

Mass Spectrometry

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A Brief History

1897- JJ Thomson recorded first mass-to-charge ratio of electrons

1951- W. Pauli and H. Steinwedel developed first quadrupole mass spectrometer

1959- K. Biemann applies electron ionisation mass spectrometry

1974- B. Mamyrin contributes to time-of-flight mass spectrometry

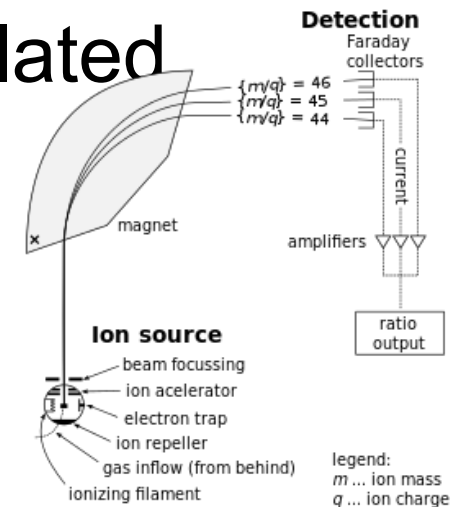
1988- K. Tanaka develops MALDI, receives Nobel prize in Chemistry

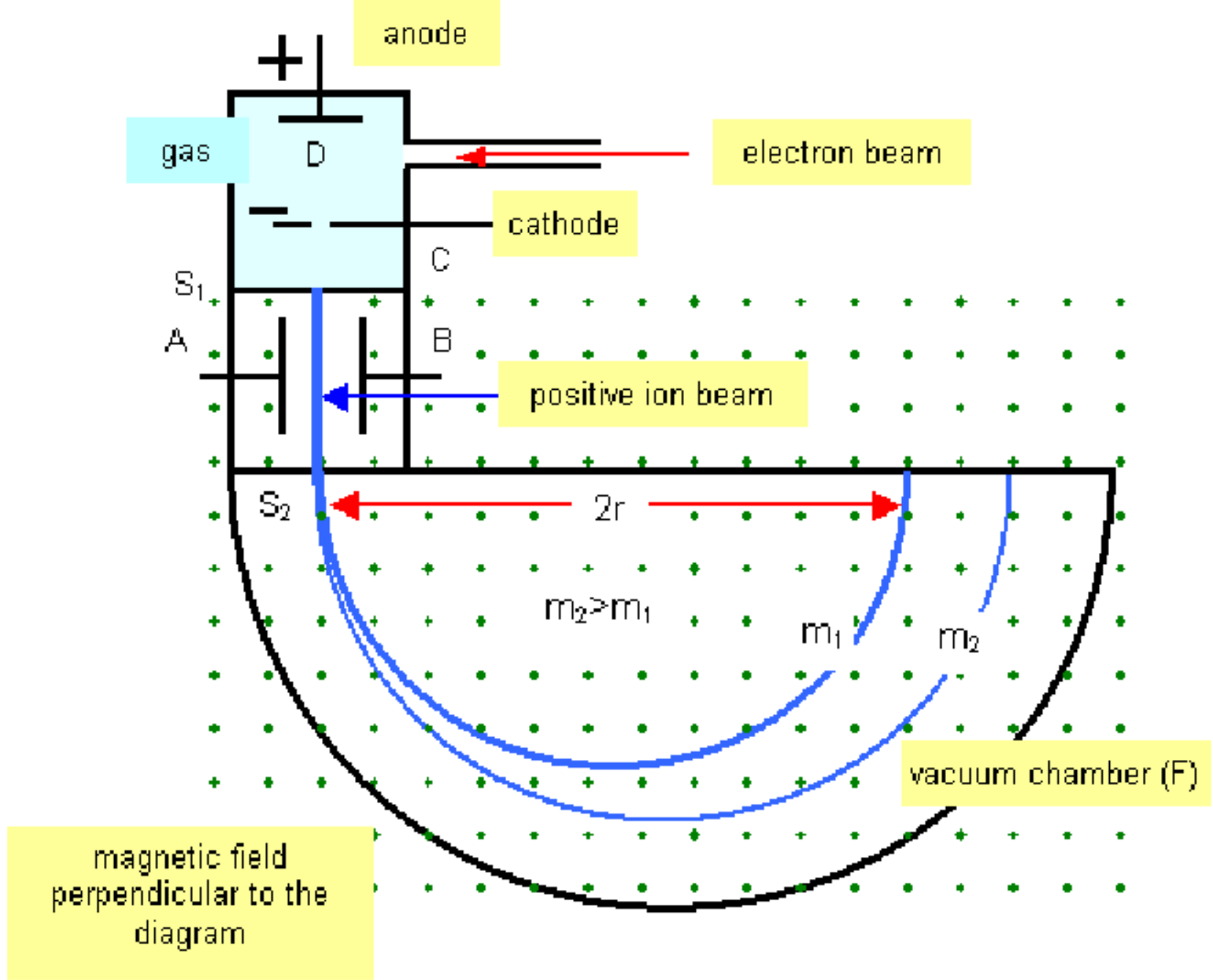
Parts of a Mass Spectrometer

1. A sample injector
2. An ionisation chamber
3. A mass analyser
4. An ion detector
5. A data handling facility

Mass Spec. For Dummies

- Cations are produced
- Cations are accelerated in instrument
- Magnetic field is introduced
- Amount of “bend” is measured
- The heavier an ion is, the less it will “bend”
- Mass/charge ratio is then calculated





The Big Equation

$$m/z = B^2 r^2 / (2V_{\text{acc}})$$

z = charge of ion

m = ion mass

B = magnetic field

r = radius

V_{acc} = potential

difference in

acceleration region

Mass Resolution

$=m/\Delta m$, m = mass, Δm = change in two neighboring masses

The higher the resolution, the better more accurate the readings are

First definition- each adjacent peak contributes 5% of the valley between them

Second definition- mass/width at half point

A resolution of 2000 for the second definition is equal to a resolution of 1000 for the first definition

Molecular Mass Accuracy

The difference between the measured and calculated masses for an ion, displayed as a percent. eg. $1000 \pm .01\%$

Peak overlap is main reason for bad accuracy

Charging the Ion

- Charging is important:
- No charge = no Lorentz force
- There are many ways to do this, including Electron ionisation (EI), Field Ionisation (FI), and Fast Atom Bombardment (FAB), Matrix Assisted Laser Desorption Ionisation (MALDI), and Electrospray Ionisation (ESI)

Electron Ionisation (EI)

Electron energy is generated by a heated filament, set to around 70eV

Gaseous molecule is sent into the energy, causes molecule to lose an electron

Cation is generated from this process

Ions are usually unstable under bombardment

Field Ionisation (FI)

Molecules are introduced in vapor state

High intense electric field is generated, which interacts with molecules

Outer shell electrons are lost, forming cations

Fast Atom Bombardment (FAB)

Argon and/or Xenon are thrown into sample surface at a 8-10 keV

Sample is placed in a glycerol matrix and bombared with Ar or Xe

Disadvantage: requires high concentration of matrix

Advantage: simple and easy to interpret

Matrix Assisted Laser Desorption Ionisation (MALDI)

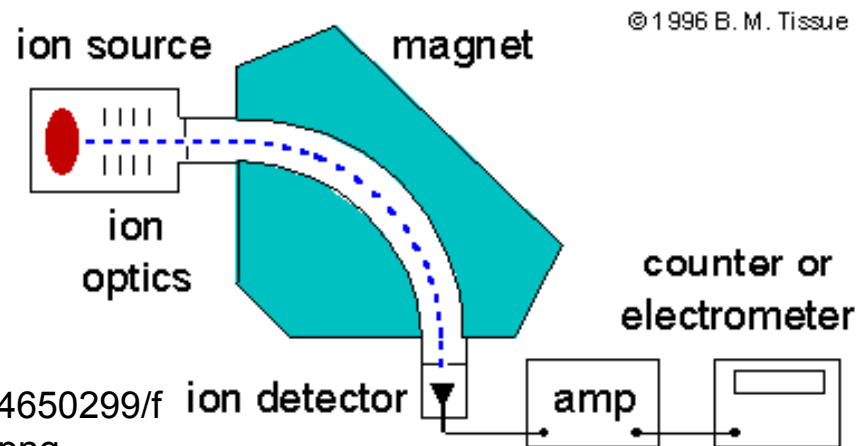
- A useful form of ionisation, more effective than FAB
- Laser energy is absorbed by chromophoric matrix, which converts molecules to gas phase
- Ionisation occurs between excited matrix molecules and sample molecules
- IR laser and UV laser are two most common lasers to use for MALDI, because they can both excite most molecules in the matrix

Electrospray Ionisation (ESI)

- Sample is put into tube and shot out in a “spray”
- Samples are hit with 1-5kV when it emerges from capillary tube
- This creates charged spray like particles
- Solvent evaporates before particles go into chamber containing mass analyser
- Cations are determined by polarity of voltage applied to capillary
- Can create multiply charged ions, which allows large mass molecules to be detected with low m/z ratio
- Higher the mass, higher the resolution

Single Focusing Mass Spectrometer

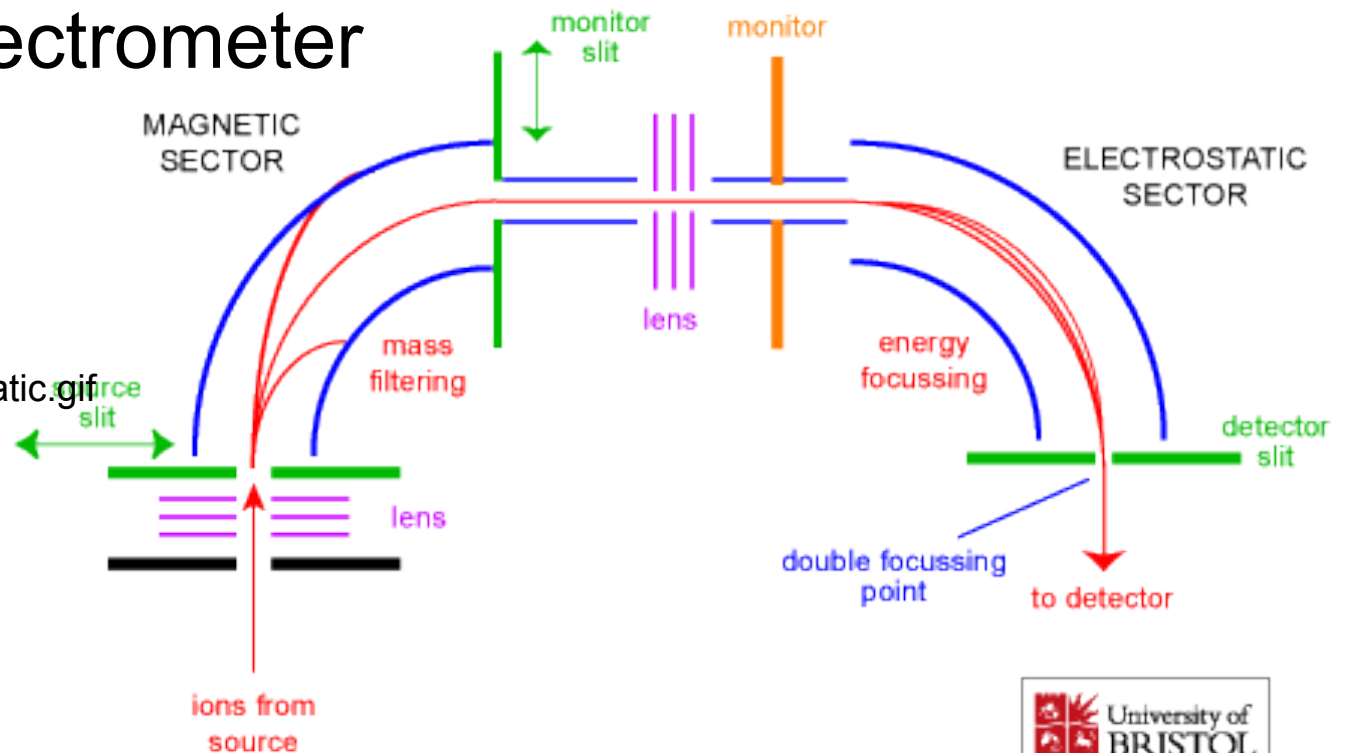
- Only one detector is present
- All ions have a constant radius
- This is done by changing B in electromagnet analyser, and V in electrostatic analyser



<http://figures.boundless.com/511edc7ce4b0c14bf4650299/full/mass-20spectrometer.png>

Double Focusing Mass Spectrometer

- Both electromagnetic and electrostatic analysers are used
- Higher resolution than a single focusing mass spectrometer



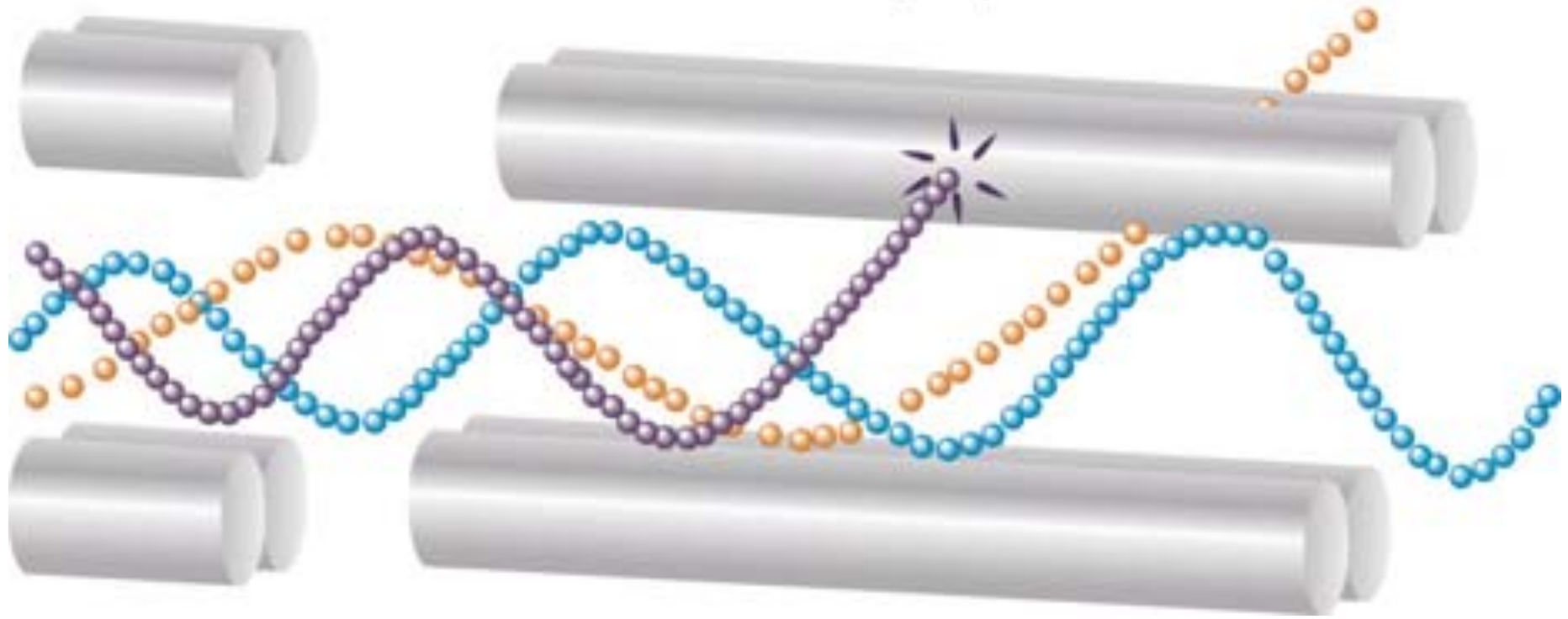
<http://www.chm.bris.ac.uk/ms/images/sector-schematic.gif>

Quadrupole Mass Filter

- Consists of four cylindrical rods
- Two have a negative direct current voltage and alternating radio frequency voltage
- Two have positive direct current voltage and also alternating radio frequency (exact opposite alternating as first two rods)
- The purpose is to disallow any ions traveling in a wrong trajectory to be filtered
- Only ions with correct radius is kept and measured

Pre Filter

Quadrupole Filter



Ion Cyclotron Resonance Mass Spectrometry (ICR-MS)

- Trapped ions in magnetic and electric field detected when frequency matches cyclotron frequency
- Ions travel in a circle and sit in machine for hours
- When you decrease the strength of the magnetic field, the heavier particles will stop traveling in circular paths and will “crash”

Another 2 Big Equations

$$F = zvB = mv^2/r$$



$$\omega = v/r = zB/m$$

Lorenz force due to moving charge through a perpendicular magnetic field

Frequency of rotation

Time of Flight Mass Spectrometer

- Bigger ions move slower than smaller ions
- Low resolution, but fast speed, high transmission, and unlimited mass range
- Uses how long it takes ion to get through instrument to measure m/z

$$u = \sqrt{2zV_{\text{acc}}/m}$$

Tandem Mass Spectrometry

- Two mass spectrometers are used one after the other
- The first mass spec. fragments the ions like normal
- One ion is chosen and sent into a collision course with the fragments of the other ions
- The second mass spec. analyses this ion and these fragments
- Allows several generations of ions to be observed

Thank You For Your Time

Mass



Spec

