

Application News

No. C111

Liquid Chromatography Mass Spectrometry

Direct Analysis of Volatile Compounds in Real Time Using DART-MS (Part 1) Analysis of Flavor Release from Chocolate-like Food

The release of flavor when food is masticated has attracted interest in the determining the compounds that affect how good something tastes or smells, which are being studied using a variety of evaluation methods. Attempts have been made to continuously measure the volatile compounds that pass through the nose during mastication. However, these involve humans as the testing medium and present various problems, such as the difficulty in repeating tests multiple times and the long data collection intervals. The DART (direct analysis in real time) system, which is able to directly ionize samples, could be used to rapidly analyze such volatile compounds if the compounds could be introduced into the ion source efficiently. This Application News describes an example of continuously measuring the volatile compounds emitted as a chocolate-like model food melts.

Analytical Conditions for Analyzing Chocolate-like Food

An LCMS-8030 system was used as the mass spectrometer. A DART-SVP (from IonSense Inc., in MA, U.S.) was used as the ion source, and a Volatimeship device (from Bio Chromato Inc. in Kanagawa, Japan) was inserted between the ion source and the mass spectrometer (Fig. 1) for efficiently analyzing the volatile compounds emitted from the model food.

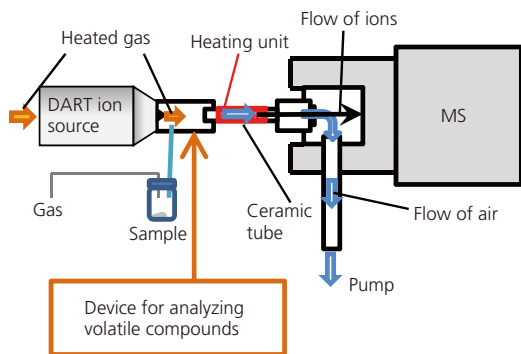


Fig. 1 Measurement System

The model food was prepared by adding different concentrations of two volatile compounds (L-carvone and D-limonene) to a solid fat base used to represent the chocolate (Table 1).

0.02 g of each sample and 1 mL of ultrapure water were placed in vials and loaded in the measurement system. Then the vials were heated by inserting the bottom of the vials in a water bath. Then the volatile compounds evolved in the headspace were measured. For the purpose of confirming the release of flavor as the sample fat melted, analysis was performed until the water temperature reached equilibrium inside the vials (about 2 minutes).

In addition to full scans in positive and negative modes, multiple MRM channels were used to identify carvone and limonene with high reliability. Due to both the ultra fast scanning (15,000 u/sec) and ultra fast polarity switching (15 msec) capabilities of the LCMS-8030, positive and negative scanning and multichannel simultaneous MRM analysis were accomplished in less than a second per data point (Table 2).

Table 1 Composition of Two Volatile Compounds in Chocolate-like Food

Sample No.	Carvone (%)	Limonene (%)
①	0.1	0
②	0.1	0.01
③	0.1	0.03
④	0.1	0.05
⑤	0	0.1

Table 2 Analytical Conditions

DART Heater Temperature	: 300 °C
Scan Type	: Q3 scan <i>m/z</i> 50 – 1500 (Positive / Negative)
MRM Transition	: Carvone 151 > 109 and 5ch (Positive) Limonene 137 > 81 and 12ch (Positive)
Drying Gas Flow	: 5.0 L/min.
DL Temperature	: 250 °C
Block Heater Temperature	: 400 °C
Water Bath Temperature	: 65-70 °C

Analysis of Volatile Compounds in Chocolate-like Food

A total ion current chromatogram (TICC) of samples (1) to (5) is shown in Fig. 2. For each sample, a peak begins to rise immediately after loading the sample vial (labeled "Load sample" in Fig. 2). One minute after loading the vials, immediately after starting to heat the vials in a water bath, an increase in an even larger peak is shown. Presumably, this is due to the heat promoting the volatilization of volatile components.

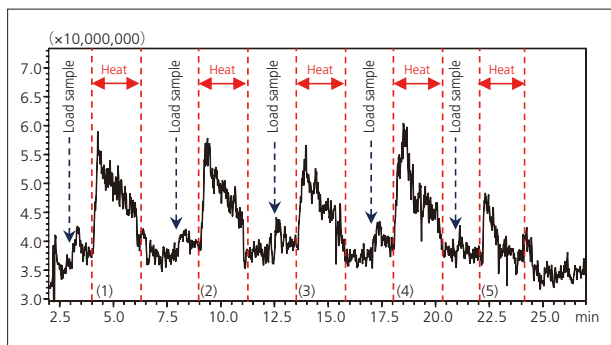


Fig. 2 Total Ion Current Chromatogram of Chocolate-like Food

The MRM mode was used for analyzing samples to detect limonene and carvone with high sensitivity and high selectivity and also to avoid effects from contaminant compounds. MRM chromatograms for representative limonene and carvone transitions during the analysis of samples (1) to (5) are shown in Fig. 3.

As shown in Table 1, identical carvone concentrations were added to samples (1) to (4) and none to sample (5). Consequently, the resulting MRM chromatograms for samples (1) to (4) include similarly strong peaks for the carvone transition at Q1/Q3 = 151/109, whereas that peak was not detected for sample (5). In the case of limonene, increasing concentrations levels were added to samples (1) to (5). Consequently, the resulting MRM chromatograms show corresponding increasing signal intensity from the limonene transition in samples (1) to (5), which indicates a correlation between the concentration added and the signal intensity.

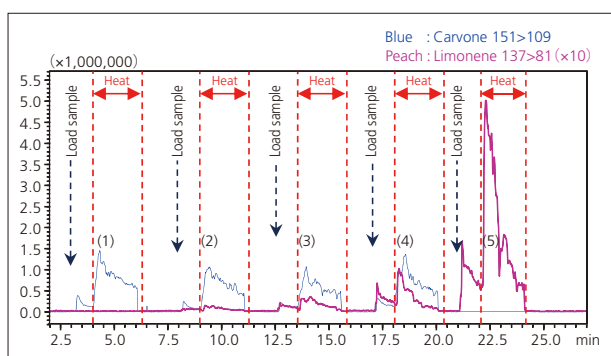


Fig. 3 MRM Chromatogram of Chocolate-like Food

To confirm the change in temperature inside the vials containing samples, water was placed in a vial instead of a sample and the water temperature was measured as a function of time. Those results, shown in Fig. 4, confirm that the temperature increased to 50 °C in about 20 seconds after applying heat.

An enlargement of the MRM chromatogram for sample (4) from zero to 20 seconds after heating is shown in Fig. 5. This confirms that the ion intensity from the carvone transition increased immediately after heating. This behavior is almost the same as the water temperature behavior in Fig. 4. In contrast, the signal intensity increase from the limonene transition occurs later than for carvone and then decreased after reaching its maximum intensity, about 15 seconds after heating.

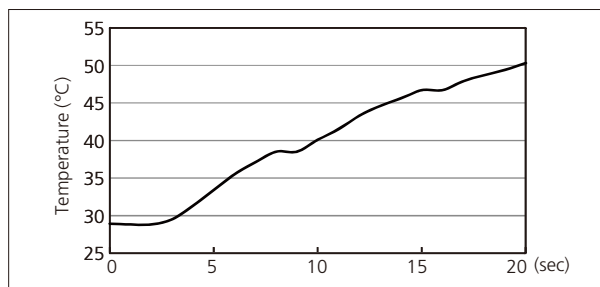


Fig. 4 Water Temperature Inside Vial

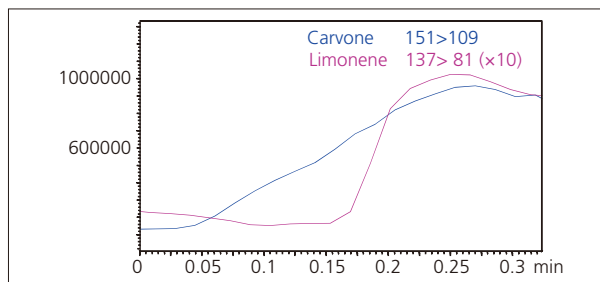


Fig. 5 MRM Chromatogram of Sample (4)

Each sample was measured three times in a row. The corresponding MRM chromatograms for samples (3) and (4) are shown in Fig. 6. This confirms the reproducibility of the behavior shown in Fig. 5.

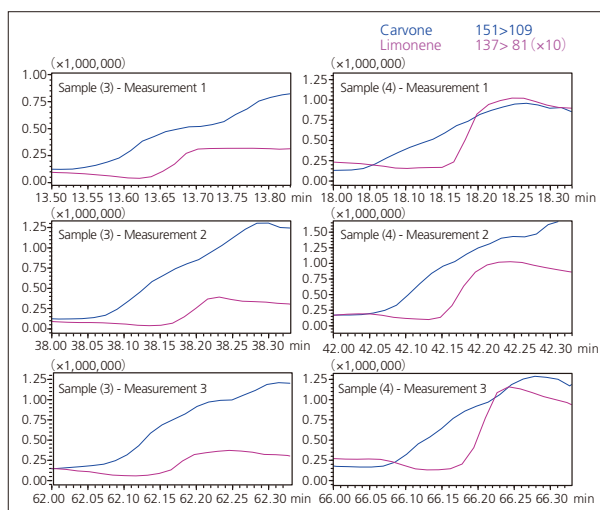


Fig. 6 MRM Chromatograms of Samples (3) and (4) (n = 3)

Thanks to the short data acquisition time of less than one second per sample, it was possible to clearly show differences in behavior of volatile compounds during a short period. This suggests the system's potential for measuring flavor-release phenomena.

Data was provided and analyzed with the generous cooperation from Mr. Takehito Sagawa at S&B Foods.

[References]

Takehito Sagawa et al., Continuous Analysis of Volatile Compounds from Foods During Flavor Release Using Direct Analysis in Real Time Mass Spectrometry, Journal of the Japanese Society for Food Science and Technology, 62 (7), 335-340, 2015

DART is a product of IonSense Inc.
(<http://www.ionsense.com/>).