Hybrid Electronic Tongue based on Multisensor Data Fusion for Discrimination of Beers

Juan Manuel Gutiérrez[a], Zouhair Haddi[b], Aziz Amari[c], Benachir Bouchikhi[b], Aitor Mimendia[d], Xavier Cetó[d], Manel del Valle[d,*]

[a] *Bioelectronics Section, Department of Electrical Engineering, CINVESTAV, 07360 Mexico D.F., Mexico*

[b] *Sensor Electronic & Instrumentation Group, Physics Department, Faculty of Sciences, Moulay Ismaïl University, B.P. 11201, Zitoune, Meknes, Morocco*

[c] *Department of Physics, Faculty of Sciences, Mohammed V- Agdal University, B.P. 1014, Rabat, Morocco*

[d] *Sensors and Biosensors Group, Department of Chemistry, Universitat Autònoma de Barcelona, 08193 Bellaterra, SPAIN*

Abstract

This paper reports the use of a hybrid Electronic Tongue based on data fusion of two different sensor families, applied in the recognition of beer types. Six modified graphite-epoxy voltammetric sensors plus 15 potentiometric sensors formed the sensor array. The different samples were analyzed using cyclic voltammetry and direct potentiometry without any sample pretreatment in both cases. The sensor array coupled with feature extraction and pattern recognition methods, namely Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), was trained to classify the data clusters related to different beer varieties. PCA was used to visualize the different categories of taste profiles and LDA with *leave-one-out* cross-validation approach permitted the qualitative classification. The aim of this work is to improve performance of existing electronic tongue systems by exploiting the new approach of data fusion of different sensor types.

Keywords: Data fusion; Hybrid electronic tongue; Linear Discriminant Analysis; Beers classification

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(*) Author for correspondence; e-mail: manel.delvalle@uab.es

1. Introduction

Beer is a popular alcoholic beverage, and probably one of the oldest manufactured by mankind. Brewing is based on the fermentation of starches, commonly derived from cereal grains such as barley, wheat, maize and rice. Most beers are flavored with hops, which add bitterness and aroma besides acting as a natural preservative and occasionally, other flavorings such as seasonings, herbs or fruits may also be included in its elaboration [1]. The direct effect of the use of hops is the release of α-acids, which during the boiling process are converted into the iso-α-acids, whose significance is relevant not only for foam stability, but also for their bactericidal effects [2].

Up to now, different styles of beer have been created around the world. These types of beers vary in characteristics such as flavor, color and aroma. Related to this, beer is generally classified into two main kinds based on the yeast used for fermentation. These two styles are Ales, which use top-fermenting yeast, and Lagers which are brewed with bottom-fermenting yeast. On the one hand, some common varieties of Ales include the Indian Pale Ale (IPA) variety, which commonly have a nutty or fruity state, and Stout which is easily identified by its very dark color and roasted taste. On the other hand, some beers categorized as Lagers include the following varieties: Pilsner which is widely produced industrially and could be considered the most popular type of beer in the world (identified by its light yellow to golden color and usually balanced taste) or the American style Lagers, mostly produced in America, and characterized by their light color and flavor as well as their high carbonic acid content [3].

An important characteristic of beers is bitterness. Bitterness determination is related with the total amount of iso-α-acids. This property is currently quantified in the European Bitter Units (EBU) scale. There are several methods related to the determination of iso-α-acids in beers (i.e. using techniques as UltraViolet spectrophotometry (UV) and High Performance Liquid Chromatography (HPLC) coupled to UV or Mass Spectrometry (MS) detection [4, 5]). However, these analytical methods often require long analysis time, complicate sample pretreatment and the use of sophisticated and expensive equipment. In this sense, due to its characteristics, working methodologies as Electronic Tongues (ETs) represent promising chemical analysis systems for the analysis of foods and beverages [6]. ETs are analytical systems consisting in an array of electrochemical sensors coupled to advanced data processing tools, able to interpret the complex chemical signals and provide the sought information of the analyzed samples [7]. 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 milk, fruit juices, coffee, wine and beer [8, 9]. Applications of ETs related to beer analysis are focused on the discrimination of samples and the prediction of some taste attributes [2, 10], in the correlation of features described by a sensory panel and ETs [11], and more recently, on the monitoring of beer aging and its fermentation process [12, 13].

Data analysis and pattern recognition in particular, are a fundamental part of any sensor array system [14]. For instance, ETs that incorporate non-linear chemometrics such as ANNs have been demonstrated in various applications. Many ANN configurations and training algorithms have been used to build up ETs; these include Probabilistic Neural Networks (PNN) with Radial Basis Functions (RBF) or Feed-Forward Networks with Backpropagation (BP) learning method [12], Fuzzy ARTMAP Neural Networks [15] or Support Vector Machines (SVM) [16]. Apart, linear pattern recognition methods namely Principal Component Analysis (PCA), the K-Nearest Neighbor (KNN) and Linear Discriminant Analysis (LDA) have been commonly used in ET systems [17].

A key principle in designing ETs is the selection of sensors forming the array and their ability to provide a useful chemical fingerprint from the samples. This potential might be increased if using sensors with different measuring principles (e.g. potentiometry, voltammetry, impedance, etc). However, the use of multiple source sensing demands more effective data processing tools. Thus, sensor data fusion is a strategy that combines and analyzes the multisource data to take advantage of their characteristics and that improves the representation of information to build a prediction or decision model [18]. Data fusion is therefore a tool that permits to make compatible measurements originated from very different nature. The research of data fusion in chemistry is in a development stage, although there are few reports describing its benefits in this field [19].

The aim of the present work is to use a hybrid ET based on potentiometric and voltammetric sensors, furnished with a data fusion processing tool, to attempt the classification of beers. Considered beer samples for this study were selected taking into account three main classes: IPA, Lager and Stout. The electrochemical sensor array was composed by fifteen solid-state potentiometric sensors employing polymeric membranes with common cations and anions ion formulations and six voltammetric bulk-modified sensors using metallic nanoparticles and conducting polymers, in order to obtain differentiate catalytic responses. Electrochemical responses obtained from potentiometric measures and Cyclic Voltammetry (CV) were used as departure information; data processing stages including feature extraction, Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), were used till discrimination of the different types of beer was possible.

2. Experimental

2.1 Study case

Samples under study were acquired at a craft brewery (Art Cervecers Company, Canovelles, Barcelona, Spain) and at a local supermarket. A total of 25 samples of beer from different brands and varieties were selected. Samples were chosen according with the mentioned types of beer (IPA, Lager and Stout) and also taking into account its production method (craft or commercial), in order to have a diversified sample set. In this way, the formed set included 17 Lager, 3 IPA and 5 Stout beers. Table 1 summarizes detailed information about the brands and beer types used.

2.2 Sensor preparation

Due to the complexity of the case, samples were independently processed using two different arrays of electrochemical sensors (i.e. potentiometric and voltammetric) and their corresponding techniques.

The 15 potentiometric sensors used were all solid-state ion-selective electrodes (ISEs) with a solid contact from a conductive epoxy composite. This configuration has been extensively used in our laboratories [20]. The PVC membranes were formed by solvent casting the sensor cocktail dissolved in THF. The formulation of the different membranes used (components supplied by Fluka, Switzerland) is outlined in Table 2.

The voltammetric sensor array was formed by 6 graphite-epoxy voltammetric sensors made with different modifiers added to the bulk mixture, selected according to previous experience in our laboratory [21]. Five of them were modified by adding components as nanoparticles of copper and platinum, conducting polymer in powder like polypyrrole, phtalocyanine and Glucose Oxidase (Sigma-Aldrich, St. Louis, USA) – one component per sensor (Table 2). The last sensor (GEC) did not incorporate any. Standard graphite-epoxy composites were prepared using 50-µm particle size graphite powder (BDH laboratory Supplies, UK) and Epotek H77 resin and hardener (both from Epoxy Technology, USA). Surface of the electrodes in contact with the samples was 28 mm^2.

2.3 Electrochemical measurements

Each beer bottle was opened just before starting the measurement, thus to avoid oxidation and loss of CO_2 in the sample; and to ensure there is no history effect. Also, each beer sample was diluted by mixing it with distilled water in a ratio 30:70 of beer and water respectively, in order to reduce matrix effect and to minimize the apparition of bubbles on the electrode surface. Potentiometric and voltammetric readings were carried out immediately after this sample dilution.

Potentiometric measurements were performed using a laboratory constructed data-acquisition system, consisting of 32 input channels implemented with amplifier-follower circuits employing operational amplifiers (TL071, Texas Instruments), which adapt the impedances of each sensor. Measurements were unipolar, with the reference electrode connected to ground, and were referred to an Orion 90-02-00 double junction Ag/AgCl reference electrode. Each channel was noise-shielded with its signal guard. The outputs of each amplifier were filtered using a passive low-pass filter and connected to an A/D conversion card (Advantech PC-Lab 813, Taiwan) installed into a Pentium PC. The readings were obtained employing custom designed software programmed with QuickBASIC 4.5 (Microsoft). Readings with the potentiometric electronic tongue were taken 5 min after dipping the sensors in the sample, once the emf values were stabilized.

The voltammetric measurement cell was formed by the 6-sensor voltammetric array, a reference double junction Ag/AgCl electrode (Thermo Orion 900200) plus a commercial platinum counter electrode (Model 52–67, Crison Instruments). Using the same diluted beer samples, CV measurements were done using a 6-channel AUTOLAB PGSTAT20 (Ecochemie, Netherlands). Cyclic voltammograms were carried out at room temperature (25ºC) under quiescent condition. Potential was cycled between -1.0 V and 1.2 V vs Ag/AgCl, with a scan rate of 100 $mV \cdot s^{-1}$ and a step potential of 9 mV. All experiments were done without any physical regeneration of electrode surfaces. Instead, and to prevent the accumulative effect of impurities on electrode surfaces, an electrochemical cleaning stage was done between samples applying a conditioning potential of +1.4 V for 40 s after each measurement, in a separate cell containing 50 ml of distilled water.

2.4 Feature extraction

Feature extraction is an important stage in many signal treatment procedures. In the case of potentiometric ETs, this stage is not employed if departure information is formed by steady-state potentials coming from ion-selective electrodes. Nevertheless, this situation is different for voltammetric ETs, given the nature of their signals involves the recording of currents generated in the solutions under study related to an applied potential, i.e. one vector is generated per each sensor. Voltammetric signals contain hundreds of measures and usually overlapping regions with non-stationary characteristics. Thus, their high complexity should be reduced in order to avoid redundancies in the information and achieve proper mathematical models with correct generalization ability [9, 17]. In other words, by retrieving particular information from the original voltammogram, extracted features might be obtained that can confer more selectivity to voltammetric sensors. On the other hand, it is not uncommon that the number of original features may exceed the number of measurements available to train the pattern recognition methods; this is a dangerous situation because there is a high risk of overfitting. In this sense, the aim of feature extraction stage in a data fusion procedure is not only focused to making compatible the nature of the two distinct signals for each sensor (discrete values from the potentiometric ET and vectors from the voltammetric ET) and to facilitating the computation, but also in retaining the relevant information from each signal type. To achieve this goal, seven representative features from the cyclic voltammogram of each sensor on the array were extracted as can be seen in Figure 1. The complete list of these features are: (1) I_{mean} [-1, -0.50]: the average value of the anodic current measured in the potential range [-1 V, -0.50 V]; (2) I_{mean} [-0.75, -0.50]: the average value of the anodic current measured in the potential range [-0.75 V, -0.50 V]; (3) I_{mean} [-0.25, 0]: the average value of the anodic current measured in the potential range [-0.25 V, 0 V]; (4) I_{mean} [0.25, 0.50]: the average value of the anodic current measured in the potential range [0.25 V, 0.50 V]; (5) I_{mean} [0.75, 1]: the average value of the anodic current measured in the potential range [0.75 V, 1 V]; (6) $\Delta I(-0.75\ V) = I_{max}(-0.75\ V) - I_{min}(-0.75\ V)$: the current change calculated as the difference between the cathodic and anodic values in the specific potential of -0.75 V and (7) $\Delta I(1\ V) = I_{max}(1\ V) - I_{min}(1\ V)$: the current change calculated as the difference between the cathodic and anodic values in the specific potential of 1 V.

These 7 features were extracted from the voltammograms of each sensor. Since there were 6 voltammetric sensors within the array, each measurement from the voltammetric ET was described by 42 variables. Whereas 15 potentiometric sensors were used to characterize beer samples, each potentiometric measurement was described by 15 variables. The data fusion matrix considered had 25 rows (i.e. samples) and 57 columns (i.e. variables). In order to reduce the variability associated to possible fluctuations in both electronic tongue signals, and to minimize other sources of variance also affecting the total signal of the voltammetric and potentiometric sensors, normalized signals rather than absolute signals were used to construct PCA and LDA models. For variable normalization, each variable value was divided by the square of the maximum value in the same column. Although this procedure could assure obtaining centered values, redundant information it is not avoided. For final application, it is advisable to choose the most relevant features from the extracted ones using some feature selection process.

2.5 Linear discriminant analysis

Linear discriminant analysis (LDA) is one of the most used classification algorithms. It has been widely used and proven successfully in many applications of electronic nose [22, 23] and electronic tongue [24, 25]. In fact, using this method, data are separated in *k a priori* defined classes by using linear combinations of the variables in each group to create *k*-1 new discriminant axis. LDA is widely recognized as an excellent tool to obtain vectors showing the maximal resolution between a set of previously defined categories. In LDA, vectors minimizing the Wilks' lambda (λ_ω) are obtained [26]. This parameter is calculated as the sum of squares of the distances between points belonging to the same category divided by the total sum of squares. Values of λ_ω approaching zero are obtained with well-resolved categories, whereas overlapped categories approach a λ_ω of one. Hence, LDA tries to find a linear discriminant function along which the classes are best separated. For theoretical background and details of the algorithm, reader is referred to [27]. Performance of the final LDA model was evaluated using *leave-one-out* cross-validation method.

2.6 Feature selection

Feature selection is motivated by the need of using the best set of input variables which will allow the pattern recognition method to achieve the correct *a posteriori* classification of the data in their *a priori* groups [28, 29]. The selection of the features to be included in the LDA models was performed using the SPSS stepwise algorithm v.11.0 (SPSS Inc., Chicago, IL, USA). According to this algorithm, a feature is selected when the reduction of λ_ω produced after its inclusion in the model exceeds F_{in}, the incorporation threshold of a test of comparison of variances or Fisher's F-test. However, the incorporation of a new feature modifies the significance of those features which are already present in the model. For this reason, after the inclusion of a new feature, a rejection threshold, F_{out}, is used to decide if one of the other features should be removed from the model. When all the features in the model meet the criterion to be kept and none of the other features meet the criterion to enter, the stepwise selection process is stopped.

Then, after proper selection of features to be included in the classification model, LDA model is built and its accuracy is evaluated by means of leave-one-out cross validation method. At this point, based on obtained predictive capabilities and previous experience, F_{in} and F_{out} values are modified so that final performance of the model is optimized (maximum classification success rate).

2.7 Data Processing

Extracting the seven aforementioned features from each voltammogram and pre-processing the resulting data matrix were an automated process via written-in-house MATLAB® v. 2012a routines (Math Works, Inc., Natick, MA). The Linear Discriminant Analysis (LDA from SPSS software) was applied on data grouping features of all the sensors and all the measurements.

3. Results and discussion

The data obtained by the process mentioned above was subjected to different pattern recognition techniques such as PCA and LDA. First, resolution of the case was attempted using potentiometric sensors only, then voltammetric sensors alone and finally with the hybrid ET approach.

3.1 Use of Potentiometric ET

Radar plot was built in order to observe wether any patterns (i.e. fingerprints) were present in beer samples. Fig. 2A shows a representative case. This helped visualizing some ionic characteristics of the beers, although no clear pattern variation existed between IPA, Lager and Stout types. As it can be seen in Fig. 2A, differentiated response was obtained for the different type of sensors and beers. It should be noticed the differences obtained especially for Na^+ sensor, also in the case of pH and Ca^{2+} ISEs. Other sensors like Cl^-, NO_3^- or NH_4^+ displayed distinct responses for at least two beer types, even clear differences were not as noticeable. Other sensors like K^+ ISE or some with generic response to cations did not present such distinguishable signals, probably due to their comparable content in beers.

In this sense, the importance of those sensors could be expected given there are some ions in water (i.e. carbonate, calcium, magnesium, sodium, chloride and sulphate plus its pH) whose concentration can determine the type of beer obtained and to which much attention is paid during brewery [3]. Nevertheless, it should be noticed that the use of an array of cross-sensitive sensors with slightly different sensitivities (those non autocorrelated) forms an overdetermined system which would permit the simultaneous determination of a number of analytes in a complex mixture, although not clearly distinguished responses were individually obtained [7].

Before performing PCA using the potentiometric electronic tongue measurements, the data matrix was mean-centered. PCA is a powerful linear unsupervised pattern recognition method that reduces the dimensionality of a multivariate problem and helps to visualize the different categories of taste and odor profiles [15, 21, 30] by highlighting similarities and differences between sample clusters. The results showed that the total variance of the first three principal components (PC1, PC2 and PC3) was 86.48%. Based on PCA, similarities and differences between Lager, Stout and IPA beers were not easy to find. The three kinds of beers cannot be accurately identified at all; the reason for this may be that the relationship among the used potentiometric sensors does not express a cross-sensitivity to the studied beers.

To estimate the success rate in sample identification, a LDA classifier using *leave-one-out* cross-validation was implemented, given the small sample set available. LDA was trained 25 times using 24 training samples and validated using the sample that had been left out. In this re-sampling approach all measurements available act as validation sample once. Performance of the model, estimated as the average performance over the n tests, can be summarized in that only 48% of the 25 samples from the three different beer types were correctly classified. Hence, the employed electronic tongue using such potentiometric sensors coupled to LDA model was not able to demonstrate the proper ability to differentiate between beer samples.

3.2 Use of Voltammetric ET

It is observed that the different voltammetric electrodes used (e.g. Figure 2B-2G) displayed differentiated signals for each kind of beer. As can be seen, different response profiles were obtained depending on the nature of the modifier employed (not only in the voltammogram shape, but also in the obtained currents); thus different fingerprints could be extracted with each type of sensor. Although similarities were observed, in general, some differentiated responses could be seen at both extreme potentials in the oxidation and reduction zone.

A feature extraction-pattern recognition strategy was then chosen in order to reduce the huge amount of data contained in the whole voltammetric data set and to achieve correct recognition of the beer type. In this way, 7 different features representing major differences observed in those regions were selected from each voltammogram; these, from an electrochemical point of view, could be taken as indicator of the compounds that can be easily reduced such as flavonols or oxidized such as saccharides. A mean centering pre-processing technique was applied to the voltammetric data matrix. As first step, PCA was applied to the dataset obtained with the 42 extracted variables (6 sensors x 7 features). Results show that the first three principal components captured 81.7% of data variance, while overlapping between the beer classes was observed.

As before, LDA model was performed on the voltammetric electronic tongue data to estimate the classification success rate in sample identification using *leave-one-out* cross-validation approach. A very low success rate in classification was obtained, with only seven samples classified correctly among 25 beer samples leading to 40% of classification success rate. Therefore, the used electronic tongue with the employed voltammetric sensors, and the information extracted coupled to LDA approach, was also not able to distinguish between the three kinds of beer.

3.3 Hybrid ET

Before performing pattern recognition with the hybrid ET, we attempted a variable selection using LDA stepwise technique separately on each data set in order to discard features that may disturb the classification task. Unfortunately, a clear area of overlapping still exists for the potentiometric ET measurements. Moreover, variable selection was quite suitable for voltammetric ET in terms of LDA classification success rate which increased significantly from 40% to 84%. However, this improvement was not sufficient to yield a good classification of the beers. In an attempt to further enhance this finding, we suggest to carry out data fusion technique.

In order to perform the fusion of data from the two ETs, a low level of abstraction was chosen [31, 32]. In our case, this means that the voltammetric and potentiometric ETs data sets are combined together to make a single data matrix, with number of rows equal to the number of samples and number of columns equal to the number of features extracted from both voltammetric and potentiometric channels. The low level of abstraction for the feature selection is in connection with the fact of the different sensors signal dimensionality [31]. Nevertheless, merging measurements from the two sensor types could potentially provide increased redundancy connected with identification ability. The idea behind the data fusion approach was to observe the classification performance when using single sensors from the two sensor families. Besides, it is obvious that the number of features from the two sources would be similar when low-level abstraction data fusion is performed. If the number of variables from one instrument is significantly larger, they could dominate the fused data set [32]. Hence, in the low level fusion approach, the data set obtained from each sensor family (i.e. voltammetric and potentiometric) were merged in a single matrix of 25 samples by 57 features (the 42 previous features from the voltammetric ET plus the 15 emf potentials from the potentiometric sensors used). Afterwards, stepwise LDA was applied to the merged set to select the features with highest discriminating power while removing the ones that did not contribute to the classification. This extra-step, not performed in previous models, seeks to avoid irrelevant or redundant features from the low-level abstraction data fusion set. In this manner, the stepwise technique used the Wilk's lambda method with F_{in}=1.7 for a feature to be added and F_{out}=0.6 for a feature to be deleted from the model. These threshold values were chosen as a balance between keeping the number of selected features small and obtaining high classification success rate by LDA. For a given combination of F_{in} and F_{out} values, the algorithm used a leave-one-out resampling method within the training subset to select features and estimate the weights for the LDA classifier. The % of correct classification was used as the figure of merit for optimizing values of F_{in} and F_{out}. Out of the whole set of features only 15 features from the initial data set (14 from voltammetric data set and 1 from potentiometric data set) were finally required to achieve the best classification ability.

Despite the efforts made to keep a similar number of features for both families (i.e. the use of a low-level abstraction for feature selection), a higher proportion of voltammetric features were finally taken; this may be explained by the higher dimensionality of voltammetric sensor data (490 current values$\cdot$sample$^{-1}\cdot$sensor^{-1}, i.e. a total of 2940 data points$\cdot$sample^{-1}) when compared to potentiometric sensors (1 potential value$\cdot$sample$^{-1}\cdot$sensor^{-1}, i.e. a total of 15 data points$\cdot$sample^{-1}). Besides, results of this feature selection stage suggest that slightly richer information related to beer composition (e.g. polyphenols, flavonols, saccharides, etc.) can be deduced from the voltammetric array, but still not enough to achieve the best classification. In this manner, by using the hybrid ET, complementary information may be obtained; that is, potentiometric sensors provided information related to ionic composition while amperometric sensors provided information more related to electroactive compounds present. Thus, when joining both data sets, complete information was obtained that allowed the correct discrimination of beer samples.

The resulting data matrix (25 samples x 15 features) was mean-centered before the PCA was performed. The score plot of the first three principal components for the three kinds of beers is shown in Figure 3. As can be appreciated, samples of the three different classes are well separated by the first three components (PC1, PC2 and PC3), which cover the 82.44% of the total variance. Because of this satisfactory result, it can be deduced that the combined data set contains now enough information and displays a high cross-sensitivity to the beer samples.

Linear discriminant analysis (LDA) was conducted on the merged data set as classification tool, at a 5% significance level. Initially, the model was built using all the available samples as training set, in order to check the classification capability of LDA. It was found that all the samples were correctly classified in their origin group. LDA results are shown in Figure 4. The two first factors accounted for ca. 100 % of the variance in the data. Plots of the first two discriminant functions show high separation of the three groups. Function 1 seemed to discriminate mostly between Stout beer from Lager and IPA beers. In the vertical direction (Function 2) there was an evident discrimination between Lager from IPA and Lager from Stout. The classification results of LDA leave-one-out cross-validation approach, in terms of the confusion matrix, are reported in Table 3. Rows indicate expected beers class and columns predicted ones. As it can be noticed in this table, only one beer sample was misclassified: specifically, one sample belonging to Stout was misclassified as IPA class. Hence, the classification success rate of the three kinds of beer reaches 96% of accuracy. The efficiency of the classification obtained was also evaluated according to its sensitivity, i.e. the percentage of objects of each class identified by the classifier model, and to its specificity, the percentage of objects from different classes correctly rejected by the classifier model. The value of sensitivity, averaged for the three classes considered was, 93.3%, and that of specificity was 98.5%.

Finally, to verify the significance of the feature from the potentiometric data on the final performance of the LDA treatment, we applied LDA on the data set formed with only the 14 features selected from the voltammetric sensors. As a result, the classification rate was demoted to 84% of correct classification. This confirms best performance of LDA (96%) obtained when all LDA stepwise selected features were taken: 14 selected features from the voltammetric data set and one selected feature from the potentiometric data set.

4. Conclusions

A hybrid electronic tongue based on the combination of potentiometric and voltammetric sensors was developed in order to create a tool capable of distinguishing between different kinds of beers. The sensors array coupled with feature extraction and pattern recognition methods, namely Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), were trained to classify the data clusters related to different beer types. PCA was used to visualize the different categories of taste profiles and LDA with leave-one-out cross-validation approach permitted the qualitative classification. According to the LDA model, 96% of beer samples were correctly classified. Moreover, the performance of hybrid electronic tongue systems by exploiting the new approach of data fusion of different sensor families, in comparison of simple electronic tongue, was illustrated.

Acknowledgments

Financial support for this work was provided by S*panish Ministry of Science and Innovation* trough the projects CTQ2010-17099, AECID A/023678/09, program ICREA Academia and by the *Mexican National Council of Science and Technology* CONACYT (Mexico) through the project 154243. A. Mimendia thanks Universitat Autònoma de Barcelona (UAB) for a PIF studentship, X.Cetó thanks the support of Dept. d'Innovació, Universitats i Empresa de la Generalitat de Catalunya for the predoctoral grant. The authors wish to thank Francisco Sanchez and Art Cervecers Company - Cervesa Artesanal (Canovelles, Barcelona, Spain) for providing samples to carry out this work.

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Biographies

Juan Manuel Gutierrez received his PhD in Electrical Engineering from the CINVESTAV, Mexico in 2008 and then he did a postdoctoral research on electronic tongues at the Sensors & Biosensors Group of of the Autonomous University of Barcelona, Spain. He is currently a Research Professor at the Bioelectronics Section of the Department of Electrical Engineering in CINVESTAV, Mexico City. His research interests are focused on the developing of Bio-inspired Systems employing portable instrumentation and advanced data processing tools.

Zouhair Haddi is currently a PhD student at the Laboratory of Electronics, Automatic and Biotechnology, University Moulay Ismaïl, Faculty of Sciences in Meknes, Morocco. His research interests include Pattern recognition methods, sensors networks and electronic noses for food analysis.

Aziz Amari received his PhD in electronics and artificial intelligence from the University Moulay Ismaïl (Meknes, Morocco) in 2009. He is currently an assistant professor at the University Mohamed V, Faculty of Sciences (Rabat, Morocco). He is member of the Laboratory of Electronics, Automatic and Biotechnology at the University Moulay Ismaïl (Meknes, Morocco). His research interests include chemical sensors, artificial neural networks, features selection, food analysis, aroma extraction techniques and pattern recognition methods applied to electronic noses and electronic tongues, instrumentation and measurement systems.

Benachir Bouchikhi received the Ph.D. degree from the Université de droit, d'Economie et des Sciences d'Aix Marseille III, in 1982. Benachir Bouchikhi was awarded a Doctor of Sciences degree in 1988 from the University of Nancy I. Dr. Bouchikhi got a position of titular professor at the University of Moulay Ismaïl, Faculty of Sciences in Meknes, Morocco since 1993. He is the director of the Laboratory of Electronics, Automatic and Biotechnology. His current research interests involve metal oxide sensors for electronic noses and their application to food analysis and the control of the climate and drip fertirrigation under greenhouse. He is author and co-author of over 44 papers, published on international journals. During the last 10 years he has coordinated a dozen national and international projects, in the area of food safety, the control of the climate and drip fertirrigation under greenhouse. He is a member of the Editorial Board of Journal of Sensors.

Aitor Mimendia completed his PhD in Environmental Sciences from the Autonomous University of Barcelona (2012). His research topics deal with the application of electronic tongues and flow systems to environmental applications.

Xavier Cetó received the MSc degree in Chemistry in 2009 from the Universtitat Autònoma de Barcelona, where he is at the moment finishing his PhD in analytical chemistry. His main research topics deal with the application of Electronic Tongues and chemometric tools for data analysis, mainly employing voltammetric sensors and biosensors, albeit also potentiometric ones.

Manel del Valle received his PhD in chemistry in 1992 from the Universtitat Autònoma de Barcelona, where he got a position of associate professor in analytical chemistry. He is a member of the Sensors & Biosensors Group where he is a specialist for instrumentation and electrochemical sensors. He has initiated there the research lines of sensor arrays and electronic tongues. Other interests of his work are the use of impedance measurements for sensor development, biosensors and the design of automated flow systems.

Table 1. Beer samples under study.

Brand	Beer type
AK Damm	Lager
Amstel	Lager
Bock Damm	Stout
Budweiser	Lager
Carlsberg	Lager
Cervesa Montseny Lupulus	IPA
Cervesa Montseny Malta	Lager
Cervesa Montseny Negra	Stout
Cervesa Pilsen Bonpreu	Lager
Estrella Damm	Lager
Flama Art 2A	IPA
Flama Art 2B	IPA
Fosca Art 2A	Stout
Fosca Art 2B	Stout
Glimbergen	Lager
Guinness	Stout
Heineken	Lager
Moritz	Lager
Orus Art 2B	Lager
Orus Art 2C	Lager
Orus Art Lager 2A	Lager
Pilsner Urquell	Lager
Saaz	Lager
San Miguel	Lager
Voll Damm	Lager

Table 2. Composition of the voltammetric and potentiometric sensors used in the study.

Potentiometric sensors

Sensor	PVC(%)	Plasticizer (%)	Ionophore (%)	Reference
Na$^+$	22	NPOE (70)	CMDMM (6)*	[33]
K$^+$	30	DOS (66)	Valinomycin (3)*	[33]
NH$_4^+$	33	BPA (66)	Nonactin (1)	[33]
Ca^{2+} I	32.9	o-NPOE (66)	Tetronasin (1.0)*	[34]
Ca^{2+} II	33.3	o-NPOE (65.2)	ETH1001 (1.0)*	[34]
Ca^{2+} III	30	DOPP (65)	BBTP (5.0)	[34]
Mg^{2+}	32.7	o-NPOE(65.6)	ETH4030(1.0)*	[34]
Ba^{2+}	27	DBS (70)	Monensin (3.0)	[34]
H$^+$	32.8	DOS (65.6)	tri-N-dodecylamine (1)	[35]
Generic Cations I	29	DOS (67)	Dibenzo-18-crown-6 (4)	[35]
Generic Cations II	27	DBS (70)	Lasalocide (3)	[35]
NO$_3^-$	30	DBP (67)	TOAN (3.0)	[36]
Cl$^-$	28.3	o-NPOE (70)	TDMAC (0.3)	[36]
SO$_4^{2-}$	33	o-NPOE(66)	1,3[bis(3-phenylthioureidomethyl)]benzene(1)	[36]
Generic Anions	29	DBP(65)	Tetraoctylammonium bromide(4)	[36]

Amperometric sensors

Sensor	Modifier	Reference
GEC	Graphite-epoxy composite	[21]
Ph	Phthalocyanine	
Pt	Platinum nanoparticles	
Cu	Copper nanoparticles	
Ppy	Polypyrrole	
GOX	Glucose Oxidase biosensor	

* The formulation includes potassium tetrakis(4-chlorophenyl)-borate as additive.

Table 3. Confusion matrix for LDA using leave-one-out cross-validation approach in the classification of beer samples

Expected	**Predicted**		
	Lager	Stout	IPA
Lager	**17**	0	0
Stout	0	**4**	1
IPA	0	0	**3**

Figure captions

Figure 1. Features extracted from voltammograms in the experiments with voltammetric sensors.

Figure 2. Average responses for beer classes obtained with the sensor array, both potentiometric (radar plot) and voltammetric (cyclic voltammograms obtained for each sensor). (A) All potentiometric sensors, (B) Graphite-epoxy composite, (C) Phtalocyanine sensor, (D) Platinum nano-particle sensor and (E) Copper nano-particle sensor, (F) Polypyrrole sensor and (G) Glucose Oxidase biosensor.

Figure 3. 3D-Score plot of PCA performed from data fusion of voltammetric and potentiometric sensors array. A total of 25 samples were analyzed. As can be observed, a correct discrimination is obtained for the different types of beers: (1) Lager, (2) Stout and (3) IPA.

Figure 4. Projections of beer samples in the space defined by the LDA Discriminant Function (DF) 1 and 2. The centroid on each class is indicated as the asterisk.

Figure 1

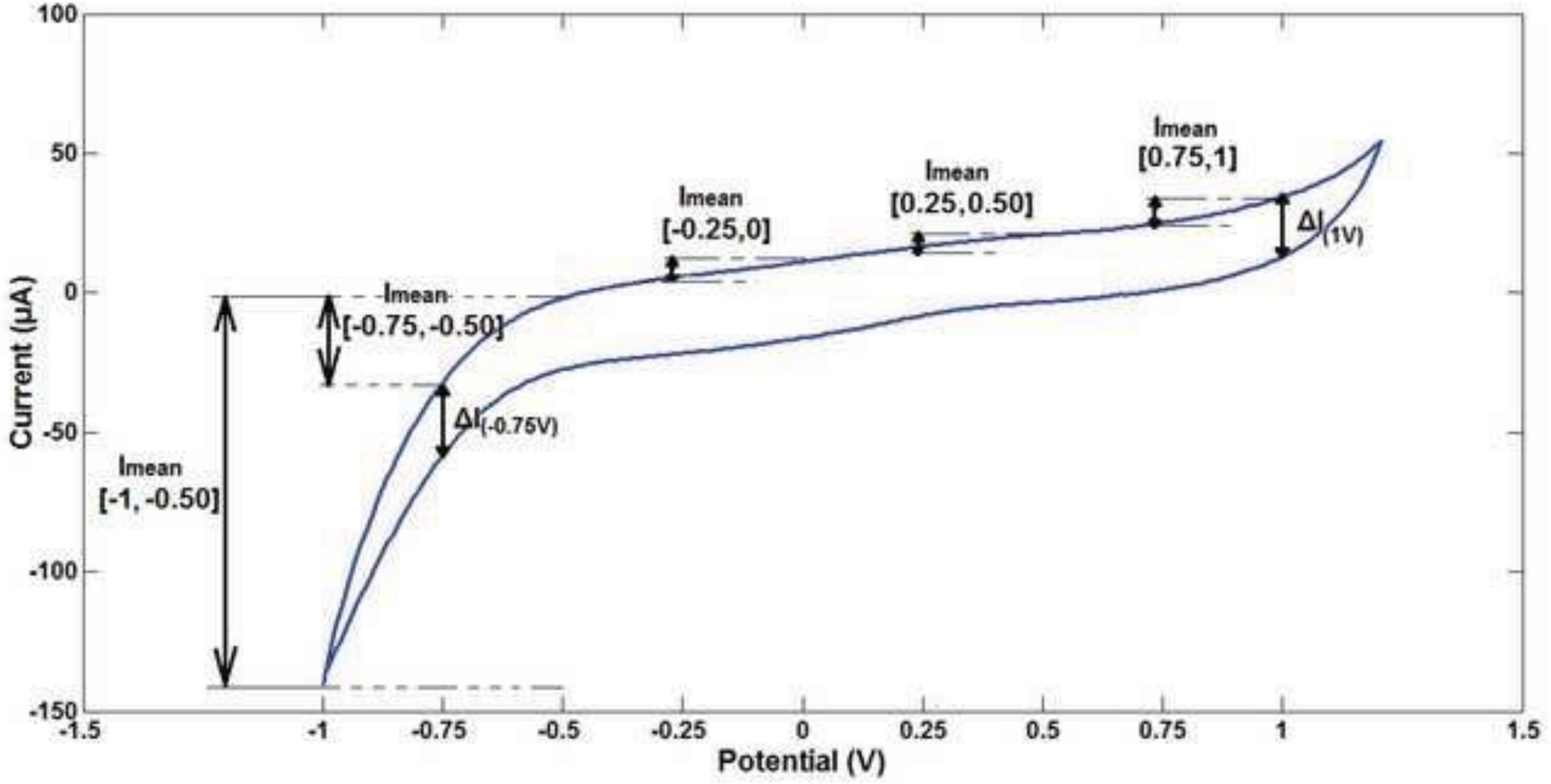
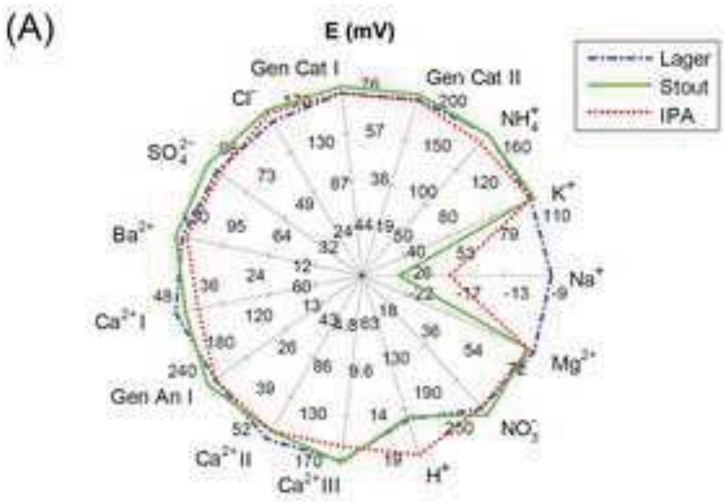

Current (µA)
100
50
0
-50
-100
-150
Potential (V)
-1.5
-1
-0.75
-0.5
-0.25
0
0.25
0.5
0.75
1
1.5
Imean [-1, -0.50]
Imean [-0.75, -0.50]
ΔI(-0.75V)
Imean [-0.25,0]
Imean [0.25,0.50]
Imean [0.75,1]
ΔI(1V)

Figure 2

Potentiometric sensors



Amperometric sensors

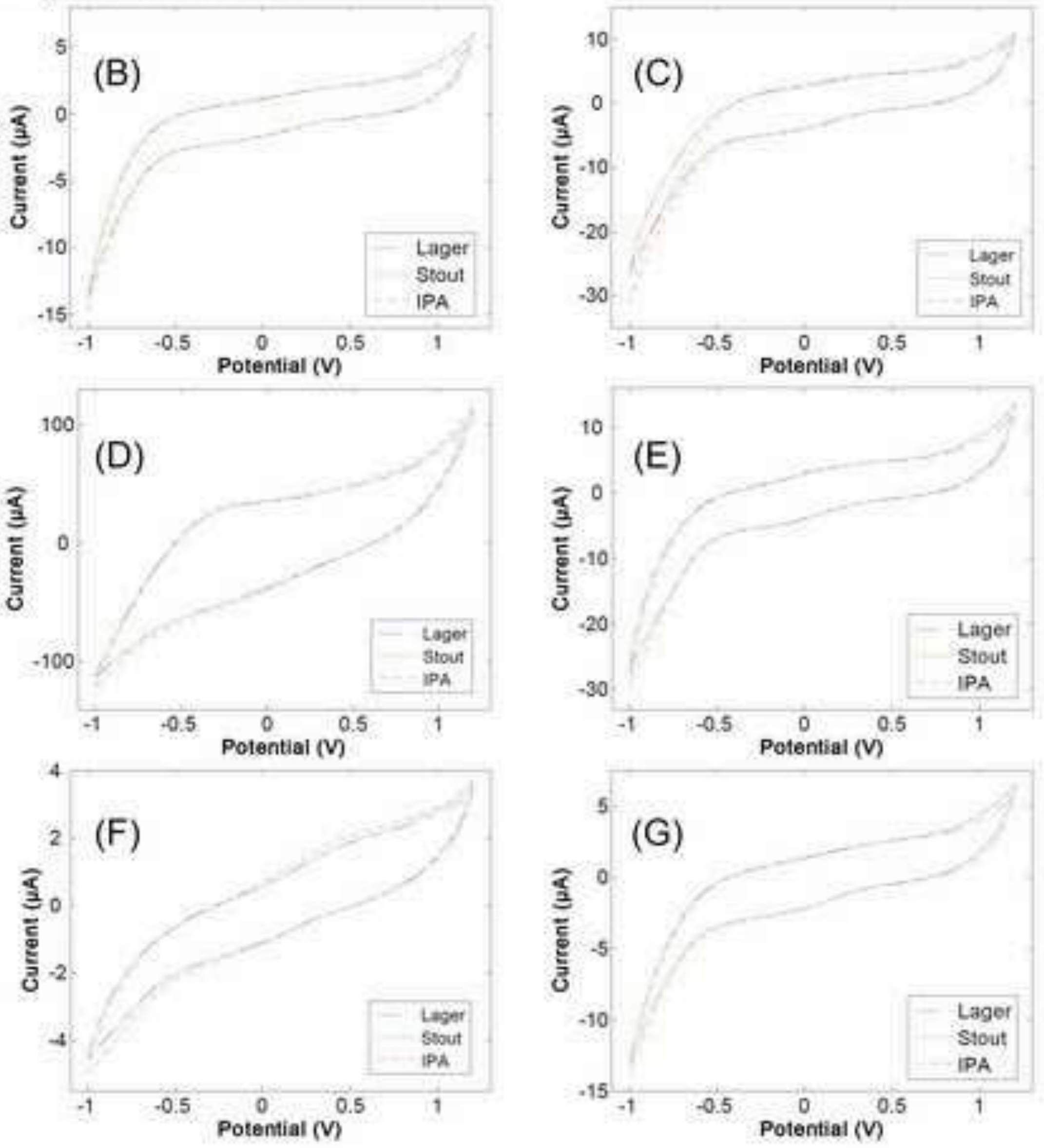


Figure 3

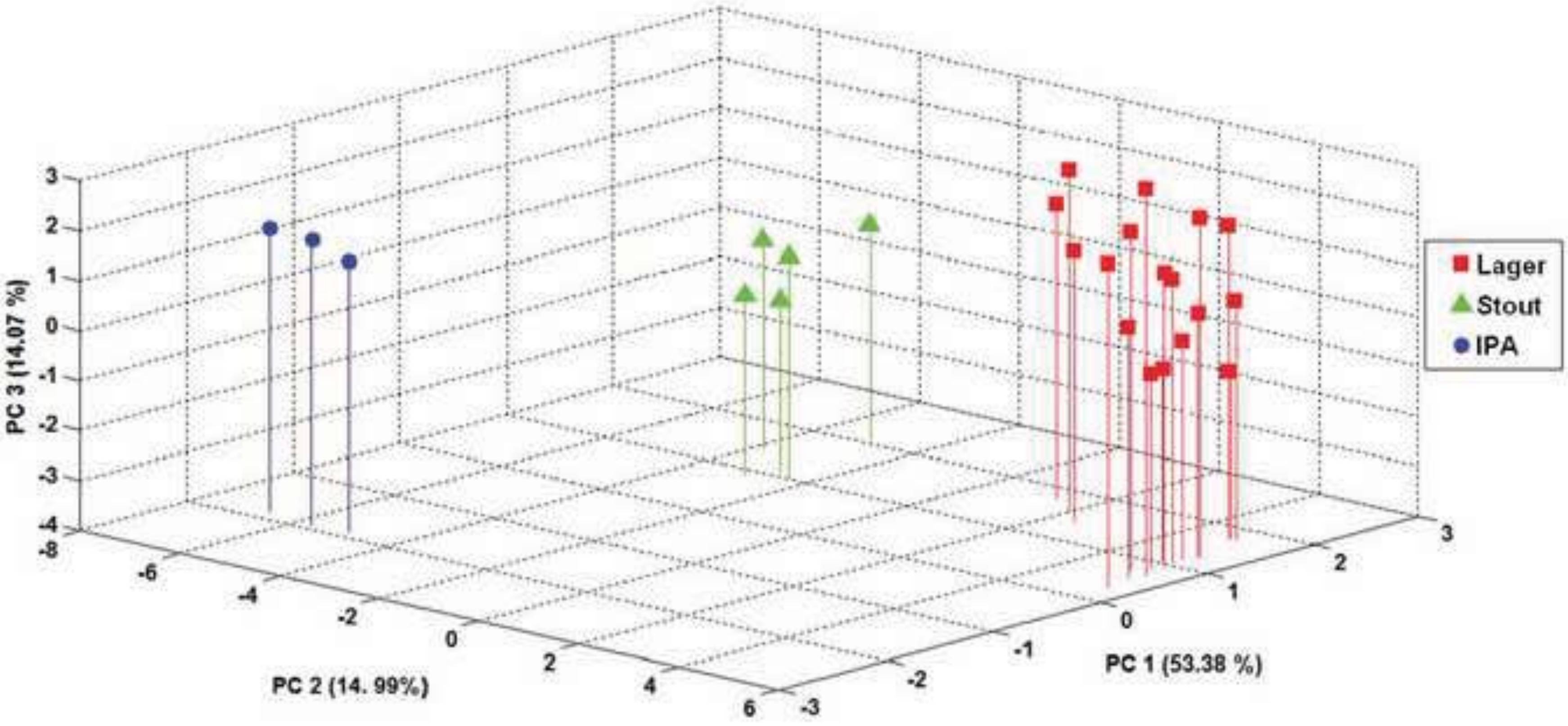

PC 3 (14.07 %)
3
2
1
0
-1
-2
-3
-4
-8
-6
-4
-2
0
2
4
6
PC 2 (14. 99%)
-3
-2
-1
0
1
2
3
PC 1 (53.38 %)
🟥 Lager
▲ Stout
● IPA

Figure 4