Gas Chromatography (GC)

Gas Chromatography (GC) can be discussed by following headings.

⇒ Introduction & origin
⇒ Basic principle
⇒ Theory of separation
⇒ Instrumentation.
- The Cassier Gas System
- Sample injectors.
- The Columns
- The oven
- Detectors
- Data System

⇒ • Advantages of GC
⇒ • Disadvantages of GC
⇒ • Applications

Introduction & Origin Of GC

The development of GC as an analytical tool was pioneered by A.J.P Martin & Richard L.M Synge in 1941. But unfortunately little notice was taken of their suggestion. They continued their work to bring the concept to practical reality in 1951 when they published their epic paper by separating & quantitatively determining. the 12 components of a $C_1 - C_5$ fatty acid mixture. Since then GC has ~~been~~ undergone tremendous development. It is quite suspising that T.A Berger in 1996 published a paper in Journal Chromatogsaphia and showed separation of 970 components in a gasoline ~~mixture~~ sample.

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Basic Principle

In GC, the components of a vapourized sample are separated as a consequence of being partitioned b/w a mobile gaseous phase and a liquid or solid stationary phase held in a column. In performing a gas chromatographic separation, the sample is vapourized and injected onto the head of a chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase. In contrast to most other types of chromatography, the gaseous mobile phase does not interact with molecules of the analyte, its only function is to transport the analyte through the column.

Brief Theory of GC Separations

There are two types of gas chromatography

⇒ Gas Solid Chromatography (GSC)

In GSC, the stationary phase is a solid packed in a column on which retention of analytes occurs because of physical adsorption. GSC is quite limited in applicability because of

- Semipermanent retention of active or polar molecules
- Severe tailing of elution peaks.
- Difficulty in reproducing surface areas.

Thus GSC is not widely used except for the separation of certain low molecular mass gaseous species.

⇒ Gas Liquid Chromatography (GLC)

In GLC, the stationary phase is ~~an immobilized~~ Friends

a liquid immobilized on the surface of an inert solid packing or on the walls of a capillary tubing. In gas chromatography, the sample is converted into the vapour state if it is not already a gas by injection into a heated port situated at the head of the chromatographic column. As a result, the components having finite solubility in the stationary liquid phase distribute themselves between this phase and mobile gas phase. Elution is then carried out by forcing an inert gas e.g He, N_2 through the column. The rate of movement of various components through the column depends upon their tendency to dissolve in the stationary liquid phase. Components having a negligible solubility in the stationary phase move rapidly through the column while those components having appreciable solubility in the liquid phase move with a low rate through the column. In this way, the components present in a sample get separated.

Instrumentation Of GC

Instrumentation for gas chromatography (GC) comprises of well-defined components, each of which contributes to the overall chromatographic performance. The key parts of a gas chromatograph include

- A source of gas as the mobile phase
- An inlet to deliver sample to a column.

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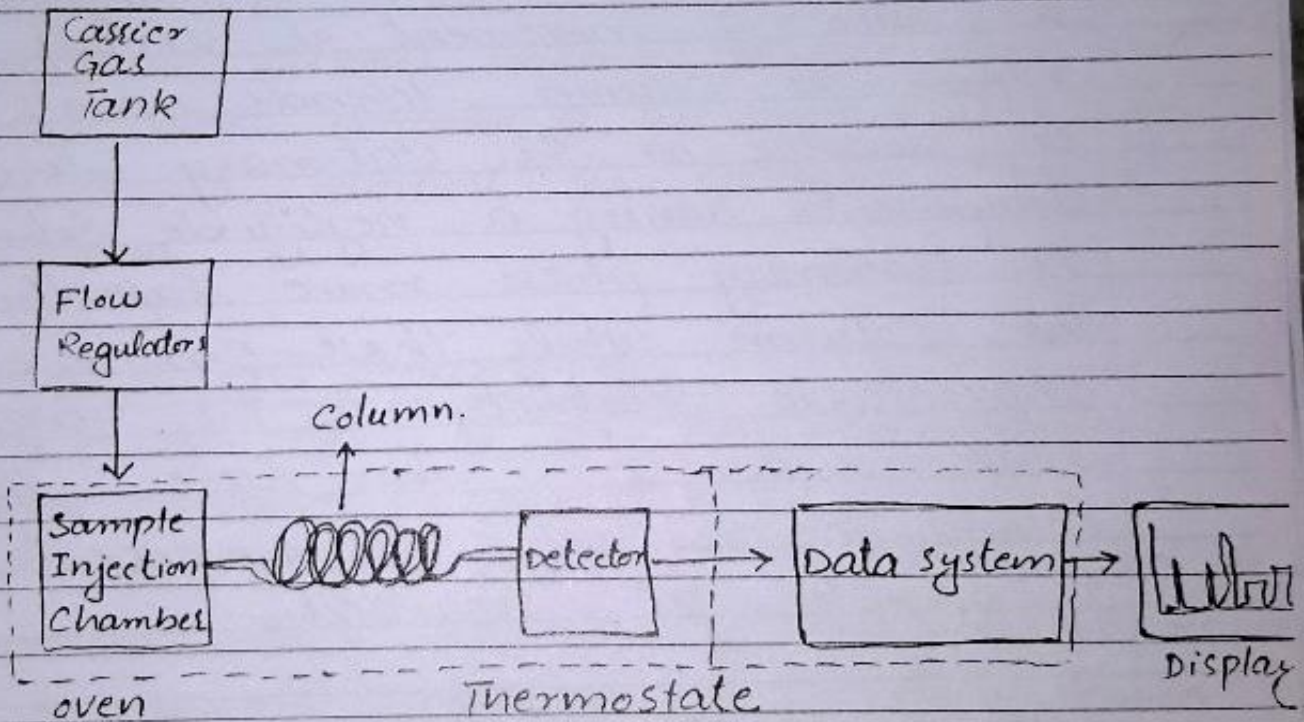
- The column where separation occurs
- An oven as a thermostate for the column
- A detector to register the presence of a chemical in the column effluent.
- A data system to record and display the Chromatogram.

The arrangement of these components is shown in a block diagram below.



The detailed description of each component is discussed below.

(1) The Carrier Gas System.

The mobile phase in gas chromatography is called the carrier gas which is present in compress form in a high pressure gas cylinder. These gas cylinders are often associated with pressure regulators, guages, flow meters and

molecular sieves to remove impurities and water.
A carrier gas should have the following properties
i. Highly pure (> 99.9%)
ii. inert i.e do not react with stationary phase, instrumental components or the analyte molecules
iii. Low cost because large quantities are used.
iv. high density
v. Compatible with the detector.
He and N_2 Fulfill all the above requirements and hence these gases are most commonly used as carrier gas although CO_2, Ar and H_2 have also been tried.

2. Sample Injectors:
In order to achieve high column efficiency, the sample must be of a suitable size and introduced as a plug of vapours. Slow injection or oversize samples cause band broadening and poor resolution. Therefore the samples injected range from about 10-20 µL for packed columns and much smaller volumes for capillary columns.
The various devices used for introducing samples ~~include~~ into the heated sample post located at the head of the column include
- Microsyringes
- Sample splitters
- On-Column inlets.
- Switching valve

Another inlet option which is now routine in certain specific applications of material sciences

is that of sample pyrolysis where solid samples are rapidly heated to a point of thermal decomposition. At temperatures in excess of 600°C, substances thermally decompose to smaller molecular weight stable species that provide a chromatographic profile which is unique to certain materials. This is called pyrolysis and is applied for substances like lignin, synthetic polymers, Rosin glycerin esters, Chlorinated polyethenes, coating materials etc.

(3)- The Columns.

The column is the heart of chromatography where components of the injected sample get separated. Two types of columns are commonly employed in Gas Chromatography

i. Packed Columns:.

Packed columns were the first type and were used for many used but now ~~their uses~~ they are less commonly used for applications that do not require high resolution. Packed columns can be in any shape that will fill the heating oven. Column shapes include coiled tubes, U-shaped tubes and W-shaped tubes but coils are most commonly used.

These packed columns are made up of glass, stainless steel, teflon or metal tubings. They are typically 2 to 3 m long and have inside diameter of 2–4 mm.

The columns are packed with uniform,

finelly divided particles of diatomaceous earth that may serve as the stationary phase for GSC or may act as support for liquid stationary phase for GLC.

ii. Open tubular or Capillary Columns

The capillary columns are the most widely used columns that can provide very high resolution as compared to packed columns.
The capillaries are made up of stainless steel or thin fused silica (SiO_2) coated on the outside with the polyimide polymer for support and protection allowing the capillaries to be coiled. This polyimide layer imparts brownish color to capillaries and is often darkens on use.
The capillary columns have 0.10 to 0.53 mm internal diameter with lengths of 15 to 100 m due to which they offer high resolution with narrow peaks, short analysis time and high sensitivity.

Open tubular or capillary columns are of two basic types

- Wall coated open tubular (WCOT) Columns.
- Support coated open tubular (SCOT) Columns.

The WCOT columns are made up of glass which are internally coated with a thin layer of liquid stationary phase.
In SCOT columns, the inner surface of the capillary is lined with a thin film (~30 um) of a support material e.g diatomaceous earth upon which thin layer of liquid stationary phase is bonded. Friend::

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(4)- The Oven :-

Liquids or solid samples must be converted to vapour state and maintained as vapour throughout the GC separations. Therefore all gas chromatographs are equipped with ovens to keep the columns at temperatures from 40 to 350°C. Early gas chromatographs were equipped with isothermal oven. Today, temperature programmed ovens are used in which the column temperature is increased either continuously or in steps as the separation proceeds.

(5) Detectors

The role of detectors in GC is pivotal because the separation process will have been wasted if the analyte cannot be detected.
Any physical or chemical property which varies widely from one gas to another and which can easily be monitored can be made the basis of detector. The most important physical properties are

- Thermal conductivity
- Velocity of sound
- Gas density
- Magnetic susceptibility
- ionization by α or β- rays or heat
- & Absorption of UV or IR radiations.
- Mass to charge ratio etc.
- Electron capture

Based on these properties, detectors are of

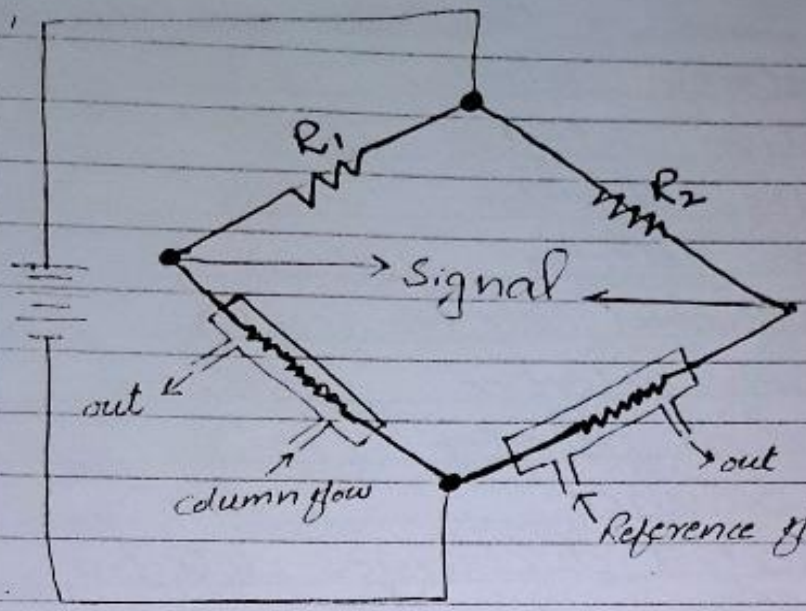
various types. Some of these are listed below

i. Thermal conductivity detector (TCD)
ii. Flame ionization detector (FID)
iii. Electron capture detector (ECD)
iv. photoionization detector (PID)
v. Nitrogen-phosphorous detector (NPD)
vi Atomic emission detector (AED)
vii. Argon ionization detector (AID)
viii. Gas density Balance
ix. Microwave excited discharge detector
x Flame photometric detector.

Thermal Conductivity Detector (TCD):-

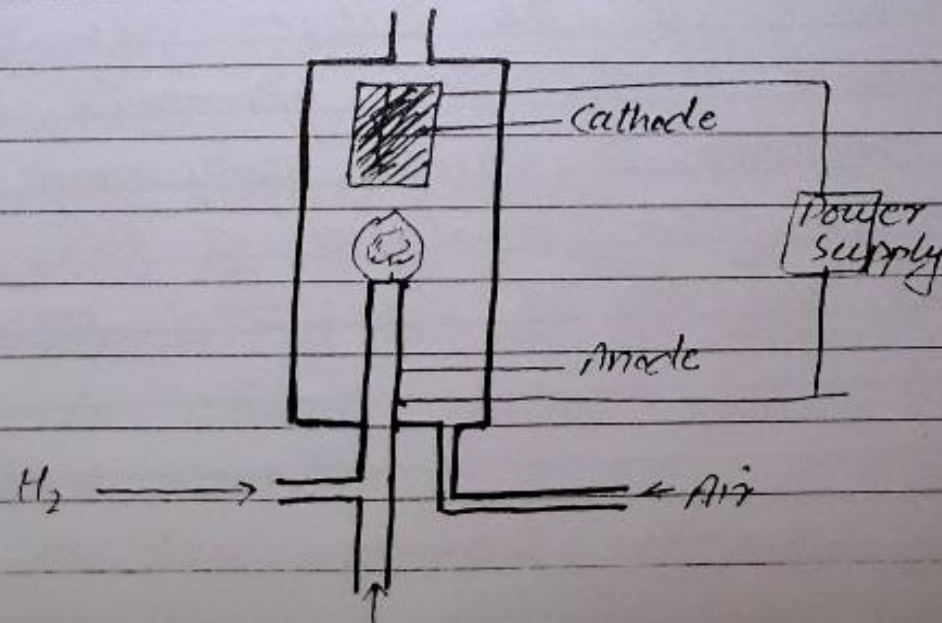
The thermal conductivity detector (TCD) which was one of the earliest detectors for GC, is still widely used. It is based upon changes in the thermal conductivity of the cassier gas stream by the presence of analyte molecules.

It comprises of a pair of electrically-heated A gold, platinum or Tungsten filaments having some value of resistance. One filament is connected to column flow and the other with reference flow. Whenever there is no sample constituent in the cassier gas flow, the resistance of the two filaments will be same. But whenever a sample component emerges from column flow, the resistance of that ~~col~~ filament increases which is registered on the recorder.

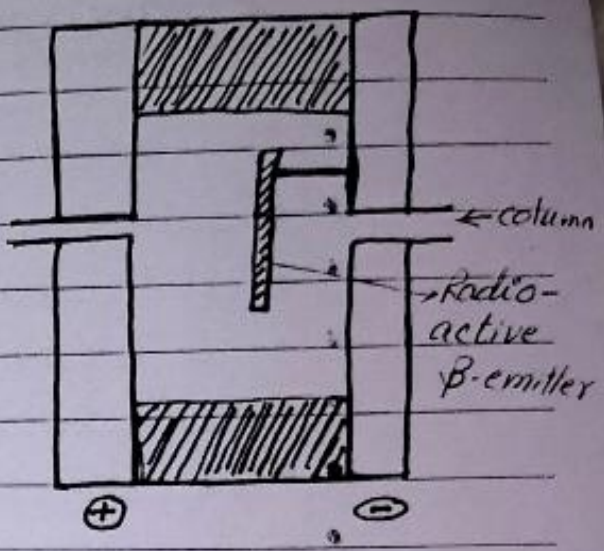


Flame Ionization Detector (FID)

Most organic compounds form ions, generally cations such as $CHO^{\oplus}$ when introduced into a hydrogen oxygen flame. These ions and lost electrons are collected at charged electrodes and produce electric current which is measured by an electrometer amplifier. As the composition of the gas in the flame changes, the number of ions and electrons will also change. Thus the current flow will vary with the change in composition of the gas eluted from GC column.



Electron Capture Detector (ECD)



The electron capture detector (ECD) has become one of the most widely used detector for environmental samples having halogen containing compounds e.g pesticides, PCBs. The Sample eluate from the column is passed over a Radioactive β-emitter usually Ni-63. An electron from the emitter causes ionization of the carrier gas producing cations and burst of electrons. These cations and electrons are collected as cathode and anode with the generation of constant standing current. However in the presence of ~~electro~~ organic compounds having electronegative groups e.g halogens, peroxides, quinones, nitro compounds, the current decreases significantly because these groups tend to capture electrons.

(6)- The Data System

The data system receives the signal from the detector and digitalizes it to form the record of the chromatographic separation known as the chromatogram. The data system can also be used to perform various quantitative and qualitative operations on the chromatogram- assisting with sample identification and quantification.

Advantages Of GC

The various important advantages of GC include
- Both qualitative & quantitative analyses are possible
- Fast analysis
- The instrument is simple to use.
- High sensitivity upto ppb level.
- The technique is applicable to about 60% of known compou
- High efficiency of separations.
- Requires small samples.
- Well established with extensive literature.
- Separations which are very difficult or virtually impossible by other techniques can be simple and straightforward with GC.

Disadvantages of GC.

GC suffers from some disadvantages e.g
- Limited to volatile samples.
- Not suitable for samples that degrade at elevated temperatures.
- Not suited to preparative chromatography.
- Requires MS detector for analyte structure elucidation.
- Most of the detectors are destructive.

Applications of GC

Since the development of GC instruments in the earl to mid 1950s, GC has found applications in G most of industrial, environmental, pharmaceutical and biotechnology analytical laboratories.