

Application of Electronic Nose Based on Fast GC for Authenticity Assessment of Polish Homemade Liqueurs Called *Nalewka*

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Abstract The possibility of application of electronic nose based on fast GC for differentiation of three types of cherry liqueurs, namely Polish homemade liqueurs called *nalewka*, commercially available liqueurs labeled as *nalewka*, and commercial liqueurs, was investigated. This device was equipped with two parallel connected columns with different stationary phases coupled to two ultrasensitive flame ionization detectors (μ -FIDs). Four data analysis methods were used, namely principal component analysis (PCA), discriminant function analysis (DFA), soft independent modeling of class analogies (SIMCA), and statistical quality control (SQC). Application of electronic nose based on fast GC system allows identification of volatile organic compounds and compare aroma profiles of all three types of cherry liqueurs. Only DFA allows for full discrimination of all groups of samples. Application of PCA, SIMCA, and SQC analysis allows only for the differentiation of homemade and commercial liqueurs, but not for separation between two groups of commercial liqueurs. The electronic nose based on fast GC provides a possibility of effective and rapid aroma profile comparison (the total time of analysis is 93 s) of selected alcohols. In addition, the identification and tentative semiquantitative comparison of the amount of selected compounds of the volatile fraction of these beverages using the HS-SPME/GC \times GC-TOFMS technique

were done. This work presents the proposal of protection of this traditional product through elaborated methodology and rapid authentication assessment of Polish *nalewka* made from cherries.

Keywords Electronic nose based on fast GC · Cherry liqueurs · Nalewka · Authenticity test · Chemometrics

Introduction

Poland is one of the biggest cherry producers. Information from the FAOSTAT shows that in Poland, ca. 41,063 t of this fruit was produced in 2012 (FAOSTAT 2012). Due to such amount of cherries produced, it is necessary to process the fruit into foodstuff, namely juices, jams, and liqueurs. According to legal regulations, liqueur is a colorless or colored sweetened spirit drink produced by flavoring ethyl alcohol or distillate of agricultural origin. The required minimum content of ethanol in liqueurs is 15 % vol. (Regulation [EC] No. 110/2008). The production of liqueurs is based very often on the use of products of agricultural origin (herbs, fruits, and fruit juices) or the foodstuff such as dairy products and wines. In addition, natural or synthetic flavorings or essential oils can also be used to the production. Liqueurs are mostly colored by the addition of caramel and honey (Hallgarten 1983; Śliwińska et al. 2015).

Production of homemade liqueurs is Polish centuries-long tradition. The original name of this alcohol is *nalewka*. Till now, in Poland, the *nalewka* name is still in use. The first mention of this drink can be found in 18th century literature. Homemade liqueurs were mainly prepared in the manor houses of Polish noblemen as well as in the households of townsfolk and peasants. In general, the traditional Polish *nalewka* is made exclusively from fruits, grain alcohol, and sugar. A broadly defined *nalewka* is a homemade alcoholic drink prepared by pouring spirit over the fresh

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fruits in the proportion which allows for obtaining the alcoholic strength of the final product of ca. 30–60 % (Fiedoruk 2006). Traditional homemade liqueurs called *nalewka* do not contain artificial flavors and colors.

Till now, cherry liqueurs were analyzed in relation to the content of phenolic compounds using a high performance liquid chromatography coupled to different types of detectors, such as electron capture detector (ECD), diode-array detector (DAD), mass spectrometry (MS), and MS/MS (Rødtjer et al. 2006; Ieri et al. 2012). The contents of phenolic compounds in liqueurs produced from different varieties of *Prunus cerasus* cv. Stevens cherry (Rødtjer et al. 2006) and *P. mahaleb* L. variety were compared with those measured in commercially available Mirinello di Torremaggiore liqueur (Ieri et al. 2012). Additionally, two samples of commercial Polish cherry liqueurs were studied for antioxidant properties using electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and ultraviolet–visible (UV–VIS) spectroscopy (Polak and Bartoszek 2015). Also, the contents of flavonoids in German liqueurs made from cherries and prunes were analyzed by using HPLC–CRD (de Pascual-Teresa et al. 1998).

Articles describing the investigations of another spirit drink made from cherries, so-called cherry spirit, can be found in the published literature (Śliwińska et al. 2015). This spirit type is produced exclusively via alcoholic fermentation of stone fruits, fruits without stones, and must, which is followed by distillation (Regulation [EC] No. 110/2008; Wiśniewska et al. 2015a). Cherry spirits are mainly analyzed in relation to ethyl carbamate content (Lachenmeier et al. 2005; Lachenmeier et al. 2006; Andrey 1987). Ethyl carbamate is carcinogenic; it forms during the fermentation of foodstuff (Zimmerli and Schlatter 1991). The highest concentrations of this compound were determined in spirits made from stone fruits (Dennis et al. 1989). The content of ethyl carbamate in cherry spirits was measured by means of gas chromatography (Śliwińska et al. 2015; Lachenmeier et al. 2005; Dennis et al. 1989; Lachenmeier 2005) and Fourier transform infrared spectroscopy (Lachenmeier 2005). In literature, there are information about comparison of the volatile fractions of cherry spirits produced from different varieties of Obláčinska, Celery's, Rexle, Heiman's Ruby, and Heiman's Conserve cherries by using GC–FID and GC–MS. In addition, all samples were subjected to sensory evaluation, while the content of benzaldehyde was analyzed by means of HPLC (Nikićević et al. 2011).

Nowadays, more and more often, instead of the traditional gas chromatography, the fast gas chromatography (fast GC) in food analysis is used. The main advantage of the application of fast GC is the possibility to obtain a short time of analysis. Until now, this technique was used several times to provide the analysis of major volatile compounds in distilled alcoholic beverages (Namara et al. 2005), differentiation of the types of beer, wine, vodka, whisky, and tequila (Ragazzo-Sanchez et al. 2008) and for classification of Chilean wines of different vintages and geographic origin (Beltrán et al. 2008). Most of

fast GC systems are traditionally equipped with one chromatographic column. However, the devices with different designs are also manufactured. One of the examples is the Heracles II electronic nose based on fast GC equipped with two independent chromatographic columns with stationary phases of different polarity and two flame ionization detectors. This type of electronic nose was used for the study presented in this paper. In literature can be found an information about application of this equipment for comparison of aroma profiles of whiskey originating from different distilleries (Kundu et al. 2006), differentiation of grape wine varied of age and brand (Yang et al. 2012), comparison and discrimination of aroma profiles of Chinese liqueurs (Peng et al. 2015; Xiao et al. 2014), and discrimination spirits according botanical origin (Wiśniewska et al. 2015b). There is minor information about the application of electronic nose based on fast GC for the analysis of homemade *nalewka* and commercial liqueurs made from cherries.

The aim of this work was to report for the first time the application of electronic nose based on fast GC for the authenticity assessment of three types of cherry liqueurs: homemade *nalewka*, commercially available alcohols labeled as *nalewka*, and commercial liqueurs. Determination of the similarities and possibility of differentiation of the aroma profiles of the aforementioned spirit drinks by applying four statistical methods of data analysis, i.e., PCA, DFA, SIMCA, and SQC were another objectives in this work. In addition, the additional investigation was done connected with identification and tentative semiquantitative comparison of the amount of selected compounds of the volatile fraction of these beverages by the use of headspace solid-phase microextraction combined with two dimensional gas chromatography (HS–SPME/GC×GC–TOFMS).

Materials and Methods

Materials

Samples

The studies were performed on 14 liqueurs made from cherries. There were three different groups of liqueurs: homemade liqueurs called *nalewka* ($n=5$), commercial liqueurs labeled as *nalewka* ($n=5$), and commercial liqueurs ($n=4$). Homemade liqueurs in 2014 were produced in Pomeranian voivodeship in Poland. Cherries (*P. cerasus*) used for the production of liqueurs called *nalewka* were harvested in August 2014 in the same region. These homemade liqueurs were produced exclusively with cherries, spirit, sugar, and water. Homemade liqueurs called *nalewka* have been prepared according to one of the most popular recipes, but the amount of ingredients used was different. After harvest, cherries were

thoroughly washed, placed in to the jars, and covered with sugar. Jars were sealed tightly for a range of 1–4 days. After that, spirits and water were added. Again, jars were closed and left in a warm place. Maceration process took 30 days. After this time, homemade liqueurs were filtered through gauzes and the remaining liquids were poured into tightly sealed glass bottles. All commercial beverages were produced in large distilleries of Poland and these beverages were purchased in local markets in 2014. During the research for each sample, three repetitions were performed. All samples were stored in glass bottles for 1 month prior to analysis.

Chemicals

Deionized water of high purity from MilliQ A10 Gradient/Elix System (Millipore, Bedford, MA, USA) was used throughout the research. The mixture of n-alkanes of carbon chain lengths from C6 to C16 from Sigma-Aldrich, (St. Louis, MO, USA) was utilized. The following chemical compounds, namely ethanol, acetic ester, 1-butanol, propanoic acid ethyl ester, 3-methyl-1-butanol, butanoic acid ethyl ester, 1-octen-3-one, and octanal, were also included as a standards purchased from Sigma-Aldrich (Poznań, Poland).

Sample Preparation

Samples were prepared in the proportion of 1.75 ml of liqueur and 6.25 ml of deionized water and were then transferred into 20-ml vials. All samples were sealed with caps closing with 20 mm thick PTFE/silicone membrane.

Headspace Generation

Headspace Generation According to Electronic Nose Based on Fast GC

For the headspace generation, in the case of using electronic nose based on fast GC system, the following analytical procedure was applied. The vial with the liquid sample was introduced into the autosampler (Odor Scanner HS 100, Gerstel, Mülheim, Germany). Gas gained from the headspace of the sample was used for the analysis. The incubation time was 20 min in 40 °C and agitation speed was maintained on the level of 500 rpm. After the incubation process, the gas sample was taken from the headspace of the sample and transferred from vial to the GC injector port at 200 °C (Plutowska and Wardencki 2008).

Headspace Generation According to GC×GC-TOFMS

The headspace generation for GC×GC-TOFMS procedure was preceded by HS-SPME extraction. A Gerstel autosampler (MPS autosampler, Gerstel, Mülheim, Germany) with agitator

and SPME fiber conditioning station was used to extract the volatiles from the *nalewkas* and liqueurs. Before the extraction, the samples were kept at 40 °C for 5 min and agitated with a magnetic stirrer at 700 rpm. Extraction was carried out at 40 °C for 20 min using a DVB/CAR/PDMS SPME fiber of 50/30- μm thickness and 2-cm length (Sigma-Aldrich, Munich, Germany). After the extraction, the fiber was removed from the vial and transferred to the injector of a gas chromatograph for thermal desorption of the analytes at 250 °C for 5 min (Plutowska and Wardencki 2008).

Instrumentation

The electronic nose based on fast GC called Heracles II (Alpha M.O.S., Toulouse, France) equipped with two parallel connected columns with different stationary phases coupled to two ultra sensitive flame ionization detectors ($\mu\text{-FIDs}$) was used for the analysis. The first non-polar column was MTX-5 (10 m \times 0.18 mm \times 0.4 μm film thickness) and the second column with medium polar stationary phase MXT-1701 (10 m \times 0.18 mm \times 0.4 μm film thickness) was applied. The separation of analytes was performed using the following temperature chromatographic program: initial temperature 40 °C (kept for 18 s) then ramped at 3 °C/s to 270 °C (kept for 30 s). The hydrogen N5.0 class (Linde Gaz, Poland) was used as a carrier gas. Detector temperature was 270 °C in. The alkane C6–C16 standard solution was used for the calculation of Kovat's indices and the identification of VOCs. The identification was confirmed using AroChemBase library.

The GC×GC system (Agilent 7890A) equipped with liquid nitrogen-based quad-jet cryogenic modulator and a split/splitless injector, coupled with Pegasus 4D time-of-flight mass spectrometer (LECO Corp., St. Joseph, MI, USA), were used for the analysis. The first non-polar column was Equity-1 (30 m \times 0.25 mm i.d. \times 0.25 μm film thickness) purchased from Supelco (Bellefonte, PA, USA). The second column with polar stationary phase SolGel-Wax (2 m \times 0.1 mm i.d. \times 0.1 μm film thickness) was purchased from SGE Analytical Science (Austin, TX, USA). The separation was performed using the following temperature program for the primary oven: initial temperature 40 °C, kept for 3.5 min, ramped at 7 °C/min to 250 °C, and held for 5 min. The secondary oven temperature was programmed from 45 °C, kept for 3.5 min, ramped at 7 °C/min to 255 °C, and held for 2 min. The carrier gas was helium (N6.0 class) at a constant flow rate at 1.0 ml/min. The MS transfer line and the MS source temperature was 250 °C. The modulation time was 6 s. The mass spectra data acquisition rate was 125 spectra/s. The data were collected over a mass range of 40–400 m/z and the voltage was 1600 V.

Data Analysis

Four chemometric methods, principal component analysis (PCA), discriminant function analysis (DFA), soft

independent modeling of class analogies (SIMCA), and statistical quality control (SQC) have been used for data analysis of results obtained by the use of electronic nose based on fast GC. All these methods were performed in Alpha Soft (V12.4, Alpha M.O.S, Toulouse, France).

Principal component is a chemometric linear unsupervised and pattern recognition technique used for analyzing and reducing the dimensionality of numerical datasets in a multivariate problem (Ragazzo-Sanchez et al. 2009). PCA is used to reduce the number of descriptive variables or detecting relationships between the variables. This statistical procedure is based on determining a set of components that are linear (Wilson et al. 2000; Ragazzo-Sanchez et al. 2009; Ghasemi-Varnamkhasti et al. 2012a).

Discriminant function analysis is a multivariate technique for describing a mathematical function and it allows distinguishing among predefined groups of samples. DFA is used when the assumptions of a linear regression are met. The cases are classified into groups using a discriminant prediction equation to examine differences between or among groups. The primary aim of DFA is the prediction of group membership based on linear combination of interval variables. This statistic method determines whether groups differ from each other and identifies the possible subgroups (Śliwińska et al. 2014).

The method of soft independent modeling of class analogy is used to compare unknown samples with the reference group. In the SIMCA model, such comparisons are made with one specific group from database. In this method, a separate model is created for each class, which is based on the principal component analysis. For each group, the number of significant components of the model is selected individually in accordance with the method used. In case only one principal component is significant for the entire class, the mean value of this

component together with the associated vector becomes the model for a given class. SIMCA classifier is usually used when we deal with two or more classes that consist of tight or less tight clusters of objects (Śliwińska et al. 2014; Ghasemi-Varnamkhasti et al. 2012b). The classifier of statistical quality control is an effective tool for conducting the statistical monitoring of product quality. The obtained data indicate the distances between analyzed samples and the profile of product being compared.

Analysis of the data obtained by the use of the GC×GC-TOFMS system was done using the algorithm for peak deconvolution implemented in the ChromaTOF software (LECO Corp., version 4.24). Analytes were tentatively identified through the use of NIST 2011 mass spectral library with minimum similarity value of 90 %.

Results and Discussion

Chromatography Analysis

The radar maps obtained on column MTX-5 and MTX-1701 of electronic nose based on fast GC for different groups of cherry liqueurs are shown in Fig. 1. The comparison of radar maps showed significant differences in volatile compounds profile between three groups of liqueurs. Radar maps show that homemade liqueurs called *nalewka* have higher amount of volatile compounds (Fig. 1) than other types of liqueurs. The smallest number of peaks was collected in group samples of commercial liqueurs labeled as *nalewka*. This situation can lead to the conclusion that application of electronic nose based on fast GC is useful to rapidly demonstrate that aroma profiles of three groups of liqueurs are different.

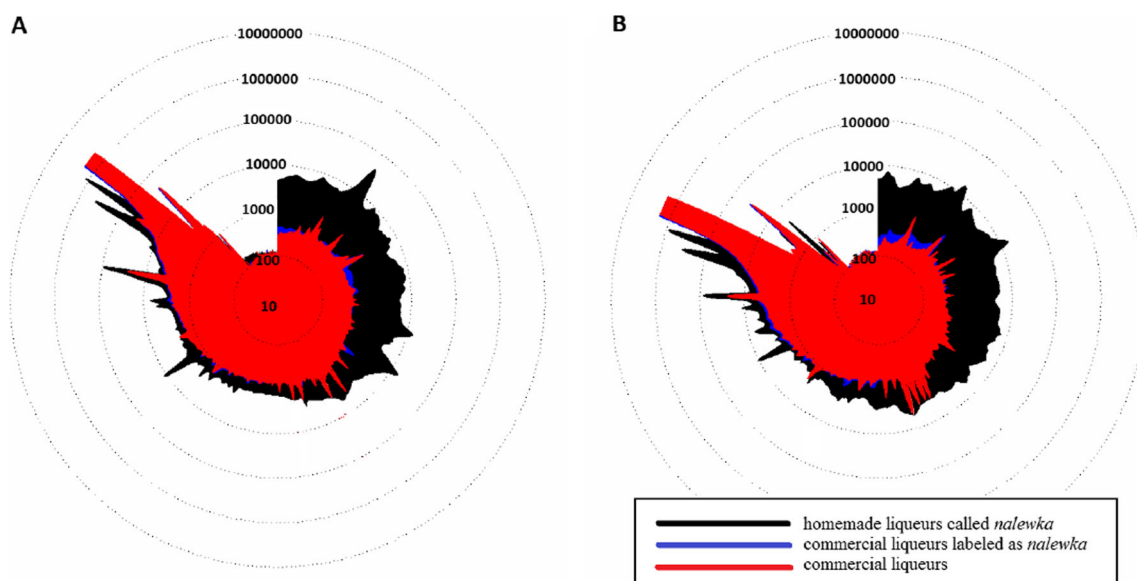


Fig. 1 Radar maps of different kinds of cherry liqueurs collected by electronic nose based on fast GC with two different separation columns: MTX-5 (a) and MTX-1701 (b)

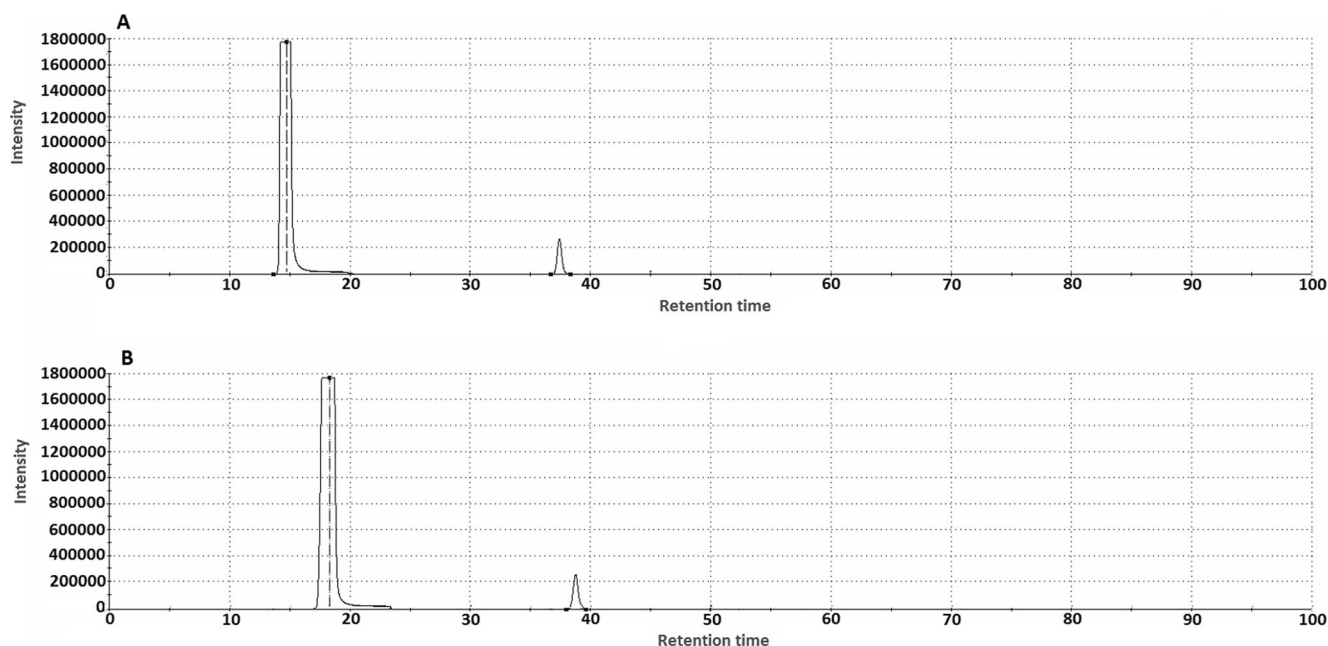
Table 1 Compounds identified in the volatile fraction of homemade liqueurs called *nalewka*, commercial liqueurs labeled as *nalewka*, and commercial liqueurs detected by electronic nose based on fast GC

Compound	Retention time		Kovats RI_{EXP}		Kovats RI_{LIT}		Sensory discription	References
	C. I	C. II	C. I	C. II	C. I	C. II		
Ethanol	15.24	18.29	435.22	566.55	437	564	Alcoholic, pungent	Allegrone et al. (2006)
Acetic ester	22.09	24.66	614.19	685.03	609	673	Fruity, orange, pineapple, pungent, sweet	Bosch-Fusté et al. (2007); Demyttenaere et al. (2003); Pino et al. (2005); Echeverría et al. (2003); Jordán et al. (2002); Quijano et al. (2007); Mattheis et al. (2005)
1-butanol	25.54	31.15	661.34	770.60	651	768	Cheese, fermented, fruity	Jordán et al. (2002); Da Porto et al. (2003)
Propanoic acid ethyl ester	29.55	31.08	711.38	771	709	766	Acetone, fruity	Da Porto et al. (2003); Pino et al. (2003)
3-methyl-1-butanol	31.26	36.06	730.60	832.23	728	842	Alcoholic, bitter, fermented, fruity, malty, pungent	Da Porto et al. (2003); Echeverría et al. (2003); Pino et al. (2003); Maia et al. (2004)
Butanoic acid ethyl ester	37.32	38.42	798	861.25	799	864	Fruity, banana, pineapple, strawberry, sweet	Demyttenaere et al. (2003); Pino et al. (2005); Maia et al. (2004); Joulain et al. (2004); Mahattanatawee et al. (2005)
1-octen-3-one	52.74	54.81	977.80	1073.41	979	1066	Herbaceous, metallic	Buettner (2004); Rouseff et al. (2009)
Octanal	54.36	56.72	997.14	1091.1	998	1090	Citrus, floral, fruity, green	Bosch-Fusté et al. (2007); Buettner (2004) Culleré et al. (2004); Gürbüz et al. (2006)

C. I chromatographic column MTX-5, C. II chromatographic column MTX-1071, Kovats RI_{EXP} Kovats Retention index_{EXP}, Kovats RI_{LIT} Kovats Retention index_{LIT}

Volatile compounds detected in the headspace of cherry liqueur samples were investigated using their Kovats retention indices and standard substances. Table 1 lists the identified volatile compounds in all kinds of cherry liqueurs. The main peak is ethanol because the range of ethanol content in all samples was 30 %

vol. to 40 % vol. During the production process of liqueurs, the fruits kept are for a limited period in ethanol. Ethyl esters such as acetic ester, propanoic acid ethyl ester, and butanoic acid ethyl ester are compounds which can be characterized by a fruity flavor (Bosch-Fusté et al. 2007; Demyttenaere et al. 2003; Pino et al.

**Fig. 2** The chromatogram of butanoic acid ethyl ester solution with ethanol content obtained by the use of electronic nose based on fast GC with two different separation columns: MTX-5 (a) and MTX-1701 (b)

2005; Echeverría et al. 2003; Jordán et al. 2002; Quijano et al. 2007; Mattheis et al. 2005; Da Porto et al. 2003; Escudero et al. 2007; Pino et al. 2003). Ethyl acetate is ester present in a wide variety of fruits and natural food products. This compound is responsible for the fresh and fruity aroma of ripening fruit. On the other hand, in the case of high concentration, acetic ester has unpleasant aroma which might be associated with the polish nail remover (Tešević et al. 2009). Butanoic acid ethyl ester and acetic ester are commonly present esters in foodstuff. These compounds have no specific aroma of any one type of fruit, but they can be connected with sweet aroma. Similar properties have butanoic acid ethyl ester and propanoic acid ethyl ester and for this reason, they can be used as flavors in cherry, rum, and chewing gum (De Rovira Sr 2008; The Good Scents Company Information System). Acetic ester is another flavor ester. It has unpleasant (Brenntag Food and Nutrition Europe) or pleasant flavor (fruity flavor) which is consistent with other ethyl esters, e.g., propanoic acid ethyl ester, butanoic acid ethyl ester (Bosch-Fusté et al. 2007; Demyttenaere et al. 2003; Pino et al. 2005; Pino et al. 2003). It

depends on the amount of this compound in food product. Higher alcohols are formed, interalia, from sugars during the alcoholic fermentation process. Higher alcohols have positive (fruity) and negative (fermented) impacts on aroma of alcohol beverages (Tešević et al. 2009; De Rovira Sr 2008; Quijano et al. 2007; Demyttenaere et al. 2003). 1-Butanol is one of the compounds important for authenticity assessment of raw materials of spirit beverages (Christoph and Bauer-Christoph 2006). The compound 1-octen-3-one has unpleasant flavor (herbaceous, metallic). Most often, it occurs in beverages made from grapes (Buettner 2004), but also in other fruits (Rouseff et al. 2009). Octanal is an aldehyde compound characterized by fruity and pleasant aroma (Bosch-Fusté et al. 2007; Buettner 2004; Culleré et al. 2004; Gürbüz et al. 2006). All these compounds are present in cherries and beverages produced with cherry (Nikićević et al. 2011; Sun et al. 2010).

For verification of the identification of substances presented in Table 1, the standard water solutions of each single compound were prepared only with addition of 30 % etanol

Table 2 The identification of selected compounds from the volatile fraction of homemade liqueurs called *nalewka*, commercial liqueurs labeled as *nalewka*, and commercial liqueurs using HS-SPME/GC×GC-TOFMS.

Compound	RT _I	RT _{II}	U.m. ^a	Peak area ^b			Sensory discription	References
				H. liqueurs called <i>nalewka</i>	C. liqueurs labeled as <i>nalewka</i>	C. liqueurs		
1-hexanol	748	4.80	56	***	***	*	Fruity, floral, green, herbaceous, sweet	Setkova et al. (2007); Seung-Joo et al. (2006); Bianchi et al. (2007); Fan and Qian (2006); Bonvehí and Coll (2003)
1-octanol	1054	4.22	56	***	*	*	Floral, green, herbaceous	Mahattanatawee et al. (2005); Setkova et al. (2007); Carasek and Pawliszyn (2006); Tsakiris et al. (2004)
Heptanoic acid ethyl ester	1084	3.04	88	***	**	**	Fruity	Pino et al. 2005; Mahattanatawee et al. (2005)
Benzoic acid ethyl ester	1180	4.48	105	***	*	*	Fruity, minty, musty, tea	Perestrelo et al. (2006); Carasek and Pawliszyn (2006); Sampaio and Nogueira (2006)
1-nonanol	1186	4.07	56	*	*	***	Floral, fruity, green	Mahattanatawee et al. (2005); Narain et al. (2007)
Linalool	1198	2.79	71	***	*	**	Floral, fruity, green, lemon, sweet	Da Porto et al. (2003); Gürbüz et al. (2006); Alissandrakis et al. (2005); Lermusieau et al. (2001); Murakami et al. (2003); Lee and Noble (2003)
Benzeneacetic acid ethyl ester	1264	4.64	91	**	*	***	Floral, fruity, spicy, sweet	Pino et al. 2005; Setkova et al. (2007); Alissandrakis et al. (2007); Xu et al. (2007)
Nonanoic acid ethyl ester	1336	3.02	88	***	*	**	Waxy	Pino et al. (2005)
Decanoic acid ethyl ester	1450	3.03	88	**	*	***	Fruity, grape	Setkova et al. (2007); Chen et al. (2006); Riu-Aumatell et al. (2006)

U.m. (unique mass)—unique ion (m/z) used for peak area determination, identified as the unique ion by ChromTOF data analysis. ***, **, * symbols are the representation of the values of chromatographic peak areas in the range of 90.1–100 %, 30.1–40 %, and 0.1–10 %, respectively, regarding the highest value of chromatographic peak area for given compound

RT_I first dimension retention time, RT_{II} second dimension retention time, H. liqueurs called *nalewka* homemade liqueurs called *nalewka*, C. liqueurs labeled as *nalewka* commercial liqueurs labeled as *nalewka*, C. liqueurs commercial liqueurs

content. The concentration of these substances in the solution was 10 ppm v/v.

Comparing two chromatograms obtained by the use of MTX-5 and MTX-1701 columns, it can be noticed that peaks with different retention times are observed in Fig. 2, which presents peaks of butanoic acid ethyl ester and ethanol. This is due to different polarity of stationary phases of these columns (Xiao et al. 2014). The difference in retention times between the two columns was about 1.5 s.

Additionally, the comparative analysis of volatile fraction of homemade liqueurs called *nalewka*, commercial liqueurs labeled as *nalewka*, and commercial liqueurs using HS-SPME/GC × GC-TOFMS was made to explain the basis of discrimination of these alcohols.

In Table 2, the identification of selected compounds present in volatile fraction of three concerned alcohols was presented. The identification was confirmed by the comparison of experimental data with mass spectra included in the NIST 2011 mass spectral library. The threshold value of similarity parameter was established at 900 (which means 90 % of conformity of obtained experimental spectrum with the mass spectrum from the database). Additionally, in this table, the tentative semiquantitative comparison of the amount of the abovementioned compounds was shown. All these compounds have been previously described in the literature concerning cherry studies (Sun et al. 2010) and can be evaluated with a fruity and floral aroma. Seven out of the ten of selected compounds, namely 1-hexanol, 1-octanol, heptanoic acid ethyl ester, benzoic acid ethyl ester, linalool, and nonanoic acid ethyl ester, appear in the nearly close concentration in each type of sample of three investigated group: homemade liqueurs called *nalewka*, commercially available alcohols labeled as

nalewka, and commercial liqueurs. Probably all of these compounds are originating from fruits, because during the preparation of *nalewka*, the fruits, sugar, and ethanol addition are used exclusively. The manufacturing process of homemade liqueurs called *nalewka* is followed by three main steps and is much more complex than production of commercial beverages. The first step of production of homemade *nalewka* is when fresh fruits are covered with sugar; subsequently, the maceration process which most often takes 3–8 weeks is the middle step and filtration of beverage is the last step.

In the production of commercial beverages, especially in the case companies possessing large distilleries, the fruit concentrates are usually used to reduce production costs (Hernández Gómez Sun et al. 2009). This is one of the main reasons of the occurring differences in composition of homemade liqueurs and commercial beverages. Differences of the amount of compounds can be found, for example, in the case of decanoic acid, 1-nonanol, and benzeneacetic acid ethyl esters.

Statistic Methods

Using electronic nose based on fast GC, the chromatographic peak area is treated as an input data, for chemometric analysis. All samples are plotted in space and clustered according to the degree of similarity and difference in the data. These parameters are related to the number and size of chromatographic peaks recorded by the electronic nose based on fast GC. To compare aroma profiles of three groups of cherry liqueurs, all chromatographic peaks were used. The chromatographic profile could be represented as an odor map using PCA, DFA, SIMCA, and SQC.

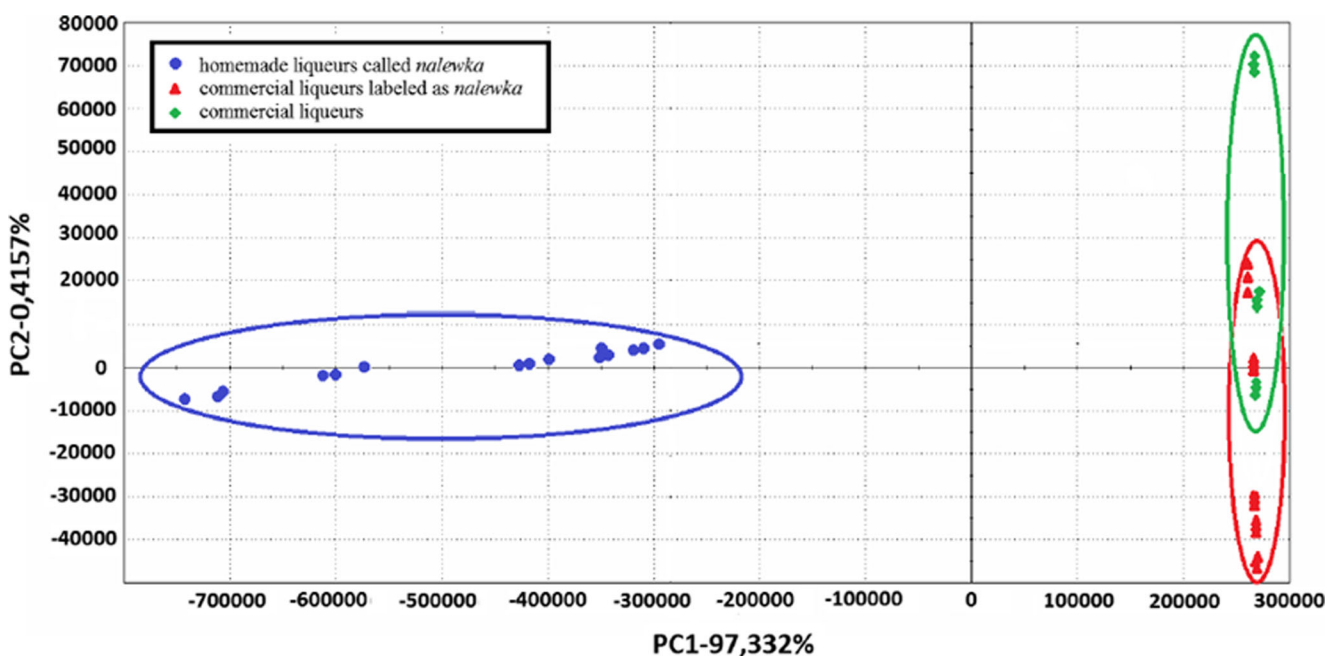


Fig. 3 PCA plots of three groups of cherry liqueurs using electronic nose based on fast GC

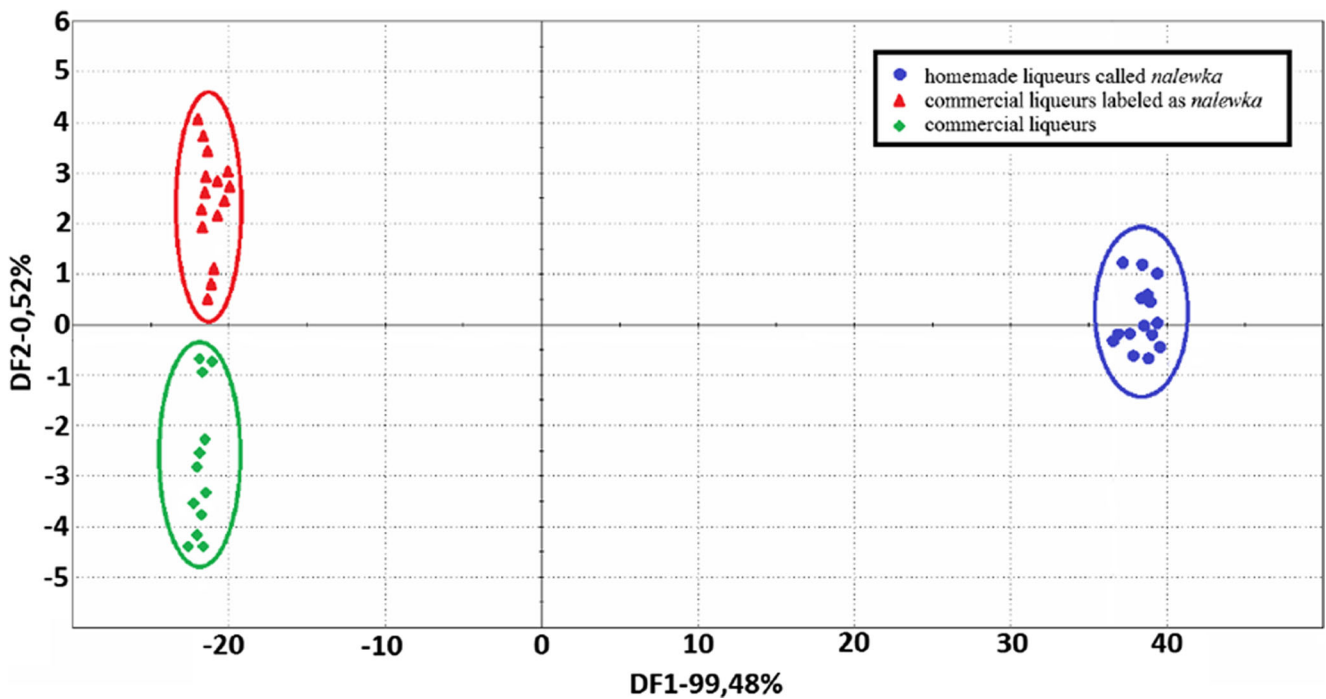


Fig. 4 DFA plots of three groups of cherry liqueurs using electronic nose based on fast GC

Principal component analysis was performed to identify patterns of correlation with individual composition variables involved in the discrimination among three groups of cherry liqueurs. The odor map based on PCA showed clear discrimination of homemade and commercial cherry liqueurs based on their volatile composition. In Fig. 3, the PCA score plot of comparison aroma profiles of different kind of cherry liqueurs is represented. PCA results showed that the first two principal components accounted for 97.75 % of total variance. Liqueur samples appear grouped into two classes: homemade liqueurs called *nalewka* are situated on the second and third quadrants of the diagram whereas the samples of commercial liqueurs are located on the first and fourth quadrants of graph. Points corresponding to the two groups of commercial liqueurs intersect, so it is not possible to distinguish them from each other.

The DFA diagram corresponding to the same data and sensors which provided the PCA diagram is shown in Fig. 4. The DFA method identifies DF1 and DF2 which explain 99.48 and 0.52 % of the variability in the initial data set, and which are represented as the axes of the DFA plot. Similarly to PCA, the graph is divided into two parts. Homemade liqueurs called *nalewka* are situated on the first and fourth quadrants of the graph. However, application of DFA analysis allows distinguishing between all three groups of liqueurs. There is a clear separation between commercial liqueurs labeled as *nalewka* and commercial liqueurs (Fig. 3).

SIMCA classification and PCA can be used to visualize the distance between the classes (Olsson et al. 2000). The area corresponding to the given class is shown on each plot as the blue rectangle in the left corner. As shown on the plots,

Fig. 5 SIMCA classification plot of three groups of cherry liqueurs using electronic nose based on fast GC

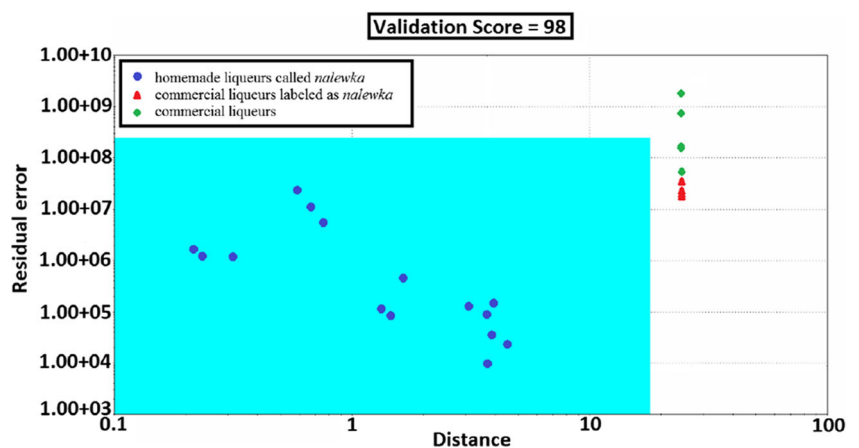
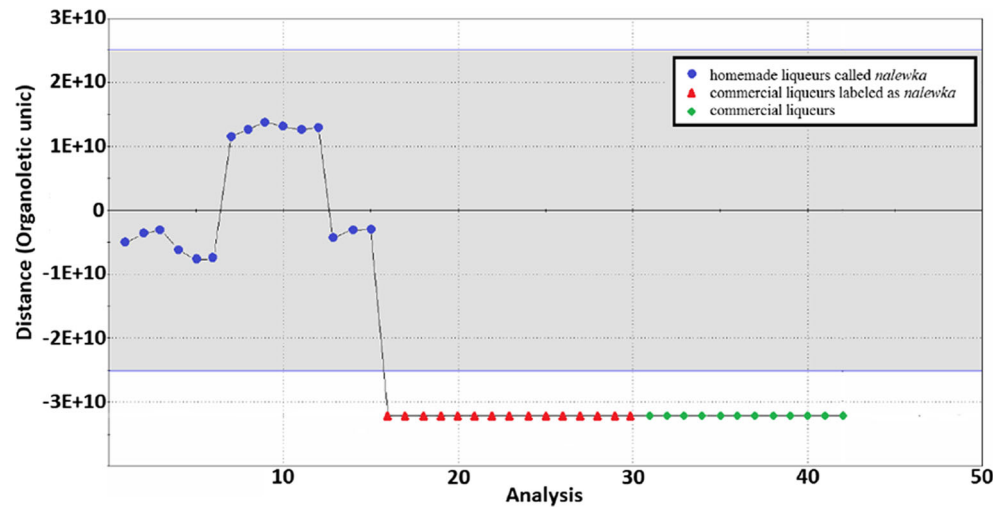


Fig. 6 SQC classification plot of three groups of cherry liqueurs using electronic nose based on fast GC



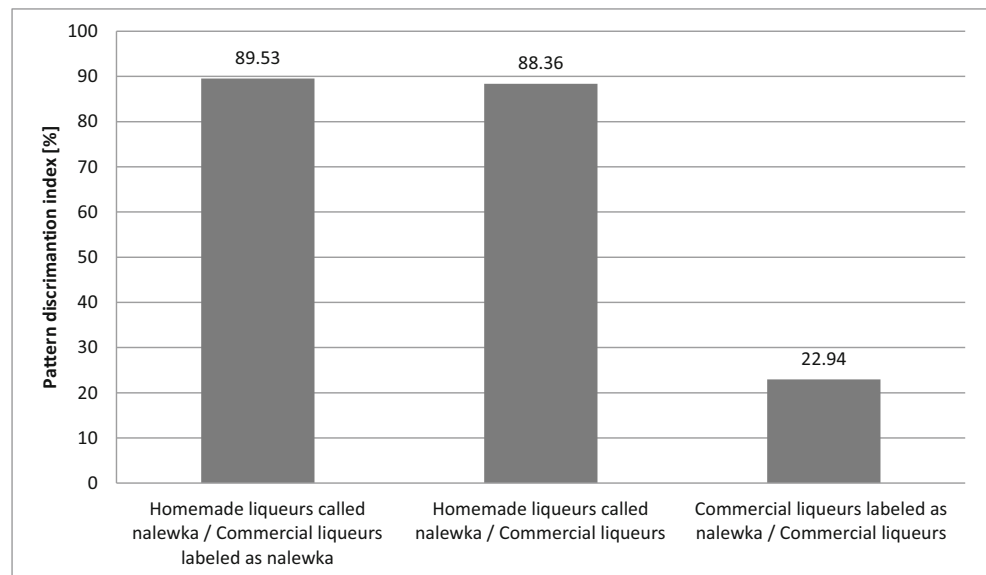
all liqueur samples were assigned correctly to the corresponding class. In Fig. 5, validation score is 98 and obtained a significant distinction between of homemade and commercial groups of cherry liqueurs. Very small distance between the two groups of commercial liqueur samples can be observed. Points relating to both groups of commercial liqueur samples are located in a narrow cluster. On the other hand, the points relating to homemade liqueur samples are arranged in a large space, which may be indicative of diverse aroma profile of these drinks. The result of SIMCA classification is similar to the results obtained by using PCA.

The statistical quality control (SQC) representation allows for rapidly evaluating quality control with a simple visual assessment of the sample quality. Figure 6 shows the result of the SQC depending on homemade liqueurs as reference group. As in the case of PCA and SIMCA, points relating to homemade liqueur samples are located in a large area. On the

other hand, samples belonging to both groups of commercial liqueurs are on the same line and are difficult to distinguish. It can be assumed that commercial liqueurs have minimal differences in the aroma profiles.

The verification on chemometric methods regarding suitability were obtained by the use of comparison of aroma profiles of all the data that obtained chromatogram interpretation (Fig. 7). Pattern discrimination index is an indicator which takes into account differences between groups obtained from investigated volatile fractions of samples. Index closer to 100 % means that there is a greater distance between centers of gravity and smaller dispersion within groups. In this case, pattern discrimination index is only 22.94 % in comparison between commercial liqueurs labeled as *nalewka* and commercial liqueurs. For this reason, it can be concluded that the two groups of commercial beverages from large distilleries have very small differences of aroma profiles. The results

Fig. 7 Results of comparison pattern discrimination index of three groups of cherry liqueurs



obtained using PCA, DFA, SIMCA, and SQC classification are consistent with all data obtained by means of interpretation of the chromatograms.

Conclusion

In this work, it has been reported for the first time the utilization of electronic nose based on fast GC for the authenticity assessment of Polish homemade liqueurs called *nalewka*. Application of this equipment allows for identification of volatile organic compounds present in all three groups of cherry liqueurs and for comparison of aroma profiles of different types of liqueurs. The PCA, SIMCA, and SQC analysis are useful for clear visualization of the differences between homemade and commercial liqueurs. In turn, DFA analysis was the only statistical analysis using which the discrimination of all three groups of liqueurs was possible. Difficulty with distinguishing between these two groups of commercial liqueurs can be explained by the minor differences in aroma profiles. This fact can be explained on the basis of conducted HS-SPME/GC×GC-TOFMS analysis. The main focus of this work is to broaden knowledge and recognition of Polish traditional product named *nalewka* and, in future, to propose protection of this traditional product in compliance with the guidelines of the European Union concerning the protection of local and traditional food products.

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Compliance with Ethical Standards

Conflict of Interest Magdalena Śliwińska declares that she has no conflict of interest. Paulina Wiśniewska declares that she has no conflict of interest. Tomasz Dymerski declares that he has no conflict of interest. Waldemar Wardencki declares that he has no conflict of interest. Jacek Namieśnik declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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References

- Alissandrakis E, Kibaris AC, Tarantilis PA, Harizanis PC, Polissiou M (2005) Flavour compounds of Greek cotton honey. *J Sci Food Agric* 85:1444–1452
- Alissandrakis E, Tarantilis PA, Harizanis PC, Polissiou M (2007) Comparison of the volatile composition in thyme honeys from several origins in Greece. *J Agric Food Chem* 55:8152–8157
- Allegre G, Belliardo F, Cabella P (2006) Comparison of volatile concentrations in hand-squeezed juices of four different lemon varieties. *J Agric Food Chem* 54:1844–1848
- Andrey D (1987) A simple gas chromatography method for the determination of ethylcarbamate in spirits. *Z Lebensm Unter Forsch* 185:21–23
- Beltrán NH, Duarte-Mermoud MA, Soto Vicencio VA, Salah SA, Bustos MA (2008) Chilean wine classification using volatile organic compounds data obtained with a fast GC analyzer. *IEEE* 57:2421–2436
- Bianchi F, Careri M, Mangia A, Musci M (2007) Retention indices in the analysis of food aroma volatile compounds in temperature-programmed gas chromatography: database creation and evaluation of precision and robustness. *J Sep Sci* 39:563–572
- Bonvehí JS, Coll FV (2003) Flavour index and aroma profiles of fresh and processed honeys. *J Sci Food Agric* 83:275–282
- Bosch-Fusté J, Riu-Aumatell M, Guadayaol JM, Caixach J, López-Tamames E, Buxaderas S (2007) Volatile profiles of sparkling wines obtained by three extraction methods and gas chromatography-mass spectrometry (GC-MS) analysis. *Food Chem* 105:428–435
- Brenntag Food & Nutrition Europe. Acidulants in food industry—a practical guideline. http://www.brenntag-nordic.com/fi/downloads/Hapot_TB_Acidulants_FN201310.pdf Accessed 4 November 2015
- Buettner A (2004) Investigation of potent odorants and afterodor development in two chardonnay wines using the Buccal Odor Screening System (BOSS). *J Agric Food Chem* 52:2339–2346
- Carasek E, Pawliszyn J (2006) Screening of tropical fruit volatile compounds using solid-phase microextraction (SPME) fibers and internally cooled SPME fiber. *J Agric Food Chem* 54:8688–8696
- Chen HC, Sheu MJ, Wu CM (2006) Characterization of volatiles in guava (*Psidium guajava* L. cv. Chung-Shan-Yueh-Pa) fruit from Taiwan. *J Food Drug Anal* 14:398–402
- Christoph N, Bauer-Christoph C (2006) Flavour of spirit drinks: raw materials, fermentation, distillation, and ageing. In: Berger RG (ed) *Flavours and fragrances chemistry, bioprocessing and sustainability*. Springer, Berlin, pp 219–239
- Culleré L, Escudero A, Cacho J, Ferreira V (2004) Gas chromatography-olfactometry and chemical quantitative study of the aroma of six premium quality Spanish aged red wines. *J Agric Food Chem* 52:1653–1660.
- Da Porto C, Pizzale L, Bravin M, Conte LS (2003) Analyses of orange spirit flavour by direct-injection gas chromatography-mass spectrometry and headspace solid-phase microextraction/GC-MC. *Flav Fragr J* 18:66–72
- De Pascual-Teresa S, Treutter D, Rivas-Gonzalo JC, Santos-Buelga C (1998) Analysis of flavanols in beverages by high-performance liquid chromatography with chemical reaction detection. *J Agric Food Chem* 46:4209–4213
- De Rovira SD (2008) *Dictionary of flavors*. John Wiley & Sons, Iowa
- Demyttenaere JC, Dagher C, Sandra P, Kallithraka S, Verhé R, De Kimpe N (2003) Flavour analysis of Greek white wine by solid-phase microextraction-capillary gas chromatography-mass spectrometry. *J Chromatogr A* 985:233–246
- Dennis MJ, Howarth N, Key PE, Pointer M, Massey RC (1989) Investigation of ethyl carbamate levels in some fermented foods and alcoholic beverages. *Food Add Contam* 6:383–389

- Echeverría G, Fuentes MT, Graell J, López ML (2003) Relationships between volatile production, fruit quality and sensory evaluation of Fuji apples stored in different atmospheres by means of multivariate analysis. *J Sci Food Agr* 84:5–20
- Escudero A, Campo E, Fariña L, Cacho J, Ferreira V (2007) Analytical characterization of the aroma of five premium red wines. Insights into the role of odor families and the concept of fruitiness of wines. *J Agric Food Chem* 55:4501–4510
- Fan W, Qian MC (2006) Identification of aroma compounds in Chinese ‘Yanghe Daqu’ liquor by normal phase chromatography fractionation followed by gas chromatography/olfactometry. *Flav Fragr J* 21:333–342
- FAOSTAT (Food and Agriculture Organization of the United Nations Statistic Division). 2012. Production quantity of cherries in Poland in 2012. Available from: <http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor>. Accessed 25 October 2015
- Fiedoruk A (2006) Polskie nalewki i wódki (English translation: Polish nalewkas and vodkas). Dragon, Bielsko Biała
- Ghasemi-Varnamkhasti M, Rodríguez-Méndez ML, Saeid Mohtasebi S, Apetrei C, Lozano J, Ahmadi H, Hadi Razavi S, De Saja JS (2012a) Monitoring the aging of beers using a bioelectronic tongue. *Food Control* 25:216–224
- Ghasemi-Varnamkhasti M, Saeid Mohtasebi S, Rodríguez-Méndez ML, Gomes AA, Ugulino Araújo MC, Galvão RKH (2012b) Screening analysis of beer ageing using near infrared spectroscopy and the successive projections algorithm for variable selection. *Talanta* 89: 286–291
- Gürbüz O, Rouseff JM, Rouseff RL (2006) Comparison of aroma volatiles in commercial Merlot and Cabernet Sauvignon wines using gas chromatography—olfactometry and gas chromatography—mass spectrometry. *J Agric Food Chem* 54:3990–3996
- Hallgarten PA (1983) Spirits and liqueurs. Faber and Faber, London
- Hernández Gómez LF, Úbeda J, Arévalo-Villena M, Briones A (2009) Novel alcoholic beverages: production of spirits and liqueurs using maceration of melon fruits in melon distillates. *J Sci Food Agr* 89: 1018–1022
- Ieri F, Pinelli P, Romani A (2012) Simultaneous determination of anthocyanins, coumarins and phenolic acids in fruits, kernels and liqueur of *Prunus mahaleb* L. *Food Chem* 135:2157–2162
- Jordán MJ, Margaría CA, Shaw PE, Goodner KL (2002) Aroma active components in aqueous kiwi fruit essence and kiwi fruit puree by GC-MS and multidimensional GC/GC-O. *J Agric Food Chem* 50: 5386–5390
- Joulain D, Casazza A, Laurent R, Portier D, Guillamon N, Pandya R, Le M, Viljoen A (2004) Volatile flavor constituents of fruits from Southern Africa: mobola plum (*Parinari curatellifolia*). *J Agric Food Chem* 52:2322–2325
- Kundu K, Mitra S, Mazumdar D, Pal SK (2006) Perception and machine intelligence. Springer, New York
- Lachenmeier DW (2005) Rapid screening for ethyl carbamate in stone-fruit spirits using FTIR spectroscopy and chemometrics. *Anal Bioanal Chem* 82:1407–1412
- Lachenmeier DW, Frank W, Kuballa T (2005) Application of tandem mass spectrometry combined with gas chromatography to the routine analysis of ethyl carbamate in stone-fruit spirits. *Rapid Commun Mass Spectrom* 19:108–112
- Lachenmeier DW, Nerlich U, Kuballa T (2006) Automated determination of ethyl carbamate in stone-fruit spirits using headspace solid-phase microextraction and gas chromatography-tandem mass spectrometry. *J Chromatogr A* 1108:116–120
- Lee SJ, Noble AC (2003) Characterization of odor-active compounds in Californian chardonnay wines using GC-olfactometry and GC-mass spectrometry. *J Agric Food Chem* 51:8036–8044
- Lermusieau G, Bulens M, Collin S (2001) Use of GC-olfactometry to identify the hop aromatic compounds in beer. *J Agric Food Chem* 49:3867–3874
- Mahattanatawee K, Goodner KL, Baldwin EA (2005) Volatile constituents and character impact compounds of selected Florida’s tropical fruit. *Proc Fla State Hort Soc* 118:414–418
- Maia JGS, Andrade EHA, Zoghbi MB (2004) Aroma volatiles from two fruit varieties of jackfruit (*Artocarpus heterophyllus* Lam.). *Food Chem* 85:195–197
- Mattheis JP, Fan X, Argenta LC (2005) Interactive responses of gala apple fruit volatile production to controlled atmosphere storage and chemical inhibition of ethylene action. *J Agric Food Chem* 53: 4510–4516
- Murakami A, Goldstein H, Navarro A, Seabrooks JR, Ryder DS (2003) Investigation of beer flavor by gas chromatography-olfactometry. *J Am Soc Brew Chem* 1:23–32
- Namara KM, Leardi R, Sabuneti A (2005) Fast GC analysis of major volatile compounds in distilled alcoholic beverages: optimisation of injection and chromatographic conditions. *Anal Chim Acta* 542:260–267.
- Narain N, De Sousa Galvão M, Madruga MS (2007) Volatile compounds captured through purge and trap technique in caja-umbu (*Spondias* sp.) fruits during maturation. *Food Chem* 102:726–731
- Nikićević N, Veličković M, Jadrantin M, Vučković I, Novaković M, Vujisić L, Stanković M, Urošević I, Tešević V (2011) The effects of the cherry variety on the chemical and sensorial characteristics of cherry brandy. *J Serb Chem Soc* 76:1219–1228
- Olsson J, Börjesson T, Lundstedt T, Schnürer J (2000) Volatiles for mycological quality grading of barley grains: determinations using gas chromatography–mass spectrometry and electronic nose. *Intl J Food Microbiol* 10:167–178
- Peng Q, Tian R, Chen F, Li B, Gao H (2015) Discrimination of producing area of Chinese Tongshan kaoliang spirit using electronic nose sensing characteristics combined with the chemometrics methods. *Food Chem* 178:301–305
- Perestrelo R, Fernandes A, Albuquerque FF, Marques JC, Câmara JS (2006) Analytical characterization of the aroma of Tinta Negra Mole red wine: identification of the main odorants compounds. *Anal Chim Acta* 563:154–164
- Pino J, Marbot R, Vazquez C (2005) Volatile constituents of genipap (*Genipa americana* L.) fruit from Cuba. *Flav Fragr J* 20:583–586
- Pino JA, Almora K, Marbot R (2003) Volatile components of papaya (*Carica papaya* L., maradol variety) fruit. *Flav Fragr J* 18:492–496
- Plutowska B, Wardencki W (2008) Determination of volatile fatty acid ethyl esters in raw spirits using solid phase microextraction and gas chromatography. *Anal Chim Acta* 613:64–73
- Polak J, Bartoszek M (2015) The study of antioxidant capacity of varieties of nalewka, a traditional Polish fruit liqueur, using EPR, NMR and UV–vis spectroscopy. *J Food Comp Anal* 40:114–119
- Quijano CE, Linares D, Pino JA (2007) Changes in volatile compounds of fermented cereza agria [*Phyllanthus acidus* (L.) Skeels] fruit. *Flav Fragr J* 22:392–394
- Ragazzo-Sanchez JA, Chalier P, Chevalier D, Calderon-Santoyo M, Ghommidh C (2008) Identification of different alcoholic beverages by electronic nose coupled to GC. *Sens Actuators B* 134:43–48
- Ragazzo-Sanchez JA, Chalier P, Chevalier-Lucia D, Calderon-Santoyo M, Ghommidh C (2009) Off-flavours detection in alcoholic beverages by electronic nose coupled to GC. *Sens Actuators B* 140:29–34
- Regulation [EC] No (2008) 110/2008 of the European Parliament and of the Council on the definition, description, presentation, labelling and the protection of geographical indications of spirit drinks and repealing
- Riu-Aumatell M, Bosch-Fusté J, López-Tamames E, Buxaderas S (2006) Development of volatile compounds of cava (Spanish sparkling

- wine) during long ageing time in contact with lees. *Food Chem* 95: 237–242
- Rødter A, Skibsted LH, Andersen ML (2006) Antioxidative and prooxidative effects of extracts made from cherry liqueur pomace. *Food Chem* 99:6–14
- Rouseff R, Jella P, Bazemore R, Yang J (2009) Aroma active internal standards for gas chromatography-olfactometry of grapefruit juices. *ACS Symp Ser* 782:73–87
- Sampaio TS, Nogueira PCL (2006) Volatile components of mangaba fruit (*Hancornia speciosa* Gomes) at three stages of maturity. *Food Chem* 95:606–610
- Setkova L, Risticovic S, Pawliszyn J (2007) Rapid headspace solid-phase microextraction-gas chromatographic-time-of-flight mass spectrometric method for qualitative profiling of ice wine volatile fraction II: classification of Canadian and Czech ice wines using statistical evaluation of the data. *J Chromatogr A* 1147:224–240
- Seung-Joo L, Jang-Eun L, Hyeon-Wee K, Sung-Soo K, Kyung-Hee K (2006) Development of Korean red wines using *Vitis labrusca* varieties: instrumental and sensory characterization. *Food Chem* 94: 385–393
- Śliwińska M, Wiśniewska P, Dymerski T, Namieśnik J, Wardencki W (2014) Food analysis using artificial senses. *J Agric Food Chem* 19:1423–1448
- Śliwińska M, Wiśniewska P, Dymerski T, Wardencki W, Namieśnik J (2015) The flavour of fruit spirits and fruit liqueurs: a review. *Flav Fragr J* 30:197–207
- Sun SY, Jiang WG, Zhao Y (2010) Characterization of the aroma-active compounds in five sweet cherry cultivars grown in Yantai (China). *Flav Fragr J* 25:206–213
- Tešević V, Nikićević N, Milosavljević S, Bajić D, Vajs V, Vučković I, Vujisić L, Dorđević I, Stanković M, Veličković M (2009) Characterization of volatile compounds of “Drenja”, an alcoholic beverage obtained from the fruits of cornelian cherry. *J Serb Chem Soc* 74:117–128
- The Good Scents Company Information System, <http://www.thegoodscentscompany.com/data/rw1004931.html>. Accessed 4 November 2015
- Tsakiris A, Sipsas V, Bekatorou A, Mallouchos A, Koutinas AA (2004) Red wine making by immobilized cells and influence on volatile composition. *J Agric Food Chem* 10:1357–1363
- Wilson DM, Dunman K, Roppel T, Kalim R (2000) Rank extraction in tin-oxide sensor arrays. *Sens Actuators B* 62:199–210
- Wiśniewska P, Śliwińska M, Dymerski T, Wardencki W, Namieśnik J (2015a) Application of gas chromatography in analysis of spirit beverages. *Crit Rev Anal Chem* 45:201–225
- Wiśniewska P, Śliwińska M, Dymerski T, Wardencki W, Namieśnik J (2015b) Differentiation between spirits according to their botanical origin. *Food Anal Met.* doi:10.1007/s12161-015-0280-x
- Xiao Z, Yu D, Niua Y, Chen F, Song S, Zhu J, Zhu G (2014) Characterization of aroma compounds of Chinese famous liquors by gas chromatography–mass spectrometry and flash GC electronic-nose. *J Chromatogr B* 945–946:92–100
- Xu Y, Fan W, Qian MC (2007) Characterization of aroma compounds in apple cider using solvent-assisted flavor evaporation and headspace solid-phase microextraction. *J Agric Food Chem* 55:3051–3057
- Yang Y, Zhao Y, Zhang S, Ni Y, Zhan J (2012) Qualitative analysis of age and brand of unblended brandy by electronic nose. In: Li VD, Chen Y (eds) *Computer and computing technologies in agriculture V, IFIP advances in information and communication technology*. Springer, Berlin, pp 619–628
- Zimmerli B, Schlatter J (1991) Ethylcarbamate: analytical methodology, occurrence, formation, biological activity and risk assessment. *Mutat Res Gen Tox* 259:325–350