Beer Aroma: Detection of Analyte Differences with GC-TOFMS and the Reference Feature in ChromaTOF®

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1. Introduction

Comparisons of food and beverage products can be useful for screening to identify samples and/or aroma analytes that differ from a target condition. This can be a quality control tool to monitor for adulterants, off-flavors, or the presence of desired analyte characteristics. Utilizing a non-targeted analytical approach allows the analyst to reliably determine what is in their sample without being limited to what is already known or expected. GC-TOFMS is a powerful tool for performing non-targeted volatile analyses of aroma and flavor analytes in food and beverage products that uncovers what a targeted analytical approach may have been missing. LECO's *ChromaTOF* brand software with *True Signal Deconvolution (TSD)* provides the analyst with automated peak finding and sample comparison tools, such as "Reference", to take the analysis further. Here, these tools are demonstrated to determine differences between commercially available craft beers, specifically a stout and coffee-flavored stout. Samples were collected with headspace solid-phase micro-extraction (HS-SPME) and subsequently analyzed by GC-TOFMS. As demonstrated, this information builds brand awareness, but the workflow is readily transferrable to other analyte screening approaches for off-flavors, adulterants, or desired aroma characteristics.

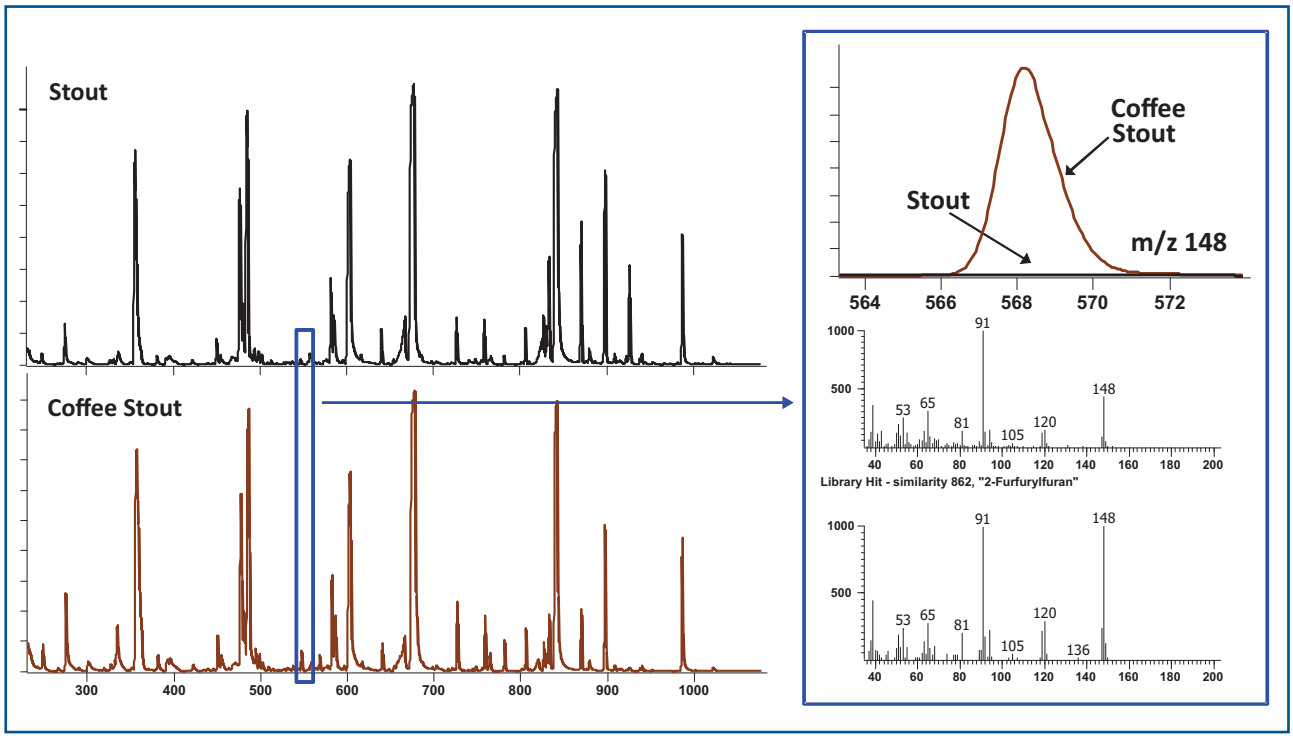

Figure 1. Representative TIC chromatograms for a stout and coffee-flavored stout are shown. The TIC chromatograms are quite similar and few, if any, analytes stand out as differing between the two from visual comparison of TIC data alone. Data processing tools, such as ChromaTOF's Reference, help identify analyte differences that are hidden in the TIC, but visible in XIC chromatograms. For example, 2-furfurylfuran that has rich and roasted odor properties and is known to naturally occur in coffee is observed in the coffee stout with XIC m/z 148 and not the stout.

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2. Experimental

Sample Preparation: Two commercially available stout beer samples were analyzed. Aliquots of 4.0 mL were pipetted into 10 mL SPME vials and sealed with septum caps. HS-SPME sampling was performed with a 50/30 μm DVB/CAR/PDMS fiber (Supelco, Bellefonte, PA, USA) at 50°C. Samples were incubated for 10 min prior to 10 min of extraction.

Table 1. GC-TOFMS (Pegasus HT) Conditions

Injection	SPME desorption for 2 min in GC inlet, splitless @ 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. *True Signal Deconvolution,* peak identification, and relative quantification for individual analytes within the samples were performed with automated data processing. *ChromaTOF's* Reference feature calculated relative concentrations of analytes between samples and was used for sample comparisons. Analytes that were present in both the user-specified reference and sample were tagged "Match" or "Out of Tolerance" depending on the relative concentrations compared to a user-specified threshold. "Not Found" and "Unknown" indicated analytes that were only present in the reference or the sample, respectively.

3. Results and Discussion

This non-targeted volatile analysis characterized stout and coffee-flavored stout beer samples. Representative TIC chromatograms from each sample are shown in Figure 1. Very few distinctions are obvious through visual comparison of the TIC chromatograms due to the many similarities of these two samples. However, there were clear sensory differences, and when individual analytes (determined through automated peak finding) were compared, many differences were apparent that related to these observations. *ChromaTOF's* Reference feature was utilized for this automated comparison through data processing. In this case, the stout was specified as the reference and the coffee-flavored stout was specified as the sample such that "Unknown" peaks were indicative of the coffee-flavored stout. Figure 1 shows an example of an "Unknown" analyte, 2-furfuryl furan that was identified through library matching to the NIST database. An XIC for m/z 148 shows that 2-furfuryl furan was only present in the coffee-flavored stout and absent in the stout. This analyte occurs naturally in coffee, has rich and roasted odor properties, and is a likely contributor to the consumer's sensory experience.

In some cases, the analytes that distinguished the samples were coeluting, and deconvolution was required to isolate information for each. For example, 2-furfuryl methyl ether and methyl pyrazine coelute and required deconvolution to distinguish, as shown in Figure 2. The TIC peak shape is dominated by the contribution of methyl pyrazine because it is present at higher levels than 2-furfuryl methyl ether.

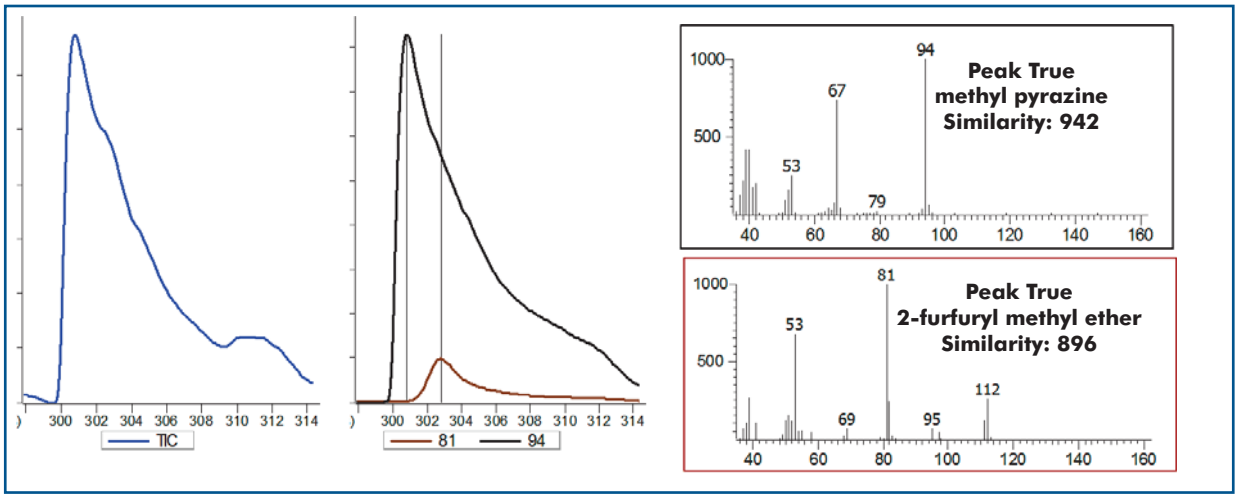

Figure 2.* ChromaTOF's TSD *algorithms isolate pure chromatographic profiles and mass spectral information for analytes that chromatographically overlap. Methyl pyrazine and 2-furfuryl methyl ether chromatographically overlap in the coffee flavored stout sample and are not distinguished in the blue TIC trace. XICs for unique masses from each analyte, black and brown, show the corresponding peak profile information for each analyte. Peak True (deconvoluted) mass spectral information is also determined and was matched to library data bases.

When the TIC chromatograms were overlaid for this region, shown in Figure 3, there did not appear to be a dramatic difference between the stout and coffee-flavored stout. With peak finding and deconvolution, however, the two coeluting analytes could be compared independently with Reference. Methyl pyrazine, that has "nutty" and "slightly roasted" odors, was tagged a "Match" with the area in the coffee stout reported at 150% of the area in the stout. 2-furfuryl methyl ether, that has "roasted coffee" odor, was tagged "Unknown" and only measured in the coffee stout. While both analytes are likely important odor contributors, without non-targeted TOFMS detection and deconvolution, the presence of 2-furfuryl methyl ether and its coffee flavor contributions may have been missed.

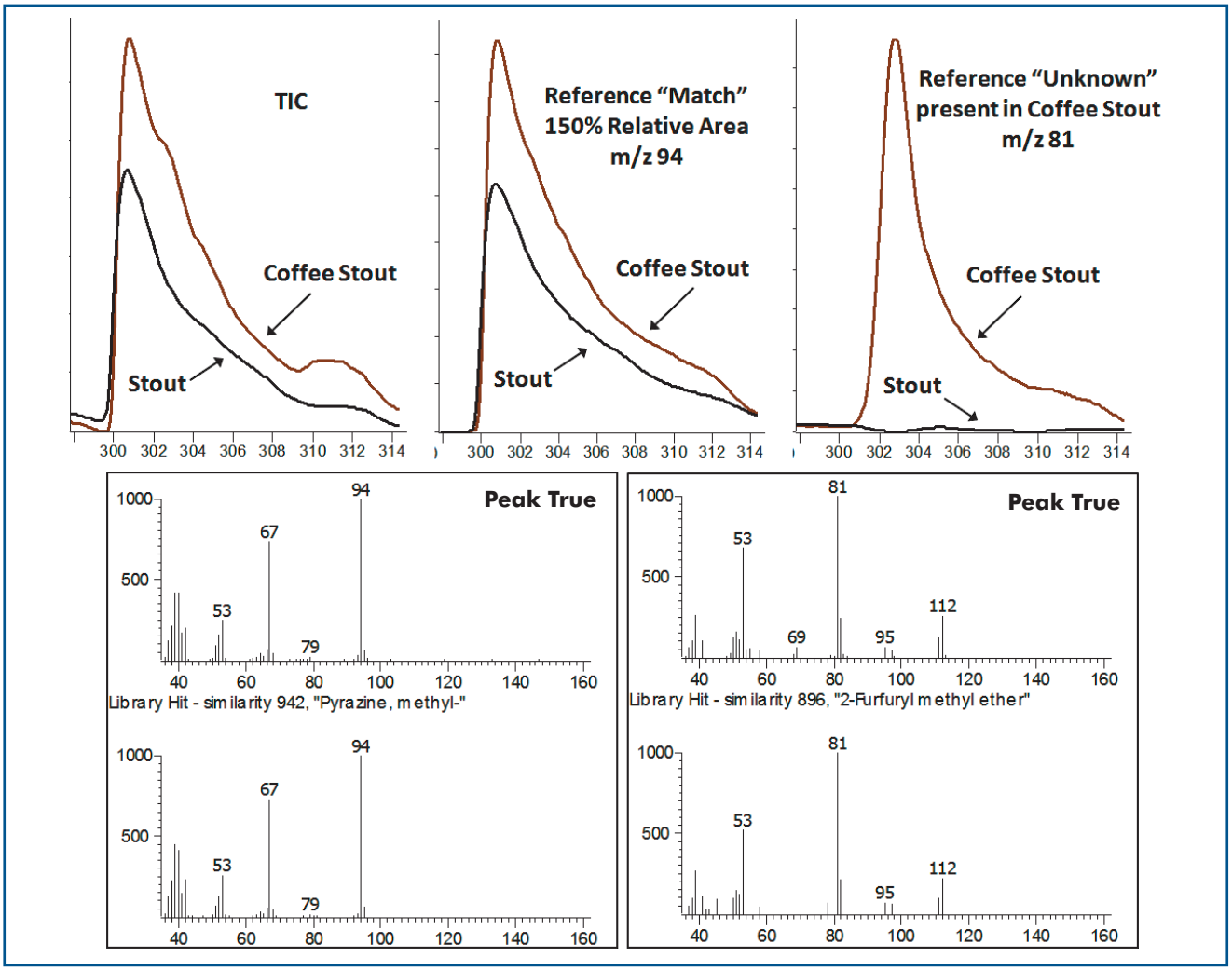

Figure 3. The coffee-flavored stout (brown trace) and stout (black trace) are compared for TIC, m/z 94, and m/z 81. There is not a dramatic difference between the samples apparent in the TIC or with m/z 94, corresponding to methyl pyrazine, an analyte with nutty and slightly roasted odor properties that was determined a "match" between the samples by the Reference feature. 2-furfuryl methyl ether, visualized with m/z 81, was tagged "unknown" indicating its presence only in the coffee flavored stout. Differentiating this important roasted coffee odor analyte required non-targeted detection and deconvolution.

Delivering the Right Results

4. Conclusion

This study demonstrates a non-targeted volatile analyte screening approach with HS-SPME and GC-TOFMS that was applied to characterize and compare beer samples. These methods along with *ChromaTOF*'s automated processing tools, including "Reference," provide the ability to isolate and identify individual analyte differences. Further, this analytical approach allowed for reliably determining unknown differences between the samples without limitations to what was already known or expected. In particular, a coffee-flavored stout was compared to a stout to screen for specific analytes only present in the stout that contribute to the coffee odors and sensory notes. Example analytes were highlighted that would likely contribute to the sensory experience that may have been missed with a targeted approach or with an approach lacking deconvolution. A collection of representative differences were highlighted here with many more observed in these data, including several analytes with coffee or roasted odor properties only detected in the coffee stout. By allowing analysts to discover what they've been missing in their samples, this workflow is readily applied as a quality control approach to monitor for adulterants, off-flavors, or the presence of desired analyte characteristics and is broadly applicable in the food and beverage industry.

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