Mass Spectrometry

From Avogadro to Zeptomole

Dr Mick Cooper

Technique for

- Determining masses of particles, atoms or molecules
- Determining the elemental composition of a sample or molecule, and for elucidating the chemical structures of molecules.

Used in

Analytical Chemistry

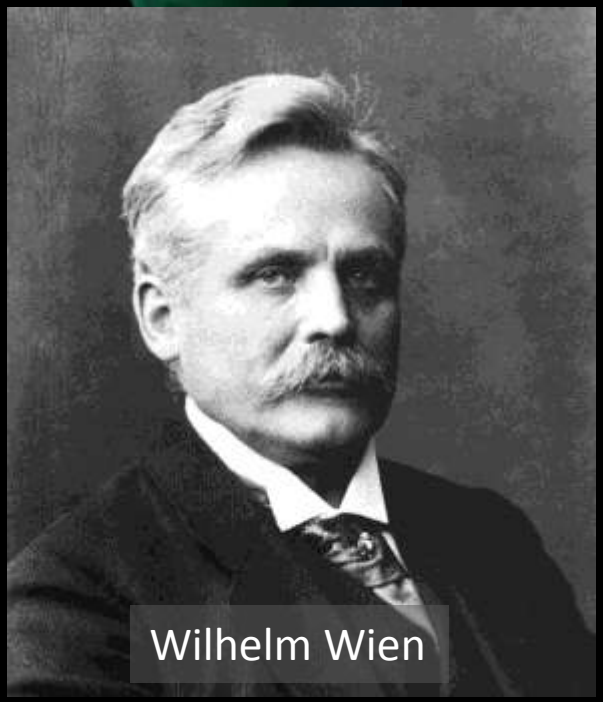
Life Sciences

Earth Sciences

Space exploration

A mass spectrometrist is someone who figures out what something is by smashing it with a hammer and looking at the pieces.

A (very) Brief History of Mass Spectrometry


Wilhelm Wien


John Joseph Thompson


Francis William Aston

The 5 stages of MS

The 5 stages of MS

- Volatilisation – turns the samples to a vapour

The 5 stages of MS

- Volatilisation – turns the samples to a vapour
- Ionisation – creates ions from the sample molecules

The 5 stages of MS

- Volatilisation – turns the samples to a vapour
- Ionisation – creates ions from the sample molecules
- Acceleration – injects the ions into the MS

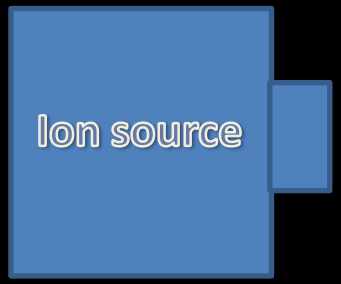
The 5 stages of MS

- Volatilisation – turns the samples to a vapour
- Ionisation – creates ions from the sample molecules
- Acceleration – injects the ions into the MS
- Deflection – separates ions according to their mass

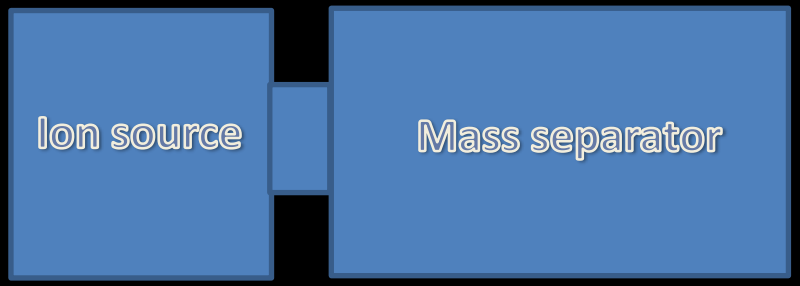
The 5 stages of MS

- Volatilisation – turns the samples to a vapour
- Ionisation – creates ions from the sample molecules
- Acceleration – injects the ions into the MS
- Deflection – separates ions according to their mass
- Detection – produces the mass spectrum

The workings of a mass spectrometer

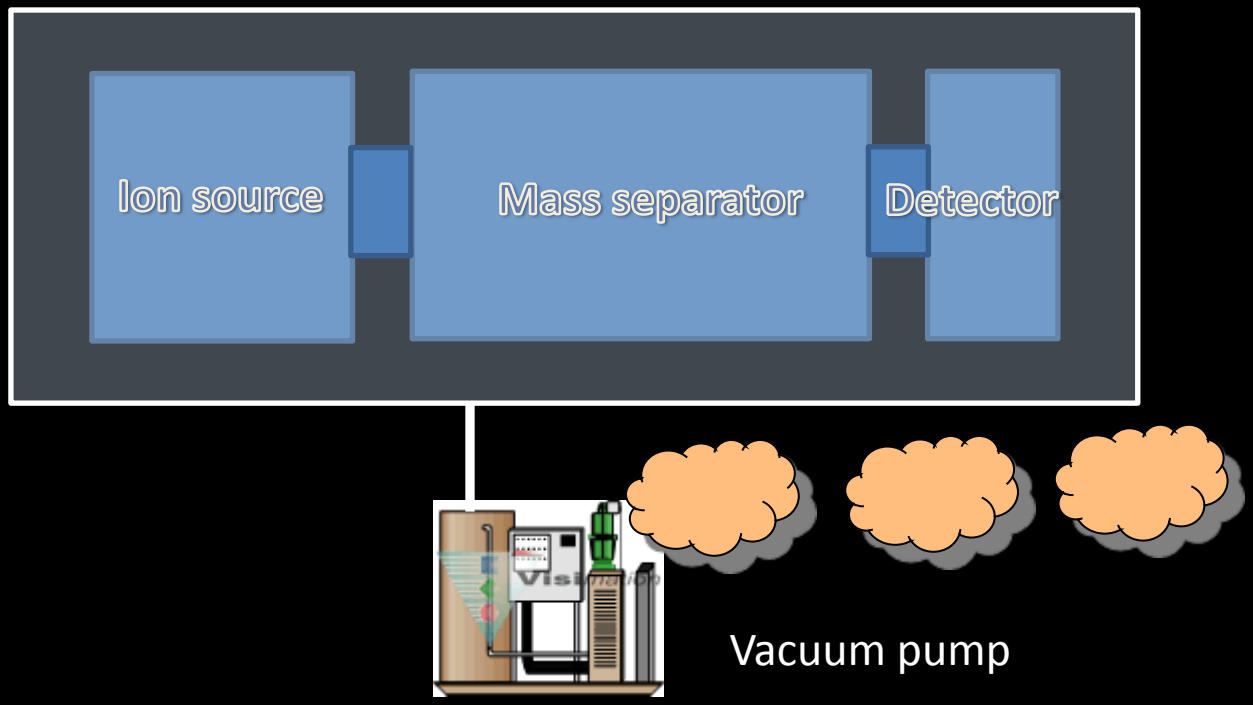


The workings of a mass spectrometer

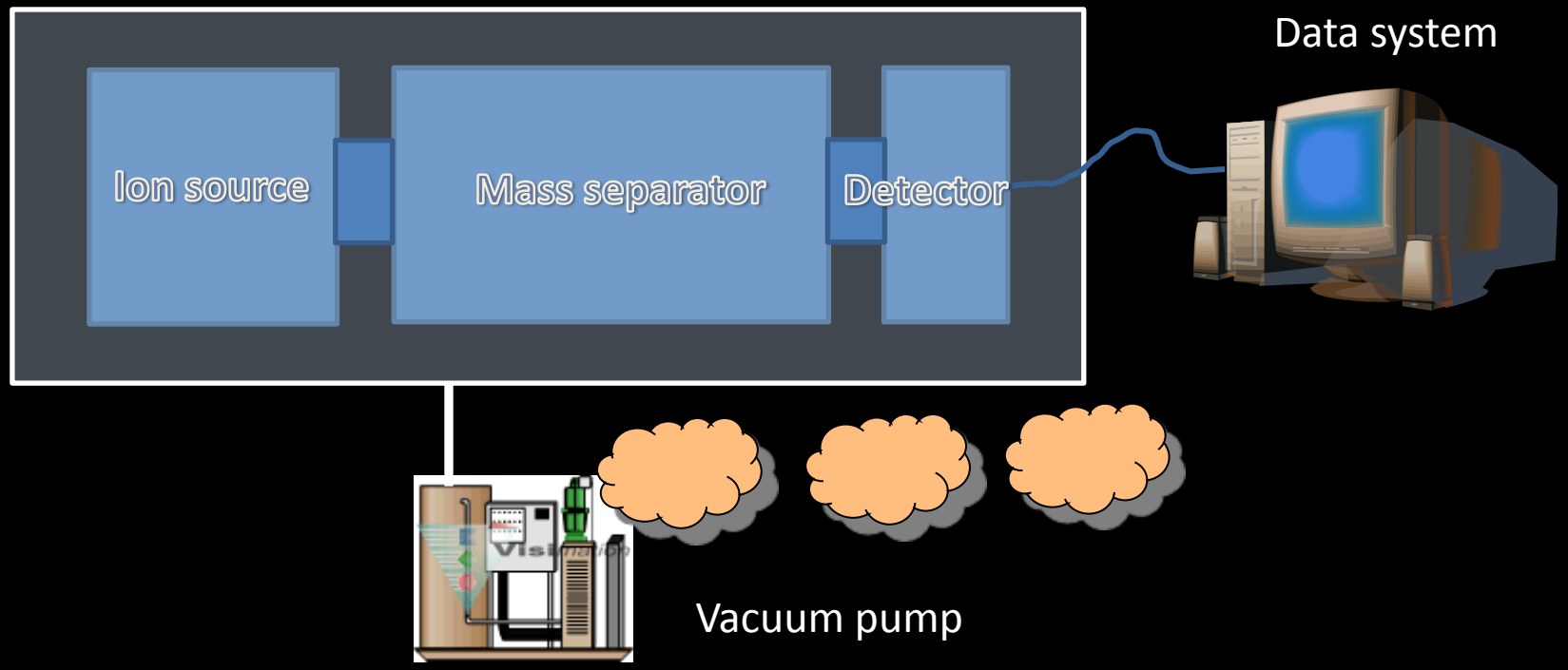


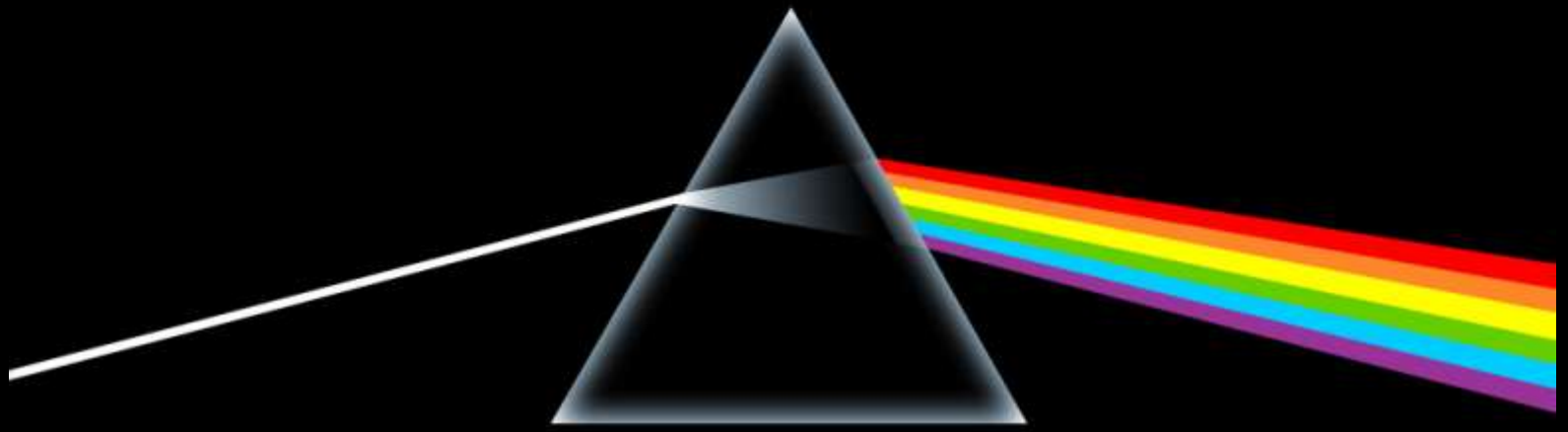
The workings of a mass spectrometer

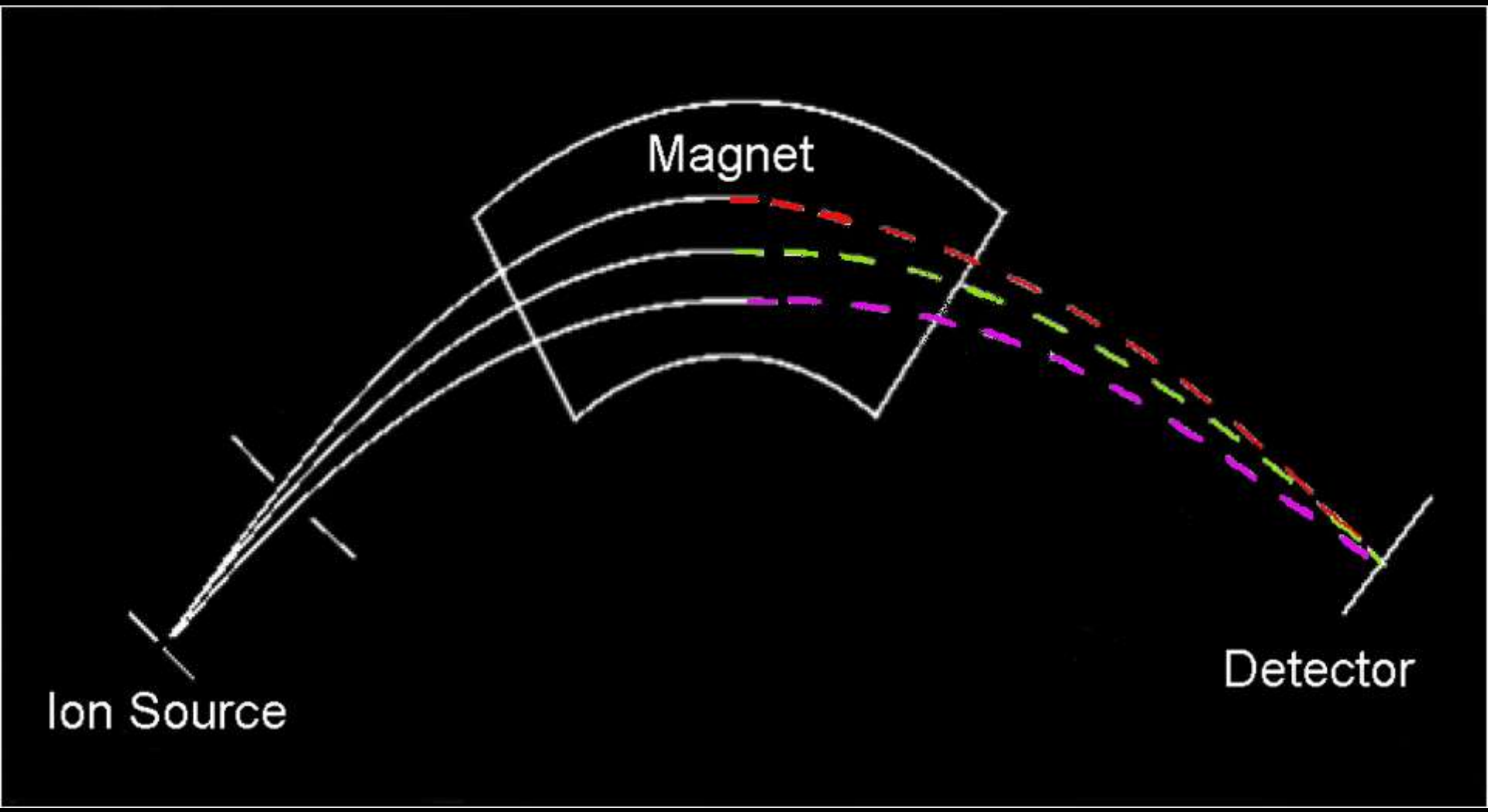
The workings of a mass spectrometer

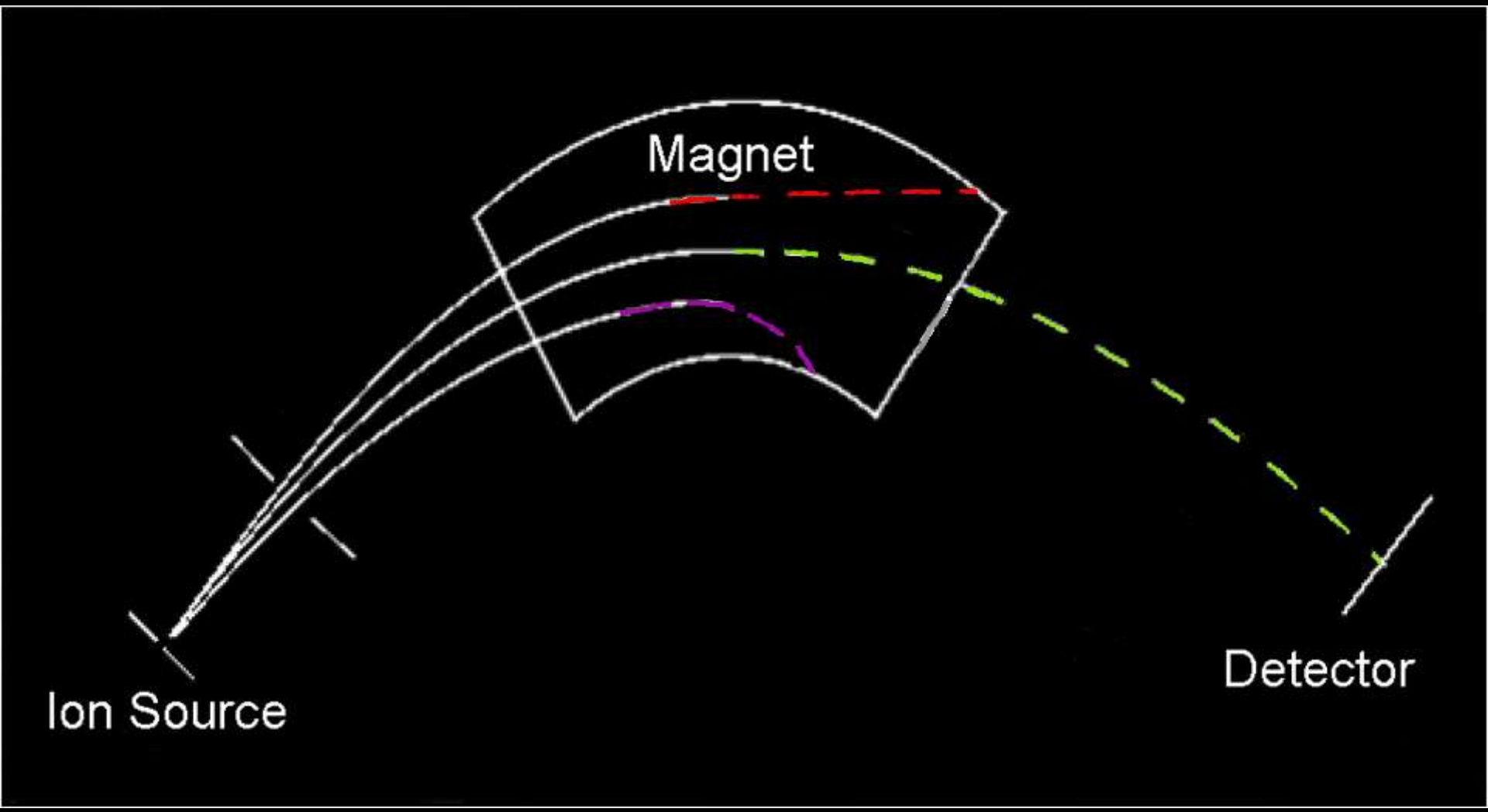


The workings of a mass spectrometer





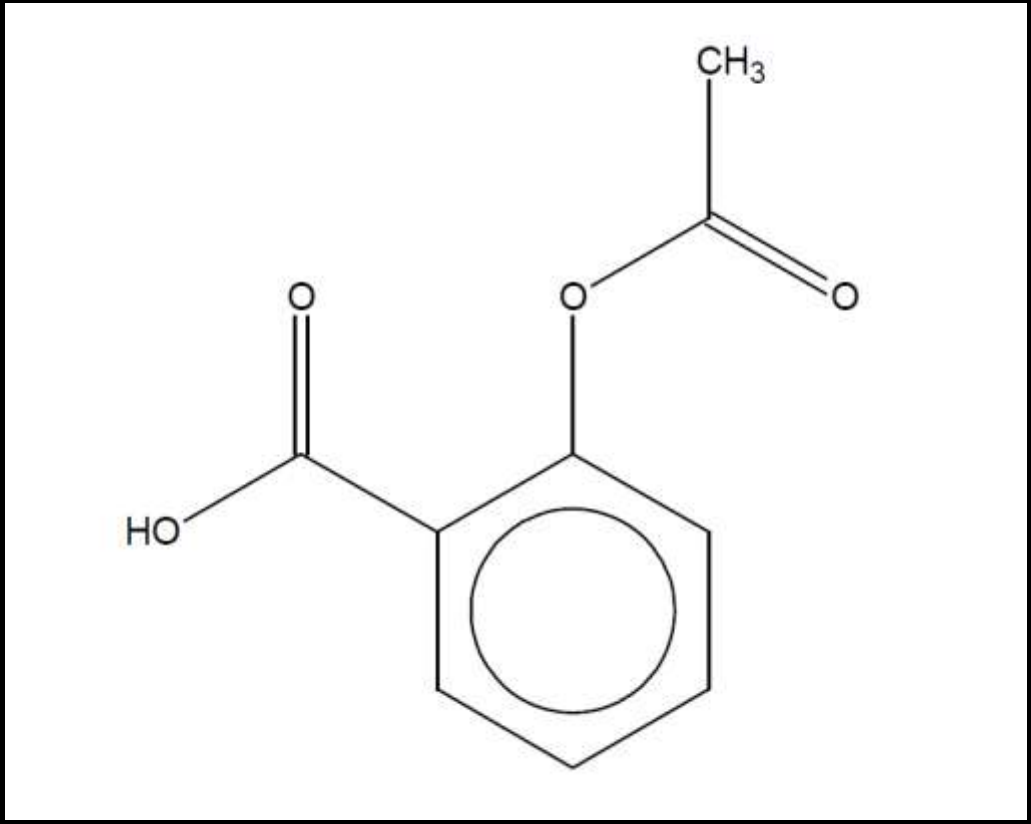

Magnet
Ion Source
Detector


Magnet
Ion Source
Detector

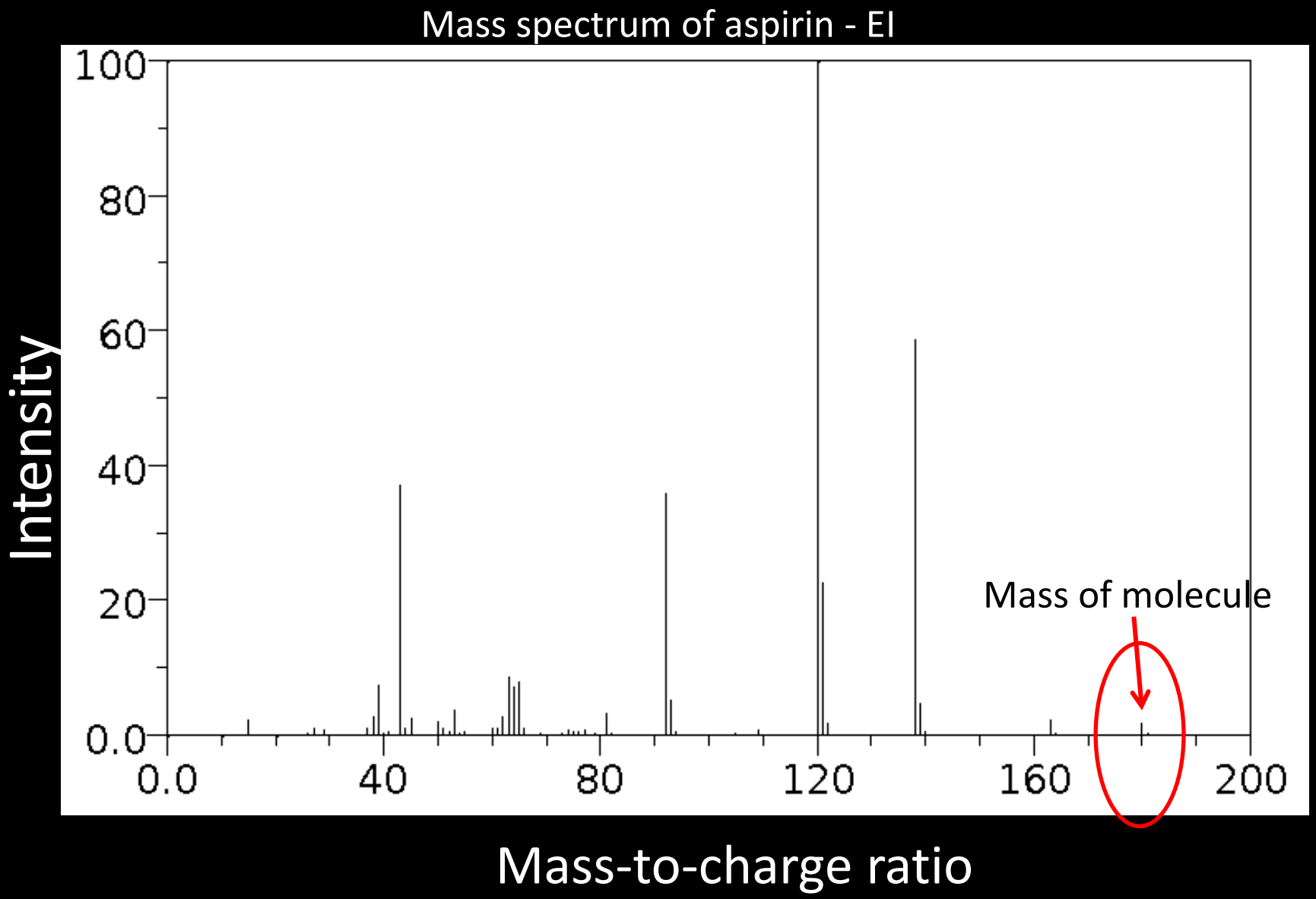
Aspirin

$C_9H_8O_4$

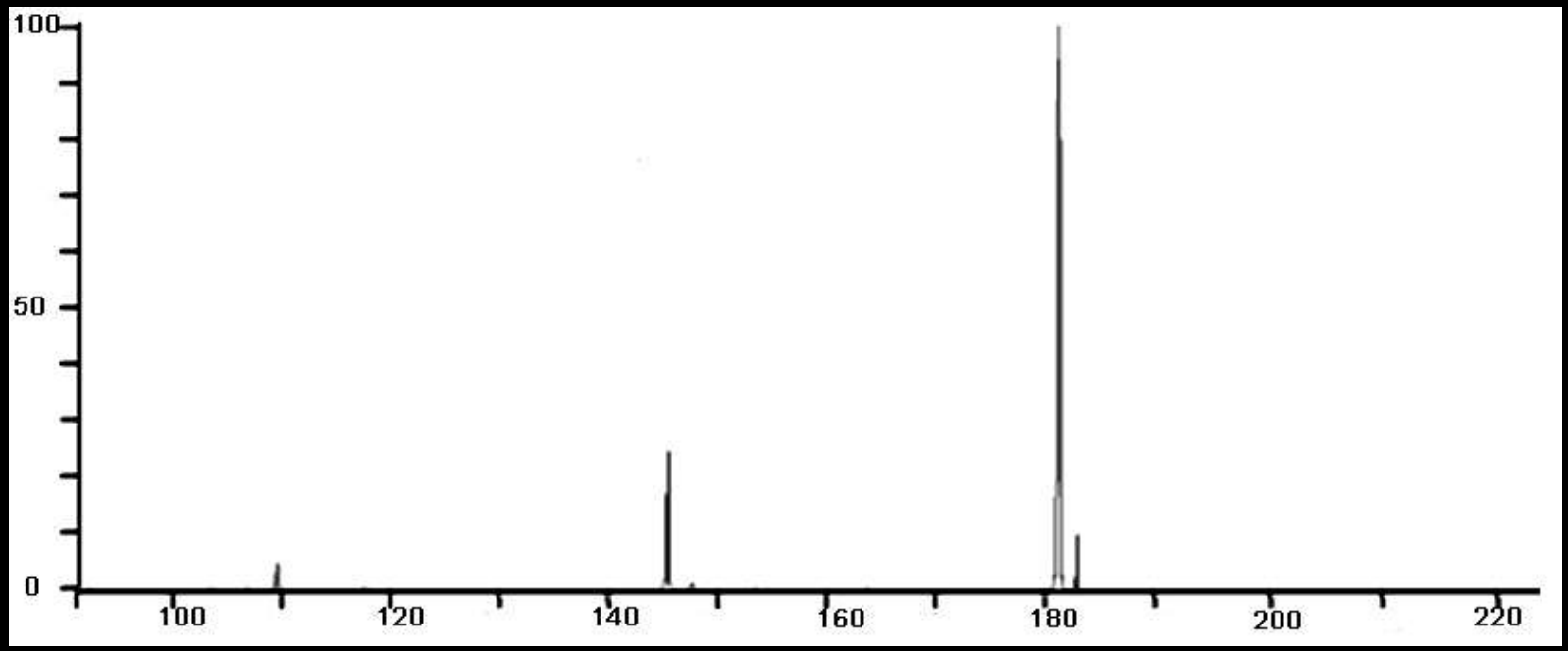
Molecular mass = 180



The end result – a mass spectrum



Mass spectrum of aspirin - ESI



Relative isotopic masses of selected elements

^{1}H 1 1.007 825 032 07(10)

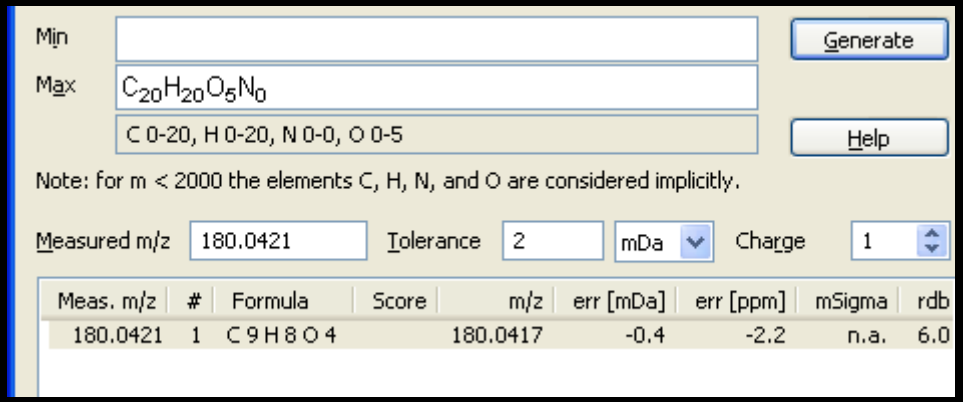
^{12}C 12.000 000 0(0)

^{14}N 14.003 074 004 8(6)

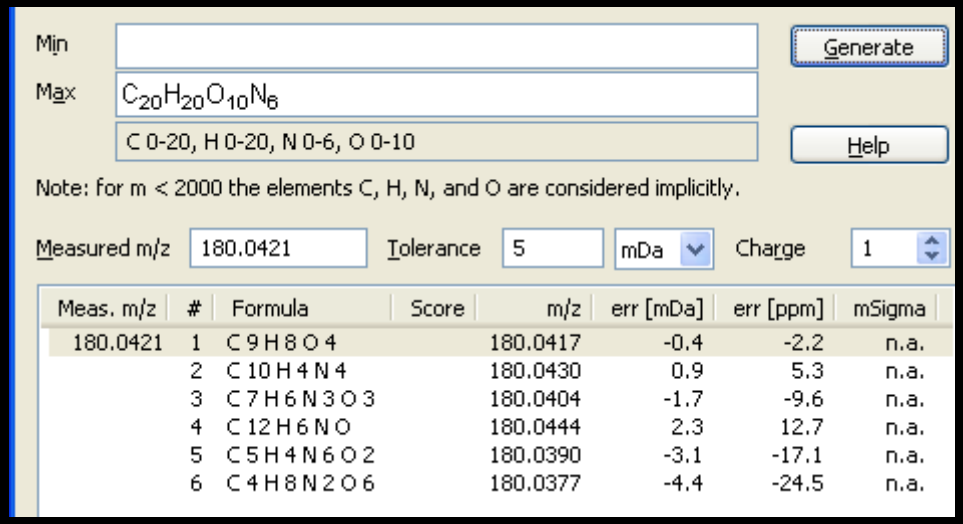
^{16}O 15.994 914 619 56(16)

Mass of electron 0.000548579909 43(23)
Mass of proton 1.007 276 466 77(10)

Measuring masses very accurately



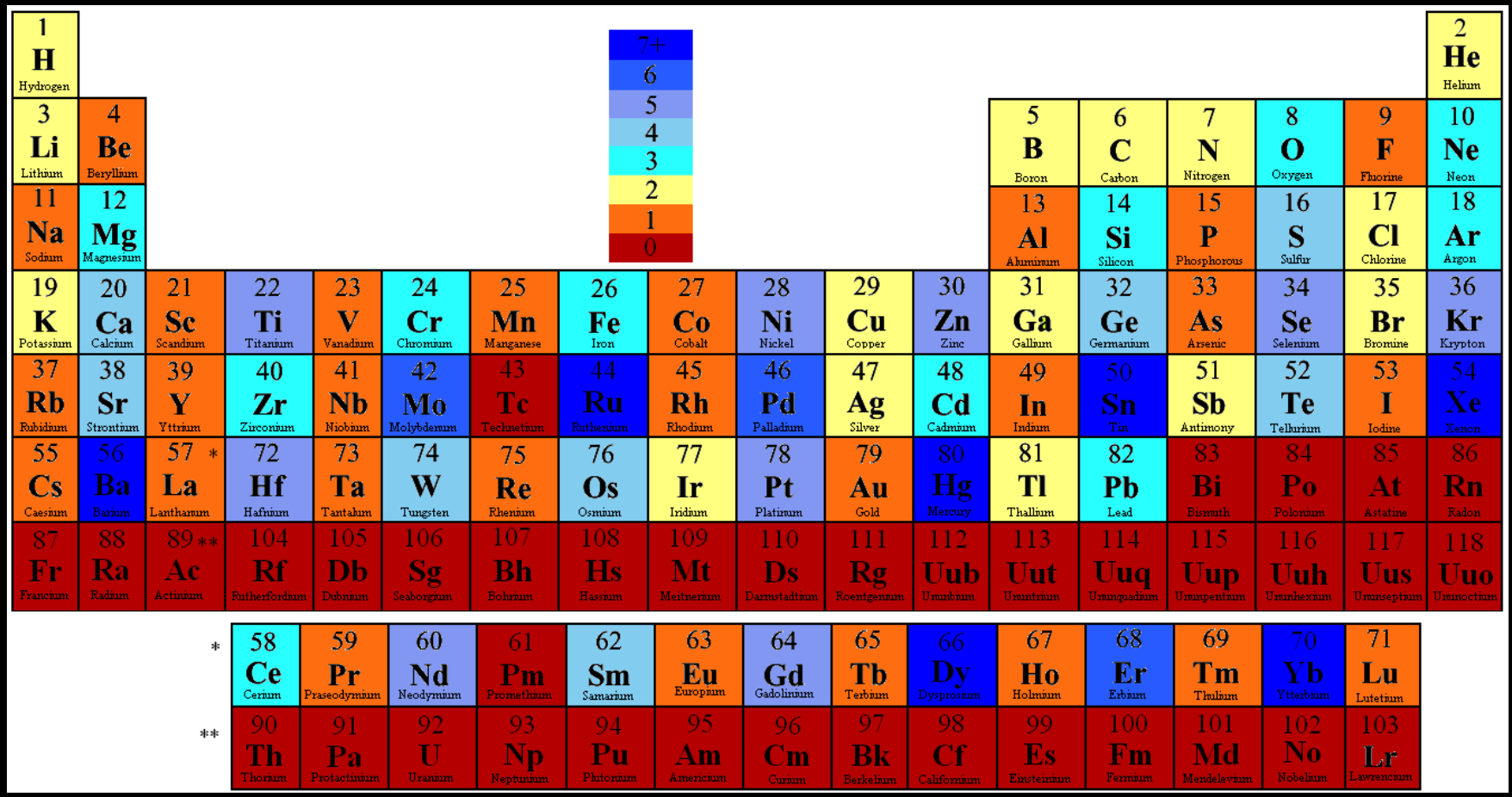
Only C,H and O
2 mDa error

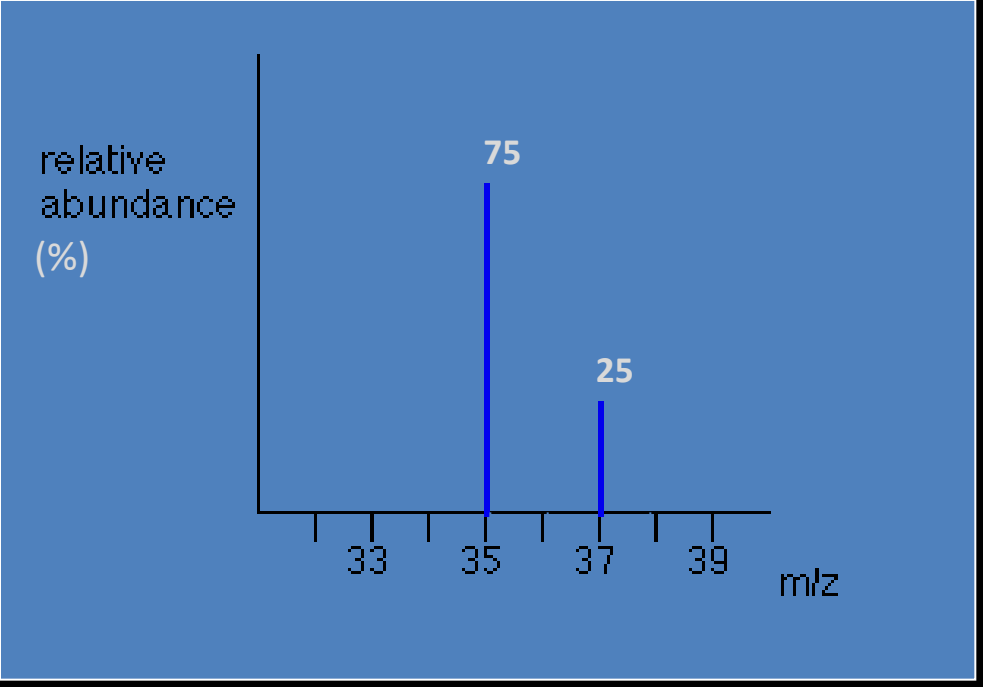


C,H,O and N
5 mDa error

Back to the Lab!

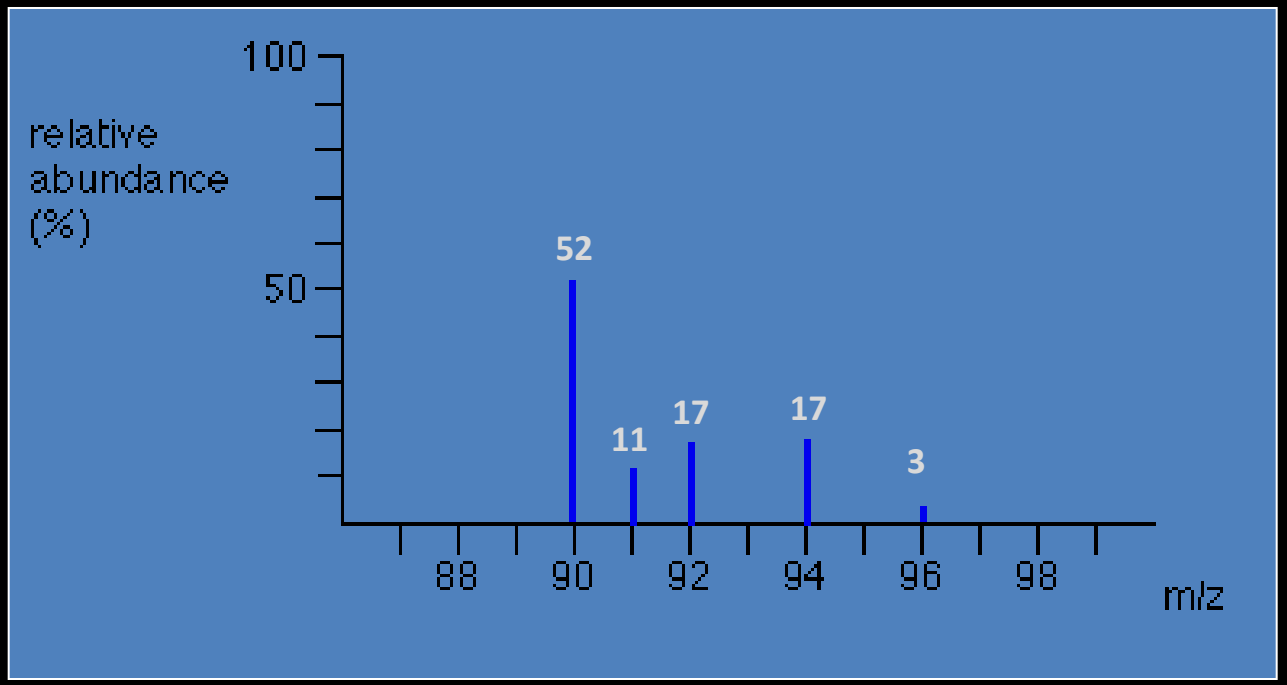
Isotopes of the Elements

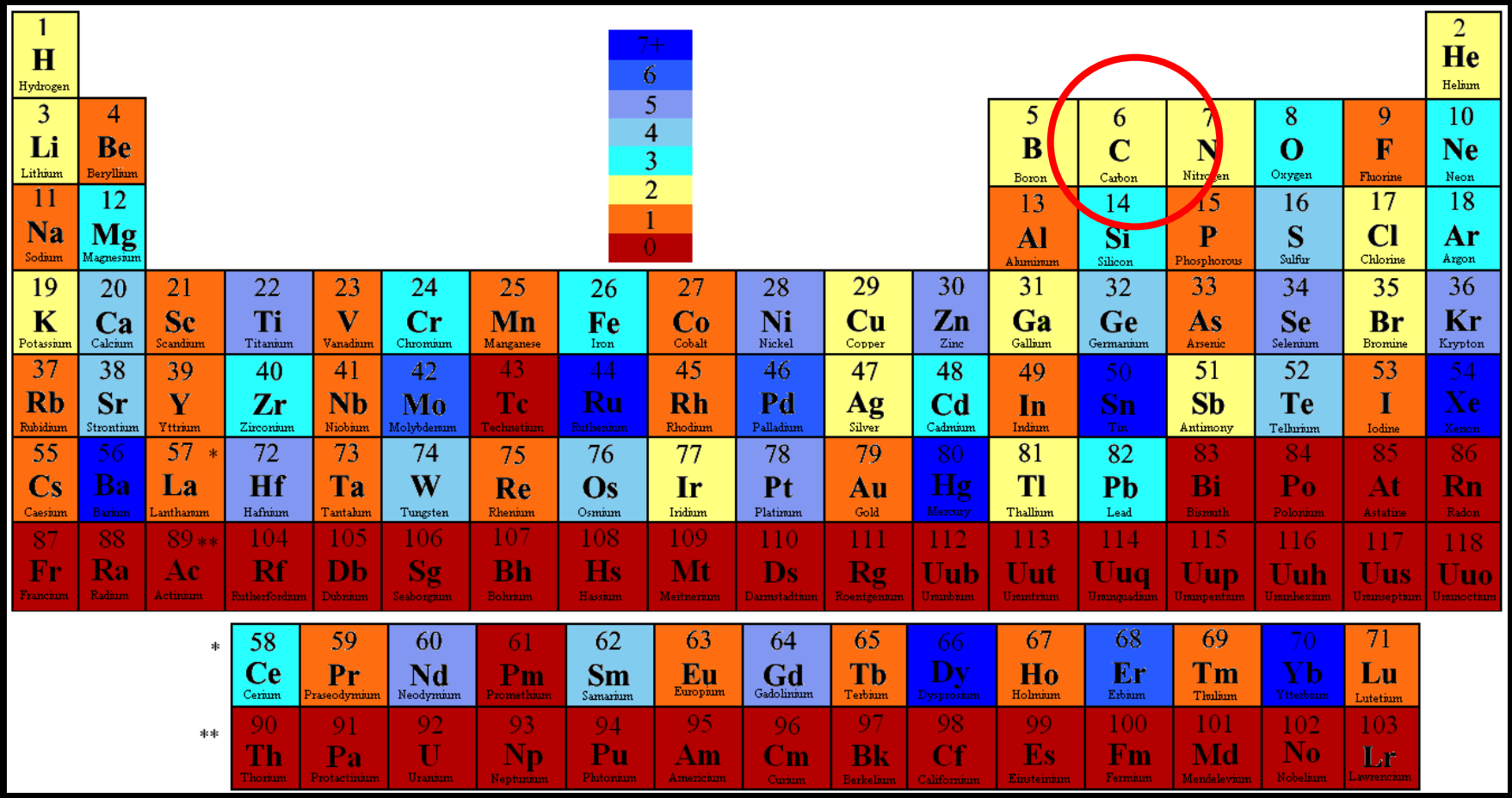




Chlorine isotope pattern

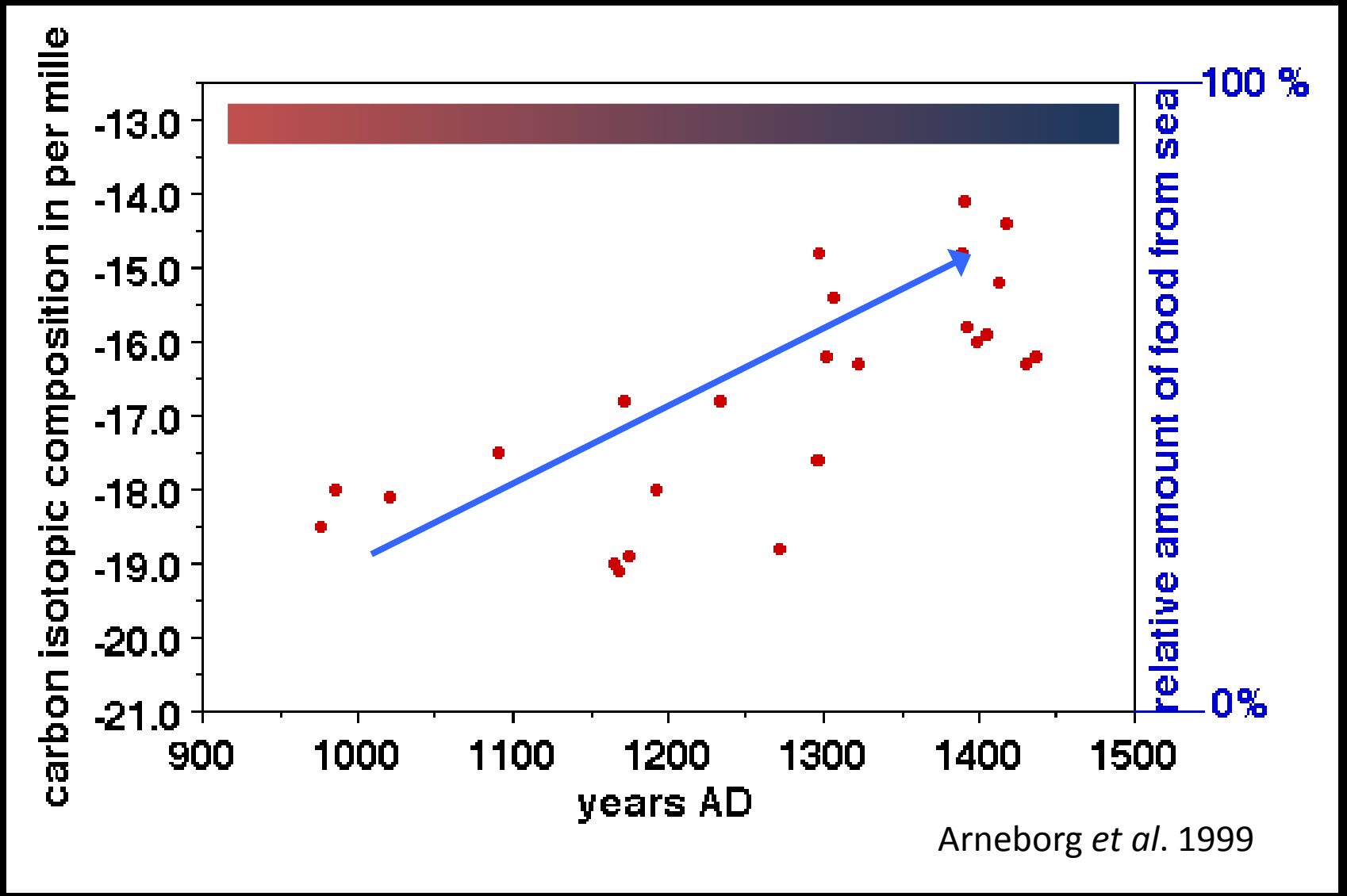
Zirconium isotope pattern




7+
6
5
4
3
2
1
0
1 H Hydrogen
2 He Helium
3 Li Lithium
4 Be Beryllium
5 B Boron
6 C Carbon
7 N Nitrogen
8 O Oxygen
9 F Fluorine
10 Ne Neon
11 Na Sodium
12 Mg Magnesium
13 Al Aluminum
14 Si Silicon
15 P Phosphorous
16 S Sulfur
17 Cl Chlorine
18 Ar Argon
19 K Potassium
20 Ca Calcium
21 Sc Scandium
22 Ti Titanium
23 V Vanadium
24 Cr Chromium
25 Mn Manganese
26 Fe Iron
27 Co Cobalt
28 Ni Nickel
29 Cu Copper
30 Zn Zinc
31 Ga Gallium
32 Ge Germanium
33 As Arsenic
34 Se Selenium
35 Br Bromine
36 Kr Krypton
37 Rb Rubidium
38 Sr Strontium
39 Y Yttrium
40 Zr Zirconium
41 Nb Niobium
42 Mo Molybdenum
43 Tc Technetium
44 Ru Ruthenium
45 Rh Rhodium
46 Pd Palladium
47 Ag Silver
48 Cd Cadmium
49 In Indium
50 Sn Tin
51 Sb Antimony
52 Te Tellurium
53 I Iodine
54 Xe Xenon
55 Cs Caesium
56 Ba Barium
57 * La Lanthanum
72 Hf Hafnium
73 Ta Tantalum
74 W Tungsten
75 Re Rhenium
76 Os Osmium
77 Ir Iridium
78 Pt Platinum
79 Au Gold
80 Hg Mercury
81 Tl Thallium
82 Pb Lead
83 Bi Bismuth
84 Po Polonium
85 At Astatine
86 Rn Radon
87 Fr Francium
88 Ra Radium
89 ** Ac Actinium
104 Rf Rutherfordium
105 Db Dubnium
106 Sg Seaborgium
107 Bh Bohrium
108 Hs Hassium
109 Mt Meitnerium
110 Ds Darmstadtium
111 Rg Roentgenium
112 Uub Ununbium
113 Uut Ununtrium
114 Uuq Ununquadium
115 Uup Ununpentium
116 Uuh Ununhexium
117 Uus Ununseptium
118 Uuo Ununoctium
* 58 Ce Cerium
59 Pr Praseodymium
60 Nd Neodymium
61 Pm Promethium
62 Sm Samarium
63 Eu Europium
64 Gd Gadolinium
65 Tb Terbium
66 Dy Dysprosium
67 Ho Holmium
68 Er Erbium
69 Tm Thulium
70 Yb Ytterbium
71 Lu Lutetium
** 90 Th Thorium
91 Pa Protactinium
92 U Uranium
93 Np Neptunium
94 Pu Plutonium
95 Am Americium
96 Cm Curium
97 Bk Berkelium
98 Cf Californium
99 Es Einsteinium
100 Fm Fermium
101 Md Mendelevium
102 No Nobelium
103 Lr Lawrencium

Carbon stable isotope MS

- Carbon has 3 isotopes
- ^{12}C – naturally occurring - 98.9% of all C atoms
- ^{13}C - naturally occurring – 1.1% of all C atoms
- ^{14}C – radioactive – produced by nuclear explosions and by cosmic rays. About 1 part per trillion of all C atoms



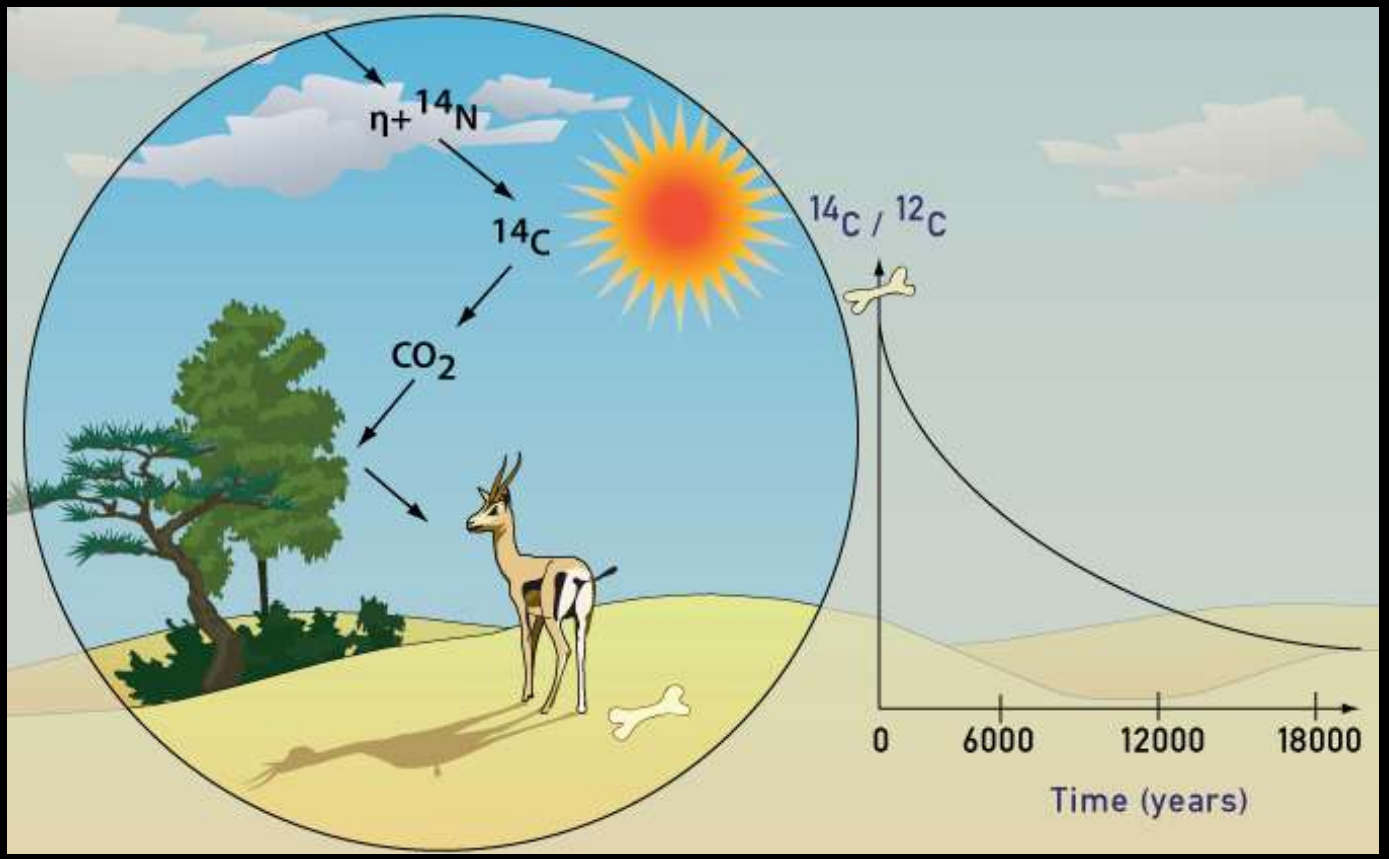
Arneborg *et al*. 1999

‘You are what you eat’

‘(Plus or minus a few per mil)’

But, what about ^{14}C?

- ‘Radiocarbon’ dating



- Carried out by Accelerator Mass Spectrometry (AMS)

Accelerator mass spectrometer at ANSTO, Australia


7
8
9
10

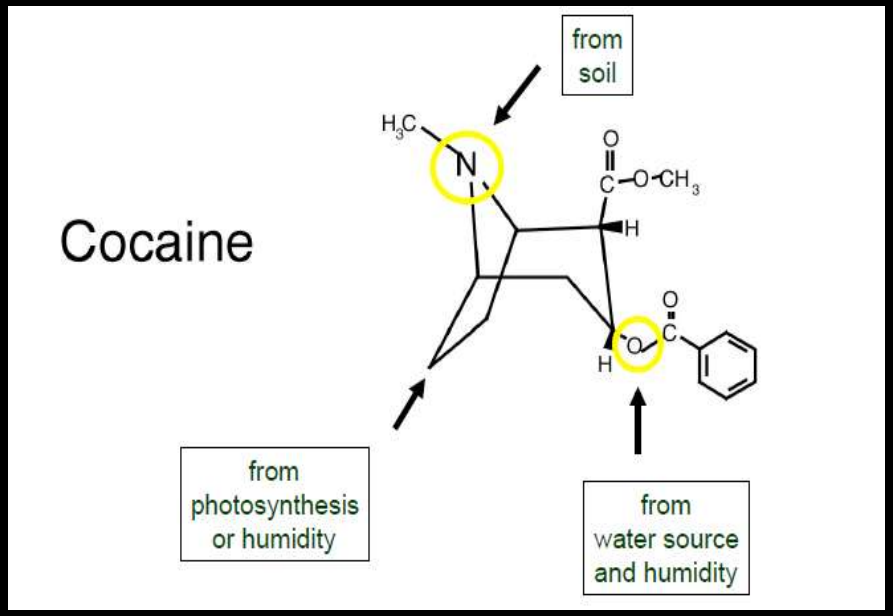
Any other things that Isotope Mass Spectrometry can do?

- Food adulteration analysis

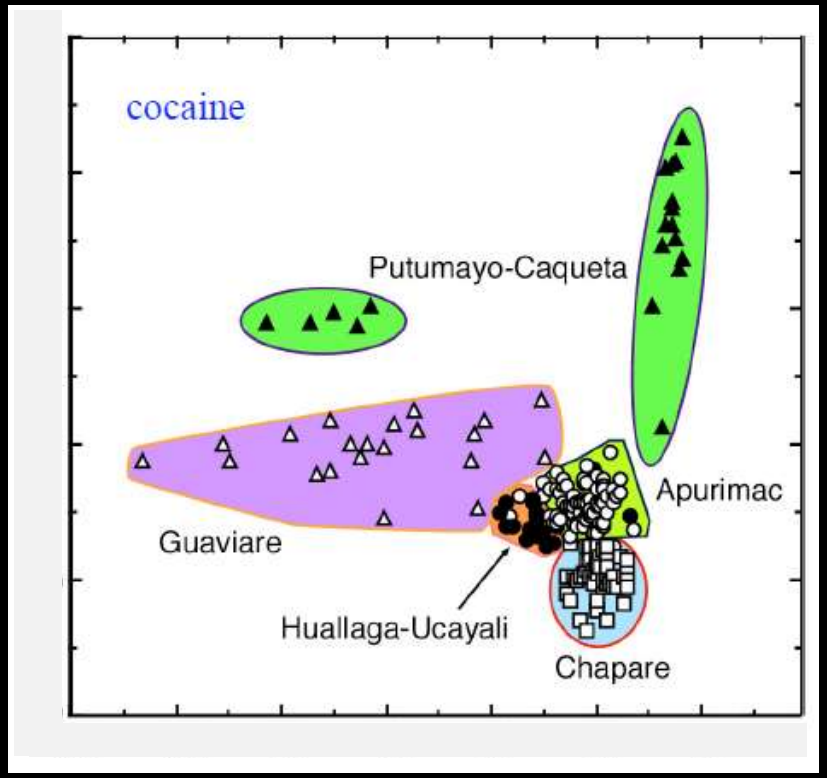
Fruit juice

Wine

- Food origin studies
- Source apportionment of pollution
- Drug doping analyses



^{15}N

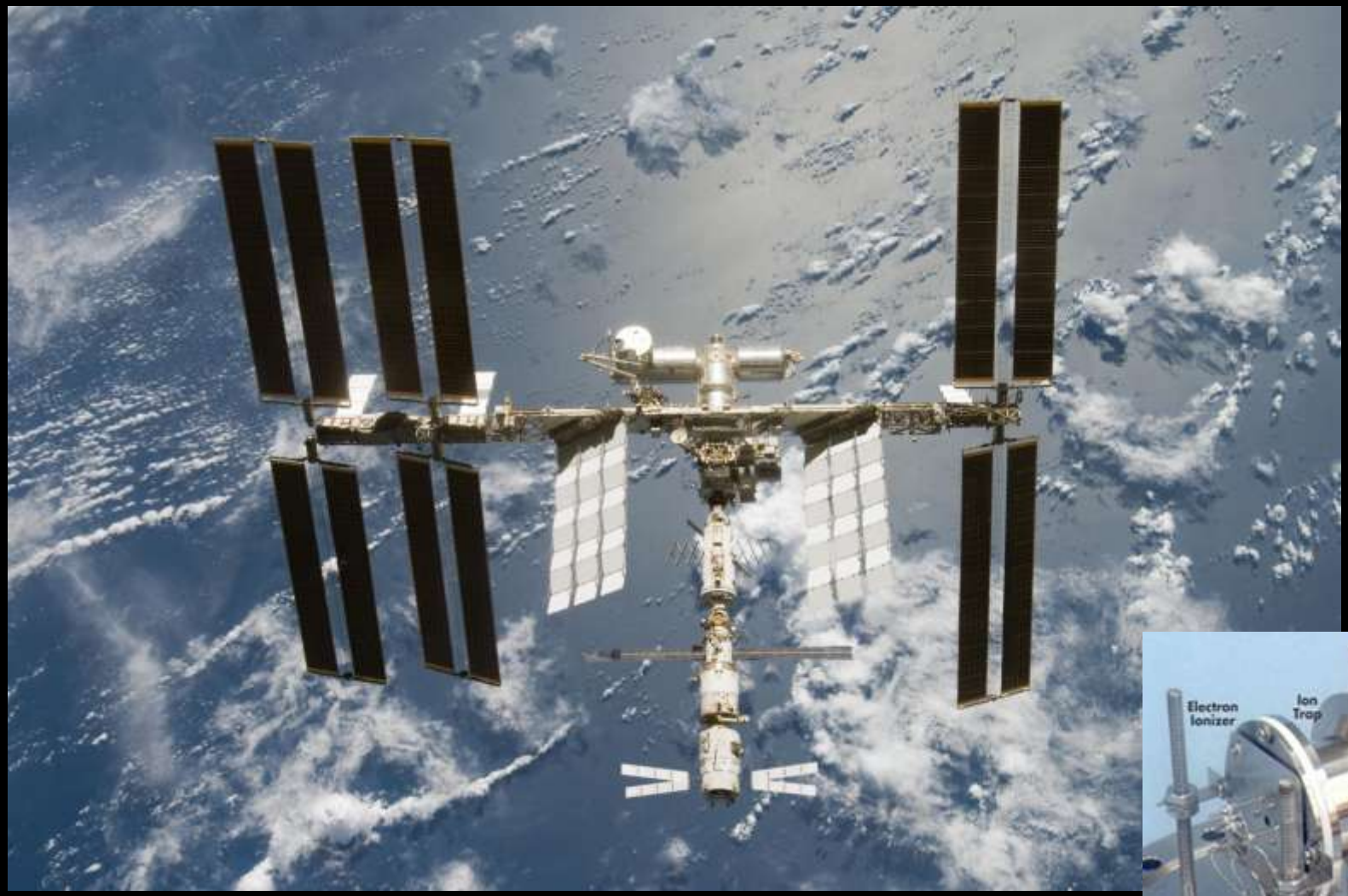


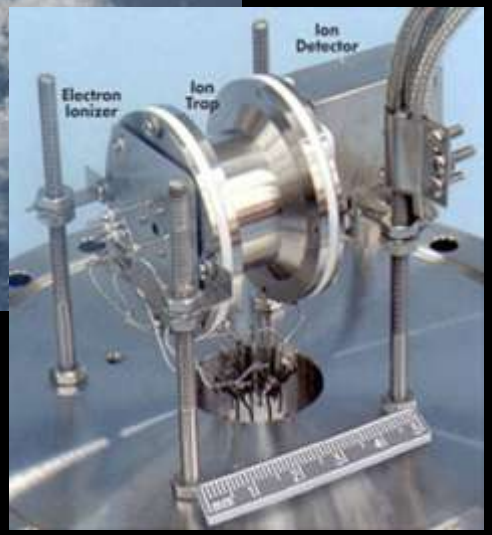
^{13}C

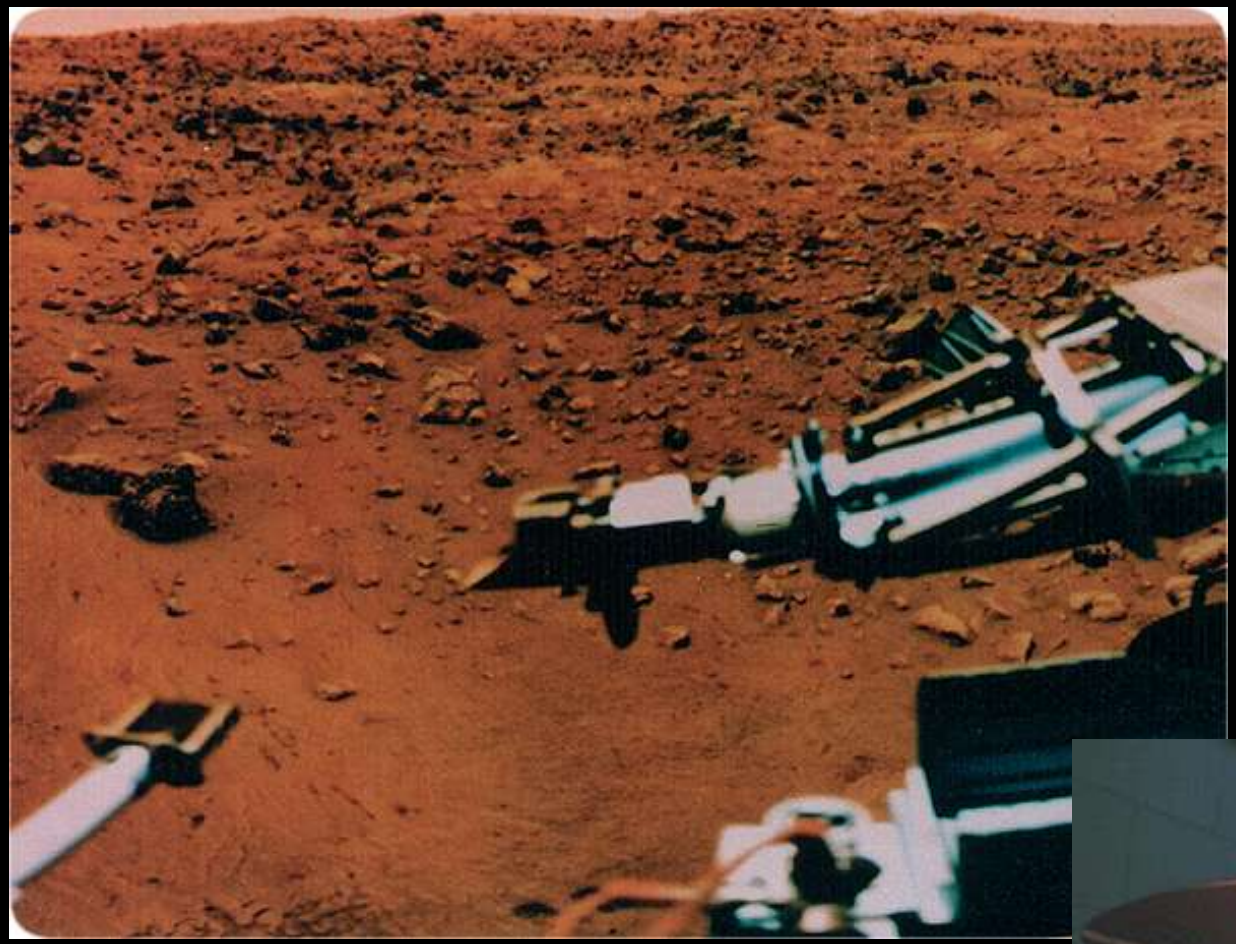
IsoForensics Inc.

Mass Specs in Spaaaaaace!!

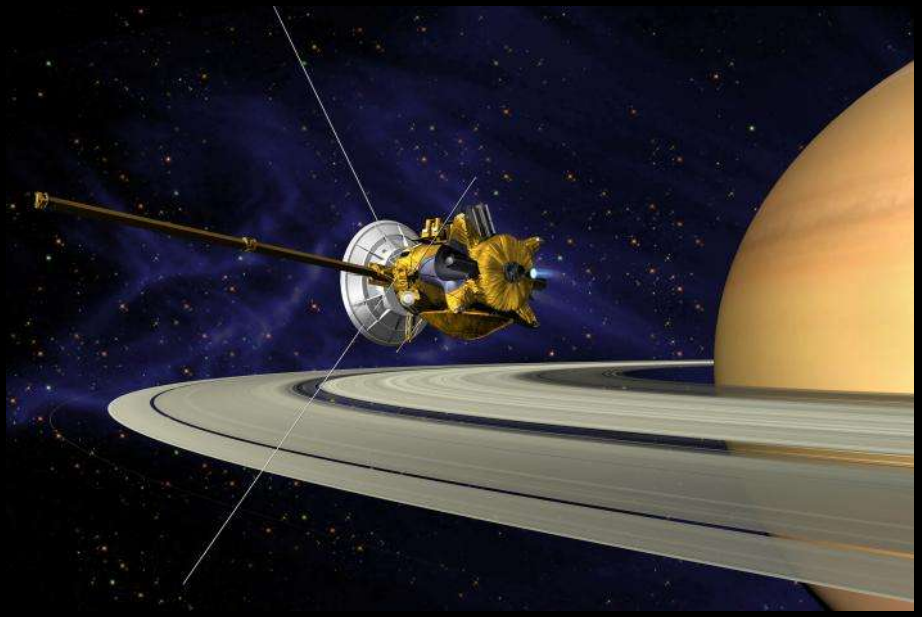
(With apologies to the Muppets)

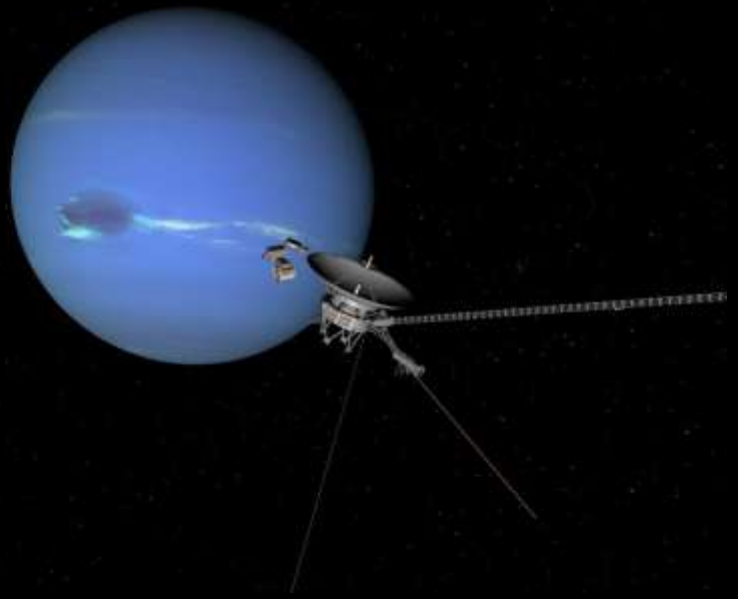



Ion
Detector
Electron
Ionizer
Ion
Trap




CCCP

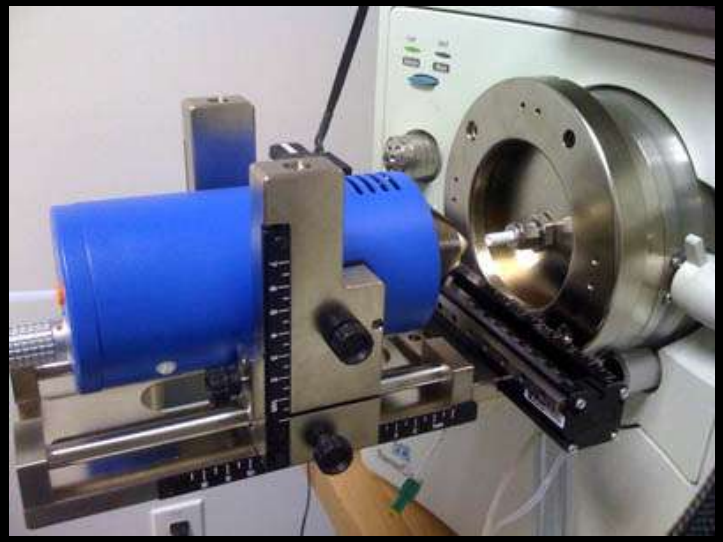




Another demonstration - if time allows

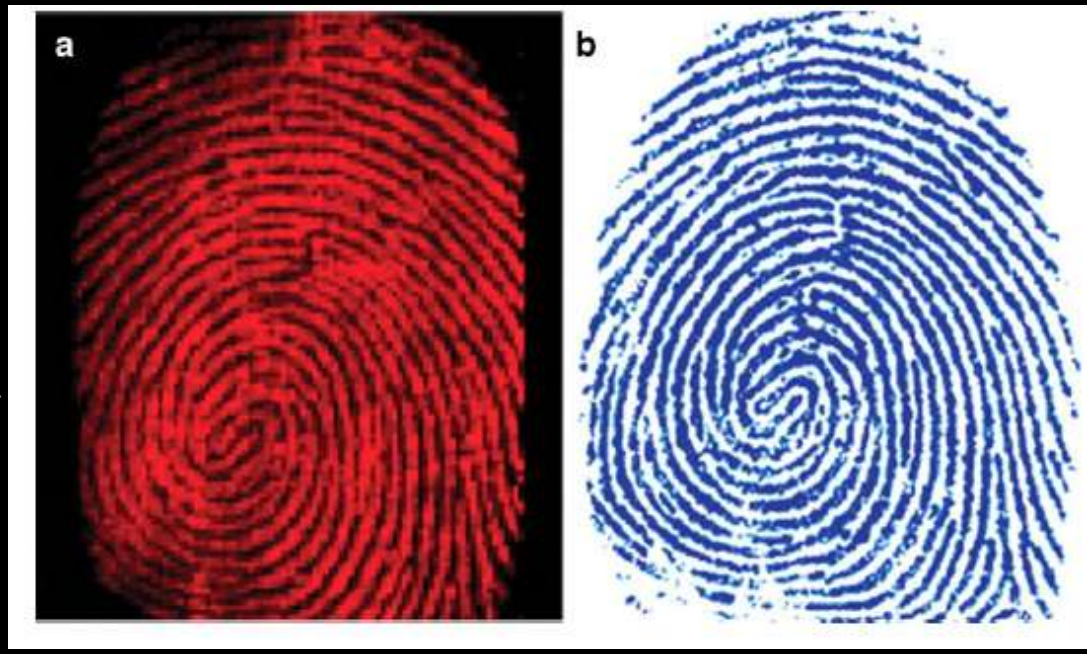
The future of MS

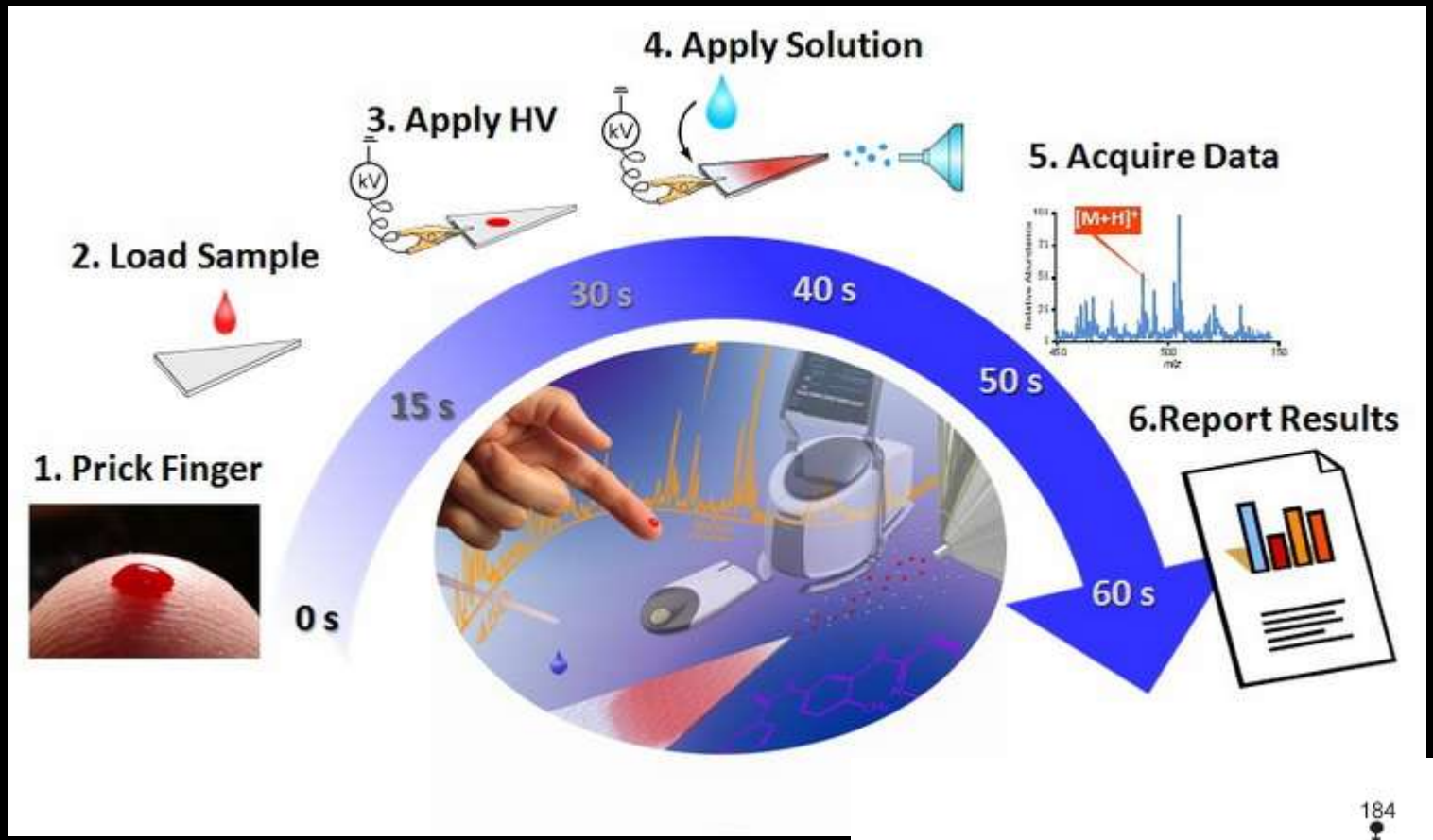
Ambient MS



MS detection of cocaine on a latent fingerprint on a glass window

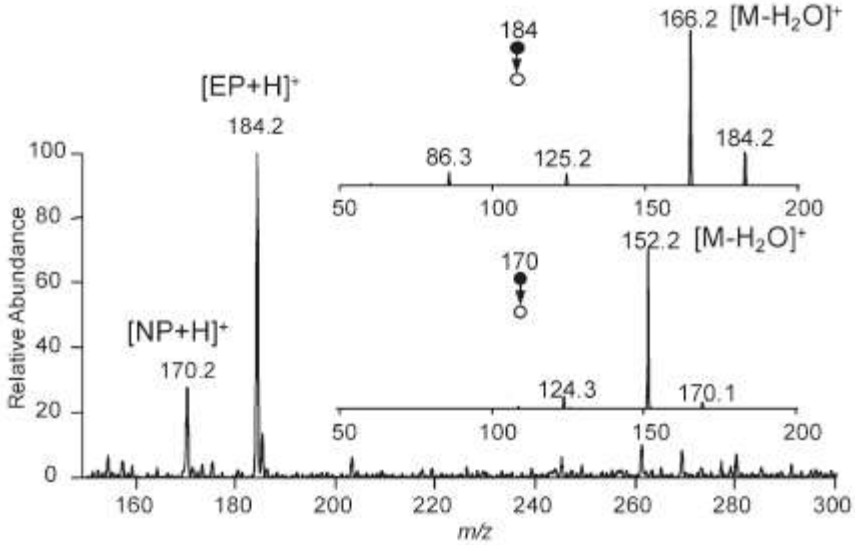
Alberici *et al*., Anal Bioanal Chem (2010) **398**:265–294





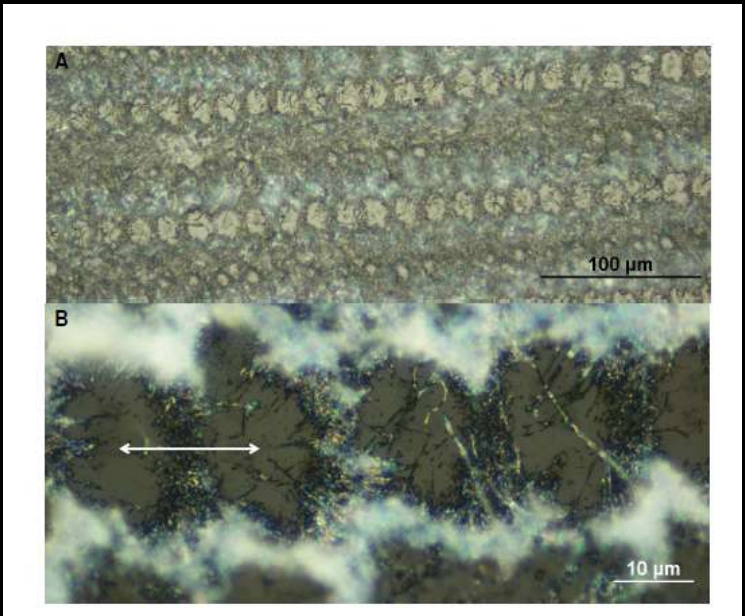
Paper Spray Ionisation

Ouyang *et al.*, Purdue Univ.

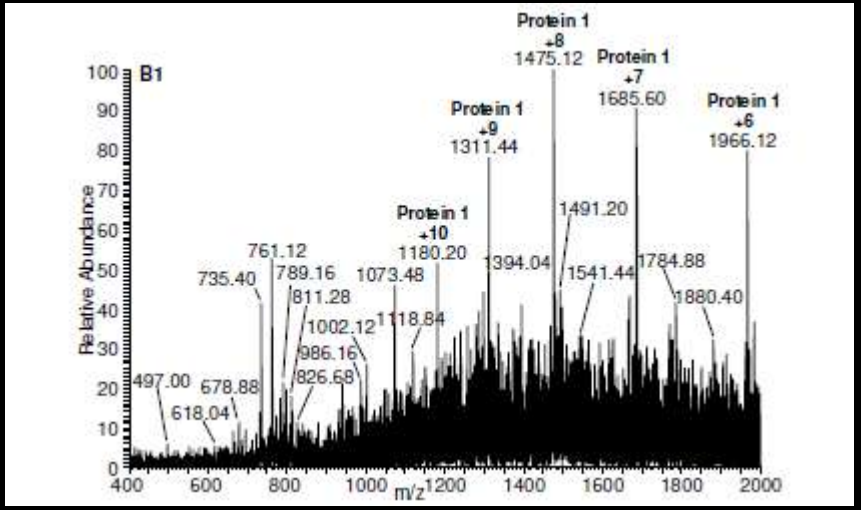


STOP PRESS!

- LaserSpray Ionisation (Inutan *et al*., Wayne State Uni)

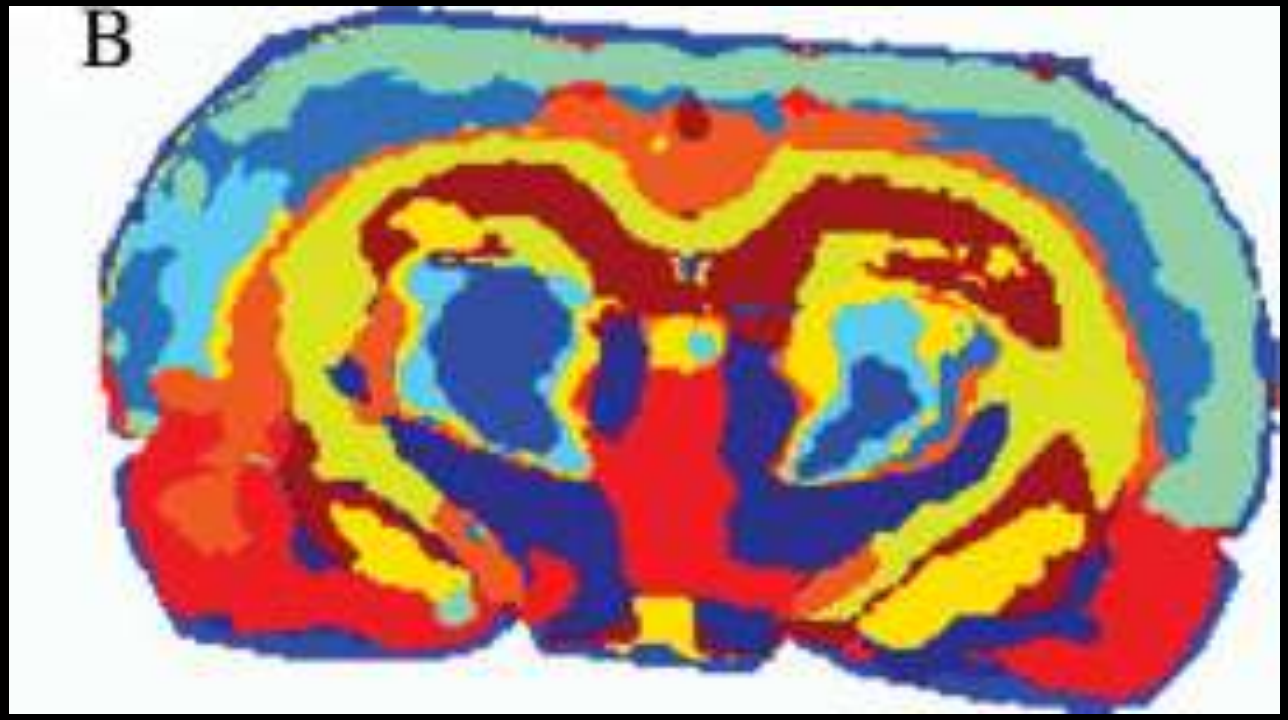


Section of mouse brain

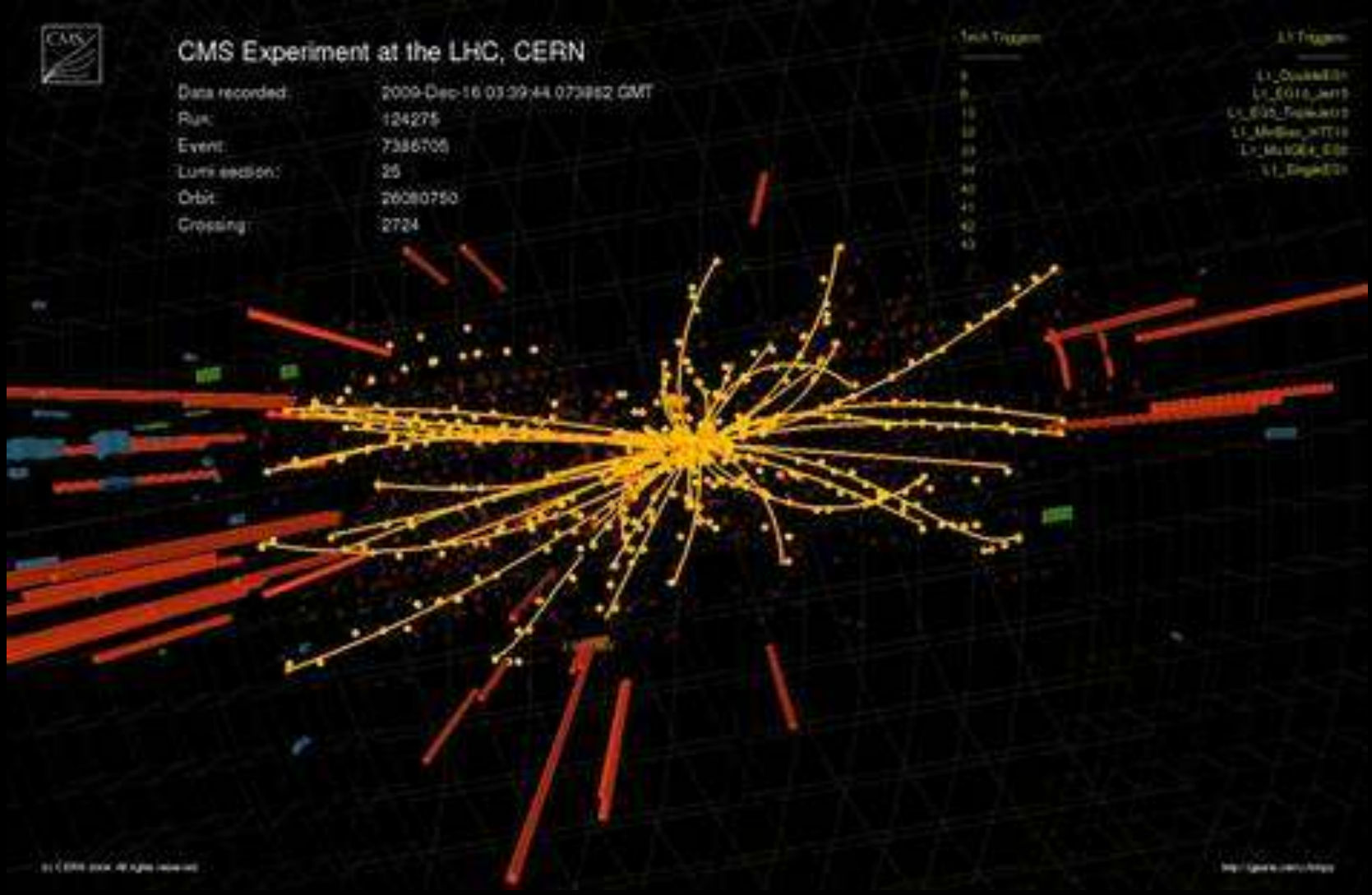


STOP PRESS!

- MS imaging (Watrous *et al*., UCSD)



The ultimate mass spectrometer?


CMS Experiment at the LHC, CERN
Data recorded: 2009-Dec-16 03:39:44.073862 GMT
Run: 124275
Event: 7386705
Lumi section: 25
Orbit: 26080750
Crossing: 2724

Papers in the scientific literature about MS analyses

Food	Oil	Air pollution	pharma*	drug	genom*
6838	5184	2639	4510	20039	1169
8206	5706	1318	12446	34345	2089
24615	12982	15666	15776	59764	8416

- *Source: ISI Web of Knowledge*

Science Citation Index 1899-present

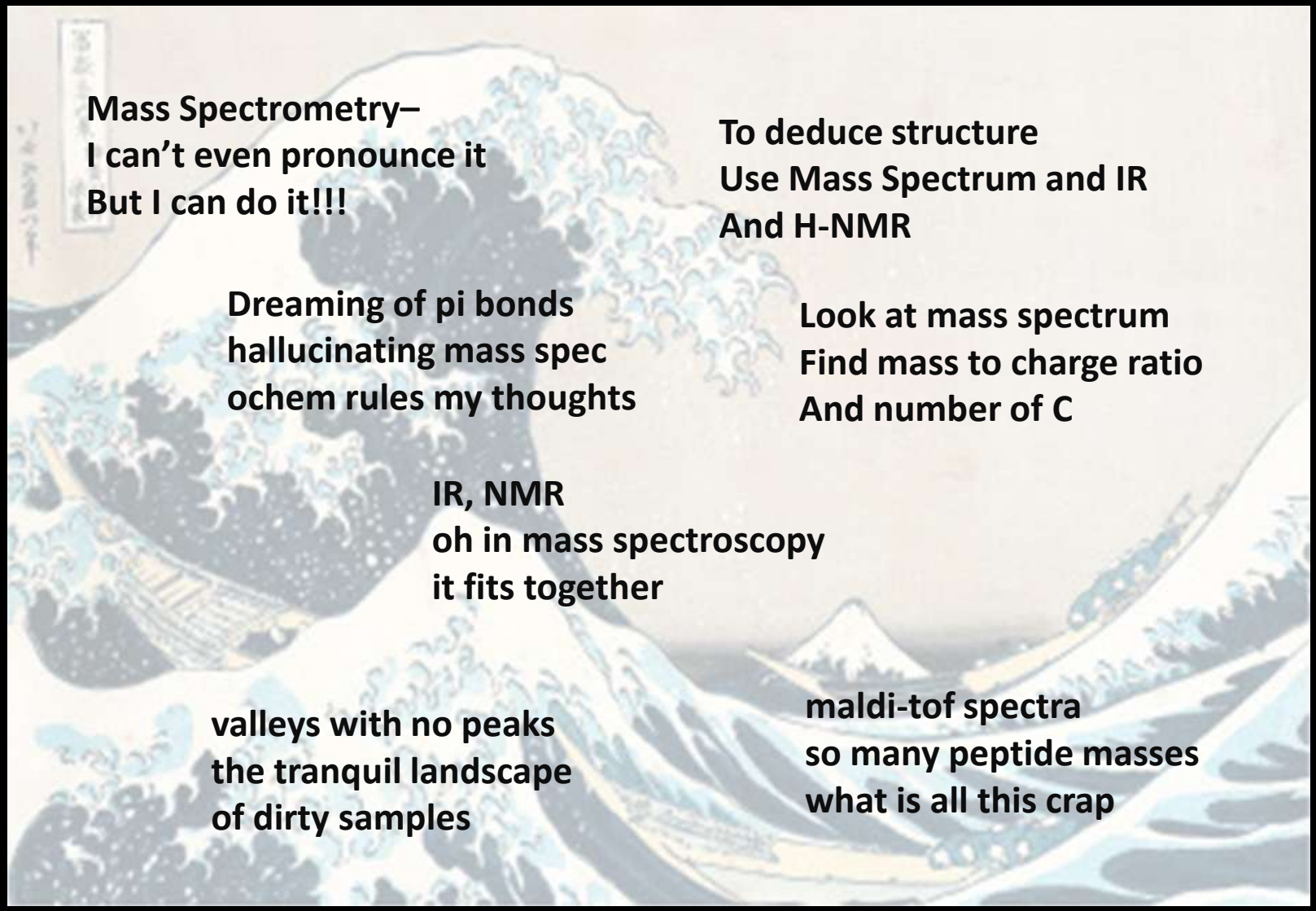
Key:

Infrared spectroscopy

Nuclear Magnetic Resonance spectroscopy

Mass Spectrometry

Haiku-MS



Mass Spectrometry–
I can't even pronounce it
But I can do it!!!

To deduce structure
Use Mass Spectrum and IR
And H-NMR

Dreaming of pi bonds
hallucinating mass spec
ochem rules my thoughts

Look at mass spectrum
Find mass to charge ratio
And number of C

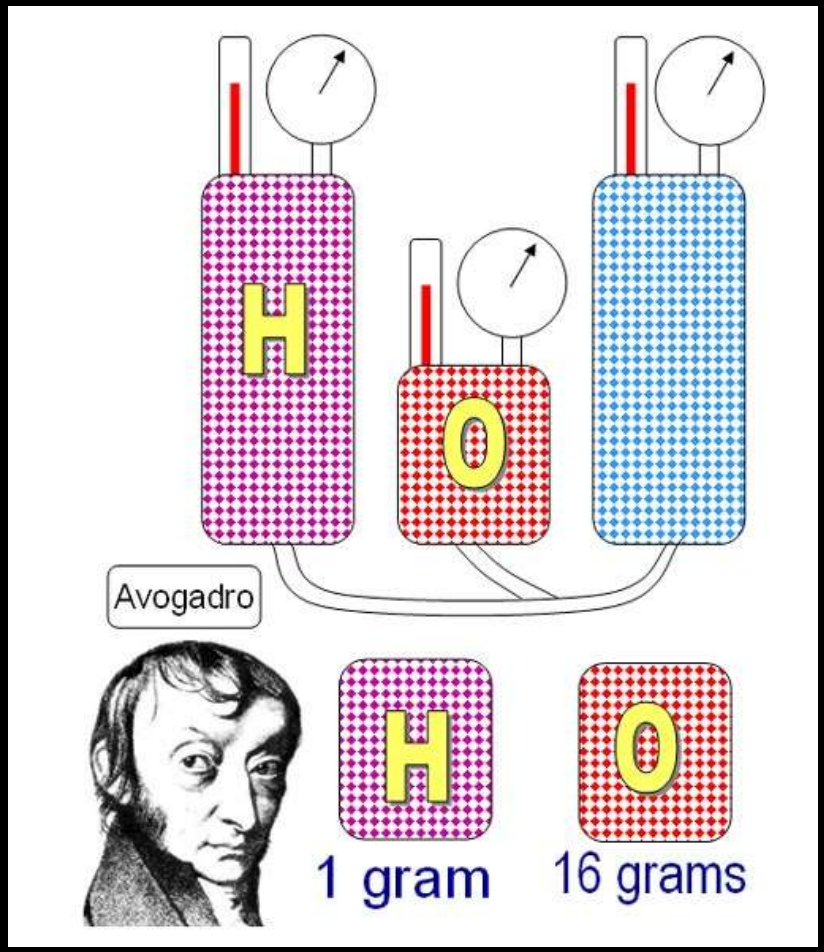
IR, NMR
oh in mass spectroscopy
it fits together

valleys with no peaks
the tranquil landscape
of dirty samples

maldi-tof spectra
so many peptide masses
what is all this crap

Steven A. Hardinger, Department of Chemistry & Biochemistry, UCLA

No, I haven't forgotten about Avogadro (or zeptomole)

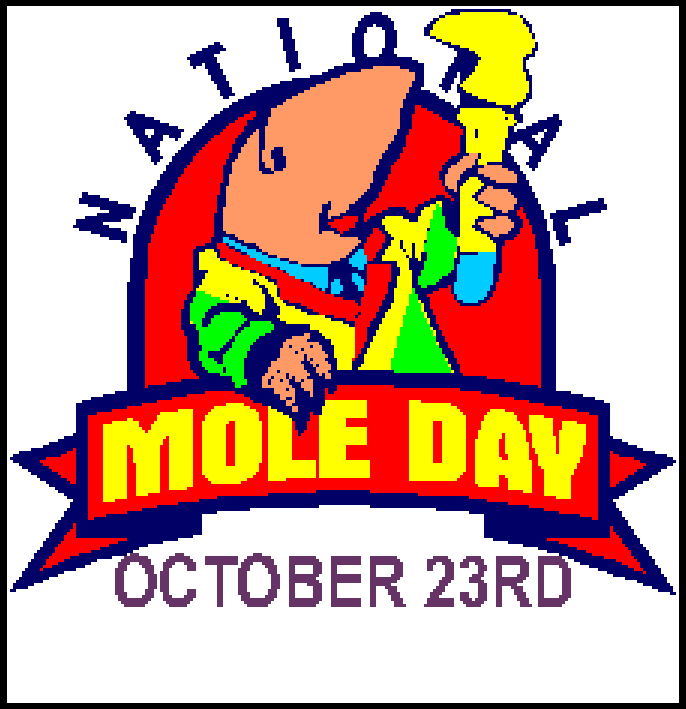


Chemistryland.com

Q: What do you call a tooth in a glass of water?

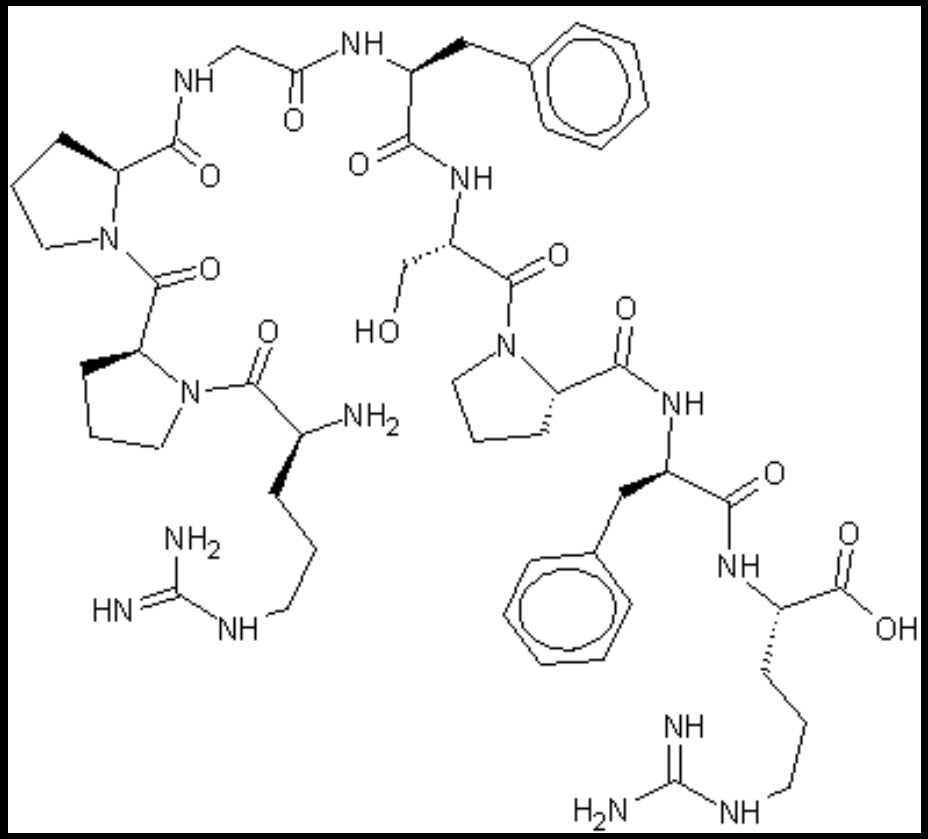
Q: What do you call a tooth in a glass of water?

A: A one-molar solution.



Celebrated annually on October 23 from 6:0 a.m. to 6:02 p.m. (6.02×10^{23})

http://www.moleday.org/index.htm



Bradykinin

10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	µ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y

Thanks to

Graham Coxhill
Sam Tang
June McCombie
Martyn Poliakoff
Peter Morgan-Tansley
Patrick Hutchinson
IS-teaching Support
Fellow Technical Support Staff