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Fluorescence excitation–emission matrix spectroscopy as a tool for determining quality of sparkling wines

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ABSTRACT

Browning in sparkling wines was assessed by the use of excitation–emission fluorescence spectroscopy combined with PARAllel FACtor analysis (PARAFAC). Four different *cava* sparkling wines were monitored during an accelerated browning process and subsequently storage. Fluorescence changes observed during the accelerated browning process were monitored and compared with other conventional parameters: absorbance at 420 nm (A_{420}) and the content of 5-hydroxymethyl-2-furfural (5-HMF). A high similarity of the spectral profiles for all sparkling wines analyzed was observed, being explained by a four component PARAFAC model. A high correlation between the third PARAFAC factor (465/530 nm) and the commonly used non-enzymatic browning indicators was observed. The fourth PARAFAC factor (280/380 nm) gives us also information about the browning process following a first order kinetic reaction. Hence, excitation–emission fluorescence spectroscopy, together with PARAFAC, provides a faster alternative for browning monitoring to conventional methods, as well as useful key indicators for quality control.

1. Introduction

Sparkling wine is a special wine whose most important characteristic is the effervescence. This characteristic is due to the presence of CO_2 produced by a second alcoholic fermentation of a still wine (Martínez-Rodríguez & Pueyo, 2009). The most famous sparkling wines include *champagne* from France or *cava* from Spain among others (Kemp, Alexandre, Robillard, & Marchal, 2015). A special production method named *Traditional* is employed to obtain these high quality sparkling wines in which the second fermentation takes place in the bottle. Thus, *cava* is a premium sparkling wine (designation of origin), which undergoes a biological ageing for at least 9 months in contact with lees under anaerobic conditions in bottle (Commission Regulation, 2009). It is during its second fermentation process when *cava* wines develop their complex organoleptic characteristics, which include aroma, colour, and their capacity of creating foam. Among these, colour is of especial relevance since it is one of the first sensory attributes observed by manufactures and consumers.

The grape phenolic compounds that remain in these wines following the elaboration process are the primarily responsible for their colour, giving to the wines a yellowish or even a brownish colour when oxidized (Buxaderas & López-Tamames, 2010). However, after their elaboration, colour can also be affected during shipment and commercial storage, where *cava* wines are usually exposed to uncontrolled temperature conditions that may lead to an increase of non-enzimatic browning processes (Serra-Cayuela et al., 2000; López-Tamames, 2014). Browning is an oxidative process involving sugars, lipids, amino acids and phenols (Li, Guo, & Wang, 2008), which decreases the sensorial quality of wines (loss of colour, flavour and aroma, and increment of astringency) (Ferreira, Escudero, Fernández, & Cacho, 1997). Thus, since quality is of prime relevance for *cava* wines, browning has to be controlled during processing and storage. In this sense, several methods have been suggested to quantify the degree of browning, based on the measurement of different quality markers, by colorimetry, Ultra Violet-Visible (UV–Vis) spectroscopy and high performance liquid chromatography (HPLC).

Tristimulus colorimetry using the *CIELab* or *Hunter Lab* color systems has been widely used to measure the browning degree. Nevertheless, these methods are often influenced by chemical

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(browning) as well as physical changes. Absorbance, in particular at 420 nm (A_{420}), has been also extensively used as a fast parameter for browning monitoring, mostly in white wines (Kallithraka, Salacha, & Tzourou, 2009; Peng, Duncan, Pocock, & Sefton, 1998), where an increase in the A_{420} parameter value is used to indicate increased browning (Serra-Cayuela et al., 2000). However, Serra-Cayuela, Aguilera-Curiel, Riu-Aumatell, Buxaderas, and López-Tamames (2013) demonstrated that the value of the A_{420} parameter has low sensitivity and low specificity as a quality marker of *cava* sparkling wines. Instead, they proposed the use of the 5-hydroxymethyl-2-furfural (5-HMF) content as a more effective marker. This compound is an intermediate product in the formation of brown pigments during the Maillard reaction, which increases linearly with time and temperature following a zero-order reaction (Özhan, Karadeniz, & Erge, 2010). Nevertheless, laboratory analyses of this quality marker by chromatographic methods are expensive, time and reagent-consuming as well as destructive.

Therefore, finding fast and accurate methods for monitoring the extent of browning reaction as well as alternative quality markers would be of utmost importance for *cava* producers. In this sense, fluorescence spectroscopy has been more and more applied in the last decades as a fast, non-destructive and environmentally safe analyzing method in food science, due to its high sensitivity and specificity (Andersen, Wold, & Engelsen, 2009).

In wines, several substances exhibit intrinsic fluorescence (stilbenes, anthocyanins, amino acids, vitamins, flavanols and tannins), but most of them are related to polyphenols (Sádecká & Tóthová, 2007). This offers a valuable alternative of wine characterization and monitoring. Dufour, Letort, Laguet, Lebecque, and Serra (2006) demonstrated the potential use of direct single front-face fluorescence measurements combined with chemometric methods for discriminating different French and German wines according to variety, typicality and vintage (i.e. ageing). Later, Airado-Rodríguez, Galeano-Díaz, Durán-Merás, and Wold (2009) employed fluorescence Excitation–Emission Matrix (EEM) spectroscopy linked to a resolution method such as PARAllel FACtor analysis (PARAFAC) for fingerprinting of red wines, where the main groups of fluorescent compounds detected were also tentatively identified by high performance liquid chromatography. Further, Airado-Rodríguez, Durán-Merás, Galeano-Díaz, and Wold (2011) explored the feasibility of the autofluorescence of wine for the purpose of discrimination of wines according to the appellation of origin. Moreover, their PARAFAC analysis revealed four groups of fluorophores in red wines, assigning two of them to benzoic-like phenolic acids and phenolic aldehydes, and to monomeric catequins and polymeric proanthocyanidin dimers, respectively.

On the other hand, fluorescence has been pointed out as an alternative tool to assess the progress of browning in foodstuff (Park & Kim, 1983) in the same way as the browning index at 420 nm (Morales, Romero, & Jiménez-Pérez, 1996). In this sense, FLuorescence Relative Index (FLRI) values (measured using maximum emission and excitation wavelengths at 493 and 400 nm, respectively) were introduced by Cohen, Birk, Mannheim, and Saguy (1998) to monitor the quality deterioration of apple juice during thermal processing. Later, front-face fluorescence spectroscopy was applied to study the development of Maillard browning in milk during thermal processing (Schamberger & Labuza, 2006), pointing out a high correlation between the emission spectra and the 5-HMF content as well. Furthermore, Zhu, Baoping, Eum, and Zude (2009) used front-face fluorescence excitation–emission matrix combined with chemometric methods as a sensitive indicator of the non-enzymatic browning in thermally processed apple juices, suggesting also that fluorescence spectra could be used to predict the 5-HMF concentration.

The aim of this study is to assess the browning in sparkling wines by the use of fluorescence excitation–emission matrix spectroscopy combined with PARAFAC analysis. Four different *cava* sparkling wines were monitored during an accelerated browning process at a temperature of 65 °C and subsequently storage. In order to assess the potential use of the proposed methodology, the fluorescence trends observed during the accelerated browning were tested and compared with those obtained by means of different common quality parameters, such as the A_{420} and the 5-HMF content. Furthermore, the fluorescence monitoring was studied to determine whether any fluorophore could be used as an aging marker for quality controlling in *cava* sparkling wines.

2. Materials and methods

2.1. Sparkling wine samples

A set of four commercial *cava* sparkling wines (*Brut*, *Brut Reserva*, *Brut Gran Reserva* and *Semiseco*) were purchased in local supermarkets, coming from several *cava* brands. These *cava* wines, mostly produced from a blending of three grape varieties (*macabeu*, *xarel·lo*, and *parellada*), were selected based on two criteria: sugar content and ageing, to cover most of types of marketed *cava* wines. Thus, *Brut* (sugar content <12 g L^{-1}) and *Semiseco* categories (sugar content between 32 and 50 g L^{-1}) were selected according to the sugar content; whereas *Reserva* and *Gran Reserva cava* wines corresponding to the *Brut* category were chosen based on the ageing periods. The term *Reserva* applies to wines that have been kept in contact with the lees for at least 15 months, while *Gran Reserva* refers to wines that have been kept in contact with the lees for at least 30 months. These two qualities of *cava* wines have a different price in the market due to the fact that the longer ageing time the better quality and higher cost of production.

The enological parameters of each type of *cava* wine at the initial sampling point (time zero) are shown as Supplementary Material (Table I). The total sugar content, alcohol content, pH, free and total sulfur dioxide were measured using the established standard methods (OIV, 2009).

The accelerated browning test was carried out in total darkness conditions for each *cava* wine (4 series). Once the bottles were opened, 10 mL of wine were aliquoted into 20 mL amber vials and were degassed under a N_2 stream. All vials, expect those belonging to time zero (initial sampling point), were subjected to heating at a constant temperature of 65 ± 1 °C in an oven (Selecta, Barcelona Spain). Sampling points were at 48 h intervals over a period of 10 days, i.e. after 0, 2, 4, 6, 8 and 10 days (6 sampling points). Three replicates were taken for each type of *cava* at each sampling time point. Hence, the heating experiment resulted in a total of 72 samples (6 sampling points × 4 cava series × 3 replicates). After that, to monitor the evolution of heated samples during storage, the heated samples were stored at room temperature for a further 10 days, and measured at 2, 4, 6, 9 and 10 days, giving a total of 60 samples (5 sampling points x 4 cava series x 3 replicates). All samples, 132 in total, were stored at 4 °C until analysis. The sampling procedure is shown as Supplementary Material (Table II).

2.2. Analytical procedures

2.2.1. Absorbance spectroscopy

The absorbance spectrum of each sample was measured in the range 200–700 nm (spectral resolution of 1 nm) in a Shimadzu® UV-3600 spectrophotometer (Duisburg, Germany), using a 10 mm path length quartz cuvette and double-distilled water as