Journal of Chromatography A, 1216 (2009) 5061–5068

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Determination of carbonyl compounds in beer by derivatisation and headspace solid-phase microextraction in combination with gas chromatography and mass spectrometry

Daan Saison*, David P. De Schutter, Filip Delvaux, Freddy R. Delvaux

Centre for Malting and Brewing Science, Faculty of Bioscience Engineering, K.U.Leuven, Kasteelpark Arenberg 22, Box 2463, 3001 Heverlee, Belgium

ARTICLE INFO

Article history:
Received 5 February 2009
Received in revised form 15 April 2009
Accepted 24 April 2009
Available online 3 May 2009

Keywords:
Beer
Carbonyl compounds
Derivatisation
In-solution
On-fibre
Solid-phase microextraction
Gas chromatography
Mass spectrometry

ABSTRACT

Headspace solid-phase microextraction (SPME) followed by gas chromatography and mass spectrometry was applied for quantification of 41 chemically diverse carbonyl compounds in beer. Therefore, in-solution derivatisation with o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) combined with SPME was optimised for fibre selection, PFBHA concentration, extraction temperature and time and ionic strength. Afterwards, the method was calibrated and validated successfully and extraction efficiency was compared to sampling with on-fibre derivatisation. In-solution derivatisation enabled the detection of several compounds that were poorly extracted with on-fibre derivatisation such as 5-hydroxymethylfurfural, acrolein, hydroxyacetone, acetoin, glyoxal and methylglyoxal. Others, especially (E)-2-nonenal, were extracted better with on-fibre derivatisation.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Carbonyl compounds are widely found in food products. They can originate from raw materials, alcoholic fermentation [1,2] or from a wide range of chemical reactions such as lipid oxidation, Maillard reactions, Strecker degradation and aldol condensation [3]. As a consequence, they are widespread in alcoholic beverages and spirits such as beer [3,4], wine [5,6], vodka [7], calvados and cognac [8]. Although their concentrations are generally very low, these compounds are designated an important, mostly unwanted contribution to the flavour profile because of their low flavour thresholds [9]. Although this contribution is mostly unnoticeable in fresh beverages, the aforementioned reactions can occur during storage, resulting in the formation of a whole range of carbonyl compounds and accordingly, the deterioration of flavour [3]. Besides, quantification of some carbonyls can be used for the evaluation of a complete and proper fermentation [1]. As a result, the quantitative determination of the volatile carbonyl content is very important.

Detecting carbonyl compounds in beer is very difficult because of their extremely low concentrations, their low volatility and high reactivity owing to the polar carbonyl group, and the presence of more abundant esters and alcohols. Therefore, it has always been a challenge to develop methods with high extraction recoveries in order to obtain adequate sensitivity. Previously, the easiest and most successful technique to overcome these problems was by derivatisation of the carbonyl group [4,10], thereby improving selectivity and rendering carbonyls less polar and less responsive for interactions. In gas chromatography (GC), the derivatisation is mostly performed with o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) or pentafluorophenyl hydrazine (PFPH), followed by electron capture or mass spectrometrical (MS) detection. The use of PFBHA is more common and it was already shown to give better results in aqueous samples [10,11]. After derivatisation, derivatives can be extracted using liquid–liquid (LLE) or solid-phase extraction techniques [5,10,12] and one study reports extraction with stir bar sorptive extraction [13]. Although these methods provide good reproducibility, they involve an extensive work-up, and mostly, the use of solvents.

Solid-phase microextraction (SPME) is a simple, solvent-free, reliable and fast extraction technique developed by Pawliszyn and co-workers [14,15]. When this technique is applied in combination with derivatisation, 3 strategies can be followed: either derivatisation is performed in-solution, combined with headspace (HS) [2,7,16–19] or liquid SPME [20], or on-fibre derivatisation can be used by loading the derivatisation agent onto the fibre and subse-

* Corresponding author.
E-mail address: daan.saison@biw.kuleuven.be (D. Saison).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.04.077

quent exposal to the HS of the sample [4,15,21–23]. Application of liquid SPME for beer analysis is less suitable, since it contains lots of non-volatile compounds such as sugars, proteins and polyphenols that can interfere with the extraction and damage the fibre. Consequently, the reproducibility should be doubted and the lifetime of the fibre would be reduced substantially [14,24]. On-fibre derivatisation on the other hand, has been widely used with PFBHA for sampling of various aqueous matrices: around 20 aldehydes with varying structures were quantified in beer [4,21,22], several C1–C10 aldehydes in white wine [11], around 25 aldehydes in water [20,23], acetone in human plasma [25] and hexanal and heptanal in human blood [26]. Finally, in-solution derivatisation with HS SPME has been applied for the analysis of around 30 aldehydes and 5 (di)ketones in water samples [18–20], acetaldehyde, diacetyl and acetoin in wine [17] and around 10 C1–C6 aldehydes in spirits such as vodka [2,7,16].

The use of on-fibre derivatisation increased the sensitivity for aldehydes in beer as compared to in-solution derivatisation followed by LLE [22]. However, arising problems for the detection of carbonyls are only partly met and method detection limits (MDLs) (defined as a general term for limits of detection and quantification) for polar aldehydes and ketones, such as methyl isobutylketone (MIBK) and acetylfuran already appeared to be quite poor in beer [4]. In addition, the technique proved to be unsuccesful for the detection of glyoxal, methylglyoxal and hydroxylated aldehydes in aqueous solutions [11,20]. Indeed, application of on-fibre derivatisation improves the selectivity for carbonyls greatly by up-concentration on the fibre and decreasing the interference of more abundant alcohols and esters. However, the advantage of improving the volatility of carbonyls by means of derivatisation is not applicable. This is supported by some fundamental studies suggesting that the kinetics of on-fibre derivatisation is limited by the mass transport rate of underivatised carbonyls to the fibre [11] and the observation that more polar carbonyls could be detected in water after in-solution derivatisation [20]. Thus, the bottleneck appears to be occurring at the sample/headspace interface and extraction efficiency is consequently greatly determined by the volatility of a compound. The latter is defined by the interplay of the boiling point and the interactions with the sample. Consequently, troublesome extraction of less volatile carbonyl compounds, owing to their interaction with aqueous solutions, might be improved by first rendering them more volatile with in-solution derivatisation and subsequent HS SPME.

The overall aim of this study was to develop an adequate method for the determination of a wide range of carbonyl compounds in order to be able to characterise the carbonyl content of beer. Therefore, sampling by in-solution derivatisation, combined with HS SPME was optimised and validated for 41 carbonyl compounds in beer. The carbonyl compound selection was based on their chemical diversity and their relevance for beer flavour. Afterwards, the validation was extended to on-fibre derivatisation and finally, the possibilities of both techniques were studied by comparing the extraction efficiency and MDLs for the selected compounds in beer.

2. Experimental

2.1. Reagents

All chemicals were purchased from Sigma (St. Louis, MO, USA) with the highest purity available.

2.2. Instrumentation

GC-MS was carried out using a Trace GC Ultra gas chromatograph coupled to a dual stage quadrupole MS (both from Thermo, Austin, TX, USA). A Rtx-5SilMS column (60 m × 0.25 μm I.D.) with a film thickness of 1 μm was used. The GC was equipped with a split-splitless injector which was held at 250 °C. Compounds were analysed following 2 min desorption and splitless injection. The GC program started at 60 °C for 2 min, then increased in 4 steps: 60–165 °C at 50 °C/min; 165–200 °C at 2 °C/min, 200–260 °C at 4 °C/min and 260–290 °C at 5 °C/min and was held at 290 °C for 6 min. During the GC run, a constant flow rate (1.5 mL/min) of the carrier gas (Helium) was maintained. The mass spectra were obtained by electron impact (EI) ionisation at 70 eV and the ion volume and the transfer line were held at 250 and 290 °C respectively. The detector was set in TIC mode from *m*/*z* 35 to 400. The results were analysed using Xcalibur software (Thermo, Austin, TX, USA).

2.3. HS SPME with on-fibre derivatisation

The extraction with on-fibre derivatisation and HS SPME was performed as described by Saison et al. [4]. A PDMS-DVB fibre was loaded with PFBHA (10 min 45 °C, 250 rpm) and subsequently exposed to the headspace of a vial containing 10 mL beer and 3.5 g NaCl (30 min 45 °C, 250 rpm).

2.4. Optimisation of the procedure using in-solution derivatisation and HS SPME

After filtration, 10 mL beer was added to a 20 mL vial and an aliquot of 50 μL ethanol containing 100 mg/L *p*-fluorobenzaldehyde was added as internal standard. Afterwards, the defined amount of PFBHA solution (20 g/L) was added to the vial. Six parameters were optimised: fibre coating, added amount of PFBHA solution, extraction temperature, pre-incubation and extraction time and salt addition. After thermal desorption in the injector, the fibre was conditioned for 12 min at the temperature defined by the manufacturer. Finally, calibration was performed and MDLs were determined.

2.4.1. SPME fibre coatings

The SPME fibres tested in this work were polydimethylsiloxane 100 μm (PDMS), polydimethylsiloxane-divinylbenzene 65 μm (PDMS-DVB), Carboxen-polydimethylsiloxane 85 μm (CAR-PDMS), Carbowax-divinylbenzene 70 μm (CW-DVB), and divinylbenzene-Carboxen-polydimethylsiloxane 50/30 μm (DVB-CAR-PDMS). The fibres were conditioned according to the manufacturers' instructions by inserting them in the desorption unit of the Combi PAL autosampler (CTC Analytics, Zwingen, Switzerland).

2.4.2. PFBHA concentration

The concentration of PFBHA in the sample was optimised by adding different amounts of PFBHA solution (20 g/L) (20, 50, 100, 250, 500 and 1000 μL). The vials were equilibrated for 20 min at 50 °C and a stirring speed of 500 rpm. Afterwards, the fibre was introduced automatically through the septum and was exposed in the HS for 30 min at 50 °C under continuous stirring at 250 rpm. The extraction efficiency was evaluated by the chromatographic peak areas of the compounds.

2.4.3. Extraction temperature

To study the effect of temperature on the extraction of the derivatised carbonyl compounds, 7 temperatures (30, 40, 45, 50, 55, 60 and 70 °C) were examined. The samples were equilibrated for 20 min at 500 rpm and subsequently extracted for 30 min under continuous stirring at 250 rpm.

Download English Version:

https://daneshyari.com/en/article/1210674

Download Persian Version:

https://daneshyari.com/article/1210674

Daneshyari.com