Chromatography, which means color-writing, is a commonly used procedure for separation of chemical compounds and their analysis (Fig. 26-1). Chemical separation is based on the **differences** in partition equilibria of various compounds between the stationary phase (e.g. column packing material) and mobile phase (e.g. water or He).

A gas chromatograph consists of the carrier gas supply, sample injection system, column oven, detection system (Fig 27-1 or equiv)

**Carrier gas**

The choice of gas (among He, N\textsubscript{2}, H\textsubscript{2}), which must be chemically inert, is partly determined by the type of detectors used. Flow rates (1-25 mL/min in open-tubular columns and 25-150 mL/min in packed columns) can be established accurately by a soap-bubble flow meter (Fig 27-2 or equiv). Flow rates as determined by gas pressure (10-50 psi above room temperature) are normally controlled by a two-stage pressure regulator at the gas cylinder.

**Sample injection system**

A microsyringe is used to inject a liquid sample (1-10 µL) or gaseous sample (larger volume) through a self-sealing, silicone rubber septum into a flash vaporizer direct injector (Fig 27-3 or equiv). It is
ordinarily maintained at a temperature to ensure complete vaporization (~50 °C above the highest boiling component).

For more reproducible injection for samples (especially gases), a rotary sample valve is used (Fig 27-4). The sample volume is fixed by the size of the sample loop.

To avoid overloading capillary columns which require much smaller samples (10^{-3} \mu L), a sample splitter system is employed (R5 Fig. 5.14).

**Column oven**

Column temperature is controlled (to a few tenths of a degree) using a thermostatted oven for precise work. A temperature equal to or slightly above the average boiling point of a sample results in a reasonable elution time (2-30 min).

**GC column**

**Packed column** (i.d. 2-4 mm): stationary phase is a liquid film adsorbed or bonded on the surface of a finely divided, inert solid support tightly packed in coiled columns (of length 2-50 m).

The columns are made of glass, metal or Teflon. The most widely used solid support is diatomaceous earth – skeleton of single-celled plants, diatoms. The particle size needs to be small (dia. 0.15-0.26 \mu m) for high efficiency, but cannot be too small to create a high back pressure (i.e. a max. of 50 psi)

**Capillary column** (i.d. 100-750 \mu m): stationary phase is a liquid film coated on the interior wall of capillary tubings which are open-tubular and unpacked.

See Table 27-1 for comparison of various columns.

Support-coated open-tubular (SCOT): thin liquid film (~ 30 \mu m) of stationary phase is coated on support material lined on the capillary wall.

Wall-coated open-tubular (WCOT): thin liquid film of stationary phase is coated on capillary wall.

WCOT columns have lower capacity, but higher separation efficiency, than SCOT ones. Early WCOT columns were constructed of SS, Al, Cu, plastic or glass. Nowadays, they are made of fused silica (FSOT) which contain minimal amount of metal oxides. To add strength, an outside polyimide coating is applied to the external capillary wall as the capillary tubing is being drawn.

**The stationary phase**

Desirable properties of stationary phases are:

1. Solvent characteristics (i.e. to give appropriate \(k'\) and \(\alpha\))
2. Low bleeding (i.e. in bonded or cross-linked phase)
3. Low volatility (i.e. 100 °C higher than the maximum column operating temperature)
4. Thermal stability and chemical inertness

Generally, the polarity of the stationary phase should match that of the sample components (“like dissolves like”). Then, the elution order is determined by the boiling points of the analytes.

The most widely used stationary phase is siloxane-based (Table 27-2). The more polar is the substituent groups (and the higher is the extent of substitution) on stationary phase, the higher is the suitability for it to resolve polar analytes.

**Deactivation of silicate surfaces of support materials**: To reduce adsorption of polar analytes (e.g. alcohols) on the silicate surfaces of column packings or capillary walls, the silanol groups needs to be deactivated by silanization (e.g. using DMCS – dimethylchlorosilane) (Sec 27C-3).
For GSC: the stationary phase is the column packing itself (e.g. molecular sieves or porous polymers) which should have large surface area to adsorb gaseous analytes (e.g. CO, H$_2$S, NO). Commercial molecular sieves come in pore sizes of 4, 5, 10, 13 Å. Gas molecules smaller than these dimensions penetrate into the interior of the particles and adsorbed (retained). Porous polymer beads are manufactured from styrene cross-linked with divinylbenzene. The pore size is uniform and is larger when the extent of cross-linking is greater. When porous polymers are used in open-tubular column, it is called PLOT.

**Detection system**

Characteristics of an ideal GC detector are:
1. adequate sensitivity (R1* Fig 18-11), similar response factor to various analytes
2. good stability and reproducibility, high reliability and ease of use
3. large dynamic (or linear) range (R1* Fig 18-11)
4. operation temperature from room temperature to at least 400 °C
5. short response time that is independent of flow rate
6. selective to one or more classes of solutes, non-destructive

**Flame ionization detector (FID)**

Most organic compounds, when pyrolyzed (or decomposed) at a high temperature H$_2$/air flame (O$_2$-rich flame), produce positively charged ions in the flame. This leads to a measurable current (~$10^{-12}$ A) when a voltage (a few hundred volts) is applied across the burner tip (positive) and a collector electrode (negative) located above the flame (Fig 27-6 or R5 Fig 5-19).

Since the FID responds to the number of C atoms entering the detector per unit time, it is a mass-sensitive detector. The FID is insensitive to organic compounds with functional groups, such as carbonyl, alcohol, halogen and amine, because they yield few ions or none at all in a flame. In addition, the detector is insensitive to non-combustible gases such as H$_2$O, CO$_2$, SO$_2$ and NO$_x$. The detector has a high sensitivity (~$10^{-13}$ g/s), large dynamic range (~$10^7$), low noise, and is rugged and easy to use. But it is destructive of the sample.

**Thermal conductivity detector (TCD)**

The detector is based on changes in the TC of the gas stream containing the analytes. The sensing element is an electrically heated metal wire (e.g. Pt). If the TC of the eluent is lower, the temperature (and hence resistance) of the wire increases (Fig 27-7 or R5 Fig 5-21). Low background signal can be obtained by selecting a carrier gas (e.g. H$_2$ or He) with a high TC (R2 Table 19-2). The TCD is simple, responsive to both organic and inorganic species, has a large dynamic range (~$10^5$), non-destructive. But it has a low sensitivity (~$10^{-8}$ g solute/mL carrier gas), and is a concentration-sensitive detector.

**Electron capture detector (ECD)**

The detector is selective toward compounds containing electronegative groups (e.g. halogens, peroxides, nitro groups). In the absence of organic species, a high background current is created between a pair of electrodes with voltage applied because of the ionization of the carrier gas (often N$_2$) by a β (or e$^-$) emitter (e.g. Ni-63). In the presence of halogen-containing organic analytes, which capture the electrons, the current decreases markedly. (Fig 27-8 or R5 Fig 5-20).

The ECD is highly sensitive and is non-destructive. But it has limited dynamic range (~$10^2$).
Flame photometric detector (FPD)
The eluent is passed into a low-temperature H₂/air flame (H₂-rich flame) where P-containing compounds produce HPO species which emits the 510 nm and 526 nm bands, and S-containing compounds produce S₂ species which emits the 394 nm bands (R5 Fig 5-23). Like a FID, the eluent in a FPD is burnt, but the radiation, not ion current, is measured. Separation between S- and P-containing compounds is required.

Photoionization detector (PID)
The eluent is irradiated with an intense UV radiation (106-149 nm). This causes ionization of molecules, leading to the flow of an ion current when a voltage is applied across the column and a collector plate (R5 Fig 5-24). Like a FID, an ion current is collected in a PID, but the eluent is irradiated, not burnt for ionization.

Thermionic emission detector (TID or TED) or nitrogen-phosphorus detector (NPD)
The eluent is burnt and ionized around the plasma created at an electrically heated rubidium silicate bead. An ion current is measured when a voltage is applied across the bead and a collector plate (R5 Fig 5.22 or R1* Fig 18-9). Comparing to the FID response, the TID response is 500-fold for P-containing compounds, and 50-fold for N-containing ones. This makes TID particularly useful for detecting organophosphorus pesticides.

An hyphenated technique: GC-MS
GC-MS is widely used, among GC-FTIR and GC-AES.

Interfacing: For packed and megabore capillary columns, the carrier gas must be removed from the analyte (e.g. using a jet separator, Fig 27-14). In this device, the carrier gas molecules are so light that they cannot make their way to the skimmer and are thus pumped away. For capillary columns, the flow rate is low enough that the eluent can be fed directly into the ionization chamber of the MS (Fig 27-13).

Mass analyzer:
1. quadrupole: The is compact, commonly used, and with low scan time (<100 ms). It consists of 4 long rods where an rf field is applied. Only the ions with a certain m/z value will pass through the region without striking the rods and being neutralized.
2. Magnetic sector: most versatile and expensive
3. Ion-trap detector (ITD): This is the simplest and least expensive. The ions are trapped in an rf field.
   Then they are consecutively ejected to a detector (e.g. electron multiplier) according to their m/z ratio.

Display (See diazinon example):
1. Total ion current (TIC): a plot of the sum of all ion currents as a function of time
2. Mass spectra of compounds in individual peaks.
3. Selected ion monitoring (SIM): a plot of ion currents for one or a few ions as a function of time.