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Volatile composition of raw spirits of different botanical origin

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The main purpose of the research was to determine the volatile composition of raw spirits, on the basis of trace compound isolation from their volatile fraction, as well as a comparison of the obtained volatile profiles of agricultural distillates of different botanical origins (maize, wheat, triticale, rye). This approach was chosen to improve methods of quality control and quality assurance in the spirit industry. Volatile composition of all raw spirit samples derived from different raw materials (rye, triticale, maize and wheat) were formed using headspace solid-phase microextraction (HS-SPME) and capillary gas chromatography–mass spectrometry (GC-MS). Performed studies indicated the presence of over 100 compounds in the raw spirit volatile fraction. The richest volatile profile was obtained from samples produced from wheat and the poorest from those produced from corn. Moreover, on the basis of performed discriminant analysis (using the variables 2-methylbutanol + 3-methylbutanol, 3-methylbutyl hexanoate, ethyl dodecanoate, ethyl heptanoate and 3-methylbutyl octanoate), it was possible to distinguish between agricultural distillates originating from triticale and distillates produced from wheat.

Keywords: alcoholic beverage processing; raw spirits; volatile compounds; botanical origin; solid-phase microextraction

Introduction

Agricultural distillates are an unrefined ethanol obtained by distillation after fermentation of different agricultural materials. These products are mainly derived from potatoes, white beets or grain materials, including maize, rye, wheat, triticale or barley. Sometimes, materials such as stale bread, spoiled jams or chocolate are also used for their production *(1)*. Apart from ethanol, a series of by-products such as organic acids, esters, higher alcohols, sulphur compounds and carbonyl compounds are formed during the alcoholic fermentation process *(2–4)*. Quantitative and qualitative composition of agricultural distillates is affected by many factors, including the raw material used during the production process, fermentation conditions as well as processing parameters, including even the condition of the processing installation *(5–9)*. Some of these pollutants occur in specific concentrations and are characteristic for the raw materials used in the production process. Raw spirits are semi-products of vodka processing and their average annual production reaches 3 million litres. The fact that raw spirits are used for the production of unflavoured and flavoured alcoholic beverages makes these products responsible for the final chemical composition of spirit drinks. Therefore, spirit drink producers require complex characterization of raw spirit samples in order to ensure quality control and quality assurance.

Numerous methods have been developed and successfully applied for analysing impurities in alcoholic beverage samples. However, most of the research has been focused on quality control *(10)*, authentication *(11)*, characterization *(12–17)* and classification according to the geographic origin *(18)* of the final products – alcoholic beverages. Procedures for the determination of principal by-products in semi-products such as raw spirits have not been sufficiently developed to date.

The idea of using instrumental analysis for the assessment of semi-products (agricultural distillates) was chosen owing to the numerous constraints of currently used methods proposed by Polish standards. Determination of total parameters (e.g. the total amount of aldehydes, expressed as acetaldehyde) is not a sufficient approach in light of the development of instrumental analytical techniques. Instrumental techniques that are reliable, environmentally friendly and easily adaptable to any industrial laboratory could allow consistent characterization of the composition of spirits samples. This methodology had been already successfully applied for the discrimination of quality of raw spirits *(19)*.

With Poland's accession to the European Union, spirit producers are now also obliged to follow EU quality standards *(20,21)*. To meet the demands of the European Union, producers intend to indicate on the label information about the raw material that was used for the production of alcoholic beverages. This approach is possible only when the producers are confident about the raw material used for the production of alcoholic beverages. Very often distillery plants do not have their own facility to produce agricultural distillates; thus they buy them from local agricultural distilleries. Therefore, it is very difficult for distillery plants to control the production of raw spirits at every stage.

Keeping this in mind, the objective of this study was to determine the composition of good quality raw spirits, on the basis of the isolation of volatile compounds from their volatile fraction as well as a comparison of volatile profiles of agricultural distillates of different botanical origins (maize, rye, triticale and wheat). The presented research constitutes a new approach to detailed and

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reliable quality control, in order to ensure a better method for verifying and maintaining a desired level of quality for raw spirit and beverages produced from them.

Methods and materials

Samples and chemicals

Samples of raw spirits used in the investigation were produced from four different raw materials – rye, wheat, triticale and maize – and were collected from several different agricultural distilleries located in the Pomeranian region of Poland. All of the samples were collected during the same calendar year. Raw spirits selected for these studies were characterized by good quality consistent with Polish Standard requirements (PN-A-79528-2:2002) *(22)*. Ethanol concentration in samples was approximately 90% (v/v). Samples were sealed with parafilm and stored at 5 °C. All of the high-purity standards (>97%) selected for the identification of compounds, as well as a homologous series of alkanes with a chain length of C_5–C_{20} (used for the calculation of retention indexes), were purchased from Sigma-Aldrich (Steinheim, Germany). In this work, deionized water was used (MilliQ A10 Gradient/Elix System, Millipore, Bedford, MA, USA). All standard solutions were prepared by dissolving standards in anhydrous ethanol and were stored at 5 °C.

HS-SPME/GC-MS conditions and data analysis

For the analysis of volatile compounds in the investigated samples, a gas chromatograph coupled with a mass spectrometer (GC-MS) was used (7890A GC System, 5975C Inert MSD Agilent Technologies). For the isolation and preconcentration of volatile by-products present in samples, HS-SPME was applied. All raw spirit samples were dissolved in high-purity water to obtain 8 mL of 20% ethanol (v/v). HS-SPME was performed under optimal parameters used for highly efficient isolation of volatile compounds from raw spirit samples. This procedure was a small modification of a procedure that was used in previous studies *(19)*. The prepared sample was placed in a block heater at 40 °C and kept for 5 min for stabilization of the headspace. After this, extraction of the volatile fraction using a DVB/CAR/PDMS fiber (2 cm length, 50/30 μm film thickness) was performed. Extraction was carried out for 40 min at 40 °C. During headspace stabilization and extraction, the sample was agitated. After this step, the SPME fiber was removed from the vial and placed into a GC injector heated at 250 °C for 5 min for thermal desorption of the absorbed/adsorbed analytes. Thermal desorption was carried out in the splitless mode of the injector. The fibers were conditioned daily before the experiments by placing them into a GC injector at 250 °C for 15 min. Separation of impurities was achieved on a DB-WAX capillary column with polyethylene glycol (PEG) bonded stationary phase (30 m × 0.25 mm i.d., 0.5 μm film thickness). The column temperature program was as follows:

$$40^{\circ}\mathrm{C}\ (1\ \mathrm{min}) \xrightarrow{6^{\circ}\mathrm{C/min}} 80\mathrm{C}^{\circ} \xrightarrow{5^{\circ}\mathrm{C/min}} 180^{\circ}\mathrm{C} \xrightarrow{7^{\circ}\mathrm{C/min}} 220^{\circ}\mathrm{C}\ (5\ \mathrm{min})$$

The carrier gas was helium with a flow rate of 1.5 mL/min. The transfer line temperature was 240 °C and the mass spectrometer operated in electron impact mode (70 eV) at 220 °C. Detection was carried out in scan mode in a range between 40 and 400 *m/z*. All data were acquired and processed using ChemStation software. For statistical purposes, discriminant analysis (together with supporting tests, e.g. the Shapiro–Wilk test) with the use of the Statistica 10 software was applied.

Results and discussion

Twenty-four raw spirit samples produced from four raw materials such as maize (seven samples), rye (eleven samples), triticale (three samples) and wheat (three samples) were chosen for this study. Each sample was analysed with three repetitions. An organoleptic quality test of all samples was performed in accordance with the Polish Standard PN-A-79528-2:2002 *(22)* and scaling method ISO 4121:1998 *(23)*. Because the amount of by-product is influenced by quality, only good quality samples consistent with Polish Standard requirements were chosen for this research *(19)*. Poor quality raw spirits are usually characterized by mouldy, musty, pungent and cabbage flavours. In comparison, good quality samples are characterized only by sweet, fruity and solvent like descriptors *(24)*. Average acidity of the samples was in a range of 0.02–0.5 g/L, whereas total aldehyde concentration was in a range of 0.02–0.06 g/L. These parameters were determined according to PN-A-79528-7:2001 *(25)* and PN-A-79528-4:2000 *(26)*.

Identification of volatile compounds present in samples of agricultural distillates was achieved by a comparison of mass spectra obtained for each compound, with spectra which are available in the NIST Database of spectra (National Institute of Standards and Technology). Moreover, the retention indexes were calculated with the use of a homologous series of alkanes with a chain length from C_5 to C_{20}. Calculated retention indices were compared with indices presented in the literature. Additionally, the identification of some compounds was confirmed with uniformity of their retention times and mass spectra with standard compounds.

Figure 1 presents typical chromatograms obtained for samples of agricultural distillates derived from wheat, triticale, rye and maize. By comparison of volatile profiles obtained for each group of raw spirits, some differences in the number and intensity of peaks can be noticed. Thus, the most characteristic chromatograms were obtained for raw spirits produced from wheat. This group was characterized by the richest profile of volatile compounds in terms of quality and quantity of isolated compounds. On the other hand, the poorest chromatograms were obtained for raw spirits produced from maize. The detector response towards isolated and identified compounds was smaller in raw spirits produced from maize than in case of other samples. It should also be noted that the chromatogram of raw spirits obtained from triticale (hybrid of wheat and rye) gave, at first glance, a more similar image to the characteristics of distillates produced from wheat rather than rye. It would seem that the distillates produced from triticale have more in common with distillates produced from wheat.

The presented studies indicated the presence of over 100 fermentation by-products in the volatile fraction of the investigated raw spirit samples (Table 1). Compounds belonging to esters, higher alcohols, aldehydes, acetals and furans were the main constituents of the raw spirits profile. Figure 2 shows the percentage of four identified groups presented in the volatile fraction of the analysed samples in relation to raw materials used during the production process. Among all identified

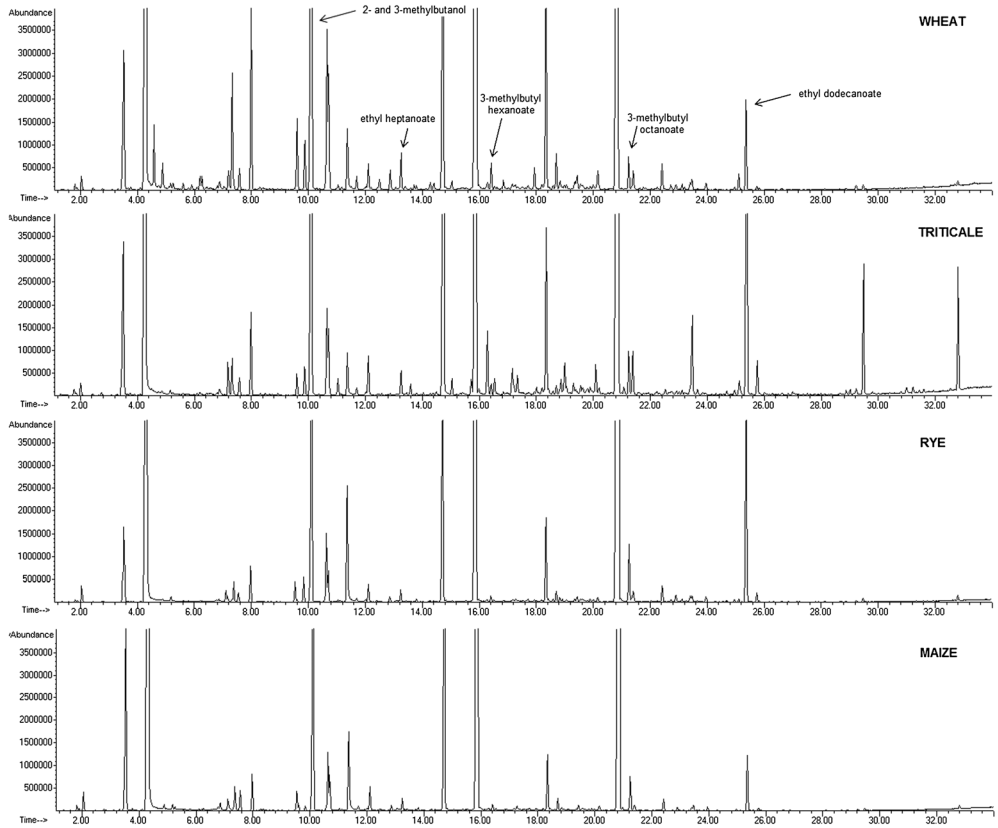

Figure 1. Typical chromatograms obtained for raw spirit samples produced from wheat, triticale, rye and maize.

Table 1. Volatile compounds identified in raw spirits of different botanical origin: maize, triticale, rye and wheat. The fragment ions masses used during peak integrations are given in brackets

No.	Compound name	$RI_{Calc.}$	$RI_{Lit.}$ *(27–53)*
1	Ethoxy ethene *(44)*	676	679
2	Acetaldehyde *(45)*	717	706; 713; 721
3	Ethyl formate *(45)*	720	728
4	1-Ethoxybutene (57)	836	870
5	2-Methylfuran (82)	891	876; 877; 893; 895
6	Ethyl acetate *(43)*	895	893; 898; 902; 906; 908
7	1,1-Diethoxyethane (73)	905	906
8	3-Methylfuran (82)	911	915; 832
9	2-Methylbutanal *(47)*	931	862; 914; 935; 936
10	3-Methyl butanal (58)	933	912; 917; 935
11	2,5-Dimethylfuran (96)	961	952; 974; 976
12	Ethyl propanoate (57)	965	950; 957; 978
13	1,1-Diethoxy-2-methylpropane (103)	973	969; 991
14	3-Methyl-2-butanol (103)	996	1094
15	2,3-Dihydroxypropanal (61)	997	
16	*n*-Propyl acetate (61)	998	969; 976
17	2-Methylpropyl acetate *(56)*	1028	1005; 1007
18	2-Butanol (59)	1040	1020; 1022; 1026; 1035
19	α-Pinene (93)	1041	1030; 1035
20	1-(2-Furanyl)-ethanone (95)	1042	
21	2-Ethyl-5-methylfuran (95)	1043	1028; 1052
22	Ethyl butanoate (71)	1047	1036; 1037; 1047; 1057
23	Toluene (91)	1051	1040; 1062; 1071
24	1-Propanol (59)	1052	1035; 1038; 1045; 1052

(Continues)

Table 1. *(Continued)*

No.	Compound name	$RI_{Calc.}$	$RI_{Lit.}$ *(27–53)*
25	1,1-Diethoxy-2-methyl butane (103)	1058	1063; 1083
26	1,1-Diethoxy pentane (103)	1059	
27	1,1-Diethoxy-3-methyl butane (103)	1059	1068; 1086
28	Dimethyl disulfide (94)	1080	1075; 1078; 1094
29	Hexanal *(56)*	1085	1110; 1104
30	2-Methyl-1-propanol *(43)*	1096	1097; 1124
31	1-(1-Ethoxyethoxy)-pentane (73)	1106	
32	*β*-Pinene (93)	1107	1118; 1176
33	3-Methyl-1-butanol acetate (70)	1124	1140
34	*p*-Xylene (91)	1130	1127; 1149; 1162
35	Ethylbenzene (91)	1131	1124; 1125; 1149
36	2-Butylfuran (81)	1132	1056; 1140; 1151
37	*m*-Xylene (91)	1140	1132; 1150; 1168
38	*o*-Xylene (91)	1143	1182; 1216
39	3-Carene (93)	1144	1127; 1144; 1157
40	7-Metyl-3-metylen-l,6-oktadien (93)	1198	
41	Heptanal (70)	1205	1186; 1197; 1208
42	D-Limonene (68)	1206	1194; 1208; 1212; 1216; 1218
43	2-Metylobutanol + 3-metylobutanol (58)	1216	1212; 1215; 1218; 1219
44	2-Ethyl-phenol (107)	1226	
45	2-Pentylfuran (81)	1237	1240; 1252
46	Ethyl hexanoate (88)	1239	1238; 1252
47	Styrene (104)	1246	1261; 1273; 1287
48	3-Methylbutyl 2-methylpropanoate (71)	1258	1187
49	Hexyl acetate *(56)*	1277	1268
50	4-Carene (121)	1290	1128
51	1,1,3-Triethoxypropane (59)	1292	
52	1-Adamantanol (95)	1305	
53	1,5-Dimethyl-1-vinyl-4-hexen butyrate (71)	1326	
54	Propyl hexanoate (99)	1326	1324
55	2-Tetradecene (57)	1331	
56	1,1-Diethoxyheptane (103)	1335	
57	2,5-Dimethylpyrazine + 2,6-dimethylpyrazine (108)	1338	1318; 1325; 1361
58	Ethyl heptanoate (88)	1343	1331; 1353
59	1,2,4-Trimethylbenzene (105)	1352	1316
60	2-Methylpropyl hexanoate (99)	1364	1369
61	Hexanol *(56)*	1369	1369; 1354
62	Ethyl 2-furancarboxylate (95)	1379	
63	Heptyl acetate (70)	1390	1406; 1415
64	Cyclohexanecarboxylic acid, 3,5-difluorophenyl ester (111)	1396	1433
65	2-Pentylthiophene (97)	1398	1438; 1452; 1486; 1509
66	Hexyl butanoate (71)	1426	1438; 1462; 1497
67	Pentylbenzene (91)	1446	
68	Ethyl octanoate (88)	1493	1438; 1462; 1497
69	Isopentyl hexanoate (70)	1497	
70	Furfural (96)	1501	1432; 1485; 1499; 1500
71	Octyl acetate *(56)*	1507	1478; 1496
72	Nonyl-cyclopentane (69)	1523	
73	Propyl-octanoate (145)	1531	1530
74	Benzaldehyde(105)	1539	1525; 1528; 1562
75	Ethyl nonanoate (88)	1555	1528; 1556
76	2-Undecanone (58)	1561	1606
77	2-(1,2-Diethoxyethyl)-furan (125)	1562	1562
78	*n*-Caprylic acid isobutyl ester (57)	1565	
79	Ethyl 2-octenoate *(55)*	1568	1579
80	1-Octanol *(55)*	1571	1539; 1561; 1575
81	4-(2-Butenyl)-1,2-dimethyl benzene (145)	1582	

(Continues)

Table 1. *(Continued)*

No.	Compound name	$RI_{Calc.}$	$RI_{Lit.}$ *(27–53)*
82	Nonyl acetate *(43)*	1584	1585; 1598
83	2,2-Bifuran (134)	1561	1635
84	β-Caryophyllene (93)	1604	1608; 1618; 1625
85	1-(2-Butenyl)-2,3-dimethylbenzene (145)	1605	
86	Ethyl decanoate (88)	1632	1630; 1636; 1647; 1680
87	3-Methylbytyl octanoate (70)	1647	1688
88	α-Caryophyllene (93)	1665	1625; 1680
89	Propyl decanoate (61)	1699	1743; 1948
90	Ethyl undecanoate (88)	1715	1760
91	α-Farnesene (93)	1722	1697; 1769
92	2-Tridecanone (58)	1781	1835
93	Acetic acid 2-phenylethyl ester (104)	1792	1803
94	1-Methylethyl dodecanoate (60)	1799	1849
95	Ethyl dodecanoate (88)	1810	1822; 1882
96	3-Phenylfuran (144)	1827	
97	3-Methylbutyl pentadecanoate (70)	1827	
98	Ethyl tridecanoate (88)	1903	1966
99	2-Pentadecanoate (58)	1995	>2000
100	Isopropyl myristate (102)	>2000	>2000
101	Ethyl tetradecanoate (88)	>2000	>2000; 2029
102	Ethyl hexadecanoate (88)	>2000	>2000; 2229

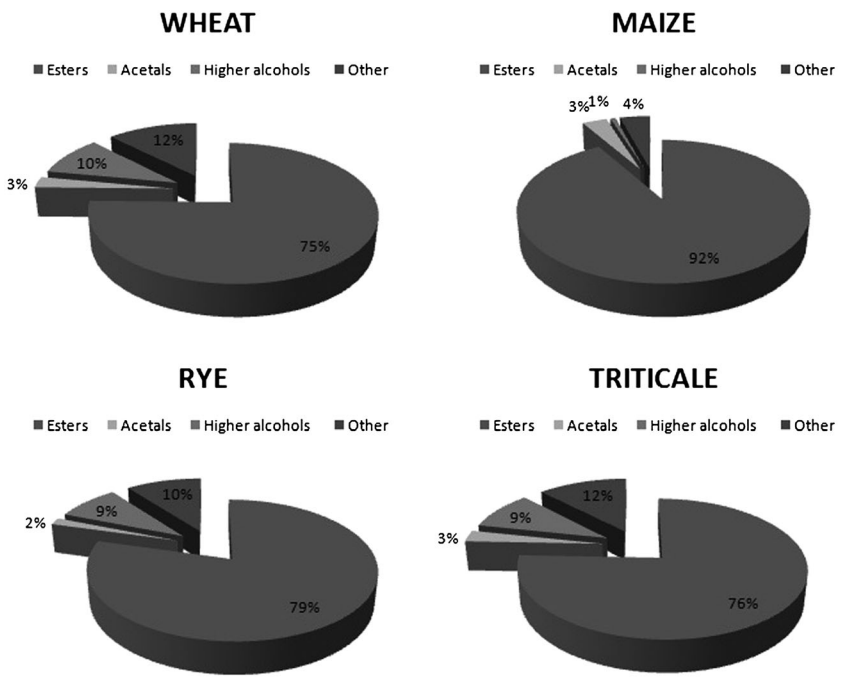

Figure 2. Percentage amount of selected groups of compounds which appear in volatile fraction of raw spirits of different botanical origin.

compounds, the largest group present in all samples was the esters, which emerge from activated fatty acids and higher alcohols *(54)*. This fact can be explained by the selectivity of the stationary phase of the fiber, since mixed-fibre-type PDMS/CAR/DVB were very good sorbents to extract esters. Similar extraction properties towards esters have been confirmed by studies conducted by other scientists. For example, analysis of the volatile fraction of white wine 'Jutrzenka' using SPME fibres coated with different stationary phases showed that the highest efficiency of esters was achieved with the use of the PDMS/CAR/DVB fiber (among all tested fibres) *(55)*. In relation to esters, samples produced from maize could be distinguished. In this group of samples, esters were present in much larger quantities (92%) than in other groups of samples (>75%), both in terms of diversity of compounds and the level of concentration at which they occur. Another significant group

of compounds that could be distinguished from the composition of volatile fractions of distillates of agricultural origin was the higher alcohols. Here again, raw spirits originating from maize, by the lowest content of higher alcohols, could be easily distinguished from other groups of raw spirits. About 10 times smaller amounts of fusel alcohols could be explained by the high amount of esters present in maize-based raw spirits. The concentration of fusel alcohols in distillates produced from rye, triticale and wheat was relatively similar, as well as the amount of esters present in them. The amount of fusel alcohols was smaller than the amount of esters in terms of their concentrations and variety of compounds. Apart from esters and alcohols, all raw spirit samples contained a relatively high amount of acetals. This group of compounds was present in every group at the same level and their diversity was not very high. Compounds that do not belong to any of the above-mentioned groups were placed in a group named 'others'. In addition, derivatives of benzene and furans were also isolated from the volatile fraction of raw spirits. These compounds may be formed during the pyrolysis of carbohydrates, dehydration of sugars as a result of the Maillard reaction and the caramelization process *(56)*.

Because the aim of the study was to analyse the whole volatile fraction of the agricultural distillates in order to identify potential marker compounds, no attempts were made to determine the actual concentrations of all identified compounds. In order to determine the difference in the amount of individual compounds, the average values of the area of the three measurements for each of the identified compounds in the distillate were taken into account. Depending on the type of raw material used for production, some differences in the appearance of individual compounds can be observed. A detailed analysis of the results based on a comparison of peak areas for particular compounds allowed potential botanical origin markers to be pointed out. Considering the results for individual samples, it was very easy to identify several compounds that were present or not present (or were below the detection limit of the procedure) in all samples or only in one variety of distillates. These compounds may represent potential marker compounds, although only the analysis of more samples would confirm the hypothesis. Table 2 presents all substances that may be considered potential origin markers. The '+' sign refers to substances that were identified in all samples of distillates obtained from selected raw material, whereas the '−' sign refers to the fact that a particular compound has not been identified in samples of the same origin.

Table 2. Potential botanical origin markers of raw spirits produced from maize, rye, triticale and wheat

Compound name	Botanical origin			
	Maize	Rye	Triticale	Wheat
1,1,3-Triethoksypropan	−	−	−	+
2,5-Dimethylfuran	−	+	−	−
2-Butylfuran	+	+	−	+
2-Pentylfuran	−	+	+	+
Butan-2-ol	−	−	−	+
Propyl decanoate	+	+	−	+
Furfural	+	+	+	−
2-Methylpropyl acatate	−	−	−	+
Hexyl acetate	−	−	−	+
Propyl acetate	−	−	−	+
Propyl octanoate	+	+	−	+
Ethyl propanoate	−	−	−	+

Because the appearance of the results in the table is very complicated, and the dependencies between individual samples are difficult to observe, it was decided that chemometric methods of data interpretation would be used. For this reason, discriminant analysis with the Statistica 10 program was used. Because some of the identified compounds were only present in a few samples, it was decided that all of the variables (compounds) that lacked many observations would be rejected. After that step, correlation occurring between the variables was checked (Pearson correlation). Strongly correlated variables, variables carrying the same information, were rejected from the statistic model. Subsequently, with the use of the Shapiro–Wilk test, confirmation of the normality of the distribution of variables in the model was performed and stepwise discriminant analysis was performed. The analysis performed pointed out five variables selected for this model:

- 2-methylbutanol + 3-methylbutanol;
- 3-methylbutyl hexanoate;
- ethyl dodecanoate;
- ethyl heptanoate;
- 3-methylbutyl octanoate.

The value of Wilk's λ was low enough to conclude that the selected variables should be well differentiated in all samples. In addition, a sufficiently low value of partial Wilk's λ and significance of the regression indicate that each variable is important as a discriminant variable. In order to examine the relationship occurring between selected variables, a canonical analysis of the results was performed. Based on the coefficients of the canonical variables, three functions can be defined:

$$D_1 = -2.58154 \times p_1 + 0.77962 \times p_2 - 1.02665 \times p_3 - 1.40409 \times p_4 + 0.81859 \times p_5 + 6.06247$$

$$D_2 = -0.19454 \times p_1 - 1.44144 \times p_2 + 0.42182 \times p_3 + 0.66842 \times p_4 + 0.81946 \times p_5 + 1.92116$$

$$D_3 = -0.471565 \times p_1 + 0.314317 \times p_2 + 0.770510 \times p_3 + 0.849513 \times p_4 - 0.134980 \times p_5 - 0.135035$$

where p_{1-5} is the peak area of each variable (1, 2-methylbutanol + 3-methylbutanol; 2, 3-methylbutyl hexanoate; 3, ethyl dodecanoate; 4, ethyl heptanoate; 5, 3-methylbutyl octanoate)

A graphical display of samples from different botanical origins is shown in Fig. 3. The chi-square test (χ^2) confirms the importance of each canonical function. The discrepancies in a particular group of raw spirit samples (maize, triticale, wheat and rye) with consideration of the discriminant function are presented in Fig. 3(a, b). Fig. 3(a) shows how the observations are spread when the first two functions are used, whereas Fig. 3(b) displays the observations spread when the first and third functions are applied. It can be clearly seen that the best differentiation of triticale samples is achieved when the first two functions are selected. Moreover, with the use of the same set of functions, it was also possible to distinguish samples produced from wheat. Because of the small amounts of wheat and triticale samples (only three for each group), it was not possible to

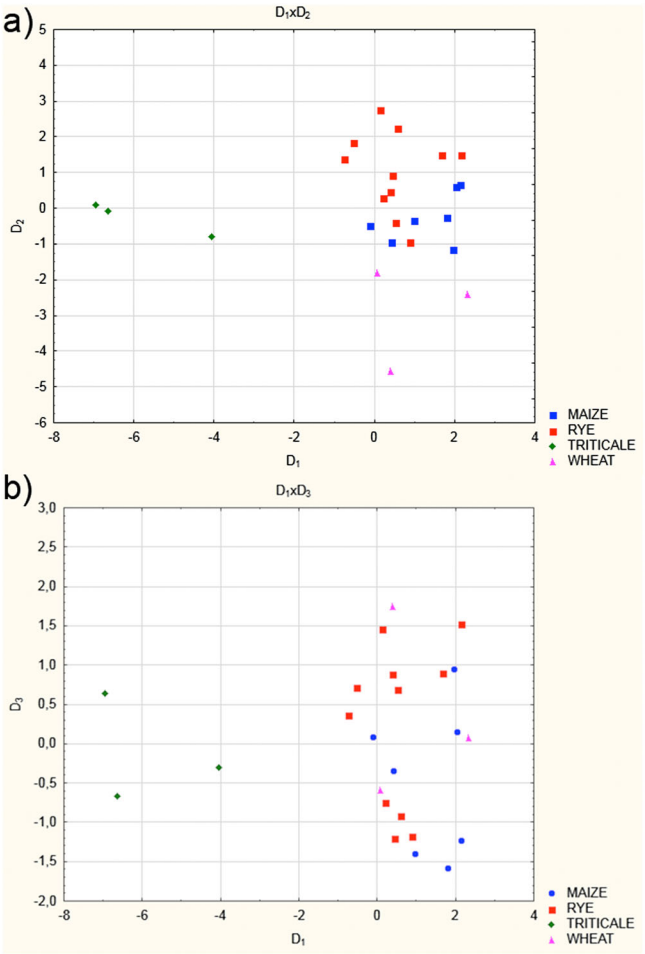

Figure 3. A graphical representation of the discriminant function analysis of the agricultural distillates samples using Canonical Discriminant Analysis data. a. - projection of function 1 vs. function 2, b. - projection of function 1 vs. function 3.

indicate more than five variables. Other authors have presented different approaches for distinguishing the origin of raw spirit – the SPME-MS method. On the basis of selected ions and linear discriminant analysis, they were able to discriminate raw spirits produced from potato, rye and maize. This approach has its own advantages, but does not state specific compounds that are typical of raw materials used during processing (*57*).

The presented studies have shown on the basis of five compounds presented in the raw spirit that it is possible to easily distinguish raw spirits derived from triticale from other groups of samples and gives quite good discrimination of wheat samples. Discrimination of rye and maize samples from each other was more difficult. However, further investigations should be performed with a greater number of samples to confirm the selected samples and indicate more origin-markers, which could allow for discrimination between rye and maize samples.

Conclusions

The main objective of the study was a detailed analysis of semi-product in the spirit industry to improve quality control and quality assurance methods. Composition of the volatile fraction of good quality raw spirits produced from different raw materials (maize, rye, triticale and wheat), and the identification of differences occurring in it, depending on the type of raw material from which the distillate is obtained, were verified. In addition, an attempt was made to identify origin markers specific to the type of raw material used to produce distillate, which might in the future allow producers of alcoholic beverages to determine the botanical origin of the raw spirits. The HS-SPME/GC-MS technique is useful for isolation, preconcentration and determination of the compounds present in the volatile fraction of raw spirits. On the basis of the markers selected in these studies, it is possible to distinguish raw spirits produced from triticale and to discriminate the raw spirits derived from wheat. Implementation of HS-SPME/GC-MS as a routine method in industrial laboratories for the establishment of raw spirit origin appears to be a good solution. However, additional studies should include experiments on a greater number of samples.

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