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Application News

GC-MS GCMS-TQ™8040 NX

Highly Sensitive Analysis of Fragrance Allergens in Cosmetics Using Triple Quadrupole GCMS

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User Benefits

- Fragrance allergens in cosmetics can be analyzed with high sensitivity using the MRM mode of the triple quadrupole GCMS.
- Improved analysis sensitivity allows for greater sample dilution, which can lead to reducing contamination in the injector.
- The use of MRM mode improves selectivity in analysis, leading to less labor-intensive data analysis and more stable laboratory operations.

■ Introduction

Fragrances in cosmetics contain compounds that can potentially cause allergic reactions depending on their concentrations, necessitating their control at appropriate levels. The EU Cosmetics Regulation (EC 1223/2009)[1)] currently regulates 24 fragrance compounds in cosmetics as fragrance allergens. However, there are considerations to expand this regulation to include more than 80 compounds. In this context, it is critical for cosmetic manufacturers to accurately track the fragrance compounds contained in their finished products or raw materials.

In Application News 01-00526, the article "Quantitative Analysis of 57 Fragrance Allergens in Cosmetics Using Twin Line MS System", introduced an example of analysis for fragrance allergens in cosmetics using a single quadrupole GCMS. However, in complex matrix samples like cosmetics, accurate quantitation can be hindered by the interference of impurities. In such cases, performing MRM analysis with a triple quadrupole GCMS is expected to improve measurement accuracy. This Application News presents the results of investigation on how to further enhance sensitivity, accuracy, and analytical stability using a triple quadrupole GCMS.

Fig. 1 AOC-30i + GCMS-TQ™8040 NX

■ System Configuration and Analytical Conditions

The analysis was conducted using the GCMS-TQ8040 NX triple quadrupole system in MRM mode. The system configuration and analytical conditions are shown in Table 1.

Standards were prepared by diluting solutions of 57 fragrance allergens in the range of 0.05 to 5 mg/kg with MtBE. 1,4-Dibromobenzene and 4,4'-Dibromobiphenyl, each prepared at 5 mg/kg, were used as internal standards. For the sample, commercially available hair oil (0.1 g) was made up to 10 mL with MtBE. In addition, the diluted hair oil was spiked with standards at a concentration of 0.1 mg/kg to confirm the detection of each compound,

Table 1 System Configuration and Analytical Conditions

System	
GCMS Model:	GCMS-TQ8040 NX
Autoinjector:	AOC-30i
Column:	SH-1 (30 m × 0.25 mm I.D., 0.25 µm)
GC Conditions	
Injection Mode:	Splitless
Sampling Time:	1 min
High Pressure Injection:	200 kPa (1.5 min)
Injection Volume:	1 µL
Injector Temp.:	280 °C
Carrier Gas:	He
Carrier Gas Control:	Linear velocity (40 cm/s)
Column Temp. Program:	40 °C (4 min)_15 °C/min_105 °C (2 min) _4 °C/min_150 °C_10 °C/min_280 °C (2 min)
MS Conditions	
Ion Source Temp.:	200 °C
Interface Temp.:	280 °C
Emission Current:	20 µA
Data Acquisition Mode:	MRM
Loop Time:	0.3 sec

■ Calibration Curves and Repeatability

Calibration curves were prepared in the range of 0.05 to 5 mg/kg, and the linearity and repeatability (N = 6) at the minimum concentration were verified. Fig. 2 and Table 2 show the linearity and repeatability at the minimum concentration.

The results showed that except for Sclareol, the linearity of the calibration curve for all compounds was excellent (R^2 > 0.995). Even for Sclareol, the linearity was sufficient for quantitative analysis (R^2 > 0.994). Additionally, the repeatability at the minimum concentration was excellent for all compounds (area %RSD < 10 %).

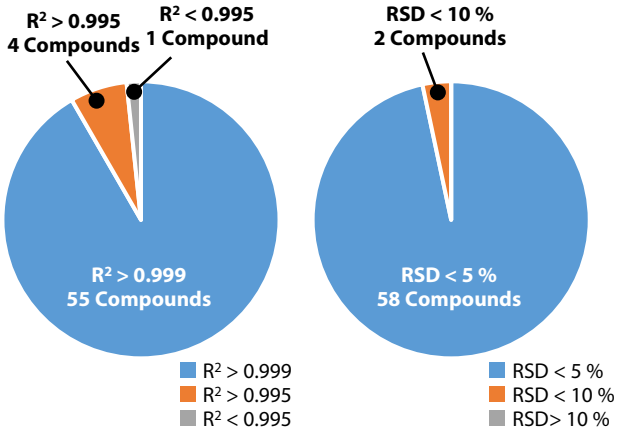

Fig. 2 Linearity of Calibration Curve and Area Repeatability

Table 2 R^2 and Area RSD of Smallest Concentration for Each Compound

ID	Compounds	R^2	%RSD
1	α-Pinene	0.99996	1.7
2	β-Pinene	0.99999	1.9
3	α-Terpinene	0.99999	1.8
4	Limonene	0.99996	3.4
5	Benzaldehyde	0.99999	1.5
6	Terpinolene	0.99998	2.0
7	Linalool	0.99994	3.0
8	Benzyl alcohol	0.99983	1.5
9	Salicylaldehyde	0.99945	1.5
10	Menthol	0.99999	3.2
11	Camphor	0.99998	1.4
12	α-Terpineol	0.99999	2.8
13	Citronellol	0.99969	4.4
14	Linalyl acetate	0.99989	2.3
15	Methyl 2-octynoate	0.99991	4.3
16	Geraniol	0.99942	3.6
17	Methyl salicylate	0.99994	2.9
18-a	Neral	0.99995	3.8
18-b	Geranial	0.99998	2.8
19	Carvone	0.99996	2.6
20	Hydroxycitronellal	0.99990	1.6
21	trans-Anethole	0.99999	3.2
22	Dimethylbenzylcarbinyl acetate	0.99997	2.0
23	β-Caryophyllene	0.99996	2.0
24	Cinnamaldehyde	0.99991	2.1
25	Geranyl acetate	0.99982	2.7
26	δ-Damascone	0.99988	4.3
27	Anise alcohol	0.99978	4.0
28-a	Ebanol 1	0.99994	1.6
28-b	Ebanol 2	0.99989	3.0
29	Cinnamyl alcohol	0.99965	2.9
30	α-Damascone	0.99995	4.6
31	β-Damascenone	0.99999	2.0
32	Eugenol	0.99975	2.9
33	β-Damascone (E)	0.99992	3.2
34	Trimethyl-benzenepropanol	0.99992	2.1
35	α-Isomethylionone	0.99990	1.9
36	Isoeugenol	0.99972	2.4
37	Vanillin	0.99871	4.5
38	Butylphenyl methylpropional	0.99988	2.4
39	Amyl salicylate	0.99956	1.6
40	Coumarin	0.99998	2.7
41	Geranyl acetate	0.99997	2.8
42	β-Tetramethylacetyloctahydronaphthalene	0.99996	2.4
43-a	α-Santalol	0.99967	3.7
43-b	β-Santalol	0.99920	3.2
44	3-Propylidene phthalide	0.99998	2.3
45	α-Amyl cinnamaldehyde	0.99968	3.4
46	trans,trans-Farnesol	0.99589	3.7
47	Isoeugenyl acetate	0.99997	2.3
48	Hydroxyisohexyl 3-cyclohexene carboxaldehyde (major)	0.99969	3.4
49	α-Amylcinnamyl alcohol	0.99892	2.8
50	α-Acetyl cedrene	0.99996	4.6
51	α-Hexylcinnamaldehyde	0.99981	8.2
52	Galaxolide 1+2	0.99997	2.6
53	Benzyl benzoate	0.99997	2.1
54	Hexadecanolactone	0.99988	3.2
55	Benzyl salicylate	0.99909	2.3
56	Benzyl cinnamate	0.99944	3.0
57	Sclareol	0.99428	5.6

■ Hair Oil Analysis

Commercial hair oil diluent was measured in both SIM and MRM modes, and the chromatograms of the fragrance allergens in the hair oil were confirmed.

Figure 3 shows examples of chromatograms of fragrance allergens in hair oil. In SIM mode, the detection of the Methyl salicylate peak was significantly affected by impurities, making an accurate detection impossible. However, in MRM mode, the impact of impurities was lessened, leading to better results.

On the other hand, while peaks for Benzyl salicylate were detected in both SIM and MRM modes, a comparison of the quantitative values showed a difference of more than twice. In SIM mode, it's possible that an accurate quantification was not achieved due to the elution of impurities at the same retention time as the target compound. Conversely, in MRM mode, due to improved selectivity, it's believed that the target concentration could be quantified more accurately.

Thus, the use of MRM mode enhances the selectivity in mass spectrometry, enabling high-sensitivity analysis through splitless injection. It also leads to improved quantification accuracy, hence more stable operations can be expected compared to analyses performed in SIM mode.

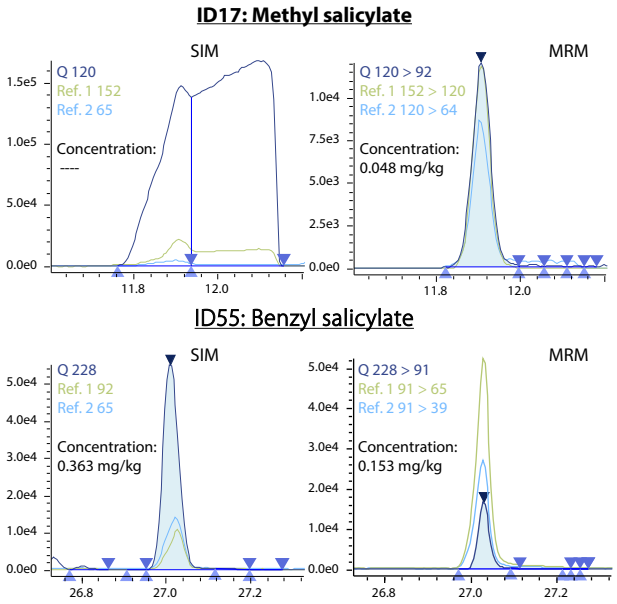

Fig. 3 Chromatograms of Fragrance Allergens in Hair Oil

■ Conclusion

This Application News introduced an example of MRM analysis of 57 fragrance allergens in hair oil using the GCMS-TQ8040 NX.

Compared to SIM analysis, MRM analysis is less influenced by impurities, making it a particularly effective method for analyzing complex samples like cosmetics. This leads to labor-saving in analysis and more accurate quantification. In addition, because MRM analysis can detect target components with high sensitivity, it is possible to increase the dilution factor of the sample. This reduces contamination in the injector and allows for more stable quality control.

In Application News 01-00526 "Quantitative Analysis of 57 Fragrance Allergens in Cosmetics Using Twin Line MS System" introduced an analysis method using a single quadrupole GCMS. By using two columns and MRM mode, it is possible to maximize the stability in quantitative analysis.

< References >
1) Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products
https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32009R1223&from=EN
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