Determination of (E)-2-nonenal in beer using Purge & Trap extraction and GC-MS analysis

Thomas M. Hartlein, Teledyne Tekmar, Mason, Ohio, USA.

Abstract

A new method to determine (E)-2-nonenal in beer based on Purge & Trap extraction and GC-MS analysis was developed. In the Purge & Trap technique the liquid samples are continually purged by an inert gas to extract the volatile sample components which are subsequently trapped by a sorbent material. The trapped components are then thermal desorbed and transferred to a gas chromatograph for analysis. The developed method was well evaluated for the determination of mid µg/mL levels of (E)-2-nonenal in beer.

Figure 1. Atomx Automated VOC Sample Prep System

Introduction

Numerous compounds contribute to changes in beer flavor as it becomes stale. One of these compounds, the unsaturated aldehyde (E)-2-nonenal, has been investigated as a major source of the papery/cardboard flavor that develops in aged beer.

Several methods for the extraction of aldehydes from beer have been reported, such as liquid-liquid extraction, low-pressure or steam distillation, however, these methods are rather laborious and prone of errors. As chromatographic signals of trace components may be masked by high concentrations of major components, the majority of the procedures involve preconcentration followed by a derivatization step and separation by HPLC or GC, but derivatization of the carbonyls is an additional step to complicate the analysis.[1]

This work presents a new method to determine (E)-2-nonenal in beer based on Purge & Trap extraction and GC-MS analysis. Purge & Trap, also known as dynamic headspace, is a technique of extraction and concentration which principle is to pass an inert, pure gas through a (heated) closed purging vessel whereby the volatile organic compounds (VOCs) are driven from the sample. The expelled volatile compounds are transported with the gas to an adsorbing material in a trap. After the step of adsorption, the trap is heated and the components are thermal desorbed and transferred by the carrier gas to the capillary column in the GC where the components are separated and detected. Purge & Trap is ideal for dirty samples, solid materials, and samples with high boiling point analytes of no interest, high water content, analytes too low in concentration, and samples that are difficult to handle by conventional GC.

Experimental

The automated VOC sample preparation system Teledyne Tekmar Atomx that combines an autosampler and Purge & Trap into a single instrument was used to extract and concentrate (E)-2-nonenal from samples of beer using the soil method. Tenax was used as adsorbent material in the trap. Some parameters of the Purge & Trap method are presented in Table 1. The conditions listed are one set of numerous possible conditions that accomplishes the separation and detection of these compounds. This does not preclude a scientific laboratory from operating this analysis with alternate conditions utilizing the Atomx soil method. The analyses were done in a GC-MS quadrupole system in the Selected Ion Monitoring (SIM) mode. The GC-MS parameters are presented in Table 2.

Table 1. Atomx Modified Soil Method Parameters

Purge Variable	Value	Purge Variable	Value
Valve Oven Temp	200 °C	Condensate Purge Temp	70 °C
Transfer Line Temp	210 °C	Dry Purge Time	0.50 min
Sample Vial Temp	50 °C	Dry Purge Flow	50 mL/min
Soil Valve Temp	120 °C	Dry Purge Temp	70 °C
Standby Flow	25 mL/min	**Desorb Variable**	**Value**
Purge Ready Temp	70 °C	Sweep Needle Time	0.50 min
Condensate Ready Temp	70 °C	Desorb Preheat Temp	220 °C
Purge Mix Speed	Fast	Desorb Temp	225 °C
Purge Time	10 min	**Bake Variable**	**Value**
Purge Flow	25 mL/min	Bake Time	8 min
Purge Temp	70 °C	Bake Flow	200 mL/min
		Bake Temp	230 °C

Table 2. GC-MS System Settings

GC Settings	
Column	Rtx®-VMS, 20 m x 0.18 mm ID x 1 µm, 0.9 mL/min Constant Flow, Helium
Inlet	230 °C, Split Ratio 60:1
Transfer Line	230 °C
Oven Program	95 °C, 3.5 °C/min to 145 °C, 15 °C/min to 240 °C, 3 min final hold, 21.7 min Run
MS Settings	
Scan	35 to 200 m/z Gain Factor 1, ATune, 1.4 min Solvent Delay
SIM (m/z)	55, 70, 83, 96, 111, Dwell Time 100
Temperatures	Source 230 °C Quad 150 °C

Results

Five lots of a commercial pale lager beer were analysed. Aliquots of 10 mL were sampled, degassed, and added with 6 g NaCl to improve the extraction by the salting out effect. Solutions with 0.27 to 5.4 ppb of (E)-2-nonenal in 5% (v/v) ethanol were prepared for calibration. Figure 1 presents the SIM Total Ion Chromatograms of a beer sample in triplicate, and the overlap of a sample spiked with (E)-2-nonenal. The concentrations of (E)-2-nonenal determined in five lots of a commercial pale lager beer are presented in Table 3.

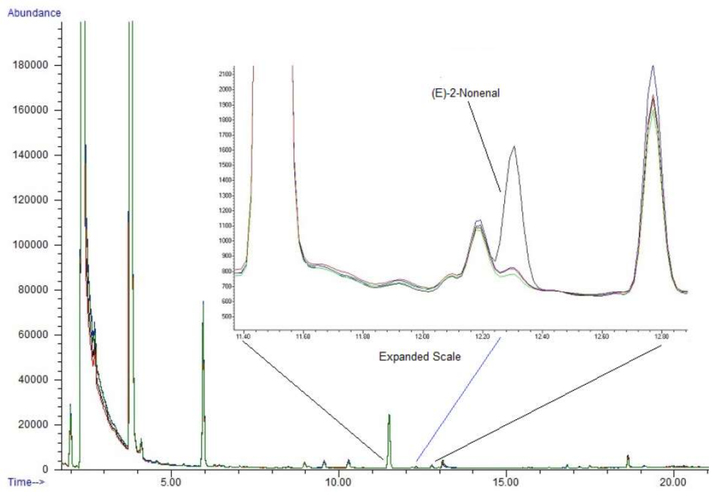

Figure 2. Comparison of the SIM Total Ion Chromatograms of a Beer Sample (in Triplicate, Lower) to its Spiked Sample (Upper)

Table 3. Concentration of (E)-2-nonenal in five lots of a commercial pale lager beer

Sample Lot	ng/mL
A	0.180
B	0.463
C	0.261
D	0.184
E	0.082

Conclusion

The initial results presented in this work suggest that the Purge & Trap extraction technique coupled to GC-MS analysis is an adequate new method to determine mid µg/mL levels of (E)-2-nonenal in beer. A validation study has yet to be developed with this method.

References

1. Scherer, R.; Wagner, R.; Kowalski, C.H.; Godoy, H. T. (E)-2-Nonenal Determination in Brazilian Beers using Headspace Solid-Phase Microextraction and Gas Chromatographic Coupled Mass spectrometry (HS-SPME-GC-MS). *Ciência e Tecnologia de Alimentos*, Campinas, 30(Supl.1): 161-165, Maio 2010.