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## Wood Degradation on Historic Shipwreck Sites: The Use of FT-IR Spectroscopy to Study the Loss of Hemicellulose

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### ABSTRACT

Analysis of waterlogged wood excavated from marine shipwreck sites show that variations in shipwreck physical environments and micro-environments produce differing extents of wood degradation. Significant differences in the degree of wood deterioration exist across a shipwreck site and even over different parts of the same timber. The extent and type of deterioration in waterlogged wood can significantly affect the results of conservation procedures. Many different analytical techniques have been utilised in attempts to quantify the extent of deterioration. Fourier transform infra-red (FT-IR) spectroscopy was used in this study to measure the extent of degradation of waterlogged wood recovered from shipwreck sites. This method can be considered as a rapid, non-destructive method of analysis which defines changes in the lignin-carbohydrate complex of archaeological waterlogged wood in comparison to undegraded wood. The results showed that decreases in the hemicellulose content of waterlogged wood can be semi-quantitatively calculated from the FT-IR traces and directly related to the extent of wood degradation.

### INTRODUCTION

Biological, chemical and physical changes occur, to different extents, in waterlogged wood during submersion and burial in marine environments. The chemistry and biology of the shipwreck environment, the wood species, the initial wood condition, time of submersion and the presence of metal corrosion products will have an effect on the extent of wood degradation. Therefore, it is important to measure the extent of degradation of waterlogged wood so appropriate conservation treatments can be applied to the wooden shipwreck artefacts. Many different analytical techniques have been developed and utilised to measure the extent of wood deterioration. At present, there is basically no reasonably rapid and uniform standard procedure for evaluating the extent of degradation in waterlogged wood [Jagels 1981]. Some of the analytical methods that have been used are maximum water contents, shrinkages, physical measurements such as bending and compressive strengths and wet chemical techniques. Instrumental analytical techniques include microscopy, thermoanalysis, infra-red (IR) spectroscopy, ultra-violet (UV) spectrophotometry, nuclear magnetic resonance (NMR) spectrometry and pyrolysis-gas chromatography (py-GC). Fourier transform infra-red (FT-IR) spectroscopy was used to measure the extent of degradation of the metal impregnated waterlogged wood samples analysed in this study.

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Infra-red (IR) and Fourier transform infra-red (FT-IR) spectroscopy can be considered as a rapid, non-destructive method of analysis which defines changes in the lignin-carbohydrate complex of archaeological waterlogged wood in comparison to undegraded wood. These methods provide considerably higher sensitivity than wet chemical methods and samples of microscopic proportions can be analysed. With FT-IR spectroscopy, the speed of spectrum measurement is increased and the mathematical treatment of results becomes much easier due to installed computers. Occasionally, IR and FT-IR spectroscopy is used to analyse the carbohydrate and lignin fractions of degraded wood separated by chemical procedures. This method of analysis can also be used to distinguish between condensed guaiacyl lignin units and syringyl lignin units. Hence, this method of analysis can be used to distinguish between hardwoods and softwoods [Allen et al. 1992; Faix et al. 1991; Fengel 1991; Hon et al. 1986; Kim 1991; Kirillov & Mikolajchuk 1990; Klyukanov et al. 1987; Laantera et al. 1993; Lau & Ibrahim 1992; Lindberg et al. 1992; Martoglio et al. 1990; Mikolajchuk et al. 1989; Owen & Thomas 1989; Pavlikova et al. 1993; Wang & Lin 1991; Wilson et al. 1987, 1993; Zaitseva et al. 1987].

Owen & Thomas (1989) studied twenty four different wood species by FT-IR analysis and the spectra obtained from all wood samples studied showed the same basic features (Figure 1). They were a strong, broad OH stretching band centred around  $3400\text{cm}^{-1}$ , a prominent C-H stretching absorption at about  $2900\text{cm}^{-1}$  [Owen & Thomas 1989; Pavlikova et al. 1993] and a strong broad envelope in the region from  $1750$  to  $1000\text{cm}^{-1}$  where there are many sharp and discrete absorptions. It is mainly in this 'fingerprint' region where distinctive differences can be identified between spectra of different woods [Owen & Thomas 1989].

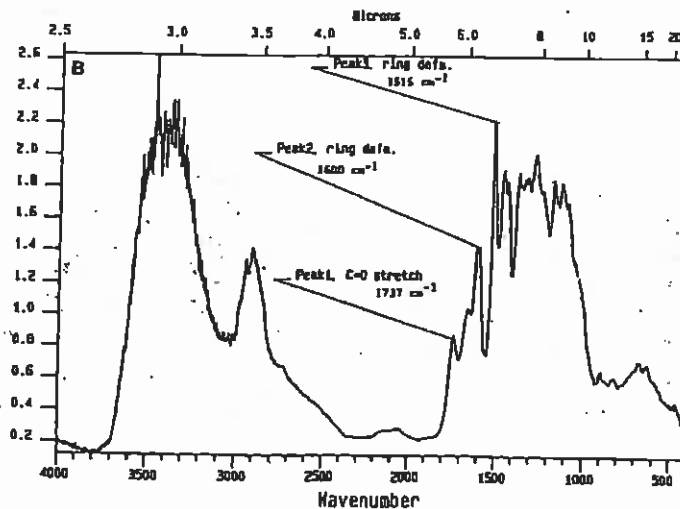


Figure 1. FT-IR spectra of redwood [Owen & Thomas 1989].

The relative amounts of cellulosic and lignin components can vary from one tree species to another and in general, the ratio of lignin to holocellulose is found to be higher in softwoods than hardwoods. Additionally, in comparison with recent wood, waterlogged archaeological wood contains higher amounts of lignin and lesser quantities of holocelluloses. Hence, the ratio of lignin to holocellulose increases as degradation proceeds, in comparison with the ratio of the recent wood. The intensities and positions of many absorptions are of particular interest when identifying the spectra of different woods, however, there are only a few particular absorptions that are used primarily to

identify the carbohydrate and lignaceous portions of the wood and hence, the extent of degradation.

Kirillov and Mikolajchuk (1990) have used the ratio of cellulose to lignin as a qualitative measure of the degree of archaeological wood degradation. These authors measure the intensity of the band at  $898\text{cm}^{-1}$  characteristic of carbohydrates and the absorption band at  $1510\text{cm}^{-1}$  indicative of lignin and quantitatively calculate the ratio of the concentration of cellulose to lignin. They also suggest that this method is suitable for wood of different species and degradation degree. Alternatively, Hon et al. (1986) quantitatively analysed the change in carbohydrate and lignin absorption bands using the typical glucopyranose ring vibration at  $1160\text{cm}^{-1}$  as an internal reference. Our research programme involved analysing ten metal impregnated wood samples recovered from four shipwreck sites and comparative unimpregnated wood samples of the same wood genus by FT-IR. The hemicellulose content, measured by the intensity of the absorption bands at about  $1740\text{cm}^{-1}$  and  $1220\text{cm}^{-1}$ , was used as a semi-quantitative measure of the degree of degradation of these metal impregnated waterlogged wood samples.

## EXPERIMENTAL

Ten metal impregnated wood samples were obtained from wrecks of the *Vergulde Draeck* (1656), *Rapid* (1811), *Favourite* (1867) and the *Hadda* (1877). Following excavation, all samples were permitted to air dry with associated warping, shrinkage and collapse. Four samples of modern, undegraded hardwoods and two samples of softwoods were also collected for comparative analyses. The wood species of all waterlogged samples were identified by polishing the end-grains to a 1200 SiC grit finish and microtome sections were cut from the radial and tangential longitudinal surfaces. Slides of these latter two surfaces were prepared for transmission microscopy and examined by Ian Godfrey of the Materials Conservation Department of the Western Australian Museum.

The corrosion products in the outer and inner regions of the metal impregnated wood samples were analysed and characterised by scanning electron microscopy (SEM) and x-ray diffraction (XRD). Dry sample sections were firstly examined by SEM using a Jeol JSM-2 SEM with EDAX using the backscattered low vacuum mode in an environmental cell at the Mineral Processing laboratories of CSIRO in Perth. This mode of SEM operation requires no sample preparation [Robinson & Nickel 1979]. Prior to XRD analysis, CSIRO technicians prepared the samples using standard mineralogical techniques. The corrosion products were then analysed by XRD on a Philips 1140 x-ray diffractometer. The resolution of the complex mixtures of corrosion products was effected through a combination of comparisons with traces of standard spectra of phases identified by SEM and a search using the Hanawalt search manual. The corrosion products identified were given their mineralogical name when the XRD pattern was coincident with that reported in the JCPDS index for such compounds, otherwise the chemical name alone was reported.

Small sub-samples of wood were taken from the outer, aerobic surfaces, the middle and inner, low oxygenated regions of each bulk section and samples were also removed from the modern, undegraded wood sections. These samples were then analysed by FT-IR spectrophotometry at the Chemistry Centre of Western Australia (CCWA) using a FTS-40 Biorad-Digilab division single beam FT-IR spectrophotometer equipped with a mercury cadmium telluride detector. Analysis of the organic materials involved positioning a

small sample between the two diamonds of a diamond anvil cell (DAC) (high pressure diamond optics). The DAC was mounted directly in the sample compartment and the spectrum recorded without the aid of beam condensing optics, ratioing against a stored background of the empty DAC. The spectra were manipulated utilising a Galactic Grams 386 programme.

Two brass fastenings, surrounded by wood, recovered from the *Hadda* wreck site were sampled for wet chemical analysis. The wood was carefully removed from around the fastening then samples of the residual fastening metal were collected by drilling into the exposed aerobic region of the fastening, not covered by wood and the low oxygenated area, that was previously in intimate contact with the wood. The four samples of corroded brass were analysed at the CCWA for aluminium, antimony, arsenic, bismuth, copper, iron, lead, tin and zinc using inductively coupled plasma atomic emission spectrometry (ICP-AES) after total dissolution in dilute nitric acid.

## RESULTS AND DISCUSSION

### Analysis of Undegraded Wood Samples

The 1800-500 $\text{cm}^{-1}$  region of the spectra of undegraded hardwood, North American white oak (Figure 1) and the softwood, Longleaf pine (Figure 2) will be used to identify the major absorption bands and the distinctive differences between hardwood and softwood spectra.

The absorption at approximately 1740 $\text{cm}^{-1}$  originates in the stretching of the free carbonyl groups that occur fairly abundantly within the branched chain hemicellulose polymer matrix of wood. Consequently, this absorption can be considered strongly characteristic of the low molecular weight component of the carbohydrate part of the wood and the intensity, a reflection of the relative concentration of this component. In addition, the C-O-C stretching vibration of acetyl and carboxyl groups in xylan, which is a hemicellulose, occurs at about 1240 $\text{cm}^{-1}$  [Hon et al. 1986; Lau & Ibrahim 1992; Owen & Thomas 1989].

The absorption bands of hardwood and softwood hemicelluloses are different. The carbonyl bands at about 1740 $\text{cm}^{-1}$  and 1240 $\text{cm}^{-1}$  are generally, more intense in undegraded hardwoods than softwoods because hardwoods contain greater concentrations of hemicelluloses than softwoods [Faix et al. 1991; Wang & Lin 1991]. This is obvious when comparing the hardwood (Figure 1) and softwood (Figure 2) spectra. Additionally, most softwoods have a carbonyl absorption lower than 1738 $\text{cm}^{-1}$ , whereas most hardwoods have a carbonyl absorption higher than 1738 $\text{cm}^{-1}$ . For the hardwood, North American white oak, the carbonyl absorption does not occur at a wavenumber higher than 1738 $\text{cm}^{-1}$  but at 1735 $\text{cm}^{-1}$ . However, this absorption is still greater than the carbonyl absorption of the softwood, Longleaf pine at 1732 $\text{cm}^{-1}$ . The shift in the carbonyl absorption to a lower wavenumber for softwoods is primarily due to the relative increase in concentration of lignin to cellulosic components in softwoods [Owen & Thomas 1989; Pavlikova et al. 1993].

Absorptions in the 1000 to 1200 $\text{cm}^{-1}$  region refer mainly to the carbohydrate part of the wood. The most intense bands are predominantly due to the valence fluctuations of the C-O bonds and the skeletal fluctuations of the chain of cellulose [Faix et al. 1991; Mikolajchuk et al. 1989; Wang & Lin 1991; Wilson et al. 1993].

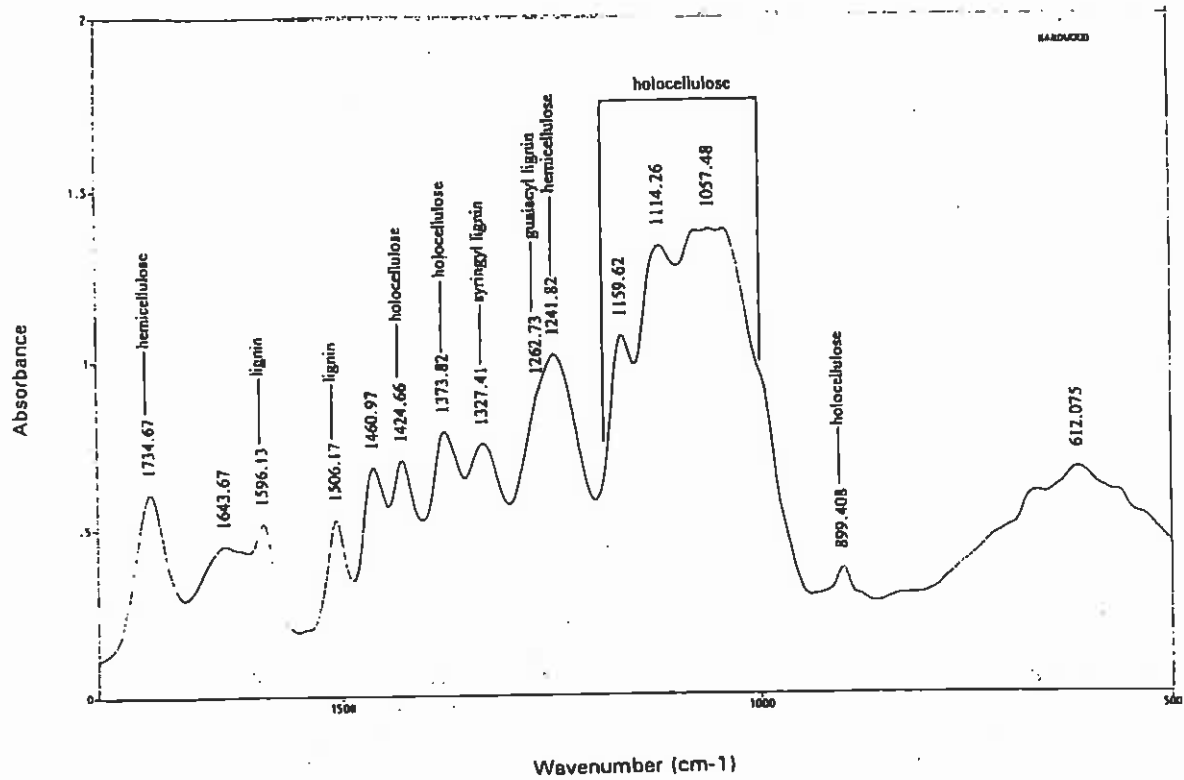


Figure 1. FT-IR spectrum of modern, undegraded North American white oak (*Quercus alba* L.).

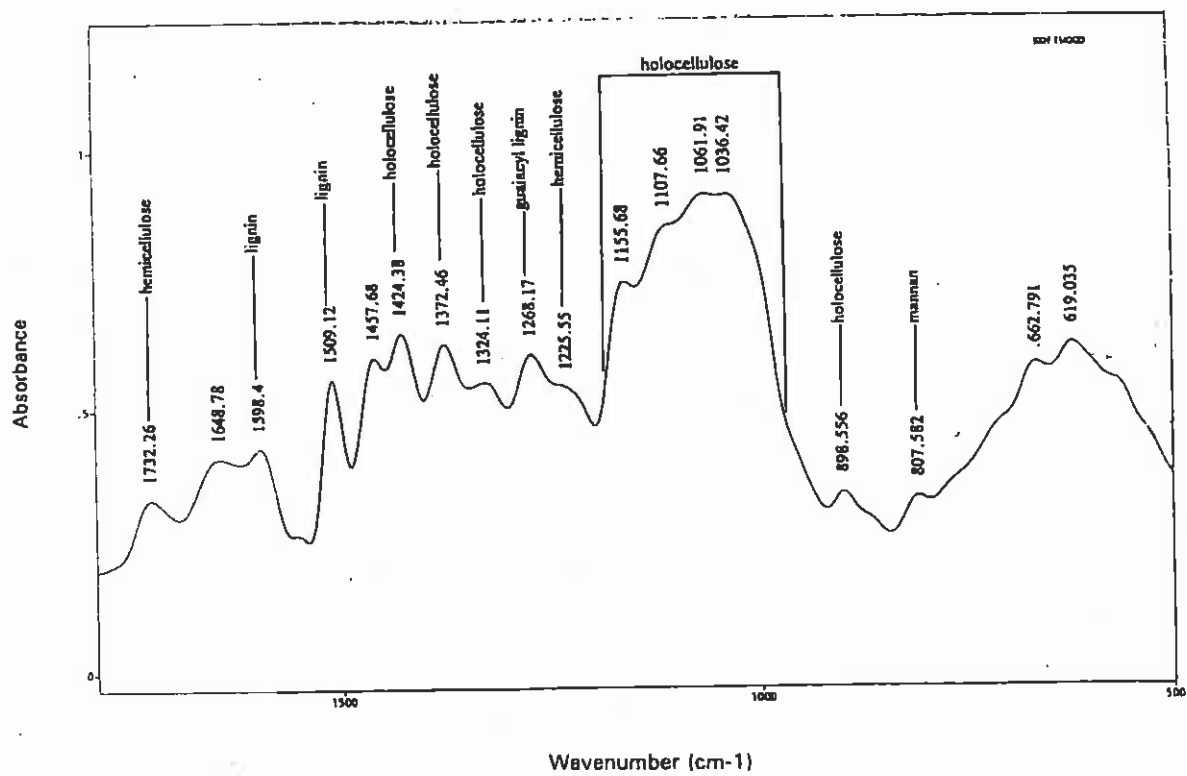


Figure 2. FT-IR spectrum of modern, undegraded Longleaf pine (*Pinus palustris* Mill.).

The bands in the 1200-1600cm<sup>-1</sup> part of the spectra arise primarily from lignin [Wilson et al. 1993]. The intensity ratio of the two absorptions, 1600 and 1510cm<sup>-1</sup> arising from lignin, as well as the position of the absorption at about 1510cm<sup>-1</sup>, varies significantly with respect to wood type. Softwoods usually show the typical aromatic ring deformation mode absorbing above 1509cm<sup>-1</sup>, whereas hardwoods typically absorb below 1509cm<sup>-1</sup>. For example, aromatic ring deformation occurs at 1509cm<sup>-1</sup> for the Longleaf pine and 1506cm<sup>-1</sup> for the North American white oak. The band at approximately 1270cm<sup>-1</sup>, which arises from guaiacyl ring breathing with C-O stretching, has also been used for the determination of total lignin content. Softwoods contain guaiacyl lignin units in the wood matrix, however, hardwoods contain both guaiacyl and syringyl lignin units. Therefore, hardwood spectra, such as the North American white oak, show a pronounced band at about 1330cm<sup>-1</sup> which is associated with syringyl lignin [Faix et al. 1991; Lau & Ibrahim 1992; Wang & Lin 1991].

In general, softwoods have more lignin but less holocellulose than hardwoods. As a result, in FT-IR spectra of softwoods, such as the Longleaf pine (Figure 2), the intensity of the absorption bands at about 1510 and 1270cm<sup>-1</sup> will be greater than those absorption bands arising from the cellulose and hemicellulose previously described [Owen & Thomas 1989; Wang & Lin 1991]. Additionally, softwoods contain more lignin than xylan and the intensity of the band at 1270cm<sup>-1</sup> of the lignin is much stronger than that of the band at 1220cm<sup>-1</sup> of xylan. The opposite applies for hardwood FT-IR spectra, such as for the North American white oak (Figure 1) [Wang & Lin 1991]. Hence, it is relatively simple to distinguish hardwoods from softwoods using FT-IR spectroscopic analysis.

#### **Analysis of Degraded Waterlogged Metal Impregnated Wood Samples**

##### General

The metal impregnated wood samples were recovered from the wreck sites of the *Vergulde Draeck* (1656), the *Rapid* (1811), the *Favourite* (1867) and the *Hadda* (1877). All wreck sites were open circulation, aerobic marine environments with an average water depth and temperature of 6 ± 2m and 23°C ± 2°C, respectively. Therefore, the shipwrecks have been subjected to similar marine environments and water depths. The wood species of the metal impregnated wood samples were identified and the results are presented in Table 1.

Table 1. Wood identification of the metal impregnated waterlogged wood samples.

Sample	Wood Type
<i>Rapid</i> (RP1.1 and RP1.2)	<i>Quercus sp.</i> American white oak
<i>Rapid</i> (RP2.1 and RP2.2)	hard pine of the pitch pine type
<i>Hadda</i> (HA30056.TOP and HA30056.BOT)	<i>Quercus sp.</i> European white oak
<i>Hadda</i> (HA30057.TOP and HA30057.BOT)	<i>Fagus sp.</i> European beech
<i>Favourite</i> (FAV 3075)	<i>Ulmus sp.</i> Elm
<i>Vergulde Draeck</i> (GT 6154)	pine of the red deal type

The results of the XRD analyses of the corrosion products collected from both the outer regions of the wood samples, which were fully exposed to the aerobic marine environment and the inner regions of the wood, which were in low oxygenated

environments, in intimate contact with the residual metal are described in Table 2. The predominant corrosion product identified in the outer regions of the copper impregnated waterlogged wood samples was paratacamite. This is one of the major copper corrosion products formed by the aerobic corrosion of copper alloy fastenings in intimate contact with wood. Calcite and aragonite are very common minerals present in concretions. In the inner, low oxygenated regions of the wood samples the major copper corrosion products were copper sulphides, with chalcocite being the more common phase. The formation of these copper sulphides is common on copper alloys corroding under anaerobic conditions. The major corrosion product identified in the outer, exposed areas of the iron impregnated wood sample was goethite. Iron oxyhydroxides are common iron minerals formed by the corrosion of iron in oxidising marine environments and are often found in wood which has been in close proximity to corroding iron.

Table 2. Identification of the major corrosion products in the outer and inner regions of the metal impregnated wood samples.

Sample	Description and Position	Mineral Name	Mineral Formula
<i>Hadda</i> white oak (HA30056.TOP) (HA30056.BOT)	blue/green crystals (outer)	paratacamite	$\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$
	off-white powder (outer)	aragonite calcite	$\text{CaCO}_3$ $\text{CaCO}_3$
	black mineral (inner)	copper sulphides	-
<i>Hadda</i> beech (HA30057.TOP) (HA30057.BOT)	blue/green mineral (outer)	paratacamite	$\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$
	white mineral (outer)	hydrozincite	$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$
	black mineral (inner)	copper sulphides	-
<i>Favourite</i> elm (FAV3075)	green mineral (outer)	paratacamite	$\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$
	black mineral (inner)	chalcocite digenite	$\text{Cu}_2\text{S}$ $\text{Cu}_9\text{S}_5$
	white powder (inner)	anglesite	$\text{PbSO}_4$
<i>Rapid</i> white oak (RP1.1) (RP1.2)	green crystals (outer)	paratacamite	$\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$
	olive green vein (outer)	paratacamite	$\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$
	black mineral (inner)	copper sulphides	-
<i>Rapid</i> pitch pine (RP2.1) (RP2.2)	green mineral (outer)	paratacamite	$\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$
	off-white mineral (outer)	aragonite	$\text{CaCO}_3$
	black mineral (inner)	chalcocite	$\text{Cu}_2\text{S}$
<i>Vergulde Draeck</i> red deal pine (GT6154)	black mineral (outer) <sup>1</sup>	goethite	$\gamma\text{-FeO.OH}$

<sup>1</sup> There were no corrosion products in the inner regions of this wood sample.

Characterisation of the corrosion products shows that there is a wide range of micro-environments existing within the waterlogged wood samples and this will have an effect on the deterioration of the metals and the wood. In addition, the nature of these corrosion products will effect the mechanical strength, the chemical stability of the wood structure and the rate of biological degradation.

In FT-IR spectra, as waterlogged wood degrades, the intensities of the absorption bands mainly associated with the carbohydrate portion will decrease and the intensities of the bands associated with lignin will increase indicating the degradation of the carbohydrates with preservation of the lignin portion of the wood matrix. Very small samples of wood, removed from the outer, middle and inner areas of each metal impregnated waterlogged

wood sample, were analysed by FT-IR spectroscopy. Only the 1800-500cm<sup>-1</sup> region of future FT-IR spectra will be presented as this area is the most important region for analysing the extent of degradation of wood samples. Peak heights of the major absorption bands were measured from a computer generated baseline between 1770-870cm<sup>-1</sup> and these results assisted in measuring the degree of wood deterioration.

#### Copper Impregnated Waterlogged Wood Recovered from the Hadda Site

At the time of sample recovery the *Hadda* wreck had been immersed for 115 years. The first wood sample was found surrounding a copper alloy fastening. The wood was removed and sectioned into two samples. The two wood samples were given identification codes, HA30056.TOP recovered near the head of the fastening and HA30056.BOT collected from the shank of the bolt.

Wet chemical analysis was performed on two drilled metal core samples collected from an exposed aerobic area of the copper alloy fastening and from the low oxygenated area in intimate contact with the wood. The major elements present in this brass fastening were copper, zinc and lead. Iron was a minor constituent at 0.1%. The percentages of copper, zinc and lead in the two samples were normalised to 100%. The concentration of these elements in the metal sample from the aerobic area were 72%, 27% and 1% (total metal composition 90%), respectively, while for the sample from the anaerobic region the results were 84%, 15% and 1% (total metal composition 95%), respectively. These results indicate that the fastening could be a 70/30 brass, i.e. 70% copper and 30% zinc with other small concentrations of impurities. In addition, there has been preferential corrosion of the zinc at the grain boundaries of the zinc rich  $\beta$  phase of the brass in direct contact with the wood in the anaerobic section. Primarily, this dezincification process occurs under anaerobic conditions and is accelerated by high temperatures, high chloride contents of water and low water speeds [Gilbert 1976; MacLeod 1985].

The HA30056 samples were identified as European white oak (Table 1) and the recent, undegraded comparative wood sample was European white oak. The FT-IR traces of the HA30056 wood samples were similar, therefore, only the spectra of the HA30056B.BOT sample are shown in Figure 3. The peak heights of the major absorption bands are presented in Table 3.

Table 3. Absolute peak heights (cm) of diagnostic absorption bands (cm<sup>-1</sup>) from the FT-IR spectra of European white oak, HA30056A.TOP and HA30056B.BOT.

Wood Sample	hemicellulose		holocellulose			lignin		
	1740	1220	1370	1160	896	1510	1330	1260
European white oak	0.24	0.53	0.62	0.84	0.13	0.29	0.64	0.48
HA30056A.TOP								
inner	0.04	0.34	0.36	0.48	0.06	0.31	0.38	0.32
mid	0.06	0.26	0.25	0.21	0.07	0.16	0.29	0.26
outer	0.05	0.25	0.30	0.33	0.02	0.25	0.31	0.26
average % loss	79	46						
HA30056B.BOT								
inner	0.04	0.41	0.41	0.62	0.04	0.40	0.44	0.37
mid	0.07	0.37	0.46	0.67	0.07	0.40	0.46	0.37
outer	0.06	0.30	0.37	0.42	0.08	0.28	0.38	0.30
average % loss	76	32						



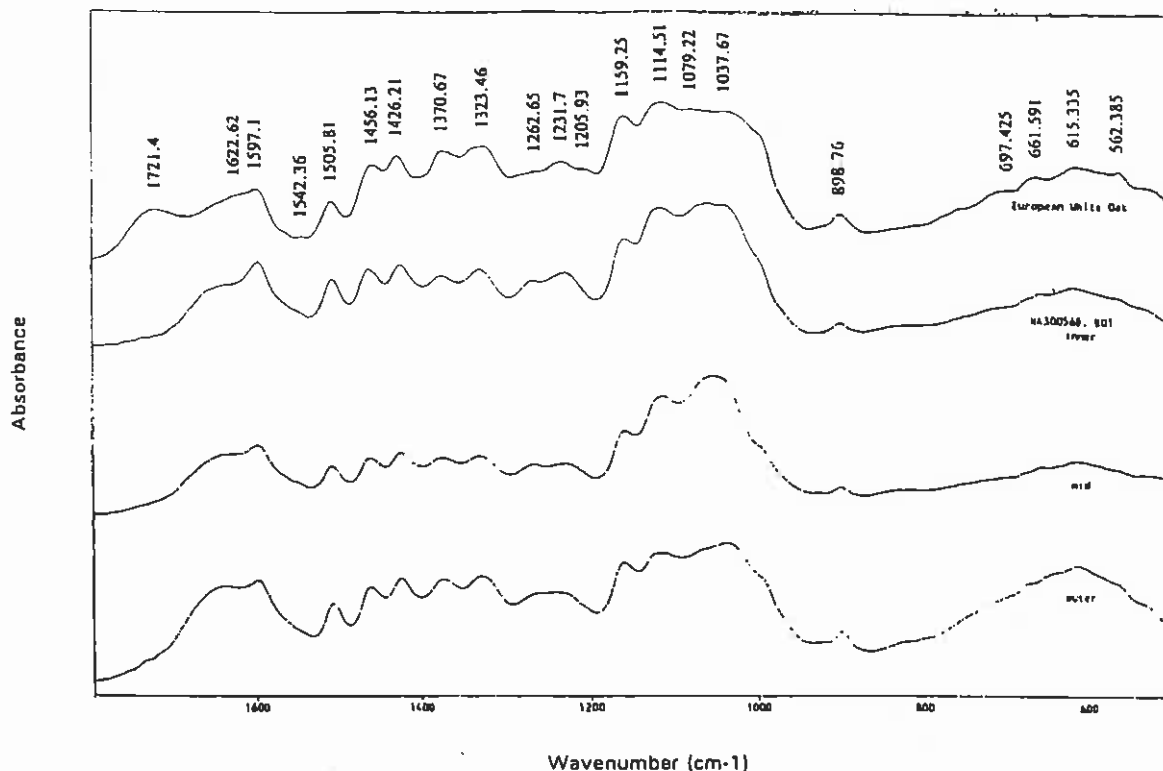


Figure 3. FT-IR spectra of copper impregnated waterlogged wood (HA30056B.BOT) recovered from the *Hadda* site and modern undegraded European white oak.

The intense band at about  $1330\text{cm}^{-1}$  corresponds to syringyl lignin units, which are present in hardwoods but not in softwoods and the fact that the lignin peak is absorbing below  $1509\text{cm}^{-1}$  is also diagnostic of hardwood. The absolute heights of the appropriate peaks of the *Hadda* wood samples compared to the undegraded European white oak show the intensities of the absorption bands associated with the hemicellulose and holocellulose have decreased while the average heights of the lignin absorption bands at  $1510\text{cm}^{-1}$  have remained stable or increased slightly. Hence, the ratio of lignin to holocellulose has increased in the waterlogged wood samples indicating some degree of deterioration.

The marked decrease in the intensity of the absorption band at about  $1740\text{cm}^{-1}$  for all waterlogged wood spectra indicates that extensive degradation of the hemicellulose fraction has occurred. Semi-quantitative analysis of the changes in hemicellulose content showed that there was a 79% average percentage loss of hemicellulose at  $1740\text{cm}^{-1}$  in the HA30056A.TOP sample and 76% in the HA30056B.BOT sample. There has also been a 32% and 47% loss of xylan, respectively, which is depicted by the decrease in the peak heights band at about  $1220\text{cm}^{-1}$ . Similarly, the holocellulose content of the waterlogged wood samples has decreased significantly. The fact that there has been some decrease in the intensities of the guaiacyl and syringyl bands at about  $1260\text{cm}^{-1}$  and  $1330\text{cm}^{-1}$ , respectively may indicate some loss of lignin character in the waterlogged wood samples. In addition, there has been a greater average percentage loss of syringyl lignin compared to guaiacyl for the waterlogged wood samples. This is not surprising as guaiacyl lignin is more stable to chemical and biological degradation than syringyl lignin.

The average percentage loss of hemicellulose indicates that the HA30056A.TOP wood sample is slightly more degraded than the HA30056B.BOT sample. This would be expected as the more deteriorated sample was sectioned near the head of the fastening where it would have been subjected to a more oxidising micro-environment. Overall, it appears that the outer and middle areas of the copper impregnated waterlogged wood samples are the most degraded sections and the inner regions are only slightly degraded.

The second copper impregnated wood sample (HA30057) was also removed from around a brass fastening. Again, as with the HA30056 sample, this wood sample was sectioned into two samples and given the identification codes, HA30057.TOP, recovered near the head of the fastening and HA30057.BOT collected lower on the shank of the bolt.

The HA30057 fastening was sampled for wet chemical analysis in the same fashion as the HA30056 fastening and the concentration of copper, zinc and lead normalised to 100%. Iron was a minor element at 0.1% in both metal samples. The percentages of copper, zinc and lead in the sample collected from the aerobic region were 71%, 29% and <0.5% (total metal composition 100%) and from the deoxygenated area were 66%, 34% and <0.5% (total metal composition 100%), respectively. It is likely that the basic composition is the same as the HA30056 fastening and is a low leaded 70/30 brass. The variation in the metal composition of the HA30057 fastening is not uncommon for copper alloys and is due to different microstructures where the solid metal was sampled. The dezincification corrosion processes that occurred beneath the wood of the HA30056 brass fastening were not occurring on the HA30057 bolt indicating a more oxidising micro-environment beneath the wood.

The wood from this *Hadda* sample was identified as a beech (Table 1). European beech cannot be readily separated from American beech. However, the German origin of the *Hadda* vessel suggests that the beech is more likely to have a European provenance. Hence, the recent, undegraded comparative sample was European beech (*Fagus sylvatica* L.). The FT-IR spectra for the outer, middle and inner regions of HA30057.BOT are shown in Figure 4. The inner and mid sections of the HA30057.TOP sample were heavily impregnated with dark anaerobic copper corrosion products and the FT-IR spectra could not be obtained. The absolute peak heights of the major absorption bands in the wood spectra are presented in Table 4.

Table 4. Absolute peak heights of diagnostic absorption bands from the FT-IR spectra of European beech and HA30057A.BOT.

Wood Sample	hemicellulose		holocellulose			lignin		
	1740	1240	1370	1160	896	1510	1330	1260
European beech	0.21	0.45	0.40	0.57	0.06	0.11	0.39	0.44
HA30057A.BOT								
inner	0.02	0.35	0.44	0.65	0.06	0.25	0.47	0.33
mid	0.02	0.23	0.25	0.45	0.03	0.11	0.30	0.21
outer	0.02	0.16	0.20	0.32	0.04	0.12	0.21	0.15
average % loss	90	45						

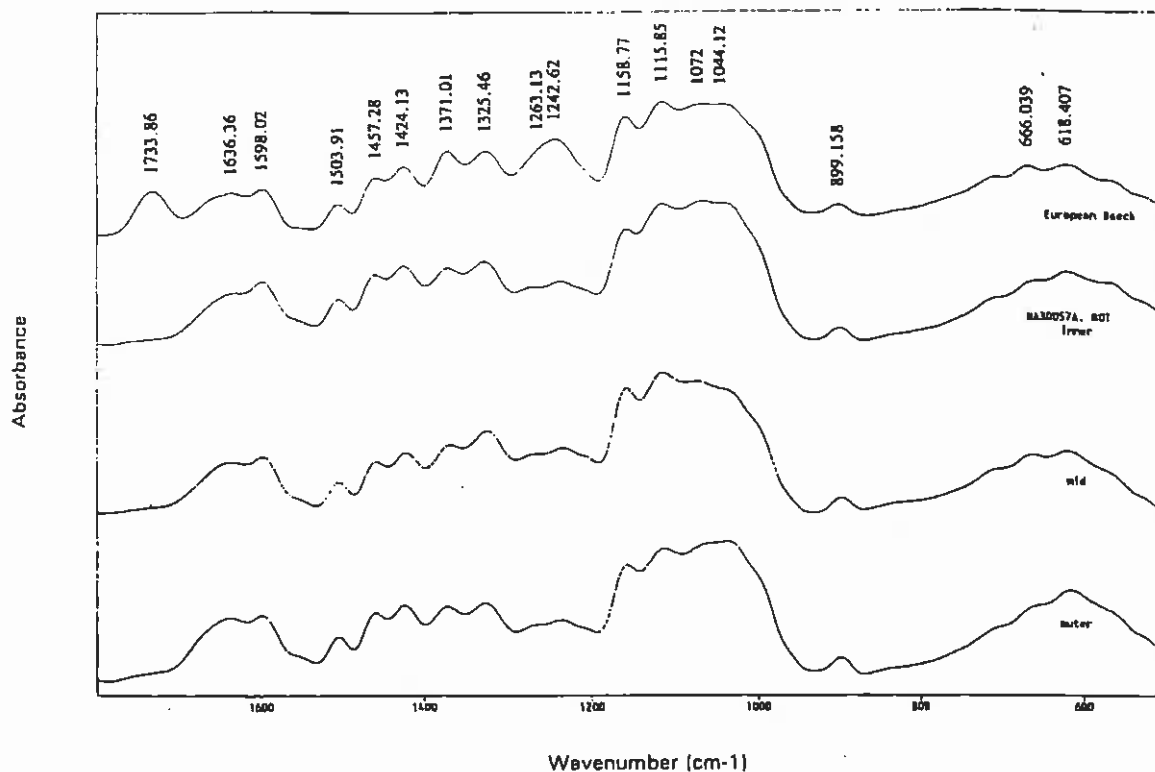


Figure 4. FT-IR spectra of copper impregnated waterlogged wood (HA30057A.BOT) recovered from the *Hadda* wreck site and modern undegraded European beech.

From the spectra, the *Hadda* wood sample was a hardwood evident from the pronounced syringyl lignin band at about  $1325\text{cm}^{-1}$  and the lignin band absorbing below  $1509\text{cm}^{-1}$ . The relatively small increase in the ratio of lignin to holocellulose for the waterlogged wood samples indicate there has been some deterioration of the carbohydrate fraction but overall, the extent of degradation of the wood is only slight. There has been a 90% loss in the hemicellulose fraction of this sample and a 45% loss in xylan. The intensities of the major absorption bands associated with the holocellulose and hemicellulose decreased in order from the inner to outer regions of the HA30057.BOT wood sample. This indicates that the inner region was the least degraded with the extent of deterioration increasing towards the outer surface of the copper impregnated wood sample. There may have been some small loss of lignin character in the outer regions of the wood denoted by decreases in the intensity of the peaks at  $1325\text{cm}^{-1}$  and  $1263\text{cm}^{-1}$ .

From the results obtained from the FT-IR spectra, it appears that there has been significant selective degradation of the copper impregnated waterlogged wood samples recovered from the *Hadda* site in comparison to the modern, undegraded wood samples. The extent of degradation is greater in the outer surfaces of the waterlogged wood samples than in the inner regions and the major wood polymers effected are the carbohydrates, especially the hemicellulose fraction. This degradation trend can be simply explained by the increase physical degradation, such as water and sand blasting and the rate of chemical hydrolysis and oxidation reactions that occur on the outer surfaces due to the exposure to the open, oxygenated marine environment and the presence of copper corrosion products. It is interesting to note that the extent of degradation of the outer and middle surfaces is relatively small and this would probably

be due to the precipitation of copper corrosion products in these areas, which are biologically toxic and protect the wood in these regions from further aerobic biodeterioration.

There was also some small loss of lignin character in the outer regions of the copper impregnated wood samples. Lignin is relatively stable and resistant to hydrolysis, however, aerobic bacteria and soft rot caused by certain marine fungi may cause modifications in lignin structure and some slight loss of lignin components. The inner surface would be expected to be the least degraded, as the lower oxygen environment would retard biological attack. However, under low oxygenated conditions some bacteria are capable of degrading wood, albeit much slowly, where marine fungi and wood borers are completely excluded because of the limited oxygen supply. The presence of copper sulphides in the inner regions will not retard biodeterioration but the formation of acidic hydrogen ions from copper sulphide precipitation may cause some acidic hydrolysis of the polysaccharides.

There are definitely some differences in the degradation of the copper impregnated wood samples with respect to wood species. The degraded white oak sample HA30056B.BOT lost 76% of the hemicellulose at 1740cm<sup>-1</sup> and 32% of the xylan (1220cm<sup>-1</sup>) while the beech sample, HA30057A.BOT lost 90% and 44%, respectively. That is, the waterlogged white oak was less degraded than the beech. Both European white oak and beech are hardwoods and have similar chemical compositions [Fengel & Wegener 1989] however, white oak heartwood is very resistant to biodeterioration because of the tyloses which block vessels and subsequently, the flow of water and microbe access. In addition, the differences in the extents of deterioration of these wood samples could be due to changes in local micro-environment.

#### Copper Impregnated Waterlogged Wood Recovered from the *Favourite* Site

This wood sample (FAV3075) was recovered from the wreck of the *Favourite* (1867) and was recovered after 117 years. The wood surrounded a bronze gudgeon. The *Favourite* wood sample was identified as an elm (Table 1) and the vessel may be of American provenance but this is not conclusive. The undegraded sample used for FT-IR comparison was European elm (*Ulmus procera* Salisb.) as an American elm was not available for analysis. The FT-IR spectra of the FAV3075 samples and the undegraded European elm are shown in Figure 5. The absolute peak heights of the major bands attributed to holocelluloses and lignin are presented in Table 5.

Table 5. Absolute peak heights (cm) of diagnostic absorption bands (cm<sup>-1</sup>) from the FT-IR spectra of European elm and FAV3075.

Wood Sample	hemicellulose		holocellulose			lignin		
	1740	1240	1370	1160	896	1510	1330	1260
European elm	0.20	0.40	0.33	0.51	0.06	0.16	0.29	0.40
FAV3075								
inner	0.10	0.78	0.95	1.10	0.18	0.59	1.00	0.72
mid	0.09	0.41	0.42	0.69	0.07	0.31	0.45	0.38
outer	0.04	0.22	0.21	0.36	0.05	0.17	0.24	0.20
average % loss	62							

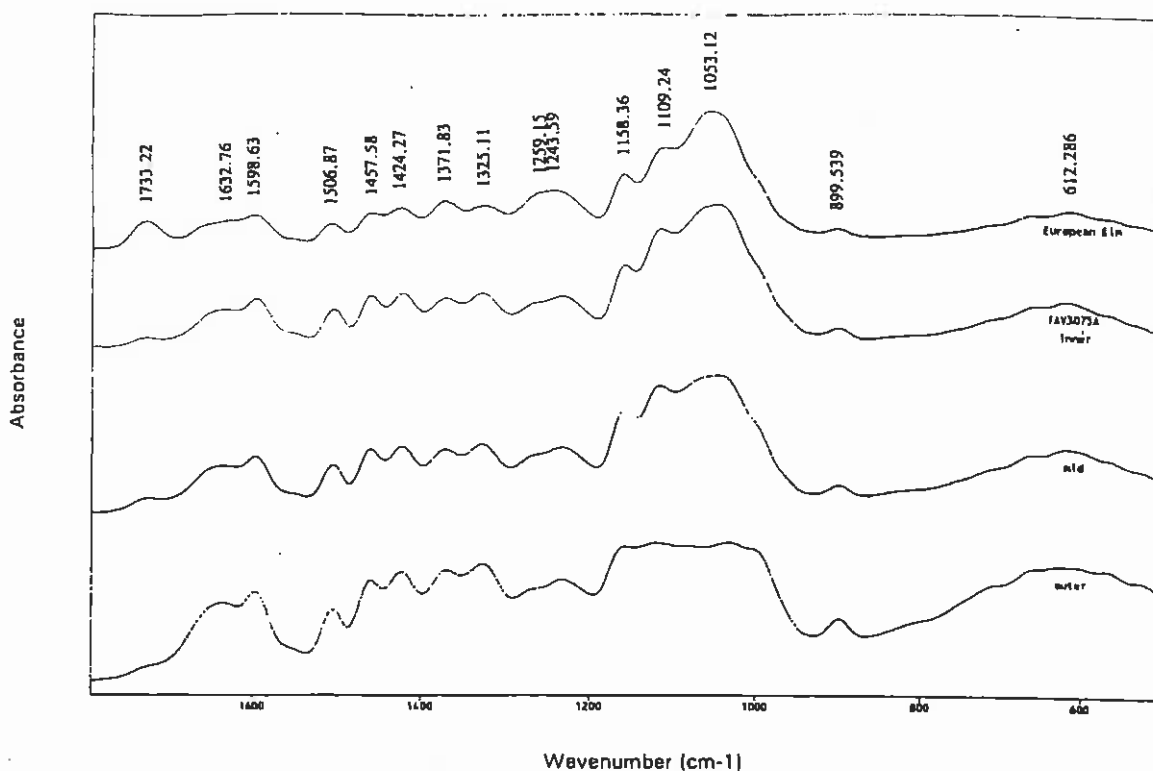


Figure 5. FT-IR spectra of copper impregnated waterlogged wood (FAV3075) recovered from the *Favourite* wreck site and modern undegraded European elm.

The FAV3075 sample is a hardwood evident from the pronounced syringyl band at  $1325\text{cm}^{-1}$  and the lignin band occurring lower than  $1509\text{cm}^{-1}$  at  $1507\text{cm}^{-1}$ . The absolute peak heights of the major absorption bands of the undegraded wood sample compared to the inner, least degraded area of the waterlogged wood, seems to suggest that the FAV3075 sample is not an elm of European origin which agrees with the archival information.

There are some distinct differences in the absolute peak heights of the major absorption bands for the FAV3075 waterlogged wood sample. There has been an overall decrease in the intensities of the peaks assigned to the polysaccharides, while the peak heights of the lignin bands have remained stable or increased. Hence, the ratio of lignin to holocellulose has increased, indicating degradation of the carbohydrates and selective preservation of the lignin in the wood matrix. In addition, the polysaccharide loss is also apparent from the decrease in the intensity of the xylan band at  $1244\text{cm}^{-1}$  and the emergence of the band at about  $1259\text{cm}^{-1}$  resulting from the preservation guaiacyl lignin.

On further inspection of Figure 5, the intensities of the holocellulose, hemicellulose and lignin bands decreased from the inner to the outer region of the waterlogged wood sample. This trend implies that the extent of deterioration of these wood chemicals increases as the wood is traversed towards the outer regions. Observing the overall decrease in the height of the band at  $1733\text{cm}^{-1}$ , there has been a 62% loss in the hemicellulose fraction of the FAV3075 sample however, this is not as dramatic as the polyose deterioration in the *Hadda* wood samples. Again, the extent of degradation of the hemicelluloses increases from the inner to the outer regions of the copper impregnated FAV3075 wood sample.

The FAV3075 waterlogged wood sample was relatively undegraded with the extent of deterioration of the wood matrix decreasing from the outer to the inner regions of the sample. Both wreck sites were subjected to a similar range of micro-environmental parameters and time of submergence. Therefore, the explanation for the general degradation patterns observed in the FAV3075 wood sample will be similar to that proposed for the previously described copper impregnated *Hadda* wood samples. However, the degree of degradation of the FAV3075 wood sample was less than that of the wood samples recovered from the *Hadda* site and this would be due, in part, to the differences in wood species.

#### Copper Impregnated Waterlogged Wood Recovered from the *Rapid* Site

The next two copper impregnated samples were recovered from the *Rapid* wreck site which is situated off Point Cloates, near the North West Cape of Western Australia. The wood had obviously surrounded a copper fastening at one time and had been immersed for 169 years. The *Rapid* wood was sectioned into two samples, identified as RP1.1 and RP1.2. The site is a relatively shallow site, experiencing occasional exposure and reburial cycles during cyclones which occur at irregular intervals in the north west of this state. These changes in burial state subject objects to a wide range of micro-environments, from aerobic to anaerobic conditions. In addition, the cyclonic activity causes unusually violent sand and water movement during these periods [MacLeod 1982, 1991].

The *Rapid* was an American China trader and this waterlogged wood sample was identified as an American white oak. Therefore, the comparative undegraded wood sample was North American white oak (*Quercus alba* L.). The FT-IR spectra of the copper impregnated waterlogged wood sample, RP1.1 and the reference are shown in Figure 6. The absolute peak heights of the major absorption bands associated with lignin and holocellulose are presented in Table 6.

Table 6. Absolute peak heights (cm) of diagnostic absorption bands ( $\text{cm}^{-1}$ ) from the FT-IR spectra of North American white oak, RP1.1 and RP1.2.

Wood Sample	hemicellulose		holocellulose			lignin		
	1740	1220	1370	1160	896	1510	1330	1260
American white oak	0.42	0.78	0.57	0.82	0.10	0.32	0.52	0.75
RP1.1								
inner	0.04	0.44	0.55	0.85	0.07	0.42	0.60	0.41
mid	0.00	0.17	0.21	0.34	0.05	0.20	0.20	0.15
outer	0.04	0.01	0.30	0.00	0.00	0.00	0.22	0.11
average % loss	94	74						
RP1.2								
inner	0.08	0.67	0.92	0.95	0.12	0.74	0.91	0.61
mid	0.04	0.41	0.48	0.66	0.07	0.39	0.51	0.39
outer	0.02	0.40	0.39	0.38	0.09	0.38	0.37	0.45
average % loss	89	51						

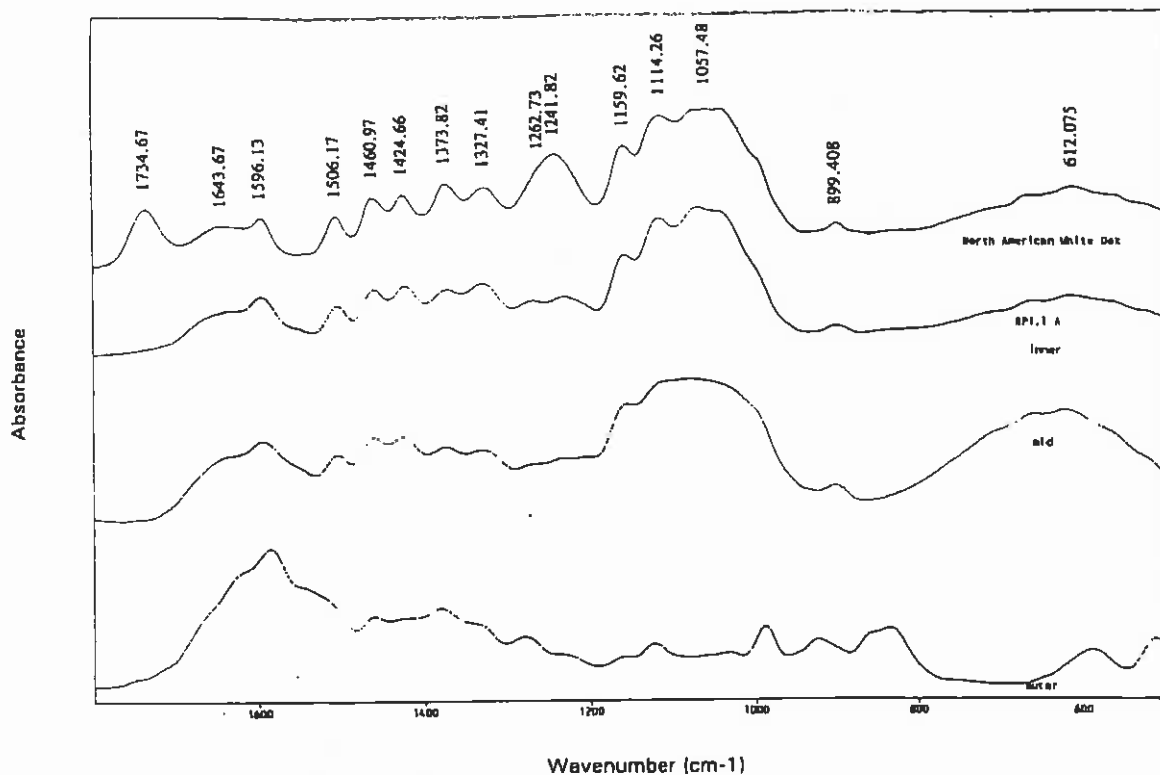


Figure 6. FT-IR spectra of copper impregnated waterlogged wood (RP1.1) recovered from the *Rapid* wreck site and modern, undegraded North American white oak.

The presence of the syringyl lignin band at  $1327\text{cm}^{-1}$  and the lower absorption of the lignin band at  $1506\text{cm}^{-1}$  indicates the *Rapid* sample is a hardwood. This agrees with the microscopic identification of the sample wood species as the hardwood, North American white oak.

Generally, in comparison to the undegraded wood, these *Rapid* waterlogged wood samples have higher lignin to carbohydrate ratios which indicates that the holocellulose fraction of the wood matrix has been preferentially degraded with respect to the lignin portion. The absorption bands at  $1735\text{cm}^{-1}$  arising from hemicellulose are almost entirely non-existent which indicates that there has been considerable destruction and dissolution of the polyoses in these *Rapid* wood samples. There has been a 94% hemicellulose loss in the RP1.1 sample and a 89% loss for RP1.2. In addition, the intensities of the bands at  $1242\text{cm}^{-1}$  representative of xylan, have decreased substantially representing a 74% loss in the RP1.1 sample and a 51% loss in RP1.2. This decrease has unmasked the guaiacyl lignin peak at about  $1261\text{cm}^{-1}$ .

The lignin to holocellulose ratios increased from the inner to the outer regions of the *Rapid* wood samples. This trend indicates that the inner areas are only slightly degraded and the degree of deterioration increases as the outer surfaces are approached. The outer surface of samples RP1.2 appears to be only slightly more degraded than the middle and inner regions of the same sample, however, the outer sample of RP1.1 was extensively degraded. Very few peaks attributed to carbohydrate absorptions remain in the FT-IR trace of the outer region of RP1.1, denoting extensive holocellulose degradation. The band emerging at about  $1120\text{cm}^{-1}$  is usually observed for very degraded hardwoods with

low carbohydrate contents. This band arises from the aromatic C-H in plane deformation of syringyl lignin structures but it is usually masked by any strong C-O stretching vibrations of holocellulose in this area of the spectrum. Furthermore, the large decrease in the intensities of the bands at 1506, 1327 and 1261 $\text{cm}^{-1}$  verifies significant deterioration of the lignin matrix in the outer RP1.1 sample.

The same arguments used to explain the degradation mechanisms applied to the other copper impregnated wood samples will apply to these *Rapid* samples however, the major difference in the extents of degradation of these *Rapid* wood samples was the high level of deterioration in the outer region of RP1.1. The fact that there was very little wood polymer remaining would explain the brittleness of this outer surface. Since these two copper impregnated waterlogged wood samples, were sectioned from the same wooden object, this increase in deterioration of the outer surface must be due to an increase in the physical, chemical and biological degradative forces effecting this particular area. The outer surface of the RP1.1 was only lightly impregnated with paratacamite and this lower copper concentration may not significantly retard attack from wood borers, soft rot fungi and aerobic bacteria. Aerobic biodeterioration can rapidly breakdown wood surfaces. These outer surfaces can then be more easily degraded by chemical and physical means.

The copper impregnated waterlogged wood samples, RP2.1 and RP2.2, were also recovered from the *Rapid* wreck site and sectioned in the same way as the previous *Rapid* wood sample. These waterlogged wood samples were identified as a hard pine of the pitch pine type (Table 1). An example of this softwood type includes Longleaf pine (*Pinus palustris* Mill.) which is the undegraded reference used for comparison. The FT-IR spectra of the inner, mid and outer sections of RP2.2 are shown in Figure 7. The peak heights of the major absorption bands are outlined in Table 7.

Table 7. Absolute peak heights (cm) of diagnostic absorption bands ( $\text{cm}^{-1}$ ) from the FT-IR spectra of Longleaf pine, RP2.1 and RP2.2.

Wood Sample	hemicellulose		holocellulose			lignin	
	1740	1220	1370	1160	896	1510	1260
Longleaf pine	0.12	0.32	0.40	0.50	0.08	0.33	0.37
RP2.1							
inner	0.04	0.34	0.37	0.37	0.08	0.35	0.38
mid	0.04	0.44	0.48	0.40	0.09	0.47	0.47
outer	0.02	0.40	0.39	0.38	0.09	0.38	0.45
average % loss	72						
RP2.2							
inner	0.03	0.46	0.58	0.87	0.11	0.44	0.61
mid	0.03	0.29	0.33	0.37	0.07	0.28	0.35
outer	0.00	0.00	0.00	0.02	0.00	0.00	0.00
average % loss	83						

From the FT-IR spectra, these *Rapid* samples can be recognised as a softwood evident from the greater intensity of the 1268 $\text{cm}^{-1}$  absorption band arising from guaiacyl lignin units, than the xylan band at 1225 $\text{cm}^{-1}$ . In addition, the lignin absorption is at about 1509 $\text{cm}^{-1}$  which is indicative of softwoods. There is also a quite distinctive peak at about 807 $\text{cm}^{-1}$  corresponding to mannan (O-acetyl-galactoglucomannan), which is prevalent in softwoods but not hardwoods.



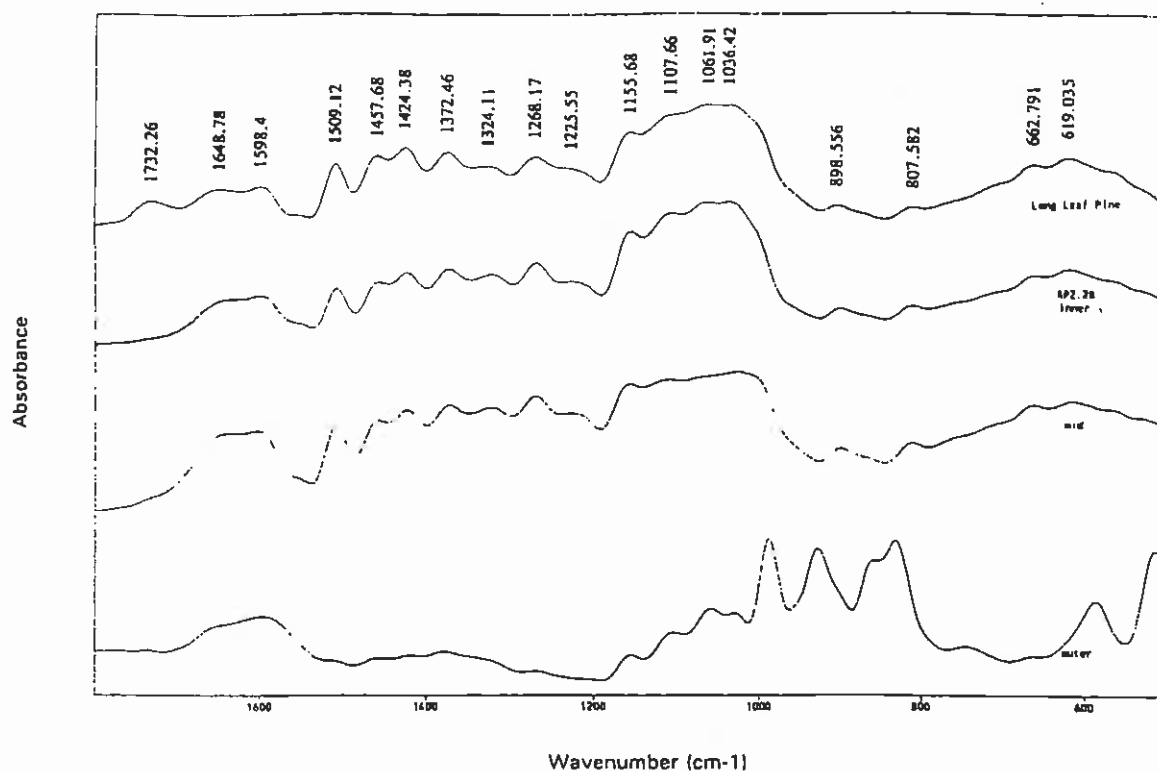


Figure 7. FT-IR spectra of copper impregnated waterlogged wood (RP2.2) recovered from the *Rapid* wreck site and modern, undegraded Longleaf pine.

From the general increase in ratios of lignin to holocellulose, the carbohydrate fractions of these copper impregnated *Rapid* wood samples have been deteriorated while the lignin has essentially remained undegraded. There has been marked decomposition of the hemicelluloses in all samples. That is, a 72% loss in the RP2.1 sample and an 83% loss in RP2.2. Overall, RP2.1 is considerably less degraded than RP2.2 and the extent of deterioration increases from the inner to the outer regions in both wood samples. Pronounced decreases in the carbohydrate and lignin content for the outer surface of RP2.2 indicates that there is extensive wood degradation in this area. Only wood decomposition products remain in this outer region and the mechanical strength has decreased significantly.

The trends in the extents of degradation for these copper impregnated waterlogged wood samples are very similar to those observed for the RP1 samples. That is, RP2.1 is relatively undeteriorated while RP2.2 is extensively degraded suggesting exposure to a more aggressive micro-environment. Therefore, the same interpretation and arguments used to explain the different degrees of degradation in the RP1 samples will apply to these samples. In addition, it seems that the different wood species of RP1 and RP2 did not have a dramatic effect on the comparative extents of degradation between these wood samples. However, from the average percentage loss of hemicellulose at  $1740\text{cm}^{-1}$  it appears that the RP2 pine samples were slightly less degraded than the white oak (RP1) samples. This is because some softwoods have lower hemicellulose and higher lignin contents than certain hardwoods. Under marine conditions, the hemicelluloses are the most readily degraded wood chemical in the wood matrix while lignin is relatively stable to deterioration. Therefore, softwood species are often more resistant to chemical and biological degradation than hardwoods.

### Iron Impregnated Waterlogged Wood Recovered from the *Vergulde Draeck* Site

The GT 6154 sample was obtained from a heavily iron impregnated wooden billet box recovered after 326 years from the *Vergulde Draeck*, a Dutch East Indiaman, which was wrecked in 1656 on a shallow reef at Ledge Point. The *Vergulde Draeck* wood sample was identified as a pine of the red deal type (Table 1) and a sample of European redwood (*Pinus sylvestris* L.) was used as the undegraded comparative sample.

The combined FT-IR spectra of the outer, middle and inner sections of the iron impregnated waterlogged wood sample and the undegraded reference are shown in Figure 8.

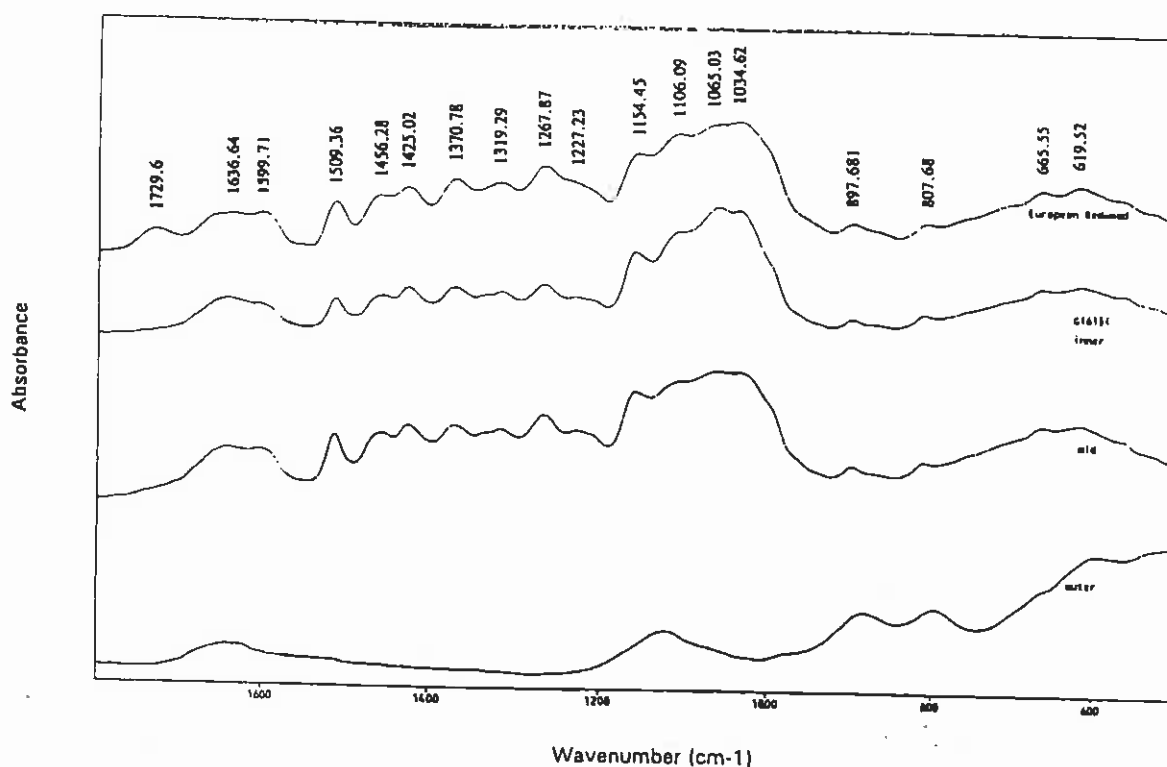


Figure 8. FT-IR spectra of iron impregnated waterlogged wood (GT6154) recovered from the *Vergulde Draeck* wreck site and modern, undegraded European redwood.

Table 8. Absolute peak heights (cm) of diagnostic absorption bands ( $\text{cm}^{-1}$ ) from the FT-IR spectra of European redwood and GT6154.

Wood Sample	hemicellulose		holocellulose			lignin	
	1740	1220	1370	1160	896	1510	1260
European redwood	0.13	0.42	0.42	0.56	0.09	0.28	0.49
GT6154							
inner	0.02	0.24	0.30	0.53	0.06	0.23	0.32
mid	0.04	0.31	0.35	0.51	0.06	0.32	0.40
outer	0.00	0.00	0.00	0.00	0.00	0.00	0.00
average % loss	85	56					

From examination of the FT-IR spectra, the waterlogged wood sample is a softwood. This is evident from the pronounced band at about  $1268\text{cm}^{-1}$  corresponding to guaiacyl lignin units and the other lignin absorption that occurs at  $1509\text{cm}^{-1}$ , which is typical of softwoods.

All of the iron impregnated waterlogged wood sections show a great decrease in the intensity of the band at about  $1740\text{cm}^{-1}$  showing a hemicellulose loss of 85% (Table 8). In addition, there has been a 56% loss of xylan in the waterlogged wood samples. Generally, the ratios of lignin to holocellulose for the inner and mid sections of the waterlogged wood samples have increased indicating a slight decrease in the holocellulose concentration of the sample and a subsequent preservation of the lignin portion of the wood matrix. On the other hand, the outer surface of GT 6154 is extensively degraded. The intensity of the absorption bands in the  $1000\text{-}1200\text{cm}^{-1}$  region arising primarily from carbohydrates, are severely decreased indicating extensive degradation and removal of the polysaccharides in the softwood. The broad band at  $1120\text{cm}^{-1}$  is usually observed in wood samples with very low carbohydrate contents. There has also been some modification and deterioration of the lignin matrix supported by the loss of the major peaks at  $1509\text{cm}^{-1}$  and  $1268\text{cm}^{-1}$ . The extent of degradation of this waterlogged wood sample decreased significantly from the outer to the inner surface and the inner surface appears to be only slightly degraded.

The degradation trends observed for the iron impregnated waterlogged wood sample are not unexpected. The outer surface of the sample should be heavily degraded as the wood had been exposed to the open, aerobic marine environment for about 326 years prior to excavation. The rate of physical, chemical and biological deterioration will be fastest in the outer regions of the wood sample. In addition, the presence of high concentrations of iron corrosion products in the outer surface will tend to increase biodeterioration and chemical degradation of the wood tissue. The main reactions occurring are acidic hydrolysis and metal catalysed oxidation of the holocellulose fraction of the wood. The lignin skeleton is only very slightly effected.

Metal catalysed oxidative degradation of carbohydrates is a chain reaction involving free radicals and molecular oxygen catalysed by metal ions. The reactions involved with oxidation proceed at the initial stages by the formation of peroxides, the decomposition of which is catalysed by certain metal ions, such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  [Allen et al. 1992; Marian & Wissing 1960]. This results in oxidation of the cellulose molecule to oxycellulose, which leads to a reduction in tensile strength [Barkman 1975].

The degradation of the iron impregnated waterlogged wood will decrease moving towards the inner regions of the wood because it is subjected to a lower oxygenated micro-environment, which will subsequently, decrease the rate of chemical and biological deterioration. Physical deterioration will be minimised because of the protection provided by the outer layers of wood to excessive water movement.

## CONCLUSIONS

FT-IR spectroscopy can be used to differentiate between hardwoods and softwoods and this is very useful as extensive degradation of the wood tissue can lead to unreliable wood identifications by the classical optical microscopic technique. Additionally, the extent of degradation of wood can be semi-quantitatively estimated by this technique. The results showed that these samples of metal impregnated waterlogged wood recovered from

different shipwreck sites had been degraded to some extent by immersion in the marine environment when compared to modern, undegraded wood of the same genus. Generally, the polysaccharide fractions were degraded in preference to the lignin structures and the rate of deterioration of hemicellulose was faster than cellulose. In many samples the lignin portion of the wood matrix appeared relatively undegraded. However, the FT-IR spectra of all wood samples showed very slight increases in the intensity of the band at about  $1650\text{cm}^{-1}$ . This absorption is attributed to carbonyl and carboxyl groups formed in the lignin part of the wood in the position conjugated to the lignin aromatic nuclei, indicative of lignin oxidation in the waterlogged wood. The extent of this degradation seemed to decrease from the outer to the inner regions of the wood samples. These results support the fact that wood carbohydrates are chemically and biologically degraded in preference to lignin and hemicelluloses undergo hydrolysis and oxidation faster than cellulose in wood tissues.

The extent of degradation of these wood samples was greater in the outer more exposed surfaces than in the lower oxygenated inner regions. This would be expected because the outer surfaces would be subjected to more severe water and sand impingement, higher levels of dissolved oxygen and increased attack by wood deteriorating marine organisms which would increase the rate of physical, chemical and biological degradation of the outer wood tissue. It is well known that aerobic degradation of wood is considerably faster than deterioration under anaerobic conditions.

The extent of degradation of the outer regions of the iron impregnated *Vergulde Draeck* wood sample was significantly greater than the outer regions of the copper impregnated wood samples. This observation can be partly explained by the fact that iron corrosion products will increase the rate of wood deterioration caused by acidic hydrolysis and catalysed oxidation of wood components. The presence of iron will also increase microbiological activity unlike copper and zinc corrosion products which are biologically toxic.

More importantly, since the general conditions of each different wreck site and the micro-environments of the wood samples were very similar, the difference in the extents of degradation of the metal impregnated waterlogged wood samples must be primarily due to the time of submergence and the wood species.

Generally, the most degraded wood sample, recovered from the *Vergulde Draeck* site was impregnated with iron corrosion products and had been exposed to the marine environment for 326 years. The *Rapid* copper impregnated wood was the next most degraded and had been immersed for approximately 169 years, while the copper impregnated *Hadda* and *Favourite* samples were only slightly degraded being submerged for about 116 years. The results show that the longer the wood is exposed to aerobic marine conditions the greater the extent of wood degradation.

The annualised percentage loss of hemicellulose for each copper impregnated wood species was calculated by dividing the average percentage loss of hemicellulose at  $1740\text{cm}^{-1}$  by the numbers of years of submersion on the shipwreck site. The results take into account the time of submergence for each wood type, effectively normalising the hemicellulose loss. The rate of hemicellulose loss for the pine (RP2) and white oak (RP1) recovered from the *Rapid* site were  $0.43\%y^{-1}$  and  $0.54\%y^{-1}$ , respectively. The *Favourite* elm (FAV3075) sample was  $0.53\%y^{-1}$ . Similarly, the *Hadda* white oak (HA30056) and beech (HA30057) samples were  $0.67\%y^{-1}$  and  $0.78\%y^{-1}$ , respectively.

These results indicate that the pine sample (RP2) recovered from the *Rapid* site was slightly less degraded than the white oak sample (RP1). This agrees with the fact that softwoods are, generally, more resistant to degradation in the same local micro-environment than hardwood species due to increased proportions of lignin and lower quantities of hemicelluloses in softwoods compared to hardwoods. Overall, the extent of degradation of the copper impregnated waterlogged hardwood samples recovered from the *Hadda* and the *Favourite* wreck sites appeared to be very similar. However, from the annualised percentage losses of hemicellulose, the *Hadda* white oak (HA30056) and beech (HA30057) samples were more degraded than the *Favourite* elm (FAV3075) and *Rapid* oak (RP1) samples. The loss of hemicellulose had been corrected for the number of years of immersion on each specific shipwreck site, hence, the differences in the extents of degradation would be mainly due to the wood species. Therefore, for wood subjected to these similar local micro-environments, a tentative order for decreasing wood species resistance would be pine > elm ≥ white oak > beech.

It is the chemistry and biology of the wreck site that are the determining factors in the extent of deterioration of wood recovered from shipwreck sites. However, if these factors are similar, then it is the age of the wood, the species and the presence of metal corrosion products in the wood matrix that have the most effect on the durability of wooden ships' timbers. Finally, it is essential to understand the deteriorating aspects that will effect the condition of wood in a marine environment and to measure the extent of degradation of the wood so appropriate conservation treatments can be applied to the wooden artefacts.

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**Jens Glastrup:** When you use a FTIR, do you think it is a good instrument to use for any sort of quantification of the loss of hemicellulose? Could there be any other possible method to do that?

**Ian MacLeod:** One of the problems that I will be comparing tomorrow is using the carbon<sup>13</sup> NMR. The fact is, there, you are using a bigger sample so you get more of an average value for the degradation but FTIR, because you are taking a small sample, it is prone to some sampling error. We have gone and looked, for example, at the intensities of the bands with different anvil pressures and found that you have to be very careful with anvil pressures with the diamond cells with some of the spectra of the waterlogged leather [and] with the waterlogged wood. By the way all the samples were dry. They had air-dried by the time they got to the FTIR. So you may get differences with wet samples. The results were quite reproducible and the spectra are incredibly reproducible. You can pick up, for example, differences in absorption of different parts of the structure of the timber from one wood species to another. You can pick up a difference of 0.7 centimetres or something in the peak and it will be reproducible. You go and bung another sample of timber in there and if it is the same species, the lines just go "britttttt" and mesh in together really well. When I was a young lad, which is a hundred centuries ago, people scanned too fast and since you didn't have the computers for averaging the scans you got crappy resolution. Now, because all the data is recorded digitally you can use, although we have not done it with this, de-convolution programs so that, for example, where you have some of the cellulose-stretching vibrations overlapping with some of the carbon-carbon stretches from the lignins you will be able to put in that data, put it through a de-convolution program and be able to actually get measurements on more of the individual peak heights and the components within the wood. Basically this is just a very simple analysis of a particular peak which we found was a very good indicator of degradation. You could perhaps go back and spend another year going through the spectra, de-convoluting them and working out more precisely what is happening. I do believe it is a very good technique for waterlogged wood as well as waterlogged leather, waterlogged baskets and waterlogged cork, cause we are the wet organic archaeological materials group, not just wood. It is a technique that is very useful.

**Haydn Sutcliffe:** Ian, a very interesting paper. Can you tell me what your scanning range was? Did you go as far as 1600 cm<sup>-1</sup>?

**Ian MacLeod:** I left that detail out. We had the full IR range from 600 up to 4000 cm<sup>-1</sup>. Up at the higher end it is just full of water and relatively boring stuff. The reason why we concentrated in the fingerprint region was that is where you get all your gutsy information out about your celluloses and your lignins.



**Haydn Sutcliffe:** What I was interested in was whether you got any absorptions around about  $1600\text{ cm}^{-1}$ , which is not near the water although you would get some water banding. But was there any evidence for carboxylate groups?

**Ian MacLeod:** Hmm, without looking at... I will bring them in tomorrow to show you.

**Khoi Tran:** I am pleased that Ian has offered us, today, a new technique. A low cost and a non-destructive technique for the assessment of the degree of deterioration of archaeological wood. I would like to take this opportunity to say some words about our common research project with the York Archaeological Wood Centre. Jim Spriggs, Ian Panter and our laboratory have a research project which we would like to submit to the European Commission next year on the topic of the development of non-destructive testing techniques, if possible low cost techniques, to study, to analyze and to quantify the degree of deterioration of archaeological wood. I think that the FTIR technique must be in the range.

**Ian MacLeod:** Yes, once you have got the instrument the scans are dead cheap to run but the instrument costs about \$32,000 Australian.

**Khoi Tran:** So I would like to invite people working in the same field to join us for the discussion of the program or with different opinion panels to present something next year to the European Commission.

**Malcolm Bilz:** I just wanted to mention that just recently we have gotten an FTIR machine that is portable. You can take it in the field and run it off a generator or solar panel. Scott Williams is just starting to look into its capabilities. It has a fibre optic type probe where you can touch things and get the scan back. He has tried it on various things. He is working on plastics and solutions. This may be an incredible step in terms of in the field work, assessing things. Otherwise you go back to the lab and if you didn't get a good sample then, as you say, it is often hard to get back to your object.

**Ian MacLeod:** Actually it would be fun water-proofing an FTIR and taking it down on a wreck site.

**Amanda Sutherland:** This rate of decay over time, that you mentioned at the end of your talk, do you think this would be exponential or linear?

**Ian MacLeod:** No, no, no. I don't know about land because I am not a land-based person, apart from when I am standing on it. The thing is with shipwrecks once you get the material into the marine environment it appears to, certainly with the corrosion of metals which is what I based my approach on, adopt a steady state decay process. Unless there is a major site disturbance like a cyclone coming through. For example, with iron corrosion you can more or less know what you can find and develop equations that tell you for every year more of immersion you are going to get another 360 g of corrosion product on your average 2 ton cannon. What I thought when we started looking at this data to see, ok, is oak being degraded by the same bugs in the sea, at the same rate, in similar sorts of wreck sites? The numbers, when you look at them in the raw data, might vary from 54% to 87% or 94 % however when you divide them by the number of years

of immersion they all start balancing out to being roughly the same annualized rate of decay. It is going to be linear. For a newly wrecked vessel it is certainly not going to apply but once something has been in the ground or in the sea for one, two or three hundred years, life settles down. Look at us we are all growing older. We are all settling down to a nice steady rate of activity and we are only 30, 40, 50 or 60 years old. After a hundred we would really be settled down.