Oxygen Attachment Dissociation MS/MS for Differentiation between Cis and Trans Fatty Acids

Hidenori Takahashi[1]; Yuji Shimabukuro[2]; Daiki Asakawa[3]; Shosei Yamauchi[1]; Shinichi Iwamoto[1]; Motoi Wada[2]; Koichi Tanaka[1]

[1] Shimadzu corp., Kyoto, Japan; [2] Doshisha University, Kyoto, Japan; [3] AIST, Tsukuba, Japan;

ASMS 2019
ThP-400

1. Overview

We have developed novel MS/MS techniques:

HAD-MS/MS
Hydrogen **A**ttachment/**A**bstraction **D**issociation

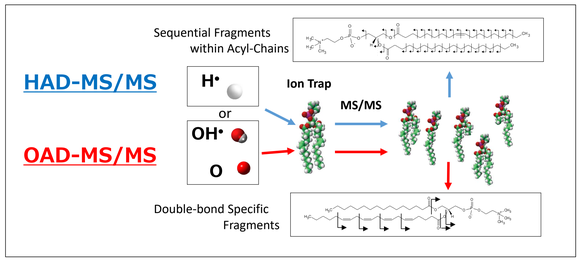
*Takahashi, H. et al. *Anal. Chem.*, 2016, 88, 3810-.

OAD-MS/MS
Oxygen **A**ttachment **D**issociation

*Takahashi, H. et al. *Anal. Chem.*, 2018, 56, 7230-.

2. Introduction

Instead of using the collision gas (Ar/N_2) for CID-MS/MS, neutral reactive radical gas is introduced into an ion trap.



3. Methods and Materials

HAD-MS/MS and OAD-MS/MS were performed using a LC-ESI-MS and a prototype MALDI-IT-TOF-MS. H• was generated by passing H_2 gas through a heated tungsten capillary. OH • and O were generated by a microwave discharge of water vapor.

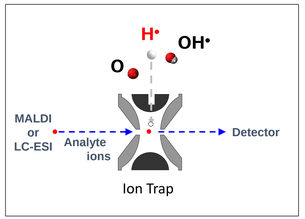


Fig.1. Schematic diagram for HAD-MS/MS and OAD-MS/MS using the LC-ESI-MS and MADLI-IT-TOF-MS.

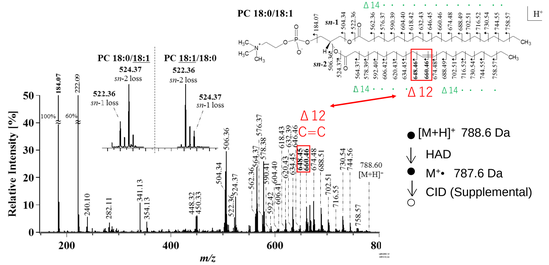
Lipid name (Phosphatidylcholine:PC)	Exact Mass
PC(18:0/18:0)	789.625
PC (18:1(9Z)/16:0)	759.578
PC (18:0/18:1(9Z))	787.609
PC (14:1(9Z)/14:1(9Z))	673.468
PC (16:1(9E)/16:1(9E))	729.531
PC (18:1(6Z)/18:1(6Z))	785.593
PC (18:3(9Z,12Z,15Z)/18:3(9Z,12Z,15Z))	777.531
PC (16:0/20:4(5Z,8Z,11Z,14Z))	781.562

Table 1. List of model phospholipids used in this study.

4. Result

4-1. HAD-MS/MS for C=C and *sn*- position determination

The HAD-MS/MS spectrum of the model phospholipid shows a continuous series of fragment ions with the mass difference of 14 Da, which represents a CH_2 group. Meanwhile, the fragment ions corresponding to the C=C position shows a characteristic mass difference of 12 Da. These diagnostic product ions enables the structural analysis of C=C isomers.

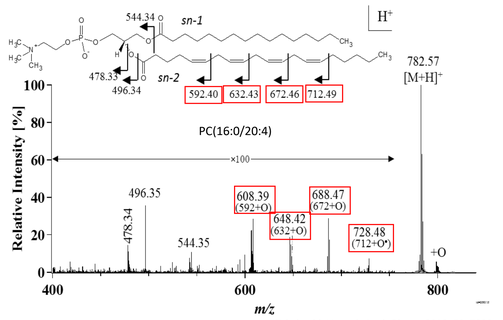


*Takahashi, H. et al. *Anal. Chem.*, 2016, 88, 3810-.

Fig.2. HAD-MS/MS spectrum of PC 18:0/18:1(9Z).

4-2. OAD-MS/MS for C=C position determination

The OAD-MS/MS spectrum provides the C=C specific fragmentation. The methylene bridges adjacent to C=C positions were selectively dissociated, accompanied by oxidation of the double bonds.



*Takahashi, H. et al. *Anal. Chem.*, 2018, 56, 7230-.

Fig.3. OAD-MS/MS spectrum of PC 16:0/20:4(5Z,8Z,11Z,14Z).

4-3. Mixture of C=C position isomers

Since the OAD-MS/MS provides straightforward double-bond specific fragmentation, OAD can be applied to the analysis for mixture of C=C position isomers, based on the product ion intensity.

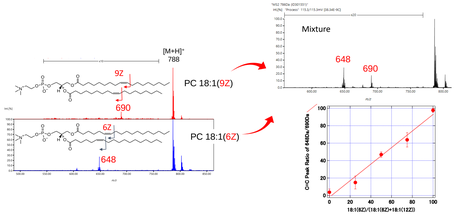
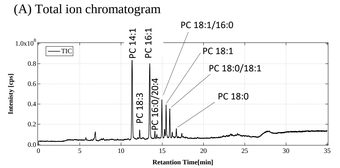


Fig.4. OAD-MS/MS spectrum for the mixture of C=C position isomers of PC 18:1(9Z) and PC 18:1 (6Z).

4-4. LC-OAD-MS/MS for C=C position assignment

Auto-MS/MS mode with a cycle time of 1 s was used for LC-OAD-MS/MS. Double bond position assignment in a mixture of eight standard samples with multiple saturated fatty acyl chains was carried out successfully.



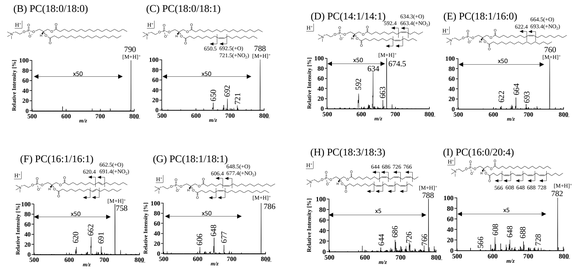


Fig. 5. (A) TIC of phospholipid mixture and (B)-(I) OAD-MS/MS spectra of each phospholipid obtained with the acquisition time of 0.5 s.

5. Differentiation between Cis and Trans fatty acids

Focusing on the intensity of non-dissociative oxidized ion $[M+H+O]^+$, cis and trans fatty acids can be differentiated. The intensity of $[M+H+O]^+$ of *trans* fatty acid is higher than that of *cis* fatty acid by a factor of around 2. Since the reproducibility of the peak intensity is quite good, this technique can be applied to cis/trans mixture (Fig.7.).

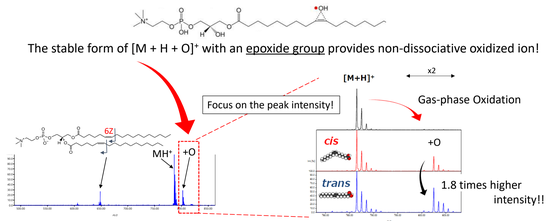


Fig.6. Comparison between the intensity of $[M+H+O]^+$ of *trans* fatty acid and that of *cis* fatty acid.

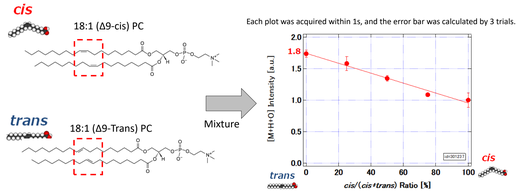


Fig.7. Differentiation between cis and trans fatty acids for cis/trans mixture.

6. Conclusions

We have demonstrated OAD-MS/MS, in combination with LC, for the detailed structural analyses of several phospholipids. OAD-MS/MS is a promising analytical technique for the assignment of C=C positions and the discrimination of cis/trans fatty acids.