Tin-glazed tiles in Surrey
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INDUCTIVELY-COUPLED PLASMA SPECTROMETRY ANALYSIS (ICP) OF TEN TIN-GLAZED DECORATED FLOOR TILES IN THE COLLECTIONS OF GUILDFORD MUSEUM, by M J Hughes

Modern scientific techniques can indicate the place of production of ceramics, and ten tin-glazed tiles in the collections of the Guildford Museum were selected for chemical analysis, nine believed to be products of the Low Countries and one Spanish. Chemical analysis for provenance studies is an established technique (Orton & Hughes 2013, 18–20 and 168–82), and in recent years inductively-coupled plasma spectrometry (ICP) has proved a popular technique replacing neutron activation analysis because of its ready availability and the large numbers of elements analysed in the body fabric. Examples of its application include Haggerty *et al* (2011), Hughes (2010) and the many reports and publications by the late Alan Vince (Vince 2010). Here the approach follows the pattern for the comparable project on ICP analysis of London delftware, where more detailed discussion can the found (Hughes 2008, esp 120–4).

The analysed tiles comprised four from the present catalogue including 4 (corner fleur-de-lis) from Limpsfield, New Hall, and 5 (floral) and 6 (floral, flower head) possibly from the same site; and 7 (floral) from 16 Tunsgate, Guildford. Three other tiles were of the same design and from the same locality respectively as examples in the catalogue: 2 (designated 2a in the figures, grasshopper – S8279 analysed) and 3 (3a, floral – S8284) from Limpsfield, New Hall; and 8 (8a, chequerboard pattern – 203/16.TUN) from 16 and 17 Tunsgate, Guildford. Another tile similar to 8 (8b, C1 10A) from 17 Tunsgate, but of a different internal/central design was also analysed. A tenth, Spanish, tile was also analysed (1993 25) from 15 Tunsgate, Guildford (Betts 2008, 56). Since the ICP analysis was not published, it has been included here for the sake of completeness. It showed a heraldic design and ICP analysis confirmed it as Valencian. It was similar, though not identical to, the analysis of another heraldic tile of the same design from Woking Palace (Betts 2008, 56; design I, tile 21A), which may indicate chemical differences in the source, location or chronology of production.

ICP and statistical analysis

Drilled samples of powder were obtained from the body fabric of each tile and the powder analysed by ICP−atomic emission spectrometry at Royal Holloway, University of London, Department of Geology; the results are given in table 1. Details of the sampling, analysis and statistical treatment of ICP data have been given elsewhere (Hughes 2008, esp 120–4).

Because ICP analyses for many elements, interpretation uses multivariate statistical methods, ie computer programs that examine all the elemental results simultaneously (Orton & Hughes 2013, 175–82). Methods widely used in archaeological science are principal components, discriminant and cluster analysis (Baxter 1994; 2003; Shennan 1997). Here, principal components proved very suitable, using the program SPSS version 10.1. A plot of pairs of principal components arising from ICP is a type of map of the overall chemistry of the sample, based on many elements. Sherds that have very similar overall analyses will plot close to each other, indicating a common clay source, and suggesting manufacture at the same production site.

Comparison with ICP analyses of Low Countries tiles and pottery

The fabric of all the polychrome tiles were notably calcareous (they contain 16–22% calcium oxide–lime), typical of tin-glazed tiles. Ceramic provenance studies include statistical comparison of the analyses of the ceramics in question against a database of analyses of similar type and from known production centres. In this case, while there are relevant analyses of Antwerp and other Low Countries (and English) tin-glazed ceramics of the period by neutron activation analysis (NAA – Hughes & Gaimster 1999) – see the next section – no systematic programs of ICP analysis of production centre material exist. However, there are a growing number of analyses of tiles and pottery assigned to Antwerp production on stylistic grounds, from the Low Countries and the UK. To date this amounted to 52 samples and includes: two Antwerp-type tiles from the Chateau Rameyen in Belgium (Nicaise 1939: one from the collections of the Musee Royaux d'Art et d'Histoire, Brussels (LR08) is of the same type as Nicaise figure 4 and the other (L?32) is a triangular tile, possibly part of a large multi-tile design (cf fig 3). See Dumortier 1999, 108); eight tiles found at Hill Hall, Epping, Essex, (Hughes 2009); a tile of Herkenrode-type found at Whitehall Palace, Banqueting House, London (Hurst & Le Patourel 1999, 181–3: it incorrectly states there that the analysis was done by neutron activation, whereas it was by ICP−AES and was partly quoted in Hughes & Gaimster 1999, 178, Table 1 – its analysis was similar to NAA analyses of tiles known to have been made in Antwerp, including one from Herkenrode Abbey, Belgium (Musee Royaux d'Art et d'Histoire, Brussels inv 2878)); a 'Malling' jug found at Southampton (analysed by the late Alan Vince, V357: site code 124, context 225. See Gutierrez & Brown 1999); and an early 'Malling jug', mottled purple, blue and pale orange from Shapwick House, Somerset (Gerrard 1999; site code 73/94/64 – analysis by Alan Vince, AG136); and a Low Countries jug found at Cleeve Abbey (Allan 1998, 68–9, fig 8: code 534). Further examples included three glazed floor tiles and a wall flower pot from Carew Manor, Surrey (Hughes 2013); seven pottery sherds from Glastonbury Abbey (Allan *et al* 2015); four tiles from Godolphin House, Cornwall (Allan 2009–10); a sherd of pottery from Crediton Vicarage (unpublished analysis); five tiles and seven pottery sherds from Jeffrey Street, Edinburgh (Franklin 2011, 32); and unpublished analyses of tiles from Buckland Abbey, Rider House (1); River Taw, Barnstaple (2); and Tawstock Court, Devon (2). These comprise all the examples of Low Counties ceramics analysed by ICP known at present to the author; it is hoped in due course to build up analyses from the production centres themselves.

The first stage in examining the analysis results was to apply principal components analysis to the ICP analyses of the ceramics. A selection of 25 of the elements in table 1 was made to include in this principal components (indicated in the table by single and double asterisks), based on previous experience of reliably discriminating elements, and chosen to include as wide a cross-section of chemically different elements from the Periodic Table as possible. In common with much general practice in ceramic provenance studies, the element concentrations were converted to logs before entering them in the multivariate statistics. The first component was proportional to the concentrations of most elements, indicating it was mainly influenced by the amount of diluting temper in the fabric of the ceramics, so the second and third principal components (where temper proportions are absent) were plotted for figure 1. Samples with higher sodium, magnesium, calcium and strontium, and lower titanium and rare earth elements plot more to the left of figure 1, while those with higher amounts of chromium, vanadium, titanium and europium and lower amounts of potassium plot towards the lower part of the figure. The first principal component contained 44% of all the chemical variation between pottery samples in the whole dataset; the second component a further 10% and the third 9%. Thus the first three principal components contained 63% of all the chemical variation in the samples, and plots such as figures 1 and 2 effectively extract much of the chemical information in the ICP analyses.

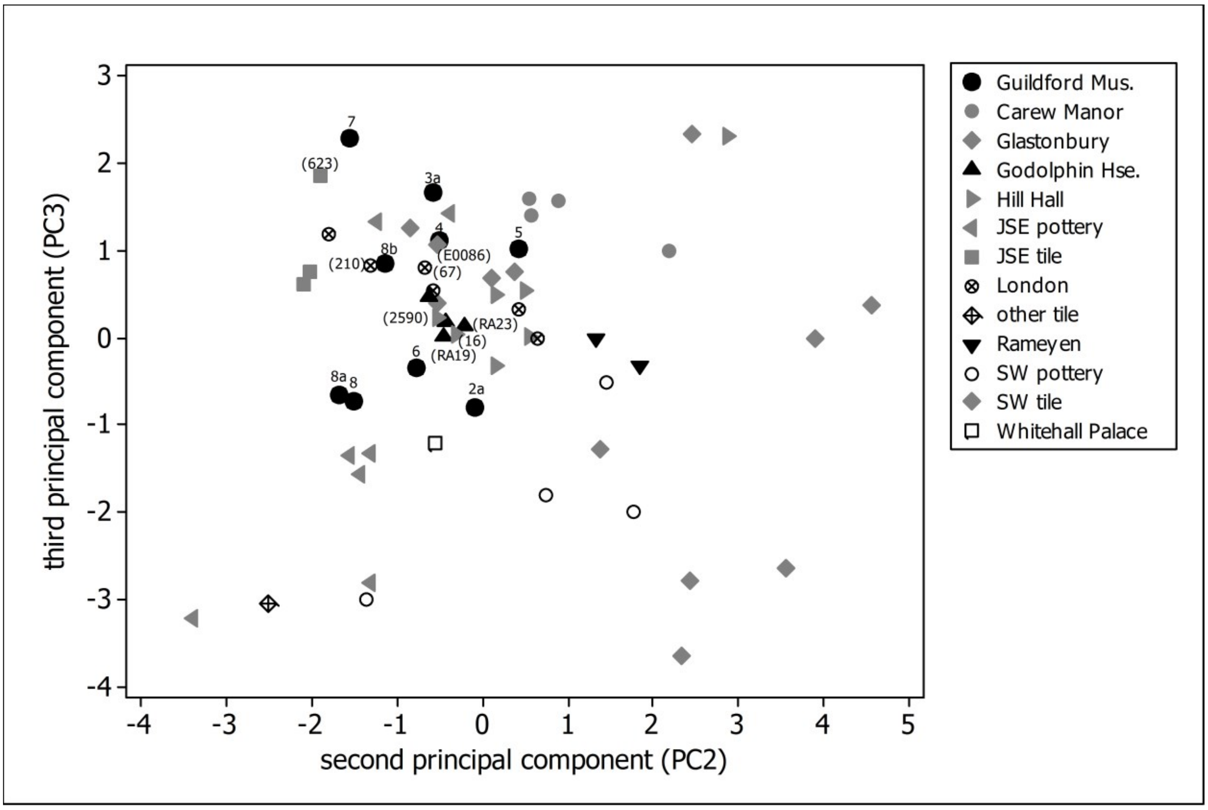

Fig 1 Principal components analysis of ICP-only analyses on tin-glazed tiles from Guildford Museum and a selection of Low Countries tiles and pottery. In the figures, the numbers alongside the Guildford Museum symbols refer to the present catalogue number; numbers in brackets next to other symbols refer to catalogue/find numbers of other tiles referred to in the text.

The distribution of points indicates there is only one broad clay source involved for all the tiles and pottery included. To aid in interpreting the statistical plots produced in this project (figs 1 and 2), each individual item analysed has been shown by symbols indicating its findspot. Labels indicate the present tile catalogue numbers for the Guildford Museum tiles listed earlier (2–8b) and bracketed numbers for tiles from elsewhere that were most similar chemically to these nine.

A central cluster of points suggests their production using the same clay source and paste production methods, but ICP analyses of definite production centre material is required to explore this further. Close grouping of tiles from the same findspot occurs to some degree, suggesting a single production centre and clay batch, for example the seven Hill Hall tiles, four from Godolphin House and the three from Jeffery Street, Edinburgh (JSE tile in fig 1). The closeness of the Guildford Museum tiles to previously-analysed Antwerp ceramics strongly points to all these tiles being of Antwerp origin. The two chequerboard tiles 8 and 8a are very close to each other in this figure, suggesting they may be from the same production firing. Another chequerboard design from Hill Hall (2590) lies more in the centre, close to another from Hill Hall (16 – flower design) and two tiles from Godolphin House (analysis nos RA19 and RA23 – circular medallion). Tile 6 from Guildford Museum lies between this group and 8/8a. It has design similarities to a tile believed to have been made at Rotherhithe (Betts & Weinstein 2010, cat no 160), but there are significant chemical differences between 6 (the analysis of which fits well with the Antwerp-produced tiles –

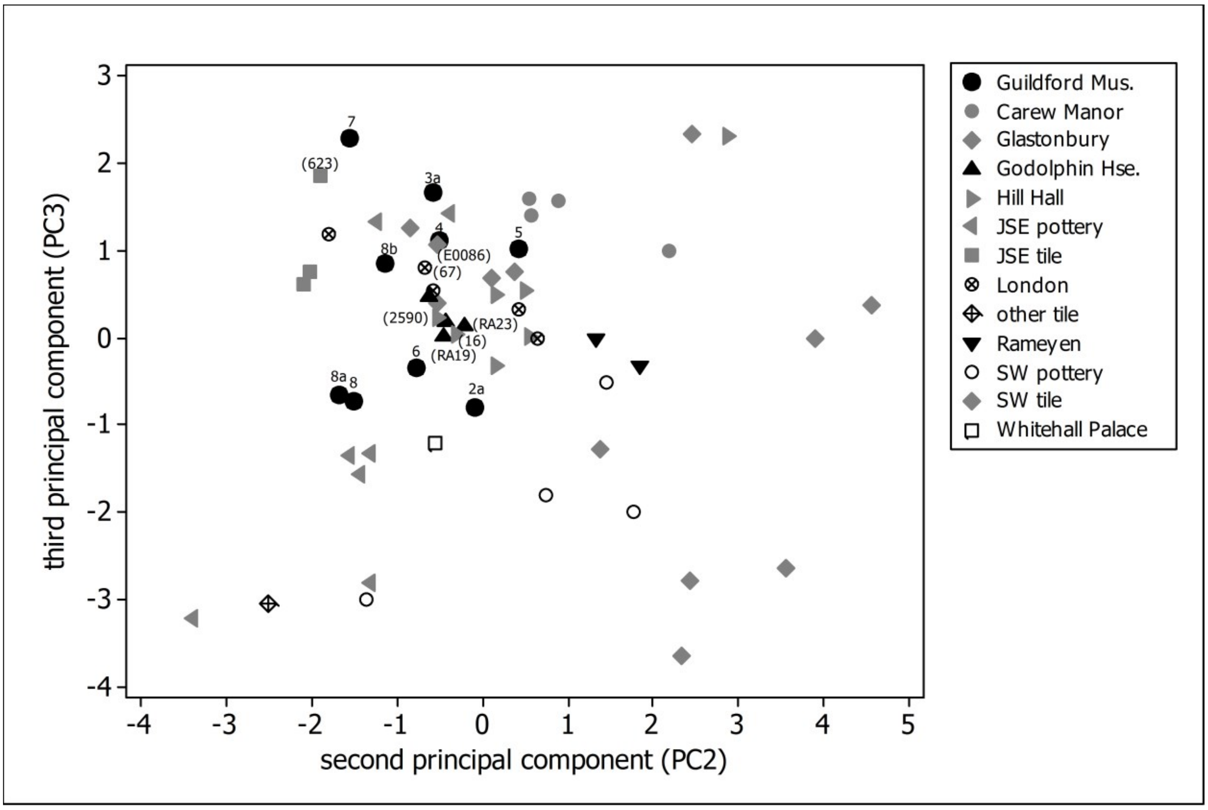

Fig 2 Principal components analysis of combined ICP and neutron activation (NAA) analyses on Guildford Museum tin-glazed tiles and a selection of Low Countries tiles, pottery, including ceramics from three production centres in Antwerp.

fig 1) and ICP analyses of tiles produced at Rotherhithe (Hughes 2008 – cf the discriminant analysis results, p 129, fig 172). A slightly different chequerboard design tile (8b) is some distance from this pair, therefore different in chemistry, but closer to a group of three tiles of similar composition, namely 4 (corner fleur-de-lis), a tile from Tawstock Court, Devon (E0086, quadrilateral/floral) and one London tile (Betts & Weinstein 2010, cat 67, heraldic shield from Anchor Iron Wharf, Greenwich). Tile 3a (floral) is close to the top of the figure, slightly above this latter group of four tiles. Tile 7 (floral) is further away still, in the top left and near a tile from Jeffrey Street, Edinburgh (JSE cat 623, combed red and white slip glazed pale green/purple).

Comparison with ICP and NAA analyses of Low Countries tiles and pottery

In an attempt to be more specific about the sources of the tiles, the analysis results were combined with a much larger body of analyses by neutron activation analysis of pottery and tiles produced in the Low Countries, which included local production centre material (Hughes & Gaimster 1999). These neutron activation analyses included ten examples of Antwerp-type tiles found in London, (‘London tiles’ in fig 2: two figure tiles, geometric and floral tiles, Hughes 2010; see also Betts 1999); five from Broad Arrow tower of the Tower of London (Gaimster & Hughes 1999a); two relief-moulded polychrome stove tiles found on the site of the Abbey of St Mary Graces, London (Gaimster *et al* 1990; the analyses were further considered by Gaimster & Hughes 1999b and concluded to be Antwerp products); and sherds of waster pottery from three production sites in Antwerp (Steenhowersvest, STE; Schoytestraat, SCH; and near the site of the National Museum of Navigation, NMN). Also

Table 1 List of analyses by inductively-coupled plasma atomic emission spectrometry of ten tiles from the collections of the Guildford Museum. Element symbols: Al_2O_3:aluminium; Fe_2O_3: iron; MgO: magnesium; CaO: calcium; Na_2O: sodium; K_2O: potassium; TiO_2: titanium; P_2O_5: potassium; MnO: manganese; Ba: barium; Co: cobalt; Cr: chromium; Cu: copper; Li: lithium; Ni: nickel; Sc: scandium; Sr: strontium; V: vanadium; Y: yttrium; Zn: zinc; Zr: zirconium; La: lanthanum; Ce: cerium; Nd: neodymium; Sm: samarium; Eu: europium; Dy: dysprosium; Yb: ytterbium (La to Yb are rare earth elements); Pb: lead. The elements from Al_2O_3 to MnO inclusive are quoted in weight percent, and the rest in parts per million. The first principal components used elements denoted with either one or two asterisks; the second principal components used only those with a double asterisk.

Catalogue no	**Lab no**	**Museum cat no**	**Al_2O_3***	**Fe_2O_3****	**MgO***	**CaO***	**Na_2O****	**K_2O****	**TiO_2***	**P_2O_5**	**MnO ***	**Ba**	**Co****	**Cr***	**Cu***	**Li***
2a	C2	S8279	13.90	6.51	1.67	17.04	0.29	1.90	0.70	0.21	0.08	318	23	75	153	74
3a	C3	S8284	12.18	5.24	1.60	20.34	0.19	1.98	0.59	0.16	0.05	257	34	51	29	69
4	C1	S8286	9.71	4.42	1.16	18.64	0.25	1.76	0.49	0.18	0.05	265	29	64	22	50
5	C10	AG21678	9.59	4.63	0.93	21.00	0.18	1.91	0.53	0.07	0.03	194	10	70	17	47
6	C9	AG21677	13.59	5.97	1.91	16.03	0.46	1.69	0.71	0.58	0.08	342	16	70	29	70
7	C7	204/16.TUN	9.73	3.49	0.89	21.72	0.23	2.40	0.42	5.83	0.05	263	31	47	55	42
8	C6	203/16.TUN	12.07	5.11	1.48	19.49	0.23	2.08	0.57	3.21	0.07	375	20	80	112	66
8a	C5	203/16.TUN	11.64	5.36	1.39	18.87	0.23	2.06	0.56	5.26	0.10	347	41	78	67	60
8b	C8	C1 10A	12.39	5.32	1.53	22.08	0.26	2.10	0.61	0.14	0.06	263	27	48	55	70
(Spanish)	C4	1993, 25	14.21	4.81	2.45	15.98	0.79	2.64	0.60	0.25	0.06	368	23	39	85	70

Catalogue no (contd)	**Ni***	**Sc****	**Sr***	**V***	**Y***	**Zn***	**Zr**	**La****	**Ce****	**Nd***	**Sm***	**Eu***	**Dy***	**Yb***	**Pb**
2a	56	15	472	112	35	88	103	42	85	43	8.0	2.0	5.8	2.8	985
3a	46	13	387	81	29	73	90	36	61	37	4.4	1.6	4.7	2.2	149
4	33	10	340	66	21	58	68	27	43	27	2.6	1.1	3.3	1.6	445
5	40	9	334	88	22	69	68	31	50	31	5.0	1.2	3.2	1.6	159
6	49	15	458	101	30	93	97	38	64	38	6.1	1.6	4.6	2.3	1207
8	45	13	431	93	29	268	74	34	51	35	4.9	1.5	4.5	2.2	293
7	39	9	442	53	31	138	30	32	42	32	3.0	1.2	3.9	1.8	338
8a	48	13	463	84	30	414	79	34	91	35	4.2	1.6	4.7	2.1	495
8b	46	13	434	102	32	85	92	35	63	36	4.4	1.6	4.7	2.3	337
(Spanish)	40	11	234	76	25	88	68	39	69	39	7.0	1.4	4.1	1.7	961

included were examples of Antwerp pottery found in London ('London pottery') and non-production site pottery from Antwerp ('Antwerp'). This database was combined with the ICP analyses of tiles from the Guildford Museum and the Hill Hall and Whitehall Palace tiles, representing a selection of those included in the first principal component analysis (81 items in all), and the two sets of data were normalised to each other using adjustment factors allowing for the different standardisations of the two techniques (given in Guttierrez *et al* 2003). One limitation caused by combining data analysed by two different methods is that different sets of chemical elements were measured by the two methods. In this case just eight elements were in common, so the statistics had to be carried out on this reduced-elements set (indicated in table 1 by double asterisks). With fewer discriminating elements for the statistical program to use, assignment of ceramics to sources becomes less certain.

A principal components analysis was run and the resulting plot of the first two components is shown in figure 2. Samples with more scandium, iron, cerium, chromium and lanthanum tend towards the right of the figure (first component), while towards the top of the figure (second component) are samples with higher sodium, potassium and cerium. Figure 2 showed similarities to an earlier analysis of the neutron activation results on the comparative material alone (Gaimster & Hughes 1999a, 179: fig 16.3 – Broad Arrow and London tiles and sherds from three production sites in Antwerp). The Broad Arrow tiles are in the lower part of the figure, slightly overlapping the London finds of Antwerp tiles, while the Hill Hall tiles are slightly above them and partly mix with the Guildford tiles and some of the Antwerp pottery found in Antwerp. Tile 4 is close to the analysis of the picture tile from Hill Hall (625 picture), while 5 is close to two relief-moulded stove tiles from St Mary Graces (catalogue nos 1821 and 1940; the analyses were published in Gaimster & Hughes 1999b, 186, table 1). The two tiles 8 and 8b (chequerboard) are very close to each other and close to 3a, and tile 2590 (chequerboard) from Hill Hall is close to these three. Slightly further away on the right, beyond the main spread of points is tile 6, close to a Hill Hall tile (16, flower design). Further out in the lower right are tiles 2a and 8a.

No samples from the three Antwerp production centres analysed were tiles, so it is not significant that the Guildford tiles differ from them in chemistry, as do the Hill Hall and Broad Arrow tiles, for example. In the original publication of the neutron activation study the statistical testing showed that a minority of the consumer site ceramics from Antwerp and London overlapped with the production centre material (Hughes & Gaimster 1999, 86, fig 3.8).

It therefore appears that the Guildford tiles, like others analysed by ICP and NAA were produced at as-yet untested kilns in Antwerp. This would provide a focus for future ICP research. Significant chemical groupings appear within the Guildford Museum tiles, with links to the analysis of other Antwerp tiles. The evidence from ICP is sufficiently strong that the Guildford tiles can be assigned to production at Antwerp, sharing similar chemical features to Antwerp tiles found elsewhere in southern and south-western England.

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