Assigned Reading: Nier mass spectrometry paper

Extra Reading:

1) Introduction

a) We are now on to the heart of the mass spectrometer. How do you separate ions of different mass, so that you can detect/quantify them.

b) In all cases this involves manipulation of a charged particle in electric and/or magnetic fields.

c) This is really the realm of ion physics, we'll touch on it only superficially to understand how they work. Designing ion optics is not a trivial task.

2) Types of Mass Analyzers - Overview

a) Quadrupole
   i) 4 charged rods oscillating in pairs at RF frequency, 180° out of phase
   ii) causes ions to take a spiral path; stability of that path (ie, expanding outward or not) depends on m/z
   iii) those with stable path make it through, those without do not. Thus acts as a mass filter, not actually separating in space.
   iv) Pros: small, simple, cheap, easy to operate, very rapid scan rate, useful filter for MS-MS
   v) Cons: throwing away most ions, limited mass resolution, limited to modest ion currents

b) Ion Trap
   i) Works a bit like a quadrupole bent into a circle. Inject ions into cavity, set up oscillating frequency, trap them all in stable orbits. Now ramp the AC frequency and sequentially eject ions in order of mass, measuring them as you go.
   ii) Can also eject all ions but one (or a range), then oscillate it with He collision gas to make it undergo further fragmentation; can then trap and sequentially eject daughter products. This is the simplest way to do MS-MS experiments, and very useful for structural identification.
   iii) One of the biggest disadvantages is that the trapping efficiency depends on the total collected charge in the trap. Thus quantification of unknowns is difficult, because the response changes depending on what else is in there…
   iv) There is also a linear ion trap design, which looks like a quadrupole with two end confining electrodes. Main advantage is said to be increased ion storage, thus better quantitation.
   v) Pros: small, simple, ability to do selected dissociation of ions
   vi) Cons: Hard to make quantitative, because stability in cavity depends in part on total injected charge

c) Ion Cyclotron Resonance
   i) Starts like an ion trap. The ions are trapped in a [Penning trap](#) (a strong magnetic field with electric trapping plates) where they are excited (at their resonant cyclotron frequencies, which depends on mass and velocity) to a larger cyclotron radius by an oscillating electric field orthogonal to the magnetic field. After the excitation field is removed, the ions are rotating at their cyclotron frequency in phase (as a "packet" of ions). These ions induce a charge (detected as an image current) on a pair of electrodes as the packets of ions pass close to them.
   ii) Measure ions by detecting the time-varying current induced by circulating ions. Signals from all the different ions are convolved in this image current. Then do a Fourier Transform to get from the time domain back to the frequency domain. Frequency of each peak then tells you mass of circulating ion.
   iii) Note: bigger magnetic field allows higher-frequency cyclotron resonance, which can be measured more precisely in the same amount of time and so ultimately achieves higher mass

resolution (time limit is that coherent ion packets decay, or thermalize, after a few seconds). Trend in field toward HUGE magnets, just like NMR.
  iv) The longer you watch, the better your precision in frequency. Can achieve phenomenal precision in measuring frequency, which translates to very high mass resolution. Allows working out exact elemental formula even for huge molecules.
  v) Pros: Mass resolution >1 million, detects all ions all the time (Fellgett's Advantage)
  vi) Cons: Huge, very expensive, superconducting magnets
d) Time of Flight
  i) Arrange ions into a packet or bundle, shoot them down flight tube with constant energy, measure how long they take to arrive at detector (microseconds)
  ii) Do this at kHz speed, then average down to a few tens of Hz data rate.
  iii) Detection has to be digital, no Faraday cups, so need small number of ions to avoid simultaneous arrivals
  iv) Very simple in principle, only possible with modern high-speed electronics.
  v) Pros: Reasonable cost, very high mass resolution, infinite scan speed, measures all ions all the time (Fellgett's advantage)
  vi) Cons: Only handles very small ion currents, no filtering ability; doesn't give classical mass spectra for database-matching
e) Sector-Field instruments
  i) Oldest type of spectrometer; originally called a 'spectrograph' because they literally used photographic plates as the detector.
  ii) Charged particle moving in an electric or magnetic field feels a force (Lorentz Force), which changes its direction.
  iii) Force depends on charge, but deflection of path depends on mass, so this physically separates ions into different beams.
  iv) Pros: can handle huge ion beams, very stable, multi-detection possible, filtering possible
  v) Cons: big instruments, very slow scan speed, throws away most ions, inherent tradeoff between resolution and beam size/transmission
f) Summary: Just about the only thing sector instruments excel at is creating very large, very stable ion beams. But that is the most important thing for high-precision isotope ratios.

## 3) Sector-Field Spectrometers; basic physics

a) Acceleration
  i) Ion has a potential energy of $\mathbf{E_p = zU}$
    (1) E_p = potential energy
    (2) z = elemental charge (+1)
    (3) U = electric field strength
    (4) Example: in a 3kV accelerating field, CO_2^+ ion has 3keV potential energy
      (a) Recall: eV is unit of energy, an electron transiting a 1V potential
      (b) In SI units: need charge in coulombs, so use q = ze where e is charge of an electron (1.6e-19), U in volts, Ep now in Joules
      (c) So the conversion of electron-volts to Joules is 1.6e-19
  ii) If we allow ion to move down the electric potential, all that potential energy gets converted into kinetic energy. Now has $E_p = E_k$, and $\mathbf{E_k = \frac{1}{2}\,mv^2}$
    (1) SI units are Ek in Joules, mass in kg, v in m/s
    (2) Solve for v = sqrt(2E$_k$/m)
    (3) Example: z = +1, m=44 Da (convert to kg, 1 Da = 1.66E-27kg), E_k = 3keV (convert to Joules, 1 eV = 1.6E-19J)
    (4) Gives v = 1.1e6 m/sec (about 1/3000 the speed of light)

   (5) Halving the mass would double the speed. H_2 molecule is going 22-fold faster (nearly 1% the speed of light?)

 b) Deflection

  i) Moving through an EM field, our ion experiences the Lorentz Force: $\mathbf{F = q[U + (v \times B)]}$

   (1) U is electric field

   (2) B is the magnetic field

   (3) v is velocity (a vector)

   (4) x is the cross product of velocity and magnetic field, not the variable x

   (5) q is electronic charge in SI units; =ze as above

   (6) direction of force is orthogonal to field and velocity vectors, following right-hand rule

  ii) In simplest design, have a magnetic field and no electric field, so simplifies to

   (1) $\mathbf{F_m = zevB}$, with the force applied orthogonal to vectors v and B

  iii) This force is balanced by the ions momentum, which wants to keep it moving straight. Quantified as the 'centripedal force'

   (1) $\mathbf{F_c = mv^2/r}$

  iv) The path that the ion will take through the magnetic field is defined by where these forces balance. So:

   (1) $F_c = F_m$

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

    (a) Knowing v from above, we could now solve for r (radius of curvature); in the interest of a more unified equation, we continue…

   (3) $v = Bzer/m$

    (a) Note that r is proportional to mv, which is momentum. Often called a 'momentum filter' to distinguish from electric sector.

   (4) Plug (3) into equation for kinetic energy ($zeU = \frac{1}{2} mv^2$)

   (5) $zeU = 1/2m \left(\dfrac{Bzer}{m}\right)^2$

   (6) $zeU = \dfrac{B^2 z^2 e^2 r^2}{2m}$

   (7) $\dfrac{m}{z} = \dfrac{B^2 r^2 e}{2U}$ - this is the key eqn for sector instruments

  v) General: Note that separation always depends on m/z, not just m

   (1) Old spectrographs scanned the mass spectrum by varying r, putting a photographic plate across the image plane

   (2) We can change the position of any ion beam by changing B or U

    (a) Use B to scan over large ranges, U to fine-tune over small ranges

  vi)

  vii) Example: for our system, assume B= 0.25 Tesla, U = 3kV, m=44Da

   (1) Calculate r as 0.209 meters.

   (2) For the real instrument, you can measure r (fixed by the geometry), I want you to calculate field strength at which you would see masses 2, 28, 44, 146

4) Ion optical concepts

 a) Previous analysis of the physics considers ion beam as an infinitely narrow, perfectly collimated beam. Real ion beams are not like that. Our ability to distinguish masses (and so measure them) depends on beam size, focus, divergence, etc.

 b) Terminology: A lot of this derives from equivalent terms in optical systems. Think of the analyzer as a lens…

i) The "object" is the thing you are looking at (objective lens), for us = the ion source, think of this as imaging the ion source
    (1) For an optical microscope, you want this to be flat, because you can only focus on a particular distance
    (2) For our IRMS, want the ion beam to come into focus for all masses on the "object plane" at the entrance slit
ii) The "image" is the transmitted light, refocused by the magnetic sector at a different place = the detectors
    (1) Called the image plane, or focal plane. Want it to come to focus at the exit slit (if one exists), diverges slightly into detector.
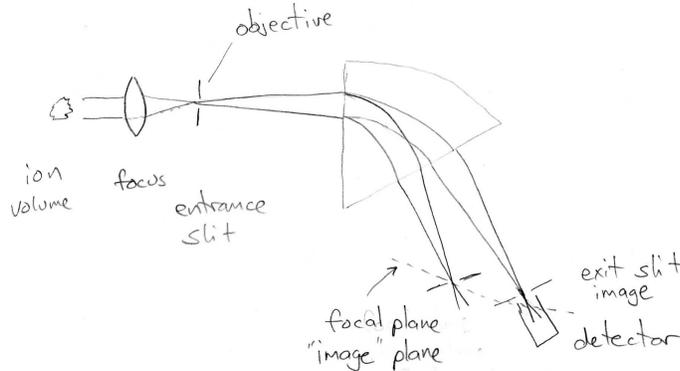
(2)
c) Focal plane distance (D) – where is the focal point of the magnet?
    i) Object and image focal points given by $D = r_{eff}/\tan(\theta/2)$ where theta is sector angle.
        (1) For 90° sector, $D = r$
        (2) But note that D now depends on mass; can only have one mass at a time perfectly in focus at one detector
        (3) Other masses will come to focus on a curved focal plane that passes through the axial point (makes it impossible to position fixed detectors that will work over a range of masses)
d) Dispersion (d) – physically how far apart are two adjacent masses on average. Very important for us doing multidetection as it determines spacing of detectors.
    i) $d = r_{eff}\Delta m/m$ (assumes a symmetrical setup, with object and image equal distance from magnet poles; approximate relationship)
        (1) m and Δm could refer to things you want to measure, say $^{28}N_2$ and $^{29}N_2$ ($\Delta m = 1$) or $^{44}CO_2$ and $^{46}CO_2$. ($\Delta m = 2$). Probably easiest to think of Δm as being "per mass unit"
    ii) depends on radius; larger the radius, the larger the dispersion. This is one good reason to build very big machines (like the ion probes)
    iii) Example:
        (1) The Neptune/Ultra has r_{eff} ~500 mm
        (2) What is the physical dispersion for N_2 (mass 28)?
            (a) 500mm/28Da = 18mm/Da
        (3) What is it for CO_2 (mass 44)?
            (a) 500/44 = 11.3mm/Da
            (b) Note! Spacing has changed. Will have to accommodate that when we install the detectors.
        (4) What is it for SF_6 (mass 146)
            (a) 500/146 = 3.4 mm/Da
e) Resolution/resolving power; ability to separate masses, includes width of beams

i)   In general, beam width is constant with mass, but physical dispersion decreases. That means it gets harder and harder to separate masses (can think of this as their relative difference getting smaller). How to quantify this ability to separate masses? Resolution.

ii) $R = m/\Delta m$

iii) Now, Δm refers to the ~beam width; more precisely, the distance (in mass units) over which the ion beam drops to 10% of its intensity. Two peaks that are Δm apart would have 10% of their tails overlapping, and be just barely "resolved".

iv) A Resolution of 1000 means that mass 1001 will be one beam-width away from mass 1000 (unit resolution); they are resolved. Or that you could cleanly separate (with 10% overlap) masses 10.00 and 10.01.

v)   What limits resolution?
   (1) Can also write $R = r_{eff}/2w$ (w = beam width)
   (2) Obviously physical dispersion; a larger geometry can achieve higher resolution
   (3) On our machines, mainly beam width. Combination of ability to focus perfectly, and size of the ion beam (more intense beams have to be physically larger because of coulomic repulsion)
   (4) Can we estimate the resolution of our machine just from physical measurements?

vi) Tradeoff: In a sector instrument, the way you get better resolution is to have a physically narrow beam. Typically achieved by a narrower object or image slit, but this clips the beam and results in lower transmission. For a fixed geometry, doubling resolution will halve transmission. Low-resolution machines typically value transmission over resolution. On the Ultra, they are equally important, starts to depend on which isotope you are measuring.

vii) Tend to think of resolution as a constant. For a sector instrument with constant radius, it is roughly constant with mass. Not true for a lot of other types of spectrometers (often R scales strongly with mass).

5) Nier-type geometry

a)   Focusing
   i)   Why don't we use a magnet that is a square shape? Instead they are always ~triangular (sectors of a circle, which gives the system its name of "sector"). Discovering the advantages of this shape was one of the seminal contributions of Al Nier. Previous instruments (Aston, Dempster, etc) had used circular or semi-circular magnets, had terrible beam shapes.
   ii) Real ion beams will not be perfectly collimated, they will have some divergence. One of the properties of a sector magnet is to provide modest ("first-order") focusing. This was one of Nier's big discoveries.
   iii) Nier-geometry
      (1) A triangular magnet in which magnet poles are sectors of a circle (traditionally 60° or 90°), ion beam enters at 90°,
      (2) Ions going deeper into the magnet spend more time in the field, have the same radius but turn for a little longer.
      (3) will have the object focus (source) and image focus (detector) on a line that passes through the apex of the magnet. (How can this be true for all masses?)
      (4) Advantages: simple to make and build, very compatct footprint (especially for 90°), source and detectors further from magnetic (important for stability)
      (5) Disadvantages: curved focal plane, small dispersion, focusing limits resolution (typical beam width at focal point is 50% larger than at source exit slit

b)   Homogeneity
   i)   Calculations assume a perfectly homogeneous field with sharp boundaries; of course, real magnets have fields that decay at their edges, called "fringing fields". These tend to cause defocusing and loss of resolution in the 'z' direction.

6) Extended geometry

   a) First proposed by Cross in 1951, but not really achieved until the MAT-250 in 1977 (first instrument with true stigmatic focusing). General idea is to have ion beam hit pole faces at some angle, and use fringing field as a focusing element.

      i) Can be easily modeled with modern computers, but cannot be done by simple ray-tracing methods. In the 1960's had to be done largely by trial and error, so took a long time.

   b) Most companies seem to have settled on following solution: Ions enter and exit the pole faces at 26.5°, magnet is no longer a true circular sector.

   c) Advantages:

      i) focal plane becomes nearly flat over wide mass range, enables single set of fixed detectors to be used for a variety of masses

      ii) effective radius of curvature is doubled over that of Nier-type (for same field strength); doubles the distance of the focal plane from the source (D), and thus also doubles dispersion (d) and improves resolution, without needing a bigger magnet.

      iii) Achieves second-order focusing (in the y-direction) as well as basic focusing in z-direction (esp in combination with z-focus in ion source); refers to focusing in the vertical direction on our instrument

        (1) Single-focusing sector can achieve resolution up to maybe 500-1000

        (2) Big advantage here is that less of the beam is clipped, so get higher transmission and better abundance sensitivity

   d) Disadvantages:

      i) Slightly larger footprint

      ii) Focal plane at an angle to beam, so detectors must be staggered 'en echelon'

7) Double focusing

   a) These systems all called "single focusing", because they have one stage of focusing in the magnetic field. Deals with beam directional divergence (directional focusing), but does nothing about energy divergence of beam (fact that ions from the source will have a distribution of energies). The latter will end up with different r_{eff} because they have different momentum.

   b) Employ an electric sector; two curved plates with DC potential between them

      i) Lorentz force is now qU (rather than qvB), when we do force balance and solve for radius we have $qU = \frac{1}{2} mv2$ and find that r is proportional to mv^2 (rather than mv), which is kinetic energy, so we call this an 'energy filter' not a 'momentum filter'. Only ions with the proper kinetic energy will make it through, all others hit the wall. So this operates as a filter, not a spectrograph. This solves the energy divergence problem.

      ii) The electric sector also has focusing properties, with respect to energy (not direction). However, turns out that the focal plane for energy filtering is at an angle to the focal plane for direction (figure). Only a single point in space where both are perfectly in focus.

      iii) Called the "double-focusing condition", and can be used to generate very high resolution (up to 100,000) in a sector instrument (i.e., the Thermo DFS)

   c) Note that the Triton/Neptune/Ultra instruments use the ESA simply to filter the energy distribution, not true double-focusing condition (which you cannot achieve with multi-detectors)

      i) With this they can achieve resolution of up to ~25,000

8) Collisions and Abundance Sensitivity

   a) All of the preceding assumes perfect ion optical behavior in a perfect vacuum. In reality, you will not get perfect collimation, energy distribution, and there will be some collisions with neutral gas molecules in the imperfect vacuum. Two endmembers:

   b) Head-on collisions. These do not change the direction of the ion, but do change the velocity (energy).

i) If after the magnet, no problem.
ii) If before the magnet, will make ion appear to be lower mass (lower v means lower momentum). So appears as a tail on low-mass side of peak.
iii) This tail can be significant even a full AMU away. Remember, separate from resolution because this is a non-ideality, whereas resolution is theoretical based on optics.
    (1) Makes it very hard to measure rare isotopes on low-mass side of abundant ones
    (2) Classic examples are ^{234}U next to ^{235}U; HD next to ^{4}He
c) Glancing collisions. Change mainly the direction rather than energy.
  i) Changes in direction are symmetric, will result in tails on high and low side.
  ii) Large deviations not possible, because ions don't make it through magnet.
d) Quantify these effects as Abundance Sensitivity
  i) $A = I(M-1)/I(M) \times 10^{6}$
    (1) I = ion current at mass M and M-1
    (2) Factor of 10^{6} means reported in ppm
  ii) Typical values for Triton are 1-10 ppm
    (1) Means an isotope ratio below 10^{-5} would be hard to measure
  iii) Depends mainly on quality of the vacuum. Hard to get much below 1E-9, so how to improve abundance sensitivity?
e) Energy filter
  i) Electrostatic lens at some fraction of nominal kinetic energy (70-80%).
    (1) Rejects any ions with less than nominal energy. But fairly crude.
    (2) Does nothing to improve directional abberations from glancing collisions
    (3) Typical improvement of ~10x
f) WARP/RPQ
  i) Combine an electrostatic aperture (like above) to reject low-energy ions with a quadrupole or long aperture to reject ions entering at the wrong angle (the glancing collisions)