Scientific Papers of the University of Pardubice,
Series A; Faculty of Chemical Technology
26 (2020) 147–156.

UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY

Classification of the alcoholic beverages by using electronic nose technique based on ultra-fast GC

Silvie Surmová[1], Paulina Wiśniewska[2], Magdalena Śliwińska[2], Tomasz Dymerski[2], Waldemar Wardencki[2], Jacek Namieśnik[2], Karel Ventura[1], Martin Adam[1], and Aleš Eisner[1]*

[1] *Department of Analytical Chemistry, The University of Pardubice, CZ–532 10 Pardubice, Czech Republic*

[2] *Department of Analytical Chemistry, Gdańsk University of Technology, PL–80-233 Gdańsk, Poland*

Received: May 29, 2020; Accepted: August 24, 2020

Each alcoholic beverage has its own distinct aroma and unique flavor. An Electronic nose (E-nose) is an instrumental tool which allows one to analyze the aroma of samples. This work illustrates the use of E-nose for the determination of characteristic aromas of seven different alcoholic beverages (bourbon, brandy, cognac, vodka, liqueurs made from pears, and fruit spirits made from lemon). The following chemometrics methods for the data analysis were employed for the classification of alcoholic beverages: principal component analysis (PCA), discriminant factorial analysis (DFA, and soft independent modelling of class analogies (SIMCA). The results show that chemometrics methods PCA and DFA allow us the determination of the individual alcoholic groups of fruit spirits, bourbon, cognac, and brandy but there is a difficulty with separation of liqueur, gin, and vodka points from one group. Only the SIMCA method allowed to distinguish the point belonging to all groups without any approximation of graph fragments.

Keywords: Alcohols; Gas chromatography; Chemometrics methods; Sensors

* Corresponding author, ✉ ales.eisner@upce.cz

Introduction

The quality of alcoholic products is determined by composition and content of odorous substances. The fact that we can smell the specific odor of alcohol depends principally on its composition. Every alcoholic beverage comprises a great number of chemicals occurring in a wide range of concentrations. The chemical composition of odors depends on the type of raw materials and upon their quality, as well as on conditions of the fermentation process [1].

During the fermentation, byproducts affecting the sensory properties are produced, including carbonyl compounds, alcohols, esters, acids and acetates, terpenes, and sulfur compounds. All the afore-mentioned compounds can influence the quality of a final product. Moreover, such products are derived from the raw materials containing simple sugars (molasses, raw and refined sugar, fruits, sugarcane, etc.), starchy raw material (potatoes, cereals, rice, etc.) or other materials containing polysaccharides [1,2].

Distilled spirits are characterized by the content of ethanol. Some spirits can be purely aqueous alcohols, e.g. vodka, the others are flavored products, such as whiskey, cognac, rum, and brandy. A wide range of volatile compounds with different polarities and volatilities ensures that the flavor of a spirit is very complex and therefore, the combinations of all these compounds represent the character of spirit and differentiate one spirit from another [3,4].

The analysis of volatile aroma compounds in alcohol products is very popular. Nowadays, an extensive research exists being focused on the determination of aroma compounds in alcoholic beverages, such as wine, beer, brandy, whiskey, spirits or flavored vodkas [5–10].

One of many options for analysis of alcoholic products is an application of an Electronic nose (E-nose) which utilizes an array of chemical sensors. Such a system is equipped with sensors capable of reacting and adequately responding to the volatile organic compounds present in the gas form and therefore, it enables the identification of complex odors [11,12]. Chemical sensors work in a similar way as a human nose. The human olfactory system is very complex as each receptor cell of this kind possesses only one type of odorant receptor, and each receptor unit can detect a limited number of odorant substances. Due to this, the human olfactory receptor cells are highly specialized for only few odors [13–15]. The E-nose technique is fast, reliable, and a robust technology which is very useful in many practical applications. Such technology can be applied, for example, in analysis of food (fish and meat) or beverages, also in various chemical processes, pharmacy, biomedicine, clinical chemistry, and industrial safety applications [11,16,17].

The E-nose device usually consists of a wide scale of different metal-oxide semiconductors (MOS) and gas sensors with overlapping sensitivities towards the volatile gaseous components [17] allowing one a pattern recognition. Chemometrics methods are used to extract the relevant information from a series of signals obtained by the system. Because of a large amount of the data obtained, there is need for a multivariate analysis [18,19]. E-nose produced by Alpha MOS Co. uses multivariate statistical analysis and chemometrics to acquire, compute, and interpret E-nose measurements. One of these methods is a principal component analysis (PCA) which can transform the original variables into a smaller set of latent variables (principal components) in order to maximize the explained variance of the data. The PCA is mainly used to model, compress, and visualize complex data by dimension reduction [20]. In the following work, we focused our attention on additional methods also allowing multivariate analysis, such as discrimination factorial analysis (DFA) or soft independent modelling of class analogy (SIMCA). When using discriminant analysis, the objects are characterized by numerous variables and classified according to independent criteria (usually expressed as a linear combination of values of measured variables). The SIMCA, on the other hand, provides an additional information about different groups, such as the relevance of different variables and measures of separation [21,22].

This report focuses on a comparison of alcoholic beverages, attempting to explore hidden relationships while using statistical methods. We also evaluate the applicability of E-nose for analysis of different types of alcoholic beverages.

Materials and methods

Materials

The studies were performed with 11 commercial spirits beverages: 1 bourbon, 2 brandy, 1 cognac, 1 gin, 4 liqueurs (made from pears), 1 fruit spirit (made of lemon) and 1 vodka. These beverages were acquired in 2014 in local supermarkets.

Methods

Sample preparation

All samples were prepared in the following proportions: 1.75 mL of beverages and 6.25 mL of deionized water in 20 mL headspace vial and closed by a cap with a Teflon® septum.

Analysis with electronic nose

Analysis of samples was conducted by using an electronic nose Heracles II (Alpha MOS Co., Toulouse, France) coupled with a Scanner HS 100 autosampler (the same manufacturer) allowing to transfer a volume of 2.5 mL gas from the volatile fraction of sample to the split/splitless injector. After this step, the analytes were adsorbed on

Tenax TA sorption trap placed behind the injector. The analytes were released from the trap and directed to the two parallel connected chromatographic columns with MXT-5 (non-polar) and MXT-1701 (semi-polar) stationary phases (10 m length; 18 μm internal diameter). After elution from the columns, the analytes were transferred into two ultra-sensitive Flame Ionization Detectors (μ-FIDs). Fast GC E-nose conditions were as follows: time of injection, 15 s; temperature of injection, 200 °C; temperature of trap on the beginning of the run, 40 °C. The GC program included the following sequences: keeping at 40°C for 2 s, increase of the temperature ramp up to the 270 °C at a slope of 3 °C s^{-1}, and final setting at 280 °C for 18 s. The FID detectors were maintained at 270 °C.

Results and discussion

Raw-data sensor response of alcoholic beverages detected by E-nose was analyzed by multivariate statistical methods (PCA, DFA, SIMCA) and the individual results in graphic presentation are discussed.

Principal component analysis

Principal component analysis (PCA) is used to explore the data and to assess the discrimination performance (i.e., a capability to determine which of the differences are important and into which degree [23]). Fig. 1 (A) shows that the PCA chemometric method enabling to distinguish three separated groups that represent fruit spirits, bourbon, cognac and one bigger group containing brandy, plus vodka, gin and liqueurs.

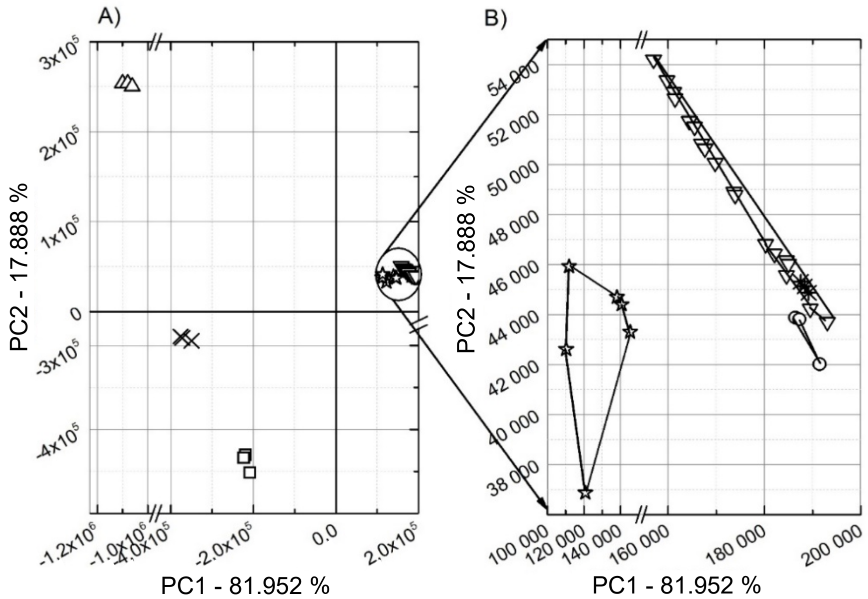

Fig. 1 A) PCA analysis: × – bourbon, ☆ – brandy, □ – cognac, ∗ – gin, ▽ – liqueurs, Δ – fruit spirits, ○ – vodka B) cutout of bigger group

Points belonging to brandy are slightly separated from vodka, gin and liqueurs points. This fact is also shown in Fig. 1 (B), which is a cutout of bigger group.

Discriminant factorial analysis

Discriminant factorial analysis (DFA) is used to identify the unknown samples into one of the training groups. To elaborate this, a reliable model for new samples identification — the electronic nose — must be practiced with a training sample set being representative for all the occurrences. The model is considered as valid if the percentage of recognition is higher than 90 % [23]. Fig. 2 (A) shows the results of the DFA method which are similar with the results of the PCA methods. However, the DFA allowed to distinguish the brandy point in the main graph without a cut-out, and as a result, it was possible to determine four separate groups representing the fruity spirits, bourbon, cognac, brandy and one mixed group standing for gin, liqueurs, and vodka.

The approximation of a fragment in the graph, where the unseparated group is located, allowed to distinguish vodka, liqueurs, and gin points. This fact is shown in Fig. 2 (B) and a proximity of these three groups can be related to similar composition and a method of their production.

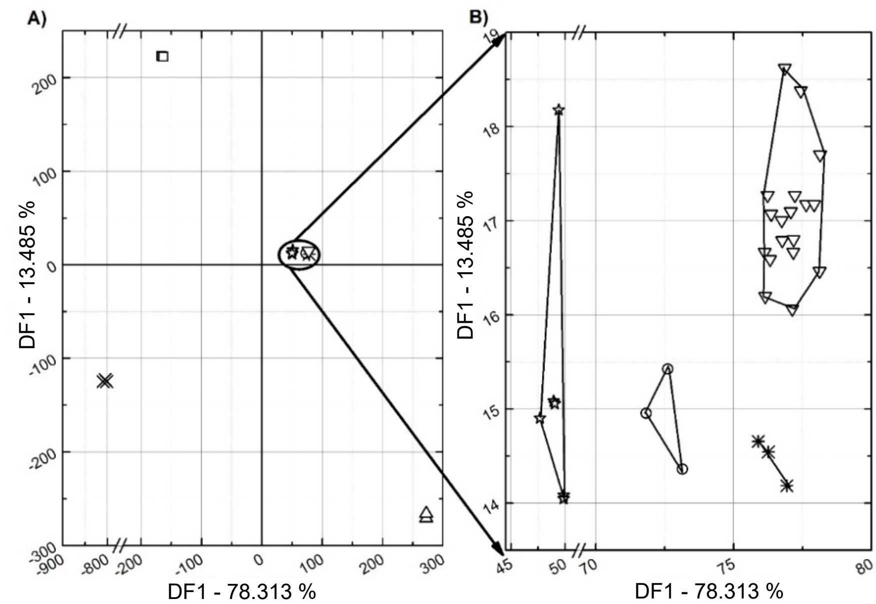

Fig. 2 A) DFA analysis: × – bourbon, ☆ – brandy, □ – cognac, ∗ – gin, ▽ – liqueurs, Δ – fruit spirits, ○ – vodka B) cutout of bigger group

Soft independent modelling of the class analogy

Soft independent modelling by the class analogy (SIMCA) is used to compare the unknown samples to a reference. The model is assembled by considering one group to be the “gold reference”. The model is going to identify the unknown samples as belonging or not to the one and the only group defined previously. The advantage of the SIMCA model is that it is not necessary to collect the sample from different groups but only within the group of interest [23]. The last chemometric method applied was the SIMCA, allowing us, almost clearly, to distinguish a point belonging to all alcoholic groups as shown in Fig. 3. Only in the case of Fig. 4, where the reference group are liqueurs, the points representing gin are located very close to the area defined by the points representing liqueurs and vice versa.

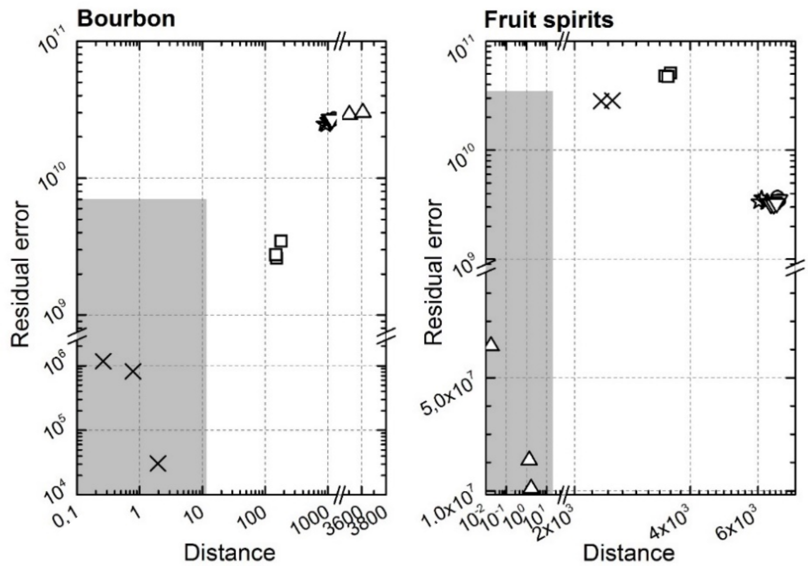

Fig. 3 SIMCA analysis: × – bourbon (reference group), ☆ – brandy, □ – cognac, ∗ – gin, ▽ – liqueurs, Δ – fruit spirits (reference group), ○ – vodka

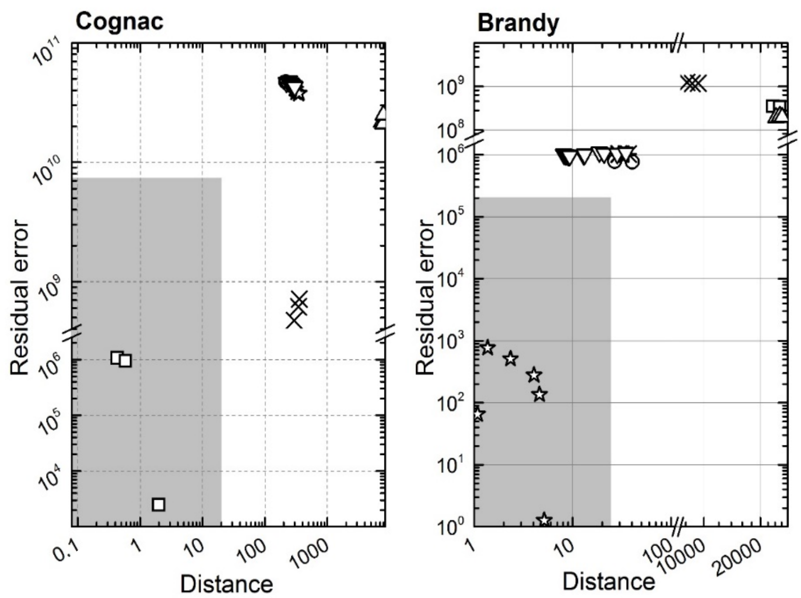

Fig. 4 SIMCA analysis: × – bourbon, ☆ – brandy (reference group), □ – cognac (reference group), ∗ – gin, ▽ – liqueurs, Δ – fruit spirits, ○ – vodka

The liqueur points are relatively close to the reference ones of gin as shown in Fig. 5. In connection with the graphical results of the PCA and the DFA methods, it is obvious that there is very likely a strong similarity between these two alcohols. In other figures, all the points belonging to the reference group are in a large distance to the points belonging to the other groups. Finally, it is worth mentioning that points belonging to vodka are the most compact as the reference group (see Fig. 6).

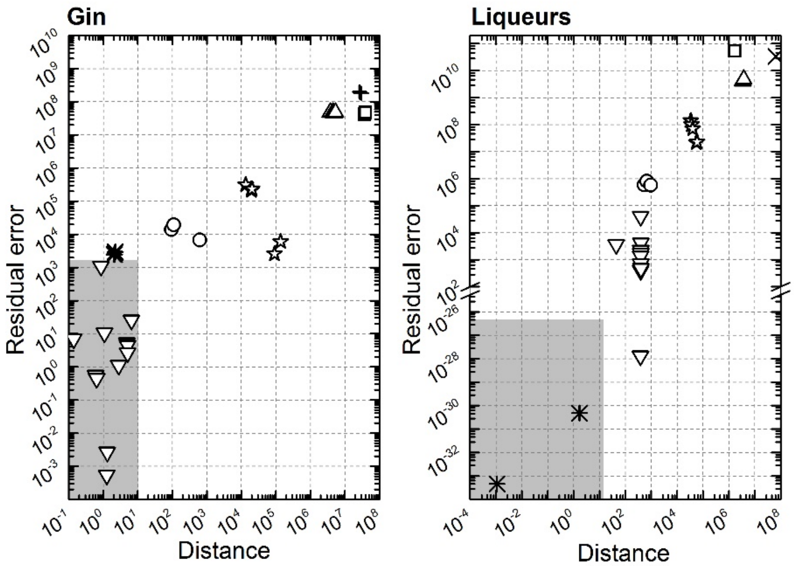

Fig. 5 SIMCA analysis: × – bourbon, ☆ – brandy, □ – cognac, ▽ – gin (reference group), ∗ – liqueurs (reference group), Δ – fruit spirits, ○ – vodka

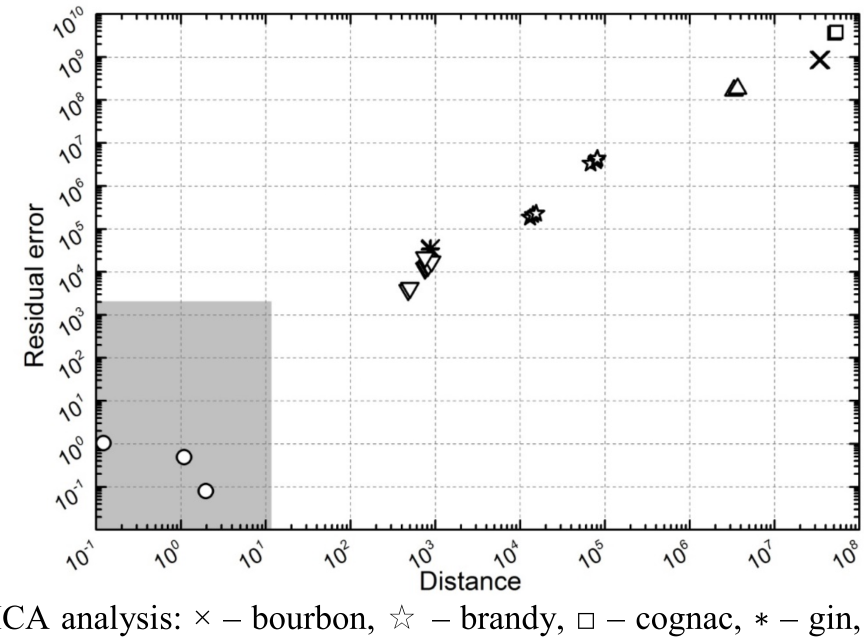

Fig. 6 SIMCA analysis: × – bourbon, ☆ – brandy, □ – cognac, ∗ – gin, ▽ – liqueurs, Δ – fruit spirits, ○ – vodka (reference group)

Conclusions

The E-nose based on ultra-fast gas chromatography was used for fast analysis of alcoholic beverages chosen. The signals from E-nose were analyzed by multivariate statistical methods via the determination of characteristic group areas. The DFA and the SIMCA methods allowed a differentiation of all studied groups of alcohols while the DFA method enabled to distinguish among them after approximations of the respective fragment of a DFA graph. The PCA analysis did not permit the classification between gin and liqueurs. This is probably related to a high degree of similarity in the composition of the tested samples. The results of analysis have shown that the E-nose based on ultra-fast gas chromatography coupled with the DFA or the SIMCA method enables a rapid differentiation of alcoholic beverages studied. Due to this, E-nose presents an interesting way to approve the authenticity of various alcoholic beverages. In conclusion, we believe that, in the future, such a use of E-nose can be useful for fast and objective detection of adulterated alcoholic beverages.

References

[1] Plutowska B., Wardencki W.: Application of gas chromatography-olfactometry (GC-O) in analysis and quality assessment of alcoholic beverages - A review. *Food Chemistry* **107** (2008) 449–463.

[2] Biernacka P., Wardencki W.: Volatile composition of raw spirits of different botanical origin. *Journal of the Institute of Brewing* **118** (2012) 393–400.

[3] Ng L.-K.: Analysis by gas chromatography/mass spectrometry of fatty acids and esters in alcoholic beverages and tobaccos. *Analytica Chimica Acta* **465** (2002) 309–318.

[4] Tešević V., Nikićević N., Milosavljević S., Bajić D., Vajs V., Vučković I., Vujisić L., Dordević I., Stanković M., Veličković M.: Characterization of volatile compounds of "Drenja", an alcoholic beverage obtained from the fruits of cornelian cherry *Journal of the Serbian Chemical Society* **74** (2009)117–128.

[5] Plutowska B, Biernacka P, Wardencki W.: Identification of volatile compounds in raw spirits of different organoleptic quality. *Journal of the Institute of Brewing* **116** (2010) 433–439.

[6] Cardeal Z.L., Marriott P.J.: Comprehensive two-dimensional gas chromatography - mass spectrometry analysis and comparison of volatile organic compounds in Brazilian cachaca and selected spirits. *Food Chemistry* **112** (2009) 747–755.

[7] García-Martín S., Herrero C., Peña R.M., Barciela J. Solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME-GC-MS) determination of volatile compounds in orujo spirits: Multivariate chemometric characterisation. *Food Chemistry* **118** (2010) 456–461.

[8] Jaitz L., Siegl K., Eder R., Rak G., Abranko L., Koellensperger G., Hann S.: LC-MS/MS analysis of phenols for classification of red wine according to geographic origin, grape variety and vintage *Food Chemistry* **122** (2010) 366–372.

[9] López-Vázquez C., Herminia Bollaín M., Berstsch K., Orriols I.: Fast determination of principal volatile compounds in distilled spirits. *Food Control* **21** (2010) 1436–1441.

[10] Rodríguez Madrera R., Blanco Gomis D., Mangas Alonso J.J.: Influence of distillation system, oak wood type, and aging time on composition of cider brandy in phenolic and furanic compounds. *Journal of Agricultural and Food Chemistry* **51** (2003)7969–7973.

[11] Zohora S., Khan A.M., Hundewale N.: Chemical sensors employed in electronic noses: A review, in: Meghanathan N., Nagamalai D., Chaki N. (Eds.): *Advances in computing and information technology, advances in intelligent systems and computing*. Springer, Berlin-Heidelberg 2013.

[12] Chatterjee D., Bhattacharjee P., Bhattacharyya N.: Development of methodology for assessment of shelf-life of fried potato wedges using electronic noses: Sensor screening by fuzzy logic analysis. *Journal of Food Engineering* **133** (2014) 23–29.

[13] Gardner J.W., Bartlett P.N., Dodd G.H., Shurmer H.V.: The design of an artificial olfactory system, in: Schild D. (Ed.): *Chemosensory information processing*, Springer, Berlin-Heidelberg 1990.

[14] Lozano J., Santos J.P., Horrillo M.C.: Classification of white wine aromas with an electronic nose. *Talanta* **67** (2005) 610–616.

[15] Press Release: The Nobel Assembly at Karolinska Institutet has today decided to award The Nobel Prize in Physiology or Medicine for 2004 jointly to Richard Axel and Linda B. Buck for their discoveries of "odorant receptors and the organization of the olfactory system" http://www.nobelprize.org/nobel_prizes/medicine/laureates/2004/press.html (accessed on 21 Sept 2016).

[16] Di Natale C., Davide F., Damico A., Nelli P., Groppelli S., Sberveglieri G.: An electronic nose for the recognition of the vineyard of a red wine. *Sensors and Actuators B* **33** (1996) 83–88.

[17] Jiang H., Chen Q., Liu G.: Monitoring of solid-state fermentation of protein feed by electronic nose and chemometric analysis. *Process Biochemistry* **49** (2014) 583–588.

[18] Gutierrez-Osuna R.: Pattern analysis for machine olfaction: A review. *IEEE Sensors Journal* **2** (2002) 189–202.

[19] Ragazzo-Sanchez J.A., Chalier P., Chevalier D., Ghommidh C.: Electronic nose discrimination of aroma compounds in alcoholised solutions. *Sensors and Actuators B: Chemical* **114** (2006) 665–673.

[20] Varmuza K.: Applied Chemometrics: From chemical data to relevant information. http://classifion.sicyon.com/References/chemometrics2000.pdf (accessed September 21, 2016)

[21] Daszykowski M., Kaczmarek K., Stanimirova I., Vander Heyden Y., Walczak B.: Robust SIMCA-bounding influence of outliers. *Chemometrics and Intelligent Laboratory Systems* **87** (2007) 95–103.

[22] Deswal A., Deora N.S., Mishra H.N.: Electronic nose based on metal oxide semiconductor sensors as an alternative technique for the spoilage classification of oat milk. *International Journal of Agricultural and Biosystems Engineering* **8** (2014) 506–509.

[23] Goodner K. Rouseff R.: *Practical analysis of flavor and fragrance materials*. John Wiley, Chichester 2011.