Application Note GCMS-08

Improved Determination of Allergenic Fragrances in Detergents and Personal Care Products in Multiple Reaction Monitoring GC-MS/MS

Abstract

A study was carried out using the Bruker EVOQ GC-TQ gas chromatography triple quadrupole mass spectrometer in multi reaction mode (MRM) to screen for allergenic fragrances within cleaning fluids and personal care products (PCPs). Compound based scanning (CBS) was used to target compounds listed in EU Directive No. 76/768/EC.

CBS provided rapid and simple method development and managed the duty cycle for optimized screening. The high performance EVOQ GC-TQ delivered excellent sensitivity and signal to noise ratio (s/n) at sub ppb levels.

Introduction

Many of the compounds commonly added to improve the aroma of cleaning agents and personal care products (PCP) are classified as allergenic. Quantifying the risk of these components to personal safety is complicated as even sub ppb levels may invoke a serious immunogenic response in hypersensitive individuals. For this reason EU Directive No. 76/768/EC stipulates that a number of allergens should be labelled if they exceed 0.001% (w/w) for rinse-off products and 0.01% (w/w) for stay on products [1]. Developers therefore require analytical techniques that can accurately and reliably screen for low level fragrance residues.

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Cosmetics	
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Gas chromatography (GC) coupled with a triple quadrupole mass spectrometer (GC-MS/MS) operating in multiple reaction monitoring (MRM) mode is regarded as the gold standard for low level multiple residue analysis, particularly in matrices containing samples such as cleaning agents and PCPs. MRM determination delivers greater levels of sensitivity and signal to noise ratio (s/n) over single quadrupole (SQ) or selected ion monitoring (SIM) techniques. However MRM set up and method develop-ment is traditionally a complicated and time intensive process.

Typically two or three MRM runs are required to confirm each residue. As many peaks overlap within a single chromatographic run the dwell time for each MRM target must be carefully optimized. GC-MS/MS techniques based on compound based scanning (CBS) greatly simplify this process, combining enhanced sensitivity, reliability and robustness with rapid method development and simple sample preparation.

Rather than targeting each individual MRM, the CBS workflow focusses on the compounds themselves. CBS libraries contain more than 2500 MRM transitions for more than 900 common contaminants, including the majority of allergenic fragrances listed within the EC regulations. These are linked with retention time, primary and secondary MRM transitions. Using this library, CBS automatically builds a screening method and manages the triple quadrupole duty cycle during analysis and data acquisition. This provides faster and easier method development and reduces the analytical cycle.

To illustrate the speed and sensitivity of employing this method for allergen screening, the EVOQ GC-TQ was used to screen for allergenic compounds within a number of commercially available cleaning agents. CBS software automatically built the screening method while advanced GC-MS/MS hardware delivered excellent sensitivity at trace ppb levels.

Methods

25 cosmetics from local and foreign retail markets were analyzed for a mixture of 27 potential allergenic compounds. Samples were spiked with an internal standard and diluted in a ratio of 1:1000. The detergents and cleaning agents within the samples were extracted in a water bath at 55°C in the presence of an internal standard. Solid phase extraction was performed on a C18 column.

Experimental Details

GC: Bruker GC 456 EVOQ GC-TQ; S/SI-injector temp: 250°C; Split: 1:20; Column: BR-5ms, 30 m x 0.25 mm x 0.25 µm; Oven program: 50°C (1 min) -> 250°C (12°C/min); 3.33 min; Injection volume: 1 µL; MRM measurements with optimized transitions for all compounds (at least 2 transitions per compound); Data system: Bruker MSWS 8.0 SP2

Results

After a small number of initial runs to locate the retention time window for each compound, CBS software used a comprehensive MRM database to automatically select optimal scan times for the 27 allergen compounds (Figure 1).

For compounds listed in Figure 2a calibration curves from 5 ppt to 250 ppb could be measured. Figure 2b shows the detection limits for each compound alongside the chromatograms recorded for d-limonene at a range of concentrations, illustrating excellent sensitivity. Due to the methodic and regulatory definition only the high end of the calibration curve is used.

Figure 3 shows an example of a full scan and MRM-trace for one of the commercially available perfume samples. The MRM trace clearly identifies the presence of ten prohibited allergenic compounds screened for using the CBS method.

Analysis was also performed using the Bruker EVOQ GC-TQ in single quadrupole SIM mode to illustrate the improvements in selectivity in matrix samples. Figure 4 show the ion trace for anisylacohol within vanishing cream measured with both techniques. SIM struggles to resolve the analyte peak. Usage of a triple quadrupole MS/MS offers greater s/n ratio and improved peak shapes.

Conclusion

The Bruker EVOQ GC-TQ in MRM mode delivered excellent sensitivity, selectivity and linearity for trace level fragrance analysis within PCPs and cleaning products using GC-MS/MS analysis in MRM mode.

The majority of allergenic compounds listed in the EC regulation have been optimized in CBS scanning, which provided fast and robust method development, showing the method to be ideal for product developers and quality control (QC) laboratories.

Compound Based Scanning Software (CBS)

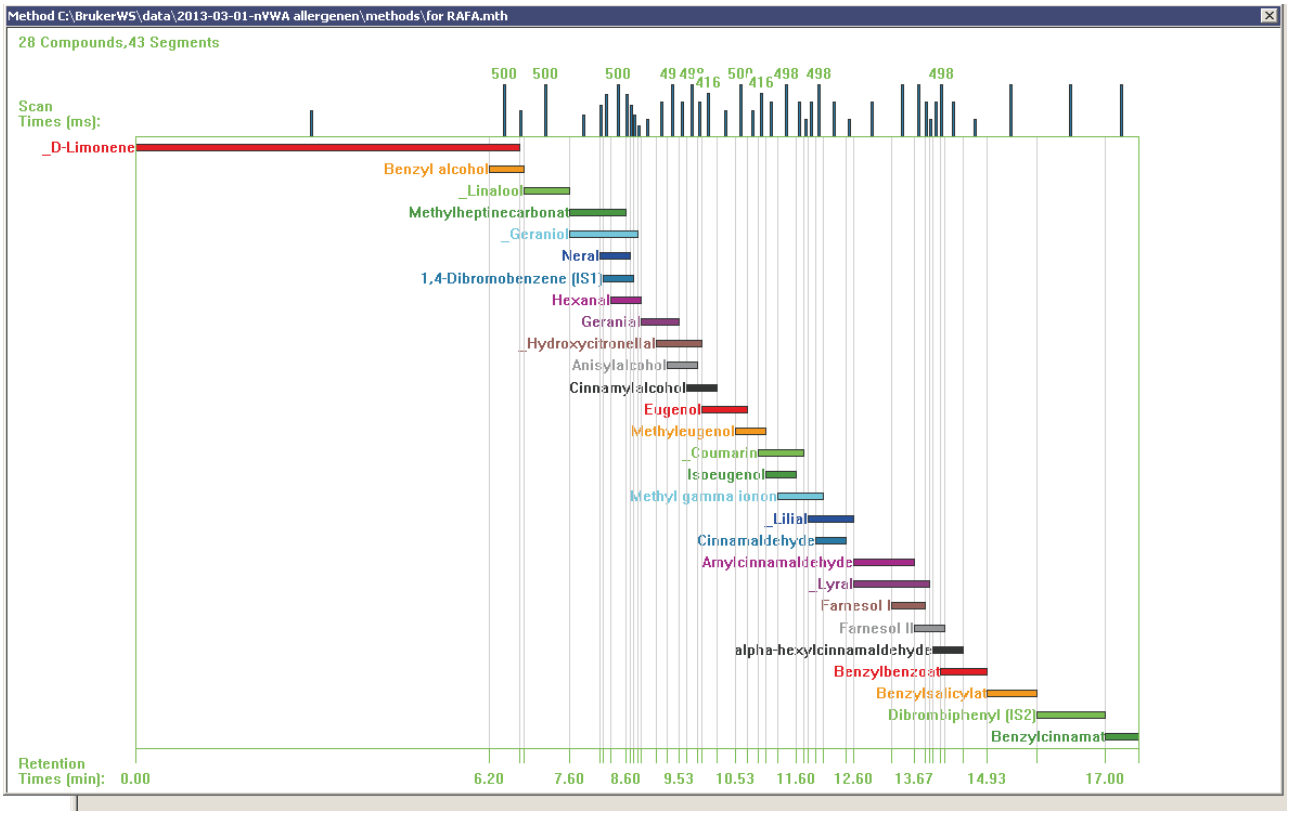

Figure 1: CBS software calculates the optimal scan times for the 27 allergens, providing more rapid method development over conventional techniques.

Calibration Curve Results

Compound name	R^2	øRRF	% RSD
alpha-Amylcinnamylalcohol	0.9869	0.0733	13.56
alpha-Amylcinnamylaldehyde	0.9972	0.2829	8.05
alpha-Hexylcinnamaldehyde	0.9986	0.2507	4.81
gamma-Methylionon	0.9968	0.3446	22.04
Anisyl alcohol	0.9982	0.2173	5.38
Benzyl alcohol	0.9979	0.2719	6.66
Benzyl benzoate	0.9991	0.6014	3.38
Benzyl cinnamate	0.9995	0.3270	1.86
Benzyl salicylate	0.9996	0.7666	3.49
Cinnamaldehyde	0.9996	0.6523	2.68
Cinnamylalcohol	0.9986	0.3364	3.63
Citral	0.9996	0.9507	2.15
Citronellol	0.9998	0.3645	3.25
Coumarin	0.9999	1.0559	4.64
Eugenol	0.9996	0.4772	8.20
Farnesol	0.9994	0.6219	16.29
Geraniol	0.9991	0.5530	5.69
Hydroxycitronellal	0.9995	1.2990	1.68
Isoeugenol	0.9997	0.7074	2.52
Lilial	0.9996	0.9517	4.30
D-Limonene	0.9998	0.5672	2.80
Linalool	0.9999	0.1636	8.64
Lyral	0.9993	0.6403	15.27
Methyleugenol	0.9995	0.4606	13.60
Methyl heptyn carbonate	0.9912	1.3013	8.40
4,4-dibromobiphenyl (IS1)	0.9993	0.4375	15.05
1,4-dibromobenzene (IS2)	0.9999	0.3189	2.74

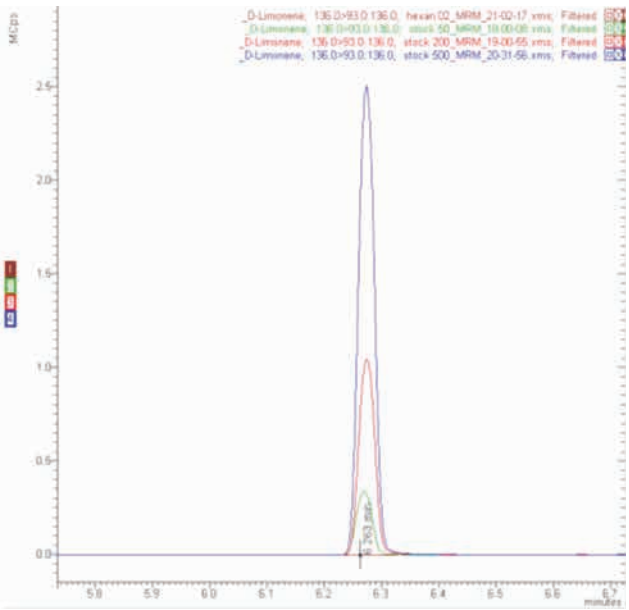

Figure 2: Results for calibration of 27 compounds (2a, left). Excellent linearity is achieved for each compound enabling calibration from 5 ppt to 250 ppb. Peaks were detected for D-limonene from 5 ppt to 250 ppb (2b, right).

Analysis of perfume sample

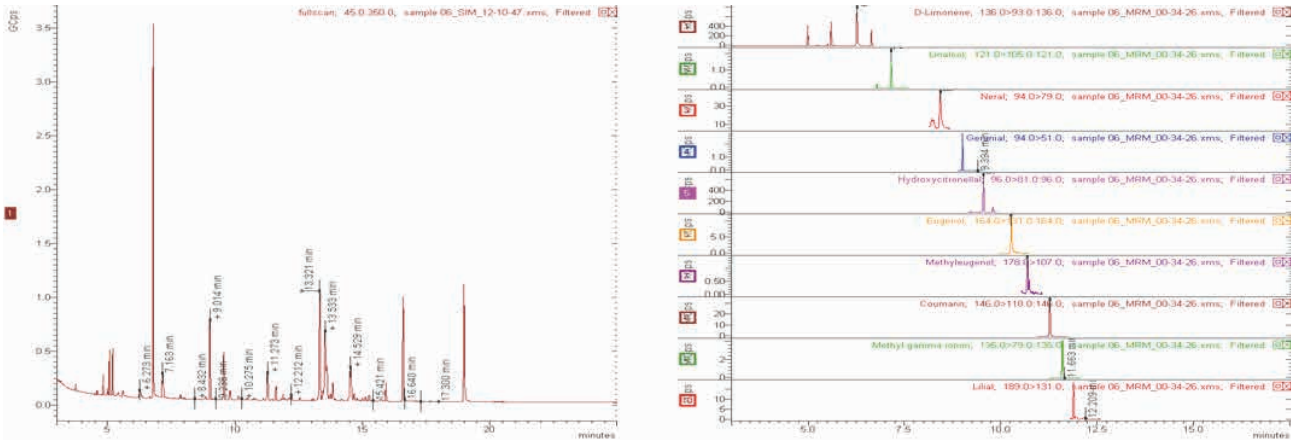

Figure 3: Peaks were detected for D-limonene from 5 ppt to 250 ppb (right). Calibration curves could be measured for all targeted allergens.

Analysis of vanishing cream

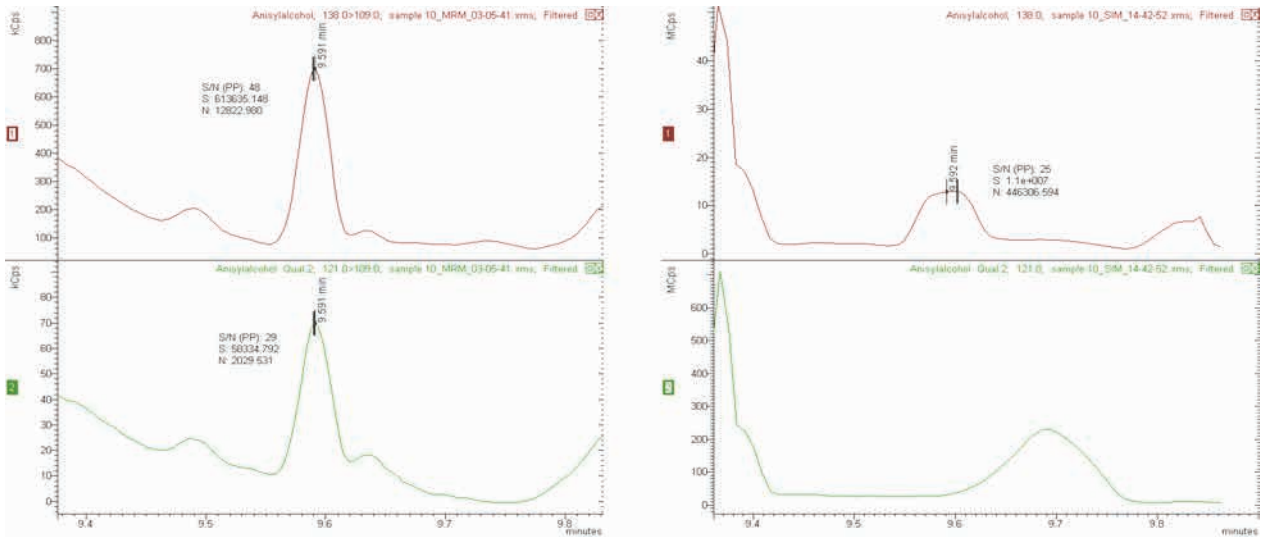

Figure 4: Comparison of exemplary ion trace for target allergen anisylalcohol in vanishing cream with triple quadrupole MS/MS (left) and single quadrupole MS (right). Triple quadrupole MS achieves excellent resolution in the heavy matrix sample.

References

[1] http://www.epa.govt.nz/Publications/gs-cosmetic.pdf

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