

Fragrance analysis using Fast GC– and GC×GC–TOFMS



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Introduction

Samples analysed in flavour & fragrance studies are by their very nature extremely complex. Being able to detect unknowns, allergens and/or pesticides in these matrices presents major issues for the analyst. Additionally, matrix interference and the levels at which specific analytes need to be reported compound these difficulties. This poster discusses the use of Fast GC- and GC×GC–TOFMS in this context.

The benefit of Fast GC–TOFMS is that all full range mass spectral information is always collected. By taking advantage of high data acquisition rates (up to 500 spectra sec⁻¹) chromatographic peaks do not require baseline separation for quantification and closely eluting peaks are readily resolved by deconvolution algorithms. Using this approach removes the need for single ion monitoring (SIM).

Comprehensive gas chromatography (GC×GC) enables the continuous flow to one detector from a single sample injection and offers an enormous benefit to the analyst. For quantification, an additional benefit of using GC×GC is the ability to choose a lower intensity, but higher *m/z* ion as a quantification mass due to the re-focusing effect of thermal modulation increasing peak height.

Analyses by GC×GC–TOFMS used a primary column (VF5-ms, 30 m x 0.25 mm x 0.25µm) as a boiling point separation and a secondary column (VF17-ms, 2 m x 0.18 mm x 0.2 µm) as a polar separation. Using this column set allergens were automatically identified and quantified in four different high-quality perfumes. Furthermore, issues associated with matrix effects can also be overcome by optimising peak separation in both dimensions.

Using GC– & GC×GC–TOFMS it is possible to achieve both non-target and target analysis in one sample run. The acquired raw data are simply processed according to what result is required – specific allergens or alternatively to provide a data set that can investigate ‘unexpected’ or ‘unknown’ analytes similar to the analytical approach of the Metabolomics community.

Modern methods that use Time-of-Flight mass spectrometers (TOFMS) such as GC- & GC×GC-TOFMS vastly increase the information gleaned from a single sample injection [1]. Dallüge *et al.* [2] reported that only detectors able to acquire fifty or more spectra per second enable effective reconstruction of the two dimensional chromatogram and subsequent quantification. Currently, the only compatible MS is time-of-flight mass spectrometry (TOFMS) and Cochran [3] describes the advantage of GC×GC for eliminating potential quantification bias when the matrix contains the same *m/z* ions used to quantify analytes of interest. Furthermore, Dallüge *et al.* [4] and Shellie *et al.* [5] concluded that GC×GC–TOFMS provides a reliable basis for the automated analysis of complex samples.

Key terms: GC–TOFMS, GC×GC–TOFMS, comprehensive GC–MS

Instrumentation & Method parameters

MPS 2 Autosampler (GERSTEL)
6890 GC (Agilent)
1st Column: VF5 30 m x 0.25 mm x 0.25 µm
2nd Column: VF17 2 m x 0.18 mm x 0.2 µm

Pegasus 4D GC×GC-TOFMS system

Sample volume.....1 µl
Constant flow.....2 ml/min
Ion source temperature.....200 °C
Data Acquisition rate.....200 spectra/sec
Splitless & Split injections (10:1)
GC run time.....23 min

GC Oven modifications for GC×GC
Quad Jet - Built by LECO under license
from Zoex Corporation

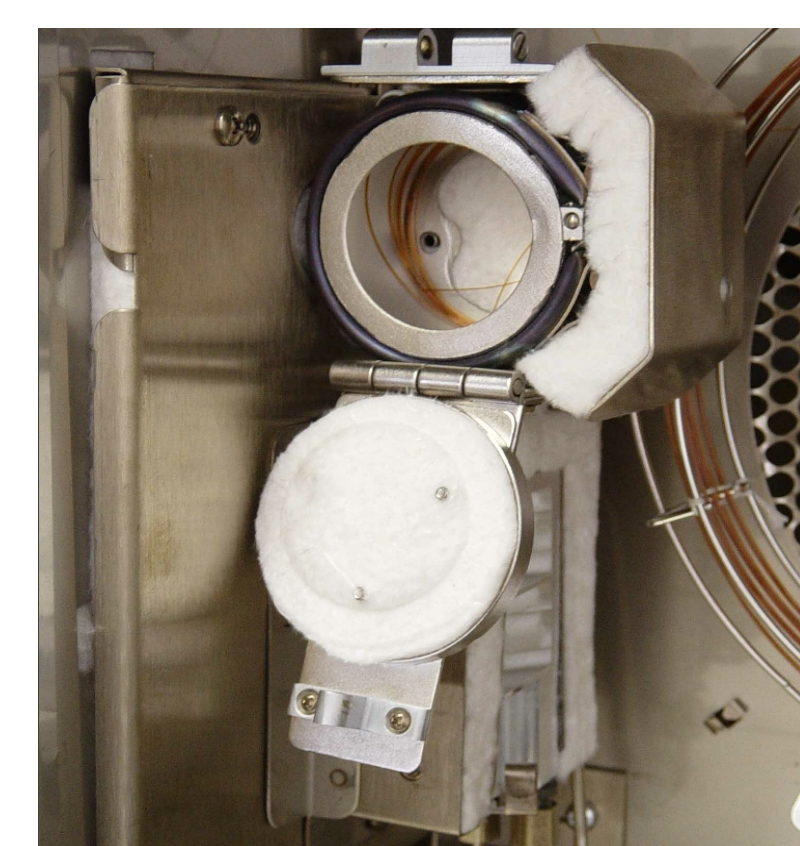


LECO Pegasus 4D GC×GC–TOFMS

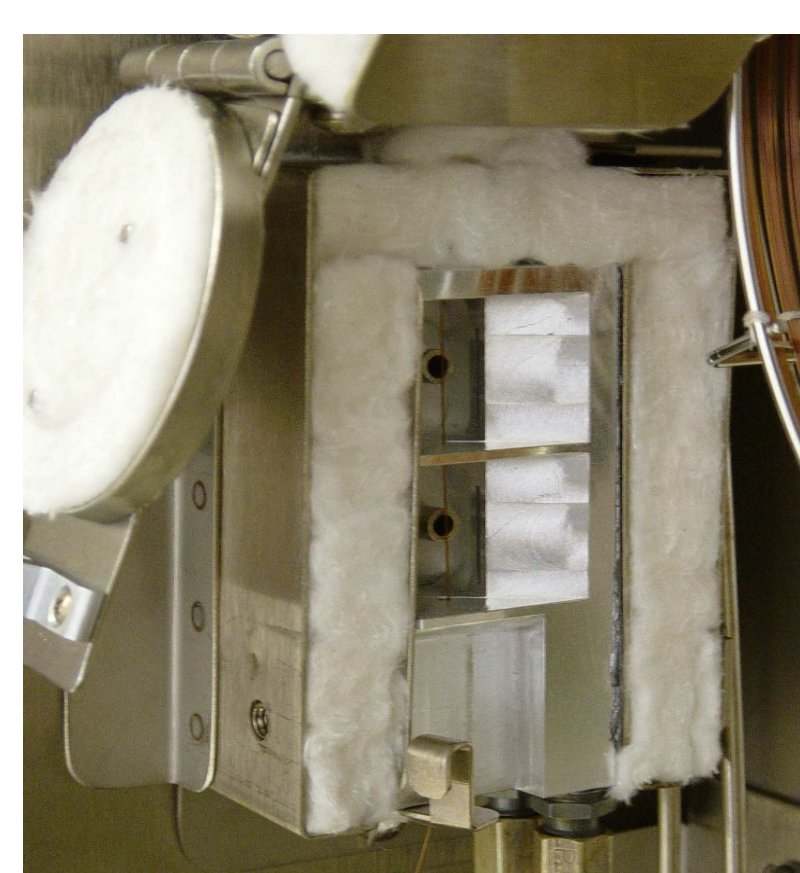
Allergenic compounds in Perfume

Linear calibration data for 32 analytes over the 0.05 – 20 ppm range were used to quantify known allergens.

Each perfume was analysed for allergens using a Pegasus 4D GC×GC-TOFMS. Identified allergens can automatically be quantified using ChromaTOF® software.



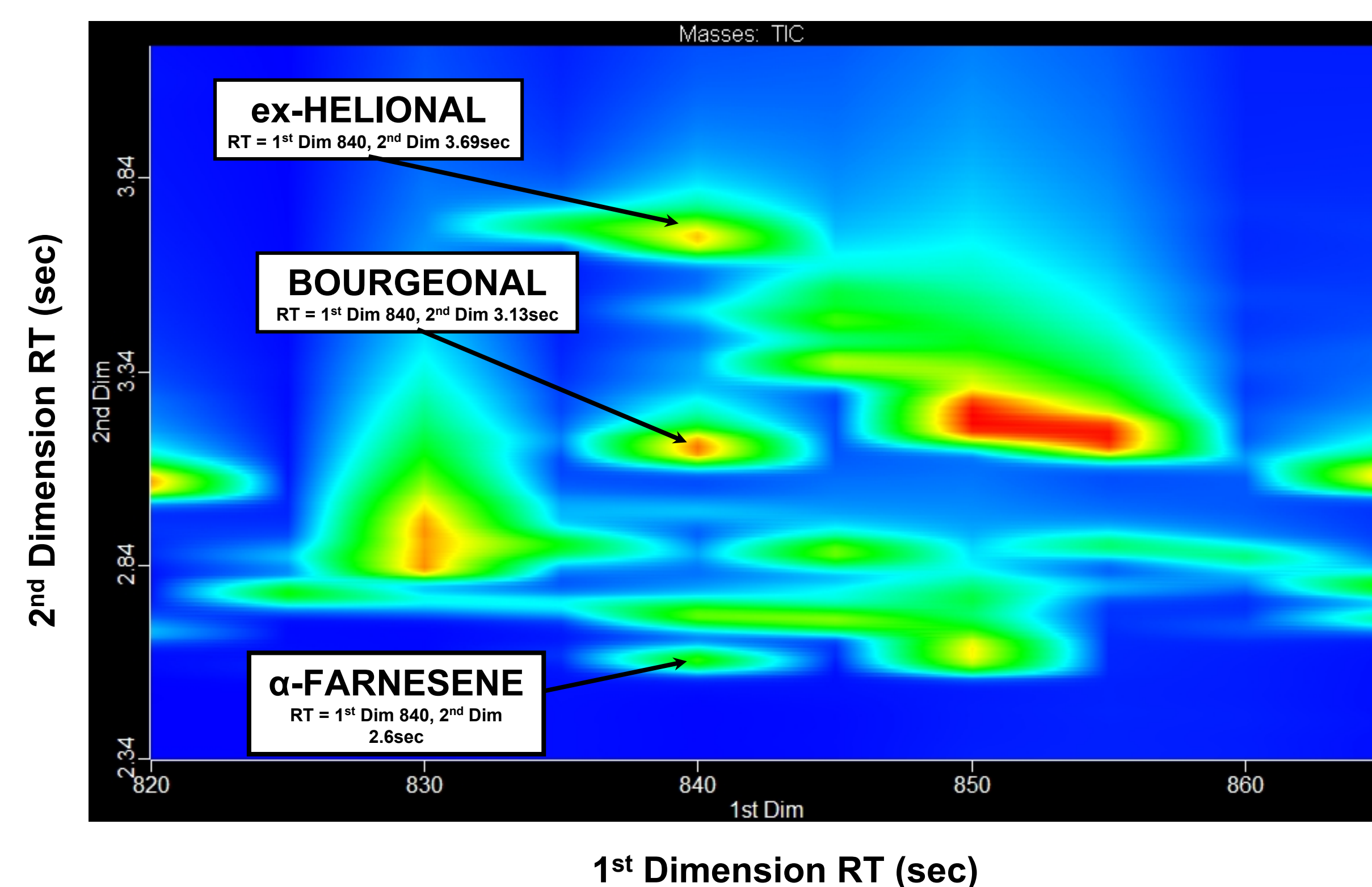
Second dimension oven for more chromatographic flexibility



Two-stage cryogenic quad-jet modulator

Fingerprinting approach for Fragrance analysis using GC×GC–TOFMS

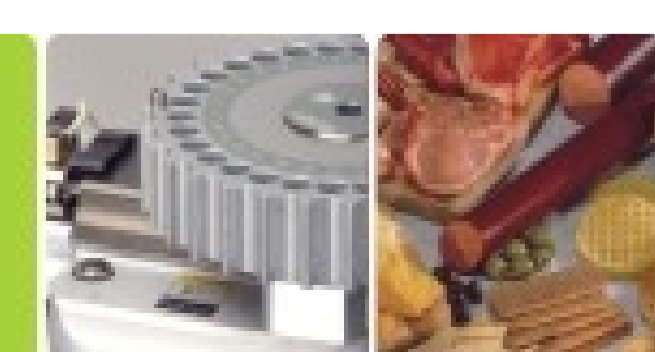
- > Fingerprinting is a non-target approach to analyses extremely complex samples that exhibit a wide dynamic range of analyte concentration
- > Each perfume chromatogram was hence re-processed using a fingerprint approach to investigate all analytes
- > Using comprehensive GC×GC-TOFMS the separation of over 7 800 chromatographic peaks was achieved
- > Of the separated peaks 657 had over 80% similarity to a spectrum of a in-house library
- > The zoomed contour plot shows analytes from one perfume sample with identical 1st dim RT (840 sec) that separated easily in the 2nd dimension
- > ex-Helional, Bourgeonal & α-Farnesene had spectral library matches of 74%, 88% & 95% respectively



GC×GC-TOFMS analysis of a high quality perfume showing coelutions of three analytes in the 1st dimension that are easily separated in the 2nd dimension.

Instrumentation & Method parameters

- [1] P. J. Schoenmakers, J.L.M.M. Oomen, J. Blomberg, W. Genuit, G. Van Velzen, *J. Chromatogr. A.*, 892 (2000) 29.
[2] J. Dallüge, R.J.J. Vreuls, J. Beens, U.A.Th. Brinkman, *J. Sep. Sci.*, 25 (2002) 201.
[3] J. Cochran, *J. Chromatogr. A.*, 1186 (2008) 202.
[4] J. Dallüge, L.L.P. van Stee, X. Xu, J. Williams, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, *J. Chromatogr. A.*, 974 (2002) 169.
[5] R. Shellie, Ph. Marriot, *J. Flavour Fragr.*, 18 (2003) 179.



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