

The Determination of Allergens in Fragrance Products

Fast GCMS with narrow bore Columns

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The determination of 24 Allergens in cosmetic products has become an important issue due to the procedure described by the IFRA (International Fragrance Association) [1]. Where fragrance products like perfumes can be diluted and measured with GCMS directly products like creams and lip sticks need preparation. The latter can be done either by the difficult matrix introduction technique [2] or by SPME/GCMS [2]. The analysis time needed to separate 24 allergens is rather large. This can be seen from fig 1. where a TIC from a standard is shown by using a 50 m, 0.25 µm, 0.25 mm column.

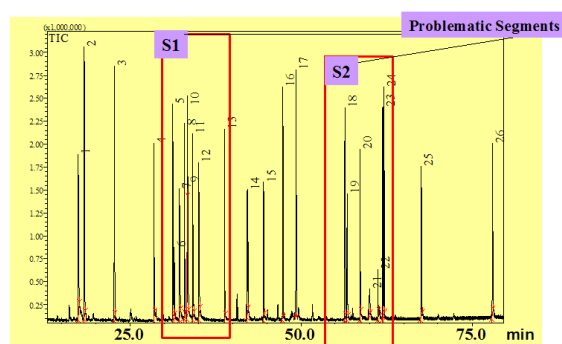


Fig.1: Full scan of an allergen standard containing 24 allergens. Column oven: 50 °C 1min, 2 °C/min to 210 °C then 10 °C/min to 280 °C, 10 min, He 34 cm/s, split ratio 300:1, 200-400 ppm

Fast GCMS by using narrow bore columns has become a reliable routine tool by maintaining most of the chromatographic resolution. Here very often a factor of about 10 can be achieved in reduction of analysis time. The GC and MS hardware however need to fulfil some requirements for effectively using the resolving power and to get accurate and reliable data. Regarding the GC the parameters are described elsewhere [3]. For the MS part both the scanning rate (amu/s) as well as the number of scan (or SIM) data points are important. This is the case as in full scan the spectrum quality need to be high in order to get good library search results. The number of data

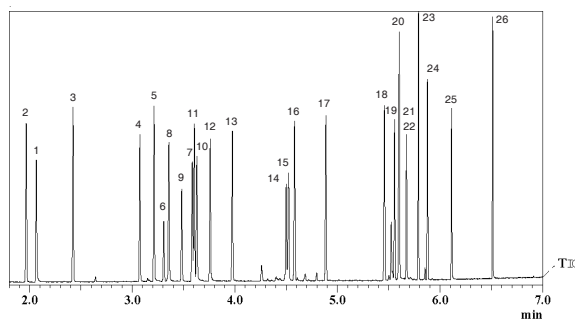


Fig 2: Full scan analysis of the allergen standard by using a SPB5 10 m, 0.1mm, 0.1 µm column. Column oven: 50 °C 1 min, 25 °C/min to 180 °C then 80 °C/min to 250 °C, linear velocity 50 cm/s. Split ratio 300:1, MS: 20 spectra/s at 10000 amu/s, scan range 30 – 350 Da.

1. Benzyl Alcohol	14. Coumarin
2. Limonene	15. Iso-Eugenol
3. Linalol	16. Methyl Gamma Ionone
4. Methyl HeptinCarbonate	17. Lillial
5. Citronellol	18. Amyl Cinnamic Aldehyde
6. Citral (Neral)	19. Lyrall
7. Cinnamic Aldehyde	20. Amyl Cinnamic Alcohol
8. Geraniol	21. Farnesol 1
9. Citral (Geranial)	22. Farnesol 2
10. Anisic Alcohol	23. Hexyl Cinnamic Aldehyde
11. Hydroxy Citronellal	24. Benzyl Benzoate
12. Cinnamic Alcohol	25. Benzyl Salicylate
13. Eugenol	26. Benzyl Cinnamate

points acquired across a peak need to be high enough to have reproducible data. In figure 2 the TIC data of the standard is shown by using a SPB5 10 m, 0.1 mm, 0.1 µm column.

The analysis time is less than 7 min without loss of resolution. The peak width at half maximum for linalool for instance is about 0.6 s and the MS was set to acquire 27 data points across the peak. The resulting scan speed was then 10000 amu/s. To show that there is no skewing of the spectrum in the peak rise, top or descent figure 3 shows the spectra of 3 points for linalool after background subtraction.

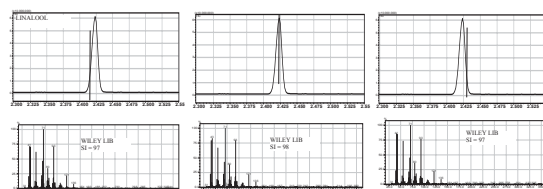


Fig.3: Spectra quality within the peak of linalool as an example at peak rise – top – descent after background subtraction

The similarity index is 97 – 98 - 97 at rise - top - descent, respectively indicating the high quality of the spectra at any data point.

To have quantitative results calibration curves were measured between a minimum of 10 and maximum of 410 ppm with 6 replicates each level. This is shown in figure 4 for the compounds limonene and lyrall.

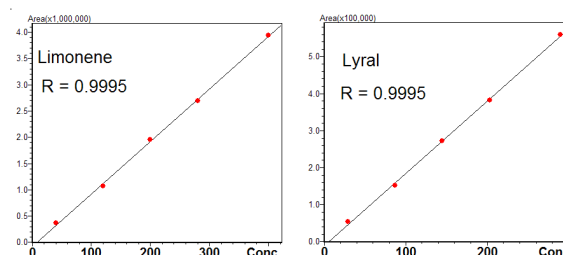


Fig.4: Calibration curves for limonene (40 to 400 ppm) and lyrall (29 to 290 ppm)

The correlation is R = 0.9995 for most of the compounds. The method was then adapted to real samples. The figure 5 shows full scan data of an eau de toilette diluted in acetone.

Eau de Toilette diluted in Acetone 1:100

Name	Conc.	SI
Methyl-Gamma-Ionone	74.5 ppm	94
Lillial	129.7 ppm	93
Lyrall	99.4 ppm	98
Benzyl Salicylate	96.6 ppm	95

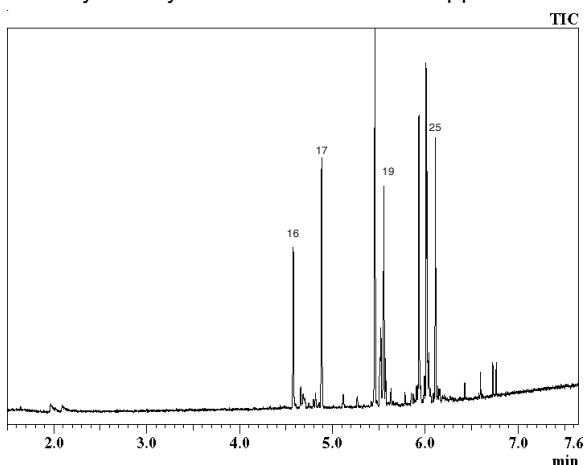


Fig.5 : Full scan of an eau de toilette diluted in acetone 100:1 recorded with fast GCMS. Split ratio 300:1

In the procedure given by the IFRA a SIM method is described and therefore the reproducibility of the above method was tested in SIM as well.

Figure 6 shows 6 successive runs of amyl cinnamic aldehyde as an example. Sim traces were measured with 41, 91, 145, 202 Da. The reproducibility was less than 1.5 %RSD.

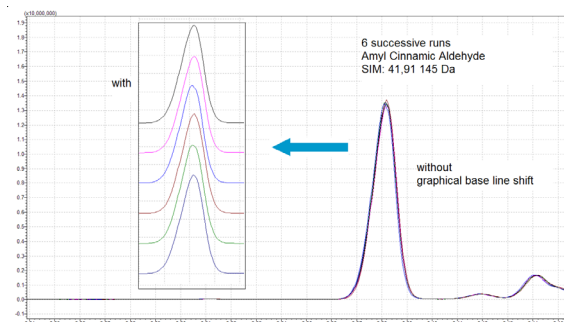


Fig. 6: SIM traces of 6 successive runs. 41, 91 and 145 Da. The Graphs represent the TIC of all three.

Conclusion

Fast and high resolution GCMS analysis can be done very reproducibly with the GCMS-QP2010. The %RSD values for replicates for Scan and SIM data were better than 2%. The above method therefore is suitable for routine analysis of allergens in fragrance products

- [1] <http://www.ifra.org/Enclosures/News/AnalyticalProcedureFragAllerfinal.pdf>
- [2] H.-U. Baier, (DMI with ATAS Optic 3), to be published
- [3] H.-U. Baier, poster p125 ISEO 2004