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Volatile profile characterisation of Chilean sparkling wines produced by traditional and Charmat methods via sequential stir bar sorptive extraction

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ABSTRACT

The volatile compositions of Charmat and traditional Chilean sparkling wines were studied for the first time. For this purpose, EG-Silicone and PDMS polymeric phases were compared and, afterwards, the most adequate was selected. The best extraction method turned out to be a sequential extraction in the headspace and by immersion using two PDMS twisters. A total of 130 compounds were determined. In traditional Chilean sparkling wines, ethyl esters were significantly higher, while acetic esters and ketones were predominant in the Charmat wines. PCA and LDA confirmed the differences in the volatile profiles between the production methods (traditional vs. Charmat).

1. Introduction

Chile is currently among the top ten wine producing countries worldwide. Among the different types of wine produced in Chile, sparkling wine is becoming increasingly popular. It is estimated that its consumption will continue to grow rapidly, leading to a growth of Chile's wine production. For this reason, it is of great interest to characterise Chilean sparkling wines.

The sparkling wine production process is based on the second fermentation of base wine in which yeast produces a significant quantity of CO2 (Liger-Belair, 2005; Martínez-Rodríguez & Pueyo, 2009). There are two main production processes: Traditional and Charmat methods. In the traditional procedure, the second fermentation of the base wine is carried out within the bottle and results in high quality wines (Torresi, Frangipane, & Anelli, 2011). Some of the most popular sparkling wines, such as Champagne and Cava, are produced by the traditional method. Regarding the Charmat method, the second fermentation is carried out in hermetically sealed tanks. This process involves faster and cheaper production techniques than the traditional method. In Chile, most sparkling wines are produced employing the Charmat method. Depending on the method employed, the sparkling wine has different characteristics (Caliari, Panceri, Rosier, & Bordignon, 2015; Stefenon et al., 2014).

Aroma is one of the most important indicators of sparkling wine quality (Kemp, Alexandre, Robillard, & Marchal, 2015). Therefore, due to the relevance of the aroma in the acceptability of a product by consumers, it is very interesting to know what volatile compounds are involved in its aroma. In general, the volatile profile of sparkling wines produced by the traditional or Charmat method is mainly composed of esters, alcohols, and acids, and also some terpenes, such as limonene, linalool, or lilial have an important role in the overall aroma (Bosch-Fusté et al., 2007; Coelho, Coimbra, Nogueira, & Rocha, 2009; Riu-Aumatell, Bosch-Fusté, López-Tamames, & Buxaderas, 2006). In this context, comparative studies on the effects of the two types of production methods on the volatile compositions of sparkling wines are scarce. A recent publication showed that the sparkling wine produced by the traditional method has higher concentrations of terpenes, alcohols, acids, and especially, ethyl esters (Caliari et al., 2015).

The determination of volatile compounds may require an extraction stage prior to analysis. To date, different extraction techniques have been employed to study the volatile profiles of

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sparkling wines: Liquid–liquid extraction (Perez-Magarino, Ortega-Heras, Martinez-Lapuente, Guadalupe, & Ayestaran, 2013), solid phase extraction (Caliari, Burin, Rosier, & Bordignon-Luiz, 2014), stir bar sorptive extraction (SBSE) with liquid desorption (Coelho et al., 2009), and headspace solid phase microextraction (SPME) (Gallardo-Chacón, Vichi, López-Tamames, & Buzaderas, 2009; Ganss, Kirsch, Winterhalter, Fischer, & Schmarr, 2011). The headspace SPME method is the most employed extraction technique for this purpose. However, SBSE has a greater extraction capacity than SPME (David & Sandra, 2007). In the SBSE technique, the analyte can be extracted by a direct immersion of the sorptive stir bar into the sample (Zalacain, Marin, Alonso, & Salinas, 2007) or placing the stir bar into the headspace (HSSE) (Callejón et al., 2010). This technique is primarily performed by employing a stir bar known as the Twister®, which is traditionally coated with polydimethylsiloxane (PDMS) as a non-polar phase. Different types of extraction phases have been synthesized in-house to improve the extraction of more polar compounds. Among these phases, monolithic materials (Huang, Lin, & Yuan, 2010), molecular imprinted polymers (Xu, Hu, Hu, Pan, & Li, 2012), C18 (Yu & Hu, 2012), and polyurethane (PU) (Rodriguez, Glories, Maujean, & Dubourdieu, 2012) have been successfully tested. In most cases, these polymers are not thermally stable and a liquid desorption process is required. Recently, new twisters coated with polyethyleneglycol-modified silicone (EG-Silicone) and a polyacrilate/polyethylenegly col phase (PA) have been commercialised. These new coatings offer the possibility of recovering compounds with higher polarity than PDMS (Gilart, Marcé, Borrull, & Fontanals, 2014). EG-Silicone and PA twisters have been already tested to determine the different volatile compounds in food matrices, such as scotch whisky, fruit juice, and white wine (Nie & Kleine-Benne, 2011), vegetable matrices (Sgorbini et al., 2012), and wine (Cacho, Campillo, Viñas, Hernández-Córdoba, 2014).

To improve the sensitivity of the extraction process, a good strategy is to increase the volume of the extraction phase. This volume increase can be achieved by increasing the number of twisters used for the extraction because it is possible to analyse the compounds retained in several twisters in a single chromatographic analysis. Moreover, the combination of twisters with different coatings may extend the range of polarity of the compounds to be determined, which increases the total number of determined compounds. In this sense, Ochiai, Sasamoto, Ieda, David, and Sandra (2013) obtained better recovery percentages with the combined use of PDMS and EG-Silicone twisters.

SBSE has been widely used for analysing volatile and semi-volatile compounds in wines (Zalacain et al., 2007), and HSSE has also been successfully applied for this purpose (Callejón et al., 2010; Weldegergis, Tredoux, & Crouch, 2007). An advantage of the HSSE method is an increase in the lifetime of the stir bar. The SBSE method extracts a large amount of aromatic compounds from samples, but HSSE has been shown to be more efficient in extracting compounds that are more volatile, such as methyl acetate, acetaldehyde diethylacetal, and ethyl 2-methylbutyrate among others (Callejón et al., 2010). Therefore, using both extraction methods, i.e., by immersion and in the headspace, to analyse the aroma may extend the volatility range of the extracted compounds.

The goal of this work is to determine for the first time the volatile composition of Chilean sparkling wines produced by the Charmat and traditional methods. For this purpose, a method for determining a large number of compounds is established by comparing the use of EG-Silicone and PDMS polymeric phases, both by immersion, as well as in the headspace, and by a simple and sequential extraction procedure combining both coatings.

2. Material and Methods

2.1. Reagents, materials and samples

Ethanol, methanol, and acetonitrile, which were used for the twister cleaning procedure, and 4-methyl-2-pentanol (internal standard) were purchased from Merck (Darmstadt, Germany). Sodium chloride was obtained from Sigma–Aldrich (Madrid, Spain).

The polymeric phases employed for this study were polyethyleneglycol-modified silicone (EG-Silicone) and polydimethylsiloxane (PDMS). These materials were obtained from Gerstel (Müllheim and der Ruhr, German). The length of EG-Silicone Twisters was 10 mm, and they had a 32 μL coating; the length of the PDMS Twisters was 10 mm, and they had a 24 μL (0.5 mm) coating.

Sixteen Chilean sparkling wines were analysed; eight were produced by the Charmat method and eight by the traditional method. These wines were donated by six main wineries producing Chilean sparkling wines. The Chilean wines came from four different production zones: Leyda, Casablanca, Curicó, and Maipo. Among the sparkling wines analysed were monovarietal wines (Pinot noir, Chardonnay) and varietals wines (Chardonnay/Pinot noir and Chardonnay/Pinot noir/Semillon).

In addition, to test different sampling procedures, a representative sparkling wine was used. This sample was a common sparkling wine made using Chardonnay and Pinot meunier grapes by the traditional method.

2.2. Sampling procedures

Two sampling procedures, i.e., headspace (HSSE) and immersion (SBSE), were tested. In these assays, two different polymeric phases, i.e., polydimethylsiloxane (PDMS) and Ethylene glycol (EG-Silicone), were used. Moreover, two types of sequential extraction methods were carried out using two twisters in each sample, i.e., first SBSE and then HSSE. In these methods, we combined the use of PDMS and EG-Silicone twisters in the following manner: SBSE-EG-Silicone/HSSE-PDMS and SBSE-PDMS/HSSE-EG-Silicone.

In all cases, 7.5 mL of the sample were placed in a 20 ml vial, and 2.25 g of NaCl (30%) plus 10 μL of the internal standard 4-methyl-2-pentanol (405 mg/L) were added. A special device made of stainless wire was designed to maintain the integrity and to extend the shelf life of the polymer as much as possible. This device was fixed to the septum of the stopper. The extraction by immersion was performed by placing the twister in the stainless wire device and stirring the sample with a conventional magnetic stir bar (non-coated stir bar) for one hour at 200 rpm at room temperature. The headspace extraction was performed by placing a new twister in an open glass insert inside the vial and heating the sample in a water bath at 62 °C for one hour (Callejón et al., 2010). In both cases, the vial was tightly capped and, after extraction, the stir bar was removed with tweezers, rinsed with Milli-Q water, and dried with a lint-free tissue paper. Then, it was thermally desorbed in a gas chromatograph/mass spectrometer (GC/MS).

2.3. Thermal desorption and GC–MS conditions

Gas chromatography analysis was carried out using a 6890 Agilent GC system coupled to an Agilent 5975 inert quadrupole mass spectrometer and equipped with a thermo desorption system (TDS2) and a cryo-focusing CIS-4 PTV injector (Gerstel). The thermal desorption was performed in splitless mode with a flow rate