A-104

2014 ASBC Annual Meeting

Chemical Profile Analysis of Beer Using Direct Analysis in Real Time Mass Spectrometry (DART-MS)

Darrin L. Smith, Ph.D.

Eastern Kentucky University, Department of Chemistry, Richmond, KY 40475

75th ASBC Annual Meeting
June 4–6, 2014
Palmer House, a Hilton Hotel
Chicago, IL

Introduction

Analysis with an ambient ionization source, Direct Analysis in Real Time (DART), coupled with a mass spectrometry system was performed to determine the chemical profile of an ale (after maturation in a bourbon oak barrel). The DART-MS was employed to determine if different congeners in the beer after maturation could be rapidly identified (compared to a brew water control sample). In addition to the direct analysis of the ale, solid phase micro-extraction (SPME) fibers were also employed.

The DART source is a surface desorption technique where direct desorption of non-volatile and volatile analytes from solid, liquid, or gas samples is possible for mass spectral analysis in the gas phase. [1] The DART source can ionize analytes from samples through mechanisms mainly depending on the reaction gas used in conjunction with the proton affinity and ionizing potential of the analytes to form positive (+) cations or negative (-) anions. It has also been demonstrated that ions can be formed through adduct formation. [2] The ionized products can eventually be identified through molecular weight determination as well as structure elucidation with tandem mass spectrometry using collision-induced dissociation. [3]

Experimental

Sample Preparation: Ale and brew water (as a control) were each placed in a separate oak barrel after being used for bourbon maturation. Samples were taken from the barrels on a weekly basis and placed in a headspace vial and crimped sealed. The samples were then placed in refrigeration (~4ºC) until used for analysis.

The headspace vials were brought to room temperature. A 1 – 2 mL aliquot were then extracted from each with a syringe and placed into a clean glass vial. For direct analysis, solution was applied to a glass 'Dip-It' rod by dipping and then introduced into the ionization region of the ion source by hand.

For SPME analysis, an octadecyl (C18) or polydimethylsiloxane (PDMS) fiber was placed in a 50:50 methanol : water solution for conditioning (30 minutes) and then placed in a sample solution and allowed to incubate for 30 minutes, Figure 1. After incubation, the fiber was inserted into the ionization region of the source by hand. Data was collected during analysis, which was completed within 1 – 2 minutes for each sample.

Figure 1. SPME fiber in ale sample

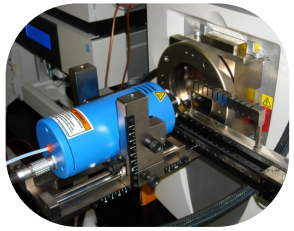

Figure 2. DART-MS System

Instrumentation: The DART source coupled to the mass spectrometer used to analyze the ale samples is shown in Figure 2. The IonSense DART ion source was coupled to a Thermo LTQ XL linear ion trap mass spectrometer. The reagent gas was helium and had a purity of >99.99%. The gas heater temperature, helium pressure, grid voltage for the ion source were set at 350°C, 80psi, and 200V, respectively.

Data / Results / Discussion

Brew Water Control

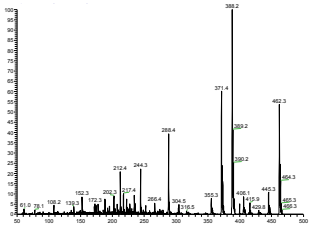

Figure 3. Mass spectrum (+) of water control after 3 weeks maturation in barrel analyzed directly with Dip-It

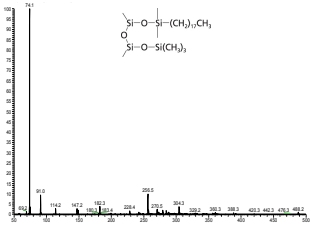

Figure 4. Mass spectrum (+) of water control after 3 weeks maturation in barrel analyzed after SPME C18 (insert)

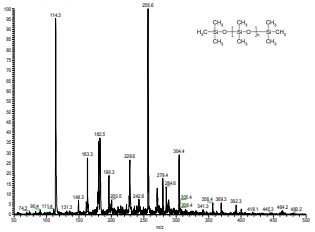

Figure 5. Mass spectrum (+) of water control after 3 weeks maturation in barrel analyzed after SPME PDMS (insert)

Ale Sample

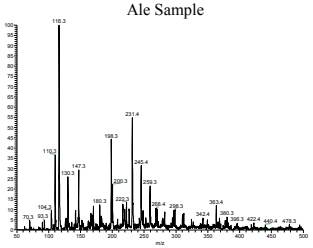

Figure 6. Mass spectrum (+) of ale after 3 weeks maturation in barrel analyzed directly with Dip-It

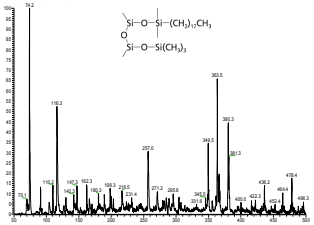

Figure 7. Mass spectrum (+) of ale after 3 weeks maturation in barrel analyzed after SPME C18 (insert)

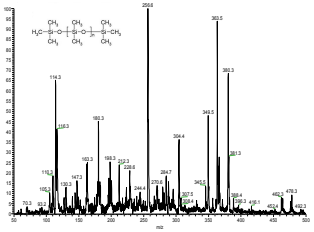

Figure 8. Mass spectrum (+) of ale after 3 weeks maturation in barrel analyzed after SPME PDMS (insert)

Positive (+) mass spectra (Figures 3, 4, and 5) were generated from water control samples (taken after three weeks in barrel) using three different methods: i) direct insertion, ii) C18 and iii) PDMS SPME fibers. For direct insertion, formed ions may be formed with compounds and water clusters since the peak pattern is unique for these samples. With SPME, the available bulk matrix is no longer present and ions are potentially derived from compounds extracted from the bourbon / barrel. For Figures 6, 7, and 8, the (+) mass spectra are generated with the ale sample (also taken from the barrel after three weeks). Comparing against water controls, one can determine the origin of the compounds of the ale from the ale itself and those compounds derived from the bourbon / barrel. Similar to water samples, using SPME removes and isolates compounds from the matrix. Identification of the ion adducts to the specific corresponding compounds are currently being investigated. Confirmation of compounds through fragmentation will occur using tandem mass spectrometry.

Data / Results / Discussion

Brew Water Control

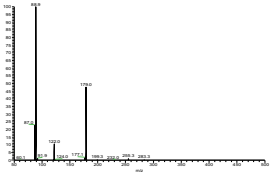

Figure 9. Mass spectrum (-) of water after 3 weeks in barrel analyzed directly with Dip-It

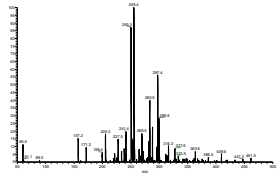

Figure 10. Mass spectrum (-) of water after 3 weeks in barrel analyzed after SPME C18

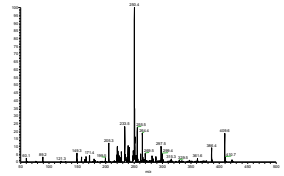

Figure 11. Mass spectrum (-) of water after 3 weeks in barrel analyzed after SPME PDMS

Ale Sample

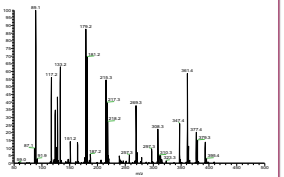

Figure 12. Mass spectrum (-) of ale after 3 weeks in barrel analyzed directly with Dip-It

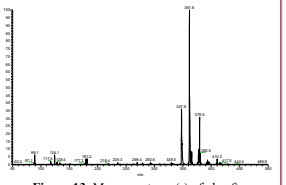

Figure 13. Mass spectrum (-) of ale after 3 weeks in barrel analyzed after SPME C18

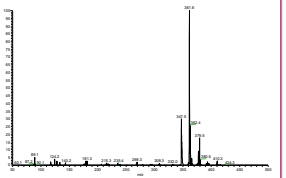

Figure 14. Mass spectrum (-) of ale after 3 weeks in barrel analyzed after SPME PDMS

Chemical profiles were also rapidly observed with negative (-) mass spectra. Figures 9, 10, and 11 mass spectra were generated for the water controls while Figures 12, 13, and 14 were generated with ale samples using the different methods of analysis. Once again, removal of bulk matrix using SPME results in different spectral patterns. Further investigations of the ion adducts to determine the specific corresponding compounds is still being pursued.

References

1. Cody, R.B.; Laramée, J.A.; Durst, H.D., *Anal. Chem.*, **2005**, *77*(8): 2297-2302.
2. Saang'onyo, D.; Smith, D.L., *Rapid Commun. Mass Spectrom.*, **2012**, *26*, 385-391.
3. Watson, J.T. "Introduction to mass spectrometry: instrumentation, applications, and strategies for data interpretation", 4th Ed., Wiley, **2008**

Acknowledgements

Samples were generously provided by Mr. Jordan Stitch. The SPME fibers used for analysis were kindly provided by IonSense, Inc. This research has been funded in part by the ***EKU Department of Chemistry***.

EKU EASTERN KENTUCKY UNIVERSITY CHEMISTRY