

Componential analysis of pepper of various origins using DART-MS using ultra-fast polarity switching

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Introduction

DART (Direct Analysis in Real Time), a direct atmospheric pressure ionization source, is capable of analyzing food samples with little or no sample preparation. Time of flight mass spectrometers, which have been a common choice to interface DART, were not suitable in carrying out simultaneous detection of compounds with different polarities from the same sample due to its limitation in

switching between positive and negative ion modes in terms of time required to do so. Analysis of different parts of pepper (exodermis, endodermis and seeds) along with olive oil and soy sauce of different types and origins were carried out using the DART combined with a mass spectrometer with ultra-fast polarity switching capability to conduct chemometric analysis.



Fig. 1 DART-SVP ion source LCMS-2020

Materials and Methods

Commercially available peppers from different origins were introduced to the DART gas using tweezers. Glass capillary was used to dip and transfer olive oil to the ionization area, and soy sauce was spotted on a metal mesh to scan with the DART beam. The DART-SVP ion source (IonSense Inc., MA, USA) was interfaced onto the single quadrupole mass spectrometer LCMS-2020 (Shimadzu Corporation, Kyoto,

Japan). Ultra-fast polarity switching was utilized on the mass spectrometer to collect full scan data. LCMS-2020 can achieve the polarity switching time of 15 msec and the scanning speed of up to 15000 u/sec, therefore the loop time can be set at less than 1 second despite the relatively large scanning range of 100-1000 u.

Results

Peppers

Capsaicin ($C_{18}H_{27}NO_3$, MW 305), which is responsible for the spicy flavor of pepper, is usually most abundant in placenta. Commercially available peppers from Korea,

China and several areas in Japan were cut and separated to each part of the exodermis, endodermis and the seed and each sample was analyzed by DART-SVP LCMS-2020.

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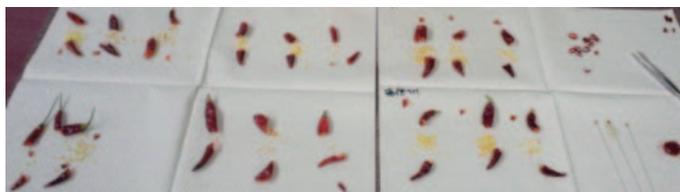


Fig. 2 Commercially available peppers from different origins and sample preparation for DART-MS

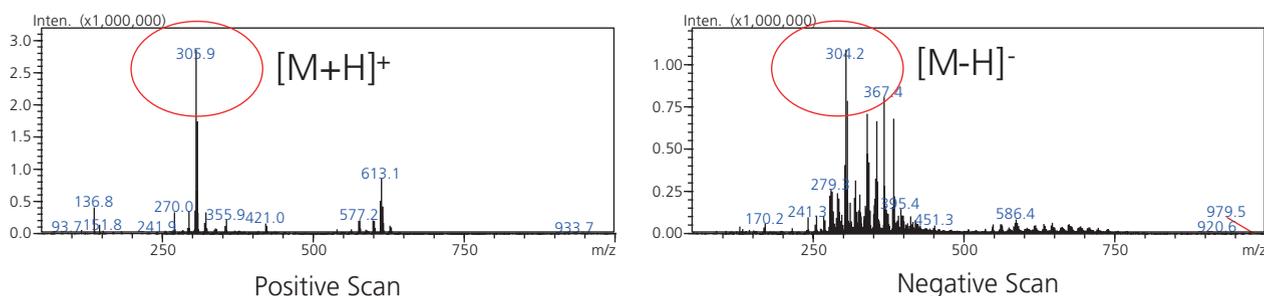


Fig. 3 Positive/Negative mass spectrum of pepper seed @350°C

The signal indicating capsaicin was detected in both polarities; at m/z 306 in positive ion mode, m/z 304 in negative mode. The signal in positive ion mode was more intense than in negative ion mode. After careful

optimization of analytical conditions using different DART gas heater temperatures at 200°C, 350°C and 500°C, it was determined that 350°C was the suitable temperature setting to analyze capsaicin.

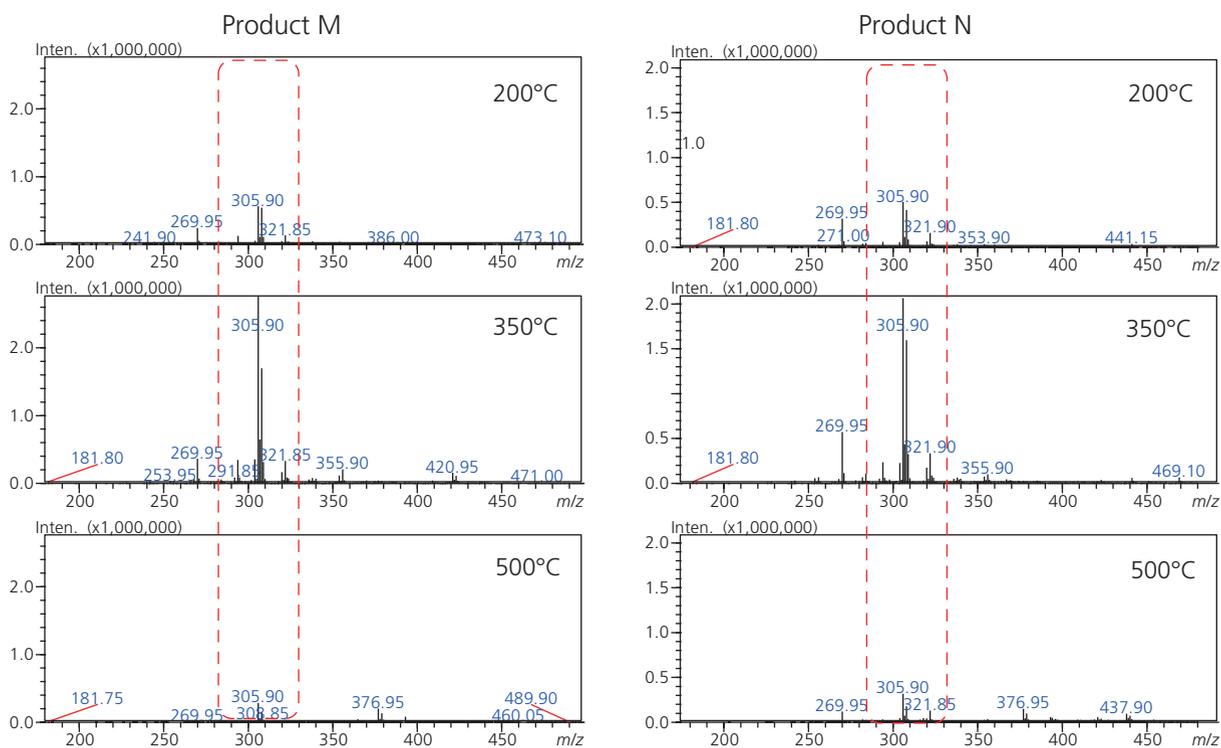


Fig. 4 DART gas heater temperature comparison; 200°C, 350°C, 500°C
Mass spectra in positive ion mode of product M, N pepper seeds

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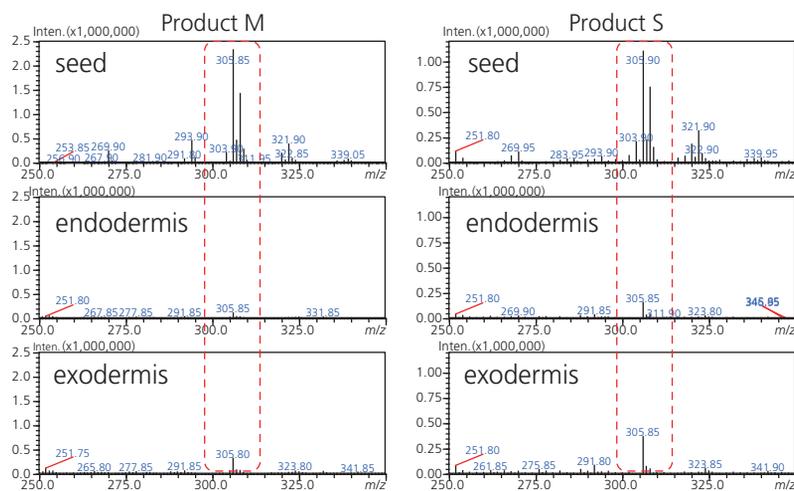


Fig. 5 Capsaicin localization comparison; seeds, exodermis, endodermis
Mass spectra in positive ion mode of product M, S pepper seeds

In most of the samples, the signal of capsaicin was most intense in seeds, which implicates that there were placental fragments on the surface of the seeds, which, even in small quantity, was giving out the intense signal for capsaicin.

Soy Sauce

Next, soy sauces and fish sauces from different origins were analyzed. Low molecular weight spectra were observed in different profiles depending on the sample ingredients, indicating the different balances in amino acid contents.

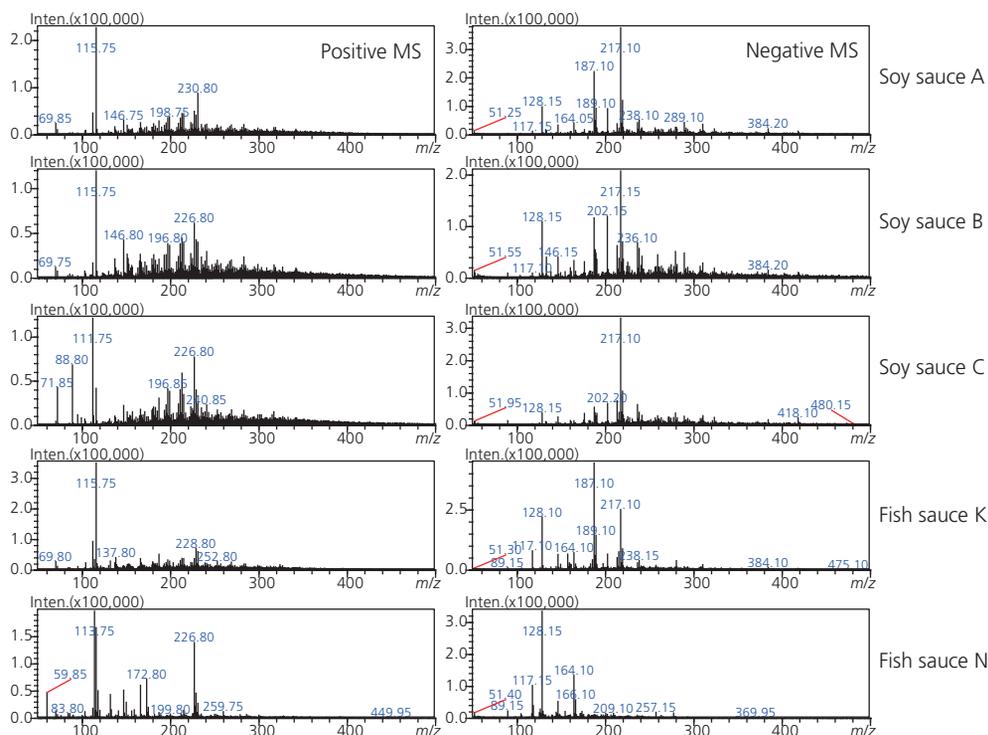


Fig. 6 Various soy sauces and fish sauces DART-MS analysis results
There found different spectrum pattern between soy sources and fish sources.

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Olive Oil

For olive oil and grape seeds oil samples, high molecular weight spectra were more dominant in both polarity at temperature setting of 500°C than 200°C and 350°C, suggesting the possibility to analyze the differences in triglycerides contents.

Multivariable analyses were conducted using these spectral

data to distinguish different food samples from different origins and/or deferent ingredients. This indicates that DART-MS can be a powerful tool for origin determination/ authentication of agricultural produce and processed goods. (data not shown)

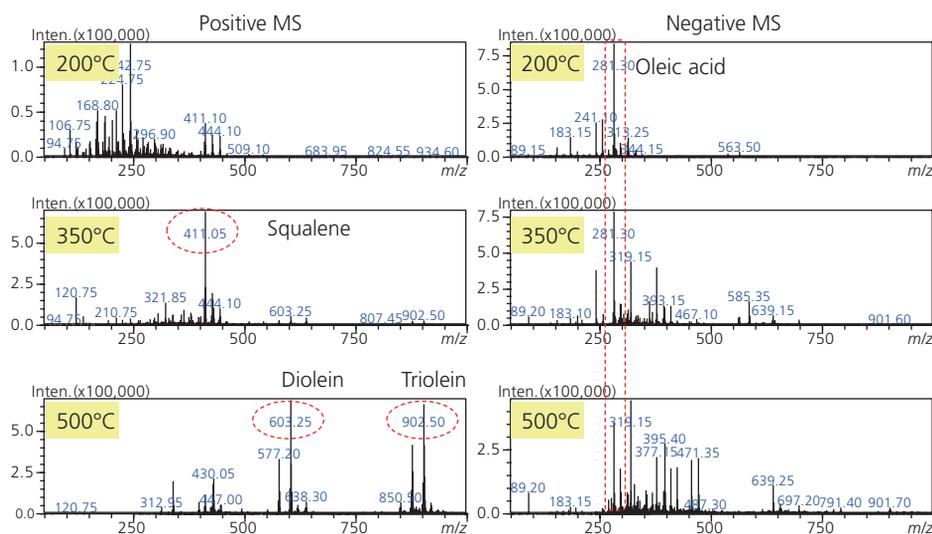


Fig. 8 Mass spectra in positive/negative ion mode of an olive oil sample ; DART gas heater temperature comparison (200 - 500°C)

Conclusions

- Ultra-fast polarity switching is useful for DART analysis of food samples.
- Some compounds have optimum DART gas heater temperature.
- Rapid DART analysis of food samples using ultra-fast polarity switching and its chemometric analysis is available to distinguish their origins.