Staffordshire Hoard
Research Report 8

XRF Analysis of Silver Foils from the Staffordshire Hoard

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Information about this report

This report was produced in 2014 as part of Stage 1 of the project, i.e. before fragments were joined and catalogued. The concordance of the K numbers given in the report to the catalogue numbers as they appear in the final publication is as given below. The list also includes the names of the objects as used in the final publication.

It should be noted that it was not until the end of Stage 1 that nomenclature was standardised. What are described as 'foils' here are now 'die-impressed sheets'.

The work reported on here was a short exploratory programme to establish whether composition could be used to distinguish between the different die-impressed sheets. The main programme of analysis for the silver objects took place in Stage 2 and is reported on in:-

Research Report 14 – Blakelock, E.S. 2015. *Pilot XRF Study of the Silver Hilt-plates from the Staffordshire Hoard.*

Research Report 15 _ Blakelock, E.S. 2015. *XRF Study of Silver Objects from the Staffordshire Hoard.*

K number	Catalogue number	Name in publication
75	600	[Helmet] Large sheet covering in silver with multiple panels of animal art and gilded borders (part).
785	600	[Helmet] Large sheet covering in silver with multiple panels of animal art and gilded borders (part).
1383	597	[Helmet] Multiple sheet panels in silver-gilt showing three warriors marching left (part).
1400	595	[Helmet] Sheet panel in silver-gilt showing a mounted warrior (part).
1406	594	[Helmet] Sheet band in silver-gilt showing a continuous process of creatures (part).
1412	594	[Helmet] Sheet band in silver-gilt showing a continuous process of creatures (part).
1423	597	[Helmet] Multiple sheet panels in silver-gilt showing three warriors marching left (part).
1476	596	[Helmet] Multiple sheet panels in silver-gilt showing three warriors marching right (part).
1556	593	Helmet-band in cast silver-gilt, inset with a silver-gilt sheet band, showing a continuous procession of kneeling or running warriors (part).
1624	595	[Helmet] Sheet panel in silver-gilt showing a mounted warrior (part).

The British Museum

DEPARTMENT OF CONSERVATION AND SCIENTIFIC RESEARCH

XRF analysis of silver foils from the Staffordshire Hoard

Science Report PR07444-14

E. S. Blakelock

Abstract:

A number of fragmentary silver foil friezes have been identified within the artefacts of the Staffordshire Hoard. Surface X-ray fluorescence (XRF) analysis was carried out on the fronts and backs of a number of fragments from several of these friezes. This was to determine whether the foil fragments could be grouped based on composition. If the friezes showed distinctive compositions, it was hoped that this would support conservators in the reconstruction of the friezes from the many fragments of foil.

With the exception of the interlace foils (frieze 10), the analysis of the front of all the foils revealed the presence of gilding: XRF analysis detected the presence of mercury indicating that they were mercury gilded. The analysis of the uncleaned surfaces of the backs of the foils showed a range of results, which overlapped between friezes and were not sufficiently distinctive to allow identification of compositional groups linked to specific friezes. Evidence was also noted of contamination from the gilding process on the back of the foils. This study overall shows that a rapid surface XRF survey is not an appropriate technique to identify frieze groups.

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20 February, 2014
External Registration Numbers: Staffordshire Hoard K75, K785, K1383, K1406, K1412, K 1423, K1476, K1556, K1624 and K1400

Introduction

This pilot study forms part of a larger English Heritage-funded research project on the Staffordshire Hoard. The Staffordshire Hoard is a large collection of Anglo-Saxon gold and silver metalwork, discovered in a field near the village of Hammerwich, near Lichfield, in Staffordshire, England on 5 July 2009. Within the Hoard assemblage a number of fragmentary silver foil friezes were found, some with designs similar to those found on the Sutton Hoo and other helmets (Bruce-Mitford 1978, 146-150).

Twelve different sequences of decorative motifs were originally identified by David Symons (Birmingham Museums Trust) (Figures 1 to 3). Most depict warriors (Figures 1 and 2(b)), while one shows 'duck' or 'beaked' heads with serpentine bodies (Figure 3) and another is an interlace design (Figure 2(a)). For some of the silver foil fragments, joins were obvious and therefore several friezes were partially reconstructed at an early stage. Some foil fragments are however difficult to assign correctly to specific friezes based on style alone. The aim of this study was to determine whether surface X-ray fluorescence (XRF) analysis can be used to help identify groups of foil fragments from individual friezes, and therefore aid in the conservation work.

Figure 1. The small running/kneeling warriors of frieze 7 (K1556).

(a) ***(b)***

Figure 2.(a) K75, a silver interlace foil from frieze 10. **(b)** K1624, the horseman from frieze 8.

Figure 3. K1383 and K1412, part of frieze 9 'beaked' quadrupeds, which have 'duck' or 'beaked' heads and serpentine bodies.

Methodology

Unprepared surfaces of the foils were analysed qualitatively using a Bruker ARTAX spectrometer using the following operating conditions: 50 kV, 500 μA current, 0.65 mm diameter collimator and 200 second counting time. A number of alloy standards of known composition were also analysed under the same conditions. The XRF results were quantified using a pre-existing silver standardisation method which also calculates the concentrations of zinc, tin and lead.[1]

Where possible, both the fronts and backs of the foil fragments were examined. While the front surfaces of the foils had been swab-cleaned to remove soil, the backs had not been cleaned and the presence of soil and corrosion deposits on the backs will affect the results. The possible compositional variability across the surface of a single fragment was checked by carrying out multiple analyses on the same foil. Three friezes had multiple pieces that had identified joins; therefore analysis of multiple foil fragments from the same frieze was carried out. Other fragments which had been identified as belonging to the same frieze scheme due to their similar designs were also examined. Table 1 notes the K numbers of the foil fragments analysed from each frieze.

Frieze	K Numbers
F1 and F2 Feet and bodies	K1423, K1476
F6 Eagle crested helmet	K1420
F7 Small warriors running	K1556
F8 Horsemen	K1624, K1400
F9 'Beaked' quadruped creatures	K1383, K1412, K1406
F10 Un-gilded interlace	K785, K75

Table 1. K numbers of the foil fragments analysed that make up each frieze.

[1]When quantifying the data from a spectrum, the British Museum in-house software uses a maximum of four accepted or certified alloy compositions to standardise against, producing compositional data in weight percentage. As with all analytical methods it is important that the compositional range of the standards covers that of the samples of interest to minimise the potential error due to extrapolation.Therefore, standards with similar alloy compositions were used to create a method (Cowell 1977).

Results

Fronts of the foil fragments

The front of thirty-seven foil fragments was analysed from across seven different friezes, with all but two of these fragments (Frieze 10 with interlace foils) being gilded. Of the gilded pieces, all revealed traces of mercury indicating that the mercury amalgam method of gilding had been used.

The gilding on the front of the foils fall into the composition ranges 50-79 wt% gold, 20-49 wt% silver and 0.5-1.2 wt% copper. The compositional differences seen are likely to be related to the thickness of the gilding layer, with part or most of the silver detected being located in the base sheet underneath. The variable thickness of the gilded layer may be affected by a different manufacturing process or the design itself, but is equally likely to relate to wear during use or in the post-depositional environment.

The silver foil fragments with interlace design had no gilding present, and analysis of the surface indicated a silver content of approximately 96-97 wt% silver with 1-2wt% gold and the remainder being copper and lead.

Variability in composition across the back of a single foil fragment

The possible compositional variability of the surface of a single foil fragment was measured by carrying out multiple analyses. In the majority of cases, gilding was clearly visible on the fronts of the foils but no gold was visible on the backs of any of the foils. Five analyses on the back of one foil fragment (K1556) with a running/kneeling warrior showed a large variation in composition (Table 2). The large variation in gold content is likely to be mainly due to splashes of gold, not visible on the surface, from the gilding process. Another contributing factor to the variability in composition will be the irregular thickness of the surface silver corrosion layers

	Wt% Au	**Wt% Ag**	**Wt% Cu**	**Wt% Zn**	**Wt% Pb**	**Wt% Sn**
1	1.7	92.3	5.4	n.d.	0.6	n.d.
2	1.7	93.0	4.9	n.d.	0.5	n.d.
3	11.2	81.5	6.6	n.d.	0.7	n.d.
4	1.9	91.2	6.2	n.d.	0.7	n.d.
5	15.0	80.7	3.8	n.d.	0.5	n.d.
Average	**6.2**	**87.2**	**5.3**		**0.6**	
Standard Deviation	*6.31*	*6.04*	*1.10*		*0.14*	
Standard Deviation without 3 and 5	***0.12***	***0.91***	***0.66***		***0.10***	

Table 2. Normalised table of results showing the variation in composition at the surface on the back of a foil fragment. Note that areas 3 and 5 have a high gold content, and therefore lower silver and copper contents, which has increased the standard deviation. n.d. indicates that the element was not detected.

Variability of the composition of the backs of the friezes

The backs of nineteen different foil fragments from seven different friezes were analysed (Table 3). The majority of the foil friezes were composed of *c*.93-97 wt% silver, 1-2 wt% gold and 0.7-2.5 wt% copper. Traces of lead were present in all of the foils. The full results of the foil analysis are included in table 4 in the appendix.

Several of the analyses on the small running warriors frieze fragments (F7) had a high gold

content. As mentioned above, this is probably due to splashes of gilding from the front. These analyses have been excluded from table 2 and figure 4.

The non-gilded interlace decorated foils appear to be distinctive with their relatively lower copper content, resulting in a higher silver content, compared to the other foils.

	Analysed Areas		Wt% Au	Wt% Ag	Wt% Cu	Wt% Zn	Wt% Pb	Wt% Sn
F1 and F2 Feet and bodies	2	Average	0.9	96.1	2.8	n.d.	0.2	n.d.
		Standard Deviation	*0.15*	*0.06*	*0.2*		*0.02*	
F6 Eagle crested helmet	3	Average	1.2	93.6	4.7	n.d.	0.5	n.d.
		Standard Deviation	*0.45*	*2.61*	*3.07*		*0.03*	
F7 Small warriors running	3[1]	Average[2]	1.7	91.6	5.5	n.d.	0.6	n.d.
		Standard Deviation	*0.15*	*0.94*	*0.67*		*0.15*	
F8 Horsemen	2	Average	1.1	95.9	2.8	n.d.	0.2	n.d.
		Standard Deviation	*0.06*	*0.21*	*0.12*		*0.04*	
F9 'Beaked' quadruped creatures	6	Average	1.3	95.6	2.9	n.d.	0.2	n.d.
		Standard Deviation	*0.54*	*1.07*	*0.91*		*0.05*	
F10 Interlace	2	Average	1.9	97.0	0.7	n.d.	0.4	n.d.
		Standard Deviation	*0.37*	*0.37*	*0.02*		*0.01*	

Table 3. Normalised table of results showing the average composition and standard deviation of the backs of the foil fragments analysed and grouped by the different friezes. [1]Three separate foil fragments were analysed. [2] This excludes four possible outliers which have much higher gold contents than the others. n.d. indicates that the element was not detected.

Discussion

Plots of gold concentrations versus copper and silver contents of the backs of the foil fragments analysed showed that most friezes were made from a similar silver alloy and therefore the alloy compositions of the different friezes were not distinctive (Figure 4). The non-diagnostic nature of the alloy composition is further reinforced by the overlap of error bars which emphasises the degree of variation between foil fragments within one frieze (Figure 4). Frieze 7, with the running warriors, is slightly more distinctive in this plot, but if the outliers are included it is more variable in composition.

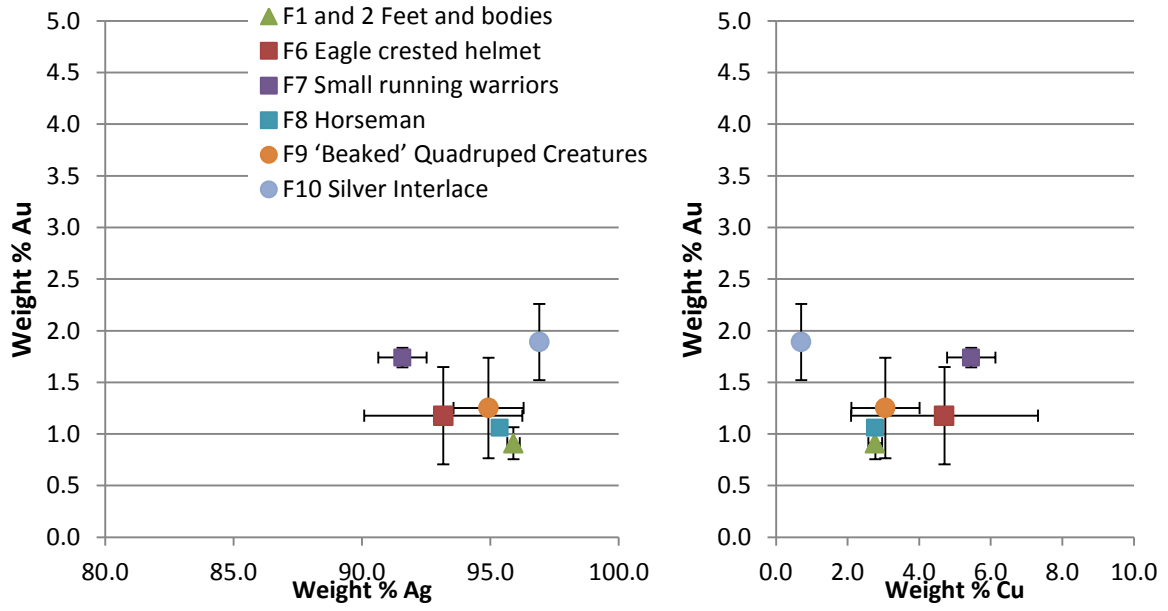

Figure 4. Scatterplot showing the average composition of the backs of the fragments of the different friezes analysed. The error bars show a single standard deviation from the average.

The non-gilded interlace foil fragments from frieze 10 are analytically different but they are easily distinguished from other fragments by their lack of gilding, so XRF analysis is unnecessary. If more types of non-gilded friezes are present within the Hoard assemblage, XRF analysis may be able to help distinguish between them. A relatively small number of fragments from the friezes were examined in this study, but analysis of more of these foil types may also result in additional compositional overlap with the other foil friezes. Overall the results show that surface XRF is not an appropriate method for grouping the foils, and it cannot be used as an aid for conservators in this case.

Conclusion

The composition of most of the foil fragments fell in the range of *c*.93-97 wt% silver, 1-2 wt% gold and 0.7-2.5 wt% copper. Traces of lead were present in all of the foils. With the exception of the interlace foils (frieze 10), the XRF analysis of the fronts of all the foils revealed the presence of mercury gilding which prevents direct access to the silver alloy below. Surface XRF of the fronts of the foils therefore cannot be used to group them. The analysis of the backs of the foils showed a range of compositions, which overlapped between friezes and therefore did not help in the identification of compositional groups linked to specific friezes. There was also evidence for contamination from the gilding process on the back of the foils although it was not always visibly present. This study overall shows that a rapid surface XRF survey is not the appropriate technique to identify frieze groups.

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Eleanor Blakelock Aude Mongiatti Susan La Niece Catherine Higgitt

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References

Bruce-Mitford, R., 1978. *The Sutton Hoo Ship-burial. Volume 2, arms, armour and regalia*. British Museum Publications Limited, London.

Cowell, M., 1977. *Energy dispersive X-ray fluorescence analysis of ancient gold alloys*. PACT Journal of the European study group on physical, chemical and mathematical techniques applied to archaeology **1**, 76-85.

Appendix

	Wt% Au	Wt% Ag	Wt% Cu	Wt% Zn	Wt% Pb	Wt% Sn
F1 and 2 Feet and bodies	0.8	95.7	2.9	n.d	n.d.	n.d.
F1 and 2 Feet and bodies	1.0	96.1	2.6	n.d	n.d.	n.d.
F6 Eagle crested helmet	0.7	96.7	2.1	n.d	0.4	n.d.
F6 Eagle crested helmet	1.7	91.9	4.7	n.d	0.4	n.d
F6 Eagle crested helmet	1.1	91.0	7.3	n.d	0.5	n.d.
F7 Small running warriors	1.7	91.7	5.3	n.d	0.6	n.d
F7 Small running warriors	1.7	92.4	4.9	n.d	0.5	n.d
F7 Small running warriors	11.1	81.1	6.6	n.d	0.7	n.d
F7 Small running warriors	1.8	90.6	6.2	n.d	0.7	n.d
F7 Small running warriors	14.9	80.2	3.8	n.d	0.5	n.d
F7 Small running warriors	5.2	86.9	6.1	n.d	0.8	n.d
F7 Small running warriors	20.7	77.1	1.7	n.d	n.d.	n.d
F8 Horseman	1.1	95.3	2.9	n.d	n.d.	n.d
F8 Horseman	1.0	95.4	2.7	n.d	n.d.	n.d
F9 ‘Beaked’ quadruped creatures	1.3	96.3	1.9	n.d	n.d.	n.d
F9 ‘Beaked’ quadruped creatures	1.0	93.8	4.2	n.d	n.d.	n.d
F9 ‘Beaked’ quadruped creatures	1.2	93.1	4.1	n.d	0.3	n.d
F9 ‘Beaked’ quadruped creatures	2.2	94.7	2.8	n.d	0.3	n.d
F9 ‘Beaked’ quadruped creatures	1.1	95.1	3.2	n.d	n.d.	n.d
F9 ‘Beaked’ quadruped creatures	0.8	96.6	2.2	n.d	n.d.	n.d.
F10 Un-gilded interlace	1.6	97.1	0.7	n.d	0.4	n.d.
F10 Un-gilded interlace	2.2	96.7	0.7	n.d	0.4	n.d.

Table 4. Normalised table of all of the surface XRF results from the analysis of the backs of the foil fragments.

Staffordshire Hoard Research Reports

Staffordshire Hoard Research Reports were produced by the project

Contextualising Metal-Detected Discoveries: Staffordshire Anglo-Saxon Hoard

Historic England Project 5892

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