Ancient Monuments Laboratory Report 87/97

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Summary

A number of plated iron objects from medieval Bedern and Coppergate were analysed qualitatively by X-ray fluorescence to identify the plating metal or metals used. Most non-ferrous coatings were tin or tin-lead, the rest being various copper alloys. Gilded silver was found on three pieces of ironwork from Bedern.

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Analysis of non-ferrous platings and deposits on ironwork from Bedern and Coppergate, York

Tim Horsley

Introduction

In medieval York, The Bedern was the name given to an area to the south-east of York Minster, and bounded on three sides by Goodramgate, Aldwark and St. Andrewgate. It is known from documentary evidence and surviving standing buildings that this area formed the precinct of the College of the Vicars Choral. Between 1973 and 1980, the site was excavated by the York Archaeological Trust, and the remains of a medieval industrial complex were uncovered (Richards, 1993).

16-22 Coppergate was excavated between 1976 and 1980. The site lies on the spur of land between the rivers Ouse and Foss. It is bounded to the east by the banks of the Foss, and to the west by Coppergate, a street leading towards the only bridge across the Ouse in the medieval period (Hall, 1992).

The Analyses

Following conservation at YAT Conservation Laboratory, a number of iron objects from Coppergate and Bedern, with traces of metal plating, were submitted for analysis by qualitative X-ray fluorescence (XRF) to identify the metals present in the platings.

The XRF spectrometer used was a Link Analytical XR400 energy dispersive system. Analyses were carried out under the following conditions: a tube voltage of 35kV; a current of 30-50uA; a collimator size of 4mm; and a collection time of 100 seconds. This size of collimator allows the analysis of a fairly large area, (about 1cm²), which is often necessary when dealing with the non-homogeneous tracings of metal platings. The greater the analysis area, the better the detection of these metals. For each analysis, both peak height and peak area were recorded as a measure of elemental signal strength.

Low levels of copper were detected on most objects, even in areas where no non-ferrous metal was apparently present. As pointed out by Wilthew (1984), this is likely to be the result of contamination during burial, and therefore is not evidence that the object was originally plated. This trace level of copper was often detected with both the tin and tin-lead platings, and so was also assumed to be due to contamination and ignored.

The analyses of a number of different tin-lead alloy and copper alloy standards allowed the identification of mathematical relationships between the recorded peak heights and the percentage of metals present in the different alloys. These findings were then used as a guide to give an indication of the proportions of non-ferrous metals present on the analysed ironwork.

Since the results obtained were qualitative in nature, this necessitated a level of interpretation before the original proportions present could be estimated. The

strength of signal (peak height) for a particular metal is affected by many factors, including the shape, size and surface texture of the object, its position during analysis, the composition and distribution of the metal plating, and the analytical conditions used. Corrosion processes may have altered the relative proportions of metals in an alloy, adding further complications (Ottaway, 1992, 724). The combination of these factors makes it impossible to give more than a rough idea of composition.

The terms used in Tables 1 and 2 have the following meanings:-

		and 2 have the following meanings
	tin	Tin was the only non-ferrous metal detected, and
		therefore the plating was essentially pure tin.
,	tin, trace lead	A trace of lead was detected, probably representing a
		lead level of about 1%. At such a low level, this may
		well be the result of contamination, either during
		manufacture or burial.
	tin, a little lead	The level of lead was up to about 10%, and is more
		likely to represent the deliberate addition of lead to the
		tin rather than contamination.
	leaded tin	The amount of lead was 'significant', that is, was
		greater than about 10%.
	tin-lead alloy	This term has been used where both lead and tin were
	•	detected, but since the levels of both were extremely
		low, no attempt has been made to estimate their
		relative proportions.
	lead	Lead was the only non-ferrous metal detected. Most of
		the objects which gave this result were not coated.
		The lead was present as lumps or droplets of metal
		adhering to the object.
	copper	Copper was the only non-ferrous metal detected; the
		plating was essentially pure copper.
	leaded copper	'Significant' amounts of lead were detected in addition
		to the copper.
	bronze	Copper and significant amounts of tin were detected.
	leaded bronze	Bronze with significant lead.
	brass	Copper with significant amounts of zinc.
	ternary	In addition to copper, significant amounts of zinc and
		tin were detected. This is effectively a gunmetal,
		though the term 'ternary' has been used instead to
		indicate that the relative proportions of these three
		metals in the alloy appear to vary considerably.
	quaternary	A ternary alloy with significant amounts of lead (leaded
		gunmetal).

Any other non-ferrous metals detected are mentioned in the tables by their elemental name.

The analytical results from the Bedern and Coppergate ironwork may be found in Tables 1 and 2 respectively.

Table 1: Analysis of Non-Ferrous Platings and Deposits on Ironwork from Bedern

164keyplatingtin168pinplatingbron	nze, trace lead
168 pin plating bron	nze, trace lead
708 bit plating tin v	with a little lead
708 " adhering metal lead	ed tin
743 riveted plate perforation tin	
858 bit plating silve	er, gold, tr. mercury
1344 object inlay silve	er, gold, tr. mercury
1505 key plating lead	ed tin
2801 key plating tin	
3108 object plating tin v	with a trace of lead
3114 object plating lead	ed tin
3215 perforated disc plating tin v	with a trace of lead
3218 object cleaned iron tin	
3237 ring fragment plating bron	ze
3275 strip plating leade	ed tin
3285 strip adhering droplet lead	
3285 " cleaned iron none	e detected
3296 padlock bolt plating quat	ternary
3308 buckle fragment corrosion leade	ed tin
3318 object cleaned iron brase	S
3319 knife shoulder plate tin, a	a little lead
3327 fitting plating none	e detected
3329 arrow tip plating leade	ed bronze
3335 object adhering droplet copp	ber
3335 " plating tin	
3336 metal droplet metal leade	ed copper
3338 fitting plating tin	
3346 fragment cleaned iron none	e detected
3353 strip corrosion layer lead	
3355 ring fragment plating tin, p	possible trace of lead
3397 object plating tin	
3398 strip area around rivet trace	e copper and lead
3398 " plating tin-le	ead alloy

SF No.	Object	Area Analysed	Plating
3411	fitting	cleaned iron	none detected
3416	scale tang	cleaned iron	none detected
3419	key	plating	tin, trace lead trace copper
3424	hinged object	plating	tin
3426	strip	plating	tin
3437	pin	pin head	tin, trace copper
3454	key	plating	tin with a trace of lead
3456	plate	cleaned iron	tin with a trace of lead
3459	bar	adhering metal	lead
3466	fitting	plating	ternary, trace lead
3469	nail	cleaned iron	tin
3471	fitting	plating	tin
3471	13	corrosion	brass
3474	arrow tip	plating	leaded bronze
3479	knife	plating	tin with a little lead
3480	scale tang knife	shoulder plate	ternary
3480	11	rivets	brass with a little lead
3480	н	end cap	ternary with a little lead
3483	spur fragment	cleaned iron	tin
3487	key	plating	trace tin
3497	object	plating	tin and lead
3511	buckle	plating	tin with a trace of lead
3512	plate	adhering metal	tin, some lead
5095	fitting	plating	tin
50 99	fitting (buckle frag?)	plating	tin
5100	strips	plating	tin
5109	ring fragment	cleaned iron	tin
5115	object	plating	tin
5124	strip	plating	leaded tin
5129	blade; scale tang	cutler's mark	brass with a trace of lead
5129	11	shoulder plate	brass with a trace of lead
5129	21	scale rivet	brass with a trace of lead
5132	strip	plating	tin

Table 1: Analysis of Non-Ferrous Platings and Deposits on Ironwork from Bedern

SF No.	Object	Area Analysed	Plating
5133	blade; whittle tang	overlay - tang end	silver, gold, mercury
5133	н	overlay - tip end	silver, little gold & mercury
5135	object	adhering metal	lead
5143	plate	adhering droplet	lead
5146	barrel padlock top	plating	quaternary
5149	object	plating	tin
5151	padlock fragment	plating	leaded bronze
5152	tube	cleaned iron	quarternary
5165	rotating buckle arm	cleaned iron	leaded tin
5167	hinge	plating	tin
5208	nail head?	cleaned iron	tin
5209	buckle frame?	plating	bronze with a little lead
5217	padlock bolt	plating	leaded bronze
5228	fitting	cleaned iron	tin
5242	object	corrosion	copper with a trace of lead
5256	blade?	corrosion	lead
5260	arrow tip	plating	bronze with a little lead

Table 1: Analysis of Non-Ferrous Platings and Deposits on Ironwork from Bedern

SF No.	Object	Plating
176	(i) ring	lead
176	(ii) strip	lead
198	nail	lead
220	pierced fitting	no non-ferrous metal detected
263	fitting	tin
328	pin	tin
474	padlock barrel	leaded bronze
568	punch?	trace lead?, trace copper?
741	hinge strap	tin, a little lead
917	plate	quaternary
931	nail fragment	tin
989	arrow head	tin
1028	twisted ring	leaded tin
1073	key	tin
1281	horse bit	tin (trace copper?)
1368	padlock	copper
1393	padlock bolt	quaternary
1469	knife	no non-ferrous metal detected
1482	buckle	tin
1549	perforated strip	leaded copper
1617	padlock key	tin-lead alloy
1695	padlock fragment	quaternary
1714	padlock barrel	quaternary
1759	buckle - (i) front	quaternary
1759	buckle - (ii) back	leaded tin, a little copper
1759	buckle attachment	leaded tin, a little copper
2028	needle fragment	tin
2127	nail	tin, a little lead
2545	ring	quaternary
2621	lock	brass
2716	key	leaded tin, trace copper

Table 2: Analysis of Non-Ferrous Platings and Deposits on Ironwork from Coppergate

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SF	Object	Plating
2949	strip	tin, trace lead and copper
2979	fitting - knob	no non-ferrous metal detected
2979	fitting - finial	quaternary
2979	fitting - shaft	copper, lead, trace zinc
2982	padlock barrel	quaternary
3004	buckle frame	tin, trace lead and copper
3137	iron rivet, lead strip	lead, a little tin, trace copper
3314	iron strip	tin, trace copper
3802	padlock arm	leaded bronze
3816	fitting	no non-ferrous metal detected
3984	fitting	silver
4211	V-eyed hinge	tin, trace copper
4370	spur fragment - (i) body	tin, trace lead
4370	spur fragment - (ii) rivets	brass/ternary? - over a tin layer
4440	pierced fitting	tin
4819	padlock spring	bronze
6163	object	tin, trace lead
6458	hinge pivot	tin
6897	iron strip	tin, a little lead, trace copper
11296	plate	leaded tin
14778	iron strip	tin
14853	spur	no non-ferrous metal detected
15290	pierced fitting	tin
15373	object	copper, (trace tin?)
15968	hinge fitting	leaded tin
16104	iron nail + leather	trace lead

Table 2: Analysis of Non-Ferrous Platings and Deposits on Ironwork from Coppergate

Discussion of results

These analyses of the ironwork indicate that tin or tin-lead alloys were more frequently used to plate ironwork than copper alloys (in total 39 tin/tin-lead compared to 25 copper alloy). This compares with the results from the analyses of Anglo-Scandinavian plated ironwork from Coppergate, where copper alloy plating (brazing) was far less common (Wilthew and Ottoway, 1992).

As stated by Wilthew and Ottoway (1992) pure tin produces the best decorative effect; tin-lead alloys produce a frosted effect. There are a few examples of objects from both sites which have been plated with a tin-lead alloy. Apart from the visual effect, the lead would not have affected the properties of the plating to any noticeable extent. The lead may have been added accidentally, or with the intention of making the more expensive tin go further.

Where no non-ferrous metals were detected on the area of the object cleaned by conservation, the adjoining corrosion was analysed (labelled "corrosion" in the 'area analysed' columns of Table 1). It should be noted that the metals detected in these cases might not have been used to coat the object, and instead maybe unassociated metal which has become trapped in the corrosion during burial (for example from Bedern, SF No. 5256, the possible blade with lead detected).

In addition to producing a decorative effect, ironwork was plated to give it a corrosion resistant surface. Therefore it is likely that the whole object would have been coated. This point is important, as many of the objects analysed here appeared to have non-ferrous metals only in the decorative grooves; for example, from Coppergate the spur fragment SF No 4370, and all the keys from both sites. The plating metals from these and various other objects have been worn off during their useful lives, but was retained in grooves and similar areas better protected from general abrasion. Evidence of keying is visible on some areas of these objects where non-ferrous metals are not, indicating more extensive coverage. Key SF No 2801 from Bedern appears not to have been totally plated: part of the decoration may have been left to contrast the 'white' tin decoration with the 'black' iron background.

SF No 5133, from Bedern, is part of a whittle tang knife with decorated blade. Visual inspection indicated that the decoration was a white metal inlay, becoming yellow in colour towards the tang. Analysis of the two differently coloured areas showed them both to be rich in silver, with the yellow metal richer in gold. Mercury was also detected in both areas. Closer examination revealed traces of keying, visible where the metal inlay has worn down exposing alternate bands of inlay and the iron of the blade. It appears that following the preparation of a portion of the blade by keying (scoring the surface to roughen it), a thin silver wire was laid on this area in the desired pattern. To attach this wire to the knife, it was then hammered, a process which flattened both the silver wire and the keying. Once secured to the blade, the silver pattern was gilded using mercury, to give the appearance of a solid gold overlay. During use, the gold has become partially worn off exposing the silver wire, except in the area next to the handle where the blade was slightly better protected.

Mercury gilded silver was identified on two other objects from Bedern: the bit SF No 858, and the unidentified object SF No1334. The white-yellow metal was visible as a few small patches on the bit, but it is probable that either the whole object, or at least portions of it were plated in this way. The unidentified iron

object has very small traces of gilded silver present in linear fragments. They appear to be the remains of gilded silver wire which, like the decorated blade discussed above, had been arranged in a pattern. It is possible that it is not inlay, but traces of the plating surviving in keying, although keying is not visible elsewhere on the object.

One knife from Coppergate, SF No 1469, has a punched decoration consisting of a line of semi-circles along both sides of the back of the blade. XRF of both the decoration and corrosion within the decoration gave no evidence for the use of non-ferrous metals as an inlay.

All the padlock parts analysed here, both cases and mechanisms, were plated only with a range of copper alloys and not with tin-based alloys. Two padlock barrels, SF Nos 474 and 2982 from Coppergate, were plated with a brazing metal which also attached decorative iron strips. This technique results in a relief decoration.

Either tin- or copper-based alloys were used to plate the various buckles analysed. A buckle from Coppergate, SF No 1759, had been plated all over with a leaded tin, and then had a copper-alloy metal plating overlaying just the front, to give a two-colour decoration. XRF identified the copper-rich plating as a quaternary alloy, but since this layer was on top of leaded tin, it could be a brass, ternary or quaternary metal. This object was the only example of use of two contrasting-coloured non-ferrous metals side by side.

SF Nos 5135 and 5143, from Bedern, both have lead adhering to them. This addition of metal was probably not intentional, and may be the result of molten lead having been spilled onto these iron objects either because they were used near to a metal working area or perhaps in a building that burnt down.

The metal droplet, SF No 3336, was found in the corrosion crust on a medieval wedge, and was identified as leaded copper. Although it is too small to say anything definite, it may be an indication of metalworking on the site.

Conclusion

XRF analysis of the plated ironwork submitted from Bedern and Coppergate indicates that a range of tin and copper alloys were in use as plating metals in medieval York; tin or tin-lead alloys being the more frequently used metal. Three objects, all from Bedern, had been decorated with gilded silver, with examples of both silver wire inlay and surface coating. Apart from these gilded plates, the rest of the plated ironwork had been coated with non-ferrous metal so that the iron was completely sealed. This implies that the plating was as much functional (protecting the iron from corrosion) as decorative. One key was almost totally plated but with iron left exposed to contrast with tin used to decorate the cut grooves.

The padlocks were all coated with copper alloys, this presumably being for a functional reason; it is more resistant to wear than a tin-based alloy. Two of the padlock barrels were decorated with iron strips held in place by the brazing metal.

Lead was detected in every type of alloy, and in varying amounts.

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