COMPARISON OF THE PERFORMANCE OF TWO DIFFERENT E-NOSES IN HOPS CLASSIFICATION

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INTRODUCTION

Hops, the female inflorescences of the hop plant (Humulus lupulus L.), are used in the brewing industry to add bitterness and aroma to the beer. Their flowers aroma and bouquet derive from their essential oils that represent among 0.5 - 3% of the dry weight of the cone. Approximately 300 different chemical components [1] characterize these oils. However, during the elaboration process, only a small proportion of them is present in the beer due to volatilization.

The hop suffers a continuous process of deterioration after the crop due to oxidative processes when exposed to ambient air. Thus an early alarm of oxidative processes is an important parameters for the brewing industry. The hops essential oils are currently analyzed with gas chromatography coupled to gas spectroscopy [2].

Since their appearance, electronic noses have been widely employed in the food industry as a rather costless and efficient method, specially aimed to screening techniques for, among others, quality control purposes [3]. Due to requirements of local beer industries which demand rigorous and yet not very expensive quality control techniques to successfully compete within the beer market, we have studied the feasibility of electronic noses, to perform some of the tasks currently undertaken by conventional gas chromatography.

A serious obstacle for the use of an electronic nose for beer control is the difficulty in the detection of some odors when they are masked by the presence of alcohol. Thus as a first step in the feasibility study, we have considered the analysis of the hops as a raw material, either as flowers or preprocessed as pellets.

The two aspects we address in this work are the quick discrimination of various types of pellets through their aroma and the detection of departures from the desired aroma due to aging processes or lousy storage.

EXPERIMENTAL

Two different noses, based on different sensor technologies, were employed in this study. The first one is one of the LibraNose series from the University of Rome 'Tor Vergata' and Technobiochip [4]. This instrument is based on eight thickness shear mode quartz resonators (TSQR) each with a fundamental frequency of 20 MHz. Each sensor is coated with a molecular film of pyrrolic macrocycles. The choice of this molecular family is based on the fact that most of the odorous compounds are excellent ligands for metal ions. The other nose is the first prototype (PampaNose 1) of an electronic nose that has been developed in our laboratories. It has six metal oxide sensors (MOS) of tin dioxide whose resistivity changes according to the reducing properties of the sensed gaseous sample. Distinct electric behavior of the corresponding sensible film is achieved through doping some of these sensors with Au and others with tetra t-Butyl Zinc Phthalocyanine. Two commercial sensors, for temperature and relative humidity control, are included inside the sensor chamber, to keep track of these important parameters during the measurements.

For hop analysis, 7 grams of each sample were put inside 250 cm3 glass bottles. The headspace air was pumped into each of the two noses. Measurements with these noses were done consecutively and they were repeated during several days to check variability in the detection process. For both noses ambient air was used as the carrier gas.

RESULTS AND DISCUSSION

Our first analysis was the comparison of the performance of these electronic noses for discrimination between different types of hops. Four classes of hops were considered: Cascade pellets and flowers, Hallertau pellets and U.S Golding pellets. We have analyzed the relative peak signal from each sensor, i.e. the normalized difference of the maximum signal when the sample is present with respect to the corre-
sponding one for ambient air. Figures 1a and 1b display the score plane for the Principal Component Analysis (PCA) for the LibraNose and the PampaNose respectively. The percentage of the overall variability taken into account by the first two principal components is greater than 94% for both cases. We have verified that, for both noses, pellets from various types are nearly discriminated. Hops flowers are located around the origin of the score plane for the LibraNose. This is consistent with the fact that this nose response was near zero for Cascade flowers.

![Figure 1: Score plot; a) for the LibraNose and b) for the Pampa nose. Both cases with more than 94% accounted in the first two principal components.](image)

The other analysis we performed was the measurement of the changes in the aroma of a given type of hop with the aging of the sample. For this purpose, samples of a single type of hop were kept inside a freezer at a temperature of 20°C in closed recipients. They were taken from their recipients and kept in ambient air during one day (m1), 15 days (m15) and 30 days (m30) before the measurement day. They are labeled m1, m15 and m30 respectively. This process was repeated several times. Figure 2 displays the results for the PCA analysis of the relative signal of each sensor only for the PampaNose, since similar results are obtained with the LibraNose. More than 93% of the nose response is accounted in the first two principal components. As it is evident from Figure 2, samples of up to 15 days of aging in ambient air conditions are not discriminated with only the first two principal components while the 30 days samples were clearly distinguished. We have then studied an alternative analysis. The approach used consists of the two dimensional mapping of the relative signals using Self Organized Maps (SOM) [6]. A network of 13x10 neurons, with euclidean distances and gaussian neighbourhood function was used. Results are shown in Figure 3. The SOM classification was able to discriminate between samples corresponding to one and fifteen days of storage with only two dimensions.

![Figure 2: Score plot of the first two principal components for different days of storage.](image)

![Figure 3: Results for the different samples correspondint to 1 day, 15 days and 30 days of storage using SOM](image)
CONCLUSIONS

The results obtained so far show that electronic noses provide an adequate tool for detection of hops properties by measuring of their aromas in ambient air conditions. We were able to discriminate between different varieties of hops with a simple PCA analysis of the nose response and we found a similar behaviour for the two noses although they are based on different sensor technology.

The aging process required a nonlinear mapping (SOM), a further step beyond linear projection (PCA), to better discriminate departures from the reference (one day) aroma and visualize it in a two dimensional plane as required for future implementations in working conditions.

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