

# Analytical instrumental techniques to study archaeological wood degradation

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## Running head: Analysis of archaeological wood

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## Abstract

Historically, a very large variety of everyday artifacts were made of wood, which makes them representative of their historical period or social context, and valuable for archaeologists and historians. In order to preserve degraded wood and to develop and apply suitable conservation treatments, chemical and physical characterization of archaeological wood is needed. This review provides the reader with a survey on state-of-the-art of instrumental analytical tools available to understand the morphology and the chemical composition of archaeological wood. The focus is on microscopic and spectroscopic techniques as SEM, FTIR, Raman, NMR, and analytical techniques based on pyrolysis, such as DE-MS, Py-MS, Py-GC/MS, with emphasis on their respective potentialities and limitations. The advantages of techniques based on synchrotron radiation are also discussed. In addition, the applicability of each examined technique is illustrated and discussed through specific examples from the literature.

34 **Keywords:** archaeological wood, microscopy, spectroscopy, pyrolysis, degradation

35

## 36 **Introduction**

37 Archaeological wood can be defined as wood that carries traces of the past cultural or  
38 technological activities related to human history. Historically, a very large variety of  
39 everyday artifacts were made of wood, which makes them representative of their historical  
40 period or social context, and valuable for archaeologists and historians. Wooden objects  
41 provide information on human technical development and culture [1]. Archaeological  
42 wooden objects are rare in museums, due to the instability of wood to moisture and to  
43 degradation caused by fire, microorganisms, fungi, and insects [2].

44 Wood is preserved for long periods of time only under particular conditions. For instance,  
45 wet environments favor wood preservation, because in a waterlogged environment,  
46 characterized by low temperatures and oxygen concentrations, the activities of fungi,  
47 insects and bacteria are limited. Consequently, wooden artifacts can survive underwater,  
48 in some cases, in a surprisingly good state of conservation, as sometimes happens for  
49 shipwrecks. A very famous example is the 17<sup>th</sup> century Swedish warship “Vasa” [3], which  
50 was found in good condition after 333 years in Stockholm harbor, and is now in the Vasa  
51 Museum (Stockholm, Sweden). Other cases are the “Bremen Cog” (1380 AD) in the  
52 Deutsches Schiffahrtsmuseum (Bremerhaven, Germany) [4], the “Ma’agan Mikhael” ship  
53 (end of the 5th century BC) in the Hecht Museum (University of Haifa, Israel) [5], the “Mary  
54 Rose” (1500 AD) in the Mary Rose Museum (Portsmouth, England) [6], and the ships (2nd  
55 century BC to 4th century AD) in the site of San Rossore (Pisa, Italy) [7].

56 Even underwater, anaerobic bacteria and soft rot fungi can still slowly degrade  
57 waterlogged wood [8-10], which in some cases is also exposed to wood borer worms [11].  
58 Anaerobic microorganisms above all attack the cellulose and hemicelluloses, while,  
59 although they modify the lignin in the cell middle lamella, they do not completely degrade  
60 it. Hence, the lignin-rich compound middle lamella survives, and the cell form is kept intact  
61 by water replacing the degraded parts of the cell. Thus waterlogged wood is often in a very  
62 good state of preservation, archaeologically speaking, as all surface and structural details  
63 are preserved. However, from a conservation/structural and chemical perspective, it can  
64 still be extensively degraded, presenting a porous and fragile structure, poor in  
65 polysaccharides and mainly composed of residual lignin [8, 12, 13].

66 Drastic dimensional changes, structural distortions and cracking can occur during drying.

67 Consequently, conservation treatments of waterlogged archaeological wood aimed at

68 fixing these phenomena are needed [1, 3-5, 14, 15]. The chemical and physical state of  
69 archaeological wood can vary from near sound to heavily degraded. The variability of  
70 degradation of wood can be explained by many factors, not yet fully assessed, such as the  
71 wood species, the history of use and fabrication, the burial time, and the burial  
72 environment [1, 15]. Inorganic salts can also heavily impact on wood degradation [16-20].  
73 Usually, the central portion of wooden pieces is better preserved than the external layers,  
74 which can be easily degraded showing a high content of water, inorganic inclusions and  
75 loss of biopolymers. The content of water in the wood increases with a relative decrease in  
76 cellulose and hemicelluloses. The water content in weight, compared with the  
77 corresponding value for sound wood, is an important decay parameter for waterlogged  
78 wood, which can reach 1000% in weight [19, 21-23].

79 In order to preserve degraded wood and to develop and apply suitable conservation  
80 treatments, the chemical and physical processes occurring during degradation need to be  
81 completely understood [22, 24, 25].

82 Many different analytical techniques have been developed and employed in order to  
83 measure the extent of wood deterioration. The measurements of residual density and of  
84 water content in waterlogged wood have become an essential parameter to assess the  
85 state of preservation and to plan the conservation of archaeological waterlogged wood [21,  
86 23, 26, 27].

87 In addition, the wet chemical methods of wood analysis, developed in the field of pulp and  
88 paper industry, can be used to calculate the concentration of wood components after their  
89 isolation and purification. By these classical methods, only the amounts of main wood  
90 components are determined: cellulose, hemicelluloses, lignin, extractives and ashes. An  
91 array of classical, wet chemical procedures, in some cases officially standardized, and a  
92 growing number of more recent instrumental methods are available for the analysis of  
93 wood [28, 29]. The CPPA (Technical Section, Canadian Pulp and Paper Association,  
94 Montreal, P Q, Canada), TAPPI (Technical Association of the Pulp and Paper Industry,  
95 Atlanta, GA) [30, 31], and ASTM (American Society of Testing and Materials, Philadelphia,  
96 PA) have issued new or revised test methods for the analysis of pulp and paper materials.  
97 There are excellent reviews covering analytical techniques for wood and its components  
98 [29, 32]. These methods have only in a few cases been applied to archaeological and  
99 historical wood artifacts. Chemical analysis using the international standard methods of  
100 wood analysis TAPPI was performed on waterlogged archaeological wood from the San  
101 Rossore site, Pisa (Italy) [19, 33, 34], and from the Biskupin site in Poland [35]. Other

102 examples of the wet chemical analyses of archaeological wood artifacts were applied to a  
103 range of archaeological artifacts from Northern Europe [26] and also to three Roman ships  
104 found in Naples [36]. Methods based on extraction require extensive chemical  
105 modifications of wood to obtain soluble fractions of the various components. It is difficult to  
106 completely separate the wood components, and so the results obtained tend to depend on  
107 the method applied. Wet chemical treatments are also reagent and time consuming, and  
108 require a substantial amount - several grams - of sample, whereas in the field of the  
109 cultural heritage sampling should be minimized, and the risk of contamination reduced.  
110 Analytical instrumental techniques are thus a more attractive strategy: they provide  
111 detailed information by minimizing the sample amount and avoiding sample preparation. In  
112 terms of archaeological wood analysis, several instrumental techniques have been used,  
113 from microscopic and spectroscopic observations, to hyphenated techniques including a  
114 chromatographic separation step. For example, the degree of crystallinity of cellulose in  
115 archaeological wood can be obtained by X-ray diffraction [26]. FT-IR spectroscopy was  
116 used to analyze the carbohydrate and lignin fractions of degraded wood separated by  
117 chemical procedures [37, 38]. Gel permeation chromatography (GPC) analysis applied to  
118 lignin extracted from archaeological waterlogged wood has been used to determine the  
119 molecular weight distribution of lignin [39-41]. Gas chromatography coupled with mass  
120 spectrometry (GC/MS) has been applied to study organic extractives in wood [40].  
121 Quantitative evaluation of methoxy groups in lignin extracted from archaeological  
122 waterlogged and sound wood has been assessed using gas chromatography using a  
123 flame ionization detector (GC-FID) [39]. Multi-analytical approaches combining several  
124 techniques, such as NMR, Py-GC/MS, GPC, have also been used [39, 41] to investigate  
125 archaeological wood from different points of view. Other analytical methods have been  
126 used to characterize inorganic compounds in archaeological wood, including mainly X-ray  
127 based techniques [42] such as X-ray fluorescence (XRF) [13, 43], X-ray diffraction (XRD)  
128 [18, 44], X-ray absorption (XANES) [45] and SEM-EDX [46]. Their applications to  
129 archaeological samples are not discussed here, given that the characterization of  
130 inorganics is beyond the scope of this review.

131 This review provides the reader with the state-of-the-art instrumental analytical tools  
132 available to understand the morphology, the chemical composition and the state of  
133 degradation of archaeological wood. It is the first review publication resulting from a  
134 detailed study on the applications of instrumental methods in archaeological wood studies.  
135 The focus is on microscopic and spectroscopic techniques (SEM, FTIR, Raman, NMR)

136 and analytical pyrolysis techniques (DE-MS, Py-MS, Py-GC/MS), with emphasis on their  
137 potentialities and limitations. The advantages of techniques based on synchrotron  
138 radiation are also discussed. In addition, the applicability of each examined technique is  
139 illustrated and discussed through specific examples from the literature.

140

## 141 Microscopy

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### 143 Light microscopy

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145 Light microscopy (LM) is a simple and practical method for observing the morphology of  
146 the wood surface with minimal to moderate specimen preparation [47], thus obtaining  
147 information on the species of wood, the nature of microbiological attack, and the extent of  
148 the decay [48-50]. Species determination is a crucial step in the diagnostic process of  
149 wooden artefacts. It provides valuable information on craftsmanship and construction  
150 technologies, and it also represents the basis for evaluating the physical, chemical and  
151 mechanical properties. Knowledge of the timber(s) used provides basic information for any  
152 study, conservation or restoration [51].

153

### 154 Ultraviolet microscopy

155

156 UV microscopy is used in wood analysis exploiting the fact that the characteristic  $\pi\text{-}\pi^*$   
157 transitions of the aromatic moieties in lignin cause a stronger UV light absorption from  
158 lignin than from carbohydrates [52, 53]. UV microscopy was applied to the study of lignin  
159 fraction separated by classical wet methodology, in order to assess the state of lignin  
160 preservation in archaeological bamboo [38]. Li et al. observed a reduction in the  
161 absorbance at 311 nm, assigned to the conjugated phenolic groups, such as p-coumaric  
162 and ferulic acids, compared to reference wood, indicating a decrease in the content of  
163 these moieties, which are covalently bonded with lignin and polysaccharide components  
164 [54] and act as linkage units. The cleavage of the aromatic linkage units can facilitate  
165 the degradation of carbohydrates, leaving non-bonded cell-wall carbohydrates sensitive to  
166 degradation [38].

167 A evolution of UV microscopy is scanning UV microspectrophotometry (UMSP), which is  
168 based on the ultraviolet illumination of semi-thin transverse sections of woody tissue.

169 UMSP is useful for the topochemical detection of lignin and phenolic extractives in situ and

170 for its semi quantitative determination in the layers of the wood cell walls. It enables direct  
171 imaging of lignin distribution within individual cell wall layers with a resolution of  $0.25 \mu\text{m}^2$   
172 [55]. Lignin displays a characteristic ultraviolet absorbance spectrum with maxima around  
173 212 nm and 280 nm due to the presence of associated phenylpropane groups with several  
174 chromophoric structural elements [56]. Cufar et al. applied UMSP for the first time to  
175 waterlogged archaeological wood in 2008 [50] in order to evaluate the state of  
176 deterioration of the cell walls. They investigated the cell wall structure and topochemistry  
177 of selected 5200 and 4500-year-old ash and oak? wood using light microscopy (LM),  
178 transmission electron microscopy (TEM) and cellular UV-microspectrophotometry (UMSP).  
179

## 180 Scanning electron microscopy

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182 Scanning electron microscopy (SEM) is an excellent method for observing the morphology  
183 of the surface of a wood sample [9]. The super-molecular structure (i.e. the ultrastructure)  
184 of wood is a double composite system. At a microscopic level, it consists of tracheids,  
185 fibers, vessels and parenchyma cells interconnected by the matrix of the middle lamella. At  
186 a sub-microscopic level, it consists of a reinforcing network of microfibrils embedded in an  
187 interfibrillar matrix. Any failure of the microfibrils or the matrix or the loss of adhesion  
188 between microfibrils and the matrix results in an alteration of the properties of the wood  
189 [57, 58]. Microbiological attack is one of the main causes of degradation in archaeological  
190 wood. Fungal (white rot, brown rot, soft rot) and bacterial (erosion, tunneling, cavitation,  
191 scavengers) attacks can be observed and classified by SEM in archaeological and  
192 historical wood, showing typical degradation signature [8, 59-61] (Figure 1).

193 The information obtained by SEM analysis is important in order to better understand the  
194 degradation processes and interpret the chemical results obtained by other techniques.

195 Thus SEM is commonly used as an essential complementary technique to obtain  
196 information on the wood species and the nature of microbiological attack, as well as to  
197 verify the extent of structural decay [38, 62, 63]. In combination with energy dispersive X-  
198 ray spectrometry, it can also offer information on the localization of inorganic products  
199 inside the wood [46].

200

## 201 Spectroscopy

202

## 203 X-rays Computed Tomography

204

205 Computed tomography techniques are able to look inside an object and reconstruct its  
206 three-dimensional microstructure in the form of imaging. The data are collected under  
207 ambient conditions, in a non-destructive way, without any need for specimen preparation  
208 [64]. This is crucial when the fragility of samples makes cutting a surface to be examined a  
209 critical step, bringing the risk of deformations and artifacts, as often happens in degraded  
210 archaeological wood.

211 Steppe et al. [65] successfully applied X-CT in wood anatomical research. Svedström et al.  
212 studied the degradation of oak wood of the warship Vasa [66]. PEG-impregnated samples  
213 were analyzed and the results compared to those of recent oak. They observed that the  
214 cellular structure of the Vasa oak was surprisingly well preserved at the micrometer level.  
215 X-ray micro-tomography has also been used to investigate the fungal attack of wood [67],  
216 and for the dendrochronological analysis of wooden artifacts from the Middle Ages [68].  
217 Figure 2 compares images obtained by  $\mu$ -X-CT for different sections of recent and  
218 archaeological beech wood, highlighting the capability of the technique to investigate the  
219 wood structure [68].

220 Laboratory or clinical CT has proven to be an extremely valuable tool in morphological  
221 analyses where its main advantage is related to a completely non-intrusive, non-invasive  
222 approach. Data extraction is straightforward and can be treated digitally in several ways.  
223 The X-ray CT of 17 historical violins and cellos crafted between 1633 and 1872 by  
224 Cremona masters, such as Guarneri del Gesù, Amati and Stradivari [69], led to the non-  
225 invasive detection of varying degrees of damage (such as wormholes, air gaps, wood  
226 deformations) and of past reparation interventions (glue linens, filling materials, wooden  
227 cleats and patches), invisible to external examination.

228 Despite significant technical advances in bench-top X-ray CT instruments, spatial  
229 resolution is still relatively low. To achieve high resolution in X-ray microtomography,  
230 synchrotron radiation (SR) as X ray source has been proposed. SR- $\mu$ CT features a higher  
231 spatial resolution, image contrast and dynamic range, dramatically increasing the quality of  
232 the final result [70]. The new possibilities offered by the latest generation synchrotron  
233 sources, together with the development of novel X-ray detectors and faster computers,  
234 have increased the interest in this technique for studying cultural heritage objects.

235 Synchrotron radiation SR- $\mu$ CT has been used to study the deformations in the cellular  
236 structure of wood [71]. Synchrotron radiation X-ray Tomographic Microscopy with phase-  
237 contrast mode (srPCXTM) was applied to the observation and identification of spruce

238 anatomy at a cellular length scale [72]. srPCXTM has been exploited to assess the  
239 structural degradation of archaeological wood by investigating anatomical features,  
240 measuring residual density, and penetration of consolidating agents [73, 74]

241

## 242 Raman spectroscopy

243

244 Raman spectroscopy provides fundamental knowledge on organic materials at a chemical  
245 level, and does not require any chemical treatment of the sample. It is thus widely used in  
246 the cultural heritage for non-destructive, qualitative, and quantitative analyses of materials.  
247 The area of interest is analyzed at a microscopic level using a laser excitation beam, and  
248 the collected molecular-specific scattered light is evaluated. In the area of micro  
249 investigations, imaging of fiber cell walls, and cellulose and lignin distributions in the plant  
250 cell walls, have provided useful information on the compositional and organizational  
251 features of woody tissues [75]. Although the specificity of Raman spectroscopy is very  
252 high, its sensitivity is somewhat poor, because only a small number of the incident laser  
253 photons are inelastically scattered. Sensitivity can be improved by Raman signal-  
254 enhancing techniques such as the resonance Raman effect and surface-enhanced Raman  
255 scattering (SERS), however applications to archaeological wood artifacts have not yet  
256 been described in the literature.

257 Although Raman spectroscopy does not belong to the most commonly used techniques in  
258 the analysis of archaeological wood, it has been applied to study both softwoods and  
259 hardwoods in their native states. Signals in Raman wood spectra have been assigned to  
260 various wood polymeric components [75-78].

261 One of the few studies on archaeological waterlogged wood using Raman spectroscopy  
262 was conducted by Christensen and co-workers [79] on both consolidated and untreated  
263 archaeological waterlogged wooden artifacts, comparing the results with those obtained  
264 from sound wood. The techniques resulted suitable to highlight a more extensive  
265 degradation of polysaccharide than lignin.

266 Petrou et al. [80] investigated archaeological Neolithic waterlogged pine and oak wood,  
267 and identified characteristic absorption Raman peaks related to cellulose, hemicelluloses  
268 and lignin. Although FT-Raman results cannot be considered as quantitative, on the basis  
269 of a comparison with the relative changes in the intensities of spectral bands associated  
270 with lignin and carbohydrates resulting from decay, the authors concluded both the  
271 softwood and hardwood samples had deteriorated extensively. FT-Raman spectroscopy

272 enabled Petrou et al. to identify the depletion of carbohydrates in archaeological samples  
273 at various stages of deterioration. They observed that Raman data on their archaeological  
274 samples did not support the fact that heartwood is expected to be more stable to decay  
275 than sapwood, and that lignin is expected to be relatively stable to degradation in  
276 waterlogged conditions. They underlined how Raman spectroscopy should be used in  
277 combination with other complementary and supplementary analytical techniques to  
278 achieve an insight into the chemistry of archaeological wood.

279 Marengo et al. used Raman spectroscopy to monitor the surface of wooden boards dating  
280 back to the 16th century subjected to simulated degradation [81], also with a pigmented  
281 layer [82]. The originality of these studies is the attempt to borrow statistical quality  
282 assessment tools from quality control approaches, and to apply the principles from  
283 statistical process control in order to treat degradation as a deviation from the initial “in-  
284 control” state, characterized by the absence of damage. They used principal component  
285 analysis of Raman spectra to build control charts to represent the situation of the system  
286 during degradation. This approach showed how multivariate data analysis techniques are  
287 valuable for data simplification when studying a complex system such as degraded wood,  
288 and for identifying the spectral regions involved in the changes induced by degradation.

289

## 290 Fourier Transform Infrared Spectroscopy

291

292 Infrared spectroscopy (FTIR) is a fast, sensitive, non-destructive method for the analysis of  
293 solid wood micro-samples, requiring minimal sample preparation and widely available  
294 instrumentation. It can be used as a qualitative tool to identify functional groups, to  
295 differentiate between hardwoods and softwoods, and to evaluate the extent of degradation  
296 of wood semi-quantitatively. FT-IR spectroscopy has been used to analyze the chemical  
297 changes in wood during weathering, decay, chemical treatments [83], and biodegradation  
298 [84]. It has permitted to hypothesize chemical modifications in archaeological wood  
299 components by observing the presence or lack of selected bands [85].

300 FT-IR wood spectra show a fingerprint region at  $800\text{--}1700\text{ cm}^{-1}$  and a large OH band  
301 ( $2900\text{--}3400\text{ cm}^{-1}$ ). Specific bands can be assigned to wood components (cellulose,  
302 hemicelluloses and lignin) and degradation products. Comprehensive assignments of  
303 infrared bands for wood are presented in papers by Faix [86, 87], Pandey [88] and  
304 Schwanninger et al. [89].

305 FTIR permits to differentiate between hardwood and softwood on the basis of differences  
306 in hemicelluloses and lignin bands.

307 The carbonyl bands at about  $1740\text{ cm}^{-1}$  and  $1240\text{ cm}^{-1}$ , assigned to hemicelluloses, are  
308 generally more intense in undegraded hardwoods than softwoods, because hardwoods  
309 contain greater concentrations of hemicelluloses than softwoods [90]. Additionally, most  
310 softwoods have a carbonyl absorption at frequency lower than  $1738\text{ cm}^{-1}$ , whereas in most  
311 hardwoods the frequency of carbonyl absorption is higher than  $1738\text{ cm}^{-1}$ . Pavlikova et al.  
312 found that the shift in the carbonyl absorption to a lower wavenumber for softwoods is  
313 primarily due to the relatively higher concentration of lignin [91].

314 The bands in the  $1200\text{-}1600\text{ cm}^{-1}$  region of the spectrum arise primarily from lignin [92].  
315 The relative intensity of the ratio of the two absorptions,  $1600$  and  $1510\text{ cm}^{-1}$ , as well as  
316 the position of the absorption around  $1510\text{ cm}^{-1}$ , varies significantly according to wood  
317 type. Softwoods usually show the typical aromatic ring deformation mode above  $1509\text{ cm}^{-1}$ ,  
318 whereas hardwoods typically absorb below  $1509\text{ cm}^{-1}$ . The band at approximately  $1270$   
319  $\text{cm}^{-1}$ , which arises from the guaiacyl ring breathing and C-O stretching, has also been used  
320 for the determination of total lignin content in softwoods, whereas hardwood spectra show  
321 a pronounced band at about  $1330\text{ cm}^{-1}$  which is associated with syringyl lignin [86, 90]. In  
322 addition, FT-IR spectra of softwoods, in which lignin content is relatively higher than  
323 hardwoods, show a higher intensity of the absorption bands at about  $1510$  and  $1270\text{ cm}^{-1}$   
324 than those from cellulose and hemicelluloses. Additionally, softwoods contain more lignin  
325 than xylans, and the intensity of the band at  $1270\text{ cm}^{-1}$  is stronger than the band at  $1220$   
326  $\text{cm}^{-1}$  of xylans. The opposite trend is observed for hardwood

327 FT-IR has often been used for the semi-quantitative evaluation of the degradation state of  
328 historical/archaeological wood. The data evaluation consists in choosing characteristic  
329 bands for each wood component (hemicelluloses, cellulose and lignin) and in measuring  
330 the heights and the areas of the selected bands. The ratio between two heights or areas  
331 can be correlated to the ratio between the components that generated those peaks.

332 Macleod and Richards [90] measured the absolute peak heights of different absorption  
333 bands for hemicelluloses in archaeological wood at  $1740$  and  $1220\text{ cm}^{-1}$ , for cellulose at  
334  $1370$ ,  $1160\text{ cm}^{-1}$  and  $896$ , and for lignin at  $1510$  and  $1260\text{ cm}^{-1}$ , and compared the values  
335 with those obtained for undegraded wood of the same species. The same procedure was  
336 applied in other works [91, 93, 94], some of which are listed in Table 1.

337 The attenuated total reflectance (ATR) device in the IR analysis has several advantages  
338 over the more traditional transmission IR technique using KBr pellets, thus allowing the

339 acquisition of spectra with a reduced pretreatment of the wood. However, the wood needs  
340 to be milled beforehand in order to obtain robust and reliable results in dry matter, mainly  
341 because of the quality of the contact between the material and the crystal. Picollo et al  
342 [100] compared the data acquired for the same wooden materials (ancient wooden  
343 artifacts) by applying the traditional KBr pellet transmission mode and the ATR mode.  
344 They obtained similar quality spectra with both techniques. However, compared to the  
345 ATR technique, the KBr pellet transmission mode generally showed a lack of sensitivity in  
346 the  $1640\text{ cm}^{-1}$  region, commonly assigned to  $\text{H}_2\text{O}$  absorption [102]. ATR-FTIR has also  
347 been used to analyze archaeological waterlogged wood in wet conditions without drying.  
348 The results showed more resolved peaks, thanks to a better contact with the crystal  
349 compared to dry conditions. In addition, the results obtained by wet chemical analysis  
350 were used to perform a calibration, and the calibration model was based on multivariate  
351 statistical analysis through partial least-squares regression. ATR-FTIR in these conditions  
352 was thus successfully used to quantitatively evaluate the content of wood components in  
353 archaeological wood samples [101, 103]. Figure 3 compares spectra obtained by ATR-  
354 FTIR analyses of archaeological and sound elm wood, highlighting significant differences  
355 in the bad and good states of preservation of the material.

356 The FT-IR studies have, in general, been achieved by sample destruction or physical  
357 modification (e.g., use of milled samples). Near-infrared (NIR) spectroscopy has shown an  
358 interesting potential in obtaining mechanical, physical, and chemical information from  
359 wood, while retaining its anatomical/biological structure [98, 104]. NIR signals depend on  
360 the particle size, thus not only molecular, but also physical information can be obtained. If  
361 this information in the spectra is irrelevant and undesired, it is possible to extract the  
362 chemical information, by applying transformation techniques that remove baseline shifts,  
363 slope changes and the curvilinearity of spectra, thus reducing the influence of particle size,  
364 scattering and other influencing factors. The transformation techniques generally used  
365 include calculating first and second derivatives, due to the variability of the particles in the  
366 structure of wood [105].

367 The drawback of NIR spectroscopy is the difficulty in interpretation of the NIR spectrum  
368 due to the chemical complexity of the wooden material. However, some researchers have  
369 tried to clarify such information-rich spectroscopic signals. Michell and Schimleck [106]  
370 investigated the origins of bands in the NIR spectra of *Eucalyptus globulus* wood.  
371 Takayama et al. [107] applied NIR Fourier transform Raman (FT-NIR) spectroscopy to

372 characterize lignin. Tsuchikawa and Siesler [108, 109] analyzed the location of OH groups  
373 in different states of cellulose in wood using the FT-NIR polarization spectra.  
374 The simplicity and ease of application, without destroying the sample, has led to  
375 application of FT-NIR for the characterization of archaeological wood. In 2003 Yonenobu  
376 and Tsuchikawa applied FT-NIR spectroscopy to investigate an old wooden building from  
377 the 7<sup>th</sup> century [95]: they calculated the second derivative of absorption spectra and  
378 examined the characteristic bands for polysaccharides and lignin. They concluded that the  
379 cellulose crystallinity of historical wood was almost comparable to modern wood. There  
380 was also a relative decrease in cellulose and increase in lignin. Another study [97]  
381 exploited variation of NIR spectra after deuterium exchange to investigate chemical  
382 changes induced by ageing in archaeological wood, with respect to sound wood.  
383 Sandak et al. [98] performed FT-NIR measurements on archaeological waterlogged wood  
384 from different sites. They repeated every measurement fifteen times and calculated  
385 second derivatives of absorption spectra. In order to validate FT-NIR techniques as a tool  
386 to evaluate the conservation state of archaeological waterlogged wood samples,  
387 spectroscopic results were correlated with those from classical wet analysis (TAPPI  
388 methods) and XRD measurements. The results were then processed by PCA and Partial  
389 Least Square (PLS) statistical methods. The authors used the NIR technique for a rapid  
390 estimation of the cellulose and lignin contents. Equally important was the match between  
391 the near infrared spectroscopic methods and x-ray diffraction in the potential assessment  
392 of the cellulose crystallinity - the most stable structure within carbohydrates in wood [98].  
393 Figure 4 shows the NIR spectra (second derivatives) for several archaeological  
394 waterlogged oak wood samples compared with an undegraded oak wood.  
395 Other examples of applications of FT-IR and FT-NIR techniques for the analysis of  
396 historical or archaeological wood material are presented in Table 1.

397

## 398 Nuclear Magnetic Resonance

399

400 Nuclear magnetic resonance (NMR) has been one of the most important analytical  
401 techniques for the characterization of organic materials in the last 50 years. Until recently  
402 its impact on archaeology had been minimal for two reasons well described by Lambert  
403 [110], mainly concerning the sensitivity and resolution of the technique. Instrumental  
404 developments have drastically changed this situation, and now NMR is used with good  
405 results in the field of cultural heritage. Thanks to the wide diversity of measurement assets

406 and methodologies developed, several applications of NMR to the study of archaeological  
407 wood have been recently reported in the literature.

408 Solid state NMR does not require sample pre-treatment, however its low sensitivity, and  
409 consequently the high amount of sample needed, means that it has only been rarely used  
410 to investigate archaeological artifacts.

411 In the last few decades, important innovations such as cross polarization (CP) and magic  
412 angle spinning (MAS), have provided information on the state of conservation of wood, the  
413 loss of cellulose and lignin demethylation through the observation of specific bonds.

414 Molecular motions can be studied by relaxation and diffusion measurements, in which a  
415 probe molecule (usually water) is used to study the response in the wood matrix, thus  
416 obtaining information on porosity.

417 Hatcher et al. [111] were the first to use NMR to examine the effect of burial on  
418 archaeological wood. They used CPMAS  $^{13}\text{C}$  NMR to compare the spectrum of a modern  
419 spruce sample with those of a 450-year-old spruce wood pile and of 10000-year old wood  
420 remains from a *Sequoia* tree. By assigning the peaks in the NMR spectra to specific  
421 carbons from cellulose or lignin, they noticed the depletion in carbohydrates in the buried  
422 wood, as well as differences between the outer and the inner parts of the pile. A more  
423 homogeneous degradation of carbohydrates and an almost perfect conservation of lignin  
424 was found for the 10000-year old tree.

425 Hedges et al. [112] demonstrated by CPMAS  $^{13}\text{C}$  NMR that wood components follow this  
426 order of stability during degradation in buried wet environments: guaiacyl and p-hydroxyl  
427 lignin > syringyl lignin > pectin > alpha-cellulose > hemicelluloses. In 1987 Saiz-Jimenez et  
428 al. [113] compared these results with those obtained by Py-GC/MS, and found a good  
429 match.

430 In 1993 Wilson et al. [92] used CPMAS  $^{13}\text{C}$  NMR to study the waterlogged wood from  
431 several shipwrecks dating back to the 17<sup>th</sup> to 19<sup>th</sup> centuries, assessing differences in the  
432 loss of carbohydrates among the samples and highlighting the presence of  $\beta$ -O-4 linkages  
433 (Figure 5) in lignin.

434 In the same year Pavlikova et al. [91] compared wood natural degradation with acid  
435 hydrolysis artificial degradation, and found that artificial degradation can affect the lignin  
436 structure more than natural degradation.

437 A systematic work on the application of high resolution solid state CPMAS  $^{13}\text{C}$  NMR to  
438 archaeological wood was accomplished by Bardet and co-workers. They assessed the

439 resonance assignment of the peaks in the NMR spectra, as shown in Figure 6, which  
440 compares a modern beech wood and two archaeological beech woods [114].  
441 The main observation of Bardet's work was the preservation of the most abundant  
442 intermonomeric bond in the lignin structure, the so-called  $\beta$ -O-4 linkages (Figure 5), in a  
443 saturated water environment. On the other hand, the degradation of cellulose and other  
444 sugars was enhanced, particularly hemicelluloses since its characteristic signal at 21 ppm  
445 was no longer visible in the corresponding spectra. Bardet's method provided quantitative  
446 results, and the amount of sample necessary for the analysis was 6-10 mg, thus making  
447 the technique more competitive to work on archaeological artifacts than before [114, 115].  
448 Interactions between polyethylene glycol and archaeological wood components were also  
449 studied [116], proving that the degradation state of wood can also be assessed in the  
450 presence of the consolidating agent. Bardet summarized most of his outstanding work on  
451 wood analysis by solid state CPMAS  $^{13}\text{C}$  NMR in 2009 [117].  
452 Other authors have used the same technique on archaeological wood, mainly observing  
453 different levels of carbohydrates and lignin degradation [63, 99, 118-123].  
454 Solid state  $^{13}\text{C}$ -NMR appeared to be a useful technique to quantitatively investigate the  
455 differences between wood components and to assess the preservation of the most  
456 abundant intermonomeric bond in the lignin structure. However, the technique is not  
457 sensitive enough to characterize and quantify the other important intermonomeric bonds in  
458 the lignin structure, and does not enable functional groups to be observed and quantified  
459 as carboxylic and alcoholic moieties.

460 To overcome these problems Colombini et al. [40] applied NMR analytical tools, already  
461 used for the study of lignin in the pulp and paper industry [124, 125], to samples of lignin  
462 extracted from archaeological wood. These methods were quantitative  $^{13}\text{C}$ -NMR after  
463 acetylation of extracted lignin, quantitative  $^{31}\text{P}$ -NMR analysis after phosphitylation of  
464 extracted lignin, qualitative and quantitative 2D-HSQC (bidimensional heteronuclear  
465 single-quantum correlation), which is currently the most powerful tool for characterizing  
466 lignin [126]. The authors concluded that the extracted archaeological lignin were rich in  
467 arylglycerol  $\beta$ -O-4 units and also contained amounts of  $\beta$ -5 and  $\beta$ - $\beta'$  units, whereas the 5-  
468 5'-O-4 unit was not observed [40], reinforcing Bardet's conclusions. It was also possible to  
469 identify  $\beta$ -O-4 units in which oxidation of the carbon at the benzylic position had occurred,  
470 connecting the phenomenon to white rot fungi degradation. The analysis by  $^{31}\text{P}$ -NMR led  
471 to the quantification of condensed phenolic and carboxylic units, thus obtaining further  
472 evidence of an oxidative effect on the lignin as a consequence of the action of white rot

473 fungi. In addition, unusual intermonomeric bonds 4-O-5' were observed in significant  
474 amounts. The same techniques were applied to other works on extracted lignin [39], and  
475 on unprocessed wood [41], highlighting the presence of lignin-carbohydrate complexes.  
476 Information on the backbone of lignin has also been obtained by 2D homocorrelated NMR  
477 spectroscopy (HOHAHA). Lignin from a wooden coffin dating back to the Graeco–Roman  
478 period in Egypt was studied [127]. The main degradation patterns were identified along  
479 with the structural details of the degraded lignin.

480 The most important drawback of high resolved solution state NMR is that it requires  
481 samples to be dissolved in a deuterated solvent. Thus the wood samples need to be pre-  
482 treated (e.g. powdering, extraction, dissolution, acetylation) before performing a  
483 characterization. This means there may be a chemical alteration in the lignocellulosic  
484 polymers, which makes an interpretation of the results quite delicate.

485 Cole et al. [128] investigated for the first time the potential of NMR imaging for the study of  
486 archaeological waterlogged wood by determining the distribution of water in waterlogged  
487 samples. High-quality images of internal wood structures were obtained, with a resolution  
488 of 25 $\mu$ m. The authors observed that the possibility of achieving this resolution was limited  
489 by the paramagnetic effect of the iron, which was present as iron II and III salts, products  
490 of the oxidation and dissolution of nails. However NMR proton imaging enabled the iron to  
491 be associated with advanced degradation, and also the iron removal and uptake of  
492 consolidating polymers to be monitored.

493 Robertson et al. [129] performed 1-D  $^1\text{H}$  NMR profile experiments on an oak timber of the  
494 Mary Rose ship, one of the most important findings of the 20<sup>th</sup> century. They monitored the  
495 diffusion of  $\text{D}_2\text{O}$  into the matrix of degraded wood. By studying samples from different  
496 depths and orientations, they found that the longitudinal orientation was the most suitable  
497 for penetration, because of the presence of vessels and tracheids, and that the penetration  
498 was proportional to the decay because of the increased porosity.

499 Unilateral NMR is a portable non-invasive technique, which allows measurements to be  
500 performed *in situ* without any sampling. It has recently been used for numerous  
501 applications in the field of cultural heritage [122]. The magnetic field is applied to one side  
502 of the object, therefore measurements can be performed directly on large objects such as  
503 wall paintings, monuments and buildings, fully preserving the integrity and the dimension  
504 of the object under investigation. The technique has also been applied to the analysis of  
505 archaeological wood [121]: in particular spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times  
506 can be measured.  $T_2$  was proved to be sensitive to wood degradation.  $T_1$  was sensitive to

507 the possible presence of paramagnetic elements. Depth profiles, spanning several  
508 millimeters in depth were also acquired (Figure 7). The technique provided information on  
509 the water content and proved to be a powerful screening tool for plan sampling.

510 The results obtained with this technique can be assimilated to those achievable by low  
511 resolution solid state  $^1\text{H}$  NMR measurements [120], however unilateral NMR has the  
512 enormous advantage of being portable and not invasive, thus it is likely to be increasingly  
513 used in the future.

514 Table 2 summarizes the most relevant applications of NMR spectroscopy to  
515 archaeological wood.

516

517 Analytical Pyrolysis (Py-MS, Py-GC/MS, DE-MS)

518

519 Analytical pyrolysis is the thermal fission (commonly in a temperature range between 300  
520 and 800°C) of a sample into molecules (pyrolysis products or fragments) of a lower mass,  
521 yet large enough to provide analytical information on the original sample. The pool of  
522 fragments provides a fingerprint that is characteristic of a particular sample, in terms of  
523 both the fragment nature and relative distribution [131]. Analytical pyrolysis (Py) based  
524 techniques are very useful for investigating wood, cellulose, lignin isolated from softwoods,  
525 hardwoods and grasswood, and residual lignin from paper pulping [113, 131-136].

526 Recently, analytical pyrolysis has also proven to be helpful for obtaining chemical  
527 information on archaeological wood [40, 137-140].

528 Pyrolysis of wood produces a mixture of low molecular weight compounds derived from  
529 polysaccharides, which also lead to the formation of levoglucosan, and relatively simple  
530 phenols resulting from the cleavage of ether and C-C bonds of lignin [141-143]. The  
531 phenols produced retain their substitution patterns from the lignin polymer [144], thus it is  
532 possible to identify components from the *p*-hydroxyphenylpropanoid (H),  
533 guaiacylpropanoid (G) and syringylpropanoid (S) lignin units.

534 Analytical pyrolysis can be easily coupled to MS or GC/MS, thus allowing the online  
535 thermal degradation of the macromolecule followed by the identification of pyrolysis  
536 products and of their relative amounts by techniques such as GC, MS and GC/MS.

537 Analytical pyrolysis is attractive for characterizing lignocellulosic polymers in  
538 archaeological findings due to (i) high sensitivity, (ii) small sample size (usually few tenths  
539 of  $\mu\text{g}$ ), (iii) negligible sample preparation, and (iv) short analysis time (from minutes for Py-  
540 MS to typical 40 minutes for Py-GC/MS).

541 Techniques that directly identify pyrolysis products by MS, without chromatographic  
542 separation, are based on a set of experimental assets. They thus have names such as Py-  
543 MS, direct exposure – mass spectrometry (DE-MS), and direct temperature resolved mass  
544 spectrometry (DTMS). Coupling pyrolysis directly to mass spectrometry reduces analysis  
545 times and extends the range of detectable pyrolysis fragments to structures that would be  
546 too large for analysis by gas chromatography.

547 All these techniques require minimal or no pre-treatment of the sample. The sample is  
548 placed onto a filament (such as a solid, as a solution or as a dispersion in a suitable  
549 solvent) or in a cup. The sample is desorbed or pyrolyzed by controlled heating [113, 145-  
550 153] directly into the ion source. Due to the difficulty in interpreting the results, multivariate  
551 analysis of mass spectral data has sometimes been used to compare, differentiate and  
552 classify the samples [145, 152-156].

553 For instance, DE-MS together with Principal Component Analysis (PCA) was successfully  
554 used in the study of degradation undergone by archaeological waterlogged wood and  
555 lignin derived from objects recovered from the Ancient Harbour of Pisa San Rossore in  
556 Tuscany (Italy) and from shipwrecks found in the Tantura Lagoon (Haifa, Israel) and  
557 Epave du Grand Conglouè recovered near Marseille (France) [137, 156], and waterlogged  
558 wooden objects from two archaeological sites, *Biskupin and Żółte* in Poland [157]. The  
559 data were compared to those relative to sound native wood of the same species: pine  
560 (*Pinus pinaster*), elm (*Ulmus minor*), beech (*Fagus sylvatica*), alder (*Alnus glutinosa*) and  
561 oak (*Quercus roburs*).

562 The technique can be used to differentiate between guaiacyl and syringyl lignin. Figure 8  
563 presents the mass spectra obtained for an archaeological sample (Figure 8a) from the  
564 Żółte site and for reference (Figure 8b) alder (*Alnus glutinosa*). These spectra are  
565 characterized by the occurrence of peaks indicative of a guaiacyl-syringyl lignin. Table 3  
566 lists the m/z identified and their assignment. Peaks at m/z 55, 60, 69, 73, 97, 114 and 126  
567 are due to polysaccharide pyrolysis products. The peak at m/z 69 is formed in the  
568 fragmentation of furan derivatives; m/z 114 can be attributed to xylans, while 55, 60 and 73  
569 are derived from levoglucosan [145, 151].

570 The main difference observed between the mass spectra of the native and archaeological  
571 wood is the presence in native wood of intense peaks derived from the pyrolysis of  
572 polysaccharides (cellulose and hemicelluloses), which are considerably reduced in the  
573 archaeological wood.

574 In all the mass spectra obtained for hardwood and softwood, in addition to the peaks

575 derived from the guaiacyl and syringyl monomer structures, peaks attributable to fragment  
576 ions derived from dimeric structures of lignin macromolecule were observed. The peaks at  
577  $m/z$  272, 302, 332, and  $m/z$  358, 418 indicate that these compounds are guaiacyl-guaiacyl  
578 (G-G), guaiacyl-syringyl (G-S) and syringyl-syringyl (S-S) containing dimeric lignin  
579 pyrolysis products. For example the peak at  $m/z$  272 corresponds to the molecular peak of  
580 the G-G dimer compound with a stilbene-like structure (3,3'-dihydroxy-4,4'-dimethoxy-  
581 stilbene) [151].

582 Due to the complexity of the mass spectra obtained in the DE-MS analysis of wood, PCA  
583 was used as a pattern recognition technique to compare the obtained mass spectra and to  
584 highlight differences and similarities between the various samples. The resulting score plot  
585 for the first two principal components is shown in Figure 9. PCA succeeded in separating  
586 the samples between softwoods and hardwoods (PC1), and between sound and  
587 archaeological wood (PC2).

588 The PC1 loadings show that PC1 is positively correlated to the intensities of the peaks due  
589 to the fragmentation of syringyl monomers ( $m/z$ : 167, 181, 210) and negatively correlated  
590 to the intensities of the peaks due to the fragmentation of guaiacyl monomers ( $m/z$ : 124,  
591 137). Therefore, PC1 gives a rapid indication of the ratio between the amounts of syringyl  
592 and guaiacyl fragments, and on the type of wood, discriminating between softwoods and  
593 hardwoods. Examination of PC2 loadings shows that PC2 is positively correlated to the  
594 intensities of the peaks ( $m/z$  55, 69, 73, 85, 97, 114, 126) due to the fragmentation of  
595 polysaccharides. This means that PC2 differentiates the samples on the basis of the  
596 polysaccharide content, and gives an indication of the degree of wood decay. All  
597 archaeological samples are located in the lower part of the PC2/PC1 score plot, which  
598 highlights their lower polysaccharide content compared to native samples of the same  
599 species.

600 Direct coupling of Py with MS is a rapid technique which is suitable for the screening of  
601 many samples, however more commonly pyrolysis products are transferred into a  
602 chromatographic system and separated before MS analysis. The more common  
603 configuration is the coupling with gas chromatography and a mass spectrometry detector :  
604 Py-GC/MS. This approach means that the chemical composition of a sample can be  
605 reconstructed on the basis of a detailed interpretation of the chromatographic molecular  
606 profile of the thermal degradation products of the original components, and on the  
607 recognition in the chromatogram of specific molecular markers or of characteristic  
608 molecular patterns, which act as molecular fingerprints of the pyrolyzed material.

609 Over the last decades, Py-GC/MS has been enhanced in order to improve analytical  
610 efficiency and to widen its applicability. As in conventional GC, derivatisation reagents  
611 have been introduced to improve the chromatographic separation and analytical response  
612 of polar compounds [159-161]. Conventional pyrolysis of organic matter releases many  
613 compounds that are not volatile enough to be efficiently separated in a gas  
614 chromatographic column. For example, in the case of degraded wood, acidic pyrolysis  
615 products such as vanillic acid are not detected in GC without derivatisation. Thermally-  
616 assisted derivatisation reactions, which can be performed *in situ* in the pyrolyzer by adding  
617 reagents, render polar pyrolysis products sufficiently volatile for gas chromatographic  
618 separation. Thus it is possible to separate and detect much more structurally significant  
619 products than observed by conventional pyrolysis techniques, with a better  
620 chromatographic performance and longer column lifetime.

621 The most common derivatization approach in analytical pyrolysis coupled with GC/MS is a  
622 trimethylation reaction, where tetramethylammonium hydroxide (TMAH) is used  
623 simultaneously with pyrolysis [162]. The method is based on the high temperature reaction  
624 of the quaternary alkylammonium hydroxide with molecules containing functional groups,  
625 carboxylic acids, ethers and especially esters, which are susceptible to hydrolysis and  
626 methylation. Thermally-assisted hydrolysis and methylation using TMAH have been  
627 successfully applied to a variety of samples ranging from natural organic substances to  
628 synthetic polymers [162, 163]. TMAH has been widely used for the characterization of  
629 wood and its components [164-166]. However it is not ideal because the methylation of  
630 phenolic groups makes them indistinguishable from methoxylic groups, unless isotopically  
631 labelled reagents are used. For this reason, the use of silylating reagents for *in situ*  
632 derivatisation reactions is of particular interest in the Py-GC/MS analysis of wood [39,  
633 167].

634 Silylation reduces the polarity of hydroxylic and carboxylic groups present in pyrolysis  
635 products by transforming them into the corresponding TMS ethers and esters, replacing  
636 active hydrogens by silyl groups. Silylated derivatives are thus more volatile and stable  
637 than the corresponding underivatized precursors, and GC/MS analysis is enhanced. The  
638 trimethylsilyl (CH<sub>3</sub>)<sub>3</sub>Si- group is the most popular for gas chromatographic applications  
639 [168] and the two adopted reagents for thermally assisted *in situ* trimethylsilylation in Py-  
640 GC/MS system are hexamethyldisilazane (HMDS) [39, 137-139, 169, 170] and N,O-bis-  
641 (trimethylsilyl)-trifluoroacetamide (BSTFA) [167, 171, 172].

642 Py-GC/MS, with and without derivatisation, has been used to study the chemical  
643 alterations of wood components [113, 173, 174] induced by fungi [175] such as brown-rot  
644 [176] and white-rot [177, 178], and also by chemical [179-181] and enzymatic treatments  
645 [182-184] for the pulp and paper industry by highlighting diagnostic markers of the various  
646 lignin units.

647 Py-GC/MS has been also used to investigate the degradation in archaeological wood from  
648 a chemical point of view [39, 137-140, 157, 158, 185, 186]. Table 4 shows a list of  
649 applications of Py-GC/MS for the study of archaeological and fossil wood, including the  
650 relative pyrolysis conditions.

651 Literature data demonstrate that Py-GC/MS achieves semi-quantitative results on the  
652 extent of cellulosic loss, and highlights the chemical modifications undergone by  
653 polysaccharides and lignin. Differences between the archaeological wood of several  
654 historical periods and sound wood have been found in the relative amounts of pyrolysis  
655 products, which above all show a polysaccharide degradation/depletion compared to lignin  
656 [39, 137-139, 158, 169]. The relative loss of polysaccharide pyrolysis products, in terms of  
657 peak areas, from sound to archaeological wood, was observed up to 90%.

658 The loss of polysaccharides induced by degradation can be semi-quantitatively estimated  
659 by interpreting the pyrograms and calculating parameters such as the Holocellulose/Lignin  
660 (*H/L*) pyrolytic coefficient, defined as the ratio between the relative abundances of  
661 holocellulose (cellulose and hemicelluloses) and lignin pyrolysis products. *H/L* coefficients  
662 of different samples analyzed in the same conditions can be compared, achieving a  
663 quantitative evaluation of decay processes. *H/L* coefficients reported in the literature for  
664 sound wood vary from around 1.0 for softwood up to 3.0 for hardwood, depending on the  
665 species. Pyrolytic *H/L* of extensively degraded archaeological wood have been reported to  
666 be significantly low (0.2-0.3) [138, 139]. Figure 10 shows the pyrograms of sound maple  
667 wood in comparison with an archaeological maple wood, in which the loss of  
668 polysaccharide pyrolysis products is clear from the changes in the pyrolytic profile.

669 The information obtained by the interpretation of pyrolysis products or lignin are not limited  
670 to the depletion of carbohydrates, because the comparison or the increase in specific  
671 pyrolysis products that are markers of degradation or alteration can also be evaluated. A  
672 study carried out on archaeological oak (*Quercus* sp.) wood samples, ranging from the  
673 16<sup>th</sup> century AD to 6000 BP, provided the first unequivocal evidence that the demethylation  
674 of syringyl units occurs very early in wood degradation [140]. The GC/MS pyrograms  
675 revealed a number of methoxycatechols, directly related to syringyl units, which are

676 characteristic building blocks of angiosperm lignin. A Py-GC/MS study of a sample of  
677 waterlogged beech from the excavation of the site at San Rossore (Pisa, Italy) confirmed  
678 the formation of catechols and methoxy catechols, which are derived from the  
679 demethylation of both guaicyl and syringyl lignin [137].

680 In another recent study [139], archaeological waterlogged wood remains from the roof of a  
681 Roman villa buried in AD 79 by the eruption of Vesuvius, were analyzed by pyrolysis-gas  
682 chromatography/mass spectrometry (Py-GC/MS), enabling the authors not only to  
683 highlight the loss of polysaccharides and the demethylation undergone by lignin, but also  
684 its oxidation. The analyzed samples revealed a relatively high abundance of vanillin,  
685 acetovanillone, vanillic acid and coniferylaldehyde, indicating that lignin monomers had  
686 also undergone oxidation reactions in the course of ageing in buried conditions. This could  
687 be clearly observed by using the O/L coefficient taken as an indicator of the degree of  
688 oxidation of lignin and calculated as the sum of the normalized areas of vanillin,  
689 acetovanillone, vanillic acid and coniferylaldehyde divided by the sum of the areas of all  
690 the lignin pyrolysis products. The O/L coefficient values shows that the O/L for sound wood  
691 is 0.07 and most archaeological samples showed a coefficient higher than 0.1, thus  
692 revealing a higher degree of oxidation.

693 Table 4 summarizes the literature regarding the application of pyrolysis-based techniques  
694 for the analysis of artificially and naturally degraded wood.

695

## 696 **Conclusions**

697

698 The chemical changes produced by decay and ageing in archaeological wood can be  
699 studied by various microscopic, spectroscopic, and hyphenated techniques including a  
700 chromatographic separation and mass spectrometric detection, thus providing different  
701 types of information.

702 Microscopic and imaging techniques achieve essential morphological information including  
703 species identification and decay of the wood cell structure.

704 There has been an increase in applications of instrumental chemical analyses based on  
705 light spectroscopy, mass spectrometry and NMR. These methods assess the degradation  
706 of archaeological wood at a molecular level, including the loss of polysaccharides, lignin  
707 oxidation and defunctionalization. In addition, all these analytical techniques have been  
708 implemented and adapted to use a minimum amount of sample, in some cases less than 1

709 mg, thus becoming particularly suitable to study cultural heritage objects where sampling  
710 is a crucial aspect.

711 From the surveys described in the literature, this review concludes that a multi-analytical  
712 approach to evaluate the state of preservation of archaeological and historical wooden  
713 objects is the best method in order to obtain a complete and complementary array of  
714 information. A reliable diagnostic evaluation helps us to understand the properties of  
715 decayed wood, to classify the material according to its current level of decay, to identify  
716 ongoing degradation and to select the most appropriate methodologies for  
717 conservation/restoration.

718

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1209 **Captions**

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1211 **Figure 1** Bacterial degradation in wood from the Uluburun shipwreck, Turkey (1400 BC)  
1212 (A-C) and the Goldcliff intertidal site, Wales (200-100 BC) (D-F). (A and B) The secondary  
1213 walls have been altered extensively. The residual cell walls are porous and contain minute  
1214 holes. (C) The decayed wood has lost its normal strength and easily collapses and  
1215 becomes distorted. (D) Tunnels formed by bacteria are evident within the secondary cell  
1216 walls. (E and F) Cells with advanced decay have extensive degradation and remnants of  
1217 tunnels can be seen within secondary walls. The degraded secondary wall often consists  
1218 of a residual, degraded wall matrix, which is often disrupted and in various stages of  
1219 disintegration. A-C SEM, D-F TEM. Bar = 100  $\mu\text{m}$  in A-C, and 5  $\mu\text{m}$  in D-F (Reproduced  
1220 from Ref. [8] with permission of Elsevier.)

1221 **Figure 2** Comparison between Sub- $\mu$ -XCT images obtained for archaeological (left) and  
1222 recent (right) beech wood. A) Diffuse-porous wood (cross section); B) thickened medullary  
1223 ray at tree ring boundary (cross section); C) multiseriate medullary ray (tangential section);  
1224 D) heterogeneous medullary ray (radial section). (Adapted from Ref. [68] with permission  
1225 of Elsevier.)

1226 **Figure 3** Comparison between ATR-FTIR spectra of sound elm wood and of two  
1227 archaeological elm wood samples: Cm5 in a good condition and Pp B17 in a bad condition  
1228 of preservation. (Reproduced from Ref [103] with permission of Elsevier.)

1229 **Figure 4** Overlaid NIR spectra a) (second derivatives) and magnifications of selected  
1230 areas b) and c) for archaeological waterlogged wood samples (Q1-Q5) and sound oak  
1231 wood (Q6). (Reproduced from Ref [98] with permission of Elsevier.)

1232 **Figure 5** Major structural units in lignin polymer  $\beta$ -O-4 (A),  $\beta$ -5 (B),  $\beta$ - $\beta'$  (C), 5-5' (D),  
1233 5-O-4 (E),  $\beta$ -1 (F) and 5-5'-O-4 (G).

1234 **Figure 6** 100-MHz CP/MAS  $^{13}\text{C}$  high-resolution solid-state NMR spectra of beech: modern  
1235 wood (A) and archaeological samples with water contents of 82% (B) and 91% (C).  
1236 Signals 1, 8, 9, 12, 13 and 16 at 172, 104.8, 88.7, 72.17, 64.7 and 21 ppm were assigned  
1237 to carbohydrates respectively; signals 10 and 11 at 83.8 and 74.75 ppm respectively were  
1238 assigned to both lignin and carbohydrates and the other signals (152.6, 147, 136, 134.3,  
1239 121, 114-106, 61.58 and 55.65 ppm) derived from lignin. (Reprinted with permission from  
1240 [114]. Copyright (2015) American Chemical Society.)

1241 **Figure 7** (a) Results obtained by using an aperiodic saturation recovery sequence to  
1242 measure T1 on areas of the inner side of a wood panel with green monochrome

1243 decorations (IP1 and IP8), and on unpainted areas (IP3, IP4, and IP6). (b) Results  
1244 obtained by using an aperiodic saturation recovery sequence to measure T1 on areas of  
1245 the outer side of the panel (HP2, HP3, HP4 and HP7). (c) CPMG decays reported in a  
1246 semi-logarithmic scale measured on areas of the inner side of the panel (IP4 and IP7), on  
1247 areas of the outer side (HP2 and HP3) and on a seasoned yew wood. (d) T2 distributions  
1248 obtained by applying a Laplace transformation to CPMG decays measured on seasoned  
1249 yew wood, on areas IP7 and HP2. (e) Comparison between depth profiles measured on  
1250 areas of the inner side of the panel (IP5 and IP7). (f) Comparison among depth profiles  
1251 measured on areas of the outer side of the panel (HP3, HP4 and HP5). (Reprinted from  
1252 [121] with kind permission from Springer Science and Business Media.)

1253 **Figure 8** DE-MS mass spectra of a reference sound alder wood, b archaeological alder  
1254 wood from the Žólte site [158].

1255 **Figure 9** PCA score plot of PC1 and PC2 of mass spectral data obtained by DE-MS  
1256 analysis of archaeological wood from different sites and of reference wood. The first two  
1257 principal components account for 72.9% of total variance of the data set, represented by  
1258 the mass spectra in the range  $m/z$  50-500. Sound wood:  $\nabla$ -Pinus,  $\circ$ -Ulmus,  $\triangle$ -Alnus,  $\square$ -  
1259 Fagus,  $\diamond$ -Quercus; Archaeological wood:  $\blacktriangledown$ -Pinus,  $\bullet$ -Ulmus,  $\blacktriangle$ -Alnus,  $\blacksquare$ -  
1260 Fagus,  $\blacklozenge$ -  
Quercus [158].

1261 **Figure 10** Py(HMDS)-GC/MS profiles obtained for the analysis of sound maple wood (a)  
1262 and archaeological maple wood (b). C-carbohydrates; G-guaiacyl lignin; S-syringyl lignin.

1263 **Table 1** The most relevant applications of Infrared spectroscopy to archaeological wood.

1264 **Table 2** The most relevant applications of NMR spectroscopy to archaeological wood.

1265 **Table 3** Lignin pyrolysis products observed in DE-MS mass spectra [158]

1266 **Table 4** The most relevant applications of Py-GC/MS to archaeological and fossil wood.

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**Table 2** The most relevant applications of Infrared spectroscopy to archaeological wood.

Sample description	Instrumental conditions	Ref.
Shipwrecks: Batavia (1629), Vergulde Draeck (1656), Rapid (1811), James Matthews (1841) and the Day Dawn (1886) <b>Species:</b> White oak ( <i>Quercus alba</i> )	FT-IR; KBr pellet; region: 700-2000 $\text{cm}^{-1}$ , 256 scans at 4 $\text{cm}^{-1}$ resolution. <b>Complementary techniques:</b> solid-state NMR; Py-GC/MS	[92]
Buried hardwoods dated 2000 and 10 000 years B.P; from the fluvial sediments of the river Elbe <b>Species:</b> Oak ( <i>Quercus</i> sp.)	FT-IR; KBr pellet; 100 scans at 2 $\text{cm}^{-1}$ resolution. <b>Complementary techniques:</b> solid-state NMR, EPR Spectroscopy,	[91]
Shipwrecks: Vergulde Draeck (1656), Rapid (1811), Favourite (1867) and the Hadda (1877) <b>Species:</b> White oak ( <i>Quercus alba</i> ), Longleaf pine ( <i>Pinus palustris</i> ), Beech ( <i>Fagus sylvatica</i> ), Elm ( <i>Ulmus minor</i> )	FT-IR; region: 1800-500 $\text{cm}^{-1}$ , in diamond device. <b>Complementary techniques:</b> SEM, XRD, ICP-AES	[90]
Upright pillars of an old building with a construction dated around A.D. 750 <b>Species:</b> Hinoki cypress ( <i>Chamaecyparis obtuse</i> )	FT-NIR; monochromatic light range: 1100-2500 $\text{cm}^{-1}$ at 2 $\text{cm}^{-1}$ resolution. Second-Derivative Spectra of the samples.	[95]
Fossil wood from Kiso region site, Nagano, Japan (1588-838 AD) <b>Species:</b> Hinoki cypress ( <i>Chamaecyparis obtuse</i> )	FT-NIR; monochromatic light range: 1100-2500 $\text{cm}^{-1}$ at 2 $\text{cm}^{-1}$ resolution. Second-Derivative Spectra of the samples	[96]
Roman shipwrecks from .San Rossore site, (Pisa, Italy)from <b>Species:</b> Pine ( <i>Pinus</i> sp.), Olive ( <i>Olea europaea</i> ), Ash ( <i>Fraxinus angustifolia</i> ), Oak ( <i>Quercus</i> ), Fig ( <i>Ficus</i> sp.), Poplar ( <i>Populus</i> sp.), Elm ( <i>Ulmus minor</i> ), Fir ( <i>Abies</i> sp.)	FT-IR; KBr pellets; range of 4000– 400 $\text{cm}^{-1}$ at 4 $\text{cm}^{-1}$ resolution. <b>Complementary techniques:</b> TAPPI methods, SEM-EDX, XRD, GC–MS, C.E.C.	[19]
Pillar of Todaiji Temple, Nara Prefecture) in Japan (late 7th century - AD 750) <b>Species:</b> Hinoki cypress ( <i>Chamaecyparis obtuse</i> )	FT-NIR; range 8000–4000 $\text{cm}^{-1}$ ; 128 scans at 8 $\text{cm}^{-1}$ resolution. Second-Derivative Spectra of the samples.	[97]
Sample from icon supports <b>Species:</b> Lime tree ( <i>Tilia</i> sp.)	ATR FT-IR; KBr pellets; range 4000–600 $\text{cm}^{-1}$ at 4 $\text{cm}^{-1}$ resolution. <b>Complementary techniques:</b> TG/DTG and DSC	[93]
Buried wood aged 5910±250 BP in the Ría Villaviciosa area, Spain. <b>Species:</b> Oak ( <i>Quercus</i> sp.)	FT-IR; KBr pellets; 128 scans at 4 $\text{cm}^{-1}$ resolution <b>Complementary techniques:</b> XRD, thermodynamic characterisation	[85]

<p>Archaeological waterlogged wood from different sites in Poland dating back from VII BC to XX AD. <b>Species:</b> Pedunculate oak (<i>Quercus robur</i>)</p>	<p>FT-NIR; range 4000 - 10000 cm<sup>-1</sup>; 25 scans at 8 cm<sup>-1</sup> resolution in. Second-Derivative Spectra of the samples <b>Complementary techniques:</b> PCA, Classical wet analysis, wide-angle X-ray scattering diffractometer (WAXS).</p>	[98]
<p>Waterlogged wood from rostrum (naval ram), Messina (Italy) <b>Species:</b> unknown</p>	<p>FT-IR; KBr pellets, range 800 and 4800 cm<sup>-1</sup>, <b>Complementary techniques:</b> ICP-OES, ICP-MS GC-MS-SPME, EDX, XRD, <sup>13</sup>C CP MAS NMR</p>	[99]
<p>Wooden roof structures in Venice dated for larch about 1295-1525 and for spruce about 1334-1477 <b>Species:</b> Norway spruce (<i>Picea abies</i>), Larch (<i>Larix</i> sp.)</p>	<p>ATR FTIR; range 4000-400 cm<sup>-1</sup>, 40 scans; at 4 cm<sup>-1</sup> of a spectral resolution; KBr pellets, range 4000-400 cm<sup>-1</sup>, 64 scans at 4 cm<sup>-1</sup> of spectral resolution.</p>	[100]
<p>Viking Age archaeological wooden object <b>Species:</b> Poplar (<i>Populus</i> sp.)</p>	<p>ATR-FTIR; range 1800-700 cm<sup>-1</sup>, 32 scans at 4 cm<sup>-1</sup> of resolution in diamond device</p>	[18]
<p>Waterlogged wooden from ancient pile-dwelling village of the Bronze Age, Fiave' Carera site (Trentino, Italy); <b>Species:</b> Norway spruce (<i>Picea abies</i>), Silver fir (<i>Abies alba</i>), larch (<i>Larix</i> sp.)</p>	<p>ATR-FTIR; range 4000 to 400 cm<sup>-1</sup>; 40 scans at 4 cm<sup>-1</sup> of resolution in diamond device. <b>Complementary techniques:</b> classical wet analyses, statistical analysis</p>	[101]
<p>The icon 8228, a „Diptych” Wood Icon, dated near the XIX century, from Transylvanian Ethnographic Museum collection <b>Species:</b> Lime tree (<i>Tilia</i> sp.)</p>	<p>FT-IR; KBr pellets, range 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. <b>Complementary techniques:</b> Differential scanning calorimetry (DSC)</p>	[94]
<p>Waterlogged archaeological wood: from site of the Mado, Korea shipwreck No. 1, dated to 1208. <b>Species:</b> Bamboo (<i>Bambuseae</i>)</p>	<p>FT-IR; KBr pellets, 100 scans; at 4 cm<sup>-1</sup> of a spectral resolution. <b>Complementary techniques:</b> TEM, SEM, CLSM, classical TAPPI, Solid state NMR, X-Ray diffraction;</p>	[63]
<p>Waterlogged archaeological wood from the sites of the Song Dynasty (A.D. 960-1279), the Three- Kingdom Dynasty (A.D. 220-280), the Han Dynasty (B.C. 202~A.D. 220) and the Qin Dynasty (B.C. 221~B.C.206); Hubei, China. <b>Species:</b> Bamboo (<i>Bambuseae</i>)</p>	<p>FT-IR; range 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. <b>Complementary techniques:</b> wet chemical methods, UV analysis; XRD, SEM, TEM</p>	[38]
<p>Short-term degraded waterlogged wood samples 99-year old <b>Species</b> :Scots pine (<i>Pinus sylvestris</i>), Penduculate oak (<i>Quercus robur</i>)</p>	<p>FT-NIR; range 4000-12000 cm<sup>-1</sup> at 8 cm<sup>-1</sup> resolution. Second-Derivative Spectra of the samples <b>Complementary techniques:</b> UV-Vis, XRF</p>	[13]

**Table 2** The most relevant applications of NMR spectroscopy to archaeological wood.

Archaeological samples description	Instrumental NMR conditions	Ref.
<p>450 years old pile buried under a building in Rotterdam (inner and outer portions). 10 000 years part of a tree from Northern Michigan and buried in anaerobic lacustrine sediments <b>Species:</b> Spruce (<i>Picea Abies</i>), tree of sequoia family</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 60 MHz; contact times 1-2 msec; radiofrequency field strengths for cross polarization and high power proton decoupling between 56 and 64 kHz.</p>	[111]
<p>Two 2500 years old wood samples excavated in a silty clay horizon along the bank of the Hoko river (near the Strait of Juan de Fuca, Washington State, U.S.A.). One 25 000 years old wood sample obtained at a sediment depth of 100 m in a drill hole on the continental slope of the Gulf of Mexico off the coast of Louisiana. <b>Species:</b> Spruce (<i>Picea sitchensis</i>), Alder (<i>Alnus rubra</i>), Oak (<i>Quercus</i> sp.)</p>	<b>CPMAS <sup>13</sup>C NMR</b>	[112]
<p>Shipwrecks of the Batavia (1629), Vergulde Draeck (1656), Rapid (1811), James Matthews (1841) and Day Dawn (1886) <b>Species:</b> white oak (<i>Quercus</i> sp.)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 22.5 MHz; recycle time 1 s; 90° pulse 4 μs; contact time 1 ms.</p>	[92]
<p>Wood samples from the sediments of the Elbe river valley dating back to 2000 and 10000 years BP <b>Species:</b> white oak (<i>Quercus</i> sp.)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 50.32 MHz; contact time 1 ms; recycle delay 3-4 s; sweep width 20 and 29 kHz; line broadening 75 Hz spinning speed of 5 kHz; number of scans 1800 for altered woods/ 5000-15 000 for hydrolyzed samples.</p>	[91]
<p>Waterlogged wood samples from some warships (La Trinidad Valencera, Dartmouth) <b>Species:</b> Ash (<i>Fraxinus</i> sp.), Birch (<i>Betula</i> sp.), Balsa (<i>Ochroma pyramidale</i>), Oak (<i>Quercus</i> sp.)</p>	<p><b>NMR imaging:</b> 7.05T magnetic field; sample chamber 25 mm; voxel size 25 x 25 x 50 pm.</p>	[128]
<p>An oak timber taken from the Mary Rose Trust, Portsmouth, UK. <b>Species:</b> Oak (<i>Quercus</i> sp.)</p>	<p><b><sup>1</sup>H NMR profiles:</b> 20 MHz and equipped with a pulsed field gradient capacity.</p>	[129]
<p>Two archaeological samples with different degrees of deterioration collected from the 11<sup>th</sup> century excavation site in the lake Paladru at Charavines, France. <b>Species:</b> Beech (<i>Fagus</i> sp.)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 100.6 MHz at room temperature; 90° pulse 2.5 μs; number of scans 1600; probe 2.5 mm; transients 8000; contact times 10 μs-20 ms</p>	[114]
<p>Samples from Portuguese medieval dugout canoes. <b>Species:</b> Oak (<i>Quercus</i> sp.)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 100.6 MHz at room temperature; 90° pulse 2.5 μs; number of scans 1600; probe 2.5 mm; transients 8000; contact times 10 μs-20 ms</p>	[115]

<p>Two ancient samples from the trussed rafter of the Castle of Valentino, XV century (Turin, Italy)  <b>Species:</b> Larch (<i>Larix</i> sp.), Fir (<i>Abies</i> sp.)</p>	<p><b>CPMAS <math>^{13}\text{C}</math> NMR, 2D WISE:</b> 200 MHz; spinning rate 8 kHz. [120]  <b><math>^1\text{H}</math> dipolar filtered <math>^{13}\text{C}</math> CPMAS:</b> 400 MHz; spinning rate 4 kHz; contact time 300 <math>\mu\text{s}</math>.  <b><math>^1\text{H}</math> low-resolution NMR:</b> 65 MHz  <b>Relaxometric measurements:</b> 18.153 MHz</p>
<p>Wooden archaeological specimens from excavations in the Vesuvian area of Pompeii (62 BC)  <b>Species:</b> poplar (<i>Populus</i> sp.), oak (<i>Quercus</i> sp.), silver fir (<i>Abies alba</i>)</p>	<p><b>CPMAS <math>^{13}\text{C}</math> NMR:</b> 100.613 MHz; spinning rate 4.0 kHz; Line broadening 64 Hz; Number of scans 1024; 90° pulse 10 <math>\mu\text{s}</math>; contact pulse 2 <math>\mu\text{s}</math>; delay time 2 s [118]</p>
<p>A fragment of archaeological waterlogged wood from the excavation of the San Rossore Roman Harbour (Pisa).  A wooden piece from a shipwreck found under 0.5 m shallow waters in Tantura Lagoon (Haifa, Israel) and dated from the 8–9<sup>th</sup> century AD</p>	<p><b>2D-HSQC:</b> 400 MHz and 308 K; spectral width 5–25 kHz; transients 128; number of scans 256; polarization transfer delay set at the assumed coupling of 140 Hz; relaxation delay 2 s [40]  <b>CPMAS <math>^{13}\text{C}</math> NMR after acetylation:</b> 400 MHz and 308 K; relaxation delay 10 s; Line broadening 2–5 Hz was; number of scans 8000  <b>Quantitative <math>^{31}\text{P}</math> NMR</b></p>
<p>Fragment of a halyard slade excavated from the Italian 17<sup>th</sup> century shipwreck “La Lomellina” in the Mediterranean sea (Villefranche sur Mer).</p>	<p><b>CPMAS <math>^{13}\text{C}</math> NMR:</b> 50.3 MHz at room temperature; 90° pulse 2.5 <math>\mu\text{s}</math>; transients 1600; Spinning rate 4000 Hz; contact times 10 <math>\mu\text{s}</math>–20 ms [116]</p>
<p>Archaeological wood from a 16<sup>th</sup> century shipwreck found at Zakynthos (Greece).  <b>Species:</b> Oak wood (<i>Quercus conferta</i>)</p>	<p><b>CPMAS <math>^{13}\text{C}</math> NMR:</b> 100.63 MHz; spinning rate 2.5 kHz; temperature 25°C; number of scans 1000; delay time 60 s; 90° pulse 5 <math>\mu\text{s}</math>; acquisition time 40 ms; contact time 2 ms; recycle delay 10 s. [119]</p>
<p>Archaeological waterlogged wood samples from bollards recovered from the excavations at the site of the Ancient Ships of Pisa (Tuscany, Italy) dated from a period between the 2<sup>nd</sup> century BC and the 4<sup>th</sup> century AD  <b>Species:</b> Beech (<i>Fagus sylvatica</i>), Elm (<i>Ulmus minor</i>), Pine (<i>Pinus pinaster</i>)</p>	<p><b>2D-HSQC:</b> <math>^1\text{H}</math>–<math>^{13}\text{C}</math> correlation spectra recorded on a 500 MHz instrument operating at 308 K; spectral width 5–25 kHz; transients 128; number of scans 256; polarization transfer delay 140 Hz; relaxation delay 2 s. <math>^1\text{D}</math>–<math>^{13}\text{C}</math> correlation spectra recorded at 333 K using a 400 MHz instrument. [39]  <b>CPMAS <math>^{13}\text{C}</math> NMR after acetylation:</b> 400 MHz; relaxation delay 10 s; line broadening 2–5 Hz; number of scans 16000</p>
<p>Archaeological sample taken from a wooden coffin, dating back to the Graeco–Roman period in Egypt.  <b>Species:</b> Cypress (<i>Cupressus sempervirens</i>)</p>	<p><b><math>^1\text{H}</math>-, <math>^{31}\text{P}</math>- and 2D-NMR (HOHAHA):</b> 400 MHz [127]</p>
<p>Archaeological waterlogged wood samples from bollards recovered from the excavations at the site of the Ancient Ships of Pisa (Tuscany, Italy) dated from a period between the 2<sup>nd</sup> century BC and the 4<sup>th</sup> century AD  <b>Species:</b> Beech (<i>Fagus sylvatica</i>), Elm (<i>Ulmus minor</i>), Pine (<i>Pinus pinaster</i>)</p>	<p><b>2D-HSQC:</b> <math>^1\text{H}</math>–<math>^{13}\text{C}</math> correlation spectra recorded on a 500 MHz instrument at 308 K. <math>^1\text{D}</math>–<math>^{13}\text{C}</math> spectra recorded at 333K using a 400 MHz instrument. [41]  <b>Quantitative <math>^{31}\text{P}</math> NMR:</b> 400 MHz</p>

<p>Two samples taken from a Rostrum with a wooden part in the inside, Messina (Italy), dating back in a time range from the 4<sup>th</sup> to the 1<sup>st</sup> century BC</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 100.63 MHz; spinning rate 13 kHz; 90° pulse 4.5 μs; contact time 1.5 ms; repetition delay 2 s; number of scans 4096 [99]</p>
<p>Analysis performed on a decorated wooden Egyptian sarcophagus dating from the XXV–XXVI dynasty, Third Intermediate Period <b>Species:</b> Yew (<i>Taxus baccata</i> L.)</p>	<p><b>Unilateral NMR:</b> Two probe-heads: one at 18.15 MHz, for measurements within the first millimeter of the sample, and the other at 16.3 MHz, for measurements at a depth of 0.5 cm inside the sample. [121] <b>CPMAS <sup>13</sup>C NMR:</b> 100.63 MHz; spinning rate 12 Hz; contact time 1.5 ms; recycle delay 3 s; 90° pulse 3.5 μs; line broadening of 8 Hz.</p>
<p>Archaeological samples with different degrees of deterioration collected from the 11<sup>th</sup> century excavation site in the lake Paladru at Charavines, France. <b>Species:</b> Oak (<i>Quercus</i> sp.)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 50.3 MHz; 90° pulse 3.4 μs; transients 1600; spinning rate 5000 Hz. [130]</p>
<p>Two historic wood samples from icon supports from different particular collections kept in normal indoor environmental conditions. One sample taken from a decoration of a rood screen from a church. One sample taken from a decoration of a rood screen from a monastery. <b>Species:</b> Lime (<i>Tilia cordata</i> Mill)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 176.08 MHz; spinning rate 5 kHz; 90° pulse 2 μs; dwell time 2 μs; contact time 1000 μs; recycle delay time 5 s; number of scans 4096 [123]</p>
<p>Waterlogged archaeological samples obtained from the excavation site of the Mado shipwreck No. 1, which was estimated to have sunk in the spring of 1208, near Mado Island in Korea. <b>Species:</b> Bamboo (<i>Bambuseae</i>)</p>	<p><b>CPMAS <sup>13</sup>C NMR:</b> 100.62 MHz; spinning speed 13 kHz; contact time 1 ms; acquisition time 17.1 ms; relaxation delay 5 s [63]</p>

1273

1274

**Table 3** Lignin pyrolysis products observed in DE-MS mass spectra [158]

<b>m/z</b>	<b>Derivation</b>	<b>G: guaiacyl</b> <b>S: siringyl</b>
124	Guaiacol (M <sup>+</sup> ) Coniferyl alcohol (M <sup>+</sup> -C <sub>3</sub> H <sub>4</sub> OH)	G
138	Methylguaiacol (M <sup>+</sup> )	G
150	Vinylguaiacol (M <sup>+</sup> )	G
137	Ethylguaiacol (M <sup>+</sup> -CH <sub>3</sub> ) Propylguaiacol (M <sup>+</sup> -CH <sub>2</sub> CH <sub>3</sub> ) Coniferyl alcohol (M <sup>+</sup> -C <sub>2</sub> H <sub>2</sub> OH)	G
164	Propenylguaiacol (M <sup>+</sup> )	G
151	Acetylguaiacol (M <sup>+</sup> -CH <sub>3</sub> ) Vanillin (M <sup>+</sup> -H)	G
152	Vanillin (M <sup>+</sup> )	G
154	Syringol (M <sup>+</sup> )	S
168	Methylsyringol (M <sup>+</sup> )	S
167	Ethylsyringol (M <sup>+</sup> -CH <sub>3</sub> ) Propylsyringol (M <sup>+</sup> -CH <sub>2</sub> CH <sub>3</sub> ) Sinapyl alcohol (M <sup>+</sup> -C <sub>2</sub> H <sub>2</sub> OH)	S
178	Guaiacyl vinyl ketone (M <sup>+</sup> ) <i>E</i> -Coniferaldehyde(M <sup>+</sup> )	G
180	Vinylsyringol (M <sup>+</sup> )	S
194	Propenylsyringol (M <sup>+</sup> )	S
181	Acetolsyringone (M <sup>+</sup> -CH <sub>3</sub> )	S
208	<i>E</i> -Sinapaldehyde (M <sup>+</sup> )	S
210	Sinapyl alcohol (M <sup>+</sup> )	S
272	Stilbene-type dimer (M <sup>+</sup> )	G-G dimer
303	Stilbene-type dimer (M <sup>+</sup> )	G-S dimer
332	Stilbene-type dimer (M <sup>+</sup> )	S-S dimer
358	β-resinol type dimer (M <sup>+</sup> )	G-G dimer
388	β-resinol type dimer (M <sup>+</sup> )	G-S dimer
418	β-resinol type dimer (M <sup>+</sup> )	S-S dimer

**Table 4** The most relevant applications of Py-GC/MS to archaeological and fossil wood.

Archaeological samples description	Instrumental conditions	Ref.
Buried wood, 2500 and 25000 year old <b>Species:</b> Spruce ( <i>Picea sitchensis</i> ), Alder ( <i>Alnus rubra</i> ), Oak ( <i>Quercus</i> sp.)	Curie point pyrolyser, connected to a GC/MS (Py-GC/MS) Py T: 610°C	[113]
Wood samples from wrecks of the Batavia (1629), Vergulde Draeck (1656), Rapid (1811), James Matthews (1841) and the Day Dawn (1886) <b>Species:</b> white oak ( <i>Quercus</i> sp.)	Microfurnace pyrolyser, connected to a GC/MS (Py-GC/MS) Py T = 400, 500 and 610°C.	[92]
Fossil wood <b>Species:</b> <i>Cyrilla</i> sp. (titi bush) and (2) the fossil fruit endocarp* of <i>Nyssa fissilis</i> (gum tree).	Curie point pyrolyser, connected to a MS (Py-MS) Py T = 610°C and in-source Py-MS (the platinum-rhodium pyrolysis probe resistively heated to ca. 800°C at 15°C/s):	[187]
Coalified Lower Devonian vascular plants ( <i>Zosterophyllum</i> , <i>Psilophyton</i> , <i>Renalia</i> ) Jurassic gymnosperm: fossil xylem ( <i>Cordaixylon</i> , <i>Callixylon</i> ) and cuticle ( <i>Pachypteris</i> )	Filament (platinum coil) pyrolyser connected to a GC/MS (Py-GC/MS) Py T: 610°C	[188]
Waterlogged archaeological wood ranging from 16 <sup>th</sup> C. AD to 6000 BC <b>Species:</b> Oak ( <i>Quercus</i> sp.)	Filament (platinum coil) pyrolyser connected to a GC/MS (Py-GC/MS) Py T: 610°C	[140]
Waterlogged archaeological wood from shipwrecks: <i>Vergulde Draeck</i> (1656), <i>Rapid</i> (1811), <i>Hadda</i> (1877) and <i>the Favourite</i> (1867) <b>Species:</b> White oak ( <i>Quercus</i> sp.), Beech ( <i>Fagus</i> sp.), Elm ( <i>Ulmus</i> sp.), <i>Pinaceae</i> family.	Microfurnace pyrolyser, connected to a GC/MS (Py-GC/MS) Py T: 600°C	[186]
Mummified fossil wood	Open-system with a preheated tube furnace (Carbolite MTF12/38/250, Hope, UK) off-line pyrolysis at temperatures of 200, 250 and 300 C. Pyrolysis products collected in an ice-cooled trap containing MeOH/DCM (1:1), derivatised with BSTFA+1%TMCS and analyzed by GC/MS	[189]
Fossil woods older than 41,000 years. <b>Species:</b> ( <i>Sequoiadendron giganteum</i> Lindl.)	Filament (platinum coil) pyrolyser connected to a GC/MS (Py-GC/MS) Py T: 450°C	[173]

Fossil leaf and wood from late Paleocene–early Eocene and middle Eocene <b>Species:</b> <i>Metasequoia</i>	Filament (platinum coil) pyrolyser connected to a GC/MS (Py-GC/MS) Py T: 610 °C	[174]
Wood from painting supports, from different age and with various ageing characteristics <b>Species:</b> Lime wood ( <i>Tillia cordata</i> Mill)	Filament (platinum coil) pyrolyser connected to a GC/MS (Py-GC/MS) Py T: 500 °C	[190]
Waterlogged archaeological wood from the excavation of San Rossore site, Pisa(Italy) 4 <sup>th</sup> century BC-2 <sup>nd</sup> AD <b>Species:</b> Pine, beech, elm	Filament (platinum coil) pyrolyser connected to a GC/MS using HDMS as derivatising agent (Py-(HMDS)-GC/MS) Py T: 600°C And Direct Exposure Probe (rhenium filament resistively heated to ca. 1000°C at 20°C/s) coupled with MS (DE-MS)	[155]
Waterlogged archaeological wood from the excavation of San Rossore site, Pisa(Italy) and from a shipwreck from Tantura Lagoon (Haifa, Israel) dated 8–9th century AD <b>Species:</b> <i>Pinaceae</i> , Oak ( <i>Quercus</i> sp.)	Microfurnace pyrolyser, connected to a GC/MS (Py-GC/MS) Py T: 600°C	[40]
Waterlogged archaeological wood from the excavation of San Rossore site, Pisa(Italy) 4 <sup>th</sup> century BC-2 <sup>nd</sup> AD <b>Species:</b> Pine, elm	Microfurnace pyrolyser, connected to a GC/MS (Py-GC/MS) Py T: 500°C and Direct Exposure Probe (rhenium filament resistively heated to ca. 1000°C at 20°C/s) coupled with MS (DE-MS)	[137]
Lignin extracted from Waterlogged archaeological wood from the excavation of San Rossore site, Pisa(Italy) 4 <sup>th</sup> century BC-2 <sup>nd</sup> AD <b>Species:</b> <i>Fagus sylvatica</i> (G, beech), <i>Ulmus</i> cfr. <i>minor</i> (D, elm), <i>Pinus pinaster</i> (F, pine)	Filament (platinum coil) pyrolyser connected to a GC/MS using HDMS as derivatising agent (Py-(HMDS)-GC/MS) Py T: 500°C	[39]
Waterlogged wood from the Zótte historical site (Poland), settlements dating to a period between the 9th and the 12th centuries AD <b>Species:</b> alder ( <i>Alnus glutinosa</i> ), oak ( <i>Quercus roburs</i> ), beech ( <i>Fagus sylvatica</i> )	Filament (platinum coil) pyrolyser connected to a GC/MS using HDMS as derivatising agent (Py-(HMDS)-GC/MS) Py T: 550°C	[138]
Archaeological waterlogged wood remains from the roof of a Roman villa and carbonized wood (samples from House of the Telephus Relief, two from a carbonized bed in the House of Carbonized Furniture and one from a carbonized bed in the House of the Alcove.) 79 AD, Herculaneum site, Italy <b>Species:</b> silver fir ( <i>Abies alba</i> Mill.)	Filament (platinum coil) pyrolyser connected to a GC/MS using HDMS as derivatising agent (Py-(HMDS)-GC/MS) Py T: 550°C	[139]