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Beer discrimination using a portable electronic tongue based on screen-printed electrodes

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ABSTRACT

There is a wide variety of Lager beer styles that differ, among others characteristics, in their alcohol content and color. Beer contains a high concentration of electrochemical active compounds, some of them related to the color of these beverages. In the present work, the applicability of a portable electronic tongue based on an array of electrochemical screen-printed electrodes was applied to the analysis of *Lager* beers. Multivariate analysis of the obtained signals allowed establishing mathematical models able to predict the European Brewery Convention (EBC) color index and the alcoholic strength with an accuracy of 76% and 86% respectively. Moreover, a discriminant model was established, able to classify beer by styles with 100% degree of accuracy.

1. Introduction

Beer is an alcoholic beverage obtained by fermentation of a starch-rich wort from cereal grain such as malted barley, wheat, maize and rice. Depending on the yeast used, beers can be classified in Lager beer (*Saccharomyces Pastorianus*) or Ale (*Saccharomyces cerevisiae*). Ales are traditionally fermented at warmer temperatures (14/19 °C), while lagers are typically fermented at cooler temperatures (4–9 °C). The cooler fermentation and lower aging temperatures used with lager yeast slow down the yeast activity and require a longer maturation time. The cold environment inhibits the production of fruity aromas and other fermentation byproducts common in ales.

There is a wide variety of Lager beers with pronounced differences among them. The characteristics of each type of beer depend on the raw material used and the parameters employed in the different steps of the production process, including the alcoholic content, which affects the defects of taste in alcohol-free beer (Blanco et al., 2014). Therefore, despite sharing certain steps in their processing, there are some differential aspects in the composition and organoleptic characteristics among the different Lager styles, including color and alcoholic strength. The color of a beer is an important visual cue and part of the overall sensory appeal of evaluating a brew.

Among the substances that contribute to beer characteristics, especially to color, there are a large number of electrochemically active compounds, substances that can be detected by means of electrochemical techniques. These include polyphenolic compounds, natural antioxidants present in plants. Approximately 80% of these compounds come from the malt and 20% from the hop used in the elaboration process. Some of the major phenolic compounds present in beer are phenolic acids (ferulic, cinnamic, chlorogenic, vanillic, gallic, caffeic, and p-coumaric, syringic), derivatives of flavan-3-ol (catechin, epicatechin, procyanidin, prodelphinidin) and flavone glycosides (Leitao et al., 2011). Hodžić et al. showed that there is a relationship between the content of polyphenols and color so that by increasing the content of polyphenols, the intensity of the color of beer increases. A relationship has also been established between polyphenol content and the antioxidant activity (Hodžić et al., 2007).

In addition, several studies have established a relationship between the malting process used and the antioxidant content in beers. Pale malts, subjected to mild heat treatment, exhibit greater antioxidant activity and have a higher content of phenolic compounds than roasted malts, subjected to higher temperatures during drying and roasting (Samaras et al., 2005; Amarowicz, 2009). Recently, it has been shown that antioxidant capacity varies with the type of beer, and this difference could be attributed to different contents of polyphenols, free phenols and phenolic acids (Piazzon et al., 2010). Some beers categorized as Lagers include the following styles: pilsener, which is widely produced industrially and could be considered the most popular type of beer in the world

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(identified by its light yellow to golden color and usually balanced taste); doppelbock, which is a very dark brown version of lager and is exceptionally malty, with very little bitterness; European strong lager, which is a variation of a Malt Liquor, contains more malt for fermentation but it has relatively low hop levels, and lastly alcohol-free beer, which has lower polyphenol and other antioxidant compounds content than other types of beers and whose antioxidant activity is, therefore, also lower.

Although there are traditional methods of analysis for the control of beer production, which include the official analysis methods, recent years have witnessed the increase in the use of cleaner, faster and more economical techniques. In this sense, working methodologies such as electronic tongues (ETs) represent promising chemical systems for the analysis of foods and beverages (Deisingh et al., 2004).

ETs are analytical systems consisting of an array of electrochemical sensors coupled with advanced data processing tools able to interpret the complex electrochemical signals (Cetó et al., 2014a,b, 2012; Gutiérrez et al., 2013; del Valle, 2010; Escuder-Gilabert and Peris, 2010; Winquist, 2008). Their use is becoming more widespread in food analysis, given the advantages offered in tasks such as recognition and classification, quantification of components and prediction of properties. In this sense, there are many reports using ETs for the analysis of beer during its production (Gorjanović et al., 2010). Applications of ETs related to beer analysis are focused on the discrimination of beers and the prediction of some important parameters (Rudnitskaya et al., 2009; Arrieta et al., 2010; Polshin et al., 2010; González et al., 2001), on the monitoring of beer aging and its fermentation process (Ghasemi-Varnamkhasti et al., 2012; Kutyła-Olesiuk et al., 2012) and on the quantification of certain compounds present in beer (Escobar et al., 2013; Ghasemi-Varnamkhasti et al., 2011; Cetó et al., 2013a,b).

In this work, miniaturized Screen-Printed Electrodes (SPEs) which are cheap, disposable and suitable for working with sample microvolumes (Tymecki et al., 2004; Washe et al., 2013), have been used. Their disposable character avoids cleaning stages, typical of conventional electrodes, and have even demonstrated better properties than other kinds of electrodes in the quantitative determination of some of the compounds present in beer (Matemadombo et al., 2012), including alcoholic strength (Patel et al., 2001; Avramescu et al., 2002) and polyphenol content (Cummings et al., 2001), among others.

The present work has been undertaken to develop a portable electronic tongue formed by Screen-Printed Electrodes (SPE) built commercially with different sensing materials and without any modification. The system has been used to analyze several styles of Lager beers in a wide range of color index and alcoholic strength. The voltammetric signals have been pre-treated using the kernel method and as the input variable of multivariate analysis. This method attempts to be a real tool for classifying beer samples according to their beer style and to establish predictive correlations.

2. Experimental section

2.1. Beer samples

The measurements were made in 25 types of commercial beers (Table 1). Beers were selected attending to their alcoholic strength (from alcohol free to strong beers) and their EBC (European Beer Convention) color value (from golden to dark beers) searching for a wide range in both characteristics. All analyses were carried out from newly opened bottles.

The excess of CO_2 was removed by stirring the samples during 10 min before the measurements.

Table 1
Classification and characteristics of 25 analyzed beers.

Style	Color	%Vol	Number of samples
Free alcohol beer (BS)	Golden	<1.0	8
Pilsener (BP)	Golden	4.2–5.5	9
Doppelbock (BD)	Brown/dark	>7.0	5
European strong *Lager* (*BF*)	Golden/amber	>6.5	3

2.2. Electronic tongue

Electrochemical measurements were carried out in a DropSens stat400 potentiostat (Oviedo, Spain) using four Screen-Printed Electrodes (SPEs) made by DropSens. Their dimensions were $3.4 \times 1.0 \times 0.05$ cm. Voltammograms were registered with DropView 2.0 program. All electrodes employed share a pseudo-reference Ag/AgCl electrode and electrical contacts manufactured in the same material.

- DS-110, working electrode made of carbon.
- DS-250AT, working electrode made of gold.
- DS-410, working electrode made of carbon/Co-Phtahlocyanine.
- DS-550, working electrode made of platinum.

2.3. Voltammetric measurements

Voltammograms were performed between -0.6 V and 1.0 V, with a scan rate of $100\ \mathrm{mV\,s^{-1}}$. Electrochemical measurements were performed at room temperature (25 °C). The robustness of the system was ensured by measuring the samples seven times with each sensor.

2.4. Data processing

The multivariate data analysis was performed by using the program Matlab V 7.0 and MinitabV 15. Voltammograms were pre-processed by using an adaptation of a data reduction technique based on predefined response "bell-shaped windowing" curves called "kernels" (Parra et al., 2004). The data pre-processing has been done based on a compression method described by Gutiérrez-Osuna and Nagle (1999). The voltammogram curve is multiplied by 10 smooth, bell-shaped windowing functions defined as

$$K_i(V_j) = \frac{1}{1 + \left(\frac{V_j - c_i}{a_i}\right)2b_i}$$

where a_i, b_i and c_i define the width, shape and center of the different windowing functions K_i. Subsequently, data were integrated with respect to voltage. After compression, each voltammogram has been reduced to a vector of 10 variables. Using this technique, 10 variables were obtained from each voltammogram. A data matrix formed by 175 rows (25 beer samples $\times$ 7 repetitions) and 40 columns (10 values for each one of four electrodes employed) was constructed. Principal component analysis (PCA) and linear discriminant analysis (LDS) were carried out using these 10 variables as input data source. Prediction models were performed by partial least squares (PLS). The classification models were subjected to full cross-validation by means of the "leave-one-out" method (Berrueta et al., 2007: Cetó et al., 2013c).

2.5. Color index and alcoholic strength determinations

UV–Vis spectrophotometer Shimadzu UV-1201S was used to determine the color of different beers. Photometric measurements