

THE VOLATILE COMPOUNDS COMPOSITION OF THE POLISH CARPATHIAN GOAT USING HS-SPME-GC/MS – CHEMOMETRIC CLASSIFICATION BASED ON AGE

HLAPLJIVI SASTOJCI SMJESA ZA POLJSKE KARPATSKE KOZE UPOTREBOM HS-SPM-GC/MS - KEMOMETRIČKE KLASIFIKACIJE NA TEMELJU DOBI

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SUMMARY

In order to identify the volatile compounds in Polish Carpathian goat meat, baked leg muscle samples from two groups aged 12 and 9 months were subjected to a headspace solid phase microextraction gas chromatography/mass spectrometry (HS-SPME-GC/MS). The multivariate statistics was done, which included the Fisher's ratio method for variables pre-selection, and principal component analysis together with linear discriminant analysis. 93 volatile compounds were found, out of which 49 were confirmed on two columns: non-polar ZB-5MSi and polar ZB-Wax, whereas 5 were verified by using of authentic standards. HS-SPME-GC/MS analysis together with chemometrics occurs to be the effective tool for the discrimination of the meat from the Carpathian goats aged 12 and 9 months. The first two principal components accounted for 88.8% of the total variance. These values for the first three principal components were 94.6% and the classification accuracy values for both groups were 100%.

Key words: Meat, Carpathian Goat, Volatile Compounds, SPME-GC/MS

INTRODUCTION

Goat breeding is not a large part of the agricultural economy in Poland. In the thirties of the twentieth century the goat population was some hundred thousand, but after World War II the numbers of goats gradually decreased. Since 2003, the goat population in Poland has been about 100 thousand. Poles, especially living in the country, still have a prejudice against goats, since they are associated with poverty. However, this situation has been changing over the last years. The demand for goat products is constantly increasing. They are probably eaten by people who appreciate their unusual taste and aroma, but should also be recommended for consumption by elderly, children, people with malnutrition problems and those who pay attention to a healthy lifestyle (Bagnicka et al., 2014). Carpathian goat is the old breed that was numerous in Poland

at the turn of the 19th and 20th centuries in mountainous areas, but now has been displaced by more noble goat breeds, such as Polish White Improved and Polish Fawn Improved. Carpathian goats which are white in Poland, in fact, settle the whole territory of the Carpathian Mountains.

The largest population is in Romania, but the coats of these goats are of different colors. Carpathian goats are horned and long haired animals that have forward-facing ears and a characteristic fringe.

Moreover, they are hardy and are extremely well adapted to live in the mountains and highlands. Supporting the popularity of goat meat should be of special interest, especially for its nutritional and flavor attributes. The substances that shape the taste and smell of meat are the volatile compounds that are often analyzed by a headspace solid phase microextraction gas chromatography/mass

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spectrometry (HS–SPME–GC/MS). Their composition in meat is associated with some factors, like feeding and breed (Elmore et al., 2000; Resconi et al., 2010), and ripening of meat (Yancey et al., 2006). It depends on pH value, thermal processing (Meynier and Mottram, 1995; Ames et al., 2001) and the age of the animal (Ba et al., 2012).

Multivariate statistical analysis is usually used, when the complex food samples analyses are performed. It is often utilized to authenticate and differentiate the sample groups (Majcher et al., 2015.). Prior to doing chemometrics the Fisher's ratio for variables pre-selection can be applied (Pierce et al., 2006). Then, the principal component analysis (PCA) and linear discriminant analysis (LDA), together with the classification of samples, are usually performed.

The goal of this study was to identify the volatile compounds in Polish Carpathian goat meat using HS–SPME–GC/MS and to discriminate by chemometrics the product coming from goats aged 12 and 9 months.

MATERIALS AND METHODS

Materials. Acetone ($\geq 99,9\%$), 1-octanol ($\geq 99\%$), octanal ($\geq 99\%$), toluene (99,8%), acetaldehyde ($\geq 99,5\%$), 2,3-butanedione (analytical standard), and acetic acid ($\geq 99,5\%$) were purchased from Sigma - Aldrich Co. (Poznań, Poland). The n-Paraffin mixes (3 packages): C5 to C15 (from pentane – hydrocarbon with 5 carbon atoms to pentadecane – hydrocarbon with 15 carbon atoms), and C10, C12, C14, C16, and C18, C20, C22, C24 were purchased from Supelco (Poznań, Poland).

Animal Experiment. The experiment involved 12 kids of the Carpathian goat native breed, selected from conservation herds belonging to the National Research Institute of Animal Production. All the animals were 7 months of age, with the initial body weight of the lambs at 16,5 kg. The animals were maintained in a semi-intensive system: they received meadow hay and straw ad libitum as well as about 0.4 kg of concentrate per animal. At the age of 9 months, 6 kids were slaughtered. The rest of the animals were maintained to 12 months of age. As a result, 12 animals in 2 groups aged 12 and 9 months were obtained. The carcasses were chilled for 24 h at 4 °C. Slaughter analysis was performed

according to the procedure used at the Instytut Zootechniki PIB (National Research Institute of Animal Production) as reported in NRIAP (2009).

Meat Samples. For VOCs analysis, 12 ca. 200 g leg muscle (m. biceps femoris) samples (one sample from each of the 12 animals from the groups) were taken and cut into smaller pieces (ca. 2-3 cm). Next, they were vacuum-packed in 70 – 100 g portions into polyamide/polyethylene bags, and stored at -80 °C.

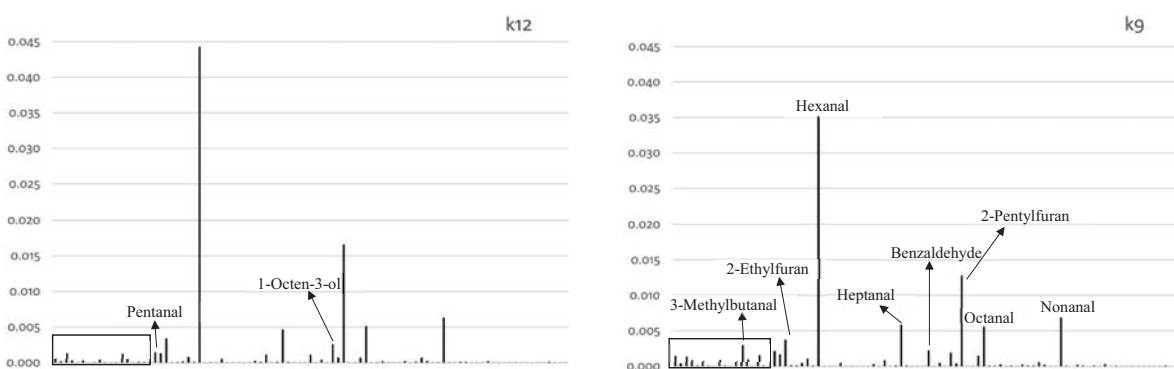
Sample Preparation and Analysis. An unthawed (-80 °C) and previously cut ca. 10 g sample was processed at a low temperature by liquid nitrogen, then homogenized and moved into a 20 ml vial sealed with an aluminum crimp cap and PTFE/silicon septum. Prior portioning of the sample, as well as using the liquid nitrogen, kept the material frozen until the heat treatment and analysis started. Then, the thawed sample was baked in the same sealed vial (170 °C, 35 min) and analyzed by HS-SPME-GC/MS using the gas chromatograph mass spectrometer GCMS-QP 2010 Plus (Shimadzu, Japan), 50/30 μ m DVB/CAR/PDMS fiber (Supelco, USA), and Zebron ZB-5MSi 30m x 0.25mm, 0.25 μ m column (Phenomenex, USA). To confirm the compound identification, a ZB-Wax column was applied (30m x 0.25mm, 0.25 μ m column, Phenomenex, USA). For a sample injection the SPME autosampler AOC-5000 (Shimadzu, Japan) was used. The conditions were as follows: equilibration time, 30 min, equilibration temperature, 50 °C, exposition time, 15 min, exposition temperature, 50 °C, and desorption was performed in the splitless port at 240 °C for 2 min. The analysis was done at helium flow (purity, 99.999; Linde Gaz Polska, 1 ml min⁻¹), oven temperature 37 °C (10 min), that was increased to 132 °C (4 °C/min) and 240 °C (8 °C/min). During the run, total ion currents in the 35–450 m/z mass range were monitored. The electron impact energy of the mass spectrometer detector was 70 eV. The temperature of the ion source was set at 250 °C. The autosampler rack was cooled to about +3 °C. The elimination of analytical trends effects was provided by setting the sample vials in a rack in an uneven manner (Calik et al., 2017). This way of proceeding was the next crucial step of the whole analysis process. The paraffins for compounds identification, standards, and blank samples – to exclude extraneous compounds – were also analyzed.

Chromatogram Integration and Peak Identification. The substances were identified based on mass spectra libraries (NIST08, NIST08s, FF NSC1.3), and by comparing retention index values (RI) with either published values from the National Institute of Standards and Technology (NIST, 2018), or those of authentic standards. These values were calculated as Kovats' RI for isothermal analysis, and as Van den Dool and Kratz RI for using temperature ramp, based on n-paraffins. After that, normalized peaks area (Area %) of the substances was calculated. The minimum area, 9000 (in area units) was taken for calculating an average for each group (n=2). The total area of all the peaks was about 5×10^8 area units.

Chemometric analysis. The differentiation between the 2 goat groups: k12 and k9 based on intensity spectral data was performed. Firstly, data (416 m/z ions, from the range between 35 and 450 m/z) were logarithmically transformed. Then the data pre-selection by use of Fisher's ratio method was done, based on basic Microsoft Excel® statistical functions. Next, PCA was used, whereby the number of variables was reduced to the first four principal components using Kaiser screen test in order to avoid the classification model overfitting. Then, the LDA analysis was performed and classification accuracy was calculated by cross validation method. The PCA-LDA analysis was executed using Statgraphics® Centurion XVI equipped with a multivariate statistics package.

RESULTS AND DISCUSSION

Identification and classes of volatile compounds. In this study, 93 volatile compounds analyzed by HS-SPME-GC/MS were found (mentioned additionally in a scientific literature), out of which 49 were confirmed on two columns: non-polar ZB-5MSi and polar ZB-Wax, whereas 5 were verified by using authentic standards (Table 1). The most abundant (Area%) substances, on average in all animal groups, were: hexanal, 2-pentylfuran, nonanal, heptanal, octanal, 2-ethylfuran, and 1-octen-3-ol. The most abundant compounds present in particular groups were as follows: in the first goat meat group k12 - hexanal, 2-pentylfuran, nonanal, octanal, heptanal, 2-ethylfuran, as well as 1-octen-3-ol and pentanal, and in the second goat meat group k9 - hexanal, 2-pentylfuran, nonanal, heptanal, octanal, 2-ethylfuran, as well as 3-methylbutanal and benzaldehyde (Graph 1). Study on goat meat (Madruga et al., 2010) shows that the largest classes of volatile compounds are aldehydes, hydrocarbons, ketones, and alcohols. It was similar in our work: 29 aldehydes, 18 hydrocarbons, 13 ketones, 12 alcohols were found. Other classes were: 11 sulfur compounds, 5 furans, 1 ester, 1 acid, and 1 lactone, as well as 1 nitrogen, and 1 nitrogen and sulfur containing compound. The greatest shares of aldehydes (above 65%) and furans (above 18%) in goat meat were found. Alcohols and ketones accounted for about 4.1% to 5.5%, whereas sulfur compounds were in amounts between 1.4% and 2.7%. A large number



Graph 1 Average (n=2 for each group) profiles of volatile compounds in 2 goat meat groups: k12 and k9. The range in the square is potentially differentiating.

Graf 1. Prosječni profili (za svaku skupinu) hlapljivih sastojaka u mesu dviju skupina koza: k12 i k9. Raspon u okviru potencijalno se razlikuje.

Table 1 Profiles (Area%) of volatile compounds in meat of Carpathian goats aged 12 months (k12) and 9 months (k9)

Tablica 1. Profili (Područje %) hlapljivih sastojaka u mesu karpatskih koza u dobi od 12 mjeseci (k12) i 9 mjeseci (k9)

	Compound ¹	RI ²		k12		k9		References ³
		ZB-5Msi	Wax	Area %x10	SD x10	Area %x10	SD x10	
1	Acetaldehyde (S)	<500	713	6.07	1.93	15.04	0.65	Kim et al. (2002)
2	Methanethiol	<500	692	1.70	0.62	3.87	0.47	Madruga et al. (2010)
3	Acetone (S)	<500	823	13.10	1.78	13.92	3.28	Kim et al. (2002)
4	Dimethyl sulfide	536	759	3.28	0.27	9.24	3.38	Kim et al. (2002)
5	Carbon disulfide	548	731	0.01	0.01	1.08	0.03	Madruga et al. (2010)
6	2-Methylpropanal	570	821	3.29	0.10	8.11	0.35	Bueno et al. (2014)
7	2,3-Butanedione (S)	600	-	0.13	0.04	0.63	0.03	Madruga et al. (2010)
8	Butanal	602	881	0.35	0.03	0.12	0.03	Kim et al. (2002)
9	2-Butanone	604	-	4.45	0.19	10.01	1.61	Rivas-Cañedo et al. (2013)
10	2-Methylfuran	613	875	0.40	0.06	0.65	0.07	Shahidi (1994)
11	Methylthioethane	628	829	0.05	0.01	0.04	0.01	Nam et al. (2003)
12	Acetic acid (S)	653	-	0.09	0.00	7.61	4.73	Rivas-Cañedo et al. (2013)
13	3-Methylbutanal	667	-	12.80	0.55	28.56	2.05	Bueno et al. (2014)
14	2-Methylbutanal	676	916	5.68	0.70	10.50	2.67	Bueno et al. (2014)
15	Thiophene	680	1019	0.16	0.04	0.26	0.21	Madruga et al. (2010)
16	1-Penten-3-ol	692	1171	1.06	0.07	15.63	5.57	Madruga et al. (2010)
17	2-Pentanone	696	-	0.77	0.10	0.81	0.37	Ba et al. (2010)
18	1-Heptene	698	-	1.06	0.25	0.37	0.05	Madruga et al. (2010)
19	Pentanal	708	981	14.61	2.56	21.51	0.45	Bueno et al. (2014)
20	Heptane (S)	710	-	13.17	0.33	16.95	4.56	Madruga et al. (2000)
21	2-Ethylfuran	711	957	34.23	0.39	37.50	3.49	Madruga et al. (2010)
22	Dimethyl disulfide	743	1067	0.36	0.22	1.54	0.65	Madruga et al. (2010)
23	Toluene (S)	770	1035	0.66	0.15	1.38	0.04	Madruga et al. (2010)
24	1-Pentanol	778	1260	1.59	0.23	4.65	5.24	Madruga et al. (2010)
25	2-Methylthiophene	779	-	7.97	0.63	10.75	3.29	Madruga et al. (2010)
26	2-Hexanone	799	-	1.04	0.11	1.30	0.21	Ba et al. (2010)
27	Hexanal	785	1079	442.7	0.57	352.8	38.15	Bueno et al. (2014)
28	3- Octene or 3-methyl-2-heptene	814	-	0.02	0.00	0.04	0.02	Madruga et al. (2010); Kim et al. (2002)
29	2-Octene	819	847	0.45	0.08	0.22	0.02	Madruga et al. (2010)
30	1,3-Octadiene	824	-	0.19	0.09	0.06	0.01	Madruga et al. (2010)
31	Pentyl formate	821	-	5.32	0.05	5.00	0.91	Rivas-Cañedo et al. (2013)
32	Furfural	827	-	0.07	0.01	0.08	0.01	Madruga et al. (2010)
33	(E)-2-hexenal	858	-	0.08	0.01	0.14	0.02	Bueno et al. (2014)
34	Ethylbenzene	861	-	0.11	0.00	0.05	0.01	Madruga et al. (2000)
35	p-Xylene	865	-	0.08	0.01	0.05	0.04	Madruga et al. (2000)
36	3-Methyloctane	872	-	0.04	0.00	0.03	0.02	Shahidi (1994)
37	1-Hexanol	871	1361	2.43	0.43	3.22	0.17	Madruga et al. (2010)

38	Styrene	882	-	0.62	0.09	0.37	0.18	Madruga et al. (2010)
39	2-heptanone	886	-	10.89	0.42	8.34	1.10	Bueno et al. (2014)
40	3-Heptanol	888	-	0.01	0.01	0.04	0.02	Baruth and Ternes (2011)
41	(Z)-4-Heptenal	895	1237	0.95	0.09	1.31	0.08	Madruga et al. (2000); Madruga et al. (2010)
42	Heptanal	896	1180	46.68	6.94	58.69	9.40	Bueno et al. (2011)
43	γ -Butyrolactone	902	1614	0.84	0.04	0.82	0.32	Rivas-Cañedo et al. (2013)
44	Dimethyl sulfone	909	1912	0.31	0.05	0.20	0.02	Rivas-Cañedo et al. (2013)
45	2-Heptenol	943	1496	0.07	0.02	0.02	0.02	Shahidi (1994)
46	3-Ethylcyclopentanone	954	-	0.14	0.00	0.17	0.03	Madruga et al. (2010)
47	Benzaldehyde	957	1514	11.18	1.83	22.41	7.48	Madruga et al. (2000)
48	Dimethyl trisulfide	963	-	0.08	0.03	0.24	0.26	Madruga et al. (2010)
49	1-Heptanol	971	1463	4.13	1.62	4.73	0.36	Madruga et al. (2010)
50	1-Octen-3-one	971	-	0.05	0.00	0.09	0.04	Bueno et al. (2014)
51	1-Octen-3-ol	977	1457	26.03	2.83	19.14	1.15	Bueno et al. (2011)
52	2,3-Octanedione	982	1325	7.22	0.81	3.76	1.51	Madruga et al. (2010)
53	2-Pentylfuran	987	1226	166.0	43.66	128.2	56.38	Bueno et al. (2011)
54	Thiophene-2-carboxaldehyde	992	1699	0.04	0.01	0.03	0.04	Shahidi (1994)
55	3-Octanol	997	-	0.05	0.01	0.04	0.01	Madruga et al. (2010)
56	2-(2-pentenyl)furan	1005	1297	6.95	3.93	14.71	7.77	Elmore et al. (2000)
57	Octanal (S)	1003	1284	51.46	5.50	55.99	7.14	Bueno et al. (2014)
58	2-Acetylthiazole	1010	-	0.33	0.08	0.82	0.23	Ba et al. (2010)
59	2,2,7,7 (or 2,2,4,4)-Tetramethyloctane	1025	-	0.38	0.17	0.57	0.62	Lee et al. (2003)
60	1,3-hexadiene, 3-ethyl-2-methyl-	1024	1406	1.69	0.10	2.63	1.37	Baruth and Ternes (2011)
61	3-Octen-2-one	1038	1402	0.08	0.03	0.04	0.05	Baruth and Ternes (2011)
62	Benzacetalddehyde	1038	-	0.30	0.01	0.78	0.23	Madruga et al. (2010)
63	2-Ethylhexanol	1046	-	0.00	0.00	0.03	0.03	Madruga et al. (2000)
64	(E)-2-Octenal	1058	1424	1.88	0.38	2.64	1.69	Ba et al. (2012)
65	2-Acetylpyrrole	1060	1982	0.03	0.01	0.79	0.10	Baruth and Ternes (2011)
66	(E)-2-Octen-1-ol	1066	1612	1.39	0.77	1.07	0.30	Madruga et al. (2010)
67	1-Octanol (S)	1069	1564	6.81	0.24	6.30	1.84	Madruga et al. (2000)
68	2-nonanone	1084	1386	2.10	0.28	1.93	0.35	Madruga et al. (2010)
69	6-Nonenal	1092	-	0.23	0.06	0.16	0.04	Narváez-Rivas et al. (2010)
70	Undecane (S)	1097	-	0.35	0.02	0.33	0.01	Madruga et al. (2000)
71	Nonanal	1102	1390	63.11	3.92	68.78	13.77	Bueno et al. (2011)
72	5-undecen, 9-methyl-	1116	-	0.49	0.11	0.60	0.39	Lorenzo et al. (2014)
73	1,2,4-Trithiolane, 3,5-dimethyl	1138	-	0.00	0.00	0.00	0.00	Shahidi (1994)
74	2-Decanone	1190	1492	1.55	0.46	1.68	0.66	Madruga et al. (2010)
75	Decanal	1203	-	1.21	0.28	1.31	1.05	Bueno et al. (2014)
76	3-Dodecyne	1222	-	0.04	0.00	0.09	0.06	Pongsetkul et al. (2016)
77	2-Decenal	1265	1627	0.08	0.08	0.74	0.55	Bueno et al. (2011)
78	2-Decen-1-ol	1284	-	0.09	0.04	0.12	0.15	Narváez-Rivas et al. (2010)
79	2-n-Octylfuran	1293	-	1.94	0.15	3.24	2.80	Ba et al. (2010)
80	Tridecane (S)	1298	-	0.21	0.01	0.30	0.15	Madruga et al. (2000)
81	Undecanal	1306	1601	0.29	0.00	0.47	0.39	Baruth and Ternes (2011)

82	2,4-Decadienal	1314	-	0.04	0.01	0.28	0.26	Bueno et al. (2011)
83	(E)-2-Undecenal	1363	1749	0.18	0.06	0.34	0.24	Madruga et al. (2000)
84	Dodecanal	1409	1704	0.11	0.11	0.19	0.25	Bueno et al. (2011)
85	5,9-Undecadien-2-one, 6,10-dimethyl	1460	-	0.03	0.00	0.01	0.01	King et al. (1993)
86	Tridecanal	1516	-	0.11	0.01	0.12	0.10	Rivas-Cañedo et al. (2013)
87	Tetradecanal	1608	1931	0.12	0.07	0.14	0.06	Madruga et al. (2000)
88	Heptadecane	1698	-	0.04	0.01	0.05	0.01	Lorenzo et al. (2014)
89	Pentadecanal	1718	2017	0.16	0.01	0.14	0.05	Madruga et al. (2000)
90	Hexadecanal	1816	2147	1.24	0.29	1.06	0.36	Madruga et al. (2000)
91	3,7,11,15-Tetramethyl-2-hexadecene	1844	-	0.00	0.00	0.00	0.00	Madruga et al. (2000)
92	Heptadecanal	1902	-	0.03	0.01	0.04	0.00	Madruga et al. (2000)
93	Octadecanal	2018	-	0.08	0.00	0.04	0.00	Madruga et al. (2000)

¹ Compound identified by mass spectrum libraries (NIST08, NIST08s, FF NSC1.3) and retention index, (S) means additional identification by use of the standard.

² RI – retention index (calculated as Kovats' RI for isothermal analysis, and Van den Dool and Kratz RI for using temperature ramp).

³ The reference from the table appears in the literature section.

of hydrocarbons did not translate into a content of these compounds (less than 2.4%). Other substances (an ester, acid, lactone, as well as nitrogen and nitrogen and sulfur containing compounds) were in smaller amounts (Graphs 2-3). The furans, the lipids-derived volatile compounds, such as 2-pentylfuran, 2-(2-pentenyl) furan and 2-ethylfuran, made a great contribution to the overall volatile compounds content. The latter ones are probably derived from the degradation of DHA and EPA upon heat treatment of the meat (Elmore et al., 2000).

The most odor-active compounds. 11 sulphur containing compounds in meat were found. Among them the dimethyl sulfide, 2-methylthiophene and methanethiol were most abundant. They come from cysteine and methionine, and, generally, have low odor thresholds. The most odor-active sulphur compounds (Madruga et al., 2010) are methanethiol (rotten, eggs) and carbon disulfide (sulfury, fruity, burnt, cabbage). The sulfur and nitrogen containing compound – 2-acetylthiazole – is also treated in the literature as an active odorant (roasted, nutty, popcorn, meaty). Hydrocarbons come from the long-chain fatty acids. They are not meaningful aroma active substances, in contrast to aldehydes, which are active odorants such as (Resconi et al., 2010): 2,4-decadienal (burnt meat, rancid), 2-methylbutanal (sweet, mushroomy), hexanal (green, floral), octanal (lemon, floral), and, according to Ba et al. (2012): 3-methylbutanal (meaty, fish, rotten, aldehyde, valeric acid, fatty), heptanal (fruity, fatty, sweet, oily), nonanal (sweet, fatty, green), and, according to Madruga et al. (2010): pentanal

(pungent, almond), benzaldehyde (roasted pepper, nutty), (Z)-4-heptenal (cream like, fatty, rancid, crabby), (E)-2-octenal (marine, green, solvent). All of them existed in these study in goat meat. Ketones and alcohols present in meat in this study can also be active odorants (2-heptanone, soapy, fruity, blue cheese, and 1-octen-3-ol and 1-octen-3-one, both with mushroomy aroma, Madruga et al., 2010), as well as other compounds, like: 2-pentylfuran (geranium, spicy, Bueno et al., 2011) and γ -butyrolactone (caramel, sweet, Flavornet, 2018).

Chemometrics. Looking at the results, seen that, especially in graph 1 it seems that they differente the k12 from k9 group. So, to avoid possible of discrimination, the Fisher's ratio-PCA-LDA statistics was applied.

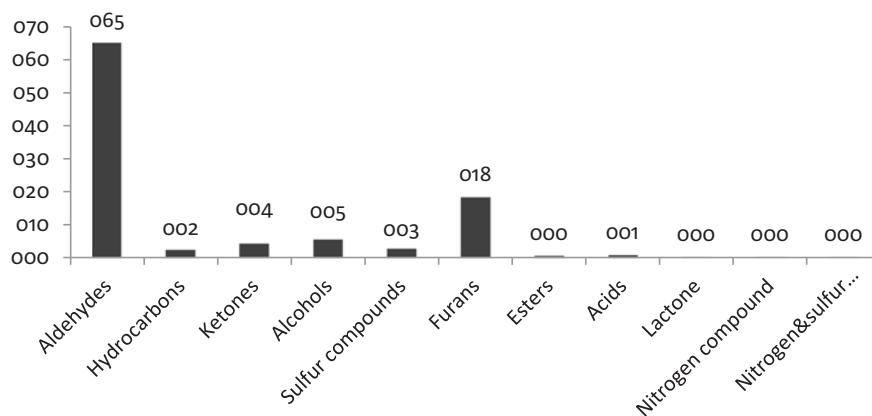
The multivariate statistics in some studies was used to differentiate animal groups based on volatile compounds composition in their food products. Vasta et al. (2010) used PCA to discriminate lambs according to the feeding treatment, based on muscle volatile compounds. The first principal component accounted for 53.1%, the second one for 25.2% of the variability. In a study of Elmore et al. (2000) the principal component analysis displayed the effect of a diet and breed on the aroma volatiles from lamb meat, where the two principal components accounted for 40.0% and 34.4% of the total variance, respectively. And finally, in the study on Rhode Island Red capons and cockerels (Calik et al., 2017) the PCA analysis was performed, based on mass spectra of volatile compounds (by

SPME-GC-MS analysis) in breast muscles, to show the differences between these groups. The first two principal components explained 88.4% of the variance. Additionally, the classification was applied. The accuracy, calculated upon cross-validation, was 100%.

In our study, the first two principal components accounted for 88.8% of the total variance. These values for the first three principal components were 94.6%. The classification accuracy values in both groups were 100%. The cross validation results of the classification model and graph 4 show perfect distinguishing the k12 group from the k9 group.

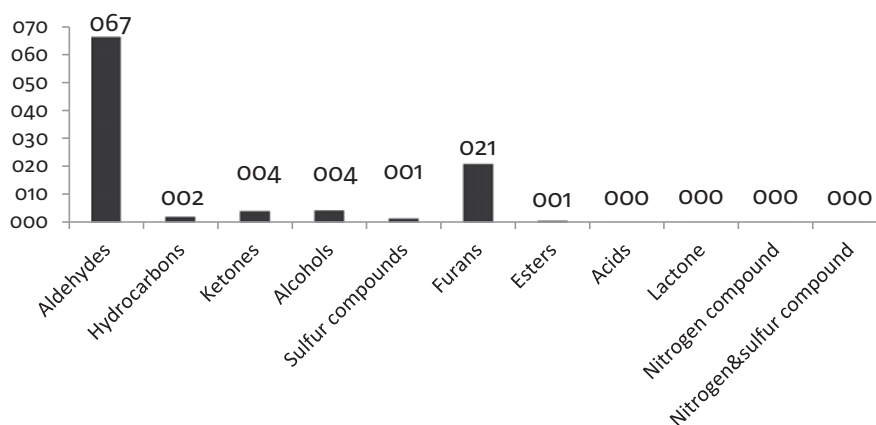
So, a very good effectiveness of the discriminant analysis is clearly visible and the accuracy over 80% is considered satisfactory (Stanimirova et.al., 2010).

In conclusion, the results from this study show that it is possible to identify in goat's leg meat 93 volatile compounds, out of which 49 were confirmed on two columns: non-polar ZB-5MSi and polar ZB-Wax, whereas 5 were verified by using authentic standards. HS-SPME-GC/MS analysis together with chemometrics occurs to be the effective tool for the discrimination of the meat from the Carpathian goats aged 12 and 9 months.



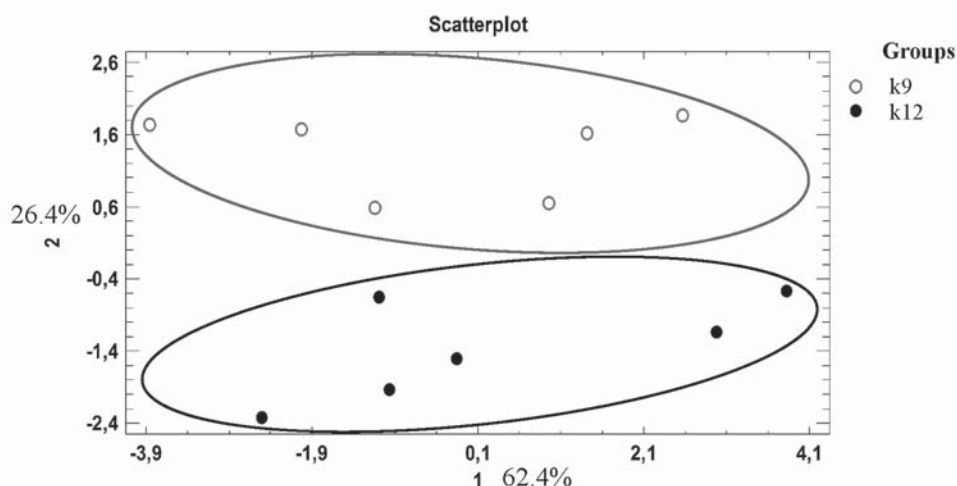
Graph 2 Classes of volatile compounds (Y-axis - averaged Area%) in goat meat group - k12.

Graf 2. Hlapljivi sastojci kozjeg mesa skupine k12



Graph 3 Classes of volatile compounds (Y-axis - averaged Area%) in goat meat group - k9.

Graf 3. Hlapljivi sastojci kozjeg mesa skupine k9.



Graph. 4 Fisher's ratio-PCA-LDA sample classification of the two Carpathian goat groups (each - $n=6$) aged 9 months (k9) and 12 months (k12), based on spectral data from volatiles analysis by HS-SPME-GC/MS.

Graf 4. Fisherov omjer -PCA-LDA klasifikacije uzorka dviju skupina karpatske koze u dobi 9 mjeseci (k9) i 12 mjeseci (k12) na temelju spektralnih podataka iz analize hlapljivosti pomoću HS-SPME-GC/MS.

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SAŽETAK

Radi utvrđivanja hlapljivih sastojaka u mesu poljske karpatske koze uzorci pečenog mišića noge u dvije skupine u dobi od 9 i 12 mjeseci podvrgnuti su plinskoj kromatografiji/masenoj spektrometriji (HS-SPM-GC/MS) mikroekstrakcije čvrste faze prostora glave. Obavljena je raznovrsna statistika uključujući metodu Fisherovog omjera za preSelekciju varijabla i analiza glavnog sastojka zajedno s linearnom diskriminantnom analizom. Pronađena su 93 hlapljiva sastojka od kojih je 49 potvrđeno u dva stupca: nepolarni ZB-5MSi i polarni ZB-Wax, dok ih je 5 potvrđeno primjenom autentičnih standarda. HS-SPME-GC/MS analiza zajedno s kemometrijom čini se da je djelotvorno sredstvo za razlikovanje mesa karpatskih koza u dobi 12 i 9 mjeseci. Prva dva glavna sastojka iznosila su 88,8% ukupnog neslaganja. Te su vrijednosti za prva tri glavna sastojka bile 94,6%, a vrijednosti točnosti klasifikacije za obje skupine bile su 100%.

Ključne riječi: meso, karpatska koza, hlapljivi sastojci, SPME-GC/MS