Voltammetric BioElectronic Tongue for the analysis of phenolic compounds in rosé cava wines

Xavier Cetó [a], Josefina Capdevila [b], Santiago Mínguez [b] and Manel del Valle [a,*]

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

[b] *Estació de Viticultura i Enologia, INCAVI, Vilafranca del Penedes, Spain*

Abstract

A BioElectronic Tongue (BioET) based on a sensor array comprising 4 voltammetric sensors plus pattern recognition and multivariate calibration data processing tools was applied towards the analysis of cava rosé wines. A total of 20 different samples were analyzed using cyclic voltammetry without any sample pretreatment. Obtained responses were preprocessed employing *windowed slicing integral* method in order to compress and extract significant features from the recorded data. Extracted coefficients were then evaluated by means of Principal Component Analysis to visualize some initial patterns, while quantification of different polyphenols indexes was achieved by an Artificial Neural Network (ANN) model. In this manner, three different classical indexes related to total polyphenol content (i.e. I_{280}, I_{320} and Folin-Ciocalteu index) plus two indexes related to more specific families of those (i.e. total tannins and anthocyanins content) were correlated with sensors responses.

Keywords: Electronic Tongue; Artificial Neural Networks; voltammetric biosensors; cava wine; polyphenols; tannin; anthocyanin

* E-mail: manel.delvalle@uab.cat; tel: +34 93 5811017; fax: +34 93 5812379

1. Introduction

Phenolic compounds in wine include a large group of chemical compounds that affect its taste, colour and mouthfeel [1]. These compounds include phenolic acids, stilbenoids, flavonols, dihydroflavonols, anthocyanins, flavanol monomers (catechins) and flavanol polymers (proanthocyanidins); which can be broadly separated into two main categories: flavonoids and non-flavonoids. Flavonoids include the anthocyanins and tannins which contribute to the colour and mouthfeel of the wine [2]; while non-flavonoids include the stilbenoids such as resveratrol, and phenolic acids such as benzoic, caffeic and cinnamic acids.

Beyond its contribution to the wine sensorial features (e.g. to its colour, body and astringency), most of these compounds are powerful antioxidants with great health benefits derived from their action as free radical scavengers and inhibitors of lipoprotein oxidation [3]. In this sense, there are evidences that wine antioxidant properties are due to phenolic components, which total content is directly correlated with their antioxidant capacity [4], and that wine without these components loses these properties.

A part from total polyphenol content, tannins and anthocyanins are two classes of flavonoids with huge importance, especially in the case of rosé and red wines, as they have a clear influence in its colour and mouthfeel, particularly in its astringency [5]. On the one hand, tannins can affect the colour, ageing ability and texture of the wine. While tannins cannot be smelled or tasted, they can be perceived during wine tasting by the tactile drying sensation and sense of bitterness that they can leave in the mouth [5]. On the other hand, anthocyanins are odourless and nearly flavourless compounds, contributing to wine taste as a moderately astringent sensation; besides concentration of those dictates the colour of the wine [5].

As a results, given its importance, several methods to quantify phenolic compounds (either total content or individual identification) are reported in the literature [6]; over those, most common ones include chromathography or specthrophotometry. However, these procedures usually require additional preparative steps, the use of heavy, dedicated laboratory instruments and are not suitable for on-site analysis.

On that account, biosensors are arising as an alternative to traditional laboratory techniques given their low cost and their ease of use to carry out on field analyses. In the case of phenolic compounds, previous attempts are based on the development of amperometric biosensors based on the immobilization of basically three different

enzymes: laccase, tyrosinase and/or peroxidise [7]. Although the applicability of biosensors to the analysis of antioxidant compounds is promising and represents an attractive alternative for their detection, further work is required to avoid and/or take into account the interference problem [8].

To overcome such difficulties, chemometric tools such as Principal Component Analysis or Artificial Neural Networks (ANNs) can be used [9, 10]. This coupling consists in the integration of an array of sensors (with marked mix-response towards the desired species) and a chemometric processing tool (able to interpret and extract meaningful data from the complex readings); an approach known as BioElectronic Tongue [11].

The present work reports the application of a voltammetric BioET towards the analysis of phenolic compounds in cava rosé wines, for the prediction of both global phenolic content and total classes content. As such, it combines the responses from an array of voltammetric biosensors, plus an advanced response model employing a specifically trained Artificial Neural Network, with pretreatment of data employing *windowed slicing integral*.

2. Experimental

2.1 Reagents and solutions

All reagents used were analytical grade and all solutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA). Tyrosinase from mushroom (EC 1.14.18.1, 4276 U mg^{-1}), laccase from Trametes versicolor (EC 1.10.3.2, 21 U mg^{-1}), copper nanoparticles (< 50 nm) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Folin-Ciocalteu's reagent and sodium carbonate were purchased from Panreac Química (Barcelona, Spain).

2.2 Samples under study

A total set of 20 rosé cava wine samples were analyzed. Those samples were selected so as to obtain a set of samples with sufficiently differentiated total polyphenol content and grape varieties (e.g. *Pinot noir*; *Grenache*; *Mourvèdre*, also known as *Monastrell*; *Trepat* or *Xarel·lo*). Moreover, although all the samples considered were from Catalonia region, different wine regions inside this were also considered; i.e. different denomination of origin (D.O.). In this context, Table 1 summarizes detailed

information about the brand of samples under study as well as analytical information of those samples.

<TABLE 1>

2.3 Standard Methods

For comparison purposes, different polyphenols indexes (related to different classes of them) were analyzed by classical methods for both subsets to extract additional quantitative analytical information that may complement ET qualitative response if their level could be modelled properly. On the one hand, three indexes related to total polyphenol content were evaluated, i.e. Folin-Ciocalteu, I_{280} and I_{320} [12]; while in the other hand, total tannins and anthocyanins (two classes of phenolic compounds) were also quantified by standard procedures.

2.3.1 Folin-Ciocalteu index

Firstly, the Folin-Ciocalteau (FC or Folin) index of the cava wines was determined spectrophotometrically [13]. Fc method is a colorimetric assay measuring the amount of phenol needed to inhibit the oxidation of the Folin-Ciocalteu reagent (a mixture of phosphomolybdate and phosphortungstate, which are reduced to the respective oxides).

The FC test was carried out according to the following procedure: 1 mL of sample (cava wines were previously diluted 1:100 or 1:50), 6 mL of deionized water, 0.5 mL of Folin-Ciocalteu reagent and 2 mL of a 20% sodium carbonate solution were added in this order to a 10 mL beaker and diluted to volume with deionized water. The resulting solution was stirred and allowed to react for half an hour at room temperature in darkness. The absorbance was then read at 760 nm using a spectrophotometer PerkinElmer Lambda 20 UV/VIS (MA, USA). Total phenolic content, expressed in gallic acid equivalents, was evaluated from the absorbance value by interpolation into the calibration plot obtained with gallic acid standard solutions, multiplying the resulting value by 10 and by the proper dilution factor. Different dilution factors were applied given when carrying out specthrophotometric measurements absorbance value should be around 0.3 [13].

2.3.2 I_{280} and I_{320} indexes

Additionally, for the determination of the total content of polyphenolic compounds in cava wines the polyphenol indexes I_{280} and I_{320} were also considered. While FC is the recommended reference method, the use of those two indexes has arisen as an alternative to the first given its shorter time of analysis and simplicity. Although between them, the most common one is the I_{280} index, I_{320} index is also considered to be important as sometimes there could be a shift on the maximum of absorbance, especially in white wines [14]. Additionally, the latter is related to hydroxycinnamate compounds, a group of phenolic compounds [12].

For its determination, cava wine was diluted with water (1:100 or 1:50) and the absorbance was measured directly at 280 nm and 320 nm. The values of I_{280} and I_{320} for each sample were given as the absorbance multiplied by the proper dilution rate.

2.3.2 Tannins and anthocyanins

Lastly, tannins and anthocyans, which are two main classes of phenolic compouds belonging to flavonoids group, were also analyzed given its clear influence in the colour and mouthfeel of the wine [5].

For the detection of tannins, the analytical method applied was the acid butanol assay [14]. This method is based on the acid-catalysed oxidative cleavage of the C-C interflavanic bondo of proanthocyanindins in butanol-HCL. On the other hand, total anthocyanins were determined by the colour variation in function of pH [15].

2.4 Electrochemical measurements

2.4.1 Voltammetric sensor array

The voltammetric array was formed by four graphite-epoxy voltammetric sensors prepared using bare graphite C and adding different modifiers such as tyrosinase, laccase and copper nanoparticles to the bulk mixture – one component per electrode plus a blank electrode without any modifier.

Electrodes were prepared following the conventional methodology previously described [16]. Electrode fabrication begins with the preparation of the composite paste. For this, resin EpoTek H77 (Epoxy Technology, Billerica, MA, USA) and its corresponding hardener compound were mixed in the ratio 20:3 (w/w); afterwards a 15% (w/w) of graphite (50 μm BDH Laboratory Supplies) and a 2% (w/w) of the modifier (either the enzyme or the catalyst) were added to the previous mixture before hardening. Then, it was manually homogenized for 60 min, and afterwards, the paste

was allowed to harden for seven days at 40 ºC. Finally, electrode surface was polished with different sandpapers of decreasing grain size, with a final electrode area of 28 mm^2.

2.4.2 Measuring procedure

The amperometric measurement cell was formed by the 4-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 taken using a 6-channel AUTOLAB PGSTAT20 (Ecochemie, Netherlands), in a multichannel configuration, using GPES Multichannel 4.7 software package. For this, potential was cycled between -0.4 V and +0.8 V vs. Ag/AgCl, with a scan rate of 100 $mV \cdot s^{-1}$ and a step potential of 9 mV.

Electroanalytical experiments were carried out at room temperature (25 ºC) under quiescent conditions, and without any pretreatment or dilution of the sample. Prior to perform cava samples measurements, electrodes were first cycled in saline solution in order to get stable voltammetric responses, ensuring reproducible responses from the BioET array. Apart, all experiments were carried out without performing any physical surface regeneration of the working electrodes. In order to prevent the accumulative effect of impurities on the working electrode surfaces, an electrochemical cleaning stage was done between each measurement applying a conditioning potential of +1.0 V for a duration of 40 s after each experiment, in a cell containing 25 ml of distilled water [17].

2.5 Data processing

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

The whole cyclic voltammograms obtained from each sensor from the proposed sensor array were included in the data processing stage. In order to reduce the multidimensional data matrix generated in each measurement, a preprocessing stage employing the *windowed slicing integral* method was used [18]. In this way, the corresponding compressed voltammograms were processed employing either Principal Component Analysis (PCA) or Artificial Neural Networks (ANNs) models. The first

allowed to visualize some initial patterns, while the second one allowed the quantification of different analytical parameters related to polyphenolic content of cava samples.

Principal Component Analysis (PCA) allows the projection of the information carried by the original variables onto a smaller number of underlying ("latent") variables called principal components (PCs) with new coordinates called scores, obtained after data transformation. Then by plotting the PCs, one can view interrelationships between different variables, and detect and interpret sample patterns, groupings, similarities or differences [19]. Moreover, PCA is a useful method to reduce the dimensionality of large data sets, such as those from voltammetric sensor arrays.

Artificial Neural Networks (ANNs) consist of a number of simple processing units (or neurons) linked by weighted modifiable interconnections [20], originally designed to mimic the function of the human brain and applied to quantitative and qualitative analysis during the last decades [11]. Imitating the biological learning, they require a training process where the weights of those connections are adjusted, and build a model that will allow to carry out the prediction of the desired parameters (either qualitative or quantitative). Then, once the corresponding model is generated, it can be further applied to the prediction of the outputs for new samples by simply introducing the readings of the sensors of those to the model, hence obtaining a powerful analytical tool for rapid analysis of cava wine samples.

In order to find the appropriate ANN model, significant effort is needed to optimize the configuration details that determine its operation. Normally, this is a trial-and-error process, where several parameters (training algorithms, number of hidden layers, number of neurons in the different layers, transfer functions, etc.) are fine-tuned in order to find the best configuration to optimize the performance of the model [21].

3. Results and Discussion

3.1 Voltammetric responses

Under the conditions described in Section 2.4, a total of 20 samples were analyzed, registering a complete voltammogram for each of the samples. As can be seen in Figure 1, where examples of the different responses obtained for each kind of sensor are shown, currents monotonously increase as FC index (and other polyphenol indexes) increases, with some differentiated behaviour for each sensor. As a general trend,

oxidation of phenolic compounds onto electrode surface could be seen in all the cases, while also some reductive currents close to the region of 0 V are obtained for both biosensors and copper modified sensors due to its catalytic effect.

<FIGURE 1>

For developing an ET, the first necessary condition is to have analytical signals responding to the phenomena to which the objective is aimed, with variability among them and the different sensors forming the sensor array. Thus, proposed BioET seems to be a very useful departure point, generating very rich data. However, the extreme complexity of the generated signals (the set of voltammograms) hinders the processing step; especially if ANNs are to be used. As already commented, all these data is pretreated using a compression step, required to gain advantages in training time, to avoid redundancy in input data and to obtain a model with better generalization ability. In our case this was accomplished by the use of the *windowed slicing integral* [18].

3.2 Qualitative approach

As deducted from the voltammograms in Figure 1, it could be stated that BioET array seems to clearly respond to polyphenolic content of samples. Nevertheless, to detect any other similarities or capabilities to distinguish some extra features of cava samples, the corresponding compressed signals were processed employing PCA analysis (Figure 2). Despite PCA cannot be considered as a properly pattern recognition method, as it only provides a visual representation of the relationships between samples and variables, it is a very useful tool due to it provides insights into how measured variables cause some samples to be similar to, or how they differ from each other.

<FIGURE 2>

Firstly, it should be noticed that with only the first two PCs, the accumulated explained variance was ca. 98.4%; a large value which means that nearly all the variance contained in the original information is now represented by only these two new coordinates. Secondly, as can be seen by simply analyzing the plot visually, some clusters are obtained after this transformation, thus indicating some similarities between those samples.

Again, an as could be expected from the voltammograms, it could be seen how samples seem to group depending on their phenolic content; e.g. cluster II seems to group samples with very low phenolic content, while cluster V seems to involve samples with the highest content. Moreover, S18 correspond to a cava from *Brut Nature* class, while almost all the others belong to *Brut* class; thus BioET seems to be able also to distinguish this fact [17]. Moreover, a part from phenolic content BioET seems to be capable to distinguish other features such as the different ageing or region. For example, S20 belongs to a low aged cava, thus it might indicate that also S17 is a young one. Another particularity of S8 is its region, which belongs to *l'Empordà* while other samples are mainly from *Penedès* region.

After constructing this preliminary visualization model which permitted recognizing some initial patterns and similarities between samples, while confirming that BioET was also responding to phenolic content of the samples, the next step is the construction of a quantitative model that allows the quantitative prediction of phenolic content of rosé cava wine samples.

3.3 Prediction of phenolic compounds

After preprocessing the recorded voltammograms with *windowed slicing integral*, the obtained coefficients fed an ANN model in order to predict the total polyphenol index in wines. After a systematic evaluation of topologies, the final architecture of the ANN model had 44 neurons (4 sensors x 11 coeffs. obtained from the preprocessing stage) in the input layer, 10 neurons and *purelin* transfer function in the hidden layer and 5 neurons and *purelin* transfer function in the output layer, providing the five phenol indexes considered.

To evaluate the BioET response, leave-one-out method was used given the reduced data set. In this manner, each sample is quantified by means of the model derived from the other samples (all cases except the case itself). This process is repeated k times (as many as samples) leaving out one different sample each time, the one to be quantified, which acts as model validation sample. Thus, with this approach all samples are used once as validation. Finally, all data is grouped depending on if it was intervening in the training process or used in the external test subset, building the response model.

<FIGURE 3>

Comparison graphs of predicted vs. expected concentration for the five indexes were built, both for train and test subsets, to check the prediction ability of the obtained ANN model. As an example of those, Figure 3 shows the obtained plot for the prediction of tannins content of rosé cava wine samples. It may be seen that a satisfactory trend is obtained, with regression lines almost indistinguishable from the theoretical ones. Also, as usual in ANN models, lower dispersion is obtained for the training subset.

<TABLE 2>

Similarly, same plots were built for the other four indexes and regression lines were fitted, which regression parameters are summarized in Table 2. As expected from the comparison graphs, a good linear trend is attained for all the cases, but with better correlation coefficients in the training subsets due to the lower dispersion. Despite this, the results obtained for both subsets are close to the ideal values, with intercepts close to 0 and slopes and correlation coefficients close to 1.

Therefore, the presented approach herein represents the obtaining of an alternative analytical tool that allowed the simultaneous determination of five different phenolic compounds index in a simply, rapid and inexpensive way. Furthermore, with the same experimental setup, the proposed approach may be alternatively applied for the quantification of other specific compounds.

4. Conclusions

In summary, a voltammetric BioElectronic Tongue has been applied in cava rosé wine analysis in order to create a tool capable of quantifying total phenolic content as well as concrete classes total content. Concretely, proposed BioET was formed by an array of four biosensors modified with enzymes such as tyrosinase and laccase on one side and copper nanoparticles on the other so as to obtain a set of electrodes responding to the phenomena to which they are aimed and with some variability and cross-response features among them. Additionally, the use of chemometric tools such as ANNs allowed the quantification of five different phenolic compounds indexes widely used in wine sector; viz. Folin-Ciocalteu, I_{280}, I_{320}, total tannins and total anthocyanins.

In this sense, such strategy has demonstrated to be a powerful and much promising approach, with huge applications in wine making industry, as it allows reducing

considerably analysis time, avoids any sample pretreatment or the use of additional reagents, and what's more, allows the simultaneous determination of several indexes at the same time. Moreover, its performance characteristics may satisfy food industry requirements of precision, rapidity, sensitivity, simplicity and low cost required to be considered as a useful analytical tool.

Acknowledgments

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Table 1. Detailed information of the cava wine samples under study.

Sample	*Folin index*	*I_{280} (arb. unit)*	*I_{320} (arb. unit)*	*Tannins ($mg \cdot mL^{-1}$)*	*Anthocyanins ($mg \cdot mL^{-1}$)*	*Producer*
S1	5	8.50	5.41	100	9	Llopart
S2	10	18.55	7.87	393	26	Colet
S3	5.1	7.84	4.21	189	11	Berberana
S4	4.7	8.51	5.36	80	11	Freixenet
S5	5.7	11.12	5.08	119	14	Dibon
S6	7	12.04	5.98	281	22	Saint Clair
S7	7.1	10.99	6.30	216	17	Canals & Munné
S8	6.1	11.19	5.40	244	23	Castell Peralada
S9	4.5	8.84	4.39	85	9	Don Román
S10	7	11.79	6.51	229	17	Mont-Ferrant
S11	5.5	8.96	5.10	116	5	Codorniu
S12	4	7.41	3.81	50	8	Canals Nadal
S13	4.9	8.89	4.59	101	10	Castell de la Comanda
S14	4.3	8.49	3.96	150	7	Oriol Rossell
S15	6.1	10.85	6.37	123	4	Titiana
S16	6	9.25	4.27	173	5	Vallformosa
S17	4.5	6.90	4.23	110	0	Raventós i Blanc
S18	7.1	11.88	6.06	173	9	Fuchs de Vidal
S19	-	8.15	4.44	-	-	Cavas Hill
S20	-	-	-	-	-	INCAVI

Table 2. Results of the fitted regression lines for the comparison between obtained vs. expected values, both for the training and testing subsets of samples and the five considered phenolic compounds indexes (intervals calculated at the 95% confidence level).

			Training subset		
Phenolic indexes	*Correlation*	*Slope*	*Intercept*	*RMSE*	*Total NRMSE*
Folin index	1.018±0.147	-0.05±0.88	0.965	0.40	
I_{280} index (arb. unit)	0.955±0.109	0.45±1.14	0.977	0.55	
I_{320} index (arb. unit)	0.896±0.236	0.61±1.27	0.895	0.49	0.077
Tannins ($mg \cdot L^{-1}$)	0.987±0.060	2.14±11.02	0.993	9.50	
Anthocyanins ($mg \cdot L^{-1}$)	0.869±0.167	1.23±2.24	0.940	2.36	
			Testing subset		
Phenolic indexes	*Correlation*	*Slope*	*Intercept*	*RMSE*	*Total NRMSE*
Folin index	0.977±0.257	0.25±1.54	0.896	0.70	
I_{280} index (arb. unit)	0.973±0.308	0.51±3.22	0.858	1.52	
I_{320} index (arb. unit)	0.872±0.358	0.82±1.92	0.791	0.74	0.151
Tannins ($mg \cdot L^{-1}$)	0.942±0.261	4.82±47.71	0.886	41.38	
Anthocyanins ($mg \cdot L^{-1}$)	0.739±0.340	1.85±4.56	0.755	4.89	

FIGURE CAPTIONS

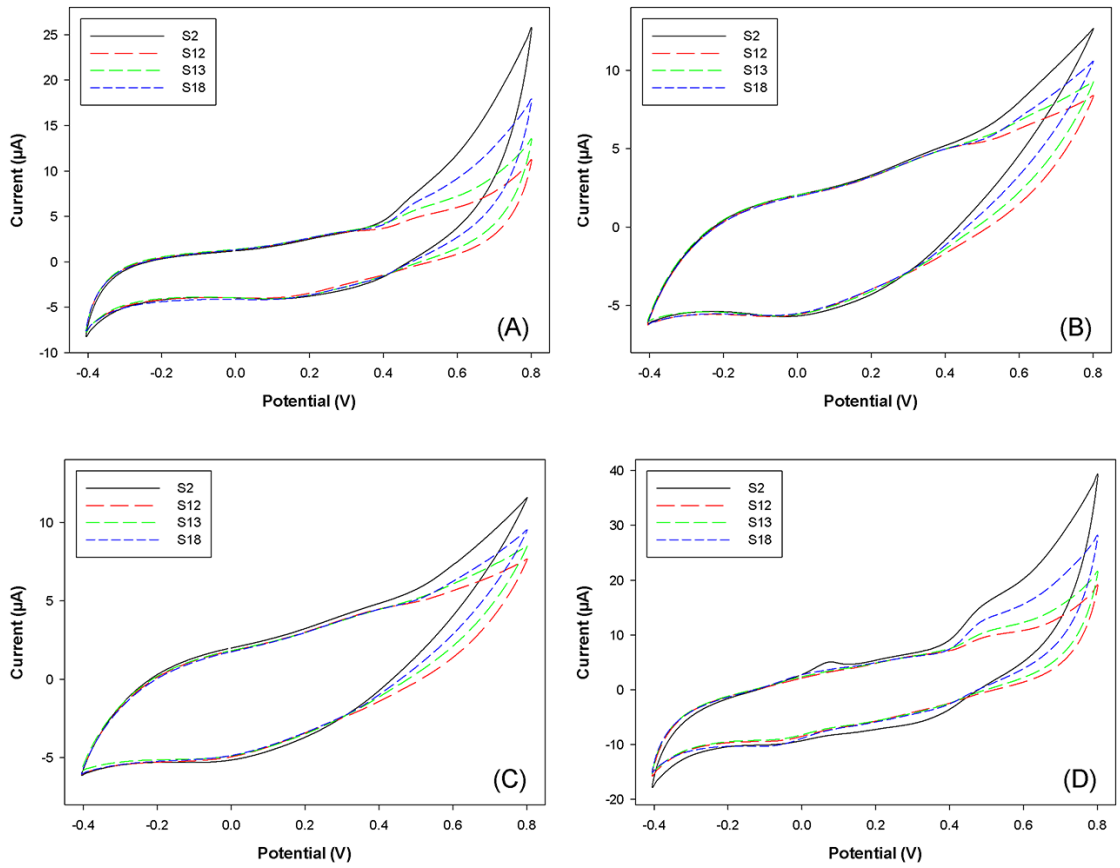

Figure 1. Example of the different voltammograms obtained with the different sensors forming the BioET array and for certain arbitrary cava wine samples are shown. Signals provided correspond to: (A) graphite-epoxy sensor, (B) tyrosinase biosensor, (C) laccase biosensor and (D) copper nanoparticle modified sensor.

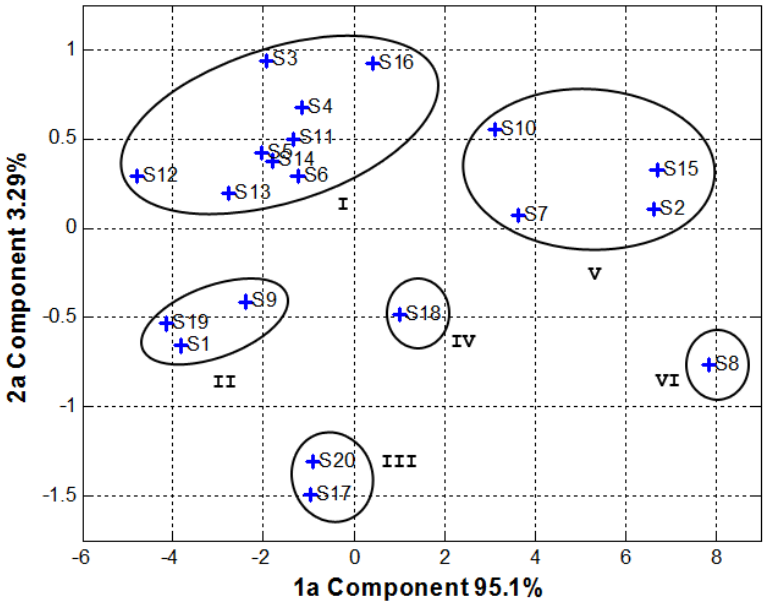

Figure 2. Score plot of the first two components obtained after PCA analysis of the cava wine samples.

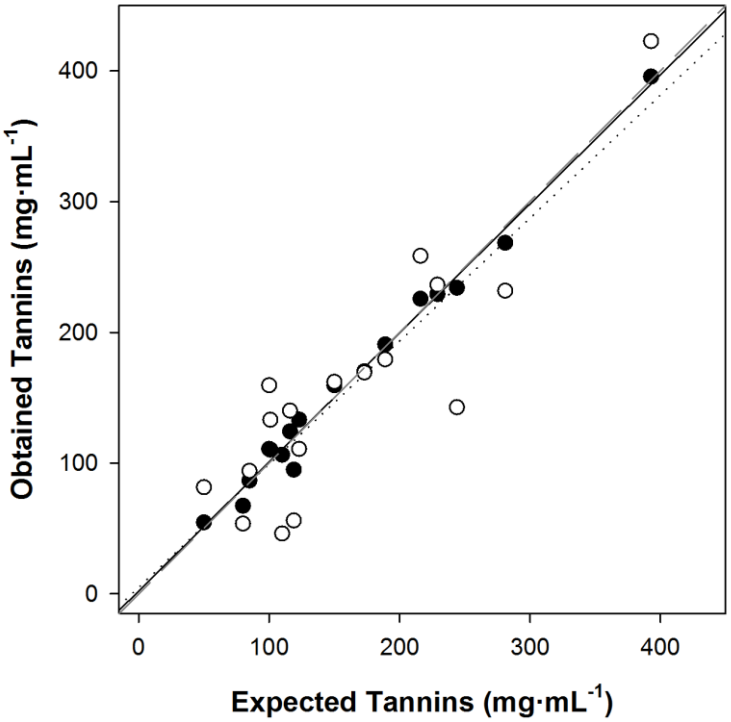

Figure 3. Example of the modelling ability of the optimized ANN showing the set adjustments of obtained vs. expected tannins content, both for training (●, solid line) and testing subsets (○, dotted line). Dashed line corresponds to theoretical diagonal line.