Quadrupole Performance: Do Quadrupoles Discriminate Against High Masses?

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It has been generally held that quadrupoles exhibit high mass discrimination. This can be interpreted to mean that the relative transmission of a quadrupole at unit mass resolution reduces dramatically as mass increases. In our laboratory, we have determined that mass discrimination is very much dependent on the relative location on the resolution-transmission curve for the quadrupole, which in turn is dependent on effective rod radius. The mass discrimination effects of quadrupoles constructed from 6 mm round quadrupole rods are typically exhibited as a dramatic change in intensity with a small change in resolution, whereas on a 19 mm quadrupole there is a much more subtle change in intensity with an equivalent change in resolution. In this presentation, we characterize the relative transmission as a function of mass for various quadrupole systems including standard quadrupoles of 9.5 mm and 19 mm rod diameters, as well as quadrupoles with RF-only pre- and post-filters. These relative transmission functions are extracted from resolution-transmission curves measured at various masses for the various systems.

I. INTRODUCTION AND THEORY

This presentation will focus on a single figure of merit for characterization of quadrupole performance: Relative Transmission. For a given set of tune parameters, the measured intensity of a mass peak will increase as the commanded mass resolution is decreased, until a point is reached where the peak gets wider but no longer increases intensity (identified as 100% transmission). (See Figure 1.) If intensity is plotted as a function of mass resolution (mass divided by peak width at half height), a characteristic curve is seen. (See Figure 2.)

For the purposes of this presentation, unit mass resolution can be defined as 0.7 amu peak width at half height, and is identified on the various plots as a large solid circle. (about 41% transmission in Figure 1.) Note that there is an inherent bias in this technique where the accurate point of 100% transmission is never reached. Instead, the 100% transmission point is taken as the point where the individual ion merges with it nearest neighbor. Thus this method will overestimate relative transmission by varying degrees for the different masses. Note also that this measurement technique normalizes out effects such as detection efficiency.

Within a quadrupolar field, the motion of the ions in the x, y, and z directions is linearly independent. At the entrance and exit of a quadrupole, however, the ions travel through some region in space where their ion motion in the three directions is coupled. The net effect of these fringing fields is two-fold. Ion trajectories are de-stabilized by the fringing field, causing some of the ions to have much larger injection angles, with a net result in ion loss when the injection angle exceeds the phase space acceptance of the quadrupole. This effect is generally more dramatic for higher mass ions than for lower mass ions. Second, some of the radial energy of the ions gets coupled into the axial direction in the fringing field, resulting in a broadening of the range of ion energies (along with a corresponding sacrifice in abundance sensitivity and resolution that is associated with too broad an ion energy).

Four distinct experimental configurations were selected to illustrate the effects that various parameters had on relative transmission. Since early quadrupoles typically operated with a grounded aperture in front of the quadrupole, experiments were performed with the entrance lens to the quadrupole grounded, with extensive mass discrimination expected and measured. If this were the only mode of operation, then clearly one would conclude that quadrupoles have dramatic high mass discrimination.

Quadrupoles are often operated with a bias voltage applied to the entrance lens to the quadrupole to help accelerate the ions through the fringing field at the entrance to the quadrupole. This, along with a biased exit lens has been determined to be quite an effective means of minimizing the effects of the fringing fields at the entrance and exit of a quadrupole. Brubaker demonstrated in the early 1960's that the use of RF-only pre-filters and post-filters at the entrance and exit of the quadru-

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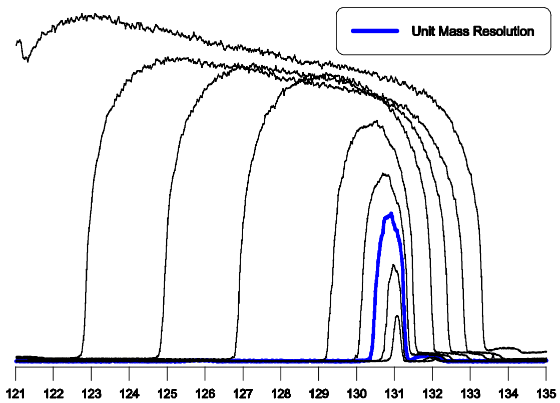

Figure 1 Transmission of m/z 131 as a function of resolution (19mm quadrupole, mass programmed entrance lens).

pole dramatically enhanced ion transmission, especially at high mass, by eliminating the de-stabilizing effects of the RF/DC fringing field, by making the fringing fields RF-only.

II. EXPERIMENTAL

The data for this presentation was gathered using the fp Extrel Merlin data acquisition and control electronics, with a 1.2 MHz 150-QC quadrupole power supply driving three separate quadrupole configurations: 9.5 mm with bias-able entrance lens, 9.5 mm quadrupole with pre-and post-filters, and 19 mm quadrupole with biasable entrance lens. The pre-and post-filters were configured such that they are capacitively coupled to the resolving quadrupoles, and hence do not have distinct RF power supplies. A 1.5 megaohm resistor was used to electrically connect each pair of pre- and post-filter rods to the quadrupole housing (ground) effectively creating a capacitive voltage divider.

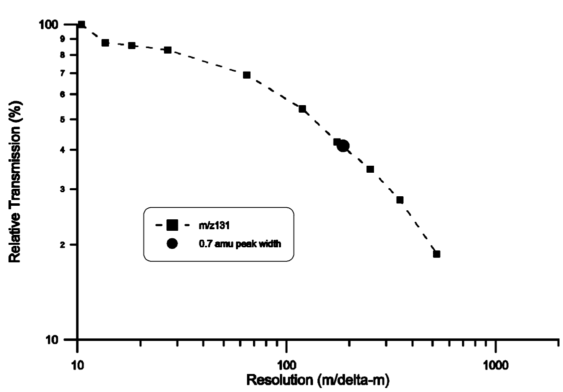

Figure 2 Relative transmission curve for m/z 131 (19mm quadrupole, mass programmed entrance lens).

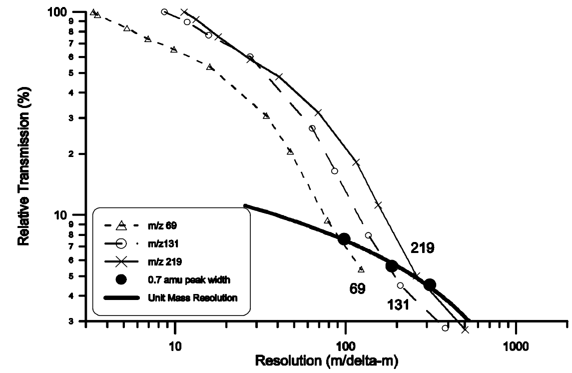

Figure 3 Relative transmission curves for 9.5 mm quadrupole (grounded entrance lens).

For the data labeled 'Grounded Entrance Lens', the entrance lens was held at 0 volts for all masses. Data was not gathered for the higher masses for the grounded entrance lens experiments due to the extremely poor transmission for such masses.

For the data labeled (Mass Programmed Entrance Lens), the voltage applied to the entrance lens was varied linearly with mass (more negative with increasing mass).

The following procedure was used to determine the optimum entrance lens voltage:

1. Set the mass programming control to 0%.
2. Set the voltage for optimum peak shape and sensitivity at m/z 18.
3. Adjust the mass programming control for optimum peak shape at m/z 502.

The resulting programmed voltages ranged from –10 to –20 volts for m/z 69, to –210 to –360 volts for m/z 502. The

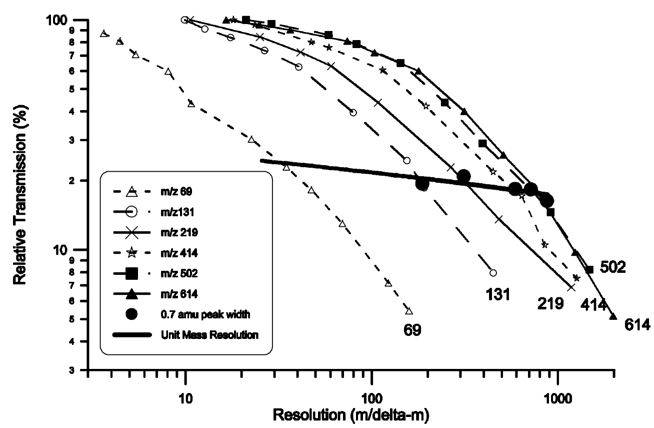

Figure 4 Relative transmission curves for 9.5 mm quadrupole (mass programmed entrance lens).

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Table 1. Summary of relative transmission for the various configurations

	m/z					
	69	131	219	414	502	614
9.5 mm quadrupole (with grounded entrance lens)	7.6%	5.6%	4.5%			
9.5 mm quadrupole (with mass programmed entrance lens)		19.4%	20.9%	18.4%	18.3%	16.3%
9.5 mm quadrupole (with pre- and post- filters)	41.3%	31.7%	43.2%	32.8%	28.8%	31.8%
19 mm quadrupole (with mass programmed entrance lens)	68.0%	41.2%	39.9%	29.2%	26.7%	

control electronics automatically interpolate between these values, and extrapolate to higher masses.

For each data set, the resolution was opened until the mass peak in question merged with its nearest lower mass neighbor. This intensity was taken as 100% transmission. All other intensities within a given experimental run are normalized to this intensity. This assumption will not overestimate transmission so long as the starting point for the curve exists on the flat part at the top of the resolution transmission curve (i.e. the next few points on the curve are almost the same intensity).

III. RESULTS AND DISCUSSION

Figures 3 through 6 contain curves of relative transmission as a function of resolution for the four configurations tested. Each of the individual curves was extracted from peak tracings similar to those seen in Figure 1.

The intensity that corresponds to unit mass resolution (0.7 amu peak width at half height) was interpolated from each curve and is identified with a large black dot. For a given configuration, these unit mass resolution relative transmissions were fit to a curve, which is displayed as a thick black line. Table 1 summarizes the values for these various unit mass resolution transmission points. In all cases, the relative transmission for heavier masses is smaller than for lighter ions, although the slope of the curve is much steeper with a grounded entrance lens, and much less pronounced when pre- and post-filters are used.

Note that the relative transmission for m/z 69 was not included in the curve fits for the two cases of the mass programmed entrance lens because the value dramatically skewed the slope of the line (both up and down.)

IV. CONCLUSIONS

This work demonstrates that the mass discrimination commonly attributed to quadrupoles can be dramatically minimized through proper analyzer design and tuning.

It is guessed that the perception that quadrupoles discriminate against high mass was generated based on early system

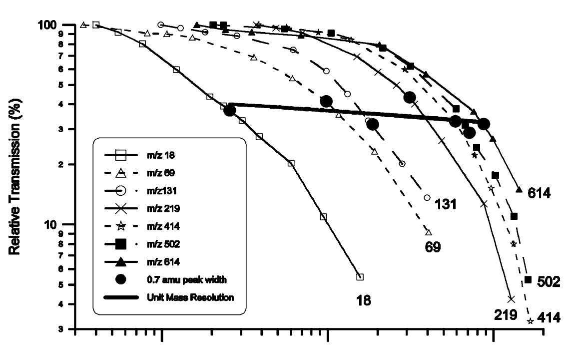

Figure 5 Relative transmission curves for 9.5 mm tri-filter quadrupole (with pre- and post- filters).

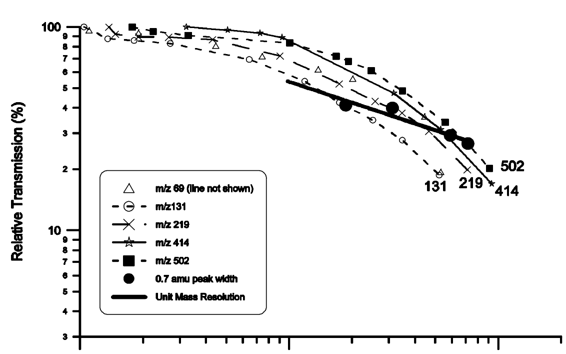

Figure. 6 Relative transmission curves for 19 mm quadrupole (mass programmed entrance lens).

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designs which did not incorporate biased entrance and exit lens, nor pre- and post-filters.

While quadrupole transmission efficiency is only slightly dependent on mass, detection efficiency using an electron multiplier is very dependent and decreases with increasing mass, leading to an apparent system bias against high mass.

Bigger is better! The relative transmission for the 19 mm quadrupole was much greater than for the 9.5 mm quadrupole, although the 9.5 mm quadrupole with pre- and post-filters was a close second. A smaller quadrupole would be expected to have much lower relative transmission than the data shown for the larger diameters.

Absolute transmission of a quadrupole (not shown) tends to match the relative transmission for a given quadrupole rod size. The 19 mm quadrupole has about four times the absolute transmission as the 9.5 mm quadrupole with programmed entrance lens, and about twice the relative transmission. The 19 mm quadrupole has slightly higher absolute transmission than the 9.5 mm quadrupole with pre- and post-filters.

Relative transmission at masses higher than shown in this presentation is expected to follow the trend shown for low masses.

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