White Paper 042
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Evaluating the authenticity of brand perfumes

This study demonstrates how the comprehensive data acquired using GC×GC–TOF MS with Tandem Ionisation® can be processed in a single, automated workflow to uncover the subtle differences between brand and imitation fragrances.

Introduction

The global perfumes market was valued at over $30 billion in 2019 and is expected to continue growing.[1] However, this has been accompanied by a rise in counterfeit products and imitation fragrances, sold at significantly lower prices compared to the luxury brands.

The packaging of such counterfeits is often so similar to the known brands that consumers may be unable to distinguish between the genuine and imitation goods. It is therefore important to have reliable quality and authenticity tests to ensure consumers do not receive an inferior product, to protect brand reputation and minimise loss of revenues.

The diverse range of chemical classes in perfumes requires advanced separations to resolve co-elutions and provide identification of the analytes present. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC–TOF MS) can tackle this challenge by coupling two columns of different selectivity to separate the analytes based on two different chemical properties (e.g., volatility and polarity).

Nevertheless, perfumes contain structurally similar compounds (such as terpenes) that can be difficult (or impossible) to speciate when using conventional 70 eV electron ionisation (EI), even with the increased separation capacity of GC×GC. The BenchTOF2-TI™ mass spectrometer used in this study not only provides excellent spectral fidelity, for matching against commercial libraries, but has the added benefit of Tandem Ionisation to provide both hard and soft EI data in a single analysis. The complementary soft EI spectra improves chemical selectivity to enhance untargeted 'discovery' workflows, as required in quality and authenticity evaluation, where you may not know what compounds can be used to differentiate between genuine and imitation products.

Here, we show how the comprehensive data acquired using GC×GC–TOF MS with Tandem Ionisation can be processed in a single, automated workflow to quickly and easily uncover the subtle differences between brand and imitation fragrances, for quality and authenticity evaluation.

Experimental

Samples: Three brand perfumes and three imitation perfumes were analysed in triplicate by GC×GC–TOF MS. The perfumes had three distinct scents – blackberry, pomegranate and lime.

GC×GC: INSIGHT® flow modulator (SepSolve Analytical); Modulation period (P_M): 3.6 s.

MS: Instrument: BenchTOF2-TI (SepSolve Analytical); Mass range: m/z 35–600; Acquisition rate: 100 Hz in Tandem Ionisation mode at 70 and 14 eV.

Software: Full instrument control and data processing by ChromSpace® with ChromCompare+ (SepSolve Analytical) for untargeted chemometrics.

Please contact SepSolve for full analytical parameters.

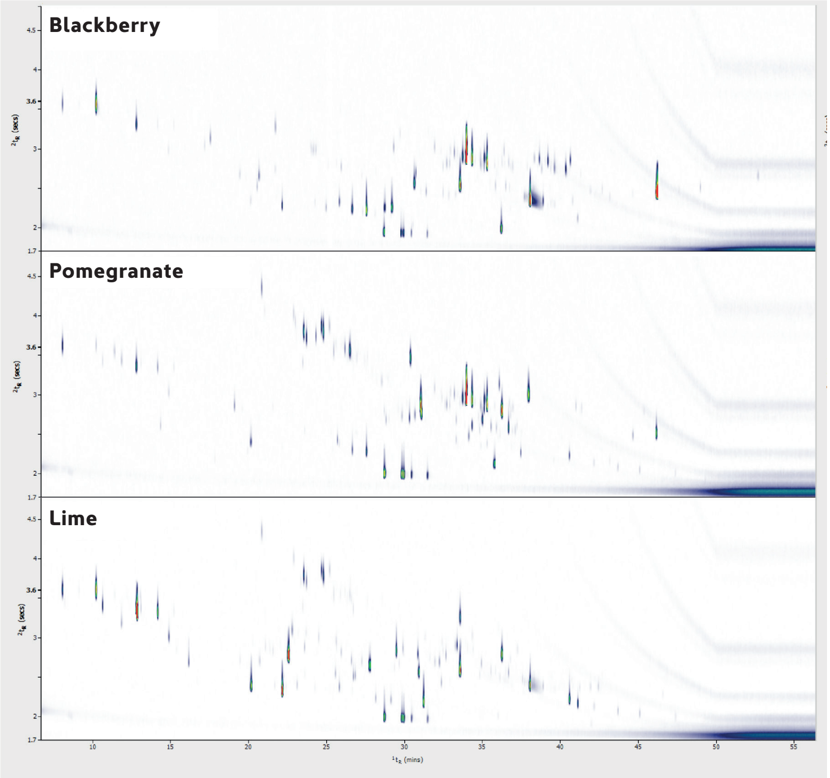
Results and discussion

In this study, three luxury brand perfumes and their imitation versions were analysed. As seen in Figure 1, the brand and imitation fragrances share similar compositions; however, there are differences that can be uncovered easily by GC×GC–TOF MS.

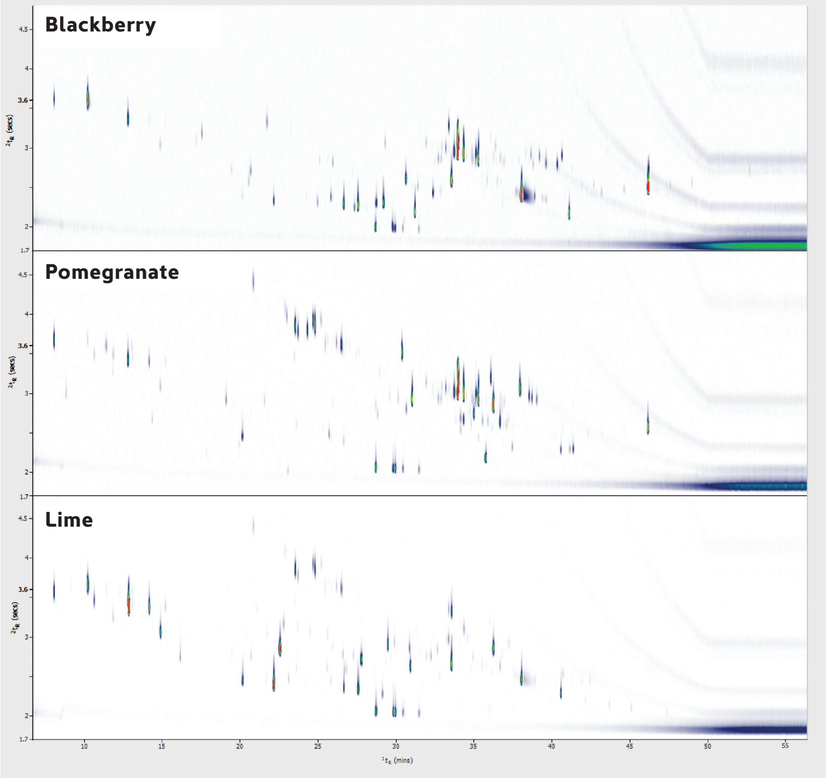
Figure 1

GC×GC–TOF MS colour plots for the three brand and imitation fragrances.

Brand fragrances



Imitation fragrances



Here, Tandem Ionisation was also utilised to improve the selectivity for compounds that share similar spectra at 70 eV (such as terpenes). This enabled both hard and soft EI data to be acquired simultaneously in a single workflow for complementary chemical information with no added analysis time. Figure 2 shows the ‘tandem’ data file, which contains both MS data blocks. Using the tandem format, both sets of spectra can be searched simultaneously against hard and soft ionsiation libraries. ChromSpace software includes simple tools for batch addition of spectra to custom libraries, further streamlining the use of soft EI data.

Name: Caryophyllene
Formula: $C_{15}H_{24}$
MW: 204 Exact Mass: 0 CAS#: 87-44-5
Other DBs: Fine, TSCA, RTECS, HODOC,
Contributor: NIST Mass Spectrometry Dat
10 largest peaks:
93 999 | 133 921 | 91 858 |
69 754 | 105 623 | 107 483 |
Experimental RI median±deviation(#data
Semi-standard non-polar: 1419±3 (983
Standard non-polar: 1419±5 (656
Polar: 1595±16 (57
Related CASNO:
8007-38-3; 1407-53-0
InChIKey:
NPNUFJAVOOONJE-WDZFZDKYSA-N
1tR:
23.76
2tR:
0.000992407798765527
Found in file:
210326_13_Copy POM rep 270eV.tander

Hit No	Name	Formula	Synon	RI	CAS	MW	Library	MF	RMF	Probability
1	Caryophyllene	C15H24	Bicyclo[7.2.0]undec-4-...	1419	87-44-5	204	mainlib	876	872	29.98 %
2	β-Caryophyllene	C15H24	Caryophyllene		87-44-5	204	ti library 14ev	844	846	73.92 %
3	Bicyclo[7.2.0]undec-4-ene...	C15H24	Isocaryophyllene	1406	118-65-0	204	mainlib	842	862	12.75 %
4	Bicyclo[7.2.0]undec-4-ene...	C15H24	Bicyclo[7.2.0]undec-4-...	1490*	13877-93-5	204	mainlib	816	834	3.82 %
5	β-Longipinene	C15H24	(1S,2R,7S,8S)-2,6,6-T...	1403	41432-70-6	204	mainlib	816	838	3.82 %
6	Longifolene	C15H24	1,4-Methanoazulene, ...	1405	475-20-7	204	mainlib	812	822	3.22 %

* -RI Matched using Other non-polar column type

Inlib: -1428

Figure 2

‘Tandem’ GC×GC–TOF MS chromatogram for a perfume showing both 70 eV and soft EI data blocks stored within a single datafile for dual library searching.

Tandem Ionisation is especially useful in the case of isomer identification, such as the diverse range of terpenes and terpenoids found in fragrances. For example, Figure 3 shows spectral comparisons for two isomers of guaiene, with enhanced differences in ion ratios obtained when using soft EI, for improved confidence in isomer speciation.

In this study, the Tandem Ionisation data was also used to improve discovery of true differences between the brand and imitation perfumes, using novel automated workflows in ChromCompare+ software.

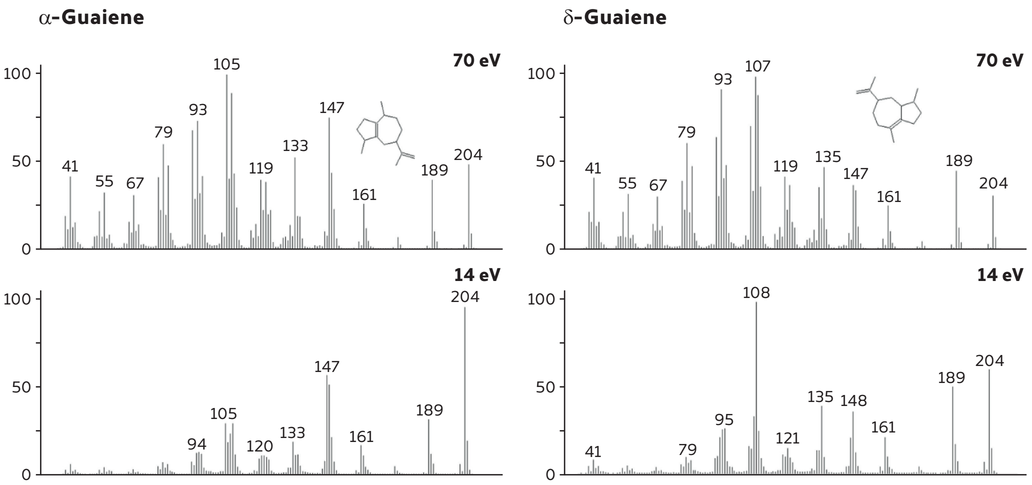


Figure 3
Comparison of the mass spectra for two isomers of guaiene found in the pomegranate fragrances using Tandem Ionisation at 70 eV and 14 eV.

This approach divides the chromatogram into small tiles and sums the signal for every individual m/z channel in each tile for comparison between samples. Time-consuming pre-processing steps, such as integration and identification, are eliminated and all of the raw data is used, minimising the risk of missing important details. By utilising both sets of MS data in a single workflow, discovery of true differences is improved through reduction of false positives. Find out more about these tandem workflows in our technical note 'Improving discovery workflows using Tandem Ionisation data'.

The principal components analysis (PCA) score plot in Figure 4 shows the comparison of all six perfumes (run in triplicate). The brand and imitation versions of the pomegranate fragrance appear to be most similar in composition as they cluster closely in the PCA plot, while those of lime and blackberry appear to be more distinct.

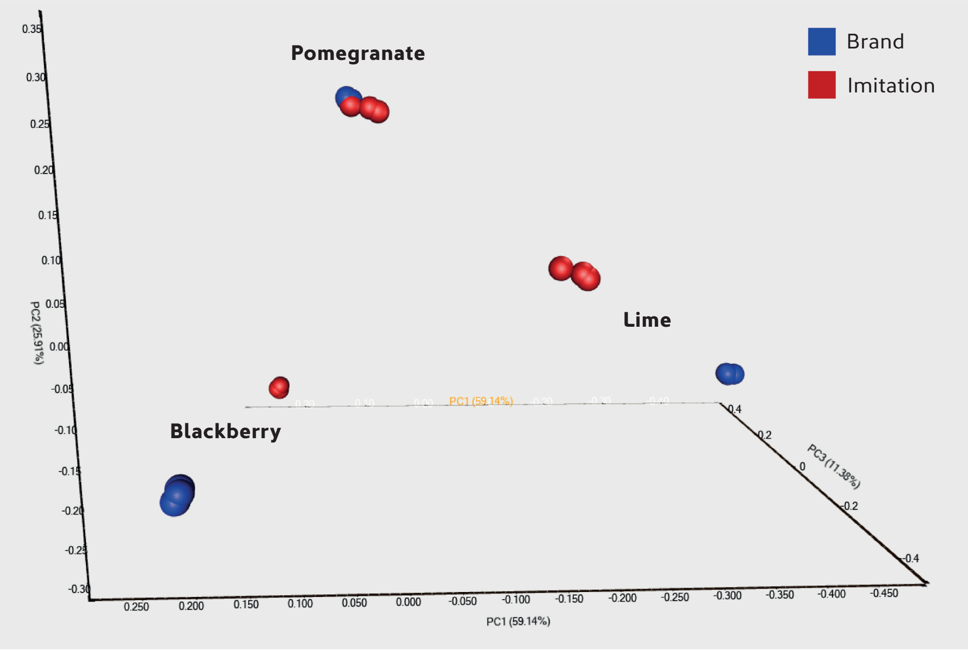


Figure 4
Principal components analysis (PCA) score plot in ChromCompare+ software for the top 15 most significant features found for the comparison of the perfume samples using tandem GC×GC–TOF MS data.

Using the Feature Discovery tool, the top 10 differentiating features between the brand and imitation versions were found for each fragrance and were identified using BenchTOF2™ MS (Figure 5).

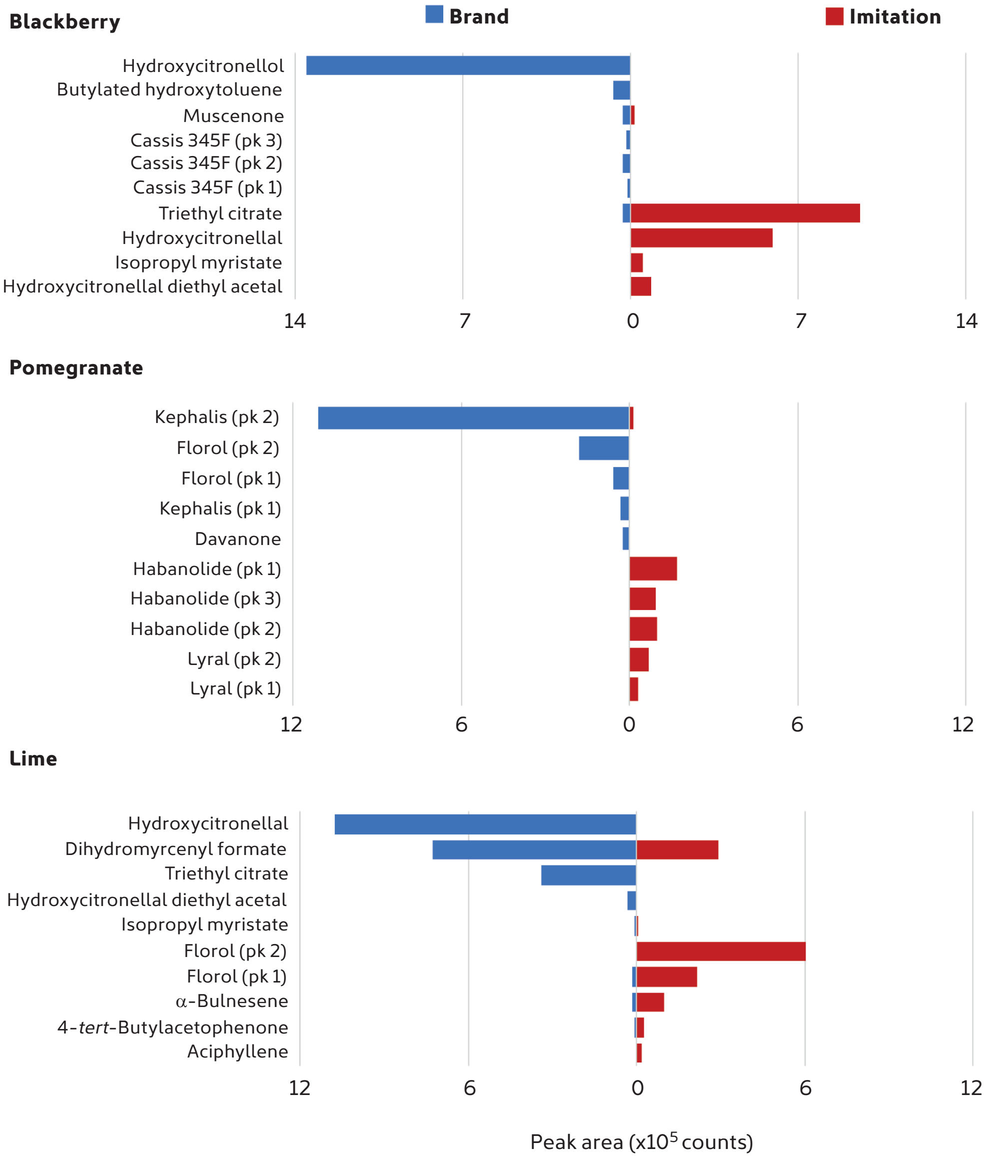


Figure 5

Comparison of extracted ion chromatogram peak areas for the top differentiators identified by ChromCompare+ for the brand and imitation versions of each fragrance.

Interestingly, the imitation pomegranate fragrance was found to contain the two isomers of lyral (also known as 3- and 4-(4-hydroxy-4-methylpentyl)cyclohex-3-ene-1-carbaldehyde, or HICC). Lyral is now banned under Regulation (EU) 2017/1410 (an amendment to Regulation 1223/2009/EC), due to the high risk of contact allergy associated with this compound.[2] The amendment calls for all non-compliant cosmetics to be withdrawn from the market by 23 August 2021.

On the other hand, a number of the differentiators found only in the brand perfumes are described as 'long-lasting' base notes – such as kephalis and muscenone – and as such, these are potential markers of quality when comparing brand and imitation products.

It is important to note that the use of tandem data to confirm positive hits during Feature Discovery improved the discovery of subtle, trace differences by suppressing false positives. When the top 50 differences for the brand and imitation fragrances were compared using the tandem data and then using 70 eV data alone, two true differences were listed for the tandem dataset that were not found amongst the top 50 differences when using 70 eV data alone. Therefore, using tandem data to cross-confirm the positive hits during Feature Discovery can provide more confidence that true differences have been found, by reducing the number of false positives for review.

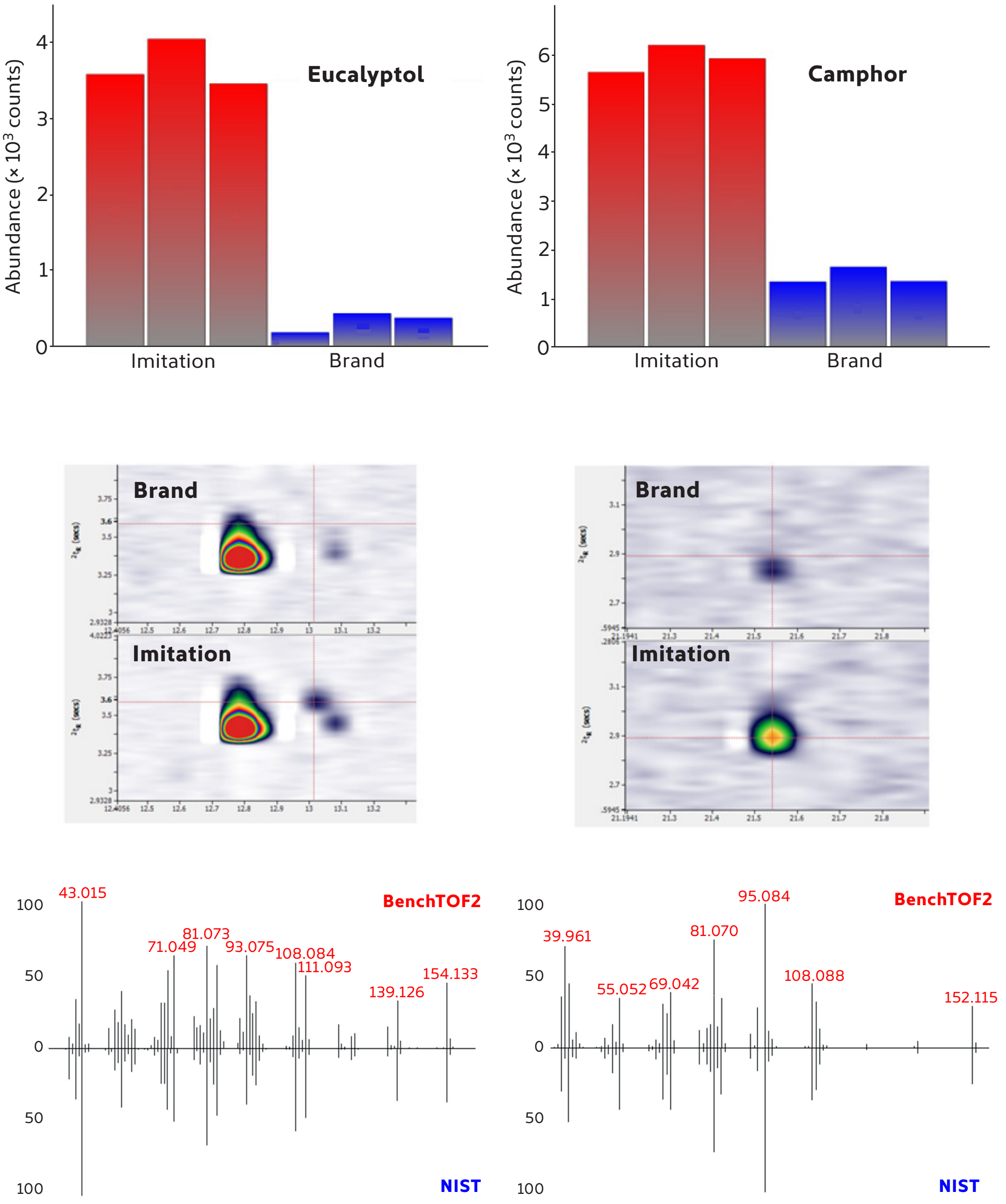


Figure 6

Two differences between the pomegranate brand and imitation fragrances that were not found using 70 eV alone. Top: Feature summary charts in ChromCompare+; Middle: GC×GC–TOF MS colour plots showing the relevant region of the chromatogram for the feature; Bottom: Feature identity revealed using comparison of BenchTOF2 spectra against the NIST20 library.

Conclusions

This study has shown that the combination of GC×GC–TOF MS with Tandem Ionisation and powerful chemometrics provides comprehensive fragrance profiling to aid quality and authenticity evaluation, specifically:

- Enhanced separation of GC×GC, combined with the excellent spectral fidelity of BenchTOF2-TI, enables confident identification of analytes in fragrances.
- Tandem Ionisation adds an extra level of confidence through complementary hard and soft EI data, with innovative tools to harness the power of both data blocks in a single, streamlined workflow.
- Fast and confident identification of key quality markers using untargeted data analysis in ChromCompare+ chemometrics software.
- An end-to-end workflow for fragrance profiling, with full instrument control and data analysis in a single user interface.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

References

[1] Perfumes Global Market Report 2020, https://www.researchandmarkets.com/reports/4900602/perfumes-global-market-report-2020.

[2] Commission Regulation (EU) 2017/1410 of 2 August 2017, amending Annexes II and III to Regulation (EC) No 1223/2009 of the European Parliament and of the Council on cosmetic products, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32017R1410.