Journal of Chromatography B, 978–979 (2015) 122–130

Contents lists available at ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/chromb

Optimization and application of headspace-solid-phase micro-extraction coupled with gas chromatography–mass spectrometry for the determination of volatile compounds in cherry wines

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ARTICLE INFO

Article history:
Received 15 June 2014
Accepted 7 December 2014
Available online 13 December 2014

Keywords:
Cherry wine
SPME
Gas chromatography–mass spectrometry
Volatiles
PCA

ABSTRACT

A simple, rapid and solvent-free multi-residue method has been developed and applied to confirm and quantify a series of volatile compounds in five cherry wines by gas chromatography coupled with mass spectrometry (GC–MS). Four parameters (e.g., coating material of fiber, temperature and time of extraction, and addition of sodium chloride in the solution) of headspace solid-phase micro-extraction (HS-SPME) were optimized, resulting in the best extraction condition including 50/30 μm DVB/CAR/PDMS fiber, 45 min and 50 °C of SPME, and 2 g of sodium chloride addition in the wine during the extraction. The SPME had LODs and LOQs ranging from 0.03 to 7.27 μg L^{-1} and 0.10 to 24.24 μg L^{-1} for analytic compounds, respectively. Repeatability and reproducibility values were all below 19.8%, with mean values of 12.7% and 10.5%, respectively. Regression coefficients (R^2) of detective linearity of the standard curves was higher than 0.9852. Moreover, relative recoveries of analytical targets were achieved in a range of 60.7–125.6% with good relative standard deviation values (≤20.6%). In addition, a principal component analysis (PCA) was used to analyze the aroma profiles of the wines, which indicated that five samples were distinctly divided into two groups based on their different geographical origins and volatile compounds.

1. Introduction

Cherry is one of the most desirable fruits in light of its unique flavor and health benefits linked with many inherent biologically active compounds [1–3]. It has been used in food industry for the production of beverages, jams, syrups and cherry wines [4]. The latter, recognized for its specific aroma and taste, are becoming more and more popular in domestic and foreign markets [4,5].

Aroma components of cherry wines determine the qualities and characteristics of the wines. Those aromas are prevailingly derived from the process of fermentation and aging, and often used as biomarkers for production process to some extent [6,7]. It was reported more than 1000 volatiles had been confirmed in wines [8], including alcohols, esters, organic acids, aldehydes, ketones, phenols, terpenes and furans, etc. which are aroma contributors [9,10].

Several pretreatment methods, such as liquid–liquid extraction (LLE) solid-phase extraction (SPE), simultaneous distillation extraction (SDE), etc. are commonly used to extract volatile compounds in wine. Generally speaking, LLE could extract more volatile compounds with higher boiling points, while SPE intends to extract more volatile small molecules. For example, seven sulfur-containing compounds in white wines were extracted by the LLE [11]. In comparison, SPE was used to extract more volatile aromas in several commercial white, red and "cream" wines [12]. Besides, a wide range of volatile compounds from aged cava sparkling wines were extracted by simultaneous distillation extraction (SDE) [13], closed-loop stripping analysis (CLSA), etc. while the aroma profile of Madeira wine was characterized with aids of SPME and stir bar sorptive extraction (SBSE) [14]. Yet, the LLE usually requires toxic organic solvents [9], SDE is criticized for its tedious time [13], and the SBSE has an expensive cost and complex process. By contracts, the SPE can simplify the extraction procedure in light of

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http://dx.doi.org/10.1016/j.jchromb.2014.12.006
1570-0232/

using less amounts of solvents compared with the LLE. Therefore, HS-SPME has been more commonly used for flavor extraction of wines because of its solvent-free, relatively fast, simple, inexpensive and safe advantages [9,15,16]. Moreover, GC–MS can detect and determine volatile components accurately and rapidly. Li et al. [17] identified a total of 41 volatile compounds in Chardonnay dry white wines. Xiao et al. [18] confirmed 86 aroma compounds in Chinese famous liquors. Riu-Aumatell et al. [19] identified and quantified 59 volatile compounds in beers. Sagratini et al. [20] identified and compared 28 volatile chemicals in red wines from two different regions of Italy.

Several studies about cherry wine have been reported in recent years. For example, Sun et al. [21] compared the influence of cultivars on aromatic compounds and polyphenols in cherry wines by HS-SPME-GC–MS and HPLC. Niu et al. [5] identified 45 aroma compounds in cherry wines, which were also classified into six sensory terms as fruity, sour, woody, fermentation, cameral and floral notes by gas chromatography-olfactometry (GC-O). Besides, aroma compounds of Marasca cherry wines produced at different fermentation conditions were determined by HS-SPME and headspace sampler (HSS) coupled with gas chromatography (GC/FID). Recently, Xiao et al. [8] have successfully discriminated nine different cherry wines based on their sensory properties and aromatic fingerprinting. However, there is still a lack of systematic study on the aroma of cherry wines originated from different regions by HS-SPME-GC–MS combined with PCA. Therefore, it is necessary to conduct more intensive flavor analysis of cherry wines.

Herein, we report our latest study of flavor analysis of cherry wines, which consisted of the following four steps as follows: (a) optimizing an extraction procedure of SPME; (b) determining regression coefficients, limits of detection and quantification, repeatability, reproducibility and recoveries of analytes; (c) identifying and quantifying volatiles of real cherry wine with the above developed method; (d) analyzing the aroma profiles of five cherry wine samples using chemometric PCA.

2. Materials and methods

2.1. Materials

Five cherry wines were analyzed. Among them, three of them were foreign cherry wines, including the wine form Germany LORCH Co., Ltd. with 20 vol% (W1), the Berentzen wild cherry wine with 16 vol% (W2) and the Germany Kirschwein with 9.5 vol% (W4). Other two domestic wines were provided by China Jiangsu hongxiangyi wine Co., Ltd. with 8 vol% (W3) and 9 vol% (W5), respectively.

Tour type of SPME fibers, including the 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) and 100 μm polydimethylsiloxane (PDMS), were purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO). Standards of ethyl acetate, 1-butanol, hexyl acetate, furfual, 3-methyl-1-butanol, phenylethyl alcohol, ethyl hexanoate, trans-2-hexenal, ethyl lactate, acetic acid, ethyl phenylactate, 4-methy phenol, 4-ethyl guaiacol, 2-octanol (internal standard) and n-alkane standards (C7–C30) were purchased from the same Sigma-Aldrich Chemical Co. (St. Louis, MO). Analytical grade ethanol 99.7% (v/v), sodium hydroxide and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tartaric acid (≥99.5%) was purchased from Merck (Darmstadt, Germany). Pure water was prepared by Milli-Q purification system (Millipore, Bedford, MA).

2.2. Preparation of simulated cherry wine

The simulated cherry wine (12% (v/v) ethanol), containing 40 mg L^{-1} mixture of all the aforementioned standards and 2 g L^{-1} tartaric acid in Milli-Q water, was used to develop and optimize a SPME method. The pH of working solutions was adjusted to 3.5 with sodium hydroxide on the basis of data measured from real cherry wine.

2.3. Optimization of extraction condition

The extraction condition was determined by optimizing a series of different parameters that affect the extraction efficiency, including the fibers in different polarity, different extraction temperatures and extraction times, and different content of sodium chloride in the wine.

2.4. Extraction of aroma compounds

Prior to first use, the fibers were conditioned according to manufacturer's guideline. A 15 mL headspace vial (Reference 27385, Supelco, Bellefonte, PA, USA) with PTFE-silicone septa (Supelco, Bellefonte, PA, USA), containing 8 mL of the simulated wine, 2 g sodium chloride and 50 μL 2-octanol (262 mg L^{-1}) was placed in a thermostatic water bath. The fiber was exposed to the headspace of the sample for 45 min at 50 °C without stirring and then desorbed into the injector port of GC apparatus for 5 min. After each analysis, the fiber was inserted into a thermal heater for 20 min at 250 °C to ensure there were no contaminants was remained. The same procedure was applied to all the five cherry wine samples, which were adjusted to 12% ethanol before the flavor extraction.

2.5. GC–MS analysis

A 7890A gas chromatograph (GC) coupled to a 5973C mass selective detector (MS) (Agilent Technologies, USA) was employed for separation and detection analyses. The HP-INNOWAX fused-silica capillary column (60m × 0.25 mm ID, 0.25 μm film thickness) was used to perform the chromatographic separations. The oven temperature program was started from 40 °C for 2 min, increased at a rate 3 °C min^{-1} to 230 °C for 2 min, along with quadrupole mass filter was operated at 150 °C, the transfer line temperature was at 250 °C and ion source temperature at 230 °C. The injector temperature was set at 230 °C for flavor desorption 5 min from the SPME fiber under a splitless mode. Helium was used as the column carrier gas with a constant flow rate of 1 mL min^{-1}. The MS parameters included electron impact ionization with electron energy of 70 eV, and mass range of m/z 30–450, using the selective ion monitoring (SIM) mode. The area of each peak was determined by ChemStation software (Agilent Technologies). A blank run was carried out to ensure no carryover of analytes from previous injections before sampling [22,23].

The compound identifications were achieved by comparing their retention indices (RI) and mass fragmented patterns with those of authentic compounds, or with mass spectrums in the Wiley7n. L Database (Hewlett-Packard, Palo Alto, CA) and NIST Database and previously reported RI in the literatures. The RI was determined for each unknown compound using a commercial mixture of n-alkanes (C7–C30) (concentration of 1000 μg L^{-1} in n-hexane). Meanwhile, quantitative data for individual target compounds were determined by the external standard method.

2.6. Statistical analysis

The quantitative data of five sample wines were analyzed by PCA using XLSTAT ver. 2010 (Addinsoft, New York, NY, USA). PCA