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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.

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