Extended Length Radial Ejection Linear Ion Traps for Higher Ion Capacity and other Modes of Mass Analysis

Poster Note 64469

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Overview

Purpose: Demonstrate the improved performance of extended length linear ion traps including higher charge capacity and other modes of mass analysis.

Methods: Utilize a modified ion trap system for evaluating various length traps with appropriate radial and axial ion detectors..

Results: 4.6x higher charge capacity is demonstrated for mass analysis along with a trap device able to perform quadrupole mass filtering, waveform mass filtering, and time of flight mass analysis.

Introduction

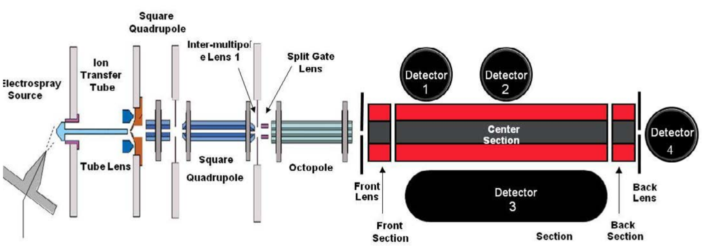
One of the significant advantages of 2D linear ion traps versus 3D ion traps is ion capacity. Space charge effects are reduced in linear traps since the ion cloud is free to extend axially throughout the length of the trapping section, versus being compacted into a more spherical (ellipsoidal) volume in the center of a 3D trap. Theoretically, the capacity of the linear trap can be increased to any desired level by simply extending the length of the trapping section. We have explored the technical challenges and complexities that occur when extending the length of the radial ejection linear ion trap, and have also investigated new mass analysis capabilities that extended length ion traps can offer.

Methods

System

The vacuum manifold and electronics of a Thermo Scientific™ LTQ XL™ ion trap mass spectrometer was substantially modified to accommodate various length linear ion traps and operational modes. The manifold also allowed various ion detector configurations including long radial, multiple short radial, and axial ion detector systems as shown in **Figure 1**. Instrument control software was modified to allow the various operational modes of the device. For Quadrupole Mass Filter mode testing, some devices were tested using a standard ThermoTSQ Quantum MS™.

FIGURE 1 - Extended Length Linear Trap Instrument Configuration with Radial and Axial detectors

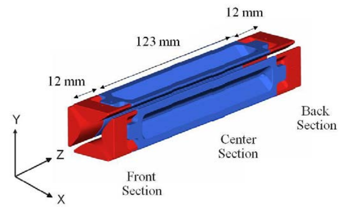


Linear Ion Traps

Three segment linear ion traps with trapping segment lengths of 2x, 3x, and 4x the standard LTQ XL ion trap[1] were constructed and are shown in **Figure 2a** with the dimensions of the segments of the 4x version shown in **Figure 2b.**

FIGURE 2a - Various Length Linear Ion Traps

FIGURE 2b - 4x Long Trap Dimensions



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Extended Length Detection Systems

Several different detector design strategies were investigated for detecting the wide ion beam radially ejected from the extended length trap. One consisted of a custom made wide funnel design made from lead silicate glass (DeTech, Inc.) shown in **Figure 3a**. Although, this design was functional, there was some detection sensitivity bias based on the ions entrance position along the length. A second design, which simply focused the exiting ion beam to a conversion dynode held at +/-15KV, while secondary electrons were subsequently focused into a discreet channel multiplier (ETP Electron Multipliers Pty LTd) worked well, and is shown in **Figure 3b**, with complete assemblies shown in **Figure 4a** and **4b.**

FIGURE 3a - Extended Funnel EM

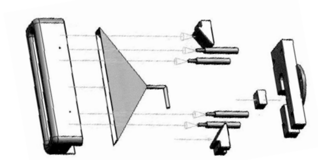


FIGURE 3b - Focused Ion Beam Concept

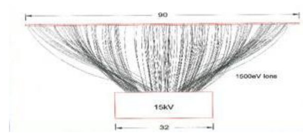


FIGURE 4a - Focused Ion Beam Detector Configuration

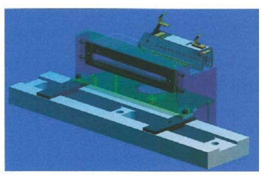
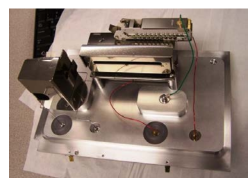


FIGURE 4b - Extended Length Radial and Axial Detectors in the System

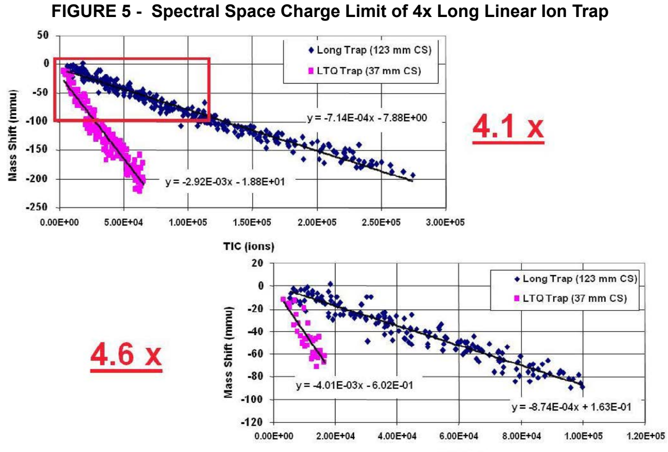


Results

Trap Charge Capacity

The most limiting, and important space charge limit for an ion trap mass analyzer is the spectral space charge limit[1] (the number of ions before space charge effects degrade the quality of mass analysis). This was evaluated for the various length traps and consists of measuring the space charge induced mass shift on m/z 524.3 as a function of TIC using a standard calibration mixture. The data for a trap which has a trapping section approximately 4x longer than a standard trap is directly compared to the standard length trap and is shown in **Figure 5**. The slopes of the curves represent the rate of m/z shifting and can be compared for the two traps to determine the improvement. When the entire range of TIC is considered, an improvement of 4.1x is shown. Due to some non-linearity in the full curves, when only the lower end of the range is fit, the gain 4.6x. This value is greater than 4x and is easily rationalized due to the effects of the field penetration of the axial trapping end section voltages, which makes the effective trapping segment increase larger than 4x (4.6 is predicted).

FIGURE 5 - Spectral Space Charge Limit of 4x Long Linear Ion Trap



Resolution

Although ion capacity clearly goes up with trap length, in many cases resolution was observed to degrade. A careful study using the resolution dependence on the axial cloud length in **Figure 6a** clearly shows that some traps have deviations of the electric field strength along the axis causing resolution degradation for large axial cloud sizes. This was verified by measurements of the X rod separation (parallelism) along the length of the device as shown in **Figure 6b**. The effects on peak width is clearly seen in **Figure 7** by looking at the variation in peak properties obtained from the various positioned detectors.

Figure 6a - Cloud Size Effect on Peak Width for Asymmetrical and Symmetrical Trap Geometries

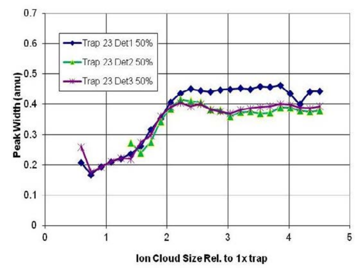


Figure 6b- X Rod Separation along the Length of a Poor Performing Extended Length Trap

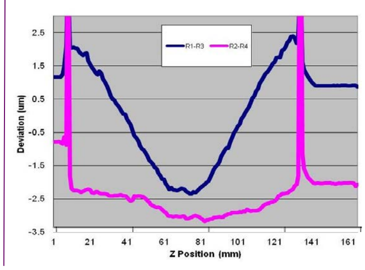
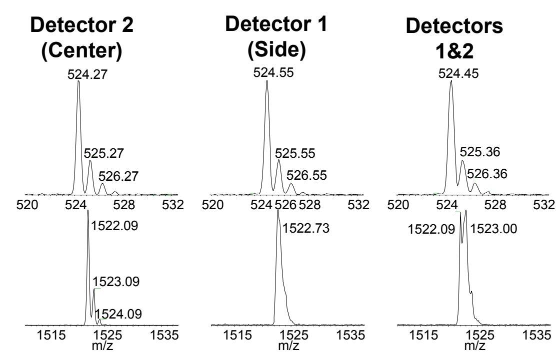
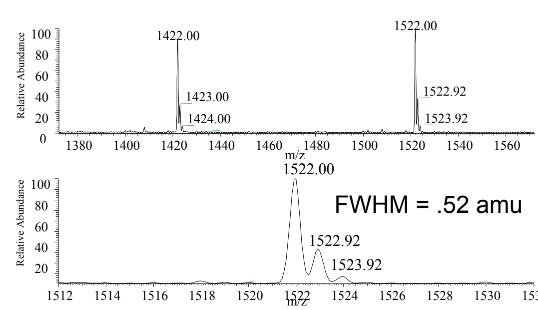


FIGURE 7 - Peak Widths For Ions Exiting at Different Axial Positions and Different Detectors



Fully symmetrical trap designs with slots in all four rods, along with improved tolerance control helped improve longitudinal uniformity and achieve the desired resolution performance as shown in **Figure 8**.

FIGURE 8 - Peak Widths Obtained with a Symmetrical 4x Extended Length Device Scanning at 33333 amu/sec using Detector 3



Other Mass Analysis Modes - QMF

With an increased length trapping section, the structure of the linear trap becomes quite comparable to a quadrupole mass filter (QMF) with pre and post filters. By having both an axial and radial detector, the performance in both ion trap and QMF mass analysis modes can be studied. Of course, field distortions due to the ion ejection slots will degrade the performance as a QMF. Simulations of various geometries for optimizing performance in both modes have been performed and several promising designs have been identified. One example is shown here.

Standard linear traps have their rods moved out 0.76 mm beyond their theoretical position to compensate for the negative effects of the field distortions caused by the ejection slots when operating in ion trap mass analysis mode[1]. However, this configuration is not optimal for QMF operation. Simulations suggest that a compromise stretch of 0.35 mm may allow the device to be operated in both linear trap and QMF modes with reasonable performance. This configuration was tested in both modes with the results shown in **Figure 9** and **Figure 10**.

FIGURE 9 – 4x Extended Length Trap with 0.35 Symmetric Stretch Operation in QMF Mode

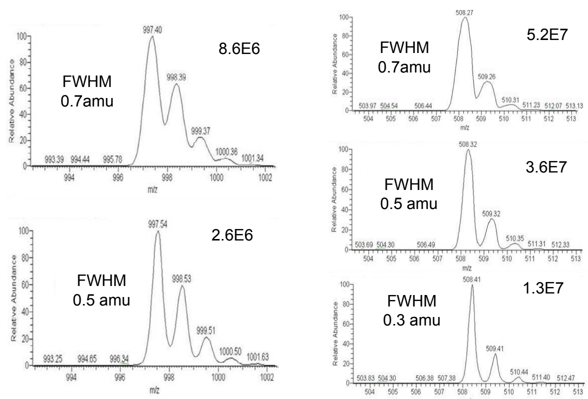
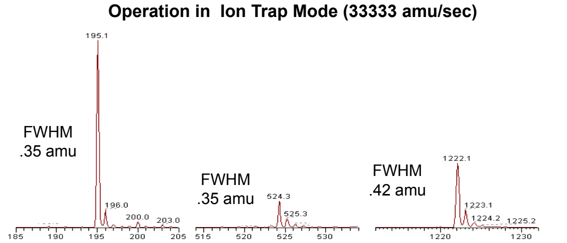


FIGURE 10 – 4x Extended Length Trap with 0.35 Symmetric Stretch Operation in Ion Trap Mode (33333 amu/sec)



However, due to non optimal field effects, peak shapes in ion trap mode at higher m/z and slower scan rates were observed to not be ideal, often having split peaks as shown in **Figure 11a**. Peak shapes were very sensitive to tuning of the resonance ejection conditions with this configuration versus than with the normal .76 mm stretch. Interestingly, at significantly slower scan rates the peak shapes were again found to be good and high resolution was able to be achieved, shown in **Figure 11b**.

FIGURE 11a – Ion Trap Operation at 1111 amu/sec Showing Split Peaks

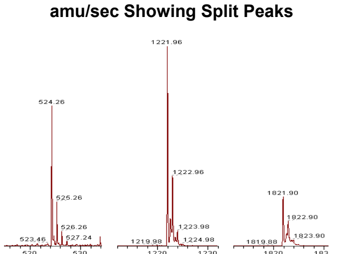
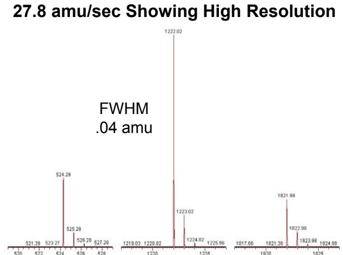


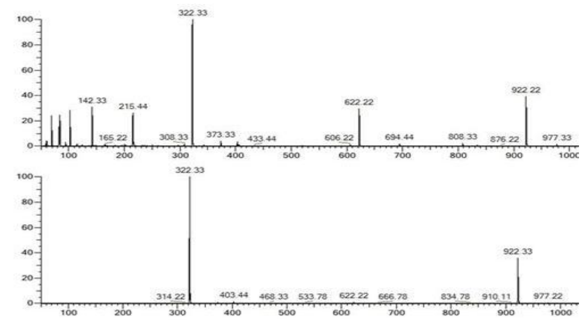
FIGURE 11b – Ion Trap Operation at 27.8 amu/sec Showing High Resolution



Other Mass Analysis Modes – Waveform Filtering

By applying dipolar multi-frequency resonance excitation isolation waveforms across the X rod pairs commonly used for m/z isolation in ion traps, axial mass filtering can be achieved[2]. A multi-notch filtering example is shown in **Figure 12**. The extended length trap offers the possibility of improved resolution for this approach and further experiments are underway.

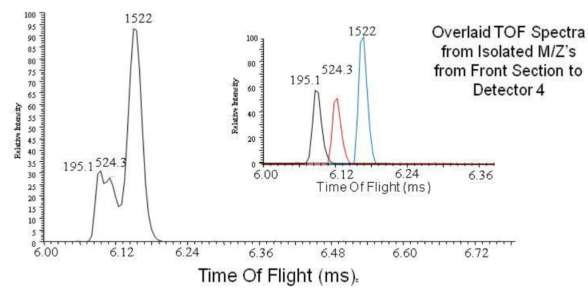
FIGURE 12 - Radial Waveform Filtering of Two m/z Windows From the Full Scan



Other Mass Analysis Modes - TOF

An additional mode of mass analysis is also demonstrated in **Figure 13**. By trapping ions in the front section of the extended linear trap, and pulsing them to the axially detector, a very low resolution time of flight mass spectrum can be obtained. Utility of this mode is still being investigated.

FIGURE 13 -TOF Spectra From Ions Pulsed from Front Section to Detector 4



Conclusion

- Extended Length Linear Ion traps (up to 4x) have been constructed, along with an appropriate detection system and shows a 4.6x increase in charge capacity for mass analysis.
- The 4x long device has the capability to operate in other mass analysis modes
- Using a symmetrical electrode "stretch" of .35 mm instead of the conventional .76 mm allows the device to work as both a quadrupole mass filter and an ion trap especially for lower m/z values
- Other mass analysis modes include using ion trap isolation waveforms applied radially to allow axial mass filtering, and a low resolution TOF by pulsing ions from the front section of the device to the axial detector.

References

1. J.C. Schwartz, M.W. Senko, J.E.P. Syka, A two-dimensional quadrupole ion trap mass spectrometer, J. Am. Soc. Mass Spectrom. 13 (6) (2002) 659-669.
2. Q. Song, S. A. Smith, L.Gao, W. Xu, M. Volny, Z. Ouyang, R. G. Cooks, Mass Selection of Ions from Beams Using Waveform Isolatin in Radiofrequency Quadrupoles, Anal Chem. 81 (5) (2009) 1833-1840

Acknowledgements

We would like to thank Jay Ray at Detector Technology, Inc and the team at ETP Electron Multipliers for their collaboration on the development of the detectors used for this work.

PN64469-EN 0615S