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Analytical Methods

Evaluation of oxygen exposure levels and polyphenolic content of red wines using an electronic panel formed by an electronic nose and an electronic tongue

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ABSTRACT

An electronic panel formed by an electronic nose and an electronic tongue has been used to analyse red wines showing high and low phenolic contents, obtained by flash release and traditional soaking, respectively, and processed with or without micro-oxygenation. Four oxygen transfer rate conditions (0.8, 1.9, 8.0, and 11.9 μl oxygen/bottle/day) were ensured by using synthetic closures with controlled oxygen permeability and storage under controlled atmosphere. Twenty-five chemical parameters associated with the polyphenolic composition, the colour indices and the levels of oxygen were measured in triplicate and correlated with the signals registered (seven replicas) by means of the electronic nose and the electronic tongue using partial least squares regression analysis.

The electronic nose and the electronic tongue showed particularly good correlations with those parameters associated with the oxygen levels and, in particular, with the influence of the porosity of the closure to oxygen exposure. In turn, the electronic tongue was particularly sensitive to redox species including oxygen and phenolic compounds. It has been demonstrated that a combined system formed from the electronic nose and the electronic tongue provides information about the chemical composition of both the gas and the liquid phase of red wines. This complementary information improves the capacity to predict values of oxygen-related parameters, phenolic content and colour parameters.

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1. Introduction

The phenolic composition and associated organoleptic properties of red wines are greatly dependent on the grape variety and the wine-making process.

The concentration of phenolic compounds can be modified by using various extraction methods (Sacchi, Bisson, & Adams, 2005). Among such methods, the flash détente (also called flash release process), allows extraction of phenolic compounds and can be used to produce polyphenol-enriched grape juices (Garrido & Borges, 2011; Morel-Salmi, Souquet, Bes, & Cheynier, 2006). Moreover, oxygen exposure during the wine-making process, for instance in operations like micro-oxygenation, can also influence the phenolic composition (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Sartini, Arfelli, Fabiani, & Piva, 2007).

It has recently been shown that sealing systems can influence the evolution of white and red wines. It has been postulated that oxygen transmission rates (OTR) through the stoppers could be the main cause of the differential wine evolution (Kwiatkowski, Skouroumounis, Lattey, & Waters, 2007; Lopes et al., 2009). Indeed stoppers can differ in oxygen barrier properties allowing different oxygen transfer rates (Pocas, Ferreira, Pereira, & Hogg, 2010). Storage under different OTR conditions actually induced differences in the wine phenolic composition (Wirth et al., 2010) and sensory properties (Caillé et al., 2010).

The influence of the oxygen exposure on the phenolic composition of wines is usually studied by means of traditional analytical techniques (mainly spectroscopic and chromatographic methods). In such works, a high number of parameters including a variety of phenols, measures of colour, and oxygen related variables are measured (Caillé et al., 2010; Dimkou et al., 2011; Wirth et al., 2010).In past years, a different method to analyse complex samples such as

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wines has been developed. Electronic noses (e-nose) (Baldwin, Bai, Plotto, & Dea, 2011; Peris & Escuder-Gilabert, 2009) and electronic tongues (e-tongue) (Del Valle, 2010; Escobar et al., 2013; Parra, Hernando, Rodriguez-Mendez, & de Saja, 2004; Riul, Dantas, Miyazaki, & Oliveira, 2010), operate in manner analogous to human senses and can perceive odors and tastes. An e-nose (or an e-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 and/or Multivariate data analysis.

Wines have been extensively analysed using e-noses based on resistive sensors (Capone et al., 2000; Lozano, Arroyo, Santos, Cabellos, & Horrillo, 2008; Villanueva, Guadarrama, Rodriguez-Mendez, & de Saja, 2008) and e-tongues based on electrochemical sensors (Gay et al., 2010; Moreno i Codinachs et al., 2008; Riul et al., 2010; Verrelli, Lvova, Paolesse, Di Natale, & D'Amico, 2007). Electrochemical e-tongues have been particularly successful in the analysis of wines due to the important role that oxygen and antioxidants play in their organoleptic characteristics (Parra et al., 2004). Both, the e-tongue and nose have demonstrated a good capability to discriminate among red wines elaborated using different extraction techniques and micro-oxygenation methods and bottled under different OTR conditions (Prieto et al., 2011).

E-noses and tongues are analytical systems that provide global information about the sample instead of information on particular components. However, if the data matrix obtained by such multisensor systems is analysed with adequate chemometric processing tools, descriptive or predictive information of particular parameters could be extracted (Oliveri, Casolino, & Forina, 2010).

The aim of this work was to establish correlations between the chemical parameters associated with the oxygen and the polyphenolic composition of red wines and the signals registered by means of an e-nose (based on resistive sensors) and an e-tongue (based on electrochemical sensors), using partial least squares (PLS1) regression analysis. For this purpose, four Grenache red wines with high and low phenolic contents, obtained by flash détente or flash release (FR) and traditional soaking (Trad), respectively, and processed with (Mox,4.6 mg l^{-1} O_2) or without (No Mox) micro-oxygenation were prepared. Four OTR conditions (0.8, 1.9, 8.0, and 11.9 μg oxygen/bottle/day) were ensured by using synthetic closures with controlled oxygen permeability and storage under controlled atmosphere.

2. Experimental

2.1. Wines

Wines were prepared from *Vitis vinifera* var. Grenache. Grapes from the first plot (22° Brix, pH = 3.6) were used for traditional wine-making and those from the second plot (25° Brix, pH = 3.7) were used for FR trial. The FR treatment consisted in de-stemming and crushing the grapes, heating them to 95 °C for six minutes, and submitting them to a strong vacuum (pressure closed to 60 hPa). Two wines were prepared by Trad and FR respectively. Each of these two wines was then divided in two batches submitted or not to micro-oxygenation (Mox/No Mox), yielding four wines in total: FR, FR + Mox, Trad, Trad + Mox.

Mox was performed with a 10-channel Oenodev system, at 5 mg O_2 l^{-1} $month^{-1}$ for 3 weeks. The No Mox modalities were stored in the same cellar in similar tanks. The total oxygen quantities introduced into these four wines (Tradmox, Trad, FRmox, FR) 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. 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. The OTR were calculated using Fibox 3 trace fibre optic oxygen meter (PreSens Precision Sensing GmbH, Regensburg, Germany) and were found to be 11.9, 8.0, 1.9 and 0.8 μg 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. Chemical measurements

2.2.1. Oxygen related parameters

Dissolved oxygen (DO) and Headspace Oxygen (HO) were measured with the Fibox 3-Trace fibre-optic oxygen meter coupled to Pst3 oxygen sensors (linearity range from the manufacturer: 0% to 50% oxygen) following a previously published procedure (Dimkou et al., 2011). The Closure Contribution (CL) parameter was defined in a previous work and indicates closure contribution to oxygen exposure of the wine (Dimkou et al., 2011). Essentially, CL is the OTR plus the amount of oxygen present at bottling.

2.2.2. Polyphenols related parameters

Anthocyanins (ACN), Hydroxycinnamic acids (HA), flavan-3-ol monomers, also called catechins (CAT), flavonols (FLV) and derived pigments were analysed by direct injection of the wines into the HPLC system. HPLC-DAD analysis were performed using a Waters 2690 system equipped with an autosampler system, a Waters 996 photodiode array detector, and a Millenium 32 chromatography manager software (Waters, Milford, MA). Separation was achieved on a reverse phase Atlantis dC18 column (250 × 2.1 mm, 5 μm packing) protected with a guard column of the same material (20 × 2.1 mm, 3 μm packing) (Waters, Milford, MA). The elution conditions were as follows: 0.250 ml/min flow rate; oven temperature30 °C; solvent A, water/formic acid (95:5 v/v); solvent B, acetonitrile/water/formic acid (80:15:5 v/v/v); elution was performed with linear gradients from 0% to 2% B in 10 min, from 2% to 10% B in 10 min, from 10% to 20% B in 20 min, from 20% to 30% B in 5 min, from 30% to 40% B in 5 min, from 40% to 50% B in 5 min, followed by washing and re-equilibration of the column. The injection volume for all samples was 5 μl. Calibration curves were established using the following external commercial standards of analytical grade: catechin and epicatechin (Extrasynthèse, France) to quantify catechin and epicatechin, respectively, at 280 nm, caffeic acid to quantify hydroxycinnamic acids at 320 nm, quercetin 3-O-glucoside (Extrasynthèse, France) to quantify flavonols at 360 nm, and malvidin-3-O-glucoside (Extrasynthèse, France) to quantify anthocyanins and red derived pigments at 520 nm. Quantifications of derived pigments were carried out on (epi) catechin-ethyl-malvidin-3-glucoside, carboxypyranomalvidin-3-glucoside (vitisin A) and phenylpyranomalvidin-3-glucoside, which are the major representatives of ethyl-bridged pigments (EB), carboxypyranoanthocyanins (CPA), and phenylpyranoanthocyanins (PPACN), respectively.

Proanthocyanidin (syn condensed tannin, TAN) composition was determined by HPLC after acid-catalysed cleavage in the presence of excess of phloroglucinol (Kennedy & Jones, 2001). The protocol was adapted for analysis of wine tannins as recently described (Ducasse et al., 2010). Total proanthocyanidin content was calculated as the sum of all units released after phloroglucinolysis, The percentage of epicatechin 3-gallate units (%Gall), percentage of epigallocatechin units (%EGC) and mean degree of polymerisation (mDP), were also calculated. The ratio of tannins to anthocyanins (T/A) was also calculated.

Absorbance measurements were performed using a UV mc2 spectrophotometer (Safas, Monaco, France) as previously described

Table 1
Wine-making process, type of closure used, % oxygen storage environment and codes of the wines used for this study.

Crush	Microoxygenation	Closure (%)	Sample
Traditional crush	No Mox	Light 21	T1
		Classic 21	T2
		Classic 4	T3
		Classic 1	T4
	Mox	Light 21	TM1
		Classic 21	TM2
		Classic 4	TM3
		Classic 1	TM4
Flash release	Mox	Light 21	FM1
		Classic 21	FM2
		Classic 4	FM3
		Classic 1	FM4
	No Mox	Light 21	F1
		Classic 21	F2
		Classic 4	F3
		Classic 1	F4

(Atanasova et al., 2002). Absorbance values at 420, 520 and 620 nm were measured directly in a 1-mm light path cell and converted to absorbance values (A420, A520, A620) with a 10-mm light path. Wine pigments (WP) were evaluated at A520. Colour intensity (CI) was calculated as the sum A420 + A520 + A620 and Hue (H) as the ratio A420/A520. Identical measurements were performed 30 min after addition of acetaldehyde to wine in order to release anthocyanins involved in bisulphite adducts, to obtain the same indexes corrected for bisulphites at wine pH [Corrected colour intensity (CIcor), Corrected Hue (Hcor)]. Total polyphenol index (TPI) and total colour of pigments (TCP) were defined as the absorbance at 280 nm and at 520 nm, respectively, of wine 4 h after a 100-fold dilution in HCl 1 M. Non discoloured pigments (NDP) were determined at 520 nm, 10 min after addition of sodium metabisulphite (3 mg ml^{-1} of wine).

Chemical age of wine (CAW) was evaluated by calculating the percentage of pigments measured after addition of acetaldehyde ($A520_{acetald}$) (Somers, 1977). The percentage of pigments discoloured by sulphites (%$PDSO_2$) was calculated as 100%-CAW.

Colour due to co-pigmentation (CC) was determined as described by Boulton (Boulton, 1996), as the difference in absorbance values at 520 nm of the wine added with acetaldehyde and the wine added with acetaldehyde and diluted 10-fold with a model wine consisting of a buffer at the wine pH and containing the same EtOH concentration as the wine.

2.3. Electronic nose

An array of 14 gas sensors was constructed using inorganic metal oxide (MOX) sensing units that were selected according to a previously published method (Villanueva et al., 2008). Sensors were polarised using a constant voltage of 5 V. The resistance was measured every 0.5 s. Data were monitored in real time and the graphs could be followed using a program written in Visual Basic software from Microsoft.

The *SPME* (Solid Phase Microextraction) sampling method was used as the injection method equipped with a bipolar fibre of polydimethylsiloxane coated with carbowax and divinylbenzene (*PDMS/CW/DVB*, *Supelco*).

Data matrix used for the different chemometric treatments had a dimension of 96 × 14, where the rows represent the wine samples analysed (six replicates per type of wine) and the columns correspond to the value of the maximum variation of the resistance registered upon exposure of each sensor to the headspace of the wine samples.

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). CPEs were used as working electrodes, a platinum wire as the counter electrode and 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, E_{sw} = 0.1 V, E_{sw} = 0.1 V, ΔE = 0.007 V (except for CoPc, ΔE = 0.005 V).

2.5. Data treatment

Data analysis involved an initial pre-processing of the signals registered with the e-nose and the e-tongue. In the case of the e-nose, maximum values of the transient responses from each of the 14 MOX sensors were selected as input variables. Voltammetric signals required a more complex pre-treatment to obtain 10 parameters per sensor. For this purpose, signals were pre-processes using a method developed previously, based on kernel functions where voltammetric curves were separated into ten bell-shaped curves (ten variables) (Parra et al., 2004). The kernel method allows the data number to be reduced without losing important information throughout the total response. The ten selected variables were used as the input parameters for statistical analysis.

The partial least squares Discriminant Analysis (PLS-DA) method was used to establish prediction models based on the polypehnol content, the effect of micro-oxygenation and closure OTR (Prieto et al., 2011).

Data were tested for statistical significance using multi-way ANOVA routines running under Matlab environment. Three factors were established: extraction technique (Trad or FR), micro-oxygenation (Mox or No Mox) and type of closure (4 degrees of OTR). Values of $p < 0.05$ were considered statistically significant. PLS1 regression was performed to model the relationships between the electronic signals and the results provided by physico-chemical analysis.

Both the X-matrix (containing the electronic panel data values) and the Y-matrix (containing the analytical parameters) were pre-processed using a normalisation routine. The optimum number of latent variables (LV) was selected by choosing the first local minimum in the residual Y variance plot. Validation of the predictive models was carried out by full cross-validation method (leave-one-out).

3. Results and discussion

Wines were analysed using the electronic systems (e-nose and e-tongue). In good accordance with previously published results (Prieto et al., 2011), our system was able to discriminate the wines according to their polyphenolic content. 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 capability of discrimination of the system is illustrated in Fig. 1, where the PLS-DA plot corresponding to the classification of wines by means of the electronic panel, according the micro-oxygenation is shown. The PLS-DA prediction and validation models using the panel test shown in the inset, demonstrate the good capability of the system to classify the wine samples according to the use of micro-oxygenation.

3.1. ANOVA studies

Red wines with different oxygen exposure levels and polyphenol contents, prepared by diverse extraction techniques (FR/Trad),

micro-oxygenation methods (Mox or No Mox) and nano-oxygenation levels (using polymeric closures with different oxygen transmission rates), were analysed by chemical methods after 10 months of bottling.

As stated before, the objective of this work was to establish correlations between the chemical parameters and the results obtained using an e-nose and an e-tongue by means of PLS1. Due to the large number of chemical variables, ANOVA studies were conducted to evaluate the importance of the vinification method in the chemical composition of wines.

In order to establish the degree of significance of the variables, three factors were defined: the extraction technique (two levels: FR/Trad); the application of micro-oxygenation (two levels: Mox/No Mox) and the OTR of the closures (four different levels). The *p*-values for chemical parameters are listed in Table 2. The results showed that the three factors had a significant influence on several of the chemical parameters analysed. Of particular relevance was the influence of the OTR on most of the chemical parameters analysed and, in particular, the association with oxygen levels (DO, HO and CL). The reason is that during storage, oxygen ingresses through the closure (OTR), causing additional oxygen uptake (Lopes et al., 2009), which has an impact on overall oxygen levels. In turn, how the wine is made influences parameters associated with polyphenolic content and colour.

3.2. Partial least squares regression (PLS1)

PLS1 was used as a prediction technique to correlate the data derived from the e-nose and e-tongue with the values obtained by means of traditional methods.

Three sets of independent regression models were performed. The first set of models correlated the results of the e-nose with each chemical parameter. The second set of models correlated the outputs of the e-tongue with the chemical parameters. The last model merged the information obtained from both the e-nose and e-tongue with the chemical parameters.

Table 3 summarises the statistical parameters for the PLS1 regression models correlating the output of the e-nose with the chemical parameters associated with the polyphenolic content, colour and oxygen levels. Table 3 shows the root mean square errors, and the correlation coefficients at calibration and prediction.

Root Mean Square Error of Calibration (RMSEC) is a measure of the average difference between predicted and measured response values at the calibration stage. Root Mean Square Error of Prediction (RMSEP) is a measure of the average difference between predicted and measured response values at the prediction or validation stage. RMSEC and RMSEP measure the calibration error and prediction error in the same units as the original response variable. In turn, R_c (and R_p) are correlation coefficients of calibration (and prediction). LV indicates the number of latent variables used in the calculations. The correlations obtained using PLS1 are illustrated in Fig. 2 were an example of the observed versus predicted graph, corresponding to the DO measured with the e-nose, is presented.

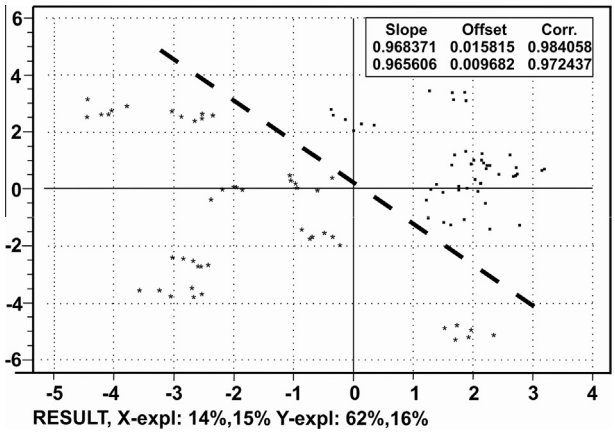

Fig. 1. PLS-DA plot corresponding to the classification of wines by means of the electronic panel, according the micro-oxygenation (black stars correspond to wines prepared using micro-oxygenation; black squares correspond to wines not micro-oxygenated. The inset shows the PLS-DA prediction and validation models using the panel test.

Table 2
ANOVA results for the chemical parameters.

	Trad/flash	Mox/No Mox	OTR
Oxygen related parameters			
DO mg l^{-1}	ns	ns	***
HO mg l^{-1}	ns	ns	***
CL	ns	ns	***
Polyphenols			
ACN mg l^{-1}	***	***	***
TAN mg l^{-1}	***	**	***
T/A	***	*	***
CAT mg l^{-1}	***	ns	***
HA mg l^{-1}	***	ns	***
CPA mg l^{-1}	***	***	***
EB mg l^{-1}	ns	ns	ns
FLV mg l^{-1}	ns	***	***
PPACN mg l^{-1}	ns	ns	ns
mDP	**	ns	***
%Gall	***	ns	ns
%EGC/	**	*	ns
Colour indices			
CI	**	*	***
CIcor	***	ns	***
Hcor	***	ns	***
TCP	ns	ns	***
TPI	***	ns	ns
NDP	ns	ns	***
CAW	***	ns	***
%PDSO$_2$	***	ns	***
WP	**	***	***
CC	**	ns	***

ns: $p > 0.05$ (not significant).
* $p < 0.05$ (significant).
** $p < 0.01$ (highly significant).
*** $p < 0.0001$ (extremely significant).

Excellent correlations (in both calibration and prediction) were found for CL and HO, which are parameters associated with the OTR, i.e. amount of oxygen that goes inside the bottle through the closure.

Surprisingly, good correlations were found between the output of the e-nose and some parameters associated with the polyphenolic content, i.e. TAN, CAT, HA, CPA or FLV, which show correlation coefficients in calibration (R_c) > 0.9 and coefficients of correlation in prediction (R_p) > 0.8, respectively. Good correlations between the e-nose signals and colour parameters were also observed for Hcor and TPI.

The good correlation found between the e-nose output and the concentration of compounds found in solution (such as polyphenols), can be explained by the working principle of the e-nose. This instrument provides global information of the composition of the headspace that, in turn, is related to the chemical composition of the liquid phase. There is also another aspect that might be worth considering: some studies have shown that the non-volatile composition of wines can alter volatility of aroma compounds. In previous papers (Caillé et al., 2010; Wirth et al., 2010), it has been observed that the different treatments applied to wines (Mox, FR, OTR) influence both the phenolic composition (TAN, CAT, HA etc.) and the aroma properties. The correlations between e-nose re-

Table 3
Results of the PLS1analysis with data obtained from the e-nose and oxygen related parameters polyphenolic content and colour indices.

Parameter	RMSEC	RMSECV	R_c	R_p	LV
Oxygen related parameters					
DO mg l^{-1}	0.0094	0.0114	0.804	0.701	4
HO mg l^{-1}	0.123	0.148	0.912	0.873	4
CL	0.603	0.740	0.935	0.901	5
Polyphenols					
ACN mg l^{-1}	7.988	13.561	0.858	0.529	3
TAN mg l^{-1}	112.399	178.869	0.953	0.878	3
T/A	1.999	3.377	0.904	0.703	3
CAT mg l^{-1}	4.506	7.555	0.933	0.800	3
HA mg l^{-1}	22.988	39.984	0.948	0.843	3
CPA mg l^{-1}	12.98	86.081	0.947	0.947	10
EB mg l^{-1}	0.030	0.038	0.669	0.471	2
FLV mg l^{-1}	2.447	4.606	0.903	0.630	3
PPACN mg l^{-1}	0.162	0.237	0.792	0.502	3
mDP	0.254	0.289	0.520	0.304	1
% Gall	0.405	0.626	0.845	0.582	2
%EGC	1.421	2.111	0.709	0.329	4
Colour indices					
CI	0.280	0.457	0.899	0.598	3
CIcor	0.131	0.167	0.744	0.568	3
Hcor	0.013	0.023	0.901	0.662	3
TCP	0.904	1.218	0.688	0.396	4
TPI	2.626	3.914	0.901	0.866	3
NDP	1.185	1.366	0.677	0.548	5
CAW	1.149	2.009	0.902	0.700	4
%$PDSO_2$	1.186	2.082	0.992	0.668	4
WP	0.175	0.251	0.752	0.436	2
CC	0.072	0.156	0.904	0.531	5

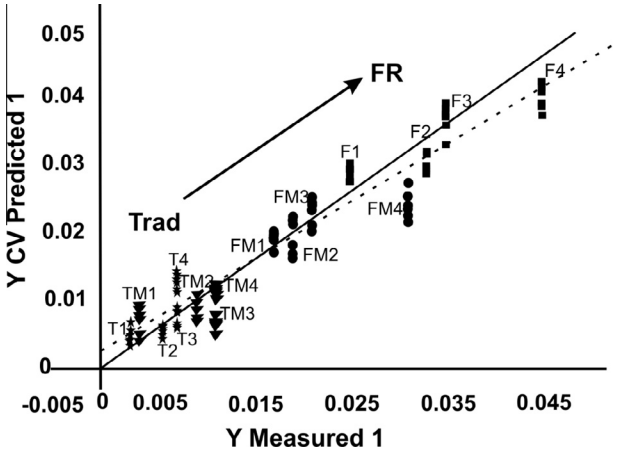

Fig. 2. PLS1 regression model for the estimation of DO in a red wine using the electronic nose, for calibration (dotted line) and validation (solid line).

sponse and phenolic composition are mostly due to the fact that differences in oxygen exposure alter simultaneously phenolic composition and volatile composition (i.e. (1) higher oxygen levels in the headspace, (2) lower SO_2 levels in the headspace, (3) differences in the aroma profiles detected by sensory analysis) (Caillé et al., 2010). It has also been shown (Zapata, Lopez, Herrero, & Ferreira, 2012) that the non-volatile composition of the wine can alter transfer of some aroma compounds into the gas phase.

So the e-nose is sensitive to the aroma differences, which happen to be correlated with the different composition of the liquid phase. By changing the phenolic composition of the wines (through Mox and FR), the volatility of aroma compounds is also affected. For these reasons, although the instrument is not able to detect directly non-volatile compounds such as tannins, a correlation can be found between the signal provided by the gas phase and the concentration of those non-volatile compounds present in the wine matrix.

PLS1 regression models were also applied to correlate the e-tongue data set with chemical data (Table 4). The e-tongue showed excellent correlations with the parameters associated with oxygen and in particular with the closure contribution parameter (CL) (R_c = 0.972 in calibration and R_p = 0.935 in prediction) and with the oxygen in the headspace, HO (R_c = 0.952 in calibration and R_p = 0.886 in prediction). The capacity of the e-tongue to predict chemical values of several parameters related with the polyphenolic content with R_c higher than 0.9 (ACN, TAN, CAT, HA CPA, PPACN) and with parameters related with the colour (Hcor, TPI and CC) is also remarkable. The good predictions achieved by the e-tongue are in agreement with previous works, which indicate that the array of voltammetric sensors is particularly sensitive to the presence of redox species (i.e. polyphenols or oxygen) and, on average, to the antioxidant capability of wines (Apetrei et al., 2007).

Bearing in mind that flavour perception is based on two components: taste and aroma, it can be assumed that flavor could be analysed using a combination of an e-nose and an e-tongue. Several attempts have been made to combine e-noses and e-tongues (Rodríguez-Méndez et al., 2004; Winquist, Lundström, & Wide, 1999). It has been demonstrated that the simultaneous use of e-noses and e-tongues can increase the amount of information extracted from a certain sample. Moreover, using different transduction principles, lower correlation between the responses of different sensor types is assured.

In this last part of the work, PLS1 was used to establish a model between the data provided by both electronic systems (e-nose and e-tongue), and all the data obtained from chemical analysis (oxygen content, polyphenols and colour). As observed in Table 5, an improvement of the prediction capabilities is obtained. Almost all the variables showed calibration errors (R_c) than 0.9 while the errors of validation (R_p) were higher than 0.8. The explanation is that measuring in the liquid and in the gas phase, complementary information about the chemical nature of the wines can be extracted. Finally, it is important to mention that excellent correla-

Table 4
Results of the PLS1 analysis with data obtained from the e-tongue and oxygen related parameters polyphenolic content and colour indices.

Parameter	RMSEC	RMSECV	R_c	R_p	LV
Oxygen related parameters					
DO mg l^{-1}	0.0091	0.0130	0.818	0.607	4
HO mg l^{-1}	0.0925	0.1413	0.952	0.886	6
CL	0.400	0.604	0.972	0.935	6
Polyphenols					
ACN mg l^{-1}	5.824	8.102	0.928	0.858	3
TAN mg l^{-1}	115.974	243.705	0.950	0.705	3
T/A	2.667	3.874	0.823	0.570	3
CAT mg l^{-1}	4.124	8.487	0.944	0.742	3
HA mg l^{-1}	21.356	44.701	0.955	0.792	3
CPA mg l^{-1}	46.822	140.217	0.970	0.694	3
EB mg l^{-1}	0.020	0.024	0.873	0.810	2
FLV mg l^{-1}	2.898	3.760	0.861	0.758	2
PPACN mg l^{-1}	0.094	0.114	0.936	0.903	3
mDP	0.137	0.182	0.886	0.794	3
% Gall	0.137	0.182	0.886	0.794	1
%EGC	0.991	1.263	0.870	0.792	2
Colour indices					
CI	0.303	0.418	0.866	0.735	3
CIcor	0.122	0.146	0.782	0.676	2
Hcor	0.651	0.023	0.917	0.651	3
TCP	0.588	0.789	0.881	0.784	3
TPI	2.093	4.07	0.938	0.744	3
NDP	0.689	0.919	0.868	0.762	3
CAW	1.240	1.725	0.885	0.779	3
%$PDSO_2$	1.272	1.717	0.875	0.767	3
WP	0.143	0.166	0.841	0.781	3
CC	0.076	0.103	0.899	0.796	3

Table 5
Results of thePLS1analysis with data obtained from the e-panel and oxygen related parameters polyphenolic content and colour indices.

Parameter	RMSEC	RMSEP	R_c	R_p	LV
Oxygen related parameters					
DO mg l^{-1}	0.0085	0.0145	0.840	0.767	4
HO mg l^{-1}	0.0874	0.1351	0.965	0.944	6
CL	0.126	0.193	0.994	0.988	6
Polyphenols					
ACN mg l^{-1}	5.465	7.997	0.937	0.864	3
TAN mg l^{-1}	96.05	166.37	0.966	0.897	3
T/A	1.575	2.496	0.942	0.849	3
CAT mg l^{-1}	3.358	5.785	0.963	0.890	3
HA mg l^{-1}	17.445	30.701	0.970	0.907	3
CPA mg l^{-1}	57.78	76.156	0.955	0.921	4
EB mg l^{-1}	0.014	0.016	0.917	0.898	2
FLV mg l^{-1}	2.141	3.042	0.928	0.847	2
PPACN mg l^{-1}	0.091	0.116	0.941	0.904	3
mDP	0.112	0.158	0.926	0.848	2
%Gall	0.327	0.391	0.902	0.858	2
%EGC	0.894	1.332	0.899	0.754	3
Colour indices					
CI	0.225	0.292	0.912	0.851	3
CIcor	0.134	0.171	0.812	0.745	3
Tcor	0.010	0.014	0.932	0.890	3
TCP	0.462	0.654	0.928	0.856	3
TPI	1.868	2.924	0.952	0.874	3
NDP	0.681	0.898	0.872	0.775	4
CAW	1.024	1.398	0.923	0.854	3
$PDSO_2$	0.391	1.394	0.988	0.851	4
PV	0.129	0.151	0.874	0.823	3
CC	0.059	0.088	0.917	0.861	4

tions have been found between the output of the electronic systems and CL (R_c = 0.994), and HO (R_c = 0.965). These results demonstrate the important role of the OTR of the closure in the chemical composition of wines and the capability of the electronic systems to evaluate the role of the oxygen diffusion during bottle storage.

4. Conclusions

In this work, correlations between the signals obtained by means of an e-nose and an e-tongue exposed to experimental wines (with different polyphenolic content) and 25 parameters obtained by traditional chemical analysis (polyphenolic composition, oxygen parameters and colour indices) have been established for the first time. Quantitative data obtained from PLS1 regression models have demonstrated that e-nose and e-tongue responses correlate well with parameters associated with the oxygen level (such as headspace oxygen or closure characteristics) and with the polyphenolic content (such as tannins or hydroxycinnamic acids) and the colour.

The combined use of an e-nose and an e-tongue improves the quality of the predictions. The correlations achieved with our electronic panel have never been reached before.

These results indicate that e-noses and e-tongues (and the combination of both instruments forming an electronic panel), are useful instruments not only to provide global information of wine samples, but also they can be used to assess chemical parameters related to oxygen levels and polyphenolic content.

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