Profiling Beer: Solid Phase Micro-Extraction (SPME) Analysis via Direct Analysis in Real Time HRMS

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Overview

Rapid profiling the chemicals in beer using DART-MS to ionize a small volume of sample is a strategy that has been used in the past for determination of authenticity. In a move to a more dynamic sampling, we took this experiment a step further by using solid phase extraction to collect key beer markers onto SPME fibers. Neat analysis of six beers provided minimal information while only showing a few of the expected acids present. Utilizing three different SPME fibers; C18, strong cation exchange (SCX, and polydimethylsiloxane/divinylbenzene (PDMS/DVB), provided a more information rich spectra showing many of the marker species that have been previously defined in the literature.

Methods

A fourth generation Direct Analysis in Real Time (DART-SVP) ambient ionization source was coupled to a high resolution mass spectrometer for full spectrum single MS data acquisition. Six beer samples were analyzed neat on a Dip-It. The same samples were exposed to three types of SPME fibers: C18, SCX and PDMS/DVB. A temperature profile was acquired to determine optimal thermal desorption of the sample. Each fiber was then analyzed in triplicate.

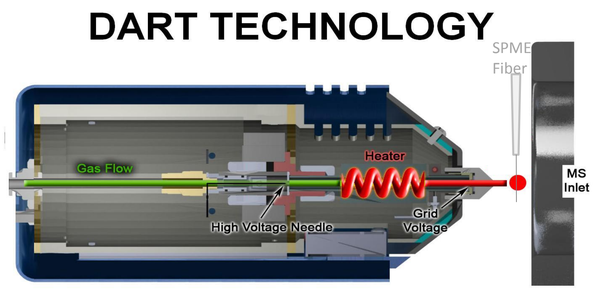
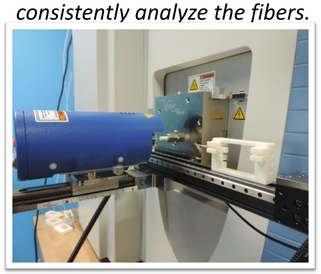
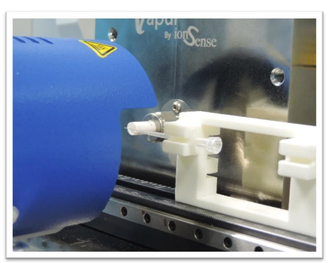


Figure 1: Above is a cutaway image of a DART-SVP source and a depiction of how the SPME fiber was used with the DART source.
Figure 2 (Below): Shows the sample apparatus that was utilized to consistently analyze the fibers.





SPME Fiber Sampling Protocol

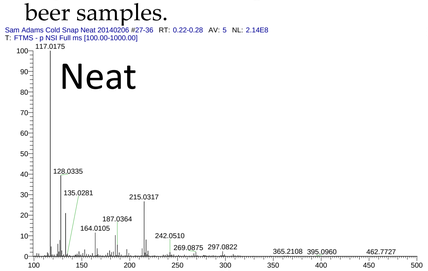
- Fibers were first conditioned in 1:1 methanol:water for 30 minutes
- Fibers were exposed to the beer sample and agitated over night
- Fibers were dipped in water and were ready to be analyzed
- Fibers were analyzed using the module shown in Figure 2

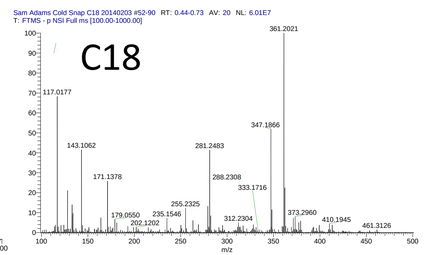
DART HRMS Method

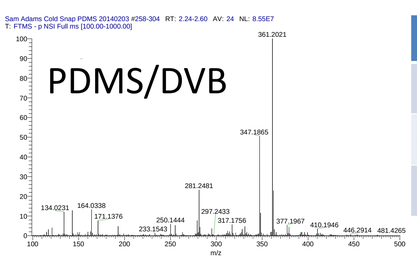
- DART-SVP ion source coupled with Exactive Plus MS
- Exactive Plus Parameters
  - Orbitrap – Full Spectra : 100-1000 amu @ 1 scan/sec
  - Capillary temp 200°C
  - Resolving power 35,000

Results

Initially, the beer samples were analyzed neat utilizing glass capillary tubes (Dip-it samplers, IonSense, Inc.) to generate a characterization profile. Upon reviewing the data it was determined that many of the ions of interest were not present in the spectra. Three SPME fiber types were chosen to enhance the profile of the six beers. After the first round of testing, it became obvious that the SCX fibers were not providing beneficial information for this particular study so they were not used after the initial tests. The C18 and PDMS/DVB fibers drastically enhanced the profile spectra , especially in negative ion mode in particular it revealed many more of the hop acids in the beer samples.







Compound	Exact Mass	$[M-H]^-$ ΔPPM
Cohumulone	348.1936	.786
Adhumulone	362.2093	.312
Humulinone	378.2042	.631

On top of extracting out the hop acids from the beer, the SPME fibers also enhanced the presence of succinic, pyrogluatmic, stearic, oleic, and palmitic acid in the sample. These other acids helped develop characterization profile spectra for each beer samples based on the absence or concentration of the ion.
We were also looking to monitor the degradation of these profiles over time, so these samples were analyzed using the same method after one month and four months. Finally the resulting spectra were exported and entered into a statistical analysis program called Analyze IQ by Analyze IQ Limited. Through this approach we were able to visually see that the hop acids had degraded over the four month period and also enter each spectra from each beer into the analysis program. Utilizing this program we were able to successfully identify a beer type based on its spectra profile within a 8% error rate.

Beer Type	Best Model Fit	% Error
Ale	Spectral Attribute Voting	8
White Ale	Weighted Spectral Linear	1.3
American Brown Ale	Linear Regression	0
Indian Pale Ale	Euclidean Distance	6
Belgian Style Ale	Polynomial 1	.5
Belgian Tripel	Weighted Spectral Linear	6

These results were acceptable for our first pass result and should improve if a larger sample set was used. Future work will include monitoring unopened beer over time and sampling multiple types of the same beer type to see if the models can identify beer type among varying brands.

Conclusions

- C18 and PDMS SPME fibers drastically improve the characterization fingerprint we obtained from a beer sample
- Statisical models can be designed to predict beer types based off of its profile spectra
- The degradation of the hop acids in the beer were monitored over time and seemed to be completely gone by the four month mark.
- SPME fibers were purchased from Supelco with funding from DHS BAA 13-007 Chemical Signature Analysis contract. The authors thank the DHS for this funding.