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The analysis of a yellow bead from Jutland

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The bead came from a woman's grave in Jutland which dated to about 400 AD (Brinch Madsen 1975). It was part of a long necklace, mostly of monochrome beads but including several polychrome ones.

The bead was analysed in the Ancient Monuments Lab. by energy dispersive x-ray fluorescence (XRF) which gave qualitative results (see table 1), and at the Universities Research Reactor by neutron activation which gave quantitative results for those elements listed. The neutron activation analysis was carried out by Gordon Gilmore and his report is given in table 2.

The reason for performing these analyses was to determine what gave the bead its colour and opacity. Two opaque yellow colourants for glass are known in antiquity; the first is lead antimonate, $Pb_2Sb_2O_7$ (Turner and Rooksby 1959, 22) and the second cubic lead tin oxide, "$PbSnO_3$" (Rooksby 1964). These colourants were identified by x-ray diffraction (XRD) which showed them both to have a cubic pyrochlore-type structure. Because of this similarity in structure the XRD patterns must be interpreted with great care to avoid confussion. For this reason elemental analysis, though not positively identifying the compounds present, can be easier to interpret as elemental tin and antimony are more easily distinguished.

Lead antimonate in opaque yellow glass is known as early as the mid 2nd millenium BC (Sayre and Smith 1967, 298) and continued in use down into the Roman period where it is found in such things as gaming counters, beads and enamels (Bateson and Hedges 1975, 181). It has also been identified in the post-Roman period (Biek and Bayley 1979, 10), but only occasionally.

Lead tin oxide was originally thought to be a mediaeval introduction (Turner and Rooksby 1959, 27) but has more recently been discovered in far earlier contexts. It has been identified in all the opaque yellow glass beads from Sewerby, an Anglian cemetery in Yorkshire dating to the 6th-7th centuries (Hirst and Biek 1981, 141 and table 2, below), in beads of a similar date from Little Chester, Derbyshire (Henderson, pers. com.) and also in crucibles found on an early Saxon site at Buckden, Huntingdonshire (Rooksby, forthcoming). Further potsherds containing lead tin glass have come from 4th century layers at Catsgore, Somerset (Biek and Kay, forthcoming). Werner and Bimson (1967) have identified lead tin yellow in a set of late 1st century BC gaming pieces found in Hertfordshire and it has also been found in glass from various parts of continental Europe, the earliest example, dated about the 5th century AD, being from Centcelles in Spain (Rooksby 1962, 24).

Leaving aside the unique 1st century BC, identification, it seems that lead tin yellow appears from the 4th century onwards in England and is known in continental Europe from the 5th century. At much the same time lead antimony yellow disappears, though isolated examples of later date are known. It is interesting that this bead from Jutland is among the earliest examples of the use of lead tin yellow. On the basis of this one analysis it can be postulated that the use of this colourant originated among the germanic peoples and spread into western Europe with their migrations. Further analyses of securely dated material might either confirm or disprove this suggestion.

One further, though unconnected point was noted during microscopic examination of the bead. Its perforation was coated with a thin black layer. A small sample of this was removed and analysed by XRF which detected only iron and zinc. The presence of the zinc was unexpected as none had been detected in the main fabric of the bead. The iron however is more easily explained: To form the bead, glass would be wound round a rod, most probably of iron. A thin outer layer of this rod could have become oxidised and adhered to the glass or have been absorbed into the glass, producing a thin layer of high iron, black glass. These black-lined perforations are found fairly commonly in Anglo-Saxon beads, especially in those made of opaque glass.

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Table 1 : X-ray fluorescence results

Elements detected	Signal strength
Si	medium
K	weak
Ca	medium
Mn	weak
Fe	medium
Cu	weak
Pb	strong
Sn	medium

NB : Na, Mg and Al were not detectable under the analytical conditions used. Other elements not detected may have been present in amounts below their detection limit which varies from one element to another but is typically a fraction of a percent.

Analytical conditions : Incident x-ray beam (Rh tube) 35 kV, 0.18 mA
Detector live time 20 secs.

Table 2 : Neutron activation results

UNIVERSITIES RESEARCH REACTOR

Source	Sewerby 12/6-14	Jutland
Weight (g)	1.4123	0.2985g
	Element Concentrations	
Co ppm	<20	<20
Ti ppm	≤170	≤520
Mn %	0.158 ± 0.006	0.55 ± 0.02
Mg %	<0.2	<1.2
Cu ppm	240 ± 40	<150
Al %	0.551 ± 0.007	1.03 ± 0.02
Na %	4.4 ± 0.2	11.5 ± 0.3
Sb ppm	890 ± 20	<95
Sn %*	5.3	2.0
Ca %	1.49 ± 0.09	2.6 ± 0.3
Cl %	0.33 ± 0.02	1.05 ± 0.04
I ppm	<9	<40
Br ppm	<20	<80
K %	<1.6	<3.7
V ppm	12.3 ± 0.6	16 ± 2
Ba ppm	<200	<600
Sr %	<0.1	<0.2

< Indicates sought but not detected.

≤ Indicates detected but not measurable.

* Sn results are perturbed by self absorption within the sample. The extent of this is, at present, unknown and consequently no uncertainty is quoted.

Analytical conditions:

30 kW Reactor power.
URR Rabbit position (10^{11} thermal) for 2 min.
Counts for 600 seconds after short decay periods.

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