

Allergen screening in commercial cosmetics by using multiple heart-cut Multidimensional Gas Chromatography with Mass spectrometric detection



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The International fragrance association (IFRA) defined 24 volatile chemicals as potential allergens which have to be labelled on commercial cosmetic products. The quantitative determination of these potential allergens with conventional gas chromatographic approaches can give imprecise or even false results due to the high complexity of the real sample. To avoid interferences of allergens with matrix compounds multidimensional gas chromatography (MDGC) with multiple heart-cutting is one powerful approach. The components of interest are transferred from the first analytical dimension to the second, which increases drastically the peak capacity. As transfer device the

recently developed Multi-Deans switching unit (MDGC-2010, Shimadzu) was used in combination with a GC-FID (GC-2010, Shimadzu) as the first analytical dimension and a GCMS (GCMS-QP2010 Plus) as the second analytical dimension. The Multi-Deans switching device consists of an advanced pressure control, which supplies carrier gas at a constant pressure, to a valve unit, which is not placed in the analytical line. With the use of a pressure-balance mechanism the analytes are either passing the first column and are detected in the FID („stand-by mode“) or are transferred to the second column and analysed with the mass spectrometer („cut mode“).

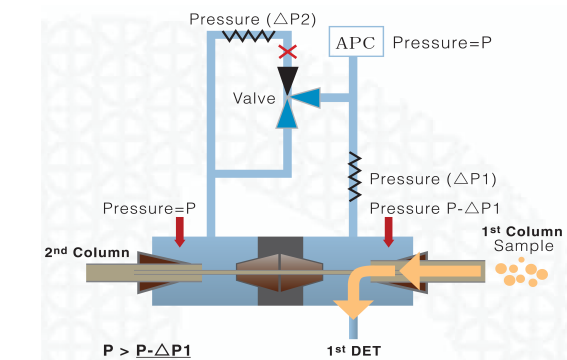


Fig. 1: Standby mode

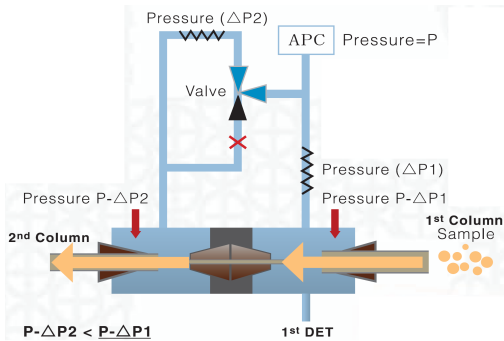


Fig. 2: Cut mode

An allergen standard is injected into the first analytical dimension to define 24 cut positions. The allergens are transferred into the second analytical dimension, where the qualitative and quantitative analysis in full scan mode is done.

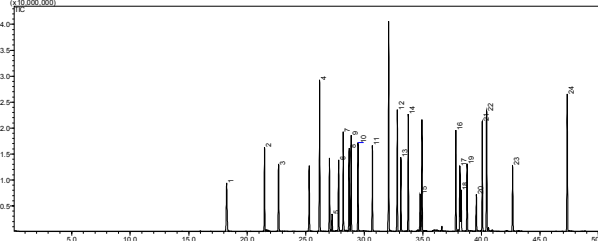


Fig. 3: TIC of 24 cut allergens

Due to the Multi-Deans switching unit only one reference chromatogram (allergen standard injection) is necessary to build up the multiple heart-cut method. A polar column (Carbowax, 30 m, 0.25 mm, 0.25 μ m) in the first analytical dimension turned out to give the best separation, which is necessary to define precise heart-cuts. An optimized temperature program from 60 °C to 100 °C with 20 °C/min and from 100 °C to 250 °C with 7.5 °C/min was used in the first GC oven. To increase the separation capacity an unpolar column (5 % Phenyl, 30 m, 0.25 mm, 0.25 μ m) in the second dimension was used with a temperature program from 40 °C to 280 °C after a holding time of 15 min at 40 °C. The identification was done with the FFNSC 1.2, a library which was specially developed for flavours and fragrances (available from Shimadzu Europa GmbH).

Calibration Curves with regression coefficients better than 0.999 have been obtained for all potential allergens, which indicates 100 % recovery of the cut allergens. The retention time precision in both analytical dimensions is the same like in standard chromatography.

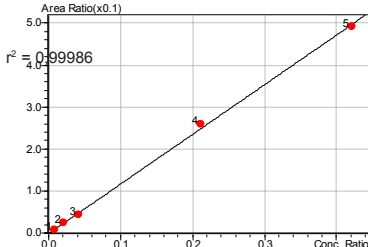


Fig. 4: Calibration Curve of Coumarin

Due to the heart-cut screening method the potential allergens in commercial cosmetic samples, perfume and extract of a crème have been analysed. The results are shown in Table 1.

ID	Allergens	Parfume	Concentration (ppm)	Extract	Concentration (ppm)
1	Limonene	x	1.236	x	0.005
2	Linalool	x	0.867	x	0.145
3	Benzyl alcohol	x	0.624	x	0.006
4	Follione				
5	Citronellol	x	1.321		
6	Citral	x	0.179		
7	Geraniol			x	0.084
8	Citronellal, hydroxy				
9	Cinnamaldehyde				
10	Anisyl alcohol			x	0.011
11	Cinnamyl alcohol	x	0.062	x	0.013
12	Eugenol	x			
13	Isoeugenol				
14	Coumarin	x	0.963		
15	Gamma-Methylionon	x	1.057		
16	Lilial				
17	Cinnamaldehyde <amyl->				
18	Lyral	x	0.026		
19	Cinnamyl alcohol <amyl->			x	0.024
20	Farnesol			x	0.017
21	Hexyl-Cinnamaldehyde				
22	Benzyl Benzoate	x	0.764		
23	Benzyl cinnamate	x	0.362		
24	Benzylsalicylate				

Tab. 1: List of allergens with determined concentrations

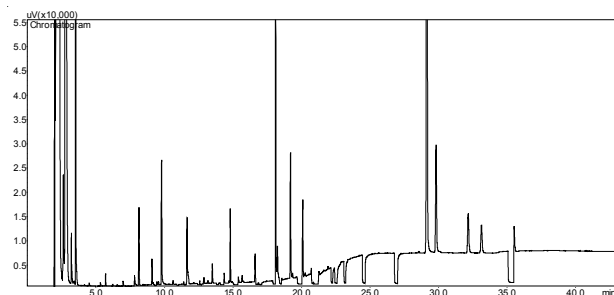


Fig. 5: FID chromatogram of real sample with cut positions

Conclusion

Multidimensional gas chromatography with Multi-Deans switching device is a powerful approach to solve interference problems in complex samples. Due to the Multi-Deans switching device (MDGC-2010) and the MDGC Software (MDGC Solution) Shimadzu Europa GmbH offers a ready to

Literature

1. L. Mondello, Luigi Mondello, A. Casilli, P. Q. Tranchida, G. Dugo and P. Dugo et al: Journal of Chromatography A, 1067 (2005) 235–243