

Analytical pyrolysis: a useful tool to analyze and evaluate consolidated archaeological wood

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Abstract.

Archaeological wooden objects can be preserved for millennia in waterlogged environments where the action of primary biodegradation agents is limited. When wooden artifacts are removed from the waterlogged environment specific stabilization or consolidation treatments are needed to prevent damage during drying.

The consolidant fills the gaps of cell lumen and supports the entire structure, improving its stability and load capacity to keep the object in shape. A large assortment of consolidation materials have been used and tested for this scope, and others are object of investigation and research, including green biomaterials as consolidants derived from lignin. Py-GC-MS is here described as a useful and promising technique to investigate complex composite waterlogged wooden objects.

Ongoing research on this topic includes the activities carried out in the context of the JPI StAr project (JPI-CH, <http://jpi-ch.eu/>).

Keywords: analytical pyrolysis, archaeological waterlogged wood, consolidation, treatment evaluation, degradation.

1 Introduction

Archaeological wooden objects can be preserved for millennia in waterlogged or extremely dry environments. The former represents the largest source of archaeological wooden finds, as the aqueous environment, being predominantly anaerobic, limits the action of primary biodegradation agents, as only particular types of bacteria are

able to degrade polysaccharides in anaerobic conditions [1]. The absence of light and the low temperatures in waterlogged burial conditions contribute to preserve wood artifacts [2].

The main degradation phenomenon for waterlogged archaeological wood artifacts in aqueous media is the depletion of the polysaccharide fraction. In these conditions, water usually fills the cavities in wood, replacing degraded carbohydrates and allowing the artefact to maintain its original shape. However, critical stabilization issues arise when a wooden artefact is removed from the waterlogged environment in order to be investigated, conserved or displayed: the drying of the delicate, spongy and porous waterlogged wood is accompanied by a high possibility of deformation, cracking and collapse of the structure [1-3].

For this reason, waterlogged wooden objects of historical or artistic value often need conservative treatments entailing stabilization or consolidation to prevent damage during drying. The consolidant fills gaps in cell walls or in lumens, thus supporting the entire structure and improving its strength and minimizing dimensional change.

In order to assess the chemical-physical preservation state of waterlogged archaeological wooden artifacts, both treated and untreated, analytical tools are needed to investigate both the lignocellulosic wood components and the consolidation materials applied in conservation.

Analytical pyrolysis has proven an extremely promising tool to achieve information on wood and consolidation materials in archaeological objects. This technique can be used for both the short- and long-term evaluation of the effects of conservation treatments.

After an overview of the treatments used in the past and at present for the consolidation of waterlogged wooden artifacts, we present case studies that prove the versatility of analytical in the characterisation of complex and composite wooden artifacts.

1.1 Conservation treatments for waterlogged archaeological wooden objects: an overview

The choice and application of effective and long-term performing consolidation materials is extremely challenging, and is currently the object of intense research [4-9]. An ideal consolidant should have good penetration capacity, low toxicity due to the need of using large amounts, chemical and thermal stability, provide wet wood with sufficient strength and support to endure drying, ensure a reasonable degree of reversibility or at least enable future retreatment. The penetration of consolidant into the object can occur by impregnation or by in situ polymerization [10, 11].

One of the first consolidation attempts, dating to the mid-1800s, was based on the treatment with concentrated solutions of alum, a potassium or ammonium aluminum sulfate ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) [8] This treatment was frequently used in Sweden and Denmark until approximately the 1950s. The artefacts were immersed in a highly concentrated, hot salt solution (90 °C), which penetrated the wood structure. Upon cooling, alum recrystallizes, providing support for the outer surface of wood and reducing shrinkage during drying. This treatment has now been completely

abandoned because in the long term it is harmful to the artefacts, as demonstrated by the conservation state of the wooden objects of the Oseberg collection [8]. Today, over 100 years after this treatment, the objects are in advanced state of degradation and show an extreme alteration of both polysaccharide and lignin fractions [5]. The cause of this extreme deterioration is due to the ability of alum to catalyze degradation reactions especially towards the polysaccharide fraction of wood during immersion in the treatment solution. The sulphuric acid generated by the treatment was absorbed by the wood and has caused further deterioration of its polymers over time.

Consolidation with carbohydrates has been also used to conserve waterlogged wood, through the formation of saccharide crystals following the removal of water from the treated wood [6]. Lactitol is the most used carbohydrate-based consolidant and in particular the addition of trehalose increases solubility and excludes the formation of hydrated crystals avoiding possible fractures of the wood structure [7].

Polyethylene glycol, PEG, has been the most used consolidation material for waterlogged archaeological wood in the last decades. Its extensive use is due to various factors such as: good penetration capacity, low cost, ease of use and low toxicity. Generally it is used with average molecular weights between 200 and 4000 g/mol: the low molecular weight PEG penetrates deeper but does not guarantee a good support to the wood, while higher molecular weight PEG provide structural support. In addition, the PEG treatment can increase wood plasticity in large load-bearing objects.

An interesting approach in the consolidation of wood is represented by methods based on in situ polymerization: low-molecular weight molecules are introduced into the pores of the object and then they are polymerized by the addition of a reagent, or by activation via heating or irradiation [5, 12].

An example of the in-situ cross-linking approach is the consolidation of shipwrecks with Kauramin, a melamine-formaldehyde resin [4, 12, 13]. The cross-linking reaction renders the consolidant insoluble in solvents, such that the treatment is irreversible. However consolidation treatments on large wooden objects are generally poorly reversible due to practical issues. Nevertheless, artefacts treated with Kauramin have good mechanical properties and there is not excessive weight gain. The treatment has been successfully applied to the Roman ships preserved in the "Museo delle Navi Antiche" of Pisa [14, 15].

To overcome the limitations presented by the consolidation treatments currently available, innovative and experimental treatments have been recently proposed and are object of research also paying particular attention to the impact on the environment and health of operators. In recent years new conservation technologies have been proposed.

Organosilicon compounds are of interest for their good water-repellent properties; in fact, their application takes place using alcohol as solvent after eliminating the water present in wood [16, 17].

Since wood degradation is mainly due to cellulose decomposition, consolidation approaches have been proposed to allow the re-introduction of this substance in archaeological wood. However, these treatments provided limited consolidating effect. For this reason, a parallel approach has been developed, which involves the synthesis of lignin-like polymers from isoeugenol [18]. The consolidation can be carried out

either by immersion in solution or by means of in situ polymerization. A promising feature of lignin-like consolidants is that the introduced polymer does not fill the pores of the wood, leaving room for future re-treatments.

More recent studies aim to directly introduce the lignin extracted from herbaceous plants using non-aqueous solutions [9]. In fact, aqueous retreatment is suitable only for objects that are not extremely degraded because otherwise there is a risk of causing irreparable damage.

Another proposed green approach is based on keratin extracted from the feathers of birds [19, 20]. The advantages of this method are that the keratin adheres to the cell walls without filling the cell lumen, and that the treatment does not alter the colour of the wood as PEG and carbohydrates.

2 Materials and Methods

2.1 Materials

Samples taken from treated and untreated archaeological artefacts, were analyzed and compared in order to assess the degradation status of the wood fraction and the consolidant. Samples include: medieval pine treated with soda lignin from wheat straw/Sarkanda grass [9]; oak from a Gallo-Roman Lyon wreck found during the building of underground car park in Lyon, Rhone region (France) contaminated by iron salt and treated with PEG 4000 [21]; alum and linseed oil treated wood from the Oseberg collection [22] and Oseberg archaeological wood which previously contained alum and linseed oil and was retreated with Kauramin 800 following the procedure described in [13].

Table 1. List of archaeological wood samples

Sample	Description	Treatment	Other information
Arch-Al-LO	alum and linseed oil treated archaeological wood	alum, linseed oil	Archaeological wood sample, unknown genus, alum treated and covered with linseed oil, belonging to the Oseberg collection [22].
Arch-PEG	archaeological oak treated with PEG	PEG, disodium sebacate	Oak fragment from Lyon ship contaminated by iron salts treated with PEG 4000 20% + disodium sebacate 10% solution and freeze-dried [21].
Arch - Kau	archaeological wood treated with melamine formaldehyde resin	Kauramin 800	Archaeological wood sample, unknown genus, retreated with Kauramin 800 and air dried, from the Oseberg collection. 10% v/v PEG 400 was added to the treatment bath to improve elasticity [13].
ArchP	archaeological pine	untreated	Discarded archaeological pine, recently discovered in Medieval Oslo in 2018 [9].
ArchP-L int/ext	archaeological pine treated with straw lignin	straw soda lignin	Archaeological pine "ArchP" (8 cm ³ cube), treated with commercial lignin from wheat straw and Sarkanda grass. The procedure of treatment was described in [9]. Analyzed samples were collected from the outer (ext) and the inner part of the cube (int).

2.2 Apparatus

Investigations were performed using a micro-furnace pyrolyzer EGA/Py-3030D (Frontier Laboratories) combined with Agilent Technologies gas chromatograph (6890) and mass spectrometric detector (5973). Pyrolysis was undertaken in the presence of hexamethyldisilazane (HMDS, Sigma-Aldrich) as derivatizing agent, and was performed at 550°C. About 100-150 µg of sample with 2 µL of HMDS were pyrolysed directly in a stainless-steel cup. Further details on set-up conditions are described in [23].

The identification of wood pyrolysis products, almost all present as TMS derivatives, was based on literature data [24-27]. Table 2 reports a list of the 105 identified compounds.

Table 2. Wood compounds identified by Py-GC-MS.

N°	Pyrolysis product	m/z	Origin*
1	1,2-dihydroxyethane (2TMS)	73,103,147,191	H/L
2	2-hydroxymethylfuran (TMS)	73, 81, 111, 125, 142, 155, 170	H
3	phenol (TMS)	75, 151, 166	p-H
4	2-hydroxypropanoic acid (2TMS)	73, 117, 147, 190	H/L
5	2-hydroxyacetic acid (2TMS)	73, 147, 177, 205	H/L
6	1-hydroxy-1-cyclopenten-3-one (TMS)	73, 81, 101, 111, 127, 155, 169	H
7	3-hydroxymethylfuran (TMS)	75, 81, 111, 125, 142, 155, 170	H
8	o-cresol (TMS)	73, 91, 135, 149, 165, 180	p-H
9	2-furancarboxylic acid (TMS)	73, 95, 125, 169, 184	H
10	m-cresol (TMS)	73, 91, 165, 180	p-H
11	2-hydroxy-1-cyclopenten-3-one (TMS)	73, 81, 101, 111, 127, 155, 170	H
12	p-cresol (TMS)	73, 91, 165, 180	p-H
13	3-hydroxy-(2H)-pyran-2-one (TMS)	75, 95, 125, 151, 169, 184	H
14	Z-2,3-dihydroxy-cyclopent-2-enone (TMS)	73, 115, 143, 171, 186	H
15	E-2,3-dihydroxy-cyclopent-2-enone (TMS)	75, 101, 143, 171, 186	H
16	1,2-dihydroxybenzene (TMS)	75, 91, 136, 151, 167, 182	H
17	3-hydroxy-(4H)-pyran-4-one (TMS)	75, 95, 139, 151, 169, 184	H
18	5-hydroxy-2H-pyran-4(3H)-one (TMS)	75, 101, 129, 143, 171, 186	H
19	2-hydroxymethyl-3-methyl-2-cyclopentenone (TMS)	73, 103, 129, 173, 183, 198	H
20	1-hydroxy-2-methyl-1-cyclopenten-3-one (TMS)	73, 97, 125, 139, 169, 184	H
21	1-methyl-2-hydroxy-1-cyclopenten-3-one (TMS)	73, 97, 125, 139, 169, 184	H
22	1,3-dihydroxyacetone (2TMS)	73, 103, 147, 189, 219	H
23	guaiacol (TMS)	73, 151, 166, 181, 196	G
24	unknown holocellulose (TMS)	73, 217, 232	H
25	3-hydroxy-6-methyl-(2H)-pyran-2-one (TMS)	73, 109, 139, 168, 183, 198	H
26	vinyl phenol (TMS)	73, 151, 177, 192	p-H
27	2-methyl-3-hydroxy-(4H)-pyran-4-one (TMS)	73, 101, 153, 183, 198	H
28	2-methyl-3-hydroxymethyl-2-cyclopentenone (TMS)	73, 103, 129, 173, 183, 198	H
29	2,3-dihydrofuran-2,3-diol (2TMS)	73, 147, 231, 246	H
30	2-furyl-hydroxymethylketone (TMS)	73, 81, 103, 125, 183, 198	H
31	5-hydroxymethyl-2-furaldehyde (TMS)	73, 81, 109, 111, 169, 183, 198	H

32	4-methylguaiacol (TMS)	73, 149, 180, 195, 210	G
33	4-hydroxy benzaldehyde TMS	73, 151, 179, 194	p-H
34	1,2-dihydroxybenzene (2TMS)	73, 151, 239, 254	H
35	2-hydroxymethyl-2,3-dihydropyran-4-one (TMS)	73, 142, 170, 185, 200	H
36	4-hydroxy-5,6-dihydro-(2H)-pyran-4-one (TMS)	73, 103, 129, 155, 171, 186	H
37	Z-2,3-dihydroxy-cyclopent-2-enone (2TMS)	73, 147, 230, 243, 258	H
38	4-methylcatechol (2TMS)	73,180, 253, 268	G
39	4-ethylguaiacol (TMS)	73, 149, 179, 194, 209, 224	G
40	syringol (TMS)	73, 153, 181, 196, 211, 226	S
41	1,4-dihydroxybenzene (2TMS)	73, 112, 239, 354	H
42	arabinofuranose (4TMS)	73, 147, 217, 230	H
43	4-vinylguaiacol (TMS)	73, 162, 177, 192, 207, 222	G
44	3-hydroxy-2-hydroxymethyl-2-cyclopentenone (2TMS)	73, 147, 257, 272	H
45	E-2,3-dihydroxy-cyclopent-2-enone (2TMS)	73, 147, 243, 258	H
46	4-ethylcatechol (2TMS)	73, 147, 179, 231, 267, 282	G
47	3-hydroxy-2-(hydroxymethyl) cyclopenta-2,4-dienone (2TMS)	73, 147, 255, 270	H
48	eugenol (TMS)	73, 147, 179, 206, 221, 236	G
49	4-methylsyringol (TMS)	73, 167, 210, 225, 240	S
50	3-methoxy-1,2-benzenediol (2TMS)	73, 153, 254, 269, 284	S
51	3,5-dihydroxy-2-methyl-(4H)-pyran-4-one (2TMS)	73, 128, 147, 183, 271, 286	H
52	1,6-anhydro-beta-D-glucopyranose (TMS at position 4)	73, 103, 117, 129, 145, 155, 171	H
53	1,6-anhydro-beta-D-glucopyranose (TMS at position 2)	73, 101, 116, 129, 132, 145, 155, 171	H
54	Z-isoegenol (TMS)	73, 179, 206, 221, 236	G
55	vanillin (TMS)	73, 194, 209, 224	G
56	1,2,3-trihydroxybenzene (3TMS)	73, 133, 147, 239, 327, 342	H
57	3-methyl-2-methoxy-1,4-benzenediol (2TMS)	73, 151, 210, 253, 268, 283, 298	S
58	4-ethylsyringol (TMS)	73, 191, 209, 224, 239, 254	S
59	E-isoegenol (TMS)	73, 179, 206, 221, 236	G
60	1,4-anhydro-D-galactopyranose (2TMS)	73, 101, 116, 129, 145, 155, 171, 217	H
61	1,6-anhydro-D-galactopyranose (2TMS)	73, 101, 116, 129, 145, 189, 204, 217	H
62	2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one (2TMS)	73, 129, 147, 155, 183, 273, 288	H
63	4-vinylsyringol (TMS)	73, 179, 222, 237, 252	S
64	1,4-anhydro-D-glucopyranose (2TMS at position 2 and 4)	73, 101, 116, 129, 155, 191, 204, 217	H
65	1,2,4-trihydroxybenzene (3TMS)	73, 133, 147, 239, 327, 342	H
66	acetovanillone (TMS)	73, 193, 208, 223, 238	G
67	4-hydroxy benzoic acid (2TMS)	73, 147, 193, 223, 267, 282	p-H
68	propenyl-syringol (TMS)	73, 205, 236, 251, 266	S
69	1,6-anhydro-beta-D-glucopyranose (2TMS at position 2 and 4)	73, 101, 116, 129, 155, 191, 204, 217	H
70	vanillic acid methyl ester (TMS)	73, 193, 224, 239, 254	G
71	cinnamic acid, 3,5-dimethoxy-4-(trimethylsiloxy) methyl ester	73, 147, 179, 222, 280, 295, 310	S
72	Z-propenylsyringol	73, 205, 236, 251, 266	S
73	1,4-anhydro-D-galactopyranose (3TMS)	73, 129, 147, 191, 204, 217, 243, 332	H
74	syringaldehyde (TMS)	73, 224, 239, 254	S
75	2,3,5-trihydroxy-4H-pyran-4-one (3TMS)	73, 147, 239, 255, 270, 330, 345,	H

		360	
76	1,6-anhydro-beta-D-glucopyranose (3TMS)	73, 129, 147, 191, 204, 217, 243, 333	H
77	1,4-anhydro-D-glucopyranose (3TMS)	73, 129, 147, 191, 204, 217, 243, 332	H
78	<i>E</i> -propenylsyringol (TMS)	73, 205, 236, 251, 266	S
79	1,6-anhydro-beta-D-glucofuranose (3TMS)	73, 115, 147, 191, 204, 216, 246, 319	H
80	vanillic acid (2TMS)	73, 253, 282, 297, 312	G
81	acetosyringone (TMS)	73, 223, 238, 253, 268	S
82	5-propyl-3-methoxy-1,2-benzenediol (2TMS)	73, 147, 179, 209, 296, 311, 326	S
83	coumaryl alcohol (2 TMS)	73, 189, 205, 267, 279, 294	p-H
84	syringic acid methyl ester (TMS)	73, 223, 254, 269, 284	S
85	vanillylpropanol (2TMS)	73, 179, 206, 221, 236, 311, 326	G
86	<i>Z</i> -coniferyl alcohol (2TMS)	73, 204, 252, 293, 309, 324	G
87	4-hydroxy-3,5-dimethoxy cinnamic acid methyl ester (TMS)	73, 147, 179, 222, 280, 295, 310	S
88	coniferylaldehyde (TMS)	73, 192, 220, 235, 250	G
89	trihydroxy cinnamic alcohol (3TMS)	73, 147, 210, 254, 368, 383, 398	S
90	syringic acid (2TMS)	73, 253, 297, 312, 327, 342	S
91	<i>p</i> -coumaric acid (2TMS)	73, 175, 203, 276	p-H
92	<i>E</i> -coniferyl alcohol TMS	73, 163, 191, 221, 237, 252	G
93	<i>E</i> -coniferyl alcohol (2TMS)	73, 132, 204, 293, 309, 324	G
94	3,4-dihydroxy-5-methoxy benzoic acid (3TMS)	73, 137, 147, 223, 253, 297, 385, 400	S
95	syringylpropanol (2TMS)	73, 210, 240, 341, 356	S
96	<i>Z</i> -sinapyl alcohol (2TMS)	73, 234, 323, 339, 354	S
97	3,4-dihydroxy cinnamyl alcohol (3TMS)	73, 205, 293, 355, 382	G
98	trihydroxy cinnamic alcohol I (3TMS)	73, 147, 210, 254, 368, 383, 398	S
99	sinapylaldehyde (TMS)	73, 222, 250, 265, 280	S
100	trihydroxy cinnamyl alcohol (3TMS)	73, 147, 210, 254, 368, 383, 398	S
101	<i>Z</i> -2-methoxy-3,4-dihydroxy cinnamic alcohol (3TMS)	73, 235, 323, 385, 412	S
102	synapyl alcohol (TMS)	73, 234, 251, 267, 282	S
103	<i>E</i> -synapyl alcohol (2TMS)	73, 234, 323, 339, 354	S
104	<i>E</i> -2-methoxy-3,4-dihydroxy cinnamic alcohol (3TMS)	73, 235, 323, 385, 412	S
105	Ferulic acid (2TMS)	73, 249, 308, 323, 338	G

* Holocellulose (H), Lignin (L), guaiacyl lignin (G), syringyl lignin (S), *p*-hydroxyphenyl lignin (p-H).

Assessment of the degradation state of the lignocellulosic fraction in consolidated archaeological wood was performed by processing the chromatographic peak areas of identified compounds formed from lignin and holocellulose. Peak areas were normalized against the total peak area of all pyrolysis products derived from wood and expressed in percent. Normalized areas were used as a semi-quantitative evaluation as described in [28]. The chromatographic peaks of lignin and holocellulose were deconvoluted and integrated using AMDIS software [29].

3 Results and discussion

The most important outcomes of the research study presented here are the identification of specific pyrolysis products, which can be correlated with specific factors or

types of degradation and demonstrate the possibility to apply Py-GC-MS to highly complex mixtures of materials, obtaining information about all organic components without previously separating them. Analytical pyrolysis of untreated wood and that treated with conservation materials was performed to characterize and assess the state of decay of archaeological woods. In this paper, conservation materials used in the past but now disused due to the preservation problems of treated wood objects such as alum (aluminium potassium (or ammonium) sulphate) or those that continue to be used for years such as linseed oil, PEG and Kauramin 800 were considered. In addition, the newly tested bio-sustainable treatment with straw lignin is also discussed.

Archaeological wood treated with alum shows a particularly advanced degradation state of both the holocellulose and the lignin fractions. A strong depolymerization of both holocellulose and lignin as well as oxidation of lignin have been found in many objects treated with alum [8, 30-32]. From the archives of the Museum of Cultural History, it is known that many Oseberg artefacts were consolidated with alum, and/or with boiled linseed oil which had the function of improving the resilience and visual appearance of the treated wood. The study of these objects has allowed to ascertain that linseed oil has not only had the function of improving the visual appearance of the treated objects but has also functioned to slightly protect the wood from degradation. Generally, archaeological wood is more degraded on the surface than in depth. However, objects treated with both alum and linseed oil were better preserved on the surface than in the underlying layer where linseed oil is not present [22]. Figure 1 reports the chromatographic profile obtained for the Oseberg collection alum and linseed oil treated archaeological wood. In addition to the peaks relating to the pyrolysis products of wood listed in Table 2, fatty acids such as: dicarboxylic azelaic acid, unsaturated palmitoleic and oleic acids and saturated myristic, palmitic and stearic acids were identified. This is in agreement with what happens with the dried oils during aging [22]. Linseed oil is a drying oil consisting of triacylglycerols (TAGs), which are highly polyunsaturated. Linolenic and linoleic acids account for about 65% of total fatty acids [33] while free fatty acids (FFAs) make up ca. 0.5–2% of the total amount. Curing and ageing of drying oils cause significant changes in their chemical composition. Some curing reactions cause bond scission, resulting in the formation of products with lower molecular weight, the most abundant of which is azelaic acid. It is possible to observe a decrease in the degree of unsaturation as well as in the amount of free fatty acids as the oil cures and ages.

The wood fraction of the analyzed sample is very depleted of polysaccharides, as can be seen from Table 2 compared to fresh wood, in which the holocellulose fraction reaches about 75% of the total lignocellulosic matter [22, 30].

Today, the most commonly used treatment of archaeological wood is based on polyethylene glycol (PEG). The pyrolysis products of PEG are easily determined by analytical pyrolysis as shown in Figure 2, where the chromatographic profile obtained for the archaeological wood of the Lyon shipwreck treated with PEG 400 and disodium sebacate is present. Application of disodium sebacate is an experimental treatment proposed by the Arc-Nucléart Institute of Grenoble (France). This treatment relies on the buffering action and metal passivation effect of disodium sebacate to compensate for the disruptive action of iron salts present in large quantities in this

artefact [21, 34, 35]. A large number of peaks derived from PEG's pyrolysis were observed, as shown in Figure 2. Despite some overlap between PEG and wood pyrolysis products, the AMDIS software allowed to identify all the compounds in the pyrogram by performing deconvolution of the mass spectra of co-eluting species. Consequently, it was possible to perform the semi-quantitative calculations for wood, even in presence of predominant pyrolysis products from PEG (Table 2). Sample Arch-PEG was strongly degraded in terms of loss of carbohydrates, with a H/L ratio 0.02, indicating almost no carbohydrates left.

Pyrolysis of archaeological wood treated with melamine-formaldehyde resin (Kauramin 800) provided very small peaks ascribable to pyrolysis products of holocellulose or lignin. The main pyrolysis products of wood treated with melamine resin, aside from ethylene glycol derivatives, are nitrogen compounds such as: 2-amino-4-methoxybenzamide 3TMS (m/z 73, 147, 205, 277, **367**), triethanolamine 3TMS derivative (m/z 73, **262**, 350), 2-amino-6-(methylamino)-4(1H)-pyrimidinone (43, 69, 111, **140**), methenamine (85, 112, **140**), 1,3,5-triazine-2,4,6-triamine (43, 68, 85, 99, 111, **126**) known as melamine and N,N,N'-trimethyl-5-azacytosine (43, 57, 83, 98, 111, 125, **154**).

The lignocellulosic matrix after in situ polymerization with melamine formaldehyde resin was almost completely transformed into a different polymeric material. Some peaks of ethylene glycol derivatives, were also present. These peaks most likely originate from the PEG 400 added in the treatment bath. At the same time, it is possible to ascertain that the in-situ polymerization of the analyzed fragment with the melamine resin was extensively achieved.

Bio-sustainable treatment with soda lignin was also discussed. Archaeological pine was treated with soda lignin as a consolidating agent. The soda lignin treatment was evaluated by the presence of lignin peaks in the chromatographic profile of treated pine, which are normally absent or present in very low abundance in native pine wood [9]. These pyrolysis products are highlighted in red in Figure 3. The archaeological medieval pine used in these experiments was found to be medium-degraded, as the fraction of holocellulose determined by Py-GC-MS was about 50%. In comparison, fresh pine has a higher percentage of polysaccharides, 60% [9]. Since the wood was treated with lignin, the H/L, normally used for the determination of the decay level of degraded wood, will in this case be used as an index of penetration of the lignin used as consolidant (Table 2). Not surprisingly, the surface of the treated fragment was richer in lignin than the core. Another way to measure extent of penetration into the pine specimens was to consider the types of lignin units present in the treated wood. As pine is a softwood, it contains primarily G-lignin. Therefore, any syringyl and p-hydroxyphenyl lignin pyrolysis product can only derive from the treatment. For this reason, the penetration could also be evaluated considering the types of lignin units. The amount of S-lignin, in the analyzed fragment, increases from 0.6% to 28.4% in the core and 33.3% on the surface.

Table 2. Percentage of wood components holocellulose (H) and lignin (L) and H/L ratios calculated for the archaeological wood samples.

Sample	Arch-AI-LO	Arch-PEG	Arch-Kau	ArchP	ArchP-L-int	ArchP-L-ext
description	alum and linseed oil treated archaeological wood from Oseberg collection	PEG treated archaeological wood from Lyon shipwreck	Kauramin 800 treated archaeological wood	Untreated archaeological pine	Lignin treated archaeological pine sampled from the core	Lignin treated archaeological pine sampled from the surface
Sum H	16.90	1.60	nd	49.94	30.23	27.92
Sum L	83.10	98.40	nd	50.06	69.77	72.08
H/L	0.20	0.02	nd	1.00	0.43	0.39

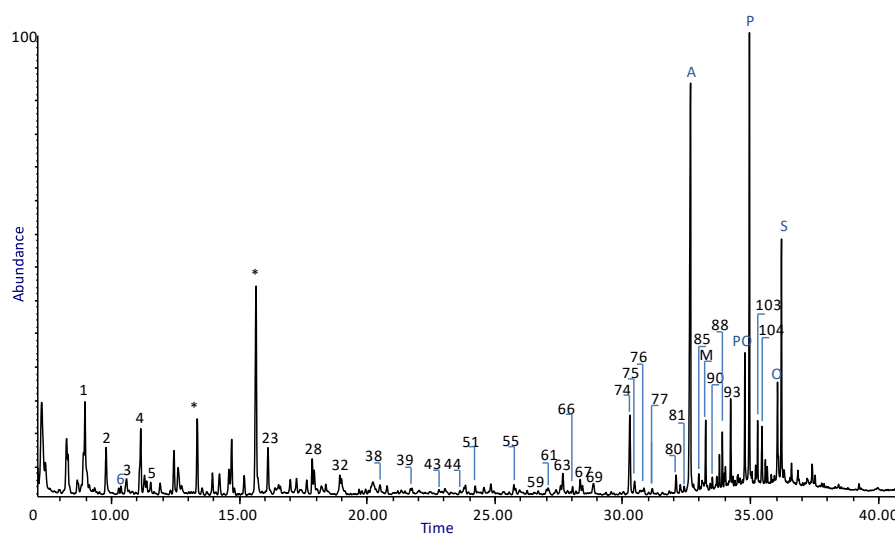


Fig. 1 Pyrogram of alum and linseed oil treated archaeological wood from the Oseberg collection, where azelaic acid-A, myristic acid-M, palmitoleic acid-PO, palmitic acid-P, oleic acid-O and stearic acid-S, (*) – peaks from HMDS. Peaks are labeled according to Table 2.

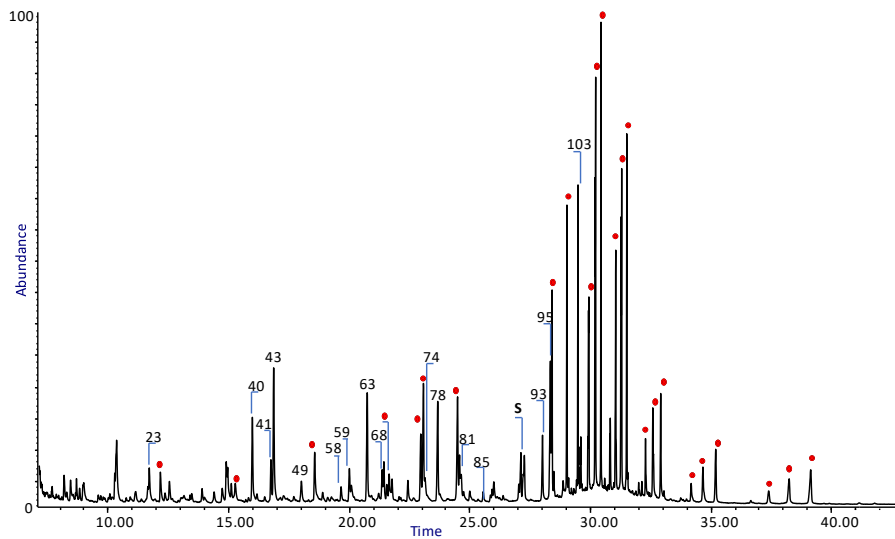


Fig. 2 Pyrogram of PEG 4000 treated archaeological wood from Lyon Ship, where: S - sodium sebacate, (•) PEG pyrolysis products. Peaks are labeled according to Table 2.

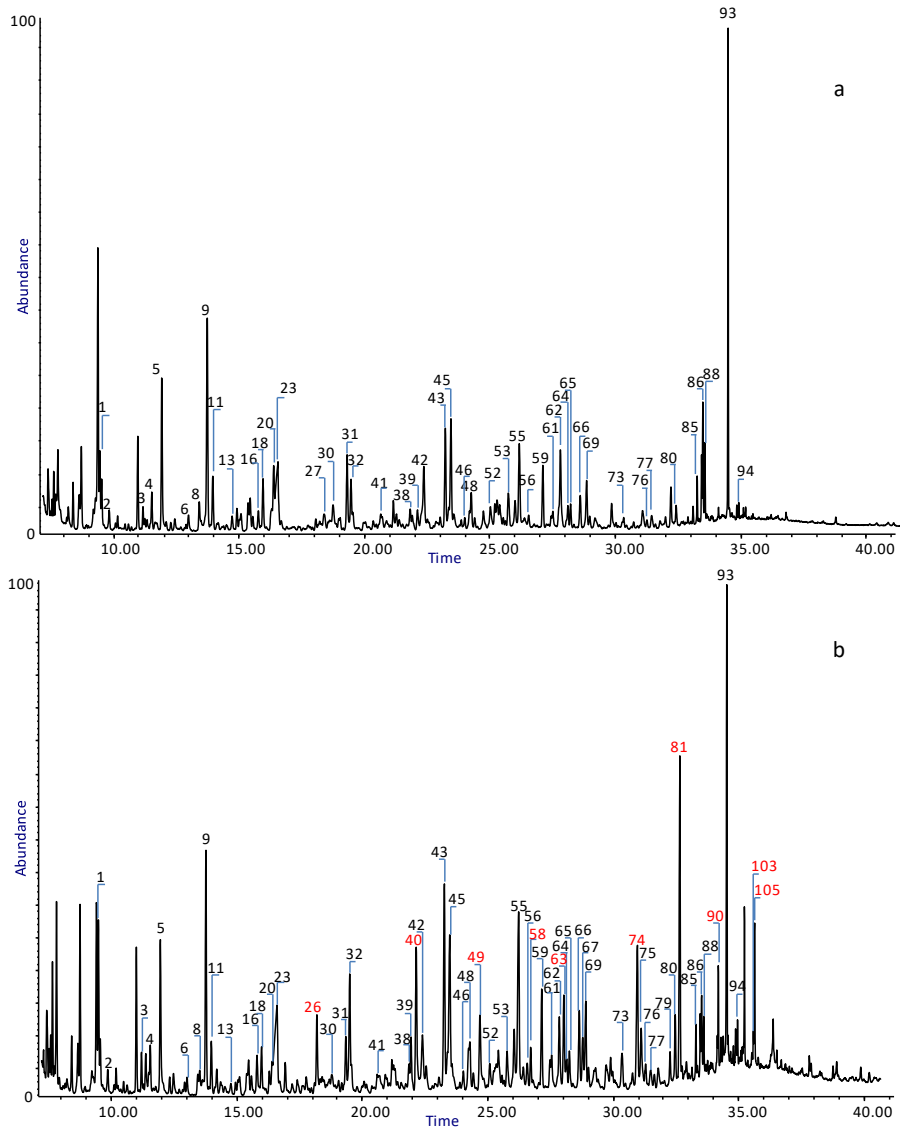


Fig. 3 Pyrograms of a) archaeological untreated pine and b) archaeological pine treated with lignin. Products labeled in red script are derived only from soda lignin and were used to assess soda lignin penetration in test fragments. Peaks are labeled according to Table 2.

4. Ongoing research and perspectives

Ongoing research on this topic include the activities carried out in the context of StAr project started in 2020 (JPI-CH, <http://jpi-ch.eu/>).

This project develops strategies that allow the stabilization of delicate organic archaeological artefacts in the waterlogged state. The project aims at developing, testing, and applying several approaches to maintain storage conditions of archaeological wood, and specific chemical-physical monitoring protocols for these wet finds. Storage experiments are planned in controlled laboratory conditions (ARC-Nucléart, France) and in a real excavation context, the Biskupin site in Poland [1].

StAr aims also to set up effective and sustainable methods to assess the short/long-term stability of archaeological organic artefacts, after conservation treatment. The goal is to develop a protocol for evaluating treated and untreated materials. These practical assessments, suitable for storage centers and museums, will be validated by complementary advanced analytical techniques to confirm the extent of degradation.

The project, coordinated by ARC-Nucléart (Grenoble, France) involves four partners from four different countries (Figure 4).

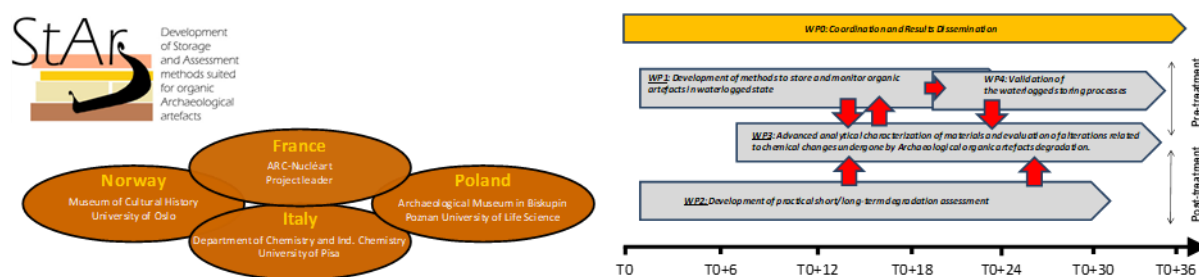


Fig. 4 Research partners involved in the StAr project – on the left, PERT Gantt diagram of StAr project on the right.

A selection of reference pieces and samples from archaeological materials treated with different consolidation treatments (PEG, Kauramin, Nucléart) exposed to natural and artificial ageing will be included in the analytical protocols which will be validated and transferrable. The assessment methods will involve pH measurements, water content, microscopy (optical microscopy, SEM), molecular characterization of organic and inorganic components by Py-GC-MS, FTIR, XRD, assessment of climate-induced response by dynamic vapor sorption (DVS). The transferable tools and protocols will be highly relevant in cases where assessment of new conservation materials need to be undertaken, which is a growing field of interest in heritage science.

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