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QUALITATIVE ANALYSES OF COPPER ALLOY OBJECTS FROM PORTWAY, ANDOVER, HANTS

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A total of 47 objects, some of them made of more than one part, were analysed qualitatively by energy dispersive x-ray fluorescence (XRF).

The peak heights (signal strengths) for the major elements (copper, zinc, tin and lead) were recorded together with the presence/absence of any other elements, e.g. silver, gold. The absolute peak heights depend on the size, shape and surface texture of the object as well as on its composition. In order to minimise the differences in signal strength that are not due to differences in composition, ratios of peak heights rather than absolute peak heights are compared. These ratios are obtained by dividing the zinc, tin and lead figures by the corresponding copper ones as copper is the most nearly constant element in the alloys being analysed.

Where objects had a visible surface plating, either gilding or white metal plating, two areas on the object were analysed, one plated and one plain. This was so the elements in the plating layer could be identified separately from those in the bulk metal of which the object was made.

As only one area on each object was analysed to give a bulk metal composition, the figures given in the table are only an indication of the composition. For this reason and because of the uncertainties inherent in converting the ratios given into absolute percentage compositions the divisions made are only into broad compositional classes; fine divisions made on the basis of only slight variations in ratios would be unsound and probably misleading.

Although most of the objects contained some lead, tin and zinc, the amounts varied from just detectable to considerable quantities. Depending on the relative amounts present the objects are described as bronze (mainly copper and tin) or gunmetal

(copper with tin and zinc) though it should be remembered that the division is an arbitrary one as there are no hard and fast boundaries between adjacent alloy types. A "(leaded) bronze" contains more lead than a "bronze" but less than a "leaded bronze" though again the dividing lines are arbitrary. An approximate conversion of ratio figures to percentages can be made by analysing objects of known composition. This suggests that the objects described here as low tin bronzes contain a few percent tin and the bronzes fall into the 5-15% tin range. The zinc contents of the gunmetals are probably mostly in the 5-10% range though some may contain more. "(Leaded)" bronzes and gunmetals probably contain 5-10% lead while "leaded" alloys contain more than this and in some cases considerably more.

Discussion of results

The results are tabulated below and the spread of tin and zinc values illustrated in the figure. The overall range of alloys in use was not extensive when compared with the range found on most Roman sites. There were no brasses (copper and zinc alloys) at all, few high tin bronzes and few heavily leaded alloys. All of the objects contained detectable amounts of lead and all but two (54-9 which was silver and 44-44B which was nearly pure copper) detectable amounts of tin. Zinc was detected in over three quarters of the objects.

As expected, none of the wrought objects (wire, thin sheet) contained much lead as this makes the metal crack when hammered because the lead is not dissolved in the copper alloy but is present as discrete droplets which are weak points in its structure.

All the gilded objects (saucer brooches) were low tin, low zinc and (with the exception of 41-2) low lead alloys. This agrees with results from other similar objects (pers. comm. Tania Dickinson; analyses by Peter Northover). The brooches from graves 41 & 48 had been mercury gilded, the technique generally used from the late Roman period on (Lins and Oddy, 1975),

(continued overleaf)

while those from grave 35 showed no sign of residual mercury. The composition of the objects probably relates directly to the surface plating as it is not possible to mercury gild on heavily leaded alloys.

However not all these low tin bronzes are gilded; other objects with similar compositions include 22-1: a disc brooch, 25-1: a small long brooch and 26-4A: a pair of tweezers.

Silver was detected at low levels in all the gilding; it is a common contaminant of ancient gold as it is relatively difficult to separate the two metals. Silver is also present at low levels (of the order of 0.1% or so) in some of the non-gilded objects. In these cases it probably just indicates that the copper came from an ore which naturally contained a little silver.

All the white metal surface platings were tinning (rather than silvering). The analytical results suggest that the applied metal was usually a tin-lead mixture rather than pure tin, though they are seldom unambiguous as both tin and lead are also found in the bulk metal of which the objects were made. Most of the tinned objects are bronzes rather than gunmetals and range from those containing nearly no lead to those containing over 10% or so.

The pairs of disc brooches from graves 1, 32 and 38 are compositionally closer than two randomly chosen disc brooches suggesting that at least some of the pairs may have been made from the same batch of metal at the same time. The same can be said for the pairs of saucer brooches from graves 35 and 48. The small long brooches are mainly found individually however the two from grave 19 do have very similar compositions although they are of different designs.

Reference

Lins, P.A. and Oddy, W.A. (1975) The origins of mercury gilding.

J. Arch. Sci. 2, 365-73.

TABLE OF RESULTS

| Grave/object no. | Element ratios | | | Other elements detected | | bulk metal alloy | Plating | Object |
|------------------|----------------|------|------|-------------------------|---------|-------------------|---------|-------------------|
| | Zn | Pb | Sn | bulk metal | plating | | | |
| 1-1 | 1.7 | 27.7 | 13.6 | Ag | | (leaded) bronze | tinning | disc brooch |
| 1-2 | 1.3 | 21.9 | 11.0 | ?Ag | | (leaded) bronze | tinning | " |
| 1-3 | 4.1 | 16.0 | 17.2 | | | gunmetal | | pin |
| 2A-1 | 8.6 | 36.3 | 5.7 | ?Ag | | (leaded) gunmetal | | disc brooch |
| 11-3 | 14.2 | 24.1 | 14.2 | | | (leaded) gunmetal | | strip |
| 12-6 | 2.4 | 67.0 | 20.9 | | | leaded bronze | | sheet cylinder |
| 13-1 | 9.0 | 36.6 | 20.0 | | | (leaded) gunmetal | | " |
| 13-2 | 5.6 | 22.3 | 11.1 | | | (leaded) gunmetal | | " |
| 16-2 | ? | 12.5 | 13.7 | | | bronze | tinning | disc brooch |
| 19-1 | 4.0 | 28.4 | 11.5 | Ag | | (leaded) gunmetal | | small long brooch |
| 19-2 | 6.6 | 35.5 | 14.9 | | | (leaded) gunmetal | | " |
| 22-1 | 0.8 | 12.1 | 3.8 | | | low tin bronze | | disc brooch |
| 22-2 | 2.3 | 58.0 | 12.8 | Ag | | leaded bronze | tinning | " |
| 25-1 | 2.0 | 2.0 | 6.3 | | | low tin bronze | tinning | small long brooch |
| 25-2 | 3.4 | 9.2 | 8.5 | Ag | | bronze/gunmetal | tinning | " |
| 26-4 A | X | 4.3 | 5.5 | | | low tin bronze | | } tweezers |
| B | X | 18.2 | 12.3 | | | bronze | | |
| 31-1 | ? | 46.0 | 8.6 | | | (leaded) bronze | tinning | small long brooch |
| 32-1 | 5.0 | 41.3 | 16.6 | | | (leaded) gunmetal | tinning | disc brooch |
| 32-2 | 4.7 | 42.9 | 15.9 | | | (leaded) gunmetal | | " |
| 33-9 | 5.9 | 16.4 | 6.2 | | | gunmetal | | scrap sheet |
| 33-10 | 5.1 | 33.2 | 9.8 | | | (leaded) gunmetal | | binding strip |
| 35-1 | 1.0 | 3.9 | 3.2 | | Au. Ag | low tin bronze | gilding | saucer brooch |
| 35-2 | 1.9 | 7.7 | 6.2 | | Au. Ag | low tin bronze | gilding | " |
| 35-3 A | 3.1 | 3.3 | 7.0 | | | bronze/gunmetal | | } buckle |
| B | ? | 6.0 | 9.0 | | | bronze | | |
| 38-1 | 3.8 | 16.1 | 7.2 | | | bronze/gunmetal | tinning | disc brooch |
| 38-2 | 1.8 | 22.2 | 10.7 | | | (leaded) bronze | tinning | " |

| Grave/object no. | Element ratios | | | Other elements detected | | bulk metal alloy | Plating | Object |
|------------------|----------------|-------|------|-------------------------|-------------|------------------------|-----------------|----------------------|
| | Zn | Pb | Sn | bulk metal | plating | | | |
| 41-1 | X | 6.4 | 7.7 | | Au.Hg.Ag | bronze | mercury gilding | saucer brooch |
| 41-2 | 3.0 | 39.4 | 7.8 | | Au.Hg.Ag | (lead) bronze/gunmetal | mercury gilding | " |
| 42-1 | 8.0 | 144.0 | 12.7 | | | lead gunmetal | tin | disc brooch |
| 44-44 A | 10.3 | 69.0 | 14.3 | | | lead gunmetal | | } chatelaine |
| B | X | 2.0 | X | | | "copper" | | |
| C | 8.7 | 88.7 | 13.1 | | | lead gunmetal | | |
| 48-2 | ? | 10.1 | 6.2 | | Au.Hg.Ag.Zn | low tin bronze | mercury gilding | saucer brooch |
| 48-3 | ? | 16.8 | 8.0 | ?Ag | Au.Hg.Ag.Zn | bronze | mercury gilding | " |
| 48-4 A | X | 242.0 | 6.7 | | | lead (low tin) bronze | | } buckle |
| B | ? | 13.8 | 18.9 | | | bronze | | |
| 48.112 A | 4.8 | 31.4 | 15.7 | | | (lead)gunmetal | | } needlecase |
| B | 5.3 | 55.9 | 20.8 | | | lead gunmetal | | |
| 50-1 | 1.1 | 30.3 | 8.9 | | | (lead) bronze | | small long brooch |
| 50-2 | 4.0 | 17.9 | 10.9 | | | gunmetal | | bucket |
| 52-1 | 10.6 | 137.0 | 14.9 | | | lead gunmetal | | disc brooch |
| 52-2 | 6.6 | 33.2 | 10.2 | | | (lead) gunmetal | | " |
| 52-3 | 3.4 | 88.3 | 24.9 | | | lead bronze | | pin |
| 53-1 | 4.4 | 17.0 | 49.2 | | | bronze | | tweezers |
| 54-9 | | | | Cu. Au. Pb | | silver | | finger ring |
| 59-1 | 2.6 | 52.2 | 17.5 | Ag | | lead bronze | | small long brooch |
| 61.15 | X | 11.7 | 16.7 | | | bronze | | strip bent into ring |
| 61-19 | 2.7 | 19.4 | 10.4 | | | bronze | | sheet strip |
| 67-2 | 0.7 | 15.3 | 17.7 | | | bronze | tin | annular brooch |
| 67-6 | X | 7.4 | 12.6 | | | bronze | | binding strip |
| SF5 | 1.9 | 22.9 | 6.1 | Ag | | (lead) low tin bronze | | saucer brooch |

Notes to table:-

(1) The ratios given are

$$\text{Zn ratio} = \frac{\text{Zn } K_{\alpha}}{\text{Cu } K_{\beta}} \times 10$$

$$\text{Cu } K_{\beta}$$

$$\text{Sn ratio} = \frac{\text{Sn } K_{\alpha}}{\text{Cu } K_{\alpha}} \times 1000$$

$$\text{Cu } K_{\alpha}$$

$$\text{Pb ratio} = \frac{\text{Pb } L_{\alpha}}{\text{Cu } K_{\alpha}} \times 1000$$

$$\text{Cu } K_{\alpha}$$

(2) ? = signal uncertain

X = not detectable

(3) Zn = zinc, Pb = lead, Sn = tin,

Ag = silver, Au = gold, Hg = mercury

(4) Object numbers:-

26-4 A = tweezers B = wire loop

35-3 A = buckle loop B = buckle plate

44-44 A = loop B = scoop C = pin

48-4 A = buckle loop B = buckle plate

48-112 A = needlecase B = loop