SHIMADZU
Excellence in Science

PO-CON1533E

Structural analysis of isomeric chemicals by using high resolution MS/MS on Curved Field Reflectron incorporated with a novel focusing technology

ASMS 2015 ThP 273

Shuuichi Nakaya[1]; Keisuke Shima[1]; Yuzo Yamazaki[1]
[1]Shimadzu Corporation, Kyoto, JAPAN.

SHIMADZU
Excellence in Science

Structural analysis of isomeric chemicals by using high resolution MS/MS on Curved Field Reflectron incorporated with a novel focusing technology

Overview

- Precise assignment of isomeric chemicals is conducted with a new MALDI-TOF/TOF MS.
- Isomeric carbohydrates and prostaglandins are differentiated successfully.
- Choice of cation is significant to obtain informative MS/MS spectrum.

Introduction

While resolution of MS has been greatly improved recently, no matter how high resolution of MS is achieved, MS/MS is essential to conduct analysis of isomeric chemicals, and the analysis is thought to be still significant task given to mass spectrometry. To date, we applied PSD and high energy CID in curved field reflectron to the analysis, since intensities of fragment ions in the reflectron were susceptible to isomeric forms. Recently, we incorporated a new focusing technology into the curved field reflectron, which enabled to obtain 10,000 resolution of MS/MS. We will apply the new curved field reflectron toward ambiguous assignment and differentiation of isomeric chemicals.

Methods

Materials

Isomeric oligosaccharides	: Lacto-N-neotetraose(LNnT)	Galβ1-3GlcNAcβ1-3Galβ1-4Glc
	Lacto-N-tetraose(LNT)	Galβ1-4GlcNAcβ1-3Galβ1-4Glc
Isomeric prostaglandin	: Prostaglandin E2(PGE_2) and prostaglandin D2(PGD_2)	
Matrix	: 10 mg/mL of DHB in methanol.	
Cation	: Li, Na, Cs, Ba.	

MALDI-tandem TOFMS

Instrument	: MALDI-7090 (Shimadzu/Kratos)
Measurement	: High-energy CID-MS/MS in positive ion mode.
Collision gas	: helium
Collision energy	: 20 keV (laboratory frame of reference).

Structural analysis of isomeric chemicals by using high resolution MS/MS on Curved Field Reflectron incorporated with a novel focusing technology

Principle of Axial Spatial Distribution Focusing (ASDF)

MS/MS resolution is improved with correcting the spatial distribution of ions in ASDF cell. This is achieved by applying a pulsed electrostatic field at the point, at which the precursor and fragments are velocity focussed but are spatially resolved.

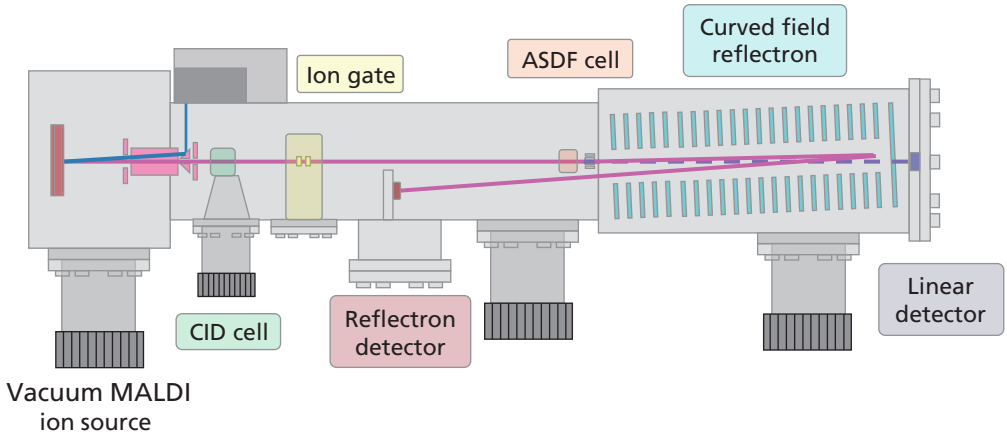

Fig.1 Inside view of MALDI-7090

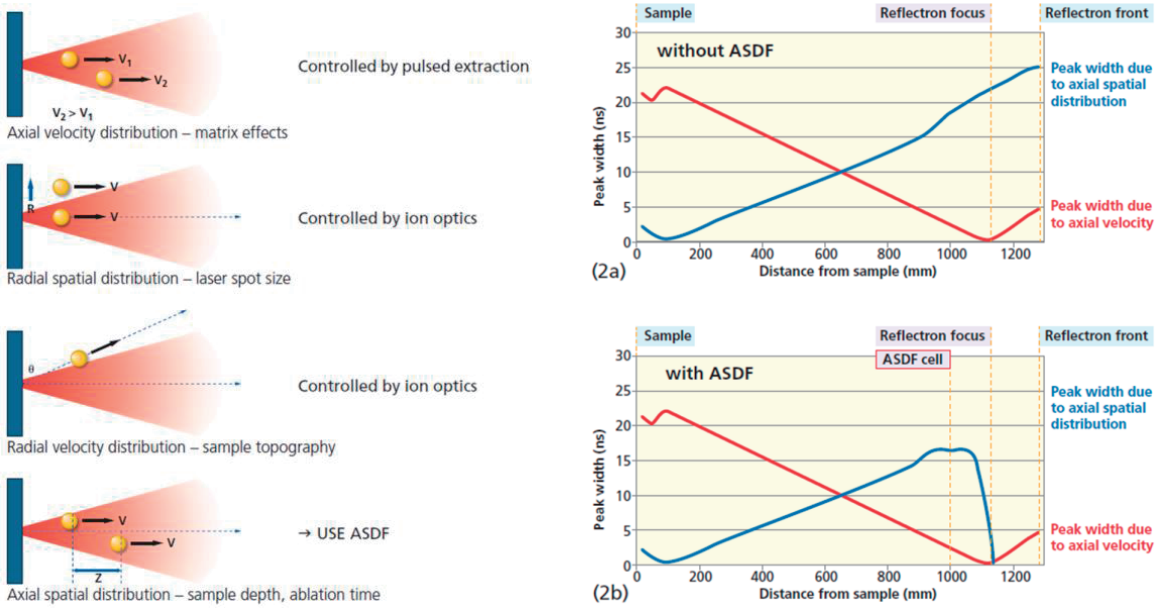

Fig.2 Axial Spatial Distribution Focusing

Structural analysis of isomeric chemicals by using high resolution MS/MS on Curved Field Reflectron incorporated with a novel focusing technology

Results

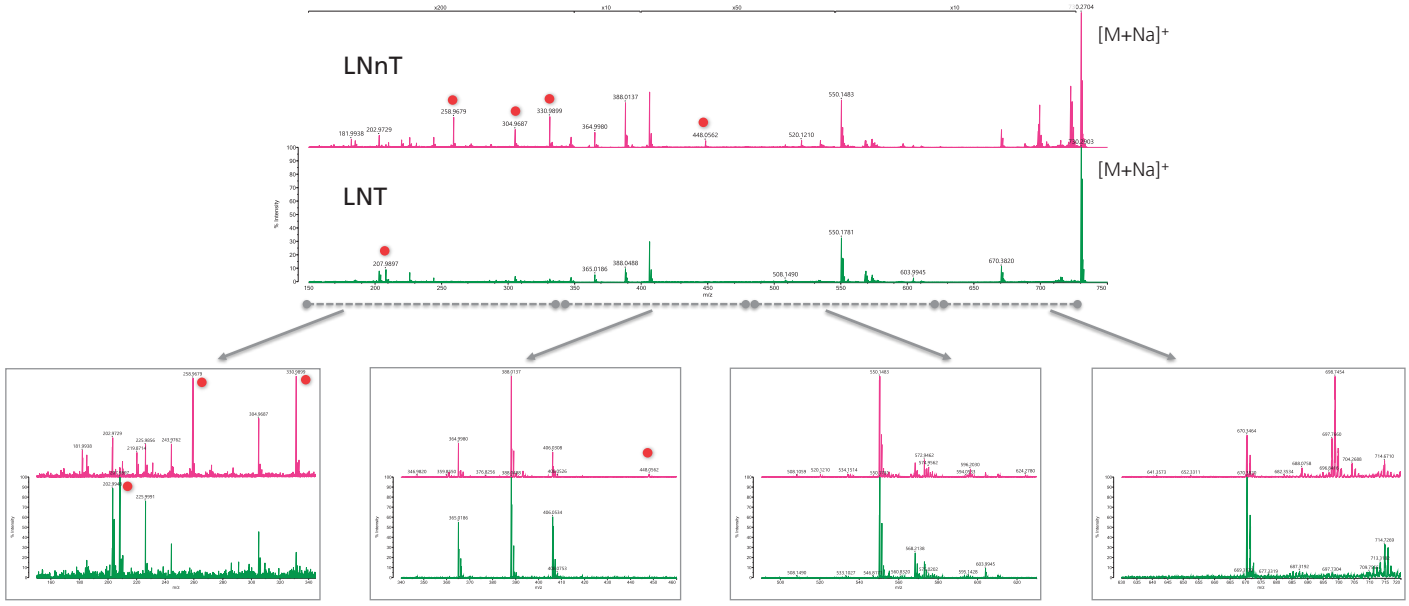

Fig.3 MS/MS of LNT and LNnT

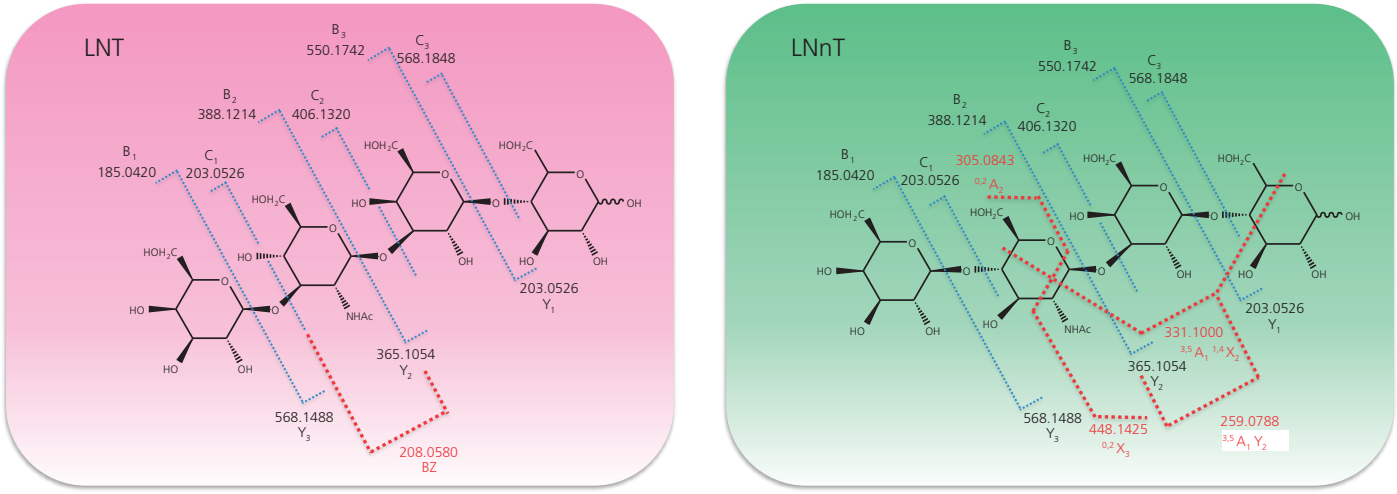

Fig.4 fragment ions of LNT and LNnT

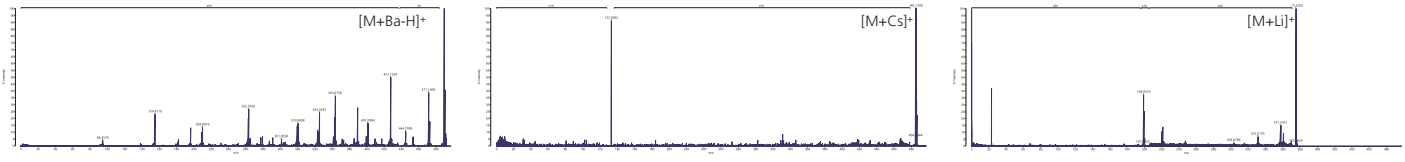

Fig.5 Effect of metal cations in MS/MS (PGE_2)

Structural analysis of isomeric chemicals by using high resolution MS/MS on Curved Field Reflectron incorporated with a novel focusing technology

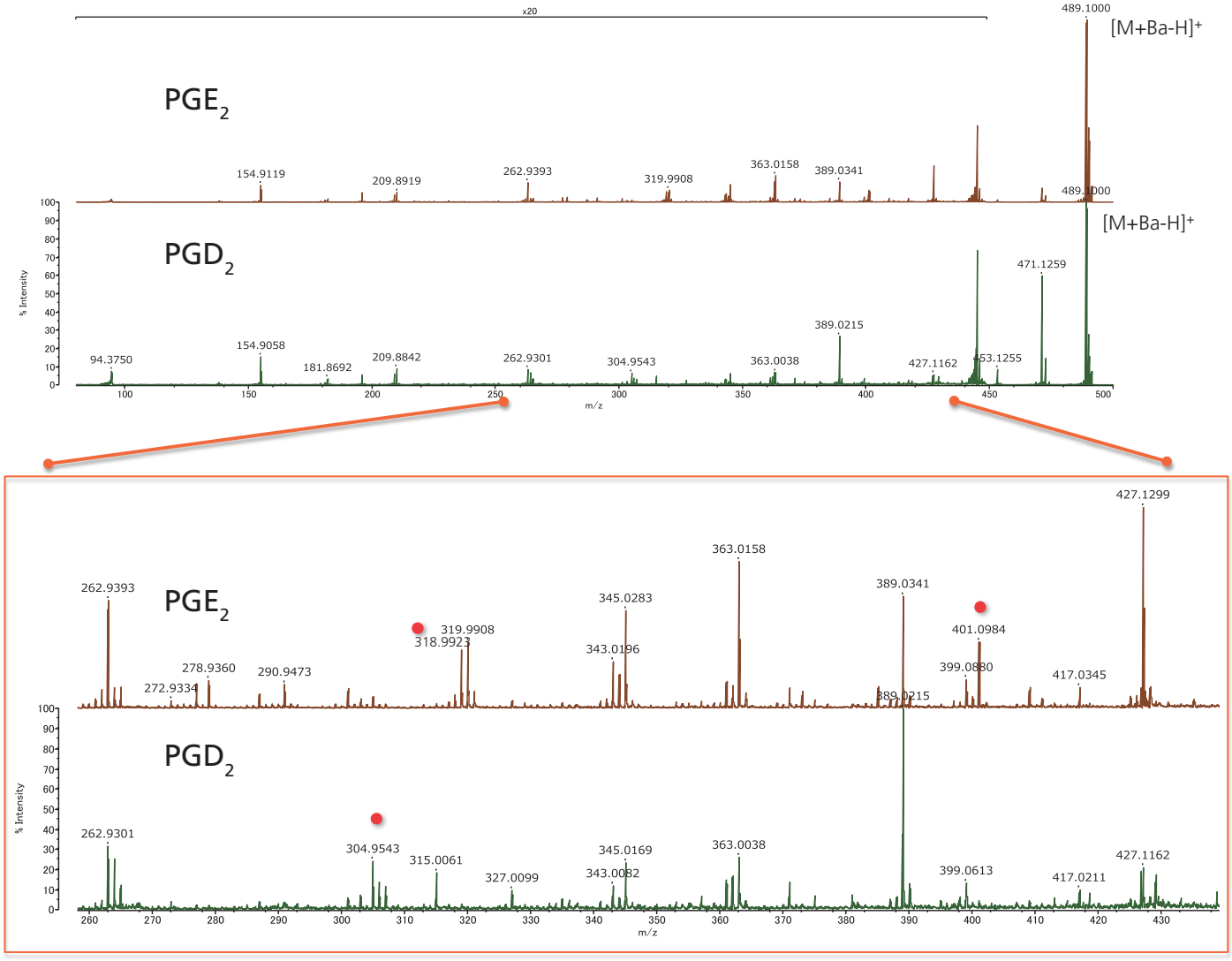

Fig.6 MS/MS of PGD_2 and PGE_2

Structural analysis of isomeric chemicals by using high resolution MS/MS on Curved Field Reflectron incorporated with a novel focusing technology

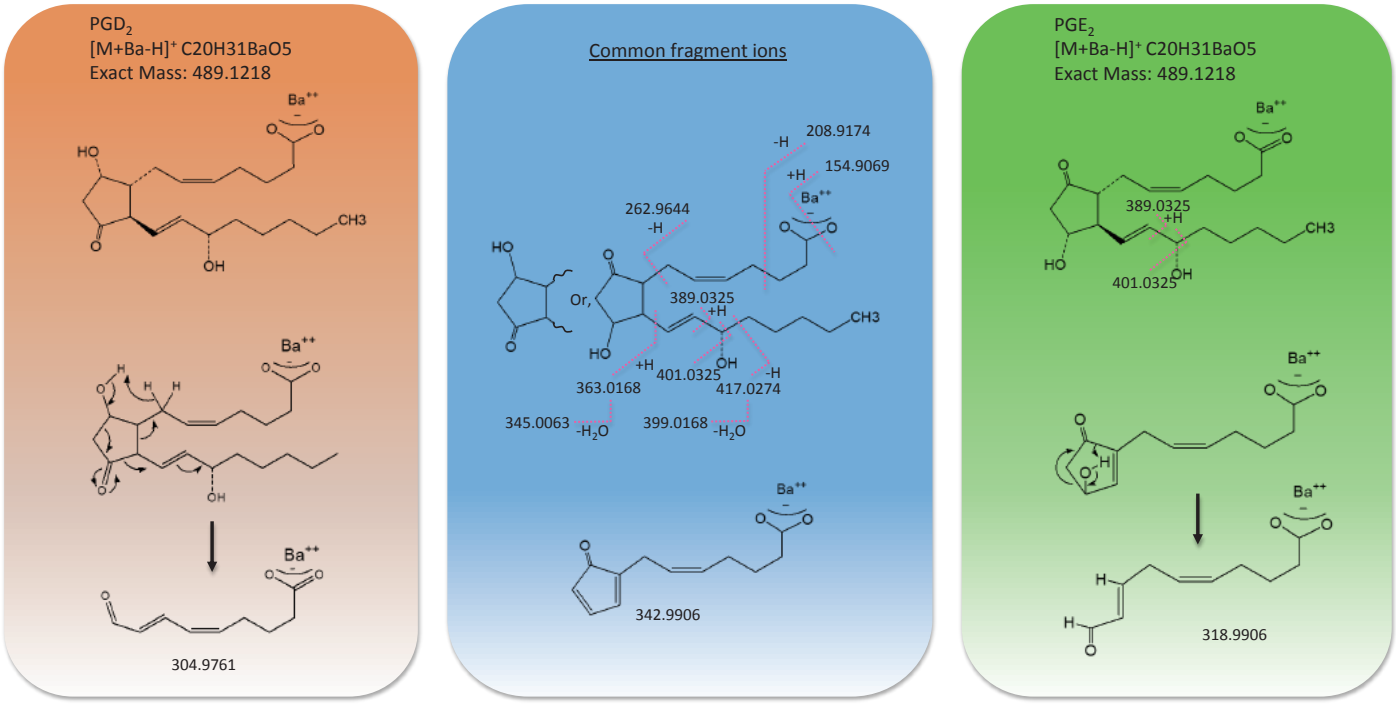

Fig.7 Conceivable pathways for fragmentations of PGD_2 and PGE_2, including reported one in ref(1).

Conclusions

- High MS/MS resolution achieved by ASDF enables to perform precise assignment in the analysis of isomeric chemicals.
- Differentiation of linkage formations between Gal and GlcNAc was conducted successfully by MS/MS of sodium adducted carbohydrates.
- Charge remote fragmentation of bariated PGD_2/PGE_2 was applied to a differentiation of the isomeric chemicals.
- Choice of cation was significant to obtain interpretable fragmentation as well as FAB-tandem MS analysis.

References

(1) Zirrolli, J.A., et al; J Am Soc Mass Spectrom., 1990, 1(4), 325-35.
(2) Yamagaki, T., et al; J Mass Spectrom., 2006, 41(4),454-62.

First Edition: May, 2015

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/