074

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BEEROMICS: UNTARGETED CHEMICAL PROFILING REVEALS A NOVEL CONTEXTUAL UNDERSTANDING OF BEER PROPERTIES

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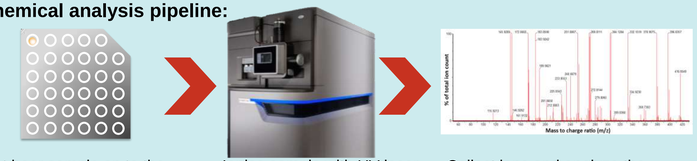
1. INTRODUCTION

- Rapid advances in mass spectrometry has provided an ever-deeper understanding of the chemistry of beer in relation a range of factors such as storage, brewing processes and the hop varieties used.
- Concurrently, the field of metabolomics, "the systematic study of the unique chemical fingerprints that specific cellular processes leave behind" has been used to study the responses of organisms to external factors at the small-molecule scale.
- Increasing numbers of studies claim to deploy metabolomics in the context of beer; few however, do so in a truly untargeted fashion that allows the emergent properties of beer chemistry to be profiled.
- This is because either the analytical technique or the resultant statistical analysis used is targeted at specific compounds.
- Here, we couple high throughput, low-cost untargeted biochemical fingerprinting of beers using Matrix-Assisted Laser Desorbtion/Ionisation Mass Spectrometry imaging (MALDI-MSi) to unsupervised and supervised statistical analysis.

2. MATERIALS & METHODS

•We sampled a diverse selection of styles of beers obtained from several breweries in the UK. Several batches from distinct brews were collected for each beer 'at the pump' after cellar conditioning. The colour of each beer was determined on an 8-point and chemically analysed using MALDI-MSi.

Chemical analysis pipeline:



Spot beer sample on to the MALDI target plate and crystalize sample with α-CHCA matrix

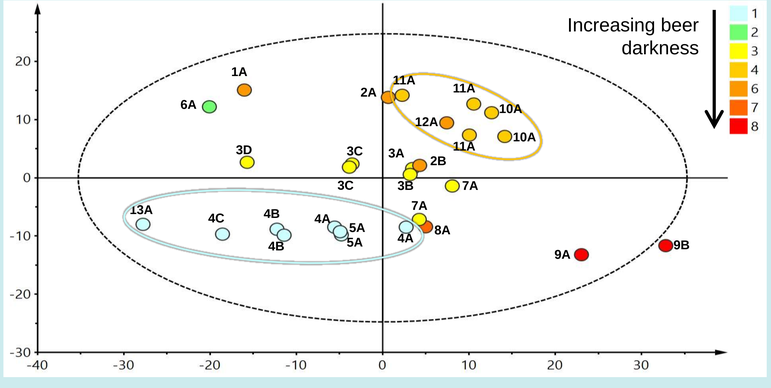
Ionise sample with UV laser using a Waters G2 synapt mass spectrometer

Collect ions and analyze the resultant chemical fingerprint by ToF-mass spectrometry

- We analysed the resultant mass spectral data using unsupervised and supervised dimensional reduction statistical analysis approaches (PCA and O2PLS-DA respectively) using the SIMCA-P package (Umetrics, Sweden).

3. RESULTS & DISCUSSION

Figure 1. Principle component analysis of beer biochemical fingerprints



- Figure 1 illustrates the differences in beer chemical composition from different breweries (different number codes on the graph) in relation to the orthogonal variables of colour, brewery and brew batch to understand the chemical similarity of similarly styled beers.
- Figure 1 reveals the principle differences in the chemistry of different beer samples and demonstrates that different batches of the same beer (same number code and different letter code on the graph e.g. beer 4A vs. beer 4C) have different chemical composition thus determining inter batch variability.
- Together, these data show that, irrespective of the individual brewery or batch, the strongest predictor of beer chemical similarity is colour (e.g. between colour category #1 [blue] and #4 [orange]). Moreover, we show that different batches of the same beer can be as chemically distinct from each other as unrelated beers from different breweries.
- As proof of concept, we investigated the compounds responsible for the separation of beers by colour in Figure 2 using O2PLS-DA in relation to colours #1 and #4. Individual beer samples clearly separate according to their chemistry.

Figure 2. OPLS-DA analysis of beer colour categories 1 and 4 biochemical fingerprints

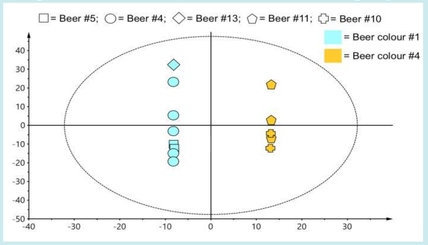
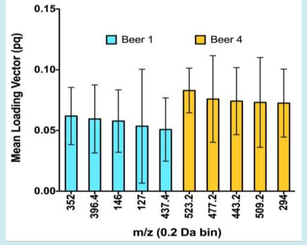


Figure 3. Loadings scores of the top 5 most discriminating m/z



- The key masses (m/z) responsible for driving the separation in multivariate space were resolved using the loadings plot summarised in figure 3.
- Compounds were then associated with putative metabolites using the 'metacyc' database with a tolerance of 10 ppm.
- Four of the 10 m/z were identified (Putative IDs: 352 ≈ 5-methylaminomethyl-2-selenouridine; 396.4 ≈ ergosterol (yeast?); 146 ≈ metabisulfite (additive?); 127 ≈ 2,3,6-trihydroxypyridine. Further bioinformatics and chemical analysis is ongoing.
- None of the compounds we putatively identified were major components of beer thus differences in the chemical composition of the beers in relation to colour is subtle and unlikely to be detected via traditional targeted chemical analysis.

4. CONCLUSION

In conclusion, we validate the MALDI-MSi approach as a high throughput/low cost method for profiling beer chemistry capable of revealing the extent of inter-batch variability. MALDI-MSi also allows quantitative analysis of beer chemistry in relation to important variables such as colour with sufficient resolution to resolve subtle differences in beer chemistry.

5. ACKNOWLEDGEMENTS

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