

Improving Mass Resolution in ortho-TOF Mass Spectrometer

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INTRODUCTION

The use of radiofrequency (RF) multipole ion guides for the efficient transport of ions produced at the atmospheric pressure into a mass analyzer operating under high vacuum is a common practice in mass spectrometry. The cooling of ions is especially beneficial in the case of a time-of-flight (TOF) mass analyzer with orthogonal acceleration (oa), where the energy spread of the ion beam exiting an RF ion guide irreversibly affects the resolution and sensitivity of TOF mass spectrometer¹.

It was pointed out² that the effect of the initial velocity spread, in the y -direction (time-of-flight), on resolution of oa-TOF mass spectrometers is probably the largest. The contribution in the peak width Δt due to this effect is determined by³:

$$\Delta t = \frac{2mv_y}{zeE} \quad (1)$$

where v_y is the velocity spread in y direction, m is the mass, ze is the ion charge and E is the strength of the electric field during the extraction.

EXPERIMENTAL

TOF Mass Spectrometer

The time-of-flight mass spectrometer with orthogonal acceleration and an ESI ion source is shown schematically in Figure 1. The atmospheric pressure (AP) interface consists of a heated capillary (0.4 mm i.d.) and a quadrupole ion guide (6.35 mm rod diameter). The pressure in the AP interface (~ 1 Torr) was maintained by a 30 m³/hr roughing pump. The octopole ion guide (3.2 mm rod diameter) was separated from the octopole by a 2 mm diameter aperture. The pressure in this region was about 10^{-3} and was maintained by a 70 l/s turbomolecular pump. The lengths of the pulser, acceleration and field free regions are 0.9 cm, 4.6 cm and 48 cm, respectively. Acceleration voltage was typically 5 kV. The ion signal was amplified and recorded by a 100 ps time digitizer (ORTEC Model 9353).

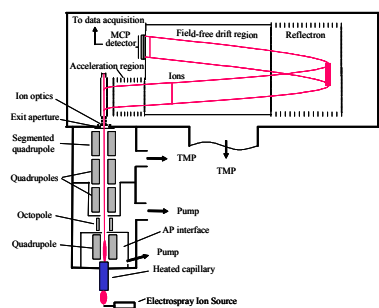


Figure 1. Schematic view of oa-TOF mass spectrometer.

A schematic of the last segmented quadrupole is shown in Figure 2. The RF divider consisting of 220 pF capacitors allowed changing the RF voltages applied to the individual rod sections. The value of 220 pF is much larger than rod capacitance thus causing minimal RF voltage variation on the quadrupole sections (less than 5%) when the same RF voltage is applied to both ends. The length of the 1-st section was 25 mm and the next 5 sections were 9.5 mm long. The sections were separated by 1 mm thick PEEK washers.

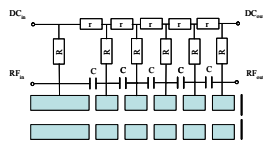


Figure 2. General schematic of the segmented quadrupole.

Numerical Simulation

The quality of the ion beam was determined by simulating the ion motion in the proposed ion guide geometry using SIMION 3D software (Fig. 3). The RF voltage on the first quadrupole section of the ion guide was set at 200 V_{0-peak} and 1 MHz frequency; eleven ions were chosen for simulation with initial energy equal to 1 eV. Ions were evenly distributed from $x=-0.125$ mm to $x=+0.125$ mm (0.25 mm dia. ion beam). Their initial velocities were parallel to the ion guide axis. After passing the exit aperture the ion beam was focused by an Einzel lens. The divergence angle of the ion beam, exiting the quadrupole ion guide, is proportional to the diameter of the beam waist at the point of beam's focus.

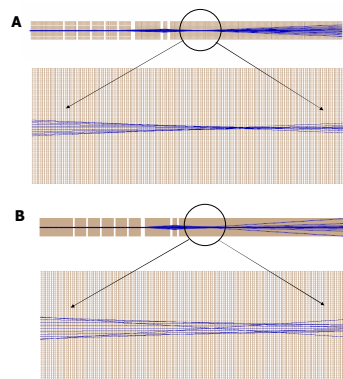


Figure 3. The results of numerical simulation of ion trajectories with reducing (A) and constant (B) RF and DC voltages.

RESULTS AND DISCUSSION

The electrospray spectra of Bradykinin 1 μ M solution were acquired on the oa-TOF instrument described above. The spectra were acquired for 10 s with the TOF repetition rate of 5 kHz. Different RF and DC voltage distributions on the segmented quadrupole ion guide were tested. The isotopic structure of the Bradykinin (2+) ion is shown in Figure 4:

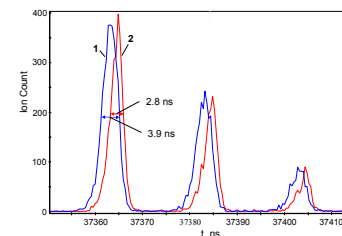


Figure 4. Isotopic structure of $m/z=531$ ion; 1 – corresponds to the same RF and DC voltages applied to quadrupole segments; 2 – RF voltages are stepwise reduced to 0 towards the ion guide exit.

As one can see from the spectra presented on Figure 4, the mass resolution (determined as $t/2\Delta t$ at FWHM) improves considerably when the RF voltages applied to the quadrupole guide sections were reduced towards the exit. Similar improvements in resolution were observed over a whole mass range of electrospray generated peptide ions. For example, for Bradykinin (3+) ($m/z=354.19$) and Bradykinin $\gamma 7$ (1+) fragment ($m/z=807.42$).

Ions moving along the ion guide typically fill a central area near the ion guide axis which is determined by the pseudopotential well depth. When ions leave the ion guide, they experience the radial kick-off effect, which is due to the cut-off of the RF ion oscillations at the arbitrary phase. The RF potential distribution between the ion guide exit and the

exit aperture can be described as⁴:

$$\Phi = V_{RF} \cos \Omega t \frac{x^2 - y^2}{r_0^2} f(z) \quad (2)$$

where $f(z) = 1 - \exp[-a(l-z)/r_0 - b(l-z)^2/r_0^2]$ is a fast decreasing ($a=2.13$ and $b=1.55$) exponential function in units of $(l-z)/r_0$; z is the coordinate along the quadrupole axis originating at the quadrupole exit; l is the distance between the rods and exit aperture. The resulting velocity gain in the y direction when the ion leaves the ion guide equals to:

$$\Delta v_y = \int_{t_0}^{t_f} 2zeV_{RF} \cos \Omega t \frac{Y(t) - 0.5qY(t) \cos \Omega t}{m r_0^2} f(z) dt \quad (3)$$

where t_0 is the time when the ion leaves the ion guide and t_f – the time when the ion reaches the exit aperture, Y – secular motion coordinate, q – Mathieu parameter.

We can estimate the value of the integral as $2zeV_{RF} \cos \Omega t_0 Y(t_0)/m r_0^2 + l/v_z$. For Bradykinin (2+) ions, in our experimental conditions, $q=0.3$ and the average $Y(t_0)=0.11$ mm. Using these values together with $l=1.5$ mm and $v_z=2.6 \times 10^3$ m/s (this velocity corresponds to 20 V acceleration), one can estimate average Δv_y as 200 m/s. For the value of $E=6 \times 10^4$ V/m, typical for our experimental conditions, this gives the value of turn-around time from equation (1) 37 ns. This would limit the resolution in the TOF mass spectrometer to ~ 500 . Since the experimental value is higher, this means that the ion beam is substantially clipped by the exit ion optics before the ions enter the pulser region.

REFERENCES

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