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Assessment of archaeometallurgical residues from Hollis Croft, Sheffield

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Abstract

The investigated materials comprised a suite of small bulk samples together a group of firebricks with a vitrified and slagged front face.

All materials were examined visually and by pXRF.

The collection is mostly formed by assemblages of residues associated with the melting of copper alloy, most likely in a crucible furnace. The volatile elements with the alloy (zinc, lead) are concentrated in the loose residues and in the firebricks behind the slagged face. The slagged face of the bricks shows a concentration of copper and nickel in the slag phase. Bulk samples <1> and <2> contained an assemblage of finely sintered (?) sand with Cu-alloy weathering products, associated with abundant small chips or spalls from bricks. Such deposits would be compatible with an origin within flues. Bulk sample <3> contain much fuel waste, along with oxidised blebs and other spills of copper alloy and fine debris from bricks, together with some small copper alloy objects. This assemblage may have derived from the ash pit of a crucible furnace.

The metal being melted can therefore be identified as a ternary alloy of Cu-Ni-Zn (with very low levels of lead), almost certainly that known as 'German silver' (later as nickel silver or nickel brass). German silver was identified in the early 19th century as a metal to which silver plating would adhere tightly. Although initially employed as an intermediate layer in 'Sheffield Plate' (placed between the silver and copper layers to aid bonding and to help conceal areas of thinning of the silver plate in the 'close plated' technique), the alloy came into its own as the core for electroplated items (as electro-plated nickel silver – EPNS). This material rapidly replaced Sheffield Plate for mass produced cutlery in the mid- to late 19th century.

The German technique for production of the metal was imported to London in c.1829. Use of the metal in close plating spread to Sheffield in the 1830s with William Hutton, who opened a works on West Street, initially close plating, but from 1843 onwards using electroplating (and employing nickel silver produced by Evans & Askin in Birmingham). Later, other lesser electroplating businesses operated in Sheffield as the close plating process became almost entirely replaced by electroplating, amongst them Joseph Elliot and Sons operating from 4 Hollis Croft until 1923.

It is extremely unlikely that any of the small businesses in the Hollis Croft area would have been involved in the primary production of German silver and the production of cutlery using the metal typically entailed machine stamping from sheet metal. The melting of German silver might possibly have been undertaken for pieces requiring a cast, rather than stamped, core, but it is more likely that melting would be undertaken as a means of recycling the metal waste from the stamping process.

Bulk sample <4> contains a different assemblage of materials, dominated by the magnetic, hard, dense, ferruginous sandy material known as 'crozzle' (the indurated slaggy material formed in steel cementation furnaces – of which several examples formerly existed in Hollis Croft).

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Methods

All materials were examined visually, using a low-powered binocular microscope where required.

Following on from the requested pXRF investigation of the slagged bricks, which revealed a non-ferrous metallurgical context, pXRF was also undertaken on the bagged bulk samples for health and safety purposes (in order to determine any problematic levels of elements such as lead, arsenic and cadmium). Injurious levels of these elements were not detected, but the analyses made were also then available for the interpretation of the samples.

The specimens were analysed on a semi-qualitative basis using a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer (instrument belonging to the Department of Archaeology, Cardiff University). The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti; this serves to maximise detection with Ti to Ag and W to Bi), at 40kV and 9.60 µA, with a filament current of 189 µA, for 60s. The instrument was controlled by a PC running Bruker's *S1PXRF* with spectra stored as txt files. The output was imported into Bruker's Spectra (*Artax*) software for production of images of the spectra (Figures 2 and 3) and for measurement of net peak areas (Table1).

Measurements were taken using the pXRF of the bulk samples within their plastic storage bags, with two measurements made for each sample. Spot analyses were taken from the brick/slag samples from locations where the sample could be as close to the face of instrument as practical.

The nature of the targets meant that quantified data could not be produced and a purely categorical approach to data presentation has been adopted.

The bulk samples were wet-sieved at 10mm, 1mm and 0.063mm. The <0.063mm fraction (i.e. the silt and clay fraction) was discarded. The results of this sorting (Table 2) should not be considered a definitive granulometric description.

This assessment was conducted in April 2024 and was commissioned by Simon Hambrook of West Yorkshire Archaeological Services.

Results

Description of the bulk samples

Sample <1>, (719)
The raw sample showed a very dark grey/brown fine matrix bearing abundant pale gritty material.

The coarser fractions mostly comprise a pale grey, sandy, possibly sintered material of ashy appearance. There are also abundant brick fragments, mostly pale (buff/cream), but red brick is common too, particularly at a slightly smaller grain size.

Sample <2>, (716) [?(718)]

This sample appeared as a brown, plastic, gritty clay before processing.

The coarser fraction of the sample is equally divided between small fragments of red (occasionally cream) brick and a sandy pale grey material, that appears partially fused or cemented and which contains abundant green flecks of copper alloy weathering products.

Context (716) is listed as a concrete surface and it appears very likely that this sample actually derives from context (718).

Sample <3>, (724)
The unprocessed sample was a very dark, coarse, sediment with abundant slaggy clasts.

The >10mm fraction produced:
32.5g (7 pieces) of rusted sheet iron;
16.7g (11 pieces) of coke, often with green Cu-alloy weathering product in the vesicles;
16.6g (8 pieces) blebs of very dark, glassy, vesicular slag, commonly with green Cu-alloy weathering;
8.2g (3 pieces) of dense prilly flows of corroded metal, the interior of often weathers green, but there is a white bloom on the external surfaces;
9.3g (5 pieces) fragmental material with coke, slag and metal in varying proportions;
0.3g (1 piece) chip of red brick; 0.3g (1 piece) angular fragment of cement. The 1-10mm fraction contains similar materials, the slag commonly in isolated drips, but also fragments of wood and charcoal.

The 1-10mm fraction contained similar materials, but also produced 4 copper alloy objects (total 1.55g). These are (from left to right in Figure 1)

a. a length of fine copper alloy rectangular-sectioned rod, 2.3mm x 0.3mm in section and 25mm long, of which last 6mm is folded back on itself,

b. a length of fine copper alloy rectangular-sectioned rod, 1.8mm x 0.5mm in section and 16mm long,

c. the tip of a copper alloy tube, forming a ferrule-like object (with a resemblance to a partial ring gland as employed in plumbing). The object was 8mm in outside diameter, approximately 0.4mm thick, with the tip bevelled inwards over a distance of 1mm to an inside diameter of 6.5mm. It is a maximum of 8mm long, but with an irregular margin, locally only 4mm long,

d. a 22mm length of curved copper alloy rod, 1.8mm in diameter. It curves gently for 16mm before bending at an approximate right angle for 5mm.

Sample <4>, (605)
The raw sample was a coarse brown gravel, with abundant large clasts.

The coarser fractions are dominated by brown, ferruginous, sandy materials that are probably almost entirely 'crozzle'. A small proportion may be natural stone, but this cannot be established with microscopic examination. A very minor component is supplied by pale and red brick fragments. There are also a few small pieces of brown glassy slag sheet (approximately 1mm thick) of uncertain origin.

pXRF analysis

Samples <1>, (719), <2>, (716) & <3>, (724)

These three samples show rather similar pXRF results (Table 1; Figure 1), with moderately elevated iron and nickel, strongly elevated copper and zinc, and slightly elevated lead. In detail, however, the pattern of enrichment varies: sample <1> shows extremely elevated zinc (with 20 times the peak area of copper), sample <2> less so (10 times the peak area of copper and with sample <3> showing the zinc peak at just 4 times the area of that of copper. The relationship between the peak areas of copper and nickel is less varied: that of copper approximately 5 time the area of that of nickel, for samples <1> and <2>, but around 10 times for <3>.

Sample <4>, (605)
This sample shows little, if any enrichment in nickel, copper, zinc or lead, but does show strongly increased levels of manganese and iron.

Slagged bricks
The bricks show very low contents of nickel, very slightly raised contents of copper, but markedly elevated zinc. The Cu:Ni peak area ratio is approximately 8. The zinc enrichment varies from within the core of the small brick, where it has a peak area around 5 times that of copper, to the original rear face of the brick where it reaches a peak area over 40 times that of copper (which is itself moderately enriched).

In contrast, the slag layers on the front of the bricks show a different pattern of enrichment, with the copper peak area being 5 times that of nickel in places, but increasing to as much as 70 times that of nickel close to the partial-melted front face of the bricks. The relative copper and zinc enrichment is also very variable, with the copper peak having an area of 6 to 15 times that of the zinc peak in the larger fragment of wall and the detached slag, but only 1 to 7 times in the slag on the smaller brick piece.

The ratio of the area of the zinc peak to the that of the nickel peak varies from 0.6 – 0.7 on the front face of the slag in the lager brick piece, 1.2 – 1.6 on the front face of the detached slag layer, but 10 – 36 in the slag of the smaller brick piece. The ratio rises to approximately 40 within the bricks and to 360 on the back face of the bricks.

Interpretation

Copper alloy working

The collection is mostly formed by assemblages (bulk samples <1>to <3> and the slagged brick samples) of residues associated with the melting of copper alloy, in a crucible furnace.

Samples <1> and <2> are very similar in their granulometry as well as both physical and chemical composition; if sample <2> is indeed from context (718), then the evidence here supports the suggestion that (718) and (719) may be laterally equivalent contexts.

The patterns of metal contamination in the furnace and its associated deposits, reflect the different behaviours of the alloy components during heating. The fractionation of the different metals has been described on a small scale by Kearns *et al.* (2010), but the principle is the same on the scale of a furnace: zinc will be lost from zinc-bearing alloys by volatilisation, and will accumulate in cooler locations, including within porous materials and within flues.

In samples <1> and <2> the approximate original ratio of copper to nickel is probably maintained, but the zinc content has been relatively enhanced by this process, in keeping with their suggested origin within flues.

Zinc is also locally concentrated in the firebricks behind the slagged face. The slagged face of the bricks shows a concentration of copper and nickel in the slag phase, locally preserving their approximate ratio in the alloy.

Sample <3> from context (724) shows a rather different composition, with much spent fuel (often showing copper alloy weathering products), as well as slag in very blebby and prilly forms. This assemblage also contains small prills of corroded metal. Such an assemblage is vey likely to have been produced in the ash pit of a crucible furnace, although an origin in the sweepings from the workshop floor cannot entirely be excluded.

The metal being melted can therefore be identified as a ternary alloy of Cu-Ni-Zn (with trace levels of lead), almost certainly that known as ‘German silver’ (Grant 2017; approximately Cu 60%, Ni 20% and Zn 20%; later, particularly post-1914, as nickel silver or nickel brass; note: German silver does not contain silver!). German silver was identified in the early 19th century as a metal to which silver plating would adhere tightly. Although initially employed as an intermediate layer in ‘Sheffield Plate’ (placed between the silver and copper layers to aid bonding and to help conceal areas of thinning of the silver plate in the ‘close plated’ technique), the alloy came into its own as the core for electroplated items (as electro-plated nickel silver –

EPNS). This material rapidly replaced Sheffield Plate for mass produced cutlery between 1840 and 1850.

The German technique for production of the alloy was imported to London in c.1829 by Percival Norton Johnson, who established a nickel refinery on Bow Common and a German silver works at Hatton Gardens. Use of the metal for close plating spread to Sheffield in the 1830s with William Hutton, who opened a works on West Street, where from 1843 he was instead using electroplating (following the licensing of Elkington & Co's patent of 1841 for their process using silver cyanide as the electrolyte). William Hutton employed nickel silver produced by Evans & Askin in Birmingham, the 19th century's foremost producers.

Later, other lesser electroplating businesses operated in Sheffield as the close plating process became almost entirely replaced by electroplating by the end of the 1840s, amongst them Joseph Elliot and Sons operating from 4 Hollis Croft until 1923.

Against this background, the question for this site is why nickel silver was being melted? It is extremely unlikely that any of the small businesses in the Hollis Croft area would have been involved in the primary production of German silver, and the production of cutlery using this metal typically entailed machine stamping from sheet metal. The melting of German silver might have been undertaken for pieces requiring a cast, rather than stamped, core, but this was a relatively rare usage compared with the widespread stamping of utensils from sheet metal. It is perhaps more likely that the melting would have been undertaken as a means of recycling the metal waste from the stamping process.

The assemblage of small copper alloy artefacts from the 1-10mm fraction of sample <3>, from context (724), might reflect items lost during charging of the crucible with such scrap material.

Steel-making

Bulk sample <4> differs from the rest of the collection and contains a different assemblage of materials, possibly including some natural stone, but dominated by the magnetic, hard, dense, ferruginous sandy material that is known as 'crozzle' (the indurated slaggy material formed from the capping to the chest containing the iron bars in a steel cementation furnaces – of which several examples formerly existed in Hollis Croft; Tuck & Rajic 2021).

Further work

Additional pXRF analysis of the metal prills and metal artefacts from sample <3> could be undertaken to enhance to interpretation established here, but such additional work is not essential.

References

GRANT, A., 2017. A British history of 'German silver': part II: 1829-1924. *Journal of the Antique Metalware Society*, **24**, 48-79.

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

TUCK, A. & RAJIC, M., 2021. Hollis Croft, Sheffield, South Yorkshire: Old site and new connections, *Internet Archaeology* **56**. https://doi.org/10.11141/ia.56.4

Figure captions

Figure 1: copper alloy artefacts from sample <3> from context (724).

Figure 2: pXRF traces for analyses on the bulk samples

Figure 3: pXRF traces for analyses on the bricks and slagged surfaces from context (

Table 1: summary of net peak areas recorded by Artax for the pXRF analyses.

Element	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Y	Zr	Sn	Pb
Peak	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	L1
large bricks (720), slagged face a	424	24074	35417	285344	25614	255	477	94	823	326	1230
large bricks (720), slagged face b	1019	57610	105799	559800	64882	253	365	127	2482	444	1488
small brick (720), slagged face a	2158	120149	60070	528956	1066910	866	813	645	1440	477	2579
small brick (720), slagged face b	2165	126261	68565	1042408	854574	545	671	516	1191	833	2571
slag sheet (720), outer a	3697	145675	53757	572497	88552	996	1947	572	4533	947	1765
slag sheet (720), outer b	2035	82083	59484	1083849	70390	194	580	182	1781	502	3250
slag sheet (720), inner ceramic a	342	20844	367	25711	3770	191	870	566	28078	936	1174
slag sheet (720), inner ceramic b	330	15990	352	15711	12595	172	662	467	17589	1001	1248
small brick (720), pale edge of broken face	512	52000	844	7006	35066	5527	6028	2290	13293	1160	1603
small brick (720), core of broken face	229	23299	410	3502	16703	2287	2601	1111	5773	454	982
small brick (720), powder on lateral face	593	64293	893	6466	15884	2465	3580	1452	17111	655	2041
small brick (720), clean rear face	748	73045	1785	14929	646562	2395	3730	1246	7263	889	2906
Sample <1> (719), a	941	137421	12326	68563	1497874	371	913	1611	1789	1081	10577
Sample <1> (719), b	959	99943	9727	58023	1138071	825	860	1090	2279	840	6676
Sample <2> (716), a	1146	104223	12816	74477	724219	285	716	456	1188	804	10898
Sample <2> (716), b	1710	144167	17532	96846	999875	276	1098	1382	2063	961	12416
Sample <3> (724), a	2862	132837	13071	149750	570107	792	2458	740	2329	627	9209
Sample <3> (724), b	3195	221681	17866	144824	579484	1179	3119	1222	3365	824	4519
Sample <4> (605), a	6778	1052395	1034	3708	3105	418	314	79	1961	407	2256
Sample <4> (605), b	5537	844370	884	3397	2267	339	472	154	1950	730	2207

Table 2: summary of investigation of the bulk samples

sample	context	sample wt (wet; g)	sample notes	fractions >10mm	1-10mm	0.063 - 1mm	remainder	description
1	719	640	dark fine matrix bearing abundant pale gritty material	5 (1%)	45 (7%)	164 (26%)	426 (67%)	the coarser fractions mostly comprise a pale grey, sandy, possibly sintered material of ashy appearance. There are also abundant brick fragments, mostly pale (buff/cream), but red brick is common too, particularly at a slightly smaller grain size.
2	716 (718?)	828	brown, plastic, gritty clay	0 (0%)	87 (11%)	181 (22%)	560 (68%)	the coarser fraction of the sample is equally divided between small fragments of red (occasionally cream) brick and a sandy pale grey material, that appears partially fused/cemented and which contains abundant green flecks of copper alloy weathering products
3	724	868	dark coarse sediment with abundant slaggy material	84 (10%)	389 (45%)	167 (19%)	228 (26%)	coarsest fraction: 32.5g (7 pieces) of rusted sheet iron; 16.7g (11 pieces) of coke, often with green Cu-alloy weathering product in the vesicles; 16.6g (8 pieces) blebs of very dark, glassy, vesicular slag, commonly with green Cu-alloy weathering; 8.2g (3 pieces) of dense prilly flows of corroded metal, interiors often weather green, white bloom on surfaces; 9.3g (5 pieces) fragmental material with coke, slag and metal in varying proportions; 0.3g (1 piece) chip of red brick; 0.3g (1 piece) angular fragment of cement. The 1-10mm fraction contains similar materials, the slag commonly in isolated drips, but also fragments of wood and charcoal. This fraction contains 4 copper alloy objects (total 1.55g).
4	605	1105	brown, with abundant large clasts	583 (53%)	163 (15%)	81 (7%)	278 (25%)	the coarser fractions are dominated by brown, ferruginous, sandy materials that are probably almost entirely 'crozzle'. A small proportion may be natural stone. A very minor component is supplied by pale and red brick fragments. There are also a few small pieces of brown glassy slag sheet (approximately 1mm thick) of uncertain origin.

Figure 1

50mm

Figure 2

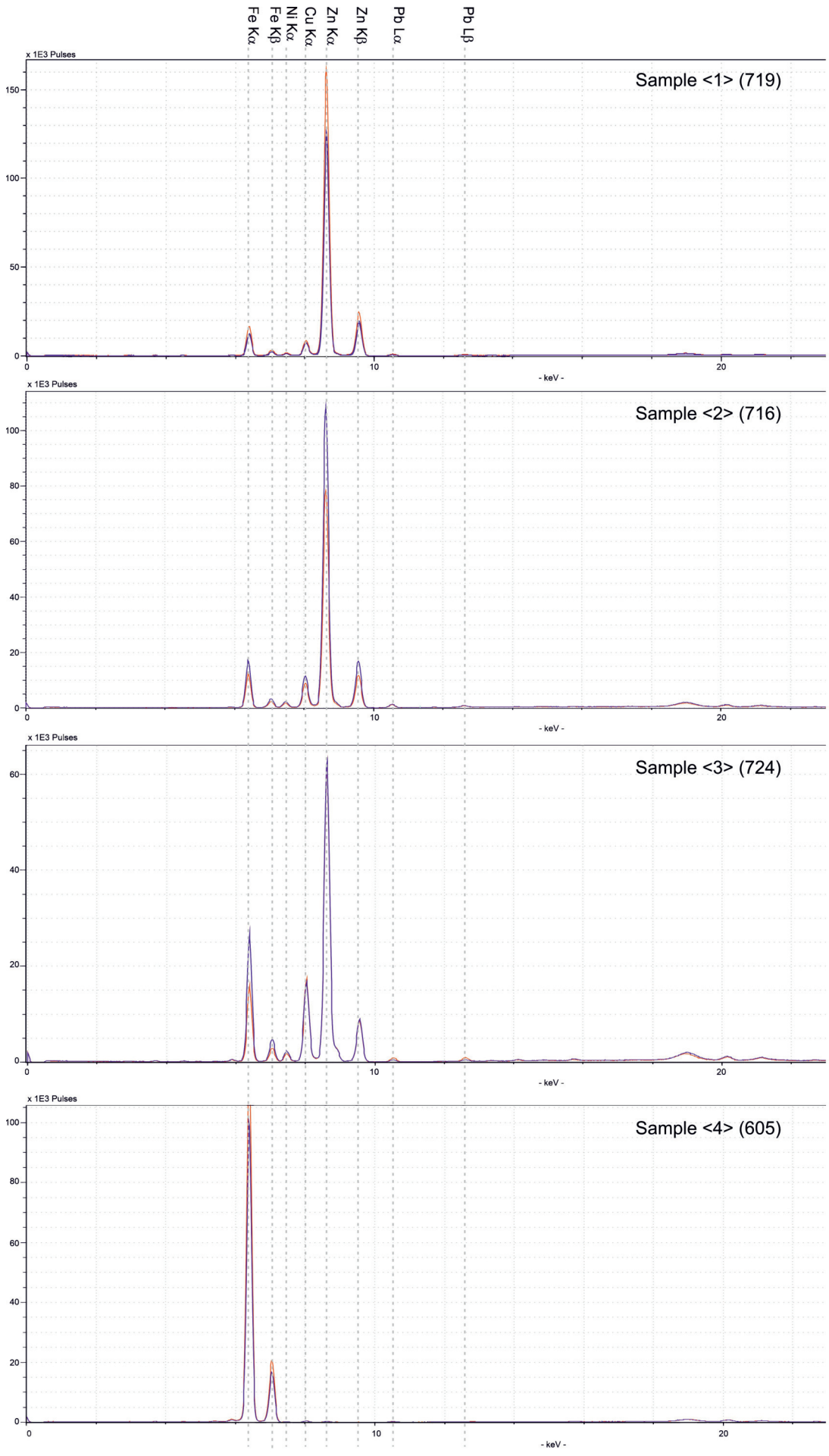
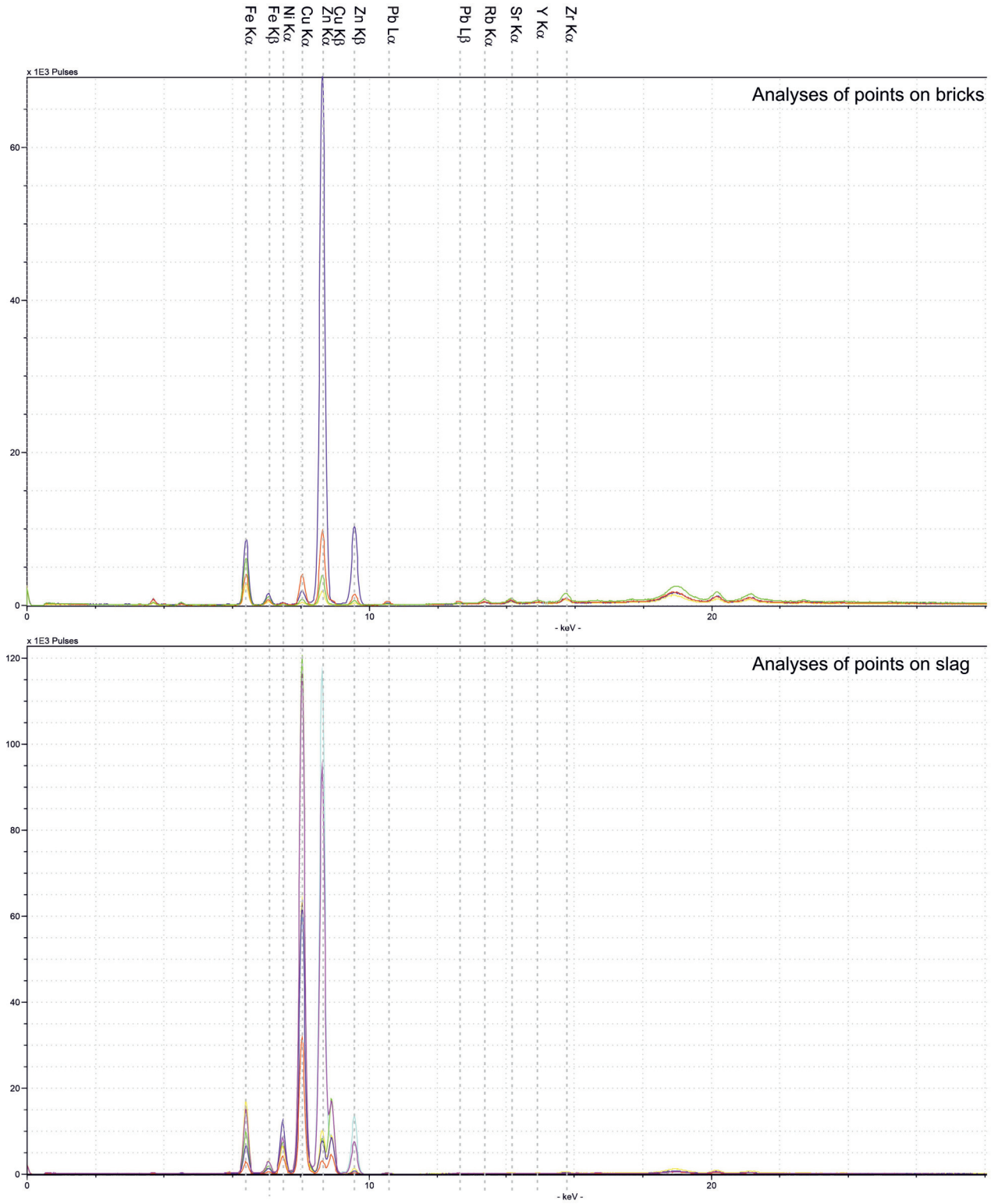

Fe Kα
Fe Kβ
Ni Kα
Cu Kα
Zn Kα
Zn Kβ
Pb Lα
Pb Lβ
x 1E3 Pulses
Sample <1> (719)
- keV -
x 1E3 Pulses
Sample <2> (716)
- keV -
x 1E3 Pulses
Sample <3> (724)
- keV -
x 1E3 Pulses
Sample <4> (605)
- keV -

Figure 3


Fe Kα
Fe Kβ
Ni Kα
Cu Kα
Zn Kα
Cu Kβ
Zn Kβ
Pb Lα
Pb Lβ
Rb Kα
Sr Kα
Y Kα
Zr Kα
x 1E3 Pulses
Analyses of points on bricks
- keV -
x 1E3 Pulses
Analyses of points on slag
- keV -

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