Gas Chromatograph Mass Spectrometer

Application News

Comprehensive and High-Sensitivity Analysis of Food Aroma by Simultaneous Scan/MRM Measurement Using Triple Quadrupole GC-MS/MS

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User Benefits

- ◆ Simultaneous scan/MRM measurement enables comprehensive search by scan measurement and high-sensitivity analysis of trace aroma compounds by MRM in a single measurement.
- ◆ With LabSolutions Insight Explore™ GCMS, deconvolution analysis of scan data and target analysis of MRM data are possible in a single software program.
- ◆ The Multi-Mode Injection Unit (MMI), which allows rapid heating, supports aroma analysis in the thermal desorption (TD) mode.

■ Introduction

The "aroma" of food products and beverages is a key factor that largely determines product quality and consumer preferences, and thus is an extremely important element in product development and quality control. Since the gas chromatograph mass spectrometer (GC-MS) provides excellent performance in qualitative analysis of volatile compounds, it is used to measure various aroma components that make up an odor. However, due to the diversity of aroma compounds and their wide concentration range, which extends from the ppm to the ppt order, an analytical method that allows efficient measurement of these substances is demanded.

Non-targeted analysis by scan measurement is an effective tool for comprehensive profiling, but in many cases, it is difficult to identify the trace components that make a significant contribution to aroma due to the limits of instrument sensitivity and matrix interference. On the other hand, although wide-target analysis by the MRM (Multiple Reaction Monitoring) mode using GC-MS/MS offers high sensitivity and selectivity for several hundred target components, MRM lacks a search capability for unknown components.

Therefore, this Application News article reports a technique that satisfies both comprehensive non-targeted search and high-sensitivity detection of trace components in a single analysis by combining the GCMS-TQ™8040 RX, which supports simultaneous data acquisition in simultaneous multi-component analysis measurements by scan measurement and the MRM mode, and the Smart Aroma Database™ for use in aroma analysis. In addition, in this experiment, the thermal desorption (TD) mode of the Multi-Mode Injection Unit (MMI) was adopted for sample introduction. This enables introduction of components tapped on the adsorbent without using a dedicated TD device, thereby achieving a simplified system configuration.

■ Sample Introduction by TD Mode Using MMI

The MMI allows sample introduction by the split/splitless (SPL) mode and large volume injection (LVI) mode, as well as the manual TD mode using a MonoTrap (GL Sciences) TD tube. The MMI offers rapid heating with a maximum heating rate of 1200 °C/min, making it possible to obtain satisfactory peak shapes even with low-boiling components (Fig. 1).

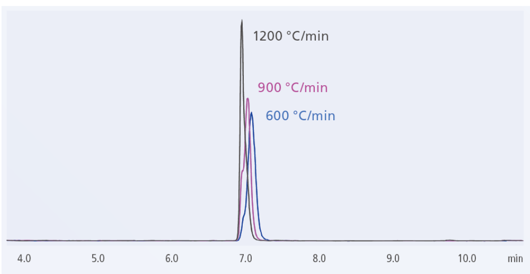

Fig. 1 Chromatograms Acquired by TD Mode with Different Heating Rates (Methyl Hexanoate)

■ Automatic Creation of Simultaneous Scan/MRM Measurement Methods by Smart Aroma Database

In this experiment, a simultaneous scan/MRM measurement method was created using Smart Aroma Database for use in aroma analysis. The analysis conditions and sensory information (aroma profile) of approximately 500 important components of compounds that contribute to aromas are registered in Smart Aroma Database (Fig. 2). In addition to retention indices and mass spectrum information, the analysis conditions also include up to 6 optimized MRM transitions.

Compound Name (E)	Ret. Index 1 IC Pure-WAX	Cas#	Comment (E) Odor Quality	MRM Transition Ion1 Type	m/z	CE	Ratio
Methyl octanoate	1382	111-11-5	orange	T	87.00>55.00	9	100.00
3-Octanol	1382	589-98-0	moss, nut, mushroom	T	83.10>55.10	6	100.00
Nonanal	1383	124-19-6	fat, citrus, green	T	82.10>67.10	6	100.00
2,3,5-Trimethylpyrazine	1387	14667-55-1	roast, potato, must	T	122.10>42.10	15	100.00
Methyl (methylthio)acetate	1387	16630-66-3	cooked potato, roasted nut	T	120.00>74.10	6	100.00
2-Ethyl-3-methylpyrazine	1388	15707-23-0	roast	T	121.00>93.10	12	100.00
2-Isobutylthiazole	1391	18640-74-9	tomato leaf, green	T	99.00>59.00	18	100.00
2-Methylanisole	1391	578-58-5	warm, flower, walnut	T	122.00>107.10	12	100.00
trans-3-Octen-2-one	1392	1669-44-9	nut, crushed bug	T	111.10>55.10	9	100.00
trans-2-Hexen-1-ol	1395	928-95-0	green, leaf, walnut	T	82.10>67.10	6	100.00

Fig. 2 Information Registered in Smart Aroma Database

Using the retention indices of various components obtained from the Smart Aroma Database and the retention time information for n-alkane measured in advance, the optimum method can be prepared automatically, without the use of reference samples. In method creation, the newly developed Smart MRM™+ function was used (Fig. 3). Smart MRM+ automatically creates a method in which the dwell time (duration of data collection) for each MRM transition is optimized. High-sensitivity MRM measurements that secure a sufficient dwell time are possible, even in simultaneous analysis of scan measurements and MRM measurements of 484 components × 2–3 MRM transitions per component (total: 1452 transitions).

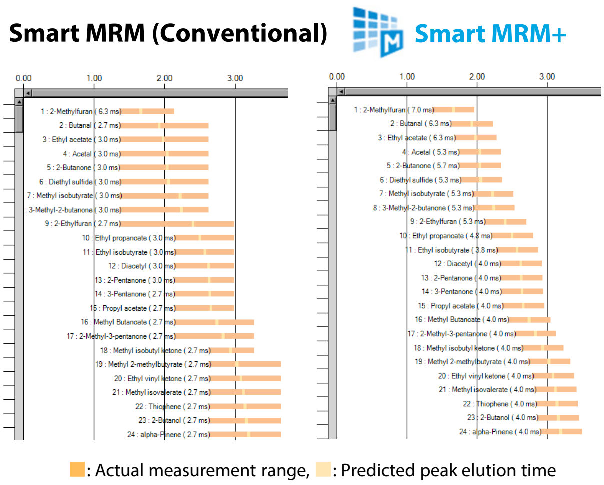

Fig. 3 Comparison of MS Measurement Time of Simultaneous Scan/MRM Analysis Methods

■ Sample Preparation and Analysis Conditions

The samples used in this experiment were two types (A and B) of commercially available soy sauce. Using MonoTrap, a monolithic silica adsorbent, the aroma components were concentrated by vapor-phase extraction and immersion (liquid-phase) extraction (Fig. 4). Specifically, 6 mL of the sample and a MonoTrap RGPS TD (GL Sciences) were introduced into a 20 mL screw vial and concentrated under either vapor-phase or immersion extraction conditions while stirring at 250 rpm at 60 ˚C for 30 min. After concentration, the excess moisture adhering to the MonoTrap was wiped off with a Kimwipe, and the MonoTrap was placed in a splitless glass insert (Xtra Inert Liner, Splitless, P/N: 227-36701-01) for use with the MMI.

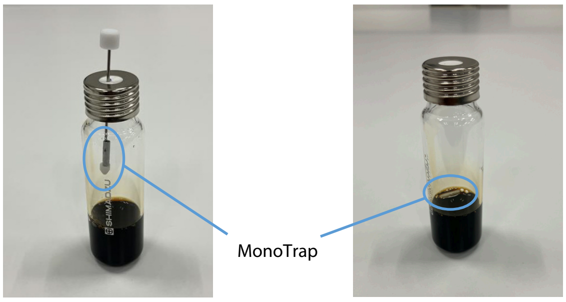

Fig. 4 Simple Concentration of Aroma Components Using MonoTrap
(Left: Vapor-Phase Extraction, Right: Immersed Extraction)

Table 1 shows the instrument configuration used here, together with the analysis conditions. A capillary tube was connected to the column as a post-column. This made it possible to prevent deterioration of the column liquid phase at the interface side, even when exchanging the insert liner, without lowering the interface temperature. Use of the Easy sTop function also made it possible to exchange the glass insert safely and reliably by displaying the permissible timing for the replacement and automatically checking for leaks.

Table 1 Instrument Configuration and Analysis Conditions

Configuration	
GC-MS	: GCMS-TQ8040 RX
Injection Unit	: MMI-U
Column	: InertCap Pure-WAX (30 m × 0.25 mm I.D., 0.25 μm) (GL Sciences Inc.) *A post-column (30 cm × 0.25 mm I.D.) was connected with a micro union.
GC	
MMI Mode	: Thermal desorption/extraction introduction method
Purge Program	: [Time] 0 min [Temperature] 35 ˚C [Split Ratio] 10
Desorb Program	: [Time] 10 min [Temperature] 250 ˚C [Heating Rate] 1200 ˚C/min [Split Ratio] 10
Carrier gas	: He
Carrier gas control	: Pressure (83.5 kPa)
Column temp.	: 50 ˚C (5 min) – 10 ˚C/min – 250 ˚C (10 min)
MS	
Ion source temp.	: 200 ˚C
Interface temp.	: 250 ˚C
Acquisition mode	: Scan/MRM (using conditions of Smart Aroma Database)
Loop Time	: Scan 0.1 s, MRM 0.2 s

■ Data Analysis

The simultaneous scan/MRM measurement data were analyzed using LabSolutions Insight Explore GCMS (Fig. 5). For scan data, this software can perform peak detection by deconvolution and a library search. The same program can also carry out targeted analysis and quantitative analysis of MRM data.

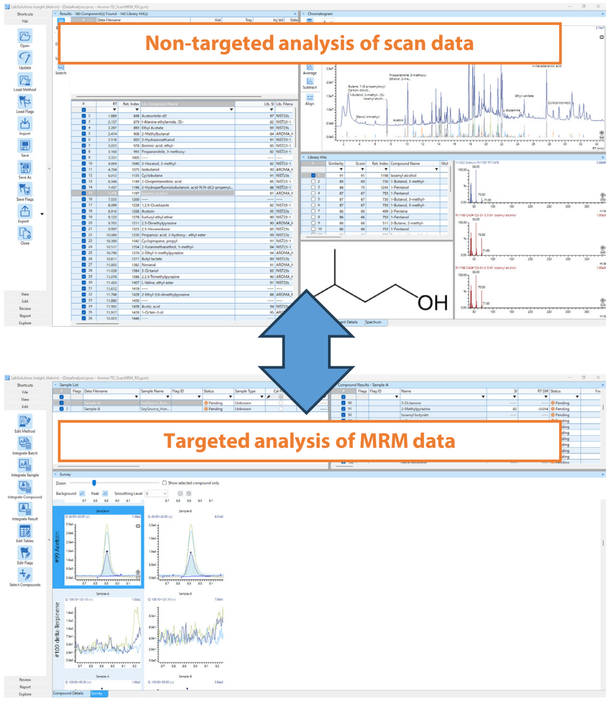

Fig. 5 Analysis Screens of LabSolutions Insight Explore GCMS

■ Comprehensive Search Using Scan Data

Peak detection by deconvolution and identification of the detected compounds by a library search were carried out for the scan data. In the mass spectrum library, the mass spectrum library (AROMA_IC-WAX) belonging to the Smart Aroma Database and the NIST mass spectrum library (NIST23) were used, and a similarity score of 80 was used as the threshold. Among the detected peaks, peaks originating from collision gas and peaks of siloxane originating from the MonoTrap were excluded from the analysis. Fig. 6 shows the total ion current chromatograms (TICC) obtained from soy sauce A by vapor-phase and immersion extraction and the peaks detected by deconvolution. Here, 138 peaks were detected in vapor-phase extraction, among which 123 components were identified by the library search. On the other hand, 201 peaks were detected in immersion extraction, and 147 hits were obtained. Based on these results, in this experiment, the compounds in the soy sauce samples could be extracted more comprehensively by immersion extraction. Although low-boiling components such as Isoamyl alcohol, Acetoin and Nonanal were common to both vapor-phase extraction and immersion extraction, immersion extraction allowed extraction of polar components and relatively high boiling components, which rarely appear in the vapor phase. The compounds that were qualitatively identified in the library search included alcohols, furans, pyrazines, and others, as well as characteristic aroma-active components of soy sauces, namely, Homofuraneol (HEMF), p-Vinylguaiacol, and Methionol. Table 2 shows the main compounds identified by the library search following immersion extraction. Among these, in some cases, the TIC included peaks and mass spectra that could be extracted by deconvolution, even though they were buried by other peaks, and the compounds could be identified by a library search (Fig. 7). These results show that comprehensive profiling of the main volatile components that exist in a complex matrix is also possible even in scan measurements by carrying out a deconvolution analysis.

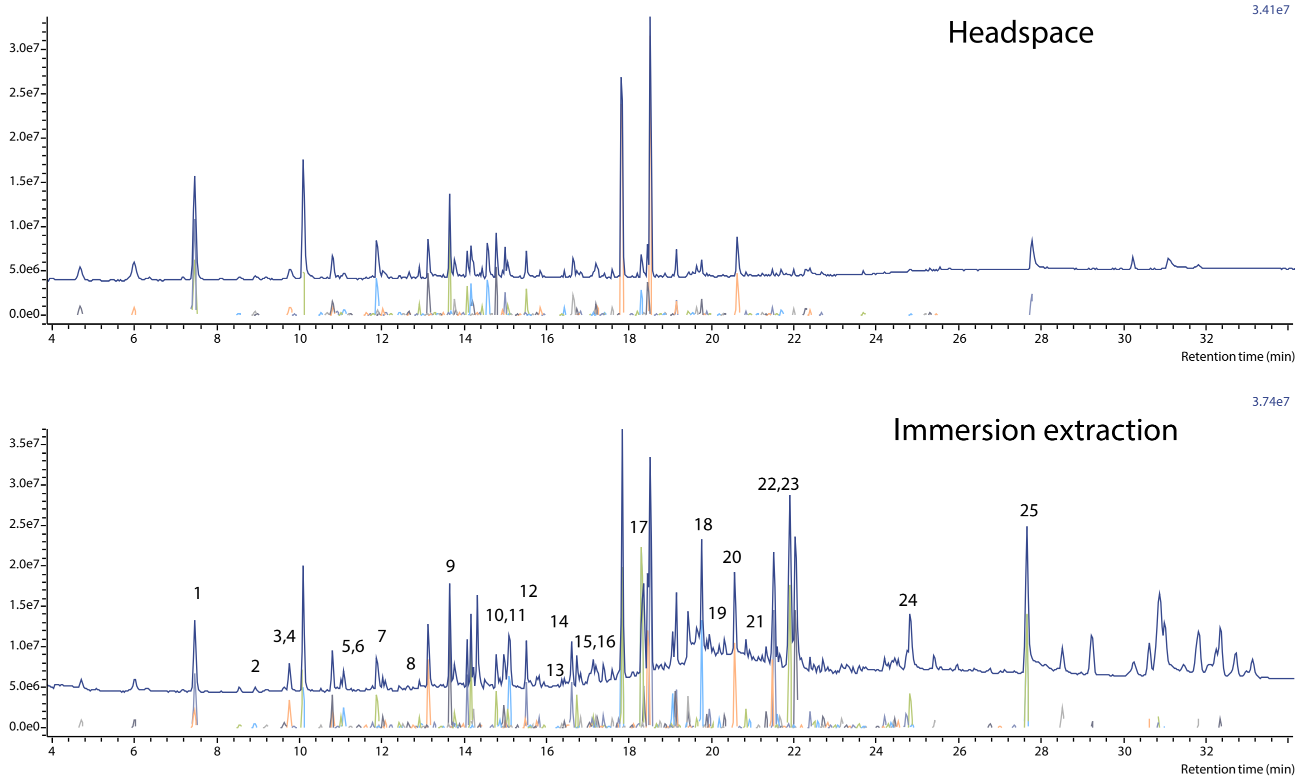

Fig. 6 TICs and Peak Detection by Deconvolution (Soy Sauce A) (Top: Vapor-Phase Extraction, Bottom: Immersion Extraction)

Table 2 Examples of Compounds with Hits in Library Search (Soy Sauce A, Immersion Extraction) (Partial Excerpt)

ID	Retention time (min)	Retention index (measured)	Compound name	Similarity	Library name	Odor*
1	7.455	1196	Isoamyl alcohol	88	AROMA_IC-WAX	whiskey, malt, burnt
2	8.906	1267	Acetoin	88	AROMA_IC-WAX	butter, cream
3	9.620	1303	2,5-Dimethylpyrazine	93	AROMA_IC-WAX	cocoa, roasted nut
4	9.747	1310	2,6-Dimethylpyrazine	95	AROMA_IC-WAX	roasted nut, cocoa
5	11.001	1382	Nonanal	88	AROMA_IC-WAX	fat, citrus, green
6	11.068	1386	2,3,5-Trimethylpyrazine	94	AROMA_IC-WAX	roast, potato, must
7	12.207	1458	Pyrazine, tetramethyl-	92	NIST23s	
8	12.636	1485	2-Acetylfuran	92	AROMA_IC-WAX	balsamic
9	13.640	1555	2,3-Butanediol	97	AROMA_IC-WAX	fruit, onion
10	14.778	1639	Furfuryl alcohol	98	AROMA_IC-WAX	burnt
11	14.957	1653	Isovaleric acid	92	AROMA_IC-WAX	sweat, acid
12	15.498	1695	Methionol	88	AROMA_IC-WAX	sweet, potato
13	16.417	1770	Ethyl phenylacetate	93	AROMA_IC-WAX	fruit, sweet
14	16.807	1802	Cyclotene	83	AROMA_IC-WAX	
15	17.231	1838	Guaiacol	90	AROMA_IC-WAX	smoke, sweet, medicine
16	17.407	1854	Benzyl alcohol	86	AROMA_IC-WAX	sweet, flower
17	19.141	2009	4-Ethyl-2-methoxyphenol	93	AROMA_IC-WAX	spice, clove
18	19.754	2067	Homofuraneol (HEMF)	89	AROMA_IC-WAX	caramel
19	19.824	2074	2-Acetyl-5-methylfuran	86	NIST23s	
20	20.564	2146	Nonanoic acid	93	AROMA_IC-WAX	green, fat
21	20.822	2171	p-Vinylguaiacol	91	AROMA_IC-WAX	clove, curry
22	21.857	2276	Sulfurol	86	AROMA_IC-WAX	sulfur
23	21.898	2281	Glycerin	92	NIST23-1	
24	24.824	2604	Ethyl vanillate	91	AROMA_IC-WAX	flower, fruit, sweet, vanilla
25	27.643	2884	n-Hexadecanoic acid	92	NIST23s	

*Information registered in Smart Aroma Database.

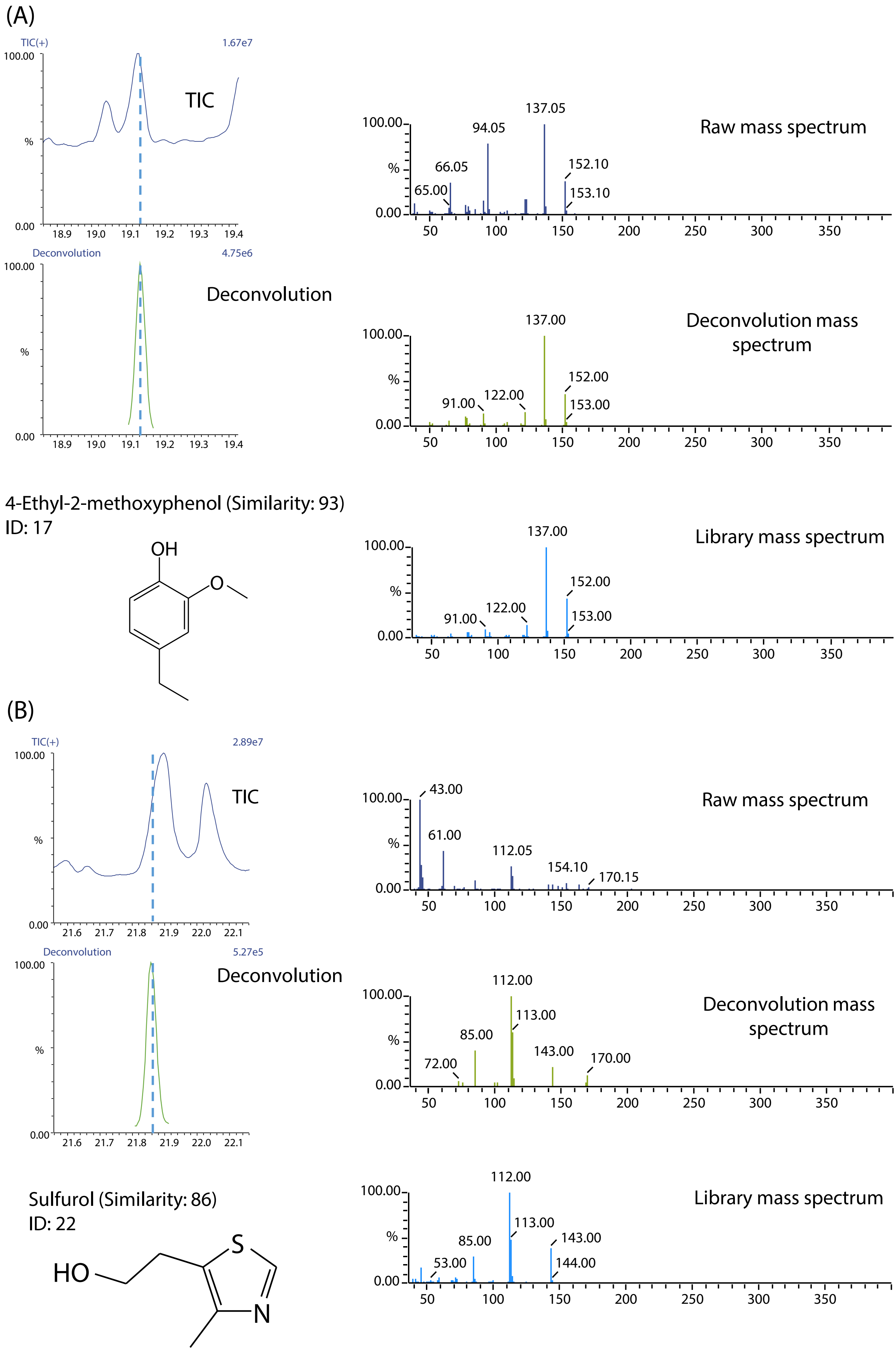

Fig. 7 Detection Results and Qualitative Analysis Results by Deconvolution Analysis
A: 4-Ethyl-2-methoxyphenol, B: Sulfurol

■ Identification of Trace Aroma Components Using MRM Data

Identification of compounds in the MRM data was carried out based on the ratio of quantitative ions and confirmation ions and the retention indices registered in advance in the Smart Aroma Database. As the mass spectra of standard substances are also registered in the Smart Aroma Database, the measured mass spectra obtained by simultaneous scan measurements were also used as reference. When the MRM data (soy sauce A, immersion extraction) obtained by simultaneous scan/MRM measurement were analyzed, it was possible to detect 113 aroma compounds including trace components that were either hidden or below the limit of detection in the scan data. In particular, key aroma components with low odor thresholds that contribute substantially to the distinctive aroma of soy sauce, such as Furaneol (HDMF), Methional, Dimethyl trisulfide (DMTS), and Methyl 2-methyl-3-furyl disulfide, were clearly detected and confirmed in the MRM chromatograms. Soy sauces A and B are produced by different manufacturing processes, and when the components of the two products were compared, differences in their peak intensities were confirmed (Fig. 8).

These results demonstrated that MRM data are effective in identification of trace aroma components with low odor thresholds, which are difficult to detect in scan data, and in analysis of differences in intensity.

■ Conclusion

This Application News article showed that it is possible to achieve both a comprehensive non-targeted analysis of food aroma and a high-sensitivity wide-target analysis of trace components in a single analysis, without carrying out complicated operations, by simultaneous scan/MRM measurement combining the GCMS-TQ8040 RX and the Smart Aroma Database. This article also demonstrated that use of the Multi-Mode Injection Unit (MMI) enables measurements in the thermal desorption (TD) mode without using dedicated TD instrumentation, and also allows a flexible response in case of budgetary or installation space limitations. A comprehensive aroma evaluation based on this approach will facilitate the discovery of important aroma components that were easily overlooked in the past, and is expected to make important contributions to product development and quality control in the food and beverage industries.

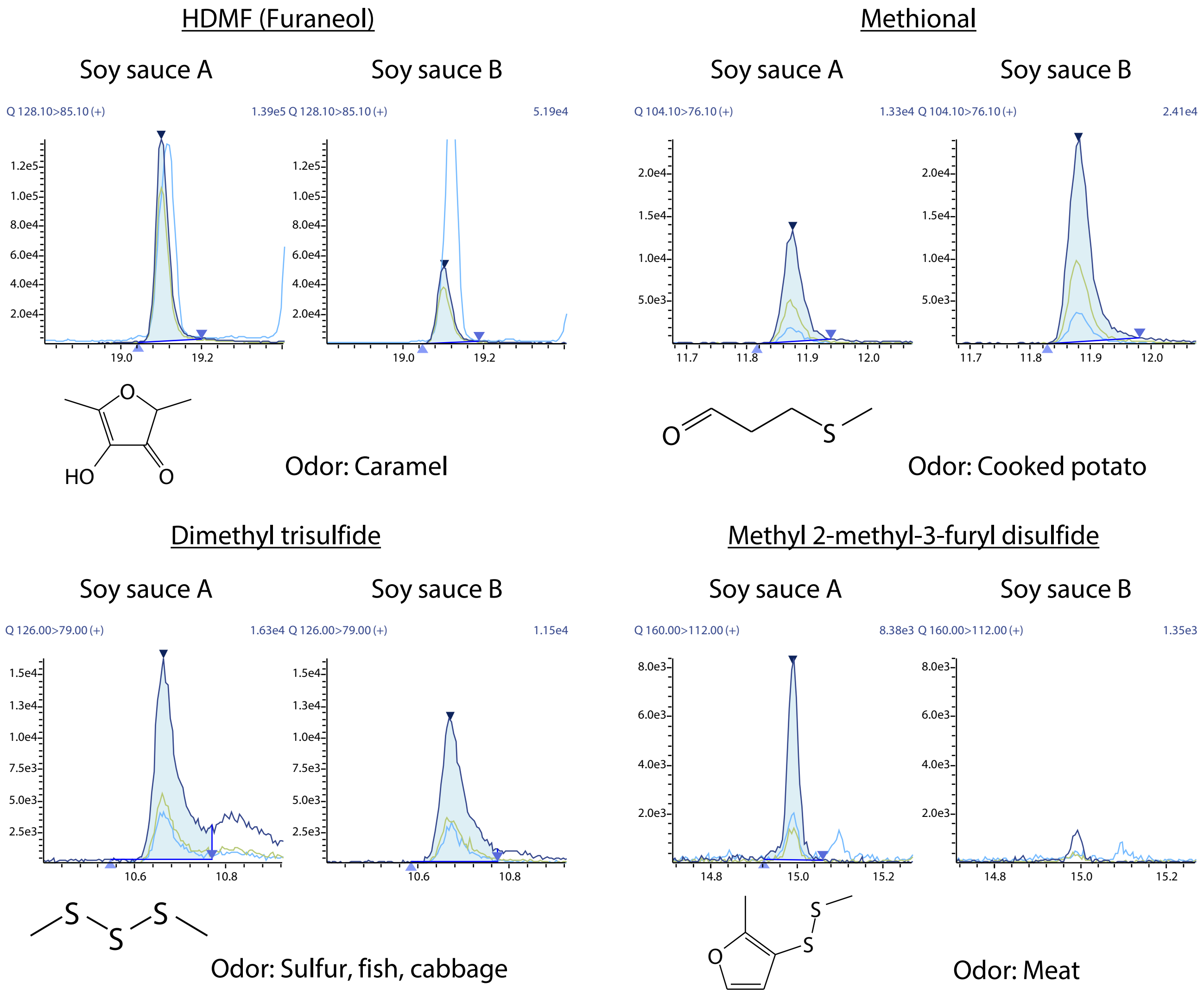

Fig. 8 Comparison of Peaks of Different Soy Sauces in MRM Data Acquired by Immersion Extraction

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01-01269-EN First Edition: Aug. 2026

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