# DUNADD ARCHIVE

# SECTION 3: ANALYSIS AND SPECIALIST REPORTS

## 3.2 *XRF results on crucibles and other material*

*By Justine Bayley*

Table 1 records the metals detected on the crucibles by the initial energy dispersive x-ray fluorescence analysis (XRF). The results are all for the inner surface of the sherds unless otherwise stated. The elements naturally present in the clay fabric of the crucibles have been omitted from the table. Those crucibles with no entry in the 'XRF Results' column were not analysed. The elements of metallurgical interest are gold (Au), silver (Ag), copper (Cu), Zinc (Zn), tin (Sn) and lead (Pb). In general the elements are written in order of decreasing signal strength, i.e. the element that gave the strongest XRF signal comes first. Where an element is written within brackets it was only just detectable. Where 'Au*' appears in the table, gold droplets were visible under the microscope although not always detectable by XRF because of their small size.

Unfortunately, different elements fluoresce more or less strongly so their order in the table is not necessarily the same as that of the relative abundance of the elements present; in particular tin and silver only fluoresce weakly. Zinc often heads the list not because it was particularly abundant in the metal being melted but because of the way it behaves. It is a very volatile metal so its vapour penetrates into the fabric of the crucible where it gets trapped. It can also become included in the slaggy surface of the crucible where it is chemically bound while the other elements or their alloys are only present as metal droplets physically held by the roughness of the surface and easily dislodged by enthusiastic washing in the finds hut!

It can be seen from Table 1 that a variety of metals were being worked on the site. Most metals at this period were not pure but were mixed, either deliberately or accidentally, with other elements. The re-use of metal would tend to reinforce this mixing though scrap would not have been used indiscriminately; even new metal usually contained some impurities. Certainly gold often contains some silver and copper, and silver usually contains copper and often other elements too. These additional elements can be looked on as either accidental inclusions or deliberate alloying or debasement. Copper is rarely used in its pure form but is normally alloyed with either tin (to give bronze) or zinc (to give brass) or both (giving alloys known as gunmetals). Copper alloys, especially those not intended for wrought work, often contain considerable amounts of lead too.

By considering these comments on the likely additions to be found in any particular alloy together with the comments on XRF signal strengths the XRF results presented in Table 1 can be assessed to identify the metal each crucible once contained. These results for the crucibles of known type are presented in Table 1. In the table the type of sherd is designated as: B-body sherd, Ba - base, L - lid, R - rim, K - knob, All - complete.

**Table 1: XRF results for crucibles**

| Find No. | Sherd Type | T. mm | Extra Layers | Vessel Type | XRF results (inside) |
|---|---|---|---|---|---|
| 105 | B | 4 | | ? | |
| 112/1 | L | 3-5 | | C | Zn |
| /2 | B | 6 | | ? | |
| /3 | B | 5 | | ? | Zn (Cu Pb ?Ag) |
| /8 | B | | | B | |
| /9 | R | | | ?C | |
| /10 | R | | | ? | |
| 163 | K | 3 | | ?C (or ?D) | |
| 187 | B | 2 | | D | |
| 188 | R+K | 2 | | D | Au* |
| 192 | R | 5 | in,out | E | Zn Cu Sn Pb |
| 193 | B | 4.5-6 | | ? | Zn |
| 195 | R | | | ?ingot mould | |
| 196 | R+Ba | 12 | | B2 | # |
| 208 | K | 2 | | C | |
| 211 | Ba | 5 | | ?C | Cu Zn Sn Pb |
| 220 | R | 6-7 | | B5 | # |
| 221/465 | R+Ba | 5-11 | | B4 | # |
| 230 | R | 9 | | ?B2 | Ag Cu Zn |
| 281 | B | 2 | | ? | |
| 303 | All | 5-6 | | E | Cu Sn Pb |
| 308 | B | 5 | ? | | Zn (Cu ?Ag) |
| 316 | B | 4-8 | | ?E | |
| 333 | B | 6 | ? | | |
| 379 | R | 3-4 | ? | | |
| 418 | K | | | C | |
| 425 | B | 2 | out? | ? | Zn Ag Cu Pb |
| 429 | Ba | 3-4 | | C | Zn Pb (Cu Sn)<br>outside = Cu Zn Sn |
| 433 | B | 7 | | ?B | |
| 445 | L | 1-3 | | C | |
| 447 | Ba | | | B4 | # |
| 454 | L | 2-3 | | C | |
| 459 | All | | | D | outside = Cu Zn Sn Ag<br>(Pb Au) Au* |
| 465 | R | 4-9 | | B4 | |
| 466 | R+L | 3-5 | | C | Zn Ag (Cu Pb) |
| 550/1 | Ba+R | 2 | | C | Zn Cu Sn Pb |
| /2-6 | B | 2-5 | | ? | Zn Ag (Au Cu Pb) |
| 600 | R | 3 | | A | Zn Cu Pb Ag<br>outside = Cu Ag Zn Pb |
| 621/1 | Ba+R | 8 | | B3 | Ag Au Zn Pb (Cu)# |
| /2 | ?L | 5 | | C | Nil |
| /3 | B | 2.5 | out? | C | Zn |
| 624 | L | | | C | |
| 630 | K | | | C | |
| 632 | B | 2.5 | | ? | Zn Pb Ag Sn Cu |
| 646/1 | R | 2.5 | out? | C | Pb Zn (Ag Sn Cu) |
| /2 | R | 4 | | ?C | Au* Zn Ag Cu (Pb Au) |
| /3 | B | 2 | | ?D | Au* |
| 666 | B | 7 | | B?4 | |
| 678 | R | 2 | | C | Zn Cu (Pb ?Ag) |
| 681 | K | | | C | |
| 697 | L | 2.5 | | C | Zn (Cu ?Ag) |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | outside = Zn Ag (Cu) |
| 753 | K | | | C/D | |
| 754 | R | 3-4 | | C | Zn Pb (Cu ?Ag ?Sn) |
| 756 | B | 2-3 | | ? | Zn Ag Cu (?Pb) |
| 782 | Ba | 2 | ?D | | Ag Zn Cu Au Au* |
| 799 | R | 4 | | C | Au* |
| 816 | R | 4 | | E | Cu Sn Zn Pb |
| 839/1 | R | 2-3 | out | C | |
| /2 | R | 3 | | C | |
| 842 | R | 3-4 | | C | |
| 846/851 | L | 4-5 | | C | Zn Pb |
| 854 | B | 5 | | ?C/D | Cu Sn Zn Pb |
| 884 | R | 3-4 | | E | Cu Sn Pb (Zn) |
| 885 | K | | | D | |
| 888 | R | 4.5 | | A/D | Cu Zn Sn Pb |
| 895 | Ba | 9 | | B | # |
| 911/1 | R | 2-3 | | C | Zn Ag Pb (Cu) |
| /2 | B | 3-4 | | C | Zn Ag Pb (Cu) |
| /3 | L | | | C | |
| /4 | | | | C | |
| /5 | L | | | C | |
| 932/1 | R | 3-4 | | C | |
| /2 | B | 2 | | ?D | |
| 944/1 | B | 2.5 | | ? | Cu Zn (Sn) |
| /2 | B | 4 | | ? | Zn Ag Zn Cu (Pb) |
| 952/1 | L | 2 | | C | Zn Pb (Cu) |
| /2 | R | 7 | | ? | |
| 963 | K | 4 | | C | |
| 989 | B | 4 | in | C | |
| 1004/2 | B | 3.5 | | ? | Cu Pb Sn Zn Ag |
| /1 | B | 4.5 | | C | Zn (?Ag) |
| /3 | L | 4 | | C | outside = (?Cu Zn) |
| /4 | L | | | C | |
| 1016 | R+Ba | | | B1 | # |
| 1030/1 | R | 2.5 | | C | Pb Sn Zn Cu |
| /2 | B | 3 | | ? | Ag Zn Cu Pb |
| /3 | B | 2.5 | | ? | Zn Pb (Cu) |
| /4 | B | 3 | | ? | Zn Cu Ag (Sn Pb) |
| 1031 | K | | | C | |
| 1034 | K | | | C | |
| 1135 | R | | | ?C | |
| 1164/1 | L | | | C | outside = Zn Cu ?Ag |
| /2 | B | | | ? | Zn Ag (Cu Pb) |
| /3 | B | | | ? | Zn Ag (Cu Pb) |
| /4 | B | | | ? | Pb Cu Sn (Zn) |
| /5 | B | | | ? | Zn Ag (Cu Sn) |
| /6 | B | | | ? | Pb Cu Sn (Zn) |
| /7 | R | | | C | |
| 1200 | ? | 4 | | ? | |
| 1221/1 | R | | | ?A/D | |
| /2-3 | B | | | ? | |
| 1232 | R | | | A/D | Zn Pb Cu Sn |
| 1261 | All | 3.5 | | E | Cu Sn Pb |
| 1282 | L | 3 | | C | Zn Ag (Cu) |
| 1334 | R | | | D/C | Zn |
| 1346 | B | 3 | | ? | Ag Zn Cu (Pb) |
| 1352/1 | R | 5 | | B5 | Cu Zn (Pb) |
| /2 | R | 3.5 | | ? | Zn Ag Cu Pb |
| /3 | R | 2.5 | | ? | Zn (Pb) |
| 1378/1 | R | 5 | | E | Cu Sn Pb (Zn) |

| | | | | | |
|---|---|---|---|---|---|
| /2 | R | 3 | | ? | Cu Zn Pb Sn |
| 1404 | K | | | C | |
| 1431 | L+K | | | C | |
| 1434 | K | 5 | in | D | Zn Ag (Cu) |
| 1435 | R | | | B4 | # |
| 1506/1 | R | 5 | | C | Zn Pb Cu (?Ag) |
| /2 | R | 4-5.5 | | A/D | Zn |
| /3 | R | 3 | | C | Zn (Cu) |
| /4 | B | 4 | | ? | Zn Ag (Cu) |
| /5 | R | 6 | | ? | |
| /6 | B | 3-4 | | ? | |
| 1514 | Ba+R | | | B1 | Pb Zn Cu Ag# |
| 1517 | R | | | B1 | |
| 1518 | Ba | 5 | | A/D | Zn Cu Pb Sn Ag |
| 1538/1 | K | | | C | |
| /2 | R | | | C | Zn |
| /3 | B | | | ? | Zn Ag Pb |
| /4 | B/Ba | | | ? | Zn Ag |
| /5 | R | 4 | | C | Zn Sn |
| /6 | R | 2 | | C | Zn Cu Ag Sn Pb |
| 1551 | R+Ba | | | ?B1 | |
| 1567 | B | 3 | | ? | Zn Cu Sn Pb |
| 1576/1 | R | | | ? | |
| /2 | B | | | ? | Au* |
| /3 | L | | | C | Zn Ag (Cu Pb) |
| /4 | R | | | ? | |
| /5 | B | | | B | |
| 1579 | R | | | B5 | # |
| 1602/1 | 2-6 | | | ? | |
| /2 | B | 4 | | ? | Zn Ag |
| /3-6 | B | 6 | | ? | Zn Ag |
| 1625 | R | 4 | ?4 | | Cu Pb Sn (Zn) |
| 1630 | R | 6 | in, out | ? | (Sn Zn Pb Cu) |
| 1632 | R+Ba | | | B1 | Au (Zn Cu)# |
| 1650/1 | B | | | ?C | Zn Ag (Pb Cu) |
| /2 | R | | in, out | ? | Zn Ag (Cu Pb) |
| 1656 | R | | | ?B | |
| 1665/1 | R | 3 | | E | Cu Sn Pb Zn |
| /2 | R | 2 | | C | Zn Cu (Pb) |
| /3 | K | | | C | |
| /4 | R | 2-3 | | ? | Zn |
| /5 | B | 4-5 | | ? | Zn (Ag Cu) |
| 1666 | B | 4 | | ? | Zn Cu |
| 1667 | B/Ba | 8 | | B3 | Au Ag Zn (Cu Pb)# |
| 1701 | Ba | | | B | |
| 1730/1 | B/Ba | 3 | | ? | Pb Sn Cu Zn |
| /2 | L | 3.5 | | C | Zn Pb Cu |
| 1731 | B | | | ? | |
| 1748 | B | 4 | | ? | Zn |
| 1815/1 | R | | | B2 | # |
| /2 | Ba | 6 | | ?E | Zn Cu (Pb) |
| /3 | R | 3-4 | | ?C | Pb Zn Cu Ag |
| /4 | R | 4 | | C | Zn ?Ag (Cu) |
| /5 | B | | | ? | |
| 1830/1 | K | | | C | |
| /2 | K+L | | | C | |
| /3 | K | | | D | 0utside = (Zn Cn) |
| /4 | ? | | | ? | (Zn) |
| 1831 | B | 3.5 | out | ? | Pb Cu Zn Ag Sn |
| 1847/1 | R | 4 | | ? | Zn |

| | | | | | |
|---|---|---|---|---|---|
| /2 | B | 3 | | ? | Zn Ag (Cu) |
| /3 | B | 3 | | ? | Ag Zn Cu (Pb) |
| /4 | B | 6 | | ? | Zn |
| /5 | B | 5 | | ? | Cu Zn Sn Ag (Au Pb) |
| /6 | Ba | | | B | |
| /7 | R | | | C | |
| /8 | B | | | C | |
| /9 | B | | | ? | |
| /10 | B | | | ? | |
| 1857 | B | 6 | out | ? | Pb Zn Ag (Cu) |
| 1926 | R | 4 | | A/D | Cu Zn Ag Pb (?Sn) |
| 1989 | L | | | C | |
| 2024 | R | 4 | | A/D | Zn |
| 2073 | B | 3 | | ? | Ag Zn Cu Pb |
| 2303 | K | | | C | |

# see additional comments below

**Table 2: XRF Metal analyses**

| Find No. | Object | Alloy |
|---|---|---|
| 44 | Ring-headed pin: ring | Brass |
| | : pin* | Gunmetal (with some lead) |
| 45 | Pin (? for penannular)* | Bronze (with some lead) also containing a minor amount of silver. |
| 148 | Dribble* | Bronze/gunmetal |
| 214 | Repousse foil | Bronze (with a little lead) |
| 215 | Needle | Bronze |
| 310 | Lump* | Low tin bronze |
| 330 | Scrap* | Copper |

(see also text chapter 5 for Atomic Absorption Analyses of objects marked with asterix)

**Table 3: Miscellaneous analyses by XRF**

| No. | XRF results | Interpretation/description |
|---|---|---|
| 728 | Calcium detected | White material. Needs further (XRF) analysis for identification. |
| 874 | Major elements: Fe,Mn,Ca | Part of a glass cane. The (Si, Na, K not detectable) colour is due to the presence of manganese. |
| 981 | 0nly iron detected | Red flecks probably haematite. |
| 1305 | Major:Pb, Cu Minor: Fe, Zn, Sb Trace: Mn (Si, Na, K not detectable) | Red glass inset. The colour is mainly due to the presence of copper. |
| 1362 | Only iron detected | Yellow and liverish red lump - colour probably due to iron oxides. |
| 1368 | Iron and titanium detected | Pink material. Needs further (XRD) analyses for identification |
| 1844 | Only arsenic detected | Orpiment - a naturally occuring mineral. |

## *Additional note on Type B crucibles from Dunadd*
## *By Justine Bayley*

These notes should be read in conjunction with the earlier report (above) on the metalworking finds from Dunadd (Bayley 1984). A review of the notes made in 1984 suggested that the unidentified process carried out in the type B crucibles was probably parting, the separation of silver from gold by heating thin sheets of the mixed alloy below its melting point while packed into a vessel interleaved with a salt-containing mixture (Bayley 1991). The Dunadd crucibles were thus re-examined in an attempt to confirm this identification.

All the type B crucibles that were seen in 1984 (with the exception of 1667) were made available for re-examination, together with a number of sherds that had not previously been identified as crucibles. All were analysed by XRF (see Table 4); the results are comparable with those previously obtained. With a larger number of pieces available, it could be seen that not all came from the shallow (c 20-25mm high), flat-bottomed vessels previously described (type B1 here). The majority of the new pieces were from deeper vessels (up to 60mm high) with an external diameter of c 100mm (type B2 here). (Editor's Note: these B1 and B2 categories differ from those used in the finds report and the list above; the categories used in the main report are noted in the table below in brackets).

**Table 4: the analysed sherds**

| Bag No | Form | Elements Detected | Previous XRF |
|---|---|---|---|
| 621 | B1(B4) | Ag Au (Pb) | Ag Au Zn Pb (Cu) |
| 1016* | B1 | Sn (Ag) | |
| 1514 + | B1 | Pb (Ag) | Pb Zn Cu Ag |
| 1632 + | B1 | Au (Ag) | Au (Zn Cu) |
| 1667 + | B(B4) | not seen/analysed | Au Ag Zn (Cu Pb) |
| 196 | B2?(B2) | - | |
| 220 | B2?(B5) | - | Poorly fired added inner and outer lay layers. ? unused |
| 221 | B2(B4) | Ag | Rim previously seen but not analysed |
| 447 | B2(B4) | Ag | |
| 895 | B2?(not B) | - | |
| 1435 | B2?(B4) | Ag | |
| 1579 | B2?(B5) | Ag Au (Pb) | |
| 1815/1 | B2?(B?0 | Ag (Pb) | |

* = extracted from this bag no
+ = previously analysed

{NB 621 joins 1667; 221, 447, 465 & 1435 are from one vessel. B4 is a high-walled variant of B1(editor)}

All samples had detectable, but very low levels of zinc and copper present; these are not included in the Table. Elements written in brackets are present in minor amounts.

All the pieces listed in the table are oxidised-fired, generally appearing buff in colour, and most have traces or iron-rich straining on either inner or outer surfaces. This discoloration runs from red (eg 1632) to maroon (eg 447) and purplish-grey (eg 895). Some pieces show more than one of these colours which are produced by iron from within the clay fabric being mobilised and then re-deposited on the surface as a by-product of the parting process (Bayley 1991).

It can be seen that the deeper, B2 vessels have silver as the main, or only element detectable, like the majority of other parting vessels previously identified. The range of elements present in the shallow B1 vessels is wider and may represent a variety of precious metalworking processes or just variants of the parting process. On the basis of the analytical results, 1667 is probably a B1 type. There was no good evidence for the presence of a lid on any of these vessels, which is surprising as one would have been necessary to present the loss of most of the silver; with a lid the silver would be trapped in the mixture packing the vessels and could be retrieved by smelting it.  In this, the Dunadd parting vessels find parallels with the apparently lidless, early Roman parting vessels from Chichester (Bayley 1978; 1991), which are also their closest parallels for form.

Four pieces seen are not thought to be from parting vessels (666: red-slipped pottery, 1517: ? clay mould fragment, 1656: rim sherd, possibly from type B2 vessel but thinner walled than the rest, 1701: clay luting from mould or crucible).  None of them had significant traces of metals, except for 1701 where a minor amount of lead was detected.

References

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