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Optimization of fiber types in the SPME technique to evaluate volatile organic compounds emitted by meranti (*Schorea* sp.) wood

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Abstract: *Optimization of fiber types in the SPME technique to evaluate volatile organic compounds emitted by meranti (Schorea sp.) wood.* The aim of this study was to select optimal parameters for the determination of volatile organic compounds (VOC) emitted by meranti (*Schorea* sp) wood. Microextraction to the stationary phase from the headspace was applied in order to isolate VOCs. An optimal adsorber (PDMS fiber and Carboxen/PDMS) was selected at extraction time of 45 min and temperature of 40°C. The composition of volatile organic compounds emitted from meranti wood was determined using a gas chromatograph coupled with a mass spectrometer (a DB-5 column, (Supelco, 25 m x 0.25 mm x 1 μm). A total of 18 compounds were identified. The greatest concentration in the mycelium headspace was found for 7 sesquiterpene hydrocarbons and their derivatives such as Copaene, β-Elemene, γ-Muurolene, α-Muurolene, Cadina -1(10),4 diene, α.-Amorphene, Cadalene.

Keywords: Scots pine, meranti wood, HS-SPME, GC-MS, VOC

INTRODUCTION

Exotic wood is currently extensively used as construction material in interior finishings. It is reported that many wood species, particularly exotic, may cause allergies among occupants of facilities, in which it is used. Volatile organic compounds (VOC) emitted by wood constitute one of the sources of allergies. These compounds are found in trace amounts; however, despite their low concentrations they reduce comfort and hygienic standard of the facilities occupied by people. At present it is attempted to determine VOCs in order to correlate them with specific diseases. A considerable analytical problem is connected with the appropriate identification of the entire VOC spectrum due to the fact that they are found in a mixture of various compounds and they are present in trace amounts. For this reason when assaying them it is important to extract and concentrate them. Several VOC extraction and concentration methods are applied, such as liquid-liquid extraction, liquid-liquid extraction with ultrasound, simultaneous stream distillation extraction, solid-phase extraction (Cai et al. 2001). Solid-phase microextraction (SPME) is an extensively used method in such analyses. This technique was presented for the first time by Arthur and Pawliszyn in 1990 (Alpendura 2000) and at present it is a method of choice in the isolation of volatile compounds. Its advantages include short extraction time, no necessity to use solvents and thus low cost, as well as simplicity of the analytical procedure. SPME consists in adsorption of compounds on the stationary phase, the absorber fiber, which is a thin, quartz fiber covered with a special polymer. Depending on the chemical character of this polymer compounds may be selectively isolated according to the principle “like with like”, i.e. polar compounds are effectively extracted on fibers coated with polymers with polar functional groups. For this reason adsorbers with various chemical and physical properties are used. In such studies it is crucial to select an appropriate adsorber, which is dependent to a considerable degree on the chemical properties of the analyte. Desorption of compounds adsorbed on the SPME fiber occurs in the injection port of the gas chromatograph under the influence of high temperature. Next the analysis was run with the use of a gas chromatograph coupled with a mass spectrometer.

The aim of this study was to optimize adsorbers applied in SPME to assess volatile organic compounds emitted by merani (*Schorea* sp) wood.

MATERIALS AND METHODS

Experimental material comprised meranti wood (*Schorea* sp.). It is a species very often used in interior design, furniture manufacture, joinery, boat making and even production of musical instruments. To date limited information has been available on VOC emissions by that wood species. Wood was provided directly by its importer. Samples of 30 × 15 × 5 mm were prepared (the first dimension along the grain, while the last - tangential). Prior to analyses wood was conditioned in a chamber at 21°C and relative humidity of 75%. Optimization of the SPME technique consisted in the selection of 5 SPME fibers by Supelco differing in the stationary phase: 100 μm polydimethylsiloxane (PDMS), 75 μm carboxen/polydimethylsiloxane (CAR/PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) 85 μm polyacrylate (PA). Detailed characteristics of adsorbers is presented in Table 1.

Table 1. Fibre coatings commercially available for SPME: use, some properties and applications

Fibre coating	Film thickness (mm)	Recommended use	Maximum injector temperature (°C)	Applications
Poly(dimethylsiloxane) (PDMS)	100	GC, HPLC	280	Nonpolar organic compounds such as VOCs, polycyclic aromatic hydrocarbons, organochlorine pesticides
Polyacrylate (PA)	85	GC, HPLC	320	Polar organic compounds such as triazines, organophosphorous pesticides and phenols
Poly(dimethylsiloxane)–divinylbenzene (PDMS–DVB)	65	GC, HPLC	270	Aromatic hydrocarbons, aromatic amines, VOCs
Carboxen–poly(dimethylsiloxane) (Carboxen–PDMS)	75	GC	320	VOCs, hydrocarbons
Carbowax–divinylbenzene (CW–DVB)	65	GC	260	Polar organic compounds such as alcohols, ketones, nitroaromatics

Extraction temperature of 40°C and time of 45 min were applied, since they had been previously optimized in view of further studies on moulds growing on meranti wood (Cofta 2010).

Analysis of volatile compounds emitted by meranti comprised qualitative analysis conducted using a gas chromatograph Trace 1300 (Thermo Scientific) with a DB-5 column (30 m × 0.25 mm × 0.25μm) by J&W Scientific. Temperature at the injection port was 260°C, while fiber desorption lasted for 5 min in the splitless mode. Separation was run at the programmed temperature: 35°C for 1.5 min, followed by an increase in temperature of 6°C/min to 200°C and 200°C were maintained for 5 min. Helium at a flow rate of 60 kPa was used as a carrier gas. Identification was run using a mass spectrophotometer, in which the interface temperature was 200°C, the source temperature was 230°C and ionization energy was 70eV. Volatile compounds were identified by comparing mass spectra of analyzed compounds with

spectra given in available mass spectrum libraries (NIST 98, Xcalibur, Flavornet, NIST Chemistry WebBook, Adams 2007).

RESULTS AND DISCUSSION

The criterion considered in the evaluation of adsorber suitability for the isolation of VOCs emitted from meranti wood was connected with the amount of isolated compounds and the area of the five greatest peaks corresponding to the dominant compounds emitted by meranti. These compounds were preliminarily selected based on literature studies, which was confirmed by the preformed chemical analyses (Nguyen 1974, Ishikawa at al. 2009, Mulyono 2010).

The first stage was to determine compounds emitted by meranti. Isolated and determined volatile organic compounds are given in Table 2. The greatest number of 18 compounds was isolated using the Carboxen/PDMS fiber, followed by PDMS, PDMS/DVB and PA fibers, on which 14, 13 and 11 compounds were extracted. The main determined compounds were sesquiterpenes. The greatest concentration in the mycelium headspace was recorded for 7 sesquiterpene hydrocarbons and their derivatives, such as Copaene, β-Elemene, γ-Muurolene, α-Muurolene, Cadina -1(10),4 diene, α.-Amorphene and Cadalene.

Table 2. Results of GC/MS analysis of VOC of meranti

Compound	CAS	Fibre coating			
		PDMS	PA	PDMS/DVB	Carboxen/PDMS
Formic acid	64-18-6				*
Acetic acid	64-19-7		*		*
3-furaldehyde	498-60-2				*
Tridecane	629-50-5				*
á-Cubene	17699-14-8				*
á-Guaiene	3691-12-1	*			
Unidentified sesquiterpene					*
α-Copaene	3856-25-5	*		*	*
Helminthogermacrene	75023-40-4	*		*	
β-Elemene	515-13-9		*	*	*
Dodecanal	112-54-9			*	
Unidentified sesquiterpene		*			*
γ-Muurolene	30021-74-0	*	*	*	*
α.-Amorphene	483-75-0	*	*	*	*
α-Muurolene	31983-22-9	*	*		*
Azulene	22567-17-5	*			
Cadinene	39029-41-9	*	*	*	*
Cadina -1(10),4 diene	483-76-1	*	*	*	*
Isolongifolene	156747-45-4	*		*	
Unidentified sesquiterpene				*	*
á-Calacorene	21391-99-1	*	*		*
Tau-Muurolol	19912-62-0		*		
á-Cadinol	481-34-5		*		
Unidentified sesquiterpene		*		*	

Unidentified sesquiterpene				*	*
Cadalene	483-78-3	*	*	*	*

The second criterion for the selection of appropriate fiber was based on the measurement of area of five peaks of isolated volatile compounds emitted from meranti wood (tab. 3). Large peak areas provide more accurate spectra and make it possible to reduce concentrations at which these compounds may be assayed.

Table 3. Percentages of selected compounds expressed by the ratio of peak area of a given compound to the greatest peak area for selected compounds

Compound name	Fiber coating			
	PDMS	PA	PDMS/DVB	Compound
Copaene	25,64	0,02	0,03	3,04
β-Elemene	88,19	0,05	0,16	100,00
γ-Muurolene	38,46	0,04	0,07	19,51
α-Muurolene	69,06	0,05	0,17	31,92
Cadina -1(10),4 diene	93,86	0,08	0,24	33,12

Based on the area below the peaks of selected compounds it may be stated that PDMS and Carboxen/PDMS fibers are best suitable for the determination of VOCs emitted from meranti wood.

CONCLUSION

The application of SPME to determine VOCs emitted by meranti wood facilitates their easy identification.

Among the five tested adsorbers PDMS and Carboxen/PDMS fibers proved to be the best. A total of 18 and 14 compounds released by wood were identified on these fibers.

Assuming areas under the peaks of five selected compounds as a criterion, adsorbers made from PDMS and Carboxen/PDMS also turned out to be the best.

The greatest concentrations in the mycelium headspace were recorded for 7 sesquiterpene hydrocarbons and their derivatives such as Copaene, β-Elemene, γ-Muurolene, α-Muurolene, Cadina -1(10),4 diene, α.-Amorphene and Cadalene.

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Streszczenie: *Optymalizacja włókien w technice SPME do oceny lotnych związków organicznych emitowanych przez drewno merani (Schorea sp.).* Celem przeprowadzonych badań był dobór optymalnych parametrów oznaczania lotnych związków organicznych (VOC) emitowanych przez drewno meranti. Do wyodrębnienia VOC zastosowano mikroekstrakcję do fazy stacjonarnej z fazy nadpowierzchniowej. Dobrano optymalny adsorber (włókno PDMS i Carboxen/PDMS) przy czasie ekstrakcji 45 min i temperaturze 40^{o}C. Oznaczenie składu lotnych związków organicznych emitowanych z drewna meranti dokonano za pomocą chromatografu gazowego sprzężonego ze spektrometrem mas GC/MS (kolumna DB-5, Supelco, 25 m x 0,25 mm x 1 μm). Wyodrębniono 18 związków. Największe stężeni w fazie nadpowierzchniowej grzybni stwierdzono dla 7 węglowodorów seskwiterpenowych i ich pochodnych takich jak: Copaene, β-Elemene, γ-Muurolene, α-Muurolene, Cadina -1(10),4 diene, α.-Amorphene, Cadalene.

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