Principles of Isotope Ratio Mass Spectrometry (IRMS)

DM Baker

basics

HISTORY

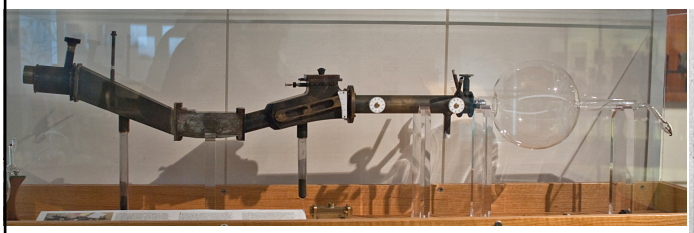
History

Harold Urey (1893-1981)

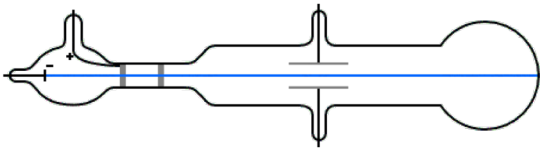
- Stable isotopes of oxygen known in the 1920s
- Urey set out to discover deuterium – Nobel Prize 1934
- Enriched H_2 via electrolysis and evaporation
- Went on to produce other enriched elements (tracers)
- Manhattan Project, paleoclimate, geochronology, origin of life

History

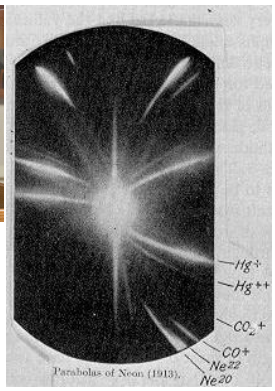
mass spectrography → mass spectrometry



3rd mass spectrometer (JJ Thompson)



Cathode rays deflected by electric field



Phosphor screen image of ions

History

Alfred O. Nier (1911-1994)

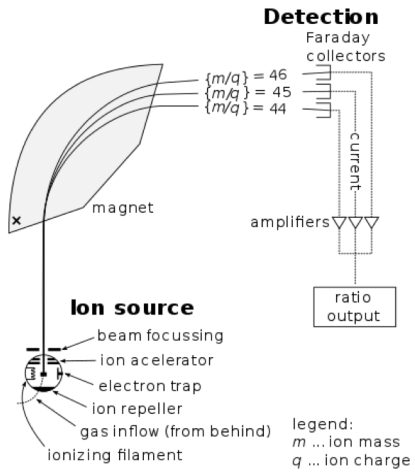
- isolated Uranium-235 and demonstrated fission
- Developed first sector-field mass spectrometer ”Nier-type” (1927)
- Manhattan Project, Viking Landers, geochronology, space sciences, etc.

basics

ANATOMY OF A MASS SPEC

anatomy

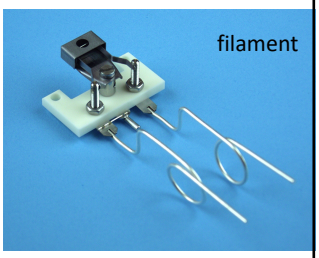
- Ion source
- Mass analyzer (sector field)
- Detector

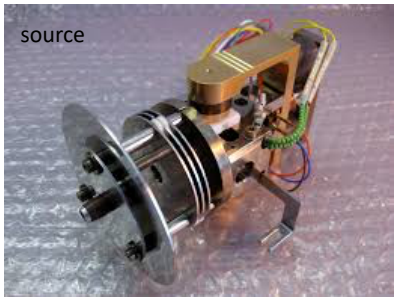


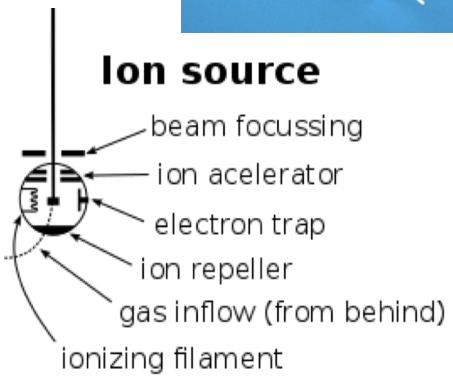
Example of an IRMS for $\delta^{13}C$ determination

Ion source

- Step 1: ion-source (the heart of the IRMS)

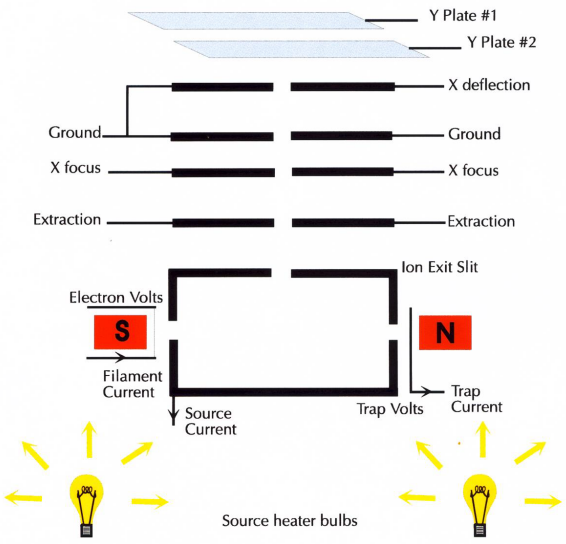






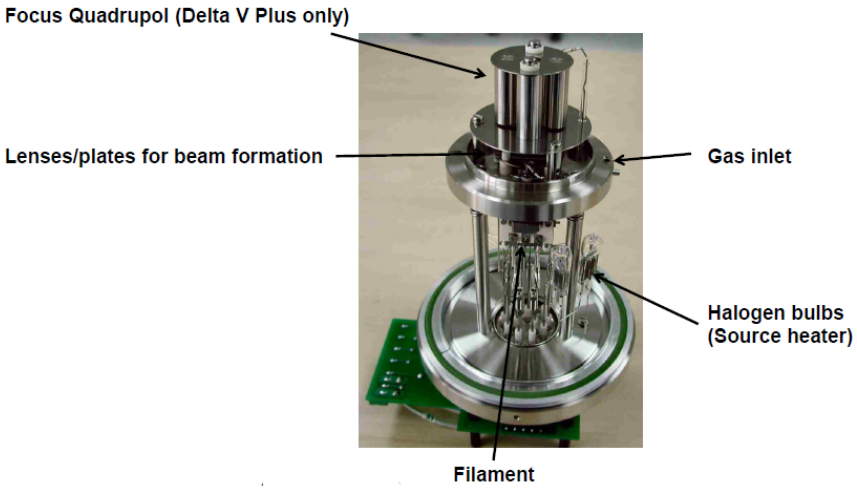
Ion source

- Gas molecules are ionized to positive ions through collision with electrons
- Ions are accelerated and focussed through a series of slits and focus planes => **tuning** parameters



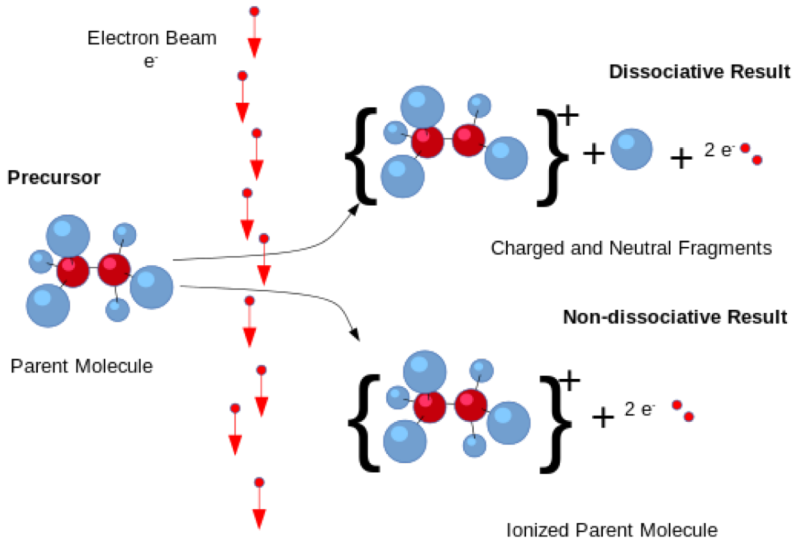
(ThermoFisher Scientific)

Ion source

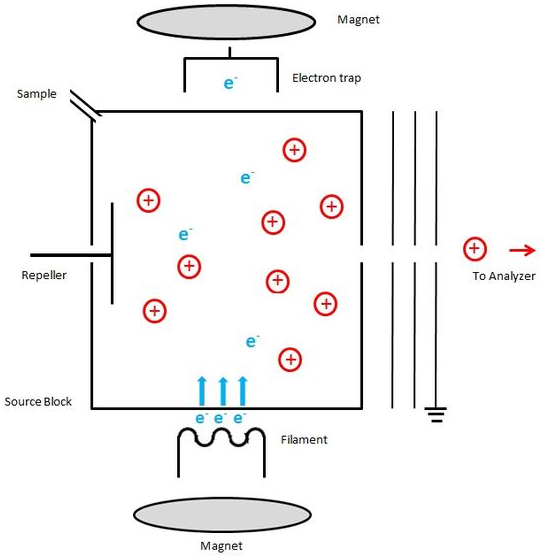


(ThermoFisher Scientific)

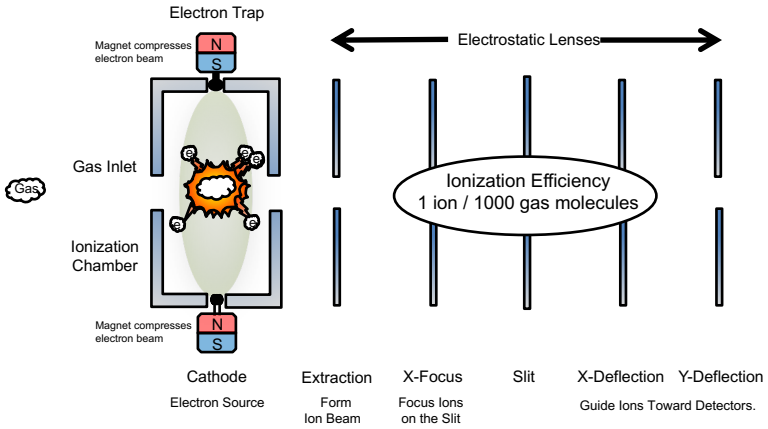
Electron ionization



Electron ionization

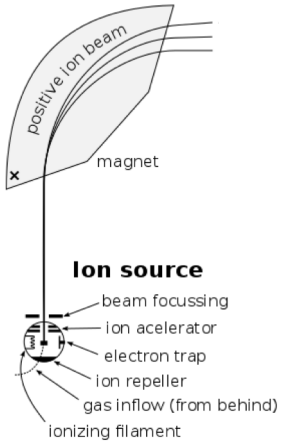


Ionization – Electron Impact Source



Mass analyzer

- Step 1: ion-source (the heart of the IRMS)
- Step 2: magnetic field



Magnet (sector)

Ions travel with radius of:

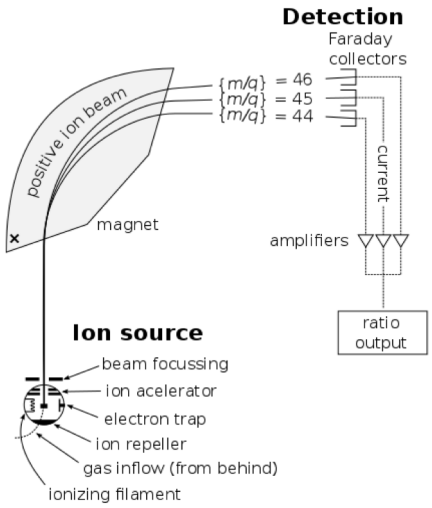
$$r = \frac{1}{H} * \left(\frac{2mV}{e} \right)^{0.5}$$

With H the magnetic field, m the mass, V the voltage and e the charge

- Ions are separated according to mass
- Changing the magnetic field according to the element so that the ions reach the detector cups

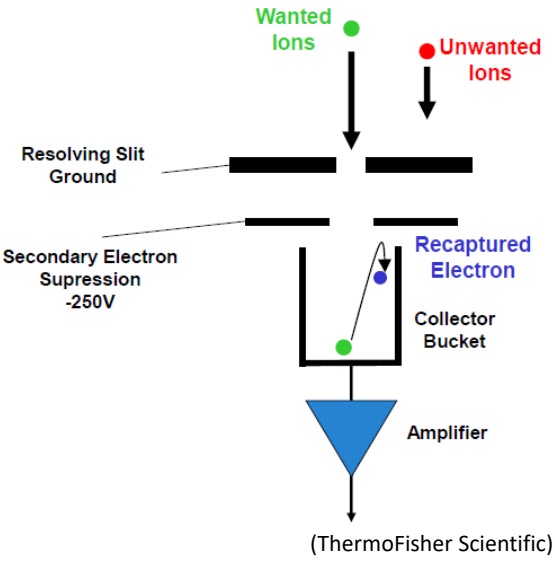
detector

- Step 1: ion-source (the heart of the IRMS)
- Step 2: magnetic field
- Step 3: Faraday collectors



Ion collectors

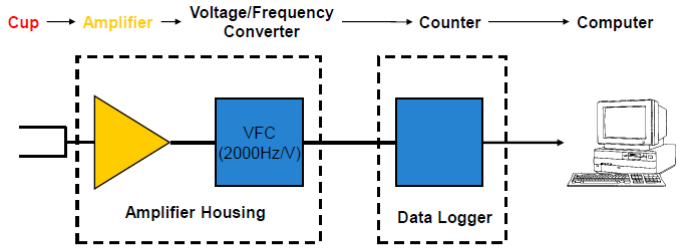
Faraday cups: generate current as ions are collected



(ThermoFisher Scientific)

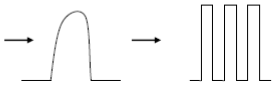
Ion collectors

Output can be in mV (Thermo) or in amps (Nu instruments)



Ohm's Law (U= R x I):

$3*10^{-9}$ A x $1*10^{9}\ \Omega$ = 3 V



(ThermoFisher Scientific)

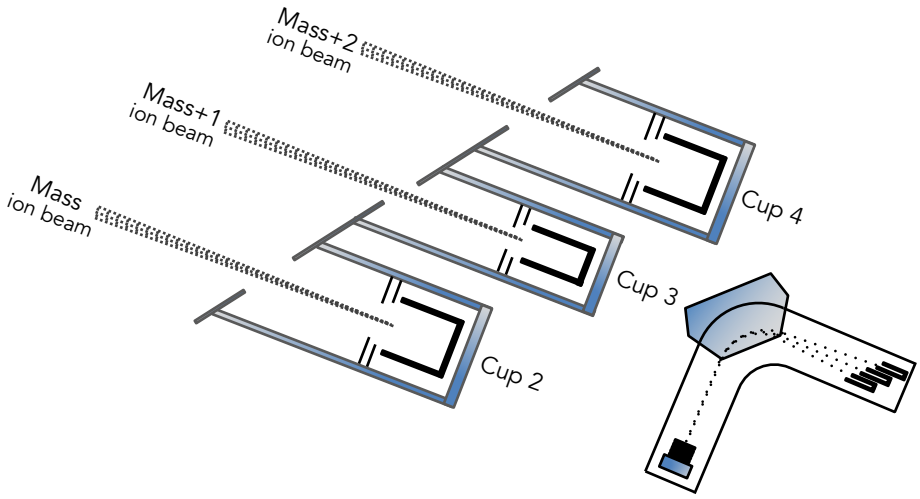
Ion collectors

- 3-5 collectors: H has separate collectors due to its low mass
- Some masses cover multiple gasses: risk of contamination
- More advanced equipment has up to 10 collectors and can measure more gasses

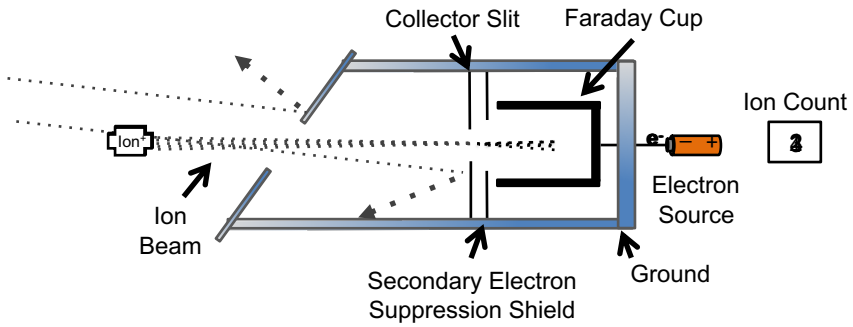
Gas	Collector Arrangements for Masses (m/z)				
H_2	2				3
N_2		28	29	30	
CO		28	29	30	
NO		30	31	32	
O_2		32	33	34	
CO_2		44	45	46	
N_2O		44	45	46	
SO_2		64	66		

(ThermoFischer Scientific)

Ion Detection: Faraday Cup Array



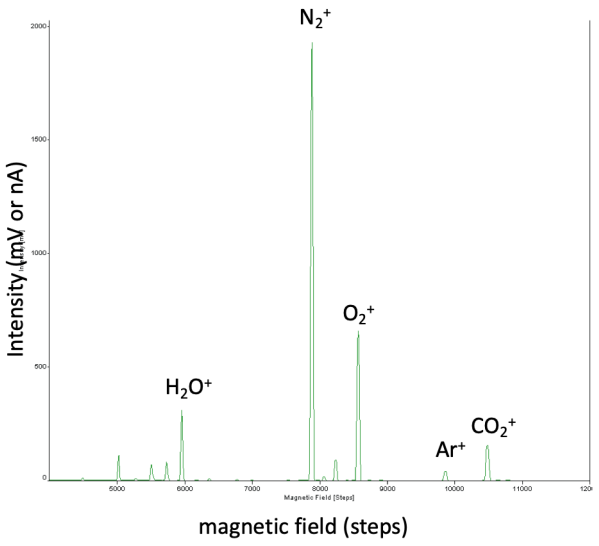
Ion Detection: Faraday Cup



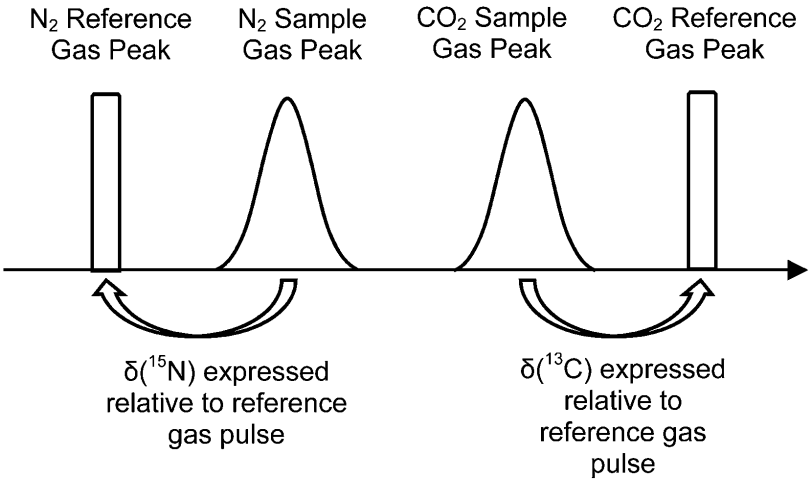
The chromatogram

- A visual “trace” of ion beam intensities as a function of time (mV or nA)
- Measured at the ion collector
- Shape is diagnostic of the process (pure gas vs. combustion/pyrolysis)
- Peak height and area used in SIA calculations

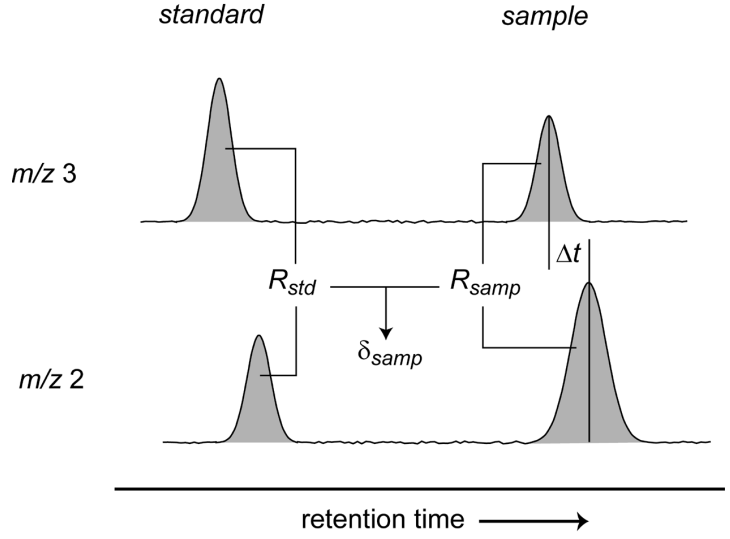
Background scan



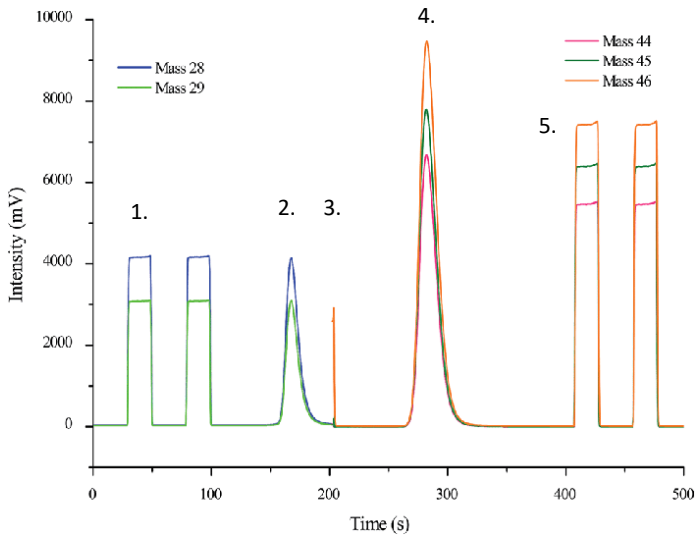
Chromatogram to delta



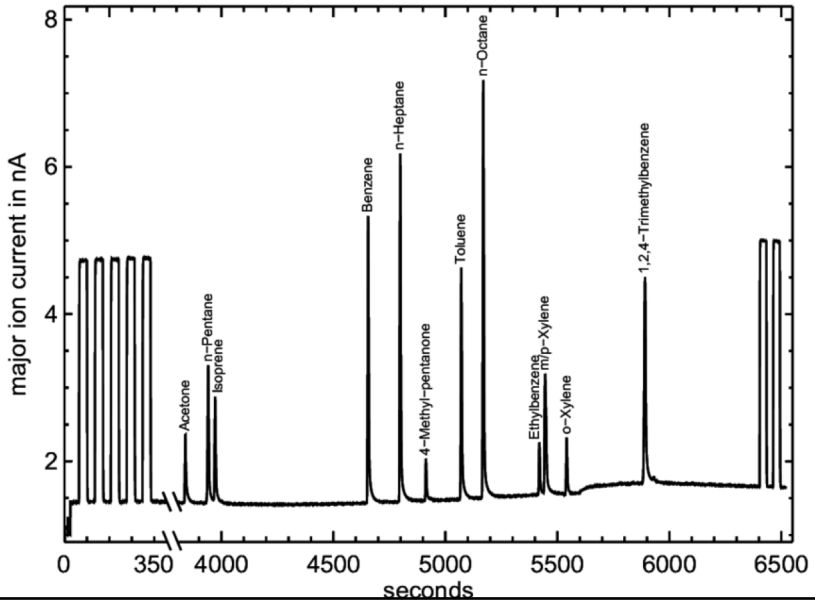
Chromatogram to delta



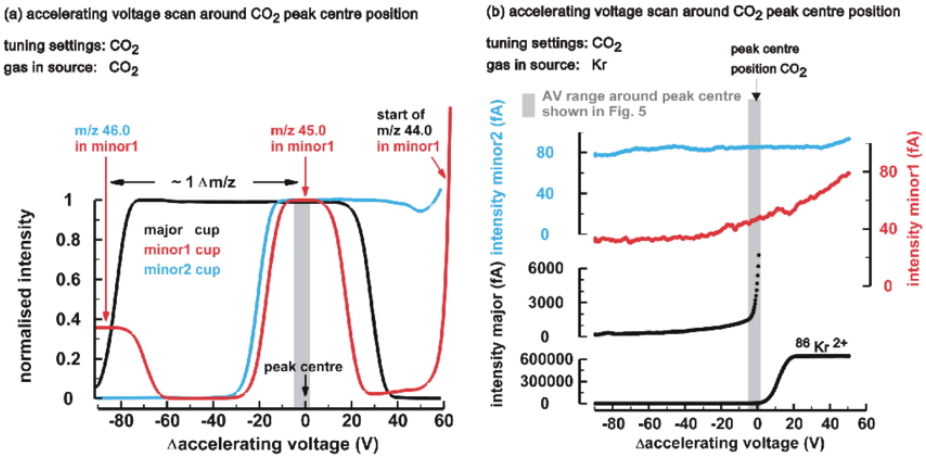
Chromatogram – EA IRMS



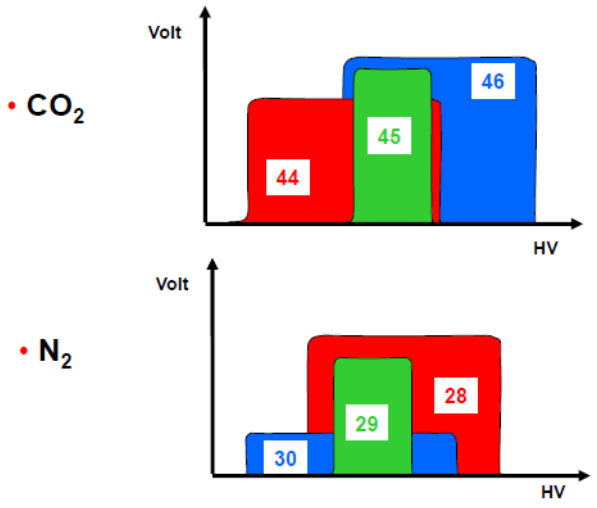
Chromatogram – GC-IRMS



Peak centering



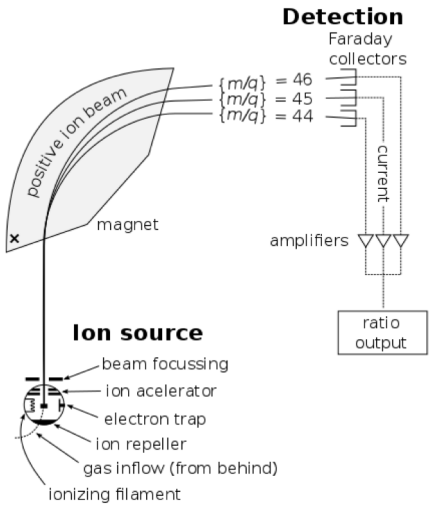
Ion collectors



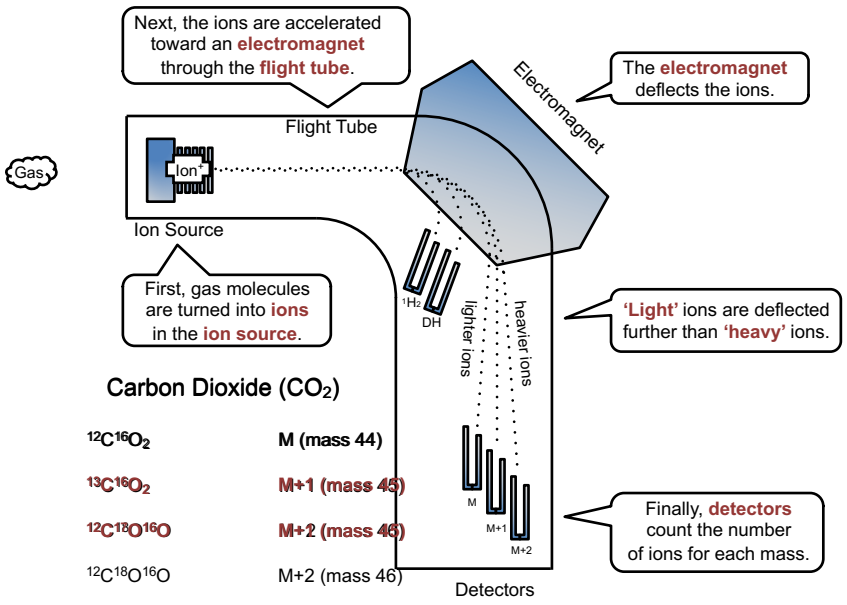
(ThermoFisher Scientific)

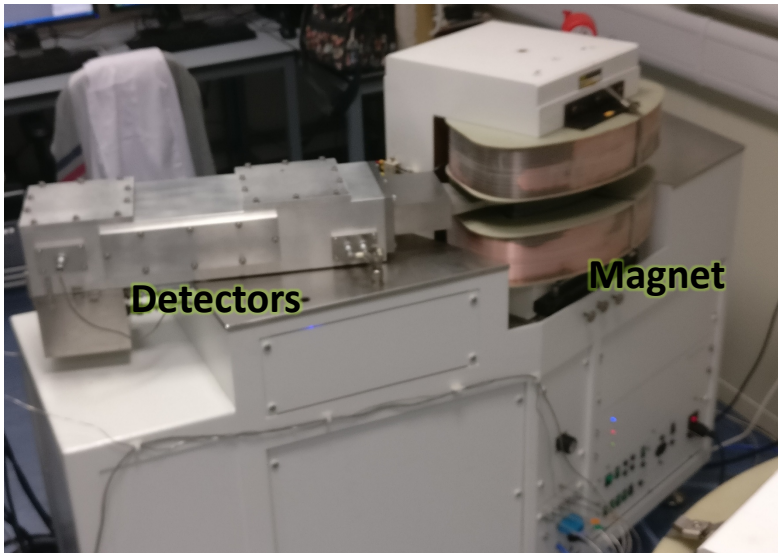
Isotope Ratio Mass Spectrometer

- Needs to have vacuum to avoid ion collisions
- Vacuum pump are essential parts



Isotope Ratio Mass Spectrometers (IRMS)





Nu Instruments “Perspective”

Mass spec in action

Non-demonic intrusions

What affects IRMS performance?

- Humidity – influences electrostatic interactions
- Temperature – can influence optics and overheated electronics, loosen connections
- Vibration – can disrupt collectors and increase noise
- Leaks!

What's in the box?

VG 'Prism'

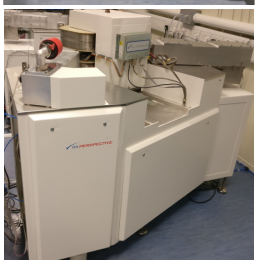
Thermo 'Delta V'

Isoprime 'PrecisION"

What's in the box?

Nu Instruments 'Panorama' – clumped isotopes

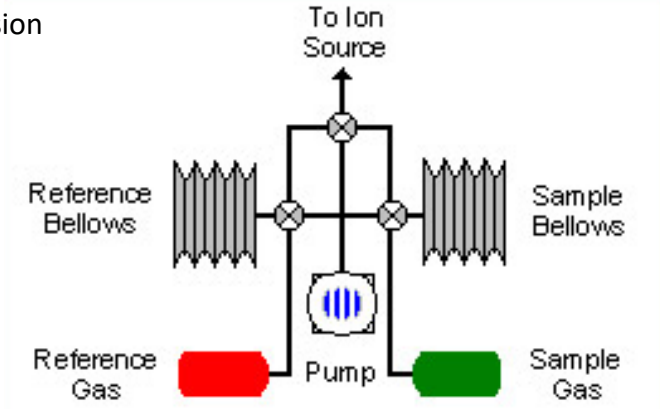
The equipment: (G-)IRMS



Requires samples in gaseous form:
CO_2, N_2, SO_2, N_2O,H_2

Dual inlet (DI)

- Samples prepared off-line
- Sample and reference gas analyzed alternatively
- Highest precision

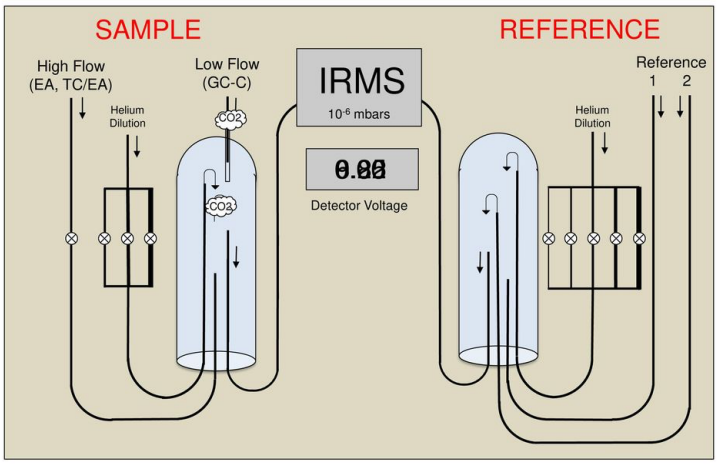


dual inlet prep

- Vacuum extraction lines
- Isolate combusted gases based on freezing point
- Move gas around, removing water and contaminants
- Trap in quartz tube and seal with a torch
- Tube can be “cracked” into dual inlet

Continuous Flow (CF)

IRMS Universal Interface (ConFlo IV)



DI vs. CF

Table 2. Comparison between dual-inlet and continuous flow techniques

	Dual-Inlet	Continuous flow
Type of gas entering the mass spectrometer	A pure gas (such as CO_2) is introduced into the ion source.	A pure gas is entrained as a chromatographic peak within a flow of helium during introduction to the ion source. Thus a mixed gas enters the ion source (e.g. CO_2 + He).
How the sample gas and working gas are introduced into the mass spectrometer	The gases are repeatedly and alternately introduced into the ion source.	The chromatographic peak of sample is preceded and/or followed by introduction of working gas.
Signal intensity of sample gas	Sample gas and working gas are carefully balanced by adjustments of bellows to produce nearly identical signals, for the major ion beam, avoiding linearity biases.	Sample gas varies in intensity across the chromatographic peak.
Amount of sample required	10s of µmol, or ~0.5 µmol using a cold finger volume. The sample size is controlled by the need for viscous flow conditions in the capillaries.	100s of nmol, smaller if systems are optimised (10s of nmol by GC-IRMS). Because viscous flow is provided by the helium stream, there is the possibility of further reduction in sample size by advancements in blank reduction, amplification and/or minimising the preparatory system.

FIRMS

basics

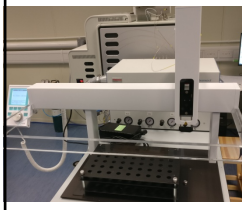
PERIPHERALS (INLETS)

Continuous flow (CF) Peripherals

(G-)IRMS

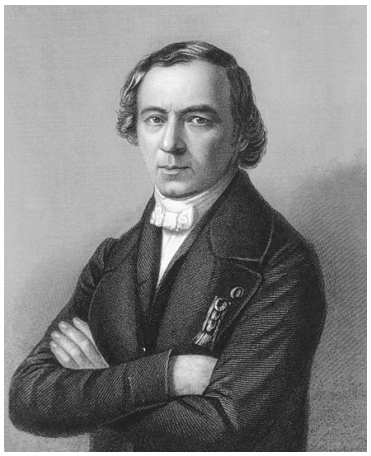
Elemental Analyzer
(HT-)EA

Gas Chromatograph
GC



Gasbench
GB

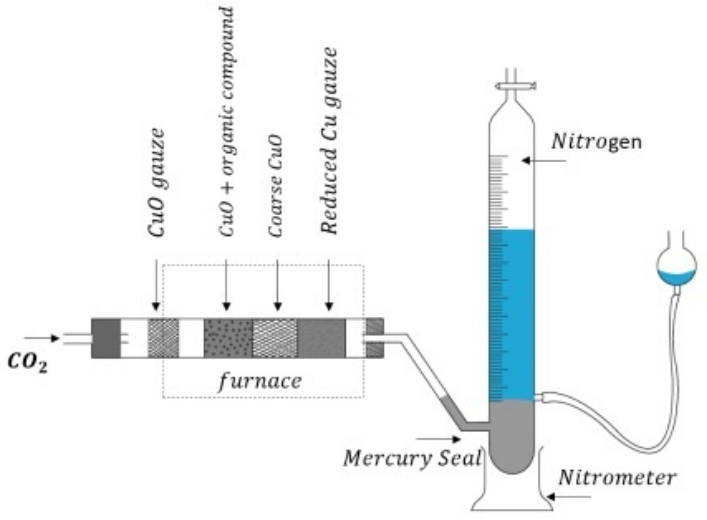
Elemental Analyzer (EA)



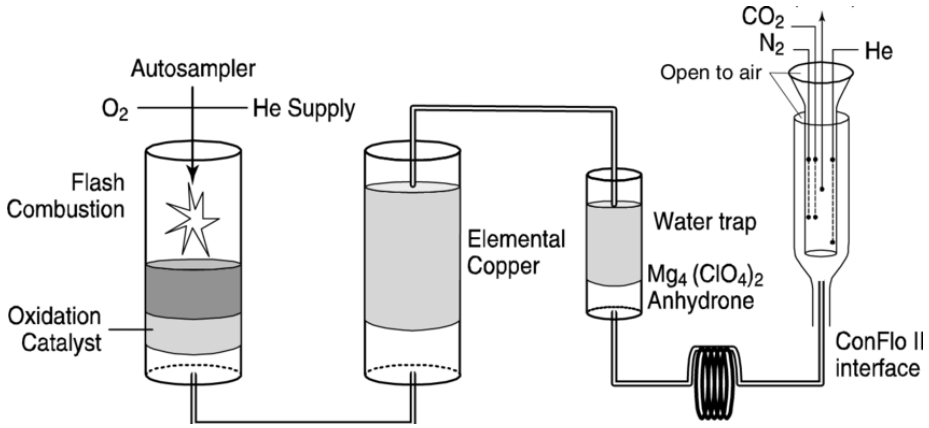
- "Dumas Method" (1833)
- Permits the liberation of N_2 from organics
- Aware of atmospheric N_2 contamination – flush with CO_2 first.
- Oxidized and reduced copper as a catalyst under high temp.

Jean-Baptiste Dumas (1800-1884)

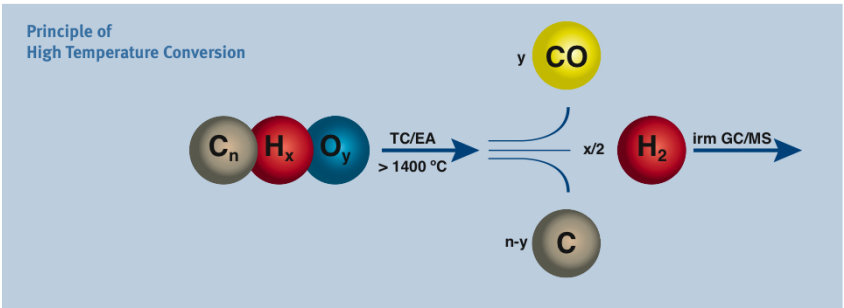
Dumas method



Elemental Analyzer (EA)

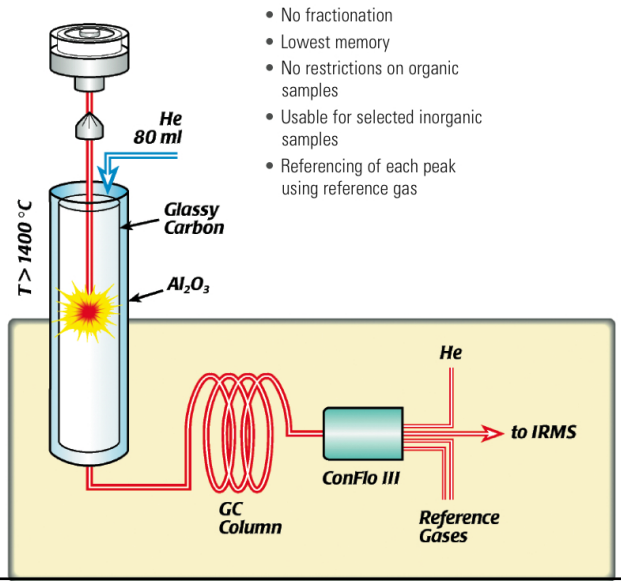


Thermal conversion (TC/EA)



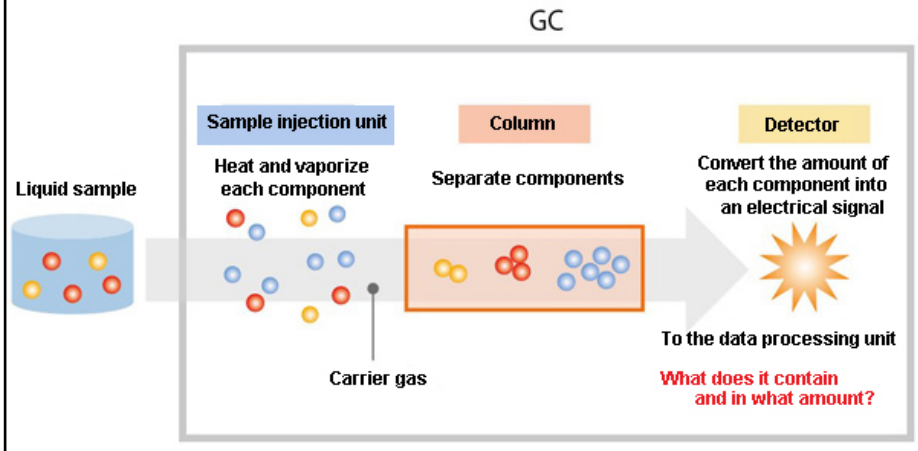
- High temperature (>1400C)
- No oxygen present
- Bonds destroyed (only surviving molecules have stronger bonds)

TC/EA-IRMS



- No fractionation
- Lowest memory
- No restrictions on organic samples
- Usable for selected inorganic samples
- Referencing of each peak using reference gas

Gas Chromatograph (GC)



GC columns

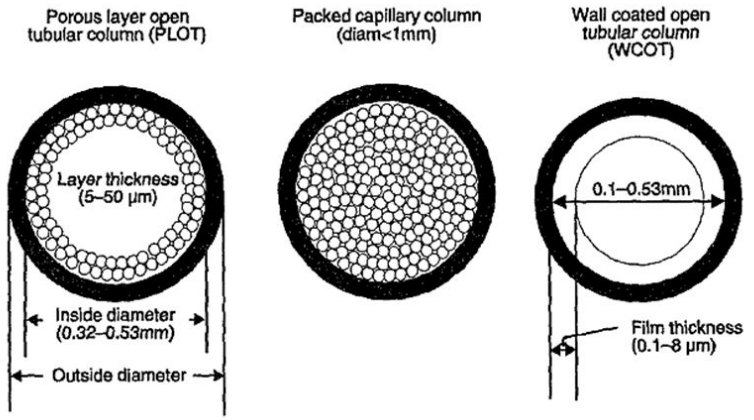
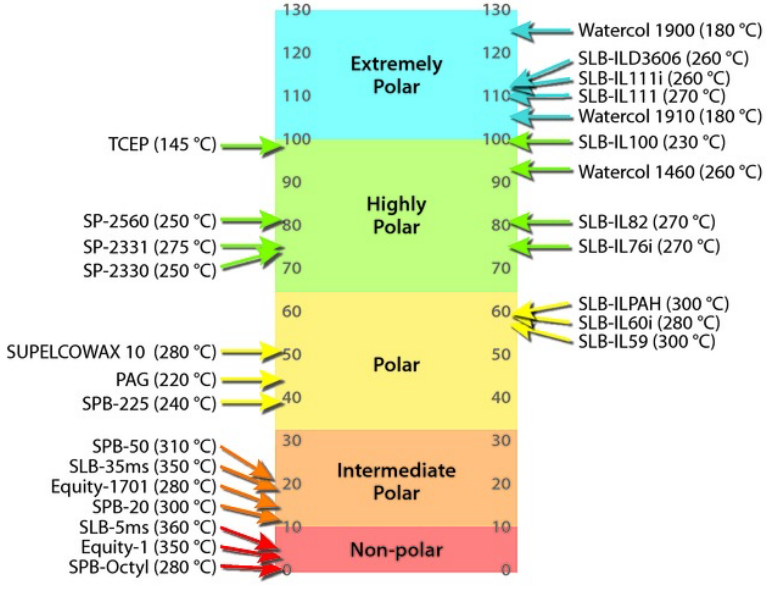
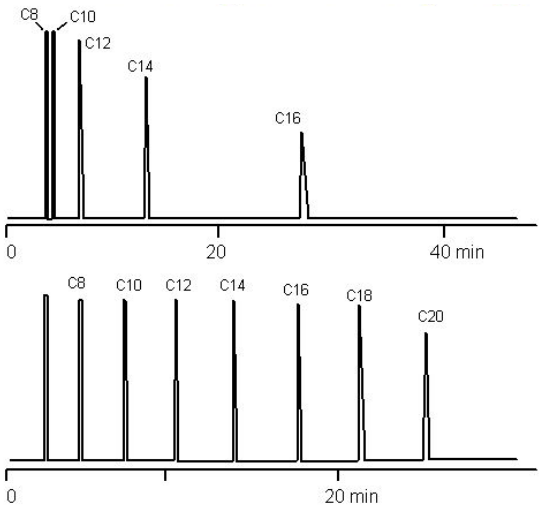


Figure 1.4 Types of capillary column

Column to fit the purpose



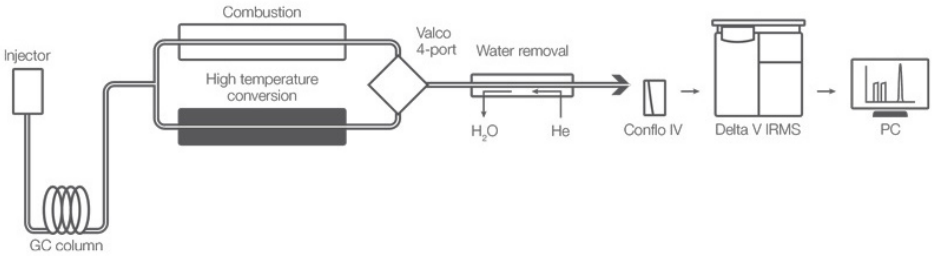
Temperature program



Constant temperature

increasing temperature

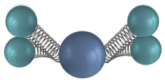
Gas Chromatograph (GC)



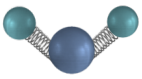
basics

LASER BASED METHODS

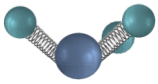
Isotope Ratio Infrared Spectroscopy (IRIS)



Bend



Symmetric Stretch



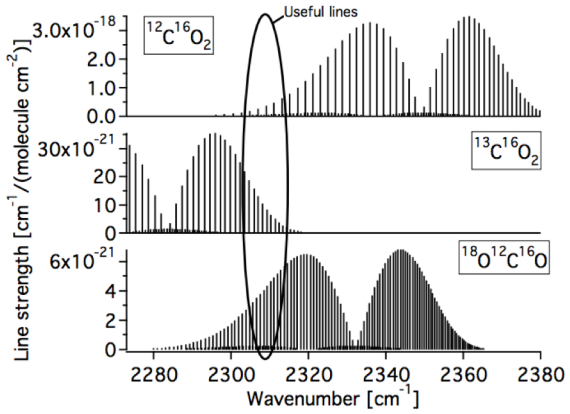
Asymmetric Stretch

- Lasers and Mirrors

Stolen from Seth Newsome

Isotope Ratio Infrared Spectroscopy (IRIS)

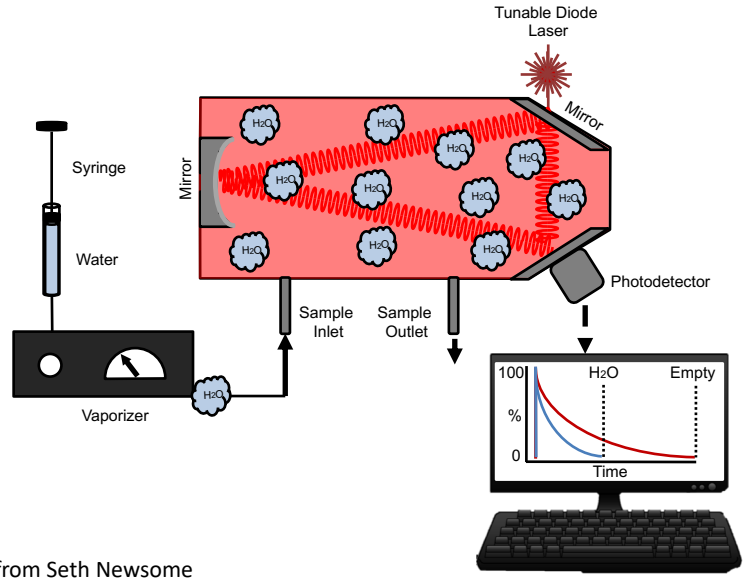
Mid-infrared absorption lines of a subset of the isotopologues of CO_2.



Waechter 2007

Stolen from Seth Newsome

Isotope Ratio Infrared Spectroscopy (IRIS)



Stolen from Seth Newsome

Combustion – IRIS/CRDS