elementar
EXCELLENCE IN ELEMENTS

Introduction to Stable Isotope Analysis and IRMS

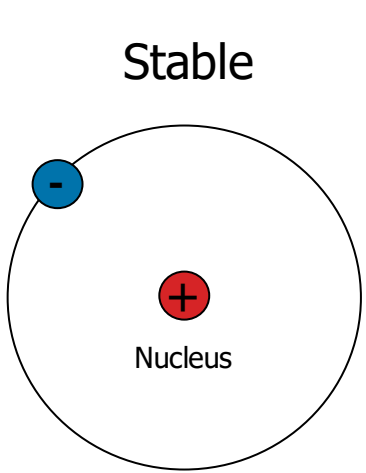
Sunday ~~18th May 2025~~ 7th June 2026

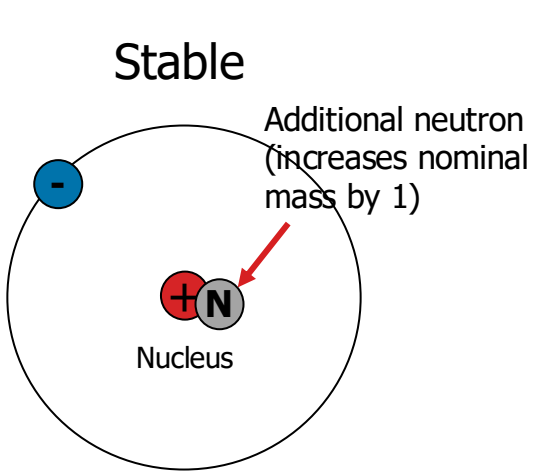
ASITA ~~2024~~ ~~2025~~ 2026

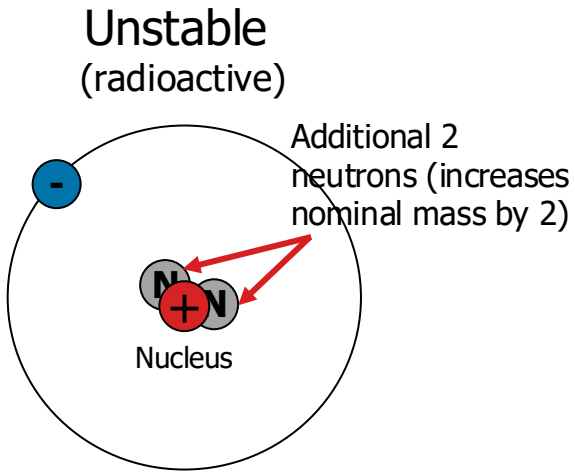
Dr Kyle William Robert Taylor

What is an Isotope?

Same element *(topos = place, re: periodic table)*, different masses







Mass Number 1
Atomic Number 1
H

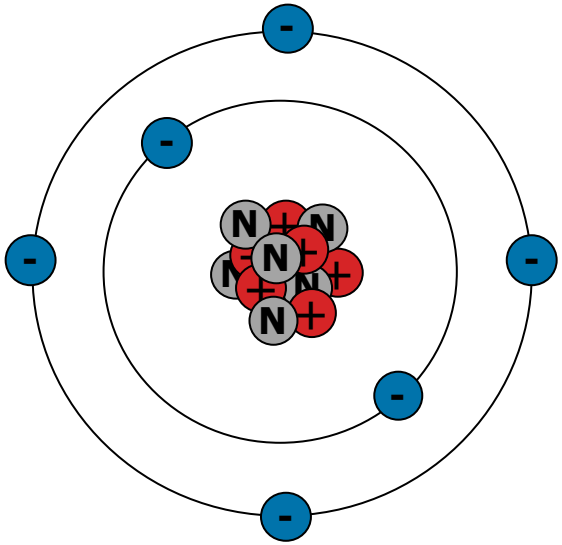
Mass Number 2
Atomic Number 1
H

Mass Number 3
Atomic Number 1
H

Too many (or too few) neutrons, and the nucleus becomes unstable, generally it's the ratio of neutrons to protons that governs the stability.

Isotopes of Carbon

Stable

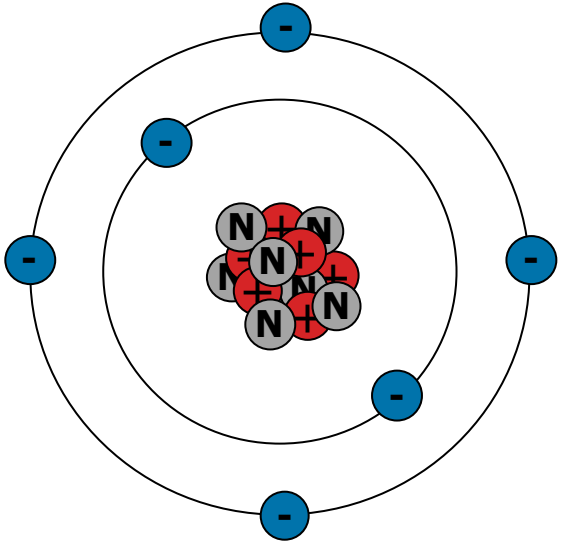


Carbon-12

Mass Number 12

Atomic Number 6 C

Stable

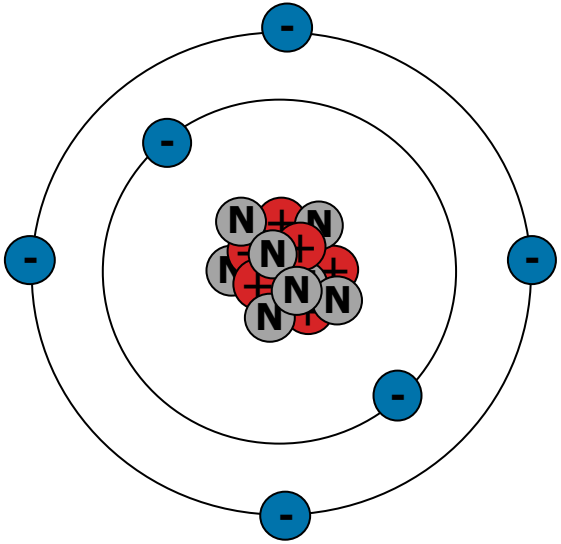


Carbon-13

Mass Number 13

Atomic Number 6 C

Unstable

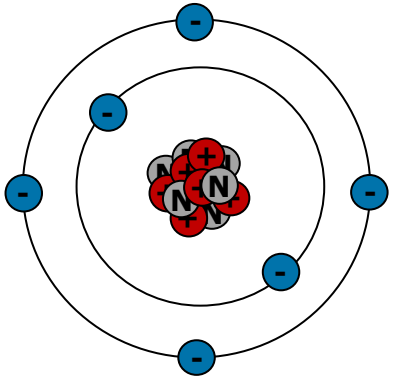


Carbon-14
("Carbon Dating")

Mass Number 14

Atomic Number 6 C

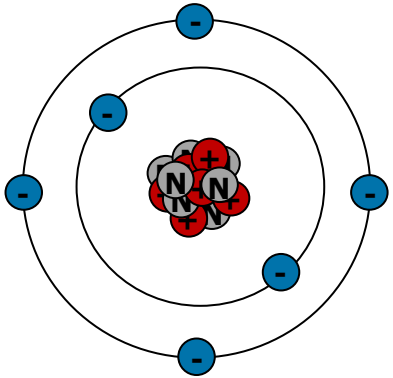
Stable Isotopes of Carbon & Atomic Mass



Natural Abundance

Mass Number 12
Atomic Number 6
C
98.93 %

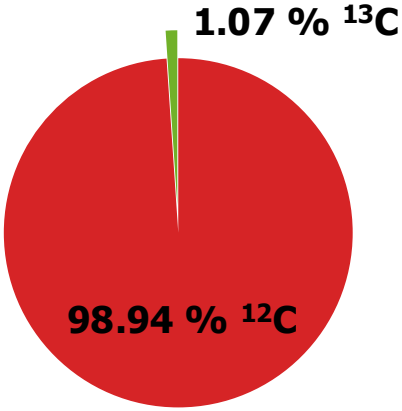
Fun note: carbon-12 has atomic mass and mass number of exactly 12.000, by definition!



Mass Number 13
Atomic Number 6
C
1.07 %

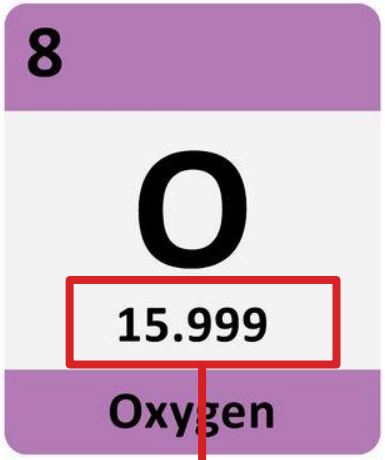
Average mass, accounting for natural abundance & mass of stable isotopes

Atomic Mass 12.011
Atomic Number 6
C

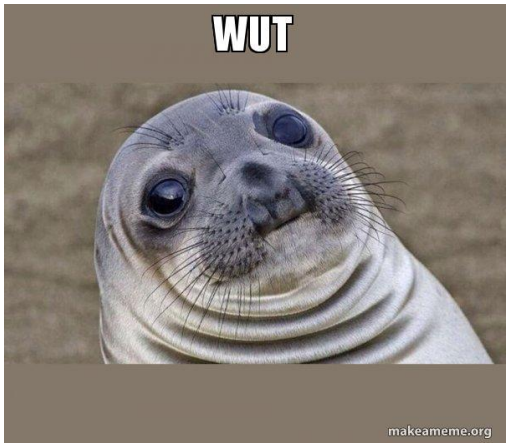


Level up the Confusion, Einstein Style

Oxygen is less massive than it should be?



	Mass Number	Atomic Number		Natural Abundance
	16	8	O	99.757 %
	17	8	O	0.038 %
	18	8	O	0.205 %



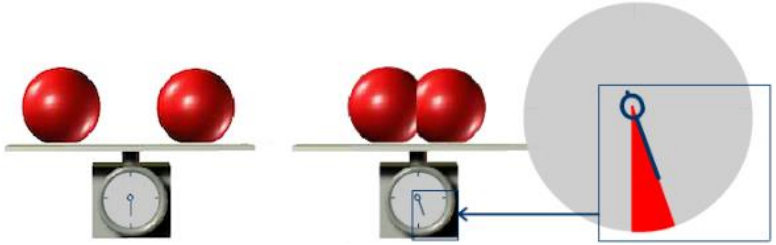
Courtesy of Frédéric Séguin

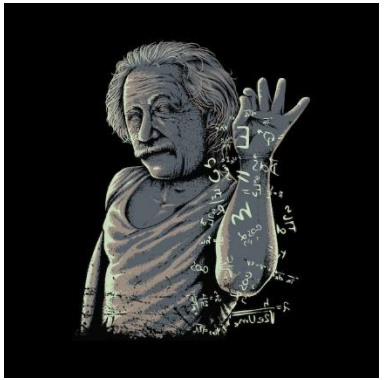
(16*0.99757) + (17*0.00038) + (18*0.00205)

= 16.00448 ***(c. 0.03% difference)***

Level up the Confusion, Einstein Style

Mass Defect & Binding Energy

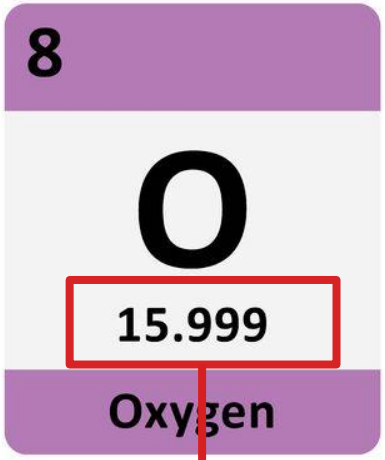




- Binding a nucleus requires energy to overcome proton-proton repulsion
- Energy and mass can be neither created nor destroyed, only converted
- Some nuclear mass therefor must be converted to provide the binding energy
- The mass of a nucleus is thus less than the sum of its parts
- "Relative Isotopic Mass" of all other individual atoms are constrained by definition that 1 atom of ^{12}C = 12 Da/amu/u (1 Da = $^{1}/_{12}$ mass of a ^{12}C atom)

Level up the Confusion, Einstein Style

Mass Number vs Relative Isotopic Mass

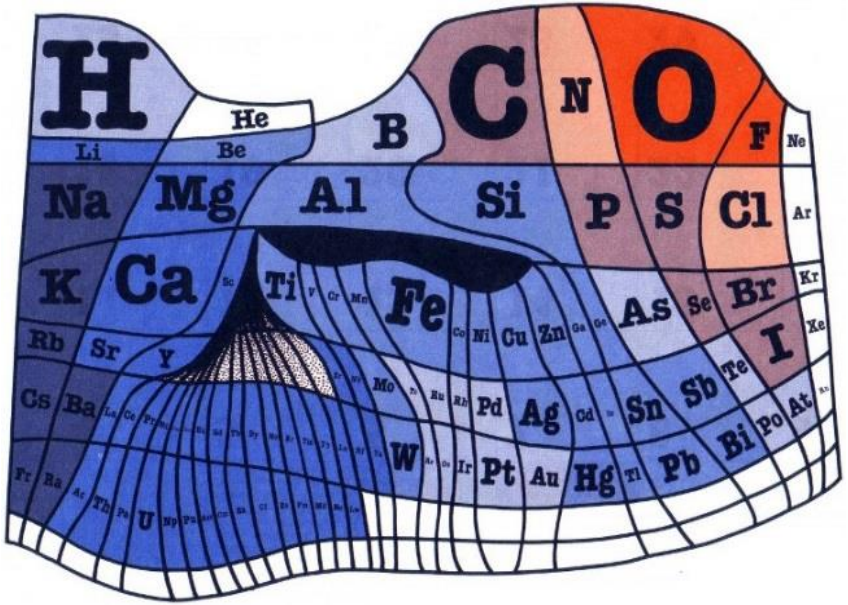


		Natural Abundance	Relative Isotopic Mass
Mass Number 16 Atomic Number 8	^{16}O	99.757 %	15.995 amu
Mass Number 17 Atomic Number 8	^{17}O	0.038 %	16.999 amu
Mass Number 18 Atomic Number 8	^{18}O	0.205 %	17.999 amu

(15.995*0.99757) + (16.999*0.00038) + (17.999*0.00205)

= 15.999

Focus on Bio-Elements (Light Elements)



Elements according to relative abundance (on Earth)

"Bio-elements"?

Really just means, integral to biology! And so, are the most abundant elements on Earth, involved in many processes

Sugars: H, C, O

Fats: H, C, O

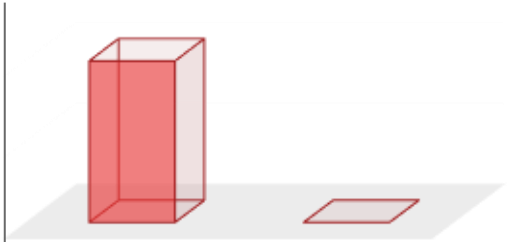
Proteins (amino acids): H, C, O, N, S

Hormones: H, C, O, N, S

DNA: H, C, O, N, P

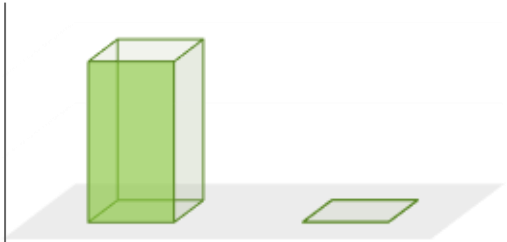
Vitamins: H, C, O, N, S, P (+ trace metals)

Natural Isotope Abundance



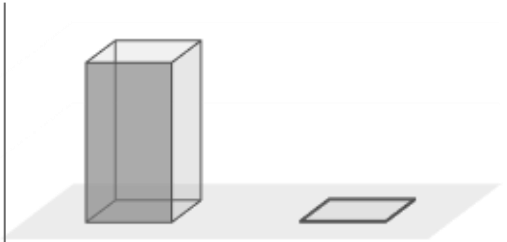
Hydrogen

- 99.9840% ^{1}H
- 0.0156% ^{2}H



Nitrogen

- 99.635% ^{14}N
- 0.3650% ^{15}N



Carbon

- 98.8920% ^{12}C
- 1.108% ^{13}C

Oxygen

- 99.7590% ^{16}O
- 0.0370% ^{17}O
- 0.2040% ^{18}O

Sulfur

- 95.020% ^{32}S
- 0.7600% ^{33}S
- 4.2200% ^{34}S
- 0.0140% ^{36}S

- These are the approximate natural abundance of isotopes
- However, there are miniscule variations in these abundances

Natural Isotope Abundance of the Light ("Bio") Elements

Why are those ratios only an average?

The average terrestrial abundance ratio of (most abundant) heavy to light isotopes:

Sulfur ($^{34}/_{32}$):	1:22
Carbon ($^{13}/_{12}$):	1:89
Nitrogen ($^{15}/_{14}$):	1:272
Oxygen ($^{18}/_{16}$):	1:500
Hydrogen ($^{2}/_{1}$):	1:6410

Different processes (biological, physical, geological, etc..) will change the isotopic composition (ratio of heavy to light isotope) of a material by a process called **"Fractionation"**

What is Fractionation?

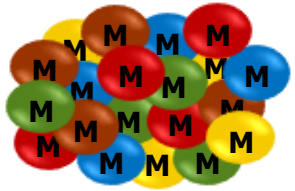
In simple terms, it's discriminating against one form of a substance as it moves from one place to another…

Van Halen were pioneers of confectionary fractionation with their famous tour rider:

"No Brown M & Ms!"

Fractionation of M & Ms

Original bag, before any consumption



Equal mix: e.g. 5 colours, 4 of each (20 M & Ms in total).

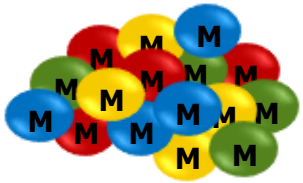
Brown:Not Brown Ratio [B:NB] = 4:16

Or decimal ratio = [B]/[N+NB] = 4/20 = 0.2 (20%)

Remaining M & M's after consumption

B:NB = 4:0
(1.0; 100 %)

M & Ms Eaten

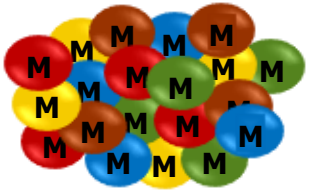


B:NB = 0:16
(0, 0 %)

How About Someone a Little Less Fussy?

In less extreme circumstances, you might have a preference, but don't *always* reject the brown M & Ms if you happen pick one up….e.g. if you reject it first time you pick a brown M & M, then eat it anyway the second time, you'd still be discriminating, just not to the same total degree:

Original Bag



B:NB = 4:16

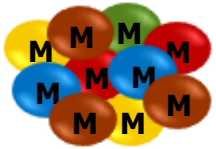
(0.2; 20%)

If selecting a brown M & M, put it back in the bag first time; second time, eat it anyway!

Eat 1/2 of the Bag

Chances of picking a brown M & M = 1 in 5; so should pick 2 brown M & Ms out of 10 when eating half the bag of 20. Put first one back, eat second one – so you'll have eaten 1 brown M & M, and 9 other colours.

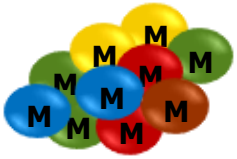
Remaining



B:NB =3:7

(0.3; 30%)

Eaten



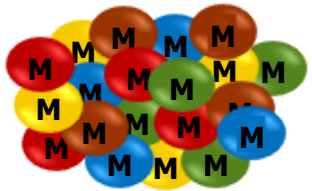
B:NB = 1:9

(0.1; 10%)

The Language of Fractionation: Enriched vs Depleted

If we want to talk about the relative changes in the proportion of discriminated material (in this case, brown M & Ms), we can use the terms 'enriched' and 'depleted', in a fairly common-sense manner: relatively more is 'enriched', relatively less is 'depleted':

Original Bag



B:NB = 4:16 (0.2; 20%)

Eat 1/2 of the Bag

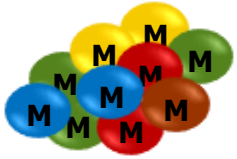
Remaining

B:NB = 3:7
(0.3; 30%)

Enriched in brown M & Ms relative to the original bag

Enriched in brown M & Ms relative to the eaten portion

Eaten



B:NB = 1:9
(0.1; 10%)

Depleted in brown M & Ms relative to the original bag

Depleted in brown M & Ms relative to the remaining portion

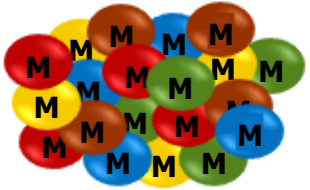
Enriched in brown M & Ms relative to the eaten portion after consuming half the bag

Depleted in brown M & Ms compared to the remaining M & Ms after consuming half the bag.

Quantifying the discrimination – Fractionation Factor

We can then express a constant that describes how the colour composition of the consumed M & Ms (*i.e. product*) differs from the original (*reactant / reagent*) for the specific approach to consumption (*reaction conditions*). This called the Fractionation Factor, denoted as "α"

Original Bag



B:NB = 4:16

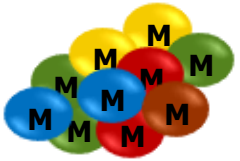
(0.2; 20%)

Eat 1/2 of the Bag

[Ratio Original] / [Ratio Eaten]

$$\alpha = {}^{0.2}/_{0.1} = 2.00$$

Eaten



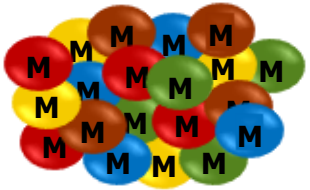
B:NB = 1:9

(0.1; 10%)

Quantifying the discrimination – Fractionation Factor

You can also define "α" with respect to the left-over remaining M & Ms *(residue),* if that's your bag.

Original Bag



B:NB = 4:16

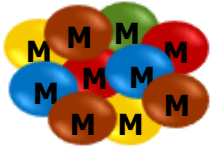
(0.2; 20%)

Eat 1/2 of the Bag

[Ratio Original] / [Ratio Remining]

$$\alpha = {}^{0.2}/_{0.3} = 0.667$$

Remaining



B:NB = 3:7
(0.3; 30%)

Quantifying the discrimination – Fractionation Factor

If the person always discriminates in the same way (i.e. α is constant), we can use that to calculate/predict the composition of the reactant, residue or product if we know 2 of the 3:

- E.g. a bag of 400 total, with 60 brown M & Ms (i.e. 15%)
- Same "put back 1st time, eat on 2nd" approach to discrimination
  - **Eaten (α = 2.00)** : $[\text{Ratio Original}] / [\text{Ratio Eaten}] = 2.00$

    ➡ $[\text{Ratio Eaten}] = [\text{Ratio Original}] / [\alpha] = [0.15] / [2.00] = \underline{0.075\ \textbf{(7.5 \%)}}$

    ➡ Total number of brown M & Ms eaten = 0.075 x 200 = **15**

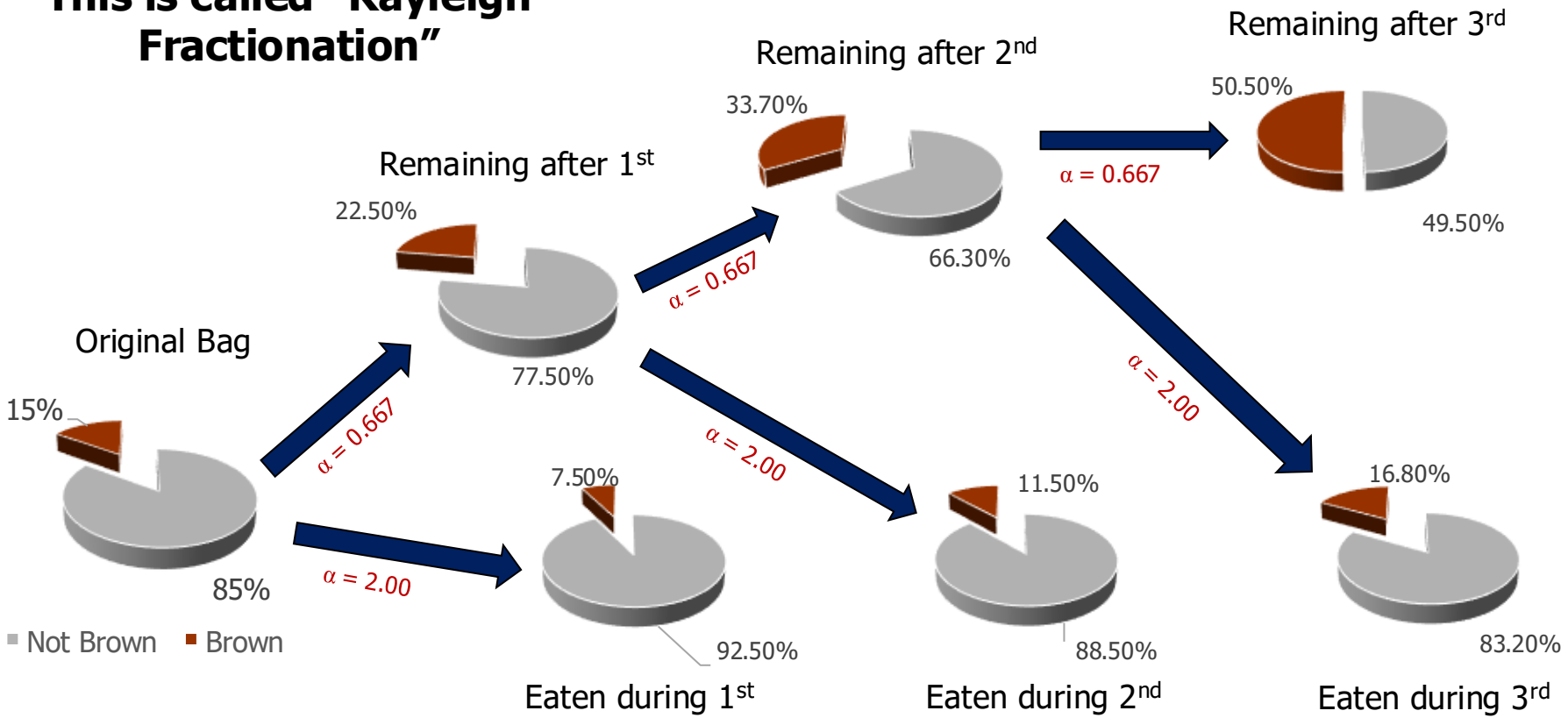
  - **Remaining (α = 0.667) :** $[\text{Ratio Original}] / [\text{Ratio Remaining}] = 0.667$

    ➡ $[\text{Ratio Remaining}] = [\text{Ratio Original}] / [\alpha] = [0.15] / [0.667] = 0.225$ **(22.5%)**

    ➡ Total number of brown M & Ms remaining = 0.225 x 200 = **45**

Brown M & M Enrichment with Successive Consumption!

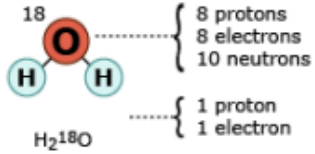
This is called "Rayleigh Fractionation"

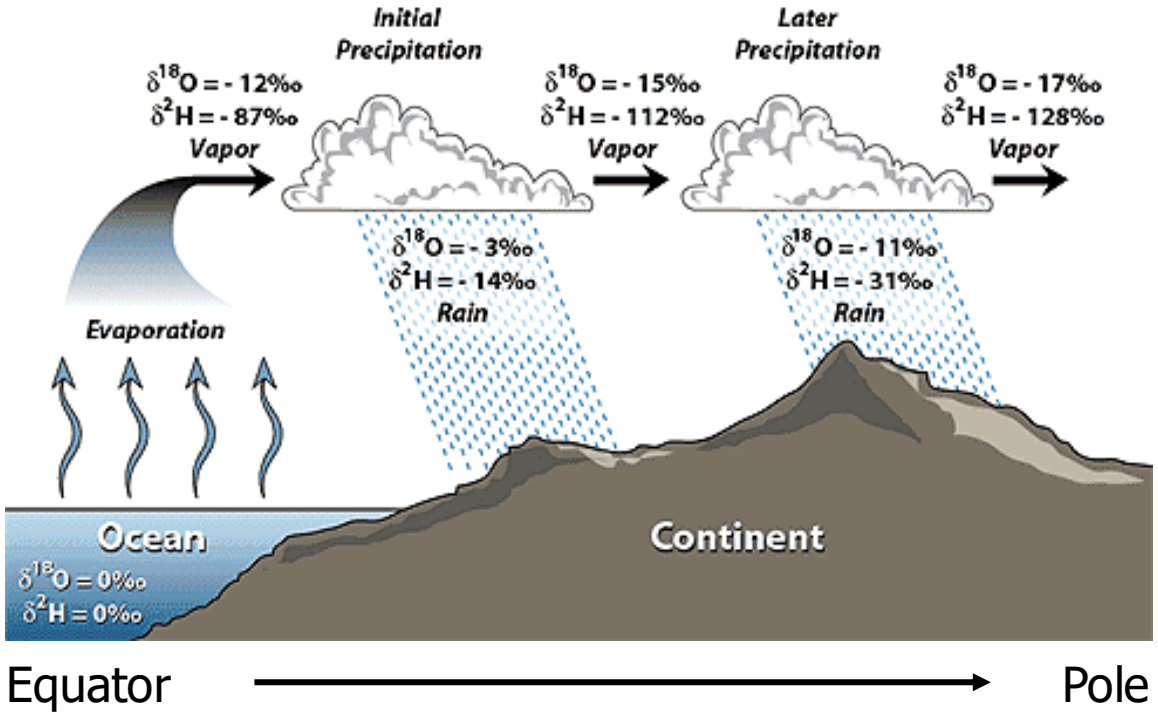


Example: Ocean water & ice cores

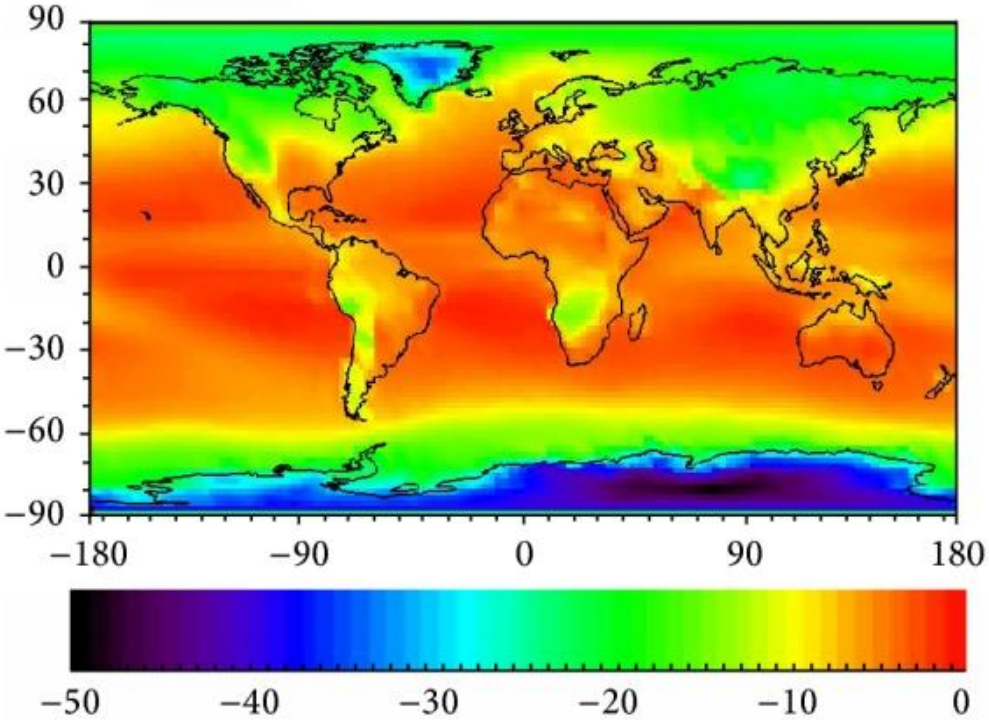
Water Molecule A

Water Molecule B





Hydrology Isotopes – Rayleigh Fractionation in Action!

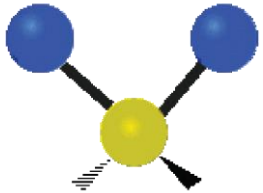
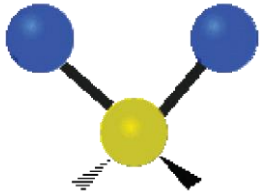
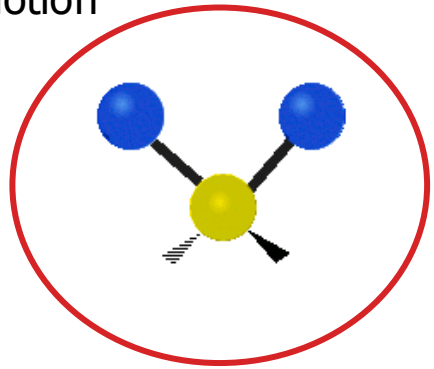


Rayleigh Fractionation means precipitation gets isotopically lighter and lighter from equator to pole…

That means you can take a fairly good guess at where water might have come from, if you measure the isotopic composition - we know the starting isotopic composition (of equatorial water), so by understanding the fractionation processes, we can estimate the source of precipitation in an unknown sample.

Why do isotopes undergo fractionation: Bond strength (chemical behaviour)

- Molecules exhibit translational, rotational, and **vibrational** motion

- Vibrational energy of a molecule is determined by its mass:

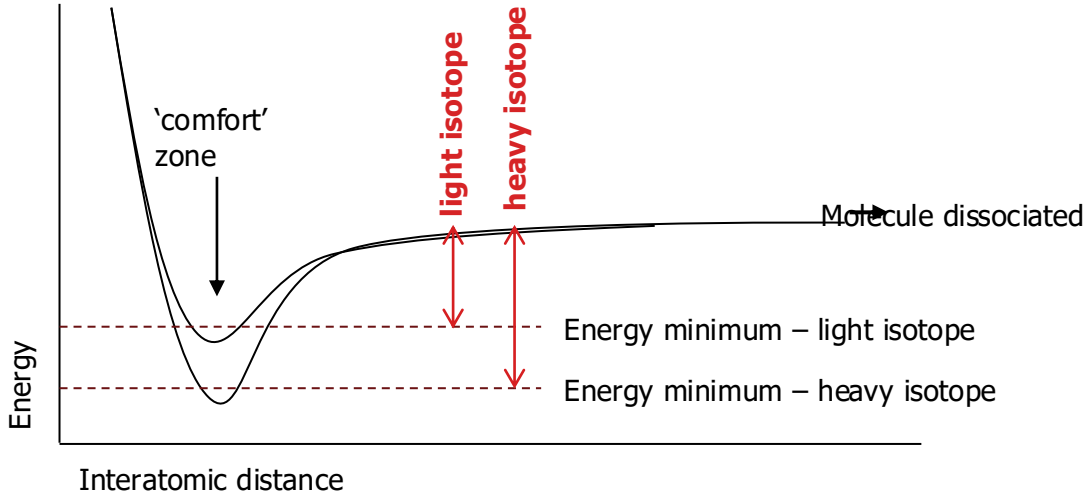
$$E_{vibrational} = \frac{1}{2} h\nu \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

h = Planck constant
v = frequency
k = Boltzmann constant
m = mass

- As mass increases, frequency and vibrational energy decrease. As a result, an isotopologue of a molecule incorporating a heavy isotope will have less vibrational energy than an isotopologue of a molecule incorporating a light isotope

Why do isotopes undergo fractionation: Bond strength (chemical behaviour)

- Isotopologues with **heavy** isotopes will have **lower** vibrational energy and form **stronger** bonds - requiring more energy to break them apart: they have a higher ***dissociation energy***



Why do isotopes undergo fractionation: Reaction Rate (physical behaviour)

- All molecules have same kinetic energy (KE) at same temperature

$$\mathrm{KE} = \frac{1}{2}mv^2 \qquad \frac{1}{2}m_L v_L{}^2 = \frac{1}{2}m_H v_H{}^2 \qquad \frac{v_L}{v_H} = \sqrt{\frac{m_H}{m_L}}$$

- **Example**: H_2O
  - $H_2{}^{16}O$ $m \sim 18$
  - $H_2{}^{18}O$ $m \sim 20$

$$\frac{v_L}{v_H} = \sqrt{\frac{20}{18}} \qquad \frac{v_L}{v_H} = 1.05$$

- Velocity of $H_2{}^{16}O$ is 1.05x faster than $H_2{}^{18}O$, irrespective of temperature
- …$H_2{}^{16}O$ will evaporate, diffuse faster

Mass Dependent Fractionation: Summary

(Most) variations in isotope ratios are due to mass-dependent fractionation processes during reactions:

- **Lighter** isotopes form **weaker** bonds and move **faster**
  - So in *kinetic* (uni-directional) reaction, light isotope **reacts faster** and concentrates in **reaction product**
  - In *equilibrium*, light isotope will concentrate in form with weaker bonds (e.g. less dense phases)

- **Heavier** isotopes form **stronger** bonds and move **slower**
  - So in kinetic (uni-directional) reaction heavy isotope reacts slower and concentrates in reaction residue
  - Or in *equilibrium,* heavy isotope concentrates in form with stronger bonds (e.g. denser phases).

Describing Isotope Ratios (so we can compare them)

- Use difference between measured ratio of sample vs. reference:

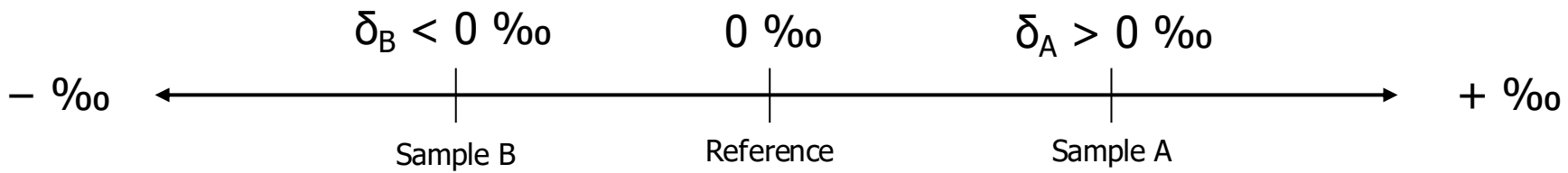
e.g $^{18}O/_{16}O$

$$\delta = \frac{R_{sample} - R_{reference}}{R_{reference}} \times 1000\ ‰$$

i.e. which isotope you are describing the ratio for

- Delta value (lowercase Greek ***delta δ***), e.g. $\delta^{18}O$ or $\delta^{13}C$
- No units, but reported in parts per thousand (***per mil ‰***)
  - 10 ‰ = 10/1000 = 1 % *(just easier to see small differences!)*
- Allows comparison of variations (rather than actual abundance)…

The Delta Scale (to be revisited – JF Hélie!)



- + δ value = Sample isotope ratio bigger than Reference (more heavy isotope)
  - E.g. $\delta^{13}C$ of +20 ‰, $^{13}C/^{12}C$ is 2% higher in sample than standard
- - δ value = Sample isotope ratio smaller than Reference (more light isotope)
  - E.g. $\delta^{13}C$ of -25 ‰, $^{13}C/^{12}C$ is 2.5% lower in sample than standard

- Sample A has ***higher*** δ value than Sample B, Sample B has a ***lower*** δ value than Sample A. Could also say Sample A is isotopically ***lighter*** than Sample B, or Sample B is isotopically ***heavier*** than sample A

- δ scales are "anchored" (0-point fixed) using international reference standards…

Anchoring the Scale: International Reference Scales

Element	Ratio	Notation	Standard	Abbreviation	Abundance ratio	δ ‰
Hydrogen	$^{2}H/^{1}H$	$\delta^{2}H$	Vienna Standard Mean Ocean Water	VSMOW	1.558×10^{-4}	$\delta^{2}H = 0$
Carbon	$^{13}C/^{12}C$	$\delta^{13}C$	Vienna Pee Dee Belemnite	VPDB	1.124×10^{-2}	$\delta^{13}C = 0$
Oxygen	$^{18}O/^{16}O$	$\delta^{18}O$	(as above)	VSMOW / VPDB	2.005×10^{-3} / 2.067×10^{-3}	$\delta^{18}O = 0$
Nitrogen	$^{15}N/^{14}N$	$\delta^{15}N$	Atmospheric N_2	AIR	3.677×10^{-3}	$\delta^{15}N = 0$
Sulphur	$^{34}S/^{32}S$	$\delta^{34}S$	Vienna Canyon Diablo Troilite (FeS)	VCDT	4.5001×10^{-2}	$\delta^{34}S = 0$

- Having an internationally-defined zero point means isotope scientists can report numbers which can be compared & discussed globally
- If we tried to measure absolute amounts of an isotope, very minor differences in e.g. instrumentation, environment could swamp any real difference!

Calibrating IRMS Data

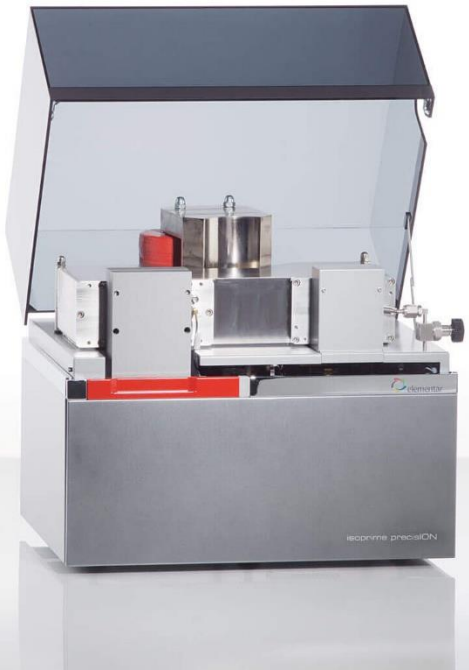
- The data output by an IRMS is not calibrated, it represents: $\delta^{Z}X_{MEASURED}$ (we denote as) $\delta^{Z}X_{(GAS)}$ – this is why we prefer to call the 'reference' gas a 'monitoring' or 'working' gas.
- In order to generate a "true" value you need to determine: $\delta^{Z}X_{CALIBRATED}$
- The calibrated δ value corresponds to a particular isotopic scale (i.e. SMOW, CDT, PDB, AIR, etc) and should be reproducible and equivalent between different labs and equipment.

Methods of Calibration

1. **Monitoring Gas Correction** – 1 point correction based upon the value of the reference (monitoring/working) gas relative to international standards
2. **Standard Correction** – Can be either 1, 2, 3+ point calibrations utilising international and in-house standards.

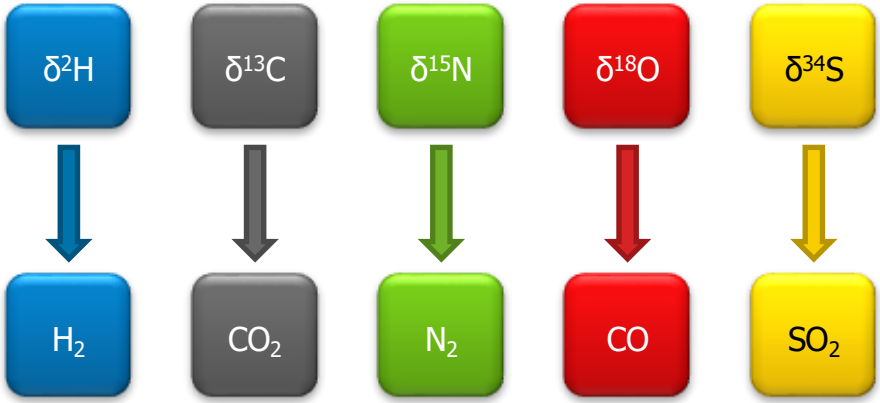
Introduction to Isotope Ratio Mass Spectrometry

What is an Isotope Ratio Mass Spectrometer?



- An isotope ratio mass spectrometer (IRMS) is designed to very precisely measure the relative abundance of isotopes in a sample of pure molecules
- Resolves integer (usually 1) mass differences (e.g. *m/z* = 44 vs 45). No need for "accurate mass" analysis (i.e. determination of mass beyond integer values) – we sacrifice accurate mass to the Deities of precision & stability.
- System will only accept the sample as a simple gas (hence "gas-source isotope ratio mass spectrometer"), , and the separation *(on a 0-5kV acceleration / 0-5A magnet current)* system cannot work with anything which has a molecular mass > 100 *(as "resolving power" is c. 100 m/Δm, so maximum mass to achieve 1 amu resolution is 100/1)*

How to analyse stable isotopes

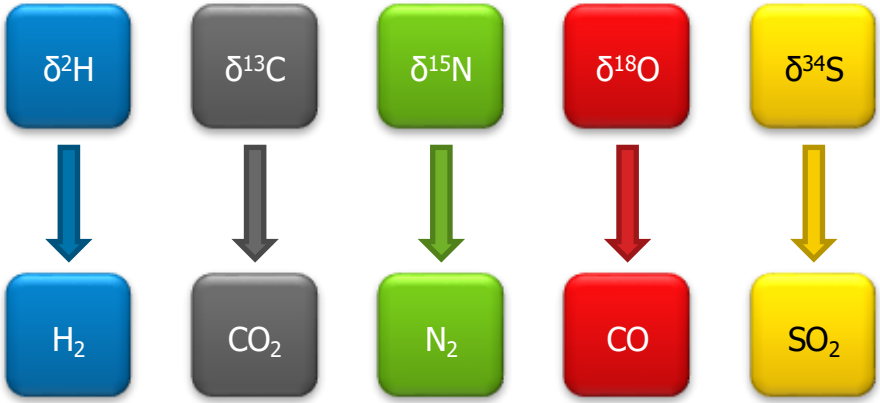


When we want to determine the isotope ratio of a sample, we measure as a **simple gaseous molecule** (i.e. turn the whole sample into these gases), and determine **R** (**isotope ratio**)

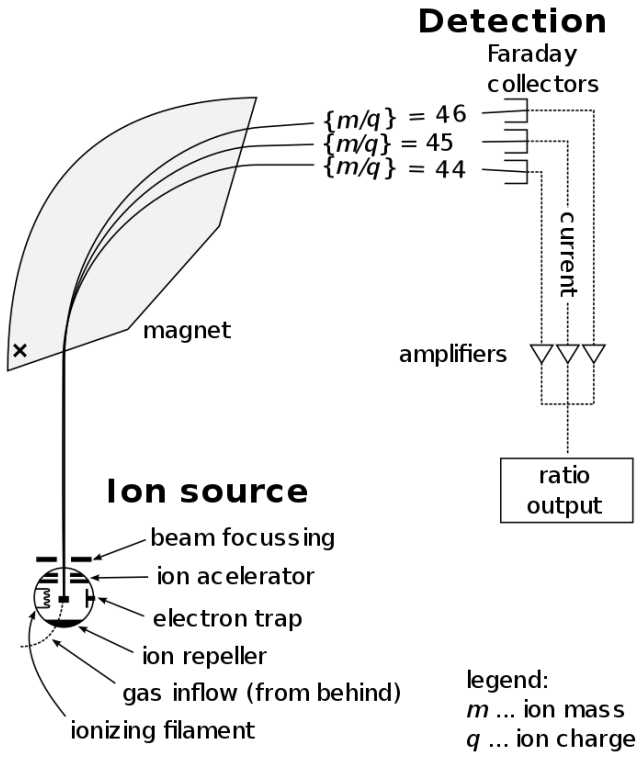
Many **billions of molecules** are generated from one small sample – e.g. a pint of water (568 ml) contains 1.9 x 10^{25} water molecules (more than the number of starts in the known universe)

Of those billions of gas molecules, some individual molecules will have heavy isotopes, some light – e.g. for natural abundance carbon isotopes, **c. 1% of the CO_2 molecules will contain ^{13}C, the rest will contain ^{12}C**. The molecules with same structure but different isotopic masses are called "isotopologues" – same compound, different mass.

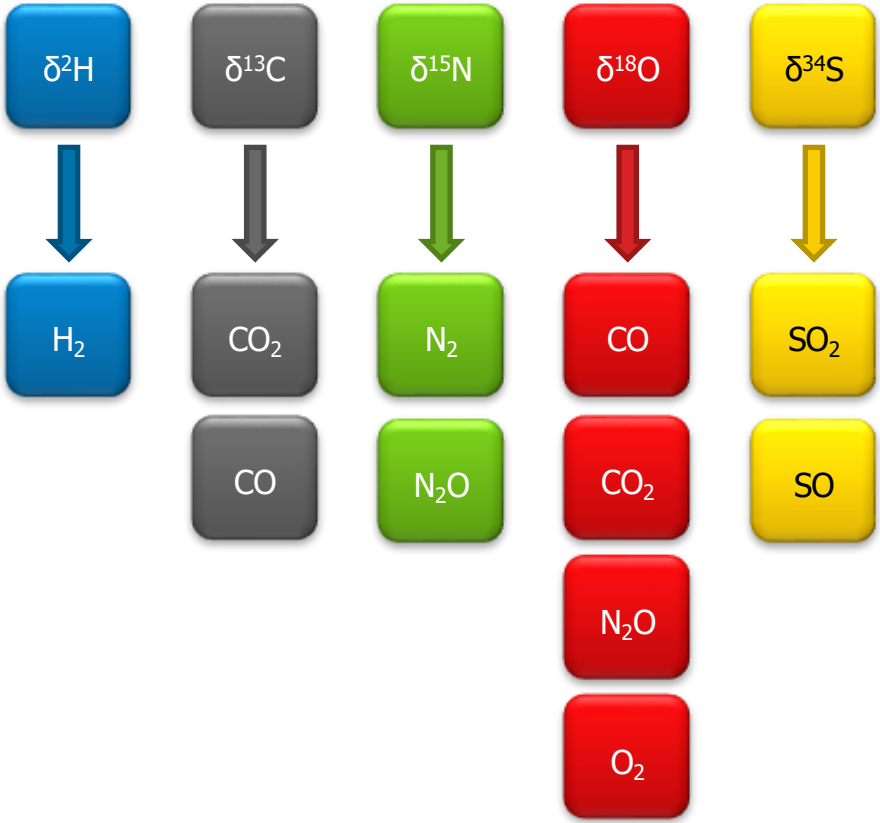
How to analyse stable isotopes



CO_2 = $^{12}C + ^{16}O + ^{16}O$ = molecular mass 44 (Major isotope)
= $^{13}C + ^{16}O + ^{16}O$ = molecular mass 45 (Minor 1 isotope)
= $^{12}C + ^{18}O + ^{16}O$ = molecular mass 46 (Minor 2 isotope)



How to analyse stable isotopes



- Depending on the sample introduction / preparation system (inlet), some isotopes have more than one possible gas molecule it can be measured in (e.g. combustion vs pyrolysis, or direct analysis of purified gas)
- For example some techniques analyse N_2O, which can provide the stable isotope ratios for nitrogen and oxygen (e.g. N_2O generated from bacterial denitrification – i.e. conversion of NO_2)
- In general we are interested in molecules which form ions with mass/charge ratio < 100, containing the isotopes of interest (so the species on the left account for almost all which are actually used for isotope analysis).

Dual Inlet & Continuous Flow Analysis

Dual Inlet analogy

- Alternating flow, controlled by traffic lights (valves)
- DI system all under vacuum (no direct traffic related analogy)
- Sample gas often prepared offline

Sample gas

Turbomolecular pump

Ion Source

Reference gas

Continuous Flow analogy

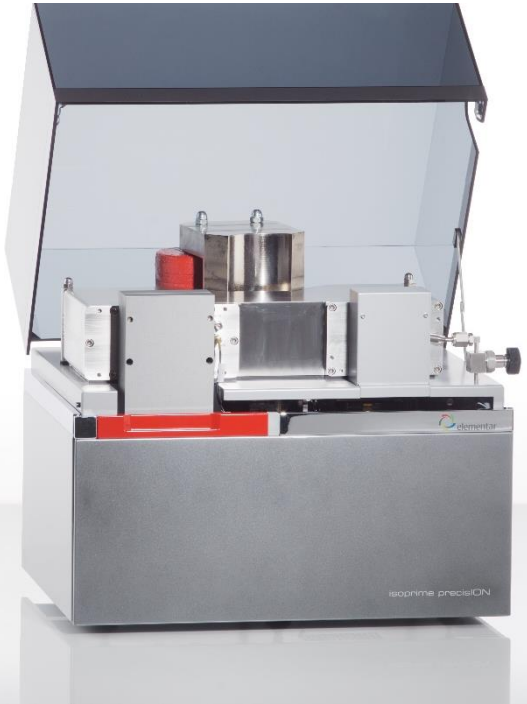
- Confluence of two continuously flowing rivers
- He continuously flows through from start (sample introduction) to end (IRMS detectors), sample or reference gas injected into stream
- Sample gas usually prepared online

Monitoring gas in helium steam

Sample gas in helium steam

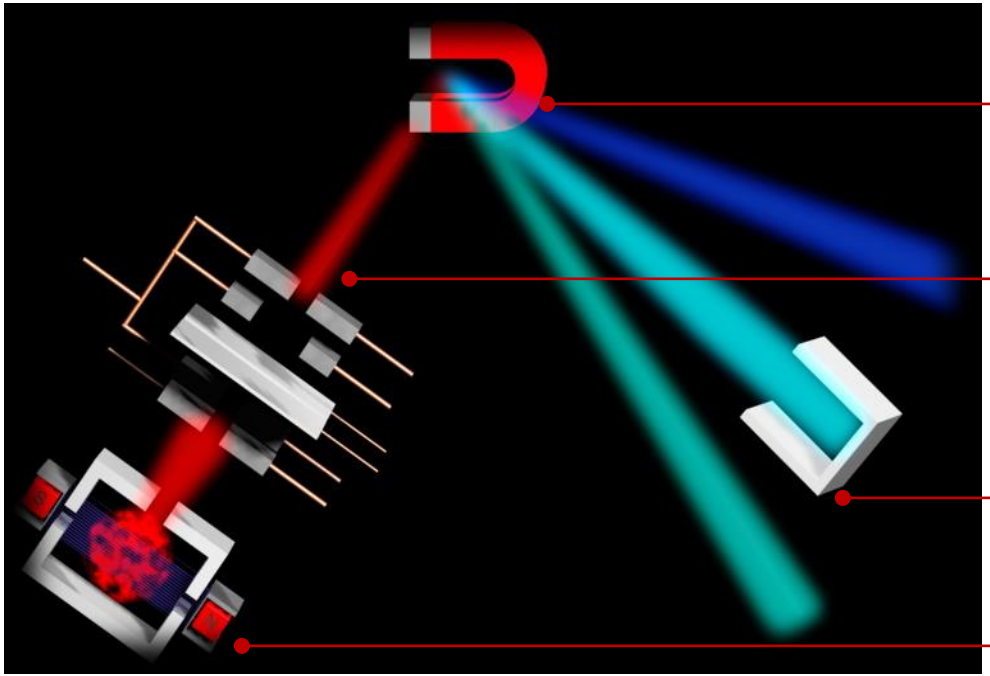
Ion Source

Introducing the stable isotope ratio mass spectrometer



- The IRMS does:
  - transmit a highly stable ion beam
  - measure multiple, fixed ion beams with very high precision
- The IRMS does not:
  - perform high frequency mass range scans
  - measure very high molecular weights
  - have high mass resolution

Mass Spectrometry: Separating and Detecting



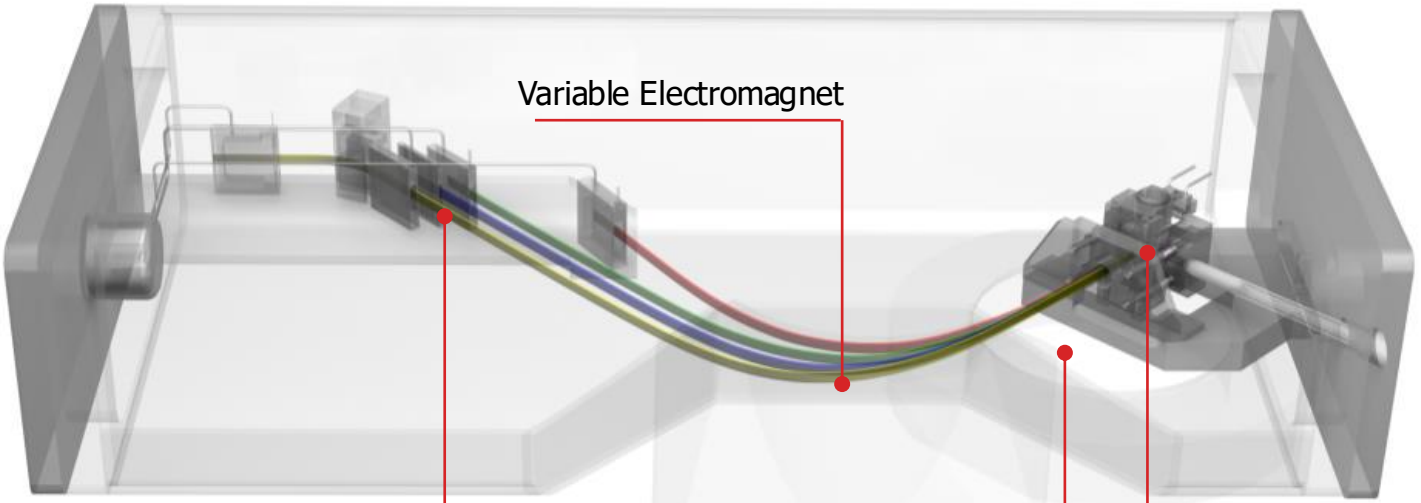
Magnetic field separates the ion beam into its constituent mass/charge ratios

Accelerated ion beam is focussed into the magnetic field

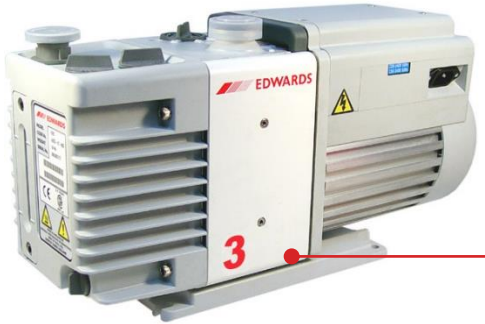
Faraday detector positioned to detect the separated ion beam

Electron impact ion source ionizes the sample gas and accelerates into the lens stack

What is an Isotope Ratio Mass Spectrometer?



Instrument Vacuum



Instrument must be held under vacuum in order to avoid collision and contamination of the ion beam with atmosphere

High vacuum is achieved using a turbomolecular pump

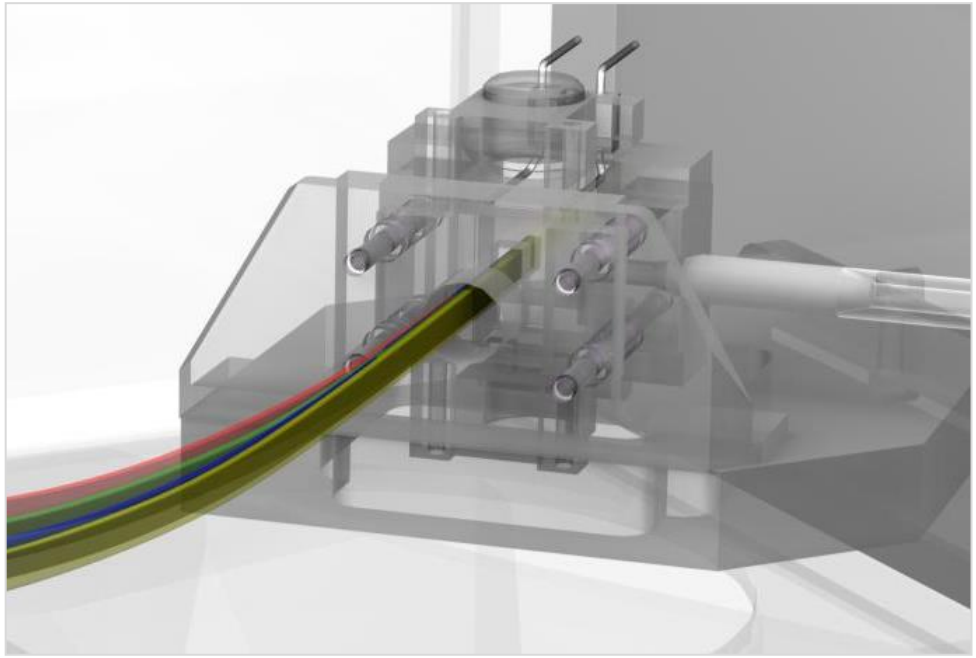
Ultimate vacuum level achieved < 5 x 10^{-8} mBar

The pump removes atmosphere from the instrument at 255L/s and spins at over 60,000 times per second

Turbomolecular pump is backed-up by an oil filled rotary pump

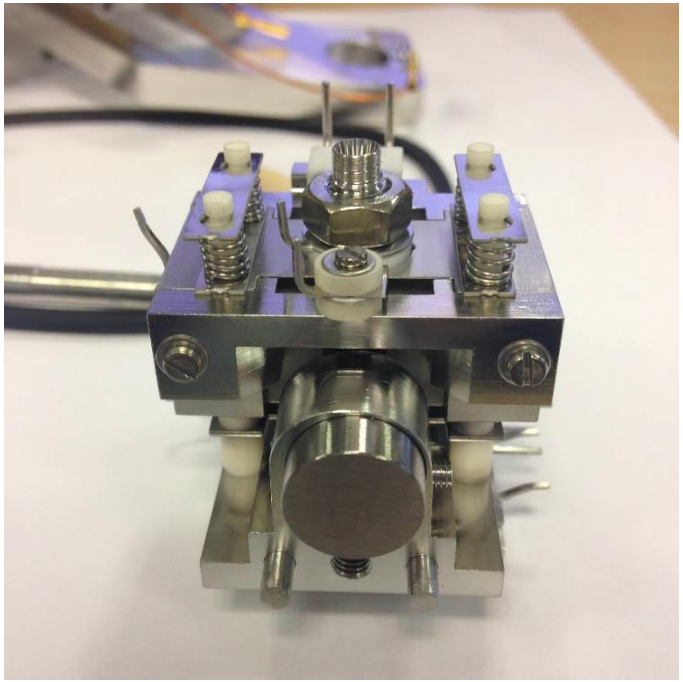
Ultimate vacuum level achieved < 5 x 10^{-3} mBar

Ionization source



- Ionization is performed via electron emission from a filament wire
- Electrons accelerated into ion source containing sample
- Ion source can only ionize gas samples
- Most raw samples are solid minerals/organic matter/fluids
- Therefore, samples must be converted into gaseous form that can be ionized by the electron beam

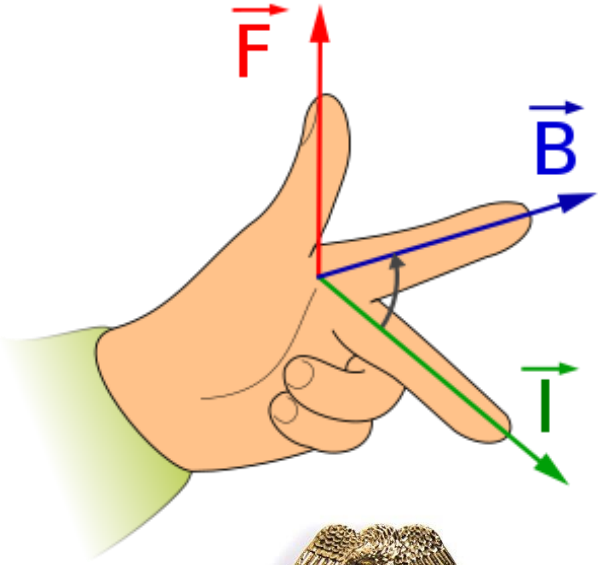
Ion Source



How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, Separation, Detection

- When moving charged species (ions) experience a magnetic field, they are deflected
- The direction of the deflection can be described by Fleming's Left Hand Rule
- The magnitude of the deflection is governed by the **momentum** of the ion
- Ions are then detected and generate an electrical signal for measurement & quantification



How does a Mass Spectrometer work?

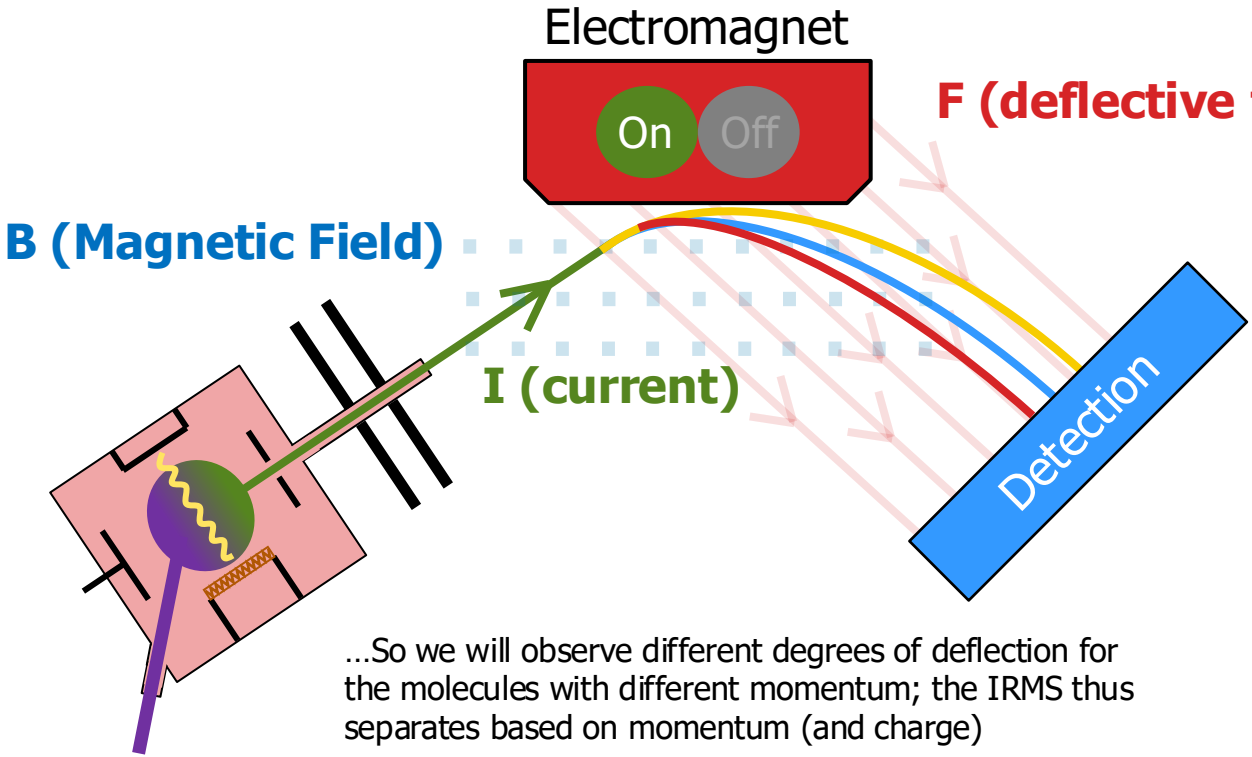
Ionisation & Acceleration, Focussing, **Separation**, Detection

Why are particles with less momentum deflected more than particles with greater momentum?

- While we usually think of 'velocity' as speed, it is a vector quantity, so a change in direction without a change in speed, or change in both speed and direction, is also change in velocity
- While we usually think of 'acceleration' an increase in speed over time, it is more precisely a change in velocity over time. So acceleration can also mean (or include) change in direction over time
- Newton's laws of motion state that force = mass x acceleration (F = mA)
- The same force is applied to all masses entering the magnetic field, so F is constant. As such, rearranging the equation will define the acceleration: A = F/m
- So we see that acceleration (A), i.e. the rate of change of speed or direction, will be different for different masses. Moreover, we can see that A will be greater for smaller mass (e.g. F/2 > F/3), explaining why lighter particles are deflected (accelerated at a greater rate) more than heavier ones.

How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, **Separation,** Detection



Molecules with a different mass will have different **momentum**

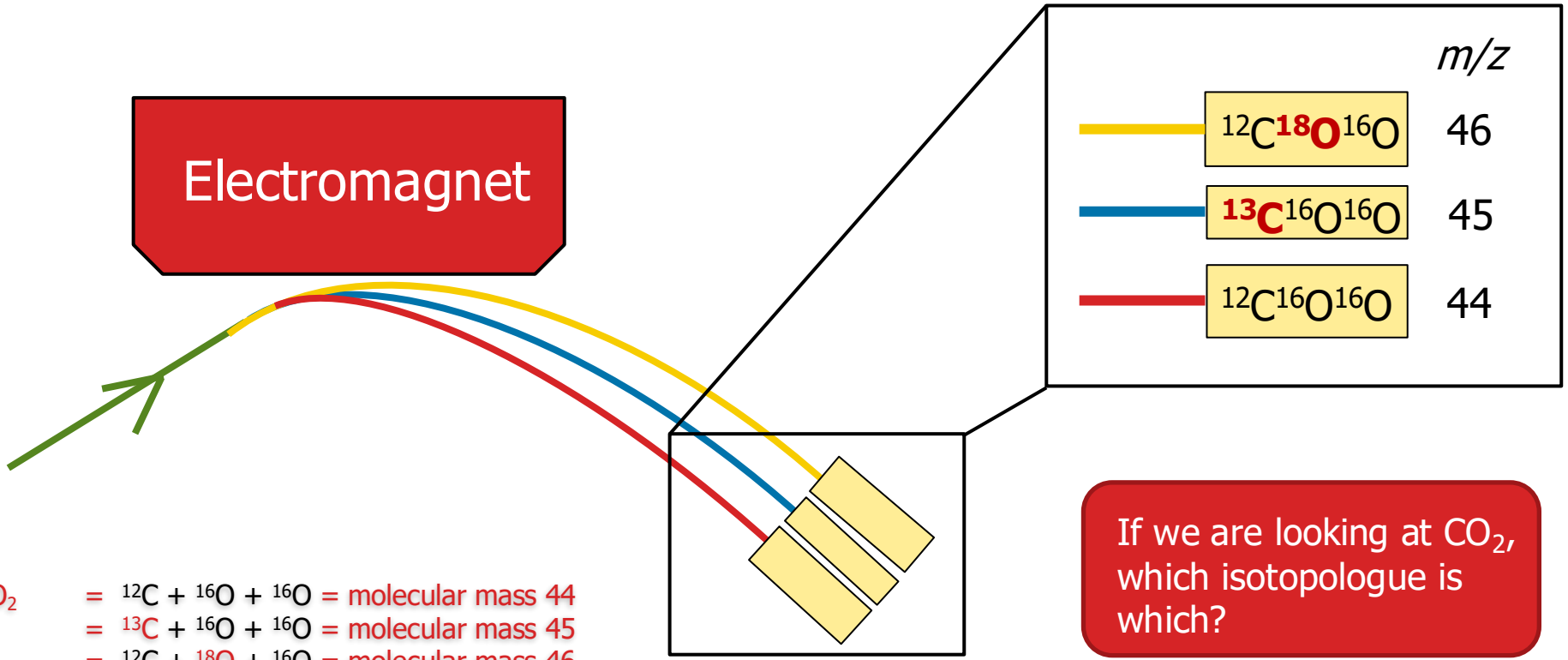
Molecules with **greater momentum** are **deflected less** by the magnetic field

…So we will observe different degrees of deflection for the molecules with different momentum; the IRMS thus separates based on momentum (and charge)

*To explain why in detail involves a few equations – see optional further reading!

How does a Mass Spectrometer work?

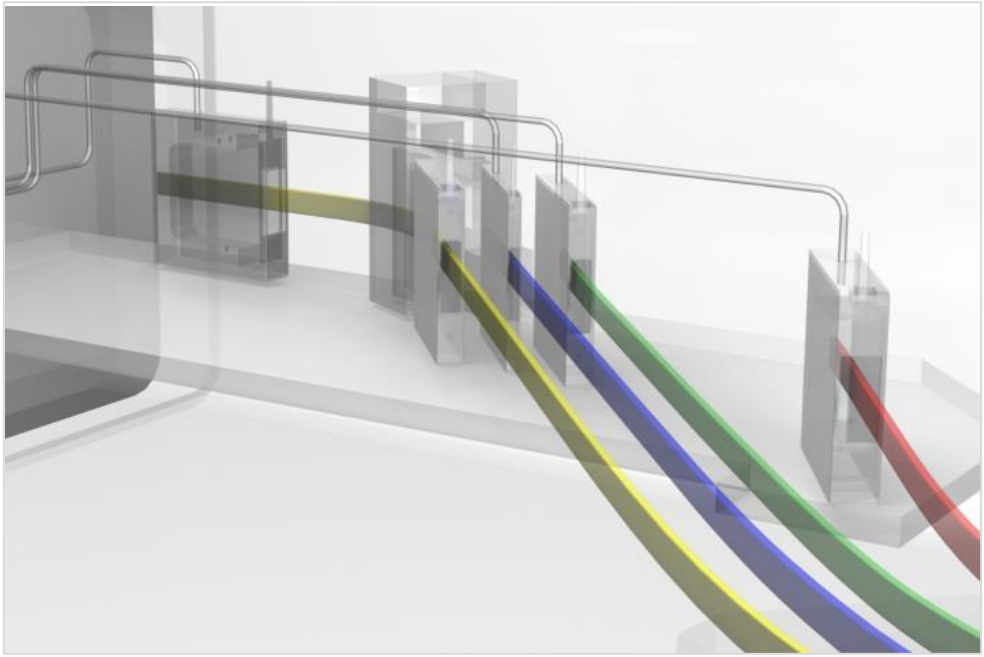
Ionisation & Acceleration, Focussing, Separation, Detection



CO_2 = $^{12}C + ^{16}O + ^{16}O$ = molecular mass 44
= $^{13}C + ^{16}O + ^{16}O$ = molecular mass 45
= $^{12}C + ^{18}O + ^{16}O$ = molecular mass 46

If we are looking at CO_2, which isotopologue is which?

Faraday detectors



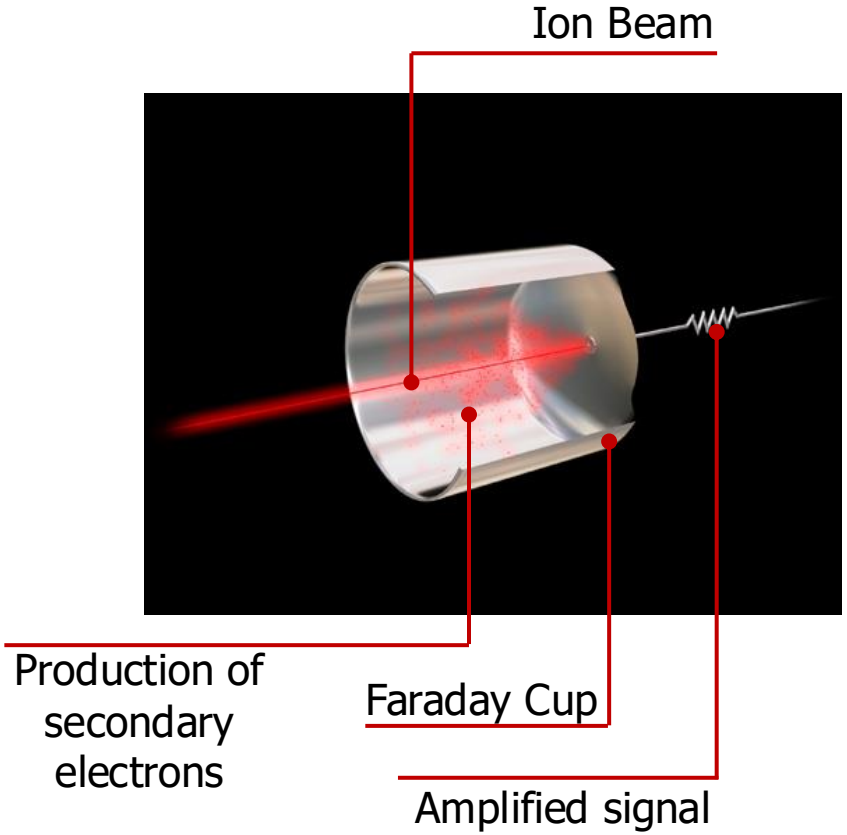
- Following ion beam separation the beams must be detected
- The detectors are fixed position
- Multiple detectors used to detect all required ion beams
- Since detectors are fixed, we must vary the relationship between the acceleration of the ion beam and the strength of the magnetic field to steer the required gas species into the detectors
- The detector array is “universal” and is able to detect all common isotopes

How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, Separation, Detection

Basic Premise:

- Ions in IRMS carry +ve charges.
- On arrival at an earthed metal plate they are neutralized by accepting electrons.
- The resulting flow of electrons constitutes a tiny electrical current which can be amplified and used to drive a recording device.
- Rather than using a plate, a cup is used allowing both primary and secondary electrons to be collected.
- One positive ion arriving at a Faraday cup needs one electron for neutralisation but causes several to be emitted.



Ion Beam Measurement Characteristics

Ionisation & Acceleration, Focussing, Separation, **Detection**

Ion current is made up of individual ions arriving at the detector at an average rate that is a measure of the number of ions generated at the source

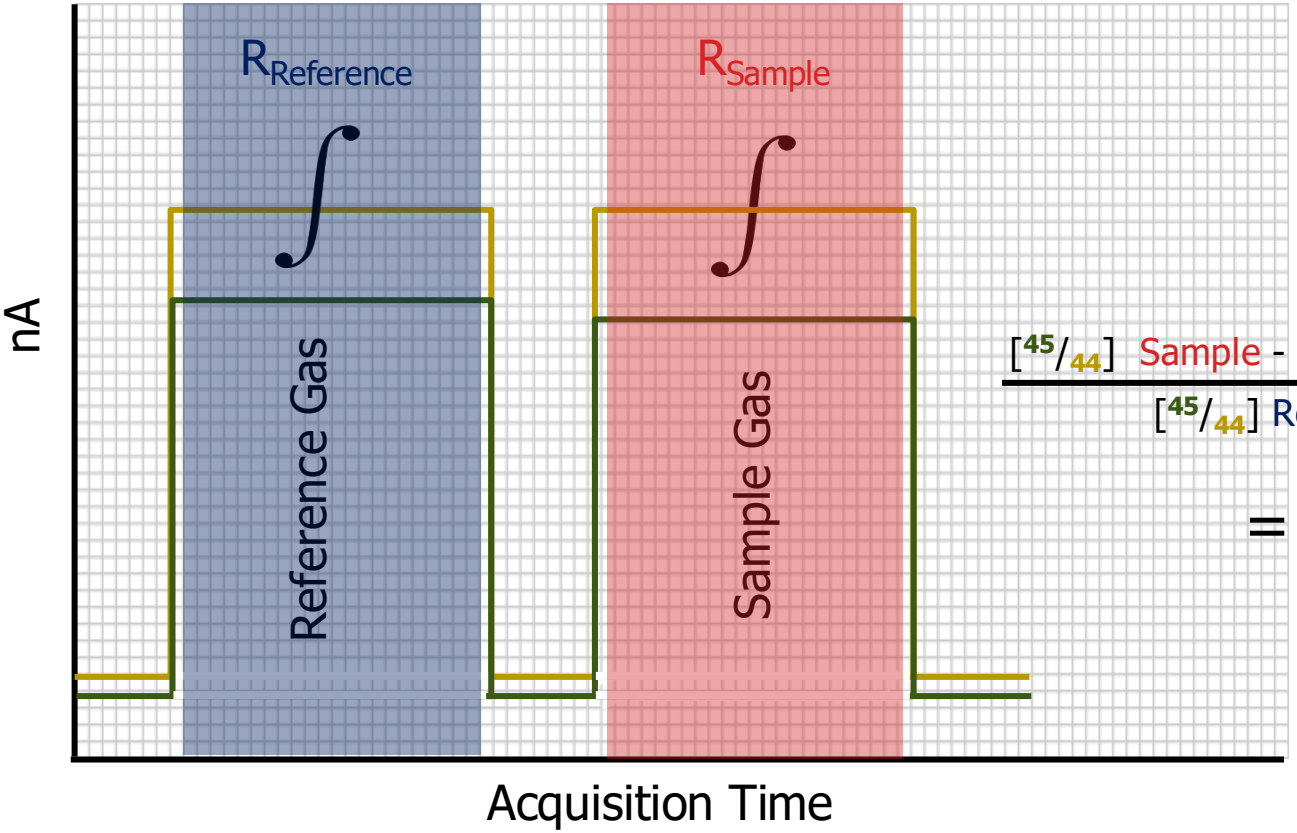
Theoretically at least the rate of ions entering the detector is a measure of the amount of that isotope in the sample

If we ratio the rates of two isotopologue ion beams, this ratio is the ratio of the two isotopes in the sample:

$$\frac{R_1}{R_2} = \frac{S_1}{S_2}$$

Where R_1 is the rate of isotope 1, R_2 is the rate of isotope 2, S_1 is the amount of isotope 1 in the sample and S_2 is the amount of isotope 2 in the sample.

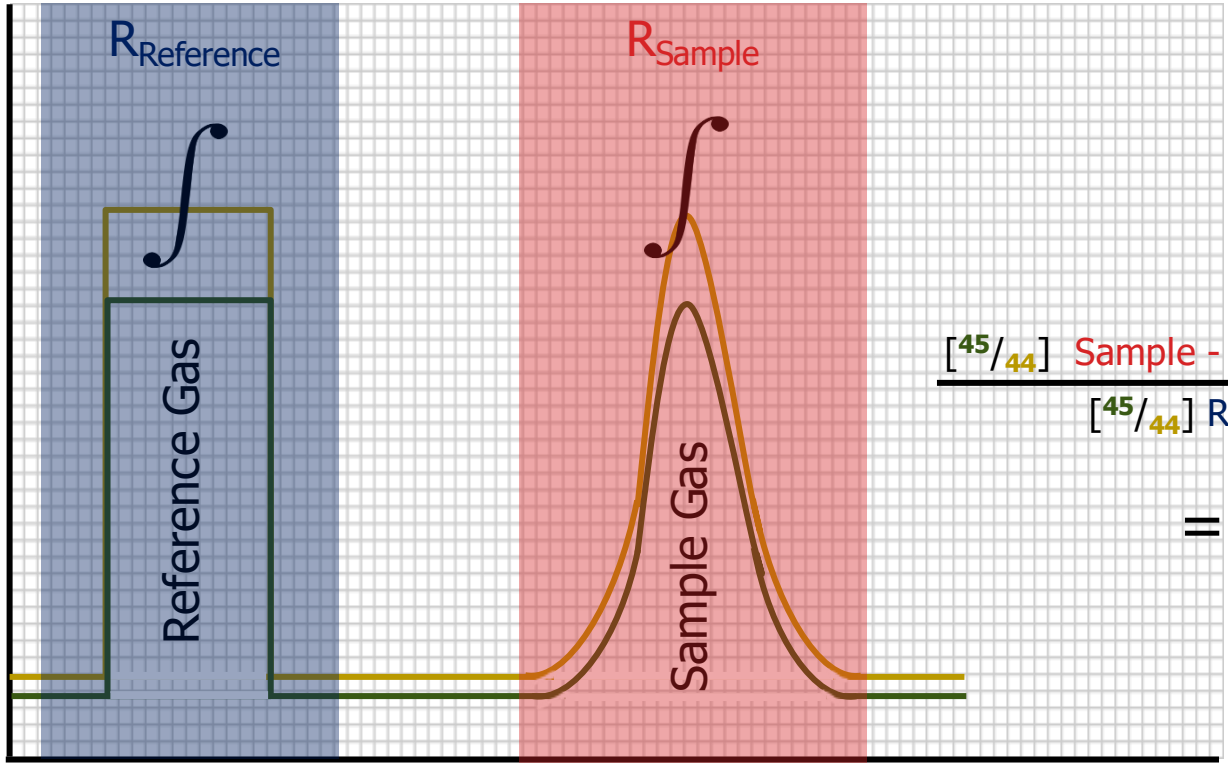
Describing Isotope Ratios (so we can compare them): Dual Inlet



m/z 45
m/z 44

$$\frac{[^{45}/_{44}]\ \text{Sample} - [^{45}/_{44}]\ \text{Reference}}{[^{45}/_{44}]\ \text{Reference}} \times 1000 = \delta^{13}C$$

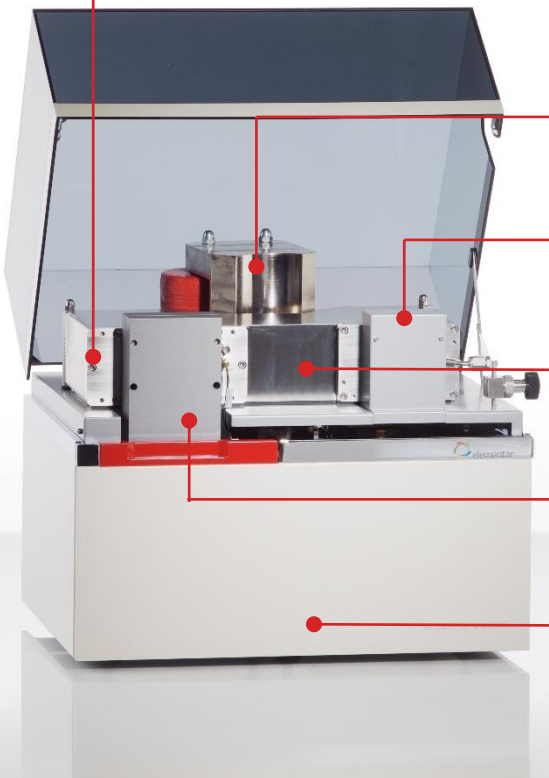
Describing Isotope Ratios (so we can compare them): Dual Inlet



m/z 45
m/z 44

$$\frac{[^{45}/_{44}]\ \text{Sample} - [^{45}/_{44}]\ \text{Reference}}{[^{45}/_{44}]\ \text{Reference}} \times 1000 = \delta^{13}C$$

Physical overview of IRMS



Faraday collectors installed in the analyser

Fixed position electromagnet

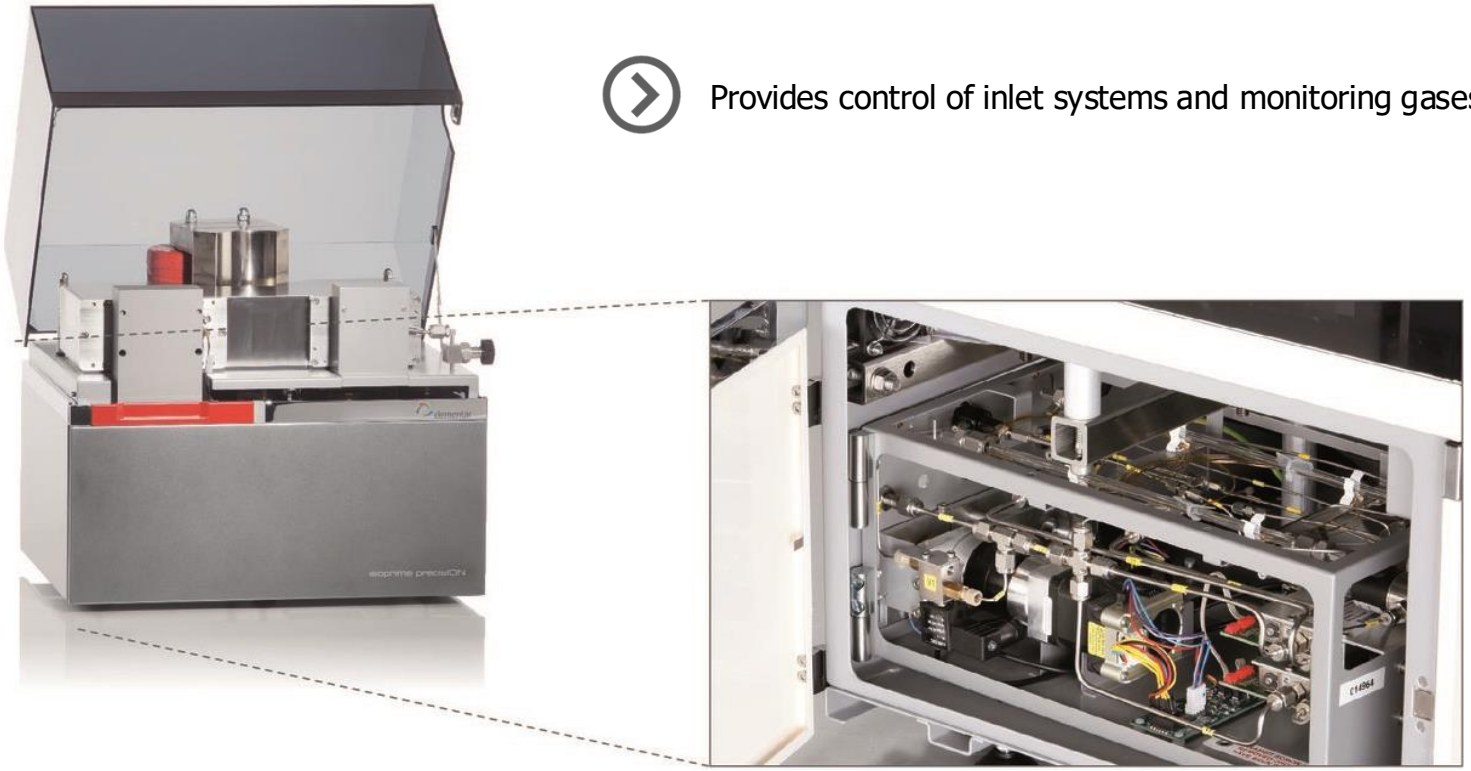
Ion source installed in the analyser

Analyser/Flight-tube held under vacuum

100V Amplifier

System controller electronics contained inside instrument chassis

Continuous Flow Gas Management/Interface System



- Provides control of inlet systems and monitoring gases, dilution, etc..

Elementar isoprime xION: Analysis! (finally!)

The IRMS itself is only able to measure purified molecules of gas i.e. CO_2, SO_2, etc… as the source can only analyse gas molecules…BUT, we add on additional kit to convert the sample into these gases, giving us almost limitless possibilities for what we can analyse!

Plant materials, food, fruit

Wood fibres

Hair, Chitin, Nails, Hooves

Water, Beverages, Liquids,

Meat, muscle Biological materials

Carbonates (e.g. forams

Soils, Sediments, Clays, Minerals

Trace Atmospheric Gases

Post-ASITA Workshops!

Wed PM: 1:30 PM - 5:30 PM
2 parallel sessions

- Source Maintenance
- LyticOS Data Processing

Thu AM: 08:30 AM - 1:00 PM *(workshops start at 9:00)*
Possibly 2 parallel sessions (depending on final numbers for source workshop)

- Source Maintenance
- EA & EA-IRMS

Thu PM: 1:30 PM - 5:30 PM
2 parallel sessions

- Source Maintenance
- iso FLOW GHG for N2/N2O

EXCELLENCE IN ELEMENTS

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How to analyse stable isotopes – Inlets

Combustion

- Convert into simple gases at high temperature in the **presence** of oxygen (form CO_2, NOx, SOx, H_2O), and reduce NOx & SOx (to N_2 & SO_2) for simplicity.
- Excess of O_2 means ^{18}O measurements are largely meaningless.
- For bulk analysis – **EA,** also **TOC**. Same principles apply to compound-specific (**LC** & **GC**); compounds separated, then combusted

Pyrolysis

- Convert into simple gas at *very* high temperature in the **absence** of oxygen, usually in the presence of carbon. Mostly useful for bulk ^{18}O analysis (forms CO) and ^{2}H (forms H_2).
- Excess carbon means ^{13}C measurements are usually meaningless.
- For bulk samples – **Pyrolysis-EA** (sometimes called TC/EA). Same principles apply to compound-specific (**LC** & **GC**); compounds separated, then pyrolyzed.

Direct Analysis

- Analyse the sample gas/headspace directly
- Trace gases, or headspace gas generated from acidification of carbonates, or equilibration of liquid samples with introduced headspace gas (e.g. CO_2 for ^{18}O, H_2 for ^{2}H in waters/liquids)

How does a Mass Spectrometer work?

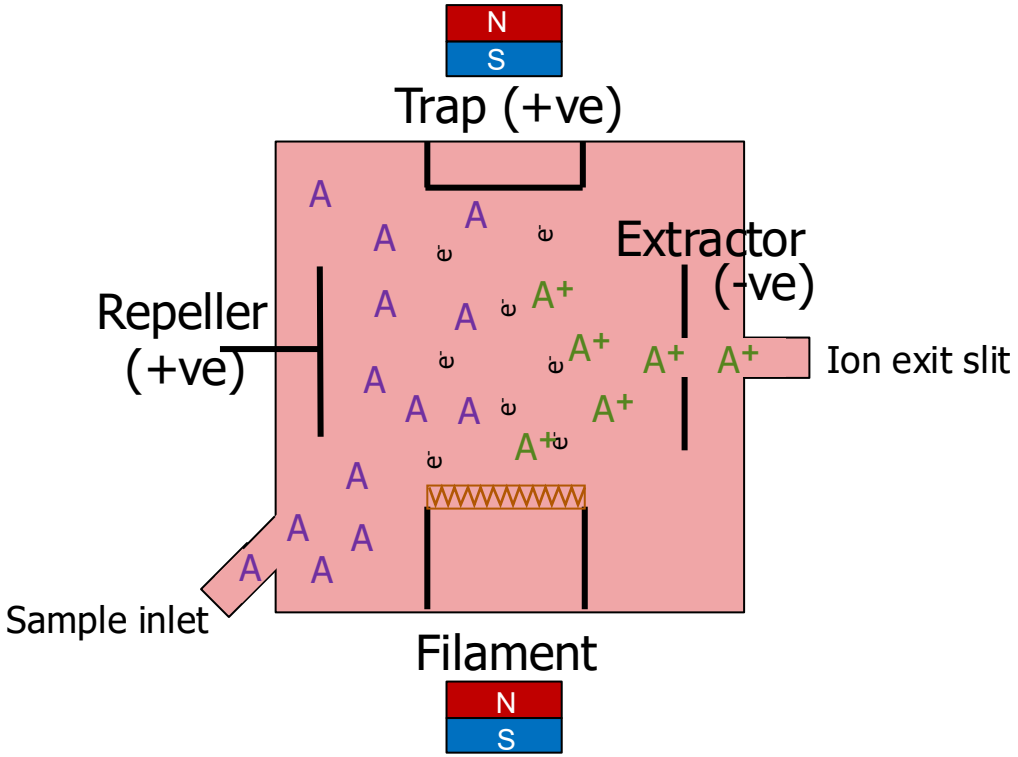
Ionisation & Acceleration, Focussing, Separation, Detection

Filament produces electrons (e^-); magnets cause electrons to move in helical path

Trap at +ve potential draws electrons to it (trap-regulated emission)

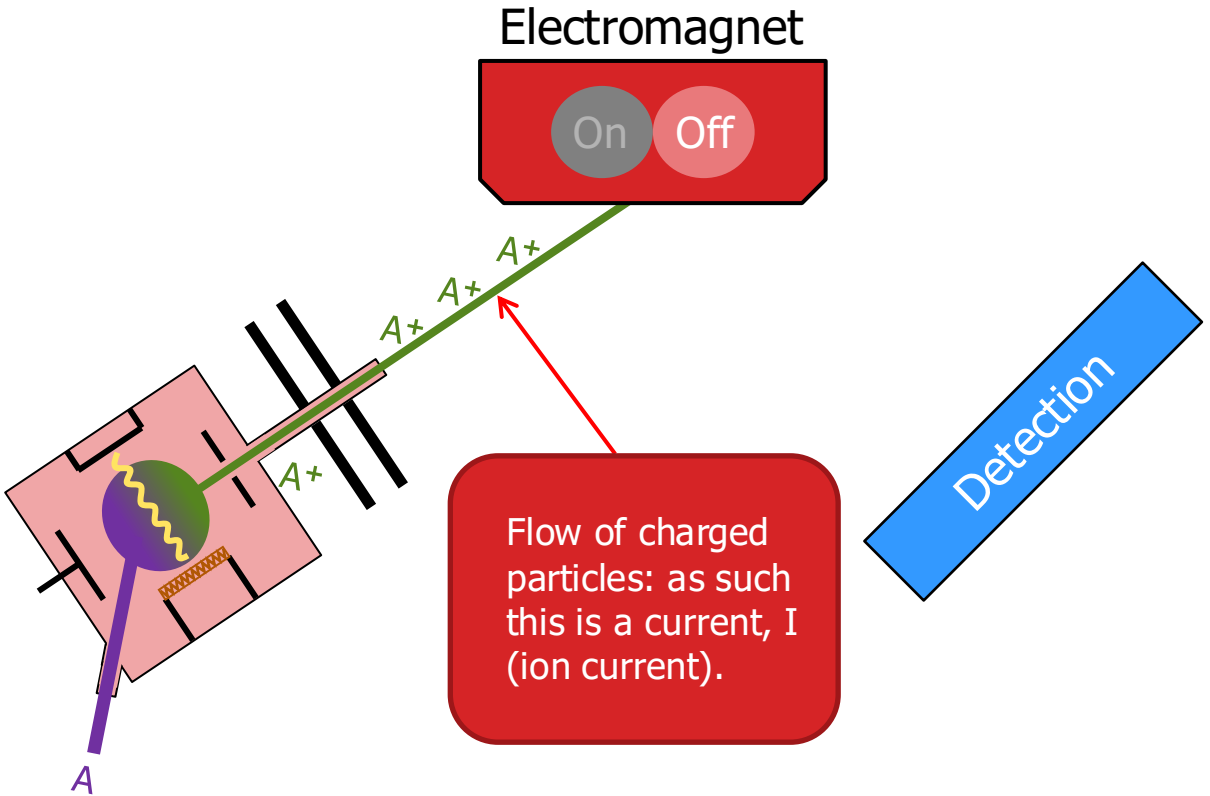
Electrons collide with analyte (A), displacing an outershell electrons and forming positively charged analyte ions (A^+)

A^+ is directed through the source by repeller and extractor (also affected by trap & source magnets)



How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, Separation, Detection



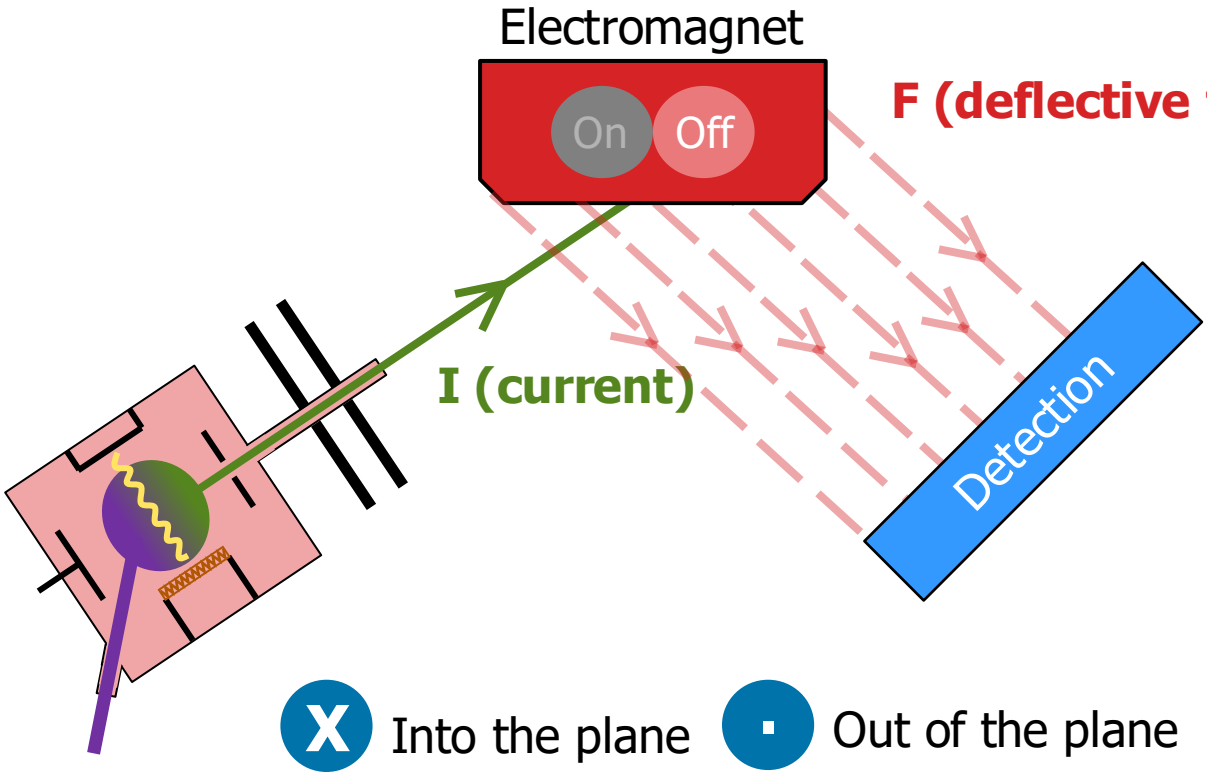
Flow of charged particles: as such this is a current, I (ion current).

Detection

Ion beams being accelerated towards the **magnetic sector** is a current, just like the flow of electrons along a wire in an electronic circuit

How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, Separation, Detection

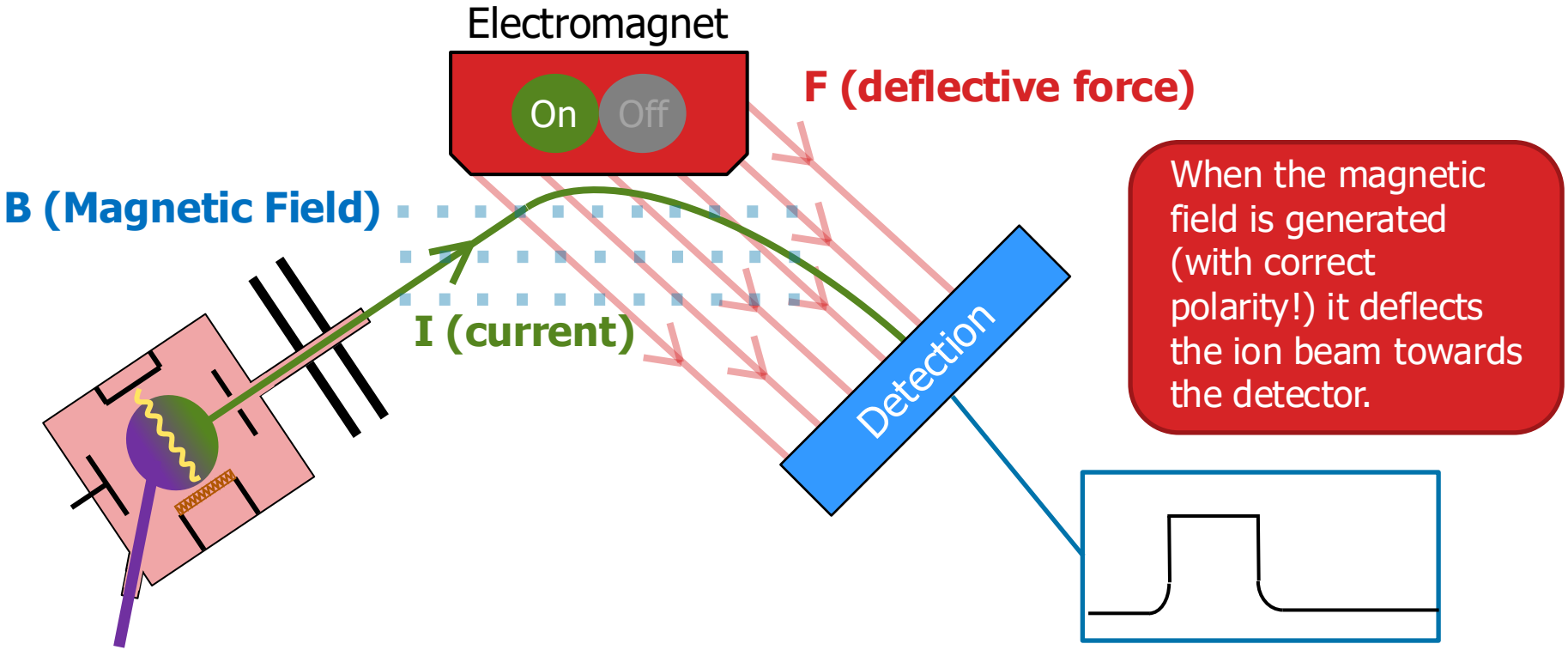


To generate a deflective force in the correct direction to send ions to the detector, a magnetic field should be applied (**magnetic sector** separation).

Using the left hand rule, we see it needs to be applied **out of** the plane (i.e. directly out of the page, towards you.

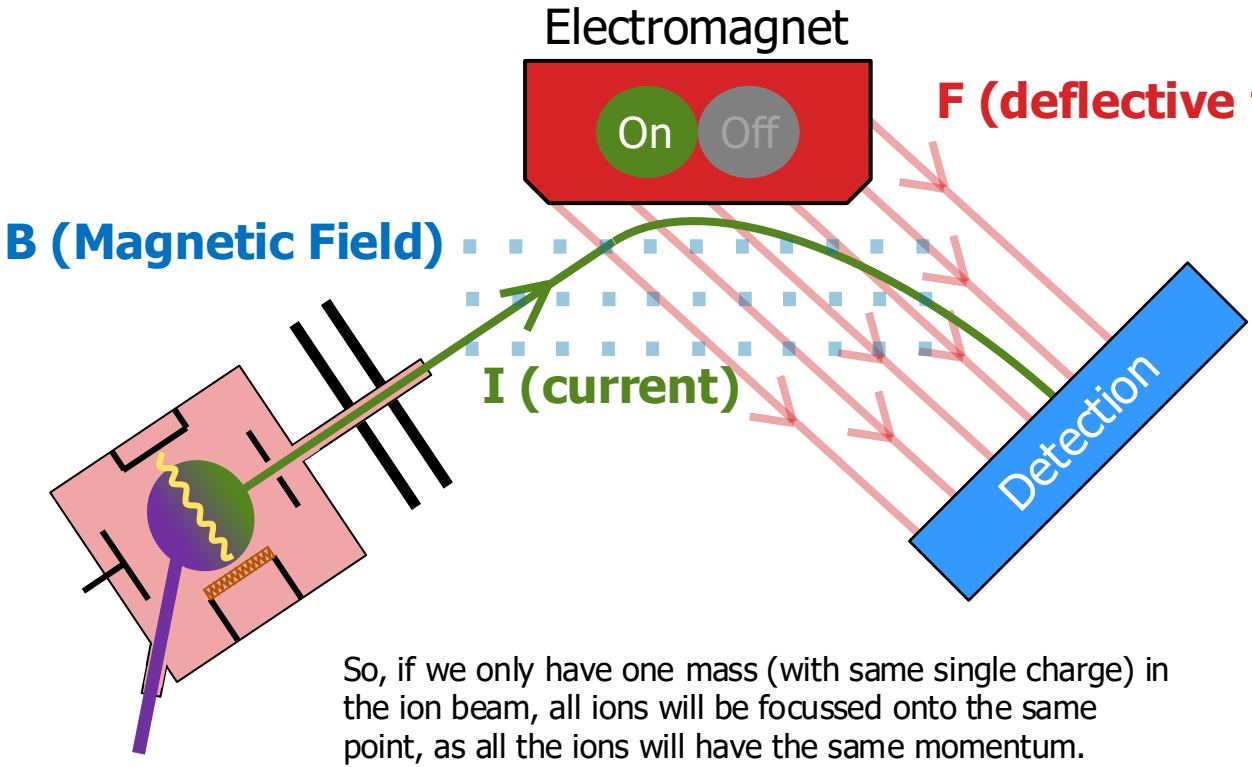
How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, Separation, Detection



How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, **Separation,** Detection



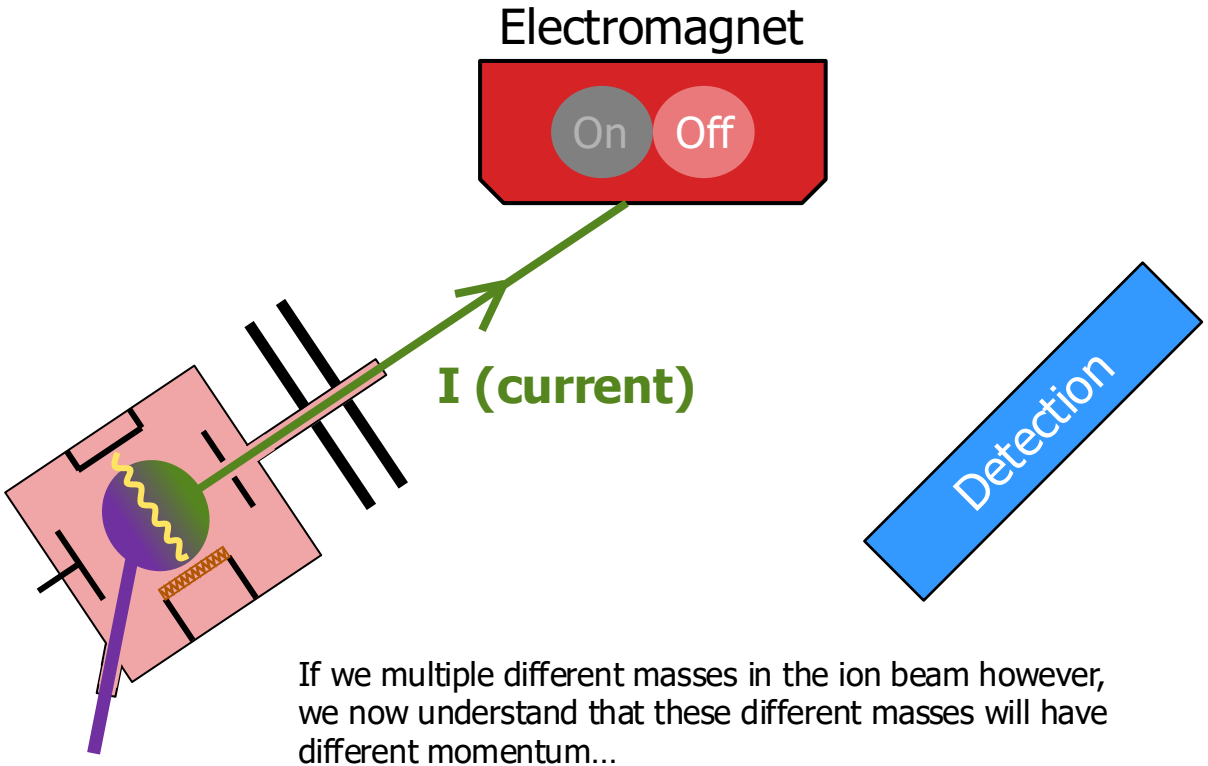
Any moving body has "**momentum**" which is the product of mass (m) and velocity (v)

All the ions will have the same velocity as they enter the magnetic field

So, if we only have one mass (with same single charge) in the ion beam, all ions will be focussed onto the same point, as all the ions will have the same momentum.

How does a Mass Spectrometer work?

Ionisation & Acceleration, Focussing, **Separation,** Detection



Molecules with a different mass will have different **momentum**

Molecules with **greater momentum** are **deflected less** by the magnetic field

If we multiple different masses in the ion beam however, we now understand that these different masses will have different momentum…

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So we now see that we can detect ions by deflecting them in a magnetic field, as they have mass, charge and velocity.

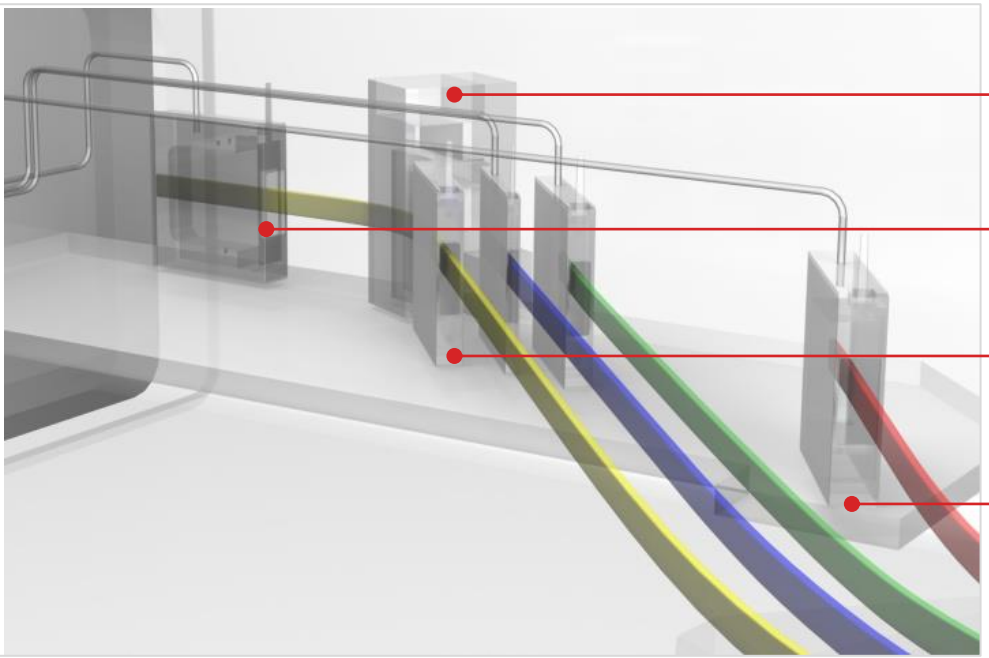
Moreover we see that lighter particles are deflected more than heavy particles by the force of the magnetic field.

For isotope analysis, we are interested in differentiating isotopologue ions based on their mass/charge ratio; we see from the previous slides that we can separate ionised isotopologues in a magnetic field due to the difference in acceleration they will experience.

e.g. $\delta^{13}C$

Species	*m/z*
$^{12}C^{16}O^{16}O^{+}$	44
$^{13}C^{16}O^{16}O^{+}$	45
$^{12}C^{18}O^{16}O^{+}$	46

Analysing hydrogen isotopes in CF mode

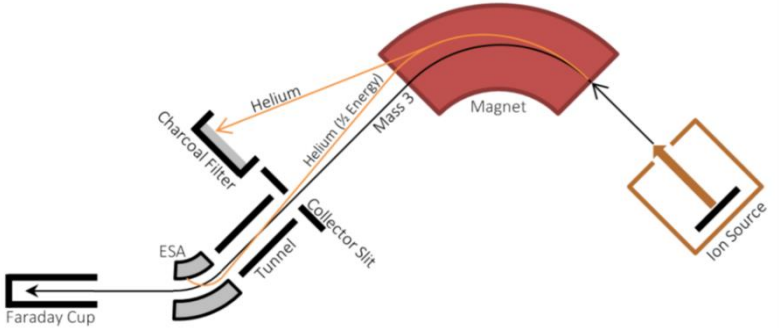


Instrument uses a secondary electrostatic filter to separate H-D from ^{4}He+ tail

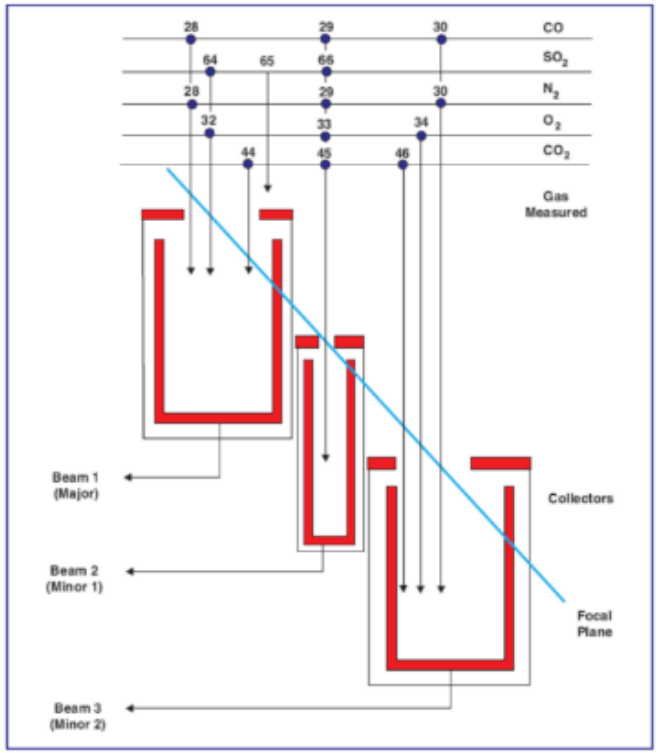
Faraday detector for analysing H-D ion beam

"Dummy" collector which the H-D and the ^{4}He ion beam tail pass through

Faraday detector for analysing H-H ion beam



Elementar isoprime IRMS: Faraday Detectors (the Universal Triple Collector)

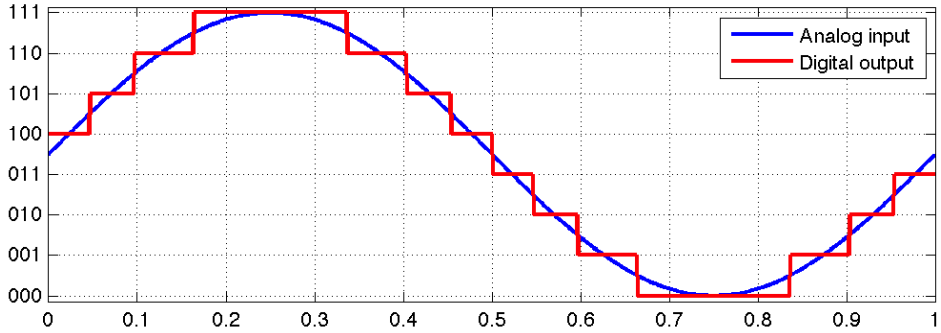


- The Universal Collector Array is comprised of 3 Faraday collectors, and is able to analyse the stable isotopes in CO_2, N_2, SO_2 and O_2 gases
- Because of the molecular weight of each gas is different, the amount of relative dispersion between the ion beams is going to be different
- Therefore, the relative widths of the three Faraday collectors must be different to ensure that all gasses can be analysed without physical movement of the collectors
- The minor1 ion beam is chosen as the axial mass and is the beam that we focus on when tuning the instrument (major, and where used minor2, are thus focussed onto the radial collectors)

So what are we *actually* measuring?

An ion beam current! This is made up of individual ions arriving at the detector at an average rate (amount per unit time) that is continuously **digitially quantified and amplified by the head amplifier**

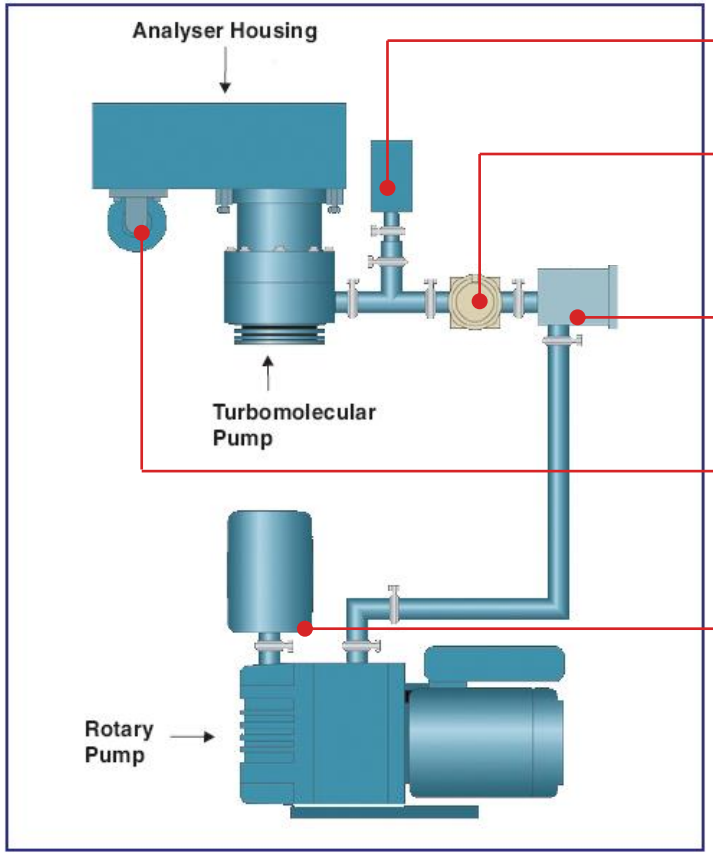
The rate of ions entering the detector for a given mass is a measure of the amount of the isotopologue at that mass in the sample at that given time.



Like converting analogue to digital music, the ion beam is continuous – but measured (quantized) at discrete intervals to generate a digital signal for processing/measurement

The ratio of two isotope beams is therefore the ratio of the two isotopes in the sample

Instrument Vacuum



Pirani gauge for low vacuum readback

Isolation valve allows maintenance to the low vacuum system without venting the instrument

Foreline trap stops oil vapor from back flowing into the analyser and contaminating the instrument

Penning gauge for high vacuum readback

Mist filter stops oil vapor escaping into the lab atmosphere

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A closer look to the Isoprime visION

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