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Predicted behaviour of QMF systems with and without prefilters using accurate 3D fields

J. Raymond Gibson*, Kenneth G. Evans, Stephen Taylor

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

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ABSTRACT

Computer simulation enables the effects of a much wider range of design parameters of quadrupole mass filters (QMFs) to be investigated than is economically possible by experiment. Large deviation from ideal behaviour arises from effects of the fringe field regions and is only predicted correctly if the three dimensional fringe fields are determined accurately.

The boundary element method, BEM, was used to compute accurate 3D electric fields for complete QMF systems with and without prefilters. Detailed examination of system behaviour without prefilters was used to determine where the effects of fringe fields are particularly detrimental. Examination was extended to systems with prefilters to investigate the required prefilter length and the improvement in performance. The results confirmed that use of a prefilter improves performance in most situations; for high m/z the improvement was large. The results support the original claims of Brubaker although behaviour is more complicated than is described by Brubaker.

The results are relevant to QMF designers and users and especially for miniature systems for portable mass spectrometry with the aim to optimise performance whilst maintaining a small instrument footprint.

1. Introduction

The construction and operation of a quadrupole mass filter, QMF, is well documented in standard references, for example Dawson [1,2] and Douglas [3]. Computer models are used to predict behaviour of proposed designs allowing design parameters to be investigated more rapidly and at lower cost than is possible experimentally. They are particularly useful for small instruments in order to optimise injection of ions from the miniature ion source into the mass filter. Failure to do this can have a detrimental effect on performance. It is also possible to use computer modelling to predict the effect of inaccuracies in manufacture.

Conventionally QMF descriptions use rectangular Cartesian coordinates with the system axis coincident with the z axis and electrodes placed symmetrically on the x and y axes. Most predictions of behaviour assume that the electric fields are generated by infinitely long electrodes. In this case the fields only have components in the x and y directions and the electric field in the direction of the z axis, E_z, is zero at all positions. That is field values do not depend on z position. We refer to such fields as 2D fields.

In practice, fields are not ideal because the electrodes have finite length and there are end caps to couple the ion source and detector to the QMF. Most end caps are flat plates with central holes coaxial with the system axis located a short distance from the ends of the quadrupole electrodes. The field extending from the end caps for a distance into the region between the quadrupole electrodes is not ideal. This is the fringe field region in which all components of the field vary in all directions. Consequently the axial direction field, E_z, is not zero in the fringe field region. We refer to electric fields with components varying in all three coordinate directions as 3D fields.

Predictions using 2D fields provide many indications of QMF design requirements and behaviour; for example minimum electrode length and optimum radius for circular section electrodes. There are large inaccuracies in such treatment; early considerations of deviations from ideal 2D fields are discussed by Dawson [1]. Brubaker [4–6] suggested that the non-ideal fringe field region at the source end cap led to loss of slow moving ions (heavy ions when operating at constant ion energy). Brubaker introduced the delayed d.c. ramp, implemented using a prefilter, to reduce such effects. Unfortunately much of Brubaker's work is in NASA reports and is not readily available.

We previously described the use of the Boundary Element Method (BEM), formulated as described by Read [7,8], to deter-

* Corresponding author.
E-mail address: jrgjrg@liv.ac.uk (J.R. Gibson).

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mine accurate 3D field values for QMF systems with finite electrode length and end caps [9]. The method avoids the need to differentiate potential distributions produced by other techniques and the inaccuracies this introduces. Using the BEM method fields, except very close to the electrodes, are very accurate.

We have extended the BEM to investigate systems with prefilters. Existing studies of the effects of fringe fields on QMF performance are limited and many ignore the important feature that E_z, is not zero. To explain effects observed when a prefilter is included we first examined the effect of fringe fields on behaviour of systems without a prefilter.

2. Effects of finite length electrodes and end caps

The fringe fields at the source end have a very large effect on filter behaviour whereas those at the exit end usually have a small effect which is further reduced if the detector is operated at high voltage. Fringe field effects vary with both geometrical and electrical parameters. It is difficult to give general rules as parameters interact affecting both the transmission of ions through the filter and the peak shape. Our formulation allows the fields to penetrate into the end cap apertures but at present we do not consider ion motion inside the apertures.

There have been several efforts to estimate the effects of finite electrode length and end caps. These involved approximations, for example [2,6,10–14]. We only know of one set of measurements of the effect of fringe fields on QMF behaviour [15].

Early computations of fringe field effects [6,10] used a simple linear approximation for the fringe field; all field components were zero at the ion source end cap and changed linearly in the axial direction to the 2D field values over some distance, typically r_0. Later work [10,11] included estimates of the effect of variation in z velocity on individual ion trajectories although the main calculations used constant z velocity. This was stated to be valid provided the ion source has a small radius (small is not defined). Examination of individual ion trajectories shows effects that may be as extreme as ions returning to the source end cap or even oscillating in the z direction; such effects correspond to large changes in the z velocity. It is also noted that there is a discontinuity where the linearly varying field changes to the 2D field; this corresponds to Laplace's Equation not being satisfied.

A more elaborate method [12,13] used a Liebmann iterative relaxation method to find the potential distribution in the source fringe region of a QMF. The calculations were performed for several values of end gap and the results fitted to an analytical expression. The potential distribution avoids the discontinuity in E_z of earlier work; a weakness is that the distribution does not satisfy Laplace's equation. The effect of the fringe field on motion in the z direction was ignored; the authors state this is adequate for ion source exit radius below $0.1r_0$ whereas we found that this is not generally true as the limit depends on ion velocity (mass for fixed energy), gap size and rf frequency.

Other than our earlier work [9] there appears to be only one other study of QMF behaviour with accurately determined 3D fields [16]; it only gives a limited range of results for one specific system with a prefilter.

Using accurate 3D fields we made extensive studies of QMF behaviour. Example results shown are for a simple system with $r_0 = 2.6$ mm, gap from planar end cap surfaces to quadrupole electrodes $0.4r_0$, electrode length $40r_0$. The frequency was 2 MHz, the source radius $0.2r_0$ was uniformly illuminated, the detector radius was r_0 and the ion injection energy 1 eV. Identical results are obtained if the system is scaled as described in Appendix A and similar general trends are observed for different parameter values. Fig. 1 shows the variation of ion transmission as a function of ion mass divided by charge (m/z) for both 2D and 3D fields using these parameters. Following the practice of other authors '*ion transmission*' values used correspond to the peak maxima of simulated mass scans. Results are shown in Fig. 1 for hyperbolic cross section electrodes (referred to as hyperbolic) and for circular cross section electrodes (circular) with radius $r = 1.127r_0$ with resolution setting $\eta = 0.9992$ where $\eta = 1.0$ corresponds to the scan line passing through the peak of the stability diagram.

All ions start at the exit of the source aperture, have the same energy and initial direction parallel to the filter axis. Initial ion conditions (using uniform distributions of position in source and rf phase) are selected randomly from the infinite set of all possible conditions. Ions are considered to be detected if they reach the central aperture of the detector end cap. Small fluctuations in results may be ignored; they arise because a large, but finite, number of ions are used at each m/z point simulated, typically 50,000–100,000.

The 2D results have the expected form; transmission falls as ion mass increases (ion velocity falls) until it reaches some constant value for hyperbolic electrodes. This is because low mass ions have high velocity and some that have unstable trajectories do not experience a sufficient number of cycles of the rf field to be ejected. However once ions are travelling slowly enough to experience a sufficient number of rf cycles (between 50 and 100 cycles depending on the filter resolution and geometry chosen) and are still within the filter they are in stable trajectories and remain within the filter regardless of how many further cycles they experience. For circular electrodes the transmission is not quite constant as mass increases but ions must experience a very large number of rf cycles for any significant fall in transmission to be observed.

It is very difficult to make direct experimental comparison of the performance with different electrode shapes. The only previous experimental investigations by Brubaker reproduced in [1] (pp. 129–130) and 2D computations [17] also show that transmission for a system with hyperbolic electrodes is higher than that of a system using circular electrodes.

Results obtained using 3D fields showed very large variations as parameters were changed and were more complicated than for 2D fields. There were also large differences between hyperbolic and circular electrodes using 3D fields. Transmission was usually higher for hyperbolic electrodes but there were situations where the reverse was true. A feature, Fig. 1, is the variation in the transmission when used in the usual mass spectrometer mode in which ions of all masses have the same energy. The choice of geometric and electrical parameters produces a more pronounced peak than our previous results [9]. The peak position and shape vary with choice of parameters; in particular reduction of the source radius reduces the sharpness of the peak and the peak position moves to a lower m/z value.[1] Variation of transmission in this manner has been previously suggested [1,11] and is supported by experiment [15]. Dawson [11] only shows a single smooth curve and states that this curve is only an estimate; Ehlert [15] incorrectly thought that the fall in transmission as m/z decreases towards zero was a fault of his instrumentation.

With both hyperbolic and circular electrodes the predicted transmission at low m/z is usually higher for 3D fields than for 2D fields and the 3D transmission increases with m/z in a non-linear manner to a peak value. For m/z above the peak value transmission falls rapidly and behaviour differs markedly for hyperbolic and circular electrodes. At high m/z the transmission using 3D fields is

[1] m/z in units of Da is commonly used to indicate the position on the x axis of a mass spectrometer scan. Note that the z in this term is not the axial position which is also commonly denoted as z.