

# Stationary phase in gas chromatography engineering essay



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Stationary phase in Gas Chromatography (GC) is the part of the chromatographic system where the mobile phase will flow and distribute the solutes between the phases. Stationary phase plays a vital role in determining the selectivity and retention of solutes in a mixture. There are two major types of GC which are gas-solid chromatography and gas-liquid chromatography.

In gas-solid chromatography, same material is used as both the stationary phase and support material. The common adsorbents used include alumina, molecular sieve such as zeolite and clay, silica and active carbon. In gas-liquid chromatography, the stationary phase is a liquid which is immobilized or adsorbed on a solid support material such as silica particles. The material of stationary phase ranges from polymers such as polysiloxanes, polyesters, polyethylene glycols to fluorocarbons, and liquid crystals. In addition, the stationary phase may consist of either porous particles, solid particles or a fibrous material such as paper.

There are various types of stationary phases available because the choice of stationary phase being the most suitable one depends on the polarity of components. The primary rule of separation is "like dissolves like" where non-polar analytes will partition strongly into non-polar stationary phases and polar analytes partition into polar phases.

Polysiloxanes, for instance are the most common stationary phases. They possess the greatest variety and are stable, robust and versatile. Besides that, they can resist oxidation and offer high solute diffusivities into the polymer coupled with excellent chemical and thermal stability. 100% methyl

substituted is the most basic polysiloxane being used and is non polar. The diagram below shows the basic structure of 100% dimethyl substituted polysiloxane.

Because a variety of groups can be incorporated into the structure, polysiloxane exhibit a wide range of polarities ranging from non polar to polar. This can be done by replacing the methyl groups with other functional groups in the polymer structure. The structure below is a general representation of substituted polysiloxane.

The R groups can be methyl(-CH<sub>3</sub>), phenyl(-C<sub>6</sub>H<sub>5</sub>), trifluoropropyl(-CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>) or cyanopropyl(-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN). X and Y indicate the percentage of an aggregate in the overall polymeric stationary phase composition. The increase in the percentage of substitution of these polar groups increases the polarity of the liquid phase to various degree.

For instance, 5% diphenyl-95% dimethyl polysiloxane.

In this structure, R<sub>1</sub> and R<sub>2</sub> are phenyl groups and R<sub>3</sub> and R<sub>4</sub> are methyl groups. M and N have the value of 5% and 95% respectively.

Table below shows some of the common stationary phases used in gas-liquid chromatography.

## **Stationary Phase**

### **Common Trade Name**

### **Temperature**

### **İŞC**

### **Applications**

Polydimethyl siloxane

OV-1, SE-30

350

hydrocarbons, drugs, steroids

Poly(phenylmethyldimethyl)

siloxane (10% phenyl)

OV-3, SE-52

350

Fatty acid methyl esters, alkaloids, drugs

Poly(phenylmethyl) siloxane (50% phenyl)

OV-17

250

Drugs, steroids, pesticides, glycols

Poly(trifluoropropyldimethyl)

siloxane

OV-210

200

Chlorinated aromatics, nitroaromatics, alkyl substituted benzene

Methyl-5% phenyl polysiloxane

SE-54, OV-23, DB-5, SPB-5, BP-5, HP-5, ULTRA 2, RTx-5, CPSil-8

50-325

Similar to methyl polysiloxane. Slightly more selective due to phenyl content.

Excellent thermal stability.

Methyl 50% Phenyl Polysiloxane

OV-17, DB-17, SPB-7, BP-10, HP-17, RTx-17, AT-50,

40-325

Added selectivity-higher phenyl content. Retains similar compounds longer than methyl silicone. Efficient separations of drugs, sugars and steroids.

Good thermal stability.

6% Cyanopropylphenyl 94% Methylpolysiloxane

DB-1301, RTx-1301, HP-1301

30-320

Selectivity for polarizable and polar compounds. Exhibits less retention of polyaromatic compounds. Good thermal stability.

Methyl 7% Cyanopropyl 7% Phenyl Polysiloxane

DB-1701, CPSil-19, RTx-1701, AT-1701

280

Unique selectivity of cyanopropyl and phenyl groups. Not truly a polar phase. Good thermal stability

Methyl 25% Cyanopropyl 25% Phenyl Polyciloxane

DB-255, HP-255, CPSil-43, RTx-225, AT-255

40-240

Polar phase. Efficient separations of fatty acids and alditol acetate derivatives of sugars. Fair thermal stability

Silicone Oil

DC-550

180-200

Moderately polar substrate, used for alkylbenzenes and naphthalene homologs

Silicone Gum Rubber

SE-30

400

Non polar, for highest temperature work. Used for steroids and polycyclic aromatics

For polydimethyl siloxane, the -R groups are all hydrophobic giving liquid the least polarity and has the following general structure.

Poly(cyanopropylphenyldimethyl) siloxanes are another polar stationary phases. They are used in separating compounds which contain several hydroxyl groups such as steroids.

Another type of stationary phase is polyethylene glycols (PEGs) which is shown below.

This stationary phase is non-silicon-containing stationary phase and is most widely used after siloxanes in the analysis of polar solutes. They are moderately polar and was considered the most polar stationary phase available due to the difficulty in coating and cross-linking of polar siloxane on the stationary phase. Besides, they are well known for their unique selectivity and high polarity as a liquid phase. The polyethylene backbone of these columns is different than polysiloxane phases. Strong polar dispersive interaction in the phase is imparted by the oxygen group in the polymer backbone. It also provides a very strong dipole interaction as the phase itself is capable of hydrogen bonding which is the bonding between a strong polar

group (OH, NH) and a compound with strong electronegativity (F, O, N)]. Stationary phases with “ wax” or “ FFAP” in their names also belong to polyethylene glycol. Polyethylene glycols stationary phases have 100% of the stated material because they are not substituted. They have several disadvantages such as less stable, less robust and limited maximum temperature compared to most siloxanes. In addition, they exhibit shorter lifetimes and have high susceptibility to damage upon over-heating or exposure to oxygen. However, the unique separation properties of polyethylene glycol have made these liabilities tolerable. Also, cross-linked PEG phase is able to overcome these deficiencies. Under GC temperature condition, PEG stationary phases must be liquids. For example, alcohols, ethers, aldehydes and other compounds with low boiling points can be separated by a suitable sorbent called PEG 400. Carbowax 20M can be used for the separation of polar compounds with higher boiling points. Other polar compounds such as amino alcohols, hydroxyl acids, dibasic acids, amines, nitrile, fatty acids, fatty acid methyl esters (FAMES), aromatic volatile compounds, and nitrosamines can also be separated using PEG columns.

Arylene-modified polysiloxanes are also known as aryl-poly or arylene stationary phase. They are similar to standard polysiloxane except having phenyl groups in the polymer backbone. This stationary phase has several advantages including lower column bleed and higher temperature limits than their polysiloxane counterparts.

Diagram 1 : Structure of arylene-modified polysiloxane



In order to prevent column bleed during GC analysis, most of the stationary phases used today are of arylene-modified polysiloxane. These stationary phases have been designed to be equivalent to a familiar stationary phase such as 5% phenylmethyl polysiloxane (BD-5ms and DB-5). They have slight differences although both the stationary phases have similar separation characteristics.

Chiral stationary phases are also used in Gas Chromatography analysis.

These stationary phases are typically used to separate individual enantiomers, stereoisomers which only differ in the spatial arrangement of their atoms and in their ability to rotate the plane of polarized light.

Separation of two substances can only occur when their standard energy of distribution differ, which means that their standard enthalpies and/or their standard entropies of distribution also differ. In general, the standard enthalpy indicates the difference in the interactive forces such as polar, dispersive and ionic interactive on the molecule in the two phases whereas the standard entropy indicates their spatial disposition. Hence, to separate chiral solutes, the stationary phase chosen must differ significantly in the spatial arrangement of its composite atoms results in the probability or proximity of interaction between the two enantiomers to be separated. Many chiral compounds are used in the preparation of chiral stationary phase (CSP). Cyclodextrin (CD) and their derivatives are the most commonly used chiral compounds. Cyclodextrin is a cyclic oligomer substituted into a conventional siloxane stationary phase. A strong interaction with the cavity in the CD is achieved when organic molecules of correct size and shape are present. Hence, these organic molecules will be more strongly retained on

the capillary column. Furthermore, modified CDs are used since they are capable of resolving chiral solutes over a high range of GC temperatures. Chiral stationary phase plays a vital role in separation especially in pharmaceutical industry because pharmaceutical compounds usually exist as enantiomers. Some rough estimations about the target compounds that are generally well dissolved into their enantiomers by using specific chiral stationary phase are illustrated below.

## **Product Name**

### **Stationary Phase**

#### **Analytes**

Cyclodextrin E

2, 6-Pentyl-3-Butyryl-gamma-Cyclodextrin

oxygenated terpenes, alcohols, epoxides

Cyclodextrin G

6-Methyl-2, 3-Pentyl-gamma-Cyclodextrin

monoterpene hydrocarbons, volatile/low temperature

Cyclodextrin H

2, 6-Methyl-3-Pentyl-gamma-Cyclodextrin

terpenes, alcohols, alkenes

Cyclodextrin 3P

2, 6-Methyl-3-Pentyl-beta-Cyclodextrin

terpenes, alcohols, alkenes

Cyclodextrin TM

6-TBDMS-2, 3-Methyl-beta-Cyclodextrin

PCB, polycyclic or chlorinated aromatics, pesticides

Cyclodextrin TE

6-TBDMS-2, 3-Ethyl-beta-Cyclodextrin

pharmacopeia separations of essential oils

Cyclodextrin TA

6-TBDMS-2, 3-Acetyl-beta-Cyclodextrin

oxygenated terpenes, aromatics, low volatile

Cyclodextrin PM

2, 3, 6-Methyl-beta-Cyclodextrin

legacy phase for many analytes

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In Gas Chromatography, there are generally two different types of column used which are packed columns and capillary columns.

Packed columns contain finely divided inert solid support material that is densely packed in the inside of the column in which the material is coated with a liquid stationary phase. This stationary phase is 3-10% by weight of the solid support and will form a thin liquid film on the surface of the material where the mobile phase will flow over and around the coated material as it travels down the column. The solid support material used is usually diatomaceous earth. To improve resolution and speed, the particles size should be small enough, ranging from less than 100-300mm and are uniform in size. Small size of particles is necessary as it increases the surface area for easier partition and separation of solutes. Besides that, the material should be inert to avoid any chemical reaction between the solutes and solid support material. However, packed columns have limited resolution where  $N < 8000$ .

Diagram 2 : Cross section of packed column

Solid support material

Packed columns are 1.5 - 10 m in length and have an internal diameter of 2 - 4 mm. They are normally constructed from stainless steel but can be glass such as Pyrex glass if a less reactive surface is desired. Pyrex glass is chosen when thermally labile solutes are being separated. Unfortunately, glass has pressure limitations and for long packed columns, stainless steel columns are chosen since they possess high pressure tolerance. The nature of the coating material which is the liquid stationary phase determines what type of solutes will be most strongly adsorbed onto it. Hence, various columns are available that are designed to separate specific types of compounds.

Open tubular columns or rather known as capillary columns are characterized by a small narrow opening in the centre of the column through which the mobile phase will travel as it moves past the stationary phase.

There is no packing of solid support material unlike packed columns.

Capillary column is constructed by fused silica which is a highly purified and inert material. There is a protective coating on the outside of the column, called polyamide that affords strength and flexibility in order to wind into small coil.

### Diagram 3 : Cross-section of capillary column

Capillary columns have a very small internal diameter, on the order of a few tenths of millimeters, are between 25-60 meters in length. Capillary columns can be divided into three classes which are wall-coated open tubular (WCOT) columns, support-coated open tubular (SCOT) columns and porous layer open tubular (PLOT) columns. For WCOT columns, the inner column walls are coated with a thin layer of liquid stationary phase. The thickness of liquid coating is 0.25 - 0.5  $\mu\text{m}$  thick leading to very fast and efficient separations (up to 300,000 plates). Other types of capillary columns exist with the stationary phase contained in different formats. These columns are typically efficient but they have a small sample capacity due to their low surface area. For SCOT columns, the inner wall of capillary columns are lined with approximately 30  $\mu\text{m}$  of a porous support material in order to allow a higher loading of stationary phase, resulting higher column capacity. Then, a thin film of liquid stationary phase is then coated on this layer of support material, providing SCOT columns a larger surface area. For PLOT columns,

they are similar to SCOT columns except solid support materials are  
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attached to the inner column wall where the particles themselves are the stationary phase. There support materials can be glass powder or microcrystalline materials rather than particulate support.

Diagram 4 : cross section of WCOT, SCOT and PLOT columns

Generally, capillary columns are favored over packed columns and WCOT columns are more efficient than SCOT columns in Gas Chromatography. The table below shows further comparison of capillary (WCOT) and packed columns.

## **Parameter**

### **Capillary Column**

### **Packed column**

Efficiency (plates/m)

> 100000

<8000

Sample size (ng)

10-75

10-1000000

Relative pressure

Low

High

<https://assignbuster.com/stationary-phase-in-gas-chromatography-engineering-essay/>

Relative speed

Fast

Slow

Chemical inertness

Best

Poorest

Column flexibility

Yes

No

Resolution

Good

Poor