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The Development of Miniature MALDI Digital Ion Trap Mass Spectrometer

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Overview

- A new miniature MALDI-DIT-MS developed
- Compact body size, wide MS range, and high-performance MS^n are achieved by a unique Digital Ion Trap (DIT) technology, along with the innovative design of the laser/ion optics.

Introduction

To analyze the structure of the bio-molecules, a large and expensive MS equipment is necessary as TOF/TOF, etc. We have reported a digital ion trap mass spectrometer (DIT-MS) which is driven by high-voltage rectangular waveform for trapping ions [1][2], and developed several DIT-based MS instrument [3] which have specific functions such as wide mass range ion scanning and rapid digital asymmetric waveform isolation (DAWI) of the precursor by adapting our driving unit of rectangular waveform [4]. The advantage of utilizing rectangular waveform is that the frequency and the duty ratio of the waveform can be changed easily and flexibly. However, the DIT itself, as well as the mass spectrometer system has kept the similar size as the conventional one.

[1] Iwamoto. S. et al. ASMS2007, WPE087. [2] Iwamoto. S. et al. ASMS2008, ThP033. [3] Iwamoto. S. et al. ASMS2009, MP202. [4] Brancia. F.L. et al. J Am Soc Mass Spectrom. 2010, 21(9), 1530.

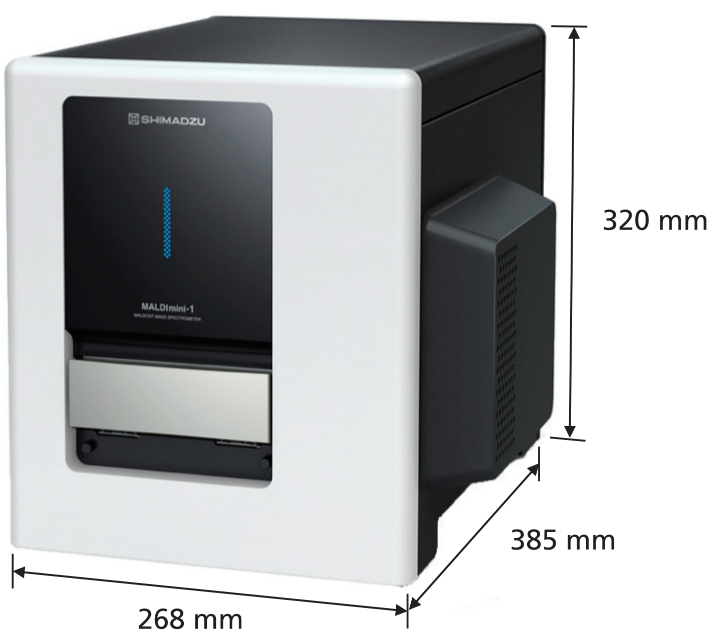

Figure 1 Appearance of the miniature MALDI-DIT-MS “MALDImini-1”

Methods

To miniaturize the instrument, we developed a new sample stage unit. A sample plate holder in a vacuum chamber is driven by a magnet which transmits the power of actuators from out of the chamber, thereby downsizing the vacuum chamber compared with a conventional unit. We employed only one optical window above the sample plate for laser irradiation and image observation by camera to simplify the optics and slim down the chamber volume. Ion trajectory was bended 90 degrees by quadrupole deflector of ion optics. The downsizing of vacuum volumes resulted in employing small size pump as well.

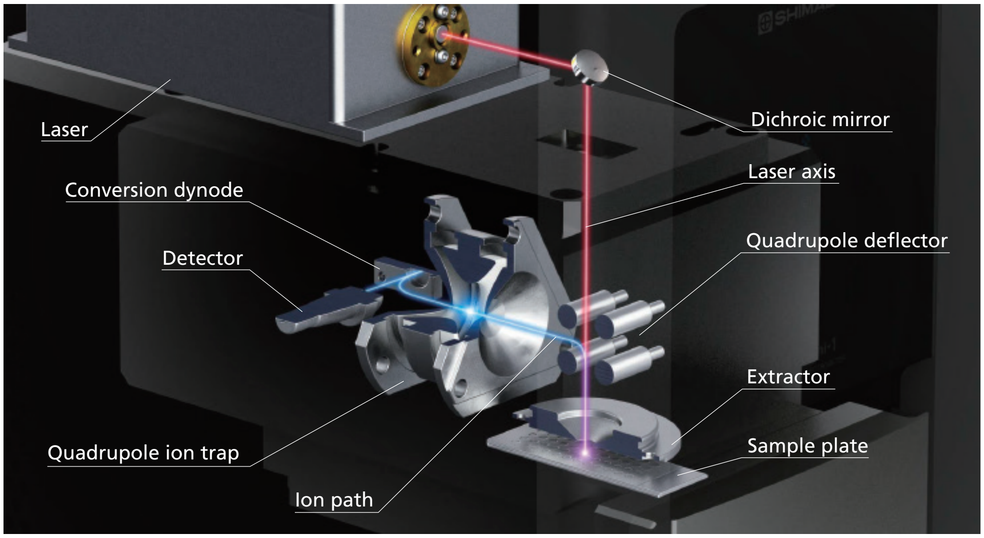

Figure 2 Laser / ion optics

One of the important benefit of DIT is that the power supply voltage of RF can be lowered than conventional IT. Because in DIT, we can modulate the frequency of trapping RF waveform easily to trap heavy ions. We used rectangular waveform RF with an amplitude under +/-500 V to drive the ion trap. This enabled us not only to make a DIT driving unit much smaller than before, but to achieve more durable, and smaller power consumption. By these improvements and many other refines, all components of new device are housed in the small body.

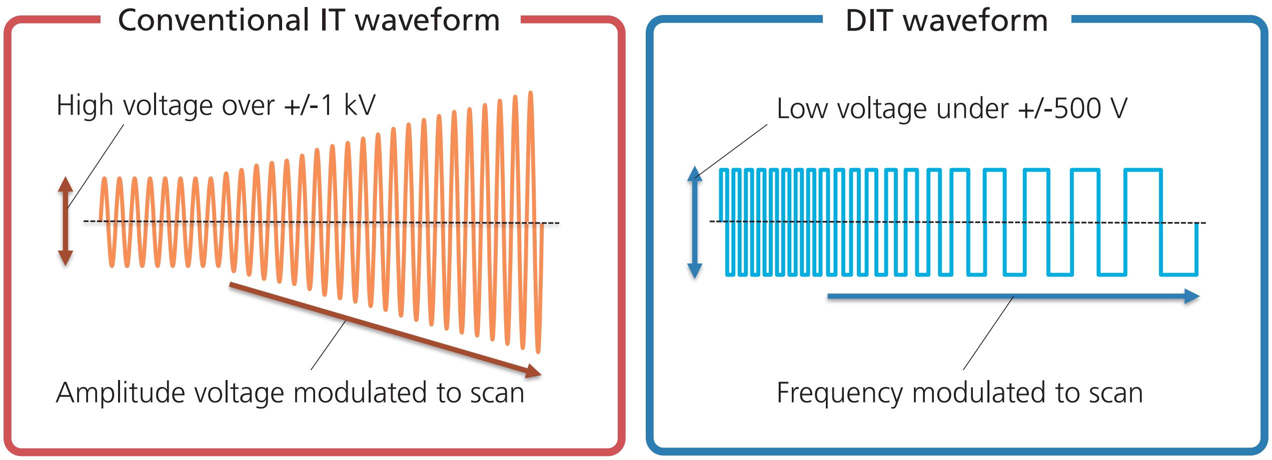

Figure 3 Difference of trapping parameters between conventional IT and DIT

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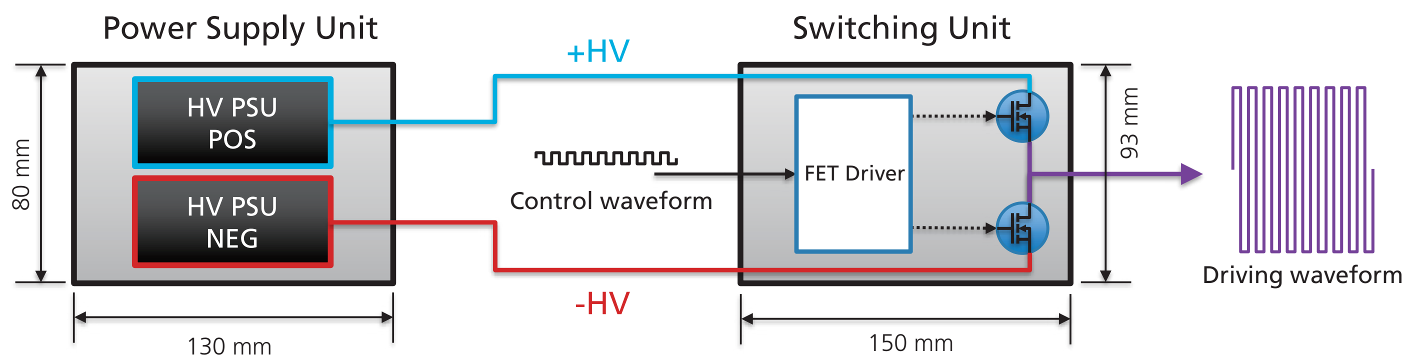

Figure 4 Diagram of the DIT driving unit

Results

Simulation study on the ion optics

To evaluate the efficiency of ion trapping through the quadrupole deflector, the ion trajectories were calculated by SIMION® 8.1. The simulation studies indicated that almost all ions ranging from m/z 600 to 5000 were injected into the ion trap, and more than 90% of them were trapped. The trapping efficiency is equivalent to the conventional ion optics considering linear ion path.

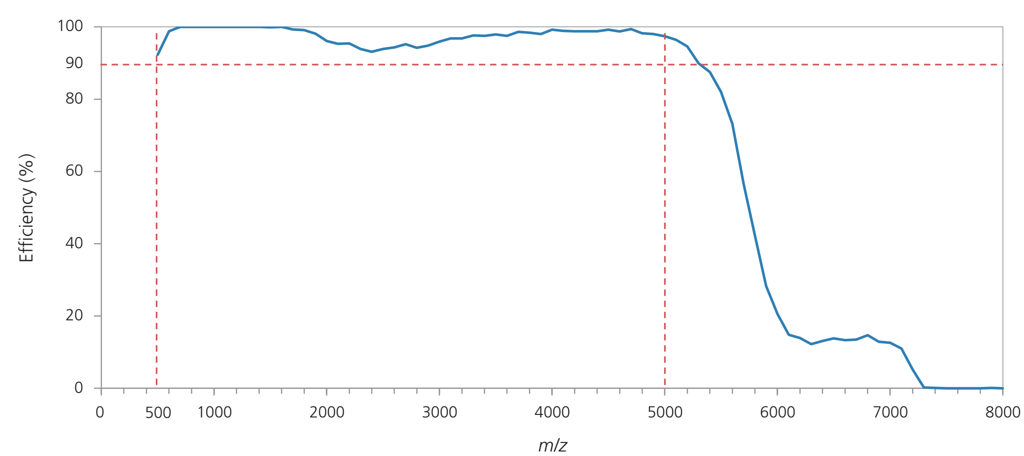

Figure 5 Simulation study on trapping efficiency by *m/z*

Performance evaluation on actual instrument

The performance of the miniature instrument was experimentally tested using standard peptide and protein. First, the sensitivity of MS was determined using Glu-1-Fibrinopeptide B (Glu-Fib, MW 1570.6) and bovine serum albumin (BSA, MW 66.5K). In the peptide analysis using α-cyano-4-hydroxycinnamic acid (CHCA) as a matrix, 1 fmol of Glu-Fib was detected at signal-to-noise ratios above 5. As an application toward large molecules, 250 fmol of BSA was tried and clearly detected as a series of singly and multiply charged species, by using sinapinic acid (SA) as a matrix and by employing a dedicated instrumental tunings.

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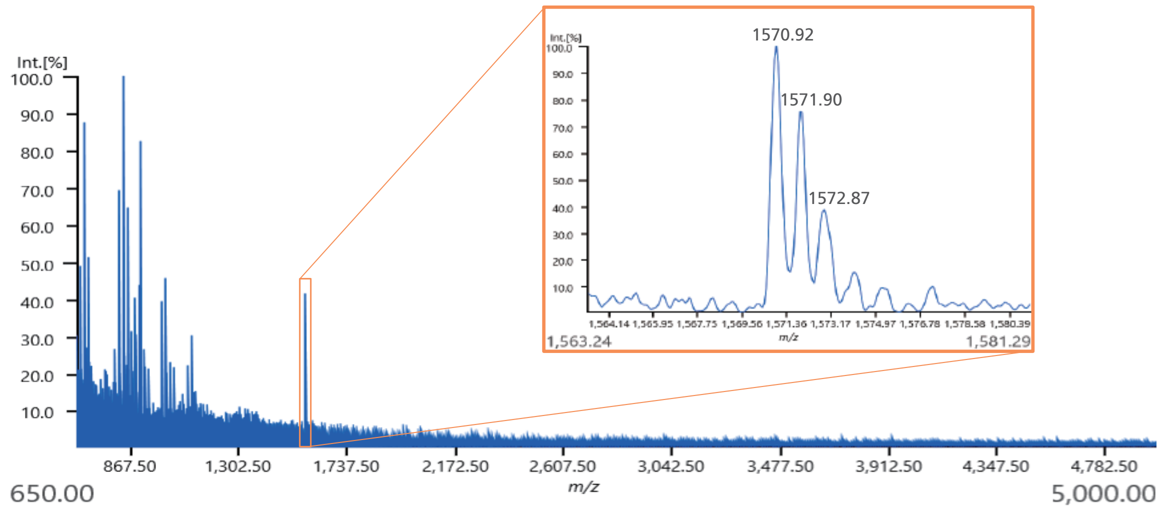

Figure 6 MS Spectrum of 1 fmol of Glu-1-Fibrinopeptide B

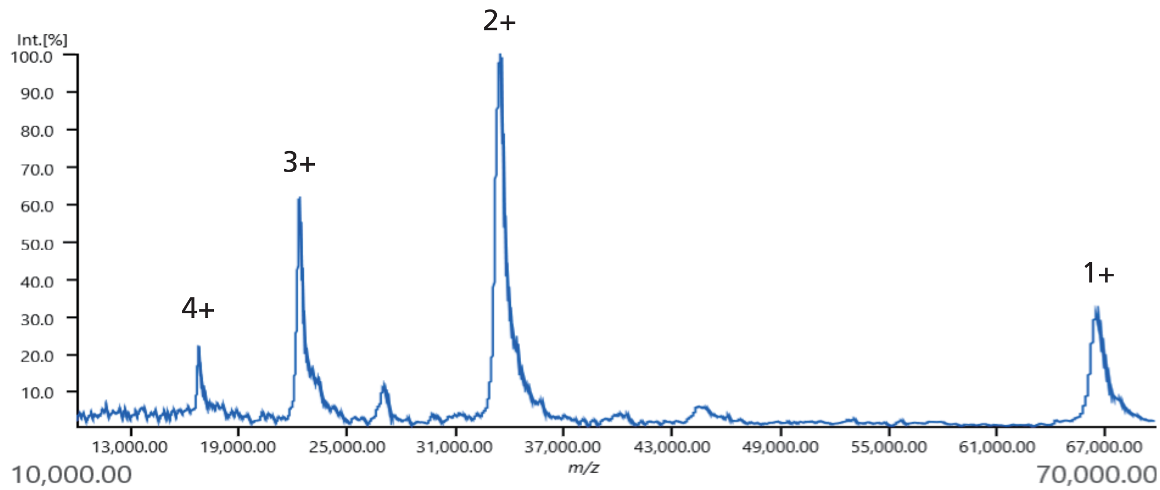

Figure 7 MS Spectrum of 250 fmol of bovine serum albumin

Next, MS^n performance was evaluated. Precursor was isolated by DAWI which instantaneously isolates the targeted ions by manipulating the duty ratio of rectangular wave trapping voltage. Product ions were produced by collision-induced dissociation (CID) of the precursor with argon gas by dipole excitation. For MS/MS performance, 10 fmol of Glu-Fib produced a beneficial product ions with a high signal-to-noise ratio.

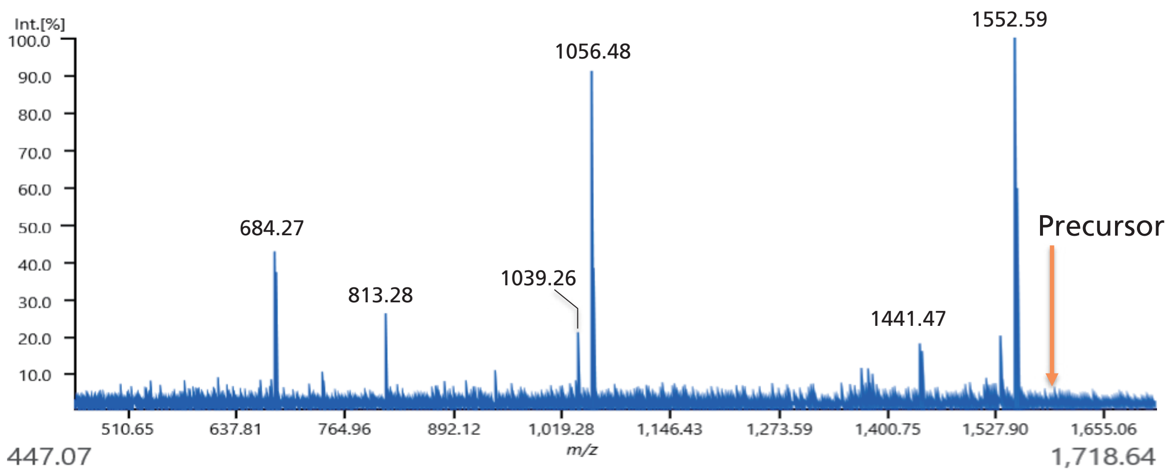

Figure 8 MS/MS Spectrum of 10 fmol of Glu-1-Fibrinopeptide B

In the case of MS^3, the fragment ion peak of *m/z* 1056 from 100 fmol Glu-Fib was further dissociated by CID and produced product ion peaks were detected.

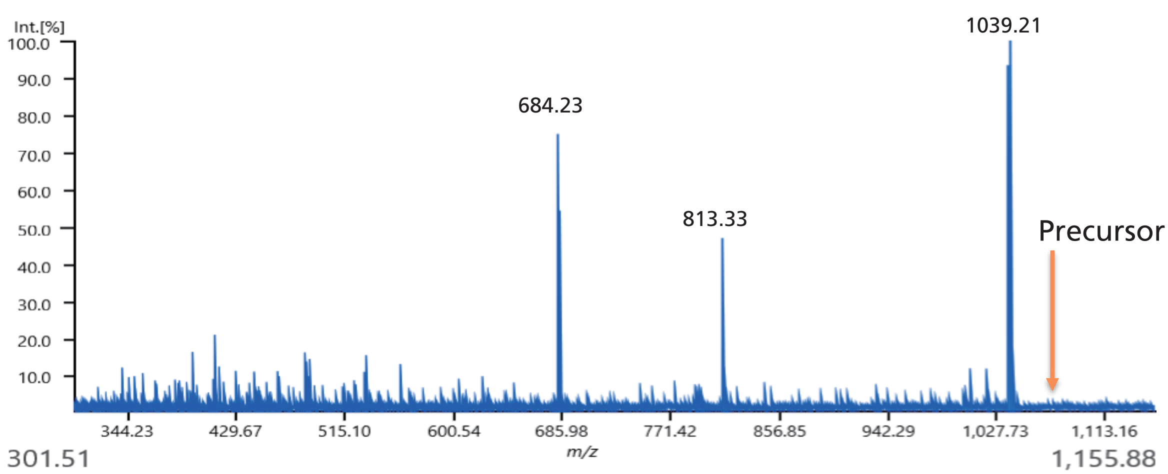

Figure 9 MS^3 Spectrum of the fragment ion peak of *m/z* 1056 from 100 fmol of Glu-1-Fibrinopeptide B

Conclusions

The new miniature MALDI-DIT-MS provides sufficiently high-performance MS and MS^n for various samples including biopolymer, despite its remarkably small size.

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