GAS CHROMATOGRAPHY

By-

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Principle

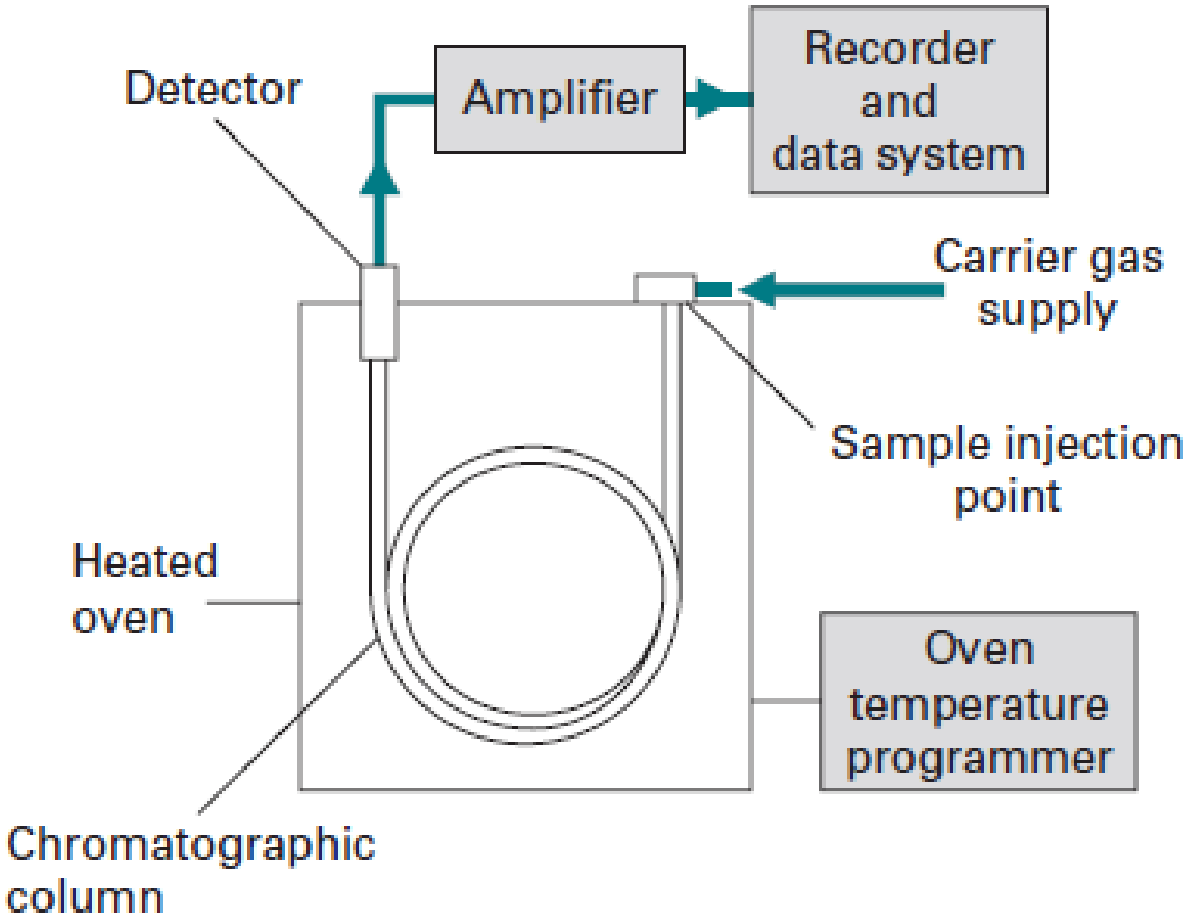
- It exploits differences in the partition coefficients between a stationary liquid phase and a mobile gas phase of the volatilised analytes as they are carried through the column by the mobile gas phase.
- Its use is therefore confined to analytes that are volatile but thermally stable.
- The partition coefficients are inversely proportional to the volatility of the analytes so that the most volatile elute first.
- The temperature of the column is raised to 50-300°C to facilitate analyte volatilisation.

- The stationary phase consists of a high-boiling-point liquid material such as silicone grease or wax that is either coated onto the internal wall of the column or supported on an inert granular solid and packed into the column.
- There is an optimum flow rate of the mobile gas phase for maximum column efficiency (minimum plate height, H).
- Very high resolutions are obtained hence the technique is very useful for the analysis of complex mixtures.
- Gas chromatography is widely used for the qualitative and quantitative analysis of a large number of low-polarity compounds because it has high sensitivity, reproducibility and speed of resolution.
- Analytically, it is a very powerful technique when coupled to mass spectrometry.

Apparatus and experimental procedure

- The major components of a GC system are:
  - a column housed in an oven that can be temperature programmed;
  - a sample inlet point;
  - a carrier gas supply and control; and
  - a detector, amplifier and data recorder system

Components of GLC



Columns

- These are of two types:
- **Packed conventional columns:** These consist of a coiled glass or stainless steel column 13m long and 24mm internal diameter.
- They are packed with stationary phase coated on an inert silica support.
- Commonly used stationary phases include the polyethylene glycols (Carbowax 20M, very polar), methylphenyl- and methylvinylsilicone gums (OV17 and OV101, medium and non-polar respectively).
- The support particles have a large surface area and an even size, which, for the majority of practical applications, ranges from
- 60-80 mesh (0.25mm) to 100-120 mesh (0.125mm).
- The smaller the particle size and the thinner the coating the less band spreading occurs.
- **Capillary (open tubular) columns:** These are made of high-quality fused quartz and are 10-100m long and 0.1-1.0mm internal diameter.
- They are of two types known as wall-coated open tubular (WCOT) and support-coated open tubular (SCOT), also known as porous layer open tubular (PLOT) columns, for adsorption work.

Capillary (open tubular) columns

- In WCOT columns the stationary phase is thinly coated (0.15 mm) directly onto the walls of the capillary,
- Whilst in SCOT columns the support matrix is bonded to the walls of the capillary column and the stationary phase coated onto the support.
- Commonly used stationary phases include polyethylene glycol (CP wax and DB wax, very polar) and methyl and phenyl-polysiloxanes (BP1, non-polar; BP10, medium polar).
- Analyte partition coefficients are particularly sensitive to temperature so that analysis times may be regulated by adjustment of the column oven, which can be operated in one of two modes:
  - Isothermal analysis: Here a constant temperature is employed.
  - Temperature programming: The temperature is gradually increased to facilitate the separation of compounds of widely differing polarity or Mr.

Application of sample

- The majority of non- and low-polar compounds are directly amenable to GC.
- But other compounds possessing such polar groups as -OH, -NH_2 and -COOH are generally retained on the column for excessive periods of time if they are applied directly.
- This problem can be overcome by derivatisation of the polar groups.
- This increases the volatility and effective distribution coefficients of the compounds.
- Methylation, silanisation and perfluoracylation are common derivatisation methods for fatty acids, carbohydrates and amino acids.
- The test sample is dissolved in a suitable solvent such as acetone, heptane or methanol.
- Chlorinated organic solvents are generally avoided as they contaminate the detector.
- It is common practice to maintain the injection region of the column at a slightly higher temperature (+20 to 50 ^{o}C) than the column itself as this helps to ensure rapid and complete volatilisation of the sample.

Mobile phase

- The mobile phase consists of an inert gas such as:
  - nitrogen for packed columns or
  - helium or argon for capillary columns.
- The gas from a cylinder is pre-purified by passing through a variety of molecular sieves to remove oxygen, hydrocarbons and water vapour.
- It is then passed through the chromatography column at a flow rate of 40-80 cm^3 min–1.
- A gas-flow controller is used to ensure a constant flow irrespective of the back-pressure and temperature of the column.

Detectors

- Several types of detector are in common use in conjunction with GC:
- **Flame ionisation detector (FID)**: This responds to almost all organic compounds.
- A mixture of hydrogen and air is introduced into the detector to give a flame, the jet of which forms one electrode.
- Whilst the other electrode is a brass or platinum wire mounted near the tip of the flame.
- When the sample analytes emerge from the column they are ionised in the flame, resulting in an increased signal being passed to the recorder.
- **Nitrogen–phosphorus detector (NPD) (also called a thermionic detector):** This is similar in design to an FID but has a crystal of a sodium salt fused onto the electrode system, or a burner tip embedded in a ceramic tube containing a sodium salt or a rubidium chloride tip.
- The NPD has excellent selectivity towards nitrogen- and phosphorus-containing analytes and shows a poor response to analytes possessing neither of these two elements.

...Detectors

- **Electron capture detector (ECD):** This responds only to analytes that capture electrons, particularly halogen-containing compounds.
- This detector is widely used in the analysis of polychlorinated compounds, such as the pesticides DDT, dieldrin and aldrin.
- When an electron-capturing analyte (generally one containing a halogen atom) emerges from the column, the ionised electrons are captured, the current drops and this change in current is recorded.
- **Flame photometric detector:** This exploits the fact the P- and S-containing analytes emit light when they are burned in a FID-type detector.
- This light is detected and quantified.

...Detectors

- **Rapid scanning Fourier transform infrared detector:** This records the infrared spectrum of the emerging analytes and can give structural as well as quantitative information about the analyte.
- **Mass spectrometer detector:** This is a universal detector that gives a mass spectrum of the analyte and therefore gives both structural and quantitative data.

THANKS