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Prediction of quadrupole mass filter performance for hyperbolic and circular cross section electrodes

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A computer model has been developed that is able to predict the performance of a quadrupole mass spectrometer (QMS) for any constant cross section electrode geometry. It has been used to predict the performance of QMS systems with both hyperbolic and circular cross section electrodes. The predictions confirm the limited previous work that indicates QMS performance is poorer when circular cross section electrodes are used rather than hyperbolic ones. There is also an indication that use of circular electrodes causes a movement of the peak position from the expected one and produces an extended tail on the low mass side of the peak. Copyright © 2000 John Wiley & Sons, Ltd.

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There have been many analytical predictions of the behaviour of quadrupole mass spectrometers (QMS); an extensive review is given in Reference 1. Except for computations by Blaum *et al*,[2] recent work[3–6] examines quadrupole ion traps (QIT); however, computational problems are closely related to those for QMS systems. Most detailed predictions of QMS behaviour are for fields created by electrodes with hyperbolic cross sections. However, with a small number of exceptions,[8,9] instruments are constructed with circular cross section electrodes. There have been a number of analytical attempts[1,10,11] to determine the effects of non-ideal construction such as the use of round rods instead of hyperbolic ones.

In a previous paper[12] we described new computations predicting QMS behaviour. Although these were for hyperbolic electrodes the results exhibited many of the features observed using instruments with round electrodes. We now report results using a revised computation method that allows any electric field distribution to be used. Using the field distribution for hyperbolic cross section electrodes the results are identical to our previous ones; however, we are also able to predict QMS behaviour for circular cross section electrodes. The results indicate that performance with circular cross section electrodes is '*poorer*' than with hyperbolic electrodes as indicated elsewhere.[8]

THE COMPUTATION MODEL

As previously,[12] a large number of ions are generated (at least 10^5 at each point on the mass scale). The ions are random in both time relative to the a.c. field and in position at the entrance of the mass filter. The ion source model has been enhanced; if required the ions may have a spread of energies instead of all having identical energy. Also ions may be generated so that they enter the mass filter with their direction of travel spread over a range of angles instead of all being parallel to the QMS axis. Both of the spread features generate ions at random within user selected truncated Gaussian profiles. Generally, for both the previous and new programs, the effect of these spreads on QMS performance is small.

The field generated by the electrodes starts immediately the ions leave the source and ions are detected if they pass through a circular disc at the exit of the filter, that is fringe field effects are ignored. Rectangular Cartesian co-ordinates are defined with the QMS axis in the z direction and the electrodes positioned as in Fig. 1 (circular section electrodes illustrated). Ions are traced through the filter by determining their motion in the field produced by the electrodes.

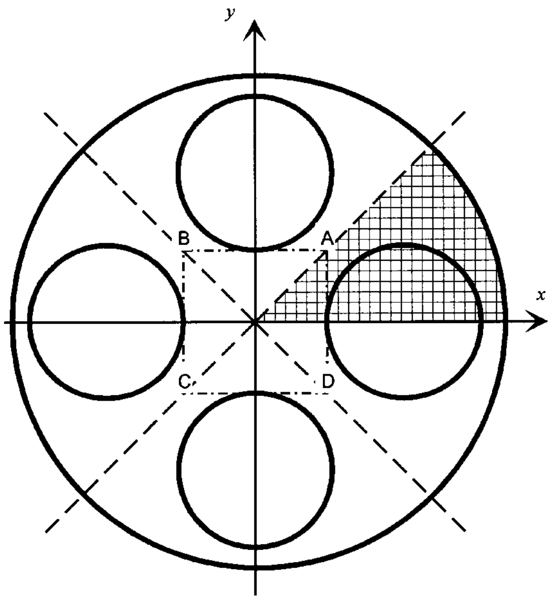

Figure 1. Cross section of the QMS, circular section electrodes illustrated.

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Because fringe fields have been ignored ions travel with constant velocity in the z direction; whenever the distance of an ion from the axis exceeds the filter radius, r_0, it is rejected. Ions that pass through the exit disc form the received signal.

The ion travel is divided into small time intervals and ion motion over each interval is computed using the instantaneous local field. It is considered that over very short time intervals the motion in the x and y directions may be examined separately. That is the motion is defined by

$$qE_x = m\frac{\partial^2 x}{\partial t^2} \quad \text{and} \quad qE_y = m\frac{\partial^2 y}{\partial t^2}$$

where q is the charge of the ion, m is its mass, and E_x and E_y are the electric field components in the x and y directions respectively at the ion position (x,y). Solution using separate x and y components over short time intervals is exact when the E_x field does not vary in the y direction and the E_y field does not vary in the x direction. This is true for the field from correctly positioned hyperbolic rods but is not strictly correct for other cases. Provided the time intervals used to evaluate ion motion are very small the approximation does not affect the results; this was tested by varying the time interval. The motion of each ion over one time interval is determined using a fourth-order Runge-Kutta algorithm. Whenever electric fields are required to evaluate the algorithm they are determined from a separate field description (in the previous program the analytical expression for the field from hyperbolic electrodes was incorporated into the equations of motion). This modification allows any field distribution to be used; however, it has the disadvantage that the new program runs much more slowly than the previous one.

ELECTRIC FIELD COMPUTATIONS

The new program requires the electric field at any position (x,y) to be available when tracing ion trajectories. The field is represented by the values of E_x and E_y at all points on a rectangular grid. The values are determined for unit voltages on the rods (x rods positive, y rods negative); field values are obtained by multiplying grid values by the instantaneous value of the rod voltages. To determine QMS behaviour values are only required at all points on a grid with sides of length $2r_0$, that is inside the square ABCD in Fig. 1. However, accurate grid value determination usually requires a much larger grid as fields must be evaluated up to known boundary values (for example the housing).

To determine ion motion the grid values may be used in several ways. The most simple method to obtain the field components seen by an ion at a particular position is to use the values at the nearest grid point. An alternative is to extrapolate values using the values at the corners of the grid square containing the ion position. Although the extrapolation process significantly slows program execution, the limits set by computer memory size restrict the maximum grid size (use of disc storage, virtual memory, to hold larger grids is slower than extrapolation). Investigations were made using a grid of field values for hyperbolic electrodes computed from analytical expressions. These showed that linear extrapolation allowed the grid interval to be more than doubled when results were required to match those from our previous program.[12] This corresponds to a reduction by a factor of four in required memory size so the extrapolation method was adopted.

The new program was used for QMS systems with both hyperbolic and circular cross section electrodes. In the case of hyperbolic electrodes the field values for the grid were calculated from the analytical expressions. In all other cases a standard '*mesh*' evaluation was used. One common method of field evaluation is the finite element technique; however, even commercial programs do not allow use of the number of elements shown to be necessary by examination of results for hyperbolic electrodes.

An alternative slow iteration method was adopted. Because the fields are only evaluated once for a particular electrode geometry this is not a serious disadvantage. There is symmetry about the axes and the diagonals so it is only necessary to determine the fields for a sector forming one eighth of the QMS (Fig. 1). The fixed potential boundaries for field evaluation are the two sector radii, the surface of one electrode and the housing. The electrode radius was $1.148 \times r_0$ which is the value usually accepted as providing the best performance.[13,14] For computational convenience, the housing used was a ground potential cylinder with radius $3.6 \times r_0$.

The region formed was divided into the required mesh, indicated with fewer elements than were actually used in Fig. 1. The field evaluation was performed by first determining the potential distribution from the solution of Laplace's equation at each grid point. The iterative method, a simple relaxation process, determined a new potential at every grid point as a quarter of the sum of that at the four adjacent points. Starting with initial zero values at all points, except the rod surface, new values were determined at all grid points in free space. Interpolation was used where electrodes intersected the mesh. This evaluation process was repeated for several days until the potentials at several, well-separated, sample points no longer changed significantly (less than 1 part in 10^8) after a further one thousand iterations. Partial differentiation of the potentials, using a linear approximation at each grid point, gave the electric field components.

SIMION, and alternative packages, used in other investigations[2–6] use over-relaxation methods; in addition SIMION uses a pixel-based electrode description. Detailed examination of results (number of ions transmitted at each point on a simulated mass peak) when the new QMS programme was forced to use the same random ion set for each run showed that small differences were obtained if the iteration was not performed to the high degree of convergence used. Attempts to use over-relaxation to achieve this very high degree of convergence tended to become unstable because rounding errors affected the projections required. A pixel-based electrode structure will also produce field variations comparable with the degree of convergence shown to be required, the interpolation method adopted here overcomes this.

The mesh size for the fields and the time interval when computing the ion trace interact. Over a limited range one can be increased if the other is decreased. As the x and y motions are not strictly independent for non-hyperbolic electrodes it was decided to use much smaller time steps than previously. With these small steps QMS behaviour was examined for hyperbolic section electrodes using different grid sizes; provided the interpolation technique was used it was found that the results were independent of the mesh interval if this was chosen to be $0.002 \times r_0$ or less.

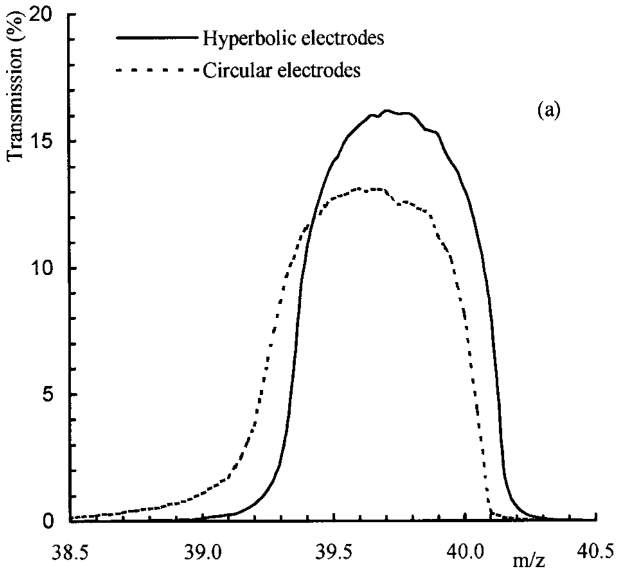
RESULTS

All computations determined the QMS peak profiles by tracing between 1×10^5 to 2×10^5 ions at about 50 to 80 different mass points. The entrance aperture radius was about $0.35 \times r_0$ and the exit aperture radius was r_0.

Previous work[12,15] has shown that QMS behaviour depends on the number of cycles of the radio frequency (r.f.) field experienced by an ion. The behaviour of the QMS filter was examined for a range of values of the number of cycles using singly charged ions of mass 40. Identical results were obtained for other mass ions that experience the same number of cycles. As previously[12] the QMS resolution setting was defined as the ratio of the d.c. to a.c. voltages denoted by η where $\eta = 1$ corresponds to the peak of the stability diagram. Figure 2 shows mass peaks for both hyperbolic and circular section electrodes using two values of η; the ions experienced 48 cycles of the r.f. field and the mass scale was defined as before.[12]

Similar differences were observed between the mass peaks for the two electrode forms for all QMS conditions except η >1.0 (outside the stable region). Transmission was lower for circular section rods and, in addition, circular rods produced a long low mass tail that was pronounced at high values of η. An unexpected feature was the reduction in the high mass side of the peak for circular rods; this caused the peak position to appear at a lower mass than expected. This peak shift would not be observed in practice as instruments are calibrated by use of known samples, rather than by absolute voltage measurements. Circular rods produced lower resolution than hyperbolic ones but the difference in peak shape means that the amount by which resolution changed varied with definition of resolution. When the common definition of width at 10% of peak height was used resolution for circular electrodes was much lower than for hyperbolic ones; however, if resolution was defined at 25% or 50% of peak height the reduction in resolution was less.

Comparison of QMS behaviour for the two electrode forms is shown as a function of η for peak width (represents resolution), Fig. 3, and transmission, Fig. 4. In general the performance of circular electrodes was *'poorer'* than that of hyperbolic ones although single values cannot be given for the difference in resolution or transmission. Transmission performance was complex. At low values of η the transmission using hyperbolic rods was not affected by number of r.f. cycles; for circular rods there was a small reduction in transmission as the number of cycles increased. Close to maximum resolution, η >0.995, transmission



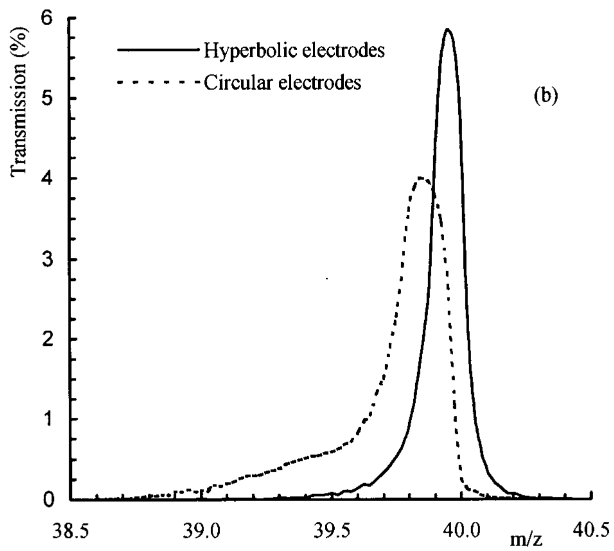


Figure 2. Computed mass peaks for ions with *m/z* 40 using (a) U/V ratio η = 0.985 and (b) U/V ratio η = 0.9975.

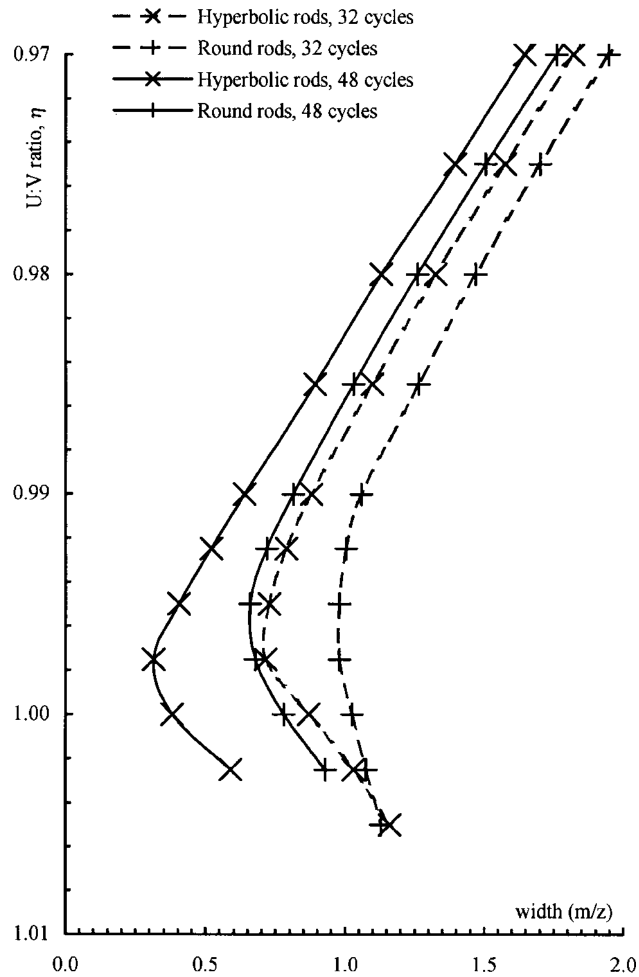


Figure 3. Variation of peak width for ions with *m/z* 40 for change in QMS resolution setting η.

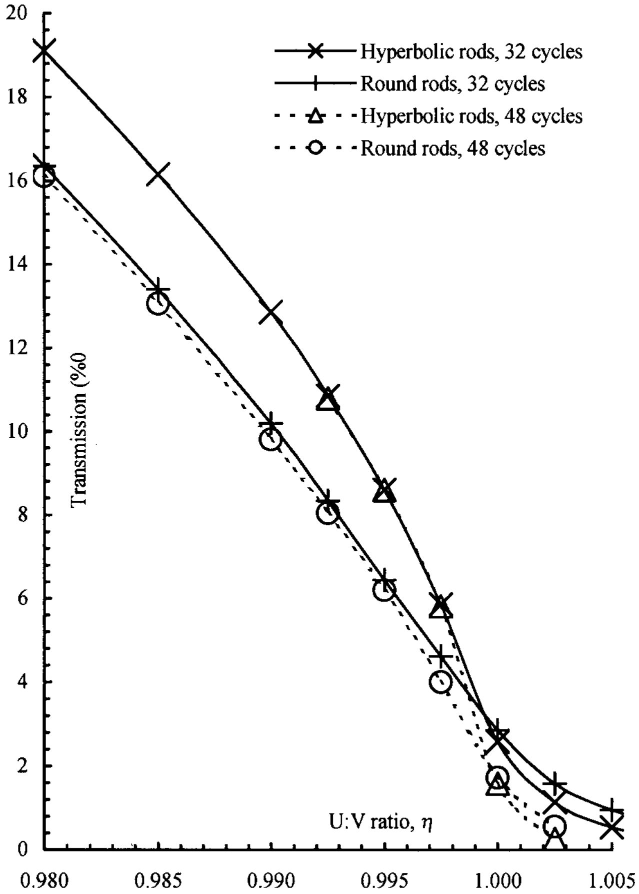


Figure 4. QMS transmission (peak height) for ions with *m/z* 40 as a function of the resolution setting η.

varied with the number of cycles for both electrode forms. The low mass tail for circular rods persists as η rises and prevents transmission falling as rapidly as for hyperbolic rods when η approaches 1. Consequently, the transmission curves for the two forms may cross near $\eta = 1$; however, for $\eta \geq 1$ peak shapes are poorly defined and transmission is very low so most instruments cannot be operated in this region.

QMS instruments are usually operated close to the maximum resolution possible (minimum peak width) provided that the signal intensity is adequate. To show the variation between the two electrode forms we chose $\eta = 0.9975\%$ and computed resolution, Fig. 5, and transmission, Fig. 6, as a function of the number of cycles. The uncertainty in peak width for circular rods above 60 cycles arises because the 10% level intersects the low mass tail, the width cannot be accurately determined when only 2×10^5 ions are used. Comparison cannot be reduced to simple numeric values but, for a high resolution instrument (many r.f. cycles), the use of round rods instead of hyperbolic ones typically reduces the resolution by a factor of 2 (as suggested in reference[2]). Change in transmission at high resolution for the case selected is also reduced by about a factor of 2 but this varies by a large amount as η is varied.

CONCLUSIONS

A computer model of a QMS has been created which allows the fields for electrodes of any geometry to be used. The model has been used to show the difference between hyperbolic and circular section electrodes. In general the hyperbolic electrodes produce a resolution up to twice that for round rods and show improved transmission. The results indicate a long tail on the low mass side of the peak for circular electrodes which can reduce the ability of an instrument to resolve small mass peaks close to large ones.

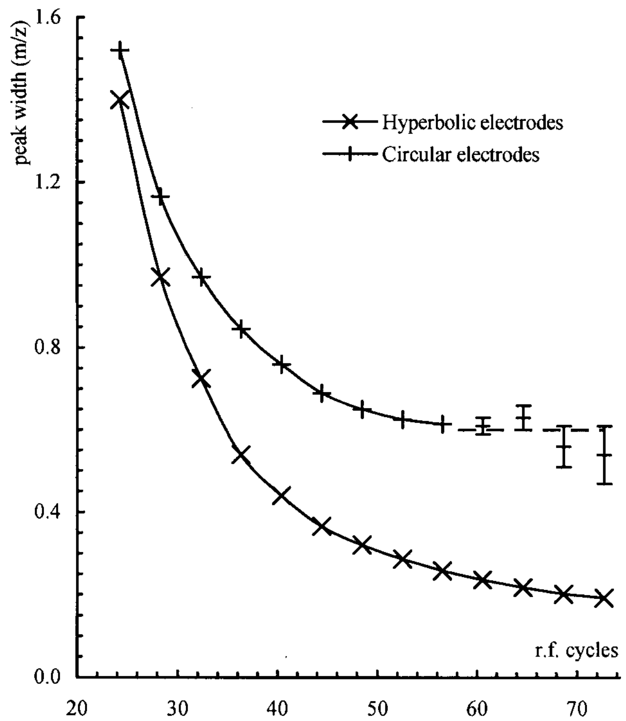


Figure 5. Predicted resolution (peak width) for ions with *m/z* 40 as a function of number of r.f. cycles; resolution setting $\eta = 0.9975$.

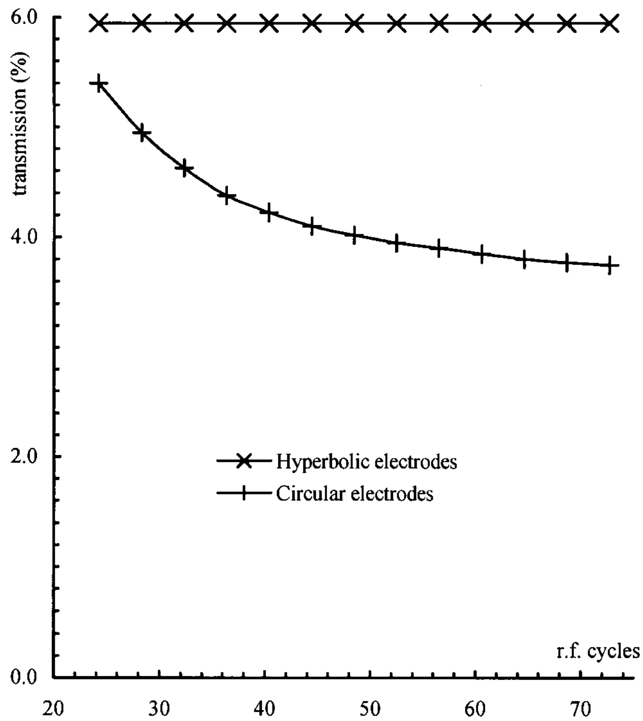


Figure 6. Predicted transmission (peak height) as a function of number of r.f. cycles; conditions as in Fig. 5.

Although a low mass tail is often observed with real circular electrode QMS systems it is usually not as pronounced as the model predicts.

The model can be applied to any QMS electrode geometry; all that is required for a different geometry is the grid of field values. The disadvantage of the model is that computation time is significantly increased, typically by five to ten times, compared with that for our previous model[12] (results for Figs 3 and 4 required several weeks of continuous computation using a 400MHz Pentium CPU and 256Mbytes of RAM).

Use of a general purpose ion optics package cannot produce some features we have shown to be necessary in a QMS model; for example, SIMION cannot model the very large number of ions previously shown to be necessary.[12] Additionally techniques such as over-relaxation and pixel-based descriptions of geometry limit field calculation accuracy but are essential for packages with unrestricted user descriptions of electrodes. However SIMION operates in three dimensions and the results of some of the QIT computations using SIMION[3,4] show that fringe fields influence behaviour, in some cases beneficially. Also Titov[7] has shown that QMS fringe fields may be the source of precursor peaks. The fringe fields may affect the region on the low mass side of the peak; it is possible that they reduce the size of the tail. Fringe fields and other features, for example source radius and exit radius, remain to be investigated with this new model.

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