

A MASS SEPARATING TRAVELLING WAVE ION GUIDE

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OVERVIEW

- A travelling wave ion guide (TWIG) has been modified to provide low resolution mass separation.
- Mass separation is obtained by forming an RF barrier within the ion guide and then using a travelling wave to eject ions past the barrier.
- Linking the device with a scanning quadrupole provides improved sampling duty cycle and hence improved sensitivity.

INTRODUCTION

The use of radio-frequency (RF) only ion guides for efficient transport of ions through regions of a mass spectrometer is commonplace in present instrumentation. Historically, such ion guides have been based upon multi-pole rod sets but there has been increased use of stacked ring ion guides over recent years, for example the travelling wave ion guide (TWIG) and the ion funnel. In the case of the TWIG, ions are propelled along the device by superimposing a train of voltage pulses upon the confining RF voltage applied to each electrode.

Here we present a novel design of travelling wave ion guide which allows ions to be ejected in a mass dependent manner and which consequently functions as low resolution mass analyser.

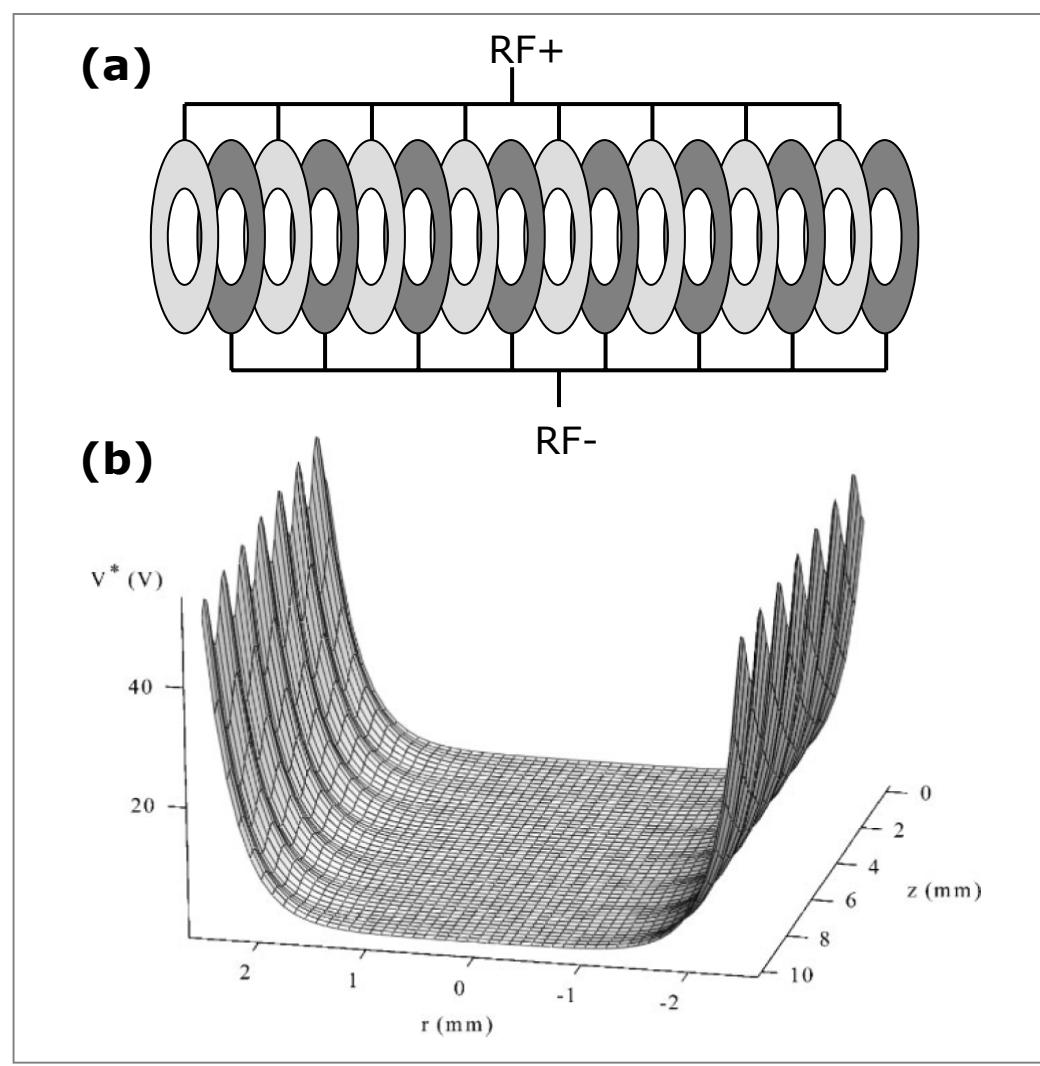


Figure 1. (a) Basic schematic of a stacked ring ion guide. (b) The pseudo-potential formed within the stacked ring ion guide.

CONCEPT

Figure 1(a) shows the basic construction of a stacked ring ion guide where opposite phases of confining RF are applied to adjacent electrodes. The resulting pseudo-potential along the device is highlighted in figure 1(b) and is characterised by steep sided walls with a relatively flat central region leading to good ion confinement and ion transport properties.

The basic concept for modifying this device to provide mass separation lies in the use of a travelling wave to axially propel ions over an RF barrier which has been superimposed upon the normal confining pseudo-potential. Unlike a DC barrier, the height of which is mass independent, the height of an RF barrier is inversely proportional to the mass to charge ratio (m/z) of a given ion, i.e. a low m/z ion will perceive a larger barrier than an ion with a large m/z for the same applied RF. If sufficiently tall, this barrier will prevent the movement of ions along the device unless driven over by the travelling wave.

Because the height of the RF barrier is mass dependent, the travelling wave will only eject ions which encounter a smaller RF barrier than the height of the travelling wave. Mass separation may therefore be effected by one of two methods; by ramping the height of the travelling wave with a fixed RF amplitude, or by reducing the height of the RF barrier with a fixed height travelling wave, or else by a combination of both methods.

RESULTS

Barrier Formation

An RF barrier may be formed by a number of different methods; for example, the internal diameter or the spacing of the ring electrodes may be adjusted or else the RF voltage or frequency may be altered. To prototype the use of an RF barrier for mass separation the internal diameter of a single pair of ring electrodes in a standard TWIG was reduced from 5 mm to 3 mm. The resultant RF barrier created within the ion guide is shown in figure 2. The mass separating ability of this modified ion guide was tested by using it in place of the standard TWIG gas cell inside a Quattro Premier XE (Waters Corporation, Manchester). Ions were accumulated within the source ion guide before periodically releasing them into the new gas cell. One of the two previously mentioned mechanisms was then used to eject ions from the gas cell.

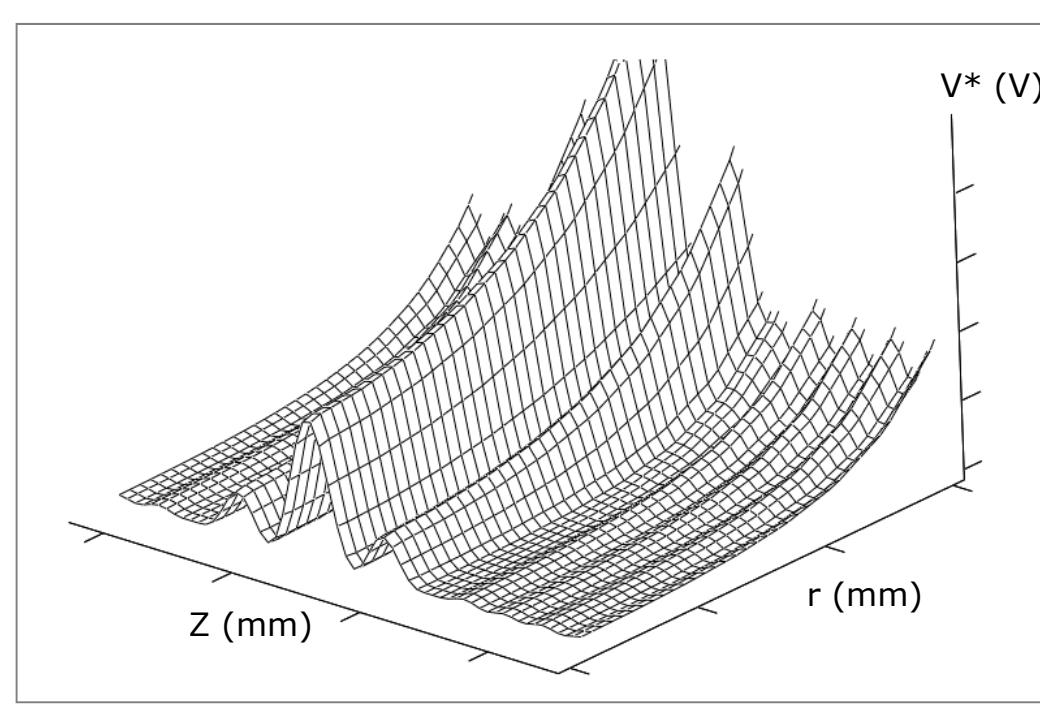


Figure 2. RF barrier formed within ion guide by replacing two standard ring electrodes with 3 mm I.D. electrodes.

Mass chromatograms for the resultant separation were obtained by measuring the time evolution of the ion current passing through the second quadrupole which was resolving at a chosen set mass. Figure 3 below is a typical example of the mass chromatograms obtained using this method. An obvious characteristic of this device is that it ejects ions in reverse mass order, i.e. ions of higher m/z are ejected first.

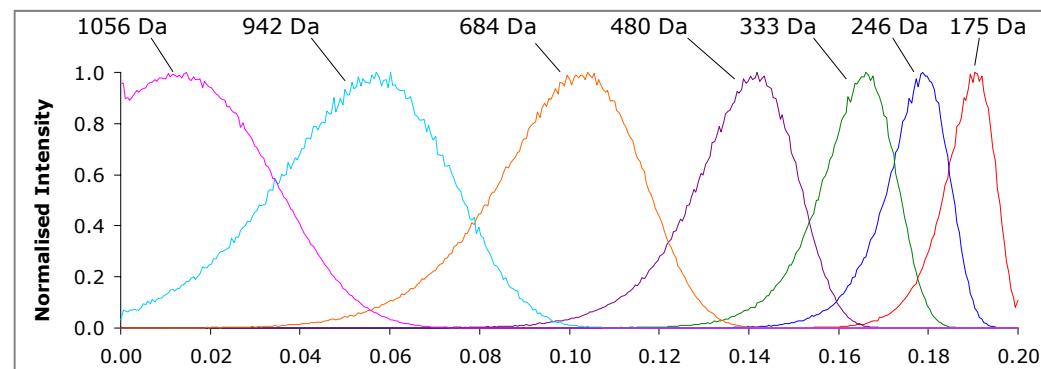


Figure 3. Typical mass chromatograms obtained by ejecting ions out of the prototype gas cell.

Ramped TW vs. Ramped RF

Both ejection mechanisms were evaluated to determine which produced the better mass separation behaviour. Typical separation data for the two mechanisms is shown in figure 4.

The separation is clearly non-linear using the ramped TW approach in comparison with that for the ramped RF separation. This may be understood by considering the basic concept that ions of a given m/z are ejected once the axial kinetic energy provided by the travelling wave equals the height of the RF barrier for that particular m/z ion. For the ramped TW ejection this leads to the equation,

$$\Delta V_{TW} t = \frac{z k}{m} V_{RF}^2,$$

where ΔV_{TW} is the rate at which the TW is ramped, t is the ejection time, V_{RF} is the RF amplitude and k is a constant defined by the geometry of the barrier and the frequency of the RF. This equation may be re-arranged to give the following relationship between m/z and time,

$$\frac{m}{z} = \left(\frac{k V_{RF}^2}{\Delta V_{TW}} \right) \frac{1}{t}.$$

The reciprocal dependence clearly explains the strong non-linear separation observed experimentally. Similarly, it can be shown that the separation behaviour for the ramped RF mode follows a quadratic dependency,

$$\frac{m}{z} = \frac{k}{V_{TW}} (V_0 - ct)^2,$$

where V_0 is the initial RF amplitude, c is the rate at which the RF amplitude is reduced and V_{TW} is the fixed travelling wave height. Although the ramped RF separation is not as strongly non-linear, it is still desirable to be able to eject masses linearly with time.

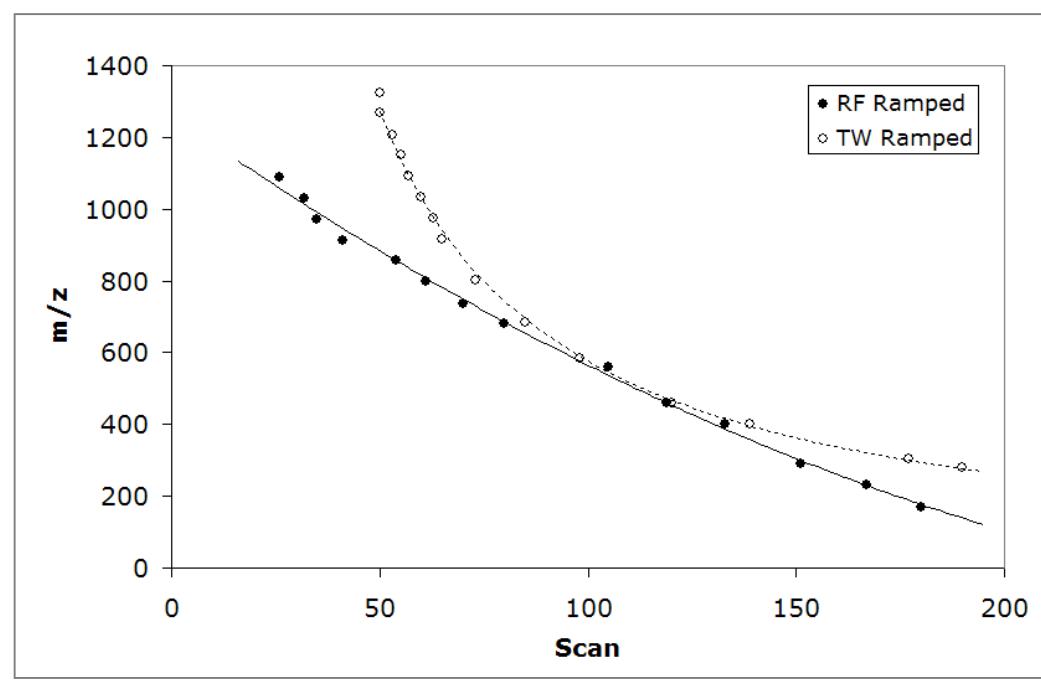


Figure 4. Mass separation profiles for the two different ejection mechanisms.

This may be achieved by calculating an appropriate non-linear RF ramp which has the form,

$$V(t) = \sqrt{\frac{V_{TW}}{k}} \left[\left(\frac{m}{z} \right)_{max} - rt \right]$$

Figure 5 illustrates a typical RF ramp calculated using the above equation. Using this ramp to produce linear mass separation then allows the resolution of the mass separation to be determined. Figure 6 below highlights the typical mass resolutions obtained as a function of mass. This figure shows that there is a well defined mass dependency with mass resolution increasing from 2 at low mass up to approximately 5 at m/z 2000 Da.

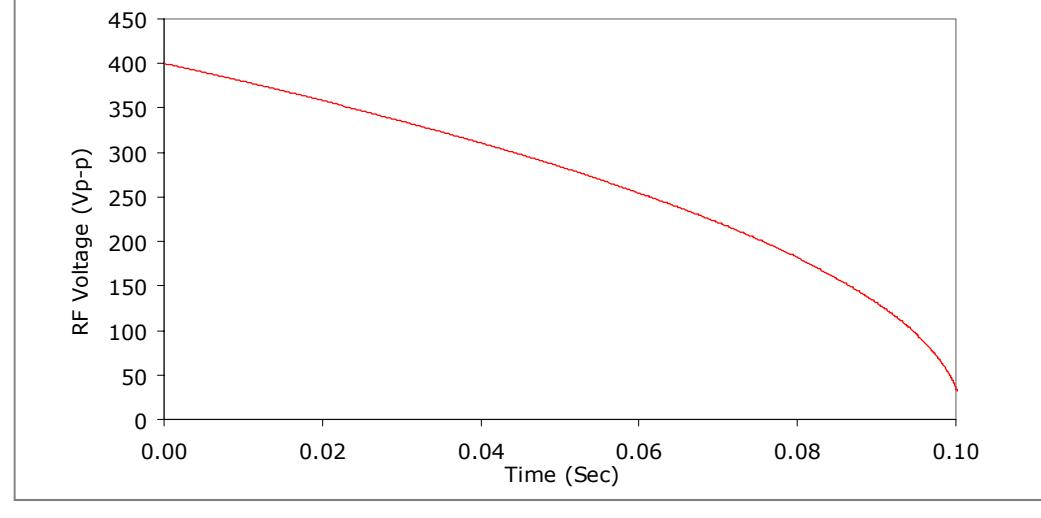


Figure 5. Non-linear RF ramp.

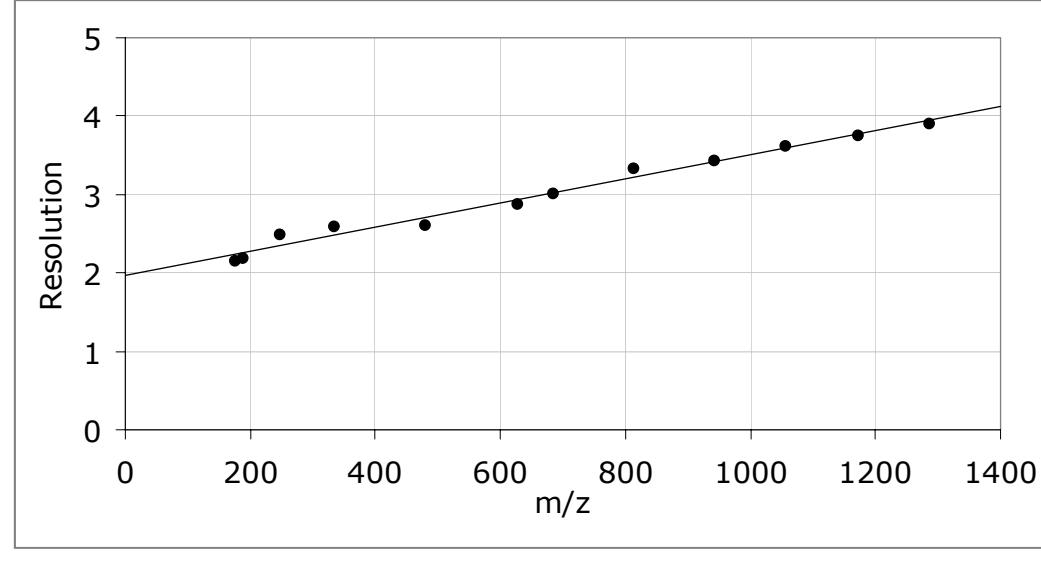


Figure 6. Typical mass resolution obtained using a non-linear RF ramp plotted as a function of m/z .

Split Gas Cell Design

To minimize the effects of space charge, a second prototype was constructed so that ion accumulation could be performed within the gas cell rather than within the source ion guide. This helps avoid accumulation losses, particularly when looking at daughter ions, as most of the ions entering the system will be removed by the first resolving quadrupole and hence minimizing the number of charges that are stored.

This was achieved by effectively splitting the gas cell in to two regions, a storage region occupying approximately the front 2/3 of the gas cell and an ejection region. This allowed the same mechanical assembly to be retained but with two independent TWIG controllers being used to control the front and back sections. A typical storage and ejection cycle is depicted in the series of illustrations in figure 7.

Linked Scan

The resolution of the mass ejection is not sufficient in its own right to act as a useful mass analyser for most applications. However, using the low resolution of the device to deliver ions to the existing high resolution scanning quadrupole allows significant sensitivity improvements to be made over a standard scanning quadrupole^{1, 2, 3}. The advantage of this linked scan operation is shown in figures 8 and 9.

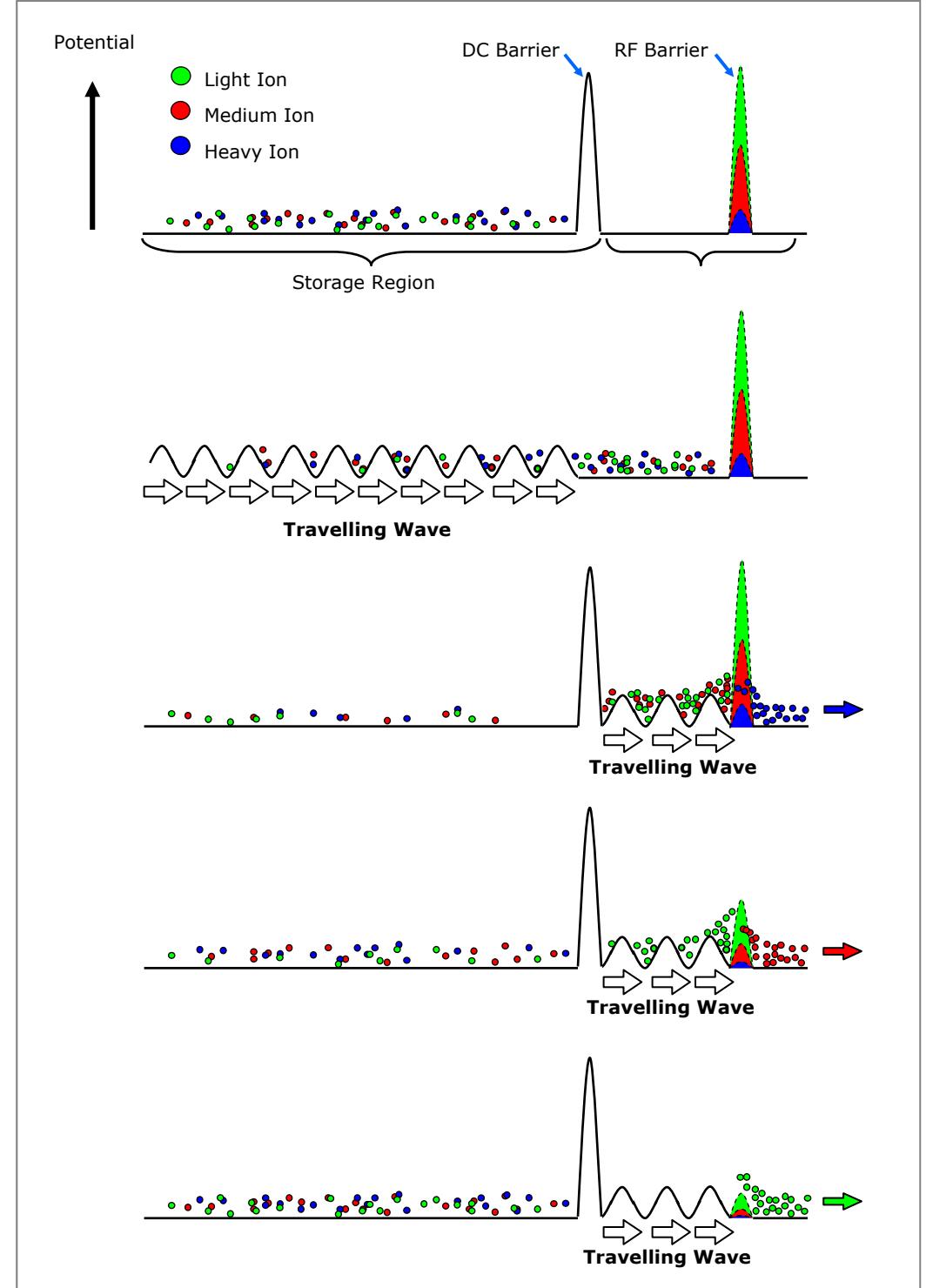


Figure 7. Time-line of an enhanced experiment where ions are accumulated before being sequentially ejected.

Figure 8 shows a daughter ion spectrum for Glu-fibrinopeptide obtained using a scanning quadrupole operating at 5000 amu/sec in (a) normal operation and (b) enhanced operation. It is immediately obvious that the enhanced spectrum shows a large improvement in sensitivity without any loss of resolution or scan speed. The gain in sensitivity between the two modes of operation are shown in figure 9. Gains of up to 16x can be seen for certain masses whilst the average gain over the whole mass range is >8x.

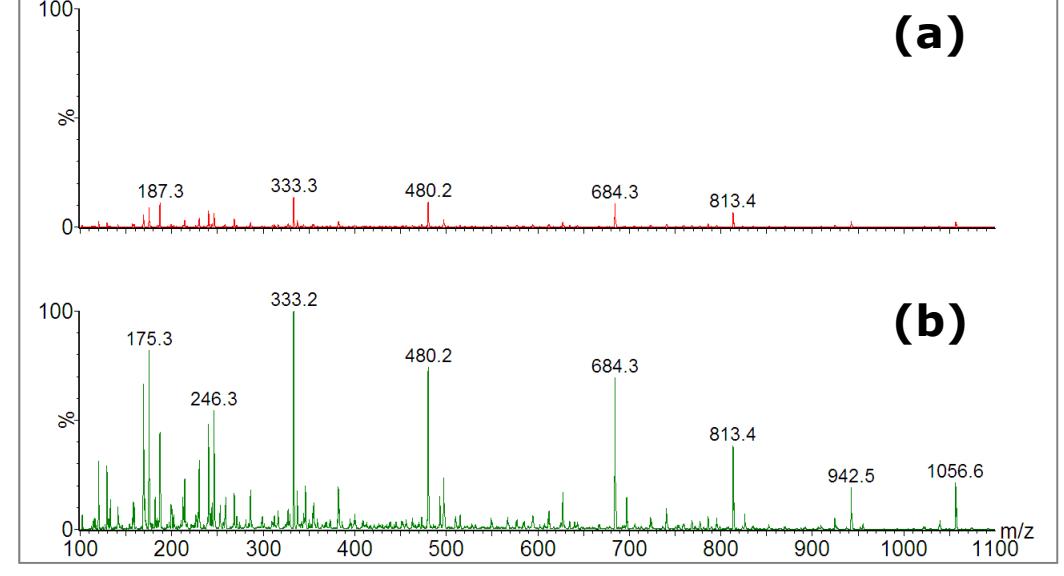


Figure 8. Comparison of scanning quadrupole mass spectra in (a) standard operation and (b) enhanced operation.

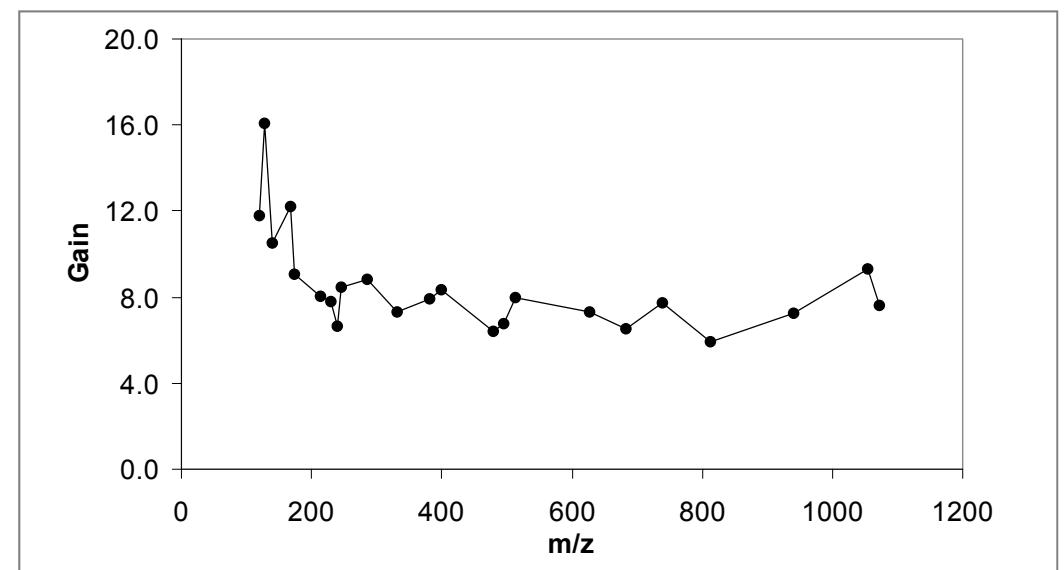


Figure 9. Sensitivity gains for enhanced over standard operation.

CONCLUSION

- Novel travelling wave based gas cell which allows mass dependent ejection of ions.
- Linking this ejection with a scanning quadrupole allows for significant sensitivity gains to be made over a standard scanning quadrupole.

References

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- A mass spectrometer with improved duty cycle, Hoyes, J.B., GB20060016878D.
- Method and apparatus for the mass-selective release of ions from an ion trap, Giles, K., Green, M., Pringle, S.D., Wildgoose, J.L., GB20060011062.