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2014 ASBC Annual Meeting

Determination of Flavor Compounds in Beer using Stir Bar Sorptive Extraction and Solid-Phase Microextraction

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ABSTRACT

Stir bar sorptive extraction (SBSE) and solid phase microextraction (SPME), two solventless enrichment techniques, were applied in combination with gas chromatography flame ionization detection (GC/FID) for the determination of flavor compounds in beer. The performance of both methods was compared for various parameters, including linearity, limit of detection, repeatability, and recovery of four compounds (isoamyl acetate, ethyl hexanoate, myrcene, benzaldehyde) typically found in beer. Both methods were characterized by high linearity (r > 0.996) and repeatability (RSD = 1.76 to 10.66%). Higher recoveries were obtained by SBSE, and limits of detection were 1.8 to 2.8 times lower when compared to SPME. When both methods were used to analyze commercial lager beers, the results showed that SBSE has higher recovery efficiency, therefore showing promise for the analysis of beer volatiles.

INTRODUCTION

The analysis of volatile flavor compounds in beer requires the use of extraction techniques prior to instrumental analysis (1). Many well-established extraction methods have limitations including requirements for expensive equipment, expensive and environmentally unfriendly solvents, multi-step sample handling that decreases accuracy, and the need to concentrate analytes of interest to detectable levels (1,2). To address some of the limitations of the available extraction and concentration procedures, solvent-less sample extraction techniques have been developed, among these developments are solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE) (2, 3). In SPME, a coated fused silica fiber is inserted into a liquid sample, or the headspace above the sample to adsorb the analytes of interest (2,4). This technique has proven to be fast, simple, reliable, enabling simultaneous extraction and concentration, and has been successfully applied in the determination of a variety of compounds in beer (3,5). Another development of solvent-less sample extraction is SBSE. The extraction is based on the sorption of analytes onto a thick film of polydimethylsiloxane (PDMS) coated on a stir bar (4). SBSE methods in beer analysis have been applied for the determination of hop derived terpenoids and esters in beer (2). Thus far, the use of SBSE using thermal desorption has not been compared to SPME for the analysis of flavor compounds belonging to different chemical groups that are present in beer. The objective of this investigation was to compare SBSE and SPME extraction methods for the determination of beer flavor compounds.

MATERIALS AND METHODS

Sample preparation. Bottles of American lager beer were purchased at a local store and kept at 4 ° C until they were analyzed to avoid significant losses of volatile compounds.

Volatile Compound Stock Solution. For method validation a volatile compound stock solution in 5% ethanol was prepared with final concentrations of: isoamyl acetate (8.44 mg/L), ethyl hexanoate (8.53 mg/L), benzaldehyde (10.29 mg/L), myrcene (7.21 mg/L).

Validation and Quantification. The linearity, limit of detection, and repeatability of the method were determined using calibration curves. The calibration curves were prepared from dilution of the volatile compound stock solution to different concentrations with 5% (v/v) ethanol. Accuracy was evaluated by conducting recovery tests on commercial lager beers.

Extraction Method Comparison. SBSE and SPME were compared for the determination of the volatile compounds in commercial lager beers.

SPME

SBSE

Samples

Gas Chromatography
Flame Ionization Detection
(GC/FID)

Statistical Analysis
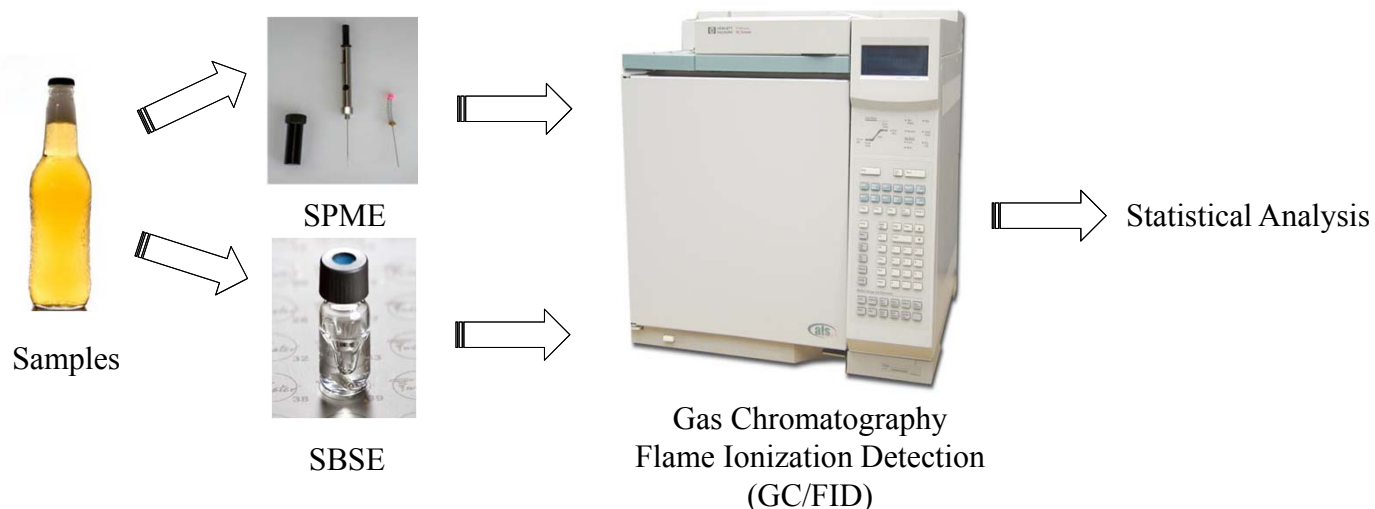
RESULTS AND DISCUSSION

For method comparison, the following parameters were determined: recovery, precision, linearity, and limits of detection (LOD). Results of these comparisons are shown in Table I. Both methods showed high linearity in the studied concentration ranges. Lower LOD and higher recoveries were obtained by SBSE when compared to SPME. The results demonstrate the increased recovery obtained by using a higher volume of extraction phase in the SBSE stir bars compared to the volumes used in the SPME fibers.

Table 1. Comparison of linearity, recovery, limit of detection and repeatability of SPME and SBSE methods

Compound	Linearity (R)		Limit of Detection (mg/L)		Recovery (%)		Repeatability (%RSD)	
	SPME	SBSE	SPME	SBSE	SPME	SBSE	SPME	SBSE
Isoamyl Acetate	0.999	0.999	0.17	0.07	96.28	102.18	10.66	3.82
Ethyl Hexanoate	0.999	0.999	0.17	0.09	85.62	90.07	4.72	1.76
Myrcene	0.996	0.998	0.21	0.11	97.41	99.19	10.24	2.93
Benzaldehyde	0.996	0.999	0.23	0.08	83.24	98.90	6.70	4.89

The RSD values were lower for SBSE. These results indicate a higher reproducibility of the SBSE technique compared to SPME. This phenomenon is very likely due to the difference in the extraction phase used by both methods. SPME uses copolymers (PDMS/DVB or PDMS/CAR) which can lead to irreproducible results because of the presence of adsorption mechanism, while SBSE uses PDMS.

Both SPME and SBSE were evaluated for the analysis of the compounds in commercial lager beer samples (Table 2). Higher concentrations were detected for all compounds when using SBSE compared to SPME (p ≤ 0.05). The higher concentrations obtained by SBSE are likely due to the higher volume of extraction phase present in the PDMS coated stir bars, suggesting that SBSE may be more suitable for volatile flavor analysis in beer than SPME.

Table II. Concentrations of flavor compounds (mg/L) as the mean of three replicates in four beer samples determined by using SBSE and SPME. Different letters in the same row indicate significant differences between compound concentrations within a sample as analyzed by Tukey's HSD (p ≤ 0.05). n.d. not detected

Compound	Beer A		Beer B		Beer C		Beer D	
	SPME	SBSE	SPME	SBSE	SPME	SBSE	SPME	SBSE
Isoamyl Acetate	1.00[a]	1.75[b]	1.50[a]	1.65[b]	2.95[a]	5.57[b]	1.44[a]	3.05[b]
Ethyl Hexanoate	n.d.	0.11	n.d.	0.26	0.18[a]	0.32[b]	n.d.	0.17
Myrcene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	0.32[a]	0.36[b]	n.d.	0.14	n.d.	0.17

CONCLUSIONS

➢Both SBSE and SPME followed by GC analysis were successfully applied for the extraction and concentration of volatile flavor compounds from beer.

➢The SBSE technique showed some advantages in comparison with SPME, including lower detection limits, higher linearity, and higher recovery for the compounds studied.

➢ SBSE shows promise for the analysis of beer volatiles. However, further research needs to be conducted to determine its suitability for the analysis of the volatile fraction of beer.

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