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Rapid detection of natural plant toxins using probe ESI unit combined with quadrupole time-of-flight mass spectrometer

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1. Introduction

Many animals and plants are known to have poisonous components (natural toxins) in their bodies. Food poisoning caused by animals and plants containing these natural toxins occurs every year, although the number of cases are not very high compared to bacterial food poisoning. However, this is extremely important from the viewpoint of food sanitation because some poisons have a high fatality rate. Therefore, rapid and effective screening methods are required to guarantee food safety. In this study, we report a method for rapid detection of natural plant toxins in *Colchicum autumnale* and *Narcissus tazetta* using DPiMS^{TM} QT equipped with probe electrospray ionization (PESI) technology. Additionally, we use a DPiMS QT mounted on the LCMS-9050, a newly designed quadrupole time-of-flight (Q-TOF) mass spectrometer that can rapidly achieve mass stability. This combination enables direct analysis and minimizes the time from sample preparation to accurate analysis.

2. Sample Preparation and Analysis Conditions

The leaves and bulbs of *Narcissus tazetta* and the bulbs of *Colchicum autumnale* were obtained from garden stores. Fig.1 shows the natural toxins contained in these plants. The sample was cut into approximately 5 mm squares with a thickness of 1 to 2 mm and set in a biological sample plate. 35 µL of 50% ethanol-water solution (v/v) was added to the well of this plate. In the PESI-Q-TOF system (Shimadzu Corporation), a probe picks up sample from the sampling plate. At the same time, by applying a voltage to the probe, the sample adhering to the probe surface is ionized and directly introduced into the mass spectrometer (Fig. 2). Table 1 shows the analytical conditions for this analysis. Qualitative analysis was performed using the LabSolutions Insight Explore^{TM} software (Shimadzu Corporation).

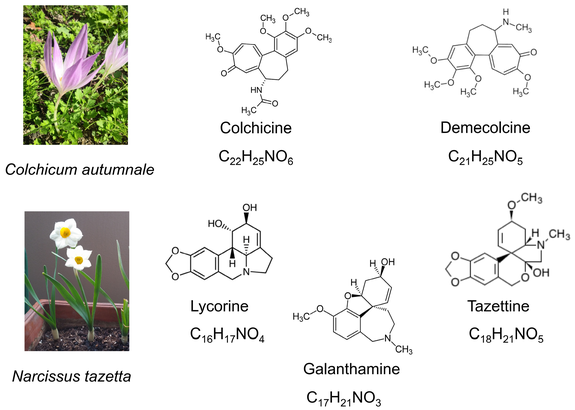


Fig. 1 Structural formula of alkaloids in *Colchicum autumnale* and *Narcissus tazetta*

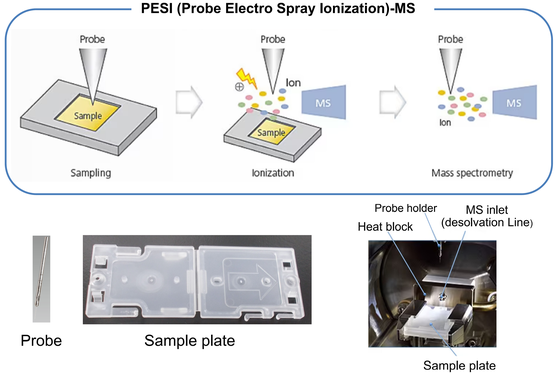


Fig. 2 Principle of PESI

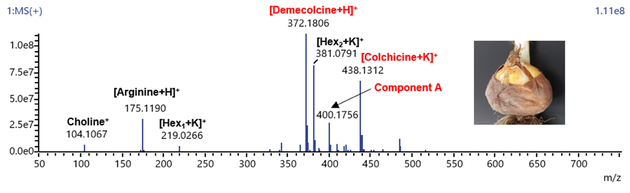
Table. 1 Analytical settings

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

3. Results

Analysis of natural toxins contained in *Colchicum autumnale*

Fig. 3 shows the mass spectrum of a *Colchicum autumnale* bulb section measured in the positive mode. By using a dedicated analytical software, component A (*m/z* 400.1756) was estimated to be $C_{22}H_{25}NO_6$ with high mass accuracy of within 1 mDa compared to the theoretical mass value (Fig. 4). When an online search was conducted using the ChemSpider database for the estimated composition formula, colchicine was suggested as a top candidate compound. Fig. 5 shows the automatically detected match between the product ions predicted from the structural formula and the product ions observed in the MS/MS spectrum. These results strongly support that component A is colchicine. In the same manner, hexose-based saccharides, metabolites choline and arginine, and the natural toxin demecolcine were also detected.



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	400.1756	0.1
Colchicine	[M+K]+	438.1314	438.1312	-0.2

Fig. 3 Mass spectrum of *Colchicum autumnale* bulb

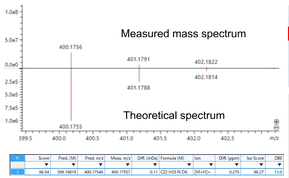


Fig. 4 Formula estimation results for component A

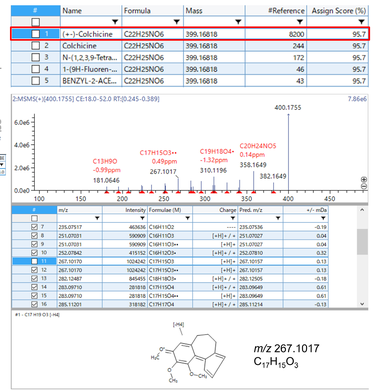
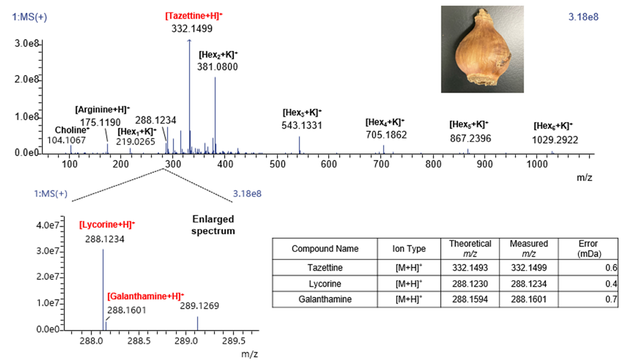


Fig. 5 Automatic assignment of MS/MS Fragments

Analysis of natural toxins contained in *Narcissus tazetta*

Fig. 6 shows the mass spectrum of a *Narcissus tazetta* bulb section measured in the positive mode. Accurate mass spectrometry was performed using analysis software, showing that saccharides composed of hexose, metabolites choline and arginine, and natural toxins tazettine, lycorine, and galanthamine, were detected. Figure 7 shows that MS/MS spectral pattern of lycorine obtained from the bulb measurement matches that of the standard. These components was also detected in a section of *Narcissus tazetta* leaf.



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
Galanthamine	[M+H]+	288.1594	288.1601	0.7

Fig. 6 Mass spectrum of *Narcissus tazetta* bulb

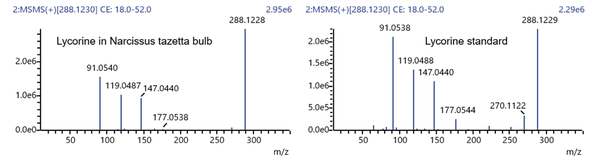


Fig. 7 MS/MS Spectra of Lycorine

4. Conclusion

・PESI and Q-TOF were combined to detect natural toxins in 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 time required for analysis compared to measurement by LC or LC/MS.

・The obtained data can be used for simple and rapid composition estimation and structural analysis of unknown components using the qualitative analysis software.