GeoArch

Report 2016/34

Possible archaeometallurgical residue from Tower Hill, Howth, Fingal

Dr Tim Young
5th October 2016

Possible archaeometallurgical residue from Tower Hill, Howth, Fingal

Dr T.P. Young

Abstract

Excavations at Tower Hill produced an unusual artefact of uncertain nature: a broken small 'trough' of fine-grained ceramic, containing the tip of a small, apparently ingot-like, mass of weathered copper-alloy residue (probably derived from dross rather than fresh metal).

The apparently processed ceramic and the tentative estimate of the elemental composition of the oxidised metal would both suggest a post-medieval origin for the piece. If the oxidised material has a composition close to that of the original metal, it suggests the metal was a lightly leaded brass, but both the poor quality of the calibration of the analysis on such a substrate and the potential difference in composition between the oxidised material (dross?) and any original metal, must mean this identification is considered extremely tentative. The level of zinc does, however, indicate that a pre-Viking age for the material is very unlikely with a higher degree of confidence.

The presence of a higher proportion of the alloying elements in analyses of the ceramic is ambiguous; although it probably supports the identification of the material as a mould, migration of those elements from metal to ceramic during weathering cannot be excluded.

In summary, identification as a post-medieval mould is most likely.

Contents

Abstract 1

Methods 2

Results
Description of the specimen 2
Analysis 2

Interpretation 2

Figure caption 3

References 3

Figure 1: pXRF spectra 5

Methods

The material described here derives from excavations at Tower Hill, Howth, Fingal, conducted by Paul Duffy.

The specimen was analysed on a qualitative basis using a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer (instrument belonging to the Department of Archaeology, Cardiff University, and the National Museum Wales). The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 100s. The instrument was controlled by a PC running Bruker's S1PXRF software and peak areas calculated using Brucker's Artax software.

Data were exported as .csv files and graph prepared for illustration in Excel.

Results

Description of the specimen

The specimen has a central core of rough-textured, green coloured copper alloy-based material. The material is granular, with broken surfaces showing the impression of small grains of cuprite encased in green hydrated alteration products. It is unclear from the external appearance whether this is corroded metal or a metal dross, but it is much more likely that this texture has evolved from dross than solid metal. This material has a crudely concave upper surface. It has a maximum length of 26mm, with an oblique fracture, a width of 14mm, 2mm thickness in the centre but rising to up to 7mm thick adjacent to the margin.

The central copper alloy is partially encased in fine pale pinkish -coloured ceramic. The paste is very fine grained, free of visible inclusions, and therefore with the appearance of having been well-processed. The surface is finely striated, apparently where it has been smoothed during manufacture. The striations run longitudinally, providing a hint that the piece has been hand-formed rather than moulded. The termination, base and one lateral face are all planar, with rounded angles between them. The upper surface of the ceramic is nowhere preserved, and it has a maximum preserved height of 17mm near the better preserved corner. The ceramic is 5mm thick below the metal, 5mm on the side and was probably 5mm on the end, giving the ceramic an overall preserved cross section of 20mm x 17mm and a preserved length of 36mm. The closed end of the trough has neatly rounded internal angles.

The contact between the copper-alloy material and the ceramic is sharp, with no signs of alteration of the ceramic surface and no change in the colour (i.e. oxidation state) of the ceramic.

Although the cross-section of the ceramic is incomplete, it would appear likely to have originally been symmetrical, giving it an overall section 24mm wide.

Analysis

Three spectra were acquired (Figure 1), one of a smooth face of the ceramic ('ceramic'), one from above of the copper alloy material (but with a distance of several millimetres between the same and instrument; 'top') and one from the exposed end of the copper alloy material (where the copper alloy could be placed close to the instrument, but where there was probably a greater impingement of the beam onto the adjacent ceramic; 'end'.

The Bremsstrahlung (background) is high for the ceramic sample, as would be expected. Because of the use of the Bruker 'yellow' filter elements lighter than titanium are poorly represented in the spectra, so that the spectrum is dominated by iron. Low levels of the expected trace elements rubidium, strontium, niobium and zirconium are present, as are trace levels of tin. Copper and zinc are both represented in the spectrum, with the copper CuKα peak only slightly taller than that of zinc. Lead is present, with a small PbLα peak of just less than half the height of the zinc ZnKα peak.

The spectrum taken with the X-Rays incident on a free surface of the copper-rich material ('end' and 'top') show spectra in which the copper CuKα peak is much larger than that of ZnKα. The PbL lines are very much lower in intensity, but significant.

Interpretation

There are two lines of enquiry that may assist with the interpretation of this artefact. The first is the form and nature of the ceramic, the second the composition of the metal.

The ceramic has not been subjected to any detailed analysis, but it shows a very fine-grained, even, inclusion-free, paste, quite unlike the coarse silty or sandy material that was employed in the fashioning of most early (pre-industrial) moulds. It is also noteworthy that the ceramic has fired to an even degree of oxidation, as indicated by its colour, across the entire width from metal to outside. These characteristics would argue against the artefact being an early mould.

Because the copper alloy material is represented neither by fresh metal nor by a smooth surface, the analytical results from pXRF cannot be calibrated to give a meaningful numerical composition. It is likely that in the oxidised state of the material it does not have a composition that would be fully representative

of the original. Nonetheless some qualitative comment may be made. Firstly, the copper peak so much larger than any other peak, that it is clear that the original metal would have a copper-rich copper alloy. Only the zinc peaks are also clearly visible on the scale of diagram presented in the upper part of Figure 1. On the detailed view of the data (Figure 1 lower), only lead appears a significant additional alloying element. Arsenic may be present (the Kα is coincident with one of the lead peaks and Kβ is very small), but appears unlikely to be present in more than trace levels. Tin is not present at a measurable (except possibly in the 'ceramic' analysis). The relative intensities of the copper and zinc do not suggest a very high zinc content. The spectra taken on the metal both show trace levels of bismuth. A very approximate calibration of the spectra was undertaken through linear correlation of the net peak areas with those recorded by Nicholas & Manti (2014) on a series of copper alloy standards, using exactly the same instrument and settings. This calibration is only qualitative when applied to a rough oxide surface, but gave the following results (normalised solely for iron, copper, zinc, lead, antimony and tin; data in wt%):

	ceramic	end	top
Fe	86%	6%	1%
Cu	4%	86%	95%
Zn	2%	6%	3%
Sn	2%	0.05%	0.03%
Pb	4%	2%	0.3%
Sb	0.8%	0.3%	0.04%

These data are only of poor quality and it is unclear whether the oxidised material would be representative of the original metal, but they tentatively suggest that the original material was a lightly leaded brass, perhaps with a rather low zinc content.

The analysis taken of the ceramic were not primarily taken to investigate the ceramic composition itself, but to investigate whether there had been any uptake of the metal into the ceramic. In this spectrum the zinc peak was relatively stronger compared to the copper than it was in the spectrum taken of the metal residue itself. The net area of the Zn Kα peak is approximately 5% of that of the CuKα peak in the 'top' sample, 9% in the 'end' spectrum, but 77% in the 'ceramic' sample. There is also a relatively stronger series of peaks for lead. Peaks for antimony and tin are also relatively stronger, but given the extremely low values involved this may not necessarily be significant.

The transfer of lead and zinc into the ceramic might be a consequence of weathering, but transfer of both may occur from metal to mould during casting (Kearns *et al.* 2010). Typically, in a mould, the transfer of zinc involves the vapour phase, whereas that of lead involves reaction with the silicate to form a slag. The apparently higher degree of enrichment of lead and tin in the ceramic than that of zinc may suggest that the enrichment did not involve transfer via vapour – providing an argument against this artefact being a mould. The specimen does not show the colour-change that commonly accompanies significant uptake of metals into a hot ceramic.

Summary

The overall form of the piece has a size and shape suggestive of a small ingot mould. However, the two strands of evidence discussed above argue against that interpretation. The piece would appear best interpreted as of relatively modern origin.

Analysis of the copper-alloy based material shows an elemental composition suggestive of derivation from a metal with the composition of a very slightly-leaded brass (perhaps not quite formally a leaded brass since the lead content is likely to have been at or below 4%). The zinc content is likely to have been low for a brass. It would appear probable that the metal contained only trace levels of tin. The analysis taken with least influence from the ceramic tentatively suggest (with a large margin of error) that the metal may have had perhaps between 1 and 10% zinc (probably in the lower part of that range), probably in the order of 1% lead, and probably less than 0.5% tin. Such a composition would be very unusual for the early medieval or high medieval periods In the later medieval and post-medieval periods leaded brasses and lead-bearing brasses are rather more common (e.g. Blades 1995, Figure 5.17). In particular, the extremely low levels of tin and the absence of silver, would be unusual characteristics in a medieval or earlier copper alloy. Zinc appears a significant alloying element in the later part of the early medieval period in Ireland, possibly as a result of contact with the Viking world, but most examples of early zinc-bearing alloys also contain tin. The ceramic appears highly processed and would therefore be most likely to be post medieval in date.

If the evidence suggests that this artefact is of probable post-medieval age, the evidence for its nature is less certain. The object looks like a small mould, even if the ceramic is very fine and even for a mould. The possible presence of the alloying elements (lead, zinc and tin) within the ceramic could be explained by migration during weathering (corrosion), as well as by migration during moulding of hot metal. The granular nature of the oxidised material is more likely to be derived from metal dross than from metal itself.

Figure Caption

Figure 1: XRF spectra for areas on the possible tuyères. The inset shows the part of the spectrum surrounding the Sn Kα and Kβ peaks, with the data normalised to their average value between 24.0 and 24.5 KeV to facilitate comparison between the different spectra.

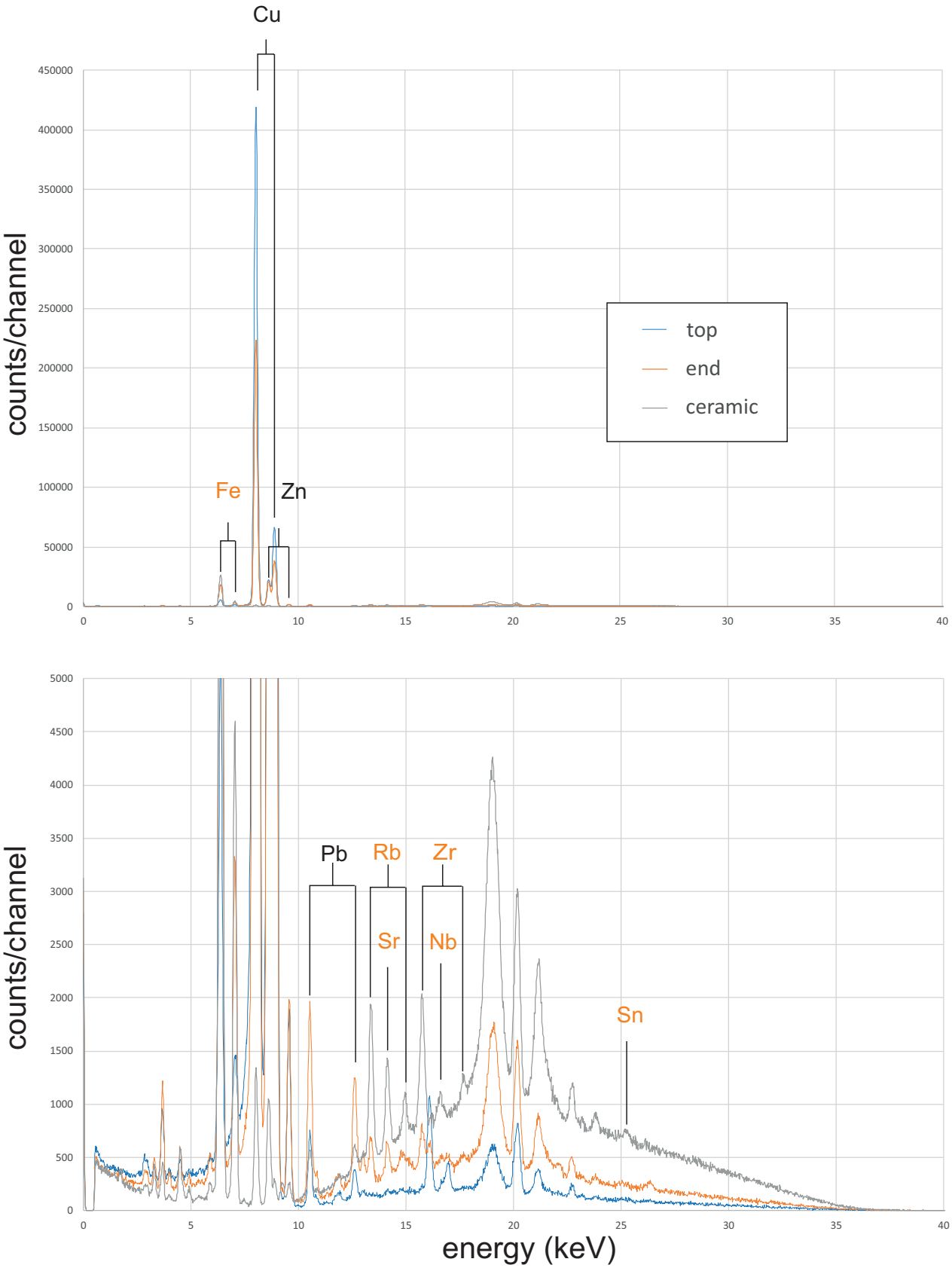
References

BLADES N.W. 1995. Copper alloys from English archaeological sites 400-1600 AD: An analytical study using ICP-AES. Unpublished PhD Thesis, Royal Holloway, University of London

KEARNS, T. MARTINON-TORRES, M. & REHREN, T. 2010. Metal to mould: alloy identification in experimental casting moulds using XRF. *Historical Metallurgy*, **44**, 48-58.

NICHOLAS, M & MANTI, P. 2014. Testing the applicability of hand held portable XRF to the characterisation of archaeological copper alloys. *In* J. Bridgland (ed) *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014*. Paris: International Council of Museums.

Figure 1


Cu
Fe
Zn
Pb
Rb
Zr
Sr
Nb
Sn
top
end
ceramic
counts/channel
counts/channel
energy (keV)

GeoArch

geoarchaeological, archaeometallurgical & geophysical investigations

Unit 6,
Western Industrial Estate,
Caerphilly,
CF83 1BQ

Office: 029 20881431
Mobile: 07802 413704

E-Mail: Tim.Young@GeoArch.co.uk
Web: www.GeoArch.co.uk