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Analytical Methods

Analysis of the influence of the type of closure in the organoleptic characteristics of a red wine by using an electronic panel

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ABSTRACT

An electronic panel formed by an electronic nose, an electronic tongue and an electronic eye has been successfully used to evaluate the organoleptic characteristics of red wines vinified using different extraction techniques and micro-oxygenation methods and bottled using closures of different oxygen transmission rates (OTR).

The three systems have demonstrated a good capability of discrimination by means of Principal Component Analysis (PCA). Partial Least Squares Discriminant Analysis (PLS-DA) has permitted to establish prediction models based on the type of closure, the polyphenol content or the effect of micro-oxygenation. The best correlations found using the e-eye and the e-nose are related to the OTR of the closure. In contrast, the electronic tongue is more sensitive to the polyphenol content. The discrimination and prediction capabilities of the system are significantly improved when signals from each module are combined. The electronic panel can be a useful tool for the characterisation and control of oxygen and antioxidant capability of red wines.

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1. Introduction

Oxygen plays a pivotal role in the evolution of wine by impacting its colour, aroma and mouth-feel properties. Managing oxygen in oenology remains critical as both excessive exposure and excessive protection lead to sensory defects known as oxidation and reduction. To efficiently manage it, oxygen must be controlled along the whole value chain from grape harvest to bottle storage. Very often oxygen introduction is uncontrolled as during pumping over and other operations of wine transfer and at bottling. New techniques were developed aiming better control of oxygen exposure. For example, a mild oxygenation process, referred to as micro-oxygenation, has been proposed to simulate the continuous low oxygen uptake taking place in barrels (Atanasova, Flucrand, Cheynier, & Moutounet, 2002). This technique has become common practice to improve the quality of red wines, enhance colour intensity and stabilize wine pigments. In bottle, oxygen exposure is usually low but can be quite variable depending on the type of closure. The wine industry can now also take advantages of engineered solutions to deliver known and reproducible amounts of oxygen into bottles through the closures, that can be manufactured with specific and controlled oxygen transfer rate (OTR).

Usually, the quality of wines is evaluated by a sensory panel composed of trained experts or by chemical analysis. In the last years electronic noses (Peris & Escuder-Gilabert, 2009; Rock, Barsan, & Weimar, 2008) and tongues (Ciosek & Wroblewski, 2007; Labrador, Olsson, Winquist, Martinez-Manez, & Sotoa, 2009; Parra, Hernando, Rodríguez-Méndez, & de Saja, 2004; Vlasov, Legin, Rudnitskaya, Di Natale, & D'Amico, 2005) have been developed to operate in an analogous manner as the human senses can perceive odours and tastes. They are based on the combination of non-selective chemical sensors endowed with sufficient cross-selectivities coupled with chemommetric methods.

Wines have been extensively analysed using arrays of resistive sensors as electronic noses combined with preconcentration techniques such as Solid Phase Microextraction (that eliminate water and ethanol) (Capone et al., 2000; Hahn et al., 2003; Lozano, Santos, & Horrillo, 2008; Penza & Cassano, 2004; Villanueva et al., 2006). In the case of electronic tongues, the use of arrays of electrochemical sensors is of particular interest due to the important role that the oxygen and the antioxidants play in the organoleptic characteristics and also in the health benefits of red wines (Moreno i Codinachs et al., 2008; Parra, Arrieta, Fernández-Escudero, Rodríguez-Méndez, & de Saja, 2006; Riul et al., 2003; Verrelli, Lvova, Paolesse, Di Natale, & D'Amico, 2007). Colour is an important part

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of the red wine quality. It is generally accepted that an increase in colour coincides with an improvement in phenol structure, an increase in aroma intensity and hence, an increase in wine quality. In the search for objective, easily quantifiable quality parameters, colour is therefore a logical option and has been investigated as a possible wine quality parameter for many years (Perez-Caballero, Ayala, Echavarri, & Negueruela, 2003).

Several attempts have been made to combine e-noses and e-tongues an even with e-eye (Cosio, Ballabio, Benedetti, & Gigliotti, 2007; Di Natale et al., 2004; Rodríguez-Méndez et al., 2004). It has been demonstrated that the simultaneous utilisation of electronic noses and electronic tongues can increase the amount of information extracted from a specific sample. In previous works, our group has developed an electronic panel purposely dedicated to the analysis of red wines (Rodríguez-Méndez et al., 2004). The electronic nose was based on an array of metal oxide sensors coupled to an SPME system. The chemical nature of the SPME fibre and the protocol of absorption and desorption of gases has been optimised to increase the amount of volatiles absorbed while minimising the absorption of ethanol and water (Villanueva, Rodríguez-Mendez, & de Saja, 2008). The electronic tongue developed by our group consisted of an array of voltammetric sensors chemically modified with electroactive substances. The sensing materials included phthalocyanines and perylenes that interact with components of wines namely with their antioxidant capability (Arrieta, Rodríguez-Méndez, & de Saja, 2003; Casilli et al., 2005). Thus, the electronic tongue has been able to discriminate wines of different qualities, grape variety or among wines aged in different types of oak barrels and oak chips (Apetrei et al., 2007; Parra et al., 2006; Rodríguez-Méndez et al., 2004). The system has been completed with colour measurement system based on CIELab coordinates calculated from spectrophotometric data (Rodríguez-Méndez et al., 2004).

The aim of this study was to monitor the influence of oxygen pick-up, before (micro-oxygenation, Mox) and after bottling (nano-oxygenation), on wine sensory evolution. The rate of nano-oxygenation was controlled by combining consistent OTR closures and different oxygen controlled storage conditions. Since oxygen consumption is known to be related to phenolic compounds (Singleton, 1987; Waterhouse & Laurie, 2006), the same experiments were performed on wines differing by their phenolic content, obtained from the same grapes either by Flash Release (FR, higher phenolic content) (Morel-Salmi, Souquet, Bes, Cheynier, & Moutounet, 2006) or traditional soaking.

The potential of the e-panel to discriminate among wines with different oxygen levels and antioxidant capabilities is evaluated by using Principal Component analysis. Partial Least Squares Discriminant Analysis (PLS-DA) is also used to investigate prediction models based on (a) the polyphenol content (b) the contribution of micro-oxygenation and (c) the closure OTR.

2. Materials and methods

2.1. Samples

Ten thousand kilograms of grapes from Vitis Vinifera var. Grenache (2007), grown at INRA Pech Rouge experimental Unit station (Gruissan, Southern France) were harvested on two plots at commercial maturity in September 2007. Grapes from the first plot (22°Brix, pH = 3.6) were used for traditional winemaking and those from the second plot (25°Brix, pH = 3.7) were used for Flash Release trial. The treatment by FR consisted in destemming and crushing the grapes, heating them at 95 °C during 6 min with biological vapour, and then submitting them to a strong vacuum (pressure closed to 60 hPa).

Two wines were prepared by traditional soaking (Trad) and Flash Release (FR) respectively. Each of these two wines was then divided in two batches submitted or not to micro-oxygenation (Mox/noMox), yielding four wines in total: FR, FR + Mox, Trad, Trad + Mox.

For both traditional soaking and Flash Release trial, the musts were distributed into two 50 hL fermentation stainless steel tanks equipped with temperature control, added with sulphite (5 g hL^{-1}) and with 500 g yeast (LBRouge, Lallemand, 10 g hL^{-1}), and fermented to dryness. The cap was punched down daily to ensure mixture of the marc with the fermenting liquid phase. A supplementation of nitrogen nutrition was done (20 g hL^{-1} DPA) after a decrease of 30 points of density. After 8 days of maceration, when alcoholic fermentation was finished (controlled by sugar analysis), the wines were racked (O_2 pickup: 0.3 ppm), transferred to 20 hL tanks and inoculated with lactic bacteria (Lalvin VP41, Lallemand) to start malolactic fermentation. At the end of the malolactic fermentation, the wines were racked into other 20 hL inox tank (O_2 pickup: 4 ppm) and sulphites were added (3 g hL^{-1}). Each of the wines was transferred from the 20 hL tank into four 2.7 hL tanks, adapted to perform Mox with a height of 3 m and a surface of wine of 0.09 m^2. Mox was performed with a 10-channels Oenodev system, at 5 mg O_2 L^{-1} $month^{-1}$ during 3 weeks. The noMox modalities were stored in the same cellar in similar tanks. The total oxygen quantities introduced (pick-up at racking and Mox) into these four wines (Tradmox, Trad, FRmox, FR) during winemaking were estimated in mg L^{-1} as follows: 8.66; 5.79; 9; 3.85, respectively. The wines were bottled in 375 mL glass bottles (Saint-Gobain bordelaise 39). Each of the four wines was divided in four batches in order to obtain four OTR conditions: one batch was closed with Nomacorc Light stoppers and stored in ambient air (21% oxygen). The three remaining batches were closed with Nomacorc Classic stoppers and stored respectively in ambient air (21% oxygen) and in stainless steel drums where oxygen levels were kept constant at either 4% oxygen or 1% oxygen. All the wines were stored in the same closed room at a constant temperature (23 °C). The OTR were calculated using Fibox 3 trace fibre optic oxygen metre (PreSens Precision Sensing GmbH, Regensburg, Germany) (Diéval, Veyret, Vidal, Aagaard, & Vidal, 2009) and were found to be 11.9, 8.0, 1.9 and 0.8 μL oxygen/bottle/day for Light 21%, Classic 21%, Classic 4% and Classic 1%, respectively. Wines included in the study are listed in Table 1.

2.2. Electronic eye

Colour measurements were made in a Shimadzu 2101 UV–Vis Spectrophotometer, using 1 mm path length glass cell (Rodríguez-Méndez et al., 2004). The CIELab coordinates (L^*, a^*, b^*, C, H, S) were calculated following the recommendations of the Comission Internationale of L'Eclairage for the CIE illuminant D_{65} and 10° standard observer conditions.

2.3. Electronic nose

The array of 15 gas sensors was constructed using inorganic metal oxide (MOX) sensing units that were selected according to the previous experience of our group (Villanueva et al., 2006). Sensors were mounted in a stainless steel test box with an internal volume of 75 mL. The test box was kept at a constant temperature (50 °C) throughout the experiments. Data collection was performed through a *PC-LPM-16* data acquisition card from National Instruments interfaced to a personal computer. Sensors were polarised using a constant voltage of 5 V provided by a *FAC-662B* programmable power supply. The scan rate used to measure the resistance was 0.5 s. Data were monitored in real time and the

Table 1
Wines prepared for this study.

	Crush	Microoxygenation	Type of closure
Grenache must	Trad low polyphenols (W and X)	Not micro-oxygenated (W)	Ligth 21% (W1) Classic 21%(W2) Classic 4% (W3) Classic 1% (W4)
		Micro-oxygenated (X)	Ligth 21% (X1) Classic 21% (X2) Classic 4% (X3) Classic 1% (X4)
	FR high polyphenols (Y and Z)	Micro-oxygenated (Y)	Ligth 21% (Y1) Classic 21% (Y2) Classic 4% (Y3) Classic 1% (Y4)
		Not micro-oxygenated (Z)	Ligth 21% (Z1) Classic 21% (Z2) Classic 4% (Z3) Classic 1% (Z4)

graphs could be followed using Visual Basic software from Microsoft.

The *SPME* (Solid Phase Microextraction) sampling method was used as the injection method. A volume of 3 mL of wine was placed in 10 mL vial that was kept at 40 °C during 15 min, with a stirring speed of 650 rpm. Then a bipolar fibre of polydimethylsiloxane coated with carbowax and divinylbenzene (*PDMS/CW/DVB*, *supelco*) was exposed to the headspace of the vial for 15 min. Then, the *SPME* fibre was placed in a heated injection port of a gas chromatograph at 250 °C. The volatile compounds were driven to the test chamber using constant gas flow of 150 mL min^{-1} (air 100 mL min^{-1}, nitrogen 50 mL min^{-1}).

2.4. Electronic tongue

An array formed by voltammetric carbon paste electrodes (CPEs) based on bisphthalocyanines and perylenes was constructed according to previously published procedures (Apetrei et al., 2007; Parra et al., 2006). Two bisphthalocyanines the lutetium bisphthalocyanine ($LuPc_2$) and the octatert-butyl substituted analogue ($LuPc_2^t$) and one monophthalocyanine, the cobalt metallophthalocyanine (CoPc) have been used as modifiers. In the case of the perylenes, the *N,N*-bis(methylpiperidine)-3,4,9,10-perylenebis(dicarboximide) (BpPTCD), the *N*-octyl-3,4,9,10-perylenebis(dicarboximide) (OcPTCMI) and the *N*-butyl-3,4,9,10-perylenebis(dicarboximide) (BuPTCMI) were included in the study. An unmodified carbon pasted electrode (CPE) and a platinum electrode were also included in the array of sensors.

The measures were carried out using three electrode cell: CPEs were used as working electrode, a platinum wire as the counter electrode and a Ag/AgCl as the reference electrode. Square wave voltammetry was performed at potential scan ranging from −1.0 to 1.3 V using f = 15 Hz, Esw = 0.1 V, ΔE = 0.007 V (except for PcCo, ΔE = 0.005 V).

2.5. Data processing

Each wine was measured with the three systems separately. In order to carry out statistical analysis, seven replicates were registered for each measurement.

Data analysis involved an initial pre-processing of the corresponding signals. The UV–Vis spectra were used to calculate CIELab parameters giving raise to six input values per sample. In the case of e-nose, the maximum values of the transient responses of each one of the 15 MOX sensors were selected as input variables. Voltammetric signals were pre-treated using a previously developed method, based on kernel functions where the voltammetric curves were divided in 10 bell-shaped curves (Parra et al., 2004). The kernel method allows the data number to be reduced without losing important information throughout the total response.

The selected variables were used as the input parameters for PCA pattern recognition analysis. The Partial Least Squares Discriminant Analysis (PLS-DA) method was used to establish prediction models based on the polyphenol content, the effect of micro-oxygenation and closure OTR. In order to establish the prediction model on the polyphenol content, samples were divided into two different classes: class 1 included Flash-Released wines (Y and Z) and class 2 included traditional soaking wines (W and X). In order to evaluate the influence of micro-oxygenation, wines were grouped in two sets: the first one included wines micro-oxygenated (wines X and Y) and wines not micro-oxygenated (wines W and Z). Finally the prediction model of the effects of the closure OTR was analysed by establishing two classes, one including high OTR (1 and 2) and wines bottled with low OTR closures (wines 3 and 4).

Validation was performed using cross-validation. The RMSEP (Root Mean Square Error of Prediction), slope and correlation coefficient of predicted versus measured correlation line were used to evaluate the efficiency of applied regression model.

Data fusion coming from the three instruments was carried out by constructing a data matrix containing the information provided by the three apparatus. Data treatment was performed with commercial Unscrambler (v. 9.1, 2004, CAMO PROCESS AS, Norway) and Matlab (V.7.2, MathWorks, USA) software.

3. Results and discussion

Wines were analysed using the three systems (electronic tongue, electronic nose and electronic eye) separately in order to study the capability of each system to analyse the organoleptic properties. Then, a data fusion procedure was followed in order to assess the performance of the whole system.

3.1. Analysis of colour: e-eye

UV–Vis spectra of wines were measured and the CIELab parameters were calculated.

Wines sealed with closures 1 and 2 showed distinct spectra. In contrast, wines bottled using closures 3 and 4 were more similar. The type of closure affected strongly the lightness (L^*) of wines; the highest L^* values corresponded to wines sealed using closures 3 and 4, and were ranged from 25.09 to 27.10. The lower L^* (darker) corresponded to wines sealed with closures 1 and 2 (values ranged from 21.10 to 24.59). Depending on oxygen permeating through the closures, wine polyphenolics undergo different reactions that will eventually end up with different types of pigments. The newly formed pigments will show new colour properties and thus intensity of colour of the wines will be modified accordingly.

CIELab coordinates were used as the input variable for PCA analysis. PCA scores plot is shown in Fig. 1. As observed in the figure, the First Principal Component (PC1), that explains 69% of the information, contrasted wines according to the type of closure. Wines 1 and 2 appear in the right side of the graph. Wines sealed with stoppers 3 and 4 were not clearly discriminated due to the similarity of the spectral features, and appear in the left side of the plot. This result is in accordance with the fact that the sealing conditions 3 and 4 are very similar (1.9 and 0.8 μL oxygen/bottle/day).

The Partial Least Squares Discriminant Analysis (PLS-DA) method was used to establish prediction models based on the polyphenol content, the effect of micro-oxygenation and the type of

closure. Results shown in Table 2 demonstrate that CIELab coordinates are not influenced by the polyphenol content and the use of microoxygenation, for this reason, errors in the predictions are high. In contrast, the model established for predicting the groups according to the type of closure demonstrated a good-quality ability in discriminating and recognising wines based on different OTR.

3.2. Analysis of odours: e-nose

The wines under study were exposed to the array of MOX sensors. The peak height was used as the input variable for PCA analysis. Fig. 2 shows the scores plot of the three first principal components (PC1 = 68%; PC2 = 18% and PC3 = 6%). The wines analysed could be clearly discriminated from each other, exception made of wines W3 and W5, that also showed very similar spectra. Wines bottled with high OTR closures (closures 1 and 2) appear on the left side of the figure (negative *X*). In the region of positive *X*, wines bottled using low OTR closures could be found. Differences caused by micro-oxygenation or polyphenol content were less marked.

In order to evaluate the prediction capability of the system, PLS-DA was conducted. A quantitative evaluation of the regression models is given in Table 2. Calibration was carried out using the test set validation. The small number of latent variables (5) and the closeness of calibration and prediction error rates demonstrate that these results were statistically valid. The model showed good percentages of correct classifications. The results indicated that the classes of wines according to the closure OTR and the polyphenolic content may be reasonably considered as separate from each other. The results obtained can be discussed in light of oenological meaning. The two extraction techniques used to get different polyphenol content also played a role in extracting aromatic compounds (free and precursor forms). These two different aromatic potentials were then submitted to different oxygen regimes through different OTR. This has created different oxygen conditions that had modified the "bouquet" of the different wines. It is known that the same wine put under different closures can evolve differently from reduced to oxidised wine.

3.3. Analysis of taste: e-tongue

The response of the array of carbon paste electrodes (CPEs) towards wine samples was analysed. As stated before, curves were pre-treated using kernel functions in order to obtain 10 variables per sensor. This pre-treatment gives rise to a high number of input variables (8 sensors × 10 variables = 80 variables). For this reason, a selection of variables (three variables per sensor) was carried out using the PCA loading plot and selecting those variables with higher correlation loadings. Using this method the total number of variables was reduced to 24. These values were used as the input parameters for PCA pattern recognition analysis. Fig. 3 shows the PCA scores plot of measurements using the electronic tongue. A partial overlapping between the wines studied could be observed; however, a certain degree of discrimination was observed between wines with a high polyphenol content (left side of the plot) and wines with low polyphenol content (right side of the plot). In addition, non-micro-oxygenated wines tend to appear in the upper side of the plot and micro-oxygenated wines appear in the lower part of the plot. The percentage the explained variance was of a 35% for PC1, 18% for PC2 and 11% for PC3.

PLS-DA models were developed for prediction of the different classes of wines: high and low polyphenol content, micro-oxygenated and not micro-oxygenated wines, and wines bottled with different types of closures. Full cross validation was used in the considered models. The discrimination results of calibration and validation sets are shown in Table 2. When grouped by polyphenolic content, the obtained prediction coefficient was 0.970801 (5 latent variables). The calculated coefficient of prediction was also high 0.933645 (6 latent variables), when classifying micro-oxygenated and not micro-oxygenated wines. In contrast, the capability of the system to classify wines according the closure OTR (6 latent variables) was clearly lower (0.877746) with a residual error of 0.240189.

These results are in good agreement with previously published results where the correlation between the sensors signals and the polyphenolic content of wines and with components with redox properties was demonstrated (Casilli et al., 2005; Parra et al., 2004). These results are also in phase with what was expected from this trial. Flash-Release is a technique known to extract a high amount of tannins. Astringency increases with tannin concentration, degree of polymerisation and galloylation (Vidal et al., 2003). Micro-oxygenation is used to stabilize colour but also to soften tannins (reduce astringency) notably through the formation of new polyphenols known as ethyl-bridged tannins (Atanasova et al., 2002). These wine tannins had been found to be bitter (Vidal et al., 2004). The mouth feel properties are thus depending on the extraction techniques but also to the oxygen treatment during winemaking. The amount of oxygen added through the closures also played a role in modelling wine mouth feel properties even if its effect was lower than those of extraction techniques and micro-oxygenation.

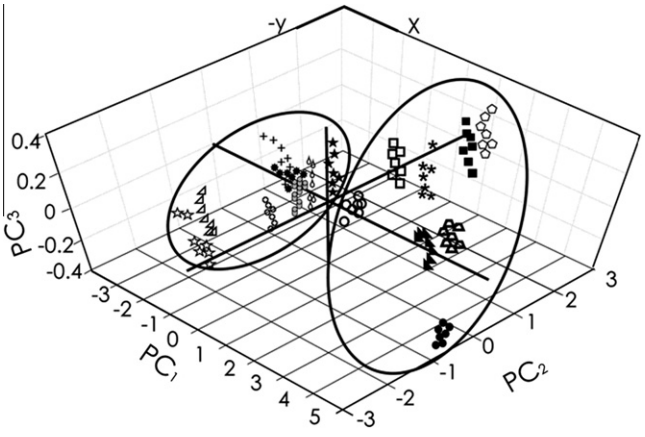

Fig. 1. PCA Scores plot of the CIELab coordinates. PC1, PC2 and PC3 bring the 68%, 31% and 1% of the variance respectively. The samples are marked with the following symbols: W1 (△), W2 (∗), W3 (+), W4 (✸), X1 (□), X2 (○), X3 (◿), X4 (☆), Y1 (●), Y2 (◣), Y3 (▯), Y4 (⬚), Z1 (⬠), Z2 (■), Z3 (★), Z4 (◊).

3.4. Sensor fusion: electronic panel

As demonstrated in previous sections each instrument provides a complementary piece of information that contributed to the discrimination of the studied wines. For instance, electronic nose and electronic eye responses are sensitive to the effects caused by the closure OTR. In contrast, the liquid sensory system can discriminate the flavour attributes which are influenced by the presence of compounds with redox activity and by the antioxidant character of wine (polyphenolic content and micro-oxygenation). Signals coming from the three systems were merged in a data matrix formed by six CIELab coordinates (colour), 15 variables extracted from the signals produced by the 16 MOX sensors (odour) and 24 data selected from the voltammetric curves provided by the electrochemical sensors (3 kernel values by sensor) were used as feature vectors for the multivariate analysis. The first principal components, shown in Fig. 4, capture 29%, 19% and 12% of the total variance, respectively. The PCA clusters were small, allowing an

Table 2
PLS-DA prediction models using the different systems.

	Slope		Offset		Correlation		Residual Error	
	Calibration	Prediction	Calibration	Prediction	Calibration	Prediction	Calibration	Prediction
Prediction models using CIELab coordinates								
Polyphenol[a]	0.402	0.383	0.300	0.310	0.634	0.605	0.387	0.398
Mox[a]	0.387	0.369	0.307	0.313	0.622	0.593	0.391	0.403
Closure[a]	0.844	0.843	0.078	0.077	0.919	0.914	0.197	0.204
Prediction models using e-nose								
Polyphenol[a]	0.732	0.702	0.134	0.150	0.855	0.826	0.260	0.282
Mox[a]	0.566	0.526	0.217	0.257	0.753	0.703	0.330	0.356
Closure[a]	0.740	0.720	0.127	0.135	0.860	0.840	0.255	0.272
Prediction models using e-tongue coordinates								
Polyphenol[a]	0.960	0.950	0.020	0.023	0.980	0.971	0.100	0.120
Mox[a]	0.914	0.888	0.043	0.933	0.956	0.933	0.147	0.180
Closure[a]	0.846	0.877	0.077	0.100	0.920	0.877	0.196	0.240
Prediction models using the panel test								
Polyphenol[a]	0.973	0.955	0.013	0.022	0.986	0.980	0.082	0.101
Mox[a]	0.923	0.902	0.039	0.050	0.961	0.943	0.139	0.167
Closure[a]	0.964	0.948	0.018	0.027	0.982	0.973	0.094	0.115

[a] Polyphenol = type of crush (Trad or FR that produces wines with high or low polyphenolic content); Mox = type of micro-oxigentation (Mox or notMox); Closure = type of closure (high or low porosity).

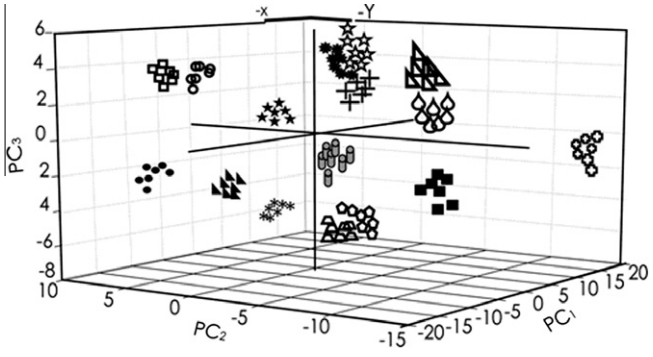

Fig. 2. PCA scores plot illustrating the discrimination between the wines using e-nose. PC1, PC2 and PC3 bring the 68%, 18% and 6% of the variance respectively. The samples are marked with the following symbols: W1 (⏢), W2 (∗), W3 (+), W4 (✸), X1 (□), X2 (○), X3 (◿), X4 (☆), Y1 (●), Y2 (◣), Y3 (⛁), Y4 (⛌), Z1 (⬠), Z2 (■), Z3 (★), Z4 (◊).

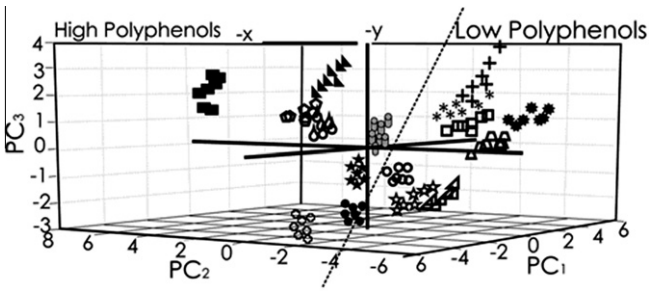

Fig. 3. PCA scores plot illustrating the discrimination between the wines using e-tongue (3 variables per sensor). PC1, PC2 and PC3 bring the 35%, 18% and 11% of the variance respectively.The samples are marked with the following symbols: W1 (⏢), W2 (∗), W3 (+), W4 (✸), X1 (□), X2 (○), X3 (◿), X4 (☆), Y1 (●), Y2 (◣), Y3 (⛁), Y4 (⛌), Z1 (⬠), Z2 (■), Z3 (★), Z4 (◊).

easy discrimination of wines. This demonstrated that fusion of the three arrays of sensors improved the discrimination of wines. Moreover, the PCA scores plot allows simultaneous discrimination of wines according to the closure OTR, the polyphenol content and the occurrence of micro-oxygenation. In the front part of the graph

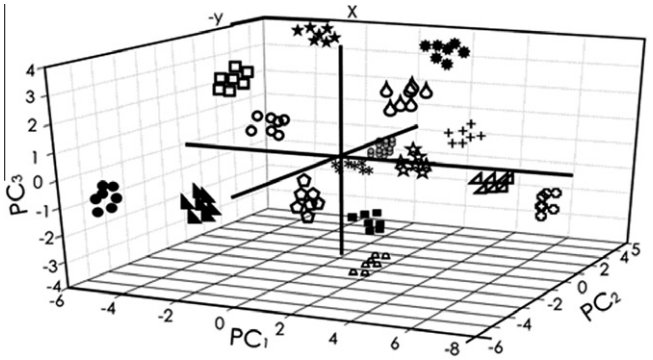

Fig. 4. PCA scores plot illustrating the discrimination between the studied wines using the e-panel. PC1, PC2 and PC3 bring the 29%, 19% and 12% of the variance respectively.The samples are marked with the following symbols: W1 (⏢), W2 (∗), W3 (+), W4 (✸), X1 (□), X2 (○), X3 (◿), X4 (☆), Y1 (●), Y2 (◣), Y3 (⛁), Y4 (⛌), Z1 (⬠), Z2 (■), Z3 (★), Z4 (◊).

(negative *X* axis) wines bottled with stoppers of high OTR to the oxygen (wines 1 and 2) could be observed, while wines bottled with low OTR stoppers (wines 4 and 5) appear in the positive *X* axis region (bottom of the image). At the same time clusters corresponding to micro-oxygenated wines (wines X and Y) tend to appear on the right part of the graph (negative *Y* axis), while wines with different polyphenols content appear in well-separated regions of the PCA scatter plot (wines Y and Z on the right side of the graph and wines X and W on the left part of the graph). This means that the combined system could discriminate simultaneously according to the type of closure (thanks to the information provided by the electronic nose and the electronic eye systems) and according to the polyphenol levels (due to the information provided by the electronic tongue). The improvement on the discrimination and prediction capabilities was confirmed by the PLS-DA models shown in Table 2.

4. Conclusions

Wines treated with different amount of oxygen have been successfully analysed using an electronic nose, an electronic tongue and an electronic eye. The changes in the sensory attributes in-

duced by the use of closures of varying permeability have been detected by the electronic nose and by the electronic eye. In contrast, the electronic tongue is more sensitive to the organoleptic properties related to the oxidation state of the wine induced by micro-oxygenation and by the polyphenolic content controlled during wine making. The discrimination capability of the system is significantly improved when the signals from each sensory subsystem are combined into a multimodal representation.

The electronic panel is a good precision and accurate multiparameter system that can be a valuable tool in estimating the organoleptic characteristics of wines and can complement the classical sensorial analysis carried out in wineries and oenological centres.

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