Quantitative Methods in Chemistry

Week 8, Lecture 2

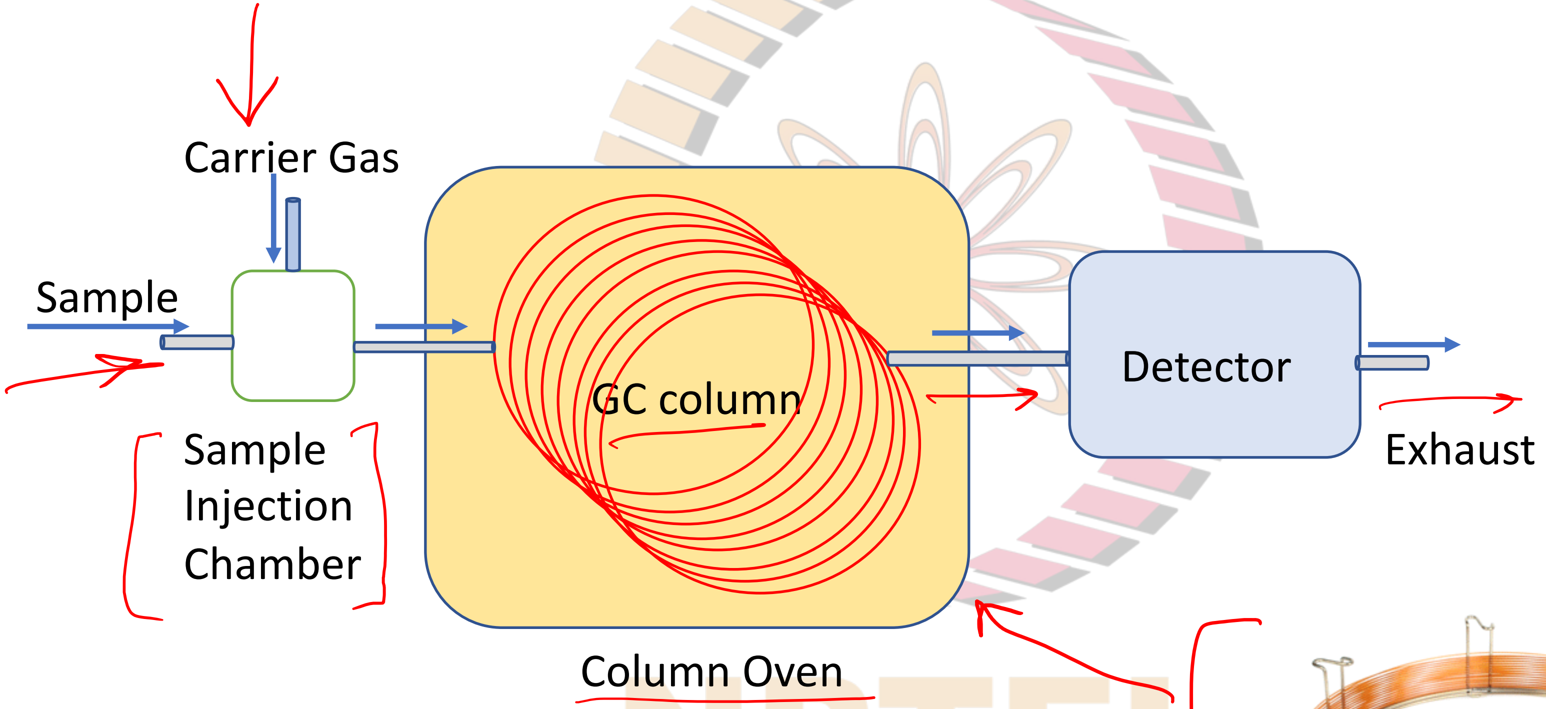
This week: Practice of Chromatography – HPLC, Gas Chromatography, Supercritical Fluid Chromatography, Detectors for analytes

This lecture: Practice of chromatography – Gas Chromatography: Principles and applications

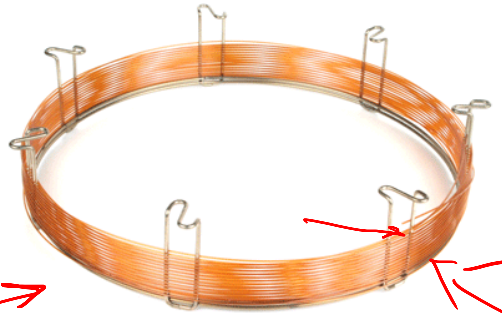
Gas Chromatography principle

- Concept first given by Martin and Synge in 1941
- Applicable only for analytes that can be easily vaporized without degradation
- For non-volatile compounds chemical functionalization may be needed
- Typically, low MW compounds are analyzed by Gas Chromatography
- Analyte is vaporized and injected into the column kept at a high temperature
- Mobile phase is a carrier gas that is non reactive. Common examples are N_2, CO_2, Ar, He.
- Mobile phase does not interact with the analyte. It only carries/ transports it through the column.
- An analyte with higher vapor pressure will move much farther than the analyte with lower vapor pressure.

Line diagram of the GC system



GC columns can be 25-100 m long!



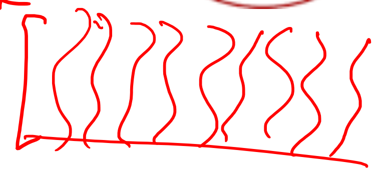
A picture of a real uninstalled GC column

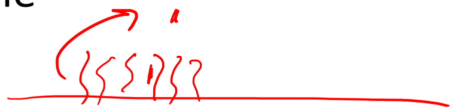
Types of Gas Chromatography

Gas-Liquid Chromatography aka Gas-Liquid Partition Chromatography (GLPC) –If the stationary phase is "liquid" and the mobile phase is gaseous.

Example of GLC is when fused silica or quartz columns coated with PDMS (polydimethyl siloxane) or methoxy-polyethyleneglycol (Carbowax) are used for separating the analytes. Thickness of the film is an important criteria for separations and may vary from 0.1 – 5 um.

thick





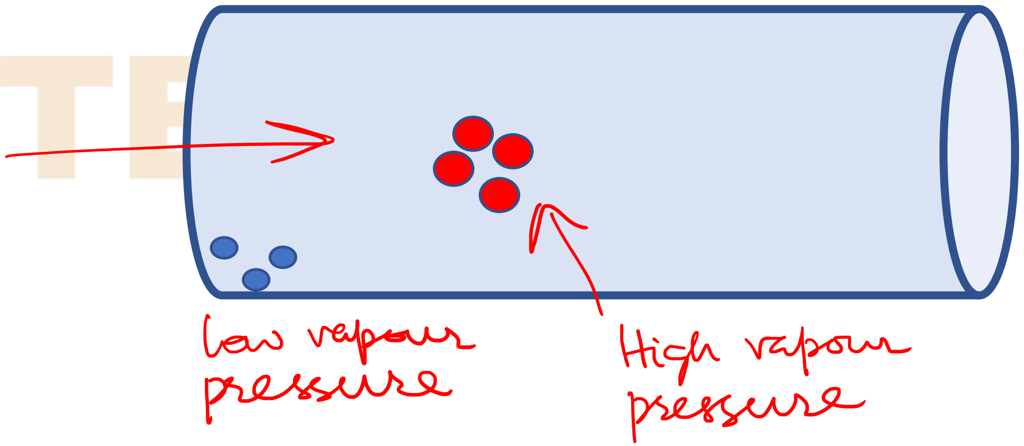
Very fast elution of analyte with high Vapour pressure

Gas-Solid Chromatography – If the stationary phase is a porous solid e.g. Diatomaceous earth or molecular sieves, and the mobile phase is gaseous. The stationary phase may be packed into the column or coated on the walls of the column.

Physical adsorption of the analyte may sometime occur on the solid phase, resulting in contamination of the column. The stationary phase may also catalyze reactions at high temperatures at which GC is undertaken.

Temperature programming in GC

- Isothermal elution in GC are analogous to isocratic elution in LC – the late peaks exhibit poor resolution and the high boiling analytes may not elute out at all!
- A Programmed Temperature GC (PTGC) is analogous to the change of composition of the mobile phase during gradient LC.
- Temperature ramps from RT to 350 ℃ are usual.
- Alters the vapor pressure of the solute in the column.
- Influences the diffusion coefficient of the solute in the mobile phase.
- Alters the movement of the solute within the column.

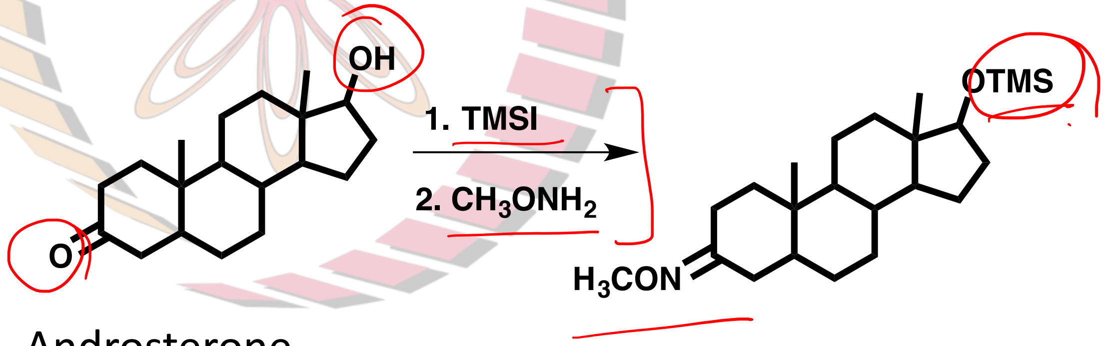


Chemical derivatization to improve GC chromatogram

Is a chemical reaction between the analyte and derivatizing reagent to produce a new compound with improved flow profile in GC.

Following derivatizations are routinely undertaken:

- Silylations
- Acylations
- Alkylations



Androsterone

Poor GC profile
(Poor peak shape
and poor separation)

Improved GC profile
(Increased separation,
better peak shape and
detector response)

Use of Open Tubular Columns in GC

Open Tubular columns are hollow tubes

The mobile phase can **travel uninterrupted** through the open tubular columns.

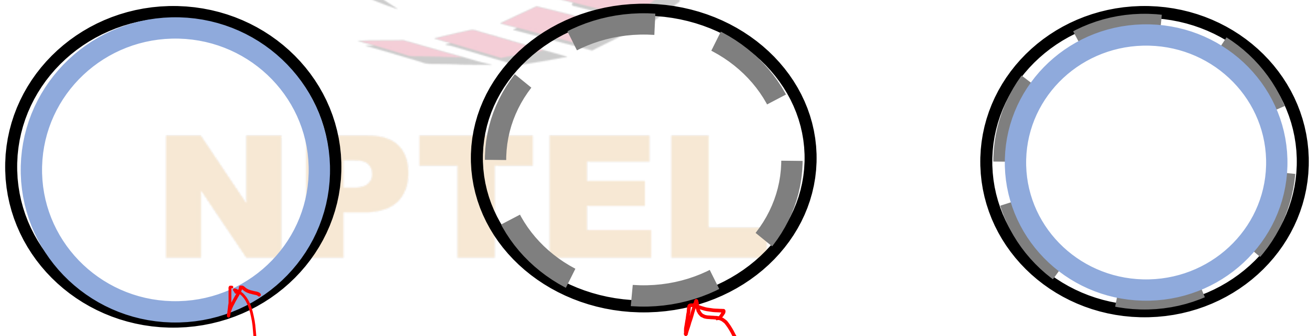
This makes the **A-term** (eddy diffusion term) of van Deemter equation become **zero** for open tubular columns and reduce the plate height.

Uninterrupted travel of the mobile phase results in almost **no pressure drops** even in the extremely long GC columns!

Open tubular columns provide much **better efficiencies** than the packed columns and are also more **chemically-inert**.

Types of Open Tubular Columns

1. **Wall Coated Open Tubular** (WCOT) – the capillary wall is coated with the stationary phase.
2. **Porous Layer Open Tubular** (PLOT) – the capillary wall is coated with porous solid material.
3. **Support-Coated Open Tubular** (SCOT) – the capillary wall is coated with a porous solid support followed by attachment of the liquid stationary phase onto it.
4. **Fused Silica Open Tubular** (FSOT) – The capillary is made from fused silica to provide mechanical strength and chemical inertness. A polyimide coating reduces the formation of moisture-induced stress regions during drawing of these capillaries.



WCOT
Liquid layer coated on wall

PLOT
Layer of Porous solid on the wall

SCOT
Contains porous solid layer and waxy liquid layer

Typical Chromatographic Parameters for GC

Parameter	HPLC (5 um particles)	GLPC (Capillary)
Column length L	~ 0.12 m	100
No. of plates (N)	~6000	300,000
Plate height (H)	~0.002 cm	~0.03 cm
Flow rates (u)	0.02 cm/s	2.0 cm/s
No. of plates per meter	~48,000	3000