

Adam PIOTROWICZ<sup>1</sup>

## IDENTIFICATION OF VOLATILE COMPOUNDS FROM A BREWERY WITH SPME TECHNIQUE

### IDENTYFIKACJA LOTNYCH ZWIĄZKÓW Z BROWARU ZA POMOCĄ TECHNIKI SPME

**Abstract:** The paper presents results of the analysis of the volatile compounds arising from the production processes in a brewery. The investigated material comprised the unhoped brewer's wort which was taken from the fermentation tanks during the industrial process. The identification of volatile compounds was conducted with the use of Solid-Phase MicroExtraction (SPME) technique by extracting the compounds from the headspace of the brewer's wort (HS-SPME). The procedure was optimized by modifying the parameters potentially influencing the process efficiency. The analytes adsorbed on the fibers were subsequently placed in the injector of a gas chromatograph, where they were released in the course of thermal desorption. Three types of fibers were chosen for the experiments: 65 µm PDMS/DVB, 50/30 µm DVB/CAR/PDMS and 100 µm PDMS. The greatest number of peaks corresponding to compounds found in the examined material was observed on the 50/30 µm DVB/CAR/PDMS fiber while the lowest was identified on the 100 µm PDMS fiber. The detected compounds are mainly the derivatives of aliphatic, alicyclic and aromatic hydrocarbons with different functional groups *e.g.* carbonyl, aldehyde or ester and possessing O-heteroatom in their structure.

**Keywords:** volatile compounds, brewer's wort, SPME, headspace, GC-MS

## Introduction

Food industry, with its diversity and a great number of food processing plants, comprises a significant source of volatile compounds arising from the ongoing production processes. Among many others, the sector includes breweries which introduce a variety of VOCs, often exhibiting odorous properties, to the environment [1, 2]. Moreover, the brewery plants are often situated within large human settlements, which causes a serious nuisance. Odors are believed to cause adverse health effects such as headaches, irritation, depression states, insomnia, lack of appetite, *etc.*

The first step of an attempt to mitigate the emission of volatile compounds into the environment involves conducting a detailed characterization of an emission source and determining the composition of off-gases [3]. A chromatographic analysis can be used for the determination of volatile compounds from environmental samples. Chromatography enables to accurately determine the chemical composition of a mixture. Apart from

<sup>1</sup> Faculty of Environmental Engineering, Lublin University of Technology, ul. Nadbystrzycka 40B, 20-618 Lublin, Poland, phone +48 81 538 41 39, email: a.piotrowicz@wis.pol.lublin.pl

a qualitative analysis, this technique also allows to identify the concentrations of substances in the examined sample. As far as aroma compounds are concerned, chromatography enables their detection at lower levels than it is possible for a human.

Prior to conducting the chromatographic analysis, it is necessary to isolate and enrich the analytes. Solid-phase microextraction (SPME) constitutes one of the most commonly used methods [4]. It was devised in the early 1990s by Pawliszyn [5, 6] and has been widely-discussed in the literature [7-9]. SPME involves a division of analytes into a gaseous phase and a solid phase in the form of thin polymer-covered quartz fiber as a sorbent. Utilizing such sorbent requires a special device, *i.e.* holder, in which a fiber is placed. The device resembles a syringe, with main components including a needle - used to pierce the membrane covering a vessel containing the sample - a fiber placed in the needle and a piston which enables to pull out the fiber.

The SPME process may be carried out in two ways: directly (Direct Solid Phase MicroExtraction - DSPME) or in the head space (HeadSpace SPME - HS-SPME). In the former, the fiber is introduced directly into the examined sample. This method usually yields compounds characterized by medium volatility. In the case of the latter, the fiber is placed in the head space and can be used to analyze the samples containing relatively high volatile substances. The amount of compounds sorbed by the solid-phase is expressed with the following formula:

$$n_f = \frac{K_{fh} \cdot K_{hs} \cdot V_f \cdot C_0 \cdot V_s}{K_{fs} \cdot K_{hs} \cdot V_f + K_{hs} \cdot V_h + V_s} \quad (1)$$

where:  $n_f$  - the amount of a compound in the solid-phase [g],  $K_{fs}$ ,  $K_{hs}$ ,  $K_{fh}$  - distribution constants, fiber/sample, head space/sample, and fiber/head space, respectively,  $V_f$ ,  $V_s$ ,  $V_h$  - volumes of: solid-phase, sample, and head space, respectively [cm<sup>3</sup>],  $C_0$  - initial concentration of the compound in the solution [g/cm<sup>3</sup>].

At present, several types of fibers are used in the SPME method. The most frequently commercially used sorbents include PDMS - polydimethylsiloxane - used for the analysis of non-polar compounds, PDMS/DVB - polydimethylsiloxane/divinylbenzene - used for compounds characterized by medium polarity, CAR/PDMS - carboxen/polydimethylsiloxane - used with non-polar compounds, PA - poly(butyl acrylate) - utilized for polar compounds, CW/DVB - carbowax/divinylbenzene - also employed for polar compounds, as well as DVB/CAR/PDMS - divinylbenzene/carboxen/polydimethylsiloxane - utilized for the analysis of a broad range of analytes. Recently, there has been a growing interest in home-made fibers [10].

The SPME technique is characterized by numerous advantages, for instance, it does not necessitate the use of expensive, often toxic, organic solvents of adequate purity, nor does it require a time-consuming and work-intensive preparation of a sample. A lengthy analytic procedure is redundant as well. The method also enables to separate analytes characterized by varying polarity and obtained from different matrices, in solid, liquid, and gaseous phases. Moreover, it is highly-sensitive, requires samples with small volume and enables to perform analyses cheaply [11]. The process can be conducted automatically. It also allows for a rapid sample collection and is characterized by the ease of transport over great distances as well as repeatability of results [12].

The SPME technique is constantly being developed; new fiber coatings are being devised, the devices used in the process are being automatized. SPME is frequently coupled with other instrumental methods, *e.g.* capillary electrophoresis (CE) [13, 14] or electronic

nose (E-nose) [15, 16]. Initially, SPME fibers were only used with gas chromatography [5]. At present, the method is also employed with HPLC, especially as the hurdles stemming from dissolution of fiber coatings in organic solvent of mobile phase, swelling of coatings and changes in flow rate during desorption have been overcome [17]. Nowadays, the swelling effect of stationary phase is used for the improvement of sorption capacity of fibers [18].

## Materials and methods

The study area involved an industrial brewery located in south-eastern Poland. Unhopped brewer's wort constituted the main study material. Samples were collected directly from the process line devices, *i.e.* from before the brewing pot, right after a 2-hour long filtration process.

SPME fibers were placed in the head space inside the vessel containing wort. The procedure was optimized by modifying the parameters potentially influencing the process efficiency, such as the fiber coating type and the duration of its exposure, as well as the temperature, sample volume, and the volume of head space in the vessel [19-21].

The analytes adsorbed on the fiber were subsequently placed in the injector of a gas chromatograph, where they were released in the course of thermal desorption. The analyses were conducted by means of Trace Ultra gas chromatograph coupled with Polaris Q mass spectrometer - both manufactured by Thermo Electron - and the RTx-5 capillary column made by Restek, with 0.25  $\mu\text{m}$ -thick stationary phase comprising 5% diphenyl/95% dimethylpolysiloxane. A mass spectrometer using electron ionization was employed as the detector. The operational conditions of the system for chromatographic analysis (Table 1) were established in line with the method proposed by Cai et al. [22].

Table 1

Operational conditions of the system for chromatographic analysis

Operational conditions of Thermo Electron Trace Ultra gas chromatograph	
Injector	PTV, constant temp. mode, splitless, temp.: 250°C
Analytical column	capillary RTx-5 (Restek), 60 m x 0.25 mm ID x 0.25 $\mu\text{m}$ ( $d_i$ )
Oven temperature programming	45°C (2 min), ramp 4°C/min to 270°C (5 min)
Carrier gas	He (99.9996%)
Linear velocity of carrier gas	40 cm/s
Operational conditions of Thermo Electron PolarisQ mass spectrometer	
Ion source temperature	250°C
Transfer line temperature	300°C
Ionization mode	EI
Scanning mode	Full Scan (42-340 u)

The injector operating parameters, *i.e.* the proper temperature and desorption time were selected with the carry-over effect taken into account, which involves carrying the remnant of analytes present on a fiber over subsequent analysis. It was observed that 2-min long desorption time in the temperature of 250°C is sufficient even for fibers with thicker coatings. Additionally, before using, each fiber was conditioned for 30 min in the temperature of 250°C.

The selection of the proper SPME fiber coatings was made on the basis of suitability test of different kinds of fibers to determine the compounds derived from the brewer's wort.

The tested fibers as well as the characteristics of respective coatings were presented in Table 2.

Table 2

SPME fibers tested with coating characteristics and recommended range of operating temperature

Coating	Symbol	Coating thickness [μm]	Operating temp. [°C]
Polydimethylsiloxane	PDMS	100	200-280
Carboxen / Polydimethylsiloxane	CAR/PDMS	75	250-310
Carboxen / Polydimethylsiloxane	CAR/PDMS	85	250-310
Polyethylene Glycol	PEG	60	200-250
Polydimethylsiloxane / Divinylbenzene	PDMS/DVB	65	200-270
Carbowax / Divinylbenzene	CW/DVB	70	200-250
Divinylbenzene / Carboxen / Polydimethylsiloxane	DVB/CAR/PDMS	50/30	230-270

The HS-SPME-GC/MS analysis has demonstrated the diversified selectivity of the tested fibers. Consequently, three types of fibers were chosen for further experiments: 65 μm PDMS/DVB, 50/30 μm DVB/CAR/PDMS and 100 μm PDMS. Due to the rich content of the examined samples, the fibers characterized by diversified types of stationary phase, and the resultant different polarity, were selected so that the proposed set of fibers could be used for marking a broad range of compounds [23].

As part of HS-SPME optimization, conical glass Supelco vessels with the volume of 25 cm<sup>3</sup> were used in the study. The investigated material (in the amount of 15 cm<sup>3</sup>) was subsequently placed in each vessel. The pH was marked as 5.39. The samples were heated to 60 ± 0.5°C, and left for an hour in order to establish equilibrium. Afterwards, the selected SPME fibers were placed in the vessel head space for 15 minutes. Throughout the experiment, the samples were mixed by means of an electromagnetic mixer operating at 500 rpm. Following the extraction, the fibers were secured against accidental sorption of organic compounds from the air and subjected to chromatographic analysis.

## Results and discussion

The greatest number of peaks corresponding to compounds found in the examined material was observed on the 50/30 μm DVB/CAR/PDMS fiber characterized by the most complex stationary phase. In turn, higher intensities of ion current were observed on the fiber coated with 65 μm PDMS/DVB. Exemplary chromatograms of total ion current for the considered fibers, constituting a basis for identification of compounds from the brewery were presented in Figure 1. For the sake of comparison, the chromatograms depicting fibers coated with 100 μm PDMS - characterized by the best sorption of non-polar compounds - were presented as well. However, in that case the number of peaks was the lowest.

In the case of the fiber characterized by mixed stationary phase 50/30 μm DVB/CAR/PDMS, 32 compounds of different chemical class were identified, characterized by molar masses of 59-147 g/mol and boiling temperatures of  $T_b = 3-218^\circ\text{C}$  (the boiling temperature was not determined in a single case). A major group of the identified compounds is aliphatic. In the samples were identified: chlorinated methane derivatives (dichloromethane), branched hydrocarbons of saturated character (3-methylpentane) and unsaturated character (cis-beta-ocimene); alcohols, *e.g.* 3-buten-2-ol, 1-hexanol or 2,3-butanediol possessing two hydroxyl groups; ketones, such as methyl vinyl ketone and

4-methyl-2-hexanone; aldehydes, *e.g.* 3-methylbutanal and esters, such as ethyl acetate, allyl acetate and isoamyl acetate. Moreover, the representative of organosulfur compounds (dimethyl sulfide) and tertiary amine (trimethylamine) were identified.

RT: 0.00 - 63.27

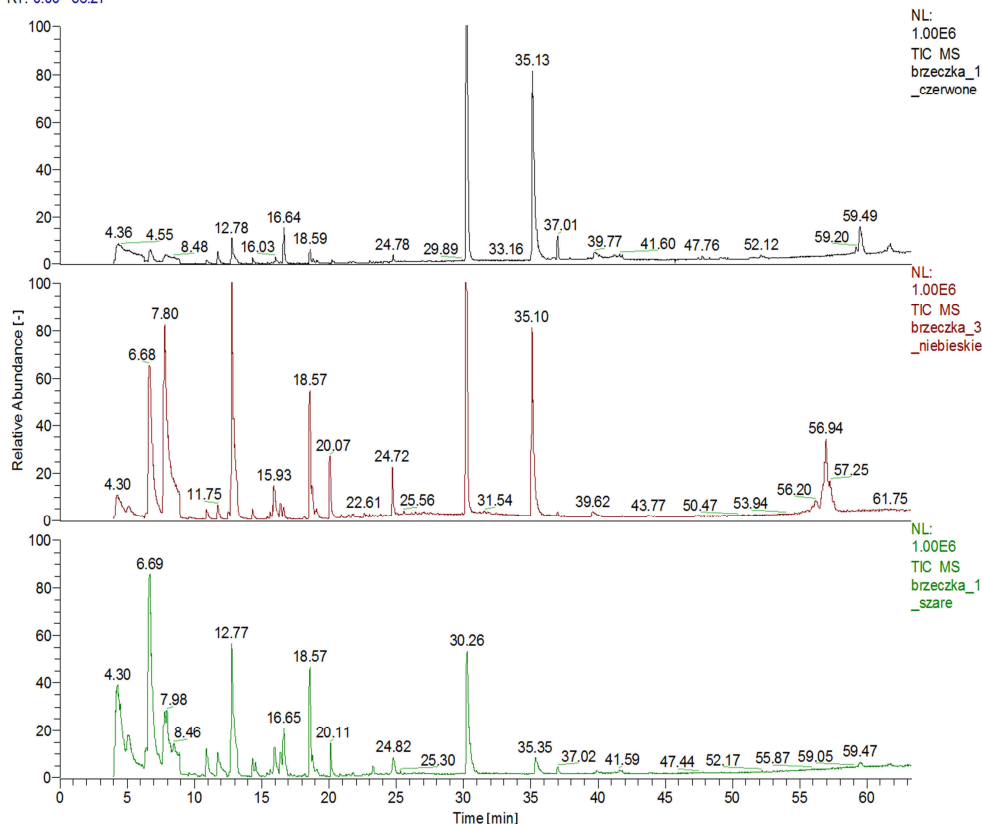


Fig. 1. Total ion current chromatograms from HS analysis of the brewer's wort samples obtained for fibers of different polarity: 100 μm PDMS (top), 65 μm PDMS/DVB (middle) and 50/30 μm DVB/CAR/PDMS (bottom)

Several compounds present in samples are characterized by cycloaliphatic structure. They include an aldehyde derivative - 4-methylcyclohex-3-enecarbaldehyde and heterocyclic hydroxyl derivative with O-heteroatom - tetrahydropyran-2-methanol. From among aromatic compounds monocyclic aromatic hydrocarbons were detected, such as benzene, o-xylene, isopropylbenzene (cumene) and a chlorinated derivative of benzene - 1,2-dichlorobenzene as well as polycyclic naphthalene. In the samples were also identified: the representative of aromatic aldehydes (benzaldehyde), an aromatic-aliphatic ether (1,3-dimethoxybenzene), the derivatives of furan (2-ethylfuran and 2-pentylfuran) as well as the derivative of phenol (4-ethylphenol). The identified compounds were presented in Table 3. It includes the retention time of particular substances (RT), the name, CAS registry number, molar mass (M), molecular formula and boiling temperature ( $T_B$ ).

Table 3

Identified compounds from HS-SPME-GC/MS analysis of the brewer's wort samples (50/30  $\mu\text{m}$  DVB/CAR/PDMS)

<i>RT</i> [min]	Name	CAS-RN	<i>M</i> [g/mol]	Molecular formula	<i>T<sub>B</sub></i> [°C]
4.10	trimethylamine	75-50-3	59.11	C <sub>3</sub> H <sub>9</sub> N	3
4.31	dichloromethane	75-09-2	84.93	CH <sub>2</sub> Cl <sub>2</sub>	40
4.31	dimethyl sulfide	75-18-3	62.13	C <sub>2</sub> H <sub>6</sub> S	38
4.32	2,3-butanediol	513-85-9	90.12	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	183
4.60	3-buten-2-ol	598-32-3	72.10	C <sub>4</sub> H <sub>8</sub> O	96
4.65	3-methylpentane	96-14-0	86.18	C <sub>6</sub> H <sub>14</sub>	64
4.89	ethyl acetate	141-78-6	88.10	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	75
5.48	benzene	71-43-2	78.11	C <sub>6</sub> H <sub>6</sub>	80
5.57	1-penten-3-ol	616-25-1	86.13	C <sub>5</sub> H <sub>10</sub> O	114
5.65	3-methylbutanal	590-86-3	86.13	C <sub>5</sub> H <sub>10</sub> O	90
5.81	pentanal	110-62-3	86.13	C <sub>5</sub> H <sub>10</sub> O	103
5.95	2-ethylfuran	3208-16-0	96.13	C <sub>6</sub> H <sub>8</sub> O	94
6.42	allyl acetate	591-87-7	100.12	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	103
6.45	methyl vinyl ketone	78-94-4	70.09	C <sub>4</sub> H <sub>6</sub> O	80
6.52	1-pentanol	71-41-0	88.15	C <sub>5</sub> H <sub>12</sub> O	137
7.23	2-propyn-1-ol	107-19-7	56.06	C <sub>3</sub> H <sub>4</sub> O	114
7.40	tetrahydropyran-2-methanol	100-72-1	116.16	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	187
9.08	hexanal	66-25-1	100.16	C <sub>6</sub> H <sub>12</sub> O	130
9.21	1-hexanol	111-27-3	102.18	C <sub>6</sub> H <sub>14</sub> O	156
10.77	isoamyl acetate	123-92-2	130.18	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	142
11.75	o-xylene	95-47-6	106.16	C <sub>8</sub> H <sub>10</sub>	143
12.20	4-ethylphenol	123-07-9	122.16	C <sub>8</sub> H <sub>10</sub> O	218
12.39	4-methyl-2-hexanone	105-42-0	114.19	C <sub>7</sub> H <sub>14</sub> O	139
14.21	isopropylbenzene (cumene)	98-82-8	120.19	C <sub>9</sub> H <sub>12</sub>	152
14.24	1-octen-3-ol	3391-86-4	128.21	C <sub>8</sub> H <sub>16</sub> O	174
14.73	2-pentylfuran	3777-69-3	138.21	C <sub>9</sub> H <sub>14</sub> O	169
15.32	benzaldehyde	100-52-7	106.12	C <sub>7</sub> H <sub>6</sub> O	179
15.55	cis-beta-ocimene	3338-55-4	136.23	C <sub>10</sub> H <sub>16</sub>	ND
16.35	1,2-dichlorobenzene	95-50-1	147.00	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	179
18.35	4-methylcyclohex-3-enecarbaldehyde	7560-64-7	124.18	C <sub>8</sub> H <sub>12</sub> O	176
22.67	1,3-dimethoxybenzene	151-10-0	138.16	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	217
23.83	naphthalene	91-20-3	128.17	C <sub>10</sub> H <sub>8</sub>	218

The lowest number of organic compounds was identified on the 100  $\mu\text{m}$  PDMS fiber - five compounds characterized by molar masses of 100-212 g/mol and boiling temperatures of  $T_B = 130\text{-}271^\circ\text{C}$  (in a single case the boiling temperature was not determined). In the samples was detected the representative of aliphatic hydrocarbons with relatively long chain (pentadecane), together with the representatives of alcohols (2-dodecen-1-ol) and aldehydes (hexanal). As was the previous case, the cycloaliphatic aldehyde derivative (4-methylcyclohex-3-enecarbaldehyde) was detected. Among aromatic compounds was identified a benzene derivative with two chlorine substituents (1,2-dichlorobenzene). The compounds identified on the 100  $\mu\text{m}$  PDMS fiber were presented in Table 4.

Utilizing fiber with the 65  $\mu\text{m}$  PDMS/DVB coating in the head space of brewer's wort 27 compounds of various physicochemical properties were identified. Their molar masses range from 62 to 147 g/mol and the boiling temperatures from 38 to  $218^\circ\text{C}$  (in one case the boiling temperature was not determined). The set of identified compounds largely agrees with the set of compounds detected with the 50/30  $\mu\text{m}$  DVB/CAR/PDMS fiber. The most numerous group is constituted by aliphatic compounds. In the samples were detected

saturated hydrocarbons, *e.g.* 3-methylpentane and unsaturated, *e.g.* 2-methyl-1-heptene; compounds with alcohol functional group, such as 1-hexanol or 1-octanol; ketones, *e.g.* 4-methyl-2-hexanone; compounds belonging to aldehydes, such as 3-methylbutanal or 2-ethylbutanal; representatives of esters - allyl acetate and isoamyl acetate.

Table 4  
Identified compounds from HS-SPME-GC/MS analysis of the brewer's wort samples (100  $\mu$ m PDMS)

RT [min]	Name	CAS-RN	M [g/mol]	Molecular formula	T <sub>B</sub> [°C]
9.14	hexanal	66-25-1	100.16	C <sub>6</sub> H <sub>12</sub> O	130
16.36	1,2-dichlorobenzene	95-50-1	147.00	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	179
18.52	4-methylcyclohex-3-enecarbaldehyde	7560-64-7	124.18	C <sub>8</sub> H <sub>12</sub> O	176
20.93	2-dodecen-1-ol	22104-81-0	184.32	C <sub>12</sub> H <sub>24</sub> O	ND
22.80	pentadecane	629-62-9	212.41	C <sub>15</sub> H <sub>32</sub>	271

Table 5  
Identified compounds from HS-SPME-GC/MS analysis of the brewer's wort samples (65  $\mu$ m PDMS/DVB)

RT [min]	Name	CAS-RN	M [g/mol]	Molecular formula	T <sub>B</sub> [°C]
4.31	dimethyl sulfide	75-18-3	62.13	C <sub>2</sub> H <sub>6</sub> S	38
4.60	2-butanone	78-93-3	72.11	C <sub>4</sub> H <sub>8</sub> O	80
4.70	3-methylpentane	96-14-0	86.18	C <sub>6</sub> H <sub>14</sub>	64
5.56	3-methylbutanal	590-86-3	86.13	C <sub>5</sub> H <sub>10</sub> O	90
5.82	pentanal	110-62-3	86.13	C <sub>5</sub> H <sub>10</sub> O	103
6.43	allyl acetate	591-87-7	100.12	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	103
6.45	methyl vinyl ketone	78-94-4	70.09	C <sub>4</sub> H <sub>6</sub> O	80
7.24	3-methyl-1-hexene	3404-61-3	98.19	C <sub>7</sub> H <sub>14</sub>	83
9.08	2-ethylbutanal	97-96-1	100.16	C <sub>6</sub> H <sub>12</sub> O	117
10.10	2-methyl-1-heptene	15870-10-7	112.21	C <sub>8</sub> H <sub>16</sub>	117
10.24	1-hexanol	111-27-3	102.18	C <sub>6</sub> H <sub>14</sub> O	156
10.79	isoamyl acetate	123-92-2	130.18	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	142
10.91	2-furylacetone	6975-60-6	124.14	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	179
11.63	styrene	100-42-5	104.15	C <sub>8</sub> H <sub>8</sub>	145
12.22	4-ethylphenol	123-07-9	122.16	C <sub>8</sub> H <sub>10</sub> O	218
12.40	4-methyl-2-hexanone	105-42-0	114.19	C <sub>7</sub> H <sub>14</sub> O	139
14.19	1-octen-3-ol	3391-86-4	128.21	C <sub>8</sub> H <sub>16</sub> O	174
14.47	1,2,4-trimethylbenzene	95-63-6	120.19	C <sub>9</sub> H <sub>12</sub>	168
14.72	2-pentylfuran	3777-69-3	138.21	C <sub>9</sub> H <sub>14</sub> O	169
15.29	benzaldehyde	100-52-7	106.12	C <sub>7</sub> H <sub>6</sub> O	179
15.80	1-octanol	111-87-5	130.23	C <sub>8</sub> H <sub>18</sub> O	195
15.86	6-methyl-5-hepten-2-one	110-93-0	126.20	C <sub>8</sub> H <sub>14</sub> O	173
16.33	1,2-dichlorobenzene	95-50-1	147.00	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	179
17.57	4-methyl-2-propylfuran	6148-37-4	124.00	C <sub>8</sub> H <sub>12</sub> O	ND
18.37	4-methylcyclohex-3-enecarbaldehyde	7560-64-7	124.18	C <sub>8</sub> H <sub>12</sub> O	176
21.66	1,3-dimethoxybenzene	151-10-0	138.16	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	217
23.63	3-ethylbenzaldehyde	34246-54-3	134.17	C <sub>9</sub> H <sub>10</sub> O	214

Similar to 50/30  $\mu$ m DVB/CAR/PDMS fiber an organosulfur compound (dimethyl sulfide) was found. From among cycloaliphatic compounds 4-methylcyclohex-3-enecarbaldehyde was identified. Moreover, several compounds with aromatic ring were

detected, such as aromatic hydrocarbons, *e.g.* styrene or 1,2,4-trimethylbenzene, also including the one with chlorine substituent - 1,2-dichlorobenzene; furan derivatives, such as 2-pentylfuran and 4-methyl-2-propylfuran, including the one with carbonyl group - 2-furylacetone; aromatic aldehydes, such as benzaldehyde and 3-ethylbenzaldehyde as well as phenol derivative - 4-ethylphenol and an aromatic-aliphatic ether 1,3-dimethoxybenzene. The information on identified compounds together with retention times, CAS registry numbers, molar masses, molecular formulas and boiling temperatures is included in Table 5.

The headspace analysis of brewer's wort samples was also conducted in the temperature of 40°C. A considerable influence of the temperature of the liquid samples during the extraction on the kind of analytes adsorbed on the fiber was noticed. Generally a similar analyte profile to that obtained in 60°C was observed. However, in lower temperature a little less compounds with higher molecular masses were sorbed on the fiber [24, 25]. In the temperature of 60°C better-defined peaks were also gained, which facilitated the identification process.

## Conclusions

As a result of HS-SPME-GC/MS analysis carried out on the brewer's wort 44 compounds were identified with molar masses of 59-212 g/mol and boiling temperature  $T_b = 3-271^\circ\text{C}$ . Detected substances are mainly the derivatives of aliphatic, cycloaliphatic and aromatic hydrocarbons with several functional groups (*e.g.* carbonyl, aldehyde, ester) and possessing O-heteroatom in their structure.

Optimization of the parameters at the stage of isolation and enrichment of analytes as well as the optimization of the GC/MS system parameters enabled the selection of conditions that allowed to obtain chromatographic peaks of high intensity.

The greatest number of compounds was identified on the basis of the analysis of the 50/30  $\mu\text{m}$  DVB/CAR/PDMS bipolar fiber coating. In contrast, the least number of compounds was detected in the analysis utilizing the 100  $\mu\text{m}$  PDMS fiber. Additionally, the compounds identified with the 65  $\mu\text{m}$  PDMS/DVB fiber, for which the highest intensities of ion current were observed, overlapped to the large extent with the compounds detected with the 50/30  $\mu\text{m}$  DVB/CAR/PDMS fiber.

A considerable influence of the temperature of the liquid samples during the headspace extraction on the kind of analytes adsorbed on the fiber was observed. At a higher temperature a little more compounds with higher molecular masses were sorbed.

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## IDENTYFIKACJA LOTNYCH ZWIĄZKÓW Z BROWARU ZA POMOCĄ TECHNIKI SPME

Wydział Inżynierii Środowiska, Politechnika Lubelska

**Abstrakt:** W pracy przedstawiono wyniki analizy lotnych związków powstających w trakcie procesów produkcyjnych w browarze. Materiałem pobieranym do badań była brzeczka przednia (niechmielona) otrzymywana po procesie filtracji w kadzi filtracyjnej. Identyfikacji lotnych składników dokonano z wykorzystaniem techniki mikroekstrakcji do fazy stacjonarnej (SPME), ekstrahując związki z fazy nadpowierzchniowej brzeczki piwnej. Procedurę optymalizowano, modyfikując parametry potencjalnie wpływające na efektywność procesu. Zaadsorbowane na włóknie anality umieszczano następnie w dozowniku chromatografu gazowego, gdzie w wyniku termicznej desorpcji następowało ich uwalnianie. Do badań wytypowano trzy rodzaje włókien: 65  $\mu\text{m}$  PDMS/DVB, 50/30  $\mu\text{m}$  DVB/CAR/PDMS oraz 100  $\mu\text{m}$  PDMS. Największą ilość związków zidentyfikowano na podstawie analizy włókna o bipolarnej fazie stacjonarnej 50/30  $\mu\text{m}$  DVB/CAR/PDMS, natomiast najmniejszą przy użyciu włókna 100  $\mu\text{m}$  PDMS. Zidentyfikowano w sumie kilkadziesiąt związków będących pochodnymi węglowodorów alifatycznych, alicyklicznych i aromatycznych, posiadających różne grupy funkcyjne, takie jak karbonylowa, aldehydowa, estrowa, oraz zawierających w swej strukturze heteroatom tlenu.

**Słowa kluczowe:** lotne związki, brzeczka piwna, SPME, faza nadpowierzchniowa, GC-MS