

Non-Targeted and Targeted Aroma Analysis of Name-Brand and Imitation Perfume Samples by GC×GC-HRT

Key Words: Pegasus® GC-HRT 4D, Perfume Analysis, Non-Targeted Analysis

1. Introduction

Quality control, process optimization, and product development are all driven by the ability to differentiate samples and the individual components within them. These tasks are sometimes done by targeted screening to monitor analytes that are expected at certain levels within the samples, but a comprehensive non-targeted analysis would instead allow for determining what else is in your sample and would not limit the analyst to what they already know. GC-TOFMS inherently provides non-targeted information through full mass range data to comprehensively describe a sample. Extending this analytical capability with GC×GC and HR-TOFMS yields even more information to determine what you've been missing. Chromatographic separation is improved with GC×GC by coupling an additional complementary column to the primary column to separate first dimension coelutions, while HR-TOFMS adds accurate mass data for formula determinations to more confidently identify unknowns. More analytes are separated and detected and more of these are confidently identified for overall superior non-targeted characterization. LECO's *Pegasus* GC-HRT 4D combines these analytical capabilities and was used here to probe differences and similarities between a name-brand and two imitation perfume samples in both a targeted and non-targeted way.

***Figure 1.** Representative GC×GC separations of each commercial perfume sample. A name-brand perfume sample was compared to two drugstore imitations of the brand. The GC×GC contour plots show good separation of the analytes within the 2D space. Many similarities and differences between the samples are observed.*

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2. Experimental

A name-brand and two drugstore imitation perfume samples were diluted in ethanol and prepared for analysis. Each sample was analyzed by GC×GC coupled to HR-TOFMS with LECO's *Pegasus* GC-HRT 4D. The instrument conditions are listed in Table 1.

Table 1. Instrument Conditions

GC×GC	**Agilent 7890 with MPS2 Autosampler**
Injection	1μL, splitless @ 250°C
Carrier Gas	He @ 1.0 ml/min, Pressure Corrected Constant Flow
Column One	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μm (Restek)
Column Two	Rxi-17SilMS, 1.20 m x 0.25 mm x 0.25 μm coating (Restek)
Temperature Program	40°C (2 min), to 280°C @ 5°C/min (10 min) Secondary oven maintained +15°C relative to primary oven
Modulation	3 s with temperature maintained +15°C relative to secondary oven
Mass Spectrometer	**LECO *Pegasus* GC-HRT 4D**
Transfer Line	250°C
Ion Source Temperature	250°C
HRT Acquisition Mode	High Resolution, R = 25,000 (FWHM)
Ionization Mode	EI
Mass Range (m/z)	33-500
Acquisition Rate	100 spectra/s

3. Results and Discussion

The *Pegasus* GC-HRT 4D effectively separated and identified hundreds of analytes contributing to the overall sensory attributes of the samples. The name-brand perfume's packaging material included an ingredient list of 16 analytes that were an important target list of what is already known and potentially important for screening. These analytes were identified and compared to determine similarities and differences of the imitator samples to the brand, but were only a fraction of the analytes detected.

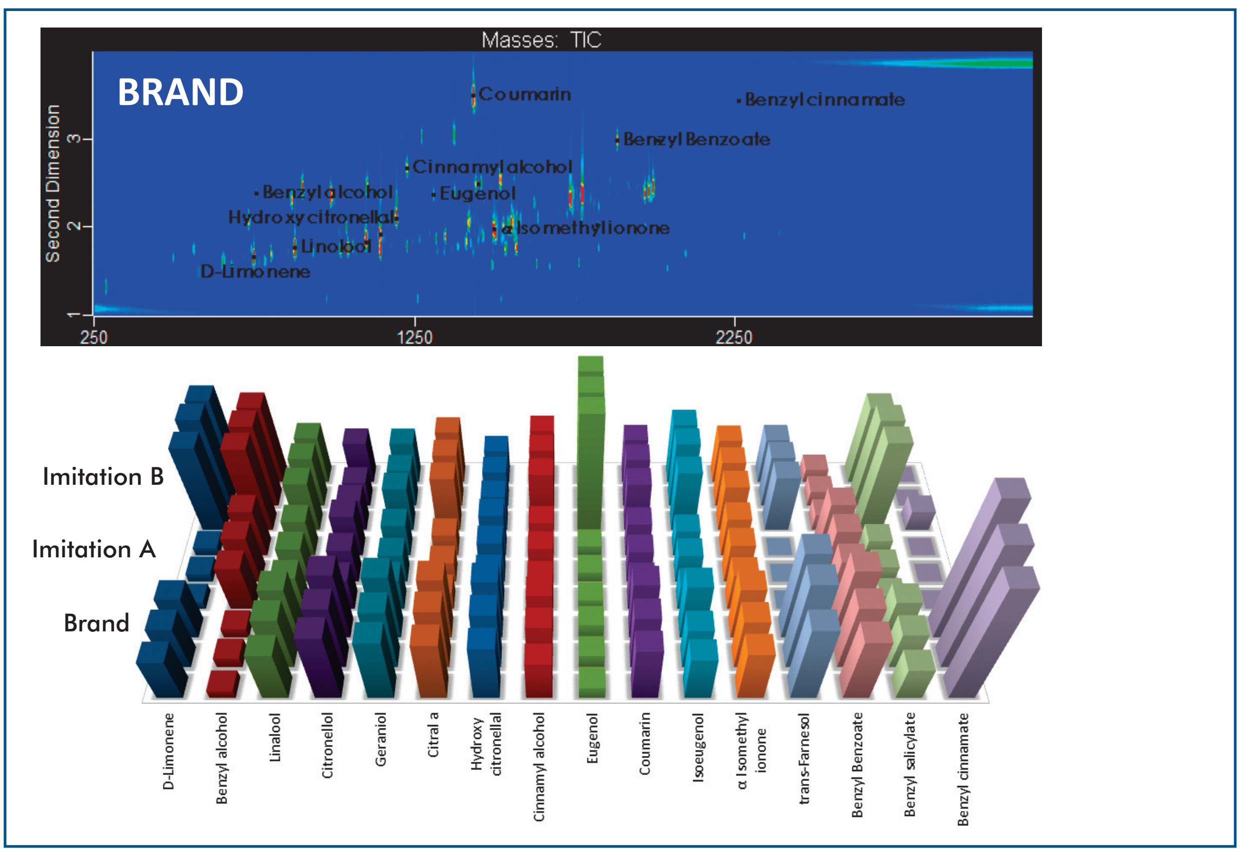
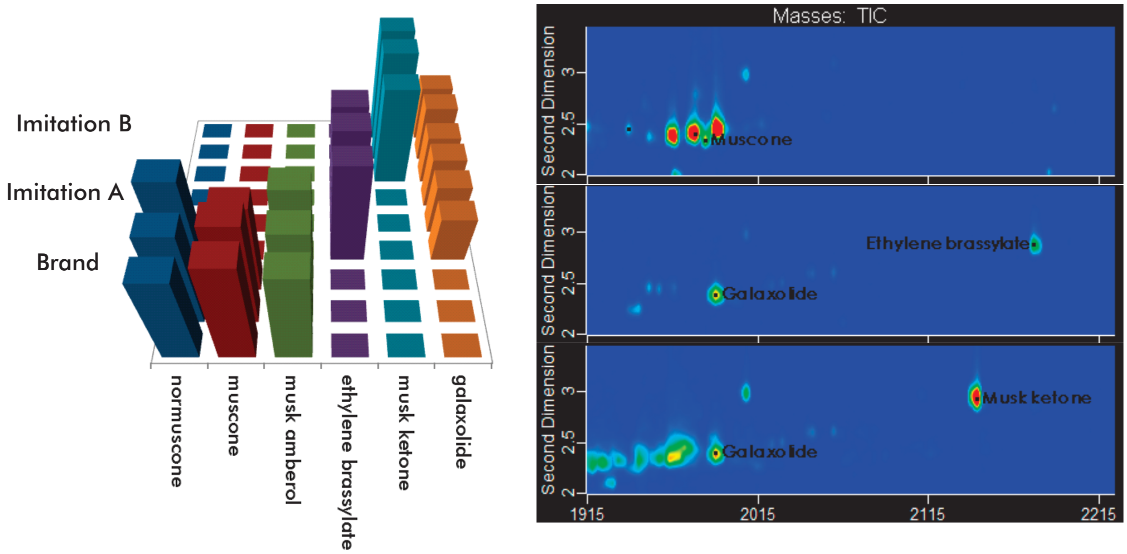


Figure 2. The name-brand ingredients were targeted and identified in each of the samples. Identifications were determined in the name-brand sample through library matching (average similarity = 893), and through accurate mass information (average mass accuracy = 0.52 ppm for molecular ion or highest m/z mass observed). The same analytes were determined in the imitator sample. Each perfume sample was analyzed in triplicate and relative peak areas (normalized to the mean) are shown. Even in the known analytes, some differences are apparent.

While the target analytes do differ, many other differences between the samples were observed both within the data and also in terms of sensory attributes. These differences were investigated through the non-targeted analysis of data, and many specific analyte differences with important odor characteristics were determined. An example of the type of insight that can be gained from this analysis is highlighted in Figure 3 and Table 2. Musk is a common base note in many perfumes and there are many natural and synthetic ways to add musk notes. A collection of analytes that are likely contributing to the musk properties were separated and identified. These are highlighted on the chromatogram in Figure 3 and the identification information is provided in the associated table. These were observed differentially between the samples with each sample having at least one unique musk aroma analyte.



Analyte (CAS)	similarity	formula	obs. mass	calc. mass	ppm	Observed in:
normuscone (502-72-2)	837	$C_{10}H_{15}$	135.11683	135.11683	0.00	**BRAND**
muscone (541-91-3)	875	$C_{16}H_{30}O$*	238.22975	238.22912	2.67	**BRAND**
musk amberol (37609-25-9)	908	$C_{16}H_{28}O$*	236.21331	236.21347	-0.65	**BRAND**
ethylene brassylate (105-95-3)	878	$C_{13}H_{23}O_3$	227.16439	227.16417	0.98	**A**
musk ketone (81-14-1)	928	$C_{14}H_{18}N_2O_5$*	294.12110	294.12102	0.25	**B**
galaxolide (1222-05-5)	878	$C_{18}H_{26}O$*	258.19790	258.19782	0.32	**A & B**

Figure 3. A variety of analytes with musk odor properties were identified within the samples. The analytes were identified through library matching and accurate mass information with metrics compiled in the associated table. Each perfume sample was analyzed in triplicate and relative peak areas (normalized to the mean) are shown. These non-targeted analytes had greater differential expression between the samples than the target analytes with several of the analytes only observed in one of the samples.

This type of information allows for more in depth comparisons of the samples and their sensory attributes. A closer look at the additional odor descriptions for these analytes can uncover important distinctions. Each of these analytes contributes musk odor properties, but also contributes other different odor characteristics. The different choices of analytes to contribute musk by the different manufacturers led to other sensory differences in the samples.

Table 2. Additional Odor Descriptors of Musk Odor Analytes

Odor Descriptor	Musk	Sweet	Animal	Powdery	Fatty	Natural	Greasy	Dry	Amber	Civet	Strong	Diffuse	Floral	Ambrette	Wood	Soapy
normuscone	X		X	X		X	X									
muscone	X	X	X	X	X	X										
musk amberol	X			X				X	X	X						
ethylene brassylate	X	X		X									X	X	X	
musk ketone	X			X	X			X								X
galaxolide	X	X									X	X	X			

4. Conclusion

This study demonstrates the benefits of including non-targeted analysis in place of (or in addition to) targeted screening when characterizing and comparing related samples. A name-brand perfume sample was compared to two drugstore imitations with many specific differences observed. The brand's ingredients were considered to be target analytes and important additional non-targeted aroma differences were also observed. LECO's analytical instrumentation, in particular the *Pegasus* GC-HRT 4D, is well-suited for providing data to determine what else is in a perfume sample. GC×GC offered exceptional separations and chromatographically resolved many analytes within the complex sample into two-dimensional space. HR-TOFMS delivered accurate mass data formula determinations and more confident identifications. More analytes were separated and detected with the improved separation, and more confident identifications of these analytes were achieved with the accurate mass data. The sample differentiation capabilities shown here are broadly applicable to other tasks such as quality control, process optimization, and product development.

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