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Application News

Imaging Mass Microscope iMScope™
Oxygen Attachment Dissociation MS/MS Option Kit

Multidirectional Analysis of Plant Alkaloids Using MS Imaging and OAD-TOF System

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User Benefits

- By combining the iMScope QT and OAD-TOF systems, it is possible to perform distribution analysis through MS imaging and structural analysis via OAD-MS/MS.
- The combination of OAD-MS/MS with CID-MS/MS for structural analysis is expected to enable more accurate identification of compounds.

■ Introduction

Plant alkaloids are naturally occurring compounds that contain nitrogen atoms and are widely distributed in plants, known for their pharmacological activities. Many alkaloids exhibit toxicity and function as defense mechanisms against herbivores and pathogens. Well-known examples include morphine obtained from poppies (used as a pain reliever) and quinine derived from the bark of the cinchona tree (used for malaria treatment). Other noteworthy alkaloids include caffeine, nicotine, and atropine. These compounds play crucial roles in medicine, agriculture, and the economy, and research on alkaloids is essential for the development of new drugs and the understanding of plant biology. In this study, we used the iMScope QT and OAD-TOF systems (Fig. 1) to perform distribution analysis of potato plant alkaloids through mass spectrometry imaging (MSI) and structural analysis by combining a unique new fragmentation technique called Oxygen Attachment Dissociation (OAD)[1-3] with traditional Collision Induced Dissociation (CID).

Fig. 1 Combination of the OAD-TOF System and iMScope™ QT

■ OAD-TOF system

OAD induces radical-based fragmentation of precursor ions using atomic oxygen and hydroxyl radicals (O/OH•), which are neutral radicals generated from water vapor. The O/OH• radicals produced by a microwave-driven source are introduced into the Q2 collision cell via a quartz tube, allowing the acquisition of OAD-MS/MS spectra. Atomic oxygen selectively oxidizes and cleaves C=C bonds, and OAD-MS/MS clearly provides positional information of the C=C bonds.

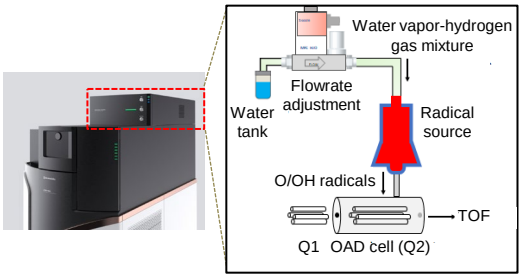


Fig. 2 LCMS-9050 equipped with OAD RADICAL SOURCE I (OAD-TOF system)

■ Pre-treatment and Analysis Conditions

We used commercially available potatoes (*Solanum tuberosum L.*) that were placed under sunlight to induce sprouting as a model. The potato sprouts were frozen, and sections with a thickness of 10 µm were cut using a cryomicrotome and mounted on ITO-coated glass slides. Using the iMLayer™ deposition system (Fig. 3), α-cyano-4-hydroxycinnamic acid (CHCA) was applied as a matrix at a thickness of 0.7 µm. MSI, OAD-MS/MS, and CID-MS/MS analyses were performed using the iMScope QT and OAD-TOF systems (Table 1). MSI data were analyzed using IMAGEREVEAL™ MS (Fig. 4 left), and MS/MS data were analyzed using LabSolutions Insight Explore™ (Fig. 4 right).

Table 1 MSI Analysis Conditions

Mass spectrometer		
System	:	iMScope QT+OAD-TOF System
Polarity	:	Positive
DL temp	:	290 ˚C
Heat block temp	:	400 ˚C
MS Range	:	MS *m/z* 270-1000 MS/MS *m/z* 100-1000
Spatial Resolution (Pitch)	:	10 / 25 / 50 µm
Laser Diameter Setting	:	1 / 2 / 4
Laser Intensity	:	38 / 46 /63
Laser Repetition Frequency	:	1k / 100 Hz
Q1 Resolution	:	5 Da
Collision Energy	:	10 / 80 V
Matrix Coating		
System	:	iMLayer
Matrix Used	:	CHCA
Coating Method	:	Deposition with 0.7 mm Thickness

Fig. 3 iMLayer™

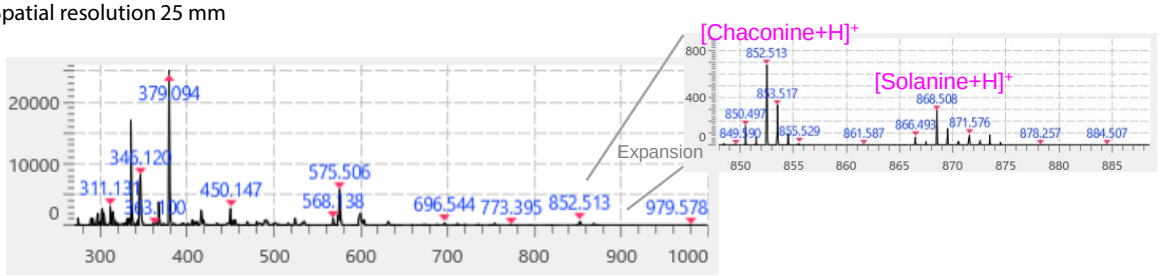
Fig. 4 IMAGEREVEAL™ MS (left) and LabSolutions Insight Explore™ (right)

■ Distribution Analysis of Plant Alkaloids Using MSI

We conducted distribution analysis of plant alkaloids in potato sprouts. The MS spectrum of the entire section was obtained with a spatial resolution of 25 μm, and the MS spectrum of the area observed with a 5x objective lens of the optical microscope was obtained with a spatial resolution of 10 μm.

Fig. 5 and Fig. 6 show the MS spectra and MS images, respectively. From the MS images, it was revealed that plant alkaloids such as solanine and chaconine are abundantly distributed in potato sprouts and the surrounding skin. These glycoalkaloids are known to accumulate in potato sprouts as a defense against herbivores and pathogens.

(a) Spatial resolution 25 mm



(b) Spatial resolution 10 mm

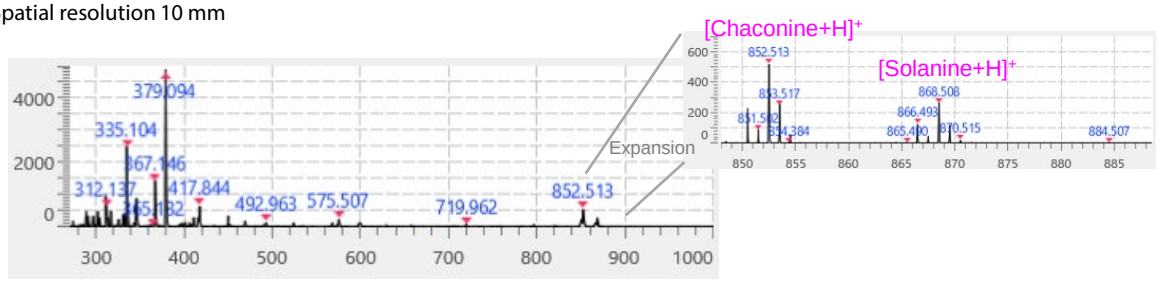
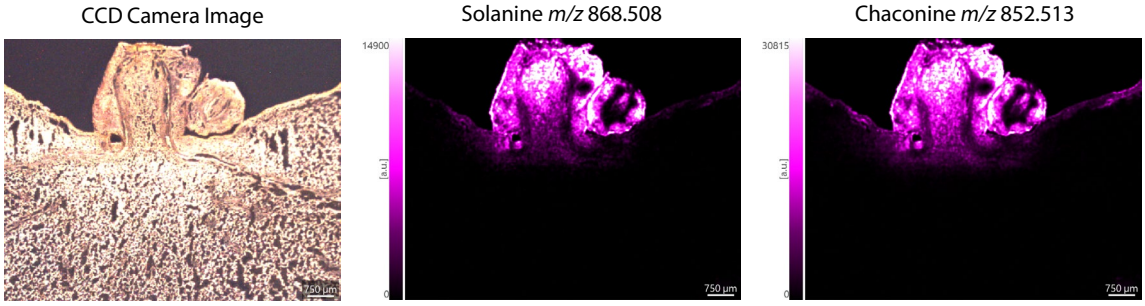


Fig. 5 Average MS Spectra of Potato Sections

(a) Spatial resolution 25 mm



(b) Spatial resolution 10 mm

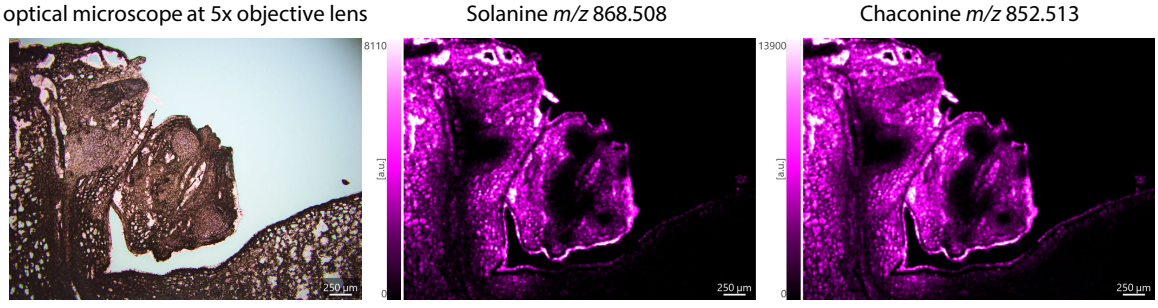


Fig. 6 MS Images of Plant Alkaloids in Potato Sections

■ Structural Analysis of Plant Alkaloids Using OAD-MS/MS and CID-MS/MS

When there are known standard compounds, identification using CID-MS/MS spectra is possible. However, elucidating the structures of novel alkaloid analogs is often challenging with CID-MS/MS spectra alone. Here, we present an example of MS/MS analysis combining CID and OAD. Solanine was treated as an unknown compound, and its CID-MS/MS spectrum was compared with in silico fragment ions generated by LabSolutions Insight Explore to derive structural candidates (Fig. 7 (c) and Fig. 8).

We then searched for compounds with the same chemical formula registered in ChemSpider. Several structurally different compounds containing solanine were proposed (Fig. 8). To narrow down these candidates, we utilized the OAD-MS/MS spectrum. In OAD, a fragment ion at m/z 150.128 was specifically detected under low collision energy, which was not observed in CID (Fig. 7 (a) and (b)). This fragment ion, unique to OAD, resulted from preferential cleavage near heteroatoms, and its precise mass value indicated a molecular formula of C10H16N. By leveraging this complementary information, we were able to narrow down the candidate compounds to solanine.

(a) OAD-MS/MS
CE: 10
CID gas: 17k Pa

(b) CID-MS/MS
CE: 10
CID gas: 230k Pa

(c) CID-MS/MS
CE: 80
CID gas: 230k Pa

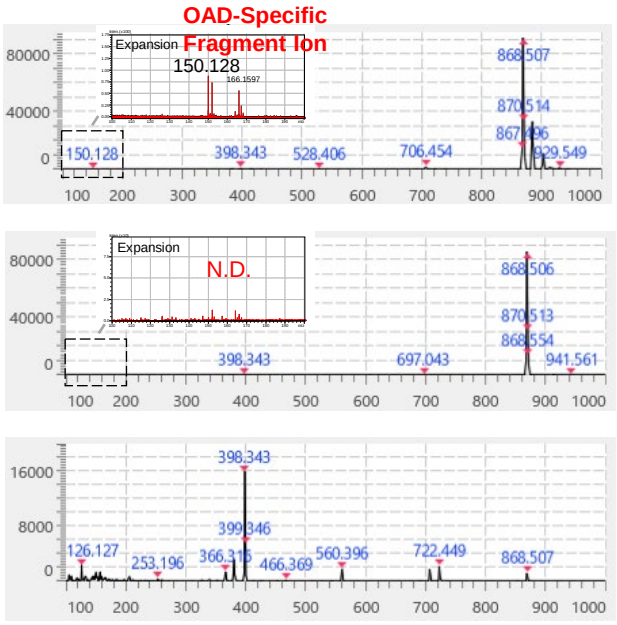


Fig. 7 OAD-MS/MS Spectrum and CID-MS/MS Spectrum of $[Solanine+H]^+$

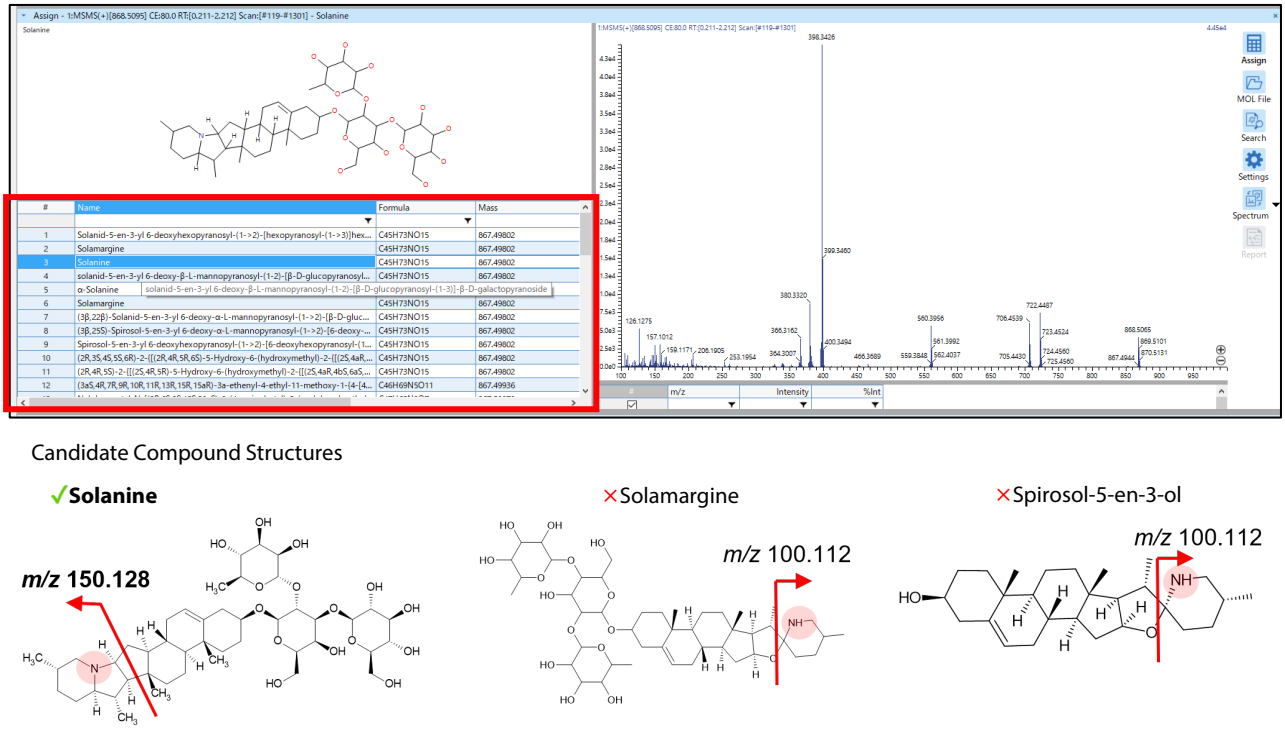


Fig. 8 Structural Analysis Results Using LabSolutions Insight Explore

■ Conclusion

In this study, we conducted distribution analysis of plant alkaloids in potatoes using MS imaging. Subsequently, by combining OAD-specific diagnostic fragment ions obtained from OAD-MS/MS with CID-MS/MS for structural analysis, we were able to enhance the identification accuracy of solanine. These results suggest that the iMScope QT and OAD-TOF systems are expected to contribute to the discovery and identification of new plant alkaloids that are biologically or pharmacologically relevant.

<References>

1) Takahashi.H et al. Anal. Chem. 2018, 90 (12), 7230-7238.
2) Takahashi.H et al. Mass Spectrometry. 2019, S0080.
3) Uchino.H et al. Commun Chem. 5, 162 (2022).

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