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INTERACTION EFFECT OF ENTRY VELOCITY AND POSITION ON QUADRUPOLE MASS FILTER RESOLUTION

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ABSTRACT

From numerical calculations of ion trajectories in a quadrupole field, upper bounds on the initial displacement and radial velocity for zero initial phase have been obtained for 100 % ion transmission in the resolution range $m/\Delta m = 100$–1000. An empirical expression relating the maximum possible resolution as a function of initial velocity and position involving a position–velocity interaction term has been obtained to fit the calculated results.

INTRODUCTION

In our earlier paper [1] we had shown how the results of ion trajectory calculations in a quadrupole field predict, for 100 % transmission and for a given resolution, higher bounds on the initial position and velocity when both of them are non-zero than when either of them is zero. This indicates that position–velocity interaction effects play a significant role in the former case. Since most of the ions which enter the radiofrequency field fall in this category, it is of considerable interest to have an estimate of the extent to which such interaction effects are operative. This information is also valuable where quadrupole mass filters are used in quantitative analysis and it is with this objective we have now extended our earlier calculations to a wider range of initial velocities and positions, and obtained a functional relationship between the mass filter resolution for 100 % ion transmission and the entry conditions.

In our earlier work we calculated the limiting resolutions for entry conditions x_0 (or y_0), x'_0 (or y'_0) being 0.005, 0.01; 0.01, 0.005; 0.01, 0.01 in units of inch and

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inch per radian respectively. In the present work we have extended the calculation for the following sets of initial conditions: 0.008,0.008; 0.01,0.015; 0.012,0.01; 0.015,0.005; 0.015,0.012.

From a plot of x,y limits in the a,q stability diagram we obtained the limiting resolutions for a given set of entry conditions. A combination of the results of the present calculations with those of the earlier ones gave eight sets of different initial conditions for (x_0, x'_0) and (y_0, y'_0) each, hence 64 different x–y combinations altogether. This leads to 64 limiting resolutions obtainable from the stability diagram. From 34 such bounds an empirical relationship between the resolution and the entry displacement and radial velocity was obtained using a least squares fit.

ION TRAJECTORY COMPUTATIONS

The methods of trajectory computation using numerical solution of Mathieu's equation have already been described in our earlier paper [1]. Various operating points were chosen with resolutions in the range $m/\Delta m = 100$–1000 and computation was carried out for about 160 cycles of ion motion using an IBM 7044 Computer.

RESULTS

Maximum amplitudes of ion motion, in both x and y directions, were computed for $m/\Delta m = 100, 200, 500, 1000$ along a range of operating points varying over $0.69 < q < 0.71$. In all calculations the initial phase ωt_0 of the radio-frequency field during ion entry was taken as zero. Maximum amplitudes have been plotted as x_m/x_0, y_m/y_0 against q for various resolutions in Fig. 1. Both x and y limits are shown in the figures with initial conditions of $x_0 = y_0$ and $x'_0 = y'_0$ in each case.

The radius of the field is taken to be 0.350 inch for finding the region of operating parameters a,q wherein the ion transmission is 100 %. The horizontal lines in Fig. 1 indicate the region of operating points on the basis of which Fig. 2 is constructed. The limiting resolutions for 100 % ion transmission are found from Fig. 2 by finding the $a_{0.706}$ of the resolution line passing through the apex of the x and y limiting lines and using the expression [2] $m/\Delta m = 0.357/(0.23699 - a_{0.706})$.

Since x and y trajectories depend on the initial conditions x_0, x'_0 and y_0, y'_0 independently, limiting resolutions for cases where the x and y initial conditions are different were found by extending the x limit and y limit lines in the stability diagram so that these intersect all other lines. With eight sets of independent x and y initial conditions (including the 3 from ref. 1) we have altogether 64 combinations between x and y initial conditions. Out of these the 9 possible combina-

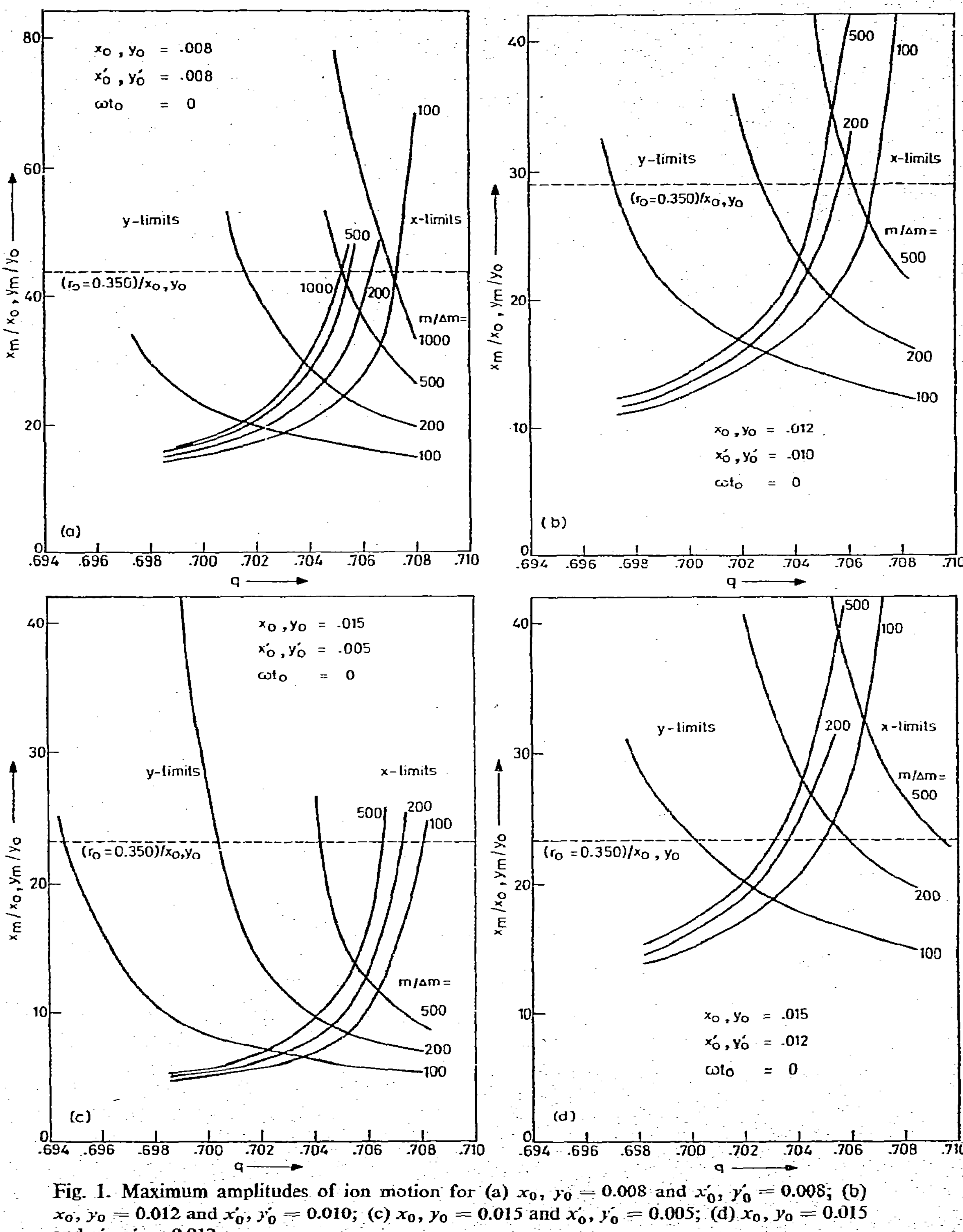

Fig. 1. Maximum amplitudes of ion motion for (a) x_0, $y_0 = 0.008$ and x'_0, $y'_0 = 0.008$; (b) x_0, $y_0 = 0.012$ and x'_0, $y'_0 = 0.010$; (c) x_0, $y_0 = 0.015$ and x'_0, $y'_0 = 0.005$; (d) x_0, $y_0 = 0.015$ and x'_0, $y'_0 = 0.012$.

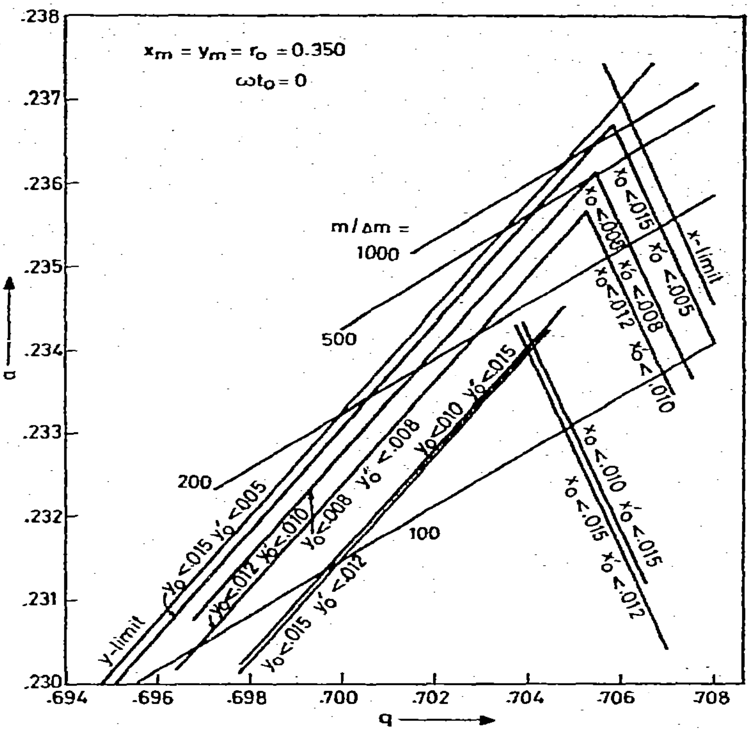

Fig. 2. Permissible entry conditions for 100 % ion transmission.

tions from the earlier work and 25 possible combinations from the present work, which gave 34 bounds of resolution, were used to calculate an empirical relationship between the resolution and the upper bound of initial displacement and velocity for 100 % ion transmission. A general expression relating the resolution with initial conditions is thus obtained.

DISCUSSION

For non-zero radial velocity and zero initial displacement the upper bound of initial radial velocity is given by [2]

$$\dot{x}_0, \dot{y}_0 \approx 0.16\,\omega r_0\,(\Delta m/m)^{0.5} \tag{1}$$

$$x'_0, y'_0 = (\mathrm{d}x/\mathrm{d}\xi)_0, (\mathrm{d}y/\mathrm{d}\xi)_0 \approx 0.32\, r_0(\Delta m/m)^{0.5}$$

whereas the upper bound for initial displacement when the radial velocity is zero is given by

$$2x_0, 2y_0 \approx r_0(\Delta m/m)^{0.5}. \tag{2}$$

Our results show that the upper bounds predicted for initial conditions for a given resolution are higher than that predicted when one of them is zero. Thus when both x and y initial conditions are identical, i.e. $x_0 = y_0$ and $x'_0 = y'_0$, and when both initial displacement and radial velocity are non-zero, we get

$$(\Delta m/m)^{0.5} = (2x_0/r_0)+(x'_0/0.32r_0)-0.59162(2x_0/r_0)^{0.5}(x'_0/0.32r_0)^{0.175} \tag{3}$$

This expression reduces to those given in (1) and (2) when either of the entry conditions is zero. When x and y initial conditions are unequal, we get for the case of non-zero initial conditions

$$\left(\frac{\Delta m}{m}\right)^{0.5} = \tfrac{1}{2}\left[\left(\frac{2x_0}{r_0}\right)+\left(\frac{2y_0}{r_0}\right)\right]+\tfrac{1}{2}\left[\left(\frac{x'_0}{0.32r_0}\right)+\left(\frac{y'_0}{0.32r_0}\right)\right]-$$

$$-0.59162\left[\left(\frac{2x_0}{r_0}\right)^{0.50}\left(\frac{x'_0}{0.32r_0}\right)^{0.175}\right]^{0.55}\left[\left(\frac{2y_0}{r_0}\right)^{0.50}\left(\frac{y'_0}{0.32r_0}\right)^{0.175}\right]^{0.45} \tag{4}$$

The standard deviation of $(\Delta m/m)^{0.5}$ values calculated using eqn. (4) from values measurable in Fig. 2 is 0.006.

Equation (4) reduces to eqn. (3) when the x and y initial conditions are equal and to that in (1) and (2) when either of the initial conditions is zero. The validity of the most general expression (4), though limited to the range of initial conditions studied because of its empirical nature, extends to almost the whole range of interest in practical mass spectrometer operation.

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