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1 Introduction

Mass spectrometry is one of the primary and most frequently used techniques in analytical chemistry and also finds many important applications in material sciences as well as fundamental research in physics, chemistry, geo-science and climatology, biology and medicine. There are several ways to perform mass selection of charged species, i.e. ions of atoms, molecules or clusters. Common are sector field magnets to the separate charged particles of different masses after electrostatic acceleration according to their mass-to-charge ratio. In a homogeneous magnetic field they follow a circular track with a radius r simply given by the equivalence of the Lorentz force as

$$e \cdot v \cdot B = m \cdot \frac{v^2}{r} \qquad (1)$$

With e the elementary charge, B the magnetic field strength, v the velocity, and m the mass of the particle. Particles of similar charge but different mass have different trajectories and corresponding deflection angles in the sector field magnet and as the result can be separated. Standard acceleration potentials for the entering ion beam are between 5 and 60 keV.

Another option for mass separation is a quadrupole mass filter (QMF) that operates usually with much lower accelerating voltages in the range of 50 to 100 V. The two-dimensional QMF structure was developed by W. Paul in 1953 and proposed as a mass spectrometer, for which he was awarded the Nobel Prize in 1989. He also considered and studied the three-dimensional quadrupole structure, which serves as ion trap with multiple applications including aside of analytics e.g. atomic clocks or quantum computers. For mass selection finally the flight time of charged particles in so called time-of-flight (TOF) mass spectrometers can be analyzed.

The goal of the experiment at the QMF is to understand the operation principle of this very typical instrument with wide range application. Analytically we shall study the elemental and molecular composition of different gases, investigate the precision on the mass scale as well as the peak height and learn about the characteristic fragmentation, which serves of calibration. The operating conditions and all parameters of the quadrupole mass filter (QMF) are to be adjusted, the QMF is to be calibrated and finally unknown substances will be identified.

2 Operation Principle of a Quadrupole Mass Filter

The particular property of a two-dimensional quadrupole field, as applied in a QMF, is the confinement of charged particles of a specific charge to mass ratio $\frac{q}{m}$ in the radial direction, while other particles are deflected out of the beam axis. As in the sector field magnet the underlying effect is the Lorentz force but this time involving alternating (AC) fields in the GHz frequency range. We restrict ourselves here to particle charge of *q = 1* without limitation of general validity.

The QMF structure and geometry is given in Fig. 1 with particles move along the z-axis. The distance between opposite surfaces of the hyperbolic electrodes is twice the free field radius, i.e. $2r_0$.

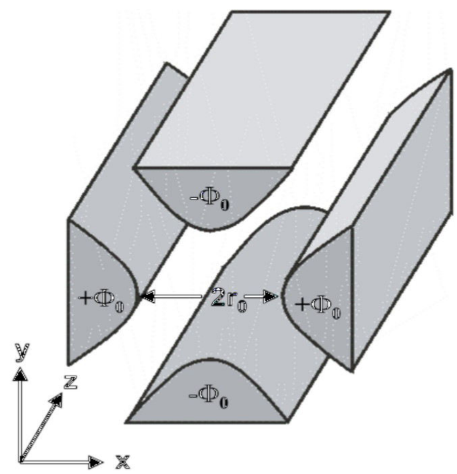

Fig.1: Spatial arrangement of the QMF electrodes

To keep the track of the desired particles along the central QMF axis, a repulsive force F is needed. For the quadrupole field this is linearly increasing with r according to $\vec{F} \propto -|r| \cdot \overrightarrow{e_r}$, which facilitates setting up the equations of movement.

The ideal quadrupole field is generated by hyperbolic electrodes, while in real systems also spherical structures are used with correction electrodes to simplify construction. Assuming that the electrodes are aligned along the z-direction and that the distance between the (0,0,z)-axis and the hyperbolic electrodes is $2r_0$, the potential can be written as:

$$\Phi(x,y,t) = \Phi_0(t)\frac{x^2-y^2}{r_0^2}, \tag{2}$$

with a potential of $\pm\Phi_0(t)$ applied to adjacent electrodes. Thus, no force is affecting the ion movement along the z-direction. The radial potential is shown in 2d and 3d representation in Fig. 2.

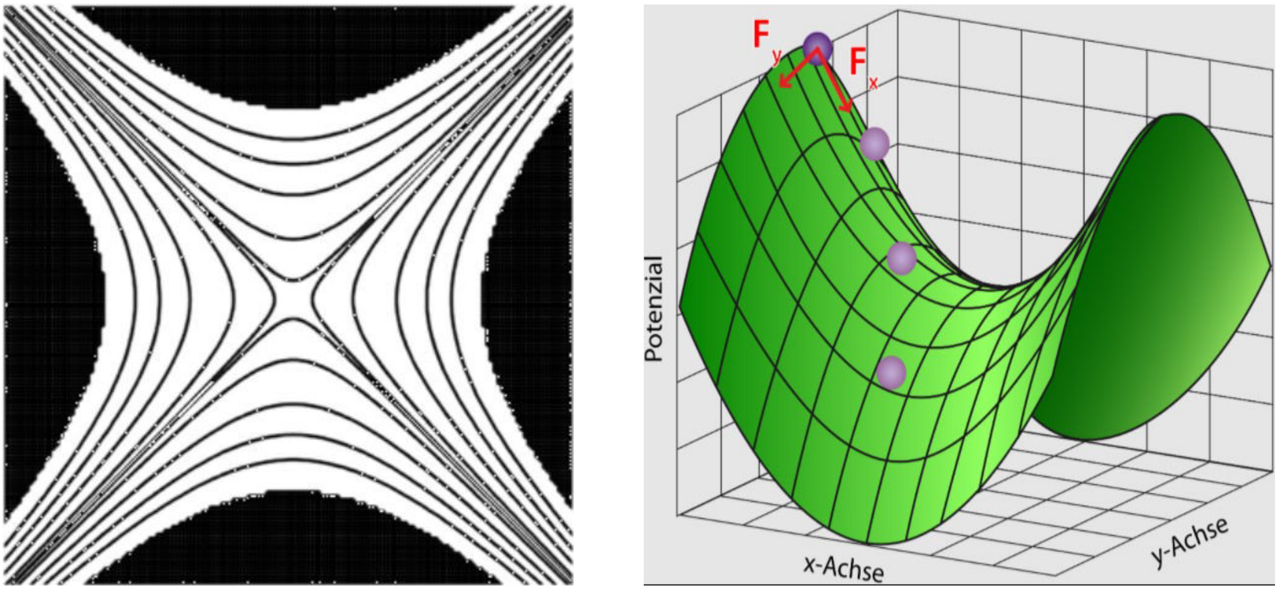

Fig. 2: a) Equipotential lines in the x,y-plane for a constant voltage applied to the electrodes.
b) 3d representation of the potential for a constant voltage applied to the electrodes. While focusing in x-direction, it is defocusing in y-direction, the corresponding movement of a charged particle is indicated.

As given in Fig. 2b, the field focuses in one direction (x-direction), while it defocuses in the other (y-direction), making an ion hit the quadrupole rods there. To prevent this an alternating (AC) voltage V is applied in addition to the constant direct (DC) voltage U, which must be properly chosen in amplitude and frequency. In this way an alternating focusing and defocusing in x- and y-direction can be realized. The resulting potential can be written as:

$$\Phi(x,y,t) = (U + V cos(\omega t)) \cdot \frac{x^2 - y^2}{r_0^2} \quad . \tag{3}$$

The equation of motion of an ion with charge e and mass m can be derived a:

$$m\frac{d^2}{dt^2}\vec{r} = e\vec{E} = -e\vec{\nabla}\Phi(x,y,t) \quad . \tag{4}$$

For the individual spatial directions, they are given by:

$$m\frac{d^2x}{dt^2} + \frac{2e}{r_0^2}(U + V cos(\omega t)x) = 0 \tag{5}$$

$$m\frac{d^2y}{dt^2} - \frac{2e}{r_0^2}(U + V cos(\omega t)y) = 0, \tag{6}$$

$$m\frac{d^2z}{dt^2} = 0 \tag{7}$$

While the third equation describes a uniform movement along z-direction as mentioned above, the first and second are homogeneous differential equations of second order, which cannot be solved analytically in this form. To solve this problem, we can use the transformations:

$$2\tau = \omega t, \tag{8}$$

$$a_x = -a_y = \frac{8eU}{m\omega^2 r_0^2} \tag{9}$$

$$q_x = -q_y = \frac{4eV}{m\omega^2 r_0^2}. \tag{10}$$

Then, the equations for x- and y-movement can be rewritten as Mathieu‘s differential equations, which are identical except for one minus sign:

$$\frac{d^2x}{d\tau^2} + (a_x + 2q_x \cos(2\tau))x = 0 \tag{11}$$

$$\frac{d^2y}{d\tau^2} - \left(a_y + 2q_y \cos(2\tau)\right)y = 0 \quad . \tag{12}$$

General solutions can be calculated as expansions of exponential functions. These can be related to the parameters $a_{x,y}$ and $q_{x,y}$, respectively, leading to parameter areas in a two dimensional *a,q* spaces for both dimensions. They either show instable or stable trajectories, the latter areas being called stability ranges. These are indicated in Fig. 3 for the y-movement.

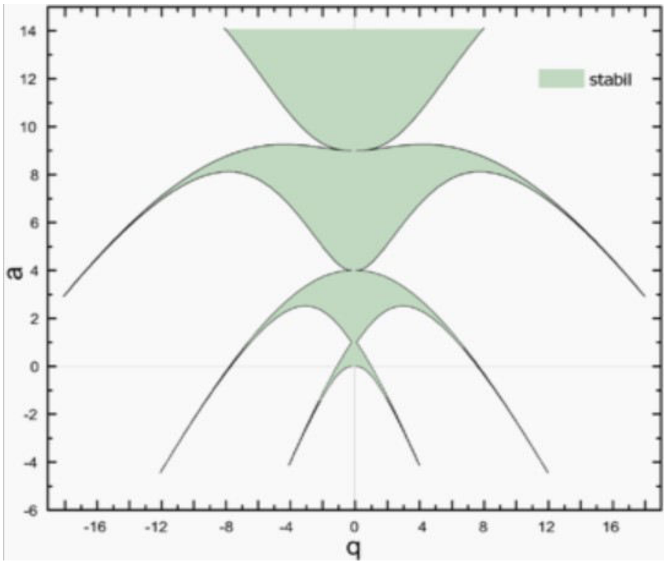

Fig. 3: Diagram of stable solutions for y-movement (green areas), the corresponding pattern for the x-movement is obtained by an inversion of the pattern at the *a = 0 and the q = 0* axes.

As only ions with stable trajectories in both, x- and y-direction can successfully transmit the mass filter, areas of stable solutions for both directions must be selected. Overlapping the stability areas for x- and y-direction leads to the overall stable solutions, as displayed in Fig. 4.

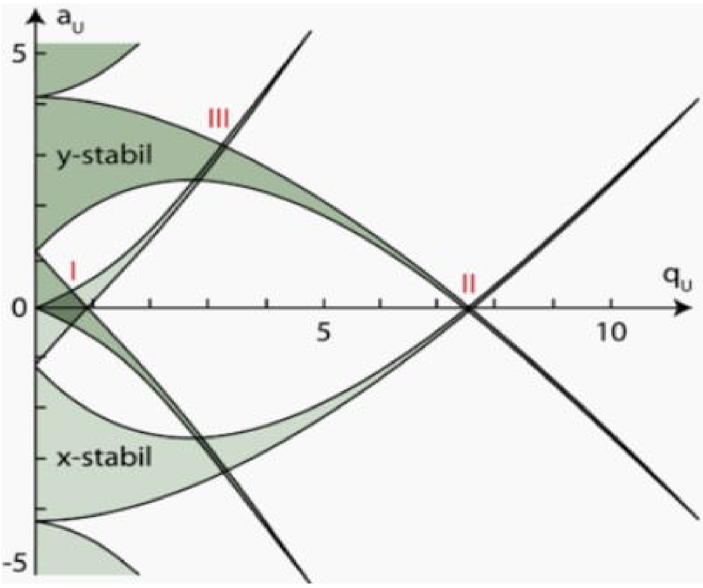

Fig. 4.: Diagram of stable solutions for x- and y-movement. The overlapping areas of stable solutions in both directions are numbered with I to III.

For a given polarity of the dc potential U and for limited voltage we are restricted to the non-negative *a* and *q* part of stable area I, resulting in the common stability triangle of a QMF. A closer look on it is presented in Fig. 5. Outside the triangle the ions show unstable movement, will hit the electrode and will be lost.

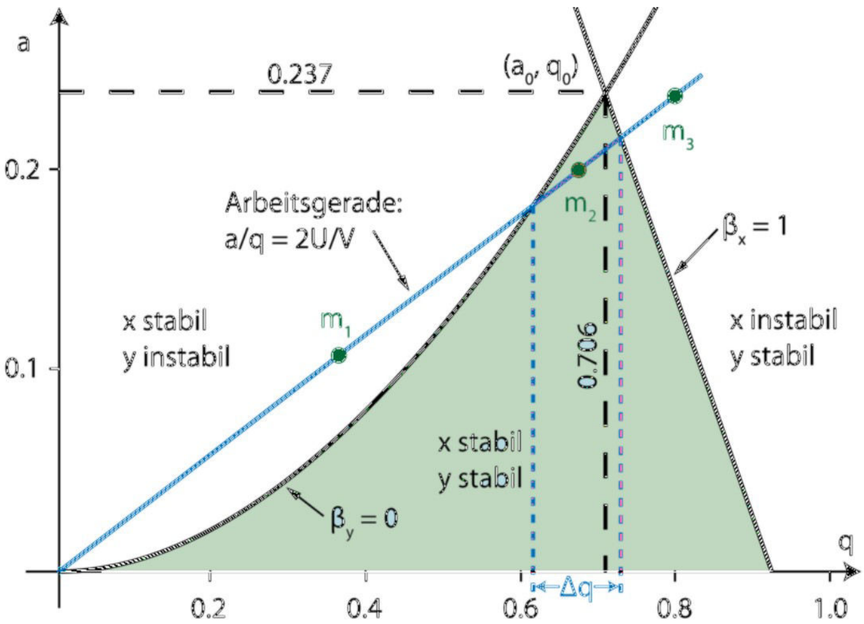

Fig. 5: According to its triangular shape, the stability area (I) is called stability triangle. The working line (solid blue) is given by the chosen value of the ratio a/q, which defines the resolution.

Fig. 5 also shows the so-called working line, which is given by a well-defined ratio $\frac{a}{q} = 2\frac{U}{V}$. According to the definition of *a* and *q* in equations 9 and 10, particles with a given mass m lie on a well-defined point on this line. For a reasonable ratio of a/q, the slope is low enough to have the working line intersect the stability triangle. In this case a variation of both potentials *U* and *V* along this line defines an interval Δq of stable movements, which can be assigned directly to a mass interval Δm. Only ions with a mass inside this interval have stable trajectories and can pass the QMF. By changing the ratio a/q the mass resolution can be adjusted via the slope of the working line as given by:

$$\frac{m}{\Delta m} = \frac{0.126}{0.1678 - \frac{U}{V}} \tag{13}$$