# Instrumental measurement of wine sensory descriptors using a voltammetric electronic tongue

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## Abstract

The approach presented herein reports the application of a voltammetric electronic tongue (ET), in contrast with a wine tasting sensory panel, as a tool for standardized wine tasting; concretely, to achieve the discrimination of different wine DOs (*Denominación de Origen*, a mark related to its geographical region and ensuring specific quality levels) and the prediction of the global score assigned by the trained sensory panel. To this aim, a voltammetric array of sensors based on bulk-modified graphite and metallic electrodes was used as the sensing part, while chemometric tools such as linear discriminant analysis (LDA) and artificial neural networks (ANNs) were used as the qualitative and quantitative modelling tools. Departure information was the set of voltammograms, which were first preprocessed employing fast Fourier transform, followed by removal of less-significant coefficients employing a stepwise inclusion method and pruning of the inputs. The trend, in global scores, was modelled successfully with a 92.9% of correct identification for the qualitative application, and a correlation coefficient of 0.830 for the quantitative one (with 14 and 20 samples for the external test subset, respectively).

**Keywords:** Electronic Tongue; Linear Discriminant Analysis; Artificial Neural Network; voltammetric sensor; wine; sensory panel

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## 1. Introduction

Over the last decades, there have been important advances in the design of new sensors and biosensors, normally directed to the implementation of new concepts, designs, or configurations, in all cases heading to improved biodevices showing perfect selectivity [1, 2]. Unfortunately, there are many factors hindering their application in the required conditions (e.g. matrix effects, secondary responses, irreversible fouling, etc.).

Opposite to that trend, there is a different approach that appeared in the late 1990s that proposes the use of arrays of sensors in order to obtain some added value in the generation of analytical information [3]. Then, generated information is processed by means of advanced chemometric tools able to interpret and extract meaningful data from the complex readings. Curiously, this approach respresents a shift of the complexity of the analysis from the chemical to the processing field [4]; this approach is known as Electronic Tongue (ET).

According to the agreed IUPAC definition [3], an Electronic Tongue is “a multisensor system, which consists of a number of low-selective sensors and uses advanced mathematical procedures for signal processing based on Pattern Recognition (PARC) and/or Multivariate data analysis [artificial neural networks (ANNs), principal component analysis (PCA), etc.]”. In this way, the underlying motivation of ETs is different from the general trend in the sensor field; that is, instead of pursuing the perfectly selective sensor, to use low-selectivity sensors or with cross-response features; a prerequisite for the development of these biomimetic systems.

Furthermore, given its biomimetic behaviour, ETs represent a straightforward solution when trying to analytically reproduce the sensory information perceived by subjects or tasters towards natural samples, food, beverages, etc. (Figure 1); e.g. a taste perception, identifying a variety, noticing a defect, etc. [5-8]. That is, even with absence of the knowledge about which compounds are primarily responsible for some sensations, the perceptions are mimicked.

<FIGURE 1>

Within this context, ETs have already been successfully applied to the classification or identification of several beverages such as mineral waters, milk, juices, wine or coffee, between others [9-12]. Within those, wine is a specially regulated beverage, being, in many cases, subjected to a PDO (protected designation of origin) status and its regulations [13]; in the case of Spain, receiving the appellation DO (*Denominación de Origen*). Therefore its identification has received special attention, together with methodologies for its characterization and elaboration control [11].

However, most of the papers devoted to the application of ETs to wine analysis deal with classification tasks or the numerical prediction of specific chemical parameters or individual taste descriptors (e.g. phenolic content or bitterness level), but to the best of authors' knowledge, none of them have achieved the correlation between ET measurements and the global score assigned to wines by a sensory panel.

DO (or PDOs as defined by the European Union Regulations) are a labelling system established to regulate the quality of Spanish (or the respective European country) foodstuffs based on its region (with well established geographical limits) and food type, which is controlled by a governing body that controls the quality, ingredients and production process of each product in order to ensure attaining specific quality levels in the final food or beverage [14]. Products labelled DO (or the respective PDO), apart from being of superior quality, are expected to carry specific characteristics of geographical region or individual producer and be derived from raw materials originating within the region. Like most of these designations, a fundamental tenet of a DO label is that no product outside of that region is permitted to bear that name.

From an analytical point of view, wine is a complex mixture of diverse substances, which exhibit considerable influence on wine's taste and other features. Although declaring the interest, its quality control is still under development and still very much based on wine tasters [11], whose taste and olfaction play an important role in the evaluation of the quality of wine. Therefore, it should be expected that the ability to simultaneously detect a large spectrum of compounds in one step and provide a comprehensive information on the sample within a few seconds can be considered as a basic feature/requirement for the design of an artificial analytical system; a situation that suits perfectly with the concept of ETs.

In this sense, the main goal of this work is to demonstrate the huge capabilities of ET-based systems to mimic the human taste perception and provide an analytical tool for its assessment. More specifically, proposed approach herein is based on the application of a voltammetric ET formed by bulk-modified graphite-epoxy composites and metallic electrodes towards the discrimination of different wine DOs and the prediction of the global score assigned by a standardized sensory panel.

## 2. Experimental

### *2.1 Reagents and solutions*

All reagents used were analytical reagent grade and all solutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA). Cobalt (II) phtalocyanine, copper and platinum nanoparticles (<50 nm), which were used as electrode modifiers, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Au and Pt metal wires were obtained from Goodfellow (Huntington, UK). Graphite powder (particle size 50 µm) was received from BDH (BDH Laboratory Supplies, Poole, UK). Epotek H77 resin and its corresponding hardener were supplied from Epoxy Technology (Billerica, MA, USA). Potassium chloride was purchased from Merck KGaA (Darmstadt, Germany).

### *2.2 Samples under study*

A total set of 71 wines from different producers were analyzed. All wine samples considered were white bottled wines produced in Catalonia region and commercially available. Those samples were selected according to its DO (that is, the region where the wine is produced), but also taking into account other factors such as grape varieties, vintage, etc. Thus, in order to have a more representative set of samples.

In this sense, Table S2 (supplementary info) summarizes information about the producers and trademarks of the wine samples analyzed; so that, complete information of them (e.g. vintage, grape varieties, DO, fermentation method, etc) can be checked in *La guia de vins de Catalunya* (The 2014 guide of Catalan wines) [15]. Besides, and if only focusing in their DO, the samples can be categorized as (number of samples belonging to each class in brackets): *Empordà* (10), *Penedès* (11), *Costers del Segre* (8) *Terra Alta* (16), *Priorat* (7), *Montsant* (7), *Catalunya* (10) and *Tarragona* (2). Detailed information on each DO (geographical, climatic, soil, etc) might be found in [16].

Additionally, parameters such as alcohol by volume (abv), volatile acidity, pH or the amount of sugar between others were analyzed following regulated methods to further characterize samples under study and to guarantee they fulfil required standards by the DO [17]. This information, although not used in this study, is presented also in Table S2.

### *2.3 Sensory panel evaluation*

Taste attributes of the wines considered were assessed by a panel of 8 wine experts under usual established procedures [18]. The panellists were professional wine tasters from the panel tasting of the different DOs included in this study. All of them were fully trained and with more than five years of experience in evaluating the wines for the different editions of the Catalan wines guide.

Briefly, the 71 wine samples were randomly divided in groups of 8, evaluating one group per day. Randomized samples of 25-30 ml were served in clear glasses NF V09-110 (AFNOR 1995) marked with three digit random numbers and covered with Petri dishes. Water was provided for rinsing the palate during tasting. Evaluations were conducted at 20-22 ºC. No information of the type of wine or its DO was provided to the panellists.

In this way, the subjects were asked to rate the global sensory quality of the wines (sight, aroma and taste) by assigning it a value ranging from 0 to 10 (for each of the three parameters); and the assigned score given to each wine was calculated as the weighted mean as follows: sight x 0.3 + aroma x 0.35 + taste x 0.35. Afterwards, the final score was obtained from the mean of the eight panellists. On that account, such information of considered samples can be found in Table S2 (supplementary info) as well as in *La guia de vins de Catalunya* (The 2014 guide of Catalan wines) [15].

### *2.4 Electronic tongue sensor array*

A hybrid electronic tongue formed by both bulk-modified graphite composites and metal wire electrodes was used for samples measurement. The latter consisted of a 1 mm diameter metal wire casted into the epoxy resin [19], while the formers were prepared by mixing the resin, graphite powder and a modifier in a ratio 83:15:2 (w/w) [20]. In both cases, resin was allowed to harden at 80 ºC for three days, and afterwards, electrode surfaces were polished with different sandpapers of decreasing grain size. Final electrodes area was 28 and 0.79 $mm^2$ for composite and metal electrodes, respectively.

In this manner an array of 6 voltammetric electrodes was prepared, consisting in two metallic Au and Pt electrodes plus four composite electrodes, one unmodified epoxy-graphite electrode and three modified with Cu and Pt nanoparticles, and cobalt (II) phtalocyanine.

Those modifiers/catalysts were selected based on previously reported studies with wines, either from other research groups or from our laboratories, in order to obtain a variety of electrodes with significant cross-selectivity and complementary electroactive properties that allow the obtaining of rich information to enhance modelling capabilities [21, 22]; this is the desired situation in ETs applications.

Electrodes modified with phthalocyanines (mainly CoPc and its derivatives) are interesting for being efficient electrocatalysts in the determination of many important inorganic, organic or biological compounds [21]; while nanoparticles have emerged as interesting electroactive material in electroanalysis; these are alternative to bulk metals, with catalytic and electrocatalytic peculiarities, mainly derived from their higher surface/mass ratio [22]. Lastly, the usage of bare metallic electrodes respond to some approaches followed by some research groups in the field of ETs [23], while also provides an opportunity to asses the differences found between those and the nanoparticles-modified electrodes.

### *2.5 Voltammetric measurements*

The measurement cell was formed by the 6-sensor voltammetric array and a reference double junction Ag/AgCl electrode (Thermo Orion 900200, Beverly, MA, USA) plus a commercial platinum counter electrode (Model 52-67, Crison Instruments, Barcelona, Spain).

Cyclic Voltammetry measurements were carried out at room temperature (25 ºC), in a multichannel configuration, using a 6-channel AUTOLAB PGSTAT20 (Ecochemie, Netherlands) controlled with GPES Multichannel 4.7 software package.

In order to get stable voltammetric responses, ensuring reproducible signals from the ET array along the whole experiment, electrodes were first cycled in saline solution (i.e. 10 mM KCl). Afterwards, an aliquot of 25 ml of wine was directly used for each measurement, without any sample pretreatment.

In this manner, a complete voltammogram was recorded for each sample by cycling the potential between -1.0 V and +1.3 V vs. Ag/AgCl with a step potential of 9 mV and a scan rate of 100 $mV \cdot s^{-1}$. Additionally, an electrochemical cleaning stage was carried out between each measurement to prevent any cumulative effect of impurities on the working electrode surfaces, and avoiding to perform any physical surface regeneration of those. To this end, a conditioning potential of +1.5 V was applied during 40 s in a cell containing 25 ml of distilled water [24]. As in the case of the panel of experts, all samples were analyzed in random order.

### *2.6 Data processing*

Chemometric processing of the data was done in MATLAB 7.1 (MathWorks, Natick, MA, USA) using specific routines written by the authors, and its Neural Network Toolbox (v.4.0.6). Concretely, principal component analysis (PCA) and linear discriminant analysis (LDA) were used for qualitative analysis of the results, while quantitative analysis was achieved by means of artificial neural networks (ANNs).

In the case considered, the large dimensionality of the data generated when voltammetric sensors are used (that is, when a complete voltammogram is recorded for each sensor from the array) hinders their treatment; especially if ANNs are to be used. This is because it is widely recommended to employ a dataset for training with larger number of samples than the number of interconnection weights that are then needed to calculate. If a single voltammogram is formed by hundreds of current values, and a sensor array is then used, the difficulty of the problem is made evident. Therefore, one solution when dealing with a set of voltammograms is to employ a preprocessing stage for data reduction. The main objective of such a step is to reduce the complexity of the input signal preserving the relevant information, which in addition allows to gain advantages in training time, to avoid redundancy in input data and to obtain a model with better generalization ability [25].

In addition, removal of less significant coefficients that barely contribute to the model (i.e. with low information content) might also improve model performance. That is, 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 the prediction task as well as possible, with as few variables as possible.

In our case, compression of voltammetric data was achieved by means of fast Fourier transform (FFT) [26], while pruning of the inputs was done either using a stepwise inclusion method for LDA [27] or Causal Index (CI) pruning for ANN model [25, 28]. More specifically, a feed-forward network with a back-propagation algorithm which is used to train the network according to a learning rule, what is known as multilayer perceptron (MLP) [29].

Sigmaplot (Systat Software Inc., San Jose, CA) was used for graphic representations of data and results.

## 3. Results and Discussion

As already commented, the aim of this work was to demonstrate the huge capabilities of ET-based systems as an analytical tool capable of reproducing the expertise of wine tasters. In this direction, we focused in two specific cases. On one hand, we evaluated the discrimination of different wine DOs; while on the other hand, we attempted the correlation of ET response with the scores assigned by a sensory panel. Both examples would show the potentialities of ET-systems to translate the subjective evaluations of a sensory panel into conventional qualitative or quantitative information (Figure 1).

As from the definition of ET of the IUPAC, the first condition for the development of an ET is that we must have an array of low-selective sensors with cross-response features that provide some added value in the generation of analytical information.

Hence, we should firstly confirm that differentiated signals are observed for the different electrodes, and that those are related to the phenomena under study. That is, generating data rich enough that can be a useful departure point for the multivariate calibration model. In our case, we can see how that can be achieved thanks to the use of the different modifiers and the metal wires (Figure 2); even in the case of Pt nanoparticles and Pt wire, where still some differences may be observed. In this case probably due to catalytic phenomena attributable to large surface to volume ratio attributable to the nanoparticles.

<FIGURE 2>

To provide an objective measure of the differences observed for the different sensors towards wine samples, correlation between their responses was evaluated by means of the comparison factor *fc* which considers the area under both signals when superimposed (Figure S1, supplementary info). Briefly, *fc* is defined as the ratio of the area intersected by both curves to the total area under both curves, and ranges from 0 to 1 depending on signals similarity; it values 0 when two signals have nothing in common and increases its value as similarity does. Thus, obtaining a unique numerical value that provides a measure of its resemblance. In our case, calculated values are summarized in Table S1 (supplementary info) where, as can be seen, those are around 0.7 and even as low as 0.54. These numeric values corroborate and objectivise what is already seen in Figure 2.

After this initial confirmation, the next step is to assess whether or not the recorded signals are related to the phenomena under study. However, this can not always be checked so easily, requiring the use of advanced chemometric tools which, as also defined by IUPAC, are the ones extracting and interpreting the relevant information. Therefore, in the next sections we will focus on discerning the richness of the generated data and its suitability for the desired outputs.

At this point, given the complexity of the generated data, FFT was used as a preprocessing step in order to reduce the high dimensionality requirements of the processing, which additionally may result in an improvement of model's performance. In this manner, each voltammogram was compressed down to only 32 coefficients without any loss of significant information (Figure 3) [30]; this allowed for a compression of the original data up to 93.75% (from 512 current values down to 32 coeffs.), prior to pattern recognition or numerical modelling.

<FIGURE 3>

### *3.1 Identification of the DO for the same grape variety*

As a first attempt to assess whether or not the ET would be capable to distinguish the wine samples based on its DO, we focused on a specific grape variety and analyzed some wine samples from that variety, but produced in different regions. Hence, reducing the source of variability and ensuring the source of the discrimination factor; that is, to asses if there is or not an effect due to its origin.

To this aim, a total subset of nine samples, all from *Garnatxa Blanca* variety, produced in three different DO regions (*Empordà*, *Terra Alta* and *Montsant*) were initially considered. Samples were analyzed as previously described in section 2.4, and an extract of the recorded signals has already been shown in Figure 2.

Once confirmed the cross-response features of the ET, we should look now for (dis)similarities along the recorded signals that might indicate whether or not analyzed samples might be distinguished by means of the ET. Hence, looking more deeply in the voltammetric responses, we can observe some distinguished features that seem to originate depending on the DO; e.g. some anodic peaks that can be observed around

+1.0 V for graphite-epoxy sensor (Figure 4), but also at the anodic wave in the region -0.5 to -1.0 V.

<FIGURE 4>

To confirm this differentiated behaviour, voltammetric responses were compressed employing FFT, and obtained coefficients were analyzed employing PCA (Figure 5); an unsupervised method which provides a better representation of samples (dis)similarities, but not performing its classification. As could be expected from the voltammograms, the PCA plot shows how some samples seem to group in clusters, thus indicating some similarities between those samples and suggesting that the ET should be capable of distinguishing such factor (i.e. the effect of the different DOs in the final wine). Moreover, it should be also noticed that with only the first two PCs, the accumulated explained variance was ca. 79.8%; a large value which means that most of the variance contained in the original information is now represented by only these two new coordinates.

<FIGURE 5>

### *3.2 Discrimination of different DOs*

Due to the satisfactory trend already observed in the previous analysis, the whole set of samples were analyzed with the ET array and recorded signals compressed employing FFT as previously done, but this time LDA was chosen for pattern recognition of the different DOs. This alternative was chosen given that, unlike PCA which only provides a visualization tool of the variability of the data, LDA is a supervised method that allows to actually build a classification model [27]. That is, LDA explicitly attempts to model the difference between the classes of data, while PCA does not.

Therefore, the whole set of 71 samples was categorized according its DO as follows (number of samples): *Empordà* (10), *Penedès* (11), *Costers del Segre* (8) *Terra Alta* (16), *Priorat* (7), *Montsant* (7), *Catalunya* (10) and *Tarragona* (2). Unfortunately, compared to the other classes, very few samples from DO *Tarragona* were available, and hence it would result problematic to build a proper classification model without overfitting it if those were included. Accordingly, those samples were not considered for further calculations.

Lastly, as LDA is a supervised method, some samples from the set must be left out when building the model so that they can be used to assess its performance. In our case, the model was trained with 80% of the data (training subset), using the remaining 20% of the data (testing subset) to characterize the accuracy of the classification model and obtain unbiased data (Tables S3 and S4, supplementary info).

<FIGURE 6>

Figure 6 displays the distribution of the wine samples along the first three new coordinates, showing an accumulated variance of 94.8%; a high value indicating that nearly all the variance contained in the original information is represented now by only these three new functions. As can be observed, discrimination of the different wines according to its DOs can be achieved with this simple analysis of the scores. Nevertheless, it should be taken into account that the actual LDA model is composed by 6 functions (number of groups - 1) and that all of them are used to perform the classification task; although not being possible to visualize it.

Despite the good clustering observed in the built pattern recognition model (Figure 6), its actual performance should be assessed employing the samples from the testing subset, and not only the ones from the training subset. To this aim, the generated model was used to predict the expected DO for the 14 samples that were left out (not being used at all) during the modelling stage and predicted classes were compared to the expected ones. The corresponding confusion matrix was then built (Table 1), allowing calculating the performance of the model by means of three different indicators: classification rate, sensitivity and specificity.

<TABLE 1>

The former corresponds to the ratio between the number of samples correctly classified and the total number of samples. While the latter two, are related to the number of false positives or false negatives. Sensitivity is calculated as the percentage of objects of each class identified by the classifier model, and specificity as the percentage of objects from different classes correctly rejected by the classifier model;

averaging those for the classes. In this case, values reached 92.9%, 92.9% and 98.8% for the classification rate, sensitivity and specificity, respectively.

Similarly, in order to evaluate if the only miss-classified sample could be an outlier, model performance was also evaluated employing the leave-one-out strategy, regardless the fact this has been sometimes criticized as overoptimistic [8]. The idea here is that the use of a larger number of samples in the training subset might improve the model generalization ability. In this manner, LDA model was rebuilt, and as it could be expected given that wines are already subjected to strict DO controls, none of the samples were now miss-classified, achieving a classification rate of 100% in terms of accuracy, sensitivity and specificity.

### *3.3 Prediction of global scores of the sensory panel*

To further assess the ability of the ET as a tool for wine tasting, the correlation between the ET measurements and the global scores assigned by the sensory panel was also attempted. That is, the average scores assigned to each wine by the sensory panel were modelled from the set of voltammetric responses, previously compressed with FFT, by means of an ANN model.

Unlike the previous cases, where qualitative information was extracted, a quantitative model was built this time. For this, ANN was selected as the modelling tool due to its superior performance compared to linear methods; i.e. more flexible modelling methodologies, since both linear and non-linear functions can be used (or combined) in the processing units [31]. Thus, ANNs are specially suitable to be used with non-linear sensor responses and allow for more complex relationships between a high-dimensional descriptor space and the given retention data; all this leads to a better predictive power of the resulting ANN model compared with other linear methods [25], although if linearity exists, a proper behaviour may be obtained also with the latter.

As before, the set of samples were split into two subsets: the training subset (49 samples, 71%) used to build the model and the testing subset (20 samples, 29%) used to assess its performance. Again, this division was randomly performed, taking as only precaution to avoid that extreme values are used in the testing subset; that is, to avoid extrapolation from the model.

After a systematic study to optimize the topology of the neural network (i.e. training algorithm, number of hidden layers, number of neurons, transfer functions, etc.), the final architecture of the ANN model had 80 neurons (corresponding to the selected FFT coeffs. after CI analysis) in the input layer, 6 neurons and *logsig* transfer function in the hidden layer and one neuron and *tansig* transfer function in the output layer, viz. the score assigned by the sensory panel.

Subsequently, comparison graphs of predicted vs. expected scores, both for the training and testing subsets, were built and the linear fitted regression parameters were calculated to easily check the performance of the ANN model (Figure 7). As it can be observed, a satisfactory trend was obtained for both subsets, with regression lines close to the theoretical ones; i.e. values of slope and intercept close to 1 and 0, respectively.

<FIGURE 7>

To numerically assess the predictive ability of the ET three different parameters were calculated: Standard Error of Prediction (SEP), Ratio of standard error of Performance to standard Deviation (RPD) and Range Error Ratio (RER) [32]; with obtained values of 0.30, 1.48 and 5.93, respectively.

However, despite the good trend observed, it is true that the observed dispersion, especially for the testing subset, is larger than desirable for a quantitative application; but, still good enough to be considered at least as a semi-quantitative approach. It should be remembered anyhow, that still correlation and the followed trend is highly significant. Moreover, considering the subjective nature of the scores, which are provided by the sensory panel.

As an additional verification of the proposed approach, a Student's paired samples *t* test for the testing subset was performed. Obtained experimental *t* value was 1.42, while the critical tabulated *t* value with 95% confidence level and 19 degrees of freedom is 2.09. Therefore, confirming the agreement observed between the ET response and the scores assigned by the sensory panel.

And last but not least, it should be taken into account the complexity of the approach and the promising capabilities that this represents; i.e. achieving to artificially reproduce the tasting perception of a sensory panel.

## 4. Conclusions

Electronic tongues have proved to be a useful tool for wine tasting, either for qualitative or quantitative analysis, especially suitable for screening purposes, with interesting advantages as might be its simplicity and low cost. Concretely, in this case we reported its application towards the qualitative discrimination of different wine DOs and the quantification of the global score assigned by a sensory panel; the latter corresponding to the first attempt to correlate such parameter in wines, to the best of author's knowledge.

Moreover, the use of both bulk-modified electrodes and metallic electrodes has also been demonstrated to be a feasible way to obtain sensors with differentiated and cross-selectivity response towards desired samples; which if required, can be easily miniaturized and mass-produced through the use of screen-printed technologies.

Finally, future efforts with this approach may involve its further validation (e.g. extending it to the analysis of wines from other regions) and the miniaturization of the system. Beyond, further work is still required to improve the biomimetic capabilities of the ET array to artificially assess the tasting score of the wines. In this direction, this might be improved through the incorporation of new voltammetric electrodes in the array or through the combination of the ET response with sensors from other nature such as would be an electronic nose or an electronic eye. That is, to better reproduce the overall perceptions perceived by the sensory panel when tasting a wine (i.e. taste, odour and colour) in what might be considered as an electronic panel.

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**Table 1.** Confusion matrix built according to the DO category obtained using the LDA model for the testing subset samples.

| | *Emp* [b] | *Pen* [b] | *CdS* [b] | *TA* [b] | *Pri* [b] | *Mon* [b] | *Cat* [b] |
|---|---|---|---|---|---|---|---|
| *Emp* [a] | 1 | 0 | 0 | 0 | 1 | 0 | 0 |
| *Pen* [a] | 0 | 2 | 0 | 0 | 0 | 0 | 0 |
| *CdS* [a] | 0 | 0 | 2 | 0 | 0 | 0 | 0 |
| *TA* [a] | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| *Pri* [a] | 0 | 0 | 0 | 0 | 2 | 0 | 0 |
| *Mon* [a] | 0 | 0 | 0 | 0 | 0 | 2 | 0 |
| *Cat* [a] | 0 | 0 | 0 | 0 | 0 | 0 | 2 |

[a] Expected; [b] Found.
Emp: *Empordà*; Pen: *Penedès*; CdS: *Costers del Segre*; TA: *Terra Alta*; Pri: *Priorat*; Mon: *Montsant*; Cat: *Catalunya*.

# FIGURE CAPTIONS

**Figure 1.** Comparison of the recognition processes of a sample by the biological (top) and the biomimetic systems (bottom).

**Figure 2.** Example of the different voltammograms obtained with the different sensors forming the ET array for an arbitrary wine sample. Signals provided correspond to: (1) graphite–epoxy sensor, (2) Pt nanoparticle modified sensor, (3) cobalt (II) phtalocyanine modified sensor, (4) Cu nanoparticle modified sensor, (5) Pt metallic sensor and (6) Au metallic sensor.

**Figure 3.** FFT data pre-processing. Representation of the coefficient of determination ($R^2$, x) and $f_c$ (○) as the measure of signal reconstruction degree, vs. the number of Fourier coefficients used. For better representation of the data, Y-axis is plotted in linear-scale, while X-axis is in log-scale.

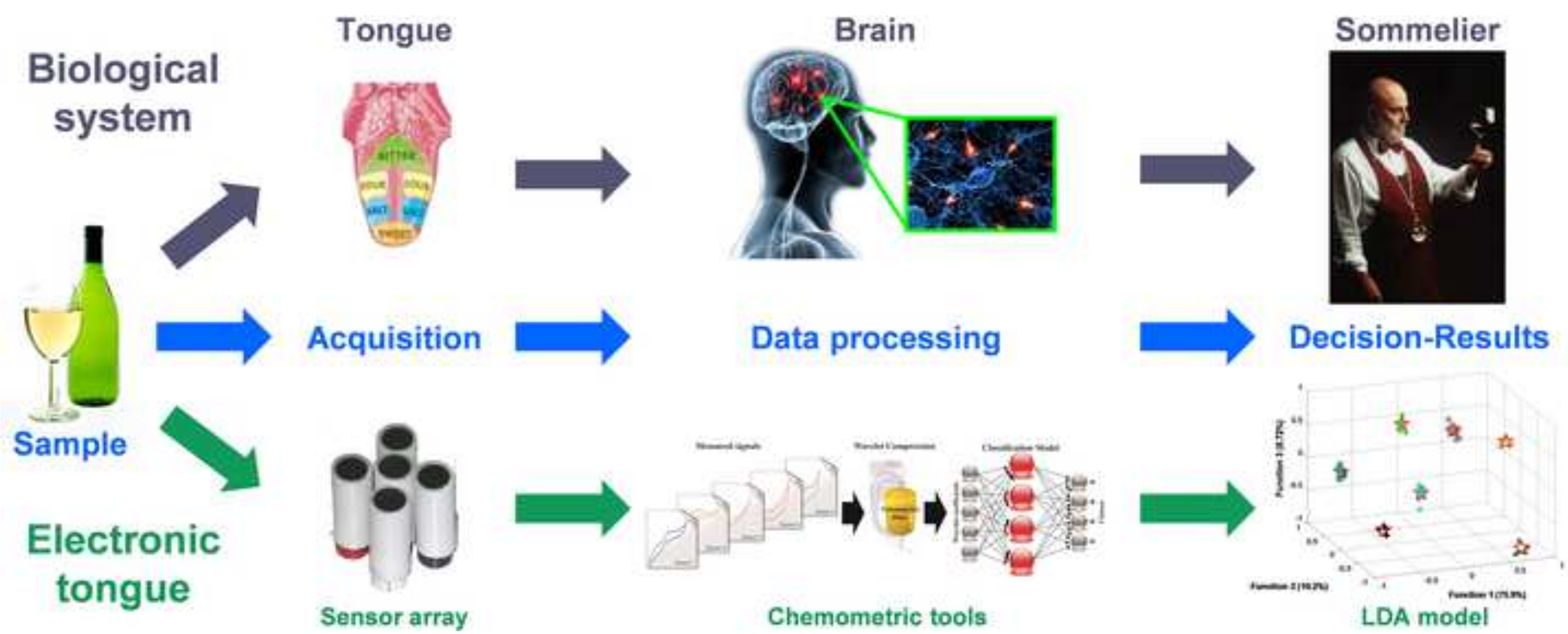
**Figure 4.** Example of the different voltammograms obtained with graphite–epoxy sensor for some samples of the same grape variety *Garnatxa Blanca*. Signals provided correspond to: (solid line) *Empordà*, (short dashed line) *Terra Alta* and (long dashed line) *Montsant* DOs.

**Figure 5.** Score plot of the first two components obtained after PCA analysis of *Garnatxa Blanca* wine samples: (■) *Empordà*, (●) *Terra Alta* and (▲) *Montsant*.

**Figure 6.** Score plot of the first three functions obtained after LDA analysis of the wine samples, according to their DO: (■) Empordà, (▼) Penedès, (♦) Costers del Segre, (●) Terra Alta, (✚) Priorat, (▲) Montsant and (✡) Catalunya; also the centroid of each class is plotted (★).

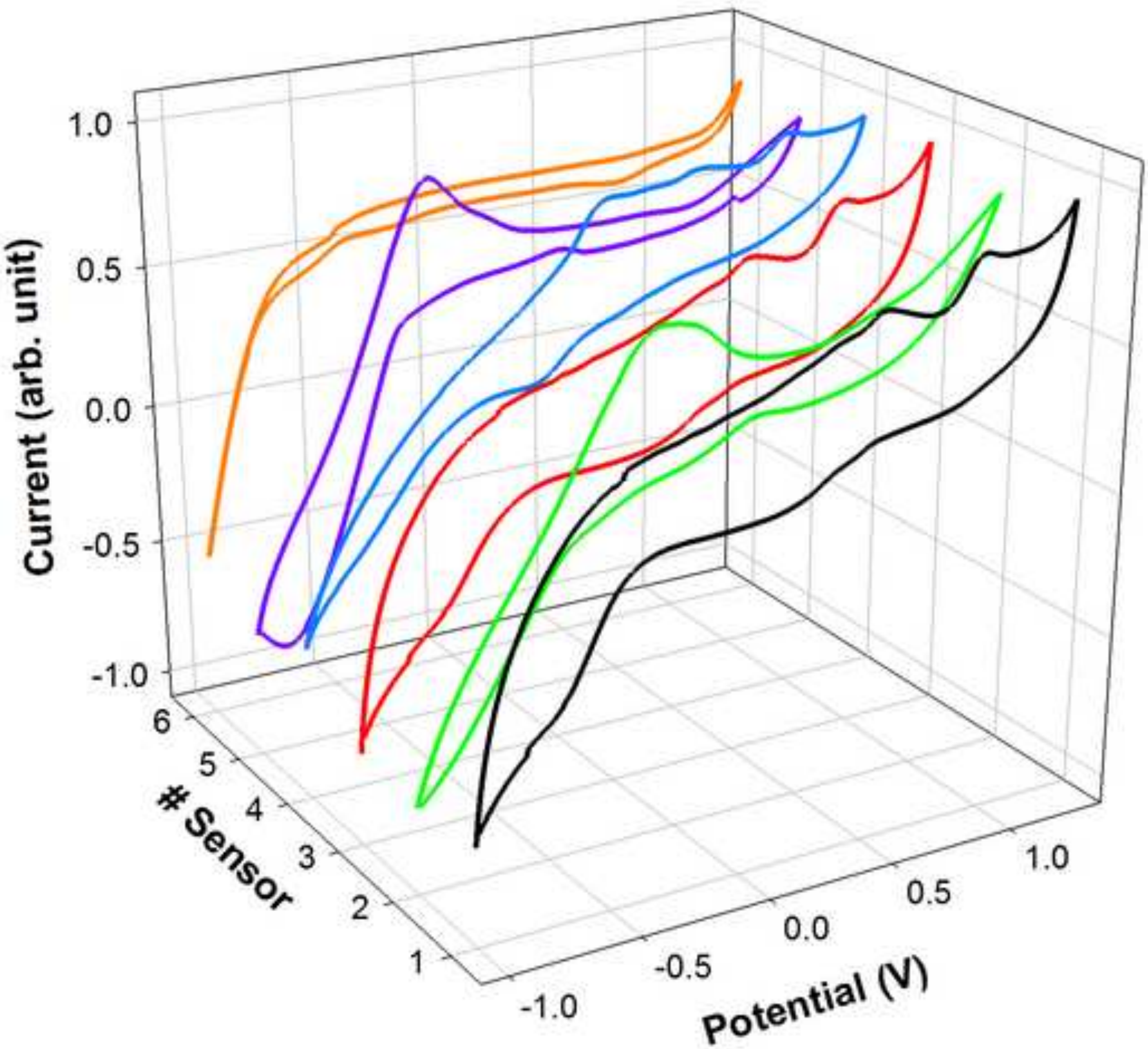
**Figure 7.** Modelling ability of the optimized FFT-ANN for the prediction of wines global scores assigned by the sensory panel. Set adjustments of obtained vs. expected values, both for training (●, solid line) and testing subsets (○, dotted line). The dashed line corresponds to theoretical diagonal line.

Figure1



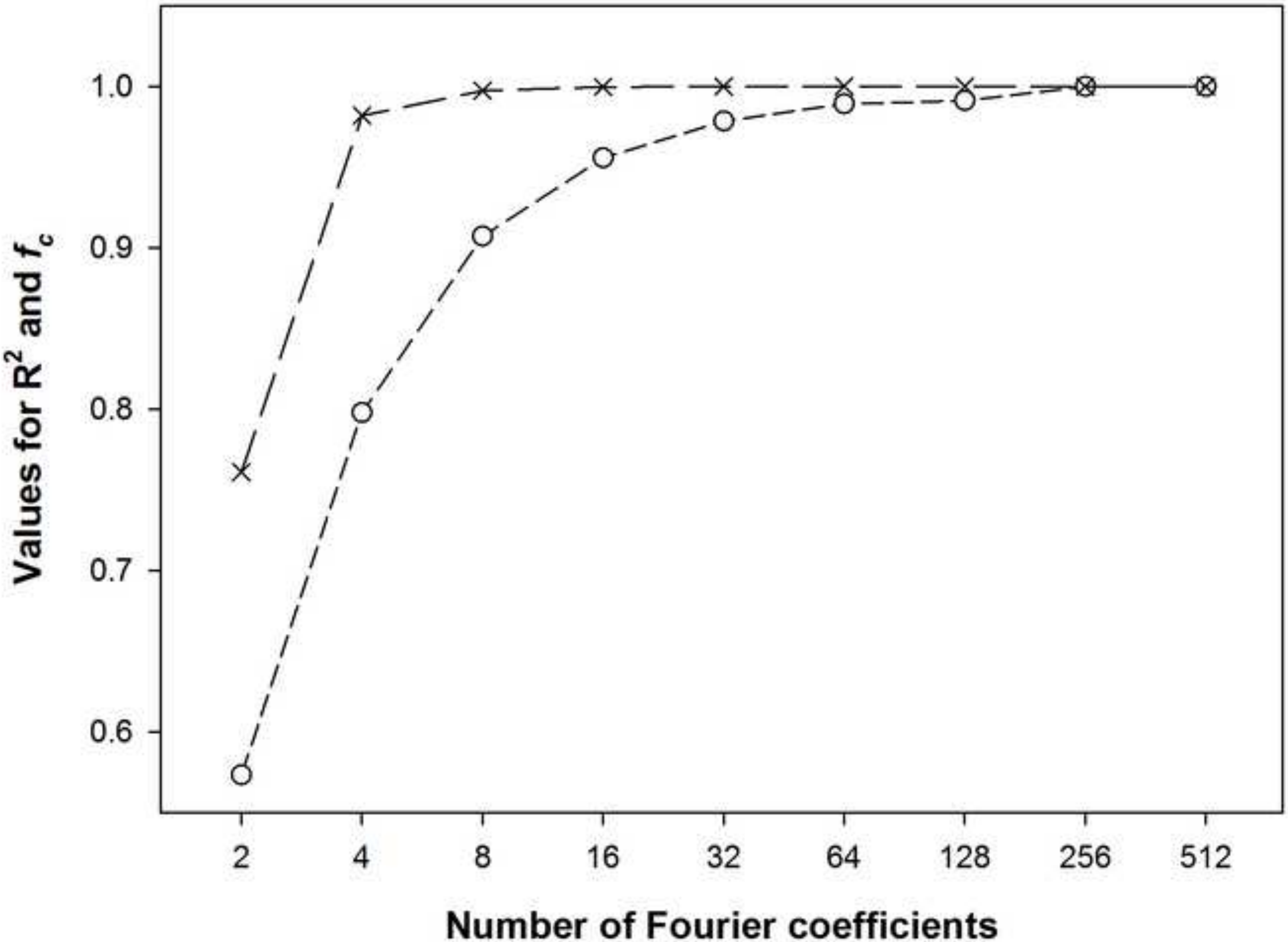
Biological system
Tongue
Brain
Sommelier
Sample
Acquisition
Data processing
Decision-Results
Electronic tongue
Sensor array
Chemometric tools
LDA model

Figure2



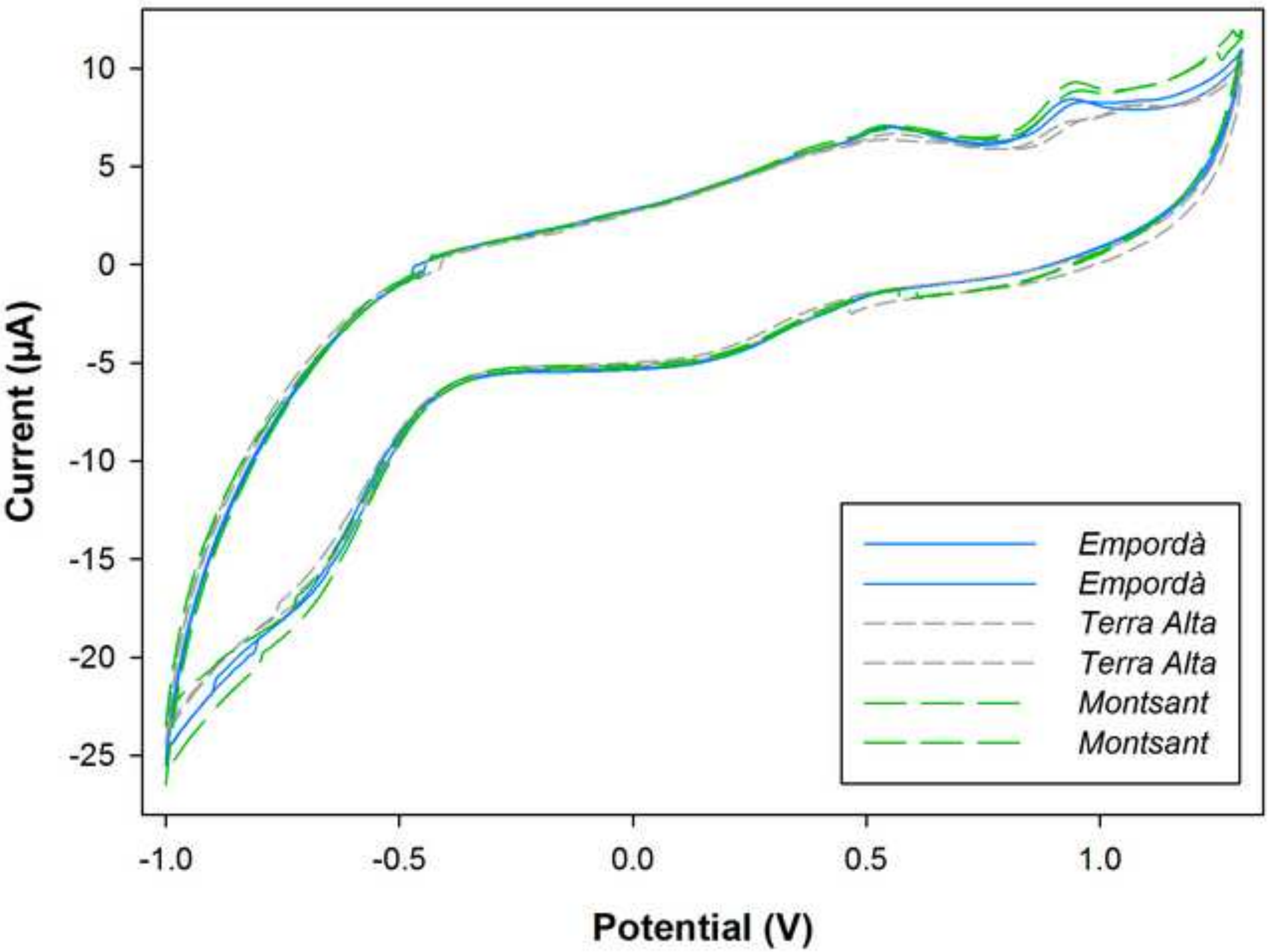
Current (arb. unit)
1.0
0.5
0.0
-0.5
-1.0
# Sensor
6
5
4
3
2
1
Potential (V)
-1.0
-0.5
0.0
0.5
1.0

Figure3



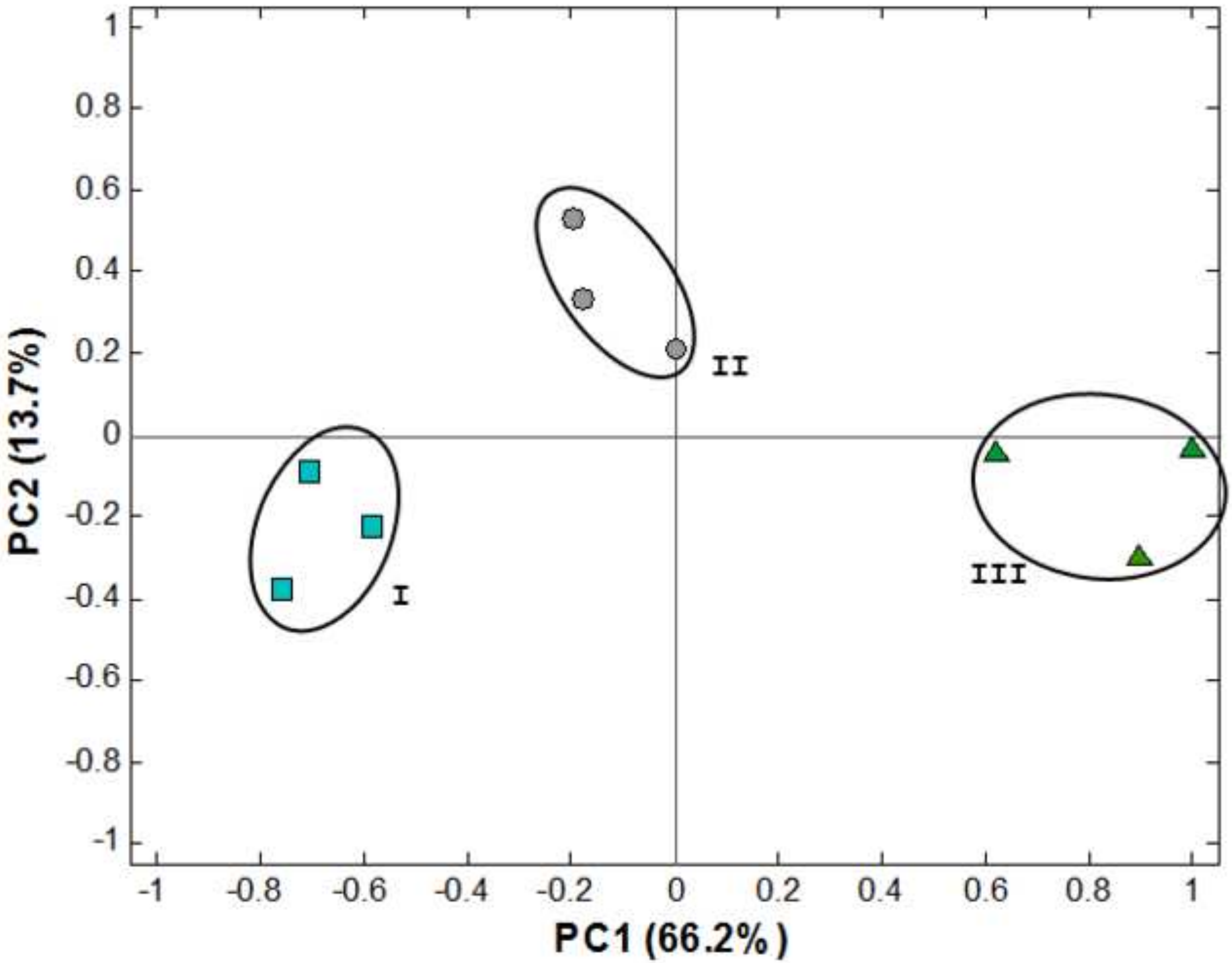
Values for R2 and fc
1.0
0.9
0.8
0.7
0.6
2
4
8
16
32
64
128
256
512
Number of Fourier coefficients

Figure4



10
5
0
-5
-10
-15
-20
-25
Current (µA)
-1.0
-0.5
0.0
0.5
1.0
Potential (V)
Empordà
Empordà
Terra Alta
Terra Alta
Montsant
Montsant

Figure5



1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
PC2 (13.7%)
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
PC1 (66.2%)
I
II
III

Figure6

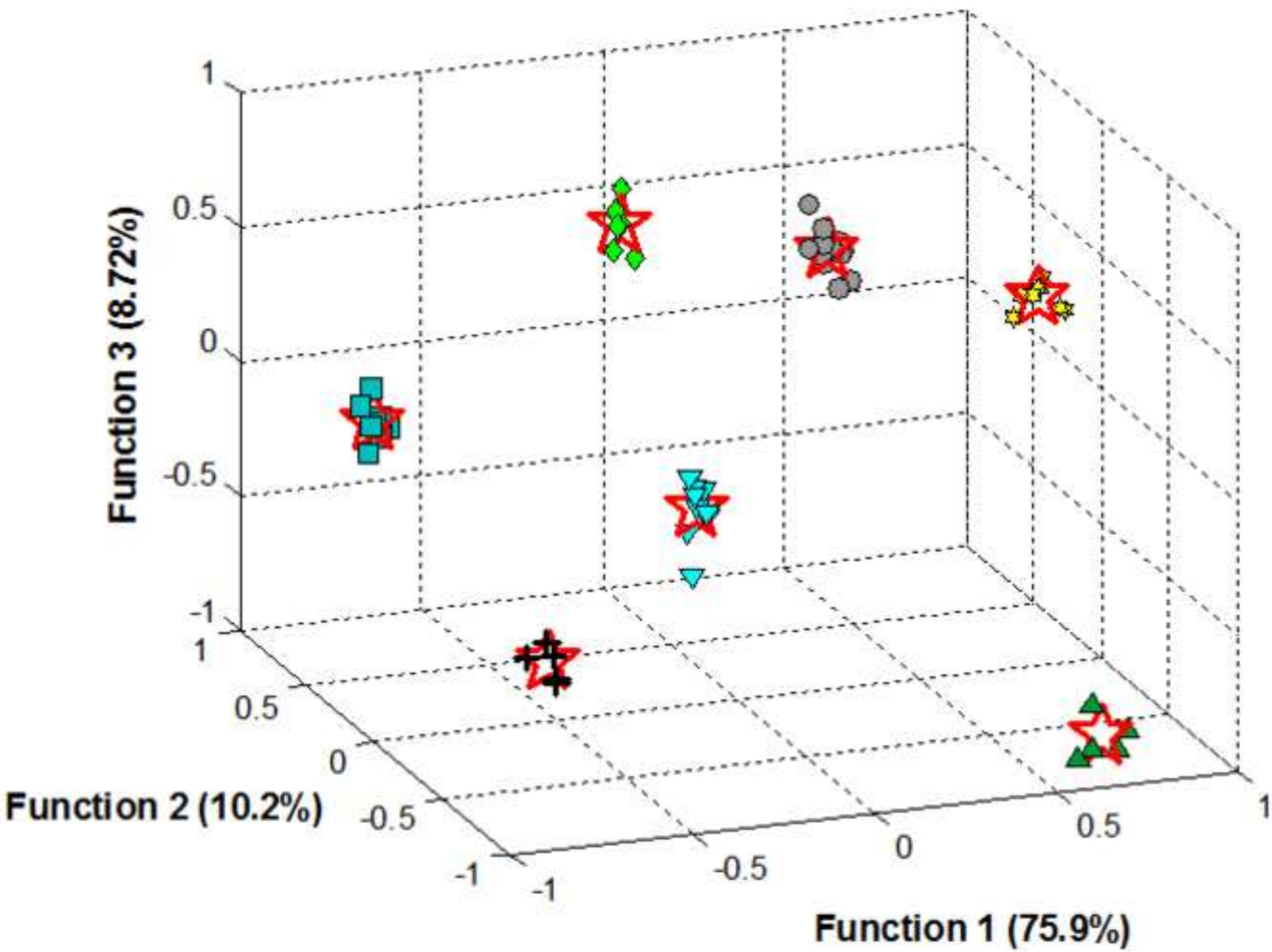
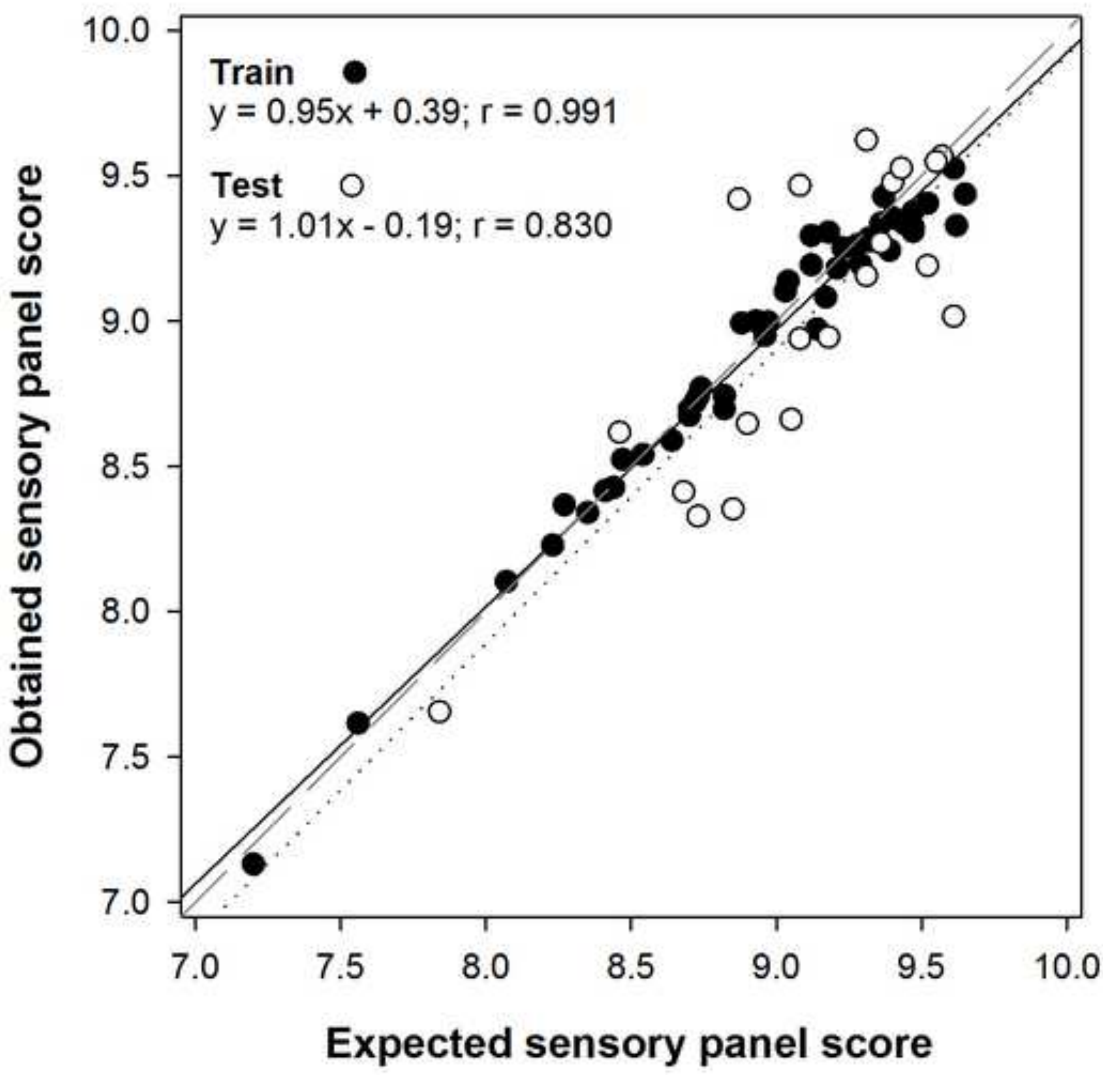

Function 3 (8.72%)
1
0.5
0
-0.5
-1
1
0.5
0
-0.5
-1
Function 2 (10.2%)
-1
-0.5
0
0.5
1
Function 1 (75.9%)

Figure7



Train
y = 0.95x + 0.39; r = 0.991
Test
y = 1.01x - 0.19; r = 0.830
Obtained sensory panel score
Expected sensory panel score
10.0
9.5
9.0
8.5
8.0
7.5
7.0

**Xavier Cetó** completed his M.Sc. degree in chemistry in 2009 at the *Universtitat Autònoma de Barcelona*, and received his Ph.D. in Analytical Chemistry in 2013 from the same university. At present, he is a postdoctoral researcher at Mawson Institute. His main research topics deal with the development of new voltammetric (bio)sensors and the application of electronic tongues and chemometric tools for data analysis, mainly employing voltammetric (bio)sensors, albeit also potentiometric ones

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