Differential Analysis of Perfumes with GC-TOFMS

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1. Introduction

Determining individual components within a perfume sample provides important information that can help maintain quality control and drive product development through both a better understanding of your own brand and through competitive analysis. GC-MS is well-suited for these studies and is an important tool in this industry. TOFMS, in particular, provides a comprehensive non-targeted view of the sample, so you are not limited to what you already know. LECO's *Pegasus* HT GC-TOFMS system allows the user to see more by providing full mass range sensitivity and speed with unparalleled deconvolution capabilities. This data allows the user to measure the anticipated analytes and also discover what they've been missing. Here, we demonstrate a comparison of a brand perfume sample to two imitation fragrances. ChromaTOF® brand software's automated data processing and analysis tools facilitate sample comparisons and many analyte similarities and differences were apparent, including analytes that would be difficult to detect without TOFMS and deconvolution. These strategies are highlighted as a competitive analysis, but the method and workflow is readily transferable to any sample differentiation task including quality control and process monitoring.

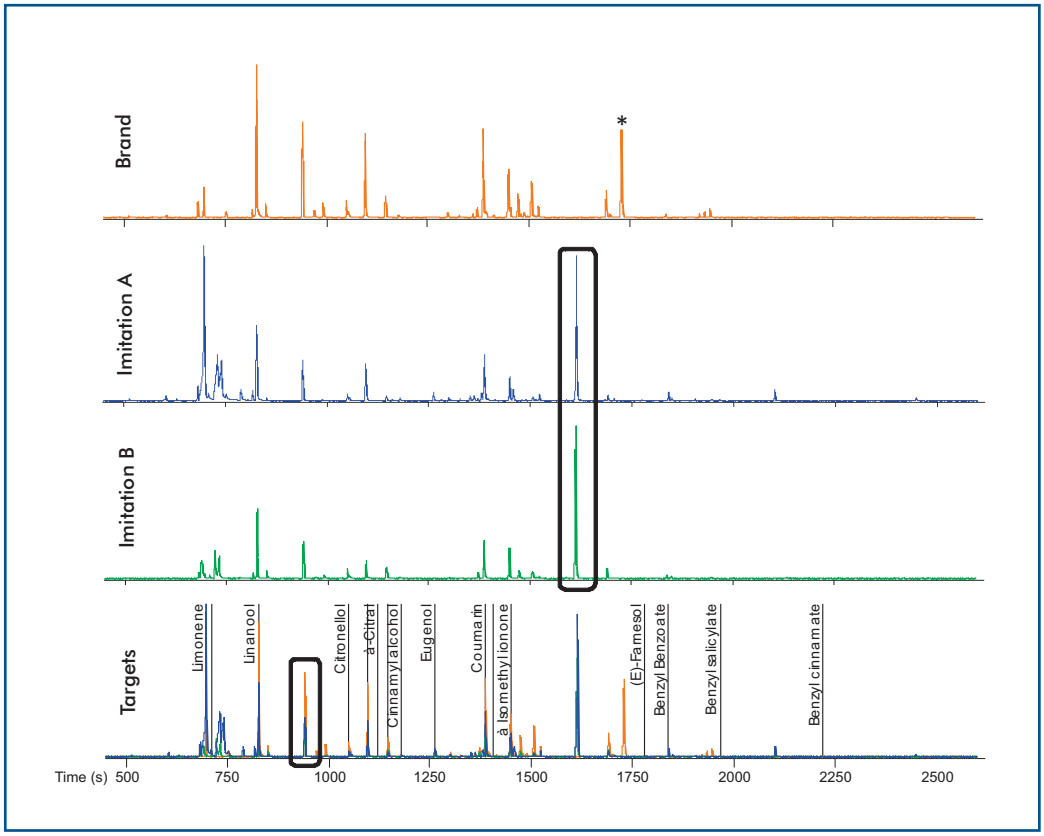

Figure 1. GC chromatograms for a brand sample (orange) and two imitations (blue and green) show many analyte similarities and differences. Sixteen analyte ingredients were listed on the packaging material for the brand sample and are highlighted with peak markers in the overlaid chromatogram. Several analyte differences and similarities between the samples in the non-targeted analytes are highlighted and described further in Figures 2-4.

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2. Experimental

Three commercially available perfume samples, a brand and two imitations, were diluted 50:1 in ethanol and analyzed with the instrument conditions listed in Table 1.

Table 1. GC-TOFMS (*Pegasus* HT) Conditions

Gas Chromatograph	**Agilent 7890 with MPS2 Autosampler**
Injection	1 µL splitless with inlet @ 250°C
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, ramped 5°C/min to 280°C, held 10 min
Transfer Line	250°C
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	250°C
Mass Range	33-500 m/z
Acquisition Rate	20 spectra/s

3. Results and Discussion

Non-targeted sample characterization is important for competitive analysis because target analytes often provide an incomplete picture of the sample. Here, *ChromaTOF's* automated peak finding tools detected nearly 200 peaks in the brand perfume with S/N >50. Of these peaks, 119 matched to analytes in the NIST library databases with similarity scores >700, and many of those had known odor properties that likely contribute to the characteristic notes of this perfume sample. The brand fragrance listed 16 specific analyte ingredients on the packaging, which are highlighted with peak markers in Figure 1. A targeted analysis of these analytes would show only a limited view of this sample. Most of the targets were found in all of the samples, but many other similarities and differences between the non-targeted analytes were also observed.

A non-targeted analyte that was observed in all three perfume samples is outlined in the overlaid chromatogram plot in Figure 1 and shown below in Figure 2. This peak was identified as benzyl acetate, with known floral odor properties. This was not listed as an ingredient, but was observed at a high level in all three perfume samples.

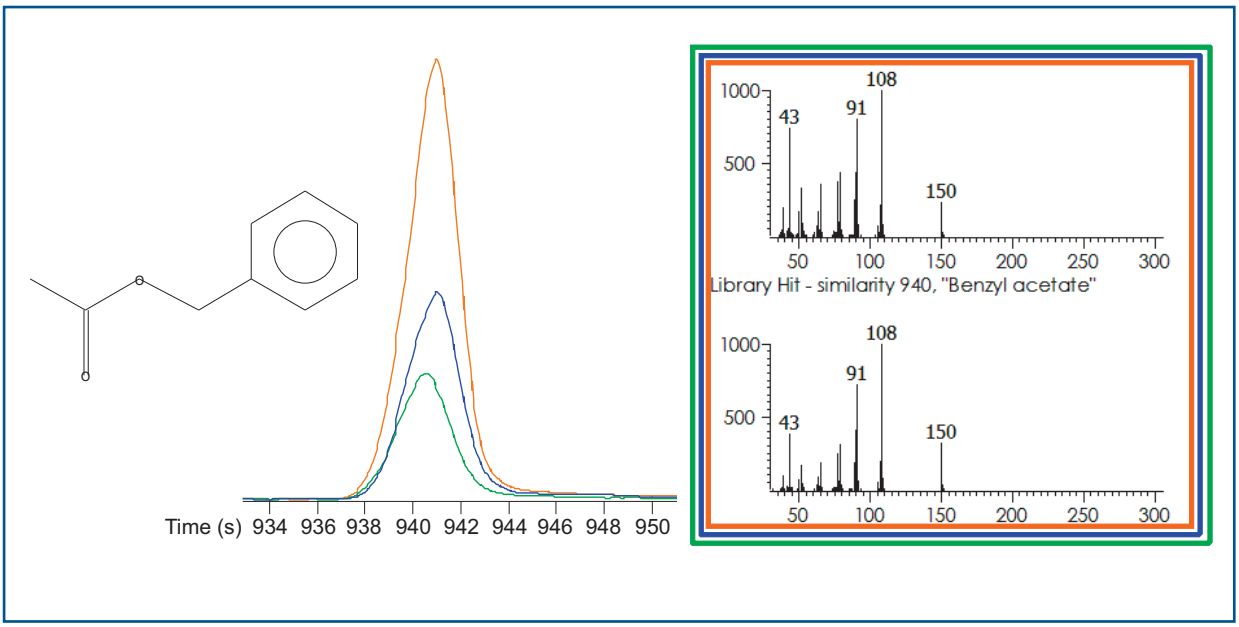


Figure 2. Benzyl acetate (CAS: 140-11-4), with floral odor properties, is a non-target analyte that was observed in the brand perfume (orange) and both imitations (blue and green). The spectral information matched to library data bases with a similarity of 940.

Representative differences that are clearly apparent in the TIC view are also highlighted in Figure 1. A large peak that is present in both imitations, but missing from the brand is encircled in Figure 1 and shown below in Figure 3. Diethyl phthalate was observed in both imitation samples and not the brand. This analyte does not contribute to odor, but could come from plastics in the packaging material or it may have been added as a diluent or solvent for the perfume sample itself. Phthalates are of interest in terms of their environmental and toxicological impact, so their presence or lack thereof is important to sample characterization and competitive analysis.

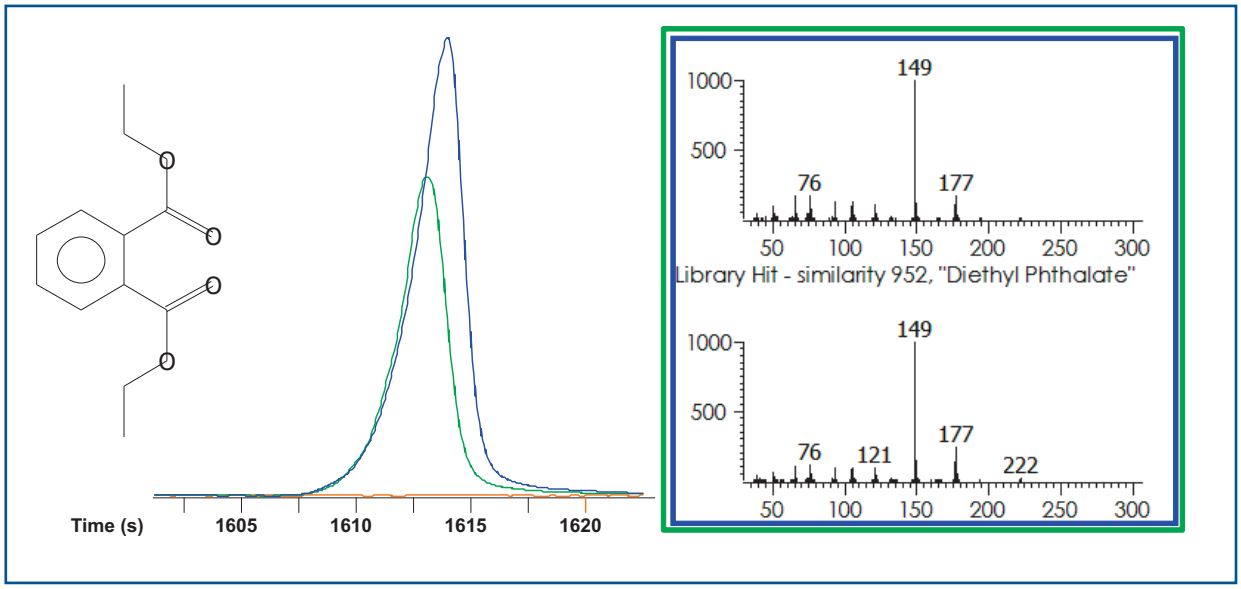


Figure 3. Diethyl phthalate (CAS: 84-66-2) is a non-target analyte that was observed in both imitation perfumes (blue and green), but not in the brand perfume (orange). This analyte does not contribute to odor properties, but is of interest due to its other potential impacts.

Another sample-distinguishing peak is marked with an asterisk in Figure 1 and shown in Figure 4. By the TIC view, it appears that there is one analyte present that is characteristic of the brand sample. A powerful capability of the *Pegasus* HT, however, is the ability to mathematically separate chromatographic coelutions with *True Signal Deconvolution*. With this aspect of data analysis, it is possible to see that there are actually two analytes coeluting here and both are only observed or present at much higher levels in the brand perfume. By plotting specific masses (m/z 94 that is a fragment for both analytes and m/z 83 that is unique to the second) it is possible to see both distinct peak shapes. The mass spectral information is also determined and the analytes were identified as α-santalol, with woody odor properties, and kharismal, with floral odor properties. Kharismal is detected at very low levels in the imitation samples, but α-santalol was only observed in the brand perfume. Both of these analytes are likely important odor-contributors and required a non-targeted analytical approach that includes deconvolution.

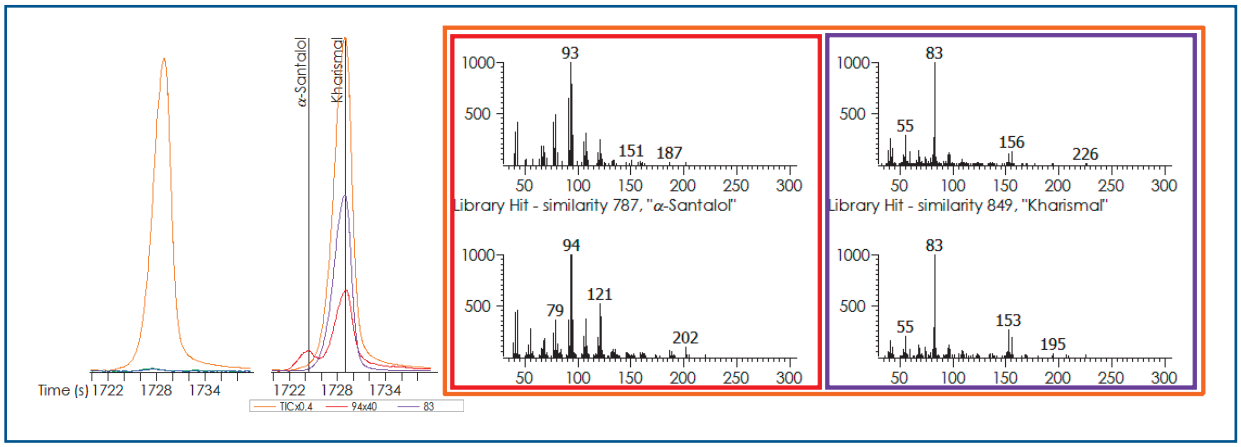
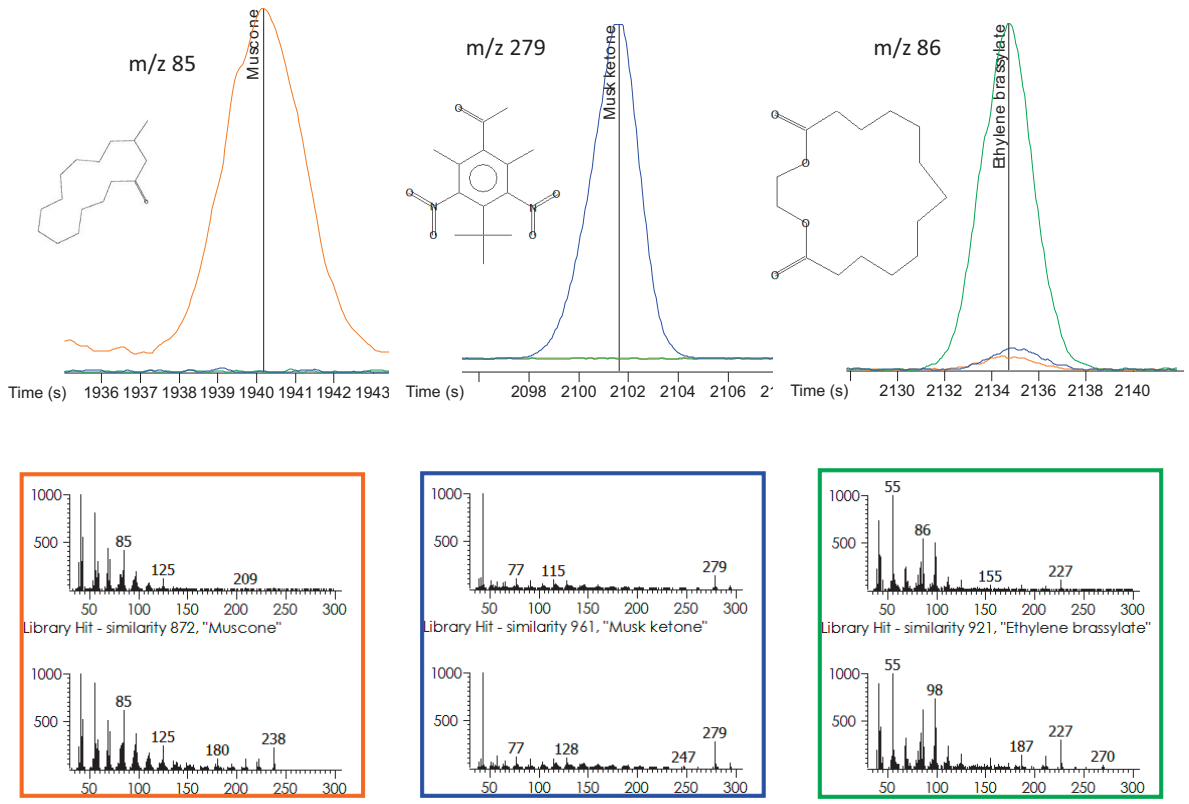


Figure 4. The TIC view shows what appears to be a single peak that is representative of the brand perfume (orange), and not observed (or much lower) in the imitations (blue and green) is actually two analytes. ChromaTOF's deconvolution determines that two unique peaks are coeluting in this region. These can be observed by plotting m/z representative of each analyte, m/z 94 (red) and m/z 83 (purple). TSD also provides the mass spectral information for each peak that can be library matched and were identified as α-santalol (CAS: 115-71-9) and kharismal (CAS: 24851-98-7).

Several other smaller peaks that differ and distinguish the samples can also be observed in these data. A representative example is shown in Figure 5. Here, three analytes, each one distinct to one of the perfume samples, are shown together. All of these analytes have musk odor properties. There could also be other sources of musk odor in the perfumes, but the naturally occurring muscone is present only in the brand sample, while the artificial sources of musk, musk ketone, and ethylene brassylate, are each only observed in one of the imitation samples. This type of information is useful to better understand the sources of specific odors and how they may compare to each other.



Sample	Analyte	Similarity	CAS	Odor Type	Natural/Artificial?
Brand	Muscone	872	541-91-3	Musk	natural
Imitation A	Musk Ketone	961	81-14-1	Musk	not found in nature
Imitation B	Ethylene Brassylate	921	105-95-3	Musk	not found in nature

Figure 5. Three analytes that have musk odor characteristics, each unique to one of the perfume samples, are shown. The analyte observed in the brand sample is found in nature while the other two are not.

4. Conclusion

This study demonstrates the benefits of using LECO's *Pegasus* HT GC-TOFMS for a non-targeted analysis to characterize and compare perfume samples relative to a targeted analysis where you are limited by what you already know. Specific analyte similarities and differences between a brand perfume sample and two imitation brands were determined. In particular, phthalates were observed in the imitation perfumes but not the brand perfume sample, and each perfume type had a different unique analyte contributing musk odor properties. Additionally, *TSD* was helpful to determine individual analyte information in regions of coelution, and highlighted that what appeared in the TIC as one analyte characteristic of the brand sample, was actually two coeluting analytes that were unique to the brand sample. This application note demonstrates a competitive analysis, but the same approach can be applied for other differential analysis comparisons, including quality control and product development.

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