

A note on the analysis of crucibles and moulds

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ABSTRACT: Crucibles and moulds are routinely analysed using energy dispersive X-ray fluorescence in order to determine the sorts of metals that may have been melted or cast in them. The interpretation of the results needs to be approached with caution as the proportions of metallic elements are not the same as those in the original melt. Data available from the thermochemical literature is explored as a first step towards understanding how metallic elements become incorporated into crucibles and moulds.

Introduction

Crucibles and moulds are routinely analysed using EDXRF (energy dispersive X-ray fluorescence) in order to determine the sorts of metals that may have been melted or cast in them (Bayley 1989, Bayley *et al* 1991, Tylecote 1980: 204, Wilthew *et al* 1991). This technique is non-destructive and allows many samples to be analysed quickly. However, the proportion of metallic elements which are detected in a crucible or mould may not be identical to those found in the original metal. The interpretation of EDXRF results for crucibles and moulds therefore needs to be approached with caution. This paper illustrates this through the analysis of a crucible and its metallic residue. Data available from the thermochemical literature is explored as a first step towards understanding how metallic elements become incorporated into crucibles and moulds.

The examination of crucible and adhering metal from Mucking, Essex

EDXRF has been used to characterise crucibles and moulds from Mucking, Essex (Dungworth and Bayley 1999). One of these crucibles (catalogue number 14, found in the fill of Anglo-Saxon *grubenhäuser* number 126) was found to have a droplet of metal adhering to its inside. The opportunity was taken to examine the relationship between the proportions of alloying elements in a copper alloy melted in a particular crucible with the proportions of those elements which then become incorporated into the crucible fabric. Figure 1

shows a typical EDXRF spectrum taken from the outer surface of the base of the crucible (40kV accelerating voltage, 75mA current, 2mm collimator and 100 seconds count time). This shows the characteristic peaks for copper, zinc, lead and tin (as well as characteristic peaks for elements in the clay and mineral temper of the crucible itself and the rhodium tube peaks and scattering peaks). This indicates that a copper-based alloy was melted in the crucible (rather than gold, silver or other non-ferrous metal or alloy). Using the spectrum to estimate the proportions of the different metals in the crucible fabric is not a straightforward process. In broad terms the area and height of a peak are proportional to

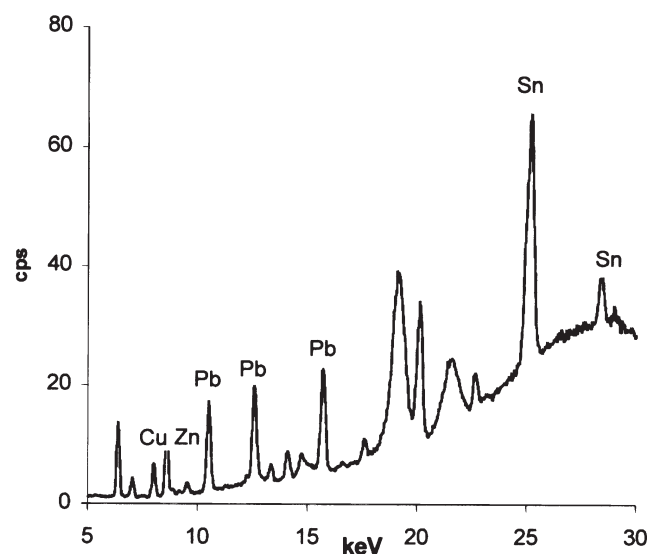


Figure 1: EDXRF spectrum taken from Mucking crucible 14

the amount of that element present. However, peak areas and heights also depend on the density, the fluorescent yield, the type of peak (K, L, M), the form of the elements (*eg* oxide) and the presence of other elements. Nevertheless, EDXRF analysis of the crucible would normally be seen as evidence for the melting of a leaded bronze (which would have also contained a small amount of zinc).

A small droplet of metal was found adhering to the inside of the crucible. A sample of this was removed, mounted and polished to a 1 micron finish. This was examined using optical and electron microscopes and analysed using EDXRF following similar procedures as for the crucible. Metallographic examination of the droplet showed that it was almost entirely metallic with only a small amount of adhering slag. The metal had a dendritic structure, with some lead and copper sulphide inclusions. Figure 2 shows the EDXRF spectrum collected from the polished sample of the metal droplet. This shows an extremely strong peak for copper and weaker peaks for zinc, tin and lead.

Table 1 shows the proportions of the four alloying elements in the crucible and the metal droplet. The crucible was analysed using EDXRF and the results calibrated using a variety of copper alloy standards (although the results are normalised for these four elements, and other elements (silicon, iron etc) and their state of oxidation are ignored. The metal droplet was analysed using a scanning electron microscope with attached energy dispersive spectroscopy. The calculated crucible to metal ratios for each element show that the

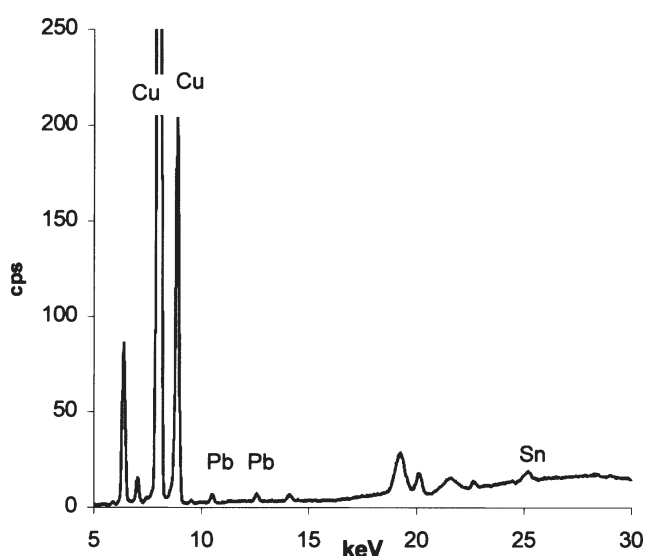


Figure 2: EDXRF spectrum taken from copper alloy droplet in Mucking crucible 14

Table 1: Proportions of copper, zinc, tin and lead in crucible 14 (crucible and metal)

	crucible	metal	crucible/metal
copper	14	95	0.1
zinc	4	0.2	20.0
lead	22	2.8	7.9
tin	60	1.8	33.3

proportions of zinc, tin and lead are greater in the crucible than the metal while the proportion of copper has fallen. This, of course, assumes that the droplet is representative of the original batch. It is possible that this droplet has been fire-refined and so contains lower levels of zinc, tin and lead than the original batch.

The EDXRF analysis of the crucible and its adhering metal has highlighted the problematical nature of this method of analysis. The problems inherent in the technique and material have been discussed before (*eg* Barnes *nd*, Bayley 1989, Bayley *et al* 1991, Wilthew *et al* 1991).

Thermochemical behaviour of copper alloys

When a copper alloy is melted in a crucible some of the metal may be oxidised, react with the crucible and become trapped within the crucible or vitrified layers on the surface of the crucible. Additionally, metallic elements (or oxides of these elements) may be volatilised and diffuse into the mould or crucible fabric. The proportions of different metallic elements in the crucible or vitrified layers are unlikely to be identical to those in the molten metal for a number of reasons. The most important factors that affect the ways in which metallic elements are trapped in a crucible are the melting regime (*ie* temperature and redox conditions) and the chemical and physical properties of the different elements (*ie* free energies of oxidation and the volatility). High temperatures will increase the volatility of metals and so their transfer to the mould or crucible fabric. The more oxidising the conditions within the crucible, the more likely it is that metallic elements will oxidise and react with the crucible fabric and/or vitrified layers.

The free energies of oxidation vary for different elements and Table 2 shows the values for copper, zinc, tin and lead at 1100°C. The greater the value for the free energy of oxidation the more energy is released when the reaction takes place. The greater the amount

Table 2: Free energies for formation of oxides (from Reed 1971)

Reaction	Free Energy (kJ/moleO ₂)
4Cu + O ₂ → 2Cu ₂ O	136
2Cu + O ₂ → 2CuO	65.3
2Pb + O ₂ → 2PbO	183
Sn + O ₂ → SnO ₂	293
2Zn + O ₂ → 2ZnO	380

Table 3: Vapour pressure for different metallic elements at 1000°C (after Brandes 1983: Table 8-13).

metal	Vapour pressure (mm Hg)
zinc	4064*
lead	4.91
copper	3.5 x 10 ⁻⁴
tin	8.7 x 10 ⁻⁴

* the value for zinc has been extrapolated as data is only available up to 727° C

of energy released the more likely it is that the reaction will take place. The values quoted in Table 2 are for pure elements rather than alloys but clearly demonstrate that all three major alloying elements in archaeological copper alloys are more easily oxidized than copper itself. In addition the amphoteric nature of the oxides of lead and zinc leads to them more readily reacting with the ceramic fabric of crucibles and moulds and so being incorporated into them.

The degree to which the different elements in a copper alloy are volatilised during melting can be assessed from the vapour pressure values. Table 3 gives values for vapour pressure for the principal elements in copper alloys. It should be noted that these vapour pressures have been determined for pure elements and values will be somewhat different in complex alloys (data for such alloys is not readily available). Nevertheless it can be seen that zinc, and to a lesser extent lead, are significantly more volatile than copper or tin and will be easily lost during melting.

Barnes noted the high volatility of zinc during casting experiments to examine mould residues (Barnes nd). Barnes cast copper alloys containing varying levels of zinc (1, 2, 3, 4 and 5%) into ceramic moulds which were then analysed using EDXRF; in each case very strong zinc peaks were noted (unfortunately no attempt was

made to quantify the results). It is likely that even minute levels of zinc in alloys can give rise to modest levels of zinc in the corresponding crucibles and moulds.

The values for the free energies of oxidation and the vapour pressures indicate that when a copper alloy is melted the alloying elements are more likely to be incorporated into a crucible or mould fabric than the copper. The behaviour of the alloying elements will vary depending on the proportions of them present in the melt, the activity being carried out (melting in a crucible or casting in a mould) and the temperature and redox conditions. It should now be possible to offer some suggestions as to what will happen under specific circumstances.

When melting a copper alloy in a crucible under oxidising conditions any zinc, tin, lead and copper present will be progressively oxidised and react with the crucible fabric to form crucible slags. When such a crucible is analysed using EDXRF the proportions of the four principal elements in copper alloys will be different to those in the original metal: zinc will be most enriched (compared to copper), then tin and then lead.

When melting a copper alloy in a crucible under suitably reducing conditions little or no metal will be oxidised and no crucible slags will be formed. However, the high volatility of zinc and lead will mean that these two elements may be detected in the crucible fabric (zinc will be more enriched than lead).

When casting a copper alloy into closed moulds the conditions within the mould itself are usually reducing and so little or no oxidation will occur. The high volatility of zinc and lead means that these two elements may be detected in the mould fabric (zinc will be more enriched than lead). The extent to which zinc and lead may be detected in a mould fabric probably relates to the length of time the cast metal remains molten (vapour pressure is dependent on temperature and physical state). A mould for a large object will remain hot longer than a small one and so may contain higher levels of zinc and lead.

The interpretation of EDXRF spectra obtained from moulds and crucibles is further complicated by a range of other problems, including alloy composition, re-use of moulds and crucibles, the presence of naturally occurring metallic elements in clays and temper and post-burial corrosion effects.

Conclusions

EDXRF has enabled the analysis of large quantities of debris associated with the melting and casting of non-ferrous metals. The technique is well suited to determining whether crucibles or moulds were used in the manufacture of precious or base metals. Where only base metals are detected, however, it is much harder to determine the exact nature of the alloy that was melted or cast. Zinc, tin, lead and copper have very different physical and chemical properties and during melting they will be absorbed by the crucible or mould in varying degrees depending on the melting and casting conditions. Where the composition of the metal melted is known, the analysis of a mould or crucible may provide information about the nature of the melting conditions. In most cases, however, the only information available about the composition of the alloy is the analysis of the crucible or mould. Reconstruction of copper alloy type from the analysis of the mould or crucible alone should be avoided. Zinc is routinely detected in crucibles and moulds even where zinc is present in the alloy melted only at minor or trace levels. The absence of an element in a crucible or mould may be due to melting conditions or because it was absent from the alloy melted.

Future work

There is clearly a need for further work to characterise the ways in which copper alloys react with crucibles and moulds. Analytical techniques, in particular scanning electron microscopy, should provide more information on the ways in which different alloying elements partition between ceramic and metal. This methodology needs to be applied to archaeological crucibles and moulds (Whewell *et al* 1996) and to modern crucibles used in replication experiments (melting different alloys under varying conditions,

casting into different sorts of moulds, co-smelting, etc).

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