Chem Factsheet

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Gas Chromatography

Gas chromatography (GC) is a routinely-used technique to separate and analyse mixtures of volatile and thermally-stable substances. Nowadays, it is more commonplace to use gas chromatography in conjunction with mass spectrometry (GC-MS) to yield structural data.

Gas chromatography is a form of **partition chromatography**.

All chromatographic techniques use:
1. A **mobile phase** - a gas or liquid, which transports the sample through the separating column
2. A **stationary phase** - tiny particles of an inert solid (e.g., silica) or an immobilised non-volatile liquid adsorbed to the surface of a solid support.

Partition-based chromatography uses:
1. A **gas or liquid** mobile phase
2. An **immobilised-liquid** stationary phase.

Partition relies on a substance having different **solubility** in the mobile and stationary phases. As the sample (X) flows through the separating column (see figure 1), substances can move from the mobile phase and into the stationary phase and vice-versa. A dynamic equilibrium is useful to understand what is happening:

$$\mathbf{X}_{(\text{mobile phase})} \rightleftharpoons \mathbf{X}_{(\text{stationary phase})} \quad \text{--- (1)}$$

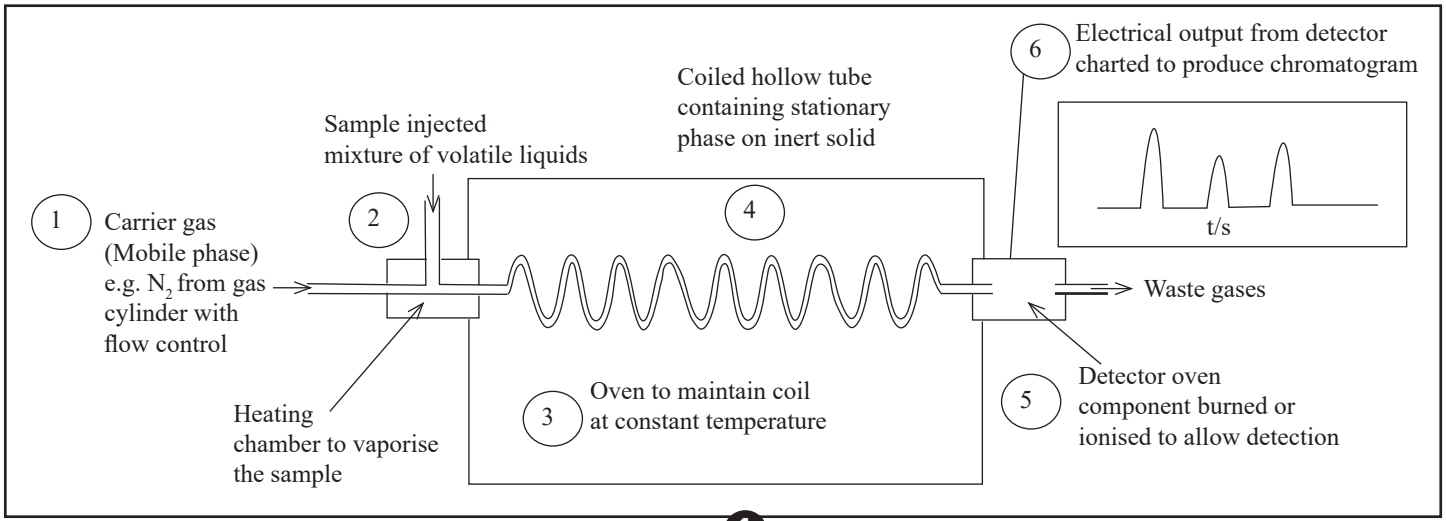
The distribution of substance X between two different solvents is termed **PARTITIONING**.

Separation of substances during chromatography occurs due to their different solubility in both phases:

More soluble in mobile phase	**More soluble in stationary phase**
Equilibrium (1) lies to the left	Equilibrium (1) lies to the right
Spends more time dissolved in the mobile phase	Spends more time dissolved in the stationary phase
Travels through column faster	Travels through column slower
Shorter retention time (R_t)	Longer retention time (R_t)
Tend to be smaller or polar substances	Tend to be larger or non-polar substances

In GC, separation of substances is related to how soluble they are in the stationary phase (as the mobile phase is a gas not a liquid) as well as how **volatile** the substance is. The more volatile a substance, the more likely it is to remain in the gas phase (rather than dissolve in or condense on to the stationary phase) and, thus, it will have a shorter retention time than less volatile substances.

Fig 1. Parts of the gas chromatograph



1. **Gas cylinder** – the mobile phase is typically an **inert gas such as nitrogen, helium or argon**. It is pushed through the chromatograph at pressure, carrying the vaporised sample with it.

2. **Sample injection port and vaporiser** – a small quantity of the mixture to be separated is injected into a vaporisation chamber. The individual substances in the sample are heated and turn into gases. These gases are then transported into the column by the inert gas carrier.

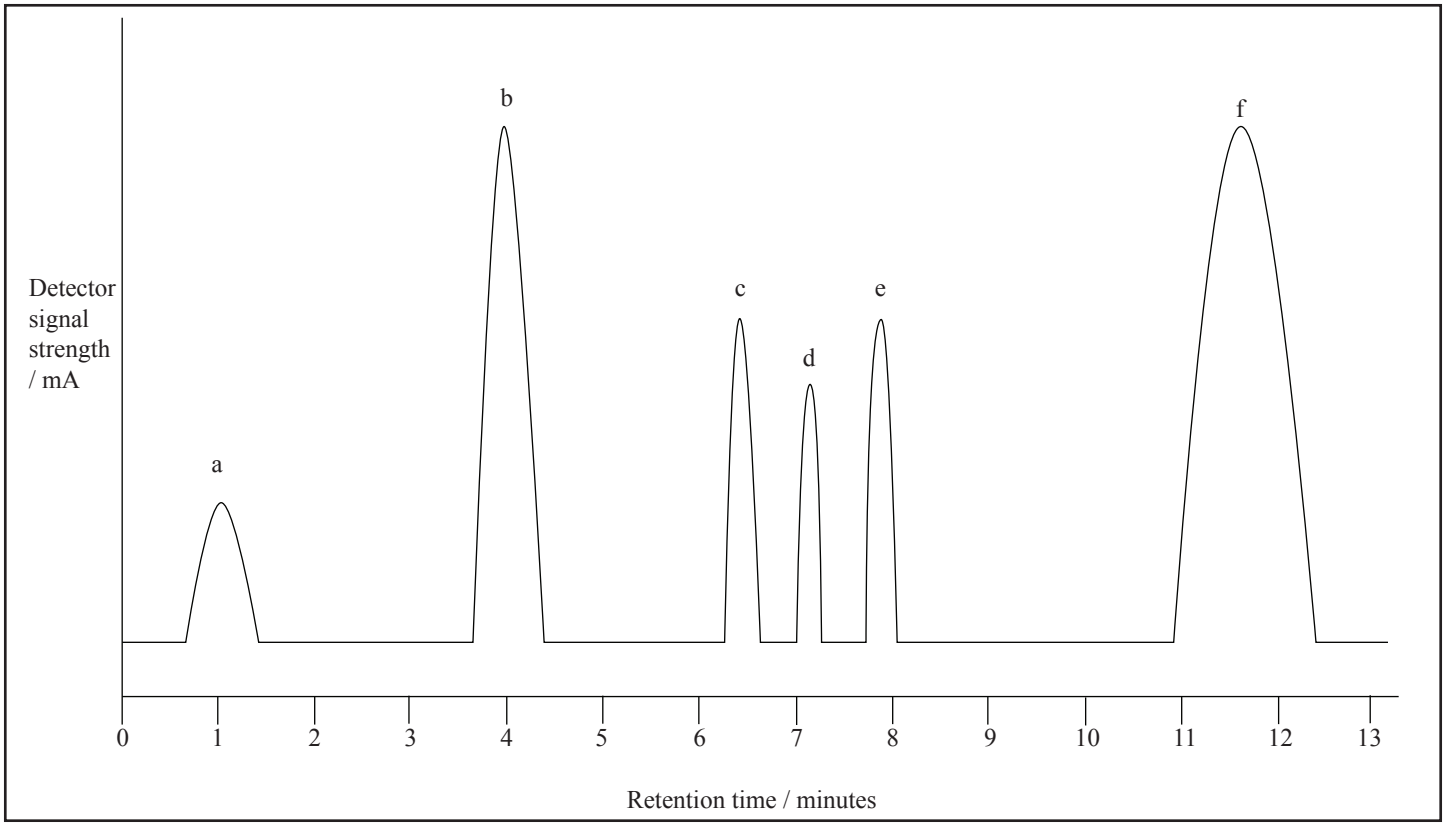
3. **Temperature-controlled oven** – depending on the nature of the sample, the temperature of the oven can be changed to ensure that the sample remains in the gas phase for the right amount of time. If the temperature is too high then substances remain gaseous and travel too quickly and are poorly separated; if it is too cool then the gases condense frequently and separation takes too long.

4. **Chromatography column** – typically the column used in GC is coiled to fit in the oven, has a very narrow bore (a few millimetres) and is extremely long (several metres), though these parameters can be varied. The column contains, for example, an immobilised long-chain alkane stationary phase attached to the surface of tiny silica particles. The longer the column, the better the separation.

5. **Detector** – there are many ways in which the eluted substances can be detected. These are some of the most common:
   a. **flame ionisation**: as the substances exit the column, they are burned in a very hot flame producing ions. The charged particles created increase the electrical conductivity of the gases exiting and this change in conductivity is recorded against the time elapsed.
   b. **thermal conductivity**: as substances exit the column the thermal conductivity of the gas decreases (gases such as helium have relatively high thermal conductivity). This drop in conductivity causes a probe to heat up and this change in temperature can be detected.
   c. **mass spectrometry**: each substance is carried directly into a mass spectrometer as it exits the column. This technique is very powerful as each eluted substance is then assigned its own mass spectrum from which structural details can be determined or identified by comparison with a database of known spectra.

6. **Recorder** – signals from the detector are amplified and recorded by a computer as a function of the time elapsed. A typical chromatogram is shown in figure 2.

Fig. 2 A typical gas chromatogram



The area under each peak in a chromatogram provides a relative measure of the quantities /concentrations of the substances present in the sample. More precise quantification can be achieved by injecting a sample of known concentration; this serves as a standard against which other substances can be measured.

Retention times can be used to determine the identities of the substances in the sample, but these vary depending on the column used, oven temperature, flow rate of gas, etc. A series of samples of known substances can be run under identical conditions to the unknown sample and retention times can be compared. However, the use of GC-MS largely makes this redundant as spectral analysis alone may be adequate to determine the identity of a substance.

Uses of Gas Chromatography

Among many others, these are some of the common applications for GC and GC-MS:

1. Detection of volatile substances in body fluids, e.g., alcohol, banned drugs.
2. Analysis of mixtures used in the cosmetics industry.
3. Analysis of food samples.
4. Analysis of air samples to check air quality.
5. Forensic and toxicological analysis.
6. Analysis of crude oil and natural gas.

Advantages and disadvantages of gas chromatography

ADVANTAGES	DISADVANTAGES
Very sensitive – only tiny quantities of sample needed	Many substances are not thermally stable or volatile enough to be analysed
Fast method – detection and analysis occurs in minutes	Cannot be used with ionic or highly polar substances
Quantitative – using appropriate standards	Expensive to purchase and maintain
Structure determination – using GC-MS	Requires training to use
High resolution - excellent separation of similar compounds	Some methods of detection (e.g., flame ionisation) destroy the sample
Wide range of applications	

Questions

1. Use Figure 2 to answer the following questions:
   a. which peak represents the substance present at the highest concentration in the original sample?
   b. which peak is most likely to represent the most volatile substance?
   c. which peak is most likely to represent the most polar molecule?

2. Briefly outline the technique of gas chromatography.

3. State and explain which, if any, of the following chemical analyses would be best suited to gas chromatography:
   (i) determining the concentration of Fe^{2+} ions in a sample of rust-contaminated water.
   (ii) determining the concentration of an anabolic steroid in an athlete's urine several weeks after it was administered.
   (iii) determining the concentrations of harmful gases present at the deepest point of a coal mine.

4. Suggest **two** ways in which the separation of substances using gas chromatography might be enhanced.

Answers

1 (a) f (b) a (c) a

2. Sample is injected and vaporised
   Vaporised sample carried through column by inert gas carrier/ mobile phase
   Inert gas such as helium, argon or nitrogen
   Column is held in a temperature-controlled oven
   Substances in sample separate due to different volatility/solubility in stationary phase
   Substances reach detector at end of the column
   Detected by flame ionisation/thermal conductivity/mass spectrometry…
   Measured signal recorded by computer as a function of time
   Least soluble/most volatile substances are detected first/shortest retention time
   Most soluble/least volatile detected last/longest retention time

3. (i) not suitable – detection of ions.
   (ii) suitable – steroids are volatile and stable enough to be heated. Detection of trace quantities remaining after several weeks requires a very sensitive technique such as GC.
   (iii) suitable – gases can be injected directly into chromatograph. Separation occurs due to different solubility in stationary phase/ volatility.

4. Column length increased.
   Temperature of oven changed.
   Flow rate of inert gas carrier changed.
   Packing material of column changed / different stationary phase.

Acknowledgements: *This Factsheet was researched and written by* ***Dr Chris Martin. Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. Chemistry Factsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***