J. Am. Soc. Mass Spectrom. (2011) 22:1381–1387
DOI: 10.1007/s13361-011-0153-5

RESEARCH ARTICLE

QMS in the Third Stability Zone with a Transverse Magnetic Field Applied

Sarfaraz U. A. H. Syed, Jeyan Sreekumar, J. R. Gibson, Stephen Taylor

Department of Electrical Engineering and Electronics, University of Liverpool, Brownlow Hill, Liverpool, L69 3GJ, UK

Abstract

We report here a study using a quadrupole mass spectrometer (QMS) in which a static magnetic field is applied transversely to the body of the mass filter operating in stability zone 3. Significant improvement in QMS performance was obtained under certain magnetic field conditions, and these have been explained in terms of our theoretical model. The theoretical approach assumed in the model is that the QMS contains hyperbolic rods as electrodes and that the magnetic field acts over the full length of the mass filter assembly. Our latest analysis also predicts for what values of operating parameters an enhancement of the quadrupole resolution is achieved when a transverse magnetic field is applied. The model predicts instrument resolution R>5000 for Ar with a 100 mm long mass filter and R>3500 for a HT and D_2 mixture with a 200 mm long mass filter via application of a transverse magnetic field.

Key words: Quadrupole Mass Filter (QMF), Magnetic field, Zone 3, Lorentz force, Runge-Kutta Algorithm, Ion trajectories, Resolution

Introduction

A quadrupole mass spectrometer (QMS) is an instrument for measuring concentrations of atoms and molecules by separating atomic and molecular ions according to their mass-to-charge ratios (*m/z*). It consists primarily of an ion source, quadrupole mass filter (QMF) and detector [1]. QMSs have found a wide range of applications in both industry and research, with applications ranging from analysis of simple gas mixtures to analysis of complex organic materials using varied resolution devices [2, 3]. The characteristics that have ensured its widespread use include versatility, low-cost, accuracy, and mass range. There are number of applications that require high resolution; example application includes the quantitative measurement of hydrogen isotopes in the presence of helium isotopes that generally requires a minimum resolution of 930 [4–6]. These resolutions, especially at the lower end of the mass range 1–6 *u*, are not readily achievable with commercially available QMS instruments.

Most commercial quadrupole mass spectrometers operate in stability zone 1 (a=0.237, q=0.706) [1]. However, there are certain advantages such as mass spectral peak shape, reduction of low mass tails, and increase resolution to be obtained if the QMS is operated in the third stability zone. Stability in zone 3 requires higher operating voltages, which have previously been seen as a disadvantage. Nevertheless, with the introduction of miniature QMFs, the increased voltage budget currently may not be considered as an economic obstacle anymore [7]. Stability zone 3 is a sloping rectangular area providing two tips, one at the upper left (a=3.16, q=3.23), and the second at the lower right (a=2.52, q=2.82) corners that enable high resolution mass scanning to be achieved [8]. With stability zone 3, the ions require a lower exposure to number of radio frequency (rf) cycles to achieve the same resolution as compared with zone 1 [9].

Since the early extensive work of Dawson, there have been numerous attempts to theoretically model the performance of the quadrupole mass filter. Examples of such types of analytical works include the prediction of behavior of QMS by tracing ion motion through the mass filter [10], simulation of ion transmission through the filter by calculating ion trajectories in rf only quadrupoles

Correspondence to: Stephen Taylor; *e-mail:* s.taylor@liv.ac.uk

Received: 22 February 2011
Revised: 28 March 2011
Accepted: 7 April 2011
Published online: 6 May 2011

[11], and the modeling of ion transmission through the filter by calculating ion trajectories in exactly determined quadrupole fields [12]. Gibson and Taylor have developed computational methods to determine the trajectories of large number of ions in QMS; their computer program generates large number of ions (at least 10^5 ions injected into the quadrupole model at each point on the mass scale), thus providing a detailed computer simulation for both hyperbolic and circular rods [13, 14]. Some workers have used commercially available software tools, such as SIMION 3D, to compute field conditions and ion trajectories of a commercial QMS with a number of imperfections, as compared to ideal hyperbolic geometry [15]. Other workers have performed elemental analysis with quadrupole mass filters operated in higher stability regions, and it was concluded that there is an increase in resolution when QMF is operated in higher stability regions [9]. Hogan and Taylor performed computer simulation with large number of ions (10^8) to investigate the operation of QMS in first and third stability zones, and it was concluded that QMS operation in zone 3 provides an improved immunity from the effects of the variation in the value of rod radius r to field radius r_0 which is referred as (r/r_0) compared with zone 1 [7]. More recently, Sreekumar *et al.* performed simulations for a QMS operated in zone 3 with large number of ions ($>10^7$) to achieve a required resolution for the qualitative and quantitative identification of low mass isotopes in the mass range 1–6 u [16].

Generally, QMS resolution can be improved by increasing the number of rf cycles of the alternating electric field the ion experiences when passing through the mass filter. This may be achieved by either increasing the frequency of the rf signal, or increasing the quadrupole rod length, or decreasing the ion energy. An alternative method to increase the QMS resolution is the application of the magnetic field to the mass filter; and was previously described for stability zone 1. This was a motivation for this investigation. Previously published experimental and theoretical results

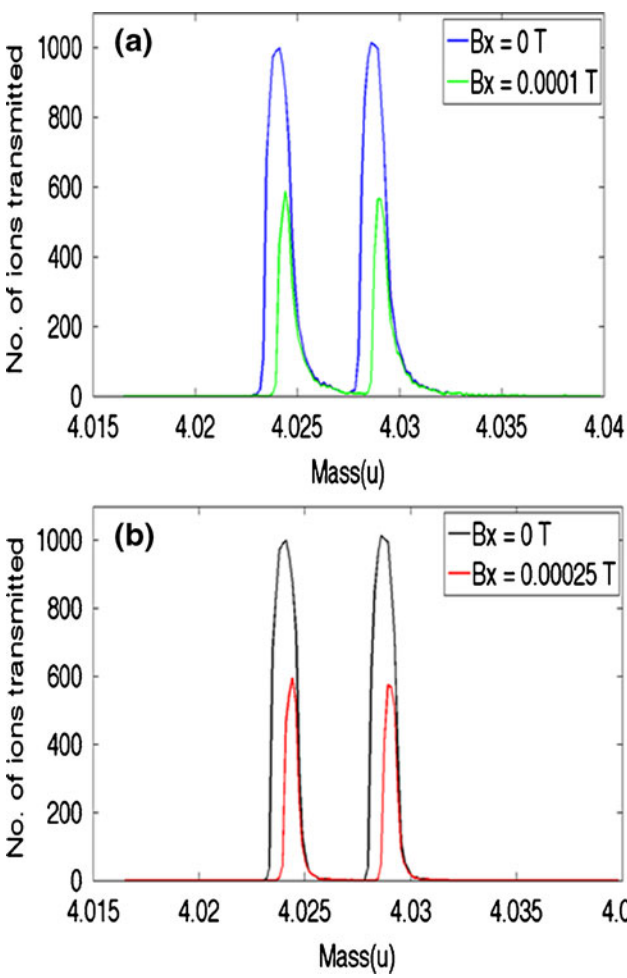

Figure 1. (**a**) Simulated mass peaks for HT^+ and D_2^+ mixture with and without magnetic field applied (B_x=0.0001 T), frequency 5 MHz. (**b**) Simulated mass peaks for HT^+ and D_2^+ with and without magnetic field applied (B_x=0.00025 T), frequency 8 MHz

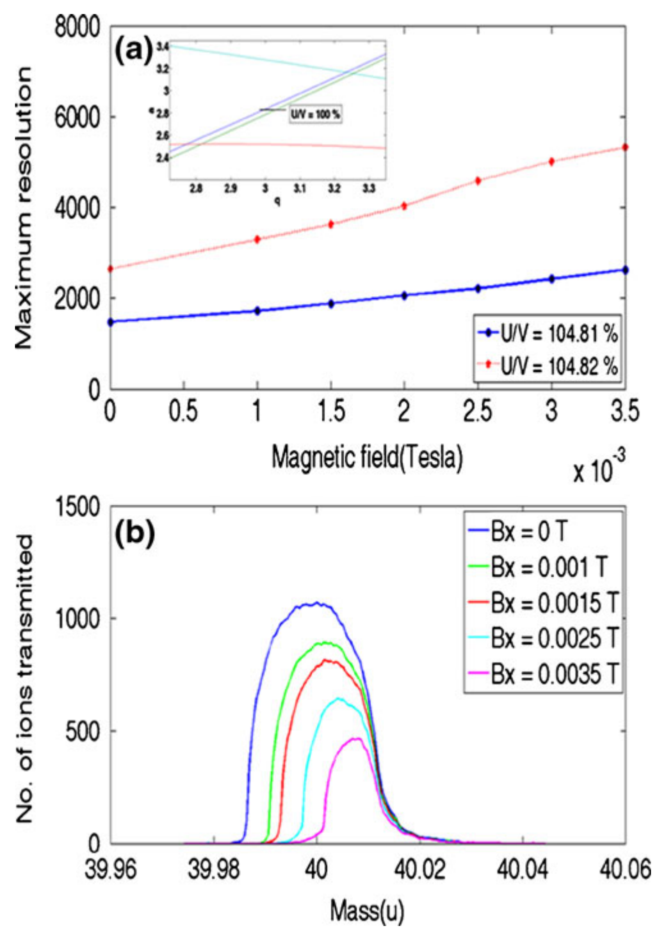

Figure 2. (**a**) The effect of magnetic field on resolution of $^{40}Ar^+$ applied in x-direction (solid line (U/V=108.81) and dotted line (U/V=104.82%), the zone 3 detail of the Mathieu stability diagram is shown in the inset. (**b**) Simulated mass peaks for $^{40}Ar^+$ with and without magnetic field

for stability zone 1 showed the effect of a transverse magnetic field on the resolution of QMS [17]; the effect of a static magnetic field on the ion trajectories [18]; and the effect of an axial magnetic field on the performance of a QMS [19]. Our original model was modified to include mass scanning for stability zone 3; and with an option to include the effect of magnetic field when operating in zone 3. In this article, the application of a transverse magnetic field to the mass filter will be considered in addition to the conventional electric fields when operating in stability zone 3. It will be assumed in the model that the QMS contains hyperbolic rods as electrodes and the magnetic field is applied along the full length of the mass filter assembly.

Theory

The theory for ion motion in a QMS with an applied magnetic field is as published previously [19], and is reproduced here for completeness. Ions oscillating tangentially to a magnetic field will experience a Lorentz force $F = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$ where v is the instantaneous velocity of the particle and is directly proportional to ion energy E_z, q is electric charge of the particle, **E** is the strength of electric field and B is the strength of magnetic field [20]. If the electric field is given by conventional hyperbolic potential where U is the amplitude of DC potential applied to rods, V the amplitude of rf potential, f the frequency of the sinusoidal field and r_0 the inscribed radius of the electrodes, for general magnetic field $\boldsymbol{B}=(B_x, B_y, B_z)$ the coupled equations of motion are given by

$$\frac{d^2x}{d\xi^2} = -x(a - 2q\cos 2\xi) + \left(\frac{dy}{d\xi}b_3 - \frac{dz}{d\xi}b_2\right) \quad (1)$$

$$\frac{d^2y}{d\xi^2} = y(a - 2q\cos 2\xi) + \left(\frac{dz}{d\xi}b_1 - \frac{dx}{d\xi}b_3\right) \quad (2)$$

$$\frac{d^2z}{d\xi^2} = \left(\frac{dx}{d\xi}b_2 - \frac{dy}{d\xi}b_1\right) \quad (3)$$

In the numerical model the above equations have been written in a dimensionless form where the only dimension that appears is that of length displacement. The time t has become $t=2\xi/\omega$ where ω is the angular frequency equal to $2\pi f$. In the absence of an applied magnetic field the direct potential U and alternating potential V are related to a and q as

$$a = \left(\frac{4eU}{mr_0^2\omega^2}\right) \quad (4)$$

$$q = \left(\frac{2eV}{mr_0^2\omega^2}\right) \quad (5)$$

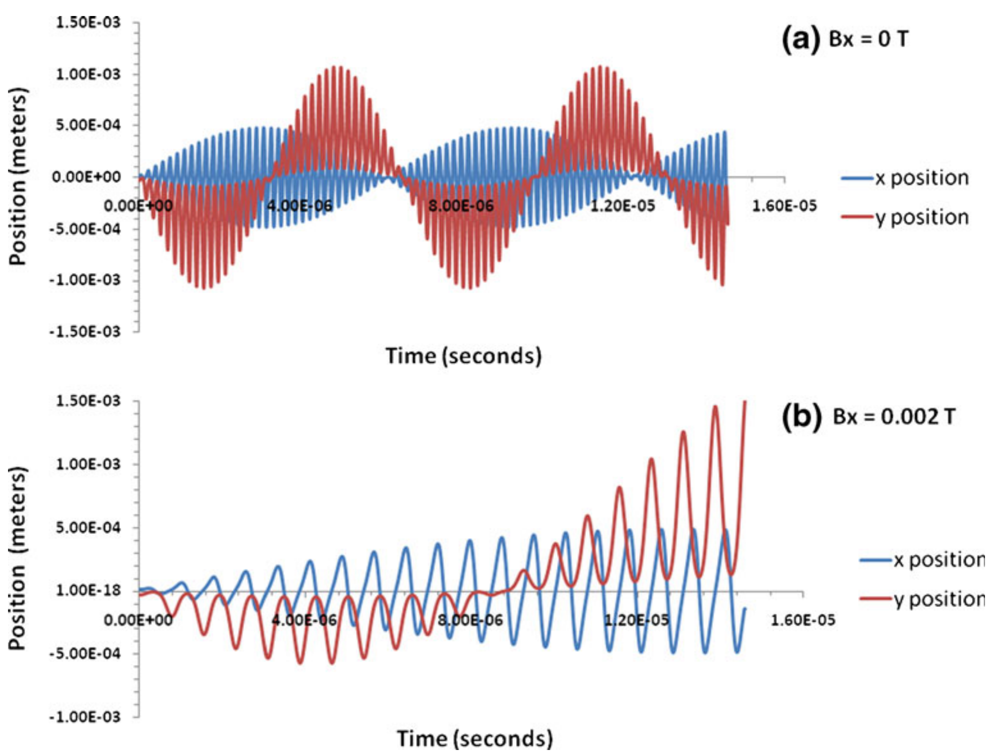

Figure 3. Numerical simulation of ion trajectories in x- and y-directions for $^{40}Ar^{+}$ with (**a**) B_x=0 T (upper trace) and (**b**) B_x= 0.002 T (lower trace)

The components of the magnetic field $\boldsymbol{B}$ are

$$(b_1, b_2, b_3) = \left(\frac{2eB_x}{m\omega}, \frac{2eB_y}{m\omega}, \frac{2eB_z}{m\omega} \right) \tag{6}$$

It can be seen from eqs 1–3 that if the magnetic field is taken to be zero the coupled differential equations reduce to the familiar Mathieu equations for a linear quadrupole. Solving numerically the coupled differential equations gives the trajectories of the ions through the mass filter. From the trajectories it is feasible to determine the conditions which give successful ion transmission for a given mass to charge ratio. This depends on the values of direct potential U, the rf potential V, the rf voltage frequency f, the inscribed radius of the quadrupole rods r_0, the magnetic field strength B, the initial velocity, initial phase, and the ion position. The first four parameters appear as the variables of a and q in the Mathieu equation for (B=0). For $\boldsymbol{B}$ non–zero there will be a further dependence of a and q upon the magnetic field, however a complete theoretical analysis is beyond the scope of this paper. From the mass spectrum obtained by the numerical simulation, the resolution R can be found by using the equation $R=M/\Delta M$, where M is the mass of the given spectral peak and ΔM is the width of the mass peak measured at 10% of its height [1].

Simulation Method

A custom software program (QMS-hyperbolic) is used in this study. The program calculates ion trajectories by solving the Mathieu equations using a fourth order Runge-Kutta algorithm. It operates by dividing the ion trajectories into small steps and assuming that over the steps the ion motion in three directions, x, y, and z, may be uncoupled. Mass scans are computed by ramping the values of U and V with fixed U/V ratio, which sets the resolution of an instrument. An option of introducing magnetic field in all the three directions (B_x, B_y, B_z), along the whole length of the mass filter is also incorporated.

A second program (IonSrc) allows entry conditions for large number of ions (typically 10^6), to be specified, which are subsequently supplied to the mass filter calculation engine to simulate individual trajectories in each case. The IonSrc file assumes a uniformly illuminated ion distribution across a user defined ion source exit radius. Each ion is injected into the QMF with random phase with respect to the rf at the time of entry. Finally, Matlab and Microsoft Excel were used to post process the data and for the generation of graphical results.

Results and Discussions

The Effect of Magnetic Field in the x Direction on the Resolution of QMS

Mass spectral studies of HT^+ and D_2^+ mixture

All the simulations are carried out in zone 3 and use 150 steps across the mass range, with 9×10^5 ion trajectories run at each point on the peak. Mass peaks for HT^+ and D_2^+ mixture are generated for a hyperbolic quadrupole mass filter with length (l) of 200 mm. The inscribed radius of the QMF was taken to be 2 mm and the ion energy was chosen as $5\,eV$. The ion source radius (r_{ie}) was selected as 0.5 mm and the exit radius was chosen as 4 mm. The operating point (U/V ratio) was selected as 104.82%, where 100% corresponds to the U/V ratio at q=3.0 and a=2.8, which is near the center of the stability zone 3. The difference in mass between the two species is 0.0043293 u, requiring a minimum resolution of 930 for mass discrimination [16].

Figure 1a shows a set of peaks obtained without and with an applied transverse magnetic field (B_x) for HT^+ and D_2^+ mixture within a hyperbolic QMF at a frequency of 5 MHz.

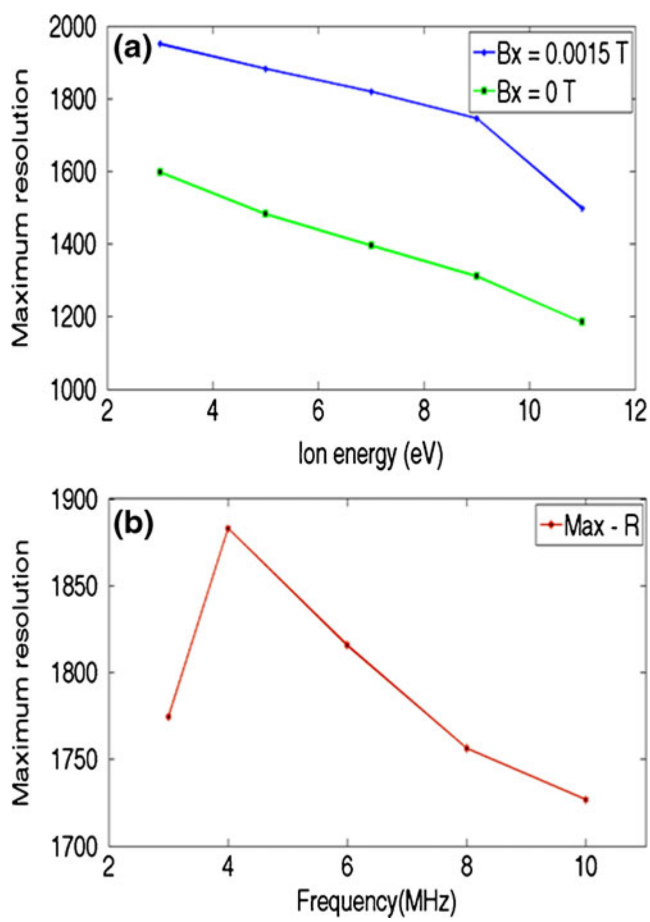

Figure 4. (**a**) The dependence of maximum resolution on ion energy with and without an applied magnetic field. (**b**) The dependence of maximum resolution on frequency with an applied magnetic field

An increase in resolution is clearly observed with an applied magnetic field of 0.0001 T, albeit at the expense of sensitivity. Figure 1b shows a set of peaks obtained without and with an applied magnetic field of 0.00025 T for HT^+ and D_2^+ mixture at a frequency of 8 MHz. From Figure 1a, it can be seen that there is a clear improvement in resolution at 10% peak height with magnetic field applied, from approximately R=1829 to R=2163 for the case with HT^+ and from R=1832 to R=2166 for the case with D_2^+. Whereas from Figure 1b, it can be seen that upon application of magnetic field the resolution increases approximately from, R=2438 to R=3860 for the case with HT^+ and from R=2517 to R=3717 for the case with D_2^+. However, it should be noted that a higher value of magnetic field was required at higher frequency to increase the resolution by a sufficient value; this effect will be explained later in the paper. The obtained resolutions are far higher than the minimum resolution required to separate the two species; this simulation result clearly illustrates the resolution enhancement provided by a transverse magnetic field.

Mass spectral studies of $^{40}Ar^+$

The simulated mass peaks for $^{40}Ar^+$ ions using the computer software are shown in Figure 2. All the simulations used 150 steps across the mass range, with 5×10^5 ion trajectories run at each point on the peak. Mass peaks for $^{40}Ar^+$ are generated for a hyperbolic quadrupole mass filter with length (l) of 100 mm. The inscribed radius of the QMF was taken to be 1.5 mm. The frequency of the rf voltage used in the simulation was 4 MHz and the ion energy was chosen as $5eV$. The ion source radius (r_{ie}) was selected as 0.5 mm and the exit radius was chosen as 3 mm. Figure 2a shows the behavior of the resolution, measured at 10% peak height as a function of transverse magnetic field for two different values of *U/V* ratios, 104.81% (solid line) and 104.82% (dotted line). The zone 3 detail of the Mathieu stability diagram is shown in the inset, where a *U/V* ratio of 100% corresponds to q=3.0 and a=2.8, which is near the center of the stability zone 3. With increasing *U/V* ratio, the scan line approaches the upper left tip of stability zone 3, so a *U/V* ratio of 104.82% corresponds to the scan line operating very close to the tip of the stability region. The resolution increases as *Bx* is varied between 0 and 0.0035 T, however, the QMS resolution will not increase indefinitely with *Bx*. This is because as *Bx* increases, the peak shape eventually degrades. In the case of *U/V* ratio=104.82%, the predicted value of resolution is in excess of 5000, if achieved in practice, thus will allow specialist high-resolution QMS applications. This results show that at any fixed value of *U/V* ratio there is a resolution enhancement by simply applying transverse magnetic field to the body of the mass filter.

Figure 2b shows a set of peaks for $^{40}Ar^+$ within a hyperbolic QMF at different values of magnetic field applied in the x-direction. An increase in resolution is clearly

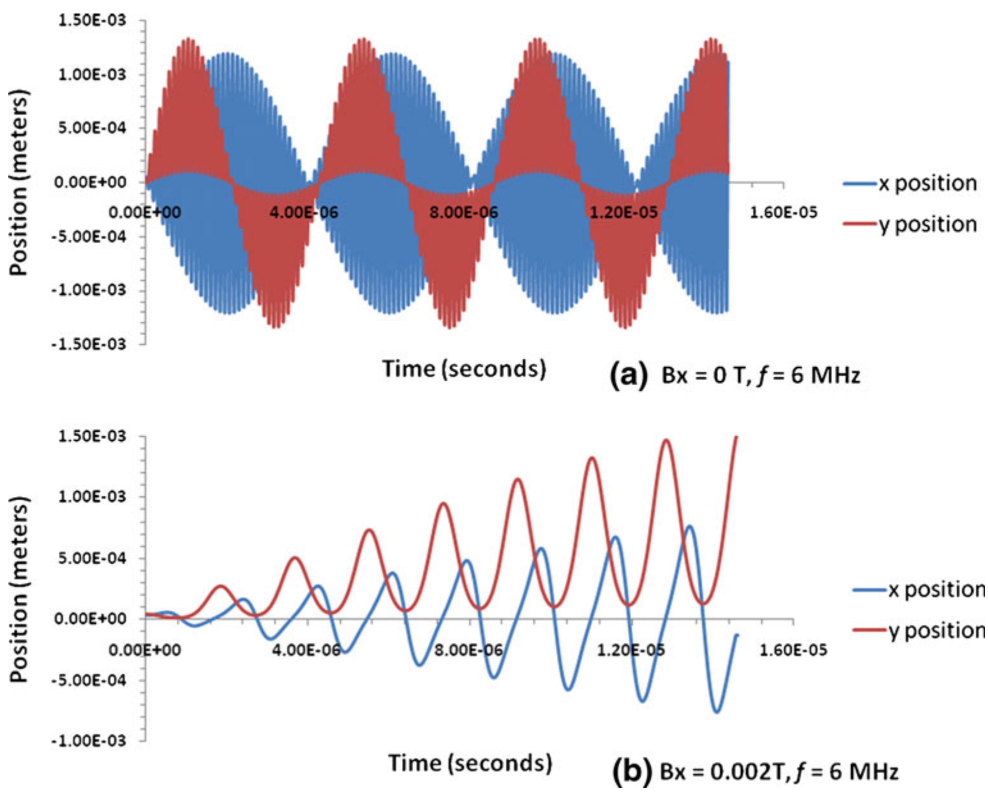

Figure 5. Numerical simulation of ion trajectories in x- and y-directions for $^{40}Ar^+$ with f=6 MHz and with (**a**) B_x=0 T (upper trace) and (**b**) B_x=0.002 T (lower trace)

observed up to a magnetic field of 0.0035 T at the expense of reduction in number of ions transmitted. There is also a reduction in the low mass tail of the mass spectra with a magnetic field applied.

The Effect of Magnetic Field in the x Direction on Ion Trajectories

The simulation program is incorporated with a trace facility and this allows the details of individual ions to be recorded. Figure 3 shows typical behavior of the ion trajectories calculated using the theoretical model for ions transmitted with and without the transverse magnetic field applied. All the simulations were carried out in stability zone 3. The corresponding traces shown in the figure are for the same ion injected into the mass filter at the same point in time (rf phase) and space and at the same point on the mass scale (m=40 u). The upper trace of the figure is for the case with no field applied and lower trace with B_x of 0.002 T. Ion motion in Figure 3 originates at $x=1.38\times10^{-5}$ *m* and $y = -3.11\times10^{-5}$ m with an initial velocity of 4.90×10^{3} m/s. In the lower trace, due to the Lorentz force provided by B_x, the amplitude of ion trajectory in *y*-direction increases; however ion trajectory in the *x*-direction remains unaffected. The application of magnetic field therefore displaces the ion in the *y*-direction so that the ion is lost through impact with the electrodes. It should be noted that ion motion in *x*-direction (parallel to field) is unaffected; it is ion motion in the *y*-direction (perpendicular to the field) that is modified, and this is to be expected since the ion motion is subjected to Lorentz force $F=q\ (E+v \times B)$ where *v* is the instantaneous velocity.

The Effect of Ion Energy and Frequency on Resolution of QMS in the Presence of Magnetic Field in the x Direction

Figure 4a shows the dependence of maximum resolution on ion energy for $^{40}Ar^{+}$ with and without magnetic field applied. As can be seen from the Figure 4a, in both the cases, resolution decreases with increase in ion energy. This feature is commonly observed for QMS systems and is due to the reduced number of rf cycles experienced by the ion as the ion energy increases. However, these results clearly indicate that the predicted performance of the QMS increases in the presence of transverse magnetic field. Figure 4b shows the effect of frequency on resolution in the presence of a magnetic field. With a transverse magnetic field applied, the effect of frequency of the rf signal on resolution is different to that normally observed in a conventional QMS. The resolution first increases by a small amount as observed from frequency 3 to 4 MHz and then decreases with increase in frequency. We attribute this effect to the Lorentz force provided in the transverse direction by the magnetic field.

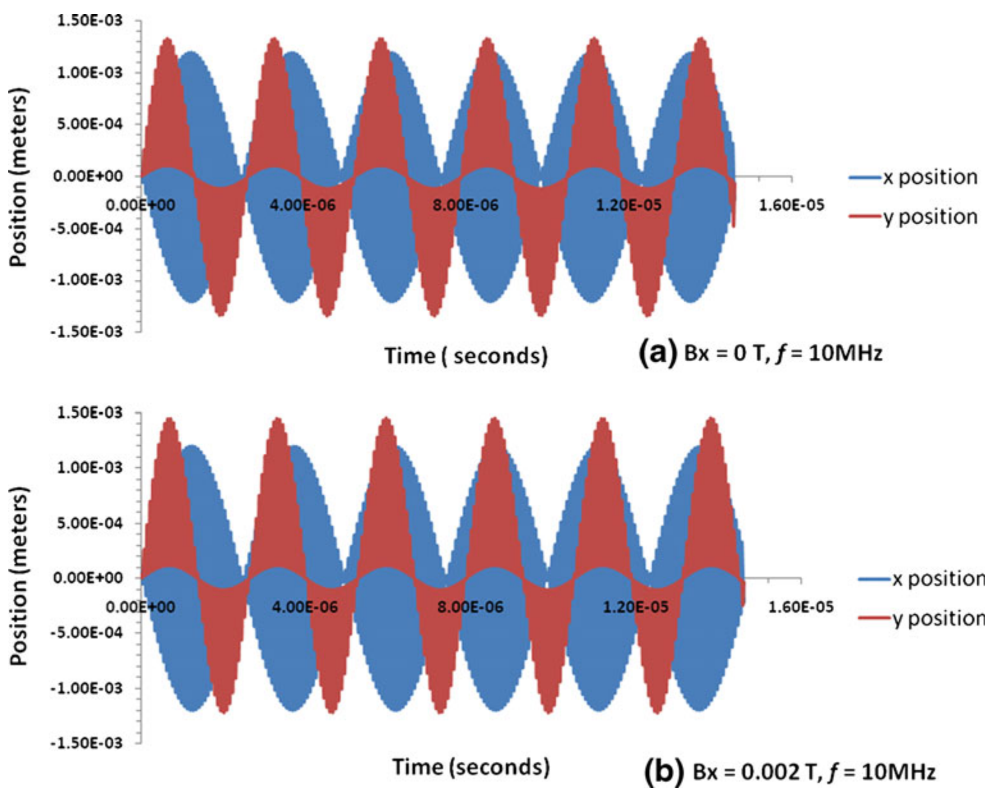

Figure 6. Numerical simulation of ion trajectories in x- and y-directions for $^{40}Ar^{+}$ with f=10 MHz and with (**a**) B_x=0 T (upper trace) and (**b**) B_x=0.002 T (lower trace)

The effect can be best demonstrated with the help of ion trajectories in the presence of a transverse magnetic field at different frequencies. Figures 5 and 6 show trajectories of ions transmitted with and without magnetic field, at frequencies of 6 and 10 MHz, respectively. The corresponding traces shown in the figures are for the same ion injected into the QMF at the same point in time (rf phase) and space and at the same point on the mass scale (m=40.00 u). In both figures the upper trace is for the case with no field applied and lower trace with B_x of 0.002 T. Ion motion in Figure 5 originates at $x=3.45\times10^{-5}$ m and $y=3.88\times10^{-5}$ m with initial velocity of 4.90×10^{3} m/s. It can be seen from the figure that in the presence of magnetic field at lower frequency (6 MHz) ion motion in both the directions is affected. It is also seen that the amplitude of ion motion in the x-direction decreases, whereas the amplitude in y-direction increases, resulting in loss of ions through impact with electrodes, and correspondingly higher resolution.

In Figure 6 the ion motion also originates at $x=3.45\times10^{-5}$ m and $y=3.88\times10^{-5}$ m with the same initial velocity of 4.90×10^{3} m/s. It can be observed from the figure that increase in frequency has a major impact on behavior of ion trajectories in the presence of magnetic field. It can be seen that ion motion in the x-direction remains unaffected and the amplitude of ion motion along y-axis only slightly increases. Therefore, the ion was successfully transmitted in the presence of the magnetic field at the higher frequency of 10 MHz. In this case although the magnetic field is same as Figure 5 (B_x=0.002 T) the ion velocity is greater since the frequency is greater, and the Lorentz force correspondingly greater. It can be concluded that for a QMF with magnetic field applied in the x-direction, the effect of magnetic field on resolution enhancement is greater at lower frequencies.

Conclusions

Simulation results for a QMS operating in the stability zone 3 have been presented showing the effect of transverse magnetic field, applied along the whole length of the mass filter. The effects of different input parameters, such as variation of ion energy and drive frequency, have been examined. The effects may be explained in each case by considering the additional Lorentz force produced by ion motion in the magnetic field. All ions entering the mass filter with trajectories not parallel to the direction of magnetic field will experience Lorentz force, which modifies their motion. The increase in resolution is ascribed to the modification of the ion motion in the mass filter by the magnetic field. This results in rejection of ions in the low mass tail, giving increased resolution for a set of operating parameters. In certain cases, however, high values of Lorentz force do not produce resolution enhancement (see Figures 5 and 6). There remains an optimum value of Lorentz force for a given QMF. High resolutions (R>3500) are predicted for low mass isotopes (1–6 u) with a QMF of length 200 mm and (R>5000) for Argon with a QMF of length 100 mm as a result of the applied magnetic field. These features suggest wider application than hitherto for such QMS instruments, e.g., applications in which extremely high QMS resolution and/or high abundance sensitivity is required. These include identification of low mass isotopes in the mass range (1–6 u), as this issue is of some importance in the nuclear industry for protecting of personnel involved in handling of radioactive material.

References

1. Dawson, P.H.: Quadrupole mass spectrometry and its applications. Elsevier, Amsterdam (1976)
2. Taylor, S., Tunstall, J.J., Leck, J.H., Tindall, R.F., Jullien, J.P., Batey, J., Syms, R.R.A., Tate, T., Ahmad, M.M.: Performance improvements for a miniature quadrupole with a micromachined mass filter. *Vacuum* **53**, 203–206 (1999)
3. Ma, F.M., Taylor, S.: Simulation of ion trajectories through the mass filter of a quadrupole mass spectrometer. *IEE Proc.-Sci. Meas. Technol.* **143**(1), 71–76 (1996)
4. Hiroki, S., Abe, T., Murakami, Y.: Separation of Helium and Deuterium Peaks with a Quadrupole Mass Spectrometer by Using the Second Stability Zone in the Mathieu Diagram. *Rev. Sci. Instrum* **63**(8), 83874–3876 (1992)
5. Hiroki, S., Abe, T., Murakami, Y.: Detection of a 10^{-4} Helium Peak in a Deuterium Atmosphere Using a Modified High-Resolution Quadrupole Mass Spectrom. *Rev. Sci. Instrum*. **65**(6), 1912–1917 (1994)
6. Frattolillo, A., De Ninno, A.: A Powerful Tool to Quantitatively Detect Tiny Amounts of ^{4}He in a Deuterium Rich Background for Fusion Research. Proceedings of the 22nd IEEE Symposium on Fusion Engineering. Albuquerque, NM, June (2007)
7. Hogan, T.J., Taylor, S.: Performance Simulation of a Quadrupole Mass Filter Operating in the First and Third Stability Zones. *IEEE* **57**(3), 498–508 (2008)
8. Douglas, D.J.: Linear quadrupoles in mass spectrometry. *Mass Spectrom. Rev*. **28**, 937–960 (2009).
9. Du, Z., Douglas, D.J., Konenkov, N.: Elemental Analysis with Quadrupole Mass Filters Operated in Higher Stability Regions. *J. Anal. At. Spectrom.* **14**(8), 1111–1119 (1999)
10. Batey, J.H.: Quadrupole gas analyzers. *Vacuum*. **37**, 659–668 (1987)
11. Muntean, F.: Transmission study for rf-only quadrupoles by computer simulations. *Int. J. Mass Spectrom. Ion Processes* **151**, 197–206 (1995)
12. Reuben, A. J.; Smith, G. B.; Moses, P.; Vagov, A. V.; Woods, M. D.; Gordon, D. B.; Munn, R.W. Ion trajectories in exactly determined quadrupole fields. *Int. J. Mass Spectrom. Ion Processes*. **154**, 43–59 (1996).
13. Gibson, J.R., Taylor, S., Leck, J.H.: Detailed simulation of mass spectra for quadrupole mass spectrometer systems. *J. Vac. Sci. Technol. A* **18** (1), 237–243 (2000)
14. Gibson, J.R., Taylor, S.: Prediction of quadrupole mass filter performance for hyperbolic and circular cross section electrodes. *Rapid Commun. Mass Spectrom*. **14**, 1669–1673 (2000)
15. Blaum, K., Geppert, Ch., Muller, P., Nortershauser, W., Otten, E.W., Schmitt, A., Trautmann, N., Wendt, K., Bushaw, B.A.: Properties and performance of a quadrupole mass filter used for resonance ionization mass spectrometry. *Int. J. Mass Spectrom*. **181**, 67–87 (1998)
16. Sreekumar, J., Hogan, T.J., Taylor, S., Turner, P., Knott, C.: A Quadrupole Mass Spectrometer for Resolution of Low Mass Isotopes. *J. Am. Soc. Mass Spectrom*. **21**, 1364–1370 (2010)
17. Tunstall, J.J., Taylor, S., Vourdas, A., Leck, J.H., Batey, J.: Application of static magnetic field to the mass filter of a quadrupole mass spectrometer. *Vacuum* **53**, 211–213 (1999)
18. Srigengan, B., Gibson, J.R., Taylor, S.: Ion trajectories in quadrupole mass spectrometer with a static transverse magnetic field applied to mass filter. *IEE Proc.-Sci. Meas. Technol*. **147**(6), 274–278 (2000)
19. Syed, Sarfaraz U.A.H., Sreekumar, J., Brkic, B., Gibson, J.R., Taylor, S.: Effect of an axial magnetic field on the performance of a quadrupole mass spectrometer. *J. Am. Soc. Mass Spectrom*. **21**, 2070–2076 (2010)
20. Kraus, J.D.: Electromagnetics. McGraw-Hill, New York (1991)