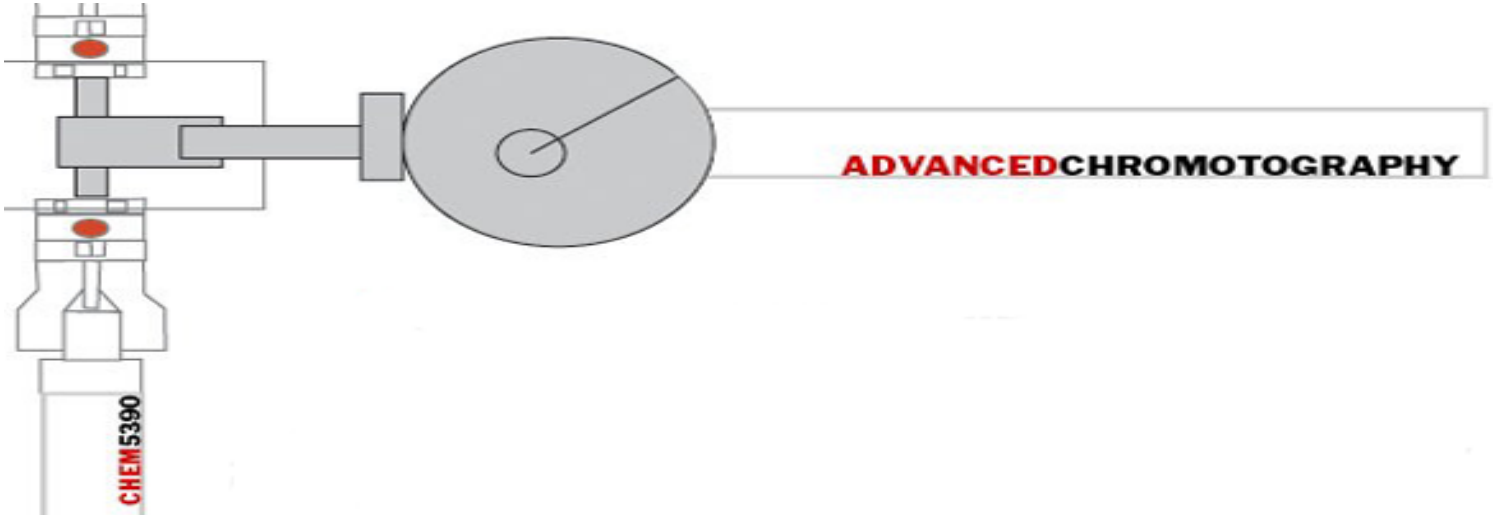
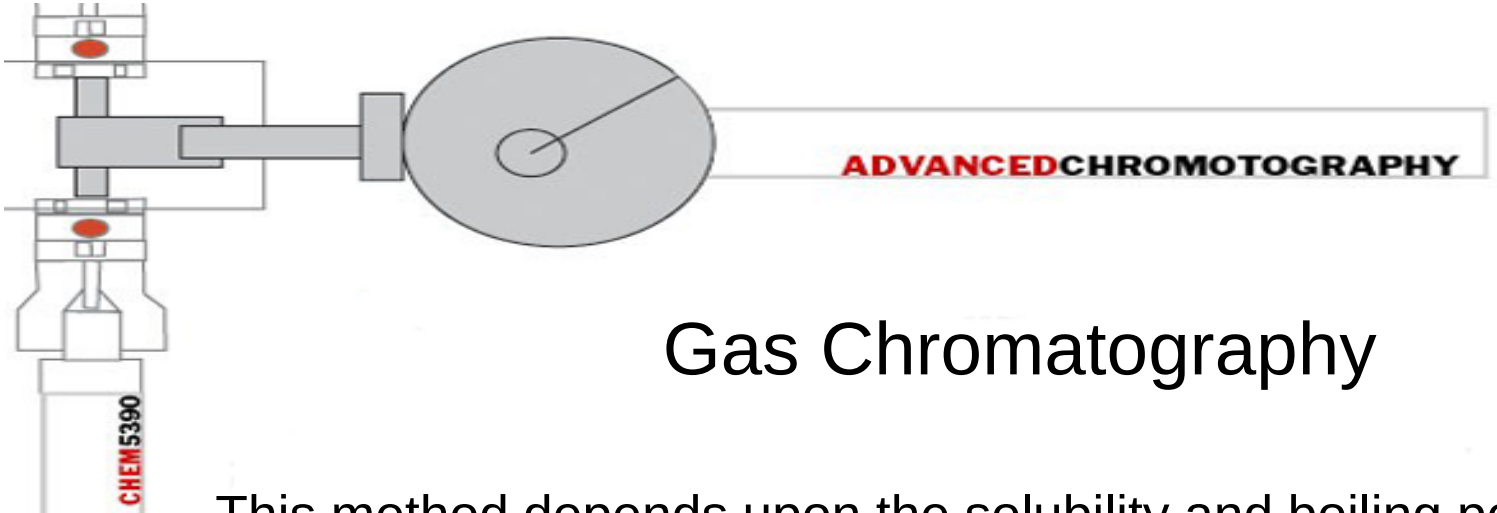


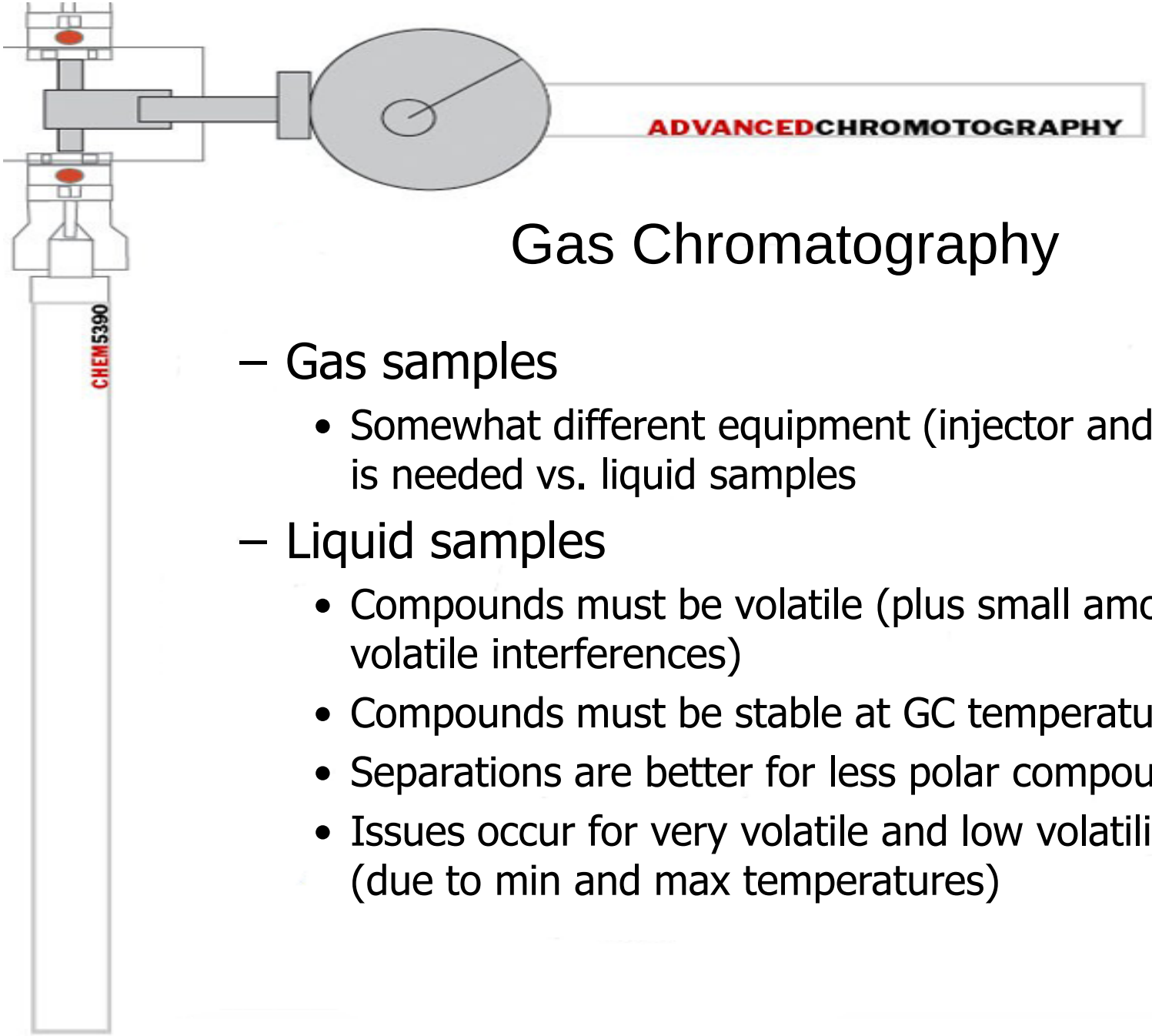
Lecture 4: Gas Chromatography Intro and Mobile Phase



Gas Chromatography

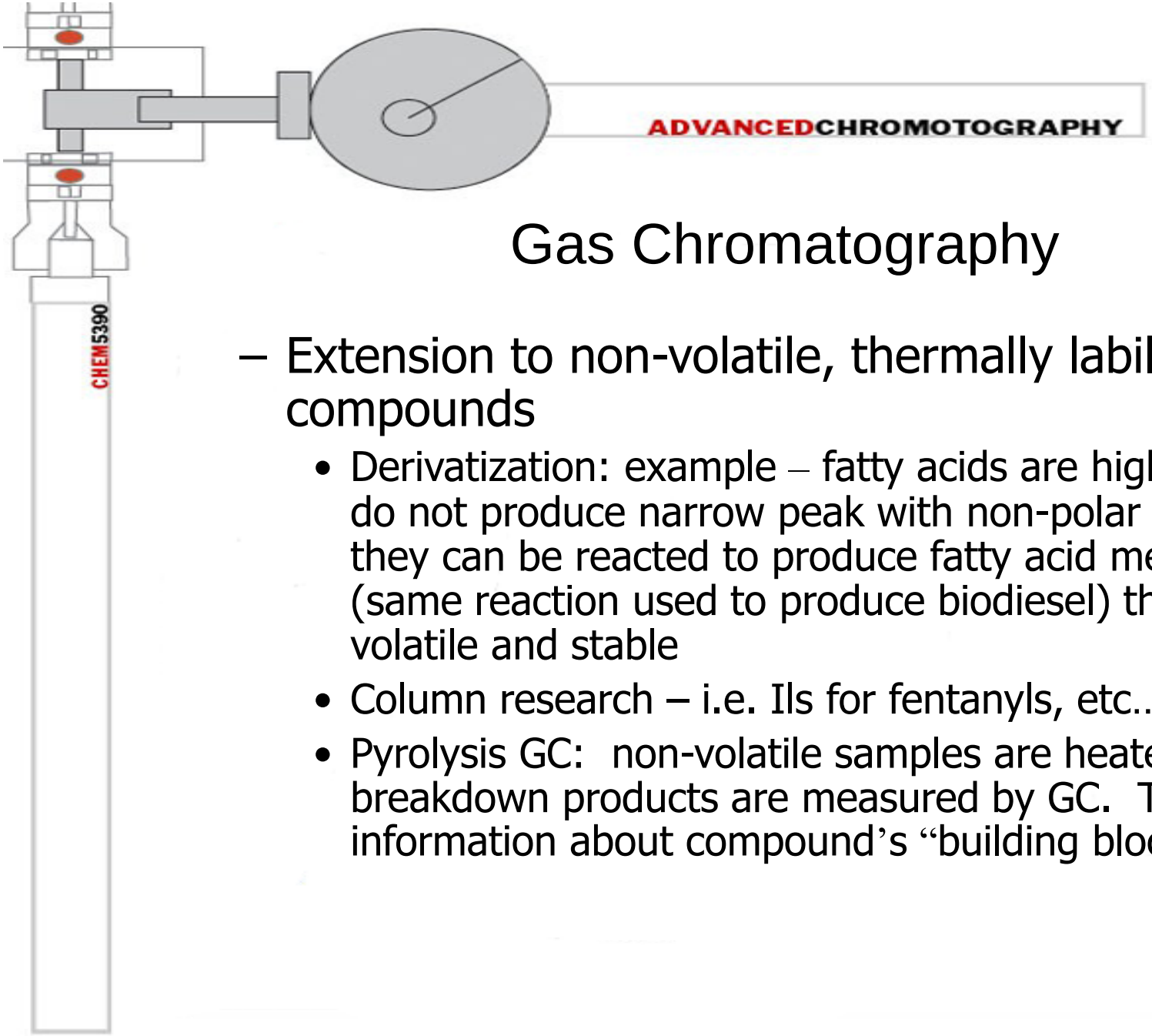
This method depends upon the solubility and boiling points of organic liquids in order to separate them from a mixture.

It is both a qualitative (identity) and quantitative (how much of each) tool.



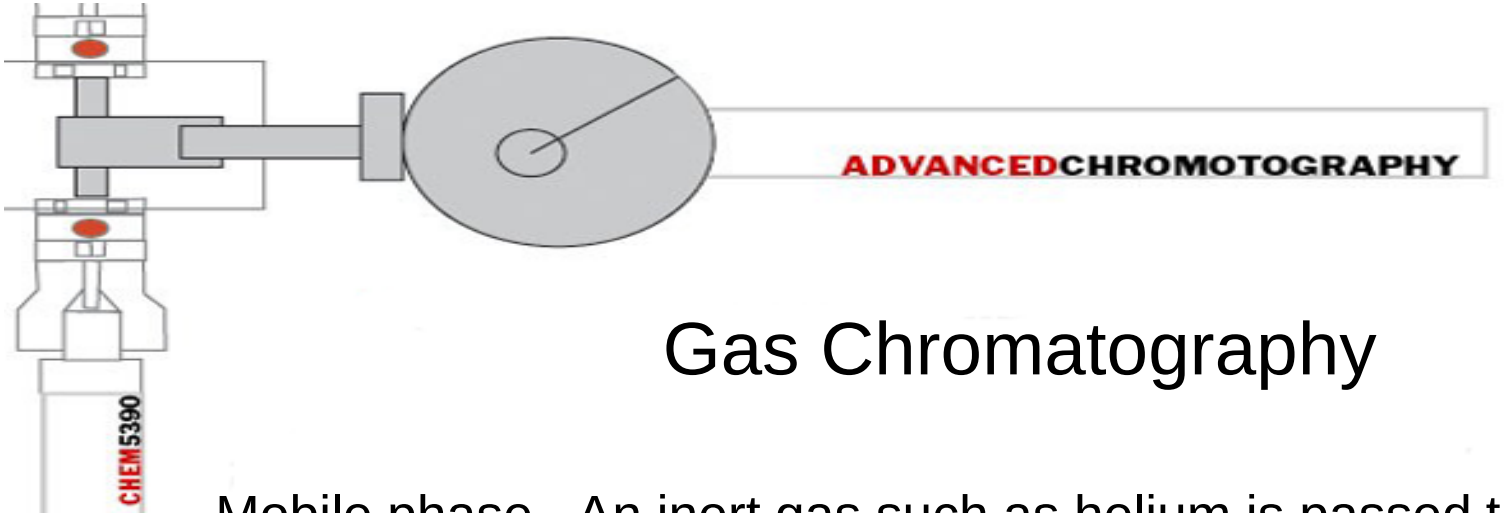
Gas Chromatography

- Gas samples
  - Somewhat different equipment (injector and oven range) is needed vs. liquid samples
- Liquid samples
  - Compounds must be volatile (plus small amounts of non-volatile interferences)
  - Compounds must be stable at GC temperatures
  - Separations are better for less polar compounds
  - Issues occur for very volatile and low volatility samples (due to min and max temperatures)



Gas Chromatography

- Extension to non-volatile, thermally labile compounds
  - Derivatization: example – fatty acids are highly polar and do not produce narrow peak with non-polar columns, but they can be reacted to produce fatty acid methyl ester (same reaction used to produce biodiesel) that are volatile and stable
  - Column research – i.e. Ils for fentanyls, etc…
  - Pyrolysis GC: non-volatile samples are heated and breakdown products are measured by GC. This give information about compound's "building blocks"

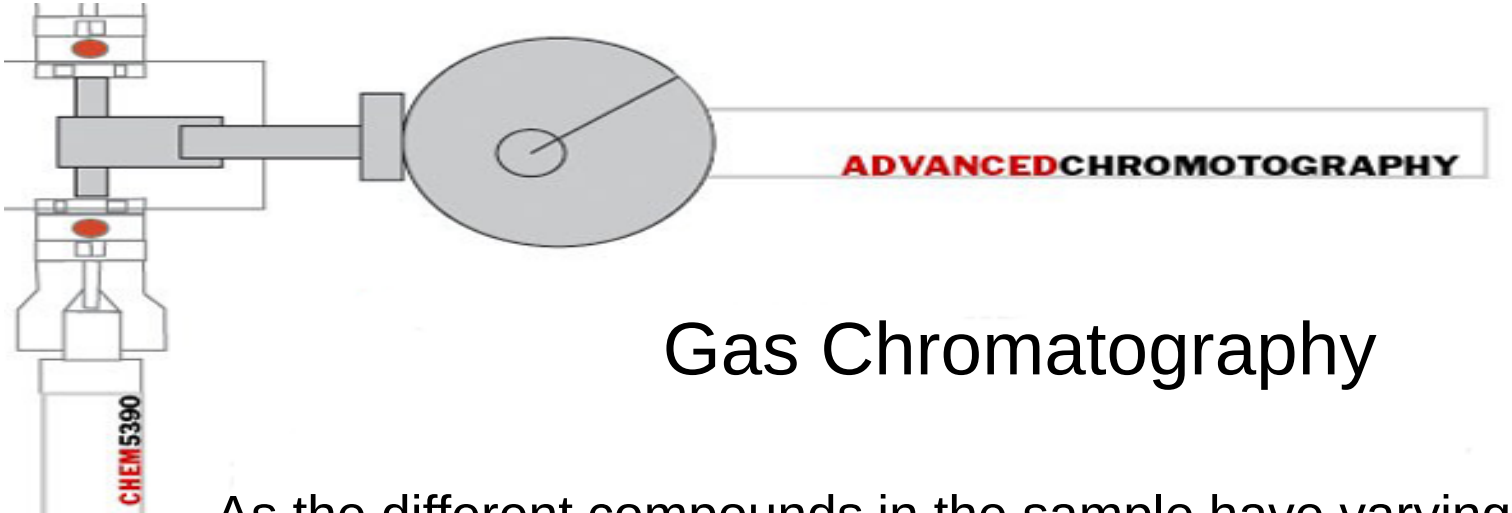


Gas Chromatography

Mobile phase - An inert gas such as helium is passed through the column as a carrier gas.

A sample is injected into a port which is much hotter than the column and is vaporized.

The gaseous sample mixes with the mobile phase and begins to travel with the carrier gas through the column.



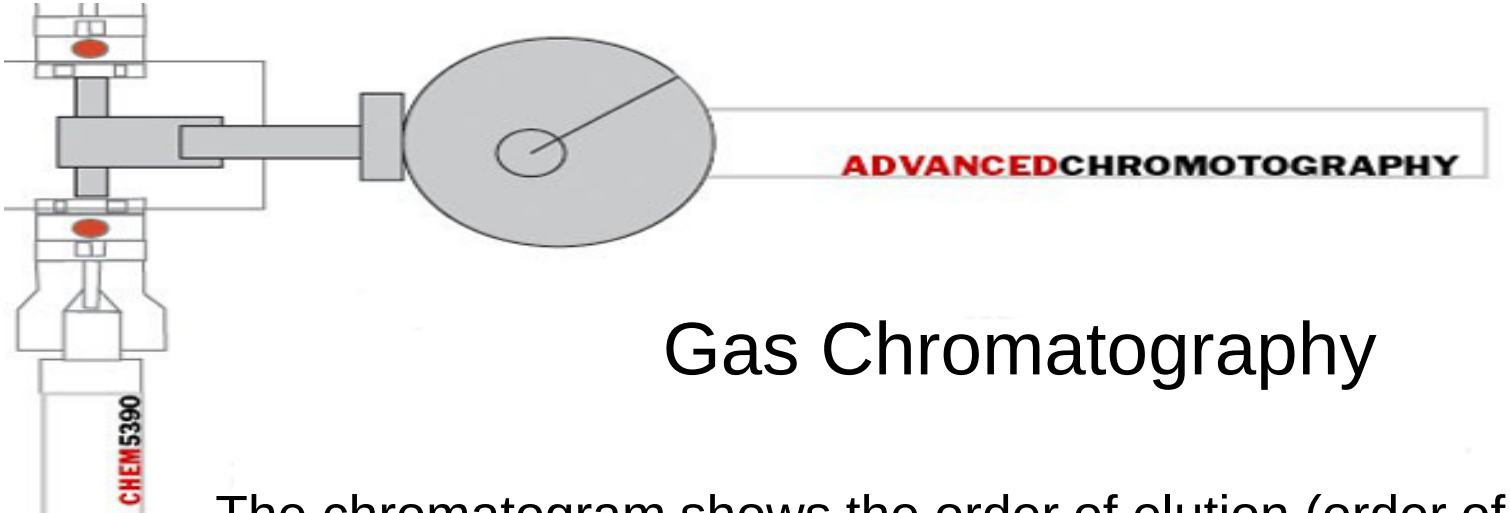
Gas Chromatography

As the different compounds in the sample have varying solubility in the stationary phase, they interact.

The process is repeated many, many times along the column. Eventually the components of the injected sample are separated and come off of the column at different times.

There is a detector at the end of the column which signals the change in the nature of the gas flowing out of the column.

The chromatogram shows the order of elution (order of components coming off the column), the time of elution (retention time), and the relative amounts of the components in the mixture.

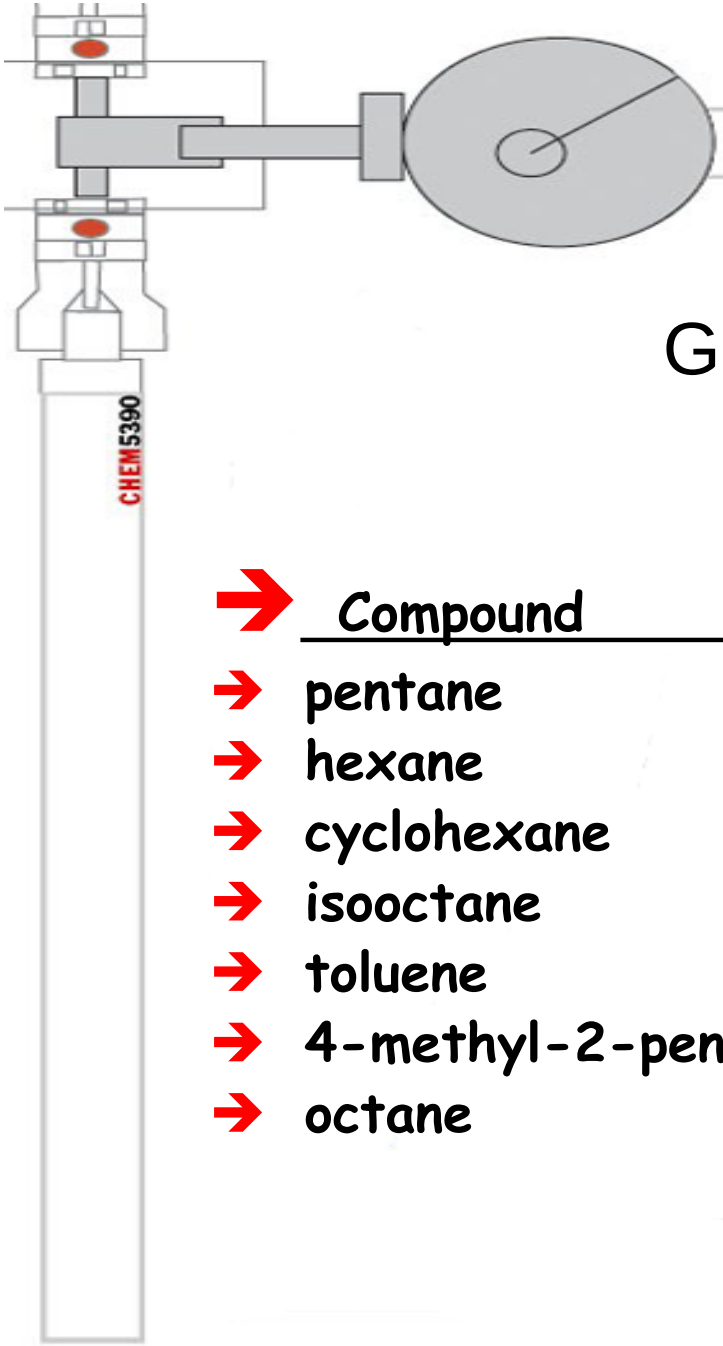


Gas Chromatography

The chromatogram shows the order of elution (order of components coming off the column), the time of elution (retention time), and the relative amounts of the components in the mixture.

The order of elution is related to the boiling points and polarities of the substances in the mixture.

In general, they elute in order of increasing boiling point but occasionally the relative polarity of a compound will cause it to elute "out of order".

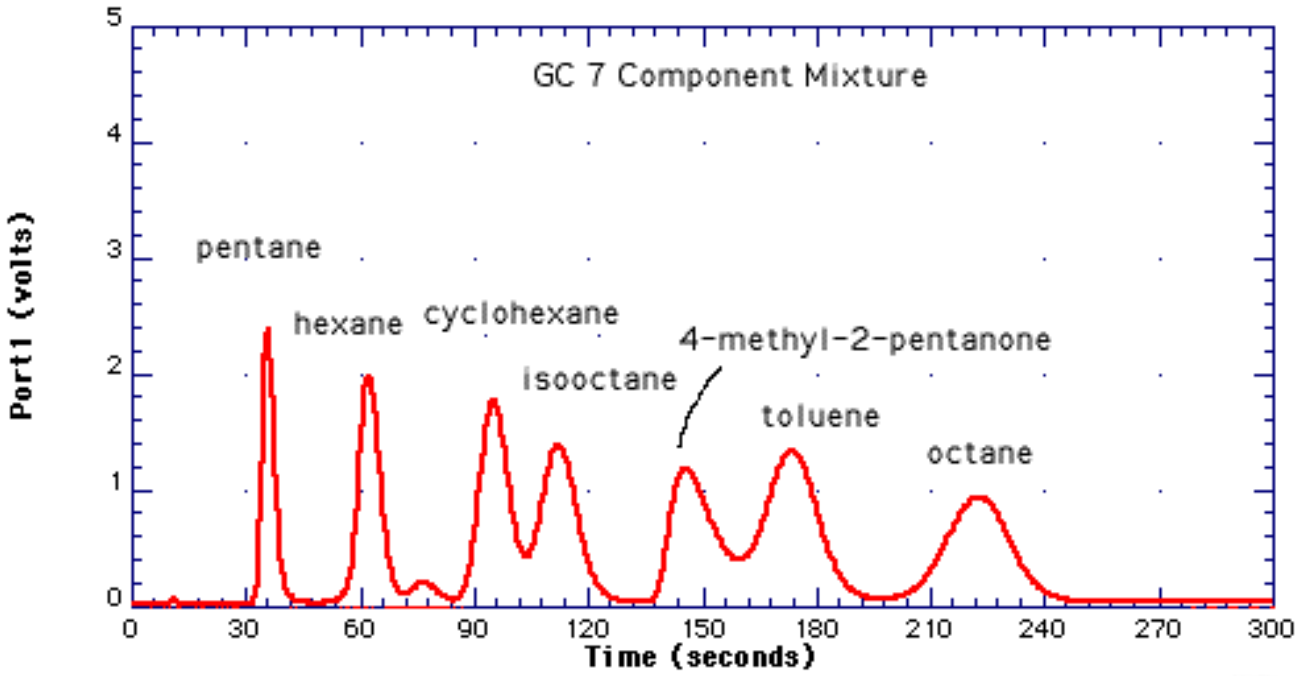


Gas Chromatography

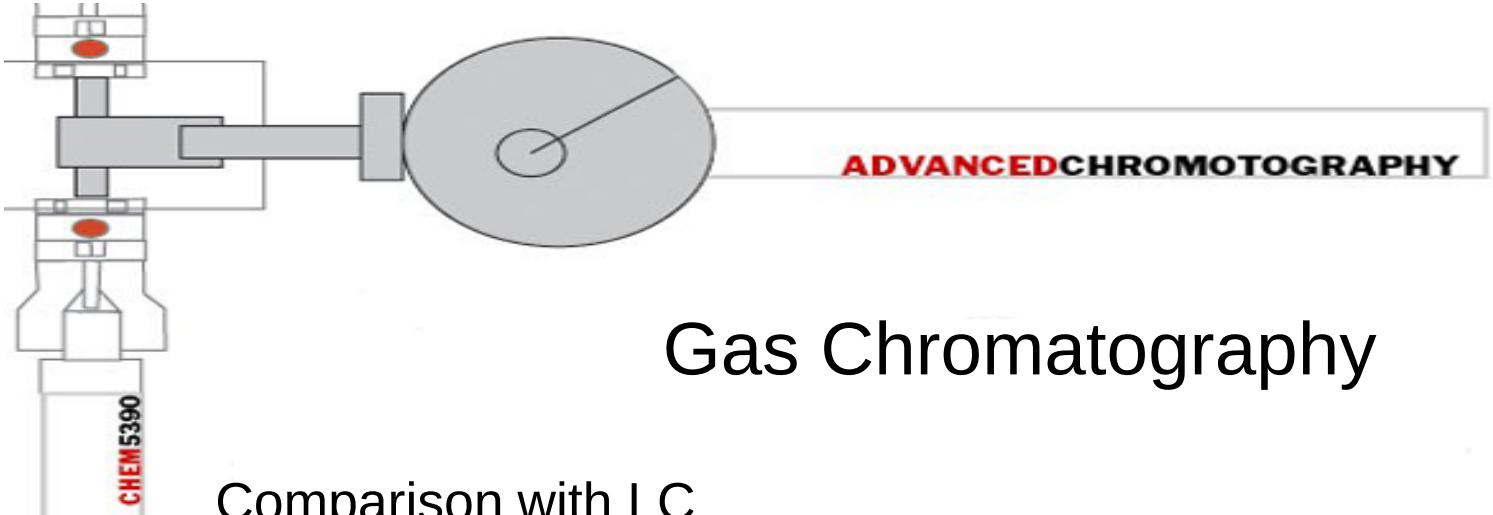
Elution Order

Compound	Boiling Point (^0C)
pentane	36
hexane	69
cyclohexane	80
isooctane	99
toluene	110
4-methyl-2-pentanone	117
octane	126

Gas Chromatography



Notice the elution of toluene and 4-methyl-2-pentanone



Gas Chromatography

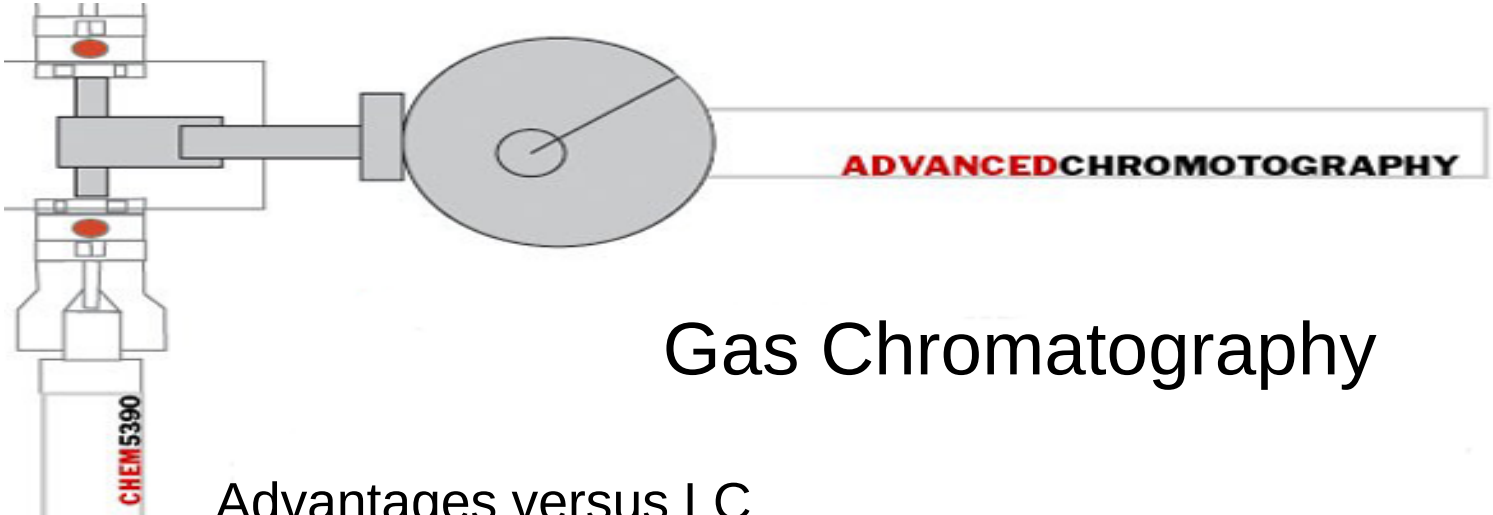
Comparison with LC

Two key differences between GC and LC:

- No analyte – mobile phase interaction in GC
- Temperature is routinely changed (and always controlled) in GC

Effects of gases (vs. liquids)

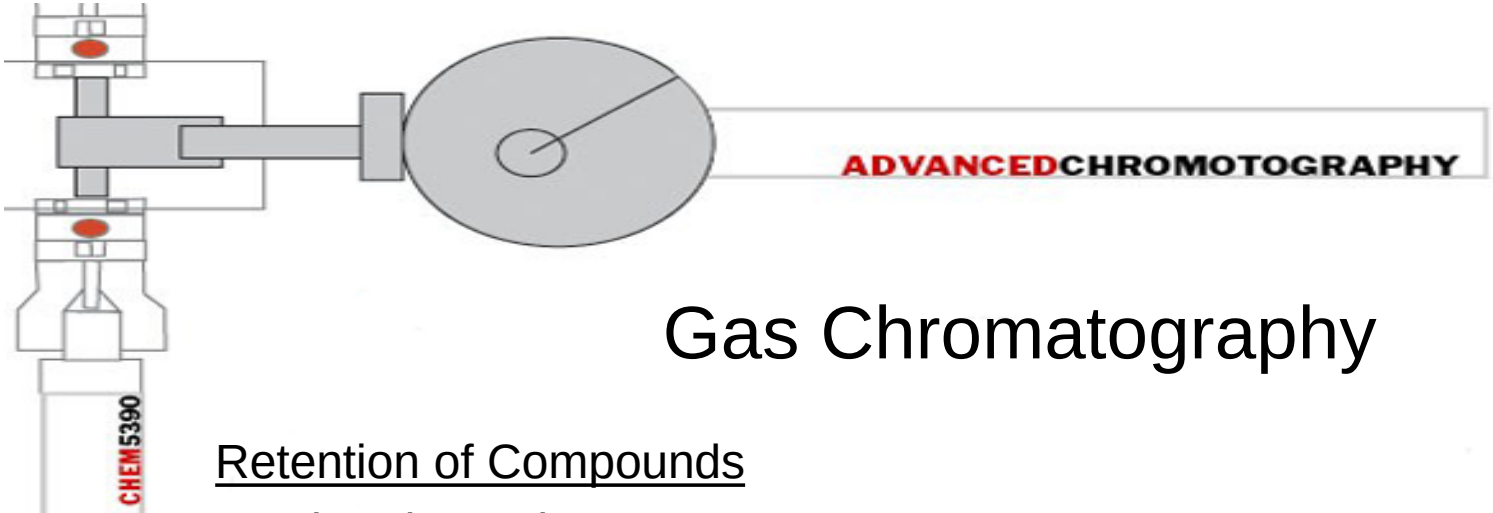
- Much higher diffusivity (larger B term of van Deemter equation but very small Cm term)
- Lower viscosity of gases (backpressure is not as big an issue)
- Much lower density (capacity of column is a big issue with liquid samples)
- Gases are compressible



Gas Chromatography

Advantages versus LC

- Main practical advantage comes from high N values (although H is usually larger) achieved with open tubular columns.
- Another advantage comes from being able to use quite long columns (60 m vs. 250 mm for HPLC) because backpressure is not a major issue
- Other advantages have to do with instrument cost and better detectors
- Main disadvantage is for analysis of non-volatile compounds



Gas Chromatography

Retention of Compounds

K value depends on:

Volatility

Polarity of analyte vs. polarity of stationary phase

Measure of volatility

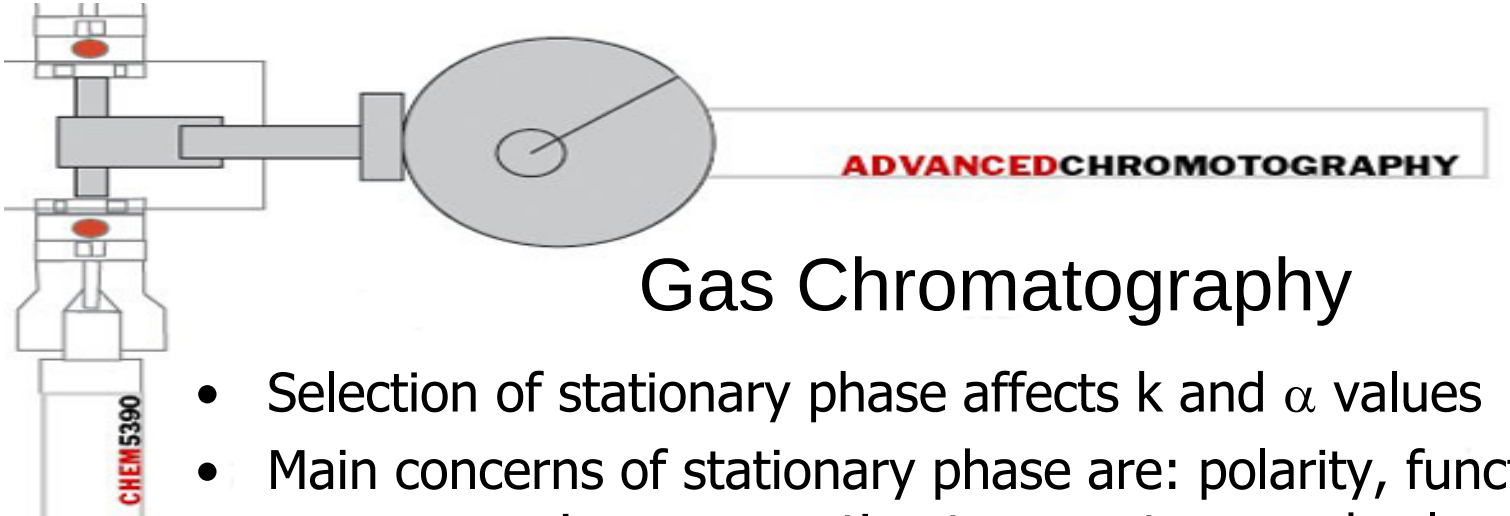
Best measure is vapor pressure at temperature

Boiling point temperature is used more frequently

Depends on molecule's size and polarity

Polarity in separations

Compounds of similar polarity as stationary phase will be more retained than similar compounds of different polarity if their boiling points are the same (ether vs. acetone example)



Gas Chromatography

- Selection of stationary phase affects k and α values
- Main concerns of stationary phase are: polarity, functional groups, maximum operating temperature, and column bleed (loss of stationary phase due to decomposition)
- More polar columns suffer from lower maximum temperatures and greater column bleed

Type	Functional Groups	Polarity
OV-1	methyl	Non-polar
OV-17	50% methyl/50% phenyl	Somewhat polar
OV-225	Cyanopropyl, methyl, and phenyl	More polar
carbowax	Ether groups	polar

Gas Chromatography

Mobile Phase

Since there is no mobile phase – analyte interaction in GC, why does the mobile phase matter?

Affects diffusion

-Smallest MW gases diffuse faster

-van Deemter B term at low flow rates (fast is worse) and C term at higher flow rates (fast is better)

-H_{min} not affected much, but u_{min} affected by gas chosen

Smallest MW allows fastest runs at minimum H

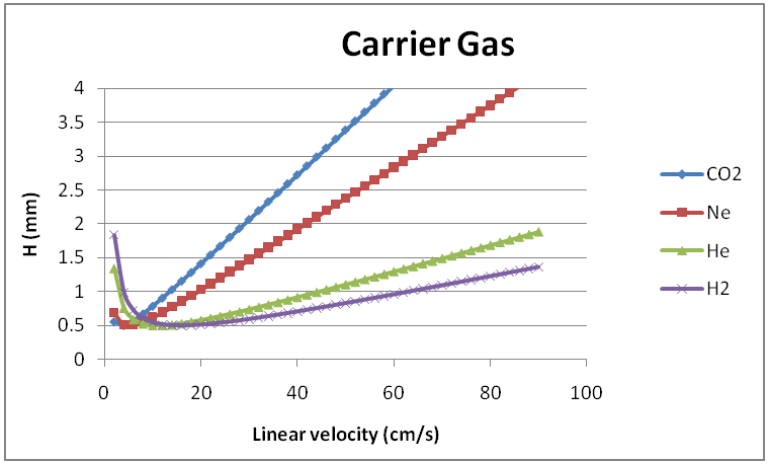
Detector requirements

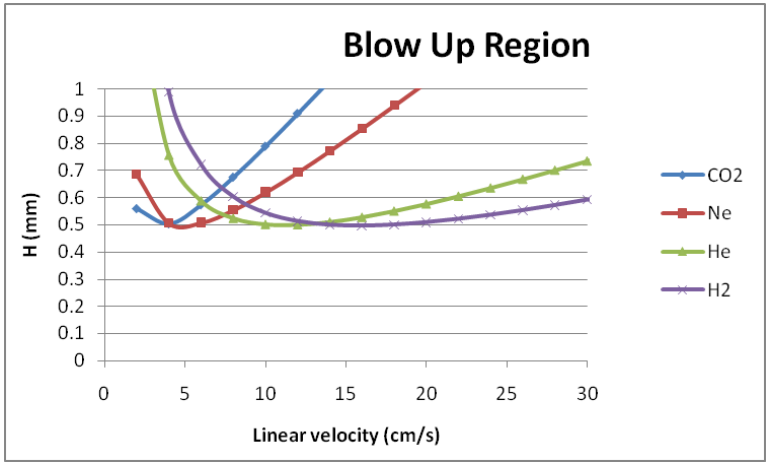
He is most common (inert, safe gas with high diffusivity for better efficiency at high flow rate)

H_2 also can be used with even better efficiency, but is less safe

Gas Chromatography

Mobile Phase





Effect of Carrier Gas Velocity

Gas flow through packed columns are generally described in terms of volumetric flow as measured at the column outlet.

Gas flow dynamics are simpler in the open tubular column and can be measured by linear velocity of the mobile phase or “average linear velocity” in cm/sec.

u – average linear mobile phase velocity

Effect of Carrier Gas Velocity

$u(cm/sec) = L(cm)/t_M(sec)$

t_M – is called the gas hold up time

<u>Unretained Compounds</u>

Methane (or butane) is commonly used with FIDs
Methylene Chloride used with ECDs
Acetonitrile is used with NPDs in nitrogen mode
Methane (or butane or <u>air</u>) is used with TCD and MS
Vinyl Chloride is used with PID and ELCD

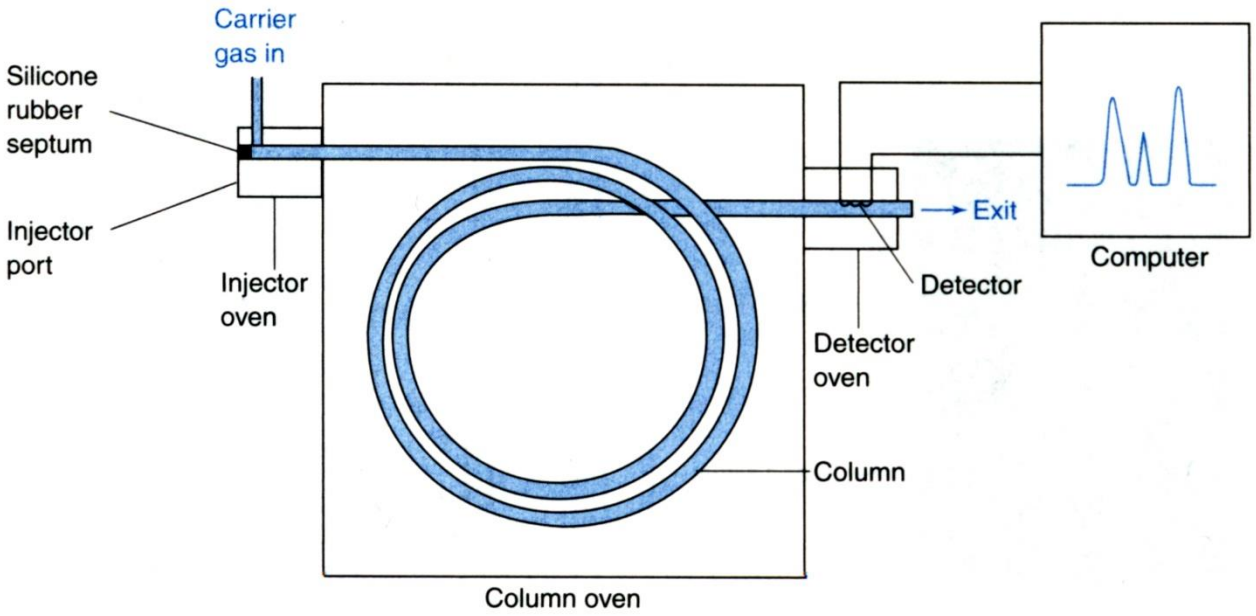
Instrumentation

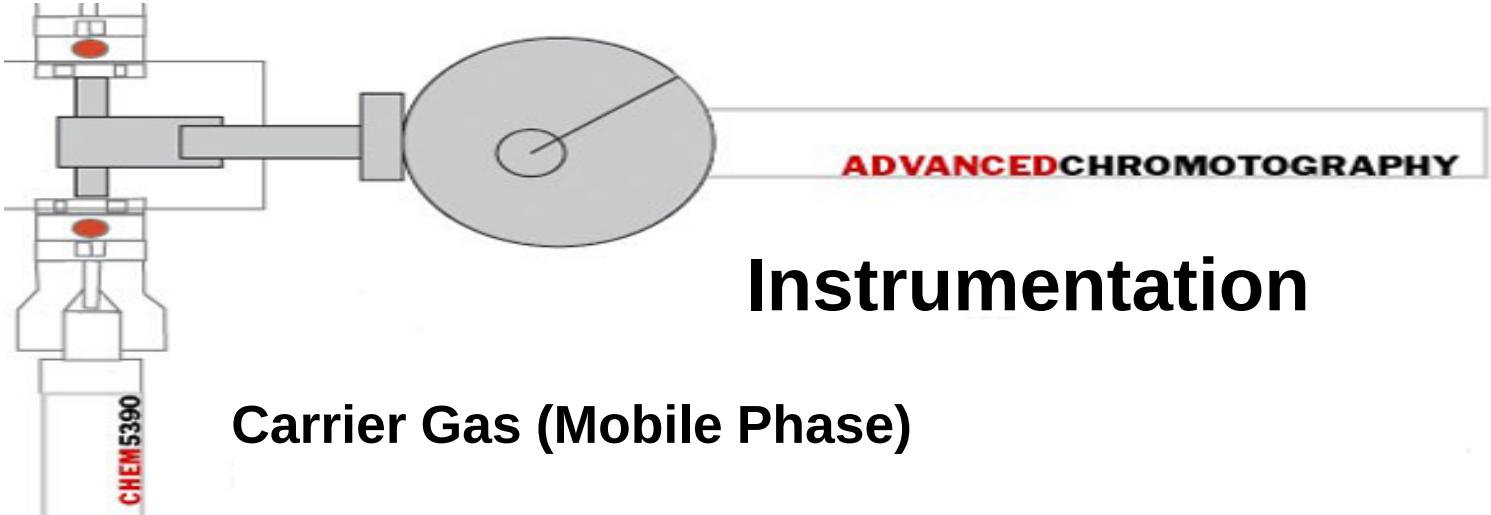
Volatile liquid or gas injected through septum into heated port

Sample rapidly evaporates and is pulled through the column with carrier gas

Column is heated to provide sufficient vapor pressure to elute analytes

Separated analytes flow through a heated detector for observation





Instrumentation

Carrier Gas (Mobile Phase)

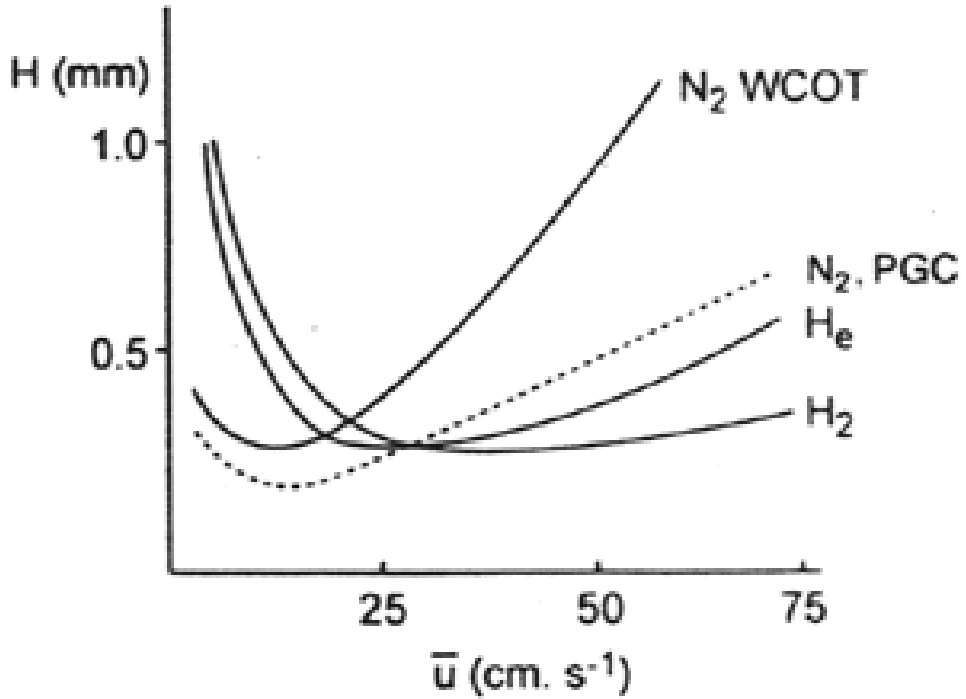
- Carrier gas usually consist of He, N, H or a mixture of argon and methane. The function of the gas is to carry the sample through the system.

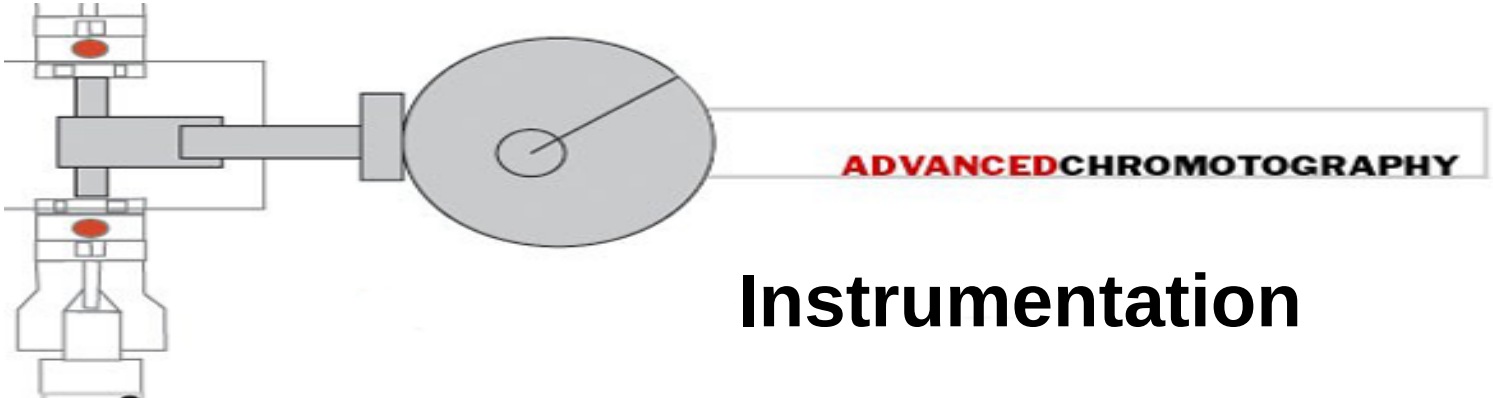
- The carrier gas must be:
  - inert toward the sample
  - dry
  - thermally stable
  - safe
  - cost effective
  - compatible with the detector

- He and N are the most popular carrier gases in GC.

Instrumentation

The most efficient separations are achieved with N_2 as a carrier gas. This can be seen with the following van Deemter curve:



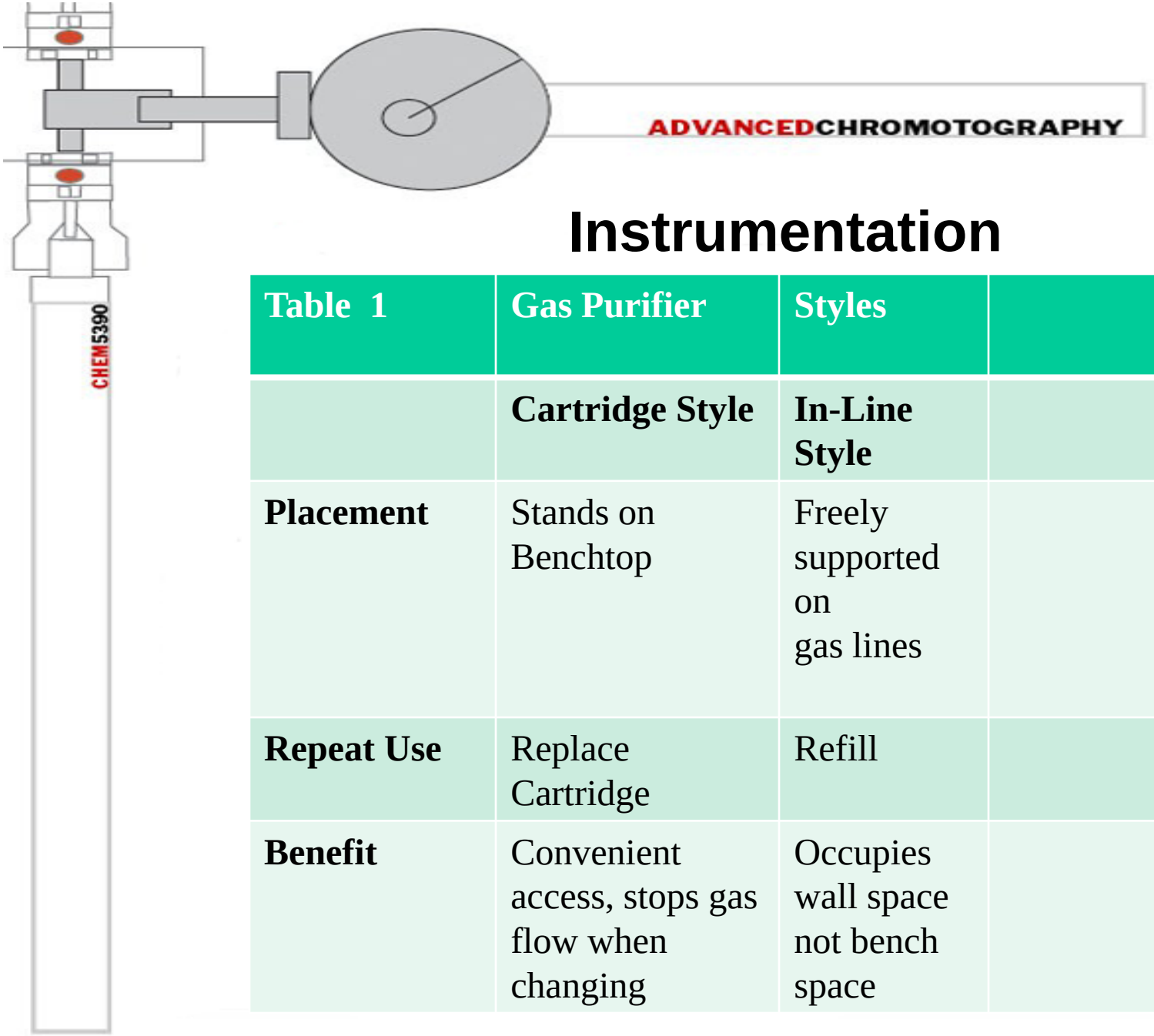


Instrumentation

- N_2 has a greater molecular weight and smaller diffusion coefficient – so lower β term, but must sacrifice analysis time. Best efficiency is at 8-10 cm/s.

- H and He have better analysis time w/ a small sacrifice in efficiency.
  He → 16-20 cm/sec H → 35-40 cm/sec

- To reduce deterioration of the stationary phase and to lessen detector noise – very high purity gas needs to be used. For this reason oxygen and moisture traps in the carrier gas lines are used.



Instrumentation

Table 1	Gas Purifier	Styles	
	Cartridge Style	**In-Line Style**	
Placement	Stands on Benchtop	Freely supported on gas lines	
Repeat Use	Replace Cartridge	Refill	
Benefit	Convenient access, stops gas flow when changing	Occupies wall space not bench space	

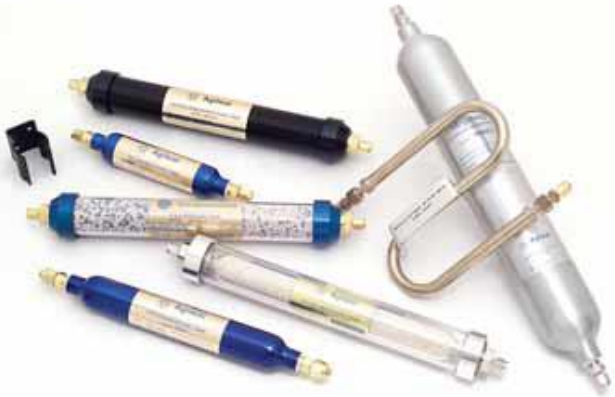
Instrumentation

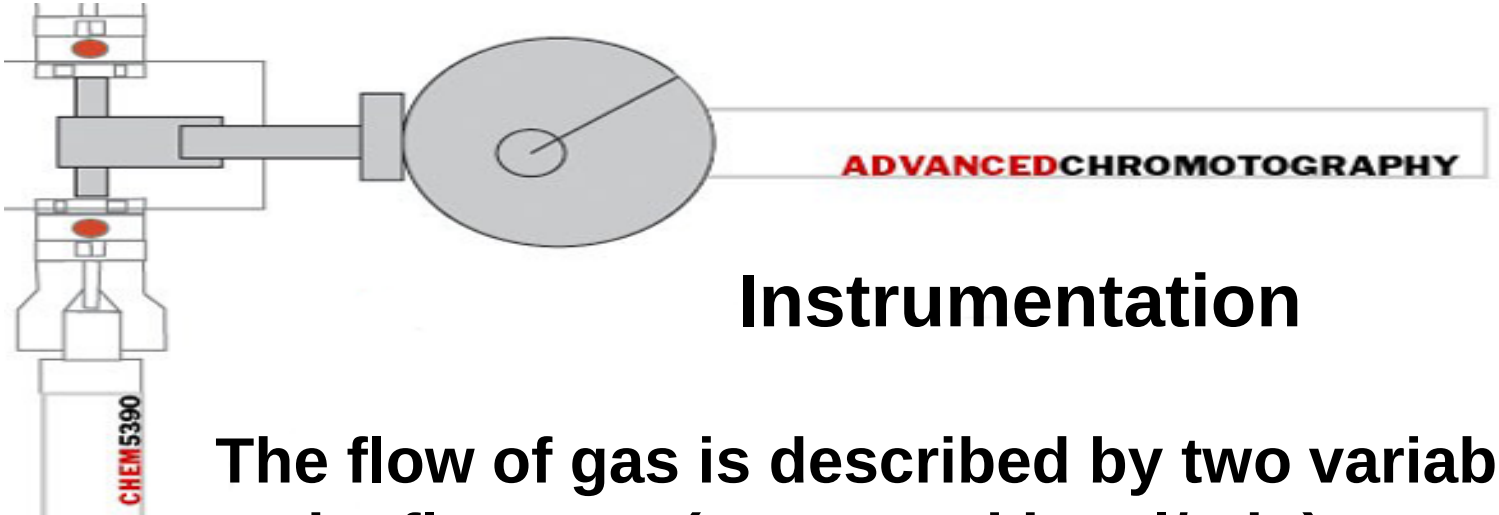
Moisture traps – molecular sieves, trap water.

Hydrocarbon traps – activated charcoal, traps organics

Oxygen traps – metal catalyst

(For multiple traps – order from gas source – moisture, hydrocarbon, oxygen, indicating oxygen)



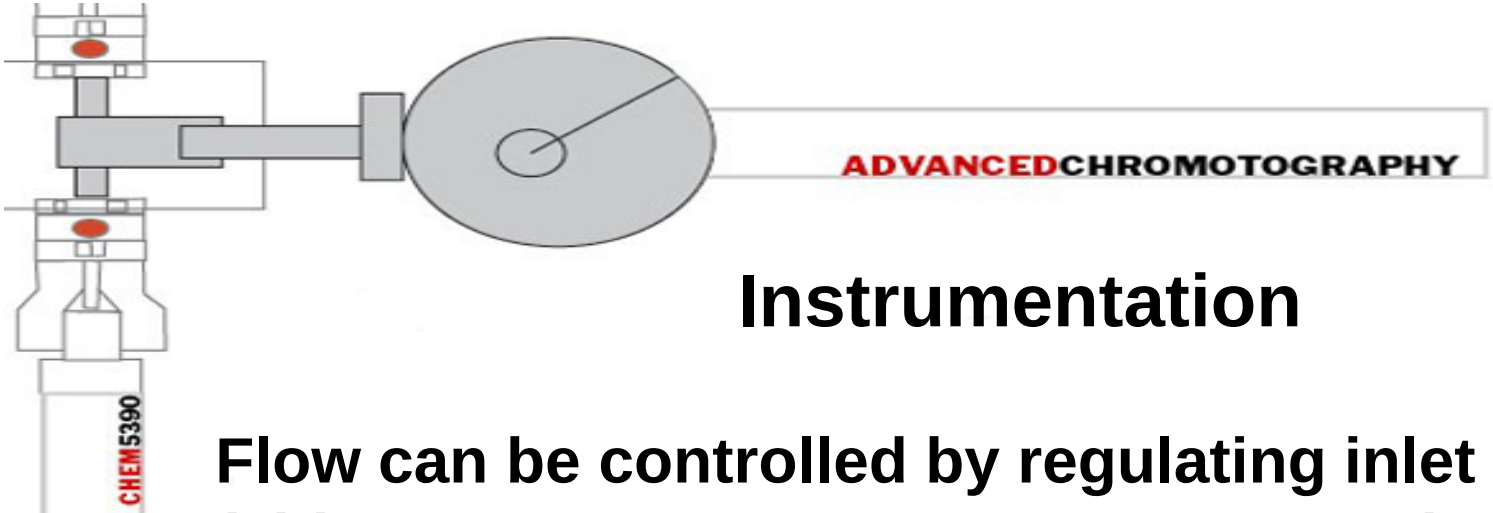


Instrumentation

The flow of gas is described by two variables

- **the flow rate (measured in ml/min)**
- **pressure drop between the injection port inlet and detector outlet**

Carrier gas is regulated by a flow controller – older flow controllers were diaphragm types with a polymeric membrane, instruments today use electronic programmable flow controllers.
(A modified thermal conductivity detector.)

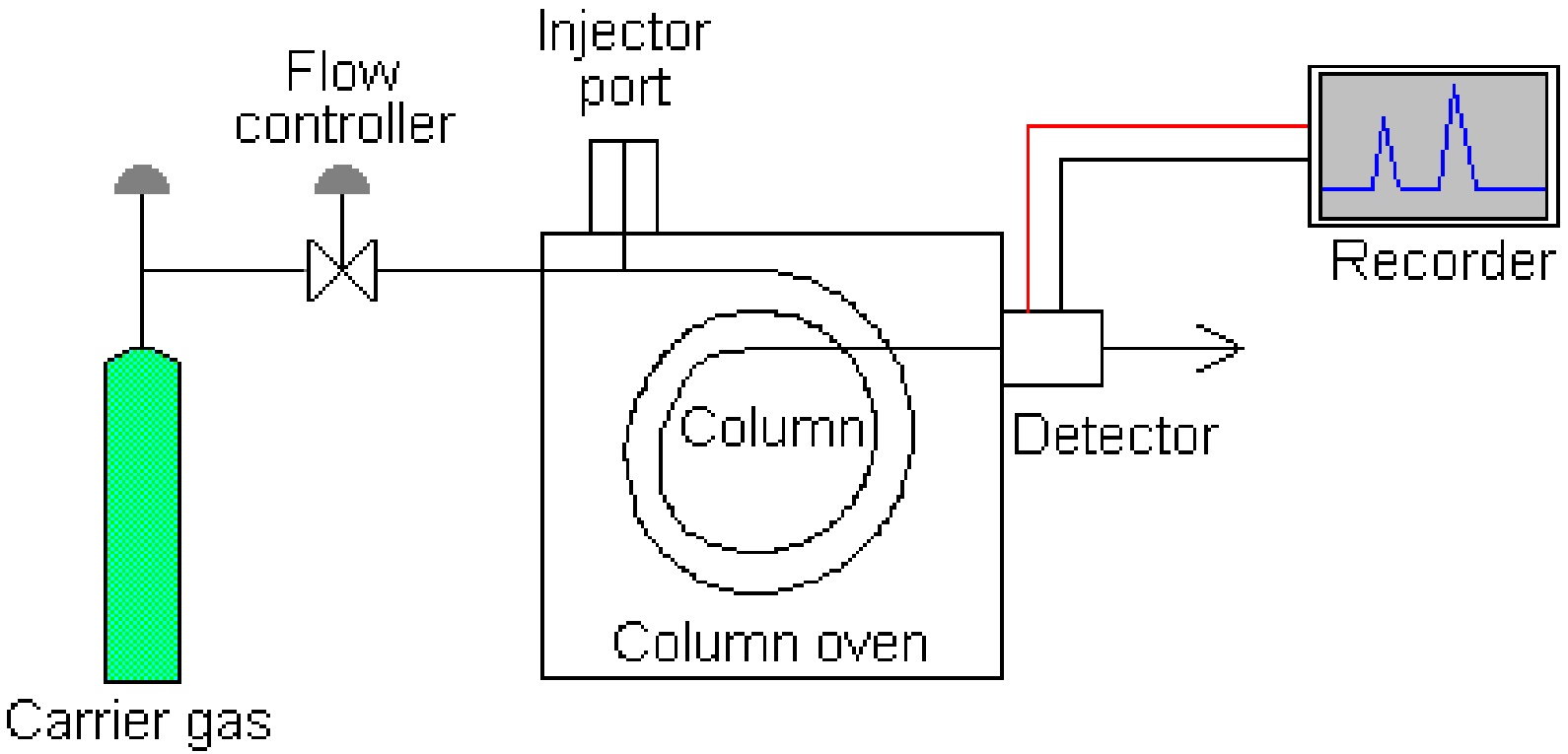


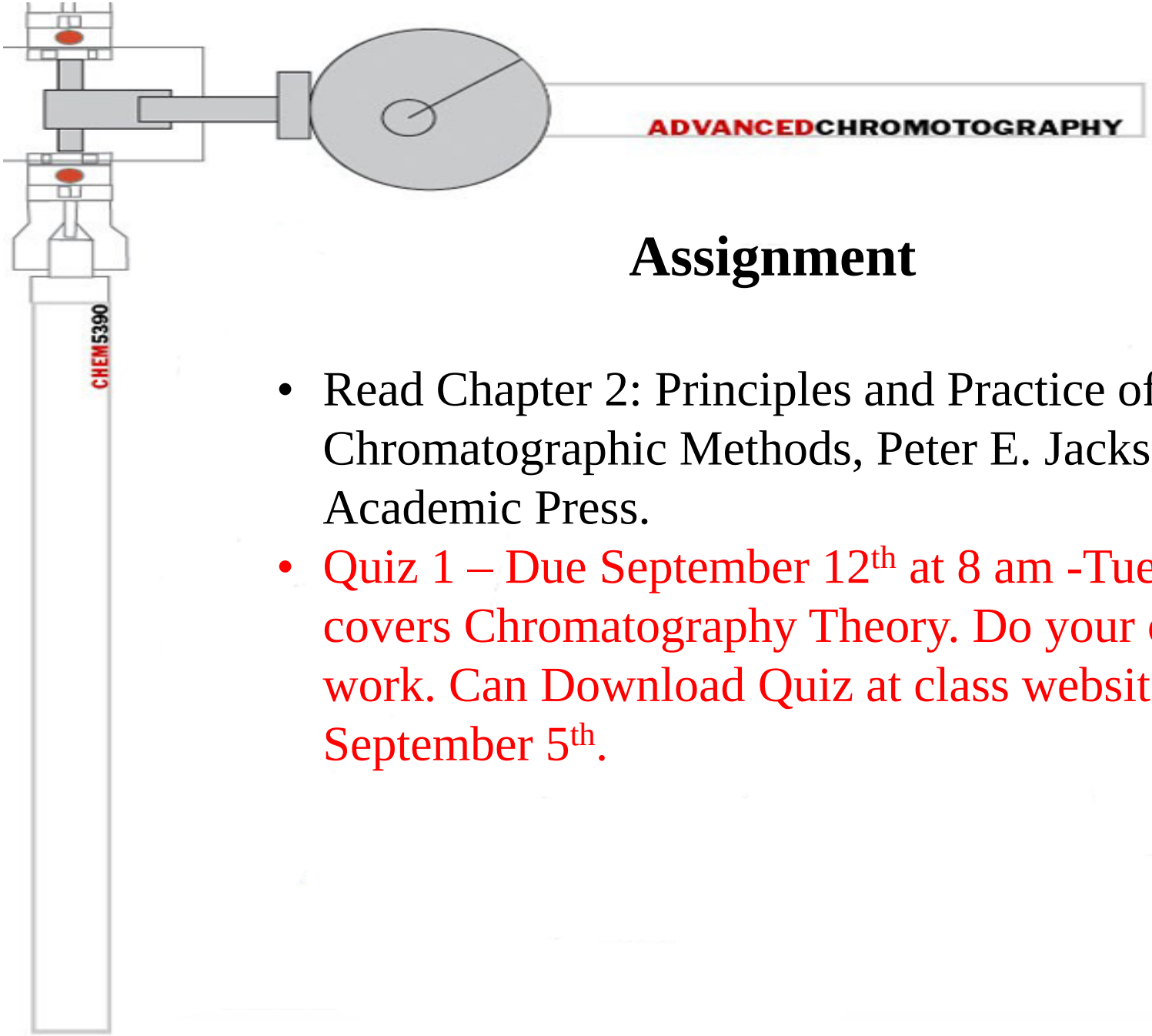
Instrumentation

Flow can be controlled by regulating inlet pressure (either constant pressure or compensation for constant linear velocity).

Equipment consists of valves for regulating pressure (constant pressure) in older instruments or electronic pressure control (solenoid valve opens or closes in response to pressure).

Instrumentation





Assignment

- Read Chapter 2: Principles and Practice of Modern Chromatographic Methods, Peter E. Jackson, Academic Press.
- Quiz 1 – Due September 12th at 8 am -Tuesday – covers Chromatography Theory. Do your own work. Can Download Quiz at class website on September 5th.