Practical Quadrupole Theory: Quadrupole Acceptance Characteristics

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In a quadrupole mass spectrometer, the ion source is coupled to the quadrupole through an entrance lens, which typically has a smaller diameter than the inscribed quadrupole diameter. (i.e. the imaginary circle one could draw which just touches the inside of each rod of the quadrupole).

Some types of ion sources (like electrospray) can be configured to have much smaller emissive areas than the quadrupole inscribed diameter.

This presentation explores, through simulation and experiment, the changes in performance when the emissivity of the ion source is limited to be much smaller than the inscribed diameter of the quadrupole.

The fringing field between an RF/DC quadrupole and a DC entrance lens voltage forces ions to traverse through a region of instability before they reach the stable region inside the quadrupole mass filter.

In 1968, Brubaker demonstrated that the use of RF-only pre-filters between the entrance lens and the RF/DC quadrupole can minimize this effect, improving absolute sensitivity, peak shape and resolution.

This presentation reviews the theory of how pre-filters work their magic.

I. INTRODUCTION

At the 2001, 2002, and 2003 ASMS conferences, the first three of this series of simple graphical introductions to quadrupole theory were presented.

This fourth presentation in the series builds on that previous work, focusing on the use of ion trajectories plotted in position-velocity space to predict the acceptance characteristics of a quadrupole, with comparisons to experimentally measured transmission functions.

In addition, the theory of operation of the use of rf-only pre-filters is reviewed.

The goal of this work is to help build an intuitive understanding of how quadrupoles work, and more importantly, how to optimize the design of experiments involving quadrupoles.

II. THE EXPERIMENT

An Extrel CMS 9.5 mm tri-filter quadrupole mass filter probe assembly (i.e. with pre-and post-filters), operated at 880 kHz, was configured with an axial molecular beam ionizer to measure spectra of perfluorotributylamine leaked into the chamber background.

Two different entrance apertures (the standard 0.3 inch diameter aperture and a smaller 0.05” diameter aperture) were installed into the probe assembly, electrically isolated from the ionizer mounting plate, and 0.1 inch from the pre-filter face.

Resolution / Transmission curves and peak shapes were monitored for these two configurations.

Ion trajectories were calculated via Runge-Kutta numerical integration of the Mathieu equation using, HyperIon, a Turbo Basic program originally developed by the author some seventeen years ago at the University of Florida.

These ion trajectories were reduced to predict quadrupole acceptance aperture areas at various mass resolutions.

See Figure 1 for a schematic view of a quadrupole.

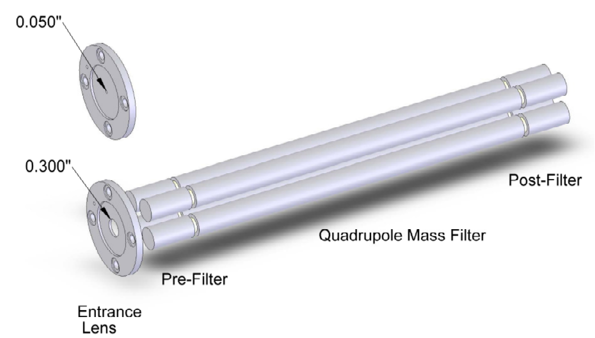

Figure 1. Schematic view of a tri-filter quadrupole with two different size entrance lenses.

III. QUADRUPOLE THEORY AND PRE-FILTERS

The traditional treatment of quadrupole theory starts with a derivation of the Mathieu equation from 'F=ma' all the way through to the final parameterized form, with the following parametric substitutions:

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0 \qquad a_u = \frac{8eU}{m{r_0}^2\Omega^2} \qquad q_u = \frac{4eV}{m{r_0}^2\Omega^2}$$

The *u* in the above equations represents position along the coordinate axes (x or y), ξ is a parameter representing Ωt/2, *t* is time, *e* is the charge on an electron, *U* is applied DC voltage, *V* is the applied zero-to-peak RF voltage, *m* is the mass of the ion, *r* is the effective radius between electrodes, and Ω is the applied RF frequency.

The family of solutions to this equation can be plotted in its parameterized form (a, q space) to become what is generally called the Mathieu stability diagram for a quadrupole. See figure 2.

Interpretation of this diagram is simple. Any a, q point within the stability diagram represents RF and DC voltages where the ion will have a stable (bounded) trajectory, and any point outside the stability diagram represents conditions where the ion trajectory will be rapidly pumped with energy by the quadrupolar field, resulting in an ion leaving the physical boundaries of the quadrupole.

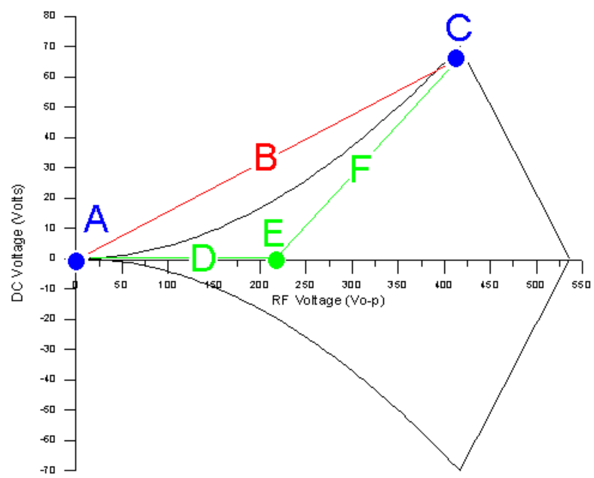

Figure 2. Mathieu stability diagram as calculated for m/z 502 for an 880 kHz 9.5 mm tri-filter.

Case 1: Entrance lens with RF-DC quadrupole:

A (entrance lens) -> B (gap, unstable region) -> C (quadrupole) .

Case 2: Entrance lens with RF-only pre-filter, followed by RF-DC quadrupole:

A (entrance lens) -> D (gap) -> E (Pre-filter) -> F (gap) -> C (quadrupole). All stable.

Consider what happens when an ion enters a quadrupole through a DC voltage entrance lens. The ion leaves the space confined by DC lens voltages, and is directed into an RF-DC quadrupole field, in which the ion has a theoretically stable trajectory.

The only problem is that in the space between the entrance lens and the quadrupole, the field is neither DC-only, nor is it the right ratio of RF to DC for stable trajectories, rather it is some combination thereof.

See figure 1 for a schematic view of an ion's path through a-q-space into the stability diagram, with and without the use of rf-only pre-filters.

With an entrance lens coupled with an RF-DC lens, ions travel from Point A (0 V RF and resolving DC) to Point C (just inside the tip of the stability diagram) through Region B (the gap between the entrance lens and the quadrupole, resulting in a symmetric DC lens voltage superimposed with quadrupolar RF and DC voltages), which is clearly outside the stability diagram. Ions traveling through a-q space along this path are either lost, or, at best, the surviving ions are accelerated radially to yield a wider cross sectional effective emittance area.

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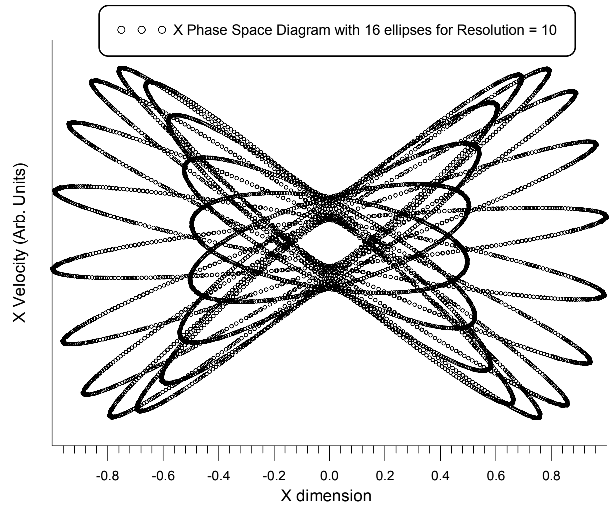

Figure 3. X-Direction phase space diagram showing sixteen acceptance ellipses for a resolution of 10. Quadrupole acceptance is 14% of the inscribed diameter.

In contrast, with an rf-only pre-filter between the entrance lens and the quadrupole, ions travel from Point A (0 V RF and resolving DC) to Point C (just inside the tip of the stability diagram) through Region D (the gap between the entrance lens and the quadrupole, resulting in a symmetric DC lens voltage superimposed with quadrupolar RF-only voltages), through the pre-filter (Point E) and then through Point F, all of which points and regions are within the stability diagram, and yield stable trajectories.

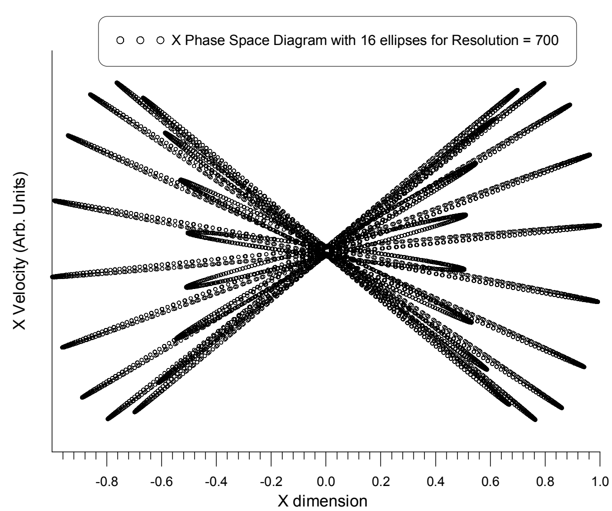

Figure 4. X-Direction phase space diagram showing sixteen acceptance ellipses for a resolution of 700. Quadrupole acceptance is 1.5% of the inscribed quadrupole diameter.

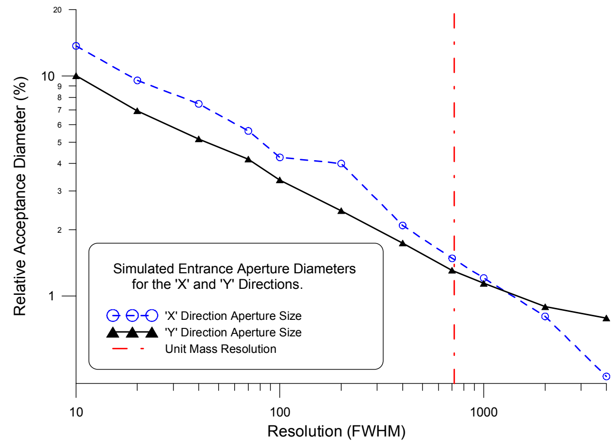

Figure 5. Calculated Quadrupole Acceptance Aperture Diameters for the 'X' and 'Y' Directions plotted as a function of mass resolution.

In this way, the use of rf-only pre-filters between the entrance lens and the RF-DC quadrupole increases sensitivity, abundance sensitivity, and resolution. RF-only pre-filters have been called by many names through the years, including 'delayed d.c. ramp', Brubaker quadrupoles, and pre-filters.

Some manufacturers also include post-filters in their quadrupole designs. The use of post-filters after a quadrupole can dramatically improve performance for certain configurations where the ions are to be coupled into a collision cell.

IV. PHASE SPACE ACCEPTANCE ELLIPSES

One could use numerical methods to integrate the solution to of the Mathieu equation, yielding a family of solutions, which, when plotted in position-velocity space, illustrates the size of the sweet spot at the center of the quadrupole. (See reference 4 for a more detailed review of this method.)

Figure 3 represents the 'X' direction phase space acceptance ellipse family for a resolution of ten, generated using 400 data points gathered at each of sixteen steps per RF cycle, (a=0.21919, q=0.706), normalized such that the furthest excursion in the positional direction exactly matches the inscribed diameter of the quadrupole.

Figure 4 was similarly generated, only for a resolution of 700 (a=0.23674, q=0.706). The 'Y' direction acceptance ellipses are similar.

These diagrams can be interpreted such that if an ion falls on any point of one of the ellipses at its corresponding RF phase, it will be seen to process through all of the other ellipses, given enough time.

If an ion falls well within said ellipse for its instantaneous initial phase, then it will have a theoretically stable trajectory through the quadrupole, with a proportionally smaller set of ellipses.

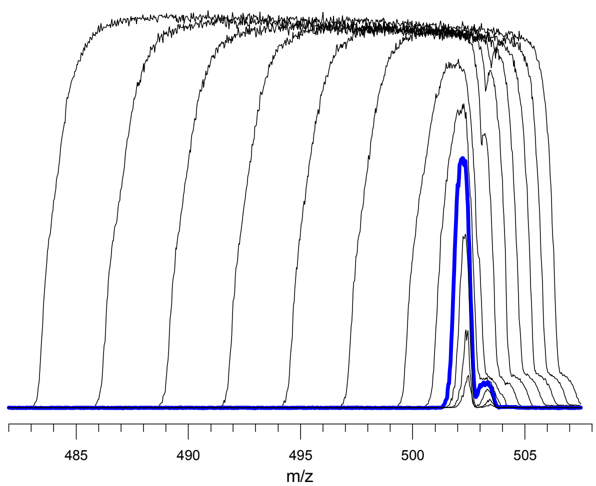

Figure 6. 0.050" aperture family of peak shapes at various resolutions. The thick blue line shows ~60% relative transmission at unit mass resolution.

What is interesting is that there is a sweet spot centered around the origin of the diagram, representing the superposition of all of the phase space acceptance ellipses. An ion injected into the quadrupole with minimal angle, and close to the center will have a stable trajectory through the quadrupole, regardless of RF phase. This sweet spot, which represents stable trajectories for all RF phases is often referred to as the acceptance of the quadrupole. Note that when resolution is increased from 10 to 700, that the relative size of the quadrupole acceptance reduces dramatically.

Figure 5 shows the relative size of the calculated acceptance of the quadrupole in both the 'X' and 'Y' directions. Note that ions which are not injected into the quadrupole within the acceptance aperture, might have stable trajectories at some RF phases, but not all of them.

Note how severely the acceptance aperture of the quadrupole restricts as resolution is increased. One could readily predict that as the acceptance of the quadrupole restricts, so should the absolute transmission.

V. PEAK SHAPES AND RESOLUTION

When the entrance aperture to a quadrupole is just smaller than the inscribed diameter of the quadrupole, one expects to see the transmission of the quadrupole to decrease as resolution is increased, since the acceptance aperture of the quadrupole decreases with increasing resolution.

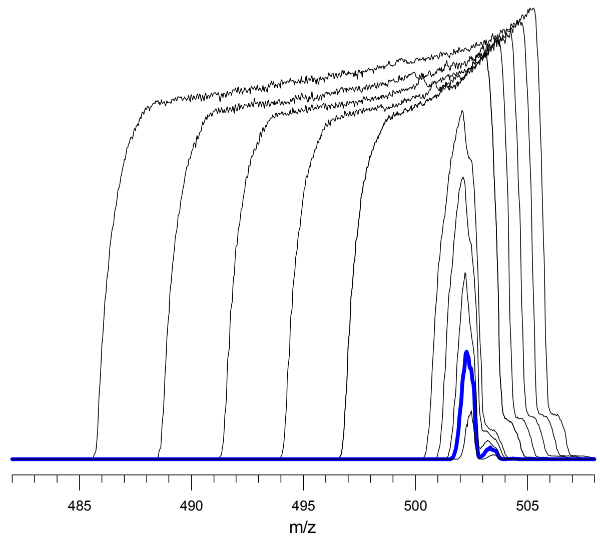

Figure 7. 0.300" aperture family of peak shapes at various resolutions. The thick blue line shows ~20% relative transmission at unit mass resolution.

When the entrance aperture to a quadrupole is much smaller than the inscribed diameter, one sees that the transmission of the quadrupole remains relatively constant as resolution is increased, until the acceptance aperture of the quadrupole for a given resolution is smaller than the entrance aperture.

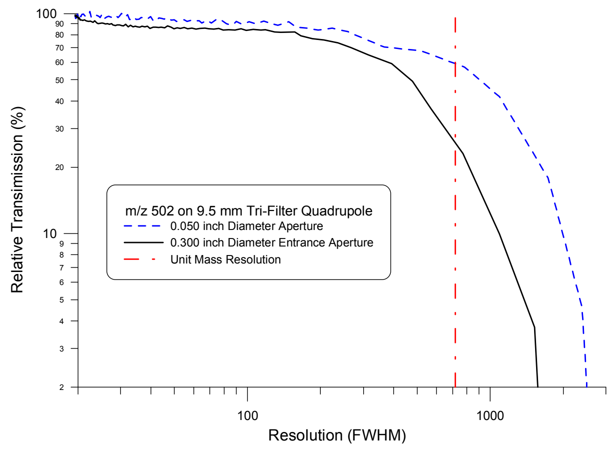

Figure 8. Experimental Resolution / Transmission curves for two different entrance aperture diameters, showing relative transmissions of ~60% and ~20% for the 0.050" and 0.300" diameter apertures respectively.

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This phenomenon is shown in the peak shapes in figures 6 and 7, with figure 8 representing the resolution/transmission curves for these two experiments.

Seeing a flat top mass peak is quite satisfying, since having the intensity to not change as mass resolution increases represents a certain immunity to sensitivity drift if there is a thermal drift in the mass resolution for a given system.

VI. CONCLUSIONS

- Quadrupole performance is dramatically impacted by the entrance conditions that ions see as they enter the quadrupole.
- The use of pre-filters in front of a quadrupole yields dramatic increases in mass resolution, abundance sensitivity and absolute sensitivity, by minimizing the negative impact of RF/DC fringing fields at the entrance to a quadrupole, replacing the de-focusing RF/DC fringing field with an RF-only fringing field followed by an RF – RF/DC fringing field, both of which yield stable trajectories.
- The acceptance of a quadrupole reduces in both the ‘X’ direction and ‘Y’ direction as mass resolution increases, causing a reduction in transmission as resolution is increased, as seen both theoretically and experimentally.
- If one were to restrict the cross sectional area of the ion source to be smaller than the acceptance of the quadrupole, then transmission would not be seen to decrease as resolution is increased, resulting in flat topped mass peaks, and flat relative transmission curves and high relative transmission at operating resolution.
- Electrospray and other high pressure ‘point’ sources naturally offer the potential for smaller emissive areas, and are therefore expected to see improved quadrupole performance compared to sources with bigger emissive areas like electron impact ion sources.

VII. REFERENCES

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3. Pedder R.E. “*Practical Quadrupole Theory: Peak Shapes at Various Ion Energies”*, Extrel CMS, L.P. Application Note RA_2011A, Poster presented at the 50th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, FL, 2002.
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