CHARACTERIZATION OF MASS SELECTIVE AXIAL EJECTION FROM A LINEAR ION TRAP WITH SUPER-IMPOSED AXIAL QUADRATIC DC POTENTIAL

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Martin R. Green, Robert H Bateman, Garry Scott.
Waters Corporation, Manchester, United Kingdom.

OVERVIEW

PURPOSE

Characterise mass selective ejection from a linear ion trap with axial quadratic DC potential well.

METHODS

Experimental device based on segmented quadrupole.

Resonance excitation and parametric excitation compared.

Effect of scan direction investigated.

RESULTS

Mass resolution of ≈ 350 (FWHM) at m/z 300 demonstrated using parametric excitation.

Performance optimised for analytical scan direction by introduction of non-linear trapping fields.

INTRODUCTION

Linear ion traps based on RF quadrupole geometries are well-established analytical devices.

Methods of both radial and axial mass selective ejection have been demonstrated. [1,2] In both these cases the characteristic frequency of ion oscillation in the radial direction is exploited to perform mass selective ejection.

More recently axial resonance ejection from a quadratic DC potential well, developed along the length of the RF multi-pole, has been demonstrated[3].

In this paper we present preliminary results from the characterisation of two different methods of mass selective ejection from an experimental axial harmonic oscillation linear ion trap.

- Mass selective resonance excitation.
- Mass selective parametric excitation.

In addition the effect of analytical scan direction on mass resolution was investigated.

METHODS

An experimental device, based on a segmented quadrupole was installed into the collision cell region of a triple quadrupole mass spectrometer. **Figure 1**

RF voltage was applied to the device to radially confine ions. A DC potential well, confining ions axially, was imposed along the length of the device by application of appropriate DC to individual segments. **Figure 2**

The segments were supplied with an additional AC potential, varying in amplitude along the length of the device.

Following accumulation of ions in the trap, the frequency of the additional AC potential was ramped to effect mass selective axial ejection. Ejected ions, passing through the second quadrupole, were recorded at the detector.

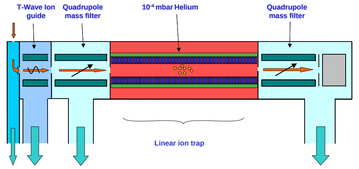

Figure 1 *Schematic of triple quadrupole mass spectrometer incorporating linear ion trap.*

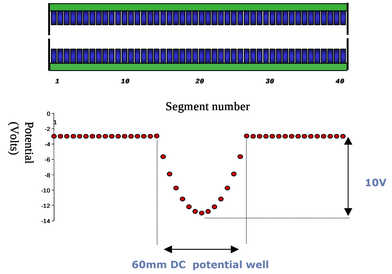

Figure 2*. Schematic of the experimental segmented quadrupole ion trap. A 10V quadratic DC potential well was imposed over the central 60mm of the device..*

RESONANCE EJECTION

Ions tapped in the axial DC well undergo Simple Harmonic Motion (SHM) oscillating at a frequency ω where

$$\omega \propto \sqrt{\frac{qV}{m}}$$

q = charge
m= mass
V=Potential well depth

Application of excitation potentials with pk-pk amplitude varying linearly along the device and at a frequency σ where σ = ω for a particular m/z value , results in resonance excitation of ions of this m/z value. (**Figure 3**)

The amplitude of oscillation of these ions increases until the ions are ejected from the ion trap.

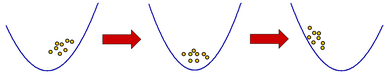

Figure 3*. Oscillation of the axial DC well at SHM frequency resulting in Resonance Ejection.*

Figure 4. shows the resonance ejection mass spectrum of a mixture of Suphadimethoxine $(M+H)^+$ m/z = 311 and a poly-ethylene glycol 400 m/z = 305.
The trap fill time was approximately 500ms. The spectra was generated from a single excitation frequency sweep with 10V axial well depth.

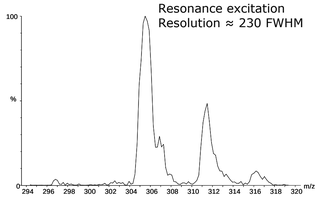

Figure 4*. Resonance ejection mass spectrum σ = ω .*

PARAMETRIC INSTABILITY

Application of excitation potentials with pk-pk amplitudes following a quadratic function along the device results in parametric excitation. (**Figure 5**)

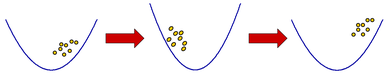

Figure 5*. Oscillation of the axial DC well at twice SHM frequency resulting in Parametric excitation.*

Stability of trapped ions during parametric excitation is described by the well known Mathieu equation. Unlike the resonance method the strongest excitation occurs when the excitation frequency σ is at twice the SHM frequency ω.

Figure 6. Shows the parametric excitation spectrum of the same sample and under the same instrumental conditions as shown in **Figure 4**.

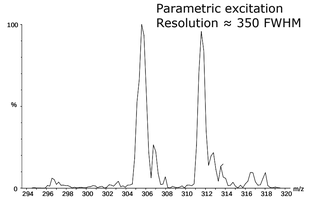

Figure 6*. Parametric excitation ejection mass spectrum σ = 2ω*

DISCUSSION

The improved resolution observed when using parametric excitation compared to resonance excitation may be attributed to the higher excitation frequency required to eject an ion of a specific m/z value.

During resonance excitation ions are ejected from the trap when the excitation frequency σ equals the SHM frequency ω.

During parametric excitation ions are ejected when the excitation frequency σ is twice that of the SHM frequency ω.

As $\omega \propto \sqrt{\frac{1}{m}}$ it may be shown that

For Resonance Excitation: Resolution = $\frac{m}{\delta m} = \frac{\omega}{2\delta\omega}$

Parametric Instability (σ = 2ω) : Resolution = $\frac{m}{\delta m} = \frac{\omega}{\delta\omega}$

EFFECT OF SCAN DIRECTION

A strong dependence was observed between mass resolution the scan direction of the excitation frequency.

Ions from a mixture of Suphadimethoxine and polyethylene glycol were mass selectively ejected using a parametric excitation frequency scan.

The profile of the DC applied to individual segments of the ion trap were optimized empirically and separately for

a) Reverse scan
High to low m/z = low to high excitation frequency.
b) Forward scan
Low to high m/z = high to low excitation frequency.

Figure 7 shows Intensity vs. Time data obtained when the shape of the potential well was optimised for a reverse scan. The figure shows the data obtained for a reverse scan **(Figure 7A)** and a forward scan **(Figure 7B)**.

Figure 8 shows Intensity vs. Time data obtained when the shape of the potential well was optimised for a forward scan. The figure shows the data obtained for a reverse scan **(Figure 8A)** and a forward scan **(Figure 8B)**.

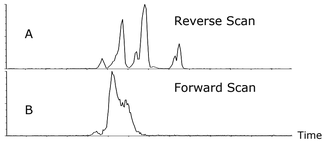

Figure 7*. DC well optimized for reverse scan.*

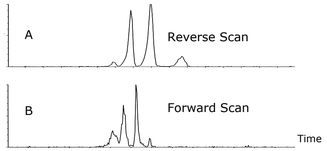

Figure 8*. DC well optimized for Forward scan.*

DISCUSSION

Introduction of small, non-linear field components, have been shown to improve performance of RF ion traps.[4] Non-linearity causes shifts in oscillation frequency with amplitude . If the frequency shift coincides with the direction of the analytical scan, ions are ejected rapidly and resolution is improved. Forward or reverse scans can be optimised by introduction of specific non-linear fields.
Figure 9 A shows the distortion applied to the DC potential well required to optimize a reverse scan.
Figure 9 B shows the oscillation frequency ω and the excitation frequency σ during a reverse scan. The frequency of ion oscillation decreases as the amplitude increases driving ions towards the excitation frequency improving mass resolution.
Figure 9C shows the oscillation frequency ω and the excitation frequency σ during a forward scan. The frequency of ion oscillation moves away from the excitation frequency retarding ejection and decreasing mass resolution.

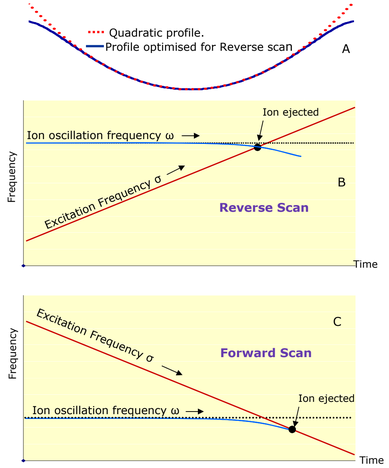

Figure 9*. Ion frequency shifts during excitation frequency scan. DC well optimized for reverse scan.*

Figure 10 A shows the distortion applied to the DC potential well required to optimize a forward scan.
Figure 10 B shows the oscillation frequency ω and the excitation frequency σ during a reverse scan. The frequency of ion oscillation moves away from the excitation as the amplitude increases retarding ejection and decreasing resolution.
Figure 10C shows the oscillation frequency ω and the excitation frequency σ during a forward scan. The frequency of ion oscillation increases driving ions towards the excitation frequency improving mass resolution.

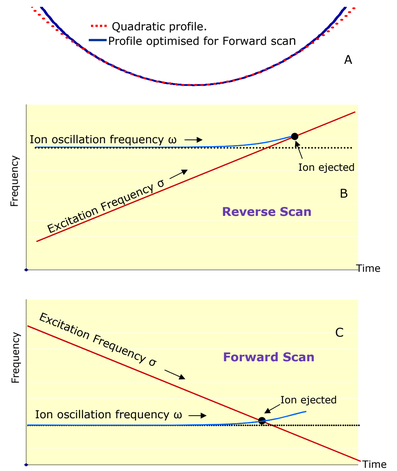

Figure 10*. Ion frequency shifts during excitation frequency scan. DC well optimized for forward scan.*

CONCLUSION

- **Acceptable analytical performance achieved using Experimental linear ion trap with axial DC potential.**
- **Parametric excitation at twice SHM frequency results highest mass resolution.**
- **Performance can be optimised for analytical scan direction by introduction of non-linear DC field.**

1. Schwartz et al. J. Am. Soc. Mass Spectrom. 2002,13,659-669
2. Hager J. et al., Rapid Commun. Mass Spectrom. 2002,16, 512-526
3. Hashimoto et al. J. Am. Soc. Mass Spectrom. 2006,17,1669-1674
4.Cooks G., McLuckey S. et al. Anal. Chem. 1994,66,725-729

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS

720002210EN

©2007 Waters Corporation