Combined pyrolysis-based techniques to evaluate the state of preservation of archaeological wood in the presence of consolidating agents

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Abstract

Chemically evaluating the state of preservation of archaeological wood in the presence of consolidating agents, such as polyethylene glycol (PEG), can be challenging. Interpreting the results obtained by the most commonly used single-shot pyrolysis method coupled with gas chromatography and mass spectrometry with *in situ* silylation (Py(HMDS)-GC/MS) is complicated, since both wood and PEG pyrolysis products are produced and poorly separated by GC.

Two new approaches based on analytical pyrolysis are here applied for the first time to consolidated archaeological wood in order to obtain information on both the degraded wood and the consolidating material. Evolved gas analysis mass spectrometry (EGA-MS) provided information on the thermal stability of the materials, as well as on the distribution of the pyrolysis products. The results showed that, for some archaeological wood samples, wood and PEG can be thermally separated. A double-shot Py(HMDS)-GC/MS procedure was also tested and the pyrolysis temperatures for the two shots were chosen on the basis of EGA-MS results. The pyrolysis products of wood and PEG were separated into two different pyrograms.

In some cases, the combination of EGA-MS and double-shot Py(HMDS)-GC/MS provided more detailed information on the material degradation compared to single-shot. Both double shot Py(HMDS)-GC/MS and EGA-MS.

Keywords: waterlogged wood, PEG, EGA-MS, double shot pyrolysis, HMDS

Introduction

Archaeological wood is an extremely valuable source of information regarding our cultural heritage, however archaeological wood findings are extremely rare, because of the long-term microbiological biodegradability of wood in many environments [1][2].

When archaeological wooden objects survive over time in sediments, they are usually in specific burial conditions, such as waterlogged environments, extremely dry conditions, or in a frozen state, where the action of aerobic microorganisms is drastically reduced [3,4]. However, waterlogged wood generally presents poor mechanical properties, and the evaporation of water during drying is an extremely dangerous and delicate conservation practice, because it runs the risk of deformations, cracking and the collapse of the structure. Consolidating agents are therefore currently applied to strengthen the structure during or after controlled drying, in order for the objects to be exhibited in museums [5]. Many classes of consolidating materials have been tested and applied, including alum salts [6,7], colophony/acetone solutions [8], sugars (sucrose, mannitol, sorbitol, lactitol, trehalose) [9-11], melamine formaldehyde resin [12], *in situ* polymerised resins [13,14], thermosetting resins (epoxy, polyester, methyl-methacrylate) [15,16], thermoplastic resins (acrylic, polyvinyl acetate, and polyvinyl acetal resins [17-20]. Polyethylene glycol (PEG) treatment followed by freeze-drying or controlled air drying is currently the preferred method for preserving degraded waterlogged archaeological wood.

PEG based consolidation methods have been applied to some of the most famous archaeological wood findings exhibited in European museums, such as the Vasa warship [21-24], the Mary Rose [25], and the Bremen Cog [26]. Over the last few decades, conservators have become aware of the fact that wood consolidated by PEG is not stable, and that this consolidation method has various drawbacks, above all linked to the sensitivity of PEG towards moisture [27]. Thus, the search for innovative consolidating agents for archaeological wood is a very active field in conservation science [12].

In order to choose the most suitable conservation treatments, the preservation condition of the object needs to be evaluated from structural, chemical and physical perspectives. The evaluation of the degradation state of archaeological wood can be performed with different levels of detail, from the macroscopic to the molecular [28], using optical microscopy, SEM, TAPPI methods, FTIR, NMR and Py-GC-MS techniques [29]. Analytical pyrolysis presents a series of advantages in terms of obtaining chemical information at a molecular level, such as the need for a very small sample size (*ca.* 100 μg), the short analysis time (*ca.* 30 min), and the negligible pre-treatment of the sample. These aspects are extremely advantageous for application in the field of cultural heritage.

A correct interpretation of the results obtained by analytical pyrolysis provides valuable information at a molecular level on the preservation of the wood components, i.e. lignin and polysaccharides (cellulose and hemicelluloses). The ratio between the sums of the chromatographic peak areas of holocellulose and lignin pyrolysis products (pyrolytic H/L ratio) is a useful parameter which has been successfully used to evaluate the degradation state of archaeological wood in terms of the loss of wood components, and to compare samples with different degradation levels [30,31].

Holocellulose [30] and lignin pyrolysis products [7,32] can be classified into groups on the basis of their chemical nature, structure and pyrolytic formation, and the relative amounts of the various categories can be evaluated. Using this approach, information on the degradation reactions undergone by the single wood components (holocellulose and lignin) can be obtained, e.g. oxidation or depolymerisation phenomena [7,32].

Due to the high number of products produced in the pyrolysis of wood, it is particularly useful to partially automize the identification and integration of peaks using specific software such as the Automated Mass spectral Deconvolution and Identification System (NIST package), whichdeconvolutes the peaks on the basis of their mass spectra and the calculation of chromatographic areas even in presence of significant peak overlapping.

Conservators and scientists are often asked to establish the state of degradation of archaeological wood in the presence of consolidating materials, which are mostly not reversible. In some cases it is necessary to investigate the effect of the presence of a consolidating agent on the degradation processes of wood, or to evaluate the degradation undergone by the consolidation materials.

The characterisation of a composite matrix such as archaeological wood consolidated with PEG is complex when using the classical flash pyrolysis approach, because of the very high number of pyrolysis products obtained, which complicate the interpretation of the pyrograms.

This paper presents various strategies to apply pyrolysis-based techniques to such composite materials. Several pyrolysis assets were tested on treated archaeological wood samples: single-shot Py(HMDS)-GC/MS, EGA-MS and double-shot Py(HMDS)-GC/MS. EGA-MS was recently applied to untreated archaeological wood [33], with interesting results. This work also represents the first application of EGA-MS and of double-shot Py-GC/MS to archaeological wood impregnated with a consolidating material.

Materials and methods

Samples

Four archaeological wood samples were analysed and compared. The samples were provided by the Arc-Nucléart Institute of Grenoble (France) within the framework of the ArCo Project: Ageing Study of Treated Composite Archaeological Waterlogged Artifacts, funded as: JPI-JHEP Joint Pilot Transnational Call for Joint Research Projects on Cultural Heritage (2014-2016).

Two samples, named Ly-A0 and Ly-A1, were taken from a shipwreck referred to as the Lyon2 ship. This is one of the sixteen wrecks discovered during the salvage excavations of the Parc Saint-Georges in Lyon, Rhone region (France), situated on what was once the right bank of the Saône River. The findings cover 18 centuries of riverboat architecture (1st-18th century AD). The Lyon2 was a Gallo-Roman river barge dated to the 2nd century AD. Sample Ly-A0 was taken from untreated softwood section, most likely pine, which showed a high degree of contamination by iron salts, mainly pyrite. Sample Ly-A1 was taken from an oak wood part contaminated by iron salts, treated with a solution of 20% PEG 4000 and 10% disodium sebacate ($SebNa_2$) and freeze-dried. This treatment is part of an experimentation carried out by the Arc-Nucléart Institute of Grenoble (France), aimed at testing the pH buffering potential and metal passivation power of disodium sebacate when added to PEG and applied to acidic archaeological wood contaminated by inorganic salts [34,35].

The two other samples, named SM-A0 and SM-A1, were taken from another shipwreck, called "L'Aimable Grenot". This is a corsair boat dating back to the 18th century which sank in 1750 near Saint Malo harbour (France). It was found in 1995 and is the first corsair boat ever found. It is still kept under the seawater, and only same parts have been recovered and submitted to treatment tests. Sample SM-A0 was taken from an oak wood fragment treated with PEG 4000. Sample SM-A1 was taken from an oak wood fragment treated with PEG 4000 and recently post-treated with a solution of 20% PEG 4000 and 10% disodium sebacate (Na_2Seb) freeze-dried. Again, the two wood fragments suffered from significant contamination and acidification by iron salts.

PEG 4000 and disodium sebacate provided by the Arc-Nucléart Institute of Grenoble (France) were used as reference materials.

Experimental conditions

The instrumentation consisted of a micro-furnace EGA/Py-3030D Multi-Shot Pyrolyzer (Frontier Lab) coupled with a 6890 Agilent Technologies gas chromatograph and a 5973 Agilent Mass Selective Detector single quadrupole mass spectrometer operating in electron impact mode (EI) at 70 eV. For all experiments the MS transfer line temperature was kept at 300°C. The MS ion source temperature was kept at 230°C and the MS quadrupole temperature at 150°C.

For single-shot Py(HMDS)-GC/MS 1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9%, Sigma Aldrich Inc., USA) was used as a silylating agent to achieve the *in situ* derivatisation of pyrolysis products. The GC oven was equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl and 95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m x 0.32 mm i.d., Agilent J&W, USA).

Approximately 50 µg of sample and 5 µL of HMDS were put into a stainless steel cup and placed into the micro-furnace. The pyrolysis temperature was 550°C and interface temperature was 250°C. The split/splitless GC injector was used with a split ratio of 1:5 at 280°C. Chromatographic conditions were as follows: initial temperature 50°C, 1min isothermal, 10°C min^{-1} to 100°C, 2 min isothermal, 4°C min^{-1} to 190°C, 1 min isothermal, 30°C min^{-1} to 280°C, 30 min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 mL min^{-1}.

For double-shot Py(HMDS)-GC/MS, a long stainless steel stick, which connects the cup with the sample holder, was used instead of the short one used for single shot analysis. This enabled the sample to be retrieved from the pyrolysis chamber after the first shot. Approximately 100 µg of sample and 5 µL of HMDS were put into a stainless steel cup and placed into the micro-furnace. The pyrolysis temperature for the first shot was 320°C, which was held for 1 min. The sample was then retrieved from the pyrolysis chamber and the chromatographic run was started. Chromatographic conditions were 50°C, 1 min isothermal, 10°C min^{-1} to 280°C, 30 min isothermal. At the end of the first run, the pyrolyser was opened and another 5 µL of HMDS were added to the cup. The pyrolysis temperature for the second shot was 600°C and the same chromatographic conditions as the first shot were used.

For the EGA-MS analysis, the GC oven was equipped with a deactivated and uncoated stainless steel transfer tube (UADTM-2.5N, 0.15mm i.d.× 2.5m length, Frontier Lab). A temperature program was set for the micro-furnace chamber: initial temperature 50°C; 20°C min^{-1} up to 200°C; 8°C min^{-1} up to 500°C; 20°C min^{-1} up to 700°C. Analyses were performed under a helium flow (mL min^{-1}) with a split ratio 1:20. The micro-furnace interface temperature was kept at 100°C higher than the furnace temperature until the maximum value of 300°C. The inlet temperature was 280°C. The chromatographic oven was kept at 300°C. A total of 200 µg of sample was put into the stainless steel cup and placed into the micro-furnace.

All the samples were oven dried for 24 h at 50 °C, and then homogenised and powdered using a ball mill made of zirconium oxide (Pulverisette 23, Fritsch GmbH, Germany) before analysis. The identification of the pyrolysis products was based on the results reported in our previous publications [7,30,32,33].

Results

Single-shot Py(HMDS)-GC/MS

The analyses of pure PEG and disodium sebacate (Na_2Seb) were preliminarily performed to collect their pyrolysis profiles and to study their pyrolytic behaviour in the adopted conditions. The single-shot Py(HMDS)-GC/MS pyrograms are shown in Figure 1.

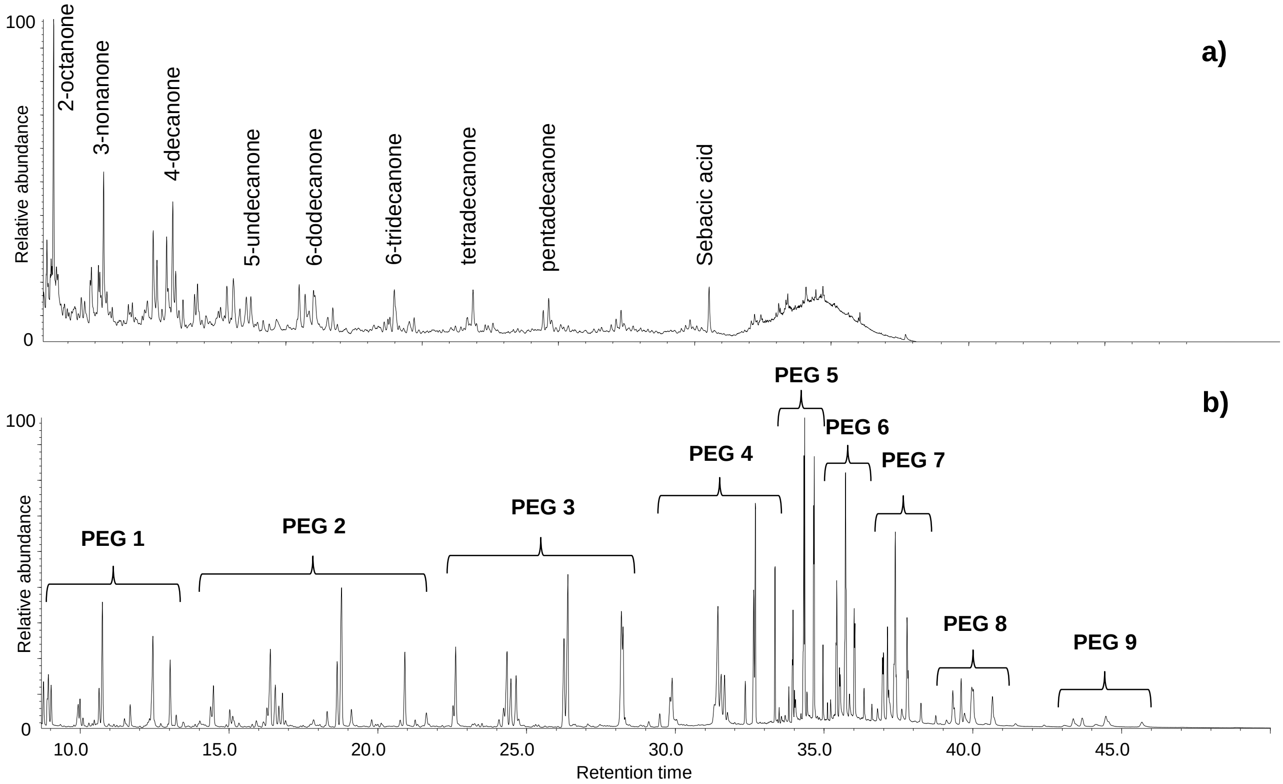

Figure 1. Pyrograms obtained by single-shot Py(HMDS)-GC/MS of **a)** disodium sebacate and **b)** PEG 4000.

The pyrolysis of Na_2Seb resulted in a few pyrolysis products, mainly ketones, with a very low abundance and a small peak related to the bis-trimethylsilyl ester of sebacic acid, as expected due to the very low volatility of carboxylates.

The pyrolysis of PEG resulted in a high number of peaks corresponding to oligomers, which were divided into clusters, as highlighted in Figure 1. Each cluster had a similar number and distribution of peaks, with some differences in their relative abundances. The products in each cluster were differentiated on the basis of their terminal groups. If one cluster is considered, the products present in the next cluster have the same structure as those in the previous one, but they increase in size and weight by one monomeric unit ($–CH_2–CH_2–O–$), whose mass is 44 uma. Thus, all the pyrolysis products of PEG can be identified if the products in one group are identified [36,37]. According to the literature, the end groups of the products are $–OCH_3$, $–OCH_2–CH_3$, $–OCH=CH_2$, –OH, –CHO, and they can combine in different ways, depending on the pyrolytic conditions [36]. The formation of a cycloether end-group has also been reported [37].

The identification of the exact molecular structure of the pyrolysis products of PEG after silylation using HMDS is not straightforward and beyond the scope of this work. In general, in the adopted conditions, the hydroxyl groups are turned into trimethysilyl ethers. The peak at *m/z* 73 is usually used to distinguish derivatised and non-derivatised compounds, since it corresponds to the trimethylsilyl radical ion, which is always present in the mass spectra of derivatised products [38]. However, the mass spectra of PEG pyrolysis products with a cycloether end-group displayed a strong peak at *m/z* 73 due to the fragmentation of the cycloether [37]. This made it impossible to distinguish between silylated products and compounds containing a cycloether end-group. In addition, the mass spectra of the PEG pyrolysis products did not clearly show the molecular peak, thus preventing the molecular weight of the single pyrolysis products from being determined.

Analysis of the archaeological samples showed the presence of the pyrolysis products originating from wood and from the consolidating materials, as shown in Figure 2.

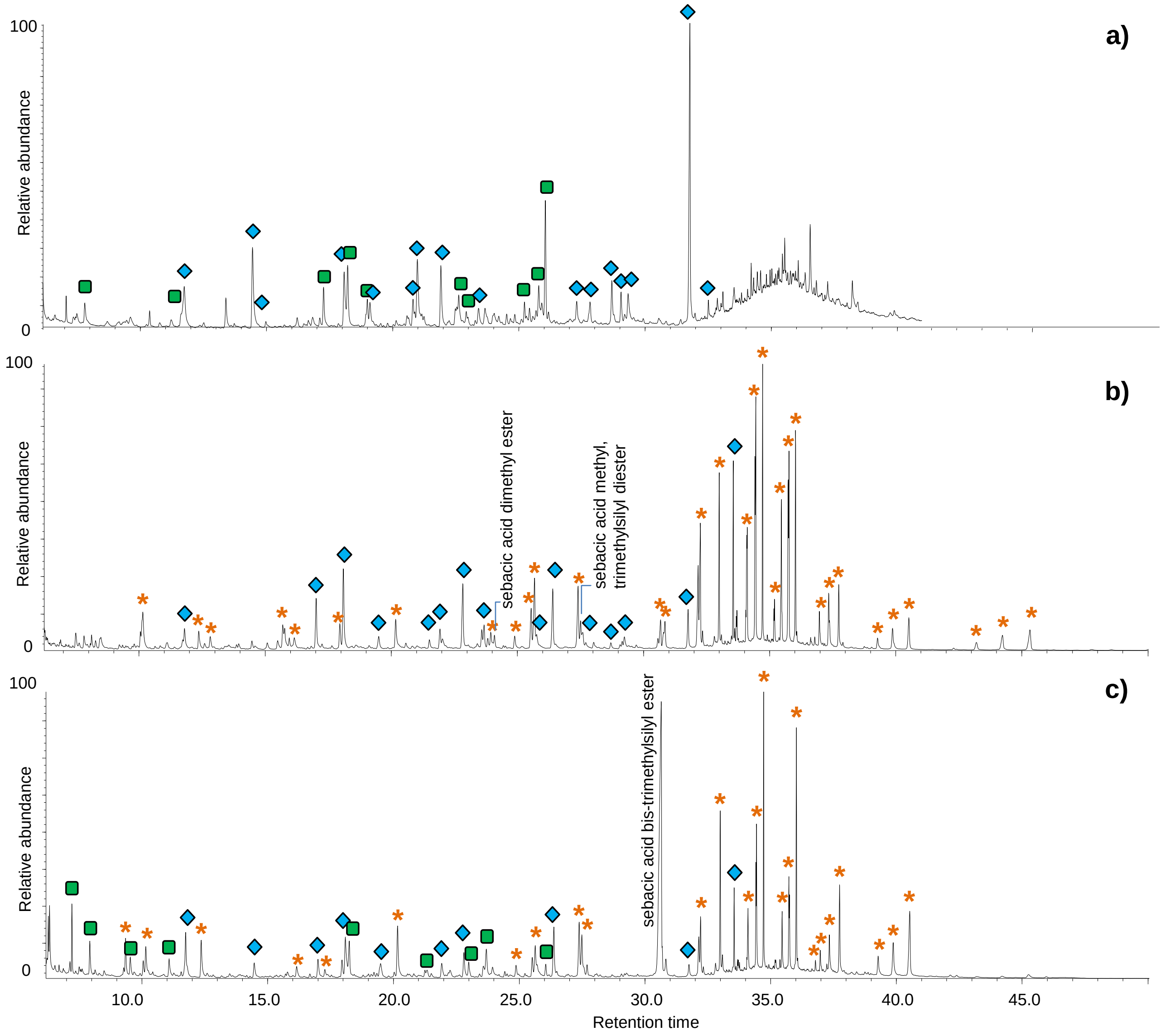

Figure 2. Pyrograms obtained by single-shot Py(HMDS)-GC/MS of samples **a)** Ly-A0 (untreated), **b)** Ly-A1 (treated with the solution of 20% PEG 4000 and 10% Na$_2$Seb), and **c)** SM-A1 (treated with the solution of 20% PEG 4000 and 10% Na$_2$Seb). 🟩: holocellulose pyrolysis products; ◆: lignin pyrolysis products; ✱ : PEG pyrolysis products

The results obtained for sample Ly-A0 (Figure 2a) showed a typical pyrolytic profile for a waterlogged wood sample, with a very low abundance of holocellulose pyrolysis products and lignin pyrolysis products as the most abundant ones. This was an indication that part of the polysaccharide component of the wood had been depleted, as usually occurs in waterlogged archaeological wood, since carbohydrates (cellulose and hemicelluloses) undergo degradation more easily than lignin in wet environments [39,40]. The complexity of the pyrolytic profile of sample Ly-A1 (Figure 2b) was clearly higher: lignin and PEG pyrolysis products were both present and showed some overlapping. A few holocellulose pyrolysis products were detected with negligible abundance, indicating an advanced degradation and depletion of carbohydrates for this sample. However the presence of PEG pyrolysis products as major peaks prevented these observations from being completely reliable, since the compounds co-eluted. Two forms of sebacic acid were also detected; a dimethyl ester and a methyl, trimethylsilyl diester. These products were formed by trans-methylation of disodium sebacate. It is known that PEG degradation leads to the release of formic acid [41], which could have reacted with the sebacate, leading to the formation of the methylated derivatives.

As regards sample SM-A1 (Figure 2c), the profile was even more complex, since wood pyrolysis products were detected with a lower abundance compared to sample Ly-A1, and both holocellulose and lignin pyrolysis products were present. In addition, an intense peak corresponding to the bis-trimethylsilyl form of sebacic acid was observed, indicating that most of the Na_2Seb was converted into the corresponding acid in sample SM-A1. A completely different analytical response of disodium sebacate in samples Ly-A1 and SM-A1 was therefore revealed. This is likely the result of the different acidity of the two samples. Although absolute pH values were very difficult to measure, preliminary pH measurements revealed that sample SM-A1 was 1-2 pH unit more acidic that sample Ly-A1. Thus it is not surprising that the sebacic acid in sample SM-A1 was prevalently in the protonated from, which has a higher yield in Py(HMDS)-GC/MS analysis, thus producing an intense sebacic acid peak These results support the on-going investigations aimed at clarifying the potentialities of the Na_2Seb treatment from a conservation point of view and the interactions between the treatment material and the wood matrix.

The results obtained in the single-shot Py(HMDS)-GC/MS analysis of sample SM-A0 (not shown) were similar to sample SM-A1, with the differences that the holocellulose pyrolysis products were slightly more abundant in sample SM-A0 and that the sebacic acid peak was not present, as this sample had not been treated with Na_2Seb.

Despite the overlapping between PEG and the chromatographic peaks of the wood pyrolysis products, the wood pyrolysis products present in the pyrograms could be identified, exploiting the AMDIS software. In fact, this software performs the deconvolution of the peaks pyrogram, and detects small differences in the mass spectra, which enabled the wood pyrolysis products to be identified, even when they had co-eluted. The identification is based on the match (a matching factor > 70 % was used) between the mass spectra present in the pyrogram and those in a mass spectral library. This mass spectral library was created after several works were performed applying Py(HMDS)-GC/MS to archaeological wood materials [7,30,32,42], and contained 117 entries corresponding to wood pyrolysis products.

AMDIS software also automatically provides the integrated areas of the recognised peaks, thus enabling semi-quantitative calculations to be performed in a few minutes. It was thus possible to calculate the pyrolytic H/L (holocellulose/lignin) ratios as the ratio between the sum of the areas of the holocellulose pyrolysis products and the sum of the areas of the lignin pyrolysis products, also in the presence of predominant pyrolysis products from PEG. This parameter was used to evaluate the degradation state of archaeological wood [29,31], since the difference between the H/L ratio obtained for sound and archaeological wood from the same species provides information on the preferential loss of one wood component (holocellulose or lignin) over the other one.

The pyrolytic H/L ratios for the archaeological samples Ly-A0, Ly-A1, SM-A0 and SM-A1 were 0.5, 0.1, 2.7 and 0.6, respectively. The same parameter ratio for sound oak wood obtained in the same conditions is 2.8 [32]. Several studies have shown that the relative standard deviation for the pyrolytic H/L ratios is below 10% [7,30,32,42]. Therefore, these results showed that samples Ly-A0, Ly-A1 and SM-A1 had undergone an extensive loss of carbohydrates, especially sample Ly-A1, whereas sample SM-A0 had a very good state of preservation.

Although the area integration performed by AMDIS can be partially controlled, in the case of co-elution it is difficult to double-check the actual section of the peak area considered. Therefore, the reliability of these values is strongly related to the complexity of the chromatogram, which influences the ability of the software to correctly perform this operation. We thus decided to test other innovative analytical approaches to separating wood and consolidating materials on the basis of their thermal stability.

EGA-MS

PEG 4000 and disodium sebacate (Na_2Seb) were preliminarily analysed by EGA-MS. Figure 3 shows the total ion thermogram obtained for disodium sebacate and the overall mass spectrum obtained.

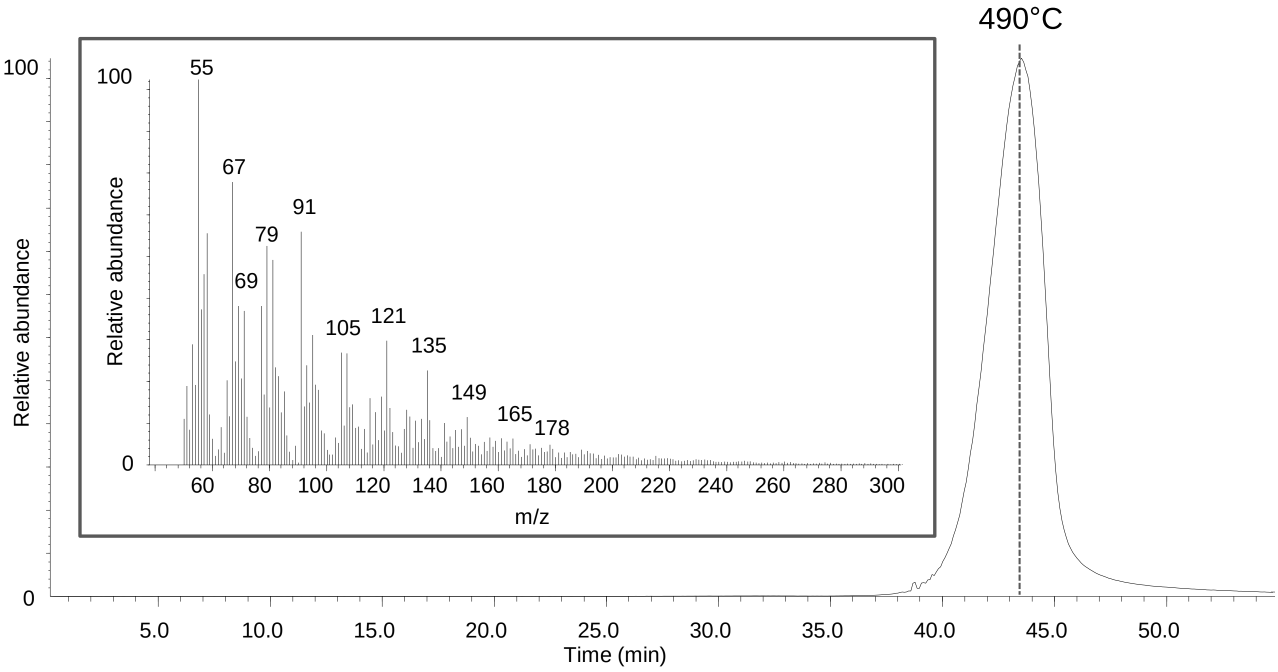

Figure 3. Total ion thermogram obtained by EGA-MS analysis of disodium sebacate Na_2Seb. Inset: overall mass spectrum obtained in the thermal degradation region.

Disodium sebacate underwent thermal degradation between 450 and 550°C. The mass spectra did not show significant changes during the temperature interval, above all highlighting the typical fragmentation of fatty acids. The most abundant were fragment ions attributed to the pyrolysis of an aliphatic chain, since the loss of the carboxyl group as CO_2 is the first pyrolytic reaction in these systems [43]. In particular, fragment ions with *m/z* 55, 69, 83, 97 from alkenes, 67, 81, 95, 109 from dienes, and 79, 93, 107, 121 from trienes were present in the spectra, as well as *m/z* 91 and 105 from aromatic rings obtained by the rearrangements of aliphatic chains at high temperatures. The fragment ion with *m/z* 81 may also derive from a double McLafferty rearrangement of the sebacate [43].

PEG 4000 underwent thermal degradation between 300 and 500°C (Figure 4). Again, the mass spectra were similar in the whole thermal degradation region. The fragment ions reflected the fragmentation of the polymeric chains and showed the *m/z* corresponding to monomers, dimers, trimers and tetramers.

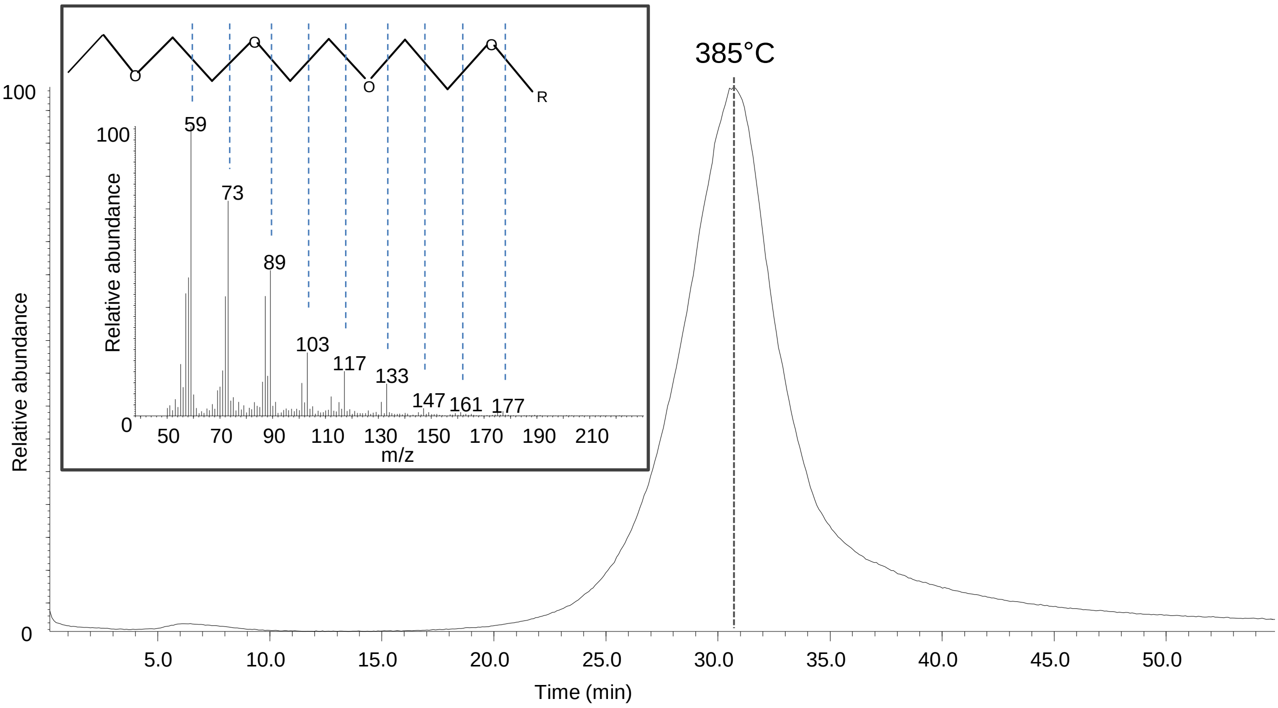

Figure 4.1 Total ion thermogram obtained by EGA-MS analysis of PEG 4000. Inset: overall mass spectrum obtained in the thermal degradation region of PEG 4000, reflecting the fragmentation of the polymeric chains.

Sample Ly-A0 was untreated, and was thus the least complex sample in the set. Figure 5 shows the results obtained by EGA-MS.

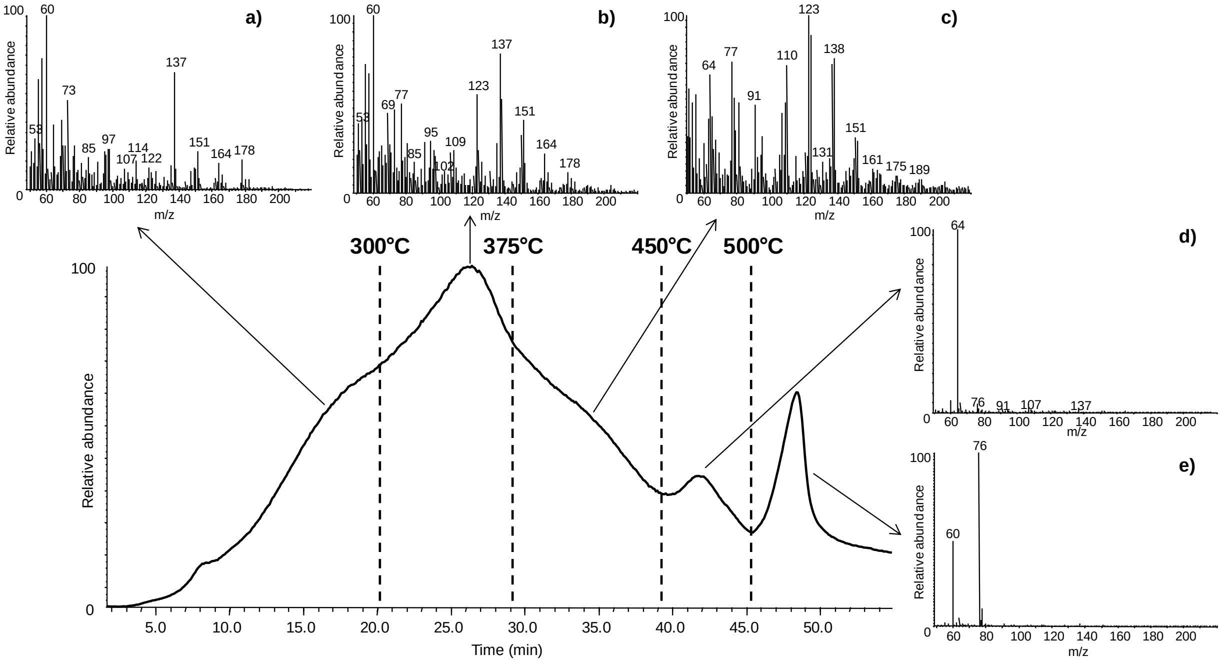

Figure 5. Total ion thermogram obtained by EGA-MS analysis of sample Ly-A0 from the Lyon2 ship and overall mass spectra obtained in the ranges a) 10-20 min, b) 22-28 min, c) 30-38 min, d) 40-45 min and e) 46-50 min.

Despite the absence of a conservation material, the total ion thermogram appeared very complex. Different regions of thermal degradation were identified. The first region was detected as a shoulder until 300°C (20 min) and the mass spectrum revealed the presence of cellulose (*m/z* 60), hemicelluloses (*m/z* 114) and guaiacyl-lignin (*m/z* 137, 151, 178), indicating the thermal decomposition of all wood components in this region. In the second region from 300 to 375°C (20-29 min), the maximum was reached. Hemicelluloses pyrolysis products were no longer detected at this temperature, whereas cellulose and lignin continued to undergo their thermal degradation. In the third region, from 375 to 450°C (29-39 min), only the pyrolysis products of lignin were identified. Benzyl, phenolic and catecholic structures (*m/z* 91, 110 and 123 respectively) were the most abundant, since these pyrolysis products have been reported to be produced during the pyrolysis of lignin at high temperatures [33]. Above 450°C another decomposition peak was revealed which corresponded to the formation of SO_2. The contamination of this sample by FeS_2 and other iron and sulphur salts was assessed in the previous analyses, thus justifying the significant presence of the evolved SO_2.

The last peak above 500°C showed the mass spectrum of thiourea. The formation of this compound during the pyrolysis of the sample is difficult to explain, especially regarding the source of nitrogen (NO_3^- content was negligible in this sample). The predominant presence of lignin pyrolysis products, as detected in the mass spectra, is an indication of the extensive degradation of carbohydrates in this sample, as assessed by single-shot Py(HMDS)-GC-MS analysis discussed in the previous section. In fact, in sound wood, *m/z* peaks attributed to carbohydrate pyrolysis products are generally the most abundant in the mass spectra [33].

Sample SM-A0 was treated with PEG 4000, thus representing a system in which archaeological wood and PEG are both present. The results obtained by EGA-MS analysis of sample SM-A0 are shown in Figure 6.

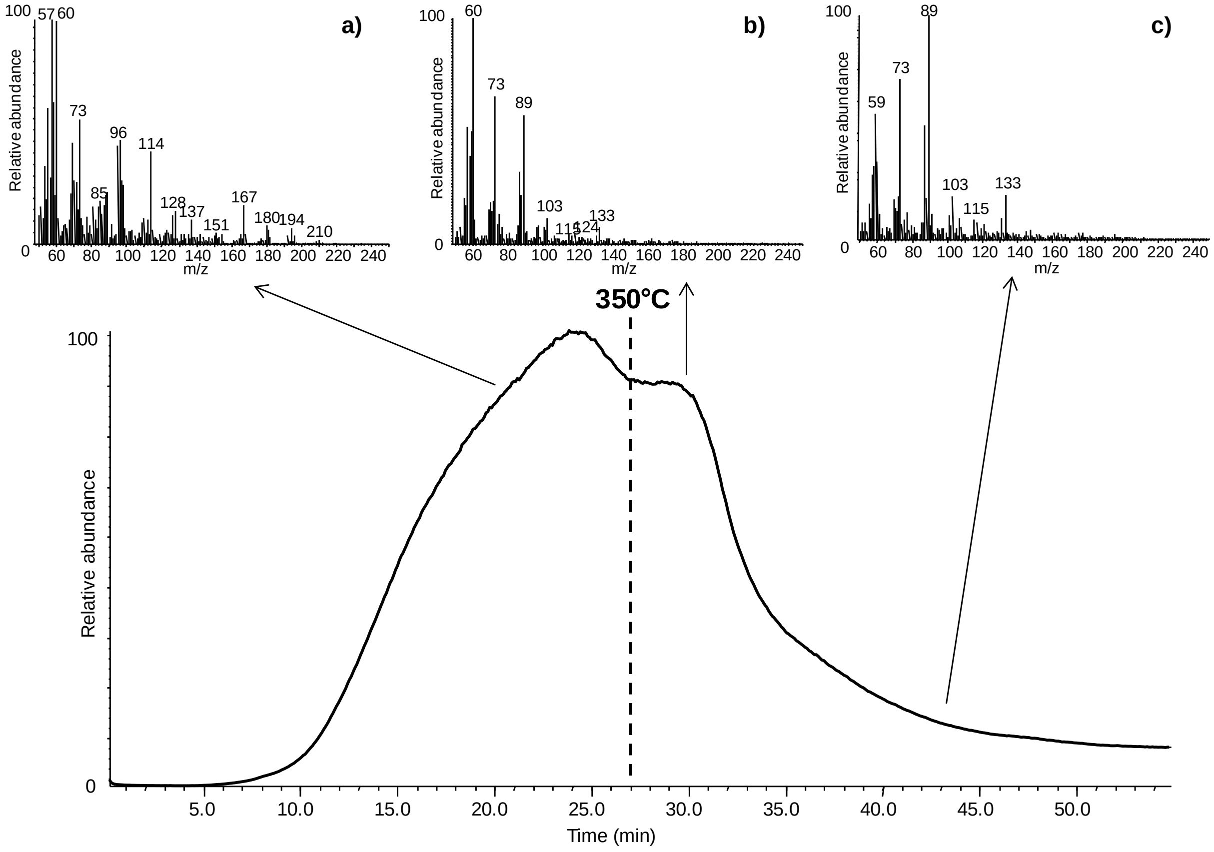

Figure 6. Total ion thermogram obtained by EGA-MS analysis of sample SM-A0 from L’Aimable Grenot and overall mass spectra obtained in the ranges **a)** 10-27 min, **b)** 27-35 min and **c)** 35-45 min.

The first region of thermal degradation up to 350°C corresponded to the main thermal decomposition of cellulose and hemicelluloses: the mass spectra showed that the fragment ions with *m/z* 60, 96 and 114 were the most abundant. The pyrolysis products of lignin were also detected with a relative low abundance in this region, thus highlighting and confirming the good preservation of carbohydrates in this sample. The second region of thermal degradation, represented by the second shoulder in the thermogram, corresponded to the thermal decomposition of PEG. In fact, up to 400°C cellulose continued to undergo its thermal decomposition, as indicated by the presence of *m/z* 60 in the mass spectrum. In the last part of the thermogram only PEG was detected.

These results thus highlighted that when archaeological wood is well preserved, there is an overlapping between the thermal decomposition of wood and PEG.

Samples Ly-A1 and SM-A1 were treated with the solution of PEG 4000 and Na_2Seb, thus representing an additional level of complexity in the system analysed.

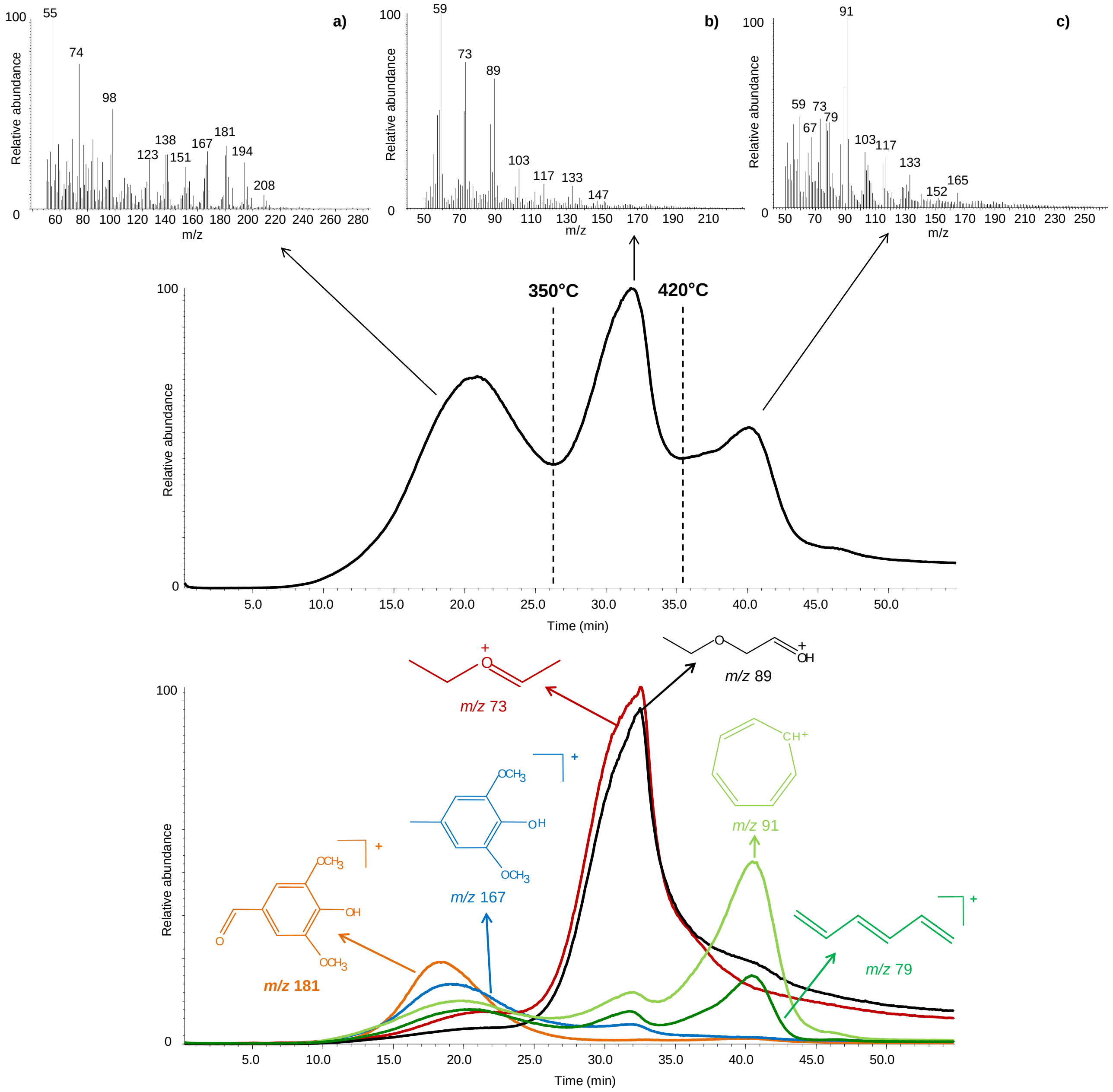

Figure 7. Total ion thermogram obtained by EGA-MS analysis of sample Ly-A1 from the Lyon ship and overall mass spectra obtained in the ranges **a)** 10-26 min, **b)** 27-34 min and **c)** 35-45 min. Extract ion thermograms of evolved gas during the thermal degradation and the molecular formula of selected ions are reported.

Three main regions of thermal degradation were identified (Figure 7). The first region was between 200 and 350°C, the second region was between 350 and 420°C, and the third region between 420 and 500°C. The mass spectra in the first region highlighted the thermal degradation of wood. In fact, fragment ions with *m/z* 123, 137, 138, 151, 167, 181, 194, 208 are produced in the pyrolysis of lignin

[33]. The fragment ion with *m/z* 98 derives from several pyrolysis products with a furan or pyran structure, produced during the pyrolysis of carbohydrates. The detection of only one fragment ion derived from the pyrolysis of holocellulose confirmed the high depletion of this wood component in the sample.

The spectra in the second region corresponded to PEG. The fragment ions detected showed some differences in the relative abundances compared to the reference sample of PEG, most likely due to differences in the degree of polymerisation of the consolidating agent. In fact, the fragment ions attributed to monomers and dimers were relatively more abundant in the spectra obtained from sample Ly-A1 compared to the PEG reference . The higher yield in the thermal production of small fragments could be associated with the degradation of the polymer.

The third region showed fragment ions derived from both PEG and Na_2Seb. The fragment ions with *m/z* 67, 79 and 91 were not present in the mass spectrum of PEG, and were indicative of the presence of Na_2Seb. Therefore, these results highlighted that the wooden material, PEG and Na_2Seb were partially thermally separated in sample Ly-A1 using EGA-MS. This separation allowed considerations on the state of preservation of wood to be made, by focusing on the first region of thermal degradation. One of the data elaboration tools of EGA-MS enables the extract ion thermograms (EIT) to be obtained, which enable specific fragment ions to be extracted in order to follow their evolution during the temperature range scanned. Two fragment ions for each component present in the sample are considered in Figure 7: *m/z* 181 and 167 for wood, *m/z* 73 and 89 for PEG, *m/z* 79 and 91 for Na_2Seb. The extract ion thermograms confirmed that there was almost no overlapping between the thermal degradation of wood and PEG, whereas there was some overlap between with PEG and Na_2Seb.

It is important to underline that the good separation between the thermal degradation of wood and PEG was obtained in this case because the archaeological wood had suffered from a poor preservation state in terms of carbohydrate loss. The thermal degradation of the archaeological wood mainly occurred in a reduced temperature range compared to that of sound or well-preserved wood, which normally occurs up to 500°C [33]. Therefore, PEG began its thermal degradation when the wood had been almost completely thermally degraded.

Very similar results were obtained for sample SM-A1. Wood, PEG and Na_2Seb showed three different regions of thermal degradation, respectively. Again, the wood was highly degraded in terms of carbohydrate loss, thus resulting in a good separation of the components by EGA-MS.

Double-shot Py(HMDS)-GC/MS

On the basis of the results obtained by EGA-MS, double-shot Py(HMDS)-GC/MS was tested on samples Ly-A1 and SM-A1. According to the extract ion thermograms discussed in the previous section, at 320°C wood and PEG pyrolysis products showed the lowest intersection (Figure 7). Therefore, this temperature was chosen to perform the first pyrolysis step, and 600°C was chosen for the second step, in order to ensure the thermal decomposition of all the remaining material. Figure 8 shows the results obtained in the analysis of sample Ly-A1.

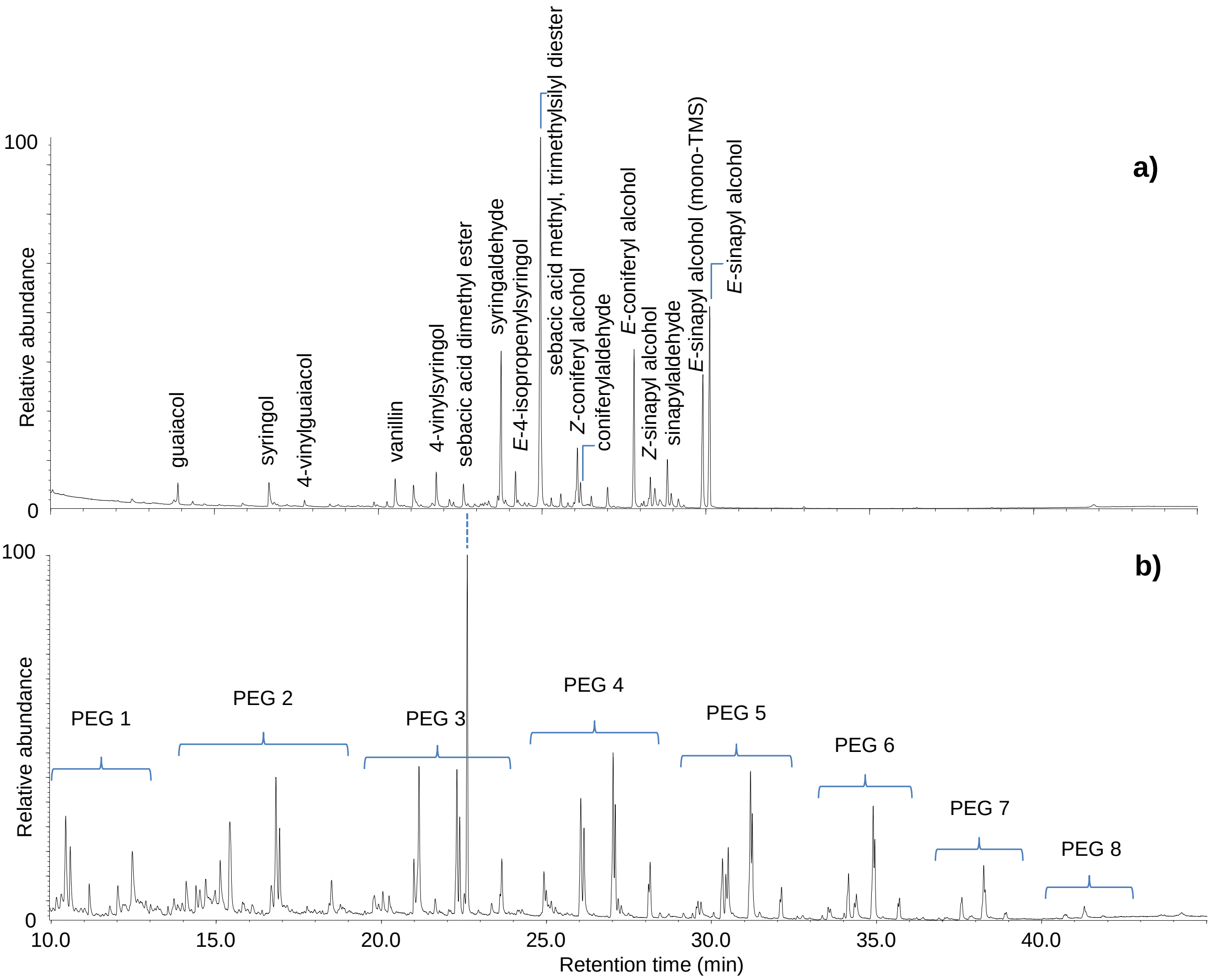

Figure 8. Pyrograms obtained by double-shot Py(HMDS)-GC/MS analysis of sample Ly-A1 at temperatures of **a)** 320°C and **b)** 600°C. The pyrolysis products are considered as fully silylated, unless otherwise indicated.

The pyrogram obtained at 320°C mainly showed lignin pyrolysis products. A few holocellulose pyrolysis products were detected with negligible abundance. The two methylated forms of sebacic acid, also detected with single shot pyrolysis, were present. The pyrogram obtained at 600°C contained PEG pyrolysis products divided into groups of n-mers (n = 1-8) with a similar pattern to that observed for single-shot pyrolysis analysis. Sebacic acid dimethyl ester was also present with a high relative abundance. A complete separation of wood and PEG pyrolysis products in the two different pyrograms was obtained. The resulting pyrograms were less complex than the pyrogram obtained using single-shot pyrolysis, and the co-elution of peaks was removed.

For sample SM-A1 (Figure 9), the result was different. Although the extract ion thermograms of samples Ly-A1 and SM-A1 obtained by EGA-MS were very similar, there was slightly more overlap at 320°C between lignin and PEG pyrolysis products in sample SM-A1 than in sample Ly-A1. However, this temperature showed the lowest overlapping between wood and PEG pyrolysis products, and thus was chosen as the first pyrolysis step temperature. However, this small difference in the thermal behaviour of lignin and PEG in sample SM-A1 resulted in an incomplete separation of wood and PEG pyrolysis products when double shot pyrolysis was applied using these conditions. The pyrogram obtained at 320°C revealed the presence of ethylene glycol and its oligomers, in addition to wood pyrolysis products. Sebacic acid in its trimethylsilyl form was also present with a high abundance, similarly to the findings in single-shot pyrolysis. On the other hand, the pyrogram obtained at 600°C showed a similar profile to that obtained for sample Ly-A1.

The difference between the two samples could be explained with the fact that sample SM-A1 was treated with PEG 4000 at two different times. The previously applied PEG probably had a worse conservation state compared to the PEG applied more recently. This resulted in a lower thermal stability of the polymer, which began to undergo its thermal degradation below 320°C. The pyrogram obtained at 320°C was indeed much less complicated than the one obtained with single-shot pyrolysis, and there was almost no overlap between peaks.

For both samples the H/L index was calculated using the pyrograms obtained at 320°C. The results perfectly matched those obtained using single-shot pyrolysis. Therefore, this approach was not only successful in estimating the preservation state of archaeological wood in the presence of PEG, but also obtained more detailed information on all the materials present in the samples.

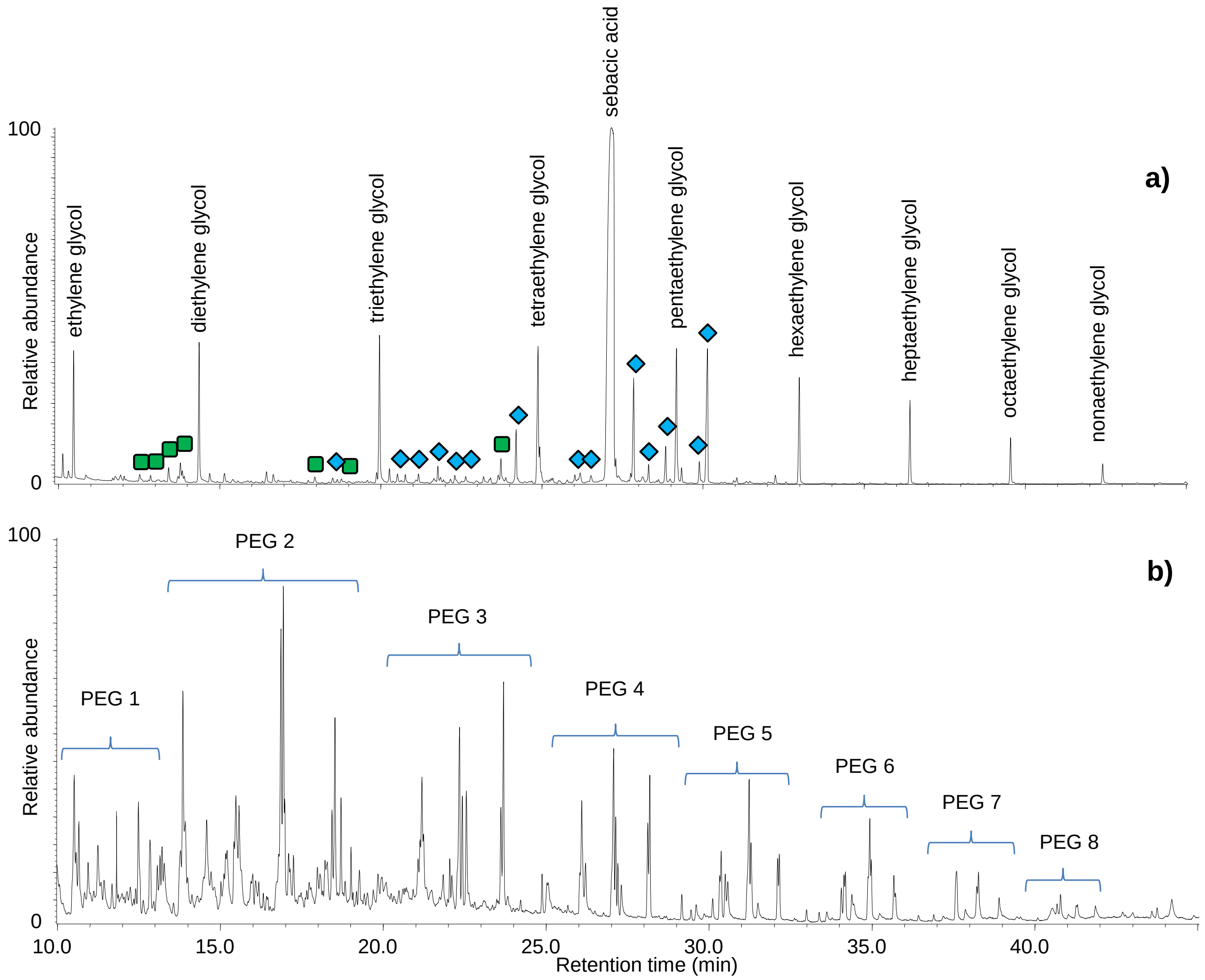

Figure 9. Pyrograms obtained by double-shot Py(HMDS)-GC/MS analysis of sample SM-A1 at temperatures of **a)** 320°C and **b)** 600°C. The pyrolysis products are fully silylated, unless otherwise indicated.

Conclusions

Analytical pyrolysis based techniques, namely single-shot Py(HMDS)-GC/MS, EGA-MS and double-shot Py(HMDS)-GC/MS, were applied to establish the effectiveness of different approaches in determining the state of preservation of archaeological wood in the presence of consolidating agents. The results showed that the combination of EGA-MS and double-shot pyrolysis has various advantages over single-shot pyrolysis and can be used in some cases to investigate such complex mixtures of materials. In fact, despite the shorter analysis time, complex pyrolytic profiles were obtained using single-shot pyrolysis, as both PEG and wood pyrolysis products were present and showed many overlapping peaks. Only the application of the AMDIS software enabled peak areas to be integrated, using an appropriate mass spectral library.

EGA-MS was applied for the first time to consolidated archaeological wood and its use highlighted the potential of exploiting the differences in the stability of materials towards thermal degradation. The results showed that degraded wood and PEG have different ranges of thermal degradation. When archaeological wood has undergone an extensive loss of carbohydrates, as is common for waterlogged wood, an almost complete separation of the thermal degradation regions of wood and PEG can be obtained. Disodium sebacate (Na_2Seb) added to the consolidating material also showed a distinct thermal degradation region at a higher temperature compared to wood and PEG. The data obtained by EGA-MS were used to set up a double-shot method, using a relatively low temperature (320°C) for the first shot. In one case the method succeeded in obtaining two pyrograms, one containing just wood pyrolysis products and the other containing just PEG pyrolysis products. In the other case, the pyrogram obtained at 320°C showed some PEG pyrolysis products, most likely due to a higher depolymerisation degree of the polymer occurring during the ageing of the materials. This aspect will be developed in future investigations, as this combined pyrolytic technique approach could lead to the evaluation of the degradation state of both wood and PEG in the same micro-sample and without any sample pre-treatment, which is extremely important in terms of conservation issues related to consolidated archaeological wood.

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