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Numerical investigation of the effect of electrode size on the behaviour of quadrupole mass filters

John Raymond Gibson* **and Stephen Taylor**
The Department of Electrical Engineering and Electronics, The University of Liverpool, Brownlow Hill, Liverpool L69 3GJ, UK

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The behaviour of a quadrupole mass spectrometer (QMS) for variation in rod size has been investigated using a numerical approach reported previously. Behaviour is found to vary significantly with the change in rod size and the optimum rod size suggested is closer to that used in some commercial QMS instruments than to the value from analytical approaches. The results allow an upper limit to manufacturing tolerances to be inferred. The present work also confirms that the size of the QMS housing has only a very small effect on QMS behaviour. Copyright © 2001 John Wiley & Sons, Ltd.

Quadrupole mass spectrometer (QMS) systems are usually manufactured with circular section electrodes although the original design assumes the use of hyperbolic section electrodes. We previously reported[1] predictions of performance when circular cross section electrodes are used instead of hyperbolic section ones. The results showed differences in predicted QMS behaviour for the two geometries. In particular, the circular section system had lower resolution, mass peaks had a long low mass tail, and the ions had to experience more cycles of the radio-frequency (rf) field for good filter performance to be obtained (longer system).

Further application of the model has allowed some design features of QMS systems to be investigated. In particular, the effects of rod size, the housing, and a few features of the low mass tail have been examined.

ROD SIZE

When hyperbolic cross section electrodes are used the surface cross section should be located on a right-angled hyperbola with its axis at the QMS axis. For a perfect system the only effect of changing electrode size is to require changed electrode separation and different applied voltages; QMS behaviour is unaffected by electrode size if the ion source is scaled such that the source radius is scaled so that the ratio of radius to rod separation remains the same. If the ion source is not scaled then transmission increases as the rod size increases because ions close to the axis have a higher transmission probability than those distant from it. When circular cross section electrodes are used they are positioned so that the electric field approximates to that for hyperbolic electrodes. The field produced depends on the ratio of the rod radius, r, to the distance from the rod surface to the QMS axis, r_0. Changes in the ratio r/r_0 affect QMS performance.

Early theoretical considerations of QMS design[2,3] determined an optimum value for r in terms of r_0. The earliest such work was an empirical treatment[2] which suggested that a value of $r = 1.148 \times r_0$ should be used. This result was incorrectly quoted by Paul *et al.*[4] as $r = 1.16 \times r_0$; this was subsequently quoted elsewhere and adopted by some QMS manufacturers.

A more formal treatment by Denison[3] expanded the field of the circular electrode quadrupole as an infinite series of multipole components with terms present only for 4-poles (quadrupole), 12-poles, 20-poles, and so on. The field was determined numerically and compared to a multipole expansion in which the coefficients of each term were varied to obtain a least-squares fit to a large number of points in the computed field. Multipole terms were added until addition of further terms resulted in no change in the coefficients previously obtained; twelve terms were required. A perfect system using hyperbolic electrodes will produce only the quadrupole field. Therefore, it was assumed that the use of the value of r/r_0 which caused the 12-pole term, the first after the quadrupole term, to be zero would provide optimum QMS behaviour; this required $r = 1.1468 \times r_0$. It was also shown that QMS sensitivity at high resolution is improved if $r = 1.1468 \times r_0$ rather than $r = 1.16 \times r_0$. Later, Dawson and Whetten[5] showed that presence of the 12-pole term can limit the maximum resolution that can be obtained.

An analysis[6] for the identical case of an ideal magnetic quadrupole system determined a marginally different value for the 12-pole term to be zero giving an optimum condition of $r = 1.14511 \times r_0$. A more recent analysis[7] is similar to this[6] (the authors appear to not have been aware of the earlier work), and again the work suggests the optimum condition occurs for $r = 1.14511 \times r_0$. Many commercial QMS instruments use values of r/r_0 found experimentally. Most values have not been published, although Blaum *et al.*[8] indicate that two particular instruments use values of 1.127 and 1.16 (in some cases instruments have auxiliary electrodes intended

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**Correspondence to*: J. R. Gibson, The Department of Electrical Engineering and Electronics, The University of Liverpool, Brownlow Hill, Liverpool L69 3GJ, UK.
E-mail: jrgjrg@liv.ac.uk

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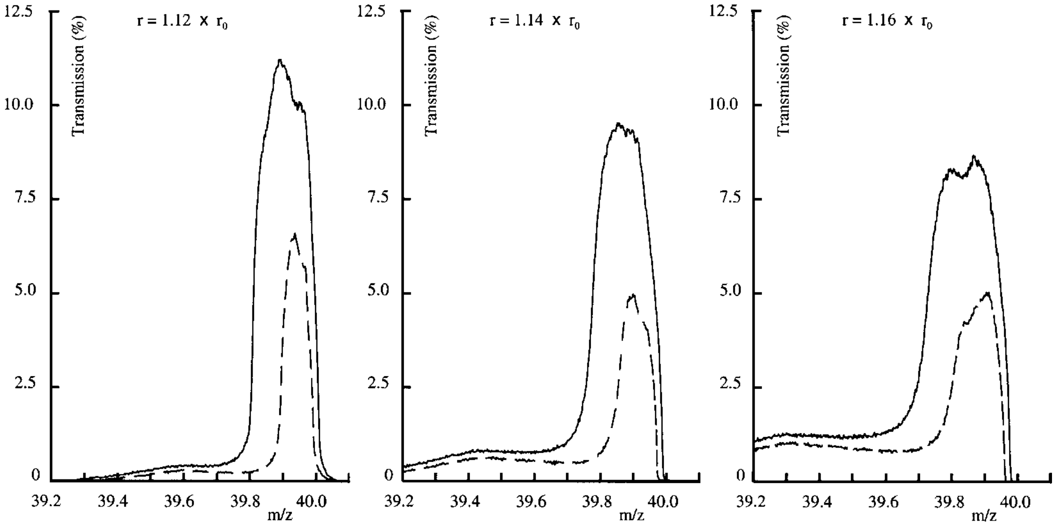

Figure 1. Computed spectra for a single ion species for three values of r/r0. Solid lines $\eta = 0.9990$, broken lines $\eta = 0.9995$.

to compensate for field deviations so direct comparison is not strictly correct).

It is reasonable to assume that the field using circular electrodes is such that effects of the 12-pole term are the most significant. For many values of r/r_0, this term produces the largest non-quadrupole contribution to the field in the central region of the QMS system which is probably the most critical field region for QMS operation. Reuben *et al.*[7] calculate the coefficients of the multipole terms exactly and also illustrate the variation of coefficients with values of r and r_0.

However, it is only an assumption that a zero value of the 12-pole term will correspond to best QMS behaviour. This is not necessarily true; an infinite number of higher order terms still exist. Although the coefficients decrease rapidly with rising order it is possible that their total contribution could be more significant than that of the 12-pole term. We have used our circular electrode model to examine QMS behaviour for values from $r = 1.110 \times r_0$ to $r = 1.160 \times r_0$. Our earlier analytical results for hyperbolic electrodes[9] suggested that mass peak shape depends on the form of the initial ion beam entering the QMS system; this dependence has also been shown for an ac-only QMS system by Muntean.[10] For a system with hyperbolic electrodes, the overall trends in behaviour (transmission and resolution) do not vary strongly with ion source characteristics; it is mainly the absolute values of these quantities that change. For circular electrodes we have found a stronger dependence of QMS behaviour on the ion source properties. Unless explicitly stated, all the present computations were made using the ion source model and QMS system defined in Table 1. The general trends in QMS behaviour were similar when different models were used.

Figure 1 shows simulated mass spectra for a single ion species at three r/r_0 values using two QMS resolution control settings. The instrument resolution setting, η, is as defined in our earlier paper[9] as the ratio of the d.c. to a.c. voltages where $\eta = 1$ corresponds to the peak of the stability diagram when hyperbolic electrodes are used. (By keeping η constant the computer model is strictly mass-independent but results are more easily compared to experimental ones if a particular mass is used. The instrument resolution in terms of mass divided by peak width is constant for varying mass. Many instruments are operated so that peak width, rather than resolution, remains constant as mass is varied. Note that Reuben *et al.*[7] showed that the stability peak conditions change slightly when round rods are used. For ease of comparison with our earlier work, we have defined the resolution setting, η, from peak conditions as if hyperbolic section rods are in use.) As previously, the calculations were performed for a medium-size QMS instrument (Table 1) using singly ionised argon.

A number of features are apparent from Fig. 1. Peak height, peak shape and the low mass tail change with r/r_0 when all other conditions are constant. The tail reduces to some extent as r/r_0 decreases; also change in resolution setting does not affect the amplitude of the low mass tail to the same extent as it affects the main peak height. Overall the behaviour of the tail is complex and requires further investigation; other effects follow more simple trends.

The variation in transmission (sensitivity, peak height) with the r/r_0 ratio is shown in Fig. 2; generally transmission increases slightly as r/r_0 falls, although there is limited evidence of a small increase at high r/r_0 values. While increased peak height improves sensitivity of a QMS system the improvement in peak height has a relatively small effect

Table 1.

Ion energy	2.000 eV
Ion energy spread	None
Ion angular spread	None
Ion distribution	Constant (uniform source)
Ion source radius	0.5 mm
QMS length	0.254 m
r_0	2.76 mm
QMS frequency	2.0 MHz
Approx rf cycles experienced	164
Exit aperture	QMS radius

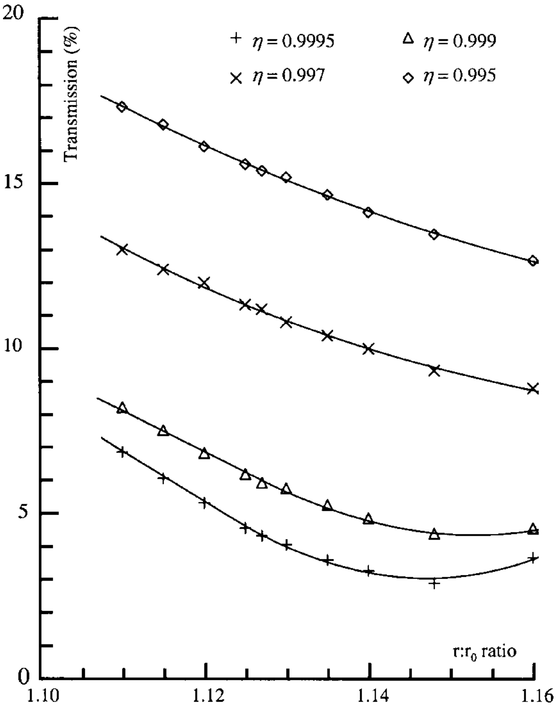

Figure 2. Transmission (peak height) as a function of r/r$_0$ at four QMS settings.

on overall performance when compared with changes in resolution and peak shape.

A more important result is that the peak width changes with r/r$_0$ exhibiting a clear minimum in the region between r = 1.120 × r$_0$ and r = 1.130 × r$_0$, particularly at high resolution. This is best illustrated by the ability of the QMS to resolve adjacent mass peaks as a function of r/r$_0$. This ability, instrument resolution, is defined here as nominal ion mass divided by the peak width at some fraction of the peak height. While QMS resolution is often measured at 10% of peak height (sometimes 5%), both the low mass side of the peak and the low mass tail vary with ion source conditions. This means that results for resolution defined at 10% of peak height are strongly ion source dependent. Precise determination of the 10% value is difficult at the highest values of r/r$_0$ as the low mass tail interferes with the side of the main peak (with some dependence on ion source behaviour). Therefore, the resolution is shown at both 50% of peak height (Fig. 3) and at 10% of peak height (Fig. 4). The results in Fig. 4 vary more than those in Fig. 3 if the ion source model is changed. Only 150000 ions are used at each mass point causing small statistical fluctuations in the results. Additionally, there are some variations in the peak shape and structure with resolution making the exact peak height difficult to determine. These effects cause some scatter in the resolution values estimated to be typically about 1% and never above 2.5%. The resolution values using 10% peak height were inferred as if the low mass tail was absent at the highest r/r$_0$ value for the ion source model used. This was because this ion source model produced an unusually large tail at this value; such large tails are not observed in practice.

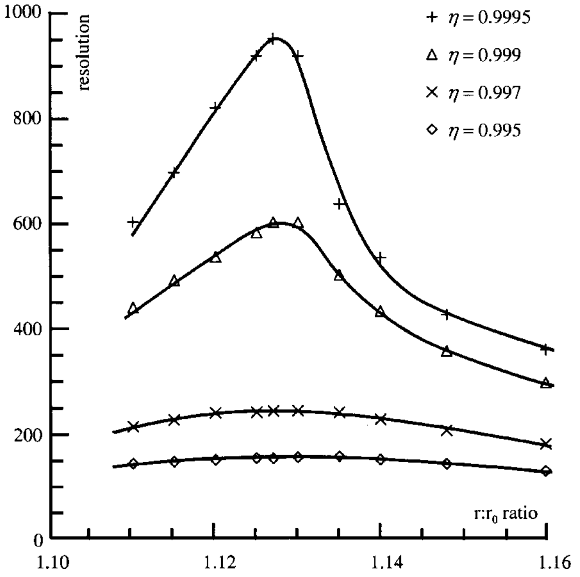

Figure 3. Resolution (mass divided by peak width) at 50% of peak height as a function of r/r$_0$.

It was considered unreasonable to reduce the statistical scatter because of the increase in computation time necessary for a significant improvement. Each peak computed at one r/r$_0$ value, one resolution setting and one ion source model requires between 8 and 30 h computation using a 933 MHz Pentium system with 768 Mb of PC133 RAM. Halving the scatter would approximately quadruple these times. Our previous result[1] showed that the resolution was nearly constant after ions had experienced about 80 cycles of the rf-field. However, the shape of the regions on both sides of the main peak at levels below about 20% transmission continued to change slightly as the ions experienced more cycles of the rf-field. For our investigations with hyperbolic rods such effects are much less significant. To produce consistent results computations were extended to about 160

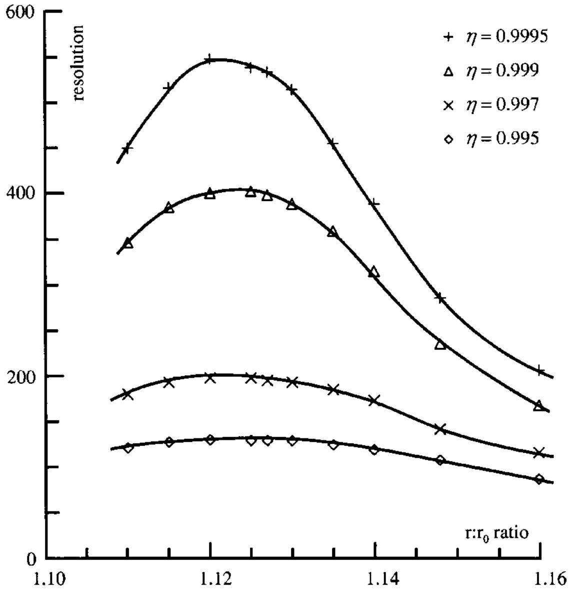

Figure 4. Resolution (mass divided by peak width) at 10% of peak height as a function of r/r$_0$.

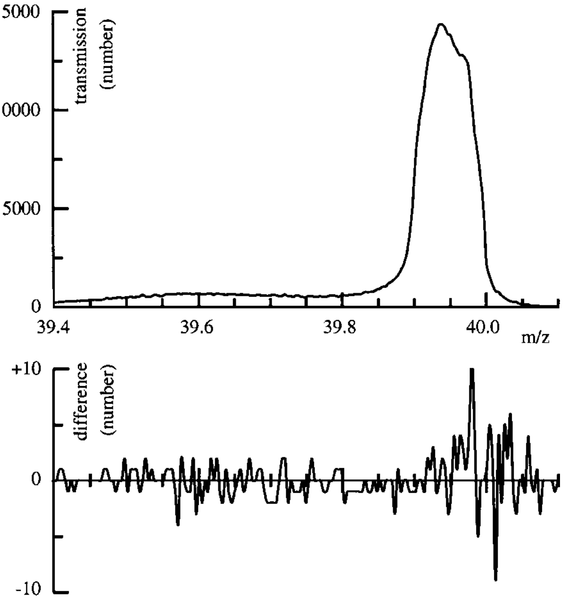

Figure 5. Typical spectrum of a single ion species and the differences in the spectrum for housing radii of 3.4 × r_0 and 4.2 × r_0.

cycles, equivalent to longer rods or higher frequency; this contributed to the high computation time.

Figures 3 and 4 suggest an optimum value near $r = 1.125 \times r_0$ rather than the previous suggestions[2,3,6,7] of around $r = 1.146 \times r_0$. Also the curves suggest the effect of varying r/r_0 is more pronounced at higher resolution settings. For example, the resolution doubles when r decreases from $1.16 \times r_0$ to $1.125 \times r_0$ with $\eta = 0.9995$, whereas it only changes by a factor of 1.2 with $\eta = 0.995$.

HOUSING

The early work by Denison[3] also considered effects of the housing enclosing the electrodes and concluded that any effect of the enclosure was small, although no estimate was given of the effect. Recent work[7] states that the optimum r/r_0 value is not affected by the housing. (Here optimum implies the best resolution, the work does not indicate if the housing has any effect on other features of QMS performance such as transmission or peak shape.)

In our computations we assumed a circular conducting housing at zero potential with housing radius 3.6 × r_0. The radius was selected as sufficiently greater than the QMS system to allow reasonable computation of fields between the outer electrode edges and the housing, but did not lead to excessive computation time for field evaluation. We also calculated fields for housing radii of 3.4 × r_0 and 4.2 × r_0 for the case of $r = 1.12 \times r_0$. The value 1.12 was chosen as this produces a larger gap between adjacent rods than a larger value, such as 1.1468. If field penetration influences the results it should be more easily detected with the lower value of 1.12. For a housing of radius 3.6 × r_0, field determination required between one and two weeks continuous computation; for a radius of 4.2 × r_0, the time increased to nearly six weeks.

We modified the QMS model so that, although the ions were still selected randomly, exactly the same random selection was used to examine performance with different housing sizes. Mass peaks were examined at a number of resolutions using 2×10^5 ions at each of 250 masses from 39.0 to 40.1 for mass 40 ions. Differences were extremely small for the cases of 3.6 × r_0 and 4.2 × r_0 (differences at only five of the 250 points exceeded a single ion). Differences between the results using 3.4 × r_0 and the other two cases were larger but still very small. They are illustrated by Fig. 5, which shows the computed mass peak at a resolution of $\eta = 0.999$ and the difference between the values for the largest and smallest housing sizes. Figure 5 rarely shows differences of more than three ions transmitted; this could easily be accounted for by rounding errors in the electric field evaluations. However, all cases examined (even the cases with very small differences) showed a small region on the high mass side of the peak where QMS transmission differs by a larger amount; Fig. 5 shows cases differing by about ten ions corresponding to a few percent of the total transmitted. As these larger differences do not occur at the peak they are not proportional to the number of ions transmitted. They correlate to the high mass side of the peak that is associated with stability in the y-direction; i.e., the housing does appear to affect the high mass side of the peak but the effect is extremely small and probably below the noise level in any real instrument.

CONCLUSIONS

Using the computer model previously reported we have shown that the optimum value of the r/r_0 ratio used in QMS design is lower than that suggested by previous work. It is not possible to give a single figure for the optimum r/r_0 ratio because results are influenced to a small extent by the form of ion beam entering the QMS. However, a value in the range $r = 1.12 \times r_0$ to $r = 1.13 \times r_0$ produces the best performance. Variation of resolution, transmission and peak shape indicates that, even for a perfectly constructed system, changes will be observed in QMS behaviour at high resolution if dimensions change by about 1% of the rod radius (about 20–50 μm for most instruments). It is probable that asymmetric imperfections in manufacture will produce larger effects; further, Titov[11] has shown that fringe field effects ignored in this work may cause precursor peaks (effects in the low mass tail). Therefore, the present results give a very approximate upper limit to the tolerances required in QMS manufacture.

The computations also produce mass peaks that match those observed in real QMS instruments with a tendency to have a small broad peak on the low mass side of the main filter peak. This small peak is affected less by the QMS resolution setting than the main peak but is affected by the form of the ion beam.

In addition we have shown that QMS performance is almost unaffected by the size of a circular section electrode housing, although an extremely small effect is observed on the high mass side of the peak.

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