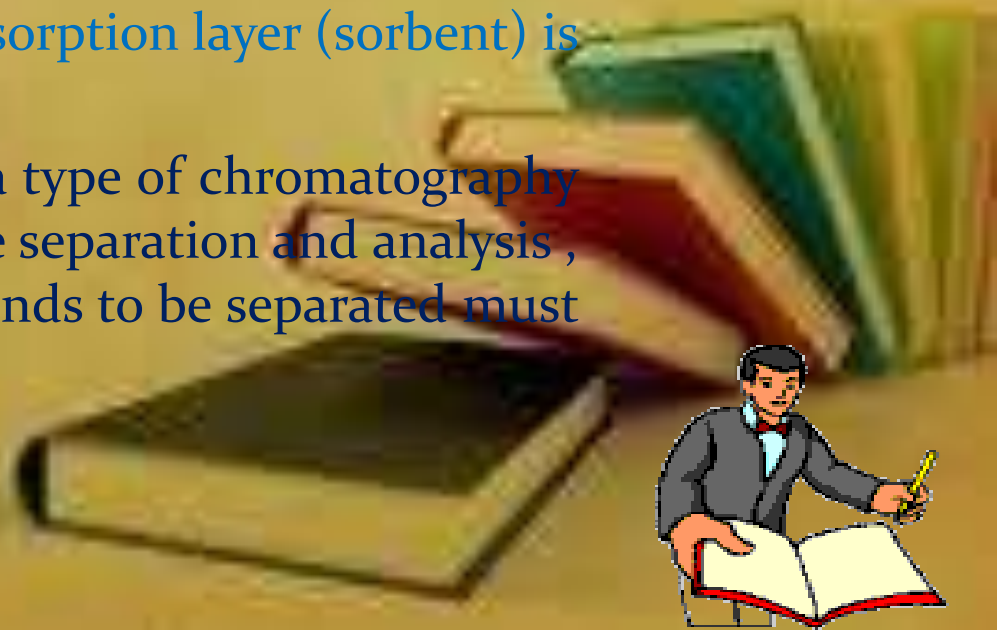
GAS CHROMATOGRAPHY

DEFINITION OF GAS CHROMATOGRAPHY

- In 1952 Martin and James publishes his first paper on gas chromatography .
- Between 1952 and the end of the 1960s developed into a gas chromatography sophisticated analytical techniques
- Etymologically , Chromatography derived from the Greek meaning "color " and "write"
- Gas chromatography is the process of separation of a mixture into its components by using gas as the mobile phase that passes through an absorption layer (sorbent) is silent
- Gas chromatography (GC) , is a type of chromatography used in organic chemistry for the separation and analysis , therefore , the chemical compounds to be separated must be in the form of gas anyway .



Introduction

- Gas chromatography - specifically gas-liquid chromatography - involves a sample being vapourised and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.

- Have a look at this schematic diagram of a gas chromatograph:

the Chromatography

- Chromatography is classified two different ways. In the first way, it is based on the physical means by that the stationary and the mobile phase are brought into contact. In column chromatography, the stationary phase is held in a narrow in tube through which the mobile phase is forced under pressure. In planar chromatography, the mobile phase moves through the stationary phase by capillary action or under the influence of the gravity to the stationary phase which is supported on a flat plate or in the interstices of paper. In the second way, the classification is based on the types of the mobile and the stationary phases and the kinds of equilibria involved in the transfer of the solute between phases; gas chromatography ",liquid chromatography, and supercritical fluid chromatography

Mobile phase

- A liquid or gas which percolates through or over the stationary bed in a definite direction. It may be a liquid (liquid chromatography, LC) or a gas (gas chromatography, GC). In gas chromatography the expression ‘carrier gas’ may be used for the mobile phase. In elution (liquid) chromatography the expression ‘eluent’ is also used for the mobile phase. Efficiency.

Analyte - The compound of interest to be analyzed by injection into and elution from an HPLC or GC column.

Stationary phase

- The stationary phase is one of the two phases forming a chromatographic system. It may be a solid, a gel, or an immobilized polymeric liquid. If a liquid, it may be distributed on a solid. This solid may or may not contribute to the separation process. The liquid may also be chemically bonded to the solid (bonded phase). The expression chromatographic bed or sorbent may be used as a general term to denote any of the different forms in which the stationary phase is used. A stationary phase which is covalently bonded to the support particles or to the inside wall of the column tubing is known as a bonded phase. Vapor pressure - the absolute pressure at which the vapor contained in a substance is at equilibrium with its liquid or solid phase

Quantitative - Chemical analysis undertaken to determine (measure) the quantity or amount of each analyte within a mixture.
Polarity - The greater the difference in electron affinity (electronegativity) between atoms ina covalent bond the more polar the bond. Partial negative charges are found on the most electronegative atoms, the others are partially positive. The molecular electrostatic potential is the potential energy of a hydrogen ion at a particular location near a molecule. Negative electrostatic potential corresponds to partial negative charges. Positive electrostatic potential corresponds to partial positive charges.

Elute - To chromatograph by elution chromatography. The process of elution may be stopped while all the sample components are still on the chromatographic bed or continued until the components have left the chromatographic bed.

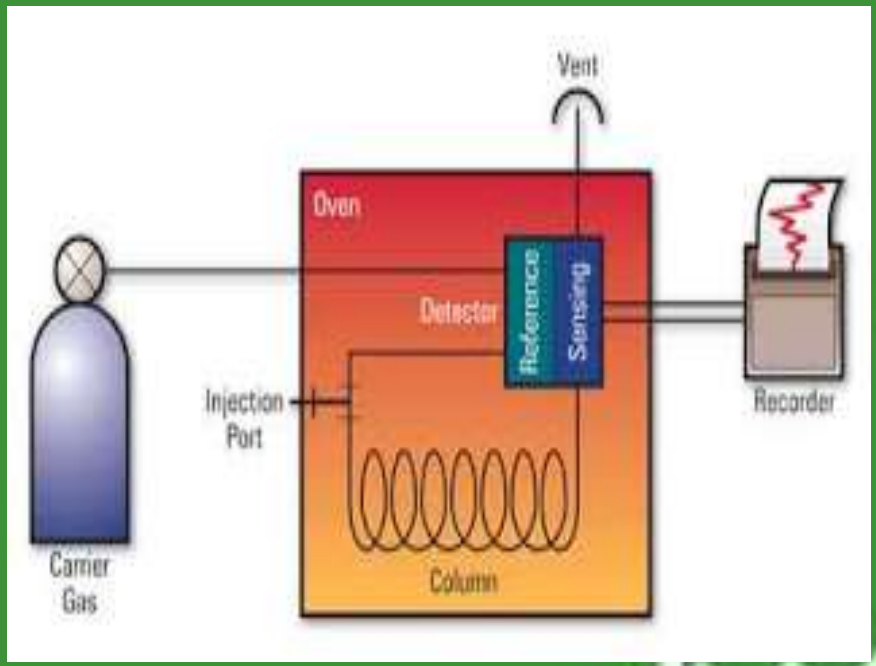
to - The volume of the mobile phase (or the corresponding time) required to elute a component the concentration of which in the stationary phase is negligible compared to that in the mobile phase. In other words, this component is not retained at all by the stationary phase. Thus, the hold-uip volume (time) is equal to the retention volume (time) of an unretained compound. The hold-up volume (time) includes any volumes contributed by the sample injector, the detector, and connectors

THE BASIC COMPONENTS OF A GAS CHROMATOGRAPH

components of a gas chromatograph:

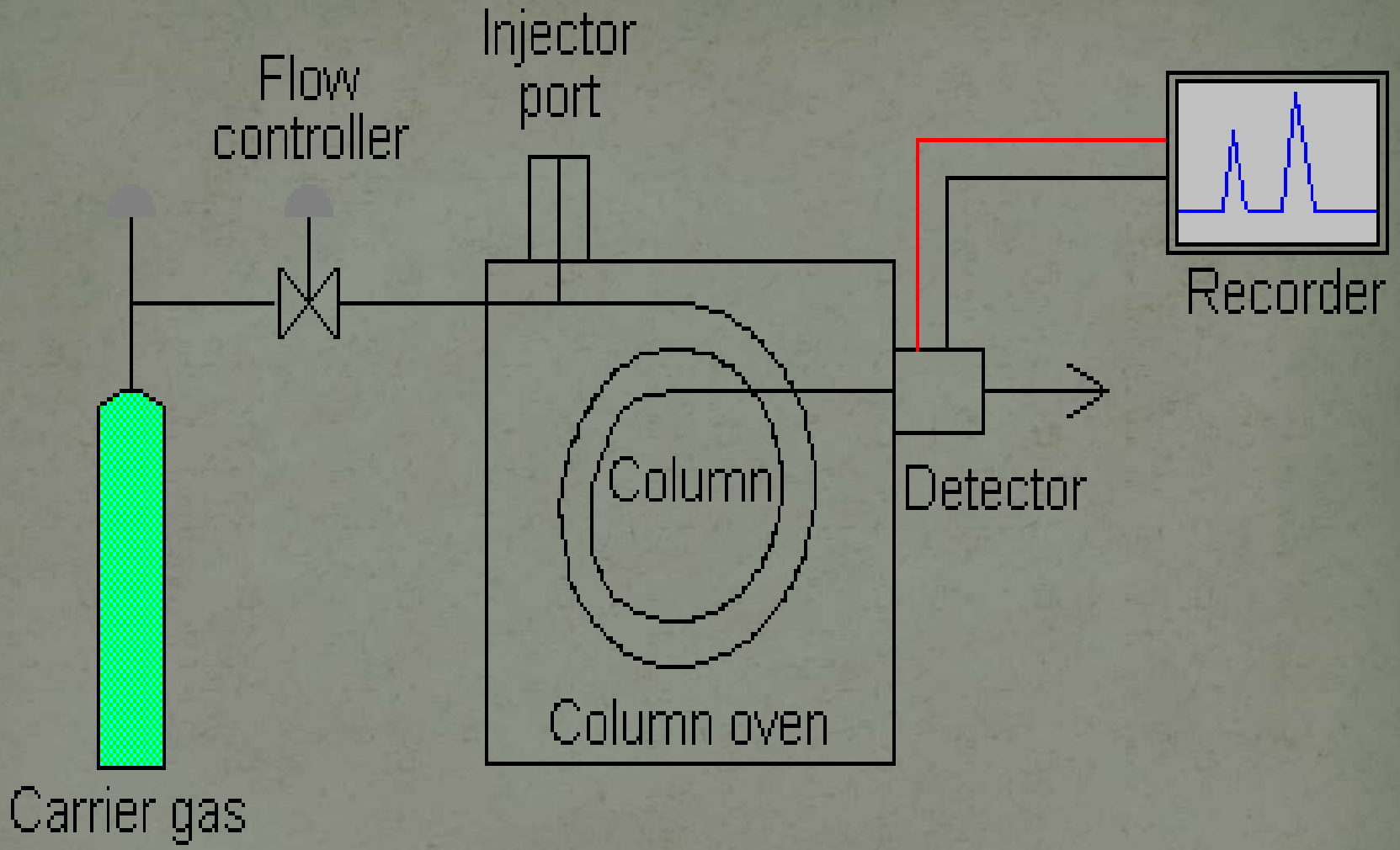
1. The carrier gas tank
2. Regulatory flow and pressure regulating
3. Injection site
4. The column
5. Detector
6. Recorder

Scheme of gas chromatography equipment



Carrier gas

- The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities.


Injector
port
Flow
controller
Recorder
Column
Detector
Column oven
Carrier gas

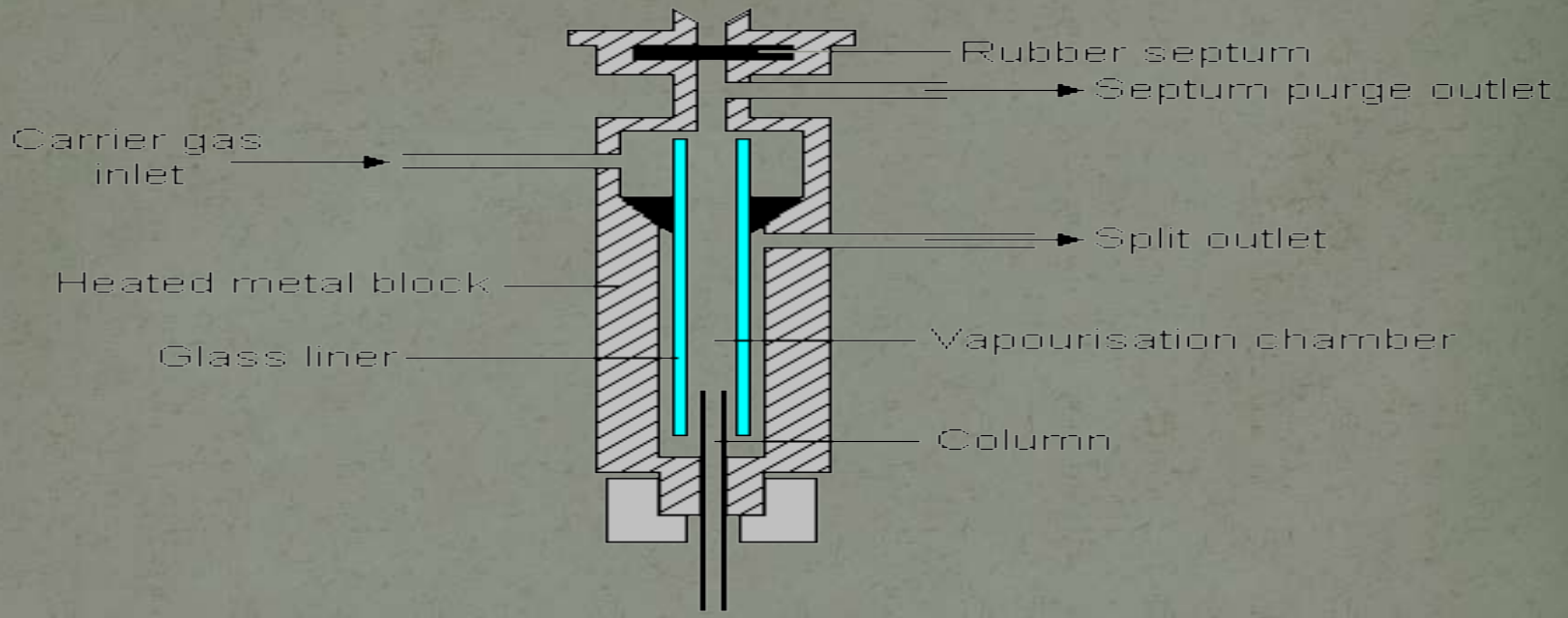
Regulatory Flow and Pressure Regulator

- This is called a regulator or deduction Drager . Drager worked well at 2.5 atm , and flow with a fixed mass flow.
- Common prices for the gas velocity for a column that has an outside diameter :
  - 1/4 " O.D : gas rate 75 ml / min
  - 1/8 " O.D : gas rate 25 ml / min

Sample injection port

- For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a "plug" of vapour - slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a microsyringe is used to inject sample through a rubber septum into a flash vapouriser port at the head of the column. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component of the sample. For packed columns, sample size ranges from tenths of a microliter up to 20 microliters. Capillary columns, on the other hand, need much less sample, typically around 10^{-3} mL. For capillary GC, split/splitless injection is used. Have a look at this diagram of a split/splitless injector;

The split / splitless injector



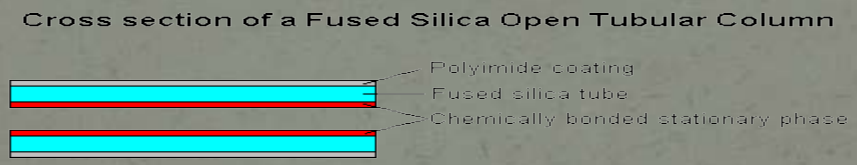
The injector can be used in one of two modes; split or splitless. The injector contains a heated chamber containing a glass liner into which the sample is injected through the septum. The carrier gas enters the chamber and can leave by three routes (when the injector is in split mode). The sample vapourises to form a mixture of carrier gas, vapourised solvent and vapourised solutes. A proportion of this mixture passes onto the column, but most exits through the split outlet. The septum purge outlet prevents septum bleed components from entering the column.

Columns

There are two general types of column, *packed* and *capillary* (also known as *open tubular*). Packed columns contain a finely divided, inert, solid support material (commonly based on *diatomaceous earth*) coated with liquid stationary phase. Most packed columns are 1.5 - 10m in length and have an internal diameter of 2 - 4mm.

Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; *wall-coated open tubular* (WCOT) or *support-coated open tubular* (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns.

In 1979, a new type of WCOT column was devised - the *Fused Silica Open Tubular* (FSOT) column;



These have much thinner walls than the glass capillary columns, and are given strength by the polyimide coating. These columns are flexible and can be wound into coils. They have the advantages of physical strength, flexibility and low reactivity.

Column temperature

- For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependant upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds.
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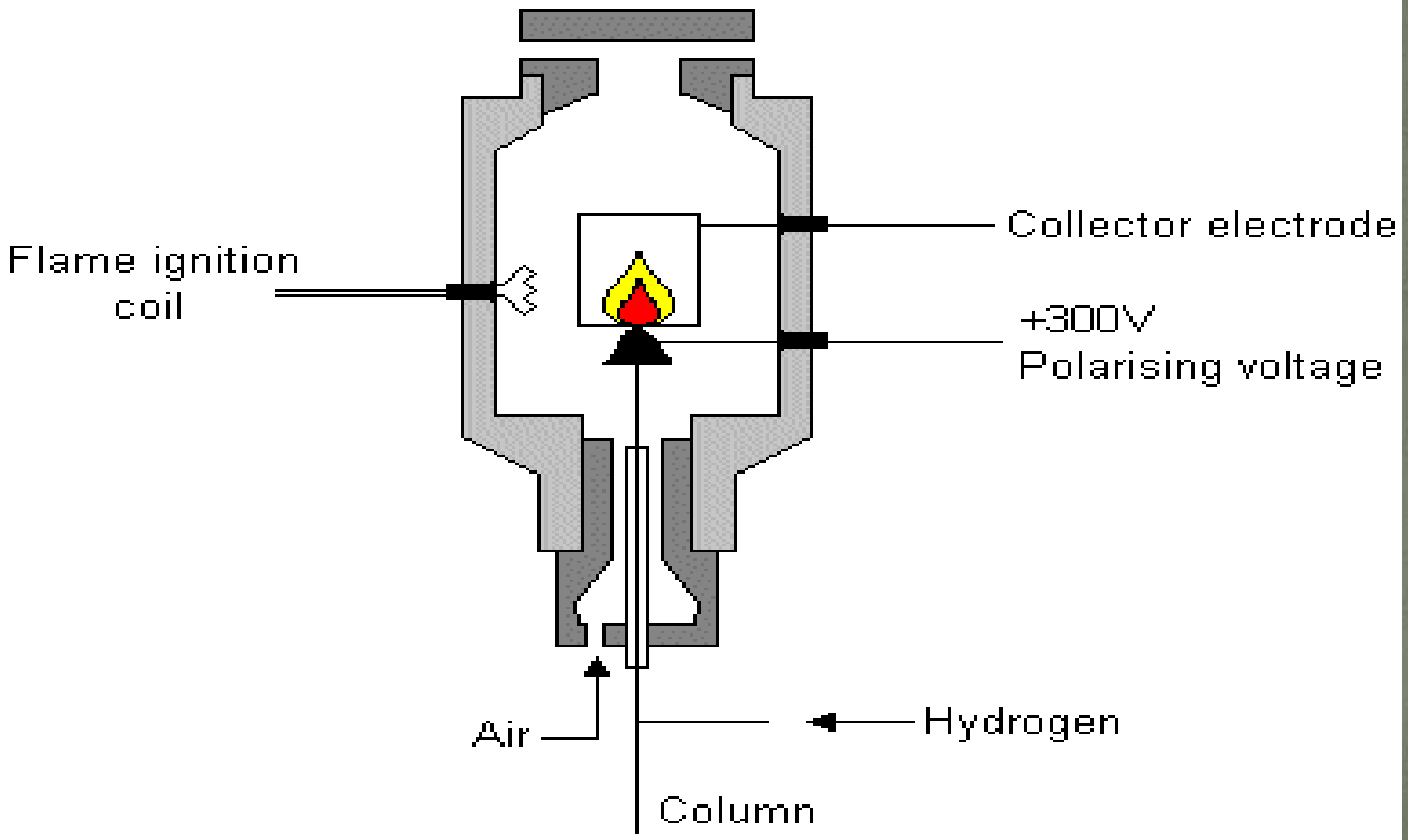
Detectors

There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity. A *non-selective* detector responds to all compounds except the carrier gas, a *selective detector* responds to a range of compounds with a common physical or chemical property and a *specific detector* responds to a single chemical compound. Detectors can also be grouped into *concentration dependant detectors* and *mass flow dependant detectors*. The signal from a concentration dependant detector is related to the concentration of solute in the detector, and does not usually destroy the sample Dilution of with make-up gas will lower the detectors response. Mass flow dependant detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependant detector is unaffected by make-up gas.

The Flame Ionisation Detector



- The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. FIDs are mass sensitive rather than concentration sensitive; this gives the advantage that changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range, and low noise. It is also robust and easy to use, but unfortunately, it destroys the sample.

Detectors

- In contrast with other analysis tools , detectors in gas chromatography are generally more diverse .
- his is due to the GC detector detects the flow of chemicals and not as the beam spectrophotometer
- Some considerations in designing a detector to dikemukan as follows :
  - GC detectors should be able to detect within a few seconds .
  - Samples were entered into the detector to be volatile and are free from the influence of the matrix . This sort of thing also happens to atomic absorption or emission spectrometry .
  - GC detector sensitivity has now significantly compared with the analysis tools in general .
  - have a GC detector dynamic range is very large , generally greater than 10^7 .
  - GC detectors can also be used as a means of identification in spite of usability in general is for the purpose of quantitative

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Recorder

- Recorder functions as a modifier of the detector signal is amplified by an electrometer into shape chromatogram.
- Chromatograms obtained from the analysis can be carried out qualitative and quantitative.
- Qualitative analysis by comparing the retention times with standard samples .
- Quantitative analysis by calculating the area or height of the chromatogram .

GC Advantages and Disadvantages

- Gas chromatography has several important advantages which are listed opposite. GC techniques produce fast analyses because of the highly efficient nature of the separations achieved – this will be studied further in the Band Broadening Section. It can be argued that modern GC produces the fastest separations of all chromatographic techniques. A column has been produced to separate 970 components within a reasonable analysis time - proving that very complex separations may be carried out using GC.2 By using a combination of oven temperature and stationary phase chemistry (polarity) very difficult separations may also be carried out – including separations of chiral and other positional isomers. GC is excellent for quantitative analysis with a range of sensitive and linear detectors to choose from. GC is however limited to the analysis of volatile samples. Some highly polar analytes can be derivatized to impart a degree of volatility, but this process can be difficult and may incur quantitative errors. A practical upper temperature limit for conventional GC columns is around 350-380 ° C. Analyte boiling points rarely exceed 400 ° C in GC analysis and the upper Molecular Weight is usually around 500 Da.

Advantages

- □ Fast analysis □ High efficiency – leading to high resolution □ Sensitive detectors (ppb) □ Non-destructive – enabling coupling to Mass Spectrometers (MS) - an instrument that measures the masses of individual molecules that have been converted into ions, i.e. molecules that have been electrically charged □ High quantitative accuracy (

Disadvantages

- Limited to volatile samples Not suitable for samples that degrade at elevated temperatures (thermally labile) Not suited to preparative chromatography Requires MS detector for analyte structural elucidation (characterization) Most non-MS detectors are destructive

Typical GC Applications

- . Since the development of GC instruments in the early to mid 1950's, GC has found applications in a host of industrial, environmental, pharmaceutical and biotechnology analytical laboratories. Modern GC techniques are able to sample from a wide variety of matrices, including solids, liquids and permanent gases. High temperature applications using specially designed columns are able to analyze relatively nonvolatile substances and Cool-on-Column injection techniques allow the sampling of moderately thermally labile materials. Purge and trap and headspace autosampling techniques are now well established and are able to desorb or extract samples collected in the most inhospitable of environments, such as the emission stacks of industrial plants. Detector technology for GC is able to detect very small amounts of pesticides for example, from environmental samples and GC-MS techniques allow structural elucidation of even the most complex analytes.

TERMS OF THE GAS CHROMATOGRAPHIC SEPARATION

- Terms of compounds that can be analyzed by GC , namely the KG operational temperatures (≤450°C) :
  1. Molecules / compounds can change the gas or vapor phase
  2. Not decomposed at the temperature
- Terms gas as the mobile phase :
  1. Inert
  2. Gaseous diffusion coefficient lower
  3. Purity High
  4. Easily available and cheap
  5. Fits the detector used

Examples of carrier gas : N_2 , He, H_2 , Ar , etc.

BASIC PRINCIPLES OF GAS CHROMATOGRAPHY

1. The workings of a gas chromatographic carrier gas is passed through one side of the detector and then enter the column
2. Near the column there is a device in which the sample - the sample can be inserted into the carrier gas (injection site) .
3. Hole injection vaporized sample is heated so quickly .
4. Subsequent gas flow to meet the column , the column is where the heart chromatography instruments takes place .
5. Column contains fine solids with a large surface area and relatively inert .
6. Before being filled into the column , the solids impregnated with the desired fluid that acts as the stationary phase or stationary indeed , this fluid must be stable and nonvolatile at the temperature of the column and must comply with certain separation .
7. After emerging from the column , the gas stream passes through the other side of the detector .
8. Then the solute elution of the column set the imbalance between the two sides of the detector are recorded electrically .


THANK
YOU