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Headspace-solid phase microextraction–gas chromatography as a tool to define an index that establishes the retention capacity of the wine polymeric fraction towards ethyl esters

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Abstract

A headspace-solid phase microextraction followed by gas chromatographic analysis (HS-SPME–GC) was developed to be applied in the study of the interactions between the wine polymeric fraction and the ethyl esters: ethyl hexanoate, ethyl octanoate, and ethyl decanoate. Wine models (WM) were prepared with 10% (v/v) aqueous ethanol at pH 3.5 with distinct wine polymeric concentrations prepared from white wine of *Vitis vinifera* L. var. Fernão-Pires: 1.0 g L^{-1} (PWM_1), with a polymeric concentration approaching the real one in wine; 10.0 g L^{-1} (PWM_{10}); and 30.0 g L^{-1} (PWM_{30}), saturated with polymeric fraction. A reference wine model (RWM) was prepared without polymeric fraction. Each volatile compound (4.0 mg L^{-1}) was added separately to the RWM and to the WM with the three levels of polymeric material (PWM). From the retention index (RI) calculated for each compound using the formula: [$RI = 1 - (C_{RWM} - C_{PWM})/C_{RWM}$], where C_{RWM} is the concentration of the compound in the RWM and C_{PWM} is the concentration of the compound in the given PWM, the retention capacity of each wine polymeric fraction towards the three esters was established. The higher retention indexes were observed for ethyl decanoate, the more hydrophobic compound, and for the PWM with higher concentration. Furthermore, this study also suggested that the retained compounds are dosed to the headspace, which may promote the perception of their aroma for a longer period of time.

Keywords: Wine polymeric fraction; Ethyl esters; HS-SPME–GC; Retention capacity

1. Introduction

Aroma compounds are important in wine as they contribute to the quality of the final product, hence to the consumer acceptance. Alcohols, esters, acids, aldehydes, ketones, terpenoids and phenols, representing more than 800 volatile compounds, have been identified in grapes and wines [1–3]. The equilibrium of the volatile compounds between the liquid and vapour phases are ruled by physico-chemical properties such as volatility and solubility [4], which, in turn, are influenced by the non-volatile wine constituents, namely, polysaccharides, proteins, and phenolic compounds. Several studies report the interactions between wine macromolecules and volatiles, as well as the ability of each type of macromolecules on the retention of volatiles [4,5–13]. These phenomena are dependent on the nature and concentration of both, macromolecules and volatiles. The interactions between volatiles and macromolecules seem to occur by sorption or inclusion phenomena dependent on the macromolecule structure and on the characteristics of volatile compounds such as molecular weight, chemical groups, polarity and relative volatility [14]. Generally, the sorption of the volatile to the macromolecules depends on their ability to form hydrogen bonds or hydrophobic interactions [6].

The interactions between volatiles–macromolecules have been studied using the dynamic exponential dilution method, which allows the determination of infinite dilution activity coefficients γ_i^{∞} of volatile components in an aqueous medium [8]. This coefficient varies with the polymeric fraction concentration and seems to be related with the nature and the strength of the interactions. Solid phase-microextraction (SPME) was also applied to study the disulfide interchange reactions between ovalbumin and volatile disulfides [15].

SPME is a sample preparation technique based on sorption (absorption and/or adsorption, depending on the fibre coating),

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used for extraction and concentration of analytes either by submersion in a liquid phase or by exposure to a gaseous phase [16]. Following exposure of the fibre to the sample, sorbed analytes can be thermally desorbed in a conventional GC injection port. This methodology is simple to use, relatively fast, does not require solvent extraction, and allows a characterisation of the headspace composition in contact with the sample [16,17]. The application of this technique requires previous knowledge of the coating fibre affinity for the volatiles under study as well as optimisation of experimental parameters to improve the reproducibility and sensitivity of the method [18]. Headspace-SPME has been widely used to the food flavour characterisation, namely for wine analysis [18–20].

In this study, a novel approach was applied to study the interactions between wine polymeric fraction and three ethyl esters based on headspace-solid phase microextraction followed by gas chromatographic analysis (HS-SPME–GC), allowing definition of an index that establishes the retention capacity of the wine polymeric fraction towards each one of the three esters.

2. Materials and methods

2.1. Materials

Four chemicals were used: absolute ethanol (purity ≥ 99.8%) from Riedel-de-Haën (Seelze, Germany), ethyl hexanoate (≥99.0%), ethyl octanoate (≥99.0%) from Aldrich Chemical Co. (Milwaukee, WI, USA), and ethyl decanoate (≥99.0%) from Fluka (Buchs, Switzerland). Relevant physico-chemical parameters of the three ethyl esters are listed in Table 1.

A SPME holder from Supelco Inc. (Bellefonte, PA, USA) was used to perform headspace-SPME manually. The SPME fibre coated with 85 μm polyacrylate was also purchased from Supelco. Polyacrylate is an absorbent liquid-phase coated fibre, which is recommended for polar organic compounds. However, according to its performance in the analysis of the esters, namely the esters used in the present study [20], and considering the future applicability of the present methodology towards other volatiles of wine, polyacrylate coating fibre was chosen. The absorptive fibres are used to extract semi-volatile compounds from the headspace. Absorptive fibres have greater capacity and linear concentration ranges than adsorptive, and utilise partitioning for the extraction [21,22]. The SPME fibre was conditioned at 300 °C for 2 h in the GC injector, according to the manufacturer's recommendations. All fibres used were from the same lot.

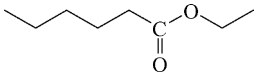
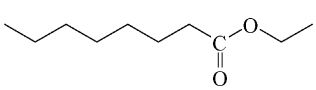
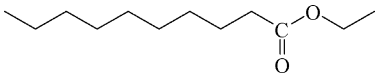
2.2. Wine polymeric origin and preparation

Vitis vinifera L. var. Fernão-Pires monovarietal wines from the Portuguese Bairrada Appellation were used. The wine (9 L) was rotary-evaporated under reduced pressure at 35 °C to eliminate the ethanol and concentrate the total solids present to a final volume of 300 mL [23]. The solid material was then dialysed (12–14 kDa cut off) to remove the tartaric acid and other small molecules. The dialysate was concentrated, frozen, and freeze-dried to give the wine polymeric fraction (WP) with a fluffy dry appearance. The chemical composition of the WP is indicated in Table 2.

2.3. Preparation of the standard solutions

Individual standard stock solutions of ethyl hexanoate (7.68 g L^{-1}), ethyl octanoate (8.78 g L^{-1}) and ethyl decanoate

Table 1
Physico-chemical characteristics of the chemical standards used: structure, molecular weight (MW), boiling point (BP), solubility in water and ethanol, log *P*, Henry's law constant and aroma descriptor (AD)

Compounds	Chemical structure	Characteristics
Ethyl hexanoate		MW = 144.21 BP = 168 °C Insoluble in water Miscible with ethanol log *P* (octanol–water) = 2.83 Henry's Law constant 0.000723 atm m^3 mol^{-1} AD: fruit, apple, banana [34,35]
Ethyl octanoate		MW = 172.27 BP = 208 °C Insoluble in water Miscible with ethanol log *P* (octanol–water) = 3.81 Henry's Law constant 0.00127 atm m^3 mol^{-1} AD: ripe fruits, pear, sweety [35]
Ethyl decanoate		MW = 200.31 BP = 245 °C Insoluble in water Miscible with ethanol log *P* (octanol–water) = 4.79 Henry's Law constant 0.00225 atm m^3 mol^{-1} AD: sweety, fruit, dry fruits [35]