Talanta 83 (2010) 294–296

Contents lists available at ScienceDirect

Talanta

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

Short communication

Determination of beer aroma compounds using headspace solid-phase microcolumn extraction

Ján Hrivňák[a], Daniela Šmogrovičová[b,*], Pavol Nádaský[b], Jana Lakatošová[a,b]

[a] The Plant Production Research Center Piešt'any, Institute of Viticulture and Enology, Matúškova 25, 831 01 Bratislava, Slovak Republic
[b] Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

ARTICLE INFO

Article history:
Received 29 April 2010
Received in revised form 24 August 2010
Accepted 26 August 2010
Available online 9 September 2010

Keywords:
Gas chromatography
Solid-phase microcolumn extraction
Beer
Volatile organic compounds
Adsorption
Tenax

ABSTRACT

A rapid sampling technique for the analysis of beer aroma compounds is described. The headspace (10 ml) is passed through the microcolumn filled with 5 mg of Tenax TA and thermally desorbed in a modified GC inlet (modification is described). Eight compounds (from acetaldehyde to 2-phenylethanol) in four beer samples were analyzed. The correlation coefficients (r^2), repeatability (RSD) and limits of detection (LOD) were 0.9973–0.9994, 2.1–6.9% and 0.00002–0.13 mg/l, respectively. The methodology can be useful for routine beer sample analysis.

1. Introduction

Beer aroma compounds are very important as they make a major contribution to the quality of the final product. A variety of flavor compounds may arise depending on the beer type and storage conditions. Reliable and sensitive analytical methodologies are required for the extraction and analysis of a great number beer aroma compounds, ranging from very volatile all the way to high boiling.

Several extraction/concentration methods have been employed for the analysis of beer volatiles. Static or dynamic headspace analysis and the purge-and-trap technique are among the most widely used sampling techniques for volatile isolation [1]. Headspace solid-phase microextraction (HS-SPME) is a simple, fast, sensitive and solvent-free extraction technique that enables the extraction and concentration steps to be performed simultaneously [2–5].

Headspace solid-phase microcolumn extraction (HS-SPMCE) is a useful and an alternative analytical tool for the analysis of both very volatile and high-boiling compounds. Among volatiles, HS-SPMCE has been successfully used for the quantitative analysis of vinyl chloride in water [6], chloroform in urine [7] and benzene in air [8].

The aim of this work was to demonstrate the performance of HS-SPMCE for the quantitative analysis of both very volatile and higher boiling beer aroma compounds in one sample run using GC-FID.

2. Experimental

2.1. Chemicals

Acetaldehyde, acetone, methyl acetate, ethyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, 2-phenylethanol, ethanol and sodium chloride (NaCl) were obtained from Merck (Darmstadt, Germany). Tenax TA was purchased from Aldrich (Deerfield, IL, USA).

2.2. Instrumentation and chromatographic conditions

Analyses were carried out on a Shimadzu GC model 14A equipped with a modified split/splitless (S/SL) inlet with capillary restrictor, new silicone septa, tubing and glass liner as shown in Fig. 1. For detailed description see also [7,9]. For the analysis, a 100-ml aliquot of the beer sample was quickly transferred (by means of a graduated cylinder) into a 500-ml volumetric flask containing 20 g NaCl and the flask was vigorously shaken by hand (approximately 0.5 min) at room temperature (22 ± 1 °C). After 10–15 min equilibration using a narrow glass tube (1 mm i.d.) connected (with

---

* Corresponding author. Tel.: +421 2 59325493; fax: +421 2 52493198.
E-mail addresses: janhrivnak@post.sk (J. Hrivňák), daniela.smogrovicova@stuba.sk (D. Šmogrovičová), pavol.nadasky@stuba.sk (P. Nádaský), xlakatosova@is.stuba.sk (J. Lakatošová).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.08.041

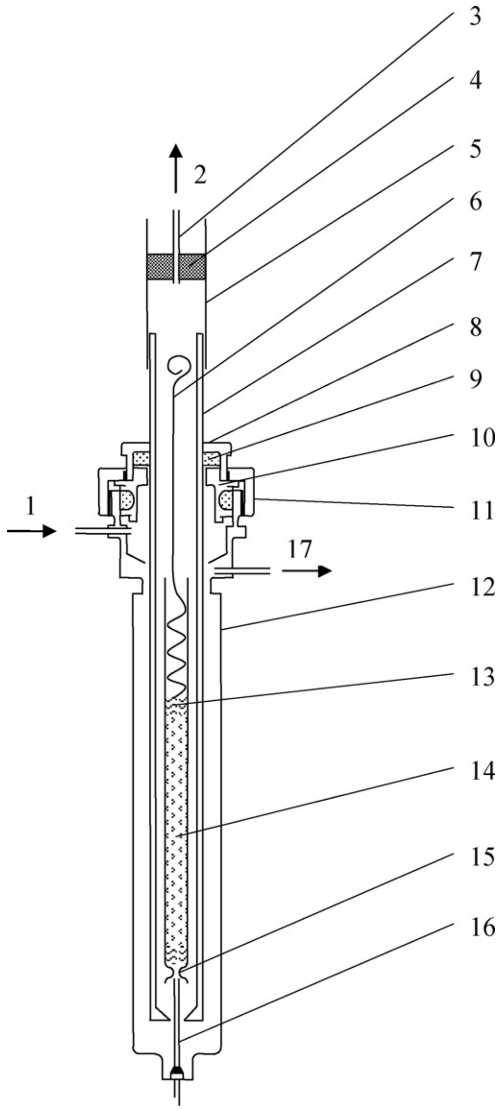

Fig. 1. Schematic diagram of the modified GC inlet for thermal desorption: (1) carrier gas, (2) septum purge, (3) capillary restrictor, (4) silicone septum, (5) silicone tubing, (6) wire eye (for manipulation), (7) glass liner, (8) septum holder, (9) silicone septum, (10) sealing ring with O-ring, (11) nut, (12) inlet body, (13) glass wool, (14) Tenax TA, (15) gas tight connection, (16) capillary column, and (17) to split valve.

a short piece of flexible tubing, glass to glass) to a 10-ml all glass syringe (Poulten & Graf, Wertheim, Germany) and 10 ml of headspace from a distance of about 1–2 cm above the liquid phase was withdrawn. The headspace content of the syringe was immediately pushed through the microcolumn (1 mm i.d. packed with 5.0 mg of 60–80 mesh Tenax TA) – parts 6, 13, 14 and 15 in Fig. 1. The loaded microcolumn was transferred to a modified GC inlet.

The trapped aroma compounds were desorbed at 10 kPa by heating the microcolumn to 230 °C for 1 min. After desorption, the carrier gas pressure was increased to 60 kPa and the temperature program was started. During the analysis run, the microcolumn remained in the GC inlet.

A computer program (Shimadzu, Class-VP.2, SP1) was used for data acquisition. The chromatograph was equipped with FID and fused silica VF-WAXms capillary column of 30 m length × 0.25 i.d. × 0.5 μm film thicknesses (Varian, Lake Forest, CA, USA). The chromatographic elution was temperature programmed as follows: isothermal at 30 °C (4 min), then increased at a rate of 5 °C/min to 200 °C and hold 10 min. The temperature of the inlet chamber was 230 °C and helium was used as a carrier gas.

Table 1
Correlation coefficients (r^2), limits of detection (LOD), limits of quantification (LOQ) and repeatability (RSD) of investigated analytes.

Compound	r^2	LOD (mg/l)	LOQ (mg/l)	SD % ($n = 5$)
Acetaldehyde	0.9989	0.039	0.24	4.9
Acetone	0.9983	0.011	0.070	5.7
Methyl acetate	0.9991	0.003	0.022	4.1
Ethyl acetate	0.9993	0.001	0.0068	2.9
Ethyl hexanoate	0.9993	0.0002	0.0015	3.2
Ethyl octanoate	0.9994	0.0004	0.0028	2.1
Ethyl decanoate	0.9991	0.001	0.0066	3.7
2-Phenylethanol	0.9973	0.13	0.79	6.9

3. Results and discussion

Acetaldehyde, acetone, methyl acetate (representatives of very volatile compounds) and ethyl hexanoate, ethyl octanoate, ethyl decanoate and 2-phenylethanol (representatives of higher boiling beer aroma compounds) were chosen to confirm the versatility and suitability of the new HS-SPMCE method.

For quantitative analysis, five-point calibration curves over the range of concentrations from 1 to 10 mg/l for acetaldehyde, 0.1–1 mg/l for acetone, methyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, 2–20 mg/l for ethyl acetate, and 1–50 mg/l for 2-phenylethanol in the 4% (v/v) of ethanol were measured. The correlation coefficients (r^2) listed in Table 1 varied from 0.9983 to 0.9996 (each calibration mixture was analyzed three times).

The repeatability of the method, determined five times for the same beer sample and expressed as the relative standard deviation (RSD) was in the range of 2.1–6.9% (Table 1) and is sufficient for the studied compounds' quantitative analyzes. Similar values have been obtained by HS-SPMCE analysis of volatile compounds in water [6] and urine [7].

The limits of detection (LOD) and quantification (LOQ) (listed in Table 1) were calculated by Adstat Calibration Program (Trilobite, Czech Republic) and show good sensitivities for the real sample analyses.

As an example, the chromatogram of the beer sample 1 shown in Fig. 2 was analyzed by the method (described in Section 2.2) and the results of the quantitative analysis of four sample results (mean value of two measurements) are listed in Table 2. In the chromatogram (Fig. 2), there are 19 peaks from very volatile compounds and 94 peaks from higher boiling compounds. We believe that many of these peaks can be used for quantitative analysis.

The results in Table 2 indicate relatively small differences between the compositions of the studied compounds in the analyzed samples. The proposed method can be useful for the analysis of real samples.

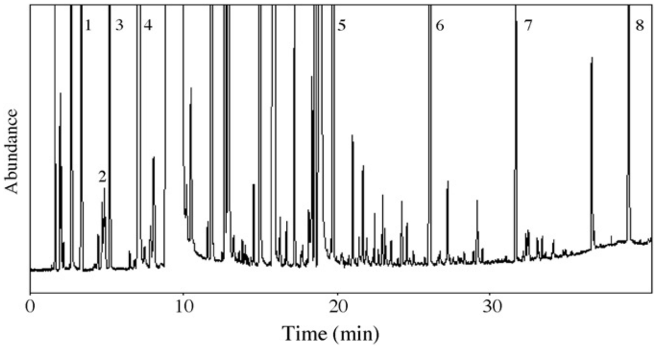

Fig. 2. Chromatogram of the beer sample 1. Peaks: (1) acetaldehyde; (2) acetone; (3) methyl acetate; (4) ethyl acetate; (5) ethyl hexanoate; (6) ethyl octanoate; (7) ethyl decanoate; (8) 2-phenylethanol.

Table 2
Four sample results (mg/l) of studied beer aroma compounds analysis.

Compound	Sample 1	Sample 2	Sample 3	Sample 4
Acetaldehyde	5.14	4.26	6.11	3.86
Acetone	0.12	0.093	0.15	0.093
Methyl acetate	0.13	0.94	0.14	0.11
Ethyl acetate	10.1	9.41	12.1	13.3
Ethyl hexanoate	0.11	0.10	0.16	0.12
Ethyl octanoate	0.31	0.34	0.33	0.33
Ethyl decanoate	0.079	0.13	0.087	0.37
2-Phenylethanol	10.3	11.4	13.3	11.8

The modification of gas chromatographic inlet for thermal desorption in the microcolumn is economic, and replaces the expensive thermal desorption unit.

4. Conclusions

HS-SPMCE is a simple, fast and sensitive method for the routine analysis of aroma compounds in beer samples. Owing to the good reproducibility of the method, it can in be used to compare the volatile profiles of different types of beers, study the development of a particular beer during aging, or correlate with sensory analysis results.

Acknowledgements

This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Academy of Sciences, registration number 1/0786/08.

References

[1] B. Vanderhaegen, H. Neven, S. Coghe, K.J. Verstrepen, H. Verachtert, G. Derdelincks, J. Agric. Food Chem. 51 (2003) 6782.
[2] C.L. Artur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[3] Z. Zang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[4] E. Ibanez, R. Bernhard, J. Sci. Food Agric. 72 (1996) 91.
[5] J. Pawliszyn, Solid-phase Microextraction: Theory and Practice, Wiley-VCH, New York, 1997.
[6] P. Tölgyessy, J. Hrivňák, K. Šilhárová, Petrol. Coal 46 (2004) 88–94.
[7] J. Hrivňák, E. Král'ovičová, P. Tölgyessy, J. Ilavský, J. Occup. Health 51 (2009) 173–176.
[8] E. Král'ovičová, J. Hrivňák, P. Tölgyessy, Petrol. Coal 48 (2006) 61–65.
[9] J. Hrivňák, P. Tölgyessy, S. Figedyová, S. Katuščák, Talanta 80 (2009) 400–402.