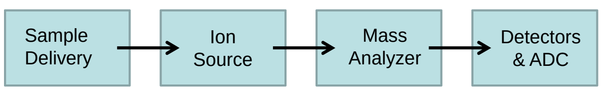
Lecture 13
Measurements I: Mass spectrometry

- Introduction
  - Uses, criteria, commonalities
- Ion Sources
  - Electron impact, TI, ICP, SI
- Analyzers
  - E & M sectors, QMS, TOF, Ion Traps
- Detectors
  - Faraday cups & electron multipliers
- Data Acquisition
  - Electrometers, ADC, statistics

Uses for Mass Spectrometers

- Trace element determination
  - sensitivity & isolation
- Quantitative analysis
  - reproducibility & separation, isotope dilution
- Molecular structure determination
  - deconstruction of molecules
- Material identification and separation
- **Isotope abundance determination**
- Isotope mass determination

Commonalities



- Sample delivery system
  - Pre-purification, optimal phase, preferably non-fractionating
- An ion source
  - Atoms must be charged to be manipulated
  - Preferably mono-energetic, but sometimes spread
  - Creates, accelerates, focuses, collimates a beam
- A “mass” analyzer (m/q)
  - Selects momentum, also maybe energy
  - Refocus & maybe collimates beam
- A detector(s) and Analog to Digital Conversion
  - Measure and discriminate beam(s), possibly isobars
  - Digitize for data acquisition.

In addition

- Sample preparation and introduction system
  - Often integrated into machine
  - Depends on sample type and machine type
- Data gathering and processing system
  - Digitization of analog signals
  - Counting of ions
- Instrument control
  - Control of all parts
  - Automation and book-keeping
  - More reliable, cost effective, humane

Decisions to make

- Sample character: gas, liquid or solid, purity?
- How abundant is the material?
- Isotopic abundance: similar or drastically different?
- Range: do isotope ratios vary a lot or a little?
- Are there isobaric (molecular or nuclear) interferences?
- Are there "matrix effects"?
- Do we need to know the "absolute" ratio?

Figures of Merit

- Resolution: smallest difference in mass
- Sensitivity: how small a signal can be discerned?
- Blank: what do you get with no sample at all?
- Abundance sensitivity: the smallest isotopic ratio
- Stability and reproducibility
- Speed and throughput
- Discrimination and accuracy
- How much does a measurement depend on the presence or absence of other species?
- Memory effect? Does the system hold a grudge?

Resolution

- Are there interfering isobars?
  - How small a mass difference can you distinguish?
- Caveat emptor: watch the definitions!
- You can separate entangled peaks if you know the peak shape very well
  - Not trivial to do…

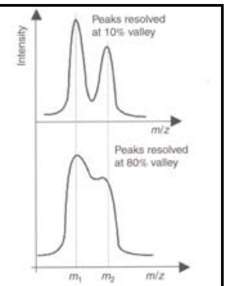
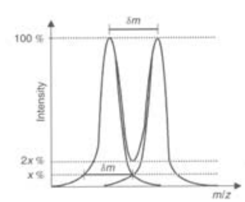


Figure 2.1
Diagram showing the concepts of peak resolution and valley



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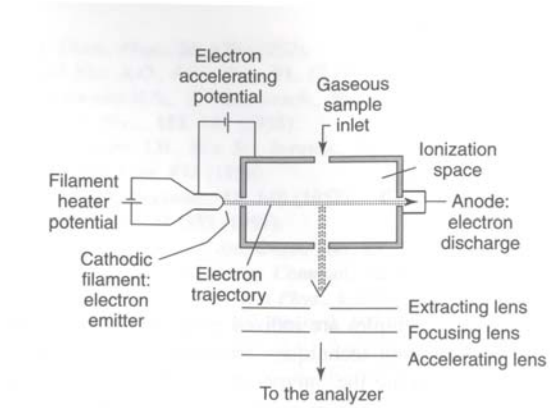
Types of Ion Sources

- Electron impact
  - Gases
- Microwave Plasma
  - Also gases
- Thermal ionization
  - solids
- Inductively coupled plasma source
  - liquids
- SIMS and Laser Ablation
  - solid surface analysis
- There are others
  - But not important for isotope work

Electron Impact Source



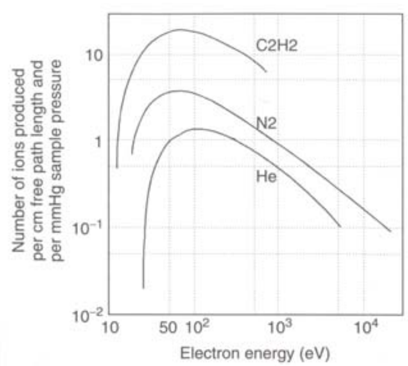
- Generally has more plates than this

Electron impact ionization

- Depends on atomic structure
- Can produce multiply charged ions
- Sensitivity generally around n x 10^{-4} amps/torr

1 amp = 6.24 x 10^{18} e s^{-1}

1 torr = 1/760 atmospheres



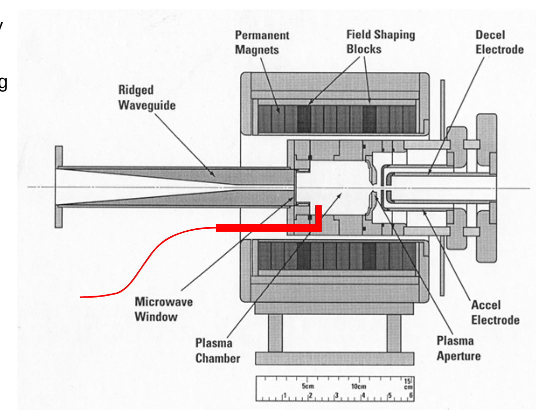
Microwave Plasma Gas Ion Source

Plasma maintained by microwave discharge,

Supported by inflowing gas through capillary

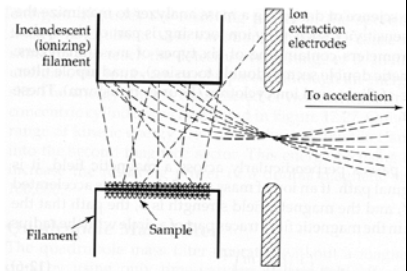
Contained by axial magnetic fields

Ions extracted and focused by electric fields



Thermal Ionization Source

- Solid sample dissolved and concentrated into a few drops
- Deposited on a refractory filament
  - Often with 2ndary coatings
- Filament heated in an ion source
  - Diffusion of material to surface
  - Volatilization
  - Ionization
  - Usually multiple filaments



Thermal Ionization Source

- Solid sample dissolved and concentrated into a few drops
- Deposited on a refractory filament
  - Often with 2ndary coatings to control release characteristics
- Filament heated in an ion source
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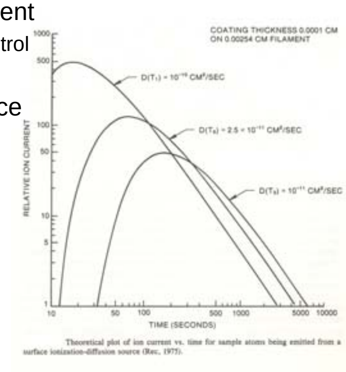
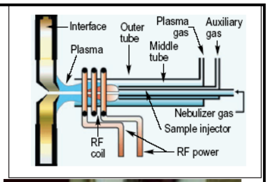
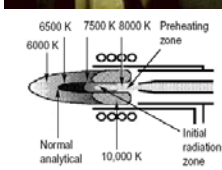


Inductively Coupled Plasma Source

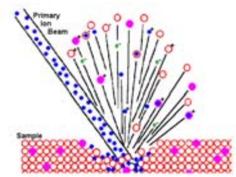
- For "direct" injection of solutions
  - Amenable to automation
  - Simpler chemistry (?)
- Ionization ~ 100%
- Process:
  - Ar from liquid Ar source
  - Torch made of quartz (high temp!)
  - electrostatic ignition of Ar
  - Maintenance of plasma by RF (1-2 KW)
  - Nebulization of solution into Ar flow
  - Coaxial flows of Ar (for cooling too)
  - Ion extraction by "skimmers" (cooled)
  - Skimmers interface vacuum to Ar pressure
- Issues: matrix effects
- Recent developments with laser ablation

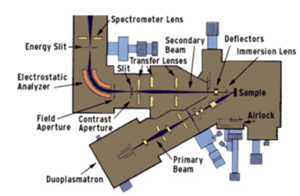




Secondary Ion Mass Spectrometry

- For surface analysis of solids
  - E.g., thin sections
- Spatial resolution ~ 10^{-6}m
  - Laterally and in depth
- Process
  - Create ion beam (Ar, Cs, etc)
  - Extract & Ionize sputtered atoms typically < 10% ionized
  - Accelerate, collimate & focus
  - Big energy spread in ions
    - Need to energy filter
- Issues: surface & ionization biases
  - Standard surfaces/matrices?





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Mass Analyzers

- Magnetic and Electric Sectors
  - Most common for isotope studies
- Time of Flight
  - Simple designs
- Quadrupolar Mass Analyzers
  - Robust rapid scanners
- Ion Traps
  - Compact and emerging tools

Magnetic and Electric Sectors

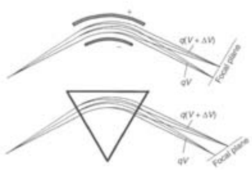
- Electric sectors:
  - Energy filters
  - Balance between:
    - Centripetal force mv^2/R
    - Electrical force qV

$$qV_{Analyzer} = \frac{mv^2}{R}$$

or

$$R = \frac{2E_K}{qV_{Analyzer}}$$

- Resolution related to R and defining slit dimensions



Energy dispersion in an electric sector (*top*) and in a magnetic sector (*bottom*)


Combination of the two sectors, electrical and magnetic

Magnetic and Electric Sectors

- Magnetic sectors:
  - Momentum filters
  - Balance between:
    - Centripetal force mv^2/R
    - Magnetic force qvB
  - Since energy = qV
    - We have

$$F_C = \frac{mv^2}{R} = qvB$$

or

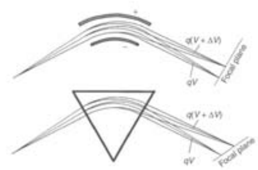
$$R = \frac{mv}{qB}$$

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

$$R^2 = \frac{2mV}{qB^2}$$

- Resolution related to R and defining slit dimensions

$$\frac{\Delta M}{M} \cong \frac{\Delta R_{Beam} + \Delta R_{Slit}}{R}$$

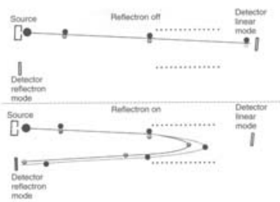


Energy dispersion in an electric sector (*top*) and in a magnetic sector (*bottom*)


Combination of the two sectors, electrical and magnetic

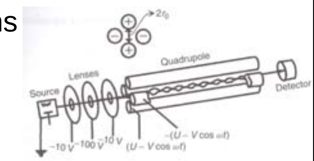
Time of Flight Instruments

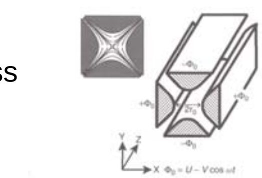
- Conceptually simple
- Not widely used for isotope studies
- Operated in pulse mode
  - "duty cycle" low
- Momentum filters:
  - □ $\Delta T = L / v$



Quadrupolar Mass Filters

- Reliant on orbital stabilty in RF electric fields:
  - Only stable orbits passed
- Complicated optical solutions
  - Integrated Mathieu equations
- Compact and robust
- Low voltage
- Fast scanners
- Wide range
- Constant resolution vs Mass





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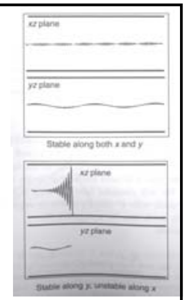
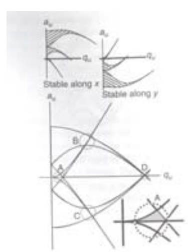
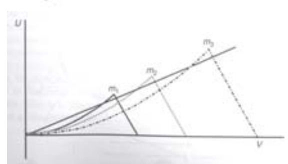
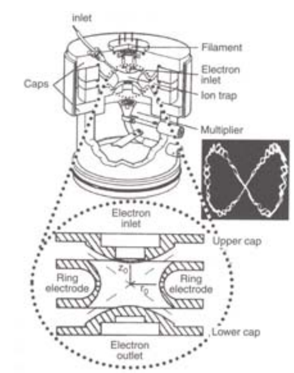






Ion Traps

- Invented by the same guy (Paul)
- Opposite to QMS
  - All ions in stable orbits
  - Desired ions ejected
  - Operated in pulse mode
- Compact & easily made
- Emerging technology



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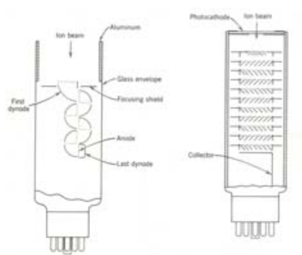
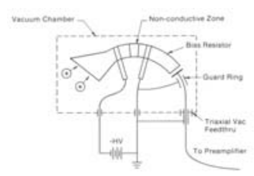
Faraday Cups

- For intense ion beams
  - From 10^{-15} – 10^{-9} ampere range
- Very simple: collect charge
  - Bleed through electrometer
  - Easily created arrays of cups
- Watch for secondary electrons
  - From beam in cup
  - From beam outside of cup
  - Secondary electron suppression plates

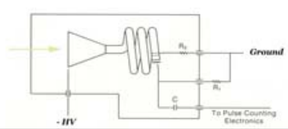
Electron Multipliers

- For ion beams < 10^{-12} amps (< 10^7 ions /s)
- Relies on secondary electron cascade
- Discrete or continuous
- Current or pulse mode
- Run at 10^2 > Gain < 10^8
- Ion feedback issues





Gain depends on high voltage applied to device



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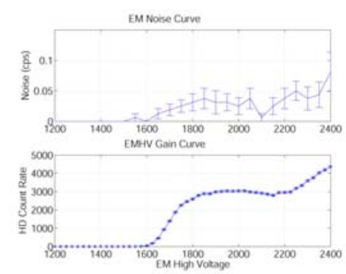
Current vs. pulse counting modes:

(a) gain dependency!

(b)dark current discrimination



Gain and NOISE depends on high voltage applied to device

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Measurement of ion currents

- From Faraday Cup
  - Electrometers (usually FET input)
    - Use feedback resistors
      - Inherent noise
      - Intrinsic time constant
- From S.E.M.
  - If "current mode", use with electrometers
    - First order gain dependence on SEM history
  - If "pulse mode", use preamplifier/discriminator and fast counting electronics

Measurement of ion currents

- Pulse mode SEM already digital (ions/sec)
- Electrometer outputs need to be converted to digital
  - Either ADC (16-24 bit DACs now available)
  - Or VFC (longer term integrators, highly linear, good for ratiometric measurements)