

Flavour & Fragrance analysis: Easy heart cut MDGC with mass spectrometric detection in 1st and 2nd dimension

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Introduction

Food, Flavour and fragrance products are well known as complex mixtures. The analyses of these matrices are carried out to determine the composition of the products, to control the quality, to determine adulteration or product counterfeiting. Proper characterisations of the enantiomeric composition can provide information's on the genuineness, geographic origin, biogenesis and the quality of the product. Chiral separation of (+) and (-) enantiomers are possible with a cyclodextrine-based capillary column.

Multidimensional GC

Due to the high level of complexity sometimes a one dimensional gas chromatographically approach is not sufficient to separate the analytes of interest. In order to separate those non separated regions they can be transferred into a second column using heart cut multidimensional gas chromatography GC/GCMS. Using a multidimensional gas chromatography system with the coupling of a non-chiral pre-column and a chiral analytical column a direct chiral analysis is possible without any further clean-up or derivatisation procedure.¹

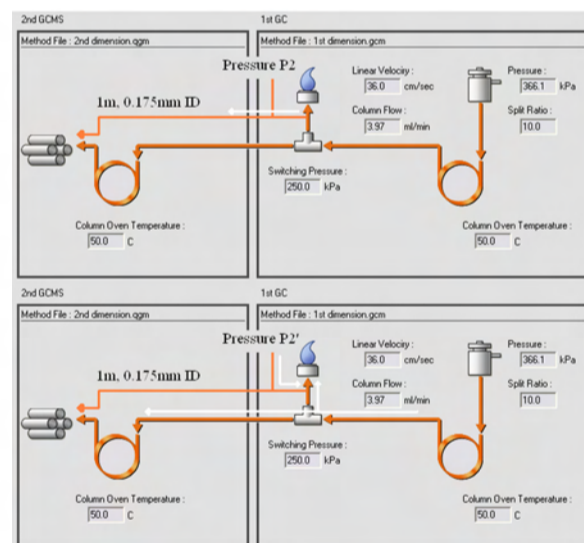


Fig 1: Flow diagram of the MDGC 2010 configuration including FID-MS splitting in standby mode (top) and no splitting in cut mode (bottom)

Multi Deans Switch

By using the recently developed multi deans switching technique (MDGC-2010 Shimadzu) the outlet pressure for the 1st column is not changed even when switching is performed. This enables an easy multiple heart cut method set up. A GC 2010 equipped with an FID for the 1st dimension was coupled with a GCMS-QP2010 Plus for the 2nd dimension. A polar column (Carbowax, 30 m, 0.25 mm, 0.25 µm) was connected via the switching device with a chiral column (RTX 30 m, 0.25 mm, 0.25 µm) in order to perform enantiomeric separation. In standby mode,

a reference run without any transfer to the second column, an FID chromatogram is achieved. This FID response can be used to perform an area normalization report and to define the cut positions.

Splitting System

To have also identification in the first dimension a FID-MS capillary split connection was installed for simultaneously FID and MS detection. Capillaries, the split connection and the second dimensional column were mounted into the MS detector using a special connector.² To prevent interferences from the FID-MS splitting and the peaks passing the second column, the split line is blocked in cut mode by an increase of the pressure P2 to P2' corresponding to Fig.1. Therefore the pressure P2 decides either there is FID-MS splitting of the 1st dimension chromatogram or not. This pressure value is stored as part of the method file and an easy change between splitting and no splitting therefore is possible.³

Analysis of lavender oil

A commercial lavender oil was injected. Fig. 2 shows the FID chromatogram of lavender oil without cut positions and the chromatogram below present the simultaneously detected MS chromatogram. The Retention time difference of a peak in the FID and MS chromatogram is less than 0.01min. The FID-MS splitting ratio is about 1:1/15.

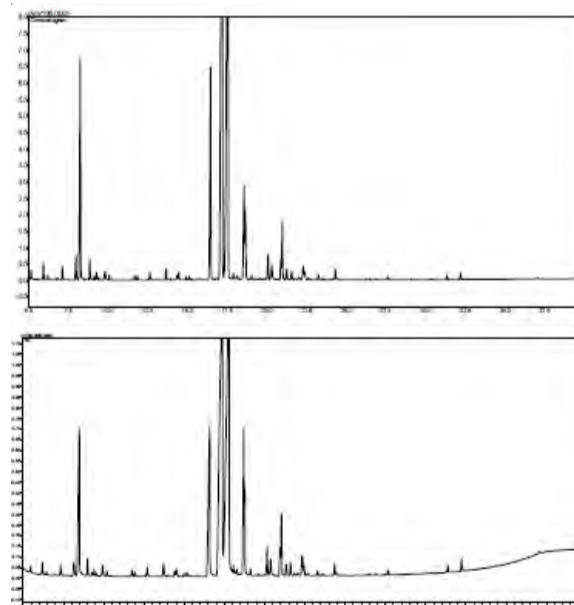


Fig. 2: Standby chromatograms of lavender oil, FID chromatogram (top), MS TIC chromatogram (bottom)

Different cut positions were defined by just double clicking in the uncut chromatogram using the MDGCsolution software.³ Fig. 3 shows the 1st dimension FID chromatogram of lavender oil in standby mode and with several cut positions. The cut peaks are totally transferred (100% recovery) to the second column, where the chiral separation can be performed. The

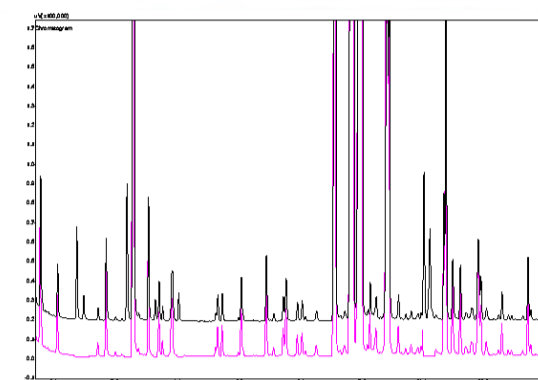


Fig.3: FID chromatogram uncut (black) and with several cuts in one run (purple)

identification was done with the FFNSC 1.3, a library which was specially developed for flavours and fragrances (available from Shimadzu Europa GmbH). Fig. 4 presents the enantiomeric separation of sabinene, beta-pinene, and limonene.

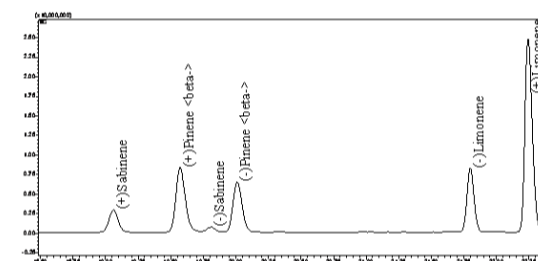


Fig. 4: Enantiomeric separation of the first 3 cut portions in lavender oil

Fig. 5 compares the enantiomeric separation of linalool. The predominance of a single linalool enantiomer indicates the natural source of linalool in this commercial lavender oil. The balanced dominance of both linalool enantiomers in the commercial peach aroma indicates a synthetic source of linalool. This multidimensional GC/GC-MS system enables easy and reliable determination of flavours and fragrances. With the parallel FID-MS detection in the first dimension both, the FID area normalisation report and a simultaneous identification, was obtained. Due to the identification in the first dimension regions of co-eluting peaks can be easily determined.

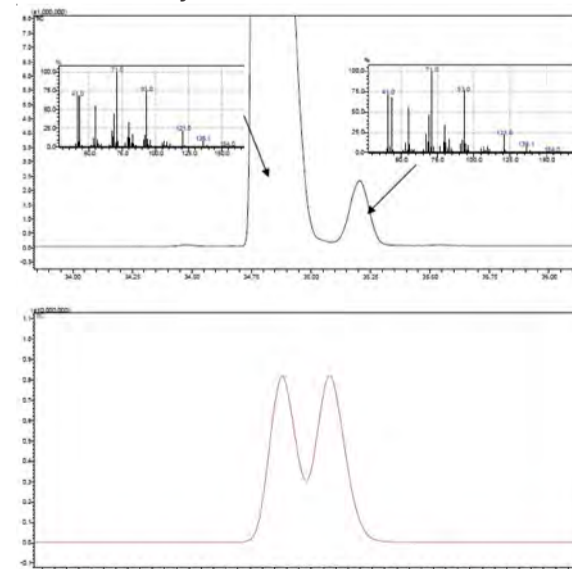


Fig. 5: Comparison of enantiomeric separation of linalool in lavender oil (black) and peach aroma (purple)

[1] L. Mondello, A.C. Lewis, K.D. Bartle Multidimensional Chromatography, 2002, (217-223)

[2] S.Böhme, H.U. Baier, „Easy Heart-cut MDGC with Mass Spectrometric Detection in 1st and 2nd Dimension LCGC Application Book July/August 2009 (31-32)

[3] Shimadzu Application note SCA-180-017 „Introduction of MDGCsolution“