

# Chapter 27: Gas Chromatography

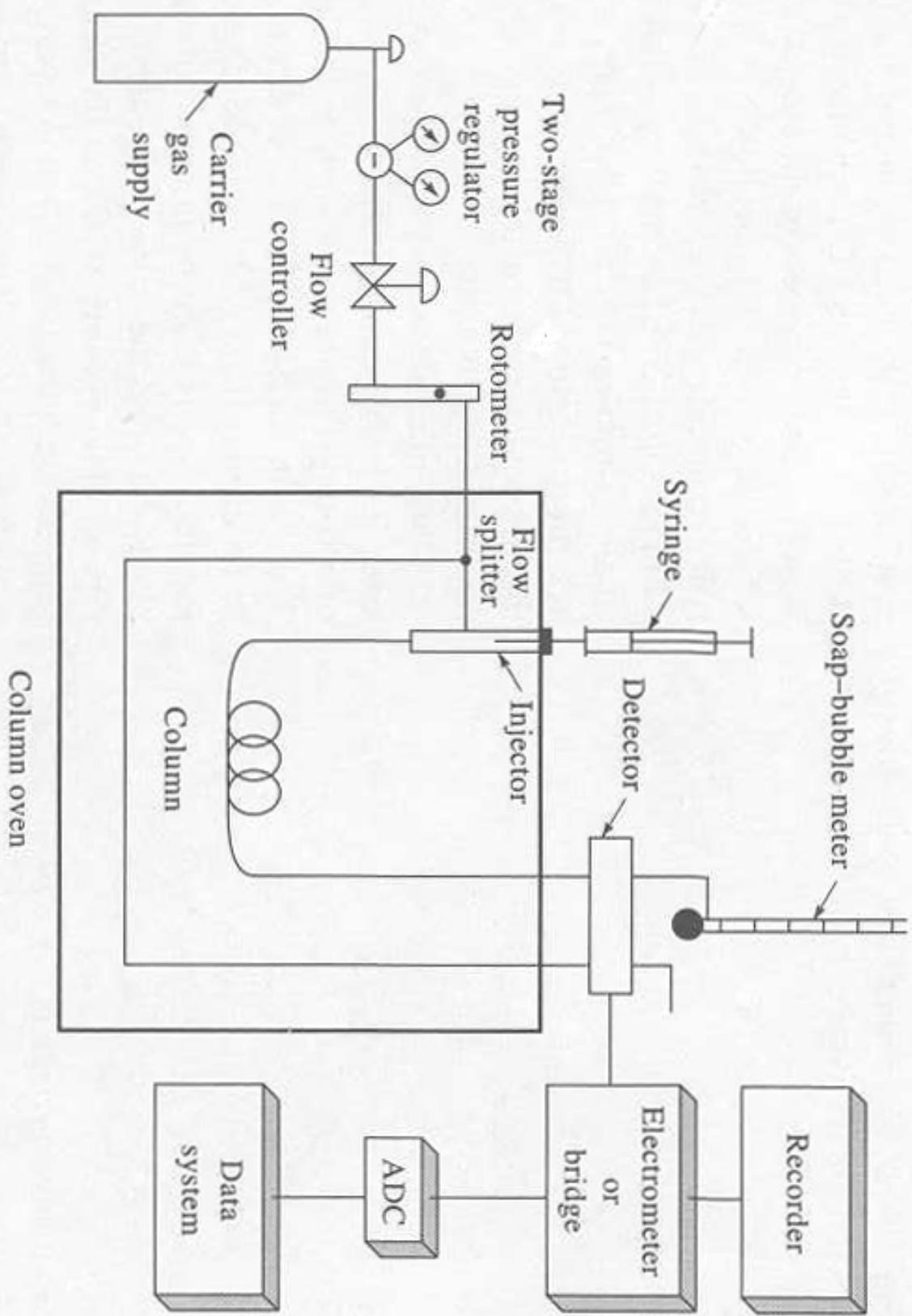
- Principles
- Instrumentation
- Detectors
- Columns and Stationary Phases
- Applications

**Basic Principle of GC** – sample vaporized by injection into a heated system, eluted through a column by inert gaseous mobile phase and detected

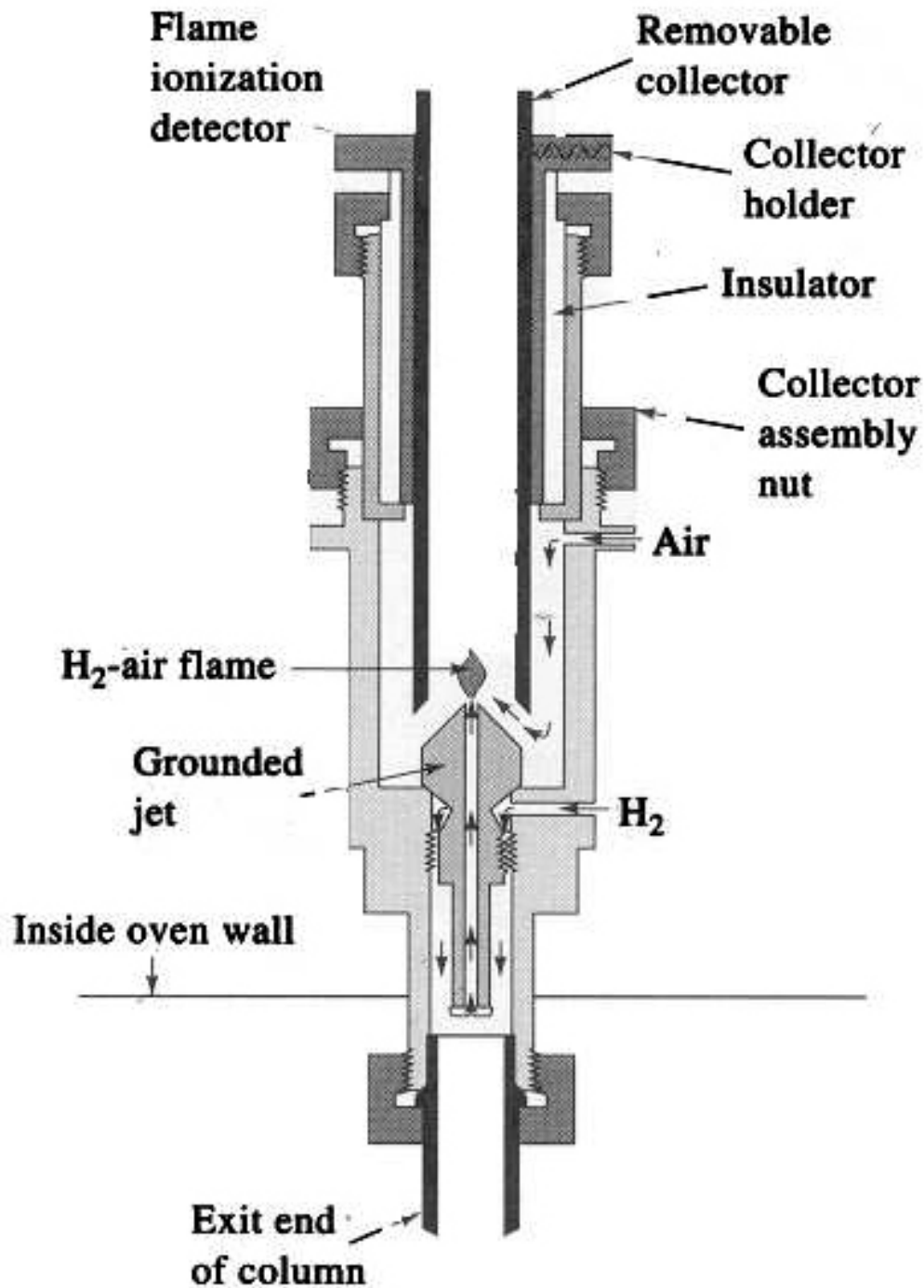
**Three types (or modes)**

- gas – solid chromatography ← early
- gas – liquid “ ← important
- gas – bonded phase “ ← relatively new

An estimated 200,000 GC in use worldwide



**Figure 27-1** Schematic of a gas chromatograph.

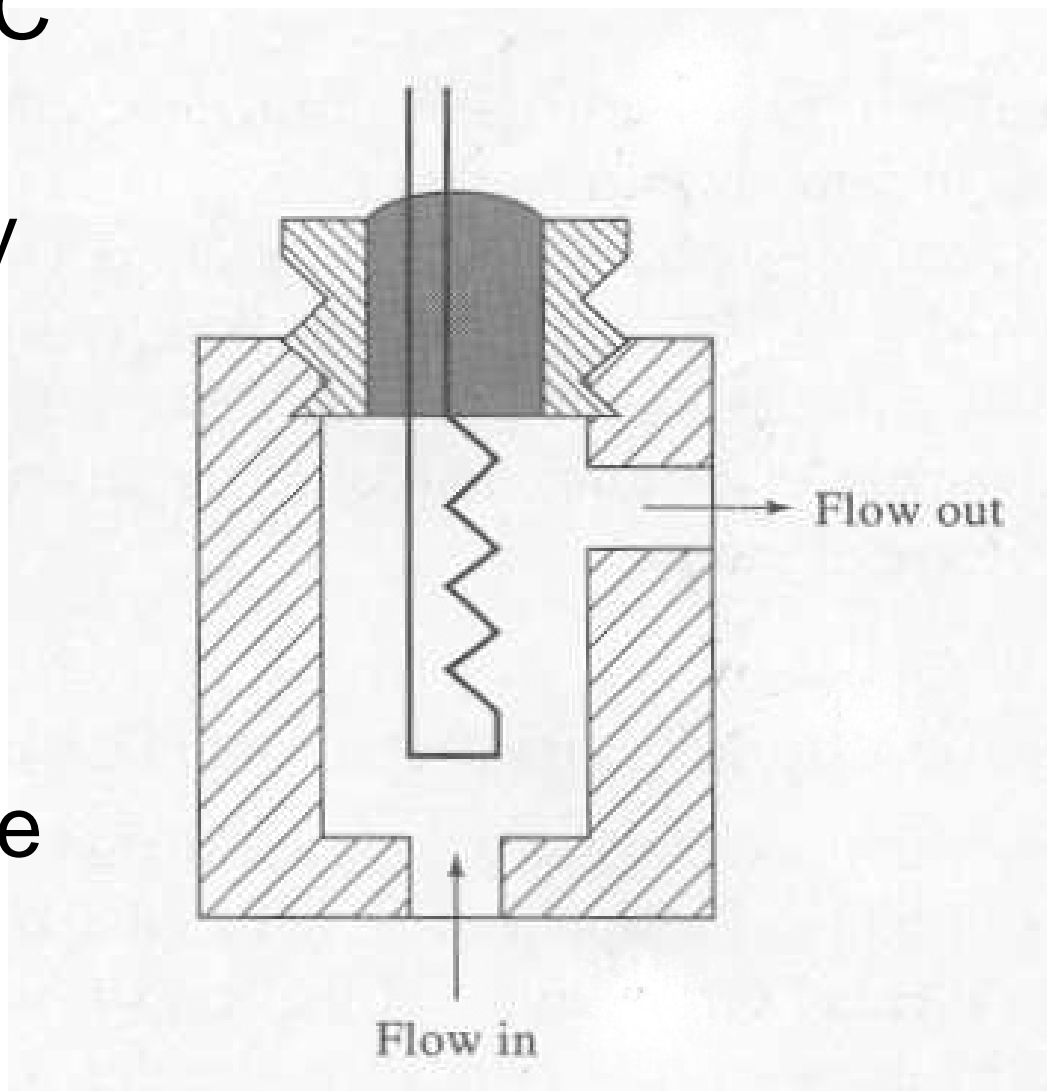


## Flame Ionization Detector (FID)

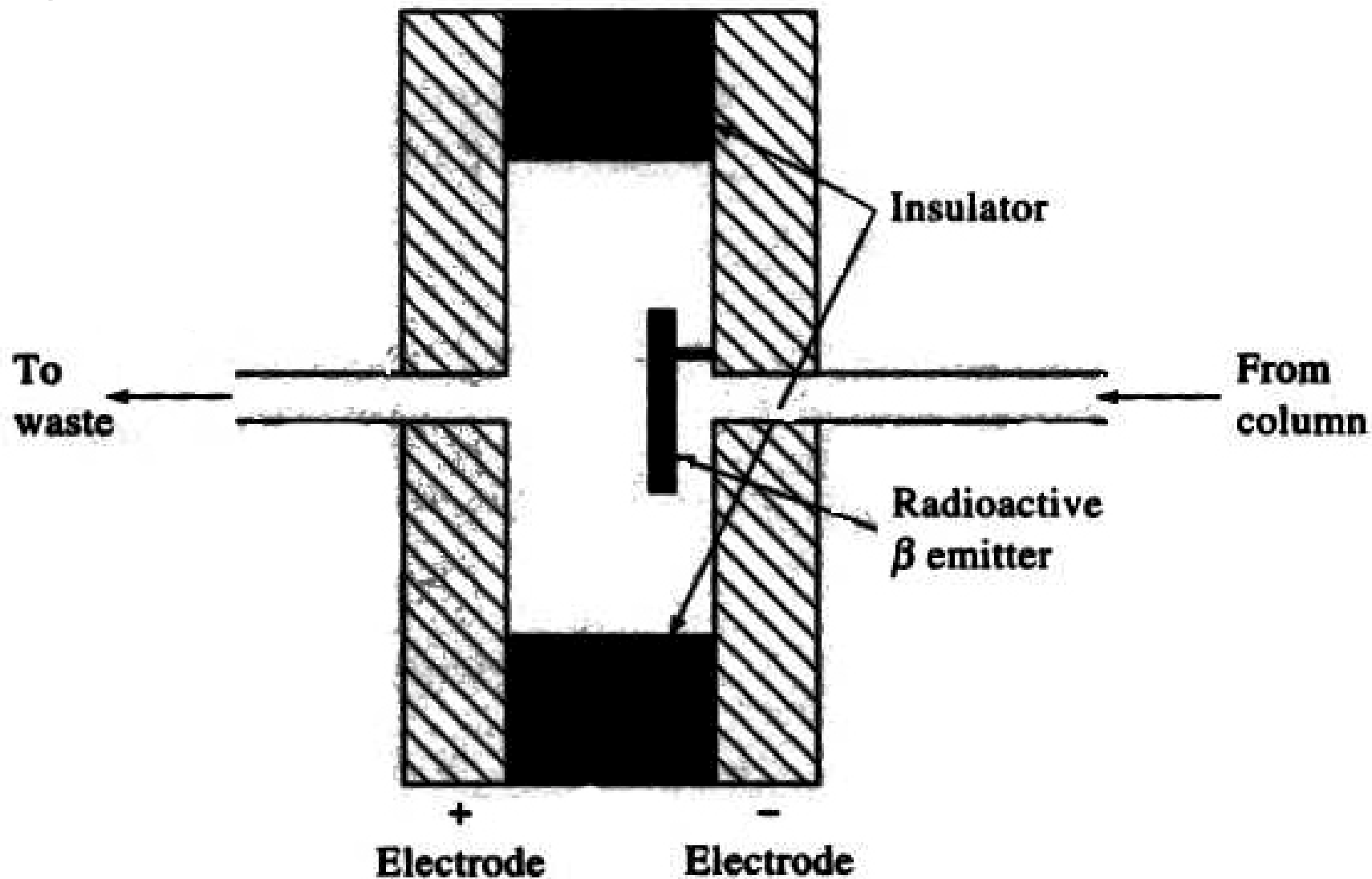
- one of most widely used GC detectors
- good sensitivity to almost all organic compounds

# Thermal Conductivity Detector (TCD)

- One of earliest GC detectors
- Not popular today
- Low sensitivity
- Several designs
- Use heated wire or semiconductor
- Resistance of wire changes with analyte vs carrier



ECD



**Figure 27-8** A schematic of an electron-capture detector.

## Electron Capture Detector

- Sample passes over  $\beta$  emitter (radioactive) like  $^{63}\text{Ni}$  foil or  $^3\text{H}$  adsorbed on Pt or Ti foil
- $\beta$  particles (i.e. electrons) hit carrier gas (usually  $\text{N}_2$ ) causing a burst of  $e^-$  to be released & measured by electrode = standing current or constant signal
- When analyte molecule that absorbs  $e^-$  passes through, current is reduced = signal
- Response is non-linear unless pulsed

## ECD Advantages

- Responds well to molecules with electronegative atoms like halogens (F, Cl, Br, I), peroxides, quinones, & nitro groups
- Insensitive to amines, alcohols, hydrocarbons
- Chlorinated pesticides are big application
- Highly sensitive
- Easy to use
- Pretty reliable, although foil can get coated
- Selective



## ECD Disadvantages

- Narrow linear range
- Radioactive
- Regular wipe test
- Bake out contaminants
- Some limits to applicability because highly selective

## Other Conventional Detectors

### Thermionic Detector (TID)

- Selective for N & P compounds
- 500 x more sensitive than FID for P
- 50 x more sensitive than FID for N
- Bad for C
- Design similar to FID with rubidium silicate bead at 180 V vs collector → get hot plasma 600 - 800 °C
- Produces large number of ions with N & P

## Flame Photometric Detector (FPD)

- Selective for P & S compounds
- Again sample goes through H<sub>2</sub>/air flame
- Observe optical emission of HPO at 510 nm & 526 nm & S<sub>2</sub> at 394 nm
- Use optical filters to isolate signal
- Can also measure halogens, N, some metals (e.g. Cr, Ge, Se)

## Photoionization Detector (PID)

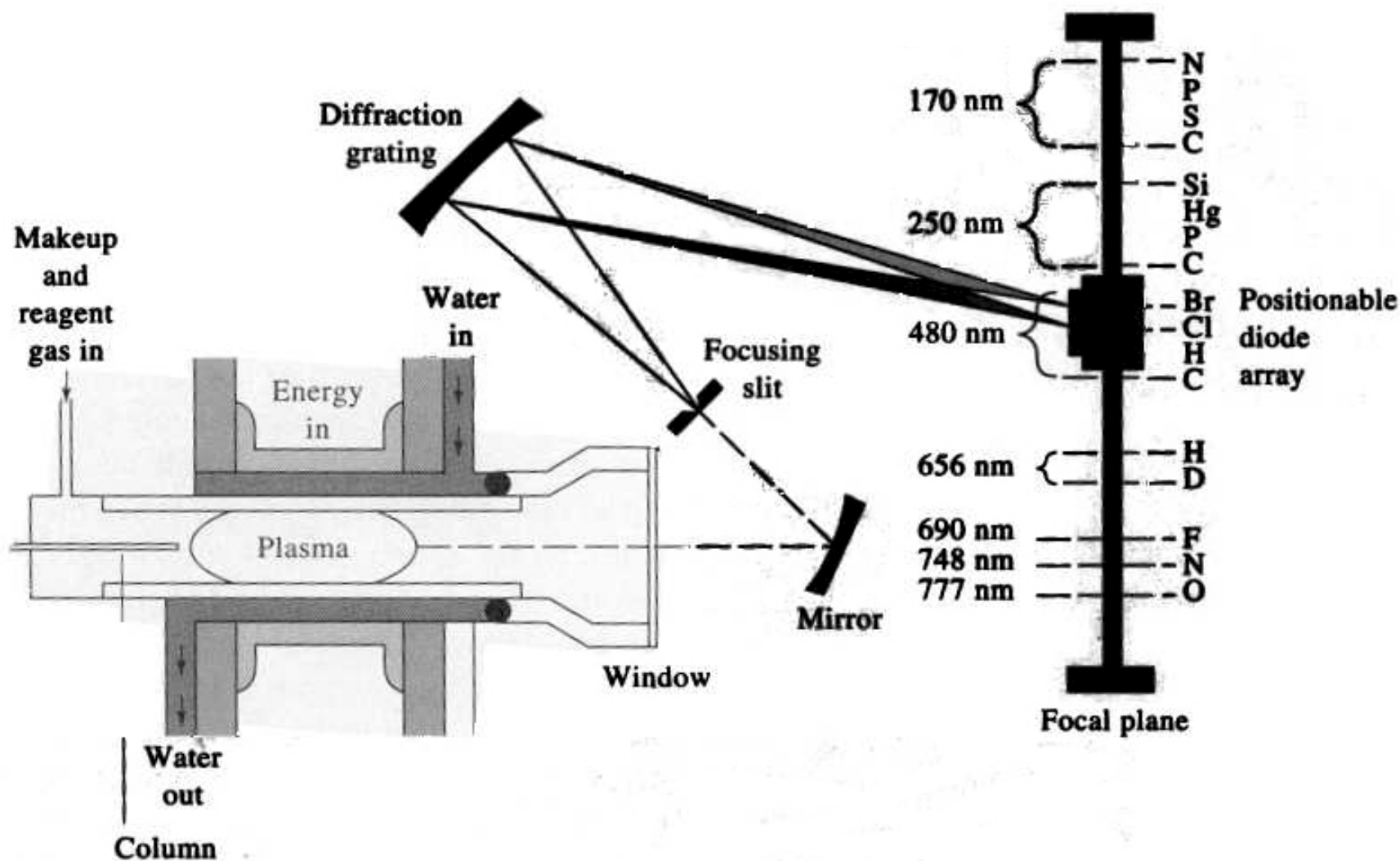
- Column effluent irradiated with intense UV light source
- Ionizes molecules
- Measure ions with electrodes in detector cell

# Unconventional Detectors (Hyphenated Techniques)

## Atomic Emission Detector (AED)

- Fairly new
- Very powerful
- Sample eluent introduced to He microwave plasma atomizing all atoms in sample
- Uses diode array detector measuring optical emission over wide spectral range (170 - 780 nm)
- Measure many elements simultaneously

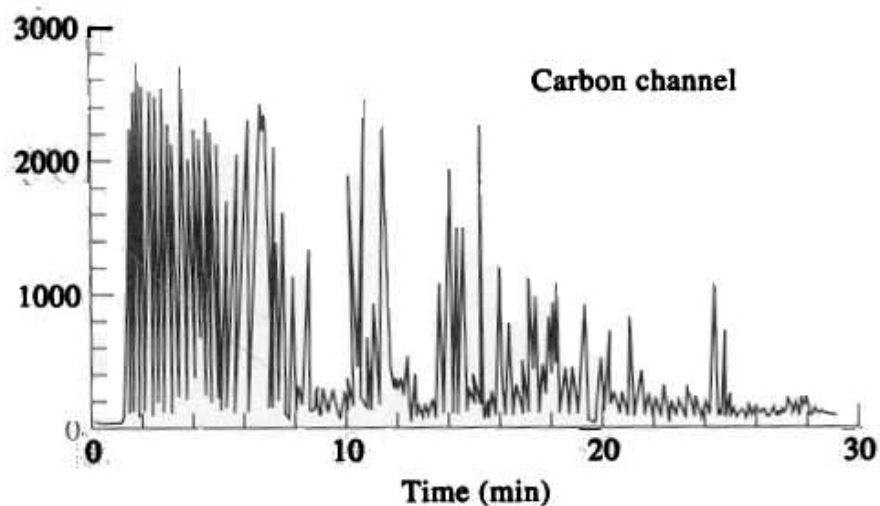
# GC-AED



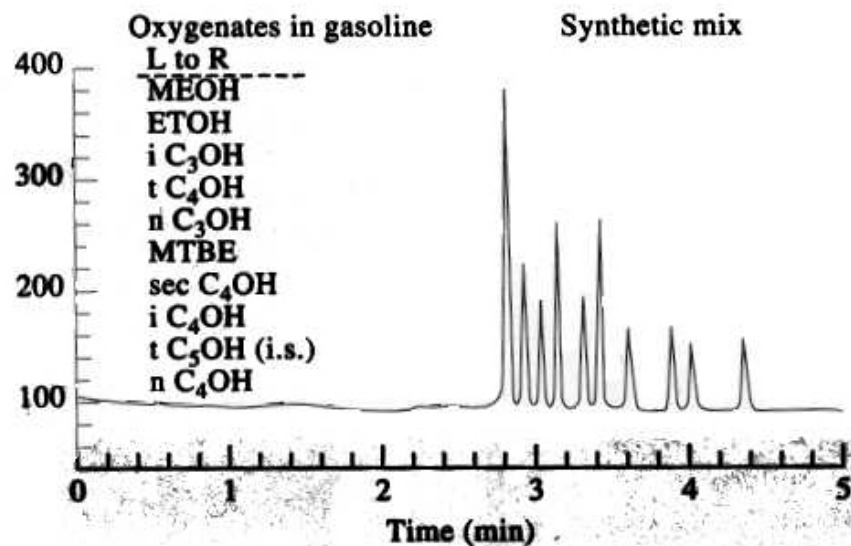
**Figure 27-9** An atomic emission detector. (Courtesy of Hewlett-Packard Company.)

## GC-AED

- Potentially can measure 70 or more elements
- If look at C signal from AED get chromatogram with hundreds of peaks
- If look at O signal get very simple chromatogram with only a few peaks



(a)



(b)

**Figure 27-10** Chromatograms for a gasoline sample containing a small amount of MTBE and several aliphatic alcohols: (a) monitoring the line for carbon; (b) monitoring the line for oxygen. (Courtesy of Hewlett-Packard Company.)

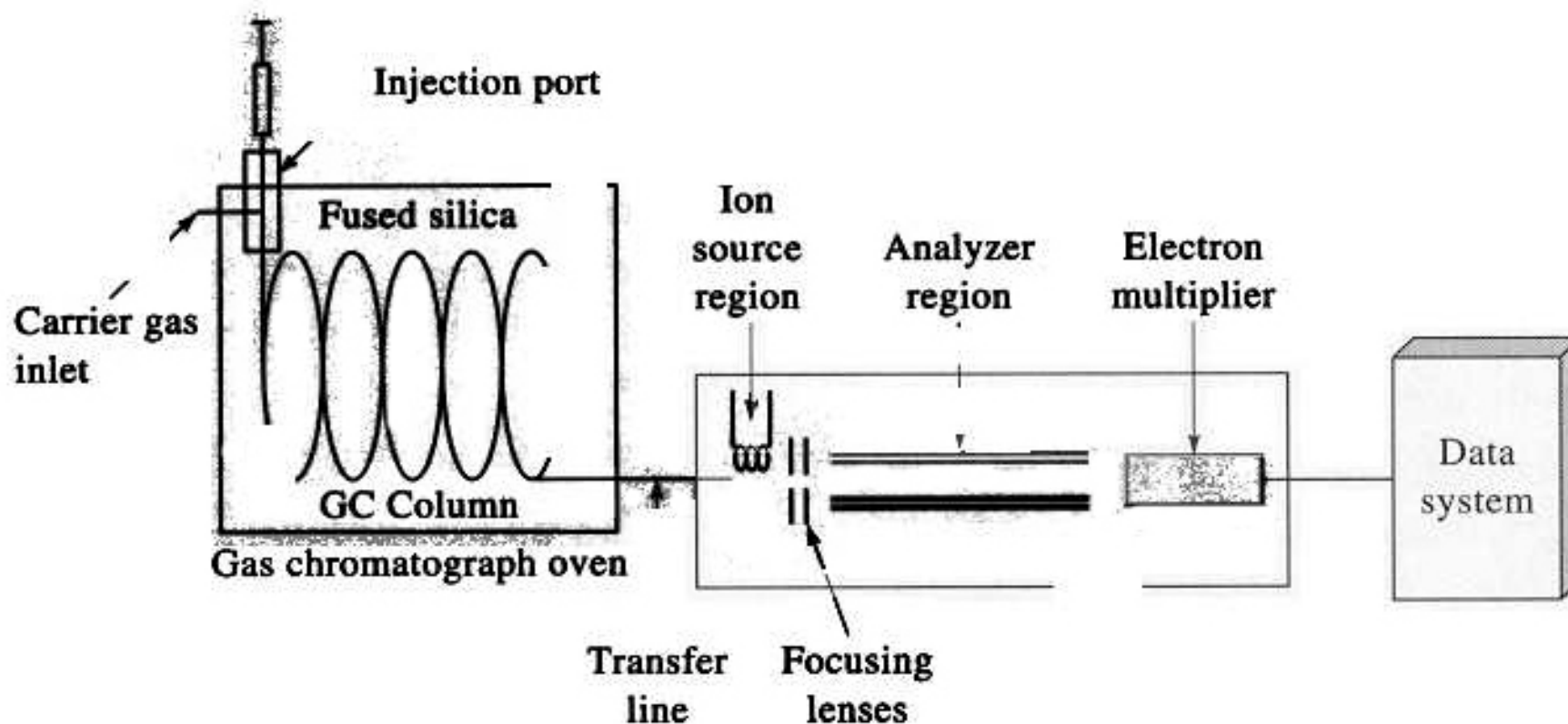
## GC – Mass Spectrometry (GC-MS)

- Already covered Mass Spec
- Interfacing GC & MS normally difficult
- GC at pressure above atmospheric while MS under high vacuum
- Need special interfaces for packed columns
  - Jet separator – discussed below
  - Membrane separator – a membrane sandwich between spiral channels, column effluent on one side under pressure, MS on other side under vacuum – relies on differential permeability of carrier gas vs analyte molecules

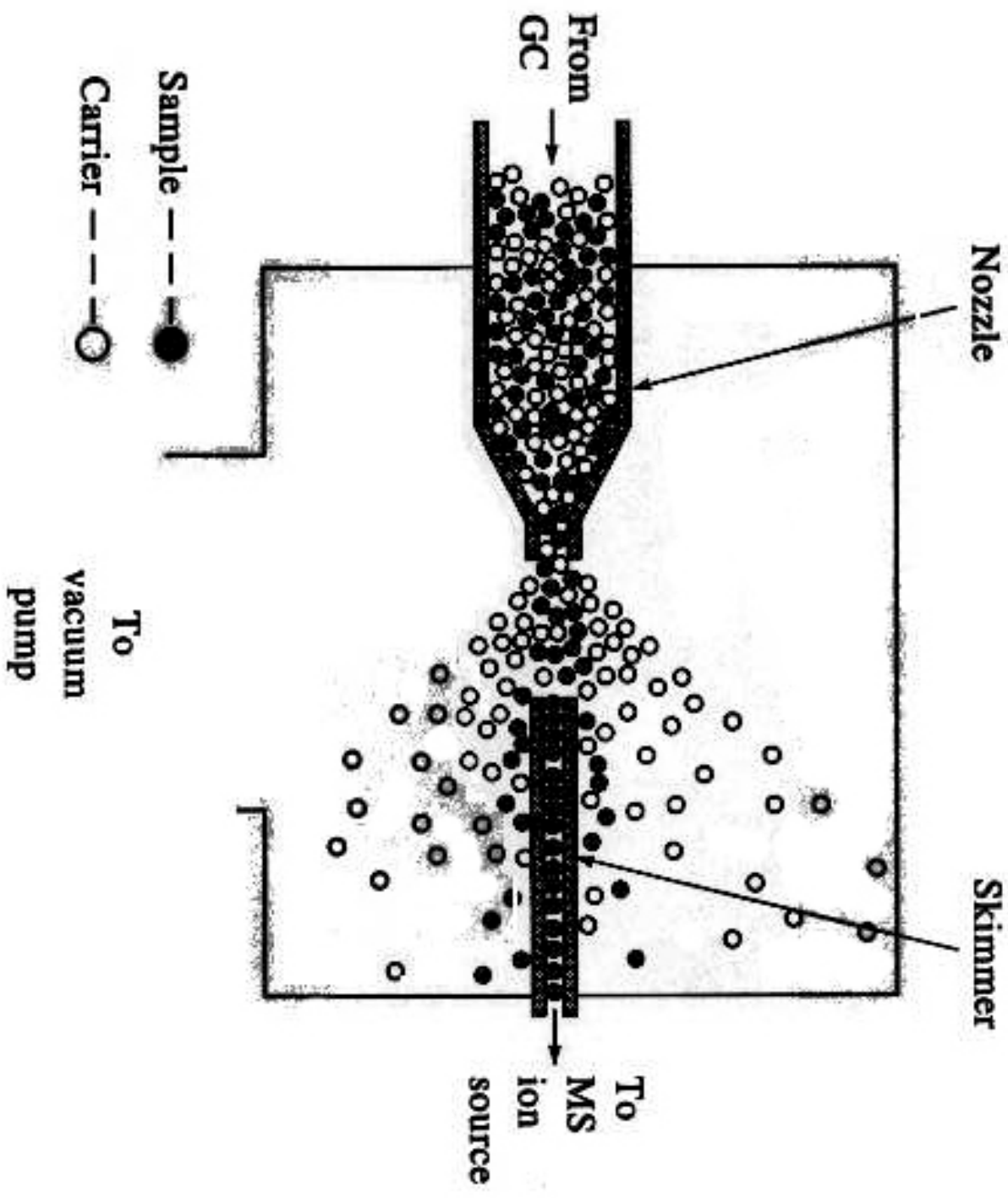


# GC-MS Schematic

Interface less critical for capillary columns



**Figure 27-13** Schematic of a typical capillary gas chromatography/mass spectrometer.



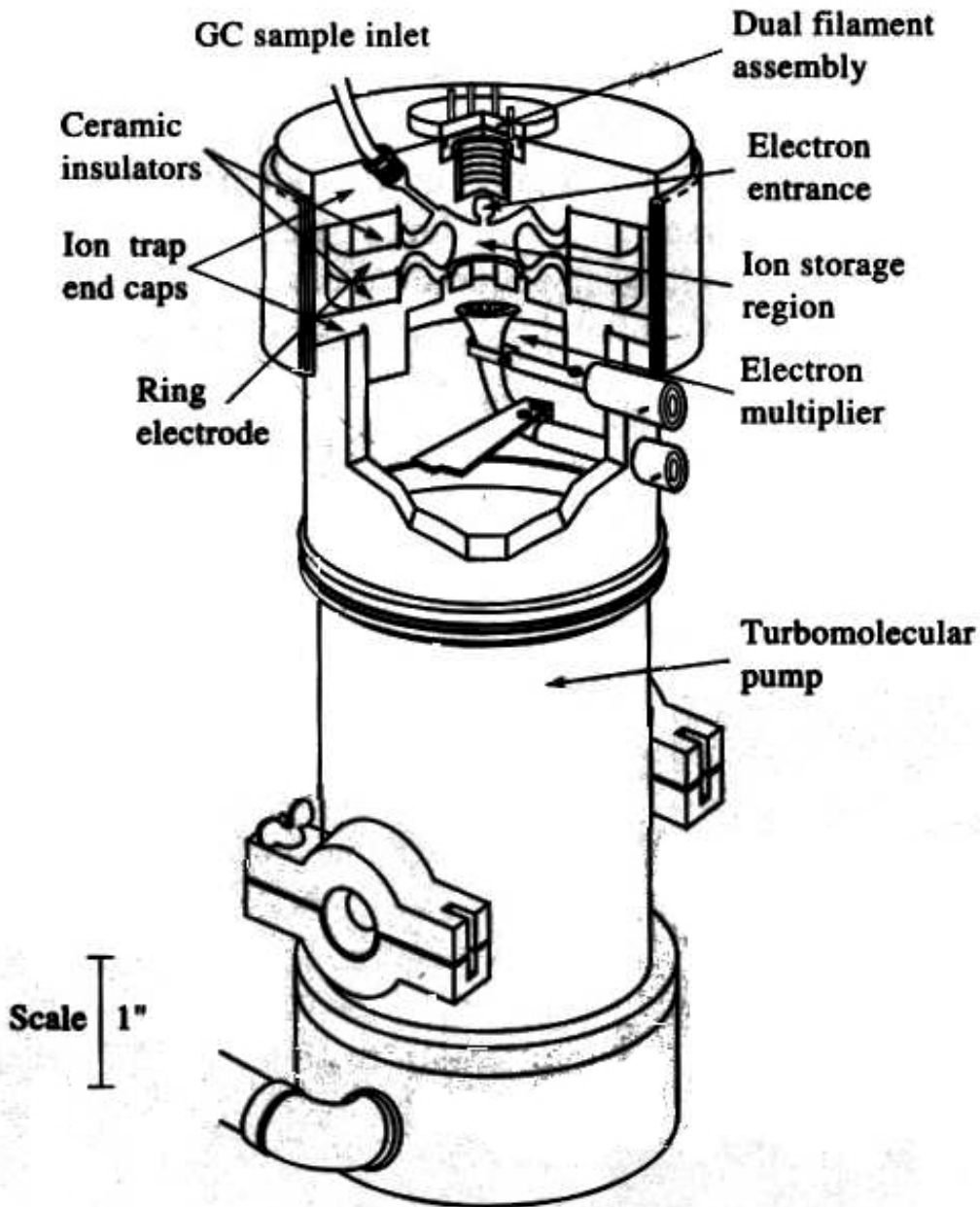
**Figure 27-14** Schematic of a jet separator. (Courtesy of DuPont Instrument Systems, Wilmington, DE.)

## Jet Separator

- Purpose is to get more analyte into MS than carrier gas
- Usually an all glass device
- Principle is that heavier atoms have greater momentum and travel a fairly straight path into the MS, lighter carrier gas molecules are deflected outward by vacuum & pumped away

## Several types of Mass Specs available

- Rarely magnetic sector or time of flight
- Usually quadrupole or ion trap for GC-MS
- Less expensive
- Less maintenance
- Easy to use
- Normally use electron multiplier as detector
- All MS systems need ion source, either electron impact or chemical ionization



Ion trap uses radio frequency to trap ions, hold or store them, then ejects them to detector

**Figure 27-15** Schematic of the ion trap detector.

## Three modes of operation for GC-MS

- 1) Spectral mode – look at mass spectrum every second or so during chromatogram - gives most information for research or method development
- 2) Total ion current – sum signal for all ions as one large signal – highest sensitivity
- 3) Selective ion monitoring – look at certain mass/charge ratios for compounds of interest – routine analysis

## GC-MS

- sensitive
- can be very selective in SIM mode
- powerful for qualitatively & quantitatively

There is also one other kind of Mass Spec  
Ion Cyclotron MS which is a very high  
resolution, Fourier transform instrument  
not used for GC