

Emissions of acetic acid and other volatile organic compounds from different species of solid wood

M. Risholm-Sundman, M. Lundgren, E. Vestin, P. Herder

The emission of volatile organic compounds (VOC) from wood and wood products are important in evaluating the impact on the indoor environment from different materials. The results from analyses of emissions from nine different wood species are presented in this article. The measurements were made with Field and Laboratory Emission Cell (FLEC) and with Head-Space (HS) analyses and the results from the different methods are discussed. The main emissions are terpenes from softwood and acetic acid from hardwood.

Die Emission von Essigsäure und anderen flüchtigen, organischen Stoffen aus dem Holz verschiedener Holzarten

Kenntnisse über die Abgabe von flüchtigen organischen Stoffen (VOC) aus Holz und Holzwerkstoffen sind wichtig, wenn die Umweltbeeinflussung von verschiedenen Materialien untersucht werden soll. Messungen an neun verschiedenen Holzarten werden in diesem Artikel präsentiert. Die Messungen wurden mittels Field and Laboratory Emission Cell (FLEC) und Head-Space (HS) Analyse durchgeführt, wobei auch die verschiedenen Methoden beurteilt wurden. Die hauptsächlichsten Abgaben an flüchtigen Stoffen sind Terpene aus Nadelholz, sowie Essigsäure aus Laubholz.

1

Introduction

Building materials, including furniture, are generally the main sources of VOC in the indoor environment (Gustavsson 1992). It is important to have good methods to determine the emission rate from different materials. Chambers of different sizes and flow through cells like FLEC have been used to determine the formaldehyde and VOC emissions (Wolkoff 1995). For the determination of volatile acids from wood chips and particle boards, the flask-method followed by ion chromatography (IC) has been used (Roffael 1989).

Most reported emission studies have been made on engineered wood products and final products (Turner 1996, Sundin 1992 and Englund 1994). The formaldehyde emission has been determined to 2–9 ppb from five different wood species of solid wood with the chamber method with a loading factor of $1 \text{ m}^2/\text{m}^3$ (Meyer 1997).

The aim of the present study was to identify the emission from untreated wood and to compare the emissions from different species.

2

Experimental

2.1

Samples

Solid wood samples from nine different wood species often used in the indoor environment were used in the study, see Table 1. The samples were taken from the wood raw material in the parquet floor production. The wood samples were felled between 0.5 to 1.5 year before the emission tests and most of them were dried to a moisture content of about 5%. All samples were planed to have a fresh surface just before the emission test started.

2.2

Methods

2.2.1

HS-GC-MS

The sample was cut with a knife to chips, about $20 \times 5 \times 1 \text{ mm}$ and put into a serumbottle, 1 g wood chips in a 22 ml bottle. The bottle was closed with a Teflon coated rubber septum and an aluminium crimp cap. After 30 min of equilibration at $80 \text{ }^\circ\text{C}$, 2 ml of the head-space (HS) gas was injected on the gas chromatograph (GC).

A GC coupled to a massspectrometer (MS) was used to identify the different components and a GC with a flame ionisation detector (FID) was used to quantify the emission.

HS-GC-MS analysis was carried out on a VG 7035 HSE MS with a 60 m DB-1701 column, 0.32 mm i.d., $1.0 \text{ }\mu\text{m}$ thickness, with the following temperature program: $40 \text{ }^\circ\text{C}$ for 2 min, heating to $270 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C}/\text{min}$ and held for 5 min. The MS was scanned over a massrange of m/z 20–320. The split injector was held at $150 \text{ }^\circ\text{C}$ and used in splitless mode for 1.5 min. During injection and splitless time, the first 0.3 m of the column was cooled to $-40 \text{ }^\circ\text{C}$.

2.2.2

FLEC with GC and IC-analysis

A stainless steel lid (FLEC) was put on the newly planed sample and the emission from a surface area of 0.0177 m^2 was collected on Tenax TA tubes or silica gel tubes during 0.5 to 8 hours.

A Tenax tube, I.D. 4 mm packed with 350 mg Tenax TA 60–80 mesh, was used to adsorb VOC in the boiling point range of $60\text{--}250 \text{ }^\circ\text{C}$ (hexane to hexadecane). The Tenax tube was thermally desorbed and analysed with FID detection for quantification and with MS for identification.

M. Risholm-Sundman, M. Lundgren, E. Vestin, P. Herder
Casco Products AB, P.O. Box 11538, S-100 61 Stockholm, Sweden

Correspondence to: M. Risholm-Sundman

The authors would like to thank Per-Eric Stridsman, Tarkett, for providing the wood samples and Birger Sundin for fruitful discussions.

Table 1. Samples used in the study

Tabelle 1. Die im Artikel untersuchten Hölzer

Wood species	Sample Origin	Moisture Content (dry weight at 103 °C) %
Ash	Parquet blocks	5.1
<i>Franxinus Excelsior</i>	Belgium/Croatian	
Beech	Parquet blocks	5.0
<i>Fagus Sylvatica</i>	Sweden	
Maple	Parquet blocks	5.8
<i>Acer Saccharum</i>	USA/Canada	
Birch	Parquet blocks	5.0
<i>Betula Pubescens</i>	Poland	
Oak	Parquet blocks	5.8
<i>Quercus Robur</i>	Sweden	
Cherry	Parquet blocks	4.5
<i>Prunus Serotina</i>	USA/Canada	
Rubberwood	Parquet blocks	5.7
<i>Hevea Brasiliensis</i>	Malaysia	
Pine	Plank	7.2
<i>Pinus Silvestris</i>	Sweden	
Spruce	Plank	13.1
<i>Picea Abies</i>	Sweden	

Table 2. Response from the HS-GC analyses of pine at different HS temperatures

Tabelle 2. Ergebnisse der HS-GC-Analysen an Kiefernholz bei unterschiedlichen HS-Temperaturen

Pine wood at different HS-temperatures	40 °C	60 °C	80 °C
Total area	33 × 10 ⁶	80 × 10 ⁶	178 × 10 ⁶
Terpenes – area%	95.6	95.4	92.4
Aldehydes & ketones – area%	1.5	2.3	4.4

Table 3. Standard deviation in the HS-GC results from different species

Tabelle 3. Standard-Abweichungen der Ergebnisse der HS-GC-Analysen an verschiedenen Hölzern

	Pine	Birch	Rubber-wood
Total area – average	188 × 10 ⁶	1.4 × 10 ⁶	1.5 × 10 ⁶
No of samples	5	3	6
CV-%	16	2.5	24

Table 4. Emission results

Tabelle 4. Ergebnisse der Emissions-Analysen

Sample	VOC HS-GC-MS		VOC FLEC-Tenax		Acetic acid FLEC-IC µg/m ² × h
	Sum of all components Relative area ¹	Major components	Emission factor µg/m ² × h	Major components	
Ash	1.4	acetaldehyde methanol 2-pentylfuran acetic acid	30	acetic acid	370
Beech	1.6	hexanal 2-pentylfuran methanol acetone	30	acetic acid hexanal	250
Maple	1.5	methanol 2-pentylfuran hexanal	20	acetic acid	270
Birch	2.4	hexanal pentanal acetone 2-pentylfuran terpene	110	acetone hexanal acetic acid	<10
Oak	1.0	methanol 2-pentylfuran hexanal	210	acetic acid	2800
Cherry	1.0	acetic acid 2-pentylfuran acetic acid methanol hexanal	60	acetic acid	2000
Rubberwood	3.4	acetic acid 2-pentylfuran 2-propylfuran methanol	50	acetic acid	640
Pine	362	α-pinene 3-carene hexanal	3700	α-pinene 3-carene β-pinene acetone hexanal	120
Spruce	46	α-pinene other terpenes hexanal	1400	α-pinene acetone hexanal	190

¹ All areas are compared with the area for cherry.

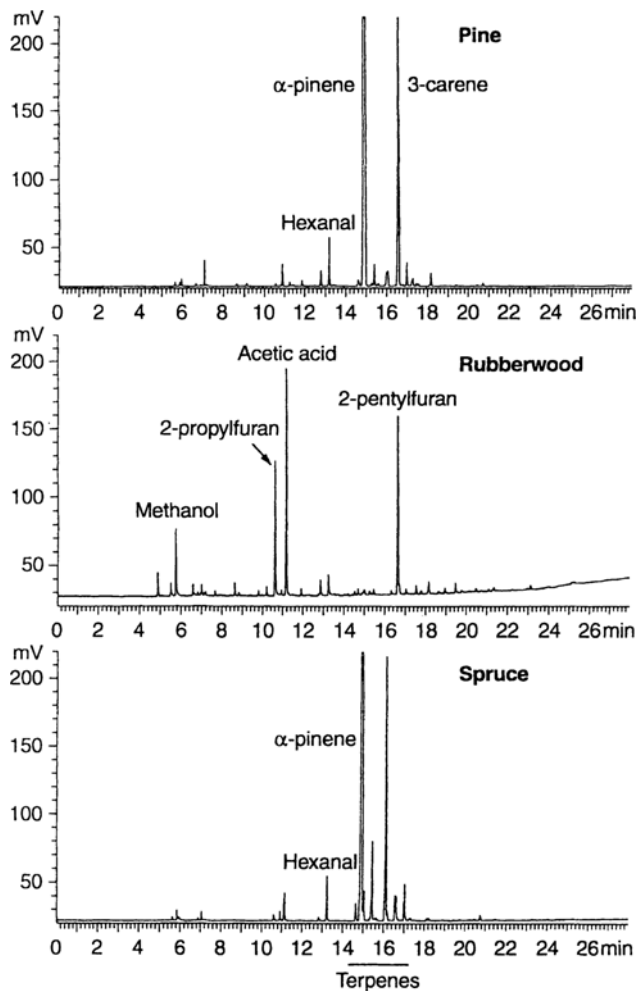


Fig. 1. HS-coldtrap-GC analyses of the emission from pine, rubberwood and spruce.
Bild 1. HS-coldtrap-GC Analyse. Die Emission von Kiefer, Gummibaum und Fichte.

The VOC-concentration was calculated in toluene equivalents. The GC-analysis was carried out on a Perkin Elmer ATD-400, GC AutoSystem and Q-mass 910 with a 30 m DB 5 ms column, 0.25 mm id, 0.25 μ m phase and the following temperature program: 45 $^{\circ}$ C for 3 min, 4 $^{\circ}$ C/min to 150 $^{\circ}$ C, 15 $^{\circ}$ C/min to 250 $^{\circ}$ C and held for 4.1 min.

A silica gel tube, 6 \times 70 mm with 75/150 mg silica gel, was used to collect volatile acids. The tube was desorbed with 0.025 M sodium hydroxide and analysed by IC on a Dionex AS10 column with 0.025 M sodium hydroxide as the eluent and with a conductivity detector.

3 Results and discussion

3.1 Head-Space method compared with FLEC-method

The HS-method gives an overview of the emission from different wood species. It is a useful method for screening the emission from different materials. It is quick and if coupled to a GC-MS gives a lot of information.

The advantage of FLEC is that it gives quantitative results, e.g. an emission rate, which can be used to estimate the concentration in a room with a known loading factor and ventilation rate. It is also common as a standard method.

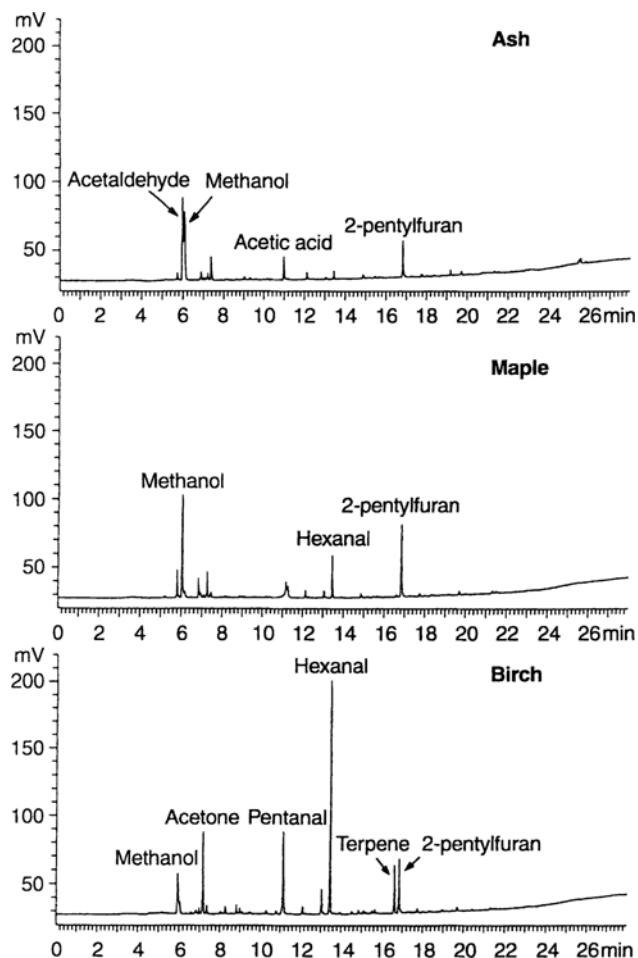


Fig. 2. HS-coldtrap-GC analyses of the emission from ash, maple and birch.
Bild 2. HS-coldtrap-GC Analyse. Die Emission von Esche, Ahorn und Birke.

In the HS-analysis the gas is collected in a cold trap and most volatile organic compounds can be analysed with the same method. In FLEC and chamber methods VOC are usually sampled on a Tenax tube and analysed by GC after thermal desorption. Only the components that are adsorbed on Tenax, thermally desorbed from Tenax and detected by GC can be measured this way. For example methanol is not detected by Tenax-GC, but it does not chromatograph well and can not be determined quantitatively in the ordinary VOC-method. Different types of adsorption materials, depending on the emission, must be used with FLEC and chambers in order to collect all types of volatile components.

Silica gel tubes and IC-analyses give good quantitative results for acetic acid. A drawback with the HS-analyses is the elevated temperature needed. Different HS-temperatures were tested and 80 $^{\circ}$ C gave a good response for most wood species. Use of a higher temperature means a risk of oxidation or formation of other degradation products. Pine samples were analysed after 30 min at 40, 60 and 80 $^{\circ}$ C and the relative amount of hexanal was found to be somewhat higher at higher temperature, see Table 2.

Multiple HS-analyses of the same sample gives a different standard deviation for different wood species, see Table 3. The variation most likely depends on the stability of the samples and how well the volatile components in the emission chromatograph.

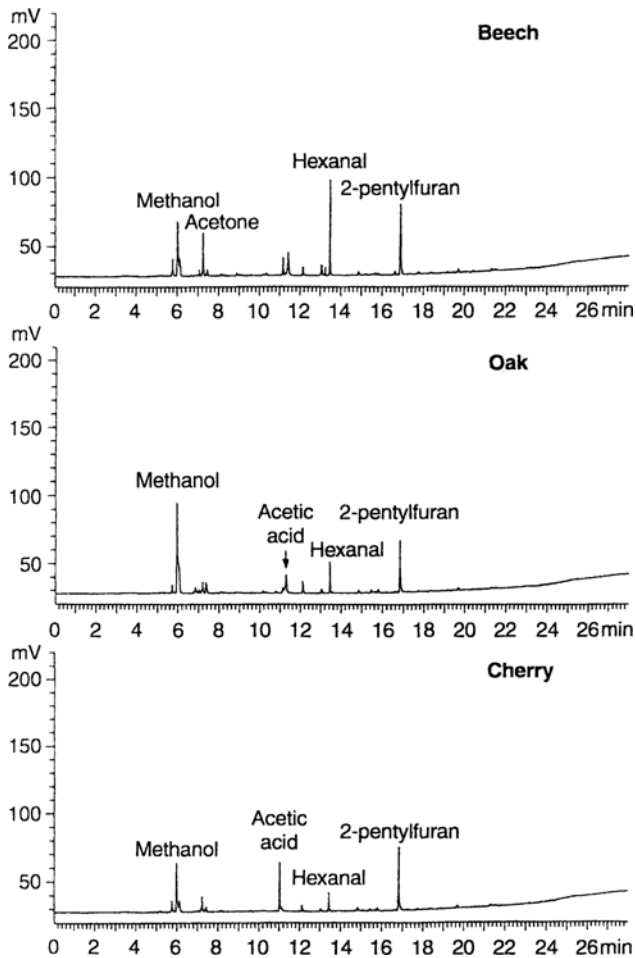


Fig. 3. HS-coldtrap-GC analyses of the emission from beech, oak and cherry.
Bild 3. HS-coldtrap-GC Analyse. Die Emission von Buche, Eiche und Kirsche.

3.2

Emission from the different wood species

Several types of compounds can be found in the emission from the different wood species, see results in Table 4 and chromatograms in Figures 1 to 6. The emission is very high from some of the samples, mainly due to the fact that the samples were planed just before the test. A surface treatment with e.g. a lacquer would in most cases lower the emission.

The main emission from softwood is terpenes. Several different types of terpenes are found in the emission, see chromatogram of pine and spruce emission in Figure 1 and 4. The MS-spectra of the different terpenes are very similar and references are needed for exact identification, but the main components are α -pinene, β -pinene and 3-carene. Terpenes give a pleasant odour but can be harmful and cause allergic reactions. Test persons have been exposed to terpene vapours in chambers and an irritation of the mucous membrane have been found (Falk et al. 1991). Terpenes give skin irritation, most likely caused by oxidation products, e.g. hydroperoxides from 3-carene. The emission of terpenes from pine and spruce are very high, 3700 and 1400 $\mu\text{g}/\text{m}^2 \times \text{h}$ respectively.

The hardwoods give a more versatile emission of carbonyl compounds and alcohols. Hexanal and a minor peak from pentanal are found in the emission from most hardwoods. They are formed by oxidation of unsaturated fatty

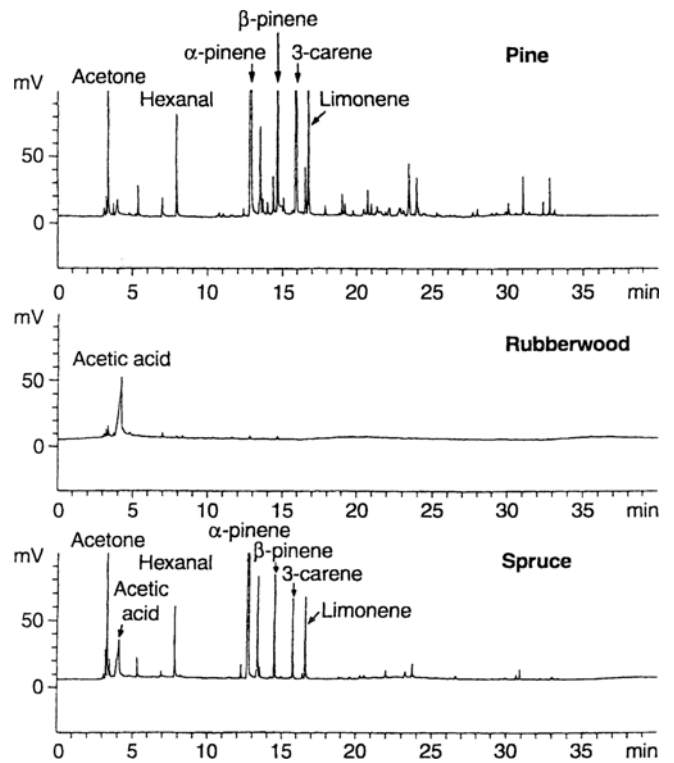


Fig. 4. FLEC-Tenax-GC analyses of the emission from pine, rubberwood and spruce.
Bild 4. FLEC-Tenax-GC Analyse. Die Emission von Kiefer, Gummibaum und Fichte.

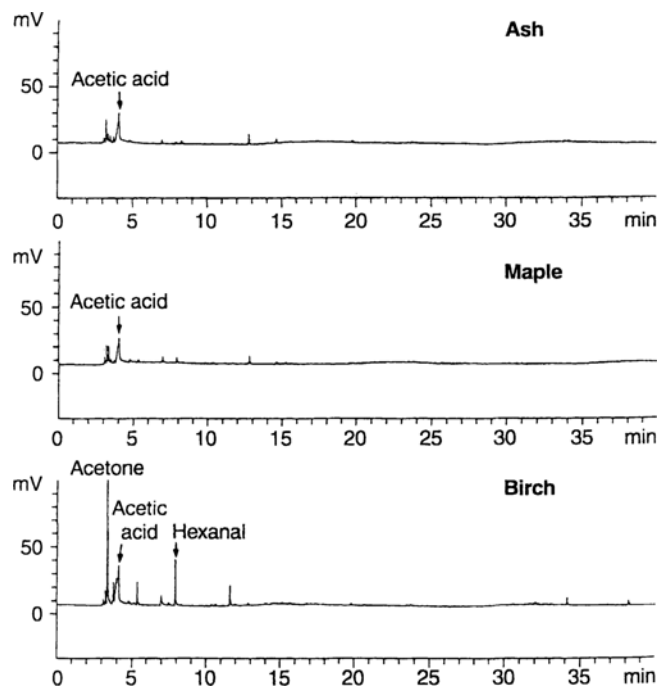


Fig. 5. FLEC-Tenax-GC analyses of the emission from ash, maple and birch.
Bild 5. FLEC-Tenax-GC Analyse. Die Emission von Esche, Ahorn und Birke.

acids. Aldehydes can cause odour problems. They are known to cause off-flavours in low concentrations in paper.

Some hardwoods give a high emission of acetic acid. It is formed from the hydrolyses of acetyl groups in hemicellulose and it can cause corrosion problems. The amount

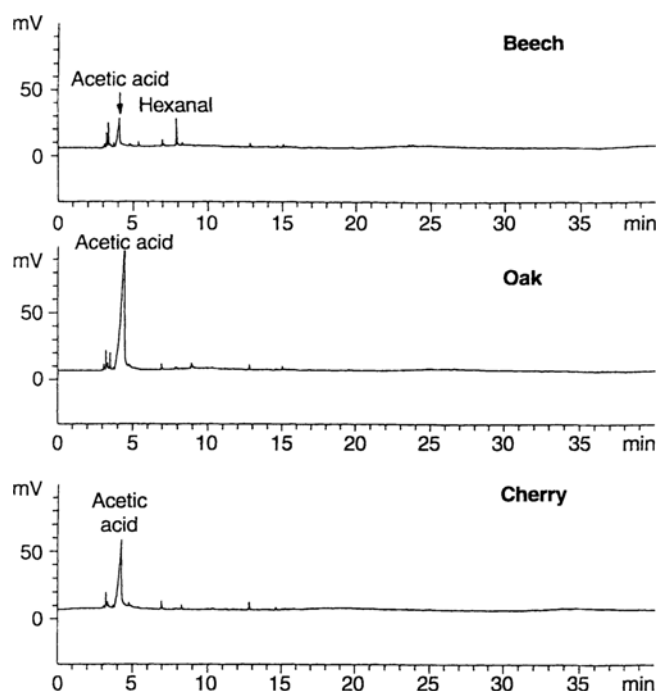


Fig. 6. FLEC-Tenax-GC analyses of the emission from beech, oak and cherry.
Bild 6. FLEC-Tenax-GC Analyse. Die Emission von Buche, Eiche und Kirsche.

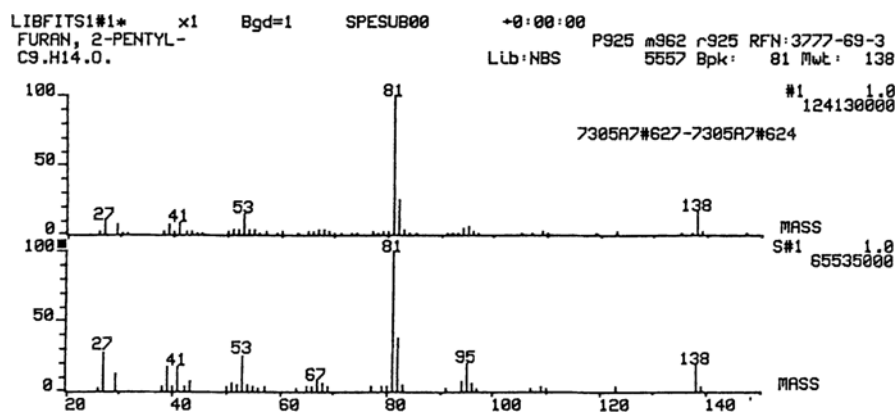


Fig. 7. Mass spectrum of 2-pentylfuran. Top: spectrum from the peak at retention time 16.4 min in the emission from beech. Bottom: reference spectrum in the NBS MS-library.
Bild 7. Massenspektrum des 2-Pentylfurans. Oben: Emissions-Spektrum von Buche, Retentionszeit 16.4 Minuten. Unten: Referenz-Spektrum aus NBS MS-Bibliothek.

of acetyl groups is higher in hardwoods than in softwoods (Fengel et al. 1989). The highest emission rate of acetic acid was found in cherry and oak, 2000 and 2800 $\mu\text{g}/\text{m}^2 \times \text{h}$ respectively.

Methanol was only found in the HS-analyses. It is most likely an important emission product from wood, but it is too volatile to be trapped on Tenax and thus not included in the emission factor, see discussion under 3.1.

Alkylfurans, like ethyl-, propyl- and pentyl-furans, are found in the HS-emission from most of the hardwoods. They are most likely formed during the analysis at an elevated temperature. The alkylfurans are only identified from the MS-library, see MS-spectrum in figure 7, but they are likely decomposition products from cellulose. Furan and furan derivatives are found among the thermal degradation products of cellulose and other polysaccharides. (Fengel et al. 1989).

References

Englund F, Andersson B-I (1994) Emissions of volatile compounds from wood and wood products. A survey of current international research (Swedish). Trätekt 9404023

Falk A, Löf A, Hagberg M, Wigaeus-Hjelm E, Wang Z (1991) Human exposure to 3-carene by inhalation: Toxicokinetics, effects on pulmonary function and occurrence of irritative and CNS symptoms. *Toxicol. Appl. Pharmacol.* 110: 198–205

Fengel D, Wegener G (1989) "Wood, Chemistry, Ultrastructure, Reactions", Walter de Gruyter

Gustavsson H (1992) Building materials identified as major sources for indoor air pollutants, BFR D10: 1992

Meyer B, Boehme C (1997) Formaldehyde emission from solid wood, *Forest Prod. J.* 47 (5): 45–48

Roffael E (1989) Abgabe von flüchtigen organischen Säuren aus Holzspänen und Holzspanplatten. *Holz Roh-Werkstoffe* 47: 447–452

Sundin B, Risholm-Sundman M, Edénholm K (1992) Emission of formaldehyde and other volatile organic compounds from sawdust and lumber, different wood-based panels and other building materials. Proc. 26th Int. Particleboard/Composite Materials Symposium, Pullman

Turner S, Martin C, Hetes R, Northeim C (1996) Sources and factors affecting indoor emissions from engineered wood products. Summary and evaluation of current literature. EPA-600/R-96-067

Wolkoff P (1995) Volatile Organic Compounds – Sources, Measurements, Emissions and the Impact on Indoor Air Quality. *Indoor Air*, supplement no 3/95