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The *London* Protected Wreck, The Nore, off Southend-on-Sea, Thames Estuary, Essex: Compositional analyses of copper alloy and pewter objects

Florian Ströbele, Jörn Schuster

Discovery, Innovation and Science in the Historic Environment



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off Southend-on-Sea, Thames Estuary, Essex

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SUMMARY

Seventeen copper alloy objects and 11 tin alloy objects from the *London* protected wreck site, Project HE PR6901, were analysed using XRF. The compositions of the objects are compared to reference material from other sites in order to show overall trends in metal composition. The results show that the alloy was chosen depending on the type of object. The copper alloy objects, including the navigational dividers, calipers and sundial, were mainly brass of consistent composition. The pins contained the highest zinc contents whereas the ring and weight were more complex alloys containing much less zinc and higher lead contents. The two spoons with touchmarks had surviving tinned areas. The pewter objects were especially heterogeneous. Most of the cutlery and tableware was made from Guild specified, tin-rich alloys, whereas other types of object, including the button, chamber pot, and the threaded spout, contained more lead.

CONTRIBUTORS

Florian Ströbele carried out the material analysis of the objects with catalogue entries by Jörn Schuster, and photographs by Angela Middleton or Eric Nordgren. The finds were recovered in a collaborative project involving Cotswold Archaeology, site Licensee Steve Ellis, licensee divers, Southend Museums, and local volunteers.

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ARCHIVE LOCATION

The archive will be deposited with Southend Museum Services. Please note that at the time of writing (Autumn 2018), the assemblage is still being worked on at Historic England, Fort Cumberland, and – in the case of the gun carriage – at York Archaeological Trust, York; so has not yet been deposited.

DATE OF RESEARCH

04 October 2018

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INTRODUCTION

The English Second Rate Ship of the Line *London* was in service for only 11 years. She was commissioned on the 3rd of July 1654 and launched in June 1656. The *London* is particularly interesting, as she was one of only three types of that ship completed. Several contemporary diary entries including Samuel Pepys (Pepys 1665) point out that she was destroyed by an explosion, presumably caused by an accident in the gunpowder magazine while preparing salutes for the boarding of Vice Admiral Sir John Lawson on 7 March 1665. The accident caused more than 300 casualties, only 24 or 25 crew members survived. The wreck was lying in the Thames estuary at only a few meters depth. She was rediscovered in 2005 and designated a protected wreck, under the Protection of Wrecks Act of 1973, in 2008.

During field work in 2014, 2015 and 2016, involving a collaboration between Historic England, Cotswold Archaeology, Licensee divers, Southend Museums, and local volunteers, over 700 objects were recovered from the seabed. The focus of this report is on the pewter spoons, vessels and a urethral syringe, as well as various objects made from copper alloys, mainly brass. Amongst those, the majority are navigational dividers and calipers, but also a weight, a metal bar and base metal spoons can be found. The objects for analysis were selected based on the Post-Excavation assessment (Walsh et al. 2017).

BACKGROUND

Brass

Brass had become a very popular and widely used alloy for a wide range of objects and purposes, like tokens and jetons (Mitchiner et al. 1985), musical instruments (Bacon 2003), all kinds of dress accessories (Heyworth 1991, Dungworth 2003, Egan 2005), tableware, lighting and cutlery (Egan 2005), as well as scientific and navigational instruments (Dungworth forthcoming; Pollard and Heron 1996), at the time the *London* sank in the Thames estuary.

The process that was used to make brass is known as cementation. In this process solid copper metal is put in a crucible together with sulphur free zinc ores (calamine, a mixture of the zinc carbonate smithsonite, $ZnCO_3$ and the zinc silicate hemimorphite, $Zn_4Si_2O_7(OH_2) \cdot 2H_2O$) and charcoal. The crucible is then sealed air tight and heated to a temperature where the zinc ores dissociate and reduce. The zinc carbonate smithsonite is especially crucial in this process as its dissociation provides additional carbon monoxide (CO) which, like the charcoal, acts as reducing agent to the zinc oxides (Bougarit and Bauchau 2010). Due to the low boiling point of metallic zinc ($907^\circ C$) the metal will instantly evaporate as it forms. The zinc fumes react with the copper to form brass. The maximum zinc content that can be achieved in brass by using this method is 28% (Bayley 1990; Craddock 1990). The temperature for this process needs to be kept in a very distinct window, above $907^\circ C$ in order to evaporate zinc and lower than $\sim 970^\circ C$, which is where the solidus of a 28% zinc brass lies, in order not to form zinc-rich partial melts and make the brass unusable. This issue is especially critical when massive copper is in the cementation process due to the diffusion speed of zinc in copper.

The process could be modified in order to achieve a higher zinc content of the brass. By using granulated copper, the reaction surface was increased, the depth zinc vapours have to diffuse through solid copper reduced, and brass with up to 35% zinc could be produced. However, recent experiments have shown that it is possible to produce brass with a zinc content as high as 40% by using the cementation process (Bougarit and Bauchard 2010). Although it was possible to obtain a high zinc content, the mechanical properties, especially hardness and tensile strength start to plateau at a zinc content of about 20% and only increase significantly again, when the zinc content exceeds 35% (Wallbaum 1964).

As the first metallic zinc from India started to pour into the European market in the 16th century (Bougarit and Bauchard 2010), it is possible to find 17th-century objects made from very high zinc brasses, but these should be considered as an exception.

Pewter

Pewter is an alloy of tin and lead as the main elements, with copper, antimony and bismuth as minor elements. The British pewter industry started to become regulated with the foundation of the pewterers' guild in 1348 (Welch 1902). By the time that the *London* was built, the pewterers' guild had defined three different alloys (grades) of pewter:

- Fine pewter, which should be lead free and have a copper content of less than 4% and was intended for tableware (sadware) and cutlery.
- Trifle also should have less than 4% copper and was allowed to contain up to 4% of lead. This alloy was also intended for eating ware (sad and hollow) but wasn't as reflective and silver-like in appearance.
- The last grade was lay pewter where the percentage of lead allowed is not exactly defined but the value was typically between 12.5 and 21% depending on the period and the reference. Lay was not to be used for sad, cutlery and drinking vessels (Hornsby et al. 1989).

In order to identify the maker and ensure the quality and use of high-grade pewter, the objects had to be stamped from the 16th century onwards (Welch 1902). Given the guild mostly had influence in the city of London, 'uncontrolled' pewter ware was still produced outside the city of London for quite a time (Hornsby et al. 1989).

Adding a certain amount of copper, antimony, bismuth, or a combination of those elements to pewter can significantly change its material properties. Adding lead to tin does not significantly increase the hardness, but it was cheaper and easier to acquire than tin. The effect of adding copper to tin is beneficial as it can harden the alloy in order to make a more durable product. An even better hardening effect is achieved by adding antimony. A 3% addition of antimony would double the hardness of tin from 5VHN to 10VHN (Vickers Hardness Scale). The same effect can be achieved by adding as little as 0.7% of bismuth (Hedges 1960). Concerning the melting temperature of pewter, the effect of antimony, lead and bismuth is only very small, lowering the liquidus of the alloy slightly. On the other hand, copper has the opposite effect on the liquidus of the alloy, which can be brought up to 350°C (from 232°C for pure tin) by adding as little as 4% copper.

The effects of various alloying elements on tin were well known and by the 17th century, the pewterers' guild advised their members to add 0.25-0.3% bismuth to their pewter. To secure the accessibility of bismuth, the Pewterers' Company provided a supply of bismuth to their members at the Pewterers' Hall in 1654 (Hatcher and Barker 1974). These years are exceptionally interesting when looking at the pewter from the *London*, and in the 1650s a French pewterer named James Taudin came to the city of London and set up his business there. Most likely, he, as other French pewterers, brought his own pewter recipe from France, of which we

have no exact information concerning its composition. By doing so he entered into a persistent conflict with the Company. He was fined in 1658 as well as being required to discharge “all his stranger workmen” and was only allowed two apprentices. In that time also British pewterers offered ‘Hard Metal’ or ‘French Pewter’. It is not clear so far what the exact composition referred to by these terms was.

AIMS

This study aims to analyse the metal objects from the *London* and compare these to contemporary objects from other studies to better understand how different alloys were used at this time. The analysed objects are shown in Figures 1 to 30.

The brass objects from the *London* assemblage are of particular interest from a metallurgical point of view, as most of the objects have a 'standard calamine brass' composition with zinc values of about 20%, but some of the objects (for example pin SF3166, Fig. 8 and one part of the sundial SF3165, Fig. 14) have very high zinc contents that were possibly made by using the 'modified calamine process' (see BACKGROUND section).

The brass objects include navigational dividers; these are an interesting object group as they survive in quite a substantial number from very different locations (e.g. Portable Antiquity Scheme unique IDs SF-41967F and SFB4F3C8, www.finds.org.uk). In particular the navigational dividers from the Stirling Castle (lost in 1703) are of interest as they have been analysed for their composition earlier and some of them are exactly the same type as the ones found on the London. Four dividers from the Stirling Castle (ID177, ID210, ID211, ID215) were analysed (Dungworth et al. forthcoming); each was made from several parts although only one of those was sampled in the course of the analysis, and these will be compared to the dividers found on the London.

Another type of object that is very common are spoons, made both from pewter and copper alloys, where a large number of analyses are available from a contemporary site, Southwark, in the city of London (Egan 2005; Dungworth 2002).

Some of the objects are outstanding and have been analysed to be able to get a better insight into the object biography. This applies for example to the pipe stopper (SF3040, Fig. 1), which is well preserved and one of the few known to be made from a base metal alloy (one very similar item is <https://finds.org.uk/database/artefacts/record/id/855349>), and the syringe (SF3394-SF3396, Fig. 26-28).

THE OBJECTS FROM THE *LONDON*

Copper alloy objects



Fig 1: SF 3040: Pipe stopper with double convex-sectioned hoop and long-oval octagonal bezel decorated with bird.



Fig 2: SF3041: Navigational dividers. Double-handed straight dividers. Straight semi-circular-sectioned arms each with arched middle forming open circle when dividers are closed. Hinged end ball-shaped.



Fig 3: SF3056: Spoon with deep, oval bowl (L 59.1mm; W 49.2mm) and flat hexagonal stem with straight end and no knob (L 105.6mm, W base 7.5mm, middle 5.8mm, end 7.6mm). Inside of bowl stamped with circular touchmark 7mm below join to stem: within beaded circle 3 spoons on belt/band ending in letter "G" one end and "I" or, more likely, "P" at the other.



Fig 4: SF3072: Disc weight, 193.7g. Raised rim (W top 5.8-6.2mm, inside base 6.8-7.1mm) with groove along inner and outer edge; inside of the disc has two concentric double lines and central pivot spot (i.e. a total of six concentric rings). Back with central casting sprue scar, several concentric flat ridges and pronounced filing marks. No verification or other marks.



Fig 5: SF3100: Thin strip, tapering to irregular, corroded ends; mostly of flat, or flat ovoid section with rounded edges, segment between two perforations (diameter 6.3-8.4mm and 3.2-3.3mm) with flat convex outer- and shallow concave inner side.



Fig 6: SF3122: Spoon with oval bowl (L 60.1mm; W 48.9mm) and flat oval/hexagonal-sectioned stem (L 107.7mm; W base 7.3mm, middle 4.6mm, end 6.4mm) with rounded end and slightly bevelled corners and no knob. Most of surface covered in black patina with greenish beige corrosion areas. White metal covering at front of stem near base. Circular touchmark in centre of bowl 6mm below stem: "G", a spoon with bowl at top, followed by possibly another, ?central stem, rest illegible (probably the same as in spoon 3056).



Fig 7: SF3135: Pair of wing calipers. Arms joined by scarf-jointed hinge with domed rivet and rove. The wing has a semicircular end with two open holes either side; marked with number scales and lettering: on side with screw arm facing, stamped "YSE[R]" (antiq. Dutch for iron) above median double line and "1" (for number 1) below, scale runs from [0] to 50, increments of 1 marked outside of upper line. Reverse of wing stamped "LOOT" (antiq. Dutch for lead) above median double line and "[..?EW]" below (possible beginning of word obscured); upper scale as obverse but visible from tick for 7, visible number markings for 10 to 50.



Fig 8: SF3166: Very fine pin with wound wire head (diameter 1.3mm; 2 coils Z twist) stamped in shape of small sphere, round sectioned shaft with faint grooves from wire drawing vice. No obvious remains of white metal coating.



Fig 9: SF3328: Sundial. Plain lid, shoulder decorated with double line above and single line below shoulder. Most of centre of lid missing, leaving hole with irregular outline. Lid rim with profiled edge creating lip on inside; some (c. 5mm) of edge split off and bent backwards inside lip. Possibly lid for sundial compass SF 3165.



Fig 10: SF3332: Spoon probe with widening spatula end (W 4.0mm, Th 0.8mm), flat end bent slightly upwards. Double-convex stem widening to flat, double-convex probe end (W 3.7mm, Th 2.1mm).



Fig 11: SF3338: Pin. Very fine pin with wound wire head (diameter 1.4mm; 3 coils Z twist).



Fig 12: SF3380: Calipers. Pair of wing calipers. Arms joined by scarf-jointed hinge with flush-set rivet; upper length of arms up to curved wing with flat inside and trapezoidal section; wing set in rectangular-cuboid section held with flush-set rivet in one arm and winged screw in other. Lower length (L 18.1mm) of arms of octagonal cross section with longitudinally set 11mm-deep rectangular notches both containing residues of iron/steel arms and tips. The wing has a profiled outer end; on side opposite screw it is marked with number scales. Scale outside arm towards end reads: 2|4|6|8|10, above scale is a ribbon of tick marks at half intervals to number boxes below. Scale between arms with visible number markings: 6|5|4|3|2|1, again with ribbon of half intervals above.



Fig 13: SF3392: Navigational dividers. Double-handed straight dividers. Straight plano-trapezoidal-sectioned arms each with arched middle forming open circle when dividers are closed; profiled scroll below arches. One arm shorter than the other: L1 105.4mm; L2 106.1mm. Hinged end ball-shaped joined by flush-set rivet.



Fig 14: SF3165: Sundial. Horizontal pocket sundial with compass disc. Chapter ring with folding gnomon over compass bowl with coloured, heavily corroded glass, needle missing. Chapter ring radially marked with numbers 4 to 11 on left and 1 to 8 on right; 12 o'clock position covered by loop holding gnomon; 6 o'clock position marked with "GC". Gnomon angle c. 48.78°.



Fig 15: SF3477: Navigational dividers. Double-handed straight dividers. Straight truncated pyramidal-sectioned arms (forming octagonal shape when closed) each with arched middle forming open circle when dividers are closed; profiled scroll below arches. Arms of equal length, section below circle has higher triangular shape than above; tips both with intentional (L1 5.4mm, L2 4.8mm) split. Hinged end double conical ball-shaped with flat equator.



Fig 16: SF3530: Ring/washer, flat rectangular-sectioned hoop with uneven outer and inner edges.



Fig 17: SF3760: Navigational dividers. Single handed dividers. Each arm with convex-arched top of 2 flat rectangular-sectioned strips, moving through each other when opening. Arched tops creating circle (diameter 38.5mm) when closed; circular hinge with flush rivet. Upper parts of straight, tapering arms rectangular-sectioned (L c. 15.3mm) with concave notch in middle of inside; lower parts of arms with bevelled outer edges. Pointed tips, one slightly bent inwards.

Pewter objects



Fig 18: SF3032: Spoon with round bowl (L 65.0mm; W 61.8mm) and hexagonal-sectioned stem (L 105.6mm; W base 10.2mm, middle 9.1mm, end 10.3mm) with straight end and no knob. No touchmark.



Fig 19: SF3039: Jug handle with 3-lugged hinge, right void containing remains of lid; plano-convex cross section. Both ends broken.



Fig 20: SF3043: Threaded spout (pre conservation). Threaded spout with wide double flange (H between flanges 4.4mm, depth 4.2-5.1mm), thread with 3 full turns (L 9.2mm). Internal L of spout: 11.3mm).



Fig 21: SF3053: Chamber pot with globular body, very slight step to narrower neck and everted, upwardly-curved rim; rim flares very slightly and has straight, horizontal edge. Circular pedestal ring soldered onto base, a gentle ridge/seam runs along upper third of pedestal. Pot now distorted and broken into 2 larger body fragments (joining along one break) and base, and 6 smaller fragments (if interpretation as chamber pot is correct, handle is missing). Corrosion pustules cover entire surface.



Fig 22: SF3099: Spoon with oval bowl (L 67.0mm; W 48.7mm) and flat hexagonal-sectioned stem (L 110.5mm; W base 8.5mm, middle 8.4mm, end 10.1mm). No discernible touchmark.



Fig 23: SF3110: Neck fragment of jug or flagon with straight, vertical rim and hinge for missing lid and upper end of profiled handle; hinge has rivet with domed ends still in place. Surfaces covered in corrosion pustules and greyish patina with off-white patches of marine organism growth.



Fig 24: SF3153: Spoon with hexagonal-sectioned stem (L 92.7mm; W base 8.3mm, middle 6.7mm, end 6.5mm) with straight end, corrosion has deformed corners; most of ?round bowl missing apart from top near stem base, base at back of bowl ends in triangular profile. No touchmark visible, but area of bowl inside below stem base obscured by corrosion pustules. Entire surface with light grey patina and corrosion pustules.



Fig 25: SF3359: Button. Solid discoidal button with recessed octofoil (or piriform); central subrectangular perforation for attachment of – now missing – separate ? iron wire shank.



Fig 26: SF3394: Syringe. Spherical knob decorated with 2 double-lines above and below equator and carnie-profile base, set on tube surrounding hollow brass tube with broken end.



Fig 27: SF3395: Syringe. Top of barrel, end of cylindrical barrel body squashed, set in cylindrical socket with raised rims of semi-circular profile at top and base and slightly domed end cap. Cap crimped onto socket, hollow pipe set slightly off-centre. attached to cap; the pipe is the lower end of plunger 3394.



Fig 28: SF3396: Syringe. Cylindrical barrel with cap/lid at one end (possibly crimped on); externally threaded nozzle (L 10mm; diameter 9.8mm) in centre of lid.



Fig 29: SF3430: Spoon with oval bowl (L 61.3mm; W >52.4mm) flat hexagonal-sectioned stem (L 101.4mm; W base 9.0mm, middle 8.3mm, end 8.4mm) no knob. May have touchmark, but inside of bowl below stem is too corroded to be certain.



Fig 30: SF3600: Spoon with oval bowl (L 72.5mm; W 49.3mm) with wider end than base and flat hexagonal-sectioned stem (L 101.4mm; W base 9.0mm, middle 8.3mm, end 8.4mm), no knob. Circular touchmark visible in x-radiograph, but no detail discernible; the letters B A appear to be stamped or ?engraved above touchmark (towards centre of bowl).

METHODS

All results presented for the *London* artefacts have been produced using an M4 Tornado XRF analyser at Historic England's material science laboratory based at Fort Cumberland, Portsmouth. Prior to the analysis, a small spot ($<1/4\text{mm}^2$) was mechanically prepared using a scalpel to expose underlying fresh metal and avoid analysing corrosion. Whenever an object was made of several parts, such as the navigational dividers or the calipers with two arms, and sometimes several rivets and additional circles, a spot was prepared for analysis on every part, provided that the respective part could be reached with the X-ray beam of the instrument. In some cases where the results of the initial spot were very heterogeneous, a second spot was selected for preparation. On every prepared spot a number of analyses were undertaken in order to negate the effects of microscopic inhomogeneities in the material.

The machine uses a rhodium tube and a 30mm^2 SDD (silicon drift detector) with a resolution of $\leq 145\text{ eV}$ for manganese $\text{K}\alpha$. The tube has a polycapillary lens with a focus spot size of $25\mu\text{m}$. All analyses were done using an acceleration voltage of 50kV and an anode current of $200\mu\text{A}$. No filter was used, and all analyses were done in a vacuum. The counting time on each analysis point was 200 live seconds. The spectra were quantified using a standard enhanced fundamental parameter method calibrated against certified reference materials of known composition.

RESULTS

Each of the values given in Tables 1 and 2 represent the chemical composition of a single piece of metal which is equivalent to one part of an object. In some cases, objects are made from a single piece of material, like the spoons or the pipe stopper. In that case the results represent the average value calculated from various single analyses (number <<N>> is indicated in tables 1 and 2 as well). In the case of objects that are assembled from several parts, for example the calipers or the navigational dividers, a result is given for each part of the object that is made from one single piece of material.

Brass

The majority of the analysed copper alloy objects from the *London* are brass (Table 1), using the alloy nomenclature published by Bayley and Butcher (2004). Only one object (ring SF3530, Fig. 16) falls into the transition field brass/gunmetal and only one object (weight SF3072, Fig. 4) can be identified as gunmetal; additional classification for this particular object will be provided below. The latter two objects have also significantly higher lead contents than the rest (22.7% for the ring and 7.3% for the weight). Among the objects analysed, no pure copper or bronze was identified. That is in good accordance with the observation that by the 17th century hardly anything other than brass was used for these types of object and only a small fraction of the copper alloys in use were gunmetal (Dungworth 2002, Fig. 6).

Homogeneity of the alloys

Several analyses were performed on a single prepared spot in order to gain information on the homogeneity of the metal. While some objects seem to be very homogeneous (arm 1 of navigational dividers SF3477, Fig. 15: 73.8%<Cu<75.8%, 21.9%<Zn<22.5%, 0.74%<Sn<1.14%, 0.60%<Pb<2.09%, N=4) others seem to be extremely heterogeneous (copper alloy object SF3332 'spoon probe', Fig. 10: 73.2%<Cu<86.9%, 11.5%<Zn<24.4%, DL<Sn<0.62%, 0.65%<Pb<1.93%, N=11). Some objects high in lead, which are more heterogeneous due to segregation, also have even broader ranges in composition (ring SF3530, Fig. 16: 45.3%<Cu<72.3%, 7.52%<Zn<11.11%, 3.14%<Sn<4.58%, 11.1%<Pb<40.7% N=5) (DL=detection limit, Sn=tin, Zn=zinc, Cu=copper, Pb=lead).

Figure 31 shows the variation in tin content amongst the brass objects. Around half of the objects have tin contents of <0.18% and the rest 0.7%>Sn>1.43%. Two of the objects (ring SF3530 and weight SF3072, Fig 16 and 4) are exceptional with Sn>3.63%. Note that some objects, like the calipers (SF3380, Fig. 12) and the navigational dividers (SF3135, Fig. 7), have both higher and lower tin parts (see DISCUSSION section for more details).

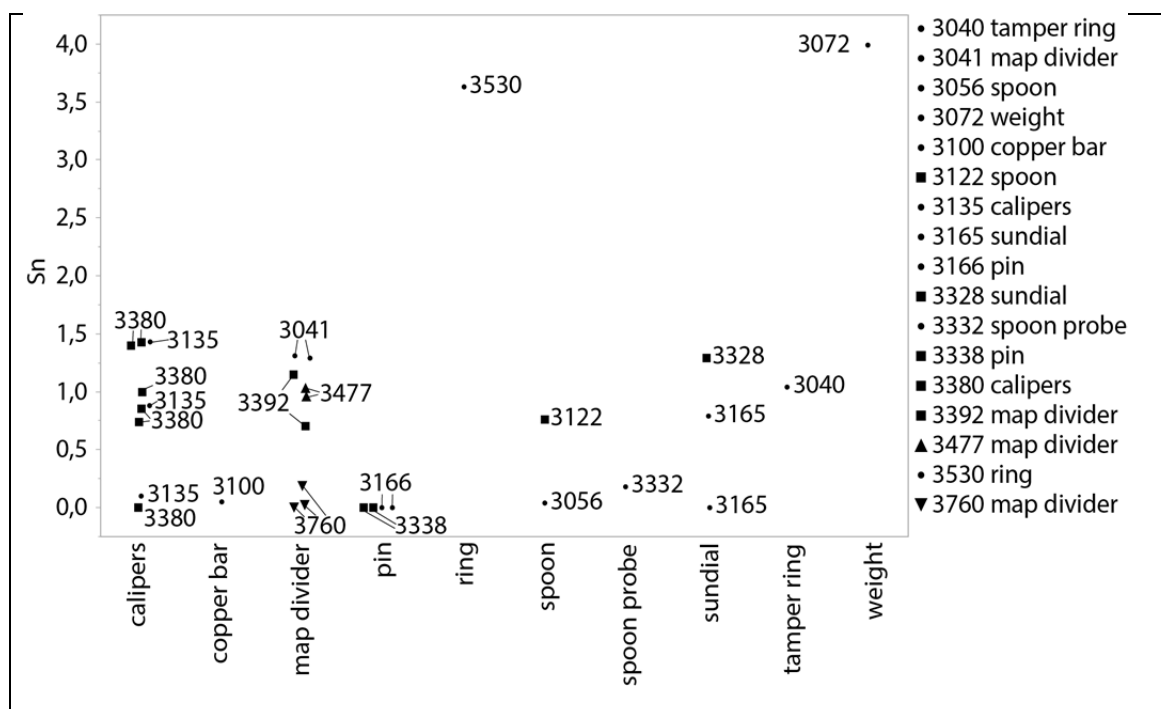


Fig 31: Diagram showing tin content (weight %) by object type. Different symbols in one object type column e.g. spoons or dividers, represent different objects and have no significance in terms of chemistry.

Most of the brasses have zinc contents between 18.5% and 26.8% with an average of 22.3 (N=27), which ties in well with the majority of the contemporary brasses (Heyworth 1991; Egan 2005). Two objects are in an exceptional position. The chapter ring of sundial SF3165 (Fig. 14) with 29.9% zinc and the head of pin (SF3166, Fig. 8) with 28% zinc are at around the limit of what is achievable with the traditional (non-granulated copper) cementation method. The zinc content of only one object (arm 2 of caliper SF3380, Fig. 12) is 13.6% and considerably lower than the zinc content of the other brass objects. With the exception of the wing of caliper SF3380 (Fig. 12, 6.6% lead) and arm 2 of the navigational dividers SF3392 (Fig. 13) with 7.1% lead, all brass objects have lead contents lower than 3.1%.

Tinning of spoons

The spoon SF3122 (Fig. 6) has some very small bright spots on the bowl as well as the stem. The spots are slightly raised and much smoother than the rest of the spoon. These spots were investigated in an unprepared state to check if they might be the residues of plating. A total of 21 analyses were performed on the spots in order to identify the material. The spots have a higher tin content (7.8% on average compared to the spoon (0.76%), the lead content is also higher (3.7%) than that of the spoon (1.1%), and the zinc contents are in good accordance (24.0% on the spots, 23.0% on the spoon).

Also, on spoon SF3056 (Fig. 3) some spots are raised from the corroded surface and are much smoother. In contrast to SF3122 (Fig. 6), these spots are dark grey-green.

Eight additional analyses were done on these spots and the zinc content is much lower (11.2%) than on the spoon (22%), while the tin content is higher (0.4% on the spoon, 8.1% on the spot). Differences in lead are also visible (1.55% on the spoon, 2.9% on the spot).

The analyses of SF3122 (Fig. 6) and SF3056 (Fig. 3) do support the interpretation of the bright spots as tinning. The conditions that are responsible for the different state of preservation are most likely also responsible for the different composition (different intensity of corrosion).

Pewter

Spoons and tableware

One pewter spoon (SF3430, Fig. 29) and a jug handle (SF3039, Fig. 19) are of a similar alloy (with more copper and bismuth), which can be considered as fine pewter (Table 2). Another spoon (SF3153, Fig. 24) is fine pewter, but almost free of copper and free of bismuth. No trifle alloy artefacts could be identified among the objects from the *London*. The jug (SF3110, Fig. 23) and one spoon (SF3600, Fig. 30) are made from a lay alloy and even higher levels of lead were detected in spoon (SF3032, Fig. 18). One spoon could not be analysed due to severe corrosion (SF3099, Fig. 22).

Other artefacts

The chamber pot (SF3053, Fig. 21), the button (SF3359, Fig. 25) and the threaded spout (SF3043, Fig. 20) are made from alloys very high in lead and are far from the threshold for fine, trifle and lay pewter. All of these objects are very inhomogeneous in terms of their composition. The button being the most compact object has tin values between 14.5% and 50.4% while its lead content varies between 47.2% and 85.4%. Copper is also variable and is between 0 and 2.8%. Also, the chamber pot has a very large spread in composition with tin ranging between 24.4% and 91.6% and lead from 6.0% to 75.6%. The threaded spout has the lowest tin values of all objects analysed. They are as low as 5.2% to 38.6% while the lead contents are the highest of the whole dataset (60.5% to 94.7%).

One artefact that is of particular interest is the syringe, recovered in three fragments (SF3394-SF3396, Fig. 26-28). As it is not in very good condition no effort was made to sample or clean the object prior to the analysis. Semi-quantitative XRF analyses (not listed here) were performed on the corroded surface in order to get an idea of the elements present. The corroded surface of the pewter parts shows lead contents between 6% and 50%. The copper content of the pewter corrosion is less than 1%. The plunger of the syringe seems to be made from a pewter-covered brass tube. A bit of the brass tube could be analysed and gave a zinc content of 20%-21%

which ties in well with the other technical brass objects from the *London*. However, the brass tube is highly inhomogeneous in terms of lead where results between 9.5% and 26% were obtained. No traces of mercury were found on any part of the syringe, thus it is unlikely that mercury was one of the liquids handled with it.

Corrosion products

All of the pewter objects are corroded and show various grades of decomposition ranging from dark grey pustules (North and MacLeod 1987; Dunkle 2002) to a light grey to light yellow, heavily disturbed surface. On all but one of the artefacts (spoon SF3099, Fig. 22) metallic pewter could still be identified after removing the corrosion mechanically. The latter spoon has been completely corroded or altered, however, and no metallic material could be found. The analysis gave equal parts of iron, copper, tin and sulphur.

DISCUSSION

Brass

The homogeneity of the material is a crucial point to the understanding of the results. A molten copper-lead alloy segregates into a lead-rich and a copper-rich phase when it solidifies. This effect is noticeable at fairly low lead levels, as copper and lead are almost immiscible in the solid state (Korojy et al. 2009). Those immiscible phases can easily reach a size where they can be picked up individually by the analytical instrument used. This results in a larger spread of the results with variable lead contents. Another effect that may influence the homogeneity of the results is corrosion in the marine environment, including dezincification and probably redeposition of the dissolved zinc close to, or directly on the objects' surface. Such heterogeneities are likely to be present on a micro scale and may be picked up by the instrument that was used in this study as it focusses the x-rays to an area of 25µm diameter.

When reviewing the results and taking the dimensions and mass of the objects into account, it appears that the objects with a small diameter or thin profile and a (relatively) high surface to mass ratio have a tendency to be more heterogeneous, like the above-mentioned spatula and ring. More consistent results were obtained for bulkier objects, like the navigational dividers. Whether this heterogeneity was caused during production, by alteration due to the marine environment and corrosion, or by a combination of these factors is uncertain at this time.

Dezincification

As is well-known from marine contexts, base metal objects may be subject to dezincification or destannification during their exposure to the marine environment (North and MacLeod 1987). No systematic pattern was observed on the objects from the *London*; comparative analyses of the corrosion products (not listed here) and the prepared metal show higher zinc contents in the corrosion products in some of the objects and higher zinc contents in the prepared spots on other objects. This shows again that corrosion can be subject to very local conditions on a micro scale and that bulk or averaged metal analyses need to be treated with caution.

Object grouping

As stated above, the brass objects have a range of tin contents, however this is not thought to be significant, rather a consequence of the variability of the alloy used and the small number of analysed artefacts. This is supported by two observations:

- Some of the objects have parts in both material groups thus two different material pools can be ruled out. It is far more likely that the variation of brass available to the founder covers the whole range.

- If the navigational dividers from the *Stirling Castle* wreck and the objects from Southwark are taken into account as comparative objects, they close the gap between the two groups.

This argument however must be seen with caution, as from the documentation of the analyses on the *Stirling Castle* dividers it is clear that the analysis was only done on one part of the object.

There do appear to be trends in the ratio of lead to tin in the brass alloys used for different types of objects however, particularly when these are compared with other contemporary assemblages, seen in the lead/tin diagram (Fig 32):

- A high tin trend that is formed predominantly by the buckles and the sheet metal waste from Southwark. The Sn/Pb ratio in these objects is approximately 2-8.
- An intermediate trend with a ratio of about 1 that is followed by most of the *London* objects.
- A high lead trend with a Sn/Pb ratio around 0.1. This trend is followed predominantly by the *Stirling Castle* dividers, the two *London* 'high lead' outliers (dividers and calipers respectively, SF3392/SF3380, Figs 13 and 12) and with the highest lead, the ring (SF3530, Fig. 16).

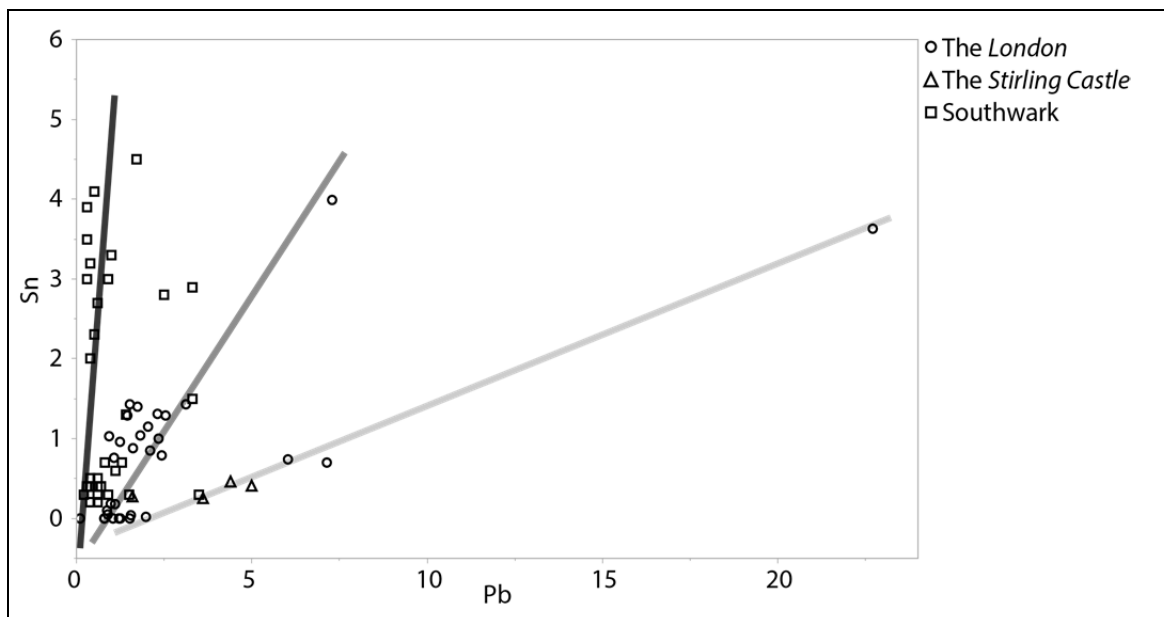


Fig 32: Tin versus lead (weight %) diagram showing the different trends in material that could be observed. Low tin trend: light grey, intermediate trend: medium grey, high tin trend: dark grey.

The weight SF3072

The weight SF3072 (Fig. 4) has a composition that is not comparable to any other object from the dataset. Using the alloy nomenclature of Bayley and Butcher (2004) this particular object would be identified as gunmetal, but Bayley and Butcher (2004) do not take elements other than zinc and tin into account for their classification. However, the composition is in very good accordance with an alloy called 'Caldarium', which is leaded antimony bronze. Caldarium is known to be a by-product of medieval and post-medieval liquation, a process that was used to de-silver copper (Dungworth and Nicholas 2004; Suhling 1976). The alloy was widely used to cast domestic vessels such as cauldrons, thus the name.

The syringe SF3394-SF3395-SF3396

Of particular interest was the question of whether the syringe (SF3394-SF3395-SF3396, Fig. 26-28) was used to handle mercury. As liquid mercury forms a stable and insoluble amalgam at room temperature (Yen et al. 2003), it is highly likely that this would have happened during the use of the syringe to handle mercury. Likewise, the reduced environment of the seabed is known to cause the formation of cinnabar (mercury (II) sulphide) (Dunkle 2002). The analysis did not provide any evidence that the syringe was used for that purpose however, as no mercury was detected.

Pewter

Pewter corrosion is a very complex topic involving various factors, for example the oxygenation rate of the seawater, the formation of (protective) concretions, direct contact with other metals and materials, as well as sedimentary movement that may cause multiple phases of burial, exposure to water and reburial. The most common phases formed during pewter corrosion are various tin oxides and hydroxides like romarchite, hydroromarchite, and cassiterite, but tin chlorides, such as abhurite, are also common (MacLeod 1991; Dunkle et al. 2004). One particular corrosion product (stannite: $\text{Cu}_2\text{FeSnS}_4$) needs to be considered when looking at spoon SF3099 (Fig. 22). Although it showed a metallic appearance after mechanical removal of the superficial corrosion, the analysis gave about equal parts of iron, copper, tin and sulphur. As the object seemed completely corroded or altered, the results were not included in this report. Stannite can form either when the object is removed from the anaerobic burial environment or when an aerobically corroded object is subsequently buried (MacLeod 1991). Thus, the results for spoon SF3099 (Fig. 22) emphasise how important local conditions are when investigating corroded pewter objects.

Object grouping

Due to the small number of pewter objects from the *London* that were analysed, the results do not form a very clear picture. When looked at together with the reference material from Southwark and the *Stirling Castle* however, a more detailed interpretation is possible (Fig. 33). In terms of the lead content most of the objects from Southwark form a tight cluster with lead contents of not more than 6.7%. Some of the objects from Southwark as well as from the *Stirling Castle* are lead free or have lead contents close to zero. The results from the *London* do not show a distinct lead free or a low lead group, thus, the border between ‘fine’ and ‘trifle’ cannot be seen clearly here. It is noteworthy that although up to 4% copper is allowed in fine, as well as trifle, alloys the majority of the spoons have copper contents of less than 2.5%, which might indicate they were intended to be fine ware.

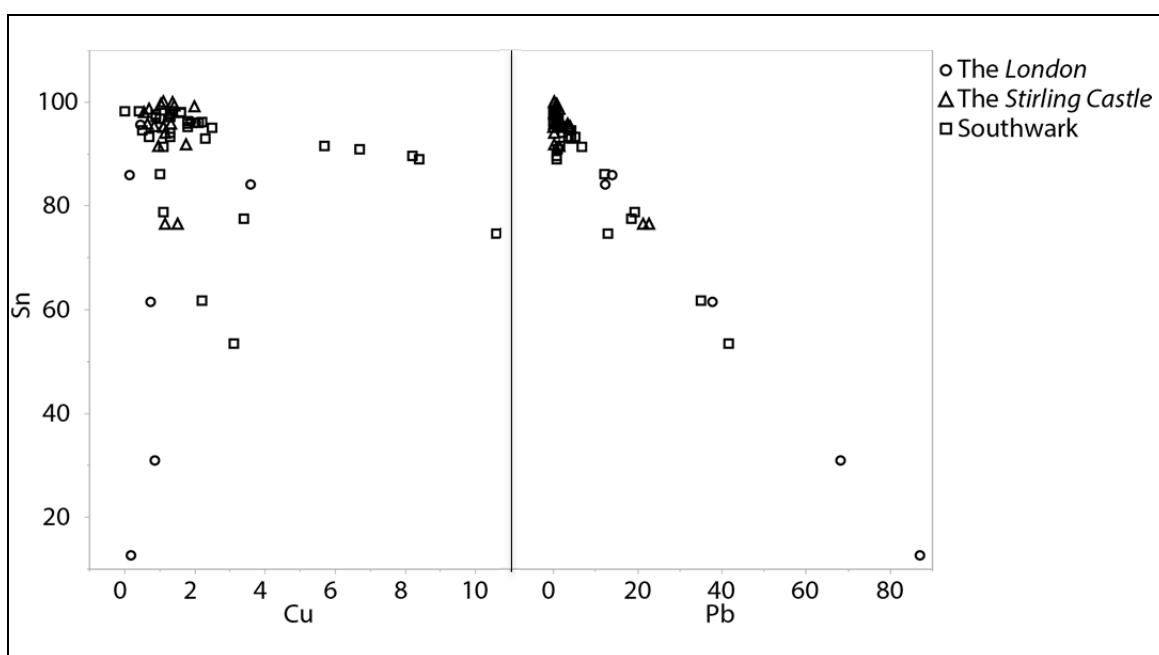


Fig 33: Comparison of the composition of the objects from the London (circles) to those from the Stirling Castle (triangles) and Southwark (squares) (in weight%).

If grouped by the antimony content (Fig. 34), the objects from the *London* have the lowest contents with $DL < Sb < 0.11\%$ (DL =detection limit, Sb =antimony), while the Southwark objects lie at $0.5\% < Sb < 1.1\%$. The highest antimony contents can be found in the *Stirling Castle* objects with $2.7\% < Sb < 5.4\%$. Except for the antimony content, the spoons from the *London*, the *Stirling Castle* and from Southwark seem to be in good overall accordance. The majority of the spoons can be categorised as fine or lay pewter; only a small number are made from high lead pewter.



Fig 34: Plot showing variable antimony content of the objects (weight %).

Two pewter spoons from the *London* (SF3153, Fig. 24; SF3430, Fig. 29) can be found within the fine/trifle cluster that is formed by the Southwark and *London* spoons. Four spoons from Southwark plot on the low lead/ high copper trend of the diagram. In addition to these, a number of spoons (6 from Southwark and SF3600, Fig. 30; SF3032, Fig. 17) are made from alloys that need to be considered as lay, or from alloys that have even higher lead contents of up to 41%.

Another important point to notice is that only three objects contain enough bismuth to regard it as an intended addition. Spoon SF3430 (Fig. 28) and jug handle SF3039 (Fig. 18) have bismuth contents of 0.73% and 0.62%, respectively, as well as lead contents of only ~1.2 % and copper contents of ~2%, and these alloys can easily be identified as either primary material or as very carefully recycled material. On the other hand, spoon SF3032 (Fig. 18) also has bismuth and copper, but at a considerably lower level and it has over 20% lead. This could be interpreted as a single or a repeated recycling step, where high grade pewter (fine or trifle) was diluted with lead. Recalculating the composition of the alloy, after subtracting the lead, would result in pewter with ~99% tin, 0.6% copper and 0.25% bismuth which would be fine pewter of excellent quality.

Buttons were made out of different materials, depending on their value, intended colour and wealth of their owner and garment they were used on. The analysis of buttons is predominantly made using a stylistic approach (Read 2010). From the excavations at Southwark, buttons made from pewter, tin, leaded gunmetal and brass/leaded brass are known (Egan 2005), but no quantitative results were published. Also, a large number of buttons (5345 database entries only for the post-

medieval period) are recorded in the Portable Antiquities Scheme database (www.finds.org.uk), but only a minute fraction of them has been analysed qualitatively in terms of chemical composition. Thus, the single analysed button from the London does not give a new insight into the topic.

CONCLUSIONS

As can be seen from the analyses of the pewter objects, in the case of tableware and cutlery the rules of the Pewterers' Company concerning the lead content of the objects were obeyed in most cases. Only spoons (SF3032, Fig. 18 and SF3600, Fig. 30) were made from higher lead alloys. Concerning the question of how these came aboard the *London*, it is interesting that spoon SF3600 appears to be a personal belonging rather than provided by the Royal Navy. The owner's mark suggests that it was owned by an unmarried man, at least at the time when the mark was applied (Cotterell 1929, 53–4). It would be interesting to see if the Navy had a 'certified' supplier of utensils or bought them as and when required. The other pewter objects that were not made from 'company grade' metal (button SF3359, Fig. 25, threaded spout SF3043, Fig. 20 and chamber pot 3053, Fig. 21) are also not intended to contain food and thus did not have to meet the restrictions.

Most of the dividers and calipers have zinc contents of around 20%, in common with instruments from other contemporary wrecks; this alloy probably had a good cost/material property ratio, as these instruments had to be precise and keep this precision on a long-term basis.

The two brass spoons (SF3056, Fig. 3, SF3122, Fig. 6) have maker's marks; the marks are similar (although the one on SF3122 is incomplete) and the spoons have similar compositions and were both tinned so the analysis supports the theory that these are from the same manufacturer. The sundial lower case (SF3165) also has a distinctive composition, with small amounts of antimony, tin and lead, closely matched by the composition of the object thought to be the sundial upper case (SF3328), confirming that they belong to the same object.

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APPENDICES

Table 1: Results of the copper alloy object analyses by XRF, wt%, where no value is reported = below detection

SF No/object/part	Material		S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	#N
3392	brass	average		0.33	0.18	76.2	19.8	0.3		1.15		2.0	0.01	3
		min		0.30	0.15	66.0	15.7	0.3		0.67		1.7		
		max		0.42	0.21	77.5	21.1	0.6		1.47		15.8	0.03	
3392	brass	average		0.78	0.17	69.1	21.8	0.3	0.01	0.70		7.1		5
	leaded	min		0.66	0.15	64.9	19.8	0.1		0.43		2.3		
		max		0.89	0.18	72.7	23.4	0.4	0.02	1.01		13.3		
3477	brass	average		0.37	0.11	75.0	22.2	0.2	0.01	0.96		1.2		4
		min		0.36	0.10	73.8	21.9	0.1		0.74		0.6		
		max		0.37	0.12	75.8	22.5	0.2	0.04	1.14		2.1		
3477	brass	average		0.33	0.10	74.8	22.7	0.1	0.01	1.03		0.9		4
		min		0.32	0.10	74.5	22.5	0.1		0.50		0.6		
		max		0.33	0.11	75.7	23.0	0.2	0.04	1.91		1.2		
3530	gunmetal	average		1.87	0.10	60.7	9.3	0.9	0.13	3.63	0.69	22.7		5
	leaded	min		1.61	0.08	45.3	7.5	0.7	0.06	3.14	0.52	11.1		
		max		2.09	0.13	72.3	11.1	1.1	0.18	4.58	0.77	40.7		

SF No/object/ part	Material		S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	#N
3122	brass	average		1.27	0.06	73.6	23.0	0.1	0.07	0.76		1.1	<0.01	4
spoon		min		0.87	0.06	72.2	22.6	0.1		0.44		0.5		
main mass		max		2.30	0.07	74.5	23.2	0.2	0.18	1.09		1.4	0.01	
plating		average	5.3	3.59	0.07	55.2	24.0	0.2	0.16	7.78		3.7		20
3760	brass	average	0.1	0.29	0.12	70.9	26.4	0.1	0.01	0.02		2.0		3
navigational		min	0.1	0.26	0.09	70.1	24.5	0.1				1.8		
dividers arm 1		max	0.1	0.30	0.13	72.6	27.4	0.1	0.02	0.03		2.2		
3760	brass	average	0.1	0.33	0.11	71.1	26.8	0.1	0.01			1.5		4
navigational		min	0.1	0.31	0.10	70.7	26.5	0.1				1.1		
dividers arm 2		max	0.1	0.34	0.11	71.5	27.3	0.1	0.03			1.8		
3760	brass	average	0.2	0.27	0.18	76.4	21.7	0.1		0.18		1.0		4
navigational		min	0.1	0.26	0.17	76.0	21.3	0.1		0.07		0.8		
dividers rivet		max	0.2	0.28	0.18	76.6	21.9	0.1		0.29		1.2		
3040	brass	average		0.67	0.13	75.6	20.5	0.2	0.02	1.04	0.02	1.8	0.04	20
pipe stopper		min		0.55	0.12	74.3	18.2	0.1		0.47		1.2		
		max		0.98	0.15	78.0	21.4	0.3	0.07	1.34	0.10	2.6	0.26	
3041	brass	average		0.93	0.12	73.2	21.9	0.2	0.06	1.31	0.02	2.3		5
navigational		min		0.51	0.08	72.1	20.0	0.1	0.01	0.77		1.8		
dividers arm 1		max		2.11	0.14	74.1	22.5	0.4	0.15	2.12	0.06	3.0		

SF No/object/part	Material		S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	#N
3041	brass	average		0.63	0.12	75.9	20.5	0.1	0.01	1.29	0.01	1.5		7
navigational		min		0.47	0.09	74.9	17.9	0.1		0.95		1.0		
dividers arm 2		max		0.99	0.13	77.3	21.6	0.2	0.40	1.90	0.05	2.3		
3056	brass	average		0.47		75.8	22.1	0.1	0.04	0.04		1.6		4
spoon		min		0.44		74.0	20.8	<0.1				0.9		
main mass		max		0.53		77.5	23.4	0.1	0.06	0.06		2.0		
plating		average	9.3	1.02		67.1	11.2	0.2	0.19	8.13		2.9		5
3072	gunmetal	average		0.67	0.46	78.0	5.8	0.9	0.07	3.99	2.72	7.3		16
weight		min		0.52	0.39	68.1	5.0	0.3	0.01	2.77	1.83	1.4		
		max		1.19	0.57	83.1	8.0	1.3	0.13	5.21	4.16	18.2	0.03	
3100	brass	average		0.67	0.08	71.5	26.8	0.1	0.01	0.05	0.00	0.9	0.01	10
strip		min		0.60	0.06	69.5	23.8	<0.1				0.4		
		max		0.75	0.13	73.9	27.7	0.1	0.03	0.26	0.00	2.2	0.03	
3135	brass	average		0.40	0.18	71.6	23.1	0.1	0.02	1.43	0.04	3.1		5
caliper		min		0.35	0.15	69.9	22.6	0.1		0.72		2.0		
wing		max		0.50	0.22	73.7	23.5	0.2	0.05	2.09	0.11	5.6		
3135	brass	average		2.16	0.18	70.8	24.3	0.1	0.02	0.88	0.00	1.6		5
caliper		min		1.51	0.16	69.8	23.6	0.1		0.67		0.8		
arm 1		max		2.95	0.20	71.8	25.1	0.1	0.04	1.11	0.02	2.5		

SF No/object/part	Material		S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	#N
3135	brass	average		0.37	0.16	73.6	24.8	0.1		0.10		0.9		5
caliper		min		0.34	0.15	71.6	21.9	0.1		0.05		0.4		
arm 2		max		0.45	0.20	76.9	26.6	0.1	0.01	0.13		1.5		
3135		average	1.4	20.71		72.8	3.4	0.1				1.6	0.03	5
caliper		min	0.5	4.57		35.5	0.4					0.4		
loose rivet		max	3.7	47.73		93.3	9.1	0.2				3.8	0.13	
3165	brass	average		0.51	0.08	76.5	19.3	0.2	0.03	0.79	0.23	2.4		5
sundial		min		0.42	0.03	72.7	10.6	0.2		0.55	0.16	1.8		
lower casing		max		0.75	0.10	84.8	22.3	0.2	0.10	1.28	0.39	4.2	0.02	
3165	brass	average		0.22	0.03	69.0	29.9	<0.1			0.01	0.8		4
sundial		min		0.20	0.01	64.3	18.0					0.3		
chapter ring		max		0.24	0.04	81.4	34.5	<0.1		0.02	0.06	1.4	0.01	
3166	brass	average		0.22	0.01	70.0	28.5	<0.1	0.01			1.2		2
pin		min		0.21		69.5	28.0	<0.1				1.2		
head		max		0.22	0.01	70.5	29.1	<0.1	0.02			1.2		
3166	brass	average		0.11	0.02	74.7	24.3	0.1				0.8		3
pin		min		0.11	0.02	73.8	23.6	0.1				0.5		
shaft		max		0.12	0.02	75.7	24.7	0.1				1.2		
3328	brass	average		0.83	0.14	73.5	21.1	0.3	0.05	1.29	0.34	2.5		4
sundial		min		0.56	0.12	71.4	20.3	0.3		1.09	0.28	1.8		
top of case		max		1.46	0.14	74.5	22.2	0.4	0.09	1.14	0.42	3.3		

SF No/object/part	Material		S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	#N
3332 spoon probe	brass	average		0.47	0.06	79.4	18.7	0.1	0.03	0.18	0.01	1.1		10
		min		0.32	0.03	73.2	11.5	0.0				0.7		
		max		0.68	0.09	86.9	24.4	0.1	0.10	0.62	0.08	1.9		
3338 pin head	brass	average		0.14		72.1	26.6	<0.1	0.05			1.0		2
		min		0.13		71.8	26.0	<0.1	0.05			0.7		
		max		0.16		72.4	27.3	0.1	0.05			1.4		
3338 pin shaft	brass	average		0.13		72.6	26.0	0.1	0.02			1.3		4
		min		0.12		72.3	25.8	<0.1				0.5		
		max		0.15		73.1	26.2	0.1	0.05			1.8		
3380 caliper arm 1	brass	average		0.67	0.12	75.6	20.4	0.3	0.02	0.85	0.01	2.1		4
		min		0.61	0.11	74.7	18.9	0.2		0.57		1.0		
		max		0.81	0.13	76.8	21.5	0.4	0.06	1.07	0.02	3.6		
3380 caliper arm 2	brass	average		0.70	0.05	82.2	13.6	0.2	0.04	1.40	0.09	1.7		4
		min		0.21	0.03	78.4	8.3	0.1	0.02	1.01		0.9		
		max		1.80	0.08	89.3	16.8	0.2	0.07	1.66	0.14	2.2		
3380 caliper wing	brass	average		0.70	0.07	72.9	19.3	0.3	0.04	0.74	0.01	6.0		4
	leaded	min		0.62	0.06	71.5	17.6	0.2	0.03	0.12		3.4		
		max		0.79	0.07	74.8	20.6	0.3	0.08	1.24	0.02	9.0		

SF No/object/part	Material		S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb	Bi	#N
3380	brass	average		0.10		79.1	20.7	<0.1				0.1		4
caliper		min		0.09		72.2	13.6					0.0		
rivet (wing)		max		0.12		86.3	27.4	<0.1				0.3		
3380	brass	average		0.56	0.11	76.9	19.3	0.2		1.43	0.03	1.5		4
caliper		min		0.34	0.11	76.0	18.0	0.1		0.79		1.2		
central rivet		max		0.90	0.12	78.7	19.9	0.2		1.83	0.13	1.8		
3380	brass	average		0.62	0.10	76.0	19.7	0.2		1.00		2.3		5
caliper		min		0.58	0.09	75.9	19.2	0.1		0.73		1.9		
screw		max		0.65	0.11	76.3	20.2	0.3		1.27		2.7		

Table 2: Results of the pewter object analyses by XRF, wt%, where no value is reported = below detection, #N = number of analyses

SFNo/object/part	Alloy		Cu	Sn	Sb	Pb	Bi	#N
3153 spoon	fine	average	1.3	96.1	0.01	2.6	0.01	8
		min	0.1	93	0.01	1		
		max	5.4	98.5	0.01	4.3	0.02	
3110 jug	lay	average	0.1	85.9	0.01	13.9	0.01	6
		min	0.1	61.3	0.01	38.6		
		max	0.3	97.4	0.01	2.6	0.1	
3359 button	lead alloy	average	0.9	31		68.2	0.1	10
		min		14.5		47.2		
		max	2.8	50.4	0.01	85.4	0.01	
3430 spoon	fine	average	2	96	0.01	1.2	0.73	10
		min	1.6	94.3	0.01	0.5	0.13	
		max	2.6	97.6	0.01	2.2	1.28	
3032 spoon	lead alloy	average	0.4	77.8	0.01	21.6	0.19	6
		min	0.2	60.4	0.01	12.5		
		max	1.1	87.2	0.01	39.4	1.08	
3039 jug handle	fine	average	1.9	96.2	0.01	1.3	0.62	4
		min	0.7	94.9	0.01	0.5	0.3	
		max	2.6	98.6	0.01	1.7	0.8	
3043 threaded spout	lead alloy	average	0.2	12.7	0.11	87	0.01	9
		min	0.1	5.2		60.5	0.01	
		max	0.4	38.6	0.5	94.7	0.01	
3053 chamber pot	lead alloy	average	0.7	61.5	0.02	37.4		28
		min		24.4	0.01	6		
		max	2.7	91.6	0.2	75.6	0.01	
3600 spoon	lay	average	3.6	84.1	0.01	12.3	0.01	10
		min		70.3	0.01	4.1		
		max	21.3	93.2	0.01	29.7	0.05	



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