Electronic tongues to assess wine sensory descriptors

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Abstract

This work reports the application of an electronic tongue as a tool towards the analysis of wine in tasks such as its discrimination based on the maturing in barrels or the prediction of the global scores assigned by a sensory panel. To this aim, red wine samples were first analysed with the voltammetric sensor array, without performing any sample pretreatment. Afterwards, obtained responses were preprocessed employing fast Fourier transform (FFT) for the compression and reduction of signal complexity, and obtained coefficients were then used as inputs to build the qualitative and quantitative models employing either linear discriminant analysis (LDA) or partial least squares regression (PLS), respectively. Satisfactory results were obtained overall, with a classification rate of 100% in the discrimination of the type of barrel used during wine maturing, a normalized NRMSE of 0.077 in the estimation of ageing time (months) or 0.11 in the prediction of the scores (0-10) from a trained sensory panel (all for the external test subset).

Keywords: Electronic Tongue; voltammetric sensors; Partial least squares regression; wine; sensory panel; ageing

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1. Introduction

Wine is a specially regulated beverage, and its characterization receives much attention from different bodies and administrations [1-3]. However and despite the interest, wine quality control is still highly dependent on wine tasters; this is due to the difficulties to reproduce human perception using classical analytical techniques. That is, the challenge is to relate wine aroma or taste to specific compounds (and later to carry out its quantification), whereas it is known that perceived organoleptic properties originate on the contribution of the many compounds present and on their interactions.

Therefore, to get a system capable to artificially reproduce the wine tasting descriptors perceived by a skilled sensory panel, it should simultaneously detect a large spectrum of compounds and provide comprehensive information of the sample [4]. These two pre-requisites perfectly suit the concept of electronic tongues (ETs) and electronic noses [5], that thanks to their bioinspired nature, represent a straightforward solution when trying to analytically reproduce the sensory information perceived by subjects or tasters towards food or beverages.

ETs are based on the usage of an array of sensors with low-selectivity and/or cross response features in order to obtain some added value in the generation of analytical information; the latter is further coupled with advanced chemometric tools that allow the interpretation and extraction of meaningful data from the complex readings [6]. Thus, instead of focusing on finding highly selective sensors, ETs are inspired and try to mimic the sensory ability of taste in mammals: in these, a few receptors can respond to a large variety of substances thanks to the combinatorial principles used, and the obtained information is later processed by the brain [7].

On this account, ETs have started to be significant in foodstuff analysis over the last years, mainly used in the identification of different types/varieties/defects of samples or in the quantification of certain components present [8]. More specifically, ETs have already been successfully applied to the classification or identification of several beverage types: mineral water, wine, beer, spirits, milk, juice, tea or coffee, among others [9-11].

In the case of wine analysis [4], reported publications are aimed mainly to classification tasks (e.g. the discrimination of samples of different varieties/origins) [12-14] or to the prediction of certain chemical parameters or individual taste descriptors (e.g. total acidity, phenolic content or bitterness level) [12, 15]. Moreover, there are also other interesting works focused on e.g. the detection of inappropriate handling practices or adulteration processes [16, 17], the use of alternative ageing methods [12, 18] or the monitoring of alcoholic fermentation [19]. However, to the best of authors' knowledge, very few attempts have been described in relation to the correlation between ET measurements and the global scores assigned to wines by a standardized sensory panel. A global score is a numerical mark, given mostly in wine marketing context in order to indicate the quality of a wine from the subjective point of view of an expert.

In this context, the work presented herein aims to demonstrate the huge capabilities of ET-based systems to mimic the human taste perception, and hence to provide an analytical tool for the evaluation of wine tasting descriptors. Among the different wine descriptors, wine maturing practices and wine tasting score were the considered scenarios to evaluate the potential of ETs in this field. To this aim, a voltammetric sensor array based on metallic electrodes and bulk-modified graphite-epoxy composites was prepared and employed for the analysis of the wine samples.

2. Experimental

2.1 Reagents and chemicals

All reagents were analytical reagent grade and all solutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA). Potassium chloride was purchased from Merck KGaA (Darmstadt, Germany). Cobalt (II) phtalocyanine, copper and platinum nanoparticles (<50 nm) which were used as electrode modifiers, were purchased from Sigma-Aldrich (St. Louis, MO, USA). The Au and Pt wires (diameter 1 mm) employed in the construction of the metallic electrodes were purchased from Goodfellow (Cambridge, UK).

Besides, graphite powder (particle size 50 µm; BDH Laboratory Supplies, Poole, UK) and Epotek H77 resin and its corresponding hardener (Epoxy Technology, Billerica, MA, USA) were also used for the construction of the graphite-epoxy electrodes.

2.2 Samples under study

To illustrate the capabilities of ETs as a tool for wine tasting, two different scenarios were considered; viz. wine maturing practices (the effect of the barrel and ageing time in its maturing) and the overall tasting attributes. For each of them, a different set of samples was considered and measured with the sensor array, building afterwards the chemometric model that correlates the ET response with the parameters of interest (class or index value).

All considered samples were red wines produced in Catalonia region, each from a different producer, selected according to the nature of the study case. Besides, other factors such as grape varieties, vintage, region, etc. were also taken into account in order to have a more representative set of samples. Overall, a total of 52 wines were obtained from different local wine shops and producers.

2.3 Wine tasting by the sensory panel

Taste attributes of the wines considered were assessed by a panel of 8 wine experts under usual established procedures [3]. The panellists were professional wine tasters from the tasting panel of the different DOs considered in this study. All of them were fully trained and with more than five years of experience in evaluating wines from the Catalan region. Briefly, the subjects were asked to rate the global sensory quality of the wines (sight, aroma and taste) by scoring them in the range from 0 to 10. To this end, wine samples were served randomized in clear glasses NF V09-110 (AFNOR 1995) marked with three digit random numbers and covered with Petri dishes. The blind evaluations were conducted at 20-22ºC, and water was provided to the panel for rinsing the palate during tasting. An average of the three features formed the score of one expert; the final global score was taken as the mean from the 8 panellists. Further information of considered samples can be found in *La guia de vins de Catalunya* (a 2014 guide of Catalan wines) [20].

2.4 Electronic tongue

The voltammetric ET was formed by an array of 2 metallic electrodes and 4 bulk-modified graphite composite electrodes acting as working electrodes, plus a reference double junction Ag/AgCl electrode (Thermo Orion 900200, Beverly, MA, USA) and a commercial platinum counter electrode (Model 52-67, Crison Instruments, Barcelona, Spain).

The metal electrodes were fabricated encasing the metal wire (Au and Pt) in epoxy resin and fixing an electrical connection in the other end, obtaining a final disk electrode of 1 mm diameter. Composite electrodes were prepared by mixing the resin, graphite powder and selected modifier in a ratio 83:15:2 (w/w) [21]. Afterwards, the mixture was allowed to harden at 80ºC for three days, and then polished with different sandpapers of decreasing grain size. In this way, cobalt (II) phtalocyanine, copper and platinum nanoparticles were incorporated as modifiers/catalysts for three of the composite electrodes, additionally one blank graphite-epoxy composite (which did not incorporate any modifier) was also prepared. The final sensor array was formed by one Pt and one Au metal electrodes, plus the four composite electrodes.

Analysis of the wine samples with the ET, was carried out using a 6-channel potentiostat AUTOLAB PGSTAT20 (Ecochemie, Netherlands) controlled with GPES Multichannel 4.7 software package. To this aim, 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 $mV \cdot s^{-1}$.

Although wine analysis did not require any sample pretreatment, some precautions were taken to guarantee sensors response stability along the whole experiment. On one side, electrodes were first cycled in a saline solution (i.e. 10 mM KCl) in order to get stable voltammetric signals prior to proceed with wine samples measurements. On the other side, an electrochemical cleaning stage was performed between each measurement to prevent any cumulative effect of impurities on the working electrode surfaces, while not performing any physical surface regeneration of those. To this end, before analyzing each sample, a conditioning potential of +1.5 V was applied during 40 s in a cell containing 25 ml of distilled water [22]. Lastly, a model wine control sample was analysed repeatedly to guarantee that no drift was observed during the experiment.

2.5 Data processing

Chemometric analysis were done in MATLAB 8.2 (MathWorks, Natick, MA, USA), by specific routines written by the authors, using its Statistics Toolbox. In particular, fast Fourier transform (FFT) was used for signal compression [23], genetic algorithms (GAs) were used as the feature selection tool [24], and linear discriminant analysis (LDA) and partial least squares regression (PLS) were used for the qualitative and quantitative modelling of the data [25, 26], respectively. Besides, Sigmaplot (Systat Software Inc., San Jose, CA) was used for graphic representations of data and results.

The usage of FFT and GAs was aimed to the reduction of the large dimensionality and complexity of the recorded voltammetric signals, which allows to gain advantages in training time, to avoid redundancy in input data and to obtain a model with better generalization ability [27]. Hence, the idea is to extract maximum information of the waveforms themselves with a smaller number of variables, while at the same time, to identify and select the ones that most contribute to the prediction task, discarding the less significant ones.

Furthermore, to guarantee that performance of the generated models was not dependant on the specific subdivision of samples between the train and test subsets, its accuracy was evaluated employing the *repeated random sub-sampling validation method* (RRSS) [28]. Briefly, a model was first trained employing 75% of the data, and its performance evaluated towards the remaining 25% of the samples (which have not been used at all during the modelling). Next, random subdivision of the data between train and test subsets was repeated again, and a new model was built and its performance evaluated. This process was repeated k times to guarantee that there was not any dependence of the predictions related to the specific subdivision of data. Then, once all responses from all the constructed models were obtained, predicted values by each model were grouped depending on if they were used in the training process or in the testing subset. To finish, average values for each sample were calculated, allowing us to estimate model uncertainties and obtain unbiased data [28].

3. Results and Discussion

To illustrate the capabilities of ETs as a tool for wine tasting, two different scenarios were considered: wine maturing practices (barrel effect and period) and prediction of the global scores from a wine tasting panel. For each of the study cases, a different set of samples was considered and measured with the sensor array, building afterwards the chemometric model that correlates the ET response with the parameters of interest (class or index value). Maximum precautions were taken to separate the training process or building of the identification model, and the fine-tuning of the response model configuration, for which a cross-validation scheme was used. Lastly, to actually assess the performance of the built model, RRSS method was used to rebuilt the model several times and used to predict the values for the external test samples that were left out (not being used at all) during the modelling stage and those compared to the expected ones, in this way avoiding any bias in performance.

Those scenarios perfectly fit in the biomimetic approach of ETs, and clearly illustrate the particularities of those over conventional analytical methods. That is, the fact that the wines' taste and flavour perceived by the skilled sensory panel is not related to a specific compound, but to a joint effect of different ones or groups of them. Besides, those compounds have sometimes not been perfectly identified, what in turn hinders the use of classical methods as those would require its targeting. In contrast, ETs combine obtained chemical information from the array of sensors to generate a model like the human brain would do; in this way, not focusing on which specific compounds are responsible for those flavours or tastes, but still being able to identify or quantify specific compounds if proper knowledge (from the expert personnel) can be isolated and proper correspondence can be established.

Thus, the idea behind the ET approach is to use an appropriate array of sensors to obtain complex information about the sample, and the chemometric tool to build a proper model that relates the former with the knowledge of the skilled sensory panel, so as to reproduce its operation. In this way, end goal would be obtaining an automated method that would allow significant reduction of wine tasting by the panel; it must be remarked that the final aim is not replacing the human expertise, but replicating it and allowing an increase of the number or frequency of samples that may be analysed.

3.1 Voltammetric sensor array

Based on the aforementioned, and according to the IUPAC definition of ET [6], we first need to have an array of low-selective sensors with cross-response features allowing us to extract rich-enough data from the sample. These data must be somehow directly or indirectly related with the analytical information finally sought, if not, building of the response model will not be feasible; if all information obtained from the wine samples is their physical characteristics, deduction of properties related to the chemical nature will be very difficult. This means the sensors to be used in a given case must not be any, but with certain connection to the information sought; as second condition these must provide non-specific measurements, this viewpoint related to the cross-response requirement.

In the present work we have combined metallic electrodes with catalyst-modified carbon electrodes; the goal is to accomplish better complementary and more varied voltammograms with the wines considered; in this sense, example of the voltammetric responses obtained for the selected sensor array are shown in Figure 1. As can be seen, differentiated response is achieved thanks to the use of the different modifiers for the epoxy graphite electrodes and the different metallic electrodes; even in the case of Pt, the responses of the electrode modified with Pt nanoparticles and the Pt metal electrode still display some differences, useful for obtaining complementary information from the voltammograms. In this case, differences are probably due to catalytic phenomena attributable to large surface to volume ratio when metal nanoparticles are used.

<FIGURE 1>

Besides, not only the cross-response features need to be checked, but also whether or not sensors responses are related to the phenomena under study. However, this is not straightforward, as the proper evaluation needs to be done by its modelling with the different chemometric tools (as from the IUPAC definition of ET [6]). Hence, on the next sections we are going to evaluate the richness of the generated data and suitability of the ET approach.

Additionally in our case, and due to the large dimensionality of the generated signals, a preprocessing stage based on the usage of FFT was also performed prior the modelling stage itself, aimed to improve model's robustness and performance [27]. In this manner, prior to the modelling, each voltammogram was compressed from the registered 512 current intensities down to 32 coefficients without any loss of significant information [23]; this allowed a compression of the original data up to 93.8%.

3.2 Effect of the barrel in wine maturing

In the first study case, we assessed whether there was or not some identifiable trend in the ET response that could be related to the type of barrel used during wine maturing; that is, the type of wood oak used for the construction of the barrel in which the wine will be aged. On this account, Fernández de Simón and colleagues demonstrated that there was a clear effect based on the type of oak used, as they found that wines with different characteristics were obtained from the same base wine after 21 months of ageing [29].

Among the different types of oak barrels, there are mainly two that are used among producers in Catalonia region; namely, French (*Quercus robur*, *Quercus petraea*) or American (*Quercus alba*) oak wood, although also their mixtures might be used. Hence, we will focus on the analysis of different wines aged on those.

As a first attempt to assess the capabilities of the ET to distinguish barrel effect in wine ageing, we initially focused only on wines aged in French and American barrels to asses if there is or not any pattern found. To this aim, a total subset of 16 samples, were initially considered. Samples were analysed as previously described by means of the sensor array. Next, obtained responses were compressed by means of FFT and obtained coefficients were analysed employing PCA (Figure 2); this, as an unsupervised method, provides a better representation of samples (dis)similarities, but it does not perform its classification.

Interestingly, the PCA plot shows how French oak samples seem to group in the left side, whereas the American ones seem to group in the opposite one; thus indicating some effect due to the oak barrel employed and suggesting that the ET should be capable of distinguishing such factor.

<FIGURE 2>

To further confirm the observed trend, some additional samples aged in mixed oak barrels were analysed as described by means of the sensor array. Obtained responses were compressed by means of FFT as before, and the whole set modelled using LDA as the pattern recognition method (Figure 3). This was chosen given that LDA is a supervised method that allows to actually build a classification model [25]. That is, LDA looks specifically for differences among the data classes, while unsupervised methods do not.

At first sight, it can be seen how the ET is able to distinguish the different types of barrels with this simple analysis of the projected coordinates; however, to numerically assess the performance of the model, cross validation was performed and three different indicators (namely, classification rate, sensitivity and specificity) were calculated [30]. To this aim, the generated model was used to predict the expected group for the test samples that were left out (28% 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), and the efficiency of the classification was evaluated for samples of the external test subset as 100% according to classification rate, sensitivity and specificity. With the goal of providing a further measure of the goodness of fit, a Pearson's chi-squared test was calculated for the contingency table (Table 1), obtaining a calculated statistic of χ^2=14.0, larger than the tabulated value at the 95% confidence level (9.49). This parameter, plus the calculated coefficient of contingency (0.8165, a 100% of the maximum value for the number of classes considered) describes numerically the ability in the identification of ageing wood used.

<FIGURE 3>

<TABLE 1>

3.3 Prediction of the wine maturing period

In the same direction, we also evaluated the capabilities of the ET not only to discriminate ageing in different types of oak barrels, but also to identify the number of months that wines were aged for; this application case is also of interest in the wine field, specially to prevent fraud, as it was already demonstrated for sparkling wines [31].

As before, another set of samples was analysed with the ET, and responses were modelled employing PLS instead of LDA to quantitatively predict their ageing time. Details of the PLS model, such as number of latent variables used (5) were derived from a leave-one-out cross-validated initial calculation. After model optimization, a more complete cross-validation stage (RRSS) with separate training and test subsets was done, whereas comparison graphs of predicted vs. expected ageing months were built to check its prediction ability (Figure 4), and regression lines were fitted. To ensure the robustness of the approach, and that the results obtained were not dependant on the specific subdivision of the samples for the train and test subsets, a repeated resampling approach was used (n=24), which in turn allowed us to assign prediction uncertainties to the different samples and to obtain unbiased data, both for training and test subsets.

<FIGURE 4>

<TABLE 2>

As can be seen in Table 2, a satisfactory trend was obtained for both subsets, with regression lines of the predicted vs. expected comparison plot almost indistinguishable from the theoretical ones; that is, with slope, intercept and correlation values close to 1, 0 and 1, respectively.

In addition, joint confidence intervals were calculated and plotted according to described methodology (Figure 5) [32]. Its usage allows to simultaneously assess the goodness of slope and intercept, and therefore represents a rapid visualization tool to detect if there are or not differences between two compared methods. In this direction, uncertainties in both axes are used to calculate the estimated covariance matrix based on an F distribution, and to examine whether or not the theoretical slope, intercept comparison point (1,0) is included in the elliptical region of the 95% joint confidence intervals of slope and intercept. Therefore, we can state that there are not significant differences between the actual ageing time and the values predicted by the ET, thus suggesting the ET as a promising approach for the obtaining of an analytical tool to assess the wine ageing process.

<FIGURE 5>

3.4 Prediction of global scores of the sensory panel

Lastly, the capabilities of the ET as a tool able to reproduce the global scores assigned by a trained human sensory panel were also evaluated. This represents a more complex approach compared to the previous ones, as those scores depend from the mouthfeel and flavours perceived when tasting the wine, and can be related to both the presence and absence of several compounds and classes of those. This is why the ET system represents an interesting straightforward approach for this scenario, as its biomimetic nature aligns with the biological scheme. Hence, the hypothesis if the ET can be trained employing the scores assigned by the sensory panel to reproduce the knowledge from the experts is thus assessed.

After analysing the wine samples with the sensor array, obtained responses were processed as previously described; a PLS model was constructed from the FFT coefficients available from each sample and optimized to correlate the ET responses with the average scores assigned to each wine by the sensory panel. Fine tuning of the PLS model, such as number of latent variables used (6) were derived from a separate leave-one-out cross-validated initial calculation. After model optimization, a more complete cross-validation (RRSS) stage with separate training and test subsets was done, whereas comparison graphs of predicted vs. expected scores assigned by the sensory panel were built to check its prediction ability (Figure 6), and corresponding regression lines were fitted. Again, to ensure the robustness of the approach, and that the results obtained were not dependant on the specific subdivision of the samples for the train and test subsets, a repeated sampling and calculation (n=30) was performed, which in turn allowed us to assign prediction uncertainties to the different samples and to obtain unbiased data, both for training and test subsets.

<FIGURE 6>

As can be observed from Figure 6, the obtained comparison results are close to the ideal values, with regression lines very close to the theoretical ones. This was further confirmed by numerically assessing the regression parameters (Table 2) and building the joint confidence intervals plot (Figure 5); which intercepts were close to 0 and slopes and correlation coefficients close to 1, and included in the 95% confidence interval. Thus, meaning there is no significant model bias or differences between the values predicted by the ET and the ones assessed by the panel.

This satisfactory trend confirms the potential of such an approach (i.e. to artificially reproduce the tasting perception of a sensory panel), even more if considering the subjective nature of the scores originated from the human sensory panel.

4. Conclusions

In this report, we have illustrated the interesting capabilities of ETs as analytical tool applicable in the tasting and sensory analysis of wine. More specifically, the proposed ET has been successfully applied in the discrimination of wine samples based on its maturing in barrels or the prediction of the global scores assigned by a sensory panel.

To this end, wine samples were analysed with the voltammetric sensor array, and obtained responses were preprocessed employing FFT and GAs for the compression and reduction of signal complexity, followed by its modelling employing LDA for the qualitative and PLS for the quantitative approaches, respectively.

Overall, ETs represent an interesting alternative to more conventional methods due to its biomimetic behaviour, which provides them with the most straightforward approach to overcome the lack of knowledge of the compounds responsible for certain wine sensations. That is, their ability to reproduce the knowledge from the experts, although not replacing them, but being highly suitable as a screening tool which would allow an increase of the number or frequency of samples that can be analysed.

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Table 1. Confusion matrix built according to the maturing category obtained using the LDA model for the testing subset. Results provided correspond to the average of the values obtained for each sample after 25 repeated calculations done with random division of samples for train/test subsets each time.

	F^{b}	FA^{b}	A^{b}
F^{a}	100%	0	0
FA^{a}	0	100%	0
A^{a}	0	0	100%

[a] Expected; [b] Found.
F: *French*; FA: *French/American*; A: *American.*

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

		Ageing time		
	Correlation	*Slope*	*Intercept*	*NRMSE*
Train	0.982	0.964±0.025	0.45±0.33	0.048
Test	0.969	1.011±0.061	0.14±0.84	0.077
		Global scores (0-10) assigned by the sensory panel		
	Correlation	*Slope*	*Intercept*	*NRMSE*
Train	0.981	0.976±0.023	0.22±0.20	0.045
Test	0.917	0.973±0.087	0.29±0.74	0.11

NRMSE: Normalized Root Mean Square Error; Intercept values are expressed in months and arb. unit (0-10), respectively

FIGURE CAPTIONS

Figure 1. Example of the different voltammograms obtained with the different sensors forming the ET array for four arbitrary wine samples. Signals provided correspond to: (a) graphite–epoxy sensor, (b) Cu nanoparticles modified sensor, (c) Pt nanoparticles modified sensor, (d) Co phthalocyanine modified sensor, (e) Au metallic sensor and (f) Pt metallic sensor.

Figure 2. Score plot of the first two components obtained after PCA analysis of the wine samples: (■) French and (♦) American.

Figure 3. Score plot of the first two functions obtained after LDA analysis of the wine samples, according to its maturing: (■) French, (●) French/American and (♦) American; with filled symbols for the training subset and empty ones for the testing subset. Additionally, the centroid for each class is plotted (★).

Figure 4. Performance of the optimized FFT-PLS model for the prediction of wines ageing time. Set adjustments of obtained vs. expected values, both for (A) training and (B) testing subsets. The dashed line corresponds to theoretical diagonal line. Results provided correspond to the average of the values obtained for each sample after 24 repeated calculations done with random division of samples for train/test subsets each time. Uncertainties calculated at the 95% confidence level.

Figure 5. Joint confidence intervals for the testing subsets: (●, short-dashed line) the ageing time and (■, long-dashed line) the global scores assigned by the sensory panel. Also the ideal point (1,0) is plotted (x); intervals calculated at the 95% confidence level.

Figure 6. Performance of the optimized FFT-PLS model for the prediction of wines global scores assigned by the sensory panel. Set adjustments of obtained vs. expected values, both for (A) training and (B) testing subsets. The dashed line corresponds to theoretical diagonal line. Results provided correspond to the average of the values obtained for each sample after 30 repeated calculations done with random division of samples for train/test subsets each time. Uncertainties calculated at the 95% confidence level.

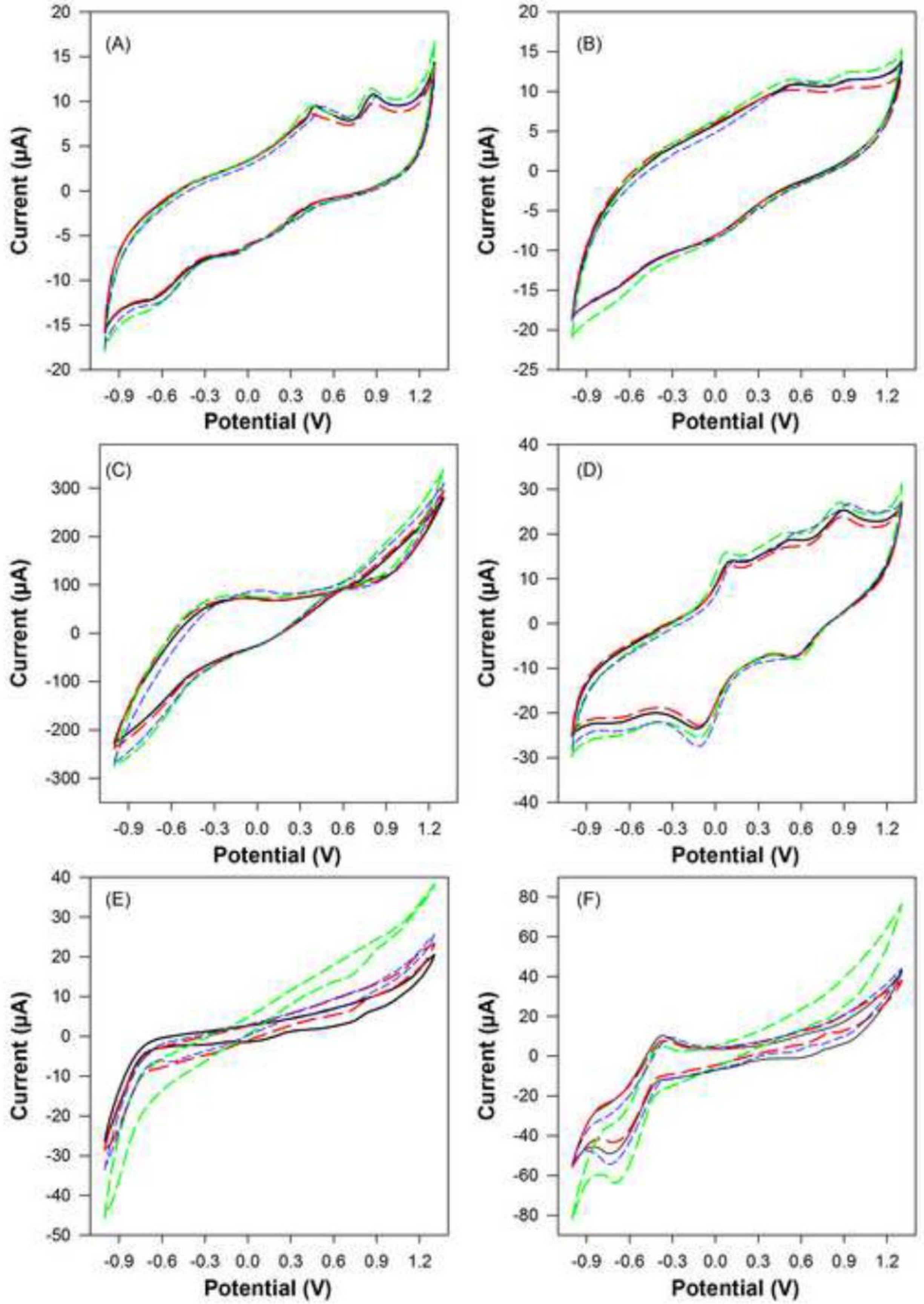


Figure 1

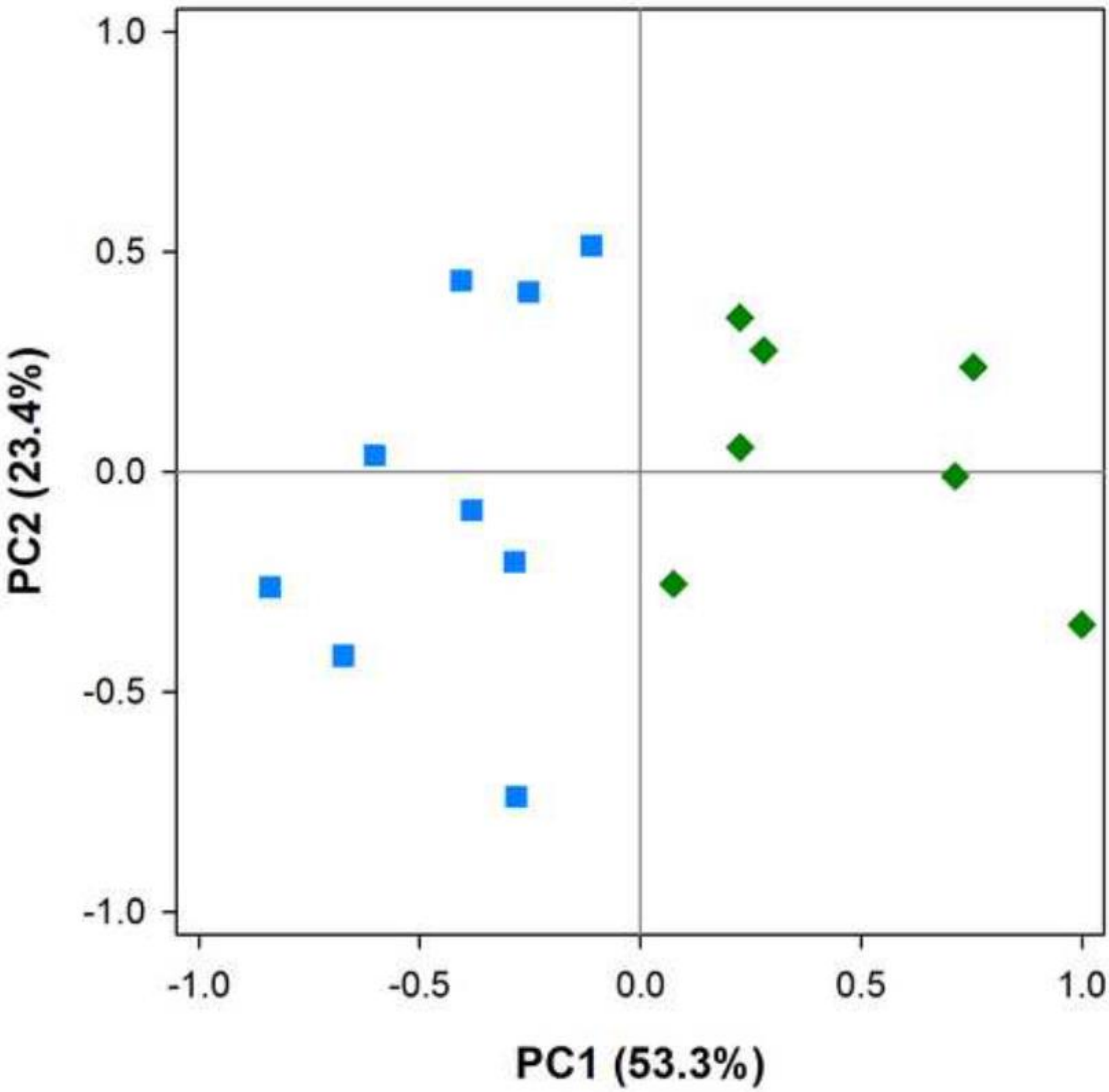


Figure 2

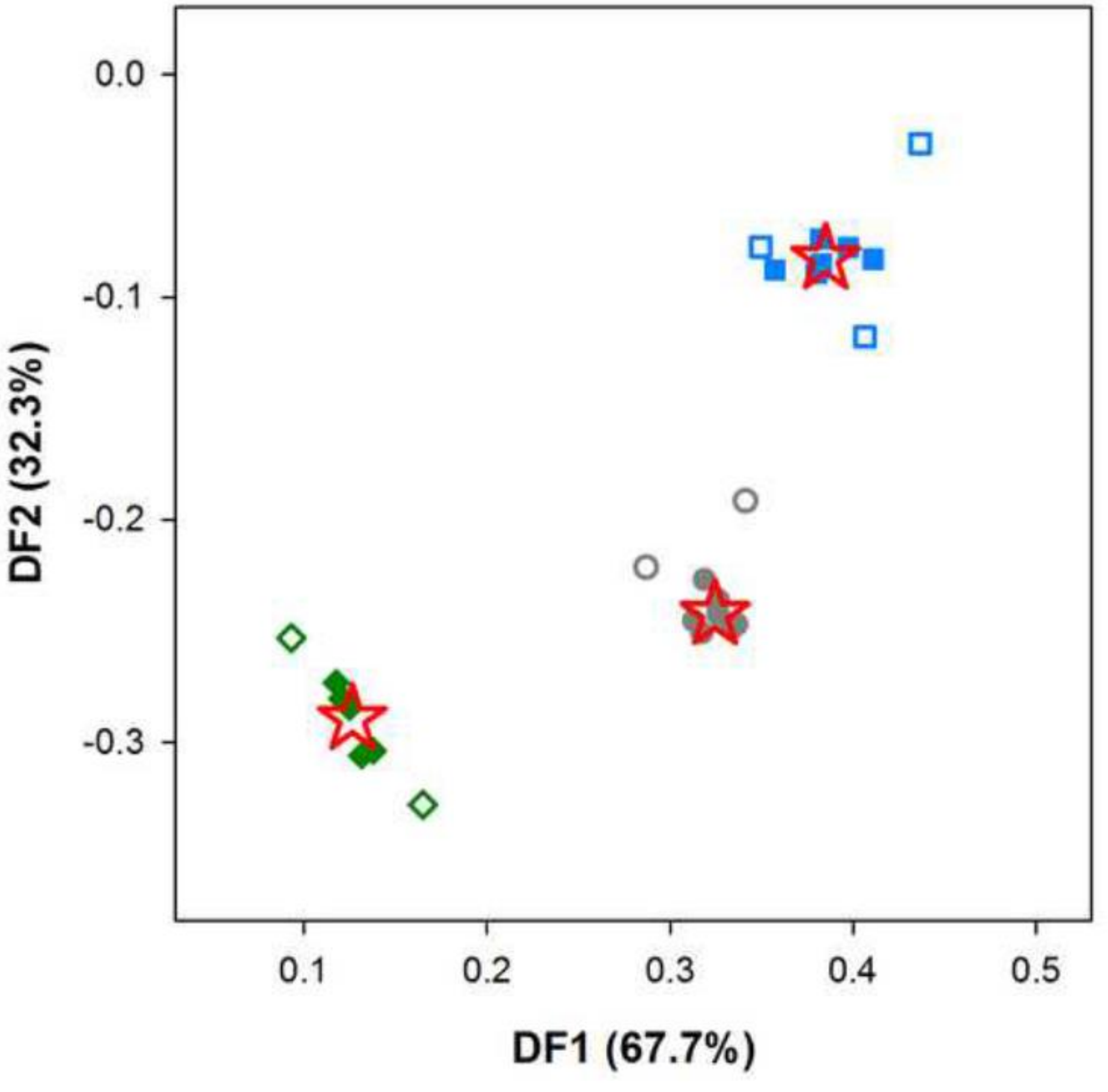
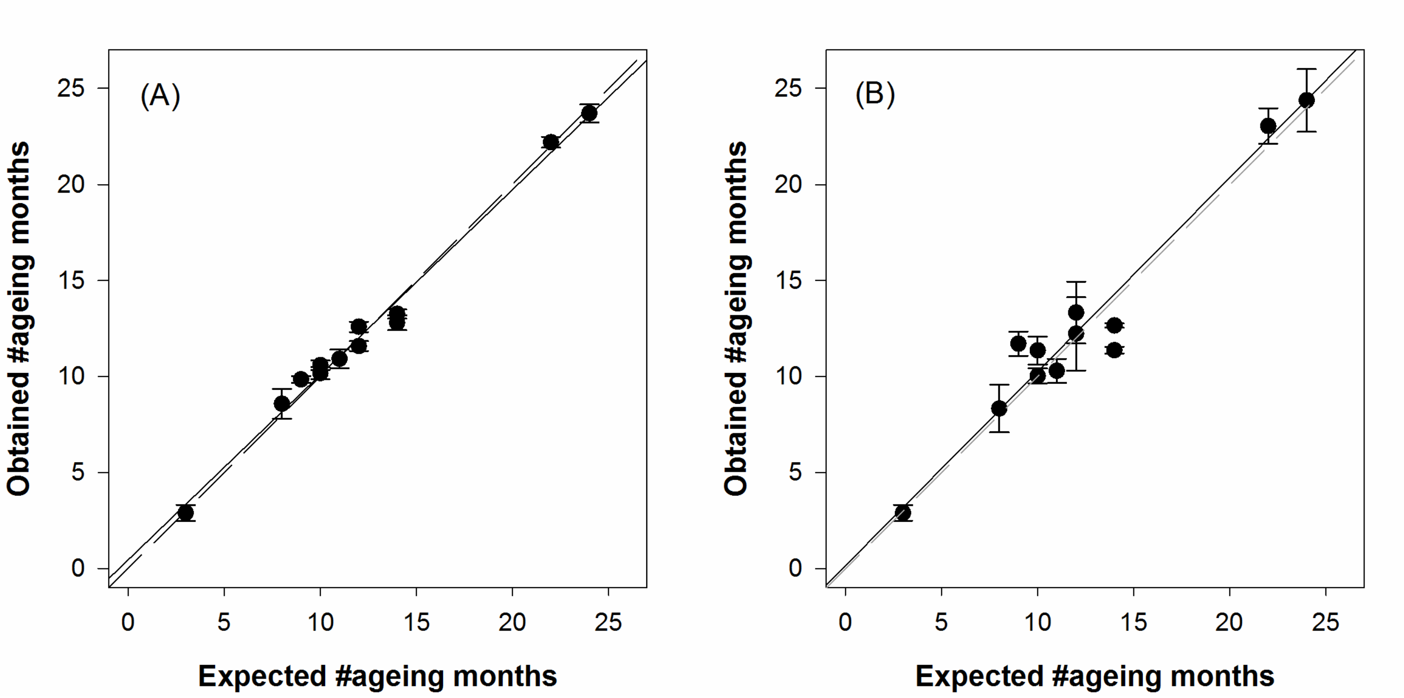


Figure 3



(A)
(B)
Obtained #ageing months
Expected #ageing months
0
5
10
15
20
25

Figure 4

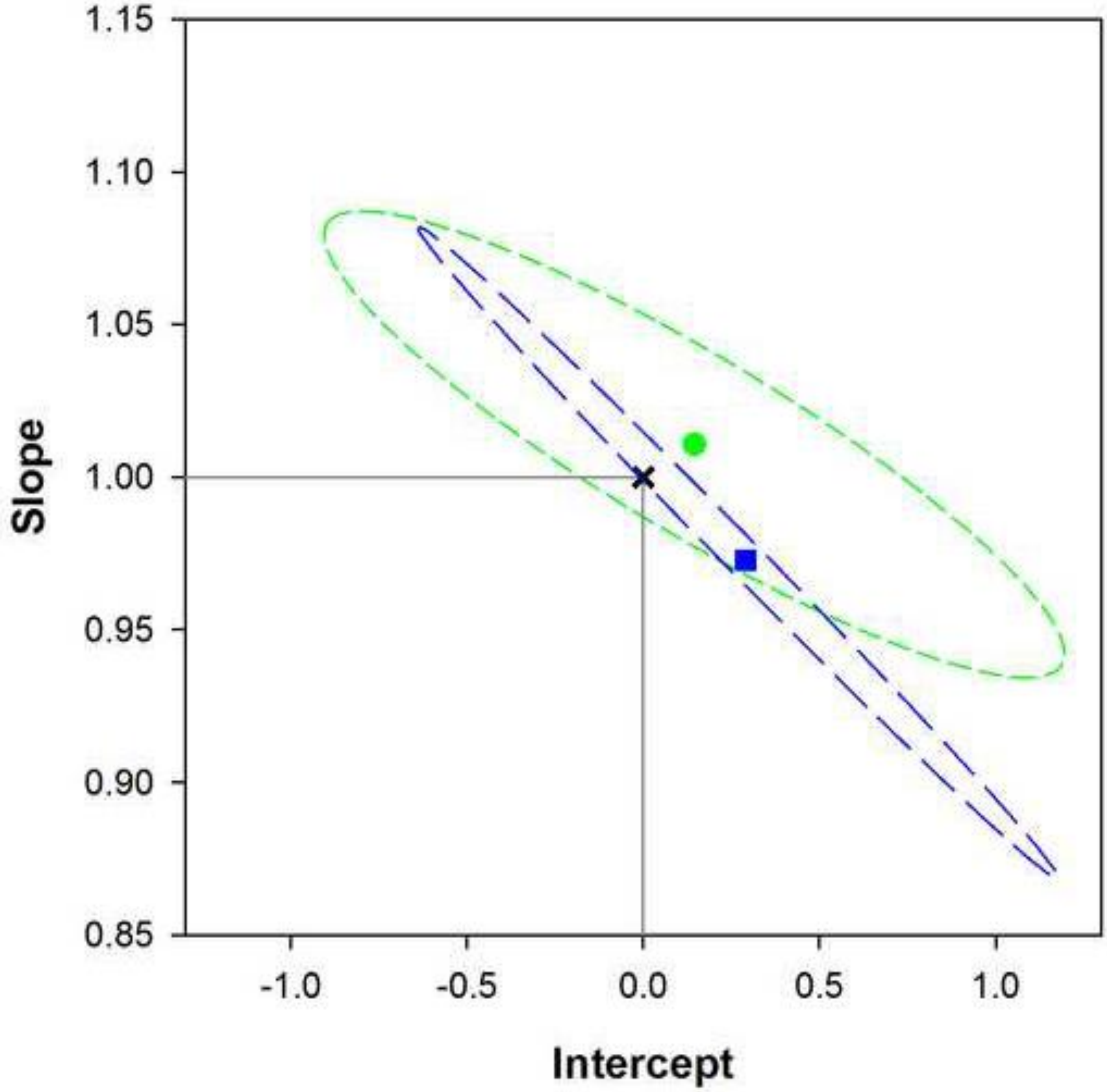


Figure 5