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Development of a simultaneous analysis method of volatile compounds by DART MS

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Introduction

Gas chromatography is typically used for analysis of the volatile compounds represented by aroma compounds. It's considered that measuring flavor release from foods within seconds at eating is important to find relationship with the results of chemical analysis and perceptive aroma. DART MS is effective as the method to monitor volatile compounds within seconds successively. On the other hand, there are a lot of structural isomers in volatile compounds, and it is difficult to specify a target compound by SIM analysis.
Here, we developed a simultaneous analysis method of flavor components which have the similar structure by combining DART and LC-MS/MS.

Methods and Materials

Gamma terpinene, 1,8-cineol, linalool, limonene and cuminal were used for volatile compounds. Gamma terpinene and limonene (molecular weight 136), 1,8-cineol and linalool (molecular weight 154) are a structure isomer, respectively. Triple quadrupole mass spectrometer LCMS-8030 (Shimadzu Corporation, Kyoto, Japan) was used for the analysis of these components.

They were ionized by atmosphere pressure chemical ionization (APCI), so MS conditions like compound-dependent parameters and MRM transitions of each compound were optimized using flow injection analysis with APCI. Next, the DART-OS ion source (IonSense Inc., MA, USA) was interfaced onto the LC-MS/MS and MRM transitions was verified.

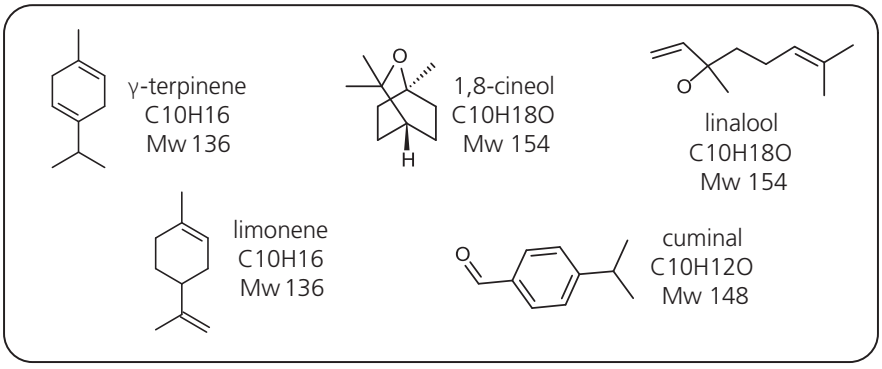

Figure 1 Structure of volatile compounds

UFMS

Ultra Fast Polarity Switching
- 15 msec
Ultra Fast Scanning
- 15,000 u/sec
Ultra Fast MRM
- Max. 555 transition /sec

Figure 2 LCMS-8030 triple quadrupole mass spectrometer

Result

Method development for volatile compounds

At first, we tried ionization ability of these components by electro spray ionization (ESI) and APCI. With ESI, they were not ionized. All components were ionized by APCI while not by ESI. Precursor ion signal was detected by positive m/z 137 both for 4 compounds except for cuminal. This means that a detected signal cannot be specified to be a certain compound even if these 4 compounds were analyzed in selected ion monitoring (SIM). Not only a molecule ion peak, but more than one precursor ion was detected. All components were ionized high-sensitively at positive ion mode and cuminal was ionized at negative ion mode as well as positive.

MS condition (LCMS-8030; Shimadzu Corporation)	
Ionization	: APCI
Measuring mode (MS)	: Q1 scanning, positive/negative simultaneously
Mass range	: m/z 50 - 500
Flow injection analysis	

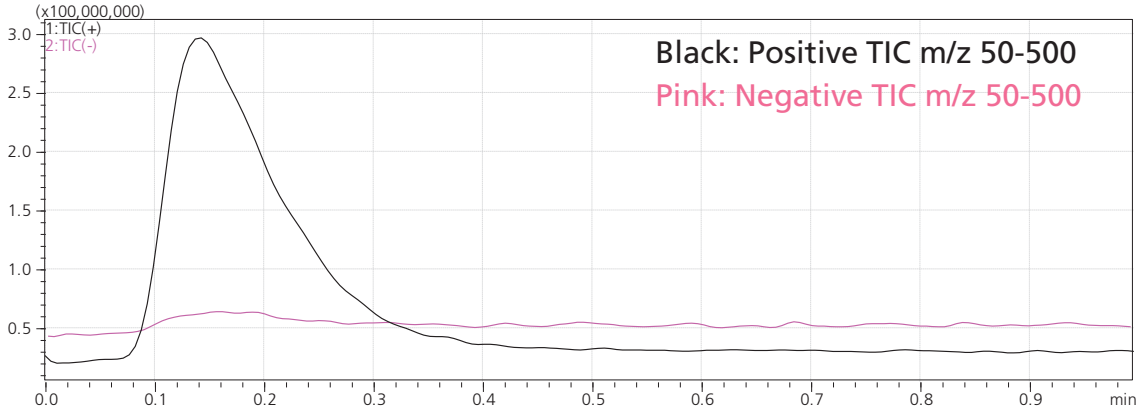

Figure 3 TIC chromatogram of gamma terpinene

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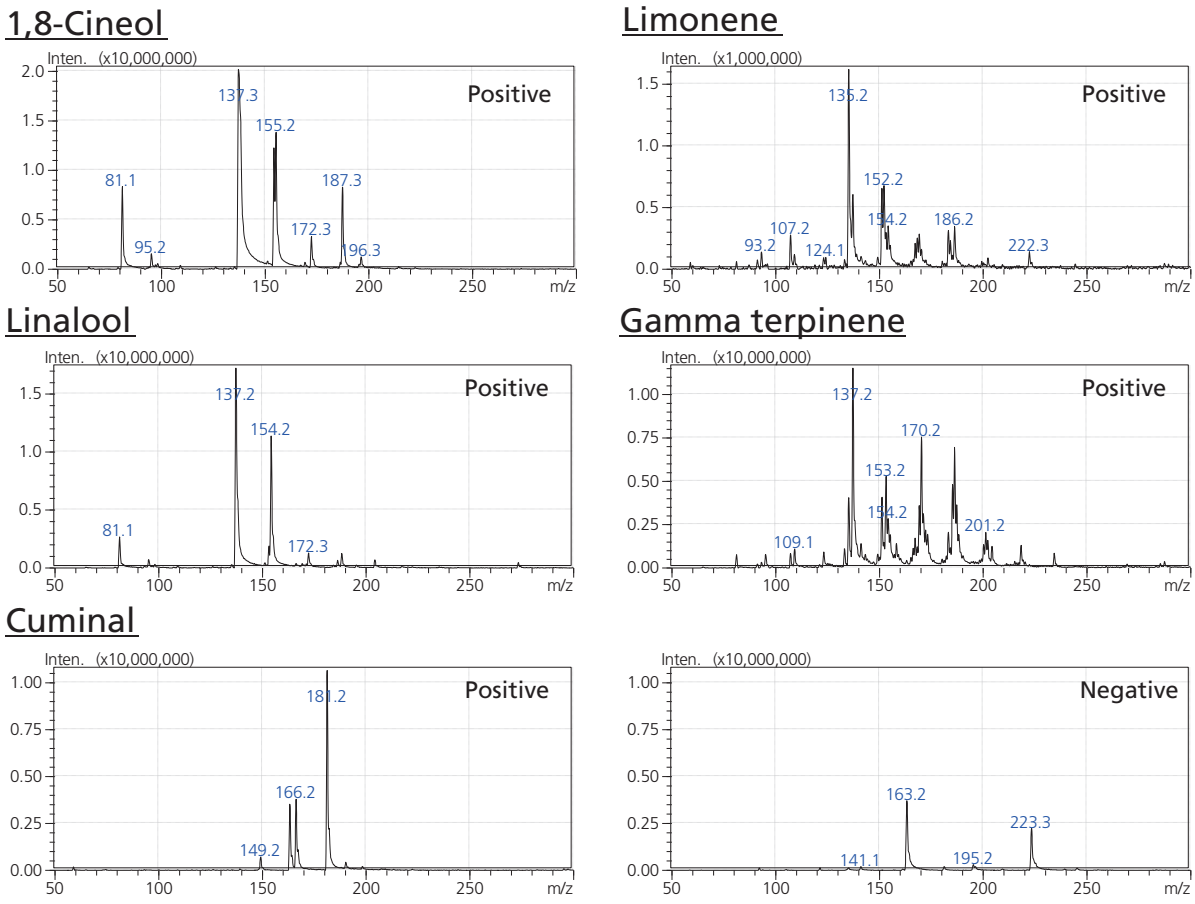

Figure 4 Mass spectra of volatile compounds

For improvement of the selectivity of these compounds, they tried to be detected in MRM mode by LC-MS/MS. MRM transition candidates of each compound were set by flow injection in APCI. Because some transitions would be similar between plural compounds and others would be unique, several MRM transition candidates were selected and compound-dependent parameters were optimized to each MRM transition.

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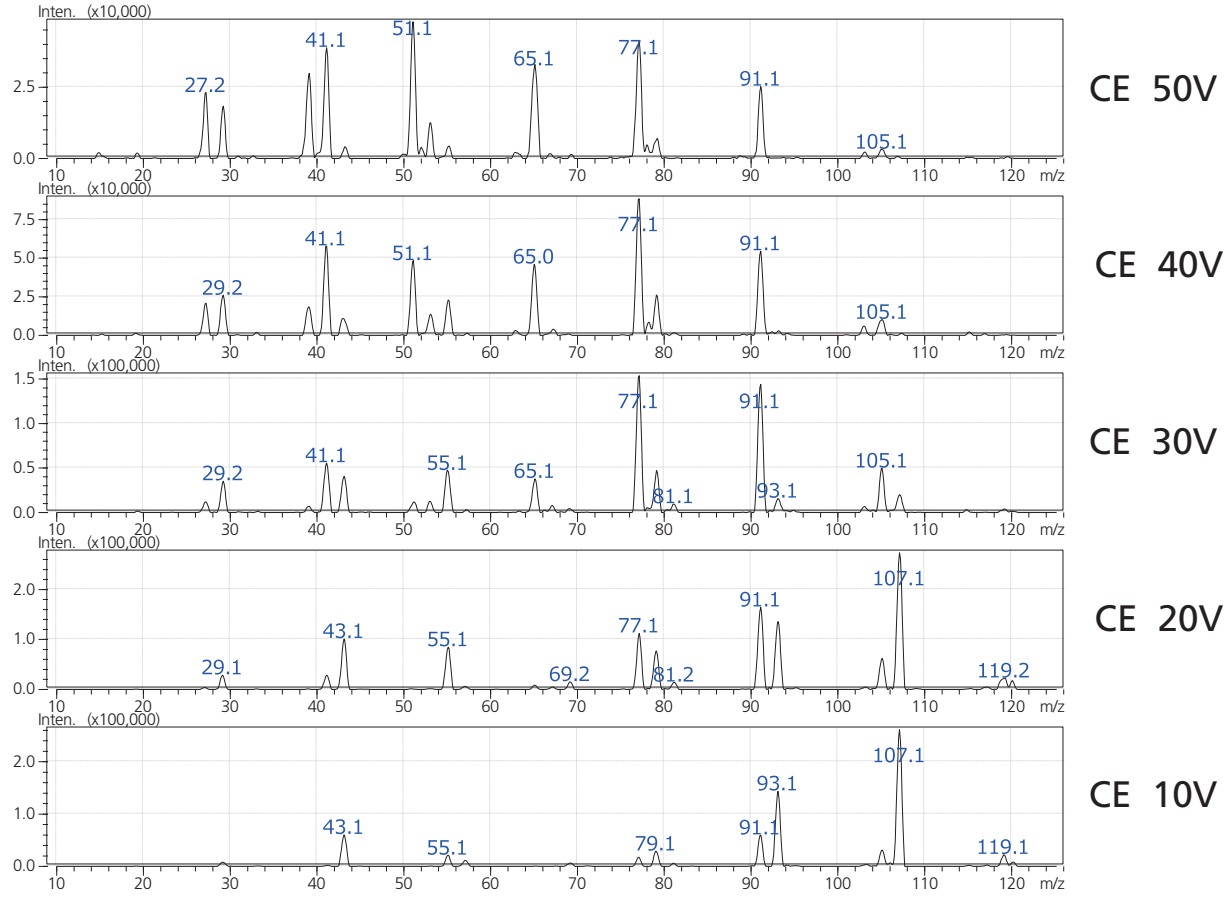

Figure 5 Product ion scan spectra of gamma terpinene (precursor m/z 135)

In the auto optimization for MRM method, multi product ion scannings are acquired for the selection of suitable fragment ions and collision energy. It is able to be executed with single flow injection analysis owing to the Ultra Fast Scanning.

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Table1 MRM transition candidates of volatile compounds

compound ID	Q1>Q3	compound ID	Q1>Q3	compound ID	Q1>Q3
terpinene135(+)	135.20>107.20	cineol155(+)	155.20>81.00	limonene152(+)	152.20>135.10
terpinene135(+)	135.20>91.00	cineol155(+)	155.20>137.05	limonene152(+)	152.20>107.10
terpinene135(+)	135.20>93.00	cineol155(+)	155.20>41.00	limonene152(+)	152.20>69.30
terpinene135(+)	135.20>77.15	cineol155(+)	155.20>95.05	limonene152(+)	152.20>93.10
terpinene135(+)	135.20>43.10	cineol155(+)	155.20>79.00	limonene152(+)	152.20>76.95
terpinene137(+)	137.20>81.20	cineol187(+)	187.20>81.05	cuminal163(+)	163.20>133.05
terpinene137(+)	137.20>95.00	cineol187(+)	187.20>155.15	cuminal163(+)	163.20>105.05
terpinene137(+)	137.20>55.05	cineol187(+)	187.20>137.15	cuminal163(+)	163.20>148.05
terpinene137(+)	137.20>57.00	cineol187(+)	187.20>41.00	cuminal163(+)	163.20>77.10
terpinene137(+)	137.20>43.00	cineol187(+)	187.20>79.15	cuminal163(+)	163.20>79.10
terpinene170(+)	170.20>153.10	linalool137(+)	137.20>81.10	cuminal166(+)	166.20>149.10
terpinene170(+)	170.20>135.10	linalool137(+)	137.20>95.10	cuminal166(+)	166.20>43.05
terpinene170(+)	170.20>43.10	linalool137(+)	137.20>41.10	cuminal166(+)	166.20>79.10
terpinene170(+)	170.20>107.10	linalool137(+)	137.20>55.00	cuminal166(+)	166.20>18.10
terpinene170(+)	170.20>93.00	linalool137(+)	137.20>67.00	cuminal166(+)	166.20>107.05
terpinene186(+)	186.20>151.05	linalool154(+)	154.20>81.10	cuminal181(+)	181.20>149.10
terpinene186(+)	186.20>169.00	linalool154(+)	154.20>137.15	cuminal181(+)	181.20>43.05
terpinene186(+)	186.20>107.10	linalool154(+)	154.20>41.10	cuminal181(+)	181.20>79.00
terpinene186(+)	186.20>43.00	linalool154(+)	154.20>95.10	cuminal181(+)	181.20>107.10
terpinene186(+)	186.20>109.10	linalool154(+)	154.20>69.10	cuminal181(+)	181.20>77.05
cineol137(+)	137.20>81.10	limonene135(+)	135.20>107.10	cuminal163(-)	163.20>119.00
cineol137(+)	137.20>95.00	limonene135(+)	135.20>90.95	cuminal163(-)	163.20>118.85
cineol137(+)	137.20>41.10	limonene135(+)	135.20>93.00	cuminal223(-)	223.20>162.95
cineol137(+)	137.20>79.10	limonene135(+)	135.20>77.05	cuminal223(-)	223.20>119.10
cineol137(+)	137.20>55.10	limonene135(+)	135.20>55.05	cuminal223(-)	223.20>59.10
cineol154(+)	154.20>81.15	limonene151(+)	151.20>109.15		
cineol154(+)	154.20>137.10	limonene151(+)	151.20>69.15		
cineol154(+)	154.20>95.00	limonene151(+)	151.20>41.10		
cineol154(+)	154.20>41.10	limonene151(+)	151.20>81.05		
cineol154(+)	154.20>79.10	limonene151(+)	151.20>43.15		

MRM transition candidates of 5 compounds were built by APCI. Each compound has a few precursor ions, which have several product ions.

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Direct analysis of volatile compounds by DART MS

Next, the DART-OS ion source with volatile analyzing option; Volatimeship (Bio Chromato, Inc., Japan) was interfaced onto the LC-MS/MS and each compound was analyzed with optimized MRM transition candidates then they were verified.

MS condition (LCMS-8030; Shimadzu Corporation)	
Ionization	: DART-OS with Volatimeship
Heater Temperature (DART)	: 350 °C
Measuring mode (MS)	: MRMs Positive/Negative simultaneously

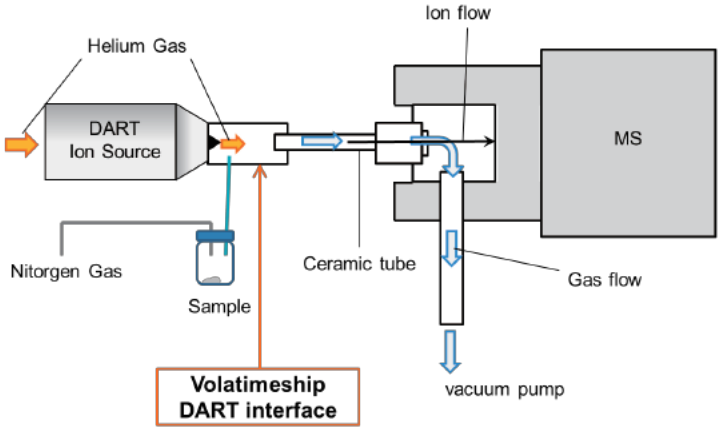

Figure 6 DART-OS ion source with volatile analyzing option & LCMS-8030

Only 1,8-cineol was detected intensively at Q1/Q3=155/81, 155/137 and 155/95 (positive) which were the MRM transition candidates optimized in 1,8-cineol. This found out that they are the transitions which can specify 1,8-cineol. In the same way, limonene showed that Q1/Q3=135/107, 135/91 and 152/107 (positive), cuminal showed that Q1/Q3=166/149, 166/43 (positive) and 163/119 (negative) are the transitions which can specified the respective compounds.

Development of a simultaneous analysis method of volatile compounds by DART MS

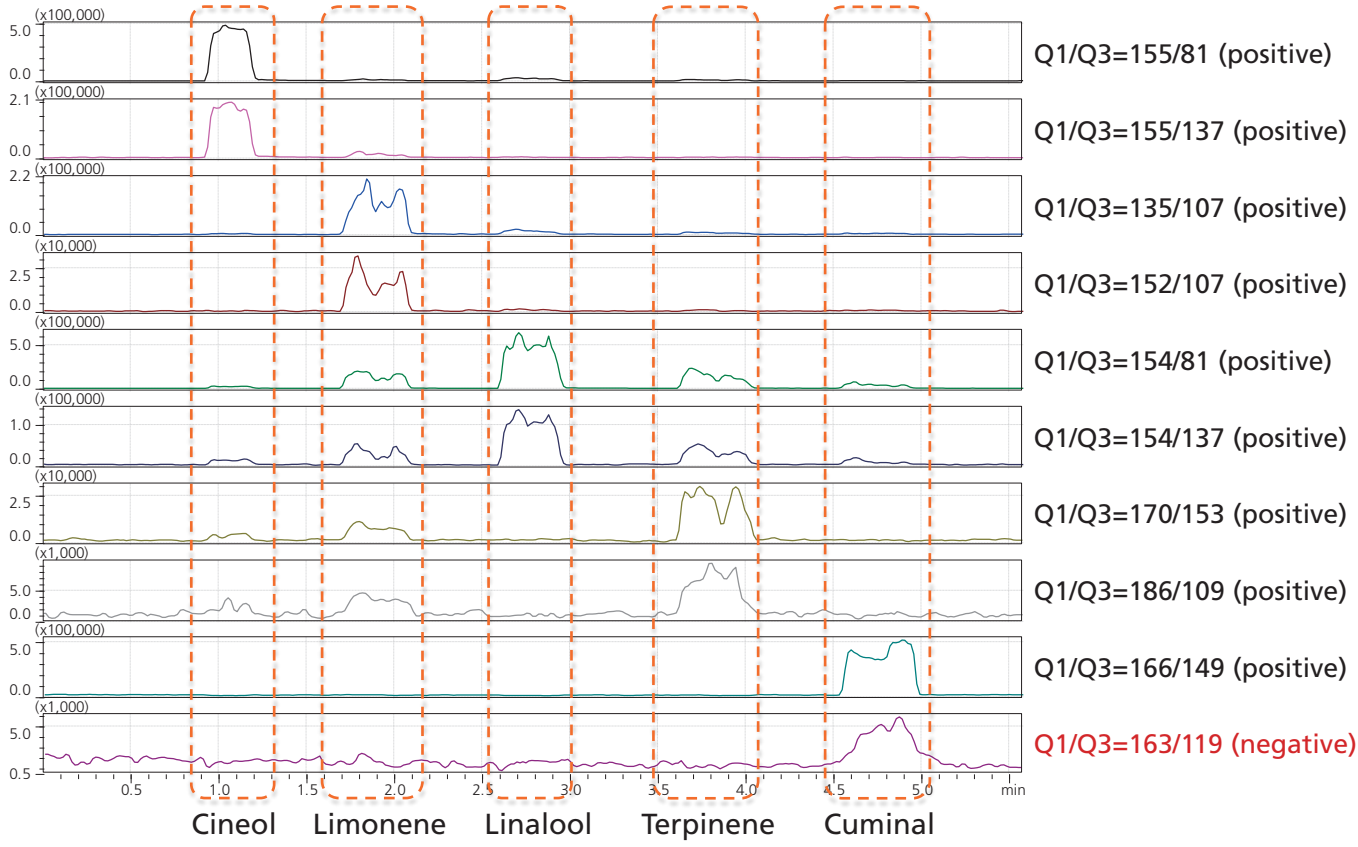

Figure 7 MRM chromatograms where a strong signal was detected only in a specific compound

Conclusions

- Volatile compounds were analyzed and detected by APCI and DART-MS with volatile analyzing option.
- Volatile compounds with the similar structure and/or the same molecular weight could be detected specifically by DART & LC-MS/MS.

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