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Comparison of Quality Evaluation of Agricultural Distillates Using Prototype of Electronic Nose and Fast/Flash GC

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The paper presents the results of investigation on quality evaluation of agricultural distillates using a prototype of electronic nose instrument and a commercial electronic nose of Fast/Flash GC type – HERACLES II. The prototype was equipped with a set of six semiconductor sensors by FIGARO Co.. In case of the prototype volatile fraction of the agricultural distillate was prepared via barbotage process. HERACLES II analysed the headspace fraction. Classification of the samples into particular quality classes was performed using linear discriminant function supported with cross-validation method. Almost 100 % correct classification of agricultural distillate was observed for the analyses with HERACLES II. The prototype of electronic nose provided correct classification of 70 % of the samples.

1. Introduction

In a number of alcohol industry plants quality control and classification of raw material are done using organoleptic analysis. Although simple in its nature it is characterized by many shortcomings originating from human sense limitations. As a consequence distillery plants may collect the agricultural distillates of low quality due to poor raw material or improper preparation technology. Processing of raw alcohol of low quality is costly and yields financial loses of the manufacturer. According to the Regulation (EC) No. 110/2008 of the European Parliament and of the Council the manufacturers of alcohols should provide customers with a product from the highest quality raw material. Literature studies as well as own research reveal that utilization of low quality agricultural distillates in further production stages yields a number of by-products: aldehydes, ketones, acids, acetals (Plutowska et al. 2010), which are presents in a very wide concentration range deteriorating quality of produced alcohols. Application of the electronic nose instrument in alcohol industry has been already investigated, however it concerned quality control of the final products such as whisky, brandy, vodka, wine, beer, their classification, storage conditions, degree of ripening of the fruits they are made of as well as their botanic and geographic origin (Di Natale et al. 1996, Guadarrama et al. 2000, Santos et al. 2004, Marti et al. 2005, Lozano et al. 2005, Garcia et al. 2006, Buratti et al. 2007). However, there is a lack of information in the literature about the analysis of agricultural distillates using electronic nose as far as their quality is concerned (Dymerski et al. 2013a). Electronic nose is a device consisting of a set of sensors, not necessarily selective with respect to particular groups of volatile compounds, which operates in a way similar to the human sense of smell. The similarity consists in the fact that the sensors are analogues of receptor proteins in nose epithelium, which change chemical information into analytically useful signal. This signal is transmitted to an identification system, which is human brain and in the case of electronic nose suitable mathematical-statistical algorithm. These devices are equipped with a compare-to-pattern system, which is capable of identification of simple or complex gas mixtures. The main advantages of electronic nose instruments are: short time of analysis, possibility of miniaturization and possibility of portable devices production. The main disadvantages of electronic nose engulf: metrological parameters of the sensors applied, complicated mathematical-statistical approach employed for measurement data analysis, necessity of database

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preparation and training in order to provide correct interpretation of the results (Rock et al. 2008, Wilson and Baietto 2009, Szczurek et al. 2011). Comparing the electronic nose with the chromatographic techniques (frequently utilized in industrial investigations of agricultural distillates quality) one can notice a significant advantage connected with practical application of electronic nose device. A single gas chromatography analysis takes about 30-50 minutes (Gewu 1997, Falqué et al. 2001, Cortes et al. 2005, Callemien et al. 2006), whereas typical electronic nose analysis lasts a few minutes. This difference can be a milestone in industrial analytics of raw alcohol. The paper presents the results of investigation on agricultural distillates quality evaluation using the prototype of electronic nose equipped with semiconductor sensors by FIGARO Co. and the commercially available HERACLES II electronic nose of Fast/Flash GC type by Alpha MOS Co.. The aim of the research was to compare the results obtained with both electronic nose devices and to verify usefulness of the prototype in this type of analysis and its potential future application in industry.

2. Experimental

2.1 Raw materials

The investigation was conducted for the agricultural distillates of different raw material origin: triticale, corn, wheat and barley. The samples of agricultural distillates originated from local distilleries of Pomeranian voivodship. The results of organoleptic evaluation performed in a laboratory of Sobieski Distillery S.A. in Starogard Gdański allowed classification of the agricultural distillates into three quality classes: high quality class: 5 distillates, which earned very high marks during sensory analysis according to the Polish standard PN-A-79528-2:2002, medium quality class: 5 distillates, for which there was a discrepancy between testers during the sensory analysis – some testers classified them as compliant with the standard, some rejected as incompliant, low quality class: 5 distillates, which were unanimously classified as incompliant.

2.2 Measurement set-up

In case of the investigations utilizing the prototype of electronic nose the measurement set-up consisted of a bottle with carrier gas, Tecfluid 2150 series flow meter, a prototype of electronic nose and a PC class computer. Compressed air of N5.0 purity (Linde Gaz Polska Ltd.) was the carrier gas. Gas mixture was prepared via barbotage of the carrier gas through a sample of diluted agricultural distillate. Then the gas mixture was directed to the sensors module of electronic nose. In case of the investigation with HERACLES II device the headspace (gas mixture) prepared in a thermostated vial was transferred into a proportioner using an automatic feeder with 5 cm^3 syringe. The proportioner was followed by a sorption trap of Tenax. The analytes were released from the trap after it had been heated to 240 °C and the stream simultaneously directed to two chromatographic columns characterized by different polarity of stationary phase and equipped with two detectors of FID type. Figure 1a presents the general scheme of the electronic nose prototype, whereas figure 1b illustrates the general scheme of HERACLES II electronic nose.

2.3 Apparatus–prototype of electronic nose

The prototype consisted of a set of six commercial semiconductor sensors by FIGARO Co. (TGS 880, TGS 825, TGS 826, TGS 822, TGS 2610, TGS 2602). All internal elements of the prototype: barbotage scrubber, connecting tubes and sensors module were thermostated in order to provide stable measurement conditions. Dedicated miniaturized electronic circuit conditioned the output signal from the sensor set of the prototype. Its task was to convert changes of sensor resistance into voltage signal measurable by analogue-to-digital converter (ADC). This step yielded a voltage signal, the changes of which within full measurement range of the converter corresponded to complete range of changes of the sensor resistance. The voltage obtained was converted into digital from in the range from 0 to 14 bits. Accurate description of the prototype electronic nose can be found in the works: (Dymerski et al. 2013a, Dymerski et al. 2013b).

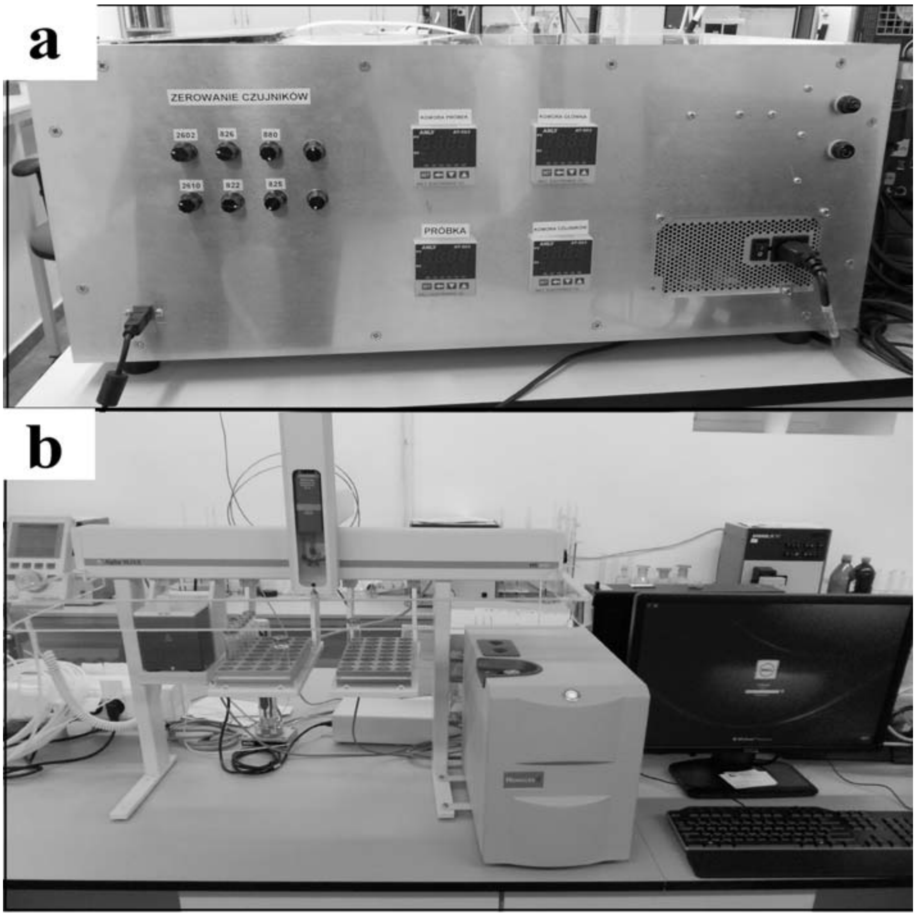

Figure 1: Prototype of electronic nose -(a), HERACLES II electronic nose of Fast/Flash GC type -(b).

2.4 Measurement methodology

The agricultural distillate samples were diluted with deionized water (Mili-Q A10 device by Millipore Co.) in 1:1000 ratio. Then 5 cm^3 of diluted samples were placed in the barbotage scrubber (prototype of electronic nose) and the vial of automatic feeder of HARACLES II device. The volume of scrubber and vial was 20 cm^3 each. The total number of prepared samples was 45 (3 types of agricultural distillates times 5 samples times 3 repetitions). The investigation was carried out for one month. Temperature of the barbotage scrubber and the vial was 20 °C. Volumetric flow rate of the carrier gas passing through the barbotage scrubber was equal 15 dm^3/h. Time of sensor signal acquisition since barbotage process onset was 60 s.

In the case of HERACLES II device the result of analysis – area of chromatographic peaks – was treated as an input for data analysis methods (situation analogous to the prototype of electronic nose equipped with a set of semiconductor sensors).

Classification of the agricultural distillates samples with respect to their quality was performed using linear discriminant analysis (LDA) employing free R software being a part of Free Software Foundation (Free Software Foundation, Boston, MA, USA).

3. Results and discussion

Table 1 presents a matrix with the results of LDA classification of all agricultural distillates samples subjected to analysis with the electronic nose prototype. 80 % of the samples were classified correctly. The samples of agricultural distillates medium quality (m) were best classified, whereas 12 out of 15 samples of high quality agricultural distillates (h) and 11 out of 15 samples of low quality agricultural distillates (b) were positively classified.

Table 1: Classification of agricultural distillate samples using LDA, b – distillates of low quality, m – distillates of medium quality, h – distillates of high quality. Electronic nose prototype.

	b - low quality	h - high quality	m - medium quality
b - low quality	11	2	2
h - high quality	2	12	1
m - medium quality	2	0	13

The LDA classification using cross-validation method, thus complete classification with training and testing sets, provided 71.1 % of correct classifications. In the case of cross-validation the entire data set is treated as both training and testing set. Having n-vector set (n=45) with explanatory variables one vector is withdrawn and treated as the testing set. The remaining n-1 vectors are subjected to classification and then the withdrawn vector is verified for its compatibility with a particular class. Afterwards the vector is returned to the n- vector set and the procedure is repeated for every vector from the set. Table 2 presents a matrix with classification of the agricultural distillates samples using the LDA classifier and cross-validation method; the samples of agricultural distillates of high quality were characterized by the biggest number (12 samples) of correct classifications.

Table 2: Classification of agricultural distillate samples using LDA supported with cross-validation, b – distillates of low quality, m – distillates of medium quality, h – distillates of high quality. Electronic nose prototype.

	b - low quality	h - high quality	m - medium quality
b - low quality	9	1	5
h - high quality	3	12	0
m - medium quality	4	0	11

Figure 2 illustrates graphical picture of classification of the agricultural distillates samples together with generated linear functions separating particular classes. Depending on selected explanatory variables (sensor response signal) characterized by the biggest variability one can notice very high separation of the samples within particular quality classes of agricultural distillates.

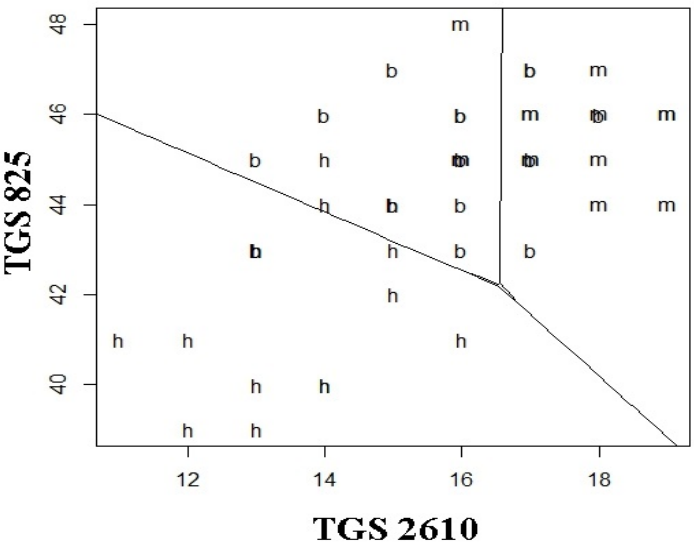

Figure 2: Classification of agricultural distillate samples using LDA as a function of selected descriptive variables (response signals of the sensors TGS 2610 and TGS 825), b – distillates of low quality, m – distillates of medium quality, d – distillates of high quality. Electronic nose prototype.

Table 3 shows a matrix with the results of LDA classification of agricultural distillates performed with HERACLES II device. This time 100 % of samples were correctly classified. Application of LDA classification together with cross-validation method yielded 97.8 % of correctly classified samples. Only the agricultural distillate sample of medium quality (m) was not properly classified.

Table 3: Classification of agricultural distillate samples using LDA, b – distillates of low quality, m – distillates of medium quality, h – distillates of high quality. HERACLES II .

	b - low quality	h - high quality	m - medium quality
b - low quality	15	0	0
h - high quality	0	15	0
m - medium quality	0	0	15

Figure 3 depicts graphical picture of classification of agricultural distillates samples together with generated linear functions separating particular classes depending on selected explanatory variables (area of chromatographic peaks) characterized by the biggest variability of the response. Applied discriminant function highly satisfactorily divided the plane into three regions (classes) and correctly assigned the samples of agricultural distillates into particular classes.

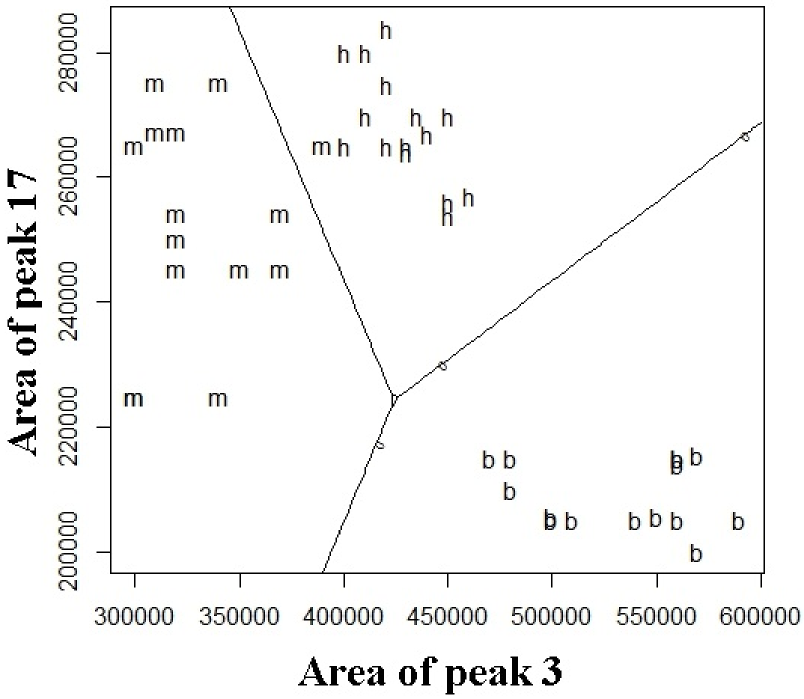

Figure 3: Classification of agricultural distillate samples using LDA as a function of selected descriptive variables (area of peak 3 and area of peak 17), b – distillates of low quality, m – distillates of medium quality, d – distillates of high quality. HERACLES II .

4. Conclusions

The aim of the investigation was to compare the results of agricultural distillates quality evaluation obtained with both types of electronic nose devices and to verify usefulness of the prototype in this type of analysis as well as its potential future application in industry.

Analysing the classification of the samples with respect to quality of agricultural distillates obtained using LDA discriminant function one could notice high number of correctly classified samples into particular quality classes: agricultural distillates of high class, agricultural distillates of medium class and agricultural distillates of low class. Application of this classifier to the results obtained with HERACLES II device provided almost 100 % correct classification (only implementation of the cross-validation method taking into account division of the samples into training and testing ones allowed correct classification of 97.8 % of samples). The results obtained with the prototype of electronic nose made correct classification of agricultural distillates samples quality possible at the level of 70 % (80 % for the entire training set, 71.1 % using cross-validation method). The aim stated by the authors was achieved because the presented prototype and applied data analysis method enabled discrimination and classification of agricultural distillates samples into particular quality classes with very high probability of success. The authors also believe that in future electronic nose device can be successful in providing routine evaluation of agricultural distillates quality and can constitute relatively cheap, fast and non-invasive technique widely applied in alcohol industry.

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