Discriminatory Power Assessment of the Sensor Array of an Electronic Nose System for the Detection of Non Alcoholic Beer Aging

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Abstract

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Many chemical changes in beer aroma occur during storage (aging), and monitoring these changes could give guidelines to the brewers how to manage and control the brewing process to obtain the final product with a high stability in flavour after packaging. In this regard, our laboratory aimed at a research into the application of an electronic nose in order to get the fingerprint of the change of non alcoholic beer aroma during aging. Th discriminatory power of the sensor array of this system was evaluated. Principal Component Analysis (PCA) and Soft Independent Modelling of Class Analogy (SIMCA) techniques were used for this purpose. The results obtained can direct us to performing other parts of our project. Considering the discriminatory power of the sensor array used, we can develop the application of a specific electronic nose system by picking up the most effective sensors or ignoring the redundant sensors.

Keywords: electronic nose; chemical change; storage; beer; aroma; food; PCA

In recent years, the quality of non-alcoholic beers has been fairly improved in such a way that the consumption of such product has become of great interest to the consumers. Brewery industries believe that non-alcoholic beers have a different flavour fingerprint compared with regular beers and many challenges should be addressed to attain an acceptable quality of non-alcoholic beers; for instance, achieving flavour stability is a critical challenge, especially the fact that what occurs with the beers between packaging and consumption (storage period) is usually out of the control in brewery. During storage (aging), flavour stability of non-alcoholic beer is diminished and off flavours are developed in aged beer accordingly. Although some methods exist, such as sensory panel and GC-MS, to evaluate and monitor these changes, due to some drawbacks, the use of other methods to evaluate the beer aroma during aging as fast and accurately as possible seems necessary (Ghasemi-Varnamkhasti *et al.* 2011, 2012). So, the employment of advanced analytical systems such as the electronic nose could be an option for this purpose. Some valuable works on the beer quality evaluation (e.g, off flavour detection) by the electronic nose have been reported in literature (Ragazzo-Sanchez *et al.* 2006, 2008, 2009). Also, a few works have been reported evaluating the aroma of beer in the aging process with the greatest emphasis having been laid in these studies on alcoholic beers (Lamagna *et al.* 2004; Sikorska *et al.* 2007). The knowledge of the aging phenomenon in non-alcoholic beer can be used to develop appropriate technological process improvements to control its particular flavour stability in brewery.

This study was aimed at the evaluation of the discriminatory power of each sensor included in the sensor array of the electronic nose for the identification of the aging process in non-alcoholic beer. There exists no study on this subject in the literature which shows the originality of this research.

MATERIAL AND METHODS

One brand of commercial non-alcoholic beer, produced on the industrial scale by a French company, was prepared and for the simulation of the long storage time, the samples were stored in an oven (at 40°C in dark). This procedure is known in the literature as forced aging (Walters *et al.* 1997; Guido *et al.* 2003). The interval time between the experiments was 5 days. The illustrations and descriptions of the system used in our laboratory had been reported previously (Delpha *et al.* 2004). Five tin oxide-based gas sensors (Figaro Engineering Inc., Glenview, USA and FIS Inc., Osaka, Japan) were used as the sensor array. These sensors were CP0: SPMW0 (tin dioxide, monitors the changes of various gases emitted during cooking), CP1: SPAQ1 (tin dioxide semiconductor sensor, with very high sensitivity to volatile organic compounds (VOCs) and solvents), CP2: TGS2620 (alcohol, toluene, xylene, other volatile organic vapours), CP3: TGS825 (hydrogen sulphide), and CP4: TGS880 (volatile vapours from food – alcohol). Moreover, a humidity sensor (Humirel Inc., humidity sensor (Humirel Inc., USA) and a temperature device (National Semiconductor) were incorporated in the array to control the ambient conditions. For the experiments, dynamic injection was considered after static headspace sampling and synthetic air was used as the carrier gas for preserving the beers. 50 ml of non-alcoholic beer sample were kept in a 250 ml bottle at 25°C for 45 min to create a vapour phase in equilibrium with the liquid. In this system, the synthetic air is brought into the sample container based on the bubbler principle and then mixed with the beer headspace. The mixture portions were controlled by a mass flow controller. These portions were considered as 100 ml/min and 80 + 20 ml/min, respectively, in the purging and injection phases. For purging the sensor array, the electric valves were switched during 1300 s and the dynamic injection of the beer headspace was then done for 300 seconds. For each aging beer sample, this experimental plan was performed randomly in seven replications. To eliminate or diminish the effects of the sensors drift, the sensor array was calibrated with blank deionised water. This approach was reported for wine by Gutierrez-Osuna (2002) and Lozano *et al.* 2008). All the sensor output signals were collected using the data acquisition board (LabView, National Instruments, Osaka, Japan) and the features relevant to the individual sensors were, therefore, extracted (Pearce *et al.* 2003; Lozano *et al.* 2008). The following relation was used for the feature extraction:

$$F = \frac{R_{\text{sample}}}{R_{\text{calibration}}} \quad (1)$$

where:

R_{sample} – minimum resistance of the sensor during performing the measurement protocol

$R_{\text{calibration}}$ – minimum resistance of the sensor exposed to blank deionised water

Autoscaling was exploited for the data preprocessing and principal components analysis (PCA) was used as the data reduction (Wei *et al.* 2009).

In this study, the discriminatory power is addressed to know how well a sensor discriminates between two aging beer classes. For this purpose, it is firstly necessary to fit each sample to both models of classes. For instance, to fit fresh beer to the PC model of both fresh and aged beers. Therefore, the residual matrices are computed, just for the discriminatory power. The theory of the discrimination power is beyond the aim of this paper, thus the reader is referred by Brereton (2006, 2007)and Otto (2007). The software of Matlab Vers.7.6 (Mathworks Inc., Natick, USA) and the Unscrambler 9.2 (Camo, Oslo, Norway) were used to analyse the data and compute the discriminatory power values of the sensor array.

RESULTS AND DISCUSSIONS

The score plot of the data collected is illustrated in Figure 1 in such a way that the two first principal components account for 88% of variance.

Clearly discriminated classes could be observed for N0, N1, N2, and N5. This reveals that the change in non-alcoholic aroma compounds is faster in the early stage. This observation agrees with that of Walters *et al.* (1997) who suggested that the changes in the beer flavour happen mostly early in the beer life and are then affected by factors such as the oxygen levels in the package at bottling, oxygen ingress during the storage, transport, agitation, temperature, and storage duration. Also, as seen in Figure 1, the discrimination between N3 and N4 is not distinct. In these circumstances, the discriminatory power of the sensors used in the electronic nose could lead to a better discrimination because, after selecting the most important sensors contributing in the recognition of the beer classes, clearly separated classes can be achieved. The discriminatory power values of the sensor array are given in Table 1.

As presented in the table, the discriminatory power is computed for each of the two classes. The values given in this table could be useful in the interpretation of the changes in beer during aging. The higher is the value, the higher is the discriminatory power. For instance, the discriminatory power of CP0 and CP3 sensor is the highest among the values associated with N0–N5. As mentioned earlier, N0 and N5 are fresh and highly aged beers, respectively. We can conclude that CP0 and CP3 have a considerable contribution to discriminate between these two classes. CP3 is responsible for H_2S concentration in the beer aroma; so, we can say the change in this certain compound, present in the beer headspace, is significant during the aging process of non-alcoholic beer. This conclusion is in close agreement with the literature (Vanderhaegen *et al.* 2006). The flavour of non-alcoholic beer is characterised largely by its taste and smell, which is affected by about 700 volatile and non-volatile compounds (Pearce *et al.* 1993) moreover the aroma changes caused by the changes in these volatile compounds are very complicated, and thus the knowledge of the contribution value of each sensor could help us to interpret what happens between the packaging and consumption of non-alcoholic beer. This information could be also useful, for example, if due to some reasons in the fabrication stage of the sensor array of the electronic nose, we want to reduce the number of sensors; by these results, the experiment could choose the most important and effective sensors which contribute more to the beer fingerprint measurement. Moreover, selecting the most important sensors contributing in the clearly discriminated classes of beer is helpful while we want to consider a transient state of the sensors other than the steady state. In this case, many variables depend on the technique used that can be extracted and it is obvious that possessing the most important variables can play a significant role in the computation stage of the data, because sometimes involving many variables in the data analysis could lead to some problems

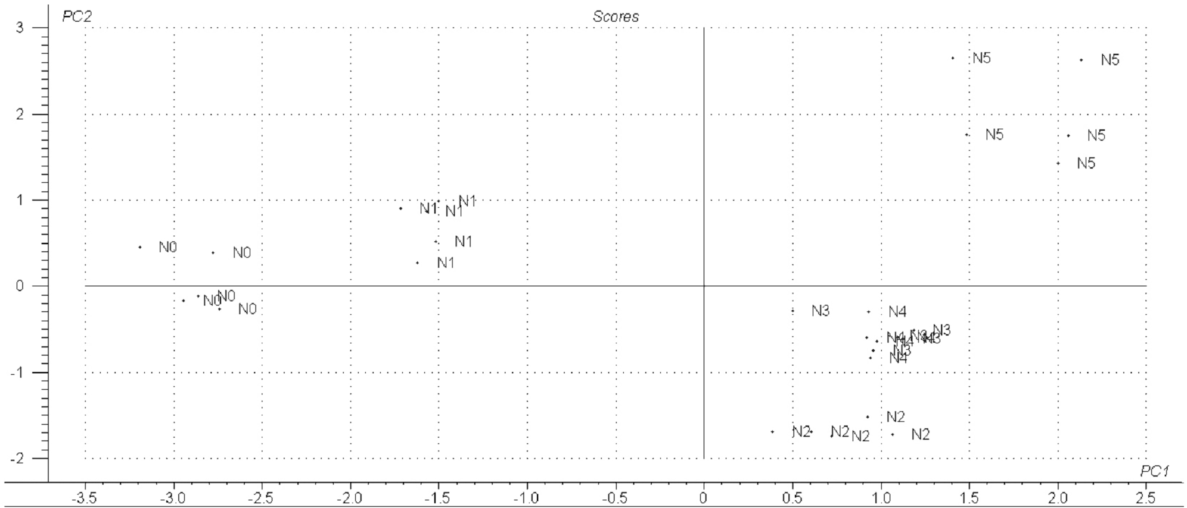

Figure 1. Score plot of the sensor array responses to non-alcoholic beer samples (N0 – fresh, N1–5 – aged)

Table 1. Discriminatory power values of the sensor array of the electronic nose used

Discriminated classes	Discrimination power of the sensors				
	CP0	CP1	CP2	CP3	CP4
N0–N1	10.7	4.4	5.6	14.8	8.6
N0–N2	25.5	21.6	5.3	18.4	22.3
N0–N3	34.1	33.1	9.2	29.1	53.2
N0–N4	48.1	20.5	36.71	47.0	21.9
N0–N5	40.1	33.6	12.1	58.6	4.71
N1–N2	30.0	25.9	5.28	25.6	24.8
N1–N3	50.7	32.5	15.3	26.0	27.9
N1–N4	53.5	14.5	25.2	33.4	9.1
N1–N5	57.7	24.4	24.9	42.3	19.0
N2–N3	21.5	1.9	4.8	14.3	30.6
N2–N4	9.3	12.55	20.1	6.6	4.3
N2–N5	12.5	14.6	6.8	27.7	22.5
N3–N4	13.0	58.3	12.1	19.2	8.0
N3–N5	17.2	43.0	4.1	19.2	28.0
N4–N5	21.0	65.2	8.21	13.4	3.1

N0 – fresh; N1–N5 – aged beers; CP0 – SPMW0; CP1 – SPAQ1; CP2 – TGS2620; CP3 – TGS825; CP4 – TGS880

like over fitting in the analysis. The results of this study could give us an insight into considering the best sensors in the future parts of our projects.

CONCLUSION

The overall flavour of non-alcoholic beer is said to be relatively poor and mild due to a very low intensity of most factors generally associated with beer, and to a special lack of complexity and balance which is attributed to the absence of alcohol. The flavour stability of beer after packing is very important to the quality management in the brewing industry and it is suggested that the aged character of beer should be maximised before it leaves the brewery, namely so that no further flavour change should occur. This study was a part of a project in our laboratory in which the aging fingerprint of non-alcoholic beer is to be detected by the use of the electronic nose system. The awareness of the discriminatory power of the sensors array could help us to make the appropriate decisions for selecting, changing, or even fabrication of the sensors relevant to the aim of our project. By performing SIMCA and computing the discriminatory power of the sensors used, we conclude that the capability of the array is acceptable to the aging fingerprint detection. The discriminatory power values computed in the current study can be used for the implementation of specific electronic nose application by picking up the effective sensors or eliminating the redundant sensors. Thus, we can use this array in other parts of the project in our laboratory.

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