Carrier Gases in Capillary GC Analysis

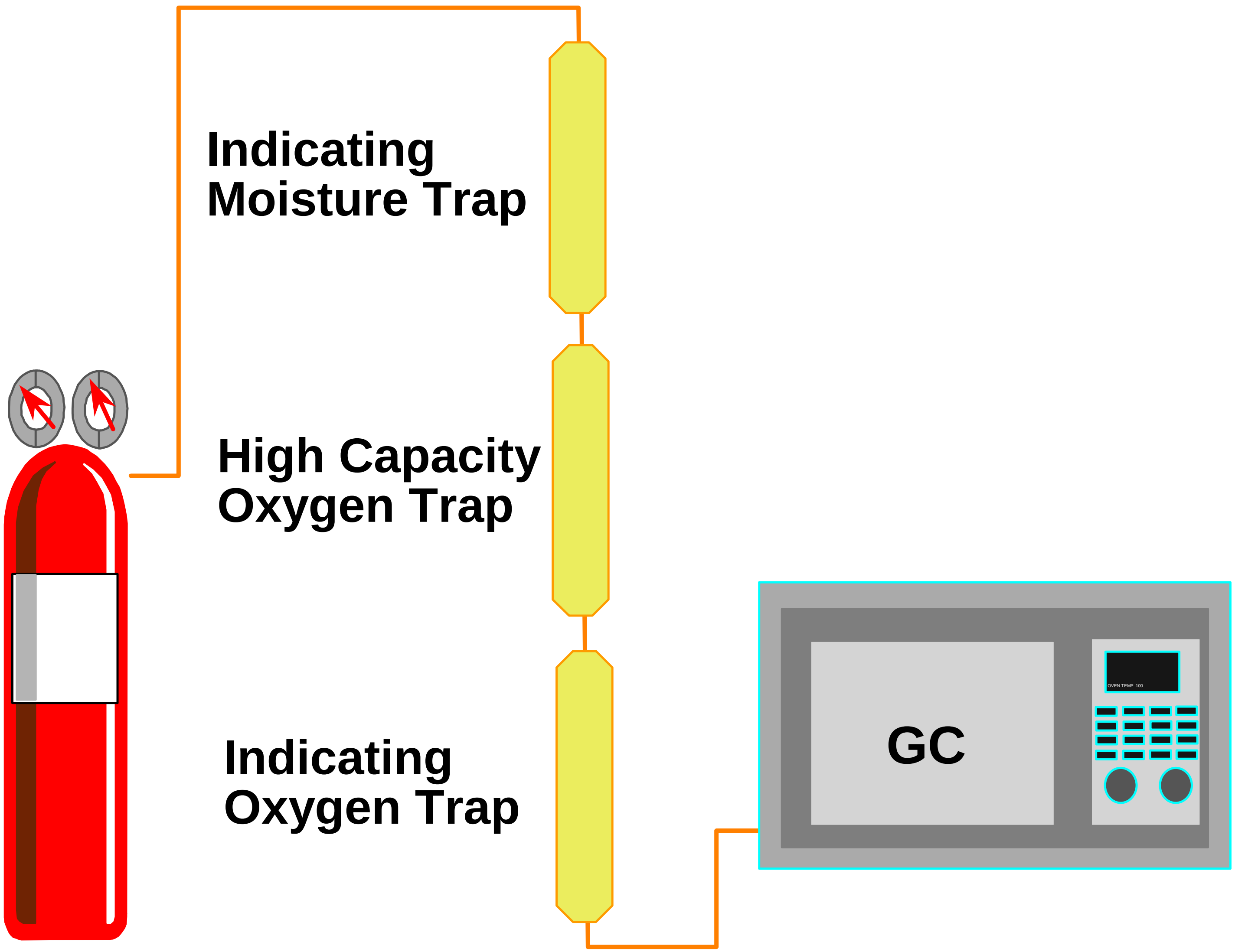
CARRIER GAS
Mobile Phase

- 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 prodigiously precise pressure delivery system

COMMON CARRIER GASES

- Nitrogen
- Helium
- Hydrogen

Configurations for Carrier Gas Purifiers



CARRIER GAS
Flow Rate (mL/min)

"Volume"

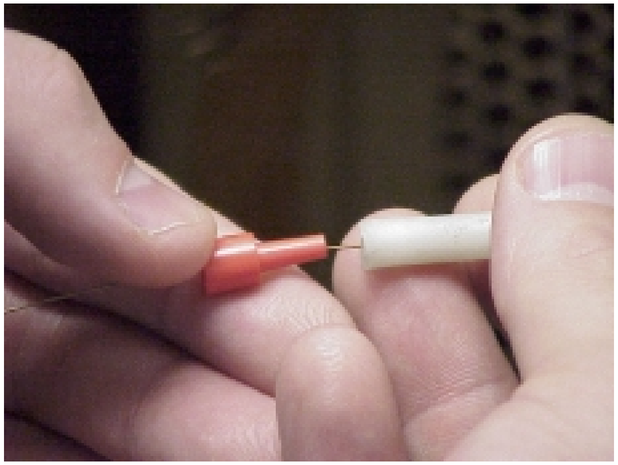
Measurement:

- 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)



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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

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

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

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

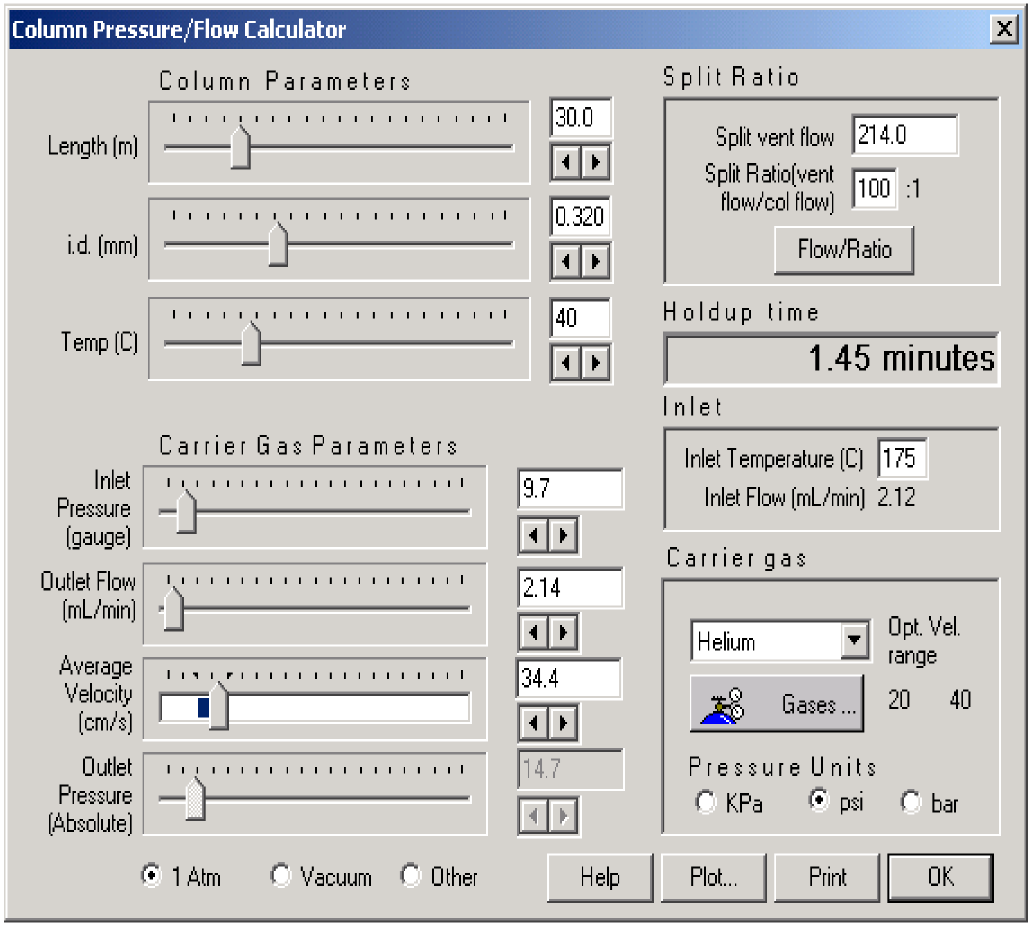
$$t_m = \frac{3000\text{ cm}}{32\text{ cm/sec}} = 93.8\text{ sec} = 1.56\text{ min}$$

tm = 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

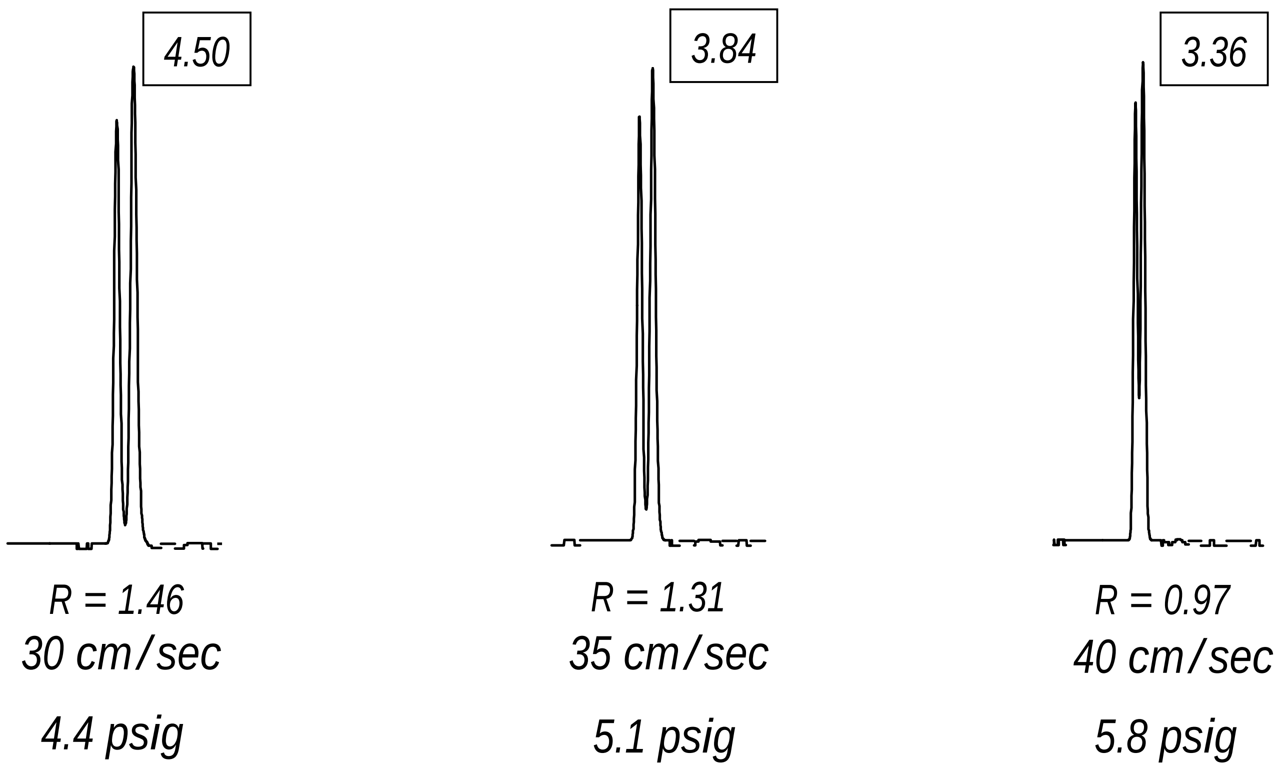
USER CONTRIBUTED SOFTWARE

- **GC Pressure/Flow Calculator Software**
- **http://www.chem.agilent.com/cag/servsup/usersoft/main.html**



RESOLUTION VS. LINEAR VELOCITY

Helium



DB-1, 15 m x 0.32 mm ID, 0.25 um
60°C isothermal
1,3- and 1,4-Dichlorobenzene

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

Calculated using Column Pressure/Flow Calculator available from Agilent (www.agilent.com/chem)

Relationship of tubing dimensions and pressure: 12m x 0.20mm ID column

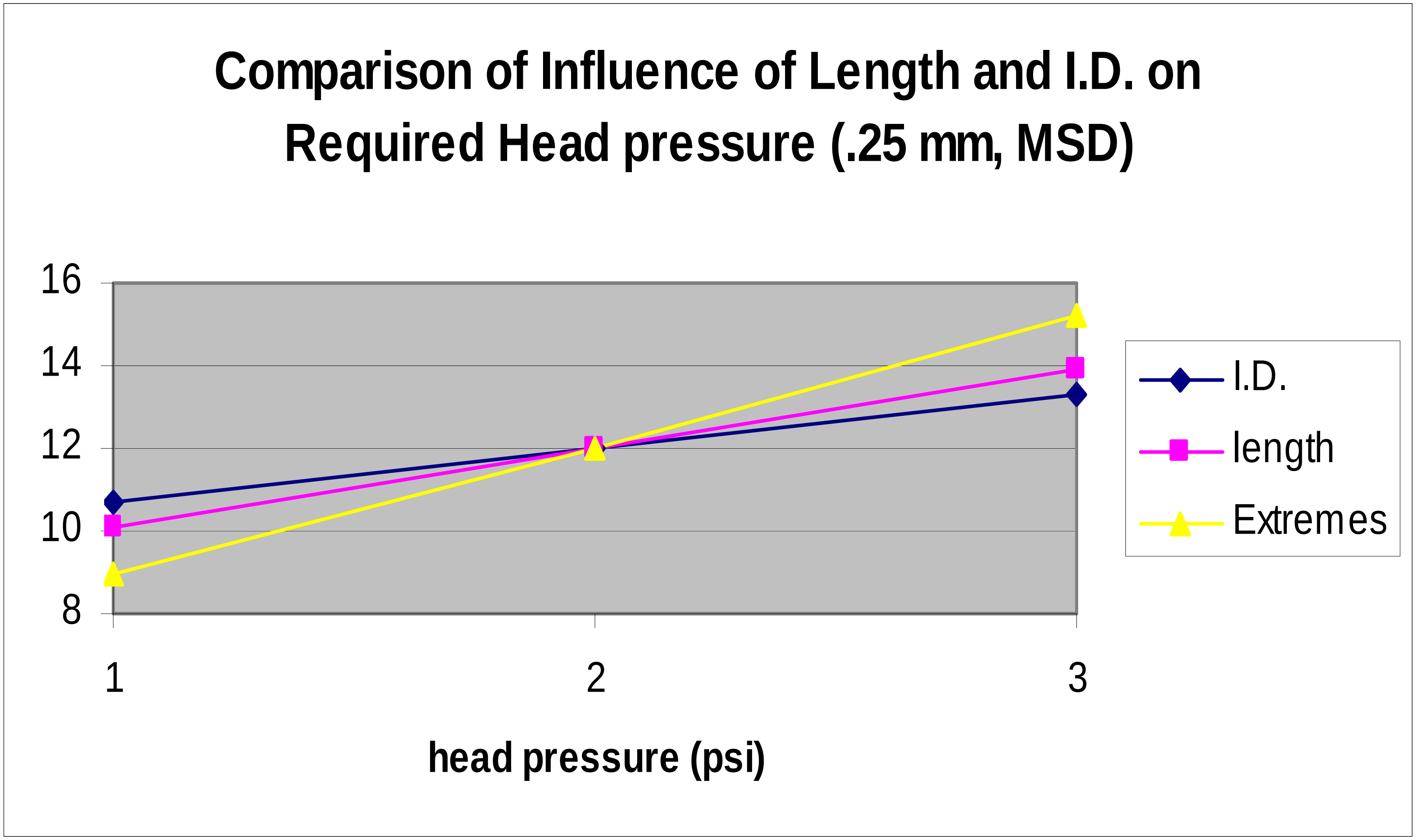
L (m)	ID (µm)	P (psi)	% of nominal P
11.5	205	6.9	69%
12.0	**200**	**10.0**	**100%**
12.5	195	13.5	135%

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

Calculated using Column Pressure/Flow Calculator available from Agilent (www.agilent.com/chem



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

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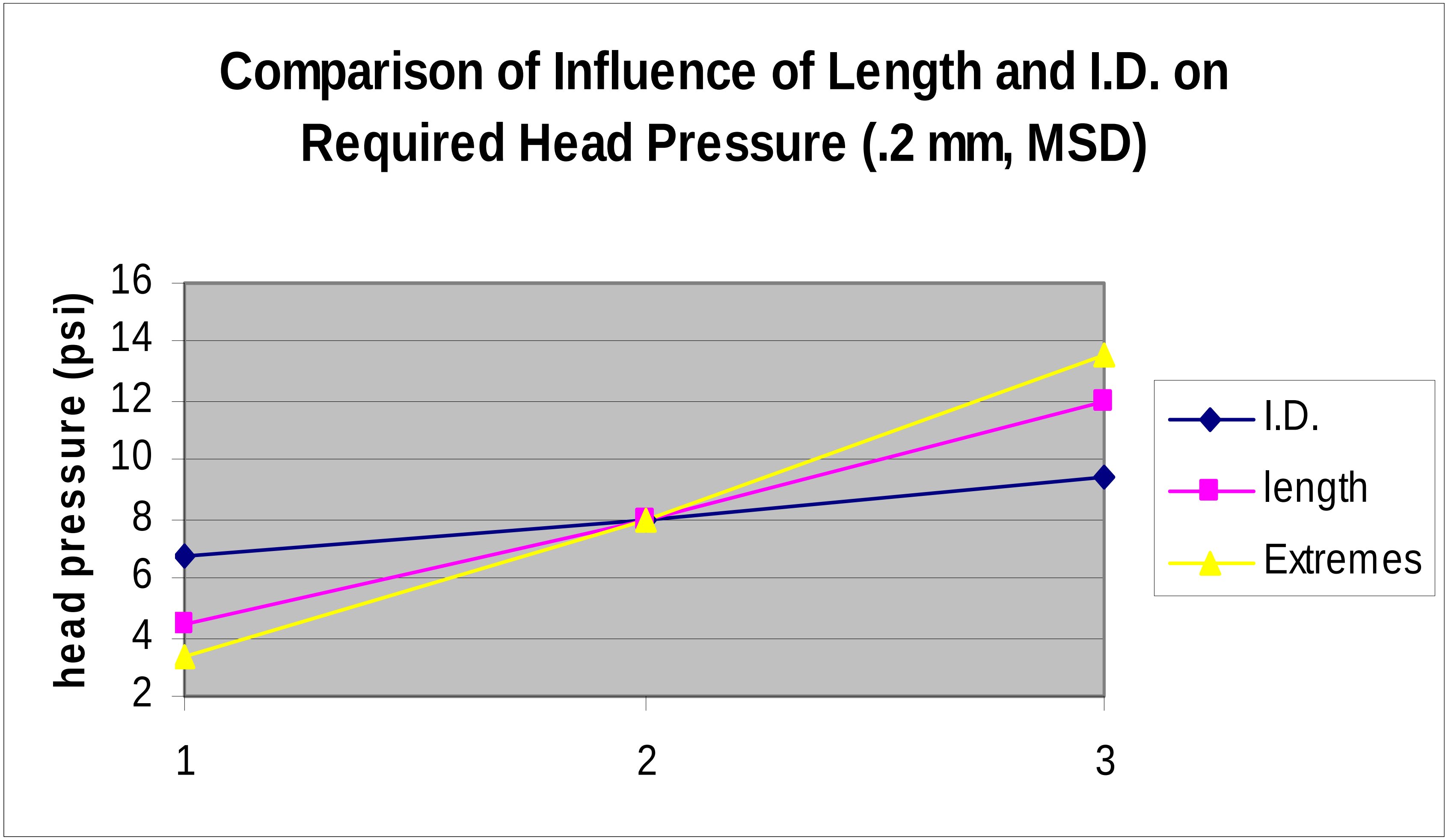


"Extremes" denotes combination of smallest ID/longest column and vice versa. (±1 m length; ±6 µm ID)

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?”

Break Number

Agilent Technologies

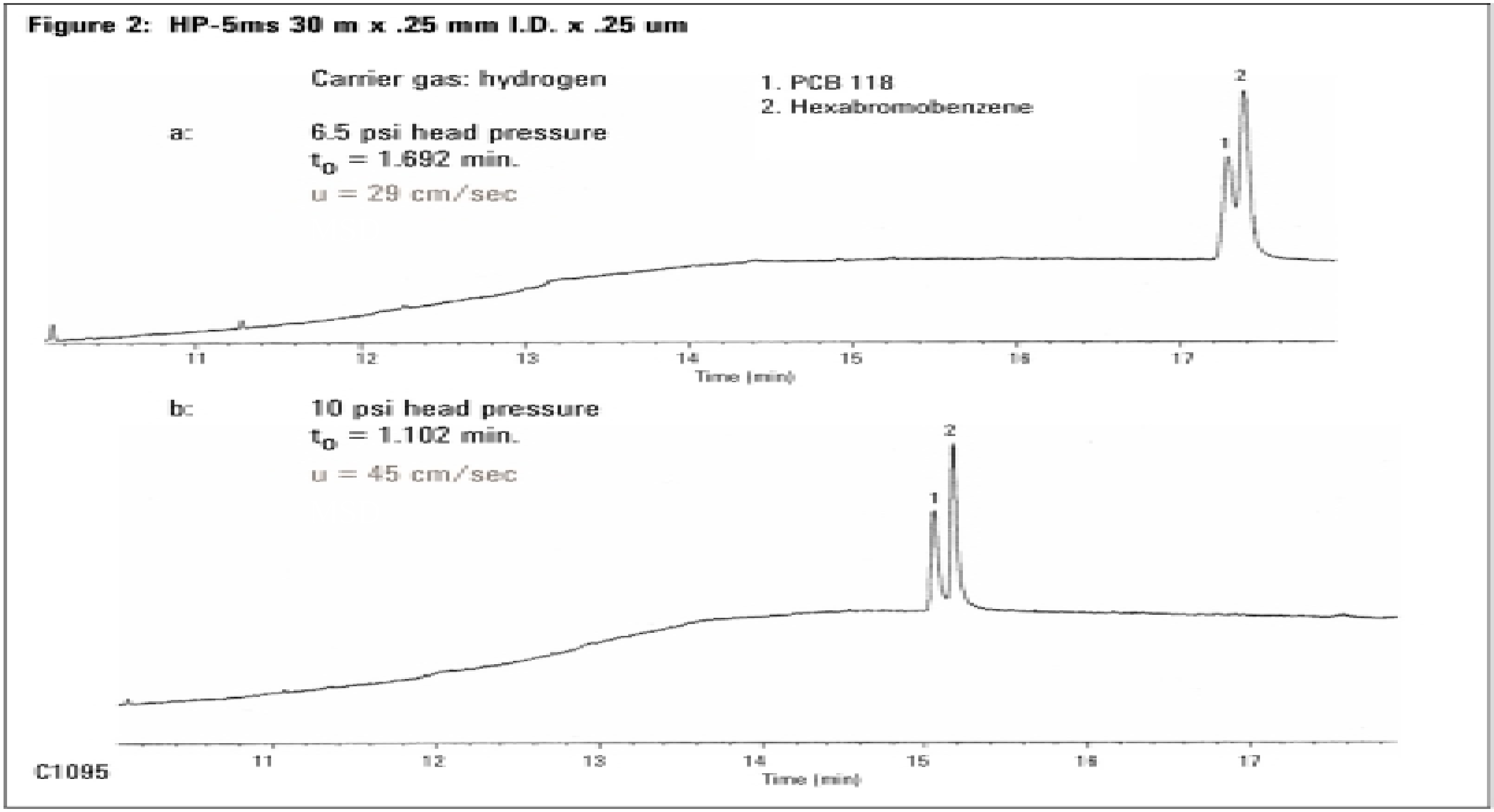
"I don't use retention time windows. Why should I care if my retention times shift?"

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)



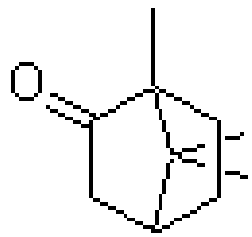
Net Vapor Pressure

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:

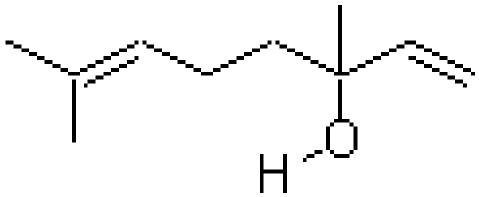
- Loss of resolution
- Complete reversal of elution
  - **More common in mixtures of disparate functionalities; it does not occur with homologues.**
  - **Also more common with solutes and stationary phases employing multiple modes of solute-stationary phase interactions.**

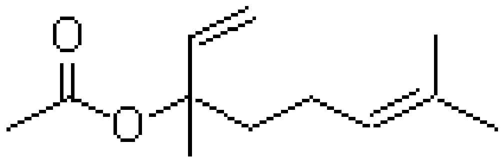
Example -- Compounds of Interest



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



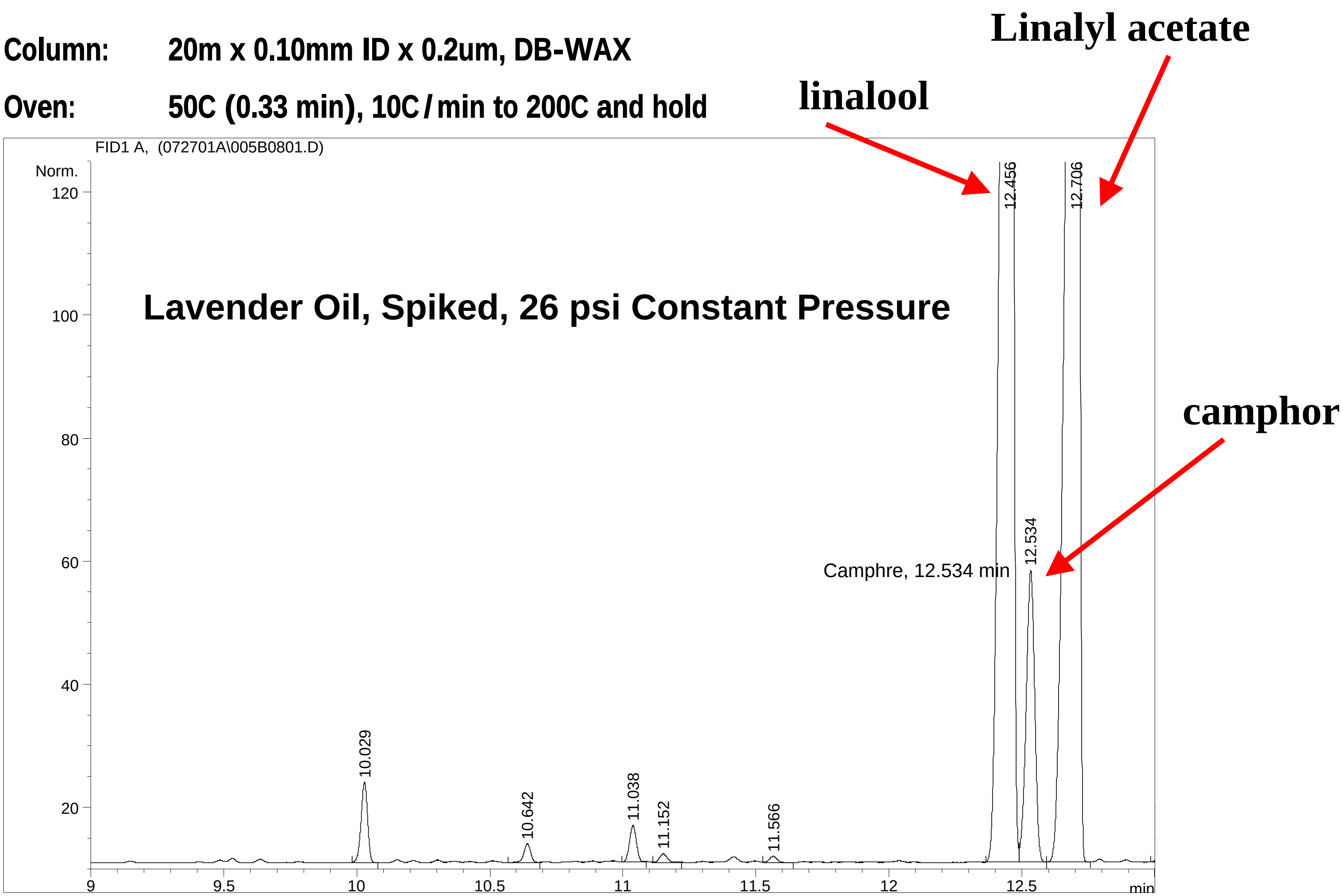


Linalyl acetate
b.p. 220°C
acid ester
and alkene functions
2 x Weak H-Bonding,
weak dipole, Van der Waals

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



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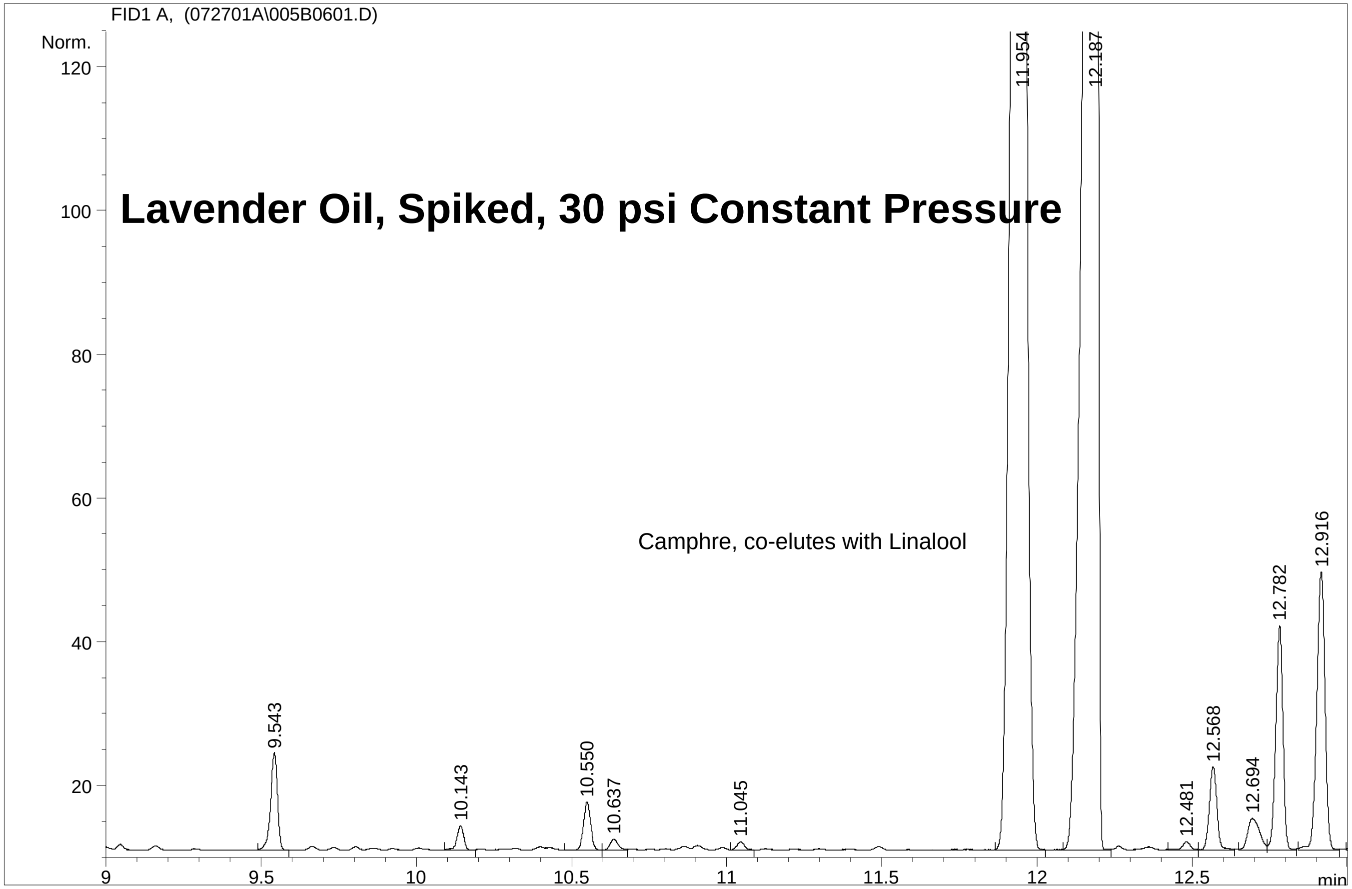
Effects of Head Pressure on Elution Order: 30 psi

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

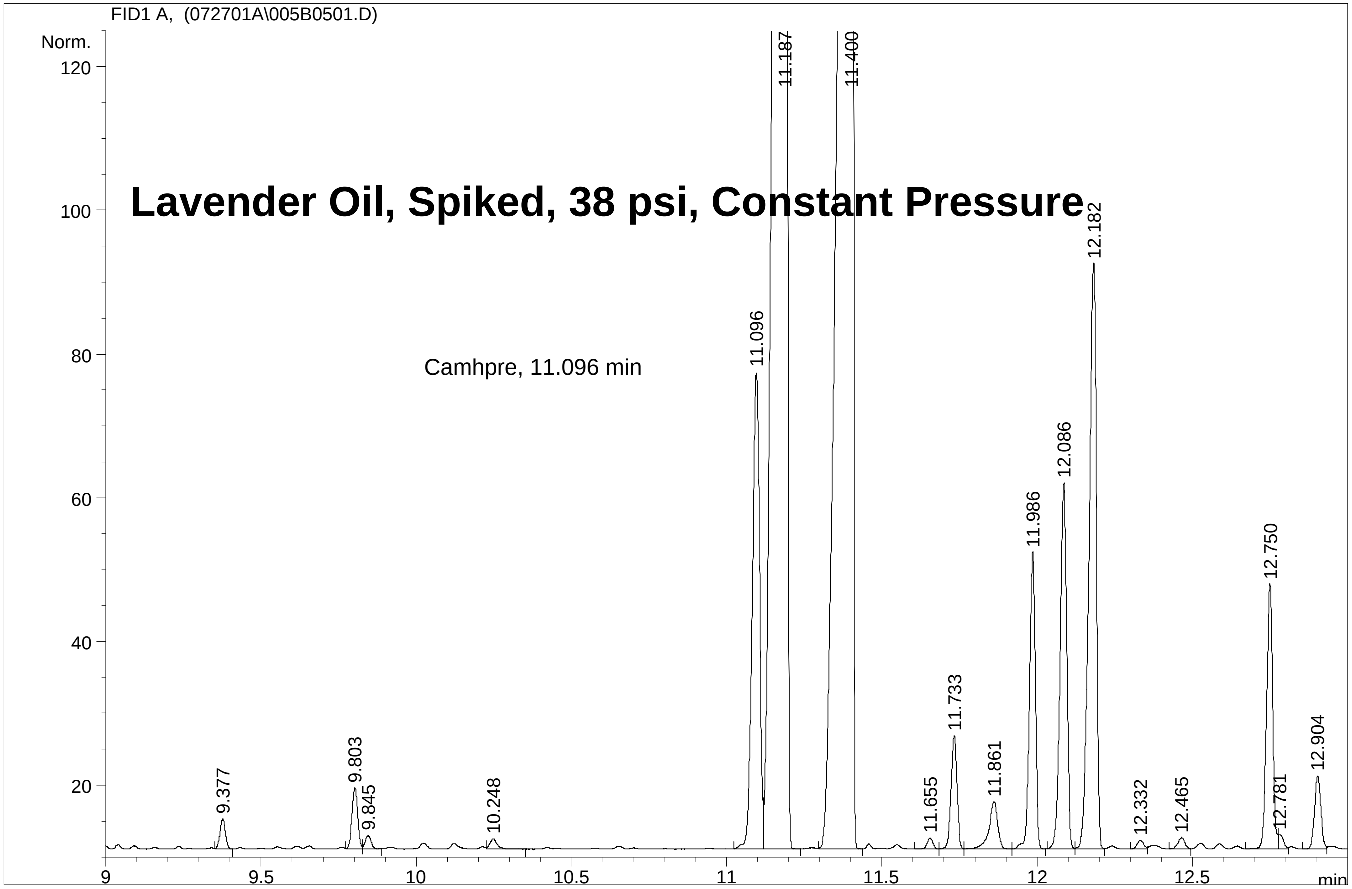
Oven: 50C (0.33 min), 10C / min to 200C and hold



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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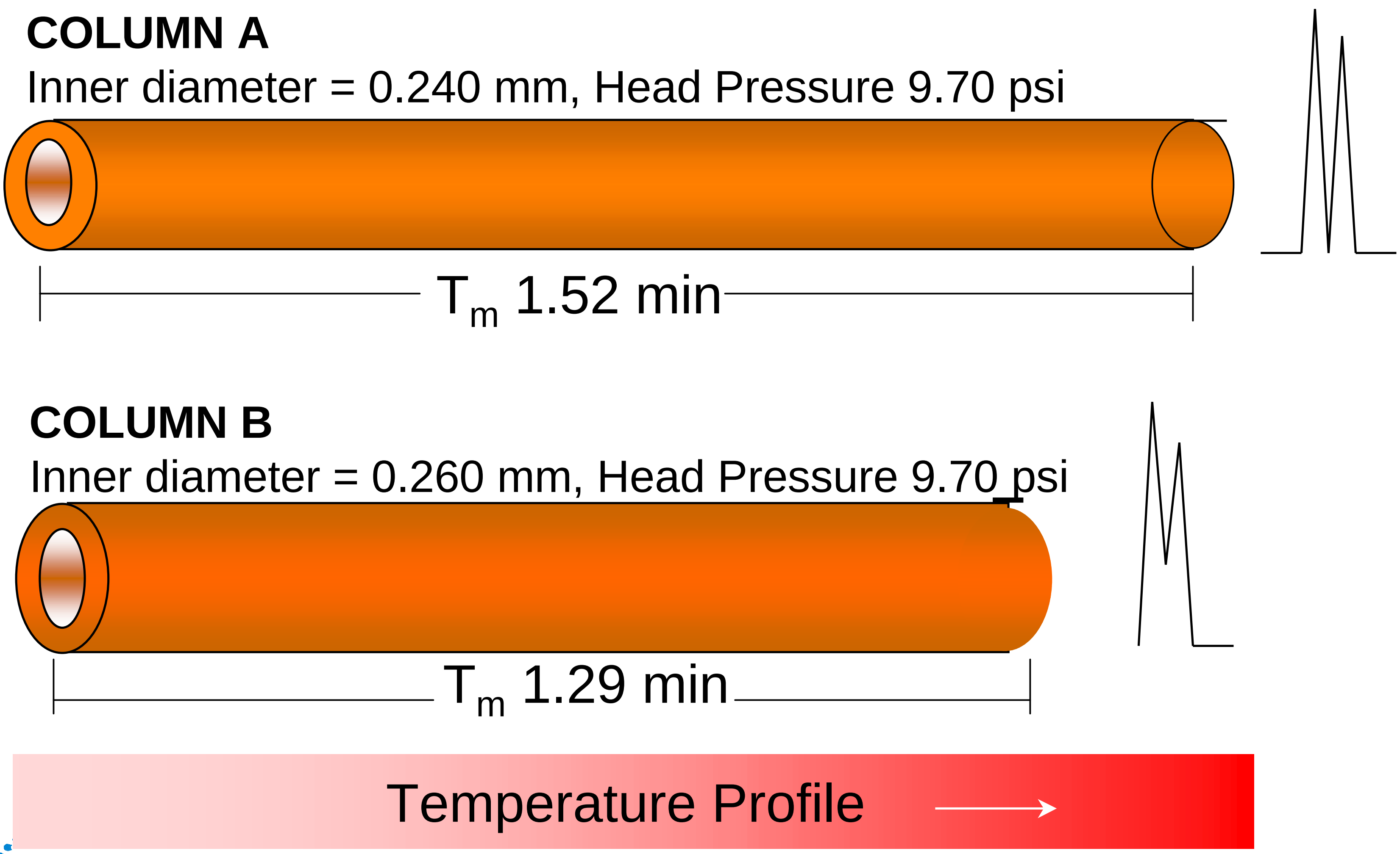
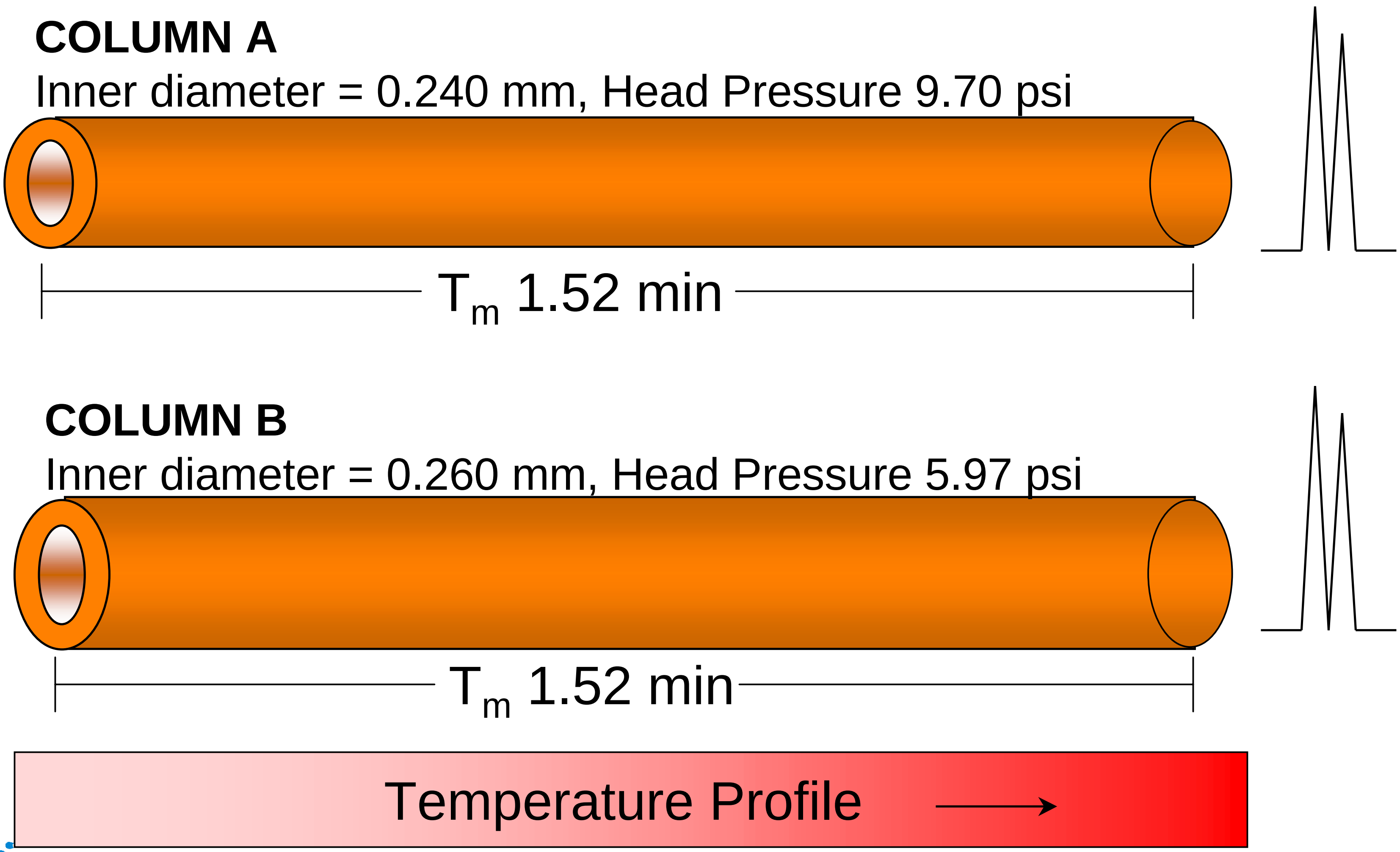
Temperature Programming

Effect Of Locking Software On Temperature Of Elution



Temperature Programming

Effect Of Locking Software On Temperature Of Elution



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Break Number 2

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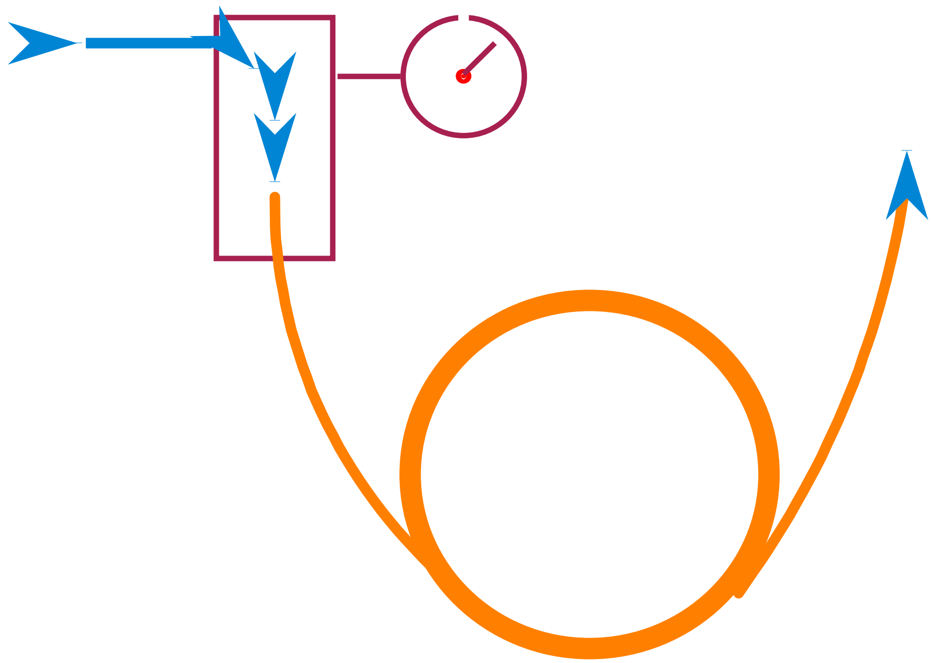
CARRIER GAS
Properties

- Compressible
- Expands with temperature
- Viscosity increases with temperature

CARRIER GAS
Constant Pressure Mode



Head pressure is constant
Flow decreases with temperature

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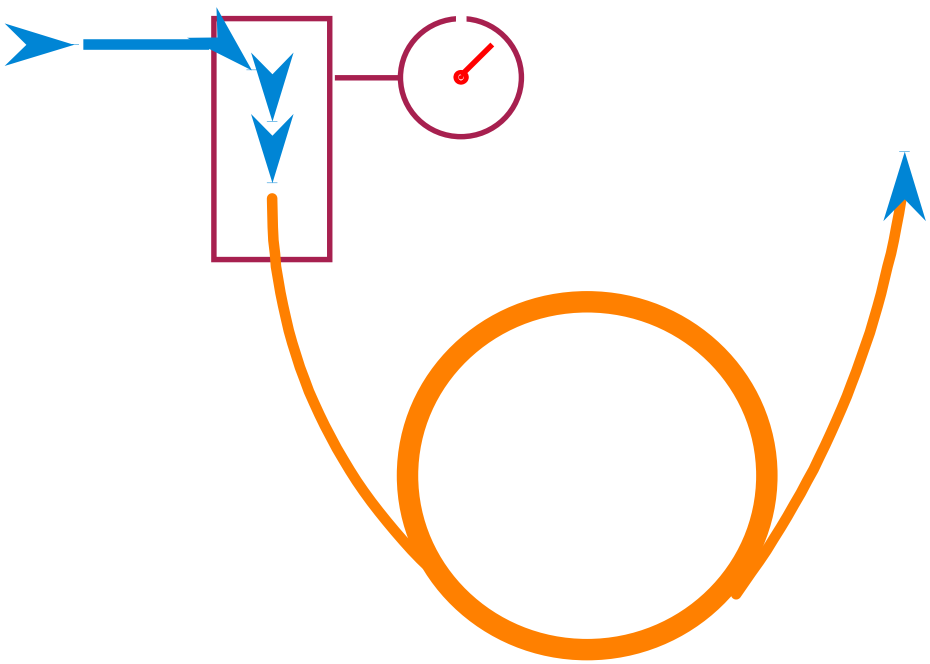
CARRIER GAS
Constant Flow Mode



Carrier gas flow is constant
Pressure increases with temperature

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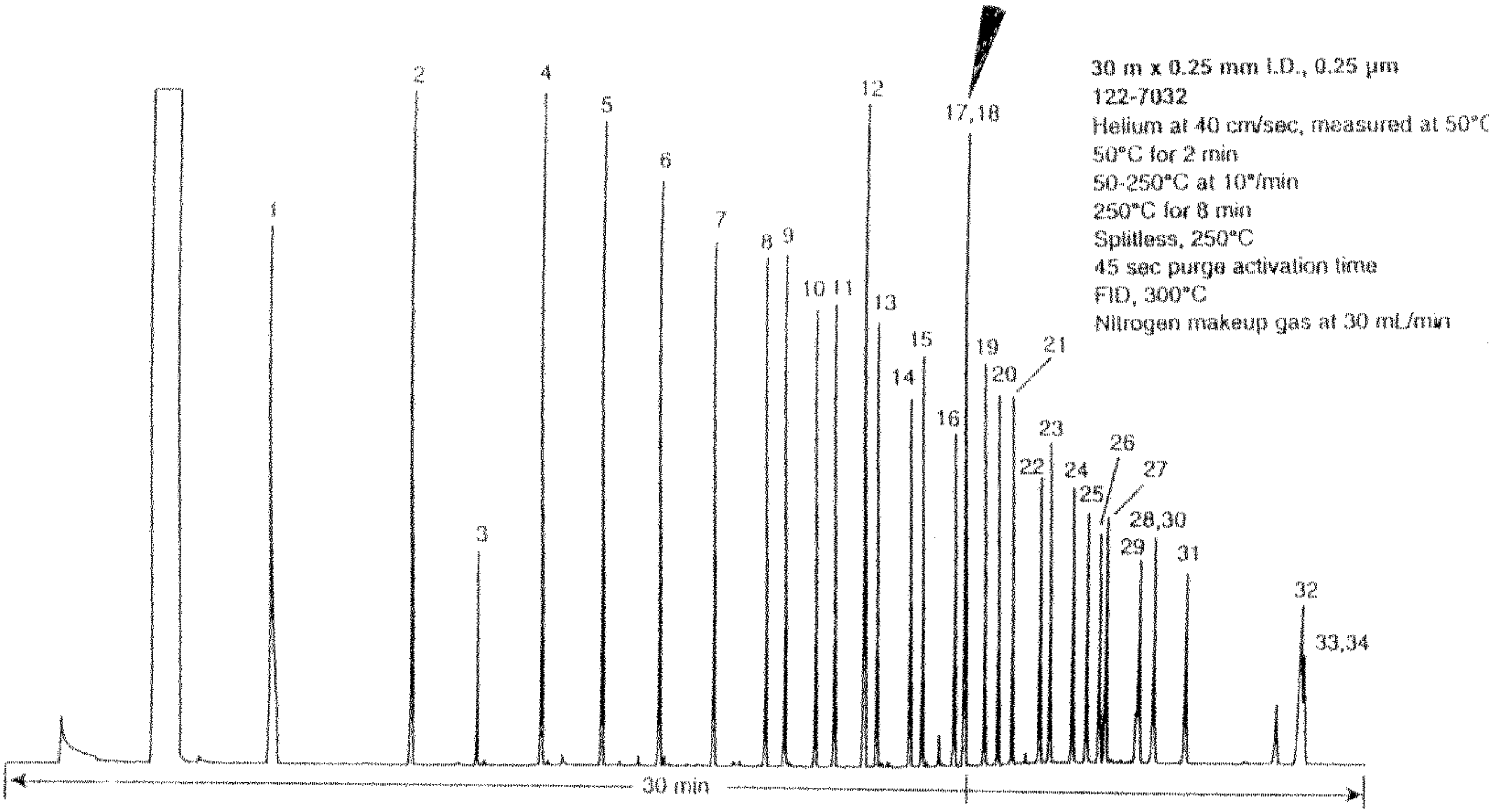
CARRIER GAS
Consistent Temperature

•Set the velocity at the same temperature

•Initial temperature is the most convenient

Optimizing ū for a specific area in programmed mode



Critical area elutes at 242°C; at 212°C, that chromatographing plug is ca. half way through the column. Set oven temperature at 212, and optimize carrier for a solute k = 7. Cool oven to 50°C starting temperature, and institute run.

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VAN DEEMTER EQUATION

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

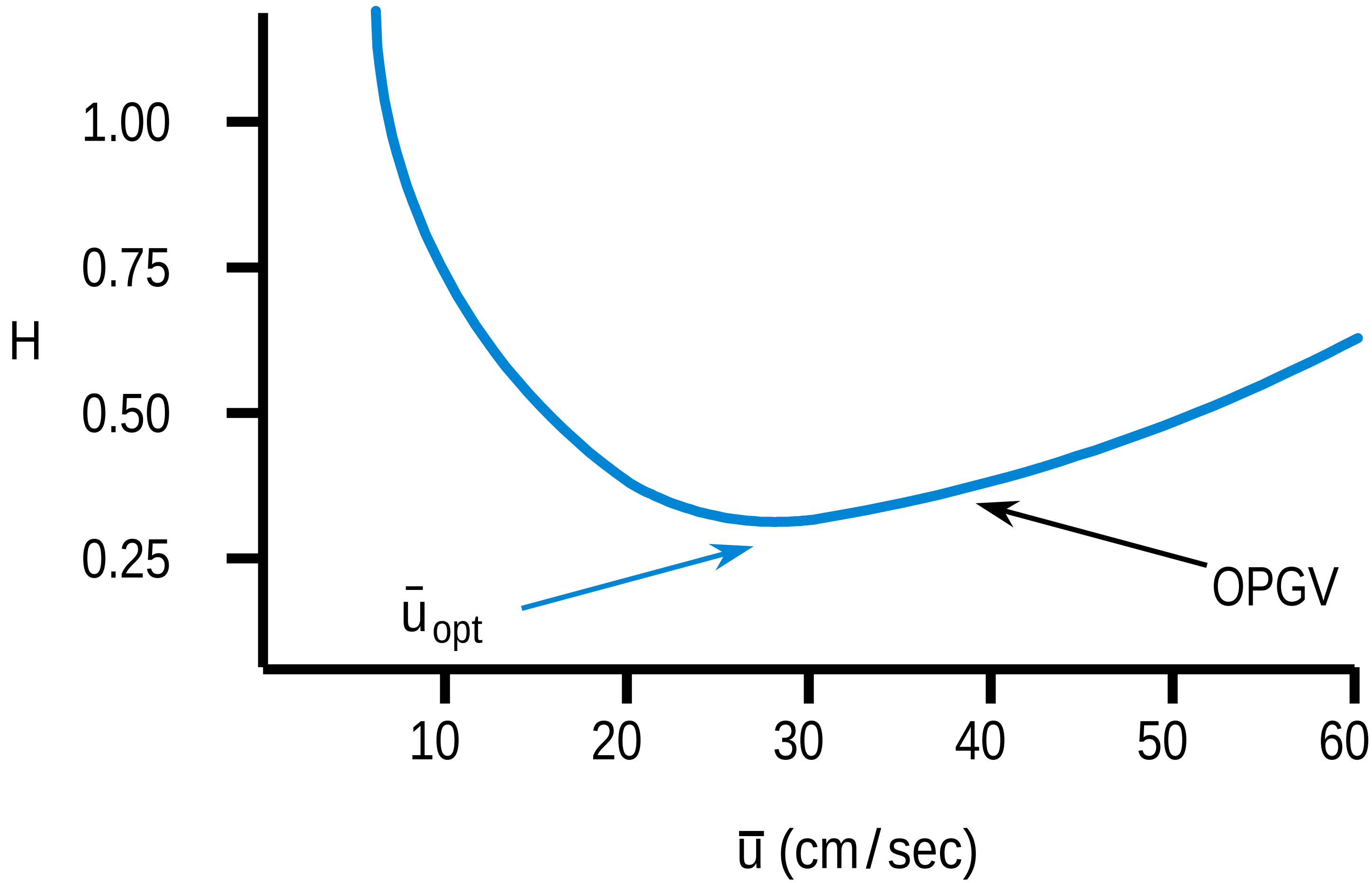
H = Height equivalent to a theoretical plate

A = Multi-path term

B = Longitudinal diffusion term

C = Mass transfer term

VAN DEEMTER CURVE



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

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

Maximum efficiency

OPGV:

Optimal practical gas velocity

Maximum efficiency per unit time

1.5 - 2x u_{opt}

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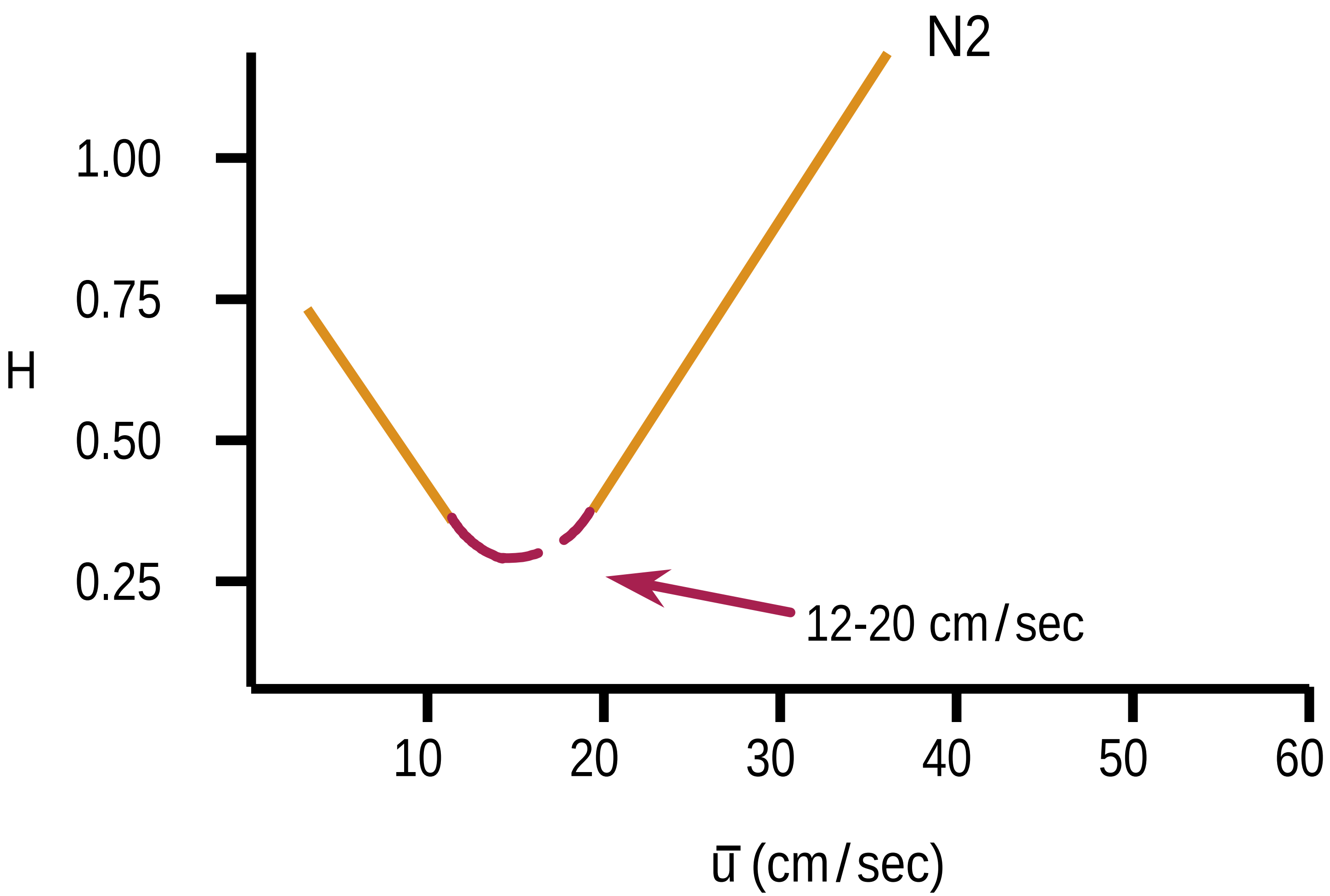
COMMON CARRIER GASES

- Nitrogen
- Helium
- Hydrogen

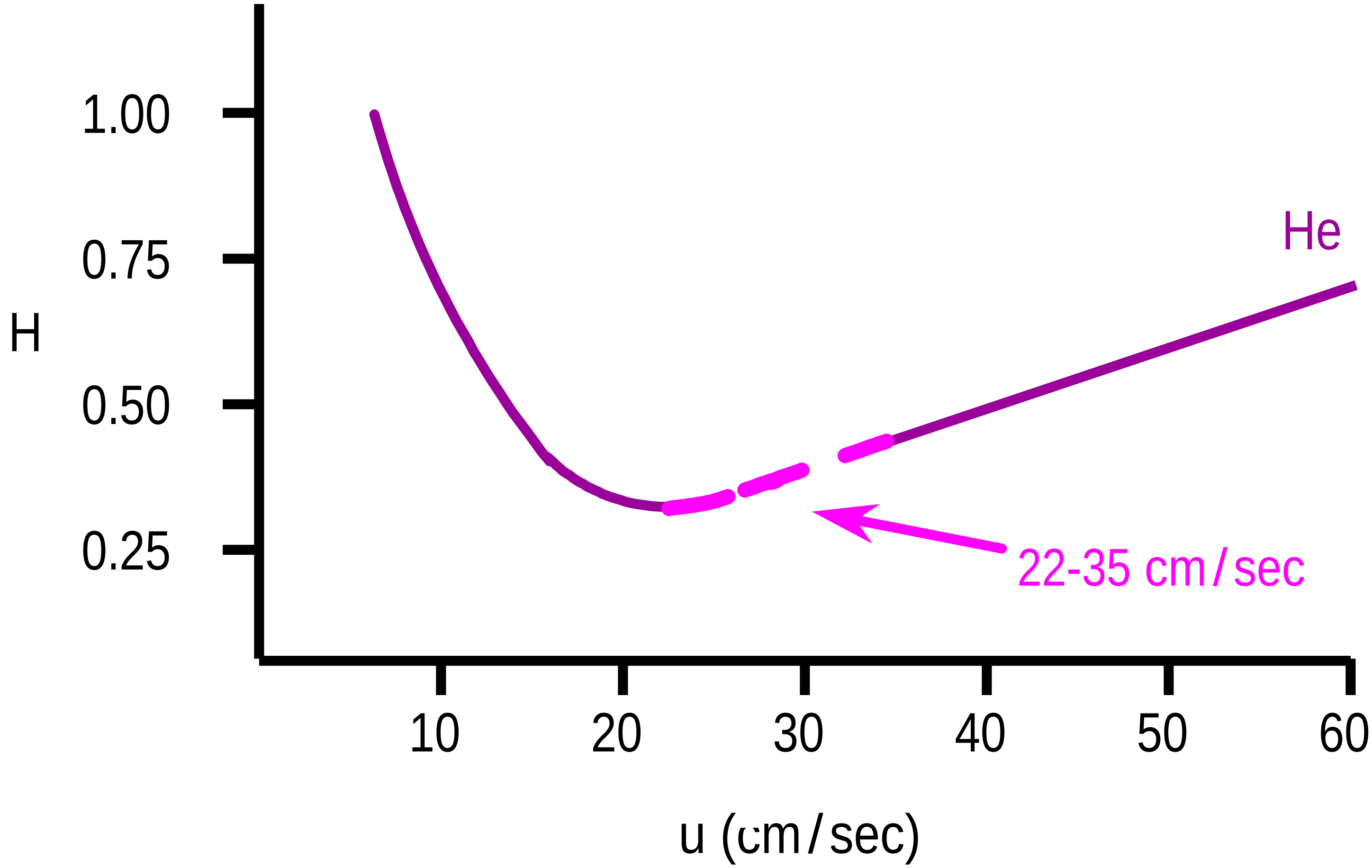
VAN DEEMTER CURVE

Nitrogen



VAN DEEMTER CURVE

Helium



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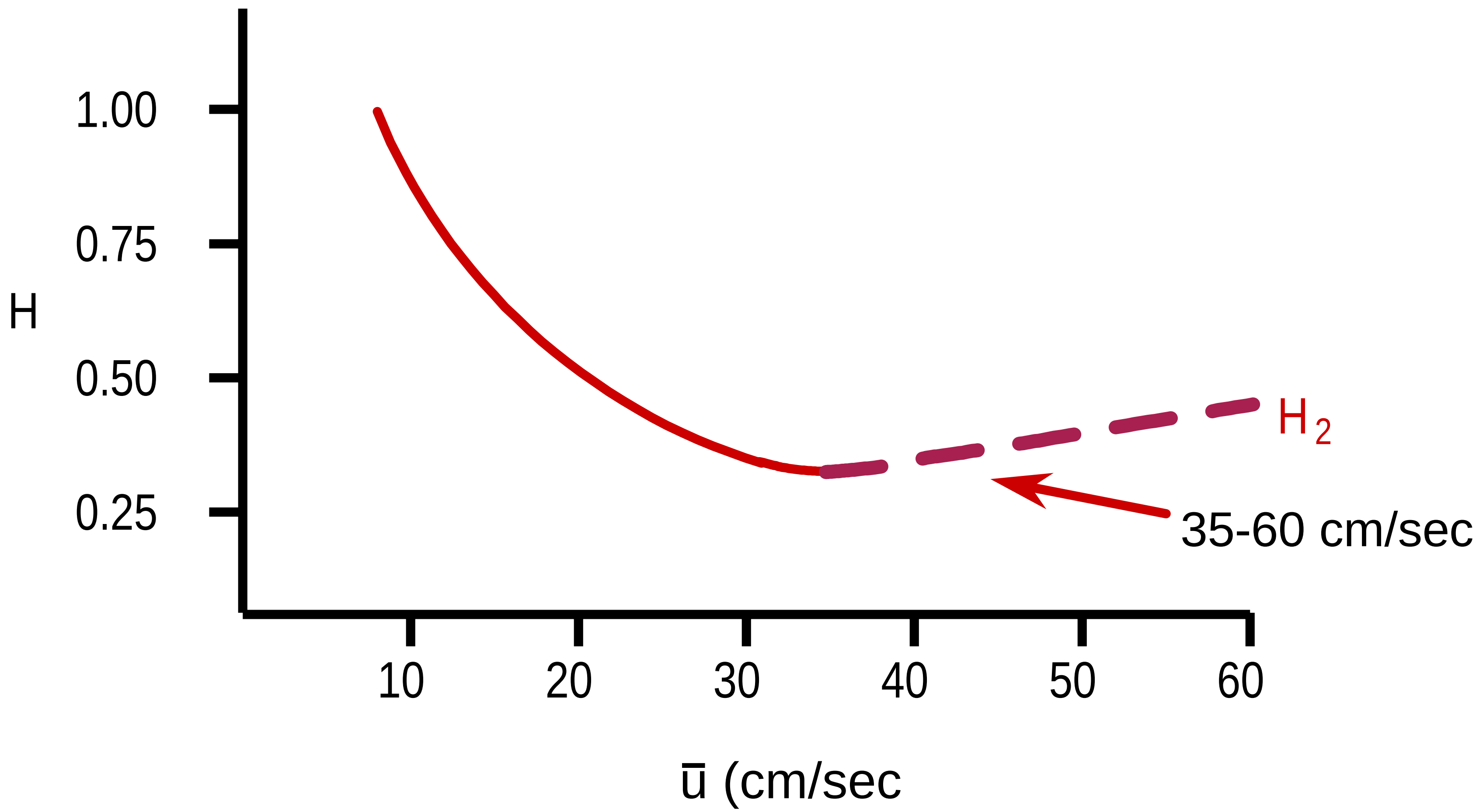
VAN DEEMTER CURVE

Hydrogen



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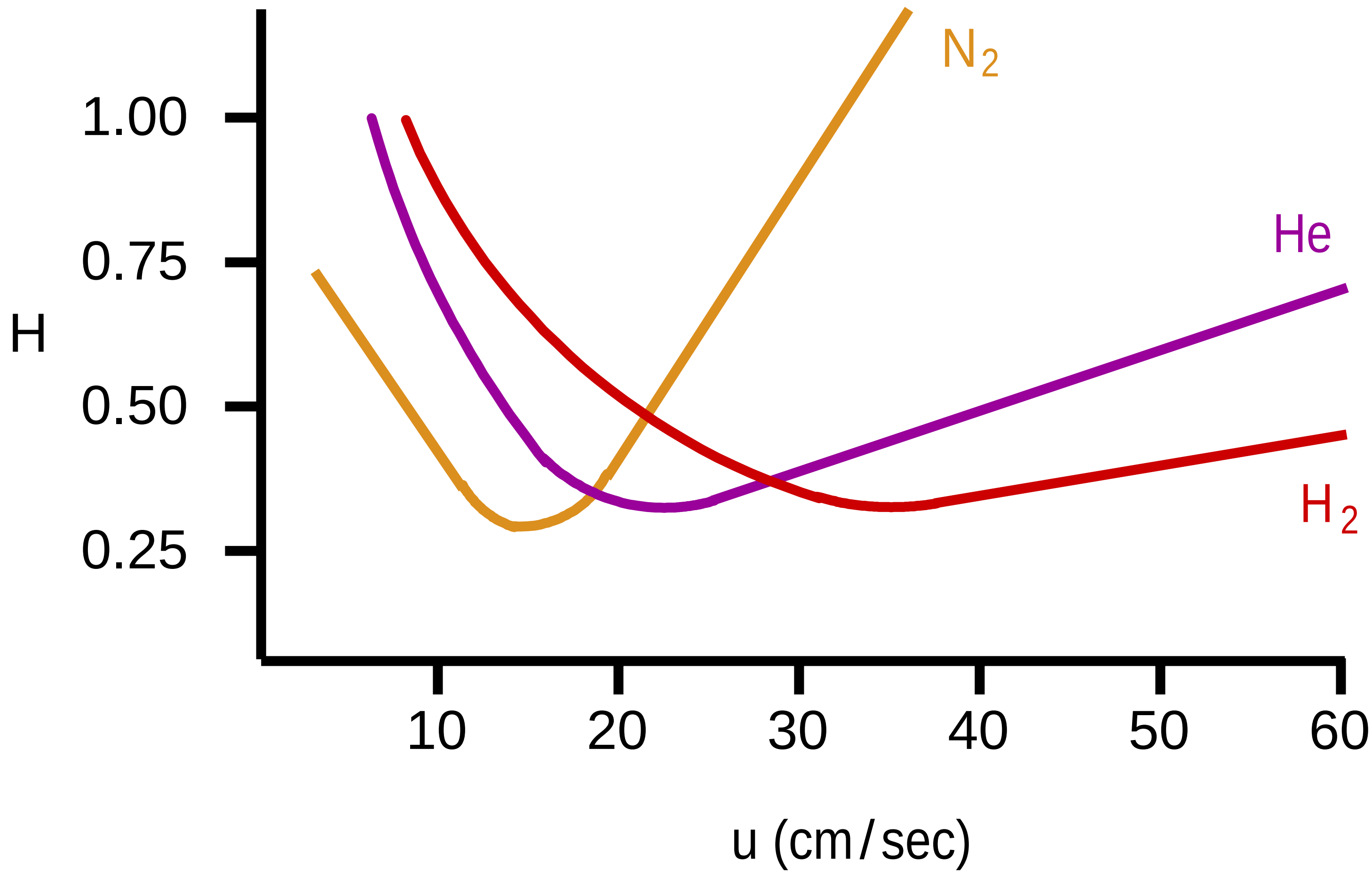
VAN DEEMTER CURVES



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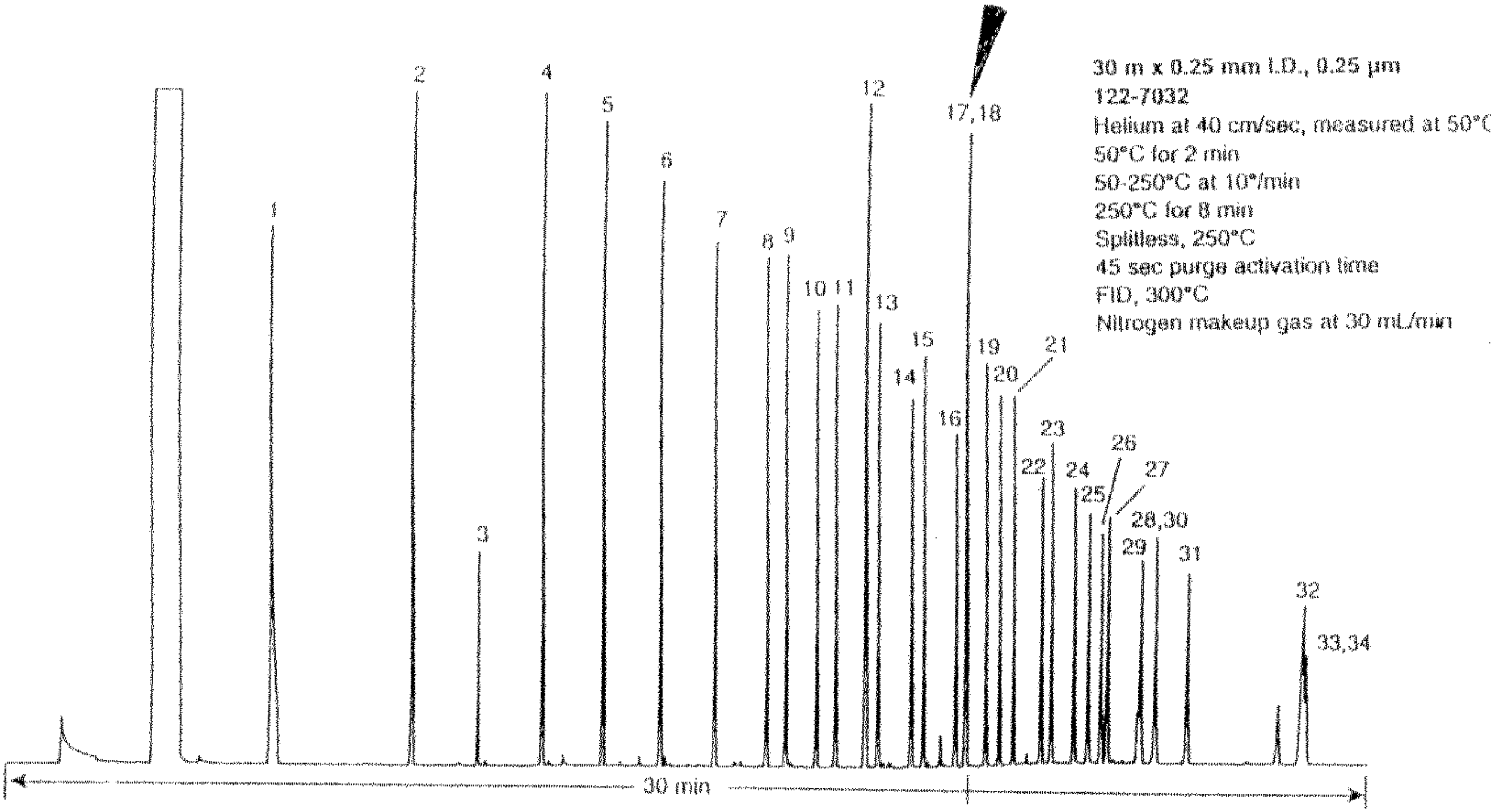
Optimizing $\bar{u}$ for a specific area in programmed mode



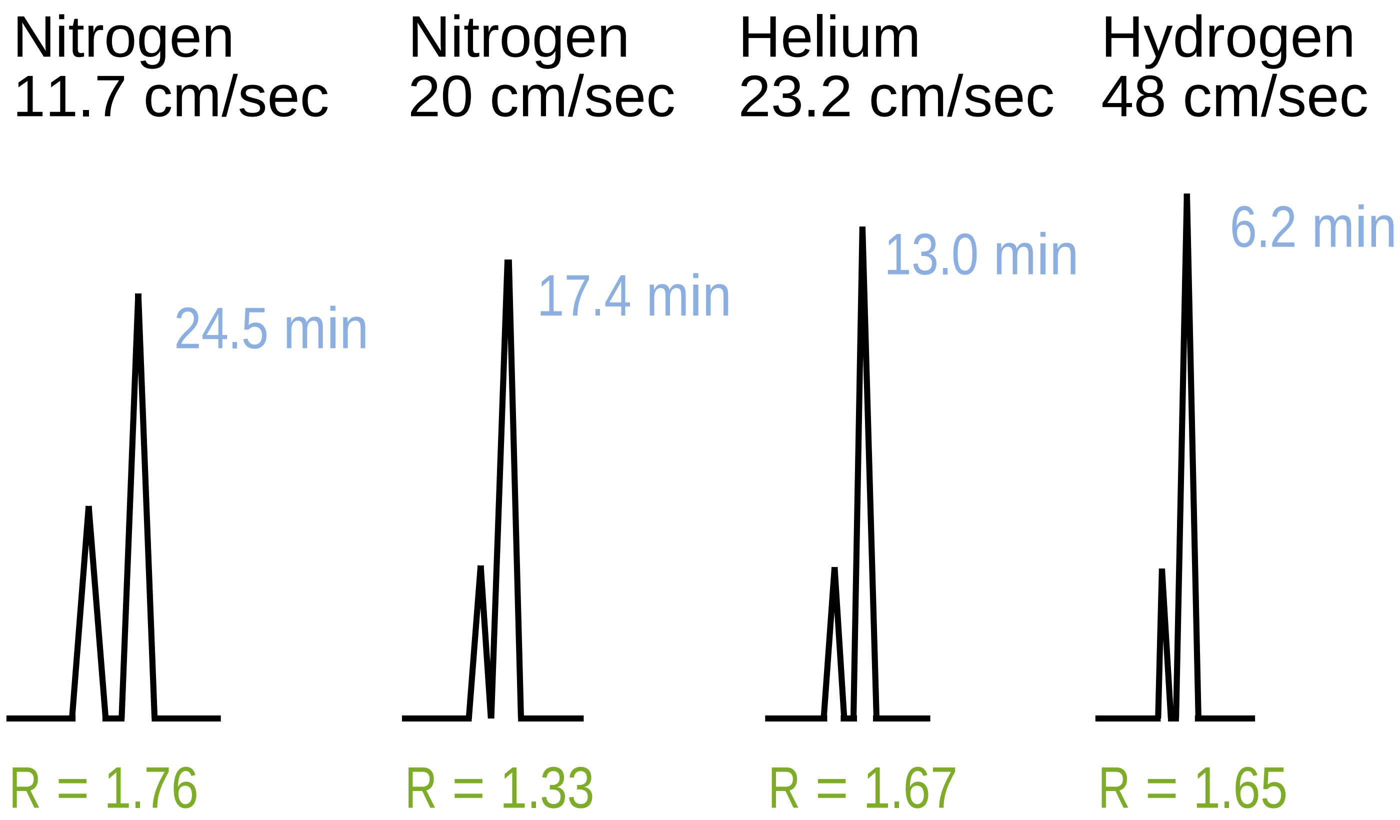
Critical area elutes at 242°C; at 212°C, that chromatographing plug is ca. half way through the column. Set oven temperature at 212, and optimize carrier for a solute k = 7. Cool oven to 50°C starting temperature, and institute run.

CARRIER GAS
Hydrogen Comments

- Hydrogen is extremely diffusive in air
- Difficult to reach explosive level of ~4 %
- Many GC's are flow regulated

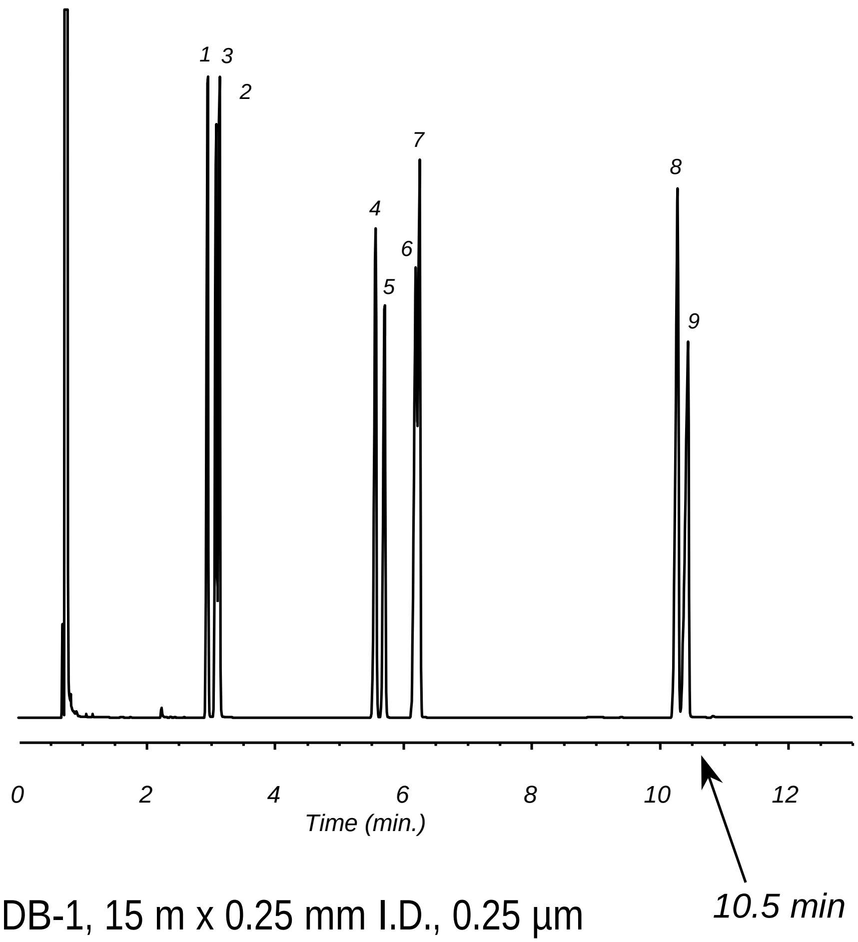
CARRIER GAS

Selection Example

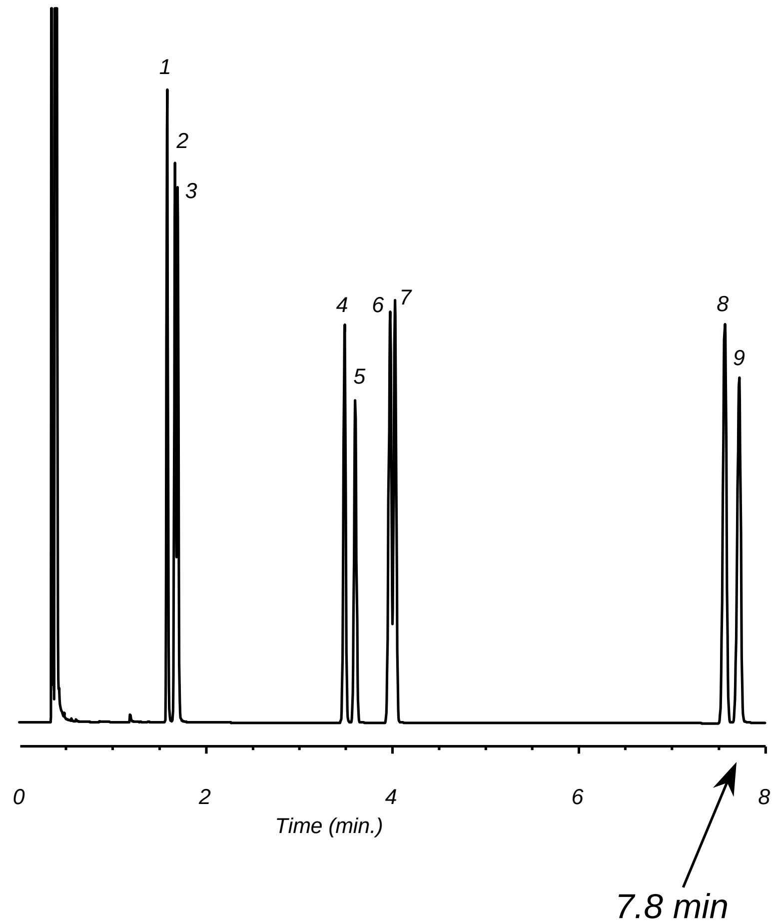


Carrier Gas
Helium vs. Hydrogen

Helium (35 cm/sec)



Hydrogen (73 cm/sec)



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

Carrier Gas

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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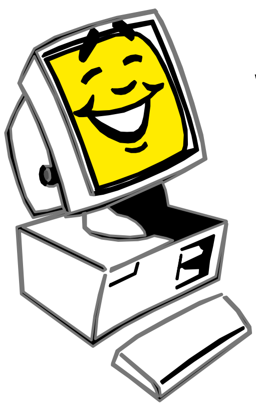
302-993-5304 (phone)*

**** Select option 4, then option 1.***

916-608-1964 (fax)



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