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Computer Simulation of the Mass Filter for a Finite Length Quadrupole†

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The development of a computer program designed to simulate the performance of the mass filter in an ideal quadrupole mass spectrometer (QMS) is described. The simulation program provides flexible input parameters to allow the user to investigate the ion trajectories and transmission efficiency for different operating conditions. The program solves the Mathieu equation in two dimensions using a 4th-order Runge–Kutta iteration routine. the program is written in Turbo-Pascal and runs under DOS on any PC. The main original feature is the ability to simulate ion trajectories through the mass filter so as to study transmission efficiency for a finite length QMS under a range of operating conditions and for different design dimensions. The program has been used to analyse the change in QMS resolution with the number of RF cycles, DC voltage, ion energies, RF voltage magnitude and phase angle. The angle at which the ions enter the mass filter is significant and the effect of RF phase on transmission probability through the filter is critical. A comparison of the computer simulation with experimental results shows excellent agreement. The program also accurately predicts the long tail observed on the low mass side of the mass peaks.

A later version of the program incorporates Fourier series analysis to examine the effect of ion energies and entrance aperture for the mass filter for both sinusoidal RF excitation and RF with added harmonics. The addition of harmonics to the RF voltage reduces the instrument sensitivity compared with the sinusoidal case. However, for certain operating conditions, there is the possibility of operating the QMS with rectangular waveforms. This may be particularly advantageous when high frequency miniature quadrupoles are used.

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The quadrupole mass spectrometer (QMS) contains three basic elements: (i) ion source, (ii) mass filter and (iii) ion detector. There has been much associated experimental work but little has been written on the modelling of the mass filter.[1–3]

The equation of motion of the ions through a mass filter with hyperbolic electrodes is given by the Mathieu equation. The mass analyser selects ions with certain charge-to-mass ratios through the application of direct and alternating electric fields to the electrodes of the mass

$$\phi(x,y,z) = \phi_0 \frac{(x^2 - y^2)}{2r_0^2} \quad \textbf{(1)}$$

filter. The potential distribution ϕ in the ideal mass filter is given by the Eq (1) where:

$$\phi_0 = U - V\cos(2\pi ft) \quad \textbf{(2)}$$

The potential satisfies Laplace's equation and is invariant in the z direction. This potential, when substituted into the Lorentz equation, gives the Mathieu, Eq (3)

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u\cos(2\xi))u = 0 \quad \textbf{(3)}$$

where $\xi = \omega t/2$, $\omega = 2\pi f$, is the frequency of the RF voltage, and

$$a_u = a_x = -a_y = \frac{4eU}{m\omega^2 r_0^2} \quad \text{and}$$

$$q_u = q_x = -q_y = \frac{2eV}{m\omega^2 r_0^2}$$

The computer simulation solves the Mathieu equation both in the x and y directions and plots the trajectories of the ions.

SOFTWARE DETAILS

The program[4,5] (a copy with supporting documentation is available from S. Taylor) was written in Turbo-Pascal and runs under DOS on any PC with a VGA monitor. The program is fully menu-driven with a menu breadth of six and a maximum menu depth of three. The entire program suite is over 2000 lines long including error handling and data handling routines. The suite can be divided into three parts, as follows:
(i) ion trajectory determination, (ii) generation of Mathieu stability diagram and (iii) transmission analysis.

Each of the above options can be accessed independently and data files generated. The program allows the reproduction of graphs using data already in files. Separate filenames can be used to keep a record of results obtained and thus allow the construction of a database for a particular QMS design and/or mode of operation. The structure of the program is given in Fig.

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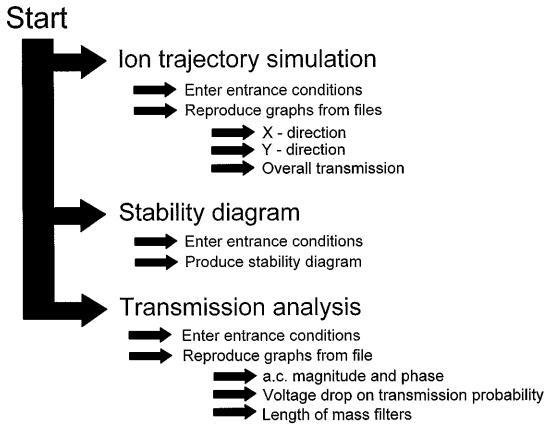

Figure 1. Tree diagram fcr simulation program.

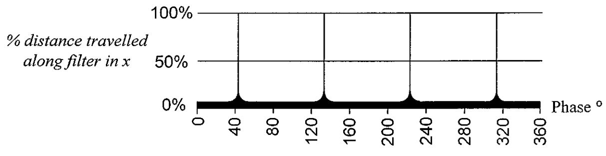

Figure 2. Ion transmission through the mass filter in the x-direction as RF phase varies from 0^0 to 360^0. $x_0 = y_0 = 0.3$ mm; $u_0 = 0$ m/s; $U = 20$ V; $V = 123.5$ V; the number of RF cycles $N = 100$.

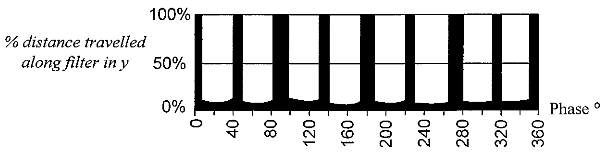

Figure 3. Ion transmission through the mass filter in the y-direction as RF phase varies from 0^0 to 360^0. $x_0 = y_0 = 0.3$ mm; $u_0 = 0$ m/s; $U = 20$ V; $V = 123.5$ V; the number of RF cycles $N = 100$.

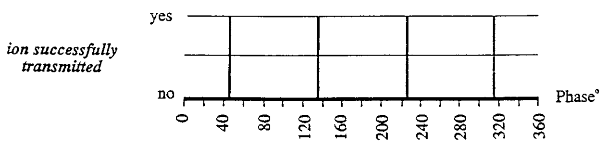

Figure 4. Ion transmission through the mass filter in the x- and y-directions as RF phase varies from 0^0 to 360^0. $x_0 = y_0 = 0.3$ mm; $u_0 = 0$ m/s; $U = 20$ V; $V = 123.5$ V; the number of RF cycles $N = 100$.

1. The following variables can be changed in the program: (i) a and q, (ii) number of ions input into the mass filter, (iii) initial phase angle, (iv) N, i.e. the number of cycles of RF voltage applied to the rods of the mass filter, (v) initial coordinate in x direction (mm) of the ion, (vi) initial coordinate in y direction (mm) of the ion, (vii) initial velocity of the ion in the x direction (m/s), (viii) initial velocity of the ion in the y direction (m/s), (ix) ion mass (amu), (x) frequency of the RF voltage (MHz) and (xi) field radius (mm).

RESULTS—TRANSMISSION ANALYSIS

Figures 2–4 show the transmission analysis for 360 ions with m/z 28 injected into the simulated mass filter. The direct and alternating voltages were taken to be $U = 20$ V and $V = 123.5$ V respectively, f (the frequency of the RF voltage was 2 MHz, and the inscribed radius was $r_0 = 2.75$ mm.

These figures reveal a number of interesting features: (i) the ion transmission probability and hence QMS performance, depends critically upon the phase of the ions of the mass filter. (ii) the RF phase has a greater effect upon the ion trajectory in one direction than in the other. (iii) Ions injected at different values of RF phase which are unstable and not transmitted through the mass filter are not equally unstable, e.g. ions at phase angle 50 ° (Fig. 2) travel further down the mass filter than ions injected at a phase angle of 100°.

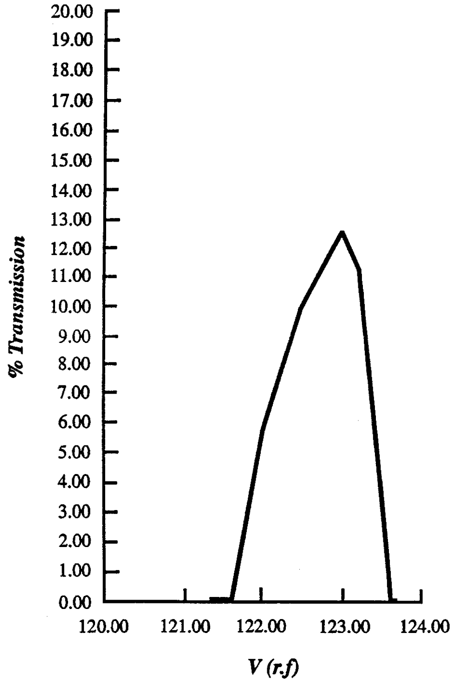

Figure 5. Simulated mass spectrum 100 ions injected with initial conditions $x_0 = y_0 = 0.3$ mm, $u_0 = 0$ m/s; $N = 100$.

EFFECT OF OPERATING CONDITIONS ON THE SIMULATED MASS SPECTRUM

By varying V, for a fixed U/V ratio, a mass spectrum can be generated. Figure 5 shows such a spectrum. Here, 100 ions with m/z 28, having zero entrance angle and velocity, were injected into the mass filter with fixed spatial location and with the same RF phase but with V varied between 120 and 124 V in 200 mV increments. The direct voltage U was kept at a constant ratio to V so that a line passing through a point below the tip of the stability peak for m/z 28 was effectively scanned. As V increases from 120 V the percentage of injected ions successfully transmitted rises to a peak at $V = 122$ V then falls sharply as V increases further. Simulation also predicts the long tail on the low mass side of the peak showing that it is not just a measurement artefact.

SIMULATION OF DIFFERENT LENGTH MASS FILTERS

Figure 6 shows the effect of altering the length of the mass filter. This is achieved by obtaining mass spectra for different numbers of RF cycles (N) experienced by the ions while keeping the frequency of operation constant, thus effectively altering the time for which ions are subject to the filter field. The curves illustrate graphically the importance of N in determining filter performance and show the dramatic improvement in resolution obtained by increasing N from 25 to 50 and

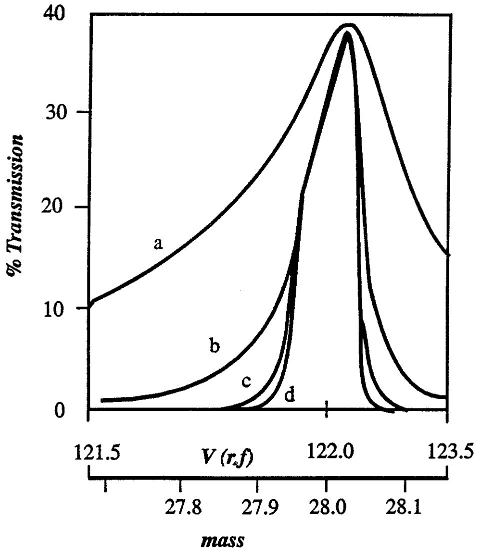

Figure 6. Effect of the number of RF cycles (N) on the mass spectra (a) 25 cycles; (b) 50 cycles; (c) 100 cycles; (d) 200 and 400 cycles.

Table 1. Effect of number of RF cycles (N) on intensity ratios. The mass and voltage scales from Fig. 6 have been multiplied by a factor of 10

Number of cycles	Ratio at m/z 279[a]	Ratio at m/z 281[b]
25	0.63	0.63
50	0.21	0.08
100	0.04	0.00
200 and 400	0.00	0.00

[a] Calculated as (intensity at m/z 279)/(intensity at m/z 280).
[b] Calculated as (intensity at m/z 281)/(intensity at m/z 280).

then to 100. However, the simulation shows no measurable improvement when N is increased beyond 200. Thus, under these particular operating conditions, $N = 200$ effectively represents an infinitely long filter. This result is particularly important as it allows the design and/or operating conditions of a mass filter to be tuned to a particular application, with a consequent reduction in manufacturing costs.

For a given mass peak it is possible to scale voltage and mass by the same fixed amounts since, in the definition of a_u and q_u in the Mathieu equation, the voltage and mass appear only as ratios. The peak height and shape will thus remain unchanged when U, V and m are ten times as large. On this basis, by multiplying the mass scale by ten, and the voltage, it is possible to calculate the abundance sensitivity data for the mass peak at m/z 280 from Fig. 6. For N to remain the same, however, the initial velocity of the ion along the major axis (z direction), must be unchanged.

Now, an indication of the abundance sensitivity at m/z 279 is given by the ratio of the peak height measured at m/z 279 to the height measured at m/z 280 and at m/z 281 by the ratio of the peak height at m/z 281 to the height at m/z 280. For the scaled curves in Fig. 6, these data are given in table 1. For increasing N it can be seen immediately that resolution of the mass peak improves and the intensity ratio decreases.

COMPARISONS WITH EXPERIMENTAL RESULTS

Figure 7 shows the results obtained from a series of

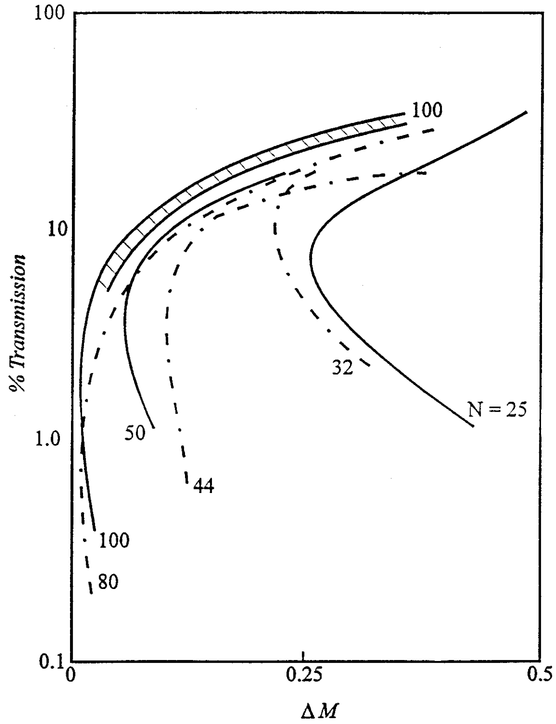

Figure 7. Comparison between experimental (broken line) and simulated (solid line) QMS performance.

experiments on an experimental QMS of length 125 mm constructed from circular rods 6.25 mm in diameter. The results are referenced to Ar^{2+}. The percentage of ions transmitted through a real mass filter cannot be easily measured. Thus, the ordinate scale was normalized to the ion transmission percentage obtained by simulation so that, at $\Delta M = 1.0$ u (the peak width at 10% peak height), the simulated and experimental percentages were approximately equal. The simulated $N = 25$ and $N = 50$ curves refer to ions injected parallel to the major axis. The results for $N = 100$ show curves for ions injected at 30° to the major axis (lower curve) as well as for ions injected parallel to the major axis (upper curve). These results show that: (i) The minimum ΔM (corresponding to the maximum resolution R_{max}) increases as the number of cycles N is increased following (approximately) the relationship $R_{max} \propto N^2$. (ii) The experimental observation that ΔM passes through a minimum as the transmission through the filter decreases, at a given N, is fundamental to the quadrupole operation and is not an artefact. (iii) The entrance angle of the ions affects the overall transmission efficiency.

THE EFFECT OF ANALYSER LENGTH ON TRANSMISSION

Figure 8 shows the percentage of ions passing through the mass filter plotted against quadrupole rod length for ions with initial energy of 1 eV and 2 eV respectively. The DC supply to the mass filter was taken to be 20.5 V and the amplitude of the RF voltage was set at 123.5 V with a frequency of 2 MHz. As the quadrupole length increases the percentage transmission decreases. The rod length is varied through the parameter N, i.e. the number of RF cycles applied to the mass filter. Thus, for shorter quadrupoles, an increased transmission of ions would be expected.

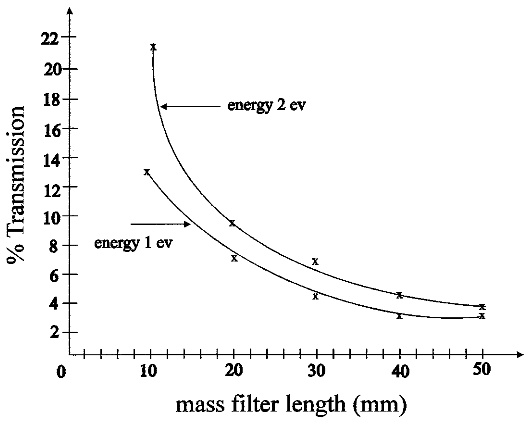

Figure 8. The percentage transmission of ions through the mass filter plotted against quadrupole rod length for ions with initial energy of 1 eV and 2 eV respectively. The DC supply to the mass filter was taken to be 20.5 V and the amplitude of the RF voltage was set at 123.5 V with a frequency of 2 MHz. The injection point of the ions was taken to be 0.3 mm in the x direction and 0.3 mm in the y direction. The inscribed field radius r_0 was 2.75 mm.

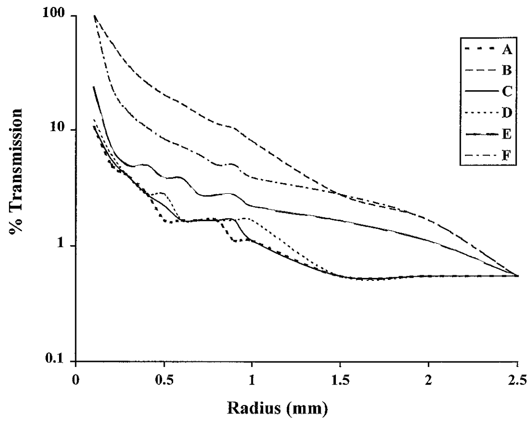

Figure 9. The percentage of ions successfully transmitted plotted against aperture radius. The DC supply to the mass filter was taken to be 20.5 V and the amplitude of the RF voltage was set at 123.5 V with a frequency of 2 MHz. The curves are labelled A to F. For certain aperture angles the plots are coincident. Curve A represents a group of coincident curves for the following aperture angles: 0^0, 45^0, 135^0, 180^0, 225^0 and 315^0. Curve B represents coincident plots for aperture angles 90^0 and 270^0. Curve C represents an aperture angle of 15^0. Curve D represents an aperture angle of 30^0. Curve E represents an aperture angle of 60^0. Curve F represents an aperture angle of 75^0.

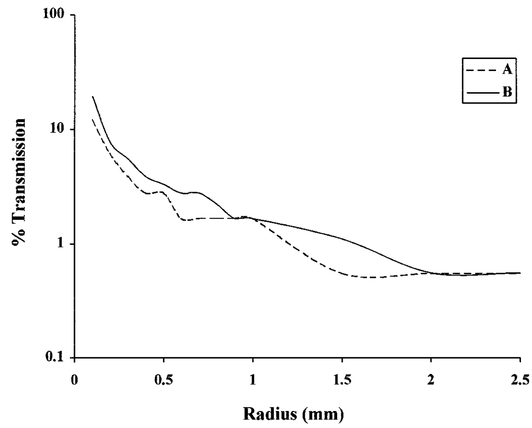

Figure 10. Plots showing percentage transmission against aperture radius for ions injected at an angle 30^0 with sinusoidal RF in curve A and ions injected at 75^0 with approximate square wave RF in curve B (sine wave with the third, fifth and seventh harmonics). The voltage and frequency conditions are the same as in the previous Fig.

EFFECT OF APERTURE PARAMETERS ON TRANSMISSION PROBABILITY

Figure 9 shows the effect of aperture angle. Percentage transmission is plotted against aperture radius for various groups of aperture angles. The aperture angle is measured in the plane perpendicular to the length of the quadrupole rods. The x and y axis connect opposite electrodes of the quadrupole in this plane and the aperture angle, essentially the polar angle, is measured from the x axis. The aperture radius is the polar radius measured in the x–y plane. The voltage conditions and the frequency of the RF potential remain the same. The number of RF cycles applied to the mass filter rods N was fixed at 38. As r increases from 0.0 mm to 2.5 mm the transmission percentage falls for each aperture angle. The following conditions were found to apply: (i) ion transmission characteristics are symmetrical about the x and y axes (ii) The percentage transmission is larger if the aperture size is small, i.e. the ion is closer to the z axis (major axis), as opposed to having injection coordinates further away from the centre. (iii) At angle 90° (or 270°) and a radius of 0.1 mm, 100% of the ions were transmitted through the simulated mass filter.

The aperture angles are important in QMS design. A lens system might be constructed so that the ions could be injected into the mass filter at certain aperture angles to give maximum transmission characteristics.

EXCITATION OF THE MASS FILTER WITH A SINUSOIDAL RF FIELD WITH HARMONICS

Instead of exciting the QMS rods with sinusoidal fields it is possible, in the simulation, to apply a rectangular wave form to the mass filter. To achieve this it is necessary to alter the Mathieu equation by removing the sine wave component of the voltage and replacing it with the Fourier series expansion of a square wave. The new differential equation must be solved numerically for a truncated Fourier series.

The computer simulation was modified to include the harmonics from series expansion of the square wave. Figure 10 shows the percentage transmission against aperture radius for ions injected at an aperture angle of 30° with a sinusoidal RF field (curve A) and ions injected at 75° with approximately square wave RF field (third, fifth and seventh harmonics) in curve B. We found that, although sine wave excitation normally results in much greater transmission than does square wave excitation,[6,7] nevertheless, for certain entrance apertures, square wave performance is equal to or greater than sine wave performance. From this we conclude that square wave operation of the mass filter is possible and in some circumstances may be an advantage.

CONCLUSIONS

A flexible computer model of the mass filter in a QMS has been formulated and shown to give valuable insight into the actual behaviour of an ion under the field within the mass filter. Sinusoidal and rectangular RF fields have been considered in the simulation to excite the QMS rods. The dependence of mass filter resolution on N, the number of RF cycles applied to the rods, was also considered. The variation of percentage transmission with aperture radius and with aperture angle was also investigated and the effect of square wave excitation, as opposed to sinusoidal excitation, on sensitivity was examined.

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