



# A hybrid sensing system combining simultaneous optical and electrochemical measurements: Application to beer discrimination

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## ARTICLE INFO

### Keywords:

Hybrid sensing system  
Voltammetry  
UV–Vis absorbance  
Beer discrimination  
Partial least squares discriminant analysis (PLS-DA)

## ABSTRACT

A hybrid sensing system, which combines simultaneous cyclic voltammetric (CV) and UV–vis absorbance measurements using a commercial carbon screen-printed electrode and a set of optical fibres in disposable cuvettes, is proposed. The hybrid system approach was applied to 27 samples of recognized beer brands, improving the classification power as compared to only voltammetric or only spectrophotometric measurements. The developed partial least squares discriminant analysis (PLS-DA) model was able to discriminate between five types of beer (lager, marzen, black/stout, alcohol-free and white/ale). The model was also successfully applied to 28 beer samples of white-label brands sold in local supermarkets, demonstrating their similarity to recognized brand beers.

## 1. Introduction

Sensors are becoming a key technology in modern quality control of food and beverages, which not only aims for reliability and sensitivity but also for easy, frequent and fast measurements [1]. In this context, the combination of non-specific electrochemical sensors in the form of electronic tongues or noses is especially relevant in the characterization, discrimination and authentication of food products [2,3]. For this purpose, the use of chemometric methods of pattern recognition is essential [4,5].

The careful selection of sensors included in the electronic tongue is an important step to ensure the desired response with the minimum number of sensors (and therefore amount of data). Thus, cross-response among sensors is essential. In most electronic tongues reported in the literature, this cross-response is achieved by introducing modifications in the same type of sensors (e.g., only potentiometric, only voltammetric, only impedimetric ...) [6–9]. However, sensors based on the same measurement principle have an intrinsic common behaviour that hinders the acquisition of completely complementary information. In this sense, the inclusion of sensors based on different measurement principles is highly desirable to gain reliability and selectivity. Such combined devices are usually known as hybrid electronic tongues (or noses) or, in a more general way, as hybrid sensing systems [10–15].

The benefits of hybrid sensing systems were long ago proved in the

field of electronic noses [13–15], demonstrating that the inclusion of different transducers provides a much better performance than selected sensors from any single sensor class [13,15]. However, the implementation of truly hybrid electronic tongues has not been fully achieved. The usual situation in hybrid systems is the combination of different types of electrochemical measurements, typically potentiometric and voltammetric [10–12]. In contrast, works combining completely different measurement principles such as electrochemical and optical are really scarce. A valuable example of this is the strategy proposed by Gutiérrez-Capitán et al. [16] for the discrimination of wines, integrating potentiometric measurements with several ISFETs, cyclic voltammograms acquired with a gold electrode and UV–vis absorbance data. Unfortunately, in this case data had to be acquired sequentially using a separate instrumentation for each type of measure, which significantly increases analysis time.

In this work we have developed a hybrid sensing system combining simultaneous voltammetric and spectrophotometric measurements. Absorbance spectra are registered with two optical fibres in the transmission mode, whereas electrochemical measurements are based on the use of screen-printed electrodes (SPE), which are cost-effective, disposable and reproducible devices that are commercially available in many formats [17,18]. The SPE unit is placed in the same disposable optical cell where the light beam is passing, allowing the simultaneous registration of absorption spectrum and cyclic voltammograms without

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<https://doi.org/10.1016/j.talanta.2022.123273>

Received 21 December 2021; Received in revised form 26 January 2022; Accepted 27 January 2022

Available online 29 January 2022

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**Table 1**

Beer brands considered in the present study. Numbers 1–27 are recognized brand beers used in the calibration and validation sets, whereas numbers 28–55 are white-label brand beers commercialised in local supermarkets and used to test the application of PLS-DA model.

Number	Name	Type	Class	% Alcohol (v/v)
1	Estrella Damm	Lager	1	5.4
2	Moritz	Lager	1	5.4
3	Cruzcampo	Lager	1	4.8
4	Mahou	Lager	1	5.5
5	Heineken	Lager	1	5.0
6	Carlsberg	Lager	1	5.0
7	Selecta San Miguel	Marzen	2	6.2
8	Amstel oro	Marzen	2	6.2
9	Daura marzen Damm	Marzen	2	7.2
10	Ambar export 3 maltas	Marzen	2	7.0
11	Bock Damm negra Munich	Black	3	5.9
12	Leffe bruin	Black	3	6.5
13	Praga dark lager	Black	3	4.5
14	Mahou maestra dunkel	Black	3	6.1
15	Guinness draught	Stout	3	4.2
16	Super bock stout	Stout	3	5.0
17	Guinness original	Stout	3	5.0
18	Buckler 0,0	Alcohol-free	4	0.0
19	San Miguel 0,0	Alcohol-free	4	0.0
20	Moritz 0,0	Alcohol-free	4	0.0
21	Paulaner	White	5	5.5
22	Erdinger	White	5	5.3
23	Patronus	White	5	5.5
24	San Miguel IPA	Ale	5	6.1
25	Cruzcampo IPA	Ale	5	5.5
26	Mahou IPA	Ale	5	4.5
27	Damm complot IPA	Ale	5	6.6
28	Adlerbrau	Lager	1	5.0
29	Argus clásica	Lager	1	4.8
30	Pilsen Condis	Lager	1	5.6
31	Clásica El Corte Inglés	Lager	1	4.8
32	Clásica Spar	Lager	1	4.5
33	Argus especial	Lager	1	5.6
34	Carrefour especial	Lager	1	5.6
35	Bonpreu clàssica	Lager	1	5.6
36	Aliada	Lager	1	4.8
37	Aurum pilsen	Lager	1	4.8
38	Pils Carrefour	Lager	1	5.5
39	Doble malta Mercadona	Marzen	2	7.4
40	Argus extra malta	Marzen	2	6.8
41	Mercadona tostada	Marzen	2	5.9
42	Alderbrau tostada	Marzen	2	5.5
43	Aurum tostada	Marzen	2	6.6
44	Black (Mercadona)	Black	3	6.0
45	Dia black	Black	3	5.6
46	Argus negra	Black	3	5.6
47	Carrefour negra	Black	3	5.0
48	Carrefour 0,0	Alcohol-free	4	0.0
49	Alderbrau sin alcohol	Alcohol-free	4	0.0
50	Aurum 0,0	Alcohol-free	4	0.0
51	Mercadona trigo	White	5	5.3
52	Aurum weissbier	White	5	5.0
53	Blanca trigo Carrefour	White	5	5.2
54	Session IPA Carrefour	Ale	5	4.5
55	IPA Tibidabo Brewing	Ale	5	5.7

any interference.

The new hybrid sensing system has been applied to the analysis of beer, a very old and popular beverage prepared from grain (usually malted barley but also other grains like wheat), hops, yeast and water [19]. Depending on the proportion of the ingredients and on the brewing methodology, many varieties of beer can be elaborated but, in general terms, they can be divided in two big families: *lager beers* produced by low fermentation (being pilsner beer its most famous variety) and *ale beers* produced by high fermentation (being IPA and white beer characteristic varieties). Ale beers usually have more fruity and bitter taste than lager beers, as well as less CO<sub>2</sub> content and more turbidity. In both families, darker beers can be obtained by using dark malt varieties, increasing the roasting of the grain or using authorised colorants, mostly

derived from caramel. In this work, we use the term *black* for dark lager beers, *marzen* for middle dark lager beers and *stout* for dark ale beers. Since beer is produced in many countries, by many brands and in a large diversity of types, and is worldwide consumed, it requires a rigorous control of its quality and authenticity. This is made by means of different analytical methods, with predominant use of spectrophotometric and chromatographic techniques [20–24] although electrochemical techniques are progressively gaining visibility in the form of sensors and electronic tongues [12,25–27].

In this work we explore the enhanced features of the combination of simultaneous electrochemical and optical measurements to go deeper in the discrimination of beers. Both measurements are recorded with the same instrumentation, which provides a data set especially rich in complementary information from two very different sources in a short analysis time.

## 2. Experimental section

### 2.1. Samples and instrumentation

Beers from 27 recognized brands and 28 white-label brands (Table 1) were purchased in local supermarkets. They were opened at room temperature (20 °C), placed in plastic containers and analysed without sample pretreatment.

Voltammetric and spectrophotometric measurements were simultaneously carried out using a SPELEC equipment by Dropsens-Metrohm (Oviedo, Spain), with the software DropView 8400 from Dropsens-Metrohm. The experimental set-up is shown in Fig. 1. Cyclic voltammetric (CV) measurements were carried out with screen-printed carbon electrodes (SPCE) of 4 mm diameter by Dropsens-Metrohm (reference DRP-C110). UV–vis measurements were performed with two optical fibres (TFIBER-VIS-UV) attached to a sample holder CUV-UV by Ocean Insight (Orlando, USA). Collimators were included in the sample holder. Samples were introduced in disposable plastic cells (macro Vis cuvette, reference 0030079345) by Eppendorf (Hamburg, Germany), with SPCE units placed in a side position. A home-made cover fabricated from a cardboard box lid was used to protect the cell from stray light, as shown in Fig. 1.

Cyclic voltammograms (CV) were registered between –0.5 and +1.1 V with a scan rate of 50 mV s<sup>–1</sup>. Absorbance spectra were acquired with wavelengths between 200 and 900 nm in comparison with a blank of pure water.

### 2.2. Data treatment

The files with the experimental voltammetric and spectrophotometric data acquired with DropView 8400 software were imported to Matlab® [28] for data treatment by means of home-made programs.

As voltammograms presented some drift due to the adsorption of substances on the electrode surface, a new SPCE was used every four samples of beer, which were measured in triplicate and in random order. Every set of four samples included a reference beer that was always the same brand (Estrella Damm) and was used to correct voltammograms according to the method developed in Ref. [26]. It essentially consists on correcting the current of every beer (*I*) with the current measured for the standard beer in the first, reference electrode (*I*<sub>1</sub>) and in the actual electrode where the considered sample is measured (*I*<sub>2</sub>):

$$I_{\text{dif}} = I_2 - I_1 \quad (1)$$

$$I_{\text{cor}} = I - I_{\text{dif}} \quad (2)$$

where *I*<sub>cor</sub> is the current of the sample corrected by means of the standard beer.

Corrected voltammetric data were combined with spectrophotometric data and submitted to chemometric methods (principal

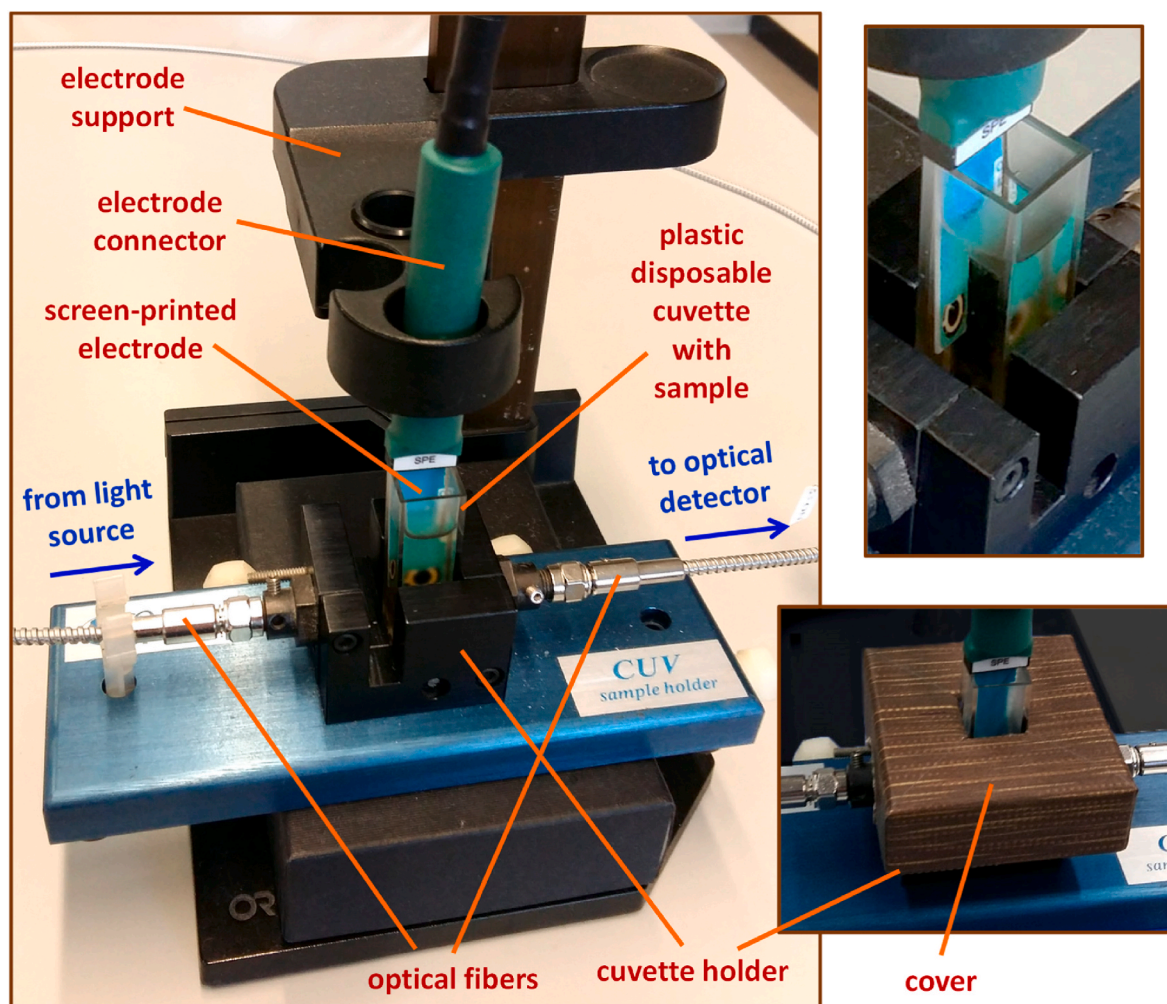


Fig. 1. Experimental setup for the simultaneous voltammetric and spectrophotometric measurements, which were made with the home-made cover shown in the bottom right photography.

component analysis, PCA, and partial least-squares discriminant analysis, PLS-DA) with PLS-Toolbox by Eigenvector Research (Wenatchee, USA) [29]. From the measured data points, a sampling was made at regular ranges: 161 out of 642 in voltammetry and 168 out of 2007 in spectrophotometry resulting in two matrices of similar size ( $I$  for voltammograms and  $A$  for UV-vis spectra). In order to have similar magnitudes, several preprocessing strategies were tested such as autoscaling or mean center but the best results were achieved by dividing  $I$  (originally in  $\mu\text{A}$ ) by 300 and  $A$  by 2.5. Then, both matrices were row-wise combined as shown in Fig. 2.

Exploratory and classification models were built by PCA and PLS-DA. For the latter, the first set of 81 samples (three replicates of 27 recognized beer brands) was divided, by means of the Kennard-Stone algorithm [30], into a calibration set with 52 measurements and a validation set with 29 measurements. As for the 28 white-label brands, the samples were also measured in triplicate and generated 84 couples of voltammetric and spectrophotometric signals that were treated according to the same procedure. This set was considered as a test set to assess the performance of the developed PLS-DA model in new samples.

### 3. Results and discussion

Beer samples from the 27 recognized brands were measured by triplicate, generating 81 measurements by both voltammetry and spectrophotometry. Fig. 2 summarizes the typical shape of the cyclic voltammetric (Fig. 2a) and spectrophotometric (Fig. 2b) signals combined

in the augmented data matrix (Fig. 2c and 2d). It should be noted that cyclic voltammograms are represented as a continuous line in the augmented data matrix.

Considering that voltammograms present a drift caused by the adsorption of beer matrix onto the SPCE surface, a correction of voltammetric data was necessary. Figure S1 in the Supplementary Material file demonstrates the effect of the correction method described in the experimental section on three cyclic voltammograms obtained for the same beer (red lines). As it can be observed, the correction using the voltammograms of a reference beer (blue lines) significantly decreases the variability among replicates as compared to the original data (red lines).

Fig. 3 shows the augmented data matrix of representative beers from each class: lager, marzen, black, alcohol-free, and ale. As it can be observed, different types of beer produce different signals, especially in the region of more positive potentials of voltammograms, corresponding to variable numbers *ca.* 60 to 90 in the augmented data matrix and in the region of spectra between 300 and 500 nm, corresponding to variable numbers *ca.* 180 to 230.

Taking advantage of these differences, an exploratory PCA was performed with all the samples (81) from the 27 recognized brands. The diagram of scores (Fig. 4) shows a clear separation between lager, marzen, alcohol-free, indian pale ale (IPA) and stout beers. However, the couples IPA/white and stout/black beers are very similar. This is not strange, considering that both IPA beers and white beers (also known as wheat beer, weissbier or witbier) are pale-coloured beverages produced

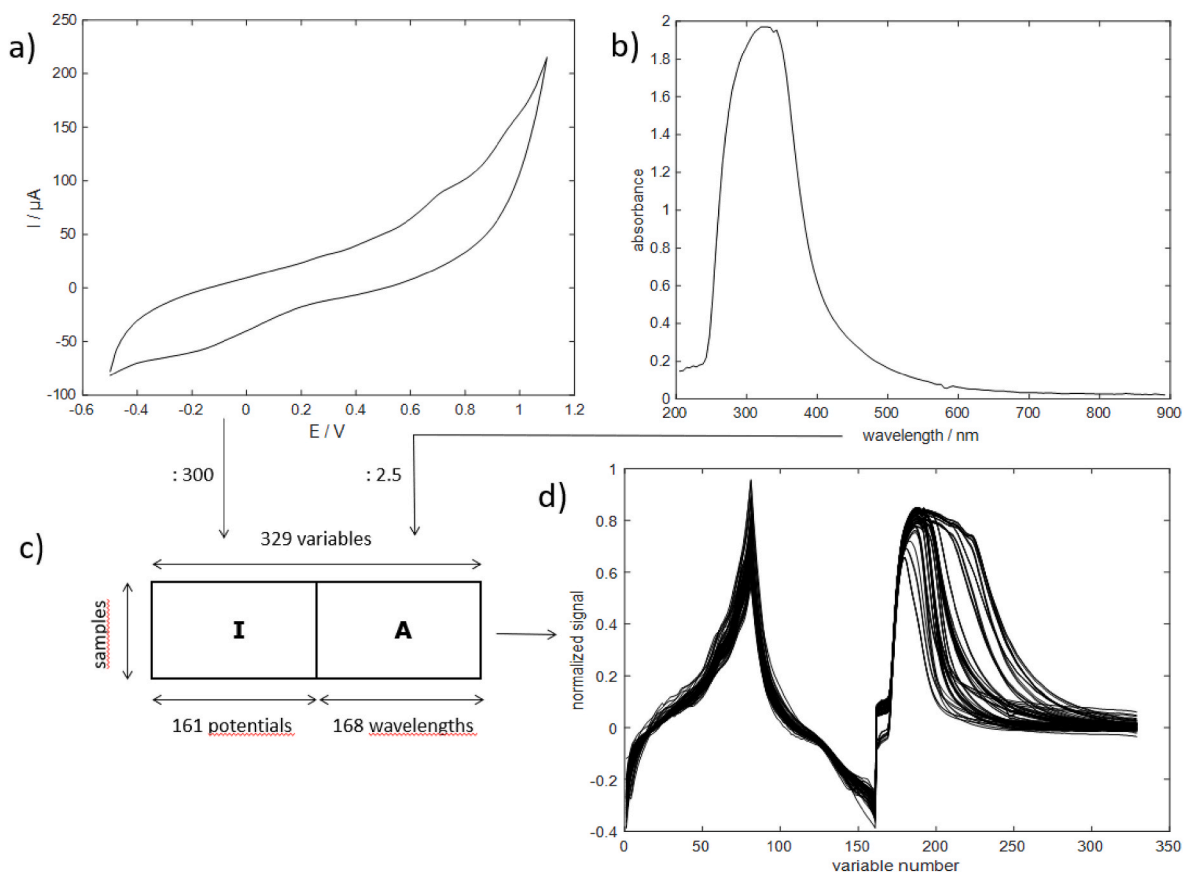


Fig. 2. Typical shape of voltammetric (a) and spectrophotometric (b) signals and their combination into an augmented data matrix (c, d).

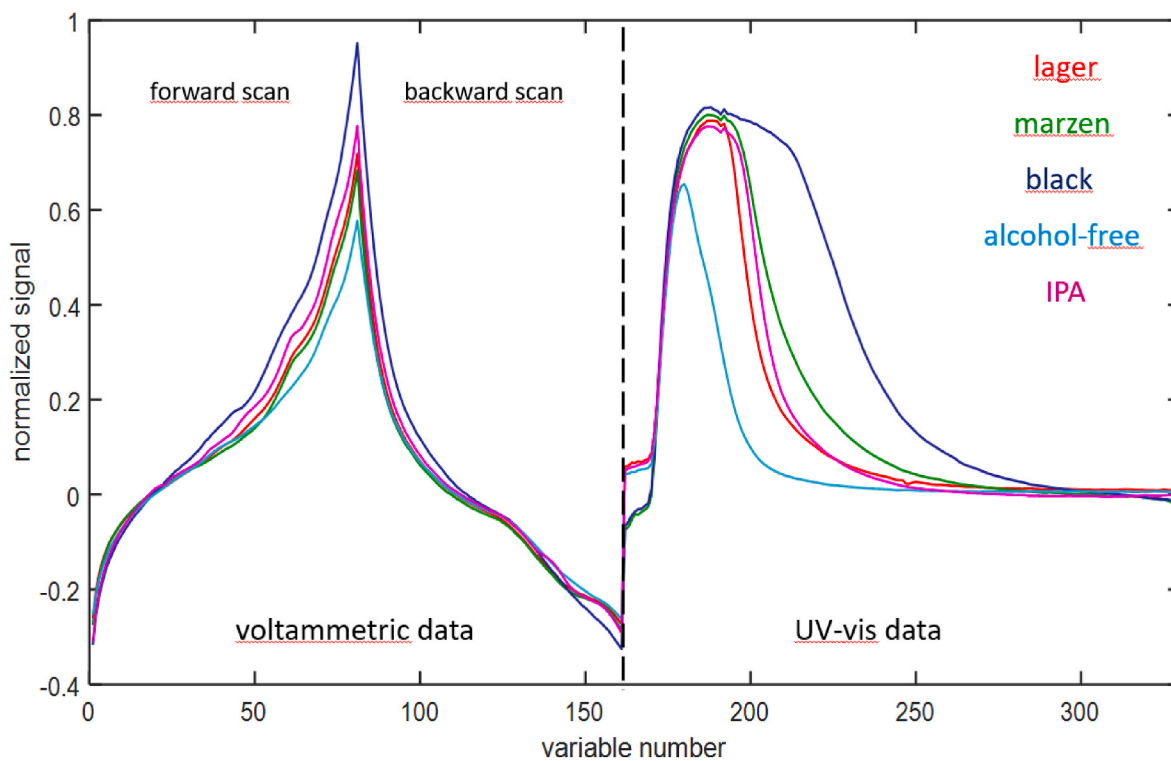


Fig. 3. Comparison of the combined signals of characteristic beers: Estrella Damm as a typical lager (red), Selecta San Miguel as a typical marzen (green), Leffe bruin as a typical black (dark blue), Moritz 0.0 as a typical alcohol-free (cyan) and Cruzcampo IPA as a typical ale (magenta). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

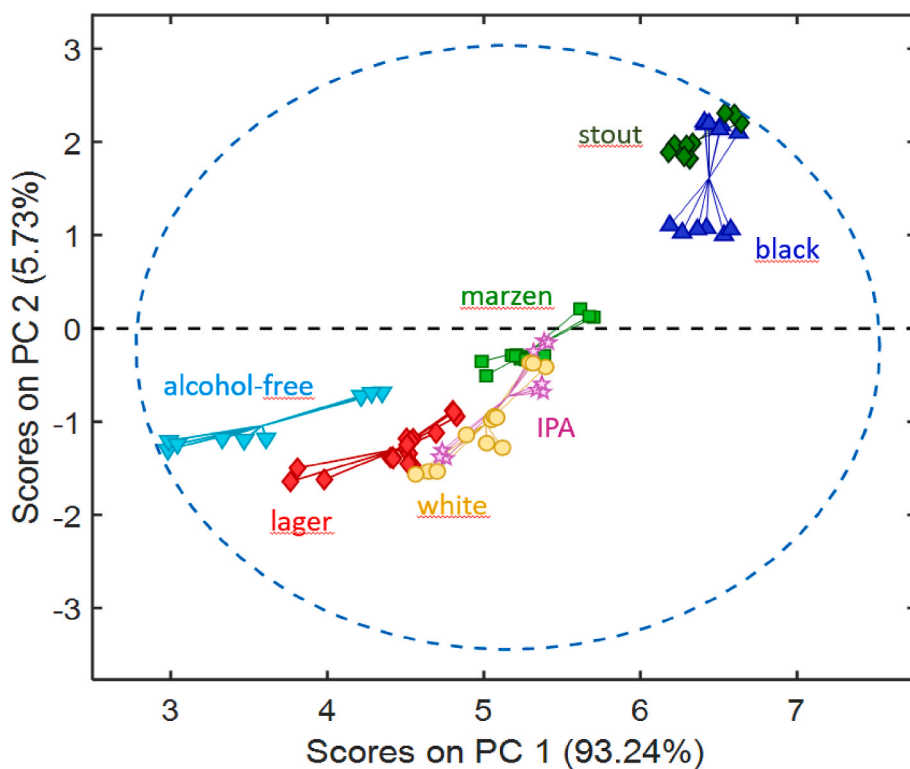


Fig. 4. Scores plot of the two first principal components of the PCA analysis of the set of 81 beer samples from the 27 recognized brand beers, containing both electrochemical and optical data. Samples have been labelled with different colours depending on their variety, which is written in the graph. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

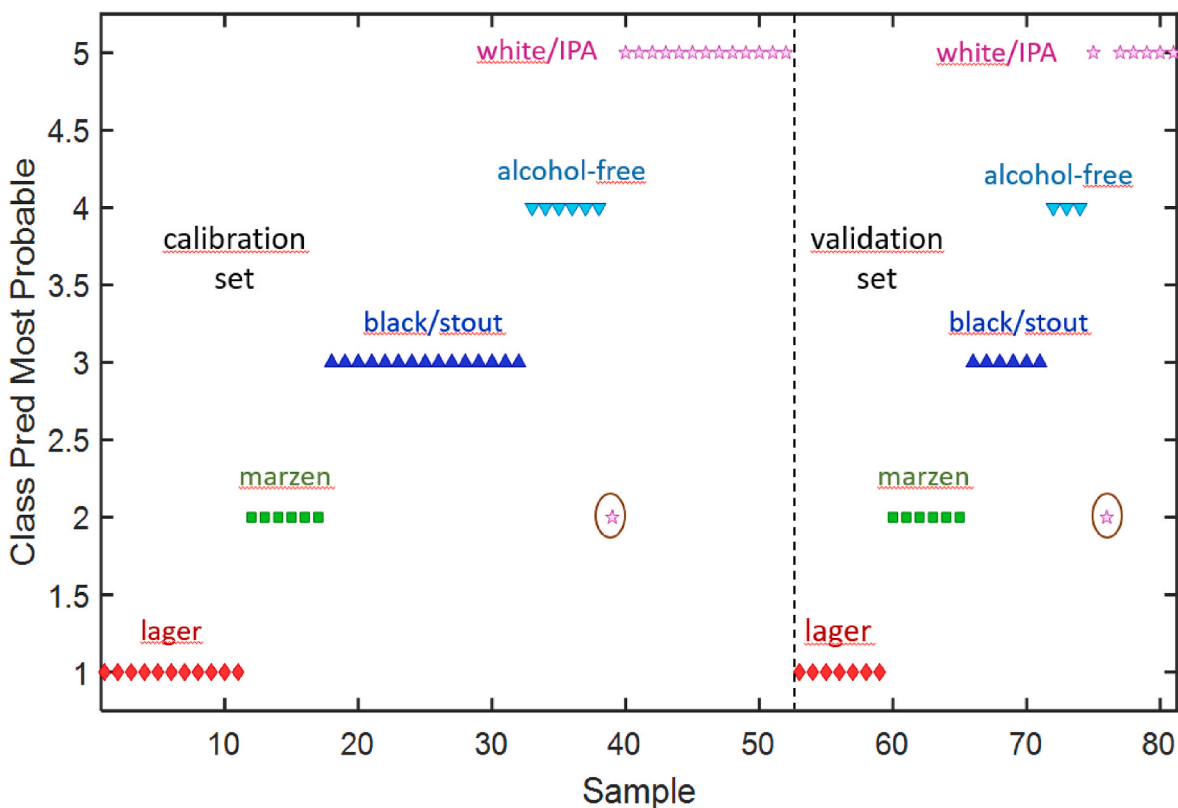
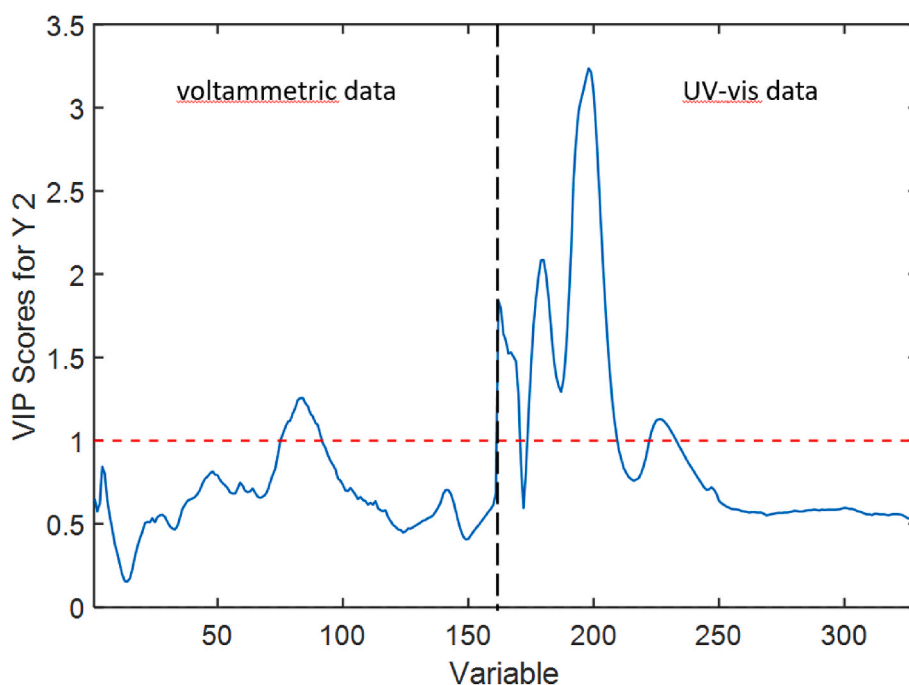


Fig. 5. Most-probable class prediction of the calibration (samples 1 to 52) and validation (samples 53 to 81) sets by using a PLS-DA model with 6 latent variables. Classes are identified with different colours and labelled in the graph. Misclassified samples are marked with a brown ellipse. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 2**

Comparison between prediction indicators obtained in the development of PLS-DA models from the recognized brand beers (calibration and validation sets) when only electrochemical or only optical data are considered and when both kinds of data are analysed together (shown in bold typing). LV indicates the number of latent variables chosen, as provided by cross-validation.

Data	LV	Class	Calibration			External validation		
			sensitivity	specificity	classification error (%)	sensitivity	specificity	classification error (%)
only electrochemical	4	1 (Lager)	0.727	0.610	33.15	0.714	0.409	43.83
		2 (Marzen)	1.000	0.717	14.13	1.000	0.478	26.09
		3 (Black/Stout)	0.467	0.838	34.77	0.167	0.826	50.36
		4 (Alcohol-free)	0.833	0.826	17.03	1.000	1.000	0.00
		5 (White/IPA)	0.714	0.842	22.18	0.143	0.955	45.13
only optical	7	1 (Lager)	1.000	0.878	6.10	1.000	0.955	2.27
		2 (Marzen)	1.000	0.804	9.78	1.000	0.739	13.04
		3 (Black/Stout)	1.000	1.000	0.00	1.000	1.000	0.00
		4 (Alcohol-free)	1.000	1.000	0.00	1.000	1.000	0.00
		5 (White/IPA)	0.857	0.842	15.04	1.000	0.591	20.45
electrochemical + optical	6	1 (Lager)	<b>1.000</b>	<b>0.902</b>	<b>4.88</b>	<b>1.000</b>	<b>0.909</b>	<b>4.54</b>
		2 (Marzen)	<b>1.000</b>	<b>0.935</b>	<b>3.26</b>	<b>1.000</b>	<b>0.783</b>	<b>10.87</b>
		3 (Black/Stout)	<b>1.000</b>	<b>1.000</b>	<b>0.00</b>	<b>1.000</b>	<b>1.000</b>	<b>0.00</b>
		4 (Alcohol-free)	<b>1.000</b>	<b>1.000</b>	<b>0.00</b>	<b>1.000</b>	<b>1.000</b>	<b>0.00</b>
		5 (White/IPA)	<b>1.000</b>	<b>0.921</b>	<b>3.94</b>	<b>1.000</b>	<b>0.864</b>	<b>6.82</b>



**Fig. 6.** VIP scores of the PLS-DA model corresponding to the second class (marzen beers). Variables above the red line are these relevant for sample classification. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 3**

Prediction indicators obtained in the application of the PLS-DA model to white-label brand beers as compared to the type of beer declared in the bottle/can.

Class	sensitivity	specificity	classification error (%)
1 (Lager)	1.000	0.765	11.76
2 (Marzen)	0.733	0.870	19.85
3 (Black/Stout)	1.000	1.000	0.00
4 (Alcohol-free)	1.000	1.000	0.00
5 (White/IPA)	0.800	0.884	15.79

by high fermentation. As for the confusion between black lagers and stouts, it seems that the dark colour in spectrophotometry and the presence of colorants or products derived from roasted malts in voltammetry are more important for discrimination than the differences generated by the type of fermentation.

As a consequence, we decided to define five classes of beer for the further supervised discriminant analysis: i) lager, ii) marzen, iii) black/stout, iv) alcohol-free, and v) white/IPA. Table 1 summarizes the classes assigned to each studied beer.

The above-mentioned five pre-defined classes were used for the construction of a PLS-DA model, splitting the total data set into calibration and validation sets (see experimental section for further details). The average cross-validation suggested the use of 6 latent variables (LV). As shown in Fig. 5, this model allowed a successful classification of all the brands, with only one sample misclassified out of 52 (1.92% of classification error). The application to the validation set produced a slightly higher error, with one sample misclassified out of 29 (3.45% of classification error). Table 2 summarizes the main features of the PLS-DA classification model. Considering the model built from both electrochemical and optical data, it is remarkable the very good sensitivity and specificity of black/stout and alcohol-free beers, the good behaviour

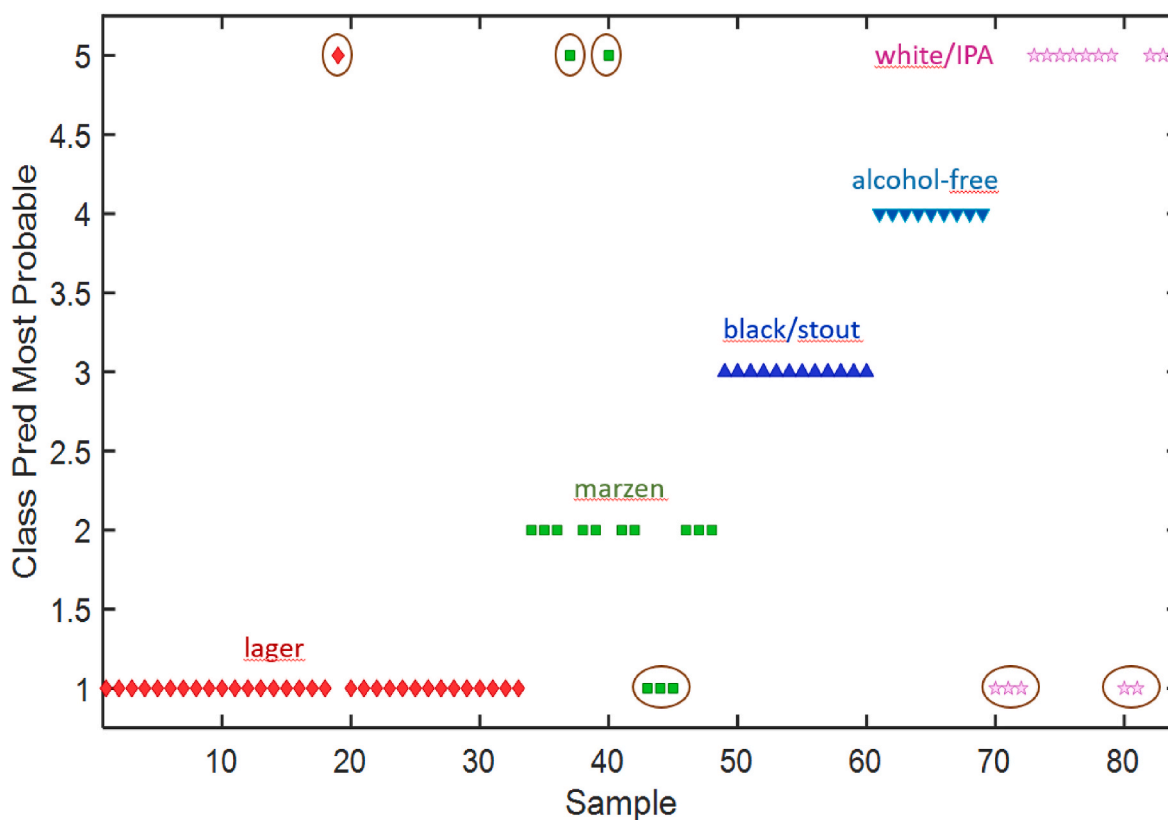


Fig. 7. Most probable class prediction of the white-label brand beers (test set) by using a PLS-DA model with 6 latent variables. Classes are identified with different colours and labelled in the graph. Misclassified samples are marked with a brown ellipse. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of lager and white/IPA beers and the reasonable classification of marzen beers, which present a moderate specificity in validation as compared to the other classes.

The analysis of VIP scores suggests a major contribution of spectrophotometric data to the discrimination of beers. However, the contribution of the region of voltammograms at higher potentials is also relevant, as shown by the VIP plot corresponding to the class of marzen beers (Fig. 6). A proof of this is the comparison in Table 2 with the results obtained with only voltammetric and only spectrophotometric data. Although the optical results are clearly better than the electrochemical ones, the combined results are the best ones. These results confirm the benefits of hybrid systems combining data coming from different measurement principles.

The developed PLS-DA model was validated with external samples using white-label brand beers purchased in local supermarkets. Reasonable predictions were achieved with only slightly higher errors as compared to calibration and validation steps (Table 3). This fact can also be seen in Fig. 7, where only 11 samples from a total of 84 were misclassified (13.10% of classification error). Moreover, it can be seen that the predictions are very accurate for lager beers, which are the most common variety in supermarkets. Most problems arise in marzen and white/IPA beers, which are ‘intermediate’ varieties, with colour and flavour intensities between the extreme types lager and black/stout. Such prediction error could be partly due to the model, but also to the higher diversity in the production of these modalities of beer. Anyway, it must be said that, in general terms, the characteristics of the white-label brands tested are quite comparable to these of recognized brand beers.

#### 4. Conclusions

The investigations described so far show the promising features for sample discrimination of hybrid sensing systems combining

voltammetric signals and UV–vis spectra simultaneously obtained with a synchronised instrumentation, especially when supported by supervised classification methods like PLS-DA. In the case of beers, the combination of complementary information about colour and oxidable substances has allowed a successful discrimination of five varieties of beers: lager, marzen, black/stout, alcohol-free and white/IPA, not only for recognized brands, but also for white-label brand beers commercialised in local supermarkets, which appear to be not much different to their homologous recognized brand beers. It is expected that in the future the implementation of new electrochemical and optical sensors in hybrid sensing systems will provide a powerful tool for fast identification, classification, and authentication of beverages and food products.

#### Credit author statement

Clara Pérez-Ràfols: Methodology; Formal analysis; Writing – review & editing; Visualization; Resources. Núria Serrano: Methodology; Formal analysis; Writing – review & editing; Visualization; Resources. José Manuel Díaz-Cruz: Conceptualization; Methodology; Formal analysis; data-treatment; Writing – review & editing; Visualization; Resources.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work is supported by the Ministry of Science and Innovation of Spain (Project PID2019-107102RB-C22) and the Generalitat of

Catalunya (Project 2017SGR311). The authors also want to acknowledge Drs. Santiago Hernández and Xavier Saurina for providing them the Ocean Insight cuvette holder.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2022.123273>.

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