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Summary

Technical examination of nine enamelled copper-alloy artefacts (brooches, buttons and studs) showed that they were made in a variety of ways. The artefacts were made of copper and brass, using high-lead enamels. The enamelling was carried out using *cloisonne* and *champleve* techniques. The artefacts are Roman through to high medieval in date and include examples which are thought to be Irish, ?Swedish and French (Carolingian) in origin. The techniques of examination are also discussed.

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# Technical examination of nine enamelled copper-alloy artefacts, found in the City of London

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The artefacts, mostly brooches, were found in a variety of contexts, including two from excavations (Billingsgate Watching Brief (BWB83) and Thames Exchange (TEX88)) but mostly from metaldetector work on spoil originating from the Vintry site (north bank of Thames, to the west of Southwark Bridge; site code VRY89). The objects are of Roman, early medieval and high medieval types and are thought to have several different origins. Examination and analysis was required to establish the alloy type, enamel type and the nature of subsequent surface treatments, but no destructive analysis was permitted.

## Research techniques

The pieces examined have enamels of various colours, and the technique of enamelling (*ie* whether *champlevé* or *cloisonné*) was established using a low-powered microscope. The colour of the enamels were recorded as accurately as possible, although corrosion on many of the pieces meant that the original colour could be only tentatively suggested.

In most cases, analysis of both the base metal and the enamel was carried out using energy-dispersive X-ray analysis in a Cambridge Stereoscan SEM (SEM-EDX). Non-conductive materials must be coated (*ie* with carbon or gold) prior to examination in the SEM to prevent charging on the object and to avoid damage to both the object and the equipment. However, as the artefacts in this project are primarily metal, they could be analysed in the SEM without coating. Organic molecules from the burial environment were also a potential danger to the equipment, since if they are not firmly attached to the surface, they could become charged by the electron beam, ejected from the surface and deposited on prominent areas within the chamber, especially if these areas are cold (*eg* the X-ray detector). This effect was minimised ensuring a good vacuum was in effect before starting analysis; the chamber was pumped down over a long period (more than 2 hours).

Electrical contact between the object and the sample table was effected using a combination of several types of conductive material. Carbon tabs, tape or putty, aluminium tape and small amounts of silver dag, were used, depending on the shape of the object and the need for support. At least two points of contact were maintained between the object and the sample table (*eg* the pin lug and one edge of the brooch, or the pin lug and the catch). Heavily corroded areas were avoided as places of attachment/electrical contact, since the adhesive from the tabs *etc.* could cause surface loss on removal; heavily corroded areas also conduct less well as they are less metallic.

The capacity of the SEM for detailed visual display and accurate positioning of the sample beam meant that very small areas of the surface to be analysed (less than 1mm square).

Care was taken to ensure that the beam did not dwell for long on any one small area of enamel because this could cause heat damage to the surface and, possibly, release material from the surface of the object into the chamber. Areas of corroded metal or enamel on which the electron beam was incident for some time often became charged to some extent. This could be seen when stepping down the magnification - the area of higher magnification left a bright (*ie* highly-charged) rectangular mark on the artefact. This mark soon disappeared whilst the surface was examined at lower magnifications and left no lasting effect.

A range of working energies were used for the SEM-EDX work. The accelerating voltage was 10 kV, where the surface was only being visually examined (*eg* to establish 'sampling' positions), and up to 20 kV, when the Lβ peaks of lead were being analysed. Some elements which were tentatively identified by their low energy X-rays could be confirmed by high energy X-rays. This versatility is especially useful in cases where important low energy X-ray peaks overlap, *eg* Pb Mα and S Kα. However, there are problems in comparing sets of analyses if analysis was carried out at different energies, since excitation efficiency varies with energy. For this reason, analysis at 20kV was carried out and recorded on disc for each sample area.

Further analysis of the base metal was carried out using surface X-ray fluorescence (XRF). A moderately large beam area (*c.* 3mm x 5mm) was used to ensure that the analysis was reasonably representative despite the variable corrosion. An excitation energy of 35kV was selected as being a good compromise value (covering low and high energy X-ray peaks) for this sort of work.

X-ray diffraction (XRD) allows the identification of crystalline materials. The technique requires samples to be taken although these can be very small (<1g). In one case (sample 3; BWB83, SF203), an area of corrosion product was already detached from the brooch and proved to be suitable for XRD analysis (details below).

## Results of examination and analysis

Details of the results of examination and analysis are given for each artefact, in Appendix 1.

### Metal technology

Six of the pieces used *champlevé* enamel (Samples 1, 2, 3, 5, 6 and 8), two *cloisonné* (Samples 7 and 9) and one of the 'saint' brooches (or *Heiligenfibeln*) has a combination of both techniques (Sample 4). The *champlevé* pieces are thought to be Roman, Irish and Carolingian. The *cloisonné* pieces are Carolingian and Scandinavian (possibly Swedish) in origin. Buckton (1991, 145) believes that saint brooches with *champlevé* and *cloisonné* together (*eg* sample 4) are likely to be contemporary with saint brooches with *champlevé* only (*eg* sample 3). The use of *champlevé* and *cloisonné* together may have been a way of mass-producing the form. Both of these forms are likely to have been in use up to *c.*900AD.

*Champlevé* and *cloisonné* enamelling have long histories in northern Europe, but both techniques had periods in which they were little used, as well as periods in which they were dominant (Campbell 1983; Maryon 1971). The choice of which technique to use is influenced somewhat by the metals used. Precious metals present fewer problems in enamelling than some copper alloys. Copper alloys should be either pure copper or copper alloys which are low in zinc and lead. *Champlevé* enamelling techniques were used in the late Iron Age and the Roman periods, but

they were less frequently used for high prestige artefacts in the immediate post-Roman period. *Cloisonné* was not used in northern Europe in the Roman period, although the technique was known much earlier. It was subsequently used on Byzantine, Lombardic and Anglo-Saxon objects during the medieval period. Although Campbell (1983, 13) says that *cloisonné* was rarely used on base (*ie* copper-alloy) metal in the 10th century, several of the pieces in this study fall into this category and may have been made at this time. Combinations of *champlevé* and *cloisonné* techniques are evident from the twelfth century Mosan (Meuse/Rhine valley area) ecclesiastical artefacts.

No gold was detected on the surfaces of any of these pieces; the gold-coloured, crusty or bubbly areas seen on samples 3 and 4 are corrosion products. X-ray diffraction analysis on gold-coloured corrosion products from sample 3 (BWB83, SF203) showed that the main constituent of these was chalcopyrite ($CuFeS_2$), with a smaller amount of galena (PbS). These compounds suggest that these pieces were in a reducing atmosphere during burial. There was a trace of quartz ($SiO_2$) and possibly a trace of free iron, although this could not be positively identified because only one diffraction line was present.

## Metal composition

Chemical analysis by XRF and SEM-EDX allowed reasonably unambiguous identification of the base metals. In most of the cases, the base metal was copper, but three of the *champlevé* pieces had brass as their base metal.

A previous XRF analysis of the Billingsgate brooch (sample 3) showed both copper and zinc to be present at significant levels (Bayley 1985), suggesting that the base metal of this brooch was brass not copper. Depending on the deposition environment, metal surfaces may be depleted in some elements whilst some other elements may be redeposited. This can lead to the surface of an artefact being extremely heterogeneous. Analysis by both XRF and SEM-EDX would be significantly affected by the effects of corrosion as these methods analyse only the surface of the object (to a depth substantially less than 1mm). SEM-EDX analysis can be carried out on very small areas, so newly-exposed metal (*eg* inside scratches) could be analysed. When a scratched area on back of sample 3 was analysed by SEM-EDX, it was shown to be copper, with a trace of lead (*ie* substantially the same as the analysis of the 'unprepared' surface).

Copper or copper-rich alloys were shown to have been used for the cell walls, on those *cloisonné* pieces where analysis was possible.

The small amount of available comparative material for this dataset shows some interesting patterning in the compositions of the base metals. The types of base metal alloy used for *champlevé* enamelled pieces were not noticeably limited during the Roman period. Copper was normally used in later periods, but this was because artefacts were often gilded; gilding should be carried out on copper with only low levels of impurities. For example, a broad range of copper alloys were used for Roman enamelled brooches (Bayley and Butcher 1981; Bateson and Hedges 1975) but a selection of twelfth- and thirteenth-century English and continental copper-alloy plaques with *champlevé* enamelling were all nearly pure copper (Oddy *et al* 1986, Table 3). It is therefore interesting that the early medieval *champlevé* artefacts examined here include examples made from brass (samples 1 and 2).

Compositional patterns for published *cloisonné* artefacts are less clearcut; a circular Carolingian brooch with gilding and *cloisonné* enamelling has a copper-alloy metal base with zinc, tin and lead present at percent levels (Oddy *et al* 1986, Appendix 1, no 89), but another *cloisonné* brooch of a similar date and probably similar decorative techniques was made with a base plate which has low levels of zinc and lead and only *c.*5% tin (*op cit*, no 90).

## Metal coatings

Examination and analysis were carried out to see if any of these examples have metal coatings, such as gilding, silvering or tinning.

It is often difficult to confirm tinning by non-destructive analysis. If tin is already present in the alloy, it will normally be present on the surface and may even be present at higher levels on the surface than inside (Tylecote 1985). In the case of sample 1, the high tin levels found on the *champlevé* cell wall may be due to tinning or to contamination from tin oxides used to opacify the enamels. It could also be from a lead-tin solder, but the *champlevé* technique would not normally have needed soldering. Tin levels in the base metal are relatively low elsewhere on the artefact (according to XRF on the back).

Silver was detected on the cell walls of sample 2 but, as a small amount of silver was also found in the area of the inlay, the significance of this finding is not clear.

## Enamel composition

Chemical analysis provided only a basic identification for glasses used for the enamels on these pieces, because only the major elements could be identified and glasses are very vulnerable to corrosion in burial. Since lead and silica were often identified in the enamelled areas, it seems likely that the enamels were silica-lead-alkali glasses. A high lead content gives a lower melting temperature, to avoid endangering the copper-alloy metals during the heating process of enamelling and to give a better 'fit' to the metal base. Silica is present in all ancient glasses.

Almost all enamels have some sort of opacifying agent and a range of colourants were used during the early and full medieval periods. Neither the opacifiers nor the colourants in these enamels could be identified by the methods of analysis employed here. Copper was often used in colouring enamels at this time (reds, greens and blues), but since the base metals for these artefacts are copper alloy, contamination from the base is highly likely to be present.

In sample 3, blue enamels are found to be higher in copper than the red ones (in the blue enamel, copper is a major element, but in the red it is only a minor element). The blue is probably partly corrosion product (possibly the iron compound vivianite), not enamel, as a white crumbly material is found underneath it.

In sample 4, blue and yellow enamels have lower lead concentrations than the green enamels. Again, it seems that several areas of enamelling are deeply corroded, producing a white or clear corrosion product in some areas. Preservation states on the enamels of samples 3 and 4 are similar, as were the types of copper corrosion seen on these samples (above).

# Discussion

## Problems encountered in examination and analysis

The analytical methods used in this project produced useful data in most cases, although the lack of surface preparation caused problems in interpreting the results of analysis. In some cases, burial had stripped off corrosion - the extant surfaces seem to be very metallic. However, surface analyses of these objects should not be considered to have a particularly strong correlation to the internal composition of the artefacts, since an environment which results in an apparently-clean surface is also likely to remove the more chemically active elements. The problems of analysing those objects which, conversely, still have significant deposits of corrosion products

are evident. Information about some of the corrosion products is potentially of interest in understanding the corrosion dynamics of copper-alloys in wet environments, although this subject is not considered in any depth here.

The burial environment also had a strong effect on the surfaces of the enamels used on these pieces. This meant that the analytical techniques used often could not provide unambigious results. Detecting colourants and opacifiers was difficult in such heavily corroded artefacts; many of the elements of interest were present on the surface of the enamel as contamination from the corroding copper-alloy base. A further problem was frequently apparent, in that enamels have often developed metal-rich 'crusts' during burial; some of these have flaked off in some areas, revealing a crumbly interior. Examination using SEM allows analysis of the crusts and of the underlying areas of highly-deteriorated enamels, both of which have potential information about the original enamelling material.

The best solution to these problems would be to take samples from the objects, mount them in resin and polish until a solid, glass-like surface is achieved. However, this was not permitted in this case. By amassing data on the elements detected at the most solid enamelled areas (and on the copper-alloy base), some useful information can still be deduced.

## Conclusions

This research showed that a careful visual examination combined with non-destructive chemical analysis can provide some useful archaeological information.

The technique of whole object analysis in the SEM has proved to be a useful way of discovering the composition of nine copper-alloy brooches. Alternative methods ofanalysis would be necessary if the composition of the enamels were to be determined.

Copper and brass were the commonest types of metal used for making the base 'plates' of these brooches and copper was normally used for *cloisons*. The enamels are lead-rich silicates, but it was not possible to determine which other significant oxides were present.

## Acknowledgements

Geoff Egan (Museum of London) supplied the artefacts and information on their dating and provenance. Malcolm Ward (English Heritage) carried out the XRD analysis.

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Appendix 1

| **Sample 1: Reference = VRY 89, V823, Box 15; Finder = P Stewart** | |
|---|---|
| **Description:** Button/brooch/stud. From the front, the object has a plain copper-alloy rim (*ie* an area of the base metal which has not been enamelled). Inside the rim, there is an inlaid ring, and inside this a quartered design with *champlevé* enamel. The enamel is now yellowy-green. The area to be enamelled was hatched, to give a 'key'. Diameter = 32mm. Probable Irish origin. | |
| **Analysis areas:** *a) SEM/EDX*:<br>1. Cell wall<br>2. Enamel<br>3. Metal from an exposed area of hatching<br>*b) XRF*<br>4. Base metal, on reverse | **Analysis results:** *a) SEM/EDX*:<br>1. Major peak: Sn. Minor peaks: Cu, Pb.<br>2. Major peaks: Pb, Si. Minor peaks: Sn, Cu, Fe.<br>3. Major peaks: Pb, Cu, Sn. Minor peaks: Si.<br>*b) XRF*:<br>4. Major peaks: Cu, Zn. Minor peaks: Sn, Pb, (Fe) (Ni) |
| **Comments:** Brass mount with significant tin content but low level of lead. Lead-rich enamels. | |

| **Sample 2: Reference = VRY 89, V735; Finders = I Smith/T Pilson** | |
|---|---|
| **Description:** Button/stud. Dark blue/grey *champlevé* inlay in spiralling design. Walls for inlay cast with the base. Diameter = 27mm. ?Carolingian | |
| **Analysis areas:** *a) SEM/EDX*<br>1. Copper-alloy base metal<br>2. Copper-alloy walls for enamel<br>3. Enamel<br>*b) XRF*<br>4. Base metal at reverse | **Analysis results:***a) SEM/EDX*<br>1. Major peaks: Cu, Zn, Sn, Pb.<br>2. Major peaks: Cu, Ag, Zn, Pb. Small Sn peak may be obscured by silver.<br>3. Major peaks: Pb, Cu, Fe, Ag.<br>*b) XRF*<br>4. Major peaks: Cu, Zn (Sn). Minor peaks: Fe, Pb. |
| **Comments:** Brass mount with significant amounts of tin, lower levels of lead. Leaded enamel. Possibly some silvering. | |

**Sample 3: Reference = BWB83 (Billingsgate Watching Brief), Context 290, SF203**

**Description:** Disc brooch with ?saint design. Copper-alloy base metal (coppery-coloured), exposed and stepped at edge. *Champlevé*. Enamel now appears either a) glossy red or b) white overlain by black/dark blue crust. Some areas of the copper-alloy surface are gold-coloured and shiny resembling gilding with a bubbly texture. Diameter = 27mm. Carolingian?

| **Analysis areas:** *a) SEM/EDX* | **Analysis results:** *a) SEM/EDX* |
|---|---|
| 1. Base metal, at edge | 1. Major peak: Cu. Minor peaks: Zn Pb Sn. |
| 2. Enamel (blue) | 2. Major peaks: Cu Pb Si Fe. Minor peaks: Ca Zn |
| 3. Enamel (red) | 3. Major peaks: Si Pb (Fe) (Cu). Minor peaks: Ca K Al |
| | 4. Major peaks: Fe Cu. Minor peak: S? |
| 4. ?Gilding | 5. Major peak: Cu. Minor peak: Pb. |
| 5. Base metal, reverse, within scratched area | *b) XRF* |
| *b) XRF* | 6. Major peaks: Cu (Zn) (Pb). Minor peaks: Fe ?Sn |
| 6. Base metal at reverse | 7. Major peaks: Cu Fe. *I.e.* no gold detected. |
| 7. Area of ?gilding | *c) XRD* |
| *c) XRD* | 8. Compounds: Mostly chalcopyrite ($CuFeS_2$). Some |
| 8. Area of ?gilding | galena (PbS). Possibly quartz ($SiO_2$) and free iron. |

**Comments:** Copper base, with traces of zinc and lead. Analysis was also attempted on a central white area, which may originally have been enamelled; this shows only Si.

**Sample 4: Reference = VRY 89, V10; Finder = L Hunt**

**Description:** Disc brooch - ?saint design. Copper-alloy base metal (coppery-coloured), *champlevé* but with additional *cloisonné* details added by the use of copper-alloy 'wire' walls within enamelling area. White face and 'bib'; ?opaque yellow 'hair'; blue or green arms and body, although some of these areas are white or clear. Small amounts of golden bubbly corrosion (as sample 3). Diameter = 24mm. Carolingian?

| **Analysis areas:** *a) SEM/EDX* | **Analysis results:** *a) SEM/EDX* |
|---|---|
| 1. Base metal | 1. Major peaks: Cu, Sn. Minor peaks: Si, Pb |
| 2. Cell walls | 2. Major peaks: Cu (Sn). Minor peaks: Pb (Ca) |
| 3. Enamel (green) | 3. Major peaks: Si Pb Ca. Minor peaks: Fe Cu K Al |
| 4. Enamel (blue) | 4. Major peaks: Si Ca Fe Cu. Minor peaks: K Pb P Al |
| 5. Enamel (green with blobs of copper colour on it) | 5. Major peaks: Si Cu Ca Fe Pb. Minor peaks: K (Al) (P) |
| 6. Enamel (yellow) | 6. Major peaks: Si Ca Fe Cu. Minor peaks: K Pb Al (Cl) ?Na |
| *b) XRF* | *b) XRF* |
| 7. Base metal | 7. Major peak: Cu. Minor peaks: Sn Pb Fe. |

**Comments:** Copper base and cell walls. Silica-lead-alkali enamels.

| **Sample 5: Reference = V186; Finder = D Elliot** | |
|---|---|
| **Description:** Crescent brooch, with rounded enamelled areas. Copper alloy base metal, heavily corroded with some blistering, some bubbly corrosion. *Champlevé*. Enamelling now greenish, crusty on surface, probably redeposited metals. Roman? | |
| **Analysis areas:***a) SEM/EDX*<br>1. Base metal<br>2. Enamel<br>b) XRF<br>3. Base metal | **Analysis results:** *a) SEM/EDX*<br>1. Major peak: Cu. Minor peak: Pb<br>2. Major peak: Si. Minor peaks: Si, Ca, Fe, Cu, ?S<br>*b) XRF*<br>1. Major peaks: Cu (Pb). Minor peaks: Zn Fe |
| **Comments:** Copper, with traces of lead. Enamel probably leaded. | |

| **Sample 6: Reference = VRY 89, V+ 63 IS/PL** | |
|---|---|
| **Description:** Circular brooch, Carolingian? with cross design? Copper-alloy base metal. *Champlevé*. Enamel now greenish on the surface, possibly with redeposited copper. Maximum diameter = 22mm. | |
| **Analysis areas:***a) SEM/EDX*<br>1. Base metal<br>2. Enamel<br>*b) XRF*<br>3. Base metal (reverse) | **Analysis results:** *a) SEM/EDX*<br>1. Major peaks<br>2. Major peaks: Si Pb. Minor peaks: K Ca Fe Cu<br>*b) XRF*<br>3. Major peaks: Cu (Pb). Minor peaks: Zn Fe |
| **Comments:** Copper with lead in minor quantities. Enamel probably leaded. | |

| **Sample 7: Reference = VRY 89, V+ 210; Finder = D Wood** | |
|---|---|
| **Description:** Circular brooch with cross-shaped enamelled design. Copper-alloy base metal. Deep *cloisonné* cells - mostly empty, remains of some enamel, now white, yellow and green, although it is not clear what colour they were originally. Carolingian? | |
| **Analysis areas:***a) SEM/EDX*<br>1. Base metal<br>2. Walls for enamelling<br>3. Enamel<br><br>*b) XRF*<br>4. Base metal | **Analysis results:** *a) SEM/EDX*<br>1. **Major peaks**: Ca Cu Si. **Minor peaks**: Zn Pb S.<br>2. **Major peak:** Cu. **Minor peaks:** Zn Si Ca Pb ?S.<br>3. **Major peak:** Si. **Minor peaks**: Fe Cu Al K Ca Na.<br>*b) XRF*<br>4. **Major peaks:** Cu Zn Pb. **Minor peaks:** Fe. |
| **Comments:** Copper base, with traces of zinc and lead. *Cloisonné* walls also copper. Lead not detected in enamelled area. | |

| **Sample 8: Reference = VRY 89, V835; Finder = R Green** | |
|---|---|
| **Description:** Flower-shaped brooch. Copper alloy base metal. Enamelling all missing from *champlevé* cells. Carolingian? | |
| **Analysis areas:***a) XRF*<br>1. Reverse | **Analysis results:** *a) XRF*<br>1. Major peaks: Cu (Zn) (Pb). Minor peaks: Fe, ?Ni, ?Sb |

**Comments:** Lightly-leaded brass. No evidence for enamel type.

| **Sample 9: Reference = TEX88, No context, SF7364** | |
|---|---|
| **Description:** Fragment of circular brooch. Copper-alloy base. *Cloisonné*. Chips or crystal-like ?enamel, now green and white/clear, not clear what colour it was originally. Scandinavian (Swedish) in origin? | |
| **Analysis areas:***a) SEM/EDX*<br>1. Cell walls<br><br>2. Enamel (green)<br><br>3. Base metal<br><br>*b) XRF*<br>4. Base metal (reverse) | **Analysis results:***a) SEM/EDX*<br>1. Major element: Cu. Minor elements: Pb (Fe) (Ca)<br>2. Major element: Si. Minor elements: Ca Cu (K) (Pb) Fe ?Na Al<br>3. Major element: Cu. Minor elements: Pb (Fe) Ca ?Sn<br>*b) XRF*<br>4. Major element: Cu. Minor elements: Pb Sn. |
| **Comments:** Copper base metal; cell walls may be copper too, but contaminated with lead from the ?enamel or from the burial environment. Normal range of glass elements in the enamels sampled. | |

**Notes to the catalogue**

Colours of metals and enamels are recorded as seen, although it is very likely that these have been substantially changed by corrosion. Specifically, it is to be expected that copper- and iron-based corrosion products will be present.

Cu = copper, Sn = tin, Zn = zinc, Pb = lead, Fe = iron, Ca = calcium, Al = aluminium, Ag = silver

Where elements are in brackets, they are present at low levels. Where elements are preceded by a question mark, they are present at very low levels, at around the limit of detection for the system.