Carrier Gases in Capillary GC

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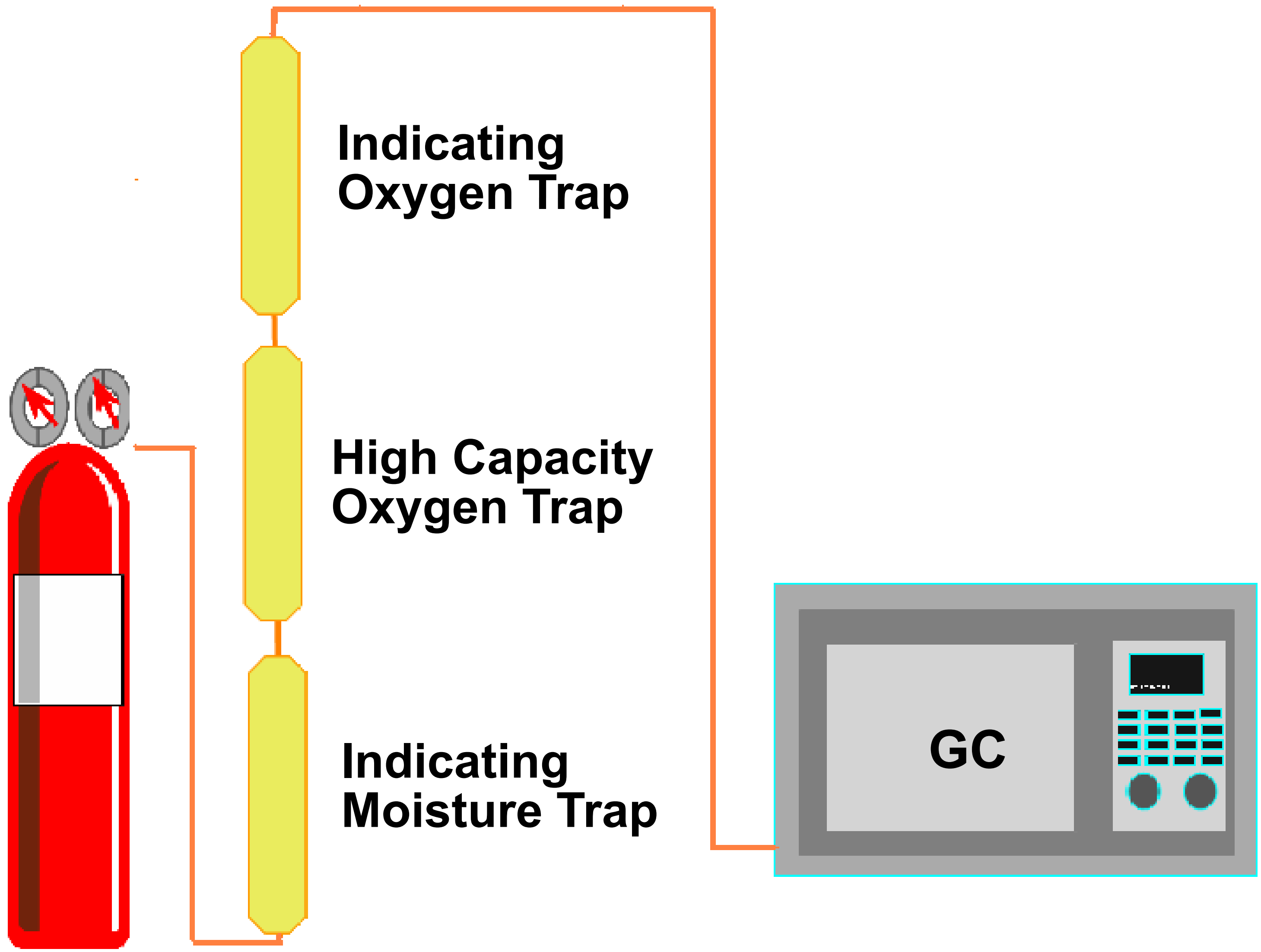
Applications Engineer
February 15, 2011

Configurations for Carrier Gas Purifiers



CARRIER GAS
Mobile Phase

Carries the solutes down the column

Selection and velocity influences efficiency and retention time

Must be inert to solutes and stationary phase

Must be free of detectable contaminants

Must have a leak free and very precise pressure delivery system

COMMON CARRIER GASES

Nitrogen

Helium

Hydrogen

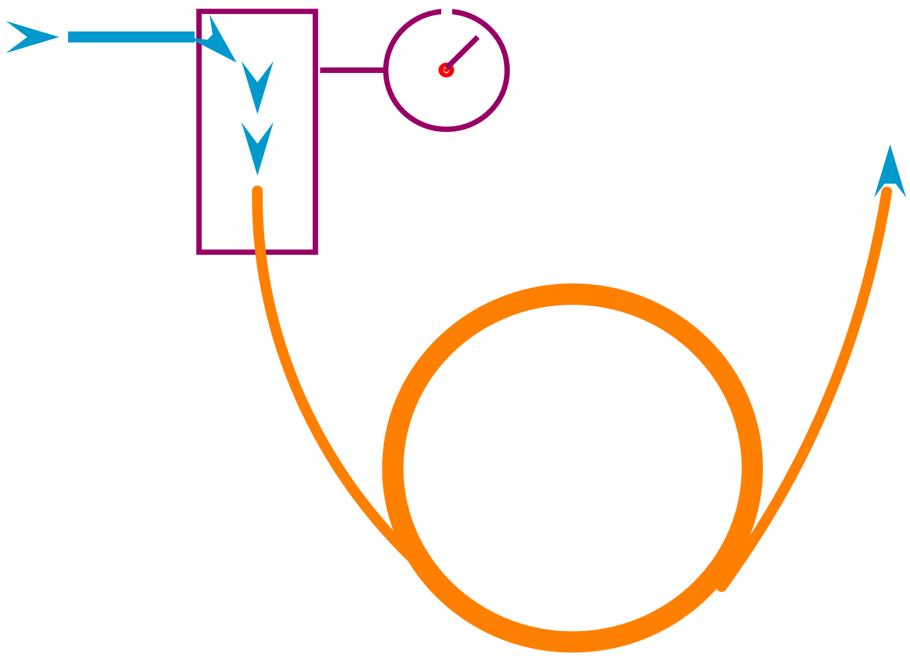
CARRIER GAS
Properties

Compressible

Expands with temperature

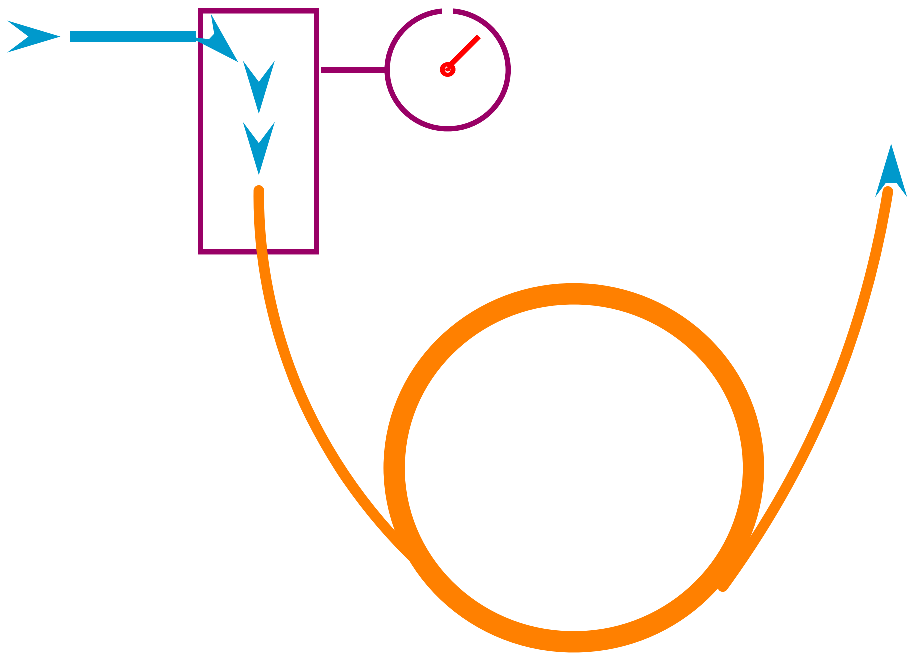
Viscosity increases with temperature

CARRIER GAS
Constant Pressure Mode



Head pressure is constant
Flow decreases with temperature

CARRIER GAS
Constant Flow Mode



Carrier gas flow is constant
Pressure increases with temperature

CARRIER GAS
Consistent Temperature

Set the velocity at the same temperature

Initial temperature is the most convenient

van Deemter Equation

h = Height equivalent to a theoretical plate

Packed Columns

$$h = A + \frac{B}{\bar{u}} + C\bar{u}$$

Open-Tubular Columns

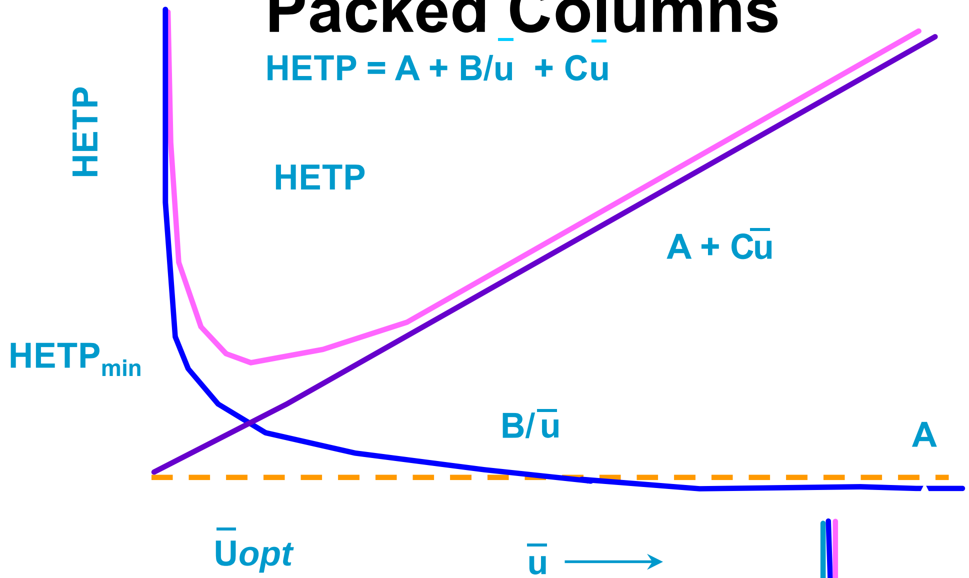
$$h = \frac{B}{\bar{u}} + C\bar{u}$$

A = Multi-path term
B = Longitudinal diffusion term
C = Mass transfer term

van Deemter Curves

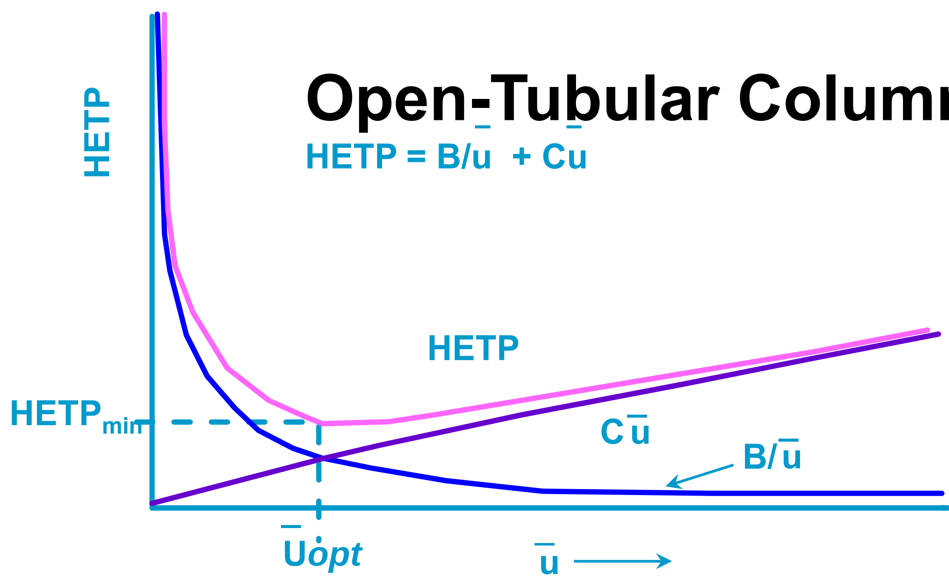
Packed Columns

HETP = A + B/$\bar{u}$ + C$\bar{u}$

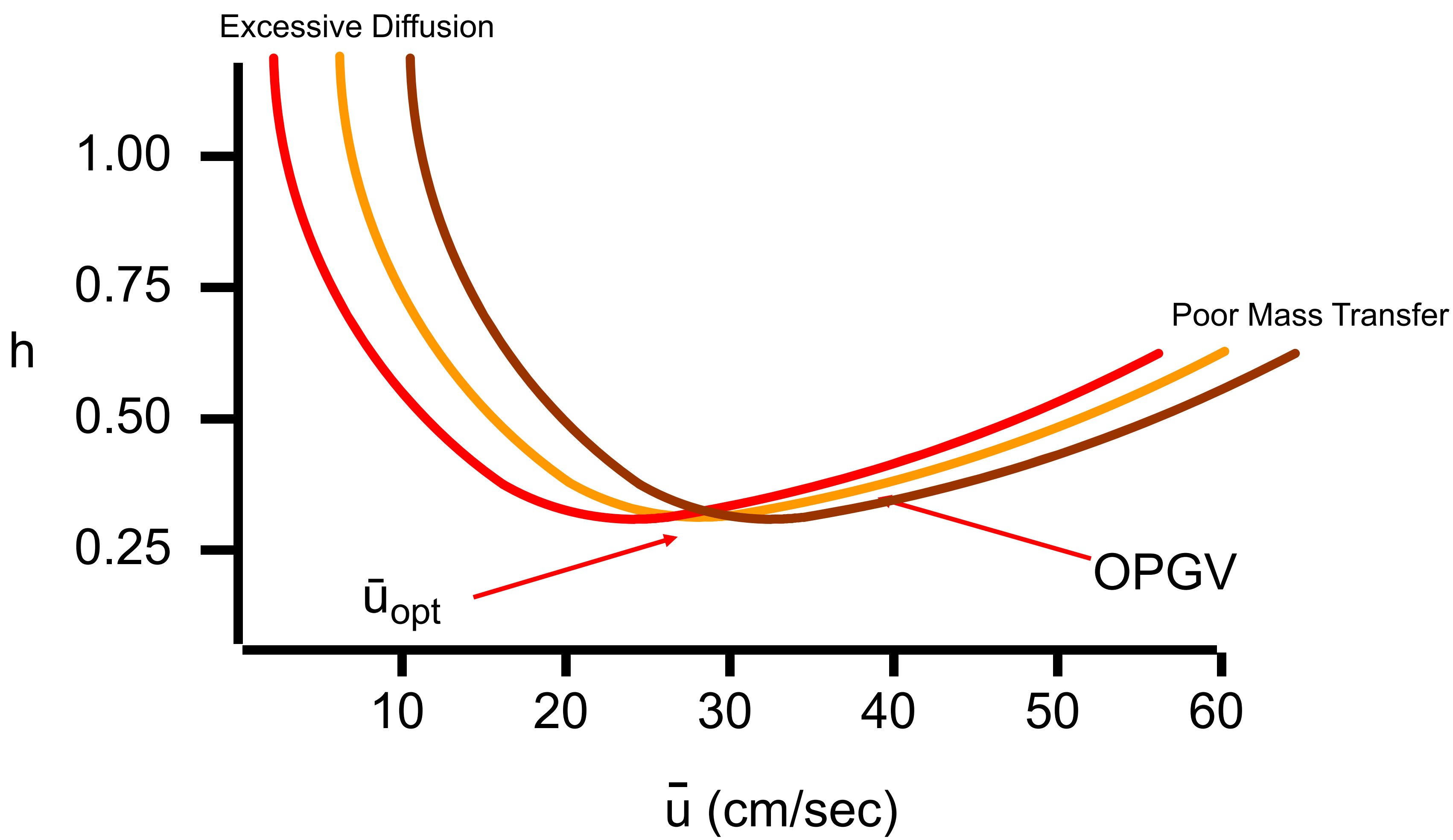


Open-Tubular Column

HETP = B/$\bar{u}$ + C$\bar{u}$



van Deemter Curve



$\bar{u}_{opt}$ and OPGV

$\bar{u}_{opt}$:

Maximum efficiency

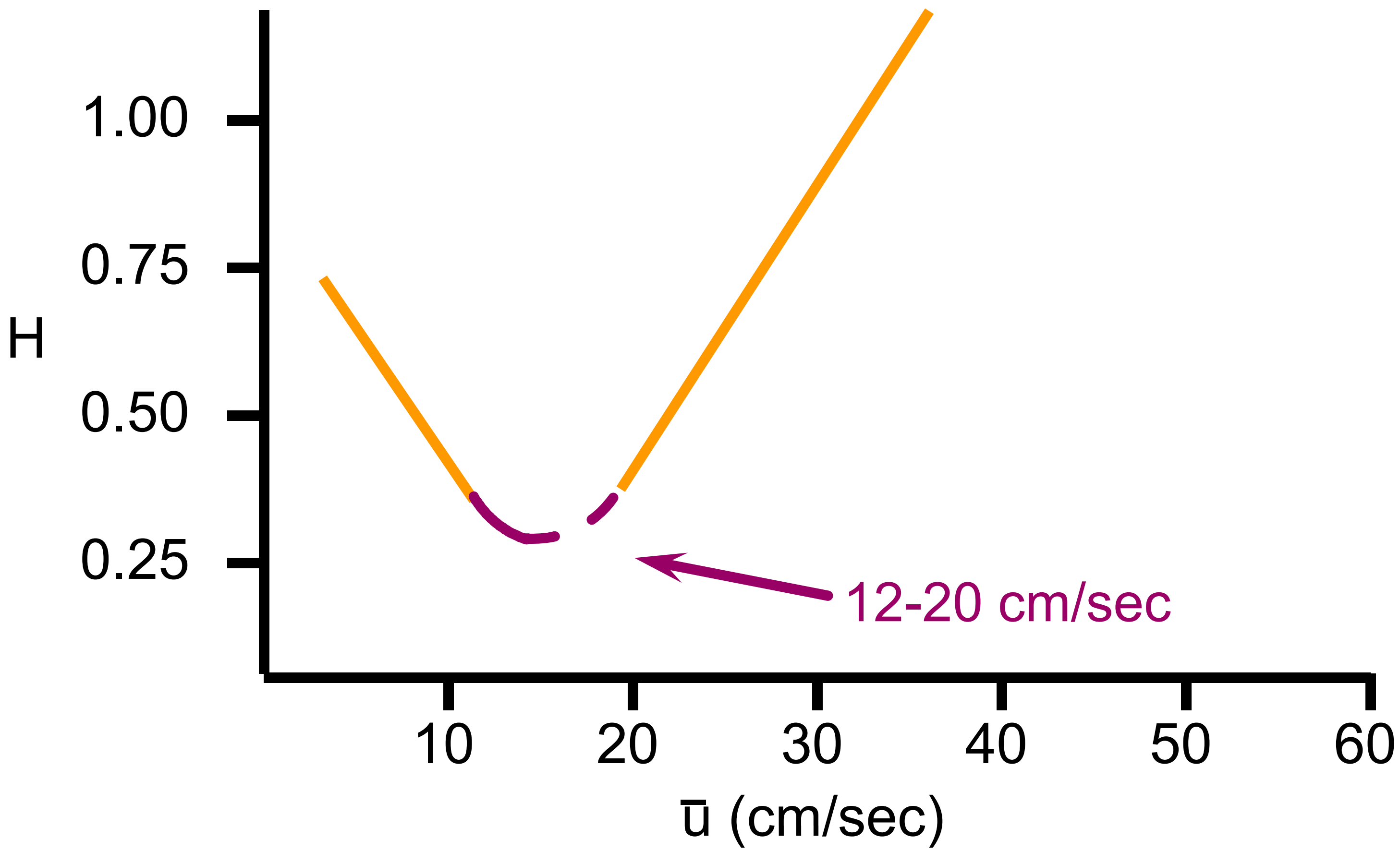
OPGV:

Optimal practical gas velocity

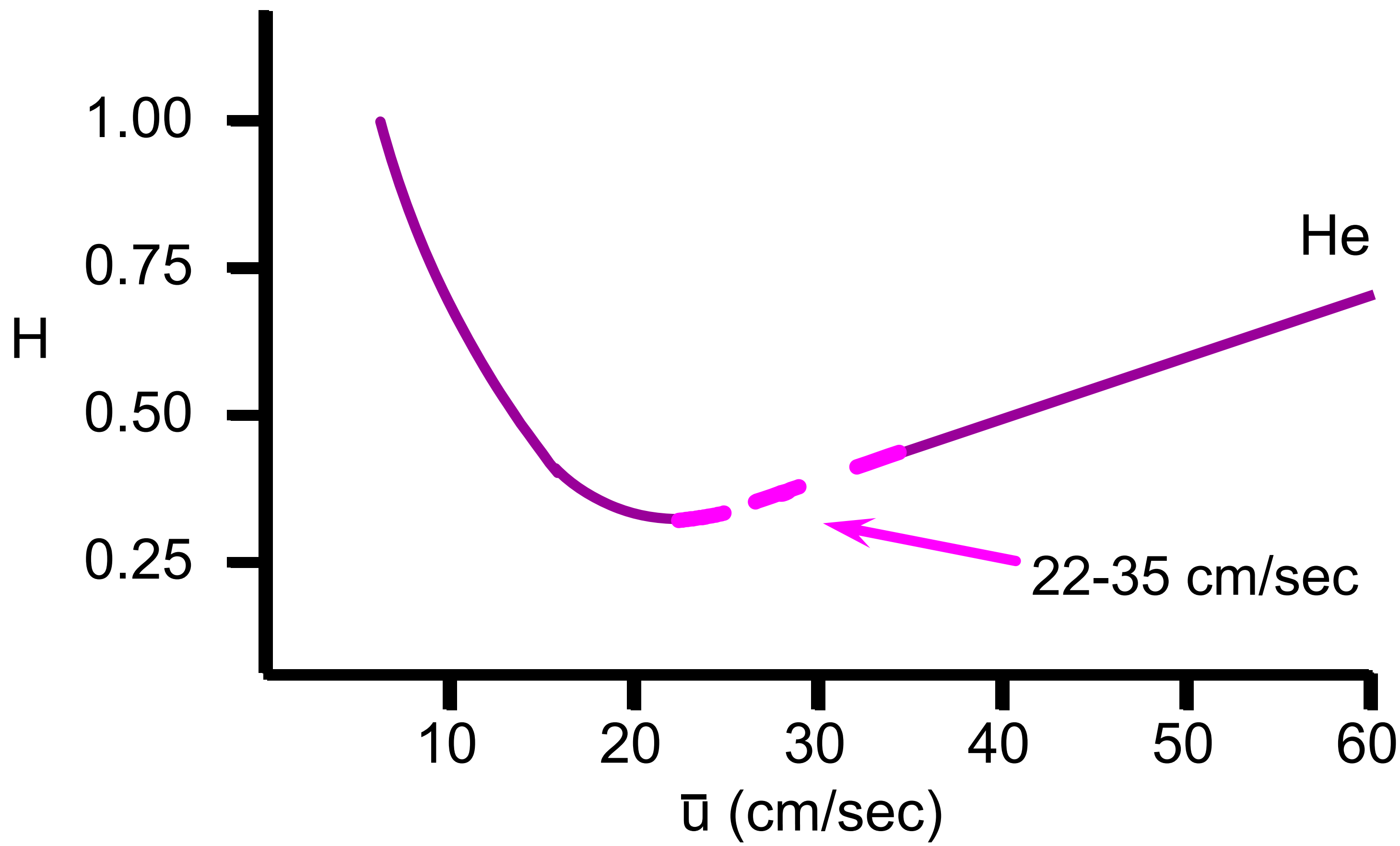
Maximum efficiency per unit time

1.5 - 2x $\bar{u}_{opt}$

VAN DEEMTER CURVE
Nitrogen

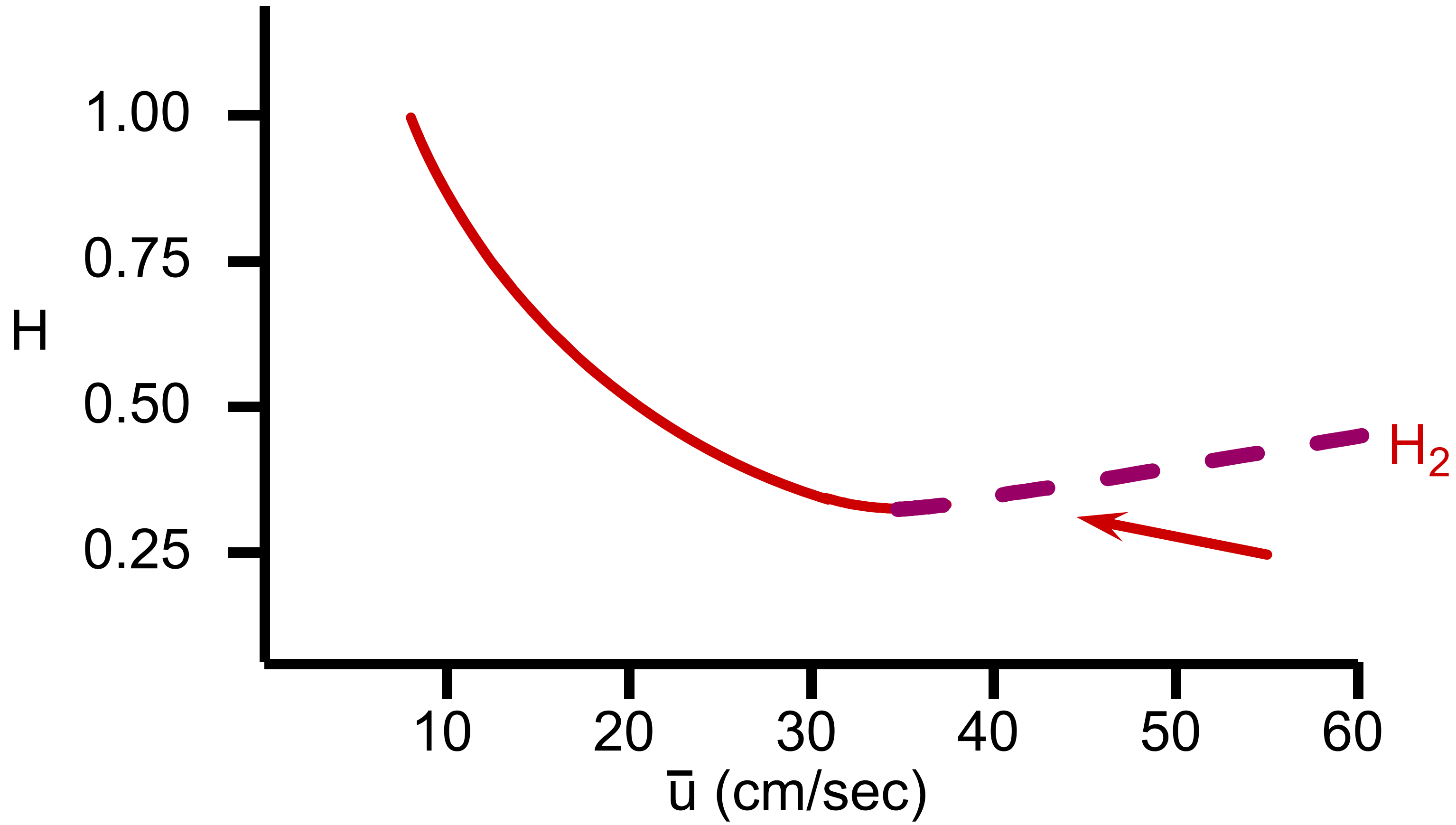


VAN DEEMTER CURVE
Helium

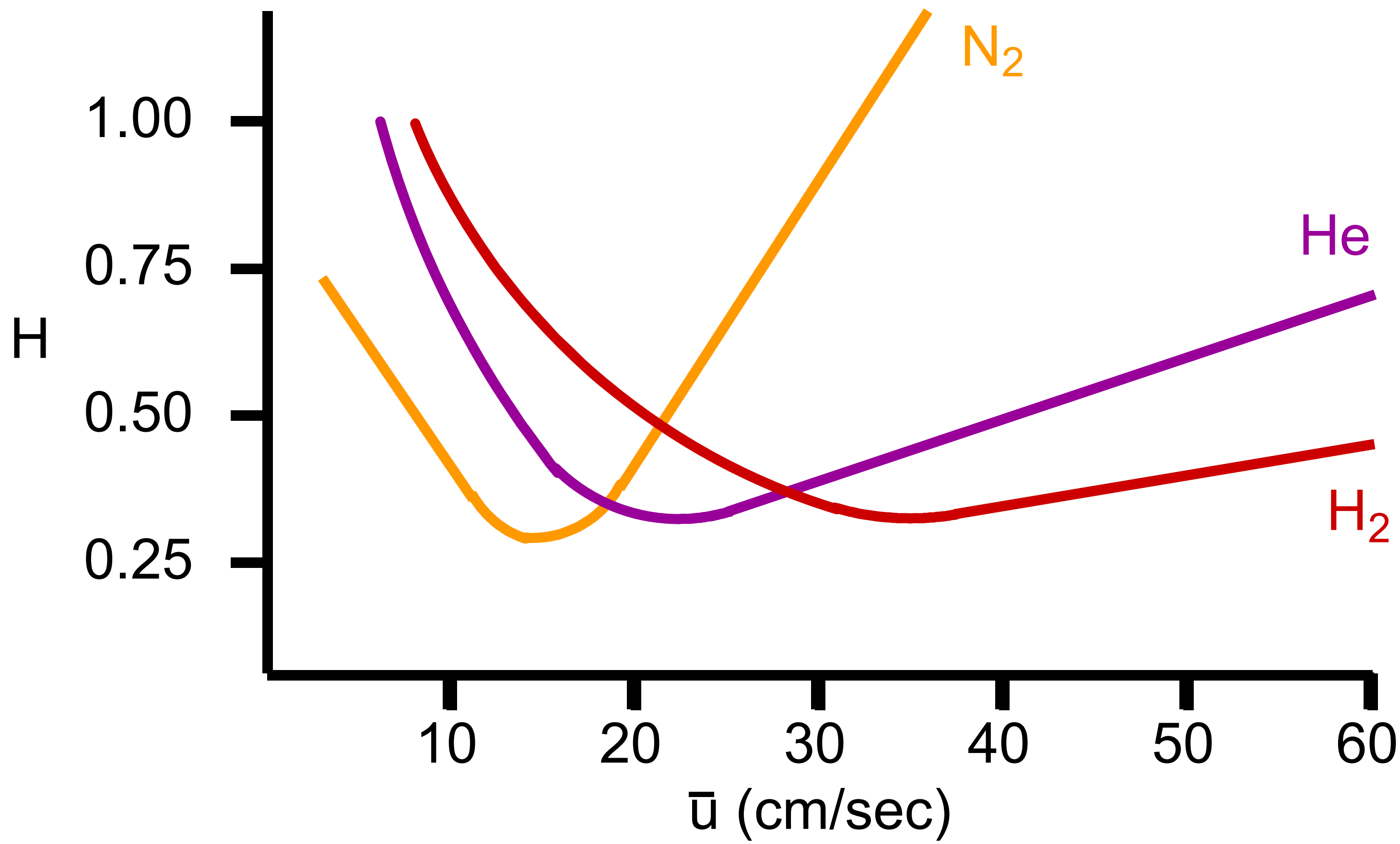


VAN DEEMTER CURVE

Hydrogen



VAN DEEMTER CURVES



CARRIER GAS

Flow Rate (mL/min)

"Volume"

Measurement:

At column exit

Calculate

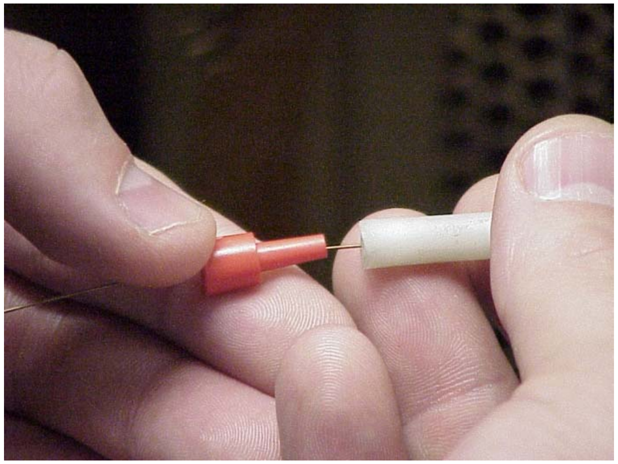
Electronic Pressure Control (EPC)

CARRIER GAS
Flow Rate (mL/min)

"Handy Gizmos" for Flow Measurement:

FID Flow Measuring Insert (p/n 19301-60660)

"Little Red Cap" (p/n 325-0506)



CARRIER GAS

Average Linear Velocity (cm/sec)

"Speed"

$$\bar{u} = \frac{L}{t_m}$$

L = column length (cm)

t_m = retention time of non-retained peak (sec)

FLOW RATE CALCULATION

Provides average flow rate

$$F = \frac{\pi r^2 L}{t_m}$$

r = column radius (cm)
L = column length (cm)
t_m = retention time of a non-retained peak (min)

NON-RETAINED COMPOUNDS

Detector	Compound
FID	Methane, Butane
TCD, MS	Methane, Butane, Air
ECD	Vinyl chloride, SF6
	Methylene Chloride (vapors)*
NPD	Acetonitrile (vapors)*
PID, ELCD	Vinyl chloride

** at elevated temperatures*

CARRIER GAS

Average Linear Velocity Calculation

$$t_m = \frac{L}{\bar{u}}$$

L = column length (cm)

t_m = retention time of non-retained peak (sec)

$\bar{u}$ = desired average linear velocity (cm/sec)

CARRIER GAS

Average Linear Velocity Calculation

$$t_m = \frac{L}{\bar{u}}$$

$$t_m = \frac{3000\ \text{cm}}{32\ \text{cm/sec}} = 93.8\ \text{sec} = 1.56\ \text{min}$$

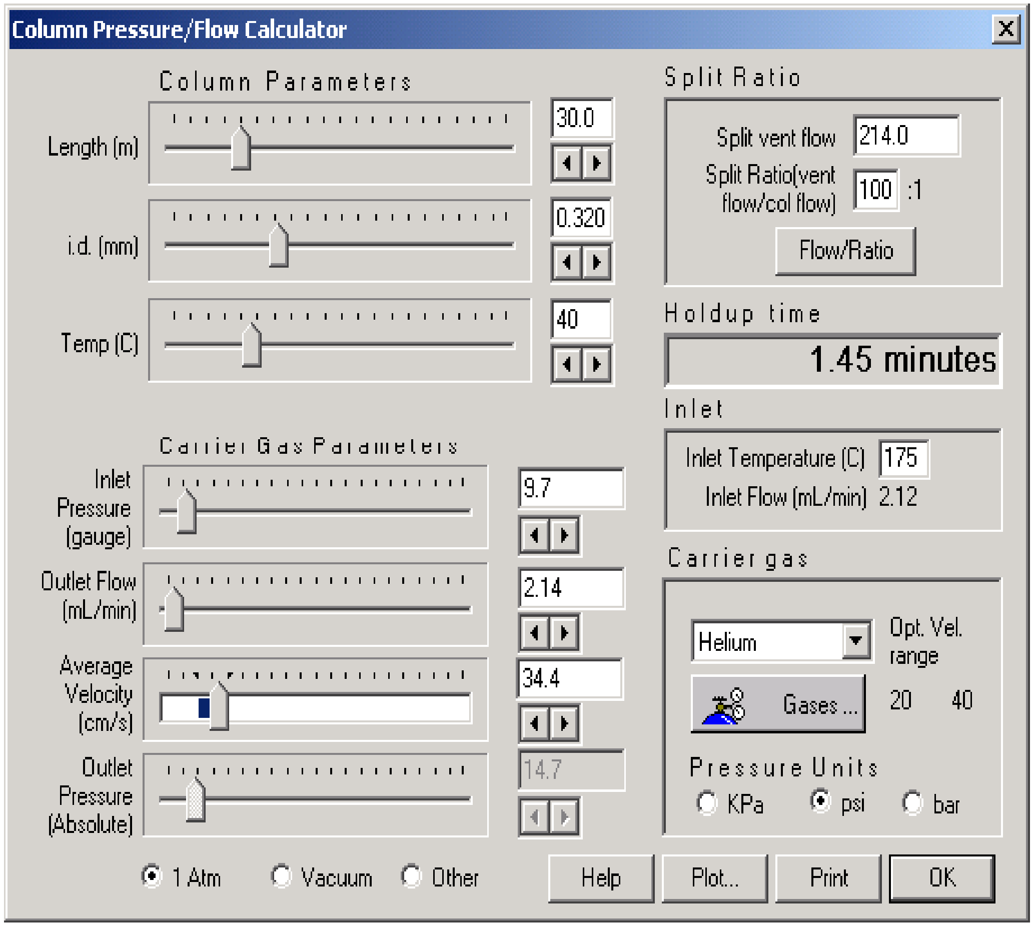
t_m = retention time of non-retained peak (sec)
L = 30 meters = 3000 cm
$\bar{u}$ = 32 cm/sec

Figuring Carrier Gas Flow Rate – the easy way

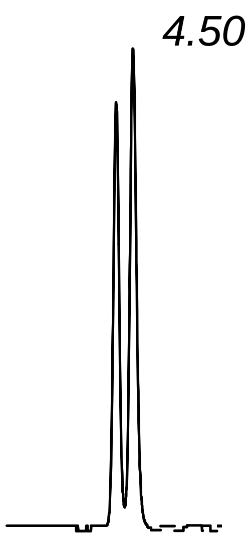
USER CONTRIBUTED SOFTWARE

GC Pressure/Flow Calculator Software

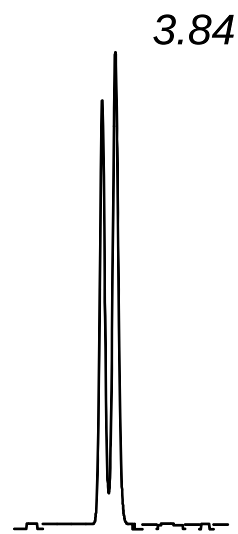
http://www.chem.agilent.com/en-US/Support/Downloads/Utilities/Pages/GcPressureFlow.aspx



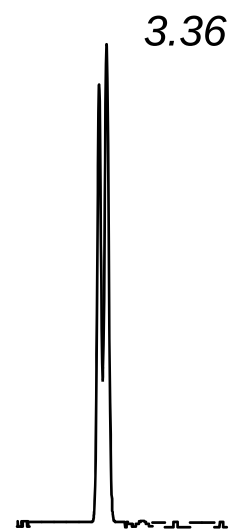
RESOLUTION VS. LINEAR VELOCITY
Helium



R = 1.46
30 cm/sec
4.4 psig



R = 1.31
35 cm/sec
5.1 psig



R = 0.97
40 cm/sec
5.8 psig

Effect of dimensional tolerances in capillary GC columns

I understand why RT changes occur with "in use" columns, but why with new columns?

- Normal dimensional differences in capillary tubing
  - Length
  - Inner diameter
- Minor differences in film thickness (β)
- Variability in phase selectivity (RI)
  - More of an issue with high polarity phases

Capillary Tubing Dimensional Tolerances

Capillary columns manufactured by Agilent Technologies have a general dimensional specification of:

- **Length** — **within about 0.5 meter (≈ 1 "loop")**
- **ID** — **± 6 μm**

Variation in internal diameter is a normal distribution around nominal. Approximating the range (12 μm) as 6 times the standard deviation, there is a 95.5% probability that tubing will be within ± 4 μm.

Let's look at the effects of these actual tubing dimensions on the pressures required to maintain retention times for a method…

Relationship of Tubing Dimensions and Pressure: 30m x 0.25mm ID column

L (m)	ID (µm)	P (psi)	% of nominal P
29.5	255	8.2	82%
30.0	**250**	**10.0**	**100%**
30.5	245	11.9	119%

Conditions: vacuum outlet **(MSD),** helium carrier, 100°C oven temperture, maintained T_m at 1.38 min

L (m)	ID (µm)	P (psi)	% of nominal P
29.5	255	9.3	93%
30.0	**250**	**10.0**	**100%**
30.5	245	10.9	109%

Conditions: atmospheric outlet **(FID),** helium carrier, 100°C oven temperture, maintained T_m at 2.60 min

Relationship of Tubing Dimensions and Pressure: 12m x 0.20mm ID column

L (m)	ID (µm)	P (psi)	% of nominal P
11.5	205	6.9	69%
12.0	**200**	**10.0**	**100%**
12.5	195	13.5	135%

Conditions: vacuum outlet **(MSD),** helium carrier,
100°C oven temperture,
maintained T_m at 0.345 min

L (m)	ID (µm)	P (psi)	% of nominal P
11.5	205	8.7	87%
12.0	**200**	**10.0**	**100%**
12.5	195	11.5	115%

Conditions: atmospheric outlet **(FID),** helium carrier,
100°C oven temperture,
maintained T_m at 0.651 min

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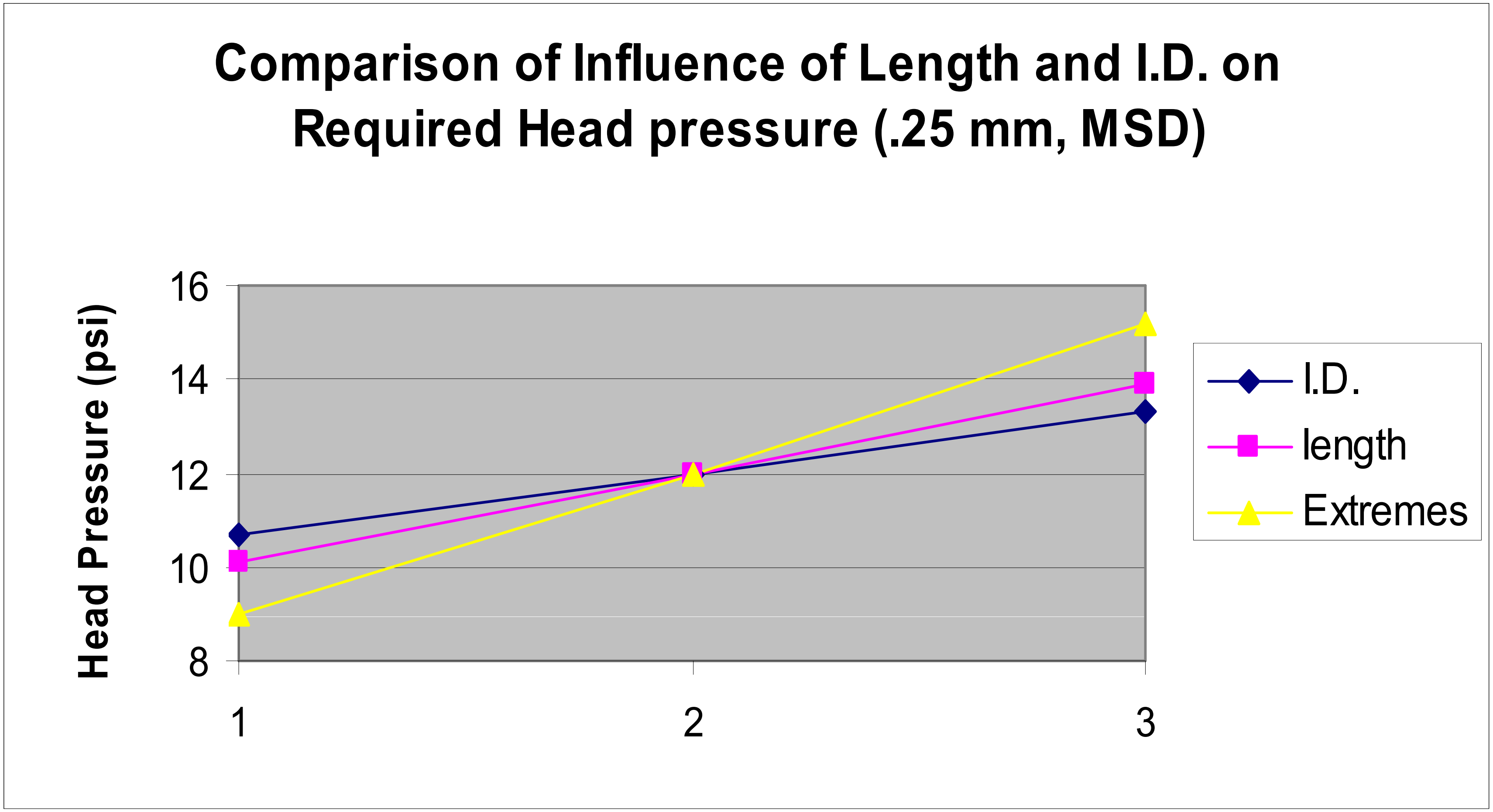
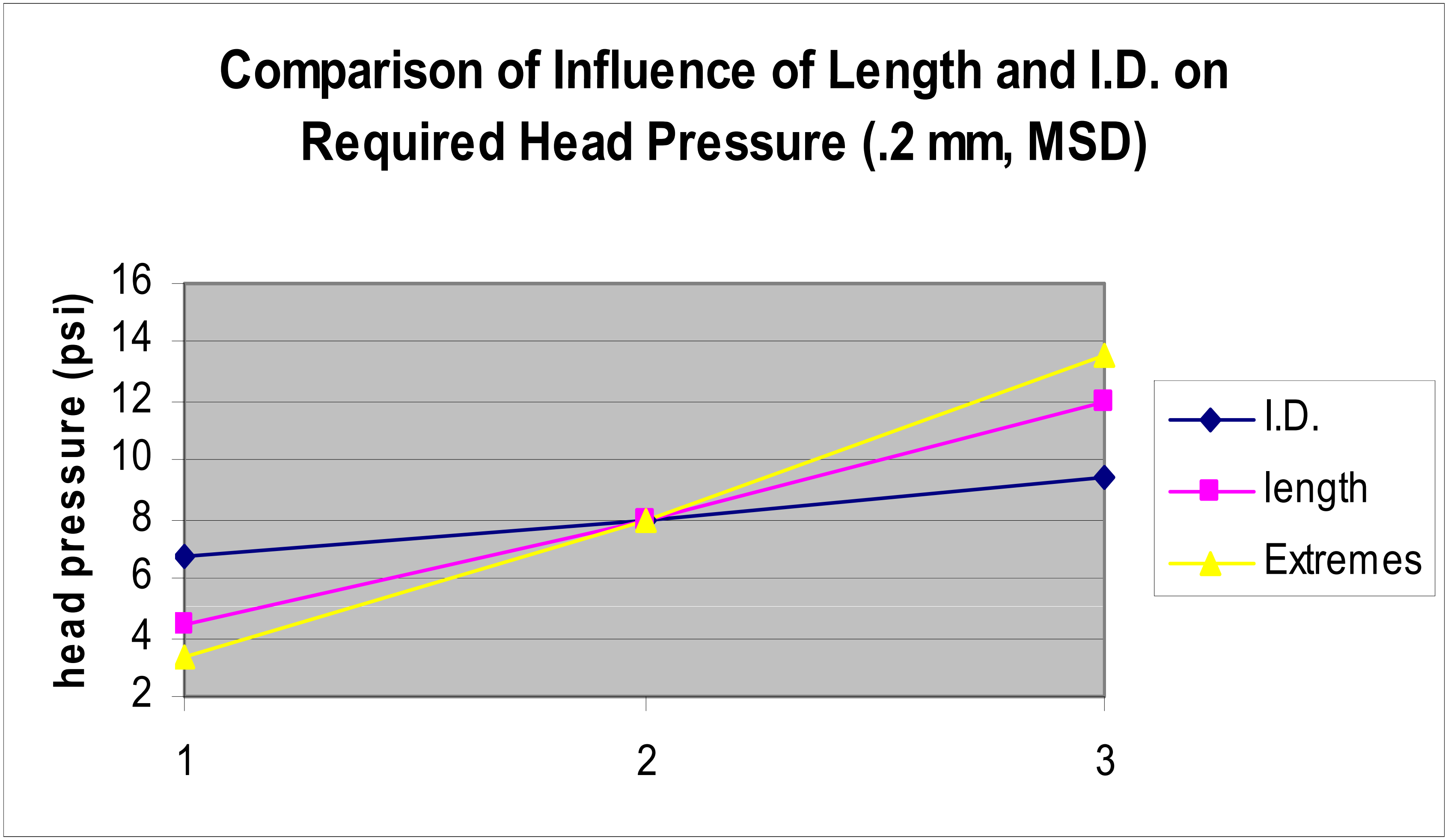


“Extremes” denotes combination of smallest ID/longest column and vice versa. (±1 m length; ±6 µm ID)



"Extremes" denotes combination of smallest ID/longest column and vice versa. (±1 m length; ±6 µm ID)

Impact of Dimensional Differences on Required P

Impact varies inversely with length and ID

- **The relative percentage of impact increases as nominal length and ID decrease.**

Additionally, vacuum outlet (MSD) greatly exaggerates pressure drop across the tubing. This in turn amplifies the differences in head pressure required to maintain T_m

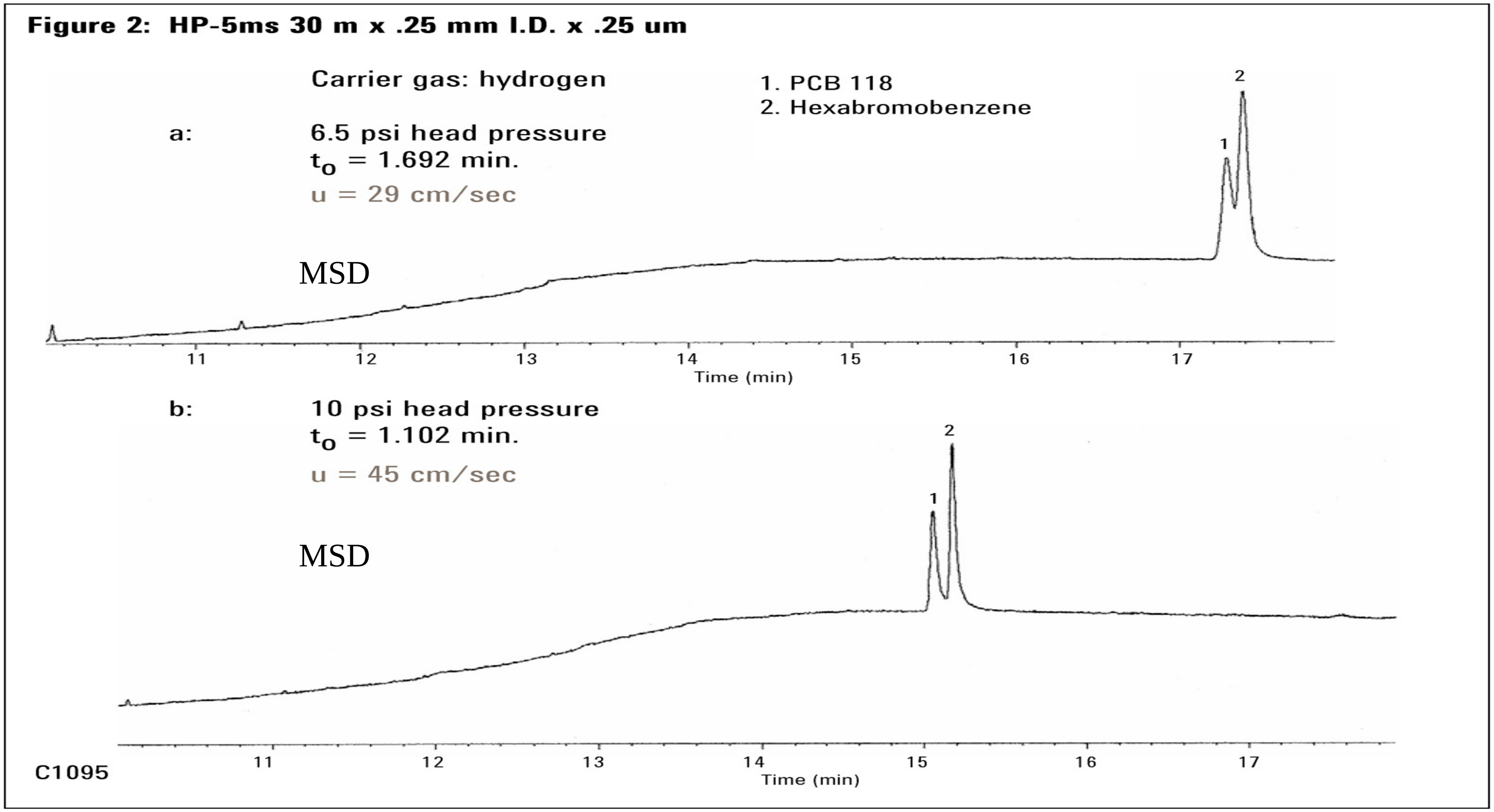
“I don’t use retention time windows. Why should I care if my retention times shift?”

Retention time changes in temperature programmed analyses can also alter the *elution sequence of solutes…*

Solutes elute in an order mandated by their *“net” vapor pressures - i.e., vapor pressures* under their gas chromatographic conditions.

Impact of Dimensional Differences on R

Not only may absolute retention times change, but resolution may change as well due to changes in carrier gas linear velocity (efficiency; HETP)



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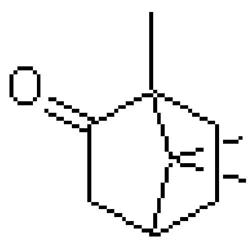
Net Vapor Pressure

The net vapor pressure is the intrinsic vapor pressure *reduced by the sum of all solute-stationary phase interactions* (e.g., dispersion, proton sharing and dipole interactions, *all of which are influenced by temperature*).

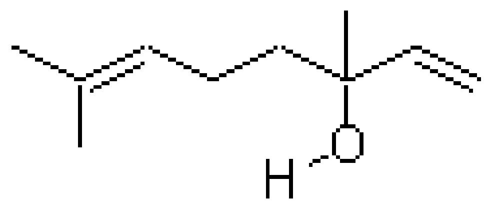
If considerations for the inter-effects of length, diameter and gas velocity are not factored into the method's Standard Operating Procedure (SOP) the end result can be:

- Loss of resolution
- Complete reversal of elution
  - **More common in mixtures of disparate functionalities; it does not occur with homologues.**
  - **Also more common with solutes and stationary phases employing multiple modes of solute-stationary phase interactions.**

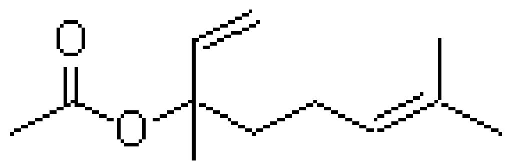
Example -- Compounds of Interest



d-Camphor,
b.p 176-180°C
keto function
Weak H-Bonding,
Van der Waals



Linalool
b.p. 199°C
hydroxy and alkene functions
Strong H-Bonding, weak dipole,
Van der Waals

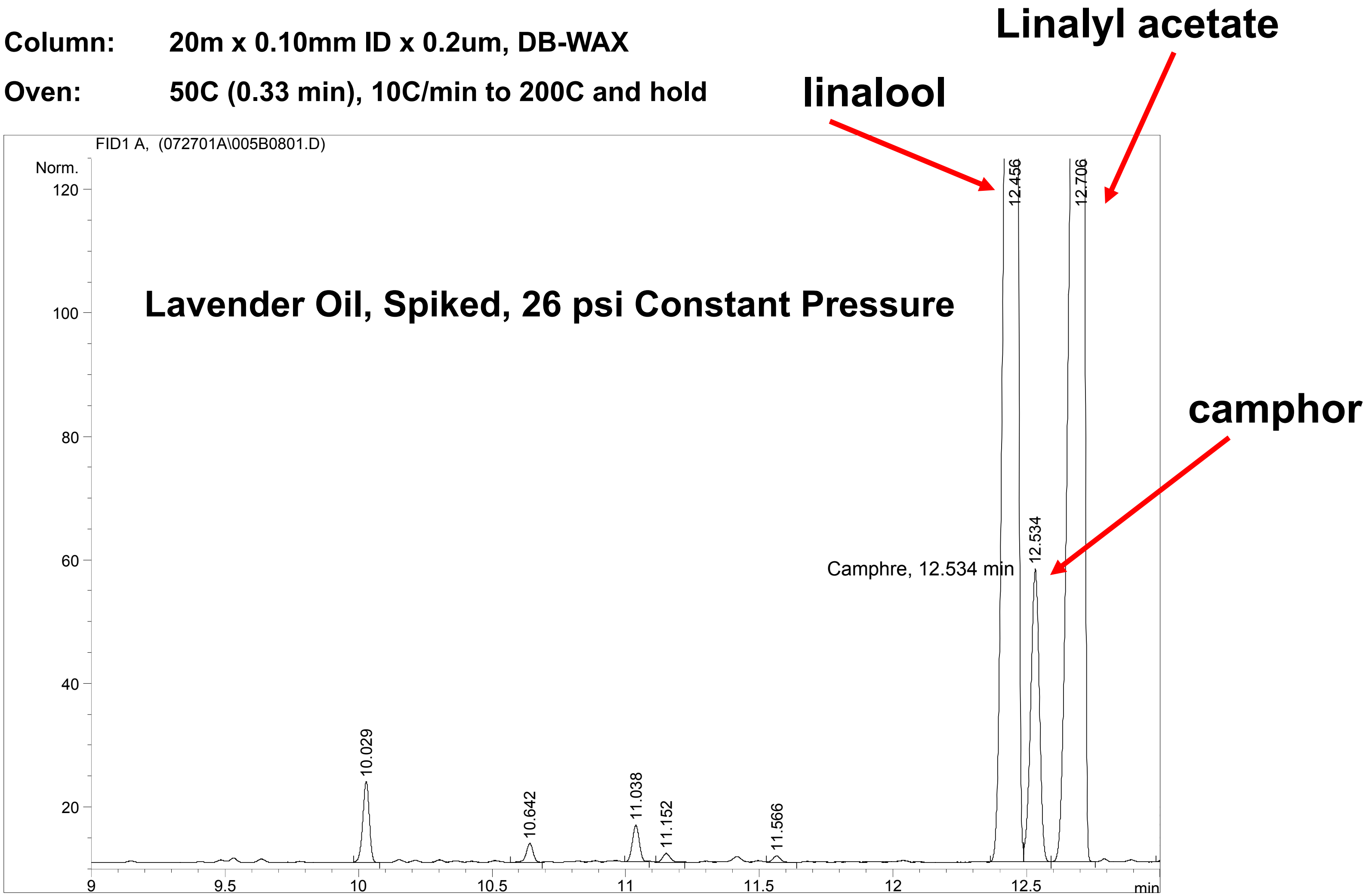


Linalyl acetate
b.p. 220°C
acid ester
and alkene functions
2 x Weak H-Bonding,
weak dipole, Van der Waals

Effects of Head Pressure on Elution Order: 26 psi

Column: 20m x 0.10mm ID x 0.2um, DB-WAX

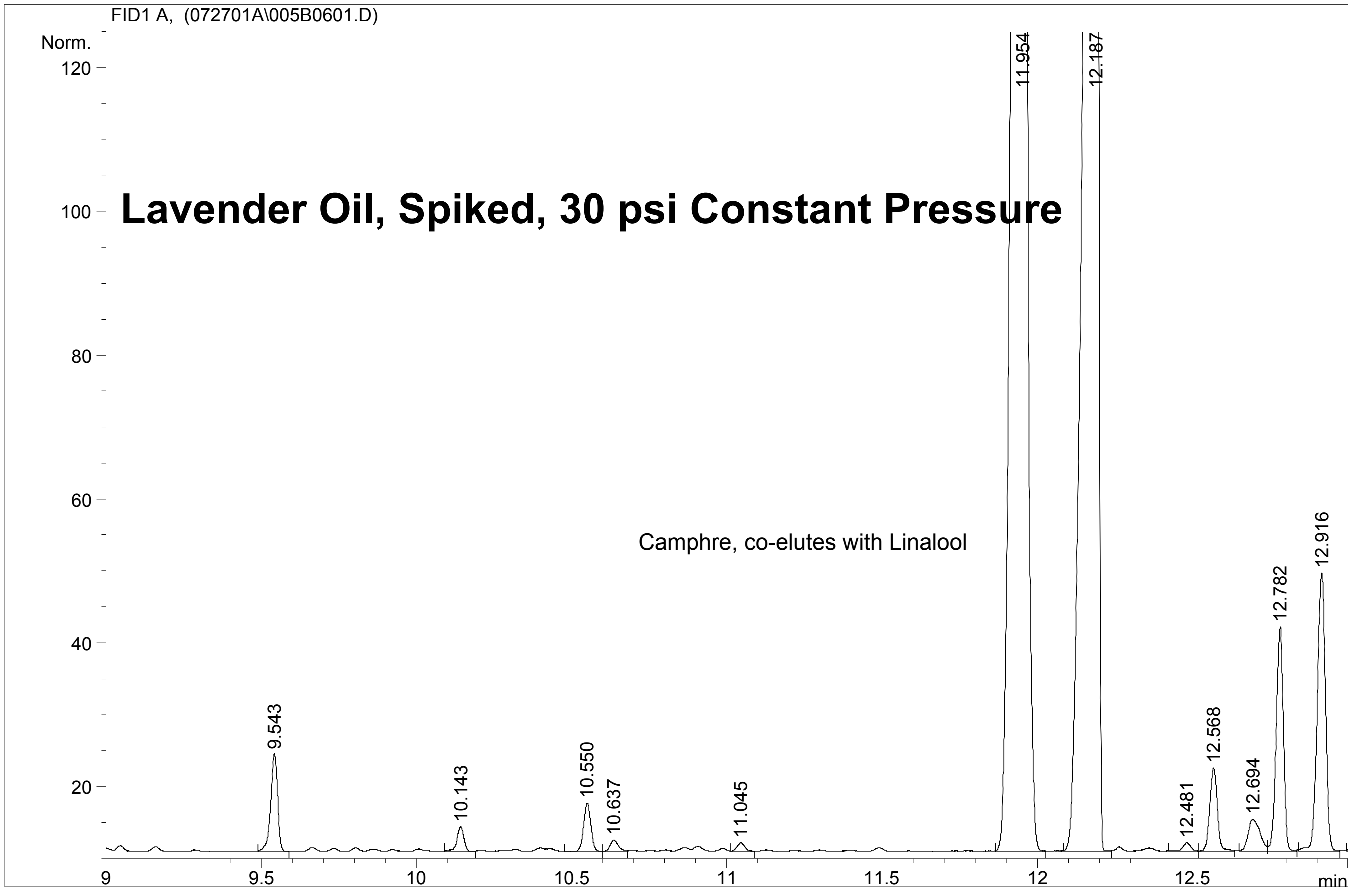
Oven: 50C (0.33 min), 10C/min to 200C and hold



Effects of Head Pressure on Elution Order: 30 psi

Column: 20m x 0.10mm ID x 0.2um, DB-WAX

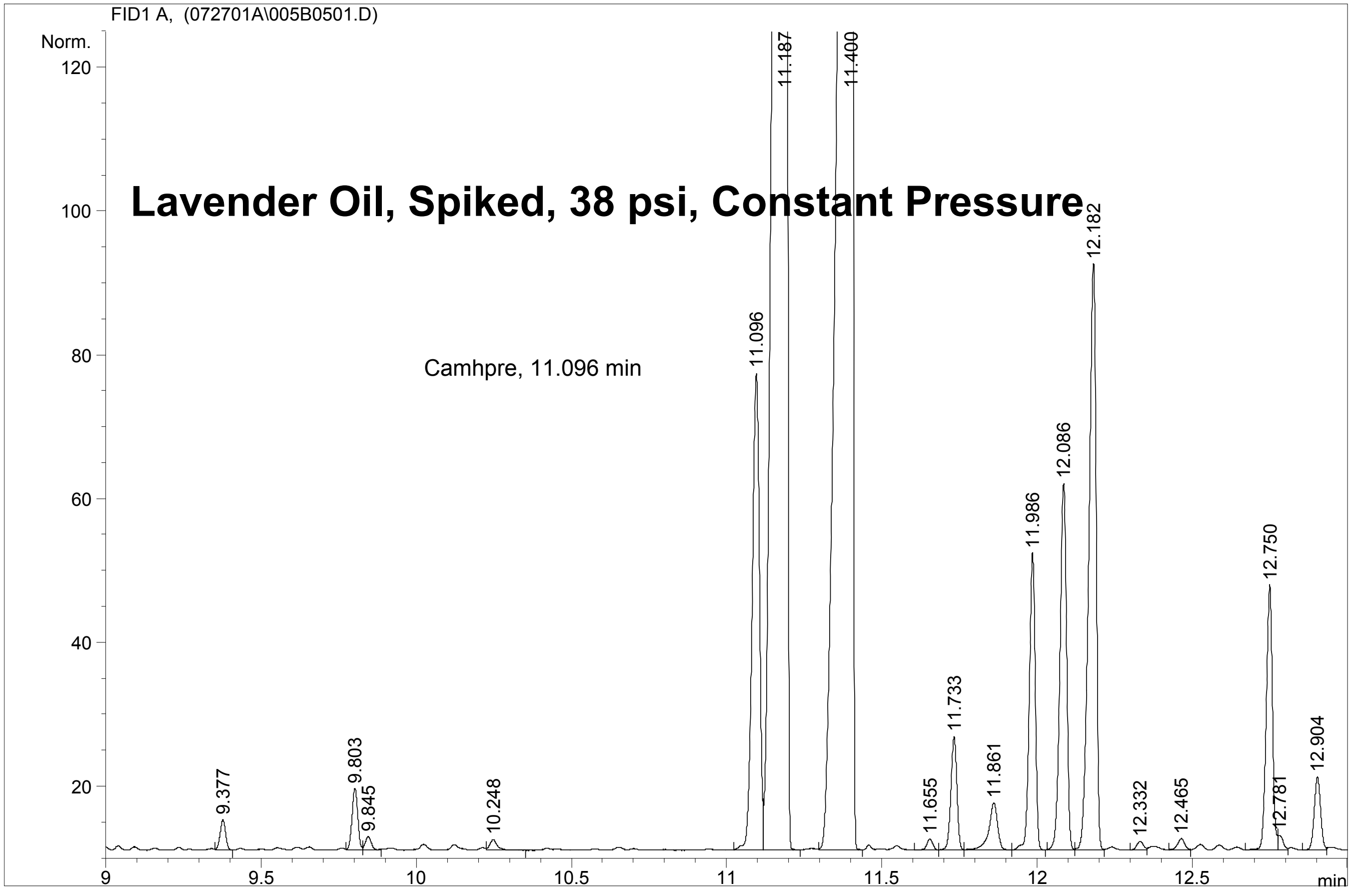
Oven: 50C (0.33 min), 10C/min to 200C and hold



Effects of Head Pressure on Elution Order: 38 psi

Column: **20m x 0.10mm ID x 0.2um, DB-WAX**

Oven: **50C (0.33 min), 10C/min to 200C and hold**



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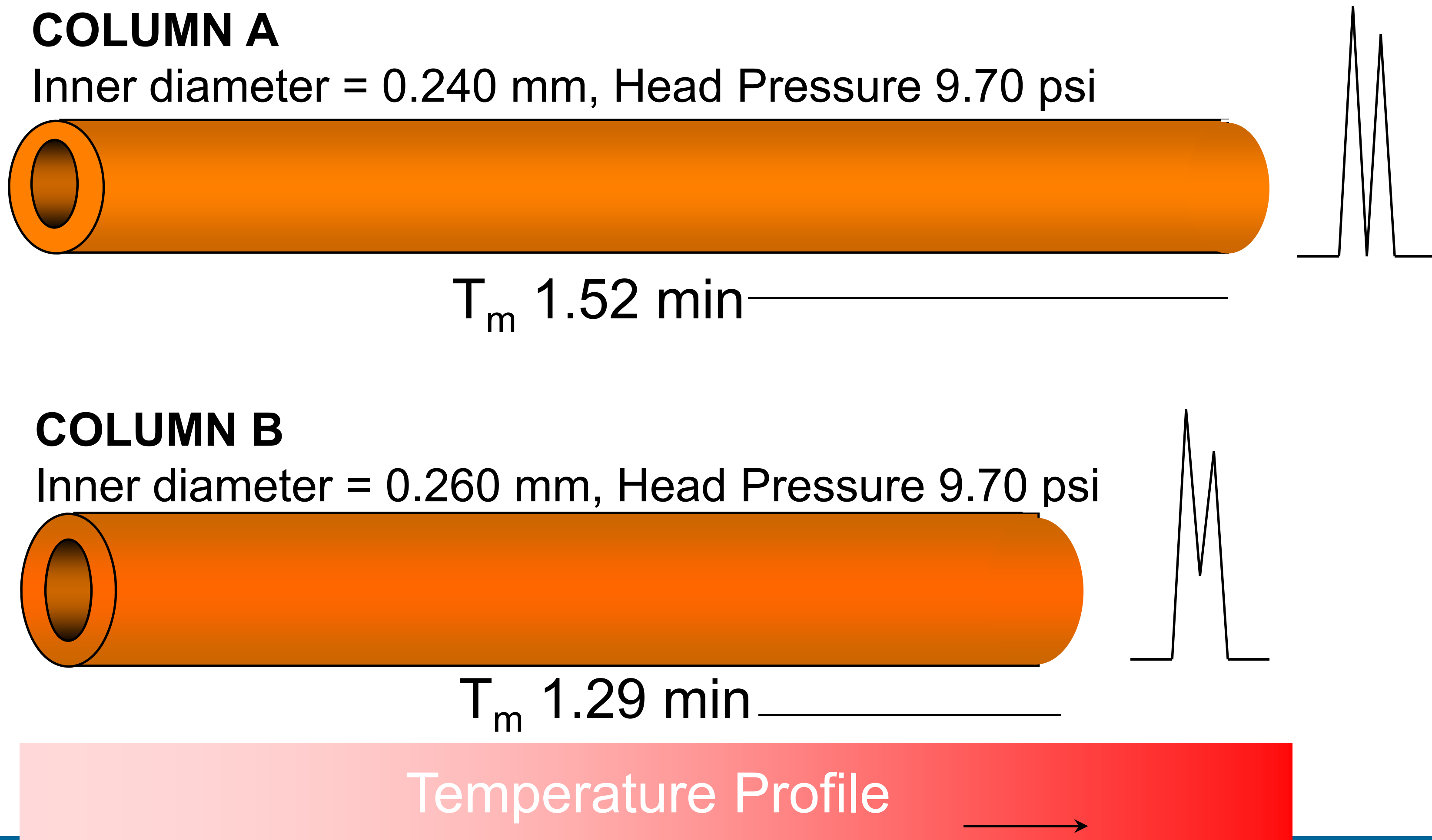
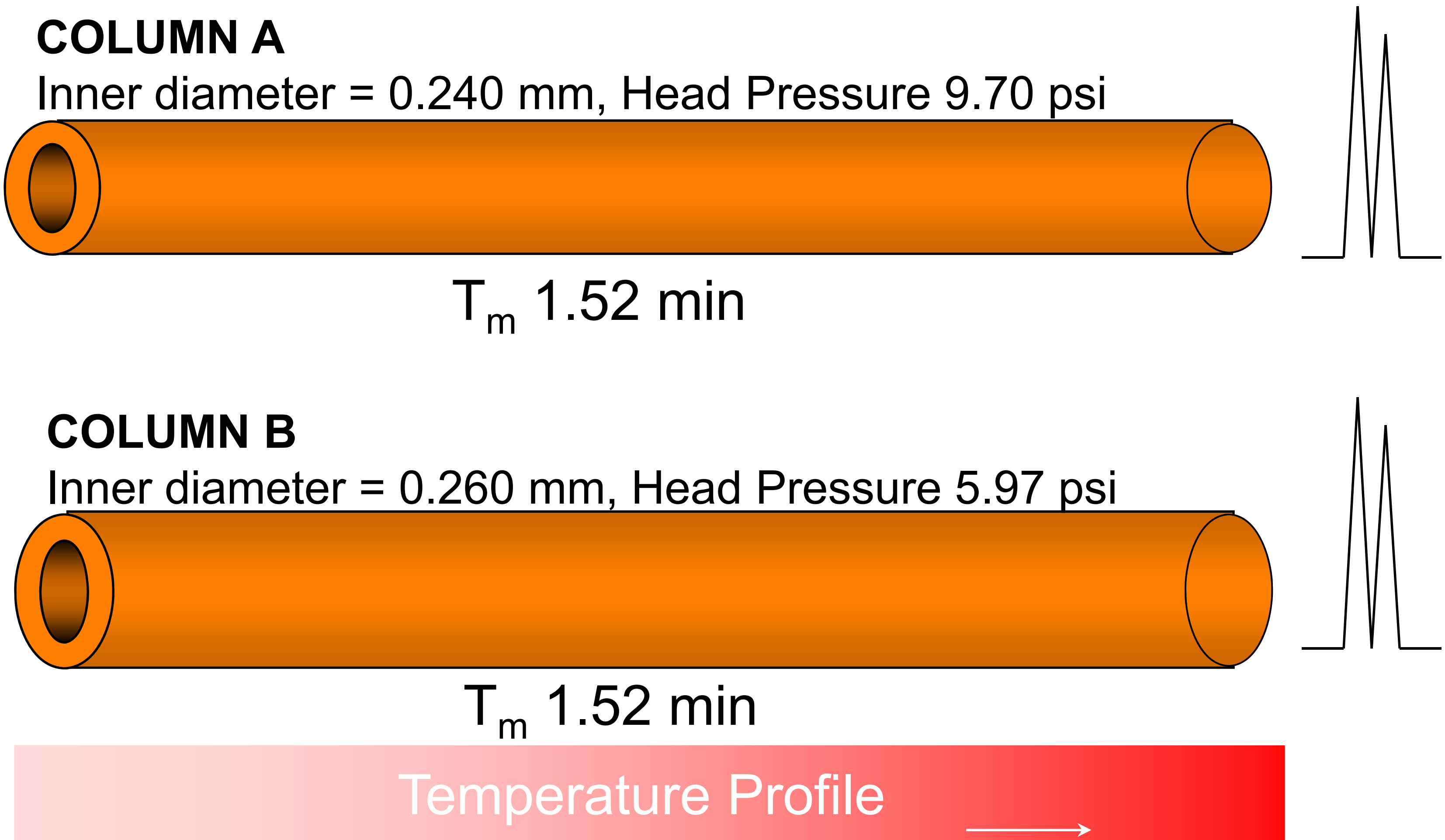
Temperature Programming

Effect Of Locking Software On Temperature Of Elution



Temperature Programming

Effect Of Locking Software On Temperature Of Elution



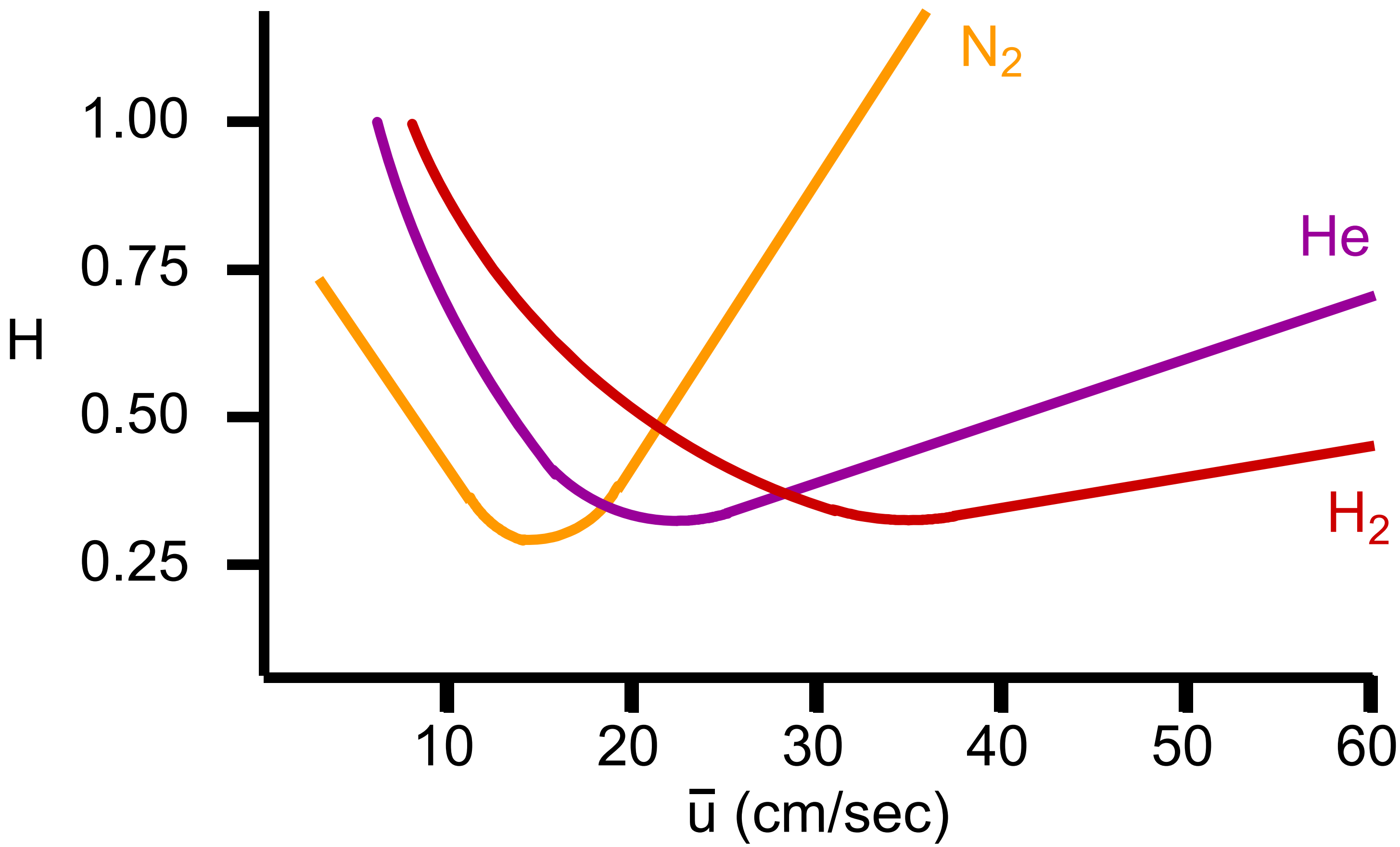
CARRIER GAS
Hydrogen Comments

Hydrogen is extremely diffusive in air

Difficult to reach explosive level of ~4 %

Many GC's are flow regulated

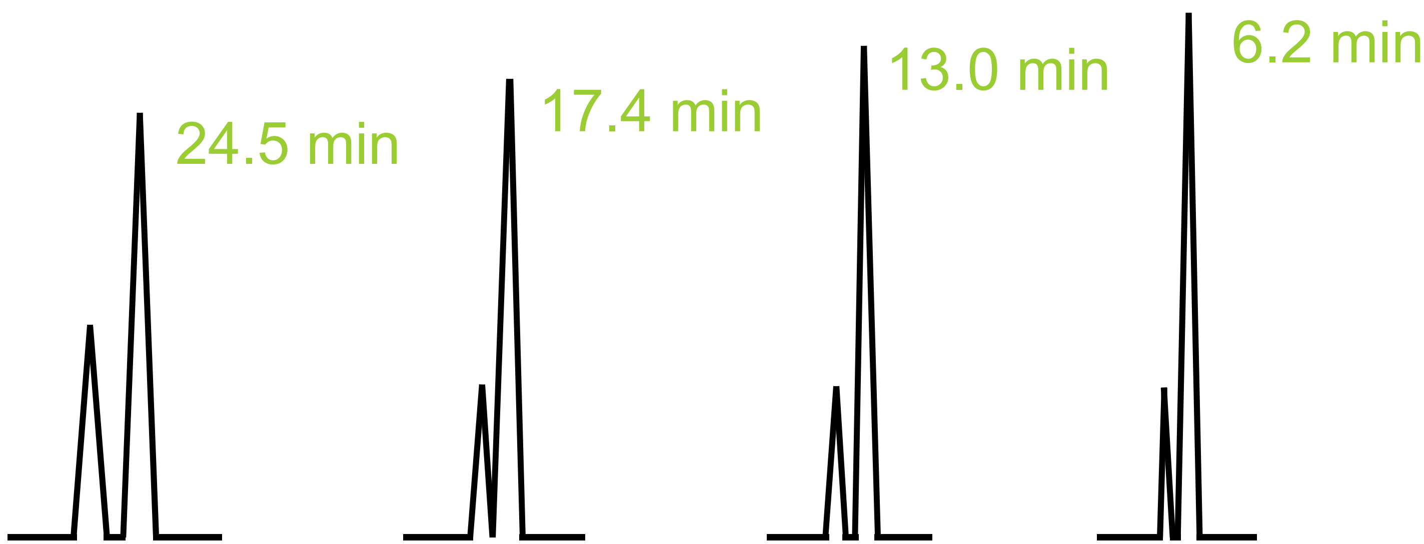
VAN DEEMTER CURVES



CARRIER GAS

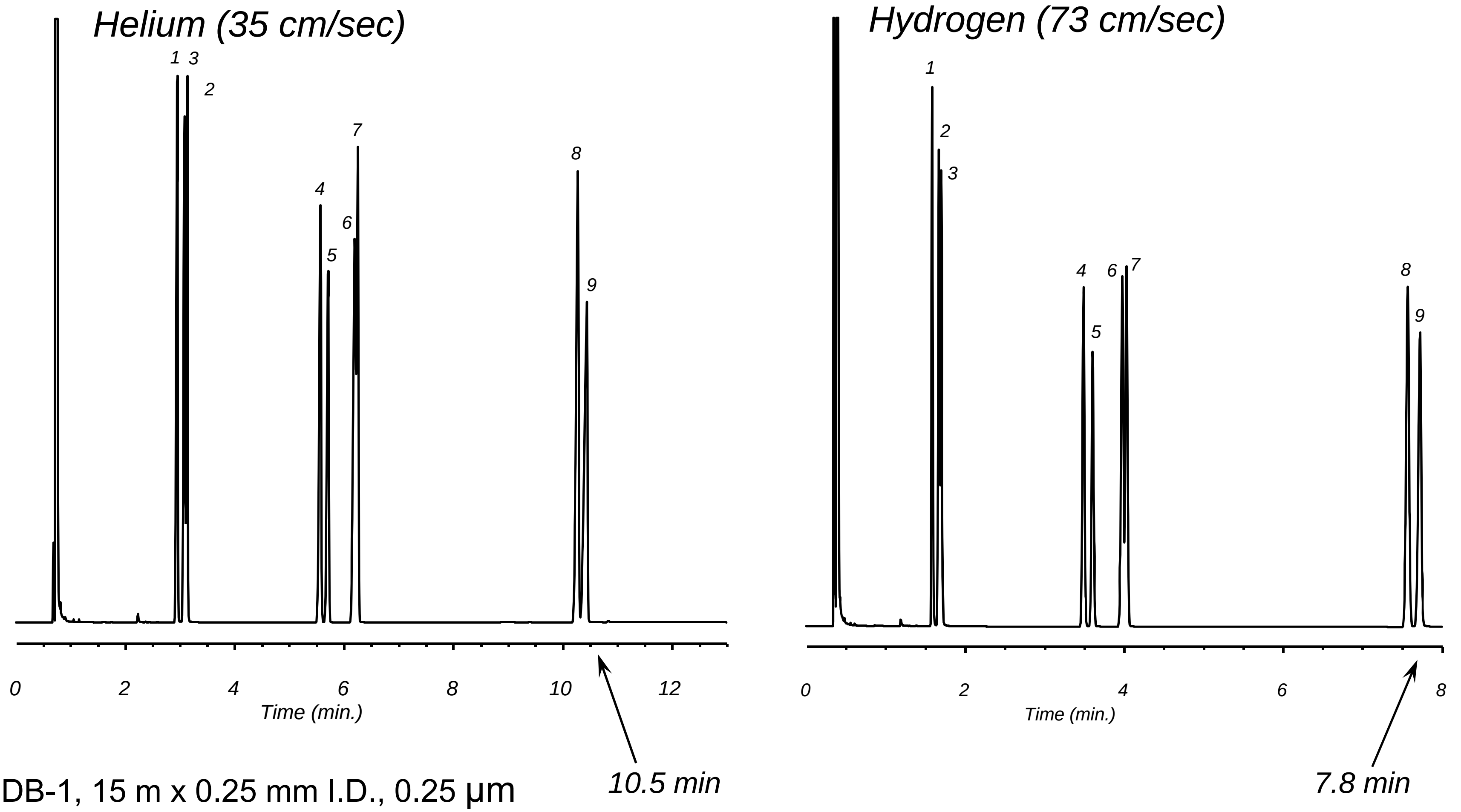
Selection Example

Nitrogen 11.7 cm/sec	Nitrogen 20 cm/sec	Helium 23.2 cm/sec	Hydrogen 48 cm/sec



R = 1.76	R = 1.33	R = 1.67	R = 1.65

Carrier Gas
Helium vs. Hydrogen



DB-1, 15 m x 0.25 mm I.D., 0.25 µm
50°C for 2 min, 50-110°C at 20°/min

Hydrogen as Carrier with MSD – Contamination?

Contamination of GC flow modules and lines.

Hydrogen acts as a scrubber.

On the MS this typically looks like Hydrocarbon contamination

Most people report that it takes 2-4 weeks to clean out, depending on flows.

The FID only sees a high background for that time.

Hydrogen seems to scrub the lines of that which Helium leaves behind.

Carrier Gas - Summary

Gas	Advantages	Disadvantages
Nitrogen	Cheap, Readily available	Long run times
Helium	Good compromise, Safe	Expensive
Hydrogen	Shorter run times, Cheap	Explosive

Hydrogen is difficult to explode under GC conditions

CARRIER GAS

Selection Summary

Hydrogen is best especially for wide k range analyses

Helium is acceptable

Nitrogen is not recommended

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*** *Select option 3, option 3, then option 1.***

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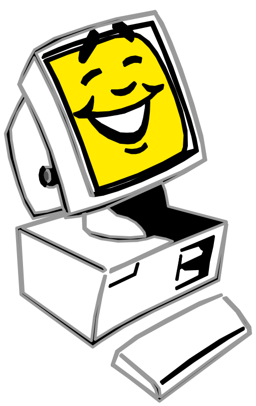

Wrap-up e-Seminar Questions

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Upcoming GC and LC Series e-Seminars

HPLC Column Troubleshooting - Series 2
February 23, 2011 – 2:00pm ET

Advanced Topic: Tips and Tricks of Injector Maintenance
March 8, 2011 – 2:00pm ET

Selection of Capillary GC Columns -
Series 3
March 24, 2011 – 1:00pm ET