Gas Chromatography

15

Abstract

In this technique, the separation of the components present in mixture is based on the partition between the gaseous mobile phase and liquid stationary phase. In this chapter, types of gas chromatography are given. The advantages and disadvantages have also been described. The instrumentation of gas chromatography along with its working has been described. The factors that affect the GC have also been discussed. At the end of this chapter, advantages and disadvantages along with its application have been given.

Keywords

Principle of gas chromatography · Components of gas chromatography

15.1 Introduction

This chromatographic technique was invented by Martin in which he suggested that liquid mobile phase which is used in liquid chromatography can be replaced by using a suitable gas as mobile phase. As he used gaseous mobile phase instead of liquid mobile phase for separation purpose of the components of the sample, therefore, the term was named as gas chromatography. It is a process of separation of the components of the given sample such as crude substances by using a gaseous mobile phase. The more classy form of gas chromatography was developed by James and Martin in 1955. In gas chromatography, the mobile is in gaseous form, whereas the stationary phase is in solid or liquid form. If the component is more soluble in stationary phase, then it travels slower in the column, whereas if the component is less soluble in stationary phase, then it travels faster. Therefore, the components present in the sample mixture are separated according to their partition co-efficient between the component of interest and stationary phase.

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15.2 Principle

In this technique, the sample is first vaporized by heating and then it is injected into the head of the chromatographic column. The sample is transferred into the column by the flow of inert gaseous mobile phase. The column has a liquid stationary phase which is adsorbed on the surface of an inert solid. It has same principle as chromatography, separation of the components due to partition between stationary phase and mobile phase.

15.3 Types of Gas Chromatography

Based on the nature of the stationary phase, gas chromatography has the following two main types:

15.3.1 Gas–Solid Chromatography

When the stationary phase (adsorbent) is solid in nature, then it is known as gas–solid chromatography (GSC). The most common examples of stationary phase used in GSC are active carbon, silica, alumina, etc. The principle of separation in GSC is adsorption. One of the main advantages of GSC is that the column life is long, while the main disadvantage of this technique is that there may be chances of catalytic changes in the chemical composition of the components present in sample mixture.

15.3.2 Gas–Liquid Chromatography

If the stationary phase is liquid in the gas chromatography, then it is referred as gas–liquid chromatography (GLC). The solid surface which may be polymer is coated with the immobilized liquid. The principle in GLC is partition. Nowadays, GLC is abundantly utilized in the form of capillary column.

15.3.2.1 Advantages of GLC

1. It provides high resolution capacity for the complex mixtures. For example, separation of methyl esters of fatty acids.
2. As capillary column is abundantly used in GLC, only few microliter samples are enough for the complete analysis.
3. The seed of analysis is quite fast because the mobile phase has the ability to attain the rapid equilibrium between the mobile phase and stationary phase.
4. Sensitivity of detection is quite high while using different types of detectors.
5. It simultaneously allows qualitative and quantitative analysis of analyte.

15.3.2.2 Disadvantages of GLC

The major disadvantage of GLC is that the immobilized liquid is slowly run out from the solid surface.

15.4 Components of Gas Chromatography

The main components of gas chromatography have been illustrated in Fig. 15.1.

15.4.1 Carrier Gas

The carrier gas must be chemically inert. The most common gases that are used include nitrogen, helium, argon, and carbon dioxide. Hydrogen has better thermal conductivity but it also has disadvantage that it often reacts with the unsaturated compounds and compounds that are inflammable in nature. Thermal conductivity of helium is excellent but it is too much expensive. Nitrogen is inexpensive but it has reduced sensitivity. The selection of carrier gas mostly depends upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities. Following characteristics should be present in carrier gas:

1. It should be chemically inert in nature.
2. It should be suitable for the detector and must enable the detector to respond in a sufficient adequate manner.

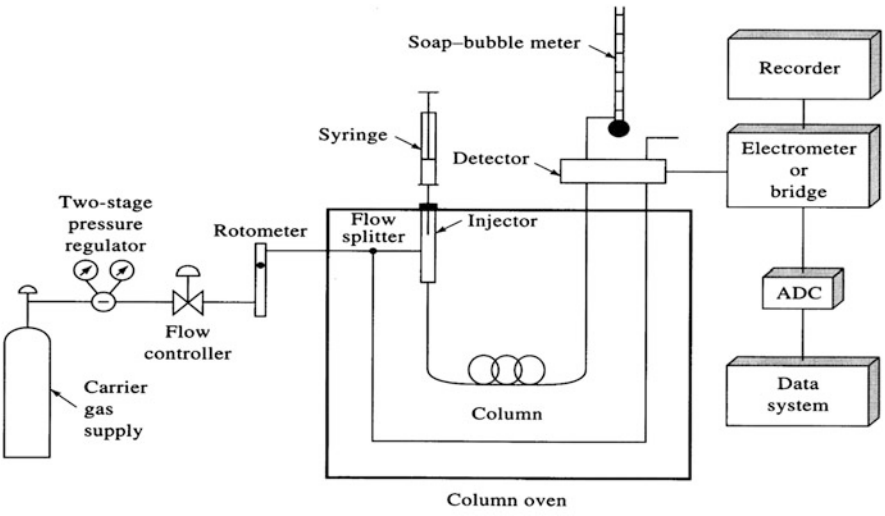

Fig. 15.1 Schematic representation of components of gas chromatography

3. The carrier gas should have the high purity.
4. It should be easily available.
5. It should be cheap.
6. It should be non-inflammable.
7. It is responsible for giving the best column performance.
8. It should be free from metallic particles.

15.4.2 Columns

The fundamental role of column is to separate the individual components present in sample mixture. There are two main types of columns that are used in gas chromatography technique.

15.4.2.1 Packed Columns

These columns contain glass or metallic tubes that are coated with immobilized liquid stationary phase. Most packed columns are 1.5–10 m in length and have an internal diameter of 2–4 mm.

15.4.2.2 Capillary Columns

These columns have very small internal diameter in millimeters but their length is between 25 and 60 m. These capillary columns have immobilized stationary phase which is liquid. The stationary phase is coated with the glass or silica in the inner sides of columns. These are also called as open tubular columns and have the following types:

1. *Wall-coated open tubular columns:* The inner walls of these columns are coated with inert active material which acts as a support on which the immobilized liquid stationary phase is adsorbed. Therefore, these columns are also known as support-coated open tubular columns.
2. *Support-coated open tubular columns*: Support-coated open tubular columns are usually coated with layer of the support material having micron size. This layer is further coated by the thin film of immobilized liquid stationary phase. These types of columns usually have more capacity for sample as compared to that of wall-coated open tubular columns.

15.4.2.3 Factors Affecting on Column Efficacy

Following are the important factors that may influence the overall efficacy of the column:

1. *Column breakage*: This column may break due to many reasons such as if coating of the column is done by the weak coating material or may be coating is not done properly. Due to variation in the temperature of the column which may increase or decrease depending upon the conditions is also a reason for column breakage. If the diameter of the column is large then breakage may occur due to this reason.

2. *Thermal damage*: Higher temperature of the column during heating may also cause the degradation of stationary phase. Due to presence of oxygen during the whole operation thermal degradation may be increased. Similarly, the presence of chemical compounds, such as non-volatile compounds, acids (HCl, H_2SO_4, HNO_3), bases (KOH, NaOH), organic compounds (perfluoro acids), may also damage the column.
3. *Column contamination*: It may be either because of the non-volatile or semi-volatile contaminants.

15.4.3 Temperature Programmer

The column of GLC is interposed in the thermostatic oven. It is temperature-controlled device which monitors and regulates the overall temperature of the column. It is recommended to use thermostatically controlled oven for efficient separation. Sometimes, preheaters are also used to convert the sample into its vapor form. These preheaters are present along with injecting devices. There are two main types of temperature programmers which as follows:

1. *Isothermal programming*: During the whole experiment, the temperature is kept constant.
2. *Gradient programming*: During the whole experiment, the temperature varies. In this case temperature may be increased or decreased depending upon the conditions.

15.4.3.1 Factors Affecting on Temperature Programming

During the operation of GC, temperature programming should be performed. The factors that affect the temperature programming are of the following:

1. *Flow rate of the mobile phase*: It affects the elution rates of the components of interest present in sample. When the flow rate of mobile phase in the column is high, then components remain for the shorter period of time in column as a result broadening the peak.
2. *Stability of the stationary phase*: If the sample shows the solubility within stationary phase, then residential time of sample in column is increased and better results can be achieved.
3. *Stability and solubility of analyte*: Temperature affects the stability and solubility of analyte. If the temperature increases, the solubility of the gas in liquid decreases and it reduces the retention time of the sample in the column.
4. *Volatility of analyte*: If the sample evaporates rapidly by applying the heat, then components of the sample are eluted rapidly.

15.4.4 Sample Injector

The sample is injected into the carrier gas flow to the column of HPLC by using sample injector. For the analysis of the gaseous samples, mostly rotary valve is used. This rotary valve is mostly used in gas chromatography but volume of sample is kept small than used in HPLC. In the case of the liquid sample, the sample is introduced into the heated lash by using the gas syringe. The sample evaporated and the carrier gas is responsible for the transferring of the vaporized sample from the injection site to the column. In the case of the solid samples, the sample is initially heated at a high temperature for the volatilization of the sample. As a result, the sample is converted into the volatile derivatives substances.

15.4.5 Detectors

There are many types of detectors which can be used in gas chromatography. Detectors can be grouped into the following two main types:

1. *Concentration-dependent detectors*: The signal detected by a concentration-dependent detector is directly related to the amount of solute in the detector. This type of detector cannot cause the destruction of the sample. The detector response may be lower due to dilution with make-up gas.
2. *Mass flow-dependent detectors*: This type of detectors mostly destroy the sample. The rate at which solute components enter into the detector affects the signals. The make-up gas has no influence on the efficiency of mass flow-dependent detectors.

Different kinds of detectors exhibit the different level of selectivity. The non-selective type of detectors can respond to all types of the components of the sample mixture except for the carrier gas. The selective type of detectors responds to a wide range of compounds having common physical characteristics. Wide range of detectors are used in gas chromatography, the most commonly used detectors are as follows:

1. *Flame ionization detector (FID)*: It is highly sensitive detector. Two different kinds of gases are placed in the cylinder, which are used for the ignition of the flame. The effluent of the column is directed towards the flame and the potential difference is detected.
2. *Thermal conductivity detector (TCD)*: This detector contains the heated filament. When the carrier gas is passed through the cell, change in the filament current which is compared with the reference cell. Due to difference in current a signal is produced.
3. *Electron capture detector (ECD)*: It specifically detects the halogen containing compound. The sample is ionized due to radioactive material. This ionization current is quenched by the compounds containing halogen compounds.

4. *Nitrogen-phosphorus detector*: This is used for the detection of the compounds having nitrogen and phosphorus. Its principle is same as flame ionization detectors.
5. *Flame photometric detector (FPD)*: It is used for the detection of the sulfur and phosphorus. The eluent is passed through the flame as a result excited species are formed and the light is produced in the flame.
6. *Photo-ionization detector (PID)*: This type of detector is used for the detection of the aromatic compounds. The eluted molecules are photoionized by the ultraviolet radiation. The compounds that have low ionization energy are detected.

15.4.6 Recorder and Read-Out Device

Signals for separated fractions of vaporized components, received from the detectors are recorded by recorder and read-out device interpret the input responses received from detector into results.

15.4.6.1 Features of Detectors

Following are the ideal characteristics of the detector:

1. It should be easily handled easily.
2. The decomposition of the sample may not occur due to the detectors.
3. It can measure the wide range of temperature.
4. The sensitivity and reproducibility of the detectors must be high.
5. The detectors must have high stability.
6. It should not produce noise.
7. Small volume of the sample can be used in order to avoid peak broadening.

15.5 Factors Affecting on Gas Chromatography

1. *Volatility of compounds*: The components of the sample that have low boiling point will travel faster than the compounds having high boiling components through the column.
2. *Polarity of the compounds*: If the polar column is used, then the components of the sample that are polar in nature will move more slowly and vice versa.
3. *Column temperature*: If the temperature is increased, then the components of the sample will eluted very rapidly.
4. *Column packing polarity*: All the components of the compounds will move slower in polar column as compared to that of non-polar column.
5. *Flow rate of mobile phase*: Speeding up the flow rate of mobile phase also increases the speed of all compounds to be moved with mobile phase.
6. *Length of column*: If the column have longer length then it will take longer time for elution of all the components present in mixture and as a result better will be the separation.

15.6 Advantages

1. This technique has strong power for the separation of even complex mixture that can be resolved into its constituents.
2. The method is highly sensitive.
3. Small sample is required for analysis.
4. It contains high sensitivity detector system.
5. It has good precision and accuracy.
6. The operation is completed in a very short interval of time.
7. Linearity is good.
8. The instrument cost is relatively low.
9. It has generally longer life.
10. The technique is relatively suitable for routine analysis.
11. Precision is high.
12. Easy to handle the equipment.

15.7 Disadvantages

1. Sensitivity is low.
2. Volatilization is required for the analysis and there may be a chance for the degradation of the sample.
3. It cannot be used for analysis of biological sample because of the high temperature of the column.

15.8 Applications

1. It is widely used for analysis of gaseous samples.
2. It is used for the estimation of amount of CO_2 present in the fuel gases.
3. It is used for the estimation of organometallics.
4. It is used for the estrogens analysis.
5. In pharmaceutical industry, it is widely used for the analysis of the following drugs:
   a. Anti-tuberculosis drugs.
   b. Antibiotics.
   c. Antiviral drugs.
   d. Anti-neoplastic agents.
   e. Ointments.
   f. Anticonvulsants.
   g. Steroids.
6. In food industry, it is also used for the analysis of dairy products.
7. It is used for the determination of pesticides in aquaculture products.
8. It is used for the diagnosis of certain diseases like cancer.
9. It is used for the analysis of plant-based bioactive compounds and essential oils.
10. It is used for the detection of narcotics and alcohols in blood.

Further Reading

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