SHIMADZU
Excellence in Science

Application News

Liquid Chromatograph Mass Spectrometer LCMS™-9030

Rapid Analysis and Structural Analysis of the Components in Foods Using DART and the LCMS-9030

J. Nakazono, T. Goda, and T. Iida

User Benefits

- The system can perform analysis without pretreatment, regardless of whether the sample is solid, liquid, or gas.
- Using this workflow, a structural analysis of the components in foods can be performed with high mass accuracy.
- Compositional formula estimates, compound searches, and fragment attribution analysis can be performed using the LabSolutions Insight Explore™ analysis software.

■ Introduction

In developing food and beverage products, obtaining information on the constituent components is important for maintaining and improving quality. Normally, however, when measuring specific components in foods and beverages, extraction and other troublesome pretreatments are often necessary.

Direct Analysis in Real Time (DART®) is a method for the direct ionization of samples. It is effective for simple screening because it enables measurements to be performed quickly without pretreatment regardless of whether the sample is solid, liquid, or gas.

In this article, the combination of DART and the LCMS-9030 quadrupole time-of-flight mass spectrometer (Q-TOF) (Fig. 1) is used to measure the components in foods, using chili oil as an example. Structural analysis of the components in the sample is performed with high mass accuracy, using the LabSolutions Insight Explore analysis software based on the MS/MS spectral information obtained. The IonSense DART-OS was used as the ion source.

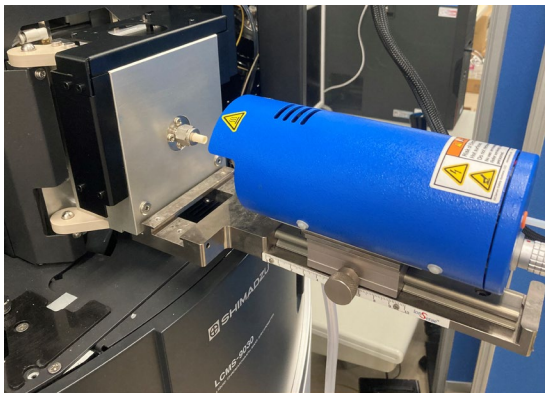


Fig. 1 LCMS™-9030 Connected to the DART Ion Source

■ Direct Analysis of the Components in Chili Oil

Commercially available chili oil was applied to a glass capillary and then measured by suspending the capillary over the DART ion source. The analysis conditions are shown in Table 1.

For measurements in negative mode, the measurement time (horizontal axis) and the peak intensity (vertical axis) are shown in Fig. 2. Peak increases were only observed while the sample was suspended over the DART ion source. In addition, Fig. 2 shows an extracted ion chromatogram (EIC) of *m/z* with the largest intensity among those ions detected in the mass spectra in negative mode.

Table 1 Analysis Conditions

DART Heater Temperature:	350 °C
Scan Type:	*m/z* 50 - 1500 (Positive, Negative)
Nebulizing Gas Flow:	0.5 L/min
Drying Gas Flow:	5.0 L/min
DL Temperature:	250 °C
BH Temperature:	400 °C

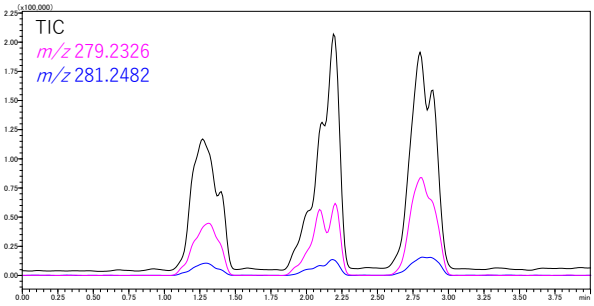


Fig. 2 TIC and EIC for Negative Mode Measurements

Chili oil was measured in positive and negative modes respectively, and the mass spectra obtained are shown in Fig. 3. In the mass spectra, the highest intensity peaks shown are for component A (*m/z* 306.2060) in positive mode, and components B (*m/z* 279.2326) and C (*m/z* 281.2482) in negative mode.

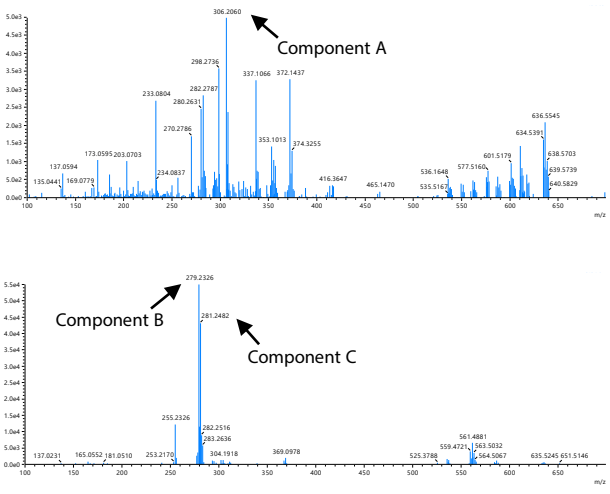
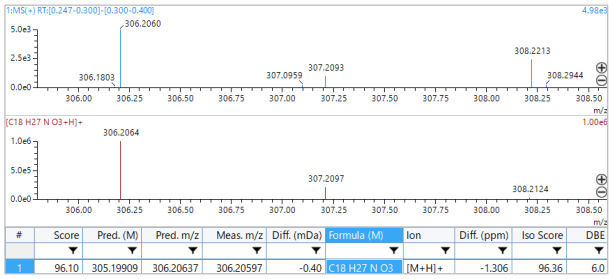


Fig. 3 Mass Spectra for Components in Chili Oil
(Top: Positive Mode Measurements;
Bottom: Negative Mode Measurements)

■ Compositional formula Estimates for the Components in Chili Oil

LabSolutions Insight Explore was used to perform a compositional formula estimate based on the mass spectral information obtained. Here, as an example, the results of a compositional formula estimate of component A (*m/z* 306.2060) are shown in Fig. 4.

The only candidate compositional formula suggested for component A was $C_{18}H_{27}NO_3$. Similarly, $C_{18}H_{32}O_2$ and $C_{18}H_{34}O_2$ were estimated as the compositional formulas for components B and C, respectively. For each component, the compositional formula estimates had high mass accuracy, with a mass error of 1 mDa max.



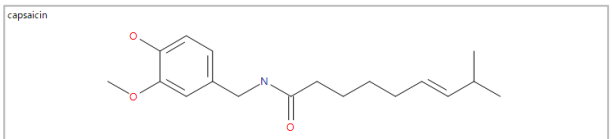
#	Score	Pred. (M)	Pred. m/z	Meas. m/z	Diff. (mDa)	Formula (M)	Ion	Diff. (ppm)	Iso Score	DBE
1	96.10	305.19909	306.20637	306.20597	-0.40	C18 H27 N O3	[M+H]+	-1.306	96.36	6.0

Fig. 4 Compositional Formula Estimation Results for Component A
(Top: Measured Mass Spectrum; Middle: Theoretical Spectrum;
Bottom: Compositional Formula Candidate)

■ Compound Searches and Fragment Attribution

The LabSolutions Insight Explore "Assign" function was used to perform further structural estimates for component A. Firstly, compounds matching with the compositional formula are listed from an online search based on the ChemSpider database. Next, for the compounds obtained, the degree of congruency ("Assign score") between the product ions observed in the measured MS/MS spectrum and the product ions obtained from fragment estimation is calculated by running the assign function.

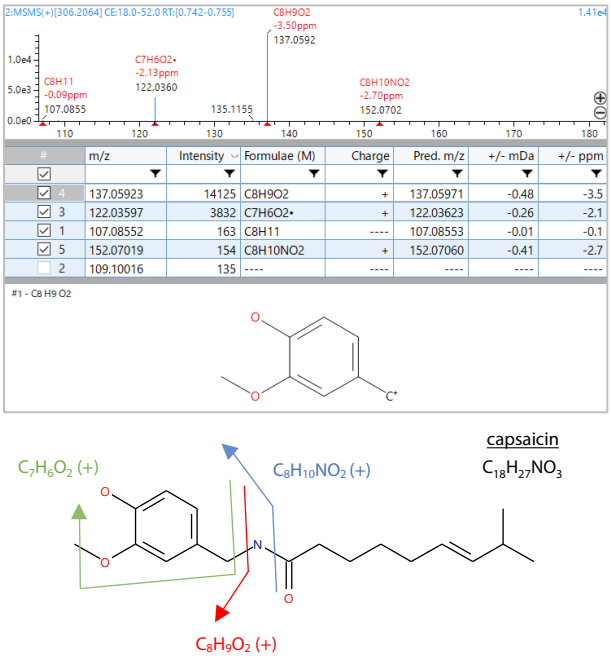
For $C_{18}H_{27}NO_3$, the compositional formula for compound A, 8,363 compounds were suggested in the results of running an online search. Further, for the MS/MS spectrum for component A, from the results of running the assign function, capsaicin (ChemSpider ID 1265957) was suggested as the compound with the highest assign score and ChemSpider reference number (#Reference). (Fig. 5) In this way, using the Insight Explore assign function makes it possible to narrow down structural formulas and compound names from a large number of candidate compounds.



#	Name	Formula	Mass	Assign Score (%)	#Reference	CSID
1	capsaicin	C18H27NO3	305.19910	80.0	5757	1265957
2	Zucapsaicin	C18H27NO3	305.19910	80.0	93	1265956
3	E-Capsaicin	C18H27NO3	305.19910	80.0	49	2452
4	AURANTIOL	C18H27NO3	305.19910	80.0	41	88590
5	2-Methyl-2-pro...	C18H27NO3	305.19910	80.0	36	27458706
6	2-(Dimethylami...	C18H27NO3	305.19910	80.0	34	147293
7	4-(4-tert-butylp...	C18H27NO3	305.19910	80.0	34	1275159

Fig. 5 Compositional Formula $C_{18}H_{27}NO_3$ Online Search Results

Next, an example of the automatic attribution of the fragment ions using the assign function is shown in Fig. 6.



#	m/z	Intensity	Formulae (M)	Charge	Pred. m/z	+/- mDa	+/- ppm
4	137.05923	14125	C8H9O2	+	137.05971	-0.48	-3.5
3	122.03597	3832	C7H6O2•	+	122.03623	-0.26	-2.1
1	107.08552	163	C8H11	----	107.08553	-0.01	-0.1
5	152.07019	154	C8H10NO2	+	152.07060	-0.41	-2.7
2	109.10016	135	----	----	----	----	----

Fig. 6 Fragment Attribution Results for Component A

Finally, the analysis results for each component are shown in Table 2. Components B and C were found to be linoleic acid and oleic acid, respectively, both of which are free fatty acids. Components A, B, and C were measured with high mass accuracy with a mass error of less than 1 mDa compared to the theoretical mass values.

Table 2 Mass Accuracy for Components A, B, and C from Chili Oil

Component	Compound Name	Compositional Estimate Results	Score	Ion Type	Theoretical *m/z*	Measured *m/z*	Error (mDa)
A	Capsaicin	$C_{18}H_{27}NO_3$	96.10	$[M+H]^+$	306.2064	306.2060	-0.4
B	Linoleic acid	$C_{18}H_{32}O_2$	97.19	$[M-H]^-$	279.2330	279.2326	-0.4
C	Oleic acid	$C_{18}H_{34}O_2$	97.14	$[M-H]^-$	281.2486	281.2482	-0.4

■ Summary

The combination of DART and the LCMS-9030 quadrupole time-of-flight mass spectrometer is capable of the direct analysis of a sample quickly and without pretreatment. Furthermore, using the LabSolutions Insight Explore analysis software enables the structural analysis of the measured components. This workflow can be applied to the analysis of components in foods and products in other fields, including chemical products and pharmaceuticals.

01-00236-EN First Edition: Sep. 2021

SHIMADZU
Shimadzu Corporation
Analytical & Measuring Instruments Division
Global Application Development Center

www.shimadzu.com/an/