Compositional analysis of non-ferrous metalwork

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Twenty of the non-ferrous artefacts from the site were analysed as part of a larger project in which 73 early Anglo-Saxon brooches from the Avon valley were analysed using X-ray fluorescence (XRF) on drilled samples (Brownsword *et al* 1984). Since then, several hundred other early Anglo-Saxon artefacts have been analysed by the same group using the same analytical technique (Hines 1997), and by other researchers using other techniques (Mortimer 1990, Blades 1995). The Wasperton data can therefore be placed within a wider picture, by comparing them with information from the enlarged dataset.

Comparing datasets

Analytical methods applied to archaeological artefacts have inevitably changed since the 1980s. Many analysts now use techniques such as electron microscopy which allow the sample to be inspected in microscopic detail before selecting a sub-sample for analysis avoiding corroded areas. More elements are also routinely analysed for, either by X-ray analysis in an electron microscopy set-up (SEM-EDX) or by inductively-coupled plasma spectroscopy (ICPS). The Wasperton artefacts will be not be re-sampled and re-analysed in this project, but the compatibility of their compositional data (and the other 53 XRF analyses in Brownsword 1984), with recent analyses can be assessed by determining whether the results of the XRF analyses conform to what is 'expected' for artefacts of the period. Nigel Blades' 1995 ICPS study of several hundred artefacts, mostly brooches, provides suitable comparison data, as it covers eight sites and several artefact types; when data from sheet metal artefacts and compositions totalling less 95% are removed, 320 analyses are available. Other datasets can also be used, such as 363 analyses of cruciform brooches, analysed using atomic absorption spectroscopy (AAS) and SEM-EDX (Mortimer 1990). Brownsword also provided 102 XRF analyses of copper-alloy great square-headed brooches for a publication by Hines (1997) which includes four Wasperton brooches. In addition to these general comparisons, three great square-headed brooches were analysed by both Blades and Brownsword allowing some direct comparison of ICPS and XRF, although too much stress should not be placed on the results of analysing only three artefacts.

Typically, copper alloy compositions of the period range from leaded bronze with low levels of zinc through to leaded brass with low levels of tin, with the majority being more bronze-like alloys. The nine elements analysed for by Brownsword have ranges which lie well within the values seen by Blades and Mortimer, as can be illustrated by histograms of the zinc, lead and tin contents (Figs 1, 2 and 3). Average values are shown in Table 1. Some significant differences were noted and these may partly be due to the differences in dataset size, since clearer patterns often emerge with increasing data numbers. It might also be suggested that they relate to real differences in metal supply or usage; for example, most of Blades and Mortimer's analyses are from sites well to the east (East Anglia) or north (Yorkshire) of the Brownsword *et al* 1986 study area; however, the great square-headed brooches have a geographical distribution similar to those of the artefacts in Blades and Mortimer, but their compositions, determined by XRF

(Hines 1997), have significant similarities – particularly the tin content - with the Avon Valley compositions. This suggests that the compositional differences between XRF and the other techniques indicate differences in analytical accuracy. The direct comparisons support this idea (Table 2). From this review, we can conclude that the XRF analyses can be used for comparison purposes, with a few precautions:

1. Using XRF, tin contents are likely to be reported at levels less than those reported by other techniques, possibly as much as 2% less.
2. XRF rarely reports very low, or 'not detected' levels of any of the analysed-for elements, probably due to signal background noise being interpreted as real signals. This means that it is not appropriate to study the minor and trace elements in detail.

Change over time

Analysis of the large cruciform brooch dataset (Mortimer 1990) suggested that the alloy range used in the early Anglo-Saxon period did not change drastically during the fifth and sixth centuries but that there was a trend towards to increasing use of 'less pure' alloys, with fewer truly bronze-like or brass-like alloys used, and more alloys with significant quantities of both zinc and tin. This change is suggested to relate to intensified recycling and to a lack of fresh metal supplies in the early sixth century. Although it is a small dataset, it is worth seeing whether the early Wasperton artefacts are perceptibly different to the later ones.

The recent chronological studies have associated the graves that the analysed artefacts came from with one or more phases within the early Anglo-Saxon period; Phase 2a (c.470-500AD), Phase 2b (c.480-530AD) and Phase 2c (c.530-580AD) – none came from earlier or later phases. Some of the XRF analyses are not attributable to particular artefacts and some artefacts come from graves without phases, but sixteen artefacts have both XRF analyses and phases (Table 3). The phases overlap each other chronologically, and some graves are allocated to more than one phase. It is also important to note that the dataset includes six analyses which are from pairs of brooches. In these pairs, the compositions are closely similar, so that the artefacts were probably cast from the same melt. Hence each pair should probably be represented by a single point in any graphical representation and the sixteen datable analyses should really be considered as only thirteen separate alloys. However, three 'group' numbers have been given here to provide three groups (roughly early, middle and later), within the analysed material.

With this small database size in mind, it is difficult to comment in detail on the Wasperton data. In a zinc-tin plot (Figure 4), it is noticeable that the three artefacts (or pairs of artefacts) thought be the earliest are amongst the 'purer' alloys – one high in zinc and relatively low in tin (the cruciform brooches from Grave 167), and the other two with moderate tin and relatively low in zinc (cruciform brooches and a small-long brooch from Graves 17 and 39 respectively). However, these are only three datapoints, and the compositions from later phases are not drastically different. Also, two out of the three points relate to cruciform brooches, prompting the question whether the previously observed pattern of increased recycling/low purity alloys is only relevant to cruciform brooches, or whether the pattern would be revealed in other larger datasets.

The alloys used for the great square-headed brooches can be reassessed to investigate this suggestion, as these have been subject to intense typological scrutiny (Hines 1997). An earlier study of the chemical dataset (Brownsword and Hines 1993) discovered some intriguing connections between pairs and groups of brooches, but no other significant patternings. The remainder of the Avon Valley brooches analysed by Brownsword *et al* have not been assessed for detailed phasing within the early Anglo-Saxon period, nor have Blades' artefacts.

Hines (1997, Table 25) proposed three overlapping phases for his 24 groups of great square-headed brooches. Few brooches belong to the first phase (Phase 1 *c* 475 – *c* 520), and only one of these was analysed by Brownsword *et al* (Alveston Manor 5); this phase probably overlaps with the period given for the earliest cruciform brooch types. However, 41 analyses are available from Phase 2 brooches (dated *c* 525 – *c* 550), and 43 from Phase 3 brooches (dated *c* 530 – *c* 570); Phase 2 overlaps with the main production period of cruciform brooches, and Phase 3 with the very latest phases. Graphs of zinc contents (Figure 5) show that the Phase 2 square-headed brooches appear to be more frequently low in zinc, compared with the Phase 3 brooches, many of which have significant quantities of zinc. If this is a real effect, this is a slightly later shift from 'pure' to 'less pure' alloys than is seen in cruciform brooches. Further research could be carried out on other datasets, if detailed chronological studies were available.

Regional patterning

The Avon Valley is distant from the main concentration of early Anglo-Saxon find-sites. The nearest site with a reasonable number of available analyses is Empingham, but even this is more than 50 miles away. At first sight, it seems that the rather low tin content at the Avon Valley sites is similar to that Empingham (Table 4), but it must remembered that the XRF analyses are likely to significantly under-estimate tin contents, so the Avon Valley artefacts actually have tin contents similar to those in East Anglia and Yorkshire (probably 6-7%). The high average zinc contents at Empingham are intriguing giving some suggestion of differences between sites or regions, although it is a small dataset (34 samples), so that the six samples with high zinc levels have a proportionally large effect (cf Blades 1996). Zinc values at the Avon Valley sites are average, however. Hence there is no clear evidence that the Avon Valley sites had a different metal supply at this period.

Surface XRF analyses

A total of 25 copper-alloy objects have white metal surfaces or areas of soldering but, for various reasons, only five objects with white metal surfaces and four objects with soldered areas were made available for analysis. These were analysed using non-destructive surface XRF analysis, comparing the white metal or solder areas with the base metal used for the main part of the artefact. Although it was not seen as necessary to investigate the gilding, two of the items available for surface XRF happened to be gilded, so these gilded areas were also analysed.

Amongst the samples with white metal surfaces, two samples with very shiny and well-preserved surfaces had strong evidence of elevated tin (A7147 and A7245) and another with a good surface had only slightly elevated tin (A7514). Two samples had poorly-preserved white metal surfaces; one showed significantly elevated levels of lead along with only slightly elevated levels of tin (A7454) and the other showed no difference between the tinned area and the tinned area (A7244). Clearly good-quality tinning is indicated in the first three samples, and the occasionally-striated appearance suggests that may well have been of the wipe tinning type (see *eg* Meeks 1986). However, it appears that for A7454, a lead-tin alloy was used for the white metal rather than a pure tin, which may explain why the preservation was not as good.

It was more difficult to detect solder using XRF. In three samples there was no discernible difference between the soldered area and background compositions (A7114, A7123, A7133) and there was only slight increase in tin in the other piece (A7123). It was particularly difficult to position samples accurately to concentrate on very small areas of soldering.

Mercury was detectable in both areas of gilding examined, showing that, as expected, mercury gilding was used to gild both the upper surface of the cast saucer brooch (A7114) and the foil for the applied saucer brooch (A7146).

References

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Appendix 1: Detailed comparison of Brownsword XRF analytical dataset and other datasets

1. Average **zinc** contents are very similar for analyses by Brownsword, Blades and Mortimer (Table 1). It is noticeable that Blades’ zinc contents appear to take the form of a one-tailed normal distribution (Fig 1a) and a very similar picture emerges from the cruciform brooches. The usual assumption about this sort of distribution pattern is that

many samples have lower concentration levels which, if detectable, would result in a two-tailed distribution, but that the analytical techniques used are not sensitive enough to detect these low levels.

Generally the Brownsword *et al* data is comparable with the other datasets, except that it has relatively few alloys with very low zinc contents. Initially this seems to be because the minimum detectable limit (MDL) for zinc is relatively high for XRF, with the lowest value recorded as 0.39%. A similar pattern is noticeable in the great square-headed brooch dataset (Hines 1997), although here the lowest recorded zinc content is 0.08%. However, there are no zero or 'not detected' values for zinc in either XRF dataset. About 10% of Blades' and Mortimer's analyses (29 out of 320 and 39 out of 363 respectively) are below 0.39% which suggests some alloys with very low zinc contents may be calculated by XRF as having detectable zinc. The lack of low and undetectable zinc values could be a regional metal supply effect, but the same feature reported amongst the great square-headed brooches which have a wide geographical distribution makes this less likely. Instead it seems possible that the XRF spectrum was sufficiently 'noisy' in the relevant area, that it provided enough signal to report detectable amounts.

2. Average **tin** contents are substantially lower (5.6%) in Brownsword *et al* and amongst the square-headed brooches (5.7%), compared to Blades and Mortimer (7.3% and 7.7%). This pattern is also obvious in the direct comparison (Table 2). In addition, it is also possible that very low tin values are under-reported; about 2% of the alloys used for cruciform brooches and those reported by Blades have tin values less than the smallest reported value in Brownsword *et al* (1.84%). However this may be a feature that is only clear due to the larger datasets.

3. Average **lead** values are slightly different with higher values reported by Blades and Mortimer. Very low and very high lead levels may be under-represented by XRF. Only one of the Brownsword brooches has less than 0.5% lead, whereas 46 cruciform brooches (16%) are below this level. However only 5 of Blade's artefacts (2%) have this low level of lead, so the pattern is not clear. Amongst the Brownsword data, there are no lead values in excess of 8%, whereas 22 cruciform brooches and 12 of Blades' artefacts are above this value.

4. Average **silver** values are similar for the four datasets, but it is notable that 86 of Blades analyses (27%) showed silver at undetectable levels (less than 0.02%), whereas only four cruciform brooches, and none of the XRF analyses had undetectable levels, or below 0.02% Ag.

5. **Iron** data from the four datasets cover similar ranges and have similar average values. Each dataset has a small number of analyses with unexpectedly high levels of iron (more than 0.6%). This might initially seem to suggest that some corrosion products from iron brooch pins may have been accidentally included, as was feared by Brownsword (p102-105). However, four samples with high iron levels were detected amongst the 131 SEM-EDS analyses, where electron microscopy should have ensured that only sub-samples which were completely metallic were used; six of the 232 AAS samples also had these high levels. Thus it is likely that a small proportion of Anglo-Saxon copper alloys had elevated iron levels. The larger ICPS and AAS/SEM-EDS datasets indicate that the iron contents follow a normal distribution with the largest number of samples containing

between 0.1 and 0.2%, and suggest that there may be quite a few samples with iron at below detectable amounts. However, a total of only eleven 'not detected' values are reported (nine in the cruciforms and two in the square-headed brooches).
6. All datasets show a one-tailed distribution for **nickel**, with a high concentration of datapoints around the lowest detectable amounts. However, given the shape of the curve and the low average values, it is surprising that 'not detectable' is only recorded amongst the cruciform brooches (in about one third of the analyses).
7. **Arsenic** shows a somewhat similar picture, although in this case, arsenic was recorded as 'not detectable' in 30 cruciform brooches (out of 131 SEM-EDX analyses), two of the great square-headed brooches and ten of Blades' analyses.
8. **Antimony** values are variable. Two datasets have average values in excess of 0.1% (Hines and Blades) and two below (Mortimer and Brownsword).
7. **Copper** values in the XRF analyses effectively allow the sample composition to total 100% ± 0.01. Hence this is not an independent variable, and it is not appropriate to compare results from the different techniques.

Appendix 2: XRF surface analysis of white metal surfacing on copper alloy objects.

Non-destructive surface X-ray fluorescence (XRF) analysis was carried out on five objects with white metal surfaces, four objects with visible soldering and two objects with gilding.

A7147, disc brooch, from Grave 89. White metal surface is shiny and mostly well-preserved, although one area shows the corroded base metal through it, and another area is black and shiny.

XRF analysis of shiny area shows a strong tin peak and a small lead peak. The blackened area also shows a strong tin peak but a rather more lead. Silver is relatively prominent, traces of zinc, antimony and arsenic are visible; these are all probably from the underlying copper alloy. Conclusion: the white metal coating was tinning, with the area with the darkened appearance being due to different burial conditions, which caused the formation of a different corrosion patina. Under higher magnification in the scanning electron microscope, the uneven texture of the tinned surface can clearly be seen; this is due to the various metallic phases being differently attacked in the burial environment.

A7245 disc brooch. With very shiny white metal coating on the front.

XRF analysis showed a very high tin peak on the front, with low levels of lead. This compares with the base metal composition where zinc and lead are present at higher levels but with tin still present.

A7244 disc brooch. Poor preservation/quality of tinning on the front.

XRF analysis on the white metal area and the comparative background area were very similar, with both spectra showing significant silver and tin peaks. This suggests the artefact is made of a silver-containing copper alloy, and that it is not possible to determine whether the white metal coating is tinning or silvering.

A7514 disc/disc brooch. Good white metal surface on the front.

XRF analysis of the white metal area shows slightly more tin than the comparative analysis area on the back.

A7454 disc brooch. Poor preservation of white metal area.

XRF analysis on the white area shows much more lead, and a little more tin than in the comparative area. Silver detectable in both areas.

A7114, cast saucer brooch from Grave 18. Faint traces of soldering visible on reverse, near catch area, probably from repaired catch (not present). Gilded.

XRF analysis of soldered area shows a good tin peak and smaller lead peaks, but there is no significant compositional difference between the soldered area and the ‘background’ (base metal) composition. Good peaks for silver and mercury as well as gold in the gilding.

A7123 Applied saucer brooch. A possible area of solder on the reverse seems to be related to a repaired catch.

XRF analysis showed there was slightly more tin in the soldered area than the comparative area.

A7133 cruciform brooch, soldered repair on back near catch area.

XRF analysis suggests a copper alloy with zinc, tin and lead. Analysis on the ?solder area and a comparative area showed little difference compositionally.

A7146 applied saucer brooch, frags. Gilded thin copper alloy sheet, with possible soldering on reverse.

XRF of the gilding had detectable mercury peaks, large gold peaks and traces of silver, copper, zinc, lead and tin, which may be from underlying copper alloy. On the reverse, there was no clear evidence for solder.

Table 1: Average values for major and minor elements

n = number of analyses, sd = standard deviation, min/max = minimum/maximum reported values
Zn = zinc, Pb = lead, Sn = tin, Ag = silver, Fe = iron, Ni = nickel, As = arsenic, Sb = antimony
ICPS = inductively-coupled plasma spectroscopy, AAS = atomic absorption spectroscopy, SEM-EDS = energy-dispersive X-ray analysis, XRF = x-ray fluorescence

Various brooch types, XRF, Brownsword *et al* 1984, n=73						**Great square-headed brooches, XRF, Hines 1997, n = 102**				
	mean	sd	min	max			mean	sd	min	max
Zn	3.34	3.80	0.39	17.58		Zn	3.34	2.98	0.08	13.00
Pb	2.86	1.37	0.46	7.46		Pb	2.03	1.18	0.49	11.40
Sn	5.56	1.74	1.84	9.63		Sn	5.71	3.02	1.19	27.90
Ag	0.11	0.07	0.02	0.56		Ag	0.13	0.09	0.03	0.84
Fe	0.31	0.31	0.03	1.73		Fe	0.25	0.20	0.00	1.16
Ni	0.05	0.03	0.02	0.19		Ni	0.06	0.06	0.01	0.49
As	0.10	0.08	0.00	0.52		As	0.16	0.17	0.03	0.93
Sb	0.06	0.03	0.00	0.17		Sb	0.11	0.06	0.00	0.57
Various types, ICPS, Blades 1995, n=230						**Cruciform brooches, AAS/SEM-EDS, Mortimer 1990, n = 363**				
	mean	sd	min	max			mean	sd	min	max
Zn	3.56	3.95	0.00	24.10		Zn	4.00	4.52	0.00	21.90
Pb	3.38	3.32	0.05	27.76		Pb	3.56	2.42	0.00	17.36
Sn	7.34	2.41	0.09	15.40		Sn	7.73	2.79	0.00	14.46
Ag	0.13	0.12	0.00	0.96		Ag	0.21	0.22	0.00	2.50
Fe	0.24	0.30	0.01	4.07		Fe	0.21	0.15	0.00	0.99
Ni	0.07	0.39	0.01	7.00		Ni	0.03	0.03	0.00	0.22
As	0.05	0.04	0.00	0.26		As	0.13	0.13	0.00	0.58
Sb	0.16	0.07	0.05	0.95		Sb	0.07	0.03	0.01	0.21

NB where minimum is 0.00 this represents ‘not detected’

Table 2: Direct comparison of XRF and ICPS, on three great square-headed brooches

	Zn			**Sn**	
	XRF	ICPS		**XRF**	ICPS
Bergh Apton 64	3.43	3.06		4.48	7.01
Bergh Apton 7	11.2	9.54		5.09	6
Spong Hill 24	2.87	2.41		4.5	7.81
	Pb			**As**	
	XRF	ICPS		**XRF**	ICPS
Bergh Apton 64	1.17	1.58		0.07	0.04
Bergh Apton 7	1.73	2.02		0.22	0.15
Spong Hill 24	1.39	1.77		0.18	0.07
	Ni			**Fe**	
	XRF	ICPS		**XRF**	ICPS
Bergh Apton 64	0.04	0.04		0.24	0.21
Bergh Apton 7	0.09	0.07		0.19	0.19
Spong Hill 24	0.06	0.04		0.52	0.39
	Ag			**Sb**	
	XRF	ICPS		**XRF**	ICPS
Bergh Apton 64	0.07	0.18		0.04	0.1
Bergh Apton 7	0.06	0.12		0.04	0.09
Spong Hill 24	0.07	0.19		0	0.1

Table 3: Wasperton compositions, grouped by phase (Phases refer to Scheschkewitz 2006)

Analysis number	**Mus. No.**	**Grave**	**Type**	**Phase**	**group**	**Sb**	**Sn**	**Ag**	**Pb**	**As**	**Zn**	**Cu**	**Ni**	**Fe**
BR1	1267/7	39	sml	2a-b	1	0.12	7.39	0.09	1.84	0.07	1.95	88.25	0.03	0.25
BR20	3616/23	167	cb, pair	2a-b	1	0.05	2.51	0.07	2.31	0.1	13.1	80.08	0.04	1.73
BR21	3616/22					0.02	2.35	0.09	1.54	0.05	13.5	81.36	0.04	1.06
BR23	1441/2	17	cb, pair	2a-b	1	0.06	5.84	0.14	3.35	0.06	0.47	90.01	0.05	0.03
BR2	1441/1					0.01	4.93	0.14	3.24	0.1	0.39	91.01	0.05	0.14
BR14	1247/1	13	sml	2b	2	0.07	5.46	0.13	2.63	0.11	0.64	90.42	0.03	0.5
BR5	3276/22	116	sml , pair	2b	2	0	5.97	0.14	2.9	0.06	1.35	88.66	0.05	0.92
BR18	3276/23					0.02	5.36	0.07	1.65	0.21	1.94	89.26	0.04	1.45
BR6	1324/2	43	sml	2b2	2	0.02	6.18	0.13	4.64	0.16	3.85	83.87	0.04	1.1
BR13	1324/1	43	gt shb	2b2	2	0.17	4.24	0.12	1.97	0.24	4.85	87.84	0.04	0.54
BR3	3247/23	111	sml	2b-c	2	0.03	3.71	0.08	2.23	0.05	11.17	82.35	0.05	0.33
BR22	3247/22	111	cb	2b-c	2	0.07	6.32	0.08	3.49	0.07	1.07	88.78	0.05	0.07
BR10	1232/4	19	sml	2c	3	0.05	4.08	0.08	2.36	0.03	8.62	84.53	0.07	0.18
BR4	1230/4	24	sml	2c1	3	0.07	6.75	0.12	3.34	0.13	1.78	87.36	0.03	0.42
BR12	2301	65	gt shb	2c1	3	0.07	7.01	0.16	2.29	0.09	3.37	86.53	0.03	0.43
BR15	1257/1	15	gilded bronze pendant	2c	3	0.06	4.56	0.09	2.33	0.08	0.51	92.13	0.04	0.21

Table 4: Average zinc, lead and tin contents, by region

	Zinc %	Lead %	Tin %
Blades East Anglia n = 234	3.11	3.28	7.78
Blades Yorkshire n = 52	3.76	3.98	6.32
Blades Empingham n = 34	6.34	3.17	5.91
Avon Valley n = 73	3.34	2.86	5.56

Data from Blades 1995 and Brownsword *et al* 1986