The Effects of the Ammonia Neutralizing Treatment on Marine Archaeological *Vasa* Wood

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Laboratory experiments with ammonia vapour on Vasa *wood have been carried out to neutralize the acidity connected to the numerous outbreaks of acidic sulfate salts occurring on the wooden surfaces of the Swedish historical shipwreck* Vasa *(1628). The effects of the ammonia treatment have been evaluated by means of pH measurements, Fourier transform infrared (FTIR) spectroscopy and size exclusion chromatography (SEC). The SEC analyses did not show any apparent effect on the cellulose in the polyethylene glycol-treated* Vasa *wood sample, while the FTIR results indicate some degradation of the holocellulose.*

INTRODUCTION

Accumulation of sulfur and iron compounds in marine archaeological wood has caused conservation concerns for decades, but research into this particular problem has increased over the past few years [1, 2]. The reduced sulfur species originate from the natural sulfur cycle that takes place in the seabed and is produced *in situ* in the wood via bacteria [3, 4]. For the famous Swedish shipwreck *Vasa*, sunk in 1628, high concentrations of sulfur and iron are found mostly in the bacterially degraded surface layers of the wooden hull [4, 5]. The accumulation in waterlogged wood occurs via competing reactions forming organic sulfur compounds and also inorganic iron (II) sulfides in the presence of corroding iron. In the presence of oxygen the sulfides primarily oxidize to sulfuric acid and acidify the moist surface wood. This reaction is catalysed by the iron (II)/iron (III) redox couple [2, 5]. It is estimated that about 2 tons of sulfuric acid may have formed in the *Vasa's* wooden hull since the spray treatment with the

conservation solution of aqueous polyethylene glycol (PEG) ceased in 1979 [6]. Recently, additional Fenton type oxidation reactions of PEG, catalysed by iron ions probably originating from corroding bolts inserted after the salvage, have been reported to form organic acids in the interior of the wood [7].

Frequent formation of sulfate salts at the wooden surfaces, such as natrojarosite, $NaFe_3(SO_4)_2(OH)_6$, gypsum, $CaSO_4.2H_2O$, melanterite, $FeSO_4.7H_2O$, rozenite, $FeSO_4.4H_2O$ and also small crystals of elemental α-sulfur was proven by X-ray powder diffraction (XRD) [1, 6]. In April 2008, 3131 areas on the *Vasa's* hull and on loose objects in storage with visible precipitates of acidic salts and with surface pHs of 3.5 or lower were registered. Such high acidity in conserved marine archaeological wood potentially constitutes a serious problem, since acid hydrolysis may eventually reduce the mechanical strength of the wood [8]. Experimental investigations are required to examine the rate of destabilization in ambient conditions [5].

The accessible acidic wooden surfaces inside the *Vasa's* hull were formerly treated with an aqueous solution of sodium bicarbonate ($NaHCO_3$) and soda

(sodium carbonate decahydrate, $Na_2CO_3.10H_2O$). This treatment increased the humidity inside the ship, removed the surface PEG and only temporarily raised the surface pH, and was therefore terminated in 2004 [5]. More recently, *in-situ* deacidification through the introduction of calcium hydroxide nanoparticles into the wood structure has been proposed [9]. However, the effects of such a highly alkaline treatment seem doubtful for marine archaeological wood. A diaminoethane treatment by Ghisalberti et al. 2002 [10] on acidic wood from the *Batavia* shipwreck (1629) showed some promise in reducing surface acidity, but the depth of penetration was minimal and dependent on the initial condition of the wood. In addition, Fourier transform infrared (FTIR) and ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopic analysis showed that the treatment reduced the hemicellulose and cellulose fractions and probably also reacted with lignin components.

Ammonia gas treatments have been shown to efficiently neutralize acid and also convert compounds that promote oxidation, e.g. hydrated ferrous sulfates, to more humidity-inert iron (III) compounds [11]. This gaseous treatment minimizes physical and mechanical damage to PEG-treated wood and has been applied with mostly positive results on *Batavia* timbers at the Western Australian Museum. The impact on the wood chemicals was described to be limited to a slight loss of hemicellulose [12]. This result is consistent with earlier studies, which mostly show degradation and possibly reorientation of partially solubilized hemicelluloses within the cell wall after ammonia treatment [13]. With guidance from the *Batavia* experiment, a test series was set up to expose *Vasa* wood to ammonia vapour. The purpose was to monitor the neutralizing effect, the post-treatment long-term pH stability and the impact on the wood structure and the PEG [14].

According to the literature, ammonia treatments may result in plasticization and changes in sorption behaviour related to structural changes within the cell wall, especially at repeated exposure [15, 16]. Native lattices of cellulose I are claimed to be converted to crystalline cellulose III in wood exposed to ammonia vapour at room temperature at saturated vapour pressure (10 atm) for 18 hours [17]. Ammonia sorption into wood seems to reach a threshold value at the relative vapour pressure near 0.5, below which no relaxation of the cellulose crystal lattice occurs [15], indicating that the degree of plasticization strongly depends on the ammonia content in the wood [15, 16]. Some reports of tests performed at elevated temperatures and pressure are not relevant for the *Vasa*. However, prolonged and repeated alkaline treatments could be detrimental and the pH should be kept sufficiently low (pH < ~9) during longer exposure periods. Ammonia has previously been shown to efficiently neutralize acid in wood [11, 12] and the neutralization should be followed by storage in a stable temperature and low humidity (RH ~55% or lower) environment. A more detailed literature review is found in Fors et al. 2009 [14].

EXPERIMENTAL

The present study sought to investigate the effects of ammonia neutralizing treatment on oak and pine wood. Samples studied included PEG-treated oak and pine material from the *Vasa*, both with and without acidic sulfate precipitates, as well as an untreated *Vasa* oak sample, and reference samples of fresh oak (*Quercus robur*) and pine wood (*Pinus sylvestris*).

The impact of ammonia neutralization treatment on the wood samples was evaluated by several methods: pH measurements; X-ray powder diffraction (XRD) of crystalline precipitates; Fourier transform infrared (FTIR) spectroscopy; and size exclusion chromatography (SEC). Details of the experimental methods are provided in the Appendix.

RESULTS AND DISCUSSION

pH Profiles

The surface pH of the wood samples increased initially from about 3 to approximately 8, then plateaued around pH 6 after gaseous ammonia treatment for 24 hours (Table 1). The initial pH increase was most marked (pH ~9) in the reference samples; fresh pine and oak and the untreated *Vasa* oak sample, which were exposed to ammonia for 48 hours. No significant differences were noted between the oak and pine samples after the experiment, but the PEG-treated wood without visible salt precipitates obtained slightly higher plateau values at the surface after ammonia treatment. For most wooden pieces with visible salt stains, the pH profile throughout the wood was lower before and after treatment. In one salt-stained pine wood sample (65365) a surface pH of 3–3.5 was measured by pH-indicator paper [pH 3.72 digitally] in one particular acid-affected area ~1000 days after treatment.

The general increase in pH throughout the wood samples indicated that the ammonia had penetrated the wood structure, though there were some variations in pH often to a depth of 5–10 mm, but this sometimes

Table 1   *The average pH values of the* Vasa *wood surfaces measured before ammonia exposure, 318 and ~1000 days after exposure*

Sample No.	Characteristics	Surface pH Before exposure (paper/digital)	Surface pH Day 318 (paper/digital)	Surface pH Day ~1000 (paper/digital)
65367	Vasa oak salt	2.2 / 3.54	6.0 / 5.90	5.3 / 5.16
26625	Vasa oak salt	1.9 / 2.53	5.7 / 6.20	5.7 / 5.19
65374	Vasa oak no salt	5.0 / 5.53	6.5 / 7.60	7.0 / 6.70
65375	Vasa oak no salt	5.0 / 5.39	6.8 / 7.06	6.0 / 6.40
21675	Vasa oak no PEG	7.8 / 7.73	6.9 / 6.94	6.2 / 6.68
65365	Vasa pine salt	2.0 / 2.82	5.6 / 5.20	5.2 / 5.63
5691	Vasa pine no salt	4.0 / 4.75	7.0 / 7.16	7.1 / 6.59
Ref 1	Fresh oak	3.8 / 3.28	6.2 / 6.31	5.1 / 5.57
Ref 2	Fresh pine	4.0 / 4.66	6.5 / 5.73	6.0 / 5.09

continued throughout the entire wood sample (Figure 1). The decrease in pH levels sometimes observed near the surface (Figure 1, lower) could be due to formation of new acid from the oxidation of iron (II) sulfides that were not neutralized by the ammonia treatment. The higher pH measurements observed close to the surface (Figure 1, top) in some of the samples could be an indication that degraded (especially non-PEG treated) wood is more susceptible to the ammonia treatment than non-degraded wood. However, the low number of samples and testing prevents more definite conclusions.

X-ray powder diffraction (XRD)

Some of the sulfate salts on the *Vasa* wood surfaces changed colour after the ammonia exposure from yellow to the characteristic red-brown of iron oxyhydroxides, identified by XRD analyses (Table 2). In addition, some of the ammonium salts identified (e.g. the Fe(III) salt ammoniumjarosite, $(NH_4)Fe_3(SO_4)_2(OH)_6$) probably recrystallized from natrojarosite and mohrite, $Fe(NH_4)_2(SO_4)_2(H_2O)_6$. Mascagnite, $(NH_4)_2SO_4$, probably formed from the hydrated Fe (II) sulfates. Some of the previously known sulfate salts (e.g. natrojarosite and melanterite) were still present after the ammonia treatment. Damaging volume expansion from the new salts is not expected considering that the volume increase per S atom is small compared to the increase when pyrite oxidizes to rozenite and melanterite (Table 2). No cracking related to the ammonia exposure was noticed in the treated wood samples. After transfer to higher RH storage, the pine samples showed signs of increased moisture upon the surfaces. Humidity is more easily transferred in softwood, but possible migration of the more hygroscopic low-molecular weight PEG could
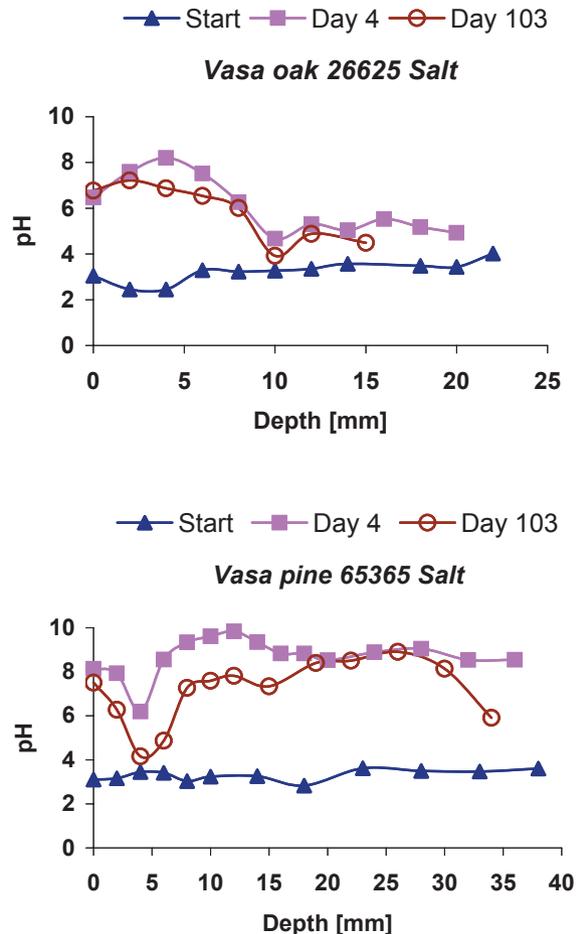
Figure 1   *pH profiles through the wood before the ammonia exposure, 4 days and 103 days after treatment.*

Table 2 *Volume expansion of salts. Text in bold denotes new salts that were identified with XRD on the* Vasa *timbers after the ammonia treatment*

Mineral	Formula	Volume per S atom/Å³	Volume factor from pyrite/ jarosite
Rozenite	$FeSO_4 \cdot 4H_2O$	163	8 / 1.2
Melanterite	$FeSO_4 \cdot 7H_2O$	244	12 / 2
Natrojarosite/	$NaFe_3(SO_4)_2(OH)_6$ /		
Ammoniumjarosite	**$(NH_4)Fe_3(SO_4)_2(OH)_6$**	**133**	7 / 1
Gypsum	$CaSO_4 \cdot 2H_2O$	124	6 / 1
Pyrite	FeS_2	20	1 / < 1
Mohrite	**$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$**	**176**	9 / 1.3
Mascagnite	**$(NH_4)_2SO_4$**	**123**	6 / <1

also be an explanation. The *Vasa* pine has been proven to be more degraded than the oak before the ammonia treatment and might have absorbed more PEG.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is a useful technique for the comprehensive analysis of whole wood without recourse to extraction and degradative techniques, allowing all components comprising the sample under examination to be analysed simultaneously. FTIR provides structural information linked to the chemical composition of wood components, thereby allowing information to be obtained on changes that have occurred to the lignin-carbohydrate complex of the wood matrix following immersion or burial in archaeological contexts and after chemical treatment. The use of the diamond anvil cell (DAC) permits the use of microscopic samples to accumulate a spectrum; however, this technique is more likely to produce unrepresentative sampling problems. These problems can be overcome by careful choice of samples for analysis and acquiring spectra on multiple sub-samples. In addition, due to inherent differences in absolute peak intensities caused by differences in the amount of sample on the DAC, the DAC pressure applied to the sample, the instrument optics, floating baselines, etc, it is not possible to directly compare absolute peak heights of diagnostic absorption bands between different spectra. Hence the relative ratios of the heights of chosen peaks assigned to certain wood chemicals are used in comparative studies and therefore this method is usually described as semi-quantitative.

Wood components show characteristic infrared absorption bands in a 'fingerprint' wave number region from about 1800 to 800 cm⁻¹, which can be used to diagnose the relative amounts of lignin, hemicellulose and cellulose [18], and thereby assist in assessing the

extent of wood degradation [19, 20]. However, one of the major problems associated with the analysis of FTIR spectra of archaeological wood samples is the incorporation of polyethylene glycol (PEG) in the wood matrix after conservation. Certain bending and stretching vibrations attributed to different chemical structures in the polyethylene glycol polymer occur at frequencies similar to those vibrations assigned to peaks for different wood components. In addition, some peaks for different wood chemicals occur at very similar frequencies. Consequently, in the raw FTIR spectra, some peaks are unresolved and often appear as one large, broad peak. In an attempt to separate these overlapping peaks, the raw spectra were manipulated using a specific deconvolution mathematical algorithm (see Appendix). Attempts were made to subtract the degraded PEG 1500 FTIR spectrum from the treated *Vasa* wood to minimize interference from the impregnated PEG 1500; however, this function gave rise to some negative peaks in the diagnostic absorption area and was not pursued further. In addition, second derivatives were applied to the raw spectra to confirm that the resultant peaks in the corresponding deconvoluted spectra were true peaks and not a consequence of over-deconvolution.

The intensities and positions of many absorption bands are of particular interest when identifying the carbohydrate and lignaceous portions of wood; however, only a few diagnostic peaks (1732 cm⁻¹, 1592 cm⁻¹, 1509 cm⁻¹, 1330 cm⁻¹, 1260 cm⁻¹ and 896 cm⁻¹) that had no or very little contribution from PEG were used during the spectral analyses in this study. The absorption at approximately 1732 cm⁻¹ originates in the stretching of the free carbonyl groups of carboxylic acids and esters 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.

Absorptions in the 1000 to 1200 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. However, many of these bands are highly mixed and coupled vibrations and it is not always possible to assign them to specific functional groups and many overlap with peaks from the PEG spectrum. However, the band at 896 cm⁻¹ represents a β-anomeric linkage between discrete cellulose and hemicellulose units which can be used to determine the

content and degree of deterioration of carbohydrates in wood [20–22].

The bands in the 1200–1600 cm^{-1} part of the spectra arise primarily from lignin. The characteristic absorption bands of lignin are at 1592 cm^{-1} and 1509 cm^{-1} and these two absorptions are caused by C=C stretching vibrations of the lignin matrix, probably associated with aromatic ring deformation modes [18, 22]. The absorption around 1592 cm^{-1} can be easily impaired by water present in the sample, thus the intensity of the lignin absorption band at 1509 cm^{-1} is the better choice for the determination of the lignin content in wood. The band at approximately 1260 cm^{-1}, 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 European white oak, show a pronounced band at about 1330cm^{-1} which is associated with syringyl lignin while it is absent in softwood spectra. In waterlogged wood, the polysaccharides generally degrade in preference to the lignin components. Hence, the ratios of the peaks assigned to lignin versus carbohydrates usually increase as degradation proceeds [20, 21]. The relative ratios of the peak intensities of the selected diagnostic absorption bands in the deconvoluted spectra were used as a semi-quantitative measure of the degree of degradation of the wood samples and most importantly, the effect of the ammonia treatment on the wood components. In order to understand the effect of the ammonia deacidification treatment on the treated *Vasa* samples, the relative ratios of each distinct set of samples before and after treatment were compared, taking into account the standard deviations in order to ascertain the statistical validity of any changes to the wood components. The peak ratios of

lignin components to carbohydrates before and after the ammonia treatment for the oak and pine *Vasa* samples are shown in Tables 3 and 4, respectively. In addition, examples of deconvoluted spectra used to calculate these peak ratios for modern, undegraded, untreated (no PEG) European oak and the PEG-treated, acidic *Vasa* oak before and after ammonia treatment are shown in Figures 2 to 4, respectively. Note that only the 1800–800 cm^{-1} region of the selected deconvoluted spectra are presented as this area is the most important region for analysing changes in the wood matrix.

Care must be taken when performing comparative analysis of relative ratios and relating these to changes in the degree of degradation of wood components. Generally, with waterlogged wood, the polysaccharides degrade in preference to the lignin components and hence, the lignin to carbohydrate peak height ratios generally increase as degradation proceeds, in comparison with the ratios of recent wood. However, if there is degradation of, for example, both the lignin and polysaccharides then interpretation of the observed changes in the relative ratios as an indication of the relative degree of deterioration of the lignocellulosic components in the wood matrix is more difficult.

There were also some discrepancies in the ratios involving the guaiacyl lignin peak at 1260 cm^{-1} and the hemicellulose peak at 1732 cm^{-1}. On closer inspection of the spectra it was obvious that the deconvolution parameters had not fully resolved the lignin peak at 1260 cm^{-1} from the overlapping PEG and hemicellulose peaks and it still appeared as a shoulder or totally unresolved in some of the spectra making the peak height integration results inconsistent. Conversely these deconvolution parameters may have over-deconvolved peaks in the 1800–1700 cm^{-1} area, which could have artificially increased the height of the hemicellulose peak at 1732

Table 3 *Average peak ratios for* Vasa *oak samples before and after ammonia treatment*

AVERAGE Peak Ratios	Description	Modern European Oak	Oak salt surface	Oak salt surface NH$_3$	Oak salt mid	Oak salt mid NH$_3$	Oak no salt surface	Oak no salt surface NH$_3$	Oak no salt mid	Oak no salt mid NH$_3$
1592/896	lignin/carbo	1.78 ± 0.07	2.63 ± 0.55	2.94 ± 0.74	2.56 ± 0.02	2.14 ± 0.10	3.88 ± 0.15	8.81 ± 4.56	4.86 ± 0.14	3.01 ± 0.12
1509/896	lignin/carbo	1.64 ± 0.09	3.04 ± 1.05	1.77 ± 0.06	2.03 ± 0.19	4.77 ± 0.46	3.27 ± 0.17	4.06 ± 1.13	4.64 ± 0.37	2.59 ± 0.03
1260/896	gl/carbo	1.24 ± 0.05	2.34 ± 0.19	1.97 ± 0.47	2.43 ± 0.00	1.52 ± 0.09	2.06 ± 0.00	4.38 ± 1.64	2.49 ± 0.17	2.57 ± 0.02
1592/1732	lignin/hemi	1.77 ± 0.04	0.96 ± 0.30	1.18 ± 0.03	1.49 ± 0.07	3.40 ± 0.27	1.98 ± 0.26	2.37 ± 0.05	1.29 ± 0.09	1.21 ± 0.08
1509/1732	lignin/hemi	1.63 ± 0.01	1.07 ± 0.19	2.40 ± 0.40	1.18 ± 0.05	1.39 ± 0.34	1.67 ± 0.24	1.17 ± 0.28	1.23 ± 0.03	1.04 ± 0.01
1260/1732	gl/hemi	1.23 ± 0.03	0.88 ± 0.38	1.45 ± 0.08	1.41 ± 0.07	3.06 ± 0.32	1.05 ± 0.10	1.23 ± 0.17	0.66 ± 0.02	1.03 ± 0.02
1260/1330	gl/sl	0.65 ± 0.02	0.60 ± 0.11	0.51 ± 0.09	0.62 ± 0.05	0.59 ± 0.03	0.60 ± 0.04	0.50 ± 0.11	0.68 ± 0.05	0.89 ± 0.04
1732/896	hemi/carbo	1.01 ± 0.06	2.98 ± 1.51	1.66 ± 0.36	1.72 ± 0.09	0.45 ± 0.06	1.98 ± 0.18	3.69 ± 1.85	3.78 ± 0.38	2.48 ± 0.06

carbo = carbohydrate; hemi = hemicellulose; gl = guaiacyl lignin; sl = syringyl lignin

Table 4   *Average peak ratios for* Vasa *pine samples before and after ammonia treatment*

AVERAGE Peak Ratios	Description	Modern European Redwood	Pine salt surface	Pine salt surface NH$_3$	Pine salt mid	Pine salt mid NH$_3$	Pine no salt surface	Pine no salt surface NH$_3$	Pine no salt mid	Pine no salt mid NH$_3$
1592/896	lignin/ carbo	1.22 ± 0.09	3.98	3.59 ± 0.75	2.96	2.00 ± 0.66	9.00			
1509/896	lignin/ carbo	2.99 ± 0.25	16.24	9.52 ± 1.31	9.69	5.90 ± 3.33	23.93			
1260/896	gl/ carbo	2.61 ± 0.14	11.83	6.24 ± 0.73	6.94	3.79 ± 2.53	14.43			
1592/1732	lignin/ hemi	1.11 ± 0.02	1.58 ± 0.38	1.93 ± 0.08	1.41 ± 0.27	1.02 ± 0.27	1.94 ± 0.49	1.99 ± 1.26	1.82 ± 0.08	1.75 ± 0.34
1509/1732	lignin/ hemi	2.72 ± 0.07	6.44 ± 1.51	5.15 ± 0.58	5.01 ± 1.45	2.98 ± 1.49	6.04 ± 2.55	5.02 ± 3.97	5.92 ± 0.15	5.13 ± 2.23
1260/1732	gl/ hemi	2.38 ± 0.01	4.32 ± 0.58	3.38 ± 0.45	3.18 ± 0.45	1.91 ± 1.16	3.80 ± 1.76	3.46 ± 2.69	4.23 ± 2.99	4.28 ± 3.03
1732/896	hemi/ carbo	1.10 ± 0.06	3.02	1.87 ± 0.47	2.43	1.94 ± 0.14	5.64			

carbo = carbohydrate; hemi = hemicellulose; gl = guaiacyl lignin
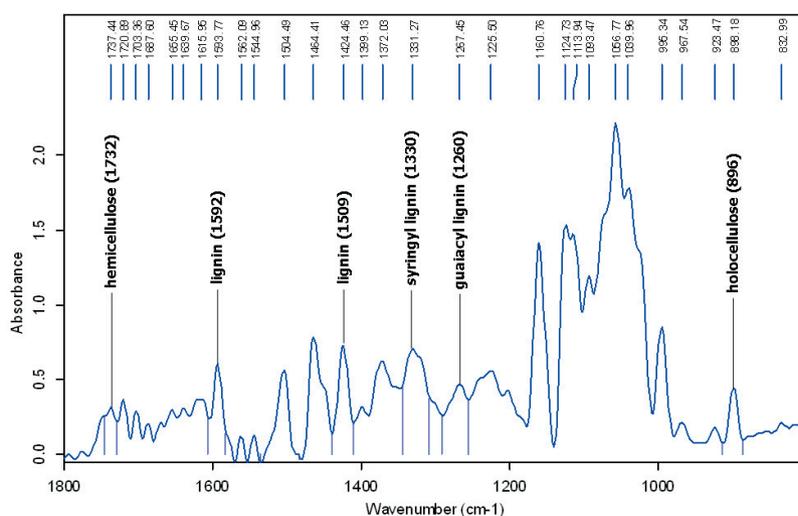
Figure 2   *Deconvoluted FTIR spectrum of modern, undegraded, untreated (no PEG) European white oak.*

cm^{-1}. However, the second derivatives of the raw spectra seemed to indicate that the resultant peaks in the corresponding deconvoluted spectra were actually true peaks and not a consequence of over-deconvolution but the peak heights may have been affected.

Another potential problem is the presence of degradation products from the deterioration of wood components, such as oxidation of polyoses, solvolysis of wood and PEG, mild hydrolysis and/or cleavage of the β-aryl ether bonds of lignin, etc, that could contribute to this peak at 1732 cm^{-1}, associated with the free carbonyl stretch, and, although conditions are conducive for hemi–cellulose deterioration, the peak height increases and therefore the ratios against lignin will decrease instead of increasing as would normally be expected.

In addition, the larger standard deviations for the ratios of the softwood samples and the outer surfaces of the hardwood samples indicated extensive variations in the extents of deterioration of these samples making any comparative analysis more difficult. It also illustrates the importance of obtaining multiple spectra on many samples and not relying on limited spectral data on a very small number of samples for interpretation. It also highlights the problems associated with representative sampling when using micron-sized particles in this particular diamond cell accessory when accumulating the FTIR data. However, even with these limitations, interpretation of the ratios from the FTIR data was attempted and the results discussed below.

Degree of degradation prior to ammonia treatment

Generally, all PEG-treated *Vasa* oak samples prior to deacidification (Figure 3; Table 3) were more degraded
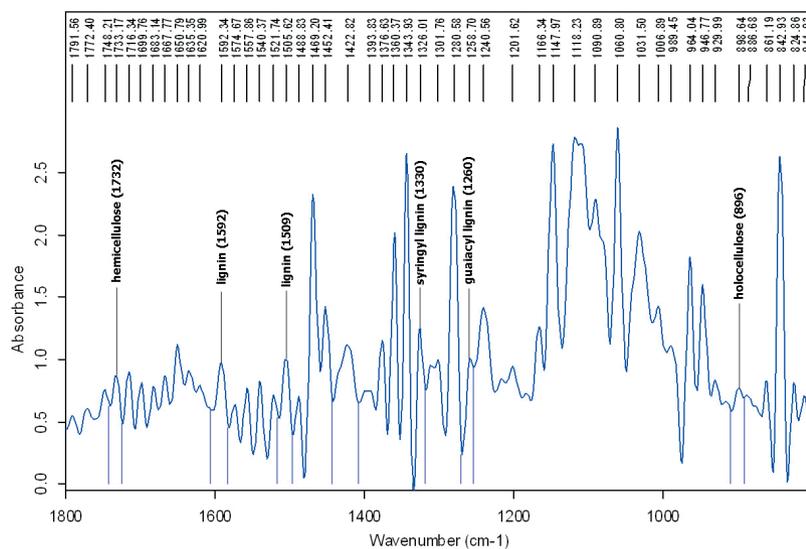
Figure 3   *Deconvoluted FTIR spectrum of the PEG-treated, acidic* Vasa *oak sample – outer surface before ammonia treatment.*
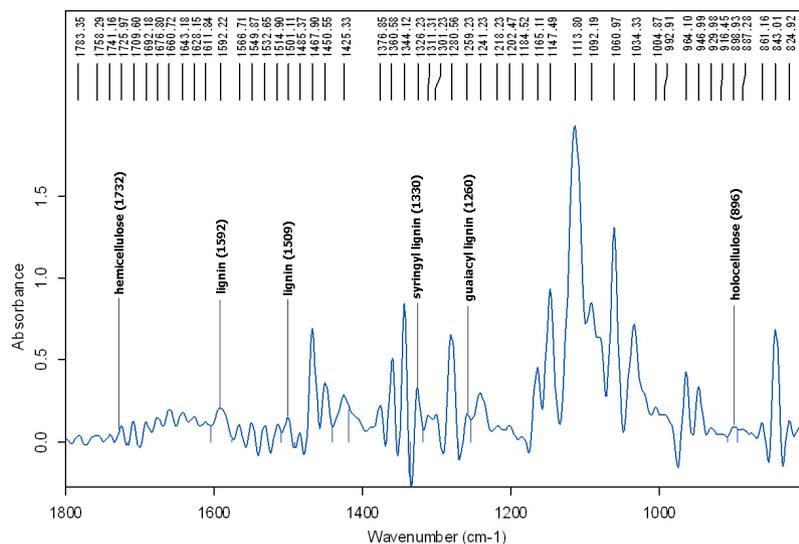

Figure 4   *Deconvoluted FTIR spectrum of the PEG-treated acidic* Vasa *oak sample – outer surface after ammonia treatment.*

with respect to the polysaccharide fraction (increase in most lignin/carbohydrate and lignin/hemicellulose ratios) and their lignin character was similar (similar 1260/1330 cm^{-1} peak ratios), in comparison to modern, undegraded European oak (*Quercus robur*) (Figure 2; Table 3), irrespective of their inherent acidity.

There appeared to be slightly more degradation of the hemicellulose in the mid region of the acidic *Vasa* oak sample than the outer surface indicated by a noticeable decrease in the 1732/896 cm^{-1} peak ratio and slight increases in the lignin/hemicellulose ratios (Table 3). The acidic oak sample appeared less degraded with

respect to carbohydrates than the non-acidic *Vasa* oak sample. In addition, it appeared that there had been more deterioration of the carbohydrate fraction in the inner regions of the non-acidic *Vasa* oak sample compared to the outer surface (increases in lignin/carbohydrate ratios and the hemicellulose/carbohydrate ratio).

Generally, all treated *Vasa* pine samples, prior to the ammonia treatment, were extensively degraded with respect to the polysaccharide fractions when compared to modern, undegraded European redwood (*Pinus sylvestris*) (Table 4), independent of their inherent acidity.

The outer surface of the acidic *Vasa* pine sample was more degraded than the inner region as shown by the increased lignin/carbohydrate and lignin/hemicellulose ratios. However, the inner region was also extensively deteriorated. The degradation of hemicellulose for the non-acid pine sample appeared to be similar, both in the outer and inner regions. However, the ratios of lignin/carbohydrate increased considerably for the outer surface of the non-acid *Vasa* pine sample and no peak was evident at 896 cm⁻¹ in the mid region indicating that there had been more deterioration of the polysaccharides in these samples compared to the acidic *Vasa* pine sample.

All treated *Vasa* oak and pine samples indicated significant degradation of the polysaccharides when compared to their modern, undegraded, untreated wood counterparts, which is entirely consistent with the well-established degradation mechanism for waterlogged wood, where the carbohydrates are preferentially degraded with respect to the lignin fraction.

All pine samples were extensively deteriorated and significantly more degraded than the oak samples with respect to the carbohydrate fractions. This could easily be explained by the fact that oak has a high resistance to microbial decay and chemical degradation. The heartwood of white oak is hard and more inaccessible due to sealed bordered pits and plugged vessels (e.g. less diffusion of metal corrosion products, such as iron sulfides) making it more resistant to deterioration compared to pine. In addition, most pine timbers tend to be thinner than their oak counterparts and therefore, degradation tends to be more evenly distributed throughout the entire width of the pine as compared to the more substantial oak structural members.

Interestingly, there appeared to be more hemicellulose deterioration in the inner regions of the acid-affected *Vasa* oak and pine samples. The preferential degradation of hemicelluloses in the polysaccharide fraction of wood tissue is evidence that chemical (non-biological)

degradation processes have occurred [8]. Hemicelluloses undergo acid hydrolysis faster than cellulose in wood tissues. This increased resistance of cellulose is due to its crystalline order system. The hemicelluloses are continuously degraded as acidic groups split off and cause further in-situ acid hydrolysis [23]. Similar phenomena have been reported earlier [7, 24].

However, another possible explanation for this observed increase in the deterioration of the hemicelluloses in the inner regions as compared to the outer surfaces of the acidic samples may be due to increases in the absolute peak heights of the hemicellulose peak at 1732 cm⁻¹ in the spectra of the outer surface samples caused by an increase in the formation of shorter chained carboxylic acids. The increase in the peak height of this diagnostic peak assigned to the free carbonyl stretching vibration of carboxylic acids and esters, may be caused through the solvolysis of the wood and incorporated PEG with sulfuric acid, which produces levulinic and formic acids and/or through the direct formation of formic acid from PEG deterioration. As the concentrations of PEG and acidic by-products are, on average, highest in the outer surfaces of the timbers and the concentrations of these compounds decrease significantly as the timber is traversed towards the inner regions, it follows that more acid formation would occur in the outer surfaces as compared to the inner regions. Hence, this increase in acid formation would increase the peak height of the 'hemicellulose' peak at 1732 cm⁻¹ and as a consequence, the relative ratios would indicate a decrease in the degradation of hemicellulose in the outer surfaces as compared to the inner regions, where acid formation would be considerably less.

There appears to be no statistically significant deterioration of the lignin content in the treated *Vasa* samples, although this is not to say that there could not have been some slight modification of the lignin component that was not observed by this instrumental analytical technique.

Effect of ammonia treatment

After ammonia treatment the acidic *Vasa* oak sample (Figure 4; Table 3) experienced a significant loss of hemicellulose (increases in lignin/hemicellulose ratios and a decrease in the hemicellulose/carbohydrate ratio) with no statistically significant effect on lignin character. For the non-acidic *Vasa* oak sample, there appeared to be some deterioration of the carbohydrates in the outer surface and possibly some effect on lignin character, especially syringyl lignin in the inner region, but the

overall effects of the ammonia treatment appeared to have been minimal on these non-acidic samples. There appeared to be no statistically significant effect of the ammonia treatment on any of the pine samples, irrespective of their inherent acidity (Table 4).

The ammonia treatment has affected the carbohydrate fractions of the treated *Vasa* oak samples as the most significant chemical change following treatment with alkalis (and acids) is a reduction in hemicellulose content and to a lesser extent deterioration of the cellulose, which is due to the more well ordered crystalline cellulose regions of the wood cells being more resistant to chemical attack. Wood carbohydrates, particularly hemicelluloses and to a lesser extent lignins, are sensitive to bases and are susceptible to hydrolysis and oxidation under alkaline conditions [25]. The most important reactions responsible for the loss of polysaccharides and reduction of the chain length under alkaline conditions are peeling of end-groups and the hydrolysis of glycosidic bonds and acetyl groups. However, lignin is also degraded under alkaline conditions, albeit slower than the carbohydrate fractions, by cleavage of the α- and β aryl ether linkages leading to depolymerization of both softwood and hardwood lignins [23]. Hence, it is not surprising that there has been some evidence of lignin deterioration in the treated *Vasa* samples, but the effect is still relatively small when compared to the effect on the polysaccharides.

The minimal effect of the ammonia treatment on the pine samples is most probably a consequence of all pine samples being extensively deteriorated with respect to the carbohydrate fraction prior to deacidification. The best woods for chemical resistance are those having high cellulose and lignin content and a correspondingly low hemicellulose content. Hence, softwoods show relatively high resistance to attack by acids and alkalis as a result of their low hemicellulosic content [23]. However, any deleterious effect on the carbohydrate fractions would be difficult to discern with such extensive initial deterioration of the polysaccharides in these pine samples. Therefore, based on these results, it is possible that acid-degraded wood is more susceptible to alkaline deterioration than non-acidic wood and the effect on extensively degraded wood is minimal, since the carbohydrate fraction is already severely affected prior to the ammonia treatment.

Hence, it would be advisable to treat more samples (oak and pine) with differing extents of wood degradation and also some degraded PEG with ammonia vapour to determine if this alkaline deacidification treatment

does, in fact, have a negative effect on the different components present in treated waterlogged wood.

Size exclusion chromatography (SEC)

SEC is an analytical technique for separating molecules according to their size. Two distinctive fractions in the molecular weight distribution (MWD) of cellulose and hemicellulose are obtained. By qualitative comparison with recent wood, changes in the MWD can be revealed. The SEC analysis results of the PEG-treated acidic *Vasa* oak wood (sample 63567 with salts) indicate very well-preserved wood before and after ammonia exposure. Both spectra are very similar to that of the 150-year-old oak piece (sample A0, no ammonia or PEG treatment) where the cellulose peak showed no visible indication of any major depolymerization with no change in the extractable fraction (Figure 5). The untreated (no PEG) waterlogged *Vasa* oak sample (sample 21675) also appeared well preserved before the treatment, but the spectra after the ammonia exposure indicated extensive depolymerization of the cellulose chains. The magnitude of the cellulose peak of the untreated (no PEG) sample after ammonia exposure (Vasa (21675) no PEG NH3) has 'shifted' to lower molecular weight, e.g. the height of the cellulose peak (to the right in the spectra) has decreased with a concomitant increase in the height of the first peak (left peak) indicating depolymerization of the cellulose as a result of alkaline hydrolysis. The fragile wood seems susceptible to the ammonia vapour and most of the extractives might have been extracted during the ammonia treatment (Table 5). This may indicate that the PEG has a protective effect during the ammonia exposure. On the other hand, the untreated (no PEG) sample (21675) was treated for 48 hours compared to 24 hours for the acidic *Vasa* oak (65367) sample. Moreover, the initial high moisture content of the 21675 *Vasa* sample (waterlogged, no PEG, before ammonia) explains the low yield of the dry weight measurement (49.5%) and the following low concentration of extractives in the water extract (Table 5).

In an earlier study on wood pulp exposed to ammonia vapour from 24 hours up to 14 days in a similar procedure as for these wood samples, ^{13}C-NMR solid state spectra indicated no major change in the cellulose structure [14]. Also, results from MALDI-TOF/GC-MS analyses of PEG solutions from the Vasa museum, which were exposed to ammonia vapour from 24 hours up to 4 weeks, showed no ammonia-related degradation [14].
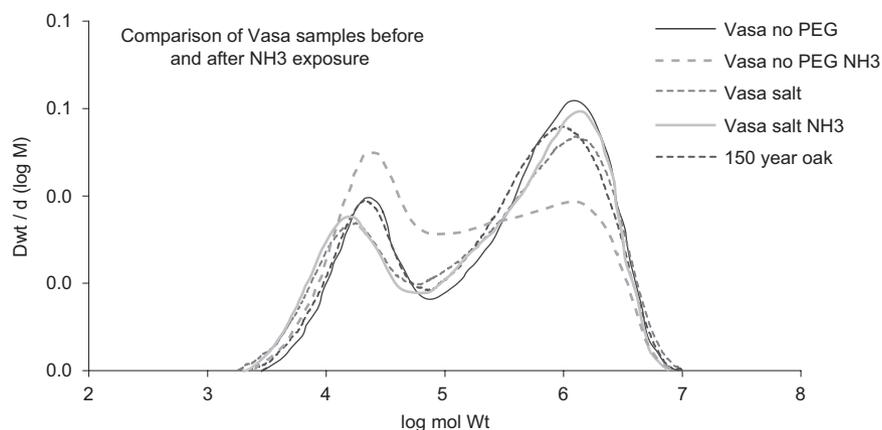
Figure 5 *The SEC analysis results for acidic* Vasa *oak (Vasa salt 65367) and untreated* Vasa *oak (Vasa no PEG 21675) before and after ammonia treatment and 150-year-old oak (150 year oak A0) with no ammonia treatment. [Left peak: hemicellulose fraction; right peak: cellulose fraction.]*

Table 5 *Wood samples for SEC analysis before and after ammonia exposure.*

Samples	Water extract, 0.3g wood to 6mL H_2O (mg.mL^{-1})	Water extract pH after 48h R.T.
Ref 150 year oak	48	3.23
Vasa 21675 No PEG	25	7.41
Vasa 21675 No PEG, after NH$_3$	45	7.60
Vasa 65367 salt	50	4.28
Vasa 65367 salt, after NH$_3$	51	6.35

SUMMARY AND OUTLOOK

Based on the results from the pH profiles, the ammonia vapour seems to have effectively penetrated the *Vasa* wood to a minimum depth of 5–10 mm. However, the pH values measured throughout the wood samples are sometimes inconsistent, which could be partly related to the heterogeneous nature of the wood with respect to both the extent of degradation and the sulfur and acid distribution throughout the samples [6]. However, more frequent pH measurements at smaller depth intervals throughout thicker wood samples using different ammonia exposure times would be required before more conclusive information regarding the maximum penetration depth of the ammonia treatment could be obtained. Increasing penetration depth by using slightly elevated temperature and pressure could also be investigated. An elemental or XRF analysis of the total nitrogen content throughout the wood could also be used to confirm the ammonia penetration depth. The high PEG concentrations in the surface layers, about 0–20 mm, in treated waterlogged wood could be an efficient barrier effectively preventing deeper penetration into the wood. The pH profile and SEC analyses of the waterlogged sample without PEG indicate that the ammonia caused extensive cellulose degradation. As a control experiment, a *Vasa* wood sample should be exposed to ammonia vapour after extracting the PEG.

More importantly, the results obtained from the different analytical methods used to measure the effect of the ammonia treatment indicates some ambiguity, which requires further investigations. No obvious degradative effect of the ammonia treatment on the wood cellulose of the acidic, PEG-treated *Vasa* samples was observed in the SEC analyses or on the PEG and wood pulp in the earlier reported MALDI-TOF and ^{13}C-NMR results, respectively [14]. Although the heterogeneous nature of the archaeological timber makes it more difficult to determine unambiguously its condition with FTIR, the results indicated degradation of the carbohydrates, especially the hemicellulose fraction, after the ammonia treatment. These anomalies require further investigation, possibly using different spectroscopic techniques, such as ^{13}C-NMR and ^{1}H-NMR spectroscopy [21] and FTIR microscopic imaging (lateral resolution about 10 μm), which could reveal the degradation on a more detailed level and without the aforementioned interference problems associated with overlapping peaks, PEG incorporation and carboxylic acid formation. Experiments investigating the length of time that wood can be exposed to ammonia before the carbohydrates

may be affected would also be useful. However, it is important to stress that these results have been produced using a very small number of wood samples from one particular shipwreck. Further work is necessary to obtain more conclusive data before these preliminary findings can be confirmed.

Furthermore, very little is known about the consequences of this alkaline deterioration of the wood components on the mechanical stability of the wood. In radial compression testing of *Vasa* oak, the modulus and strength of the PEG-treated wood decreased by 50% compared with recent oak with a significant change in the failure mechanism [26]. However, a single ammonia-treated *Vasa* wood sample had a relatively high density compared to the non-deacidified sample but the mechanical properties did not differ significantly [27]. Obviously, further testing (also including tension and bending strength and izod impact) is required to verify the effect of the ammonia treatment on the mechanical stability of the *Vasa* wood.

In addition, the long-term effects of low pH on the wood structure and the effect that variations in relative humidity has on the chemical interaction between the different components (sulfur, iron, acids and PEG) and the wood matrix are still not fully understood. If the degradative effects of the ammonia treatment are less significant than the predicted effects of long-term acid hydrolysis and Fenton oxidation reactions then this deacidification treatment may be considered justifiable despite the associated problems. Hence, the effects of the ammonia treatment on the stability and mechanical strength of the wood as a function of the degree of exposure should be further monitored and investigated. This would be very important considering the ammonia vapour would access the hidden surfaces within the different layers of the hull and the possible effects such a large-scale deacidification treatment could have on the massive *Vasa* hull. Also, any initial short-term reaction of the hull's mechanical strength during the ammonia exposure could be quite important.

The potential of the pro-oxidative properties of ammonia on iron, in order to prevent Fenton reactions, should be studied further. The increase in pH could also deactivate the iron catalysis. Iron K-edge X-ray absorption near edge structure (XANES) spectroscopy analyses could then be useful in analysing these effects. Marcus et al. 2008 [28] has recently published systematic methods for identifying iron-bearing species from K-edge XANES data. Further sulfur XANES analyses are required in order to speciate and quantify the amount of reduced sulfur compounds with different

stabilities within the wood, especially the remaining iron (II) sulfides [3]. The organosulfur in the lignin-rich parts of the wood structure is assumed to be less reactive than the more easily oxidized iron sulfides, even though the stability of the lignin-bound organosulfur requires further investigation before the rate of future acid production can be predicted [2, 5]. XRD with the aid of synchrotron radiation is in progress for this purpose and may assist in deciding if the reduced sulfur compounds can be stabilized and kept in the wood and how this might be achieved, e.g. by ammonia vapour treatment and by creating a stable micro-climate, or if partial removal of iron and sulfur compounds using wet treatments, assisted by the use of a selective oxidizing agent, should be attempted at some stage.

This preliminary study can be considered as an initial step toward finding a suitable treatment. Long-term preservation of a complex object, such as the *Vasa*, will inevitably necessitate renewed treatment at some stage. Retreatment of the *Vasa* hull by spraying or immersion would be stressful, especially for the fragile surface layers that possess much of the valuable archaeological information, and more importantly, would be a major technical, logistical and monetary undertaking. However, this must be balanced against the risk of irreversible damage to this unique archaeological object by the detrimental, yet 'natural' chemical reactions occurring in the wood, the rates of which are, as yet, unknown under ambient conditions.

APPENDIX: DETAILS OF EXPERIMENTAL METHODS

Wood samples and experimental design

Oak and pine *Vasa* wood, both with and without acidic sulfate precipitates, were studied in these experiments including an untreated (no PEG) *Vasa* oak sample, and fresh pine and oak wood as references (Table 1). The wood was suspended over vessels containing concentrated ammonia solution (28%, 31.8 g/L NH_3 AR grade, VWR Prolabo) at ambient temperature and pressure within glove bags placed in a fume cupboard. Samples were taken for analyses before and after the ammonia treatment. The ammonia vapour exposure was, as for the *Batavia* timbers, carried out for 24 hours, except for the reference samples and the PEG-untreated *Vasa* sample, which were treated for 48 hours [14].

pH measurements

The pH of the wood surfaces was measured both with pH indicator paper and by means of an electronic pH meter Model IQ150 (IQ Scientific Instruments Inc.) with a pH microelectrode (MI-411P), which is a glass sensor encapsulated in stainless steel. The wood was moistened with deionized water during the measurements. The digital pH device was also used for obtaining pH profiles into the wood, by measuring the pH in holes drilled stepwise every 2 mm to the middle of the timbers.

X-ray powder diffraction (XRD) of crystalline precipitates

The analyses were carried out at the Department of Physical, Inorganic and Structural Chemistry, Stockholm University. For experimental details, see [3].

Fourier transform infrared (FTIR) spectroscopy

Small sub-samples of wood were taken from the outer and the mid (inner) regions of each bulk *Vasa* core section and from the modern, undegraded, untreated oak and pine wood sections. The FTIR spectra were collected at the Chemistry Centre of Western Australia using a diamond cell accessory on a Biorad Excalibur FTS 300MX FTIR employing a UMA 150 microscope. Analysis of the wood involved positioning a small sample on 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. Duplicate spectra were collected for all samples. The region 1800–800cm^{-1} was selected as edges for an obvious baseline in the non-deconvoluted spectra. The spectral manipulation of deconvolution was carried out using the Biorad Merlin software over the 1800–800cm^{-1} region using a K value of 2 and a half width value of 12 to separate overlapping peaks. The baseline of best fit was then chosen between about 1800 cm^{-1} and 800 cm^{-1} for each deconvolved spectrum from which the peak heights were measured. Peak marking and peak height determination of the selected diagnostic absorption bands above the marked baseline (approx. 1800-800 cm^{-1}) were measured utilizing Bruker Opus 6.5 software.

Size exclusion chromatography (SEC)

The wood preparation and analyses of the wood was performed by STFI–Packfors, Sweden. For experimental details see [24].

Materials

Electronic pH meter Model IQ150 (IQ Scientific Instruments Inc.) with a pH microelectrode (MI-411P; glass sensor encapsulated in stainless steel: Hach Company, PO Box 389 Loveland, Colorado 80539-0389, USA.

Concentrated ammonia solution; 28%, 31.8 g/L NH$_3$ AR grade: VWR (Prolabo) International AB, Fagerstagatan 18A, 163 94 Stockholm, Sweden.

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Résumé — *On a mené des expériences de laboratoire sur du bois du Vasa en vue de neutraliser l'acidité liée aux nombreux éclosions de sels de sulfates acides se produisant sur les surfaces de bois du navire historique suédois Vasa (1628) au moyen de vapeurs d'ammoniac. Les effets du traitement ammoniaqué ont été évalués au moyen de mesures de pH, de la spectroscopie infrarouge à transformée de Fourier (IRTF) et de la chromatographie d'exclusion stérique (CES). Cette dernière méthode n'a pas révélé d'effets apparents sur la cellulose dans les échantillons de bois du navire traités au polyéthylène glycol, alors que les résultats des analyses par spectroscopie IRTF indiquent une certaine dégradation de l'holocellulose.*

Zusammenfassung — *Laborexperimente mit Ammoniakdämpfen wurden am Holz des schwedischen Schiffswracks der Vasa (1628) durchgeführt, um die durch das Ausblühen saurer Sulfate entstehende Säure auf der Oberfläche des Holzes zu neutralisieren. Die Effekte der Ammoniakbehandlung wurden mit pH-Messungen sowie mit Hilfe der Fouriertransform – Infrarotspektroskopie (FTIR) und der Gel-Permeations-Chromatographie (GPC) durchgeführt. Die GPC – Analyse erwies keinen offensichtlichen Effekt auf die Cellulose in der mit Polyethylenglycol behandelten Holzprobe der Vasa. Demgegenüber zeigten die Ergebnisse der FTIR Untersuchungen eine gewisse Degradation der Holocellulose.*

Resumen — *Ciertos experimentos de laboratorio, realizados con vapores de amoniaco en maderas procedentes del Vasa, se han llevado a cabo con el fin de neutralizar la acidez vinculada a numerosos brotes de sales de sulfatos acídicos en las superficies lígneas del navío sueco Vasa (1628). Los efectos del tratamiento con amoniaco han sido evaluados mediante mediciones del pH, por espectroscopía de infrarrojos por transformada de Fourier (FTIR) y por cromatografía de exclusión por tamaño (SEC). Los análisis SEC no mostraron ningún efecto aparente en la celulosa de la muestra de madera del Vasa tratada con polietilenglicol, mientras que los análisis FTIR indicaron cierto tipo de degradación de la holocelulosa.*