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Rapid analysis of triglycerides and fatty acids in food oils using DART-MS with high-speed polarity switching

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1. Introduction

Conventionally, common ways to analyze triglycerides have been by using liquid chromatograph or gas chromatograph. Some of the problems with those methods have been the cumbersome sample prep, lengthy analysis time and memory effect. Previous reports on DART-MS analysis of triglycerides and fatty acids have involved separate acquisitions of positive spectra and negative spectra, but this time we have successfully applied the ultra-fast polarity switching to carry out high-throughput parallel analyses of fatty acid compositions in triglycerides and free fatty acids using Direct Analysis in Real Time (DART) mass spectrometry.

2. Methods and Materials

Commercially available edible oils such as olive oil and Chinese chili oil were obtained at a local grocery store. Small amount of the samples were picked up and held in the DART ionization gas stream using glass capillaries. DART-OS ion source (IonSense, Inc., MA, USA) was coupled with triple quadrupole mass spectrometer LCMS-8030/8040 triple quadrupole mass spectrometer (Shimadzu Corporation, Kyoto, Japan), which is capable of ultra-fast polarity switching. Scan range was set between *m/z* 50 -1200 for both positive and negative mode, with which the performance of 2 scans/sec was achieved.

Analytical Conditions

DART: DART OS (IonSense, Inc., USA)
Heater Temperature: 300C - 500°C

Mass spectrometer: LCMS-8030 (Shimadzu Corporation, Japan)

Ionization: Electrospray ionization, Positive/Negative
Ultra Fast Polarity Switching 15 msec
Scan type: Q3 scan, *m/z* 50 - 1200
Ultra Fast Scanning Up to 15,000 u/sec

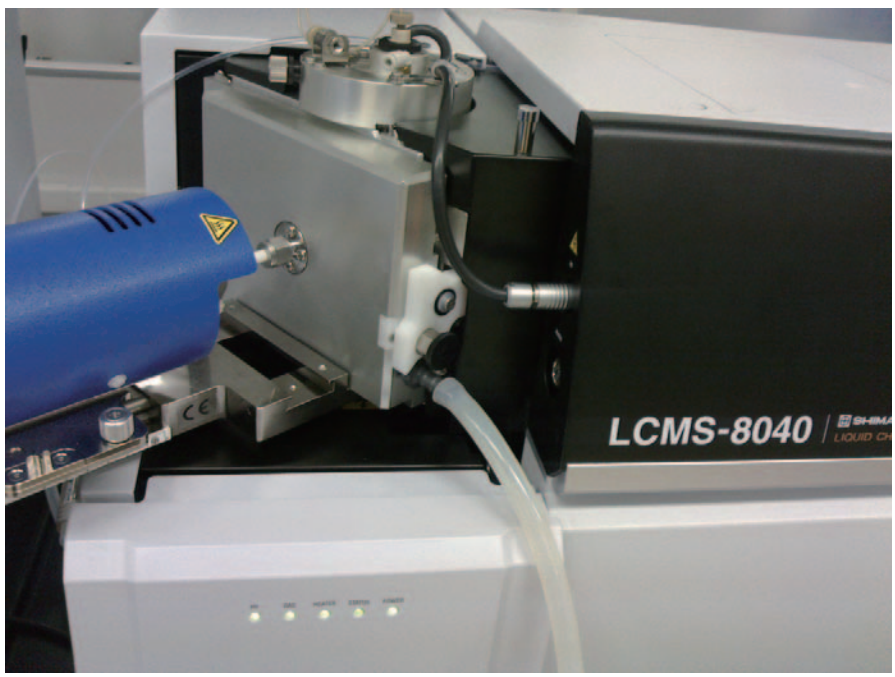

Fig. 1 DART OS ion source coupled with LCMS-8040 triple quadrupole mass spectrometer

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3. Results

3-1. Method development for oils

The samples were analyzed using three different DART gas temperature settings of 300°C, 400°C and 500°C (Fig. 2). Fig. 3 shows typical mass specta that were analyzed Chinese chili oil. From the Chinese chili oil, capsaicin (*m/z* 306, positive ion) was detected. The best temperature setting for this compound was 300°C among the three temperature settings we examined. As the heater temperature was raised to 400°C and 500°C the positive ion signals of triglycerides around *m/z* 900 became more intense. Diglycerides were detected around *m/z* 600.

Triglycerides were believed to be primarily ammonia adduct ions and diglycerides, dehydrated ions. From the negative ion spectra, signals for linoleic acid (*m/z* 279) and oleic acid (*m/z* 281) were found throughout the temperature range used in this experiment (Fig. 4).
We decided that the optimum DART heater temperature setting was 500°C for the purpose of pattern analysis of triglycerides and fatty acids, and kept the 500°C setting throughout the rest of the experiment.

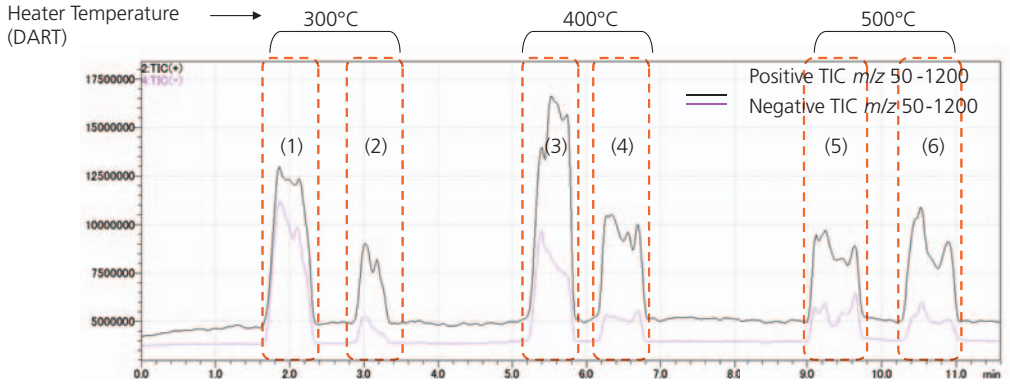

Fig. 2 Total ion current chromatograms for DART analysis of oils
(1) Chinese chili oil; heater temp. 300°C (2) Salad oil; heater temp. 300°C
(3) Chinese chili oil; heater temp. 400°C (4) Salad oil; heater temp. 400°C
(5) Chinese chili oil; heater temp. 500°C (6) Salad oil; heater temp. 500°C

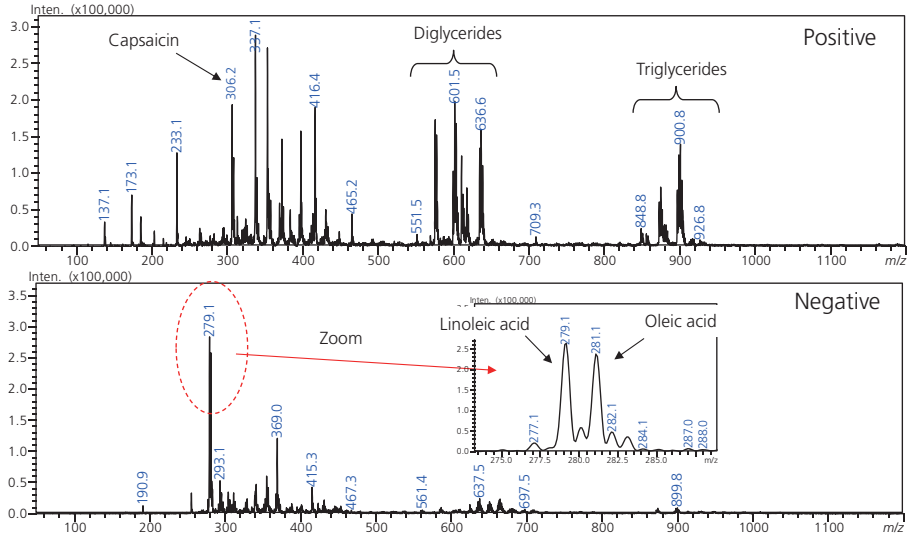

Fig. 3 Mass spectra for Chinese chili oil; heater temp. 400°C

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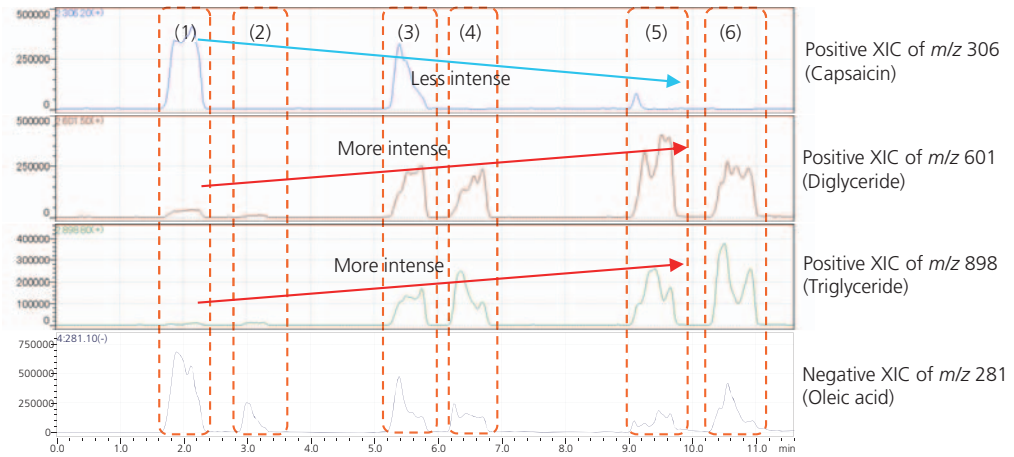

Fig. 4 Extracted Ion Current Chromatograms of typical *m/z* values

3-2. Chinese chili oil

Fig. 5 shows mass spectra that were analyzed Chinese chili oil at heater temperature 500°C. Taking a closer look at triglycerides of Chinese chili oil, it was found that there were signals of triglycerides comprised of (1) oleic acid molecules only, (2) two oleic acid and a linoleic acid molecules, (3) an oleic acid and two linoleic acid molecules and (4) linoleic acid molecules only, in similar intensity, which correlates with the balance of fatty acid signals of oleic acid and linoleic acid in the negative ion spectra. It was also possible to determine the presence of palmitic acid components by comparing the triglyceride ion clusters that appear in lower *m/z* range in the positive spectra and palmitic acid signal in the negative spectra.

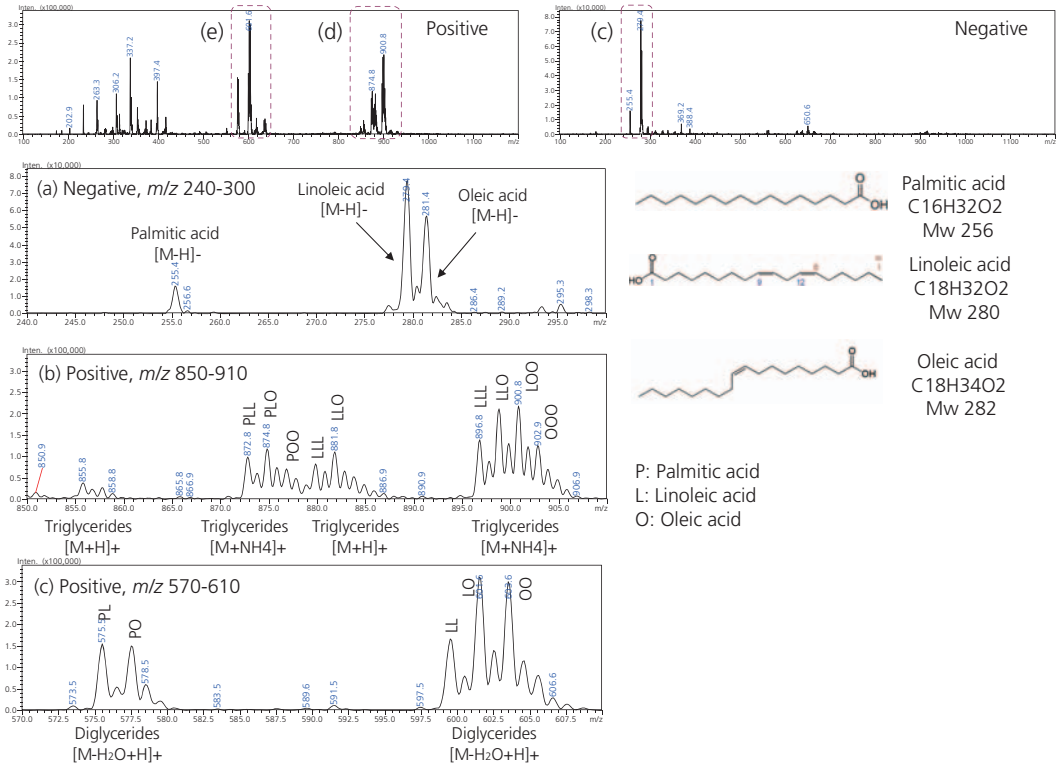

Fig. 5 Mass spectra for Chinese chili oil; heater temp. 500°C

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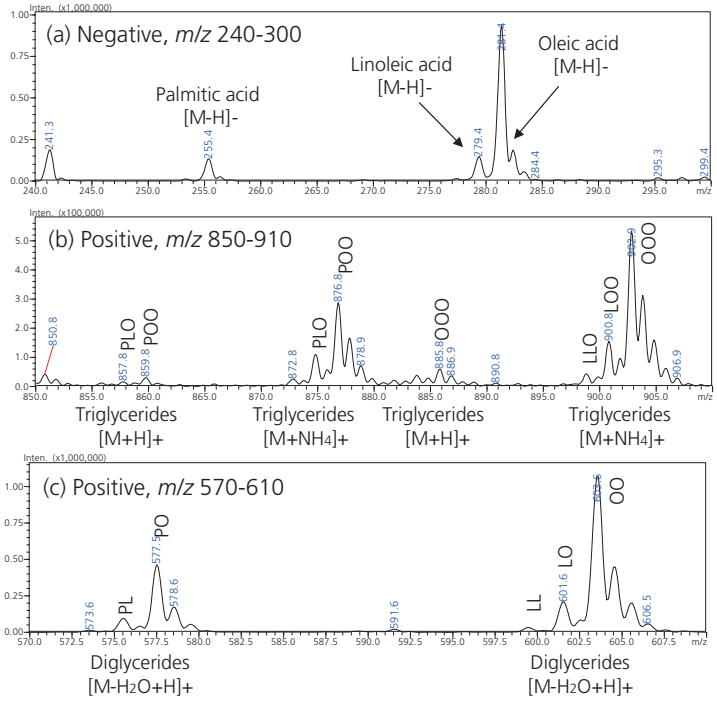
3-3. Olive oil and sesame seed oil

DART-MS analyses were carried for olive oil, sesame seed oil in the same fashion, and good correlations between triglyceride compositions in the positive ion spectra and fatty acid abundance ratio in the negative ion spectra were readily observed in one DART-MS run.

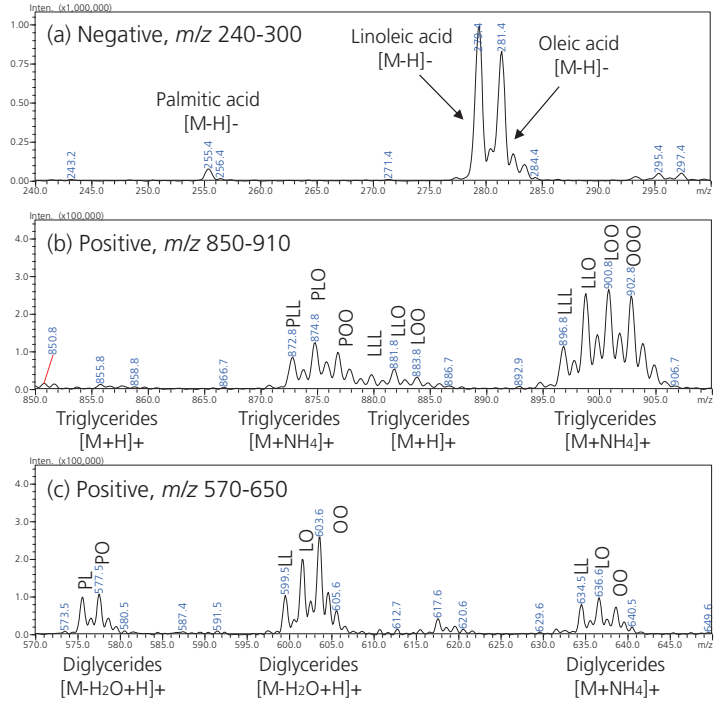
Olive oil



(a) The intense of oleic acid was higher than that of linoleic acid.

(b) (c) The intense of triglyceride and diglyceride species which included oleic acid groups was high.

Sesame seed oil



(a) The intense of oleic acid was almost equivalent to that of linoleic acid.

(b) (c) The intense of triglyceride and diglyceride species which included oleic acid groups was almost equivalent to that of linoleic acid groups.

Fig. 6 Mass spectra for olive oil and sesame seed oil

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4. Conclusions

Ultra-fast polarity switching was useful for high-throughput parallel pattern analyses of fatty acid compositions in triglycerides and free fatty acids using DART mass spectrometer.

Good correlations were seen between triglyceride and diglyceride compositions in the positive ion spectra and fatty acid abundance ratio in the negative ion spectra.

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