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APPLICATION OF COMBINED SPME AND GC/MS TECHNIQUES IN INVESTIGATIONS ON THE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM SURFACES FINISHED WITH LACQUER PRODUCTS USED IN FURNITURE INDUSTRY

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SYNOPSIS. This paper presents results of experiments on volatile organic compound emissions from waterborne and nitrocellulose lacquer coatings applied onto oak wood samples. Volatile organic compounds were analysed using the technique of gas chromatography coupled with mass spectrometry. Volatile organic compounds were identified employing the technique of solid phase microextraction (SPME) which is utilised in various scientific disciplines but so far has not been used in the analysis of volatile organic compounds present in lacquer products. The following three types of fibres were used in the performed experiments: Polydimethylsiloxane (PDMS), Polydimethylsiloxane/Divinylbenzene (PDMS/DVB), Carboxen$^{\mathrm{TM}}$/Polydimethylsiloxane (CAR/PDMS) with the aim to compare their sorption properties and determine their usefulness in investigations on volatile organic compound emissions from currently manufactured furniture.

KEY WORDS: volatile organic compounds (VOCs), lacquer coatings, solid phase microextraction (SPME)

INTRODUCTION

Finishing materials, as well as elements of interior furnishing, including furniture and other wood and wood-based products currently used in the construction and building industry, can release into the air a wide range of volatile organic compounds (VOC) which may affect negatively the health of their users (Risholm-Sundman et al. 1998, Wiglusz et al. 2002, Gaca and Dziewanowska-Pudliszak 2005, Stachowiak-Wencek and Prądzyński 2005).

VOC are determined most commonly using the method of gas chromatography coupled with mass spectrometry. Frequently, due to low or even very low concentrations of compounds emitted by the investigated elements, it is necessary to employ suitable techniques of sample collection allowing their enrichment. Among the most common techniques of sample collection used in wood industry is the adsorption of volatile organic compounds onto special sorbents, among others, on Tenax TA or active carbons through which a definite volume of air taken from a chamber in which the examined elements had been placed was passed. Depending on its size, the chamber method can be used to examine single elements or entire furniture sets. This method gives good results but it requires expensive, special equipment and is time consuming.

The solid phase microextraction (SPME) can become a competitive technique of VOC sample collection due to its simplicity, rapidity and low costs. This is a solvent-free method realised with the assistance of a simple, portable device which allows non-invasive identification of volatile compounds at very low concentrations of the order of 5-50 ppt (WITKIEWICZ 2001). It makes it possible to employ low temperatures of VOC extraction which does not result in the break up of isolated compounds and allows the examination of emission levels in conditions similar to those found in rooms in which furniture is used. The technique is based on the adsorption of compounds on the surface of an optical fibre covered with a phase. Phases covering fibres are characterised by a different polarity and properties allowing selective adsorption of compounds on their surface (JELEŃ and WĄSOWICZ 2000). Generally speaking, the SPME analytic procedure involves two stages. During the first stage, the fibre is brought into contact with the sample in the gaseous or liquid phase which leads to the sorption of analytes. In the second stage, the fibre is placed in the injector of the gas chromatographer and, in conditions of high temperature, released analytes are transferred into the chromatographic column. The SPME technique was developed by Pawliszyn and co-workers in 1990, primarily, to be employed in the analyses of environmental contamination (OUYANG and PAWLISZYN 2006). However, it was employed in many different fields of science, among others, in food industry to determine volatile compounds from vegetables and fruits (MATICH et AL. 1996, SONG et AL. 1998), for the isolation of metabolites derived from fungi (JELEŃ 2003, ZAWIRSKA-WOJTASIAK 2004) as well as in forensic medicine to determine drugs in blood (WIERGOWSKI et AL. 2002).

Despite many advantages, so far the above technique has not been applied in VOC analyses in wood industry.

Therefore, the main aim of the performed investigations was to determine the usefulness of the SPME technique in experiments on VOC emissions from currently manufactured furniture. The scope of investigations included: experiments on VOC emissions from oak wood samples finished with lacquer products currently used in the furniture sector and determination of the usefulness of SPME fibres coated with different phases for the extraction of VOCs released from furniture surfaces.

MATERIAL AND METHODS

The investigations were carried out on two colourless, single-component lacquers intended as finishers for different wood species: waterborne and nitrocellulose. Properties of the lacquers used in the experiments are presented in Table 1.

Table 1. Properties of the applied lacquers (on the basis of manufacturers' data)

Parameters	Waterborne	Nitrocellulose
Content of solids [%]	38	24
Binding agents	acrylic dispersion	modified acrylic resins, cellulose esters
Solvents	water	alcohols, esters, aromatic hydrocarbons
Density [g/cm^3]	1.05	0.92
Commercial viscosity at temperature of 21 ±1°C [s]*	57	48
Working viscosity at temperature of 21 ±1°C [s]*	23	22

*Value measured with the assistance of the Ford's cup No. 4.

Approximately 200 ±10 g/m^2 lacquers selected for investigations were applied onto oak (*Quercus* sp.) wood sample surfaces measuring 40 × 12 × 12 mm using for this purpose a brush. The moisture content of the finished wood determined with the assistance of the oven-dry method was at the level of about 5%, whereas its density determined using the stoichiometric method in accordance with the PN-77/D-04101 standard amounted to approximately 640 kg/m^3.

Samples treated with the examined lacquers were air-seasoned for the period of 24 hours at temperature of about 22 ±1°C which, according to the manufacturer's certificate, allowed them to dry sufficiently. After this period, samples were placed in vials of about 40 ml volume and thermostated for 20 min at the temperature of 22°C (typical for apartment conditions). Then fibres covered with three different phases were introduced into the gaseous phase:

– PDMS (Polydimethylsiloxane) of 100 µm film thickness
– PDMS/DVB (Polydimethylsiloxane/Divinylbenzene) of 65 µm film thickness
– CAR/PDMS (Carboxen^{TM}/ Polydimethylsiloxane) of 75 µm film thickness.

Fibres used in the presented experiments derived from Supelco Inc. Company (Bellefonte, PA), and were conditioned prior to analyses according to the manufacturer's recommendations. The extraction of volatile organic compounds released by the examined materials was carried out for 25 min.

Volatile compounds were analysed on a gas chromatograph Thermoquest Trace 2000 together with mass spectrometer working on a DB-5MS column (30 m × 0.25 mm, 0.25 µm).

The desorption of compounds adsorbed on fibres was carried out in the hot injection port of the chromatographer at the temperature of 240°C for 1 min, in splitless mode.

The GC temperature program was started at 40°C for 2 min, then increased to a rate of 7°C·min^{-1} to 200°C, further 10°C·min^{-1} to 230°C and stayed at a temperature of 230°C for 5 min.

The identification of volatile compounds was carried out on the basis of comparison of mass spectra of the identified compounds with the spectra found in the available spectrum library NIST MS Serach – program version 1.7 and later confirmed by collating mass spectra and retention times of the identified compounds with the spectra and retention times of the appropriate standards.

All mass spectra were obtained following the ionisation of molecules by electrons of 70 eV energy (EI).

Investigations on the VOC emissions were carried out in two stages: 24 and 48 hours after the application of lacquer coatings onto the surface of oak wood.

RESULTS AND DISCUSSION

On the base of the research, three types of fibres showed different ability to extract volatile compounds.

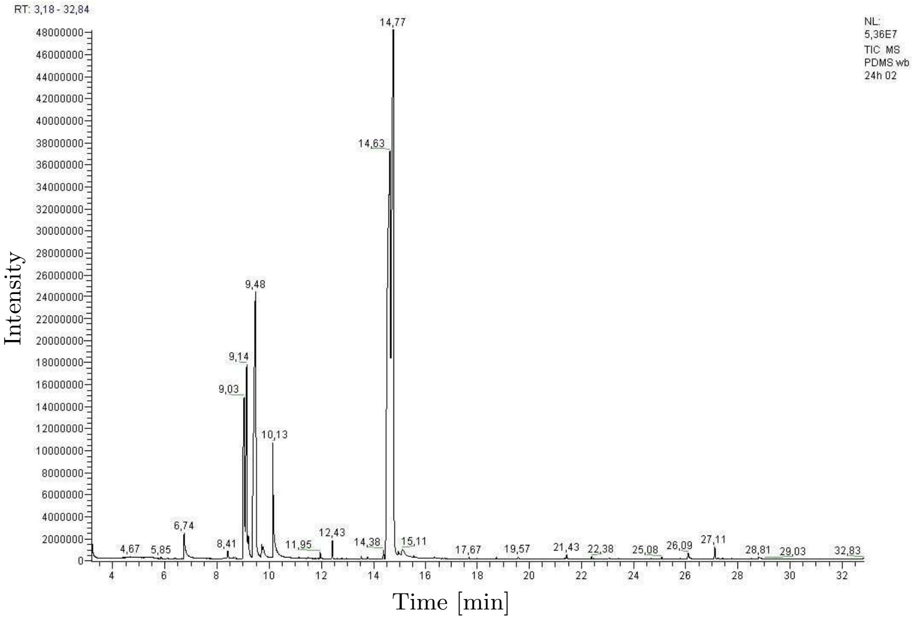
In the case of coatings obtained from the waterborne lacquer, the greatest peak areas were obtained using PDMS/DVB fibre. During the first stage of experiments, i.e. 24 hours after the application of lacquers onto sample surfaces, the amount of compounds adsorbed on the surface of the PDMS/DVB fibre (637 mln area counts) exceeded by about 24% the amount of compounds extracted by the CAR/PDMS fibre (485 mln area counts) and by over 6% the quantity of compounds isolated using the PDMS fibre (597 mln area counts).

On the other hand, in the case of coatings from the nitrocellulose lacquer, the best results, both with regard to peak intensity of isolated compounds, were obtained with the assistance of the CAR/PDMS fibre for which the largest peak areas of the emitted compounds were observed (133 mln area counts). The worst affinity for the volatile compounds released by nitrocellulose coatings was determined for fibre covered by the polydimethylsiloxane which did not adsorb hexanal emitted by these coats. The total quantity of compounds extracted from the gaseous phase using the PDMS fibre (4.7 mln area counts) was by over 28 times smaller than the amount isolated using the CAR/PDMS fibre.

Studies of fibres covered with phases of different properties allowed to observe considerable diversification of the isolation capabilities of the volatile organic compounds emitted by the examined oak wood samples. The chromatograms, presented in Figures 1 and 2 obtained during the first stage of experiments, i.e. 24 hours after the application of lacquer coatings onto sample surfaces, confirmed such diversity.

Using fibres covered by different types of phases, the same compounds were identified. However, the choice of fibre exerted a significant impact on the quantity of compounds isolated from the gaseous phase with SPME technique.

Table 2 presents a list of compounds isolated by the SPME technique with the assistance of three types of fibres from coatings of waterborne lacquer 24 and a)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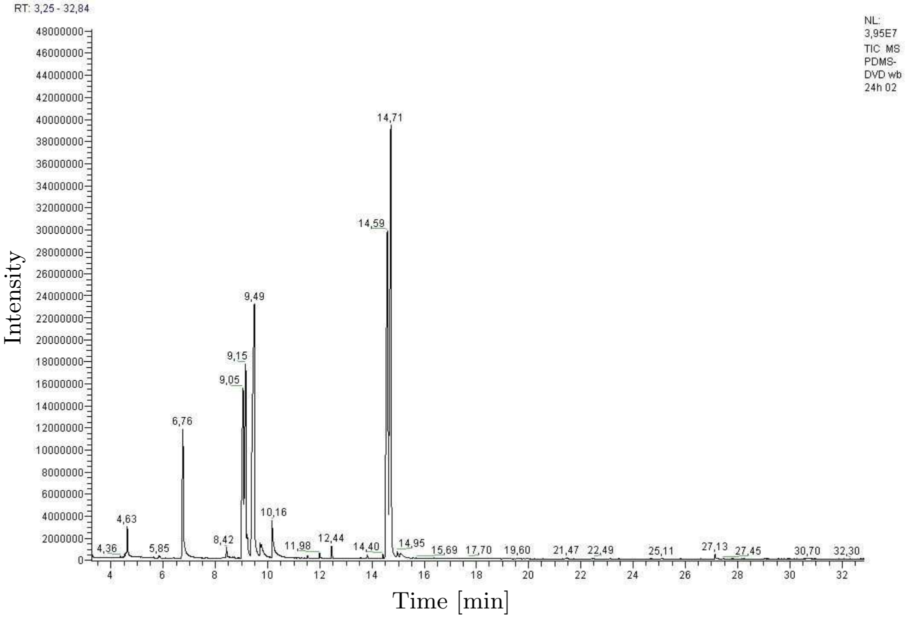
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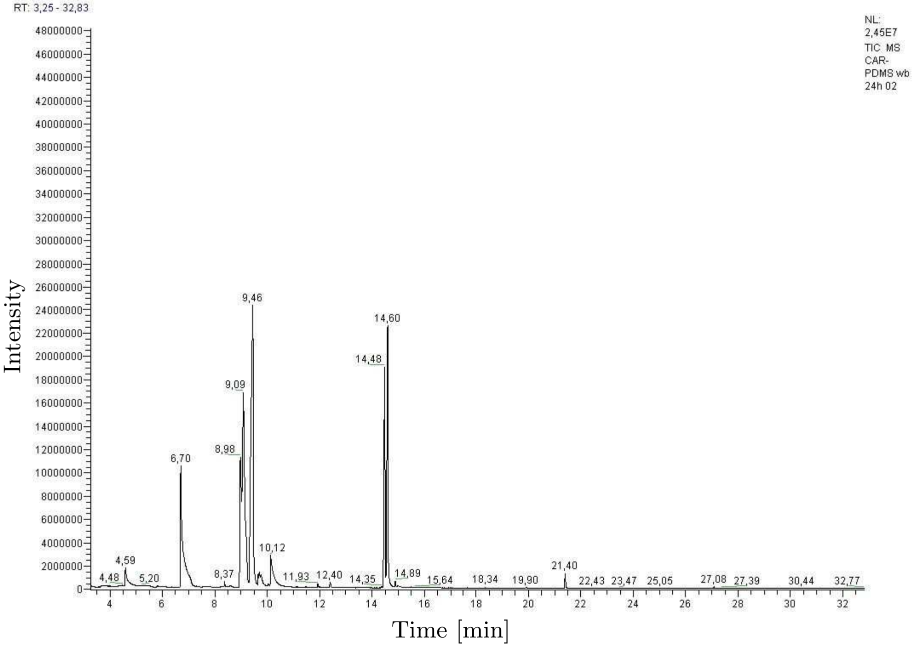
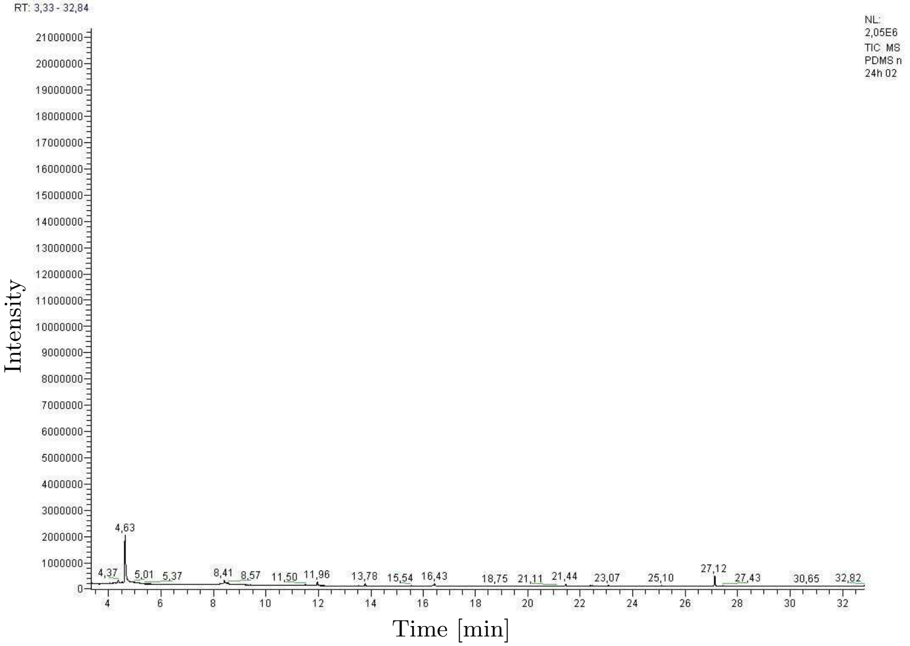


Fig. 1. Chromatograms of volatile organic compounds, adsorbed on: a – PDMS, b – PDMS/DVB, c – CAR/PDMS fibres, emitted after 24 hours by waterborne lacquer coatings applied on oak wood samples

a)



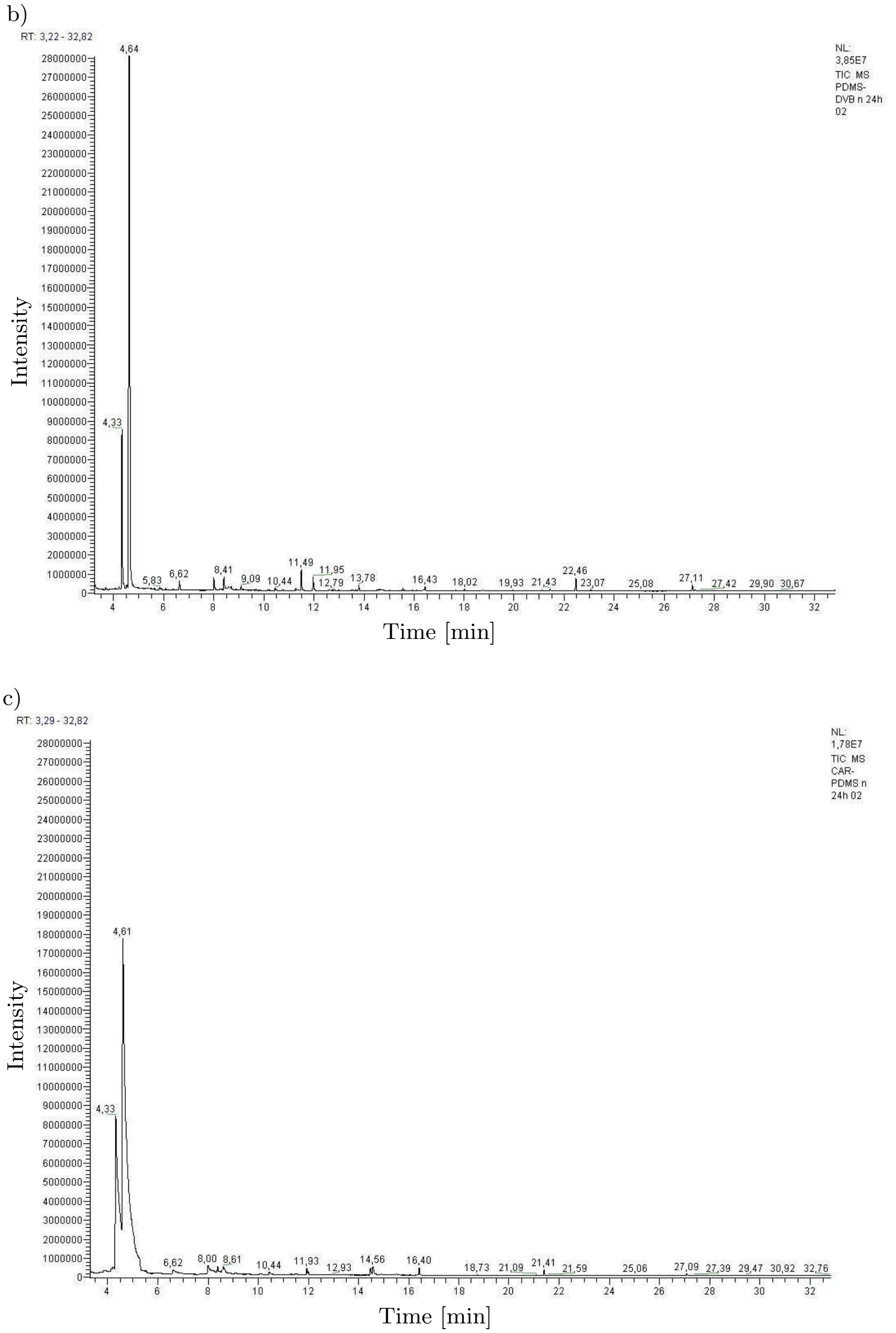


Fig. 2. Chromatograms of volatile organic compounds, adsorbed on: a – PDMS, b – PDMS/DVB, c – CAR/PDMS fibres, emitted after 24 hours by nitrocellulose lacquer coatings applied oak wood samples

Table 2. Volatile organic compounds extracted from waterborne lacquer coatings applied on oak wood, 24 and 48 hours after lacquer application, using various SPME fibres. Percentage of isolated compounds expressed as the ratio of peak area of detected substance to the total peak area of all compounds

	Compound	Rt$^{\#}$	Peak area [%]/Fibre type					
			24 h			48 h		
			PDMS	PDMS/DVB	CAR/PDMS	PDMS	PDMS/DVB	CAR/PDMS
1	Acetic acid. butyl ester	4.62	–	1.26	1.80	–	0.30	0.94
2	Ethylbenzene	5.65	–	0.03	–	–	0.02	–
3	m-xylene	5.84	0.02	0.12	0.18	–	0.08	0.07
4	p-xylene	6.40	0.01	0.03	0.02	–	0.02	–
5	Ethanol. 2-butoxy	6.73	0.98	6.93	9.81	0.93	6.87	7.55
6	2-propanol. 1-(2-methoxy-1-methylethoxy)	9.01	7.29	9.79	9.17	8.06	11.02	8.64
7	Dipropylene glycol methyl ether. isomer	9.11	7.70	10.19	21.46	8.55	11.11	23.30
8	2-propanol. 1-(2-methoxypropoxy)	9.49	17.82	21.18	29.18	19.84	24.05	31.54
9	2-pyrrolidone. 1-methyl	10.13	2.27	2.19	2.90	2.34	0.05	3.44
10	Acetic acid. 2-ethylhexyl ester	12.42	0.31	0.34	0.30	0.28	0.19	0.23
11	Dipropylene glycol	14.58	30.31	22.61	11.48	27.62	21.26	10.98
12	2-propanol. 1-(1-methyl-2-(2-propenyloxy)ethoxy)	14.71	33.29	25.33	13.70	32.38	25.02	13.31
Total peak area of all detected compounds*			$5.97 \cdot 10^8$	$6.37 \cdot 10^8$	$4.85 \cdot 10^8$	$3.96 \cdot 10^8$	$5.52 \cdot 10^8$	$3.35 \cdot 10^8$

*Mean values from three air samples did not differ by more than 10%.

Rt$^{\#}$, retention time (min).

48 hours from the moment of their application onto the surface of oak wood. Waterborne lacquer coatings released compounds belonging to: glycols, esters, ketones and aromatic hydrocarbons. The dominant group of compounds emitted by oak wood samples finished with the waterborne product comprised glycols. After 24 hours lacquer application, their share in the total emission, depending on the type of the applied fibre, ranged from 94.8% to 97.4%. The content of glycols, expressed as total peak areas observed from evaluated fibres was from 459 (CAR/PDMS fibre) to 612 mln area counts (PDMS/DVB fibre). Their highest amount was adsorbed on the surface of fibre treated with polydimethylsiloxane and divinylbenzene.

On the other hand, coatings of the examined nitrocellulose lacquer 24 hours after their application onto the surface of oak wood emitted only the following two compounds: butyl acetate and hexanal. Detailed results presenting quantities of the compounds adsorbed on individual fibres from the nitrocellulose lacquer are presented in Table 3.

During the first stage of investigations, depending on the type of the fibre applied in the experiments, butyl acetate constituted from 65.8% to 100% of the total emission. The CAR/PDMS fibre adsorbed by about 11% higher quantities of butyl acetate than the PDMS/DVB fibre. The fibre treated by the polydimethylsiloxane were characterised by the worst affinity for compounds released by the nitrocellulose coatings. Nearly 19 times less butyl acetate was extracted using the PDMS fibre than with the assistance of the CAR/PDMS fibre. In addition, no hexanal – the second compound emitted by the nitrocellulose coatings – was adsorbed on the surface of the PDMS fibre. From among fibres used in the experiments, the highest quantities of hexanal were isolated with the assistance of the CAR/PDMS fibre.

The investigations carried out 48 hours after finishing the examined materials with the selected lacquer products revealed that the quantity of VOCs emitted by these materials declined significantly in relation to the quantities determined during the first stage of the experiment.

Figure 3 presents results illustrating changes in the total amount of VOC emitted by the examined samples 24 and 48 hours after treatment with the experimental finishing materials depending on the type of the applied fibre.

Oak wood samples finished with the waterborne lacquer showed a decline of the total VOCs emissions depending on the type of the applied fibres ranging from 13% for the PDMS/DVB fibre to 34% for the PDMS fibre. The 13% decrease in emitted compounds was determined in the case of fibre which exhibited the highest affinity for compounds released by samples treated with the tested waterborne product. Analysing individual groups of compounds isolated from the gaseous phase with the assistance of the SPME technique, it was found that their concentrations, depending on the type of the applied fibres, decreased as follows: for esters – from 39 to 73%, for ketones – from 18 to 97%, aromatic hydrocarbons – from 41% to below the limit of determination. On the other hand, for glycols emitted during the first stage of investigations at the highest quantities the decrease ranged from 10 to 33%.

Table 3. Volatile organic compounds extracted from nitrocellulose lacquer coatings applied on oak wood, 24 and 48 hours after lacquer application, using various SPME fibres. Percentage of isolated compounds expressed as the ratio of peak area of detected substance to the total peak area of all compounds

	Compound	Rt$^{\#}$	Peak area [%]/Fibre type					
			24 h			48 h		
			PDMS	PDMS/DVB	CAR/PDMS	PDMS	PDMS/DVB	CAR/PDMS
1	Hexanal	4.33	0.00	19.12	34.20	–	52.14	55.91
2	Acetic acid, butyl ester	4.62	100.00	80.88	65.80	100.00	47.86	44.09
Total peak area of all compounds*			$4.68 \cdot 10^6$	$96.1 \cdot 10^6$	$133 \cdot 10^6$	$2.72 \cdot 10^6$	$47.1 \cdot 10^6$	$115 \cdot 10^6$

*Mean values from three air samples did not differ by more than 10%.

Rt$^{\#}$, retention time (min).

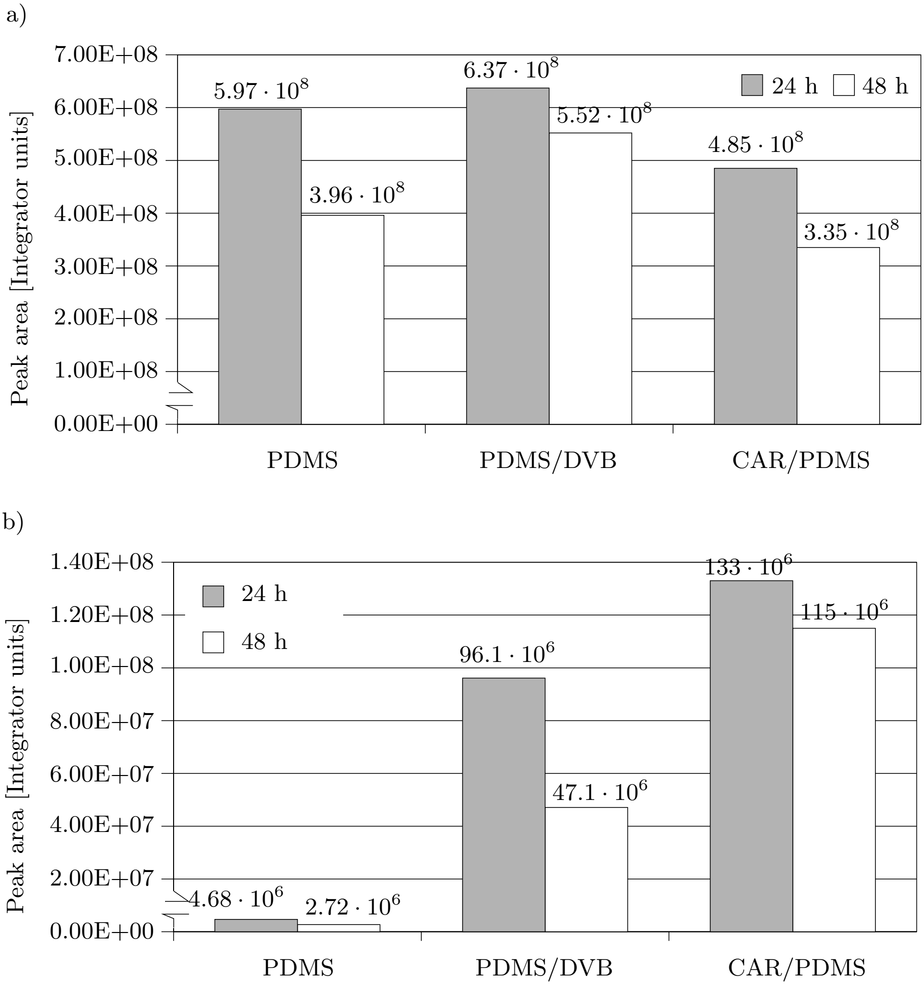


Fig. 3. Comparison of total amount of VOC released by oak wood samples 24 and 48 hours after treatment with: a – waterborne lacquer, b – nitrocellulose lacquer depending on the type of the applied fibre

Quantities of volatile organic compounds released by nitrocellulose coatings on oak wood in the course of the second stage of experiments decreased from 14% for CAR/PDMS fibre to 51% for the PDMS/DVB fibre. Similarly to the first stage of experiments, also in the course of the second stage, the highest quantities of VOCs emitted from nitrocellulose lacquer coatings were adsorbed by the CAR/PDMS fibre. In comparison with the PDMS/DVB fibre, the fibre covered by modified active carbon layer exhibited a greater affinity both for butyl acetate and hexanal emitted by these coatings.

Analysing individual compounds released by the examined materials, it was found that emissions of the majority of them decreased in the course of the first 48 hours after their application onto the surface of the experimental wood samples.

The only exception was hexanal released from the coatings of nitrocellulose lacquer which exhibited higher concentrations during the second stage of investigations than in the first one. Depending on the type of the applied fibre, the amount of hexanal emitted by samples finished with the nitrocellulose lacquer increased during 24 hours by 34 to 41%.

Different quantities of the identified volatile compounds obtained employing different types of fibres appear to confirm the possibility of selective extraction of volatile compounds with the assistance of the SPME technique. According to the manufacturer's opinion, when selecting the fibre, it is advisable to follow the principle that "similar is dissolved in similar", i.e. non-polar analytes are extracted more effectively to the non-polar fibre coating, whereas polar analytes – to the polar coating (Theodoridis et al. 2000). Fibres selected for the described experiments were covered both by a non-polar phase (PDMS) and bipolar phases (PDMS/DVB, CAR/PDMS) (Venkatachalam 1999, Zygmunt et al. 2007). The PDMS fibres, covered by polydimethylsiloxane, i.e. non-polar phase, serve mainly to extract non-polar compounds. Fibres covered by a layer of active carbon – Carboxen which utilise for the adsorption active centres situated on its surface were developed, primarily, for the analysis of low-molecular volatile compounds (Jeleń 2003). The most universal and sensitive fibre which reached the state of equilibrium during the shortest time was the fibre manufactured from polydimethylsiloxane and divinylbenzene (PDMS/DVB). According to the manufacturer, fibres covered by mixed phases, i.e. PDMS/DVB and CAR/DVB are intended mostly for the extraction of very volatile compounds (Theodoridis et al. 2000).

Bearing in mind properties of the identified compounds and remembering the above mentioned principle, mixed fibres appear to be most suitable for the extraction of VOCs emitted by the examined materials.

CONCLUSIONS

1. The combination of the solid phase microextraction technique with gas chromatography and mass spectrometry makes it possible to distinguish profiles of volatile organic compounds released by furniture surfaces.
2. The fibre choice exerted a significant influence on the quantity of extracted compounds and had a much smaller influence on their profile. The best results with regard to both peak intensity as well as the amount of the isolated compounds for samples finished with waterborne lacquer coatings were obtained in the case of the PDMS/DVB fibre. On the other hand, in the case of samples finished with the nitrocellulose lacquer, the CAR/PDMS fibre showed the highest sensitivity to the isolated compounds.
3. Wood samples treated with the tested waterborne product emitted a wider spectrum of volatile compounds than samples finished with the nitrocellulose lacquer. In profiles of volatile compounds released by waterborne coatings,

glycols were identified most commonly which, during the first stage of experiments and depending on the type of the applied fibre, constituted from 94.8 to 97.4% of all the emitted compounds, whereas during the second stage – from 95.3 to 99.3%. On the other hand, after 24 hours the nitrocellulose coatings released the highest amounts of esters. Their content in the total emissions ranged from 65.8 to 100%. After 48 hours in the case of PDMS/DVB and CAR/PDMS fibres highest amounts of emitted compounds constituted aldehydes. Their range was from 52.1 to 55.9%.

4. In the course of 48 hours following the treatment of the oak wood samples with the tested lacquers, a considerable drop in the emission levels of VOCs was observed. Depending on the type of the applied fibre, this decline ranged from 13 to 34% in the case of samples finished with the waterborne product and from 14 to 51% in samples treated with the nitrocellulose lacquer.

REFERENCES

Gaca P., Dziewanowska-Pudliszak A. (2005): Volatile organic compounds (VOC) emission of selected wood species and other materials applied in furniture manufacture. Drewno-Wood 48 (173): 119-125.

Jeleń H. (2003): Use of solid phase microextraction (SPME) for profiling fungal volatile metabolites. Lett. Appl. Microbiol. 36: 263-267.

Jeleń H., Wąsowicz E. (2000): Zastosowanie technik analizy fazy nadpowierzchniowej (Headspace) w analizie związków lotnych żywności. Aparatura Badawcza i Rozwojowa. Wyd. Centralny Ośrodek Badawczo-Rozwojowy Aparatury Badawczej i Dydaktycznej COBRABiD, Warszawa.

Matich A.J., Rowan D.D., Banks N.H. (1996): Solid phase microextraction for quantitative headspace sampling of apple volatiles. Anal. Chem. 68 (23): 4114-4118.

Ouyang G., Pawliszyn J. (2006): SPME in environmental analysis. Anal. Bioanal. Chem. 386: 1059-1073.

PN-77/D-04101: Drewno. Oznaczanie gęstości.

Risholm-Sundman M., Lundgren M., Vestine E., Herder P. (1998): Emissions of acetic acid and other volatile organic compounds from different species of solid wood. Holz Roh-u. Werkst. 56 (2): 125-129.

Song J., Fan L., Beaudry R.M. (1998): Application of solid phase microextraction and GC/TOFMS for rapid analysis of flavor volatiles in tomato and strawberry fruits. J. Agric. Food Chem. 46 (9): 3721-3726.

Stachowiak-Wencek A., Prądzyński W. (2005): Emission of volatile organic compounds from furniture surfaces finished with lacquer coatings. Acta Sci. Pol. Silv. Colend. Ratio Ind. Lignar. 4 (2): 177-185.

Theodoridis G., Koster E.H.M., de Jong G.J. (2000): Solid-phase microextraction for the analysis of biological samples. J. Chromatogr. B 745: 49-82.

Venkatachalam M. (1999): Properties of commercial SPME coatings. Applications of Solid Phase Microextraction. Ed. J. Pawliszyn. Royal Society of Chemistry, UK.

Wiergowski M., Reguła K., Szpiech B., Sein Anand J., Waldman W. (2002): Śmiertelne intoksykacje parametoksyamfetaminą na terenie województwa pomorskiego oraz możliwość szybkiego i miarodajnego diagnozowania zatruć metodą mikroekstrakcji do fazy stałej (SPME). Alkoh. Narkom. 15 (1): 37-46.

Wiglusz R., Nikel G., Igielska B., Sitko E. (2002): Volatile organic compounds from particleboard veneered with decorative paper foil. Holzforschung 56 (1): 11-26.

Witkiewicz Z. (2001): Podstawy chromatografii. WN-T, Warszawa.

Zawirska-Wojtasiak R. (2004): Optical purity of (R)-(−)-1-octen-3-ol in the aroma of various species of edible mushrooms. Food Chem. 86: 113-118.

Zygmunt B., Zaborowska A., Świłatowska J., Namieśnik J. (2007): Solid phase microextraction combined with gas chromatography – a powerful tool for the determination of chemical warfare agents and related compounds. Curr. Org. Chem. 11 (3): 241-253.

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