techniques, neutron activation has been regarded as the method of choice over the period of this review. It was growing in popularity at the beginning of the period, and interestingly the very first paper in the first issue of *Medieval Ceramics* is an outline of neutron activation analysis applied to medieval ceramics (Aspinall 1977). This reported a major project involving analyses of about 700 sherds of medieval pottery from kiln sites in Yorkshire, undertaken at the University of Bradford. While neutron activation analysis has been extensively used for provenance studies of ceramics in the past, in recent years there have been increasing moves away from nuclear-based techniques, leading to the closure of many university research reactors and the decline in laboratories that practise the method. It has been replaced by *inductively-coupled plasma atomic emission spectrometry* (ICP-AES, often shortened to ICP or ICPS). Major projects using these methods will be reviewed below.

Important programmes of neutron activation analysis have been carried out by the British Museum over the last 15 years, including three on tin-glazed ceramics. The first of these was on Hispano-Moresque and other Spanish tin-glazed wares (Hughes and Vince 1986; Blake *et al.* 1992; Gaimster *et al.* 1991; Hughes 1991a, 1995). Following this we carried out analyses of Italian tin-glazed wares, including maiolica from many centres (Hughes 1991b; Hughes *et al.* 1997), which has proved very relevant to the third major area of research, on northern European maiolica (Hughes and Gaimster 1999 and forthcoming; Gaimster and Hughes 1999a, b). The analytical techniques used in these programs have been discussed in detail by Hughes *et al.* (1991).

The aim of the investigation of northern maiolica was to see if it was possible to distinguish between maiolica produced in England and the Low Countries, and to apply the results to specific problems. The ceramics from Norwich were particularly distinctive in composition, and could be readily identified by chemical analysis. Haarlem ceramics were also distinctive in composition compared to those of other production centres in the Low Countries, such as Antwerp, Utrecht, and Amsterdam. A principal components analysis plot arising from the neutron activation analysis of reference pottery made at Antwerp is shown in Figure 1. The ellipses have been added to indicate that the pottery made in three different kilns within the city (Steenhowersvest, Schoytestraat and near the National Museum of Navigation) show slightly different chemical compositions. Test pieces compared against these include 'Malling jugs' found in London and the Low Countries (shown as star symbols), which were concluded to be Antwerp products from their analyses. This confirmed the indications from many archaeological studies of recent years.

The most unexpected result of the project was the discovery of supposed northern maiolicas that were distinctive in composition but unlike any reference sherds from England or the Low Countries.
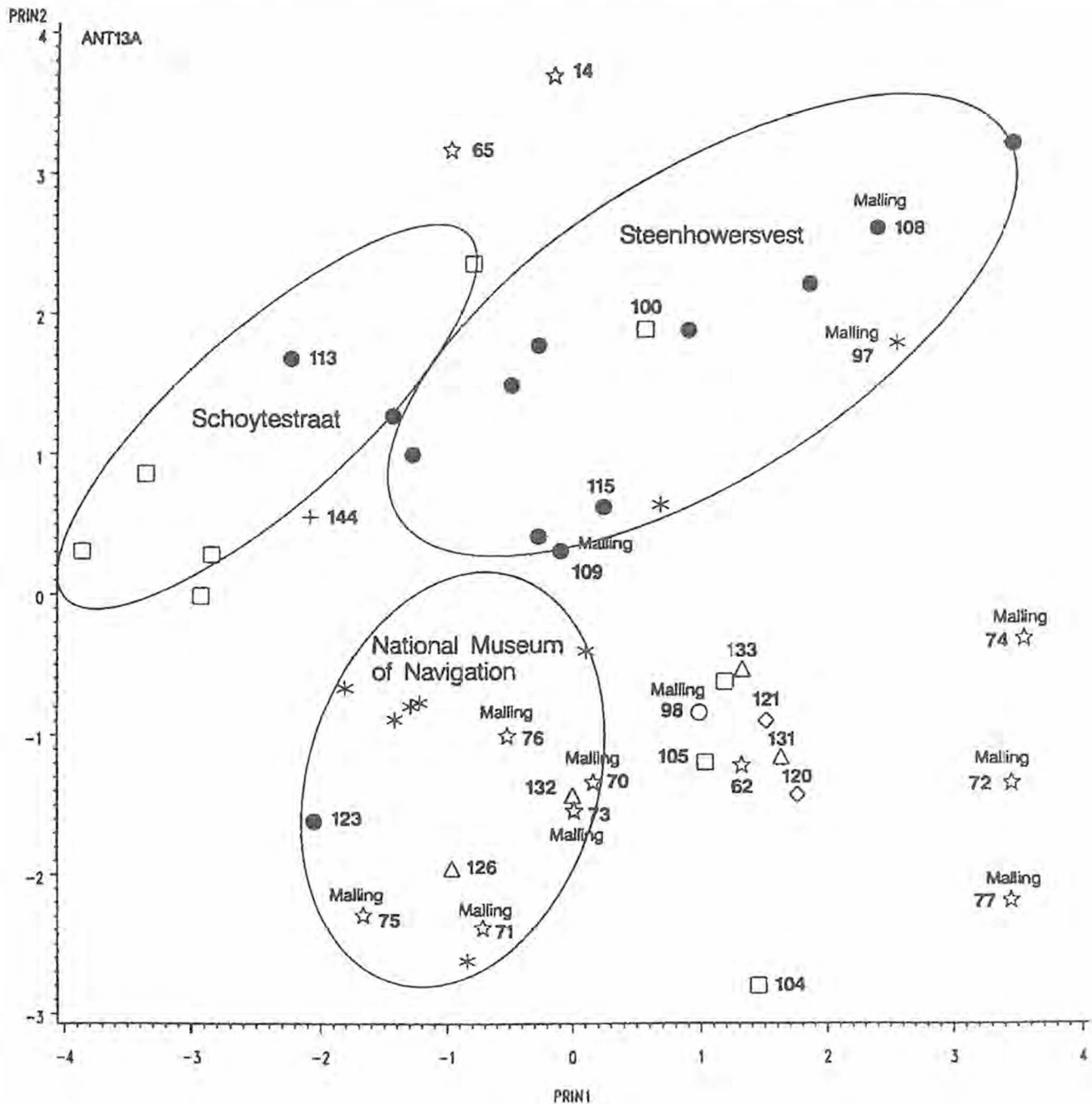
Fig. 1. Principal components analysis arising from neutron activation analyses of Antwerp tin-glazed reference ceramics. This is a kind of chemical composition 'map', with each symbol representing the analysis of one ceramic. It shows there are chemical differences between the three kiln sources: Schoytestraat (squares), Steenhowersvest (filled circles), National Museum of Navigation (asterisks) and Bishop's Palace (diamonds). Test pieces shown in this Figure (stars), mainly found in London, were assigned by analysis to the Antwerp ceramic composition, including mainly 'Malling jugs' (labelled 'Malling'). Three of the reference pieces from Steenhowersvest were also 'Malling jugs'. (After Hughes and Gaimster 1999, fig. 3.8).

Because there was already a database of ceramics of Italian origin, however, we were able to see obvious similarities in composition to northen Italian ceramics from Tuscany and Umbria. About half of the distinctive ring-handled vases analysed from London were more like reference ceramics analysed from Tuscany, specifically some from Siena. Others

appeared to be produced in the lower Arno valley, among which several different composition groups emerged. This group included in their decoration the sacred trigram (IHS or YHS), and Blake (1999) has discussed the association between such wares as commissioned pieces and locations where devotion to the Holy Name was practised.

Neutron activation projects on medieval tiles from the English Midlands have also been carried out (Hughes *et al.* 1982; Leese *et al.* 1986; Hughes and Cherry 1991), including a large-scale study of inlaid, decorated floor tiles found at Bordesley Abbey, Redditch (Leese *et al.* 1989). Other current neutron activation programmes are in course of publication on the medieval and post-medieval redwares of London and Essex.

In Germany, Hans Mommsen, of the University of Bonn, has undertaken a neutron activation analysis programme on German stoneware, especially on finds in museums. An analytical study of Mayen and Tating ware found at different locations in Denmark, Germany and the Netherlands showed that most of the Tating ware belonged to a group which was not produced in Mayen (Stilke *et al.* 1996), except for one sample, a variant of the classic ware. Stilke *et al.* (1996) note that over the last 80 years discussion about the production area has thrown up numerous opinions and hypotheses. Some petrological work was carried out in the past, but the absence of any true 'classic' Tating ware at the production site in Mayen has remained an enigma until the neutron activation study was undertaken. The careful targeting of such analytical studies can finally produce some concrete evidence on which a satisfactory solution to long-unresolved differences of opinion can be based.

The British Museum has published, in David Gaimster's book on German stoneware, a study by NAA of the compositional features of well-documented and dated finds of stoneware from specific workshops (Hook 1997).

Inductively-coupled plasma atomic emission spectrometry (ICP-AES)

The recent shift towards analysis by ICP has opened up the possibility of routinely undertaking far more projects in pottery provenance. The analyses are cheaper to obtain than NAA, and readily available from a number of laboratories acting on a commercial basis. ICP has further advantages: it does not involve radioactive material; it routinely gives high-quality analytical data for a large number of elements in a single sample (typically 27 elements; neutron activation measures slightly fewer); it analyses for both major and trace elements, whereas neutron activation analyses mostly for trace elements; it requires small sample sizes (typically 100–200 milligrams); and is a more rapid technique than neutron activation, so projects with large numbers of samples can be done in a reasonable time. It is clear that ICP-AES offers an extremely useful tool for defining the origin of pottery, including the ability to define closely several sources within a region. The data it produces are directly comparable

for a restricted range of elements (just over ten) with neutron activation. However, the chemical distinctions between pottery groups become more blurred when using fewer elements — typically, with ICP alone, about 15–20 elements would be used for statistical interpretation of the analyses. The data produced by such laboratories still needs to be interpreted by those familiar with archaeological ceramics, and using multivariate statistical methods.

Good descriptions of the technique and its applications are given by Thompson and Walsh (1989) and Potts (1987, ch. 5). The technique uses a high-temperature flame (plasma) to excite the emission lines of elements in the UV to visible range of the spectrum. The material to be analysed has first to be dissolved using acids and the solution obtained is sprayed into the plasma, where light is emitted by each element present, in proportion to its concentration in the solution (and in the original solid). By simultaneously measuring the light intensity at a range of wavelengths, the element signals can be detected, and calibrated for quantitative analysis with solutions containing known amounts of elements. From this the amount of each element in the original solution, and solid, can be calculated. A particular feature is that the intensity of light emitted per element is directly proportional to amount over many orders of magnitude. The detection system is very sensitive, so trace elements as well as major elements can be measured, normally a total of 27 or more. Each solution may only need to be sprayed into the instrument for a few minutes. When the sample preparation is scaled-up, large numbers of samples can be processed in a relatively short time; an automated sample changer presents each sample to the ICP in turn and reduces manual handling. The calculation of the concentrations of elements takes place using computers, on which the resulting data are stored for transfer to other formats such as spreadsheet programs. Applications to medieval ceramics are now beginning to be published — a recent example is the analysis of floor tiles from Cleeve Abbey, Somerset (Vince 1998).

Other elemental analysis techniques

A study of sandy and coarse utilitarian medieval wares from Dorset was undertaken by Spoerry (1990) using atomic absorption spectrometry. Although only a minimal number of elements were measured — iron, magnesium, aluminium and nickel — nevertheless the results showed chemical distinctions in the pottery. Sandy ware was produced at a small number of sites in west Dorset and south Somerset, while the chemical evidence suggested the coarse wares were produced on a large scale at fewer centres in east Dorset and west Wiltshire.

The laboratory of Maurice Picon at Lyon has undertaken numerous XRF analyses on medieval French ceramics, including early work on Spanish imports into southern France. Similarly, Daniel Dufournier, at the University of Caen, Laboratoire de Ceramologie, has made extensive analyses of groups of French medieval ceramics. These have included their recognition and analysis in the Bryggen excavations in Bergen, Norway (Deroeux *et al.* 1994). This showed the presence of a number of fabrics, which split into two major groups: ceramics from the Channel area and from the Atlantic seaboard of France, which appear to reflect the fluctuations of the wine trade. The chemical groups so defined can be compared with future analyses of sherds discovered in France. Radio-isotope sources have also been used to generate x-ray fluorescence as a method for provenance studies on medieval ceramics (La Brecque *et al.* 1998).

Electrochemical methods have also been applied occasionally to medieval ceramics (Brunc *et al.* 1994; Domenech-Carbo *et al.* 2000).

Future developments

If one can discern a trend in chemical analytical studies, it is towards methods that deliver large numbers of elemental analyses per sample. It may become more routine to use a specific version of ICP that has as the detection system a mass spectrometer (ICP-MS), where large numbers of trace elements are the main focus of the analytical results. These instruments are more expensive; not many projects based on ceramics have been carried out yet to see if they can deliver useful analytical data.

There have been developments in XRF over the last few years with micro-focus spectrometers which promise to yield better detection limits on trace elements, but again there are no major projects on ceramics for which this equipment has been used. Total reflection XRF (TXRF) is beginning to be used, though no published reports of applications to medieval ceramics have yet appeared.

POTTERY MANUFACTURE: TECHNIQUES AND RESULTS

Pertinent questions about ancient technology have been considered important to answer, benefiting greatly from the use of the scanning electron microscope. There are numerous books on methods of making pots, but from the archaeological viewpoint, particularly recommended are those of Shepard (1954) and Orton *et al.* (1993), while Arnold (1985) is well-known for his discussion of ceramic resources and technical innovation. On the fashioning of pottery from an archaeologist's viewpoint, Rye (1981) has become a standard work.

There have been a number of approaches to establishing the firing temperature of ancient pottery through scientific methods. These have included thermal analysis to try to judge the fabric's thermal history, and petrological examination and x-ray diffraction to look for the presence or absence of temperature-sensitive minerals (Tite 1972, 323–8; a recent example is Moropoulou *et al.* 1995). Mineralogical methods give only a broad indication of firing temperature, which can also be judged from scanning electron microscopy of pottery fabrics. Thermal expansion methods showed an initial promise of greater precision, which proved premature since later work has shown that many factors influence the expansion of ceramics with temperature.

Much too can be learnt from the reproduction of medieval techniques, and the series of studies by Newell on thumbed and sagging bases (1994), 'splashed glazes' (1995; also considered earlier by Griffiths and Redknap 1991), reduced wares (1998–99a) and left-leaning handles (1998–99b) have been exemplary in this respect. The very different structural features of reduced ceramics compared to oxidised ware can be explained from the combination of chemistry and practical kiln firing experience. As Newell (1998–99a) shows, reduction firing is far more common — *i.e.* easier to achieve than prevent — than many pottery specialists have believed in the past. He illustrates the different firing conditions induced by changes in the types of capping used on medieval kilns, using real firing experiments which replicate the conditions to research the actual processes.

The forming processes of pottery have also yielded to the application of radiography (Middleton 1997). Particularly useful is the more specialised version, Xeroradiography, in which the conventional photographic film is replaced by a specially charged plate to capture the image. The X-rays impinging on the plate have different energies according to the degree of absorption by the object, and so discharge differentially the electric charge on the plate. The resulting plate is 'developed' and the image has the particular feature of enhancing discontinuities. It produces informative radiographs on ceramic materials; for example, methods of fixing handles can be understood, and the orientation of voids or inclusions can indicate wheel-throwing or hand-building. Figure 2 shows a Xeroradiograph of a medieval aquamanile in Lyveden/Stanion ware, in the shape of ram, lead-glazed and dating to the late 13th to early 14th century (Nenk and Walker 1991). The Figure shows the addition of the spouts for filling (tail) and pouring (head). The body is shown to be coil-built; oblique joint lines can be seen across the body from the lower side, and the diagonal markings are incised decoration.

Scanning Electron Microscope

The scanning electron microscope (SEM) produces magnified images of outstanding quality and information, and is widely used in materials science studies. The images have great depth of field even at very high magnifications of several thousand times, far beyond that possible with optical microscopes. They appear in popular science magazines and books everywhere; a selection of typical images and brief history of the technique is given in Burgess *et al.* (1990). The technique was just being introduced to archaeological ceramics at the start of our survey period (Tite and Maniatis 1975). The practical applications to ceramics have been especially the examination of fracture or polished cross-sections; here any glaze layer is clearly visible, as well as mineral inclusions. Within the clay matrix, it is also possible to determine the degree of vitrification, shown as interlinking threads of glass formed by the melting of the more fusible of the materials in the clay. Approaching total vitrification, the fabric has effectively fused, and is typical of some 'wasters', shown by their hard, glassy outward appearance. The degree of vitrification was shown to be linked to the clay type (calcareous, non-calcareous) and to the firing temperature, estimated from the appearance of the fabric by an SEM (Tite and Maniatis 1975).

Figure 3 shows a scanning electron micrograph of a fracture cross-section through a 16th-century sherd of Turkish Iznik quartz-bodied pottery (the white scale bar shows 0.2 mm = 200 microns). The image was taken with the latest type of low-vacuum SEM, which does not require that non-conducting materials such as ceramic are pre-coated with carbon or gold to avoid charge build-up on the surface of the artefact. The image was taken with a backscattered electron detector so that the atomic number contrast is seen, representing areas of different chemical composition. Lighter regions represent areas containing mostly heavy metal ions, and darker regions represent overall lighter elements. Backscattered electron images also show less evidence of specimen charging — these and other aspects of imaging of archaeological materials in the SEM have been discussed by Meeks (1988). In Figure 3, the glaze layer, at the top, is *c.* 250 microns thick and has 'whited out' — chemical analysis using the X-ray facilities on this SEM showed that it is a lead-silica-alkali glaze (lead has a high atomic number). Below the glaze is the interaction layer between glaze and body into which the glaze has penetrated. The third layer is a white slip on which the underglaze decoration was painted. It has finer silica (quartz) grains than the body, which is the fourth layer, and which it seals. The body consists of irregular, unreacted (unmelted) quartz grains cemented by thin ribbons of lead-rich glass; the visual appearance of the fabric is white with a 'sugary' texture. The production processes of Iznik ceramics have been illuminated by the SEM and analysis studies of Tite (1989) and Atasok and Raby (1989, ch. 6).

A rare find of an unmatured glaze on 15th- to 16th-century Malvernian pottery (Hurst and Freestone 1996) provided the opportunity for a better understanding of medieval glazing technology. Sherds with a white coating were excavated in some numbers at a kiln site at Hanley Swan, Worcestershire. Cross-sections were mounted for SEM examination and quantitative chemical analysis. The white coating was a thin layer (up to 0.5 mm) consisting predominantly of lead oxide. X-ray diffraction on separate samples had shown that lead phosphate and lead carbonate were the main constituents — common weathering products of lead-bearing materials. Beneath the coating some interaction with the body had taken place, including a glassy layer just 10 microns thick (1000 microns = 1 mm), clearly visible in the SEM image. There were two other layers of similar thickness but differing degrees of vitrification. The evidence suggests the glaze had been applied as lead oxide produced by methods described by medieval writers such as Eraclius (De Bouard 1974).

Meddens and Redknap (1992) include an SEM study on the glazes on late 13th- to 14th-century kiln sherds from Mill Green, near Ingatestone, Essex. Analysis of the glazes using energy-dispersive XRF attached to the SEM showed two different techniques in use: one used iron as the colourant in a lead glaze, with colours produced by iron that ranged from yellow to olive green depending on the redox (reducing/oxidising) atmosphere in the kiln. The second form of surface treatment on jugs was the application of an opaque white slip covering the whole of the surface, under a thick bright green glaze — in this case the SEM analysis showed it was coloured by copper. Higher levels of sulphur than expected were detected in both the copper and iron greens and one iron red glaze, suggesting the use of galena (lead sulphide) for the flux.

Colourants can be easily detected, and their chemistry, morphology and particulate distribution seen. For example, on Italian Renaissance ceramics (Tite 1991) the yellow was lead antimonate, and in one example appeared as an undulating ribbon of colourant grains just below the glaze surface. The SEM allowed individual particles, only a few microns in diameter, to be analysed using the X-ray facilities on the microscope. Particles of the opacifying agent tin oxide were also seen scattered throughout the glaze layer on typical maiolica. The tin oxide was normally present at 5–10% in the glaze composition, although in some archaic maiolica, contents as high as 20% were found.

Fig. 2. Xeroradiograph of an aquamanile in the form of a ram (British Museum MLA1984,6-3,1) in Lyveden-Stanion ware, 238 mm in length. The Figure shows that the cylinder was hand-built, revealing parallel alignment of coils. The tubular filling-spout was luted over a hole pierced in the upper body. (After Nenk and Walker 1991, fig. 2).
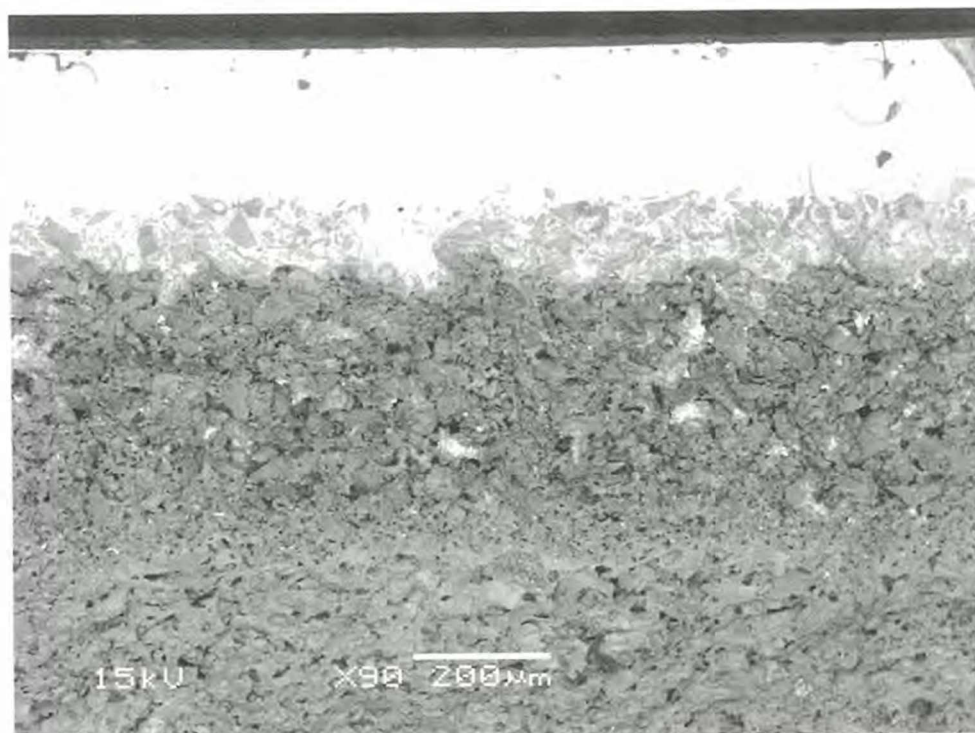

Fig. 3. Scanning electron micrograph of a fracture cross-section through a 16th-century Iznik quartz-bodied ware. The clear layer at the top is the glaze, below which is a reaction zone between glaze and body, followed by a thin slip layer lying on top of the coarser-grained quartz-rich body. The horizontal bar indicates 200 microns scale; it was taken on a JEOL JSM-5600 Low-Vacuum Scanning Electron Microscope.

An SEM and analytical study of the technology of German stoneware glazes (Freestone and Tite 1997) showed compositional changes that loosely correlate with inferred changes in kiln design and glazing technique. In recent years, the complex body structures and chemical compositions of British porcelains have become better understood as a results of examination and analysis on the SEM (Tite and Bimson 1991; Freestone 1999).

The appeal of SEM studies is that they yield an image with a mass of useful technological detail. In terms of scientific effort, a project using an SEM to examine ceramics would probably only include 6–10 samples because of the time taken, and pressures on the use of such microscopes, which are labour-intensive. By contrast, the elemental analytical data for provenance studies uses relatively short times to produce the measurements, so projects can have dozens or hundreds of samples, though interpretation then needs statistical methods.

ORGANIC RESIDUES ON POTTERY

There has been a growing interest over the last 25 years in identifying the household and industrial uses of pots using scientific analysis. A small number of research groups have studied deposits found on or in the fabric of pottery sherds using organic analysis methods. These food residues take us back to the foodstuffs originally boiled, cooked or perhaps burnt in them. The processing of non-food materials, such as dyes in ceramic containers, also leads to the deposition of organic residues whose analysis can shed light on such technological processes. Unlike inorganic materials, such as fired clay or metals, however, the problem of survival of the original organic material is severe, and it is to be expected that all are affected by degradation.

The main reason for the relatively slow development of organic analysis in archaeology in general is that the material available for analysis occurs in small amounts and is often charred or partly carbonised. Traditional methods for organic analysis are not possible and it has required the development of instrumental methods of analysis for serious research to be undertaken. Even so, one major obstacle to such studies is ensuring that the organic components of a residue are completely extracted, and that all the components can be identified. A second obstacle is ascertaining whether there has been any substantial exchange of organic substances between the residue and the environment, usually soil. A third problem is the shortage of data on the decomposition processes involved when food traces have been buried in various environments for substantial periods of time.

The first of these problems, completeness of extraction, can be satisfactorily overcome by using in sequence a range of solvents of varying polarities, usually starting with a non-polar system such as hexane. In this way not only is extraction practically complete, but also each solvent is capable of extracting a particular group of chemical compounds which makes subsequent identification somewhat simpler.

The problem of exchange appears to be rather variable. A study of medieval potsherds by Evans and Elbeih (1984) has shown that contamination by ground substances was minimal as several samples contained no detectable organic residue. However, this may be dependant on age and/or ground conditions, as other studies have raised the possibility of contamination (Condamin et al. 1976). Analysis of soil found in the immediate vicinity of excavated pottery should be undertaken whenever possible as this could give useful indications of this problem, including the likely identification of possible contaminants. Information derived from pottery excavated from middens, rubbish pits or similar environments should obviously be interpreted with some caution. Residues with vesicular surfaces, such as charred food remains, have the potential to absorb environmental substances such as humic and fulvic acids, but the author's experience (JE) is that small-scale charred residues found on potsherds do not seem to show such contamination. This may be because of a much smaller surface pore size compared to charcoal, which does show such contamination, or some protective mechanism of the pottery sherd itself.

It appears that the problem of decomposition — that is, the change in the original organic compounds to some others over time — is often less serious than usually supposed, especially in the case of charred remains. It seems that the very act of charring produces vesicles within which the original material becomes trapped. The inert wall of carbon can thus protect the trapped material from further degradation provided this is not excessive. It is also protected from bacterial attack, oxidation and other degenerative processes. Similarly, when organic substances penetrate the pottery matrix they can also be protected as the external faces of the sherd become sealed, either by some form of decomposition (e.g. bacterial lysis — such as the 'pore protection' hypothesis of Mayer 1994) or other process that shows little penetration.

Residue analysis provides the best possibility of direct evidence for the ancient use of pottery for food containment and usage. Correct sampling of residues is the cornerstone of reliable analysis. If not done satisfactorily, the time and effort involved in detailed organic analysis may be quite wasted. If the deposit appears to be heterogeneous, then multiple samples should be taken. Once the vesicular system is broken open, however, decomposition of

trapped material may well begin, so there is little to be gained by retaining some of the material as a longer-term sample. It should be obvious that many of the common assumptions involving chemical analysis of inorganic materials (*e.g.* pottery provenance studies) are not applicable to organic deposits. Where sampling is of material trapped within the fabric of the sherd itself, it is necessary to remove the first 2mm or so of the surface, which may well have been contaminated during handling the sherd. Deeper areas within the matrix should then be sampled for the residues, which are drawn there by capillary action.

Techniques which have been most useful have included thin-layer (TLC and HPTLC — high performance) and paper chromatography, gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC). Chromatographic techniques separate the components — an important feature, considering that many of the likely materials for analysis are mixtures of many different organic compounds. Non-chromatographic methods have included infra-red spectrometry (IR), including the Fourier transform version (FT-IR). Although the latter do not separate the components, they can be handled by differential infra-red techniques (Evans and Biek 1980). All these are routine methods in organic chemical analysis described in many textbooks. Their applications to problems in art and archaeology have also been described (Mills and White 1994; Derrick *et al.* 1999). Producing standards for identifying food remains (Hill and Evans 1990) requires the use of both chemical analytical and morphological features of the residues (Hillman *et al.* 1994) — morphology is best established through the scanning electron microscope to reveal the full three-dimensional features of structural remains.

The concept of the archaeological biomarker has recently received attention, namely the search for chemical fossils still present from the original material, unchanged through degradation processes. Examples include the identification of leaf waxes and lipids, resistant to decay. The identification of the remains of *Brassica oleracea* (cabbage) were found in domestic cooking vessels from the site of the late Saxon/medieval settlement of West Cotton (Evershed *et al.* 1991). The lipid extracts of a significant number of vessels yielded a distribution of lipid types that were in the correct proportions for the leaf wax of cabbage. Waxes are relatively stable chemical species in the natural environment, and are relatively resistant to degradation over time. The inference drawn was that the vessels had been used for boiling cabbage. Occasionally, non-food materials are detected: a 17th-century pharmaceutical jar was found to contain the remains of an animal fat, in the form of fatty acids detectable by infra-red spectrometry and gas chromatography (Huet and Vincotte 1997).

Immunological methods have been suggested as a means of detecting proteins in ancient pottery (Craig and Collins 2000; Craig *et al.* 2000), but it remains to be proven that such methods designed for modern samples can reliably detect ancient protein in degraded organic materials.

Another instrumental method which has applications in archaeology, though as yet not developed extensively for studies of ceramics, is the laser Raman spectrometer (Best *et al.* 1992; Bruno *et al.* 1997). This identifies chemical structures rather than individual elements, for example pigments on ceramics. It is also applicable to identifying organic compounds. Though not of the level of sensitivity of chromatographic techniques, current equipment is based around a laser microscope which can be focussed to a beam diameter of a few tens of microns. Thus it has enormous spatial resolution, and providing precautions are taken with laser intensity on organic compounds, is non-destructive and non-contact (no sample needs to be removed).

CONCLUDING REMARKS

As with all scientific projects, question formulation — project definition — is absolutely crucial to make the best use of scarce scientific resources and effort. Project definition needs to have the selection itself made in a scientific manner, for example taking enough samples to make statistically meaningful conclusions possible. Care needs to be taken because 'common sense' and statistical validity are not the same thing. The statistical sampling of artefacts themselves for scientific work has recently been addressed by Orton (2000a, ch. 7). Ceramic provenance studies using chemical and petrological methods have been a strong element of research throughout the last 25 years. In recent years there has been a growing body of research into organic materials associated with pottery, leading, for example, to the identification of foods cooked in vessels. The prevention of contamination is also an important issue, especially for organic materials. Organic chemistry is a complex area and such studies have necessarily required careful work on relatively small numbers of samples.

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Résumé

Les techniques scientifiques ont considérablement été appliquées aux céramiques médiévales depuis les 25 dernières années, et au fur et à mesure que les techniques ont été développées, les types d'information obtenus ont aussi grandi. Des progrès majeurs ont été faits dans l'étude de la provenance, provenant de plusieurs projets à grande échelle comprenant des centaines de tessons. Les scientifiques et les spécialists de la céramique se sont aussi baissé sur la question de la technologie ancienne. De plus, les emplois faits des pots ont été étudiés par l'analyse de résidus de nourriture et autres dépôts organiques en utilisant des techniques d'analyse chimique et organique.

Zusammenfassung

Während der letzten 25 Jahre wurden in großem Maße wissenschaftliche Methoden bei der Untersuchung mittelalterlicher Keramik verwendet und da die Technik sich entwickelt hat, haben sich die Arten der Information erweitert. Größere Fortschritte wurden bei den Herkunftsstudien erzielt, die auch eine Anzahl von Großprojekten einschlossen, denen Hunderte von Scherben zugrunde lagen. Die Wissenschaftler und Keramikspezialisten haben ihre Aufmerksamkeit aber auch Fragen der alten Technologie zugewandt. Zusätzlich wurden auch die Gebrauchsarten der Töpfe durch Analyse der Nahrungsreste und anderer organischer Ablagerungen mit Hilfe von in der organischen Chemie verwendeten Techniken untersucht.