Modern Analytical Instrumentation

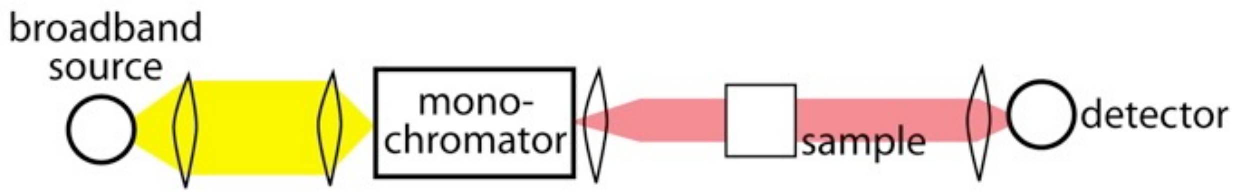
- *Atomic Absorption and Emission Spectroscopy (AAS and AES)*
- *High Performance Liquid Chromatography (HPLC)*
- *Mass Spectrometry (MS)*

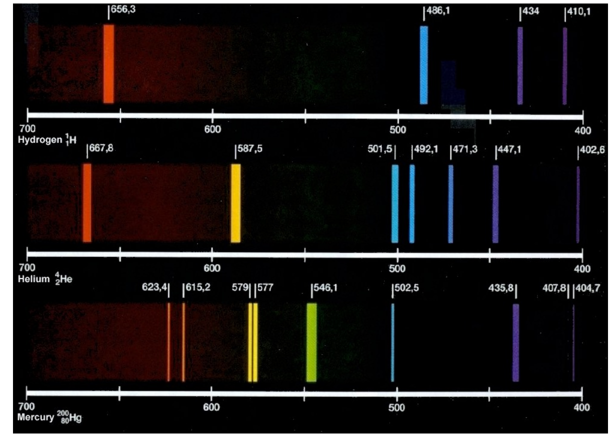
Also:
Molecular UV-Vis Spectroscopy
Fluorescence Spectroscopy
NMR
FTIR
Raman Scattering

Chem M3LC
R. Corn

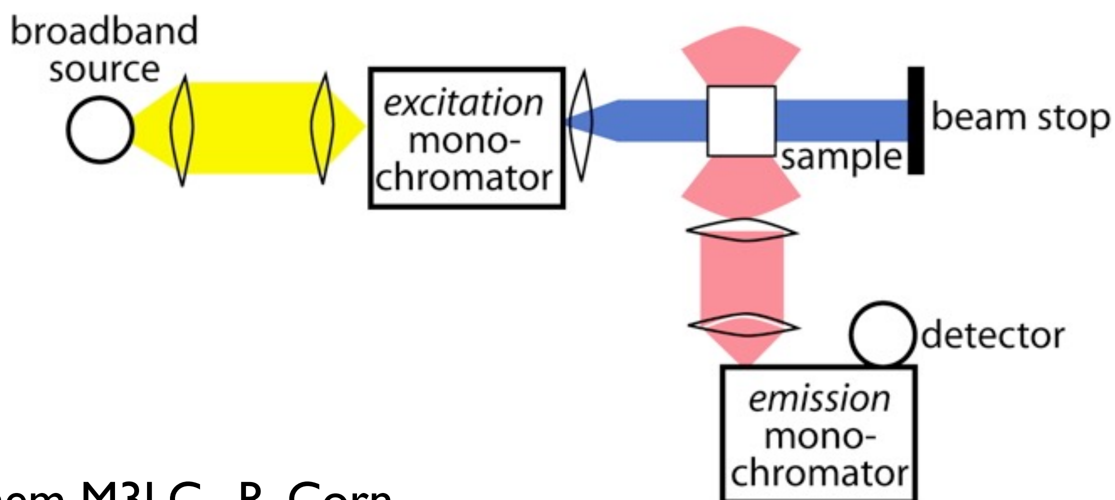
Absorption, Emission and Fluorescence Spectroscopies

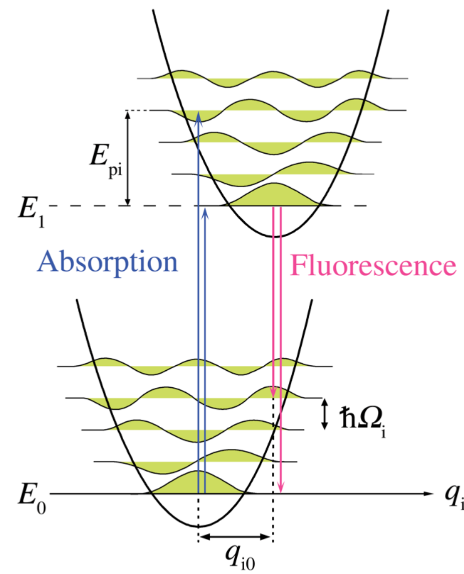
Absorption Spectrometer





Fluorescence Spectrometer





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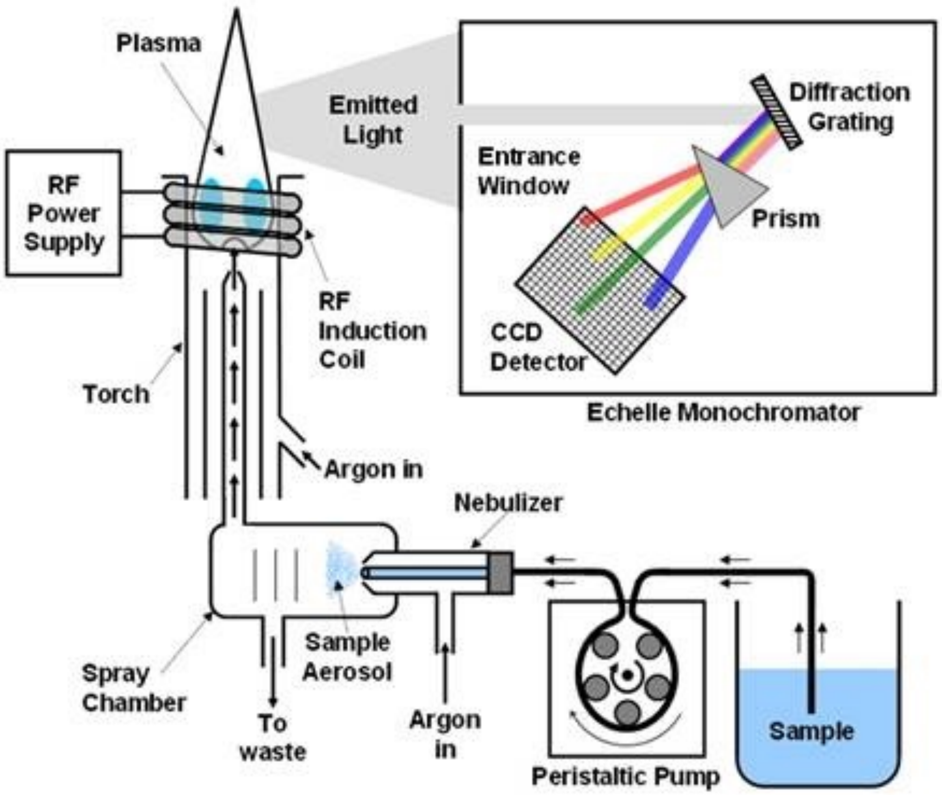
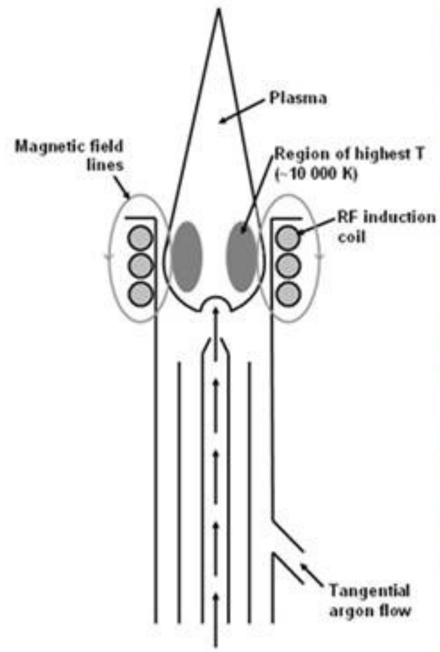
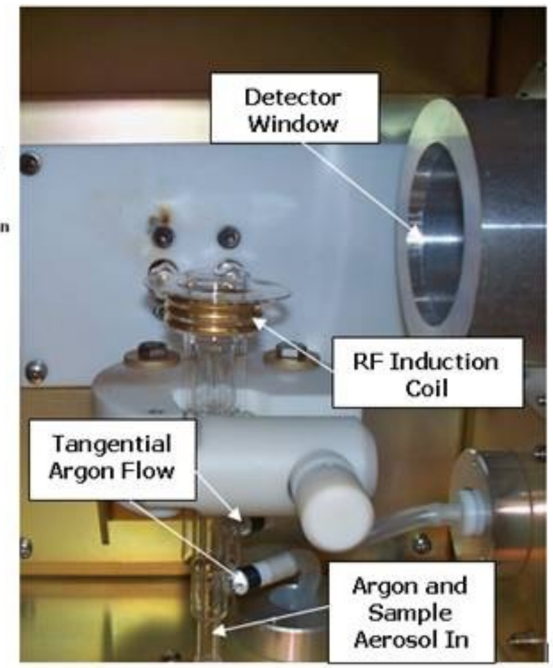
Inductively Coupled Plasma - Atomic Emission Spectrometer







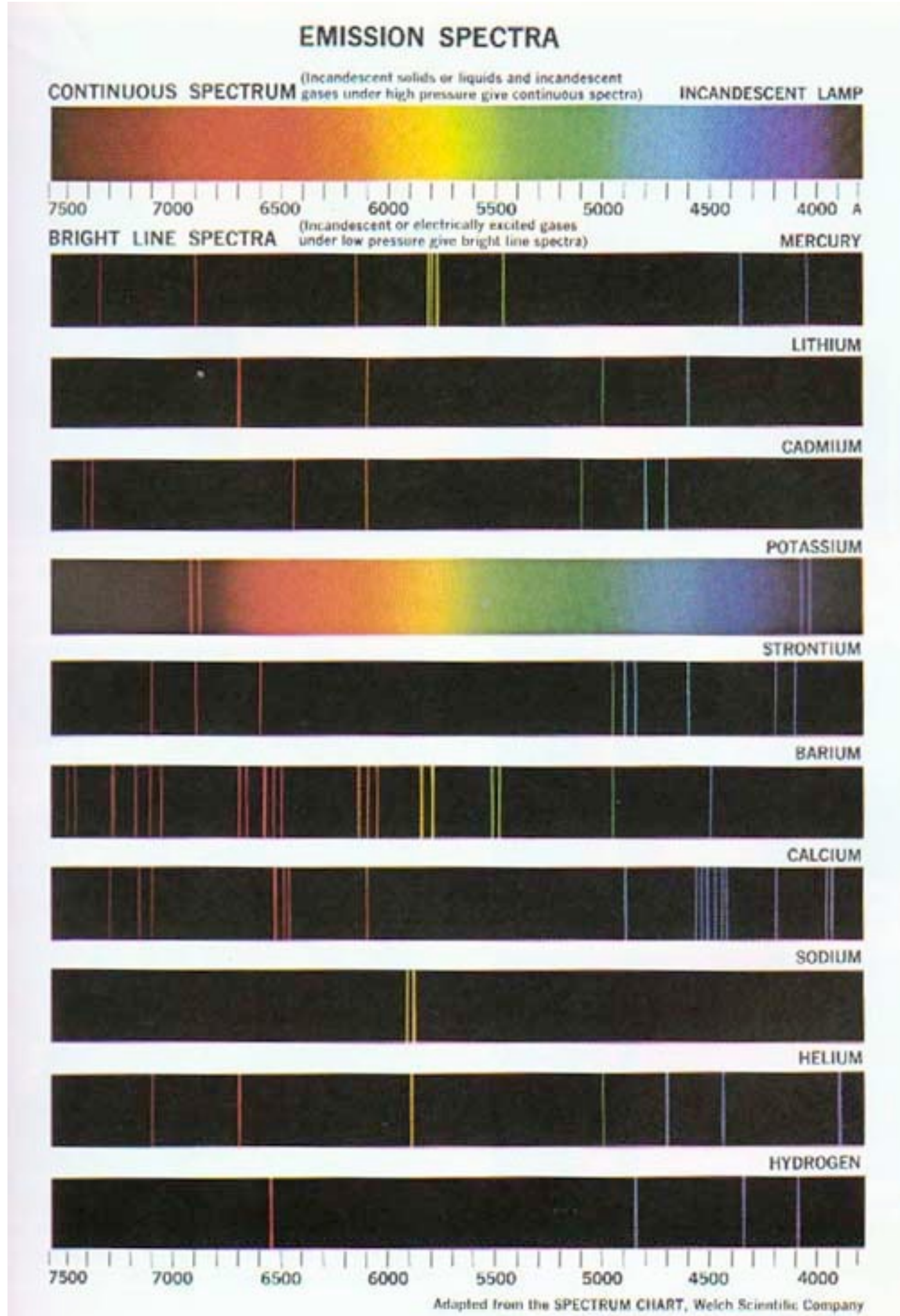
Liquid samples are nebulized into an argon plasma (10000 K) that breaks the sample into atoms and ions. Narrow band atomic emission is measured and the elemental composition is obtained.

Pictures from Concordia College (MN)
http://sites.cord.edu/chem-330-lab-manual/experiments/icp-aes

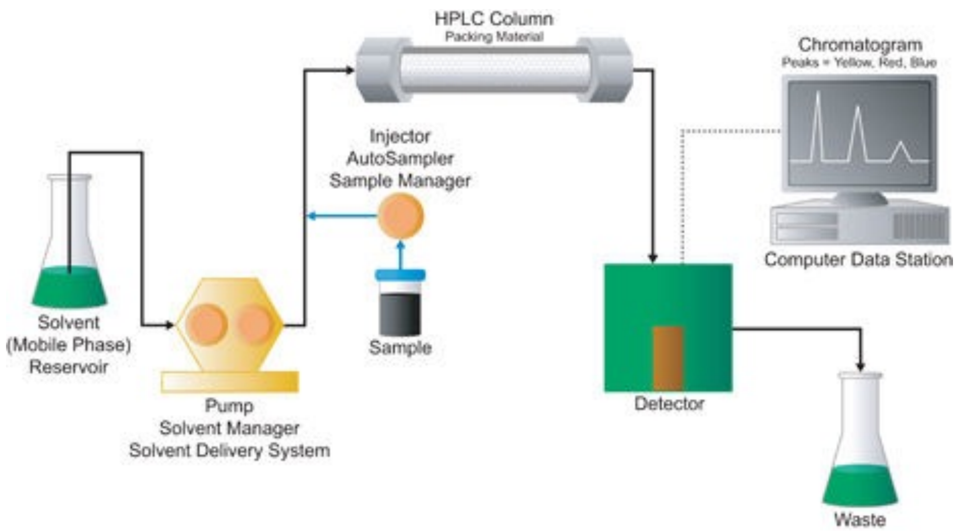
Spectroscopic Methods for Trace Metals in Seawater

Atomic Emission Spectroscopy

Each element has a unique emission spectrum



High Performance Liquid Chromatography (HPLC)

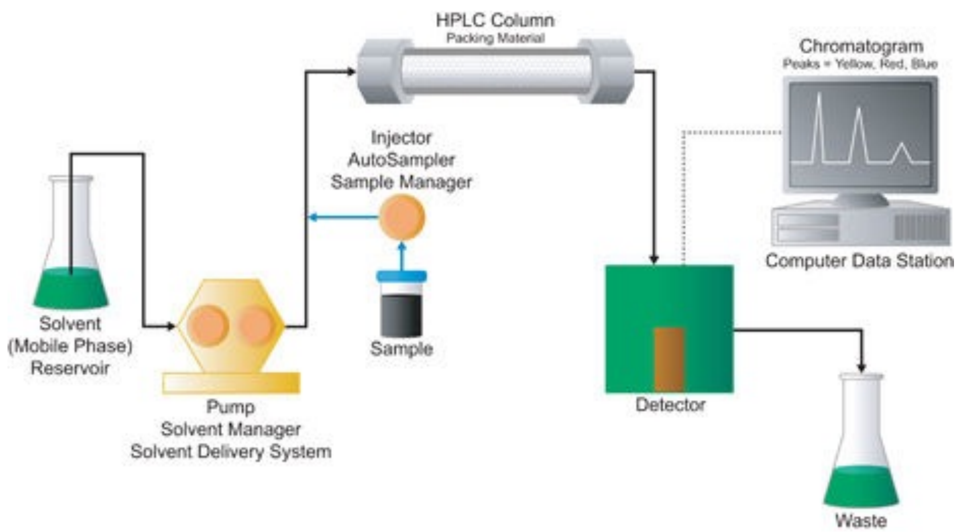


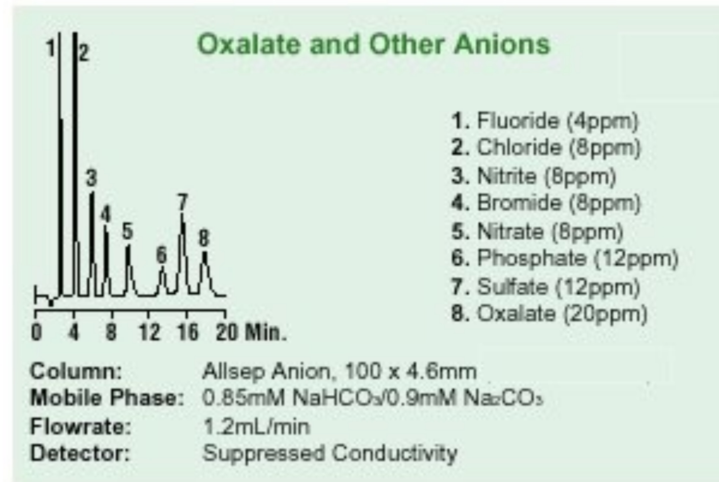
Partition chromatography
Normal–phase chromatography
Reversed-phase chromatography
Size-exclusion chromatography
Ion-exchange chromatography
Bioaffinity chromatography

Samples are passed over a packed column (stationary phase) and separated. Many types of chromatography based on different physical separation principles - the simplest is just partitioning (phase equilibria).

Picture from Waters Company
http://www.waters.com/

High Performance Liquid Chromatography (HPLC)





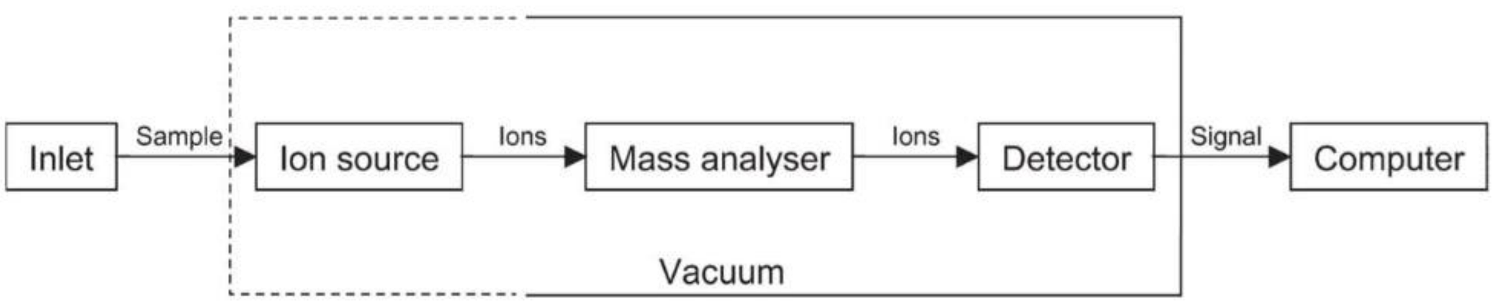
Ion-exchange chromatography is useful for the separation of organic and inorganic anions in one run. For example, samples containing oxalate and inorganic anions can be analyzed by a single method as shown in this chromatogram.

Samples are passed over a packed column (stationary phase) and separated. Many types of chromatography based on different physical separation principles - the simplest is just partitioning (phase equilibria).

IEC data from Universidad de Antioquia - Instituto de Química (Columbia)
http://quimica.udea.edu.co/~carlopez/cromatoion/ion2.html

Elements of a Mass Spectrometer

1. Device to insert sample into the mass spec.-
   sample probe, chromatograph,
   capillary
2. Source to produce ions from the sample.
3. Analyzer ($\geq$1) to separate ions by m/z.
4. Detector to count ions.
5. Computer to control instrument and
   collect & analyze data.



Ionization Methods

Characteristics:

1. Energy Imparted:

Soft Ionization (less fragmentation)-

MALDI- matrix-assisted laser desorption/ionization

ESI- electrospray ionization

Hard- EI (electron impact ionization),

FAB (fast atom bombardment),

SIMS (secondary ion mass spectrometry)

2. Sample State:

Gas- EI, CI

Liquid- nebulization to introduce droplets, **ESI**, thermospray

Solid- uses an absorbing matrix &

irradiate with particles or photons

MALDI, FAB, field & plasma desorption

Mass Spectrometry

Mass Analyzers:

1. Quadrupole Analyzer- R ~ 3000; m/z < ~2000;
   mass accuracy ~400 ppm, poor sensitivity

2. Ion Trap- R ~ 5000; m/z < ~2000;
   mass accuracy ~200 ppm; excellent sensitivity

3. Time of Flight (TOF)- R ~ 10,000; m/z < 500,000;
   mass accuracy ~10 ppm; very good sensitivity

4. Fourier-Transform Ion Cyclotron Resonance (FTICR)
   R ~ 1,000,000; mass accuracy ~1 ppm;
   Very expensive (limited availability);
   Ions are confined in a high B field;
   B field is created by a superconducting magnet;
   Circling frequency of ions ~ z/m

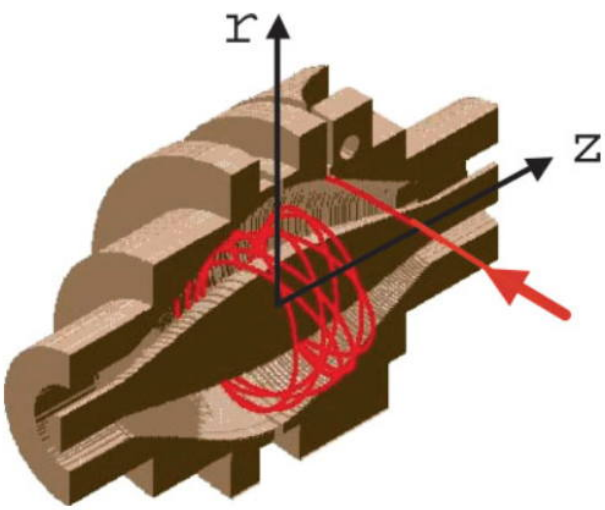


Figure 1. Cutaway view of the Orbitrap mass analyzer. Ions are injected into the Orbitrap at the point indicated by the red arrow. The ions are injected with a velocity perpendicular to the long axis of the Orbitrap (the *z*-axis). Injection at a point displaced from *z* = 0 gives the ions potential energy in the *z*-direction. Ion injection at this point on the *z*-potential is analogous to pulling back a pendulum bob and then releasing it to oscillate.

5. Orbitrap. See
Q. Hu et al., J. Mass Spectrom. 2005; 40: 430–443

Mass Analyzers – Time-of-Flight

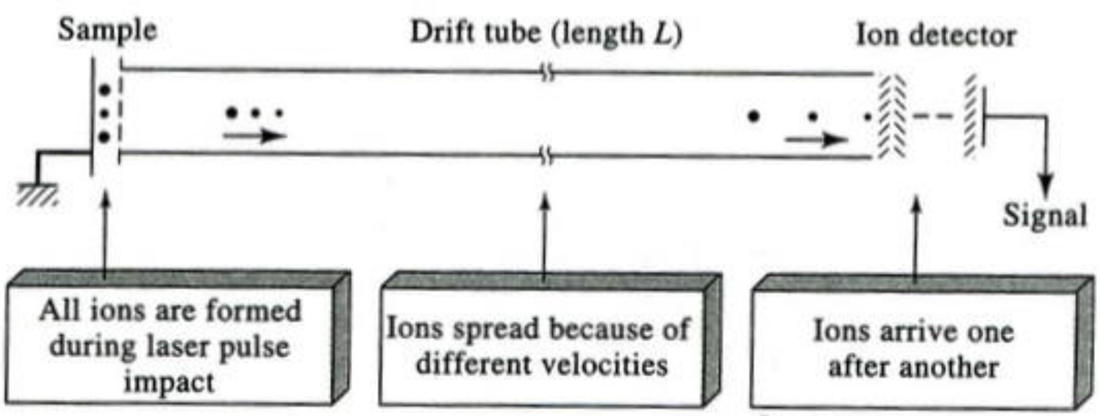


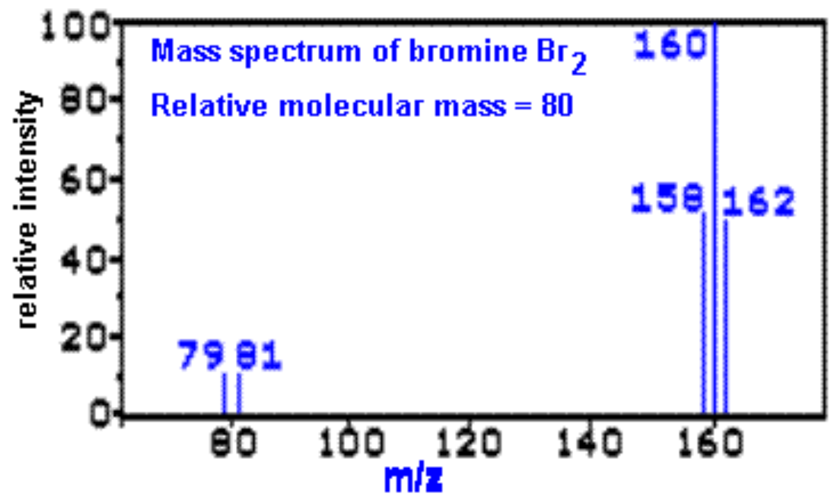
FIGURE 11-10 Principle of a TOF mass spectrometer. A spatially tightly bunched group of ions produced by a laser probe is accelerated into the drift tube where separation occurs. (From A. H. Verbueken, F. J. Bruynseels, R. Van Grieken, and F. Adams, in *Inorganic Mass Spectrometry*, p. 186, F. Adams, R. Gijbels, and R. Van Grieken, eds., New York: Wiley, 1988. With permission.)

$zeV = KE = ½(mv^2)$ $t_f = L/v = L\,(m/2zeV)^{1/2}$

Units and Numbers

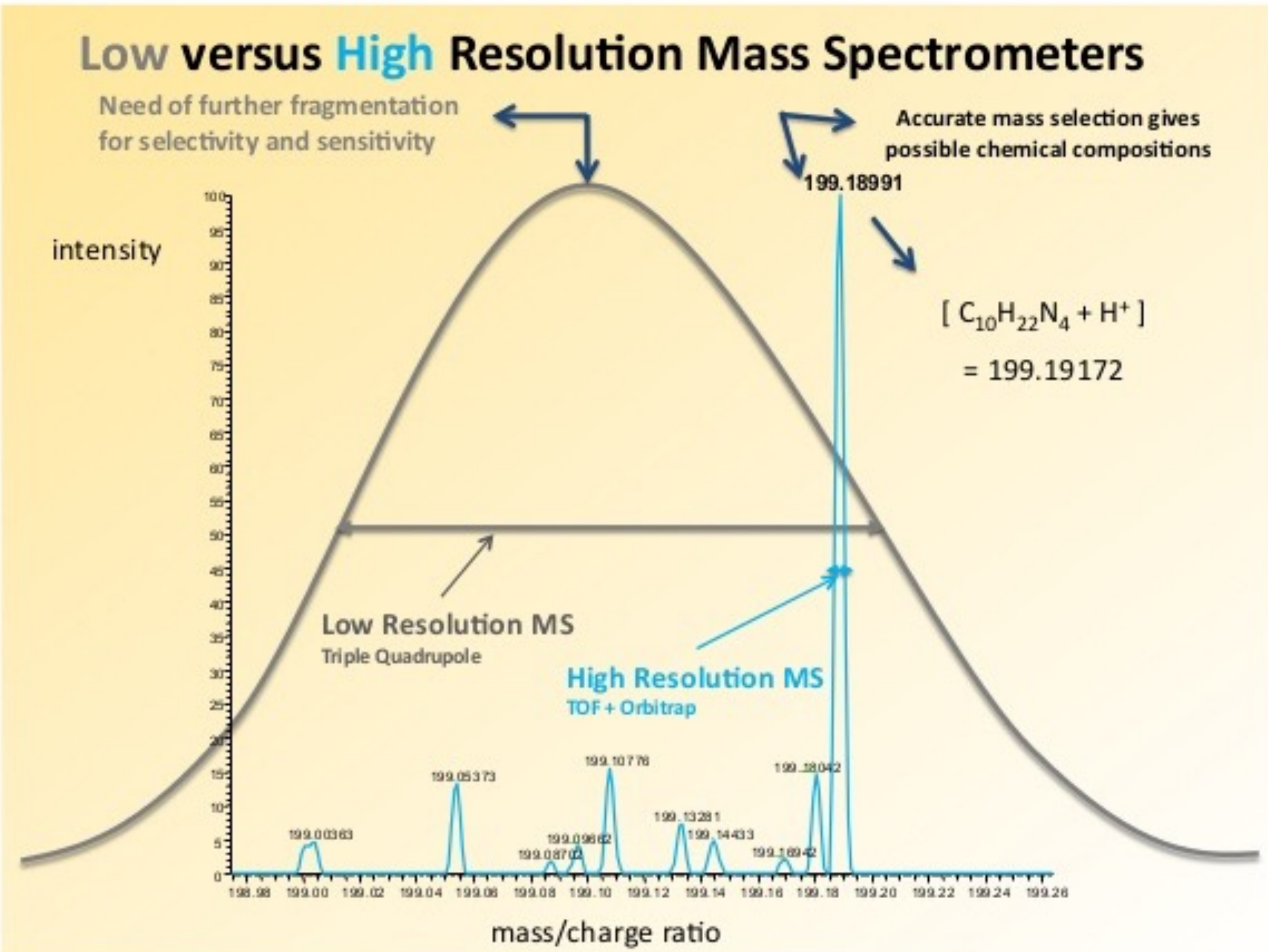
m/z = mass/(# of e charges on the ion)
m = Daltons (Da) or atomic mass units (U)
m/z units = Thompson (Th)

Bromine
50/50 mix
MW 79 and 81



Mass Spectrometry

Ultra-high resolution MS can resolve different species with the "same" molecular weight!



For example:

Hydrogen-1: 1.007825 amu
Nitrogen-14: 14.003074 amu
Carbon-12: 12.0000 amu

NH_2

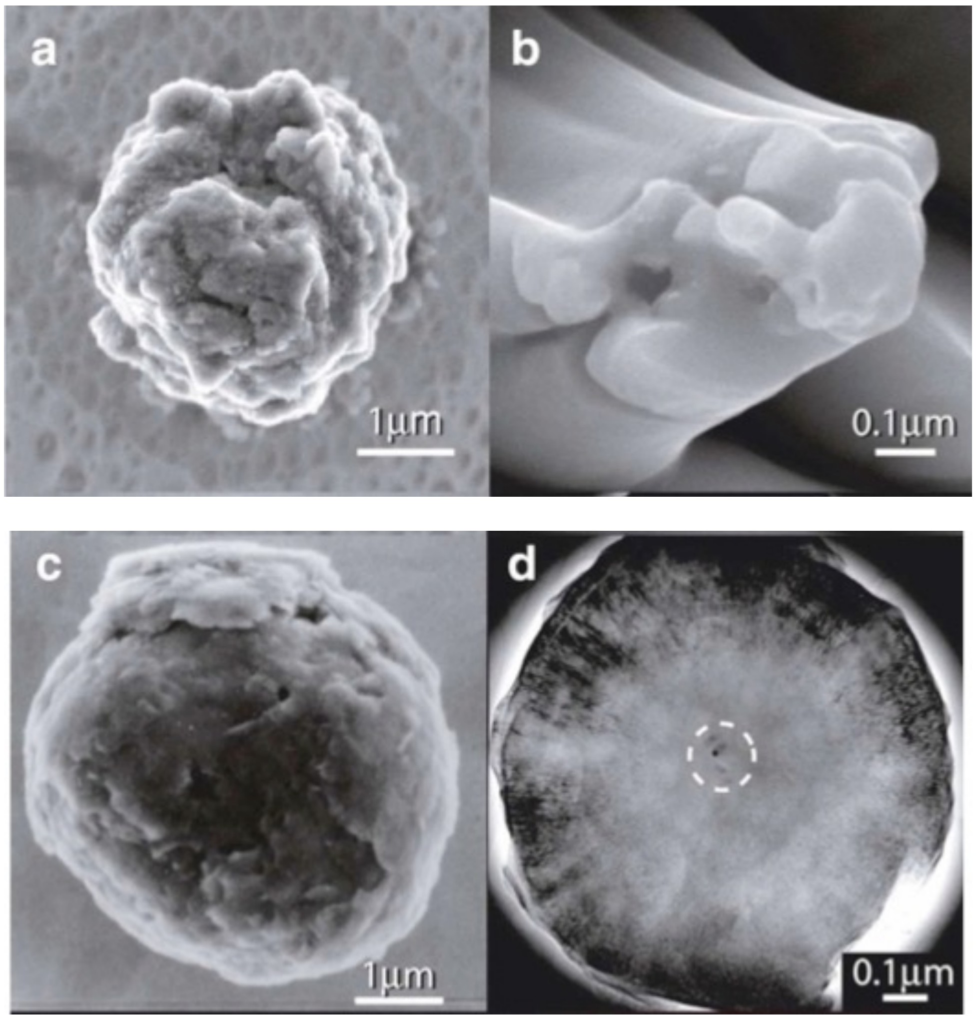
16.0187 amu

CH_4

16.0313 amu

Presolar Stardust

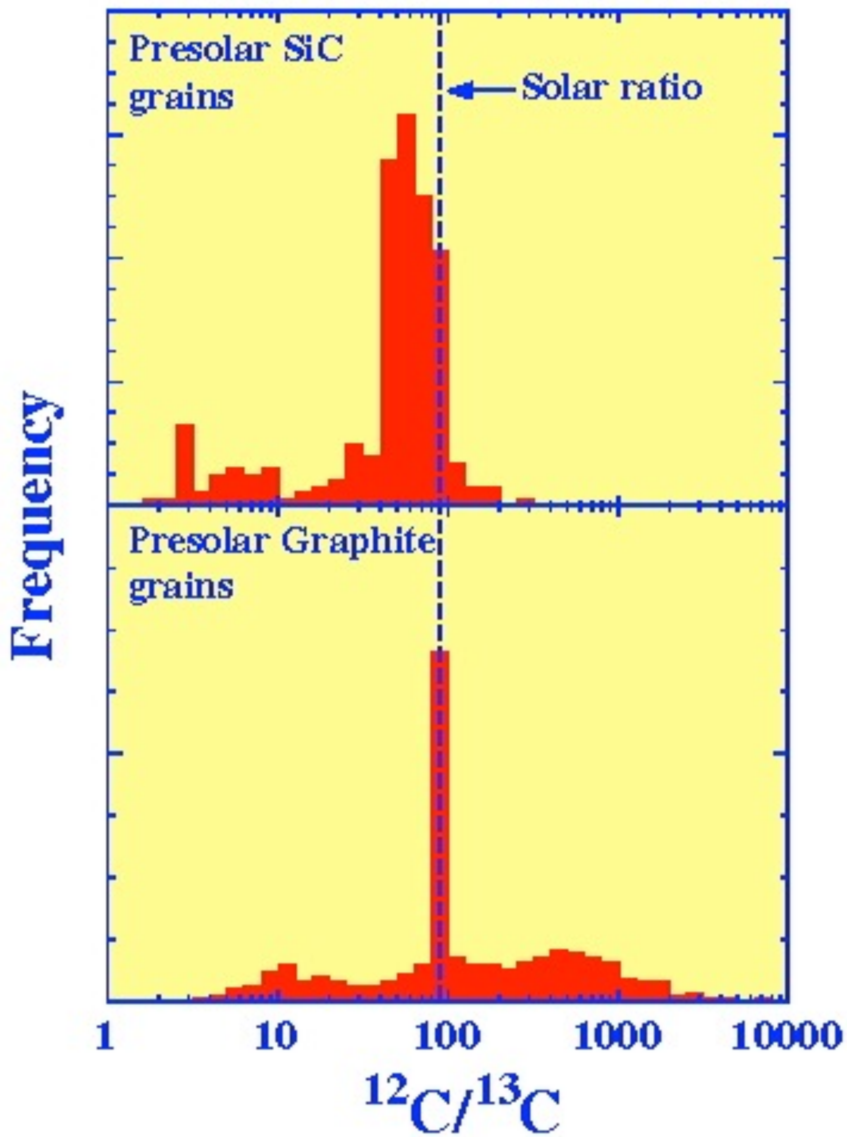
Embedded in the fine-grained dust of chondrites are **presolar grains**, which predate the formation of our solar system and originated elsewhere in the galaxy.



Larry R. Nittler, *Earth and Planetary Science Letters*, **209** 259-273 (2003). Presolar stardust in meteorites: recent advances and scientific frontiers.

C12/C13 Ratios in Presolar Grains

Carbon isotopic ratios measured in presolar grains from meteorites.



Carbon on the Sun, Earth, Moon, Mars, and the other planets has about 89 12C atoms for every 13C atom.

Presolar grains, on the other hand, contain the original atoms from their parent stars with different isotopic ratios.

Presolar silicon carbide and graphite grains have carbon isotopic ratios that range from about 3 to 10,000!

Nanodiamonds - Key to the Universe?

Nanodiamonds (ca. 2.5 nm diameter) are the most abundant, but least understood type of pre-solar grains. Scientists believe that only supernovae can form the nanodiamond or SiC grains found in presolar stardust.

Isotope Ratio Measurements

Nanodiamonds are identified as presolar on the basis of containing highly unusual Xe isotopic ratios (from Xe trapped in the nanodiamond), which seem to reflect nucleosynthetic processes in supernovae (SN).

However, their small size precludes isotopic measurement of individual grains. Making matters worse is the fact that the Xe abundance is such that only about one in a million diamond grains contains a single Xe atom!

Raman Spectrum of Diamond
One sharp band at 1332 cm^{-1}

Raman Imaging is used to map nanodiamonds in meteorites