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Beer Classification by means of a Potentiometric Electronic Tongue

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Abstract

In this work, an Electronic Tongue (ET) system based on an array of potentiometric ion-selective electrodes (ISEs) is presented for the discrimination of different commercial beer types is presented. The array was formed by 21 ISEs combining both cationic and anionic sensors with others with generic response. For this purpose beer samples were analyzed with the ET without any pretreatment rather than the smooth agitation of the samples with a magnetic stirrer in order to reduce the foaming of samples, which could interfere into the measurements. Then, the obtained responses were evaluated using two different pattern recognition methods, Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) in order to achieve the correct recognition of samples variety. In the case of LDA, a stepwise inclusion method for variable selection based on Mahalanobis distance criteria was used to select the most discriminating variables. Finally, the results showed that the use of supervised pattern recognition methods such as LDA is a good alternative for the resolution of complex identification situations. In addition, in order to show a quantitative application, alcohol content was predicted from the array data employing an Artificial Neural Network model.

Keywords: Electronic Tongue; Linear Discriminant Analysis; potentiometric sensors; classification; beer; alcohol by volume

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1. Introduction

Beer is the world's most widely consumed and probably oldest of alcoholic beverages; it is the third most popular drink overall, after water and tea (Nelson, 2008). It is produced by the brewing and fermentation of starches, mainly derived from cereal grains -most commonly malted barley, although wheat, maize (corn), and rice are maybe used. Most beer is flavoured with hops, which add bitterness and act as a natural preservative, though other flavourings such as fruits or herbs may occasionally be included. Along all the constituents of beer, one key parameter (or even the most important) is the water composition. Inasmuch the first step in every brewery is the preparation of water, which needs to be pretreated, which in turn will help to improve beer flavour and create its unique style.

While there are many types of brewed beer, their basics are shared across national and cultural boundaries. But there is an effort to differentiate and categorize beers by various factors such as colour, flavour, strength, ingredients, production method, fermentation method, recipe, history or origin. In this sense, there are certain ions in water whose concentration can determine the type of beer obtained and to which much attention is paid (Snyder, 1997).

The first one is the pH which can mainly be modified by three different compounds: bicarbonate (HCO_3^-, usually referred to it as *temporal hardness*), calcium or magnesium salts, whose concentrations are related to pH through Kolbach's formula (Fix, 1999). The addition of bicarbonate increases the pH of the water, while the salts of the other two decrease it, through separation of the carbonates. Apart from the pH, there are six additional ions whose concentrations must be taken into account and play an important role in beer flavour. Carbonate and bicarbonate, which are expressed as *total alkalinity,* are considered as the most crucial factor of water given they will affect the maceration process; e.g. its high level in Munich waters is the responsible of the mildness of Münchner dunkel beers. Sodium ion contributes to beer body and character, while chloride highlights malt sweetness, although high levels of this two will leave a seawater taste. Sulphate is the one that most influences the amount of hop added, given it enhances its bitterness; so much so that its concentration is very important and delimited depending the type of beer that must be obtained. Calcium is the most important ion in the *permanent hardness* of the water for beer brewing, and contributes to the adjustment of the pH. Finally, magnesium is mostly considered as a nutrient for the yeast.

Hence, given the importance of ionic concentration of water, measuring these ions concentration in beer samples would be a good way to develop a new classification system. Unfortunately, there are few optimally operating chemical sensors that may function without any interference or matrix effect.

In this sense, over the past decades a new concept in the field of sensors has appeared to solve these problems: Electronic Tongues (ETs) (del Valle, 2010). These systems consist in the coupling of an array of non-specific sensors plus a chemometric processing tool able to interpret and extract meaningful data from the complex readings, relating them with their analytical meaning (Vlasov, Legin, Rudnitskaya, Di Natale, & D'Amico, 2005). The idea behind this concept is to use an appropriate sensor array with some cross-sensitivity between them, which allows the simultaneous determination of a large number of species, while the chemometric treatment of the data allows the resolution of the interferences, drifts or non-linearity obtained with the sensors (Riul Jr, Dantas, Miyazaki, & Oliveira Jr, 2010). Moreover, the data processing stage may offset any matrix or interference effect from the sample itself. Thus, with this methodology, it is possible to achieve a parallel determination of a large number of different species, while any interference effect is solved using these advanced chemometric tools (A. Mimendia, Gutiérrez, Opalski, Ciosek, Wróblewski, & del Valle, 2010).

Although the use of ETs in the analysis of liquids has been widely described over the past decade, there are only some papers directly related to the world of beers and potentiometric sensors. In this fashion, this approach has already been applied in the qualitative analysis of various brands (Ciosek & Wróblewski, 2006), discrimination between different beer kinds (Haddi, Amari, Bouchikhi, Gutiérrez, Cetó, Mimendia, et al., 2011) or even the correlation with some analytical parameters (Rudnitskaya, Polshin, Kirsanov, Lammertyn, Nicolai, Saison, et al., 2009).

The present work reports the application of an ET based on potentiometric sensors to the discrimination of different beer types. The employed sensor array was formed by a total set of 21 PVC membrane ISEs, combining both specific and others with generic response. After sample measurement, the response of the sensors was evaluated by means of two pattern recognition methods, namely Principal Component Analysis (PCA) and Linea Discriminant Analysis (LDA) in order to achieve the correct recognition of sample variety. Finally, prediction of beer alcohol content was also attained by means of an Artificial Neural Network (ANN) in an illustration of the quantitative abilities of ETs.

2. Experimental

2.1 Potentiometric sensor array

The sensors used were all-solid-state ISEs with a solid contact made from a conductive epoxy composite. This is the usual configuration of our laboratories (Gallardo, Alegret, de Roman, Munoz, Hernández, Leija, et al., 2003). The PVC membranes were formed by solvent casting the sensor cocktail dissolved in THF. The formulation of the different membranes used is outlined in Table 1.

<TABLE 1>

As can be observed, the used sensor array was comprised of 20 sensors: two ISEs for ammonium, two for potassium, two for sodium, one for pH, three ISEs for calcium, with different compositions, one for strontium, one for barium, one for nitrate, five of generic response to cations, with two different compositions, and finally two blank electrodes, which were prepared without any ionophore in the membrane. These latter electrodes are inspired in the Taste Sensor concept (Toko, 2000) and will give an idea of how affects the solution to the polymeric membrane. Besides, a metallic electrode was included in order to improve the response to chloride. This chloride sensor was formed by AgCl electrodeposition on a disc of Ag, 5 mm diameter. To obtain a homogenous deposition, 0.1 mA were passed through the electrolysis cell containing 10^{-1} M NaCl for 1 hour (Gutiérrez, Alegret, Caceres, Casadesus, Marfa, & Del Valle, 2008). Thus, the array was comprised of 21 electrodes altogether.

2.2 Reagents and solutions

The ion-selective polyvinyl chloride (PVC) membranes were prepared from high-molecular weight PVC (Fluka, Switzerland), using bis(1-butylpentyl) adipate (BPA), dioctyl sebacate (DOS), o-nitrophenyloctylether (NPOE), dioctyl-phenyl-phosphate (DOPP), dibutyl phtalate (DBP), dibutyl sebacate (DBS) and tributyl phosphate (TBP), all form Fluka, as plasticizers. The recognition elements employed to formulate the potentiometric membranes were: nonactin (nonactin from Streptomyces, Fluka); valinomycin (potassium ionophore I, Fluka); bis[(12-crown-4)methyl]-2-dodecyl-2-methyl malonate (CMDMM, Dojindo, Japan), tridodecylamine (TDDA, hydrogen ionophore I, Fluka), ETH1001 (Fluka), bis(bis(4-1,1,3,3-tetramethylbuthyl)phenyl) phosphate calcium salt (BBTP, Fluka), 4-tert-butylcalix[8]aren octoacetic acid octoethyl ester (TBCOO, Acros), monensin sodium salt (Acros), tetraoctylammonium nitrate (TOAN, Fluka) and the sodium salt of the antibiotic tetronasin (provided by the University of Cambridge(Fonseca, Lopes, Gates, & Staunton, 2004)). In addition, two recognition elements with generic response for cations were used: dibenzo-18-crown-6 (Fluka) and lasalocid A sodium salt (Fluka). The ionic additives potassium tetrakis(4-chlorophenyl) borate (KpClPB, Fluka) and sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl] borate (NaTFPB, Fluka) were used when necessary for a correct potentiometric response. All the components of the membrane were dissolved in tetrahydrofuran (THF, Fluka).

Silver foil (Ag, Aldrich, USA) of 99.9% purity and 0.5 mm thick was used to prepare a Ag/AgCl based sensor for chloride.

The materials used to prepare the solid electrical electrical contact were Araldite M and Hardener HR epoxy resin (both from Vantico, Spain) and graphite powder (50 μm, BDH Laboratory Supplies, UK) for conducting filler. All other reagents used were analytical grade and all solutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA).

2.3 Beer samples

A total set of 51 samples of different brands and varieties were purchased at the local supermarket (Table 2). Initially, in order to minimize the variability coming from the manufacturer, which could be even larger that type itself and to ensure discrimination was due to beer type, all beers considered were selected from the same manufacturer (Damm S.A., Barcelona, Spain): *Voll*, *Estrella*, *Xibeca*, *Bock* (black beer), *Damm Bier* and *AK*. Additionally, 4 supplementary beer samples with some special characteristics were also used for control purposes: *Damm lemon* (shandy, a mixture of lemonade and beer), *San Miquel* (Catalan beer employing a Philippine brewer's yeast), *Heineken* (its brewing process takes around twice as long as a regular beer) and *Budweiser* (American beer). The latter were used as control samples in order to assess model’s predictive capabilities, robustness and evaluate similarities between beer classes. In addition, all the set of samples were acquired in different bottling types (33 cL can, 33 cL bottles and 1 L bottles) and from different batches, in order to provide some variability along same group samples; also, two replicas of each sample were taken and considered as independent samples when performing the measurements. Therefore, the set of samples under study will be formed by 102 samples.

<TABLE 2>

2.4 Apparatus and sample measurement

An Orion 90-02-00 double junction Ag/AgCl reference electrode (Thermo Electron, USA) was employed for the potentiometric measurements. These were performed with the aid of a laboratory constructed data-acquisition system. It consisted of 32 input channels implemented with following circuits employing operational amplifiers (TL071, Texas Instruments, USA), which adapt the impedances of each sensor. Measurements were unipolar, with the reference electrode connected to ground. 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 done employing custom designed software programmed with QuickBASIC 4.5 (Microsoft, USA).

The general procedure for the sample measurement was as follows: each beer samples was placed in a beaker and was smoothly stirred with a magnetic stirrer during 6-7 minutes in order to reduce the foaming of samples, which could interfere the measurements by distorting conductivity. No other pre-treatment or dilution was performed before the analysis. The electrodes were immersed in the beer and the signals were recorded every 30 s over 3 min duration. Two replicas were taken from each beer and considered as independent samples. Besides, all the different beers were assayed in random order to eliminate any history effect.

2.5 Data processing

Chemometric processing was done by specific routines in MATLAB 7.1 (MathWorks, Natick, MA) written by the authors, using Neural Network Toolboxes (v.4.0.6). Sigmaplot 2000 (Systat Software Inc, California, USA) was used for graphic representations of data and results.

3. Results and Discussion

3.1 Potentiometric responses

Average responses of the potentiometric sensor array towards analyzed samples are shown in Figure 1. As can be seen, differentiated response is obtained for each type of sensor and beer. This situation, with marked mix-response and differentiated signals obtained from the different electrodes, is highly desirable for studies with ET systems given very rich data is generated, which is a very useful departure point.

It should be noticed that the response obtained with blank electrodes presents a differentiated response profile for the different types of beer. Also, as expected according to most relevant ions composition of water, ISEs for Ca^{2+} and Na^{+} present a distinguished response for the different beer classes. Also, the ISE for pH shows an interesting response in terms of classification. On the other hand, the sensors with generic response to cations do not present distinguishable signals, given the similar total amount of cations of the beers. It is also the case of the sensors for anions, mainly chloride and nitrate, which show similar variation of potential for all the types of beer.

<FIGURE 1>

3.2 Classification of beer samples

Because of each sensor provides a particular response when immersed in each beer sample, its response could be used to evaluate the ET array capabilities to discriminate between the different group varieties using multivariate data analysis. For this purpose, data was analyzed using two different pattern recognition techniques: Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). LDA is closely related to PCA in that they both look for linear combinations of variables which best explain the data (Duda, Hart, & Stork, 2000). LDA explicitly attempts to model the difference between the classes of data; while PCA does not take into account any difference in class.

The main difference between these techniques is the machine learning task; that is, in the case of PCA it is an unsupervised pattern recognition method, while in the case of LDA it is a supervised one. This classification of the techniques deals on how the inferred (classifier) function that models the data is built. On the one hand, in supervised methods the training data consists of a set of training examples (a fraction of the set cases) which are used to build the model plus the desired output for these cases. Thus the model is built taking into account the parameters that best predict the desired output; then, once the model is built its response is evaluated employing the remaining cases not used in the training step. While on the other hand, in unsupervised methods only the responses of the samples are given to the learner, without any label. Thus, presenting a visual representation of the relationships between samples and variables and providing insights into how measured variables cause some samples to be similar to, or how they differ from each other. For this reason, PCA is normally used just as a visualization tool that permits to check if the samples group together in classes.

3.2.1 Principal Component Analysis

First recognition model was built using PCA given it is maybe the most powerful linear unsupervised pattern recognition method; with this we are able to reduce the dimensionality of the data, while it also helps to visualize the different categories present. Thus, samples are not grouped taking into account prior expected similarities, but based only on their response profile.

<FIGURE 2>

Figure 2 shows the results of the three-dimensional PCA score plot. As stated, clusters are formed depending on responses similarities. The accumulated explained variance with the three first PCs was ca. 91.32 %. Despite this large valour, clusters formed could not be explained by the kind of beer, but for the order samples were measured. That is, the first two PCs are mainly affected for the different aeration time of the samples (from opening the bottle to measuring it) which somehow causes an intrinsic variance along samples, and for the drift of the sensors, if any.

Indeed, the latter was controlled comparing the difference of potential obtained for each sensor passing a control sample (one sample previously opened and doubly replicated to be used as a control measure) between measurements, and the differences found were even 0 or just a few mV along all the day of measuring. Thus, this suggests that the drift found in the PCA is basically due to the samples different aeration time; being possible that some processes like the oxidation of the sample or the loss of CO_2, between others could cause an evolution of responses that is more noticeable than the differences between beer types itself.

Given this situation, where the first PCs are mostly related to the measuring scheme rather than class similarities, it was thought that perhaps discarding them and taking into account the next ones, it would be able to see some clustering trend beyond historic order of samples measurement. In this sense, the two first PC's were discarded and new score plots were built using the 3rd, 4th and 5th PC's (Figure 3).

<FIGURE 3>

In this case, despite the low accumulated variance (4.31%, 2.56% and 1.78% respectively; summing ca. 8.65%), sample scores are better grouped according to its expected class. For example, *Voll* samples are mostly grouped on top of the score plot as seen on Figure 3A, or at the left in the case of Figure 3B.

Despite no clear discrimination was achieved by the use of PCA between all the expected groups, some trend was found; thus, the next step was the use of LDA as the pattern recognition method. This was chosen given LDA, unlike PCA, is a supervised method and it was thought that its usage could improve obtained results.

3.2.2 Linear Discriminant Analysis

LDA is a supervised classification method based on Bayes' formula that builds a predictive model for group membership. The model is composed of k-1 linear discriminant function (being k the number of groups and generating one axis for each function) based on linear combinations of the predictor variables that provide the best discrimination between the groups. The functions are generated from a sample of cases for which group membership is known; the functions can then be applied to new cases that have measurements for the predictor variables but have unknown group membership. Then samples are grouped taking into account the distance of observations from the center of the groups, which can be measured using the Mahalanobis distance.

In essence, instead of generating new axis based on the directions of maximum variance of response matrix, as done in PCA, LDA generates the new axis based on the maximum discrimination between sample groups.

In our case, LDA analysis was done using a stepwise inclusion method which allows to remove the variables that have a lower contribution to the classification model (Johnson & Wichein, 2007). This method is very useful in order to select and remove the variables that do not contribute at all to the prediction success. Thus, having a list of independent variables, some of which may be useful predictors, but some of which are almost certainly useless, the aim is to find the best subset to do prediction task as well as possible, with as few variables as possible.

In this manner, and based on a statistical criteria, variables were included using Mahalanobis distance (Hand, 1981; Johnson & Wichein, 2007). This is a measure of how much a case's values on the independent variables differ from the average of all cases. A large Mahalanobis distance identifies a case as having extreme values on one or more of the independent variables. Thus, at each step, the variable that maximizes the Mahalanobis distance between the two closest groups is entered until optimum performance is reached (best separation between classes). After repeating this trial-error process, the final LDA model included the responses of 16 ISE's: two NH_4^+, two Na^+, two blank electrodes, two cation generic response (Gen Cat I B and Gen Cat II A), three Ca^{2+}, one H^+, one Sr^{2+}, one Ba^{2+}, one K^+ (sensor B) and one NO_3^- sensor.

Moreover, given this is a supervised method, classification success was evaluated using leave-one-out cross validation. In this way, each sample is classified by means of the analysis function derived from the other samples (all cases except the case itself). This process was repeated 102 times (as many as samples) leaving out one different sample each time, the one that must be classified, which acts as model validation sample. Thus, with this approach all samples are used once as validation.

<FIGURE 4>

As can be seen in Figure 4, in this case a much clearer discrimination between the six types of beer was achieved; with the first two Discriminant Functions (DFs), the accumulated explained variance was ca. 94.4%. Patterns in the figure evidence that samples are grouped according to the types of beer. Well established clusters almost separate all the main classes of samples corresponding to: (I) *Marzen*, (II) *Lager*, (III) *Pilsen*, (IV) *Munich*, (V) *low alcohol* and (VI) *Alsacien*. Only groups II and IV are slightly superimposed in this 2D representation, nevertheless it must be taken into account that the model is formed by five discriminant functions, thus this separation could be slightly improved with the other DF's which could not be visualized simultaneously, but used in the analysis.

Analyzing more deeply the obtained plot, it could be seen that samples clusters are sorted along DF1 based on beer astringency and alcohol by volume (abv) content.

That is, cluster V corresponds to a low-alcohol beer, III to *pilsen* (4.6º), II to *lager* (5.4º), IV to *bock* (5.4º) and I to *marzen* (7.2º). Meanwhile DF2 mostly discriminates cluster VI, which corresponds to an *alsacien* beer (4.8º), from the rest. The low discrimination between clusters II and IV may be attributed to the fact that the ionic composition of these beers may be similar and that both have the same abv. The discrimination between cluster VI and the rest could be due to *AK* corresponds to a special beer (Premium) prepared following the original receipt of the brand, thus its preparation is slightly different.

It must be also considered that the similarity between the rest of the clusters may be originated to the fact that samples were from the same manufacturer. This fact may be an explanation for the use of similar water in the brewing process. This is important, given it is quite well-known that ionic composition of water is a key parameter to ensure beer quality and has a large contribution into its taste and astringency (Snyder, 1997). Hence, it is very plausible that if the same water is used in the brewing process, the obtained beer has similar ionic characteristics, ergo being less easily distinguishable by the ET.

<TABLE 3>

Classification results (confusion matrix) of LDA leave-one-out cross-validation approach are summarized in Table 3. As expected from the LDA plot, except samples from groups II and IV, nearly all samples were correctly classified according to its type. The percentage of correct classifications from individual samples was calculated as 81.9%. The efficiency of the obtained classification 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 classes considered was, 83.7%, and that of specificity was 96.4%.

Furthermore, in order to assess the abilities of the proposed ET, some additional beer samples (control) were analyzed. These samples were not used in the building of the model and its objective is to prove the models response when new types of samples are measured. Thus, the model would classify them according to the type that are somehow more related, and in the case that there is no relationship leave them far away from all the clusters. Thus, evaluating these responses model's robustness could be evaluated.

<TABLE 4>

In Figure 4 these samples could be seen in the LDA plot, and Table 4 presents the assigned group by the LDA model to these additional samples. *Budweiser* samples are located between clusters IV and III, this is due to even not being a low-alcohol beer it is a soft/light one. *Heineken* samples are grouped in cluster III, which agrees from the point of view of beer type and also from the abv (4.8 and 4.6 respectively). *San Miquel* samples were located in cluster II, as before it agrees from the same points of view (abv 5.4º in both cases). Finally, *Damm lemon*, the shandy was located above cluster VI and quite far away from its centroid. Thus meaning that samples matrix is very different from the rest, which could be expected given this beer is a mixture of beer and lemonade.

3.3 Prediction of beer abv

Given the trend observed in LDA analysis, where DF1 seems to somehow discriminate abv beer content, it was thought that its quantification may be achieved from the ET responses. For this purpose, an ANN model was built employing the raw potentiometric responses.

Multiple ANN architectures and topologies were assayed employing Bayesian regularization algorithms. This was due to this is a trial-error process where several parameters (training algorithms, number of hidden layers, transfer functions, etc.) are fine-tuned in order to find the best configuration which optimizes the performance of the neural network model (Aitor Mimendia, Legin, Merkoçi, & del Valle, 2010). Once optimized, the final ANN architecture model had 5 neurons (corresponding to the scores of the five LDA model functions) in the input layer, 4 neurons and *tansig* transfer function in the hidden layer and 1 neuron and *tansig* transfer function in the output layer.

<FIGURE 5>

ANN model was trained employing 75% of the data (71 samples), using the remaining 25% (23 samples) of the data (testing subset) for the evaluation of model's performance. Comparison graphs of predicted vs. expected alcohol content (as declared by the manufacturer) were built to check the prediction ability of the ANN (Figure 5). As can be observed, the obtained comparison results are close to the ideal values, with intercepts near to 0 and slopes and correlation coefficients around 1, meaning that there are no significant differences between the values predicted by the multivariate calibration method and the expected ones.

With the ET, it was possible then to predict quantitatively a property (the alcohol content) not directly provided by the sensors used (mainly informing about ion composition), but somehow extracted from the array data by the chemometric tools, in what it can be considered a "software sensor".

4. Conclusions

An Electronic Tongue (ET) system based on an array of potentiometric sensors was developed in order to create a tool capable of distinguishing between different beers samples. The sensors forming the ET were all based on ion-selective electrodes, including as many selective as generic electrodes. Samples were measured with no more pretreatment than the mere smooth agitation of the samples with a magnetic stirrer. Preliminary analysis were done using Principal Component Analysis (PCA), which was useful to identify some initial patterns; however, an aeration time effect was observed, which must be taken into account when developing further experiments. In order to improve the recognition ability of the ET, Linear Discriminant Analysis (LDA) was used as the pattern recognition method given its superior performance. In this case, identification of the samples was achieved successfully, observing the capability of the sensor array to somehow relate beer abv with the first Discriminat Function. This trend was confirmed by building an ANN model which allowed the quantification of beer abv from LDA functions scores, in what it can be considered a "software sensor".

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Table 1. Formulation of the ISE membranes employed in the potentiometric sensor array.

Num. of sensors	Ion	PVC (%)	Plasticizer (%)	Ionophore (%)	Additive (%)	Ref.
2	NH_4^+	33	BPA (66)	Nonactin (1)	-	(Gutiérrez, Alegret, & del Valle, 2008)
2	K^+	30	DOS (68.4)	Valinomycin (1)	KpClPB (0.56)	(Gutiérrez, Alegret, & del Valle, 2008)
2	Na^+	21.8	NPOE (70)	CMDMM (6)	KpClPB (2.2)	(Gutiérrez, Alegret, & del Valle, 2008)
1	H^+	32.8	DOS (65.6)	TDDA (1)	KpClPB (0.6)	(Gutiérrez, Alegret, Caceres, Casadesus, Marfa, & Del Valle, 2008)
1	Ca^{2+} A	30	DOPP (65)	BBTP (5)	-	(Calvo & del Valle, 2007)
1	Ca^{2+} B	32.9	NPOE (66)	Tetronasin (1)	KpClPB (0.14)	(Calvo, Bartrolí, & del Valle, 2006)
1	Ca^{2+} C	33.3	NPOE (65.2)	ETH1001 (1)	KpClPB (0.36)	(Calvo & del Valle, 2007)
1	Sr^{2+}	38.9	TBP (58.4)	TBCOO (1.9)	NaTFPB (0.78)	(Calvo & del Valle, 2007)
1	Ba^{2+}	27	DBS (70)	Monensin (3)	-	(Calvo & del Valle, 2007)
3	Gen Cat A	29	DOS (67)	Dibenzo (4)	-	(Gutiérrez, Alegret, & del Valle, 2008)
2	Gen Cat B	27	DBS (70)	Lasalocid (3)	-	(Gutiérrez, Alegret, & del Valle, 2008)
2	Blank	33.3	DOS (66.6)	-	-	-
1	NO_3^-	30	DBP (67)	TOAN (3)	-	(Gutiérrez, Alegret, Caceres, Casadesus, Marfa, & Del Valle, 2008)
1	Cl^-	Ag/AgCl electrode				(Gutiérrez, Alegret, Caceres, Casadesus, Marfa, & Del Valle, 2008)

Table 2. Detailed information of the beer samples under study

Sample	**Type**	**abv**
Voll	Märzenbier style	7.2º
Estrella	Lager	5.4º
Xibeca	Pilsen	4.6º
Bock	Bockbier/Munich style	5.4º
Damm Bier	Low-alcohol beer	< 1º
AK	Alsacien style	4.8º
Damm lemon	Shandy	3.2º
San Miquel	Lager	5.4º
Heineken	Long “lagering” lager	5.0º
Budweiser	American soft beer	5.0º

Table 3. Confusion matrix built according beer kinds obtained using LDA model and leave-one-out cross validation.

Found Expected	Marzen	Lager	Pilsen	Munich	Low alcohol	Alsacien
Marzen	15	0	0	1	0	0
Lager	0	11	1	10	0	0
Pilsen	0	0	20	0	0	0
Munich	0	5	0	7	0	0
Low alcohol	0	0	0	0	16	0
Alsacien	0	0	0	0	0	8

Table 4. Confusion matrix built according beer kinds obtained using LDA model for control samples.

Found Control	Marzen	Lager	Pilsen	Munich	Low alcohol	Alsacien
Shandy	0	0	0	0	0	2
Lager	0	2	0	0	0	0
Lager, long “lagering”	0	0	2	0	0	0
American soft beer	0	0	1	0	1	0

FIGURE CAPTIONS

Figure 1. Radar plot of the average responses obtained with the potentiometric sensor array. Replicate sensors are designed as "1", "2" and "3".

Figure 2. Score plot of the first three components obtained after PCA analysis of the beer samples. As can be seen, no clear discrimination is obtained for the different beer classes: (●) *Marzen*, (▲) *Lager*, (■) *Pilsen*, (✚) *Munich,* (♦) *Low alcohol and* (X) *Alsacien*. Also control samples are plotted: (A) *Shandy*, (B) *Lager*, (C) *long "lagering" Lager* and (D) *American soft beer*.

Figure 3. Score plot of the principal components obtained after PCA analysis of the beer samples: (A) 3^{rd} and 4^{th} and (B) 4^{th} and 5^{th}. As can be seen, some improvement is achieved compared to the previous plot. The different beer classes are: (●) *Marzen*, (▲) *Lager*, (■) *Pilsen*, (✚) *Munich,* (♦) *Low alcohol and* (X) *Alsacien*. Also control samples are plotted: (A) *Shandy*, (B) *Lager*, (C) *long "lagering" Lager* and (D) *American soft beer*.

Figure 4. Score plot of the first two functions obtained after LDA analysis of the beer samples, according to its type. As can be seen, in this case clear discrimination is obtained for the different beer classes: (●) *Marzen*, (▲) *Lager*, (■) *Pilsen*, (✚) *Munich,* (♦) *Low alcohol and* (X) *Alsacien*; and the centroid of each class is plotted (★). Also control samples are plotted: (A) *Shandy*, (B) *Lager*, (C) *long "lagering" Lager* and (D) *American soft beer*.

Figure 5. Modelling ability of the optimized ANN. (A) Training and (B) external test set adjustments of the expected concentration vs. obtained concentrations for beer abv. Dashed line corresponds to the theoretical diagonal line.

Figure 1

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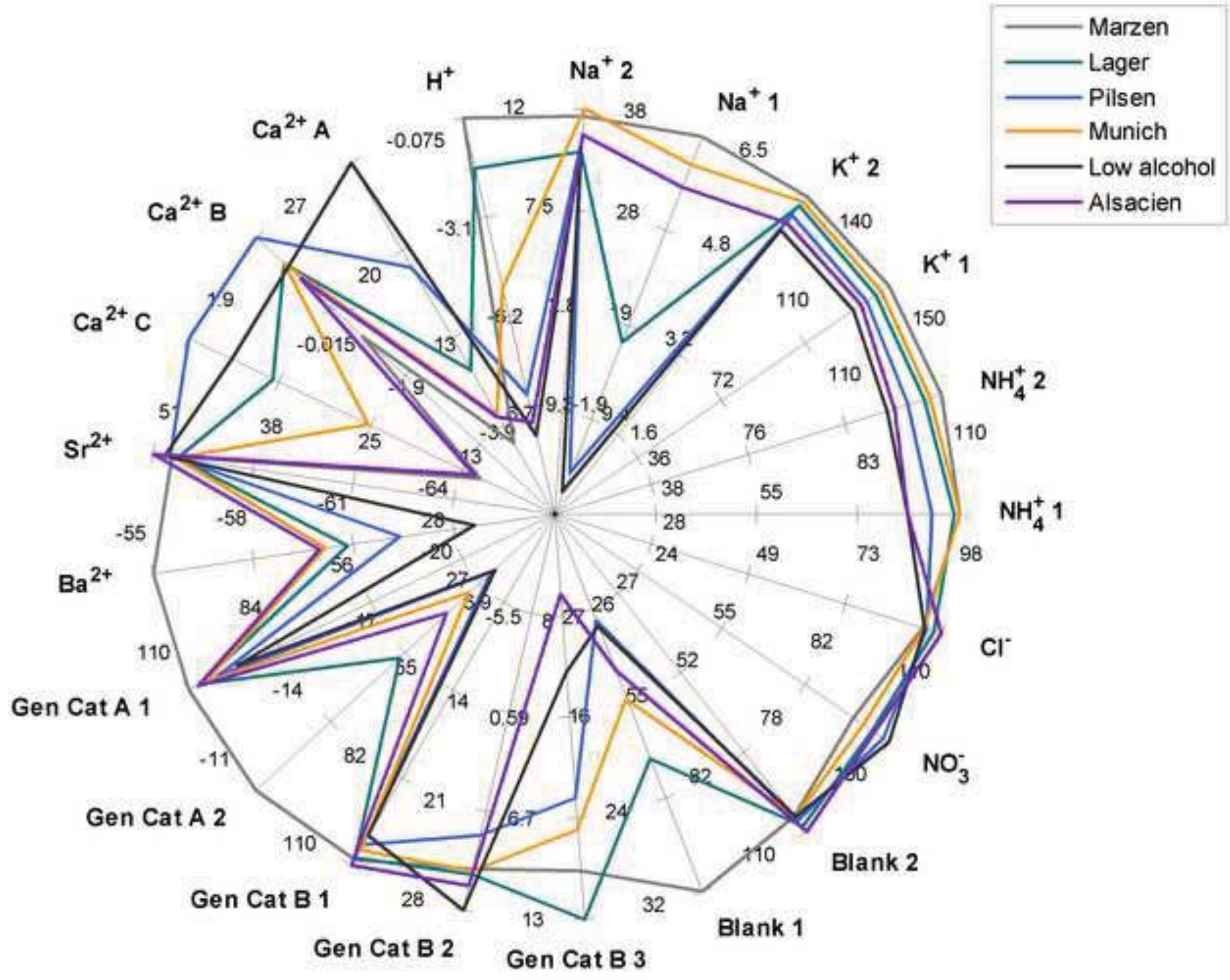

Figure 2
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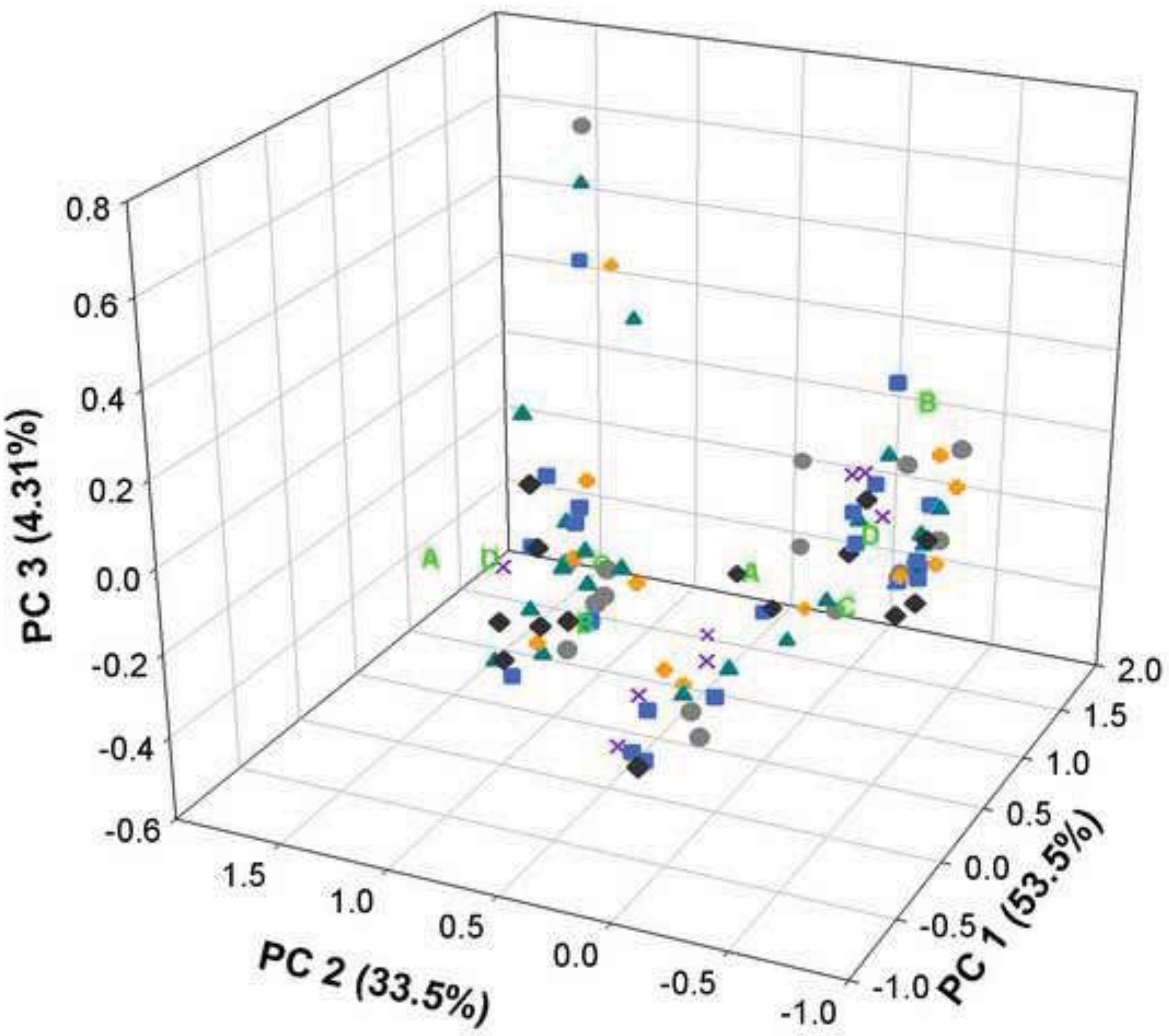

Figure 3
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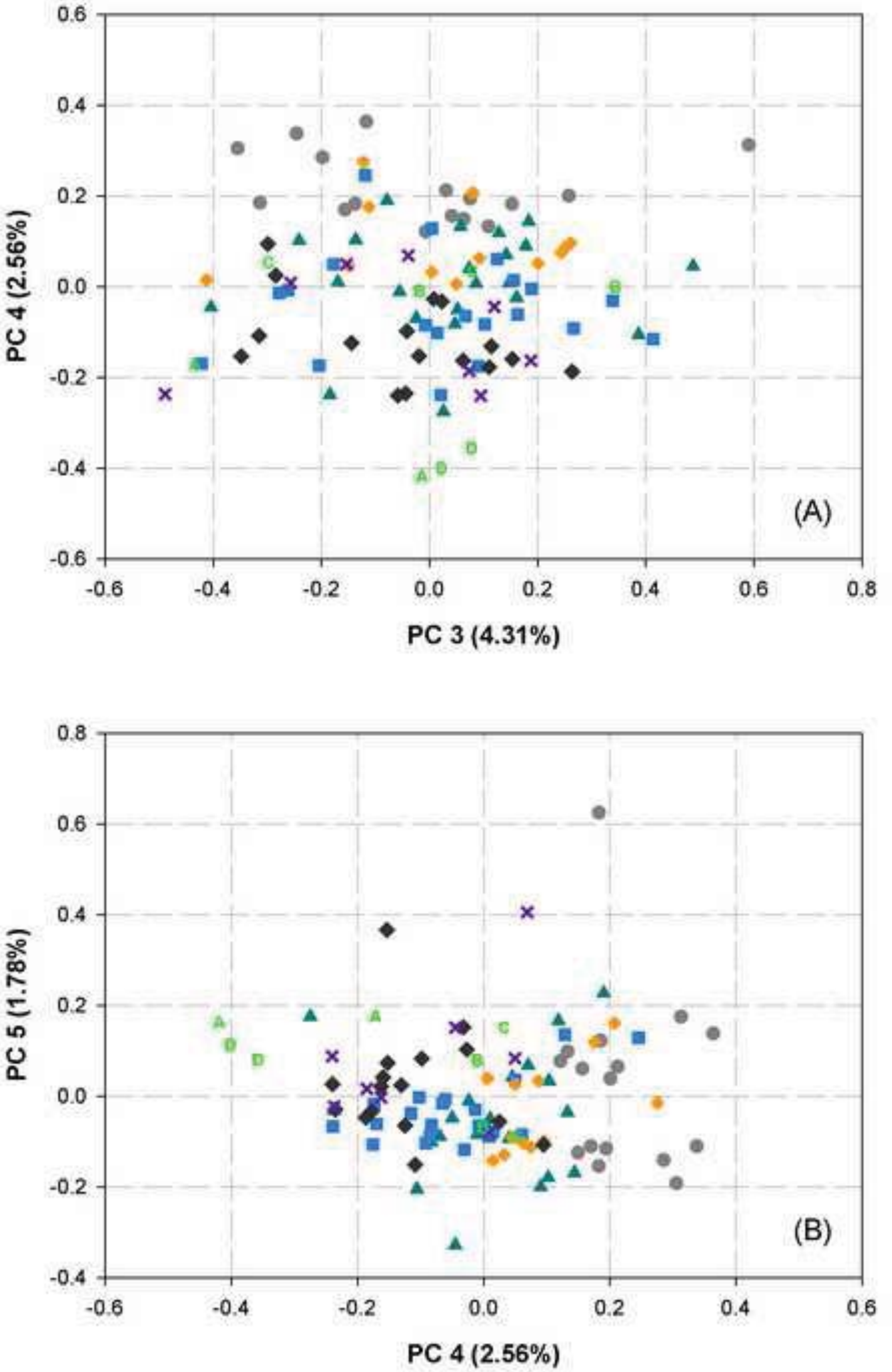
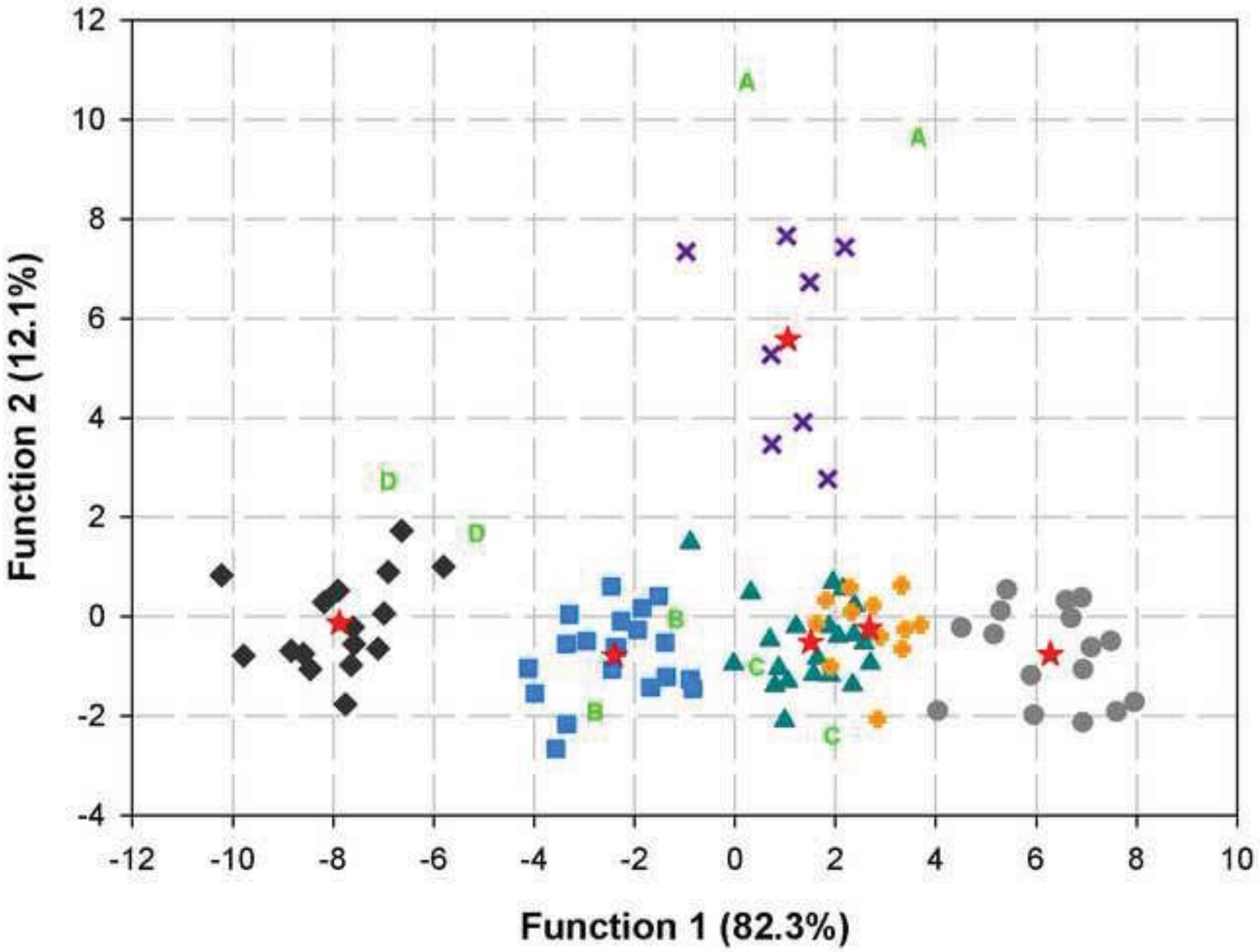


Figure 4


Function 2 (12.1%)
Function 1 (82.3%)
12
10
8
6
4
2
0
-2
-4
-12
-10
-8
-6
-4
-2
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2
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A
A
D
D
B
B
C
C

Figure 5
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