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Determination of 59 potential Allergens in Perfumes by twin-line fast GCMSMS

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Introduction

Several chemicals in fragrance products like perfumes or shower gels can cause allergic reaction. These compounds are defined as potential allergens and 24 chemicals plus 2 isomers were regulated by the EU.[1] Cosmetic products are subdivided into leave on (e.g. perfumes, cremes) or rinse off (shower gels, soaps etc.). The analytical method was using GCMS with two columns of different polarity to avoid coelutions. The most efficient setup has been to use two columns connected to two different split/splitless injectors mounted straight into the interface of one mass spectrometric detector.[2] The scientific committee on consumer safety proposed to extend that list (SCCS/1459/11).
Here we report about 59 chemical substances using a twin-line (weakly polar and WAX) GCMSMS method in order to achieve maximum selectivity applying optimized multiple reaction monitoring (MRM).[3]

Experimental

Instrumentation

All results presented on this poster were obtained with a Shimadzu GCMS-TQ8040 triple quadrupole GCMS equipped with an AOC-6000 auto-injector. Very good sensitivity combined with selectivity is achieved when MS/MS (MRM) mode is used. To increase selectivity a twin line setup was applied. From two injection units a Rxi-5SilMS and a Stabilwax (both from Restek) were simultaneously mounted to the interface of the MS without connectors. Another advantage is the choice of column by the method. No change of configuration is necessary as the AOC-6000 can inject into either line. In Table 1 the applied analytical conditions are summarized.

Table 1: Analytical Conditions

GC	
Instrument	: GCMS-TQ8040 (Shimadzu, Japan)
Software	: GCMSSolution 4.45 with smartMRM and MRM Optimization Tool
Injector 1/2	: Optic-4/SPL-2010Plus, IP deactivated split liner with glass wool
Injection conditions	: 1 µL, rapid, split ratio 1:100
Column 1	: 5Sil-MS, 20 m × 0.15 mm × 0.15 µm
Column 2	: Stabilwax, 20 m × 0.15 mm × 0.15 µm
GC Oven	: 50 °C for 1 min, 20 °C/min to 120 °C, 6 °C/min to 155 °C, 20 °C/min to 250 °C for 2 min
Flow control	: Linear velocity mode, 50 cm/sec
MS	
Interface / Ion Source	: 230 °C / 200 °C
Ionization Mode	: EI, 70 eV with 60 µA emission current
Mass Resolution in MRM	: Q1 0.8 Da, Q3 at 0.8 Da (FWHM)
CID Gas	: Argon (200 kPa)
Loop Time	: 0.15 s

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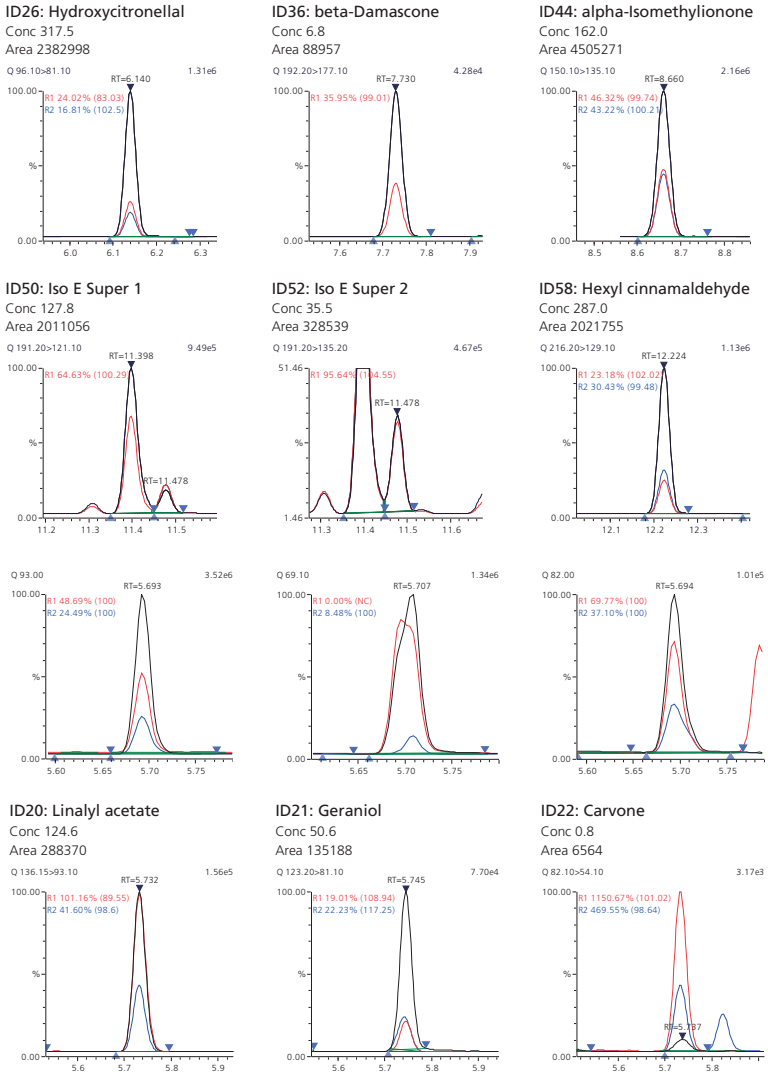
Experimental Conditions

Product ion scans (PIS) and MRM optimization were performed using Shimadzu's smartMRM and the MRM Optimization Tool. The resulting MRM transitions as well as retention times on both columns are shown elsewhere.[3] In addition, two internal standards were used. Up to a retention time of 8.5 min all targets were referred to 1,4-dibromobenzene, all other to 4,4'-dibromobiphenyl. Perfume samples were quantified by an internal four-point calibration on both columns, respectively.

Results

The regression coefficients for all calibration curves were R^2 > 0.999 for all allergens except of α-pinene (ID1, 0.998) and farnesol (ID57, 0.997) on the 5SilMS column and β-damascone (ID36, 0.996) and hexa-decanolactone (ID63, 0.995) on the WAX column.

Figure 1 shows the MRM traces of selected allergens for one of the perfume samples tested. The selectivity of these compounds in MRM mode provides good separation from matrix.



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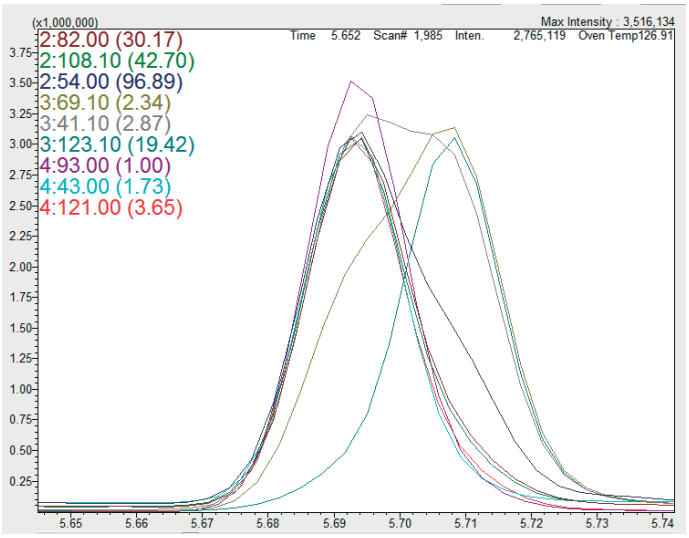
In Figure 2, a comparison of SIM and MSMS mode for three co-eluting allergens (ID 20, 21, 22) is shown. All three analytes show a fragment with m/z 93 and for ID21 it is the most abundant m/z. ID21 and 22 have m/z 69 in common, which is also the most abundant m/z for ID22.

Due to this fact, the peak shape of Geraniol is strongly influenced by the co-eluting allergens. Using MSMS mode, selectivity is increased and quantification becomes possible.



Concentrations were calculated based on the internal standard calibration and are shown in Table 2 for that sample. The quantitative results were compared to the supplier data and the results obtained with Single Quad (twin-line/SIM mode) data.

Table 2: Supplier data and results of GCMS SQ compared to MRM on two columns for one perfume matrix.

ID	Compound	% according supplier	% twin-line SIM	% 5SilMS MRM	Rel. to supplier	Rel. to twin-line SIM	% SH-WAX	Rel. to supplier	Rel. to twin-line SIM
9	Linalool	0.2701	0.2648	0.2683	-0.7	1.3	0.2713	0.4	2.5
18	Citronellol	0.4358	0.4164	0.4516	3.6	8.5	0.4443	2.0	6.7
21	Geraniol	0.4445	0.4459	0.4561	2.6	2.3	0.4808	8.2	7.8
26	hydroxycitronellal	3.1899	2.9807	2.9606	-7.2	-0.7	2.9870	-6.4	0.2
36	beta-Damascone	0.0631	0.0623	0.0615	-2.5	-1.3	0.0597	-5.4	-4.2
44	alpha-Isomethlyionone	1.5458	1.4435	1.4599	-5.6	1.1	1.5451	0.0	7.0
50	Iso E Super 1	-	1.2304	1.1514	-	-6.4	1.2069	-	-1.9
52	Iso E Super 2	-	0.3414	0.3201	-	-6.2	0.3422	-	0.2
58	Hexyl cinnamaldehyde	2.5425	2.4492	2.5854	1.7	5.6	2.5832	1.6	5.5

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ID21 and 36 show better precision on the 5SilMS column whereas Iso E Super 1 and 2 (ID50 and 52) should be quantified on the WAX column. ID44 on the 5SilMS correlated with the SIM results and on the WAX column it fits to the supplier data indicating that here MRM on the Wax is more selective. For the compounds with ID9, 18 and 58 the results on both columns match with the supplier data and the results obtained in SIM mode. Even with MSMS using one column phase the quantitative results indicate some differences of several allergens compared to supplier data. So a two-column setup is necessary.

Conclusion

Determination of 59 allergens was done for different perfume matrices and can be performed with excellent sensitivity and selectivity using the GCMS-TQ8040 applying fast GCMSMS within a runtime of 16 minutes. Other matrices will be tested in a subsequent study. Regression coefficients of the calibrations were observed to be $R^2 > 0.999$ for many allergens.
To summarize, the determination of the extended list of potential allergens in perfumes were within 8% variation on both columns relative to the expected concentrations according to the supplier data. In general the comparison to SIM data indicate a better selectivity with MRM. Twin-line setup with MS/MS provides sufficient separation efficiency and selectivity to quantify allergens in perfume matrices.
The use of fast GCMSMS allows a drastic increase in sample throughput by obtaining high quantitative precision.

Acknowledgments

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Literature

[1] EU 1223/2009.
[2] H. Leijs et al: J. Agric. Food Chem. 2005, 53, 6487
[3] Shimadzu Application Note SCA-280_089

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