

# Discrimination of beers by cyclic voltammetry using a single carbon screen-printed electrode

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## Abstract

A fast, simple and costless methodology without sample pre-treatment is proposed for the discrimination of beers. It is based on cyclic voltammetry (CV) using commercial carbon screen-printed electrodes (SPCE) and includes a correction of the signals measured with different SPCE units. Data are submitted to partial least squares discriminant analysis (PLS-DA) and support vector machine discriminant analysis (SVM-DA), which allow a reasonable classification of the beers. Also, CV data from beers can be used to predict their alcoholic degree by partial least squares (PLS) and artificial neural networks (ANN). In general, non-linear methods provide better results than linear ones.

**Keywords:** Beer discrimination, Cyclic voltammetry, Screen-printed carbon electrode, Partial least squares, Partial least squares discriminant analysis, Support vector machine discriminant analysis, Artificial neural networks

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## 1. Introduction

Food authentication is an analytical field that checks out label description about the origin, the production process and the processing technologies of foods and beverages. In the last years, strategies of food authentication have gained considerable interest due to increasing public awareness concerning food quality and safety [1]. Thus, there is a special concern in the development of robust, accurate and high-performance analytical methods to ensure the characterisation, discrimination and authentication of foods and beverages. Despite the predominant use of chromatographic techniques coupled to different detectors (UV-visible, fluorescence, mass spectrometry...) for the evaluation of characteristic compounds and fingerprints, electrochemical methods are evolving as a fast and costless alternative to chromatography. In this sense, approaches such as electronic tongue and electronic nose have been introduced for the characterisation, discrimination and authentication of different types of foods and beverages. The electronic tongue and the electronic nose use an array of non-specific sensors, that ideally must present a significant cross response with respect to taste/odour of the substances to avoid redundant information, and

pattern recognition tools to mimic the capability of human tongue and human noses to distinguish characteristic tastes and odours [2, 3].

In particular, electronic tongues, which can be potentiometric or voltammetric depending on the operating principle of the sensors involved [4], in combination with diverse chemometric methods of pattern recognition [5, 6], have been extensively applied to the analysis of food products and, especially, beverages [2, 7-13]. Regarding beverages, beers are among the world's oldest prepared and consumed drinks [14]. Beer is any fermented beverage prepared from these four primary ingredients: grain (most commonly malted barley but also other grains); hops (grown in many different varieties); yeast (responsible for fermentation, based on style-specific strains); and water (accounts for up to 95% of beer's content). All these ingredients provide beers with different attributes (colour, flavour, bitterness, aroma, strength, production method or fermentation method), which allow their differentiation and categorization. Therefore, considering the large complexity and diversity of this beverage depending on both the ingredients and the brewing process, as well as the enormous economic implications of the industrial production of beer, it seems clear that beers are one of the

main targets in the analysis of food products with chromatographic techniques, electronic tongues and chemometrics [15-21].

Electronic tongues have shown excellent abilities for beer discrimination, as it has been demonstrated in the different publications related to the subject [22-31]. But sometimes the electronic tongue approach involves a too large number of sensors in the array, which increases the fabrication time and the costs of the full device. Moreover, it leads to a high amount of data, which means a great deal of information but also a high complexity in the calculations.

Thus, in this work we try to explore the opposite direction, towards simplicity, even accepting the risk of losing some accuracy. For this purpose, we have evaluated the possibilities of a single, commercially available, disposable carbon screen-printed electrode (SPCE) as the only sensor used for cyclic voltammetric (CV) measurements. The choice of this particular material (carbon) for the screen-printed device was made not only in terms of its simplicity, reproducibility and low cost, but also considering the excellent results provided by SPCE units in previous investigations of our research group involving organic substances [32, 33].

The data have been analyzed first with pattern recognition methods in order to classify the different beers according to their fermentation process and to their different varieties. Secondly, methods of multivariate calibration have been applied to predict the alcoholic degree of the samples. In both cases, linear chemometric methods like principal component analysis and partial least squares calibration (these more 'classical' and widespread) have been compared with non-linear approaches, more recent and less popular than the linear ones but, in our opinion, best suited to deal with the characteristic non-linear behaviour of many voltammetric measurements [6, 34-36]. Among these non-linear approaches, we have selected support vector machines, based on hyperplane calculations in high-dimensional spaces to optimize classification [37, 38] and artificial neural networks, based on calculation units interconnected by parametric functions whose parameters are changing during the learning process to optimize calibration predictions [39, 40].

## 2. Materials and Methods

### 2.1. Instrumentation and apparatus

Voltammetric measurements by cyclic (CV) and differential pulse voltammetry (DPV) were made with a potentiostat  $\mu$ Autolab III (EcoChemie, Utrecht, The Netherlands) controlled with the software GPES 4.9

(Ecochemie). Disposable carbon screen-printed electrodes by Metrohm-Dropsens (Oviedo, Spain), with reference DS-110, were used as working electrode, with a surface of 50.3 mm<sup>2</sup>. Although the DS-110 units are equipped with a counter and a pseudo-reference electrode, conventional Ag/AgCl and glassy carbon electrodes by Metrohm (Herisau, Switzerland) were used as reference and auxiliary electrodes, respectively, for the sake of a better reproducibility. The DS-110 devices and the other two electrodes were connected to the potentiostat by means of a Metrohm-DropSens DSC connector (reference DRP-CAC).

### 2.2. Samples and measurements

19 beer brands of different varieties, summarised in Table 1, were considered in this study. Two or more bottles/cans of each brand were purchased in local supermarkets of Barcelona (Spain). They were stored and opened at room temperature (20 °C) and measured by CV or DPV immediately upon aperture, filling a disposable polypropylene can and immersing the electrodes there. This means that, in contrast with many conventional procedures of beer analysis, nor oxygen nor carbon dioxide were removed. Several replicates of different samples were randomly measured by using the same screen-printed unit, which was replaced every 25 measurements to ensure reproducibility standards. In the Results and Discussion section an optimised procedure of signal correction between different screen-printed units using a reference beer sample is described.

### 2.3. Data treatment

The full data set registered in every voltammogram (200 values of current including both forward and backward scans) was corrected for differences in the electrodes (as explained in Section 3.1). This was the only correction made to experimental data. Then, the corrected voltammograms of the beer samples were combined into data matrices by means of home-made programs implemented in Matlab [41]. The data matrices contained the currents measured for every beer sample replicate (in rows) at a given potential during the forward or backward scan (in columns). Calibration and validation data sets were submitted to principal component analysis (PCA), partial least squares calibration (PLS), partial least squares discriminant analysis (PLS-DA), support vector machine discriminant analysis (SVM-DA) and artificial neural networks (ANN) by means of the SOLO program by Eigenvector Research [42]. Unless otherwise indicated, autoscaling pretreatment was applied to all data sets prior to chemometric analysis.

Table 1. Main characteristics of the 19 brands of beer considered in the present study.

Brand name	Code	Fermentation	Characteristic ingredients	Variety	% Alcohol
Franziskaner	FRAN	Ale	Wheat	Witbier	5.0
1550 Weiss	155W	Ale	Wheat	Witbier	5.3
Paulaner	PAUL	Ale	Wheat	Witbier	5.5
Grimbergen	GRIM	Ale	Malt	Blonde	6.5
Leffe Brune	LFBR	Ale	Toasted malt	Dubbel	6.5
Amstel Radler	AMRA	Lager	Lemonade	Radler	2.0
Moritz Radler	MORA	Lager	Lemonade	Radler	2.8
Corona	CORO	Lager	Malt	Pilsner	4.5
Estrella Damm Original	EDOR	Lager	Malt and rice	Pale	5.4
Moritz Original	MOOR	Lager	Malt	Pale	5.4
San Miguel Manila	SMMA	Lager	Malt and hops	Indian pale lager (IPL)	5.8
Cerveza Tequila	CETE	Lager	Tequila	Tequila	5,9
Desperados Original	DEOR	Lager	Tequila	Tequila	6.0
San Miguel Selecta	SMSE	Lager	Toasted malt	Vienna	6.2
Cruz Campo Gran Reserva	CCGR	Lager	Toasted malt	Especial	6.4
Voll Damm Doble Malta	VDDM	Lager	Toasted malt	Märzen	7.2
Moritz Epidor	MOEP	Lager	Malt caramel	Blonde	7.2
San Miguel 0,0	SM00	Lager	Zero alcohol	Alcohol-free	0.0
Free Damm 0,0	ED00	Lager	Zero alcohol	Alcohol-free	0.0

### 3. Results and Discussion

#### 3.1. Preliminary study

A comparative study between CV and DPV measurements was made with several beer samples. From the study it was clear that, although DPV signals were sharper than CV ones, they were less reproducible and had less discrimination power. This could be because, unlike DPV, CV informs about both the oxidation (forward scan) and reduction (backward scan) of the samples. Thus, CV measurements were chosen for further experiments. As for the potential range, scans between -0.5 V and 0.5 V appeared to be the most convenient, being quite informative and avoiding excessive currents at extreme potentials which could favour an early deterioration of the disposable device.

An important factor to evaluate was the reproducibility and durability of the screen-printed electrodes. Figure 1a shows that the first CV scans obtained with a new screen-

printed unit were very different to the others, with quite low currents. As the electrode surface achieves equilibrium with the solution, next measurements exhibit slight current increases until they stabilise after 3-4 consecutive cycles. Then, successive scans become quite reproducible during 25-30 measurements until the electrode starts to deteriorate and voltammograms are notoriously distorted. Once a new electrode has been 'stabilised', CV voltammograms measured with it in different beers can be compared (Figure 1b). Therefore, the subtle differences in the scans can be used by pattern recognition techniques like PCA, PLS-DA or SVM-DA to discriminate among different kinds of beer.

Figure 2 summarizes the effect of the scan rate of CV measurements. As Figure 2a shows, when the scan rate increases, both the forward and backward currents increase, but the signals lose definition. This is because faradaic currents, which are the most informative about electroactive substances, increase more slowly than capacitive ones and are masked by them. A PCA study was carried out with a data set integrated by several

replicates of two beers measured by CV at different scan rates in the range 10 – 200  $\text{mVs}^{-1}$ . Figure 2b shows a scores plot, where PC1 is mostly influenced by the level

of currents (related to the scan rate) and PC3 mainly depends on the details of the signal shape (related to the type of beer).

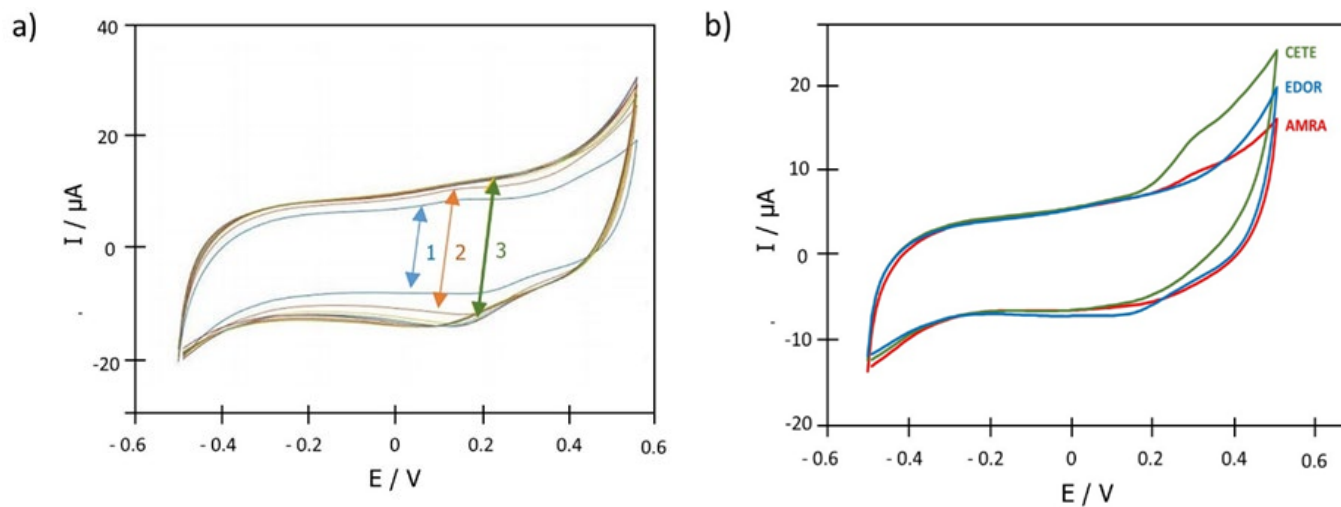


Fig. 1. (a) Successive CV scans made with a brand-new SPCE unit in a reference sample of beer (MOEP) where the three first scans have been highlighted; (b) CV scans obtained with the same SPCE unit in different beer varieties (CETE, EDOR and AMRA).

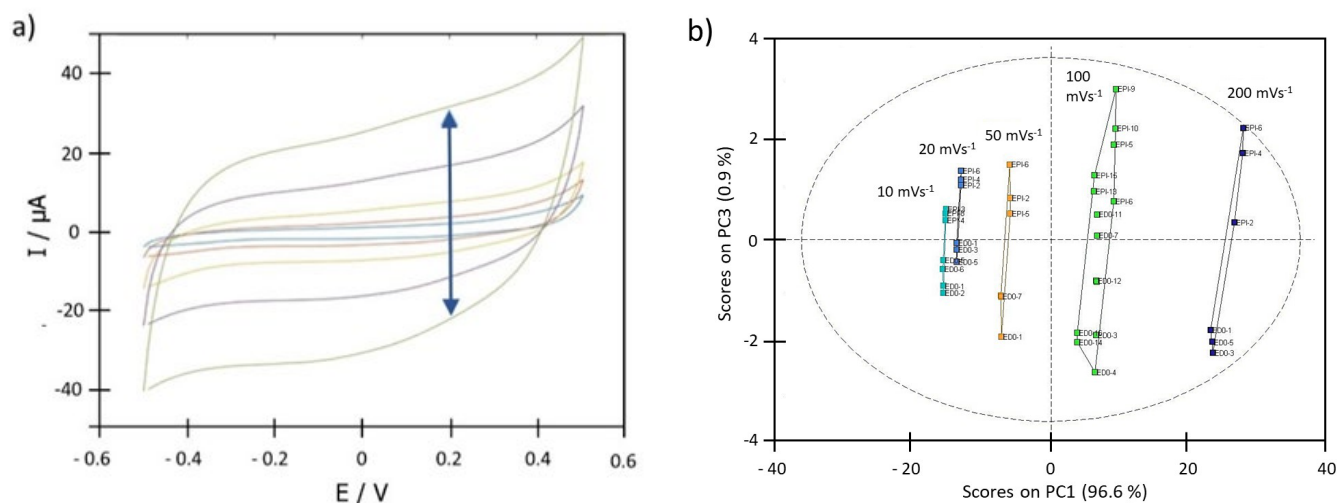


Fig. 2. (a) Evolution of the CV scans measured with a SPCE unit in a beer sample (MOEP) at increasing scan rates from 10 to 200  $\text{mVs}^{-1}$  with the arrows showing the increase of the currents as the scan goes faster. (b) PC3 vs. PC1 scores plot obtained from the overall PCA analysis of several replicates of two different beers (MOEP and ED00) measured by CV at different scan rates, which are shown in the graph. MOEP samples (here denoted as EPI) appear in the top half of the graph, whereas ED00 samples (here denoted as ED0) appear in the bottom half of the graph.

It can be seen that lower rates produce a better agreement of the replicates of the same beer (placed in the positive region of PC3) and a clearer separation from the replicates of the other beer (placed in the negative region of PC3). However, slow scans are time consuming. Therefore, an intermediate scan rate of 50  $\text{mVs}^{-1}$  was chosen as a compromise between analysis time and discrimination power.

As pointed out before, the durability of screen-printed devices is limited, and this prevented us to measure a sufficient number of replicates of all the considered beers with the same SPCE unit. To minimize the differences in the CV signals when the unit was replaced, a correction method between consecutive electrodes was developed. It consists on comparing the CV scans of a reference beer (EDOR) measured with the old and the new electrode. If

we consider every scan (including both forward and backward parts) as a vector, we can define a correction vector  $\mathbf{v}_{\text{cor}}$  in the form:

$$\mathbf{v}_{\text{cor}} = \mathbf{v}_2 - \mathbf{v}_1 \quad (1)$$

where  $\mathbf{v}_2$  and  $\mathbf{v}_1$  are the CV scans measured for the reference sample with the new and the old electrode, respectively. If we assume that this approach holds for all samples, we can correct the signal of any sample measured with the new electrode ( $\mathbf{v}_2'$ ) to predict the scan that this sample would have produced with the old electrode ( $\mathbf{v}_1'$ ):

$$\mathbf{v}_1' = \mathbf{v}_2' - \mathbf{v}_{\text{cor}} \quad (2)$$

In this way, the corrected scan would be more comparable to the measurements of other samples made with the old electrode. In practise, the percentage of

current added or subtracted by the correction is quite small, so the changes are hardly noticeable at the first sight. However, the effects of the correction are clearly visible when pattern recognition methods are applied. As an example, Figure 3 compares the scores plots obtained with PCA in the analysis of a matrix containing the voltammograms of several replicates of two different beers measured with two electrodes. In the absence of correction (Figure 3a), there is a clear difference between the replicates of the same sample measured with different SPCE units, a difference comparable to that between different beers measured with the same SPCE device. In contrast, Figure 3b shows that the application of the developed correction produces only two well defined groups of scores corresponding to both beer samples, with a good integration of the measurement of the different electrodes in the same group of samples. Thus, these results suggest the appropriateness of applying the proposed correction.

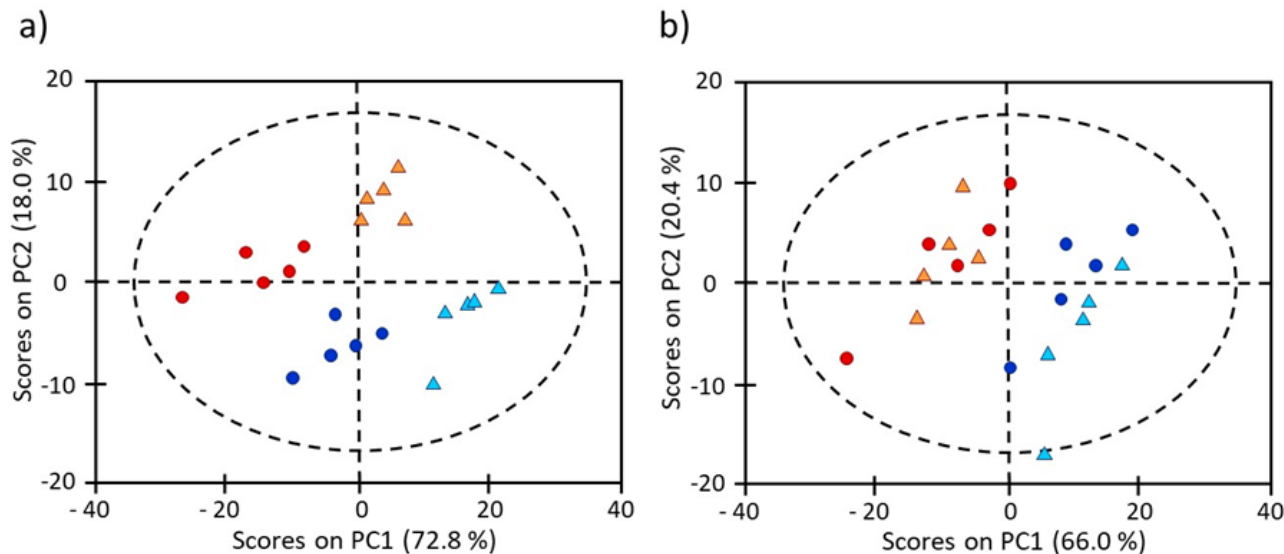


Fig. 3. PC2 vs. PC1 scores plots of a set of CV scans measured in five replicates of two different beers (beer 1: SM00; beer 2: SMSE) using two different SPCE electrodes before (a) and after (b) the proposed correction between SPCE units. (beer 1 and electrode 1 ●, beer 1 and electrode 2 ▲, beer 2 and electrode 1 ●, beer 2 and electrode 2 ▲).

Therefore, CV from -0.5 V to 0.5 V with a scan rate of 50  $\text{mVs}^{-1}$  and the above-described correction protocol was applied to measure several replicates of the brands of beer selected. Moreover, to ensure reproducibility standards, every SPCE unit was first scanned with the reference beer, then used to measure replicates of other beers in random order and finally was replaced once 25 measurements had been performed. In this way, all measurements made with all SPCE units can be compared to each other by using the initial measurements with the reference sample to correct data. The data were integrated into matrices with the samples in rows and the

potentials in columns and were submitted to different methods of sample discrimination and multivariate calibration which are described in the next sections.

### 3.2. Discrimination of beer varieties

A comparative study was made by PLS-DA and SVM-DA to discriminate among the two big groups of beers studied according to their fermentation process: ale beers and lager beers. Figure 4 and Table 2 compare the classification of 148 replicates of the 17 beers considered

according to both chemometric methods. In all cases, a calibration set of 110 voltammograms was used to build

the classification model and a set of 38 voltammograms was used for validation.

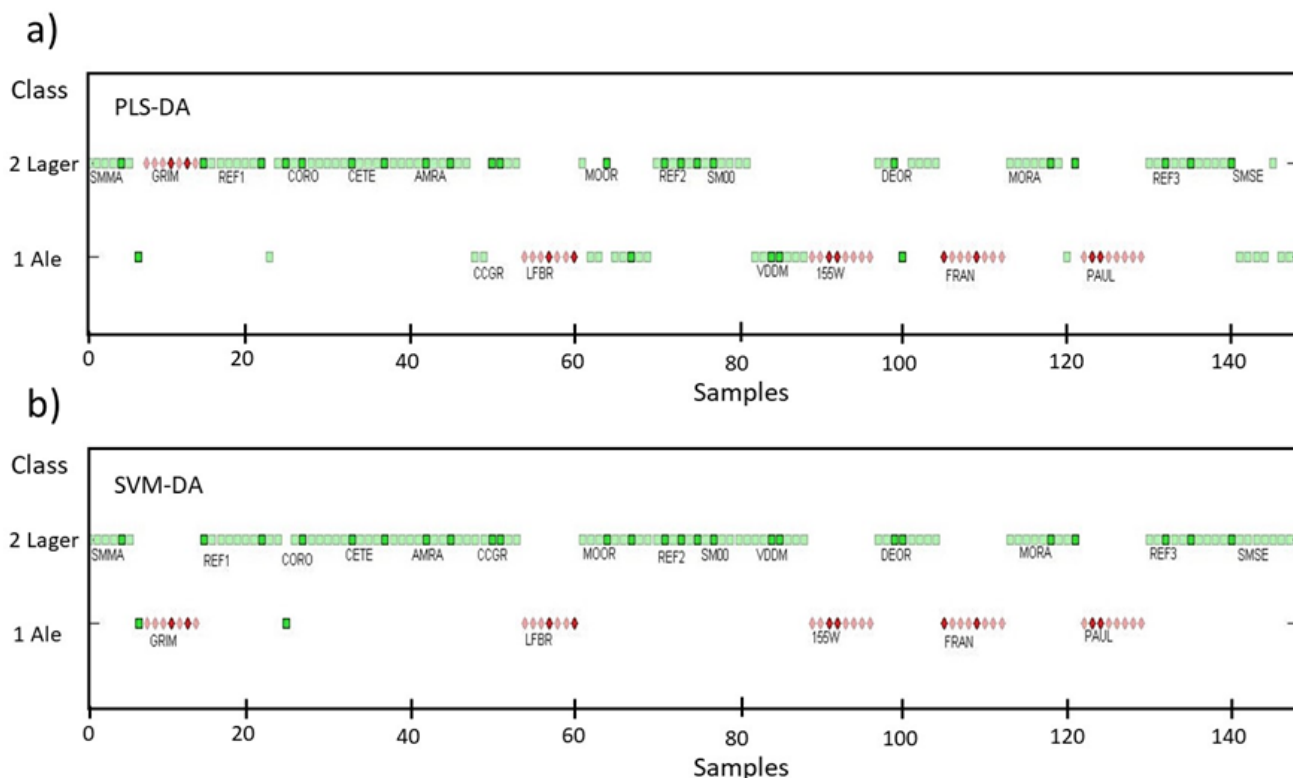


Fig. 4. Classification of the brands of beer considered according to their kind of fermentation (■ Ale or ♦ Lager) obtained from the PLS-DA (a) and SVM-DA (b) analysis of a total of 148 CV samples/scans obtained from them. The 148 replicates have been divided into a calibration set of 110 samples and a validation set of 38 samples. Validation samples are denoted with more intense colour than calibration ones. REF1, REF2 and REF3 stand for the three samples of EDOR used as a reference in the corrections of the voltammograms.

Table 2 shows that, although the results of PLS-DA are reasonable (e.g. 21.1% of classification error in validation), SVM-DA provides a much better classification (5.3% of error in the same item), maybe because it is a non-linear method which models better than PLS-DA (linear) the usual non-linearity of voltammetric data.

This difference between PLS-DA and SVM-DA is more notorious when the models try to classify the beers into 12 more specific varieties (listed in Table 1). Then PLS-DA clearly fails (graphic not shown) with classification errors of 43.6 % and 60.5 % in the calibration and validation sets, respectively. In contrast, SVM-DA provides a really accurate result, with only three samples wrongly classified out of 148 (Figure 5). This produces classification errors of 0.0 % and 7.9 % for the calibration and validation sets, respectively.

These results suggest that the use of an SPCE unit as a single sensor coupled with the analysis by SVM-DA allows an accurate classification of beer samples

according to both the kind of fermentation and the variety of beer

### 3.3. Prediction of the alcoholic degree

Multivariate calibration models obtained by means of PLS with 6 latent variables (deduced by cross-validation) and by means of ANN with two neurons in the inner layer (the default setup in the program SOLO) were applied to voltammetric data to predict the alcoholic degree of the beers in % v/v (this declared by the manufacturer). The results of both approaches are summarised and compared in Figure 6 and Table 3. As it happened in the classification study, the performance of the non-linear method (ANN) is clearly superior to the linear one (PLS). Figure 6a shows in detail the large deviations of most PLS predictions from the expected values of the alcoholic degree. Moreover, the predicted values present a high dispersion. In contrast, Figure 6b shows the accurate predictions made by ANN in a broad

range of alcoholic degrees, from 0 % to 8 %. With the exception of two beer brands (indicated by orange circles), all the predictions are uniformly and well distributed around the line indicating the real value.

Table 2. Parameters obtained in the classification by PLS-DA and SVM-DA of the brands of beer considered in the study according to their kind of fermentation, as shown in Fig. 4.

Method	Data	Parameter	Ale	Lager	Overall
PLS-DA	Calibration	Sensitivity	0.82	0.74	-
		Specificity	0.74	0.82	.
		Classification error	-	-	23.6 %
	Validation	Sensitivity	0.80	0.79	.
		Specificity	0.79	0.80	.
		Classification error	-	-	21.1 %
SVM-DA	Calibration	Sensitivity	1.00	1.00	.
		Specificity	1.00	1.00	-
		Classification error	-	-	0 %
	Validation	Sensitivity	1.00	0.93	.
		Specificity	0.93	1.00	-
		Classification error	-	-	5.3 %

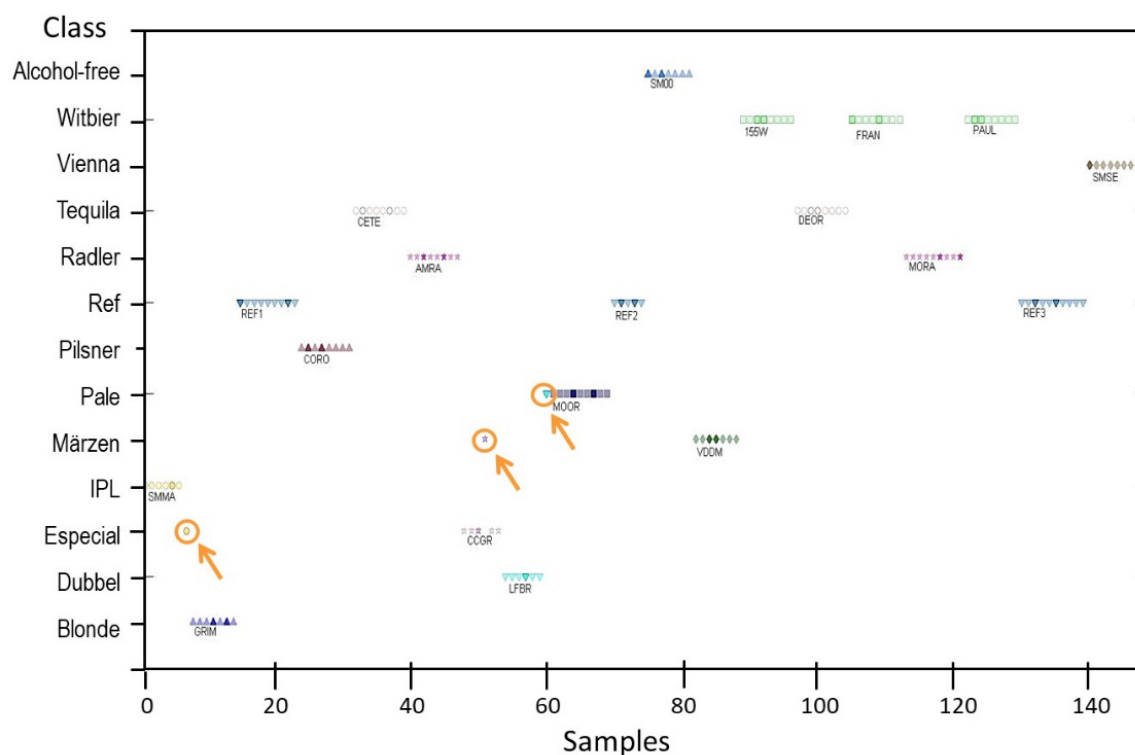


Fig. 5. Classification of the same set of 148 samples according to the 12 varieties/classes of beers (plus the reference samples) shown in Table 1 by applying SVM-DA to the corresponding CV voltammograms. All samples have been assigned to the most probable class. Samples inside the validation set are denoted with a more intense colour than these of the calibration set. Circles and arrows in orange indicate the three only samples wrongly classified by the model.

In order to carry out a comparative validation of both PLS and ANN approaches, 7 replicates of the beer SMMA were measured by CV and the data were

submitted to both PLS and ANN calibration models. Table 4 shows the average and the standard deviation of the 7 predicted values obtained in each case and



compares them with the ‘true’ value provided by the manufacturer. Figures 6a and 6b also compare the predicted values of the validation sample (in blue colour) with the expected one (in red colour). The analysis of

these data confirms the superior performance of ANN, which gets closer to the expected value than the PLS results, with a relative error of 2 %, much better than the 9% provided by PLS.

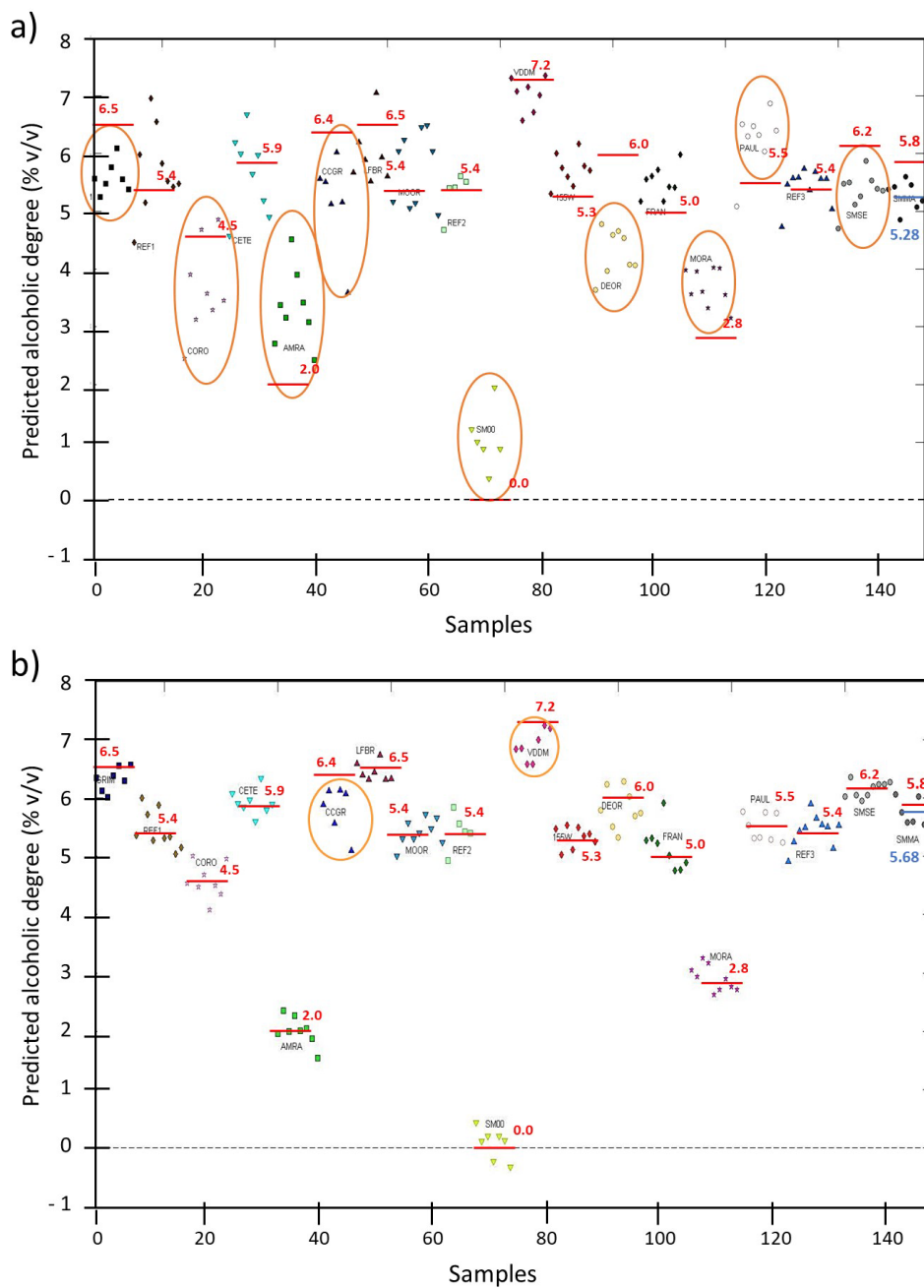


Fig 6. Prediction of the alcoholic degree (% v/v) of the beer samples considered by using a PLS calibration model (a) and an ANN calibration model with two neurones in the hidden layer (b). The alcoholic degree provided by the manufacturer is indicated in red for every brand. The average value predicted for the validation sample is indicated in blue. Orange circles indicate the brands with poor predictions (all points above or below the line).



Table 3. Comparison of the calibration (C) and cross-validation (CV) parameters of the multivariate calibration of the alcoholic degree of the beers by using PLS with 6 latent variables and ANN with 2 neurons in the hidden layer. (RMSE stands for the root mean square error, bias accounts for the systematic error and  $R^2$  is the coefficient of determination of the fitted line in the plot of predicted versus expected values)

Parameter	PLS	ANN
RMSEC	0.907	0.054
RMSECV	0.983	0.691
Bias C	$1.8 \cdot 10^{-15}$	$1.2 \cdot 10^{-3}$
Bias CV	0.014	-0.049
$R^2$ C	0.707	0.999
$R^2$ CV	0.658	0.840

Table 4. Comparison of the alcoholic degree predictions of SMMA beer made by PLS and ANN from the CV scans of 7 replicate samples. Errors are computed according to the value provided by the manufacturer, which is also shown.

Parameter	PLS	ANN	Manufacturer
Average (% v/v)	5.28	5.68	5.8
Standard deviation (% v/v)	0.26	0.28	
Error (% v/v)	-0.52	-0.12	
Relative error (%)	9.0	2.0	

#### 4. Conclusions

The results obtained in the present work show that, although maybe less accurate than the strategies based on chromatographic fingerprinting or voltammetric electronic tongues, the use of CV measurements with a single, unmodified commercial screen-printed device can be a faster, simpler and more economic tool for the preliminary screening of beers. For this purpose, carbon devices (SPCE) appear to be a good choice due to their low cost and durability. Obviously, the information provided by a single sensor is not as rich as that yielded by an array of several sensors with cross-response but, in some way, the correction between successive units and the possibility of working with the untreated sample (thus preserving the contribution of carbon dioxide and volatile substances to the signal) enhances the discrimination power of such a modest approach and easily allows the comparison of sets of measurements carried out in different days.

As for the chemometric tools tested for both classification and calibration, non-linear methods like SVM-DA or ANN seem to reflect better than the linear ones (PLS, PLS-DA) the intrinsic non-linearity of voltammetric measurements, thus providing a more accurate discrimination among different types of

fermentation and different varieties of beer, as well as a more successful prediction of their alcoholic degree.

As a general conclusion, this work suggests that in many practical applications of food characterization and discrimination, the rich information provided by an array of several electrodes constituting an electronic tongue could be replaced by a simpler and cheaper solution involving a single and disposable electrode if the loss of information is compensated by both a correction methodology to account for the different electrodes used and a non-linear chemometric method better suited for voltammetric data than linear ones. Thus, it would be interesting to test similar strategies in other relevant beverages such as wine, tea or coffee.

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for the funding required for the acquisition of disposable electrodes and reagents.

## Conflicts of Interest

The authors declare no conflicts of interest.

## Data Availability Statement

Research data are not shared.

## Figure Legends

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