Mass Analyzers: Quadrupoles

Chem-5181
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Last Update: Oct. 2014
Some slides adapted from Fall 2007 lecture by Dr. Joel Kimmel, CU-Boulder

Business Items

• We will proceed soon w Labview installation
  – Instructions coming soon
  – Getting it done on time will be part of a HW
  – Folks w Macs, Bootcamp installed?
• Questions, comments?
Quadrupole Geometry

Quadrupole consists of four parallel rods
Typical length might be 10-20 cm
Precise dimensions and spacing
Rods connected diagonally in pairs

FIG. 4.6. Schematic diagram showing arrangement of quadrupole rods and electrical connection to RF generator; a DC potential (not shown) is also impressed on the rods. The inset illustrates the ideal quadrupole electric field dispersion. From Watson

Ion Motion inside a Quad (Animation)

Voltages applied to rods define time-varying fields between rods and determine the m/z that is transmitted.

Q: what’s wrong with this animation?
Quadrupole Voltages

- Voltage of all rods have a DC component, $U$ or -$U$.
- $Q$: what would happen if there was only DC?

- All rods have RF component of voltage with MHz frequency $= \omega/2\pi$ and amplitude $V_0$.

- Potentials on the two sets are out of phase by $180^\circ$.

- Quadrupole fields cause no acceleration along $z$ axis.

\[ V_1 = V_3 = -\Phi_0 = -U - V_0 \cos \omega t \]
\[ V_2 = V_4 = \Phi_0 = U + V_0 \cos \omega t \]


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Quadrupole Electric Field

\[ \Phi = \frac{\Phi_0(x^2 - y^2)}{2r_0^2} \]

Fig. 2.1. Equipotential lines for a quadrupole field where $\phi = -1/2E_0 \lambda (x^2 - y^2)$. Fig. 2.2. The electrode structure required to generate the potential shown in Fig. 2.1. These are the ideal quadrupole mass filter electrodes having hyperbolic cross-sections.

From Dawson
An (Stable) Ion in a Quadrupole Mass Spectrometer

OUT OF PHASE
Symmetric voltages create clearly defined wells / ridges.
At any given moment one axis focuses ion to center (+), while the other pulls off center (-).
Rapid alternation between polarities.

Figure 2.8
A positive ion, represented within a dotted circle, is at the center of quadrupole rods, the potential signs of which are indicated. It goes down the potential 'valley' with respect to the negative rods and acquires some kinetic energy in that direction. However, the potentials quickly change so that the kinetic energy is converted into potential energy and the ion goes back to the center of the rods, as would happen for a ball on a horse saddle that is turned quickly. The name 'saddle field' is an allusion to this phenomenon.

Ion Motion Inside $\varepsilon$ Quadrupole

Stable along both $x$ and $y$

Stable along $y$; unstable along $x$

Figure 2.5
Stable and unstable trajectories of ions in a quadrupole.
(Reproduced (modified) from Ref. 6 with permission)
The Laplace Equation leads to:

\[ V(x, y) = \left(x^2 - y^2\right)(U + V_0 \cos \alpha) / r_o^2 \]

Applying Newton's Second Law:

\[ F = m \ddot{a} = qE \]

\[ F_x = m \frac{d^2 x}{dt^2} = -e \frac{\partial V}{\partial x} - 2e(U + V_0 \cos \alpha)x / r_o^2 \]

Substituting:

\[ \phi = \alpha / 2 \]

\[ \alpha = \frac{kezU}{r_o^2m \omega^2} \]

\[ q = \frac{kezV_0}{r_o^2m \omega^2} \]

Yields:

\[ \frac{d^2 x}{d\phi^2} = -(\alpha + 2q \cos 2\phi)x \]

\[ \frac{d^2 y}{d\phi^2} = (\alpha + 2q \cos 2\phi)y \]

Acceleration in x and y directions is described based on the terms \( \alpha \) (or \( a \)) and \( q \).

Note that:

\( \alpha \) is proportional to \( U/m \)

While

\( q \) is proportional to \( V_0/m \)

For given quadrupole, \( r_o \) is constant, \( \omega \) is held constant, and \( V \) and \( U \) will be variables.
Clicker Q

Q: To determine whether a quadrupole will transmit an ion of known m/z, one must know:

1. z
2. The length the quadrupole
3. The distance between rods of the quadrupole
4. The velocity of the ion before entering the quadrupole
5. The angular frequency of the applied RF potential

A. All of the above
B. 2, 3, 4, 5
C. 1, 3, 4, 5
D. 3, 4
E. I don’t know

Stability Diagram for a Quadrupole

\[ a_u = \frac{8zeU}{m \omega^2 r_o^2} \]
\[ q_u = \frac{4zeV}{m \omega^2 r_o^2} \]

a and q are used to define generalized stability plots. Intersections of x and y stability in a_u-q_u space define stability in quad.

Which region should we use for a quadrupole?

A. Region A
B. Regions B or C
C. Region D
D. Any of them will work similarly
E. I don’t know
Stability

An ion will have stable trajectory through quadrupole if $x$ and $y$ are always less than radius of quadrupole.

(Sim A) With no RF and positive $U$, positive ion is stable along $X$ (repelled to center), attracted to negative $Y$ rod causes instability.

(Sim C) RF field has stabilized $Y$ trajectory.

(Sim E) Instable along $x$-axis.


m/z Scanning in a Quadrupole MS

\[ \frac{U}{V_o} = \frac{1}{2}\left(\frac{0.233}{0.706}\right) \]

Increase in mass requires proportional increases in $U$ and $V_o$ to maintain this ratio and these $a$ and $q$ values.

Scan line shows

$\frac{U}{V_o} = \frac{1}{2}(0.233 / 0.706)$

Figure 2.7: Stability area as a function of $U$ and $V$ for ions with different masses ($m_1 < m_2 < m_3$). Changing $U$ linearly as a function of $V$, we obtain a straight operating line that allows us to observe those ions successively. A line with a higher slope would give us a higher resolution, as long as it goes through the stability areas. Keeping $U = 0$ (zero direct potential) we obtain zero resolution. All of the ions have a stable trajectory as long as $V$ is within the limits of their stability area. (Reproduced (modified) from Ref. 6 with permission)
Many conditions \((U, V, m)\) fall within stability region – there is more than one way for ion to pass through.

For selectivity, must also consider stability of other mass values.

Apex of generalized stability diagram is at \(\alpha = 0.237, q = 0.706\).

To select transmit narrow mass window, adjust \(U\) and \(V_o\) such that \(\alpha = 0.237, q = 0.706\) (e.g., ion B).

For any value \(m\)

\[
\frac{\alpha}{q} = 2\frac{U}{V_o}
\]

To scan values of \(m\) through narrow transmission window, hold other parameters constant and scan \(U\) and \(V_o\) with constant ratio

\[
\frac{U}{V_o} = \frac{1}{2}(0.233 / 0.706)
\]

For \(\text{any value } m\)

\[
\frac{\alpha}{q} = 2\frac{U}{V_o}
\]

For example: Reduce \(U\), Hold \(V\).

Still stable, slope of “scan line” is reduced.

What effect does this have on resolution?

A. Increase
B. Decrease
C. Keep the same
D. I don’t know
Mass Filter

Scan line shows

\[ \frac{U}{V_0} = \frac{1}{2} \left( \frac{0.233}{0.706} \right) \]

Increase in mass requires proportional increases in \( U \) and \( V_0 \) to maintain this ratio and these \( a \) and \( q \) values.

Example, bringing 202 into stability apex requires increases in \( U \) and \( V \).

Experimenting with the model

- Experiments done by 2014 students as part of the HW
  - Let’s think about their results and whether they make sense
Megan H – varying initial velocity
(variable = Vz_m_s) *5 and /5
No effect on stability diagram!

Megan H – varying initial velocity
Vz_m_s*100 default!
Everything is stable (up to and beyond reasonable voltages)
Megan H – varying initial velocity
Vz_m_s/1000 default!

**Changing Initial X Position**

- Samantha Miller
- Description of Process:
  1. Call upon Stability_Diagram function for each of the values in an initial position wave (X0, 1/3*X0, and 3*X0).
  3. Plot these values on a contour plot for each of the positions.

Comments:
X0 and 1/3*X0 produced the same stability diagram; however, the area for 3*X0 was much smaller due to a decrease in the stability at higher DC Voltages.
Varying initial Y position (Julia)

Zack Finewax: Stability Diagrams for default quadrupole diameter, three times r0, one third r0 with scaled initial x and y positions.
Megan Claflin
I adjusted the frequency from the default (2.26e6 Hz) to 3x the default (6.78e6) and to 1/3 of the default (7.53e5 Hz).

TOFMS vs Quadrupole MS

• **TOFMS**
  – Pulse packet of ions introduced into analyzer
  – All m/z in packet reach detector (“simultaneous detection”)
  – m/z determination based on dispersion in time
  – Based on static, DC fields

• **Quadrupole MS**
  – Continuous introduction of ions into analyzer
  – Transmit only specific m/z value to detector
  – m/z determination based on band-pass filtering
  – Based on time-varying, RF fields
When acquiring mass spectra with unit resolution for ions originating from a continuous source (that is, ions being presented to the mass spectrometer as a steady stream) the duty cycle of a quadrupole mass spectrometer:

A. Is nearly 100%
B. Depends on the m/z range being scanned
C. Is independent of m/z range, but depends on U, V, and ω
D. Cannot be determined
E. I don’t know

The ratio $\alpha/q$ is constant for ALL m/z values, no matter what the physical dimensions and voltage settings of a quadrupole

A. True
B. False
C. Almost True
D. I don’t know
If two mass spectra are acquired with $q = 0.706$ and different $\alpha$, and both generate stable conditions for $m/z = 100$ transmission, the spectrum collected at the ___________ $U$ is ___________ likely to generate stable conditions for $m/z = 101$ transmission.

A. Higher, More
B. Higher, Equally
C. Lower, More
D. Lower, Less
E. Need to know more about quadrupole

Quadrupole Notes

• Maximum m/z ~ 4,000
• Resolution ~ 3,000
  – Quadrupoles are low resolution instruments
  – Usually operated at ‘Unit Mass Resolution’
• Small, lightweight, cheaper
• Easy to couple with chromatography
Mass Discrimination on a quadrupole

**FIG. 4.9.** Hypothetical mass spectra recorded by an “ideal” mass spectrometer (left) and one that imposes mass discrimination (right).

From Watson

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**Clicker Question:** an RF only quadrupole is

- A. A low pass filter
- B. A high pass filter
- C. A band pass filter
- D. None of the above
- E. I don’t know

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Rf-Only Quadrupoles

Operated with \( U = 0 \), quadrupole becomes a broad filter. Such “RF-only” quads are an important tool for transferring ions between regions of mass spectrometers.

Often denoted with small “q”
A common application of RF-only multipoles involves collisional cooling.

In an ESI source, the expansion into vacuum produces a ion beam with broad energy distribution

Ion optics and TOFMS experiments rely on precise control of ion energies

Desire strategies to dampen energy from external processes

RF-induced trajectory in high pressure region yield collisions, and reduction in energy

Figure 1. Schematic diagram of the time-of-flight instrument TOF III. 1—ESI ion source; 2—heated capillary; 3—focusing electrode; 4—first aperture plate; 5—quadrupole; 6—second aperture plate; 7—grids; 8—slit; 9—the storage region; 10— extraction electrodes; 11—acceleration column; 12—electrostatic mirror; 13—deflection plates; 14—detector.

Collisional Cooling simulation paper II

Figure 4. Histograms of the ion velocity components. (A) Axial velocities at the input of the quadrupole ion guide. (B) Axial velocities at a distance of 1.5 cm inside the quadrupole ion guide. (C) Radial velocities at the input of the quadrupole ion guide. (D) Radial velocities at a distance of 1.5 cm inside the quadrupole ion guide.
Idea of MS/MS

From Watson

![Image of MS/MS](image)

FIG. 5.1. Conceptual representation of the technique of MS/MS. In this case, ions of m/z 129 are selected by the first mass spectrometer, these ions are directed into a collision chamber, and the decomposition products are analyzed by the second mass spectrometer to produce the product ion spectrum of m/z 129 (bottom).

**Triple Quadrupole Mass Spectrometer**

Q1 selects parent; q2 CID fragmentation inside RF-only quad; Q3 fragment analysis

**Fragment Ion Scan:** Park Q1 on specific parent m/z; scan Q3 through all fragment m/z to determine make-up of Q1

**Parent Ion Scan:** Park Q3 on specific fragment m/z; scan Q1 through all parent m/z to determine source of fragment

**Neutral Loss Scan:** Scan Q1 and Q3 simultaneously, with constant difference, \( a \), between transmitted m/z values (\( a = M_{Q1} - M_{Q3} \)). Signal recorded if ion of m/z = \( M_{Q1} \) has undergone fragmentation producing a neutral of m = a.
Triple Quad Animation

http://www.youtube.com/watch?v=PSFF6JJEFPE&NR=1

Q-TOF Hybrid Instrument

Figure 4.7. Schematic diagram of a quadrupole-orthogonal acceleration time-of-flight hybrid tandem mass spectrometer.
To operate a quadrupole in a scanning mode, where individual m/z values are transmitted one after the other (e.g., m/z = 100; 101; 102 …)

A. U is held constant, while V is scanned
B. V is held constant, while U is scanned
C. U and V are held constant, while $\omega$ is scanned
D. U and V are both changed
E. A or B

Clicker Q