# CHARACTERIZATION OF EMISSIONS FROM THERMALLY MODIFIED WOOD AND THEIR REDUCTION BY CHEMICAL TREATMENT

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Thermal treatment is a suitable method for improving the quality of wood types like spruce, beech, or poplar, and thus to open up new fields of application that used to be limited to tropical woods or woods treated with timber preservatives. These thermally treated woods are characterized by a typical odor caused by degradation products of miscellaneous wood components. The characterization and removal of those odorous substances were investigated using chromatographic and spectroscopic methods. Headspace gas chromatography (GC) in combination with solid-phase microextraction (SPME) was used for a qualitative analysis of volatile wood emissions, and the detectable volatiles were compared before and after solvent extraction. Wood solvent extractives were investigated by means of gas chromatography/mass spectrometry and then evaluated in terms of changes in composition caused by the thermal treatment process.

*Keywords: Thermal treatment; Wood modification; Solid-phase microextraction; Wood emissions; Gas chromatography; Mass spectrometry*

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## INTRODUCTION

As an environmentally compatible method of wood preservation against humidity and weather, thermal treatment of temperate woods can lead to their improved durability and enlarges their field of application. This treatment modifies certain structural, mechanical, physical, and chemical wood properties, resulting in increased dimensional stability (Popper et al. 2005) and durable resistance to fungi and microorganisms (Boonstra et al. 2007; Weiland and Guyonnet 2003), on the one hand, and discoloration (Bekhta and Niemz 2003) and a significant odor, on the other hand. When thermally modified wood is considered as a resource for indoor constructions or articles of daily use, there is less knowledge about the health risk posed by process products and malodorous emissions. The formation of toxic polyaromatic compounds during heat treatment has been discussed in the literature (Kamdem et al. 2000). It was supposed that the formation of these products caused resistance of thermally modified wood against fungal decomposition and microorganisms.

Increasing indoor application of thermally modified wood has led to increased interest in elucidating the chemical composition of malodorous and/or toxic emissions and to elaborate ways to reduce them. In keeping with this objective, the typical odorous components were determined in selected untreated as well as thermally modified wood

types, and changes in their composition were then verified. Emissions of heat-treated samples were reduced by methods of solvent extraction, and then the gaseous emissions as well the extracts themselves were analyzed by gas chromatography.

While static headspace analysis is a well established method for analyzing volatile emissions by gas chromatography, it is limited in its ability to evaluate low concentrations. The assumption was that potentially toxic products of the heat treatment process occur in low concentrations and cannot be properly analyzed by this method. Thus, the sampling procedure applied in the present study was the enrichment of volatile compounds by solid-phase microextraction for gas chromatography/mass spectrometry analysis (Pawliszyn 1997). When carried out in headspace mode, SPME is a fast and solvent-free sampling procedure and has recently been established in the analysis of volatiles emitted by wood (Bengtsson and Sanati 2004; Wajs et al. 2006) or paper (Lattuati et al. 2004). Volatiles from the sample matrix that equilibrate in the gaseous phase above it were absorbed on a coated SPME fiber and analyzed by gas chromatography/mass spectrometry. Results obtained by the analysis of untreated and thermally modified wood were then compared. Furthermore, the wood samples were extracted with several common solvents with the objective to reduce malodorous wood emissions after thermal treatment. The resulting extracts and wood samples were also analyzed by chromatographic and spectroscopic methods and compared with the results obtained by SPME headspace analysis.

## EXPERIMENTAL

### Samples

Four different types of wood (spruce *Picea abies*, maple *Acer pseudoplatanus*, beech *Fagus sylvatica*, and ash *Fraxinus excelsior*) obtained from Thermoholz Austria GmbH, an Austrian supplier of heat-treated wood, were investigated. Two different thermally modified samples of each species were analyzed in comparison with the respective untreated (*native*) wood. The pre-dried wood samples (8% residual moisture, maximum 60°C) were modified at 180°C (*mezzo*) and at 200°C (*forte*) in a dry three-stage heat treatment process. The process waste gas is discharged by an exhaust device and burnt.

The sample materials were ground by milling in the presence of liquid nitrogen to avoid heating, sieved to a particle size of 250-500µm, and stored at temperatures of 5°C before use.

### Sampling

*Headspace SPME*

Headspace sampling was performed manually with a Supelco SPME sample holder using an 85µm carboxen-polydimethylsiloxane coated fiber. 1g of each wood sample was placed into a 20 ml headspace vial, and the analyte was extracted by exposing the SPME fiber to the gaseous wood emissions at 70°C for 1h. Subsequently, the analyte-enriched fiber was thermally desorbed in the gas chromatograph injection port for 5min.

*Solvent-Extraction*

2-4g of sample material was soxhlet extracted for 6-8h with water, acetone, acetone/water (v:v=1:1), methanol or ethanol/cyclohexane (v:v=1:2). Identical amounts of sample material were extracted with water at room temperature for 72h or assisted by ultrasound for 1h at a maximum temperature of 40°C, respectively. Organic solvent extracts were directly transferred to GC analysis, while water extracts were analyzed after evaporation or freeze and dissolution in methanol.

## Analysis

*Gas chromatography/mass spectrometry*

GC/MS analyses were performed on an Agilent Technologies HP 6890 gas chromatograph equipped with a split/splitless injection port and an Agilent Technologies MSD 5973. The substances were separated on an Optima5 capillary column (Macherey-Nagel, 5% diphenyl - 95% dimethylpolysiloxane, 30m x 0.25mm ID, 0.25µm film thickness). Helium with a constant flow of 1ml/min was used as the carrier gas. Electron impact mass spectra were recorded at 70eV in the m/z range of 10-550. The substances were identified by analysis of the individual mass spectra and comparison with the NIST 2.0 mass spectral library. Major substances not included in the NIST 2.0 mass spectral library were identified on the basis of mass spectra of reference standards analyzed at the same conditions as the sample material.

For Headspace SPME analysis the injector initial temperature was 280°C, and chromatograms were obtained in splitless mode. Column temperature was held at 50°C for 5min, increased to 240°C at 5°C/min, and then held for 7min.

The direct injection method was used for the investigation of wood extracts. In general, 1µl of the concentrated organic solvent extracts or of the freeze-dried aqueous extracts diluted in methanol, respectively, was injected at a temperature of 280°C. Column temperature was held at 100°C for 5min, increased to 300°C at 5°C/min, and held for 15min.

*NMR*

The extracts were analyzed by $^{13}C$ HR NMR using a BRUKER DPX 400 spectrometer at a resonance frequency of 100.13 MHz. DMSO was used as solvent and $^{13}C$ chemical shifts were reported relative to TMS with $\delta_{13C}$ = 0ppm.

# RESULTS AND DISCUSSION

## Headspace SPME

It is known that emissions of untreated and thermally modified wood consist of various compounds that differ considerably in volatility. Hence, the sensitivity of SPME analysis also depends on the experimental conditions and properties of the fiber coating. In comparison with the previous experimental approach, the use of carboxen-dimethylsiloxane (CAR-PDMS) or divinylbenzene-carboxen-dimethylsiloxane (DVB-CAR-PDMS) fibers was preferable because of their good sensitivity and selectivity to volatile and semi-volatile compounds (Lattuati et al. 2004; Wajs et al. 2006). With both

fibers compared, the CAR-PDMS coating corresponded well to our requirements. To ensure good sensitivity to both volatile and semi-volatile components, various extraction times and temperatures were tested, and as a result, 1h fiber exposure to sample headspace at a temperature of 70°C was selected for the sampling procedure. Under the assumption that no state of equilibrium between sample headspace and fiber is reached, reproducible results can only be obtained by exact repetition of this procedure that was verified by duplicate SPME analyses.

The assumption was that the amount of volatiles collectable from the spruce samples with SPME generally exceeded the amount of volatiles collectable from the hardwood samples noticeably (Fig. 1). Gas chromatograms of *native* hardwood samples showed only low intensity in peak number and area even after 1h enrichment at 70°C. Thermal treatment increased the quantity of extractable volatiles in beech wood as treatment temperature rose. In the case of maple and ash wood, the total amount of volatiles in the *mezzo* modified samples was higher than in the respective *forte* samples. Contrastingly, the emissions of spruce wood decreased as treatment temperature rose, as reported in the literature on investigations of scots pine wood (Manninen et al. 2002).

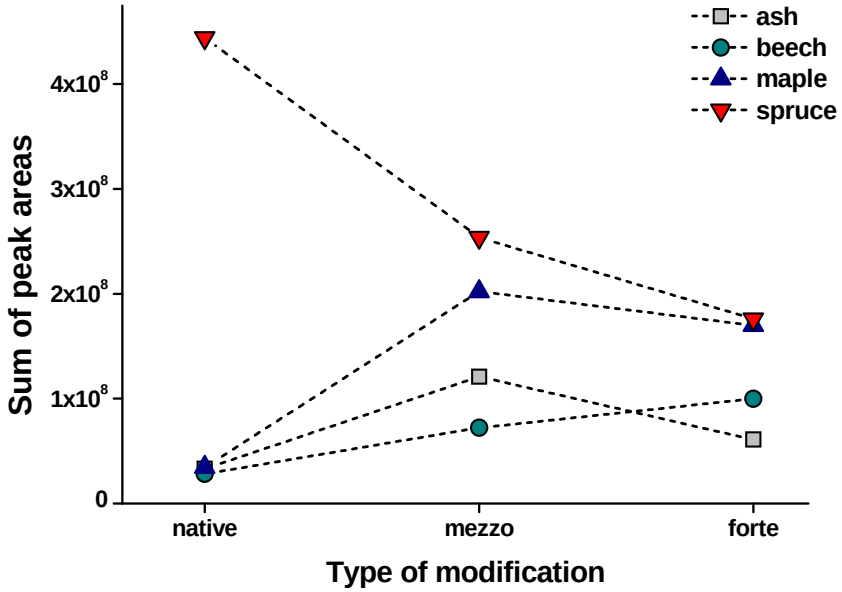


**Fig. 1.** The average sum of peak areas from the gas chromatographic analysis of solid-phase microextraction (SPME) headspace extracts for native and modified wood samples of ash, beech, maple and spruce.

As expected, the number of emission products from *native* wood samples differed significantly by wood type. SPME headspace extracts of the hardwood samples mainly consisted of aldehydes (pentanal, hexanal, furfural), carboxylic acids (acetic acid) and esters, ketones as well as aliphatic and aromatic hydrocarbons, while the volatiles emitted by *native* spruce were dominated by mono-, sesqui- and diterpenes (Fig. 2). The most noticeable changes in the chemical composition of volatiles after thermal treatment could be observed in the emission of carboxylic acids, aldehydes and – in the case of spruce wood – terpenes. Acetic acid is one of the major components formed by thermal

treatment and is well known as a degradation product of hemicelluloses that contain acetyl groups. Furthermore, the amount of acetic acid evaporating from *native* hardwood samples is significantly higher than that of spruce wood due to a greater number of acetyl groups in hardwood hemicelluloses. In addition, it should be noted that the emission of acetic acid in the *native* samples was higher than expected for untreated wood. This result can be attributed to the wood drying process which all samples have undergone (Milota 2002).

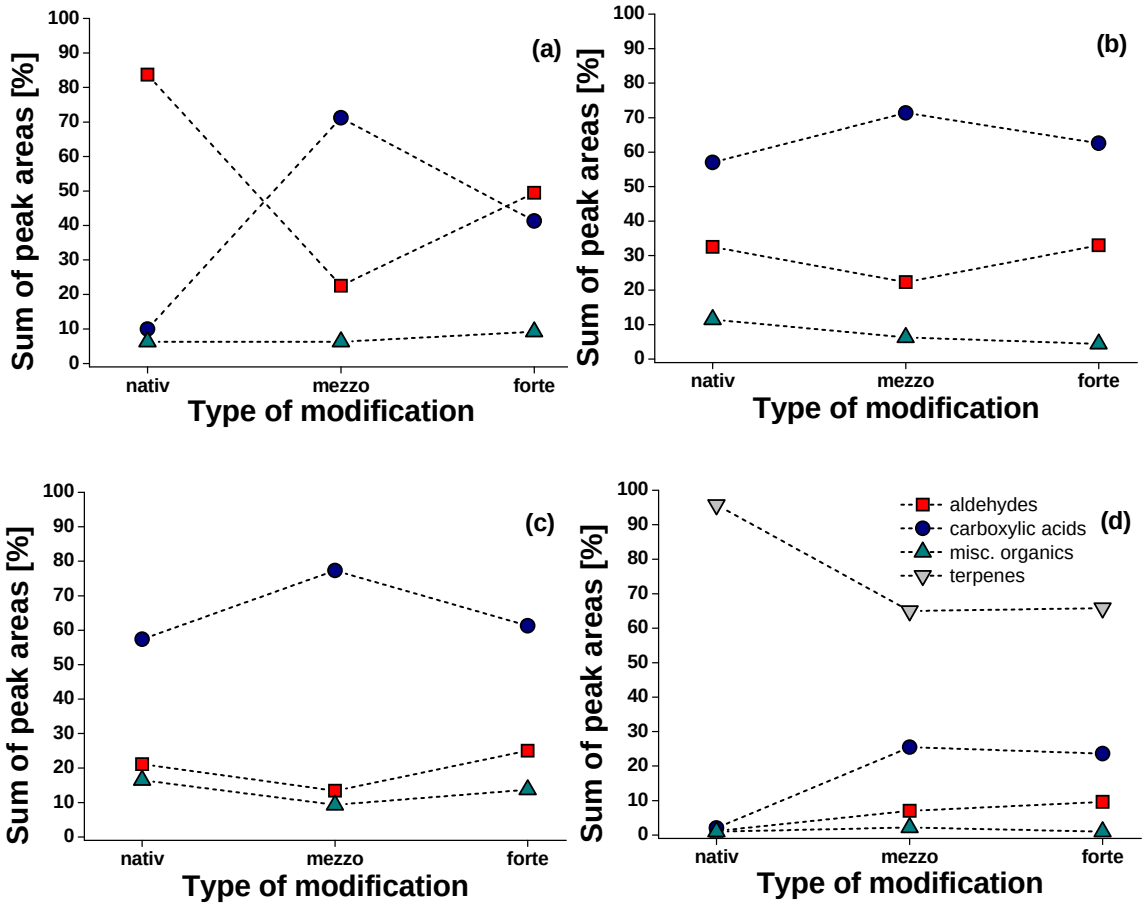


**Fig. 2.** Comparison of emission profiles of untreated and thermally modified (a) ash; (b) beech; (c) maple and (d) spruce wood.

Emissions of pentanal and hexanal, probably formed by oxidation of unsaturated fatty acids, were the prevailing aldehydes in *native* wood samples. Their amount decreased during thermal treatment, while furfural and 5-methylfurfural – degradation products of hemicelluloses – accounted for almost 100% of the aldehyde fraction (Table 1). The terpenes from *native* spruce wood trapped on the SPME fiber were numerous: more than 50 different compounds could be clearly identified, with α- and β-pinene, sylvestrene, caryophyllene, γ- and δ-cadinene as major components. The amount of terpenes emitted from spruce wood was significantly decreased in the course of thermal treatment,

but their fraction and decomposition in the volatiles of *mezzo* and *forte* wood was comparable.

**Table 1.** Changes in Aldehyde Distribution According to Thermal Modification

| Samples | Fraction of Aldehydes [%] | | | | |
|---|---|---|---|---|---|
| | Pentanal | Hexanal | Furfural | 5-Methylfurfural | Other |
| Ash *native* | - | 54.5 | 26.6 | - | 18.9 |
| Ash *mezzo* | - | 0.6 | 72.7 | 20.8 | 6.1 |
| Ash *forte* | - | 1.2 | 94.1 | 4.6 | - |
| Beech *native* | 1.4 | 91.1 | 1.4 | - | 6.2 |
| Beech *mezzo* | - | 1.1 | 83.9 | 14.8 | 0.3 |
| Beech *forte* | - | - | 83.1 | 2.3 | 2.1 |
| Maple *native* | 20.8 | 68.9 | 13.6 | - | 11.5 |
| Maple *mezzo* | - | 1.4 | 69.4 | 28.1 | - |
| Maple *forte* | - | 1.3 | 89.9 | 8.8 | .- |
| Spruce *native* | - | 70 | 11.5 | - | 18.5 |
| Spruce *mezzo* | - | 2 | 22.2 | 10.7 | 0.7 |
| Spruce *forte* | - | 1.4 | 92.8 | 4.9 | 0.8 |

The comparison of the results obtained by SPME analysis of thermally treated samples reveals that no individual component can be singled out as being the source of the typical malodor of thermally modified wood. In the investigation of specimens created by soaking pulp and untreated wood chips with a mixture of the main emission components, the odor differed from heat-treated samples. Since further investigation regarding this point was required, the odorous components were isolated and enriched by solvent extraction. Additionally, the effect of solvent extraction on the composition and amount of emissions from the wood samples was verified.

## Headspace SPME of Solvent-Extracted Wood

Based on all of the experiments considered, it can be assumed that odorous emissions of thermally treated wood can be strongly reduced by solvent extraction. Best results among the listed solvents were obtained by the ethanol/cyclohexane mixture that produces wood samples without significant odor emissions. SPME-GC analysis of the solvent-treated wood samples validates this subjective odor test (Fig. 3). In spruce wood, which can be viewed as being representative of all of the samples, no significant amount of volatiles could be detected after extraction.

Extraction not only affected the emissions from the investigated natural wood samples; process products of thermal treatment were also removed by this method, and volatiles such as acetic acid, furfural or 5-methylfurfural were no longer detectable in significant amounts (Fig. 3). The findings were that chromatograms of volatiles from different thermally modified samples were almost indistinguishable after solvent extraction. This general observation applied to all investigated wood types.

Furthermore, the reduction of odorous emissions caused by thermal treatment due to solvent extraction with different solvents is a result to be followed up, and first attempts were made to extract wood before thermal modification. It has been shown that thermally treated maple wood that had been solvent extracted on a laboratory scale led to specimens with barely noticeable odor.

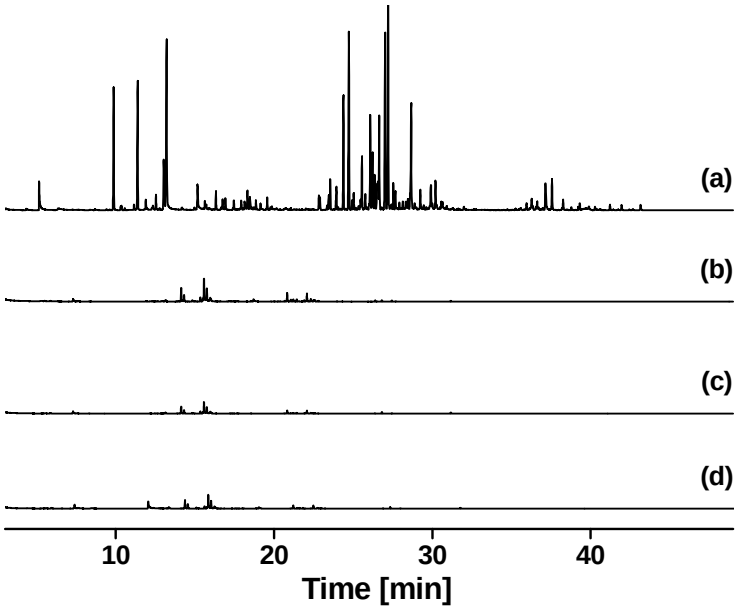


**Fig. 3.** SPME-GC analysis of (a) *native* spruce wood and extracted spruce wood samples (b) *native*; (c) *mezzo*; (d) *forte.*

## GC Analysis on Solvent Extracts

While the emissions of thermally treated wood were changed by solvent extraction, these extracts were further investigated. All solvent extracts exhibited a color change from yellow or light brown to dark brown over time, indicating degradation and condensation reactions of extracted lignin components. This observation applies to all solvents used. Taking the extracts of spruce wood in the ethanol/cyclohexane mixture once more, as an example of the variety of investigated extraction solvents, distinct changes in composition were observed depending on thermal treatment (Fig. 4).

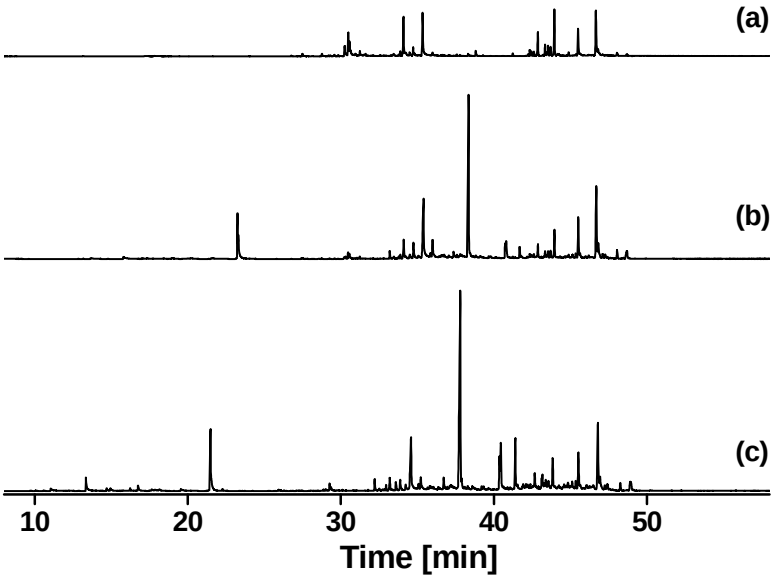


**Fig. 4.** GC/MS chromatograms of ethanol/cyclohexane extract from (a) *native*; (b) *mezzo*; (c) *forte* spruce wood.

In general, the amount of extractives in native wood was lower than in the respective *mezzo* and *forte* modified samples. While the major components in *native* spruce extract were dehydroabietic acid, linoleic acid, campestrol, and β-sitosterol, their fraction in *mezzo* and *forte* extracts was decreased, and a variety of components caused by lignin degradation was detected. These components were primarily coniferyl aldehyde, vanillin, and a component that occurred in the mass spectra with a molecular peak at m/z = 272 (retention time $t_R$ = 37,8 min). This compound was supposed to be 3,3'-dimethoxy-4,4'-dihydroxy-stilbene formed by condensation of lignin degradation products (Fig. 5).

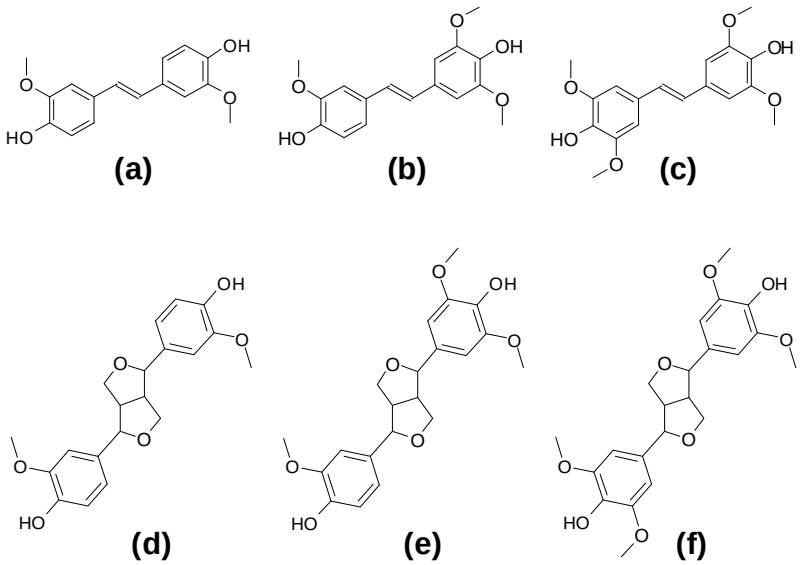


**Fig. 5.** Structural formula of selected solvent extractives from thermally modified wood (a) 3,3'-dimethoxy-4,4'-dihydroxystilbene; (b) 3,3',5-trimethoxy-4,4'-dihydroxystilbene; (c) 3,3',5,5'-tetramethoxy-4,4'-dihydroxystilbene; (d) pinoresinol; (e) medioresinol; (f) syringaresinol.

In the case of *native* hardwoods, the variety and amounts of extractives detectable by GC/MS was rather low (Fig. 6). Extractives with the highest intensity were coniferyl alcohol (molecular peak m/z = 180, $t_R$ = 21,6 min) and sinapyl alcohol (molecular peak m/z = 210, $t_R$ = 26,7 min). Further lignin degradation occurred during thermal treatment, resulting in the formation of components like coniferyl aldehyde (molecular peak m/z = 178, $t_R$ = 21,5 min) and sinapyl aldehyde (molecular peak m/z = 208, $t_R$ = 26,5 min) in large quantities, as well as of two substances with molecular peaks of m/z = 302 ($t_R$ = 41,4 min) and m/z = 332 ($t_R$ = 44,7 min), supposed to be 3,3',5-trimethoxy-4,4'-dihydroxystilbene and 3,3',5,5'-tetramethoxy-4,4'-dihydroxystilbene. This observation also applies to ash and beech extracts. Furthermore, a significant amount of different lignans could be observed in the hardwood extractives. The main component was syringaresinol with a molecular peak of m/z = 418 ($t_R$ = 54,3 min) in the mass spectra. This substance was identified earlier (Windeisen et al. 2007) in acetone extract of beech wood that had been thermally treated at 220°C. Lower amounts of medioresinol (molecular peak m/z = 388, $t_R$ = 49,0 min) and pinoresinol (molecular peak m/z = 358, $t_R$

= 45,3 min) were also detectable. Notably the amount of syringaresinol increased with higher treatment temperature, which is another indicator for degradation and condensation reactions of lignin components during the extraction procedure.

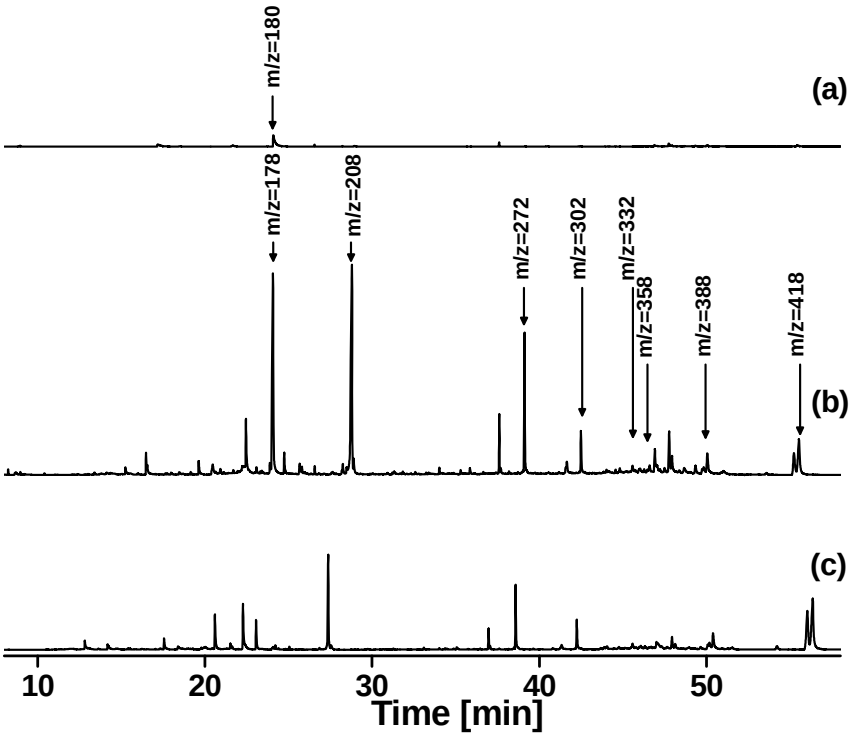


**Fig. 6.** GC/MS spectra of ethanol/cyclohexane extract from (a) *native*; (b) *mezzo*; (c) *forte* maple wood.

## NMR Analysis on Solvent Extracts

Extractives of maple wood were also characterized by $^{13}C$ NMR spectroscopy (Fig. 7). As the concentration of extractives was low, the NMR signals obtained were of poor intensity, and the method as such is not suitable in trace analysis. Since no separation of pure components was performed prior to NMR analysis, the assignment of signals to specific components was difficult, but consistent with GC/MS results.

In *mezzo* and *forte* extracts, a signal with a chemical shift of 194.7 ppm could be assigned to carbon atoms of the aldehyde C=O bonds. Signals in the range between 107 and 155 ppm could be assigned to carbon atoms in C=C double bonds of aromatic and alkene type structures represented by the stilbenes. However, the signals could not be clearly assigned to the structure of aliphatic carbon atoms because of a poor signal/noise ratio. $^{13}C$ spectra of *native* maple extract showed no signals in the range of aromatic carbon atoms. Hence, it had to be assumed that their amount was below the detection limit of this method as was the case with GC/MS. Low intensity signals in the range between 105 and 60 ppm can be explained by products of hemicelluloses degradation that cannot be measured by GC/MS.

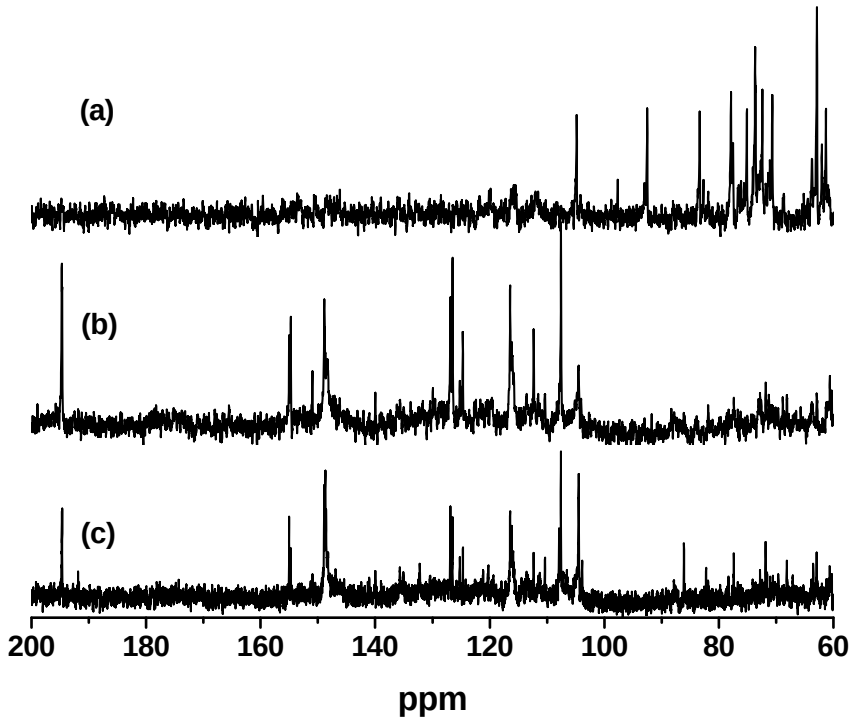


**Fig. 7.** $^{13}$C-NMR spectra of ethanol/cyclohexane extract from (a) *native*; (b) *mezzo*; (c) *forte* maple wood.

Altogether, the identification of single extractive components by $^{13}$C NMR seems to be unpromising, since it did not furnish any additional results to those that can be obtained by GC analysis, and the method was not followed up.

## CONCLUSIONS

In reviewing the results of headspace solid-phase microextraction (SPME) and solvent extract analysis, the assumption has to be made that there is no correspondence between the odorous components detected in the headspace of wood samples and the dominating solvent extractives. While the headspace analysis of thermally treated wood revealed the hemicelluloses degradation products furfural and 5-methylfurfural as main emission products, they could not be found in solvent extracts in significant amounts. Solvent extracts of thermally modified wood primarily consisted of degradation and condensation products of extracted lignin components. Advances were made in the reduction of malodorous emissions of thermally modified wood by solvent extraction, although it is obvious to the authors that this procedure is not practicable from an industrial point of view.

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