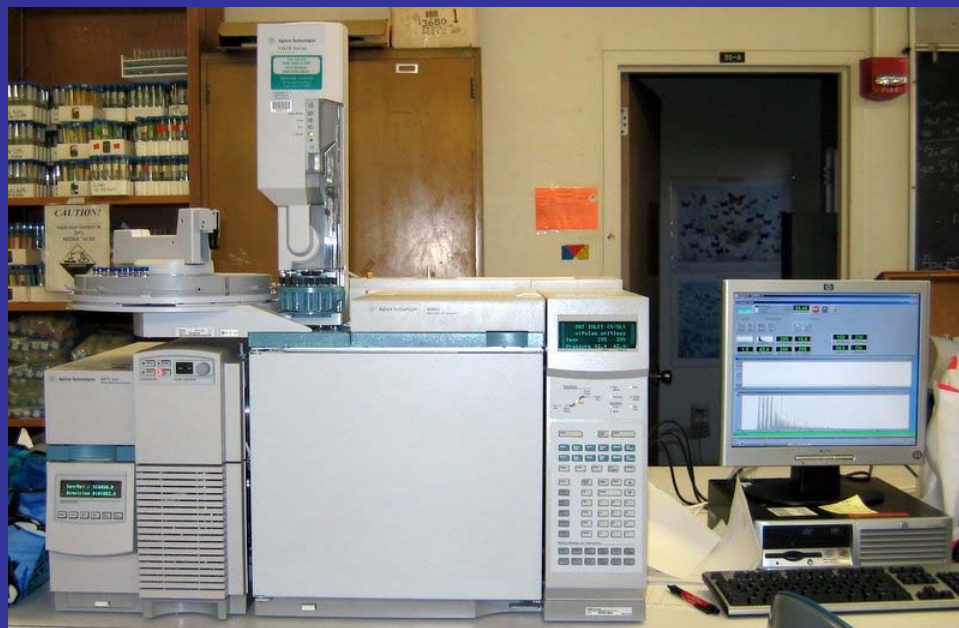
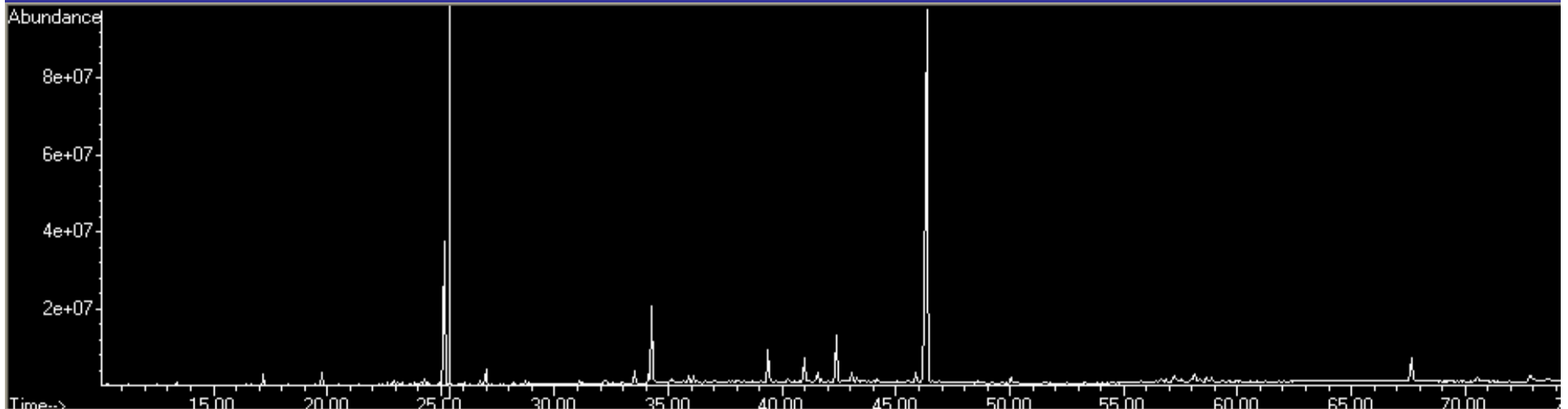


GCMS



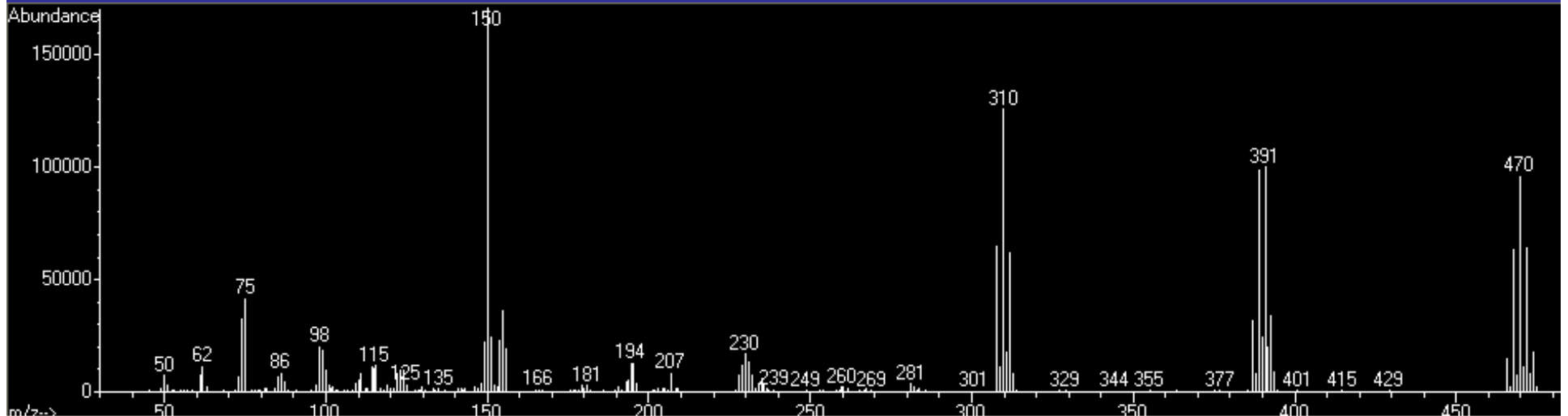
Gas Chromatography

- Used to separate components of a mixture
- Mixture is injected, vaporized and carried by an inert gas
- Compounds separate when they interact with the column at different times Retention times are based on the polarity of the substance compared to the column
- Components then pass into a mass spectrometer where they are ionized, fragmented, and detected



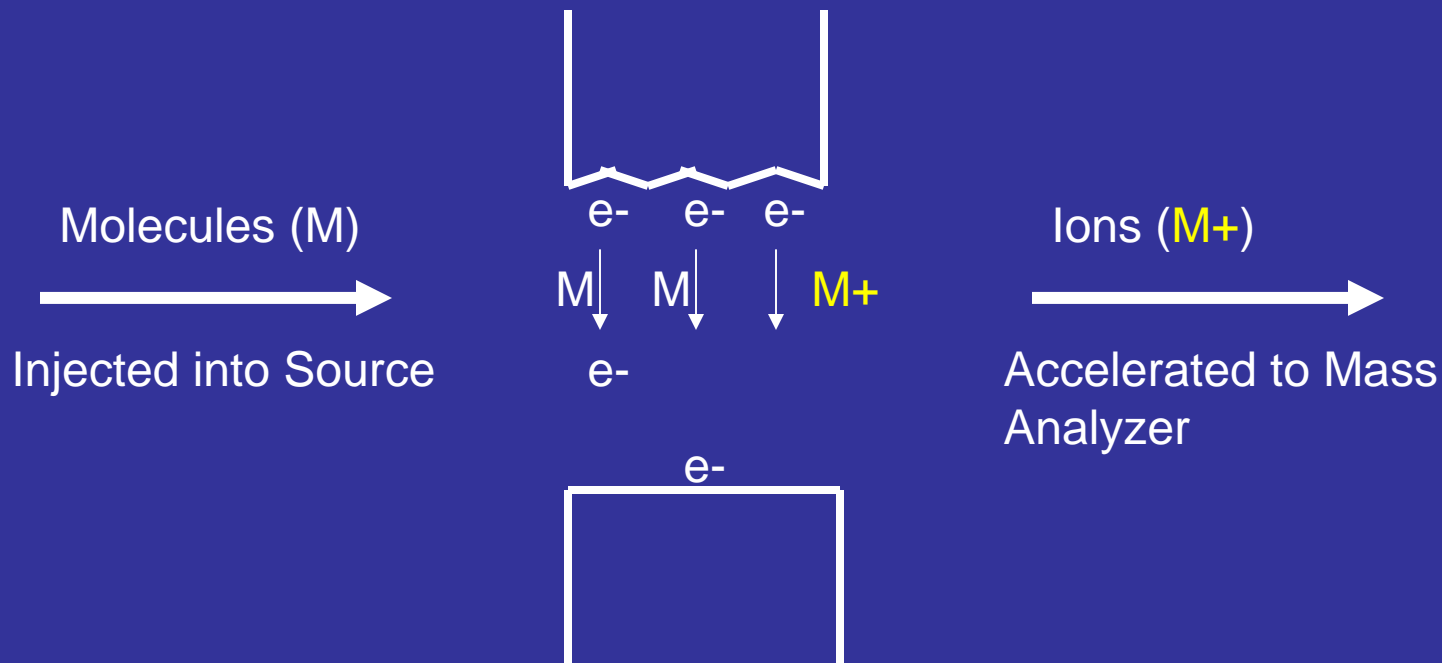
Mass Spectrometry

- Vaporized substance is ionized to form a positive ion
- Passes through ion accelerator that propels the ion through a thin slit
- Narrow beam of positive ions passed into a magnetic field which deflects ions according to mass to charge ratio
- All mass spectrometers consists of 3 regions:
 - Ionizer
 - Mass Analyzer
 - Detector



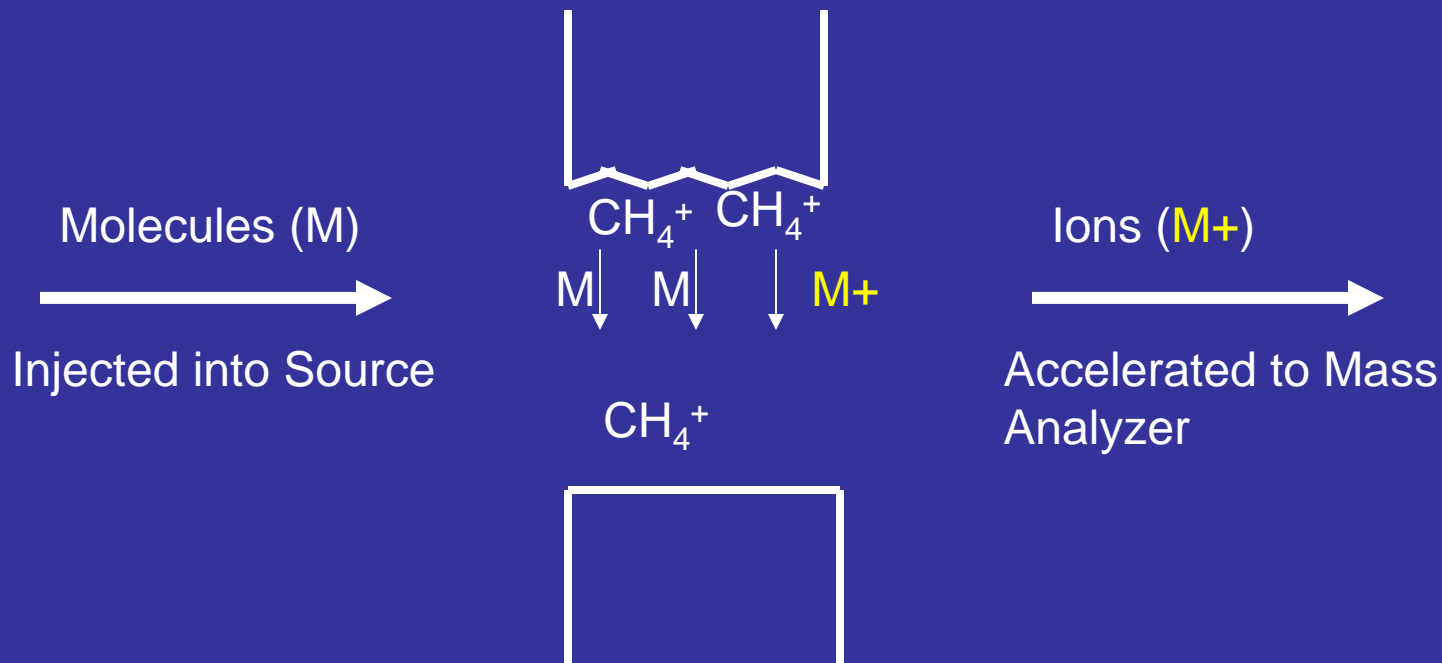
Ionizer – electron impact (EI)

- A high energy beam excites gas molecules by ejecting electrons which strikes molecules to remove an electron



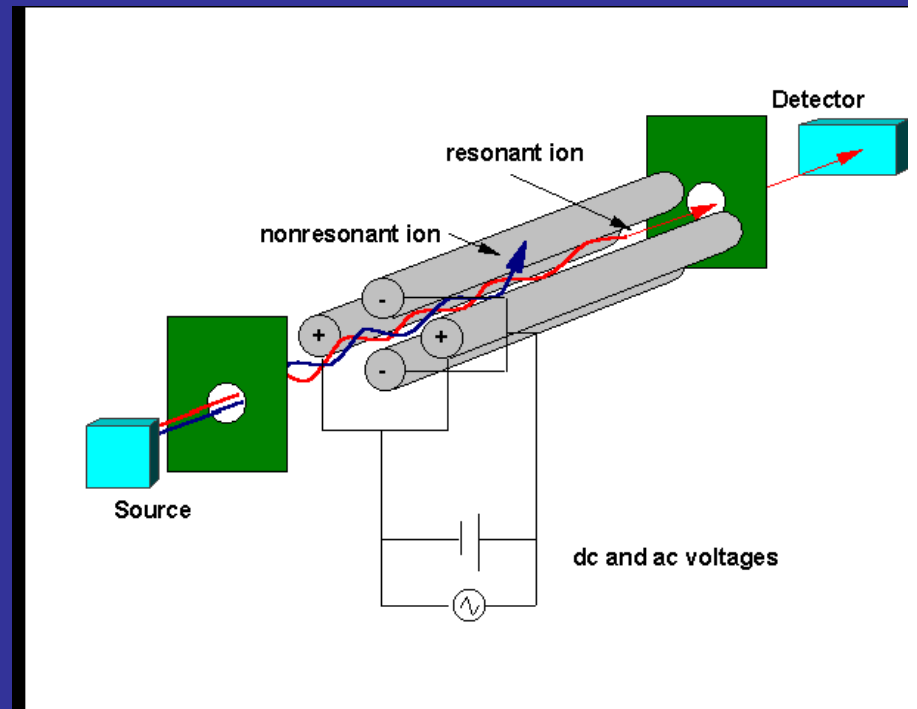
Ionizer – chemical ionization (CI)

- Ions are produced through the collision of the analyte (sample) with the ions of the reagent (or ionizing) gas that are present in the ion source
 - Fragments the molecule to a lower degree than the hard ionization of EI
 - Benefit of CI the mass fragment closely corresponds to the molecular weight of the analyte in interest



Mass Analyzer - quadrupole

- Sorts the ions according to their mass/charge (m/z) ratio
- Electric field generated by charged rods is modulated by controlled AC and DC voltage sources
- Incoming ions whose m/z meets resonate criteria will pass through quadruple filter
- A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied



Ion detector

- Counts the ions and a signal is generated that is proportional to the total number of ions

Why use GCMS data

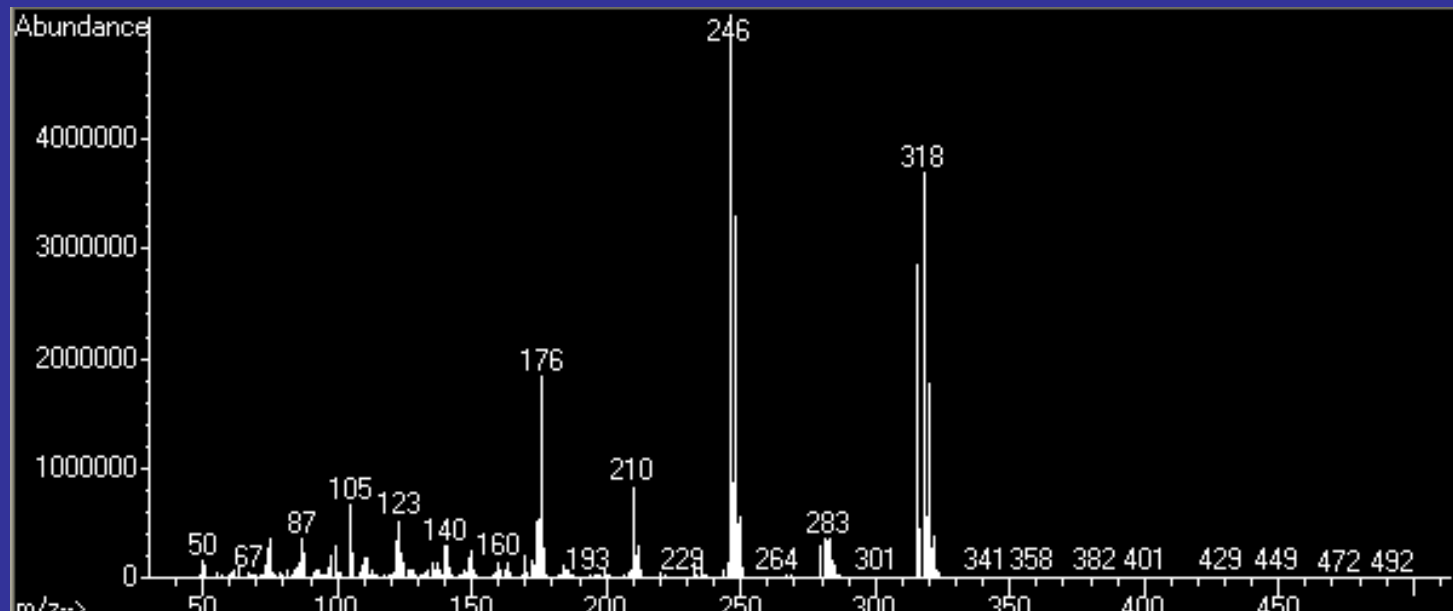
- Each mixture component is fragment uniquely by the mass spectrometer
- Information can be used to identify compounds or compare samples
- Quantitatively measure subtle differences
- Can be used for characterizing complicating mixtures such as fuel

GCMS Applications

- Data may be viewed, processed, or analyzed
 - Total Ion Chromatogram, Single Ion Chromatogram, or Mass Spectra
- Graphs respond to user interaction – clicking, adjust, contrast

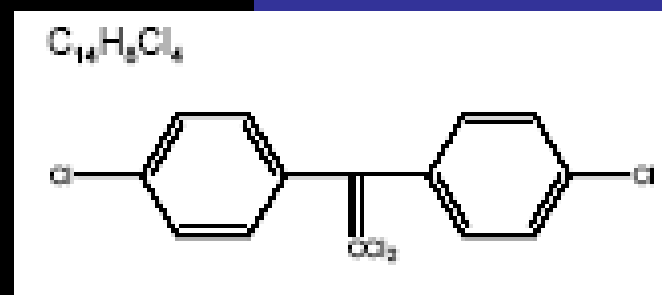
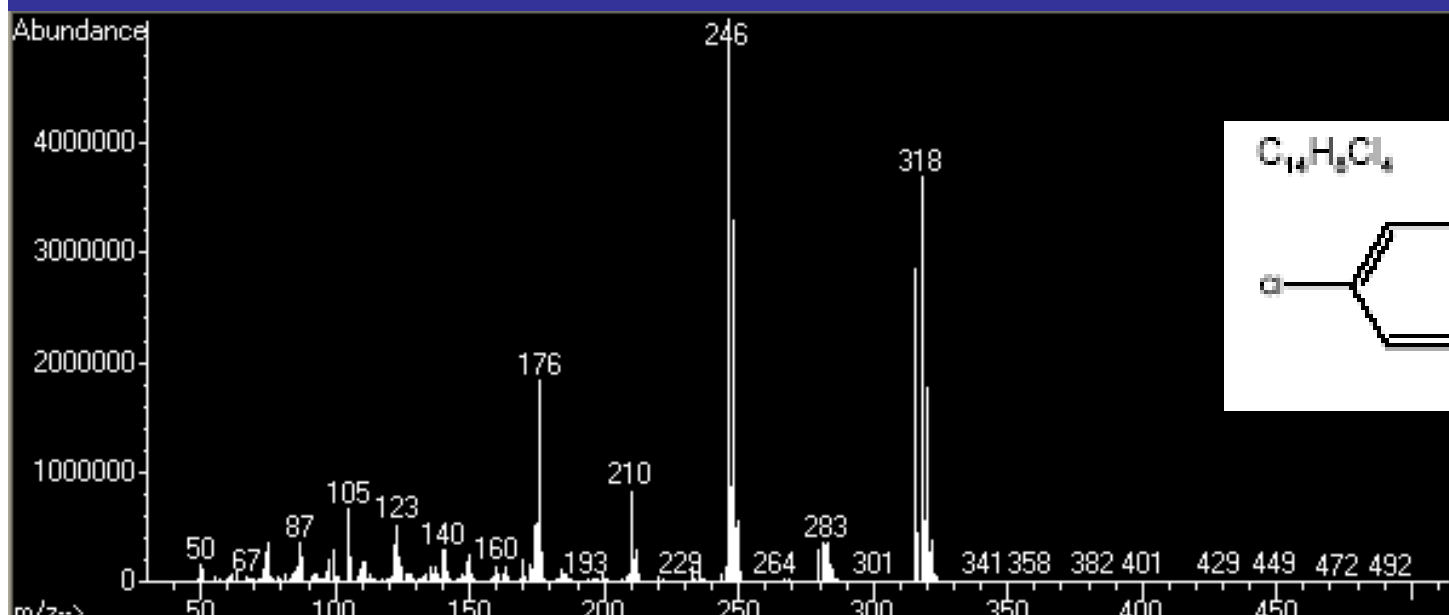
Fragmentation patterns in the mass spectra

- The tallest line in the mass spectra (in this case at $m/z = 246$) is called the *base peak*
 - The height of everything else is measured relative to this
 - The base peak is the tallest peak because it represents the commonest fragment ion to be formed



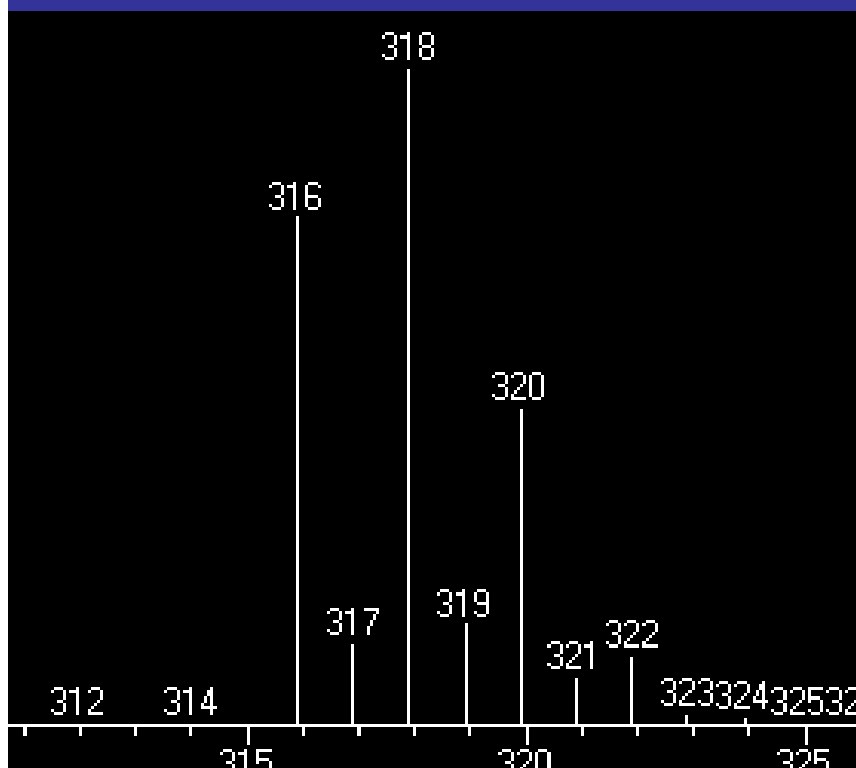
Mass Spectra – the molecular ion (M⁺) peak

- In the mass spectrum, the heaviest ion (the one with the greatest m/z value) is likely to be the molecular ion
 - Example: DDE mass spectrum
 - Because the largest m/z value is 318, that represents the largest ion going through the mass spectrometer - and you can reasonably assume that this is the molecular ion



The effect of chlorine atoms on the mass spectrum

- The lines in the molecular ion region (at m/z values of 318) arise because of the various combinations of chlorine isotopes that are possible
- Chlorine can be either of the two chlorine isotopes, ^{35}Cl and ^{37}Cl
- Chlorine contains 3 times as much of the ^{35}Cl isotope as the ^{37}Cl one
- The carbons and hydrogens add up to 176 - so the various possible molecular ions could be:
 - $176 + 37 + 37 + 37 + 37 = 324$
 - $176 + 35 + 37 + 37 + 37 = 322$
 - $176 + 35 + 35 + 37 + 37 = 320$
 - $176 + 35 + 35 + 35 + 37 = 318$
 - $176 + 35 + 35 + 35 + 35 = 316$

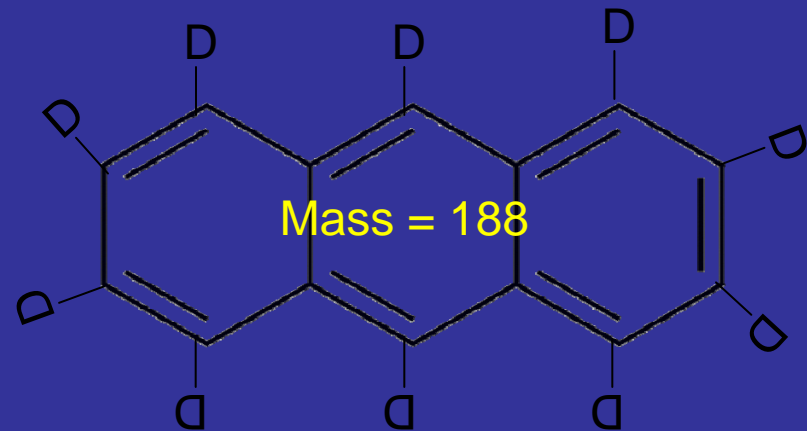
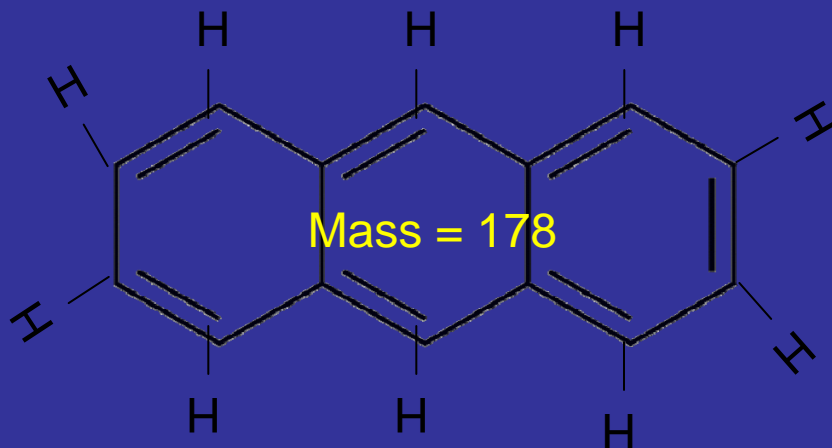


Internal standard

- A known concentration of a substance that is present in every sample (standards, blanks, QA/QC, unknown) that is analyzed
 - Dibromobiphenyl
 - Tetrabromobephenyl
 - Anthracene-d10
- Signal from analyte is compared with signal from the internal standard to find out how much analyte is present

Deuterium (D)

- Stable isotope of hydrogen
 - Mass 2.014 (common H = 1.007)
 - Contains one proton and one neutron (common hydrogen contains no neutron)
- Behaves similarly to ordinary hydrogen
- Distinguished easily from ordinary H by its mass using mass spectrometry
 - Example- Anthracene



Recovery surrogates (RS)

- Monitors extraction efficiency

Recovery surrogates	5E-SO G1S1 (A); ng/g	Spike; ng	% recovery
TCMX	176.48	400	44.12
PCB 30	318.97	400	79.74
PCB 112	367.87	400	91.97
PCB 198	496.84	400	124.21

- Acceptance range = 70-130%

Matrix spikes (MS)

- Determines the effect of the matrix on analyte recovery

Analyte	Matrix Spike 1			Matrix Spike 2			RSD
	Net	Spike Amt	% Recovery	Net	Spike Amt	% Recovery	
PCB 008	89.10	160	55.69	88.65	160	55.41	0.36
PCB 018	112.77	160	70.48	123.49	160	77.18	6.42
PCB 028	91.66	160	57.29	101.69	160	63.56	7.34
PCB 031	117.26	160	73.29	124.03	160	77.52	3.97
PCB 033	95.40	160	59.63	109.84	160	68.65	9.95
PCB 052	104.38	160	65.24	117.26	160	73.29	8.22

- $RSD = ((STDEV(MS1,MS2))*100)/(AVERAGE(MS1,MS2))$
- % recovery acceptance range = 70-130%
- RSD Acceptance < 30%

Standard Reference Material (SRM)

- Homogeneous material where analyte values have been well established to validate lab and analytical methods
 - Lake Michigan Fish Tissue (SRM 1947)
 - Sediments (1944)
 - Acceptance range = 70 -130%

Certified PCB congeners	Net µg/kg, ww	Spike Amt µg/kg, ww	% Recovery
PCB 28	13.85	14.1 ± 1.0	98.2
PCB 31	10.68	10.4 ± 1.4	102.7
PCB 52	35.85	36.4 ± 4.3	98.5
PCB 49	27.43	27.3 ± 3.8	100.5
PCB 44	21.42	20.4 ± 1.7	105.0
PCB 63	NA	4.75 ± 0.60	NA
PCB 74	32.40	33.7 ± 3.1	96.1