

The Quadrupole Mass Filter: Basic Operating Concepts

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Quadrupole mass analyzers are now widely used in many areas of chemical analysis. Although popularly referred to as quadrupole mass spectrometers, the mass-resolving properties of such devices are really much more akin to those of a tunable variable bandpass mass filter. Only ions within a narrow mass region (generally <1 amu) are allowed to pass through the device. By electronically sweeping the position of the bandpass region, a quadrupole may be used to mimic the behavior of a mass spectrometer (see Figure 1). Specifically, the mass-resolving properties of quadrupoles result from an ion's intrinsic stability or instability within the device. In contrast, true mass spectrometers resolve ions by dispersing ions in either space, as in the case of a magnetic sector instrument (see Fig. 2), or in time, as in the case of a time-of-flight instrument (see Fig. 3).

Although once considered by many to be only suitable for residual gas analysis, today quadrupole devices probably produce more mass spectra than any other type of mass analyzer found in the chemical research or industrial laboratory. High-performance quadrupole mass analyzers are now produced and marketed by no less than a half dozen reputable manufacturers. Further, in applications where extremely high resolution data or exact mass measurements are not required, quadrupoles offer a number of significant advantages over more traditional mass analyzers.

The short distance between the ion source and the detector (usually less than 15 cm) combined with the strong focusing properties of such devices make the quadrupole mass analyzer useful at comparatively high pressures (5×10^{-5} Torr). This feature has led to the widespread use of the quadrupole mass analyzer for combined gas chromatography mass spectrometry (GC-MS) (1) and liquid chromatography mass spectrometry (LC-MS) (2, 3).

In contrast to magnetic and electric sector instrumentation, quadrupoles resolve ions on the basis of their mass-to-charge ratio (m/e), rather than on the basis of momentum or kinetic energy. Thus unit mass resolution may be preserved even when sampling ion populations which have wide velocity distributions. This feature has proven to be useful in a number of practical situations including the coupling of the quadrupole mass analyzer with an inductively coupled plasma ion source (ICP-MS) (4, 5), and the successive use of quadrupole mass analyzers as a method of performing mass spectrometry-mass spectrometry (MS-MS) experiments (6-8).

A third useful feature of the quadrupole mass analyzer is the mechanical simplicity of the instrument. Unlike many other types of mass analyzers, quadrupole devices do not rely on the use of magnetic fields for their mass-discriminating properties. Thus the cost, bulk, weight, and slow scan speeds commonly associated with magnets are avoided. Further, the resolution of quadrupole devices is set electronically, rather than mechanically, through the use of slits. These facts make quadrupole instrumentation ideal for remote, mobile, or unattended operation. Examples include the adaptation of quadrupole mass analyzers for space flight (9), and the use of vehicular-based quadrupole instrumentation for real time environmental monitoring (10, 11).

Despite the widespread use of quadrupole mass analyzers in both academic and industrial laboratories, a notable void exists in the understanding of these important devices. Perhaps the single greatest obstacle to the widespread understanding of such devices is the nature of the differential equations that govern the trajectory of particles within the device. In contrast to many other types of mass analyzers,

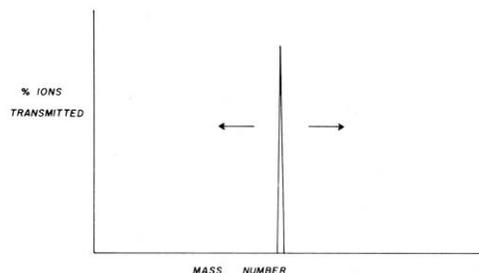


Figure 1. Mass spectra are obtained by electronically sweeping the bandpass region along a mass axis.

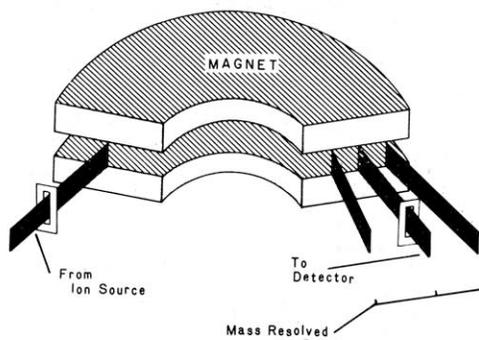


Figure 2. The magnetic sector mass spectrometer disperses ions having different mass to charge ratio spatially.

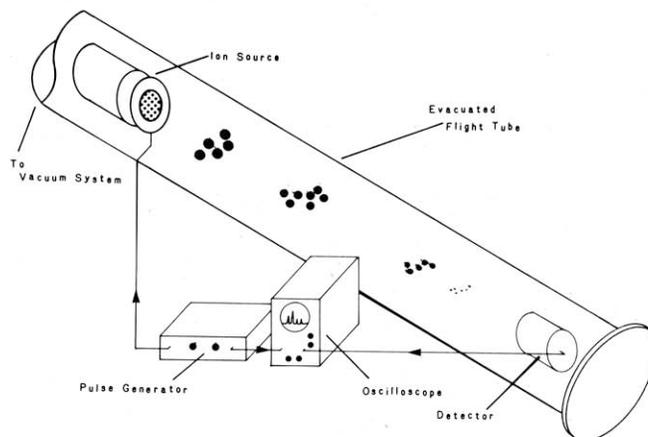


Figure 3. The time-of-flight mass spectrometer disperses ions having different mass to charge ratios temporally (in time).

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$$r = 1.148 r_0$$

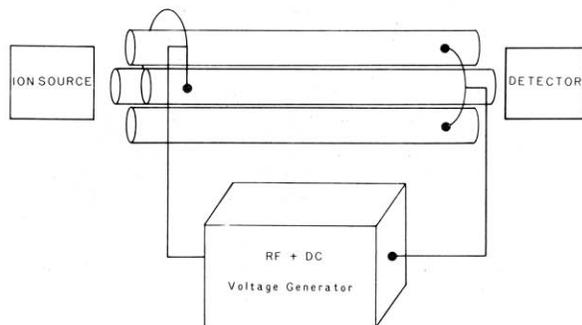


Figure 4. Experimental configuration of a quadrupole mass analyzer.

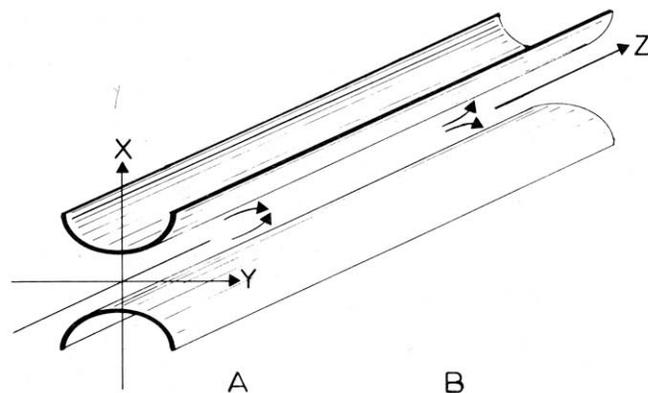


Figure 5. Operation of quadrupole in the x - z plane. a) Ions are focused toward center axis when the electrode potential is positive with respect to center axis. b) Ions are defocused when electrode potential is negative with respect to center axis.

such as magnetic or electric sector instruments, ion cyclotron resonance spectrometers, and time-of-flight instrumentation, the solutions to the differential equations that ultimately lead to the mass-resolving properties of quadrupoles are highly complex and difficult to treat analytically. Thus the operation of such devices is presented, particularly at the undergraduate level, in a manner that is not easily extended either to the explanation of related devices, such as the quadrupole ion storage trap (QUISTOR)² or the novel application of existing devices. Rather than visualizing the operation of the quadrupole mass analyzer in terms of trajectory simulations derived from analytical theory, numerical integration, or matrix calculations, it is suggested that alternative semiquantitative approaches be utilized for the introduction of the novice to the theory of the quadrupole mass filter. The purpose of this manuscript is to introduce the educator to such an explanation (12–14), which is useful to the novice yet powerful enough to be extended to the operation of related devices.

Physically the quadrupole mass analyzer consists of a set of four electrodes, ideally of hyperbolic cross section, that are accurately positioned in a radial array. For practical as well as economic reasons, most mass filters have employed electrodes of circular cross section (see Fig. 4). Denison (15) has shown that the best approximation to the ideal hyperbolic field can be obtained if the radius of the circular electrodes (r) is related to the quadrupole field radius (r_0) by the expression

although the erroneous value of 1.16 still occasionally appears in the literature.

Qualitative Description of Quadrupole Operation

The filtering action of the quadrupole mass analyzer is obtained by the application of a combination of a time-independent (dc) and a time-dependent (ac) potential. The operation of a quadrupole mass filter is best visualized by considering the effect that the electrode structure and the applied potential have on the trajectory of a charged particle in the X - Z and Y - Z planes separately. We will begin by considering the effect that a time-dependent or ac potential has on the trajectories of a beam of ions travelling in the X - Z plane. During a single period of the applied ac waveform, in the absence of a dc potential, the electrodes lying along the X axis spend $1/2$ cycle at a positive potential and $1/2$ cycle at a negative potential, relative to the center axis of the instrument. When the ac potential is positive with respect to the center axis, a beam of positive ions will be accelerated or focused onto the center axis of the electrode structure (see Fig. 5a). Conversely, when the applied potential is negative, a positive beam of ions will be accelerated toward the negatively biased electrodes. That is, positively charged ions will be defocused away from the center axis (see Fig. 5b). Whether a particular ion will strike an electrode, and thus be eliminated from the beam before it reaches the detector, is a function of how long it takes that ion to reach a negatively biased electrode. The specific dynamics of this process will be governed by a number of factors including the instantaneous magnitude of the negative potential applied to the electrodes, the period of time during which the electrodes are held at a negative potential (e.g., the frequency of the ac waveform), as well as the position, velocity, and mass-to-charge ratio (m/e) of the particle.

Let us now take into account the effect that results from adding a dc or time-independent term to the applied potential. Specifically, a positive dc potential is applied to those electrodes that lie in the X - Z plane. Consider, in a qualitative sense, the mass-dependent effect that the combined dc and ac potentials will have on the trajectories of a collection of ions. If an ion is very heavy and/or the frequency of the ac potential is very rapid, an ion will tend only to feel the effect of the average potential applied to the electrode structure. That is, heavy ions will tend only to be influenced by the positive dc potential. This means that such ions will be focused onto the center axis of the instrument. The small periods of time during which the electrodes are at a negative potential will have a negligible effect on the trajectories of heavy ions. In contrast, if an ion is very light, its path may be considerably affected by the rapidly varying ac potential. If in fact an ion is sufficiently light, it may experience a large enough acceleration, during a negative voltage excursion, to cause it to collide with an electrode and be discharged and pumped away as a neutral species. That is, ions will be filtered on the basis of their mass-to-charge ratio. In particular, ions below some critical m/e value will be filtered out of the beam, owing to speed with which they can respond to the defocusing action provided by the negative portion of the ac potential. On the other hand, those ions having a mass above the critical m/e value will be transmitted through the device and on to the detector. Thus the electrode structure and the nature of the applied potential combine to form a high pass mass filter that operates in the X - Z plane (see Fig. 6).

Let us now discuss the nature of ion trajectories in the Y - Z plane. At any instant, the potential applied to the electrodes lying along the Y axis is equal in magnitude but opposite in sign to the potential applied to the electrodes that lie along the X axis. This means that the ac (RF) waveform applied to

² Available commercially as a GC detector from Finnigan MAT Corp., 355 River Oaks Parkway, San Jose, CA.

the X electrodes is 180° out of phase with the potential applied to the Y electrodes. More important, however, is the fact that the dc potential applied to the electrodes lying in the X-Z plane is positive, while the dc potential applied to electrodes lying in the Y-Z plane is negative. Again heavy ions will only tend to be influenced by the average value of the applied potential, that is, the dc potential. In this case, however, the dc potential is negative. This means that comparatively heavy ions will tend to be eliminated from the ion beam owing to the defocusing effect caused by the negative dc potential. On the other hand, if an ion is sufficiently light, it may respond to the focusing action that results when the positive portion of the alternating field becomes larger than the static negative potential. If in fact the frequency and magnitude of the ac field are well chosen, it is useful to think of the ac potential as essentially correcting the trajectories of light ions thus preventing them from striking the electrodes along the Y axis. At first such an argument might seem contrived. An extension of a mechanical analogy given by Dawson (13) is sometimes useful in further understanding the nature of this filtering action. Consider two balls of different mass at the minimum-maximum of a saddle-like surface. Clearly with respect to the local maximum both balls are unstable. Consider, however, the situation that would occur if the saddle surface were quickly inverted from one side to the other in a periodic fashion. If the frequency and magnitude of the oscillation were well chosen, both of the balls could be made to remain in the saddle, despite their inherent instability in the static field. If the frequency and magnitude of saddle inversion were gradually reduced, clearly because of momentum considerations, the heavier ball would be lost first. Analogously, the electrodes and the applied potential combine to create a low pass mass filter in the Y-Z plane (see Fig. 7).

In order for an ion to travel from the source to the detector, clearly it must remain stable in both the X-Z and Y-Z planes. In light of the above discussion, this means that for an ion to traverse the electrode structure it must be sufficiently light such that it is not eliminated by the low pass filter operating in the Y-Z plane but not so light as to be eliminated by the high pass filter which operates in the X-Z plane. This condition of mutual stability describes a bandpass filter which is represented in Figure 8. As will be demonstrated below the width of the bandpass region, which is indicative of the mass resolution of the device, is governed by the ratio of the ac-to-dc potentials applied to the electrodes. It will be shown that the mass corresponding to the center of the mutual stability region is governed by the magnitude of both the ac and dc potentials.

A Semiquantitative Description of Quadrupole Operation

Although the qualitative description given above provides some physical insight into the nature of the mass-filtering processes that take place within a quadrupole, the interaction of the larger number of physical variables that are in-

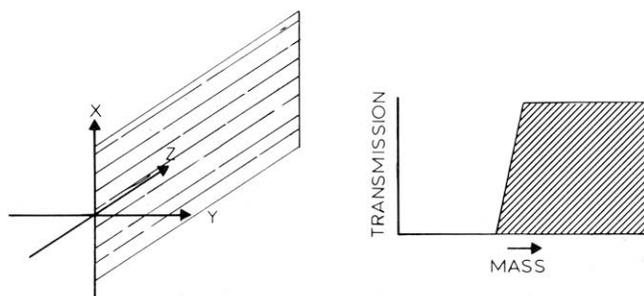


Figure 6. The quadrupole acts as a high pass mass filter in the x-z plane.

herent in the operation of any quadrupole device can only be appreciated by a somewhat more quantitative description of the device.

The Equations of Motion

Let us begin by describing the nature of the potential (voltage) distribution that ionized particles encounter as they enter the mass analyzer. This description will depend upon two factors, a spatial factor that describes the shape of the electrode structure and a second factor that describes the time-dependent nature of the voltage applied to the electrode structure. For a sinusoidally operated hyperbolic mass filter the potential distribution (Φ) at and time (t) can be described by the expression

$$\Phi = [U + V\cos(\omega t)] \frac{x^2 - y^2}{2r_0^2} \quad (1)$$

where x and y are the distances along the given coordinate axes, r_0 is the distance from the center axis (the z axis) to the surface of any electrode, ω is the angular frequency ($2\pi f$) of the applied ac waveform, V is the magnitude of the applied ac or RF waveform, and U is the magnitude of the applied dc potential.

Within the electrode structure a time-dependent electric field will be defined by the potentials that are applied to the electrode structure. The magnitude of this electric field is easily calculated by taking the partial derivative of the potential distribution as a function of the distance along any of the coordinate axes.

$$E_x = -\frac{\partial\Phi}{\partial x} = -[U + V\cos(\omega t)] \frac{x}{r_0^2} \quad (2)$$

$$E_y = -\frac{\partial\Phi}{\partial y} = [U + V\cos(\omega t)] \frac{y}{r_0^2} \quad (3)$$

$$E_z = -\frac{\partial\Phi}{\partial z} = 0 \quad (4)$$

The force (F) exerted on a charged particle is given by the magnitude of the electric field multiplied by the charge on the particle.

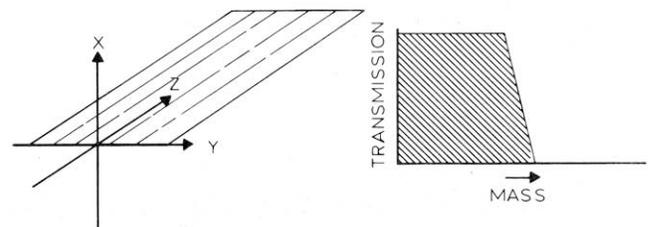


Figure 7. The quadrupole acts as a low pass mass filter in the y-z plane.

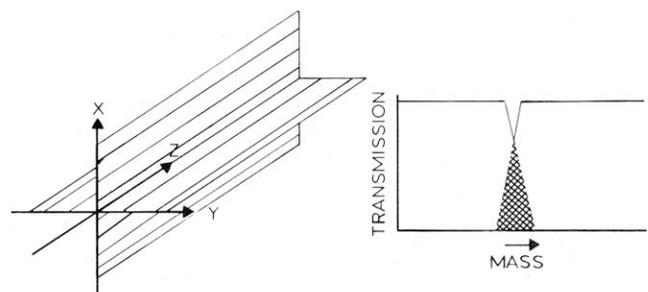


Figure 8. Operation of the quadrupole as a bandpass mass filter results from overlap of the high pass mass filter of the x-z plane and the low pass mass filter of the y-z plane.

$$F_x = -[U + V\cos(\omega t)] \frac{ex}{r_0^2} \quad (5)$$

$$F_y = [U + V\cos(\omega t)] \frac{ey}{r_0^2} \quad (6)$$

$$F_z = 0 \quad (7)$$

By Newton's law of $F=ma$,

$$\frac{d^2x}{dt^2} + \frac{ex}{mr_0^2} [U + V\cos(\omega t)] = 0 \quad (8)$$

$$\frac{d^2y}{dt^2} - \frac{ey}{mr_0^2} [U + V\cos(\omega t)] = 0 \quad (9)$$

$$\frac{d^2z}{dt^2} = 0 \quad (10)$$

The solutions to these differential equations would give a complete description of the trajectory of any ion in terms of each ion's initial conditions. The solution to eq 10 is trivial; it tells us that the position and velocity of an ion along the z axis remains unaffected by any potential applied to the electrode structure. Notice that the use of electrodes of hyperbolic cross section leads to equations of motion that contain no cross-coordinate terms. That is, the motion of the particle remains independent along each of the three coordinate axes.

If we define the parameters a and q such that

$$a = \frac{4eU}{\omega^2 r_0^2 m} \quad (11)$$

and

$$q = \frac{2eV}{\omega^2 r_0^2 m} \quad (12)$$

Then eqs 8 and 9 may be restated as

$$\frac{d^2x}{dt^2} + \frac{\omega^2}{4} [a + 2q\cos(\omega t)]x = 0 \quad (13)$$

$$\frac{d^2y}{dt^2} - \frac{\omega^2}{4} [a + 2q\cos(\omega t)]y = 0 \quad (14)$$

Equations 13 and 14 may be transformed into the canonical form of Mathieu's differential equation by the following change of variables

$$\xi = \frac{t}{2} \quad (15)$$

This implies that the quantity $d^2u/d\xi^2$ must be calculated where u represents either x (eq 13) or y (eq 14). By application of the chain rule

$$\frac{du}{d\xi} = \frac{du}{dt} \cdot \frac{dt}{d\xi} \quad (16)$$

Thus the second derivative is given by

$$\frac{d^2u}{d\xi^2} = \frac{d}{d\xi} \left[\frac{du}{dt} \cdot \frac{dt}{d\xi} \right] \quad (17)$$

applying the product rule gives

$$\frac{d^2u}{d\xi^2} = \frac{d^2t}{d\xi^2} \cdot \frac{du}{dt} + \frac{d}{d\xi} \left[\frac{du}{dt} \right] \cdot \frac{dt}{d\xi} \quad (18)$$

By referring to eq 16 it is noted that

$$\frac{d}{d\xi} \left[\frac{du}{dt} \right] = \frac{d^2u}{dt^2} \cdot \frac{dt}{d\xi} \quad (19)$$

Thus

$$\frac{d^2u}{d\xi^2} = \frac{d^2t}{d\xi^2} \cdot \frac{du}{dt} + \frac{d^2u}{dt^2} \cdot \left[\frac{dt}{d\xi} \right]^2 \quad (20)$$

Noting that

$$\frac{d^2t}{d\xi^2} = 0$$

and

$$\frac{dt}{d\xi} = \frac{2}{\omega} \quad (21)$$

allows one to write

$$\frac{d^2u}{d\xi^2} + [a_u + 2q_u \cos 2\xi]u = 0 \quad (22)$$

The Stability Diagram

Equation 22 is in the canonical form of Mathieu's differential equation, named for the French scholar E. Mathieu who introduced the use of such an equation in his 19th century discourse on the vibrational modes of a stretched membrane having an elliptical boundary. Fortunately, an understanding of quadrupole devices does not require an extensive knowledge of such solutions. In fact, the generalized behavior of the solutions of such differential equations is usually all that is needed to understand most of the salient features of quadrupole operation. In particular it can be shown that solutions of this type of differential equation may be readily classified as being either bounded solutions or unbounded solutions. Physically, a bounded solution corresponds to a case where the displacement of the particle along either the Y or X axis remains finite. Ideally, in terms of the quadrupole mass filter, such a case would correspond to a stable trajectory. That is, a particle entering the mass filter would be transmitted through the device and ultimately be registered at the detector. In contrast, an unbounded solution corresponds to a case where the radial displacement of the particle would be expected to increase without bound. Solutions of this type correspond to particles which have unstable trajectories. Such particles will be filtered out of the ion beam, due to collisions with the electrodes, before they can strike the detector. An extended analysis (16) of the pertinent differential equations reveals that the stability of the appropriate solutions depend only upon the parameters a and q , which were defined above. This fact allows one to plot regions in a - q space where solutions to the equations of motion are stable or unstable (16).

The shaded region in Figure 9 represents a collection of points in a - q space that correspond to stable solutions of the

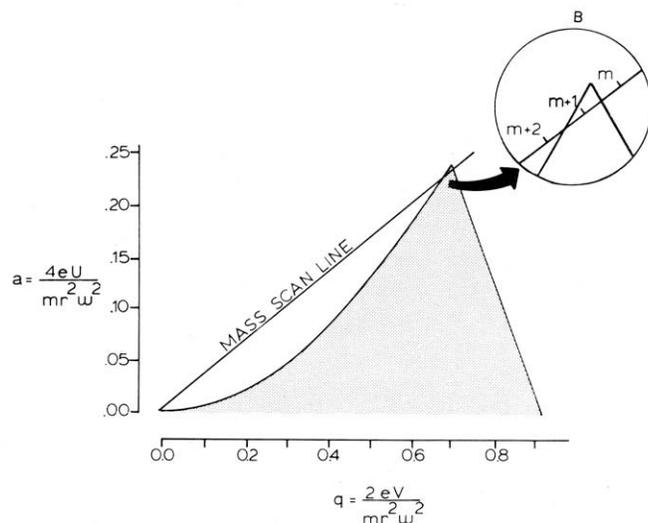


Figure 9. The a - q stability diagram: a) The shaded area represents those areas in a - q space which correspond to stable solutions of Mathieu's differential equation. b) The one amu bandpass mass filter: Notice that only ions of m/e $+ 1$ fall within the stability diagram.

equations of motion in both the X-Z plane and the Y-Z plane. In physical terms the stability diagram allows the operation of the quadrupole mass filter to be reduced from a six-dimensional problem (involving $e, \omega, r_0, m, U, \text{ and } V$) to a two-dimensional problem involving only the reduced parameters a and q . This results in a tremendous conceptual simplification that allows one to visualize readily the effect that changes in the various physical parameters will have on the operation of the quadrupole mass filter.

The Narrow Bandpass Mass Filter

Historically, the most important use of the quadrupole mass filter has been as a mass spectrometer. Recall that the quadrupole mass spectrometer is really a tunable mass filter capable of producing mass spectra. Such a distinction is particularly convenient in understanding the operation of such devices. In particular let us describe the operation of a narrow bandpass mass filter in terms of the a - q stability diagram.

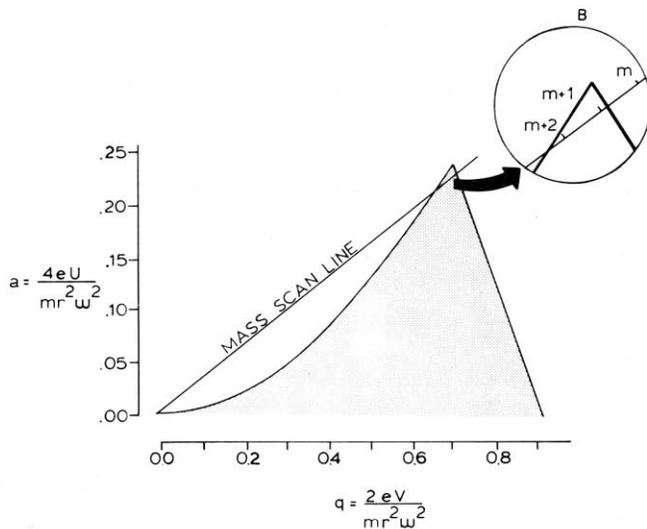


Figure 10. The variable bandpass mass filter: By adjusting the slope of the mass scan line, the bandpass region of the mass filter can be varied. The slope of the mass scan line is given by $a/q = 2U/V$.

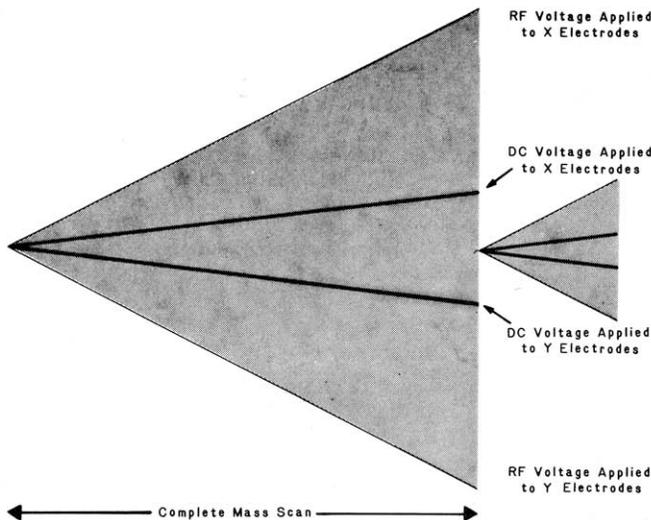


Figure 11. The nature of the potential applied to the electrode structure during a scan. The magnitude of both the ac waveform and the dc voltage are increased while keeping their ratio constant.

In principle, one could operate a quadrupole in a manner in which the parameters a and q were, at all times, independent of one another. That is, for any given mass a quadrupole could be operated at any arbitrary point in a - q space. In practice, quadrupoles are usually operated in a manner such that the values of parameters a and q are always related by a simple ratio. Specifically, this condition is established by ensuring that the applied dc is always some fraction of the applied ac potential. That is, the ratio U/V is held constant, regardless of the actual magnitude of either U or V . In terms of the a - q diagram, holding the ratio U/V constant is equivalent to restricting operation of the mass filter to a set of operating points which lie on a straight line which has a zero intercept. Such a line is known as the mass scan line (see Fig. 9). Since a and q contain a large number of common factors, the slope of the mass scan line (the quantity a/q) is given by the ratio $2U/V$.

If, for a moment, one assumes that the values of the parameters $e, \omega, U, \text{ and } V$ remain fixed, then a convenient conceptualization of the mass scan line is that of a number line which contains the mass of all particles. Recall, that mass (m) is inversely proportional to both a and q . Thus lighter particles (ions) will appear, along the mass scan line at the top right-hand portion of Figure 9, while heavier particles will appear on those portions of the mass scan line that are near the lower left-hand corner of Figure 9. Consider now if the slope of the mass scan line is suitably adjusted (by appropriate adjustment of the U/V ratio) such that only a small portion of the mass scan line falls anywhere within the stability diagram (see Fig. 9b). Physically the situation illustrated in Figure 9b would result in ions of only one mass ($m + 1$) being able to pass through the electrode structure and on to the detector. Thus the sharp tip of the a - q diagram may be used to create a narrow bandpass mass filter. The bandpass region of this filter (the resolution) is easily changed by simply altering the slope of the mass scan line (changing the value of U/V). For example, if the ratio U/V is lowered, the resolution of the quadrupole would be reduced (see Fig. 10). Commercial quadrupole instrumentation is typically able to attain a resolution on the order of about 1 part in 1500.

The most convenient method of scanning the bandpass region of such a filter is by sweeping the voltage applied to the electrode structure. Consider if the voltages V and U are simultaneously increased, while keeping their ratio constant, clearly the magnitude of the mass represented on the mass scan line at any particular coordinate in a - q space must also increase. For example, if the magnitudes of both U and V are suddenly doubled, the mass (m) that appears at the a - q coordinates that corresponds to the tip of the stability diagram must also double. Thus a voltage increase is equivalent to sliding the mass scale shown in Figure 9 upward and to the right along the mass scan line. Sweeping the voltage applied to the electrode structure (see Fig. 11) thus provides a convenient method of scanning the bandpass region of the mass filter (see Fig. 1).

The RF-only Quadrupole Mass Filter

The stability diagram is particularly powerful in that it can easily be extended to rationalize the behavior of nontraditional modes of quadrupole operation. The radio frequency only (RF-only) mode of operation provides a case in point. The RF-only mode of operation is achieved by the removal of the dc potential from the quadrupole electrode structure. In terms of the a - q stability diagram this is equivalent to operating the quadrupole under conditions where the Mathieu parameter a is always equal to zero. The mass scan line corresponding to the operation of an RF-only quadrupole device is represented by a line in a - q space that has a slope of zero and intercepts the a axis at the point $a = 0$. In contrast to the one amu bandpass mass filter, we find that a rather large portion of the mass scan line falls within the stability

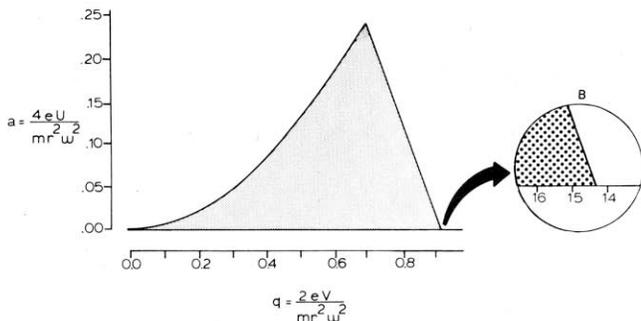


Figure 12. The a - q diagram representing the RF-only quadrupole mass analyzer. Notice, in this example ions having an m/e of 15 and 16 should have stable trajectories while ions having an m/e of 14 will be filtered out.

region of the a - q diagram. Thus a large number of ions having different m/e values would be predicted to have stable trajectories within the device. This fact has unfortunately led to the popular misconception that RF-only quadrupoles are total ion transmission devices. Examination of the a - q stability diagram (Fig. 12) reveals in fact that such devices are high pass mass filters. In actual fact the situation is further complicated by certain focusing conditions, and by the fact that each m/e ion has a unique coordinate along the q axis (17).

For many years the RF-only mode of operation remained somewhat obscure. The development of triple quadrupole mass spectrometry by Yost and Enke (6-8) has prompted recent interest in such devices. RF-only quadrupoles have also been utilized as a method of obtaining a "total ion chromatograph" in GC-MS (1) and function as part of a unique fast-scanning quadrupole device recently introduced commercially (18). Further, RF-only quadrupoles form the basis for a novel notch mass filter (19, 20).

Conclusion

The a - q stability diagram provides a powerful method of visualizing the operation of the quadrupole mass filter, and the interaction of a number of experimental variables. In addition to providing the student with a basis for understanding the many diverse operational modes of the quadrupole mass filter, the stability diagram also provides the student with the basic conceptual tools needed to understand related instrumentation such as the monopole mass analyzer (see Fig. 13) and the quadrupole ion storage trap (QUISTOR) (see Fig. 14). It is the authors' hope that the a - q stability diagram will be incorporated into the undergraduate instrumental analysis curriculum both to enlighten the interested student as well as to fight the widely held misconception that quadrupole mass analyzers are complex and incomprehensible devices.

Acknowledgment

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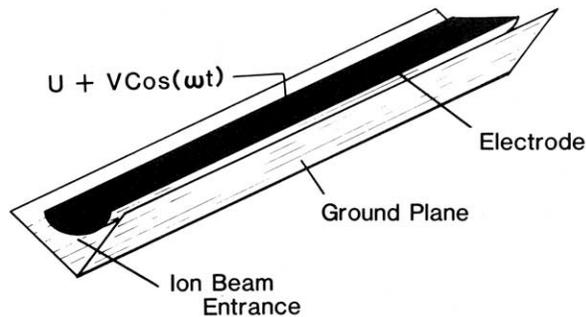


Figure 13. The monopole mass spectrometer.

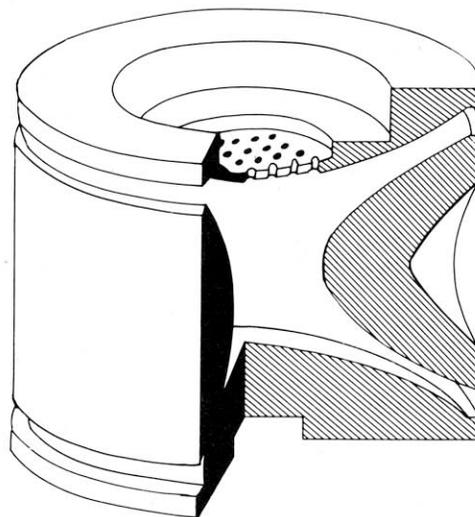


Figure 14. The quadrupole ion storage trap (QUISTOR).

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