Flavor Profiles of Imported and Domestic Beers by Purge & Trap Thermal Desorption GC/MS

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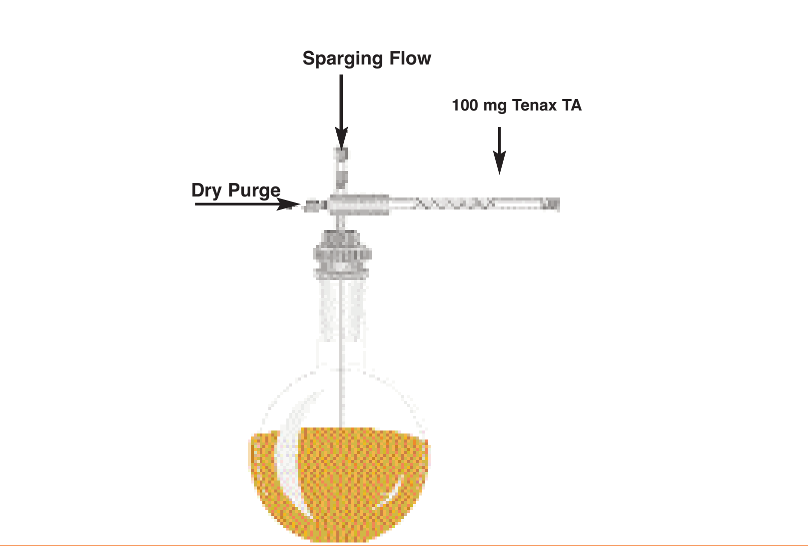
Introduction

Domestic beer sales were $99 Billion in 2012. [1] This equates to 200,028,520 barrels of product brewed and sold last year. The overall growth from 2011 was 1%, but the fastest growing segment of the beer industry is in regional craft (10,237,632 bbl), brewpubs (870,371 bbl) and microbrewers (1,905,212 bbl) with increased sales of 17% during the same period [1]. Competition in the industry is keen and keeping customer loyalty is dependent on producing a consistent high quality product. One way to aid in the art of brewing beer is to have an analytical method that is capable of detecting the differences in the flavor profiles that the brew master can use to tweak the production process to manufacture a consistent product.

Flavor qualities of beers are greatly dependent on the volatile and semi-volatile organic compounds present in the liquid matrix and headspace aroma. These compounds are also used in the manufacturing process to obtain the desired physical properties of the product. Over time beer can develop off-odors or flavors due to a number of factors including the natural aging process, variations in storage temperatures or interactions with the container. The use of purge & trap coupled with Thermal Desorption GC/MS is used to show the different flavor profiles of various types of beers.

Figure 1: Purge & Trap Setup



Materials and Methods

Five beers were sampled and analyzed. They are as follows:

1. Commercial Domestic Beer
2. Commercial Imported Beer
3. Microbrewery Ale (Brown full bodied Ale)
4. Microbrewery Ale (Blonde Ale Pilsner body)
5. Brewpub Brown Ale

Figure 2: Thermal Desorption

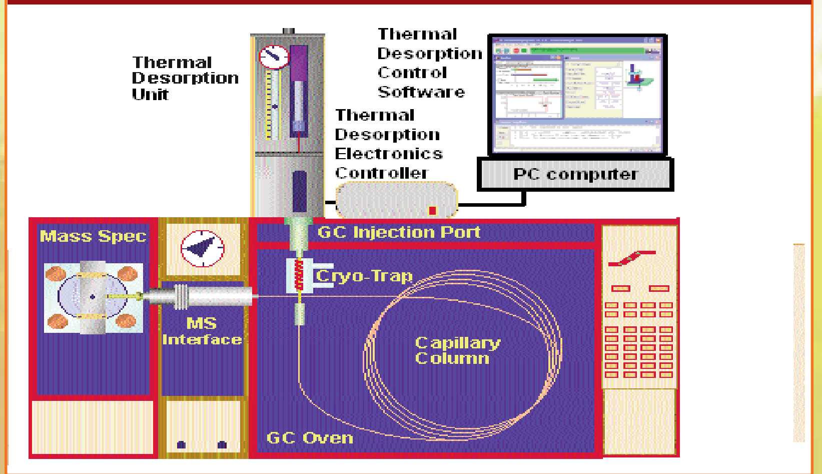


Figure 1 Shows our SIS Purge & Trap apparatus. 10 ml's of each beer (diluted 4:1 in distilled water) were purged with chromatography grade Helium with a sparge and dry purge rate of 25 ml/minute each for 10 minutes and collected on a preconditioned SIS Thermal Desorption Tube. The Thermal Desorption tubes used for the analysis were SS (0.25" x 4.0" x 4 mm ID) packed with 100 mg of Tenax TA (60/80 mesh) adsorbent. The tubes were preconditioned in a SIS conditioning oven at 320C for four hours with high purity Nitrogen flowing at a rate of 50 ml/min through the tubes.

The Desorption tube was placed in a SIS TD-5 Short-Path Thermal Desorption Instrument (**Figure 2**) and a 35 mm preconditioned SS desorption needle was attached. The TD-5 was coupled to an Agilent 6890 GC utilizing a 5973 MSD as a detector. The 6890 GC had a SIS Cryotrap installed on the injector that was cooled to -40C with liquid CO2 to cryofocus the sample during the desorption process. The TD-5 was programmed to allow for a 1 minute dry purge to reduce the ethyl alcohol concentration in the sample and then desorbed at 150C for 5 minutes. During this desorption process a divert valve is actuated by the SIS software and allows the injection port Helium flow to pass through the desorption tube that the needle has penetrated into the inlet septum. After the desorption has concluded the divert valve switches the flow back through the GC inlet in a seamless fashion. During the desorption the cryotrap remains at -40C, after the desorption period the cryotrap is ballistically heated to 200C for three minutes and the GC/MS data acquisition is initiated. The MSD was scanning a mass range of 35-350 with a 1 second scan rate.

The GC column used was a J&W DB-5MS (0.25 mm ID x 60M) with a 0.25 µm film and was operated at 40-250C at a ramp rate of 10C/minute. The GC was operated in split mode with a 5:1 split. All desorption parameters were controlled by the SIS TD-5 software integrated within the Chemstation program. Mass spectra data was compared to NIST11 AMDIS software for component identification.

Figure 3: Commercial, #1 Domestic, #2 Import

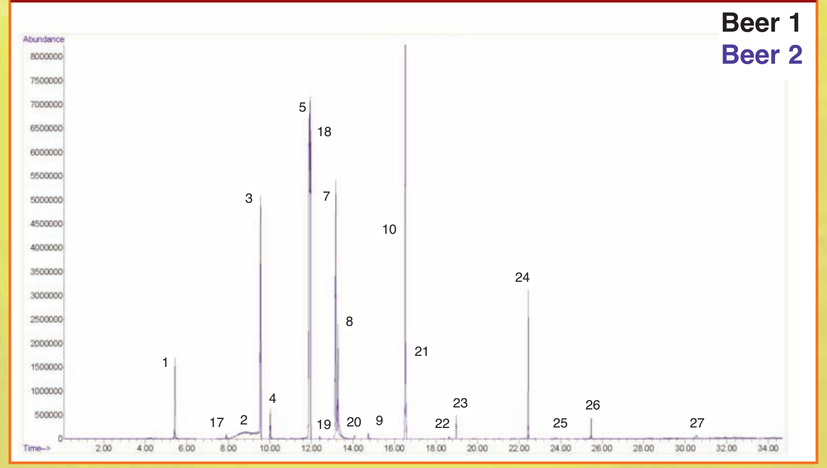
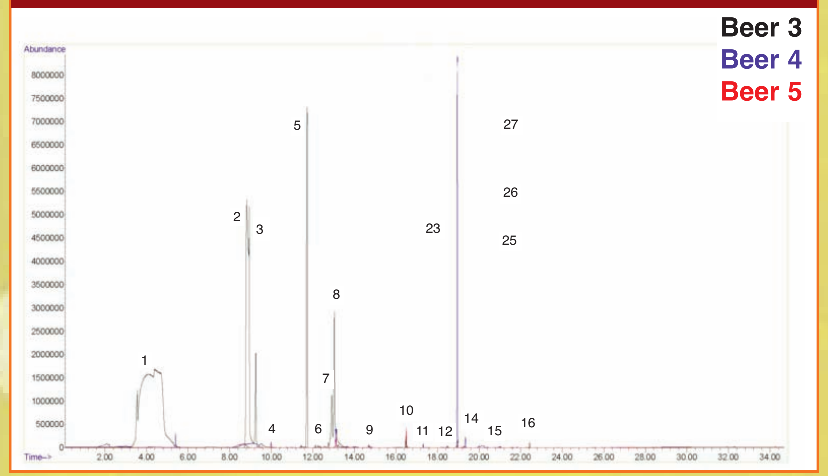


Figure 4: Microbrewery #3-4, Brewpub #5



Results & Discussions

The commercial beer samples shared similar chromatographic traits. **Figure 3** shows the overlay of the domestic (#1) and Imported (#2) beer chromatograms. The major differences arise in the increased concentrations of the longer chain alcohols, 2 & 3-methyl butanol(7&8), isoamyl acetate(10), 2-methyl propanol(4) and long chain ethyl esters of octanoic(24) and decanoic(26) acids found in the domestic beer (#1). All of these compounds are attributed with a fruity odor[2] with isoamyl acetate being the most well-known as it is banana oil. **Figure 4** is the chromatographic overlay of samples #3-5. As would be expected with a microbrewery product the profiles are quite distinct. Sample #3 had a much higher ethanol concentration than the other beers labeled at 10% by volume. Sample #4 had the most varied volatile profile with ethyl esters of propanoic(19), hexanoic(23), octanoic(24) and decanoic(26) acids as well as a higher concentration of isoamyl acetate(10). **Figure 5** is the chromatographic overlay of all five samples. All samples share some common components but in widely varying concentrations. **Table 1** shows a tabulation of the identified components.

Figure 5: Beer Samples #1-5

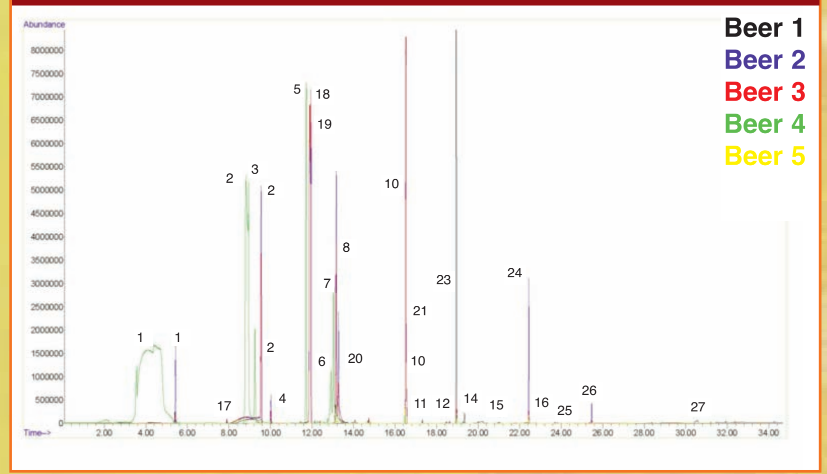


Table 1: Peak Identification

1. Ethanol	2. Ethyl Acetate	3. 2-Butanone, 4-hydroxy
4. 1-Propanol, 2-methyl	5. Pentane, 2,2, 4-4 Trimethyl	6. Heptane
7. 1-Butanol, 3-methyl	8. 1-Butanol, 2-Methyl	9. Butanoic acid, ethyl ester
10. 1-Butanol, 3-methyl, acetate (Isoamyl acetate)	11. Propanoic acid, 2-methyl-butyl ester	12. 1-Butanol, 2-methyl, propanoate
13. Beta-myrcene	14. Propanoic acid 2-methyl, 2-methyl-butyl ester	15. Glycerin
16. Octanoic acid, ethy ester	17. 1-Propanol	18. Hexane, 2, 2,Dimenthyl
19. Propanoic acid, ethyl ester	20. Acetic acid 2-methylpropyl ester	21. 1-Butanol, 2-methyl acetate
22. Phenol	23. Hexanoic acid, ethyl ester	24. Octanoic acid, ethyl ester
25. Acetic acid, 2-phenyethyl ester	26. Decanoic acid, ethyl ester	27. 1,2-Benzenedicarboxylic acid, diisooctyl ester

Conclusion

Short Path Thermal Desorption GC/MS is a valuable analytical tool to study flavor/aroma profiles of beers. The ability to use a new transfer line with each sample (The desorption needle) eliminates any cross-sample contamination and any memory effects associated with other P&T instruments. This method is a valuable asset in production to quickly determine lot-to-lot consistency of the product or to quickly determine any culprits in an off odor/taste scenario.

References

1. Brewers Association- www.brewersassociation.org
2. Merck Index, 14th edition, 2006