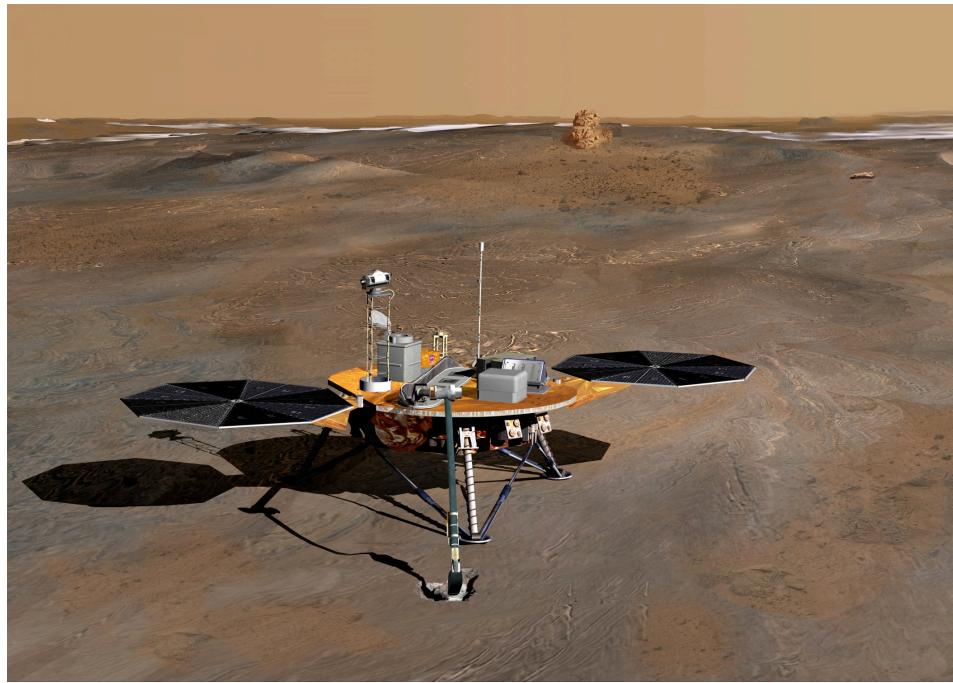


Mass Spectrometry Table of Contents

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Chemistry in Context

Life on Mars. The Viking and Phoenix landers were sent to Mars to determine if life ever existed there. What were these spacecrafts looking for and how did they perform the analyses?



Mass Spectrometry

Concept Test

The 12.01 on the periodic table for C indicates that:

- (A) A carbon atom weighs 12.01 g
- (B) A carbon atom weighs 12.01 lbs
- (C) A carbon atom weighs 12.01×10^{-24} g
- (D) It does not indicate anything pertaining to the absolute mass of a carbon atom

Mass Spectrometry

What is atomic mass?

Atomic mass units (amu) or daltons (Da): Defined relative to ^{12}C , which is assigned a mass of exactly 12 amu.

H has a mass of 1.008 relative to carbon-12, so it is assigned a mass of 1.008 amu.

1 amu = 1 Da = an absolute mass of $1.6605387 \times 10^{-27}$ kg

The mole provides the link between numbers of atoms and mass of atoms. It is defined as the amount of a substance that contains the same number of entities as there are atoms in exactly 12 g of C-12. This number is Avogadro's number.

Example: $1.008 \text{ amu} / 6.02 \times 10^{23} = 1.67 \times 10^{-24} \text{ g}$

Mass Spectrometry

A mass spectrometer is an instrument that produces ions and separates them according to their mass-to-charge ratios, m/z.

Mass to charge ratio

A unitless ratio of mass number to the number of charges, z, on the ion.

For $^{12}\text{C} \text{ } ^1\text{H}_4^+$ (methane cation) the m/z is 16.0313/1.

For $^{13}\text{C} \text{ } ^1\text{H}_4^{2+}$ the m/z is 17.0346/2 = 8.5173.

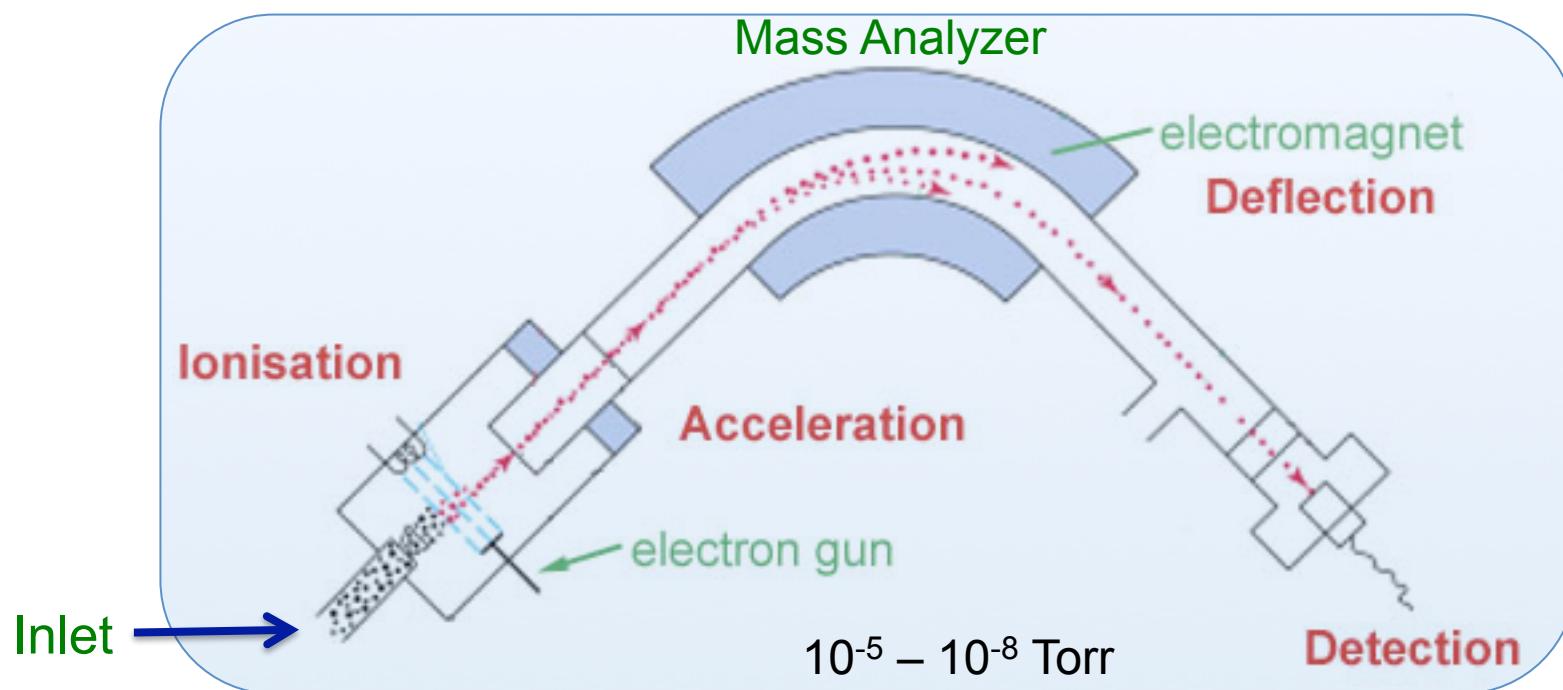
Ions in mass spec are usually singly charged so the z is frequently dropped, but this is not strictly correct.

Mass Spectrometry

General steps

- (1) Atomization
- (2) Ionization
- (3) Separation of ions
- (4) Detection-Counting the ions

General Schematic



Molecular Mass Spectra



This is often done via electron bombardment:



Where M is a molecule and m_x are fragments of M

M^+ is called the molecular ion

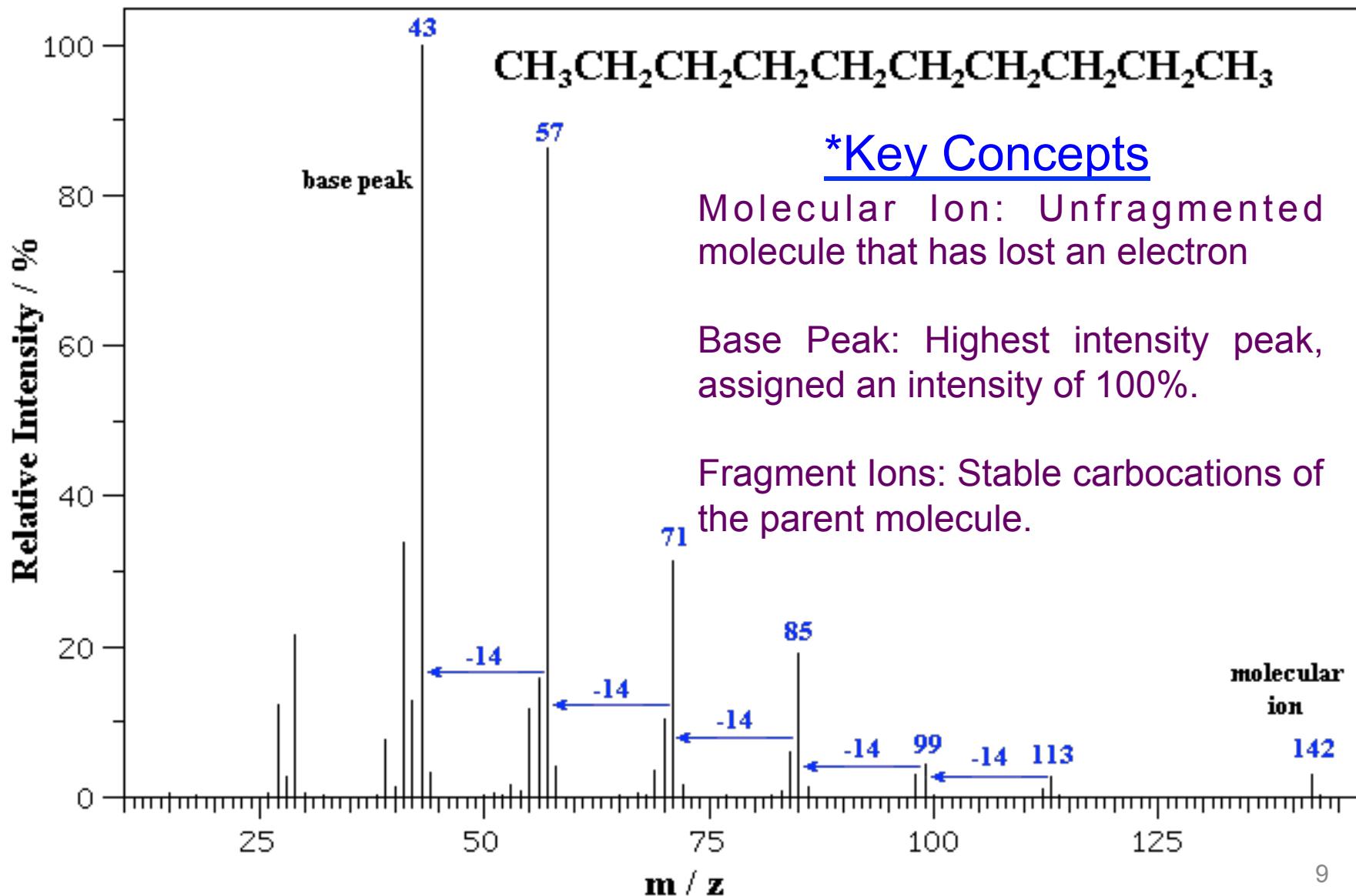
Molecular Mass Spectra

Ion-molecule collisions often occur:



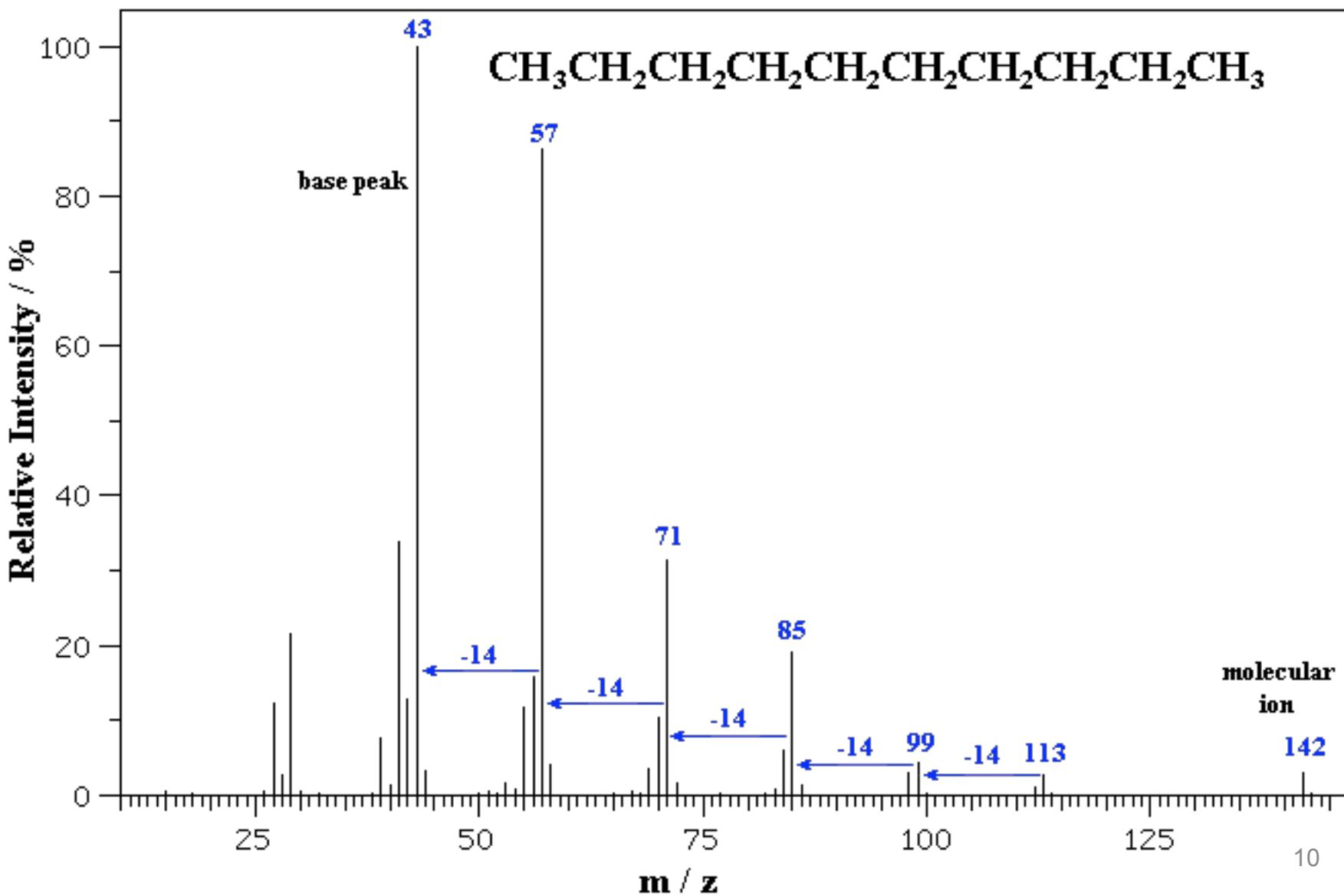
Typically only hydrogen atom transfer is observed, which yields a peak at $m/z = (M+1)^+$

Mass Spectra

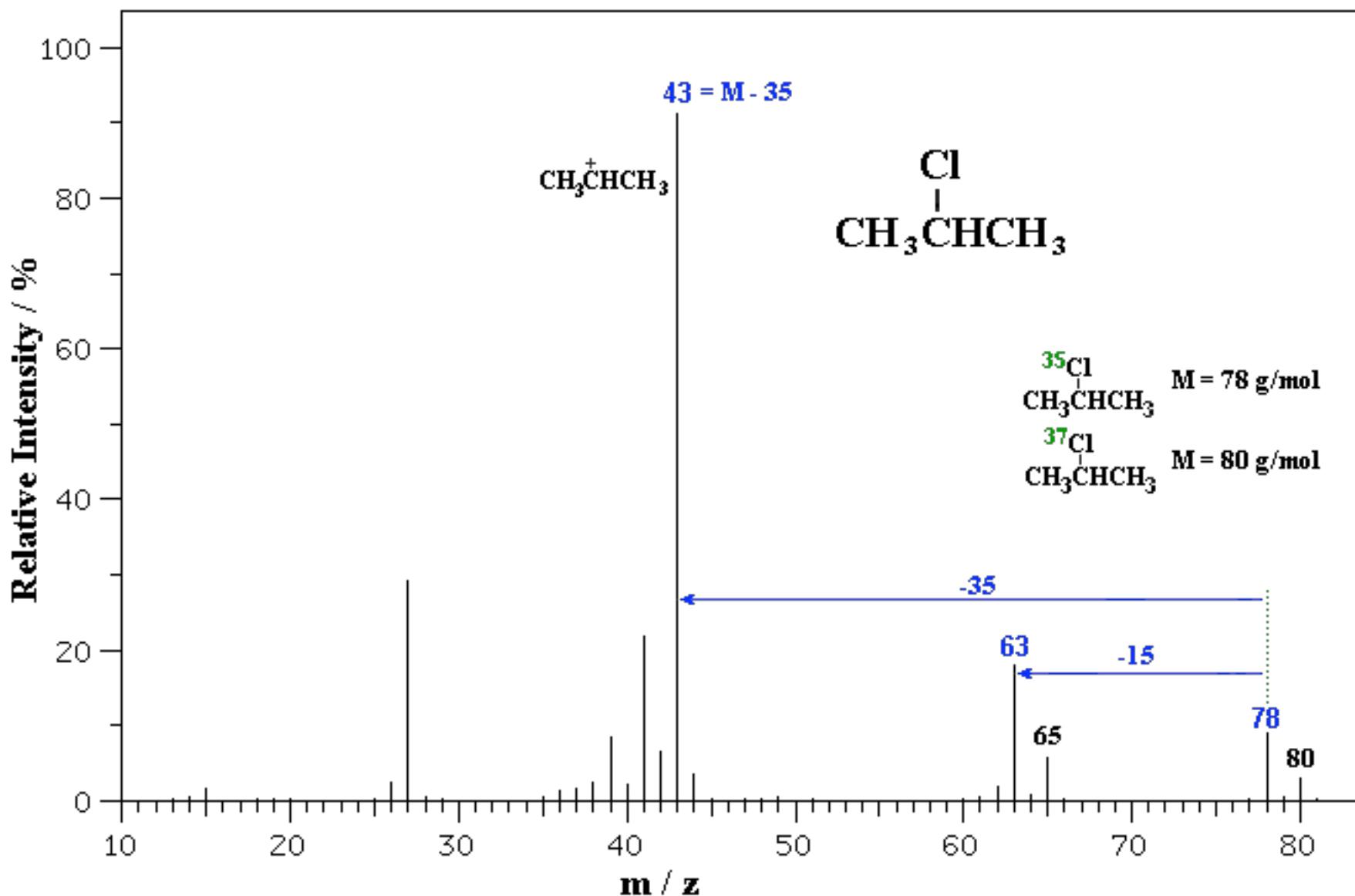


Mass Spectra

Notice the successive loss of $m/z = 14$. This corresponds to fragments of the molecular ion that have lost CH_2 .



Mass Spectra



Concept Test

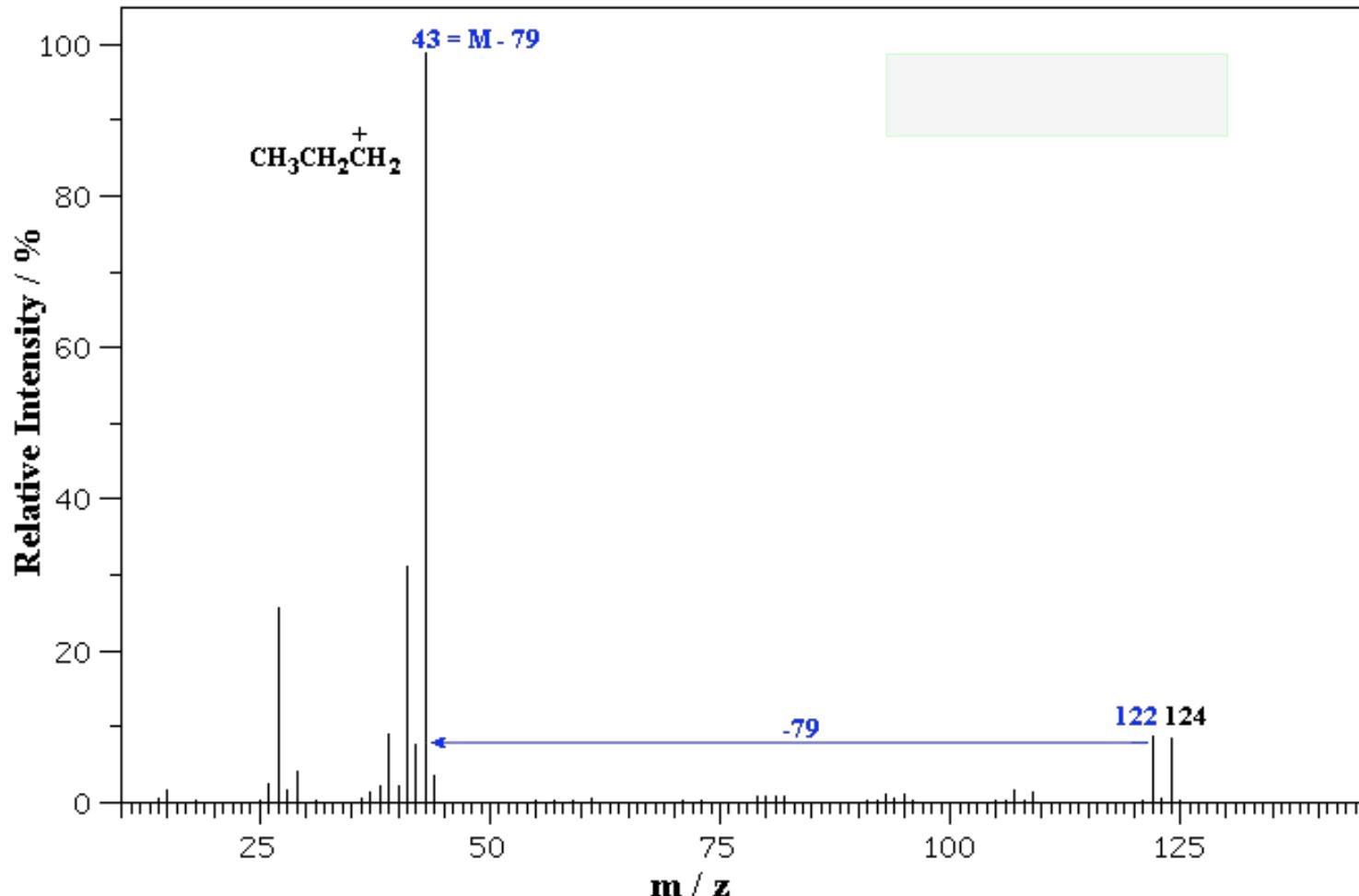
The spectrum below is from a hydrocarbon containing which substituent?

(A) Cl

(B) $-\text{C}_5\text{H}_5$

(C) Br

(D) OH



Concept Test

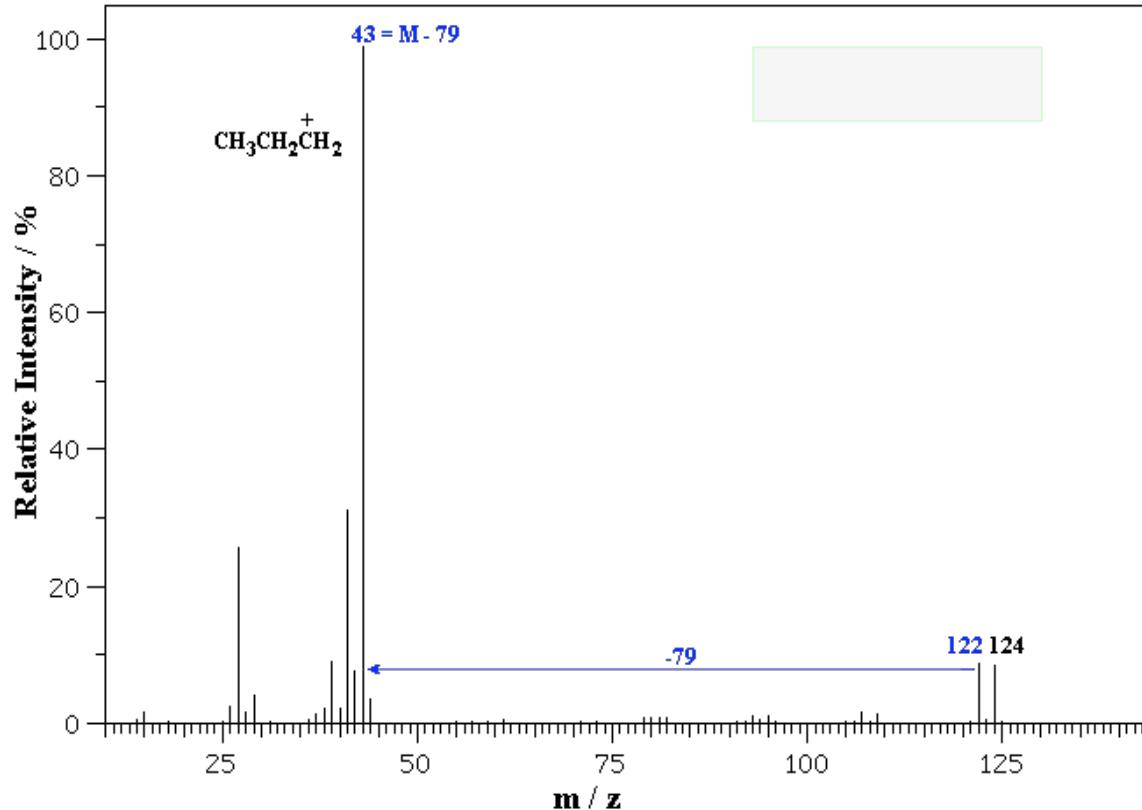
The plural form of spectrum is:

- (A) Spectra
- (B) Spectrums
- (C) Both A and B are correct

Concept Te\$t

Which of the following statements is true?

- (A) Br has only 1 significant isotope.
- (B) Br has 2 isotopes that occur in nearly a 1:1 ratio.
- (C) Br has 3 isotopes that occur in nearly a 1:2:1 ratio.



MS Resolution

Two methods

1) Resolution between mass peaks:

$$R = m/\Delta m$$

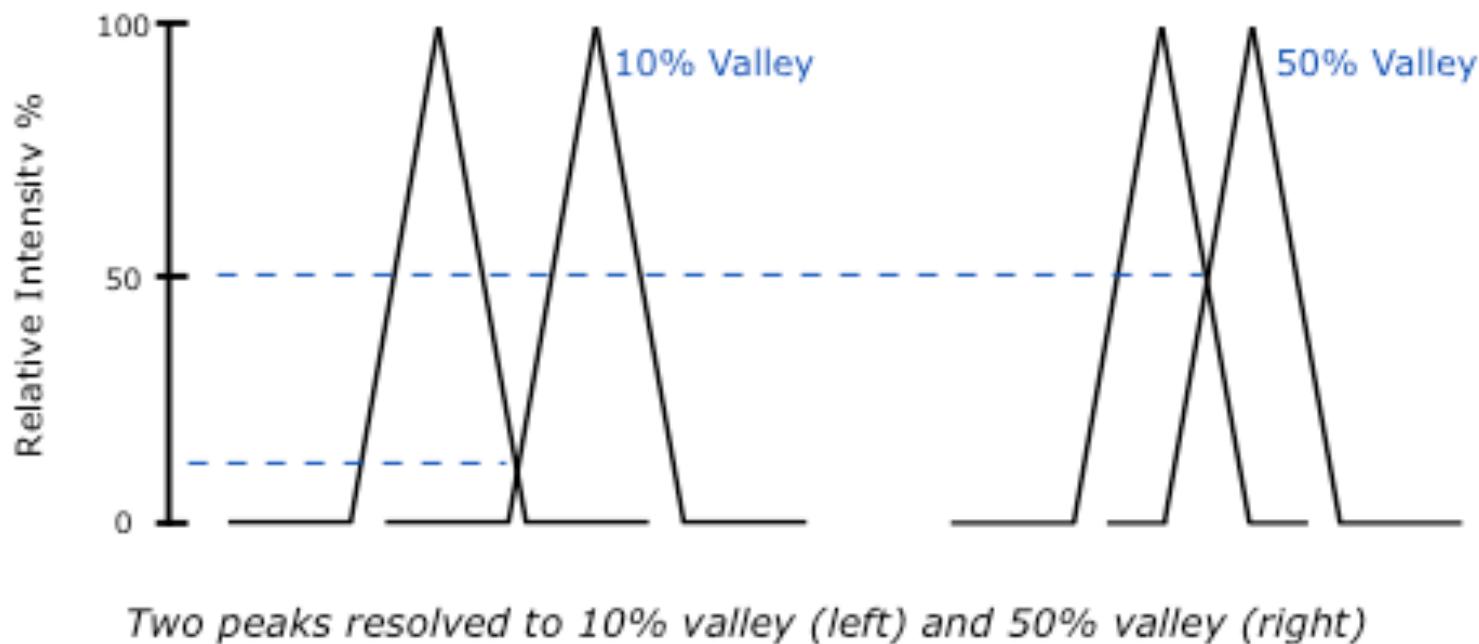
m is the average mass of the two peaks

Δm is the mass difference of the two peaks

Two peaks are considered to be separated if the height of the valley between them is no more than a given fraction of their total height (often 10%). Formally applies if the two peaks have equal height.

Thus, when determining the resolution of an instrument, the valley between two peaks must not be $>10\%$ of the total peak height. If it is not, then this definition applies.

MS Resolution



Concept Test

A spectrometer has a resolution of 2.25×10^3 . Is this resolution sufficient to resolve C_2H_4^+ and CH_2N^+ ions (masses of 28.0313 and 28.0187, respectively).

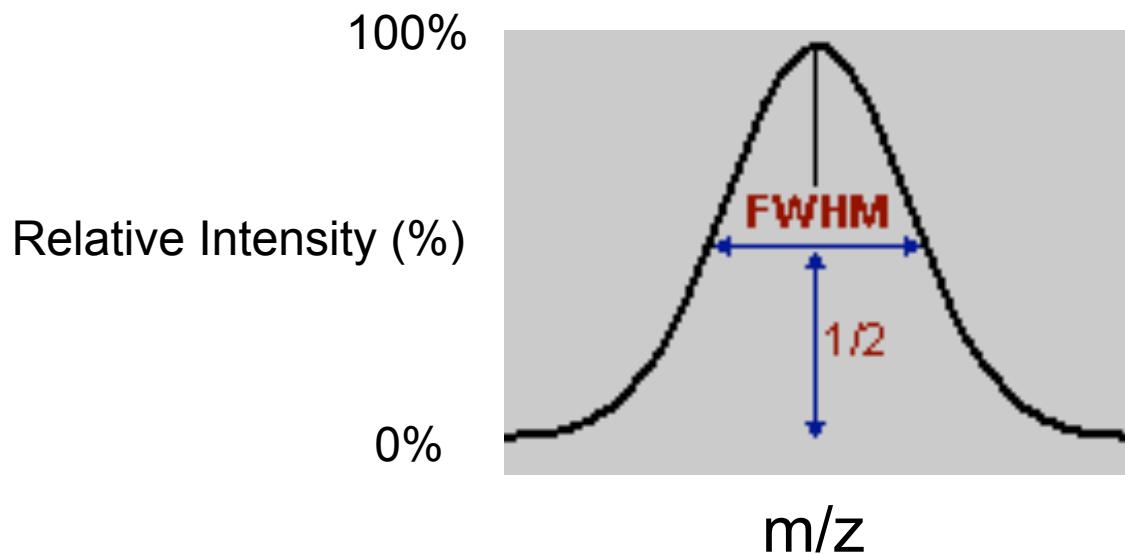
(A) Yes

(B) No

$$\text{Resolution necessary} = 28.0250/0.0126 = 2.22 \times 10^3$$

Mass Resolution

2) FWHM (Full Width at Half Max) of a single peak

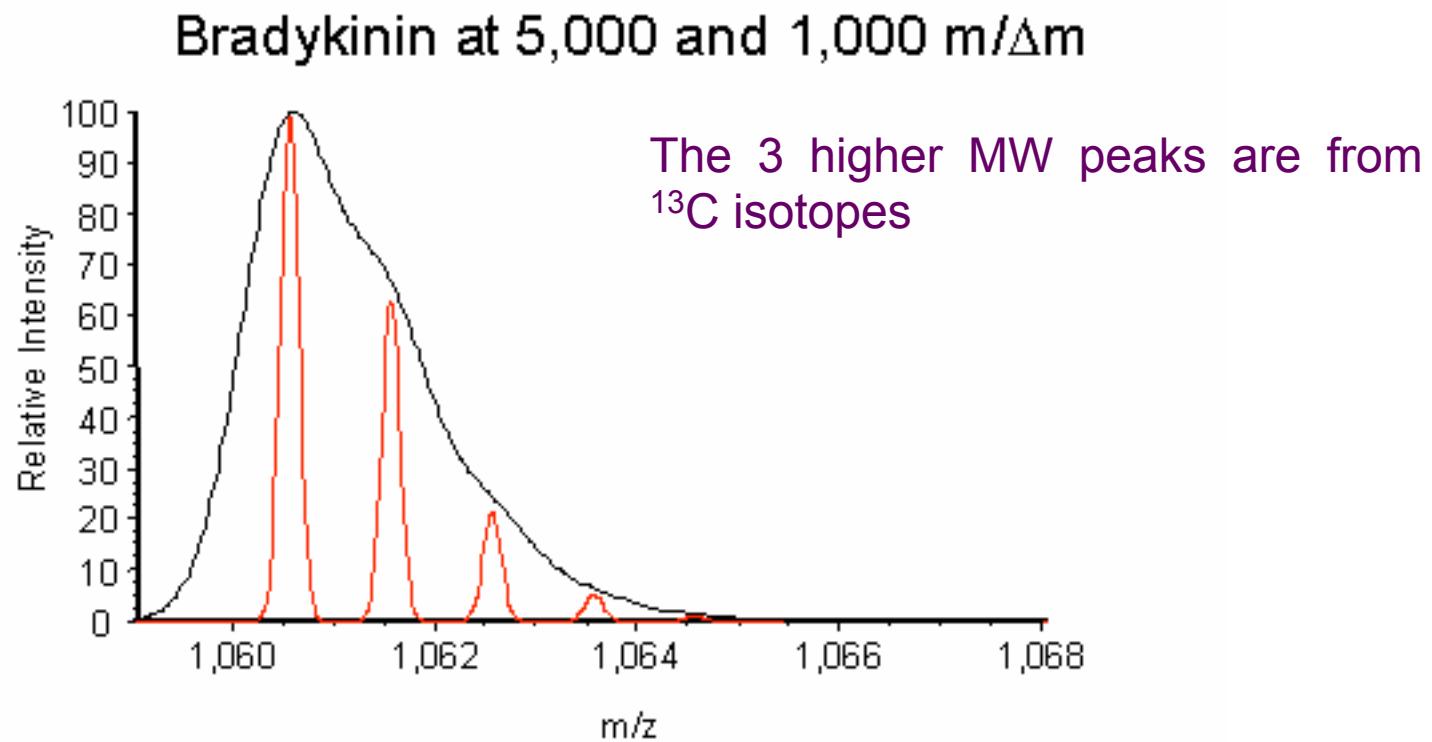


$R = m/\Delta m$ with Δm the width at 50% of the peak height

Mass Resolution

2) FWHM (Full Width at Half Max) of a single peak

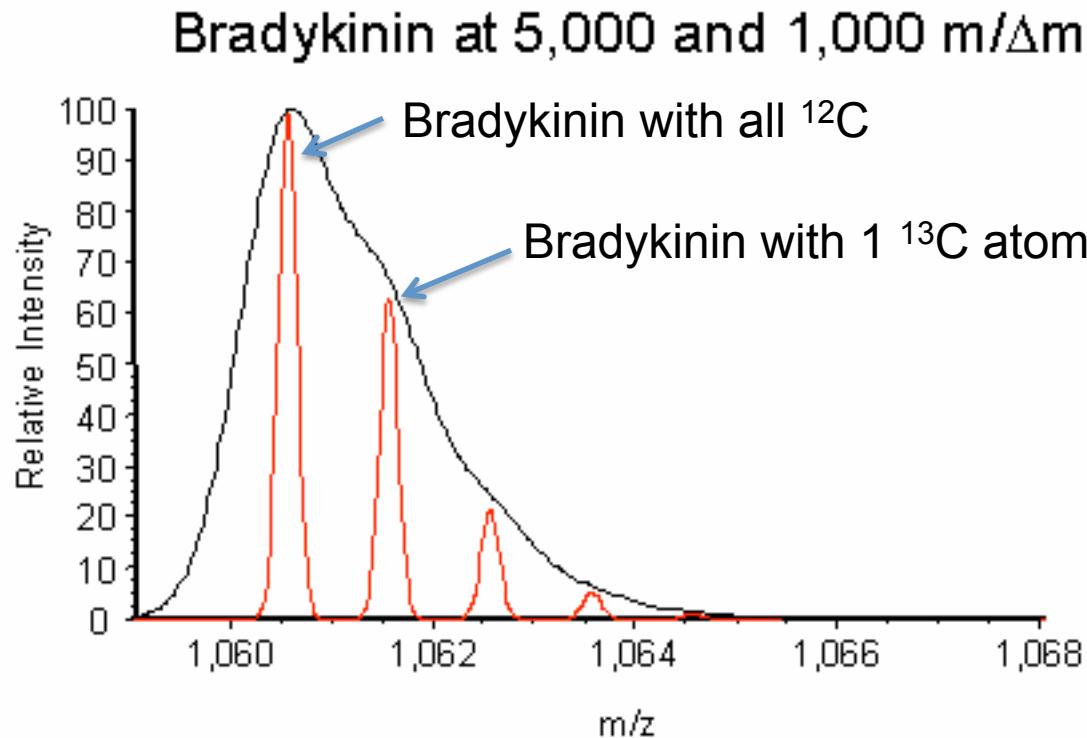
Bradykinin: Peptide that causes blood vessels to dilate (enlarge), and therefore causes blood pressure to lower. Arg - Pro - Pro - Gly - Phe - Ser - Pro - Phe – Arg
Mass = 1061.22.



As R increases, Δm decreases

Mass Resolution

For carbon, ^{13}C is roughly 1% of the ^{12}C ; therefore, for every 100 carbon atoms, 1 of them is ^{13}C . Bradykinin contains 50 carbon atoms. Approximately $\frac{1}{2}$ should have a ^{13}C atom.



$R = 1061.22/1 = 1061.22$; 1,000 won't cut it but 5,000 is plenty of resolving power.

Concept Test

Some mass spectrometers have a resolution of 1.3 million. For a mass of 28 amu what mass difference could be distinguished?

- (A) 0.00002 amu
- (B) 0.0002 amu
- (C) 0.02 amu

Mass Accuracy

$$\frac{(\text{Measured mass} - \text{True mass})}{\text{True mass}} \times 10^6 = \text{error in ppm}$$

Example:

True mass = 400.0000

Measured mass = 400.0020

Difference = 0.002

Error = $0.002/400 = 5 \times 10^{-6} = 5 \text{ ppm}$

Mass Spectrometry

Types of Mass Spectrometers

ICPMS (Inductively coupled plasma)

DCPMS (Direct current plasma)

SIMS (Secondary ion MS)

MALDI (Matrix assisted laser desorption)

Electrospray MS

Mass analyzers

Quadrupole

Double-focusing

Time of flight

Mass Spectrometry-Sample Introduction

Types of Mass Spectrometers

ICPMS (Inductively coupled plasma)

Uses an ICP torch to ionize and atomize the sample.

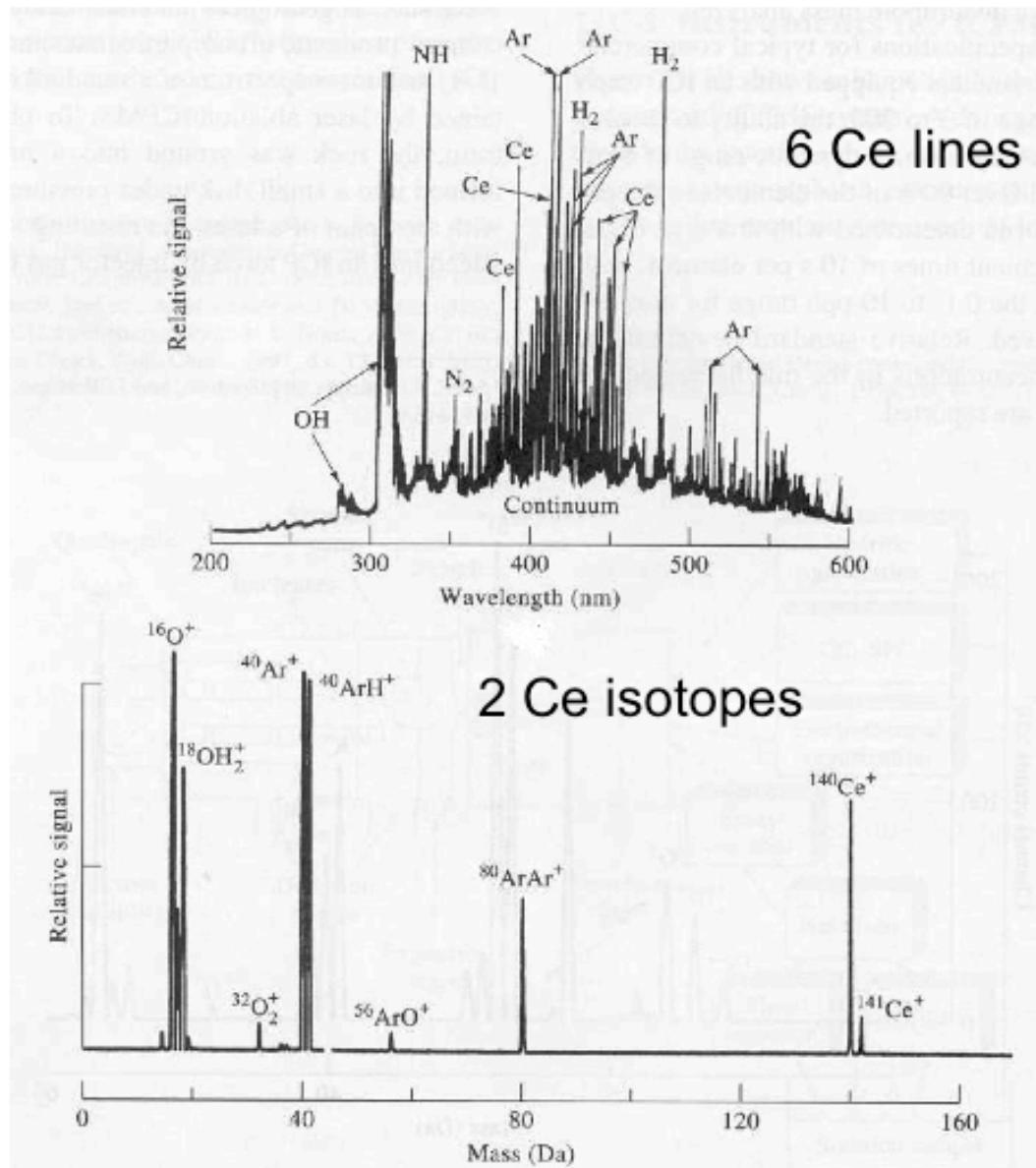
ICPMS spectra are often much simpler to interpret than ICP-OES spectra because some elements emit many lines and atmospheric contaminants such as HN, OH, N₂, and H₂ can give a high background emission.

ICPMS is not without interferences though. Oxides and hydroxides of the analytes can form in the plasma and be detected in the spectrum.

DCPMS (Direct current plasma)

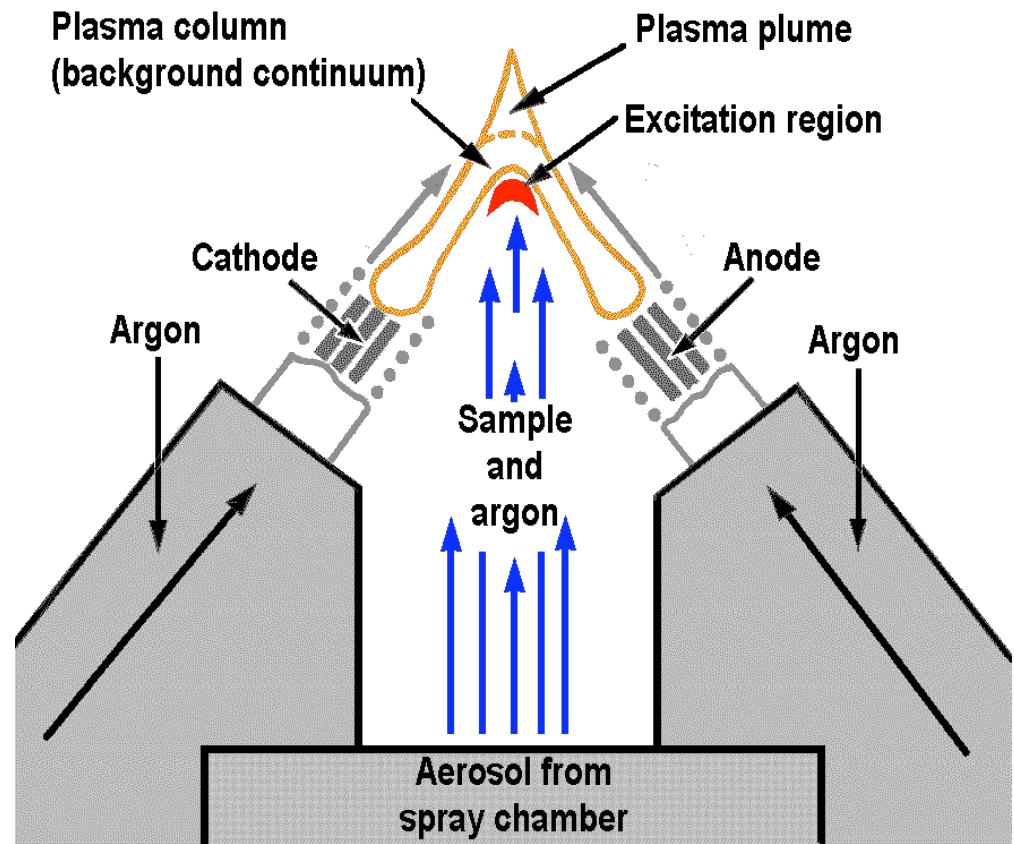
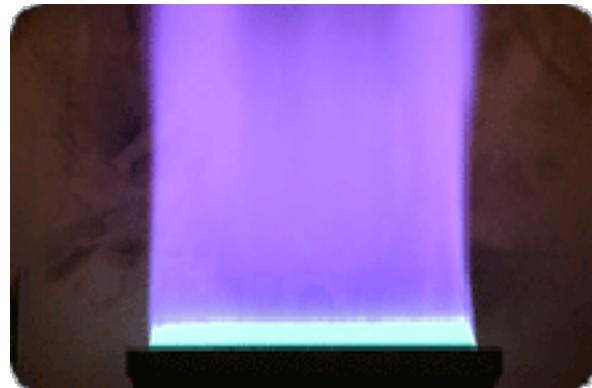
Sample deposited on a W cathode, then an electrical discharge between the cathode and two graphite anodes in the presence of Ar atomizes and ionizes the sample.

Why ICP-MS and not ICP-OES?



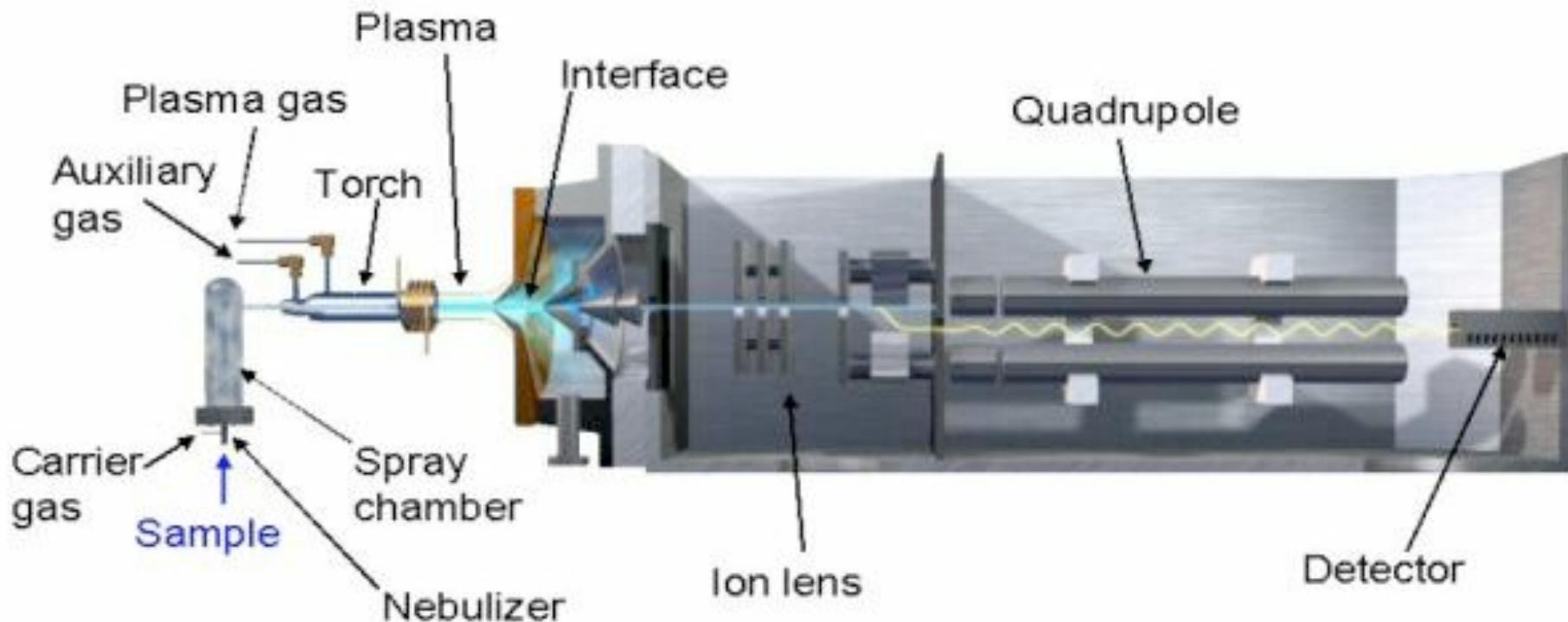
Mass Spectrometry

DCP-MS



Mass Spectrometry

ICP-MS

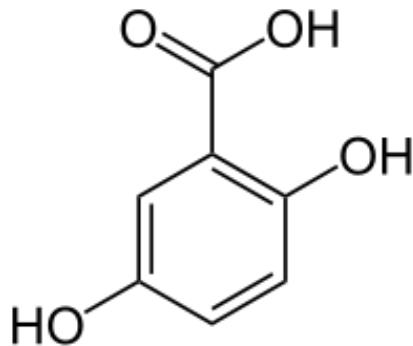


Sample Introduction: Electron bombardment is a hard ionization method that often causes so much fragmentation that the spectrum is difficult to interpret.

MALDI (Matrix assisted laser desorption; 2002 Nobel Prize)

A “soft ionization” method that is useful in studying large biomolecules and organic molecules that are difficult to atomize/ionize or are so fragile that they become so fragmented that it is difficult to determine the identity of the species being analyzed.

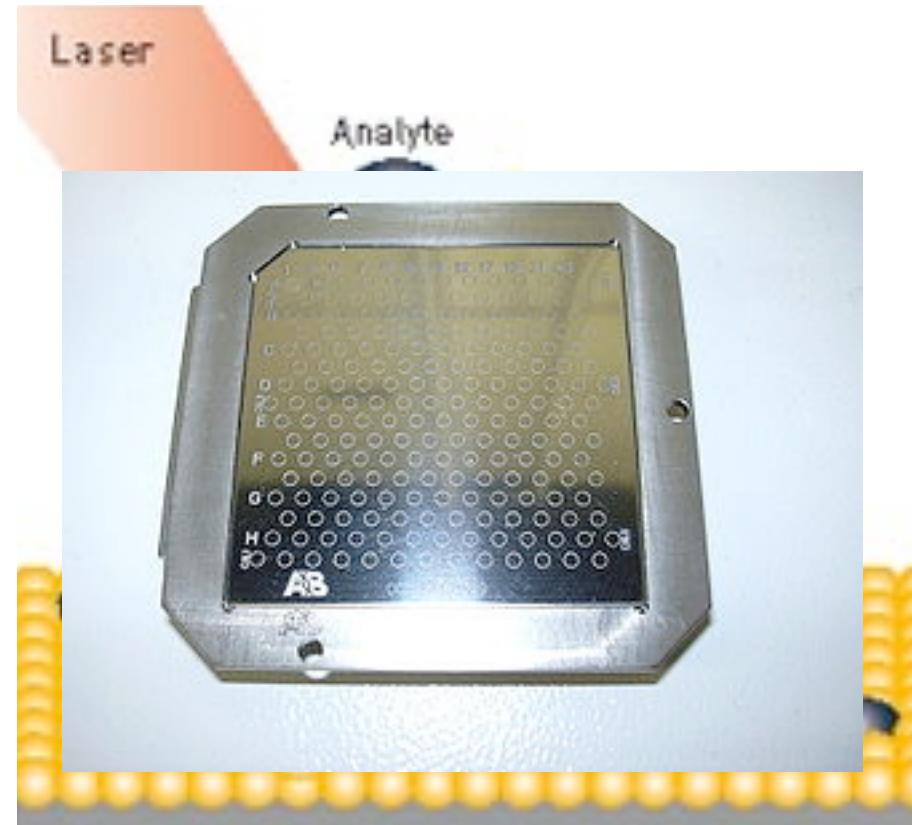
Matrix Molecule



Crystallized on a plate with the sample.

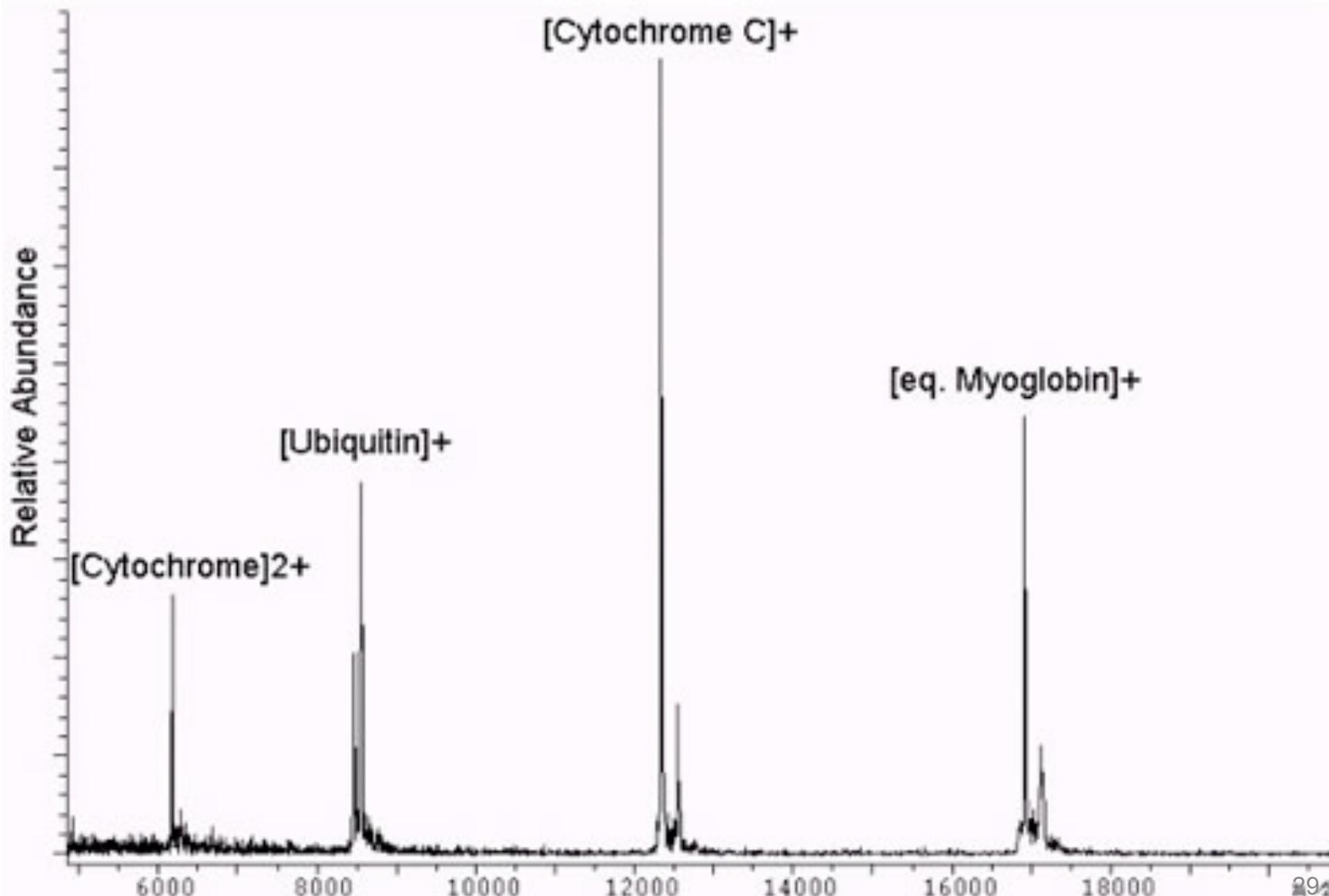
Absorb in the UV or IR.

Transfer energy to the sample, desorbing and ionizing it.



MALDI

Complex mixtures yield relatively simple spectra.

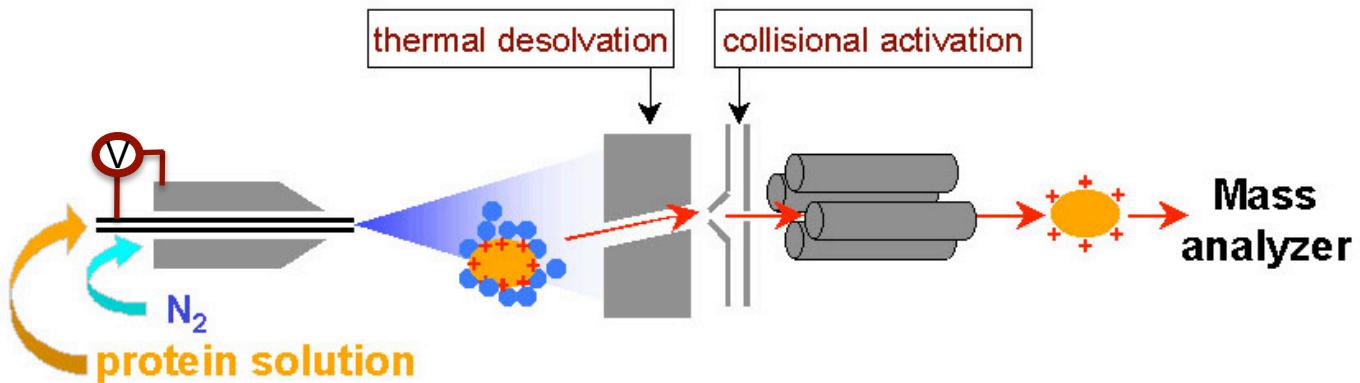
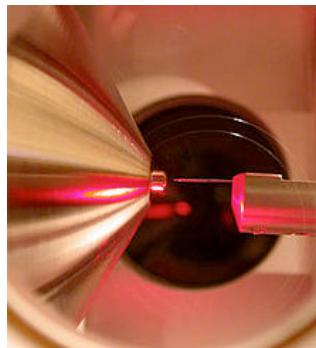


Mass Spectrometry

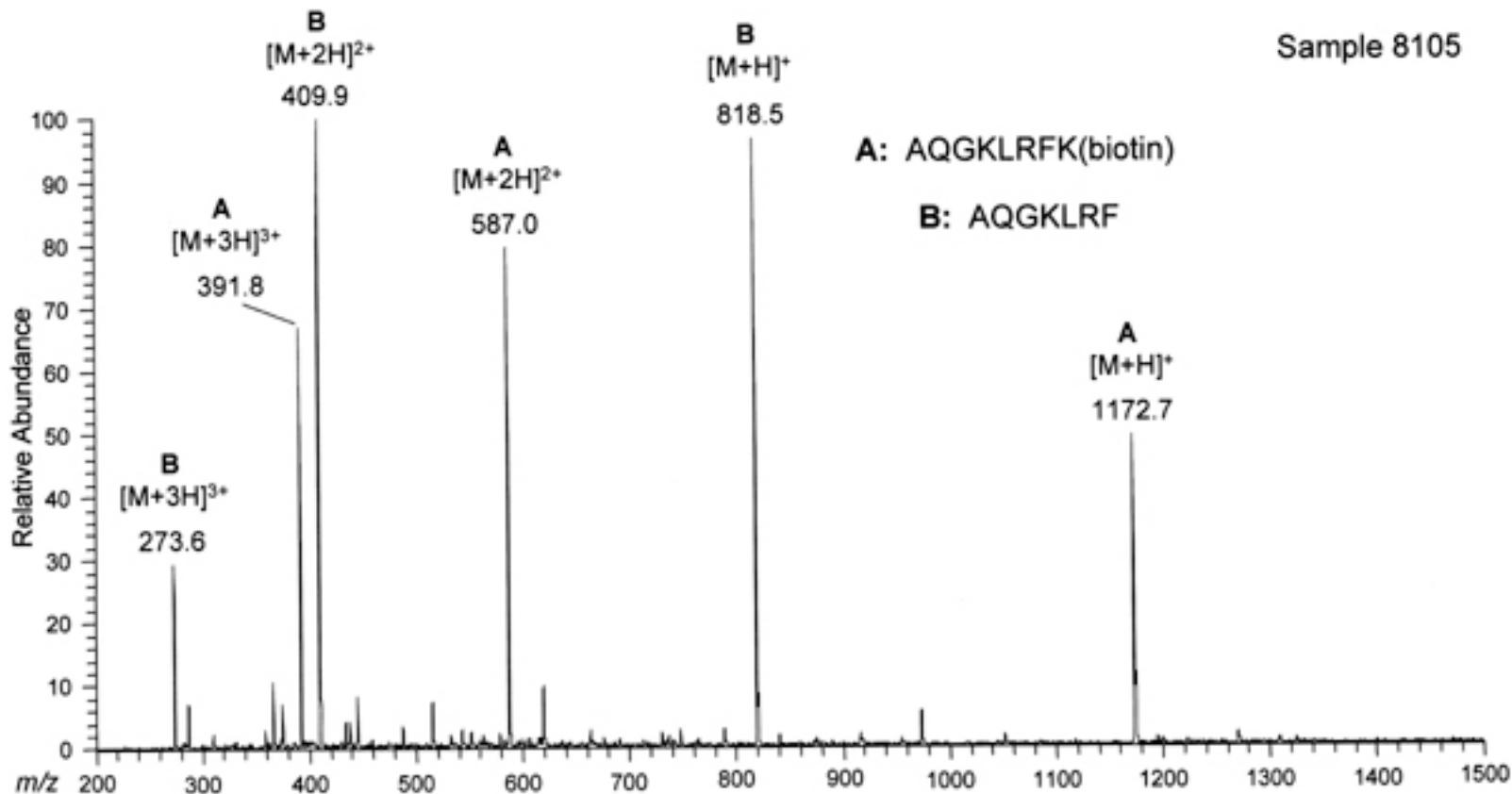
Electrospray Ionization MS; 2002 Nobel Prize)

Another “soft ionization” method that is useful in studying large biomolecules.

A liquid containing the sample is aerosolized into the spectrometer using a high voltage (kV) stainless steel needle. The fine droplets then pass through a “desolvating” capillary, where the solvent evaporates and the analyte picks up charge (H^+ or Na^+). Very little fragmentation occurs in the process.



ESI-Mass Spectrometry

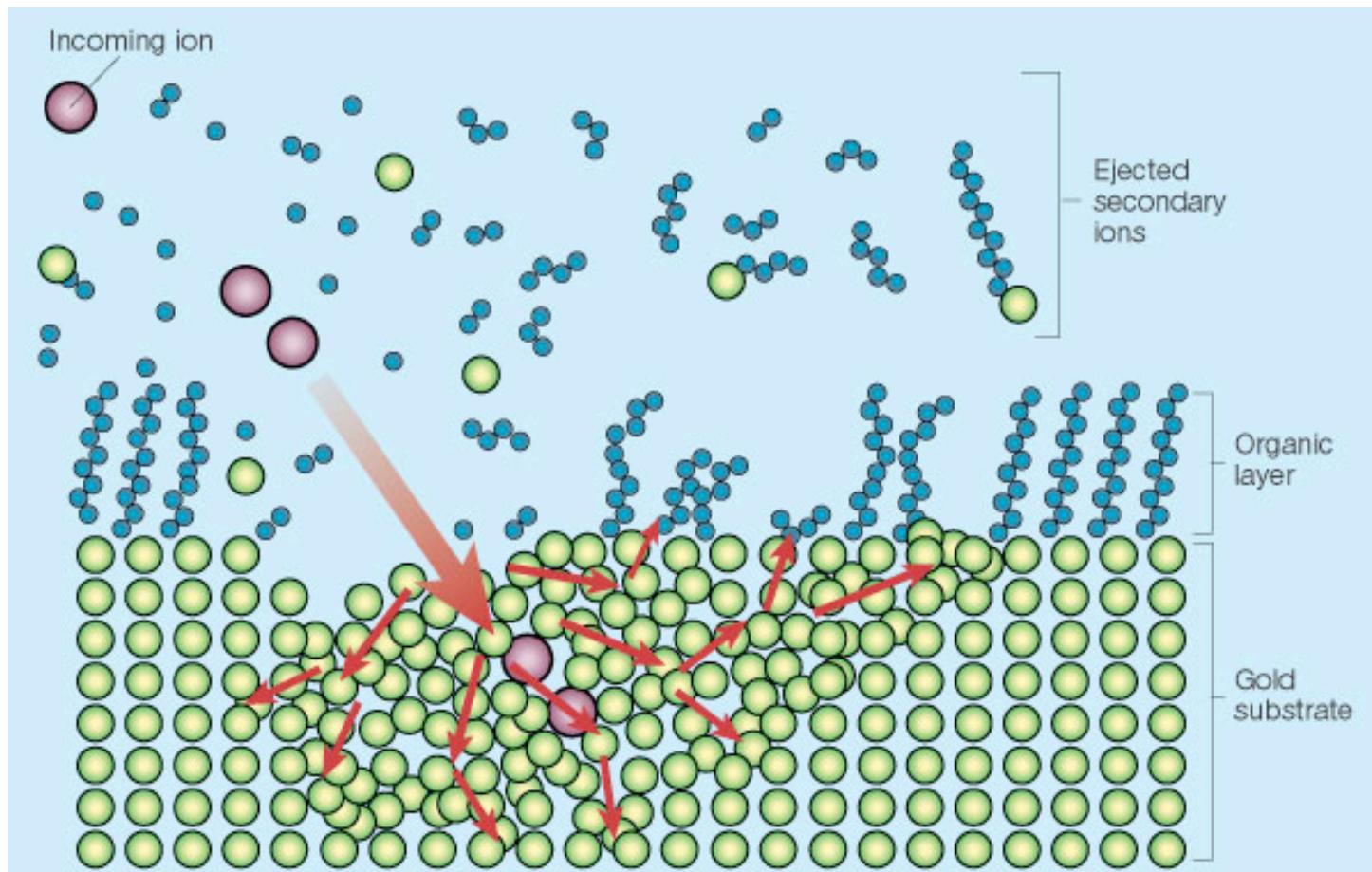


Note $M + H$ peaks and little fragmentation.

Mass Spectrometry-Sample Introduction Methods

SIMS (Secondary ion MS)

Used for analyzing solids and thin films. An ion beam (usually Ar^+ with an E of 20 keV) is focused onto a surface and the beam causes the ejection of surface molecules, atoms, and ions into the spectrometer.



Mass Spectrometry-Sample Introduction Methods

SIMS (Secondary ion MS)

Allows elemental “profiling” both along the surface and into the film (depth profiling).

Little to no sample prep (no digestion)

Only destructive to small areas of the sample surface and not the entire sample

Applications

Forensics (Hair analysis)

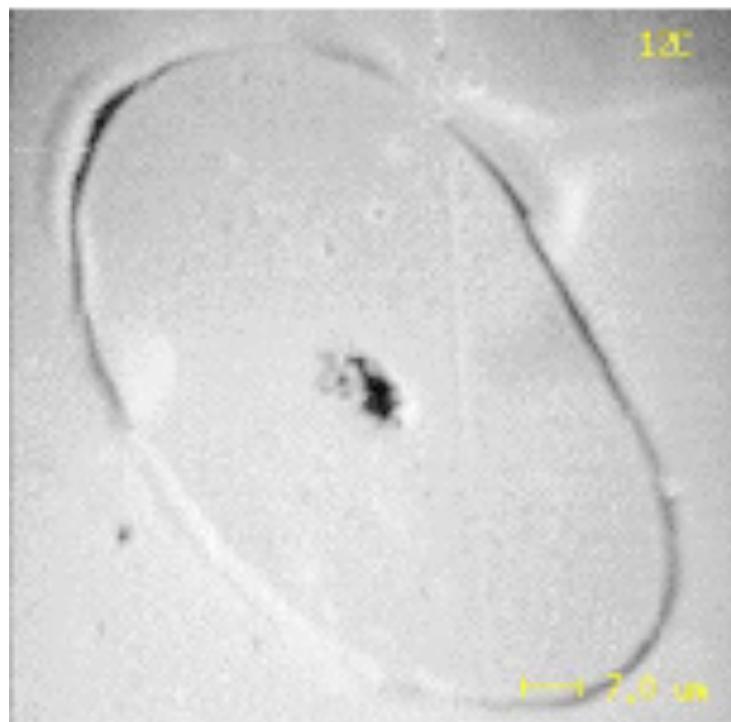
Semiconductors (doping levels)

Medical implants (has bone fused with a hip implant material?)

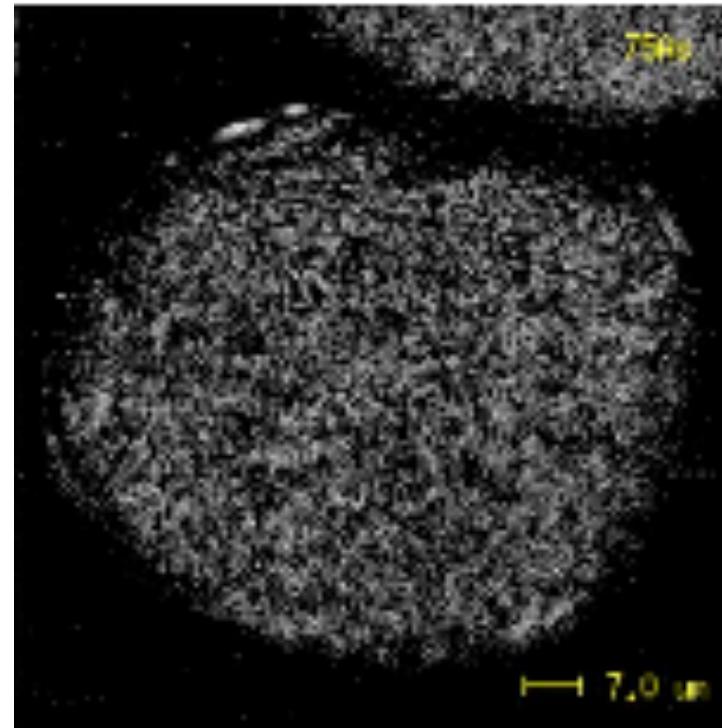
Archeology and historical artifact analysis (composition of paint from antique paintings)

Mass Spectrometry-Sample Introduction Methods

Arsenic poisoning



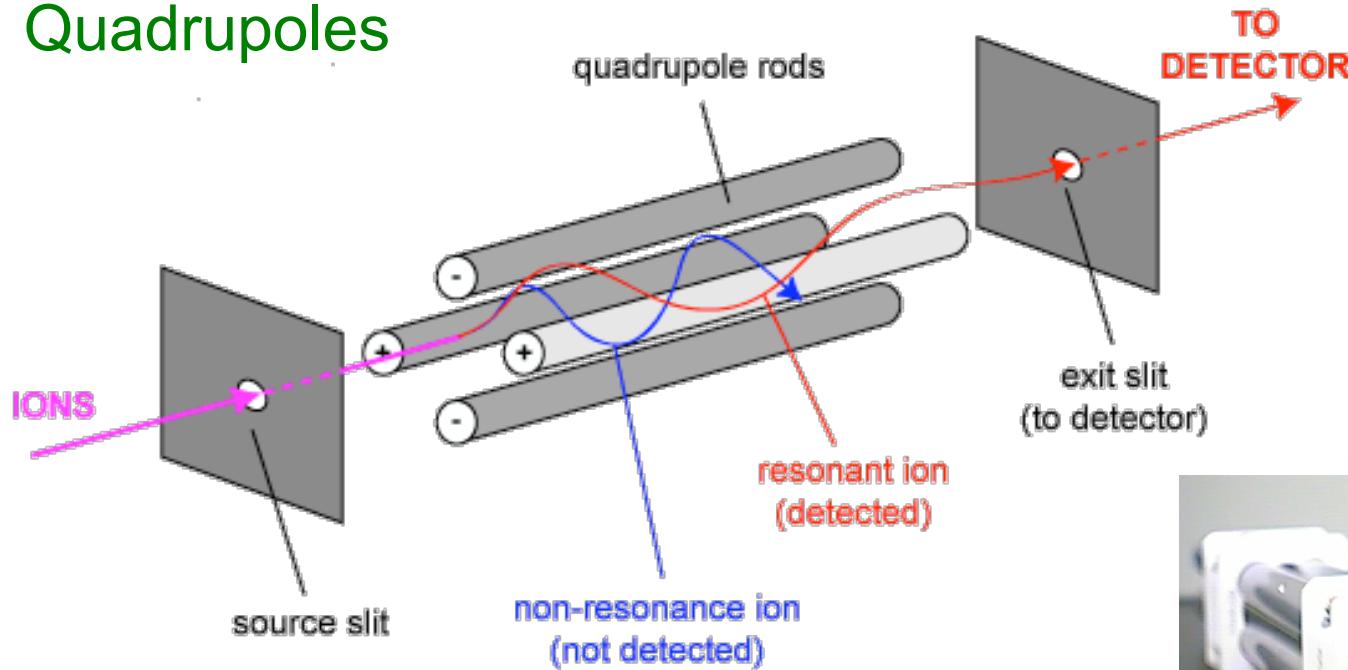
Cross section of a hair fiber



As elemental map across the hair.
Bright indicates As.

Mass Analyzers

Quadrupoles



Simple mass filters: Four metal rods, two with positive potential and two with negative potential. An alternating potential is applied and increased during the experiment. At any given moment all of the ions except those with a certain m/z run into the rods. m/z up to 4000 with 1 m/z resolution.

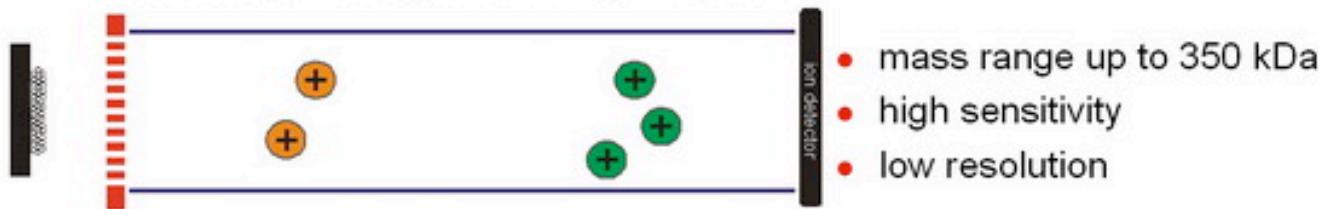
Advantages: Inexpensive and compact.

Mass Analyzers

Time-of-Flight

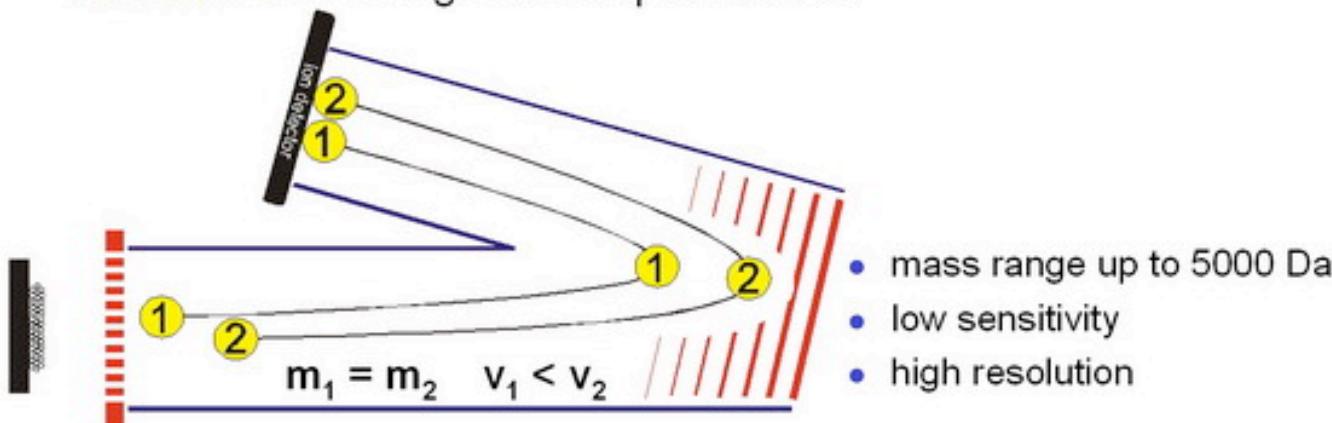
Positive ions are created by electron bombardment, lasers, or secondary ions. The ions are accelerated by an electric field and into a drift tube. The ions ideally have the same KE, but since the ions have different masses, their velocities must differ. The time it takes an ion to travel a certain distance is measured and the m/z determined from the KE and velocity. There are two types of drift tubes:

Linear time-of-flight mass spectrometer



- mass range up to 350 kDa
- high sensitivity
- low resolution

Reflector time-of-flight mass spectrometer



- mass range up to 5000 Da
- low sensitivity
- high resolution

Mass Analyzers

Time-of-Flight

When the ion enters the “drift tube”, it has a PE of

$E = zV$; where z is the charge and V the applied potential.

As the ion drifts down the tube the PE is converted to KE so

$$KE = PE; \text{ or } \frac{1}{2}mv^2 = zV$$

**z in Coulombs!
 V in J/Coulomb**

Since velocity is distance per time:

$$\frac{1}{2}m(L/t)^2 = zV; \text{ where } L \text{ is distance and } t \text{ is time}$$

$$t^2 = (L^2/2V)(m/z)$$

Time to reach the detector
depends upon drift tube length
and $(m/z)^{1/2}$

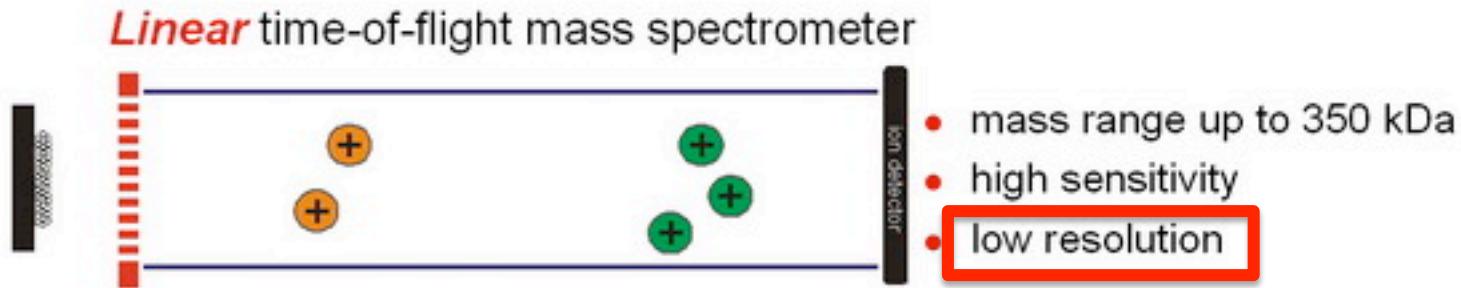
$$t = (L^2/2V)^{1/2}(m/z)^{1/2}$$

Concept Te\$t

Two ions fly down a linear TOF-MS. They have the same mass but one is a 4+ ion and the other a 1+ ion. Which one hits the detector first and what is the time delay?

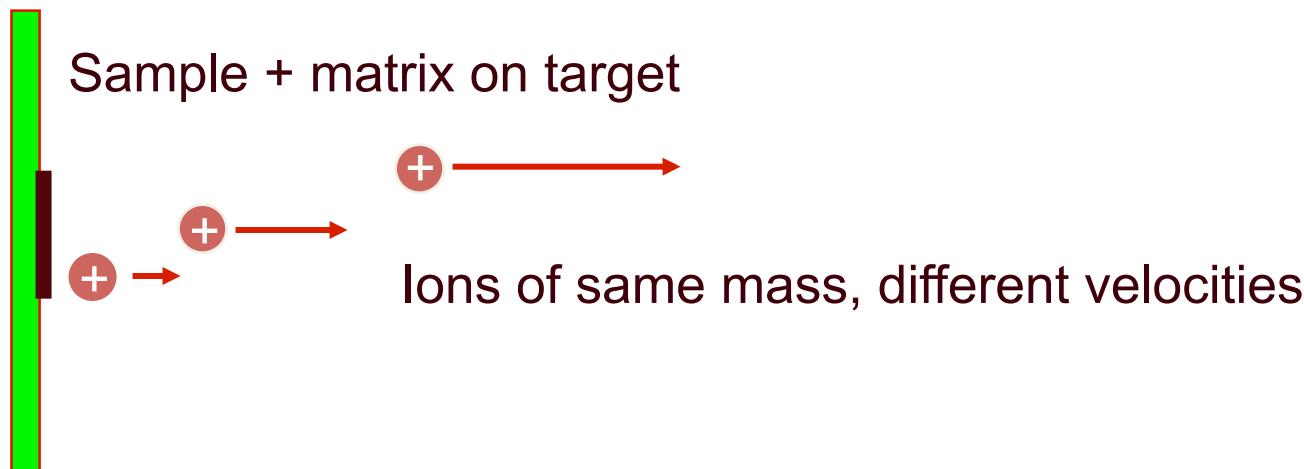
- (A) 4+ hits first and in $\frac{1}{2}$ the time of the 1+.
- (B) 4+ hits first and in $\frac{1}{4}$ the time of the 1+.
- (C) 1+ hits first and in $\frac{1}{4}$ the time of the 4+
- (D) 1+ hits first and in $\frac{1}{2}$ the time of the 4+

Linear vs. Reflector TOF



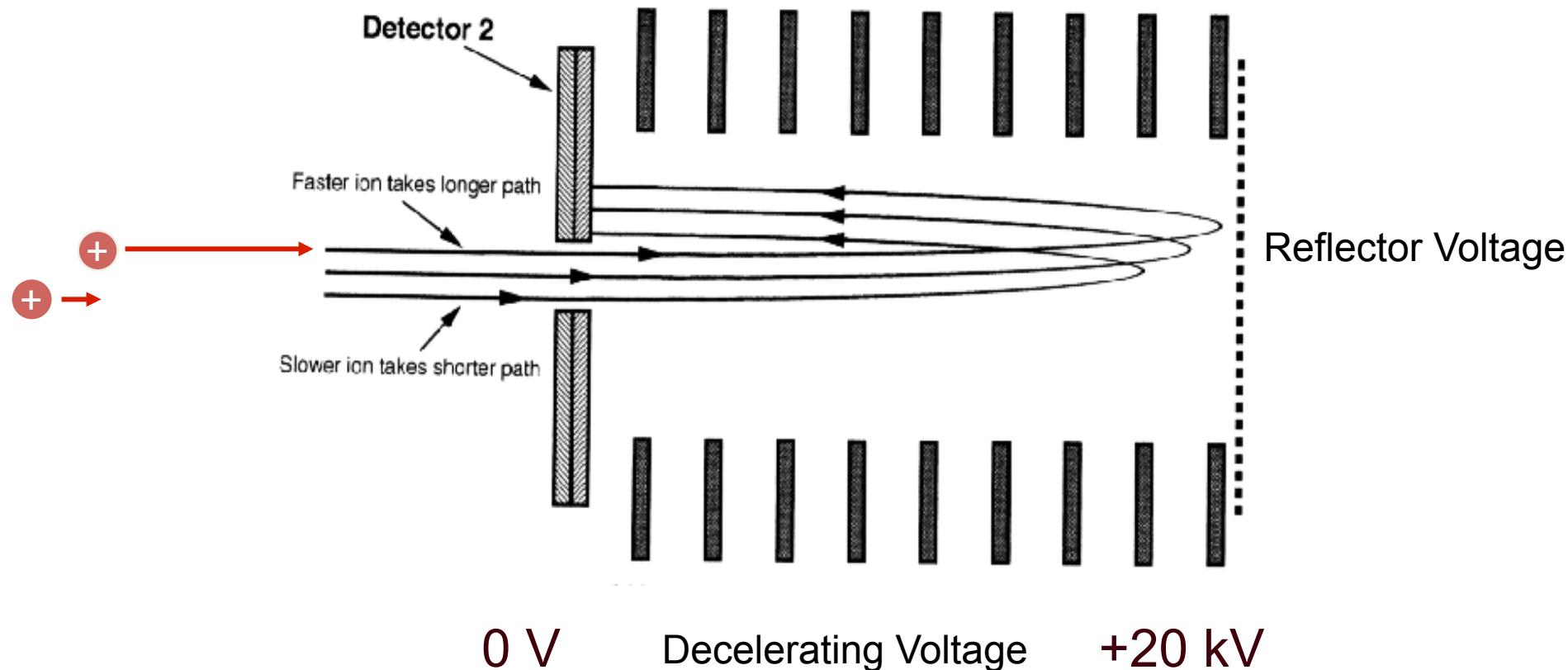
The problem: Peaks are inherently broad in MALDI-TOF spectra (poor mass resolution).

The cause: Ions of the same mass (all the green guys above) coming from the target have different speeds (and KE). This is due to uneven energy distribution when the ions are formed by the laser pulse.

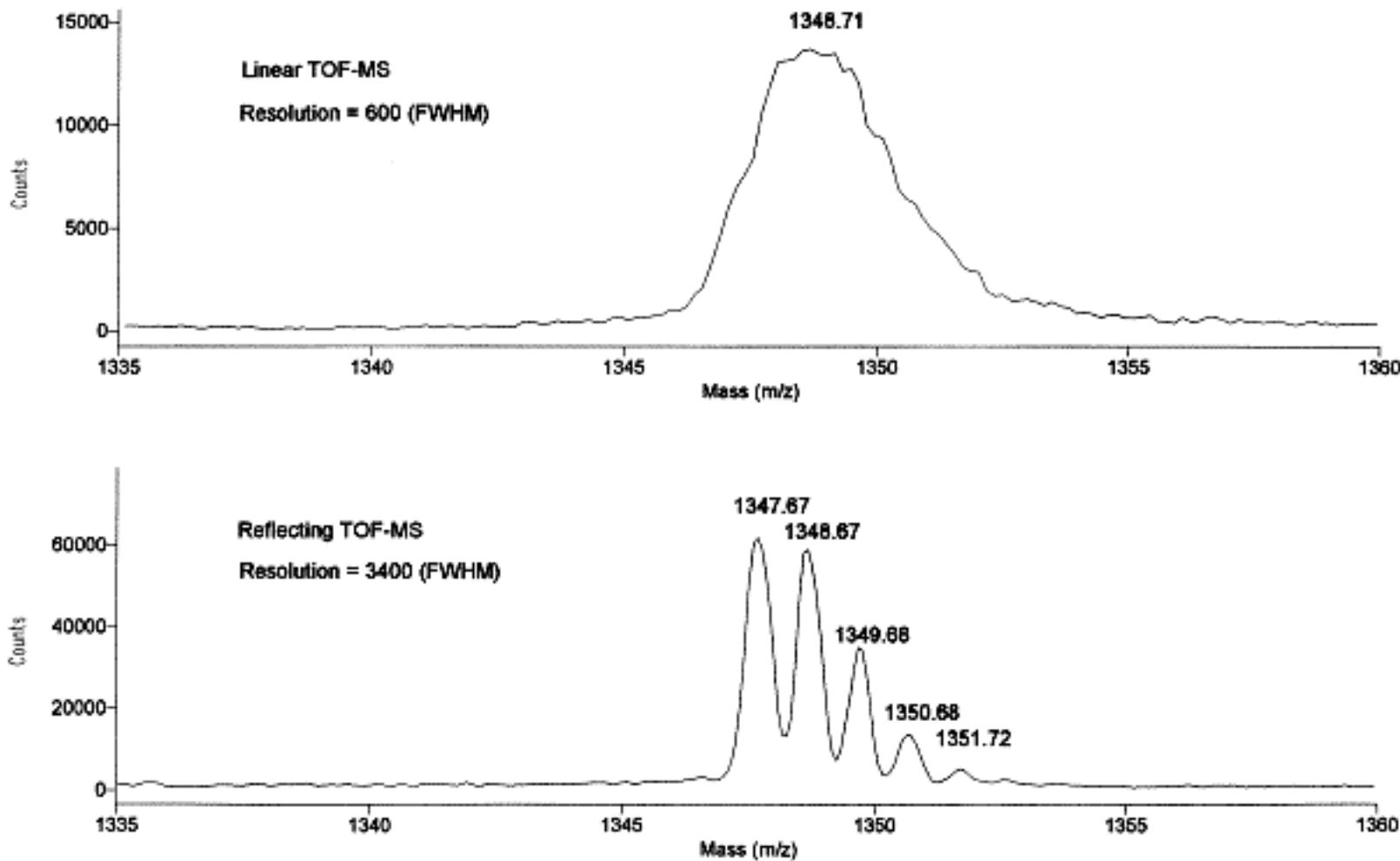


Linear vs. Reflector TOF

In reflector-TOF a “focusing” in drift time occurs because the faster ions take a longer path than the slower ions.

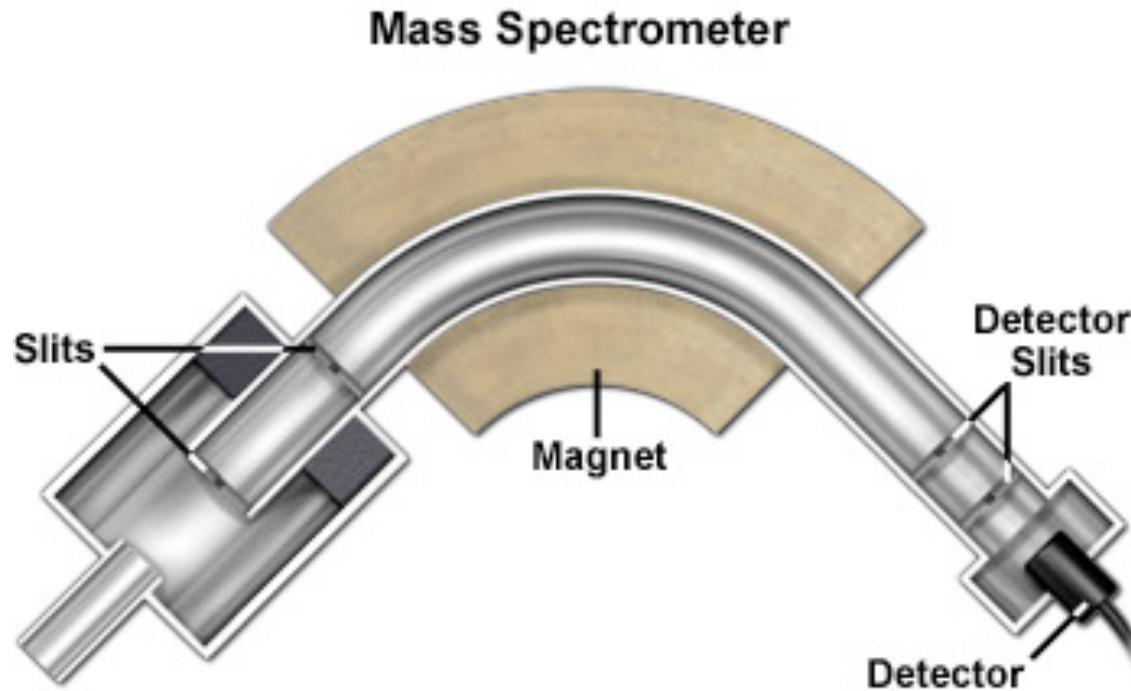


Improved Resolution with a Reflector TOF-MS



Mass Analyzers

Magnetic Sectors



The ions enter the flight tube and are deflected by the magnetic field, B.

Only ions of mass-to-charge ratio that have equal *centripetal* (F that makes an object follow a curved path) and *centrifugal* forces (F at a right angle to the centripetal force due to magnetic field, B, pass through the flight tube:

$$mv^2/r = BzV, \text{ where } r \text{ is the radius of curvature}$$

$$m/z = B^2 r^2 / 2V$$

V and r held constant and B is scanned to separate ions

Mass Analyzers

The ions enter the flight tube and are deflected by the magnetic field, B.

Only ions of mass-to-charge ratio that have equal *centripetal* (F that makes an object follow a curved path) and *centrifugal* forces (F at a right angle to the centripetal force due to magnetic field, B, pass through the flight tube:

$$mv^2/r = BzV, \text{ where } r \text{ is the radius of curvature}$$

$$m/z = B^2r^2/2V$$

Danger! z is the charge in Coulombs (1+ has a charge of 1.60×10^{-19} C)

Example

For $B = 0.126$ T (Vsec/m²), $V = 3.00 \times 10^3$ V (1 V = 1 J/C = 1 kg m²/s² C), and $r = 0.25$ m, what ion reaches the detector?

$$m = (0.126 \text{ T})^2(0.25 \text{ m})^2(1.60 \times 10^{-19} \text{ C})/[2(3.00 \times 10^3 \text{ V})]$$

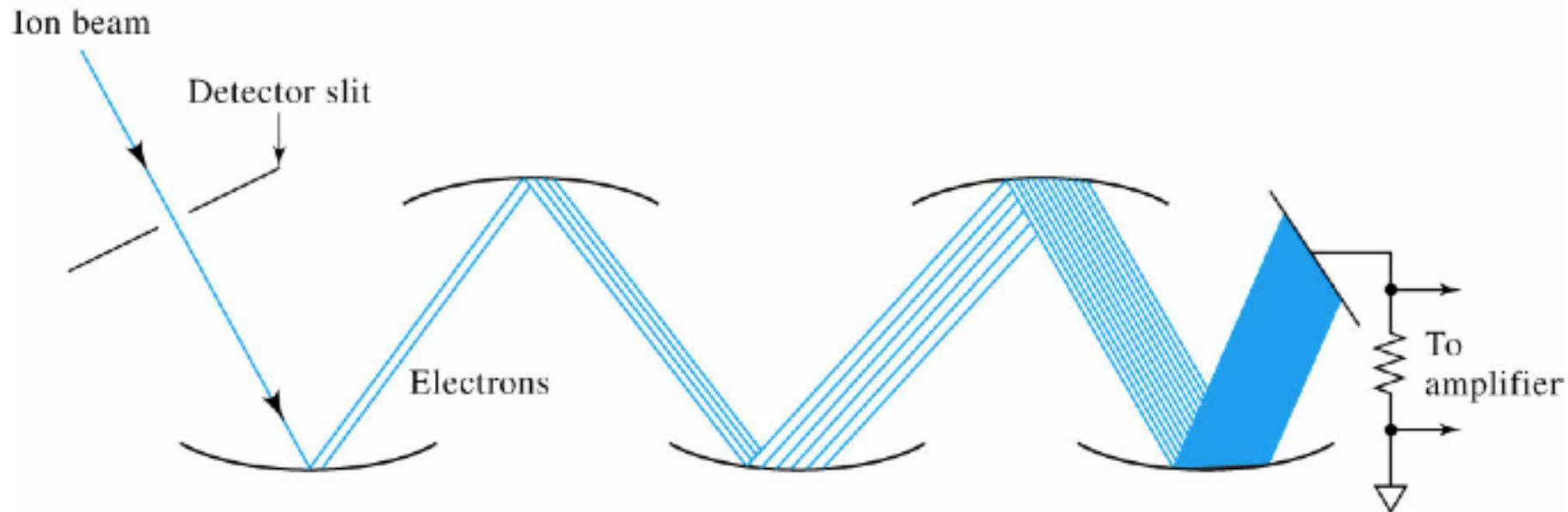
$$\begin{aligned} m &= 2.65 \times 10^{-26} \text{ kg} \\ &= 2.65 \times 10^{-23} \text{ g} \end{aligned}$$

$$\begin{aligned} 2.65 \times 10^{-23} \text{ g of ions} \times 6.02 \times 10^{23} \text{ ions/mol} \\ &= 16 \text{ amu} = \text{CH}_4^+ \end{aligned}$$

A CH_4^+ would make it through to the detector

Detectors

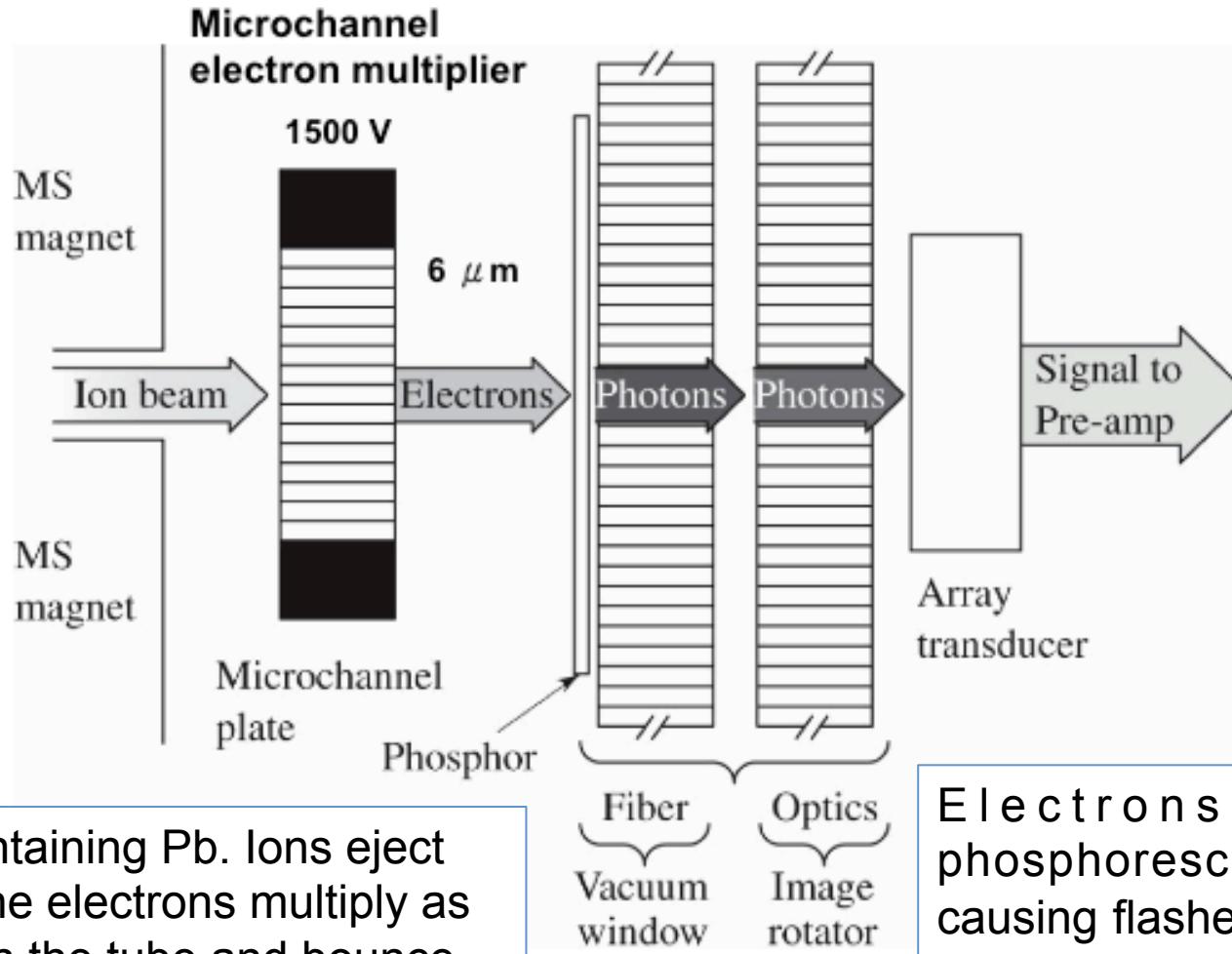
Electron Multipliers



High Gain: 10^5 - 10^8

Detectors

Array Detectors: Allow simultaneous detection of ions.
Similar to photodiode arrays in optical spectroscopy.

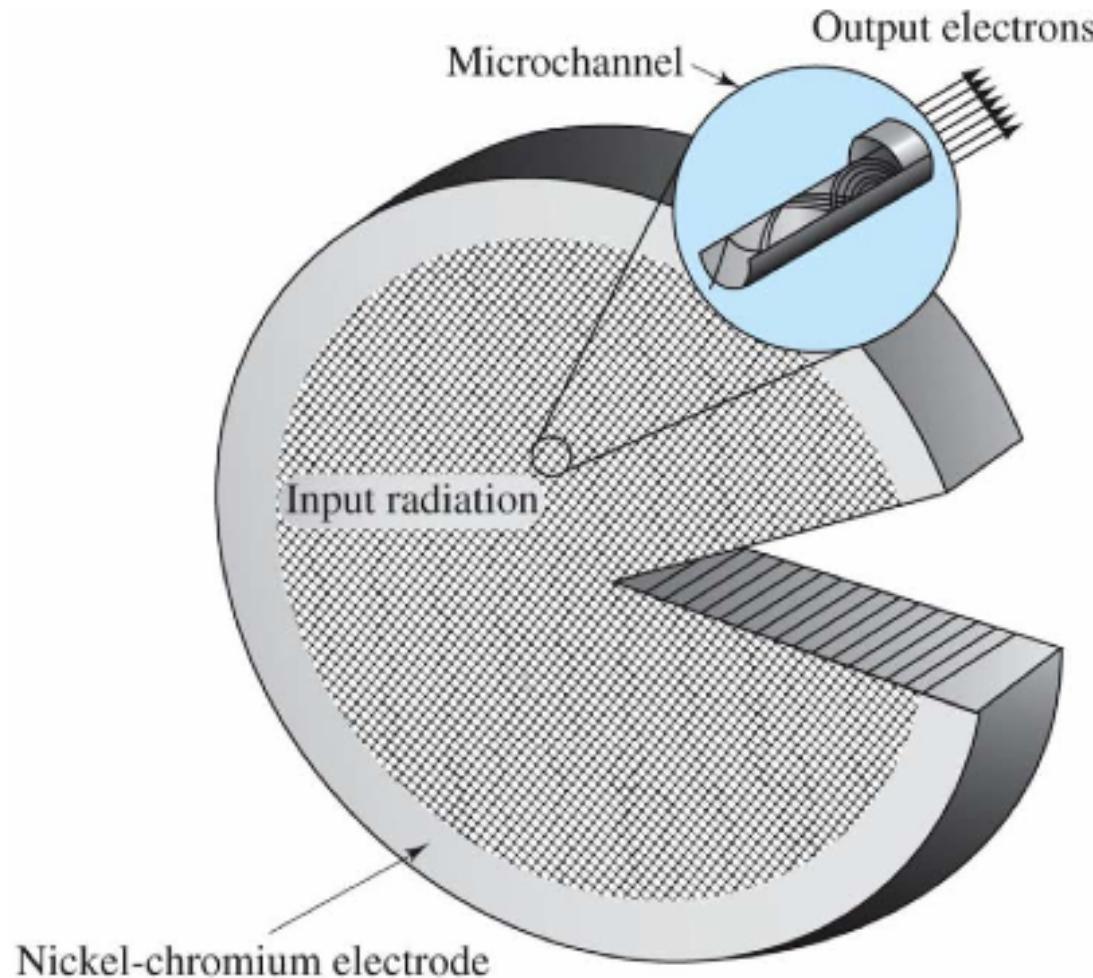


Glass tubes containing Pb. Ions eject electrons and the electrons multiply as they travel down the tube and bounce off of the Pb.

Electrons strike a phosphorescent screen, causing flashes of light that are detected diode array.

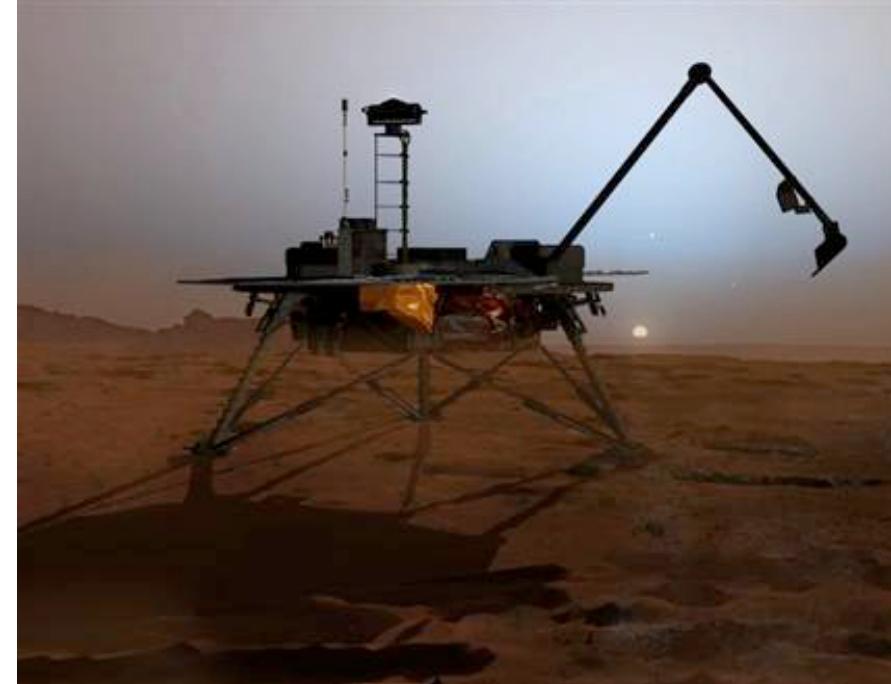
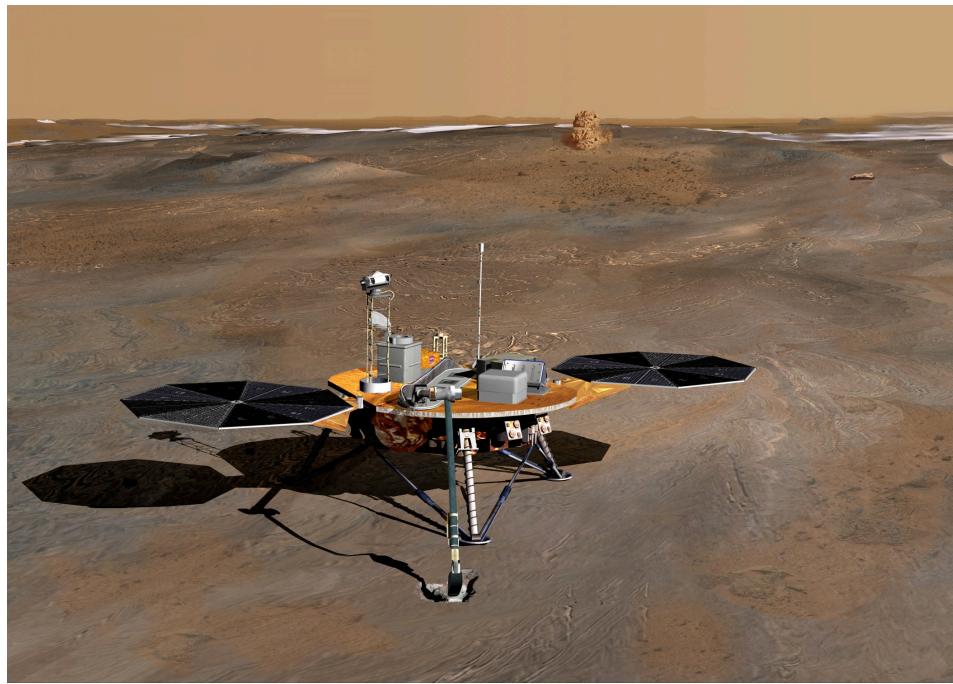
Detectors

Microchannel Plate: Each tube is an electron multiplier with a gain of 1000. Similar to a photodiode array.



Chemistry in Context

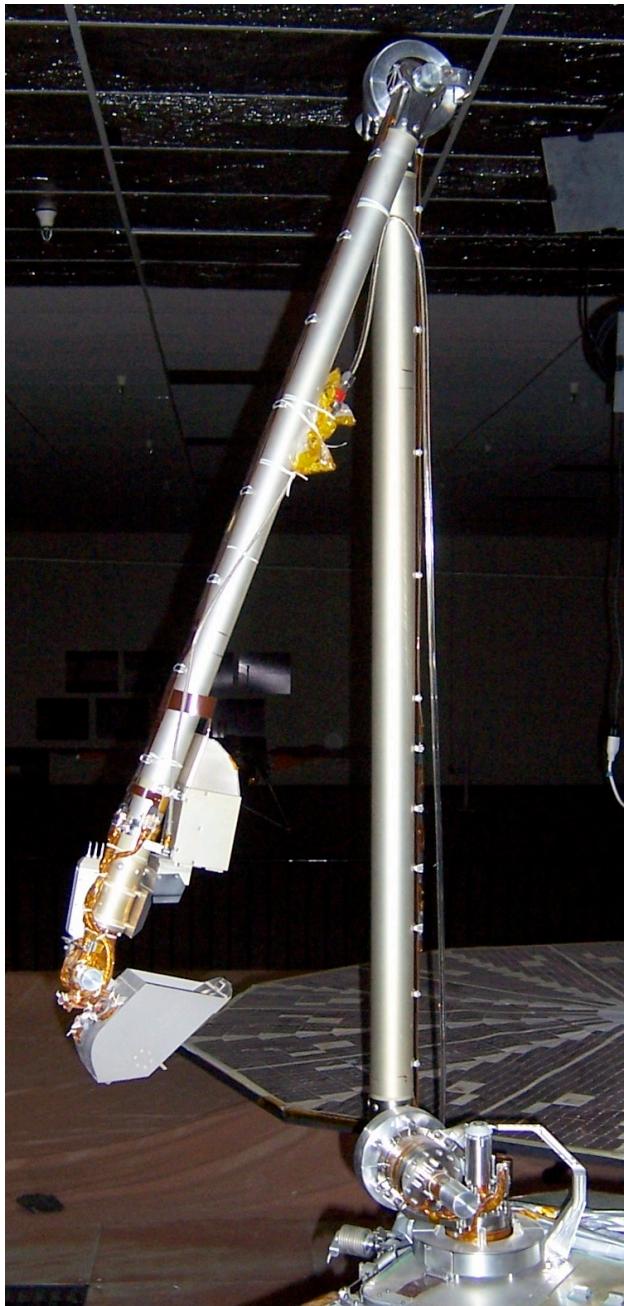
Life on Mars. The Viking and Phoenix landers were sent to Mars to determine if life ever existed there. What were these spacecrafts looking for and how did they perform the analyses?



Robotic Arm (RA)
built by the Jet Propulsion Laboratory, Alliance
Spacesystems and Honeybee Robotics

Microscopy, Electrochemistry, and Conductivity Analyzer (MECA)

By dissolving small amounts of soil in water, the wet chemistry lab (WCL) determines the pH, the abundance of minerals such as magnesium and sodium cations or chloride, bromide and sulfate anions, as well as the conductivity and redox potential. Looking through a microscope, MECA examines the soil grains to help determine their origin and mineralogy.



Thermal and Evolved Gas Analyzer (TEGA)

Built by the University of Arizona and University of Texas, Dallas

TEGA is a combination high-temperature furnace and mass spectrometer instrument that scientists used to analyze martian ice and soil samples. A robotic arm delivered samples to a container designed to feed a small amount of soil and ice into eight tiny ovens about the size of an ink cartridge in a ballpoint pen.



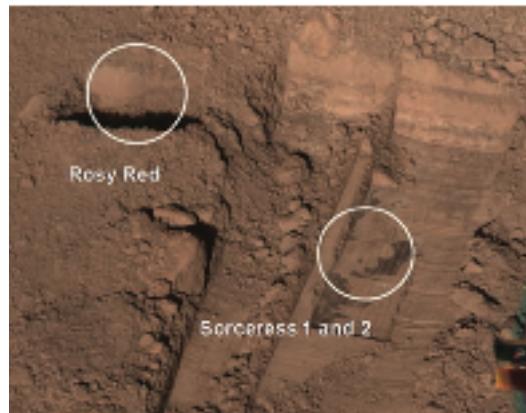
As the temperature of the furnace increases up to 1000°C (1800°F), the ice and other volatile materials in the sample are vaporized into a stream of gases. The evolved gases are transported via an inert carrier to a mass spectrometer. The mass spectrometer is sensitive to detection levels down to 10 parts per billion.

Magnetic Sector

24 cm x 23 cm x 18 cm

5.7 kg (12.6 lbs)

Chemical Composition of Martian Soil



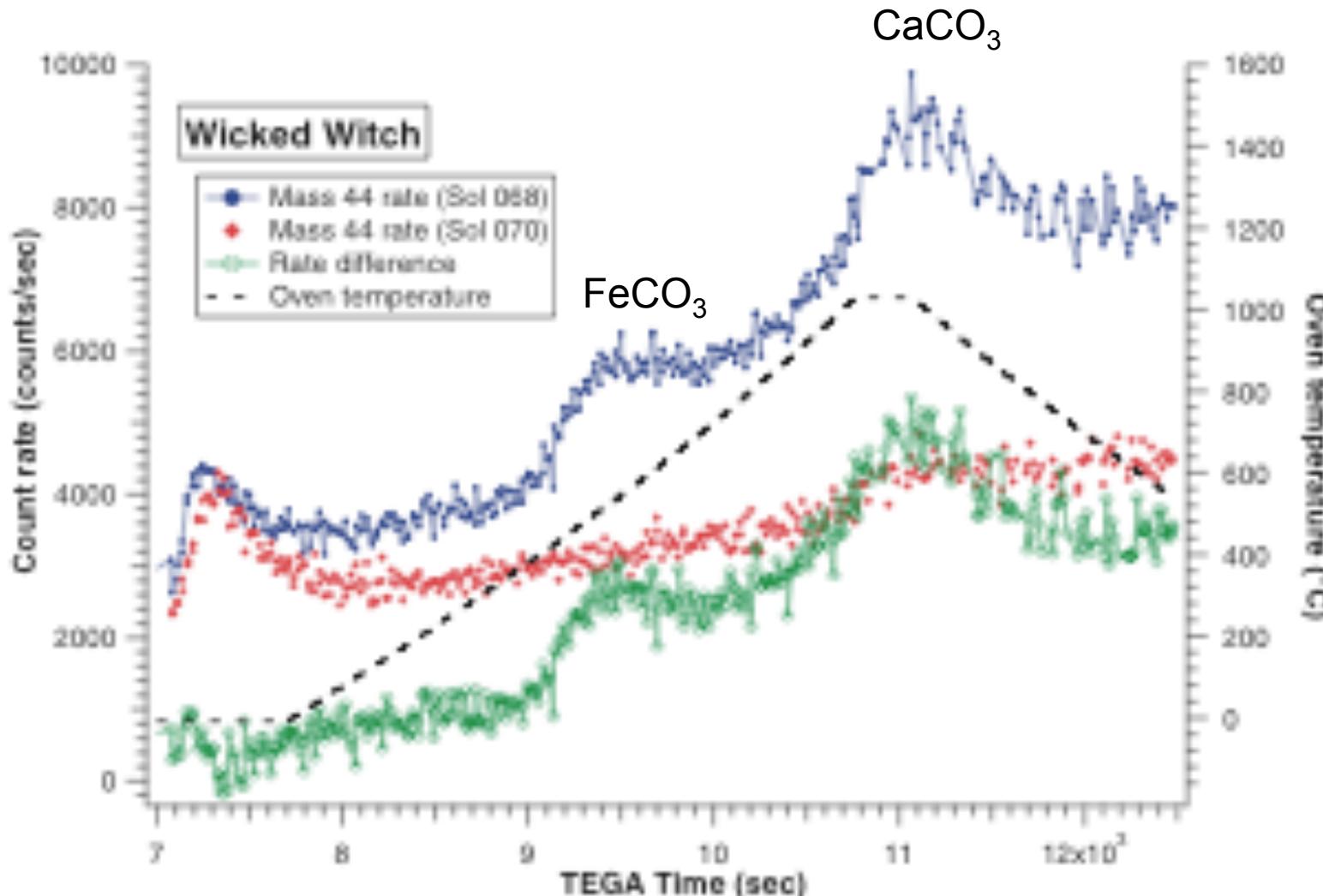
Ion-Selective Electrodes

	Rosy Red	Sorceress 1	Sorceress 2	Average
Na^+ (mM)	1.4	1.10	1.4	1.4
K^+ (mM)	0.36	0.17	0.39	0.38
Ca^{2+} (mM)	0.55	0.42	0.6	0.58
Mg^{2+} (mM)	2.9	2.20	3.7	3.3
Cl^- (mM)	0.6	0.24	0.47	0.54
ClO_4^- (mM)	2.6	2.10	2.2	2.4

Chemical Composition of Martian Soil

TEGA (thermal and evolved gas analyzer: Sample is heated, and at certain temps metal carbonates decompose and release CO_2 , which is detected by MS.

W. V. Boynton, Phoenix Landing Site Evidence for Calcium Carbonate at the Mars Science 2009, 325, 61.



Chemical Composition of Martian Soil

The ClO_4^{1-} and CO_3^{2-} are particularly significant.

Carbonates form from the reaction of CO_2 and $\text{H}_2\text{O(l)}$.
Water on Mars in the past?

Several microorganisms on Earth use perchlorate for anaerobic respiration.

"There's nothing about it that would preclude life. In fact, it seems very friendly," mission scientist Samuel Kounaves of Tufts University said of the soil.
"There's nothing about it that's toxic."

However, there was no conclusive evidence of other forms of carbon.