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Raman spectroscopic analysis of archaeological specimens from the wreck of *HMS Swift*, 1770

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Specimens from underwater archaeological excavations have rarely been analysed by Raman spectroscopy probably due to the problems associated with the presence of water and the use of alternative techniques. The discovery of the remains of the Royal Navy warship *HMS Swift* off the coast of Patagonia, South America, which was wrecked in 1770 while undertaking a survey from its base in the Falkland/Malvinas Islands, has afforded the opportunity for a first-pass Raman spectroscopic study of the contents of several glass jars from a wooden chest, some of which had suffered deterioration of their contents owing to leakage through their stoppers. From the Raman spectroscopic data, it was possible to identify organic compounds such as anthraquinone and copal resin, which were empirically used as *materia medica* in the eighteenth century to treat shipboard diseases; it seems very likely, therefore, that the wooden chest belonged to the barber-surgeon on the ship. Spectra were obtained from the wet

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and desiccated samples, but several samples from containers that had leaked were found to contain only minerals, such as aragonite and sediment.

This article is part of the themed issue 'Raman spectroscopy in art and archaeology'.

1. Introduction

The recovery and preservation of artefacts from subaqua marine archaeological excavations requires the adoption of special techniques designed to minimize the further biodeterioration of sensitive materials occasioned by their exposure to aerobic oxidation [1–3]. In particular, the desiccation of thoroughly wet specimens is not favoured archaeologically as this can cause the onset of unduly large mechanical stresses and a primary conservation exercise usually involves the spraying of an artefact with protective materials to aid the retention of water such as an aqueous solution of polyethylene glycol, as used for the ongoing preservation of excavated ships' timbers. Added to this in the depositional environment are the effects of corrosion of metal objects caused by seawater, the growth of biological colonies on a variety of substrates, the erosion of soft materials by shipworm (e.g. teredo) and wood-eating fungi, the mechanical collapse of superstructures through decay of their supports, the silting of open spaces by marine debris and damage to partially buried structures by wave motion, fishing and shipping transport in commercial lanes [4]. The analysis of artefacts from a underwater excavation must recognize and allow for these scenarios, while attempting to deliver the molecular structural information required to assist conservators in the selection of the proper protocols that need to be adopted for their ongoing preservation.

The recovery of artefacts from marine archaeological excavations is necessarily a painstakingly slow and rather dangerous process that normally occupies several years of activity; the opportunities afforded for the molecular structural analysis of materials of interest that have not already been subjected to urgent conservational invasive procedures that obscure much useful information is limited; here, we report the Raman spectroscopic analyses of a group of specimens recovered from a wooden chest, believed to possibly contain a barber-surgeon's *materia medica*, dating from the late-eighteenth century, which have been recovered recently from a marine archaeological excavation that has been ongoing for some 15 years. Preliminary data on some archaeometric results have been presented in an archaeological site report and as a case study [5,6]; we present here the full Raman spectroscopic data analysis which illustrates the application of the technique to the development of underwater archaeological excavation, artefact curation and preservation.

(a) HMS Swift

The *Swift* was one of the two sloops-of-war in its eponymous class [7], the smallest class of ship (immediately below sixth-rate) in the Royal Navy fitted out for transoceanic voyages, the other ship in the Swift class being the *Vulture*; the *Swift* was constructed in John Greaves' shipyard on the Thames at London in 1763, of displacement 263 tonnes, length 27.8 m and with a beam of 7.8 m. She had an unusual design feature of a deep underwater hull, and ports for oars located between the gun ports on the gun deck, useful attributes for heavy seas and close quarters exploration. For duty in the South Atlantic, she was ship-rigged as a three-masted with a main armament of 14 six-pounder, 2 m long iron cannon of Armstrong pattern, supplemented by 12 1 m swivel guns firing half-pound shot, eight on the quarter-deck and four on the forecastle [8]. Her ship's complement was 91 men, including a detachment of Marines, under the command of Captain George Farmer. With her consort vessel, *HMS Favourite*, she operated on coastal surveying duties out of Port Egmont in the Falkland/Malvinas Islands, which were in dispute with first French and then Spanish naval forces [9]. In the eighteenth century, the strategic exploration of the South

Atlantic was critical for the development of maritime traffic and trade between the Far East, Peru, Chile and Europe via the Cape Horn and Britain, France and Spain were active in promoting their interests in this area.

In early March 1770, the *Swift* set off from Port Egmont to conduct geographical surveys in the area. However, she faced several days with strong gales from the southwest, after which she reached the shores of mainland Patagonia. Captain George Farmer decided to enter the Deseado estuary, but they had the misfortune of stranding on a submerged rock and losing the vessel a few hours later. Ever since, HMS *Swift* lies on the bottom of the Deseado estuary, Santa Cruz Province, Argentina. Eighty-eight of the crew survived the sinking, and the body of the ship's cook was later recovered from the sea; the bodies of the two Marines missing were never recovered. It was a desperate situation, and the survivors did not have enough food or warm clothing to survive the approaching winter; hence an officer and six sailors were then dispatched in the ship's cutter 400 miles to Port Egmont where they secured help from *HMS Favourite* in the rescue of the remaining crew a month later. Captain Farmer was exonerated for the loss of his ship at court martial in London, and later in the same year he commanded the Falklands/Malvinas garrison in the first exchange of hostilities with Spanish invading forces under the command of Commandante Juan Madariaga in what later became known as the first Battle of the Falklands, June 1770. This affair ended with the honourable surrender of Captain Farmer when his ammunition was exhausted to the numerically superior force of Commandante Madariaga.

The wreck of the *Swift* was discovered in Puerto Deseado in March 1982, following an exploratory research visit in 1975 by Patrick Gower, a descendant of Lieutenant Erasmus Gower of the *Swift*, whose letter describing the loss of his ship enabled divers to find the submerged wreck [10]; she is extremely well preserved in the cold waters of the South Atlantic and lies on her port side at an angle of 60° with her bow some 10 m and stern some 20 m below the surface. There was minimal damage to the hull structure, and the site has a high archaeological integrity; the rock that caused the sinking has provided a significant degree of protection, and there has been no ocean swell damage or salvage attempted hitherto. Some 70% of the hull structure has survived and the archaeological remains cover an area of 180 m^2; owing to the significant list, the starboard side is more exposed and the best-preserved section is that of the port side, representing about 60% of the wreck [11]. Many artefacts have been recovered from the wreck and have provided a rich insight into eighteenth-century naval life at 'the edge of the world' [12,13]. In 2005, a diving team led by Dr Dolores Elkin discovered human skeletal remains near the Captain's cabin that proved to be those of one of the missing Marines; although his identity is as yet unknown, he was buried with full military honours in 2007 in Chacarita Cemetery, Buenos Aires [14]. The detailed ship's plans exist in the National Maritime Museum, Greenwich, London, and have been quite useful in determining the location of the artefacts at the wreck site [8].

Recently, further dives on the *Swift* [6] have located a wooden chest containing 12 compartments, in what is believed to be the barber-surgeon's cabin, containing several stoppered glass vials and two ceramic jars; several samples were selected for this preliminary study, using non-destructive Raman spectroscopic analysis to determine if it is a medicine chest. If so, it would confirm the proposed cabin location on the wreck as being that of the surgeon-barber. The discovery of medicinal substances is relatively rare in underwater archaeological excavations and the techniques adopted for their characterization must be scrupulously applied [15]; although small glass bottles similar to those found on the *Swift* were recovered from the wreck of *HMS Pandora*, which sank in 1771 off the Barrier Reef, Australia, there have been no published reports of their contents [16]. Following extensive excavations of a significant portion of the officers' quarters above the main deck of the *Swift* in 2006, a small cylindrical glass bottle sealed with a cork and containing a white suspension was found in a wooden chest along with personal belongings. After sequestration and drying, this was analysed by X-ray fluorescence spectroscopy [15] and identified as calomel, mercury(I) chloride, which was used for therapeutic purposes in the eighteenth century as a diuretic, an antiseptic and in the treatment of various diseases including venereal syphilis. From its location and the presence of associated material, it is believed that this glass bottle was the property of an officer on board *HMS Swift* and was not a component of the barber-surgeon's medicine chest. A comparable excavation of the privateer *Defence*, which sank during the American Revolutionary War in 1779, reported mercury(II) sulfide and mercury(II) oxide present in intact medicine bottles [17].

(b) Raman spectroscopy

Raman spectra were recorded using near infrared excitation at 1046 and 785 nm with Fourier transform and dispersive instruments, namely a Bruker IFS 66/FRA 106 interferometric and Renishaw InVia confocal microscopic instrument, respectively. In both cases, the laser power irradiance levels were selected to be minimal to avoid damaging the specimens; in previous examples of archaeologically excavated materials, the environmental exposure has caused sample deterioration, and the use of excessive laser power levels can cause severe burning, especially using focused laser beams and small sample illumination footprints. In the interferometric Fourier transform instrument, a footprint diameter of approximately 100 µm is used, whereas in the dispersive confocal microscope instrument, a 10× lens illumination objective results in a footprint diameter of about 20 µm. The wavenumber range of 3500–200 cm^{-1} was recorded in each case, using the spectral accumulations of between 20 and 200 scans to improve signal-to-noise ratios, with a spectral resolution of about 4 cm^{-1} for the interferometric instrument and about 0.5–1.0 cm^{-1} for the dispersive instrument. Each specimen was analysed at least six times at different positions to ensure that representative spectra were being obtained from possibly heterogeneous samples. In addition, several standards were run for comparison purposes to aid the identification of the unknown materials.

(c) Samples

Six specimens were taken from the vials in the suspected medicine chest, comprising

— M504: a yellow sludge; M507: a grey solid; M513: a light grey powder; M514a: a grey sludge and
— M514b: a brown sticky resin; M519: a grey-brown sludge.

The specimens were contained in several glass jars some of which were stoppered, and others had been corked; a typical example of one of these jars is shown in figure 1, with specimen M504 being extracted from it. Gentle desiccation was applied, and effected the removal of some of the liquid component which was attributed to some limited container leakage in the wreck site, leaving dry powders of unchanged colours. The Raman spectroscopic analysis of both the dried and wet specimens was accomplished successfully, and the results were found to be identical.

2. Results and discussion

The Raman spectra of samples M504 and M514b are shown in figures 2 and 3, respectively; these spectra are seen to be of reasonable quality that facilitates their assignment as follows.

Figure 2 shows the Raman spectrum of a bright yellow specimen, labelled M504, examined as dry powder and as an aqueous sludge as seen in figure 1. The major Raman bands occur at 1724, 1635, 1594, 1448 (shoulder) and 1434 cm^{-1}, and these can be attributed to a fused ring aromatic species of an anthraquinone type. Other very weak features labelled in the figure between 834 and 137 cm^{-1} are not really significant for characterization purposes but probably belong to CCH, CCO and CCC bending modes; they have an intensity just above the background emission and will not be discussed further here. The first two bands at 1724 and 1635 cm^{-1} are characteristic of the quinone moiety and the latter two of aromatic ring CCH stretching vibrations, particularly that at 1594 cm^{-1} [18]. The sharp feature at 84 cm^{-1} is a known spectrometer artefact.

Figure 1. Specimen jar with yellow sludge. (Online version in colour.)

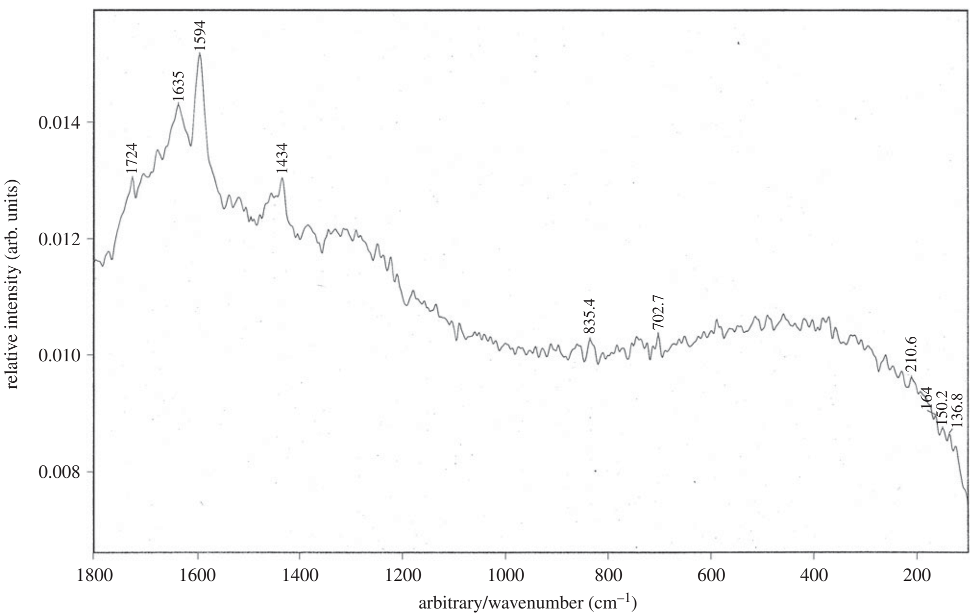

Figure 2. Raman spectrum of specimen M504, a bright yellow sludge, shown in figure 1. Excitation at 1064 nm using a Fourier-transform instrument.

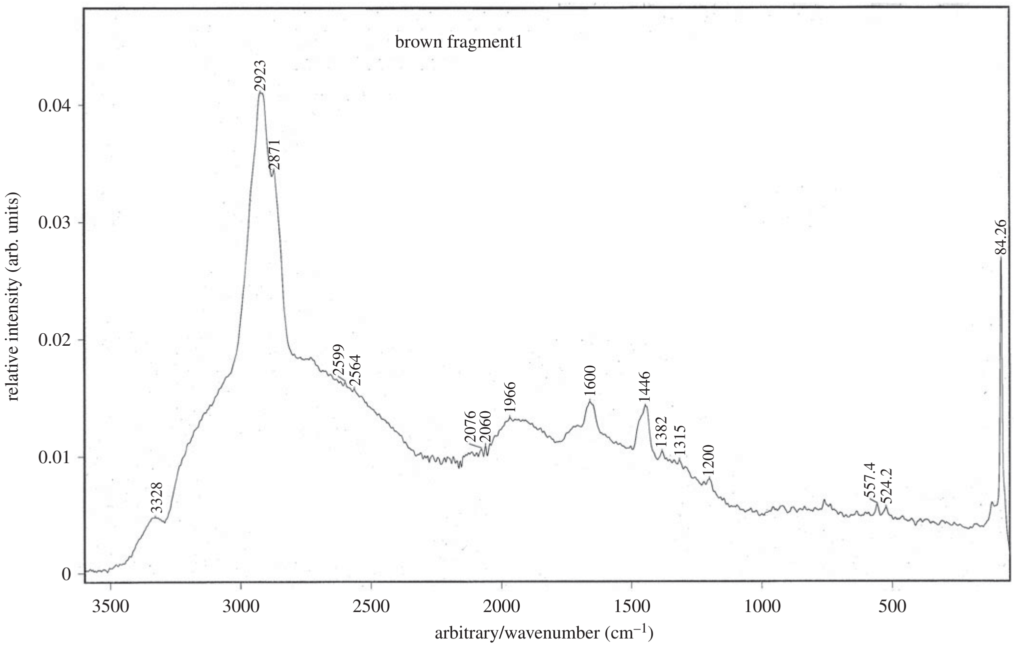

Figure 3. Raman spectrum of specimen M514b, a sticky orange-brown resin. Excitation at 1064 nm using a Fourier-transform instrument.

Figure 3 shows the Raman spectrum of an orange-brown sticky resin, labelled M514b, with Raman bands occurring at 3328 (weak, broad), 2923, 2871, 1600, 1446, 1382, 1200, 557 and 524 cm^{-1}, which correlate well with an assignment to an amber or copal resin [19]. The highest of these is characteristic of OH stretching, the next two of aliphatic CH stretching, that at 1600 is indicative of C=C unsaturation and those between 1446 and 1200 can be assigned to CH deformation vibrations. The weak bands at 557 and 542 can be correlated with ring deformations and CCH-type vibrations.

The identification of M504 as an anthraquinone extract, for example from a naturally occurring lichen species, and M514b as a young copal resin strongly suggests that the box containing the glass vials was probably a medicine chest and strongly suggestive of its location in the barber-surgeon's cabin. In eighteenth-century men-of-war, the barber-surgeon was the physician and apothecary; medical practice was still very empirical, illness was attributable to bad humours and bodily tensions, such as fevers and inflammatory disorders, which were relieved usually by copious blood-letting and bodily purging. Medicines were normally based upon empirical botanical potions and preparations; it is significant that both copals and anthraquinone extracts from natural products were well known in medical treatments at this time and indeed had been for some centuries hitherto [20]. Copals and amber resins were recommended for throat afflictions, as a treatment for alleviating jaundice, for the treatment of gum disease and for their biostimulatory role in the restoration of a stable central nervous system following trauma. The anthraquinones and related extracts from lichen species were adopted as sunscreen protectants in the tropics, were beneficial in the treatment of gastrointestinal disorders, effective in toothache relief and had significant positive effects in the treatment of ulcers, and swollen gums, and it was claimed even arrested the onset of gangrene. Anthraquinones are important constituents of epilithic lichens, where their synthesis is undertaken to provide radiation protection and to assist carotenoids in DNA repair functions; their inclusion as extracts from lichens in homeopathic body purges was a standard of eighteenth-century medicine. An agreeable purge that was popular in the late-eighteenth century was an infusion of senna pods and lichens steeped in French brandy with the addition of sugar. Of perhaps even greater significance for the current scenario on *HMS Swift*, in 1770, the presence of scurvy was prevalent in naval crews spending lengthy times at sea without fresh fruit and vegetables; scurvy arises when levels of vitamin C (ascorbic acid) are low, and if left untreated over a prolonged time results in haemorrhaging of weakened connective tissue and eventually these scorbutic episodes cause clinical exchanges in the bones. Vitamin C is essential for the hydroxylation of the amino acids lysine and proline, which are major structural components of collagen in soft tissues and bone. Buchan [21], in his classic text on the general causes of disease, first published in 1769, attributes scurvy to a 'vitiated state of the humours occasioned by long periods spent in cold, damp conditions aboard a ship' and was best treated using purges; the disease was common for populations over-wintering on stored produce and the extent of suffering is difficult to estimate as only the most serious cases actually gave observable evidential residues in excavated skeletal remains (Koon H. 2013 School of Archaeological Sciences, University of Bradford, personal communication.). Another school of thought, typified by the treatises of Lind [22] and Bisset [23] published in 1757 and 1755, respectively, suggested that poor diet lacking in fruit and vegetables was also a contributory factor to the onset of scurvy at sea. However, even by the 1790s, this was still not accepted fully and extensive blood-letting and purging were recommended as the medical treatment for scurvy—the effect of this upon an already weakened patient suffering from the ravages of scurvy can only be imagined. An idea of the terrible effect that scurvy had upon naval crews of this period can be obtained from the voyage of Admiral Anson to the South Atlantic and Pacific Oceans during 1740–1744, when only 145 men survived scurvy and returned home from an initial complement of 1029; despite this attrition, this was hailed as a highly successful voyage!

The discovery in this work, therefore, of two medicinal *materia medica* specimens used in the recommended treatment of shipboard disease at that time, especially scurvy, is highly significant and it firmly identifies the box found in the wreck of *HMS Swift* as a medicine chest. By inference, therefore, the location of the chest in the proposed barber-surgeon's cabin is also tenable. A third vial in this chest was not provided for analysis here, but we are informed that it contained mercury, which itself was used to induce vomiting, especially after the patient had ingested contaminated food [15]. Thus far, we have not identified other medicines or potions which might have been expected to be in the *materia medica* of a practising physician aboard a naval warship; we refer particularly to items that we have identified using Raman spectroscopy [24] in a medicine chest from the *Mary Rose,* King Henry VIII's flagship sunk in an engagement with French naval forces in the English Channel in 1545. Here, we also indentified several aromatic resins that were presumed to have therapeutic uses, but also found sulfur powder and amorphous carbon; the former would have been used in the treatment of open wounds and the latter in the form of *magdaleones* for the assuaging of skin burns incurred on gundecks in the heat of battle.

It is interesting that the identification of the contents of the other vials submitted for analysis here has not met with a similar success, and we can speculate on the reason for this; it is probable that the original contents of the vials have been severely affected by immersion in seawater for over two centuries—the archaeologists noted that some vials had been sealed with glass stoppers and others with corks. Clearly, the latter would not have preserved the integrity of the contents, which may have thus degraded with time through exposure to seawater over more than two centuries. The spectra of the solids and sludges remaining in the damaged vials where obtainable gave signatures only of sand, calcium carbonate and silicates, which had also been identified in our previous study of ruptured jars from the *Mary Rose* medicine chest [24], indicating that their original contents were now irretrievably lost. Nevertheless, the results from this study are positively encouraging for a more comprehensive study to now be undertaken using several molecular spectroscopic and analytical techniques, using more specimens and perhaps sacrificing small amounts of important specimens to amplify the data obtained from these first-pass analytical Raman spectroscopic studies.

3. Conclusion

The Raman spectroscopic analysis of several glass vials recovered from a wooden chest found in the wreck of *HMS Swift*, which sank off the coast of Patagonia in 1770, and now lies under 18 m of water in the South Atlantic ocean has been undertaken. Clear evidence for the presence of anthraquinones and a young copal resin in two of the glass-stoppered vials points to the probability that the chest belonged to the barber-surgeon because of the established association of these materials with homeopathic *materia medica* in the eighteenth century and their use to treat shipboard diseases. This result has therefore been instrumental in confirmation of the location of the proposed barber-surgeon's cabin on *HMS Swift*. Other specimens from vials yielded spectral signatures only of minerals such as calcite and sand, which could indicate that their original contents have now been lost by leakage of seawater through damaged corks. This case study represents one of the few examples of the application of Raman spectroscopy to underwater archaeology, and the advantages of using the technique for the first-pass analytical interrogation of wet specimens without invoking the necessity for sample desiccation are demonstrated.

Competing interests. We declare we have no competing interests.

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