A Novel Quadrupole Mass Filter Based on Rectangular Electrodes

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Abstract. A low cost and simple geometry quadrupole mass filter was developed, in which rectangular electrodes were employed instead of traditional hyperboloid or cylindrical electrodes. Modeling and simulation were accomplished in COMSOL Multiphysics. The results showed that the performance of novel quadrupole mass filter turned out to be acceptable. For the low cost, simple geometry and easy to be assembled, it had a great prospect in the field of miniature, portable and low-level mass spectrometer.

1. Introduction

Mass spectrometer (MS) is widely used in many areas, such as homeland security, medical diagnosis, pollution and environment study, molecule detection and identification from space, oil deposits detection, etc. Recently, interest in miniature, portable and low-cost MS has increased due to applications where rapid in situ or field measurements are critical, such as environmental or personal exposure monitors. Mass analyzer is a crucial part in a mass spectrometer. Thus, a simple geometry, low cost, easy to be assembled mass analyzer is of utmost significance for miniature mass spectrometer [1].

Quadrupole mass filter (QMF) is a kind of mass analyzer introduced by Paul in 1958 [2]. In a QMF, ions with different mass-to-charge are separated by quadrupole field which is formed by applying the RF potentials to four electrodes. With the development of the mass spectrometer, the mass analyzers emerge in endlessly, such as cylindrical ion trap (CIT) [3], linear ion trap (LIT) [4], rectangular ion trap (RIT) [5]. Yet QMF is still widely used.

The researches on QMF have never been stopped, though it has been invented for a long time. In the theory of QMF, the geometry of the electrodes should be hyperbolic. Nevertheless, cylindrical electrodes are widely used in practice because of the difficulty in machining a high-precision hyperboloid electrode [6, 7]. When cylindrical electrodes are used, besides quadrupole, higher-order multipole fields (A4-octapole, A6-dodecapole, etc.) are generated. Dayton [8] claims that a good approximation to a quadrupole field can be obtained when the radius of each rod $r$ is made equal to 1.148 times the desired $r_0$ value. While, Gibson and Taylor [9] question this assertion and claim that a value in the range of $r = 1.12x r_0$ to $r = 1.13x r_0$ produces the best performance. In addition, the research on the stability of Mathieu equation and mass analysis methods in higher stability regions is another active research branch [10].
2. Theoretical Modeling

2.1. Theory of Quadrupole

Theoretically, a QMF comprised four parallel symmetrical hyperbolic electrodes is shown in Figure 1. The distance between each pair of opposite electrodes is \(2r_0\) and they are electrically connected. While apply the electric potential \(\phi_0\) to the upper and lower electrodes, the electric potential \(-\phi_0\) to the left and right electrodes, where \(\phi_0 = U - V \cos \Omega t\), a two-dimensional quadrupole field in the \(x-y\) plane is established[11].

![Figure 1. Schematic diagram of quadrupole](image)

The ions enter and travel in the \(z\) direction, and oscillate in \(x-y\) plane, due to the potentials applied to the electrodes. The oscillation can be described by Mathieu equation:

\[
\frac{d^2 u}{d\xi^2} + (a_x - 2q_x \cos 2\xi) u = 0
\]

In Mathieu equation

\[
a_x = a_y = -a_y = \frac{8eU}{m^2 \Omega^2}
\]

\[
q_x = q_y = \frac{4eV}{m^2 \Omega^2}, \quad \xi = \omega t / 2
\]

where \(U\) is the potential of DC voltage, \(V\) is the amplitude of RF voltage, \(\Omega\) is the scanning frequency of the RF voltage, \(m\) is the mass of an ion, and \(e\) is the elementary charge.

The trajectories of ions in the quadrupole can be divided into two states – stability and unstability, which correspond to the stability and unstability regions of the Mathieu equation respectively. The stable ions have stable trajectories for the entire length of the quadrupole, while the unstable ions are bound to hit the electrodes when travelling in the quadrupole.

Most QMF work in first stability region, in which the range of \(a\) is 0 to 0.236 and the range of \(q\) is 0 to 0.908, as is shown in Figure 2. As for the ions with a specific mass-to-charge ratio, for a certain \(r_0\) and \(\Omega\), the \(a\) and \(q\) are confirmed by \(U\) and \(V\).

![Figure 2. First stability region and operating line](image)

The operating line is a straight line passing through the origin and almost the peak of the first stability region whose slope is defined by
3 constant \( aU = \frac{k_0}{qV} = \text{constant} \) (4)  

According to operating line, under an appropriate electrical condition, only ions of a single mass-to-charge ratio will touch the detector. Thus, by sweeping \( V \) and changing \( U \) proportionally, ions of different mass-to-charge ratio can be detected successively.

2.2. Novel Quadrupole Mass Filter

As is mentioned above, the widely-used QMF is based on cylindrical electrodes, while we proposed a novel QMF in which rectangular electrodes were used. The rectangular electrodes with low cost, simple geometry and easy to be assembled were made of stainless steel. As can be seen in Figure 3, the opposite electrodes were in pair, gaps were left between each two adjacent electrodes which guaranteed different potentials can be applied. In addition, the electrodes were fixed by electric insulating material. The length and thickness of the plate electrodes were \( \delta \) and \( L \) respectively. The distance between each two opposite electrodes was \( 2\times r_0 \). The upper and lower electrodes were electrically connected, the same as the left and the right electrodes, and the potentials were \(- (U - V \cos \omega t)\) and \(+ (U - V \cos \omega t)\) respectively.

![Figure 3. Schematic diagram of the novel quadrupole mass filter](image)

When \( r_0=5 \) mm, Table 1 shows the comparison of multipole fields distribution between cylindrical electrodes and rectangular electrodes.

| Electrode Type | Quadrupole \((A2)\) | Octapole \((A4)\) | Dodecapole \((A6)\) | Hexadecapole \((A8)\) |
|----------------|---------------------|-----------------|-----------------|------------------|
| Cylindrical    | 1.3201              | -0.0099         | -0.0378         | -0.0448          |
| Rectangular    | 1.0886              | 0.0632          | 0.2662          | 0.1142           |

Table 1. Multipole filed distribution in the two kinds of quadrupole mass filter

The data suggest that quadrupole is still dominated in the QMF with rectangular electrodes, although high-order multipole fields are higher than QMF with cylindrical electrodes. It can be predicted that the performance of the QMF with rectangular electrodes tend to be degraded, but it can still be used for mass analysis according to the theory of quadrupole.

2.3. Simulation and Discussion

COMSOL Multiphysics is a kind of CAE software based on finite element method (FEM). Such method is able to make discrete analysis of partial differential equation flexible. Therefore, it is suitable for the processing of complex domain, which ensures the accuracy of the calculation.

In this study, COMSOL Multiphysics 5.2a (trial version) was used to evaluate the performance of the novel QMF. Set the thickness of electrode \( \delta \) as 2 mm, the length of electrode \( L \) as 80 mm and the distance between the electrode and the center \( r_0 \) as 5 mm. A circular region with radius \( r_{scr}=0.5 \) mm at
the entrance center of the QMF was defined as the inlet of ions. After mesh generation, Figure 4 shows the result.

![Figure 4. Model of the novel quadrupole mass filter after meshing](image)

The simulation conditions were as follows: scanning frequency $\Omega$ was 0.768 MHz; the mass of ion $m$ was 40 amu; the initial kinetic energy of ion was 4 eV whose direction was along the $z$ direction. The ions were released 10 times during the first scanning cycle of the RF voltage, and 50 ions were released each time. Therefore, a total of 500 ions were released in each simulation process. The slope of operating line was defined as $k=a/q=2U/V=3$. When $V$ was set as 40 V, $a$ and $q$ were 0.22 and 0.67 respectively. At this condition, ions were stable. Figure 5 shows the trajectories of ions. The ions travel in the $z$ direction and oscillate in the $x$-$y$ plane after entering the QMF. Some ions pass through the QMF and touch the detector, while the others hit the electrodes due to the existence of high-order multipole fields.

![Figure 5. Ion trajectory in a novel quadrupole mass filter](image)

Then, changing the simulation conditions, two kinds of ions whose masses were 40 amu and 80 amu were released. By sweeping the amplitude of RF voltage $V$ from 0 to 100 V, we got the mass spectra, as is shown in Figure 6. In Figure 6, $x$-axis indicates the mass-to-charge ratio of ion and $y$-axis indicates the abundance expressed in transmission probability. Two peaks were generated when the $V$ were 40 V and 80 V respectively, and the max transmission probability was about 0.43. The result indicated that the novel QMF can distinguish these two kinds of ions.
For the same simulation condition, Figure 7 shows the mass spectra comparison between QMF with cylindrical and rectangular electrodes. The mass of ion is 40 amu. The dash line and solid line are the mass spectra of the QMF with cylindrical electrodes and rectangular respectively. The full width half maximum (FWHM) of the rectangular electrodes was smaller than that of the cylindrical electrodes, in addition, the transmission probability was higher. These mean that the resolving power and sensitivity of QMF with rectangular electrodes were inferior to QMF with cylindrical electrodes. However, due to its low cost, simple geometry and easy to be assembled, it still can be practiced in some miniature, portable and low-level mass spectrometer.

3. Conclusions
In this study, we proposed a novel quadrupole mass filter with rectangular electrodes. Simulation was carried out in COMSOL Multiphysics 5.2a (trial version). According to the results, the resolving power and sensitivity in QMF with rectangular electrodes were inferior to the QMF with cylindrical electrodes. However, because of the low cost, simple geometry and easy to be assembled, QMF with rectangular electrodes had a great prospect in the field of miniature, portable and low-level mass spectrometer.

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