Improved Characterization of Perfumes with GC×GC-TOFMS

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1. Introduction

GCMS is an important tool in the perfume industry because determining the components within a perfume sample provides valuable information towards quality control, understanding or modifying a product, and competitive analysis. The *Pegasus* HT GC-TOFMS system delivers full mass range sensitivity and speed with unparalleled deconvolution capabilities to allow the user to see more analytes. TOFMS inherently provides a non-targeted analysis to see what else is in the sample and offers the opportunity for retrospective examination, when necessary. The addition of a complementary secondary separation dimension with the *Pegasus* 4D GC×GC-TOFMS builds upon these benefits to allow the user to confidently discover even more about their sample. The two separations occur simultaneously, so the additional information is gained without an increase in analysis time. Here, we compare GC-TOFMS and GC×GC-TOFMS data for a representative commercial perfume sample to demonstrate the type of information that can be gained with a comprehensive two-dimensional separation.

**145 Peaks with S/N > 100
(112 with Similarity > 700)**

**375 Peaks with S/N > 100
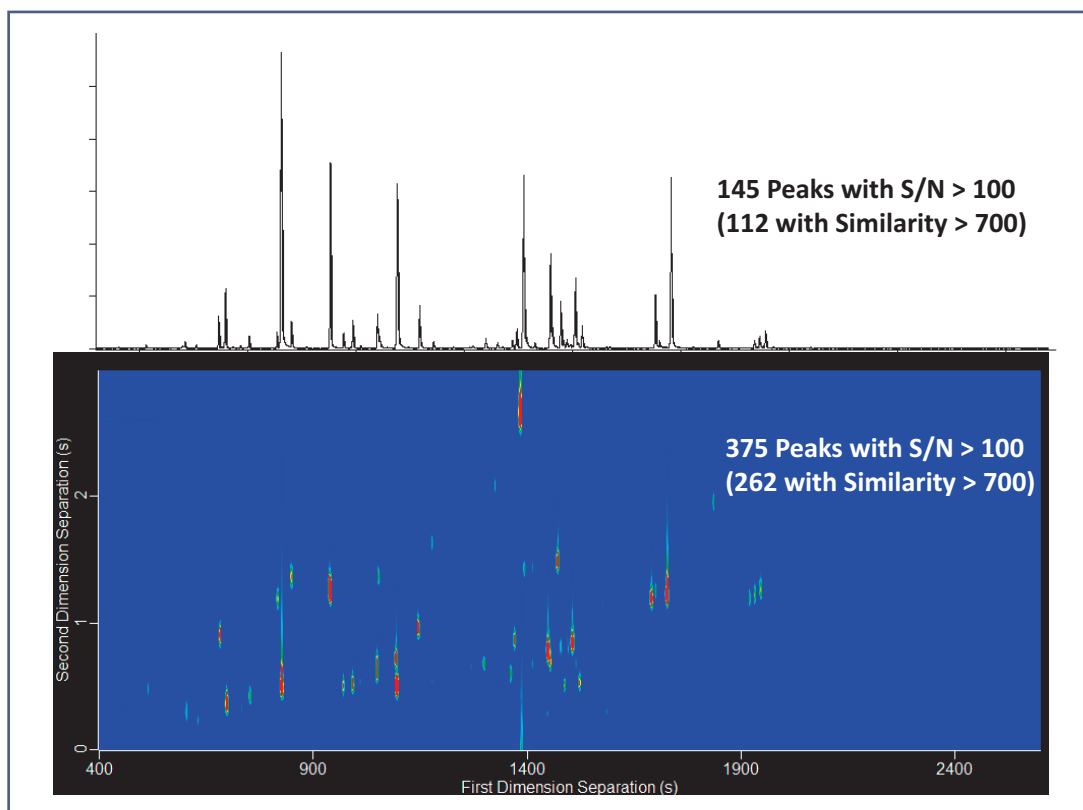(262 with Similarity > 700)**

Figure 1. GC and GC×GC separations of a commercial perfume sample. GC×GC provides improved detectability, increased peak capacity, and structured chromatograms to combine for more information on more analytes within a complex sample.

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2. Experimental

The perfume sample was diluted 50x in ethanol and analyzed with the instrument conditions listed in Tables 1 and 2.

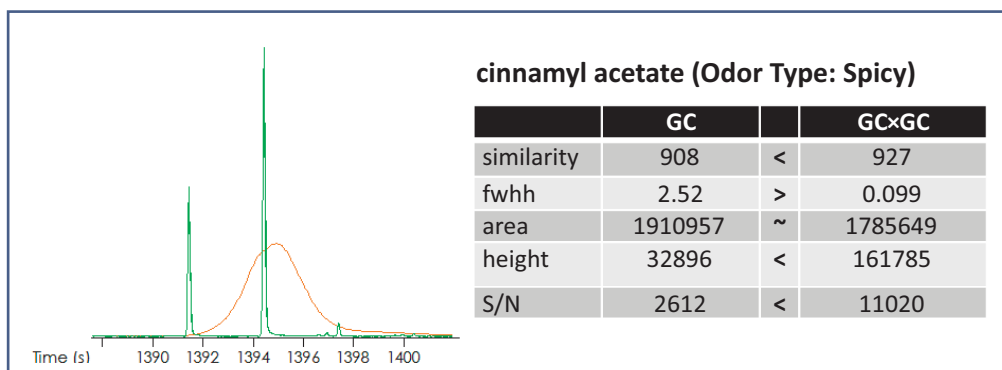**Table 1. GC-TOFMS (*Pegasus* HT) Conditions**

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

Table 2. GC×GC-TOFMS (*Pegasus* 4D) Conditions

Gas Chromatograph	Agilent 7890 with Dual Stage Quad Jet Modulator and MPS2 Autosampler
Injection	1 μL splitless with inlet @ 250°C
Carrier Gas	He @ 1.0 ml/min, Corrected Constant Flow
Column One	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μm coating (Restek)
Column Two	Rxi-17SilMS, 1.20 m x 0.25 mm x 0.25 μm coating (Restek)
Temperature Program	2 min at 40°C, ramped 5°C/min to 280°C, held 10 min Secondary oven maintained +15°C relative to primary oven
Modulation	3 s with temperature maintained +15°C relative to secondary oven
Transfer Line	250 °C
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	250 °C
Mass Range	33-500 m/z
Acquisition Rate	100 spectra/s

3. Results and Discussion

The perfume sample was characterized with GC and GC×GC, and representative chromatograms are shown in Figure 1. Both instrument platforms provided information on many analytes within this perfume sample, but analysis with GC×GC achieved an increase in the number of detected and identified peaks, as listed in Figure 1, and an improved overall characterization of the sample. One reason for the greater number of detecated analytes was the lower detection limit due to thermal focusing that occurs at the modulator, as demonstrated in Figures 2 and 3.

cinnamyl acetate (Odor Type: Spicy)

	GC		GC×GC
similarity	908	<	927
fwhh	2.52	>	0.099
area	1910957	~	1785649
height	32896	<	161785
S/N	2612	<	11020

Figure 2. Peak metrics for cinnamyl acetate in the GC (orange trace) and GC×GC (green trace) data are compiled. The linear display of the GC×GC data shows each modulation period in series and cinnamyl acetate can be observed in three subsequent modulation periods. With GC×GC, effluent is collected at the modulator for reinjection to the second column. The peak area is maintained during modulation, but the peak width is sharpened leading to an increase in peak height and S/N.

With thermal modulation, the effluent is collected and refocused for injection to the secondary column just prior to detection. The peak area is maintained during modulation, but the peak width is dramatically reduced which translates to an increased height and increased S/N for GC×GC. The increase in S/N brings low level analytes above the detection threshold, and also often provides improved spectral quality for analytes with higher S/N allowing more analytes to be detected and identified, as tabulated in Figure 1 and demonstrated in Figure 3. With GC×GC, the S/N and library similarity score increased for the three analytes that were also detected in the GC data, and two additional analytes were detected that had S/N below the same threshold in the GC data.

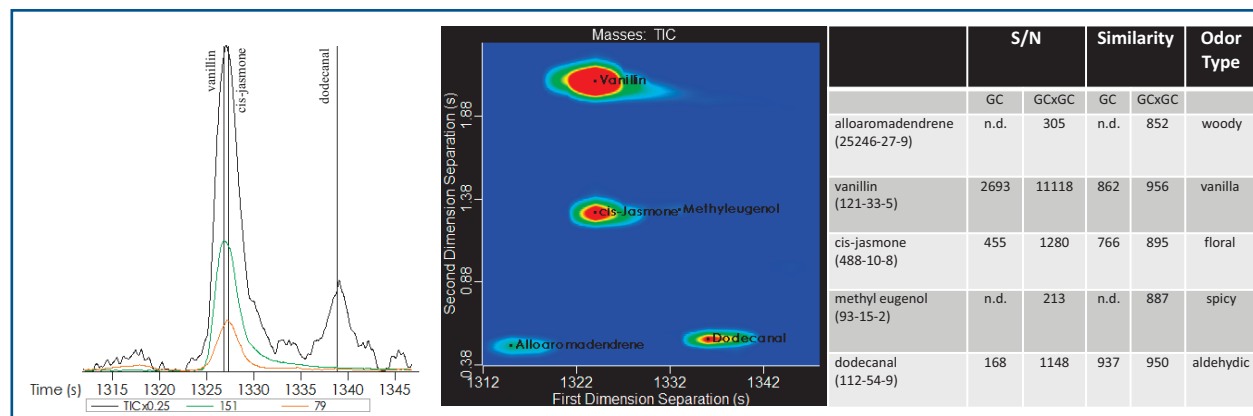|	S/N		Similarity		Odor Type
	GC	GCxGC	GC	GCxGC	
alloaromadendrene (25246-27-9)	n.d.	305	n.d.	852	woody
vanillin (121-33-5)	2693	11118	862	956	vanilla
cis-jasmone (488-10-8)	455	1280	766	895	floral
methyl eugenol (93-15-2)	n.d.	213	n.d.	887	spicy
dodecanal (112-54-9)	168	1148	937	950	aldehydic

*Figure 3. Additional analytes were detected and identified with GC×GC relative to GC, in part due to thermal focusing at the modulator. The S/N and MS similarity improved for all analytes. Vanillin (m/z 151, green trace) and cis-jasmone (m/z 79, orange trace) are deconvoluted with the GC separation and chromatographically separated with GC×GC because of an increased peak capacity. *n.d. = not detected*

In addition to the improved detectability, GC×GC has an increased peak capacity to better separate complex samples. With TOFMS, GC coelutions may be mathematically deconvoluted based on differences in the mass spectral patterns across the width of the peak, as demonstrated for vanillin and cis-jasmone in Figure 3. These first dimension coelutions are often chromatographically separated in the complementary second dimension separation with GC×GC as they were here. While deconvolution of the GC data was able to mathematically separate peaks and provide mass spectral information to identify each analyte in this case, chromatographic separation with GC×GC is particularly important in instances where the coelution exceeds mathematical deconvolution capabilities. In Figure 4, only a single analyte was found in the GC data, but two analytes were chromatographically separated in the GC×GC data.
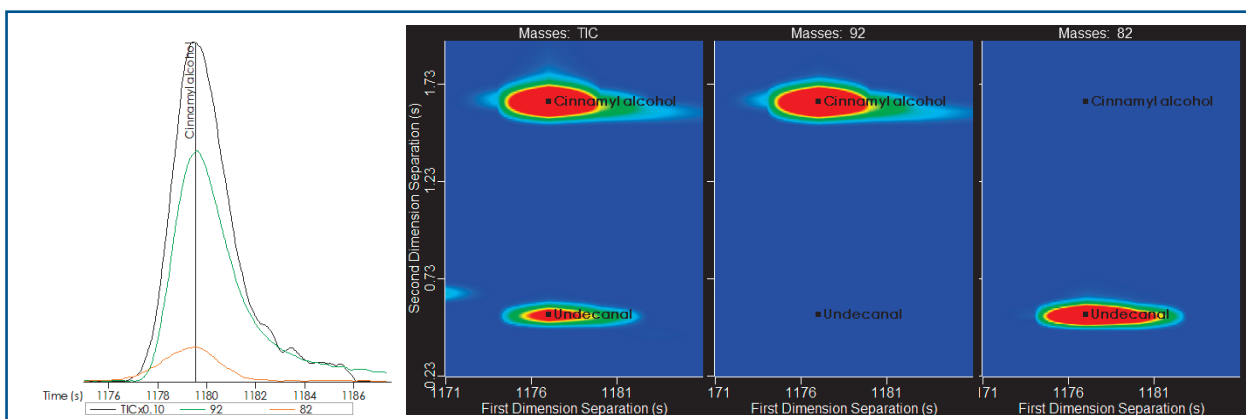

Figure 4. Increased peak capacity in GC×GC relative to GC also contributes to more detected analytes. Here, cinnamyl alohol (m/z 92, green trace) was detected and identified with GC. With GC×GC, undecanal (m/z 82, orange trace) was chromatographically separated and able to be detected and identified.

The mass spectral information for the GC peak marker and the two GC×GC peak markers are shown in Figure 5. The peak that was identified as cinnamyl alcohol with a good library similarity score of 824 with GC was chromatographically separated to two analytes, cinnamyl alcohol and undecanal, in the GC×GC data with similarity scores improving to 918 and 960, respectively. In Figure 4, the m/z unique to each analyte (m/z 92 and 82) are shown together in the single peak marker in the GC data and chromatographically separated with GC×GC. The GC mass spectrum is the combination of the two analytes. While some evidence of undecanal is apparent in the GC spectrum (with specific m/z highlighted in green), this analyte would likely be missed in this analysis. The GC×GC chromatographic separation, however, provided the ability to measure both analytes and account for the important odor characteristics of each: balsamic (cinnamyl alcohol) and aldehydic (undecanal).
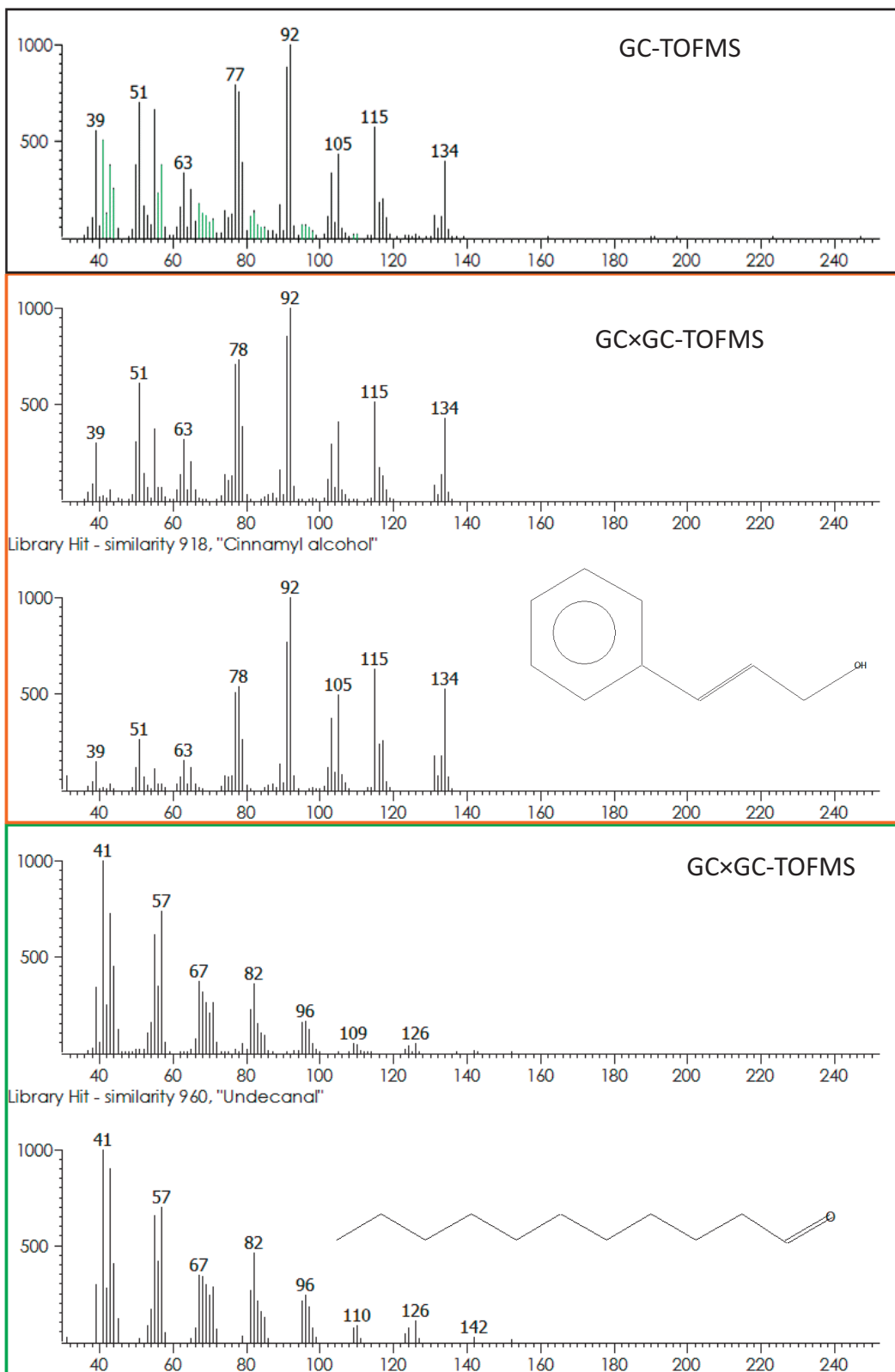
Figure 5. *GC provided information on one apparent analyte that was chromatgraphically separated to two analytes in the GC×GC data. The mass spectrum from the GC separation is the combination of the two chromatographically separated GC×GC analtyes. Undecanal masses are highlighted with green in the GCMS data.*

Along with the increased number of detected analytes from thermal focusing and increased peak capacity, another benefit of GC×GC is the generation of structured chromatograms that comes from the complementary nature of the two separations. Analytes with similar functional groups tend to elute in organized bands across the two-dimensional separation space, which is useful for general sample characterization and rapid comparison capabilities. The types of analytes present in the sample can often be determined with simple visual review because of this aspect of GC×GC. Examples of the types of analytes observed in this perfume sample, and their structured bands within the separation space, are highlighted in Figure 6.
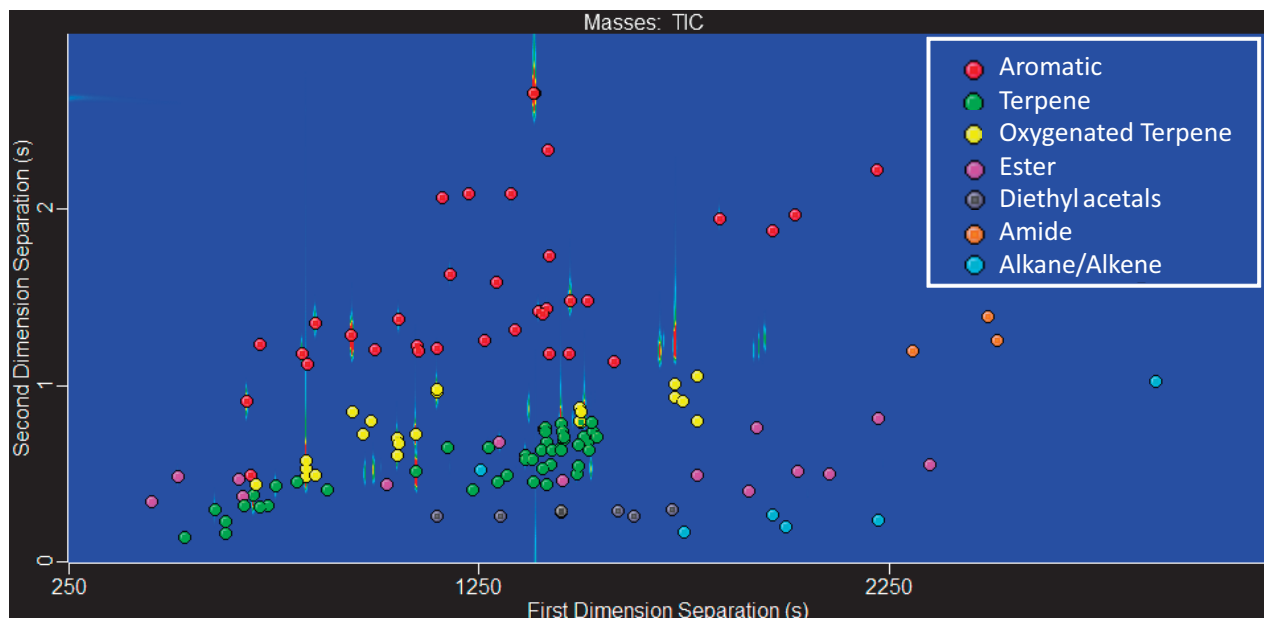
Figure 6. The structured nature of the two-dimensional space allows for rapid characterization information on the types of analytes that are present in the sample. Representative peak markers are shown.

4. Conclusion

This study demonstrates the benefits of performing GC×GC-TOFMS analysis using LECO's *Pegasus* 4D to provide more information on more analytes within a complex sample and to see what you are missing with your GC separation. A commercial perfume sample was analyzed with GC and GC×GC-TOFMS and, while good characterization was achieved with each, more information was gleaned with GC×GC. Without an increase in separation time, the GC×GC separation yielded information on 375 peaks (262 with library similarity >700) compared to the 145 peaks (112 with library similarity >700) that were observed in the GC data above the same S/N threshold. TOFMS acquisition with deconvolution allowed the user to see non-targeted analytes and mathematically separate some coelutions in the GC analysis, but the addition of a complementary separation dimension offered an increased peak capacity, improved detectability with thermal focusing, and the generation of structured chromatograms for visual characterization. Because of these benefits, analytes with important odor properties that were missed with the GC separation were detected by GC×GC, allowing the user to confidently discover even more about their sample.

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