Combining GC with MS and Olfactory Detection for Characterization of Food, Flavor, and Fragrance Samples

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LECO EMPOWERING RESULTS

INTRODUCTION

Characterization of food, flavor, and fragrance samples is important for quality control (QC), to drive product development, and for gaining a better understanding of a sample. Effectively achieving this characterization often requires identifying the individual chemical components of a sample and then linking these features to their aroma or sensory impact. The combination of gas chromatography (GC), mass spectrometry (MS), and olfactory detection provides an analytical tool that is well-suited to achieve these goals. The components most likely to contribute to the aroma of a sample tend to be volatile and semi-volatile analytes, and GC can provide effective separation of these individual analytes in complex samples. Time-of-Flight (TOF) MS detection provides important information towards the identification of these analytes. The full m/z range non-skewed spectral data is optimal for deconvolution algorithms and the resulting spectra can be library searched. The incorporation of olfactory detection (O) with this data is particularly helpful for connecting the identified features with their contributions to the overall aroma or flavor. This type of sensory directed analysis highlights chromatographic regions of interest and allows for a focused review of the data. A variety of samples were analyzed with this combination of tools, and the benefits of using the information together are highlighted.

METHOD

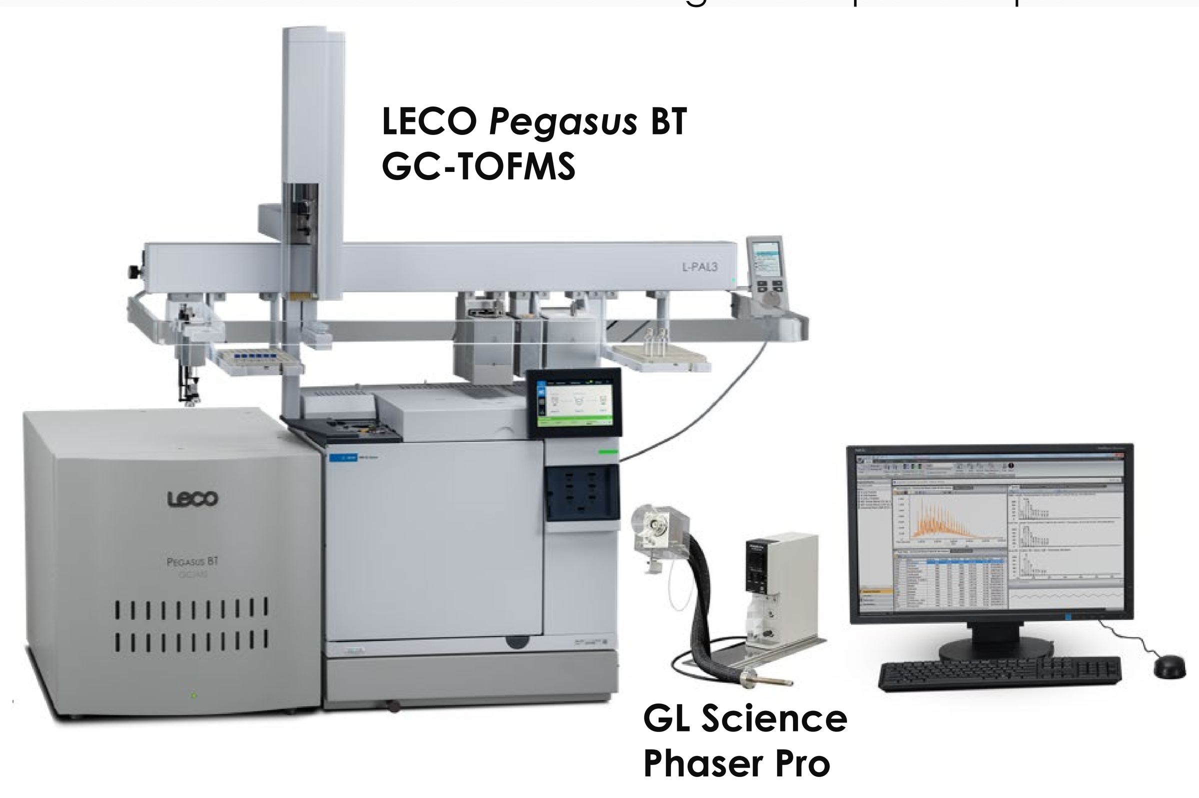
A variety of samples (essential oils, beverages, etc.) were analyzed with GC coupled to MS and an olfactory detector using LECO's Pegasus® BT and GL Science Phaser Pro.

As described below, these tools combine in a complementary way to:

- Isolate analytes in a complex mixture
- Identify those isolated analytes
- Connect analytes to their sensory impact

	GC	MS	Olfactory
Isolate analytes in complex mixture	**Chromatographic separation**	*Mathematical deconvolution of GC coelutions*	
Identify isolated analytes	*Match elution order (RI)*	**Spectral matching to libraries**	*Match known aroma attributes*
Connect analytes to sensory impact		*Literature information*	**Direct olfactory detection**

This set of tools leads to a better understanding of complex samples.



NUTMEG CHARACTERIZATION

GC-MS-O can help determine the characteristic aroma features in a sample. GC separates the individual components, olfactory data highlights those that have characteristic aromas, and MS (along with GC elution order) provides tentative identifications of the characteristic peaks. Four distinct nutmeg aroma notes were detected for the nutmeg essential oil. One was a peak with a large S/N, two were analytes with lower S/N, and one was obscured without deconvolution. These features are described in Table 1 and Figures 1-4.

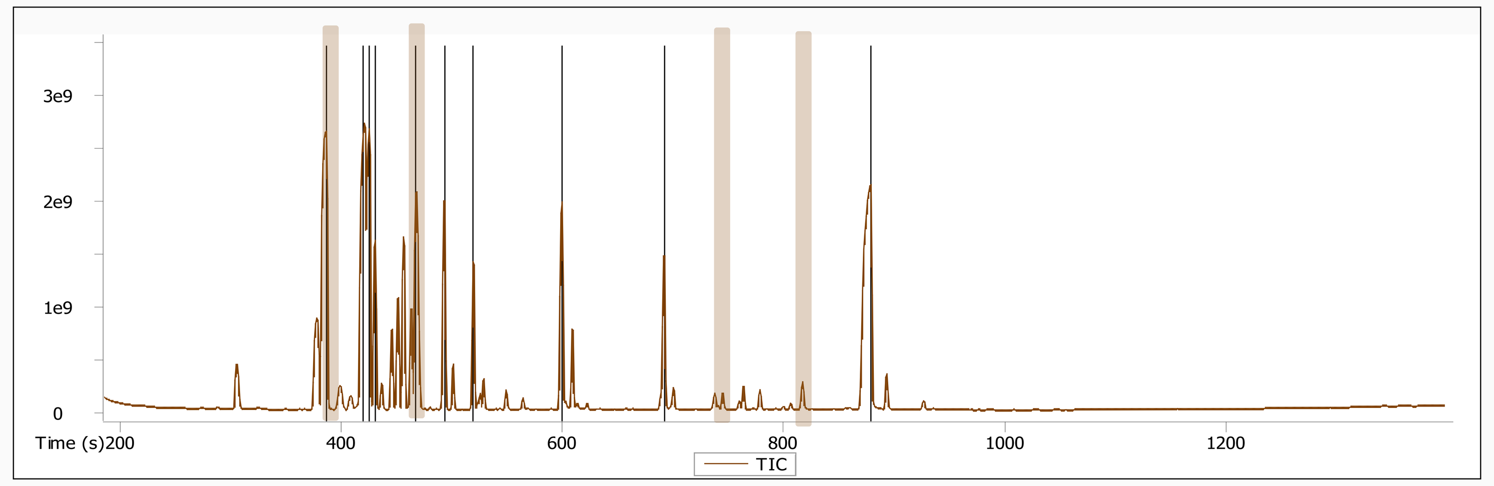


Figure 1. A representative chromatogram (TIC) for nutmeg essential oil is shown. Vertical line peak markers indicate the 10 peaks with the highest S/N and shaded brown markers indicate the most characteristic nutmeg aromas. Details for the indicated peaks are provided in Table 1.

Table 1. Peak information for Figure 1. Bold text connects to vertical line peak markers and brown shading matches brown shaded markers.

	tR	CAS	Similarity	RI	RI (Library)
α-Pinene	**386.454**	**80-56-8**	**945**	**940.7**	**937 ± 3(982)**
Sabinene	**420.205**	**3387-41-5**	**869**	**980.5**	**974 ± 2(618)**
β-Pinene	**425.597**	**127-91-3**	**937**	**986.9**	**979 ± 2(848)**
β-Myrcene	**430.827**	**123-35-3**	**923**	**993.1**	**991 ± 2(838)**
Limonene	**467.844**	**138-86-3**	**934**	**1035.4**	**1030 ± 2(986)**
β-Phellandrene	469.404	555-10-2	756	1037.1	1031 ± 2(280)
γ-Terpinene	**493.468**	**99-85-4**	**942**	**1064.5**	**1060 ± 2(734)**
Terpinolen	**519.653**	**586-62-9**	**910**	**1094.2**	**1088 ± 2(613)**
L-terpinen-4-ol	**600.006**	**20126-76-5**	**837**	**1188.2**	**1182 ± 0(3)**
Safrole	**692.082**	**94-59-7**	**926**	**1302.6**	**1287 ± 2(50)**
Eugenol	745.028	97-53-0	884	1366.9	1358 ± 3(366)
iso-Eugenol	817.255	97-54-1	919	1460.1	1450 ± 15(40)
Myristicine	**878.958**	**607-91-0**	**913**	**1544.1**	**1520 ± 4(52)**

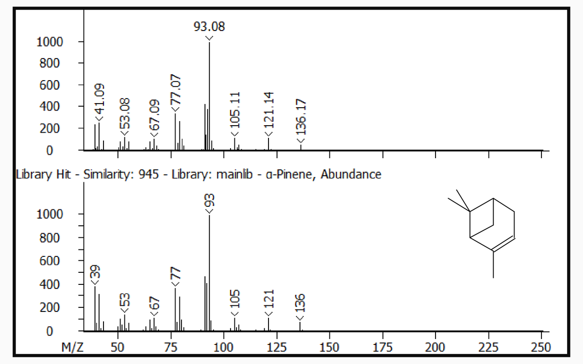


Figure 2. alpha-pinene has a large S/N and a characteristic aroma note for nutmeg.

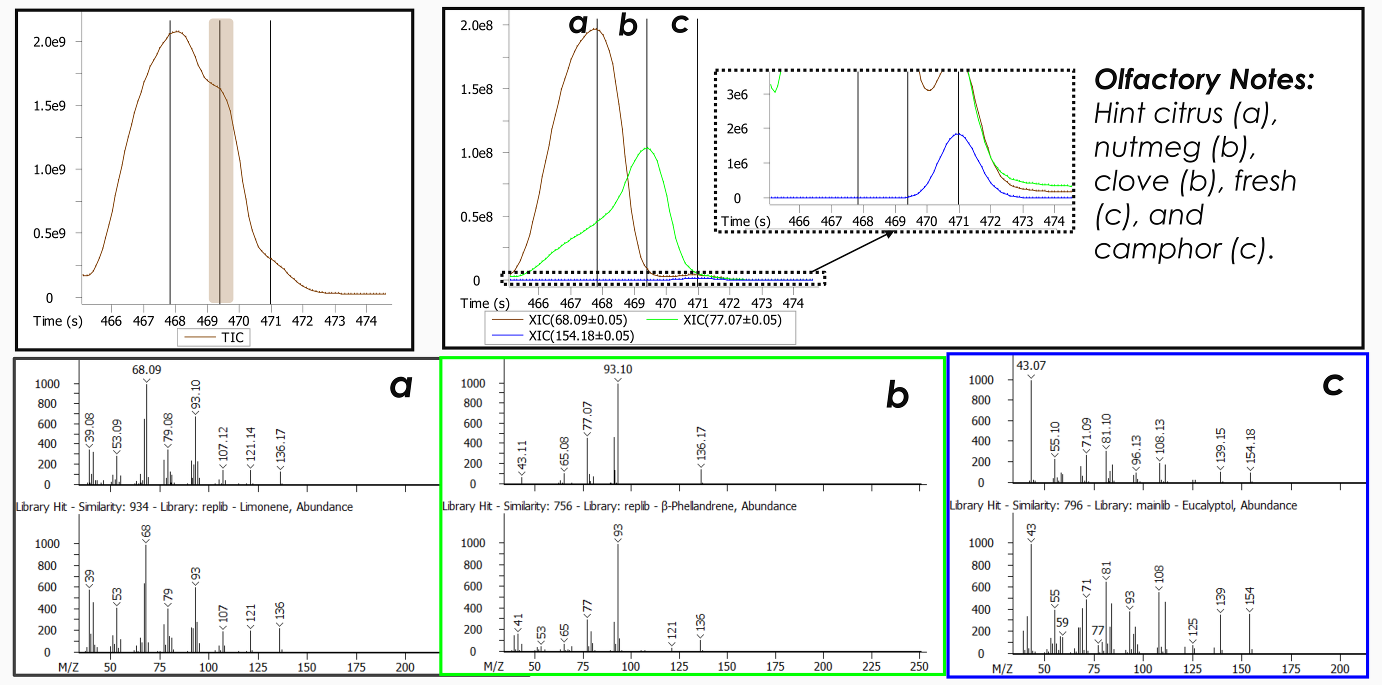


Figure 3. One of the characteristic aroma notes (peak b) was obscured by coelution with two other features (peaks a and c). Olfactory data was also a combination of aroma notes for these coeluting features. Deconvolution separated the coelution (features a, b, and c) and the olfactory notes were linked with the corresponding features.

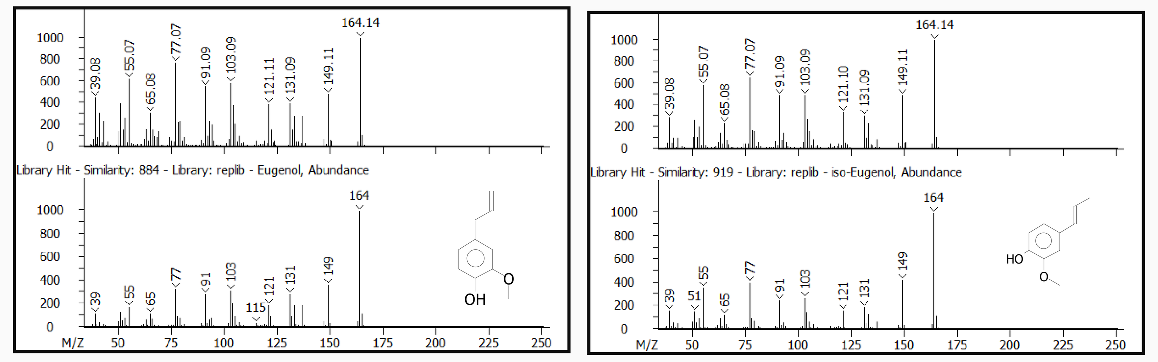
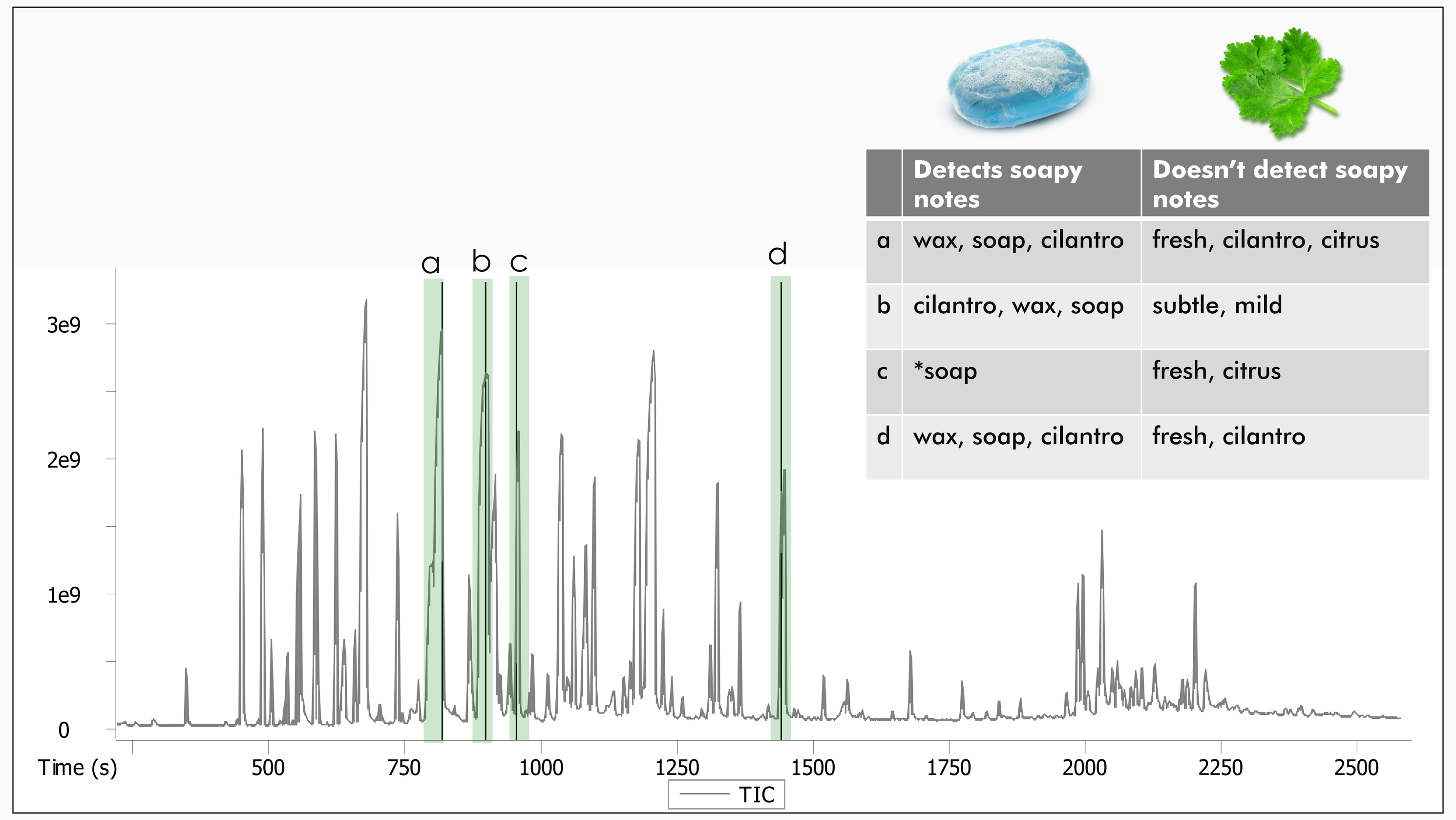


Figure 4. Two of the characteristic aroma notes were from features with low S/N. Olfactory data drew attention to these lower-level features that were determined with GC-MS.

SENSORY DIFFERENCES IN CILANTRO

GC-MS-O can also be used to help understand differences in sensory perception. Cilantro is perceived as soapy to some people and not soapy to others, based on genetics. Olfactory data revealed features that were perceived differently by people, related to this difference. Four aldehydes that were perceived as soapy by some and not by others were tentatively identified with GC-MS, as described in Figures 5 and 6.



	Detects soapy notes	Doesn't detect soapy notes
a	wax, soap, cilantro	fresh, cilantro, citrus
b	cilantro, wax, soap	subtle, mild
c	*soap	fresh, citrus
d	wax, soap, cilantro	fresh, cilantro

Figure 5. A representative chromatogram (TIC) for cilantro essential oil is shown. Green shaded markers indicate peaks (a, b, c, and d) that were perceived as soapy by some and not soapy by others. The odor descriptors from each are listed per peak.

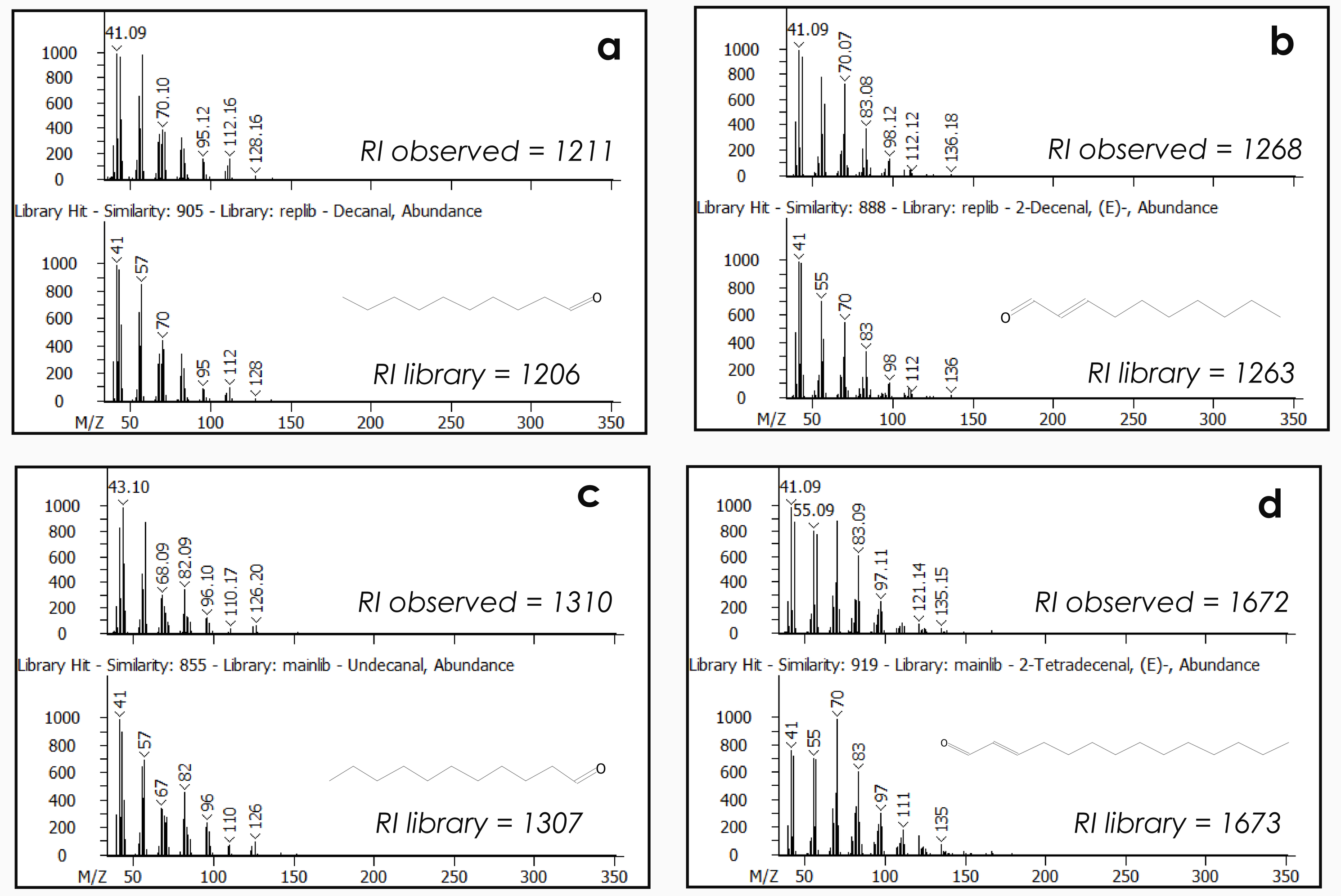
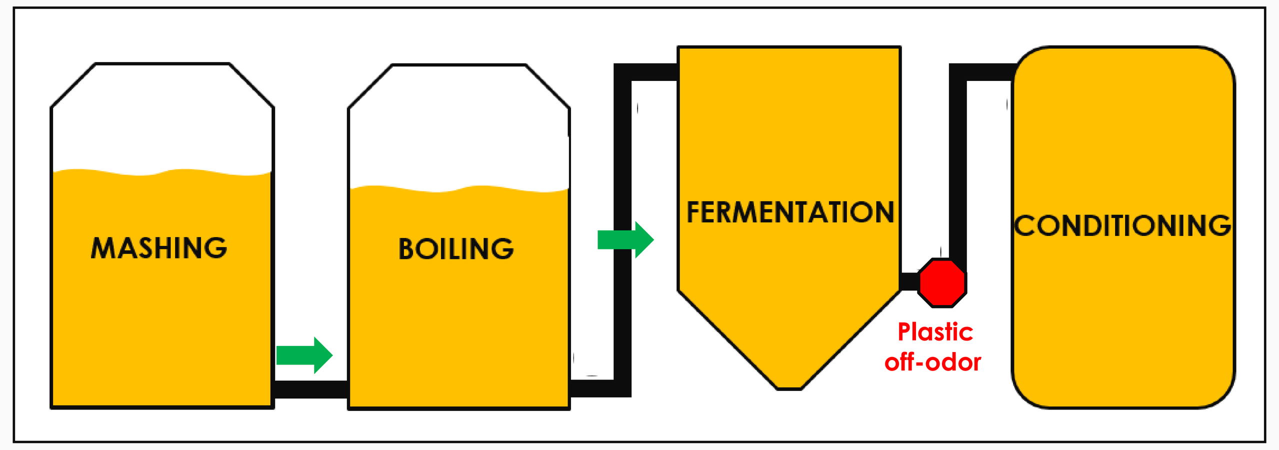
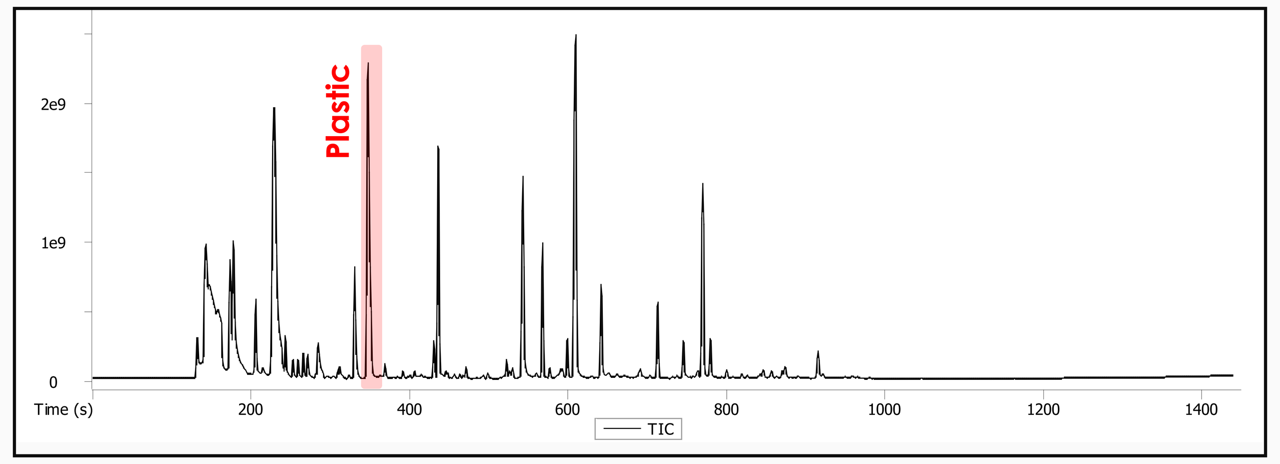


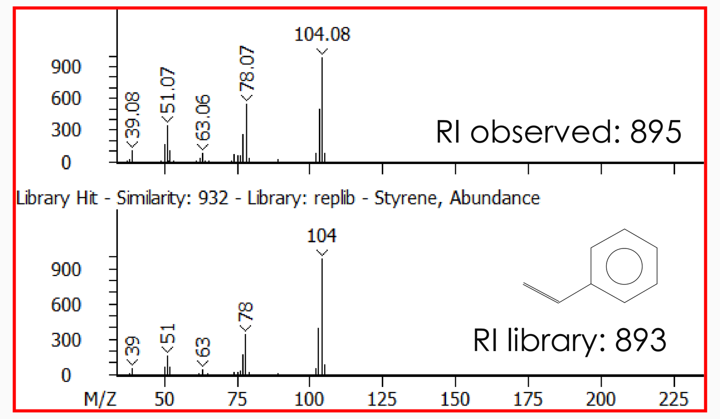
Figure 6. Spectral and retention index information for each of the peaks (a-d) are shown. These aldehydes were perceived as soapy by some and not by others, as described in Figure 5.

BEER OFF-ODOR

GC-MS-O can also help with troubleshooting off-odor and other QC issues in a sample or process. In this application, a plastic off-odor in a beer sample was determined and tentatively identified, as outlined in Figure 7. This identification gave insight to the source of the off-odor, providing direction in the trouble-shooting process.







Styrene can be formed by decarboxylation of cinnamic acid

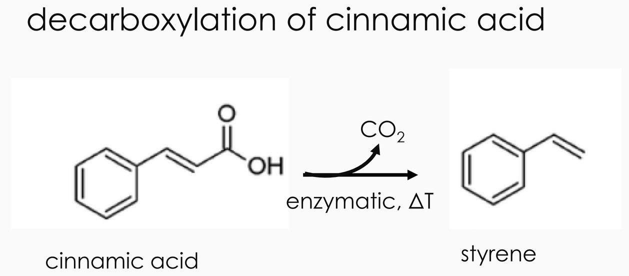


Figure 7. A plastic off-odor appeared in a small batch of beer after fermentation. The off-odor was detected in the chromatogram and identified as styrene, based on spectral and RI matching. Styrene can be formed by the decarboxylation of cinnamic acid, driven by enzymatic activity and temperature. Cinnamic acid concentration (present in the beer from added cinnamon), temperature variation, and yeast activity were all identified as directions to pursue in troubleshooting.

CONCLUSIONS

In this work, the combination of a GC separation with MS and olfactory detection provided a powerful and efficient analytical platform to isolate individual analytes, identify those isolated analytes, and connect them to their sensory impacts. The olfactory data allowed for sensory directed analysis. In each case, the GC separation and full m/z range TOFMS data were crucial for determining the identification of the feature responsible for the characteristic aroma. This collection of tools was demonstrated for the characterization of the most aroma-impacting components of a nutmeg essential oil, the distinction of sensory differences in cilantro, and the determination of an off-odor in beer.