Portable X-ray fluorescence analysis of 18th-century black-glazed pottery

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Summary

Fifty-seven sherds of 18th-century black-glazed pottery from five production and five consumption centres in the English Midlands, North-West, North Wales and the Isle of Man were subject to **XRF** analysis in an attempt to distinguish the products of individual potteries by their chemical signature. The results

Introduction

In 2009 a meeting of regional ceramicists at Norton Priory Museum identified a number of post-medieval ceramic types which are well represented in the Norton collections and in the wider region, as worthy of further research. The most crucial type seemed to be the blackglazed, usually red bodied, ware that is significant for a number of reasons:

I It is probably the single largest ceramic type present in 17th- to 19th-century assemblages whose origins cannot at present be identified with any degree of certainty.

2 It is significant in the north-west, where a number of production centres situated on coalfields have already been identified.

3 It is an issue at national level, especially given the number and geographic distribution of known production centres.

4 It is internationally important as significant quantities of this ware were exported from Britain to Ireland, America and other British colonies.

5 The ability to identify the products of individual centres would greatly assist in the clarification of trading patterns both regionally and internationally.

Pilot study

Following discussions with the Daresbury Laboratory of the Science and Technology Facilities Council, it was agreed that a pilot X-ray Fluorescence (**XRF**) study be

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produced a clear division into two chemical groupings which did not correlate with the production centres. A microscopic re-examination of the sherds suggested that the differences between the groups were the result of production choices made by the potters that outweighed any chemical variation in the clays they used.

carried out there on early 18th-century black-wares in order to see whether the chemical composition of the bodies or glazes used in different production centres could be consistently distinguished.

Methodology

Black-glazed sherds from five production sites were analysed: Prescot (7 samples), Pinfold Lane, Buckley (4), Brookhill, Buckley (2), Jackfield, Ironbridge (5) and Clayhanger Street, Burslem (14); and five consumption sites: Chester (4), Norton Village (5), Norton Priory (4), Castletown, Isle of Man (5) and Newport Street, Worcester (7). Fifty-seven sherds were tested with 212 individual analyses taken on both the glaze and edge (body fabric) of the sherds. 'Coarse' and 'fine' wares were selected in equal proportion from each site.

Scientific study of the body fabric and glaze by XRF

Analyses were carried out with a Tracer (Bruker) portable X-Ray fluorescence (p**XRF**) with silver anode and palladium collimator with resolution 140eV, operated at 15kV and 40kV to collect results on different elements. The results were obtained as uncalibrated raw peak area measurements of 20 chemical elements which could not be converted to percentages or parts per million in the original body fabric. Five of the 20 elements were excluded from all statistical tests because of a significant number of missing values (chlorine, sulphur, and vanadium), or presence in the



Figure I

Plot of the average XRF analysis of the body fabric of northern blackglazed pottery sherds for the elements rubidium (Rb) against iron (Fe), in units of raw peak area counts.

The number beside each symbol indicates the sherd $\ensuremath{\text{ID}}$ number.

X-ray tube (silver and palladium). In addition, lead was a contaminant from the glaze during firing, when it is partially volatilised into the interior fabric of the pottery. It was only included in tests to check if it was accompanied by (and correlated with) any other elements into the body fabric (especially if metallic) but none did so.

Body fabric analysis

Most often, two analyses were made on each sample and they were averaged to use in the tests. While most pairs showed reasonable consistency, thirteen diverged significantly for some elements (2-7 times the peak areas of calcium, iron, nickel, and titanium) - Prescot (nos 9, 11, 12); Buckley (17–19, 46); Norton Priory (31); Castletown (36); and Burslem (50, 54, 57, 60). Although coarse mineral grains were observed microscopically in some body fabrics, the analysis spot size of the XRF was 5 mm, so large differences between multiple analyses on a single sherd were unlikely to be from the coarseness of the body fabric. The cause may be surface roughness of the fabric, unlike analysis by conventional **XRF** (flat surface or fused bead) and solution-based plasma spectrometry (ICP) which are typically well within +/-5% relative for major elements (*ie* orders of magnitude smaller variations) (Orton and Hughes 2013, 168–89).

Results and discussion

Fourteen elements remained: iron, calcium, titanium, manganese, nickel, yttrium, zinc, chromium, copper, rubidium, strontium, niobium, and zirconium. The statistical tests used the program **MINITAB** version 16 (Ryan et al 2005), and as is common in analytical ceramic provenance studies, all the data were initially transformed to natural logarithms. A few pairs of elements showed high correlations, for example nickel and titanium (0.98) and iron and titanium (0.94).

Figure 1 shows a typical example of a scatter plot of rubidium against iron. Two broad divisions into samples with lower and higher element concentrations were immediately noticeable – a pattern repeated among other element pairs. Each division or group had representatives from all localities. A smaller group with higher content of iron and most other elements mostly contained 2–4 times that of the larger low-element group (ranging up to 8 times, Figure 1). The larger group was represented by the elongated horizontal spread at the bottom of the figure (listed in Table 1; the smaller group in Table 2).

No part of the analysis process could explain this, for example samples being analysed using different analysis regimes/settings, so it was concluded that there were two distinct fabric types among the sherds.

Table I

List of sherds forming the larger chemical composition group, Group I (low concentrations of many elements)

C consumption P production site Red body (except where shown)

ID	C/P	site	form
Ι	С	Chester	cup
3	С	Chester	chamber pot
5	С	Chester	jar
7	Р	Prescot	storage vessel (waster)
8	Р	Prescot	cup
9	Р	Prescot	cup (blistered)
12	Р	Prescot	cup (over fired)
14	Р	Pinfold Lane, Buckley	storage vessel
17	Р	Pinfold Lane, Buckley	cup
21	С	Norton Village	storage vessel
25	С	Norton Village	cup
26	С	Norton Priory	hollow ware
28	С	Norton Priory	pancheon
31	С	Norton Priory	cup
33	С	Castletown, Isle of Man	storage vessel
34	С	Castletown, Isle of Man	jar
35	С	Castletown, Isle of Man	storage vessel
37	С	Castletown, Isle of Man	storage vessel
38	С	Newport Street, Worcester	jar
40	С	Newport Street, Worcester	jar
41	С	Newport Street, Worcester	pancheon
44	С	Newport Street, Worcester	cup (buff)
45	С	Newport Street, Worcester	cup (buff)
49	Р	Clayhanger Street, Burslem	sgraffito dish
50	Р	Clayhanger Street, Burslem	storage vessel
53	Р	Clayhanger Street, Burslem	storage vessel
55	Р	Clayhanger Street, Burslem	storage vessel
56	Р	Jackfield, Ironbridge	pancheon
57	Р	Jackfield, Ironbridge	pancheon
58	Р	Jackfield, Ironbridge	bowl/jar (buff)
64	Р	Clayhanger Street, Burslem	cup
65	Р	Clayhanger Street, Burslem	bowl
66	Р	Clayhanger Street, Burslem	cup
67	Р	Clayhanger Street, Burslem	bowl
		-	

The main, larger group (named Group 1) seemed to represent a high-alumina clay relatively low in other elements (aluminium was not measured, but titanium was, which follows it geochemically in clays, and is higher in the main group than the smaller). The smaller group (2) had significantly higher concentrations of elements such as iron and calcium.

Principal Components Analysis of the XRF results on the body fabric

Detailed interpretation of the ICP analyses was carried out with multivariate statistics, which simultaneously considers the concentrations of many elements in

Table 2

List of sherds forming the smaller chemical composition group, Group 2

ID	C/P	site	form
2	С	Chester	cup
10	Р	Prescot	storage vessel
П	Р	Prescot	сир
13	Р	Prescot	pancheon
18	Р	Pinfold Lane, Buckley	jar (Fabric 47)
19	Р	Pinfold Lane, Buckley	jar
22	С	Norton Village	jug
23	С	Norton Village	storage vessel
24	С	Norton Village	bowl
27	С	Norton Priory	cup
36	С	Castletown, Isle of Man	cup
39	С	Newport Street, Worcester	storage vessel
42	С	Newport Street, Worcester	pancheon
46	Р	Brookhill, Buckley	sgraffito dish 23.11
47	Р	Brookhill, Buckley	sgraffito dish 52
48	Р	Clayhanger Street, Burslem	sgraffito dish
51	Р	Clayhanger Street, Burslem	storage vessel
52	Р	Clayhanger Street, Burslem	storage vessel
54	Р	Clayhanger Street, Burslem	storage vessel
60	Р	Jackfield, Ironbridge	press-moulded plate (buff)
61	Р	Jackfield, Ironbridge	cup (buff)
62	Р	Clayhanger Street, Burslem	jar
63	Р	Clayhanger Street, Burslem	jar

each sample. The multivariate technique of Principal Components Analysis (PCA) was used (Manly 2005; Tabachnick and Fidell 2007), with the MINITAB 'PCA' procedure. Plots of pairs of the resulting principal components are effectively chemical 'maps' for the items analysed, and pottery made of the same clay will plot in the same part of the figure.

A plot of the first and second principal components (Figure 2) showed a striking division into two chemical groups, with the main group on the left containing all the low-iron samples, exactly corresponding to the two groups of Figure 1 and Tables 1 and 2. Such elongated 'cigar shaped' distributions are very common in pottery studies – varying amounts of natural or



Figure 2

Plot of the first and second Principal Components arising from the average XRF analyses of the body fabric of northern black-glazed pottery sherds.

deliberate additions of temper, reinforced in this case by the relatively large variations in analysis on the same sample. The elements contributing to the first principal component score (PC1 – 60% of the variation in chemistry of all sherds) are positive for most of the elements, while for the second component (*ie* for PC2 – 17%) have lower concentrations of calcium, titanium, iron, nickel and copper towards the bottom of Figure 2 combined with higher amounts of zirconium and rubidium towards the top. The third principal component (contributing only 8% of the inter-sherd variation) correlated with higher amounts of zinc and strontium and lower amounts of iron and chromium. The third component was much more difficult to interpret since consistent patterns seemed to be absent.

Some within-site variations were observable within the larger and smaller groups of Figure 2, though the patterns are by no means straightforward. Internal consistency in the analysis results within a single production site would produce a single group in the plot, separate from other production sites. However, four of the Burslem sherds were in the lower left (64– 67), while others were towards the top of the main group (49, 50, 53, 55 and 57); at the top also were two Ironbridge sherds (56–7), though 58 was mid-group. The two Prescot sherds (9 and 12) separated from the rest. Within the smaller group on the right, five Burslem sherds formed a fairly consistent group (48, 51, 52, and 62–3); four of the Buckley sherds (18–19 from Pinfold Lane and 46–7 from Brookhill) were in this group, but the other two from Pinfold Lane (14 and 17) were in the larger group; three Prescot sherds (10–11 and 13) were again on the fringes of the group; and two Ironbridge (60–1) at the top.

A re-run of the principal components analysis on the larger of the two groups alone gave plots (not shown) with the points for each site rather scattered. Only the Burslem sherds seemed to show some separation from the other groups on the first and second component. Of the consumer site material, the Worcester sherds seemed separate from their nearest production site at Burslem (although no. 55 is a stray Burslem sherd close to them). The Chester sherds had different chemistries to the Castletown sherds, which split into two pairs. The two Norton Village sherds were fairly close to each other; the two Norton Priory sherds less so. A plot of the second and third components showed slightly better definition of the site groups for the Worcester, Castletown, Chester and Burslem site sherds. The Worcester sherds did not correspond to the Burslem production material, but was somewhat closer to the Chester and the Ironbridge production site, although one Buckley sherd was close to the pair 38/41 from Worcester. However, in summary, this re-run has added only slightly more interpretable information compared to the original principal components with all the sherds included.

Portable **XRF** is a relatively new technique, subject to research into its effectiveness at detecting chemical differences between material from different production sites (Orton and Hughes 2013, 19). Although there were some indications in this direction in the present study, considerable overlapping existed between sherds from different sites within the two clay types. The technique was chiefly successful in differentiating two very different chemical groups within the sherds, but seemed poorer at differentiating between production sites within the two groups, where chemical differences were smaller. The relatively large differences between the results of pairs of analyses on the same sherd points to the greater analytical errors associated with portable **XRF**.

Comparative chemical analyses of the body fabric

The late Alan Vince undertook thin section and ICP analyses on six samples of medieval whiteware jugs from Chester (Vince 2007, ICP nos AG302-7) presumed to be made at Buckley. They all showed a consistent chemical pattern of a high-alumina body containing 21-27% aluminium oxide, low levels of calcium oxide (<0.5%) and iron oxide (2-5%). Such analyses correspond to typical fireclays and would be consistent with the clay body of the low-iron **XRF** results for some Buckley black-glazed ware. These whiteware sherds showed sparse to moderate fragments of white clay, fine quartz sand in all samples and white sandstone in some. The ICP was clearly able to differentiate between the Chester sherds and examples from the kiln at Sneyd Green, Stoke on Trent. An ICP project on Midlands Purple and Cistercian wares in the west Midlands (Hurst and Wright 2011) analysed samples from production centres at Wednesbury, Burslem, Nuneaton and Ticknall and consumer sites Bordesley Abbey and Austin Friars, Leicester. These showed a consistent chemical pattern for each production centre, with Burslem Cistercian-type distinct from other centres, and of slightly different clay chemistry to Midlands Purple from Burslem (op cit 59), with the Cistercian containing slightly lower alumina (16%), calcium (1%), iron (6%) and potassium (1.5%). These may correspond to the 'high iron' Burslem black-glazed ware analysed by **XRF**, though no corresponding 'low iron' chemistry was found by ICP among any of the Cistercian wares from production or consumer sites. The west Midlands ICP project suggested that some sherds found at Wednesbury were from an unsampled kiln, possibly Wednesbury, West Bromwich or Shropshire – the Ironbridge Jackfield site (op cit p 62).

Glaze analysis

The black-glazed ware lead glaze was produced by a high temperature chemical reaction fusing a lead compound (typically lead carbonate) to the surface of the pottery. This resulted in a glaze whose composition represents a mix of element concentrations drawn from both matrices. Its interpretation is therefore complicated by the fusion; however **XRF** analysis of black-glazed ware glaze could identify the chemical elements responsible for the colour. The question arose whether the iron or manganese was deliberately added with the lead compound or is simply reflecting iron in the clay matrix. Previous analyses of black glazes on postmedieval pottery produced at Harlow (Hughes 2009a) all contained significant percentages of iron (3-5% iron oxide) and copper (2-4% copper oxide); manganese was not present to a sufficient degree to influence the colour, but zinc was always present accompanying the copper, suggesting the possible use of brass filings. By contrast, in the present study the copper, zinc and manganese peak areas in the XRF study of the glazes were not significantly different overall to those for the underlying body fabric, indicating that copper, brass or manganese compounds were not added to the northern glazes. The **XRF** analyses suggested that iron was the glaze colouring agent at all production sites studied. An **XRF** analysis of a single deep black glaze on an applied pellet on a Hedingham or Scarborough style jug showed it was coloured by iron alone (2.1%: Hughes and Hook 2012, 160 sample 5, table 15); manganese and copper were present only in trace amounts. Comparison between the iron content of body fabric and glaze on Hedingham wares showed the glaze composition followed that of the underlying clay (op cit, 162).

The technology for producing such glazes has been discussed by a number of authors (Barker 1986a; Constant and Ogden 1996; Greene 1976; and Hughes 2009a). Cardew (2002, 155) notes that if the glazing kiln is cooled quickly from its top temperature, the glaze becomes viscous and crystallisation is difficult, and then as much as 5% iron oxide can be kept in solution producing a clear bright black glaze. The black glaze does not require a reducing atmosphere in the kiln, and the more common reddish brown glaze is produced on the contrary by a slow rate of cooling over some hours. The clay used to make black-glazed ware by the Staffordshire potters was iron-rich (Barker 1986a, 60–3), and an **XRF** analysis of a black-glazed ware sherd from Norton Priory, thought to have been made at Buckley, was shown to have a glaze rich in iron (Greene 1976). An electron probe microanalysis of the glaze found an even concentration of iron throughout its cross-section which the author suggested opposed the idea that the iron had migrated from the body. However, lead glazes have a relatively low viscosity at firing temperatures, so good mixing of the glaze ingredients is expected in the molten state, including iron derived from the body fabric of the pot. A scanning electron microscope crosssection through a black-glazed ware glaze excavated at Burslem (Barker 1986a, 61: plate 1) showed a 'region of extensive crystallisation' c 50-100 microns thick probably representing an interaction zone. The overall thickness of the glaze on the Burslem sherd was of the order of 100-200 microns, and notably thinner than on a Cistercian ware pot from Hulton Abbey (Barker 1986b, 54: plate 1).



Figure 3

Plot of the XRF analyses of the glaze of northern black-glazed pottery sherds for the elements lead (Pb) against iron (Fe), in units of raw peak area counts. Note: all analyses, including multiple analyses of the same glaze are shown (eg the pair from Pinfold Lane, Buckley on the upper left; however some pairs show much greater differences).

As with the analysis of the body fabric, while there were some between-site chemical differences in the glazes, the same within-site division was found as for the body fabrics. A principal components analysis on the glaze analyses alone gave a plot of the first and second principal components very similar indeed to Figure 1: the two groups found among the body fabrics (Tables 1 and 2) were replicated in the glaze analyses for exactly the same samples. A plot of the iron and lead contents of the glazes (Figure 3) shows a very prominent cluster of samples in the lower centre (ie low iron content). Sherds with higher iron content also showed a higher lead content (most samples on the right were significantly above the baseline). Attempts to interpret further sub-groups within Figure 3 did not yield any convincing interpretations. Samples from many sites appeared in different sub-groups and it was not clear why other single samples deviated away from the rest.

Summary and conclusions of chemical analyses

The **XRF** analyses of the body fabric (edge) of the black-glazed ware sherds shows a split into two distinct chemical patterns, representing the use of two different

clay blends. The larger group had relatively low concentrations of many elements (containing significant amounts of a high-alumina fireclay and quartz) while the other was a more conventional earthenware clay with 'typical' concentrations of the major and minor elements. Examples of both types were found at all the sites investigated. While there is some evidence of chemical differences between the sherds found at the respective sites, the **XRF** did not show consistently different chemical identities for the ceramics from each production site within the two groups. It is difficult in such circumstances to make attributions of the consumer site material to the production sites. The relatively low precision of the portable **XRF** in these tests indicated it was only sufficient for detecting major chemical differences in clay type between production groups.

The analyses of the glazes showed that they split into exactly the same two chemical groups as the body fabric, supporting the view that the glaze composition was produced during firing by reaction of the lead with the underlying clay. In all cases the evidence pointed to iron alone being responsible for the black colour, produced by relatively rapid cooling of the glazed product in the kiln.

Physical re-examination of the sherds in light of the XRF results

Following the **XRF** study a microscopic examination of the body fabric at x35 proved to be consistent with the chemical analysis - Group 1 contained significantly more quartz and white clay than Group 2, which conversely contained more clay grog (Tables 3 and 4). Quartz contributes virtually pure silicon to the analysis total but lowers the overall concentrations of all other elements. The white clay was most probably fireclay, common in Coal Measures deposits, rich in alumina and whose chief minerals are poorly crystalline kaolinite (aluminium silicate), mica and quartz (Worrall 1982, 68 and 72). Minor impurities include lime and iron and titanium minerals. Typical analyses show low calcium (<1% calcium oxide), iron oxide (c 2%), and potassium (c 1.5% potassium oxide) (Worrall 1982, 75: table 14). Clay grog in Group 2, combined with a low proportion of white clay and quartz, would give the typical chemistry of Group 2.

Discussion

Given that the chemical differences between the two groups does not correlate with the production centres, or with the types of vessel involved, it seems most likely that they are the result of differing choices made by the potters themselves. Apart from the use of fillers such as quartz and grog the most influential element in discriminating between the groups is the amount of white clay involved. There is around three times as much white clay in Group 1 than in Group 2.

The use of different clays within the same vessel will affect the chemistry of the resultant pottery fabric if the clays, themselves, were significantly different in the first place. It is clear from contemporary accounts that one of the great advantages of the coalfields was the variety of clays available to the potter. Dr Plot in his *Natural History of Staffordshire* describes the range of clays found near Burslem:

where for making their several sorts of *Pots*, they have as many different sorts of *Clay*, which they dig around about the *Towne* ... and are distinguished by their *colours* and *uses* as followeth: *Bottle Clay*, of a bright white streaked yellow colour. *Hard Fire Clay*, of a duller whitish colour, and fuller intersperst with a dark yellow, which they use for their *black wares*, being mixed with the *Red Blending Clay*, which is of a dirty red colour. (Plott 1686, 3:23–9)

This mixing of clays for different types of pottery is confirmed in Shaw's *History of the Staffordshire Potteries* who, states that:

during many centuries, considerable quantities of common culinary articles were manufactured,

Table 3

Frequency of the main inclusions in chemical Group I Estimated on a 5-point scale (I rare to 5 very frequent)

Sherds ID 9 and ID 12 were over-fired

ID	quartz	white clay	shale	grog	% area
Ι	2	I	0	0	40
3	I	5	2	2	65
5	4	5	2	3	65
7	5	3	I	2	40
8	2	2	I	2	30
9	?2	?1	?	?	> 5
12	3	3	?	?	> 5
14	5	5	3	3	55
17	2	3	0	0	25
21	2	5	I	I	65
25	3	2	I	I	25
26	3	2	I	I	25
28	2	3	I	I	40
31	3	2	I	I	25
33	5	5	2	2	65
34	4	4	I	I	35
35	3	4	I	I	40
37	4	3	2	2	40

Table 4

Frequency of the main inclusions in chemical Group 2 Estimated on a 5-point scale (I rare to 5 very frequent)

ID	quartz	white clay	shale	grog	% area
2	I	I	I	3	10
10	2	I	I	3	15
П	3	I	I	2	20
13	I	I	2	3	30
18	2	2	2	2	30
19	2	2	Ι	I	25
22	3	I	2	2	30
23	2	I	Ι	2	35
25	I	2	Ι	3	20
27	I	0	0	I	5
36	I	0	0	I	5
46	I	0	Ι	I	5

of red, brown, and mottled Pottery: easily made from a mixture of different Clays found in most parts of the district. (Shaw 1829, 97).

This seems to have been the norm in all of the coalfield areas. Warner in his 1798 visit described the clays available in Buckley as follows:

the clay used for the purpose is of three kinds, differing from each other in their power of resisting the action of fire. The most tenacious is called the *fire clay* which forms the earthen receptacles and stands that receive and support the articles whilst they are baking. The second is a less-enduring species, and called the *stone clay*, of which the jars, pickling mugs, whiskey-cans, *etc* are made. The third, least capable of resisting heat, affords materials for the *smaller glazed potteries*. (Warner 1813, 246–7)

At Buckley clays were certainly being mixed together for different products:

Pot clay, 'strong clay', coated the surface and was malleable like plasticine. Fire clay was found under coal seams and, because the hand cannot press it into shape, is called 'weak clay'. The clays were chosen for their colours and every potter had his secret recipes for mixing strong and weak clays (Pritchard 2006, 69).

Storage vats for different clays have been recovered from excavations at a number of production sites such as Prescot (McNeil 1982–3, 49–51) and Buckley (McNeil 1985). The convoluted banding of red and white firing clays in some of the sherds examined, are typical of the effect of wedging two clays together. If the proportion of white clay used in the mixture is the main reason for the chemical differences between the two groups, the choices made by the potters appear to outweigh any chemical variation between the clays available in the individual coalfields. The role of the potter will need to be taken more seriously into account when ceramic bodies of this period are subject to this type of scientific examination in future.

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References

- Barker, D 1986a 'North Staffordshire post-medieval ceramics – a type series, Part two: blackware', *Staffordshire Archaeological Studies: Museum Archaeological Society Report, New series* 3, 58–67.
 Barker, D 1986b 'North Staffordshire post-medieval
- ceramics a type series, Part two: Cistercian wares',

Staffordshire Archaeological Studies: Museum Archaeological Society Report, New series, 3, 52–6.

- Cardew, M 2002 *Pioneer Pottery* (2nd edition), A&C Black, London.
- Constant, C and Ogden, S 1996 *The Potter's Palette*, Apple Press, London.
- Davey, W and Walker, H 2009 *The Harlow pottery industries*, Medieval Pottery Research Group Occasional Paper 3.
- Greene, J P 1976 'Black glazed pottery and the composition of its glaze', *Cheshire Archaeological Bulletin* 4, 15–20.
- Hughes, M J 2009a 'Scientific study of the glazes', in Davey and Walker, 159–64.
- Hughes, M J 2009b 'Report on ICP-AES and ICP-MS analysis of pottery from Harlow including medieval pottery, sherds from three 16th-century kilns and post-medieval pottery', in Davey and Walker, 174–83.
- Hughes, M and Hook, D 2012 '**XRF** analysis of glazes', in H.Walker, *Hedingham Ware: a medieval pottery industry in north Essex; its production and distribution*, East Anglian Archaeol Rep *no* 148, 160–3.
- Hurst, J D and Wright, S M 2011 'Midlands purple and Cistercian-type wares in the west midlands in the 15th–16th centuries', *Medieval Ceramics* 32, 55–64.
- Manly, B F J 2005 *Multivariate Statistical methods: a primer*, 3rd edition, Chapman and Hall, London.
- McNeil, R 1982–3 'Excavation of an eighteenth century pottery in Eccleston Street, Prescot (Site F)', *Jour Merseyside Archaeol Soc* 5, 49–95.
- McNeil, R 1985 'Clwyd: Buckley (Flintshire) SJ/275655', Post-medieval Archaeology 19, 180–1.
- Orton, C and Hughes, M 2013 *Pottery in Archaeology* 2nd edition, Cambridge University Press, Cambridge.
- Plott, R 1686 *The Natural History of Stafford-Shire*, Oxford.
- Pritchard, T W 2006 *The Making of Buckley and District*, Bridge Books, Wrexham.
- Ryan, B, Joiner, B, and Cryer, J 2005 *MINITAB Handbook* 5th edition, Thomson Brooks/Cole, London.
- Shaw, S 1829 *History of the Staffordshire Potteries*, privately published, Hanley.
- Tabachnick, B and Fidell, L S 2007 *Using Multivariate Statistics* 5th edition, Pearson, London.
- Vince, A V 2007 'Characterisation of medieval whiteware from Chester, Cheshire', (available at *Vince 2010 as avac2007007.pdf*).
- Vince, A 2010 Medieval Pottery Research Group (2010) Alan Vince Archive [data-set]. York: Archaeology Data Service [distributor] (http://archaeologydataservice.ac.uk/) (doi: 10.5284/1000382).
- Warner, R, 1813, A Second Walk Through Wales by the Revd Richard Warner of Bath in August and September 1798, Richard Cruttwell, Bath.
- Worrall, W E 1982 Ceramic Raw Materials, second edn, Pergamon Press, Oxford.

Résumé

Cinquante-sept tessons de poterie à glaçure noire du 18e siècle issus de cinq centres de production et de cinq centres de consommation - dans la région des Midlands, du nord-ouest, du nord du pays de Galles et de l'Île de Man – ont été soumis à une analyse par spectrométrie de fluorescence X (**XRF**) pour tenter d'identifier les produits des divers ateliers par leur signature chimique. Les résultats montrent clairement une division chimique en deux groupes qui ne sont pas en corrélation avec les centres de production. Un réexamen microscopique des tessons suggère que les différences d'un groupe à l'autre résultent de choix de production faits par les potiers, qui prédominent sur d'éventuelles variations chimiques des argiles utilisées.

Zusammenfassung

Siebenundfünfzig Scherben von schwarz glasierter Keramik aus dem 18. Jahrhundert aus fünf Erzeugerund fünf Gebrauchszentren in den englischen Midlands, im Nordwesten Englands, in Nordwales und auf der Insel Man wurden einer Röntgenfluoreszenz-Analyse unterzogen, mit der man versuchen wollte, die Erzeugnisse individueller Töpfereien durch ihre typische chemische Zusammensetzung zu unterscheiden. Die Ergebnisse zeigten eine klare Einteilung in zwei chemische Gruppierungen, die nicht mit den Erzeugerzentren korreliert waren. Eine mikroskopische Nachuntersuchung der Scherben deutete darauf hin, dass der Unterschied zwischen den Gruppen das Ergebnis von Herstellungsentscheidungen war, die die Töpfer trafen und die alle chemischen Unterschiede in den benutzen Tonen überdeckten.