# CHAPTER 5

# Mass Spectrometry

## 5.1 Introduction and History

The earliest forms of mass spectrometry go back to the observation of canal rays by Goldstein in 1886 and again by Wien in 1899. Thompson's later discovery of the electron also used one of the simplest mass spectrometers to bend the path of the cathode rays (electrons) and determine their charge to mass ratio. Later, in 1928, the first isotopic measurements were made by Aston. These basic experiments and instruments were presented to most readers in first-year general chemistry. More modern aspects of mass spectrometry are attributed to Arthur Jeffrey Dempster and F.W. Aston in 1918 and 1919. Since this time there has been a flurry of activity [not only concerning minor advances in components of mass spectrometers such as different types of instrument interfaces (direct injection, GC, and HPLC)] to different ionization sources (electron and chemical ionization) but also new types of ion separators. For example, double focusing magnetic sector mass filters were developed by Mattauch and Herzog in 1934 (and recently revised into a new type of mass filter), time of flight MS by Stephens in 1946, ion cyclotron resonance MS by Hipple and Thomas in 1949, quadrupole MS by Steinwedel in 1953, and ion trap MS by Paul and Dehmelt in the 1960s. Mass spectrometry was coupled with ICP as a means of sample introduction in 1980. Although not specific to ICP, even as recent as 1985, Hillenkamp and Michael Karas developed the MALDI technique (a laser-based sample introduction device) that radically advanced the analysis of protein structures and more types of mass analyzers will certainly be developed. Ion mobility spectrometers capabilities have recently advanced and are the basis of luggage scanning at airports. This chapter will deal only with basic mass spectrometer instruments that can be used in the analysis of atomic cations.

## 5.2 Components of a Mass Spectrometer

### 5.2.1 Overview:

The sample introduction systems (automatic sampler to torch) are almost identical on optical and mass spectrometry ICP units (Section 4.3.2). While the ICP-AES is interfaced with an optical grating system, the plasma in an ICP-MS instrument must enter into a vacuum so that atomic cations can be separated by a mass filter. The common components of a modern ICP-MS are shown in Figure 5.1 (the sampling interface is not shown). The torch and the plasma were discussed in Section 4.3.3 (Animations 4.1 and 4.2). For MS systems, the detector is axially aligned with the plasma to follow the flow trajectory of the argon. After the analytes are ionized in the plasma at atmospheric pressures, they must enter into a low pressure system before they can be accelerated and separated by mass to charge (m/z) ratios. This pressure difference is accomplished with a series of cones between the plasma and the mass analyzer. The first cone, the sample cone, is a protruding cone, usually made of Ni, that has a small hole (1.0 mm in diameter) at its tip to allow the cations and Ar to pass. The next chamber interface contains another cone (the skimmer cone) with an even smaller diameter hole (equal to or less than 0.1 mm in diameter) that allows less sample to enter into the low vacuum chamber (~$10^{-5}$ torr which is about $10^{-8}$ atm). The smaller hole in the skimmer cone helps maintain a lower vacuum in the mass filter chamber. As the cations enter this second chamber, they are exposed to accelerating lens (negatively charged plates) that place a fairly uniform amount of kinetic energy on the cations. Then the neutral particles and photons are filtered out by a second type of lens (Section 5.2.4). The specific design of the lens varies among different manufactures despite the fact that they accomplish the same goals. Most higher-end systems have a reaction cell placed just before the mass filter. This cell removes polyatomic interferences (that have the same mass as the analyte of interest) by gas phase chemical

reactions (Section 5.2.5). Then, the cations enter into the mass filter that separates the different atoms with respect to their mass to charge ratio (m/z) before they eventually enter into a detector. Mass analyzers that have higher than unit resolution, such as a double-focusing mass filter, bypass the reaction cell since polyatomic interferences have different masses at three or four significant figures. Given the large amount of data and the extremely short scan times of the MS, computer operation and computer enhanced data collection are required. The most variation between various ICP-MS manufactures is the presence or absence of a reaction cell and the type of mass filter.

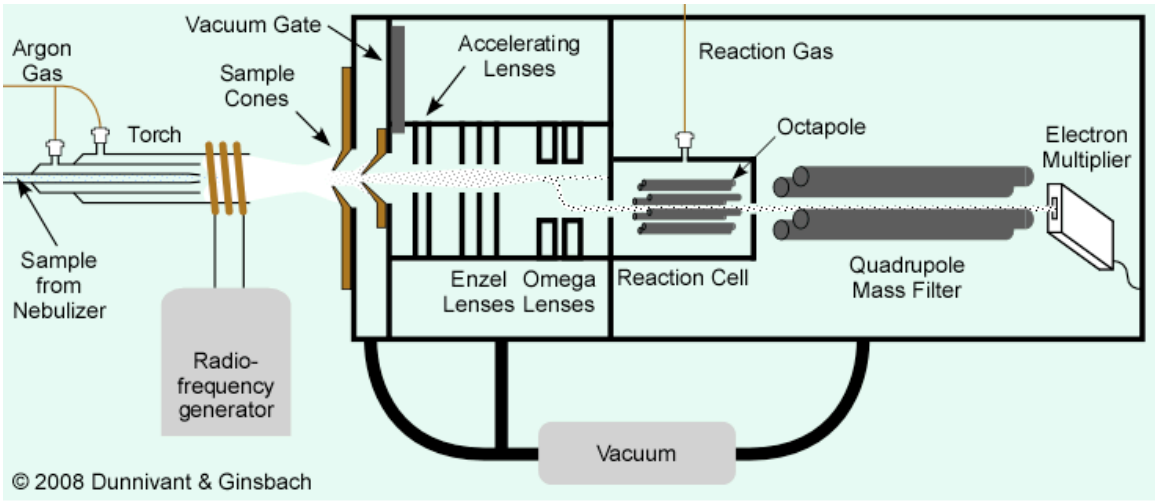



Figure 5.1. A Common ICP-MS with a Quadrupole Mass Filter.

### 5.2.2 Sample Introduction

The most common sample introduction system for an ICP-MS is made up of a nebulizer and spray chamber like an ICP-AES system (Section 4.3.2). While the majority of applications use this setup, there are some specialized applications that allow solid samples to be analyzed. Solid samples can be placed directly into the ICP with a graphite rod that contains a small quantity of sample (Section 4.3.2). Other sample introduction procedures cause solid samples to sublimate before they enter the plasma. One common form of

sample introduction not presented here is the glow discharge system that is used heavily by the semiconductor and metallurgy industries.

Another solid introduction technique is laser ablation which is becoming more common especially for geological and materials science applications. In laser ablation, the automatic sampler and peristaltic pump for liquid samples are replaced with the working components of the laser ablation system. This consists of a small chamber to hold the solid sample on a movable stage, a laser to ablate (heat and vaporize the solid), a viewing window or CCD camera to align the laser to a specific spot on the sample, and an argon gas stream to purge the ablation chamber and rapidly transport the vaporized sample to the inlet of the plasma. The laser is focused on a 10- to 25-μm section of the sample and a pulse of energy from the laser vaporizes the sample. The sample is transported to the plasma as a short pulse of vapor that is atomized and ionized in the plasma, and the generated cations are analyzed by the MS unit. Given the relatively small sampling area of the laser, numerous analyses can be conducted for a given sample and an average of analyte concentrations are determined. Common laser types include Nd-YAG, ruby, $CO_2$, and $N_2$. The only requirement of the laser is that it has sufficient power to ablate and vaporize refractory (high bond energy) sample matrixes. Obviously one of the quantitative limitations of the laser ablation technique is obtaining reference standards. While solid reference standards can be relatively easily made and obtained, it is almost impossible to match the matrix of all samples. Detection limits for this technique are in the range of 0.1 to 10 ppm which is much higher (poorer) than aqueous sample detection limits in an ICP-MS. As a result of the difficulties encountered with instrument calibration, qualitative analysis is commonly performed.

5.2.3 Mass Analyzer Interface:

Sample cations enter into the mass filter from the plasma through a series of nickel or platinum cones that contain a small hole (from 1.0 mm to less than

0.1 mm) in the center. These cones are necessary to achieve the pressure drop that is required for the mass analyzer. The low pressure of the system, $10^{-5}$ torr, minimizes the collision of the chemically reactive analyte cations with ambient gases. Thus, maintaining a confined beam of ions. A photograph of a cone is shown in Figure 5.2. Cones are one of the most maintenance intensive components of an ICP-MS since they require frequent cleaning, but the cleaning process is easy and relatively fast. After cleaning, cones must be conditioned prior to use by exposing the clean cones to a mid- to high-range reference standard via the plasma for 20 to 30 minutes. This conditioning process will avoid analyte loss on the cone and memory effects (the persistent present of an analyte in a blank run typically occurring after a high concentration standard or sample has been analyzed).

Figure 5.2. Photograph of a Sampler (the larger one) and a Skimmer Cone for ICP-MS.

The low pressure in the spectrometer chamber is maintained with two vacuum pumps. First, an external rotary vacuum pump is used to remove gas molecules down to a pressure of $10^{-1}$ to $10^{-4}$ torr; a rotary vacuum pump is a positive-displacement pump that consists of vanes mounted to a spinning rotor. After a sufficient vacuum has been reached, a turbo molecular pump takes the vacuum down to $10^{-5}$ to $10^{-6}$ torr. A molecular pump operates by using high speed (50 000 rpms today but older pumps operated at 90 000 rpms) rotating blades to literally knock gaseous molecules out of the chamber. The low vacuum pressures are needed to minimize secondary collisions between analyte cations and ambient atmospheric molecules that would deflect the cations path away

from the mass filter and detector and interfere with the desired trajectory in the mass filter.

### 5.2.4 Lenses

After entering into the evacuated region, a number of lenses are used to manipulate the path of the ions flowing from the plasma. First and foremost are the accelerator lenses. An accelerator lens consists of two to three plates with a relatively large hole in them (typically larger than the hole in the cones). Each plate has an increasingly negative charge placed across them that result in the attraction of the cations towards the plate increasing their kinetic energy. The hole in the center allows most of the cations to pass directly through the plate. The imposed kinetic energy is needed to pass the cations through the subsequent reaction cell, mass filter, and on to the detector with sufficient energy to dislodge electrons on the surface of the detector (an electron multiplier device).

The next type of lens used in the MS is a focusing lens that centers the cations into a small beam. This lens is used to focus ions into the center of the reaction cell (if present) and the mass filter. One such electrical lens is the Einzel lens that is analogous to a focusing lens in an optical spectrophotometer. An Einzel lens contains six parallel plates, three on each side of a rectangular box, that are exposed to various electric potentials (Figure 5.3). These potentials create an electrical field that bends the cations near the outside of the plates toward the focal point. The lens stretches the length of a given beam of ions since ions on the outside (near the plates) have to travel a longer distance to reach the focal point.

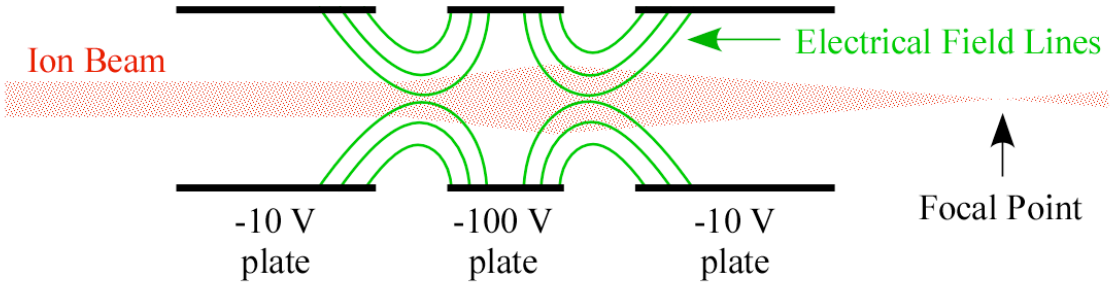





Figure 5.3. Diagram of an Einzel Lens used to focus a beam of ionic particles.

The final class of lenses removes neutral (elemental) atoms and photons that enter through the cones. Both photons and neutrals would be detected by the universal detector (an electron multiplier) and would give false signals and increase the instrumental noise if they are not filtered. Besides causing increased noise, neutrals passing through the mass filter can become adsorbed onto metal components that can interfere with their proper function. There are two major types of lenses that remove neutral particles and photons; a Bessel box and Omega lens. A Bessel box, also referred to as a photon stop, is comprised of two photon stops, an Einzel lense, and a set of three lenses (Figure 5.4). The first photon stop (located before the Einzel lense) prevents particles from flowing directly down the evacuated chamber. The Einzel lens focuses the particles into the Bessel box and around the second photon stop. The positive voltage (+4 V) on the outside of the Bessel box and the negative voltage on the second photon stop (-9 V) direct the cations back to the exit slit. Neutral particles and photons are unaffected by the electrical field and are removed.

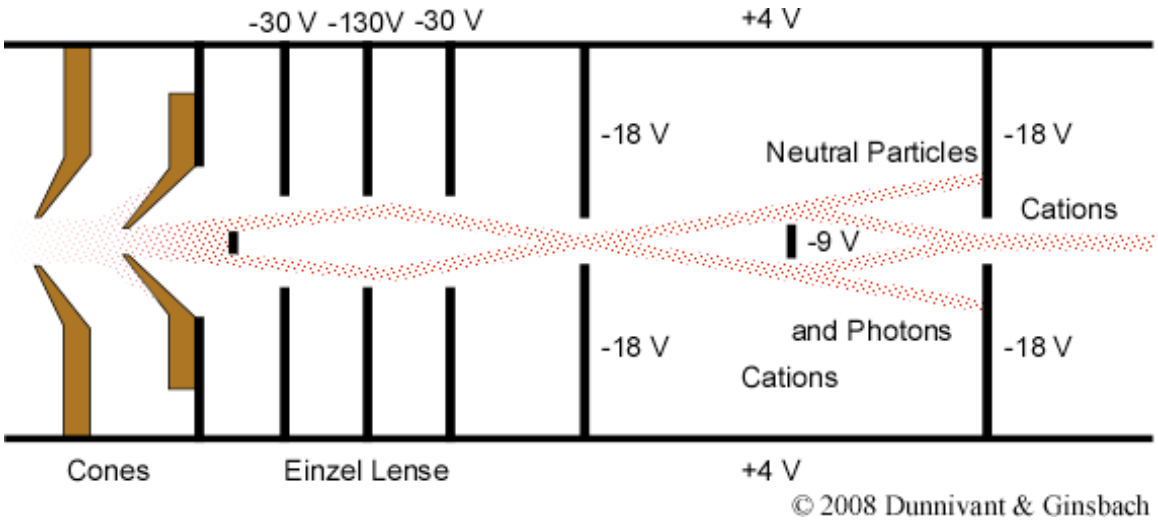



Figure 5.4. A Bessel Box photon stop.

Another type of lens, an Omega lens, filters out the photons and neutral particles. A cross-section of an Omega lens consists of four electrodes, two near the top and two near the bottom of the ion beam, and is presented in Figure 5.5. The lens works by carefully balancing the charges of the electrodes to deflect the beam of cations, but not the neutral species or the photons from the plasma. This deflection is accomplished by placing a positive charge on the first top electrode and a negative charge on the first bottom electrode that acts to deflect the beam of cations downward in the front of the lens (refer to Figure 5.4). Next the beam needs to be stabilized with respect to the horizontal direction to guide the beam into the reaction cell or mass filter, so an opposite set of electrodes is present, one with a negative charge on the top and one with a positive charge on the bottom. The net result is the deflection of the cations towards the mass analyzer in the absence of particles and photons that continue straight and collide with the end plate. Both the Einzel and Bessel systems are subject to contamination and need to be maintained (usually every six months or so depending on use).

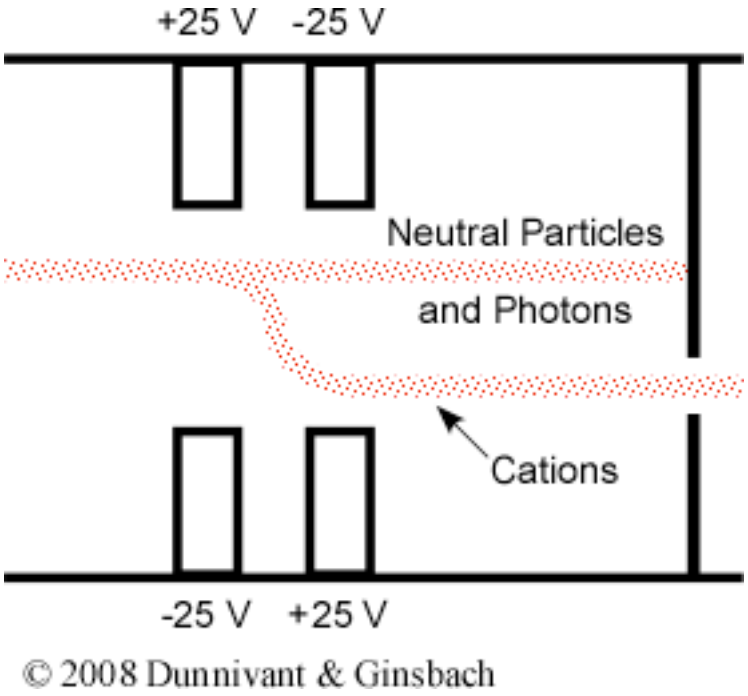



Figure 5.5. An Omega Lens.

5.2.5 Mass Interferences and Reaction Cells:

ICP-MS instruments separate and detect analytes based on the atoms mass to charge ratio. Since the plasma in an ICP system is adjusted to maximize singularly charged species, sample identity is directly related to atomic mass. While atomic emission spectrometry, ICP-AES, can be relatively free from spectral interferences (with monochromator systems that produce nm resolutions to three-decimal places), certain elements have problematic interferences in ICP-MS analysis due to the limited unit resolution (one amu) of most mass filters (especially the most common quadrupole mass filters). All ICP systems are subject to the nebulizer interferences given in the previous chapter. Spectral interferences are divided into three categories: isobaric, polyatomic, and doubly-charged species. Isobaric interferences occur in mass analyzers that only have unit resolution. For example, $^{40}Ar^{+}$ will interfere with $^{40}Ca^{+}$ and $^{114}Sn^{+}$ will interfere with $^{114}Cd^{+}$. High-resolution instruments will resolve more significant figures of the cation's mass and will easily distinguish between these elements.

Polyatomic interferences result when molecular species form in the plasma that have the same mass as the analyte of interest. Their formation can be dependant on the presence of trace amounts of $O_2$ and $N_2$ in the Ar or sample, certain salts in the sample, and the energy of the plasma. For example, $^{40}Ca^{16}O^+$ can overlay with $^{56}Fe^+$, $^{40}Ar^{23}Na^+$ with $^{63}Cu^+$, and $^{80}Ar_2^+$ and $^{80}Ca_2^+$ with $^{80}Se^+$. The final type of interference occurs with doubly charged species. Since mass analyzers separate atoms based on their mass to charge ratio, $^{136}Ba^{2+}$ interferes with the quantification of $^{68}Zn^+$ since their mass to charge ratios are identical. The presence of any of these types of interferences will result in overestimation of the analyte concentration. Fortunately there are several ways of overcoming these interferences.

The easiest, but most expensive, way to overcome all three spectral interferences is to use a high-resolution mass analyzer, but, at a minimum, this can double to quadruple the cost of an analysis. Most inexpensive alternatives include the use of interference equations to estimate the concentration of the interfering element or polyatomic species, the use of a cool plasma technique to minimize the formation of polyatomic interferences, and the use of collision and/or reaction cells prior to the entry to the mass filter. These three techniques will be discussed in detail below.

Interference Equations: Most elements are present on the Earth in their known solar abundance (the isotopic composition of each element that was created during the formation of our solar system). Important exceptions are elements in the uranium and thorium decay series, most notably lead. For these elements, the isotopic ratios are dependent upon the source of the sample. For example, lead isotope ratios found in the environment can be attributed to at least three possible sources: geologic lead, leaded gasoline, and mined lead shot from bullets.

Interference equations are mathematical relationships based on the known abundances of each element that are used to calculate the total concentration of all of the isotopes of a particular ion. Isobaric correction is relatively easy when two or more isotopes of each element (the analyte and the interfering isotope) are present in the solar abundance. There are two ways to correct for this type of interference: (1) the analyte of interest can be monitored at a different mass unit (different isotope), or (2) the interfering element can be quantified as a different isotope (mass unit) and the result can be subtracted from the analyte concentration. Polyatomic interferences can be corrected for in the same manner but to a less effective degree. This type of correction is illustrated in the following example taken from the ICP-MS primer from Agilent Technologies Company, a manufacturer of ICP-MS systems.

Example 5.1 Arsenic is an important and common pollutant in groundwater and an industrial and agricultural pollutant. The analyte of interest is $^{75}As$ but $^{40}Ar^{35}Cl$ has an identical mass on a low-resolution mass filter system, and since most water samples contain chloride, this interfering ion will be present in varying concentrations. These can be corrected for by doing the following instrumental and mathematical analysis. Note that all analysis suggested below require external standard calibration or for the instrument to be operated in semi-quantitative mode (a way of estimating analyte concentrations based on the calibration of a different element or isotope).

1. Acquire data at masses 75, 77, 82, and 83.
2. Assume the signal at mass 83 is form $^{83}Kr$ and use this to estimate the signal from $^{82}Kr$ (based on solar abundances).
3. Subtract the estimated contribution from $^{82}Kr$ from the signal at 82. The residual value should be the counts per second for $^{82}Se$.
4. Use the estimated $^{82}Se$ data to predict the size of the signal from $^{77}Se$ on mass 77 (again, based on solar abundances).

5. Subtract the estimated $^{77}Se$ contribution from the counts per second signal at mass 77. The residual value should be from $^{40}Ar^{37}Cl$.
6. Use the calculated $^{40}Ar^{37}Cl$ data to estimate the contribution on mass 75 from $^{40}Ar^{35}Cl$.
7. Subtract the estimated contribution from $^{40}Ar^{35}Cl$ on mass 75. The residual is $^{75}As$.

This process may seem complicated but is necessary to obtain accurate concentration data for As in the absence of a high-resolution mass filter. It should also be noted that this type of analysis has limitations. (1) If another interference appears at any of the alternative mass units used, the process will not work. (2) If the intensity of interference is large, then a large error in the analyte concentration will result.

Cool Plasma Technique: The ionization of Ar-based polyatomic species in the normal "hot" plasma can be overcome by operating the radiofrequency at a lower wattage (from 600 to 900 W) and therefore lowering the temperature of the plasma. This technique, a function on all modern ICP-MS systems, allows for the removal of polyatomic interferences in the analysis of K, Ca, and Fe. One downside is the tendency to form more matrix induced oxide cations.

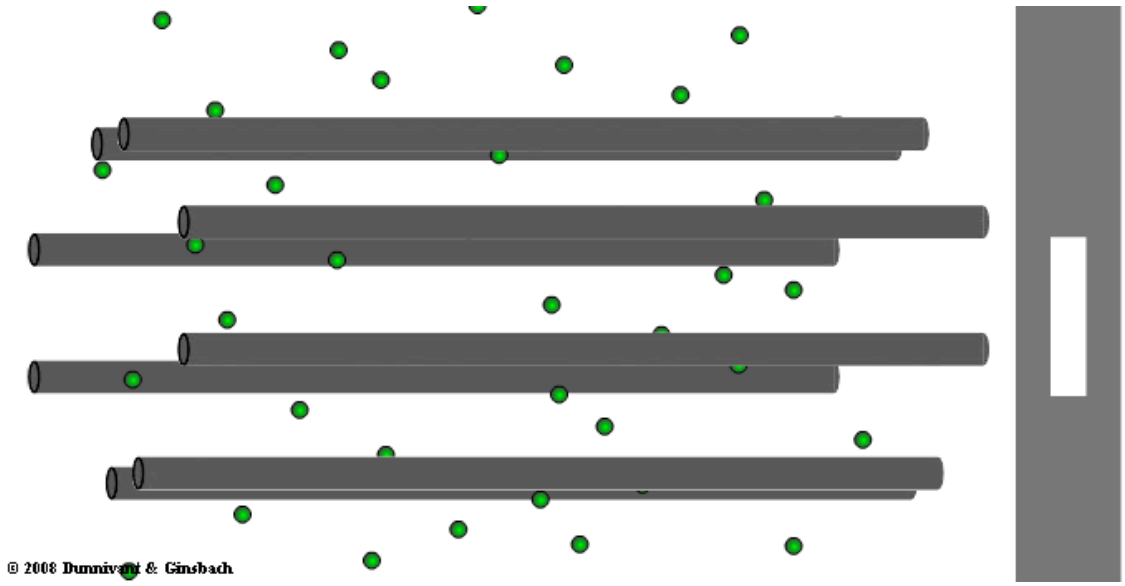
Collision/Reactor Cells: The limitations of the two techniques described above, and the price of high-resolution mass spectrometry, led to the development of collision and reaction cells in the late 1990s and early 21$^{th}$ century to remove these interferences. Numerous Ph.D. dissertations, as well as research and development programs in industry, are active in this area and there are books specifically devoted to this topic. Two basic types of approaches have been used, (1) a collision cell that uses He to select for an optimum kinetic energy by slowing interfering ions relative to the analyte and only allowing the

passage of the higher energy analyte and (2) reaction cells that promote reactions between a reagent gas and the interferences in order to remove them from detection.

The actual collision/reaction cell is a quadru-, hexa- or octa-pole that is considerable smaller than the subsequent quadrupole (mass filter) and is enclosed in a chamber that can contain higher pressures then the surrounding vacuum chamber. No mass separation occurs in the multi-pole since only a DC current is applied to the poles. Instead, the main purpose of the multi-pole is to keep the beam focused/contained to provide a space for the necessary collisions or chemical reactions to occur. While the number of poles in the reaction cell varies with different instruments, the larger number of poles allows for a more effective cell since the cross-sectional area of the ion beam is larger for an octa-pole over a hexa- or quadru-pole. The majority of collision/reaction cells can be operated in either mode by altering the gas utilized by the system. The price of the instruments increases slightly with the addition of these cells, however removing interferences with a collision cell is still less expensive than the alternative; a high-resolution mass filter.

Collision Cells: In a collision cell a non-reactive gas, usually He, is used to remove polyatomic ions that have the same mass to charge ratio as the analyte of interest. These multi-pole collisions cells are relatively small as compared to the mass filtering quadrupole and confine the ion beam from the plasma. Helium gas is added to the cell while the analyte of interest (an atomic species) and the interferent (a polyatomic species) move through the chamber. Polyatomic species are larger then atomic species and therefore collide with the He gas more often. The net result of these collisions is a greater reduction in the kinetic energy (measured in eVs) of the polyatomic species in relationship to the atomic species. As the polyatomic and analyte ions exit the collision cell, they are screened by a discriminator voltage. A discriminator voltage is the counterpart to an accelerating lens and contains a slit with a positive voltage; this process is

commonly referred to as kinetic energy discrimination. When a positive voltage is applied to this gate, only cations possessing sufficient kinetic energy will pass through the slit. Smaller cations retaining more of their energy, after being subjected to the collisions with He, will pass through the slit while larger polyatomic cations that have been slowed by the He collisions will be repelled by the voltage. The polyatomic species that do not pass into the mass analyzer collide with the walls of the chamber, are neutralized and removed by the vacuum system. Common interferences that are removed in this manner are sample matrix-based interferences such as $^{35}Cl^{16}O^{+}$ from interfering with $^{51}V^{+}$, $^{40}Ar^{12}C^{+}$ from interfering with $^{52}Cr^{+}$, $^{23}Na^{40}Ar^{+}$ from interfering with $^{63}Cu^{+}$, $^{40}Ar^{35}Cl^{+}$ from interfering with $^{75}As^{+}$, and plasma-based interferences such as $^{40}Ar^{16}O^{+}$ and $^{40}Ar^{38}Ar^{+}$. Interfering polyatomic species can be reduced down to ppt levels through kinetic energy discrimination. An animation for a typical collision cell is available on the book's web page (Animation 5.1).




Animation 5.1. A Collision Cell.

Reaction Cells: The physical structure and design of a collision cell, depending on the manufacturer, is similar or identical to that of a reaction cell. However, instead of utilizing an inert gas such as helium, more reactive gases

are introduced into the cell. $H_2$ is the most common reactive gas but $CH_4$, $O_2$, and $NH_3$ are also used. Table 5.1 shows a variety of reaction gases and their intended use.

Table 5.1 Reagent Gases used in Collision and Reaction Cell ICP-MS Systems. (Source: Koppenaal, et al., 2004, *J. Anal. At. Spectrom.*, 19, 561-570)

| **Collision Gas** | **Purpose** |
|---|---|
| He, Ar, Ne, Xe | Used as a collision gas to decrease the kinetic energy of the polyatomic interference |
| $H_2$, $NH_3$, Xe, $CH_4$, $N_2$ | Used in charge exchange reactions |
| $O_2$, $N_2O$, NO, $CO_2$ | Used to oxidize the interference or analyte |
| $H_2$, CO | Used to reduce the interference |
| $CH_4$, $C_2H_6$, $C_2H_4$, $CH_3F$, $SF_6$, $CH_3OH$ | Used in adduction reactions to remove interferences |

The purpose of the reactive gas is to break up or create chemical species, through a set of chemical reactions, and change their polyatomic masses to one that does not coincide with the mass of the analyte of interest. These cells have significantly extended the elemental range of ICP-MS to include some very important elements; the most important being $^{39}K^+$, $^{40}Ca^+$, and $^{56}Fe^+$ which had previously been difficult to measure due to the interferences of $^{38}Ar^1H^+$, $^{40}Ar^+$, and $^{40}Ar^{16}O^+$, respectively. The removal of interferences can be divided into three general categories: charge exchange, atom transfer, and adduct formation (i.e. condensation reactions).

A generic reaction for a charge transfer reaction would be

$$A^+ + B^+ + R \rightarrow A^+ + B + R^+$$

where $A^+$ is the analyte, $B^+$ is the isobaric interferent, and R is the reagent gas. An example of a charge exchange reaction is removal of the cationic Ar dimer in the analysis of selenium.

$$^{80}Se^+ + {}^{80}Ar_2^+ + H_2 \rightarrow {}^{80}Se^+ + {}^{40}Ar{}^{40}Ar + H_2^+$$

The neutral Ar dimer is now removed by the photon stop and vacuum and $^{80}Se^+$ is easily transported through the mass filter. Another specific case would be the interference of $^{40}Ar^+$ with the measurement of $^{40}Ca^+$. The reaction is

$$^{40}Ca^+ + {}^{40}Ar^+ + H_2 \rightarrow {}^{40}Ca^+ + {}^{40}Ar + H_2^+$$

In this reaction, the interfering cationic species is neutralized and removed by the vacuum and does not enter the MS. It should be noted that in charge exchange reactions, the ionization potential of the reagent gas must lie between the ionization potentials of the interfering ion and the analytes in order to promote charge transfer from the interfering ion instead of the analyte. Such a requirement is not necessary for atom transfer and adduction formation/condensation reactions. Two such reactions follow.

Atom Addition Reaction

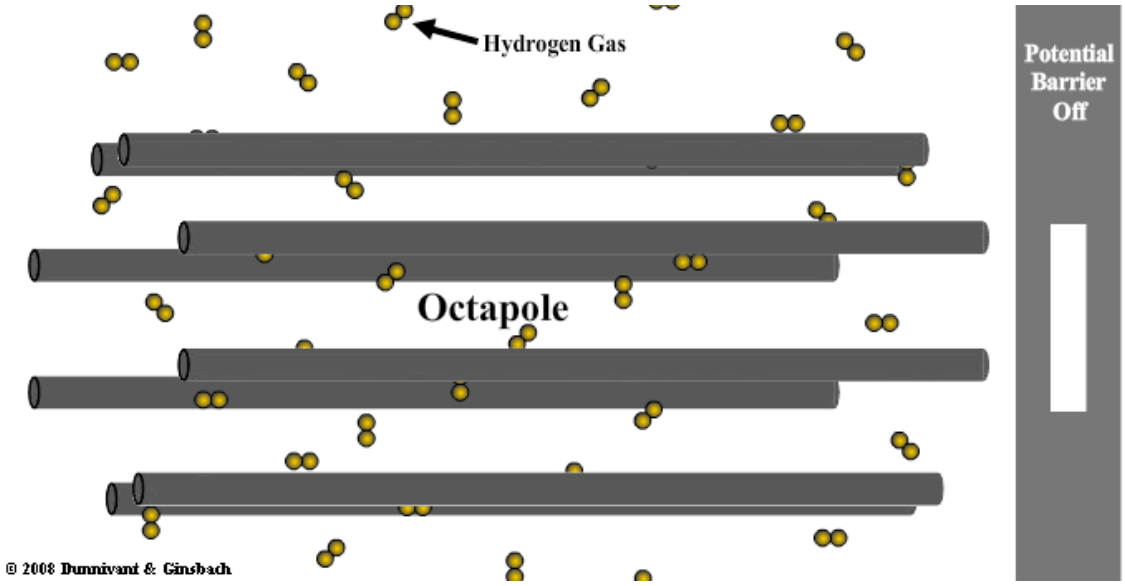
$$A^+ + B^+ + R \rightarrow AR^+ + B$$

$$Fe^+ + ArO^+ + N_2O \rightarrow FeO^+ + ArO^+ + N_2$$

In this case the interference of $ArO^+$ with the measurement of Fe is removed by oxidizing the Fe to its oxide that has a different mass from the argon oxide and quantifying Fe as $FeO^+$.. Another example is given below for the removal of $^{90}Zr$ interference in the detection of $^{90}Sr$.

$$^{90}Sr^+ + {}^{90}Zr^+ + 1/2O_2 \rightarrow {}^{90}Sr^+ + {}^{90}ZrO^+$$

These chemical reactions in the cell create cations that can potentially interfere with other analytes, hence it is not uncommon for these problematic analytes to be measured singularly (no multi-elemental analysis). As a result, the reaction cell mode is frequently utilized for singular applications or for argon interferences (ex. $^{40}Ar^{+}$ and $^{40}Ar\,^{16}O^{+}$) with hydrogen since the products of the reaction do not interfere with other analytes of interest. If possible, operating the collision/reaction cell in the collision mode is preferable since the interferences are removed from the system. After the spectral interferences have been removed by either process, the ion beam is separated by mass to charge ratio with the mass filter. An animation of a typical reaction occurring in a reaction cell with $H_2$ is available on the book's web page as Animation 5.2.




Animation 5.2. Reaction Cell.

### 5.2.6 Mass Filters (Mass Analyzers)

Mass analyzers separate the cations based on ion velocity, mass, or mass to charge ratio. A number of mass filters/analyzers are available. These can be used individually or coupled in a series of mass analyzers to improve mass

resolution and provide more conclusive analyte identification. This text will discuss the most commonly available mass filters, but not all are commercially available for ICP systems.

The measure of "power" of a mass analyzer is resolution, the ratio of the average mass (m) of the two adjacent ion peaks being separated to the mass difference ($\Delta$m) of the adjacent peaks, represented by

$$R_s = m/\Delta m$$

Resolution ($R_S$) is achieved when the midpoint between two adjacent peaks is within 10 percent of the baseline just before and after the peaks of interest (the valley between the two peaks). Resolution requirements can range from high-resolution instruments that may require discrimination of a few ten thousands (1/10 000) of a gram molecular weight (0.0001) to low-resolution instruments that only require unit resolution (28 versus 29 atomic mass units; amu). Resolution values for commonly available instruments can range from 250 to 500 000.

Before introducing the various types of mass analyzers, remember our current location of the mass analyzer in the overall ICP-MS system. The sample has been introduced to the nebulizer, atomized and ionized by the plasma, accelerated and manipulated by various lenses, sent through a collision/reaction cell, and finally enters the mass analyzer. Now the packet of cations need to be separated based on their momentum, kinetic energy, or mass-to-charge ratio (m/z). Often the terms mass filter and mass analyzer are used interchangeable, as is done in this Etextbook. But, first a controversy in the literature needed to be addressed with respect to how a mass filter actually separates ions.

Some resources state that all mass analyzers separate ions with respect to their mass to charge ratio while others are more specific and contend that only quadrupoles separate ions by mass to charge ratios. The disagreement in

textbooks lies in what components of the MS are being discussed. If one is discussing the affect of the accelerator plates **and** the mass filter, then all mass filters separate based on mass to charge ratios. This occurs because the charge of an ion will be a factor that determines the velocity a particle of a given mass has after interacting with the accelerator plate in the electronic, magnetic sector, and time of flight mass analyzers. But after the ion has been accelerated, a magnetic section mass filter actually separates different ions based momentums and kinetic energies while the time of flight instrument separates different ions based on ion velocities (arrival times at the detector after traveling a fixed length). In the other case, no matter what the momentum or velocity of an ion, the quadrupole mass analyzer separates different ions based solely on mass to charge ratios (or the ability of the ion to establish a stable path in an oscillating electrical field). These differences may seem semantic but some users insist on this clarification. For the discussions below, in most cases, mass to charge will be used for all mass analyzers.

5.2.6.1 *Magnetic sector mass filter:* It has been known for some time that the trajectory of a point charge, in our case a positively charged ion, can be altered by an electrical or magnetic field. Thus, the first MS systems employed permanent magnets or electromagnets to bend the packets of ions in a semi-circular path and separated ions based on their momentum and kinetic energy. Common angles of deflection are 60, 90, and 180 degrees. The change in trajectory of the ions is caused by the external force of the magnetic field. The magnitude of the centripetal force, which is directly related to the ions velocity, resists the magnetic field's force. Since each mass to charge ratio has a distinct kinetic energy, a given magnetic field strength will separate individual mass to charge ratios through space. A slit is placed in front of the detector to aid in the selection of a single mass to charge ratio at a time.

A relatively simple mathematical description will allow for a better understanding of the magnetic field and the ions centripetal force. First, it is

necessary to compute the kinetic energy (KE) of an ion with mass *m* possessing a charge *z* as it moves through the accelerator plates. This relationship can be described by

$$KE = \tfrac{1}{2}\, mv^2 = zeV$$

where e is the charge of an electron ($1.60 \times 10^{-19}$ C), v is the ion velocity, and V is the voltage between the two accelerator plates (shown in the Animation 1.5 below). Fortunately for the ionizations occurring in the plasma, most ions have a charge of +1. As a result, an ions' kinetic energy will be inversely proportional to its mass. The two forces that determine the ion's path, the magnetic force ($F_M$) and the centripetal force ($F_C$), are described by

$$F_M = Bzev$$

and

$$F_C = (mv^2)/r$$

where B is the magnetic field strength and r is the radius of curvature of the magnetic path. In order for an ion of particular mass and charge to make it to the detector, the forces $F_M$ and $F_C$ must be equal. This obtains

$$BzeV = (mv^2)/r$$

which upon rearrangement yields

$$v = (Bzer)/m\ .$$

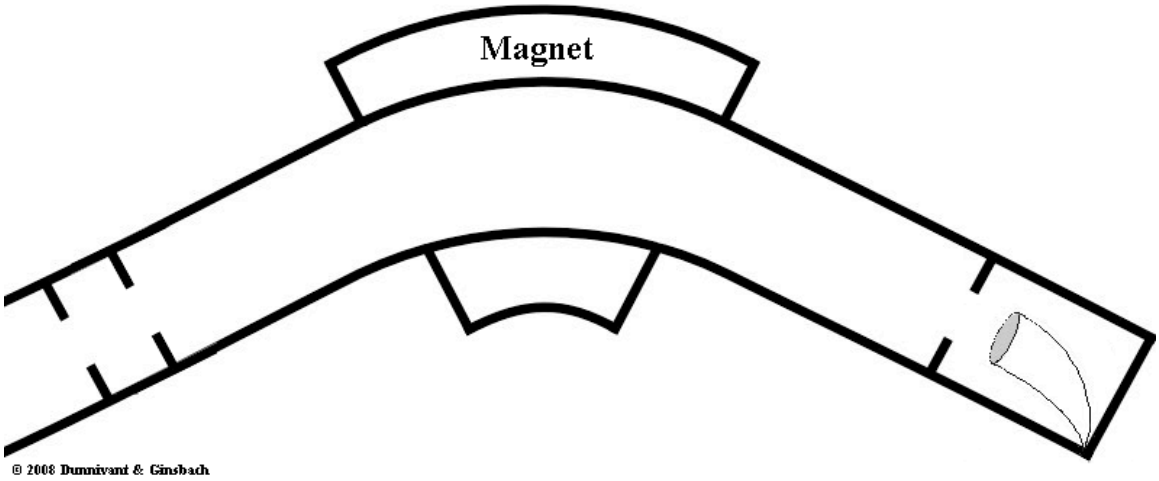
Substituting this last equation into our first KE equation yields

$$m/z = (B^2r^2e)/2V$$

Since e (the charge of an electron) is constant and r (the radius of curvature) is not altered during the run, altering the magnetic field (B) or the voltage between the accelerator plates (V) will vary the mass to charge ratio that can pass through the slit and reach the detector. By holding one constant and varying the other throughout the range of m/z values, the various mass to charge ratios can be separated. One option is to vary the magnetic field strength while keeping the voltage on the accelerator plates constant.

In general, it is difficult to quickly vary the magnetic field strength, and while this is problematic in chromatography it is of little consequence with ICP instruments. Generally, several complete mass to charge scans are desired for accurate analyte identification and this can be completed ICP analysis by simply sampling longer. This entire problem can be overcome in modern magnetic sector instruments by rapidly sweeping the voltage between the accelerator plates, in order to impart different momentums on the ions, as opposed to sweeping the field strength. Due to the operational advantages of this technique, most electromagnets hold the magnetic field strength (B) and vary the voltage (V) on the accelerator plates.

The magnetic sector mass filter is illustrated in Animation 5.3 below. As noted above, although B and r are normally held constant, this modern design is difficult to animate, so we will illustrate a magnetic sector MS where B, the magnetic field, is varied to select for different ions. After ions pass the cones at the ICP MS interface, they are uniformly accelerated by the constant voltage between the two accelerator plates/slits on the left side of the figure. As the different ions travel through the electromagnet, the magnetic field is varied to select for different m/z ratios. Ions with the same momentum or kinetic energy (and therefore mass) pass through the exit slit together and are measured by the detector, followed by the next ion, and so on.




Animation 5.3. Illustration of a Magnetic Sector MS. See the book's web site to play Animation 5.3.

While magnetic sector mass filters were once the only tool used to create a mass spectrum, they are becoming less common today. This is due to the size of the instrument and its weight. As a result, many magnetic sector instruments have been replaced by quadrupole systems that are much smaller, lighter, and able to perform extremely fast scans. Magnetic sector instruments are still used in cases where extremely high-resolution is required such as with double-focusing instruments (discussed later in this section).

5.2.6.2 *Quadrupole mass filter:* Quadrupole mass filters have become the most common type of mass filters used today due to their relatively small size, light weight, low cost, and rapid scan times (less than 100 ms). This type of mass filter is most commonly used in conjunction with ICP systems because they are able to operate at a relatively high pressure ($5 \times 10^{-5}$ torr) as compared to lower pressures required in other mass filters. The quadrupole has also gained widespread use in tandem MS applications (a series of MS analyzers).

Despite the fact that quadrupoles produce the majority of mass spectra today as mentioned earlier, they are not true mass spectrometers. Actual mass

spectrometers produce a distribution of ions either through time (time of flight mass spectrometer) or space (magnetic sector mass spectrometer). The quadrupole's mass resolving properties are instead a result of the ion's stability/trajectory within the oscillating electrical field.

A quadrupole system consists of four rods that are arranged at an equal distance from each other in a parallel manner. Paul and Steinwegen theorized in 1953 that hyperbolic cross-sections were necessary. In practice, it has been found that circular cross sections are both effective and easier to manufacture. Each rod is less than a cm in diameter and usually less then 15 cm long. Ions are accelerated by a negative voltage plate before they enter the quadrupole and travel down the center of the rods (in the z direction). The ions' trajectory in the z direction is not altered by the quadrupole's electric field.

The various ions are separated by applying a time independent dc potential as well as a time dependent ac potential. The four rods are divided up into pairs where the diagonal rods have an identical potential. The positive dc potential is applied to the rods in the X-Z plane and the negative dc potential is applied to the rods in the Y-Z plane. The subsequent ac potential is applied to both pairs of rods but the potential on one pair is the opposite sign of the other and is commonly referred to as being 180˚ out of phase (Figure 4-6).

Mathematically the potentials that ions are subjected to are described by the following equations:

$$\Phi_{X\text{-}Z} = +(U + V\cos\omega t)$$

and

$$\Phi_{Y\text{-}Z} = -(U + V\cos\omega t)$$

where Φ is the potential applied to the X-Z and Y-Z rods respectively, ω is the angular frequency (in rad/s) and is equal to 2πv where v is the radio frequency of

the field, U is the dc potential and V is the zero-to-peak amplitude of the radio frequency voltage (ac potential). The positive and negative signs in the two equations reflect the change in polarity of the opposing rods (electrodes). The values of U range from 500 to 2000 volts and V ranges from 0 to 3000 volts.

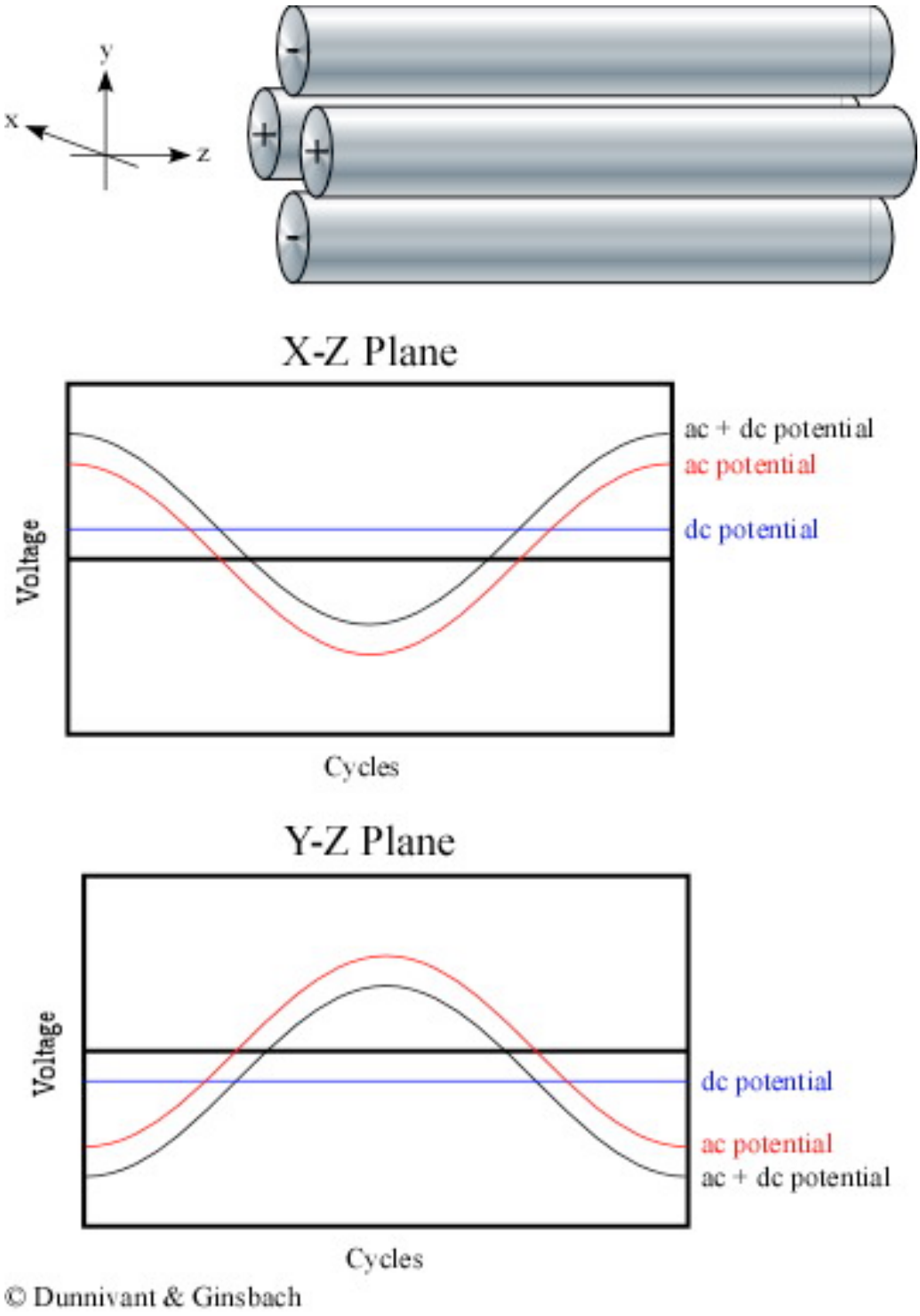



Figure 5.6. AC and DC Potentials in the Quadrupole MS.

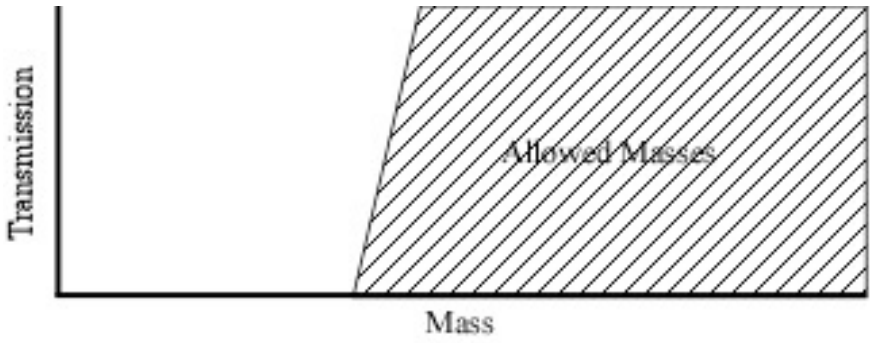
To understand the function of each pair, consider the rods in the X-Z plane in isolation. For now, imagine that only an ac potential is applied to the rods. Half the time when the potential was positive, ions (cations) would be repelled by the rod's charge and would consequently move towards the center of the rods. Likewise, when the potential was negative, ions would accelerate towards the rods in response to an attractive force. If during the negative ac potential, an ion comes into contact with the rod, it is neutralized and is removed by the vacuum. The factors that influence whether or not a particle strikes the rod during the negative cycle include the magnitude of the potential (its amplitude), the duration of time the ions are accelerated towards the rod (the frequency of the ac potential), the mass of the particular ion, the charge of the ion, and its position within the quadrupole.

Now imagine that a positive dc potential (at a fraction of the magnitude of the ac potential) is applied to the rod in the X-Z plane. This positive dc potential alone would focus all of the ions towards the center of the pair of rods. When the ac and dc potentials are applied at the same time to the pair of rods in the X-Z plane, ions of different masses respond differently to the resulting potential. *Heavy ions are largely unaffected by the alternating current and as a result respond to the average potential of the rods. This results in heavy ions being focused towards the center of the rods. Light ions, on the other hand, will respond more readily to the alternating ac current. Ions that are sufficiently light will have an unstable trajectory in the X-Z plane and will not reach the detector. Only ions heaver than a selected mass will not be filtered out by the X-Z electrodes. As a result, the X-Z plane electrodes only filter light ions and form a high pass mass filter* (Figure 5.7).

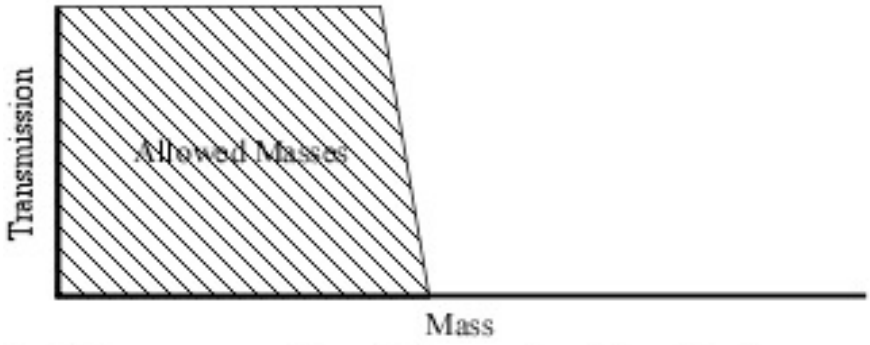
Now look at the other pair of rods or the converse of the ac/dc potential. The rods in the Y-Z plane have a negative dc voltage and the ac potential is the same magnitude but the oppose sign as the potential applied to the X-Z plane. Heavy ions are still mostly affected by the dc potential, but since it is negative,

they strike the electrode and are unable to reach the detector. The lighter ions respond to the ac potential and are focused towards the center of the quadrupole. The ac potential can be thought of as correcting the trajectories of the lighter ions, preventing them from striking the electrodes in the Y-Z plane. These electrical parameters result in the construction of a low pass mass filter.

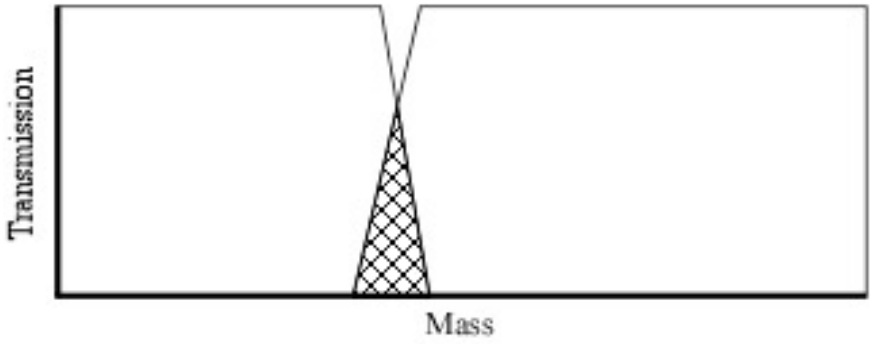
When both the electrodes are combined into the same system, they are able to selectively allow a single mass to charge ratio to have a stable trajectory through the quadrupole. *Altering the magnitude of the ac and dc potential changes the mass to charge ratio that has a stable trajectory resulting in the construction of mass spectra.* Different ions possess a stable trajectory at different magnitudes and reach the detector at different times during a sweep of the ac/dc magnitude range. The graph of the combined effect, shown in Figure 5.7c, is actually a simplification of the actual stability diagram.




a) The high pass mass filter in the X-Z plane allows heavy ions to be transmited through the quadrupole and reach the detector




b) The low pass mass filter in the Y-Z plane allows light ions to be transmited through the quadrupole and reach the detector




c) The combined effect of the dc and oscilating ac potential results in an area stability for a specific mass to charge ratio.



Figure 5.7. A “Conceptual” Stability Diagram

One way to generate an actual stability diagram is to perform a series of experiments where a single mass ion is introduced into the quadrupole. The dc

and ac voltages are allowed to vary and the stability of the ion is mapped. After performing a great number of experiments the resulting plot would look like Figure 5.8. The shaded area under the curve represents values of ac and dc voltages where the ion has a stable trajectory through the potential and would reach the detector. The white space outside the stability diagram indicates ac and dc voltages where the ion would not reach the detector.

While any ac and dc voltages that fall inside the stability diagram could be utilized, in practice, quadrupoles keep the ratio of the dc to ac potential constant, while the scan is performed by changing the magnitude of the ac and dc potential. The result of this is illustrated as the mass scan line intersecting the stability diagram in Figure 5.8. The graphs below the stability diagram correspond to specific points along the scan and help to illustrate the ions' trajectories in the X-Z and Y-Z plane (Figure 5.8). While the mass to charge ratio of the ion remains constant in each pair of horizontal figures, the magnitude of the applied voltages are changing while their ratio stays constant. As a result, examining points along the mass scan line in Figure 5.8 is equivalent to shifting the position of the high and low pass mass filters with respect to the x axis illustrated in Figure 5.7. Even though the mass is not changing for the stability diagram discussed here, the mass that has a stable trajectory is altered.

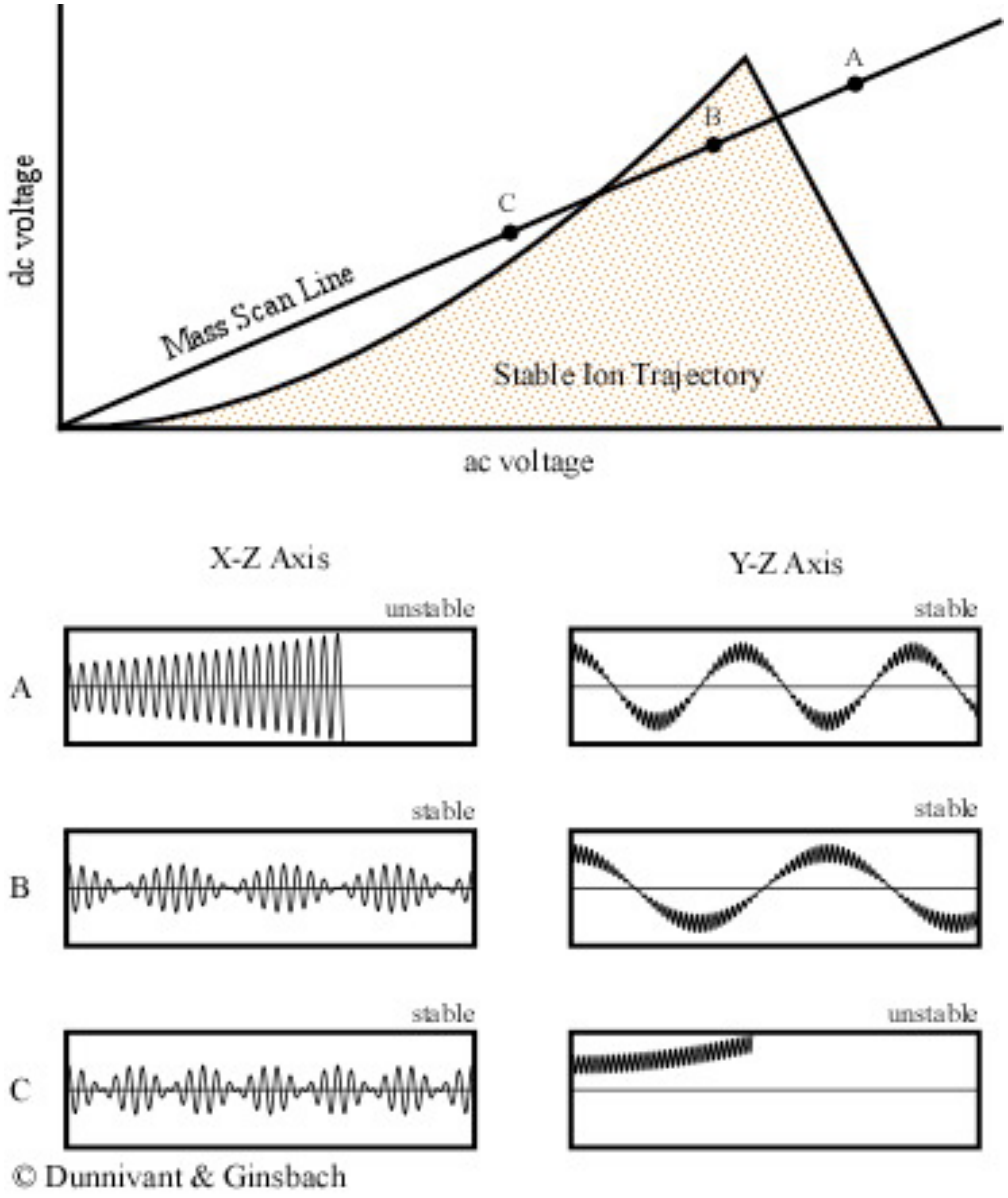



Figure 5.8. Stability Diagram for a Single Ion Mass. Used with permission from the Journal of Chemical Education, Vol. 75, No. 8, 1998, p. 1051; copyright © 1998, Division of Chemical Education, Inc.

In the above figure, the graph corresponding to point A indicates that the ion is too light to pass through the X-Z plane because of the high magnitude of the ac and dc potentials. As a result, its oscillation is unstable, and it eventually impacts the electrode/rod. The motion of the particle in the Y axis is stable because the combination of the ac potential as well as the negative dc potential

yields a stable trajectory. This is the graphical representation of the ac potential correcting the trajectory of the light ions in the Y-Z plane. At point B the magnitude of voltages has been altered so the trajectories of the ion in both the X-Z and Y-Z plane are stable and the ion successfully reaches the detector. At point C, the ion has been eliminated by the low mass pass filter. In this case, the ac potential is too low to allow the ion to pass through the detector and it strikes the rod. This is caused by the ions increased response to the negative dc potential in the Y-Z plane. The trajectory in the X-Z axis is stable since the dc potential focusing the ion towards the center of the poles overwhelms the ac potential.

Until this point, the stability diagram shown above is only applicable to a single mass. If a similar experiment were to be performed using a different mass, the positions of the ac and dc potential on the x and y axes would be altered but the overall shape of the curve would remain the same. Fortunately, there is a less time consuming way to generate the general stability diagram for a quadrupole mass filter using a force balance approach. This derivation requires a complex understanding of differential equations and is beyond the scope of an introductory text, but the solution can be explained graphically (Figure 5.9). The parameters in the axes are explained below the figure.

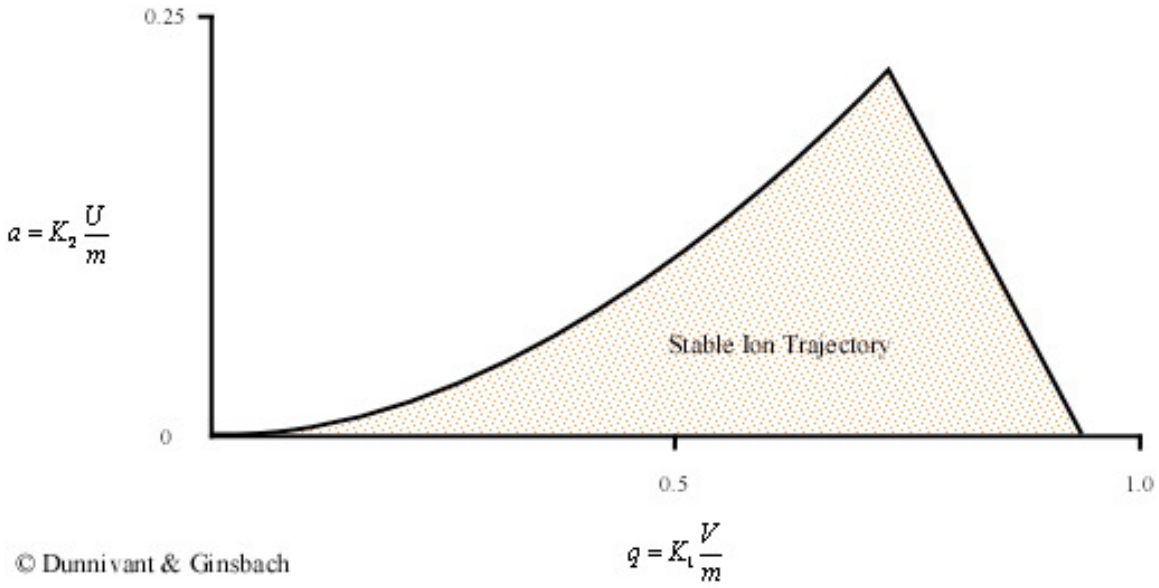



Figure 5.9. The General Stability Diagram

While this derivation is particularly complex, the physical interpretation of the result helps explain how a quadrupole is able to perform a scan. The final solution is dependent on six variables, but the simplified two-variable problem is shown in Figure 5.9. Utilizing the reduced parameters, a and q, the problem becomes a more manageable two-dimensional problem. While the complete derivation allows researchers to perform scans in multiple ways, this discussion will focus only on the basic mode that makes up the majority of mass spectrometers. For the majority of commercially available mass spectrometers, *the magnitude of the ac potential (V) and the dc potential (U) are the only parameters that are altered during run time and allows a sweep of the mass to charge ranges*. The rest of the parameters that describe $K_1$ and $K_2$ are held constant. The values for $K_1$ and $K_2$ in the general stability diagram can be attributed to the following equations:

$$K_1 = \frac{2e}{r^2\omega^2}$$

$$K_2 = \frac{4e}{r^2\omega^2}$$

The parameters that make up $K_1$ and $K_2$ are exactly what we predicted when listing the variables earlier that would affect the point charge. Both K terms

depend upon the charge of the ion *e*, its position within the quadrupole *r*, and the frequency of the ac oscillation *ω*. These parameters can be altered, but for the majority of applications remain constant. The charge of the ion (e) can be assumed to be equivalent to positive one, +1, for almost all cases. The distance from the center of the quadrupole (r) is carefully controlled by the manufacturing process and an electronic lens that focuses the ions into the center of the quadrupole and is also a constant. Also the angular frequency (ω) of the applied ac waveform can be assumed to be a constant for the purposes of most spectrometers and for this discussion.

The first important note for the general stability diagram is the relationship between potential and mass. The general stability diagram (Figure 5.8) is illustrated where there is an inverse relationship between the two. Figures 5.9 and 5.10 shows the lighter ions (m-1) are higher on the mass scan line and the heavy ions (m+1) are lower on the line. This is why in Figure 4-8 at point A, the molecule was too light for the selected frequencies, and it was too heavy at point C.

From the general stability diagram, it is also possible to explain how an instrument's resolution can be altered. The resolution is improved when the mass scan line intersects the smallest area at the top of the stability diagram (Figure 5.10). The resolution can be improved when the slope of the mass line is increased and the slope is directly related to the ratio of U and V. The resolution will subsequently increase until the line no longer intersects the stability diagram. While it would be best for the line to intersect at the apex of the stability diagram, this is impractical due to fluctuations in the ac (V) and dc (U) voltages. As a result, the line intersects a little below this point allowing the quadrupole to obtain unit resolution (plus or minus one amu).

Once the resolution has been determined, the ratio of the ac to dc potential is left unchanged throughout the scan process. To perform a scan, the

magnitude of the ac and dc voltages is altered while their ratio remains constant. This places a different mass to charge inside the stability diagram. For example, if the ac and dc voltages are doubled, the mass to charge ratio of the selected ion would also be doubled as illustrated in the second part of Figure 5.10. By scanning throughout a voltage range, the quadrupole is able to create the majority of mass spectra produced in today's chemical laboratories. But it should be noted that quadrupole mass filters have an upper limit of approximately 650 charge to mass ratios. This is of no consequence in inorganic analysis since all isotopes are well below this limit.

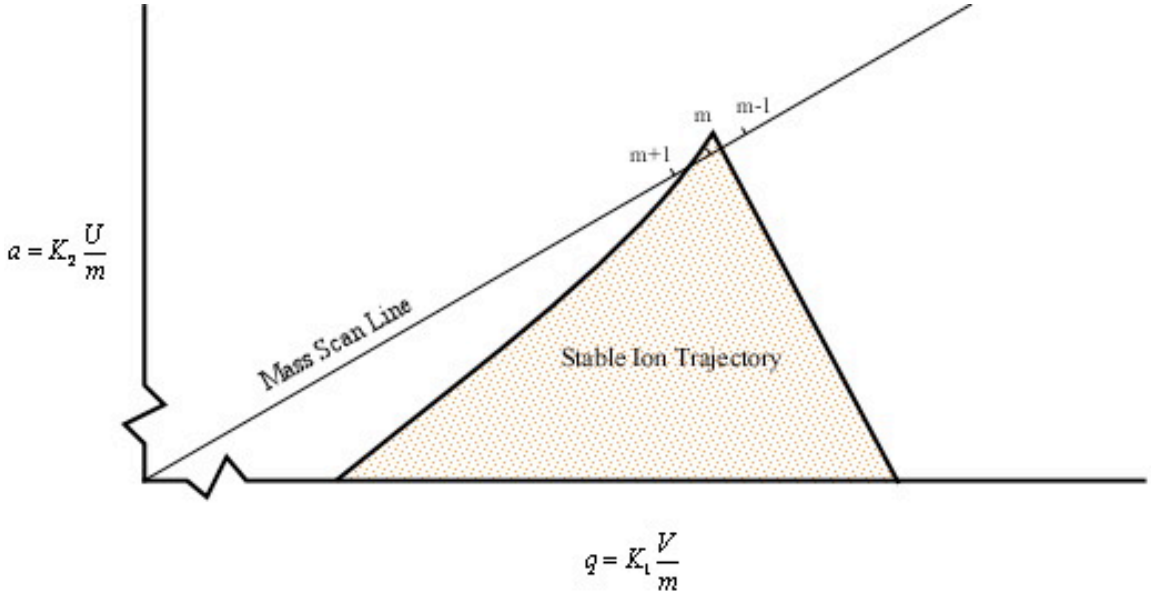
Now that we have given a detailed description of the factors influencing the movement of a charged particle through the quadrupole, it is advantageous to summarize the entire process as a physicist would do in the form of a force balance. This is the origin of the governing equation where the French scientist E. Mathieu balanced the equations for the motion of ionized particles to the potential forces (electrical potentials) encountered in a quadrupole mass analyzer. This six-parameter differential equation, known as the Mathieu equation is represented by

$$\frac{d^2u}{d\xi^2} + [a_u + 2qu\mathrm{Cos}2\xi]u = 0$$

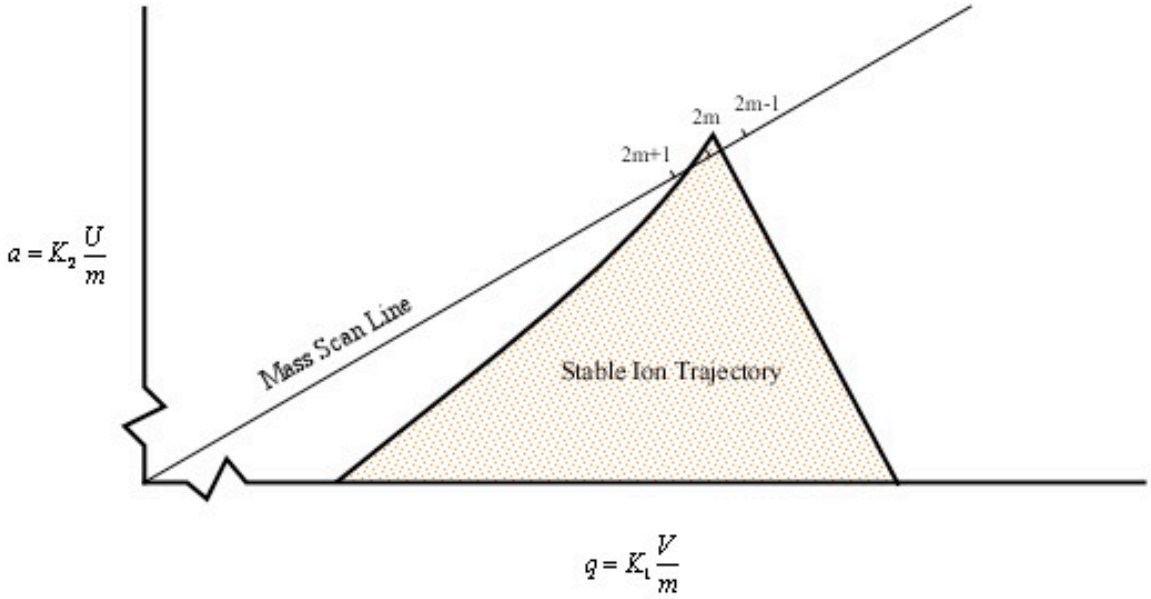
*where*

$$a = \frac{4eU}{\omega^2 r_0^2 m} \quad \text{and} \quad q = \frac{2eV}{\omega^2 r_0^2 m}$$

and where *u* is either the x or y directional coordinate, $\xi$ is the redefining of time (t/2), *e* is the charge of the ion, U is the magnitude of the dc potential, $\omega$ is the angular frequency ($2\pi f$) of the applied ac waveform, $r_o$ is the distance from the center axis (the z axis) to the surface of any electrode (rod), *m* is the mass of the ion, and V is the magnitude of the applied ac or radio frequency waveform. By using the reduced terms, *a* and *q*, the six-parameter equation (*e, $\omega$, $r_o$, m, U, and V*) can be simplified to a two-parameter equation (involving *a* and *q*). Thus, when the two opposing forces are balanced, the movement of a charged particle in an electrical field, the particle will pass through the quadrupole and strike the detector.




a) This stability diagram illustrates a single value for both U and V where only particles of mass m are allowed to reach the detector.

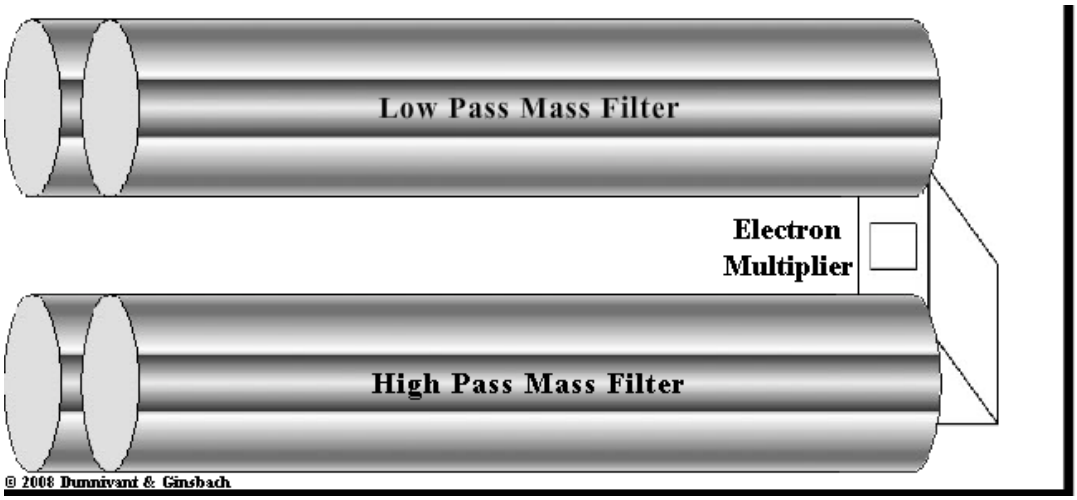



b) This stability diagram illustrates a single value for both U and V that is double the value of figure a). As a result, the particles corrisponding to a mass of 2m are able to reach the detector.



Figure 5.10 Quadrupole Mass Scan. Used with permission from the Journal of Chemical Education, Vol. 63, No. 7, 1998, p. 621; copyright © 1986, Division of Chemical Education, Inc.

View Animation 5.4, on the book's web site, for an illustration of how the trajectory of ions of different masses are changed during a mass scan.




Animation 5.4 Illustration of Cations in a Quadrupole Mass Filter.