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Prediction of bitterness and alcoholic strength in beer using an electronic tongue

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ABSTRACT

An electronic tongue based on an array of electroactive conducting polymers was developed for the analysis of beers.

The principal component analysis (PCA) of the electrochemical signals obtained by immersing the array of electrodes in 21 lager beers (dark and pale; with alcohol and alcohol free) has provided a clear discrimination between dark and pale beers and also between beers with and without alcohol. The correlations between redox processes observed in the electrodes and the iso-α-acids concentration and the alcoholic degree have been found using partial least square regression (PLS2). The Root-Mean-Square Error of Prediction (RMSEP) values for alcoholic strength and iso-α-acids prediction model were 0.603 (%vol) and 9.021 (mg L^{-1}), respectively.

1. Introduction

Beer is obtained by the brewing and fermentation of starch (mainly derived from malted barley) germinated in water in the presence of yeast (De Keukeleire, Vindevogel, Szucs, & Sandra, 1992). Cones of hop (*Humulus lupulus*) are used in the brewing process to add bitterness which comes from α-acids (humulones), that are contained in the hop cone. During wort boil, six iso-α-acids which impart about 80% of the beer bitter taste (Tanimura & Mattes, 1993) are formed from the hop α-acids. Iso-α-acids are also of interest due to their influence on foam stability (Blanco et al., 2006) and their bacteriostatic effects (Blanco, Rojas, & Nimubona, 2007).

A number of analytical techniques have been developed for determining the concentration of α-acids in hops and iso-α-acids in beers. These methods are based on lead conductance, ultraviolet spectrophotometry, and high-performance liquid chromatography (HPLC) (Lachenmeier, 2007; Llario, Iñón, Garrigues, & De la Guardia, 2006; Malfliet et al., 2008).

In spite of their interest, these methods are time consuming and require complex and expensive equipment. A promising approach to the analysis of foods and beverages consists in the use of multisensor systems (the so-called electronic tongues) (Rodríguez-Méndez et al., 2008; Toko, 2000; Vlasov, Legin, Rudnitskaya, Di Natale, & D'Amico, 2005; Winquist et al., 2005). In such systems an array of sensors which exhibit cross-selectivity to various compounds are coupled with signal processing methods, such as principal component analysis (PCA) or linear discrimination analysis (LDA) (Beebe, Pell, & Seasholtz, 1998).

Electrochemical sensors (potentiometric, impedimetric or voltammetric) are the most widely used sensing units in electronic tongues. In particular, most of the works in this field involve signal generation from potentiometric sensors where the potential value created by the diffusion of ions across a membrane is measured (Bratov & Dominguez, 2005; Gutes, Ibañez, Cespedes, Alegret, & del Valle, 2005).

The discrimination of beverages, such as coffees, juices or beers, has been attempted by using a range of sensors doped with a variety of ionophores (Rudnitskaya et al., 2009; Vlasov et al., 2005).

An electronic tongue based on voltammetry has been developed based on a number of different working electrodes made from different metals. The system has been used to evaluate several food samples (Winquist, Krantz-Rulcker, & Lundstrom, 2008; Winquist et al., 2005). Other voltammetric electrodes have also been used to discriminate phenolic derivatives, wines and teas that are characteristic of several foods (Gutes et al., 2005). Milks have also been analysed using an array of screen-printed electrodes (Collier, Baird, Park-Ng, More, & Hat, 2005).

The performance of a voltammetric multisensor system can be improved by using electrodes chemically modified with electroactive materials. Using chemically modified electrodes,

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peaks associated to the oxidation–reduction of the electrodic material and of the analytes present in the test solution can be observed. The interactions that occur between the electrode and the solution can improve extraordinarily the selectivity of the electrodes. Such interactions include: (i) the oxidant or reducing character of the solution can modify the oxidation potential of the electrodic material; (ii) the electrocatalytic activity of the electrode material can facilitate the oxidation of the compounds solved in the test solution; (iii) the response of the electrode material is related to the ability of the sensors to allow the diffusion of the counterions between the solution and the bulk material, an influx necessary to preserve the macroscopic electroneutrality of the electrode (de Saja & Rodríguez-Méndez, 2005).

Such arrays have shown to have a good discrimination capability between samples such as model solutions of basic tastes (Arrieta, Rodríguez-Méndez, & de Saja, 2003), food antioxidants (Casilli et al., 2005), wines (Parra et al., 2006) and olive oils (Apetrei, Gutierez, Rodríguez-Méndez, & de Saja, 2007). The capability of discrimination of the voltammetric system is superior to the multisensory systems based on potentiometric sensors.

In spite of the increasing number of groups working with electronic tongues, only a few works have attempted to analyse beers (Lvova et al., 2002; Toko, Murata, Matsumo, Kikkawa, & Yamafugi, 1992). All these works have used potentiometric sensors which combined with chemometric methods (e.g. principal components analysis, partial least regression (PLS), and principal component regression (PCR)) have successfully discriminated various types of beers according to their tastes. Up to now, correlations between the signals provided by the sensor and particular components of the beers have not been established.

One interesting possibility to develop arrays of sensors is to use conducting polymers as sensitive materials. Such sensors can be easily fabricated by electrodepositing a polymeric film onto a conductive surface (Sadik, 1999). This method allows the development of sensing units by using a large variety of polymers and doping agents. Conducting polymer sensor arrays have been successfully used to detect a variety of ions, simple and complex solutions such as wines (Arrieta, Apetrei, Rodríguez-Méndez, & de Saja, 2004; Cortina-Puig, Muñoz-Berbel, del Valle, Muñoz, & Alonso-Lomillo, 2007).

The objectives of this work have been twofold, (a) to evaluate the possibility of using an innovative multisensory system based on voltammetric sensors based on conducting polymers to discriminate beers according to their tastes and (b) to develop mathematical models to predict both the content of iso-α-acids and the alcoholic strength.

For this purpose, an array of six polypyrrole sensors doped with different doping agents was constructed. The array was exposed to 21 selected beers of different nationalities and characteristics (dark, pale and alcohol free). The discrimination capability of the system has been evaluated by using principal component analysis (PCA) and cluster analysis (CA). The content of iso-α-acids has also been analysed using HPLC. Prediction models to calculate the content of iso-α-acids and alcoholic strength from data registered with the electronic tongue have been constructed by means of partial least squares (PLS2).

2. Experimental section

2.1. Beer samples

The measurements were made in 21 types of commercial beers (Table 1). 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.

2.2. Chemical analysis: HPLC measurements and alcoholic strength

A calibration standard of isomerized α-acids was purchased from Labor Veritas (Switzerland). Other reactants were purchased from Merck (Germany). Deionised water (Millipore Milli Q) was used in all experiments. A Waters HPLC system with a Mod. 600 solvent delivery pump, a 996 photodiode array (PDA) detector, and a Waters HPLC U6 K injector were used. The column was a octadecyl reversed-phase column (Supelco Discovery C18, 250 mm × 4.6 mm × 5 μm).

The HPLC method used was based on Verzele, Steenbeke, Verhagen, and Strating (1990) and Biendl, Virant, and Varjú (2004), with a small modification consisting of the addition of Na_2EDTA (0.1 mol L^{-1}) to the mobile phase B to improve the resolution. The UV detector was set to a wavelength of 270 nm, which corresponds to an absorbance maximum for iso-α-acids. The injection volume was 10 μL, and the gradient flow rate was 1 mL per min at 35 °C. Mobile phase A consisted of 100% methanol, while mobile phase B contained 75% methanol, 24% H_2O, 0.9.% phosphoric acid (85%) and 0.1% Na_2EDTA (0.1 mol L^{-1}). A gradient elution was used, consisting of 0–17 min at 100% B, 17–25 min at 35% A and 65% B, 25–30 min at 100% B. The peak area was recorded by using Empower Pro software. The HPLC chromatograms were processed with PeakFit v4.11.05 for Windows software to separate and to integrate the area of the different iso-α-acids isomers (cis–trans). Using the calibration line and HPLC chromatograms processed by PeakFit software, the concentration of each iso-α-acids contained in each beer sample was calculated.

The alcoholic strength in beer samples was assessed by the EBC method 7.1 (pycnometry) (EBC, 1975).

2.3. Electronic tongue

Electrochemical measurements were carried out in an EG&G PARC 263A potentiostat/galvanostat in a conventional three-electrode cell. The reference electrode was an Ag|AgCl/KClsat and the counter electrode was a platinum plate. Sensors were obtained by polymerisation of pyrrole (0.2 mol L^{-1} in water) onto Pt disks (1 mm diameter) by chronoamperometry. Six types of sensors were obtained by doping polypyrrole with different doping agents (0.1 mol L^{-1}): 1-decanesulfonic acid sodium salt (DSA), potassium hexacyanoferrate (FCN), sulfuric acid (SO_4^{2-}), phosphotungstic acid (PWA), *p*-toluenesulfonic acid (*p*-TSA) and anthraquinone-2,6-disulfonic acid disodium salt (AQDS). Details of the preparation can be found in Ref. Rodríguez-Méndez et al. (2008).

Once prepared, the electrodes modified with conducting polymers were used as working electrodes in cyclic voltammetry experiments. Voltammograms were registered from −1.0 to 0.5 V (the scan started at 0 V) at a sweep rate of 0.1 V s^{-1}. The electrochemical experiments were performed at a controlled temperature of 25 °C.

The robustness of the system was ensured by measuring the samples eight times with each sensor. The multivariate data analysis was performed by using the program Matlab V 7.0 and Minitab V 15. Voltammograms were pre-processed by using an adaptation of a data reduction technique based on predefined response "bell-shaped-windowing" curves called "kernels" (de Saja & Rodríguez-Méndez, 2005). Using this technique, 10 variables were obtained from each voltammogram. A data matrix formed by 168 rows (21 beer samples × 8 repetitions) and 60 columns (10 values for each one of the six polypyrrole sensor) was constructed. Principal component analysis (PCA) and cluster analysis (CA) were carried out using these 10 variables as input data source. Prediction models were performed by partial least squares (PLS2). The classification models were subjected to full cross-validation by means of the "leave-one-out" method (Berrueta, Alonso-Salces, & Heberger, 2007).

Table 1
Results of quantitative estimation analysis of the isohumulone and ethyl alcohol in commercial beers using the polypyrrole sensor array; SD, standard deviation (n = 8); ME, mean error.

Commercial beers			Iso-α-acids (mg L^{-1})				Ethanol (%v/v)			
Beer code	Nationality	Type	Real	Predicted	SD	ME (%)	Real	Predicted	SD	ME (%)
BN01	Mexico	Dark	38.91	47.41	1.59	22	5.30	5.49	0.43	4
BN02	Spain		56.35	46.15	2.31	18	5.50	4.48	0.38	19
BR01	The Netherland	Pale	60.03	55.90	1.47	7	5.00	5.11	0.10	2
BR02	Denmark		38.75	47.37	2.68	22	5.00	5.18	0.20	4
BR03	Argentina		39.96	39.34	1.23	2	4.90	4.11	0.18	16
BR04	India		49.93	50.21	1.00	1	5.00	5.02	0.13	1
BR05	Germany		82.27	84.96	2.61	3	5.20	4.72	0.29	9
BR06	Morocco		107.39	102.43	7.45	5	5.00	4.97	0.31	1
BR07	Colombia		71.42	73.51	2.46	3	4.70	4.34	0.10	8
BR08	Japan		64.46	62.69	1.22	3	5.00	5.47	0.06	9
BR09	Ireland		76.48	82.48	5.32	8	5.00	4.82	0.17	4
BR10	Spain		63.48	70.57	1.86	11	5.50	5.72	0.25	4
BR11	Spain		52.86	63.30	2.32	20	5.00	4.52	0.27	10
BR12	Spain		70.47	79.48	2.24	13	4.20	4.85	0.13	15
BR13	Spain		60.53	60.87	1.20	1	5.40	5.73	0.16	6
BR14	Spain		61.38	49.61	6.68	19	6.20	6.43	0.15	4
BR15	Spain		77.94	67.33	2.11	14	4.20	3.72	0.08	11
BR16	Spain		78.62	73.22	2.37	7	4.80	4.86	0.27	1
BR17	Spain		98.77	92.53	4.88	6	7.20	7.31	0.41	2
BS01	Germany	Alcohol free	72.48	59.98	2.17	17	0.50	0.53	0.26	6
BS02	Spain		30.27	43.35	2.33	43	0.00	1.23	0.15	_

3. Results

Once prepared, the sensors were immersed in the beer samples under study and voltammetric experiments were carried out. The responses of the polymeric electrodes are illustrated in Fig. 1 where the voltammograms registered from PPy/AQDS, PPy/DSA and PPy/PWA sensors to the Club Colombia beer are shown. Voltammograms show peaks associated to the oxidation/reduction of the polypyrrole and also peaks related to the redox activity of the doping agents. For this reason, each electrode produces a particular electrochemical response permitting to construct an array of cross-selective electrodes. The shape and position of these peaks varies from one beer to another. This is due to the interactions that occur between the electrode and the solution. For instance, the reduction and oxidation of the polypyrrole that occurs during cyclic voltammetry is accompanied by a transport of ions in and out of the polymeric film. This diffusion is necessary to preserve the macroscopic electroneutrality of the layer. For this reason, the nature of the ions present in the solution and their concentration has a strong influence on the shape and positions of the peaks. The concentration of iso-α-acids is reflected in the position of the peaks.

As each electrode shows a characteristic electrochemical response towards a particular beer, the output data from the electrochemical sensor array can be used to discriminate beers according to their chemical nature.

In order to study the long term stability of the electrodes, they were exposed to an electrolytic solution of 0.1 mol L^{-1} KCl after each working day. The coefficients of variation (%CV) of the peak heights were calculated then. Polymeric electrodes showed a good level of stability up to 50 consecutive measurements, with %CV values bellow 20%. The decision of using a brand new array every 40 measures was taken from these data.

After appropriate pre-processing, the data obtained from cyclic voltammetry were used as the input variable for chemometrics. The classification capability of the system was evaluated using PCA (Fig. 2). As observed in the figure, different beers could be well discriminated in the three-dimensional space represented by the first three principal components PC1, PC2 and PC3. Even though some samples seem to overlap, there is a clear discrimination that can be observed by presenting the diagram from a different rotating angle. The array of sensors allows an improved discrimination of dark beers from pale beers. Alcohol free beers also appear apart from the other subgroups. The particular characteristics of the double malt beer also permit this sample to be easily discriminated.

The PC loading plots from the input data used to perform the PCA can provide an indication of the contribution of the variables in the discrimination of beers. As stated in previous paragraphs by pre-processing the electrochemical signals, 10 variables were obtained from each voltammetric curve. Fig. 3 represents the tridimensional PCA loading plot for the system under study. As observed in the figure, the variables are distributed in different regions of the diagram, demonstrating the complementary information provided by each variable. For instance, variables obtained from PPy/SO_4, PPy/AQDS and PPy/*p*Tol sensors showed a strong

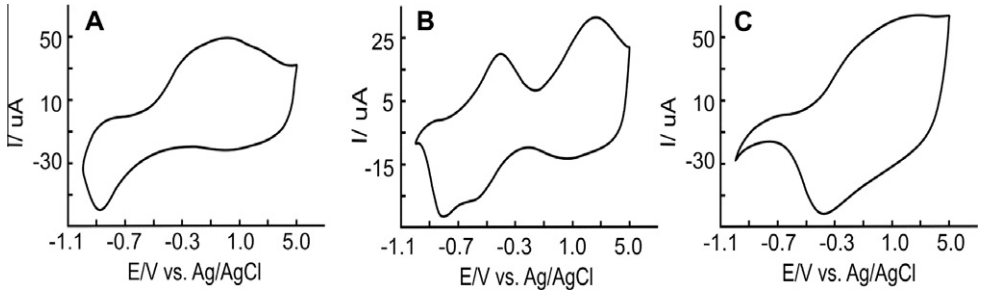

Fig. 1. Voltammetric responses of electroactive sensors immersed in a beer sample (Club Colombia) (a) Ppy/AQDS, (b) Ppy/DSA and (c) Ppy/PWA.

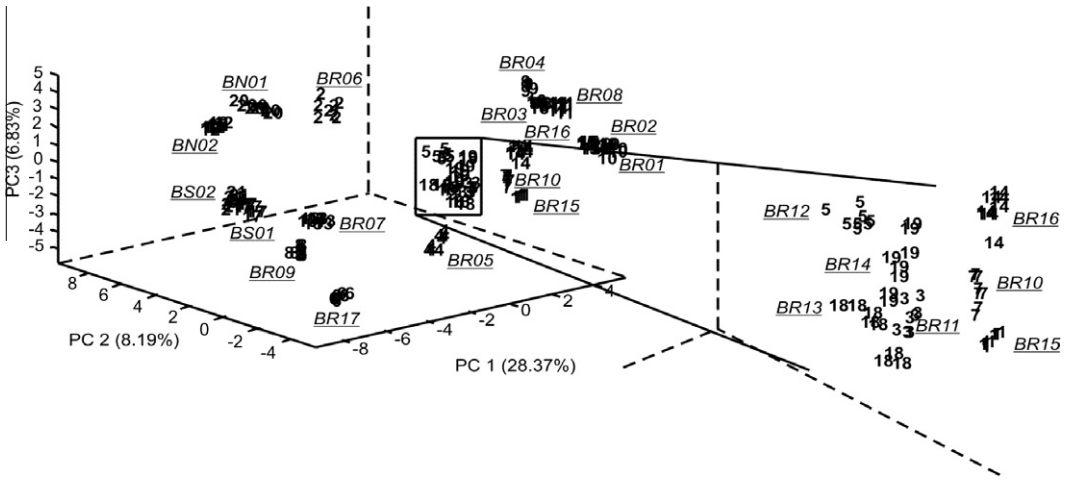

Fig. 2. PCA score plot corresponding to the 21 beers under study.

contribution to the first principal component, while variables extracted from PPy/FCN and PPy/DSA contributed strongly to the second principal component. Finally variables extracted from PPy/FCN and PPy/PWA were the strongest contributors to the third principal component. This result confirms that the sensors selected can provide complementary information to construct an array which is suitable to discriminate beers.

In the last part of the work, an attempt was made to establish a mathematical model to predict the levels of some important compounds such as the iso-α-acids and the alcoholic strength.

Partial least squares (PLS2) regressions were performed to model the relationships between the electrochemical signals obtained from the array of sensors and the concentration of iso-α-acids evaluated by HPLC and the alcoholic strength determined by the EBC method.

For PLS2 calculations, data were split into two sets, the first for calibration and validation of the model and the second for its testing. Cross-validation was used to construct a reliable calibration model. During quantitative analysis of the beers the possibility of applying the polypyrrole sensor array (i.e. electronic tongue) to measure the content of some substances such as isohumulone and ethyl alcohol were displayed, and the results are shown in Table 1. Comparing the results of quantitative analysis, it may be observed that the content of isohumulone and alcohol in the beer samples, calculated using PLS2 agree with the analytical value measured by traditional methods. Thus, using the electronic tongue based on a polypyrrole sensor array, it is possible to determine isohumulone and ethyl alcohol values necessary for the characterisation of the beer quality in a single measurement. The response of the polypyrrole sensor correlated with isohumulone content from beer estimated by HPLC with RMSEP values for alcoholic strength and iso-α-acids prediction model were 0.603 (%vol) and 9.021 ($mg\ L^{-1}$), respectively.

4. Discussion

This work reveals the first evidence that an electronic tongue based on voltammetric polymeric sensors can be used to analyse beers, e-tongues are advantageous in several ways. Their most interesting aspect is that they provide a global fingerprint of a sample instead of information about particular components. However, correlations have been found with alcoholic degree and iso-α-acids concentration. Correlations with other parameters can thus be expected to be demonstrated in future works, opening the door to further application fields within the beer sector.

In comparison with other systems, the electronic tongue analyses the sample as a whole and does not need to separate the sample in its components (as in HPLC). This allows classifying samples according to their global characteristics. Other systems that ana-

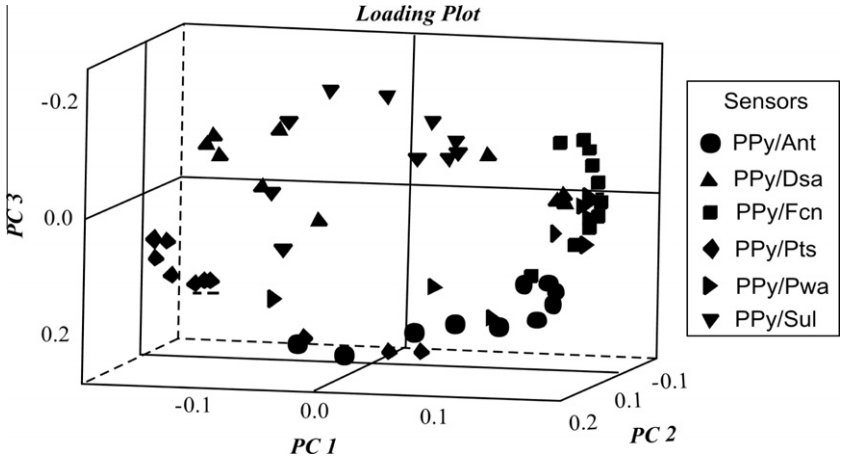

Fig. 3. PCA loading plot corresponding to the 21 beers under study.

lyse the samples in a global manner have also been described in the literature. For instance, it is possible to use commercial FTIR instruments coupled to pattern recognition techniques (Lachenmeier, 2007). The time to register a spectrum is 2 min, which is longer than the time needed by our instrument to register a voltammogram (less than 1 min). As in the case of our e-tongue, the time of training and analysis of the FTIR data is long. Similar sensitivities are found using both methods (RMSEP of 0.10% vol for alcohol using FTIR and 0.603% vol using the electronic tongue).

The electronic tongue presented in this work is not a commercial instrument. A development and improvement of these novel systems, currently in their first stages in the field of beers (the number of papers published in this field is fewer than 20), can be expected in the next years. This is our first work in this field and our objective has been to find sensors, stable, reproducible and able to provide different fingerprints for different beers. Future works will explore correlations with other parameters.

5. Conclusions

A multisensory array based on sensors chemically modified with polypyrrole sensors has allowed to discriminate 21 commercial beers. This behaviour confirms that the electrochemical signals provided by the array are related to the global properties of the beers. PCA loading plots have demonstrated that the selected sensors show a high degree of complementarity. Using the sensor responses it has been possible to build a mathematical model that has permitted to predict the content of iso-α-acids and ethyl alcohol in the beers with small residual errors.

Our prototype has been working correctly for wine in the last years, and is nowadays fully operational in some wine-producing companies. This might suggest that this prototype can lead to a more effective control of production processes in the brewing industry.

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