Archaeometry 26, 2 (1984), 237-244. Printed in Great Britain

X-RAY FLUORESCENCE ANALYSIS OF ENGLISH 13th-16th CENTURY PEWTER FLATWARE

R. BROWNSWORD and E. E. H. PITT

Faculty of Applied Sciences, Coventry (Lanchester) Polytechnic, Coventry CV1 5FB, U.K.

INTRODUCTION

In spite of the considerable output of English pewter flatware in the fifteenth to sixteenth centuries (Hatcher and Barker 1974), surviving examples in museum collections are few and earlier mediaeval examples are extremely rare. The reason for this probably lies principally in the weak nature of pewter and the consequent relatively short life of most pewter objects; this led to the widely practised habit of trading-in 'bruised' pewter as scrap for remelting when purchasing new items. Perhaps as a consequence of the scarcity of pewter objects of the period and their wide distribution around the museums of the country, there has been virtually no analytical work carried out to determine the nature of the alloys used by English pewterers in the thirteenth to sixteenth centuries. Only in the case of pewter spoons have any analyses been published but then for only a handful in total (Hilton Price 1908, Homer 1975, Brownsword and Pitt 1983b). No analysis appears to have been carried out on flatware (saucers, plates, chargers, porringers, etc. known as 'sadware' at the time) although a fair number in total has survived to the present day.

It is of interest to discover the compositions of the pewter alloys used, so that the findings may be compared with the data from literary sources of the period, particularly the records of the London Pewterers' Company. The Company had the responsibility for the regulation of the craft and a principal duty was in the maintenance of the quality of pewter manufactured in the area under its control, although it is not known to what extent this was effective. The main concern was to prevent the addition of excessive amounts of lead to the tin and, from time to time, searches of premises and at fairs were carried out to check for possible infringement of the quality standards laid down in 1348 by the Company for each type of object. Two qualities were stipulated being termed 'Fine', a tin-copper alloy to be used for flatware and 'Lay', a tin-lead alloy to be used for hollow-ware. However, confusion seems to have arisen in various published accounts of these regulations over the allowable amounts of lead in lay pewter and the amounts of copper in fine pewter.

Apart from laying down density standards in order to curb lead additions, the Company did not specifically prohibit other metals from being added to pewter to harden it, matters which were presumably left to the pewterer to decide, subject to the density constraint. The checking of such additions would have been difficult in any case. Mention has been made in Company records of the use of copper as a hardener and also of bismuth and antimony, although the amounts used are not clearly stated.

The present analytical programme was directed towards resolving some of these uncertain matters, in particular the quality of early pewter in respect of lead contents and the use of other metals as hardeners.

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ANALYTICAL TECHNIQUE

Samples for analysis were removed from the objects by careful drilling from an acceptable site, after prior removal of any surface layers at the sampling position. Sample masses of about 10 mg were typical but these ranged up to 20 mg from large objects. This has proved to be sufficient material for analysis by X-ray fluorescence spectrometry when appropriately mounted; the method of mounting samples for presentation to the X-ray source has been described elsewhere (Brownsword and Pitt 1983a). The X-ray fluorescence spectrometry equipment was used with a chromium target X-ray tube operating at 85 kV and 30 mA; further experimental details are available on request from the authors.

Samples were first subjected to qualitative analysis, for elements with Z > 25, and a semiquantitative analysis for tin, lead and copper. This involved recording the X-ray fluorescence spectra over an angular scan of $10-60^{\circ} 2\theta$ using an LiF 200 analysing crystal. The heights of the Sn K_{α}, Pb L_{α} and Cu K_{α} peaks were measured together with those given by a pewter of known composition. The approximate compositions of the samples were then calculated from these peak heights assuming that tin, lead and copper accounted for 99% of the composition in the samples.

This enabled a preliminary division of the samples into those made from 'fine metal' and those from 'lay metal'. These values also gave an additional cross-check on the full quantitative analysis when a different pewter standard was used. For the quantitative determination of the amounts of elements present, the positions of the 'peaks' were determined to the nearest $0.01^{\circ} 2\theta$ by step scanning through the 'peak' positions. Appropriate 'background' count angles were determined from the 'peak' profile. Adjustment to the counting data was made for the trace quantities of metallic elements in the Mylar/Magic tape used to mount the samples.

The effect of difference in the quantity of sample used was taken into account using a normalisation calculation. Information on reproducibility and detection limits is available from the authors.

It is appropriate to consider the relative merits of analytical techniques suitable for use in conducting alloy compositional surveys on non-ferrous archaeological metalwork. Any technique for quantitative analysis of such material is required to be comprehensive in the range of elements covered, to be able to cope with a wide variation in the levels of elemental concentration and to be non-destructive or as near that ideal as possible. If actual samples need to be taken then these must be very small.

Atomic absorption spectrometry and emission spectroscopy are techniques which have been applied to this type of work but both involve sample material being destroyed in the analytical process. Both methods are very sensitive to elements in low concentrations but the interpretation of spectra is not always easy in the latter technique. Complete solution of a sample, essential to reliable atomic absorption spectrometry and solution-based emission spectroscopy, is not always easy to achieve. In atomic absorption spectrometry only elements specifically sought are detected; there is therefore a risk of missing an unexpected element if only a few elements were included or of much effort largely unrewarded if a large number be included.

X-ray fluorescence methods are theoretically non-destructive but most archaeological metalwork requires the local removal of surface corrosion products or patination for reliable results to be obtainable by a dedicated or SEM-based energy-dispersive system. Very little additional damage need be done in taking a large enough sample (10-20 mg) for the wave-length-dispersive approach used by the authors. Quantitative analysis can be difficult by

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energy-dispersive methods when elements of adjacent atomic number are involved, particularly if the concentration of one element is several orders of magnitude greater than other neighbouring elements present. However energy-dispersive methods give almost instantaneous qualitative or semi-quantitative analytical data and require little additional time to give fully quantitative data involving the use of standards. For SEM-based energy-dispersive systems, the objects to be analysed need to be taken to the SEM and, while other systems using low-power X-ray or radioisotopic sources are car-transportable, the objects are normally taken to the instrument in these cases also. This approach does not lend itself to surveys of dispersed material, although it has been used successfully for collections.

The high-power primary X-ray generator in the wavelength-dispersive equipment used by the authors is sufficiently energetic to excite the K-radiation of relatively high atomic number elements such as tin and antimony, allowing their analysis to be conducted in an uncomplicated part of the spectrum. The method, particularly when using fine collimation, gives excellent discrimination between radiations from elements of adjacent atomic number. Occasional occurrences of unusual elements can be detected on the recorded X-ray spectrum; such elements, as with the mercury present in a pewter spoon alloy (Brownsword and Pitt 1983b) can be followed up when they are shown to be present. This analytical procedure takes longer than with the energy-dispersive methods and the equipment is costly but the sample is retained in the laboratory for possible re-checking in the light of later information and the accumulated samples can form an archive for future workers, as in the case of the present sample body.

It is believed that the analytical equipment and procedures described here probably represent the best compromise solution to the problems of routine analysis of non-ferrous metalwork which is widely dispersed in museum collections.

RESULTS

A wide variety of flatware has been sampled but all can be classed as domestic items. Saucers of about 100 mm diameter and plates of about 380 mm diameter mark the extremes of the size range. All are believed to be from the thirteenth to sixteenth centuries although close dating is difficult because of lack of precise data on makers and their marks and other information which might allow dating by style. The majority of the items were isolated finds with the exception of those from the hoard on the site of Guy's Hospital in Southwark and those recovered during excavations at Weoley Castle, near Birmingham. Thirty-six items have been analysed for the elements tin, lead, copper, antimony, bismuth, zinc and iron. Cadmium and arsenic were detected in many of the objects but at too low a level for reliable quantitative results to be obtained.

The alloy compositional data are summarised in tabular form for discussion purposes; full details are available from the authors to interested workers. It is evident from table 1 that the majority of items were made of high-quality pewter, as was required by the Pewterers' Company. Tin contents were in excess of 95% Sn for 80% of the items; those with tin contents lower than 90% Sn were all small saucers. Conversely, lead contents were below 1.5% Pb for 80% of the items and below 5% Pb for 90% of the items. Again the exceptional alloys were used in making saucers.

Copper, bismuth and antimony are alloying elements which are capable of hardening tin and are known to have been used by the pewterers for this purpose. It is clear that copper was the principal addition in the present flatware alloys; a near-normal distribution with a mean

Lab No.	Museum	Accession number	Provenance	Diam. (mm)	Sn (%)	I	Pb (%)	Cu (%)	Other (%)* Sb > 0.50 Bi > 0.35	Rim form †	Marks	Date
D34	Birmingham	WC301	Weolev Castle	188	926		0.66	6 5 1			0	
D88	Southampton	SOU163.206	Southampton	127	06.7		0.00	0.51		Angled-bead above		
D87	Leicester	A389.1973.373II33	Leicester	173	07.2		0.39	2.93		Angled-bead above	Р	c.1290
			Loicester	175	51.5		0.31	2.30		Angled-bead above		14th C
D35	Birmingham	WC309	Weolev Castle	126	72 0	2	06 5	1 20		C1		
D29	Birmingham	WC306	Weoley Castle	123	77.5	2	20.5	0.46		Groove above		
D19	Cambridge	Z15115	Cambridge	102	81.0	1	1 5	0.40	2 20 01	Groove above		2
			oumonage	102	01.0	1	4.5	1.51	2.28 50	Groove and bead		÷
D18	Cambridge	Z15114	Cambridge	100	89.9		7 6 5	1 73	0 56 Sh	Groove and head	T2C De 11. 0	
			c				1.00	1.75	0.50 50	above	I !C Portcullis?	
D9	Private	-		c.275	92.3		4.94	1.89	0.54 Sb	Bead above		0.77
										boud aborto		
D2	Coventry	49/227/93	Coventry	136	95.0		3.33	1.58		Read below	Hommon IM	z *
D3	Coventry	49/227/6	Coventry	145	97.4		1.31	1.20		Bead below	Hammer IM	110
D17	Cambridge	Z15113	Cambridge	164	97.9		1.03	0.92		Bead below	mannner	ţ
D4	Coventry	49/227/94	Coventry	250	97.9		0.16	1.48	0.49 Bi	Bead below	Hammer ?	t
D5	Coventry	49/227/95	Coventry	255	97.9		0.12	1.08	0.97 Bi	Bead below	manniner :	
D85	Leicester	389.1973.II32.132	Leicester	135	98.2		0.12	1.33	012 / 21	Bead below	Hammer	
-										boud bolow	manniner	16th C
D86	Leicester	389.1973.II32.133	Leicester	130	98.0)	0.43	1.24		Bead below	Hammer	early
DI	6										manniner	16th C
DI	Coventry	49/227/92	Coventry	120	97.4	(0.08	2.58		Bead below		Total C
D30	Birmingham	WC304	Weoley Castle	144	96.2	(0.74	2.63		Bead below	HB	
D31	Birmingham	WC303	Weoley Castle	160	97.2	(0.24	2.52		Bead below	В	
D32	Birmingham	WC308	Weoley Castle	160	97.7	(0.22	2.09		Bead below		
DIU	Private	-	-	186	97.2	(0.37	2.10		Bead below	WA?	
D46	London	8162	London	189	97.5	(0.30	2.04		Bead below	Rose? R?	
D4 I	London	81.548/16	London	378	97.0	(0.21	1.74		Bead below	E Rose &	
D42	T	011110110									Crown R	
D43	London	8144/8119	London	178	96.7	(0.82	1.64		Bead below	СМ	
D44	London	A419	Westminster	183	98.2	< (0.05	1.81		Bead below	SI (I crowned)	

 Table 1
 Pewter flatware analyses and other data

Table 1 (continued)

Lab No.	Museum	Accession number	Provenance	Diam. (mm)	Sn (%)	РЬ (%)	Cu (%)	Other (%)* Sb > 0.50 Bi > 0.35	Rim form †	Marks	Date
D45	London	A2711	London	177	98.0	0.33	1.55		Bead below	I (twice)	
D11	Private	-	-	258	97.3	0.98	1.46		Bead below	W Rowel spur l	vī
D33	Birmingham	WC302	Weoley Castle	160	98.4	0.22	1.40		Bead below	in restort spur	
D89	Peterborough	L138	Whittlesey Mere	275	98.0	0.52	1.45		Bead below	Ram's head	
D90	Peterborough	L135	Whittlesey Mere	347	97.3	0.56	1.70		Bead below	Ram's head	
D8	Private	-	Southwark	267	97.8	0.58	1.08		Bead below	Bell Crowned	
D20	London	24078	Southwark	270	98.4	0.49	0.55		Bead below	plume Bell Crowned	c.1500
D47	London	42/56/1	Southwark	268	97.8	0.36	1.52		Bead below	plume Bell Crowned	c.1500
D48	London	8166	Southwark	267	98.1	0.20	1.21		Bead below	plume Bell Crowned	<i>c</i> .1500
D80	British	1900 (2-12)1	Southwark	340	98.8	0.14	0.88		Bead below	plume Bell Crowned	c.1500
D81	British	1900 (2-12)3	Southwark	265	98.1	0.30	1.30		Bead below	plume Bell Crowned	c.1500
D82	British	1900(2-12)2	Southwark	267	98.3	0.17	0.66		Bead below	plume Bell Crowned	c.1500
										plume	c.1500

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* Full analytical data for the elements Sb, Sn, Bi, Pb, Zn, Cu and Fe are available from the authors on request. † Rim forms are illustrated in figure 1.

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content of 1.70% Cu was found and only one value exceeded 3% Cu. The distributions for the formula and antimony however were not normal and the vast majority of objects had less that 0.5% Bi and less than 0.25% Sb present. This suggests that these two metals were not delightately added, with the possible exception of the case of a saucer containing 2.28% Sb. Zine and iron levels were less than 0.2% and less than 1.0% respectively and in the majority of cases were much lower than these maxima.

DISCUSSION

Mo(t) of the objects included in this investigation do not benefit from detailed description and comment in the literature and such is not attempted here. However, some of the objects have certain stylistic features in common and it may be useful to examine the compositional data on this basis. Particular attention is paid to the rim-form and also to marks struck on the pew191.

 f_{1} (A, from Weoley Castle, has by far the highest copper content combined with a low lead content. There is some evidence from pewter spoon analyses (Brownsword and Pitt 1983b) that pewter with such a high copper content was in use in the mediaeval period, but the two object types were made by different craftsmen and they may not have used the same alloys. However, the other two items sharing the same rim-form are dated by archaeological context to the late thirteenth (Platt *et al.* 1975) or fourteenth (Clay 1983) centuries.

Four saucers D35, 29, 19 and 18 from Weoley Castle and Cambridge had in common a plain or beaded rim with a narrow, turned groove above and flat below; they shared a high lead content for flatware (7-27%) and a correspondingly low tin content. D19 was notable for the high level of antimony, probably deliberately added as a hardener. D9, a larger bowl from the West Country, had a relatively high lead content and had a beaded rim above.

The remaining twenty-eight items shared a simple rim, beaded below and flat above. These had low lead contents (all but three being lower than 1% Pb), the only other significant addition being a small percentage of copper as hardener. This rim-form has been identified from known pewterers' touch marks from the end of the sixteenth and first half of the seventeenth centuries. If the crowned-plume mark on the Guy's Hospital hoard be taken to be the insignia of Prince Arthur, then this would indicate that this rim, beaded below, was in use in c. 1500. Most of the pewter flatware recovered from the 'Mary Rose', lost in 1545, has this rim-form. It therefore appears that these twenty-eight items were made at some time in the late fifteenth or sixteenth centuries. This accords with the stylistic view which places flatware with relatively narrow rims, raised bases and small makers' marks struck singly usually on the underside (or no maker's mark at all) prior to 1600.

It is tempting to interpret the three groups separated in the table on the basis of rim-form simply in terms of a progression from three early samples, through a group of five perhaps of fitteenth-century date, to the largest group of twenty-eight perhaps of sixteenth-century manufacture; the surviving numbers might be expected to be in this relationship. This might lead on examination of the alloy compositions to the conclusion that the control exercised over the quality of pewter passed through a lax phase in the fifteenth century but was improved in the sixteenth century, by which time, if the group of twenty-eight be assigned to this period, uniformly high-grade pewter was in circulation. However, in any discussion of pew ter-metal quality, it is important to consider the extent of control likely to have been exclusived by the regulatory body as the scale and geographical distribution of pewter production

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changed with time. London, the home of the Pewterers' Company which obtained the first ordinances in 1348, probably enjoyed a virtual monopoly in pewter production in England and satisfied its slender needs up to that date. The London industry expanded over the next century, probably with reasonably tight control over quality since the pewterers all worked in a small area, although their products were sold over much of southern Britain through the fair system and other means. However, by the mid-fifteenth century, provincial pewterers were active and able to rival the London pewterers in satisfying the provincial needs. It has been suggested (Hatcher and Barker 1974) that lower quality (presumably meaning higher leadcontent) pewter was made in the provinces since the control there was not as effective as in London. In order to try to stamp out this practice and regain control of the craft, the Company spent a period from 1453 seeking corporate status which would give powers of search over the whole country. Once this was achieved in 1474 and searching became established, it appears likely that a measure of control over quality would have been exercised by the turn of the century but this was unlikely to have been effective in areas at any great distance from London.

Reference to table 1 shows that the poorest quality pewter has been found in the provinces, in or near Cambridge and at Weoley Castle, near Birmingham. However, both places have also provided some high quality pewter. All the pewter found in London was of high quality. Thus there is some evidence for classifying the flatware with rims flat below and having a tin content of less than 95% Sn as late fifteenth- or sixteenth-century provincial pewterware. In turn flatware with a bead below the rim and of tin content greater than 95% might be classified as late fifteenth- or sixteenth-century ware from London or adjacent areas in southern England. The rim with angled bead above is known to have been in use in the late thirteenth and fourteenth centuries but the form may have persisted for a long period and overlapped with other styles. Only when further material, particularly that from excavations, has been included in the study are these matters likely to be resolved.

CONCLUSION

The great majority of pewter flatware analysed has been shown to share the same rim-form, beaded below, and a high-grade alloy composition; the use of 1-3% copper as hardener for an essentially lead-free tin has been demonstrated. Most of this flatware is believed to be of sixteenth-century manufacture.

Three items having a rim with angled-bead above and of high-tin pewter are believed to be early examples, probably of the late thirteenth or fourteenth centuries.*

Five examples are thought from their variety of rim-form and generally poor quality to have been made in the provinces.

Antimony and bismuth appear to have been used only rarely as hardening additions to pewter of the period.

* Two further items, a plate WC307 and a saucer WC305 not included in the original survey of Weoley Castle pewter, share this rim-form and were made from similar high-quality alloys.

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Figure 1 Sections of some pewter flatware rim forms $(\times 1)$. (a) angled-bead above; (b) groove above; (c) groove and bead above; (d) bead above; (e) bead below.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of the following in making material available for study: J. Cherry, British Museum; J. Clark, Museum of London; Miss M. D. Cra'ster, Cambridge Archaeological Museum; P. Hornsby, Robin Bellamy Antiques Ltd, Witney; M. Howe, Peterborough City Museum; D. Janes, Coventry Museums; R. Rutland, Leicestershire Museums; D. Symons, Birmingham City Museums; R. Thomson, Southampton City Museums; Mrs R. Weinstein, Museum of London.

Thanks are due to P. Hornsby for donating a spoon for multiple sampling and for helpful discussions at various stages in the project.

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