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Analysis of copper alloys and associated materials from Berkeley

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Abstract

The submitted materials were analysed qualitatively to identify the broad characteristics of the metals involved. The qualitative nature of the analysis by portable X-ray fluorescence spectrometer (pXRF) means that precise alloy compositions cannot be determined (although it may be possible to calibrate the results to some extent in the future.

The materials had varying degrees of alteration and varied in interpreted original character from simple metal spills and a possible ingot fragment, through to more drossy (high iron) material and to material which had reacted with the hearth contents to produce a more silicate-rich slag.

Four groups of specimens were identified – a simple tin bronze composition, a leaded bronze, a strongly leaded bronze/gunmetal and slags with a high zinc content.

It is suggested that the main material being handled was a leaded tin bronze, with only very low levels of zinc. Such a material is a good casting alloy, commonly used for small items such as dress accessories, buckles and fittings. It is not particularly indicative of the age of the activity, and is not incompatible with a Saxon – Medieval age.

Contents

Methods

This report was undertaken to provide a rapid assessment of a number of fragments of what were interpreted as casting waste from the Bristol University excavations at Berkeley.

The specimens were analysed on a purely qualitative basis using a Bruker Tracer III-SD portable X-ray fluorescence spectrometer. The instrument was operated without a filter, at 40kV and 3.00 µA. The instrument was controlled by a PC running Bruker's S1PXRF with spectra stored as pdz files. These files were then compacted to 1024 channels and exported (as ASCII files) to Bruker's ARTAX software. Peak areas were generated and exported to Microsoft Excel. Data presented here include the peak area for various elements normalised against that of the Cu K peak. A visual classification of peak height is also presented.

Normalisation of the peak heights against copper allows some simple comparison of the relative abundance of individual elements in different samples, but does not indicate their absolute abundance nor allow comparison of the abundance of one element with another. The visual classification allows a 'broad-brush' indicator of relative abundance for individual elements between samples.

This project was undertaken for Peter Twinn, Bristol University.

Results

The data are illustrated in Table 1 below. The analyses have been divided into four groups, indicating clustering of material compositions. As stated above, the qualitative analyses do not permit determination of what the absolute composition of those materials actually is.

As well as the likely alloying elements lead (Pb), tin, (Sn) and zinc (Zn), there were trace level of nickel (Ni) and antimony (Sb) in some samples. These are common impurities in copper alloys. The other elements shown in Table 1 are iron (potentially an impurity in copper alloy, a major component of dross and potentially a major component of slag) and calcium (a major component of fuel ash and slag).

The first group, represented solely by an unstratified sample from Tr4 (BC10), shows a strong peak for tin, but only low peaks for lead and zinc, indicating no more than trace levels for these elements. This sample is likely therefore to be a simple tin bronze, or dross derived from such a metal.

The second group shows a lead 'L' peak and the tin 'K' peak of about similar heights. The iron content of these materials is variable – suggesting that some represent good copper alloy metal and some a more drossy material. Although there is no quantification of the alloy proportions these are likely to be slightly leaded bronzes. One of the pieces is probably a fragment of a metal charge that cooled inside a crucible, perhaps deliberately to create an ingot, of around 70mm diameter.

The third group show similar spectra to the second group but with the lead 'L' peak markedly higher than that of tin 'K' peak. These suggest high levels of lead addition to the bronze. Several of the pieces show dark coloured weathering products that are cracking open ('exploding') with weathering – and these probably represent extremely high lead contents – perhaps in an incompletely mixed state. For most of these samples zinc is effectively absent, or present at very low levels. Some of the materials with a high lead content show somewhat higher levels of zinc, and it is possible that these may approach a leaded gunmetal composition (a Cu-Pb-Sn-Zn alloy).

The final group are two samples which are more highly slagged. These materials probably contain a higher content of silicate material, and certainly show elevated levels of zinc. These materials are interesting. They probably represent residues from the working of a leaded gunmetal, but it is not impossible that the silicate materials have preferentially absorbed zinc vapour and that the metals worked during the formation of these slags were not particularly zinc-enriched – and may have been the leaded bronzes with trace zinc levels that are suggested by most analyses in groups 1 – 3.

Interpretation

The analyses suggest relatively lead-rich copper alloys, probably leaded bronze rather than gunmetal, were being cast at the site. Such a material is a good general purpose casting alloy for small items – particular dress items and fittings. It was employed (and is still employed) over a wide time period for such items.

Further work

It may be possible to improve the calibration of the current analyses and move towards at least their semi-quantification. Such an improvement would depend on the analysis of appropriate standard specimens, but it is hoped that appropriate calibration will be built up in coming months.

Even without additional calibration, the artefacts, including the potential part-finished products, could be analysed using the same configuration to establish any similarities that might exist with the casting waste.

Table 1: summary catalogue. Details of qualitative analysis of pXRF spectra. Visual classification (x – xx – XX – XXX – XXXX- XXXXX) in increasing peak height. Grey = duplicate analysis.

Sample					**peak areas (ARTAX) normalised to Cu K**							**Visual classification**					**Sample notes**
			wt		Ni K	Pb L	Sb K	Sn K	Zn K	Fe K	Ca K	Cu	Pb	Sn	Zn	Fe	
Sn K peak higher than Pb L																	
BC10	Tr4	u/s	4.4		0.00	0.01	0.00	0.03	0.03	0.06	0.00	XXXXX	x	XX	x	XX	sheet of dense, pale material
Pb L and Sn K peaks similar height																	
BC07	Tr4	409	8.0	sf45	0.00	0.02	0.00	0.03	0.01	0.04	0.01	XXXXX	xx	xx		XX	sheet of dense, pale material, prilly surfaces and charcoal
BC09	Tr8	u/s	50.0	sf177	0.01	0.02	0.00	0.04	0.01	0.01	0.01	XXXX	x	x		x	dense chunk of metal - fractured crucible ingot c70mm Ø
BC09	Tr8	u/s	12.0	sf146	0.00	0.02	0.00	0.02	0.01	0.04	0.01	XXXXX	xx	xx		XX	mass of coalesced blebs in prills
BC09	Tr8	u/s	1.9	sf140	0.00	0.02	0.00	0.01	0.02	0.02	0.00	XXXXX	xx	xx	x	xx	highly corroded small coalesced droplets
BC10	Tr8		9.3	sf11	0.00	0.02	0.00	0.04	0.01	0.08	0.01	XXXXX	XX	XX		XXX	fragment of lobate sheet, dark, 'exploding'
BC09	Tr9	u/s	2.3	sf14	0.00	0.02	0.00	0.02	0.00	0.01	0.00	XXXXX	xx	xx		x	thin sheet of rather pale material
					0.00	0.02	0.00	0.02	0.00	0.01	0.00	XXXXX	XX	XX		x	
BC10	Tr8	u/s	6.0	sf3	0.01	0.03	0.00	0.02	0.01	0.20	0.01	XXXXX	xx	xx		XX	foliated slaggy metal attached to fired ceramic
BC10	Tr8	u/s	8.7	sf112	0.01	0.04	0.00	0.06	0.00	0.02	0.01	XXXX	x	x		x	dense sheet, wrinkled surface, pale exterior
BC09	Tr8	814	6.4	sf109	0.00	0.05	0.00	0.07	0.01	0.21	0.02	XXXXX	XX	XX		XXX	coalesced dense blebs with some pale material
BC09	Tr8	u/s	7.9	sf170	0.01	0.08	0.00	0.09	0.02	0.09	0.02	XXXX	XX	XX		XX	dense dark sheet fragment with included sand
Pb L peak higher than Sn K																	
BC09	Tr9	u/s	21.0	sf12	0.00	0.08	0.00	0.00	0.00	0.06	0.01	XXXX	XX	x		XX	granular fragment, curved outer face (from crucible?)
BC09	Tr8	u/s	29.9	sf148	0.00	0.11	0.00	0.00	0.01	0.09	0.00	XXX	xx	x		xx	prilly dense mass, chilled against planar surface
BC10	Tr8	u/s	2.3	sf39	0.01	0.12	0.01	0.01	0.01	0.01	0.00	XXX	xx	x			small chip of coarsely crystalline pale material
BC09		u/s	10.1	sf009	0.01	0.20	0.00	0.03	0.01	0.07	0.01	XXX	xx	x		x	tabular flow lobe with one wrinkled surface
BC10	Tr8	851	9.5	sf85	0.00	0.03	0.00	0.03	0.02	0.02	0.00	XXXXX	XX	xx	x	XX	sheet of dense material, exploding, wrinkled pale surface
BC10	Tr8	848	9.3	sf45	0.00	0.02	0.00	0.01	0.01	0.08	0.00	XXXXX	XX	x		XX	irregular laminated dark sheet- defoliating
BC09	Tr8	u/s	11.9	sf045	0.00	0.04	0.00	0.01	0.01	0.05	0.01	XXXXX	XXX	x		XX	coalesced blebby prill
BC09	Tr8	u/s 814	8.7	sf150	0.00	0.07	0.00	0.02	0.04	0.04	0.01	XXXX	XXX	xx	x	X	dense tabular flow with smooth surface
BC08	Tr6	609	9.9	sf16	0.01	0.38	0.00	0.17	0.09	0.21	0.01	XX	xx	x	x	XX	dark 'exploding' material, crescentic, 45mm Ø crucible?
					0.00	0.28	0.00	0.07	0.06	0.11	0.01	XXXX	XXX	xx	xx	XX	
BC09	Tr8	u/s 827	9.9	sf152	0.01	0.43	0.01	0.03	0.01	0.19	0.01	XXX	XX	x		x	irregular prilly piece - chilled in fuel bed?
Zn K peak taller than Pb L																	
BC09	Tr8	u/s	24.1		0.01	0.27	0.00	0.47	0.76	0.73	0.10	XX	xx	xx	XX	XX	irregular slag fragment with charcoal
BC10	Tr8	u/s	31.8	sf102	0.01	0.35	0.00	0.58	0.57	1.37	0.08	XXX	xx	xx	XX	XXX	dense dark slaggy mass

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