크로마토그래피의 원리와 분석법

Gas Chromatography의 원리와 분석법

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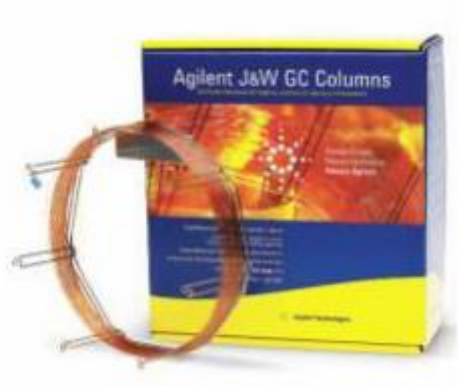
Gas Chromatography (GC)

Gas chromatography is a separation technique based on partitioning analytes between two immiscible phases: gaseous mobile phase (Carrier gas) and a stationary solid or immobilized liquid phase (packed or hollow capillary column).



상용적으로 판매하는 GC column

Autosampler가 장착된 GC
(*autosampler: 시료들을 자동으로 순서대로 주입해주는 장치)

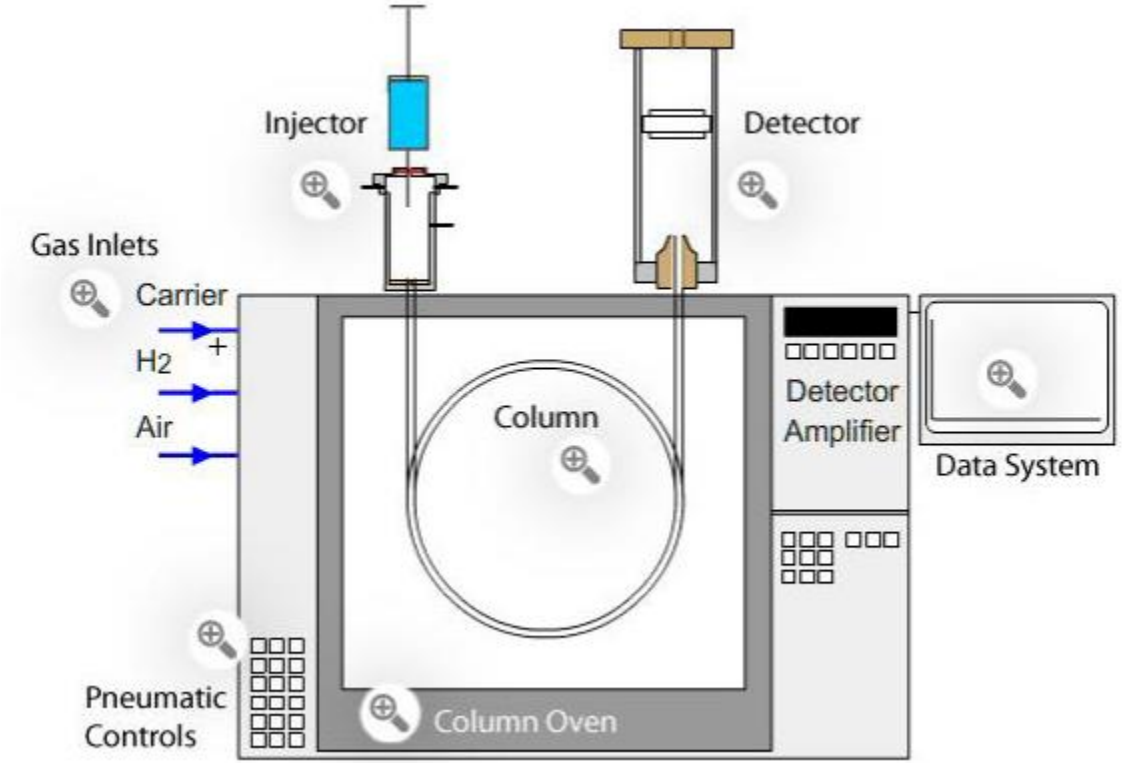
질량분석기가 장착된 GC

Gas Chromatography

- ❖ Good for volatile samples (up to about 250 °C)
- ❖ 0.1-1.0 microliter of liquid or 1-10 ml vapor
- ❖ Can detect <1 ppm with certain detectors
- ❖ Can be easily automated for injection and data analysis

- 분석하고자 하는 시료는 volatile 또는 semi-volatil해야하며, 높은 온도에서도 시료는 안정해야한다.
- 그렇지 않을 경우, 시료는 HPLC로 분석을 해야한다.
- 일반적으로 분자량 500을 넘는 물질은 GC로 분석이 어렵다.

GC Instrument



- 시료가 주사기를 통해서 주입되면 inlet system에서 고온으로 가열되어 기화된다.
- 증기화된 시료는 이동상(gas carrier)가 흐르는 GC column 안으로 주입된다.
- 시료들은 GC column내 고정상과 상호작용을 하며 시료의 종류에 다라 분리가 된다.
- 시료가 고정상에 강하게 결합될 수록 더 높은 온도로 가열시켜 용출시킬 수 있다.

Components of a Gas Chromatograph

Gas Supply: (usually N_2 or He)

Sample Injector: (syringe / septum)

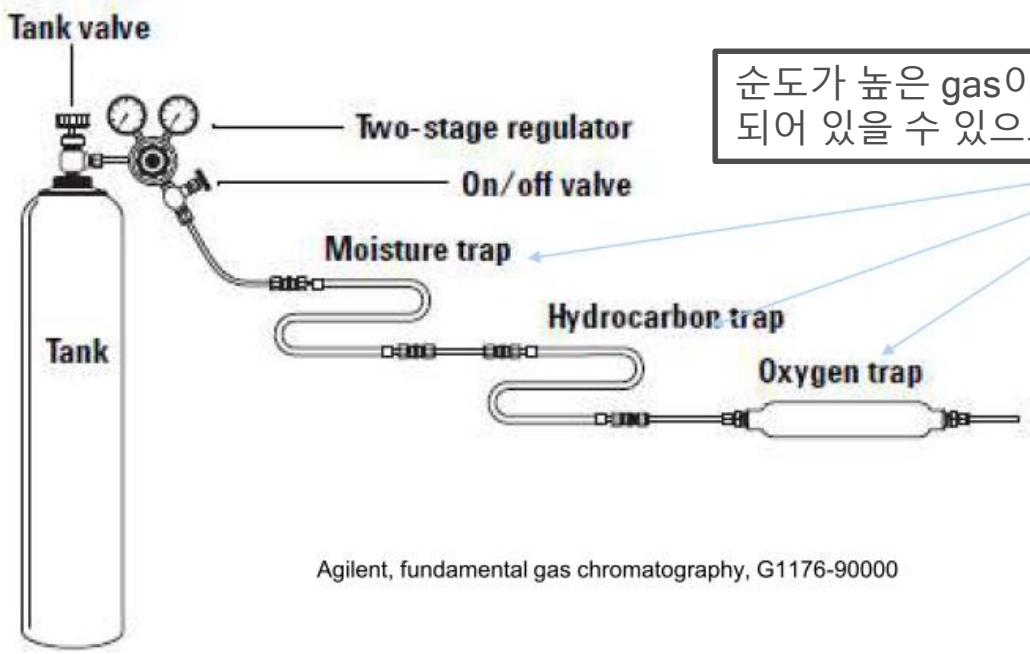
Column: 1/8” or 1/4” x 6-50’ tubing packed with small uniform size, inert support coated with thin film of nonvolatile liquid

Detector: TC - thermal conductivity
FID - flame ionization detector

Carrier Gas

- A carrier gas is responsible for carrying the sample molecules into the column and finally to the detector.

- Carrier gas must be: inert with the stationary phase, of high purity 99.999 %.



순도가 높은 gas이어도 수분이나 기타 불순물이 포함되어 있을 수 있으므로 trap의 설치는 필수이다.

Agilent, fundamental gas chromatography, G1176-90000

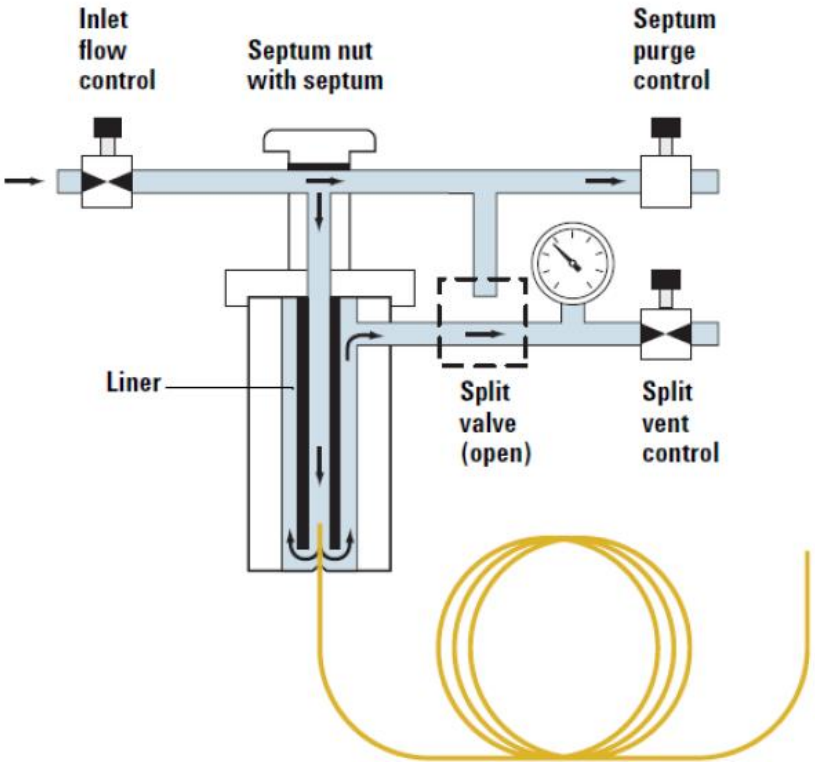
GC Injection Techniques

- Split/split-less
- Programmed temperature vaporization (PTV) injection
- Cool-on-column (COC) injection

COC injector의 경우 시료를 column에 액체로 주입한다. 높은 온도에 의한 시료의 열분해를 방지하기 위해서다.

Split Injector

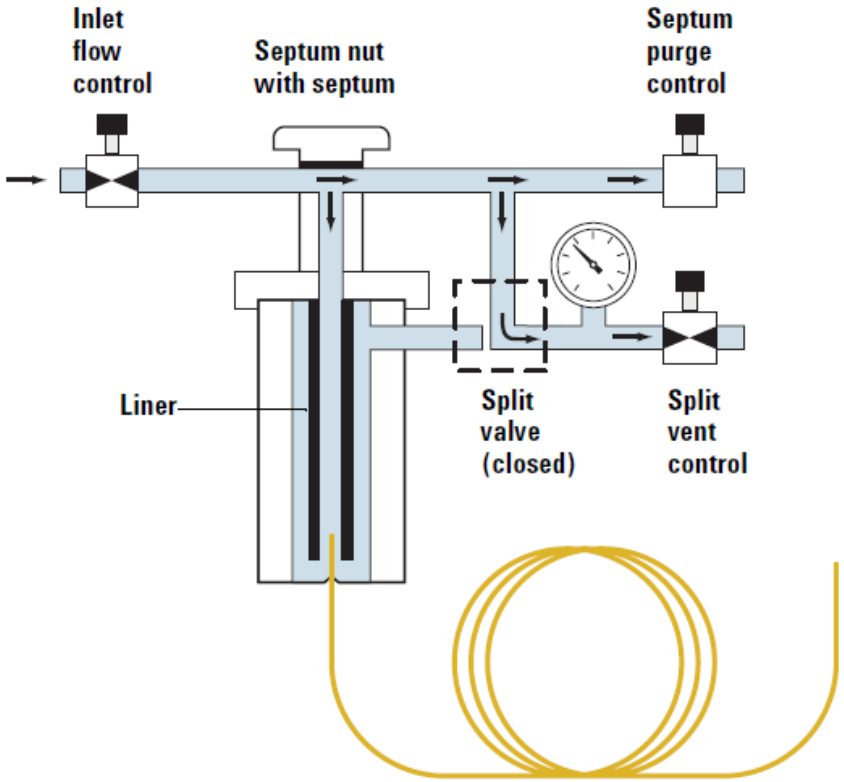
- In the split injection mode, sample enters the hot liner and volatilized rapidly.
- Vaporized sample is mixed with a carrier gas (diluted).
- Finally, a large part of the diluted vaporized sample is split away from the column, while a small part will enter the column.
- This mode of injection is used for analysis of samples of high analyte concentrations.



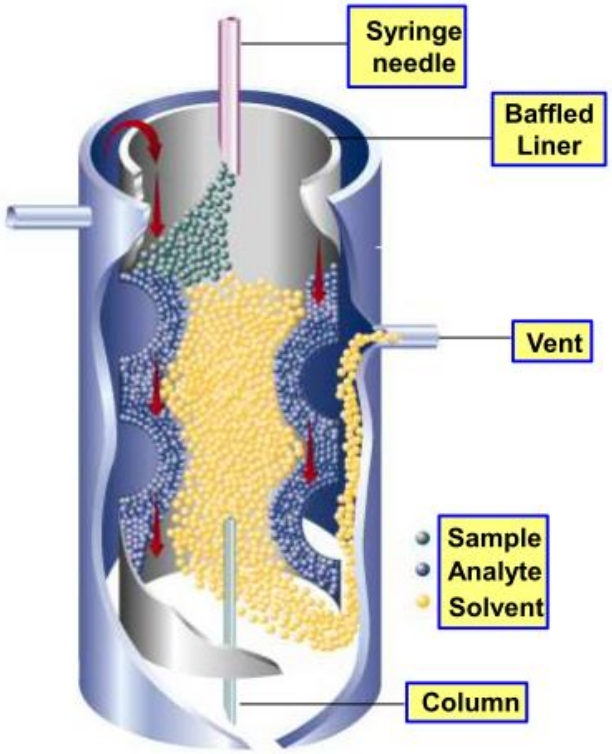
비휘발성 물질 (non-volatile substance)로 부터 분리해낼 수 있다. Column의 보호도 가능하다.

Split-less Injector

- Is the split-less injection mode, sample enter the hot liner and volatilized rapidly.
- Vaporized sample is mixed with a carrier gas (diluted).
- Finally, all the diluted vaporized sample enter the column.
- After that, the split valve is opened to remove residual vapors.
- This mode of injection is used for analysis of samples of trace analyte concentrations (residue analysis).



PTV injector



- In the program temperature vaporized injector the sample is injected in a cooled liner.

- While, the solvent will be split away. Therefore, injection in PTV should be carried out slowly.

- After that, split valve closed, and beginning ramping temperature increase (ramp PTV) to vaporize adsorbed sample matrix and analytes to be carried into the column

- 시료가 상온에서 주입되어 먼저 흡착이 된다.

- 그 후 분석에 필요하지 않은 용매를 제거한 후, 온도를 증가시켜 시료들을 기화시킨다.

GC-Column

Capillary columns
Open tubular (OT)

Agilent, fundamental gas chromatography, G1176-90000

Packed columns

Agilent, fundamental gas chromatography, G1176-90000

Packed column의 경우 (typical dimension 1.5 m X 4 mm) colum이 액체고정상 물질로 코팅된 고체물질들로 채워져 있다.

Capillary colum의 경우 (typical dimension 30 m X 0.32 mm X 0.1 mm film 두께) 매우 길고 속이 비어있으며, 안은 액체고정상물질이 여러 두께로 코팅되어 있다.

*액체고정상물질 (liquid stationary phase, GLC)

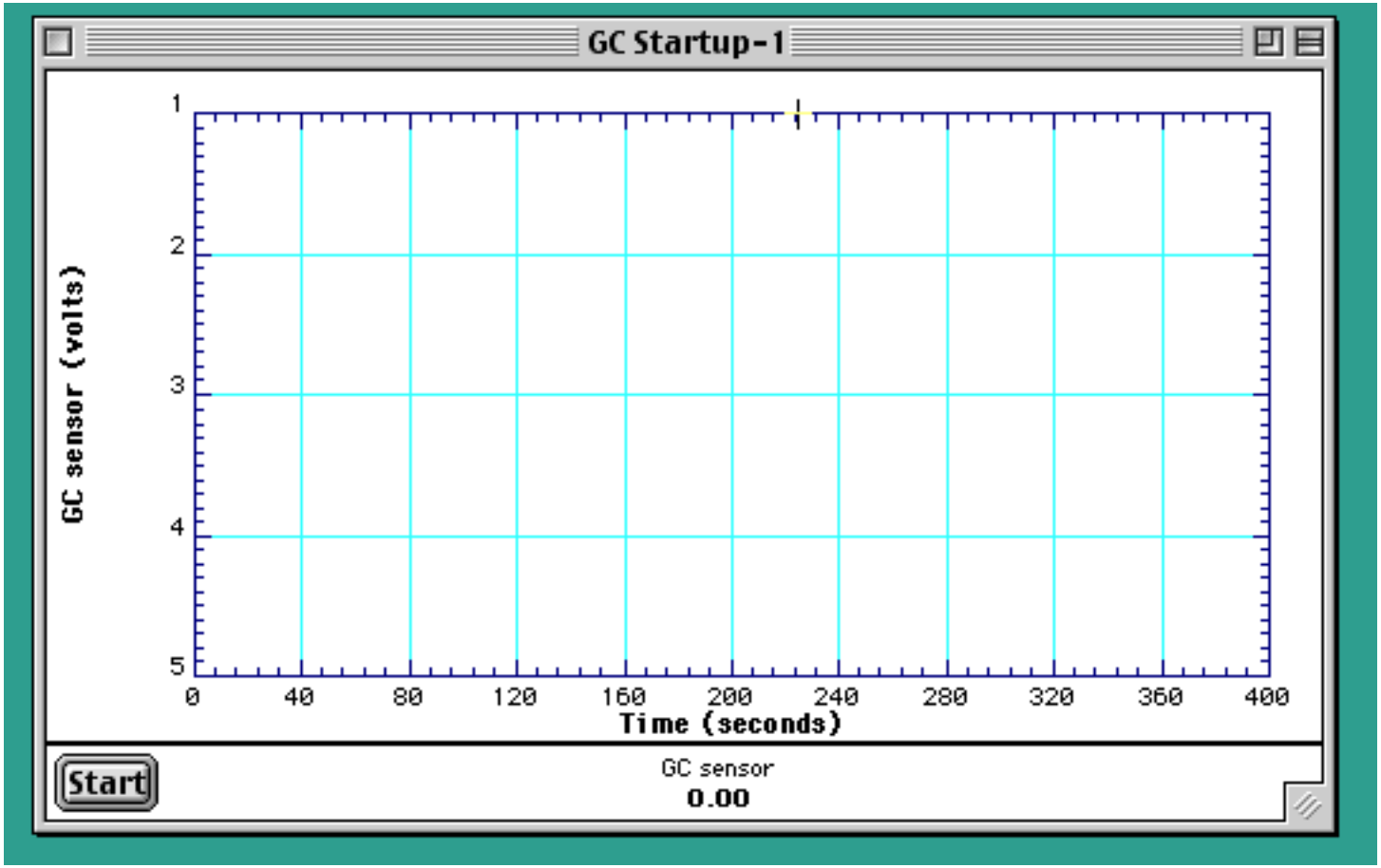
GC-Column

- A longer column will increase the resolution (selectivity), but it will also increase analysis time, and cost.

- Reduced column internal diameter double the efficiency and leads to better selectivity. This will increase retention time when using isothermal separations. such columns easily contaminated and suffer from peak broadening after routine work.

- Changes in film thickness effects retention of analyte species, interaction with the silica tubing (increased with increasing film thickness). Usually, thin films (0.10-0.25 µm)are used for trace analysis.

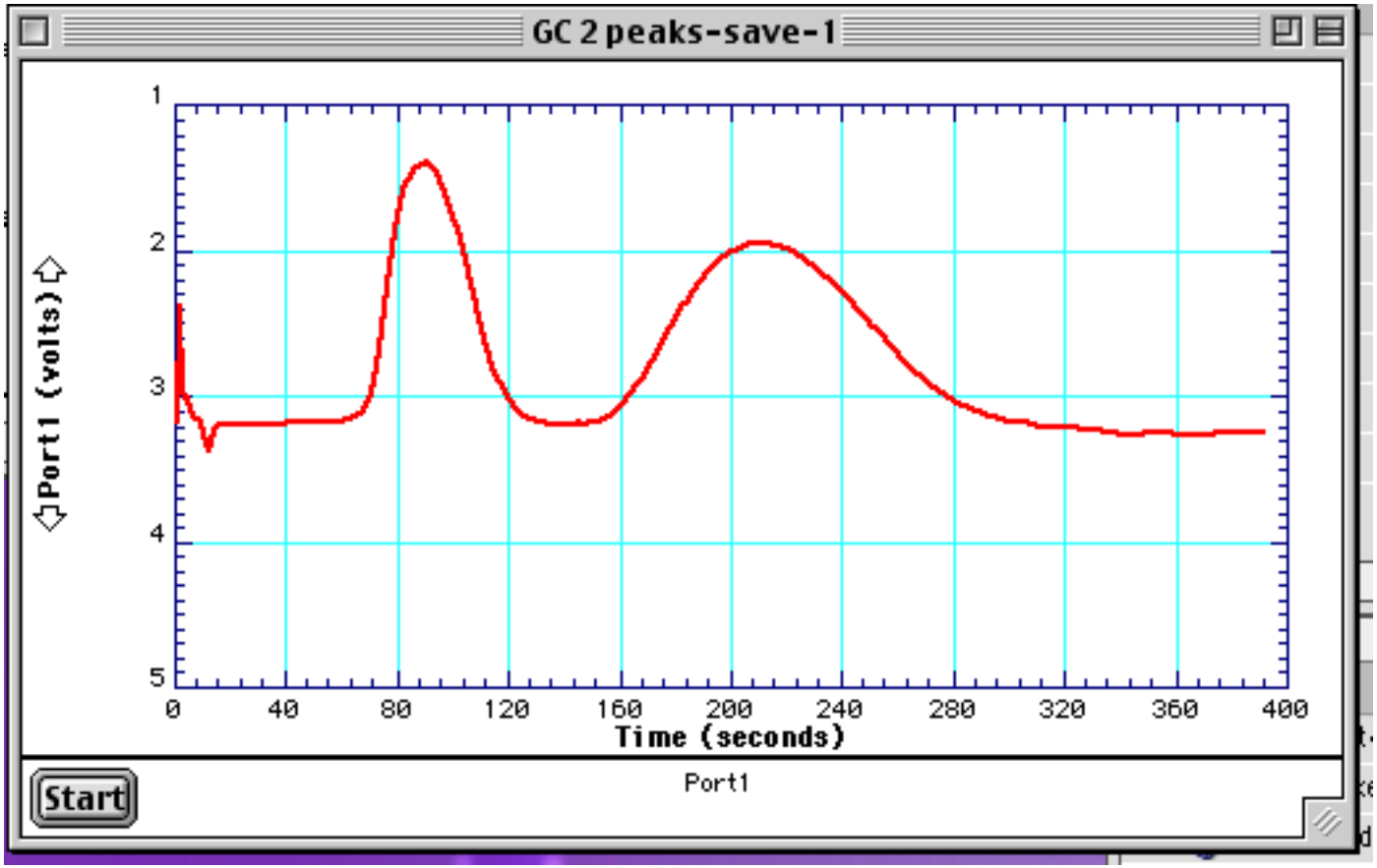
General Settings for GC Startup program



Y axis: 1-5 v (0-1 volt is in bright light, 4-5 volt is dark)

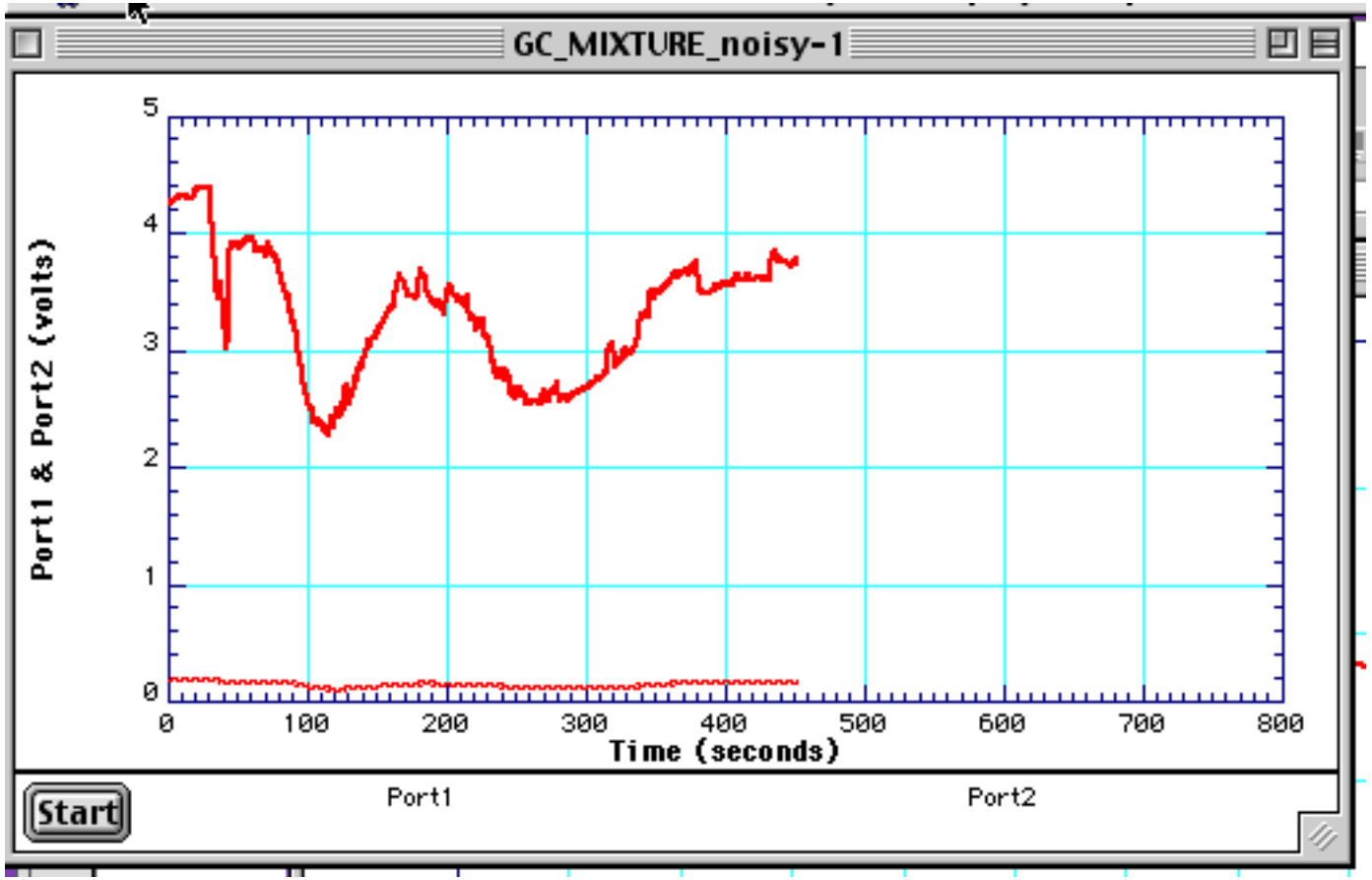
X axis: 0-400 seconds

Plot of GC Elution Data for Dichloromethane and Chloroform On 25 cm Tide Column



Good: Peaks are smooth, well separated and elute quickly

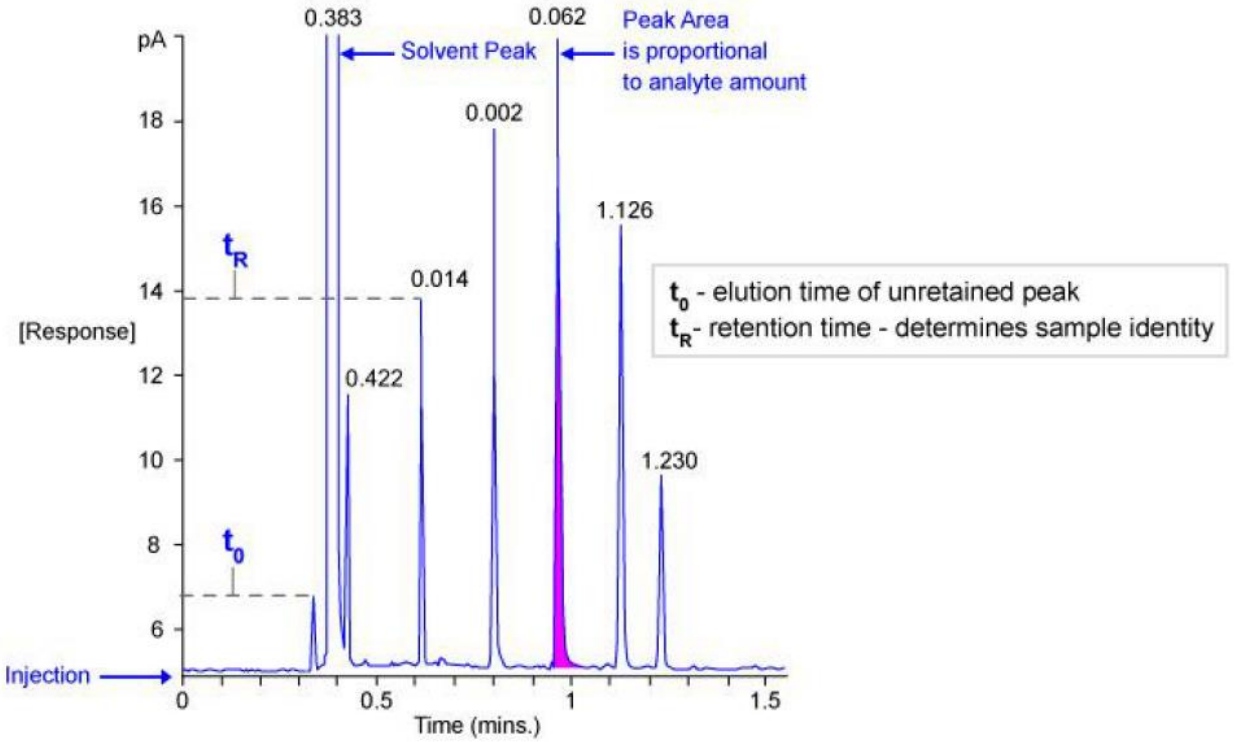
Plot of GC Elution Data for Dichloromethane and Chloroform On 25 cm Tide Column



Poor: peaks are noisy, due to flickering flame, and elute slowly.

To fix: Adjust sensor so that it is looking at the blue portion of the flame. (Verify the flame is blue.)

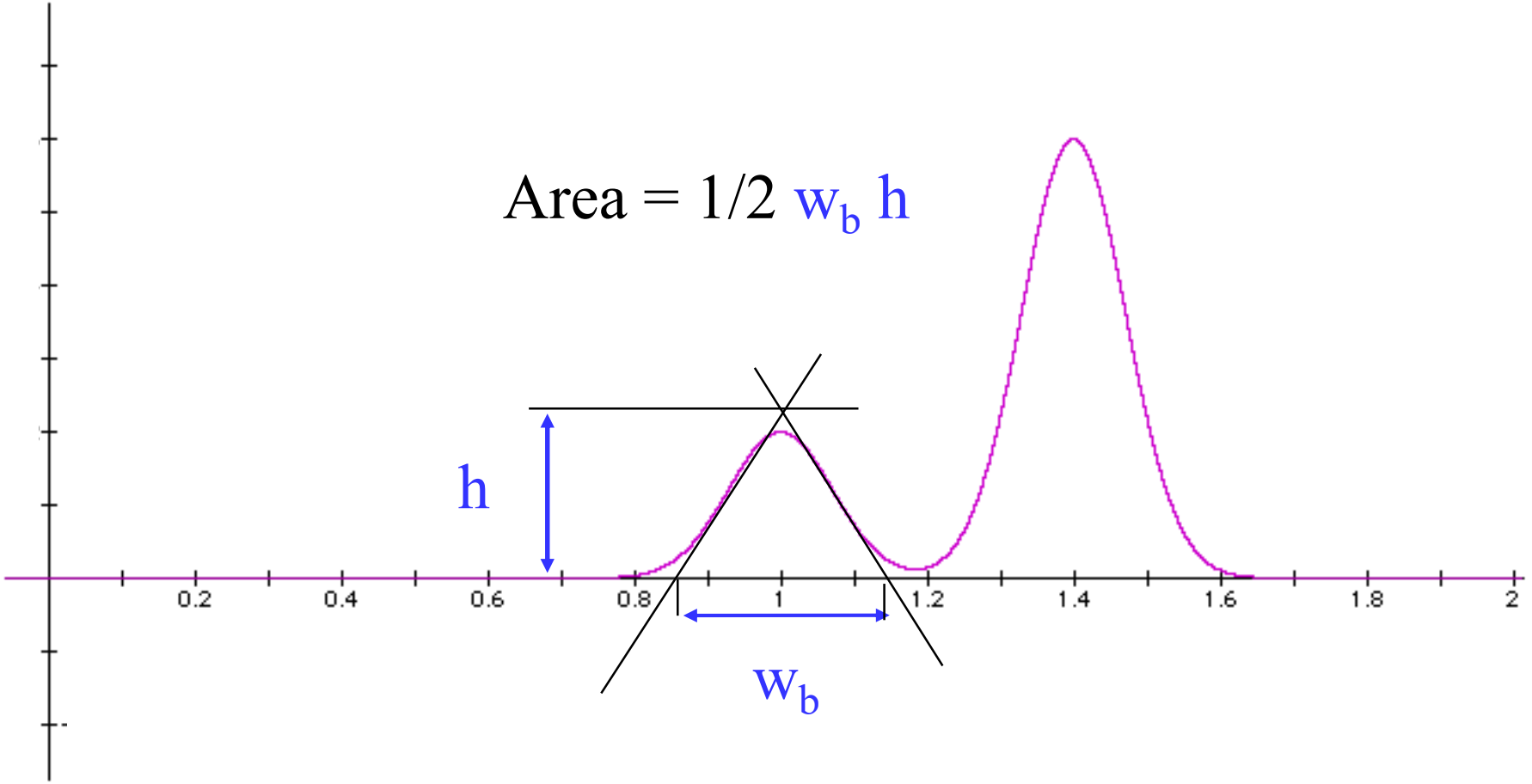
Determination of the Amount of Sample Components Present



The peak height is proportional to the amount of material eluting from the column at any given time.

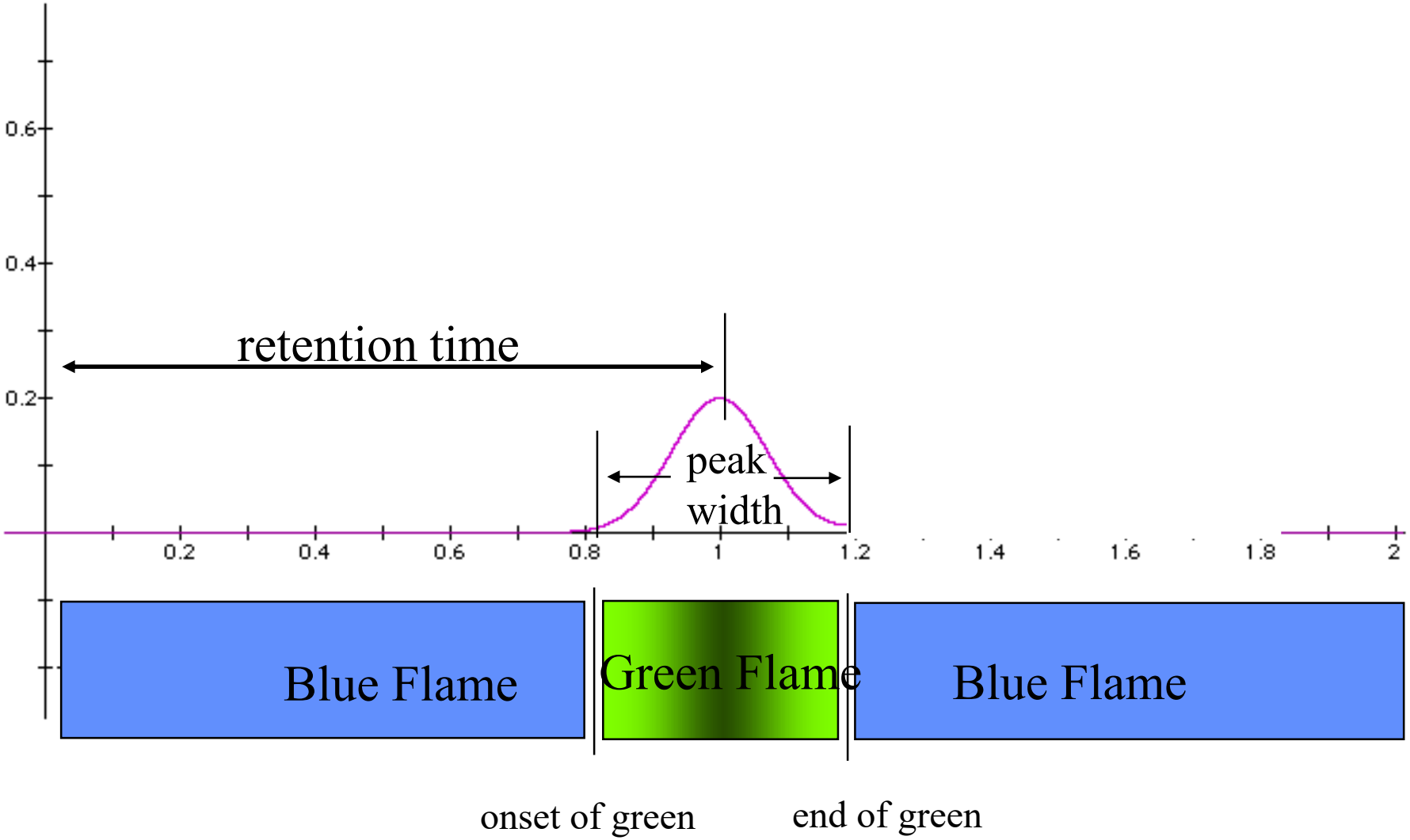
The area under the peak is a measure of the total amount of material that has eluted from the column.

The Gaussian curve can be approximated as triangular in shape, to simplify area measurement.



NOTE: the height is measured to the top of the tangents, which is above the actual curve peak.

Retention time은 같은 분석 조건 하에서는 물질마다 고유한 값을 가질 것이며, 물질의 정성분석을 가능하게 한다.



The End.