



***Staffordshire Hoard
Research Report 11***

**FTIR, Raman and GC-MS analysis of
possible organic pastes and associated
foils (K234 & 235) from the
Staffordshire Hoard**

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2014

This report forms part of
The Staffordshire Hoard: an Anglo-Saxon Treasure
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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'.

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The owners, Historic England and Barbican Research Associates are grateful to National Geographic for the funding which enabled the work to be carried out.

K number	Catalogue number	Name in publication
234	593	Helmet-band in cast silver-gilt, inset with a silver-gilt sheet band, showing a continuous procession of kneeling or running warriors
235	593	As above

DEPARTMENT OF CONSERVATION AND SCIENTIFIC RESEARCH

FTIR, Raman and GC-MS analysis of possible organic pastes within silver trays and associated foils (K234 & K235) from the Staffordshire Hoard

**Science Report
Envelope No. PR07444-18**

Rebecca J. Stacey

Abstract:

Various paste-like materials within fragments of silver trays associated with silver gilt foils from the Staffordshire Hoard have been observed during conservation. Analysis was requested to investigate the composition of these deposits prior to reconstruction of the fragments, after which they will become inaccessible for study. Five samples were examined: a black-coloured layer in the bottom of the tray; a waxy red/brown fill with impressions from the associated foil relief; a white deposit adjacent to one of the rivet holes; a sample of bright green material that occurs in various locations; soil associated with the find. The samples were analysed by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and gas chromatography-mass spectrometry (GC-MS).

The results of the analyses indicate that the materials are construction components containing organic and inorganic components. The black layer comprises carbon, protein and beeswax and the red/brown layer contains beeswax and ochre-like material. It is not clear whether these constitute two separate construction layers or if the apparent upper layer is an artefact of soil ingress. Well-preserved white beeswax was identified adjacent to a rivet hole. Green material sampled from the same area is the copper corrosion product malachite, particles of which seem to be present in all the layers and on the surface of the tray although their origin is unclear.

The composition of the pastes examined here is very similar to the backing fills within cloisonné cells from other Staffordshire Hoard fragments (K356_2; K451_5; K673 and K1003_4) and this may be significant for interpreting the manufacturing parallels between these very different metal artefacts.

CSR Project no.: PR07444-18
Staffordshire Hoard numbers: K234 and K235

January 2014

Introduction

Fragments of the silver tray (K235 and K234) associated with some of the silver gilt foil pieces from the Staffordshire Hoard have been identified during conservation. The trays and foils are thought to have once been decorative components of a helmet. The tray fragments contain various paste-like materials that may be remnants of original fillers or fixatives. Analysis was requested to investigate the composition of these deposits prior to reconstruction of the fragments, after which they will become inaccessible for study.

Five samples were examined: a black-coloured apparent fill material, a waxy red/brown fill with impressions from the associated foil relief, a white deposit adjacent to one of the rivet holes; a sample of bright green material that occurs in various locations and soil associated with the find, see Table 1. The samples were analysed by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and gas chromatography-mass spectrometry (GC-MS).

Table 1: Details of samples and analysis. Weights refer to samples prepared for GC-MS analysis

Sample	K no.	Description	Weight (g)	Analysis
1	K235 (tray)	Black layer within tray, overlaid by soil	0.00191	FTIR; Raman; GC-MS
2	K234 (foil)	White material adjacent to (?rivet) perforation on reverse of foil	0.00014	FTIR; Raman; GC-MS
3	K235 (tray)	Waxy appearing surface of red/brown material with impressions of foil relief	0.00064	FTIR; Raman; GC-MS
4	K234 (foil)	Fleck of bright green material from same location as 2	-	FTIR; Raman
Soil	Associated with K234/5 foils	Miscellaneous soil associated with foils #234 and #235	0.00417	FTIR; Raman; GC-MS

Methods

Samples were removed from the objects using a fine needle or a clean scalpel blade and collected into vials using tweezers, all under a stereoscopic microscope.

For FTIR, a small sub-sample was removed and transferred onto the window of a diamond micro-compression cell.

For Raman analysis a small sub-sample was removed and placed on a glass slide.

Samples for GC-MS were transferred to glass vials and accurately weighed prior to sample preparation. All the samples analysed by GC-MS were solvent-extracted to analyse for lipids (e.g. fats, waxes, oils, bituminous materials) using a mixture of dichloromethane and methanol (2:1 v/v). Prior to analysis they were derivatised and an internal standard was added to allow quantification.

Full details of sample preparation and analytical methods are in the Appendix.

Results

Sample 1: Black layer within K235 tray

A mixture of substances was detected in this sample using FTIR, Figure 1a. The strong, shouldered band at 1100-1000 cm^{-1} assigned to Si-O stretching vibrations compares well to the spectrum of impure burnt ochre from the IRUG database (shown in the figure for comparison). Natural earth pigments such as this ochre example typically contain clay and quartz silicates as well as the oxides (iron and manganese) that are responsible for their colour. Of the latter, only goethite displays absorption bands in the mid-IR region examined here, so spectra for earth pigments correspond primarily to their (alumino)silicate components, as seen here. Smaller sharper bands at $\sim 3600 \text{ cm}^{-1}$ are due to the presence of hydrated layered silicates, such as kaolinite. Proteinaceous material is indicated by amide bands at $c.1650 \text{ cm}^{-1}$ (C=O) and $c.1530 \text{ cm}^{-1}$ (N-H bend/C-H stretch) and the broad N-H stretch at $c.3350 \text{ cm}^{-1}$. The hydrocarbon stretches at $c.2925 \text{ cm}^{-1}$ and $c.2850 \text{ cm}^{-1}$ and just discernible bands at $c.1740 \text{ cm}^{-1}$ (ester C=O) and $c.1465 \text{ cm}^{-1}$ (C-H bending) are consistent with beeswax (Derrick *et al.* 1999).

Analysis by Raman spectroscopy showed the presence of amorphous carbon, identified from the two diffuse peaks at $c.1360$ and $c.1590 \text{ cm}^{-1}$ in the spectrum (Figure 1b). The absence of any phosphate peak at $c.960 \text{ cm}^{-1}$ rules out a burnt bone or ivory origin for the carbon, which must therefore be interpreted as lamp black or soot (produced from vegetable matter or oil) or crushed charcoal. The spectrum displays no evidence for the earth minerals observed by FTIR, probably because of the much smaller area sampled by the focused laser beam (2-3 μm) of the Raman spectrometer.

The beeswax component of the sample was clearly observed in the data obtained from analysis by GC-MS (Figure 1c), indicated by a suite of even-carbon-numbered wax esters (42–52 carbon atoms) accompanied by C_{16} and C_{24} fatty acids (Heron *et al.*, 1994; Evershed *et al.*, 1997). The alkanes that typically accompany these compounds in beeswax were only present at trace level but this is consistent with their loss by sublimation when beeswax is heated or melted (Regert *et al.* 2001). GC-MS analysis targeting amino acids, following the protein evidence from the FTIR data, was not attempted because column degradation problems resulted when such analysis was undertaken on samples from other Staffordshire Hoard items earlier in the year (Steele and Hacke, report PR07444-7).

Sample 2: White material on reverse of K234 foil

Analysis by FTIR produced a spectrum (Figure 2a) exhibiting bands typical of beeswax at $c.2925 \text{ cm}^{-1}$ (C-H asymmetric), $c.2850 \text{ cm}^{-1}$ (C-H symmetric), $c.1740 \text{ cm}^{-1}$ (ester C=O) and $c.1465 \text{ cm}^{-1}$ (C-H bending). An additional sharp doublet peak (at $c.1575/1540 \text{ cm}^{-1}$) indicates the presence of calcium salts of carboxylic acids (C-O asymmetric), which correspond well to the calcium palmitate reference spectrum shown. Calcium compounds in the sample might account for its bright white colour.

The beeswax was also detected by Raman spectroscopy (Figure 2b) with characteristic peaks at $c.1450 \text{ cm}^{-1}$, $c.1300 \text{ cm}^{-1}$, $c.1130 \text{ cm}^{-1}$ and $c.1160 \text{ cm}^{-1}$ (Vandenabeele *et al.* 2000) No features relating to the acid salts seen by FTIR and no inorganic materials were observed.

Well-preserved beeswax was observed when the material was analysed by GC-MS (Figure 2c) with abundant even-carbon-numbered wax esters (C_{42} - C_{52}) and corresponding hydroxyl esters. Characteristic fatty acids, C_{16} and C_{24} , were also observed. The *n*-alkanes and

alcohols typical of beeswax were seen only at very low abundances and the other long chain free fatty acids (C₂₂-C₂₈) were also present only at low levels. It seems likely, given the indication of acid salts in the FTIR spectrum, that the free fatty acids have been depleted by salt formation as has previously been observed in beeswax associated with archaeological metals (Stacey 2011).

Sample 3: Waxy soil-coloured material with K235 foil impressions

The FTIR spectrum obtained from this sample (Figure 3a) is dominated by a strong, broad band at 1100-1000 cm⁻¹ attributable to Si-O stretching. As for Sample 1, this is interpreted as a natural earth comprising clay and quartz silicates. The best spectral match from the IRUG library is the impure burnt ochre shown in the figure. This interpretation is supported by the evidence from Raman spectroscopy which detected the red pigment hematite (α -Fe₂O₃), Figure 3b.

Beeswax was observed when the material was analysed by GC-MS, with a composition comparable to that seen in Sample 1 (Figure 3c).

Sample 4: Bright green material from K234 foil

The FTIR analysis produced a spectrum (Figure 4a) displaying strong C-O stretches at c.1550 cm⁻¹ and c.1350 cm⁻¹ and sharp O-H bending vibrations at c.1100-1000 cm⁻¹, all attributable to hydrated carbonates. The spectrum compares well with the reference spectrum for the copper carbonate hydroxide mineral malachite (CuCO₃·Cu(OH)₂). This interpretation is supported by the results from Raman spectroscopy, see Figure 4b.

Soil associated with foils K234 and K235

The FTIR spectrum obtained from the soil (Figure 5) shows a dominant broad band at 1200-900 cm⁻¹ attributable to Si-O stretching and the smaller, sharper bands around c.3600 cm⁻¹ characteristic of hydrated layered silicates. The spectrum is consistent with a soil containing clay and quartz components and compares well with spectra for natural earth pigments from the in-house spectral library and the IRUG database. No meaningful spectrum could be obtained from the soils by Raman spectroscopy.

Only low levels of organic material were detected by GC-MS analysis and no compounds indicative of beeswax were observed.

Discussion

The results support the interpretation of the black layer as a construction material used as a fixative or filler within the void between the foils and the tray. It is unclear whether the waxy red/brown layer represents a separate upper layer of beeswax fixative or fill, or if it is formed from accumulation of soil-derived material that has mixed with beeswax from the layer below. Similar mixtures of beeswax, protein and earth minerals were observed in samples from the backing fills within cloisonné cells from other Staffordshire Hoard fragments (K356_2; K451_5; K673 and K1003_4), one of which (K673) was an undisturbed cell that was exposed during conservation treatment (Steele and Hacke, PR07444-7). It is interesting to observe such similar materials used in these different metal-working contexts and this parallel in fill technology may be significant for understanding production practices.

The malachite can be interpreted as a product of copper corrosion. There is no obvious source for this from metals represented on the helmet. As the green flecks are dispersed throughout the black layer it is possible that they may have been introduced during processing of that material at the time of manufacture rather than as corrosion products from other helmet components.

The white material is clearly distinct from the other samples, comprising well-preserved beeswax and containing no detectable mineral substances. Acid salts in the beeswax may be alteration products of the beeswax fatty acids. Similar white beeswax deposits have been reported in other Staffordshire Hoard items (K291; K546_1 and K1062_1) sometimes accompanied by calcium carbonate (Steele and Hacke, PR07444-7). The localised distribution of this white material adjacent to the rivet holes is hard to interpret but does seem to be intentional, and presumably serves a different function to other materials.

The low levels of organic material - and absence of beeswax - in the soil is a good indicator that the paste materials contain little or no contamination from soil-derived organic components. The similarity in composition between soils and earth minerals makes it hard to be certain of the extent of inorganic contamination from this source.

Conclusions

The sampled materials are construction components containing organic and inorganic substances. The lower black layer comprising carbon and protein is interpreted as a fixative or fill. The upper red/brown layer composed of beeswax and ochre-like material, may be a distinct fill or fixative layer or could be an accumulation of soil-derived material mingled with wax from the layer below. Well-preserved white beeswax identified adjacent to the rivet hole in tray/foil K234 seems to be a discrete material with a different purpose. The origin of the malachite, which is distributed as flecks throughout the layers, is unclear; it is possible that it is a component of the pastes rather than a corrosion product from metal components of the helmet.

The composition of these pastes is very similar to the backing fills within cloisonné cells from other Staffordshire Hoard fragments (K356_2; K451_5; K673 and K1003_4) and this may be significant for interpreting the manufacturing parallels between these very different metal artefacts.

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Date: 7th January 2014

Figures

Figure 1a: FTIR spectrum obtained from Sample 1 (K235) shown with library reference spectra for beeswax, hide glue (protein) and ochre.

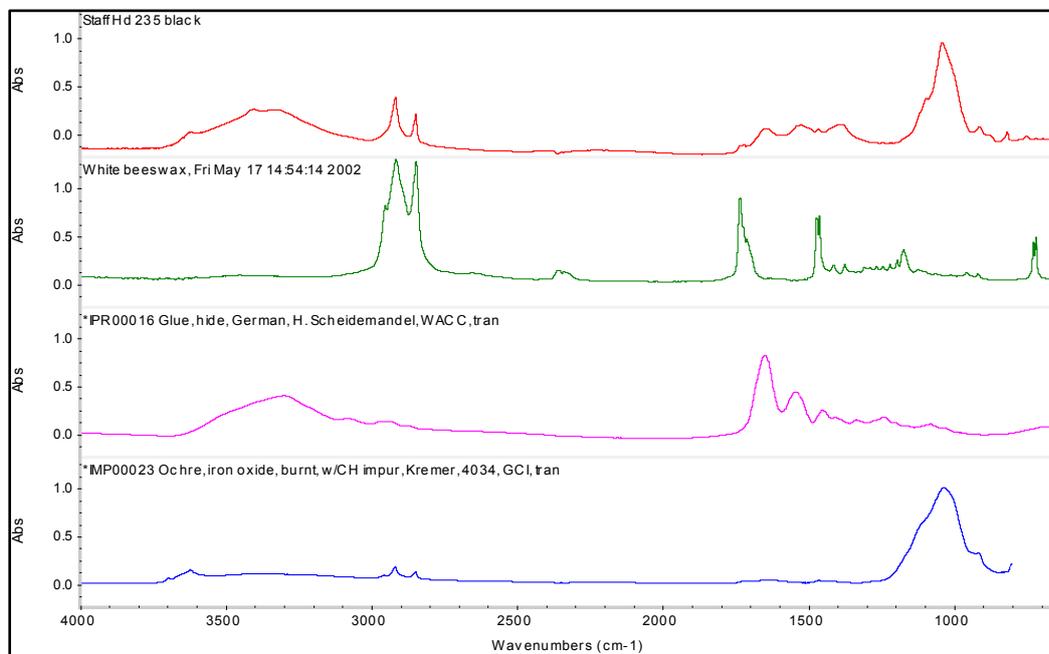
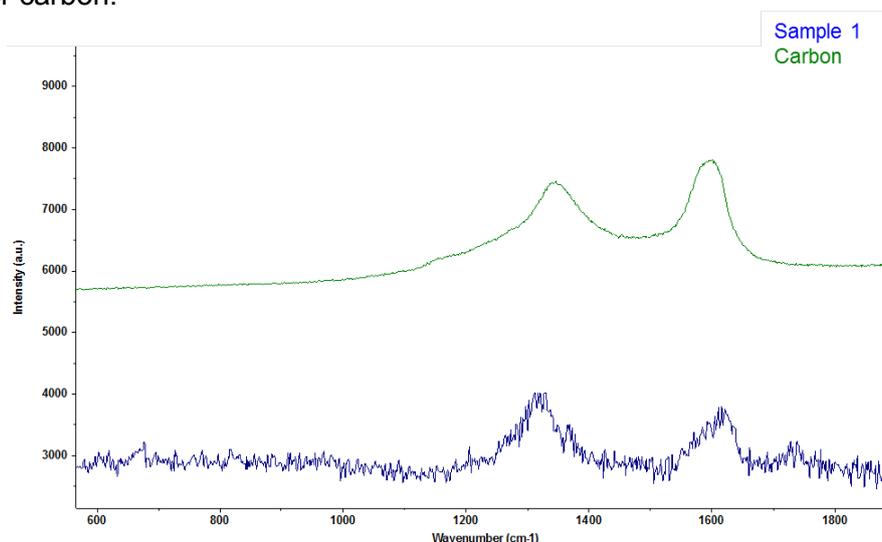


Figure 1b: Raman spectrum obtained from Sample 1 (K235) shown with library reference spectrum for carbon.



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Figure 1c: Partial (10-40 min) total ion chromatogram obtained by GC-MS analysis of Sample 1 (K235) with peaks labelled to indicate: F_n – fatty acids and W_n – wax esters where n = no of acyl carbon atoms.*internal standard (tetratriacontane).

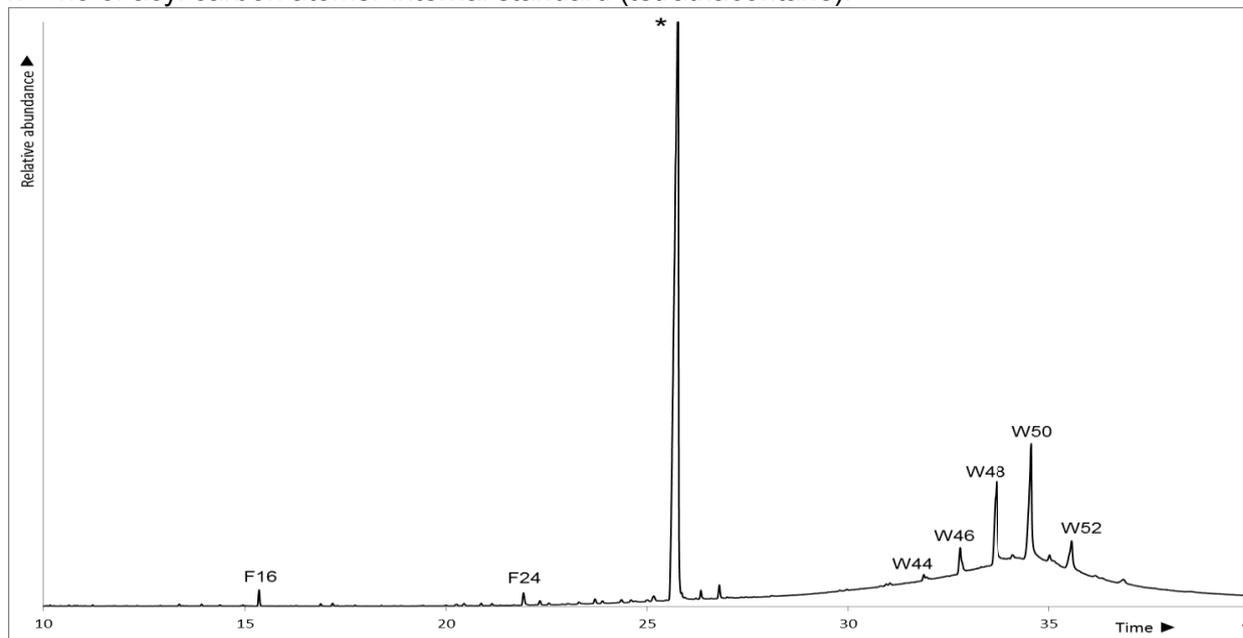
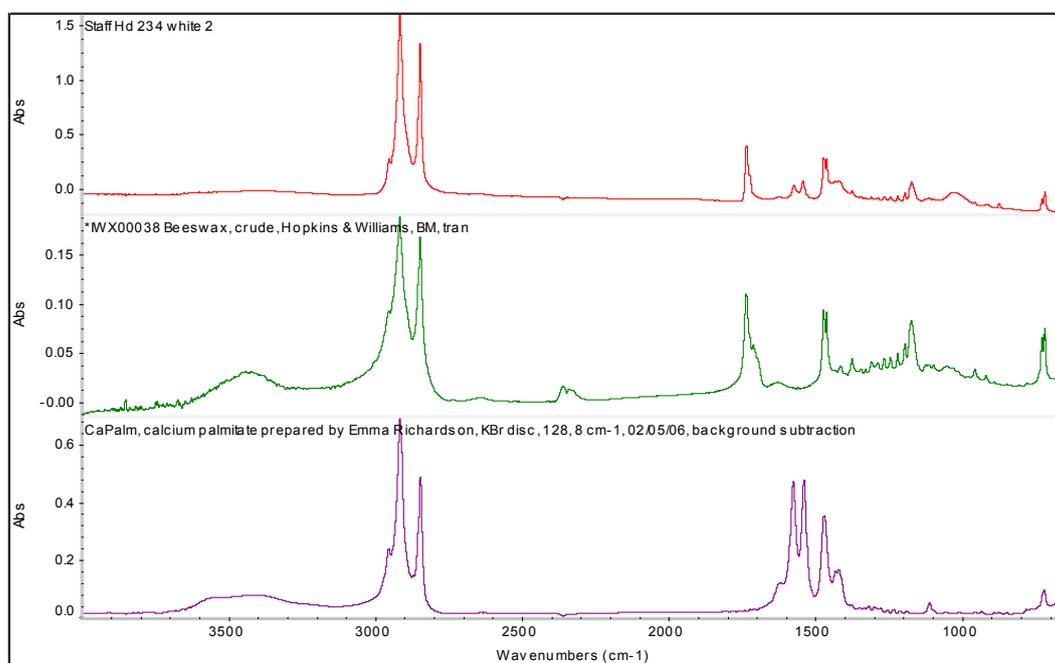


Figure 2a: FTIR spectrum obtained from Sample 2 (K234) shown with library reference spectra for beeswax and calcium palmitate.



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Figure 2b: Raman spectrum obtained from Sample 2 (K234) shown with library reference spectrum for beeswax.

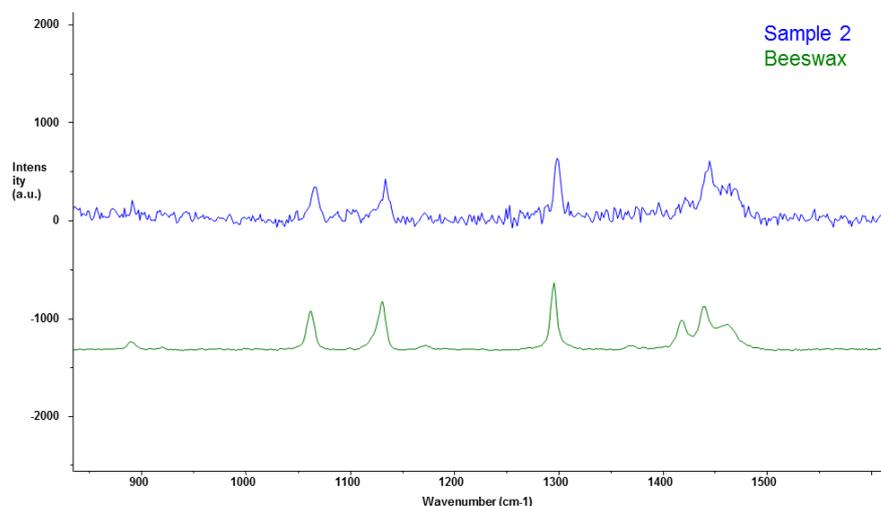
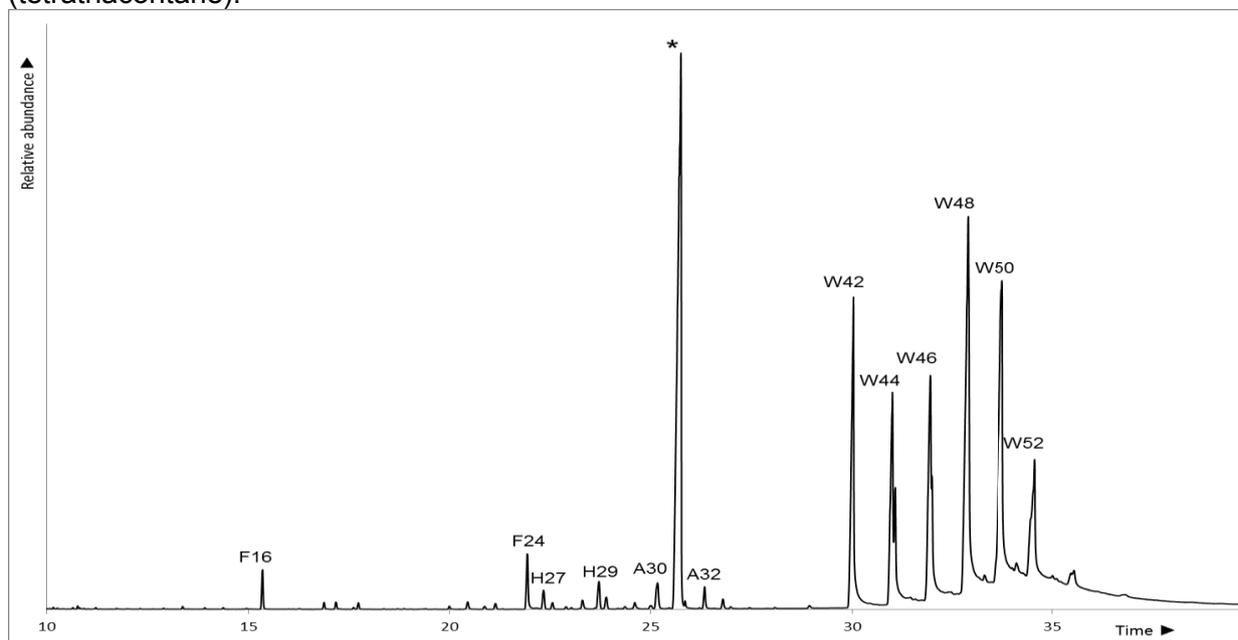


Figure 2c: Partial (10-40 min) total ion chromatogram obtained by GC-MS analysis of Sample 2 (K234) with peaks labelled to indicate: F_n – fatty acids; H_n – alkanes; A_n – alkanols and W_n – wax esters where n = no of acyl carbon atoms. *internal standard (tetratriacontane).



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Figure 3a: FTIR spectrum obtained from Sample 3 (K235) shown with library reference spectrum for impure red ochre.

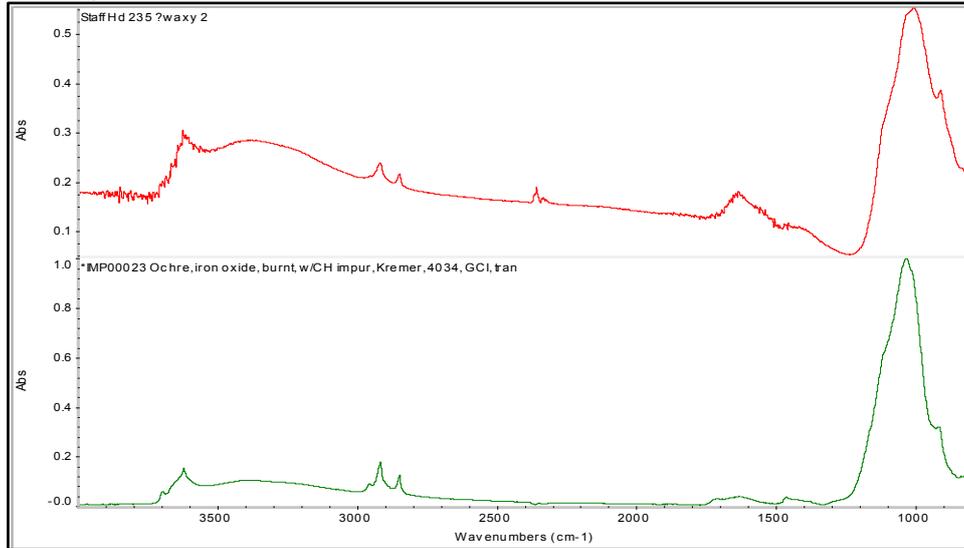
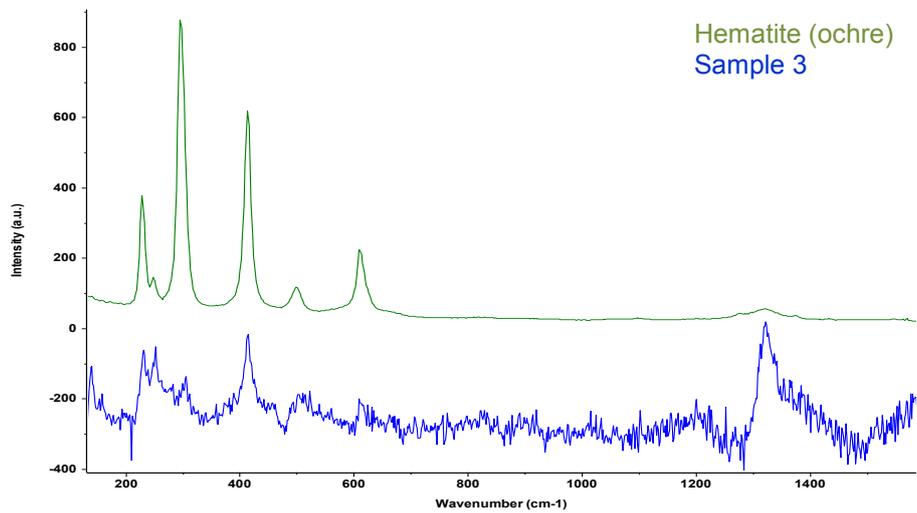


Figure 3b: Raman spectrum obtained from Sample 3 (K235) shown with library reference spectrum for hematite (red ochre).



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Figure 3c: Partial (10-40 min) total ion chromatogram obtained by GC-MS analysis of Sample 3 (K235) with peaks labelled to indicate: F_n – fatty acids and W_n – wax esters where n = no of acyl carbon atoms. *internal standard (tetratriacontane).

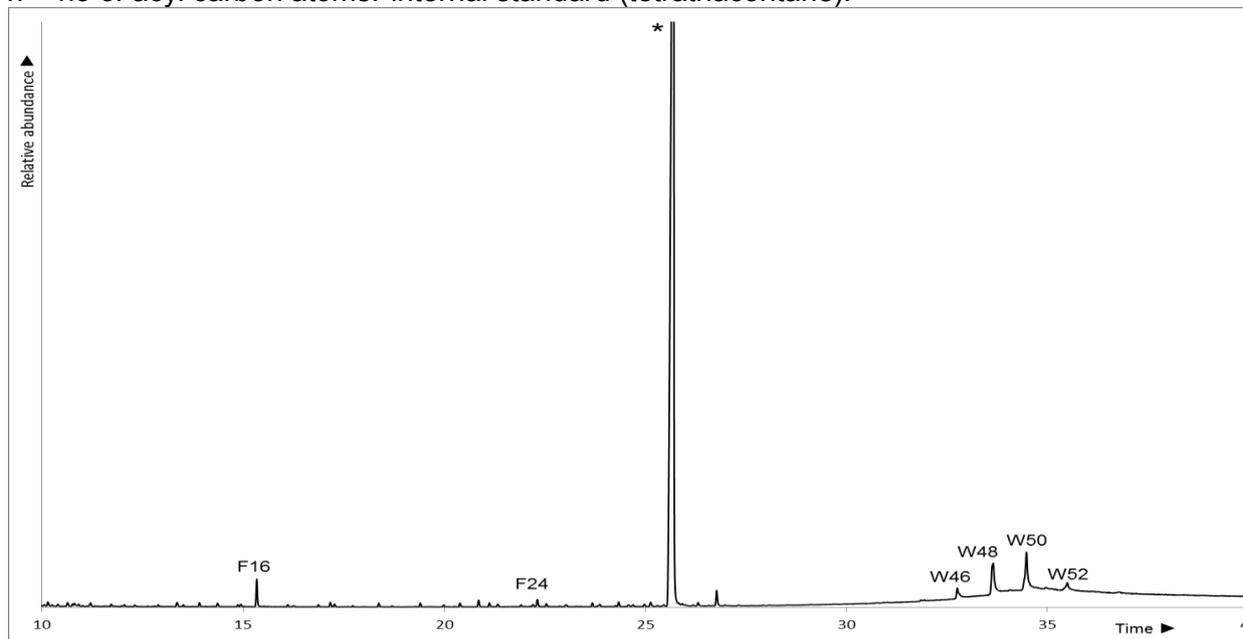


Figure 4a: FTIR spectrum obtained from Sample 4 (K234) shown with library reference spectrum for malachite.

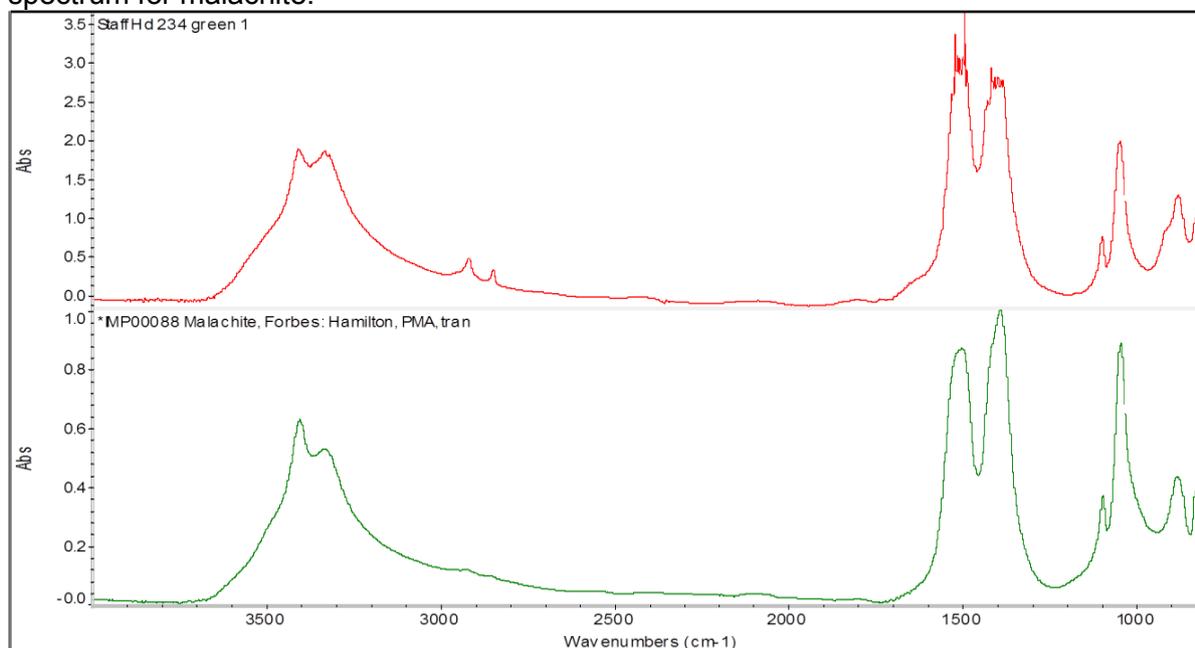


Figure 4b: Raman spectrum obtained from Sample 4 (K234) shown with library reference spectrum for malachite.

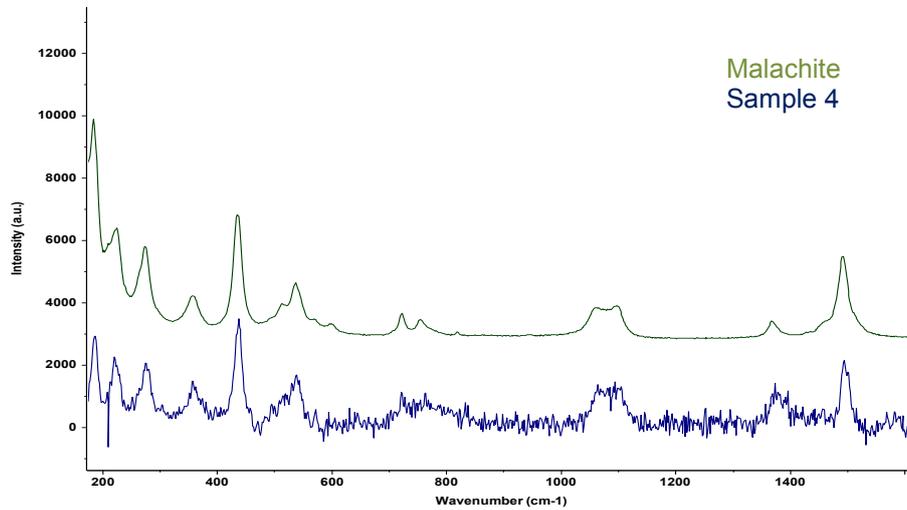
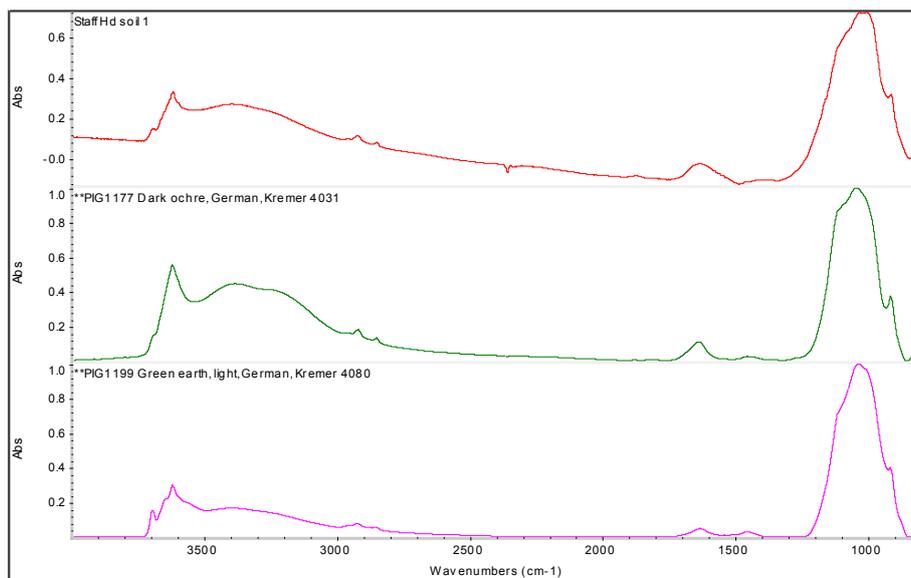


Figure 5: FTIR spectrum obtained from the soil (K234/5) shown with library reference spectra for impure ochre and green earth (kaolin).



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Appendix – Methods

FTIR

FTIR Spectroscopy was performed on a Nicolet 6700 with Continuum IR microscope equipped with MCT/A detectors. The samples were analysed in transmission mode, flattened in a diamond micro-compression cell. The cell was opened and the flattened sample supported on one diamond window, a clean area of which was used for background spectra. The field of view was controlled by the sliding aperture which, when fully open, gives a maximum area of analysis of 150x150 μm . The spectra were acquired over a range of 4000-650 cm^{-1} using 32 scans at a resolution of 4 cm^{-1} and automatic gain. The spectra produced were characterised by comparison with reference spectra from an in-house library and the IRUG database

Raman spectroscopy

Raman analysis was carried out using a Dilor Infinity spectrometer with green (532 nm) and near infrared (785nm) lasers, with a maximum power of 4mW at the sample. The spectra produced were identified by comparison with reference spectra from the in-house data base.

GC-MS

To prevent contamination during sample preparation nitrile gloves were worn at all times, all glassware and tools were washed in solvent and all reagents were Analar or HPLC grade (99.5% pure or better). Blank samples were prepared and analysed with each batch of samples to check for contamination introduced during sample preparation and analysis. Each sample was crushed in an agate pestle and mortar and accurately weighed into a

clean glass vial. Samples were then placed in an ultrasonic bath for 15 minutes with a mixture of dichloromethane (DCM) and methanol (2:1 v/v). After centrifuging for 10 minutes at 2000 rpm the supernatants were pipetted off into clean vials. This was repeated twice more, combining the three extracts of each sample. The excess solvent was evaporated off the samples under a gentle stream of dry nitrogen (N₂) while heating at 40° C. A measured amount of an internal standard, C₃₄ *n*-alkane, was added to each sample to allow quantification. Samples were derivatised for GC-MS by heating at 70° C in closed vials with 30 – 50 µl N,O-bis(trimethylsilyl)fluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS).

GC-MS analysis

These were run on an Agilent 6890 gas chromatograph attached to an Agilent 5973 mass selective detector. The gas chromatograph was fitted with an SGE HT-5 column, 12 m x 0.22 mm x 0.1 µm. The oven was programmed for an isothermal hold at 50°C for 2 minutes, rise at 10° per minute to 370°C and a final isothermal hold for 15 minutes. Helium was used as the carrier gas at a constant flow of 1.5 ml per minute. The Programmable Variable Temperature (PTV) injector was operated in on-column mode with the temperature programmed to match the oven temperature. The column was inserted directly into the mass spectrometer with the interface at 350°C. Mass spectral data was acquired in scan mode over a mass range of 50 to 750.

All data were analysed using the Agilent MSD Chemstation data analysis software. Mass spectra were identified by comparison with the NIST mass spectral database and published mass spectra.



Staffordshire Hoard Research Reports

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Contextualising Metal-Detected Discoveries: Staffordshire Anglo-Saxon Hoard

Historic England Project 5892

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