A Compendium of Food and Beverage Comparisons with Novel Benchtop GC-TOFMS System

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Introduction

GC-TOFMS is broadly applicable for food and beverage analysis. This analytical technique is useful for providing information on the volatile and semi-volatile analytes that contribute to the taste and aroma profile of raw materials, ingredients, and finished products. Among other capabilities, GC-TOFMS offers non-targeted characterization of samples for discovery applications, and maintains the ability to target specific analytes of interest for screening applications. A novel benchtop GC-TOFMS system is demonstrated here for a variety of food and beverage samples with comparisons and differentiation accomplished.

Methods

A collection of food and beverage samples (fresh and dried herbs, fresh and frozen produce, flavored candies, flavored beverages, and hops) were prepared for analysis with HS-SPME. Incubation and extraction temperatures and times are listed for each sample type in Table 1, and all applications used a DVB/CAR/PDMS fiber. The samples were subsequently analyzed with GC-TOFMS with instrument conditions listed in Table 2.

Table 1. HS-SPME sampling conditions per sample

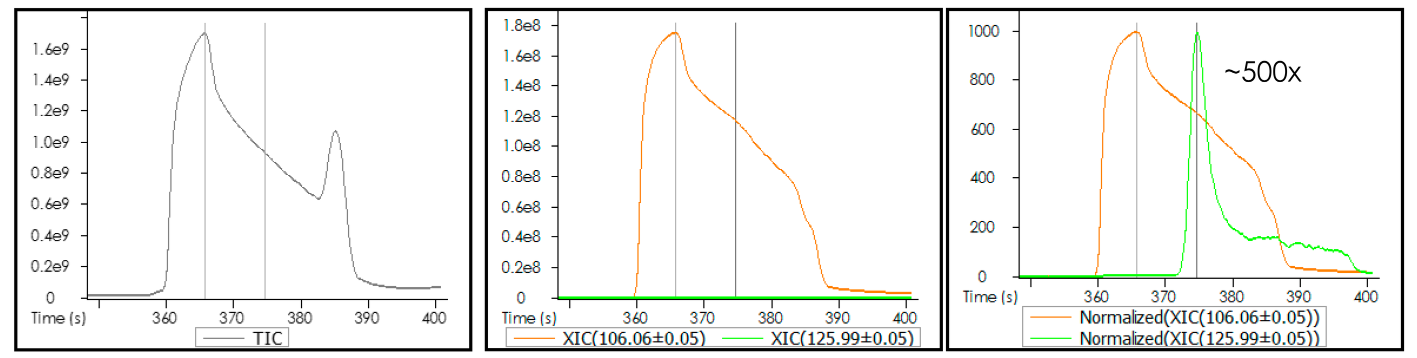
Sample	Incubation	Extraction
Basil	5 minutes at 50°C	30 minutes at 50°C
Broccoli	5 minutes at 50°C	30 minutes at 50°C
Flavored tea	5 minutes at 50°C	30 minutes at 50°C
Hops	5 minutes at 35°C	30 minutes at 35°C
Strawberry	5 minutes at 50°C	30 minutes at 50°C

Table 2. GC-TOFMS Instrument Conditions

Gas Chromatograph	Agilent 7890 with LECO L-PAL3 Autosampler
Injection	2 min desorption in 250°C inlet
Carrier Gas	He @ 1.0 ml/min, Constant Flow
Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μm coating (Restek)
Oven Program	2 min at 40°C, ramp 5°C/min to 200°C, ramp 10°C/min to 300°C, hold 1 min
Transfer Line	250°C
Mass Spectrometer	LECO Pegasus® BT
Ion Source Temperature	250°C
Mass Range	35-650 m/z
Acquisition Rate	10 spectra/s

Analytical Capabilities

GC-TOFMS provides excellent data for characterization based on individual analytes. Deconvolution offered an additional level of information based on the mathematical separation of the full m/z range TOFMS data. This aspect of the analytical approach allowed for tentatively identifying and quantifying individual analytes even when chromatographically coeluting with other analytes in the matrix. In some cases, these coelutions were important sample-distinguishing features that would be hidden without this capability.



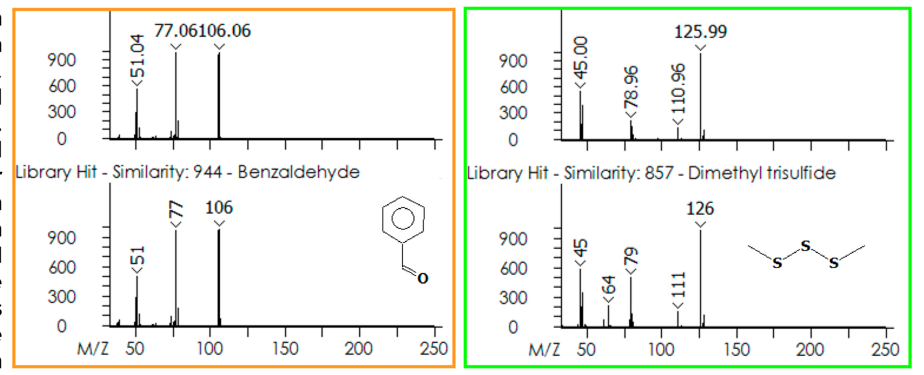


Figure 1. Deconvolution provides information for individual coeluting analytes, even when large concentration differences are present, as shown here where a small analyte is buried beneath an intense and overloaded analyte. Chromatographic peak profiles and spectral information that can be library searched for tentative identification are still found for both analytes. When XICs are plotted for each (106.06 in orange for benzaldehyde, and 125.99 in green for dimethyl trisulfide), the green trace is so much lower that the peak is not visible without normalizing the display. The peak height for dimethyl trisulfide is more than 500x less than benzaldehyde, and excellent deconvolution results were still achieved.

Flavored Beverage - Comparison

This analytical approach allows for comparisons and distinctions to learn more about a sample. Here, regular and diet fruit tea products were analyzed and compared.

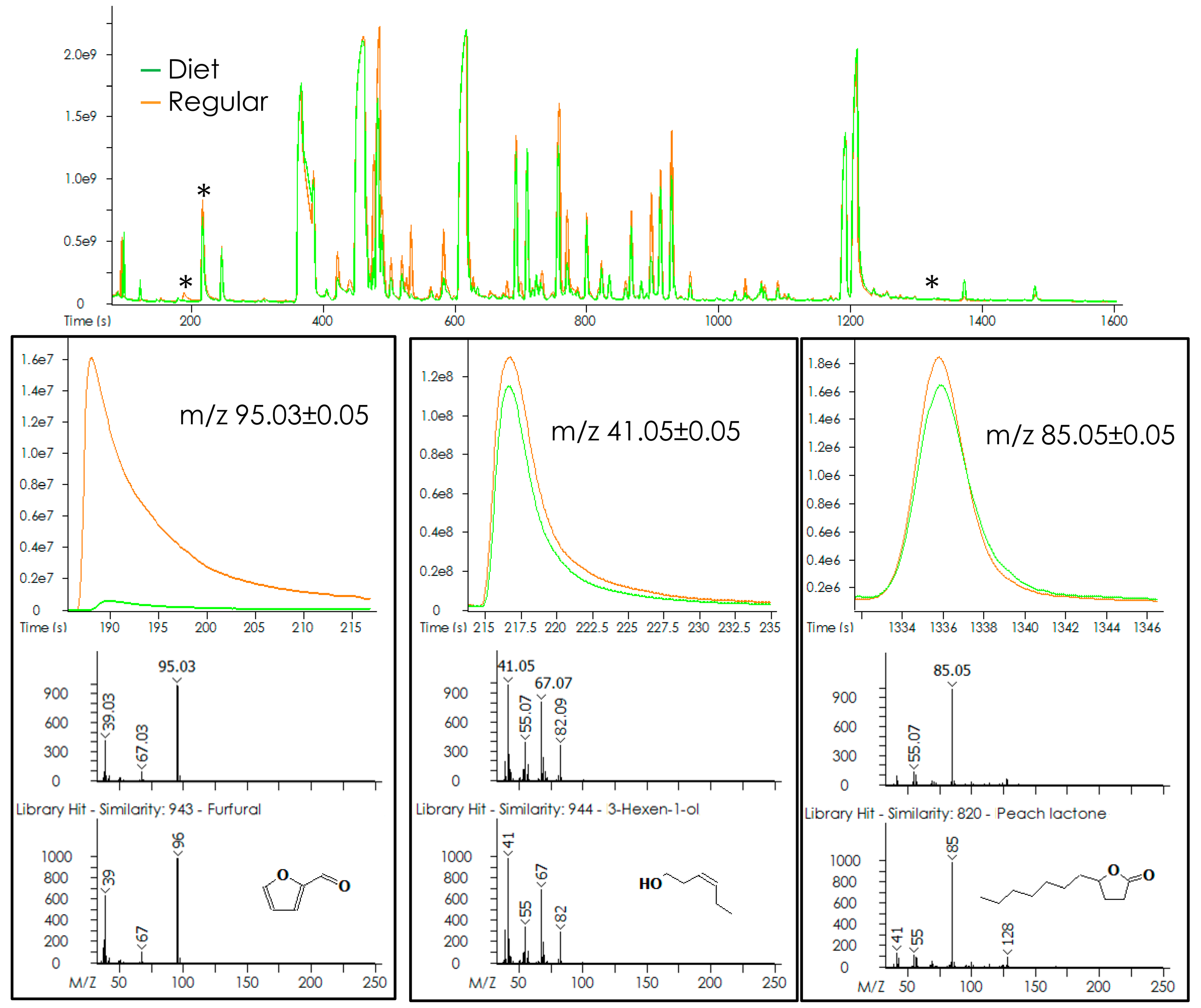
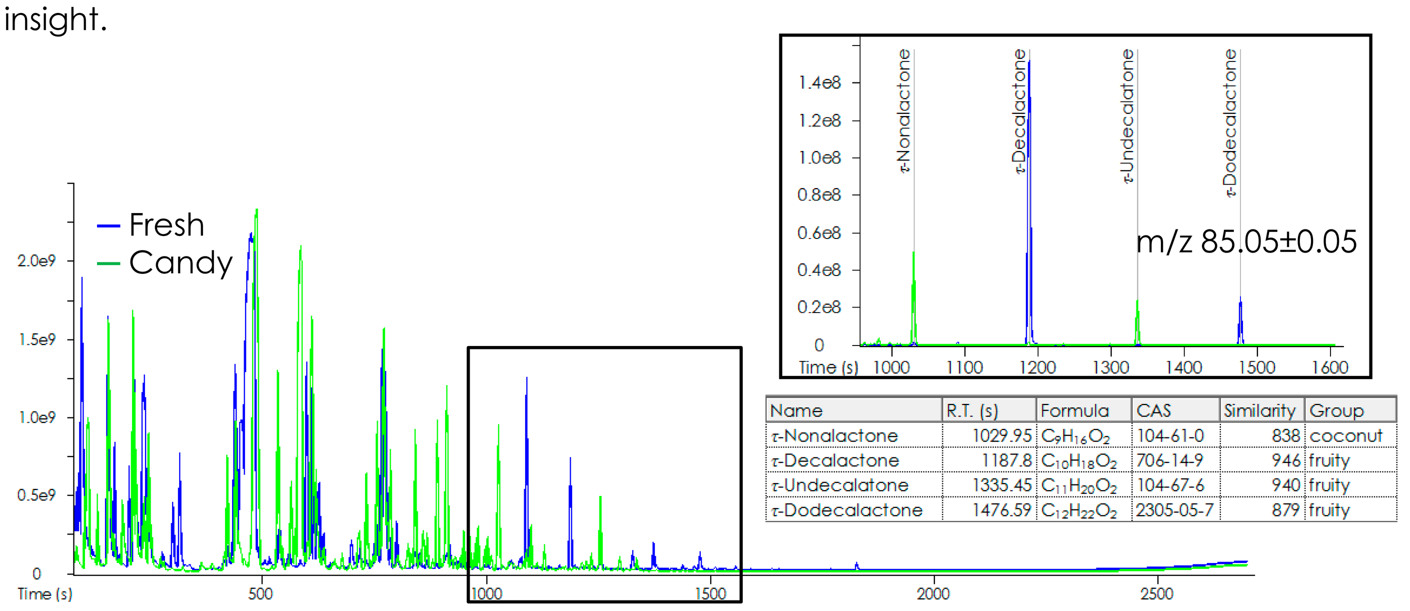


Figure 2. TIC chromatograms for a diet and regular fruit tea are shown. There are many similarities and some differences. Furfural is a sugar degradation product that was observed at higher levels in the regular tea that contains sugar compared to the diet tea that does not. 3-hexen-1-ol was observed at comparable levels in each tea. It has herbal odor properties and is known to occur in black tea. Peach lactone was observed at comparable levels. It has fruity odor properties and is known to occur in peaches.

Strawberry and Strawberry Candy

Information on specific classes of compounds can also readily be determined. Here, a series of lactones (gamma-nonalactone through gamma-dodecalactone) were compared between a strawberry-flavored candy and a fresh strawberry. These lactones contribute to the flavor of each sample, and the similarities and differences provide insight.

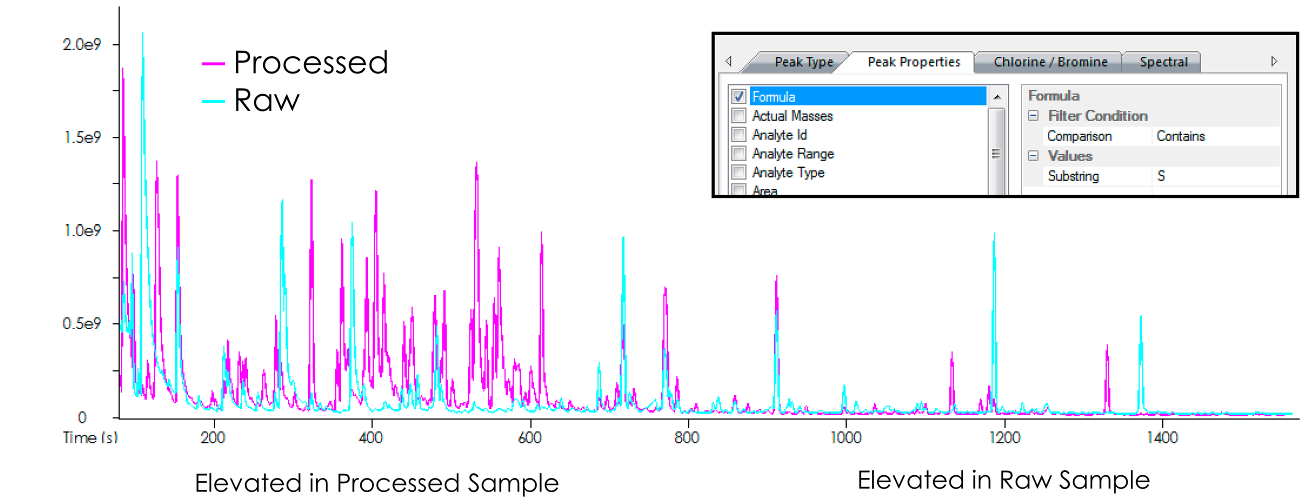


Name	R.T. (s)	Formula	CAS	Similarity	Group
τ-Nonalactone	1029.95	$C_9H_{16}O_2$	104-61-0	838	coconut
τ-Decalactone	1187.8	$C_{10}H_{18}O_2$	706-14-9	946	fruity
τ-Undecalatone	1335.45	$C_{11}H_{20}O_2$	104-67-6	940	fruity
τ-Dodecalactone	1476.59	$C_{12}H_{22}O_2$	2305-05-7	879	fruity

Figure 3. TIC chromatograms for a strawberry-flavored candy and a fresh strawberry are shown. There are many similarities and differences. A series of lactones are shown to highlight these important flavor compounds, and how they differ between these samples.

Produce – Filter for Sulfur Compounds

In other applications, there may be a specific interest in a particular type of analyte. For example, sulfur-containing compounds are often of interest because of their important contributions to taste and odor. Here, two broccoli samples were analyzed and compared. One sample was raw, and the other had been processed for freezing. Many differences were observed between these samples. To focus on the sulfur-containing compounds, peaks were tentatively identified through library searching during automated data processing. These were filtered to rapidly locate any formulae containing sulfur to then determine which were sample differentiating. A collection of some of the analytes that differed are listed in Figure 4. Several isothiocyanates were observed at elevated levels in the processed samples. These are breakdown products of glucosinolates that are found in cruciferous vegetables, like broccoli. Several other types of sulfur-containing analytes were observed at elevated levels in the raw samples, as shown here.



Elevated in Processed Sample

	Name	R.T. (s)	Formula	CAS	Similarity
	Isopropyl isothiocyanate	191.573	C_4H_7NS	2253-73-8	888
*	Isobutyl isothiocyanate	355.179	C_5H_9NS	591-82-2	927
	Butyl isothiocyanate	429.364	C_5H_9NS	592-82-5	894
	Butane, 1-isothiocyanato-3-methyl-	532.253	$C_6H_{11}NS$	628-03-5	848
	Pentyl isothiocyanate	600.396	$C_6H_{11}NS$	629-12-9	902
	4-Methylpentyl isothiocyanate	709.522	$C_7H_{13}NS$	17608-07-0	903
	Hexyl isothiocyanate	772.264	$C_7H_{13}NS$	4404-45-9	873
	3-Methylthiopropyl isothiocyanate	948.788	$C_5H_9NS_2$	505-79-3	878
	Phenethyl isothiocyanate	1180.35	C_9H_9NS	2257-09-2	899

Elevated in Raw Sample

	Name	R.T. (s)	Formula	CAS	Similarity
	Carbamimidothioic acid, methyl ester	85.1022	$C_2H_6N_2S$	2986-19-8	828
	Dimethyl disulfide	108.248	$C_2H_6S_2$	624-92-0	914
	2,4-Dithiopentane	255.112	$C_3H_8S_2$	1618-26-4	926
	Methyl thiobutanoate	257.679	$C_5H_{10}OS$	2432-51-1	847
*	Dimethyl trisulfide	374.042	$C_2H_6S_3$	3658-80-8	924
*	Hexanethioic acid, S-methyl ester	590.114	$C_7H_{14}OS$	2432-77-1	884
	Dimethyl tetrasulfide	786.572	$C_2H_6S_4$	5756-24-1	845
	S-Methyl thiooctanoate	931.149	$C_9H_{18}OS$	2432-83-9	862

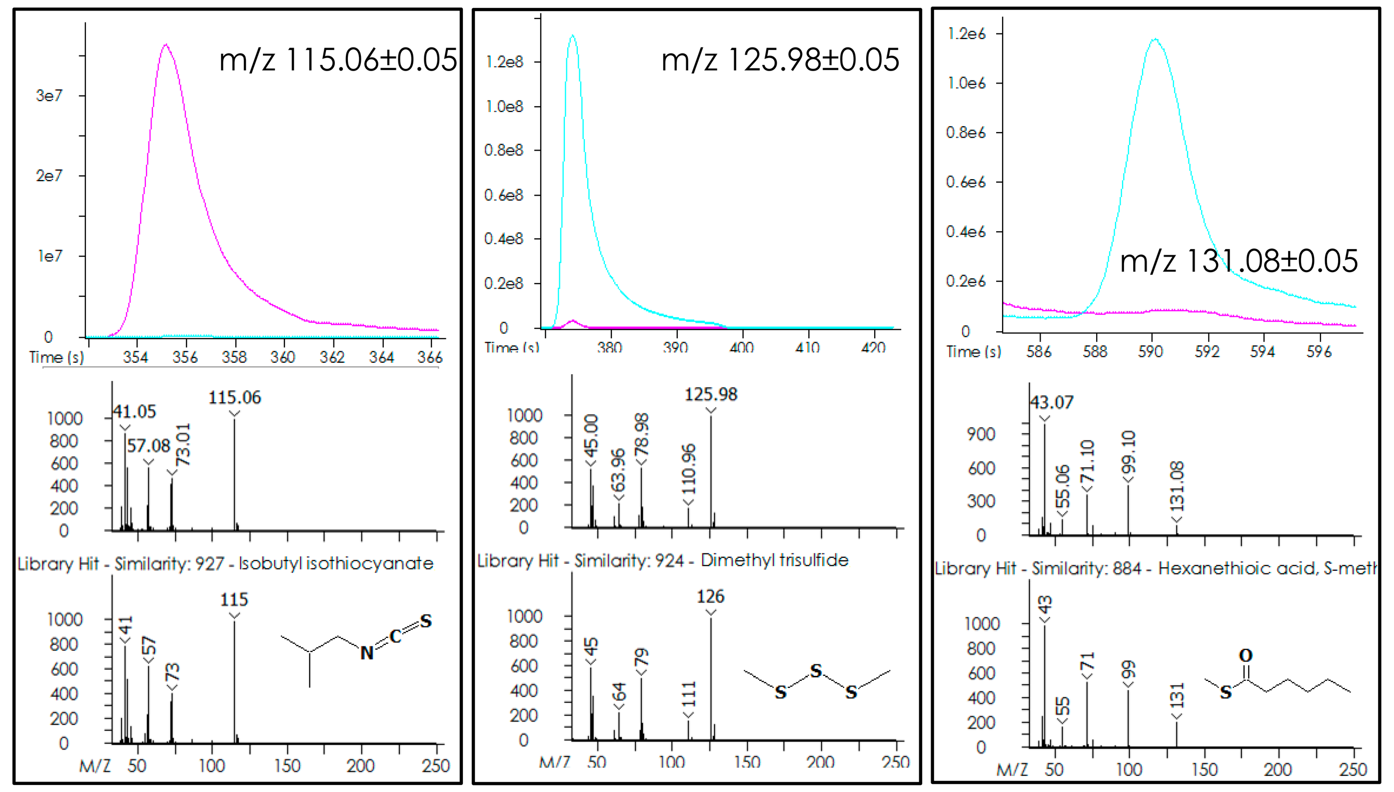


Figure 4. Extracted ion chromatograms (XICs) for a raw and processed broccoli sample are shown. There are many differences between the samples. Some of the sulfur-containing differences were highlighted with peak table filtering and a collection of those elevated in each sample are shown. Chromatographic traces and mass spectral information are shown for three specific examples (indicated with asterisks on the tables).

Hops – Fresh vs. Old

Target analysis and general screening can be accomplished in the same injection. Here, a fresh and an aged hops sample were analyzed and compared. These samples were analyzed both for a target analyte, cis-3-hexanol with grassy odors, known to be related to old and oxidized hops, and reviewed in a non-targeted way for terpenes. Cis-3-hexanol, that coelutes within a complex region of the chromatogram, was observed at elevated levels in the old sample, while the sesquiterpenes were observed at comparable levels in both.

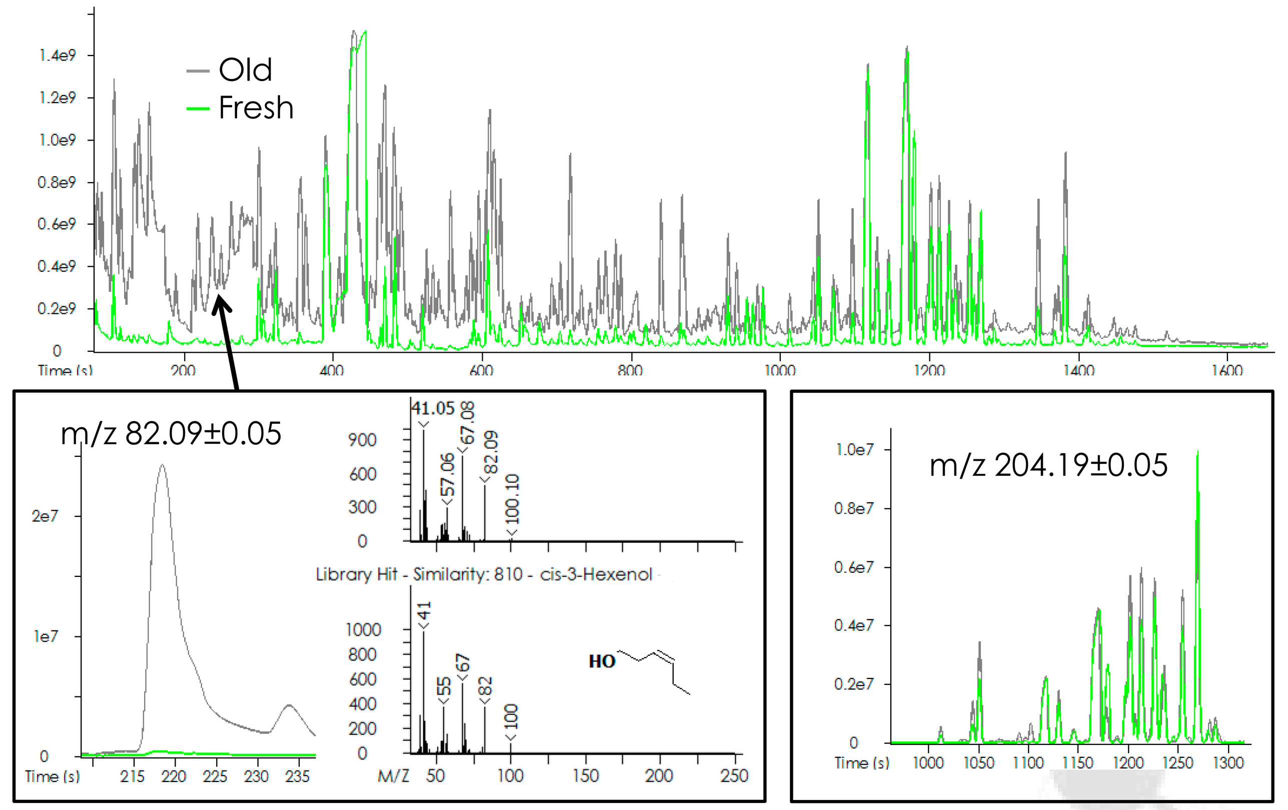


Figure 5. Deconvolution, automated as part of the data processing, effectively separates a target analyte from a complex region of the chromatogram. XICs for compound classes also provide general comparison information. m/z 204.19 is shown for a rapid comparison of the sesquiterpene region of the chromatogram.

Fresh and Dried Herb Comparison

Here, fresh and dried basil were analyzed. These are very complex samples, but with automated processing, analytes of interest can be found quickly. Cumin aldehyde is an analyte with spicy and herbal odor characteristics that was only observed in the dried basil. Many other analyte differences can be observed and could be investigated.

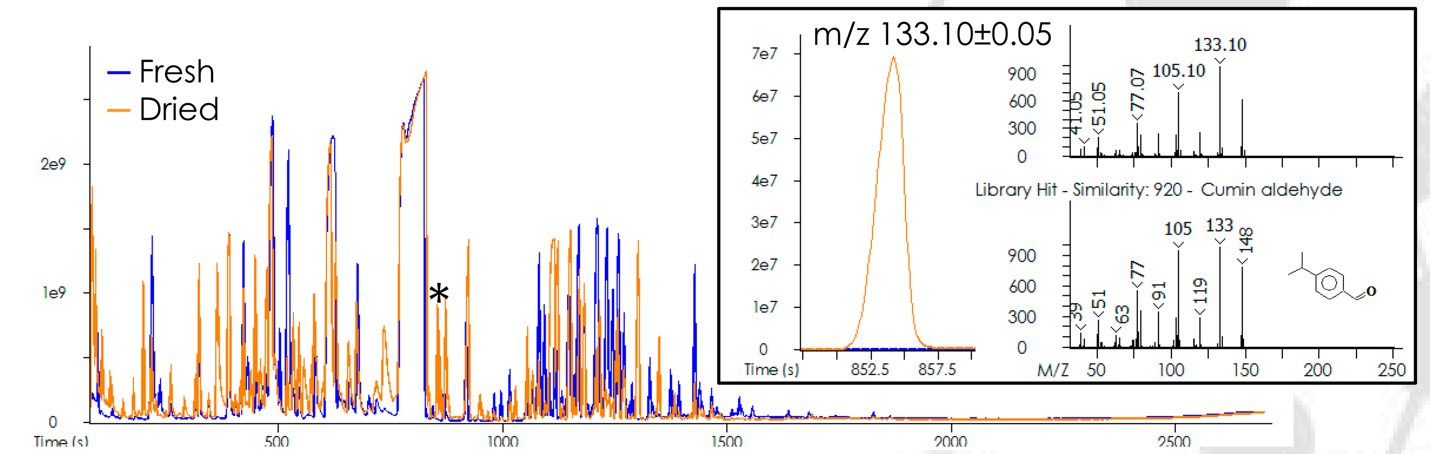


Figure 6. TIC chromatograms for fresh and dried basil are shown. Cumin aldehyde is an important odor analyte that is only present in the dried basil.

Conclusion

This study demonstrates the benefits of LECO's Pegasus BT GC-TOFMS to provide targeted screening and non-targeted characterization for a variety of food and beverage samples. Several examples were demonstrated, and the benefits of deconvolution were also highlighted.

Delivering the Right Results