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Analytical Methods for Assessing Preservation in Waterlogged Archaeological Wood: Their importance for site management decisions

Kirsty E High and Kirsty E H Penkman

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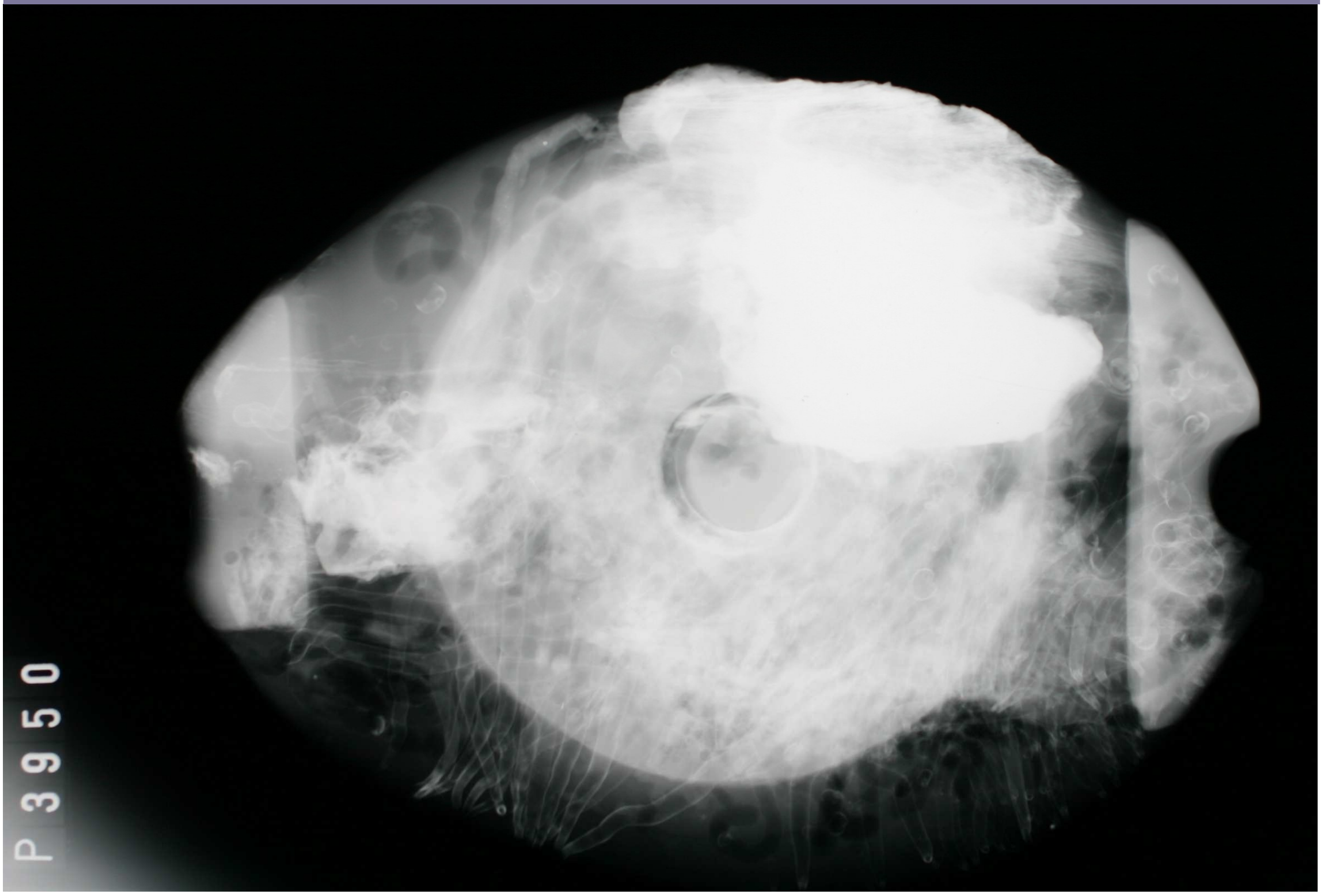

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For more information write to Res.reports@HistoricEngland.org.uk
or mail: Historic England, Fort Cumberland, Fort Cumberland Road, Eastney, Portsmouth PO4 9LD

SUMMARY

Understanding and quantifying preservation of organic archaeological materials has become increasingly important as wet or waterlogged sites are put at risk from human-driven alterations, such as land drainage, urbanisation, and climate change. Although a wide range of analytical methods can be applied to assess the state of preservation of an archaeological object, determining which of these is most appropriate can be challenging. Within the budgets and deadlines dictated by the project design, an assessment must provide useful information that aids site management and conservation decisions.

This review aims to summarise the most commonly reported methods suitable for the analysis of archaeological wood, offering an overview of the information obtained by each. Methods are evaluated in terms of the information gained weighed up against their cost, logistical considerations and time investments. Recommendations are provided to aid with the design of preservation assessment schemes.

Front Cover: X-ray image of wooden block (small find 3052), recovered from the London wreck, showing tunnels with calcareous linings created by marine wood borers. Photograph: Angela Middleton © Historic England

CONTRIBUTORS

Kirsty E High, University of York carried out this review, with input and advice from Kirsty Penkman, University of York. Jim Williams, Gill Campbell, and Karla Graham, Historic England provided advice and comments on the review content.

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2019

CONTACT DETAILS

Dr Kirsty High, University of York, Phone 07807876107

Kirsty.high@york.ac.uk / Kirsty.high@gmail.com

CONTENTS

1 INTRODUCTION AND BACKGROUND

When archaeological material is deposited, its degradation is controlled by a multitude of chemical and biological factors which depend on the material, the deposition environment, and the state of preservation prior to deposition. When we find archaeological material, it is because burial conditions have been such that deterioration is sufficiently slow; this might be due to the nature of the material itself, the way in which it was deposited, or the chemical, biological, and physical characteristics of the burial environment. In wetland or waterlogged sites, the abundance of organic material is attributed primarily to the suppression of aerobic microbial decay at a time soon enough after deposition to prevent rapid deterioration (e.g. Pollard, 1998; Caple, 2004). However, it is increasingly apparent that alteration and destruction of wetland and waterlogged sites due to human activity puts delicate organic materials at risk from degradation, despite having survived perhaps thousands of years since deposition (e.g. Kenward and Hall, 2000; Brunning et al., 2000; High et al., 2016). To fully appreciate potential risks to the continued preservation of a site, it is necessary to assess the chemical parameters of the burial environment, as well as the condition of the material present (e.g. Matthiesen, 2015). Whilst methods of monitoring geochemical and hydrological conditions are now well established and routinely implemented (see Holden et al., 2009; Williams, 2012; Mattheisen, 2015), an assessment of the state of preservation of the archaeological material itself can often be neglected, inconsistent, or occur too late to inform site management (Williams, 2012).

Assessing the current state of preservation of archaeological remains provides vital information on decay trajectories, archaeological significance (which is inherently connected to information that can be retrieved from an object), and the potential consequences of changing conditions (Gregory and Jensen, 2006). Appropriate analysis enables deterioration to be tracked over short time-periods by establishing a robust baseline of preservation assessment, for example: when a site is being monitored (e.g. Brunning et al., 2000; Sidell and Panter, 2016), when comparing material from different sites or phases of investigation (e.g. Huisman and Mauro, 2012; High et al., 2016), or when gathering experimental data on decay mechanisms (e.g. Godfrey et al., 2012; Gelbrich et al., 2012a). Analysis can also be important post-excavation; detecting slight changes in the condition of an object over periods of storage or museum display can help identify when conditions are not conducive to continued survival (Trojanowicz, 2008). Appropriate analysis can also help establish when conservation methods are themselves contributing to accelerated decay (Braovac et al., 2016; Pinder et al., 2017).

Discoveries of large wooden artefacts such as shipwrecks (e.g. Hoffman, 2001; Sandström et al., 2001) and prehistoric wooden trackways (e.g. Brunning et al., 2000), which have huge cultural importance but are challenging in terms of conservation and preservation, mean that methods of analysing and quantifying wood deterioration have been a focus of much research. Traditionally, approaches to the evaluation of preservation in organic materials have primarily consisted of cheap and readily accessible methods including visual assessment, calculation of preservation indices, and microscopic analysis (e.g. Jagels, 1981; Panter and Spriggs, 1997; Blanchette, 2000). However, over the past few decades, the interdisciplinary nature of archaeological and palaeoenvironmental research has led to the adoption of more complex methods, ranging from those that more accurately assess relative chemical compositions, to those which probe molecular changes within materials. The application of these can be used to gain a deeper understanding of how organic archaeological materials degrade, and importantly, the timescale on which this is happening. However, as these methods become increasingly available, it also becomes increasingly challenging to select an appropriate scheme for evaluation.

The aim of this review is to provide a critical overview of the techniques available for the evaluation of preservation in wood, both those already routinely used and those which may be less familiar. The methods are discussed in terms of the information they yield, how this may be useful, and how it weighs against the time and financial investments required.

2 WOOD: STRUCTURE AND DETERIORATION MECHANISMS

Waterlogged wood presents particular management challenges related to the scale of artefacts that can be uncovered (e.g. trackways and shipwrecks), and the rapidity at which it deteriorates once exposed. Preservation assessment forms a vital part of the conservation strategy for any wooden artefact, and methods of analysis are therefore well established in the fields of archaeology, heritage management and conservation (for example, see various proceedings of the ICOM-CC WOAM working group triennial conferences).

All wood is composed of three major biopolymers: lignin, cellulose and hemi-cellulose (two types of polysaccharide) arranged in fibrils (Figure 1). A variety of 'extractives' (non-structural components such as pectins, tannins, resins and oils) also contribute up to 10% by mass in fresh wood, although these tend to be present in lower concentrations in archaeological wood (e.g. Hedges, 1990). The relative proportion of each component depends on factors such as the wood species, age and growth element, but generally lignin accounts for roughly 15-35% of wood content, with the remainder made up of celluloses and extractives (for an in-depth description of wood structure see: Fengel and Wegener, 1984; Hoadley, 1990). The deterioration of wood in an archaeological context is complex, and driven by biological and chemical factors dictated by both the burial environment and the manner of deposition. Thorough reviews on deterioration mechanisms are offered by Hoffman and Jones (1990) or Blanchette (2000). In brief, the order of deterioration can often be simplified thus: non-structural components are lost first, followed by the carbohydrate components (hemi-cellulose followed by cellulose), with the polyphenolic lignin being far more robust to deterioration, particularly by biological mechanisms (Florian, 1990). As the inner cell walls are more cellulose-rich, these are often lost first, leaving a lignin-rich skeleton. Key indicators of lignin decay may include: demethylation of the phenolic syringyl (hardwoods only) and guaiacyl sub-units, an increase in guaiacyl concentration caused by preferential syringyl decay, and an increase in oxidised sub-units (Figure 1; see Section 5 for further detail).

Biological decay is the main threat to wood and this is drastically reduced (but not completely absent) in permanently waterlogged, completely dry, or very cold environments (Blanchette, 2000). Some studies demonstrate that chemical deterioration is also a significant threat, particularly under extreme conditions such as low pH (High et al., 2016; Braovac et al., 2016).

Alteration of wood chemistry, in particular loss of cellulose, results in the loss of mechanical strength (Bardet et al., 2009). This makes wood more susceptible to physical alteration (for example compression by shrinkage of the burial environment) potentially reducing the archaeological value of an object by obscuring details such as tool marks and growth ring counts (Bamforth et al., 2018).

Deterioration of wood is often characterised by alterations in the relative abundance of the main structural components, primarily alteration of the lignin: carbohydrate ratios (Martinez et al., 2005; Gelbrich et al., 2008). In the commonly used wood conservation method of polyethylene glycol (PEG) impregnation, the concentration and molecular weight of PEG applied is dictated by the amount of cellulose remaining in the wood (Hoffman, 1986). Therefore, many studies focus on establishing the carbohydrate content to inform conservation strategies. However, other chemical changes can occur in archaeological wood which are indicative of decay, for example the incorporation of inorganic material (such as metals and minerals) from the burial environment (e.g. Panter and Spriggs, 1997).

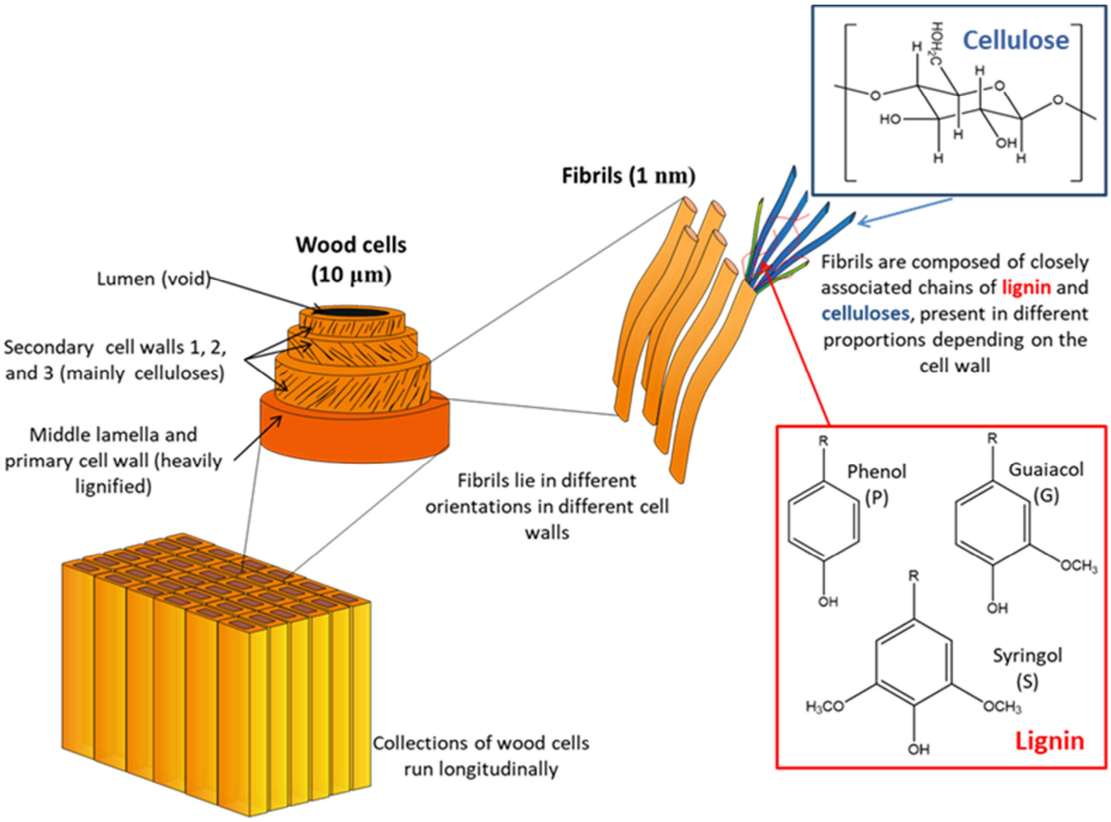


Figure 1: Schematic showing hierarchical structure of wood and the key molecular sub units present in lignin and cellulose. Methods of analysis range from those that examine the macro-structure, to those that examine the chemical structure.

The use of analytical instrumentation allows a more detailed analysis of the molecular modification of wood as it decays. The enhanced detail and sensitivity that such methods provide allow small alterations to be detected, and low levels of decay may be monitored. These methods are also particularly useful for determining modifications to the lignin skeleton in cases where cellulose is completely depleted (High et al., 2016).

3 ASSESSMENT OF MORPHOLOGICAL PRESERVATION

3.1 Physical evaluation

Descriptive characterisation of the state of preservation of waterlogged wood where features such as surface detail, colour, and texture are assessed by an experienced excavator or conservator, is the most accessible method of evaluation and is a vital component of routine excavation. In most cases physical evaluation will be the only assessment carried out, and it is used primarily as a basis for assessing the archaeological significance of the material (related to the quality of archaeological information that can be retrieved). It can also provide the basis for a further scheme of preservation assessment, or indeed dictate that further analysis would not be beneficial (Bamforth, pers. comm.). Analysis of the physical condition can identify compression damage caused by shrinkage of the surrounding deposits; this can be quantified by measuring the vertical and horizontal diameter of once-circular cross sections of wood (e.g. High et al., 2018a). The abundance of visible tool marks has also been identified as a proxy indicator of wood preservation (High et al., 2018a). Other physical features caused by decay include 'dog-leg' kinks in vertical timbers caused by variations in the degree of peat shrinkage with depth, or pointed tops of upright timbers caused by preferential decay of the outer layers of sapwood, leaving the inner pith (Panter, Bamforth, pers. comms.; Figure 2).

Figure 2: Left: Image of an upright wall post excavated from Glastonbury Lake Village, displaying the 'dog-leg' kink caused by peat shrinkage. Centre: Timber excavated from a Middle Saxon bridge near Glastonbury, exhibiting the characteristic pointed tops caused by preferential decay of the sapwood in parts of the timbers located above the waterlogged zone. Right: Root damage in a wood chip from Glastonbury Lake Village, caused when wood is weakened such that roots can penetrate through it. Images courtesy of Richard Brunning, copyright South West Heritage Trust.

Descriptive approaches have the enormous advantage of being able to be carried out immediately following or during excavations, providing a rapid assessment of preservation. The downsides of describing wood preservation are a lack of consistency between analysts and the inherent difficulties in accurately describing the appearance and texture of an object, making it hard to compare between samples. The presence of water in degraded wood cells can also make wood appear better preserved that it actually is and is not necessarily representative of how it would behave were it to dry out (e.g. Macchioni et al., 2018). The outer layers of wood can also be much more deteriorated than the inner heartwood which is often observed to resist deterioration (Hoffman and Jones, 1990).

A systemised approach to artefact description can aid comparisons. Jagels (1981) advocates the use of a standardised list of visual deterioration indicators to be reported against during each evaluation. Van de Noort et al. (1995) developed a scoring system to help characterise wood condition during a large-scale survey across the Humber Wetlands. Their system assigns each timber a value between 0-5 based on the clarity of surface information, allowing categorisation based on the level of analysis that can be carried out (e.g. species identification or tool mark analysis; Table 1). This system is closely linked to the archaeological value of an artefact rather than the chemical preservation of the wood. The use of scoring systems provides a degree of consistency and has therefore been routinely adopted by archaeological wood specialists in various large-scale excavations (e.g. Brittain, 2010; Milner et al., 2011; High et al., 2018a).

Table 1: A grading scheme for assessing the analytical potential of waterlogged wood (from Van de Noort et al., 1995 and Bamforth, M. in Milner et al., 2011). An object is assigned a grade (0-5) based on characteristics such as the visibility of anatomical features and tool marks. This grade dictates its suitability for different types of archaeological analysis; (+) = suitable (-) = unsuitable.

Grade	*Condition*	*Species ID*	*Dendro-chronology*	*Woodland Management*	*Technology*	*Museum Conservation*
0	Non-viable	-	-	-	-	-
1	Very Poor	-/+	-	-	-	-
2	Poor	+	-/+	-/+	-/+	-
3	Moderate	+	+	+	-/+	-
4	Good	+	+	+	+	-
5	Excellent	+	+	+	+	+

3.2 Advanced visualisation techniques

Illustrations and photographic records supplement visual assessment, facilitating comparison between sites and excavations. Whilst photographs and detailed plans of wooden structures are gathered as routine, advances in technologies can increasingly be exploited to provide more detailed records. An example is the use of photogrammetry software to create 3D models from digital photographs (Milner et al., 2018). These models provide an archive of the shape and surface detail of an object, which can then be stored in an online repository and are of potential use for identifying changes in the physical state of an artefact post excavation or during storage. The benefits of a digital copy include increased accessibility and the potential for enhanced analysis at a later date (for example producing 3D prints of artefacts). Digital imaging and 3D scanning when combined with traditional illustrations can reveal and record a wealth of surface detail (see Milner et al., 2016; Figure 3). 3D scanning has also been shown to be effective underwater making it possible to document large objects such as shipwrecks (Bandiera et al., 2015). Photogrammetric software is becoming more accessible and familiar, meaning that this approach is increasingly commonplace (Dawn and Biswas, 2018). Despite this, a great degree of skill is still necessary to achieve adequate lighting and contrast for observation of surface detail, particularly on wet and dark artefacts, such as waterlogged wood.

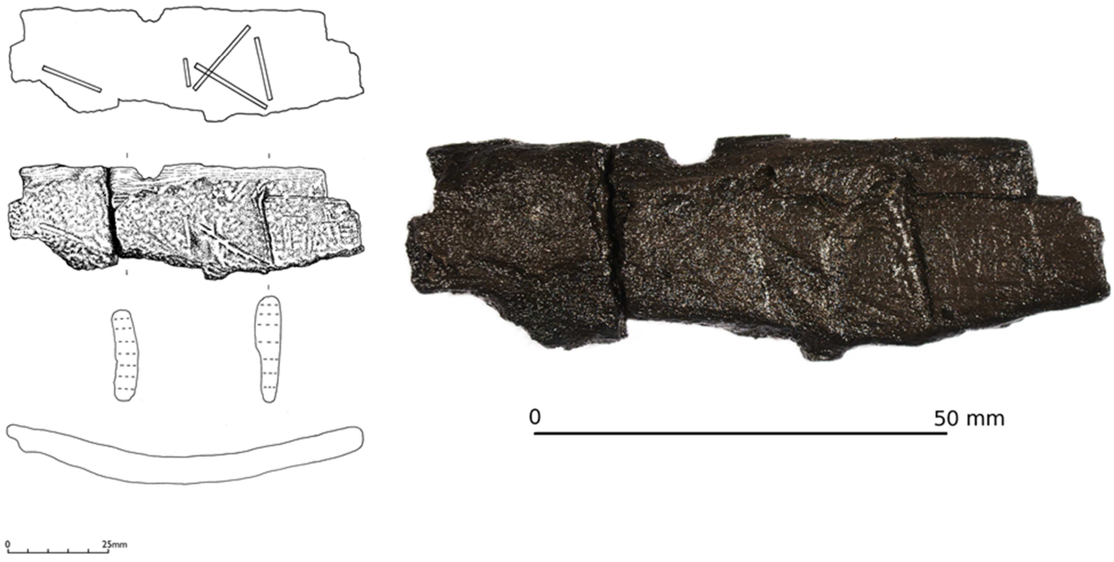


Figure 3: Illustrations and photograph of a decorated wood chip excavated from Star Carr. High quality photography clearly shows surface detail whilst illustrations allow certain features to be highlighted. Images copyright Chloe Wilson (left) and Michael Bamforth (right).

An extension of photogrammetry is high resolution laser scanning, which provides a more detailed image of surface texture, making it ideal for recording features such as surface tool marks, and again providing a digital copy of the artefacts (Lobb et al., 2010). Lobb et al. (2010) demonstrate the use of laser scanning to identify shrinkage post-excavation by comparing multiple analyses of the same object. However, laser scanning requires specialist equipment and expertise. Although analysis itself is fast (for example 307,000 data points were gathered in 2.5 seconds by Lobb et al., 2010), processing and interpretation of this data can be time-consuming (De Reu et al., 2013). It is therefore not yet accessible to most projects, but as the technique becomes increasingly common and less expensive its practical application may become more widespread in the cultural heritage sector (Dawn and Biswas, 2018).

3.3 Loss of wood substance

Assessment of the structural integrity of a wooden artefact is critical to predicting its behaviour on drying out and/or conservation treatment. It can also inform how the object might react to compression in the burial environment if left *in situ* or reburied (Jensen and Gregory, 2006). A range of different indices that indicate the 'loss of wood substance' or 'loss of density' have been traditionally applied for this purpose (Jensen and Gregory, 2006). These include maximum water content (Umax, sometimes termed MWC or µmax), basic density (Panter and Spriggs, 1997), and wood substance density (Babińksi et al., 2014). The indices are calculated from measurements of mass and/or volume of a sub-sample of the wood and all provide an indication of how much of the original wood material remains. Loss of wood substance is often considered to be caused primarily by loss of celluloses rather than lignin. However, some researchers have suggested that this is an incorrect assumption, as certain bacteria appear to consume low molecular weight products of lignin deterioration (Hedges, 1990; Zabel and Morrel, 1992).

As these indices are calculated using easily-measured parameters such as saturated mass, oven dry mass, and the wet and dry volume of wood (measured by displacement of water), no specialist equipment is required, and the analysis is therefore very accessible and cheap (Jensen and Gregory, 2006). Although the range of indices that can be applied is large, Babińksi et al. (2014) demonstrate excellent correlation between Umax and density. They suggest that measurement of only one of these parameters is sufficient and Umax tends to be the most commonly applied.

Despite the apparent simplicity of these measurements, several studies do highlight the difficulty in obtaining consistency between analysts and/or laboratories; the high porosity of wood makes an absolutely dry mass difficult to obtain, and there are inherent errors associated with weighing a sample that has a wet surface (Fengel and Wegener, 1984; Panter and Spriggs, 1997). Another major downside of these methods is the size of sample required for analysis (Jensen and Gregory (2006) recommend using at least 0.5g). This limits the ability to perform multiple analyses of an artefact, or indeed the ability to use these methods at all. Jensen and Gregory (2006) make recommendations for the standardisation and reduction of errors in these measurements, for example by using as large a sample as possible and being consistent in the way that surface water is removed. They also provide an excellent summary of appropriate equations for the calculation of these indices.

A key issue with assessing preservation based on loss of substance is that values may vary significantly through the depth of a sample. This can be addressed using mechanised equipment such as the Sibert Decay drill or Pilodyn instrument to measure resistance through the depth of a timber, which is then converted to a measure of density (Panter and Spriggs, 1997). A less mechanised version of this is the 'pin-test', long used as a standard evaluation technique in wood conservation laboratories (Christensen, 1970; Florian, 1990). In the pin-test, a steel needle is pushed into the timber and the distance it can be pushed without hindrance measured. Whilst this is clearly more subjective than mechanised methods, an experienced conservator will be able to estimate comparative degradation between samples, and it has the benefit of being widely available.

Translating a Umax value into a degree of deterioration is also highly dependent on wood species; what constitutes a highly degraded sample of oak may be a normal Umax for an undegraded piece of less dense wood (Grattan and Mathias, 1986). To accurately interpret the data, therefore, the wood species would ideally first be identified. To support parameters indicating loss of wood substance, measurements of 'shrinkage upon drying' are sometimes determined, as the degree to which a piece of wood alters on drying is dictated by its water content. Shrinkage is defined by the size of the dry sample as a percentage of the original sample size and is typically measured in all three planes of the wood (e.g. Brunning et al., 2000). Loss of cellulose can alter the ratio of shrinkage in the longitudinal: radial planes (e.g. Macchioni et al., 2012). Shrinkage measurements require a sizeable sample and can be very difficult to accurately measure in practice; however, they can provide an indication of the accuracy of the Umax and density values and a more realistic view of how wood may respond to conservation treatments (Macchioni et al., 2012).

Despite the noted drawbacks in practical application, calculation of physical parameters such as Umax and shrinkage remain easily applied, freely and widely available methods of estimating wood deterioration. They provide sufficient information to inform the treatment procedures for wood in a conservation context and are often used as the first stage in a more comprehensive scheme of preservation assessment (e.g. Hoffman and Jones, 1990; Panter and Spriggs, 1997). However, these indices are not likely to be sensitive enough to detect small variations in wood chemistry, for example over a period of monitoring or storage (Babiński et al., 2014). If this is the aim of assessment, then more sensitive methods should be considered.

3.4 Non-destructive methods for assessing physical structure

A major downside of determining the loss of wood substance using indices such as Umax and shrinkage is that these methods are destructive. Wood density (related to loss of wood substance) can also be determined using instrumental methods, which although less widely accessible, can provide the non-destructive analysis required in certain circumstances. They also allow the analysis of an entire object, reducing concerns regarding differences in preservation throughout an object, and the increasing availability of portable instruments means that analysis may sometimes be carried out during excavation rather than in the laboratory (e.g. Tuniz et al., 2013).

3.4.1 X-ray analysis

In the most well-known application of X-ray analysis, an object is placed in a high energy X-ray source and scanned, with the transmitted X-rays producing an image based on the relative density through the object. This image therefore relates to the internal structure, revealing any areas of higher or lower density (Figure 4, centre and right). Regions of increased decay can be observed, for example characteristic tunnelling caused by marine boring organisms (Southwell and Bultman, 1971; Figure 4 left) or regions affected by rot (Lechner et al., 2013). Appropriate calibration of the X-ray image enables the calculation of a quantitative value of density based on the image colour, although factors such as the moisture content and object thickness need to be accounted for (Lechner et al., 2013).

Figure 4: X-ray images of waterlogged wooden artefacts. Left: regions of low density caused by marine wood borer infestation can be clearly seen by X-ray imaging. Centre and right: a photograph compared to an X-ray scan of a wooden object, demonstrating how X-ray analysis can reveal internal features and regions of high or low density not otherwise visible. Images courtesy of Angela Middleton, copyright Historic England.

The use of X-rays from a synchrotron source rather than a traditional anode tube provides the same analysis but at much higher resolution; the higher energy of the X-rays means that contrast between even very similar materials can be obtained (Sodini et al., 2012). Although the benefit of such high-resolution analysis is clear where the significance of an object warrants an in-depth non-invasive analytical approach, the high cost and limited availability of synchrotron instruments restricts such techniques from becoming commonplace. Synchrotron instruments are also not portable and the object size may be limited, depending on the instrument available.

X-ray computed microtomography (microCT), is a version of X-ray scanning that examines cross sections through an object. When pieced together, multiples of these 2D cross sections can be built up to produce 3D images, thus providing better spatial evaluation than ordinary X-ray procedures. As instrument advances are made, microCT is becoming increasingly applied to cultural objects (e.g. Mizuno et al., 2010; Sodini et al., 2012). MicroCT can examine materials ranging from the millimetre size to large objects analysed in the field using portable instruments (although these are far less readily available; Tuniz et al., 2013). However, microCT is still primarily used for morphological characterisation (for example wood species identification), rather than an assessment of decay and state of preservation (e.g. Mizuno et al., 2010). Analysis can again be significantly enhanced by using synchrotron sources. Sodini et al. (2012) show that microCT analysis of violins using synchrotron radiation revealed the cellular structure of the wood as well as details of the manufacturing process, for example layers of adhesive.

3.4.2 Ultrasonic testing

Ultrasound has long been used in the forestry industry to characterise wood density. The method is based on the fact that sound waves travel much faster in healthy wood than in decayed timber. As such, the signal from reflected waves alters in accordance with the state of degradation of the object (Arnott et al., 2005). Ultrasound has the advantage that the effect of water can be readily accounted for, making it ideal for the study of waterlogged wood (Zisi and Dix, 2018). It is also fast, portable and non-destructive. It has been demonstrated as an ideal technique for the examination of shipwrecks, which often cannot be easily accessed for destructive examination (Zisi and Dix, 2018). However, interpretation of the data is far more complex than for example, from the indices previously described (Section 3.3). The reflected signal is affected not only by the water content, but also factors such as the orientation of the timber, and natural variabilities within the wood such as knots (Arnott et al., 2005). Despite this, it has been demonstrated that when contributory factors are adequately accounted for, there is a clear relationship between degradation state (as assessed by other parameters) and measured reflectance of ultrasonic waves (Zisi and Dix, 2018). Calibrating this signal against the known density of, for example, surrounding sediment (Arnott et al., 2005) allows a quantitative measure of wood density to be obtained.

3.5 Microscopic analysis of wood structure

Loss of wood substance, the presence of inorganic salts, and collapse of the structural integrity of cell walls can all be studied using a variety of microscopic methods (e.g. Björdal et al., 1999; Blanchette, 2000). Microscopy provides valuable information on the mechanisms and causes of deterioration that is much harder to elucidate with chemical and physical analysis. Often, microscopy techniques are used in conjunction with other analytical methods to consolidate assumptions on the state of wood preservation (e.g. Tamburini et al., 2017). An important advantage of microscopy is that it can provide spatial analysis, whereas many other techniques provide an average overview of the condition of an object (Daniel, 2016). However, this can turn to a disadvantage if the sample analysed under the microscope is not representative of the entire object. Microscopic methods are non-quantitative, so comparison between sites and/or samples is not straightforward. However, this could be addressed to some extent by applying a grading system, similarly to that widely used for physical analysis (Macchioni et al., 2013).

3.5.1 Light microscopy

Thin-section microscopy is often routinely carried out on archaeological samples for the purpose of species identification (Hather, 2000). The main advantage of light microscopy is therefore its cost effectiveness and wide availability, both of instrumentation and the expertise available to prepare and evaluate samples (Gregory and Jensen, 2006). Preparation of samples is relatively straightforward, involving cutting thin-sections with a razorblade or microtome. However, in more degraded samples this can sometimes result in damage to the structure, which needs to be considered during assessment. This problem may be addressed by first embedding the sample in paraffin or resin, or freezing prior to slicing (Daniel, 2016). In practice however, freezing has been observed to damage already degraded wood structure (Panter, pers. comm.).

Microscopic techniques are often applied to assess the nature of as well as extent of decay; in thin-section (and in more detail in electron microscopy) characteristic decay patterns (for example, tunnelling or erosion) can help identify the origin of biological attack (Björdal et al., 1999; Powell et al., 2001). The use of biological stains can further help identify biological activity by highlighting fungal hyphae and bacterial colonies (see Schwarze, 2007 for a review of commonly used biological stains; Figure 5A). Whilst this is valuable in determining the source of wood decay, it is impossible to ascertain when in the depositional history of the sample this attack may have occurred, and therefore analysis may not relate to the current burial environment.

Chemical decay is assumed to result primarily in the loss or alteration of cellulose (Hedges, 1990). As cellulose exists in two stereoisomeric forms, it displays a characteristic birefringence under polarised light (e.g. Sjöström, 1981). Therefore, viewing thin-sections of wood under polarised light can further confirm the presence or absence of cellulose as well as distinguish between the cellulose-rich inner cell walls and the lignin-rich secondary cell walls (Hoffman and Jones, 1990; Capretti et al., 2008; Figure 5B). Cellulose loss often results in the collapse of the cellulose-rich inner cell walls, which is easily identified using thin-section light microscopy (Björdal et al., 1999).

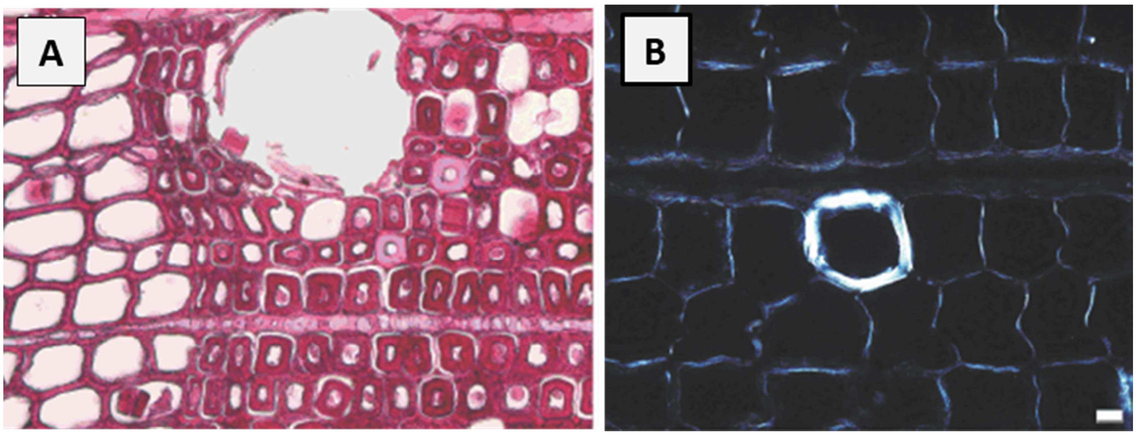


Figure 5: Examples of detail viewed by light microscopy. A: Image with biological dye showing a typical soft rot decay pattern. B: Polarised light microscopy revealing bright areas of birefringence caused by high concentrations of cellulose in cell walls. Reproduced from Capretti et al., 2008 with permission from John Wiley and Sons, copyright 2008.

Advanced versions of light microscopy include ultraviolet (UV) and fluorescence microscopy. Whilst these are less widely available, they can provide additional information on deterioration mechanisms. As the aromatic rings in lignin absorb more UV light than carbohydrates, the appearance of a wood sample under UV can indicate the relative abundance of lignin (Saka and Goring, 1988). Certain stains containing fluorescing groups preferentially bind to either lignin, cellulose or hemicellulose. They can therefore be used in conjunction with a fluorescence microscope to observe the distribution of these polymers (Daniel, 2016). The advantage of these techniques is that variations in lignin distribution across the wood microstructure can be examined (Schwarze, 2007).

3.5.2 Electron microscopy

Although still less widely accessible than light microscopy, scanning electron microscopy (SEM) is becoming increasingly commonplace in the conservation laboratory. SEM produces a very high magnification image of a sample by probing the surface with an electron beam. The high magnification, high resolution, and 3-dimensional nature of the images means that SEM can reveal greater detail than light microscopy (Figure 6). Additionally, in cases where wood has dried out and become brittle, making thin-sectioning impossible, SEM can be employed instead (Crestini et al., 2009).

Thinning of cell walls caused by loss of cellulose is typically more obvious under SEM than light microscopy (Blanchette, 2000; Powell et al., 2001; Figure 6B), although the inability to use biological stains in SEM means that experienced input is often required to identify this. Information that can be revealed by SEM but not light microscopy includes: the presence of slime deposits resulting from bacterial attack, the presence of fungal spores, and 'opening up' or separation of cell walls as wood is degraded (Powell et al., 2001; Daniel et al., 2016). Whilst this information has been critical to a general understanding of the mechanisms and process involved in wood decay, it is not always important to know this level of detail when assessing wood degradation.

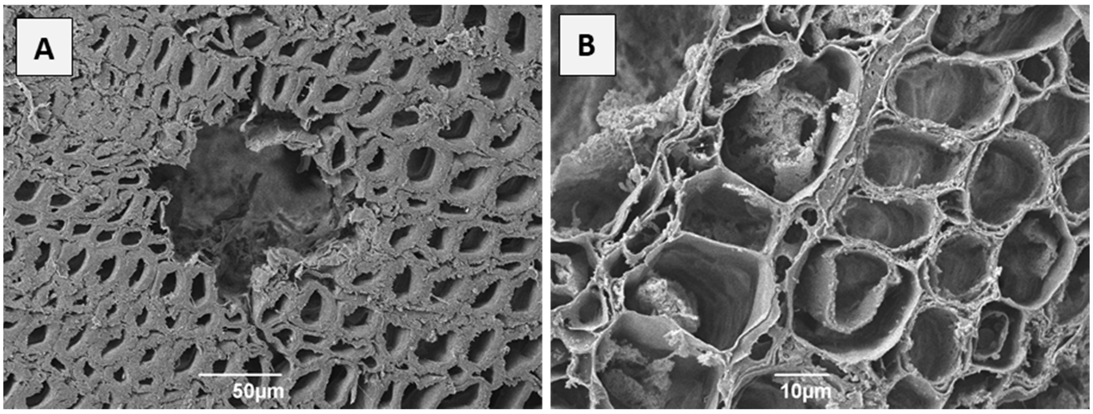


Figure 6: Examples of detail viewed by SEM. A: Wood sample from Hatfield Moor Neolithic trackway, showing good preservation of cellulose as demonstrated by the presence of thick secondary cell walls. B: Wood sample from Beccles Iron Age trackway showing heavy cellulose depletion (as observed by thinner cell walls) resulting in structural collapse. Images courtesy of Ian Panter, copyright York Archaeological Trust.

In most SEM instruments, analysis must be carried out in a vacuum, which may cause structural damage to very degraded samples. Simply cutting a piece of sample suitable for analysis may cause similar damage, as is the case with cutting thin-sections for light microscopy. Many studies have demonstrated that impregnating and 'fixing' of a sample in glutaraldehyde followed by dehydration avoids this problem, but this process does make the analysis more time consuming, adding days to the analysis time (e.g. Powell et al., 2001). SEM analysis normally also requires samples to be coated in a thin layer of metal so that they are conductive, meaning that the technique is not non-destructive (Daniel, 2016).

The development of environmental SEM instruments over the last few decades has removed some of these problems as they allow images to be collected in the absence of a vacuum and without coating. Samples can therefore be analysed moist, removing the need for lengthy sample preparations (Daniel, 2016). Although traditional SEM is typically more widespread, the usefulness of environmental SEM instruments in fields such as environmental and biological sciences means that they are becoming increasingly common in University departments. However, the presence of water can result in a lower quality of image than in traditional SEM (Macchioni et al., 2012).

Transmission electron microscopy (TEM) works by passing electrons through a sample, rather than detecting surface morphology. TEM analysis can therefore be used to examine the internal structure of wood, producing very high-resolution 2-dimensional images (Blanchette, 2000). It has been instrumental in a general understanding of the structure of wood (Daniel, 2016). However, for preservation assessment, the large expense, complexity of sample preparation, and difficulties in obtaining access to instrumentation would rarely justify the value of the information obtained (Macchioni et al., 2012).

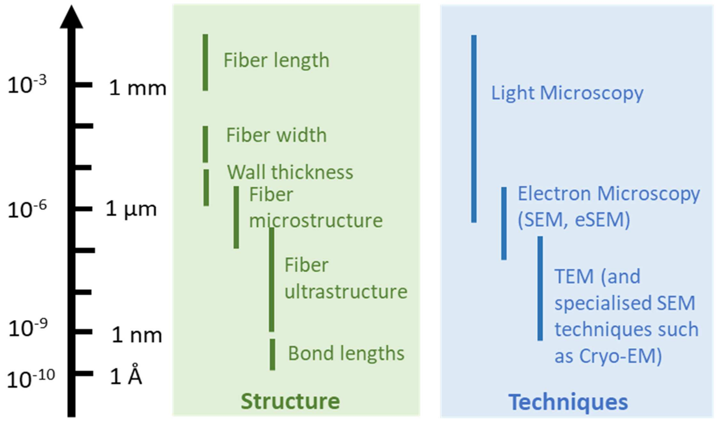


Figure 7: Simplified schematic showing the scale at which different microscopy techniques are useful. Adapted from Daniel, 2016.

3.5.3 SEM-BSE / SEM-EDX

Electron microscopy typically detects electrons emitted directly from or through a sample. However, other signals are also emitted from the sample once probed with an electron beam. If these are themselves measured using an additional type of detector, advanced analysis can be performed. Back-scattered electrons are characteristic of the atomic weight of the element present; SEM-back-scattered electron (SEM-BSE) analysis therefore provides an indication of the elemental composition of a sample. Similarly, X-rays emitted from the sample are characteristic of the element present. Detection of these in a technique termed SEM-energy dispersive X-ray (SEM-EDX), or SEM-energy dispersive X-ray spectroscopy (SEM-EDS), can provide an analysis of elemental composition (Genestar and Palou, 2006; Daniel, 2016). Both SEM-BSE and SEM-EDX provide an elemental map of the surface of the sample, which can be useful for identifying inorganic inclusions (Genestar and Palou, 2006) or investigating the effectiveness of conservation treatments (Wallström and Lindberg, 1999). Both techniques have also been shown to provide lignin distribution maps when pre-treated with a reagent that preferentially binds to lignin (Fromm et al., 2003; Xu et al., 2006). As an additional detector is required for BSE or EDX analyses, not all electron microscopes have this functionality. The analysis is therefore less easy to access. In addition, for analysis to be effective samples may have to be polished to an ultra-smooth surface, increasing sample preparation time, and potentially limiting the application on very degraded samples (Fromm et al., 2003).

3.6 Discussion and summary

An assessment of the physical condition of a wooden object is critical for assessing how it will behave during conservation or drying, and as such is an important part of the assessment procedure prior to and during excavation. Standardisation using assessment indices (e.g. Van de Noort et al., 1995), and thorough documentation (e.g. Milner et al., 2018) provide an opportunity to compare artefacts between excavations and keep a more accurate record of the levels of preservation.

Indices such as Umax and density are well-established and commonly applied in the conservation laboratory. In many cases, these cheap and accessible methods provide sufficient information on wood preservation to inform a conservation strategy (Grattan and Mathias, 1986; Hoffmann and Jones, 1990). However, the errors and insensitivity inherent in these indices have also been widely acknowledged, suggesting that they are inadequate for obtaining a clear picture of the rate and mechanisms of wood decay (Hoffmann and Jones, 1990; Panter and Spriggs, 1997; Babiński et al., 2014). Increasingly, researchers advocate that a full range of physical analyses needs to be applied to provide a reliable assessment, as single analysis methods can be misleading (Macchioni et al., 2012; Babiński et al., 2014). In particular, some measurements may be influenced by other parameters; for example Umax can be artificially lowered by a high ash content (Section 0) or by the collapse of cell walls (Macchioni et al., 2018).

Microscopic analysis is often used as a complementary assessment to preservation indices (Tamburini et al., 2017). Light microscopy is easily accessible and routinely performed, whilst using more advanced electron microscopy methods provides more detail on the nature of wood decay. Whilst critical in advising conservation treatments or a broad picture of preservation, microscopic methods are not fully quantitative and therefore are not ideal for tracking changes in preservation. A more quantitative approach to assessing the chemical composition of archaeological wood can provide greater detail on the mode of deterioration, and a clearer baseline from which to assess future change.

Table 2: Summary of techniques discussed in Section 3: Assessment of morphological preservation

	Technique	Information yielded	Advantage	Disadvantage	References
3.1 Physical evaluation	Visual assessment (descriptive approach)	Surface detail; initial assessment of quality	Done during excavation; fast; cheap; accessible	Difficult to standardise; difficult to accurately describe appearance; reveals only superficial (surface) preservation	Various older site reports
	Scoring systems	Standardised list of visual preservation indicators; comparative data on surface quality	Can be done in the field; increased level of standardisation; allows comparison across studies	Can still be open to interpretation; requires an experienced wood specialist; reveals only superficial (surface) preservation	Jagels, 1981; Van de Noort et al., 1995
3.2 Advanced visualisation techniques	Advanced photography	3D model from digital photographs; surface detail; shape; surface texture	Widely available; cheap; easy to use	Appearance may not reflect preservation; can still be open to interpretation	Milner et al., 2018
	Laser scanning	Surface quality; shrinkage if done more than once; enhanced surface detail (e.g. cut marks)	Provides a long-term digital record (ideal if artefacts will not be conserved); more detail than photography and/or illustration	Requires specialist equipment and expertise; time consuming; reveals only superficial (surface) preservation	Lobb et al., 2010
3.3 Loss of wood substance	Umax Loss of density Shrinkage	Potential behaviour upon conservation; loss of original material (assumed cellulose); broad indicator of decay	Calculated from easily measured parameters; gives numerical value allowing comparison between studies; cheap; accessible	Lack of consistency between analysts / laboratories; lack of detail on nature of decay; can vary with depth through sample; dependent on wood species	Jensen and Gregory, 2006
	Mechanised decay drill / pin test	Resistance as a measure of density	Accounts for variation with depth; allows comparison	Availability of equipment (for mechanised versions); lack of consistency (pin test)	Panter and Spriggs, 1997
3.4 Non-destructive methods	X-ray scanning / microCT	Provides information on density through the whole structure; can show characteristic decay patterns; techniques can be done using synchrotron radiation for higher resolution	Non-destructive; penetrates into a sample, providing a better analysis of the bulk; microCT provides detailed spatial evaluation; portable versions available; easy data interpretation.	Appropriate calibration required to obtain quantitative analysis; techniques not commonly used to assess state of preservation	Lechner et al., 2013; Sodini et al., 2012

	Ultrasonic testing	Provides analysis of wood density through the entire structure	Fast; portable; non-destructive; suitable for use in water	Complex data interpretation; signal is affected by multiple factors	Zisi and Dix, 2018
3.4 Microscopic analysis of wood structure	Thin-section light microscopy (LM)	Nature of deterioration (primarily biological types); wood species; collapse of wood integrity; loss of cellulose (with polarised light)	Accounts for spatial variations; readily available; cheap	Non-quantitative; requires specialist input; difficulty in preparation of degraded samples	Blanchette, 2000; Daniel, 2016
	UV/ Fluorescence LM	Lignin content (in addition to above information)	As above (and provides additional information)	Less widely available; sample preparation required	Saka and Goring, 1988; Schwarze, 2007
	Scanning electron microscopy (SEM)	Cell wall loss; nature of attack; inclusions; separation of cell walls; fungal spores	Advantages of LM, but with much higher degree of detail; easier on degraded samples than LM	Samples usually must be dry; expensive; not as widely available as LM	Powell et al., 2001; Daniel, 2016
	Environmental SEM		Not under vacuum so sample can be waterlogged	Reduced quality of images compared to normal SEM; less widely available than SEM	Daniel, 2016
	SEM-EDX (or EDS)	As for SEM, but includes elemental composition map; can obtain lignin distribution map if pre-treated	Quantitative; elemental analysis can be important	Less widely available than normal SEM; more expensive instrumentation; more complex data analysis; needs smooth sample surface	Daniel, 2016
	Transmission electron microscopy (TEM)	Examines internal structure	Very high-resolution images	Expensive; complex sample preparation; limited access to instruments and expertise	Daniel, 2016

4 ASSESSMENT OF OVERALL WOOD COMPOSITION

4.1 Acid insoluble lignin (Klason Lignin)

Cellulose components of wood are assumed to deteriorate much faster than lignin (Florian, 1990). Therefore, assessing the relative abundance of both can provide a quantitative parameter of deterioration, with a higher lignin content indicating more advanced decay. Quantification of lignin, cellulose and hemi-cellulose using wet chemical extraction is well established for the study of decay in waterlogged wood (e.g. Hoffman, 1981; Gregory and Jensen, 2006; Macchioni et al., 2012). The method that has been by far the most widely adopted in conservation laboratories is that of gravimetry, also known as 'acid insoluble lignin' or 'Klason lignin' determination (Hoffman and Jones, 1990; Babińksi et al., 2014). Typically, wood extractives (low molecular weight, non-structural compounds) are first removed from a milled sample using a combination of polar and non-polar solvents. Short chain carbohydrates (i.e. degraded celluloses) can then be removed by treatment with 1% sodium hydroxide (in reality this step is often omitted, as it has been shown to produce results contradictory to other analyses and is thought to remove degraded lignin residues as well as cellulose; Grattan and Mathias, 1986). From this 'extractives-free' sample, celluloses are then digested using hot 72% sulphuric acid, leaving behind the acid insoluble lignin (TAPPI, 1996-7). The relative abundance of different wood components can then be calculated from the accurate masses at each stage, from which quantitative indices such as lignin to cellulose (L: C) ratios can be derived.

Gravimetric methods can be viewed as providing a greater insight into wood deterioration than data such as Umax, where it is not necessarily known which component has been lost. In addition, the techniques do not require particularly expensive instrumentation, only access to a well-equipped laboratory. However, the negative aspects of gravimetric analyses are well documented. It has often been found that analysis indicates a composition of over 100%, suggesting a large degree of error (Fengel and Wegener, 1984). This can be attributed in part to the difficulties in handling small samples during multiple filtration steps (Zabel and Morrell, 1992), but studies evaluating different methods of calculating L: C ratios have also demonstrated that gravimetric methods overestimate the amount of cellulose remaining, particularly in modern wood (e.g. Łucejko et al., 2012). This is possibly due to the presence of non-polymeric extractives or short chain carbohydrates, which contribute to the apparent 'non-lignin' component, as well as the presence of inorganic compounds, termed 'ash' (Macchioni et al., 2012; see Section 4.5.1). Zabel and Morrell (1992) also suggest that the harshness of the acid digestion causes degradation of lignin, artificially inflating the cellulose content. This is of particular concern in heavily degraded archaeological woods, where lignin may already have deteriorated to some extent (Gregory and Jensen, 2006).

In a practical sense, gravimetric analysis can be extremely problematic. The use of either dangerous or environmentally damaging chemicals, such as benzene for the removal of wood extractives (e.g. TAPPI, 1996-7) has led several authors to attempt to modify the methods. However, wide variations in composition are observed depending on the solvents used (e.g. Sefara and Birkett, 2004). The procedure can also vary in terms of extraction methods (e.g. soxhlet vs sonication, extraction temperature), digestion times, and sample preparation (e.g. sieving or milling samples) (Ogilvie, 2000). Finally, the significant time required for each analysis (up to 5 days per sample) combined with the large sample quantities required if error is to be reduced, means that gravimetric methods are becoming less frequently used.

Despite the drawbacks it might sometimes be useful to employ gravimetric methods in order to compare with archive data, for example to determine increases in deterioration since previous excavations.

4.2 Lignin content by other chemical methods

Alternative methods of calculating lignin content are regularly used by researchers in fields such as plant ecology, although these are far less widely applied to the analysis of archaeological wood. Moreira-Vilar et al. (2014) compare three methods, including sulphuric acid extraction as described above, and report that large variations are observed between each.

Lignin can be preferentially dissolved (over celluloses) using acetyl bromide or thioglycolic acid and then quantified in solution using absorbance spectroscopy. Both methods involve lengthy preparation, and whilst the thioglycolic method frequently underestimates lignin content, the acetyl bromide method can overestimate it (Moreira-Vilar et al., 2014). However, due to the more straightforward preparation and consistency in analysis, Moreira-Vilar et al. (2014) recommended the acetyl bromide dissolution as the most suitable chemical method of determining lignin content.

4.3 Combustion analysis (CHN(S))

A combustion analysis system can give a measure of the relative carbon, hydrogen, nitrogen (and sometimes sulphur) content of a sample (CHN(S)) (e.g. Wilson et al., 1993). The oxygen content can be derived by correcting for the ash and moisture content, or by using an alternative, less widely available combustion system (see Pinder et al., 2017). As cellulose contains more hydrogen relative to carbon than lignin does, a decrease in the hydrogen content and increase in the carbon content can signal loss of the carbohydrate fraction (Hedges, 1990; Pinder et al., 2017). Oxygen: carbon ratios also decrease with increasing degree of decay, characteristic of preferential preservation of the carbon-rich lignin component (Spiker and Hatcher, 1987). The nitrogen content reflects the protein content (Hedges, 1990).

Elemental analysis by combustion methods requires small amounts of sample (~ 2 mg) and is quick (approx. 20 minutes per sample). However, despite its advantages, the data obtained by CHN(S) analysis is limited, with information of different decay mechanisms impossible to elucidate (Wilson et al., 1993). It must also be noted that percentage compositions can vary depending on the species of the starting material, and the method is also very heavily influenced by the presence of preserving agents, so caution should be used if the conservation history of an object is not known (Pinder et al., 2017).

4.4 Thermogravimetric analysis

In thermogravimetry (TG) a known mass of sample is heated at a constant rate and changes in the sample mass measured using specialist analytical instrumentation. Rapid changes in mass occur, for example when water or non-structural components are lost, and are visualised as steps in a plot of mass loss against temperature (Figure 8). Major benefits of TG are the small sample size required (~ 5mg; Cavallaro et al., 2011) and the fast analysis (a series of samples can be loaded into an automated instrument, with an approx. 60 min analysis time each). Instrumentation is also often commonly available in environmental or chemical research laboratories.

The application of TG to the analysis of waterlogged archaeological wood has been demonstrated by several studies (e.g. Campanella et al., 1991; Cavallaro et al., 2011; Romagnoli et al., 2018). Significant changes in the thermal activity of waterlogged wood occur first when water is lost (allowing the calculation of water content) followed by the loss of non-structural components, cellulose, and finally lignin, with the remaining mass representative of inorganic content (Campanella et al., 1991; Figure 8). The mass loss at each step can be related back to the starting mass, allowing quantitative calculation of the chemical composition. This provides the same information as chemical extraction followed by ashing (Section 4.5.1), but in a much faster process and using a much smaller sample.

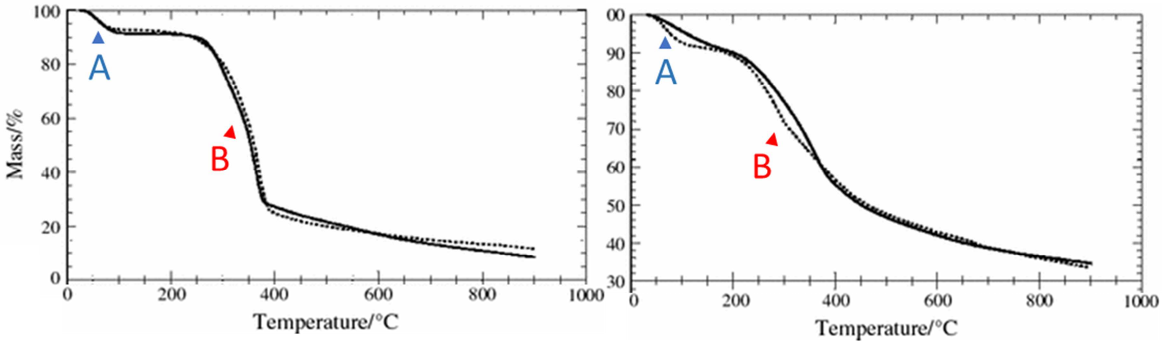


Figure 8: Plots of mass loss against temperature for modern (left) and archaeological (right) wood, obtained by TG analysis. The dotted lines represent pine, and the solid lines represent beech. The slope indicated by 'A' indicates loss of water, and the slope at 'B' relates to cellulose loss. The slow mass loss after 400°C is caused by lignin loss, and any remaining mass after 900°C is inorganic, or 'ash' components. Adapted from Cavallaro et al., 2011 with permission from Springer, copyright 2011.

Despite the advantages, TG analysis has not become a common method for preservation assessment of archaeological wood. Instead, it tends to be applied more for the assessment of the success of conservation methods, as it can be used to determine the extent to which conserving agents such as PEG have bound to the wood (Donato et al., 2010). Romagnoli et al. (2018) recently assessed TG alongside traditional methods of preservation assessment (Umax and density) and highlighted difficulties in its application, including the lack of clear transitions in archaeological data, assumedly caused by the presence of already degraded polymers. They concluded that more studies need to be carried out in order to ensure its reliability for the assessment of archaeological wood. A comparison with chemical extraction followed by ashing in a furnace similarly concluded that there were difficulties in interpreting the cellulose and lignin content (Tomassetti et al., 1987). However, the ash content could be determined with much greater precision than using traditional methods.

4.5 Analysis of inorganic components

An increased level of inorganic components (such as iron sulphides, phosphates and calcium) is often observed in archaeological wood when compared to fresh wood (Grattan and Mathias, 1986; Hedges, 1990). This is more pronounced in wood from marine contexts, but is also observed on terrestrial sites, where interaction with the burial environment leads to the incorporation of various compounds (e.g. Macchioni et al., 2012).

As they contribute to the total mass, the presence of inorganic components causes errors in measurements such as wood density, Umax, and chemical composition measured by wet chemical methods (Hedges, 1990; Macchioni et al., 2012). This is particularly notable in timbers from marine environments, where high levels of chloride will alter the density of the artefact (Oron et al., 2016). Inorganic salts have also been observed to increase the dimensional stability of a sample, leading to reduced shrinkage upon drying (Oron et al., 2016).

The identification of inorganic components is critical for predicting the success of conservation treatments and the possible effects of long term storage; for example, a build-up of iron sulphides (pyrite), particularly in artefacts from marine environments, is well known to cause problems of high acidity when exposed to air (e.g MacLeod and Kenna, 1990; Almkvist and Persson, 2011). The presence of sulphur compounds is often also associated with microbial deterioration, so can be indicative of certain mechanisms of decay (Fors et al., 2012). Crystallisation of inorganic salts upon drying, either post-excavation or due to loss of waterlogging in the burial environment, can lead to structural damage within timbers (MacLeod and Kenna, 1990; Sandström et al., 2001).

The analysis of inorganic components is therefore often a vital component of preservation assessment. Methods of determining the exact structure of inorganic components rely on instrumental techniques (e.g. X-ray analysis, Section 5.5; ICP-AES, Section 5.7). However, basic quantification can aid in the correction of other analytical data and provide a qualitative comparison of inorganic content between samples.

4.5.1 Ash content

The inorganic content of archaeological wood is most often determined by burning a known mass of wood at 600 °C (TAPPI, 1996-7). This process removes all organic components, leaving behind an ‘ash’ composed of oxidised inorganic compounds, which can then be weighed to provide a percentage ash composition, often termed ‘mineral content’ (Hedges, 1990; Shen et al., 2018). An alternative method of determining the ash content is to use TG analysis (see Section 4.4).

Determination of ash content does not reveal the chemical composition of the ash but is often sufficient in allowing the correction of other analytical methods (Tamburini et al., 2017). If necessary, the composition of this ash can be further analysed, for example by chemical extraction or instrumental methods suitable for elemental analysis (e.g. Giachi et al., 2003; see Section 5).

4.5.2 X-ray fluorescence

The quantification of trace elements in wood can be carried out using X-ray fluorescence (XRF; Sandak et al., 2014). XRF is increasingly used in heritage applications due to the ease of application, wide availability of instruments, and range of applications. It is an ideal technique for use in the field as some instruments are largely portable (Tuniz et al., 2013) and data outputs are immediate (Sandak et al., 2014). XRF measurements are made across the surface of a sample, recording the concentration of various elements. In wooden artefacts, the depth of penetration of contaminants can be determined if a core is extracted and analysed along its depth (an analysis usually performed in the laboratory; Fors et al., 2012; Figure 9).

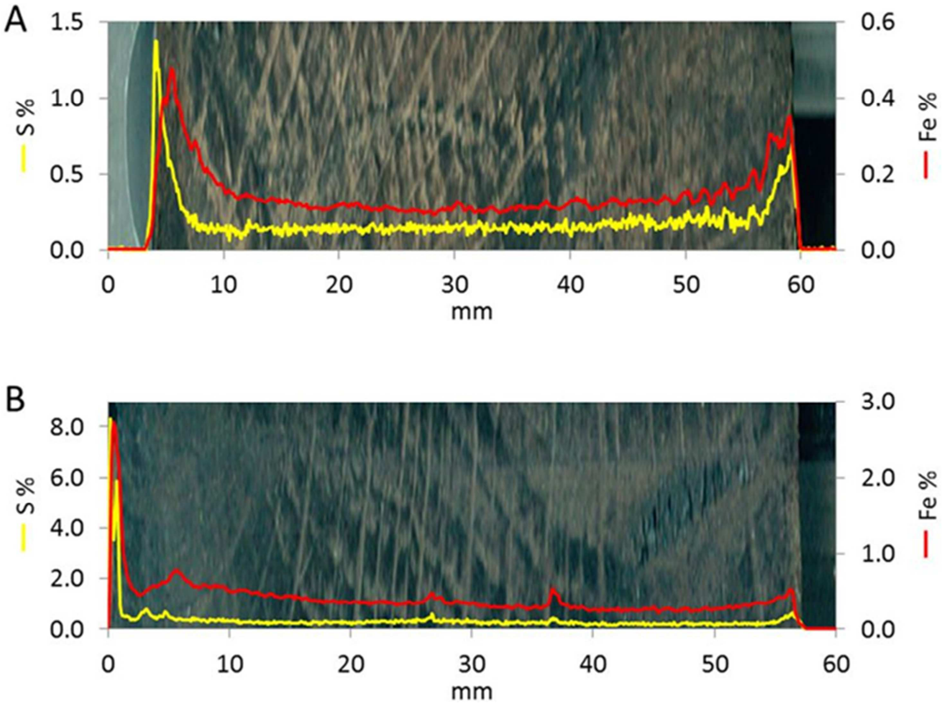


Figure 9: XRF scans of two wood samples from the Sword shipwreck. The concentrations of both sulphur and iron have been measured across the artefact surface, providing spatial analysis. Higher concentrations of both elements were observed on the outer surfaces. Reproduced from Fors et al., 2014 under a creative commons licence.

The identification of these trace elements is important in certain cases (for example in informing specialist conservation requirements). However, XRF is less useful for assessment of organic components and does not allow an assessment of the lignin and cellulose itself.

4.5.3 Microscopic analysis

Inorganic components and crystal formations can be identified using SEM (Pinder et al., 2017; Section 3.5.2). Elemental analysis of these inclusions using SEM-BSE or SEM-EDX can reveal the presence of elements such as Cl, Na, Mg and Zn and allow confirmation of their chemical structure (Almkvist and Persson, 2011). The advantage of applying microscopic methods is that they can also be used to evaluate deterioration in the wood itself (Section 3.5), and therefore contribute to a more comprehensive analysis. However, analysis is not quantitative, and as such should be considered alongside a method such as determination of ash content.

4.6 Discussion and summary

Establishing the relative quantities of lignin, cellulose, and inorganic components in archaeological wood offers a more quantitative analysis of the degree of degradation than physical and microscopic assessment. Analysis of compositional changes, for example alteration of L: C ratios and increased ash content, provides information on which components have been lost and to what degree. The techniques discussed here also tend to be widely available and require minimal expertise or specialist equipment, generating easily interpreted comparative data. Many are also very familiar and have a long history of use for the assessment of archaeological wood.

However, in general there is a lack of detailed information from these methods on the mode of decay (e.g. chemical vs biological). Interpretation of compositional changes relies on certain assumptions, particularly that cellulose decays before lignin. Compositional changes also need to be interpreted in the context of the starting composition, for which the wood species should be known, and this is not always possible in highly degraded material. The biggest limitation of determining compositional changes is in cases where cellulose has been completely lost. In these cases, modification to the lignin needs to be assessed in order to identify further changes to the state of preservation over time. In cases where a more detailed assessment is needed, methods can be applied which allow the identification of minor changes to the chemical structure of the wood, usually involving advanced analytical instrumentation.

Table 3: Summary of techniques discussed in Section 4: Assessment of changes in wood composition.

	Technique	Information yielded	Advantage	Disadvantage	References
4.1 Acid insoluble lignin	Klason lignin	Relative chemical composition of extractives, carbohydrates and lignin in wood	Numerical values allows comparison; well-established technique; cheap; more detail than loss of wood substance	Time consuming; large degree of error (particularly carbohydrate content); potentially dangerous chemicals; too harsh for heavily degraded samples	Zabel and Morrell, 1992; Gregory and Jensen, 2006
4.2 Lignin content (other methods)	Acetyl bromide extraction	Lignin content	Less dangerous than Klason Lignin; more straightforward preparation	Time-consuming; can overestimate lignin content; less commonly used for wood	Moreira-Vilar et al., 2014
	Thioglycolic acid extraction	Lignin content	Less dangerous than Klason Lignin; more straightforward preparation	Time-consuming; can underestimate lignin content; less commonly used for wood	Moreira-Vilar et al., 2014
4.3 Combustion analysis	CHNS composition	Provides relative concentrations by mass of CHN (and S)	Straightforward data interpretation; readily available	No structural information; large amounts of sample required; oxygen content not directly analysed	Hedges, 1990; Spiker and Hatcher, 1987
4.4 Thermogravimetric analysis	Thermo gravimetry	Rapid changes in mass when heated, related to different structural components	Small sample size; relatively fast (compared to extraction and combustion)	Less familiar than many techniques; requires specialist equipment	Campanella et al., 1991
4.5 Analysis of inorganic components	Ash content by combustion at 600°C	Identifies relative amount of inorganic components, a critical parameter for correcting many other analyses.	Widely used; straightforward analysis; quantitative; ease of data interpretation	Does not give detailed elemental composition	Hedges, 1990
	X-ray fluorescence	Elemental composition; can scan an object, for example a core taken from a wooden object	Non-destructive or small sample sizes; easy data interpretation; wide availability	May not detect low concentration contaminants	Sandström et al., 2001
	Electron microscopy – EDX or EDS	Elemental composition map on SEM image; can obtain lignin distribution map if pre-treated	Can conduct simultaneous SEM analysis; spatial analysis; more detailed information	More expensive; less widely available than normal SEM; requires expertise	Almkvist and Persson, 2011

5 ASSESSMENT OF CHANGES AT THE MOLECULAR LEVEL

5.1 Introduction

As heritage science research becomes increasingly multidisciplinary and collaborative, advanced methods of chemical analysis are becoming more widely available. As a result, studies into wood deterioration now often utilise a combination of the more well-known methods of physical, microscopic and bulk chemical analysis alongside analysis using specialist analytical instrumentation, which can provide greater detail regarding the mechanisms of decay (e.g. Wilson et al., 1993; Oron et al., 2016; Tamburini et al., 2017).

Łucejko et al. (2015) provide an excellent review demonstrating the value of applying techniques such as spectroscopy, mass spectrometry, and chromatography to the study of changes in archaeological wood on a molecular level. They highlight the main benefits of such analysis being the (often) small sample sizes and minimal sample preparation required, making them attractive alternatives to wet chemical methods. Instrumental techniques (and in particular using a combination of approaches) can reveal detailed information on degradation pathways and the chemical structure of wooden artefacts. This has a great advantage in cases where, for example, small changes in artefact condition during *in situ* preservation, storage, or museum display need to be monitored (Brunning et al., 2000; Pinder et al., 2017).

However, it must be noted that limited availability of both the instrumentation and the expertise required to interpret the data from these techniques is often a barrier to their routine use. There are also financial concerns which are not always adequately justified by the additional information provided. Molecular analysis of chemical modifications does not always simply translate into a “degree of degradation”; further interpretation is required. The lack of familiarity and widespread use of these techniques in the wider heritage science community can also complicate the interpretation of data and limit the ability to compare between studies.

The range of instrumental and molecular analysis applied to the study of archaeological wood is vast. In this review, some of the more common and increasingly used ones are discussed in terms of the information they yield, and the practical considerations involved in their application.

5.2 Fourier transform-infrared spectroscopy

Spectroscopic analytical methods exploit the fact that molecules absorb specific frequencies of light depending on their chemical structure. In Fourier transform infrared spectroscopy (FTIR), the absorption of infrared light by a material is used to infer information about the presence or absence of certain chemical bonds and functional groups. FTIR is semi-quantitative, as relative concentrations of these groups are reflected by the relative intensities of the associated peaks.

FTIR has long been used to assess ligno-cellulosic materials in the wood, paper, and pulp industries (e.g. Faix et al., 1991; Pandey and Pitman, 2003). Traditionally, IR light needed to be transmitted through a sample, requiring preparation in a potassium bromide (KBr) matrix prior to analysis, demanding expertise, time, and large quantities of sample. However, the development of FTIR spectrometers fitted with an attenuated total reflectance (ATR) unit means that it is now possible to directly analyse a sample with no prior preparation, reducing both the time and quantity of sample required (analysis can now be performed in a matter of minutes using < 10 mg of air-dried wood). As such, the technique has been increasingly adopted for use in the conservation and archaeological science laboratories (Gelbrich et al., 2008; Tamburini et al., 2017).

Whilst analysis of wood by ATR-FTIR is straightforward in a practical sense, the complexity of the material can mean that interpretation of the data can vary greatly. In addition, only a very small part of the sample is being measured (a factor common to most instrumental methods, and one that needs to be considered in a sampling strategy). In FTIR this effect is exacerbated by the very small depth of penetration (0.5- 3 μm) meaning that only the surface of a sample is really being analysed. However, the low cost and speed of analysis means that these issues could be resolved by analysing samples from multiple locations across an object.

Despite the downsides, FTIR analysis is an attractive alternative to the much more laborious method of chemical extraction, and theoretically more accurate than loss of wood substance indices.

5.2.1 Peak assignment

Interpretation of an FTIR spectrum requires first assignment of the peaks (sometimes referred to as bands) to the functional groups that they represent. These can then be attributed to the different components of wood. Whilst most FTIR absorbance peaks contain contributions from each polymer, some can be attributed to solely lignin, cellulose or hemi-cellulose and can therefore be examined to provide information on the relative abundance of each (Rodrigues et al., 1998; Pandey and Pitman 2003; Gelbrich et al., 2012b). Changes in the relative composition compared to fresh wood indicate the degree of decay, and comparing different peaks within the same spectrum makes this semi-quantitative, lending the ability to compare between samples. Although peak assignments have varied between studies, a cross reference of literature sources shows that certain peaks can be confidently assigned (Table 4).

However, the position of some peaks can shift to a different wavenumber depending on wood species, with hardwood and softwoods in particular having quite different spectra (Rodrigues et al., 1998). Prior knowledge of the wood species is therefore helpful in correctly interpreting spectra. The presence of inorganic salts such as gypsum and pyrite may lead to additional absorption peaks, further complicating spectra (Genestar and Palou, 2006). Pizzo et al. (2015) also demonstrate that signals attributed to non-structural compounds such as lipids and pectins (extractives) may overlap with those attributed to structural components, greatly influencing the apparent intensity of peaks related to cell wall material. In practice, assigning peaks in archaeological wood can be extremely challenging, as the spectrum of an archaeological sample can look completely different to a modern standard.

Table 4: Typical peak assignments for FTIR spectra of angiosperm wood (hardwood). Peaks attributed to more than one component can rarely be used for quantification of their relative composition.

cm^{-1}	**Assignment**	**Component**	**Reference**
898	C-H deformation	Cellulose	Pandey and Pitman, 2003; Rodrigues et al., 1998; Faix and Böttcher, 1992
		Low MW carbohydrates	Wilson, 1993
1040	C-O stretch	Cellulose / hemicellulose	Pandey and Pitman, 2003; Rodrigues et al., 1998; Faix and Böttcher, 1992
1158-1162	C-O-C vibration (identified at 1116 by Emandi et al., 2011)	Cellulose / hemicellulose	Pandey and Pitman, 2003; Rodrigues et al., 1998; Faix and Böttcher, 1992
	C-O vibration	Lignin and xylan	Emandi et al., 2011
1230	C-O stretch (methoxy)	Lignin, some hemicellulose contribution	Pandey and Pitman, 2003; Emandi et al., 2011
		Cellulose	Rodrigues et al., 1998
1268	C-O stretch (ring) and methoxyl groups	Lignin	Pandey and Pitman, 2003; Emandi et al., 2011
1325	C-H and C-O vibrations	Cellulose, syringyl groups in lignin	Pandey and Pitman, 2003; Emandi et al., 2011
	C-O vibrations	Syringyl groups in lignin	Rodrigues et al., 1998; Faix and Böttcher, 1992
1375	C-H deformation	Cellulose / hemicellulose	Pandey and Pitman, 2003; Rodrigues et al., 1998; Emandi et al., 2011; Faix and Böttcher, 1992
1425	C-H deformation	Cellulose and lignin	Pandey and Pitman, 2003; Rodrigues et al., 1998
1462	C-H deformation	Cellulose and lignin	Pandey and Pitman, 2003; Rodrigues et al., 1998
1505	C=C aromatic	Lignin	Pandey and Pitman, 2003; Rodrigues et al., 1998; Faix and Böttcher, 1992
1596	C=C aromatic	Lignin	Pandey and Pitman, 2003; Rodrigues et al., 1998;
	Conjugated C-O vibration	Lignin	Emandi et al., 2011
1738	C=O xylans	Hemicellulose	Pandey and Pitman, 2003; Rodrigues et al., 1998

5.2.2 Loss of cellulose

Many wood characterisation techniques assume that cellulose is degraded before lignin, resulting in an elevated lignin: cellulose (L: C) ratio compared to fresh wood. L: C ratios (derived from the intensity of the FTIR peaks) are perhaps the most commonly employed parameter in FTIR studies of archaeological wood (Gelbrich et al., 2008; Emandi et al., 2011). L: C ratios calculated from FTIR spectra have been shown to correlate well with those calculated by chemical extraction (Gelbrich et al., 2012b). Ratios can be calculated from either the peak heights or areas, of two or more of the assigned peaks. The peaks used vary between studies, although most use the characteristic aromatic ring peak at 1505 cm^{-1} as a reference from which cellulose content can be calculated using the peaks at 1375 and / or 898 cm^{-1} (Rodrigues et al., 1998; Emandi et al., 2011; Table 5).

Table 5: Summary of commonly used equations to calculate L: C ratios from FTIR data, taken from a review of literature sources. (H) indicates that peak heights were used, (A) indicates the use of peak areas.

Parameter	**Information given**	**Reference**
1505/1158	Lignin skeleton: cellulose and hemi-cellulose	Rodrigues et al., 1998 (H); Pandey and Pitman, 2003 (H, A)
1505/1375	Lignin skeleton: cellulose and hemi-cellulose	Pandey and Pitman, 2003 (H, A); Emandi et al., 2011 (A)
1505/1738	Lignin skeleton: xylan ratio	Pandey and Pitman, 2003 (H, A); Faix et al., 1991 (H)
1505/898	Lignin skeleton: cellulose	Pandey and Pitman, 2003 (H, A)

The peak at 1738 cm^{-1} is attributed to the C=O groups in xylan (a type of hemi-cellulose) and is often observed to have decreased in intensity or even been lost completely before significant cellulose loss has occurred (Oron et al., 2016). Changes to this peak, caused either by total loss of xylans or oxidation of the C=O groups, can therefore be indicative of the very early stages of decay. The C-O-C related band at 1024 cm^{-1} can also significantly alter with increasing degradation (Figure 10). This is attributed to cellulose hydrolysis leading to increased concentrations of carbonyl groups (Durmaz et al., 2016).

In practical terms, L: C ratios are much easier to calculate using FTIR than chemical extraction. However, the analysis does not give detailed chemical information on any residual cellulose component (Faix et al., 1991). In cases when this is required, a more comprehensive analysis might be necessary, for example py-GC (Section 5.3) or NMR (Section 5.4). In addition, assigning peaks and accurately calculating heights and areas can be difficult in a complicated spectrum with overlapping peaks (Lansley et al., 2018).

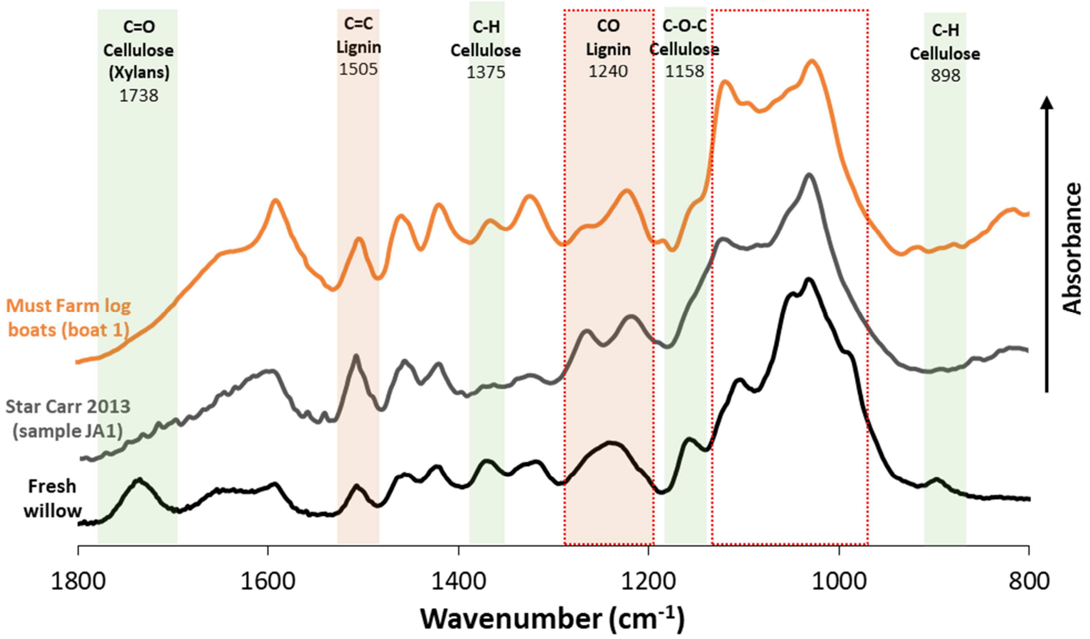


Figure 10: Stacked FTIR spectra for modern untreated willow compared to heavily degraded wood from Star Carr and moderately degraded wood from Must Farm (author's own data). Commonly used diagnostic peaks relating to cellulose (green) and lignin (red) are highlighted. Whilst degradation can be indicated by relative changes in intensity of these peaks, peak shapes can also change (highlighted by red dotted box). These differences are less easy to quantify but are nevertheless diagnostic of changes to the molecular composition.

5.2.3 Lignin deterioration

There is an increasing awareness that lignin deterioration can occur alongside cellulose deterioration, challenging the assumption that L: C ratios alone are a good indicator of preservation (Faix et al., 1991; Filley et al., 2002). Other situations where L: C ratios may not be sufficient include cases where cellulose has already been completely degraded, or where small changes need to be evaluated. Whilst a more comprehensive view of lignin deterioration can be achieved with more sensitive instrumental methods, some studies demonstrate that FTIR analysis can also highlight alteration of lignin (Faix et al., 1991; Gelbrich et al., 2012b).

Lignin deterioration is complex and dependent on the cause of deterioration, but several broad indicators of decay have been identified (see Figure 13). During bacterial degradation, methoxyl groups are removed (Filley et al., 2002). This can be observed by an increased intensity of the lignin skeleton peaks (1505 / 1596 cm^{-1}) compared to the lignin functional group stretches (1230 / 1268 cm^{-1}; Faix et al., 1991; Gelbrich et al., 2012b). Whilst in undegraded wood the peaks at 1230 and 1268 cm^{-1} appear as one broad peak, increasing degradation of lignin results in the separation of these two peaks (Pandey and Pitman, 2003; Figure 10). Durmaz et al. (2016) also report a shift of the peak at 1268 cm^{-1} to 1264 cm^{-1} with increasing degradation, as well as an increase in intensity of the C-H peaks in lignin at 1425 and 1462 cm^{-1}.

The loss of aromatic rings can theoretically be identified by loss in intensity of the aromatic absorbances (1505 / 1596 cm^{-1}). However, these peaks are usually used as internal standards, so this is difficult to assess by comparison with other peaks. In cases where lignin is deteriorated before cellulose, lignin content is therefore often underestimated by FTIR analysis, as the decrease in intensity of these peaks is not perceived (Faix et al., 1991).

5.2.4 Data collection and interpretation

Treatment of data to derive a measure of deterioration can differ greatly between studies, potentially making it difficult to directly compare data. In some cases, spectra are smoothed, normalised or baseline corrected prior to evaluation (Rodrigues et al., 1998; Pizzo et al., 2015), whereas in others spectral manipulation is kept to an absolute minimum (Traoré, 2016; High et al., 2018b). The method of calculating peak areas can also vary: Pandey and Pitman (2003) derive peak areas by drawing a baseline between the minima either side of the peak and measuring the distance to the top of the peak, whereas Rodrigues et al. (1998) measure from the peak minimum to the peak maximum (Figure 11). Some researchers have suggested that comparing the overall area of a cluster of peaks removes the difficulties encountered in accurately assigning peaks which are significantly altered from modern standards (Lansley et al., 2018). A robust investigation of the potential effect of these differences is currently lacking; however, analysts should be aware of these differences when comparing data between studies.

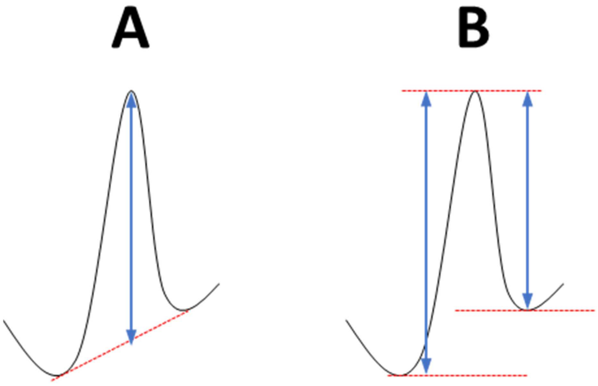


Figure 11: Schematic indicating how methodologies for calculating peak heights can vary (e.g. A by Pandey and Pitman, 2003; B by Rodrigues et al., 1998). Values obtained from each will also vary depending on data manipulation methods such as peak normalisation. In method A the placement of the baseline is critical; method B suffers from lack of consistency in whether heights are calculated from the baseline to the left or the right of the peak.

Whilst most studies combine an analysis of peak ratios with visual identification of changes in the spectra, researchers are increasingly employing chemometric methods (such as partial least squares modelling or multivariant analysis) to model changes in the entire spectrum (Ferraz et al., 2000; Pizzo et al., 2015). As most of the peaks in an FTIR spectrum of wood contain contributions from more than one polymer, taking this statistical approach to quantify overall changes can better discriminate between wood with varying degrees of deterioration (Ferraz et al., 2000). Whilst statistical analyses require expert input as well as suitable software, if applied correctly these methods can easily help identify outliers, as well as characterising differences in chemical composition between samples (Ferraz et al., 2000; Carballo-Meilan et al., 2014).

Although FTIR analysis using an ATR unit can be performed directly onto the surface of a sample, some studies report milling samples to provide a better contact with the crystal window (Durmaz et al., 2016). This also homogenises the sample, meaning that it is (slightly) more representative of the artefact. Some studies analyse wet samples, minimising sample preparation time and the potential for further chemical changes caused by drying methods (Oron et al., 2016). However, as the presence of water can obscure some of the FTIR peaks, drying samples prior to analysis is more common (Rodrigues et al., 1998; Pecoraro et al., 2015; Traoré et al., 2016). Although Faix and Böttcher (1992) recognised the importance of a standard particle size for FTIR spectra obtained using the KBr technique (as well as highlighting a need for standardised approaches in data manipulation), similar studies comparing the effect of these differences in FTIR-ATR experiments are lacking.

5.2.5 Advanced infrared techniques

FTIR analysis typically focuses on the wavelength range of 2-25 μm; a variation of the technique is near infrared spectroscopy (NIR) which utilises light in the 1-2.5 μm region. The higher energy light exploits different vibration states within a molecule, thus providing different but complementary structural information (Pasquini, 2003). NIR retains many of the practical advantages of mid-IR spectroscopy, and whilst the spectra can be more complicated the light penetrates much deeper into a sample, thus providing a slightly better representation of the bulk (Pasquini, 2003; Pecoraro et al., 2015). Due to the complexity of NIR spectra, statistical methods are normally employed to distinguish differences between samples (Pecoraro et al., 2015). NIR spectroscopy tends to be less well established in the analytical laboratory, and therefore it is as yet a less accessible technique than FTIR.

FTIR microscopy offers the ability to record multiple spectra across the surface of a sample as it is viewed under a microscope (Emandi et al., 2011). FTIR microscopes are far less widely available than ordinary FTIR spectrometers due to the much greater cost. However, they provide a spatial dimension to the analysis which can be valuable in certain situations. FTIR microscopy also allows the analysis of much smaller samples, if this is required.

5.3 Pyrolysis gas chromatography

Pyrolysis coupled with gas chromatography (py-GC; sometimes termed Curie-point py-GC) is a technique where a sample is exposed to high temperature (> 500°C) in the absence of oxygen, breaking the constituent polymers into small fragments via thermal cleavage. These sub-units are then separated based on their mass and chemical nature using GC, generating a chromatogram characteristic of the concentrations of various fragments (building blocks) of each polymer present (Hatcher et al., 1995; van Bergen et al., 2000). Fragments are identified using either flame ionisation detection (FID) or mass spectrometry (MS).

Py-GC provides a semi-quantitative analysis of wood degradation products as well as intact polymers, thus yielding a greater depth of information about wood decay than techniques which focus only on changes in the relative abundance of different polymers (e.g. Vinciguerra et al., 2007). Compared to FTIR, py-GC provides a more sensitive analysis; much more subtle changes to the polymeric structure can be detected. This depth of information is valuable in particular scenarios, for example when detecting very small changes in molecular composition during periods of storage, conservation or preservation *in situ* (Pinder et al., 2017; High et al., 2018b), or in trying to determine the exact source of degradation (Filley et al., 2002). There is also evidence that detailed analysis could allow the determination of wood species or element (Challinor, 1995; Traoré et al., 2017). Analysis by py-GC is also reproducible (Łucejko et al. (2012) report a standard deviation of 10% from four replicates). It requires minimal sample preparation and only a very small amount of sample (approx. 100 µg; Tamburini et al., 2017).

The major factors limiting the routine use of py-GC analysis in the cultural heritage sector are: analysis requires substantial expert input, long analysis times (typically between 40 minutes and two hours per sample compared to only minutes for FTIR analysis (Łucejko et al., 2015; Pinder et al., 2017)), and it is more expensive than many other routinely used techniques in terms of both the initial cost of instrumentation as well as the ongoing maintenance. There are also limitations to the data obtained; as the polymeric structure is broken down during pyrolysis, the degree of overall polymerisation is not obtained (this is instead inferred from the resultant fragments; Zoia et al., 2017). Furthermore, Wilson et al. (1993) highlight that variations in data can be observed between different analytical systems. Despite these drawbacks, py-GC is becoming increasingly used for the examination of archaeological wood, either on its own or as part of a multi-analytical study (Łucejko et al., 2012; Tamburini et al., 2014; Traoré et al., 2017).

5.3.1 Sample preparation

Dry wood samples can be analysed by py-GC with minimal preparation. However, milling or grinding the sample to a powder is often necessary to facilitate weighing into the small (approx. 2mm internal diameter) quartz crucible used for pyrolysis (Pinder et al., 2017). Some studies remove non-wood related components via solvent extraction prior to analysis, which results in less complex chromatograms (van Bergen et al., 2000). Another advantage of including this step is that non-wood components can be retained and analysed separately, although in many cases the usefulness of this additional information would be limited (Colombini et al., 2007). A faster method of removing non-polymeric components prior to analysis is to include a thermal desorption step by heating the sample to approx. 300°C (Pinder et al., 2017). However, it must be considered that highly degraded structural components could also be removed during this process.

Derivatisation is the process of transforming analytes into more reactive or more easily detectable compounds prior to analysis and is commonly used in chromatography. For py-GC, derivatising agents can be added to the wood sample in the analysis crucible and as such, total analysis time is not significantly extended. Co-pyrolysis of wood with tetramethylammonium hydroxide (TMAH) causes methylation of the pyrolysis products (Challinor, 1995). This results in products that are more directly attributable to the polymer structure, and in theory should provide a more sensitive analysis, for example suitable for the identification of wood species (Challinor, 1995). An alternative derivatisation method using hexamethyldisilizane (sylation) has been demonstrated to intensify the analytical response of sub-units and improve reproducibility when used with mass spectrometric detection (Colombini et al., 2009; Łucejko et al., 2012). Zoia et al. (2017) declare sylation a critical step in ensuring that polar compounds can be detected. However, accurately interpreting the data obtained from derivatised material arguably requires a more in-depth knowledge of wood chemistry. In addition, derivatisation is sometimes only partially complete, resulting in even more complex chromatograms (Colombini et al., 2009).

As with FTIR, when such a small amount of sample is used attention needs to be paid to where the sample is taken from, as great variations in preservation can be observed through a sample (Challinor, 1995). However, the small sample sizes provide the opportunity to simply sample in more locations.

5.3.2 Data analysis

Following separation by GC, products of the combustion process can either be detected by flame ionisation detection (py-GC-FID) or mass spectrometry (py-GC-MS). Each has advantages and both have been used to study the preservation of archaeological wood (Tamburini et al., 2014; Pinder et al., 2017). Pyrolysis products can also be analysed directly by MS without prior separation by GC, although this results in a highly complex chromatogram and is rarely done (Łucejko et al., 2015).

FID is often the cheaper detection method. It is highly quantitative and allows good reproducibility between samples (Pacchiarotta et al., 2010). In comparison, MS detection is determined by the ability of a species to be ionised, and therefore is not fully quantitative and is not capable of detecting all compounds. However, MS detection allows a more confident identification of the different sub-units, as it is based on their molecular mass as well as retention time (Łucejko et al., 2012). In contrast, compounds detected by FID are identified based solely on their retention times compared to standards and published literature, and the complexity of chromatograms obtained from wood can make this difficult.

Following detection, each peak in the spectrum is assigned to a degradation product or sub-unit of either lignin or celluloses (e.g. van Bergen et al., 2000; Traoré et al., 2017). Theoretically, the relative intensity of each peak reflects the abundance of that compound, and changes in the relative intensity of certain compounds can provide information on degradation mechanisms occurring within the sample. Peak areas of each wood degradation product can be calculated, summed if necessary, and percentage compositions derived (Łucejko et al., 2012). This analysis is arguably more accurate using FID data than MS, as the intensity of peaks in MS chromatograms is related to the ability of the compound to be ionised as well as its concentration. This can be corrected for using a 'response factor' if known for that compound, but this difficult to do when multiple compounds are present.

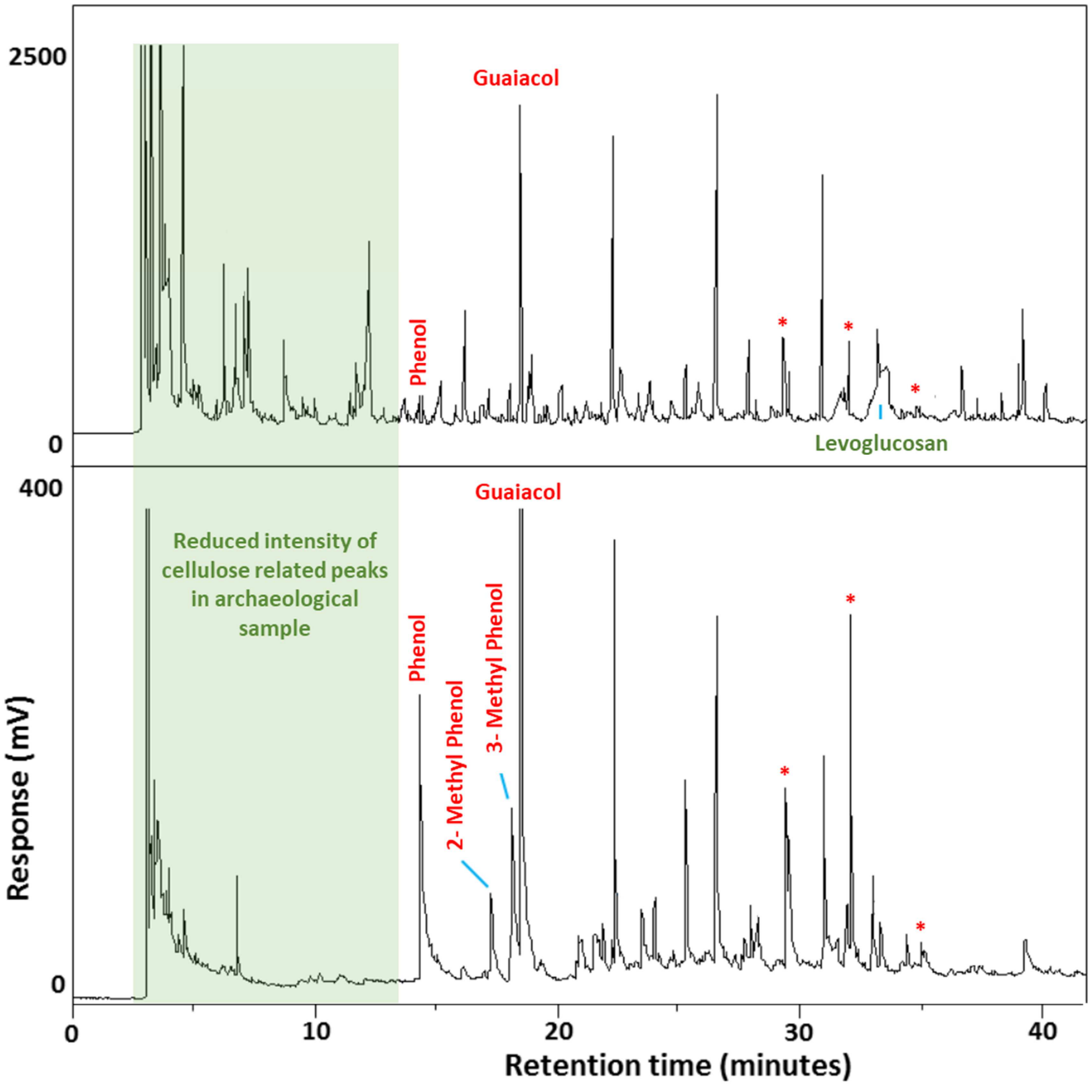


Figure 12: Partial py-GC-FID chromatograms from modern pine (top) and archaeological wood from a heavily decayed archaeological coffin (bottom). A decrease in the relative intensity of cellulose-related peaks at the start of the chromatogram and a decrease in the relative intensity of levoglucosan (a cellulose pyrolysis product) in the degraded sample indicate loss of cellulose. An increased intensity of short chain degradation products (e.g. phenol, 2-methyl phenol and 3-methyl phenol) and an increased intensity of oxidised compounds (*) in the degraded sample signify lignin modification. Image courtesy of Adam Pinder.

5.3.2.1 Cellulose loss

The relative abundance of cellulose-related peaks decreases with increasing wood deterioration (e.g. van Bergen et al., 2000; Tamburini et al., 2014; Figure 12). Łucejko et al. (2012) used GC data to calculate L: C ratios (summing the peak areas of cellulose-related products and lignin-related products) and demonstrated an excellent correlation with cellulose content as determined by wet chemical extraction. This method of calculating L: C ratios has been adopted by other studies and proves a useful parameter for comparing samples (e.g. Braovac et al., 2016;

Zoia et al., 2017). Traoré et al. (2017) show that resistant compounds derived from cellulose can be detected in even the most decayed archaeological samples; these are not observable in FTIR.

Despite this, L: C ratios calculated by py-GC analysis may have little extra to offer when compared to the much faster analysis by FTIR. Rather, the strength of py-GC is the ability to examine structural changes to the lignin, which is somewhat lacking in the techniques discussed thus far.

5.3.2.2 Lignin decay

As cellulose can often be present in only a highly degraded state, or completely absent in some archaeological samples, lignin characterisation may be of the utmost importance (Colombini et al., 2007). Recent research also demonstrates that lignin decay occurs even when cellulose preservation is good, challenging long-held assumptions about the order of decay (Zoia et al., 2017).

Py-GC analysis allows the identification of several key molecular changes that are indicative of decay in lignin. These changes include demethylation (removal of the methoxy groups) of syringyl and guaiacyl sub-units, leading to conversion of syringyl to guaiacyl, and subsequent further conversion to 1,2-benzenediol followed by phenol (van Bergen et al., 2000; Figure 13). Decay is therefore characterised by changes in the relative abundance of these compounds or derivatives of these compounds containing various side chains (e.g. van Bergen et al., 2000; Figure 12).

Preferential syringyl decay (over guaiacyl decay) has been noted by several py-GC studies (Łucejko et al., 2012; Zoia et al., 2017). This has led to the use of a syringyl: guaiacyl (S: G) ratio derived from the sum of all of the peak areas related to each compound, which decreases with increasing wood degradation (e.g. Vinciguerra et al., 2007). An increased concentration of phenol also indicates that parts of the lignin have been defunctionalised (Martinez et al., 2005; Figure 13). Braovac et al. (2016) cite the presence of oxidised products (such as 4-hydroxy benzoic acid in wooden artefacts treated with alum from the Osberg shipwreck) as confirmation of

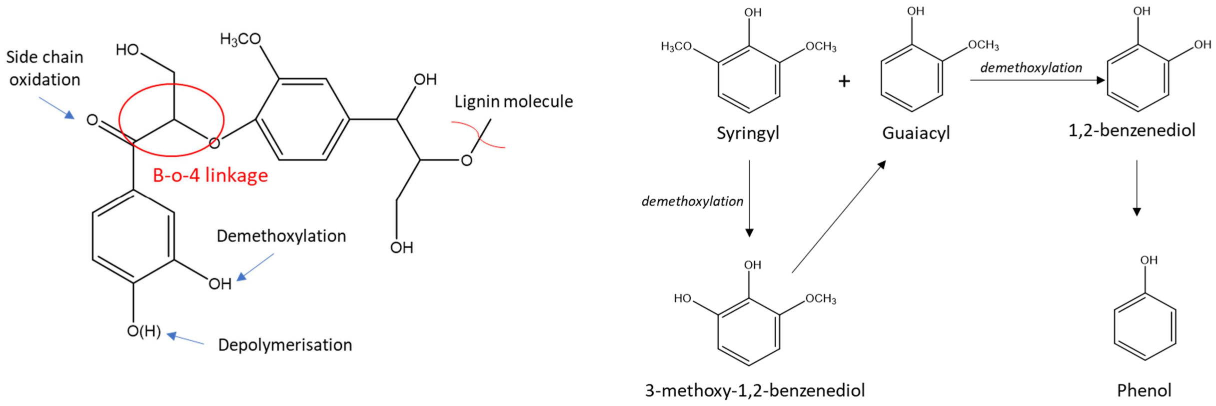


Figure 13: Simplified schematic showing some of the major diagenetic reactions occurring in lignin (left) which result in altered concentrations of different types of sub-units (right) Summarised from various sources including van Bergen et al., 2000 and Filley et al., 2002.

oxidation reaction mechanisms occurring within the lignin structure. Tamburini et al. (2014) interpreted an increased concentration of oxidised sub-unit in wood samples from Roman villas in Herculaneum as demonstrating fungal decay, suggesting that an increase in oxidation products is a valuable marker.

Oxidation of lignin is also identified by an increase in the acid: aldehyde ratio, again calculated by summing the relevant peak areas (Hatcher et al., 1995; Łucejko et al., 2012). An increased concentration of compounds with short side chains compared to those with long side chains also signifies increasing degradation. To quantify these changes, an increasingly common assessment of py-GC data is to group the decay products into types of monomer, for example: short chain, long chain compounds, acids, aldehydes etc., and compare the relative abundance of each (Zoia et al., 2017).

5.3.2.3 Statistical analysis

Several studies have employed principal component analysis (PCA) to better investigate differences between degraded and sound wood (Vinciguerra et al., 2007; Tamburini et al., 2014). In PCA, the amount of variation in peak areas for different samples is plotted in two dimensions, highlighting differences. Vinciguerra et al. (2007) used PCA to assess differences in the chromatograms obtained from both fresh and rotted wood, with significant differences attributed to several different chromatographic peaks (components).

5.4 NMR spectroscopy

Although nuclear magnetic resonance (NMR) spectroscopy has long been used for the structural elucidation of organic compounds, its use for the analysis of archaeological materials was initially limited by the need for samples to be in solution. However, over the past 30 years or so advances in instrumentation have opened up the technique to a broader range of applications.

NMR spectroscopy reveals information about the chemical environments of certain target nuclei (most commonly ^{1}H, ^{13}C and ^{31}P). It can provide information both on the structural and spatial arrangement of organic molecules, making it ideal for the analysis of complex polymers such as those present in wood (Bardet et al., 2009). Whilst proton (^{1}H) NMR requires samples to be in solution and as such is not commonly used for the analysis of wood, ^{13}C NMR has been demonstrated as a valuable technique for the examination of both celluloses and lignin in solid-state archaeological samples (Brunning et al., 2000; Bardet et al., 2002; Colombini et al., 2009). As the field advances, studies applying ^{31}P NMR and 2-dimensional NMR continue to demonstrate the power of NMR analysis to yield detailed information on the changes in polymeric structure as wood deteriorates (Colombini et al., 2009; Zoia et al., 2017).

Similarly to FTIR and py-GC analysis, alteration of the relative peak areas and chemical shifts in NMR spectra indicate alteration of the chemical environments. However, NMR analysis also reveals information on how the various sub-units relate to each other spatially, and the abundance of key linkages. This makes it ideal for examining mechanisms of decay and the degree of polymerisation (Bardet et al., 2009). NMR analysis also penetrates into the core of a sample, in contrast to techniques such as FTIR which examine only the sub-surface (Alesiani et al., 2005). NMR can be quantitative if an internal standard is added; this better allows comparison of data between laboratories and different studies. Another benefit of NMR when carried out in the solid state, is the lack of sample preparation required, meaning it is more likely to reflect the true nature of the sample compared to methods such as py-GC where the preparative or analytical process may cause significant chemical alteration.

The limitations of NMR techniques lie primarily in the lack of availability of appropriate instruments, their expense both initially and in terms of maintenance, and the high-level of expertise required to run them (Hedges, 1990). The complex nature of wood also results in highly complex spectra. As such, assignment of the peaks is not straightforward, and any errors can lead to substantial over or under-estimation of L: C ratios (e.g. Bardet et al., 2002). NMR also requires approximately 25-50 mg of sample (compared to ~ 0.1 mg required for py-GC; Zoia et al., 2017). The technique is usually destructive due to the need to cut the sample to fit into the analysis chamber (a sample of approx. 75 x 30 x 25 mm is typically required; Brunning and Watson, 2010). The influence of contaminants on the NMR spectra also needs to be considered during interpretation (for example, iron is known to cause peak broadening, and non-structural organic inclusions will also cause interference; Bardet et al., 2009).

5.4.1 ^{13}C NMR

The most commonly used type of NMR spectroscopy for the analysis of lignin-cellulosic material is ^{13}C NMR (Wilson et al., 1993; Bardet et al., 2002). Signal enhancement by cross-polarised magic angle spinning (CPMAS) means that samples can be analysed in the solid state: a massive advantage both in terms of sample preparation time and the ability to retain the natural chemical and physical state of the sample. Samples cut to the right size can be analysed whole providing they fit into the instrument. Whilst powdering samples may be more practical in terms of loading into the instrument, this has been observed to cause a reduction in signal intensity (Alesiani et al., 2005). In principle very little starting material is required (4-7 mg; Bardet et al., 2002). However, in practice more material and longer acquisition times are needed to get high enough resolution for quantification. Typically, analysis times range from 10 minutes to several hours, with longer times generating higher resolution data (Hedges, 1990).

Although ^{13}C-CPMAS is generally carried out on untreated samples, preparative methods have been reported to improve the quality of the data. Zoia et al (2017) demonstrate that first removing non-structural components by solvent extraction results in more simplified spectra that are representative of only the structural polymers. It is also possible to first chemically separate the lignin from the cellulose, resulting in a higher resolution assessment of the lignin alone (Colombini et al., 2009). Acetylation (derivatisation) of the material before analysis can improve resolution; however this is a complex process that involves first dissolving the wood in an ionic liquid and treating with acetic acid and pyridine (Crestini et al., 2009). Solubilisation using similar methods can also allow ^{1}H NMR analysis (for example for 2D experiments; see Section 5.4.3) but is highly likely to result in alteration of the chemical structure (Bardet et al., 2009).

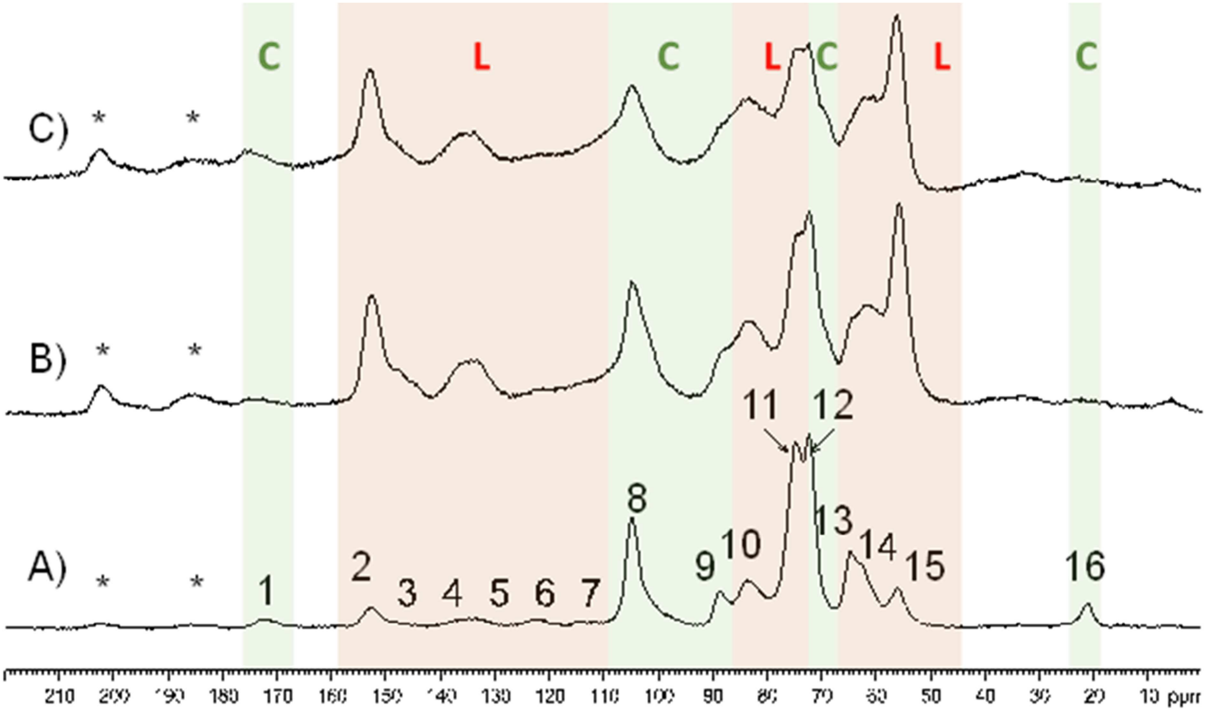


Figure 14: Examples of typical CP-MAS ^{13}C high-resolution solid-state NMR spectra of modern beech (A) and archaeological beech samples with water contents of 82% (B) and 91% (C). Peaks highlighted in green related to the carbohydrate components (C) and those in red relate to lignin (L) (a full assignment can be found in Bardet et al., 2002). An increase in relative intensity of the lignin compared to carbohydrate peaks is observed in the archaeological samples. Signal 16 relates to CH_3 groups in hemicellulose and is completely absent in the archaeological samples. Signal 2 relates to β-O-4 linkages and is retained in all samples. Adapted from Bardet et al., 2002 with permission from American Chemical Society, copyright 2002.

Due to the complexity of spectra, the interpretation of ^{13}C NMR analysis can require a high level of expertise (Figure 14). Assignment of the most abundant peaks and an excellent review of ^{13}C NMR applied to archaeological wood can be seen in Bardet et al. (2009). Comparative heights of certain peaks can be used to derive an L: C ratio, as for other instrumental techniques. However, the strength of NMR is that it can also be used to examine bonds between sub-units in lignin. A typical characteristic of decayed wood is a decrease in abundance of β-O-4 linkages in relation to the methoxy groups with increased lignin degradation (Colombini et al., 2009; highlighted in Figure 13). Colombini et al. (2007) attempted to use NMR to calculate the number of methoxy groups per phenol ring; an overlap in the signals makes this difficult, but the value appears to decrease with increasing degradation. These structural changes are less clearly observed in FTIR and may be destroyed by the pyrolysis process in py-GC.

Despite the benefits, Colombini et al. (2009) highlight that ^{13}C NMR is not sensitive enough to identify all indicative characteristics of lignin decay; in particular, it cannot reveal carboxylic acid and alcohol groups, increases in which indicate oxidative decay. The lack of homogeneity of wood can also cause significant peak broadening even with the use of CPMAS, making it difficult to assign peaks (Alesiani et al., 2005). As with many other instrumental techniques, comparison between modern and archaeological woods by NMR spectroscopy is much improved when the species is known, enabling a like-for-like comparison with modern analogues (Bardet et al., 2009). Colombini et al. (2009) suggest that despite its advantages, ^{13}C NMR should not be used in isolation, but alongside other techniques.

5.4.2 ^{31}P NMR

By first isolating the lignin, solubilising it and derivatising with a phosphating agent, ^{31}P NMR can be used as a complementary analysis to ^{13}C NMR, allowing the identification of a greater range of functional groups (Crestini et al., 2009; Colombini et al., 2009). From ^{31}P NMR spectra, guaiacyl, syringyl, p-hydroxyphenyl, and aliphatic OH groups can be assigned and the relative intensities of each compared. This can be used to quantify changes such as increased concentrations of phenol and carboxylic acid groups with increased levels of oxidative decay (Colombini et al., 2009; Zoia et al., 2017).

The disadvantage of ^{31}P NMR analysis is the intensive sample preparation required, demanding additional expertise. It is possible that the relatively harsh solubilisation steps result in significant alteration of the chemical structure (Bardet et al., 2009). Analysis has typically been carried out only on isolated lignin, meaning that the carbohydrate fraction is not evaluated. However, Zoia et al. (2017) recently demonstrated the use of ionic liquids to solubilise the complete sample, both reducing the opportunity for preparative structural modification and allowing the analysis of all components. Despite these advances, ^{31}P NMR tends to be carried out as part of a multi-analytical approach rather than in isolation (Crestini et al., 2009; Colombini et al., 2009).

5.4.3 2D NMR

Once in solution, it is possible to conduct both ^{13}C and ^{1}H NMR analysis of wood (or isolated lignin) in tandem, providing the benefits in sensitivity of ^{1}H NMR combined with the resolution of ^{13}C NMR (Sette et al., 2011). These ‘2-dimensional’ experiments allow the identification and quantification of additional structural features (such as the different inter-monomeric bonds present), providing a greater degree of structural detail than traditional NMR (Colombini et al., 2009). The two most common types of experiment are: 2-D heteronuclear single quantum coherence NMR (2D-HSQC; Colombini et al., 2009; Zoia et al., 2017) and 2D heteronuclear multiple-quantum correlation (2D-HMQC; Sette et al., 2011). Both produce a ‘map’ where the NMR signals are dispersed along two axis relating to the two different nuclei (^{1}H and ^{13}C), and analysis can be carried out on the same instruments as traditional ^{13}C or ^{1}H NMR experiments (Sette et al., 2011; Figure 15). Other 2-D techniques include homo-correlated NMR, which provides valuable information about the overall structural backbone of residual lignin (Crestini et al., 2009), and variations on 2D-HSQC/HMQC known at ‘quantitative’ or ‘quick quantitative’ methods (Q or QQ – HSQC/HMQC; Sette et al., 2011).

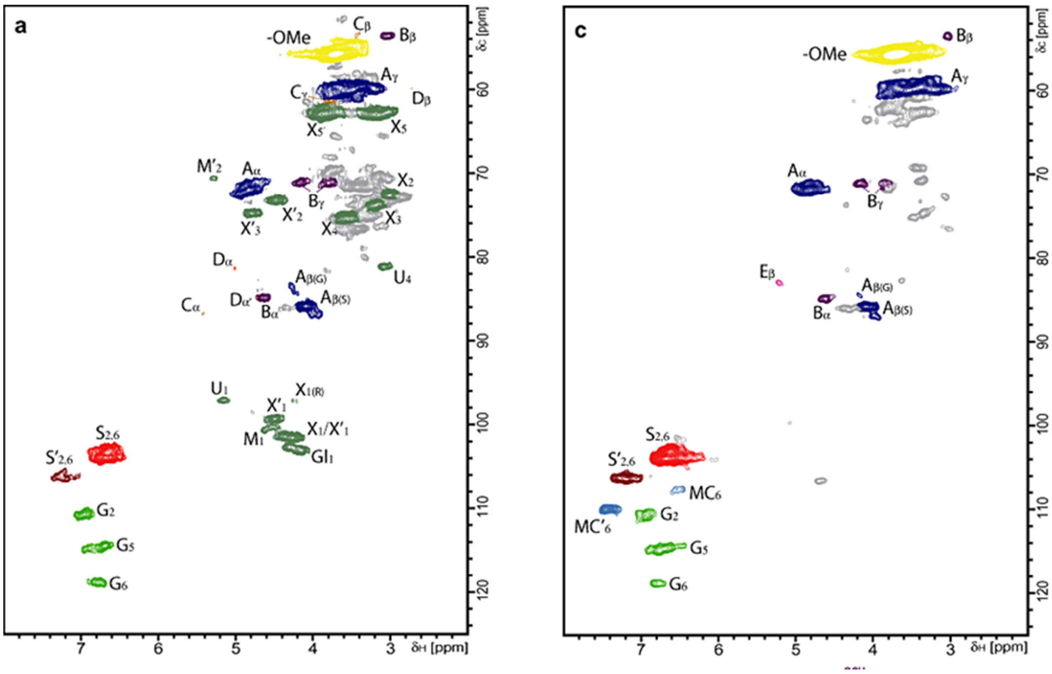


Figure 15: Example of HSQC 2D NMR spectra obtained from fresh wood (left) and wood degraded by brown rot fungi (right). The major inter-monomeric bonds present in lignin can be identified using a combination of ^{1}H and ^{13}C NMR; the size and colour of the peak in the plot relates to the abundance of those linkages. Loss of key linkages in the degraded sample are clear. Reproduced from Martinez et al., 2011 with permission from John Wiley and Sons, copyright 2011.

Some 2D NMR experiments can take a very long time: for example the QQ-HSQC/HMQC variations reported by Sette et al. (2011) take upwards of 40 hours. Additional complications of 2D analysis include the complexity of the sample preparation (samples need to be first dissolved and acetylated) and the level of expertise required to both obtain and interpret the data. 2D NMR experiments are therefore normally employed as part of a detailed multi-analytical study rather than routine characterisation (e.g. Zoia et al., 2017). Sette et al. (2011) conclude that even the most advanced NMR techniques should be combined with other methods such as chemical extraction in order to confirm interpretations.

5.4.4 Portable NMR

Traditional NMR instruments are large and immobile, containing large super-cooled electromagnets to provide the sensitivity required for routine analytical experiments. This limits their application to samples which can be brought to the instrument and placed within it. However, as advances are made in controlling the required magnetic field, portable instruments are increasingly available, opening up the application of NMR spectroscopy.

'Stray field' or 'unilateral' NMR instruments use a permanent magnet (rather than an electromagnet) open on one side, meaning that they can be brought into direct contact with a stationary object, penetrating up to 25 mm into a sample (Blümich et al., 2010). Continued advances in shaping the magnetic fields and refining the design of these instruments so that different depths can be probed has resulted in their application to the analysis of a range of cultural heritage objects, including paper and wood (Blümich et al., 2010). The application of portable NMR to archaeological wood is currently rare. One example is the use of portable ^{1}H NMR in a multi-analytical study to examine the state of decay of a wooden Egyptian sarcophagus and inform the design of an appropriate conservation scheme (Proietti et al., 2011). However, as ^{1}H NMR is somewhat less sensitive than ^{13}C NMR, structural characterisation was better achieved using different techniques. Nevertheless, as the field of portable NMR instrumentation advances, opportunities for more in-depth analysis may emerge.

5.5 X-ray analysis

Whilst the instrumental techniques discussed so far analyse a small sub-sample (e.g. 0.1 mg for p-GC), or probe only the surface of an object (e.g. FTIR), X-ray techniques penetrate the depth of an object and reveal information about the long-range internal structure (Lehmann and Mannes, 2012). The application of X-ray analysis to determine physical state of preservation and basic elemental composition has already been outlined (Sections 3.4.1 and 4.5.2). However, X-ray analysis can also provide an assessment of the chemical structure of a sample.

5.5.1 X-ray diffraction

X-ray diffraction (XRD) uses X-rays to probe the long-range arrangement and geometry of crystals within a material. XRD is commonly used in the paper and pulp industry to determine the arrangement of cellulose fibrils within wood (or paper) and calculate the overall percentage of the material that is in a crystalline form (e.g. Howell et al., 2009). As cellulose is crystalline, wood decay can be observed by an initial increase in crystallinity as non-crystalline hemi-cellulose is lost, followed by a significant decrease with loss of cellulose (Howell et al., 2009). This is identified in an XRD pattern by comparing the sharp peak caused by the crystalline fraction (at 23 $^{\circ}2\theta$) with the broader peaks related to amorphous wood components (Figure 16). From this a crystallinity index is calculated (Park et al., 2010; Popescu et al., 2011). The use of XRD to examine cellulose loss in archaeological wood has been demonstrated by Giachi et al. (2003) and Li et al. (2014), although it often comprises only one part of a multi-analytical assessment. This is because it gives an average assessment of decay so the exact location of deterioration cannot be determined (although microscopy can be used to elucidate the nature of the decay once it has been quantified by XRD; Giachi et al., 2003). Conversely, the fact that analysis focuses on a much larger area than many other analytical techniques can result in a more reliable assessment of the overall preservation state.

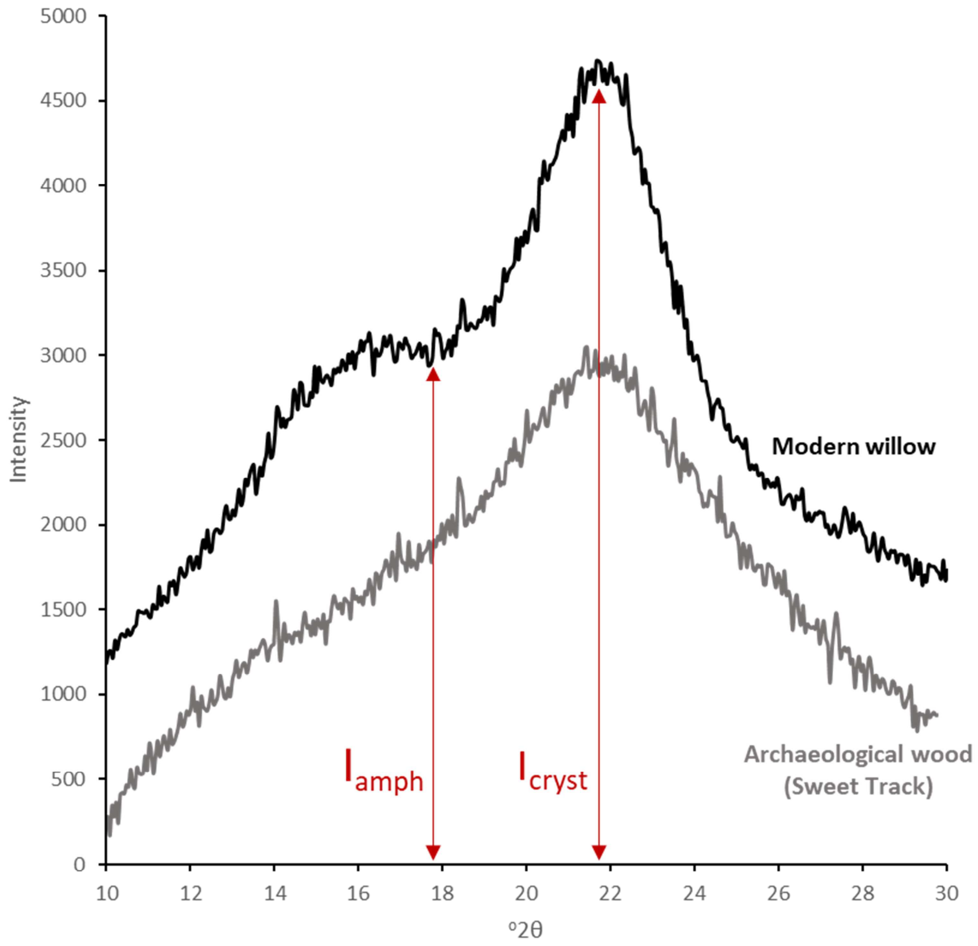


Figure 16: p-XRD patterns obtained from modern willow compared to archaeological wood excavated from the Neolithic site of Sweet Track (Somerset, UK) (author's own data). A loss of crystallinity with increasing decay is indicated by a decreasing depth of the 'trough' between the two peaks. A crystallinity index can be calculated from the height of the trough (I_{amph}) and the height of the crystalline peak at 23°2θ (I_{cryst}).

The downside of XRD analysis to quantify cellulose loss is that it can underestimate the amount of cellulose present if, having been degraded to a certain extent, residual cellulose exists in an amorphous (non-crystalline) state (Li et al., 2014). Similarly to in NMR, although the sample is not destroyed in the process it will likely need to be cut to fit into the instrument (the exact size depends on the instrument used). In addition, although an untreated sample can be analysed, sensitivity is much higher when a powdered or milled sample is used; however, results can be influenced by the method of milling (Segal et al., 1959). XRD instruments are commonly available in chemical research laboratories but are expensive in terms of initial cost and ongoing maintenance.

Powder XRD is also used to identify crystalline contaminants in archaeological wood (e.g. MacLeod and Richards, 1997; Wetherall et al., 2008). This is particularly useful in marine woods where high concentrations of pyrite, gypsum and other sulphur-based minerals may be present (MacLeod and Richards, 1997; Sandström et al., 2001). As direct analysis of the wood may fail to detect components that are present at low concentrations, XRD can also be performed on the residual ash left after burning at 600°C, reducing signal interference from the wood itself (e.g. Giachi et al., 2003). In these cases, a reasonably large amount of sample is required for destructive analysis, depending on the percentage ash content. The major benefit of applying XRD to determine inorganic components is that it is diagnostic of the crystal structure, in contrast to techniques such as SEM-EDX (Section 3.5.3), XRF (Section 4.5.2) or ICP-MS/AES (Section 5.7), where only an elemental composition is obtained. This may be valuable information for informing a strategy to remove such compounds prior to conservation, or predicting how they might behave with changing environmental conditions (Sandström et al., 2001; Shen et al., 2018).

5.5.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy is a technique that targets certain elements, measuring the energy of absorbed X-rays to discern the local environment of those elements, specifically their charge state (Figure 17). This provides more detailed analysis than, for example, determining elemental composition by XRF. X-ray absorption techniques consist of X-ray absorption near edge spectroscopy (XANES) which cover the lower energy range, and extended X-ray absorption fine structure (EXAFS) which measures higher photon energies. Both are carried out using a synchrotron source, which allows the fine tuning of the X-ray source required. XANES has been used in several studies to examine the inorganic content of waterlogged wood (e.g. Sandström et al., 2001; Fors et al., 2012). It is highly quantitative and specific, but although the value of this information is critical in isolated cases, the expense, lack of widespread availability, and complexity of the data mean that XANES is currently unsuitable for the routine assessment of artefacts. X-ray absorption studies are often carried out alongside other techniques, such as microscopy, allowing an in-depth understanding of the arrangement of inorganic inclusions within the wood structure (e.g. Almkvist and Persson, 2011).

X-ray techniques have been critical in fully understanding ‘the sulphur problem’ leading to acidification in a number of shipwrecks including the Vasa (Almkvist and Persson, 2011) and the Mary Rose (Wetherall et al., 2008). A combination of techniques in both cases has allowed researchers to unravel the complex iron and sulphur reactions leading to the acidification of ship timbers. XANES can be used to identify the various oxidation states of both iron and sulphur present through the depth of the timbers, and XRD used to confirm the compounds present (Wetherall et al., 2008; Almkvist and Persson, 2011). These studies have allowed researchers to identify the active deterioration mechanisms occurring within the ship timbers, as well as identify potential future changes, and adapt conservation strategies accordingly.

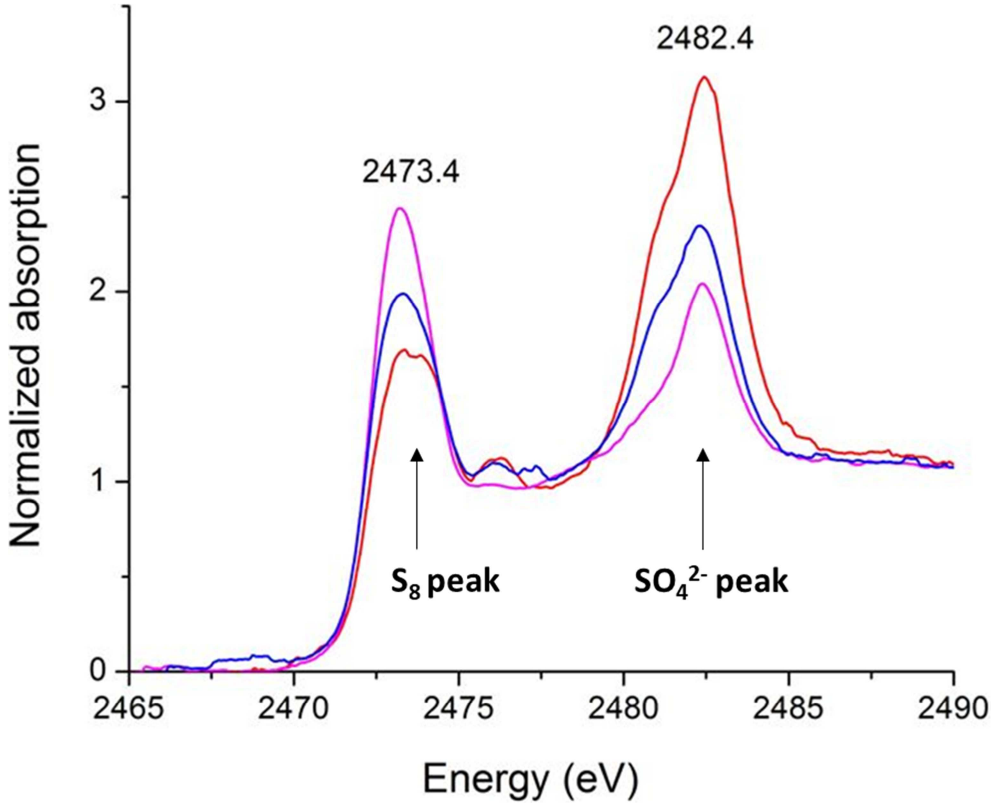


Figure 17: Sulphur K-edge XANES spectra recorded from three wood samples from the Ghost shipwreck (red = outer surface; blue = sub-surface; magenta = interior). The energy of an absorption edge (peak) increases with increasing oxidation state of the atom. Thus elemental sulphur is observed at a lower energy than sulphate. The analysis shown here demonstrated an increase in sulphates compared to elemental sulphur in the outer surface of the wreck. Reproduced from Fors et al., 2014 under a creative commons licence.

5.6 Raman Spectroscopy

Spectroscopic methods are particularly appealing for the analysis of cultural objects due to their ability to be used in a non-destructive way. Raman spectroscopy uses light from a LASER, which interacts with chemical bonds within a sample to produce a characteristic spectrum based on the light that is scattered. For wood, a 633-nm laser has been demonstrated to reveal characteristic scattering patterns for both cellulose and lignin (Agarwal, 1999). The major benefits of Raman analysis are that no sample preparation is required, and analysis times are in the region of minutes, similarly to FTIR. Raman can also be used in imaging mode when equipped with a microscope, allowing elucidation of the location of both lignin and cellulose within the cell walls (Agarwal, 2006). As it is less familiar and less widespread than FTIR spectroscopy, Raman has been far less widely applied to the analysis of archaeological wood, with only a few examples (Christensen et al., 2006; Petrou et al., 2009). Despite this, Raman spectroscopy can provide complementary information to FTIR as it interacts with different molecular bonds. It is also less affected by the presence of water, and less peak overlap makes assignment of the spectra more straightforward (Agarwal, 2006; Figure 18).

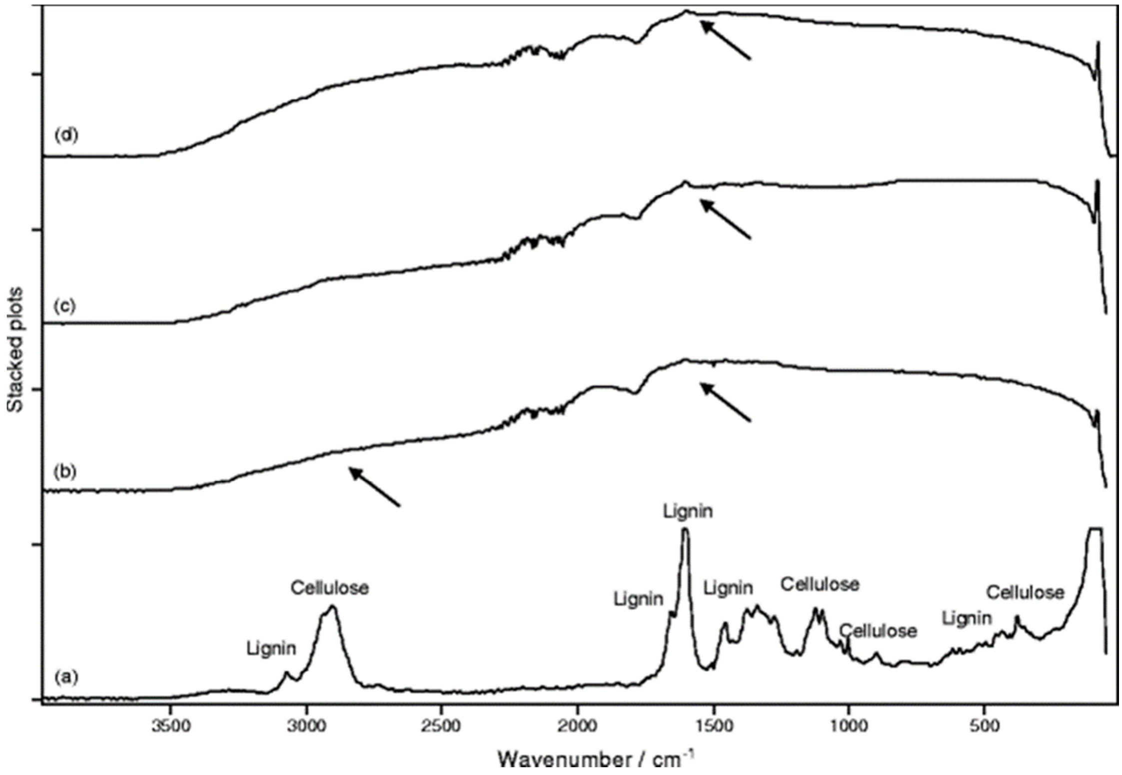


Figure 18: Raman spectra of modern pine sample (a) and highly degraded wood from the Neolithic site of Anargyroi, Greece (b, c and d). Arrows indicate the remaining characteristic peaks of lignin and carbohydrates. The loss of peaks at 1341 cm^{-1}, 496/521 cm^{-1} and 897 cm^{-1} indicate the complete loss of carbohydrates. Lignin is also highly decayed, with loss of the peak at 1190 cm^{-1} indicating loss of phenol. Reproduced from Petrou, 2009 with permission from Springer, copyright 2009.

Several Raman scattering peaks have been assigned to either cellulose or lignin by researchers working in wood and plant science; a comprehensive list can be seen in Agarwal (1999). Key indicative peaks are those between 1100-1150 cm^{-1} characteristic of cellulose and those at 1600 and 1650 cm^{-1} attributed to lignin (Christensen et al., 2006; Figure 18). As for many instrumental methods, a reduction in intensity of the cellulose related peaks relative to the lignin related peaks signifies decay (Petrou et al., 2009; Figure 18). Alteration of the lignin can also be observed by a reduction in the height of the peak at 1650 cm^{-1} (C=C) relative to that at 1600 cm^{-1} (phenol ring; Christensen et al., 2006; Figure 18). The peak at 93 cm^{-1} has been shown to correlate to the crystallinity of the cellulose, as independently determined by XRD methods (Agarwal et al., 2018). Raman spectroscopy is also suitable for the detection of inorganic components such as iron corrosion products in archaeological wood (Rémazeilles et al., 2009), and its use has been demonstrated for assessing the degree of penetration of conserving agents such as PEG (Christensen et al., 2006).

As it measures only scattered light, Raman is a fairly insensitive technique. In surface enhanced Raman (SERS), the surface of a sample is first coated in an electrochemically active substance, heightening the degree of scattering and increasing the sensitivity of the analysis. However, the process of coating is irreversible making the technique destructive, and SERS has not yet been fully demonstrated on archaeological wood. Statistical analysis may also improve the application of Raman spectroscopy; Marengo et al. (2003) used PCA to demonstrate that differences in wood chemistry following different decay treatments could be detected using Raman.

5.7 Inductively coupled plasma - atomic emission spectroscopy (ICP-AES)

Identifying metals that are present in high concentrations can be critical in determining which conservation methods will not cause subsequent reaction (Broda and Frankowski, 2017). Inductively coupled plasma analysis with atomic emission spectroscopy (ICP-AES; sometimes termed optical emission spectroscopy, OES) is an advanced method of elemental analysis. It provides a sensitive and highly quantitative assessment of a range of inorganic elements, and has been used for the identification of metal contaminants in wooden artefacts (Braovac et al., 2016; Broda and Frankowski, 2017). ICP-AES was used alongside py-GC analysis in the study of alum-treated artefacts from the Osberg shipwreck, allowing researchers to associate regions of lignin decay with the presence of aluminium and potassium from the treatment (Braovac et al., 2016). Zoia et al. (2015) demonstrate how the sensitivity of the technique can be further improved by first extracting the inorganic components by combustion (ashing).

Several methods of identifying inorganic contaminants exist and some have already been discussed. Whilst ICP-AES is a stand-alone technique, methods such as SEM-EDX can provide a greater detail of information regarding the object in general, and XRF is cheaper, more widely available, and non-destructive (whereas ICP-AES requires samples in the mg range). However, ICP-AES provides a more sensitive and quantitative assessment, which may be critical in certain cases, for example when solving a complex conservation problem such as in the case of the Osberg shipwreck (Braovac et al., 2016).

5.8 Gel-permeation chromatography (GPC)

Gel-permeation chromatography (GPC) is a technique used to determine molecular weight distribution. In wood this can be expected to correlate to the degree of lignin degradation, as shorter chains will be present if the polymers have broken down (Colombini et al., 2007). Zoia et al. (2017) used GPC as part of a multi-analytical study examining alum preserved objects from the Osberg shipwreck. Whole wood samples were dissolved in tetrahydrofuran and analysed by GPC with UV detection, allowing the analysis of both lignin and celluloses.

Due to the complexity of the lignin structure, GPC analysis can be very complicated (Colombini et al., 2009). Samples also need to be in solution and derivatised in order to increase the sensitivity of the instrument, meaning that large amounts of sample are required, and sample preparation is not straightforward. However, as information on the degree of overall polymerisation is difficult to gain using some instrumental techniques (e.g. FTIR, Raman or py-GC), GPC analysis may offer crucial complementary analysis in part of a multi-analytical study.

5.9 Discussion and summary

Analysis of the molecular structure of waterlogged wood using analytical instrumentation allows a detailed picture of the nature (i.e. chemical vs biological) and mechanisms of deterioration to be elucidated. Molecular analysis gives a far more accurate picture of the condition of the wood than techniques discussed in Sections 3 and 4, where analysis is often qualitative or semi-quantitative, and based on assumptions of the order of deterioration. Conducting such an accurate assessment provides a baseline against which future changes can be monitored. In particular, in cases where cellulose has been completely lost analysis of L: C ratios is not sufficient, and modifications to the polymeric structure of the remaining lignin can offer a valuable marker in monitoring increased deterioration.

However, many of these methods are not typically available in the standard heritage laboratory and require the input of specialised expertise in both operation and interpretation. Therefore, selecting which one will provide the required information is not easy, and requires weighing up the availability and cost of the instrumentation alongside the quality of the data obtained.

Table 6: Summary of techniques discussed in Section 5: Assessment of changes on the molecular level.

	Sub-category	**Summary**	**Advantages**	**Disadvantages**	**Assessment parameter**	**References**
Infrared Spectroscopy	Transmission	Provides information about relative abundance of functional groups; approx. **10mg** sample required (ATR only); transmission mode requires preparation in a KBr matrix; ATR mode allows direct surface analysis; techniques provide comparable data	Can be portable; fast; cheap; accessible; increasingly common; can be non-destructive (ATR only); no sample preparation (ATR only); large exisiting body of literature meaning that data can be compared between studies; suitable for chemometric studies	Complex data leading to inconsistencies in data interpretation; peak overlap and alteration of archaeological wood makes peak assignment difficult; only semi-quantitative; only a very small part of the sample is assessed; fairly insensitive as it does not give detailed assessment of degraded components; underestimates lignin content	L: C ratios calculated by comparing peaks related to cellulose (e.g. 898 or 1375 cm^{-1}) to those for lignin (1505 or 1596 cm^{-1})	Gelbrich et al., 2008; Emandi et al., 2011
	Attenuated total reflectance (ATR)				Lignin decay assessed by comparing peaks related to lignin functional groups (1230-1260 cm^{-1}) to lignin aromatic structure (1505 cm^{-1})	Faix et al., 1991; Gelbrich et al., 2012b
					Oxidation and hydrolysis observed by changes in peak shape (at 1260-1280 cm^{-1} and 950-1150 cm^{-1})	Pandey and Pitman, 2003;
					Loss of hemicellulose (peak at 1738 cm^{-1})	Oron et al., 2016
	Near IR	As for IR, but higher energy (gives different information)	Light penetrates deeper into sample than normal FTIR	Complex spectra; less widely available	Similar observations as for normal IR; chemometrics often employed	Pecoraro et al., 2015
	IR microscopy	As for IR; viewed with a microscope	Provides spatial analysis at the same time	Less widely available than normal FTIR instruments	As for normal FTIR, but parameters can be plotted spatially	Emandi et al., 2011
Pyrolysis-GC	Flame ionisation detection / Mass spectrometry	Sample is combusted in the absence of oxygen, breaking it down into small sub-units which are then separated by GC and detected by either FID or MS; sample sizes are approx. **100µg**	Small sample size, so minimally destructive; gives information on degradation products as well as intact polymer, so more subtle changes can be observed; reproducible; minimal sample preparation; products are easily identifiable (MS);	Derivatisation steps are recommended but rarely used; instruments are not widely available; needs to be compared against libraries or standards (FID); different response ratios for different compounds (MS); expertise needed to interpret data; slow analysis compared to FTIR	L: C ratios calculated by comparing intensity of cellulose related peaks to lignin	Van Bergen et al., 2000; Łucejko et al., 2012
					Loss of methoxy groups from lignin signified by increased guaiacyl, 1,2-benzenediol and phenol	Van Bergen et al., 2000; Filley et al., 2002
					Presence of oxidation products indicate lignin decay; quantified by an increase in the acid: aldehyde ratio	Hatcher et al., 1995; Łucejko et al., 2012

			analysis is highly quantitative (FID); allows detailed lignin characterisation	(> 40 mins); instruments more expensive	Increased concentration of short-chain compounds signifies lignin decay	Zoia et al., 2017
NMR spectroscopy	^{13}C	Uses the magnetism of nuclei to determine the chemical environment of target nuclei; less widely available but a fast-evolving field with increasing range of applications; sample sizes and analysis times vary widely depending on the information needed	Provides highly detailed information about structural changes; lack of sample preparation gives a more direct analysis (^{13}C); analysis probes into the depth of a sample; small (**4-7 mg**) samples sizes, although better resolution is achieved with larger amounts; can examine bonds between sub-units	Samples must be in solution, requiring harsh preparation (^{1}H, ^{31}P and 2D); lack of availability of instruments and expertise; expense of instruments; complexity of spectra; spectra influenced by contaminants; cannot detect oxygen containing groups (^{13}C)	Increased abundance of β-O-4 linkages in relation to the methoxy groups signifies degradation *(^{13}C)*	Colombini et al., 2009
	^{1}H				L: C ratios calculated by comparing intensity of cellulose related peaks to lignin *(^{13}C, ^{1}H, ^{31}P, 2D)*	Bardet et al., 2009; Colombini et al., 2009
	^{31}P				Increased concentrations of phenol and acids signify decay *(^{31}P)*	Colombini et al., 2009; Zoia et al., 2017
	2D techniques	Probe both the ^{13}C and ^{1}H nuclei in one experiment, giving much greater detail	Allows identification of additional structural features	Highly complex spectra; long experiment times (up to several days)	Comprehensive assessment of degradation mechanisms	Zoia et al., 2017
X-ray analysis	X-ray diffraction	X-ray techniques penetrate a sample, providing a better analysis of the bulk; information relates to long range internal structure	Small sample sizes; gives detailed structural information about inorganic inclusions; analyses a larger range than many other techniques	Lack of availability of synchrotron instruments (X-ray absorption); exact location of decay difficult to elucidate; may not detect low concentration contaminants	A decrease in cellulose crystallinity signifies decay *(XRD)*	Howell et al., 2009
	X-ray absorption				Highly quantitative analysis of inorganic content, including charge states (structural information *(X-ray absorption)*	Fors et al., 2012
Raman	Raman spectroscopy	Characteristic spectrum from light scattered from laser, providing complementary information to FTIR	Non-destructive; fast analysis times; can detect inorganic components; less affected by presence of water	Not as familiar or widely available as FTIR; not very sensitive	Cellulose: lignin composition by comparing peak heights at 1100-1150 cm^{-1} (cellulose) and 1600-1650cm^{-1}	Agarwal, 1999; Petrou et al., 2009

	Raman microscopy	Raman spectroscopy used in imaging mode	Provides spatial dimension to analysis, allowing cell wall compositions to be plotted	Less widely available than traditional Raman	(lignin) Wood crystallinity changes indicated by changed to band at 93 cm^{-1} Inorganic components detected	Agarwal, 2006
	SERS	Raman spectroscopy where signal is enhanced by coating	Enhanced signal by coating	Coating process is irreversible, therefore destructive		
ICP-AES	Atomic Emission Spectroscopy	An advance method of elemental analysis	Highly quantitative and highly sensitive	Not widely available; no structural information given	Highly quantitative analysis of inorganic content	Braovac et al., 2016
GPC	Gel permeation chromatography	Determines molecular weight distribution	Additional information not gained by other methods	No molecular detail; complicated sample preparation	Lower MW distribution signifies decay	Colombini et al., 2009

6 DESIGNING A SCHEME OF PRESERVATION ASSESSMENT

The level of detail required from an assessment depends on several factors, which need to be considered on a site by site basis. Macchioni et al. (2018) suggest that multiple phases of diagnosis must be considered. The first of these is a basic assessment of the general appearance and aspect of the artefact, and will generally be carried out in the field. If deemed necessary, a more detailed examination will then be carried out detailing the state of preservation of the artefact. The depth of this analysis is dictated by a multitude of factors, but the information revealed by different analytical techniques weighed up against their time and financial investments must play an informed role in this decision. Some of the major considerations are discussed here, although this discussion is by no means exhaustive. Further considerations can be found in Brunning and Watson (2010).

6.1 The purpose of analysis

The major consideration in determining what level of assessment is warranted is the aim of analysis. This can range from determining the archaeological information that can be obtained from an artefact, to detailed molecular characterisation in order to solve complex conservation problems. Identifying the aim of the assessment helps to determine what questions need to be answered, and in what level of detail (Figure 19). Following this, appropriate analytical methods can then be selected based on the information that they yield (Figure 20).

6.1.1 Analysis to assess archaeological significance

An assessment of the physical state of preservation of waterlogged wood plays an important role in informing the next steps in either analysis or conservation (Section 3). It is also critical for assessing the archaeological significance of an object, as it is closely related to the quality of information that can be retrieved (for example: the interpretation of cut marks, suitability for dendrochronology etc; Brunning and Watson, 2010).

A basic assessment is likely to be limited to things that can be carried out in the field, such as visual analysis. In the majority of cases, it will be concluded that this basic assessment is sufficient, or a fast assessment in the field will be all that is possible within the time and financial constraints of excavation. Therefore, assessment should be thorough and use the most up to date techniques available. The use of semi-quantitative preservation indices such as those defined by Van de Noort et al. (1995), or the use of advanced visualisation techniques, will significantly improve the ability to compare preservation between sites. The recording of even basic information on the preservation of objects might provide important data against which other sites can be compared.

6.1.2 Analysis for conservation

If the aim is to advise a method of conservation, assessment tends to use analytical approaches that are commonly understood and widely applied. In most cases, applying several of the techniques described in Sections 3 and 4 will be sufficient;

for example, establishing the Umax, density or cellulose content is often adequate in establishing general trends and informing a conservation strategy. In cases where a high concentration of inorganic salts may affect conservation, this should also be determined using ash content, or SEM-EDX which allows the determination of spatial variations.

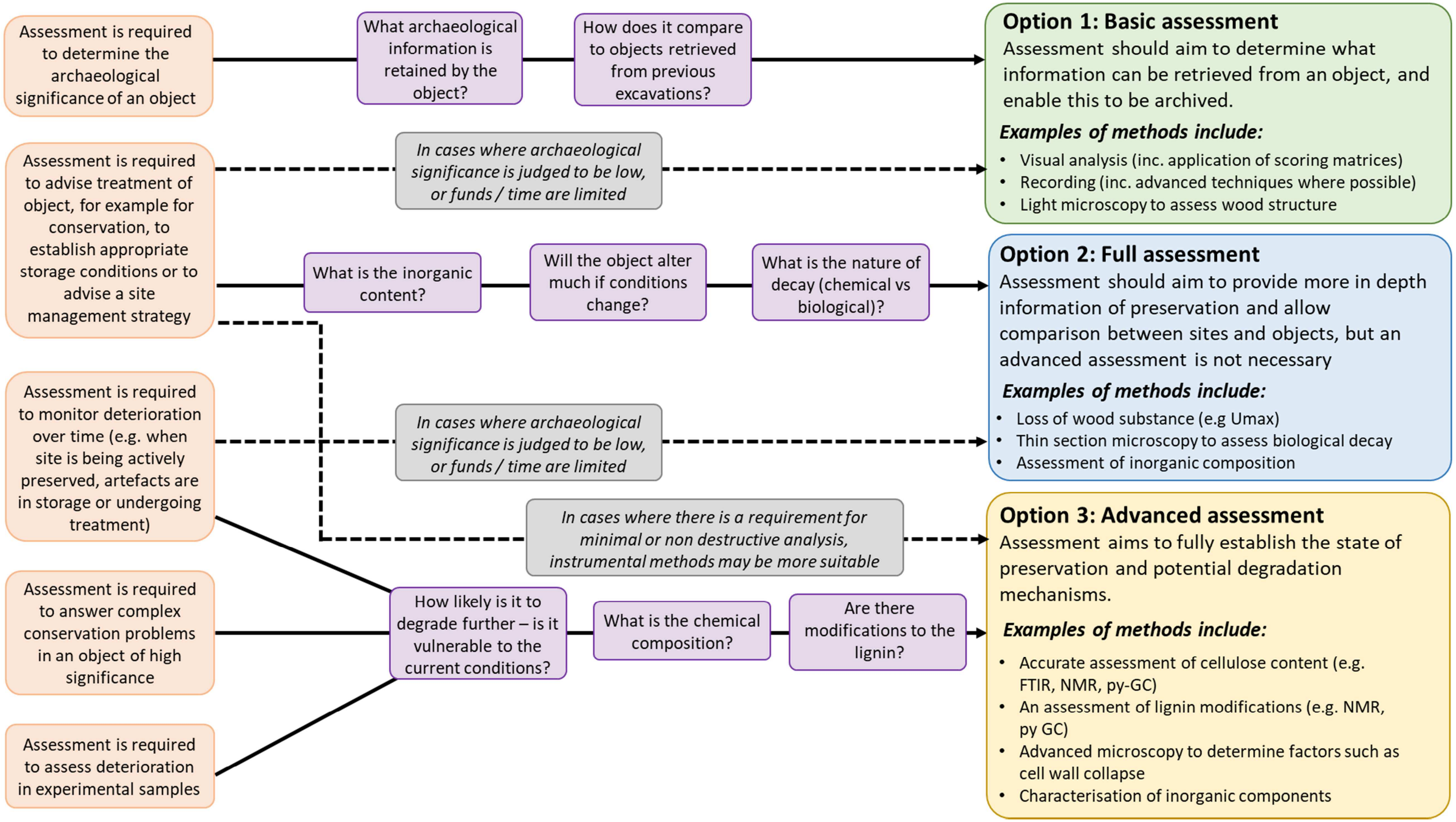
In cases where an object is considered of high archaeological significance or conservation is likely to be complex, a more advanced assessment of the molecular composition may be considered, using methods described in Section 5 (Figure 19).

6.1.3 Analysis to monitor deterioration

If the aim of assessment is to monitor deterioration, establishing the best possible picture of the state of preservation is critical for establishing a baseline against which future changes can be compared. Examples of when deterioration needs to be monitored include when a site is to be preserved *in situ* under active management, when the effect of changes in the burial conditions needs to be assessed, or when investigating the deterioration of an artefact in storage or on display. Such situations demand that preservation assessment is quantitative and provides a greater amount of detail. In these cases, analytical instrumentation should be considered, in order to fully document molecular modification within the wood structure (Section 5).

Advanced analysis may also be necessary for wooden artefacts where there is no cellulose remaining, as this makes L: C ratios misleading or useless in terms of monitoring further deterioration. Whilst archaeological wood containing no cellulose can still be conserved and archaeologically interpreted, if lignin starts to then decay, the artefacts can rapidly be lost. In such cases, it may be necessary to examine molecular alteration of any remaining lignin component (e.g. Colombini et al., 2007).

If the aim is to compare the material with material from past analysis, it is important to carry out the same analysis as far as possible, as different methods are not necessarily comparable. If possible, reanalysis of the original artefact may also be useful.



Option 1: Basic assessment

Assessment should aim to determine what information can be retrieved from an object, and enable this to be archived.

Examples of methods include:

- Visual analysis (inc. application of scoring matrices)
- Recording (inc. advanced techniques where possible)
- Light microscopy to assess wood structure

Option 2: Full assessment

Assessment should aim to provide more in depth information of preservation and allow comparison between sites and objects, but an advanced assessment is not necessary

Examples of methods include:

- Loss of wood substance (e.g Umax)
- Thin section microscopy to assess biological decay
- Assessment of inorganic composition

Option 3: Advanced assessment

Assessment aims to fully establish the state of preservation and potential degradation mechanisms.

Examples of methods include:

- Accurate assessment of cellulose content (e.g. FTIR, NMR, py-GC)
- An assessment of lignin modifications (e.g. NMR, py GC)
- Advanced microscopy to determine factors such as cell wall collapse
- Characterisation of inorganic components

Figure 19: Schematic outlining some of the most common reasons for conducting a preservation assessment, and the questions linked to those. The aim of assessment will determine the level of information required by assessment, although other factors also need to be evaluated (e.g. costs and availability of methods). Further details on methods linked to options 1, 2 and 3 are summarised in Figure 20.

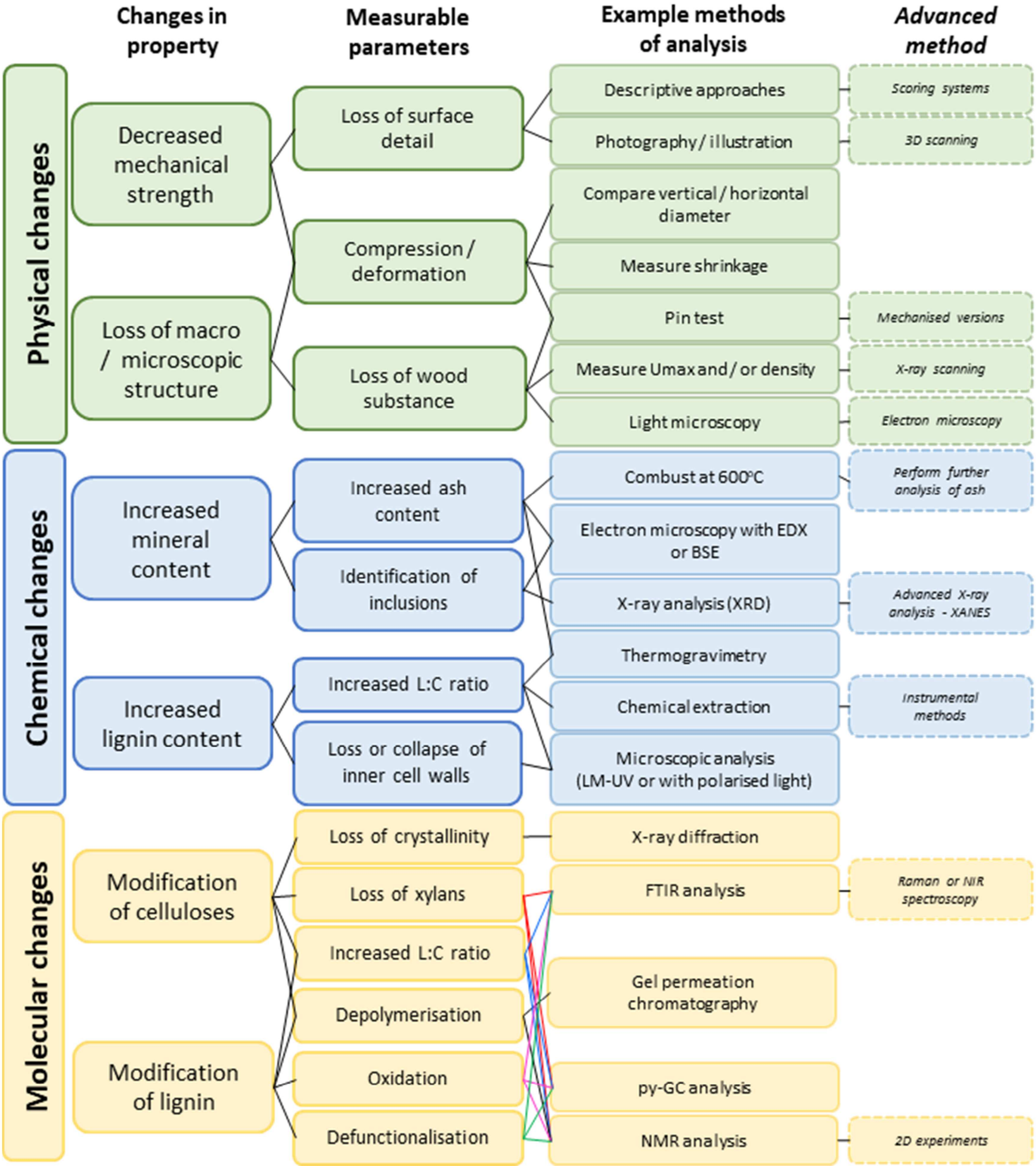


Figure 20: Summary of changes in property that might be measured in a preservation assessment, depending on the level of assessment required. Some examples of methods that can be used to determine these properties is provided, although this is not exhaustive and the decision should also be based on considerations such as cost and availability of the methodologies. The assessment of more than one change in property should be considered where possible.

6.2 Sampling concerns

The availability of material for destructive analysis is an important consideration in selecting an assessment method. This could be limited by factors such as the significance or size of an object and may demand that non-destructive (e.g. X-ray analysis or spectroscopy), or minimally destructive techniques (e.g. py-GC) are used.

The use of minimally or non-destructive methods also allows for the analysis of a greater quantity of samples. These may all be from one object, or from different locations across a site and would better reveal differences in preservation. Differences in preservation can occur for many reasons, including:

- The depth of burial: whether the artefact is located at a depth with good preservation potential (preservation horizon). This might differ through an object, for example vertical timber stakes where the sections nearer the ground surface have had a greater exposure to oxygen will likely be more decayed in the upper surfaces (Panter, pers. comm.).
- The history of the object: factors such as how soon it was buried after being discarded, its use before burial, and changes in the burial environment over the burial history may result in differences in preservation.
- The origin / species of the wood: for example, differences between the inner heartwood and outer sapwood can be stark (Hoffman and Jones, 1990). Decay will be particularly heterogenous in ring porous woods such as oak and ash.

Regardless of whether methods of assessment use only a very small sub sample or a larger piece of the whole timber, one analysis is unlikely to be representative of the entire object. An appropriate sampling strategy therefore needs to be considered. This may involve taking cores through a sample, dividing this up into zones and performing multiple analysis (McConnachie et al., 2008; Macchioni et al., 2013). If availability is limited, it may be possible to analyse samples taken for other purposes, for example species identification or dendrochronology.

6.3 Constraints on analysis

The methods used for preservation assessment are highly likely to be limited by external factors, such as the time and finances available. However, this does not necessarily mean that instrumental analysis needs to be ruled out; FTIR analysis is much quicker than chemical extraction for example and can provide a quantitative assessment. Another limiting factor may be the availability of both instrumentation and expertise, which is more of a concern for some instrumental methods than others (e.g. NMR requires highly specialist instrumentation and data interpretation can be complicated, whilst FTIR instruments are increasingly common and L: C ratios can be fairly easily derived).

6.4 The benefits of a multi-analytical approach

An increasing number of studies highlight that no single technique is best for determining the level of deterioration in waterlogged wood, mainly due to the inherent complexity of the material, and many advocate a multi-analytical approach (e.g. Faix et al., 1991; Wilson et al., 1993; Colombini et al., 2007; Crestini et al., 2009). Most of these studies employ a range of instrumental and non-instrumental methods and demonstrate that different methods provide complementary information. As an example, analysis using instrumentation rarely distinguishes between chemical and biological deterioration, whereas thin-section light microscopy easily reveals characteristic patterns of biological decay. Using the two methods together can determine both the nature and extent of decay.

In a few high-profile cases, a vast array of analytical techniques have been used to fully characterise the molecular structure of the wood, as well as any deterioration products and contaminants. Examples include the Vasa shipwreck where synchrotron radiation has been used to examine sulphur oxidation states within ship timbers (Almkvist and Persson, 2011) or the Osberg ship where a previous alum-based conservation treatment has caused acidification (Braovac et al., 2016). Such examples serve to demonstrate the value of a comprehensive analytical assessment in critical cases, although it is unlikely that such an approach will become standard.

Macchioni et al. (2012) demonstrate that using only one technique may lead to misinterpretation of the degree of preservation, and a multi-analytical approach can aid a better diagnosis. Tamburini et al. (2017) highlight that some techniques do not account for the presence of degraded polymer that have remained *in situ*. Other studies attempt to compare two or more techniques: studies comparing the level of deterioration determined by Umax and NMR (Bardet et al., 2002), wet chemical extraction compared to py-GC (Łucejko et al., 2012); and chemical extraction compared to FTIR (Gelbrich et al., 2012b) have all shown discrepancies between the techniques, without confirming which of the methods is ‘wrong’. Zoia et al. (2017) concluded that singular techniques provide only partial information, strongly advocating the use of multiple techniques where possible.

6.5 Summary

The aim of this review is to provide an overview of the various methods available for the preservation assessment of waterlogged wood. This information is important for designing an appropriate scheme of evaluation based on the detail of information revealed by certain techniques, although the value of this information needs be weighed up against factors such as their cost and availability, as well as the significance of the site and aims of analysis.

However, the value of undertaking a robust and thorough assessment of materials in guiding site management and conservation decisions should not be underestimated. In cases where the future of a site or object is uncertain, an assessment should employ the best available methods, providing a robust baseline for monitoring future change.

7 FURTHER INFORMATION

Further information related to designing a scheme of assessment can be obtained from the following freely available resources:

- Historic England guidance on Preserving Archaeological Remains *in situ*

  https://historicengland.org.uk/advice/technical-advice/archaeological-science/preservation-in-situ/

- Institute of Conservation guidance on sampling

  https://icon.org.uk/groups/heritage-science/guidance-documents

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