Combining GC with MS and Olfactory Detection for a Variety of Food, Flavor, and Fragrance Analyses

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LECO EMPOWERING RESULTS

INTRODUCTION

Gas chromatography (GC) coupled with mass spectrometry (MS) is an important tool for the characterization of a wide range of food, flavor, and fragrance samples. The components most likely to contribute to the aroma of a sample tend to be volatile and semi-volatile analytes, and GC-MS is well-suited for this type of analysis. Complex samples are effectively separated into the individual analyte components with GC. Time-of-Flight (TOF) MS detection provides important information towards the identification of these potentially important components of the sample with full m/z range data that can be library searched and that is also optimal for deconvolution algorithms. The incorporation of olfactory (O) detection 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 regions of interest and leads to specific analytes of interest for a focused review of the data. This combination of tools can separate and identify analytes and then determine those that are most important for contributing to the sensory characteristics of the sample. A variety of samples were analyzed with this combination of tools, and the benefits of using the information together are highlighted.

METHOD

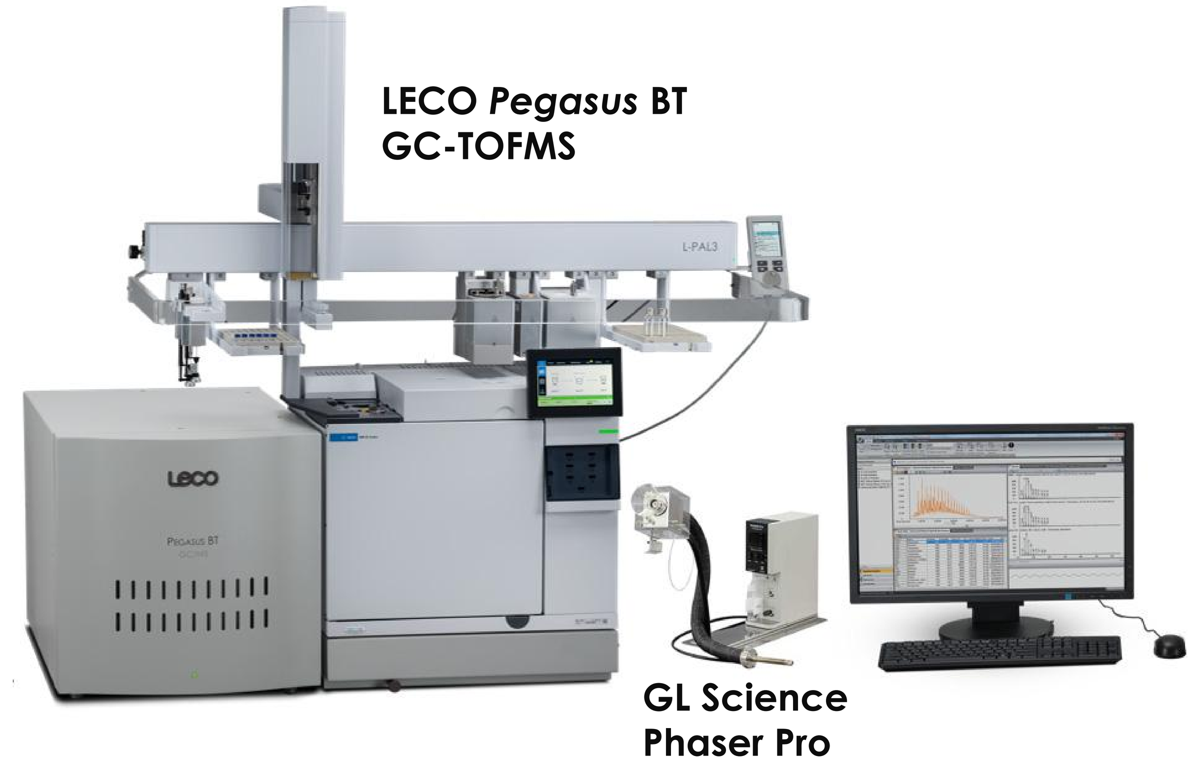
A variety of samples (essential oils, beverages, etc.) were analyzed with GC coupled to MS and O detection using LECO's Pegasus® BT and GL Science Phaser Pro.

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	O
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, O highlights those that have characteristic aromas, and MS (along with GC elution order) provides tentative identifications of the characteristic peaks. In the case of the nutmeg chromatogram shown in Figure 1, there were four distinct aroma notes. 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 2-4.

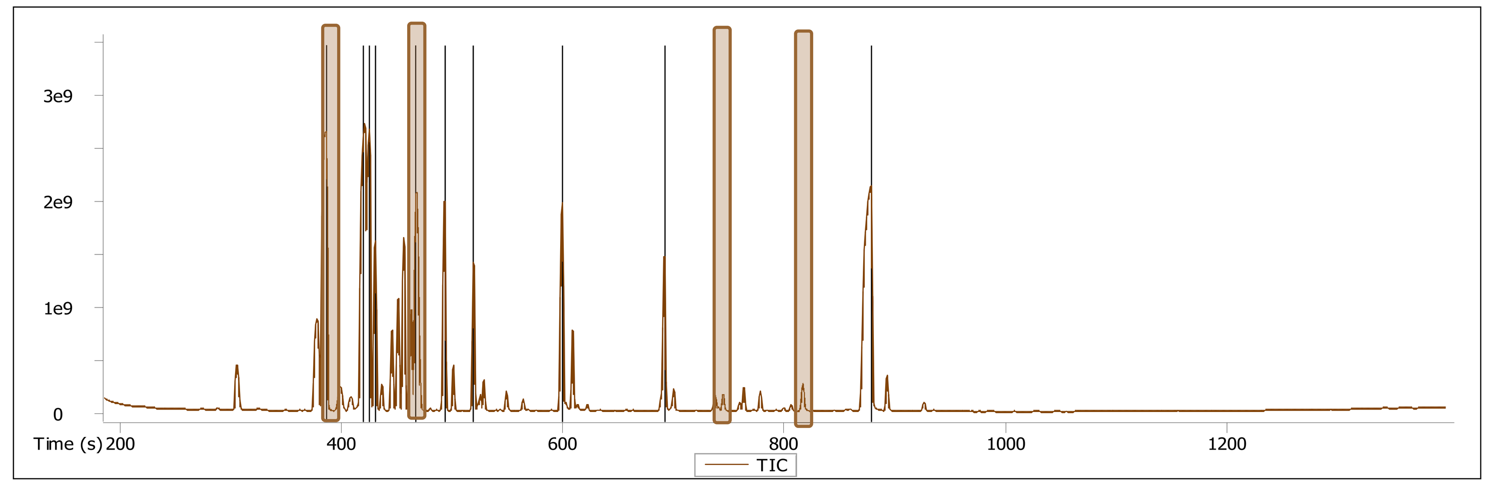


Figure 1. A representative chromatogram (TIC) for nutmeg essential oil is shown. Vertical line peak markers indicate the 10 peaks with the highest S/N and shaded brown markers indicate the most characteristic nutmeg aromas. Details for the indicated peaks are provided in Table 1.

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)**

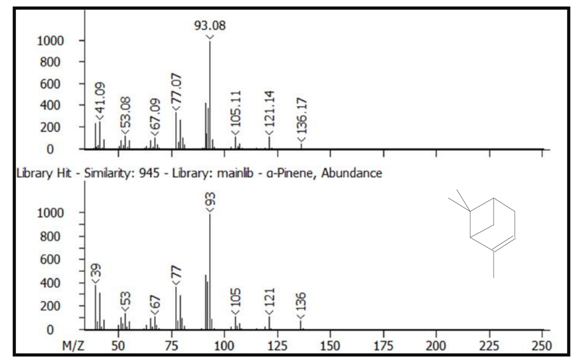


Figure 2. alpha-pinene has a large S/N and a characteristic aroma note.

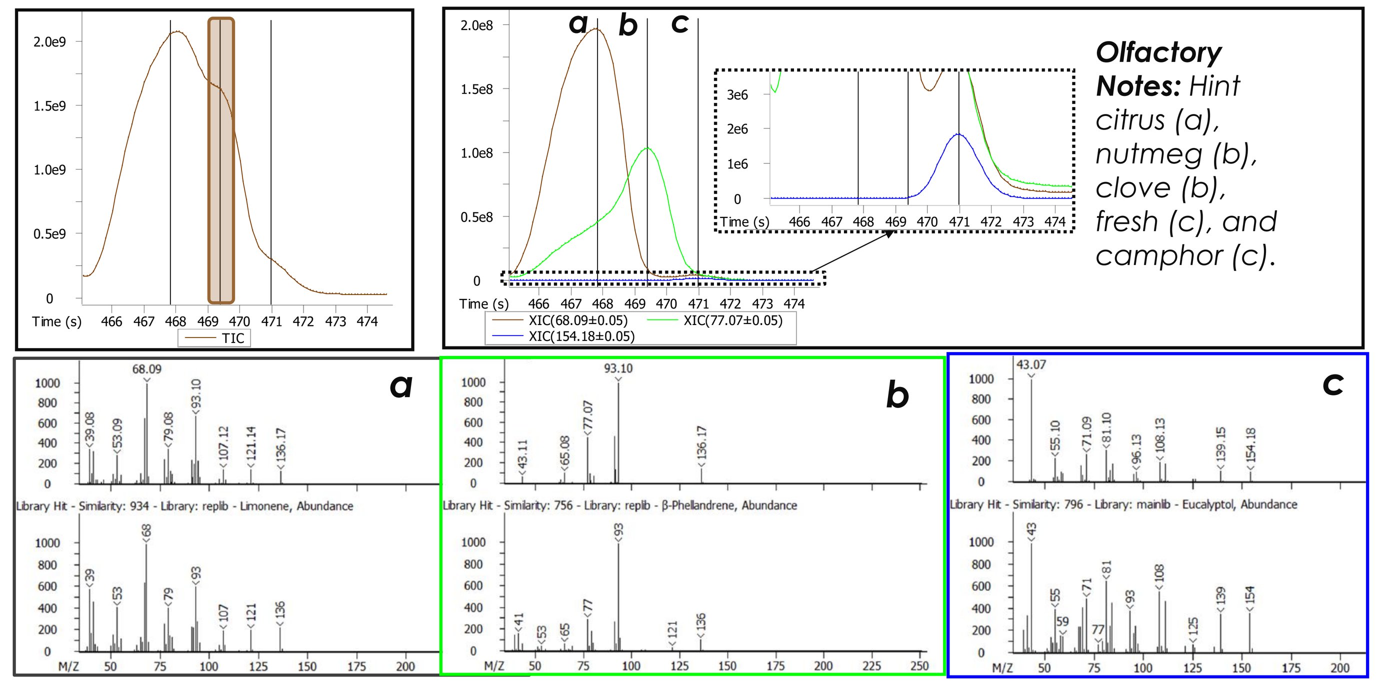


Figure 3. One of the characteristic aroma notes (peak b) was obscured by coelution with two other features (peaks a and c). Olfactory data also was a combination of aroma notes for these coeluting features. Deconvolution separated the coelution (features a, b, and c) and the olfactory notes were linked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

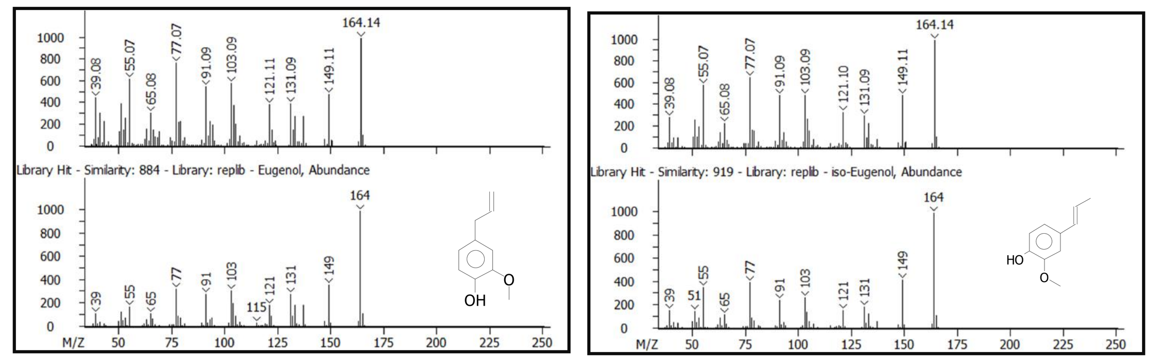


Figure 4. Two of the characteristic aroma notes were from features with low S/N. Olfactory data drew attention to these lower-level features that were determined with GC-MS.

SENSORY DIFFERENCES IN CILANTRO

GC-MS-O can be used to help understand differences in sensory perception. Cilantro is sometimes perceived as soapy based on a person's genetics. Olfactory data revealed features that had different olfactory descriptors depending on whether the person doing the detection found cilantro soapy. Those features were then tentatively identified with GC-MS. The four aldehydes are highlighted and identified, as described in Figures 5 and 6.

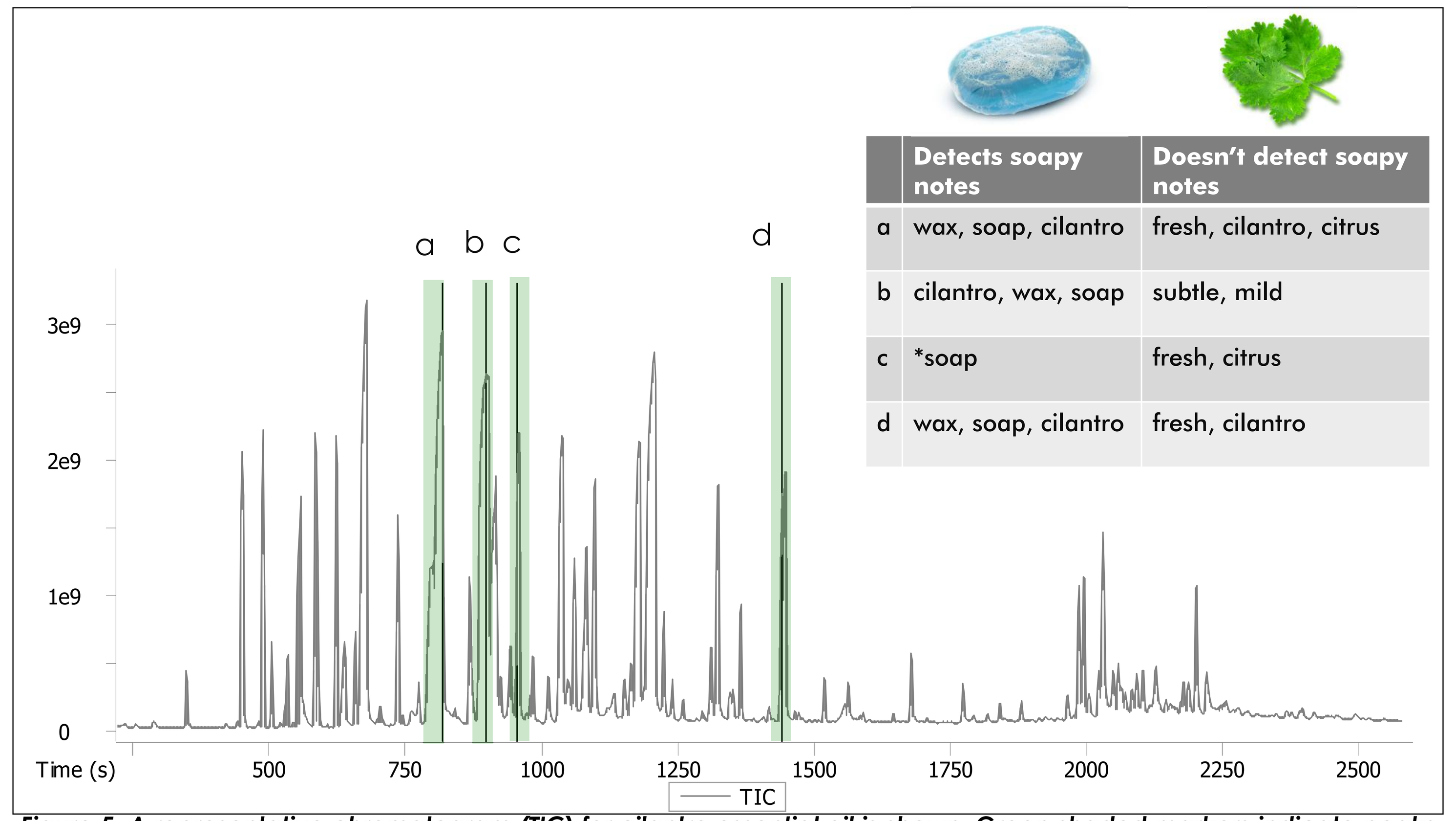


Figure 5. A representative chromatogram (TIC) for cilantro essential oil is shown. Green shaded markers indicate peaks (a, b, c, and d) that were perceived as soapy by some and not soapy by others. The odor descriptors from each are listed per peak.

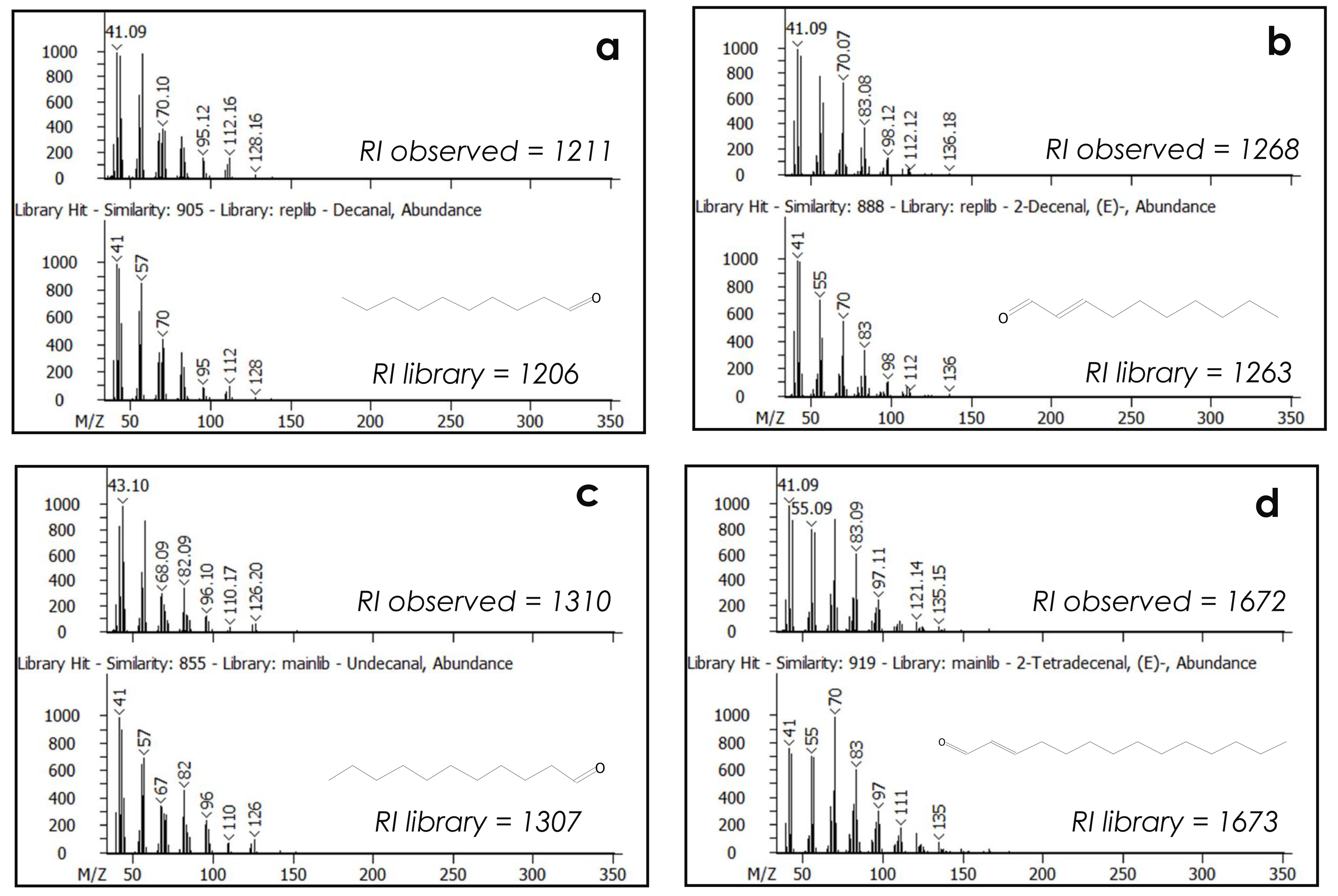


Figure 6. Spectral and retention index information for each of the peaks (a-b) are shown. These aldehydes were perceived as soapy by some and not by others, as described in Figure 5.

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.

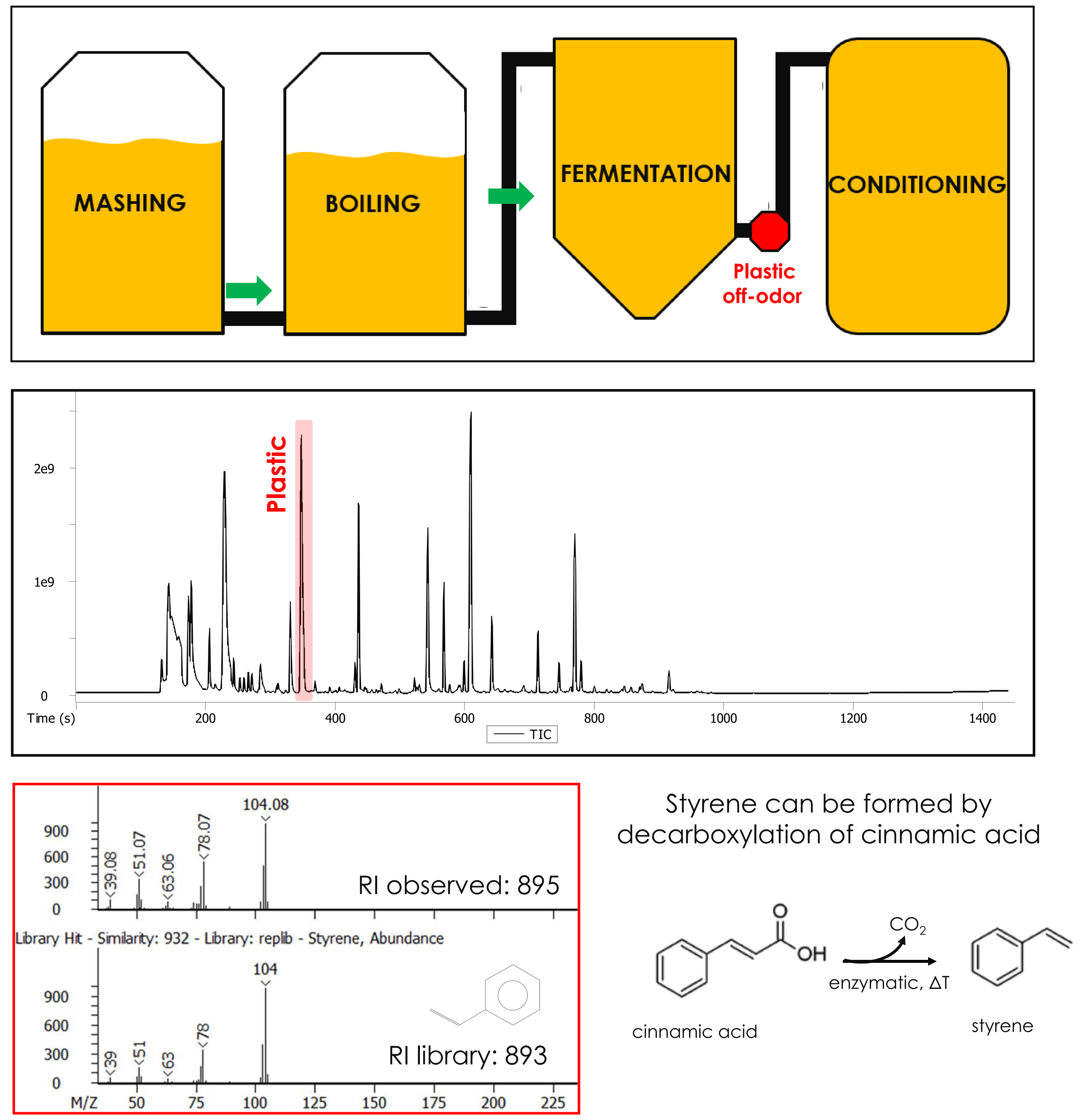


Figure 7. A plastic off-odor appeared in a small batch of beer after fermentation. The off-odor was detected in the chromatogram and identified as styrene, based on spectral and RI matching. Styrene can be formed by the decarboxylation of cinnamic acid, driven by enzymatic activity and temperature. Cinnamic 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 O for 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.