

# **Advanced Methods in Analytical Chemistry**

Given in 2020-2021 by

Dr. Alex Gordin

Teaching Assistant: Ms. Ksenia J. Margolin Eren

The course is arranged in five main subjects:

1. Chromatography and GC.
2. Gas chromatography detectors.
3. Liquid chromatography.
4. Mass spectrometry including GC-MS and LC-MS.
5. Atomic spectroscopy and elemental analysis.

*The figures can also be viewed and downloaded from the course web site:*

<http://www.tau.ac.il/~instanal/Instrumental%20Analytical%20Chemistry.htm>

## Internet Links

### Chemistry-Based

QuickTime, Shockwave Flash

GIF Animations, and Streaming Audio

(PDF and HTML augmentations of many of these are also [available](#).)

Contains informative short animation clips describing a range of analytical instrumentation, including GC (in general, split splitless injection, detectors), HPLC 6-port injector, GC-MS and Atomic Absorption.

Some of the clips include audio narrations [http://www.shsu.edu/~chm\\_tgc/sounds/sound.html](http://www.shsu.edu/~chm_tgc/sounds/sound.html)



The Virtual Mass Spectrometry Laboratory. Includes general

information, tutorials (GC-MS), and case studies <http://svmsl.chem.cmu.edu/vmsl/>



<http://www.ionsource.com/tutorial/chromatography/rphplc.htm#Introduction>



An informative and user-friendly site. HPLC, LC-MS and FTIR courses, including short clips.

<http://shula-lc.co.il/>



Including news from the field of chromatography, several training tests and links. <http://www.separationsnow.com>



<http://www.lcms.com/>

*You can download this page from the website of the course (<http://www.tau.ac.il/~instanal/Instrumental%20Analytical%20Chemistry.htm>), and then just click on the links.*

*Please let us know at [gordina@tauex.tau.ac.il](mailto:gordina@tauex.tau.ac.il) or [kсения@mail.tau.ac.il](mailto:kсения@mail.tau.ac.il) on any other website that you find as useful and informative for next year's links.*

# *Books*

**Principles of Instrumental Analysis**, 7th Edition;

Douglas A. Skoog, F. James Holler, Stanley R. Crouch

<https://chemistry.com.pk/books/principles-of-instrumental-analysis-7e/>

**Chemical Instrumentation**

H.A. Strobel, - Addison - Wesley Publishing Co.

**Undergraduate Instrumental Analysis**, 7th Edition;

James W. Robinson, Eileen Skelly Frame, George M. Frame II

<http://www.uvm.edu/~gpetrucc/courses/Chem219/Random%20docs/Undergraduate%20Instrumental%20Analysis.pdf>

# *Introduction*

## **“The qualitative and quantitative characterization of matter”**

“Wet chemical methods” - volumetric and gravimetric analyses: acid–base titrations, oxidation–reduction titrations, and gravimetric determinations (high degree of skill, time consuming, destructive...)

Grooving demands:

- Environmental (ozone depletion, sulfur in fuels...)
- Food and Drugs (drug metabolites, etc.)
- Quality Control

Computers and technology improvement (Electrospray, MALDI)

“Instrumental Analysis” - interaction of electromagnetic radiation and matter, or of some physical property of matter, to characterize the sample being analyzed.

## Analytical Approach may include:

1. Defining the problem and designing the analytical method
2. Sampling and sample storage
3. Sample preparation
4. Performing the measurement
5. Assessing the data
6. Method validation
7. Documentation

## Instrumental Analysis:

1. Separation - mostly chemical properties: TLC, LC, GC, SFC, EP.

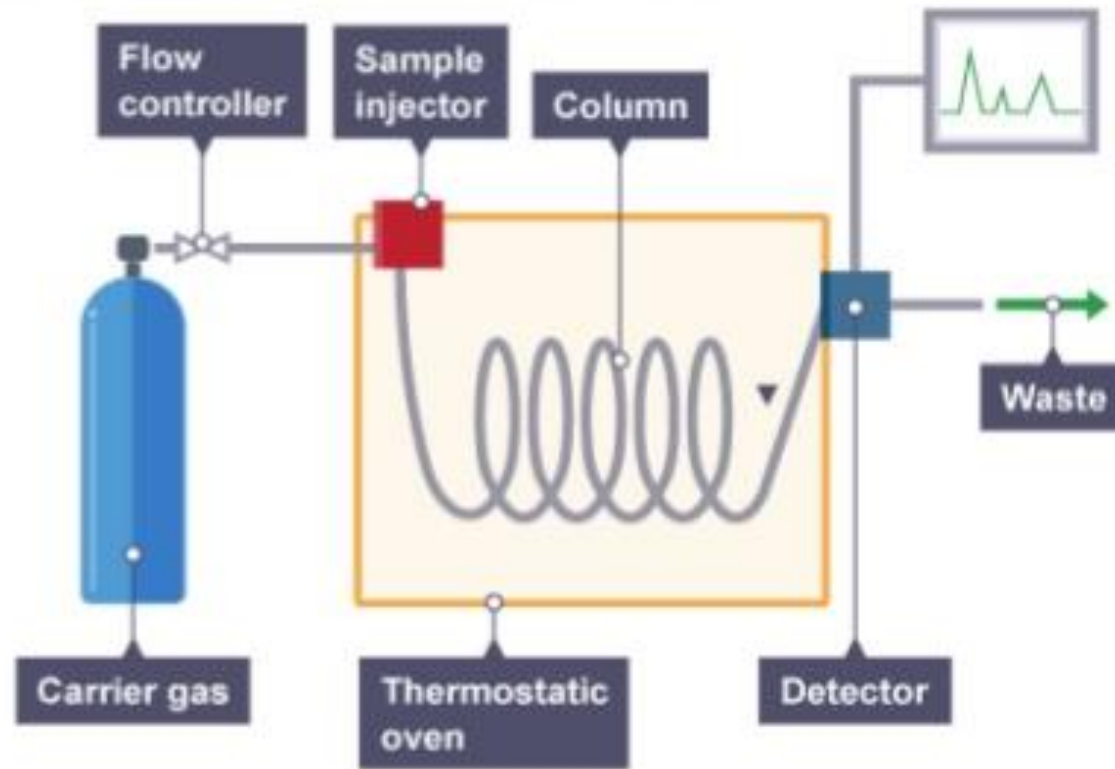
1. Detection (registration): solid state, electrochemical, TCD/FID/ELSD, ECD/PFPD,  
UV/Vis/IR, RI...

1. Identification: NMR, IR, MS, Elemental spectroscopy, XRF...

1. Quantification

# *Chromatography and GC*

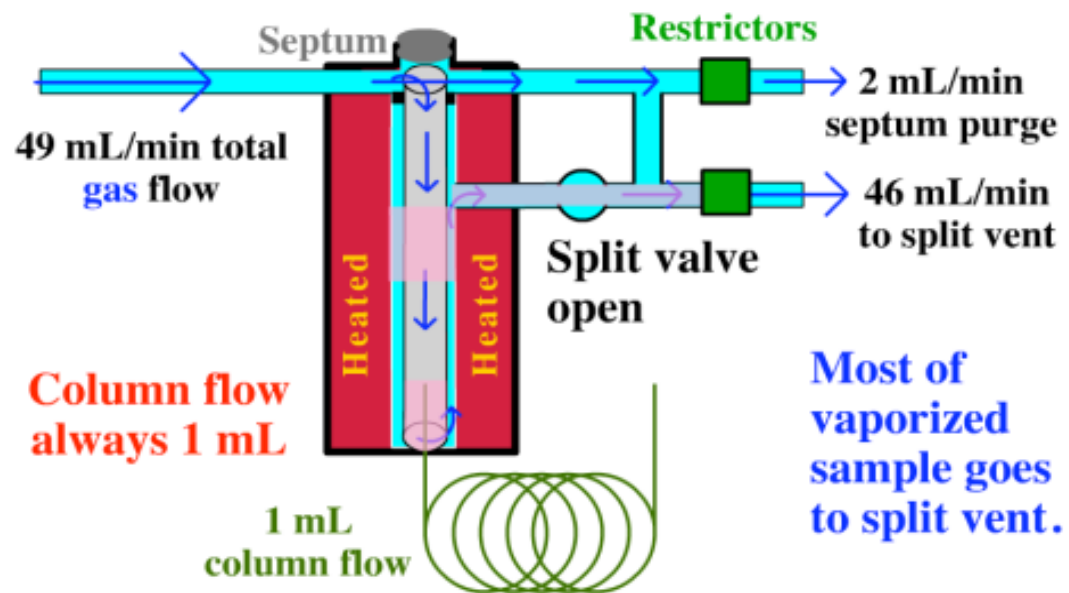
## BLOCK DIAGRAM OF GAS CHROMATOGRAPHY





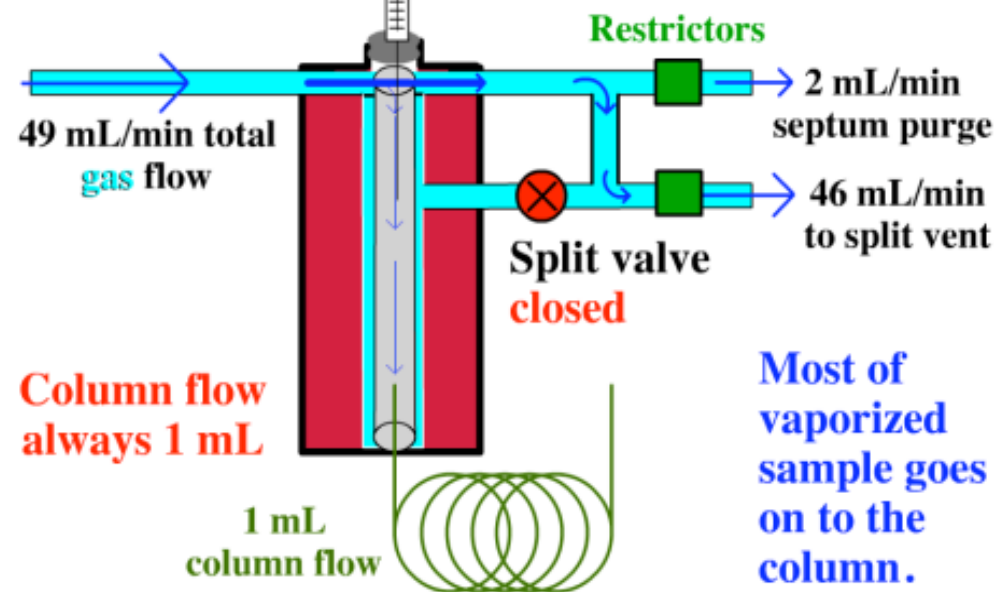
## Split/Splitless Injector

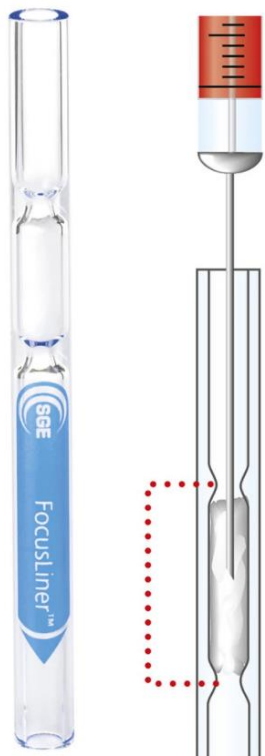
### Split Mode



## Split/Splitless Injector

### Splitless Mode





Double Taper  
Cyclo

Straight



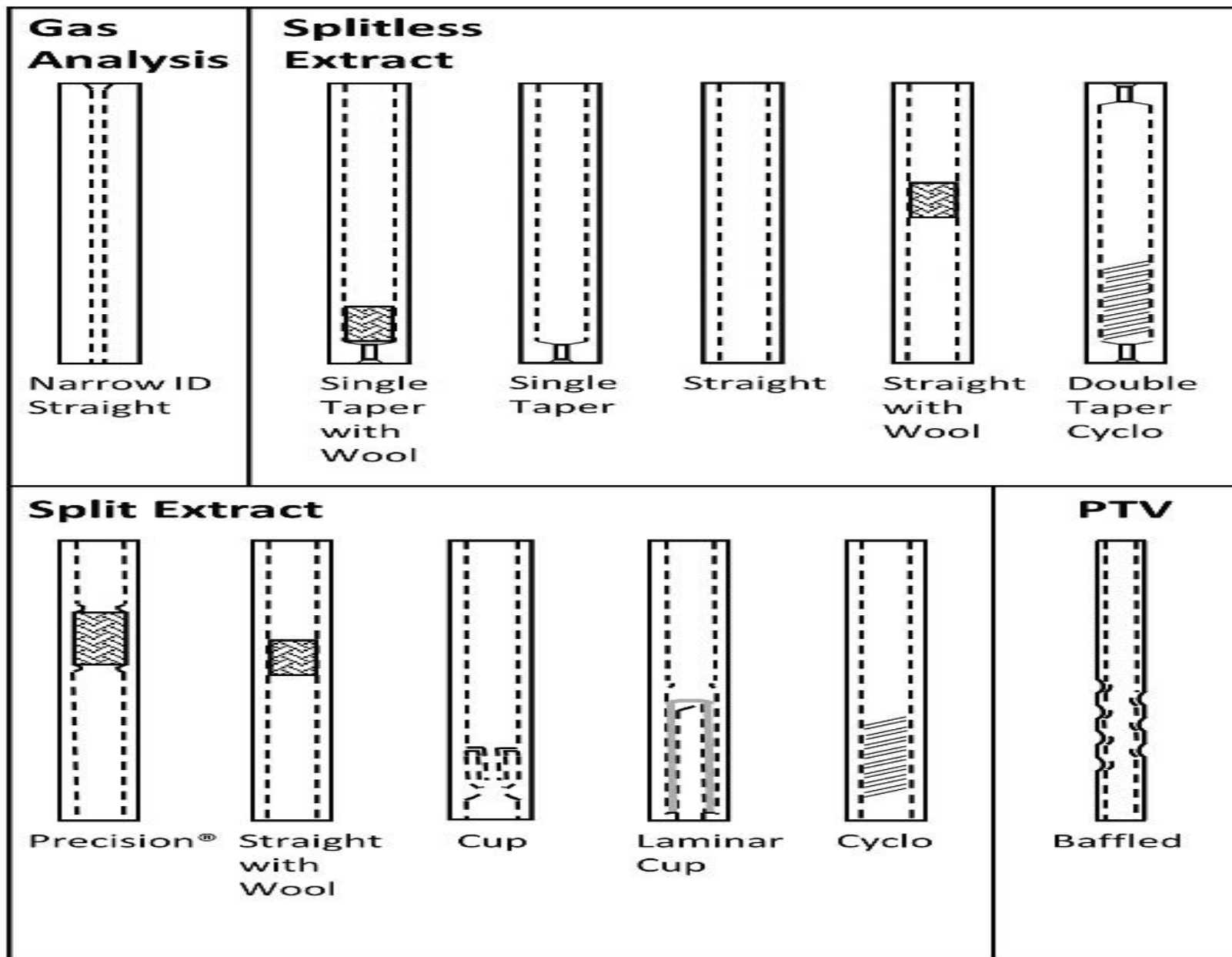
Single Taper w/  
Wool

Single Taper

Low Pressure  
Drop

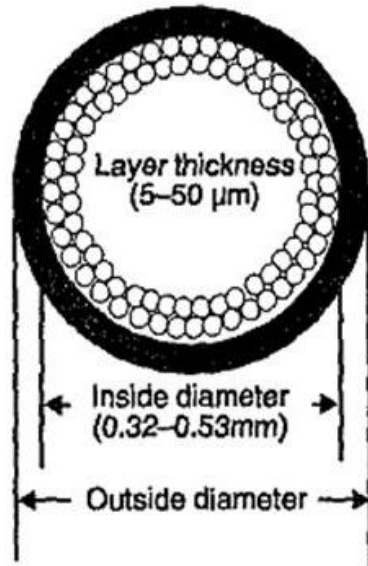


Liner	Catalogue #
Topaz 4mm Single Taper Liner w/ Wool	23303
Topaz 4mm Double Taper Cyclo Liner	23310
Topaz 4mm Single Taper Liner	23302
Topaz 4mm Straight Liner	23301
Topaz 4mm Low Pressure Drop Liner	23467

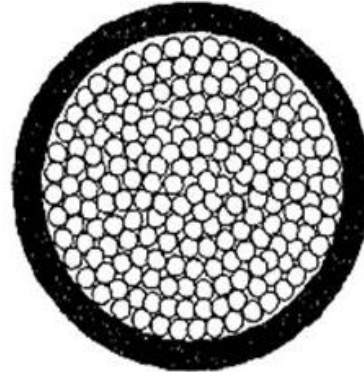


## Choice of GC Columns

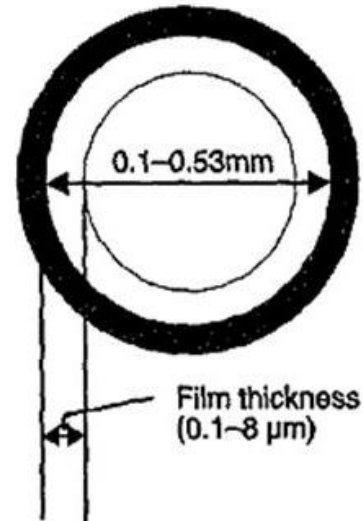
Porous layer open  
tubular column (PLOT)



Packed capillary column  
(diam < 1 mm)



Wall coated open  
tubular column  
(WCOT)



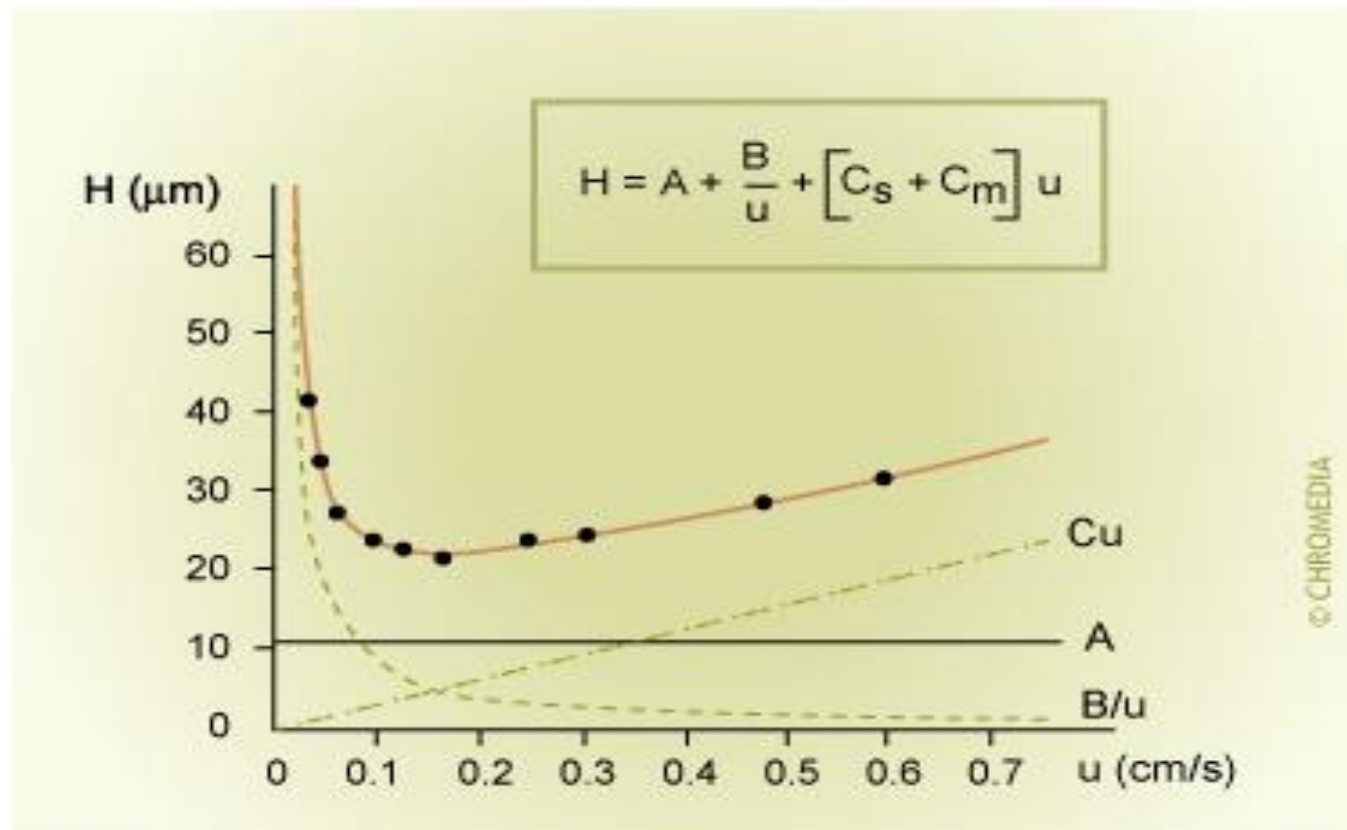




# van Deemter Equation

The efficiency of a column is measured by theoretical plates number,  $N$ , and can be normalized with the length of the column to give the **Height Equivalent Theoretical Plate**, called HETP or  $H$

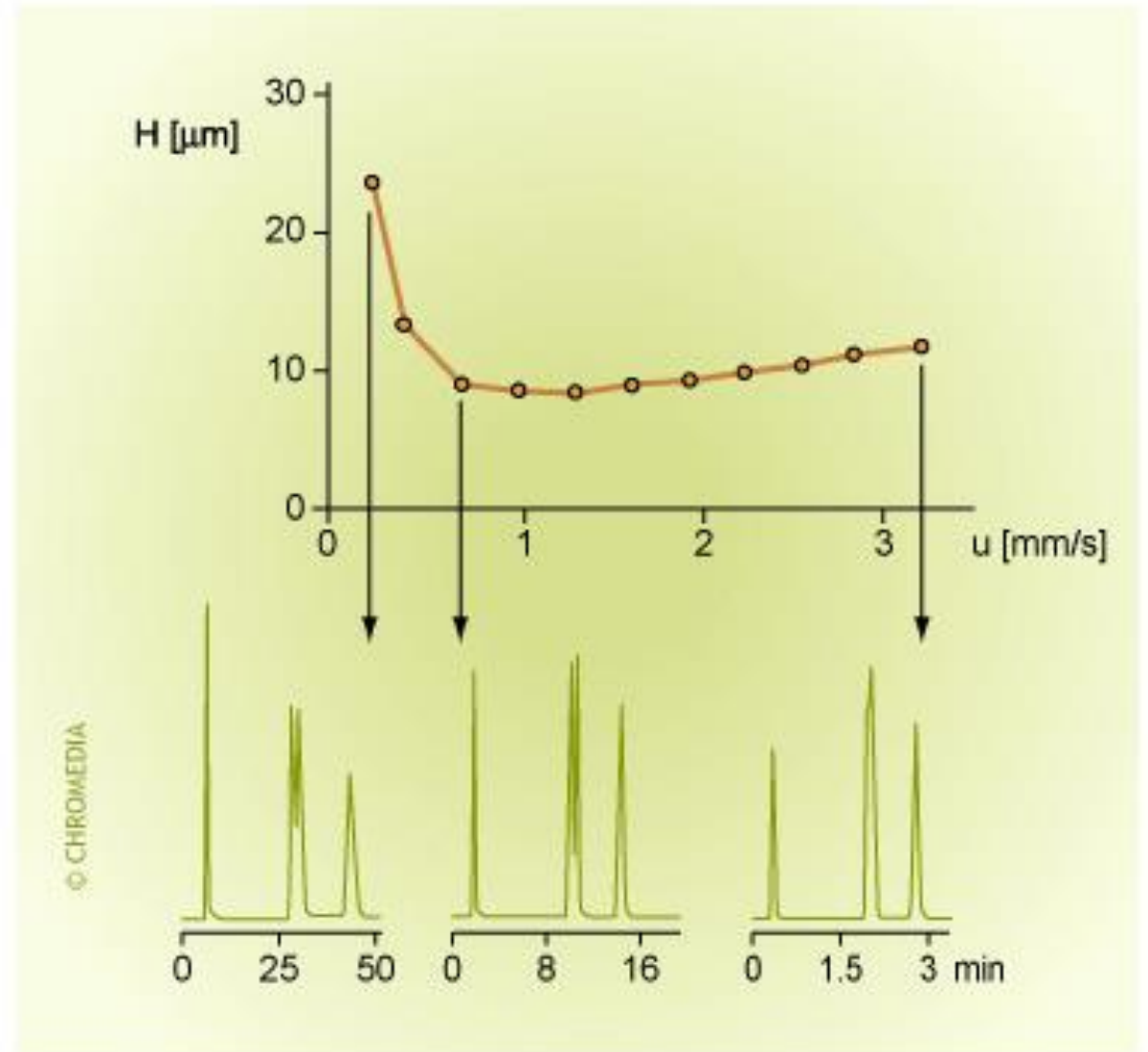
## van Deemter $H/u$ curve



## General rules of thumb:

- The smaller the plate height  $H$ , the more efficient the column. However, **at the optimum flow rate** (with the lowest  $H$ ), the analysis time will in most cases be unacceptably long.
- **Below the optimum flow rate**, the analysis time is too long and the quality of the separation suffers because of longitudinal diffusion (contribution of the B-term).
- **At extremely high flows**, both the separation quality and the pressure drop across the column will become unacceptable.
- **The practical flow is often two or three times the optimum velocity.** At these values, the minor loss of efficiency is still acceptable.
- **Small particles** ( $< 5 \mu\text{m}$ ) allow an increase in the flow to reduce the analysis time without significantly lowering resolution between the peaks of interest.

## Separation and (optimum) velocity



## Eddy Diffusion (A-term)

### Peak broadening due the presence of stationary phase particles in the column

Eddy diffusion occurs as a result of multiple flow paths through a **packed** column bed

- **Particle size**  $d_p$
- **Particle shape** (regular or irregular?)
- Particle pore structure / shape
- Quality of the column packing
- Wall effects (material, roughness, column diameter)

## Longitudinal Diffusion (B-term)

- Linear velocity of the mobile phase
- Diffusion coefficient of analyte in the mobile phase  $D_m$
- Mobile phase viscosity  $\gamma$
- Temperature
- Type of analyte (molecular mass)



## Mass Transfer (C-term)

mass transfer of sample components between the stationary phase and the mobile phase during separation

**$C_m$ -term**, peak broadening in the mobile phase.

Because the linear velocity of the mobile phase is lower closer to the column wall (or the stationary phase particles) than in the center (or further away from the particles), the analyte molecules experience different velocities.

- **Particle size  $d_p$**
- **Linear velocity  $u$  of the mobile phase**
- Diffusion coefficient in the mobile phase
- Porosity of the packing particles
- Viscosity of the mobile phase
- Retention factor  $k$
- Temperature

**$C_s$ -term**, peak broadening in the stationary phase.

The  $C_s$ -term is determined by the amount of stationary phase (low is advantageous for the efficiency) and the extent of interaction of the sample on the phase (represented by the retention factor) and the distances the sample molecules have to travel.

- Quality of stationary phase
- Diffusion coefficient in stationary phase
- Retention factor  $k$
- Temperature
- Particle size
- Mobile phase velocity