SHIMADZU

WP 227

Rapid Characterization of Alkaloids using Probe ESI Q-TOF LCMS-9050 in OAD-MS/MS

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1. Introduction to OAD-MS/MS

- While low-energy CID-MS/MS is one of the most effective fragmentation techniques for structural analysis, it may not be ideally suited for the analysis of certain isomers.
- Several novel fragmentation techniques have been proposed to complement low-energy CID-MS/MS.

Table 1. Example of proposed novel fragmentation techniques

Electron-based fragmentation
EIEIO, ECD(Electron Capture Dissociation) by Zubarev et al. (1996)
Anion-based fragmentation
ETD(Electron Transfer Dissociation) by Syka et al. (2004)
Photon-based fragmentation
IRMPD (Infrared), UVPD (Ultraviolet), BRID (Blank body infrared)

- We have introduced neutral radical-based fragmentation techniques to structural analysis of biomolecules, peptides and lipids, since 2016.

Neutral radical-based *Takahashi et al., *Anal. Chem.* 2018, 90, 12, 7230.

Charge-neutral radical-induced dissociation is available in both positive and negative ion modes!

OAD (Oxygen Attachment Dissociation)-MS/MS
$[M+H]^+ + O^\bullet \rightarrow [M + H + O]^{+\bullet} \rightarrow$ *fragments*

HAD (Hydrogen Abstraction Dissociation)-MS/MS
$[M+H]^+ + H^\bullet \rightarrow M^{+\bullet} + H_2 \rightarrow$ *fragments*

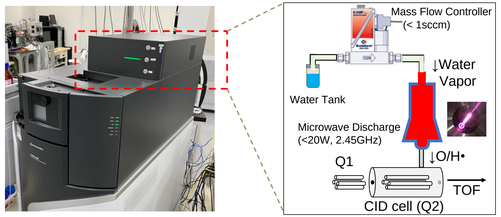

Fig. 1. Shimadzu LCMS-9050 (Q-TOF) with OAD unit.

2. Introduction to a direct ionization of PESI

- Probe Electro Spray Ionization (PESI) is one of the direct ionization techniques. Fig. 2 shows the scheme of the PESI system.

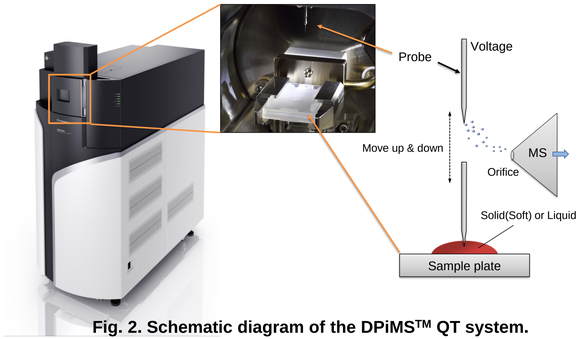

Fig. 2. Schematic diagram of the DPiMS™ QT system.

3. PESI-OAD Synergistic Lipid Analysis

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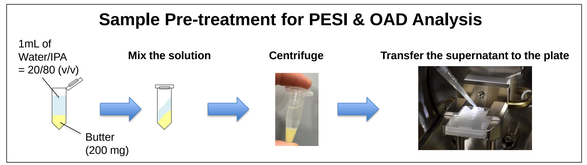
- **OAD-MS/MS** reveals double-bond (C=C) positions not accessible with CID-MS/MS. Atomic oxygen selectively oxidizes and cleaves at C=C.



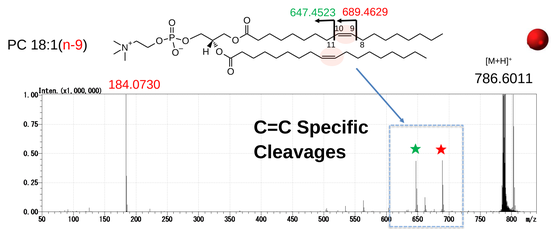
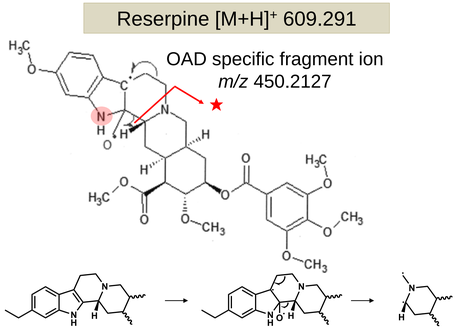


Fig. 3. Typical OAD spectrum of a model lipid of PC (18:1).

4. PESI-OAD Synergistic Alkaloids Analysis

- Atomic oxygen selectively oxidizes carbon atoms adjacent to nitrogen in nitrogen-containing heterocycles, leading to OAD-specific fragmentation distinct from CID, as shown in Fig. 4 (*m/z* 450.2127).

Scheme 1. Proposed OAD mechanism of nitrogen-containing heterocycles



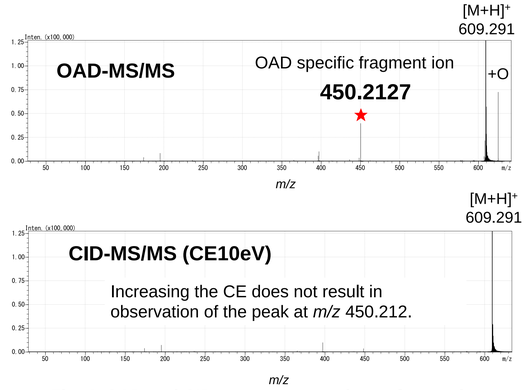


Fig. 4. OAD and CID spectra comparison of reserpine.

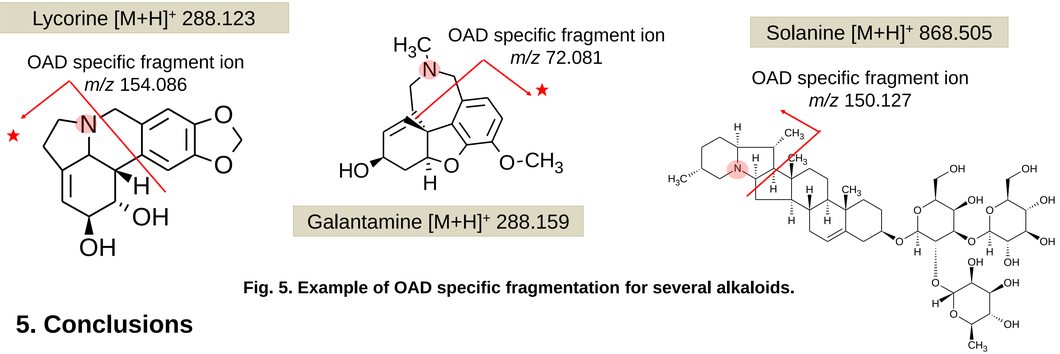


Fig. 5. Example of OAD specific fragmentation for several alkaloids.

5. Conclusions

- We have successfully developed the LCMS-9050 system integrating OAD and PESI.
- OAD provides unique structural information on nitrogen-containing heterocycles, which is distinct from CID, particularly observed in alkaloids.
- OAD specific fragment ions observed in alkaloids offer the potential for rapid characterization of alkaloids.