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Identification of the Botanical Origin of Raw Spirits Produced from Rye, Potato, and Corn Based on Volatile Compounds Analysis Using a SPME-MS Method

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Determination of the botanical origin of raw spirit used for alcoholic beverage production is of great importance for rectifying units, control laboratories, and proper product labeling. Raw spirit samples (138) produced from rye, corn, and potato were analyzed using a solid phase microextraction−mass spectrometry (SPME-MS) method, which involved volatiles preconcentration by SPME with subsequent volatile fraction characterization by MS without particular compounds separation by GC. Obtained data were treated using principal component analysis and linear discriminant analysis (LDA) to test the possibility of sample classification. SPME sampling conditions allowed rapid extraction in 2 min at 50 °C using a carboxen/divinylbenzene/polydimethylsiloxane fiber, followed by rapid MS analysis. Use of LDA made possible the classification of raw spirits based on the material they were produced from. The classification ability of the developed SPME-MS method was 100%, whereas its prediction ability was 96%.

KEYWORDS: SPME-MS; raw spirits; authentication; botanical origin

INTRODUCTION

Ethyl alcohol of agricultural origin is used for the production of alcoholic beverages, among which vodka is a predominant one. To fulfill the requirements of European Community (EU) regulations, ethyl alcohol of agricultural origin has to be of alcoholic strength of >96% by volume and be characterized by specified concentrations of regulated compounds, mainly esters, aldehydes, higher alcohols, and methanol (*1*). The raw material used for vodka production is usually specified on the label. Due to a Directive of the European Parliament and Council No. 178/2002/EEC (*2*), producers are obliged to label food products and declare their origin. EU regulations on the definition, description, presentation, labeling, and protection of geographical indications of raw spirit and other spirits drinks are given in Directive of the European Parliament and Council No. 110/2008 (*3*).

For vodka production neutral taste and odor are acclaimed, so rectified spirit is used for its production after dilution to usually 40% (volume). The rectified spirit is produced from raw spirits, which are distillates derived from the fermentation of various cereal grains, mainly rye, corn, and potatoes. These sources of raw spirit dominate in central/eastern Europe. Rye is the material with the longest tradition in vodka production in Poland and is also a main raw material for vodkas produced, potato spirit is highly praised for the characteristic flavor of potato vodkas, and corn is increasingly popular, as a relatively cheap ethanol source. In Poland small distilleries, producing raw spirits, localized in rural areas, still prevail. The product quality in terms of the contents of fermentation byproduct can vary substantially from distillery to distillery. Rectifying units that purchase raw spirits from distilleries control their quality by monitoring selected compounds, volatile congeners, usually by gas chromatography with flame ionization detection (*4*).

The main groups of volatile fermentation byproduct that raw spirits contain are carbonyl compounds, higher alcohols (fusel alcohols or oils), esters, and acetals. Some of them, such as fusel alcohols and ethyl acetate, are present in relatively large amounts (often several hundred milligrams per liter) and can be determined by direct injection of the sample without a preconcentration step, whereas others, such as carbonyl compounds (except acetaldehyde) and fatty acid ethyl esters, occur at microgram per liter concentrations and require specific isolation or detection procedures. For the characterization of volatile compounds present at low concentrations in spirits, solid phase microextraction (SPME) has been applied for vodka volatiles (*5*) and esters and aldehydes determination (*6*−*9*). Because of its sensitivity and robustness, SPME is a common method also for the characterization of various alcoholic beverages of high ethanol contents (*9*−*12*).

The development of techniques for the determination of biological origin of raw spirits is of concern to production plants, rectifying units, control laboratories, and, overall, consumers. It provides consumers with information concerning the specific character of a product and also protects the product name from misuse and imitation (*2*). For the determination of origin of alcoholic beverages stable isotope ratio analysis (SIRA) is a state-of-the-art method based on the determination of D/H values by ^{2}H NMR and δ^{13}C and δ^{18}O values for ethanol by IRMS (*13*, *14*). Often SIRA is additionally accompanied by analysis of volatile compounds (*15*). The main drawback of the SIRA approach is the very high cost of the instrumentation; therefore, it is still far from routine use.

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For sample discrimination based on the profile of volatile compounds either methods based on comparison of chromatographic peaks or profiles (*16*−*18*) or methods that utilize an electronic nose approach are used (*19*). Electronic noses do not provide information on the amounts or even type of specific aroma compounds; they make a global estimation of aroma profile, in this respect resembling the human olfactory system. The electronic noses developed so far are basically classified into two groups: "classical" electronic noses, in which solid state sensors, usually in the form of sensor arrays, are used, and instruments that utilize a mass analyzer (spectrometer) as an "array of sensors". They were introduced at the end of the 20th century and gained wide acceptance in various food testings (*20*−*22*). Classical electronic noses have been used for alcoholic beverages since 1991; the majority of applications are on wine differentiation. As the MS-based electronic noses were developed later, the first paper on its use for alcohols analysis emerged in 2002. A detailed review on the application of electronic noses for the analysis of alcoholic beverages has been published (*19*). In the MS-based electronic nose an "averaged" headspace spectrum is acquired, which can provide some additional information of chemical compounds in the headspace based on uniqueness of certain abundant and discriminant ions (*23*, *24*). For the analysis of alcoholic beverages, especially spirits, the MS-based electronic nose has one more important advantage over "classical" electronic noses: it can withstand the high concentrations of ethanol that often interfere with solid state sensors (*19*).

The aim of this study was to develop a rapid method for the biological origin determination of raw spirits based on the profile of their volatile compounds in order to check the authenticity of the producer's declaration. For this purpose a SPME-MS approach that combines fast extraction with profiling of volatile compounds without their separation was tested, with subsequent treatment of the data by multivariate statistical analysis.

MATERIALS AND METHODS

Raw Spirits. Raw spirits samples (138) of different plant origin, rye (84), corn (27), and potato (27), were used in the study. All spirits were produced by distilleries from the Wielkopolska region in western Poland. The majority of them (4/5) were obtained from small distilleries located in villages to supply the raw spirit (about 91% ethanol) for further rectifying process in specialized rectifying units. The remaining samples were produced by industrial-scale distilleries able to produce spirit up to 96%.

Chemical Reagents, SPME Fibers. The following standards were used to prepare calibration curves for the determination of volatile impurities in raw spirits using a GC method with FID: acetaldehyde, butanal, 1-butanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2-butanol, butyric acid ethyl ester, decanoic acid ethyl ester, ethyl acetate, furfural, hexanoic acid ethyl ester, isovaleric acid ethyl ester, methanol, octanoic acid ethyl ester, propanal, propenal (acrolein), 1-propanol, octanoic acid butyl ester, 1-propanol-2-methyl, 1-pentanol, 2-pentanol, and 2-hexanol as an internal standard. They were obtained, in GC standard purity, from Sigma-Aldrich (Poznań, Poland). All SPME fibers were purchased from Supelco (Poznań, Poland). The following fiber coatings were tested: polydimethylsiloxane (PDMS), polyacrylate (PA), carboxen/polydimethylsiloxane (CAR/PDMS), divinylbenzene/polydimethylsiloxane (DVB/PDMS), and carboxen/divinylbenzene/polydimethylsiloxane (CAR/DVB/PDMS). The last fiber was a 2 cm version developed for the analysis of off-odors; the remaining ones were 1 cm in length. SPME analysis was performed using a manual holder. All fibers were preconditioned according to the producer's manual.

Analytical Equipment. For determination of the main volatile impurities of analyzed raw spirits, a method routinely used in spirits quality control was used. Spirits were injected directly into GC system with FID. A Hewlett-Packard HP 6890 with 6890ALS autosampler was used for these analyses. Compounds were resolved on a CP Wax 57B capillary column (50 m × 0.25 mm × 0.20 μm, Varian, Palo Alto, CA). Hydrogen was used as a carrier gas.

For SPME-MS analysis a Hewlett-Packard HP5890II coupled to a Hewlett-Packard 5971 quadrupole mass spectrometer was used. A capillary analytical column was replaced by a fused silica capillary tubing with no phase coating (fused silica, 5 m × 0.2 mm, Supelco, Bellefonte, PA). All systems used in this study were equipped with split/splitless injection ports.

Analytical Methods for Volatile Compounds. *GC-FID Analyses*. Raw spirit was placed in a 25 mL metering flask with the addition of 5 μL of internal standard (2-hexanol). The concentration of internal standard in the sample was 50 mg/L. One microliter of such a prepared sample was injected using an autosampler into the GC in split (1:25) mode. Compounds were resolved in programmed temperature starting from 35 °C (6 min), with subsequent increase to 60 (30 °C/min), then to 120 °C (8 °C/min), and to 220 °C (20 °C/min). Carrier gas (H_2) flow was 5 mL/min in a constant flow mode. Compounds were quantified using an internal standard method using Chemstation A.10.02 version. Data on method repeatability and limits of quantitation are provided in **Table 1**. The linearity for all analyzed compounds was 0.999.

SPME MS Analyses. Raw spirit (2 mL), 18 mL of distilled water, and 10 μL of internal standard (2-hexanol) in rectified ethanol (to obtain a final concentration of 50 mg/L) were placed in a 40 mL vial, and the vial was then tightly capped with a PTFE/silicone septum. Such settings were used for all preliminary experiments in which extraction conditions were elaborated and also for the sampling using SPME-MS. SPME sampling parameters were a subject of investigation and are discussed under Results and Discussion. All SPME extractions were performed at 50 °C. Compounds were desorbed for 5 min at 260 °C in a splitless mode (1 min split valve closing time) into GC-MS. GC-MS operating conditions were as follows: helium flow, 0.4 mL min^{-1}; oven temperature, 200 °C (isothermal). The spectrometer operated in electron ionization (EI) mode (70 eV). The ion source was indirectly heated by a transfer line set to 280 °C. Detection was carried out in full-scan mode in a range of m/z 29−289. All samples were run in five repetitions from the same vial to simplify sample preparation steps.

Statistical Analysis. All tests were performed using Statistica 8.0 software (Statsoft, Tulsa, OK) equipped with a multivariate statistics package. Principal component analysis (PCA) was used in the first step of data analysis to visualize information and detect patterns in data, and linear discriminant analysis (LDA) was used to calculate classification rules for samples discrimination. Feature selection was performed by stepwise linear discriminant analysis (SLDA). In this study, an external validation method was used, dividing each data set into a training set (used to calculate the recognition ability) and a test set (used to evaluate the prediction ability of rules and models).

RESULTS AND DISCUSSION

Raw Spirits Characterization by GC-FID. Analysis of spirits fermentation byproducts (volatile congeners) by GC-FID is routinely used for quality control, providing information on fusel alcohols, esters, aldehydes, and methanol and also on unwanted compounds in raw spirits, such as acrolein or furfural. In this study it was used for raw spirits characterization. **Table 1** lists ranges of the main volatile compounds in all analyzed raw spirits. The contents of analyzed compounds in analyzed samples varied in a very broad range from a few milligrams per liter to several grams per liter. The reason for this wide range is that raw spirits originated from small distilleries, where the efficiency of distillation units provides concentration of ethanol to only approximately 91%, and usually ethanol is accompanied by many fermentation byproducts present in high (tens or hundreds of milligrams/L) concentrations. On the other hand, a few high-efficiency distilleries produce raw spirits of high purity (they can produce > 94% ethanol). The most characteristic feature, known for potato raw spirits, is the high amount of methanol, compared to corn or rye spirits. It could be an indication of the origin of a potato spirit; however, high methanol contents can be misleading. The highest concentration of methanol among analyzed samples was observed for a rye spirit sample, not a potato spirit. Compounds with the highest concentration in analyzed spirits were fusel alcohols,

Table 1. Average Contents of Main Volatile Compounds in Raw Spirits Determined by GC-FID[a]

compound	LOQ (mg/L)	RSD (%)	average contents of volatile compounds (mg/L) range (mg/L)		
			rye spirit	potato spirit	corn spirit
acetaldehyde	1	2.4	47 6−1009	25 8−59	29 22−36
ethyl acetate	2	2.0	199 1−563	350 3−453	324 2−492
methanol	2	12.6	218 nd−7499	1173 899−1799	154 147−170
propanol	1	1.8	303 nd−1850	865 586−1286	340 222−439
1-butanol	1	1.8	15 nd−458	55 7−148	8 7−9
2-pentanol	2	2.3	10 nd−339	11 nd−42	7 6−7
2-methyl-1-propanol	1	1.6	876 nd−3509	754 689−1178	734 646−785
isoamyl alcohol	1	1.7	2019 nd−4166	1122 109−2141	2314 2217−2469
1-pentanol	1	1.7	2 nd−65	12 nd−40	2 1−2
hexanoic acid ethyl ester	1	1.8	3 0.4−73	3 1−7	2 1.8−2
octanoic acid ethyl ester	1	2.1	194 nd−1026	350 147−946	324 311−344
decanoic acid ethyl ester	1	2.3	20 nd−1341	0.3 nd−1.4	3 2−3
furfural	2	4.0	78 nd−5701	9 nd−15	5 4−7

[a] LOQ, method limit of quantification; RSD, relative standard deviation determined for compounds in concentrations ranging from 1 to 2 mg/L ($n = 5$); nd, not determined (below LOQ).

mainly isoamyl alcohol (sum of 2-methyl-1-butanol and 3-methyl-1-butanol) and propanol.

Raw Spirits Characterization by SPME-MS. *Elaboration of SPME Parameters*. SPME is used for preconcentration of volatiles difficult to detect/quantify using direct injection (*6*); therefore, it was chosen as a method for the introduction of volatiles into the mass spectrometer. A series of experiments was run to determine optimal conditions for the SPME-MS method. Spirit samples were diluted 1:9 with double-distilled water. Dilution was done to minimize the interference of ethanol in the extraction process by SPME. The high concentration of organic solvents (> 90% ethanol in spirits) can influence the extraction of other compounds, especially on polymer-based fibers. The other reason for dilution was to improve the partition of higher alcohols and other compounds for which their solubility in the liquid phase can be reduced by increasing the water concentration, improving the partition of these compounds into the headspace.

Several extraction parameters were examined and included different fibers, extraction times, and multiple extractions testing. For maximum extraction efficiencies different fiber coatings were tested (**Figure 1**). Extraction for each fiber was performed for 20 min at 50 °C. Of the five tested fibers carboxen/divinylbenzene/PDMS provided the highest responses measured for the peak area, with the best reproducibility of all tested fibers. As this fiber guaranteed the highest amount of compounds transferred to the mass spectrometer, all subsequent experiments were carried out using this fiber. The highest extraction efficiency of this fiber is related probably to the amount of coating available for adsorption, as only this fiber was of 2 cm length compared to 1 cm for the remaining ones. In earlier studies on the adsorption of polar volatiles from water the fiber indicated as providing the highest extraction efficiency was DVB/PDMS (*25*), whereas for whiskeys CAR/PDMS and CW/PDMS provided the highest efficiency (*26*). As three of five fibers adsorb compounds, contrary to PDMS and polyacrylate fibers, with which absorption prevails, the fiber coatings area is probably more important than coating volume for the extraction of spirit volatiles. The relatively high responses of polyacrylate fiber can be attributed to its high affinity for alcohols.

To provide a sufficient number of replicates for the statistical procedures, each sample was analyzed five times. Instead of using five different vials, volatile compounds were extracted from the same vial. This simplified the sample preparation step, which is of a special importance in potential industrial application of the

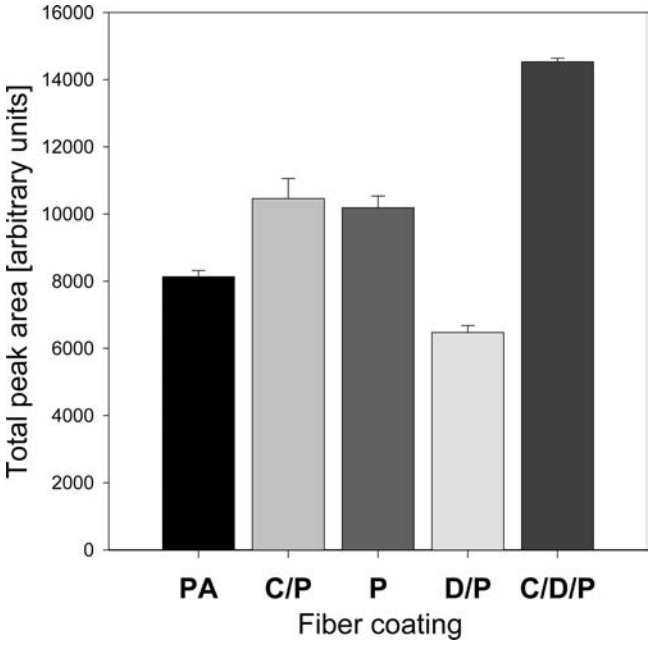

Figure 1. Selection of SPME fibers for extraction of volatile compounds from raw spirits. PA, polyacrylate; C/P, carboxen/polydimethylsiloxane; P, polydimethylsiloxane; D/P, divinylbenzene/polydimethylsiloxane; C/D/P, carboxen/divinylbenzene/polydimethylsiloxane. Extraction was performed at 50 °C for 20 min.

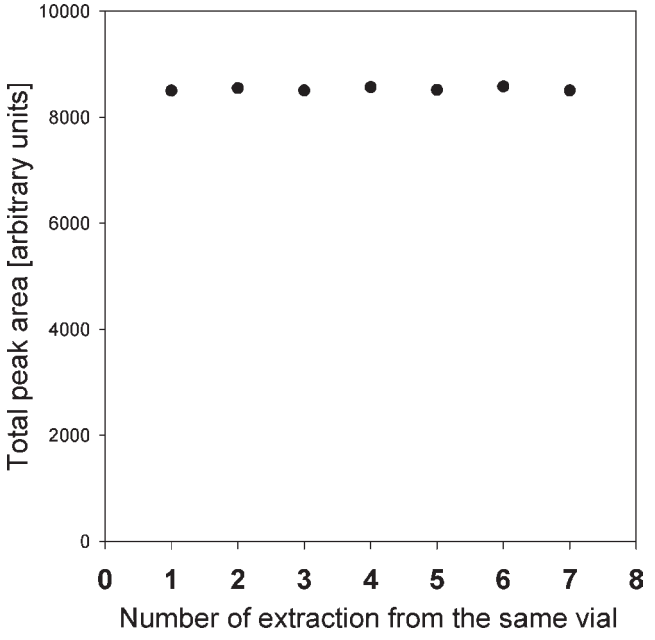

Figure 2. Influence of subsequent extractions from the same vial on amount of extracted volatiles. Extractions were performed at 50 °C for 20 min.

method. It had to be determined whether the extraction will exhaust significantly the amount of analyte in the sample. To test this, seven subsequent extractions, 20 min each, were performed from the same vial. **Figure 2** shows that there are no significant changes in the amounts of adsorbed compounds on a fiber surface, and the extraction process does not exhaust significantly analytes from the solution. On this basis, all SPME-MS experiment extractions were made from the same vial.

The SPME-MS method employs no chromatographical separation, the collection of data in the mass spectrometer lasts only the few minutes required for the elution of a single peak of unresolved volatile compounds desorbed from the fiber. The peak eluted between 0.3 and 1.3 min, so the total MS analysis was set to 5 min. For this reason SPME time should not be a limiting step in total analysis time. Extraction times ranging from 2 to 30 min were compared. An extraction time of 2 min provided highest total area responses and the best reproducibility (1.2% RSD). Interestingly, longer extraction times provided lower levels of adsorbed compounds (after 20 min, −79% of that in 2 min). This can be attributed to the desorption process, which can take place on prolonged exposure of the fiber to the 50 °C temperature. Desorption can dominate over adsorption in this case. For polymer-based fibers, such as carboxen/divinylbenzene/PDMS, extraction efficiency can be attained in a relatively short time, and often no equilibrium is achieved, due to displacement processes taking place on the fiber surface.

Optimal sampling parameters for the SPME-MS method were the following: extraction performed at 50 °C (sample preheated for 10 min prior to sampling) for 2 min with the carboxene/divinylbenzene/PDMS fiber, with all five repetitions performed from the same vial. Spirit was diluted to 10% before analysis.

Discrimination of the Raw Spirits of Different Origins Using SPME-MS. The MS-based electronic nose has many advantages over conventional sensor arrays (contrary to CP sensor arrays): it is not sensitive to water vapors and has high resistance to ethanol (contrary to MOS and MOSFET sensors). However, it has also some disadvantages, which are related to the nature of the mass spectrometer itself and the signal instability. It is caused by the ion source contamination, aging of the electron multiplier, and filament switching. Some of these obstacles can be eliminated; due to the SPME sampling, the contamination of ion source is negligible, and the corrected (normalized) response of the electron multiplier (EMV gain) within a long period of time can be set in some insruments. All data used for this paper have been collected over a 3 month period. The instrument was tuned several times in that period; the filament was not changed, nor was the electron multiplier replaced or the ion source cleaned.

As a result of SPME sampling a single peak with an average spectrum reflecting volatile compounds adsorbed was obtained. Average spectra were similar for examined spirits of different biological origins. **Figure 3** shows a typical average spectrum of rye spirit. In almost all spectra the ion of m/z 88 is a base peak. This ion is characteristic for ethyl esters and is formed via the McLafferty rearrangement. Raw spirits contain ethyl esters mainly: ethyl hexanoate, octanoate, and decanoate. These compounds are selectively enriched using the SPME fiber and result in abundant ions in the average spectra. In the same McLafferty rearrangement the ion m/z 74 is formed for methyl esters and m/z 44 for aldehydes. Alcohols generally show molecular ions of weak intensity (methanol and ethanol are exception): for higher alcohols, significant ions at m/z 59, 45, 41, 31, and 32 can be observed; for ethanol, m/z 45 prevails; in methanol, m/z 32. All of these ions can be found on a spectrum. The most abundant alcohol ions are 45 and 31, which is in accordance with the contents of, respectively, ethanol and straight-chain primary alcohols in the analyzed spirits. Abundant ions at m/z 43 can be related to acetates contribution (together with m/z 61), m/z 44 can be related to aliphatic aldehydes, and m/z45 can be attributed to the presence of secondary alcohols and butyrates. Ions that were obtained obviously from the GC column (i.e., 207) were not considered for sample differentiation.

The first approach tested was PCA. This technique of unsupervised learning is used for the discrimination of samples and visualizing eventual grouping of samples. It is often used as the first step in sample discrimination, often followed by more

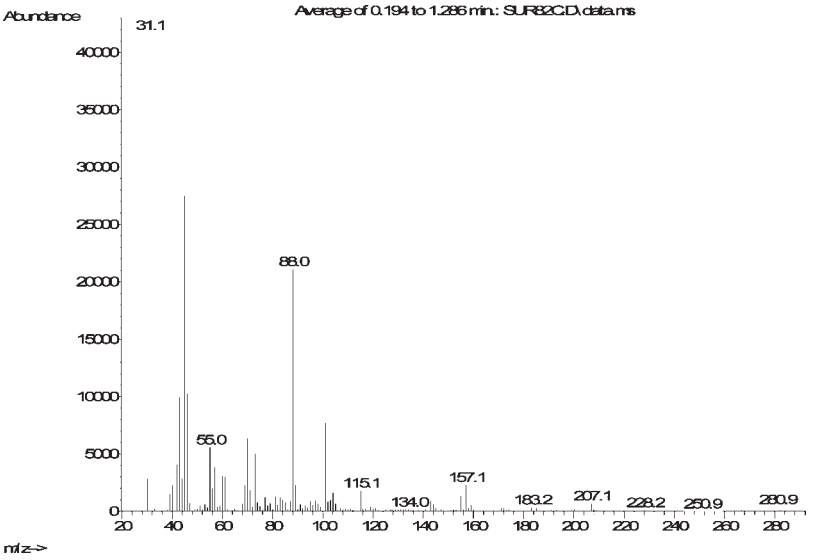

Figure 3. Average mass spectrum of rye spirit obtained using the SPME-MS method described.

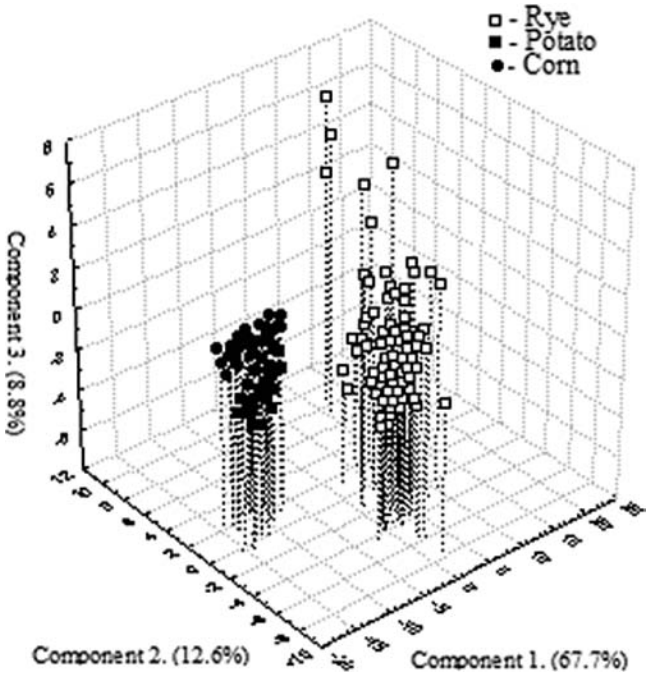

Figure 4. PCA recognition of raw spirits based on correlation analysis.

advanced statistics used for subsequent prediction studies and model construction. To perform PCA all m/z signals from tabulated spectrum were transferred to Excel, and a table was built with intensities over m/z values. At this stage, ions that exhibited an intensity of 0 for $>50\%$ of the samples were eliminated. Logarithmic transformation ($\log x + 1$) was performed because of significant differences in the ion intensities and the occurrence of zero values of matrix data. Subsequently, all variables were autoscaled (*27*). The other scaling methods, such as range transformation and constant row sum, were also tested, but the results obtained by these classification models were less satisfactory. Data prepared in this way were transferred to Statistica v. 8.0. Results of PCA grouping of samples are shown in **Figure 4**, based on correlation. The first three components explaining $>89\%$ of the total variance were taken into account, and the first three principal components were used to plot the graph. The first principal component separates rye spirits from the others, whereas the third component separates the corn from the potato spirits. In the case of potato spirits most of the factor value loadings were <0. In the case of corn spirits all values of factor loadings were >0. A differentiation of samples into the group of rye spirits and a cluster formed by unsatisfactorily resolved potato and corn spirits was obtained.

To the same data set, classification techniques were applied to calculate classification rules allowing discrimination among classes. The goal of supervised pattern recognition techniques is to create classification/discrimination rules using a set of training samples of known origin and then using the created rules to predict the "belongingness" of new samples of unknown origin to the available classes. LDA is a supervised classification technique based on the determination of linear discriminant functions, which maximize the ratio of between-class variance and minimize the ratio of within-class variance and which was applied for collected data (*27*). In LDA, classes are supposed to follow a multivariate normal distribution and be linearly separated. The criterion of LDA for selection of latent variables is maximal differentiation between the categories and minimal variance within the categories.

For LDA a data matrix having as many rows as spirit samples (138) and 137 columns (number of ions detected in the volatile fraction of spirit samples) was built. Preliminarily, the columns corresponding to compounds present in $<50\%$ samples were deleted, because the data matrix would have shown too many missing data. The new data matrix contained 138 rows and 108 columns. Features were selected by forward stepwise selection (SLDA), which selects the variable producing the highest F value and the highest decrease of Wilks' λ. To assess the discriminating capacity of the variables, the Wilks' λ and F tests were performed. The F value for a variable indicates its statistical significance in the discrimination between groups. The higher this value for a variable, the higher the discrimination power is. Also, the smaller the value of Wilks' λ, the higher the discrimination capacity of the variable is. Ions with the best discrimination power based on this assumption are listed in **Table 2**.

It has to be remembered that a group of ions is used for sample discrimination, and they are not necessarily related to those characteristics responsible for the presence of particular characteristic compounds. Ion m/z 88 originating from ethyl esters was detected as an abundant ion in all samples; however, when ions having the highest discriminant power were selected, it was not considered to be important.

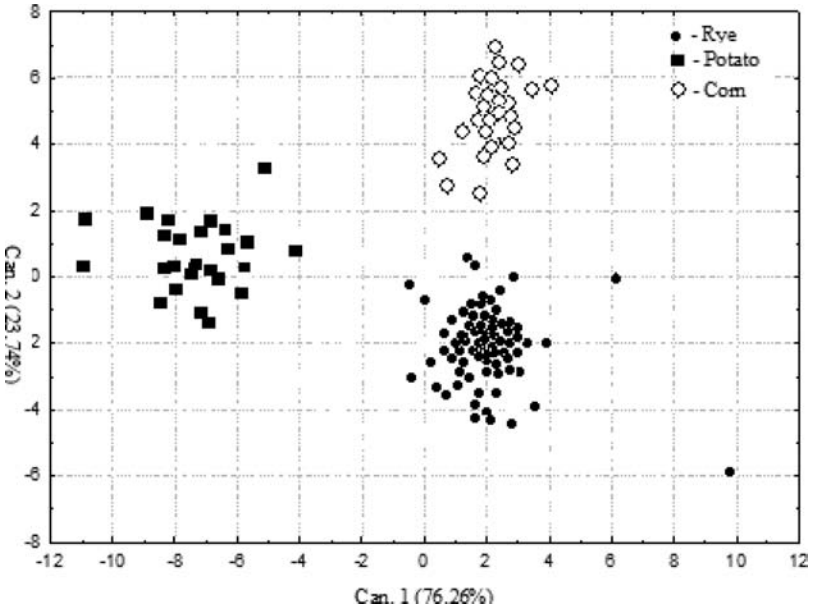

Figure 5. LDA sample classification obtained from data collected using the SPME-MS method.

Table 2. Wilks' λ and *F* Tests of Group Means

ion (*m*/*z*)	*F*	Wilks' λ
72	39.3325	0.27
95	33.1400	0.29
94	18.9767	0.38
107	18.3401	0.38
93	17.0241	0.41
54	16.1048	0.42
172	15.2807	0.44
145	13.3344	0.45
85	13.2494	0.45
159	12.2417	0.47
133	11.4140	0.48
108	11.3394	0.49
51	11.2685	0.50
104	10.1907	0.51
91	9.6579	0.52
119	8.4676	0.53
53	8.3603	0.54
147	7.4677	0.56
58	7.2022	0.56
191	7.0274	0.56
50	6.6051	0.58
116	3.0948	0.71
96	1.4028	0.79

LDA was performed independently from the previously described PCA. LDA as a supervised learning technique allows building models and sample classification, but also prediction of unknowns to a particular group. The model was cross-validated by constructing training and test sets: Classification rules were obtained by the training set of 107 samples. The remaining samples were used as a test set (31 samples = 16 rye + 8 corn + 7 potato). Both sets (all samples) are shown in **Figure 5**. In this case recognition and prediction ability were 100%. Ions with the highest discrimination ability were selected as predictors of sample affiliation to each class. Afterward, model performance was repeatedly tested (10 times) under different sets of training set and test set. Classification was performed several times to check the influence of selection of learning and a test set performance of the model. Samples for tests were randomly selected. Unfortunately, the prediction ability of the model depends on which samples were chosen as training set and which as test set. It might have been related to the relatively low number of samples in test sets. Among 310 samples (test sets), 298 were classified correctly, which gives a result of approximately 96%.

The described tools and method for the determination of raw spirit origin allows an unequivocal classification of samples considering the raw material they were produced from. Isolation of volatiles using SPME from aqueous solution of raw rye, corn and potato spirits provided high preconcentration of analytes, which in consequence provided sufficient data to be analyzed by a mass spectrometer working as an "electronic nose". This combination (SPME-MS) provides very fast sampling due to the lack of chromatographic separation and, as a consequence, can provide results in a short time, which is important if the approach is to be utilized for rapid raw spirit botanical evaluation. Presented spirits classification (and prediction) is based on analyses obtained from a single instrument. This is advantageous over methods that provide classification based on data combined from various techniques (NMR, HPLC, ICP, and GC) for the classification of spirits (*28*, *29*). However, it has to be stressed that this approach does not provide any information on particular chemical compounds present in a sample and is not related to any of the compounds listed in EU regulations. For the method performance it is of a great importance to have access to sufficient numbers of samples of reliable botanical origin to construct learning sets.

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