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THE HELMSDALE BOWLS, A RE-ASSESSMENT

R M SPEARMAN

X-ray fluorescence analysis of the Helmsdale Bowls

P Wilthew

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Method

The bowls were examined visually and using low power optical microscopy, but metallographic sections were not prepared. Selected areas were analysed elementally using an energy dispersive X-ray fluorescence system with a Rhodium target X-ray tube and silicon (lithium) detector. The beam diameter at the surface of the object was about 1.5mm.

Evidence for gilding and gross inhomogeneity in the metal was sought by qualitative or semi-quantitative analysis of several unprepared areas of each bowl. For these analyses the X-ray tube was run at an anode current of 0.3mA and spectra were collected over 200 seconds. Spectra for quantitative analyses were collected over 500 seconds with a X-ray tube anode current of 0.5mA. The X-Ray tube was run at 46KeV for all analyses.

The fundamental parameters programs FUN1 and FUN2 similar to the programme described by Cowell (1977 76-85), calibrated with alloy standards (for copper, zinc, tin and lead) and pure element standards (for nickel, iron, arsenic, silver and antimony) were used to obtain quantitative results. The areas to be quantitatively analysed were degreased using acetone and then successively abraded with 500 grit silicon carbide paper, degreased, and analysed until consistent results were obtained. Early analyses included analysis of the area before abrasion followed by four or five abrasion/analysis cycles, but it was found that after one abrasion the results did not change significantly and for later analyses two consistent results for abraded surfaces were considered adequate. Multiple analyses of each object were not possible because of the effect on the appearance of the objects and limitations of time. However semi-quantitative analysis of unprepared areas did not suggest that inhomogeneity was a major problem.

All nine elements listed above were analysed for, but nickel, silver and arsenic were not detected at levels above the minimum detection limit (see below) in any overall result and they are not listed in Table 1. The figures are subject to a relative error (error as a percentage of the quoted figure) due to the counting statistics. For any particular element the relative error increases as the absolute percentage present decreases, and it also depends on the matrix in which the element is present. It should be remembered that any errors due to uncertainties in calibration are not included in the relative error, and that internal comparisons are more reliable than comparisons with other published data. An estimate of the relative error (one standard deviation) is given below for each element detected at significant levels together with the minimum detection limits assumed for each element:

Element	Relative Error	Detection Limit
Cu	0.5%	0.05%
Zn	2.0%-10.0%	0.2%
Pb	5.0%-10.0%	0.1%
Sn	1.0%-2%	0.2%
Ni	-	0.2%
Fe	20%+	0.1%
As	-	0.2%
Ag	-	0.2%
Sb	20%+	0.2%

<u>Table 1 : Composition of the Helmsdale Bowls</u>

Object	Area	Fe	Cu	Zn	Pb	Sn	Sb
xL 1986 .4	Body	-	90.0	4.0	0.9	4.9	-
	Patch	-	89.7	1.7	1.2	7.3	0.2
	Rivet 1	-	88.5	4.2	0.5	6.6	0.1
	Rivet 2	-	88.5	4.3	0.7	6.3	0.2
	Rivet 3	-	87.9	4.4	0.8	6.8	0.2
	Rivet 4	-	87.9	4.2	0.9	6.8	0.2
	Rivet 5	-	87.8	4.3	0.9	6.7	0.3

xL 1986 .5		-	88.2	0.6	1.5	9.7	-
xL 1986 .6		-	87.2	-	1.0	11.9	-
xL 1986 .7	Bowl	-	85.3	-	1.2	13.4	-
	Patch	0.2	86.5	0.5	1.2	11.7	-
xL 1986 .8		-	88.3	-	0.5	11.2	-
xL 1986 .9		-	85.2	-	1.9	12.8	-
xL 1986 .10	Bowl	0.1	86.1	3.7	0.5	9.5	0.1
	Rim	-	87.6	-	0.5	11.6	0.1
	Handle	0.2	85.8	5.9	1.6	6.4	0.1
	Rivet 1	0.1	87.3	0.2	0.9	11.5	-
	Rivet 2	-	87.5	-	1.0	11.2	0.2
	Rivet 3	-	87.6	-	0.9	11.3	-
	Rivet 4	0.1	86.5	0.8	2.0	10.4	0.1

- = mean value was below the minimum detection limit.

Note: Because of the way the above figures were obtained, some of the analyses do not sum to 100%

Lead was present at low levels in all the areas analysed. It is often distributed inhomogeneously through a copper alloy and variations at the levels observed in these objects are not therefore of great significance.

Iron is a common contaminant of surface analyses on buried material and it is difficult to assess the significance of low levels of iron (Mortimer, Pollard & Scull, 36-42) in XRF analyses of this type. In the present work, therefore, the variations in iron levels detected could not be regarded as significant.

Bibliography

Cowel, M 1977
'Energy dispersive X-ray fluorescence analysis of ancient gold alloys', PACT, 1 (1977), 76-85

Mortimer, C, Pollard, A M, & Scull, C 1986
'XRF Analysis of some Anglo-Saxon copper finds from Watchfield, Oxfordshire', in Journal of the Historical Metallurgy Society, 20.i (1986), 36-42.

Appendix - full list of all analytical results (normalised to 100%)

Object	Area	Abrasions	Fe	Cu	Zn	As	Pb	Ag	Sn	Sb
L1986.4	Bowl	0	nd	88.98	3.86	0.07	0.35	0.01	6.46	0.27
L1986.4	Bowl	1	nd	90.08	3.86	0.06	0.90	nd	4.96	0.07
L1986.4	Bowl	2	0.04	89.94	4.06	0.11	0.92	nd	4.91	0.02
L1986.4	Patch	1	nd	89.84	1.69	0.03	1.03	0.01	7.13	0.27
L1986.4	Patch	2	0.02	89.46	1.66	nd	1.27	nd	7.52	0.07
L1986.4	Rivet 1	1	0.02	88.35	4.22	0.08	0.61	nd	6.60	0.12
L1986.4	Rivet 1	2	0.06	88.59	4.12	0.07	0.46	nd	6.68	0.12
L1986.4	Rivet 2	1	0.03	88.55	4.30	0.04	0.64	nd	6.27	0.17
L1986.4	Rivet 2	2	0.02	88.49	4.25	nd	0.77	nd	6.28	0.19
L1986.4	Rivet 3	1	0.05	87.92	4.31	0.06	0.75	nd	6.79	0.12
L1986.4	Rivet 3	2	nd	87.78	4.42	0.06	0.75	nd	6.81	0.18
L1986.4	Rivet 4	1	0.09	88.09	4.12	nd	0.80	nd	6.73	0.17
L1986.4	Rivet 4	2	nd	87.68	4.26	nd	0.93	nd	6.94	0.19
L1986.4	Rivet 5	1	0.03	87.69	4.38	0.07	0.86	nd	6.65	0.32
L1986.4	Rivet 5	2	nd	87.88	4.14	nd	0.96	nd	6.68	0.34
L1986.5		0	nd	88.54	0.63	nd	1.19	nd	9.61	0.03
L1986.5		1	0.03	88.10	0.61	nd	1.44	nd	9.72	0.10
L1986.5		2	nd	88.25	0.57	nd	1.45	0.02	9.70	0.01
L1986.5		3	0.04	88.05	0.64	nd	1.54	nd	9.73	nd
L1986.6		0	nd	87.15	nd	nd	0.78	0.02	12.05	nd
L1986.6		1	0.02	86.86	nd	nd	0.97	nd	12.15	nd
L1986.6		2	0.02	87.12	nd	0.12	0.89	nd	11.85	nd

L1986.6	3	nd	87.25	nd	nd	1.01	nd	11.74	nd
L1986.6	4	nd	87.10	nd	0.01	0.93	nd	11.96	nd
L1986.7 Bowl	0	nd	85.58	nd	nd	1.02	nd	13.40	nd
L1986.7 Bowl	1	nd	85.37	nd	0.05	1.09	0.03	13.46	nd
L1986.7 Bowl	2	0.02	85.34	nd	nd	1.24	nd	13.40	nd
L1986.7 Bowl	3	nd	85.20	nd	nd	1.40	nd	13.30	0.10
L1986.7 Patch	0	0.08	87.74	0.56	0.07	0.84	nd	10.71	nd
L1986.7 Patch	1	0.06	87.17	0.52	nd	1.08	nd	11.17	nd
L1986.7 Patch	2	0.10	86.74	0.55	nd	1.16	0.05	11.40	nd
L1986.7 Patch	3	0.12	86.26	0.54	nd	1.14	nd	11.94	nd
L1986.7 Patch	4	0.19	86.70	0.43	nd	1.19	0.02	11.47	nd
L1986.8	0	nd	89.13	nd	0.10	0.31	0.02	10.44	nd
L1986.8	1	nd	88.14	nd	0.11	0.36	nd	11.39	nd
L1986.8	2	nd	88.20	nd	0.09	0.44	0.01	11.26	nd
L1986.8	3	nd	88.34	nd	0.07	0.51	nd	11.08	nd
L1986.9	0	nd	85.62	nd	nd	1.43	0.06	12.89	nd
L1986.9	1	nd	85.57	nd	0.01	1.61	0.08	12.73	nd
L1986.9	2	nd	85.41	nd	nd	2.07	nd	12.52	nd
L1986.9	3	nd	85.05	nd	nd	2.13	0.03	12.70	nd
L1986.9	4	0.04	84.68	nd	nd	1.90	0.05	13.21	0.03
L1986.9	5	nd	85.64	nd	0.07	1.75	0.06	12.48	nd

Object	Area	Abrasions	Fe	Cu	Zn	As	Pb	Ag	Sn	Sb
L1986.10	Bowl	1	0.13	86.13	3.62	0.11	0.39	nd	9.47	0.15
L1986.10	Bowl	2	0.02	86.07	3.75	0.04	0.60	nd	9.52	nd
L1986.10	Rim	1	nd	87.77	nd	0.13	0.40	0.05	11.65	nd
L1986.10	Rim	2	nd	87.48	nd	0.11	0.55	nd	11.61	0.25
L1986.10	Handle	1	0.21	85.77	6.02	0.06	1.57	nd	6.37	nd
L1986.10	Handle	2	0.19	85.82	5.82	nd	1.55	0.05	6.41	0.16
L1986.10	Rivet 1	1	nd	87.48	0.21	0.10	0.72	nd	11.49	nd
L1986.10	Rivet 1	2	0.12	87.08	0.22	nd	1.00	nd	11.58	nd
L1986.10	Rivet 2	1	0.03	87.65	0.03	nd	1.00	0.03	11.26	nd
L1986.10	Rivet 2	2	0.05	87.44	0.05	0.02	0.92	nd	11.18	0.34
L1986.10	Rivet 3	1	0.05	87.77	0.05	0.11	0.81	0.01	11.20	nd
L1986.10	Rivet 3	2	nd	87.46	nd	0.05	1.05	nd	11.38	0.06
L1986.10	Rivet 4	1	0.06	86.58	0.88	nd	2.12	nd	10.36	nd
L1986.10	Rivet 4	2	0.11	86.51	0.77	nd	1.95	0.06	10.37	0.23

Note : Nickel was not detected in any analysis

The results above represent the raw data obtained and the fact that they are quoted to 0.01% does not imply that the method used is accurate to 0.01%. Table 1 gives the best estimate of the actual composition of the objects obtainable by the method used.