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Excavation & Analysis

Osborne House, East Cowes, Isle of Wight
Scientific Examination of the Terrace Statues

Sarah Paynter and David Dungworth

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OSBORNE HOUSE
EAST COWES
ISLE OF WIGHT

SCIENTIFIC EXAMINATION OF THE TERRACE STATUES

Sarah Paynter and David Dungworth

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SUMMARY

A survey of selected metal statues was carried out to determine the nature of the metal, as well as any coatings applied to them in the past or more recently, to inform future conservation work. Portable XRF (X-ray fluorescence) was used to confirm the existing identifications of zinc and 'bronze' metals given in the curatorial report (Hunter 2015). Bronze is an alloy of copper and tin, but the term is often used more broadly when referring to decorative metalwork or art, encompassing a range of copper alloys.

Documentary accounts describe how the zinc statues were originally plated with a copper alloy (Hunter 2015), a process repeated in 1860, some of which still survived at the time they were conserved in 1991. The zinc statues were also coated in a protective coating in 1991, which gave the otherwise grey metal a 'bronze' appearance. This coating is now cracking and is lifting in places, exposing grey metal beneath.

Two fragments of failed protective coating were characterised using a Scanning Electron Microscope (SEM).

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INTRODUCTION

Osborne House, Isle of Wight, was a formal residence for Queen Victoria and her family. It was constructed between 1845 and 1851 and following the death of Queen Victoria (1901) it was used as a naval college. The house was initially opened to the public in 1954 and since 1986 has been managed by English Heritage.

The terrace on the south side of Osborne House is decorated with 29 metal statues, collected and commissioned by Prince Albert specifically for this location. Some of the statues are zinc and others copper alloy, referred to generically as 'bronze' (Hunter 2015). Zinc is a grey metal so the zinc statues were originally electroplated with copper, however accounts show that the plating had to be repeated within a short timeframe (Hunter 2015). More recently they have received a protective surface coating to again give them the appearance of bronze.

English Heritage curators and conservators requested scientific analysis of the statues and protective coatings in order to inform wider conservation decisions.

METHODOLOGY

Portable X-ray fluorescence (pXRF) was used for the statues themselves because it provides a rapid semi-quantitative analysis of the surface, and is non-destructive. The pXRF is a Niton XL3t with pre-set methods, each analysing for a particular range of elements. The two methods used for the statues were:

1. General Metals

Light (20 seconds): Magnesium (Mg), Aluminium (Al), Silicon (Si), Phosphorus (P), Sulphur (S)

Low (20 seconds): Titanium (Ti), Vanadium (V), Chromium (Cr)

Main (20 seconds): Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Selenium (Se), Zircon (Zr), Niobium (Nb), Molybdenum (Mo), Ruthenium (Ru), Palladium (Pd), Silver (Ag), Cadmium (Cd), Tin (Sn), Anitmony (Sb), Hafnium (Hf), Tantalum (Ta), Tungsten (W), Rhenium (Re), Gold (Au), Lead (Pb), Bismuth (Bi)

2. Cu/Zn Mining

Light (30 seconds): Mg, Al, Si, P, S

Low (10 seconds): Potassium (K), Calcium (Ca), Ti, V, Cr

Main (10 seconds): Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rubidium (Rb), Sr, Zr, Nb, Mo, Hf, Ta, W, Re, Au, Pb, Bi, Ba

High (10 seconds): Pd, Ag, Cd, Sn, Sb, Barium (Ba)

The General Metals method was used primarily to analyse the metal alloys, while Cu/Zn Mining mode was used to investigate the coatings applied to the statues because this mode includes a greater range of elements (such as Ca and Ba), which are present in the coating. Further consideration of the XRF analyses is provided in the appendix.

SEM-EDS (scanning electron microscopy – energy dispersive spectrometry) was used to analyse a detached fragment of the coating. This technique provides a high magnification image of the sample. The images show areas with different compositions as different shades in a grey-scale. These areas can be targeted for analysis, allowing the different components in the coating to be identified. The instrument used was an FEI InspectF SEM (analytical conditions, 25kv and 1.2nA) fitted with an Oxford Instruments X-act X-ray detector.

The coating and adhering corrosion products were also analysed by X-ray diffraction (XRD). This technique identifies crystalline phases, and is useful for investigating corrosion products and paint pigments. The machine used was a Bruker D8 (analytical conditions, 40kV and 40mA) with a Lynx Eye detector.

RESULTS

The 'bronze' statues

Eight statues are copper or copper alloy, generically referred to as 'bronze' (Table 1).

Table 1: Chemical composition of 'bronze' statues from Osborne House Terrace (not normalised to 100wt%), all using GM (General Metals) method.

Statue	Ref	Workshop	Cu	Sn	Zn	Pb	Bi	Fe	Si	P	S
Eos	79704828	Francis	88.6	<0.1	0.2	0.3	<0.1	4.4	3.8	<0.3	0.8
Boy with Goose	79704829	Francis	91.8	<0.1	0.1	1.0	<0.1	0.8	1.8	0.5	2.4
Infant on sea monster 1		Theed	88.8	<0.1	0.1	0.1	<0.1	1.6	<0.5	<0.3	<0.2
Infant on sea monster 2		Theed	98.9	<0.1	0.1	0.1	<0.1	0.9	3.4	<0.3	4.8
Ocean	79704822	Braun	98.5	<0.1	<0.1	0.4	<0.1	0.9	<0.5	<0.3	<0.2
Caesar	79704819	Braun	99.6	<0.1	<0.1	0.1	<0.1	0.3	<0.5	<0.3	<0.2
Brutus		Braun	99.4	<0.1	0.1	0.2	<0.1	0.4	<0.5	<0.3	<0.2
Andromeda		John Bell	86.6	5.1	2.5	2.2	0.2	1.3	<0.5	<0.3	1.5

The pXRF analysis indicates that the majority of the 'bronze' statues are fairly pure copper; alloying elements that would normally be expected in castings, such as tin, zinc and lead, are largely absent. The implications of this are discussed later (see Discussion). Some iron, silicon, sulphur and phosphorus were also detected, reflecting the fact that these results also include surface corrosion and contamination.

The John Bell statue of Andromeda however contains tin, zinc and lead in addition to copper, so is slightly leaded gunmetal (gunmetal is a term for copper alloys containing both tin and zinc whereas a bronze, in metallurgical terms, is an alloy of copper and tin). Such alloys have been widely used in copper alloy casting for centuries (Heyworth *in* Egan and Pritchard 1991).

The zinc statues

The zinc statues were originally copper plated but this plating degraded quickly and the statues now have a bronze-effect coating, which was applied during conservation work in the 1990s. The binder in the current coating cannot be identified with this equipment, but it is likely to be polymer based. This bronze-effect coating has lifted and detached in many small areas (Figure 1). No evidence of the original 19th-century copper plating was observed on any of the exposed metal. One statue (Venus) has had a new coating applied recently, which may differ from the rest.

Where possible each statue was analysed twice: once on a spot with an intact coating and once on a spot where the grey metal beneath was exposed. Nevertheless, some of the exposed areas of metal were smaller than the area analysed by the pXRF (approximately 3mm diameter), and rarely flat, and so even areas listed as 'metal' could include a contribution from the coating. In some instances each spot was analysed using both modes (General Metals and Cu/Zn mining) for the reasons discussed previously. Higher levels of zinc were consistently reported using General Metals. Analyses with very low analytical totals were omitted.

Fig 1: Osborne House statue (Urania) showing areas where the bronze-effect coating has deteriorated, exposing the underlying zinc metal.

The pXRF analyses confirm that the statues are made from zinc. Low levels of zinc were also detected when analysing coated areas due to the primary X-ray beam completely penetrating the coating, giving a composite analysis of the coating and the underlying metal.

The pXRF results show the presence in some instances of copper, lead and iron, but this may be because there are low levels of these elements in the bronze-effect coating (see SEM-EDS analysis of the coating below, Table 3). This is also consistent with the fact that higher levels of copper were typically detected in the coated areas (Table 2), and because the results for Venus, which has been recoated more recently, are higher than for the other statues. Small amounts of copper may be present as surviving traces of the 19th-century copper plating; although no traces of the plating were observed, these might be obscured by subsequent corrosion. Small amounts of these elements may also be present as part of the metal alloy itself.

Tin is occasionally detected, but always with elevated levels of lead, and so the spots analysed in these instances may have been close to soldered joints.

Table 2: Chemical composition of zinc statues from Osborne House Terrace (not normalised to 100wt%). Methods used are Cu/Zn (copper/zinc mining) and GM (General Metals); S = statue, P = Plinth.

Statue	Ref	Workshop	Method	Analysis	Zn	Cu	Sn	Bi	Pb	Fe	Mn
Urania		Miroy	Cu/Zn	Coating	34.7	10.5	0.6	<0.1	1.1	1.7	0.1
			GM	Metal (S)	70.8	0.5	<0.1	<0.1	1.6	2.6	0.1
			GM	Metal (P)	59.2	6.7	0.7	<0.1	3.7	8.5	0.2
Ceres	79704791	Geiss	GM	Coating	65.2	3.2	<0.1	<0.1	4.2	4.4	0.1
			Cu/Zn	Metal	17.1	0.4	0.1	<0.1	1.0	2.4	0.1
			GM	Metal	25.7	4.8	16.4	<0.1	16.4	7.4	0.3
Enterpe	79704782	Geiss	GM	Coating	62.3	5.0	<0.1	<0.1	1.9	4.9	0.2
			GM	Metal	29.9	1.1	0.3	<0.1	1.5	9.6	0.8
Juno		Geiss	Cu/Zn	Coating	35.5	<0.1	<0.1	<0.1	0.4	1.8	0.1
			GM	Coating	62.8	5.6	<0.1	<0.1	3.3	3.5	0.2
			GM	Metal	70.5	5.9	<0.1	<0.1	2.2	2.3	0.1
Urania	79704783	Geiss	GM	Coating	66.6	4.9	0.1	<0.1	1.3	4.8	0.2
			GM	Metal	49.5	2.4	0.3	<0.1	1.0	5.9	0.3
Venus		Geiss	GM	Coating	43.7	14.3	1.8	<0.1	4.8	6.0	0.3
			GM	Coating	51.9	12.4	3.8	<0.1	3.4	4.7	0.1
			Cu/Zn	Metal (S)	23.8	9.2	0.8	<0.1	1.1	2.5	0.1
Autumn		Moreau	GM	Coating	60.9	5.7	0.2	<0.1	1.7	4.5	<0.1
			GM	Metal	58.8	1.0	0.8	0.1	2.8	10.4	<0.1
Summer	79704831	Moreau	GM	Coating	51.5	6.3	0.9	0.1	5.1	6.8	<0.1
			GM	Metal	62.4	0.3	1.3	0.2	6.8	3.7	<0.1

THE BRONZE-EFFECT COATING

Small fragments of coating had detached from the statue of Urania, which were analysed using scanning electron microscopy (SEM) with an energy dispersive x-ray spectrometer (EDS) (Table 3). The SEM images (Figures 2 and 3) show that the coating is made up of a binder packed with angular and fibrous particles, mostly less than 25 microns in diameter. The binder is probably a polymer, which this technique is unable to detect. The coating is around 200 microns thick.

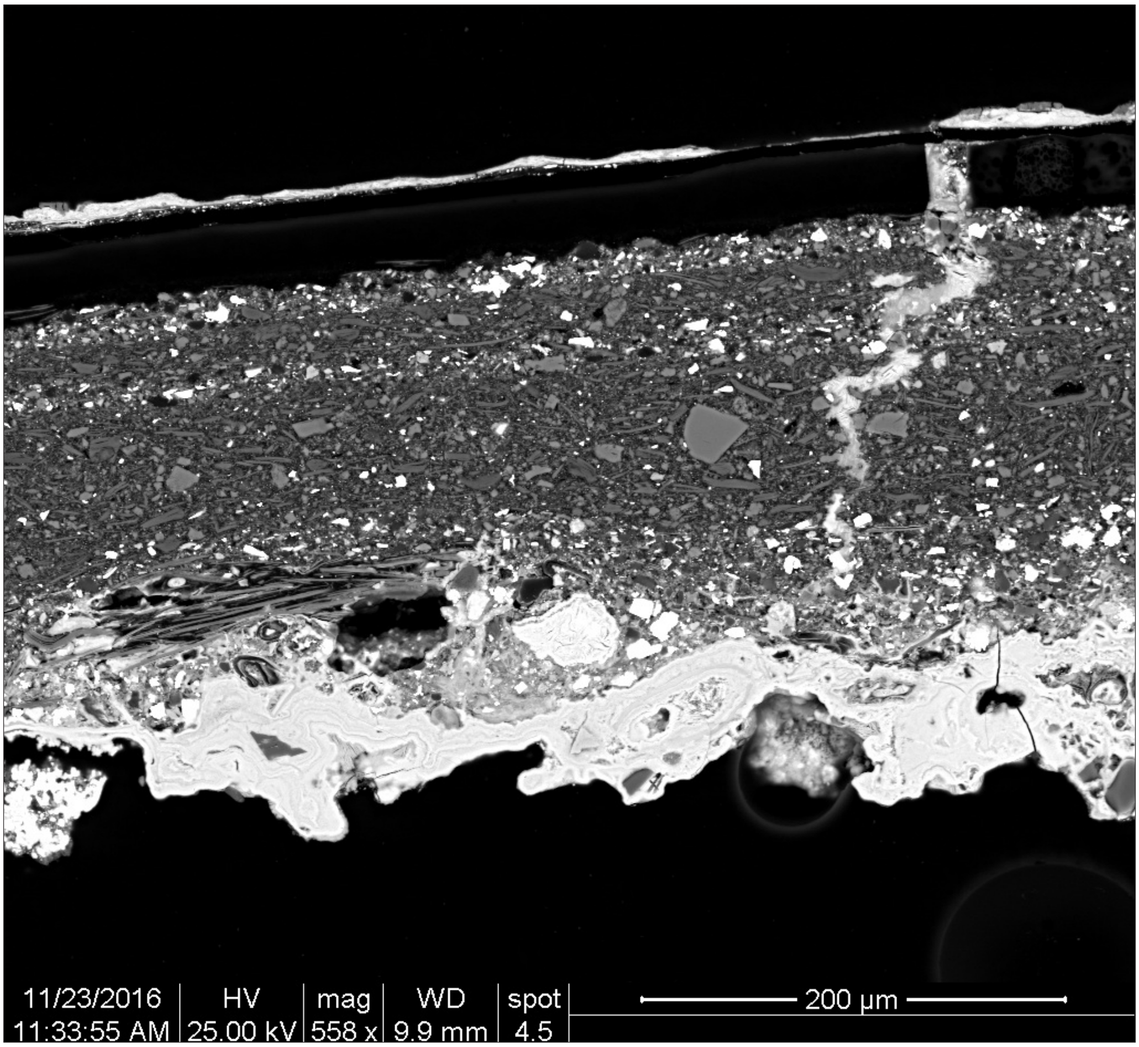

Fig 2: Back-scattered SEM image of the coating, with adhering metal corrosion layer at the bottom (white), and an applied surface layer, perhaps wax, at the top (black). The filler particles in the coating are barytes (white), calcite (grey angular) and magnesium silicate (grey plates). There appear to be at least two applications of the coating. The crack to the right has filled with precipitated material.

The particles in the binder are barium sulphate (an opaque white pigment), calcium carbonate, and a platey magnesium silicate mineral (possibly talc [$Mg_3Si_4O_{10}(OH)_2$], also commonly used in coatings). Some aluminium oxide was detected, which is present in the platey silicates, and lead was detected in the barium sulphate.

Titanium and iron oxides were also present; some associated with the silicate filler, but there may be more dispersed finely in the matrix. Low levels of copper are present.

A further layer has been applied over the top of the coating (Figure 3). This is again made up of light elements that cannot be detected, but it is visible in the SEM images. It is unstable under the electron beam so maybe wax or polish, applied as part of the protective maintenance programme. This layer is about 50 microns thick.

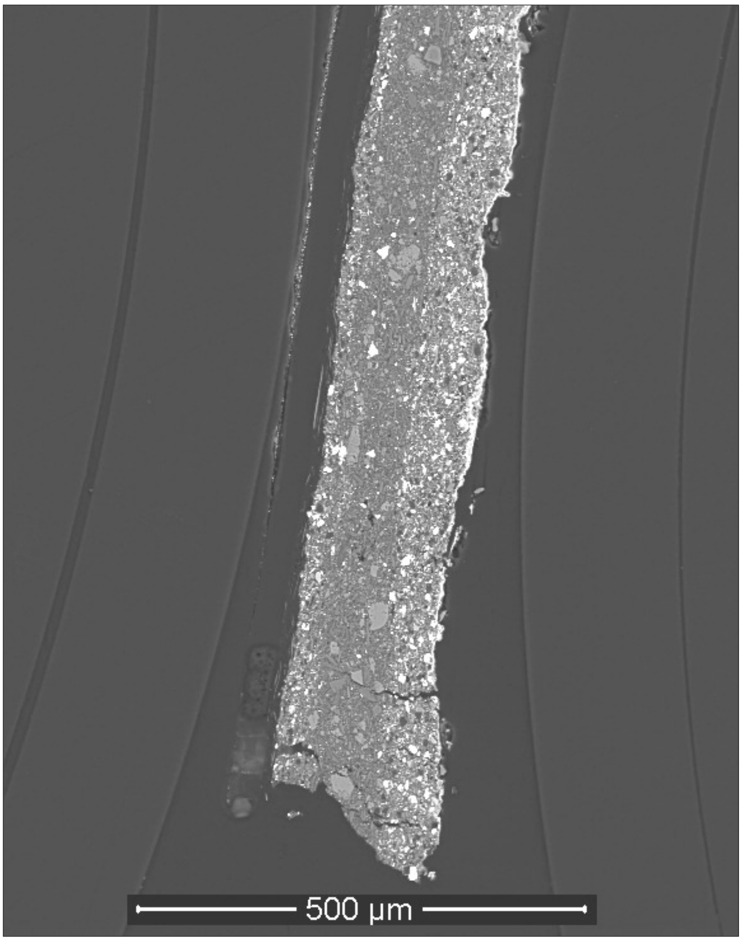

Fig 3: A sample from the body of the statue, showing the protective maintenance layer (possibly wax) on the left (black) and probably two layers of bronze-effect coating – the metal surface would have been on the right (the fragment of paint has been held upright in the epoxy resin by a plastic clip which is visible as the curved regions on either side of the sample).

A layer from the surface of the metal is still attached to the coating, and some corrosion products have also filled a crack in the coating shown in Figure 2. Areas of corrosion adhering to the metal are comprised mainly of zinc, and may be zinc carbonate, which forms as a passivating layer on the surface of zinc metal, inhibiting further corrosion. However the precipitated material in the crack, which was probably originally in solution, contains a significant proportion of sulphur and some chlorine.

Table 3: Average composition of the bronze-effect coating by SEM-EDS, normalised (not including the polymer component, which constitutes approximately 40wt%), (Mn, Co and K below detection).

MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	CaO	TiO_2	Fe_2O_3	CuO	ZnO	BaO	PbO
16.3	3.5	28.0	0.9	2.7	2.1	24.8	10.2	2.3	0.11	2.3	5.4	1.4

THE SURFACE DEPOSITS

XRD analysis was used to analyse the deposits on the reverse of the surface coating. The only additional compound identified using this method was halite, indicating the presence of salt at the interface between the surface coating and metal. Otherwise only the fillers in the bronze-effect coating fillers were detected.

DISCUSSION

The ‘bronze’ statues

Casting pure copper is technically difficult as the molten metal tends to absorb air and readily forms defects (Coghlan 1975, 65). Therefore the purity of the copper used for the majority of the ‘bronze’ statues, indicated by the pXRF analyses, suggests that these statues were not formed by casting. Instead they are probably electrotypes, made by depositing copper from a solution onto a mould by applying an electrical current.

The electrotyping process became popular in the 19th century, and was of particular interest to Prince Albert, who was given a demonstration of the process at Elkingtons in Birmingham in 1843 (Jones 2012). Emil Braun contacted Elkingtons about the process in 1846, and a large group of Braun’s models were used subsequently by Elkingtons (Marsden 2012). Jones (2012) reports that a number were purchased by Prince Albert for the Royal Collection in the 1840s and the Exhibition of Industrial Manufacturers in Birmingham, in 1849, featured three electrotype busts by Braun, lent by Prince Albert, including *Brutus* (RCIN 41881).

The Braun pieces at Osborne include Jupiter (RCIN 41489) and Ocean, and busts of Caesar and Brutus, all from around 1847 (Marsden 2012, Hunter 2015), contemporary with Braun’s electrotyping collaboration with Elkingtons. The Infants Riding Sea Monsters (*c*1858-1860) are by Giovanni Franchi, who was also a leading electrotypist (Hunter 2015). Although there is less information about the manufacture of the Boy with a Goose (1846) and Eos (1848) by John Francis, the composition of these statues is similarly copper-rich. Therefore the composition, date and route of procurement are all consistent with these being electrotypes, also known as electrocasts, rather than conventional castings. The exception is the John Bell statue of Andromeda, made by Coalbrookdale, which has a conventional cast composition and is unlikely to be an electrotype.

The zinc statues

Some 19th-century manufacturers referred to the use of ‘white bronze’, an alloy of copper, zinc and tin; however, in most cases this appears to a misnomer as they supplied more-or-less pure zinc (Day 1998, 152; Grissom and Harvey 2003). Analyses of over 300 zinc statues in the US, and also contemporary statues in Germany, has shown that these are typically 98wt% zinc with only 0.01wt% copper, 0.11wt% iron, 1.8% lead, 0.2% tin and traces of cadmium (Grissom 2009). The pXRF analyses indicate that the Osborne statues are of a similar, fairly pure zinc composition.

Tin was occasionally detected in the statues, but the highest concentrations found were with similarly elevated levels of lead. Although the construction of the Osborne statues was not studied here, lead-tin solder was commonly used for joining segments of zinc statues and these tin-rich analysed areas may have been on or near seams. Seams are points of weakness in zinc statues and degradation can contribute to deformation (Grissom 2009); zinc metal is also prone to creep.

The coating had a complex composition, including barium sulphate, calcite and magnesium silicate fillers, as well as low levels of lead and copper. Traces of copper may also remain from the original copper plating, although none was seen during the analyses.

Salt was detected in deposits from the statues, and both chlorine and sulphur were detected in the surface layer. The results of previous studies investigating the impact of salt water, and sea proximity, on zinc statue corrosion, may therefore be helpful in planning future conservation in view of the seaward-facing position of the Osborne terrace (Grissom 2009, 106).

Further work

English Heritage conservation scientists plan to use additional analytical techniques in future to identify the polymer component of the coating and the corrosion products formed on the surface of the zinc statues.

CONCLUSIONS

The pXRF analysis of metal statues at Osborne House confirms that Urania (one by Geiss and another by Freres), Ceres, Enterpe, Juno, Venus, Autumn and Summer, and by extrapolation others by the same manufacturers (Hunter 2015), are zinc castings. Andromeda by Coalbrookdale is a copper alloy casting (containing low levels of lead, zinc and tin). The remainder (Brutus, Caesar, Jupiter, Ocean, Eos, Boy with a Goose, and Infants Riding Sea Monsters) are copper electrotypes.

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APPENDIX

The benefit of pXRF analysis is that it is rapid and non-destructive, however there are several issues that need to be considered when interpreting the results: limitations of XRF spectral resolution and the effects of x-ray beam penetration.

Spectral resolution is an important consideration because it is difficult for the software to accurately identify (de-convolute) closely overlapping peaks. For example, almost all of the zinc statue analyses indicated the presence of tungsten, but the two relevant X-ray peaks (Zn = 8.63kV and W = 8.40kV) are close enough to cast doubt on this. Similar spectral overlaps exist between barium (4.47kV), titanium (4.51kV), vanadium (4.95kV) and chromium (5.41kV) (Figure 4). The two methods used for the analyses utilise slightly different elements lists; in particular, the General Metals analysis mode does not contain barium whereas the Cu/Zn Mining method does. As a consequence, spuriously high values for Ti, V and Cr resulted from the General Metals mode, but little or no vanadium was detected using the Cu/Zn mining mode.

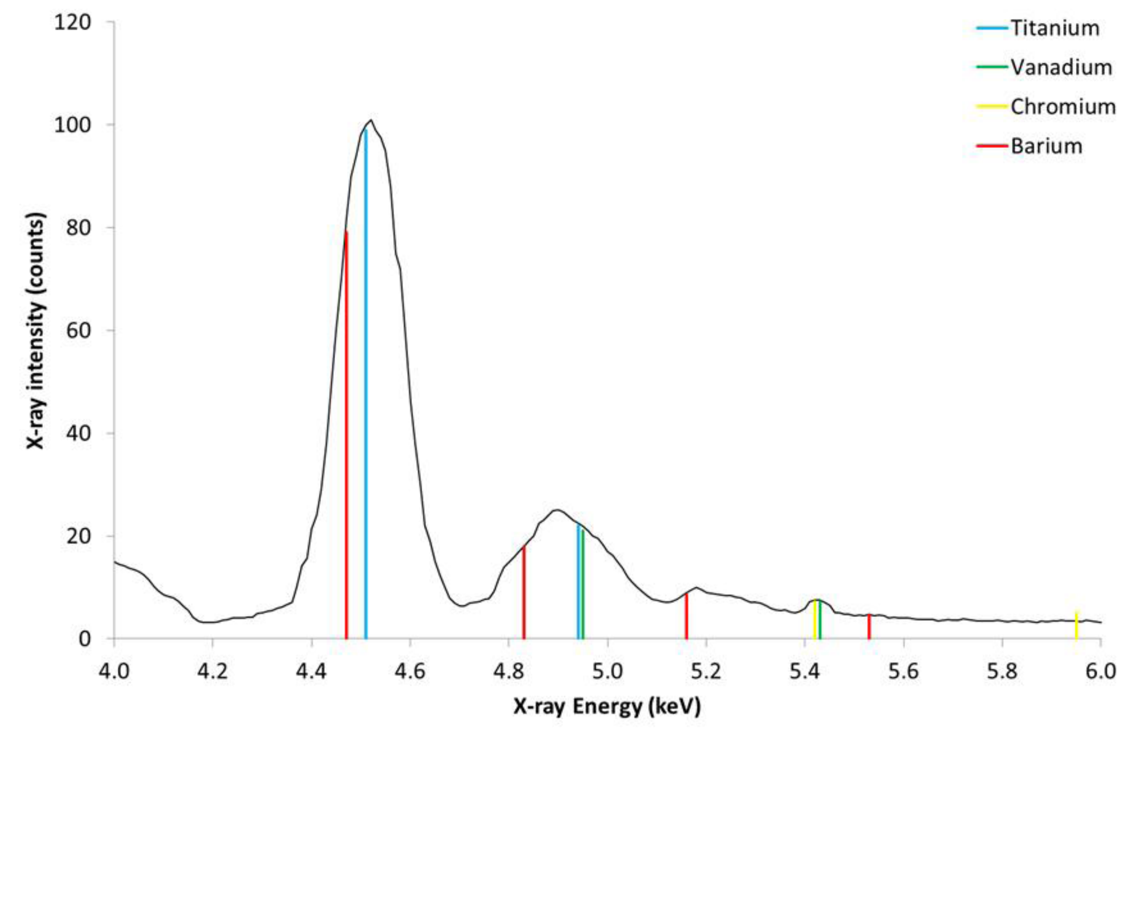

Fig 4: Extract of a pXRF spectrum (Ceres, including bronze-effect coating) showing peak overlaps between various elements (General Metals – Main).

The second issue to consider is X-ray beam penetration. X-rays penetrate into materials to varying depths depending on the energy (kV) of the primary beam and the density of the material being analysed. Where a material has a thin surface coating of a relatively light density material (such as a resin or wax), the primary beam may penetrate through this coating, and provide a combined result for the coating and any underlying material. Also, the statues are all hollow and it is possible that a proportion of the primary X-ray beam passed through into the central core; this would result in an analysed total that would fall short of 100wt%.






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