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Raman spectroscopic analysis of a unique linen artefact: the *HMS Victory* Trafalgar sail

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The Battle of Trafalgar took place in 1805 and is generally accepted to mark the last occasion of combat between major fleets of sailing ships, when a combined Franco-Spanish force of 33 battleships was defeated by a British fleet of 27 battleships blockading Cadiz and the approaches to the Mediterranean Sea. The *HMS Victory* Trafalgar sail, the fore-topsail from Admiral Lord Nelson's flagship, was severely damaged and has since suffered significant natural deterioration. As the only extant early 19th century sail in the world, it is a unique artefact and arguably Britain's foremost maritime textile treasure. Prior to its display at the bicentennial exhibition in 2005, the sail was analysed by Raman spectroscopy. Complementary tensile tests were also completed on loose yarn from around the damaged areas. The mechanical data and Raman spectral comparisons suggest a good correspondence between the historic sailcloth and surrogate specimens. The latter were prepared by subjecting modern linen canvas to a four-stage regime of artificial ageing in an attempt to reproduce the weakened state of the 200-year-old sailcloth, and provide model material to help appreciate the properties of the historic canvas. Detailed analysis suggests that certain Raman signatures are characteristic of ageing and may correlate with reduced performance of the fabric, suggesting that the technique could offer a non-destructive approach to informing the preservation of a national textile heritage. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: *HMS Victory*; linen; ageing; textile

PROLOGUE

At noon on 21 October 1805, the last great open-sea battle of the 'age of fighting sail' took place when the combined Franco-Spanish fleet (Admiral Villeneuve, *Bucentaure*, 100 guns, and Admiral Gravina, *Santissima Trinidad*, 144 guns) left Cadiz and met the blockading British fleet under the command of Admiral Lord Nelson (*HMS Victory*, 100 guns) off Cape Trafalgar. The 27 battleships of the British fleet were inferior numerically and in firepower to the 33 battleships of the Franco-Spanish fleet, but a daring strategy adopted by Nelson in defiance of the accepted rules of naval engagement operating at that time resulted in an overwhelming victory in which by 4.30 P.M. 27 battleships of the Franco-Spanish fleet had been captured or sunk without loss to the Royal Navy. The death of Admiral Nelson from musketry directed from the *Redoutable* overshadowed the cessation of the battle. In the following days, several skirmishes between British prize-crews and Franco-Spanish naval squadrons led by Commodore Cosmao and Admiral Dumanoir with the six surviving Franco-Spanish battleships led to the recovery of three of the captured, badly damaged vessels but incurring a loss of a further five Franco-Spanish battleships sunk or captured.

The implications for European history of the defeat of the Napoleonic fleet at Trafalgar were profound: Napoleon's army of 90 000 men in the Netherlands, poised for the invasion of Britain, was isolated and the Emperor turned his attention east to Russia, with dire consequences some years later.

Nelson's bold stratagem involved the division of his fleet into two forces, the Weather Column led by Admiral Nelson in *HMS Victory* comprising 12 battleships and the Lee Column of 15 battleships led by Admiral Collingwood in *HMS Royal Sovereign* (100 guns). Both columns sailed in-line-astern and engaged the enemy fleet orthogonally; this meant that the British ships were receiving hostile gunfire without being able to return fire for some 30 min before they broke through the Franco-Spanish lines and retaliated with

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broadsides fired into the unprotected flanks of the enemy ships. The *Bucentaure* was taken out with the first broadside from the *Victory* and the *Royal Sovereign* accomplished the same with the *Santa Ana*. The close proximity of the naval action resulted in almost total destruction of the masts, sails and rigging of the opposing warships[1] and in severe losses to the naval crew on both sides; in this action the Royal Navy lost 449 killed and 1241 wounded, with 4408 killed, 2545 wounded and 7000 captured in the Franco-Spanish fleet.

A painting by J.M.W. Turner depicting the *Victory* engaging with the *Bucentuare*, having broken through the Franco-Spanish line is shown in Fig. 1. It depicts the foremast with fore-topsail attached being brought down by gunfire from the French battleship *Neptune*[1]; French naval tactics centred on the broadside firing 'on the roll', which caused disproportionate destruction to the sails, spars and rigging of the enemy warships.

INTRODUCTION

The *HMS Victory*, constructed as a First-Rated battleship in 1765, is now preserved in a dry dock at Portsmouth. In a complementary exhibition to mark the bicentenary of the Battle of Trafalgar in 2005, the fore-topsail (hereafter known as the *Victory sail*) is being displayed. It is the only surviving sail from the 60 battleships, and one of the 37 carried by the *Victory* into the engagement. The fore-topsail, ravaged by the battle with over 90 shot holes and tears, was cut from the rigging by the crew and stowed to await repair, but this was never carried out, and the 24×17 m sail survives to bear witness to the late 18th/early 19th century sailmakers' art.

In preparation for the display, the sail has recently undergone first-phase conservation by the Conservation Services staff at the Textile Conservation Centre. At the same time, the Conservation Science Group was asked to assess the condition of the canvas to address concerns over the handling of the sail and to inform decisions on the display methodology.

To determine the performance of the sailcloth, we carried out extensive tensile testing of loose yarn samples taken from around areas of damage.[2] As such tests are destructive, we also prepared surrogate material for more comprehensive studies by subjecting modern linen canvas to four stages of artificial ageing. The accelerated ageing regimen adopted was designed to mimic the rigours through which the sail had been put, including exposure to the marine environment during its working life and subsequent storage and occasional display over the intervening 200 years. We hoped to reproduce not only the weakened state of the

Figure 1. *HMS Victory*, Nelson's flagship at the battle of Trafalgar, 1805, leading the Weather Column against the Franco-Spanish Fleet, engaging with the *Bucentaure* and *Redoutable*, from a painting by J.M.W Turner (1822–1824). The fore-topsail, subject of this paper, is shown being brought down by gunfire from the *Neptune*; the battle ensign from the fore-topmast also survived the engagement and was later used in the funeral of Admiral Nelson in Westminster Abbey. This subject is the largest ever painted by Turner and was commissioned by King George IV for St. James' Palace. It is now in the National Maritime Museum, Greenwich. Reproduced with permission of the Curators of the National Maritime Museum, Greenwich, Ref. ID BHC0565.

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sailcloth but also the particular micro-structural and chemical changes within the linen fibres. A well-matched model material would then help us to appreciate the immediate properties of the historic canvas, and, following further destructive investigations, allow us to predict its future behaviour and make recommendations for its preservation.

Here, we report the results of Raman spectroscopy carried out on selected yarns from the *Victory sail* and the surrogate canvas. These have confirmed the match between the historic linen and the model specimens in the later stages of accelerated ageing. A detailed analysis of the spectra has further provided insight into the particular degradative damage incurred by the sailcloth, and has additionally revealed apparent signatures of ageing that may correlate with its physical condition. Since Raman spectroscopy has the potential for *in situ* application, this suggests that the technique may offer a non-invasive approach to monitoring similar marine textiles, informing their long-term preservation.

BACKGROUND

The cloth for *HMS Victory's* fore-topsail was woven from Scottish flax at the end of the 18th century. The bast fibres of cultivated flax, *Linum usitatissimum*, and hemp, *Cannabis sativa*, had been used for sailcloth for centuries, sometimes admixed with jute. The two-foot-wide bolts of canvas were supplied to the Admiralty by Baxter Brothers of Dundee and sewn together in the sail loft at Chatham Dockyard. It was rigged in 1803 when *HMS Victory* was prepared 'fit for sea for war'. Besides the obvious gross damage suffered during the Battle (Fig. 2), the linen canvas has since suffered further deterioration. The national importance of the sail and the need for its active preservation were registered only relatively recently. The ageing of the cloth during the last 200 years is a consequence of the action of degradative environmental factors on the constituent biopolymers, perhaps exacerbated by initial exposure of the linen to the brine-laden sea air.

The major chemical components of bast fibres like linen are cellulose and hemicellulose, which together comprise about 90% of the total content, and several percent of lignins, pectin materials, proteins and waxes.[3–5] Cellulose is a disperse polymer of high molecular weight, typically 6×10^5 to 1.5×10^6 Da, which consists of long chains of α-D-glucose units joined by β-1,4-glycosidic linkages[3] (Fig. 3). Intra-molecular and inter-molecular hydrogen bonding confers a highly ordered arrangement upon structural aggregates comprising about 100 cellulose chains, which constitute a micelle. The structural hierarchy continues through elementary fibrils, micro-fibrils and macro-fibrils, which are in turn wound around the wall of the fibre cells. A number

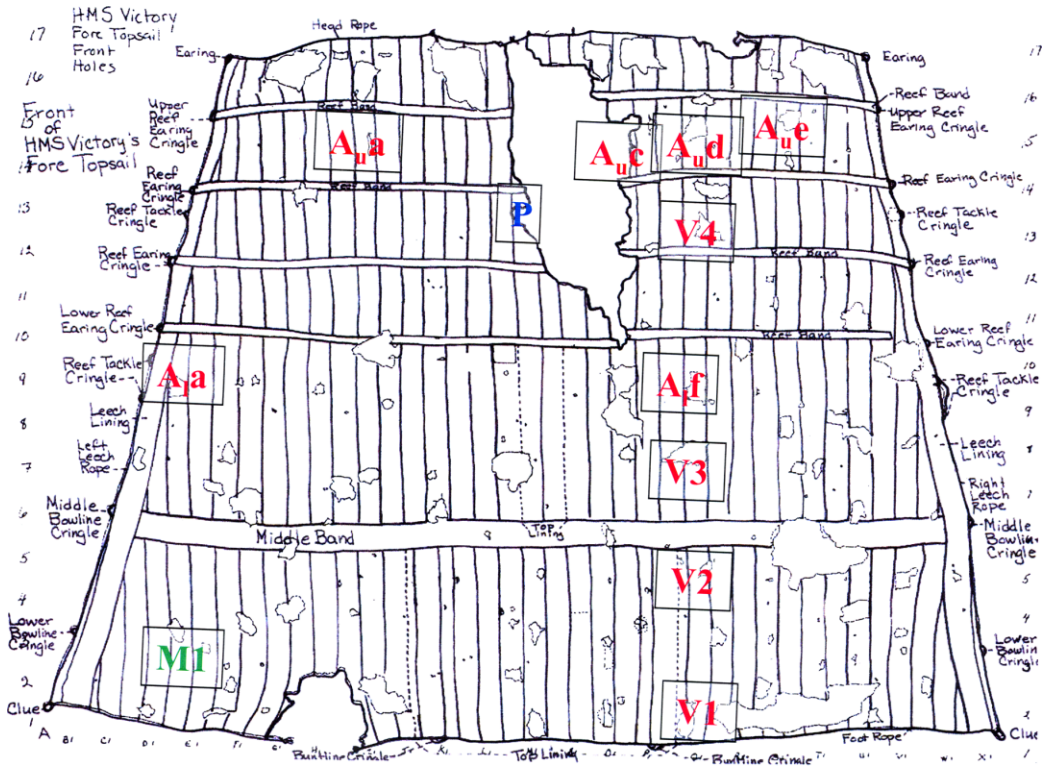

Figure 2. The fore-topsail of *HMS Victory*, from a conservator's sketch. After the Battle of Trafalgar this sail was put into storage and is now in need of conservation. It is the only sail to have survived this engagement and the battle damage is clearly seen. Specimen sample positions for spectroscopic and mechanical testing are indicated and tabulated in Table 2.

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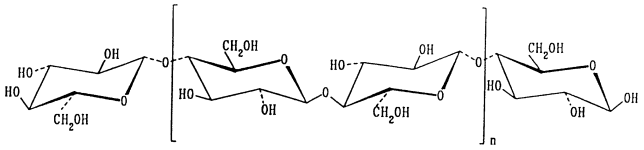

Figure 3. Molecular structure of cellulose, based on α-D-glucose units with β-1,4-glycosidic linkages.

of such cells are bound together to form the fibre. The hemicelluloses, pectins and lignin constitute the matrices in this intricate biocomposite.

Environmental exposure will result in chemical and biological deterioration.[6] Oxidation results in ring fission at the molecular level and therefore higher-order fibre damage, whereas thermal effects can cause inter-chain cross-linking and embrittlement in the woven fibres. Hydrolysis results in fission at the (1,4)-glycosidic links and formation of detritus from fragmentation (chain shortening) with consequent fibre weakening: this is accelerated in acidic environments. Further damage to linen artefacts is caused through biological cellulolytic action, induced, for example, by mould-exuded enzymes, which attacks the cellulose chains at the β-1,4-glycosidic bonds, removing cellobiose from the chain ends or causing intra-chain scission. This can occur under anaerobic or aerobic storage conditions and, in addition, causes the formation of coloured mucilage and acidic debris.[4,7] Evidence for such damage to linen artefacts has been adduced from earlier Raman studies.[3]

In this study, we sought to provide answers to the following questions:

- Can Raman spectra be obtained for yarn from the *Victory sail*, a well-aged, brown-coloured marine textile?
- How does the *Victory sail* compare spectroscopically with modern and ancient linen textiles that have been analysed using Raman techniques?
- Are the spectra of artificially aged modern sailcloth distinct and characteristic for each phase of ageing?
- Are the microstructure and chemistry of the *Victory sail* matched by the surrogate cloth, as evidenced by their Raman spectra?
- Are there any spectral signatures that correlate with the physical condition of the linen sailcloth?

The detailed results of experiments designed to address these questions and our conclusions are presented below.

EXPERIMENTAL

Specimens

Short lengths of loose yarn specimens of the *Victory sail* were taken from around areas of damage at the locations shown in Fig. 2 and, together with samples of aged modern sailcloth, were submitted for Raman spectroscopic analysis. The surrogates were prepared by subjecting 10×10 cm squares of modern linen (*Banks* sailcloth) to the following accelerated ageing regimen:

(1) Brine exposure – 24 cycles of soaking in brine for 1 h each, followed by drying at 70 °C for 1 h, over a period of 1 week;
(2) Light exposure – ageing for 1 week with 120 klux UV radiation, 200 W m^{-2};
(3) Heat exposure – thermal ageing for 7 weeks at 70 °C at 100% RH;
(4) Further exposure to high-intensity simulated sunlight, as above, for a further week.

This ageing regimen was chosen to mimic the known history of the *Victory sail*: use at sea (1) and exposure to sunlight (2), followed by almost two centuries of storage (3) and, most recently, limited exposure to light again during display (4).

Raman spectroscopy

Raman spectra of ancient degraded textiles are generally found to have strong fluorescent emission backgrounds when excited with visible and low-wavelength radiation, as exemplified in the stack-plotted Raman spectra shown in Fig. 4; hence, from our previous experience with ancient linens such as those from the Egyptian XIIth Dynasty rock tomb burials (*ca* 2000 B.C.), we selected FT-Raman spectroscopy with excitation at 1064 nm for recording the spectra from the *Victory sail* specimens and surrogates in this study.[7,8]

The FT-Raman spectra were excited with the 1064-nm radiation from a Nd^{3+}: YAG laser using a Bruker IFS 66/FRA 106 instrument, which gave a sample footprint of about 100 μm diameter in the macroscopic mode of

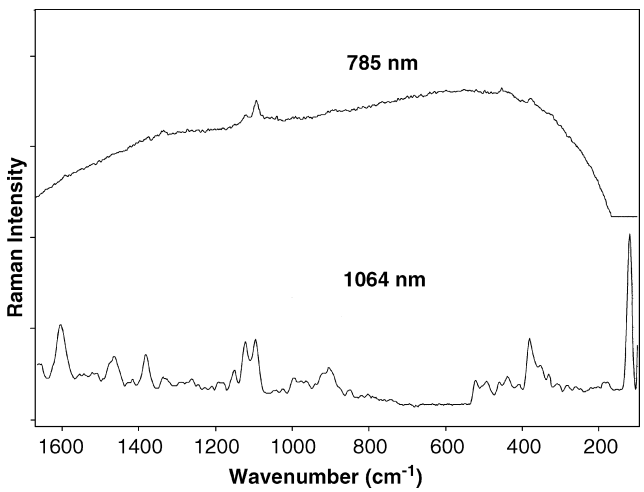

Figure 4. Raman spectra (excitation, 785 nm) of an ancient linen specimen, the *Victory sail*, with a spectrum obtained at below 1064 nm. The fluorescence emission background upon which the strongest Raman bands are superimposed at 785 nm should be noted.

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illumination. Because the spectral emission background of the ancient linen specimens is significant even with near-infrared excitation and low laser powers of only several milliwatts are necessary to minimise the onset of sample damage, 2000 spectral scans with a resolution of 4 cm^{-1} were required to obtain satisfactory spectral data with reasonable signal-to-noise ratios. An advantage of FT-RS in this mode of operation is that the full wavenumber range from 3500 to 100 cm^{-1} is recorded, which gives analytical access to the CH stretching modes and the skeletal CC, CO and CH bending modes of cellulose (Table 1) in each spectral scan.[9] Spectral measurements of relative band intensities were achieved using baseline correction (GRAMS software); in the case of weaker features spectral enhancement was also undertaken.

Table 1. Wavenumber (cm^{-1}) and vibrational Raman band assignments for cotton cellulose

ν (cm^{-1})	Approximate description of vibrational mode
172 w	τ (COH)
252 w	τ (COH)
333 vw	δ(CCC) ring deformation
349 mw	δ(CCC) ring deformation
380 m	δ(CCC) ring deformation
437 m	δ(CCC) ring deformation
460 mw	δ(CCC) ring deformation
496 w	δ(COC) glycosidic linkage
520 mw	δ(COC) glycosidic linkage
542 w	δ(COC) glycosidic ring, in-plane
900 mw, br	ν(COC) in-plane, symmetric
972 w	$\rho(CH_2)$
999 mw	$\rho(CH_2)$
1026	δ(OH)
1038	ν(CO), 1° alcohol groups
1059	ν(CO), 2° alcohol groups
1072	ν(CO)
1097 s	ν(COC), asymmetric, glycosidic link
1122 ms	ν(COC), symmetric, glycosidic link, ν(COC) ring breathing
1153 mw	ν(CC) ring breathing, asymmetric
1294 mw	$\delta(CH_2)$ twisting
1338 mw	$\delta(CH_2)$ wagging; δ(OH)
1380 m	$\delta(CH_2)$
1410 vw	$\delta(CH_2)$
1462 mw, sh	δ(COH), 1° and 2° alcohol groups
1478 mw, br	$\delta(CH_2)$ scissors
2723 w	ν(CH) methine
2870 mw, sh	$\nu(CH_2)$
2894 s	$\nu(CH_2)$ symmetric and asymmetric
2910 m, sh	$\nu(CH_2)$
2948 mw, sh	$\nu(CH_2)$
2957 mw, sh	$\nu(CH_2)$
2970 mw	$\nu(CH_2)$
3270 w, br	ν(OH), COH groups, hydrogen-bonded

Mechanical testing

Yarn samples from the *Victory sail* and the surrogates were subjected to mechanical testing: a gauge length of 2.5 cm was employed. Sections of yarn of approximate length 3.5–4 cm were taken, and the ends set between pairs of acetate squares using LR white (medium grade) resin, leaving the central 2.5 cm of the sample free. All the samples were woven with a paired warp; where warp yarns were tested, a single warp from the pair was taken.

The samples were loaded on an Instron 4301 mechanical tester, equipped with a 100 N load cell capable of a force resolution of 0.4% of the maximum load. The tests were carried out under ambient conditions (~23 °C and 55% RH) at an extension rate of 10 mm/min and a data capture of 20 points/min.

In the case of yarns of the *Victory sail*, four replicates were assessed; ideally a greater number of samples should have been used, but the size of these specimens was limited. For the Standart and Banks samples, where a greater quantity of material was available, six samples were tested.

RESULTS AND DISCUSSION

The advantage of near-infrared excitation at 1064 nm in the case of the *Victory sail* degraded linen yarns is readily demonstrated by the Raman spectra obtained with 785 nm and 1064 nm excitation, shown in Fig. 4. Although several stronger features can be identified in the upper spectrum, the fluorescence emission swamps most of the weaker bands. This effectively distorts the spectral appearance compared with the spectrum obtained at 1064 nm; hence, although both excitation wavelengths are described as near-infrared, it is clear that the longer wavelength excitation is superior for Raman spectroscopy of these degraded samples. In both cases, the laser powers incident upon the sample were low enough to prevent thermal damage to the specimens.

The Raman spectrum of cellulose as recorded from a pure, natural cotton boll, *Gossypium hirsutum*, which contains about 97% cellulose, has been reported previously,[4,9,10] and assignments are as shown in Table 1; the Raman spectrum of modern linen is very similar to this, as seen in Fig. 5 for the *Banks* sailcloth, but several new features are observed that can be related to the presence of additional constituents within linen and perhaps interwoven jute, such as lignin. For example, the band at 1605 cm^{-1} in modern linen is attributed to the ring-stretching mode of the phenolic lignin. This feature is absent from the spectra of ancient linens,[6] such as those analysed from the XIIth Dynasty Egyptian mummy wrappings (*ca* 2000 B.C.), but is seen with much reduced spectral intensity in the stack plot of historic marine sail specimens from *HMS Victory* studied here and shown in Fig. 5 for comparison. The latter could indicate a lower initial lignin content, for example, as a result of a lower jute admixture, but would also be consistent with the anticipated

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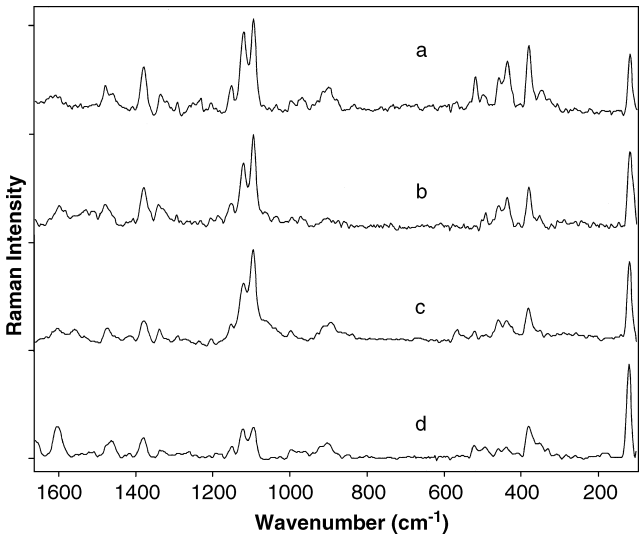

Figure 5. FT-Raman spectral stack plot of *Victory sail* specimens (a) V1, (b) V2 and (c) V3 along with a specimen of new sailcloth (*Banks*) shown in (d): 1064-nm excitation, 4 cm^{-1} spectral resolution and 2000 scans accumulated.

progressive modification of lignin, which is susceptible to light-promoted oxidative deterioration.

Spectra from three of the *Victory sail* specimens (V1–V3, Fig. 2) are stacked above that from the *Banks* modern sailcloth in Fig. 5; the most striking comparisons are as follows:

- There is marked diminution in the spectral band intensity of the C═C stretching mode at 1605 cm^{-1} for the historic sailcloth specimens, which may be attributed to oxidation in use and storage and on display.
- There is variation between the spectra of the historic specimens, exemplified by the relative band intensities of the ν(COC) symmetric and anti-symmetric glycosidic stretching modes of the cellulose chains at 1097 and 1122 cm^{-1}. The 1122 cm^{-1} band consists of a COC symmetric stretching coupled with the breathing mode of the glucopyranose rings. Here, the band intensity ratio (I_{1122}/I_{1097}) covers the range 0.64–0.84. This indicates that hydrolytic fission of the cellulosic chains at the glycosidic COC ether bonds is not constant for different parts of the sail, as expected, perhaps in view of the size of the relict sailcloth. Further experiments are in progress to assess the potential use of this band intensity ratio as an indicator of specimen ageing.
- The relative intensities of the band at 120 cm^{-1}, which has not been recorded for linen or cotton spectra hitherto, and the glycosidic doublet near 1100 cm^{-1} are approximately 30% of the same ratio for these bands in new sailcloth. The decreased tenacities (Table 2) measured for the *Victory sail* specimens relative to the modern sailcloth are also of this order. Empirically, therefore, a potential signature of linen ageing could be provided in this band ratio. The assignment of this low wavenumber band is not possible without undertaking detailed force-field and quantum mechanical calculations, but it probably arises from the tertiary structure of the cellulose biopolymer. For this reason, this band has not been identified in Table 1.
- An increased intensity in the 1338 cm^{-1} band relative to the stronger feature at 1380 cm^{-1} in modern sailcloth represents a larger contribution from OH bending modes in the degraded specimens, as predicted from the effects of hydrolytic fission of the cellulose chains.
- Complex band intensity changes in the low wavenumber region of the Raman spectrum between 300 and 600 cm^{-1} can be attributed to CCC deformations and a breakdown of the rigid cellulose rings in the COC-linked chains. Again, it is not realistic to attempt a vibrational assignment of this spectral region without resorting to detailed force-field and quantum mechanical calculations.

Table 2. Calculated tenacities (standard deviations), cN tex^{-1}, for yarn samples from the *Victory sail* and surrogate canvas

Samples	Tenacity
S1-warp (V1)	5.2
S2-warp (V2)	6.3
S3-warp (A_lf)	3.7
S4-weft (A_uc)	4.8
Average across the sail ($n = 10$)	5.1 (2.5)
Banks (new sailcloth)	17.6 (2.1)
Surrogate A	14.4 (1.6)
Surrogate B	6.9 (0.9)
Surrogate C	5.1 (0.4)
Surrogate D	3.4 (0.2)

Raman spectroscopic data were also obtained successfully from *Victory sail* fibres that have been selected as originating from the *warp* and the *weft* patterns in the sail linen construction. By orienting these in the sample illuminator, and recording the spectral band intensities for vertical and horizontal alignments of the fibres with respect to the polarization vector of the irradiating laser beam, some clear changes in the relative intensities of key bands are observed as represented in Fig. 6(a) for the A_1f specimen. These can be summarised as follows:

- The intensity ratios of the 120 and 1122/1097 cm^{-1} bands are approximately constant, as are the ratios of the latter with the CH deformation mode at 1380 cm^{-1}, but the COH deformation mode at 1338 cm^{-1} is stronger in the horizontal alignment.
- The spectral signature of jute at 1736 cm^{-1} due to the ester carbonyl group appears stronger here in the horizontal alignment, unlike the spectra of V1, V2 and V3 recorded under a similar orientation and shown in Fig. 5. This probably reflects the variability of survival of the C═C and C═O moieties with location on the ancient sail specimen.

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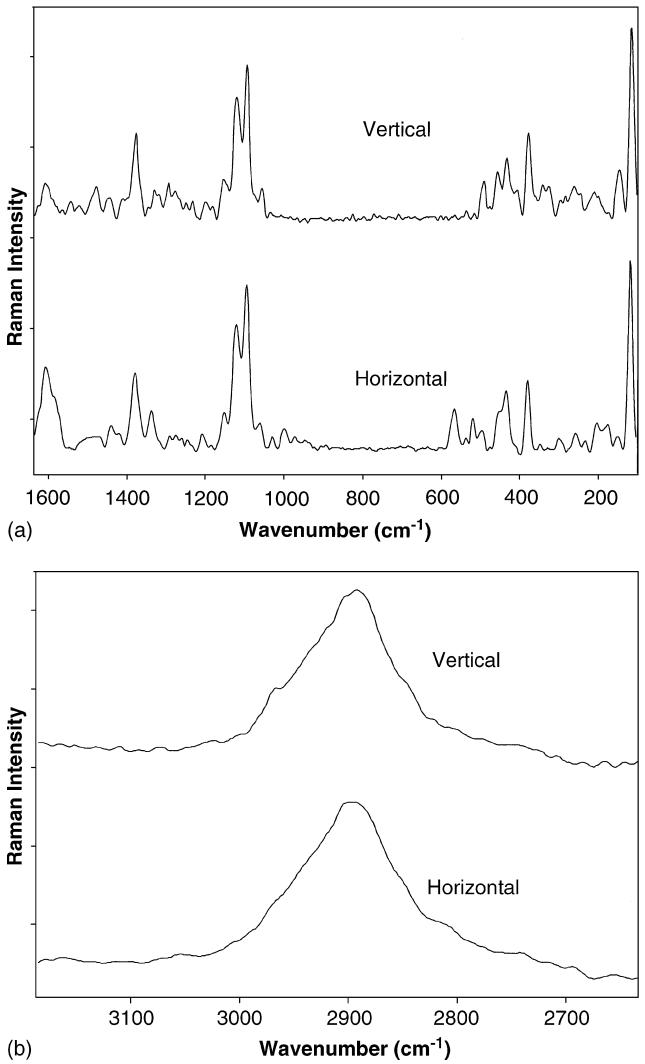

Figure 6. FT-Raman spectral stack plot of a single fibre of *Victory sail* specimen labelled A_1f under conditions similar to those given in Fig. 5: upper spectrum, fibre horizontal in the sample illuminator; lower spectrum, fibre vertical in sample illuminator. (a) Wavenumber range 100–1650 cm^{-1}, (b) wavenumber range 2600–3200 cm^{-1}.

- Several complex differences occur in the CCC deformation region of the Raman spectra near 400 cm^{-1}, which can be attributed to the greater freedom of movement for the ring motion in degraded cellulosic chains in the degraded sailcloth.
- The presence of a band at about 170 cm^{-1} in the vertical orientation, and at a similar wavenumber in the horizontal orientation but with much reduced intensity, can be ascribed to COH torsional modes in the degraded sail specimen fibres.
- There is little difference to be observed between the fibre orientations in the CH stretching region near 3000 cm^{-1}, as seen in Fig. 6(b); again, this is perhaps not unexpected in view of the accepted ideas of the mechanism of cellulose degradation, which will involve primarily the ring modes and glycosidic bonds.

The results of this spectral analysis therefore indicate that significant degradation of the cellulose and the matrix in the fibres of the *Victory* sailcloth have occurred through hydrolytic and oxidative mechanisms. The surface pH of the *Victory* sailcloth is generally quite low (3.3–4.0) and this is also consistent with oxidative deterioration. Cellulose will have suffered a reduction in the degree of polymerisation, some cross-linking of the shortened chains but reduced inter-chain secondary bonding.[11] The modifications will have led to inefficient load transfer throughout the hierarchy of the composite fibres and embrittlement. It is not surprising then that the results of the mechanical testing, which show a significantly reduced performance for the *Victory sail* yarns, reflect these ageing effects arising from environmental exposure.

A stack plot of the Raman spectra obtained from the non-aged and artificially aged surrogate sailcloth is shown in Fig. 7. A progressive diminution of the relative band intensity ratio of the 1122 and 1097 cm^{-1} features is seen over the range from 0.95 for the non-aged material to 0.60 for the last spectrum, which represents the most severely aged material, exposed successively to brine, light, heat and light.

This clearly is in accord with the reasoning that the glycosidic ring modes reflect a major progressive change in rigidity of the cellulosic structure with environmental deterioration. A decrease in intensity of the C═C mode of lignin at 1605 cm^{-1} is observed from spectra (a) to (c) followed by a dramatic decrease from (c) to (e), and this is correlated with the susceptibility of lignin to the degradative attack. Though the 120 cm^{-1} band (normalised

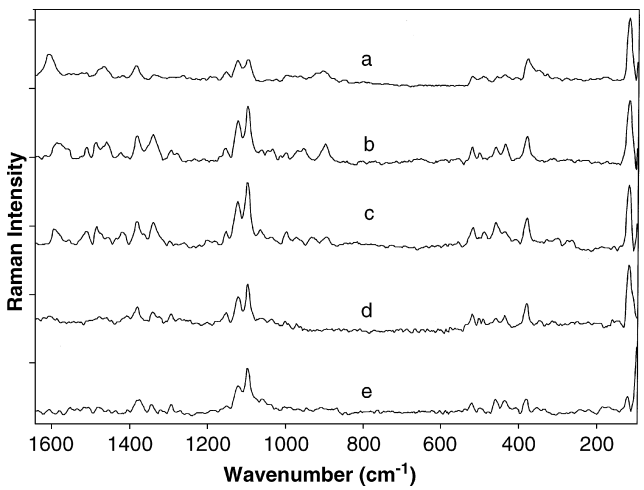

Figure 7. FT-Raman spectral stack plot of artificially aged new sailcloth specimens labelled (a)–(e), representing consecutively the non-aged, brine treated, brine and light treated, brine, light and heat treated and brine, light, heat and light treated specimens, respectively. The details of the ageing cycles are provided in the text.

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to that at 1380 cm^{-1} (due to $\delta(CH_2)$) seems to have changed little up to this point, a significant change is seen in the stack-plotted Raman spectrum shown in Fig. 7 for specimen (d), at the extreme of the accelerated ageing process. For (d), the 120 cm^{-1} band is reduced to about 30% of its starting value in the non-aged specimen.

The complete ageing cycle results in a sample (d) with a spectrum that matches quite closely with those recorded for the *Victory sail* yarns. We deduce from this that both the microstructure and chemistry of the *Victory* sailcloth is matched well by that of the modern canvas taken through the ageing regimen detailed above.

Both the intensity ratio of the 1122 and 1097 cm^{-1} bands and the intensity of the 120 cm^{-1} band seems as though they may be useful Raman signatures of ageing. Although neither signature alone shows a simple correlation with the tenacity of the yarns (Table 2), the trends are suggestive. More detailed analyses with further well-defined, progressively aged models are certainly warranted.

CONCLUSIONS

The results of this non-destructive Raman spectroscopic study of an important historic marine textile have provided some novel information on the degradation of linen fibres and have suggested a means of monitoring the extent of textile deterioration.

- Near-infrared excitation minimised background fluorescence, permitting the acquisition of good-quality spectra for short lengths of individual yarns from the *Victory sail*.
- The spectra are suggestive of hydrolytic and oxidative degradation of the constituent fibrous cellulose polymer and matrix components of the biocomposite fibres, which have been observed previously for other linen artefacts.
- Raman spectra of the surrogate canvas appear distinct, according to the particular progressive stage of accelerated ageing.
- Spectra of these comparator specimens have demonstrated that the more extreme procedures may give good replicates of the degradation suffered at the molecular and microstructural level by the sailcloth in its actual working lifetime and subsequently on storage and occasional display.
- Two particular key Raman signatures of ageing were identified: the intensity at 120 and the intensity ratio of the 1122 and 1097 cm^{-1} bands. While a simple quantitative correlation with reduced performance is not readily evident, these markers may have some immediate application in the qualitative assessment of condition.

This sequence of extreme accelerated ageing described here for modern canvas appears then to be a reasonable comparator for the exposure conditions that must have been operational for the fore-topsail of the *HMS Victory* as she maintained her blockading vigil for months at the approaches to Cadiz and subsequently suffered damage at Trafalgar, and later stored as a useless sail, and then occasionally displayed before more recently being treated appropriately as a unique historical artefact. This will lend conservators some confidence in predicting the future behaviour of the *Victory* fore-topsail and developing recommendations for its optimum preservation, based upon the results of further detailed studies of the surrogates.

The comparison of spectral indicators of degradation provides a non-invasive approach to characterising organic heritage such as textiles. Raman spectroscopy offers much potential for on-site condition monitoring of artefacts such as the *Victory sail*, to ensure the long-term preservation of a national textile heritage for the benefit of our own and future generations.

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