



Non-Targeted Aroma Profiling by GC-TOFMS to Compare Beer Samples

LECO Corporation; Saint Joseph, Michigan USA

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1. Introduction

The sensory experience of a food or beverage item is largely determined by the volatile aroma analytes associated with the product. Profiling aroma analytes by GC-TOFMS offers a non-targeted analysis of the volatile and semi-volatile components for a comprehensive understanding of what is in your sample. In contrast to a targeted approach, the analyst is not limited to monitoring what they already know and can discover what they've been missing in their samples. The characterization of aroma compounds offers useful information to the food and beverage industry on analytes that contribute to the sensory experience and can also lead to improvements in quality control, process optimization, and better brand awareness. Here, a variety of commercially available craft beer styles were characterized and compared with GC-TOFMS. Samples were collected with headspace solid-phase micro-extraction (HS-SPME) and subsequently analyzed by GC-TOFMS. Individual analytes were isolated chromatographically and full mass range TOFMS data were utilized for identification and relative quantification. The GC-TOFMS chromatogram was treated as a fingerprint for principal component analysis (PCA), which was used to investigate the similarities and differences of the samples with clear sample groupings. These methods allowed for comparing sample types by their overall chromatographic features and by individual analyte differences in order to differentiate and characterize these beer varieties.

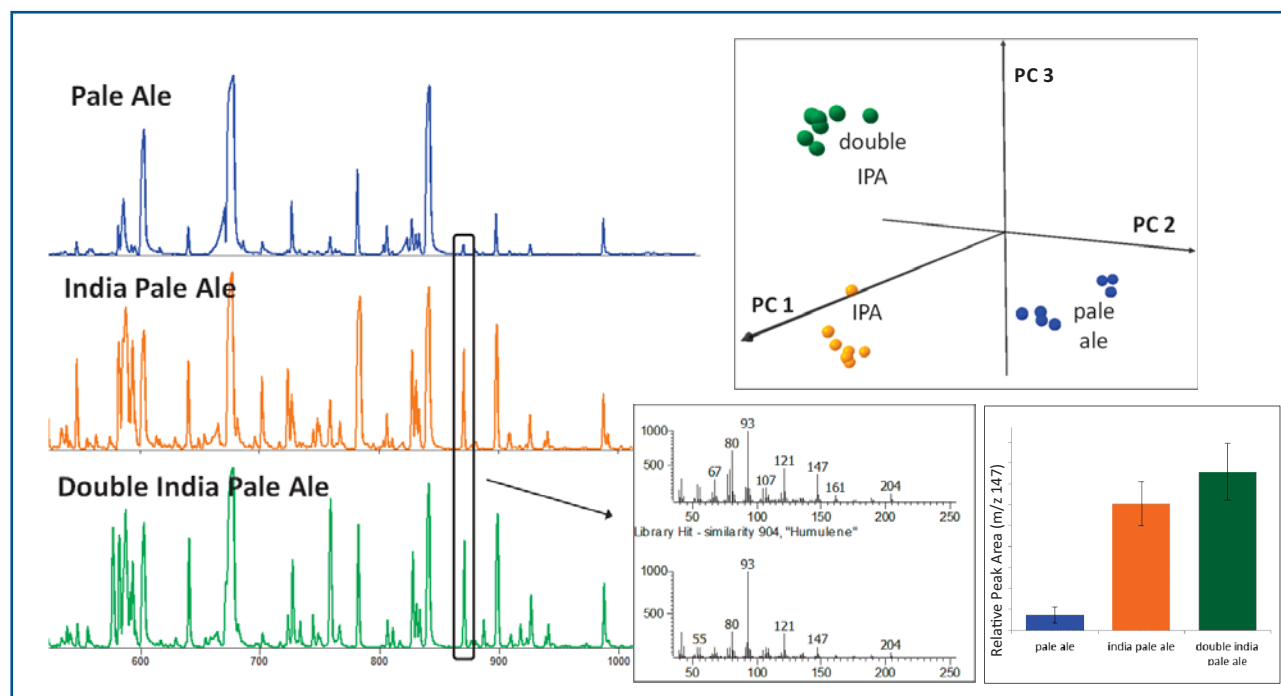


Figure 1. Representative TIC chromatograms for three beer types, pale ale (blue), IPA (orange), and double IPA (green) are shown. The chromatographic traces were submitted as fingerprints to PCA, resulting in distinct clusters of the samples by type shown in the scores plot. Humulene corresponded to one of the more highly loaded variables and was observed at different levels in each beer variety. The relative peak area is shown for each sample with highest levels observed in the double IPA. The isolated mass spectral information matched to humulene in the library with a similarity score of 904.

2. Experimental

Samples: A variety of commercially available craft beer styles including pale ales, India pale ales (IPAs), and double IPAs were analyzed. Eight separate bottles/replicates of each variety were sampled. Aliquots of 4.0 mL were pipetted into 10 mL SPME vials and sealed with septum caps.

HS-SPME conditions: HS-SPME sampling was performed with a 50/30 μm DVB/CAR/PDMS fiber (Supelco, Bellefonte, PA, USA). Each sample was incubated at 50°C for 10 min and then extracted for 10 min at the same temperature.

Injection	SPME desorption for 2 min @ 250°C
Carrier Gas	He @ 1.0 ml/min
Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μm coating (Restek, Bellefonte, PA, USA)
Temperature Program	2 min at 40°C, ramped 10°C/min to 250°C, held 2 min
Transfer Line	Temperature set to 250°C
TOFMS Conditions	33-510 m/z at 15 spectra/s with source temp of 250°C

Data analysis: Data were analyzed with LECO's ChromaTOF® brand software. Automated data processing performed background subtraction, peak finding, peak identification, and relative quantification for individual analytes within the samples. Additionally, TIC chromatographic traces were exported from the ChromaTOF brand software to be used as chemical fingerprints. TIC data were compiled into a matrix in Microsoft® Excel® and PCA was performed with XLStat™ (www.XLStat.com).

3. Results and Discussion

The non-targeted volatile analysis of aroma analytes by HS-SPME and GC-TOFMS was performed for a variety of commercially available craft beers with representative TIC chromatograms from each sample shown in Figure 1. Hundreds of peaks were detected in these samples and matched to library standards in the NIST databases, including many esters, alkanes, aldehydes, carboxylic acids, and terpenes, among others. Many of these analytes have odor properties commonly associated with hops or beer and would be expected to contribute to the consumer's sensory experience.

The TIC traces were exported as chemical fingerprints for overall sample comparison. The chemical fingerprints of all the samples were compiled and submitted to PCA. The samples clustered by type in the scores plot, shown in Figure 1. The corresponding loadings provided information on the variables that were responsible for the sample groupings on each PC. In these data, the variables correspond to retention times in the GC-TOFMS data. The ChromaTOF data processing results were reviewed and analytes at those retention times were further investigated. Humulene, shown in Figure 1, was one of the more highly loaded variables and was observed at different levels in each beer type. Humulene is known to be present in hops, so these differences could be due to differences in the hop variety and/or the amount of hops used for brewing each beer variety.

A collection of additional representative analytes that correspond to some of the more highly loaded variables are listed in Table 2 and shown in Figures 2-4. The retention time, similarity to library, known odor properties, and relative levels are compiled for each example analyte. Many other analyte differences were observed.

Analyte	tR (s)	Similarity	Odor Properties
humulene	898.2	904	Present in hop oil, wood odor
2-nonanone	576.9	937	Present in beer, fruity odor
isobutyl isobutanoate	396.2	951	Present in hop oil, fruity/green apple odor
ethyl heptanoate	582.5	921	Present in beer, fruity/pineapple/cognac odor

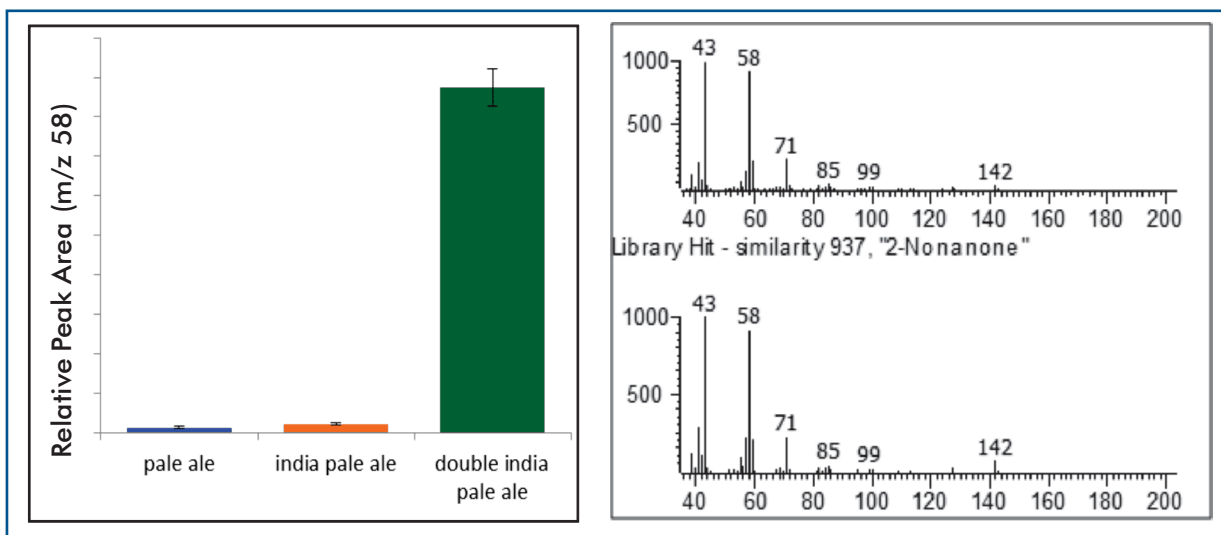


Figure 2. 2-nonanone was one of the analytes found to differ between samples. The relative peak area is shown for each sample with highest levels observed in the double IPA. The isolated mass spectral information matched to the library with a similarity of 937.

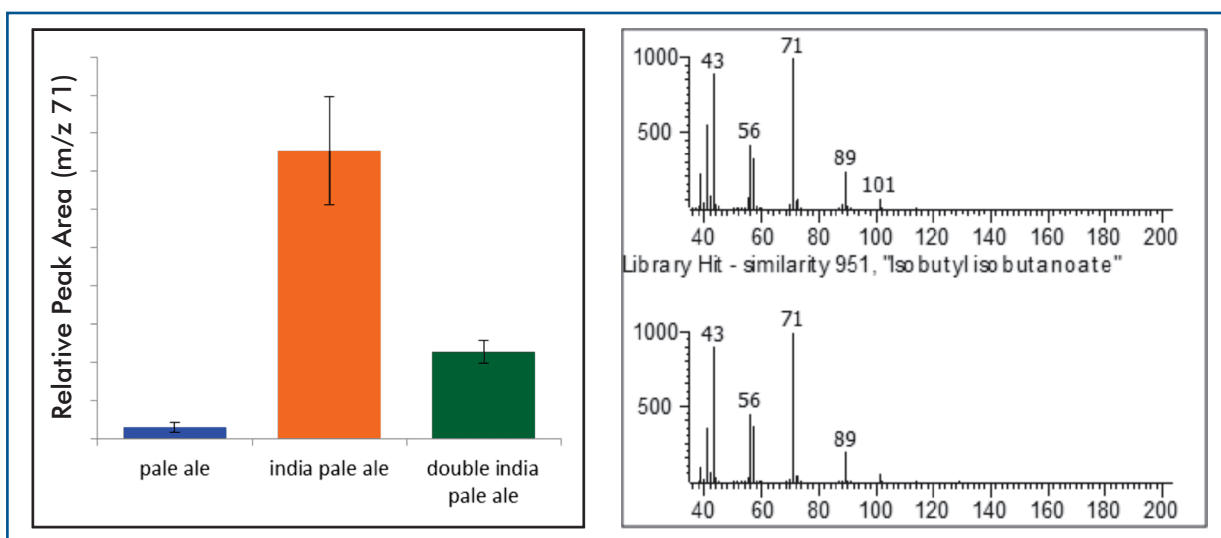


Figure 3. Isobutyl isobutanoate was another analyte found to differ between beer samples. The relative peak area is shown for each sample with highest levels observed in the IPA. The isolated mass spectral information matched to the library with a similarity of 951.

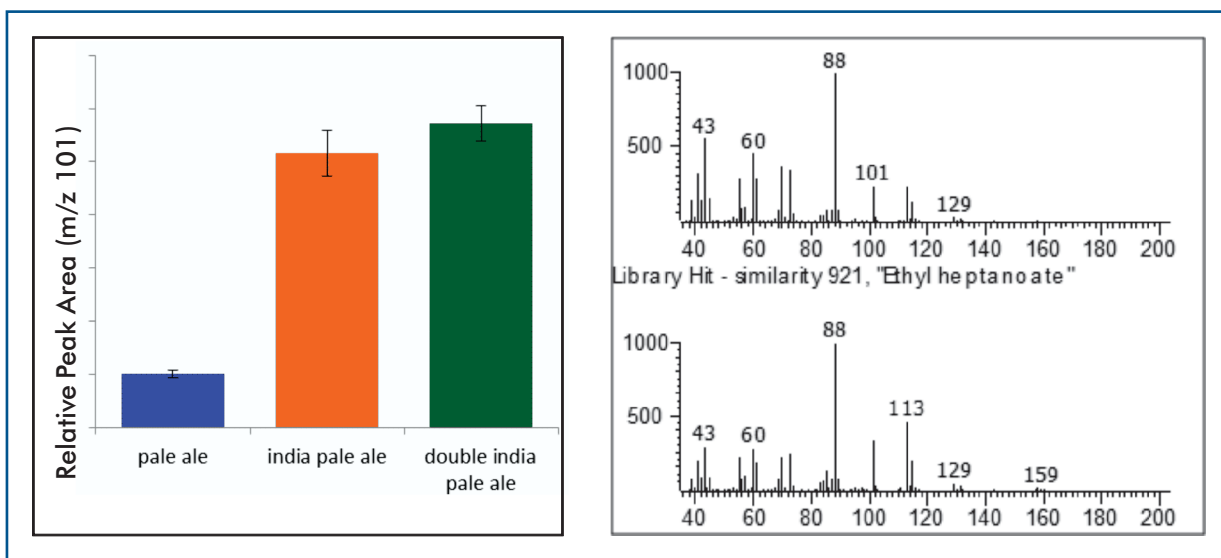


Figure 4. Ethyl heptanoate was another analyte found to differ between beer samples. The relative peak area is shown for each sample with highest levels observed in the IPA and double IPA. The isolated mass spectral information matched to the library with a similarity of 921.



4. Conclusion

In this application note, a non-targeted aroma profiling method by HS-SPME and GC-TOFMS was demonstrated and provided a comprehensive picture of the volatile and semi-volatile components of these beer samples. A variety of commercially available craft beer styles were analyzed and characterized with these methods. These methods allowed for characterizing sample types by their overall chromatographic features and by individual analyte differences in order to differentiate and characterize these beer samples. By providing a better understanding of what is in your sample, this type of aroma profiling information can be useful for quality control purposes, connecting sensory observations to chemical properties, brand awareness, screening for off-flavors or adulterants, and for product development to adjust or mimic particular flavors. In contrast to a targeted approach, the analyst is not limited to monitoring what they already know and can discover what they've been missing in their samples.



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