INTRODUCTION TO INORGANIC ISOTOPE RATIO MASS SPECTROMETRY

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Olszewski-Day 1

PURPOSE OF THE COURSE

To introduce the basic physics of mass spectrometers

To understand the methods of ion generation, mass separation and ion detection

To look at the various geometries and designs of some mass spectrometers

To understand the construction of the mass spectrometer and its associated electronics

To get an appreciation for both the power and limitations of modern isotope ratio mass spectrometer

SCOPE OF THE COURSE

- Concentrate on Thermal Ionization Isotope Ratio Mass Spectrometers
- Inorganic Materials
- “Nuts and Bolts” approach to the mass spectrometer

What is a Mass Spectrometer?

- A mass spectrometer is an instrument for separating atoms or ions according their mass (really mass to charge ratio).
- This separation can be accomplished by either electric or magnetic fields or some combination of both.
- The separation can be a separation in space, time or some other parameter (e.g., oscillation frequency).

Why High Precision Isotope Ratio Mass Spectrometry?

- Many important scientific problems in the earth sciences, physics, chemistry and the biological sciences can be answered through the measurement of the ratios of the isotopes of different elements
- Mass Spectrometers are uniquely designed to answer many of these questions by separating isotopes and measuring their ratios
- In the earth sciences, the use of isotope ratios ranges from age dating (Sr, Pb, Nd and others), petrogenetic indicators and tracers (Sr, Nd, Pb, O, H, S and others), temperature and other environmental indicators (again many of the same elements)
- As our understanding of these systems has improved the need for higher precision has increased, e.g. the need for high precision measurements in age dating the stratigraphic time scale
- There are many kinds of mass spectrometers but we will discuss mainly magnetic sector machines which are the dominant kind used in high precision work

Review of Some Basic Concepts in Mass Spectrometry

Mass

- Kilograms and grams are too large!
- Unified atomic mass unit is used
- Symbol: u or amu
- Defined as 1/12 the mass of an atom of the isotope ^{12}C, thus it includes the masses of the electrons as well as the nucleus.
- The currently accepted value (1998) is 1.660 538 73 x 10^{-24} grams.
- 1 amu equals approximately 931.494 MeV
- The term Dalton (Da) can be used interchangeably with the amu, most commonly used by the organic community

Mass (continued)

- ^{12}C is the only isotope with an exact integral mass
- All other isotopes have non-integral masses, e.g. :

  ^{1}H: 1.00783 amu

  ^{40}Ar: 39.96238 amu

  ^{88}Sr: 87.90562 amu

  ^{238}U: 238.05079 amu
- So two isotopes or compounds that nominally have the same mass number will differ slightly in weight:

  ^{40}Ar: 39.96238 versus ^{40}Ca: 39.96259

  Methane, $^{12}C^{1}H_4$: 16.03132 versus

  ^{16}O: 15.99491
- At mass number 28:

  $^{14}N_2$: 28.00614

  $^{12}C^{16}O$: 27.99491

  $^{12}C_2{}^{1}H_4$: 28.03132

Mass (Continued)

- And polyatomic species made of multi-isotopic element can have nominal mass overlaps:

  $^{28}Si^{18}O$: 45.97609 versus $^{30}Si^{16}O$: 45.96868
- Note that the mass of any isotope is not the sum of the masses of the individual electrons, protons and neutrons that make up the isotope. The binding energy that is released when the nucleons and electrons come together to form the isotope manifests itself as a change in mass (remember $E = mc^2$).
- So for example, 6 electrons + 6 protons + 6 neutrons (a disassembled ^{12}C atom) weighs 12.0989397 amu not 12 amu.

Review (Continued)

Energy

- Joule is too large an energy unit at the level of single atoms. So the electronvolt is used

- one electronvolt is the work required to move an electron (or any singly charged particle) through a potential difference of one volt (or gained by the particle if it falls through a one volt potential difference). The currently accepted value (1998) is 1.602 176 462 x 10^{-19} joule.

- Mass spectrometers today operate in the range of 0 to > 10 Mev.

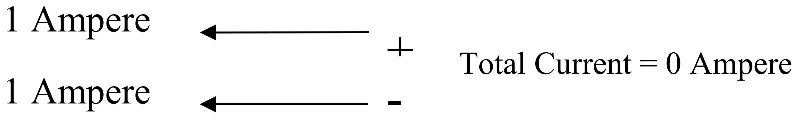
Review (Continued)

<u>Charge and Current</u>

- Official SI unit of charge is the Coulomb (C) which is equivalent to 6.241 506 x 10^{18} electron charges (e), so one electron (or proton) charge is equivalent to 1.602 177 x 10^{-19} C.

- At the level of the atom, it is easier to use multiples of the electron charge (+/- 1 e).

- Official SI unit of current is the ampere (A) which equals 1 C/s. This is net charge, so



1 Ampere ← +

1 Ampere ← -

Total Current = 0 Ampere

- +/- 1 e/s = 1.602 177 x 10^{-19} A.

- Current will be left in Amperes.

Review (continued)

Some Other useful Terms

- Magnetic Fields: 1 Tesla (T) = 1 x 10^4 Gauss (G)
- The earth's field is about 0.5 G
- Voltage : 1 V = 1 J/C

BASIC PHYSICS OF CHARGED PARTICLES IN MAGNETIC AND ELECTRIC FIELDS

Symbols:

- q = charge of ion
- $\vec{v}$ = ion velocity
- $\bar{B}$ = magnetic field
- V = Voltage
- $\overline{\underline{\ }}$ = voltage gradient = $\nabla V = \frac{d}{dx}Vi + \frac{d}{dy}Vj + \frac{d}{dz}Vk$

Force on a charged particle in an electric field

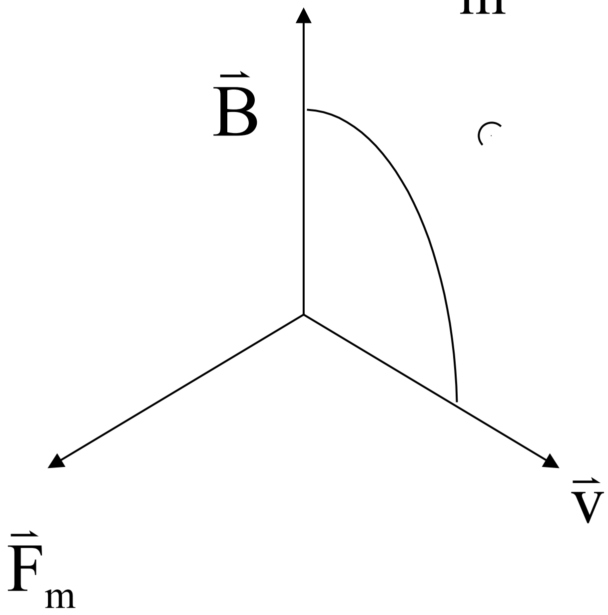
$$\vec{F}_e = -q\vec{\Phi}$$

$$\vec{F}_e \longrightarrow$$

$$\vec{\Phi} \longleftarrow$$

Force on a charged particle in a magnetic field

$$\vec{F}_m = q(\vec{v} \times \vec{B}) = qvB\sin\varphi$$



$\vec{F}_m$ is at right angles to the plane formed by B and v, use the right hand rule for direction, reverse for negatively charged ions.

For the case where $\varphi = \pi/2$ (90°) $\vec{F}_m = qvB$

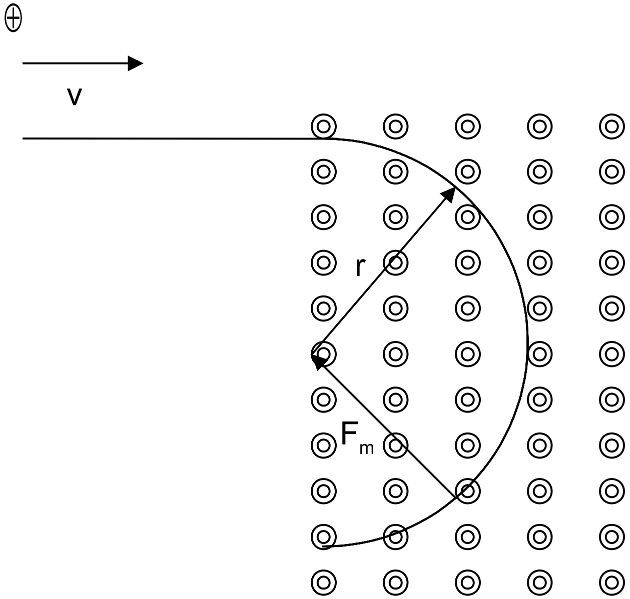
OTHER USEFUL EQUATIONS

- Kinetic Energy gained by a charged particle accelerated through a Voltage:

$$KE = qV = \frac{1}{2}mv^2$$

where m = the mass of the charged particle

Basic Magnetic Sector Mass Spectrometer Equation



Equation for Forces:

$$F_m = qvB = F_c = \frac{mv^2}{r}$$

Equations for Energy:

$$\mathrm{KE} = \frac{\mathrm{mv}^2}{2} = \mathrm{E_a} = \mathrm{qV_a}$$

Solving for v and combining equations yields the following versions of the mass spectrometer equation:

$$m = \frac{qB^2r^2}{2V_a} \qquad \mathrm{r} = \frac{\sqrt{\frac{2\mathrm{V_a m}}{\mathrm{q}}}}{\mathrm{B}} \qquad \frac{\mathrm{m}}{\mathrm{q}} = \frac{\mathrm{B^2 r^2}}{2\mathrm{V_a}} \qquad \mathrm{r} = \frac{\mathrm{mv}}{\mathrm{qB}}$$

A Magnetic Sector Mass Spectrometer is basically a momentum separator

However:

$$mv = \sqrt{2mqV_a} = \sqrt{2mKE}$$

Magnetic Sector (continued)

Some words about units:

- For q in Coulombs, B in Teslas, r in meters and V in Volts:
  m is in kilograms

- In more useful units:
  For q in electrostatic units (+/-1 e), B in gauss, r in centimeters and m in amu there is a units constant of 9.64853×10^{-5}

$$m = 9.64853 \times 10^{-5} \cdot \frac{qB^2r^2}{2V_a}$$

Some Properties of the mass spectrometer equation

- For constant B and V the radius of curvature varies as the square root of the mass to charge ratio, so larger masses have larger radii of curvature.
- As mass get higher adjacent masses get closer together.
- For fixed V, q and r the mass (m) at radius r will depend on B^2.
- The magnetic mass spectrometer is essentially a momentum separator (see last equation above). However, since all ions have the same energy, momentum is only mass dependent.

An Aside

As it stands the mass spectrometer equation is not quite right, it predicts behavior that doesn't really happen.

- The equation predicts that a charged particle in a magnetic field should circle endlessly.
- In reality a charged particle in a magnetic field radiates away energy and consequently its radius of curvature decreases

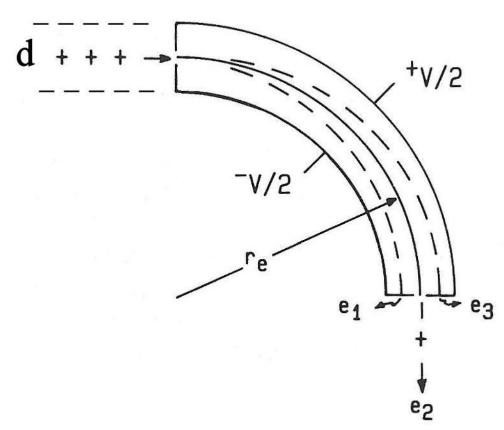
$$r = \frac{\sqrt{\frac{2V_a m}{q}}}{B}$$

- The opposite can also happen; a charged particle can absorb electromagnetic energy and increase its radius of curvature.
- In most mass spectrometers this effect is small; however some mass spectrometers have to take this into account and others exploit this property.
- Going under various names such as cyclotron resonance, ion cyclotron resonance, they use RF energy to determine the radius of curvature for charged particles in strong magnetic fields

- One version called Fourier Transform Mass Spectrometry (FTMS) has the highest resolution of any mass spectrometer technique (> 100,000). It uses an RF signal to energize low energy ions into following circular paths in an intense magnetic field (>5T). The ions are then allowed to relax and radiate away energy which is measured. Since each m/q ratio generates a characteristic set of frequencies, the resulting signal is a mixture of all of the different ions in the mass spectrometer. The Fourier transform is then used to separate the individual frequencies and generate a mass spectrum.

Equations for an Electrostatic Analyzer

Force Equations: $F_e = -q \cdot \Phi$



a) Electrostatic Analyser

For a simple parallel plate ESF:

$$\Phi = \frac{V_e}{d}$$

So:

$$F_e = \frac{q \cdot V_e}{d} = F_c = \frac{m \cdot v^2}{r}$$

Energy Equations (same as for magnetic sector):

$$KE = \frac{mv^2}{2} = E_a = qV_a$$

The following equations can be derived:

$$r = \frac{2 \cdot d \cdot V_a}{V_e}$$

$$r = \frac{d \cdot m \cdot v^2}{q \cdot V_e} = \frac{2 \cdot d \cdot KE}{q \cdot V_e}$$

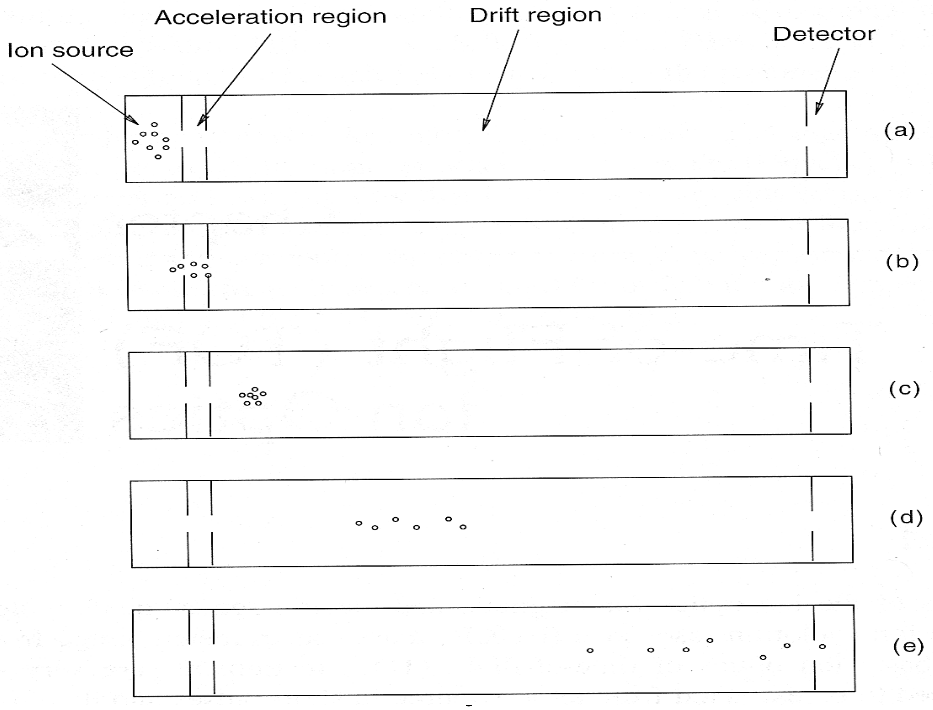
Some Properties of the Electrostatic Analyzer

- Mass does not enter into the equation for radius (except as a kinetic energy term), so an electrostatic analyzer does separation by kinetic energy. Since in most mass spectrometers all of the ions have the same KE, there is no mass separation.

- Electrostatic Analyzers are used to narrow the energy spread of ion beams to improve magnetic sector resolution. We will look at this in more detail later.

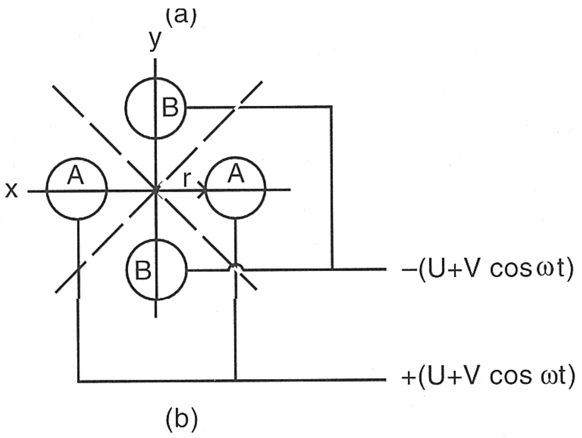
A Digression on Electrostatic Separation

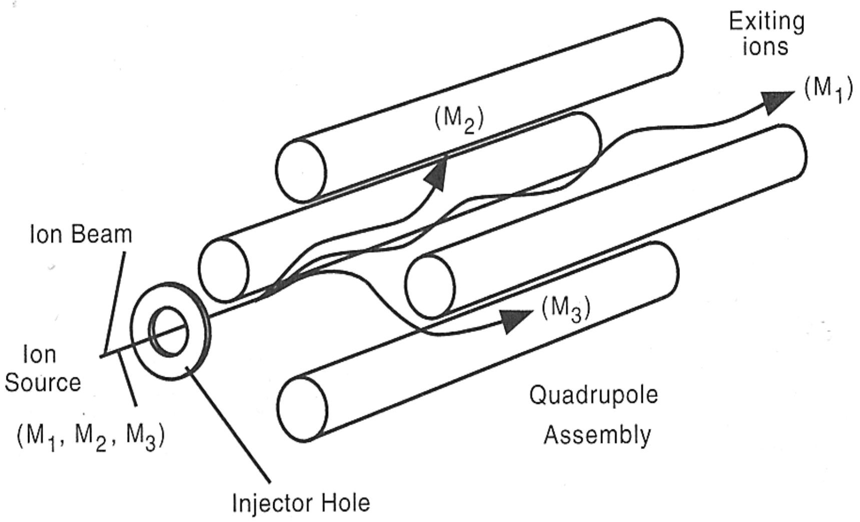
- Electric fields can be used to separates masses.
- If all the ions have the same energy their velocity depends on mass (at the same charge), so if the ions are allowed to move in free space they will separate by velocity, i.e. mass. This separates masses as a function of time rather than space (as in a magnetic sector mass spectrometer). This is the basis of Time of Flight Mass Spectrometry (TOFMS).



Digression (continued)

- For Quadrupole Mass Spectrometry (QMS) ions are subjected to a DC Voltage combined with an AC Voltage. The ions follow complex helical trajectories that are either stable (i.e. the ions stay in the Quadrupole) or unstable (the ions leave the spectrometer before detection). The trajectories are m/q dependent, so mass separation can be done. This is effectively a time dependent spatial separation of masses.





Basic Mass Spectrometer Layout

- A real mass spectrometer is usually separated into three sections:
- An ion source where ions are generated, formed into a beam (usually rectangular in cross section and diverging in the x-direction), given a specific energy and directed toward the next part of the mass spectrometer,
- The analyzer where the single ion beam is separated into beams of varying m/q ratio and the individual beams are brought to a focus (for reasons to be discussed below) outside of the analyzer where they enter,
- The collector of the mass spectrometer. Here the ions of each beam are collected and measured either as individual ions or as an integrated electrical current. This beam intensity is then a measure of the amount of that isotope in the sample.

Source

Analyzer

Collector

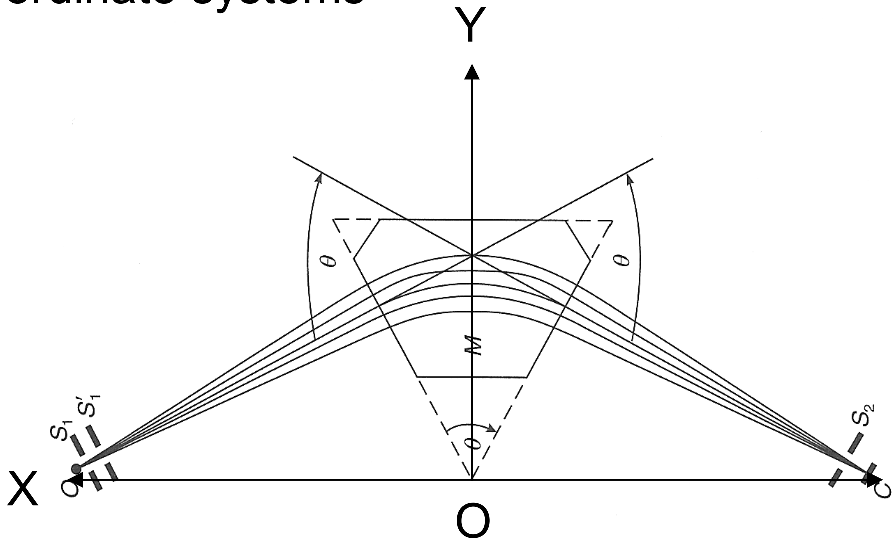
The ion generation and collection (detection) are usually done separate from the analyzer to avoid the effects of the strong magnetic (or electric) fields on the source or collector.

- It sounds simple but in practice it can be very complicated to accomplish these things and produce a high precision isotope ratio.

- The rest of this course will look at each of these parts of the mass spectrometer in detail to see how this is accomplished.

A Few Words About Mass Spectrometer Coordinate Systems

- In Magnetic Sector Mass Spectrometers (which we are mainly dealing with here), there are two main coordinate systems
- A magnet centered system:



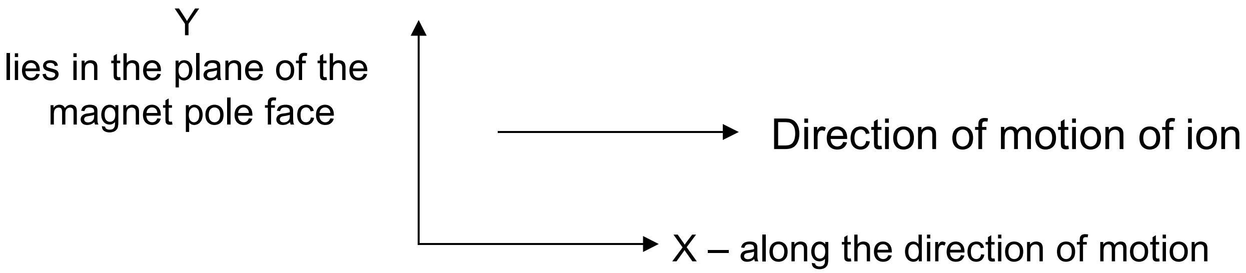
Z direction is perpendicular
To the X and Y coordinates

This coordinate system can also be used for Electrostatic Analyzers

Origin lies on the apex of the Magnetic sector

Coordinate Systems (Continued)

- A Beam Centered system:
- In this system the coordinates move along with the beam



Y
lies in the plane of the
magnet pole face

Direction of motion of ion

X – along the direction of motion

The Z direction is perpendicular to X and Y

This coordinate system allows us to talk about the geometry of the beam without having to specify its position