Naval metals from mid 18th- to early 19th-century European shipwrecks: a first analytical approach

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ABSTRACT: This article gives the preliminary results of a study of metal artefacts recovered from European shipwrecks dating from the mid 18th- to early 19th-century. The analytical approach included optical emission spectrometry (OES), atomic absorption spectrometry (AAS) and infrared spectroscopy (IR) which determined the main constituents and trace element contents of the materials. Based on the latter, and other sources of information, a technological assessment was performed. Such data provides information on the functionality of artefacts, the quality of the alloys and their possible provenance.

Introduction

The importance of metallurgical analyses for showing the composition and the manufacturing techniques of the artefacts recovered from shipwreck sites has been stated by McCarthy (2005, 130). The application of specific analytical methods to the study of metallic remains from historical shipwrecks has contributed to the description of the temporal and spatial variation of materials, the identification of the technical characteristics of the objects (*eg* manufacturing methods and alloys), and the knowledge of certain aspects of their socio-cultural context (*eg* Samuels 1983; 1992; MacLeod 1994; Stanbury 1994; Viduka and Ness 2004; Bethencourt Núñez 2008–9; Mentovich *et al* 2010). In Argentina, several studies of these characteristics have been performed, mainly on objects recovered from archaeologically studied shipwrecks of the 17th to 19th centuries (*eg* Marconetto *et al* 2007; Murray *et al* 2009; De Rosa *et al* 2011; Ciarlo 2014).

This brief report presents the first results of the chemical analysis of an assemblage of iron, copper and copper alloy artefacts recovered from the following European shipwrecks: *Swift* (1763–1770), *Triunfante* (1756–1795), *Fougueux* (1785–1805) and Deltebre I (–1813) site. This work is part of a larger project dedicated to studying the innovations in traditional (experimental) and scientific practices and knowledge of metallurgy, and their application to European warships during the mid 18th- to early 19th-century.

The study of the samples was carried out by optical emission spectrometry (OES), atomic absorption spectrometry (AAS) and infrared spectroscopy (IR). All these analytical techniques have a high sensitivity, so they allowed the qualitative and quantitative determination of the main constituents and trace element contents of the materials. The analyses were performed at the Instrumental Chemical Division of the Metallurgy Department of the ABS Corp Company (Argentina). The following equipment was used: For OES, a Spectro Spectrotest TXC 25 (portable equipment) and MAXx LMF05; for AAS, a Varian Spectrometer AA5; and for IR a LECO CS 400 (for carbon and sulphur determination). Due to the corrosion of the surface of the materials, the measurements were made on the unaltered, underlying microstructure – as seen by optical microscopy.

Figure 1: Some fastenings from the Camposoto site, identified as the Fougueux (1805), in situ. Scale bar divisions 100mm.

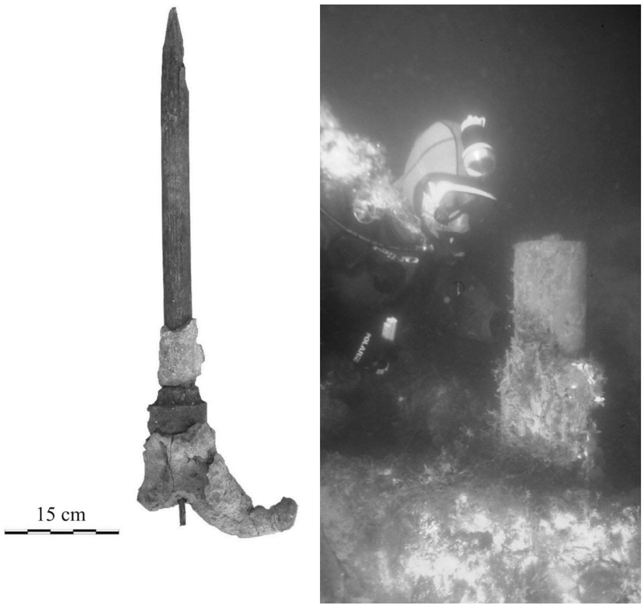

Figure 2: (left) Iron grapnel (grappling iron), (right) copper alloy pipe from one of the suction pumps standing upright in front of a diver, both from the Swift (1770).

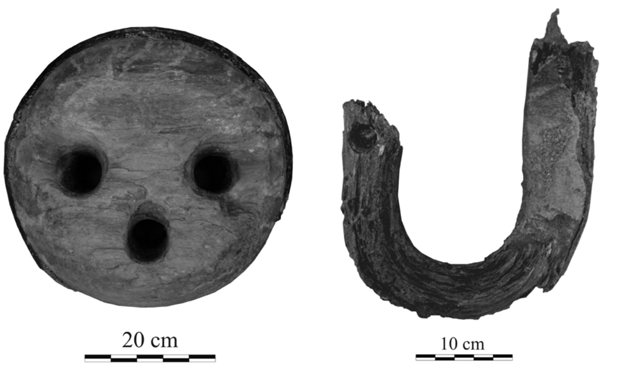

Figure 3: (left) Deadeye with iron strap, (right) iron hook from a single sheave block, both from the Triunfante (1795).

The analysed artefacts include fastenings of structural elements (Fig 1), equipment related to the anchoring, pumping and steering systems (Fig 2) and rigging components (Fig 3).

Brief review of the shipwrecks

The shipwrecks from which the samples under analysis were taken have been the subject of detailed studies as part of different maritime archaeology research projects. A succinct introduction to the sites is given below.

HMS *Swift* was a British sloop-of-war, part of the small fleet commissioned to Port Egmont (the first British operating base at the Malvinas/Falkland Islands). In March 1770, after strong gales forced her to reach the continental coast (province of Santa Cruz, Argentina), the crew decided to enter the Deseado estuary, where the vessel ran aground on a rock and sank. Since 1997, the ship has been studied by the Underwater Archaeology Programme (Programa de Arqueología Subacuática, PROAS) of the National Institute of Anthropology (Instituto Nacional de Antropología y Pensamiento Latinoamericano, INAPL), under the direction of Dr. Dolores Elkin (Elkin *et al* 2007; 2011).

The *Triunfante* was a 74-cannon Spanish ship, which carried out several military, scientific and diplomatic missions in the service of the Navy. In her last days she was under the command of Gravina, and sank in the Gulf of Roses (Catalonia, Spain) during the local defence against the French military forces (de la Fuente 2005). The archaeological work at the site (in 2008, 2009 and 2010) was led by the Catalan Centre for Underwater Archaeology (Centre d'Arqueologia Subaquàtica de Catalunya, CASC) of the Archaeological Museum of Catalonia (Museu d'Arqueologia de Catalunya, MAC), under the direction of Dr Gustau Vivar (Pujol i Hamelink *et al* 2011; Nieto *et al* in press).

The *Fougueux* was a 74-cannon ship, one of the vessels of the combined Franco-Spanish fleet which on 21 October 1805 fought against a British fleet at the battle of Trafalgar. The already dismasted ship was caught by the British, but sunk in shallow waters at Sancti-Petri (Cadiz, Spain) in a strong storm (Márquez Carmona 2000). The research on the Camposoto site, carried out by carried out by a team from the Centre for Underwater Archaeology (Centro de Arqueología Subacuática, CAS) of the Andalusian Historical Heritage Institute (Instituto Andaluz de Patrimonio Histórico, IAPH), under the direction of archaeologist Nuria Rodríguez Mariscal, links the underwater remains to the *Fougueux* (Rodríguez Mariscal *et al* 2010).

The Deltebre I site corresponds with the remains of a British Navy store ship, which sank in a storm in the delta of the Ebro river (Catalonia, Spain). The vessel was part of a combined fleet of Sicilian, British and Spanish forces, commanded by Lieutenant John Murray, who in June 1813 tried fruitlessly to liberate Tarragona from Napoleonic troops. Since 2008, the team of the Catalan Centre for Underwater Archaeology has carried out research on the site, surveying and recording the structure and excavating part of the ship's cargo (Vivar *et al* in press).

Chemical composition

The characteristics of an artefact, *eg* its mechanical and chemical properties, are usually the product of multiple variables. The decisions of the producers could have been conditioned by the available resources, their knowledge about the relationship between the properties of an object and its composition, the technical facilities available, traditional practices and the manufacturer's preferences, among other things. In the cases considered here, due to the essentially utilitarian nature of the objects, it is the conditions to which they were meant to be subjected that probably strongly influenced the decisions regarding the materials used to manufacture them.

The chemical composition of the objects, especially the proportions of the main elements, was related to the manufacturing process. It was an important issue because of the close relationship between composition and mechanical and chemical properties (*eg* melting point, malleability, toughness, and corrosion resistance). The relative quantities of some elements might be linked to certain beneficial qualities for manufacture (*eg* in case of cast copper alloy pieces, a low melting point) or the production of artefacts with specific properties (*eg* in case of some structural fastenings, strength and stiffness).

On the other hand, the consistency found in the amounts of some trace elements (<1000ppm) might be considered as a fingerprint or chemical signature. On this basis, it would be possible to obtain meaningful information about the impurities in the ore and/or the particular characteristics of the process by which the raw material was obtained (*eg* the fuel used for the smelting of the mineral), which in turn could be used to link them to the geographical provenance of the material and/or of the fuel.

The analytical results for the chemical composition of the artefacts are given in Tables 1, 2 and 3. In most cases, optical microscopy of the samples helped to identify the main methods used for manufacturing each piece, whether it was forged, rolled or cast.

Iron artefacts

The analysed artefacts show heterogeneous concentrations of carbon. In most cases, this element is present at less than 0.1%, though in one piece it reaches 0.45% (Table 1). The carbon contents recorded are consistent with the metallographic structure of these objects (Ciarlo *et al* in press; Ciarlo 2014). This variation is associated with a non-uniform distribution of carbon in the metal, which is characteristic of the wrought iron used during this period. Depending on the process used, carbon was introduced or eliminated with no regular pattern during the smelting of the ore and the later refining of the metal produced (see Samuels 1992; Buchwald and Wivel 1998).

Regarding the quality of the raw material, it is necessary to emphasize the concentrations of phosphorus and sulphur. According to Samuels (1992), the iron produced in England was characterized by phosphorus contents of

Table 1: Chemical composition of the iron samples.

Shipwreck	Artefact	Manufacture	Analyses	Composition (wt%)									
				Fe	C	P	S	Mn	Si	Cu	Al	Ca	Ni
Swift (1770)	Grapnel	Forged	AAS, IR C&S	Bal	0.110	0.056	0.033	0.097	0.115	bd	0.005	<0.001	bd
Swift (1770)	Tiller	Forged	OES, IR C&S	99.500	0.103	0.062	0.007	<0.005	<0.005	0.014	<0.001	<0.001	0.225
Triunfante (1795)	Single sheave block hook	Forged	OES, IR C&S	99.800	<0.010	0.059	0.012	0.008	<0.005	0.070	0.002	<0.001	<0.003
Triunfante (1795)	Deadeye strap	Forged	AAS, IR C&S	Bal	0.040	0.052	0.003	0.138	0.179	bd	0.005	<0.001	bd
Triunfante (1795)	Bolt	Forged	OES, IR C&S	99.400	0.457	0.015	0.006	0.013	0.015	0.060	0.006	0.007	0.006

Notes:
Bal = balance, bd = below detection limit

over 5000ppm and sulphur contents over 300ppm, which usually had certain disadvantages. Phosphorus made iron brittle when worked at low temperatures, known as cold-short, while sulphur – with a low manganese content – had a similar effect at high temperatures, being referred to as red or hot-short. In contrast, iron produced in Spain and Sweden had very low contents of these two elements. The British Navy used to import iron from these countries to make certain objects due to its very good quality (Samuels 1992). The relative proportions of phosphorus and sulphur recorded in three 18th-century British anchors are examples of this (MacLeod 1989; Samuels 1992; Ciarlo *et al* 2011).

Taking this into account, the values found in the pieces from the *Triunfante* are consistent with the provenance of the remains (Spain). In case of the *Swift*, the amounts of phosphorus and sulphur present in the tiller are typical of foreign (not British) iron. The sulphur content of the grapnel is slightly over 300ppm, though the phosphorus content is similar to that of the pieces from the *Triunfante*. It is probable that both pieces from the Swift were made in Britain but from imported iron. Although it is not possible to specify any particular source, it must be considered that Swedish iron predominated in the European market due to its high quality and relatively low cost (Santana *et al* 1999; Urteaga 1999).

Copper artefacts

In general terms, the purity of the copper pieces recovered from the British cargo ship (≥ 99.3%) is slightly superior to that of the artefacts from the other two vessels. Nonetheless, taken together, the copper contents of these artefacts are lower than those recorded for several samples of sheathing from two French shipwrecks (one of them the *Fougueux*) which have a purity of around 99.8% (Bethencourt Núñez 2008–9; 2010). This difference might be related to a more rigorous control of the quality of the material used for manufacturing the sheets, a control which does not seem to have been applied to other pieces (*eg* nails and sheathing tacks). Accordingly, the analyses of other copper sheathing samples of shipwrecks from the 17th to 19th centuries seem to point to a trend to improve the purity of the materials, presumably due to developments in the technology of copper refining (Samuels 1992, 97).

In this regard, it is worth noting the study by MacLeod (1994, 268) on the copper sheathing of HMS *Sirius* (1790). One analysis indicates a composition of 98.9% Cu, which is notably different from the 99.4% Cu detected in two other fragments. The main impurities in the three samples are lead and arsenic, though in different concentrations; 0.826% As in the first one (*ibid*, 268). This variability is probably associated with the fitting out and refurbishing of the ship, when different materials were introduced (*ibid*, 274–275). Likewise, it is possible

Table 2: Chemical composition of the copper samples.

Shipwreck	Artefact	Manufacture	Analyses	Composition (wt%)										
				Cu	Sn	Zn	Pb	Bi	As	Sb	Fe	Si	Ni	Ag
Deltebre (1813)	Cask strip	Rolled / Forged	OES, AAS	99.400	0.014	<0.003	0.037	0.082	>0.410	0.023	0.002	0.002	0.018	0.085
Deltebre (1813)	Sheet with holes	-	OES, AAS	99.300	0.009	<0.003	0.007	0.201	0.363	0.018	0.004	0.002	0.003	0.085
Deltebre (1813)	Bolt	-	OES, AAS	99.300	0.010	0.024	0.027	0.050	0.374	0.038	0.011	0.004	0.029	0.080
Deltebre (1813)	Bolt	Rolled	OES, AAS	99.400	0.008	0.026	0.033	0.057	0.387	0.033	0.003	0.002	0.020	0.068
Fougueux (1805)	Bolt	Forged	OES, AAS	97.600	0.008	0.029	0.493	0.240	0.257	0.036	0.002	0.005	0.043	bd
Fougueux (1805)	Spike	Forged	OES, AAS	99.200	0.008	<0.003	0.593	0.002	0.095	0.075	0.013	0.002	0.038	0.014
Fougueux (1805)	Spike	Forged	OES, AAS	99.300	0.017	<0.003	0.129	0.023	0.160	0.210	0.011	0.003	0.045	0.060
Triunfante (1795)	Spike	Forged	OES, AAS	99.200	0.006	0.021	0.052	0.101	0.256	0.204	0.003	0.001	0.065	0.055
Triunfante (1795)	Pipe jacket (indet)	Rolled / Forged	OES, AAS	99.000	0.008	<0.003	0.440	0.005	0.108	0.310	0.003	0.003	0.033	0.054

Notes:
bd = below detection limit

that the materials came from different foundries, which would be associated with the usual practice of supply by contract (Stanbury 1994, 37). This is an example of the variability that morphologically similar pieces within a particular site can exhibit (*eg* Samuels 1992; McCarthy 2005).

The samples analysed for this report show some differences in lead content, which seems to be related to their provenance (under 400ppm in the case of Deltebre I but always over 1000ppm for the *Fougueux* with some values over 5000ppm). The possible intentional incorporation of lead is discounted due to its very low content (even in the cases of the pieces with *c*0.5% Pb). Both the lead and the other trace elements could be associated with ore impurities, with some stage of the process of copper production or even with the manufacture of the pieces. Meanwhile, the arsenic is higher in the pieces from Deltebre I (>3500ppm) than in those of the other two shipwrecks (max 2500ppm). This element, which in larger quantities produces an increase in the metal hardness during cold-working (Samuels 1983, 72; MacLeod 1994, 274), is in the usual range for artefacts of this date.

The variability in the concentrations of certain elements such as lead and arsenic in the artefacts from these shipwrecks is probably related to the different place of origin of the raw material used in each case. Arsenic content has also been considered in the case of some copper sheathing tacks from one site, that of the HMS *Bounty* (1790) (Viduka and Ness 2004, 163). Nickel appears in very low concentrations, but in general they are greater in the *Fougueux* and *Triunfante* than in the samples from the Deltebre I wreck. In contrast, silver is present in higher amounts in the pieces from the British ship. Probably both elements are impurities which were associated with the mineral used to produce the copper.

Copper alloy artefacts

The copper alloy pieces analysed were made by casting, mainly using ternary or quaternary alloys. The contents of the three main alloying elements (tin, zinc and lead) might be linked with the producers' choices, who searched for specific characteristics related to the materials' behaviour during the manufacture process and in use. The high lead content of some fastenings could have been added to reduce the melting point, thus making the casting process easier. On the other hand, the tin concentrations in most of the copper-zinc artefacts would have improved performance, particularly resistance to marine corrosion.

The variations of the three main alloying elements present in the fastenings from one site (*eg* Deltebre I and *Triunfante*) might be related to restrictions in the available technology, and in the standards of the usual manufacturing process; for instance, a variable or low level of control of the composition of these kinds of

Table 3: Chemical composition of the copper alloy samples.

Shipwreck	Artefact	Manufacture	Analyses	Composition (wt%)										
				Cu	Sn	Zn	Pb	Bi	As	Sb	Fe	Si	Ni	Ag
Swift (1770)	Suction pump pipe	Cast	OES, AAS	69.900	7.900	0.114	>20.5	0.141	>0.480	0.356	0.030	<0.001	0.160	0.105
Swift (1770)	Sheave coak	Cast	OES	Bal	3.200	0.063	>20.5	0.056	bd	bd	0.091	<0.004	bd	bd
Deltebre (1813)	Bolt ring	Cast	OES, AAS	93.500	0.190	4.700	0.550	0.131	>0.480	0.049	0.105	0.002	0.040	0.095
Deltebre (1813)	Spike	Cast	AAS	Bal	6.700	3.400	4.700	0.060	0.130	0.019	0.020	0.009	bd	bd
Deltebre (1813)	Nail	Cast	AAS	Bal	7.700	9.950	2.250	<0.008	0.190	0.220	0.320	<0.004	bd	bd
Triunfante (1795)	Sheave of treble block	Cast	OES, AAS	79.900	9.330	3.250	5.900	0.037	>0.480	0.376	0.245	<0.001	0.155	0.080
Triunfante (1795)	Sheathing tack	Cast	AAS	Bal	10.500	4.200	7.920	0.030	0.185	0.014	0.332	0.041	bd	bd
Triunfante (1795)	Small nail (wooden sheathing)	Cast	AAS	Bal	5.620	0.015	0.341	0.012	0.049	0.230	0.080	0.019	bd	bd
Triunfante (1795)	Small nail (wooden sheathing)	Cast	AAS	Bal	6.800	0.240	0.150	0.060	0.180	0.090	0.030	0.015	bd	bd

Notes:
Bal = balance, bd = below detection limit

objects, which could include recycled metal. Samuels (1992, 92) emphasises that the manufacturers might have had different opinions as to which was the best composition for an artefact. Nevertheless, as the author indicates for other cases, the artefacts analysed here would have performed well in the environment where they were supposed to work.

It is interesting to note the high lead content of the suction pump pipe and of the sheave coak of the *Swift*, in both cases Pb >20.5%. This amount of lead would not only have assured a lower melting point than that that of pure copper, but it would have been incorporated with the purpose of improving some metal properties, such as the ductility (better than a bronze with high tin content), the strength (better than pure lead), and the friction resistance. These characteristics are consistent with the stresses to which the pieces would have been subjected. In other cases, such as some of the rudder fittings of HMS *Sirius* (1790), the presence of low percentages of lead (see Stanbury 1994, 103) would have served to relieve the friction on the wearing surfaces (McCarthy 2005, 136–137).

The trace elements are all present in concentrations that suggest a non-intentional incorporation. As in the case of pure copper artefacts, it is possible that they correspond to impurities associated with the ores, the copper smelting process, and the manufacture of the pieces. Samuels reported that bronzes with iron contents above 0.3% (*ie* particles of ferrite, which are anodic in relation to copper), can suffer preferential corrosion. This author argued that the values recorded for the cannons he studied, can be explained by the fact that they were usually cast from recycled bronze artefacts –among them, bells and old cannons – which could contain some ferrous component that would be then incorporated into the new melt (Samuels 1992, 99). The present study shows low percentages of iron in the copper alloy objects which would not have had harmful effects.

Some observations about the relation between these trace elements and the provenance of the materials can be made. It should be noted the bismuth and arsenic concentrations show some differences between the sites; the highest values of these two elements appear in many of the British artefacts (from the *Swift* and Deltebre I). However, it is worth noting that the arsenic and silver contents of one of the pieces from the *Triunfante* site (the treble block) are within the range for the artefacts found in the former shipwrecks.

Final comments

The analysis by means of OES – together with AAS and IR – allowed obtaining detailed information about the chemical composition of many metallic objects recovered from some mid 18th- to early 19th-century European warships. Based on these results, and taking into account the historical and archaeological information available for these sites, it was possible to discuss some issues related to the functionality of artefacts, the quality of the alloys and their possible provenance. Some trace elements allowed the grouping of artefacts from each vessel, according to its country of origin, and might indicate the provenance of the material used to make them. Likewise, it was possible to identify some objects that would have been manufactured with foreign (imported) raw materials. Further studies on samples from other sites will allow the development of these and other questions regarding the knowledge and practices associated with naval metallurgy of this period.

Acknowledgments

The study was carried out thanks to the Coghlan Bequest Grant awarded in 2012 by the Historical Metallurgy Society. Thanks are also due to my advisors, Dolores Elkin and Horacio De Rosa, for their support in this research and valuable comments on the manuscript; to Gustau Vivar Lombarte, director of the Catalan Centre for Underwater Archaeology, for offering the possibility of working with the materials from the *Triunfante* and Deltebre I sites; to Carmen Garcia Rivera, head of the Andalusian Centre for Underwater Archaeology (CAS-IAPH); to Nuria Rodríguez Mariscal and Milagros Alzaga García, directors of the *Fougueux* research project, for providing the materials of the site for their analysis; and to Mr Andrés Boero, president of the Company ABS Corp, for his generous collaboration with the analytical techniques and instrumentation. Figure 1 reproduced by courtesy of the CAS-IAPH, Figure 2b is by S Massaro, and Figs 2a, 3a and 3b are by the author.

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