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Monitoring of evolution during red wine aging in oak barrels and alternative method by means of an electronic panel test

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ABSTRACT

A combination of the data obtained by means of an e-nose (based on resistive MOX sensors), an e-tongue (based on voltammetric sensors) and an e-eye (based on CIE Lab coordinates) has been used to monitor the aging of a red wine. The changes in the chemical composition of wines that occur during maturing have permitted the system to discriminate among wine samples collected after one, three, six and ten months of aging. The discrimination capability of the electronic panel test obtained by means of Principal Component Analysis (PCA), Partial Least Squares Discriminant Analysis (PLS-DA) is even higher than the discrimination achieved by means of traditional chemical analysis.
After ten months of aging it has been possible to discriminate between the wine aged in a French oak barrel and the same wine soaked with oak chips of the same origin and toasting level and treated with microoxygenation.

1. Introduction

Recently, alternative methods to the maturing of wine in oak barrels have been developed in order to simplify the aging process while ensuring that the wood-originated volatiles are released into the wine (Arapitsas, Antonopoulos, Stefanou, & Dourtoglou, 2004). One of these techniques consists in the addition of small oak wood pieces (chips or staves) to the wine kept in a stainless steel tank. The fast diffusion of these techniques makes necessary to carry out studies that analyze the influence of these techniques in the chemical and organoleptic characteristics of wines and to evaluate and characterize the differences between wines aged by the traditional system and wines treated by the alternative methods (Maga, 1989).

Several authors have studied the effects that produce the addition of wood pieces to wine by means of traditional chemical analysis such as chromatography (Fernández de Simón, Cadahía, Muiño, Del Álamo, & Nevares, 2010; Gay et al., 2010; Koussissi et al., 2009; Sanza, 2006).

Several authors have reported that the differences related to the phenolic composition could be used as the basis of a chromatographic method to detect the use of oak chips in the process of aging (Arapitsas et al., 2004; Rodríguez-Bencomo, Ortega-Heras, & Pérez-Magariño, 2010).

One of the most promising approaches for the analysis of wines consists in the use of arrays of sensors where several sensing materials, which exhibit different responses to various gases/liquids, are coupled with signal processing methods based on pattern recognition or artificial neural networks. Such systems are called electronic noses/tongues (Chen, Zhao, & Vittayapadung, 2008; Gardner & Bartlett, 1999) and analyze the sample as a whole without need of separating it in simple components. After an appropriate optimization, these systems have been adapted to the analysis of red wines.

Several groups have applied electronic noses to the analysis of red wines with different organoleptic characteristics: different varieties of grape, vintage or type of oak wood (Buratti et al., 2011; Santonico, Bellincontro, De Santis, Di Natale, & Mencarelli, 2010). Usually, these systems are based on multiarrays of resistive Metal Oxide (MOX) sensors coupled to an injection technique such as Solid Phase Microextraction (SPME) (Prieto et al., 2011; Villanueva, Guadarrama, Rodríguez-Mendez, & de Saja, 2008), head space (Apetrei et al., 2010; Cynkara, Cozzolino, Dambergsa, Janika, & Gishena, 2007; Muenchmeyer, Walte, & Matz, 2000). The preconcentration technique is necessary to eliminate or at least diminish the concentration of water and ethanol in the volatile mixture that interferes in the response of resistive sensors (Aleixandre et al., 2008; Berna, Trowell, Clifford, Cynkar, & Cozzolino, 2009). Electronic

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tongues based on voltammetric, potentiometric or impedance measurements have also been used to discriminate wines with different qualities (Apetrei et al., 2007; Cetó, Gutiérrez, Moreno-Barón, Alegret, & del Valle, 2011; del Valle, 2010; Escuder-Gilabert & Peris, 2010; Gutiérrez et al., 2011; Lvova et al., 2006; Riul et al., 2004; Žeravík et al., 2009).

The simultaneous use of an electronic nose and an electronic tongue can increase the capability of discrimination of the electronic systems (Di Natale et al., 2000).

Our group presented the first electronic sensory system, specifically designed for the characterization of wines, which combined three sensory modalities: an array of gas sensors, an array of electrochemical liquid sensors and an optical system to measure color by means of CIE Lab coordinates (Rodríguez-Méndez et al., 2004).

In spite of the potential applications of the electronic instruments in the organoleptic analysis of wines, few attempts have been carried out to use electronic noses or electronic tongues to discriminate between red wines aged in oak barrels and red wines treated with oak chips. This is due to the difficulties to detect the subtle differences between wines with similar characteristics. Regardless of the difficulties, an electronic tongue based on voltammetric sensors has been able to discriminate between red wines aged in oak barrel and red wines treated with oak chips (Apetrei et al., 2007). However, that study was carried out in wines aged during a large period of time (twelve months). In addition, wines soaked with oak chips and staves were introduced in a tank without microoxygenation. It would be of considerable interest to monitor periodically the changes of wines aged by different methods and to evaluate the rate of maturing in each case. Moreover, the comparison between wines aged in oak barrels and wines soaked with oak chips in stainless steel tanks is more interesting if wines introduced in the tanks are micro-oxygenated to simulate as much as possible the conditions of the oak barrel.

The objective of this work is to monitor and to compare the aging of a red wine aged in traditional oak barrels and the same wine treated by adding oak chips and microoxygenation to the aging vessel by means of an electronic panel formed by an electronic nose, and electronic tongue and an electronic eye. The capability of discrimination of the electronic panel and the conventional chemical analysis will be compared. For this purpose, a red wine of the D.O. Toro (Spain) has been aged by both methods using French oak barrels of three different degrees of toasting. The obtained wines have been analyzed by standard chemical analysis and by an electronic system developed in our laboratory. The capability of discrimination and classification of both methods has been evaluated by using Principal Component Analysis (PCA) and Partial Least Square Discriminant Analysis (PLS-DA).

2. Experimental

2.1. Wine samples under study

A red wine of the variety *Tempranillo* coming from the D.O. Toro (Spain) was elaborated. Then, the wine was divided into batches. The first batch (W0) was kept in a stainless steel tank (no contact with wood). This wine has been used as a control.

The red wine was stored into three different aging systems: six oak barrels (samples W10 to W15) with a 225 L capacity and nine stainless-steel 100 L tanks with oak chips (samples W1 to W9). The quantity of oak chips and staves necessary to reproduce the surface/volume relation of a 225 L barrel was calculated accordingly to the 2.04 m^2 inner surface of the barrels. Thus, 600 g of chips for each tank was used. One stainless-steel tank has been used as control system for the wine. The barrels and the wood of alternative aging systems were manufactured by the same cooperage (S.L. Magreñàn, La Rioja, Spain) with mild, medium and strong toasting degrees, respectively.

In oak barrel aging, the natural properties of the wood allow for a gentle aeration of the wine to occur over a prolonged period (Lorenzo, Garde-Cerdán, Pedroza, Alonso, & Salinas, 2009; Oliveira, Silva Ferreira, De Freitas, & Silva, 2011). This aids in the polymerization of tannin into larger molecules, which are perceived on the palate as softer (Cano-Lopez, Pardo-Minguez, Lopez-Roca, Fernandez-Fernandez, & Gomez-Plaza, 2006).

The process of microoxygenation aims to mimic the effects of slow barrel maturation within a shorter period and for less of the long-term cost associated with oak barrels. The usual rate of permeation of oxygen into a new French oak barrels is between 2.0 mL of O_2 per liter of wine per month (1.66 mL L^{-1} $month^{-1}$) (Moutonet, Mazauric, Saint-Pierre, & Hanocq, 1998) and 2.5 mL L^{-1} $month^{-1}$ (Kelly & Wollan, 2003).

In our case the microoxygenation in the range 2.0–3.0 mL L^{-1} $month^{-1}$ O_2 was conducted in order to simulate the conditions of natural aging of wine in oak barrel. Dissolved oxygen was measured by means of electrochemical systems based on Clark's electrode.

Table 1 summarizes the characteristics of the aging methods used in the study. In order to monitor the aging process, samples were collected every three months: month 1 (S1), month 4 (S2), month 7 (S3), month 10 (S4).

2.2. Chemical analysis

Conventional chemical analyses of the wines were carried out following international regulations (OIV, 1990).

Conventional parameters included: Reducing sugars (S, $g\cdot L^{-1}$), dry extract (DE as $g\cdot L^{-1}$), alcoholic grade (AD %v/v), relative density (DEN) and potassium (K, as $mg\cdot L^{-1}$), volatile acidity (VA, as $g\cdot L^{-1}$ of acetic acid), total acidity (TA as $g\cdot L^{-1}$ of tartaric acid) and tartaric acid (T as $mg\cdot L^{-1}$of tartaric acid), glycerol (G as $g\cdot L^{-1}$of glycerol) pH, Free-SO_2 (F–SO_2, as $mg\cdot L^{-1}$), Combined-SO_2 (C–SO_2, as $mg\cdot L^{-1}$) and total-SO_2 (T–SO_2, as $mg\cdot L^{-1}$). The results of chemical parameters are summarized in Table 2.

2.3. Electronic panel

The gas sensor array was constructed using fourteen inorganic sensors purchased from Figaro and FIS. The sensors were mounted in a stainless steel chamber with a volume of 150 mL. The analyses were conducted using a custom-made odor-delivery system combining the gas sensor array with a preconcentration system based on solid-phase microextraction (SPME) according to a previous procedure specifically adapted to wine (Prieto et al., 2011; Villanueva et al., 2008).

Three milliliters of the wines was placed in 10 mL vials, and the SPME fiber coated with 100 μm of polyacrylate (PA, Supelco) was introduced in the gas-phase of the vial for 15 min at room temperature (25 °C). The fiber was then placed in a heated injection port and desorbed in two steps. The first desorption was carried out at 50 °C to eliminate traces of water and ethanol adsorbed by the fiber. This eluent was discarded. A second thermal desorption was carried

Table 1
Characteristics of the wines under study.

Sample	Aging system	Origin of wood	Toasting level
W0	Control wine aged in Stainless steel tank	None	–
W1, W2, W3	Stainless steel tank with Chips	French	Mild
W4, W5, W6	Stainless steel tank with Chips	French	Medium
W7, W8, W9	Stainless steel tank with Chips	French	Strong
W10, W11	Oak barrel	French	Mild
W12, W13	Oak barrel	French	Medium
W14, W15	Oak barrel	French	Strong

Table 2
Results of the wines main chemical parameters.

Wine	T	G	K	PT	AD	DE	TA	VA	T–SO_2	F–SO_2	S	DEN	pH
Month 1 — S1													
W0	1.8	8.7	1060	85	14.03	30.4	5.38	0.42	31	11	1.3	0.994	3.32
W1	1.8	8.8	1070	86	14.04	30.4	5.39	0.41	16	7	1.3	0.994	3.33
W2	1.8	9.0	1100	86	14.05	30.2	5.41	0.39	26	10	1.3	0.994	3.33
W3	1.8	8.9	1090	86	14.02	30.3	5.41	0.40	16	7	1.3	0.994	3.33
W4	1.9	9.0	1070	85	14.04	30.4	5.39	0.39	19	12	1.3	0.994	3.33
W5	1.9	8.9	1100	85	14.02	30.3	5.45	0.42	31	7	1.3	0.994	3.33
W6	1.8	9.0	1070	85	14.08	30.8	5.38	0.41	16	7	1.3	0.994	3.32
W7	1.8	9.0	1040	86	13.98	30.2	5.39	0.39	26	13	1.3	0.994	3.33
W8	1.8	8.9	1050	86	14.02	30.6	5.40	0.42	26	7	1.3	0.994	3.32
W9	1.8	9.2	1080	86	14.04	30.4	5.39	0.41	25	8	1.3	0.994	3.32
W10	1.7	8.6	1020	87	14.05	30.6	5.42	0.49	24	9	1.3	0.995	3.32
W12	1.8	8.5	1060	87	14.11	30.4	5.40	0.48	25	8	1.2	0.995	3.33
W14	1.8	8.7	990	87	14.05	30.5	5.43	0.46	26	7	1.3	0.995	3.33
Month 4 — S2													
W0	0.7	8.5	960	83	14.19	34.2	5.28	0.36	79	47	1.2	0.995	3.30
W1	0.7	8.5	990	85	14.12	34.8	5.41	0.34	64	27	1.2	0.995	3.31
W2	1.9	8.5	1040	85	14.13	35.3	5.41	0.35	69	32	1.2	0.995	3.32
W3	1.9	8.5	1050	85	14.13	34.5	5.41	0.35	70	32	1.3	0.995	3.33
W4	1.9	8.2	1060	84	14.12	35.3	5.40	0.36	70	27	1.2	0.995	3.34
W5	1.9	8.4	1030	85	14.14	34.3	5.43	0.35	62	24	1.3	0.995	3.33
W6	1.9	8.4	1020	84	14.22	36.9	5.40	0.35	77	31	1.3	0.995	3.32
W7	1.9	8.6	1030	86	14.21	35.3	5.43	0.33	76	32	1.2	0.995	3.32
W8	1.9	8.6	1060	85	14.15	34.6	5.43	0.34	80	29	1.2	0.995	3.32
W9	1.9	8.6	1060	85	14.16	36.4	5.41	0.35	86	37	1.2	0.995	3.32
W10	1.7	8.7	1030	86	14.16	35.6	5.52	0.48	74	25	1.2	0.995	3.33
W12	1.9	8.4	1050	86	14.10	34.4	5.50	0.38	84	34	1.3	0.995	3.33
W14	1.9	8.6	980	86	14.19	36.5	5.49	0.43	80	28	1.3	0.995	3.32
Month 7 — S3													
W0	1.3	8.6	1110	82	14.05	33.3	5.59	0.65	100	20	1.4	0.995	3.47
W1	1.4	8.8	1080	84	14.11	33.7	5.59	0.58	66	16	1.3	0.995	3.55
W2	1.5	8.9	1140	84	14.14	34.0	5.63	0.61	93	17	1.3	0.995	3.56
W3	1.3	8.8	1050	84	14.24	34.3	5.62	0.64	88	16	1.4	0.995	3.56
W4	1.5	8.9	1150	84	14.11	34.2	5.72	0.68	96	16	1.2	0.995	3.56
W5	1.5	8.7	1130	84	14.16	34.3	5.68	0.61	84	17	1.2	0.995	3.56
W6	1.4	8.8	1010	83	14.19	34.7	5.71	0.63	0	18	1.2	0.995	3.53
W7	1.4	9.0	1090	85	14.20	34.7	5.70	0.61	101	18	1.5	0.995	3.55
W8	1.4	8.7	1120	84	14.16	34.6	5.69	0.64	103	18	1.5	0.995	3.55
W9	1.3	8.8	1110	84	14.17	35.1	5.75	0.65	112	20	1.3	0.995	3.55
W10	1.5	9.0	1120	85	14.21	35.3	5.80	0.69	112	19	1.4	0.995	3.55
W11	1.4	8.8	1110	85	14.16	35.1	5.79	0.69	103	18	1.2	0.995	3.54
W12	1.4	8.8	1040	84	14.15	35.4	5.73	0.67	104	20	1.3	0.995	3.55
W13	1.2	9.0	1080	84	14.25	35.9	5.74	0.70	108	19	1.2	0.996	3.55
W14	1.3	9.0	1100	84	14.21	36.4	5.74	0.68	110	20	1.4	0.996	3.55
W15	1.3	9.0	1100	84	14.27	37.1	5.70	0.69	110	19	1.5	0.996	3.53
Month 10 — S4													
W0	1.2	9.3	1180	83	13.34	30.8	6.40	1.70	95	13	1.2	0.995	3.43
W1	1.8	9.2	1110	84	13.52	30.8	5.27	0.10	113	61	1.4	0.994	3.46
W2	1.7	9.1	1120	84	13.47	30.0	5.35	0.41	118	49	1.4	0.994	3.45
W3	1.8	9.1	1110	84	13.51	30.3	5.31	0.39	122	48	1.4	0.994	3.44
W4	1.6	9.3	1120	83	13.49	30.1	5.37	0.50	111	35	1.3	0.994	3.44
W5	1.6	8.8	1110	84	13.49	30.2	5.34	0.42	107	39	1.4	0.994	3.45
W6	1.5	9.0	1140	83	13.58	30.4	5.35	0.43	107	37	1.3	0.994	3.45
W7	1.6	9.2	1120	84	13.50	30.0	5.33	0.41	122	44	1.4	0.994	3.44
W8	1.5	9.5	1120	84	13.45	30.6	5.35	0.48	134	42	1.4	0.994	3.46
W9	1.7	9.2	1130	84	13.49	30.5	5.41	0.50	132	43	1.4	0.994	3.45
W10	1.3	9.7	1010	84	13.70	31.9	5.48	0.60	124	34	1.5	0.995	3.43
W11	1.4	9.5	1000	86	13.80	33.0	5.45	0.56	120	36	1.4	0.995	3.43
W12	1.4	9.8	1040	86	13.71	32.8	5.41	0.55	130	41	1.4	0.995	3.45
W13	1.3	9.3	1040	85	13.58	33.0	5.31	0.55	125	38	1.4	0.000	3.43
W14	1.3	9.6	1050	85	13.77	32.9	5.42	0.60	127	36	1.5	0.995	3.44
W15	1.3	9.5	1050	86	13.63	31.1	5.48	0.60	124	31	1.5	0.994	3.43

out at 250 °C for 30 min. The eluted vapors were injected in the test chamber. Data collection was performed through a commercial data acquisition card (PC-LPM-16, National Instruments). The sensors were polarized using a constant voltage of 5 V provided by a programmable power supply (FAC-662B). The scan rate used to measure changes in the resistance of the sensors was 0.5 s.

An array of liquid sensors was constructed formed by 6 voltammetric sensors: four carbon paste electrodes (CPE) were prepared as previously reported (Apetrei et al., 2007) using different electroactive materials as modifiers. The four electroactive materials included were two rare-earth bisphthalocyanine molecules with different central lanthanide ions, lutetium ($LuPc_2$) and gadolinium ($GdPc_2$) bisphthalocyaninates. In addition a cobalt (II) monophthalocyanine (CoPc) (Fluka) and ferrocene (Fluka) were also used as modifiers of the CPEs. Finally, one unmodified carbon paste electrode and one unmodified platinum electrode were also included in the array.

Electrochemical measurements were carried out using a conventional three-electrode cell. The reference electrode was an Ag|AgCl/KCl_{sat} and the counter electrode was a platinum wire. Pt, unmodified CPE and chemically modified CPEs were used as the working electrodes. The electrochemical experiments were carried out following a previously published method (Apetrei et al., 2007; Rodríguez-Méndez et al., 2004). Square Wave Voltammetry (SWV) was performed at a potential scan ranging from −1.0 to 1.3 V, by using $f = 15$ Hz; $E_{sw} = 100$ mV; $\Delta E_s = 7$ mV. The electrochemical experiments were performed at a controlled temperature of 25 °C.

Transmittance spectra were recorded using a series of eleven light-emitting diodes (LEDs), selected to cover the range from 780 nm to 380 nm. The spectrum of each wine was reconstructed and the CIElab coordinates were calculated.

2.4. Statistical analysis

Data obtained from chemical analysis were analyzed by Principal Component Analysis (PCA) and Partial least squares-Discriminant Analysis (PLS-DA). (Matlab v5.3. Natick, MA, USA, and The Unscrambler v9.1, CAMO ASA, Norway). In all figures X axis represents PC1; Y axis represents PC2; X-expl represents the percentage of variance explained by first three components, in the case of PCA. In the case of PLS-DA, X-expl represents the percentage of variance explained by first three latent variables in calibration; Y-expl represents the percentage of variance explained by first three latent variables in validation.

All samples were measured seven times with each sensor. In order to improve the robustness of the experiments, the samples were measured in a random order.

3. Results and discussion

3.1. Discrimination and classification of wines using traditional oenological parameters

Wines aged in oak barrels and wines treated with oak chips were analyzed by chemical methods. In addition, a series of phenolic compounds that have an influence in the taste and flavors of wines was also included in the study. In order to establish the ability of the chemical analysis (including phenolic compounds and color parameters) to discriminate between the different aging methods, Principal Component Analysis (PCA) was carried out. Fig. 1 shows the scores plot of the principal components. The results indicated that the first PC contained 28% of the information; the second PC contained 21% and the third PC contained 12%. The scores plot shows that the aging of wine can be followed through statistical analysis of the data obtained by traditional chemical analysis. However, it is difficult to discriminate between wines aged in oak barrels and those treated with chips, due to the similar chemical composition. A certain degree of discrimination was attained only after seven months of aging, with stronger correlation of the data after 10 months of aging. However, use of more data obtained by means of other techniques, such as chromatography (Koussissi et al., 2009), could help for discrimination of wines aged by traditional and alternative technique.

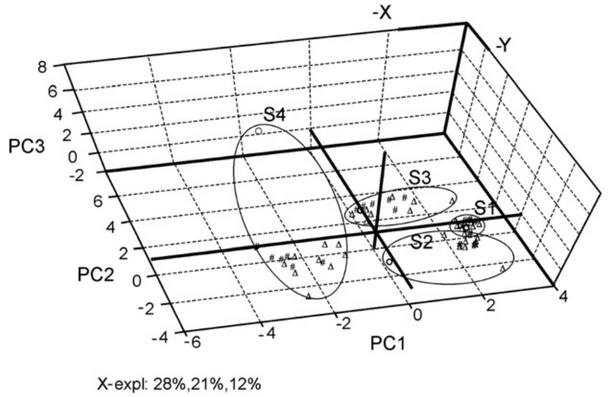

Fig. 1. PCA score plot of the oenological parameters of the wines under study. o — control wine, Δ — wine with oak chips, # — wine in oak barrel. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

3.2. Discrimination and classification of wines by means of the electronic panel

3.2.1. Discrimination studies

As stated before, the objectives of this work were to establish whether our electronic panel is able to monitor the aging of wines and to discriminate the particular characteristics induced in red wines by aging in oak casks or by soaking with oak chips or staves.

Fig. 2 presents the PCA scatter of the variations of the resistances of the array of gas sensors from the electronic nose (e-nose). The first three principal components capture 47%, 22% and 19% of the variance respectively.

As observed in the figure, the changes in the chemical composition of wines that occur during maturing induce changes in the composition of the headspace of the samples and for this reason the e-nose can monitor the aging of wines.

When analyzing the results in more depth, it can be observed that after one month of aging a reduced degree of discrimination can be obtained and wines aged in oak barrels and wines treated with oak chips. Surprisingly, next sampling (4 months of aging) samples matured using both methods were more similar and could not be discriminated. In fact, clear discrimination could not be achieved until a period of 10 months of aging elapsed.

In the case of the electronic tongue, it has been observed that the intensity and the positions of the redox processes registered during the voltammetric experiments are influenced by the chemical nature of the tested solution. For these reasons the electrochemical signals could be used to discriminate among wines with different characteristics.

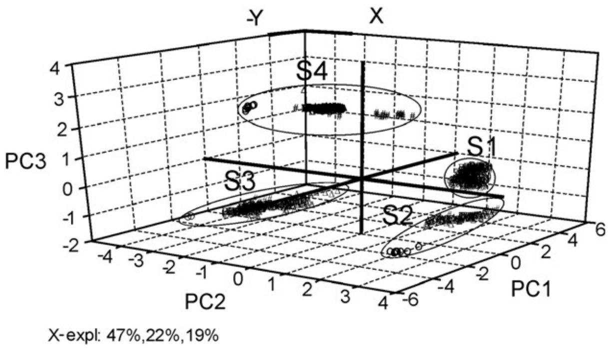

Fig. 2. Score plot of the PCA of the array of resistive sensors (e-nose) exposed to the wines aged by different methods. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

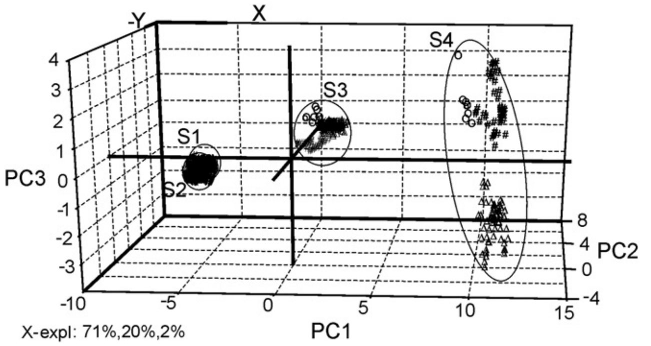

Fig. 3. Score plot of the PCA of the array of electrochemical sensors (e-tongue) exposed to the wines aged by different methods. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

With the objective to evaluate the capability of the electronic tongue to discriminate among wines aged by different methods, PCA was conducted using the electrochemical signals as the input variable. Fig. 3 shows the PCA scores plot (PC1 vs. PC2 vs. PC3). The first PC accounts for the 71% of the variation in the electrochemical signal, and the second principal component accounts for the 20% and the third principal component 2%. Overall, PC1, PC2 and PC3 explained 93% of the total variance between the samples. Fig. 3 demonstrated that the electronic tongue is also able to monitor the aging of wines. Moreover, after 10 months of aging wines aged in oak barrels could be totally discriminated from wines where pieces of wood were soaked and to the wine control.

As observed in Fig. 3 wine samples appear grouped into four classes in the clusters corresponding each sampling time. Samples in contact with oak chips appear separated from the samples aged in oak barrel. The wine sample used as a control (no contact with wood) appeared apart from the rest of the wines analyzed. The results indicate that after 10 months it is clearly possible to discriminate wines aged by traditional methods from wines flavored with pieces of wood (i.e. chips) with the differences between the samples aged by different methods increased with time.

Additionally, the differences between the samples aged by different methods were increased with the time. These results can be easily observed in the cluster corresponding to the S4 in Fig. 2 and Fig. 3. Moreover, wine samples treated with chips appear more dispersed in the plot than those aged in oak barrels. The observed differences are probably caused by the difficulty to control the microoxygenation process in the case of oak chips.

Regarding the visual aspects, the fourteen transmittance values of each wine sample were used to calculate the CIE Lab coordinates that were used as a feature vector for the multivariate analysis for

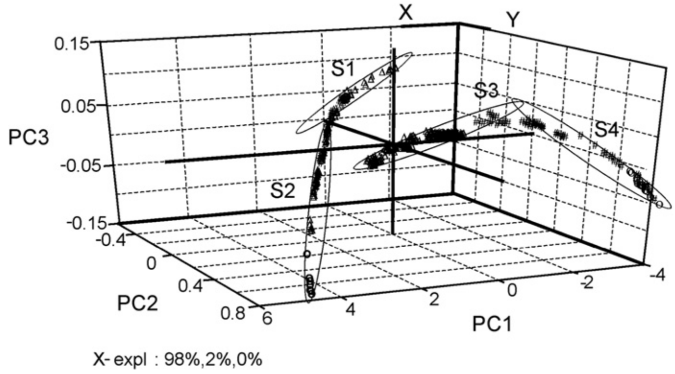

Fig. 4. Score plot of the PCAs of the CIE Lab coordinates (e-eye) exposed to the wines aged by different methods. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

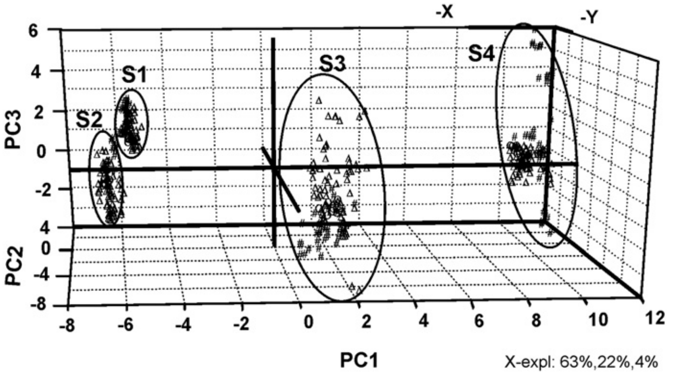

Fig. 5. PCA scores plot during the aging process obtained from the data obtained with electronic panel. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

electronic eye. The first principal components capture 100% of the total variance as shown in Fig. 4 (PC1 = 98.066%; PC2 = 1.891%; PC3 = 0.037%). As can be observed in the figure, the aging process can be easily followed by means of e-eye. However, the discrimination between the wines treated with oak chips or kept in oak barrel cannot be achieved by color monitoring.

The capability of discrimination achieved by means of the electronic nose is similar to that obtained by using the electronic tongue. Both systems have been capable to detect the use of oak chips after ten months of wine aging. However, the changes induced by the chips in the color are less effective to detect the use of such practice.

The next step in this study was to combine the data provided by individual multisensor systems in order to improve quality of the monitoring process of wine aging. The electronic wine panel test allows a simultaneous following of aging process regarding to aroma, taste and color. PCA score plot presented in Fig. 5 shows how by increasing the number of variable discriminating the samples evaluated at different times. Moreover, the discrimination between the wines in contact with oak chips and barrel can be observed with time and compared with those observed in the case of e-nose or e-tongue.

3.1.2. Classification of the samples

Partial least squares-Discriminant Analysis (PLS-DA) was used as a deterministic classification technique. PLS-DA is a classification method based on the PLS2 algorithm that performs a dimension reduction just as PLS does, but the predictions in a PLS-DA model are used to classify unknown samples, i.e. to predict the class membership of each sample (Apetrei et al., 2010; Barker & Rayens, 2003).

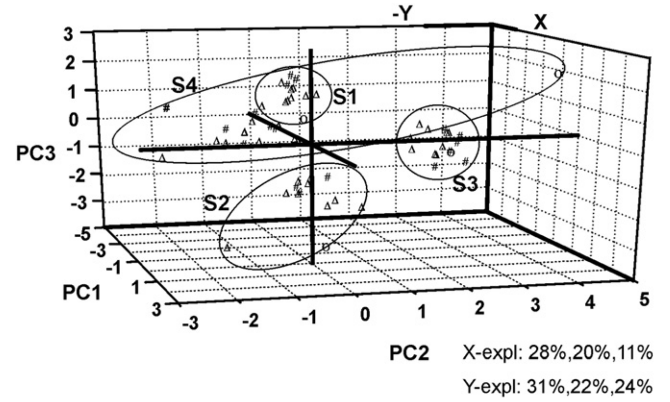

Fig. 6. PLS-DA scores plot corresponding to the monitoring of aging process by means of physicochemical analyses. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

Table 3
Quantitative data of the PLS-DA regression using physico-chemical analyses data.

Classification criteria	Calibration				Validation			
	Slope	Offset	R_c	RMSEC	Slope	Offset	R_p	RMSEP
S1	0.815	0.033	0.903	0.165	0.780	0.050	0.876	0.185
S2	0.742	0.060	0.861	0.215	0.665	0.065	0.814	0.246
S3	0.630	0.107	0.794	0.275	0.567	0.139	0.669	0.347
S4	0.872	0.037	0.933	0.162	0.803	0.046	0.907	0.190

PLS-DA is capable of separating “tight” classes of observations on the basis of the X-variables (namely, sensors), according to a Y-vector that encodes the class membership in a set of categorized variables, denoted as positive and negative (1 and 0 values, respectively).

The physicochemical analyses were used as input in the PLS-DA (supervised technique) classification. For validation, full cross method (leave-one-out) was used. The score plot of first three presented in Fig. 6 shows that following the aging process just by using principal oenological parameters cannot be efficient. The first three latent variables explain 59% of variance in calibration and 77% in validation that confirm the relative reduced quality of the model.

Table 3 collects the quantitative data derived from the PLS-DA regression model. As observed, both the calibration and the validation values involved a relative reduced-quality model performance. RMSEC (root mean square error of calibration) and RMSEP (root mean square error of prediction) values are in the range 0.162–0.347.

As shown in Fig. 6, the score plots of the three latent variables, of the fully cross-validated PLS-DA model, revealed a clear identification of the four classes of wines.

As can be observed in Fig. 7, a clear discrimination between aging steps is achieved when the data collected with the electronic panel test was used, superior of that observed in the case of individual sensory systems. The first three latent variables explain 88% of information in calibration and 93% in validation that confirm the excellent prediction capacity of the model.

Table 4 collects the quantitative data derived from the PLS-DA regression model obtained from electronic panel test signals. As observed, both the calibration and the validation values involved a

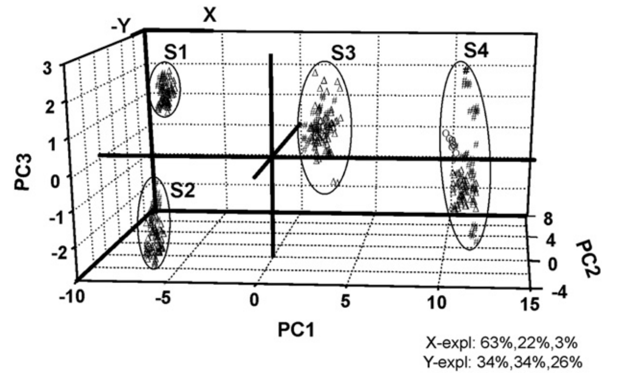

Fig. 7. PLS-DA scores plot corresponding to the monitoring of aging process by means of electronic panel. S1 — after 1 month of aging; S2 — after 4 months of aging; S3 — after 7 months of aging; S4 — after 10 months of aging.

Table 4
Quantitative data of PLS-DA regression using electronic panel data.

Classification criteria	Calibration				Validation			
	Slope	Offset	R_c	RMSEC	Slope	Offset	R_p	RMSEP
S1	0.966	0.007	0.982	0.076	0.964	0.008	0.981	0.079
S2	0.965	0.007	0.983	0.076	0.964	0.007	0.982	0.078
S3	0.990	0.002	0.995	0.044	0.989	0.003	0.994	0.044
S4	0.996	0.001	0.998	0.023	0.996	0.001	0.998	0.023

good-quality model performance (slope near 1, off set near 0 and large correlation between sensors and categorized variables). In addition, low RMSEC (root mean square error of calibration) and RMSEP (root mean square error of prediction) values were accomplished.

PLS-DA has demonstrated that measurements with the electronic panel test system allow predicting the method used to age the wines. Measurements are faster since each wine is analyzed in a single step instead of measuring a number of chemical parameters.

These results indicate that this new methodology is able to carry out an efficient monitoring of aging process of red wines in oak barrels and by alternative method.

4. Conclusions

An electronic panel test formed by combination of an e-nose, e-tongue and e-eye has permitted the aging monitoring of a red wine D.O. Toro (Spain). Additionally, the system permits discrimination between the wines aged in the French oak barrels and wines aged by using oak chips and microoxygenation.

The measurements carried out with the electronic panel test could be used in the prediction of the method employed for red wine aging after 7 months of the beginning of the process.

The results obtained by means of physico-chemical analysis were similar. Therefore, the use of electronic panel test has some advantages such as the rapidity, measurements in one step, minimum preparation of the sample etc. Additionally, the artificial sensorial measurements carry out one global analysis of wine concerning the color, the aroma and the taste in a similar way to human experts.

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References

Aleixandre, M., Lozano, J., Gutiérrez, J., Sayago, I., Fernández, M. J., & Horrillo, M. C. (2008). Portable e-nose to classify different kinds of wine. *Sensors and actuators, B*, *131*, 71–76.

Apetrei, C., Apetrei, I., Nevares, I., del Alamo, M., Parra, V., Rodríguez-Méndez, M. L., & de Saja, J. A. (2007). Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods. Correlation between electrochemical signals and analytical parameters. *Electrochimica Acta*, *52*, 2588–2594.

Apetrei, C., Apetrei, I. M., Villanueva, S., de Saja, J. A., Gutierrez-Rosales, F., & Rodriguez-Mendez, M. L. (2010). Combination of an e-nose, an e-tongue and an e-eye for the characterisation of olive oils with different degree of bitterness. *Analytica Chimica Acta*, *663*, 91–97.

Arapitsas, P., Antonopoulos, A., Stefanou, E., & Dourtoglou, V. G. (2004). Artificial aging of wines using oak chips. *Food Chemistry*, *86*, 563–570.

Barker, M., & Rayens, W. (2003). Partial least squares for discrimination. *Journal of Chemometrics*, *17*, 166–173.

Berna, A. Z., Trowell, S., Clifford, D., Cynkar, W., & Cozzolino, D. (2009). Geographical origin of Sauvignon Blanc wines predicted by mass spectrometry and metal oxide based electronic nose. *Analytica Chimica Acta*, *648*, 146–152.

Buratti, S., Ballabio, D., Giovanelli, G., Zuluanga Dominguez, C. M., Moles, A., Benedetti, S., & Sinelli, N. (2011). Monitoring of alcoholic fermentation using near infrared and mid infrared spectroscopies combined with electronic nose and electronic tongue. *Analytica Chimica Acta*, *697*, 67–74.

Cano-Lopez, M., Pardo-Minguez, F., Lopez-Roca, J., Fernandez-Fernandez, J., & Gomez-Plaza, E. (2006). Effect of microoxygenation on anthocyanin and derived pigment content and chromatic characteristics of red wine. *American Journal of Enology and Viticulture*, *57*, 325–331.

Cetó, X., Gutiérrez, J. M., Moreno-Barón, L., Alegret, S., & del Valle, M. (2011). Voltammetric electronic tongue in the analysis of cava wines. *Electroanalysis*, *23*, 72–78.

Chen, Q., Zhao, J., & Vittayapadung, S. (2008). Identification of the green tea grade level using electronic tongue and pattern recognition. *Food Research International*, *41*, 500–504.

Cynkara, W., Cozzolino, D., Dambergsa, B., Janika, L., & Gishena, M. (2007). Feasibility study on the use of a headspace mass spectrometry electronic nose (MS e_nose) to monitor red wine spoilage induced by *Brettanomyces* yeast. *Sensors and Actuators, B*, *124*, 167–171.

del Valle, M. (2010). Electronic tongues employing electrochemical sensors. *Electroanalysis*, *22*, 1539–1555.

Di Natale, C., Paolesse, R., Macagnano, A., Mantini, A., D'Amico, A., Ubigli, M., Legin, A., Lvova, L., Rudnitskaya, A., & Vlasov, Y. (2000). Application of a combined artificial olfaction and taste system to the quantification of relevant compounds in red wine. *Sensors and Actuators, B*, *69*, 342–347.

Escuder-Gilabert, L., & Peris, M. (2010). Review: Highlights in recent applications of electronic tongues in food analysis. *Analytica Chimica Acta*, *665*, 15–25.

Fernández de Simón, B., Cadahía, E., Muiño, I., Del Álamo, M., & Nevares, I. (2010). Volatile composition of toasted oak chips and staves and of red wine aged with them. *American Journal of Enology and Viticulture*, *61*, 157–165.

Gardner, J. W., & Bartlett, P. N. (1999). *Electronic noses, Ed.* Oxford: Oxford University Press.

Gay, M., Apetrei, C., Nevares, I., del Alamo, M., Zurro, J., Prieto, N., De Saja, J. A., & Rodríguez-Méndez, M. L. (2010). Application of an electronic tongue to study the effect of the use of pieces of wood and micro-oxygenation in the aging of red wine. *Electrochimica Acta*, *55*, 6782–6788.

Gutiérrez, M., Domingo, C., Vila-Planas, J., Ipatov, A., Capdevila, F., Demming, S., Büttgenbach, S., Llobera, A., & Jiménez-Jorquera, C. (2011). Hybrid electronic tongue for the characterization and quantification of grape variety in red wines. *Sensors and Actuators, B*, *156*, 695–702.

Kelly, M., & Wollan, D. (2003). *Microoxygenation of wine in barrels. The Australian & New Zealand Grapegrower & Winemaker*, *473a*. (pp. 29–32).

Koussissi, E., Dourtoglou, V. G., Ageloussis, G., Paraskevopoulos, Y., Dourtoglou, T., Paterson, A., & Chatzilazaroua, A. (2009). Influence of toasting of oak chips on red wine maturation from sensory and gas chromatographic headspace analysis. *Food Chemistry*, *114*, 1503–1509.

Lorenzo, C., Garde-Cerdán, T., Pedroza, M. A., Alonso, G. L., & Salinas, M. R. (2009). Determination of fermentative volatile compounds in aged red wines by near infrared spectroscopy. *Food Research International*, *42*, 1281–1286.

Lvova, L., Martinelli, E., Mazzone, E., Pede, A., Paolesse, R., Di Natale, C., & D'Amico, A. (2006). Electronic tongue based on an array of metallic potentiometric sensors. *Talanta*, *70*, 833–839.

Maga, J. A. (1989). The contribution of wood to the flavour of alcoholic beverages. *Food Research International*, *5*, 39–99.

Moutonet, M., Mazauric, J. P., Saint-Pierre, B., & Hanocq, J. F. (1998). Gaseous exchange in wines stored in barrels. *Journal des Sciences et Techniques de la Tonnellerie*, *4*, 131–145.

Muenchmeyer, W., Walte, A., & Matz, G. (2000). Improving electronic noses using a trap and thermal desorption unit. *Sensors and Actuators, B*, *69*, 379–383.

OIV (1990). *Recueil des méthodes internationales d'analyse des vins et des mouts, Paris.*

Oliveira, C. M., Silva Ferreira, A. C., De Freitas, V., & Silva, A. M. S. (2011). Oxidation mechanisms occurring in wines. *Food Research International*, *44*, 1115–1126.

Prieto, N., Gay, M., Vidal, S., Aagaard, O., de Saja, J. A., & Rodriguez-Mendez, M. L. (2011). Analysis of the influence of the type of closure in the organoleptic characteristics of a red wine by using an electronic panel. *Food Chemistry*, *129*, 589–594.

Riul, A., Jr., de Sousa, H. C., Malmegrim, R. R., dos Santos, D. S., Jr., Carvalho, A. C. P. L. F., Fonseca, F. J., Oliveira, O. N., Jr., & Mattoso, L. H. C. (2004). Wine classification by taste sensors made from ultra-thin films and using neural networks. *Sensors and Actuators, B*, *98*, 77–82.

Rodríguez-Bencomo, J. J., Ortega-Heras, M., & Pérez-Magariño, S. (2010). Effect of alternative techniques to ageing on lees and use of non-toasted oak chips in alcoholic fermentation on the aromatic composition of red wine. *European Food Research and Technology*, *230*, 485–496.

Rodríguez-Méndez, M. L., Arrieta, A., Parra, V., Vegas, A., Villanueva, S., Gutierrez-Osuna, R., & de Saja, J. A. (2004). Fusion of three sensory modalities for the multimodal characterization of red wines. *IEEE Sensors Journal*, *4*, 348–354.

Santonico, M., Bellincontro, A., De Santis, D., Di Natale, C., & Mencarelli, F. (2010). Electronic nose to study postharvest dehydration of wine grapes. *Food Chemistry*, *121*, 789–796.

Sanza, M. D. (2006). Wine aging in bottle from artificial systems (staves and chips) and oak woods — Anthocyanin composition. *Analytica Chimica Acta*, *563*, 255–263.

Villanueva, S., Guadarrama, A., Rodríguez-Mendez, M. L., & de Saja, J. A. (2008). Use of an array of metal oxide sensors coupled with solid phase microextraction for characterisation of wines: Study of the role of the carrier gas. *Sensors and Actuators, B*, *132*, 125–133.

Žeravík, J., Lacina, K., Hlaváček, A., & Skládal, P. (2009). State of the art in the field of electronic and bioelectronic tongues — Towards the analysis of wines. *Electroanalysis*, *21*, 2509–2520.