

Comparison of ultrasound-assisted extraction and direct immersion solid-phase microextraction methods for the analysis of monoterpenoids in wine

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Abstract

Ultrasound-assisted extraction (UAE) and direct immersion solid-phase microextraction (DI-SPME) were evaluated for the monoterpenic compounds determination in wine samples. The wine extracts obtained were analyzed by gas chromatography–mass spectrometry (GC–MS). The optimization of the variables affecting UAE and SPME methods was carried out in order to achieve the best extraction efficiency. Both UAE and SPME are quantitative (recoveries in the range 93–97% and 71.8–90.9%, respectively), precise (coefficients of variation below 5.5%), sensitive (limits of detection between 30–39 $\mu\text{g L}^{-1}$ and 11–25 $\mu\text{g L}^{-1}$, respectively) and linear over one order of magnitude. The application of both methods to red wine samples showed that UAE provided higher extraction of monoterpenic compounds than SPME. Although SPME remains an attractive alternative technique due to its speed, low sample volume requirements and solvent free character. © 2005 Elsevier B.V. All rights reserved.

Keywords: Ultrasound-assisted extraction; Direct immersion solid-phase microextraction; Gas chromatography–mass spectrometry; Monoterpenoids; Wine

1. Introduction

The composition of wine depends on many factors, some of which are related to the specific production area: grape varieties, soil and climate, culture, yeasts, and wine making practices. Different type of wine compounds were used as variety markers, however, the most promising results were obtained from the volatile fraction [1–3]. Several hundred chemically different aroma compounds such as alcohols, esters, organic acids, aldehydes, ketones, terpenes and others, have been found in wines at different concentration levels. Therefore, certain compounds could be analyzed by direct injection gas chromatography while others need to be extracted and concentrated before chromatographic analysis. The sample pre-treatment for flavor and fragrance compound analysis usually involves the analyte concentration using headspace technique [4], steam distillation and supercritical

fluid extraction [5], trapping over porous polymer [6], solid–liquid extraction over resins [7], purge-extraction techniques [8], simultaneous distillation–extraction [9] or batch and continuous solvent extraction [10]. The use of solvent-free systems such as dynamic headspace with or without cryofocusing has been proposed only in a few papers [11,12]. These methods have various drawbacks including excessive preparation time and the use of organic solvents. The primary disadvantage of static headspace technique is its poor sensitivity for low volatile compounds and traces. Instead, it may be increased by purge and trap techniques. Simultaneous distillation–extraction is not time-consuming, but presents the inconvenience of artifacts formation due to thermally induced changes. Likewise, distillation and liquid–liquid extraction are well-fitted practices for monitoring aroma compounds. In the case of monoterpenoid analysis in wine samples, the latter was the most used technique but it requires multistage time-consuming procedures for the quantitative extraction of monoterpenes from must or wines.

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Ultrasound-assisted extraction is used for the isolation of volatile compounds from natural products at room temperature with organic solvents. Ultrasonic radiation is a type of energy that aids the sample pre-treatment facilitating and accelerating operations such as the extraction of organic and inorganic compounds from solid and liquid samples. Ultrasonic-assisted extraction methods proved to be useful and rapid procedures for wine analysis in comparison to the traditional methods [13–17].

Solid-phase microextraction (SPME) was developed in 1989 by Pawliszyn in order to facilitate a rapid sample preparation. Solid-phase microextraction is a solventless extraction technique based on the exposure of an immobilized stationary phase into the matrix containing the analytes (which could be liquid, solid, or gas) followed by their thermal desorption in the injector of a gas chromatograph [18]. Compared to traditional techniques, especially solid–liquid and liquid–liquid extraction, SPME shows significant advantages: high sensitivity and reproducibility, low cost, solvent-free extraction, no previous sample preparation, and the possibility of automatization [19]. Due to these issues, SPME is considered a promising useful technique for the analysis of flavor compounds in solid and liquid samples. This technique has been successfully used for the analysis of volatile flavor compounds in several matrices [20–22] and wine [23–30].

Taking into account that UAE and SPME methods are successful extraction procedures for aroma compounds, the objective of this work was to evaluate the performance of both techniques for the analysis of certain monoterpenoids in wine.

2. Experimental

2.1. Wine samples

Ten samples of Galician (NW Spain) red wine were used in this study. All of them are monovarietal, 2000 harvest, *Ribeira Sacra* Certified Brand of Origin (CBO) wines. Wines were elaborated using more than 70% of *Mencía* grape variety and following the wine making practices established by the *Ribeira Sacra* CBO Council. Samples were collected in 750 mL glass bottles and stored in darkness at 3–4 °C before analysis.

The enological characteristics of *Ribeira Sacra* CBO wines are: minimum alcoholic content 11%, total acidity between 4.5 and 6.5 g L⁻¹ of tartaric acid, maximum volatile acidity 0.65 g L⁻¹, maximum total sulphurous dioxide level 120 mg L⁻¹, minimum free sulphurous dioxide 15 mg L⁻¹ and maximum residual sugar 3 g L⁻¹ [31].

2.2. Apparatus

2.2.1. Ultrasound device

An ultrasonic bath Ultrasons-H 3000838 P-Selecta (J.P. Selecta, Barcelona, Spain) equipped with a 2 L vessel and temperature control was used.

2.2.2. Rotary evaporator

The organic extracts obtained in UAE method were concentrated using a rotary evaporator Labo-Rota C-311, Resona Technics, Buchs, Switzerland.

2.2.3. Gas Chromatographic system

An Agilent 6890 gas chromatograph coupled to 5973N quadrupole mass spectrometer (Agilent Technologies Deutschland GmbH, Waldbronn, Germany) was employed. The capillary column used was a HP-Innowax (Agilent Technologies) (30 m × 0.25 mm i.d., film thickness 0.25 μm).

2.2.4. Data acquisition

The chromatographic data were processed on a HP-Chemstation version D.00.00.38 (Agilent Technologies).

2.3. SPME fibers

The SPME manual holders and fibers were obtained from Supelco (Bellefonte, PA, USA). In this work, all analyses were performed using a polydimethylsiloxane (PDMS) fiber with a 100 μm film thickness. This fiber was conditioned before being used by inserting it into the GC injector port for 1 h at 250 °C. Between injections, the fiber was desorbed during 10 min at 250 °C in split mode in order to prevent any contamination.

2.4. Reagents

Monoterpenoids (linalool, α-terpineol, citronellol, nerol, and geraniol) were supplied by Aldrich Flavor and Fragrances (Alcobendas, Madrid, Spain). Methyl hexanoate (internal standard), and sodium chloride (ionic strength buffer) were supplied by Panreac (Barcelona, Spain). The solvents employed were absolute ethanol (Panreac, Barcelona, Spain) and Milli-Q ultra-pure water (Millipore Co., Bedford, USA). All solvents and reagents used were analytical grade. For ultrasound-assisted extraction dichloromethane and ethanol were obtained from Panreac (Barcelona, Spain) and anhydrous sodium sulphate was obtained from Merck (Darmstadt, Germany).

Stock standard solutions (100 mg L⁻¹) were prepared for each monoterpene by solving the appropriate amount in 10% ethanol. Standard solutions were stored at 4 °C in darkness. Working solutions were prepared daily.

2.5. Ultrasound extraction

The ultrasound-assisted extraction procedure applied in this work is based on the method described by Cocito et al. [14] with some modifications. One hundred milliliters of a standard solution (or the wine sample) containing 5 mg L⁻¹ of each monoterpene was placed into a 200 mL spherical flask and was extracted three times by means of ultrasounds for 10 min with 30, 10, and 10 mL of dichloromethane, respectively. The three extractions were performed at 20 °C. The

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