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ARCHAEOLOGICAL WOOD FROM THE SWEDISH WARSHIP VASA STUDIED BY INFRARED MICROSCOPY

Master Project

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Abstract (English)

The Swedish warship Vasa is one of the largest marine archaeological artefacts in the world. It was salvaged from the bottom of the Baltic Sea after 300 years. During the time spent in the sea as well as in a museum hall, the wood of the Vasa experienced a lot of changes. These changes cause degradation of the wood. Studies of the complex chemical composition of the Vasa have been carried out in order to determine patterns of the degradation as well as discover optimal path for preservation of waterlogged wood.

Fourier transform infrared (FTIR) spectroscopy is applied for investigation of the Vasa in this work. After infrared spectra of the wood have been recorded and analysed, several conclusions could be made. With the aid of FTIR microspectroscopy, degradation of polysaccharides and lignin could be monitored. Spectral changes indicate oxidation of organic molecules in the wood occurring in the presence of iron ions. Differences in chemistry between surface and inner samples, for example, the amount of polyethylene glycol (PEG) – the preservation material - in the wood can be observed as well. When assigning spectral bands, DFT (density function theory) calculations of molecular structure and vibrations of modelled wood polymers are helpful.

All in all, infrared spectroscopy is a suitable method for the studies of marine archaeological artefacts in order to determine the changes in their chemistry in the course of degradation and to choose a proper path for preservation.

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Arkeologiskt trä från regalskeppet Vasa, undersökt med infraröd mikroskopi

Abstrakt (Svenska)

Regalskeppet Vasa är ett av världens största marina arkeologiska objekt och det enda välbevarade skeppet från 1600-talet. Det bärgades 1961 efter att ha legat på botten i Stockholms hamn i över 300 år. Tiden under vattnet och tiden på museet har utsatt träet i skeppet för många påfrestningar som har resulterat i en nedbrytning av skeppets trä. I syfte att utveckla metoder för bevarande och konservering av arkeologiskt trä har en lång rad studier av den kemiska sammansättningen i Vasas ekträ genomförts.

I detta arbete har Fourier transform infrared (FTIR) spektroskopi använts för att undersöka trä från Vasa. Resultaten visar att metoden ger insikt i ett antal processer. Nedbrytning av polysackarider och lignin kan följas. Vidare så ses indikationer på en ökad oxidering av organiska molekyler i närvaro av järnjoner. Skillnad mellan ytträ och bulkträ kan också se med metoden, likaså mängden av konserveringsmedlet, PEG. För att förbättra förståelsen av de uppmätta spektra har modellräkningar genomförts med hjälp av täthetsfunktionalteori (DFT).

Sammanfattningsvis så har vi visat att metoden, fourier transform infraröd spektroskopi är utmärkt för studier av arkeologiskt trä. Metoden gör det möjligt att följa kemiska förändringar och deras orsaker i träet vilket på sikt kan leda till att nya metoder för konservering och bevarande av marinarkeologiskt trä kan utvecklas. Ett område som idag i hög grad är outforskat.

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Introduction

The preservation of archaeological artefacts is a major consideration for scientists excavating material from archaeological site. Without or with improper conservation the valuable historical data could be lost. Artefacts that have been buried under salty sea water such as shipwrecks can be rather well preserved, but are very fragile and sensitive to environmental changes. Thus, a proper conservation method must be found in order to preserve the artefact for future generations [1].

The Swedish warship Vasa is one of the largest marine archaeological artefacts in the world. After the salvage in 1961, after more than 300 years in the sea, it has been preserved by spraying polyethylene glycol – one of the first reliable and relatively simple methods for preservation [1, 2]. The Vasa is now displayed to visitors in a museum in Stockholm.

During its time at the sea bottom as well as in a museum hall, the wood of the Vasa experienced a lot of changes. These changes cause degradation of the wood which may not be visible at first sight. It is important to determine the main causes to the deterioration of the wood condition in order to preserve it properly; thus many studies have been carried out on the Vasa [2].

Fourier transform infrared (FTIR) spectroscopy is applied for investigation of the Vasa in this work. Infrared spectra are like 'fingerprints' of the materials. Thus by analysing the spectra one can determine chemical composition or, as in this case, chemical changes occurring compared to the reference sample. The advantage of FTIR is the simplicity of the method: the equipment does not require much of adjustment, the spectra can be recorded in a fracture of a minute and small samples can be investigated if the FTIR microscope is used. In addition, it is a non-destructive method thus the samples can be preserved for further studies.

The aim of this work is to explore the usefulness of FTIR for investigation of the Vasa wood as well as determine chemical changes appearing in it compared to the reference sample of the fresh oak wood. The changes caused by oxidation reactions in the presence of iron ions in the wood are of particular interest. They cause the formation of new functional groups which in turn give rise to changes in the spectra of the oxidised wood compared to the reference one. DFT (density functional theory) calculations are made in order to specify assignments of the spectral bands.

Theory

Warship Vasa

The Swedish warship Vasa (Fig. 1.) is one of the largest marine archaeological artefacts in the world. The ship sank in 1628 on its first journey in the Baltic Sea, even before it had managed to leave the Stockholm harbour. It was recovered from the sea only after more than 300 years – in 1961. Now it is displayed in a museum in Stockholm and is a very popular tourist attraction [2].

Fig.1. Swedish warship Vasa in a museum in Stockholm [3]

Due to many environmental effects of the sea water as well as preservation treatments after the salvage the wood of the ship (oak wood *Quercus Robur*) has experienced a lot of changes. Iron was introduced to the timber from cannon balls and iron bolts, sulphur – from bacterial activity in the surroundings, salts from the sea water penetrated into the wood as well. After the excavation, large quantities of polyethylene glycol were sprayed onto the Vasa as a mean to prevent it from shrinking during evaporation of water. All these chemical changes in the wood, along with other environmental factors, such as pH, humidity or oxidation, causes degradation of polysaccharides of the wood over time. The aim of the vast studies of the Vasa is to determine these factors in order to preserve the ship for future generations [2].

Chemistry of the Vasa wood

Originally, wood consists of three main polymers: cellulose, hemicelluloses and lignin, and a small amount of inorganic mineral compounds. The oak wood used for building the Vasa is a hardwood. That means that it has a complex structure of vessels for transporting water from the roots to the leafage. The cell walls of these vessels are made of the polymers mentioned above, arranged in a specific way (Fig. 2.).

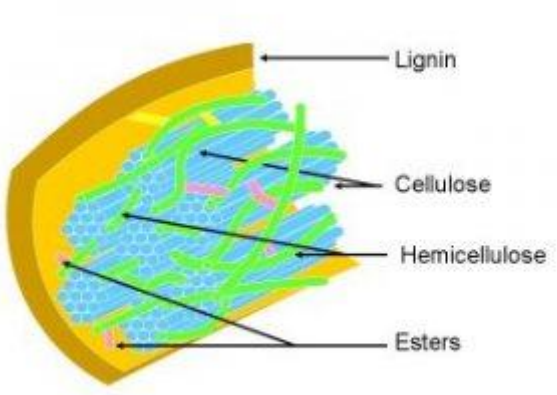

Fig. 2. Structure of plant's cell walls [4]

Cellulose is a polysaccharide consisting of a linear chain of β(1→4) linked glucose units (up to several thousands). It is a structural compound of the cell walls in the wood. The polymers of the

cellulose are aggregated to form microfibrils that in turn make complexes with hemicelluloses and lignin [2].

Hemicellulose is a smaller and branched polysaccharide. In the oak wood it mainly consists of glucuroxylan made from a backbone of β-D-xylopyranosyl residues and a side group of 4-O-methyl-D-glucuronic acid. Hemicelluloses link the cellulose microfibrils with lignin [2].

Lignin is a large, complex polymeric structure made of a network of phenolic rings linked together with C-C or ether bonds. The main feature of lignin in the hardwood is that it is composed from two types of aromatic rings - syringyl and guaiacyl (Fig. 3.) [5]. Lignin consist the cell walls of the plant along with cellulose and hemicelluloses [2].

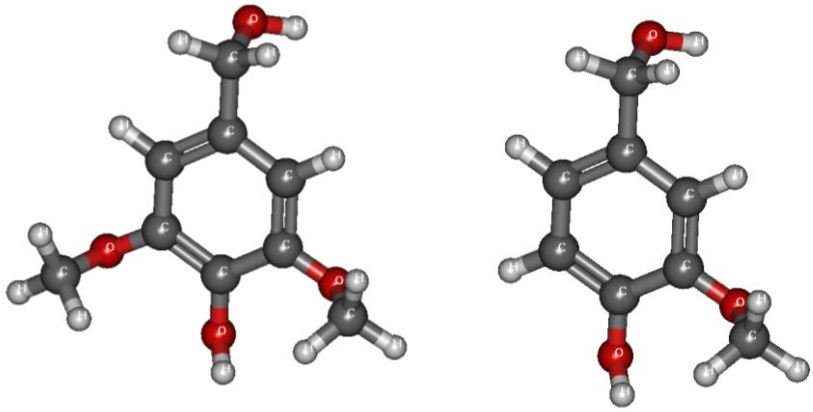

Fig. 3. Syringyl (left) and guaiacyl (right) aromatic rings

Lastly, there are small amounts of other organic materials present in the wood, such as fatty acids, tannin, terpenes, etc. [2].

During its time in the sea, the chemical composition of the oak wood of the Vasa has changed a lot. The sea water and various salts present in it have penetrated into the wood. Naturally, the opposite processes took place as well and materials like low molecular mass acids diffused in the water. As mentioned above, the iron ions from the corroded iron bolts and cannon balls, sulphur compounds produced by bacteria in the sea water had also entered the timber over the years. Iron ions present in the wood reacted with sulphur compounds and formed iron sulphides [2].

After the salvation, some chemical components were introduced into the timber as well. The Vasa ship was sprayed with polyethylene glycol (PEG) in order to prevent it from shrinking during the time of drying. The PEG was chosen as it is inert, non-volatile, water soluble polymer with low hygroscopicity. In addition, the wood of the Vasa was treated with large amounts of fungicides: boric acid ($B(OH)_3$) and borax ($Na_2B_4O_7 \cdot 10H_2O$) [2].

Lastly, the influence of the oxygen in the air (the level of which is considerably higher than under the sea water) must be considered. As it will be discussed further in this work, oxidation is probably one of the main causes of degradation of wood components [2].

Degradation of the wood

The degradation of the wood appears due to various chemical, physical or biological factors. The extent of microbial degradation is highly dependent on the species of the bacteria or fungi that affect the wood. In the case of the Vasa, the determined microbial degradation patterns were those of erosion bacteria and soft rot fungi which affected only the outermost layers of the wood. The faster and more severe degradation was prevented by environmental factors in the Baltic Sea, such as small amounts of oxygen [2].

Chemical degradation is rather slow and less effective than microbial degradation as components of the wood are chemically stable. However, when new elements like iron and sulphur are introduced into the wood, chemical reactions can take place. The outcomes of some of these reactions can highly influence the degradation processes of the wood polymers. One of the reactions is oxidation. While oxygen itself does not or only slowly react with wood polymers, the presence of iron ions in the timber can result in formation of hydroxyl radicals which affect organic molecules. The process is called Fenton's reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH,$$

$$RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O.$$

Here RH is an organic molecule containing hydrogen. Hydrogen peroxide can also be formed during interactions between iron (II) ions and oxygen.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + {}^{\cdot}O_2^-,$$

$$Fe^{2+} + {}^{\cdot}O_2^- \rightarrow Fe^{3+} + H_2O_2.$$

Oxidation could be prevented by antioxidants which would react with hydroxyl radical before it affected the wood polymers. Natural lignin and tannin are good examples of antioxidants in the wood. In the case of the Vasa, reduced sulphur compounds react with the radicals thus protecting the wood constituents [2, 6].

Hydrolysis is one of the causes of the wood degradation. It is a process which takes place in either acidic or alkaline environment. It causes chemical bonds to break in the reaction of the compound with water. The process is initiated by protonation of the glycosidic oxygen (oxygen atom binding fragments of the carbohydrates). The process can evolve in different paths leading to the breakage of the glycosidic bond. While cellulose and lignin are rather resistant to hydrolysis, it has been shown that hemicelluloses can be highly affected by it [2].

Studies of the Vasa

Many studies have been performed on the Vasa in order to determine the rate and causes of its degradation which include nuclear magnetic resonance (NMR) spectroscopy, X-ray absorption spectroscopy, mass-spectroscopy, various chemical analysis, etc. Each of these methods can provide relevant information about the state of the Vasa wood. The knowledge of the degradation extent and factors that causes it can help preserve the Vasa as well as influence the selection of preservation method for other marine archaeological artefacts [2].

Methods mentioned above have their advantages and disadvantages. For example, NMR spectroscopy can be used to determine the structure of the wood as well as quantify the chemical components. However, this technique is mainly suitable to detect hydrogen atom bearing materials thus making it impossible to detect compounds, such as sulphates which do not have hydrogen in them, in the wood. Therefore, only combination of various methods used for the analysis can yield desirable results [2].

In this study, Fourier transform infrared (FTIR) microspectroscopy was used to analyse the samples form the Vasa. Infrared radiation interacts with molecular vibrations in the matter and absorption occurs at the frequencies of the light that resonate with those vibrations. Every material has its own unique vibrational level system thus FTIR spectra yields information about chemical composition of the analysed object. This method has an advantage to other techniques as the spectra can be obtained very quickly and relatively little adjustment is needed to the equipment. In addition, by using FTIR microscopy one can record data from very small samples. FTIR microspectroscopy is a non-destructive technique; thus the samples remain intact during the investigation and can be kept for further studies.

Infrared spectroscopy

Infrared (IR) radiation has wavelengths in the region from 1 to 100 μm (corresponding wavenumbers are from 10000 to 100 cm^{-1}). This region is further divided into three smaller intervals: near infrared (NIR) – 10000÷4000 cm^{-1}, middle infrared (MIR) - 4000÷200 cm^{-1} and far infrared (FIR) – 200÷10 cm^{-1}. Many fundamental vibrational transitions are found in the mid infrared region (usually referred to simply as the infrared region). For this reason MIR spectra are used the most to study chemistry of objects. Some vibrational transitions can also appear in NIR (mostly overtones of fundamental vibrations) or FIR (vibrations with heavy atoms involved or inter-molecular vibrations) regions. [7]. We used MIR spectra for the analysis of chemistry of the Vasa.

Vibrational absorption spectra are recorded when, during interaction of the radiation with matter, a photon is absorbed and the molecule is excited into higher vibrational energy level. The

intensity of the radiation decreases with every absorption. The decrease in intensity is proportional to the intensity of the incident radiation and the thickness of the sample (l):

$$\mathrm{d}I = -b\,\mathrm{d}lI\,, \tag{1}$$

here *b* is an absorption coefficient. When integrating formula (1), Beer-Bouguer-Lambert's law is obtained:

$$I = I_0 \exp(-bl)\,. \tag{2}$$

A ratio $T = \frac{I}{I_0}$ is defined as transmission. Optical density (quantity of absorption) is defined as:

$$D = \lg\frac{1}{T}\,. \tag{3}$$

Either transmission or optical density can be measured when recording a spectrum [7, 8].

For recording infrared spectra FTIR spectrometers are used. 'The heart' of these spectrometers is an interferometer (Michelson interferometer in most cases) which replaces dispersive optics used in other spectrometers. The scheme of Michelson interferometer is presented in figure 4.

The most common source of IR radiation is a globar – a bar of SiC (silicon carbide) heated up to 1600-2400 K temperature.

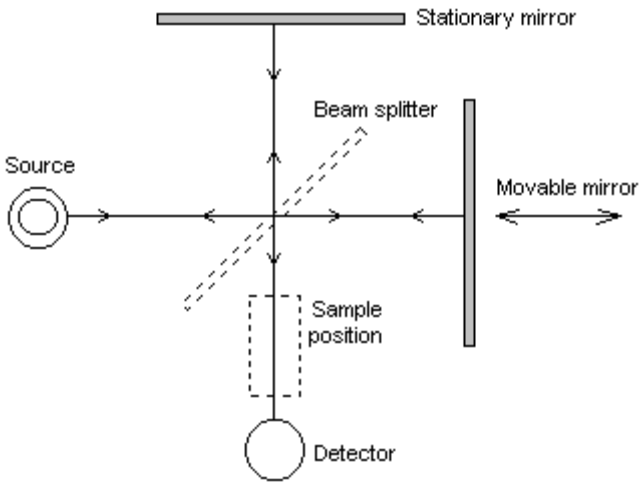

Fig. 4. Michelson interferometer [9]

Thermal or semiconductor detectors are used in the IR spectrometers. The former absorb infrared radiation and heats up. The flux of absorbed radiation is recorded. An example of thermal detectors could be pyroelectric deuterated triglycine sulphate (DTGS) detectors. They can be used to record spectra in the wavenumber interval between 5000÷200 cm^{-1}. However, DTGS detectors have low sensitivity. For this reason, the most popular detectors used in IR spectroscopy are liquid nitrogen cooled mercury cadmium telluride (MCT) semiconductor detectors. The operation of these detectors is based on the internal photo-effect phenomenon. They operate at 77 K temperature and are generally used to record spectra above 600 cm^{-1} wavenumbers [7].

One important factor should be mentioned when talking about infrared spectroscopy: glass which is usually used for laboratory dishes and sample cells is not transparent in the IR region. Thus

other materials such as NaCl, CsI, KBr must be used to make sample cells and windows. Many of these ionic crystals are hygroscopic and as water has intensive absorption bands in the IR region the spectrometer must be kept under as dry conditions as possible (usually the optics chamber as well as sample chamber are evacuated) [7].

In the FTIR spectrometer, the radiation from the light source is directed into the beamsplitter in the interferometer. Approximately half of the radiation is transmitted through the beamsplitter and hits the moving mirror while the other part is reflected to the fixed mirror. Reflected from the mirrors, these two beams interfere. The interference can be either constructive or destructive – it depends on the position of the moving mirror. The radiation then hits the sample and the transmitted radiation is directed into the detector – an interferogram is recorded (Fig 5.). In order to obtain spectrum, a Fourier transform of the interferogram must be carried out:

$$F(\nu) = \frac{1}{2\pi}\int_0^{\infty} f(\Delta x)\exp(-i\nu\Delta x)d\Delta x\,. \qquad (4)$$

Thus, in only one measurement a whole spectrum is obtained. As can be seen in formula (4), in order to obtain an ideal interferogram and an ideal spectrum, a moving mirror should scan to infinity. Naturally, this is not possible, for this reason the interferogram and the spectrum are somewhat distorted. The shorter the path of the moving mirror the greater the distortion, the larger the width of the spectral bands and the lower spectral resolution [7].

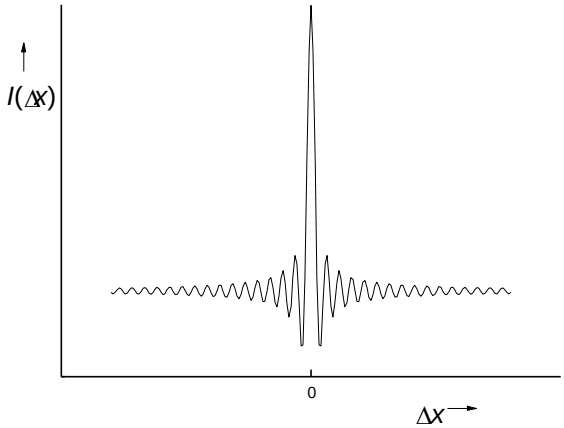

Fig. 5. Interferogram

FT spectrometers have two main advantages compared to grating spectrometers. The first one is called Fellgett's advantage. It rises from the fact that the whole spectrum is recorded simultaneously with FT spectrometer rather than point by point. This way, not only the measurement time is reduced significantly, but also the signal-to-noise ratio is enhanced. The second advantage is called Jacquinot's advantage. As the FT spectrometer does not contain any entrance or exit slits as grating spectrometer more light can pass through the instrument [7, 8].

In order to avoid environmental factors, background spectrum is recorded. The spectrum of the sample is then divided by it and the influence of, for example, the atmospheric absorption bands are compensated.

In order to expand the capabilities of the infrared spectrometer it can have various attachments. The FTIR microscope is an example of an attachment like that. It is very useful when very small samples (up to 100 μm^2) are analysed. The operation of infrared microscope is somewhat similar to the optical one. However, due to reasons mentioned above the objective of the infrared microscope cannot be made of glass lenses. Thus, Cassegrain mirror system is employed. The main mirror in the Cassegrain system is concave. The secondary mirror is convex and placed in the focus of the main one. The radiation path in the objective in the reflection and transmission modes can be seen in the figure 6. To focus the radiation onto the sample, visible radiation is used as well. It propagates in the same path as IR radiation, but is detected with CCD (charge-coupled device) camera instead of the MCT detector [10].

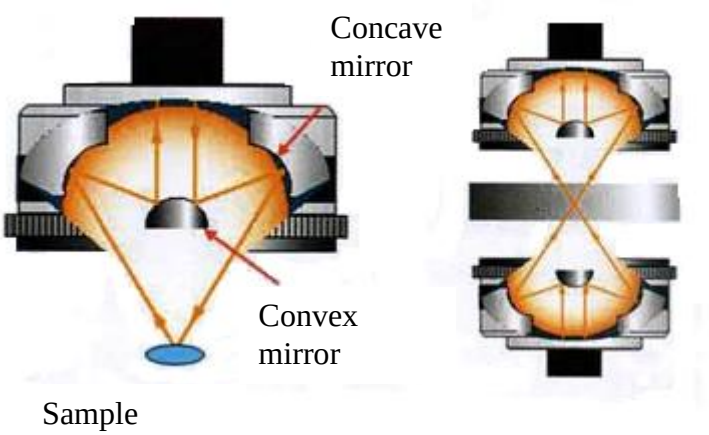

Fig. 6. Radiation path in cassegrain objective in reflection (left) and transmission (right) modes

Method

The samples for FTIR analysis were taken from various areas of the Vasa ship with different extent of degradation, salt precipitations, iron and sulphur levels. A sample from fresh oak wood *Quercus Robur* was used as a reference. The wood was converted into powder by using sand paper. In order to obtain as qualitative spectra as possible, we also tried sieving the powder of the wood to extract particles no larger than 150 µm. Spectra of the samples were taken using a Hyperion 3000 IR microscope connected to an IR spectrometer IFS66V/S from Bruker with globar IR light source and a single channel MCT (mercury cadmium telluride) detector. The resolution used was 4 cm^{-1} and 128 scans were averaged to obtain a spectrum. The measurements were carried out by choosing a point in the sample that contains a grain of wood which is thin enough to transmit IR radiation. The samples were prepared using the KBr (potassium bromide) pellet technique.

In this study data analysis of IR spectra of warship Vasa was performed. All the analytical procedures such as curve fitting and integral intensity calculations were carried out using OPUS software.

Some spectra of another archaeological marine artefact – ship Elefanten – has been analysed and compared to the spectra of the Vasa. These spectra where taken in some previous measurements.

To confirm band assignments and to evaluate possible band shifts due to degradation, calculations of cellulose vibrational properties were performed using Gaussian 09 software. In order

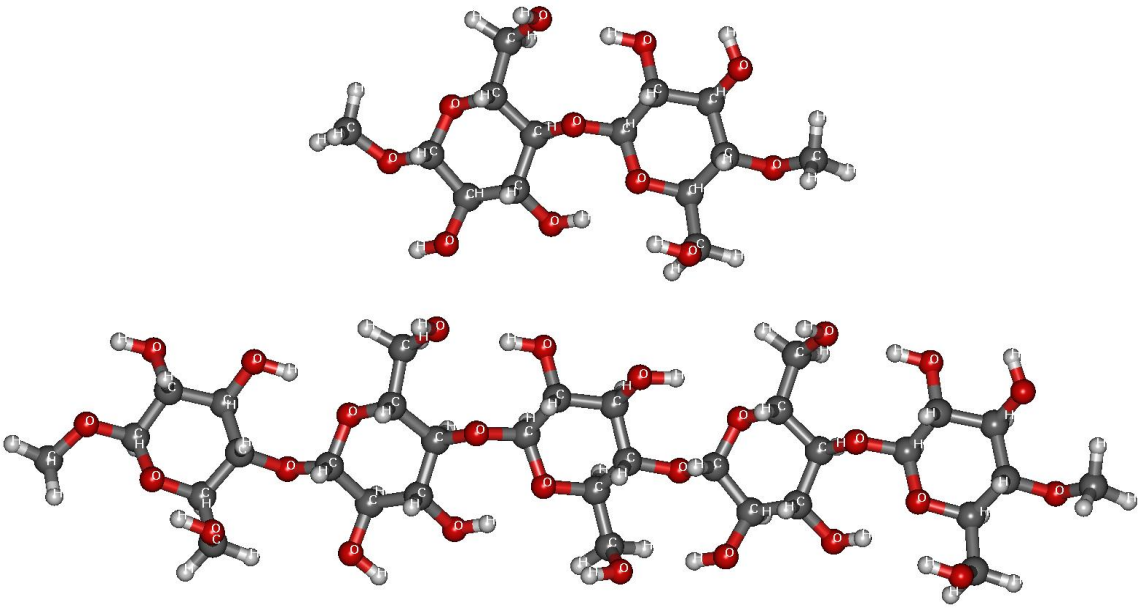

Fig. 7. Cellulose molecule models used for calculations

to simplify the calculations, systems from two and five D-glucose units were constructed. Based on the research of *M. P. Andersson* and *P. Uvdal* B3LYP/ 6-311+G(d,p) method was chosen for the calculations [11]. The calculations were made at the Center for Scientific and Technical computing LUNARC of Lund University. Optimized structures of the molecules calculated are presented in figure 7.

Results and discussion

Analysis of IR spectra

In order to determine the degradation patterns as well as other chemical changes in the Vasa wood different samples were analysed and the results compared to the ones found in the literature (obtained by different methods). The vibrational bands in the 'fingerprint' (1800-800 cm^{-1}) region were mainly analysed as they are the most sensitive to the occurring chemical changes. The assignments of the bands in this region are summarized in Table 1. They were made based on the literature and calculations [12-15]. The assignments are somewhat approximate as the chemistry of the wood is very complex and many different vibrations have the input to the positions and intensities of the bands.

In figure 8 spectra of oak wood *Quercus Robur* and of unpreserved (not treated with polyethylene glycol (PEG)) Vasa hull wood are presented. It can be seen in the picture that the relative intensity of the band at 1740 cm^{-1} is decreased in the spectrum of the Vasa wood compared to the spectrum of the fresh wood. This band is associated with the C=O vibration in functional groups (acetyl, carbonyl) in hemicelluloses.

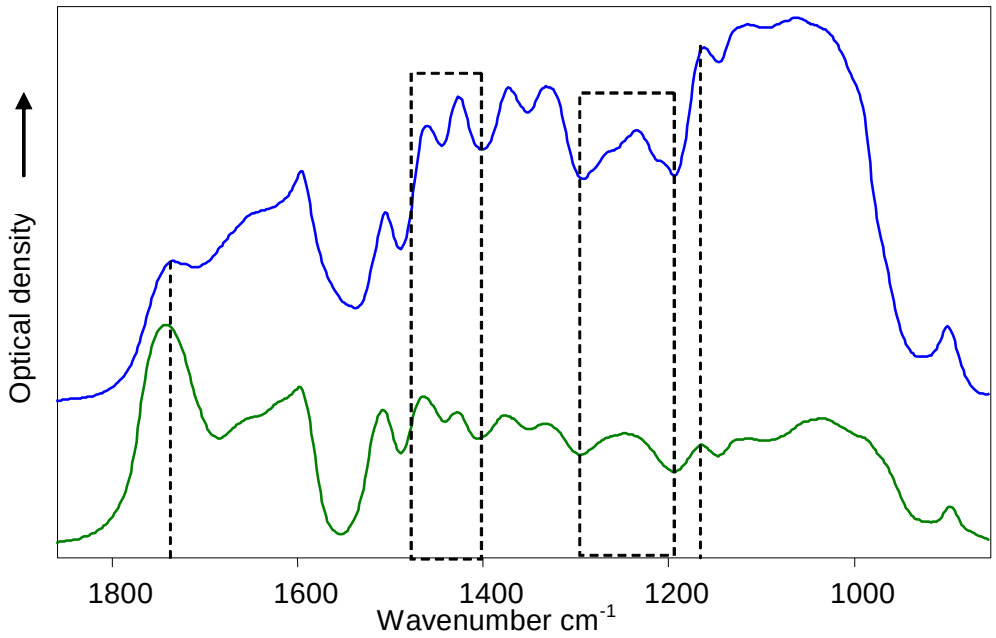

Fig. 8. Infrared spectra of non-preserved Vasa hull wood (blue) and oak wood Quercus Robur (green); spectra were shifted from each other in vertical direction for clarity

Table 1. Assignments of spectral bands of the Vasa wood according to the literature and calculations

Observed, cm^{-1}	Assignment	Calculated*, cm^{-1}	Calculated**, cm^{-1}
1740	C=O stretch in functional groups in hemicelluloses		
1666	Conjugated C=O stretch in lignin (present in the Vasa samples containing iron)		
1643	H-O-H deformation of absorbed water		
1591	C=C stretch of aromatic ring in lignin		
1506	C=C stretch of aromatic ring in lignin		
1465	C-C stretch, CH and OH wag in cellulose and hemicellulose, CH deformation in lignin	1486	1467
1426	CH and OH wag in cellulose and hemicellulose, CH deformation in lignin	1422	1420
1374	C-C stretch, CH and OH wag in cellulose and hemicellulose	1363	1363
1326	C-O stretch in syringyl ring in lignin, CH and OH wag in cellulose and hemicellulose	1299	1309
1265	C-O stretch in guaiacyl ring in lignin and xylan, CH and OH wag in cellulose and hemicellulose		
1230	C-O stretch in syringyl ring in lignin, CH and OH wag in cellulose and hemicellulose		
1205	CH and OH wag in cellulose and hemicellulose		1207
1167	C-O-C bridge vibration, asymmetric C-O stretch in cellulose and hemicellulose	1168	1163
1126	CH deformation in lignin		
1110	C-O and C-C stretch in cellulose and hemicellulose	1110	1111
1053	C-O stretch in cellulose and hemicellulose	1058	1041
1032	C-O stretch in cellulose and hemicellulose	1026	1011
987Sh	C-O stretch in a ring in cellulose and hemicellulose	999	975
898	C-H deformation in amorphous cellulose	900	900

* Two units of D-glucose, non-scaled

** Five units of D-glucose, non-scaled

Diminished intensity of this band could be a sign that hemicelluloses in Vasa wood is degrading. However, diminished intensity of this band does not necessarily indicate the degradation of

hemicellulose chains but rather the changes in functional group giving rise to it. The pattern of changes of hemicelluloses is visible not only in the unpreserved Vasa wood but in the sample of preserved wood as well (Fig. 9). However, they are to the smaller extent in these samples.

Changes in the region 1300-1200 cm^{-1} can be observed in the spectrum of the unpreserved Vasa wood as well. The band at 1265 cm^{-1} decrease in intensity compared to the band at 1230 cm^{-1}. The changing ratio of these bands can be explained by degradation of guaiacyl lignin and xylan in hemicelluloses. This kind of behaviour is observed in other spectra as well. It is the most pronounced in the spectra of the acidic, more degraded Vasa samples both preserved with PEG and not.

The change of ratio of the bands 1465 cm^{-1} to 1428 cm^{-1} is decreased in the spectra of the more degraded samples of the Vasa as well. This indicates the degradation of hemicelluloses and probably lignin contributing to the 1465 cm^{-1} spectral band.

The bands assigned to cellulose in the wood show the smallest changes. It can be deduced that while hemicelluloses and lignin are susceptible to the degradation (hemicellulose more than lignin), cellulose remains relatively stable.

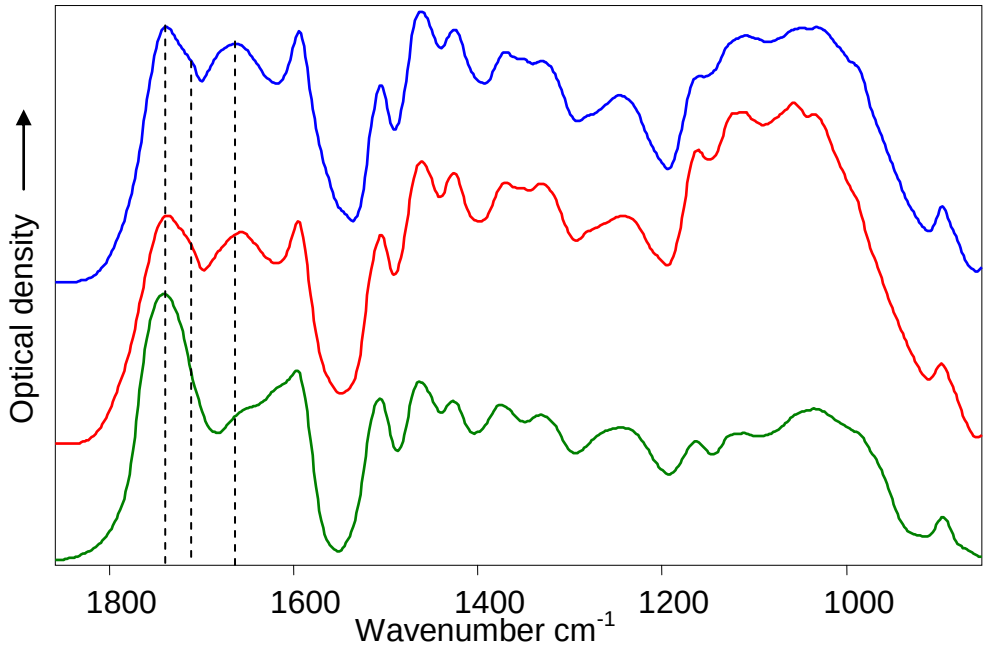

Fig. 9. Infrared spectra of oak wood Qercus Robur (green) and of preserved with PEG Vasa hull wood: blue – surface, red – inner; spectra were shifted from each other in vertical direction for clarity

The samples containing large amounts of iron were investigated as well. The spectra of one of these samples (surface and inner) are presented in figure 9. These samples have been preserved with PEG. Characteristic bands of polyethylene glycol can be observed at 1467, 1345, 1281, 1243, 1113, 952 and 841 cm^{-1} (the positions are approximate) [16]. As mentioned above, it can be

deduced from the spectra that the 1740 cm^{-1} band has changed in intensity much less than in the unpreserved sample's spectrum. Also, the overall spectrum looks much more like the reference spectrum, few changes can be observed at the first sight. This could indicate that the wood is less degraded in these samples. On the other hand, comparing the spectra of the sample to the reference spectrum of the fresh oak wood, some changes can be observed. The band at 1666 cm^{-1} appearing in the spectra could be due to conjugated C=O stretching vibration in lignin. The carbonyl functional group can form during successive oxidation reactions in the presence of iron ions in acidic environment (see chapter 'Degradation of the wood'). In the course of oxidation reactions conjugated C=O bonds in lignin can be created which gives rise to a spectral band at 1666 cm^{-1} (Fig. 9) [17]. A small shoulder at 1712 cm^{-1} can be seen in these spectra as well. It could be assigned to the carbonyl group vibration of oxidation products as well. Carbonyl group in celluloses can be one of the products in the oxidation reactions and give rise to this peak [18].

The assumptions made about the formation of conjugated carbonyl group in lignin are difficult to prove as a band of water adsorbed to cellulose appears in the same spectral region (1640 cm^{-1}). For this reason, the samples were dried in an oven of approx. 110^0C for a week. Spectra of the dried samples were recorded and analysed. The decrease in absorption at approx. 1640 cm^{-1} was observed supporting the hypothesis that vibrations of water contribute to this band. However, the band at 1666 cm^{-1} remained after the drying. The conclusion can be made that both degradation

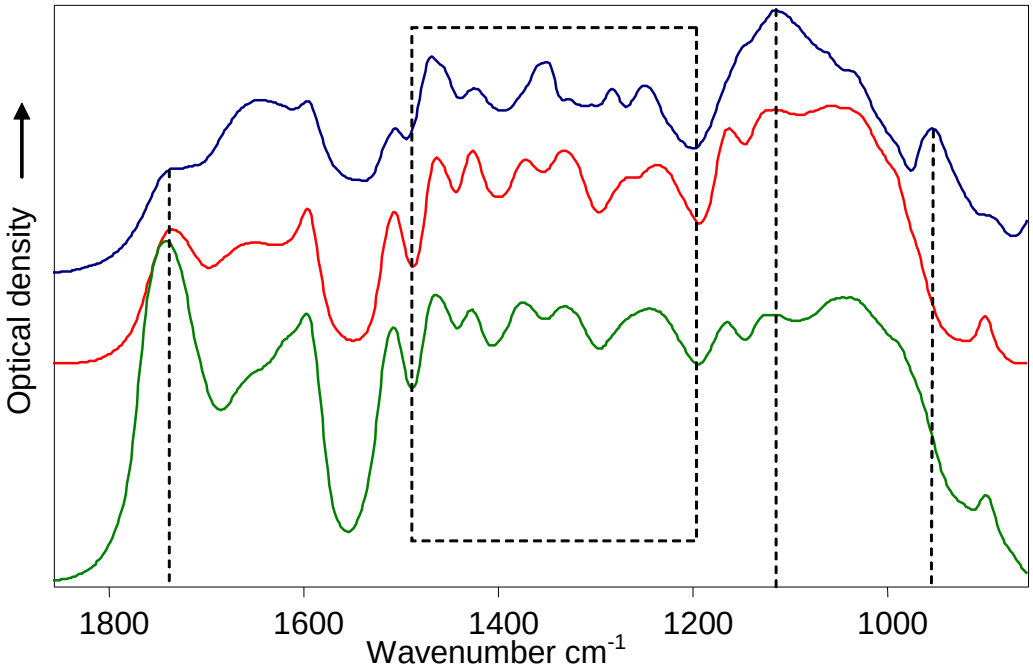

Fig. 10. Spectra of oak wood Quercus Robur (green), inner (red) and surface (blue) samples of Vasa hull contaminated with iron and sulphur and preserved with PEG

products of lignin and water adsorbed to the cellulose probably contributes to the absorption in this spectral region.

Comparison between surface and inner samples were made in this work and differences in spectra of such samples are presented in figure 10. First, the amount of hemicellulose in the surface sample is much smaller compared with the inner one according to the band at approximately 1740 cm^{-1}. Also, the intensity of the PEG vibrational bands is much higher in the spectrum of the surface sample. As it can be seen from spectra in figure 9, these differences do not apply to all the samples but rather depend on many various factors such as the state of the wood before its preservation with PEG. However, infrared spectroscopy allows differentiating between inner and surface samples of the Vasa.

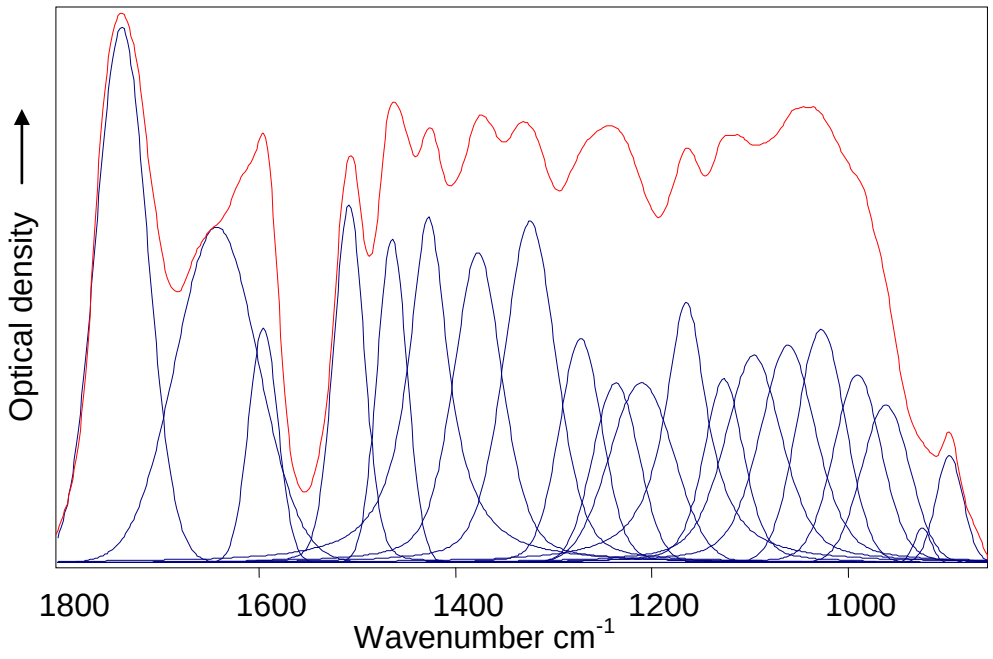

Fig. 11. Infrared spectra of oak wood Qercus Robur (red) and its fitted bands (blue)

In order to evaluate the changes appearing in the spectra, fitting procedure was applied using software OPUS to some of the samples and ratios of integral intensities of certain bands were calculated [19]. Ratios and not integral intensities themselves were taken in order to avoid dependence on different absorbance for different samples as the thickness of the samples was not known. Ratios of the bands 1740 cm^{-1} to 898 cm^{-1} (hemicellulose/cellulose), 1506 cm^{-1} to 898 cm^{-1} (lignin/cellulose), 1740 cm^{-1} to 1506 cm^{-1} (hemicellulose/lignin) and 1326 cm^{-1} to 1265 cm^{-1} (syringyl/guaiacyl) were calculated. The fitting results are presented in figure 11 while the ratios are presented in a graph in figure 12. It can be seen from the graph that samples 2 and 3 (treated with PEG) shows the smallest deviations from the fresh oak wood. The ratios of wood components in

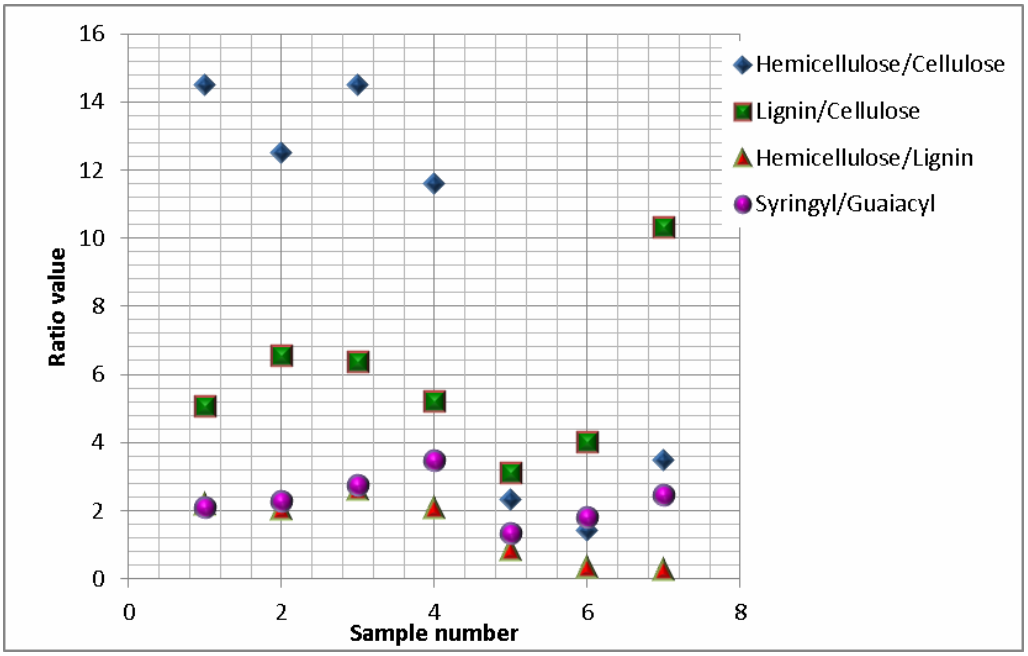

Fig. 12. Change in relative intensities of spectral bands between various samples: sample 1 - oak wood Quercus Robur; sample 2 - Vasa, iron and sulphur, PEG, surface; sample 3 - Vasa, iron and sulphur, PEG inner; sample 4 - Vasa, iron, acidic; sample 5 - Vasa, iron and sulphur, unpreserved; sample 6 - Elefanten, no iron, high sulphur, surface; sample 7 - Elefanten, no iron, high sulphur, inner

other samples differ highly from the reference sample. This could indicate that preservation of wood with PEG leads to smaller extent of degradation. The most significant changes are observed in sample 5 which is unpreserved Vasa wood containing iron and sulphur. The ratio of hemicellulose to cellulose is reduced the most by degradation suggesting that cellulose is much less susceptible to degradation than hemicellulose. The decreasing ratios of lignin to cellulose and hemicellulose to lignin indicate that both polymers are experiencing changes in the course of degradation, but lignin is more stable than hemicellulose. The decreased ratio of syringyl to guaiacyl lignin in this sample (sample 5) indicates that guaiacyl lignin is probably more stable and more resistant to degradation. The much increased lignin to cellulose ratio is probably influenced by errors of fitting procedure. In order to make solid conclusions more samples should be analysed.

Calculations

As mentioned in the Method part of this work, calculations of cellulose molecule models were carried out in order to confirm assignments and to possibly deduce the origin of band shifts in the spectra. The model was formed according to the literature [20]. Calculated vibrational frequencies are presented in Table 1. It can be seen in the table that the calculated vibrational

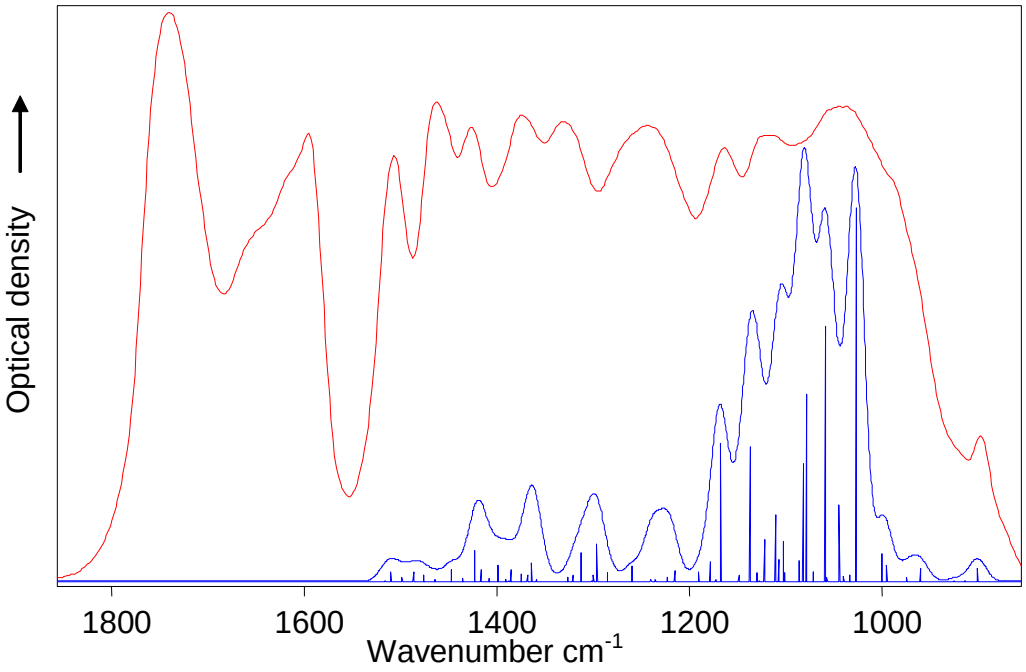

Fig. 13. Experimental spectrum of oak wood Quercus Robur (red) and calculated non-scaled spectrum and peaks of cellulose model with two D-glucose units (blue)

frequencies correspond to the experimentally obtained positions of the vibrational bands. For example, frequency of band at 1167 cm^{-1} deviate only by 1 cm^{-1} in the two D-glucose units system and 4 cm^{-1} in the five D-glucose units system. As the DFT calculations include only harmonic

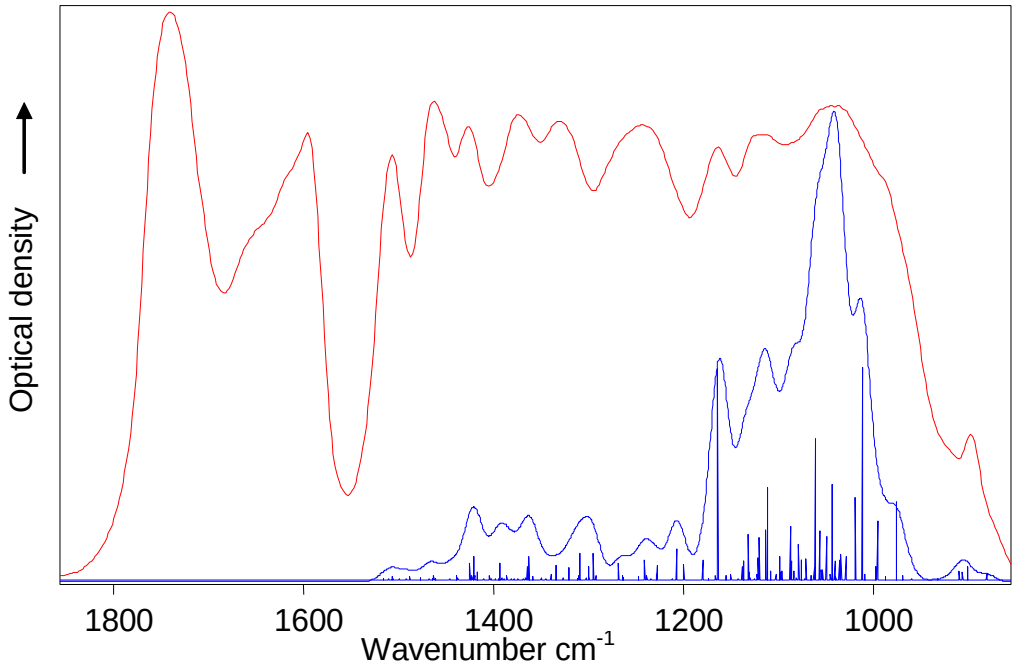

Fig. 14. Experimental spectrum of oak wood Quercus Robur (red) and calculated non-scaled spectrum and peaks of cellulose model with five D-glucose units (blue)

oscillations into account, some error is introduced into the obtained results and scaling factor should be used in order to obtain better assignments. However, no scaling factor was used in this work. As there are many differences between the model system and the real wood, such as polymer chain length, environment, etc. which affect various vibrational modes in different ways, the optimal scaling factor could not be determined. Due to the same reasons, deviations of the calculated frequencies from the experimentally obtained ones are not uniform – some frequencies are shifted to the higher wavenumbers while others – to the lower.

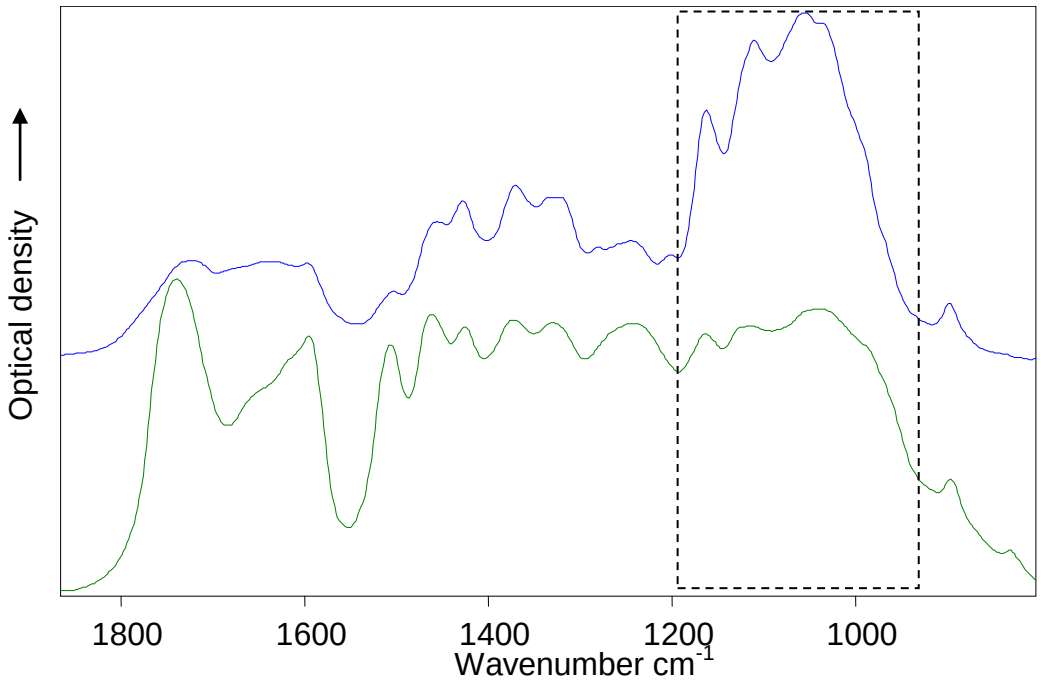

Fig. 15. Spectra of fresh oak wood Quercus Robur (green) and of Vasa wood (iron, acidic)(blue)

Probably the most sensitive region for cellulose degradation is around 1000 cm^{-1} where vibrations of linkage (C-O-C) between D-glucose units are expected. In this region, small shifts to lower wavenumbers appear in more degraded samples in comparison with the reference one (Fig. 8). The same shifts can be observed in the calculated spectra where the five-ring model represents less degraded cellulose and the two-ring model represents more degraded cellulose (Table 1, Fig. 13-14). This could imply that degradation of the wood causes dissociation of cellulose into shorter chains. The cellulose chains contain several thousand of D-glucose units even after the degradation thus it is difficult to evaluate the changes in the spectra. The changes in intensity in the spectral region 1200-1000 cm^{-1} can be noticed when comparing reference and Vasa spectra as well. Spectral bands in this region are of higher intensity in the spectra of the Vasa wood. However, the reasons for the occurrence of these changes are still unclear.

Conclusions

The usefulness of applying Fourier transform infrared spectroscopy to the investigation of the chemistry of marine archaeological artefact – the warship Vasa – has been explored in this work. Several conclusions can be made:

1. By analysing infrared spectra of the Vasa wood and comparing them to the spectra of the fresh oak wood (*Quercus Robur*) the degradation extent due to changes in functional groups of polysaccharides and lignin could be monitored.
2. New bands appearing in the spectral region 1750-1600 cm^{-1} in the spectra of the Vasa wood compared to the reference spectra of fresh oak wood could be a sign of oxidation of organic molecules in the wood as a consequence of Fenton's reaction occurring in the presence of iron ions.
3. Differences in chemistry between surface and inner samples can be observed in the IR spectra (if such differences are present). Qualitative estimations of the amount of PEG in the wood can be made.
4. DFT (density function theory) calculations of cellulose model systems (two and five D-glucose units) are helpful when assigning spectral bands as well as determining spectral changes caused by cellulose degradation.

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