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Application News

Probe Electrospray Ionization Kit
Quadrupole Time-of-Flight Liquid Chromatograph Mass Spectrometer

Detection of Plant-Derived Natural Toxins by Probe Electrospray Ionization Kit and LC-MS

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User Benefits

- Components in plants can be detected with simple pretreatment.
- Highly polar to medium polar compounds can be measured quickly without column separation.
- Mass data can be acquired with stable mass accuracy without requiring internal standard substances for mass calibration.

■ Introduction

Some plants that live in nature possess toxic components (natural toxins) that are harmful only to other organisms. Some of these toxic plants look very similar to edible plants, such as vegetables and wild plants, and cases of food poisoning due to accidental ingestion are reported every year. Some natural toxins have a high mortality rate, which is important in food hygiene. Therefore, rapid and effective screening methods are required.

This article describes a new analytical method using the probe electrospray ionization kit DPiMS QT and the quadrupole time-of-flight mass spectrometer LCMS-9050 (Fig. 1). The DPiMS QT uses the Probe Electro Spray Ionization (PESI) technique, which enables direct analysis with minimal time from pretreatment to analysis.

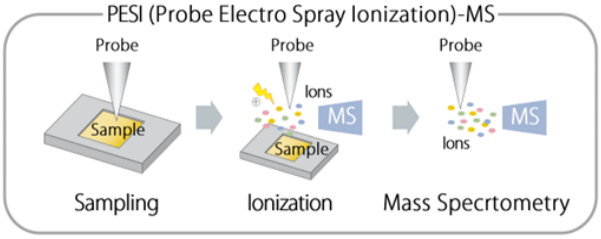
Fig. 1 Appearance of DPiMS™QT and LCMS-9050

■ Sample Pretreatment and Analytical Conditions

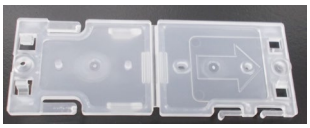
The bulbs of *Colchicum autumnale* and the bulbs and leaves of *Narcissus tazetta* were obtained from a gardening store. Plant sections were cut into pieces approximately 1-2 mm thick and 5 mm square and placed on a dedicated biological plate. Additionally, 35 µL of a 50 % ethanol aqueous solution was added to the plate wells for measurement. In the DPiMS QT, the attached probe repeatedly samples the specimen. Simultaneously, by applying voltage to the probe tip, the sample adhered to the probe surface is ionized and directly introduced into the mass spectrometer. Table 1 shows the analytical conditions, and Fig. 2 illustrates the principle of PESI. Fig. 3 shows the structural formulas of the natural toxins characteristic of *Colchicum autumnale* (colchicine, demecolcine) and *Narcissus tazetta* (lycorine, tazettine, galantamine).

Table 1 Analytical Conditions

Mass Spectrometer	
System:	DPiMS QT+LCMS-9050
Polarity:	Positive
DL Temp.:	250 °C
Heat Block Temp.:	50 °C
Interface Voltage:	3.5 kV
TOF-MS:	MS *m/z* 50-2000
	MS/MS *m/z* 50-2000
Measurement Time:	0.5 min



Probe

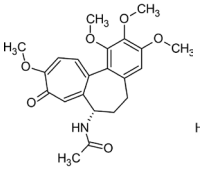


Biological Sample Plate

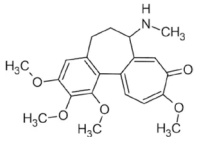
Fig. 2 Principle of Probe Electro Spray Ionization Method

A probe is inserted into the sample on the biological plate, and molecules are ionized by applying voltage to the sample attached to the probe surface.

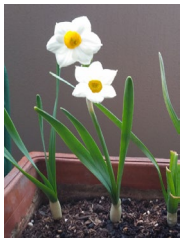
Colchicum autumnale



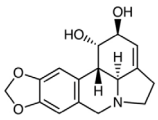
Colchicine
$C_{22}H_{25}NO_6$



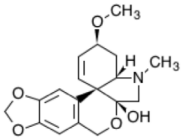
Demecolcine
$C_{21}H_{25}NO_5$



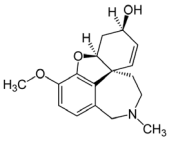
Narcissus Tazetta



Lycorine
$C_{16}H_{17}NO_4$



Tazettine
$C_{18}H_{21}NO_5$



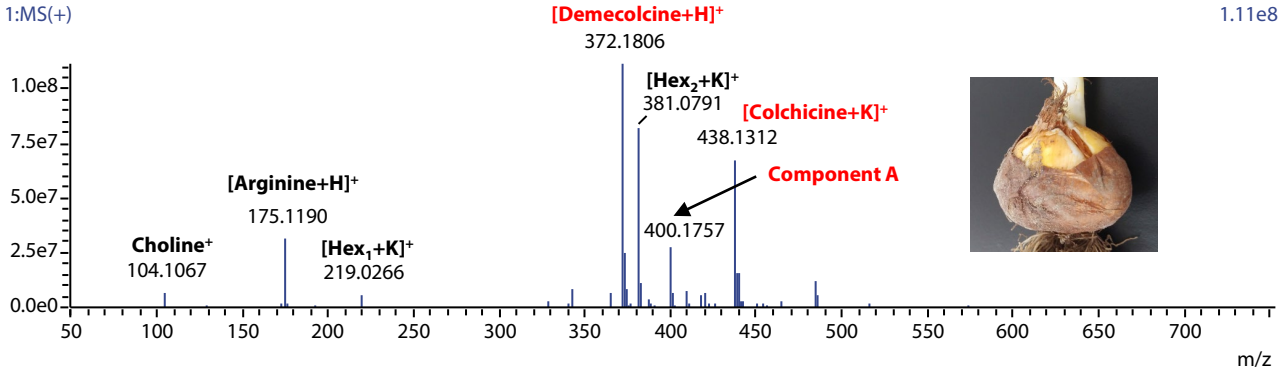
Galantamine
$C_{17}H_{21}NO_3$

Fig. 3 Structural Formulas of Natural Toxins Characteristic of *Colchicum Autumnale* and *Narcissus Tazetta*

■ Analysis of Natural Toxins in *Colchicum Autumnale*

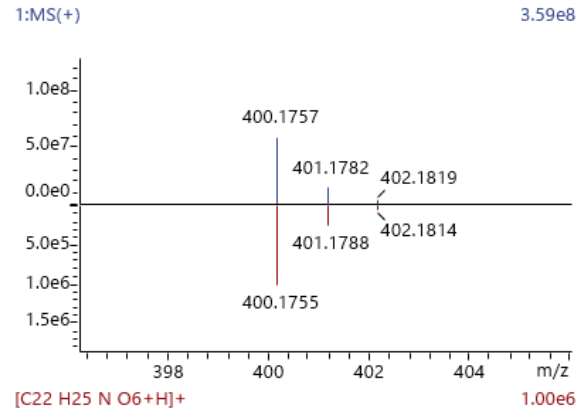
Fig. 4 shows the mass spectrum obtained by measuring the bulb sections of *Colchicum autumnale* in positive mode. In addition to metabolites such as choline, arginine, and sugars composed of hexose (Hex), components considered to be the natural toxins demecolcine and colchicine, characteristic of *Colchicum autumnale*, were detected. LabSolutions Insight Explore™ is useful for structural estimation. An example of the analysis of component A (*m/z* 400.1757) is shown.

Based on the obtained mass spectrum information, the composition formula was predicted, estimated to be $C_{22}H_{25}NO_6$ with high mass accuracy within a mass error of 1 mDa. The accuracy of the weak second and third isotopes was also high, contributing to a high score (Fig. 5). Furthermore, an online search using the ChemSpider database (assign function) for the estimated molecular formula suggested colchicine as the top candidate compound. Fig. 6 shows the matching results (fragment assignment) of the product ions predicted from the structural formula and the product ions observed in the MS/MS spectrum.



Compound Name	Ion Type	Theoretical *m/z*	Measured *m/z*	Error (mDa)
Demecolcine	$[M+H]^+$	372.1806	372.1806	0
Colchicine (Component A)	$[M+H]^+$	400.1755	400.1757	0.2
Colchicine	$[M+K]^+$	438.1314	438.1312	-0.2

Fig. 4 Mass Spectrum of *Colchicum Autumnale* Bulb



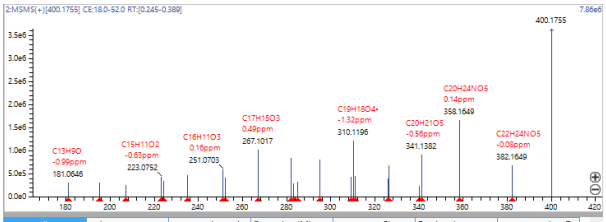
#	Score	Pred. (M)	Pred. m/z	Meas. m/z	Diff. (mDa)	Formula (M)	Ion	Diff. (ppm)	Iso Score	DBE
1	97.12	399.16819	400.17546	400.17568	0.22	C22 H25 N O6	[M+H]+	0.550	97.05	11.0

Fig. 5 Formula Estimation Results for Component A

Top: Comparison Plot of Measured Mass Spectrum (Blue/Upper Section) and Theoretical Mass Spectrum (Red/Lower Section)

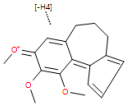
Bottom: Candidate Molecular Formula

#	Name	Formula	Mass	#Reference	Assign Score (%)
1	(+-)-Colchicine	C22H25NO6	399.16818	8204	95.7
2	Colchicine	C22H25NO6	399.16818	249	95.7
3	N-(1,2,3,9-Tetram...	C22H25NO6	399.16818	172	95.7
4	1-(9H-Fluoren-9-...	C22H25NO6	399.16818	53	95.7
5	BENZYL-2-ACETA...	C22H25NO6	399.16818	46	95.7



#	m/z	Intensity	Formulae (M)	Charge	Pred. m/z	+/- mDa
7	235.07517	463636	C16H11O2	----	235.07536	-0.19
8	251.07031	590909	C16H11O3	[+H]+ / +	251.07027	0.04
9	251.07031	590909	C16H11O3••	[+H]+	251.07027	0.04
10	252.07842	415152	C16H12O3•	[+H]+ / +	252.07810	0.32
11	267.10170	1024242	C17H15O3	[+H]+	267.10157	0.13
12	267.10170	1024242	C17H15O3••	[+H]+	267.10157	0.13
13	282.12487	845455	C18H18O3•	[+H]+ / +	282.12505	-0.18
14	283.09710	281818	C17H15O4	[+H]+ / +	283.09649	0.61
15	283.09710	281818	C17H15O4••	[+H]+	283.09649	0.61
16	285.11201	318182	C17H17O4	[+H]+ / +	285.11214	-0.13

#1 - C17 H19 O3 [-H4]



m/z 267.1017
$C_{17}H_{15}O_3$

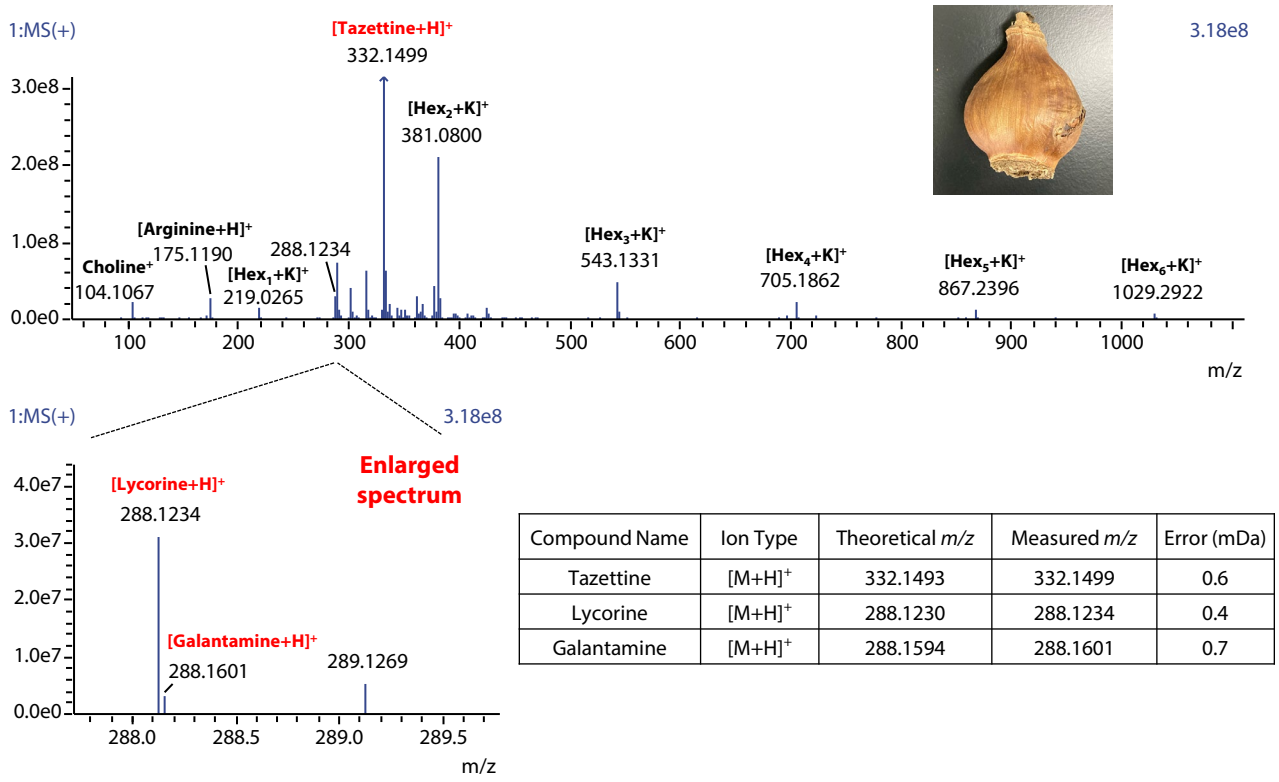
Fig. 6 Automatic Fragment Attribution Results for Component A

■ Analysis of Natural Toxins Contained in *Narcissus Tazetta*

Fig. 7 shows the mass spectrum of a *Narcissus tazetta* bulb section measured in positive mode. Accurate mass analysis was performed using LabSolutions Insight Explore, and it was considered that metabolites such as choline, arginine, and sugars composed of hexose, as well as natural toxins characteristic of *Narcissus tazetta* such as tazettine, lycorine, and galantamine were detected. The same components were also detected in a section of *Narcissus tazetta* leaf. Fig. 8 shows that the lycorine MS/MS spectrum pattern obtained from the bulb measurement matches that of the standard compound.

■ Conclusion

In this article, DPiMS QT and LCMS-9050 were combined to rapidly detect natural toxins in higher plants with high mass accuracy. The time required for pretreatment was approximately 5 minutes, and the measurement time was 0.5 minutes, significantly reducing the analysis time compared to measurement by LC or LC/MS. The accurate mass data acquired allows for easy estimation of the composition and structural analysis of unknown components using the LabSolutions Insight Explore. This method can be applied to any sample that can be sandwiched in a plate, and its utilization is expected in various fields.



Compound Name	Ion Type	Theoretical *m/z*	Measured *m/z*	Error (mDa)
Tazettine	$[M+H]^+$	332.1493	332.1499	0.6
Lycorine	$[M+H]^+$	288.1230	288.1234	0.4
Galantamine	$[M+H]^+$	288.1594	288.1601	0.7

Fig. 7 Mass Spectrum of *Narcissus Tazetta* Bulb

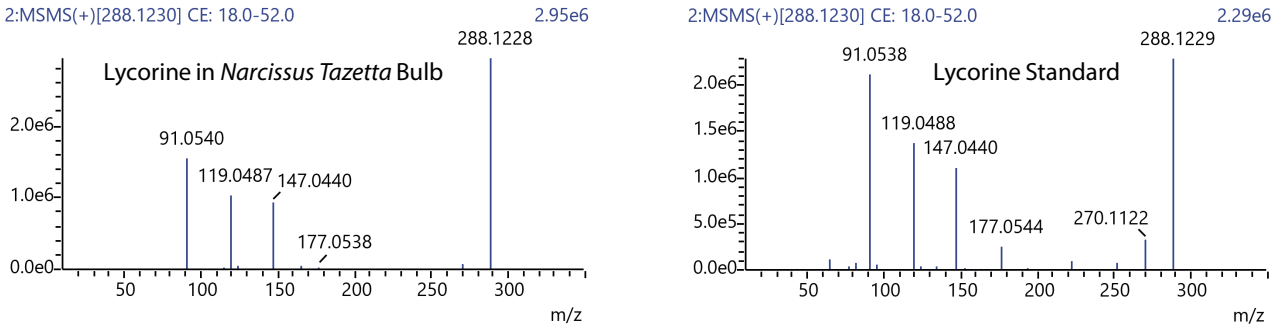


Fig. 8 MS/MS Spectra of Lycorine

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