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Rapid Communication

A rapid method for simultaneously determining ethanol and methanol content in wines by full evaporation headspace gas chromatography

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ABSTRACT

This work reports on a full evaporation headspace gas chromatographic (FE HS-GC) method for simultaneously determining the ethanol (EtOH) and methanol (MeOH) content in wines. A small sample (10 μL) was placed in a headspace sample vial, and a near-complete mass transfer of ethanol and methanol from the liquid sample to the vapor phase was obtained within three minutes at a temperature of 105 °C, which allowed the measurement of the EtOH and MeOH content in the sample by GC. The results showed excellent precision and accuracy, as shown by the reproducibilities of 1.02% and 2.11% for EtOH and MeOH, respectively, and recoveries that ranged from 96.1% to 104% for both alcohols. The method is efficient, accurate and suitable for the determination of EtOH and MeOH in wine production and quality control.

1. Introduction

Wine is a complex mixture obtained from the complete or partial fermentation of fresh grapes or grape must, containing water, alcohols, acids, sugars, mineral salts, pigments and aromatic compounds (Cheynier, Schneider, Salmon, & Fulcrand, 2010). Ethanol (EtOH) is the second largest component (after water) in wine, with concentrations ranging from 10% to 20% v/v (Pinney, 2012). The EtOH content is one of the most important parameters for process and quality control in wine industries (Collins, Miller, Altria, & Waterhouse, 1997). In addition to EtOH, there is a small amount of methanol (MeOH, also called "wood alcohol") in wines that is produced as a by-product of the acetification involving the enzymic hydrolysis of pectin methoxyl groups during fermentation (Ribereau-Gayon, Glories, Maujean, & Dubourdieu, 2000). Since MeOH is toxic to humans (Bindler, Voges, & Laugel, 1988; Robins, Angell, & Kumas, 1981), the MeOH content of wines is strictly regulated by the International Office of Vine and Wine (OIV) at <400 mg/L for red wines and <250 mg/L for white or rose wines (OIV, 2011). Clearly, routine methods that can quantify the contents of these alcohols efficiently are desirable in both production and quality control.

There are several methods available for quantifying alcohol species in wines. Densimetric methods (European Commission, 2000; OIV, 2009), based on pycnometry, and hydrostatic balance (or hydrometry) have been used traditionally for the determination of alcohols in wine, measured as the percentage by volume. However, these methods use distillation to separate the alcohols from other coexisting species (e.g., sugars) prior to the densitometry. This distillation process is time-consuming, and the sensitivity is poor, which can cause significant errors, especially in wines with low alcohol content. Several other analytical methods have been developed to quantify specific alcohol components in wines and beverage products; e.g., titrimetric methods (AOAC, 1990), enzymatic methods (Gulce, Gulce, Kavanoz, Coskun, & Yildiz, 2002; Mizgunova, Zolotova, & Dolmanova, 1996), and colorimetric (spectrophotometric) methods (AOAC, 1990). The titrimetric and enzymatic methods have low reproducibility and accuracy, while the colorimetric methods are subject to interferences by colored substances in wine. Because of the ability to separate chemical species and high sensitivity of the detector, the combination of high performance liquid chromatography (HPLC) (Chen et al., 1998; Kuo, Wen, Huang, Wu, & Wu, 2002) and gas chromatography (GC) (Liu, Liu, Zhang, & Zhang, 2001; Wilson, Ding, & Woods, 1991) is regarded as the best method for the quantification of these alcohol species. Unfortunately, HPLC or GC analysis requires sample pretreatment to minimize the species (such as natural polymers, salts and sugars) that might deteriorate or contaminate the instruments.

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The pre-treatment procedures, typically filtration and solvent extraction, are not only complicated and time-consuming but also can easily introduce significant errors in the quantification.

Conventional headspace gas chromatography (HS-GC), based on vapor–liquid partition equilibrium of the analytes, has also been used for the determination of EtOH (Wartts & McDonald, 1987) and MeOH (Chai, Dhasmana, & Zhu, 1998) in complicated liquid matrices. The major advantage of HS-GC is that it can usually be used without sample pre-treatment, because the analytes are released in a relatively pure form into the headspace. Thus, HS-GC analysis is not only simpler but is also more efficient than the techniques mentioned above. However, the HS-GC cannot simply be applied to quantify the EtOH content in wines, because the equilibrium of EtOH between vapor and liquid phases does not follow Henry's Law (Teja, Gupta, Bullock, Chai, & Zhu, 2001) due to the relatively high concentration of alcohol in wines. Although this problem can be solved by the internal standard calibration; i.e., spiking a known amount of analyte into the sample (Chai et al., 1998), this additional step makes the method less efficient, especially in the case of batch sample analysis.

Unlike the conventional HS-GC, the full evaporation (FE) technique is based on a near-complete mass transfer, other than phase equilibration, which means that the vapor analytes are independent of the sample matrices (Kolb & Ettre, 2006). In FE conditions, Henry's Law is no longer a factor, which makes the calibration step much simpler. Also, compared with the conventional HS-GC methods, the time for headspace equilibration required in FE HS-GC is much shorter, due to the very small samples used (Kolb & Ettre, 2006).

In previous studies, we developed two related FE HS-GC methods: one for the determination of MeOH in a pulping spent liquor (Li, Zhan, Fu, Liu, & Chai, 2007) and the other for determination of EtOH in a fermentation process solution (Li, Chai, Deng, Zhan, & Fu, 2009). In this work, we report on the development of a rapid method to simultaneously quantify the EtOH and MeOH content in wines based on the FE HS-GC technique. The main focus is on the optimization of the conditions during the analysis, with emphasis on the sample size and headspace equilibration time and temperature. The reproducibility of the method and the recovery of spiked analytes are also evaluated. The goal is to demonstrate a rapid method that can provide timely information during the wine making process and accurate data for quality control purposes.

2. Experimental

2.1. Chemicals and materials

All chemicals used in the experiments were analytical grade and purchased from commercial sources without further purification. A set of mixed standard solutions (EtOH concentrations of 0–16.0% v/v and MeOH concentrations of 0–396 ppm (w/v)) were prepared by adding different amounts of pure EtOH and MeOH to distilled water

Wine samples used in the experiments were purchased from a local commercial source.

2.2. Apparatus and operations

HS-GC measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, US) equipped with a flame ionization detector and a DB-5 capillary column (30 m long, 0.35 mm ID), operating at a temperature of 30 °C for 2.8 min with nitrogen carrier gas (flow rate = 3.8 mL/min). Headspace operating conditions were as follows: 3 min of strong shaking for sample equilibration at 105 °C; sample loop temperature = 110 °C; transfer line temperature = 115 °C; pressurization pressure = 2.00 bar; carrier gas pressure = 1.50 bar; vial pressurization time = 15 s; sample loop fill time = 10 s; and transfer time = 20 s.

2.3. Procedures of sample preparation

10 μL of the sample solution was placed in a headspace sample vial (21.6 mL) by a micropipette. The sample vial was immediately sealed with a PTFE/silicone septum and aluminum cap. The FE equilibration was conducted at 105 °C for 3 min prior to HS-GC measurement.

3. Results and discussions

3.1. Chromatogram of a wine sample measured by FE HS-GC

Unlike the analysis in our previous work (Li et al., 2007, 2009), in order to separate the EtOH and MeOH signals, generated by large concentration differences but similar retention times, the GC conditions had to be selected carefully. Fig. 1 shows a GC chromatogram of the FE HS-GC analysis of a wine sample under the selected conditions. Fig. 1a is an enlargement of Fig. 1b and shows that some minor volatile species (including MeOH) were well separated from EtOH under these conditions. Clearly, EtOH is the dominant species in the vapor phase due to its high content in the sample. Although MeOH is a minor component in wines, the GC detector (FID) is sufficiently sensitive to quantify its content using the FE HS-GC method.

3.2. Conditions for full evaporation

3.2.1. Equilibration temperature

In order to achieve a near-complete mass transfer of the volatile analytes from the liquid phase to vapor phase (i.e., a full evaporation), it is essential to equilibrate the sample at a high temperature so that more volatile solutes can leave the liquid phase and enter the headspace. However, if the temperature is too high, the resulting high pressure increases the risk of the sample leaking from or even bursting the vial.

In our previous studies (Li et al., 2007, 2009), we found that full evaporation of aqueous samples at 105 °C (greater than water boiling point) worked well with a sample size <100 μL. Therefore, we chose 105 °C as the equilibration temperature in the present study.

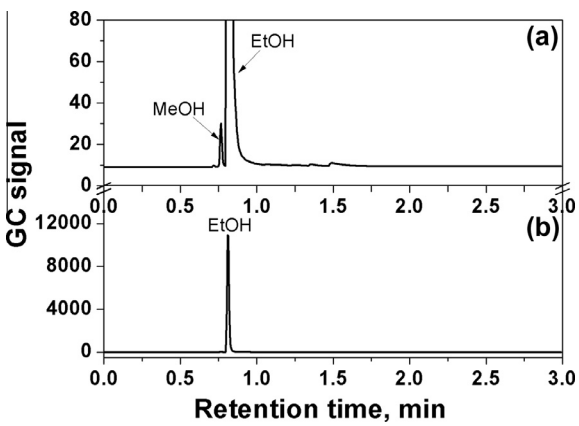

Fig. 1. GC chromatogram from FE HS-GC analysis for a wine sample.