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TRAVELLING WAVE ION PROPULSION IN COLLISION CELLS

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OVERVIEW

Aim

- To provide a means of propelling ions through an rf-only collision cell to enhance fast acquisition performance of a tandem quadrupole mass spectrometer.

Methods

- A stacked-ring rf-only collision cell has been designed which utilizes an axial travelling wave to propel ions and reduce transit time.

Results

- The travelling wave based collision cell significantly reduces ion transit time enabling short dwell MRM acquisition with minimal cross-talk and fast scanning precursor/neutral loss without degradation in performance.
- A new mode of ion fragmentation using the travelling wave indicates that use of generic settings might be possible for a variety of different compounds.

INTRODUCTION

The use of rf-only ion guides in collision cells operated at relatively high pressure (>1x10^{-3}mbar) is the current practice in tandem mass spectrometers. Reduction of axial ion velocity in such cells due to multiple collisions can affect performance in modes of operation where fast scanning or switching are required. Previous approaches to overcome this problem have been based on providing an axial voltage gradient to increase the axial velocity of ions and hence reduce their residence time in the cell. A new approach to propel ions through collision cells is presented here which utilizes a travelling wave superimposed on the confining rf of the ion guide. Additionally a new method of ion fragmentation is presented which results from increased velocity of the travelling wave.

EXPERIMENTAL

These experiments were performed using a Waters® Micromass® Quattro Premier™ tandem quadrupole mass spectrometer with electrospray ionization, shown schematically in Figure 1.

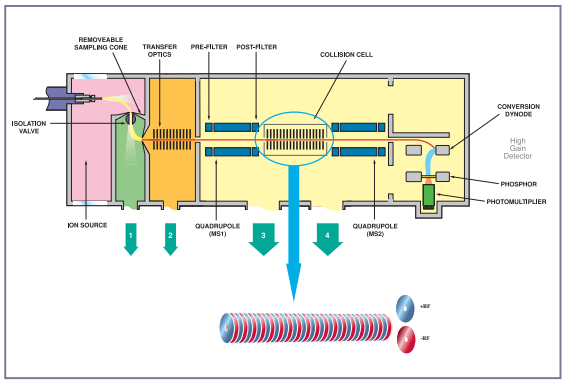

Figure 1: Schematic diagram of the Quattro Premier showing the stacked-ring collision cell.

The collision cell is based on a stacked-ring ion guide with opposite confining rf phases being applied to adjacent rings. In addition to the rf voltage each ring electrode has a constant DC offset (collision energy voltage) and may also have a transient DC potential applied. The transient DC voltage produces a local change in the electric field causing the ions to move away from the electrode in both the forward and reverse directions. To propel ions in one direction along the axis, the DC voltage is switched to an adjacent ring after a given time and so on along the guide as shown in Figure 2. This provides a moving electric field or "travelling wave" on which the ions "surf", reducing their residence time in the cell.

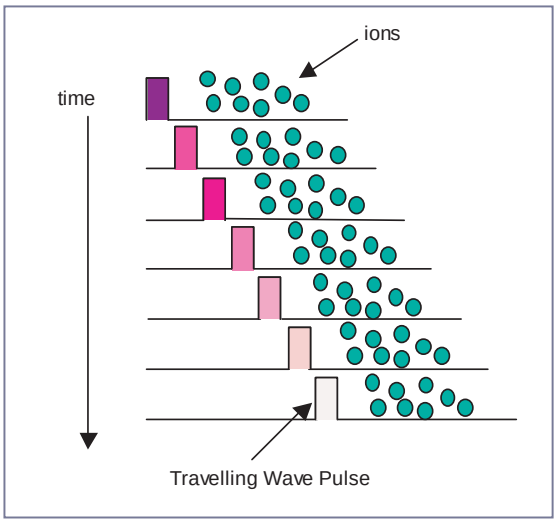

Figure 2: Schematic of the principle of operation.

The collision cell used in this study has 122 ring electrodes mounted between two printed circuit boards (PCB). Each ring has an internal diameter of 5 mm, a thickness of 0.5 mm and a 1 mm inter-electrode spacing. A photograph of the device is shown in Figure 3. The collision cell is terminated by DC only lenses with 2 mm diameter apertures.

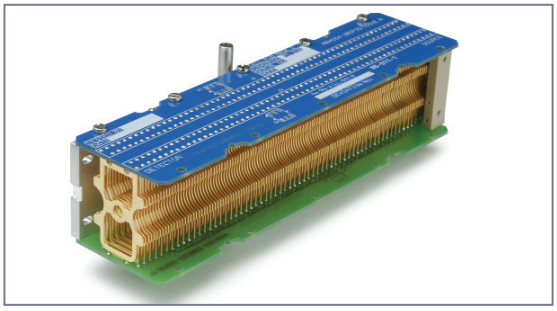

Figure 3: Photograph of the collision cell used in this study.

Rather than individual control of each electrode in the collision cell the electrodes were divided into repeat sections with interconnections made using tracks on the supporting PCB's. In this manner repeat groups of seven pairs of electrodes are produced. Each pair of electrodes are connected to separate high voltage DC amplifiers which supply both the collision energy and transient voltages. The phase and anti-phase rf voltages were superimposed onto the DC voltage via secondary windings of an rf transformer. The amplitude, velocity and pulse pattern are controlled via a programmable logic device (PLD) connected to a PC. Figure 4 shows a schematic diagram of the system, the electrode grouping is shown using matching colors.

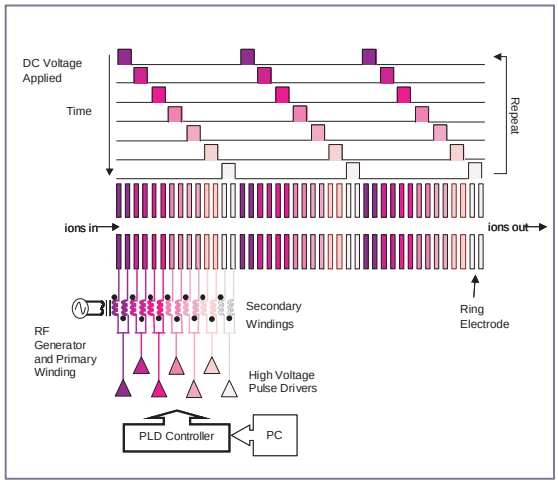

Figure 4: Schematic diagram of the travelling wave system.

RESULTS

The physical operation of the device may be clearly demonstrated by varying the travelling wave velocity and observing its effect on the mass spectrum peak shape of a product ion. Figure 5 shows two spectra taken at a scan speed of 20 amu/s at two travelling wave velocities. They both show the most intense product ion of verapamil (precursor ion = 455 amu).The collision energy was 29 eV and the travelling wave voltage was 10 V. The collision cell pressure used in all experiments was $3x10^{-3}$ mbar of argon.

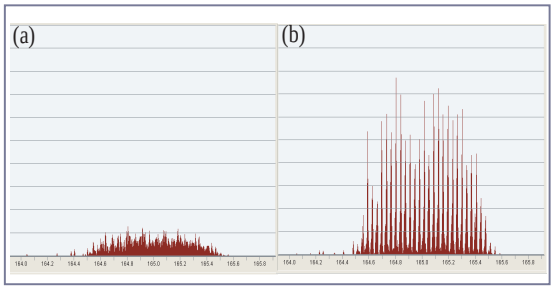

Figure 5: Product ion spectra of verapamil taken at different travelling wave velocities (a) 120 ms^{-1} and (b) 11 ms^{-1}.

In Figure 5 (a) the ions are arriving at the detector in an almost continuous stream where as the relatively slow travelling wave velocity in (b) bunches the ions into packets. The higher intensity observed in (b) is due to increased trapping of ions on injection between the more slowly moving pulses.

MRM Acquisition

When operating in MRM mode in order to operate at very short dwell time it is essential that the residence time of ions in the collision cell is minimal to avoid cross-talk between successive transitions. Previous approaches to minimize this effect have been to drop the confining rf to zero between successive channels allowing the ions to disperse. However this can affect sensitivity if the cell has not completely refilled before acquisition recommences.

The benefit of the travelling wave in reducing the level of cross-talk observed between MRM channels is illustrated in Figure 6 by loop injection of Sulfadimethoxine. Further, Figure 7 shows that no loss in sensitivity occurs when reducing the dwell time to 10 ms with the travelling wave operating.

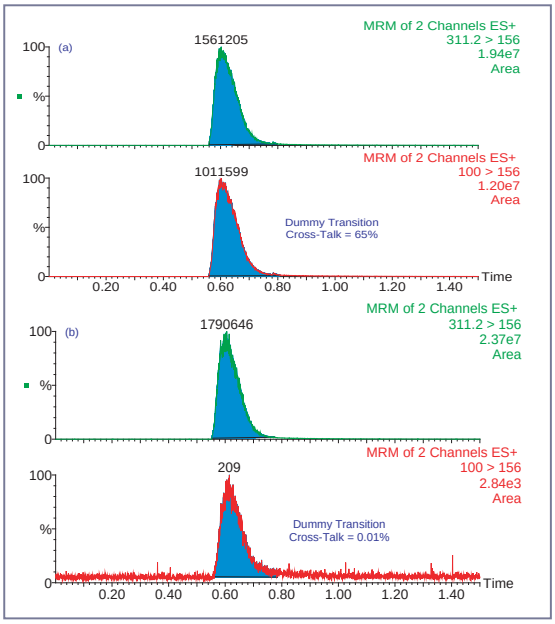

Figure 6: Effect of the travelling wave on the observed inter-channel cross-talk for MRM transitions with 10 ms dwell and inter-channel delay; (a) without travelling wave and (b) with travelling wave (2V pulse height, velocity 300ms^{-1}).

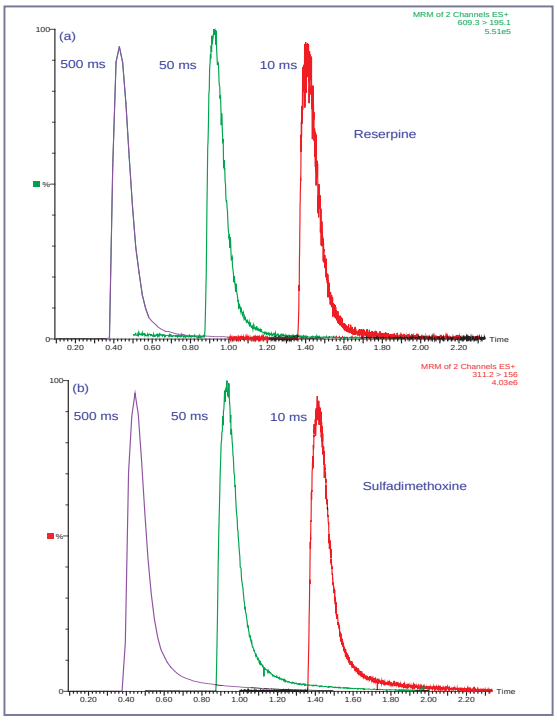

Figure 7: Effect of the travelling wave on the intensity as the dwell time is reduced, two channels were used (a) Reserpine and (b) Sulfadimethoxine. (travelling wave: 2V pulse height, velocity 300 ms^{-1}).

Precursor Ion Scanning

Figure 8 shows the performance enhancement of precursor ion spectra using the travelling wave. Note that with no travelling wave almost complete loss of resolution occurs even with very slow scan speed due to the slow transit time of ions through the cell.

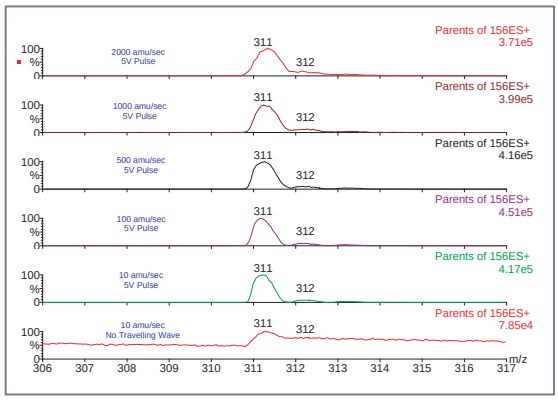

Figure 8: Precursor ion spectra at different scan speeds, with and without the travelling wave. (travelling wave: 5V pulse height, velocity 300 ms^{-1}).

Neutral Loss Scanning

Figure 9 shows the performance enhancement of neutral loss spectra using the travelling wave. Note that with no travelling wave the signal intensity is significantly reduced even at very slow scan speed.

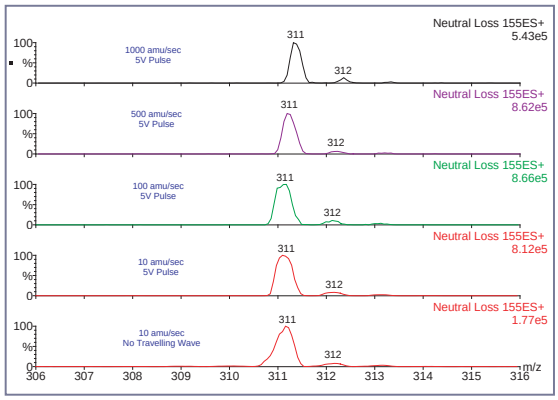

Figure 9: Neutral Loss spectra with and without the travelling wave. (travelling wave : 5V pulse height, velocity 300 ms^{-1})

Travelling Wave Induced Fragmentation

The benefits of operating the travelling wave device at certain pulse heights and velocities to enhance performance when performing fast acquisitions have been shown above. At velocities in excess of the optimal values presented above it has been found possible to induce fragmentation in the ions of interest, moreover it has been established that use of generic travelling wave parameters can provide optimal fragmentation for ions requiring notably different conventional collision energies.

In Figures 10 and 11 the fragmentation of Sulfadimethoxine and Reserpine are presented using both conventional 'collision energy' and travelling wave approaches. It is apparent that Sulfadimethoxine fragmentation is optimal at a collision energy of 20 V and Reserpine at 39 V, however both compounds are optimally fragmented with a travelling wave velocity of 1500 ms^{-1} and pulse height of 10 V.

A velocity of 1500 ms^{-1} translates to collision energies of 3.6 eV for Sulfadimethoxine and 7.1 eV for Reserpine.

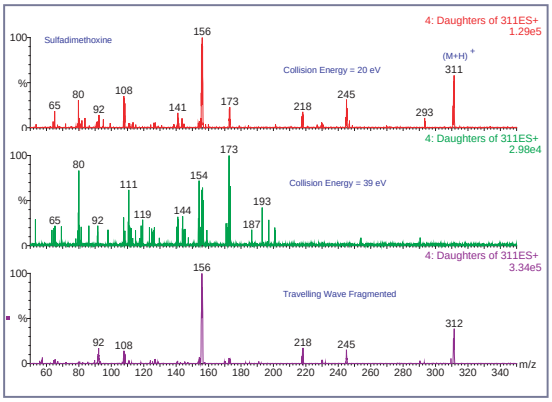

Figure 10: Comparison of conventional and travelling wave induced fragmentation for sufadimethoxine. (Travelling wave: velocity 1500 ms^{-1}, pulse height 10 V.)

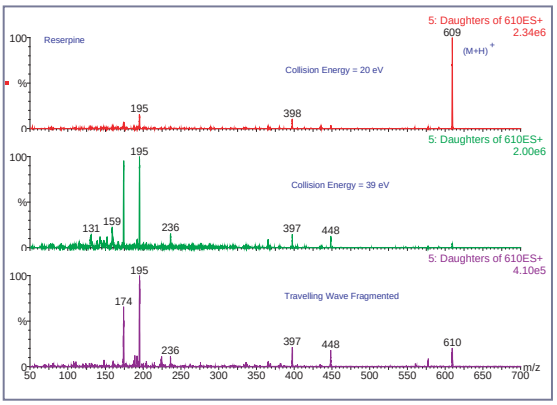

Figure 11: Comparison of conventional and travelling wave induced fragmentation for Reserpine. (Travelling wave: velocity 1500 ms-1, pulse height 10 V.)

CONCLUSIONS

The travelling wave approach to propelling ions through a collision cell has been shown to significantly enhance the performance of a tandem quadrupole mass spectrometer when fast scanning or short dwell time acquisitions are used. Notably, cross-talk is reduced to 0.01% for fast MRM acquisitions, without loss in sensitivity, further, resolution and sensitivity are maintained for fast scanning precursor ion and neutral loss modes of operation.

A different mode of fragmentation has been presented using the travelling wave which may be extremely useful in that a generic velocity and pulse height can provide optimal results for compounds nominally requiring different conventional collision energies.

It has been shown that the travelling wave device transports ions in discreet packets through the collision cell, future work will involve synchronization of the acquisition system with ion arrival time at the detector to enhance performance.

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