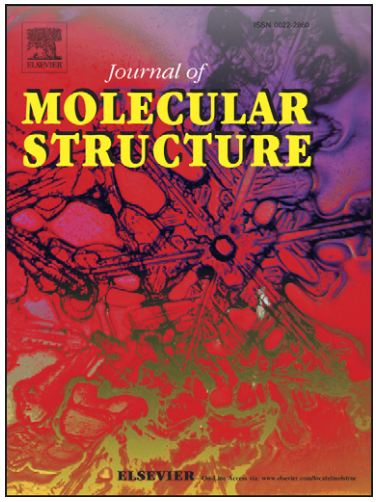

Characterization of cultural remains associated to a human skeleton found at the site HMS *Swift* (1770)

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Characterization of cultural remains associated to a human skeleton found at the site HMS *Swift* (1770)

M.S. Maier[a,*], B.A. Gómez[a], S.D. Parera[a], D. Elkin[b], H. De Rosa[c], N. C. Ciarlo[b,c], H. Svoboda[d],

[a] UMYMFOR (CONICET-UBA), Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria (C1428EGA) Buenos Aires, Argentina
[b] Programa de Arqueología Subacuática, Instituto Nacional de Antropología y Pensamiento Latinoamericano, 3 de Febrero 1378 (C1426BJN) Buenos Aires, Argentina.
[c] Laboratorio de Materiales, Departamento de Ingeniería Mecánica, INTECIN, Facultad de Ingeniería, Universidad de Buenos Aires, Paseo Colón 850 (C1063ACV) Buenos Aires, Argentina
[d] Laboratorio de Materiales y Estructuras, INTECIN, Facultad de Ingeniería, Universidad de Buenos Aires, Las Heras 2214 (C1127AAR), Buenos Aires, Argentina.

Corresponding author. Tel 541145763385; fax: 541145763385.
E-mail address: maier@qo.fcen.uba.ar (M.S. Maier)

Abstract

Different types of materials found in association with a human skeleton found in an 18th century shipwreck in Patagonia (Argentina) were analyzed by means of OM, SEM-EDX, HPLC, and chemical analysis. Alizarin and purpurin, the main anthraquinones of the dye plant *Rubia tinctorum* L. (madder) were identified as the coloring matter of a red fabric attached to the skeleton. Metallographic and chemical analysis of one of the dome-shaped buttons associated to the human bones revealed that it was composed of a Pb-Sn-Cu alloy known as pewter. The results obtained support the hypothesis that the remains originally were part of a private marine uniform.

Keywords: HPLC-DAD, SEM-EDX, madder, pewter, HMS *Swift*, underwater archaeology

1. **Introduction**

On March 13th 1770 the British sloop of war HMS *Swift*, commissioned to Port Egmont in the Falkland/Malvinas Islands, struck a sumberged rock and sank in the estuary of what is currently Puerto Deseado, in Argentinean Patagonia. The complement of a 14 gun sloop of war of this period would normally be of around 110-125 men. It was formed by Commissioned and Warrant Officers, Petty Officers, Servants, and 37 to 50 Seamen. Adittionally, there would be about 25 Marines on board, under the command of their own Sargeant and the Second Lieutenant of the ship [1]. The only men who wore uniforms were the Commissioned and Warrant Officers, characterized by their blue jackets, and the Marines, characterized by their red jackets. The rest of the crew did not wear a uniform at that time, and their clothing was quite simple, lacking the distinctive colours of the officers and the Marines [2]. At the moment of the sinking, the historical documents state that the Swift had a complement of 91 men including the group of Marines. Only three of them –the cook and two private marines– died in the wrecking [3].

The wrecksite of HMS *Swift* was discovered in 1982 by local divers from Puerto Deseado, and since 1998 it is being excavated by the underwater archaeology team of the National Institute of Anthropology. The remains of the Swift are characterized by its outstanding preservation, and the excavation conducted so far has revealed a great variety of artifacts [4]. In one of the latest field seasons a complete human skeleton was found, and several studies were carried out in order to test the hypothesis that the remains correspond to one of the private marines who died in the accident.
The aim of this work was to investigate the chemical composition and microstructure of different types of materials found in association with the skeleton, mainly fragments of fabric and buttons.

2. Experimental

2.1. Materials

The wreck lies at a maximum depth of 18 meters, and the surrounding environment is characterized by low water temperature and relatively strong currents. The human skeleton considered here, located inside the captain's cabin, was covered by a thick layer of compact, fine-grained sediment, which favored its preservation. Once in the laboratory of the local museum of Puerto Deseado (Santa Cruz province, Argentina) the bones were gently rinsed with tap water but there was no intention to desalinize them completely, as is the standard procedure with all the artifacts, given that the remains would be subsequently interred. As for the material associated with the bones and described in this paper, some of it was attached to the skeleton and some was loose. The fabric was sampled at the National Institute of Anthropology once the bones were dry, while the buttons were studied –either as a whole or sampled if necessary– once they were completely desalinated and dry.

Samples INA EHB (grayish) and INA EH7 (see Fig. 1) correspond to unidentified material attached to the skeleton's skull and scapula, respectively, and presumed to be traces of fabric. The archaeological assemblage associated to the human bones included 32 dome-shaped buttons (see Fig. 2) of at least three different types (Table 1), one stock buckle, both shoes with their respective buckles, and fragments of leather spatterdashes.

2.2. Methods

SEM-EDX analysis of samples INA EHB and INA EH7 was performed using a Philips XL 30 ESEM. Analytical HPLC was carried out on a Gilson 506C HPLC system using a Phenomenex Gemini 5 µm column (25 cm x 4.6 mm i.d.). Compounds were detected using a 170 photodiode array detector set at 254 nm, operated in series with an Unipoint System software, recording the absorption spectrum in the range 190 - 700 nm. Gradient elution was performed using two solvents, A: MeOH and B: 1% (v/v) aqueous ortophosphoric acid. The gradient started with 36% A during 5 min and was raised to 90% A within 10 min, followed of 20 min at this condition. Solvents utilized in the HPLC were filtered through a 0.2 µm filter prior to use. The flow rate was 0.8 $mL.min^{-1}$. Sample INA EH7 was treated with hydrochloric acid 37% (HCl, Riedel-de Häen) and methanol (MeOH), Merck) according to the following procedure. The sample was immersed in 400 µL of H_2O:MeOH:37%HCl (1:1:2, v/v) and kept at 100 ºC for 15 min. Then the liquid phase was evaporated (50-60 ºC) under gentle nitrogen flow. The dry residue was dissolved in MeOH. Finally, the methanolic solution was filtered through a 0.2 µm inorganic Whatman membrane filter (Schleicher-Schell) and submitted to HPLC. TLC analysis of the fibers of samples INA EHB and INA EH7 was performed on precoated Si gel F254 (butanol:AcOH:H_2O (80:20:20)) and detected by spraying with ninhydrin 0.2% in EtOH [4].

Acid hydrolysis of samples INA EHB and INA EH7: Each sample (1 mg) was heated in a Pierce vial with HCl 6 N (0.5 ml) at 100 ºC for 24 h. After evaporation under nitrogen, the residues were dissolved in HCl 0.1 N and analyzed by TLC on precoated Si gel F254 (*n*-butanol:AcOH:H_2O (80:20:20)) and detected by spraying with ninhydrin 0.2% in EtOH.

SEM-EDX analysis of one of the small buttons with the "T" and "L" marks (see Table 1) was performed using a Philips 505 microscope. Optical microscopy was performed with a Reichert MEF II metallographic microscope. The sample was cut by its middle part and the surface of the resulting section was polished with alumina 0.05 µ granulometry and then etched with a solution of AcOH:HNO_3:glycerol (1:1:8).

3. Results and discussion

As a preliminary investigation, samples INA EHB and INA EH7 were analyzed for the presence of a protein fabric. Both samples were submitted to acid hydrolysis and analyzed by TLC [5], confirming the presence of wool as the textile adhered to the skull and scapula. Analysis by SEM-EDX of sample INA EH7 showed the presence of carbon and oxygen in high concentrations with minor amounts of silicon, aluminium, sodium, magnesium, iron, calcium, sulfur, chloride and potassium. This elemental composition suggested the presence of an organic dye as the coloring matter of the woolen fabric attached to the scapula. In order to characterize the red dye components, sample INA EH7 was hydrolyzed to extract the dyestuff [6] and the extract analyzed by reverse phase HPLC-DAD. The chromatogram is given in Fig. 3. Two peaks corresponding to alizarin and purpurin (see Fig. 4) were observed. These chromophores are present in the roots of a variety of plants from the Rubiaceae family, which are arranged under the general name of madder [7]. As alizarin (1,2-dihydroxyanthraquinone) and purpurin (1,2,4-trihydroxyanthraquinone) are the main colouring compounds in *Rubia tinctorum* L. [8], it is probable that the dye was an extract of this plant, as the other members of the species, e.g., *Rubia peregrina* or *Rubia munjista* contain other predominating substances [7]. The identification of madder-dyed red wool associated to the part of the skeleton corresponding to the torso constitutes an

evidence of a red jacket, almost certainly part of the uniform that was only worn by the private marines on board the ship [9].
Fig. 2 shows the front and back view of one of the buttons associated with the human skeleton. Metallographic and spot chemical analysis revealed a microstructure formed by an eutectic compound with intermetallic particles (see Fig. 5). Elemental analysis by SEM-EDX (Table 2) showed the presence of lead and tin with some copper, which corresponds to an alloy known as pewter. SEM-EDX analysis (Table 2) of one of the cavities on the back of the button (see Fig. 2) revealed the presence of iron indicative of a completely corroded iron shank. No structural differences were detected at the joint between the front and back part of the button. This observation and the presence of a diametral line at the back part, suggest that it was manufactured as a single piece using a casting mold formed by various components. This latter aspect is noticeable since the bibliography states that they were made in two separate pieces (dome and base) which were later welded together [10,11]. In the 18th century there were various garments which included buttons, such as vests, shirts, trousers, neck cloths, spatterdashes, and hats [12], and in many cases the buttons could be made of metal. By the time of the *Swift*, the dome shaped buttons were used in several components of the uniform which had been regulated for the British Navy officers since about two decades before [13]. Although metal buttons and shoe buckles could be part of many types of clothing, the number and type of buttons, as well as the stock buckle, indicate that the person was very probably wearing a uniform. Each leather spatterdash, for instance, had at least nine buttons. Also the standardized metal buttons, which had a relatively high economic value, as well as the stock buckle, were rarely used among ordinary seamen.

4. Conclusions

Application of SEM-EDX and HPLC-DAD to the analysis of inorganic and organic materials found in association with a human skeleton found in the wrecksite of HMS *Swift* provided useful information about the analytical composition of the materials. The combination of chemical results and archaeological evidences strongly supports the hypothesis that the skeleton corresponds to one of the private marines who died in the wrecking of HMS *Swift*.

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Fig. 1. Human skull from HMS Swift with traces of gray fabric (a) and human scapula from HMS Swift with traces of red fabric (b).

Fig. 2. Front (a) and back (b) view of one of the buttons associated with the human skeleton from HMS Swift. Image of the button section showing the place where iron was identified (c).

Fig. 3. HPLC chromatogram of the extract of sample INA EH7. Peak 1 corresponds to alizarin, peak 2 is purpurin.

Fig. 4. Chemical structures of alizarin (**1**) and purpurin (**2**).

Fig. 5. Microstructure formed by globules of Lead-rich solid solution (dark) and white particles of a Copper-Tin compound in a matrix of Tin-rich solid solution.

Figure 1

Figure 2

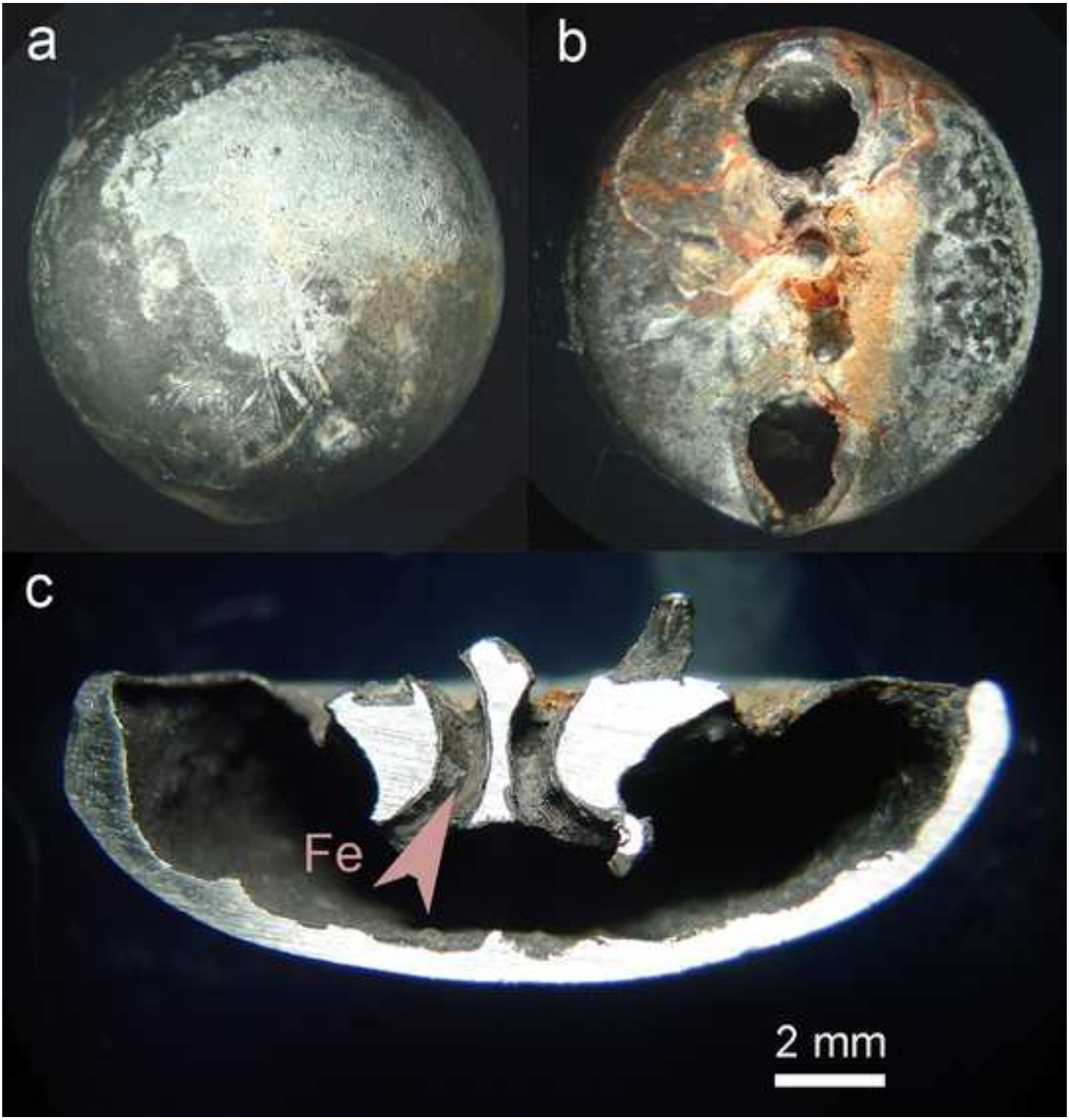


Figure 3

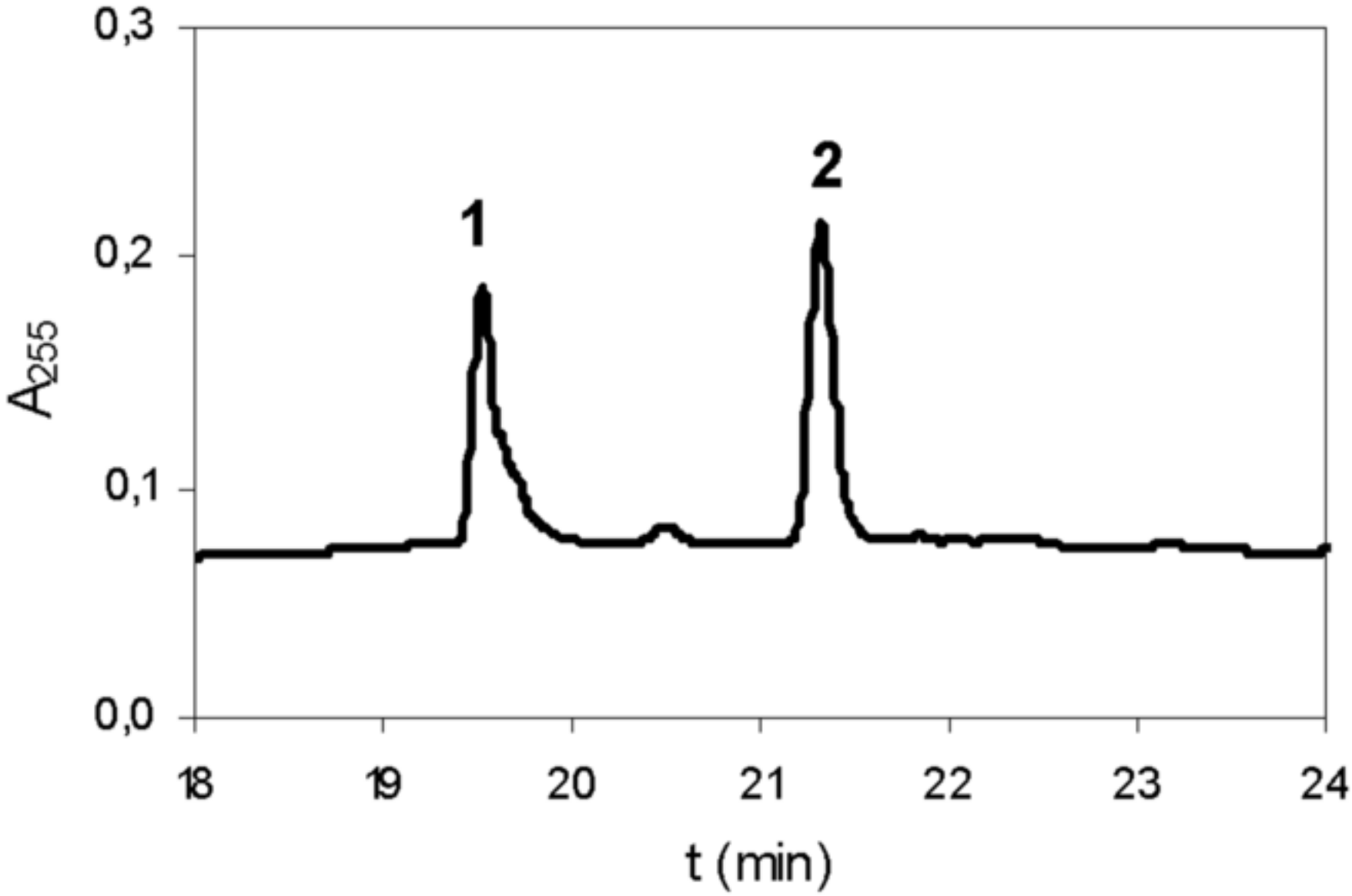
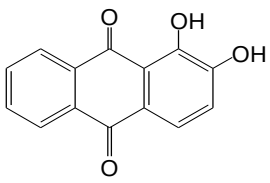


Figure 4



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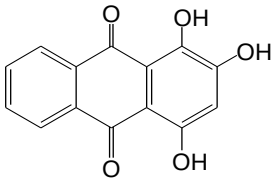

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Figure 5

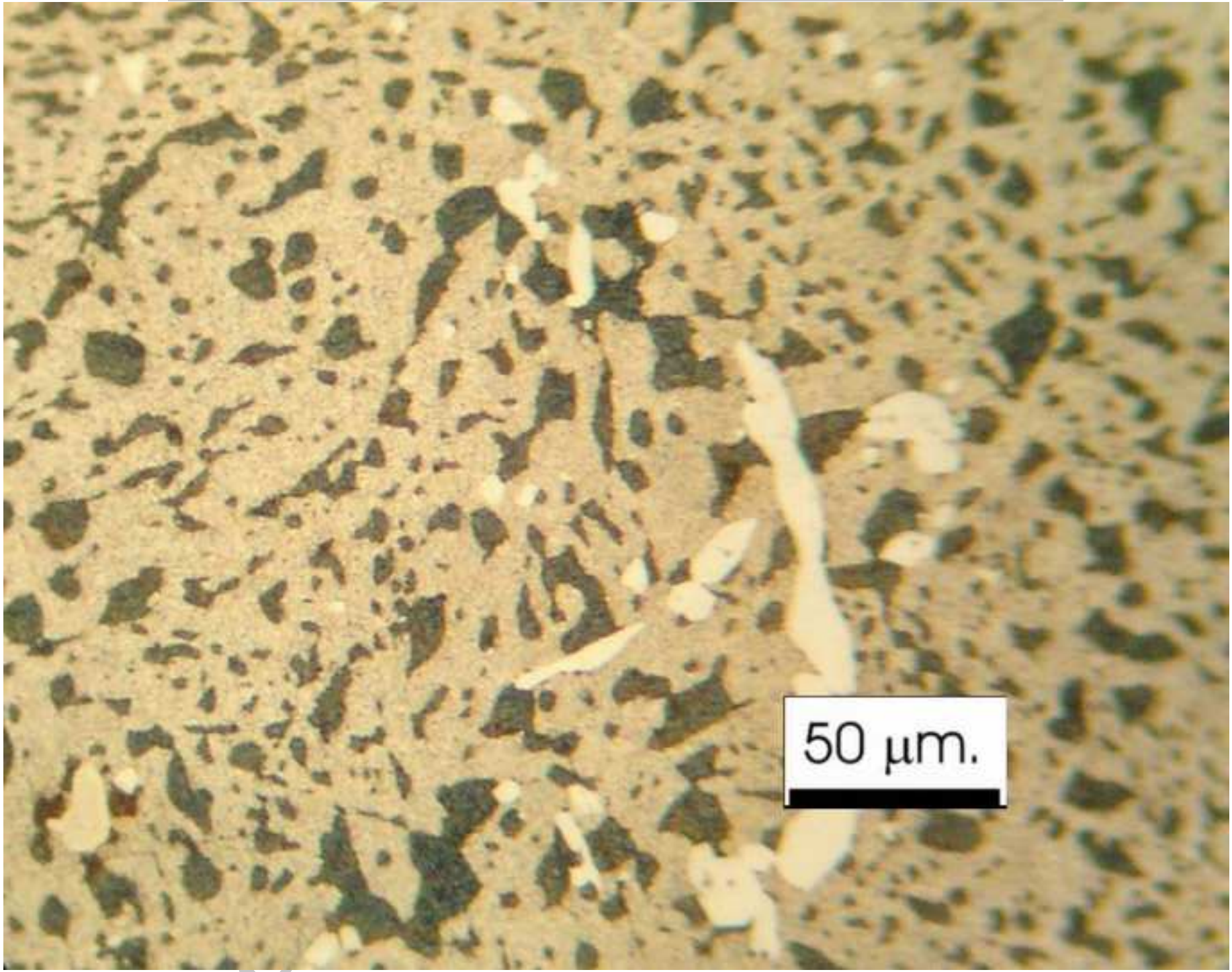

Table 1. General characteristics of the dome-shaped pewter buttons found in association with the human skeleton from HMS *Swift*.

Buttons	**Quantity**	**Average Diameter (mm)**	**Average thickness (mm)**	**Iron shank**	**Observations**
Big	6	21.4	8.9	No	No superficial marks. One of the buttons is slightly bigger (d: 22.4 mm; t: 10.5 mm)
Small type A	14	17.7	7.1	No	"T" and "L" marks on the obverse
Small type B	12	17.1	5.7	No	No superficial marks

Table 2. Elemental composition detected in different parts of the button section, according to EDS results (weight %).

Zone of measurement	Sn	Pb	Cu	Fe	Others
Tin-rich solid solution phase	97.55	2.45			
Lead-rich solid solution globules	8.75	91.25			
Copper-Tin compound	65.89	1.28	31.14	0.96	Ni, 0.73
Cavity left by the corroded shank	41.89	21.05	2.41	34.65	