

Reflections on quadrupole simulation

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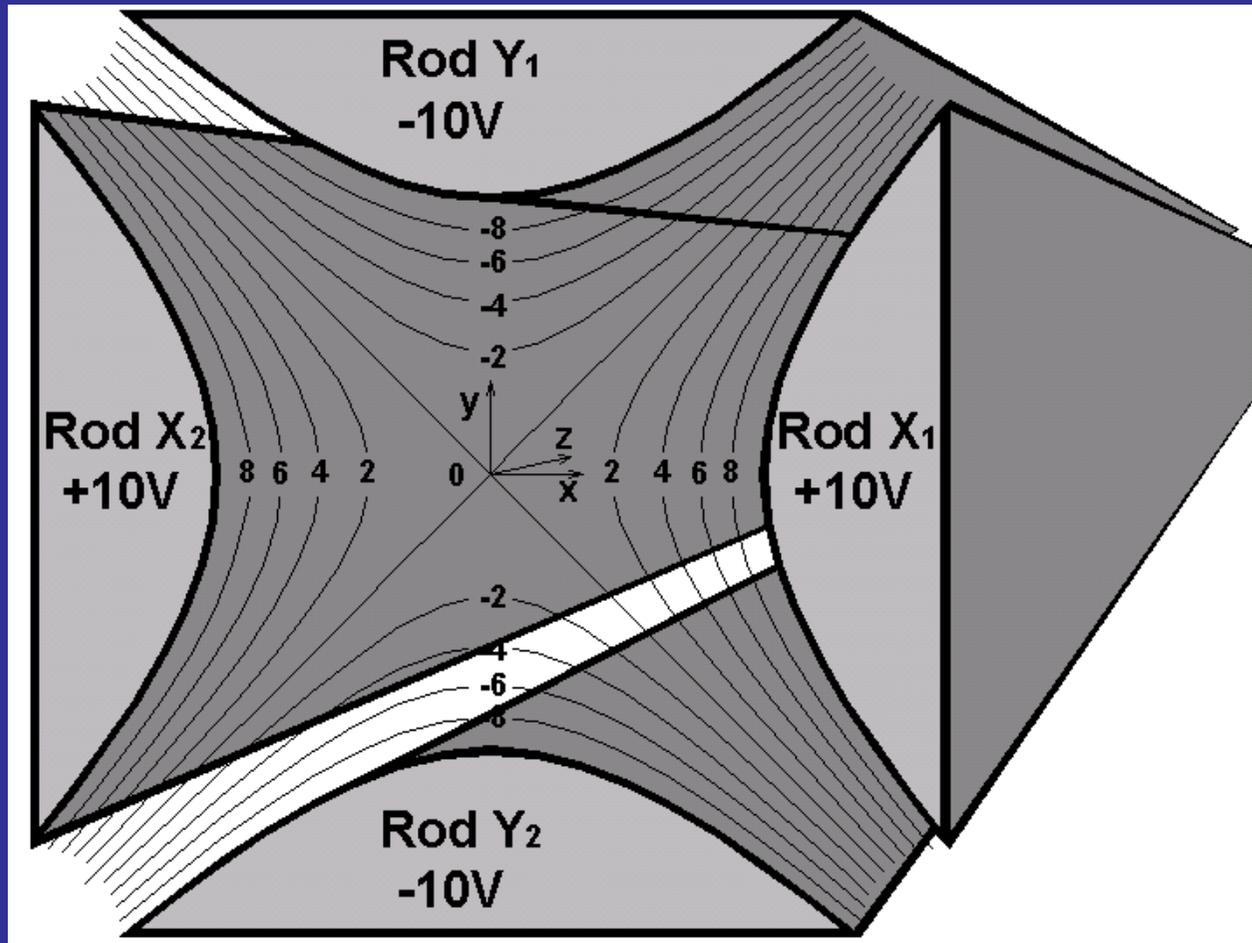
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Ion trajectories in a quadrupole can be resolved into independent equations for the X and Y motion, and uniform drift along the Z axis.

$$\frac{d^2U_x}{dt^2} = -(e/(mr_0^2)) \cdot (U - V \cos(2\pi f(t - t_0))) \cdot U_x$$

$$\frac{d^2U_y}{dt^2} = (e/(mr_0^2)) \cdot (U - V \cos(2\pi f(t - t_0))) \cdot U_y$$

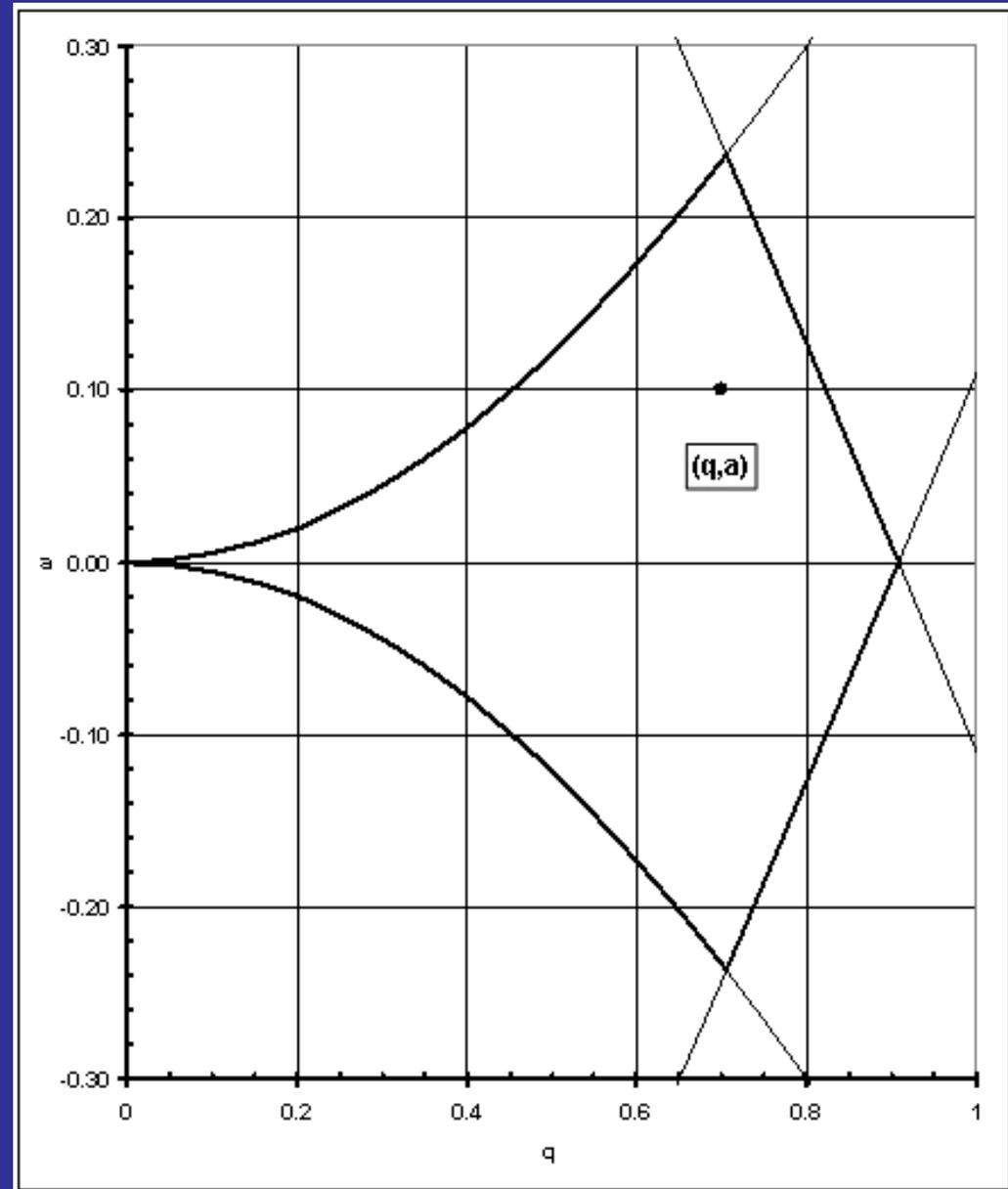
$$\frac{d^2U_z}{dt^2} = 0$$



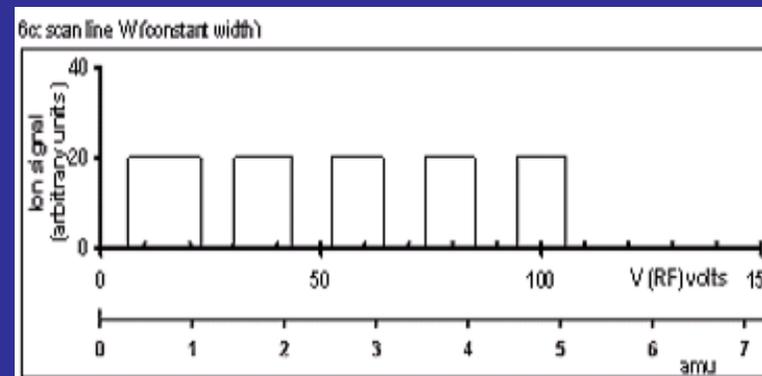
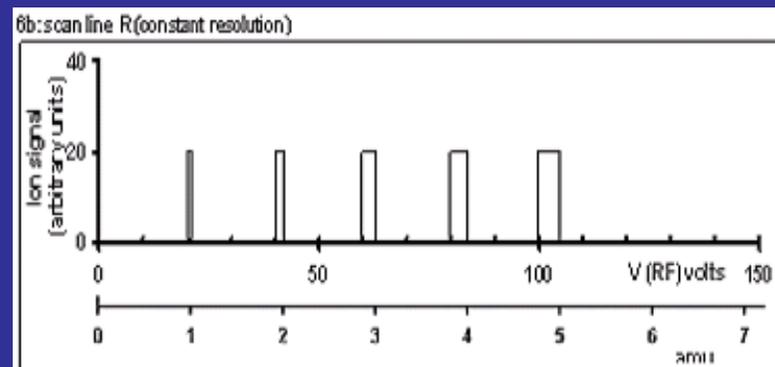
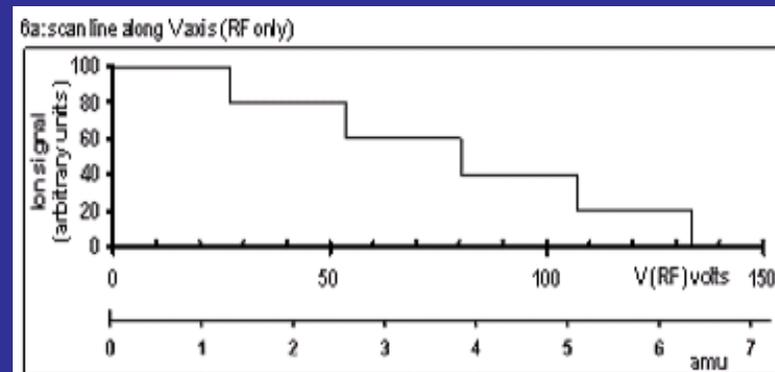
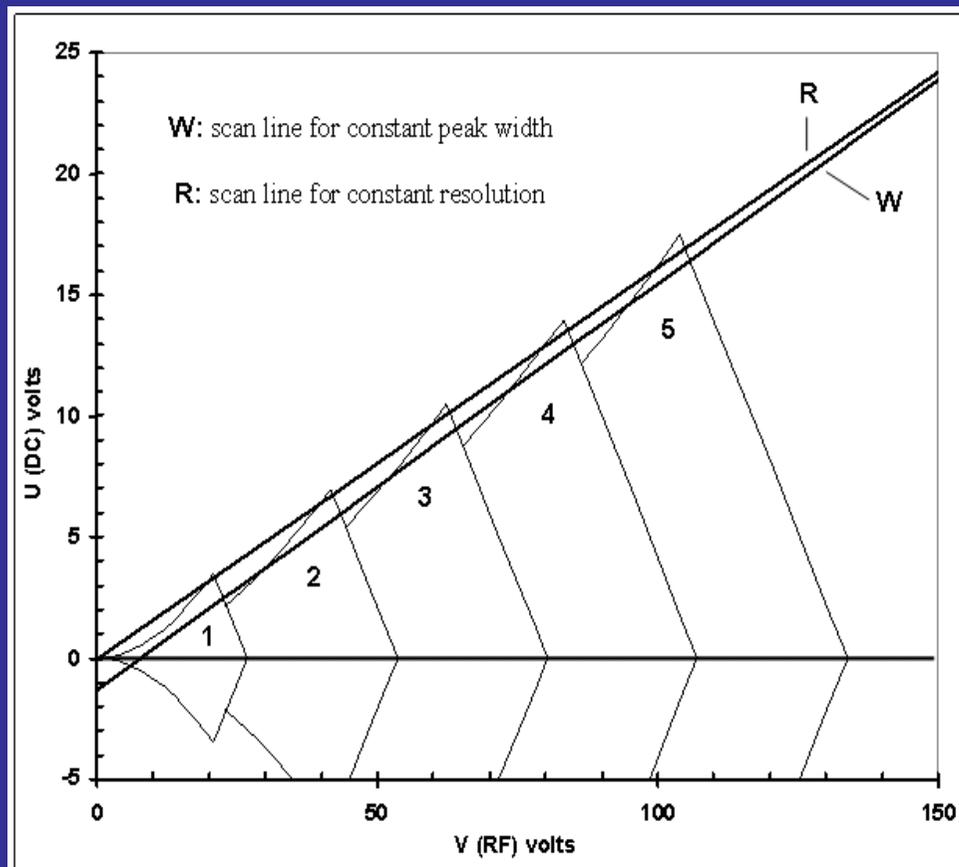
The equations for the X and Y motion are both of the form

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos(2(\xi - \xi_0)))u = 0$$

which is the Mathieu equation. From it can be derived the Mathieu stability plot, which is used to predict quadrupole RF and DC drive voltages to good accuracy and to simulate tolerably realistic peaks.



This data is for $r_0 = 6\text{mm}$ and $f = 2\text{MHz}$ (typical quadrupole ICP-MS).



Ion trajectories can be calculated by numerical integration

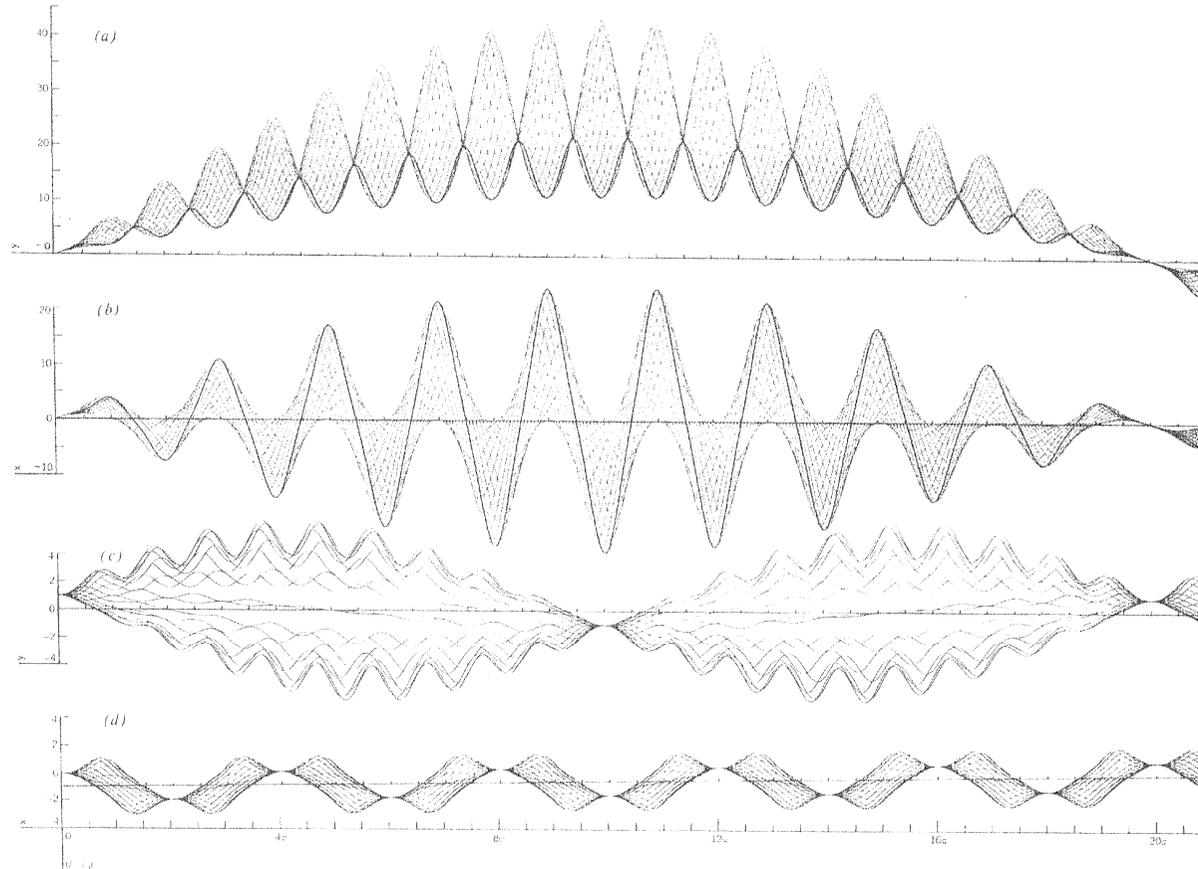
Figure 4 Ion trajectories computed for various initial conditions. The abscissae are $(\xi - \xi_0)$ where ξ_0 is the initial value of ξ . In this and subsequent figures, 17 plots are superimposed corresponding to $\xi_0 = 0, \pi/16, 2\pi/16, \dots, 15\pi/16, \pi$ with the plots for $\xi_0 = 0$ and $\xi_0 = \pi$ being identical. For the purpose of visualizing the spatial trajectories, $(\xi - \xi_0)$ may be regarded as equivalent to the spatial coordinate z (Fig. 1). They are related by $z = 2v_r^{-1} \omega (\xi - \xi_0)$.

Plot a . . . y trajectory for $y_0 = 0, y_0 = 1; a = -.233982; q = -.704396; s = 20; p = 19.$

Plot b . . . x trajectory for $x_0 = 0, x_0 = 1; a = +.233982; q = +.704396; s = 20; p = 19.$

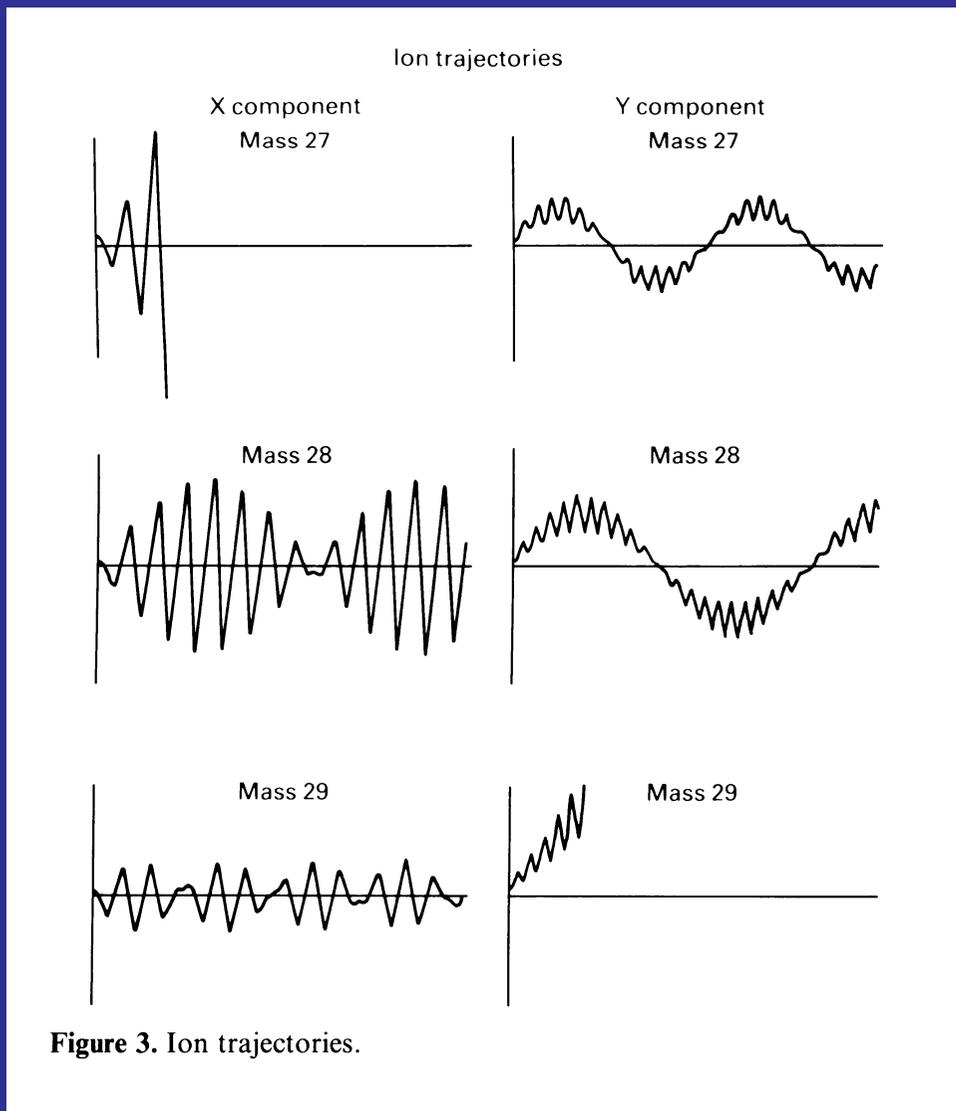
Plot c . . . y trajectory for $y_0 = 1, y_0 = 0; a = -.225041; q = -.699745; s = 10; p = 9.$

Plot d . . . x trajectory for $x_0 = 1, x_0 = 0; a = +.225041; q = +.699745; s = 10; p = 9.$



These trajectories are actually for a double-focusing monopole mass filter, but the equations are the same as for the quadrupole.

My first attempt at quadrupole simulation.

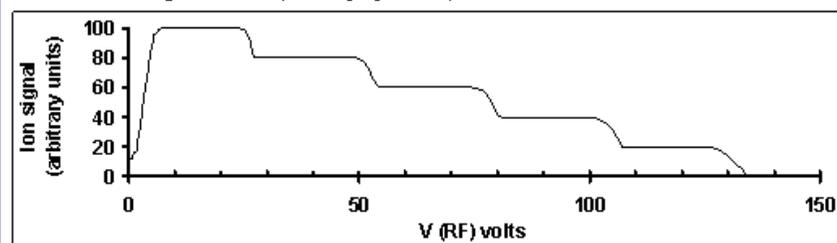


Apple IIe computer
“Paper Tiger” printer
“Cut & paste” ... literally

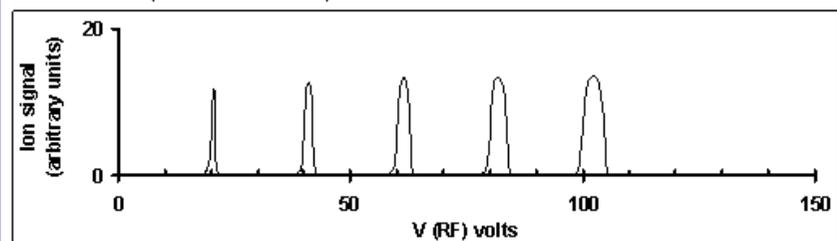
Mass peaks simulated by numerical integration of equations of motion.

Figure 9: Simulated mass spectra

9a: scan line along the V axis (RF only spectrum)



9b: scan line **R** (constant resolution)



9c: scan line **W** (constant peak width)

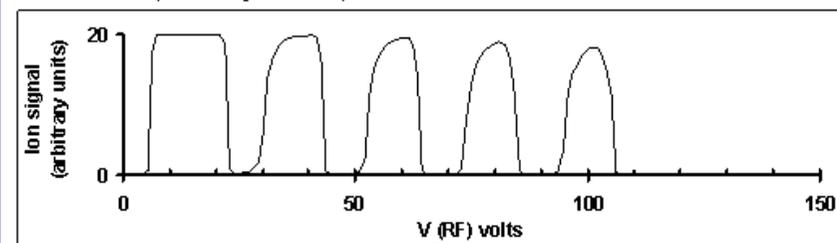
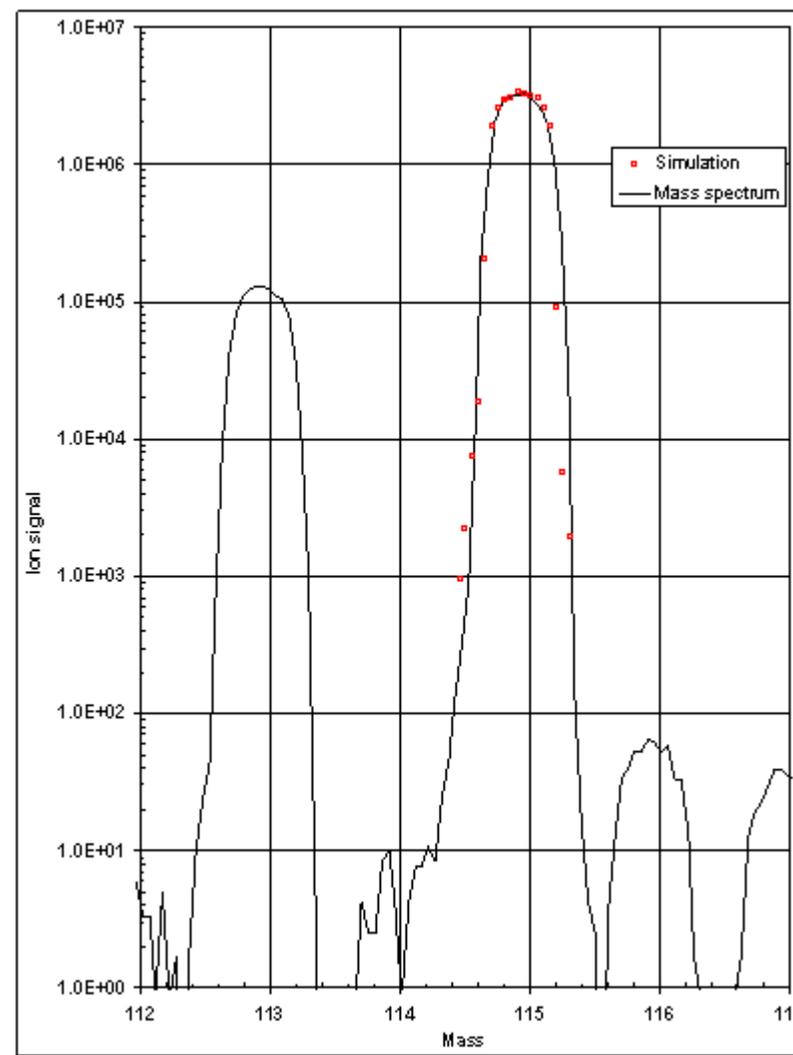
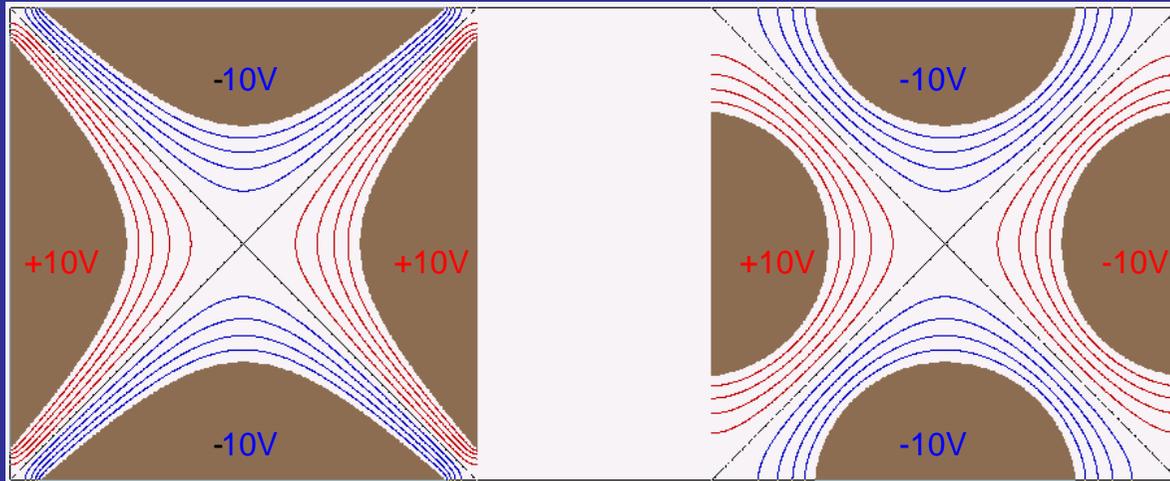


Figure 10: Spectrum from a quadrupole ICP-MS

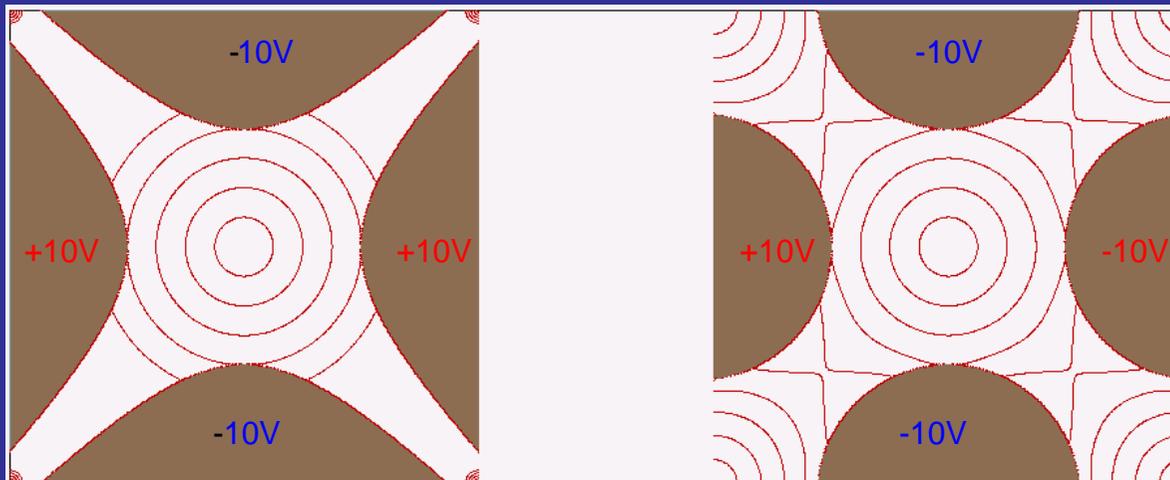


Quadrupole theory assumes a hyperbolic field. But round rods are widely used. They give a field that is essentially hyperbolic near the axis, but away from the axis, the field is quite different.



Potential contours at intervals of 2V

The effect is more clearly seen if we plot gradient contours, rather than the more familiar potential contours.



Gradient contours, at intervals of 1V/mm

The size of the rods relative to their spacing is important. Denison (1971) calculated an optimum ratio $r/r_0 = 1.1468$. With this value the stability diagram is very similar to the Mathieu diagram. Varying the ratio r/r_0 changes the stability diagram, and gives a shift in mass scale and resolution. In practice (i.e. a real instrument) this is unlikely to be noticed, because the mass scale is calibrated from known mass peaks and the resolution is tuned to give the desired peak width.

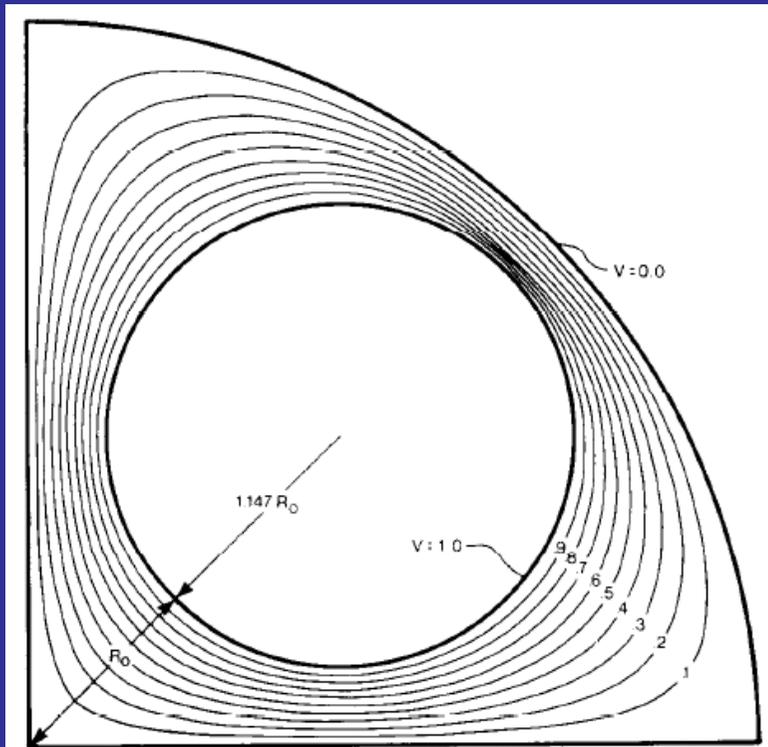


FIGURE 1. One quadrant of the potential distribution in a quadrupole with circular cross-section electrodes within a cylinder at zero potential.

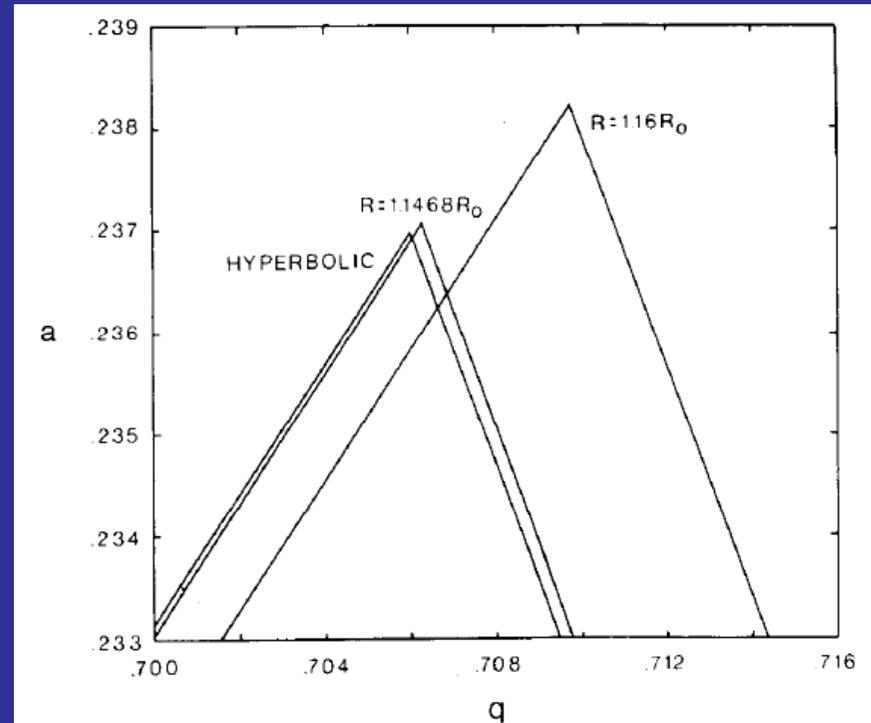


FIGURE 3. Location of the tips of the stability diagrams of a hyperbolic electrode quadrupole and circular electrode quadrupoles with rod radii of $1.1468r_0$ and $1.16r_0$.

More detailed simulation studies reveal effects on the peak shape:

- Mass shift
- Low mass tailing
- Peak top structure?

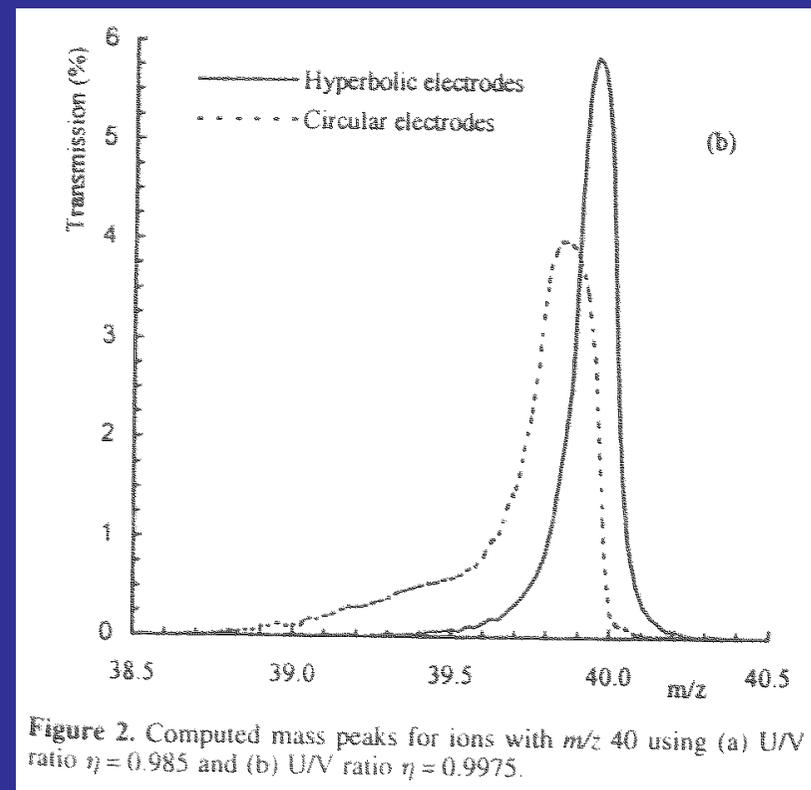
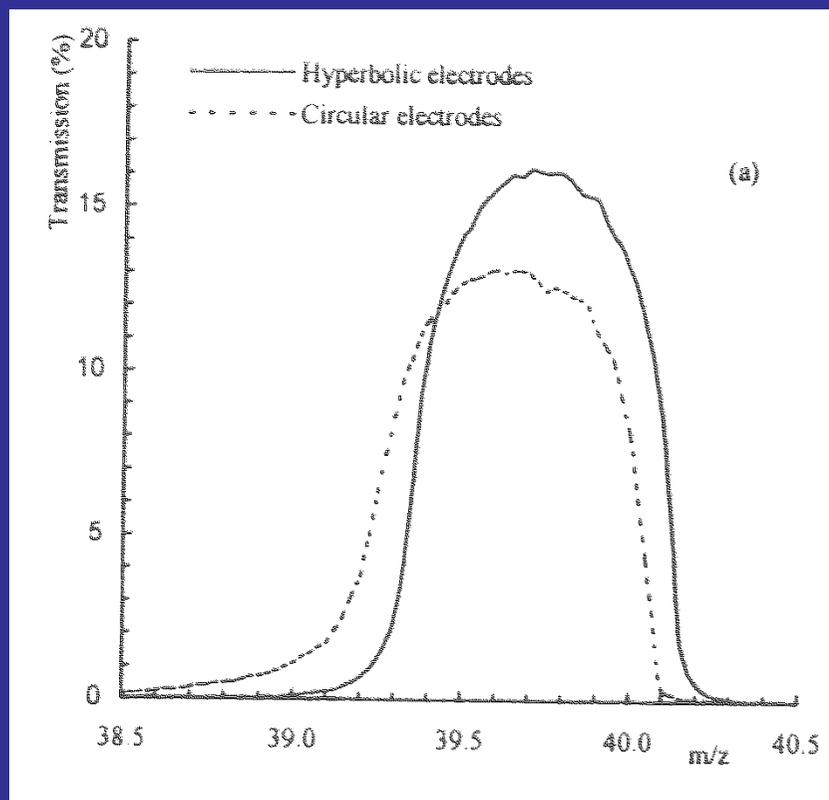
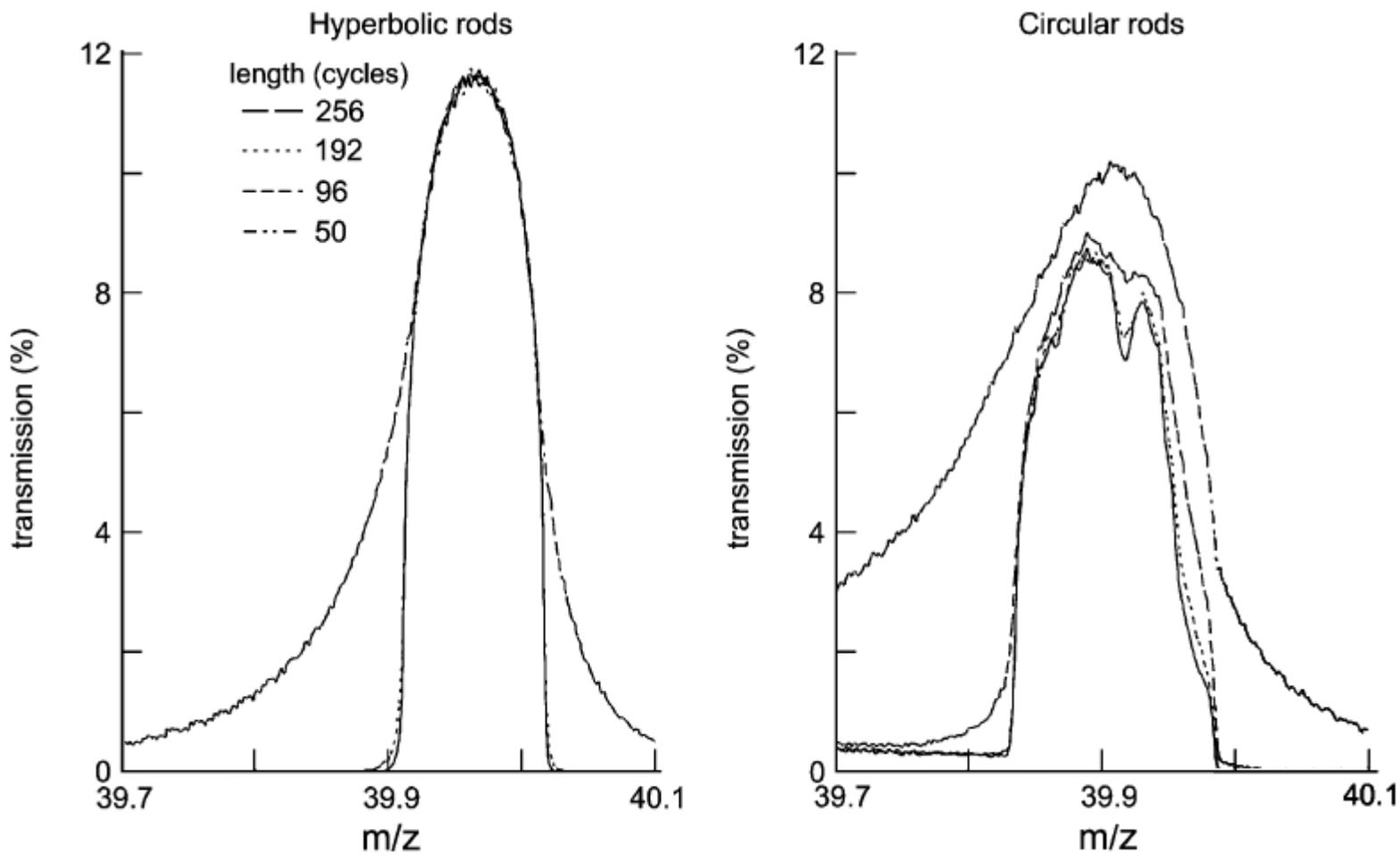


Figure 2. Computed mass peaks for ions with $m/z = 40$ using (a) U/V ratio $\eta = 0.985$ and (b) U/V ratio $\eta = 0.9975$.

This shows the altered peak structure more clearly:



Variation of QMS filter performance with QMS length.

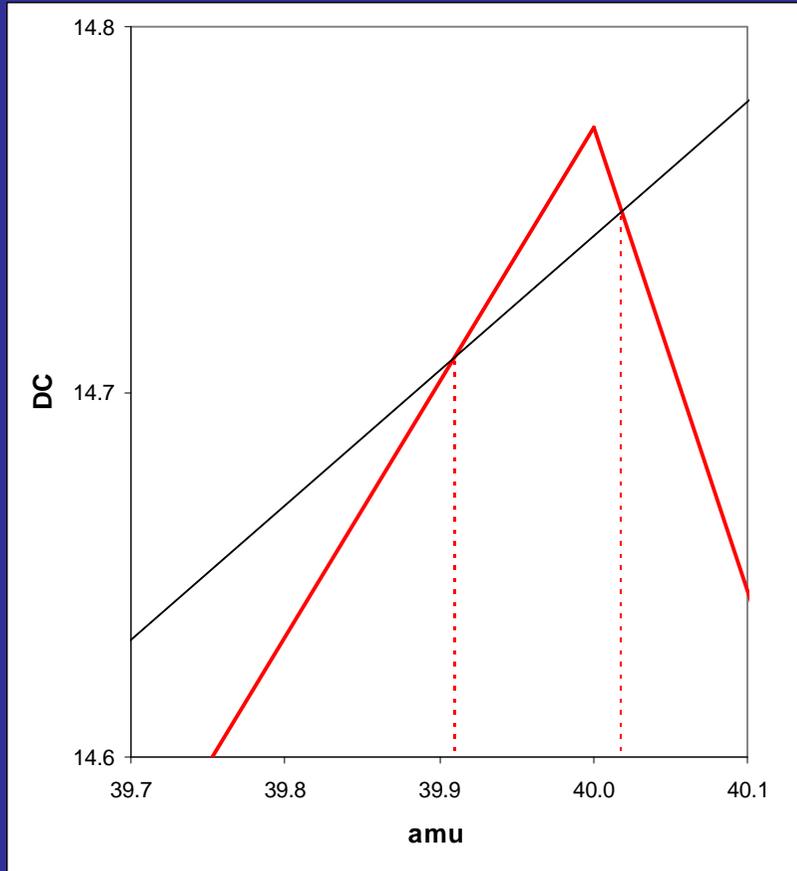
What are the requirements for quadrupole simulation? Can we use a commercially-available package such as SIMION or CPO?

	SIMION	CPO
Electrostatic field solver	✓	✓
Accuracy	✓	✓ ✓
3D display	✓ ✓	✓
Trajectory calculation	✓	✓
Randomised starting conditions	✓	✓
Time-varying potentials	✓	✓
User programming	✓ ✓	X

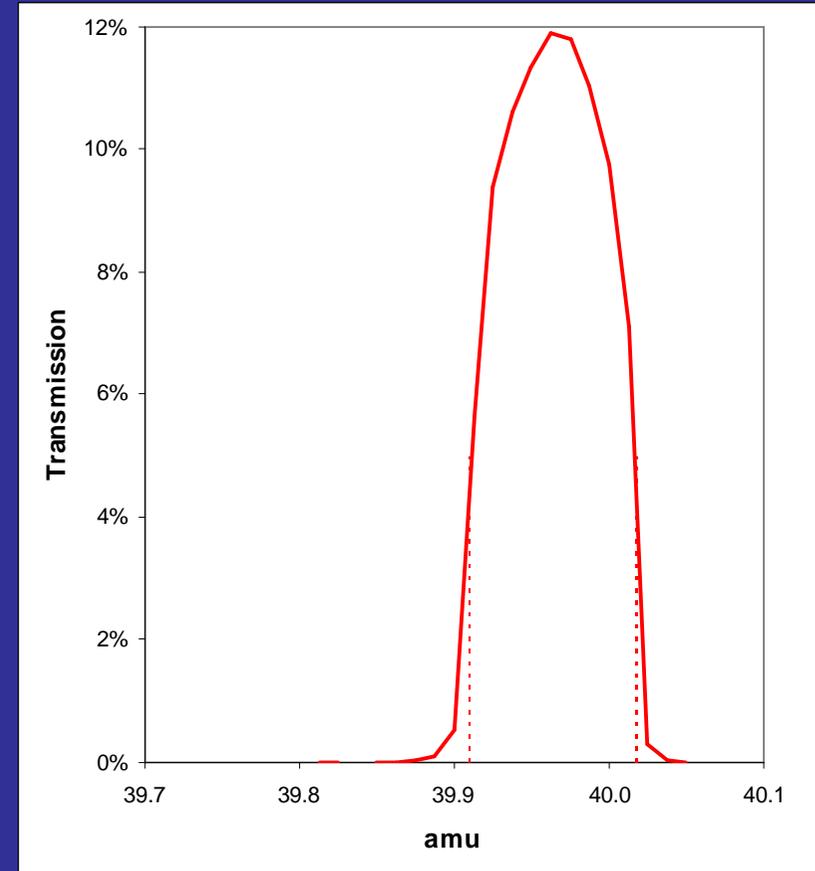
One can use a high-accuracy package like CPO to generate fields; then write a dedicated program that uses the field data to calculate ion trajectories. This involves detailed and complex programming. By using SIMION's user programming facility one can develop a model relatively quickly.

But are the results accurate enough to be useful?

First, we look at the results of a simulation based entirely on the Mathieu equation. The quadrupole parameters are taken from a case studied by Taylor & Gibson (see later slide).



Mathieu stability region and scan line



Peak

From the stability plot we calculate the peak width is 0.108 amu, corresponding to a resolution of 370.

A basic quadrupole model is supplied with SIMION. Earlier versions used the rather awkward PRG language to program electrode voltages and manipulate ions. In the latest embodiment (version 8) the Lua language is used – it is much easier to program in Lua than in PRG.

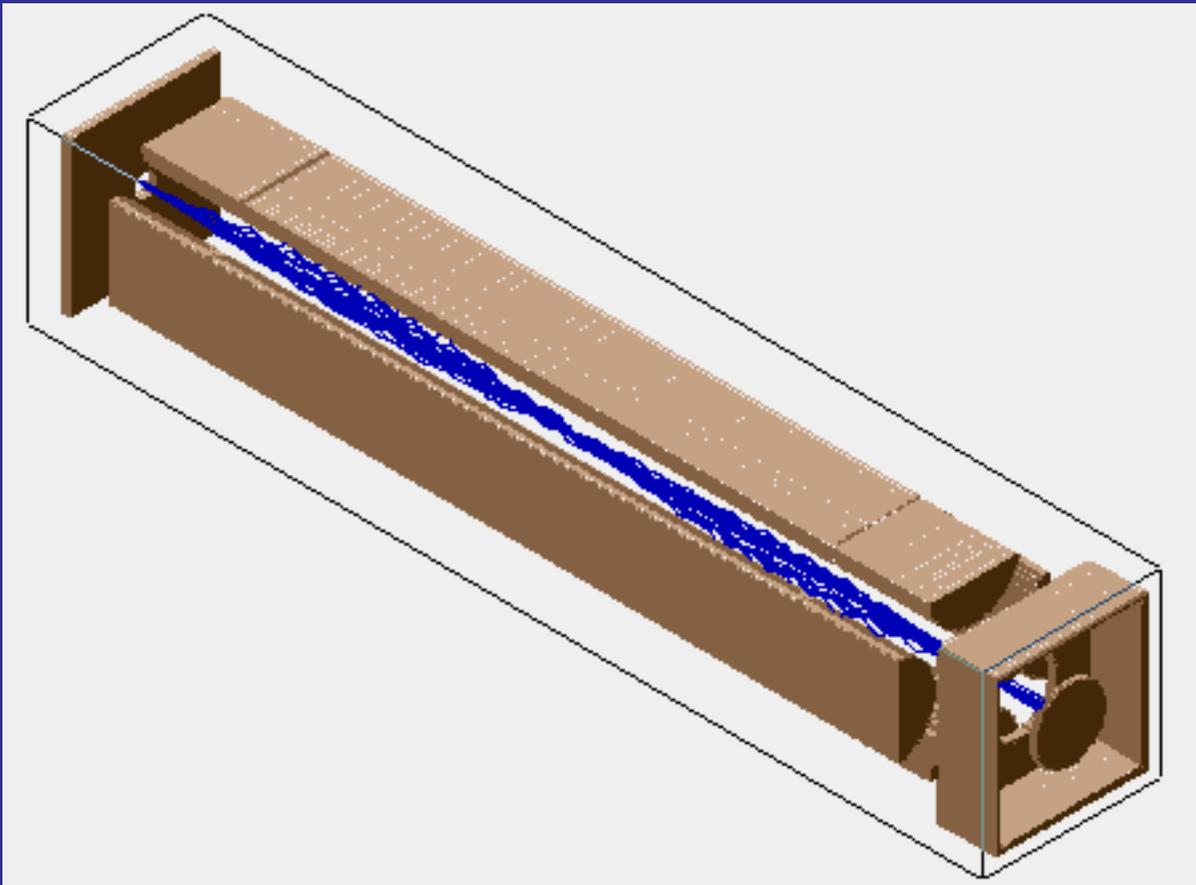
↓

```
adj_elect01 = _quad_axis_voltage + tempvolts1  
adj_elect02 = _quad_axis_voltage - tempvolts2
```

→

```
sto tempvolts  
rcl Quad_Axis_Voltage +  
sto Adj_Elect01
```

```
rcl Quad_Axis_Voltage  
rcl tempvolts -  
sto Adj_Elect02
```



Hyperbolic electrodes; otherwise the quadrupole is the same as the one described by Taylor & Gibson. Here we use a 2-D potential array, reflected about the X and Y axes – to reduce file size by a factor 4. Even so, the potential arrays take up 32 MB for a grid size of 0.005 mm (corresponding to 0.0018 times r_0).

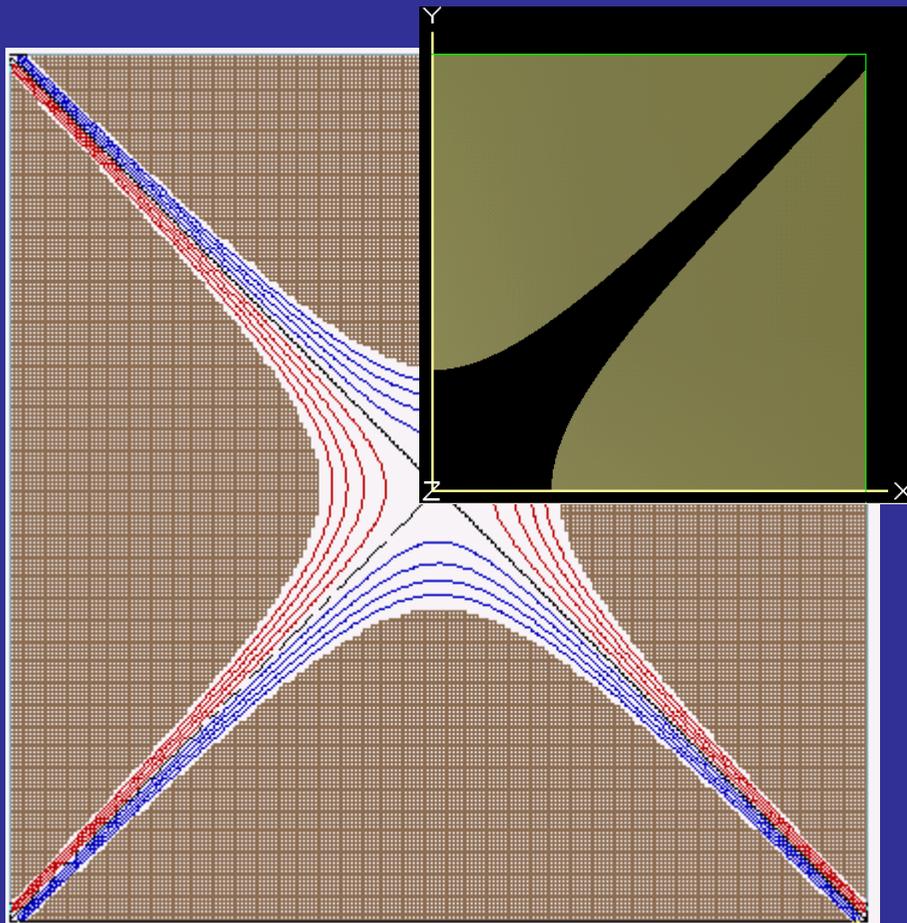
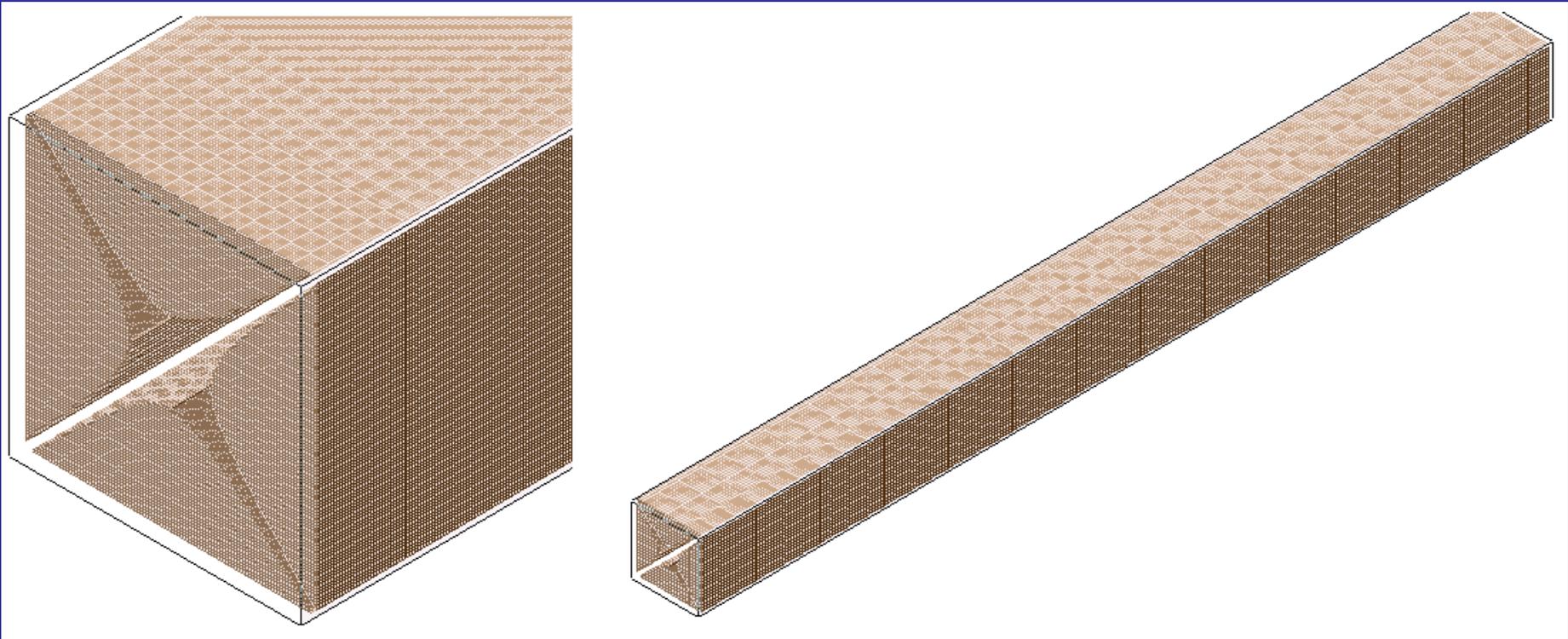


Table 1. QMS parameters used to compute Figs 2–8

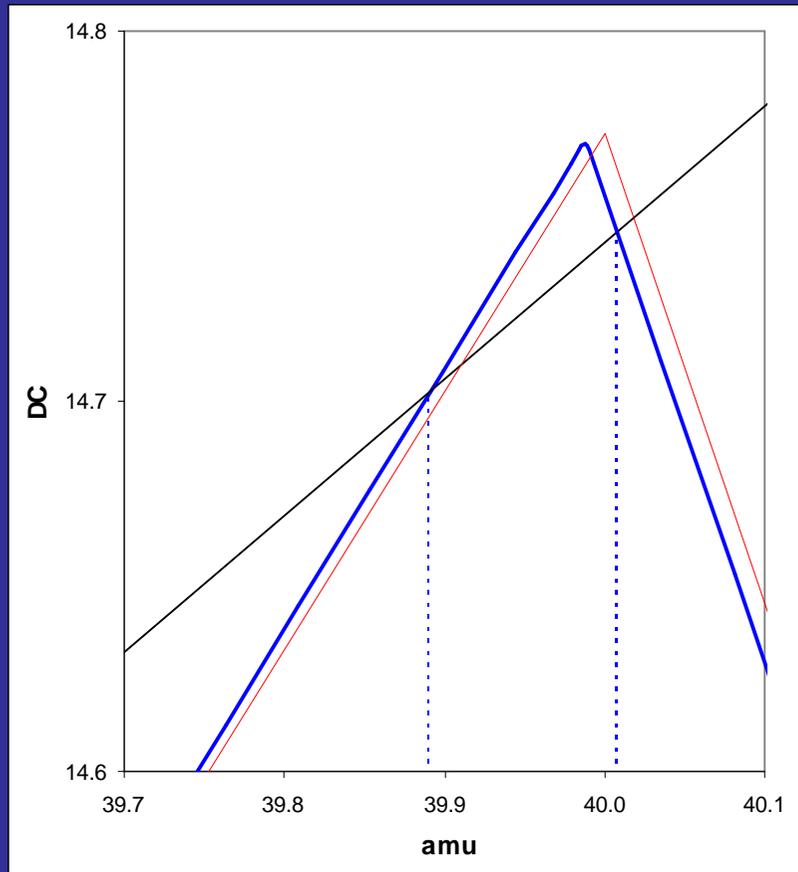
Parameter	Value
Rod length	254 mm
r_0	2.76 mm
r/r_0	1.127
Housing radius ($3.6 \times r_0$)	9.936 mm
Frequency	2 MHz
Resolution setting η	0.998
Ion m/z	40.0
Number of ions injected at each mass point	10^5
Ion source radius (uniformly illuminated)	0.5 mm
Ion energy	2.0 eV
Ion beam divergence	0 (ions parallel to z-axis)

S Taylor & JR Gibson, J Mass Spectrom 2008; **43**: 609–616

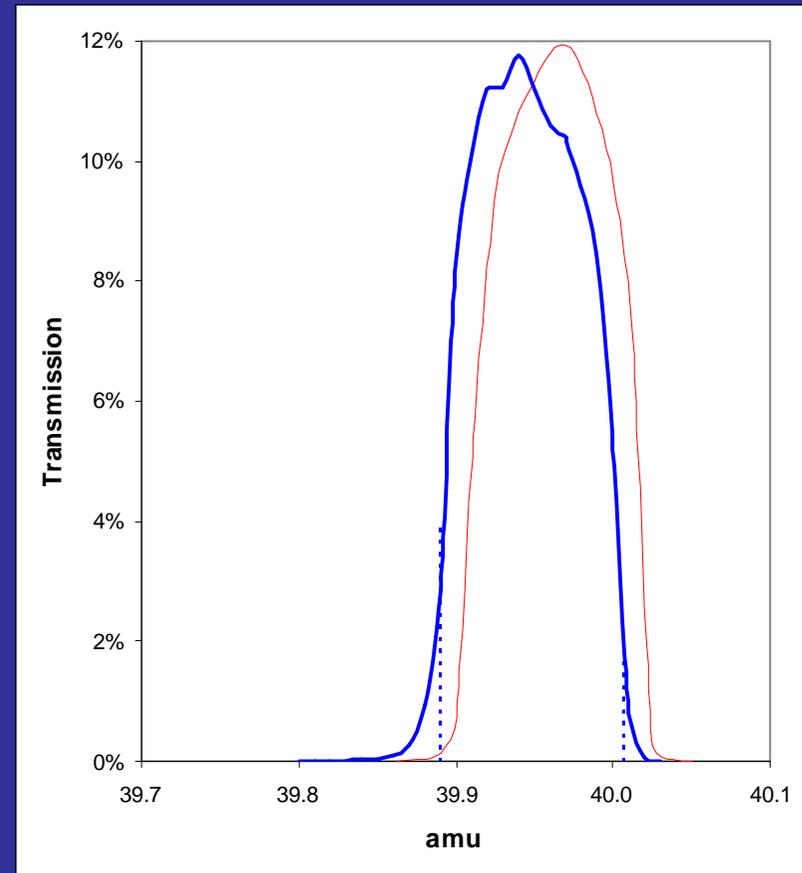
The model is 2D, but we extrude along the Z axis to represent a 3D quadrupole – ignoring any fringing fields. It is possible to set up a true 3D model, but the potential arrays get very large. A complete 3D model with the same spatial resolution would need some 650 GB of storage – not yet a practical proposition for an office PC.



This data is from the SIMION model with hyperbolic electrodes.



Mathieu stability region and scan line



Peak

The peak width is 0.117 amu, corresponding to a resolution of 343. The peak is shifted to lower mass by 0.015 amu; presumably a smaller grid size would give a smaller shift.

Now we change to round rods. The quadrupole is now the same as Taylor & Gibson's example.

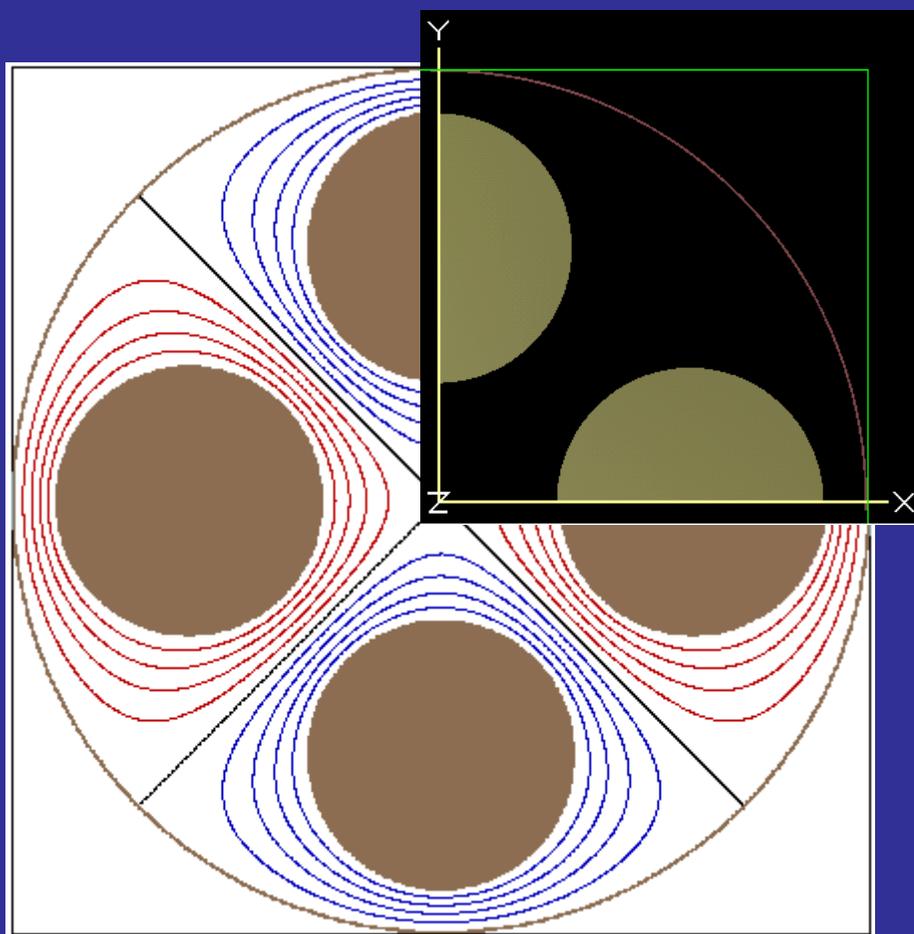
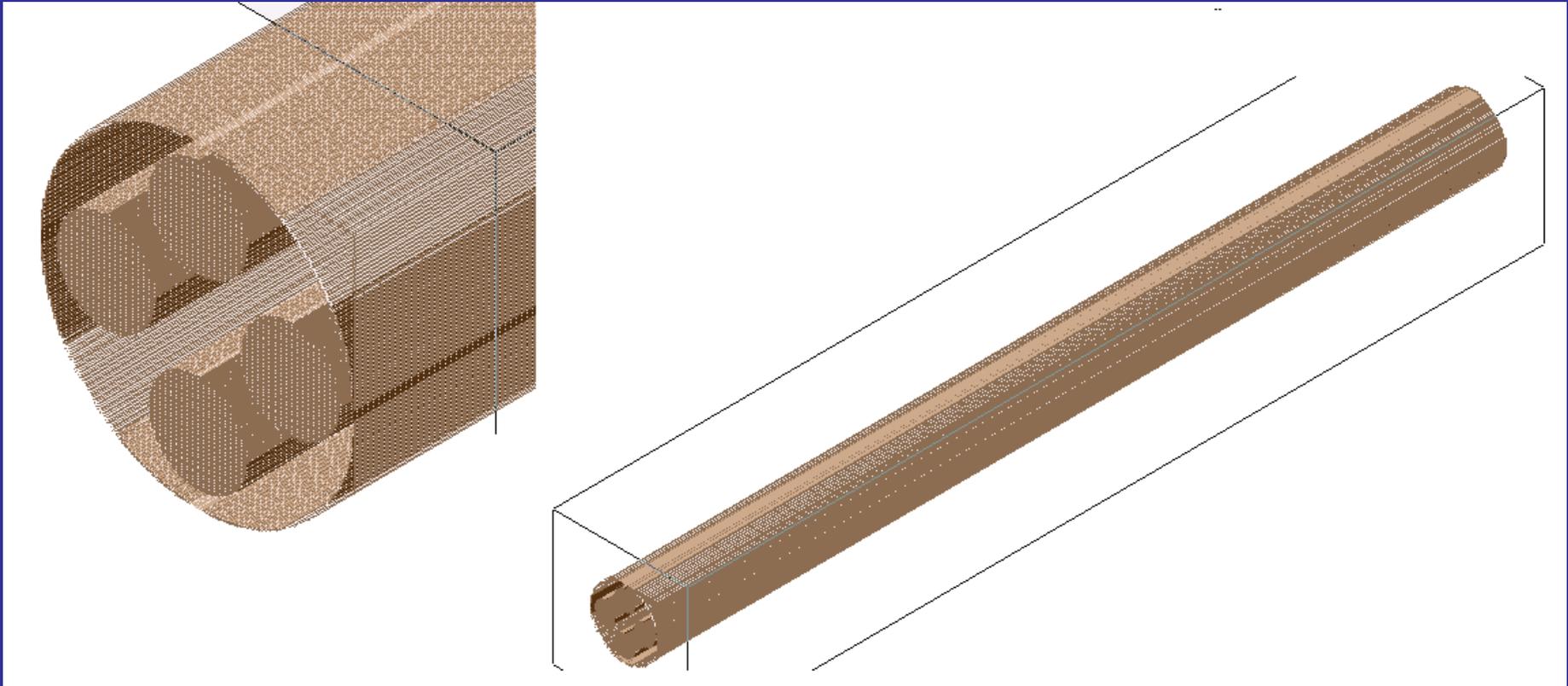


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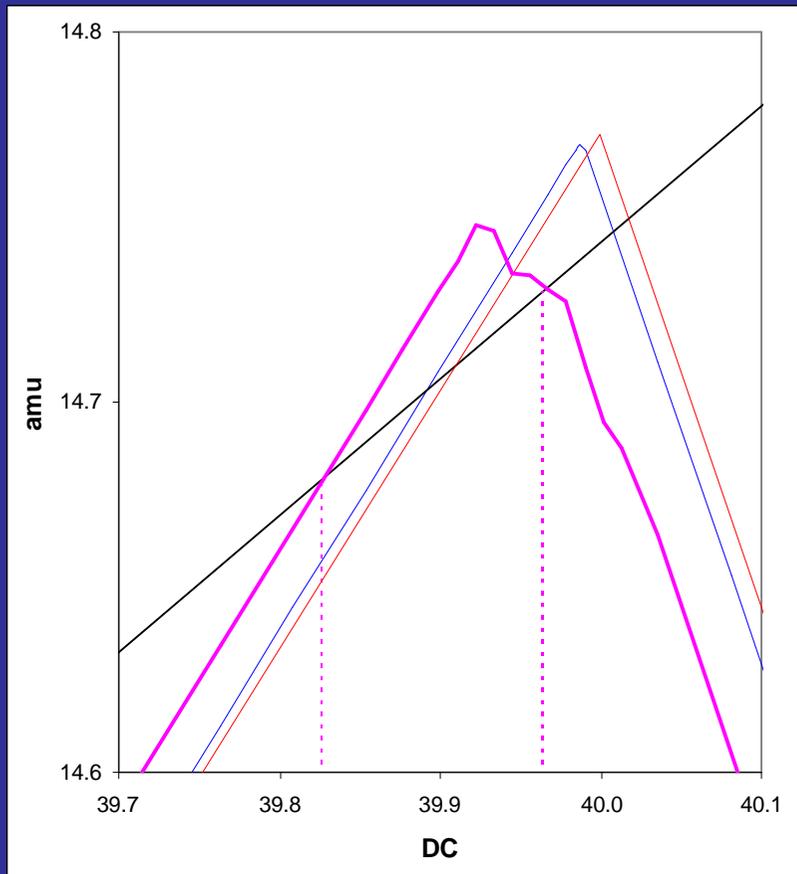
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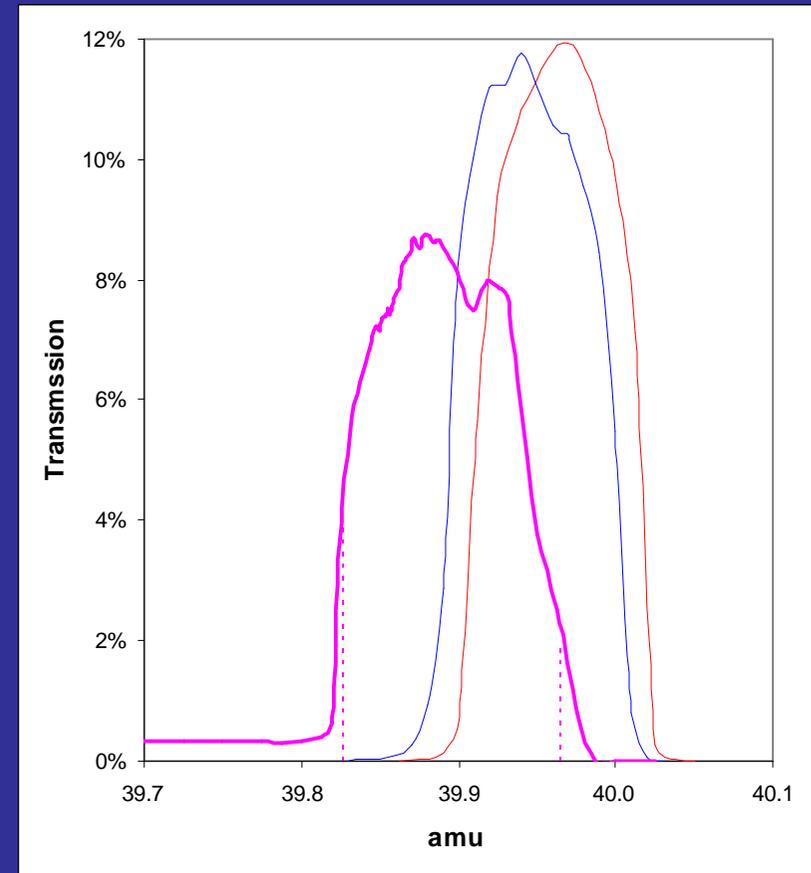
... again the model is 2D, but we extrude along the Z axis as before ...



... and finally, here is data from the SIMION model with round electrodes.



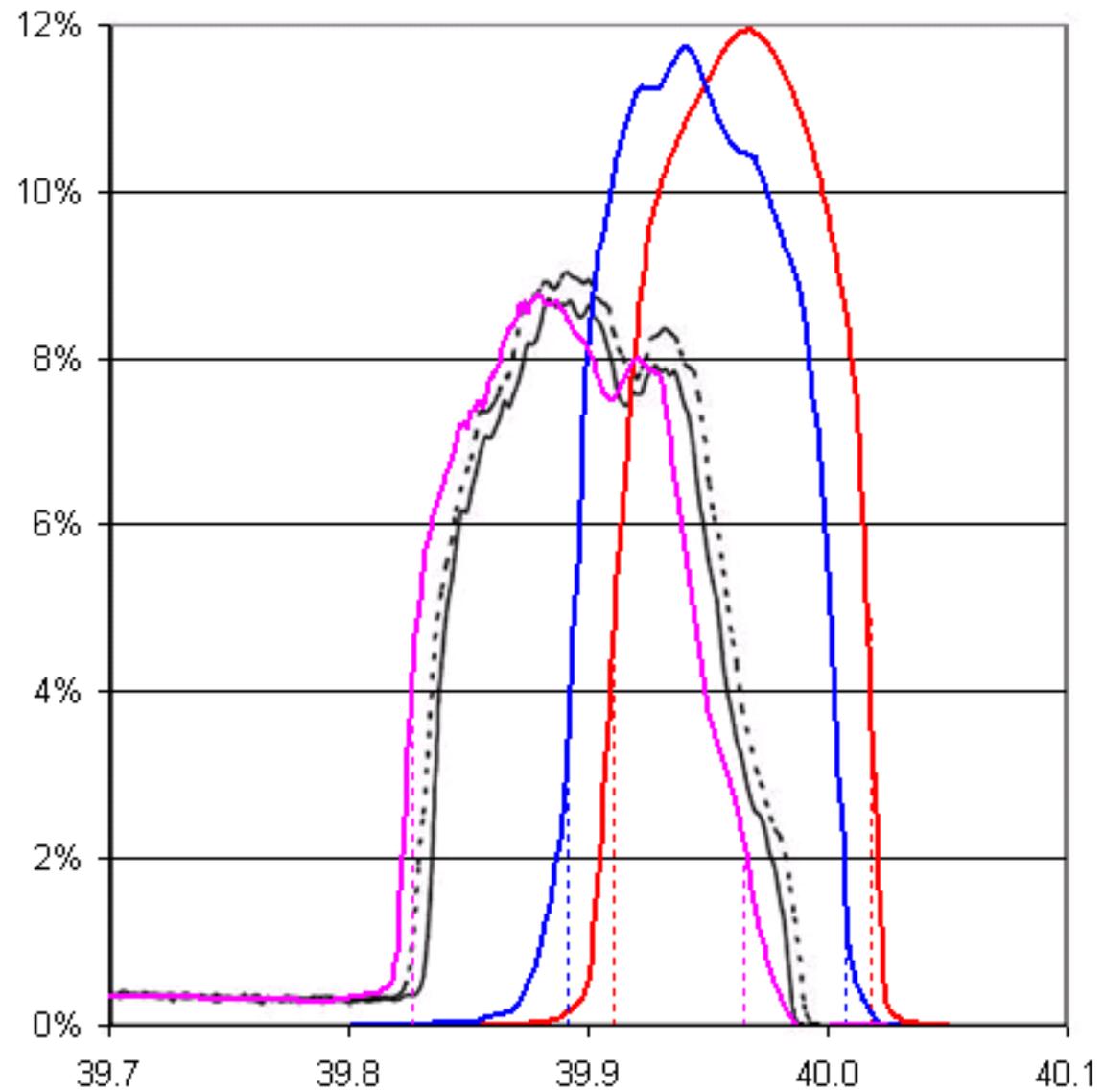
Mathieu stability region and scan line



Peak

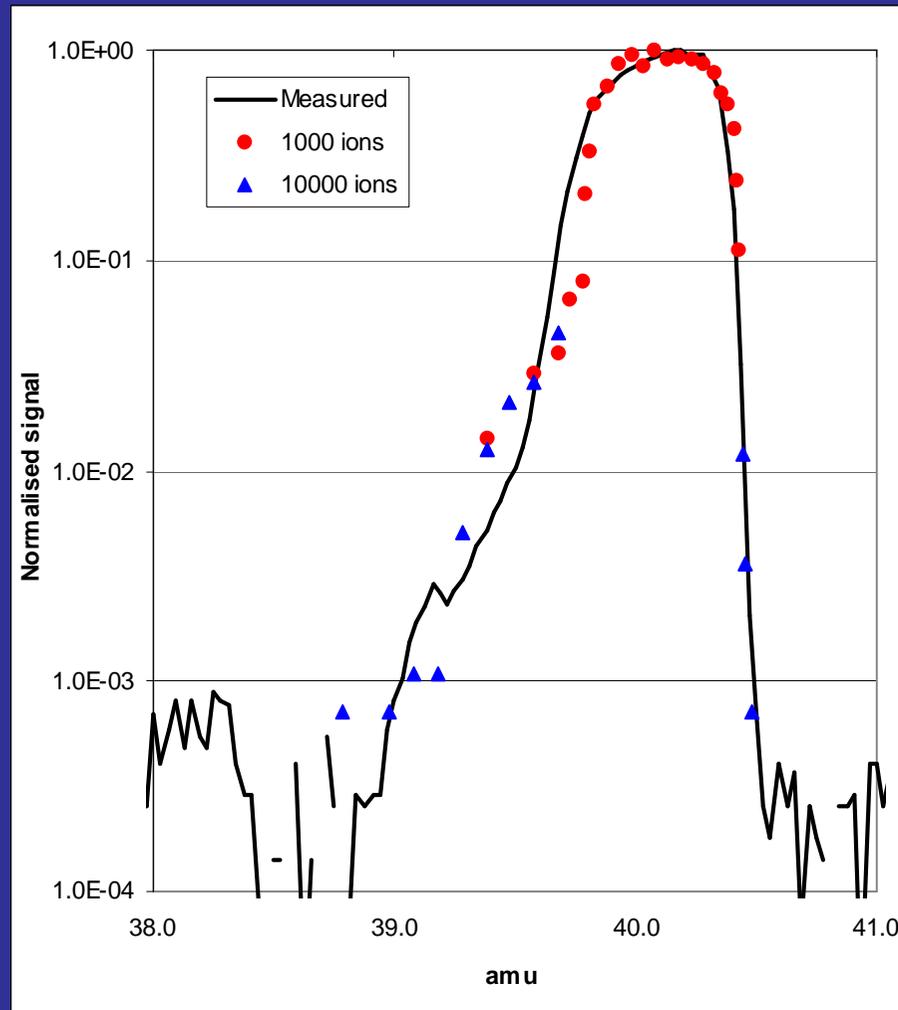
The stability region is shifted to lower mass by 0.068 amu, and the boundary is more complex near the tip. There is structure on the top of the peak, and a persistent low mass tailing effect. The peak width is broader (0.139 amu) and the transmission is reduced.

The result agrees well with data from Taylor & Gibson



This shows atmospheric argon monitored by a typical small quadrupole[†]. Also plotted are points from the round rod SIMION model already described, which is not the same as the quadrupole used for the measurement. So the scan line and ion energy have been adjusted to give a reasonable fit to the experimental data. However,

there are clear differences on the low mass side of the peak. Adjusting the ion energy distribution and/or the ion beam divergence might improve the comparison.



Scan line slope:	0.1678 V
Scan line offset:	0.1639 V
Ion energy:	7 eV
Number of ions:	1000 (10000)

[†] Cirrus: MKS Spectra Products

Conclusions

- A quadrupole with non-ideal electrodes can be modelled tolerably well using SIMION to perform all the calculations.
- In principle the same approach can be applied to a true 3D model (thus allowing for fringing fields) but the potential arrays would become prohibitively large.
- Nevertheless it would be instructive to set up a 3D model with coarse grid spacing.
- A disadvantage of this approach is that the simulations run quite slowly – in this study it took several hours to trace 100,000 ions.