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A novel ion optical device to improve duty cycle of a Q-TOF mass spectrometer

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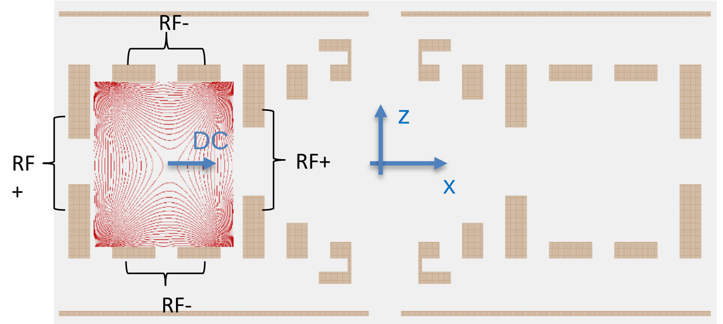
1. Introduction

Duty cycle of orthogonal Q-TOF mass spectrometer is limited by its mass range. The reason is that ions would disperse in space prior to enter the extraction region of TOF, due to ions' velocity varying according to m/z. We proposed a new strategy to address the issue, by using a novel ion optical device "RF carpet trap". Ions are firstly trapped in the device, and then being sequentially scanned out in a slow speed (~200Hz) by a reversed m/z order. A fast ion gate (~8kHz) followed can chop the ejected ion cloud and synchronize with the TOF pulser. Duty cycle of Q-TOF can be improved to be >50% in a wide mass range.

2. Design & Simulation

With the purpose to improve duty cycle of a Q-TOF mass spectrometer, while its dynamic range cannot be compromised, we designed a new ion optical device which has a large ion capacity: RF carpet trap. It consists several concentric ring electrodes which form a toroidal RF quadrupole field. **Principle for mass separation:** A DC gradient is used to counterbalance the RF barrier inside the trap. Ramping down the RF voltage, ions can be released sequentially from high to low mass.



Principle for mass separation in RF carpet trap

$\nabla V_{eff} = E_{DC}$

$\nabla V_{eff} = \nabla \frac{q}{4m\Omega^2} E^2(x) = \frac{q}{2m\Omega^2} \cdot k_1 x$ (Quadratic field)

$E_{DC} = k_2 x$

Therefore, $\frac{q}{2m\Omega^2} \cdot k_1 = k_2$ → Independent on **x** position.

On the other side, quadrupole field compresses ions well in **z** direction.

Figure 1 Geometry for RF carpet trap: "RF+" and "RF-" are RF voltages with opposite phase to apply on ring electrodes to form a toroidal RF quadrupole filed. A DC field (E_{DC}) is formed by applying DC biases on ring electrodes.

The upstream device of RF carpet trap can be a collision cell, and the downstream can be an orthogonal TOFMS. Operation of RF carpet trap was shown in Figure 2.

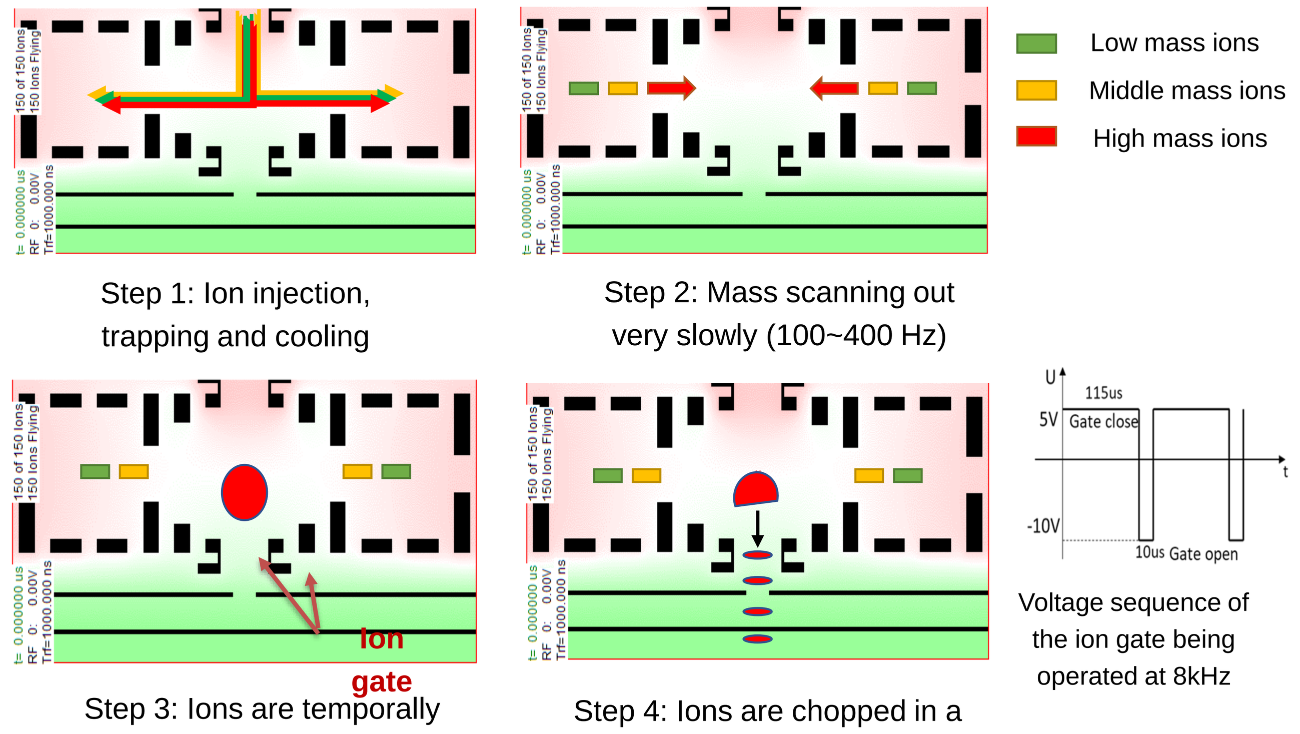


Figure 2 Operation of RF carpet trap by 4 steps, and voltage sequence on ion gate

Ion optics simulation verified the feasibility of mass separation and fast gating effect in RF carpet trap. Figure 3 shows one of simulation results.

(1) Ions with a 20% difference in m/z can be baseline separated.

(2) After the fast gating, peak width of ions is reduced to be 3.5~9.0 μs for a m/z range from 250 to 1500.

(3) Axial energy dispersion of ejected ions is around 5 eV, which is acceptable for a Q-TOF instrument.

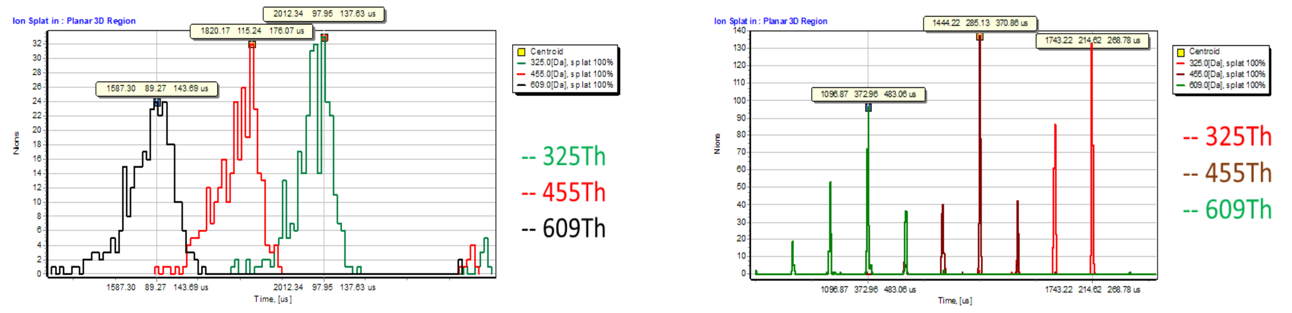


Figure 3 Simulated mass spectrum of RF carpet trap. Left: before the ion gate; Right: after the ion gate. In simulation, RF carpet trap was scanned at 200Hz and the ion gate was operated at 8kHz.

3. Fabrication & Instrumentation

RF carpet trap consists of two "RF carpets" in a face to face manner. To make sure good robustness and mechanical accuracy, we used ceramic PCB as the substrate to load concentric ring electrodes. Ring electrodes were fixed on substrate by through-hole soldering. PCB technology also ensures wire connections to electrodes very convenient.

The fabricated device was shown in Figure 4. It is a very compact and delicate device: diameter of the device is only ~45mm, and its axial length from ion inlet to ion outlet is ~16mm.

Figure 4 Photo of fabricated RF carpet trap. Left: ring electrodes loaded on ceramic PCB substrate; Right: two piece of RF carpets consist the RF carpet trap.

RF carpet trap was aimed to improve duty cycle of Shimadzu Q-TOF mass spectrometer. But for its basic performance test, RF carpet trap was firstly mounted on a modified Shimadzu triple quad LCMS8040® between the collision cell and the ion detector, by removing the Q3 part.

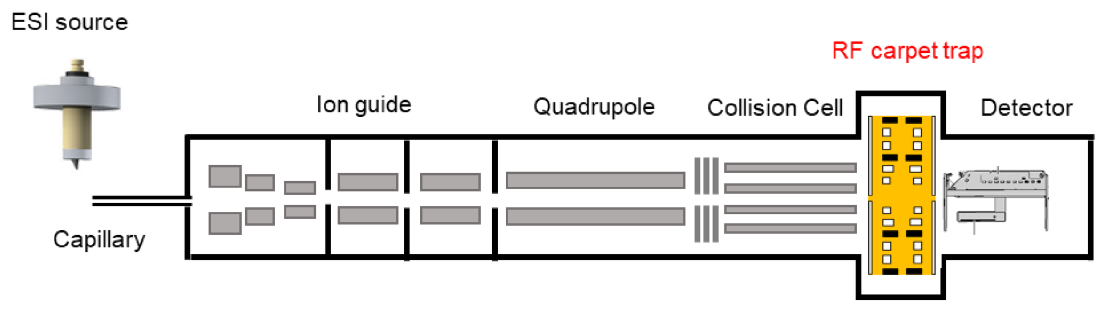


Figure 5 RF carpet trap was located just after the collision cell and followed by a SEM detector

4. Experimental results & discussion

4.1 Mass separation of RF carpet trap

In experiment, Q1 was set in SIM mode to transfer only targeted ions. The collision cell was used to temporally trap ions. RF carpet trap was operated in scan mode, which included ion injection from collision cell, ion trapping and cooling, and then being scanned out slowly. The ejected ion signal after RF carpet trap can be measured on detector to form a spectrum, with or without fast chopping (gating) mechanism. The combined spectrum for several targeted ions were shown in Figure 6. Results agreed with our simulation well. To alleviate the space charge effect due to high ion density in the "slow scan", we can increase the scan speed to 400Hz, as shown in Figure 6 (c).

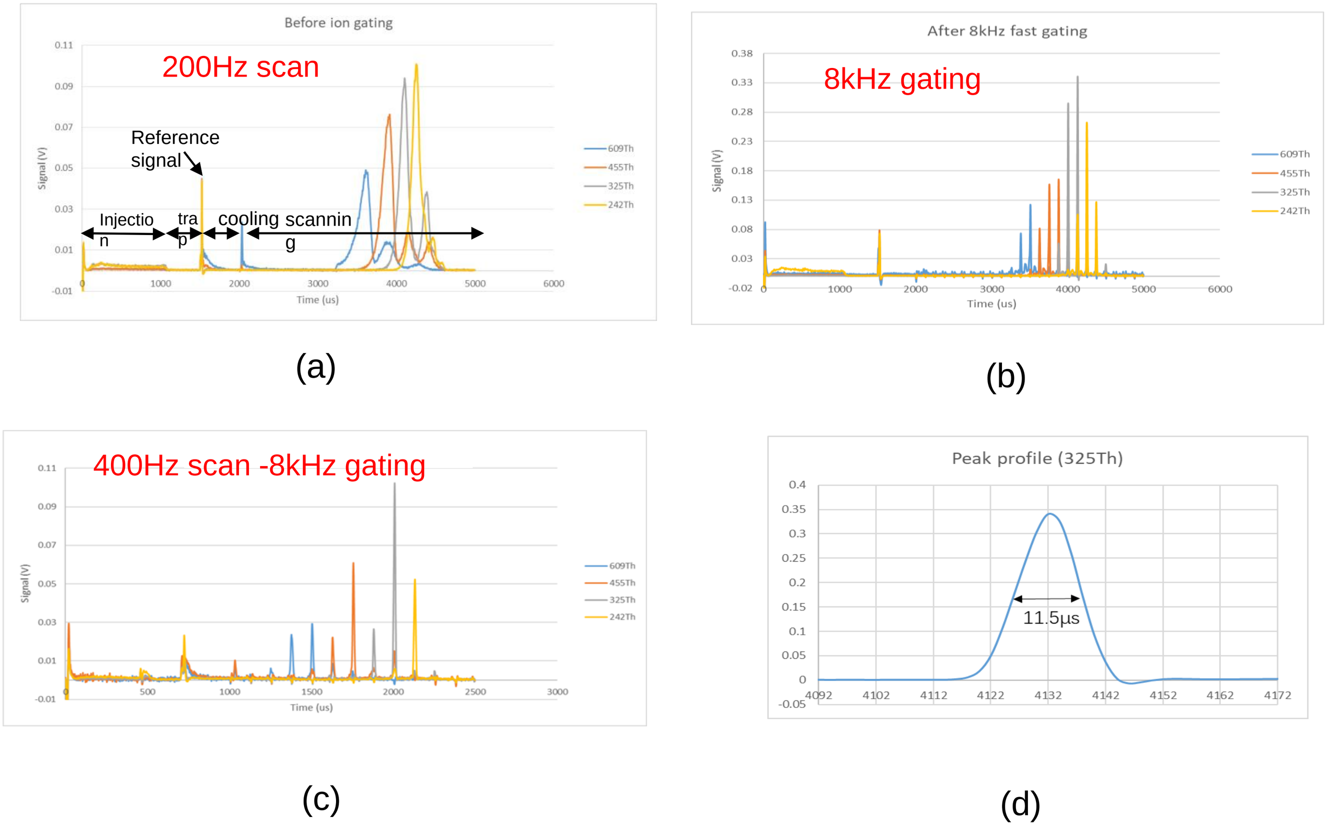


Figure 6 Mass separation by RF carpet trap: (a) before and (b) after the ion chopping mechanical and chopped peaks by the fast gating mechanism. (c) Increase the slow scan speed to 400Hz. (d) Peak width of one ion species after ion chopping.

4.2 Duty cycle enhancement

If coupling with a Q-TOF instrument, the duty cycle can be calculated by:

$$\text{Duty cycle}=\frac{\text{Ion\_peak\_width}_{\text{FWHM}}}{0.5*\text{Pusher\_width}} \times 100\%$$

With RF carpet trap, measured peak width (FWHM) on detector, and the calculated duty cycle for each ion species based on Shimadzu's Q-TOF dimensions were shown in Figure 7. For all of ions, >50% duty cycle can be achieved.

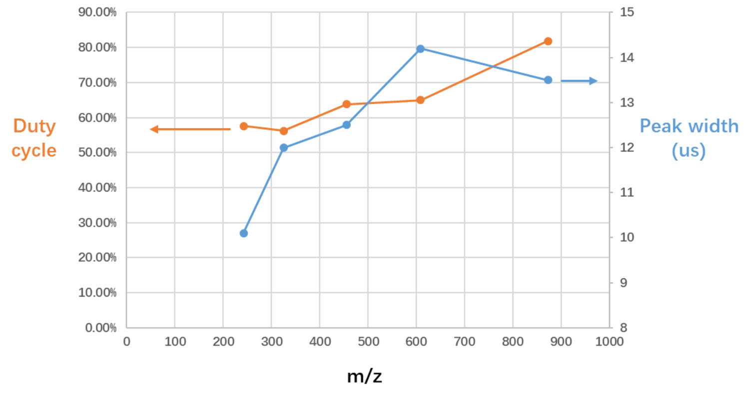


Figure 7 Peak width (FWHM) and the calculated duty cycle for ions with a wide m/z range

4.3 Comparison with the fast scan method

If without the gating mechanism but simply to improve the scan speed of RF carpet trap to 2kHz, it is also possible to improve duty cycle of a Q-TOF MS. The scheme is similar to the Zeno trap which was introduced by Loboda et. al. in the patent US7456388.

Limitations to Zeno trap mechanism: (1) The repetition rate of TOF analyzer has to be lowered down to 1~2kHz; (2) The distance from exit of collision cell to the extraction region should be long enough to make lighter ions can catch up the heavier ions.

Instead, by the slow scan -fast chopping mechanism, we can not only match the ultrafast repetition rate of TOF analyzer (8kHz), but also lower down the requirement to said distance, so that a compact instrument is possible.

5. Conclusions

A novel ion optical device "RF carpet trap", as well as with a new ion manipulation strategy, was developed to improve duty cycle of a Q-TOF mass spectrometer. A rough mass separation in RF carpet trap in a slow scan speed is followed by an 8kHz fast gating mechanism. After the RF carpet trap, ion peak width (FWHM) was chopped to be 8~15 μs, which corresponds to 50%~80% duty cycle, depending on m/z.

Acknowledgement

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