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

Discuss components starting here

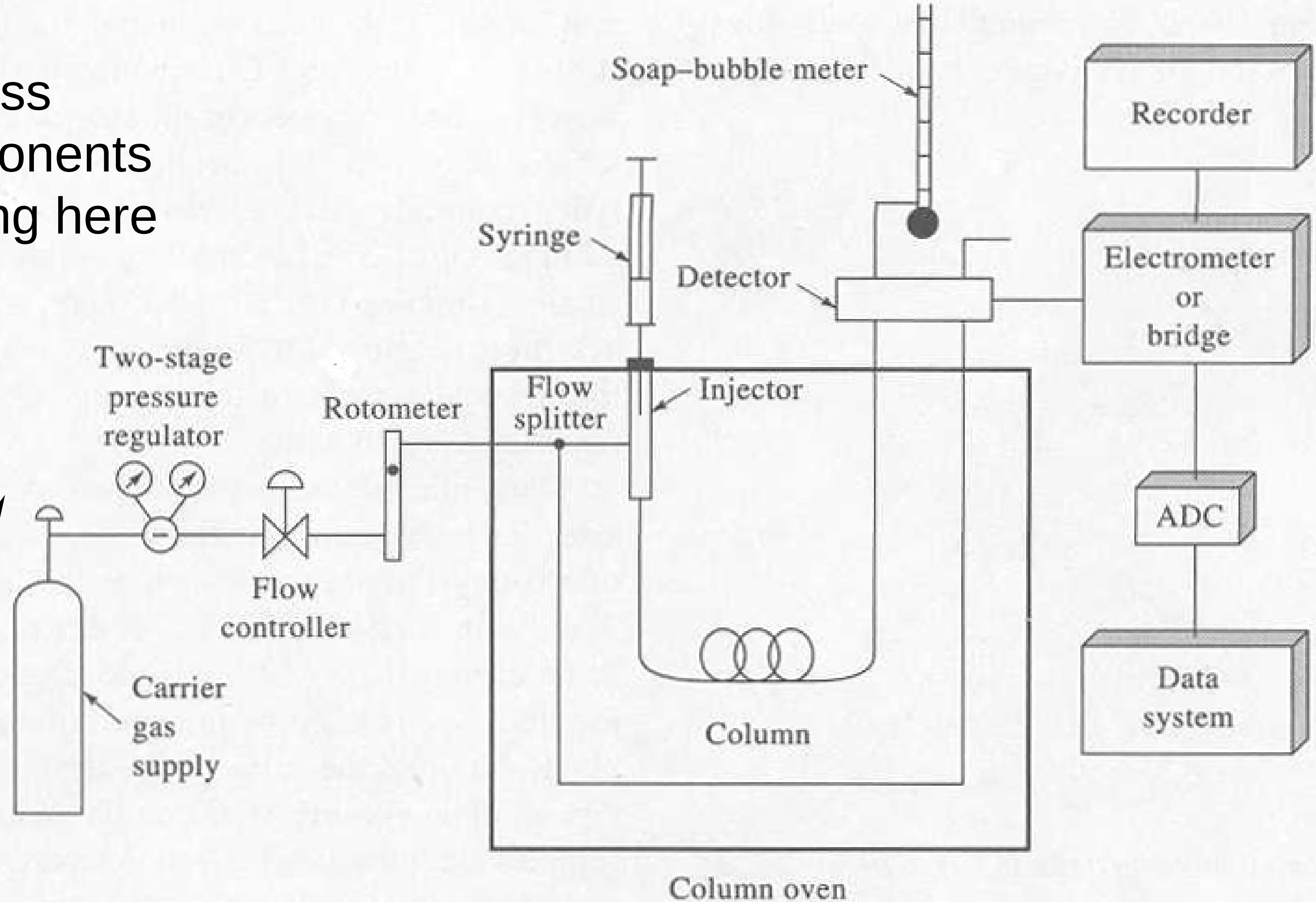


Figure 27-1 Schematic of a gas chromatograph.

Carrier gases (mobile phase) – must be chemically inert He, Ar, N_2, CO_2 even H_2 and mixtures 95/5 N_2/CH_4

Often detector dictates choice of carrier gas

In GC sample doesn’t really interact with carrier gas (unlike HPLC), temp controls partitioning

Often necessary to purify cylinder gas with a trap, scrubber or cartridge of molecular sieves (or buy high purity gas) O_2 ppm Hc

The move today is away from gas cylinders toward gas generators (extract pure carrier gas from air)

Next is gas
flow control
In this region

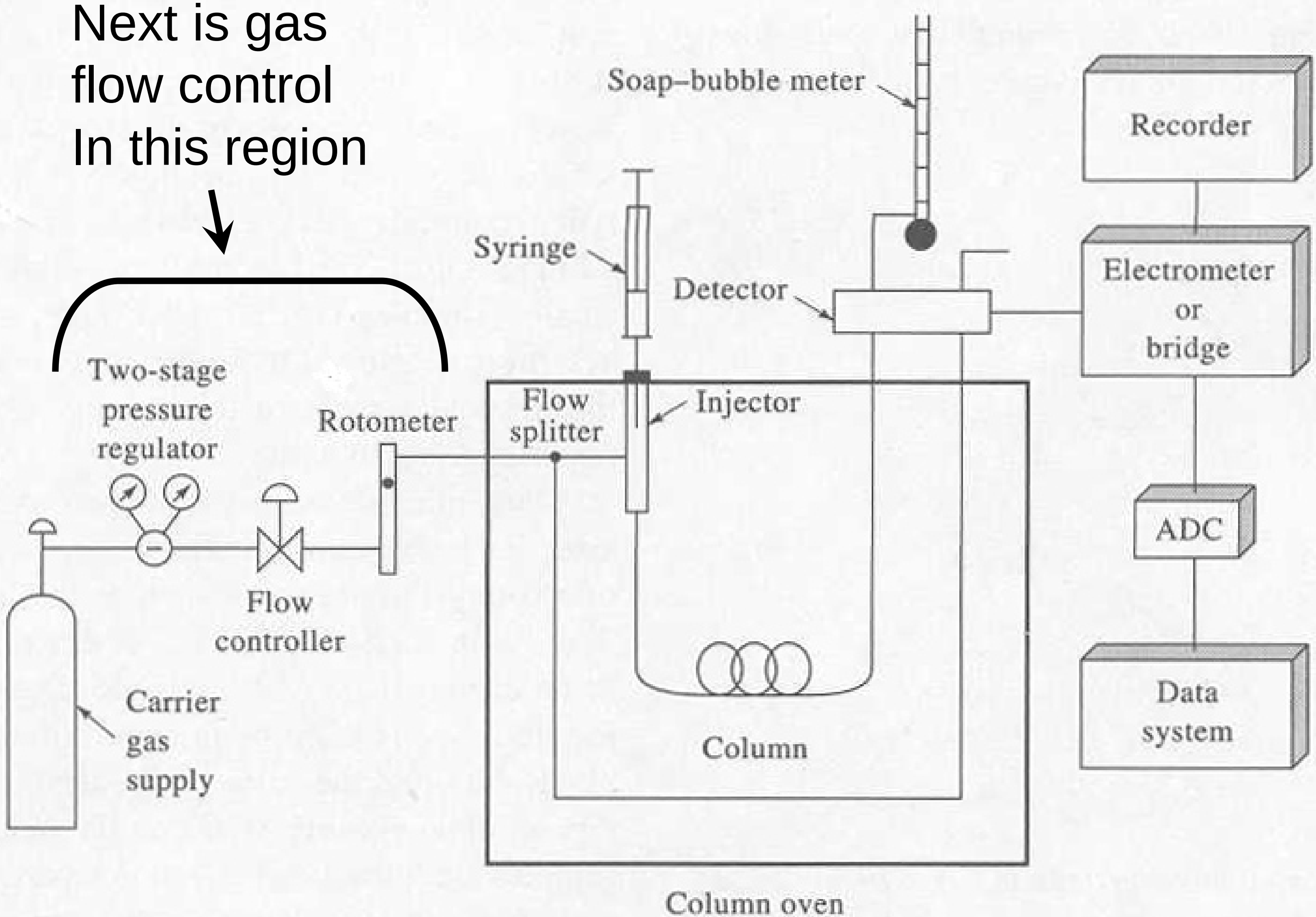


Figure 27-1 Schematic of a gas chromatograph.

Flow control – 10 to 50 psi with regulator

Regulators vary in quality, material & control, typically use a 2 stage regulator with the best material being stainless steel

Ultimately flow rate is checked by a soap bubble meter for accurate flow

Figure 27-2 A soap-bubble flow meter. *(Courtesy of Chrompack Inc., Raritan, NJ.)*

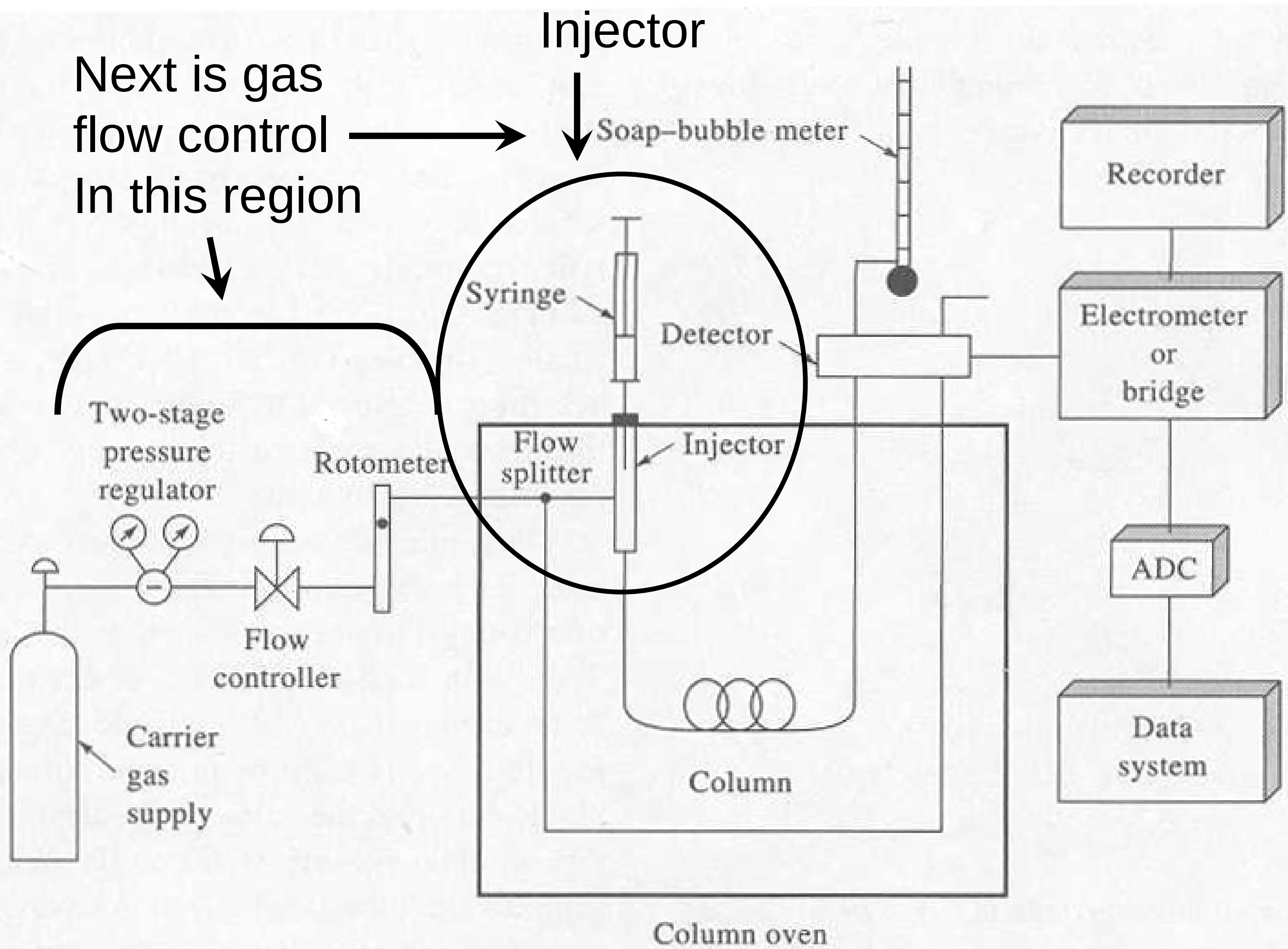


Figure 27-1 Schematic of a gas chromatograph.

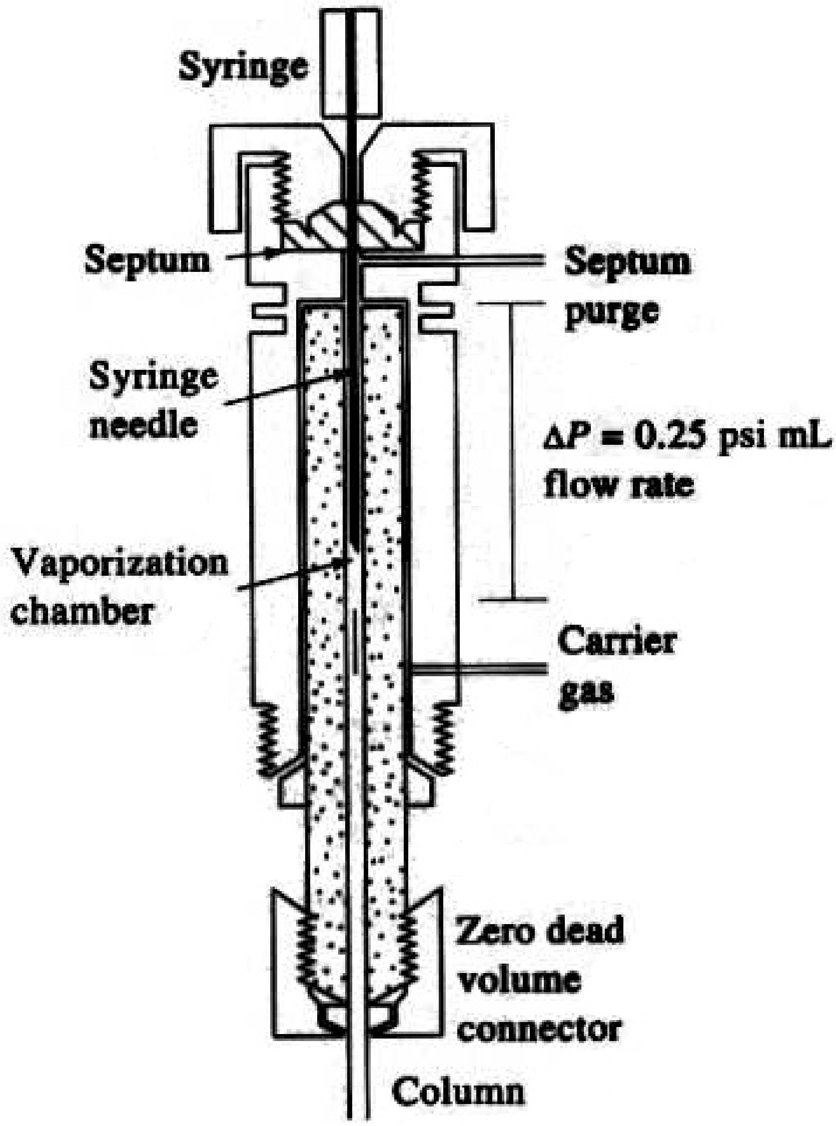


Figure 27-3 Cross-sectional view of a microflash vaporizer direct injector.

Injector – use micro syringe 99.9 % of the time injecting 1 to 20 μL, rapidly shoot in plug of sample

Old GCs had separate injection area

Today use on-column & microflash vaporizers – all have septum of synthetic rubber which is punctured by syringe

Injector usually 50 ^{o}C hotter than boiling point of sample – also hotter than column

Can use rotary injector valve (as for HPLC)

Rotary Injection Valve
Common for HPLC, rare in GC

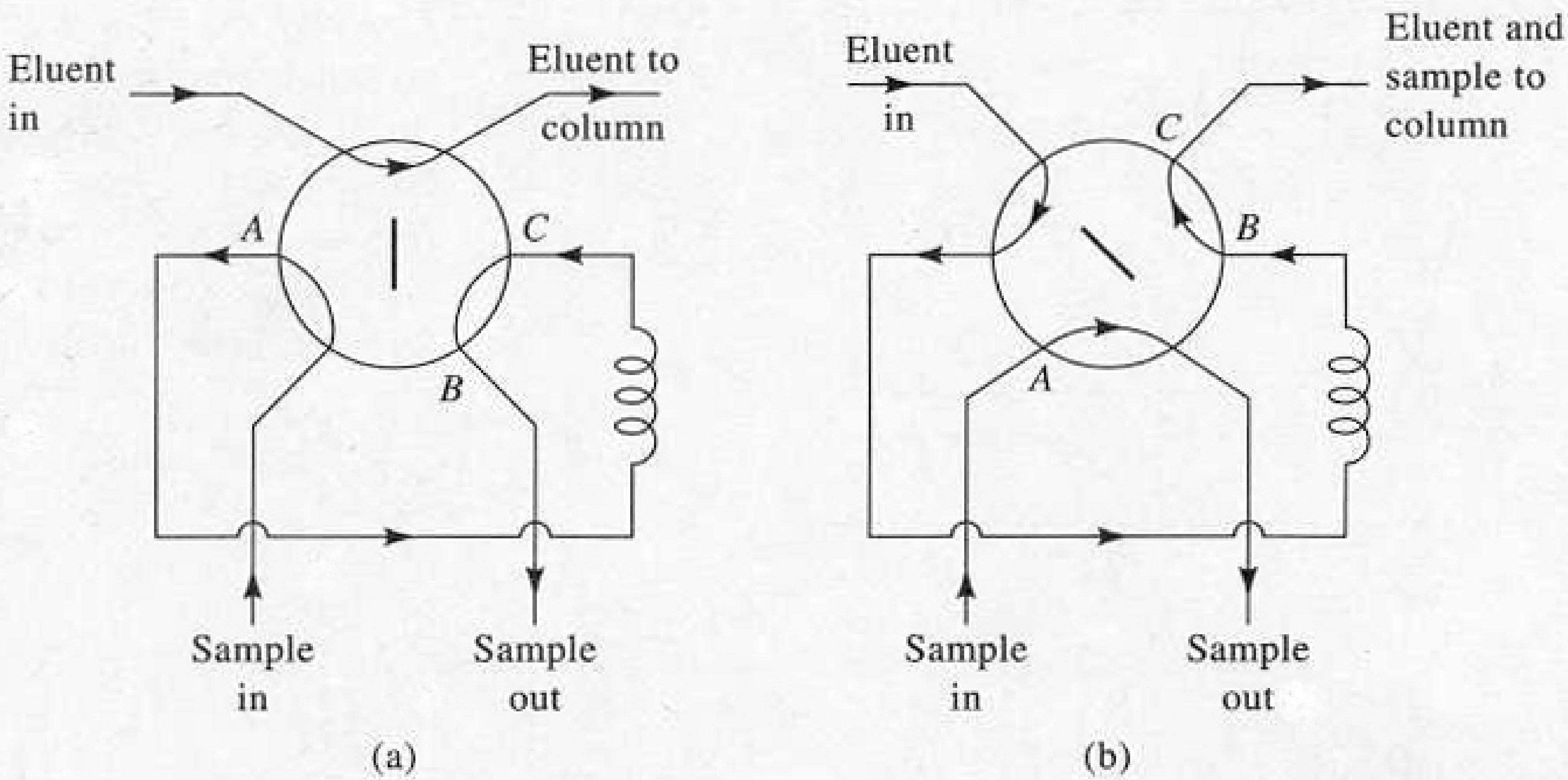
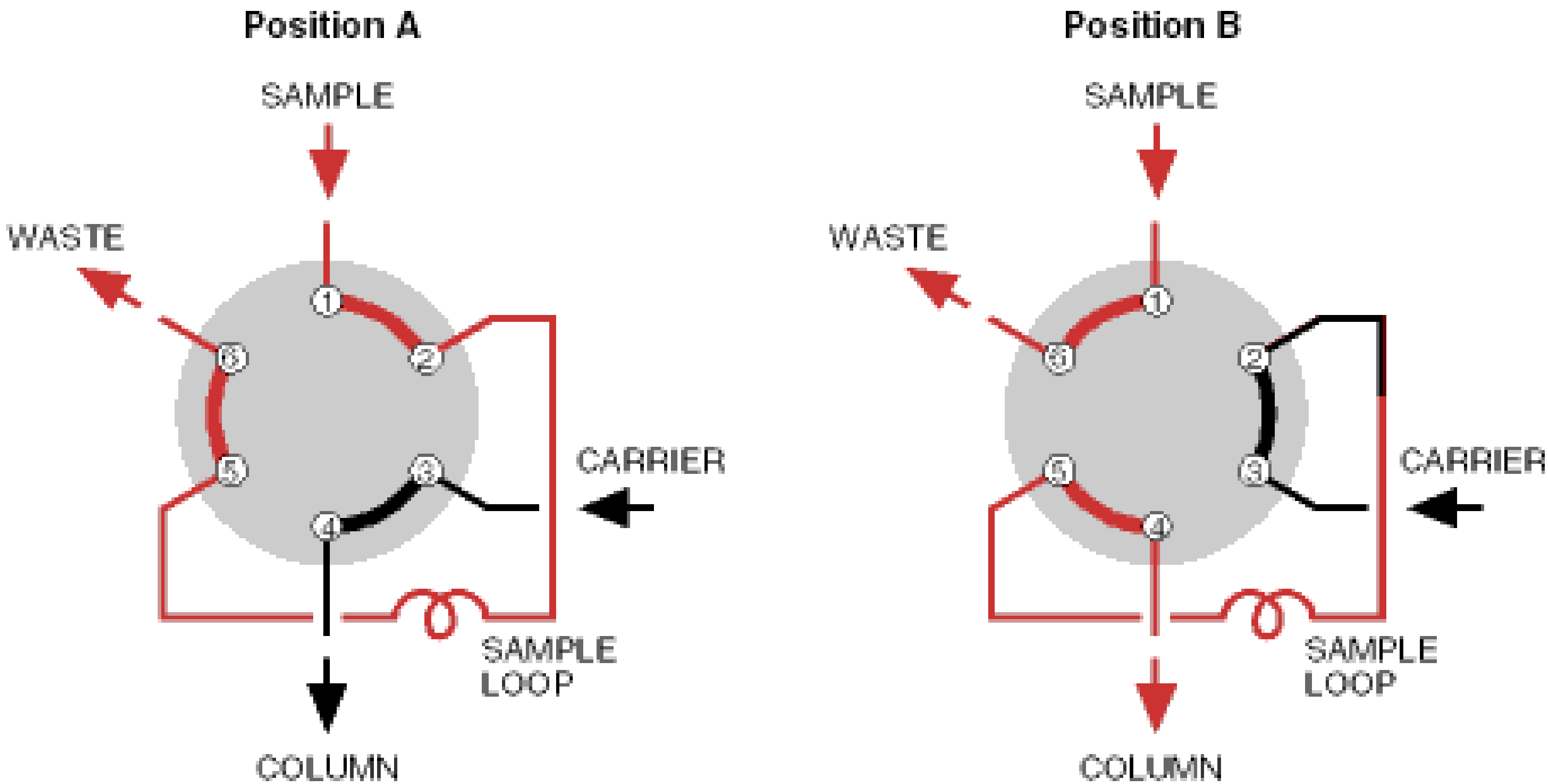


Figure 27-4 A rotary sample valve: valve position (a) for filling sample loop *ACB* and (b) for introduction of sample into column.

Alternate view of injector valve

Position A = Load (i.e. fill loop)

Position B = Inject (sample swept onto column)



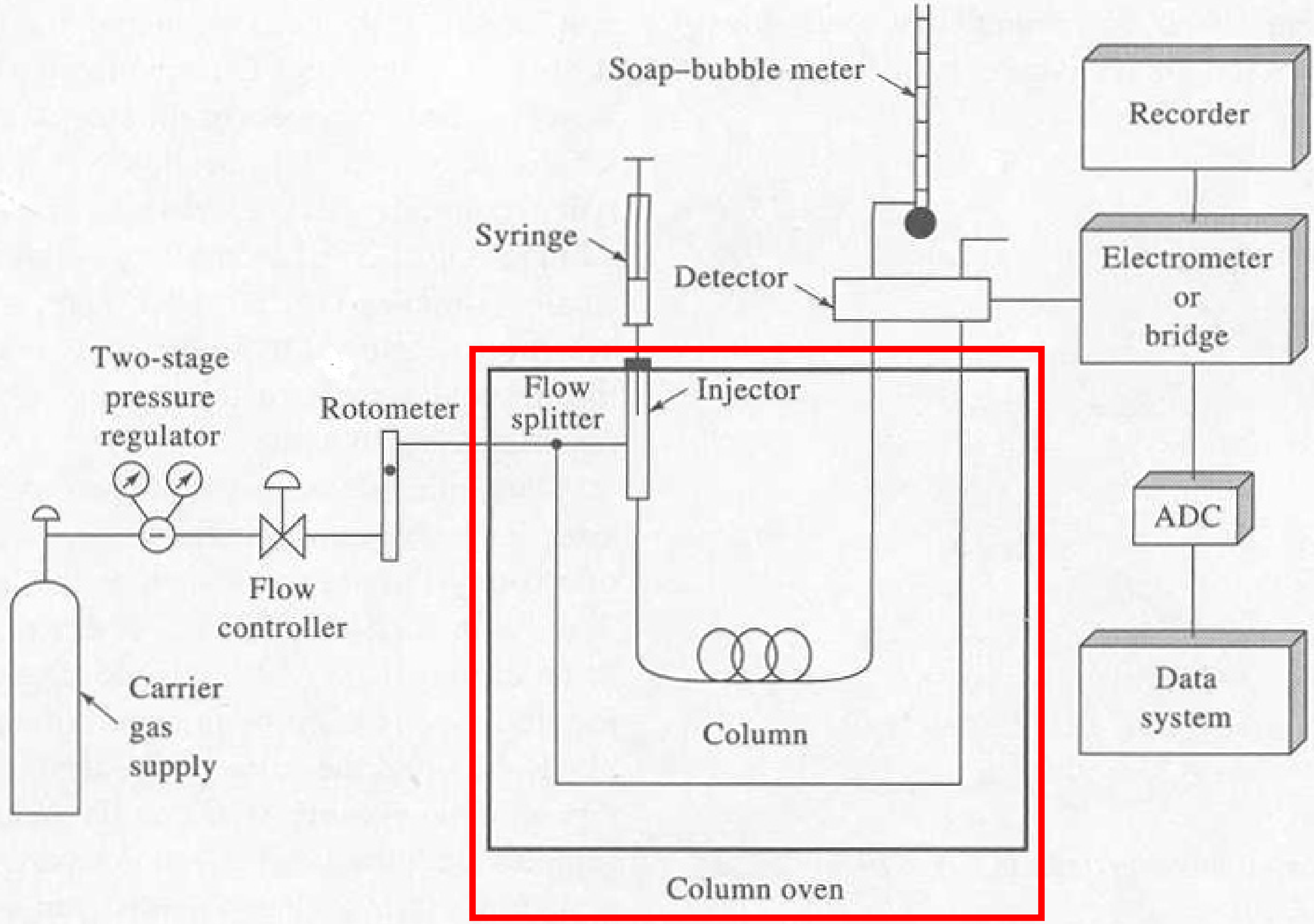


Figure 27-1 Schematic of a gas chromatograph.

Column housed in Column Oven to maintain temperature

Types – packed, open tubular, capillary

oldest ------------------- newest

Capillary columns will take over completely

Packed – tube (steel, glass, **fused silica**, Teflon) packed with material

Open Tubular – coated on walls

Capillary – coated on walls, long & narrow

Length range – 2 to 50 m (typically 30 m)

Column Concepts

In GC since mobile phase is under pressure & we operate at various temperatures

given that P V is proportional to T

Sometimes use retention volumes (V_R, V_M)

$V_R = t_R F$ for retained species t_R = retention time

$V_M = t_M F$ for unretained F = flow rate

Problem - pressure drop across a column

Pressure at head of column may be 5 atm & at end of column may be 1 atm

Need a correction factor

$$j = \frac{3[(P_i/P)^2 - 1]}{2[(P_i/P)^3 - 1]}$$

Where P_i = inlet pressure &

P = outlet pressure (atmospheric)

Can define specific retention volume (V_g)

$$V_g = \frac{V_R^o - V_M^o}{W} \times \frac{273}{T_c}$$

Where W = mass of stationary phase

T_c = column temp. (^oK)

$$V_R^o = j\, t_R\, F \qquad\qquad V_M^o = j\, t_M\, F$$

Can relate V_g to K (partition ratio)

$$V_g = \frac{K}{\rho_s} \times \frac{273}{T_c} \qquad \rho_s = \frac{W}{V_s}$$

Detectors – dozens of detectors available

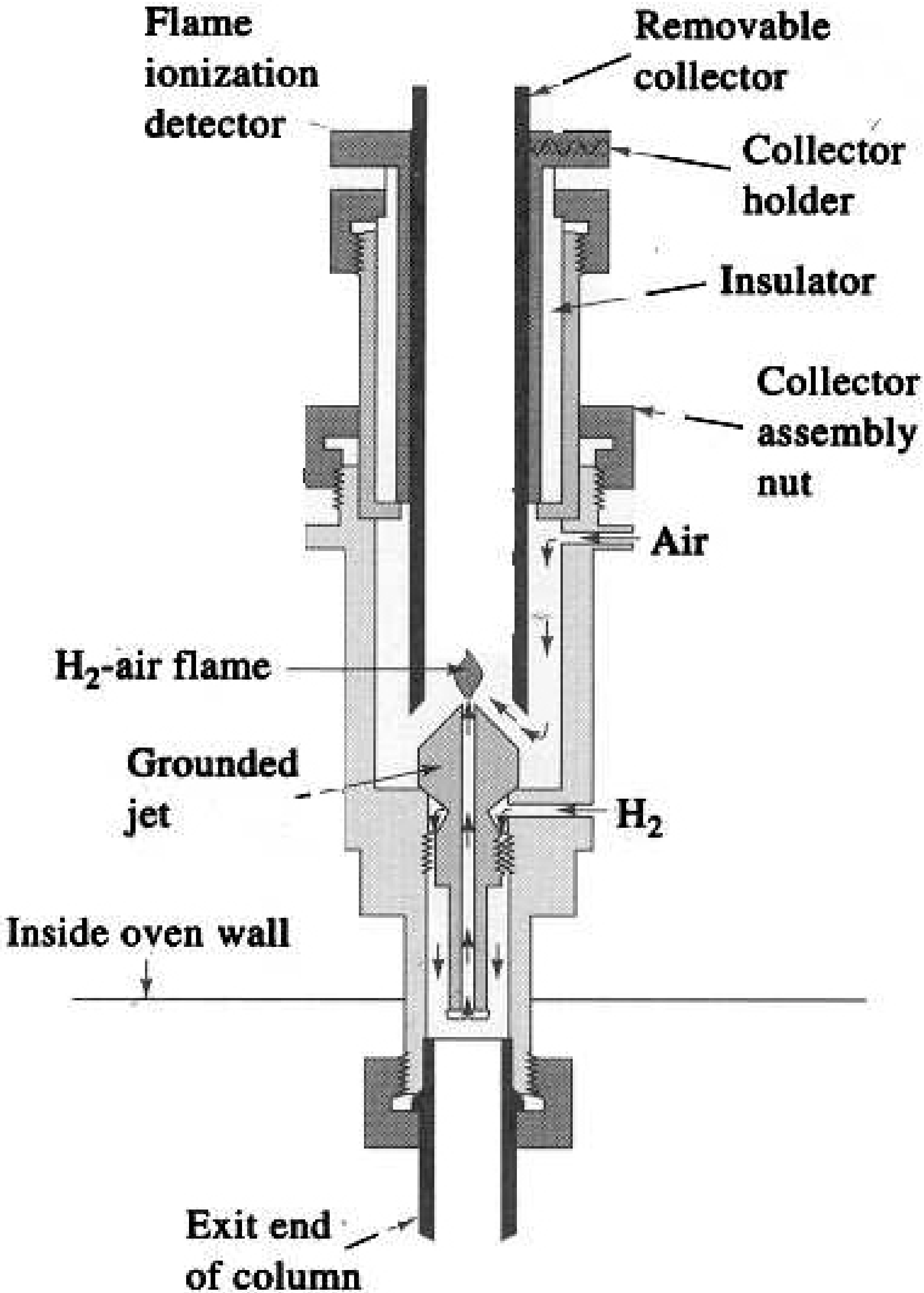
Characteristics of an ideal detector:

1) Adequate sensitivity for desired analysis (typical 10^{-8} to 10^{-15} g analyte/sec)
2) Stable – background constant with time
3) Reproducible – good precision
4) Linear response over several orders of magnitude
5) Temperature range – room temp - 400 ^{o}C

Characteristics of ideal detector: (continued)

6) Rapid response time
7) Independent of flow rate
8) Reliable
9) Easy to Use – inexperienced operators
10) Either selective or universal response
11) Nondestructive

No detector exhibits all these characteristics



Flame Ionization Detector (FID)

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

FID Basics

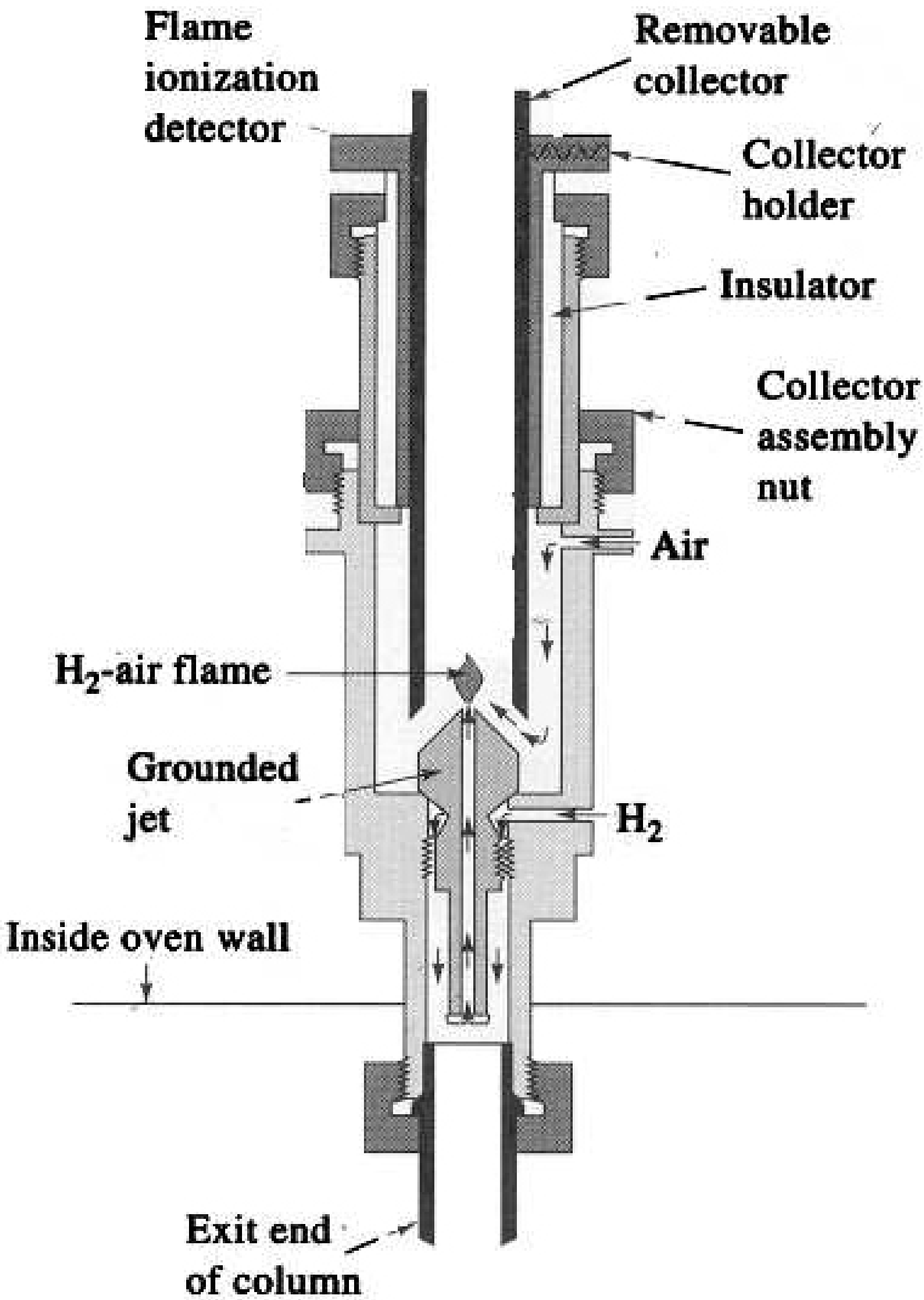
- column effluent mixed with air and burned in H_2 flame producing ions & electrons that conduct electricity
- a few hundred volts applied between burner tip & a collector electrode above the flame producing currents on the order of 10^{-12} amps
- amplify & measure
- signal approximately proportional to number of reduced carbon atoms in flame

FID Basics (continued)

- mass sensitive rather than concentration
- insensitive to non combustible gases – H_2O, CO_2, SO_2, NO_x

FID exhibits

- High sensitivity
- Large linear response range 10-13 g/s
- Easy to use
- Rugged
- DESTRUCTIVE

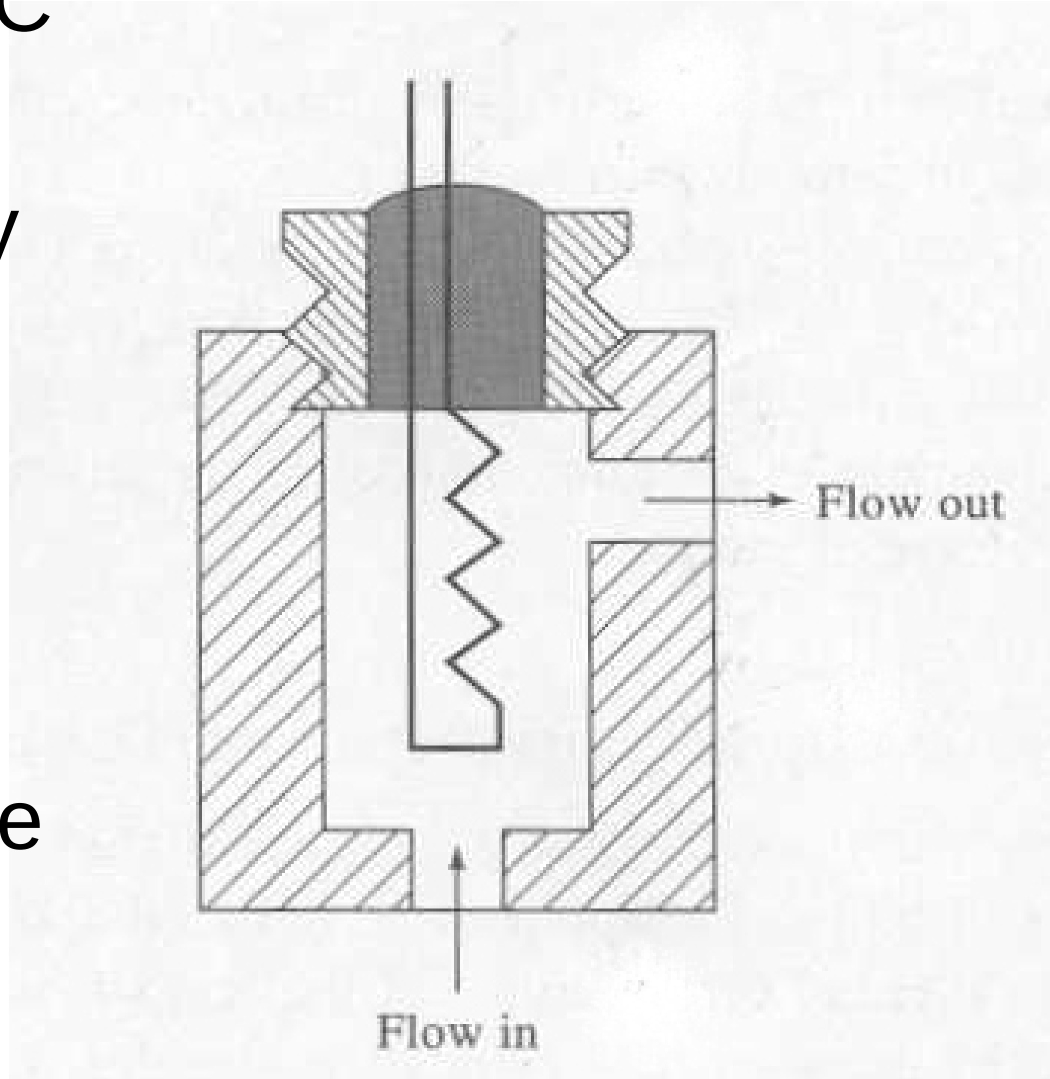


Flame Ionization Detector (FID)

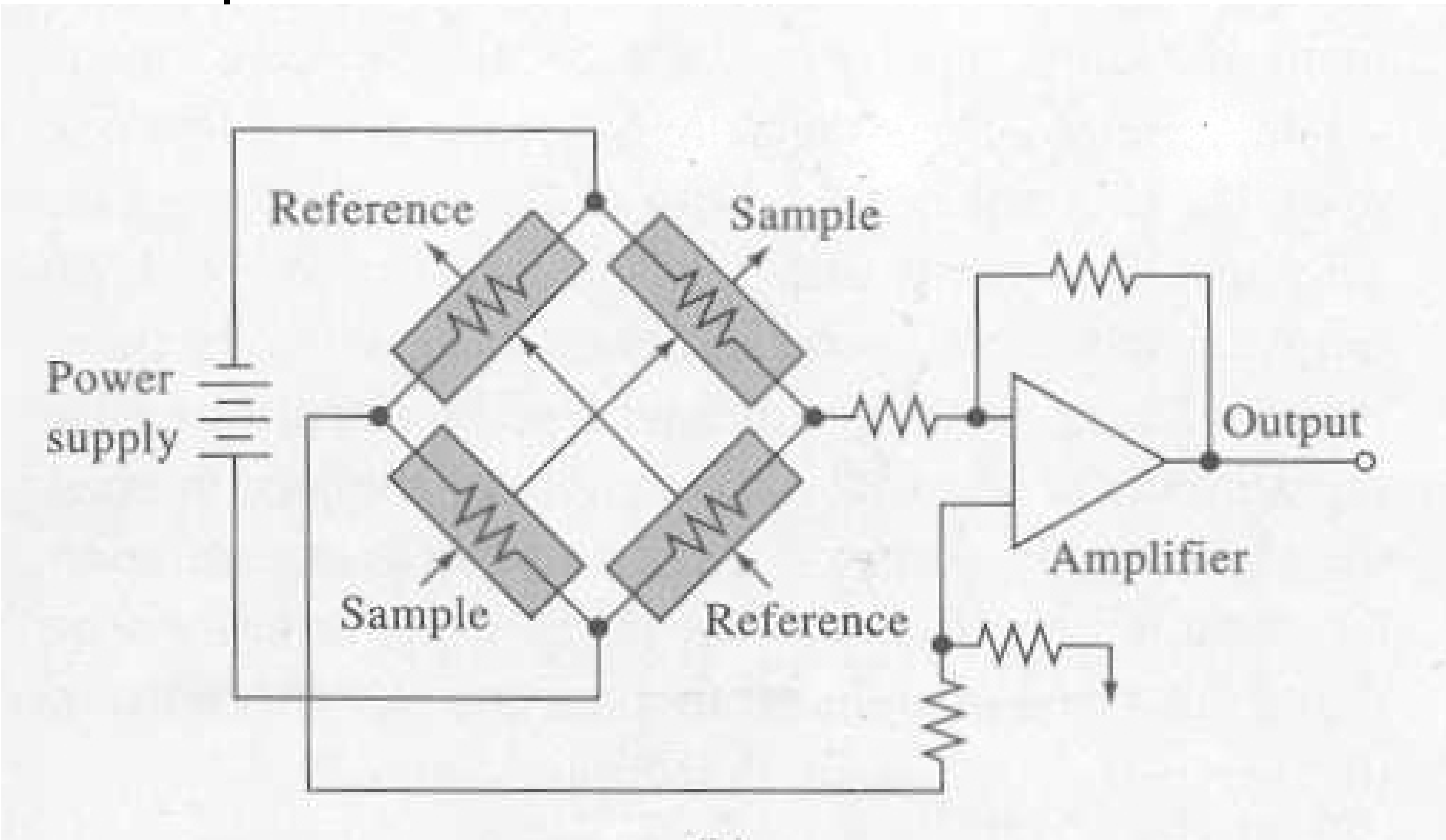
- one of most widely used GC detectors
- good sensitivity to almost all organic compounds

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



TCD uses bridge circuit with
Sample & Reference Cells



TCD

- New TCDs use pulsed current to increase sensitivity & reduce drift
- Thermal conductivity of He & H_2 are about 6 to 10 times greater than most organic compounds (must use these carrier gases)
- Other carrier gases (N_2, Ar, etc) have thermal conductivities too close to organics

Advantages of TCD

- Simple → Reliable & Easy to use
- Universal response (organic & inorganic)
- Large linear dynamic range 10^5
- Nondestructive, can use in tandem
- Older instruments have built-in TCD

Disadvantages

- Low sensitivity
- Often can’t use with capillary columns because amount of analyte is small