

# Quadrupoles: How do they work?

## Mass Spectrometer

The mass spectrometer is essentially an instrument used to measure the mass, or more correctly the mass/charge ratio, of ionized atoms or other electrically charged particles. Mass spectrometers are found in chemistry, biology, forensic and medicine laboratories to determine compositions, to measure isotopic ratios or identify contaminations.

The first mass spectrographs were invented almost 100 years ago, by A.J. Dempster, F.W. Aston and others, and have therefore been in continuous development over a very long period. However, the principle of using electric and magnetic fields to accelerate and establish the trajectories of ions inside the spectrometer according to their mass/charge ratio is common to all the different designs.

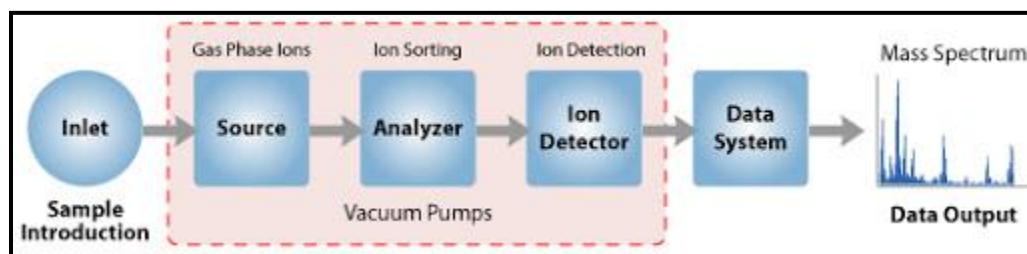


Figure 1: Schematic of a mass spectrometer system.

## Quadrupole Mass Spectrometer

In practice, it is difficult to achieve very stable and spatially uniform magnetic fields, especially with permanent magnets. These difficulties can lead to degradation of the mass resolution and drifts in the calibration of the instrument. In addition, the presence of stray magnetic fields can affect other instruments that may be used in conjunction with a mass spectrometer, for example, electron energy analyzers. In the early 1950's it was realized, by W. Paul (shared Nobel Prize in Physics, 1989) that use of magnetic fields could be eliminated altogether by a clever design which uses alternating quadrupolar electric fields rather than magnetic fields, hence the name Quadrupole Mass Spectrometer. This is the design that is currently in widespread use for residual gas analysis. It is highly stable and has excellent mass resolution. The operation of the Quadrupole Mass Spectrometer (QMS) is not quite so simple to understand as the magnetic sector design, but it is extremely elegant and involves some beautiful mathematics, and therefore the details are worth appreciating.

First, the overall quadrupole layout:

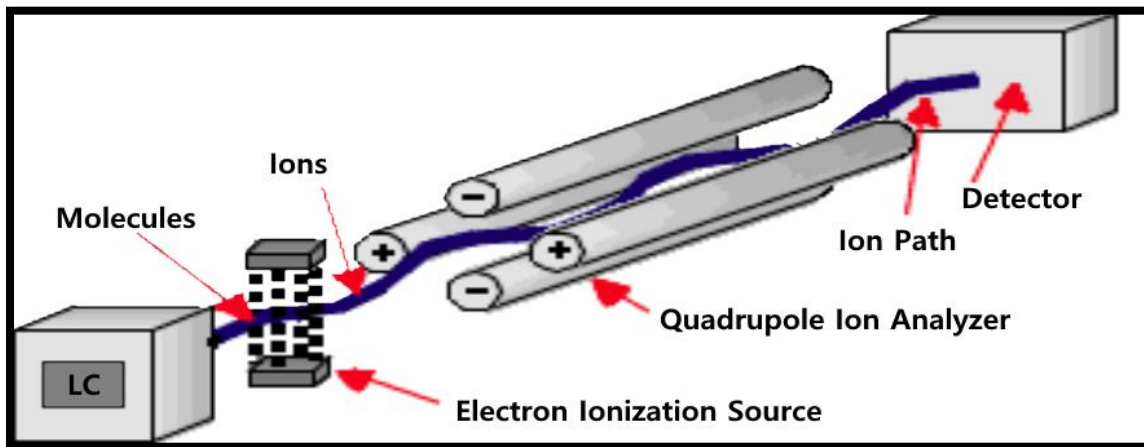


Figure 2: Schematic of a quadrupole mass filter.

A quadrupole mass spectrometer consists of an ionizer (bombardment by electrons from a hot filament), an ion accelerator, and a mass filter consisting of four parallel metal rods arranged as in the figure above. Two opposite rods have an applied potential of  $(U+V\cos(\omega t))$  and the other two rods have a potential of  $-(U+V\cos(\omega t))$ , where  $U$  is a dc voltage and  $V\cos(\omega t)$  is an ac voltage. The applied voltages affect the trajectory of ions traveling down the flight path centered between the four rods. For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path. A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied. There are two methods: varying  $\omega$  and holding  $U$  and  $V$  constant, or varying  $U$  and  $V$  with  $(U/V)$  fixed for a constant angular frequency,  $\omega$ .

The general principle of operation of the mass filter can be visualized *qualitatively* as follows: light ions (low mass to charge ratio) are able to follow the alternating component of the field. For the X-direction, those ions will stay in phase with the RF drive, gain energy from the field and oscillate with increasingly large amplitude until they encounter one of the rods and are discharged. Therefore the X-direction is a **high-pass mass filter**: only high masses will be transmitted to the other end of the quadrupole without striking the X-electrodes. On the other hand, in the Y-direction, heavy ions will be unstable because of the defocusing effect of the DC component, but some lighter ions will be stabilized by the AC component if its magnitude is such as to correct the trajectory whenever its amplitude tends to increase. Thus the Y-direction is a **low-pass mass filter**: only low masses will be transmitted to the other end of the quadrupole without striking the Y electrodes. By a suitable choice of RF/DC ratio, the two directions together give a mass filter which can resolve individual atomic masses.

The attractive features of the quadrupole as a mass analyzer are evident from the above discussion: the quadrupole provides a convenient filter which can be tuned to the desired mass by varying the amplitude of the RF voltage,  $V$ ; the mass selectivity (i.e. resolution) can also be varied electronically by simply adjusting the DC/RF ratio. Simultaneously varying the amplitude of the DC and RF voltages (at fixed  $\omega$ ) allows the entire mass spectrum to be scanned.

The X- and Y-motions of an ion with mass  $m$  and charge  $q$  are described by the Mathieu's equation of motion for the three separate coordinate axes:

$$\frac{d^2x}{dt^2} = - \frac{(e)}{(m)} \frac{[U + V \cos(\omega t)]}{r_0^2} x, \quad \frac{d^2y}{dt^2} = + \frac{(e)}{(m)} \frac{[U + V \cos(\omega t)]}{r_0^2} y, \quad \frac{d^2z}{dt^2} = 0$$

Equation 1: Mathieu's Equation in QMS

The Mathieu equations can only be solved numerically. The important characteristic of the solutions is that they are only stable (real) for a certain range of values of  $U$  and  $V$ . The regions of stable solutions are shown below as a function of  $U$  and  $V$ . The region where the stable solutions of both x-motion y-motion intersect is where the quadrupole mass filter operates. More details on the application of the Mathieu equations to the QMS can be found in an excellent review by R.E.March, An Introduction to Quadrupole Ion Trap Mass Spectrometry, Journal of Mass Spectrometry 32, 351-369 (1997).

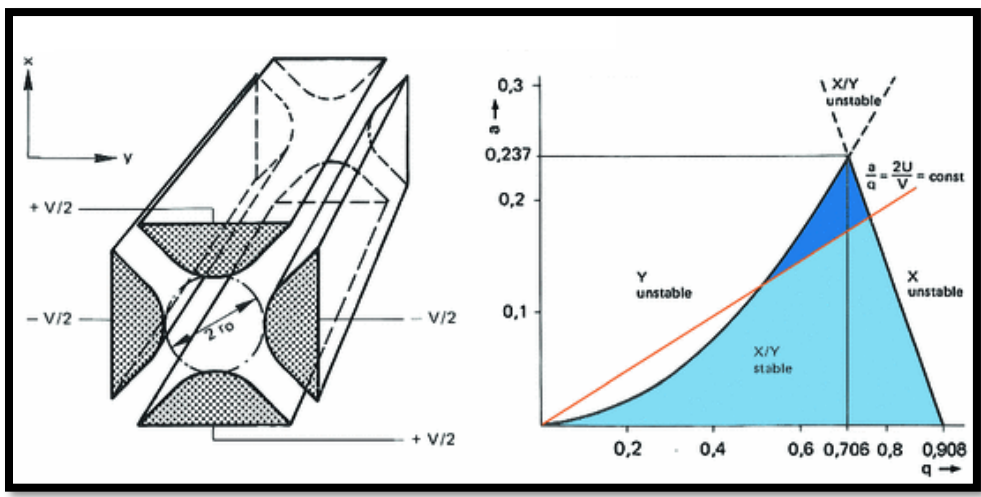


Figure 3: Stability trajectories obeying Mathieu's Equation in QMS

Contact the TRACES Manager for full details.