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Determination of semi-volatile additives in wines using SPME and GC–MS

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ABSTRACT

Parameters of headspace solid-phase microextraction, such as fiber coating (85 μm CAR/PDMS), extraction time (2 min for white and 3 min for red wines), temperature (85 °C), pre-incubation time (15 min) were optimized for identification and quantification of semi-volatile additives (propylene glycol, sorbic and benzoic acids) in wines. To overcome problems in their determination, an evaporation of the wine matrix was performed. Using the optimized method, screening of 25 wine samples was performed, and the presence of propylene glycol, sorbic and benzoic acids was found in 22, 20 and 6 samples, respectively. Analysis of different wines using a standard addition approach showed good linearity in concentration ranges 0–250, 0–125, and 0–250 mg/L for propylene glycol, sorbic and benzoic acids, respectively. The proposed method can be recommended for quality control of wine and disclosing adulterated samples.

1. Introduction

Adulteration of wines has become widespread around the world. In 2009, >1 million adulterated Amarone wine bottles were sold in Italy (Holmberg, 2010). According to the "Regulations of the Customs Union of Russia, Kazakhstan and Belarus on the safety of alcoholic beverages" (2010), wine shall be produced as a consequence of complete or partial fermentation of a grape must without adding ethanol. Addition of certain chemical substances to wine is acceptable at permissible concentrations (Avram, Bratu, & Sandu, 2013). Elevated levels of additives of natural or synthetic substances may change sensory properties of wine. Such wines are considered as adulterated. Among additives, special attention is paid to propylene glycol (PG), sorbic (SA) and benzoic (BA) acids. The presence of propylene glycol in wine may indicate an addition of flavors (Guguchkina, Oseledceva, Yakuba, & Reznichenko, 2011). Sorbic and benzoic acids at concentrations higher than permissible values can be detrimental for human health. According to the "Regulations of the Customs Union of Russia, Kazakhstan and Belarus on safety of alcoholic beverages" (2010), the maximum permitted concentration of propylene glycol in wines is 1 g/kg, for sorbic and benzoic acid – 300 mg/kg. According to "EU Regulation No 1129/2011" (2011), the maximum permissible value of sorbic acid in fruit and made wines, and aromatized wine drinks is 200 mg/kg, while according to "EU Regulation No 1130/2011" (2011), the maximum acceptable concentration of propylene glycol as a carrier for flavorings in beverages (including alcoholic) is 1000 mg/kg.

Concentrations of SA and BA are typically determined by direct injection into a liquid chromatograph with ultraviolet (LC-UV) (Lino & Pena, 2010; Saad, Bari, Saleh, Ahmad, & Talib, 2005) or tandem mass-spectrometric detectors (LC–MS/MS) (Goren et al., 2015). PG is a very polar compound featuring a strong affinity to water and poor retention by reversed-phase LC. Its determination by LC-UV involves time-consuming derivatization with phenyl isocyanate (PIC) reagent (Rychłowska, Zgoła, Grześkowiak, & Łukaszewski, 2003), *p*-toluenesulfonyl isocyanate (Zhou, Zhang, & Duan, 2007) or benzoyl chloride (Holcapek, Virelizier,

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Chamot-Rooke, Jandera, & Moulin, 1999). Direct quantification of PG in wines was successfully conducted by gas chromatography with flame ionization detector (GC-FID) (Guguchkina et al., 2011). SA and BA may be determined by GC as well; however, direct injection of samples containing high concentrations of water and non-volatile matrix into the GC is not recommended due to a decrease in a column lifetime and contamination of a system.

Headspace (HS) solid-phase microextraction (SPME) is the simplest sample preparation approach for GC or GC–MS, based on a consequent transfer of analytes from a sample to a headspace and further to a polymer coating followed by their thermal desorption in the injection port. SPME combines extraction, concentration and clean-up into a single step (Risticevic, Lord, Górecki, Arthur, & Pawliszyn, 2010). Determination of polar semi-volatile compounds in wines by GC and SPME is complicated because of (a) strong retention of analytes by ethanol and water, (b) matrix effect and (c) competition for sorption sites at the fiber with more volatile and hydrophobic wine constituents (e.g., esters and alcohols).

Dong and Wang (2006) applied anhydrous sodium sulfate to reduce the matrix effect when determining SA and BA in wines by GC-FID in combination with HS-SPME. Authors optimized SPME parameters to decrease detection limits: extraction time 40 min, extraction temperature 50 °C, desorption temperature 260 °C, desorption time 5 min, addition of 2.5 g of anhydrous sodium sulfate. Twenty and fifty times dilutions of wine samples were conducted to overcome the problem of matrix competition of volatile wine constituents with each other for sorption sites at the fiber. Authors found out that the addition of sodium hydroxide and heating in a water bath at 80 °C to remove volatile interferences for 5 min led to an increase in extraction recovery to 82.2%. PG and SA were identified by Giraudel, Setkova, Pawliszyn, and Montury (2007) and Setkova, Risticevic, and Pawliszyn (2007) along with other volatile and semi-volatile wine constituents by GC-TOFMS in combination with SPME, but that research was not focused on method optimization. The goal of that paper was qualitative profiling of ice wines volatile fraction. Authors analyzed wine samples by HS-SPME with addition of sodium chloride, in order to isolate volatile compounds from the wine matrix. Comparison of existing methodologies for determination of propylene glycol, sorbic and benzoic acids by SPME is presented in Table S1.

The aim of this research was to develop a method to determine PG, SA and BA in wines by GC–MS in combination with SPME after evaporation of ethanol, water and most volatile wine constituents. Extraction time and temperature, pre-incubation time and fiber type were optimized. The developed method was successfully applied for screening PG, SA and BA and other semi-volatile constituents in different wines.

2. Experimental

2.1. Reagents and supplies

Propylene glycol (purity >99%) and benzoic acid (>99.5%) were obtained from Sigma-Aldrich (Munich, Germany). Sorbic acid (>99%) was obtained from AppliChem (Darmstadt, Germany). Ethanol (>95%, Talgar-Spirt, Talgar, Kazakhstan) and 40% ethanol solution were used for preparing standard solutions.

2.2. Wines

All wine samples were purchased from supermarkets located in Almaty, Kazakhstan. To develop the method, semi-dry white wine "Familiae Piccini" ("Vino Bianco D'Italia", Italy), semi-sweet red wine "Toro Negro" ("Tinto Semidulce", Spain), red dry wine "Damskiy Ugodnik" (Bacchus, Kazakhstan) and dessert red wine "Kagor" ("Bacchus", Kazakhstan) were chosen. Twenty-five wine samples of different types (dry, semi-sweet, dessert white and red) and origin (Table S2) were chosen for screening of semi-volatile wine constituents using the proposed method.

2.3. Sample preparation

2.3.1. Samples for experimental optimization

Experimental samples were spiked with 100 μL of the standard solution of PG, SA and BA to a final concentration of 100 mg/L. To prepare the standard solution, 0.025 g of each analyte were weighed and quantitatively transferred to a 5-mL volumetric flask followed by filling the flask by ethanol (>95% purity) up to the graduation mark. Then, 2 mL of the obtained solution were diluted with a 40% ethanol solution to 10 mL in a volumetric flask. To prepare samples for experimental optimization of SPME parameters, 100 μL of prepared standard solution were added to 900 μL of wine sample in a screw-cap 20-mL vial.

2.3.2. Samples for quantitative analysis using standard addition method

To determine concentrations of PG, SA and BA in three wine samples (white semi-dry, red semi-sweet, red dessert) using SPME-GC–MS, the standard addition method was used. Samples were prepared by adding 50 μL of a standard solution of analytes to 450 μL of both red and white wines in a 20-mL screw cap vial (Supelco, Bellefonte, PA). Standard solutions were prepared by diluting stock solution of analytes to concentrations 500, 1000, 2000 and 2500 mg/L for PG and BA, and 250, 500, 1000 and 1250 mg/L for SA.

2.3.3. Evaporation conditions

Before SPME, all experimental samples were evaporated in a drying oven (80-01; Smolensk Special Engineering Department of Programming Management System, Smolensk, Russia) at 90 ± 5 °C, in order to remove the volatile wine matrix (water, ethanol and other volatile wine constituents). The temperature of evaporation was chosen in order to accelerate the process, shorten the time of the sample preparation and to be below the boiling point of water and temperatures of transformation and caramelization of sugars present in all wines – fructose (110 °C), galactose (160 °C), glucose (160 °C), sucrose (160 °C) and maltose (180 °C). At evaporation temperatures below 90 °C, no changes in analytes' responses and new peaks that could indicate the analytes decomposition were observed. The time of the evaporation was not fixed because it depended on the sugar content in the sample, and varied between 45 and 60 min. Evaporation was performed until the obtained residue was free from any liquid. Evaporation of the volatile wine fraction was faster for samples with a higher sugar content. After evaporation, vials were sealed with magnetic caps with PTFE/silicone septa (Agilent, USA) and placed onto the autosampler tray for analysis using SPME-GC–MS.

2.4. Solid-phase microextraction

Extraction was performed in headspace mode. Most important SPME method parameters were experimentally optimized - fiber coating, extraction temperature, extraction and pre-incubation time. The desorption time was set to 5 min for each experiment. All the experiments (optimization of parameters, screening and quantification of PG, SA and BA) were performed in two replicates.

2.4.1. Selection of a fiber coating

Experiment was conducted on a red dry wine. Three different fibers were tested: 100 μm polydimethylsiloxane (PDMS), 50/30 μm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/