LAAN-A-LM-E083

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Application News

No.C112

Liquid Chromatography Mass Spectrometry

Direct Analysis of Volatile Compounds in Real Time Using DART-MS (Part 2)
Analysis of Volatile Compounds in Spices, Herb Tea, and Flavored Oils

When food is cooked, it emits a variety of aromas that can stimulate appetite. To study the science of such food aromas, there has been interest in analyzing the volatile compounds of such aromas. Because the volatile compound profile varies extremely quickly immediately after cooking food, samples must be collected in a timely manner and efficiently introduced into the analytical instrument.
Application News No. C111 described an example of continuous measurements of flavor compounds released when a chocolate-like model food melts, using the DART (direct analysis in real time) method, capable of ionizing samples directly, in combination with a Volatimeship volatile compound measurement device and an LCMS-8030 mass spectrometer system.
This article describes an example of using the same system to continuously measure the flavor compounds released from spices, herb tea, and flavored oils that provide a pleasant cooling sensation.

■ DART-MS Analytical Conditions

An LCMS-8030 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 components emitted from the food sample.
Due to both the ultra fast scanning (15,000 u/sec) and ultra fast polarity switching (15 msec) capabilities of the LCMS-8030, multichannel scanning and multichannel simultaneous MRM analyses were accomplished in less than a second per data point (Table 1).

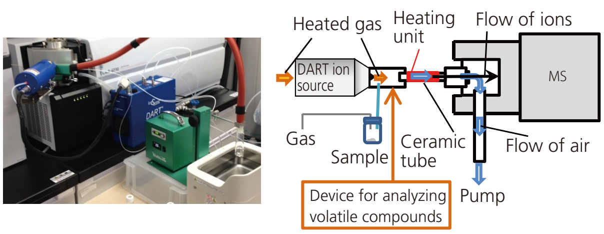

Fig. 1 Measurement System

Table 1 Analytical Conditions

DART Heater Temperature	: 300 °C
Scan Type	: Q3 scan *m/z* 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

Two kinds of spices (clove and allspice), herb tea made from fresh spearmint leaves, and two kinds of flavored oils were used for measurements.
The spices and flavored oils were placed directly in vials, sealed, and loaded in the measurement system. The vials were heated by inserting the bottom of the vials in a water bath. Then the Volatimeship device was used to inject the volatile compounds from the headspace into the ion source for measurement.
Raw leaves of the herb tea were placed in a vial with boiling water and sealed. After 1 to 3 minutes of steeping, the bottom of the vial was heated in a water bath, in the same manner as for the spices. Then the volatile compounds in the headspace were measured.

■ Analysis of Volatile Compounds in Spices

The positive mass spectra from analyzing the clove and allspice are shown in Fig. 2.
By connecting the Volatimeship device to the DART-MS system for analysis, the volatile compounds in the spices were able to be analyzed in real time and with high sensitivity, without having to collect the volatile compounds first. The volatile compounds were identified from the detected signals based on standard sample spectral patterns for the volatile compounds. From the clove, signals for compounds presumed to be 1,8-cineole, eugenol, eugenol acetate, and caryophyllene were detected. From the allspice, compounds presumed to be 1,8-cineole, eugenol, methyl eugenol and caryophyllene were detected.

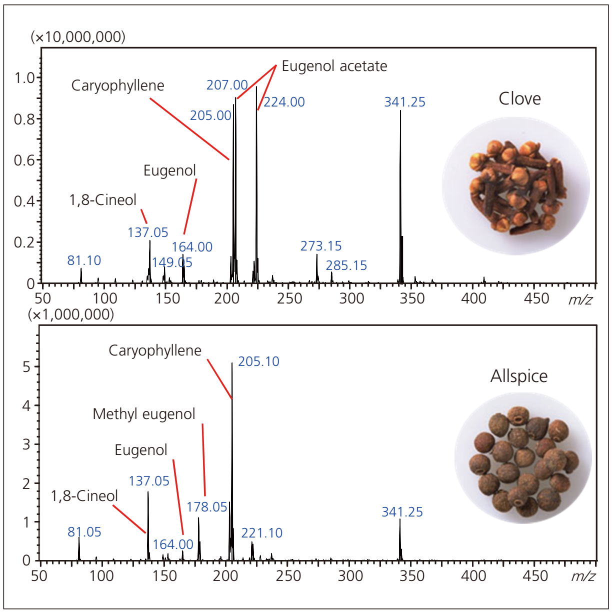

Fig. 2 Mass Spectra (positive) of Two Kinds of Spices

Analysis of Volatile Compounds in Herb Tea

Analysis was performed to simulate the change in volatile compounds as they escape a teapot when the lid is removed after steeping the herb tea in the teapot for a given time. Measurement targeted the compounds that typify spearmint, namely a mild sweet fragrance (carvone) and a ground tangerine peel fragrance (limonene). MRM transitions optimized for standard samples of carvone and limonene were used for detection. After steeping the herb tea for 3 minutes, it was heated in a water bath for 2 minutes and measured by MRM. The results are shown in Fig. 3.
The ion intensity increased for both carvone and limonene immediately after starting the measurement. The ion intensity for carvone showed no major changes until the measurement was finished, whereas the ion intensity for limonene dropped sharply about 20 seconds after starting the measurement, after which it remained constant. The results confirmed that the composition of the herb tea fragrance changed with time.

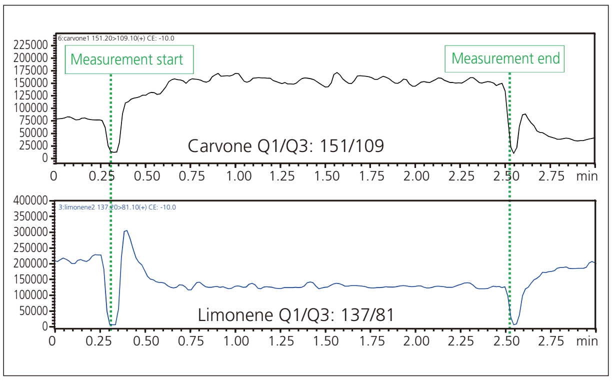

Fig. 3 MRM Chromatograms of Herb Tea (steeped for 3 min)

MRM chromatograms for two types of volatile compounds (carvone and limonene) emitted from herb tea steeped 1, 2, or 3 minutes are shown in Fig. 4 (the portion up to 10 seconds after starting heating is shown enlarged).
All herb tea steeping times produced similar results of the ion intensity for limonene sharply increasing and then decreasing, whereas the carvone ion intensity increased and then remained constant. However, the results showed that the longer the steeping time, the higher carvone ratio with respect to limonene. This showed that the fragrance of herb tea changed depending on the length of steeping time.

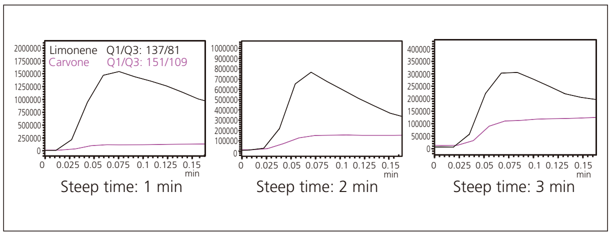

Fig. 4 MRM Chromatograms of Herb Tea (steeped for 1, 2, or 3 min)

Analysis of Volatile Compounds in Flavored Oils

Differences in the aroma that depend on the base material that includes volatile compounds were investigated. Fig. 5 shows MRM chromatograms obtained when a spearmint essential oil and a flavored oil with a medium-chain triglyceride (MCT) base material, both containing roughly equal amounts of carvone, were heated in a water bath.
The carvone MRM signal intensity from the essential oil gradually increase, whereas it dramatically increases about 3 seconds after starting the analysis for the MCT-based flavored product. The analytical data confirms that even if samples contain the same volatile compounds, differences in the base material potentially can affect how the product smells.

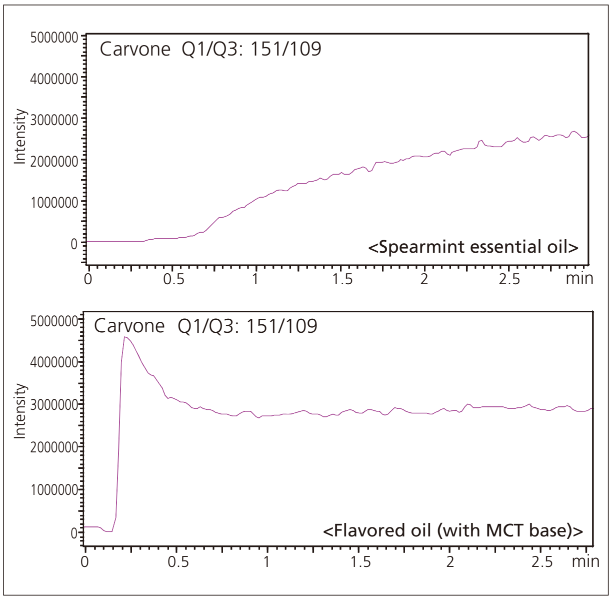

Fig. 5 MRM Chromatogram of Flavored Oils

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/).

First Edition: Oct. 2015

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