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**APPLICATION OF GAS CHROMATOGRAPHY,
MASS SPECTROMETRY AND OLFACTOMETRY
FOR QUALITY ASSESSMENT
OF SELECTED FOOD PRODUCTS**

**ZASTOSOWANIE CHROMATOGRAFII GAZOWEJ,
SPEKTROMETRII MAS I OLFAKTOMETRII
W OCENIE JAKOŚCI WYBRANYCH PRODUKTÓW SPOŻYWCZYCH**

Abstract: The volatile compounds in spirits and honeys were determined by headspace solid-phase microextraction as sample preparation technique and gas chromatography (GC) with mass spectrometry (MS) and olfactometry (O) detection. Identification of spirits and honey volatiles was made by comparison mass spectra with data in NIST Mass Spectral Database. Additionally, flavour compounds detected by sensory-panel were registered in the form of olfactograms by fingerspan method. Analysis of raw spirits indicated the presence of over 200 compounds, of which a significant number were identified (including esters, higher alcohols, aldehydes, acetals, as well as furanes, sulphur compounds, terpenoids and benzene derivatives). Among them over 50 were identified whose presence or high content can decrease the quality of distillates. In the result of performed analysis of honeys, 163 volatile and semi-volatile compounds were identified (aliphatic and aromatic acids, aldehydes, ketones, alcohols and phenols, terpenoids, furane and pyrane derivatives). In the midst of them markers of each type of honeys were indicated. Formed determinant lists can be useful for distinguish and quality control (for example finding adulterations) of Polish honeys. Besides, application of GC-MS technique coupled with olfactometry make possible creating aroma profiles of investigated honeys. Employed techniques were characterized by high sensitivity and repeatability, furthermore they are less time-consuming.

Keywords: volatile compounds, aroma, raw spirits, honeys, solid-phase microextraction, gas chromatography, mass spectroscopy, olfactometry

Volatile (odorous) compounds perform a vital role in shaping the organoleptic quality of many food products [1-3]. For consumers, an organoleptic quality is equally important and often decisive in the purchase. From chemical point of view, the aroma of

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most food products is a complicated mixture, sometimes consisting of several hundred compounds. The analysis of aroma, ie the presence, content and composition of volatile substances, can constitute a valuable source of information on the health quality of food.

A classical approach to the evaluation of organoleptic quality is based on the exploitation of sensory analysis, carried out by a group of trained assessors. This analysis is a perfect tool in carrying out marketing tests of consumers but because of great human participation it has many limitations [4]. Because of these deficiencies a good supplement of the evaluation of organoleptic food properties is instrumental analysis. Appropriate instrumental methods allow a detailed and complex qualitative and quantitative analysis of volatile components, which influence on the flavour composition of food products [5]. The methods employed most often, allowing the creation and recognition of aromagrams are chromatographic techniques, in particular gas chromatography and so called electronic nose [6-9].

In recent years, intensive studies have been carried out regarding sensory activity of the individual volatile components of various food products and the dependence between the odour and the chemical composition of the volatile fraction of these products, using gas chromatography with olfactometric detection (GC-O) [10-12].

The purpose of this work was identification and comparison of volatile compounds present in headspace fraction of different raw agriculture spirits and honeys of different origin and attempt finding the relation between flavour compounds content and quality of these products.

Materials and methods

Investigated objects

Raw spirits

For this study 39 samples of raw grain spirits with an ethanol concentration of approximately 90% (v/v) were collected from local agricultural distilleries (Pomeranian province). All the samples, divided into three groups after the sensory analysis in accordance to Polish Standard PN-A-79528-2:2002, were investigated. The first 13 samples did not fulfil the Polish Standard demands. Following 13 samples obtained divergent evaluation marks. Some of the panelists reckoned them in accordance, some others without accordance to Polish Standard demands. The last group of 13 samples fulfilled Polish Standard requirements and obtained the highest organoleptic quality assessment.

High purity water (MilliQ A10 Gradient/Elix System, Millipore; Bedford, MA, USA) as well as standard substances and alkanes with a chain length from C₅ to C₂₀ (Sigma-Aldrich Poland, Steinheim, Germany) were also used in the research.

Honeys

Investigation was performed for 40 samples of several popular unifloral Polish honeys (8 samples for each type), namely: acacia (A), buckwheat (B), lime (L), honeydew (H) and rape (R). Honey samples satisfied quality requirements of PN-88/A-77626. Rest of reagents was identical like in case spirit analysis.



Sample preparation (Headspace solid phase microextraction)

Raw spirits

Raw spirits were diluted with water to an ethanol concentration of 20% (v/v). 8 cm³ of sample were placed in a 15 cm³ vial with magnet stirring bar and capped with teflon lined septa. During extraction the temperature of the vial was kept at 45°C, and the sample was stirred (700 rpm) without the addition of salt. The SPME-fiber (DVB/CAR/PDMS, 50/30 µm, 2 cm) was inserted for 40 min into the headspace of the vial and immediately after the end of extraction placed in the injection port of the GC for 5 min for thermal desorption of the analytes.

Honeys

Weighed amount of honey (approx. 2.5 g) was placed in 15 cm³ vial with 0.5 cm³ water addition in order to receive homogeneous solution, then volatile compounds were easier and faster crossed over to headspace. The vials were closed by PTFE/Silicone lined septa to prevent losing volatiles. To ensure phase equilibrium, samples were kept at 60°C for 10 min. The SPME-fiber (like in case raw spirits) was exposed at the same temperature for 40 min. Afterwards fiber was put into the GC injection port for 5 min at 250°C for quantitative desorption of the analytes. Isolation and pre-concentration stage was supported by agitation (850 rpm).

Separation and detection (Gas chromatography)

A TRACE GC 2000 (Thermo Finnigan, Waltham, MA, USA) gas chromatograph equipped with a split/splitless injector, an olfactometric detector (Sniffer 9000 System, Brechbühler, Houston, TX, USA) and a TRACE DSQ quadrupole mass spectrometer was used for identification of extracted volatiles. Separation was achieved on two different columns for raw spirits analysis and one for honeys. Columns parameters were as follows: Stabilwax-DA (Restek, Bellefonte, PA, USA) polar capillary column with a modified polyethylene glycol bonded phase (30 m x 0.32 mm I.D., 0.5 µm film thickness) and HP-5MS (Agilent Technologies, Santa Clara, CA, USA) non-polar capillary column with a (5%-diphenyl/95%-dimethyl)-polysiloxane bonded phase (30 m x 0.25 mm x 0.25 µm). The first one was used for both, raw spirits and honeys, whereas the second only for agricultural distillates. The Stabilwax-DA column temperature program for raw spirits was as follows: 45°C held for 1 min and then ramped up 6°C min⁻¹ to 120°C, then increased 5°C min⁻¹ to 180°C and once again ramped up 8°C min⁻¹ to 240°C and held for 7 min in this temperature. The total runtime was 40 min. For honey different oven program was applied: starting temperature was 50°C for 1 min, next temperature increased 5°C min⁻¹ up to 200°C, then grown 10°C min⁻¹ to 240°C and held for 15 min in this temperature. The total runtime was 10 min longer than in spirits analysis. The initial oven temperature for the HP-5MS column program was 40°C held for 10 min and then ramped up 3°C min⁻¹ to 120°C, and once again ramped up 10°C min⁻¹ to 250°C with a final isothermal period of 5 min. The total runtime was 55 min. The temperature of the injector was 250°C in both cases. The carrier gas was helium with a flow rate of 1.5 cm³ min⁻¹ (raw spirits) and 2.2 cm³ min⁻¹ (Stabilwax-DA column) or 1 cm³ min⁻¹ (HP-5MS column). Additionally auxiliary gas - moist nitrogen



(flow rate - $12.5 \text{ cm}^3 \text{ min}^{-1}$) was used in order to prevent drying up nose mucous sensory evaluator. The detector operated in electron impact mode (70 eV) at 240°C . The transfer line temperature was 240°C . Detection was carried out in scan mode in a range of m/z 40-400. For better characterization of volatile fraction the analysis were carried out with the use of two detectors: olfactometric and mass spectrometer.

Results

Raw spirits

The chromatograms for a typical agricultural distillate sample with a low organoleptic quality analyzed on two columns (non-polar HP-5MS and polar Stabilwax-DA) are presented in Figure 1. The raw spirits volatile fraction analysis indicated the presence of over 200 compounds of which a significant number were identified. Identification was achieved with using various methods, but most importantly on the basis of comparing their mass spectrums with spectrums available in the NIST spectrum library. In addition, retention indexes were also calculated with the use of a homologous series of alkanes with a chain length from C_5 to C_{20} . The identification of some of the compounds was additionally confirmed by the consistency of their retention indexes with values in literature, as well as on the basis of uniformity of retention times and mass spectra with standard substances.

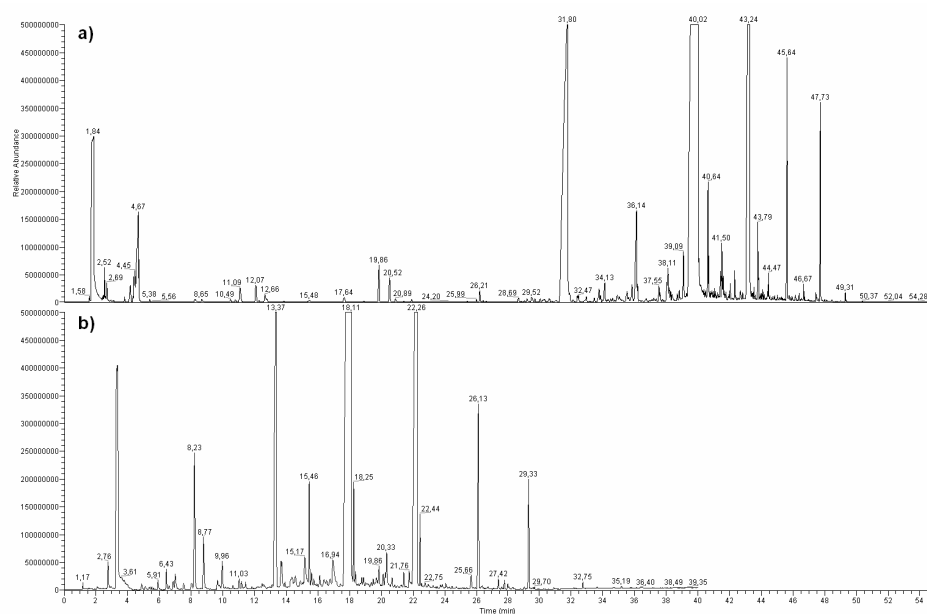


Fig. 1. Typical chromatograms of a raw spirit volatile fraction obtained using: a) non-polar HP-5MS and b) polar Stabilwax-DA columns

With the aim of determining the dependence between the composition of the volatile fraction of a product and its sensory quality, studies were conducted which were to make possible the discovery of differences in the composition of the volatile fractions of aroma compounds in agricultural distillates with different organoleptic quality. For the analysis, raw spirits were chosen which differed in evaluations obtained during the sensory analysis - 13 samples which obtained a high evaluation and fulfilled Polish Standards requirements, 13 samples which obtained a low evaluation and were deemed to not meet required Polish Standards by a portion of the panel as well as 13 samples, which did not fulfill standard requirements and did not qualify for further rectification and the production of spirits.

In the results of the conducted studies, over 100 compounds were identified which appeared in distillates with a low organoleptic quality, which fulfilled the requirement that the peak surface area of a given compound on a low quality sample's chromatogram is larger than any peak surface area of the same compound on chromatograms for samples with a high organoleptic quality. Table 1 presents a list of selected exemplary compounds (their retention indexes and references), whose high content or presence could be the cause of poor quality of distillates. The fragment ions masses used during peak integrations are given in brackets. For confirmation of this statement, olfactometric detector and Stabilwax-DA capillary column were used. The GC-O analysis combined with GC-MS analysis allowed for identification some of the flavours which are the cause of decreasing quality. Identified flavours appeared most often in raw spirits samples are listed in Table 2. Odours were identified by comparison of the retention times obtained by GC-MS and GC-O. Empirical aroma description was compared with the literature aroma description for confirmation of identified compounds. The olfactometric analysis has shown that in spite of similarities in volatile fraction composition some relationships in raw spirits quality were observed. Performed studies revealed the most general conclusion: the richer the profile of the volatile compound is, the lower the quality of the distillate. Despite the fact that practically every sample contains a unique set of volatile compounds, a few relationships were observed between the chemical composition of a distillate sample and its sensory properties. These conditions relate most of all to a higher content of compound groups, such as acetals and esters, as well as two compounds, dimethyl trisulfide and geosmin (2 β ,6 α -dimethylbicyclo[4.4.0]decan-1 β -ol). Except for the above-mentioned compounds, the composition of the volatile fraction of distillates with a low quality also includes aldehydes, terpenes, thiophene, furan or guaiacol derivatives, xylenes as well as a very large group of other identified and unidentified pollutants. Most of the discussed components are counted as aroma compounds, and some, such as dimethyl trisulfide and geosmin, are characterized by a very low sensory threshold. These compounds were confirmed by GC-O analysis as those which decreases quality of raw spirits samples the most. The results obtained with the use of two detectors were in good correlation. Dimethyl trisulfide's aroma is described in literature as a spoiled food-type smell, spoiled cabbage, garlic, onion-like, musty, sulphuric, pungent. This compound was identified in beverages such as wine, tequila and Yanghe Daqu (a Japanese wheat-based alcoholic beverage), and its sensory detection limit in a 10% ethanol-water solution was 0.2 $\mu\text{g dm}^{-3}$ [18, 25-27]. Geosmin is a compound with an earthy and musty aroma, which is detectable practically in ultra-trace quantities - its detection limit in wine is 60÷90 ng dm^{-3} [28]. Both compounds



are not typical fermentation products and are volatile metabolites produced by different undesirable microorganisms, such as fungi or many types of *Actinomycetes*, which develop in raw materials or as a result of infections during the fermentation process. From the conducted studies, it appears that their increased content in agricultural distillates significantly correlates with sensory analysis results and in most cases is even a disqualifying attribute. All of the distillates with the worst sensory properties, except for sample number 13, contain a significantly high quantity of at least one of these compounds. Whereas dimethyl trisulfide appears in small quantities in both, high and medium quality spirits, the geosmin peaks appear only on chromatograms for the worst-quality distillates (GC-MS detection). However GC-O detection was characterized by higher sensitivity for geosmin than GC-MS detection. Olfactometric detection revealed that geosmin was detected in every medium and low quality samples. Even trace quantity of geosmin and dimethyl trisulfide found in raw spirits influence on the quality of rectified spirits as well as alcoholic beverages obtained from them.

Table 1
Selected compounds considered as responsible for decreasing organoleptic quality of raw spirits samples

Retention Indexes		Compound	References	
HP-5MS	Stabilwax-DA		IR _{non-polar}	IR _{polar}
<500	713	Acetaldehyde* (43)	435 [13]	718 [14]
613	906	Ethyl acetate* (61)	615 [13]	902 [14]
648	935	3-Methylbutanal* (58)	649 [15], 650 [13]	936 [14]
658	935	2-Methylbutanal (58)	658 [15], 660 [16]	
704	870	1-Ethoxy-1-butene (57)		
726	906	1,1-Diethoxyethane* (45)	726 [17,18]	
859	991	1,1-Diethoxy-2-methylpropane (103)	859 [18]	
864	1162	<i>p</i> -Xylene* (106)	861 [15], 864 [19]	
864	1168	<i>m</i> -Xylene* (106)	860 [20]	
875	1010	1-(1-Ethoxyethoxy)-2-methylpropane (73)		
931	1035	α -Pirene* (93)	931 [20]	1045 [14]
960	1086	1,1-Diethoxy-3-methylbutane (103)	955 [10]	
961	1083	1,1-Diethoxy-2-methylbutane (103)		
964	1412	Dimethyl trisulfide* (126)	970 [21], 972 [22]	
977	1116	1-(1-Ethoxyethoxy)-3-methylbutane (73)		
978	1106	1-(1-Ethoxyethoxy)-2-methylbutane (73)		
1002	1252	Ethyl hexanoate* (88)	1003 [20]	
1057	1265	γ -Terpinene* (93)	1058 [20]	1274 [14]
1097	1244	1,1-Diethoxyhexane (103)		
1158	1486	2-Pentyl thiophene (97)		
1208	1462	Ethyl octanoate*(88)	1199 [20]	
1269	1565	2-(1,2-Diethoxyethyl)-furan (125)		
1399	1680	Ethyl decanoate* (88)	1398 [20]	
1467	1692	7,11-Dimethyl-3-methylene-1,6,10-dodecatriene (69)	1459 [23], 1466 [24]	1711 [14]
1483	NF	2-Methyl-6- <i>p</i> -tolyl-2-heptene (119)		
NF	1862	Geosmin* (112)		
1599	1882	Ethyl dodecanoate* (88)	1597 [20]	

* - identification confirmed on the basis of uniformity of retention times and mass spectra with standard substances

Table 2

Identified odours during GC-O analysis

Odour description	Compound name
sweet, fruity	ethyl acetate + 1,1-diethoxyethane
sweet, musty, aldehydic	2-methylbutanal + 3-methylbutanal
sweet, rum	ethyl propionate
sweet, synthetic	2-methylpropyl acetate
sweet, fruity, pineapple	ethyl butyrate
vegetable, boiled cabbage, onion	dimethyl disulfid
sweet, fruit drop, fruity *	2-methyl-1-butyl acetate + 3-methyl-1-butyl acetate
sweet, fruity	
sweet, cheesy, musty *	2-methyl-1-butanol + 3-methyl-1-butanol
sweet, fruity, pineapple *	ethyl hexanoate
sweet, unpleasant, sickening	
sweet, acidulous	
fresh, citrus, sweet	
pungent, synthetic	
vegetable, boiled cabbage, boiled onion *	dimethyl trisulfide
sweet, plastic, synthetic	
sweet, pungent, citrus, fruit drop *	ethyl octanoate
green, peas, grass *	
bread peel, synthetic *	
pungent, bread peel	
cabbage	
synthetic, bread peel *	
bread peel, pungent *	
green, geranium	
musty, pungent	
green tea, citrus	
mould-ripened cheese	
green, floral *	
sweet, pungent *	ethyl decanoate
unpleasant, mousy, animal *	
green, floral, geranium	
medicine, vitamin, boiled chicken *	
fresh, wet soil, geranium, green *	
boiled cabbage, vegetable	
musty	
flowery, sweet champagne *	acetic acid phenylethyl ester
green, sweet, pungent *	ethyl dodecanoate
wet basement, mouldy, musty, wet soil *	geosmin
pungent, aniseed *	
creamy, processed cheese	
almond, synthetic	
floral, green, geranium	

* - odours which appeared most often in aroma profiles

Honeys

Figures 2A and 2B presents typical honey chromatograms analysed by developed methodology. At the first look, obtained volatile profiles of particular honey types differ each other. The most characteristic chromatograms were received for buckwheat and lime honeys.

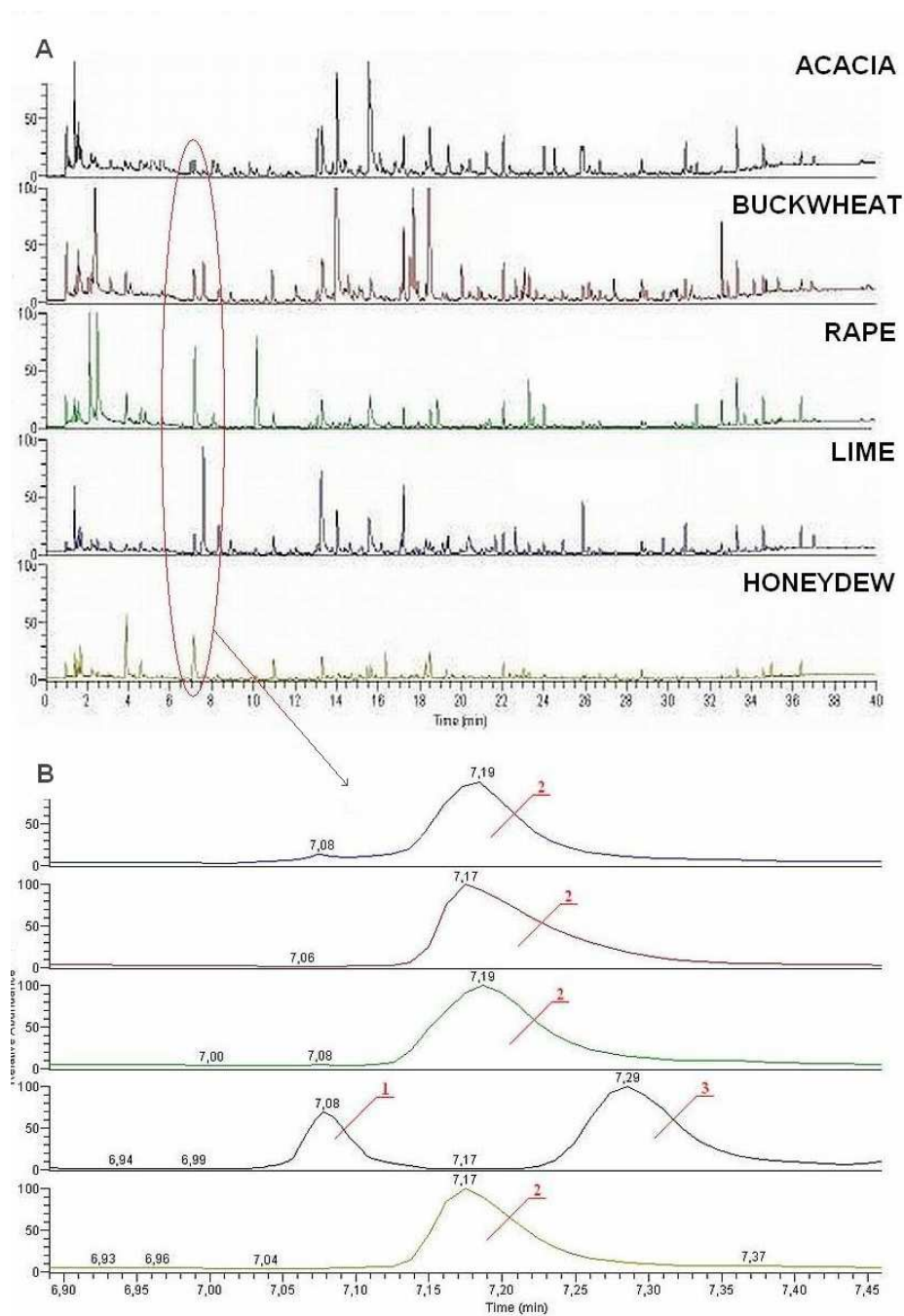


Fig. 2. Comparison of chromatograms - five samples of honey types: A) full profile, B) exemplary variety markers lime honey: 1 - limonen, 2 - 2-methylbutanol + 3-methylbutanol, 3 - phellandrene

Compounds in volatile fraction were identified by comparison of mass spectra with data in NIST Mass Spectral Data Base (like spirit samples). Identity of chosen volatile compounds was additionally verified on the basis of conformity of retention times and mass spectra with standards. In result, 163 volatile and semi-volatile compounds (aliphatic and aromatic acids, aldehydes, ketones, alcohols and phenols, terpenoids, furane and pyrane derivatives) [29, 30] were identified from which the characteristic compounds for each honey variety were indicated.

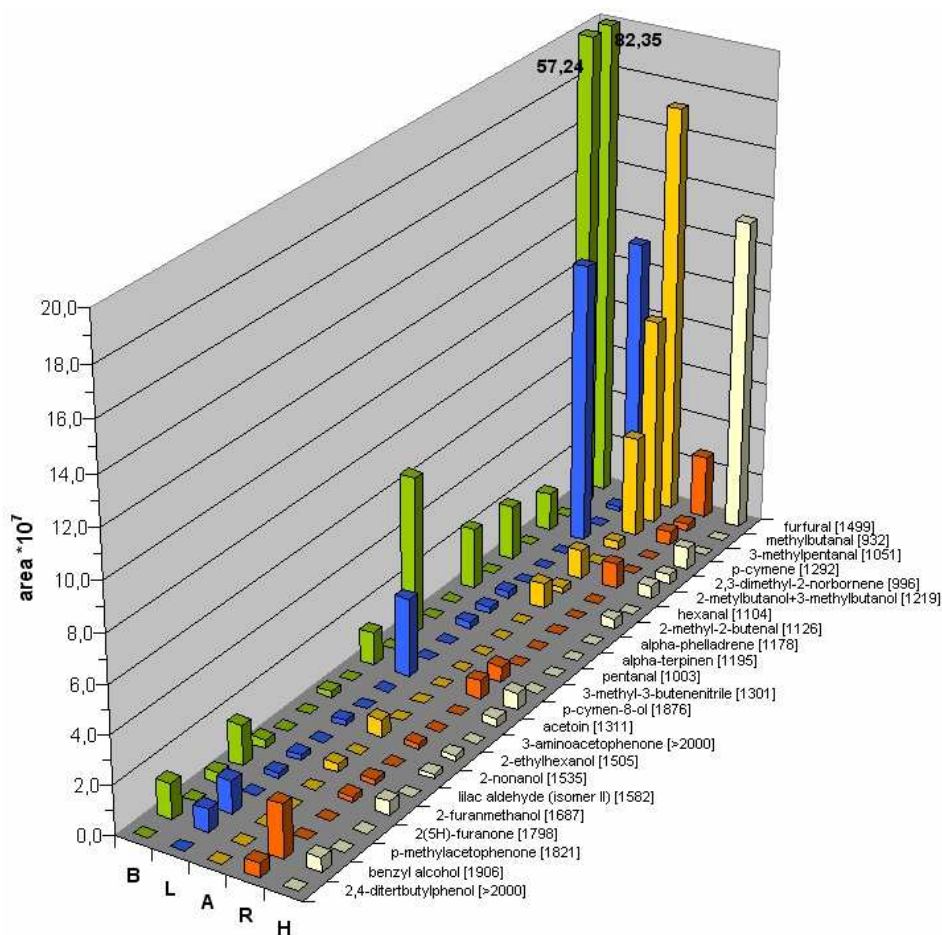


Fig. 3. Selected variety of honey markers: bukweat (B), lime (L), acacia (A), rape (R), honeydew (H)


Figure 3 presents 23 from 163 identified compounds of Polish honeys. It can be seen that some compounds were found in two, three, four or even in all honey varieties, for example benzyl alcohol, furfural. On the other hand, some compounds were present in only one type of honey suggesting that they can be the markers, eg buckwheat honey determinant can be pentanal, acacia hexanal and lime *p*-methylacetophenone.

Absence in only one type of honey have suggested that given compound can be a marker, eg 2-ethylhexanol for buckwheat honey, methylbutanal (two isomers) for honeydew [30] and *p*-cymene for rape variety. It is worth to notice that lilac aldehyde that was not existed in a few honey types (acacia, rape and honeydew) can be honeydew marker, in case of absence of all isomers in this type of honey. Furfural and methylbutanal [30] were found in buckwheat honey in five and seven times greater quantity than in the rest of honey types. The same situation was with *p*-cymen existing sevenfold greater in lime honey. It can allow for distinguishing honey varieties in respect of this characteristic amount. Like in spirits samples, Kovats retention indexes, useful information in comparing interlaboratory results [30], were calculated and are shown in square brackets in Figure 3.

Table 3

Selected flavour compounds identified in the investigated honeys.

RT _{GC-MS}	RT _{GC-O}	Compound name	A	B	L	H	R	Aroma description
1.22; 1.28	1.71	methanethiol + acetaldehyde	+	+	+	+	+	acidic, faint, cooked cabbage, addled eggs, acetic
1.40	1.91	dimethyl sulfide	+	+	+	+	+	sweet, honey, acidic, cooked vegetables, sulphuric
2.37	3.07	2-methylbutanal + 3-methylbutanal	-	+	-	+	-	sweet, almond, fermented, apple, cheese
3.11	3.91	2,3-butanedione	+	+	+	+	+	sweet, butter, cream
4.32	5.24	3-methylbutanoic acid ethyl ester *	-	+	-	-	-	sweet, acetic, strawberry, raspberry juice
9.36; 9.41	10.58	acetoin + octanal	+	+	+	+	+	sweet, tart, orange skin, sweetie, cream
10.91	12.06	rose oxide	-	+	+	+	-	sweet, acidic, tart, fragrant
11.78	12.98	dimethyltrisulfide	+	+	+	+	+	sulphuric, vegetable, cooked cabbage, onion, rotten
12.02	13.18	nonanal	+	+	+	+	+	synthetic, gummy, wax, mouldy, starched
13.30	14.42	dimethylstyrene *	+	+	+	+	+	acidic, horseradish, anise
14.05	15.19	furfural	-	+	-	-	-	sweet, fruit, cherry, soft almond
15.59	16.74	benzaldehyde	-	+	-	+	-	sweet, almond, marzipan
15.65	16.80	linalol	+	+	+	+	-	sweet, citrus, forest, geranium
16.16	17.38	3,9-epoxy- <i>p</i> -mentha-1,8(10)-diene *	-	-	+	-	-	fruit, herbal, dill
17.21	18.36	hotrienol *	-	+	-	-	+	sweet, tropic, ginger, herbal, geranium, green
18.36	19.56	phenylacetaldehyde	+	+	+	+	+	sweet, honey, floral, herbal, chocolate, lilac
18.88	19.96	benzoic acid ethyl ester	+	+	+	+	+	sweet, multivitamin, apple, coumarin
22.08	23.24	beta-damascenone	+	+	+	+	+	sweet, herbal, delicate and apple, raspberry
23.31	24.63	benzyl alcohol	+	+	+	+	+	sweet, honey, floral, rose
24.02	25.23	2-phenylethyl alcohol	+	+	+	+	+	sweet, floral, rose, violet
26.94	28.05	<i>p</i> -anisaldehyde	+	+	+	+	+	sweet, anise, marzipan, cherry
30.30	31.41	3-aminoacetophenone	+	+	+	+	+	sweet, raspberry-currant syrup, grape, gummy

 - the biggest peak on the olfactogram.

* - compounds detected by one person of sensory-panel

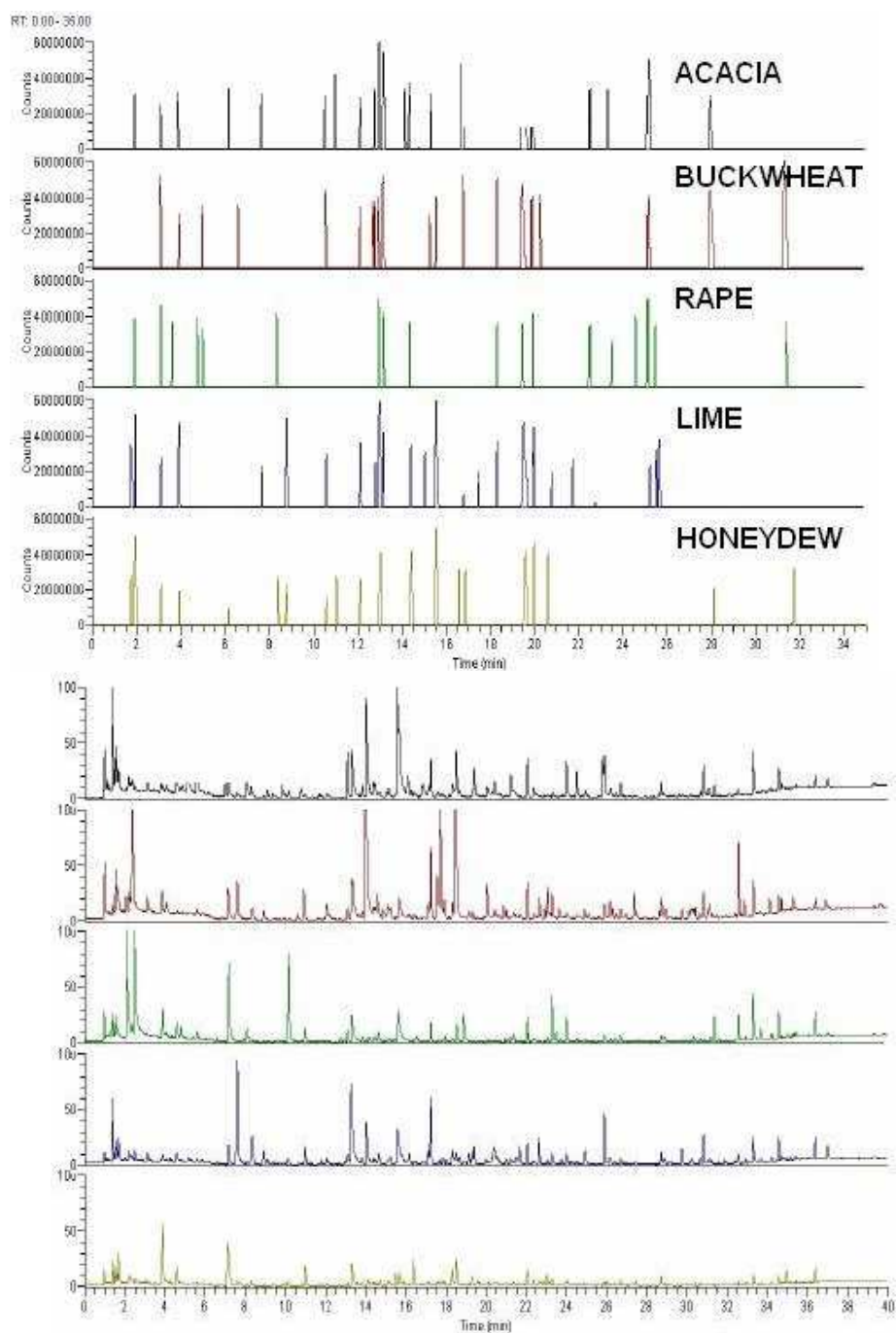


Fig. 4. Comparison of olfactograms and chromatograms of honey samples

Flavour compounds detected by sensory-panel (3 estimators) were registered in the form of olfactograms by fingerspan method. 37 volatile flavour compounds were identified after comparison of their retention times from olfactogram with chromatogram (Fig. 4). Retention time differences (between GC-MS and GC-O) were determined by passing standard mixture through the chromatographic system. It was caused by fact that olfactometer was coupled with chromatographic column using longer transfer line in comparison with mass spectrometer interface, different flow rate mobile phase in proportion to auxiliary gas and various conditions in both systems. Additionally, for the purpose of confirmation of the identity of detected flavour compounds their sensory panel aroma description (Tab. 3) was compared with literature data. Identified flavour compounds might be useful for distinguishing different types of honeys (eg furfural for buckwheat and linalol for honeydew).

Conclusions

The use of headspace stationary-phase microextraction (HS-SPME) and capillary gas chromatography/mass spectrometry (GC-MS) allowed not only for finding the dependence between the composition of the volatile fraction of agricultural distillates and their sensory quality, but also allowed for the discovery of differences between the composition of aromatic volatile compounds in agricultural distillates, originating from different sources.

The elaborated procedure, based on HS-SPME-GC-MS and GC-O [30, 31], applied for analysis of several popular Polish honeys (lime, acacia, buckwheat, rape and honeydew) after determination the volatile fraction allowed to distinguish honeys botanical origin. Differences in the volatile and flavour fraction composition of various Polish honeys were observed, especially for buckwheat honeys, which contain characteristic compounds (eg furfural). Created volatile profiles and unifloral type of honey markers might be useful in adulteration detection and quality assessment of honeys but in future greater amount of samples need to be analysed.

The obtained results have shown that instrumental analysis can complete or substitute organoleptic analysis of spirits and honeys or pollen analysis.

Acknowledgements

This research was financially supported by the Department of Scientific Research of the Polish Ministry of Scientific Research and Information Technology (grant no. N312 056 31/3446).

References

- [1] Plutowska B., Wardencki W.: *Aromagrams - Aromatic profiles in the appreciation of food quality*. Food Chem., 2007, **101**, 845-872.
- [2] Majewska E. and Delmanowicz A.: *Profile związków lotnych wybranych miodów pszczelich*. Żywność. Nauka. Technologia. Jakość, 2007, **5**, 247-259.
- [3] Plutowska B. and Wardencki W.: *Application of gas chromatography-olfactometry (GC-O) in analysis and quality assessment of alcoholic beverages - A review*. Food Chem., 2008, **107**, 449-463
- [4] Cayot N.: *Sensory quality of traditional food*. Food Chem., 2007, **101**, 154-162.

- [5] Aznar M., López R., Cacho J.F. and Ferreira V.: *Identification and quantification of impact odorants of aged red wines from Rioja. GC-Olfactometry, quantitative GC-MS, and odor evaluation of HPLC Fractions*. J. Agric. Food Chem., 2001, **49**, 2924-2929.
- [6] Čačić F., Primorac L., Kenjerić D., Benedetti S. and Mandić M.L.: *Application of electronic nose in honey geographical origin characterization*. JCEA, 2009, **10**, 19-26.
- [7] Ampuero S., Bogdanov S. and Bosset J.-O.: *Classification of unifloral honeys with an MS-based electronic nose*. Eur. Food Res. Technol., 2004, **218**, 198-207.
- [8] Benedetti S., Mannino S., Sabatini A.G. and Marcazzan G.L.: *Electronic nose and neural network use for the classification of honey*. Apidologie, 2004, **35**, 1-6.
- [9] Ghidini S., Mercanti C., Dalcanale E., Pinalli R. and Bracchi P.G.: *Italian honey authentication*. Ann. Fac. Medic. Vet. di Parma, 2008, **28**, 113-120.
- [10] Falcão L.D., Revel G., Rosier J.P. and Bordignon-Luiz M.T.: *Aroma impact components of Brazilian Cabernet Sauvignon wines using detection frequency analysis (GC-olfactometry)*. Food Chem., 2008, **107**, 497-505.
- [11] Lermusieau G., Bulens M. and Collin S.: *Use of GC-Olfactometry to identify the hop aromatic compounds in beer*. J. Agric. Food Chem., 2001, **49**, 3867-3874.
- [12] Berdagué J.L., Tournayre P. and Cambou S.: *Novel multi-gas chromatography-olfactometry device and software for the identification of odour-active compounds*. J. Chromatogr. A, 2007, **1146**, 85-92.
- [13] Pino J.A., Marbot R., Rosado A. and Vázquez C.: *Volatile constituents of Malay rose apple [Syzygium malaccense (L.) Merr. & Perry]*. Flavour Frag. J., 2004, **19**, 32-35.
- [14] Chung T.Y., Eiserich J.P. and Shibamoto T.: *Volatile compounds isolated from edible Korean Chamchwi (Aster scaber Thunb.)*. J. Agric. Food Chem., 1999, **41**, 1693-1697.
- [15] Rembold H., Wallner P., Nitz S., Kollmannsberger H. and Drawert F.: *Volatile components of chickpea (Cicer arietinum L.) seed*. J. Agric. Food Chem., 1989, **37**, 659-662.
- [16] Loon W.A.M., Linszen J.P.H., Legger A., Posthumus M.A. and Voragen A.G.J.: *Identification and olfactometry of French fries flavour extracted at mouth conditions*. Food Chem. 2005, **90**, 417-425.
- [17] Ledauphin J., Guichard H., Saint-Clair J.-F., Picoche B. and Barillier D.: *Chemical and sensorial aroma characterization of freshly distilled calvados. 2. Identification of volatile compounds and key odorants*. J. Agric. Food Chem., 2003, **51**, 433-442.
- [18] Fan W. and Qian M.C.: *Headspace solid phase microextraction and gas chromatography-olfactometry dilution analysis of young and aged Chinese "Yanghe Daqu" liquors*. J. Agric. Food Chem., 2005, **53**, 7931-7938.
- [19] Isidorov V. and Jdanova M.: *Volatile organic compounds from leaves litter*. Chemosphere 2002, **48**, 975-979.
- [20] Ansorena D., Gimeno O., Astiasaran I. and Bello J.: *Analysis of volatile compounds by GC-MS of a dry fermented sausage: chorizo de Pamplona*. Food Res. Int., 2001, **34**, 67-75.
- [21] Kubec R., Drhová V. and Velíšek J.: *Thermal degradation of S-methylcysteine and its sulfoxide-important flavor precursors of Brassica and Allium vegetables*. J. Agric. Food Chem. 1998, **46**, 4334-4340.
- [22] Tellez M.R., Schrader K.K. and Kobaisy M.: *Volatile components of the cyanobacterium oscillatoria perornata (Skuja)*. J. Agric. Food Chem., 2001, **49**, 5989-5992.
- [23] Javidnia K., Miri R., Safavi F., Azarpira A. and Shafiee A.: *Composition of the essential oil of Nepeta persica Boiss from Iran*. Flavour Frag. J., 2002, **17**, 20-22.
- [24] Larsen T.O. and Frisvad J.C.: *Characterization of volatile metabolites from 47 Penicillium taxa*. Mycol. Res. 1995, **99**, 1153-1166.
- [25] Cullere L., Escudero A., Cacho J. and Ferreira V.: *Gas chromatography-olfactometry and chemical quantitative study of the aroma of six premium quality spanish aged Red wines*. J. Agric. Food Chem., 2004, **52**, 1653-1660.
- [26] Guth H.: *Quantitation and sensory studies of character impact odorants of different white wine varieties*. J. Agric. Food Chem. 1997, **45**, 3027-3032.
- [27] Benn S.M. and Peppard T.L.: *Characterization of tequila flavor by instrumental and sensory analysis*. J. Agric. Food Chem., 1996, **44**, 557-566.
- [28] Darriet P., Pons M., Lamy S. and Dubourdieu D.: *Identification and quantification of geosmin, an earthy odorant contaminating wines*. J. Agric. Food Chem. 2000, **48**, 4835-4838.
- [29] Odeh I., Abu-Lafi S., Dewik H., Al-Najjar I. and Imam A.: *A variety of volatile compounds as markers in Palestinian honey from Thymus capitatus, Thymelaea hirsuta, and Tolpis virgata*. Food Chem., 2007, **101**, 1393-1397.

- [30] Wolski T., Tambor K., Rybak-Chmielewska H. and Kędzia B.: *Identification of honey volatile components by solid phase microextraction (SPME) and gas chromatography/ mass spectrometry (GC/MS)*. J. Apicult. Sci., 2006, **50**, 115-125.
- [31] Soria A.C., Sanz J. and Martinez-Castro I.: *SPME followed by GC-MS: a powerful technique for qualitative analysis of honey volatiles*. Eur. Food Res. Technol., 2009, **228**, 579-590.

ZASTOSOWANIE CHROMATOGRAFII GAZOWEJ, SPEKTROMETRII MAS I OLFAKTOMETRII W OCENIE JAKOŚCI WYBRANYCH PRODUKTÓW SPOŻYWCZYCH

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Abstrakt: Stosując mikroekstrakcję do fazy stacjonarnej z fazy nadpowierzchniowej jako metodę przygotowania próbek i chromatografię gazową (GC) ze spektrometrią mas (MS) i olfaktometrią (O) jako metodę oznaczeń końcowych, oznaczono lotne związki w spirytusach i miodach. Identyfikację przeprowadzono przez porównanie widm masowych z widmami z biblioteki NIST. Dodatkowo, wykrywane przez panel oceniający związki zapachowe rejestrowano w formie olfaktogramów, stosując metodę „odcisku palca”. Analiza surowych spirytusów wykazała obecność ponad 200 związków, z których większość została zidentyfikowana (estry, wyższe alkohole, aldehydy, acetale, a także furany, związki siarki, terpenoidy i pochodne benzenu). Stwierdzono, że ponad 50 związków z tej grupy to związki odpowiedzialne za pogorszenie jakości destylatów. W rezultacie przeprowadzonej analizy miodów zidentyfikowano 163 lotne i średniolotne związki (alifatyczne i aromatyczne kwasy, aldehydy, ketony, aldehydy i fenole, terpenoidy, pochodne furanu i piranu). Spośród tych związków wskazano markery każdego typu miodu. Lista markerów pozwala rozróżnić i kontrolować jakość (np. stwierdzić zafałszowanie) polskich miodów. Zastosowanie dodatkowo metody GC-MS połączonej z olfaktometrią pozwoliło stworzyć profile związków zapachowych badanych miodów. Zastosowane metody charakteryzują się dużą czułością i powtarzalnością, a ponadto są względnie szybkie.

Słowa kluczowe: lotne związki zapachowe, spirytusy rolnicze, miody, mikroekstrakcja do fazy stacjonarnej, chromatografia gazowa, spektrometria mas, olfaktometria