chemosensors

Article

Method Comparison for the Identification and Characterization of Odorants from Scots Pine (*Pinus sylvestris* L.) and Oriented Strand Boards (OSB) Made Thereof by GC-MS and GC-FID/O Using Different Headspace Techniques

Valentin Schierer [1,2], Cornelia Rieder-Gradinger [1] and Erwin Rosenberg [3,*]

[1] Competence Center for Wood Composites and Wood Chemistry–Wood K Plus, 4040 Linz, Austria; v.schierer@wood-kplus.at (V.S.); c.rieder-gradinger@wood-kplus.at (C.R.-G.)
[2] Institute of Chemical, Environmental and Bioscience Engineering, Vienna University of Technology, 1060 Vienna, Austria
[3] Institute of Chemical Technologies and Analytics, Vienna University of Technology, 1060 Vienna, Austria
* Correspondence: egon.rosenberg@tuwien.ac.at

Abstract: Volatile organic compounds (VOCs) from wood and wood composites are important contributors to odor profiles of indoor environments and can significantly influence human health and well-being. GC-MS/FID and gas chromatography (GC) with olfactometric detection (GC-O) are employed for the identification and characterization of odorants. Four different sample preparation methods are evaluated on wood strands and isocyanate adhesive–based oriented strand boards (OSBs) made from *Pinus sylvestris* L.: among these, dynamic headspace extraction thermal desorption ((dynamic) HS-TD), head space solid phase microextraction (HS-SPME), head space solid phase microextraction Arrow (HS-SPME Arrow), and liquid injection of a CH_2Cl_2 solvent extract. The olfactometric investigation revealed over 30 odor-active substances of cyclic and acyclic monoterpene, monoterpenoid ketone, monoterpenoid aldehyde, monoterpenoid alcohol, monoterpenoid ester, aliphatic aldehyde, alcohol, and acid and phenolic chemistry. Compared to liquid injection, (dynamic) HS-TD was found to result in a similar number of odorants (20 vs. 24), whereas HS SPME Arrow shows good performance with minimal instrumental effort, notably for monoterpene and aldehyde compounds. Native wood vs. OSB showed high concentrations of saturated and unsaturated aldehydes for the wood board sample. These findings demonstrate the capability of headspace methods for odorant detection and their suitability for standardization towards a database for wood and wood composites.

Keywords: *Pinus sylvestris*; headspace techniques; odorant detection

Citation: Schierer, V.; Rieder-Gradinger, C.; Rosenberg, E. Method Comparison for the Identification and Characterization of Odorants from Scots Pine (*Pinus sylvestris* L.) and Oriented Strand Boards (OSB) Made Thereof by GC-MS and GC-FID/O Using Different Headspace Techniques. *Chemosensors* **2023**, *11*, 543. https://doi.org/10.3390/chemosensors11100543

Academic Editors: María José Aliaño-González and Bruno Medronho

Received: 1 September 2023
Revised: 10 October 2023
Accepted: 16 October 2023
Published: 19 October 2023

1. Introduction

The perception of wood and wood materials as warm and comfortable [1] and their pleasant smell [2] lead to the material's high appreciation by consumers and manufacturers. Especially in indoor environments, wood materials find increased appreciation. Since every piece of furniture or construction piece exhibits its own characteristics regarding smell, the specific control of odor profiles to meet consumer demand, as well as to influence the perception of indoor spaces in a positive way, is of great interest [1].

Wood is made up of cellulose, hemicellulose, and lignin, which are its main (insoluble) components. Furthermore, there are extractives, such as proteins, amino acids, fatty acids, terpenes, resin acids, steroids, and phenols, which are defined as being extractable by organic solvents [3]. From these fractions, volatile organic compounds (VOCs) released directly from the extractable fraction or as products from conversion processes are the main contributors to the odorous profile of wood and wood materials and define our olfactory perception [4].

Oriented strand boards (OSBs) and particle boards, in which particular softwoods are used in manufacturing [5], present important wood materials used in indoor spaces. *Pinus sylvestris* L. (Scots pine) especially receives growing attention as raw material for the European wood industry, as spruce (*Picea abies* L.) sees a decline because of dryer climates and increased likelihood of beetle damage [6]. The increased amount of pine in wood products brings about its own challenges since the emission of volatile compounds from Scots pine amounts to approximately twice the emission of volatile organic compounds from Norway spruce [7].

One approach for the study of odorous compounds from different matrices is the application of GC in combination with olfactometry as a detection method, either as a substitute or as a complement to classical detectors, such as FID and MS [8]. This technique allows the direct evaluation of odor compounds by test persons to determine the start and end time in the chromatogram, as well as the specific quality and intensity of a perceived odor [8]. Different methodologies of GC-O have been reported, such as direct intensity analysis, dilution to threshold, and frequency analysis [8]. Culleré et al. investigated odorous compounds in barrel wood from five different toasted hardwood types by extraction and analysis by gas chromatography-olfactometry and mass spectrometric detection [9]. This investigation yielded odor compounds of aldehyde, phenol, acid, and, to a lesser extent, terpene chemistry. Here, the treatment and its effects on the transformation of the volatile profile of wood was reviewed. Thermal degradation of lignin mainly produces phenolic substances, such as vanillin, guaiacol, or eugenol [10], whereas the degradation of polysaccharides can give rise to furan and pyran derivatives, such as cis/trans–whisky lactone. The autooxidation of fatty acids, or enzymatic peroxidation, produces various volatile aliphatic saturated and unsaturated aldehydes [11,12]. Terpene emissions, on the other hand, derive directly from fresh wood, where they are present in resinous channels, primarily in softwoods, that extend between heart- and sapwood [13]. The biosynthesis of terpenes is started by a condensation reaction of two molecules of acetyl coenzyme A, where the compound acetoacetyl-coenzyme A is produced [14]. Further steps include the phosphorylation of mevalonic acid, which then undergoes decarboxylation and dehydration to form isopentenyl pyrophosphate (IPP). This compound, together with dimethylallyl diphosphate (DMAPP), represents the building block for the further synthesis of mono-, di-, sesqui-, triterpenes, etc.

Terpenes fulfill a multitude of functions in biological systems, such as acting as signaling compounds in plant-to-plant communication [15], as well as having important antibacterial or antifungal properties [16]. Fatty acids and esters were also detected as volatile odorous compounds, which most likely derive from fresh wood [9].

An effort to identify odorant compounds in softwood has been made by Schreiner et al., where different softwood species were investigated by the successful application of gas chromatography-mass spectrometry, and olfactometric detection [17,18]. In these approaches, a liquid extraction method with dichloromethane was proposed for the extraction and enrichment of odorous compounds. This method of sample preparation allowed the detection of 44 odor compounds for pinewood and 22 compounds for cedarwood with aldehyde, acid, terpene, furanoic, and phenolic chemistry.

Although liquid extraction presents itself as a powerful extraction technique for polar and nonpolar analytes and can produce high extraction efficiencies, it suffers from the disadvantage of high usage of solvent and multiple clean-ups, as well as enrichment steps. Headspace techniques, in contrast, exhibit a multitude of benefits, including ease of automation, reduced number of sample preparation steps, and solvent-free handling [19]. In comparison to techniques using organic solvents, headspace sampling also allows artifact-free investigation, as well as mitigation of volatile losses during the concentration of liquid extracts [20]. Furthermore, static headspace methods such as SPME in principle, resemble the biological process of orthonasal smell, by which volatile compounds are incorporated through the nose and absorbed by the mucus membrane by transport proteins, where they are then transported to the olfactory receptors [21]. In contrast, thermal desorption is

closely attributed to the process of retronasal smell, by which odorant molecules diffuse or are transported by exhalation to the mucus membrane [20,21].

The different headspace techniques investigated in this work, therefore, present a valuable alternative to solid-liquid extraction as sample preparation methods. Among these, chosen for the present investigation, were (dynamic) headspace thermal desorption with Tenax® TA as an adsorbent, (classical) headspace solid-phase microextraction, and HS-SPME Arrow. SPME has already been applied very successfully in earlier investigations regarding volatile organic compounds and aroma substances from different matrices [22,23]. It was, therefore, considered a promising method for the detection of odorous compounds in wood. More recently, SPME Arrow was proposed as an alternative to conventional SPME, offering increased sensitivity, thus allowing a larger number of compounds to be detected [24].

2. Materials and Methods

2.1. Materials

UV/IR Rotisolv® grade dichloromethane, hexane for synthesis, sodium sulfate, >99%, and anhydrous were purchased from Carl Roth (Carl Roth GmbH + Co KG, Karlsruhe, Germany). C8 to C20 *n*-alkane standard solution in hexane (40 mg L^{-1}) and TraceCERT® toluene-d8 solution in methanol (2000 µg/mL) were purchased from Supelco (Bellefonte, PA, USA). The reference substances pentanal (≥97%), hexanal (≥98%), heptanal (≥92%), α-pinene (96%), β-pinene (99%), β-myrcene (≥90%), octanal (99%), 3-carene (≥95%), α-terpinene (≥95%), p-cymene (99%), d-limonene (95%), γ-terpinene (≥97%), 2-octenal (≥95%), 1-octanol (≥98%), α-terpinolene (85%), p-cymenene (≥98%), l-fenchone (≥98%), nonanal (≥95%), dl-camphor (≥95%), 2-nonenal (≥95%), endo-borneol (98%), α-terpineol (≥95%), myrtenal (98%), 2-decenal (≥95%), bornylacetate (≥99%), and methyleugenol (%) were purchased from Merck (Merck KGaA, Darmstadt, Germany).

A divinylbenzene (DVB)/carbon wide range (WR)/polydimethylsiloxane (PDMS) SPME Arrow fiber of 20 mm length and 1.1 mm outer diameter and 110 µm phase thickness was obtained from Restek Corporation (Bellefonte, PA, USA). A Restek SPME Manual Injection Kit (Restek Corporation, Bellefonte, PA, USA) was employed for the extraction and injection of volatiles. A conventional divinyl benzene (DVB)/carboxen (CAR)/polydimethylsiloxane (PDMS) SPME fiber of 20 mm length and 30 µm (CAR/PDMS)/ 50 µm (DVB) film thickness was purchased from Supelco (Bellefonte, PA, USA). The fiber was attached to a manual SPME holder. Thermal desorption tubes with a length of 8.89 cm (=3.5″) and 6.35 mm (1/4″) outer diameter, filled with 200 mg Tenax® TA adsorption material, were purchased from Markes (Markes International, Bridgend, United Kingdom).

Samples of pinewood strands (sample A) and isocyanate binder-based OSB made thereof (sample B) were stored in the freezer at −20 °C and pretreated prior to headspace extractions by conditioning for 24 h at a relative humidity of 50% in a desiccator with a constant stream of air so that one half of the volume was exchanged in 1 h. The samples were further ground as described in the results.

2.2. GC and Thermal Desorption Methods

Experiments were conducted using a GC-MS system consisting of a 7890A gas chromatograph coupled to a 5975C inert mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). An uncoated, deactivated capillary 2.5 m × 0.25 mm ID (Restek Corporation, Bellefonte, PA, USA) was connected to a Rtx-5MS column 30 × 0.25 mm ID, 0.25 µm d_f, (Crossbond 5% diphenyl-95% dimethyl siloxane) (Restek Corporation, Bellefonte, PA, USA). Two identical columns of this configuration were connected to two individual split/splitless injectors and used with a splitter for FID/olfactometric detection with two 20 cm capillaries connected to each detector and connected with an uncoated capillary 30 cm, 0.25 µm ID serving as a transfer line to the EI source. A flame ionization detector (FID) operated at 300 °C and an olfactory detection port SIM ODP (Scientific Instruments Manufacturer GmbH, Oberhausen, Germany), which was connected to the GC-oven with a transfer line

that was constantly kept at 280 °C, were used for detection and evaluation of odorants. The GC oven was held at a temperature of 40 °C for 3 min, and subsequently, the temperature was raised by 4 °C/min to 120 °C and then by 20 °C/min to 250 °C, where the temperature was held for 5 min. Liquid extract in the amount of 1 µL was injected at 280 °C. For HS–SPME and HS-SPME Arrow, samples were desorbed for 3 min in the injector at 270 °C. For sample introduction via indirect thermal desorption, a combination of a Series 2 Ultra thermal desorption autosampler and a Unity 2™ thermal desorption unit (both: Markes International, Bridgend, United Kingdom) was used. Sorbent tubes onto which the volatiles emitted from wood or OSB samples were previously collected were initially desorbed at a temperature of 280 °C for 8 min with a flow of 50 mL/min onto a Peltier-cooled cryogenic trap, which was held at a temperature of 25 °C. This internal trap was desorbed to the GC with a flow of 1 mL/min He at 280 °C for 5 min. For all sample introduction methods, the split was altered between the splitless mode and at ratios of 2:1, 5:1, 10:1, 20:1, and 30:1, respectively, to account for the different sensitivity of detection.

Method development was additionally conducted on a second Agilent GC/MS system (7890A GC/5975C MS, Agilent Technologies, Santa Clara, CA, USA) with an HP-PONA (DB-1, Crossbond 100% dimethyl siloxane) column of 60 × 0.25 mm ID with 0.25 µm df (Agilent Technologies, Santa Clara, CA, USA) in combination with a TD-100 integrated autosampler and thermal desorber (Markes International, Bridgend, UK). A solution of toluene-d8 in methanol was added to each thermal desorption tube prior to analysis. Detection was performed by the splitting of two parts to an FID operated at 280 °C and one part to the EI source by an auxiliary EPC unit. The oven program was as follows: a starting temperature of 45 °C was held for 3 min and subsequently raised to 160 °C by 10 °C/min, upon which the temperature was raised to 260 °C by 20 °C/min and held for 10 min. Column flow was 1 mL/min He.

2.3. Data Analysis

Data Analysis was conducted using the software MassHunter (Agilent Technologies, Santa Clara, CA, USA). For (dynamic) HS-TD, FID peak areas were normalized to the area of the internal standard toluene-d8 and further divided by the sample mass and the flow rate at the thermal extractor. In the case of HS-SPME and HS-SPME Arrow, FID peak areas were normalized to sample mass. EIC chromatograms were integrated, and the peak area of individual components was divided by the sum of EIC peak areas to obtain a relative fraction for each compound. Venn diagrams were constructed using the software OriginPro 2023 (OriginLab Corporation, Northampton, MA, USA).

The identification of volatiles was conducted by search in/comparison with mass spectra libraries provided by the U.S. National Institute of Standards and Technology (NIST20) and published by Wiley/NIST (W9N11). Furthermore, linear temperature-programmed retention indices (LTPRIs) for the analytes were calculated and compared to literature values. Last, analytical standards were analyzed where available.

2.4. Extraction Methods

The following extraction methods were performed at room temperature (23 °C) for the extraction of volatiles (Table 1) from pinewood strands (sample A) and OSB made thereof (sample B). Headspace extractions were performed for 1 h after samples underwent conditioning for 1.5 h at room temperature.

Table 1. Abbreviations for extraction methods.

Method	Abbreviation
Solid-liquid extraction	SLE
Dynamic headspace extraction thermal desorption	(dynamic) HS-TD
Headspace solid-phase microextraction	HS–SPME
Headspace solid-phase microextraction Arrow	HS–SPME ARROW

2.4.1. Solid Liquid Extraction (SLE)

SLE was conducted by extraction of 20 g of wood shavings three times with 50 mL dichloromethane each time. The extract was then dried over sodium sulfate and placed into a setup for high vacuum distillation [25], where it was distilled at 40 °C. The distillate was collected in two cold traps immersed in liquid nitrogen. The purified extract was then concentrated to a final volume of 250 µL under a stream of nitrogen. This procedure was based on previous work on the isolation of odor compounds from wood by Schreiner et al. [17].

2.4.2. Dynamic Headspace Extraction Thermal Desorption ((Dynamic)-HS-TD)

The headspace of 0.6 g of powdered sample (representing the smallest mass of sample that ensured reproducible sampling conditions as the floor of the sample chamber was fully covered) was thermally extracted using a Micro-Chamber/Thermal Extractor™ (µ-CTE™) with a volume of 45 mL (Markes International, Bridgend, UK), where a gas stream of about 55 mL/min of purified dry air was used to condition the sample for prior to sampling via Tenax® TA adsorption. Toluene-d8 was used as an internal standard to monitor both adsorption and desorption efficiencies.

2.4.3. Headspace Solid Phase Microextraction (HS–SPME)

HS–SPME was performed by exposing the fiber for 60 min to the headspace of 0.6 g of powdered samples in a 20 mL headspace vial. Used as an internal standard, 3 µL of toluene-d8 solution in methanol was added prior to extractions to a piece of filter paper and introduced into the sample vial.

2.4.4. Headspace Solid Phase Microextraction Arrow (HS–SPME ARROW)

HS–SPME ARROW was conducted by exposing the Arrow fiber for 60 min to the headspace of 0.6 g of powdered sample in a 20 mL headspace vial at room temperature. Additionally, 3 µL of a solution of toluene-d8 in methanol was added to a filter paper prior to extractions as an internal standard.

3. Results

3.1. Method Optimization of Sample Homogeneity

Two different sample homogenization methods were tested. For the first procedure, the sample was cut into shavings with an edge length of 1 cm. In the second preparation method, the precut samples were further milled in a centrifugal mill to a final particle size of 250 µm with the addition of liquid nitrogen. This homogenization method represents a relatively gentle way of sample preparation [26], which greatly enhances the sensitivity of volatiles compared to non-cryogenic milling (Figure 1).

In comparison, the two sample preparation methods showed a significant increase in sensitivity of 340% for sample A and 130% for sample B (Table 2). Furthermore, improved repeatability, as evidenced by reduced relative standard deviation, shows a significant increase in homogeneity for the fine-ground sample. It was, therefore, concluded to use the powdered samples for further investigation for all extraction methods since it can be assumed that the observed behavior in repeatability (already reported previously for classical SPME [27]) is independent from the headspace extraction technique actually applied.

Table 2. Comparison of two different sample preparation methods for the detection of volatiles in terms of their mean values and (relative) standard deviations, expressed as µg toluene-d8 equivalents per g sample and m^3 sampling volume.

Sample	Mean	Standard Deviation TVOC	RSD/%
A coarse	1.622	1.425	88
A fine	6.883	0.505	7
B coarse	1.112	0.2871	26
B fine	2.497	0.2877	12

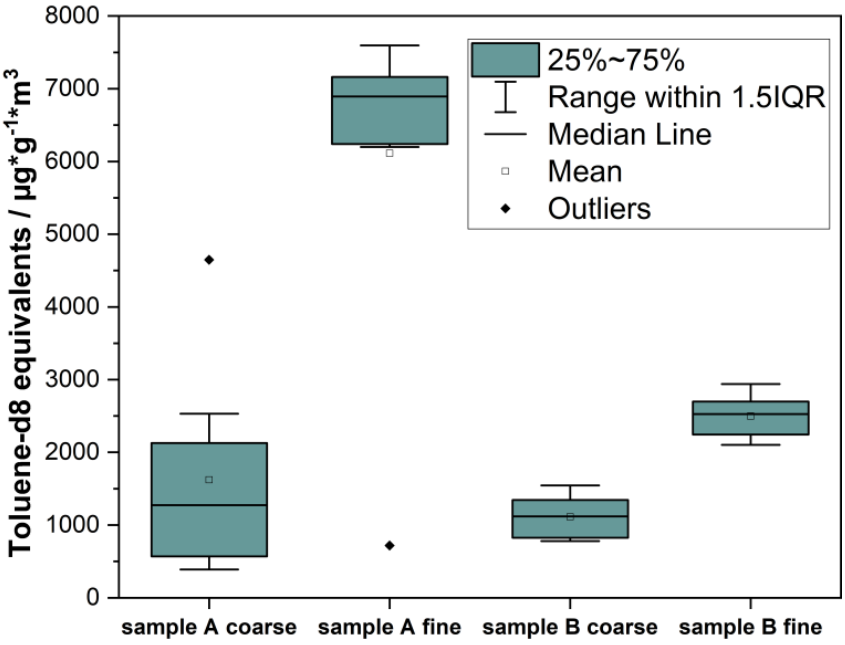

Figure 1. Boxplots of major volatile organic compounds for coarse and fine homogenized samples, eight repetitions. A Dixon's Q-test found a significant outlier at the $p = 0.05$ level for sample "A fine", which was excluded in further calculations.

3.2. Optimization of Extraction Times for Conventional SPME

Conventional HS-SPME has been shown to accomplish sample preparation for a multitude of tasks, including extraction of volatiles for GC-O [28]. For the detection of odorants by human sensory evaluation, however, a capacity as large as possible is needed [20]. The advantage of HS-SPME Arrow is therefore apparent when a direct comparison of the phase volumes is made (Table 3) [29,30]. Thermal desorption tube sampling (using Tenax® TA), in turn, offers excellent capacity due to the adsorptive material's high surface area of 3.8 m^2 for 200 mg [31].

Table 3. Comparison of the phase volume of the two static headspace techniques.

Technique	Phase Chemistry	Phase Volume/µL
HS–SPME	DVB/CAR/PDMS	2.2
HS-SPME Arrow	DVB/CAR/PDMS	7.4

Testing of extraction times was conducted for (classical) HS-SPME, as it represents the benchmark for comparison. In this study, the extraction time for SPME of volatiles from powdered samples (pinewood strands and OSB), in combination with an internal standard (toluene-d8), was varied between 5 and 120 min, and the peak area of 20 volatile compounds was monitored.

As can be seen from Figure 2, the total peak area of all volatiles reaches equilibrium at a time of 30 min for sample A. For sample B, this point is not reached even within 120 min for the sum of volatiles reviewed. However, a constant value can be seen after 60 min for individual compounds such as α-pinene, 3-carene, and β-myrcene, which represent three of the important odor compounds found in the sample (Figure 3) [17].

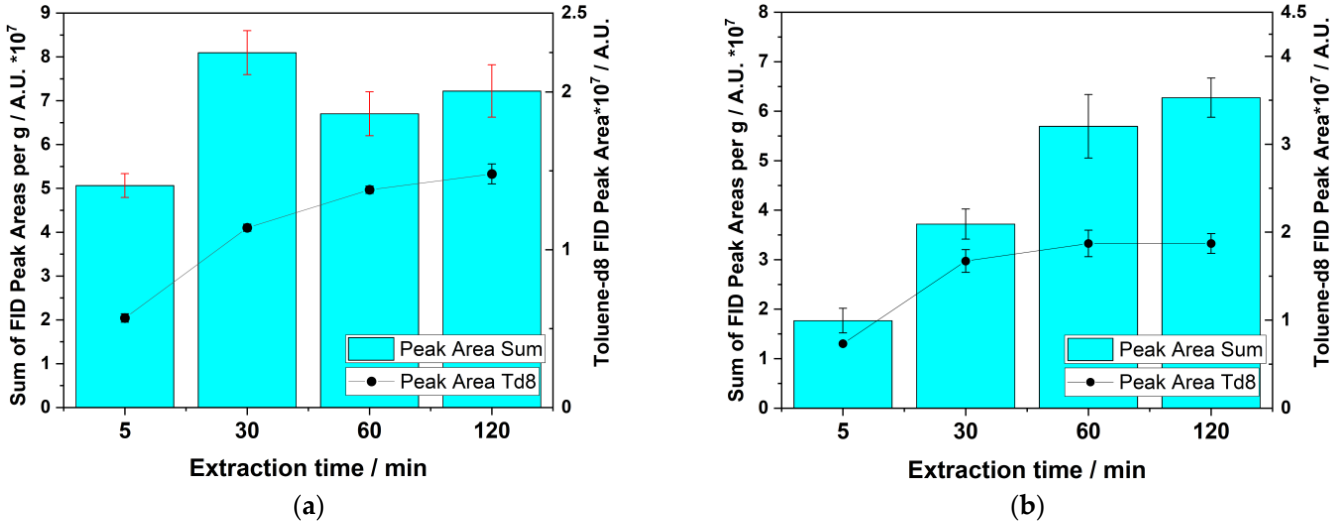

Figure 2. Sum of peak areas for major volatile compounds (Pentanal, hexanal, α-pinene, camphene, β-myrcene, β-pinene, 3-carene, p-cymene, d-limonene, γ-terpinene, p-propenyltoluene, α-terpinolene, 2-nonanal, α-campholenal, terpinene-4-ol, α-terpineol, myrtenal, verbenone, bornylacetate, longifolene) for different extraction times and peak area of the internal standard Toluene-d8; (**a**) Sample A; (**b**) Sample B.

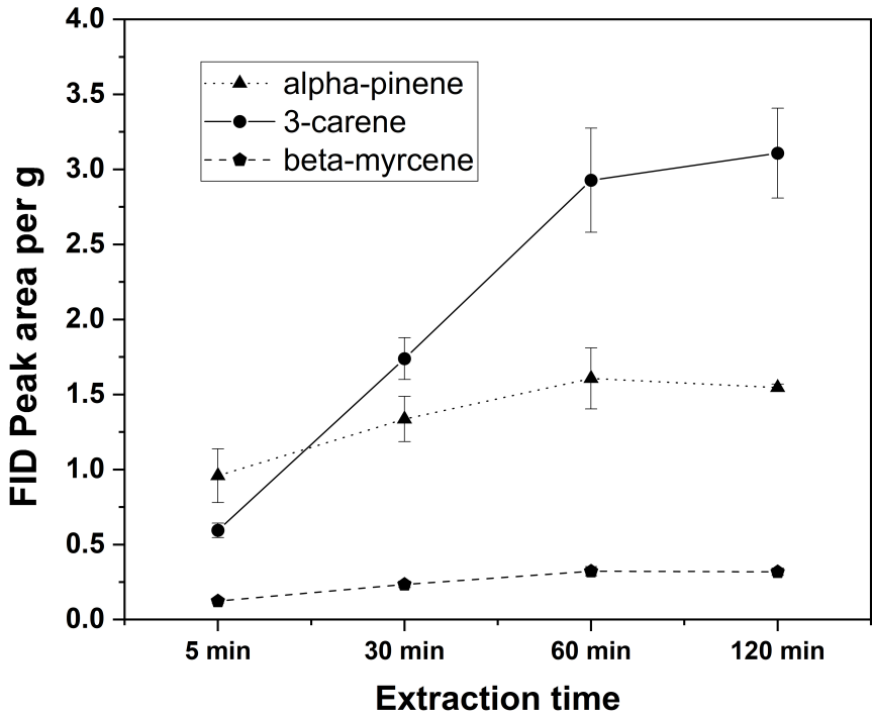

Figure 3. Peak area standardized to sample mass for classical HS-SPME of sample B for different extraction times for α–pinene, 3–carene, and β–myrcene.

3.3. Comparison of Extraction Methods

Relative fractions of detected compounds (Tables 4 and 5) were grouped into compound classes, which were represented by bicyclic monoterpenes, monocyclic monoterpenes, aliphatic aldehydes, monoterpenoid ketones, monoterpenoid aldehydes, acids, monoterpenoid alcohols, monoterpenoid esters, acyclic monoterpenes, and phenol ethers (Figure 4). Bicyclic monoterpenes, comprising α-pinene, β-pinene, and 3-carene, dominated the chromatogram for both samples and all tested methods. In the case of (dynamic) HS-TD, the relative peak area for bicyclic monoterpenes is significantly reduced in comparison

to the other methods. Additionally, the relative peak area of all other compound classes besides monocyclic monoterpenes is increased for (dynamic) HS-TD, which suggests a better representation and higher sensitivity over a wider variety of chemical classes in comparison to the other headspace methods, as well as the liquid extraction reference method. This distribution could in part be attributed to compounds of higher polarity, which were also shown by other authors to be favored in dynamic headspace sampling [32]. Classical HS-SPME and HS-SPME Arrow show a very similar distribution in peak fractions for individual compounds with a comparably high percentage in bicyclic monoterpenes. The correspondence of HS-SPME results with the reference method (SLE) is better in the case of sample A (Table 4) while dynamic HS-TD yields results more comparable to the reference method for sample B (Table 5). Both this observation and the RSD% values observed for both samples and the different extraction techniques reflect the large differences among sample constituents in terms of concentration and chemical nature/polarity. As a general trend, it can be concluded from the data that RSD% values of the fractions of individual constituents would become larger with decreasing concentration and increasing polarity of the analyte, which appears plausible, considering the relatively apolar nature of the sorbent phases used in all extraction schemes applied.

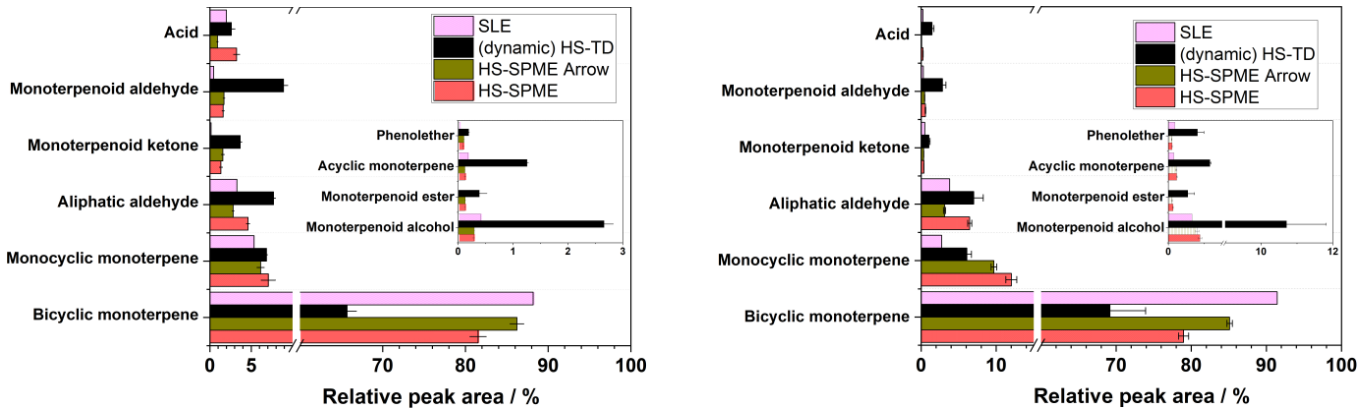

Figure 4. EIC area percentages comparison of compound classes for three different headspace methods, and SLE as reference method; (**a**) sample A; (**b**) sample B.

3.4. Olfactometric Detection of Odor Compounds

It was possible to detect a total of 34 individual odor compounds across different chemical compound classes (mono- and bicyclic monoterpenes, acyclic monoterpenes, monoterpenoid ketones, aldehydes, alcohols, and esters; and aliphatic aldehydes, acids, alcohols, and phenol ethers). SLE was used as a reference method based on [17]. The findings of these chemical groups [17,33,34] reflect the volatile fraction of extractives of pinewood (*Pinus sylvestris* L.), as well as degradation/conversion products thereof [17,33,34]. As shown in Figure 5, HS-SPME Arrow shows a larger number of detected compounds (15) vs. classical HS-SPME (10) for sample A. HS-SPME Arrow was able to detect a similar number of compounds for aliphatic aldehydes and monoterpenes, but an increase in the number of oxygenated monoterpenoids was observed. Additionally, one phenol ether was detected for sample A. In the case of sample B, only two monoterpene compounds could be additionally observed with SPME Arrow; otherwise, the two static headspace methods showed similar results. Thermal desorption in comparison to injection of the solid-liquid extract was found to result in a lower yield in odorants for sample A (20 vs. 24) due to the contribution from the higher number of acids and oxygenated monoterpenes detected with SLE. Acetic and pentanoic acid were only found by SLE for sample A, as well as octanal, α-campholenal, and bornyl acetate (Table 6). For sample B, fewer compounds (22 vs. 17) were found by SLE in comparison to TD, with a decrease in the number of detected aldehydes and phenol ether species for SLE and the appearance of the linear

alcohol 1-octanol in the case of thermal desorption. Furthermore, two aldehydes were only found by TD in sample B (pentanal and 2,4-decadienal). Similar to sample A, the detection of acids was favored by SLE, revealing butanoic acid as the only detectable species derived from this chemical class for sample B.

As can be seen in Figure 6, SLE yielded the most uniquely detected compounds in the case of native pine strands, which was in part due to the number of volatile organic acids found. The overlap in compound number is most pronounced between SLE and (dynamic) HS-TD, with the two techniques sharing a total of five unique compounds for samples A and B.

Table 4. Relative peak areas of major odor compounds from sample A (measured on a DB-5 column with four repetitions; SLE as a reference method was conducted in one repetition) with the following chemical groups: 1, bicyclic monoterpenes; 2, monocyclic monoterpenes; 3, aliphatic aldehyde; 4, monoterpenoid ketone; 5, monoterpenoid aldehyde; 6, acid; 7, monoterpenoid alcohol; 8, monoterpenoid ester; 9, acyclic monoterpene; 10, phenol ether. STD: standard deviation; RSD: relative standard deviation.

Compound	LRI	Chemical Group	HS–SPME			HS–SPME ARROW			(Dynamic) HS-TD			SLE
			Mean (%)	STD (%)	RSD (%)	Mean (%)	STD (%)	RSD (%)	Mean (%)	STD (%)	RSD (%)	(%)
Acetic acid	655	6	2.05	0.24	11.50	0.24	0.07	27.73	1.16	0.15	13.29	0.00
Pentanal	704	3	0.26	0.01	3.30	0.06	0.00	6.82	0.26	0.01	3.93	0.05
Propanoic acid	731	6	0.63	0.07	11.17	0.19	0.02	10.50	0.87	0.07	8.25	1.08
Butanoic acid	804	6	0.45	0.06	12.85	0.34	0.03	8.15	0.36	0.11	32.25	0.74
Hexanal	813	3	3.55	0.14	3.98	1.79	0.11	6.19	3.45	0.13	3.73	0.75
Pentanoic acid	900	6	0.10	0.01	14.17	0.14	0.01	8.95	0.21	0.13	59.36	0.18
Heptanal	907	3	0.14	0.01	8.04	0.13	0.01	4.12	0.28	0.01	4.79	0.02
α-Pinene	942	1	40.15	1.40	3.48	46.20	0.89	1.93	38.28	1.10	2.88	48.61
β-Pinene	984	1	1.49	0.01	0.47	1.79	0.07	4.07	0.99	0.02	2.20	2.07
β-Myrcene	993	9	0.13	0.02	15.87	0.12	0.01	5.07	1.25	0.03	2.07	0.17
Octanal	1011	3	0.23	0.02	7.97	0.27	0.02	6.44	0.72	0.03	3.77	0.03
3-Carene	1020	1	39.88	0.84	2.12	38.23	0.15	0.40	26.43	0.25	0.96	37.50
α-Terpinene	1023	2	0.12	0.01	12.39	0.09	0.00	5.55	0.06	0.00	6.25	0.25
p-Cymene	1030	2	3.86	0.48	12.52	3.13	0.30	9.69	2.20	0.15	6.77	2.91
D-Limonene	1035	2	1.88	0.25	13.39	1.70	0.10	5.73	0.90	0.02	2.51	1.72
γ-Terpinene	1064	2	0.14	0.02	11.04	0.15	0.01	7.48	0.14	0.00	2.60	0.02
2-Octenal	1065	3	0.02	0.00	10.35	0.03	0.00	12.66	0.05	0.01	13.65	2.01
α-Terpinolene	1094	2	0.68	0.09	13.70	0.87	0.08	9.08	0.54	0.01	2.65	0.13
p-Cymenene	1095	2	0.37	0.02	4.80	0.19	0.02	11.30	3.01	0.07	2.24	0.32
L-Fenchone	1096	4	0.31	0.06	20.39	0.34	0.05	14.42	0.20	0.01	2.78	0.04
Nonanal	1109	3	0.32	0.02	7.02	0.38	0.02	5.91	2.63	0.13	4.91	0.13
α-Campholenal	1138	5	0.79	0.07	8.36	0.79	0.04	4.79	4.63	0.31	6.66	0.23
Camphor	1161	4	0.45	0.06	13.58	0.58	0.06	10.61	2.19	0.13	6.01	0.00
2-Nonenal	1173	3	0.09	0.01	14.84	0.11	0.01	13.04	0.04	0.00	10.77	0.22
Pinocarvone	1178	4	0.57	0.07	12.29	0.65	0.07	10.76	1.28	0.07	5.69	0.10
endo-Borneol	1181	7	0.14	0.01	7.71	0.14	0.00	1.90	1.21	0.12	9.88	0.18
α-Terpineol	1198	7	0.15	0.02	12.85	0.15	0.01	4.94	1.56	0.06	4.11	0.23
Myrtenal	1208	5	0.83	0.07	8.19	0.92	0.06	6.28	4.26	0.25	5.78	0.23
2-Methoxy-p-cymene	1244	10	0.08	0.01	13.05	0.09	0.01	13.89	0.09	0.01	10.91	0.00
2-Decenal	1276	3	-	-	-	0.02	0.00	21.82	0.27	0.01	3.64	0.04
Bornylacetate	1296	8	0.12	0.01	9.89	0.13	0.01	9.81	0.38	0.14	36.67	0.00
(E,E)-2,4-Decadienal	1301	3	-	-	-	-	-	-	-	-	-	0.02
Methyleugenol	1364	10	0.01	0.00	25.15	0.02	0.00	7.06	0.10	-	3.15	0.02

Table 5. Relative peak areas of major odor compounds from sample B (measured on a DB-5 column with four repetitions; SLE as a reference method was conducted in one repetition) with the following chemical groups: 1, bicyclic monoterpenes; 2, monocyclic monoterpenes; 3, aliphatic aldehyde; 4, monoterpenoid ketone; 5, monoterpenoid aldehyde; 6, acid; 7, monoterpenoid alcohol; 8, monoterpenoid ester; 9, acyclic monoterpene; 10, phenol ether.

Compound	LRI	Chemical Group	HS–SPME			HS–SPME ARROW			(Dynamic) HS-TD			SLE
			Mean (%)	STD (%)	RSD (%)	Mean (%)	STD (%)	RSD (%)	Mean (%)	STD (%)	RSD (%)	(%)
Acetic acid	655	6	0.17	0.01	8.15	-	-	-	0.61	0.02	3.98	-
Pentanal	704	3	0.40	0.02	5.24	0.09	0.01	5.61	0.24	0.05	21.31	0.12
Propanoic acid	731	6	-	-	-	-	-	-	0.32	0.14	43.62	-
Butanoic acid	804	6	-	-	-	-	-	-	0.24	0.14	60.29	-
Hexanal	813	3	5.18	0.23	4.39	2.22	0.10	4.46	3.10	0.41	13.36	1.35
Pentanoic acid	900	6	0.09	0.01	13.53	0.07	0.01	8.90	0.27	0.04	15.27	0.24
Heptanal	907	3	0.16	0.00	2.30	0.11	0.01	4.70	0.22	0.03	14.20	0.06
α-Pinene	942	1	35.00	1.74	4.96	42.80	0.89	2.07	41.21	4.53	10.99	56.92
β-Pinene	984	1	1.15	0.06	5.08	1.59	0.04	2.70	0.91	0.06	6.27	1.60
β-Myrcene	993	9	0.23	0.01	6.42	0.22	0.01	4.21	1.16	0.02	1.74	0.16
Octanal	1011	3	0.22	0.01	3.40	0.20	0.01	4.16	0.59	0.13	22.03	0.09
3-Carene	1020	1	42.83	1.18	2.75	40.71	0.60	1.47	27.04	0.58	2.15	32.93
α-Terpinene	1023	2	0.45	0.04	8.66	0.38	0.02	5.06	0.13	0.02	12.19	0.19
p-Cymene	1030	2	4.62	0.27	5.93	3.13	0.15	4.64	1.40	0.23	16.58	1.30
D-Limonene	1035	2	2.16	0.12	5.44	1.87	0.09	4.74	0.83	0.07	8.06	0.90
γ-Terpinene	1064	2	0.86	0.07	7.77	0.83	0.04	4.43	0.34	0.04	11.15	0.11
2-Octenal	1065	3	0.06	0.00	7.54	0.07	0.00	5.96	0.10	0.02	15.96	1.76
α-Terpinolene	1094	2	3.20	0.23	7.09	3.09	0.12	3.86	1.25	0.12	9.41	0.19
p-Cymenene	1095	2	0.71	0.03	4.92	0.39	0.01	3.57	2.13	0.17	8.02	0.03
L-Fenchone	1096	4	0.10	0.01	8.68	0.08	0.00	3.86	0.09	0.03	30.34	0.24
Nonanal	1109	3	0.36	0.02	5.14	0.33	0.02	5.42	2.15	0.53	24.82	0.22
α-Campholenal	1138	5	0.38	0.03	7.19	0.29	0.02	5.56	1.54	0.31	20.17	0.09
Camphor	1161	4	0.19	0.01	4.55	0.19	0.01	4.48	0.72	0.08	11.22	0.02
2-Nonenal	1173	3	0.06	0.01	10.02	0.06	0.00	5.03	0.05	0.01	19.69	0.04
Pinocarvone	1178	4	0.08	0.00	5.02	0.06	0.00	4.15	0.23	0.04	19.54	0.23
endo-Borneol	1181	7	0.38	0.02	6.43	0.32	0.02	5.83	3.61	0.95	26.25	0.53
α-Terpineol	1198	7	0.50	0.04	7.18	0.48	0.03	6.68	6.30	1.29	20.40	0.13
Myrtenal	1208	5	0.19	0.01	3.78	0.17	0.01	5.96	1.30	0.14	10.89	0.21
2-Methoxy-p-cymene	1244	10	0.07	0.00	6.60	0.06	0.00	5.16	0.21	0.05	21.59	0.08
2-Decenal	1276	3	0.02	0.00	7.24	0.04	0.00	9.56	0.47	0.08	17.69	0.06
Bornylacetate	1296	8	0.13	0.01	5.04	0.10	0.00	4.56	0.54	0.18	33.12	0.00
(E,E)-2,4-Decadienal	1301	3	-	-	-	-	-	-	0.09	0.01	15.85	0.10
Methyleugenol	1364	10	0.03	0.00	11.55	0.04	0.00	6.40	0.59	0.15	25.18	0.10

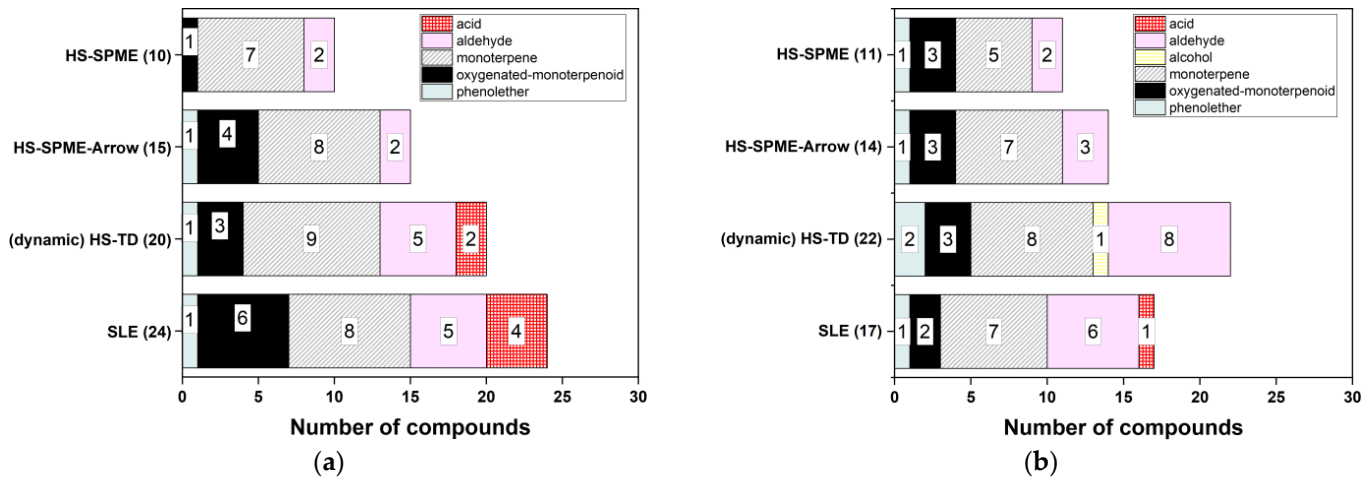

Figure 5. Number of compounds according to chemical classes and sample preparation method as detected by GC–O; (**a**) sample A; (**b**) sample B.

Table 6. Comparison between all compounds detected by GC-O and identified via their mass spectra and linear retention indices (LRI) for the sample preparation methods: 1, HS-SPME; 2, HS-SPME Arrow; 3, Thermal desorption; 4, Solid liquid extraction. Compounds detected by at least three of four methods were marked bold.

			Pine Strands				OSB			
Compound	**Odor Characteristics**	**LRI**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Acetic acid	acidic, fresh	655				x				
Pentanal	fresh, pungent	704			x				x	
Propanoic acid	acidic, putrid	731			x	x				
Hexanal	green, grassy	804	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
Butanoic acid	acidic, putrid	813			x	x				x
Pentanoic acid	acidic, cheese-like	900				x				
Heptanal	green, oily, grassy	907							x	x
α-Pinene	fresh, resinous	942	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
β-Pinene	fresh, resinous	984	**x**	**x**	**x**	**x**	**x**	**x**	**x**	
β-Myrcene	sweet, mushroom-like	993	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
Octanal	fresh, fatty	1011				x				
3-Carene	terpenoid, solvent-like	1020	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
α-Terpinene	woody, pine, sweet	1023			x	x				x
p-Cymene	spicy, pungent, solvent-like	1030	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
D-Limonene	citrus, fresh	1035	x	x		x				
γ-Terpinene	sweet, green	1064	x	x	x	x			x	x
2-Octenal	fatty, oily	1065			x	x			x	x
1-Octanol	flowery, citrus	1079							x	
α-Terpinolene	lemon, floral	1094	x	x	x	x		x	x	
p-Cymenene	phenolic, coffee	1095		x	x			x	x	x
L-Fenchone	herbal, woody	1096		x	x	x				
Nonanal	cucumber, sweet	1109	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
α-Campholenal	green, spicy, leafy	1138				x	x	x		x
Camphor	medicinal, camphorous	1161	**x**	**x**	**x**	**x**		**x**	**x**	**x**
2-Nonenal	fatty, cucumber	1173							x	x
Pinocarvone	sweet, herbal	1178	x	x	x	x				
endo-Borneol	camphorous, spicy	1181				x	x	x	x	
α-Terpineol	resinous, flowery, citrus	1198		x					x	
Myrtenal	sweet, cool, spicy	1208		**x**	**x**	**x**	**x**	**x**	**x**	**x**
2-Methoxy-p-cymene	smokey, phenolic	1244		x	x	x	x	x	x	
2-Decenal	fatty, fruity	1276			x	x		x	x	x
Bornylacetate	spicy, metholic	1296				x				
(E,E)-2,4-Decadienal	fatty, oily	1301							x	
Methyleugenol	clove, spicy	1364							x	x

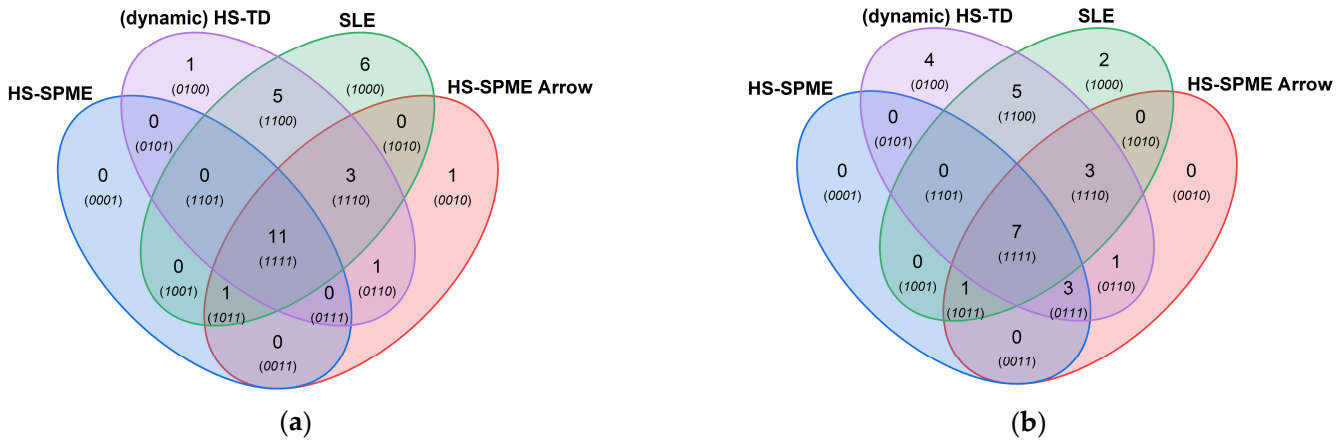

Figure 6. Venn diagrams of all compounds by method to indicate the number of compounds detected by only one or by several techniques used; (**a**) sample A; (**b**) sample B.

4. Discussion

In order to obtain reproducible and meaningful results, notably for the analysis of volatile fragrant compounds, sample homogeneity has a crucial role in sample preparation. It was, therefore, necessary to homogenize samples to achieve acceptable repeatability. As has been shown, grinding under liquid nitrogen is a suitable way of homogenizing the wood and wood-based samples under mild conditions. This procedure ensures low to negligible heating during the milling process and avoids thermal alteration of the sample composition or the creation of temperature-induced artifacts [26]. On the other hand, although a significant increase in repeatability was seen for sample A (88% vs. 7% RSD), for B the effect was less pronounced (26% vs. 12% RSD). It could be therefore argued that, for OSB, a just-acceptable decrease in repeatability could be traded in for minimizing sample preparation time. Nevertheless, it should be noted that sensitivity halved with the sampling of the coarse type sample, and consequently would lead to a lower total number of observed compounds in olfactometry. This result is of special concern if a direct adsorption of volatiles from OSB headspace is considered [35].

It was possible to identify and characterize a total of 34 odorants in native pinewood strands (*Pinus sylvestris* L.), as well as OSBs constructed by GC-O. Compounds in the chemical classes of bicyclic monoterpene, monocyclic monoterpene, acyclic monoterpene, monoterpenoid ketone, monoterpenoid aldehyde, aliphatic aldehyde, alcohol, acid, and phenol ethers were found. These results represent the volatile fraction of extractives in pine species and essential oils thereof, and the detected compounds are in alignment with reported results [17,34,36–39], with the exception of myrtenal and 1-octanol. The occurrence of both compounds can, however, be expected due to degradation/conversion processes in plant species [12,40,41] as they were also detected previously by GC-O [42,43].

In comparison to previous work by Schreiner et al. [17], deviations in odorants are primarily seen in the absence of lactones and the detection of a greater number of terpenes and terpenoids in the present study. These differences can be explained in part by the use of a standard polar FFAP (100% polyethylene glycol) column in contrast to a semi-standard apolar DB-5 (5% phenyl-/95% dimethyl siloxane polymer) column, affecting separation [44,45]. Furthermore, other deviations in methodology, such as the application of solvent-assisted flavor evaporation (SAFE) [25] and the employment of a cold-on-column technique, which were not employed in this study, can significantly influence the composition of detected odorants [46]. Last, due to the variability of the extractive content in wood, a different spectrum of volatiles within one wood species is to be expected, as can be seen by the results of previous studies on the composition of volatiles from pine wood [34,39].

When comparing the tested samples, OSBs, in contrast to the untreated wood strands, revealed a larger number of aliphatic saturated and unsaturated aldehydes, which may contribute significantly to their odor profile [47]. This finding can be attributed to enzymatic and atmospheric oxidation processes during manufacturing and storage [12]. The native wood sample, however, exhibited an increased number of organic acids. Of these compounds, butyric acid was reported as of great importance to odor profiles [48,49], but also the other members of this substance class found in this study were reported as significant odorants [50,51].

Dynamic headspace extraction thermal desorption was described as a suitable tool for the analysis and characterization of odor compounds from different matrices [52]. Furthermore, its potential for quantitative GC-O was demonstrated [53], allowing an investigation of flavor dilution factors (FD-factors) in the form of AEDA [54]. When compared to HS-SPME and HS-SPME Arrow, the higher phase ratio in (dynamic) HS-TD is advantageous in this regard. Hereby the number of odorants detectable at higher split ratios can be maximized, leading to a more pronounced classification by FD factors. In this study, (dynamic) HS-TD allowed the detection of 20 odorants for fresh pinewood strands and 22 in the case of OSB. HS-SPME in turn provides acceptable performance (10 and 11 odorant compounds detected) as well as good representation among compound groups. SPME Arrow, on the other hand, offers a significant improvement in odorant

output (16 and 14 compounds). As was shown, the total number of compounds belonging to the class of acids was maximized with the use of the solid-liquid extraction method. This finding is in accordance with a recent study [55]. It could be demonstrated, however, that (dynamic) HS-TD achieved a comparable number of odorants for sample A (20 vs. 24) and, in the case of sample B, even a higher total number of detected odorants (22 vs. 17). This increase was partially due to an increase in detected aldehydes for (dynamic) HS-TD (8 vs. 6), where 2,4-decadienal, a compound of high relevance for odor profiles, was only found after dynamic headspace extraction.

5. Conclusions

We have been able to demonstrate here that the application of the headspace methods HS-SPME, HS-SPME Arrow, and (dynamic) HS-TD shows them to be suitable tools for the analysis of odorous compounds from wood and wood composites. With these findings, it could be shown that a comprehensive evaluation of odor compounds with the use of dynamic headspace extraction thermal desorption is possible. The technique showed similar performance to SLE in compound output but outperformed the latter for the investigation of OSB. Classical HS-SPME is a well-established technique that offered good performance in this investigation (10 and 11 compounds). With minimal instrumental effort, aside from alterations in the inlet liner, sample preparation for GC-O is therefore possible, and a nuanced picture of a wood sample in regard to odorants is possible. HS-SPME Arrow in turn offers an improvement in the number of odorants and can be implemented with comparable ease for a given system. On the other hand, dynamic headspace extraction thermal desorption offers the detection of a high number of odorants with the combination of a highly automated sample preparation system. This finding is especially beneficial for high sample throughput and more streamlined modes of operation. A method comprising the latter technique could be envisioned therefore for the development of a standard method for the detection and characterization of odor compounds from wood. This method could, furthermore, pave the way for an odorant database for wood and wood composites for manufacturers, consumers, and relevant industries.

Author Contributions: The conceptualization of this work was done by E.R.; formal analysis and investigation by V.S.; writing and original draft preparation by V.S.; writing review and editing by E.R.; supervision by E.R. and C.R.-G.; funding acquisition by C.R.-G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Austrian research agency (FFG) in the framework of the COMET (Competence centers for excellent technologies) program (FFG project WOOD, number: 892416).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: All new data is contained within the article.

Acknowledgments: We thank Ewald Srebotnik for providing access to analytical equipment and helpful discussions. Furthermore, the support of the Restek Corporation for this work in the frame of the Restek Academic Support Program (RASP) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Li, J.; Wu, J.; Lam, F.; Zhang, C.; Kang, J.; Xu, H. Effect of the Degree of Wood Use on the Visual Psychological Response of Wooden Indoor Spaces. *Wood Sci. Technol.* **2021**, *55*, 1485–1508. [CrossRef]
2. Watchman, M.; Potvin, A.; Demers, C.M.H. A Post-Occupancy Evaluation of the Influence of Wood on Environmental Comfort. *Bioresources* **2017**, *12*, 8704–8724. [CrossRef]
3. Rowell, R.M.; Pettersen, R.; Tshabalala, M.A. Cell Wall Chemistry. In *Handbook of Wood Chemistry and Wood Composites*, 2nd ed.; CRC-Press: Boca Raton, FL, USA, 2016; Volume 110, pp. 33–71.
4. Leon, M.; Johnson, B.A. Olfactory Coding in the Mammalian Olfactory Bulb. *Brain Res. Rev.* **2003**, *42*, 23–32. [CrossRef]

5. Zhuang, B.; Cloutier, A.; Koubaa, A. Physical and Mechanical Properties of Oriented Strand Board Made from Eastern Canadian Softwood Species. *Forests* **2022**, *13*, 523. [CrossRef]
6. Jandl, R. Climate-Induced Challenges of Norway Spruce in Northern Austria. *Trees For. People* **2020**, *1*, 100008. [CrossRef]
7. Kovačević, M.; Rieder-Gradinger, C.; Teischinger, A.; Srebotnik, E. Volatile Organic Compounds Emitted from Scots Pine and Norway Spruce Wood. *Eur. J. Wood Wood Prod.* **2022**, *81*, 699–712. [CrossRef]
8. Delahunty, C.M.; Eyres, G.; Dufour, J.P. Gas Chromatography-Olfactometry. *J. Sep. Sci.* **2006**, *29*, 2107–2125. [CrossRef]
9. Culleré, L.; Fernández de Simón, B.; Cadahía, E.; Ferreira, V.; Hernández-Orte, P.; Cacho, J. Characterization by Gas Chromatography-Olfactometry of the Most Odor-Active Compounds in Extracts Prepared from Acacia, Chestnut, Cherry, Ash and Oak Woods. *LWT-Food Sci. Technol.* **2013**, *53*, 240–248. [CrossRef]
10. Faix, O.; Meier, D.; Fortmann, I. Thermal Degradation Products of Wood. *Holz Roh Werkst.* **1990**, *48*, 281–285. [CrossRef]
11. Ishino, K.; Wakita, C.; Shibata, T.; Toyokuni, S.; Machida, S.; Matsuda, S.; Matsuda, T.; Uchida, K. Lipid Peroxidation Generates Body Odor Component Trans-2-Nonenal Covalently Bound to Protein In Vivo. *J. Biol. Chem.* **2010**, *285*, 15302–15313. [CrossRef]
12. Song, S.; Zheng, F.; Tian, X.; Feng, T.; Yao, L.; Sun, M.; Shi, L. Evolution Analysis of Free Fatty Acids and Aroma-Active Compounds during Tallow Oxidation. *Molecules* **2022**, *27*, 352. [CrossRef]
13. Granström, K.M. Wood Processing as a Source of Terpene Emissions Compared to Natural Sources. *WIT Trans. Ecol. Environ.* **2007**, *101*, 263–272.
14. Breitmaier, E. *Terpene: Aroma, Düfte Pharmaka, Pheromone*, 2nd ed.; Wiley-VCH: Hoboken, NJ, USA, 2005; pp. 3–9.
15. Rosenkranz, M.; Chen, Y.; Zhu, P.; Vlot, A.C. Volatile Terpenes—Mediators of Plant-to-Plant Communication. *Plant J.* **2021**, *108*, 617–631. [CrossRef]
16. Masyita, A.; Sari, R.M.; Astuti, A.D.; Yasir, B.; Rumata, N.R.; Emran, T.B.; Nainu, F.; Simal-Gandara, J. Terpenes and Terpenoids as Main Bioactive Compounds of Essential Oils, Their Roles in Human Health and Potential Application as Natural Food Preservatives. *Food Chem. X* **2022**, *13*, 100217. [CrossRef]
17. Schreiner, L.; Bauer, P.; Buettner, A. Resolving the Smell of Wood—Identification of Odour-Active Compounds in Scots Pine (*Pinus sylvestris* L.). *Sci. Rep.* **2018**, *8*, 8294. [CrossRef]
18. Schreiner, L.; Loos, H.M.; Buettner, A. Identification of Odorants in Wood of *Calocedrus decurrens* (Torr.) Florin by Aroma Extract Dilution Analysis and Two-Dimensional Gas Chromatography–Mass Spectrometry/Olfactometry. *Anal. Bioanal. Chem.* **2017**, *409*, 3719–3729. [CrossRef]
19. Belinato, J.R.; Dias, F.F.G.; Caliman, J.D.; Augusto, F.; Hantao, L.W. Opportunities for Green Microextractions in Comprehensive Two-Dimensional Gas Chromatography/Mass Spectrometry-Based Metabolomics—A Review. *Anal. Chim. Acta* **2018**, *1040*, 1–18. [CrossRef]
20. Mayol, A.R.; Acree, T.E. Advances in Gas Chromatography-Olfactometry. In *Gas Chromatography-Olfactometry: The State of the Art*, 1st ed.; Leland, J.V., Schieberle, P., Buettner, A., Acree, T.E., Eds.; American Chemical Society: Washington, DC, USA, 2001; Volume 782, pp. 1–10.
21. Sell, C.S. *Chemistry and the Sense of Smell*, 1st ed.; Wiley & Sons: Hoboken, NJ, USA, 2014; pp. 32–51.
22. Nicolotti, L.; Cordero, C.; Bicchi, C.; Rubiolo, P.; Sgorbini, B.; Liberto, E. Volatile Profiling of High Quality Hazelnuts (*Corylus avellana* L.): Chemical Indices of Roasting. *Food Chem.* **2013**, *138*, 1723–1733. [CrossRef]
23. Rega, B.; Fournier, N.; Guichard, E. Solid Phase Microextraction (SPME) of Orange Juice Flavor: Odor Representativeness by Direct Gas Chromatography Olfactometry (D-GC-O). *J. Agric. Food Chem.* **2003**, *51*, 7092–7099. [CrossRef]
24. Ferracane, A.; Manousi, N.; Tranchida, P.Q.; Zachariadis, G.A.; Mondello, L.; Rosenberg, E. Exploring the Volatile Profile of Whiskey Samples Using Solid-Phase Microextraction Arrow and Comprehensive Two-Dimensional Gas Chromatography-Mass Spectrometry. *J. Chromatogr. A* **2022**, *1676*, 463241. [CrossRef]
25. Engel, W.; Schieberle, P.; Bahr, W.; Bahr, G.; Engel, W.; Bahr, W.; Schieberle, P. Solvent assisted flavour evaporation—A new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. *Eur. Res. Technol.* **1999**, *209*, 237–241. [CrossRef]
26. Sharma, L.K.; Agarwal, D.; Rathore, S.S.; Malhotra, S.K.; Saxena, S.N. Effect of Cryogenic Grinding on Volatile and Fatty Oil Constituents of Cumin (*Cuminum cyminum* L.) Genotypes. *J. Food Sci. Technol.* **2016**, *53*, 2827–2834. [CrossRef] [PubMed]
27. Cheng, Z.; Mannion, D.T.; O'sullivan, M.G.; Miao, S.; Kerry, J.P.; Kilcawley, K.N. Comparison of Automated Extraction Techniques for Volatile Analysis of Whole Milk Powder. *Foods* **2021**, *10*, 2061. [CrossRef] [PubMed]
28. Frank, D.C.; Owen, C.M.; Patterson, J. Solid Phase Microextraction (SPME) Combined with Gas-Chromatography and Olfactometry-Mass Spectrometry for Characterization of Cheese Aroma Compounds. *LWT-Food Sci. Technol.* **2004**, *37*, 139–154. [CrossRef]
29. SPME Fiber Assembly Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS). Available online: https://www.sigmaaldrich.com/AT/en/product/supelco/57348u (accessed on 30 August 2023).
30. SPME Fibers and Arrows. Available online: https://at.vwr.com/store/product/22785727/spme-fibers-and-arrows (accessed on 30 August 2023).
31. Alfeeli, B.; Jain, V.; Johnson, R.K.; Beyer, F.L.; Heflin, J.R.; Agah, M. Characterization of Poly(2,6-Diphenyl-p-Phenylene Oxide) Films as Adsorbent for Microfabricated Preconcentrators. *Microchem. J.* **2011**, *98*, 240–245. [CrossRef]
32. Elmore, J.S.; Erbahadir, M.A.; Mottram, D.S. Comparison of Dynamic Headspace Concentration on Tenax with Solid Phase Microextraction for the Analysis of Aroma Volatiles. *J. Agric. Food Chem.* **1997**, *45*, 2638–2641. [CrossRef]

33. Schreiner, L.; Ortner, E.; Buettner, A. Nosy Confirmation: Reconstitution of the Characteristic Odor of Softwood via Quantitative Analysis and Human Sensory Evaluation. *Anal. Bioanal. Chem.* **2020**, *412*, 1137–1149. [CrossRef]
34. Allenspach, M.; Valder, C.; Flamm, D.; Grisoni, F.; Steuer, C. Verification of Chromatographic Profile of Primary Essential Oil of *Pinus sylvestris* L. Combined with Chemometric Analysis. *Molecules* **2020**, *25*, 2973. [CrossRef]
35. Note 100: Volatile and Semi-Volatile Profile Comparison of Whole Versus Cracked Versus Dry Homogenized Barley Grains by Direct Thermal Extraction. Available online: https://www.sisweb.com/referenc/applnote/app-100.htm (accessed on 27 August 2023).
36. Ankney, E.; Swor, K.; Satyal, P.; Setzer, W.N. Essential Oil Compositions of *Pinus* Species (*P. contorta* Subsp. *contorta*, *P. ponderosa* Var. *ponderosa*, and *P. flexilis*); Enantiomeric Distribution of Terpenoids in *Pinus* Species. *Molecules* **2022**, *27*, 5658. [CrossRef]
37. Szmigielski, R.; Cieslak, M.; Rudziński, K.J.; Maciejewska, B. Identification of Volatiles from Pinus Silvestris Attractive for Monochamus Galloprovincialis Using a SPME-GC/MS Platform. *Environ. Sci. Pollut. Res.* **2012**, *19*, 2860–2869. [CrossRef]
38. Komenda, M.; Kobel, K.; Koppmann, R.; Wildt, J. Comparability of Biogenic VOC Emission Rate Measurements under Laboratory and Ambient Conditions at the Example of Monoterpene Emissions from *Scots pine* (*Pinus sylvestris*). *J. Atmos. Chem.* **2003**, *45*, 1–23. [CrossRef]
39. Alapieti, T.; Castagnoli, E.; Salo, L.; Mikkola, R.; Pasanen, P.; Salonen, H. The Effects of Paints and Moisture Content on the Indoor Air Emissions from Pinewood (*Pinus sylvestris*) Boards. *Indoor Air* **2021**, *31*, 1563–1576. [CrossRef] [PubMed]
40. Dragomanova, S.; Tancheva, L.; Georgieva, M. A review: Biological activity of myrtenal and some myrtenal containing plant essential. *Scr. Sci. Pharm.* **2018**, *5*, 22–33. [CrossRef]
41. Noma, Y.; Asakawa, Y. 3.19—Biotransformation of Monoterpenoids. In *Comprehensive Natural Products II*, 1st ed.; Liu, H.W., Mander, L., Eds.; Elsevier: Amsterdam, The Netherlands, 2010; Volume 3, pp. 669–801.
42. Niu, Y.; Ma, Y.; Xiao, Z.; Zhu, J.; Xiong, W.; Chen, F. Characterization of the Key Aroma Compounds of Three Kinds of Chinese Representative Black Tea and Elucidation of the Perceptual Interactions of Methyl Salicylate and Floral Odorants. *Molecules* **2022**, *27*, 1631. [CrossRef] [PubMed]
43. Kesen, S.; Kelebek, H.; Sen, K.; Ulas, M.; Selli, S. GC-MS-Olfactometric Characterization of the Key Aroma Compounds in Turkish Olive Oils by Application of the Aroma Extract Dilution Analysis. *Food Res. Int.* **2013**, *54*, 1987–1994. [CrossRef]
44. Sharp, M.-E.E. A Comprehensive Screen for Volatile Organic Compounds in Biological Fluids. *J. Anal. Toxicol.* **2001**, *25*, 631–636. [CrossRef] [PubMed]
45. Welke, J.E.; Manfroi, V.; Zanus, M.; Lazarotto, M.; Alcaraz Zini, C. Characterization of the Volatile Profile of Brazilian Merlot Wines through Comprehensive Two Dimensional Gas Chromatography Time-of-Flight Mass Spectrometric Detection. *J. Chromatogr. A* **2012**, *1226*, 124–139. [CrossRef]
46. Giardina, M.; Mccurry, J.D. Comparison of Temperature Programmable Split/Splitless and Cool On-Column Inlets for the Determination of Glycerol and Glycerides in Biodiesel by Gas Chromatography with Flame Ionization Detection. *J. Chromatogr. Sci.* **2016**, *55*, 683–688. [CrossRef]
47. Tsuzuki, S. Higher Straight-Chain Aliphatic Aldehydes: Importance as Odor-Active Volatiles in Human Foods and Issues for Future Research. *J. Agric. Food Chem.* **2019**, *67*, 4720–4725. [CrossRef]
48. Sheridan, B.A.; Curran, T.P.; Dodd, V.A. Biofiltration of N-Butyric Acid for the Control of Odour. *Bioresour. Technol.* **2003**, *89*, 199–205. [CrossRef]
49. Reyes, J.; Toledo, M.; Michán, C.; Siles, J.A.; Alhama, J.; Martín, M.A. Biofiltration of Butyric Acid: Monitoring Odor Abatement and Microbial Communities. *Environ. Res.* **2020**, *190*, 110057. [CrossRef] [PubMed]
50. Toshio, M.; Mlchele Gallagher; George, P.; Wise, P.M. Odor Detection of Mixtures of Homologous Carboxylic Acids and Coffee Aroma Compounds by Humans. *J. Agric. Food Chem.* **2009**, *57*, 9895–9901.
51. Wang, G.; Jing, S.; Song, X.; Zhu, L.; Zheng, F.; Sun, B. Reconstitution of the Flavor Signature of Laobaigan-Type Baijiu Based on the Natural Concentrations of Its Odor-Active Compounds and Nonvolatile Organic Acids. *J. Agric. Food Chem.* **2022**, *70*, 837–846. [CrossRef] [PubMed]
52. Clausen, P.A.; Knudsen, H.N.; Larsen, K.; Kofoed-Sørensen, V.; Wolkoff, P.; Wilkins, C.K. Use of Thermal Desorption Gas Chromatography–Olfactometry/Mass Spectrometry for the Comparison of Identified and Unidentified Odor Active Compounds Emitted from Building Products Containing Linseed Oil. *J. Chromatogr. A* **2008**, *1210*, 203–211. [CrossRef] [PubMed]
53. Feng, Y.; Cai, Y.; Sun-Waterhouse, D.; Cui, C.; Su, G.; Lin, L.; Zhao, M. Approaches of Aroma Extraction Dilution Analysis (AEDA) for Headspace Solid Phase Microextraction and Gas Chromatography-Olfactometry (HS-SPME-GC-O): Altering Sample Amount, Diluting the Sample or Adjusting Split Ratio? *Food Chem.* **2015**, *187*, 44–52. [CrossRef] [PubMed]
54. Grosch, W. Evaluation of the Key Odorants of Foods by Dilution Experiments, Aroma Models and Omission. *Chem. Senses* **2001**, *26*, 533–545. [CrossRef] [PubMed]
55. Zhang, Y.; Stöppelmann, F.; Zhu, L.; Liang, J.; Rigling, M.; Wang, X.; Jin, Q.; Zhang, Y. A Comparative Study on Flavor Trapping Techniques from the Viewpoint of Odorants of Hot-Pressed Rapeseed Oil. *Food Chem.* **2023**, *426*, 136617. [CrossRef]