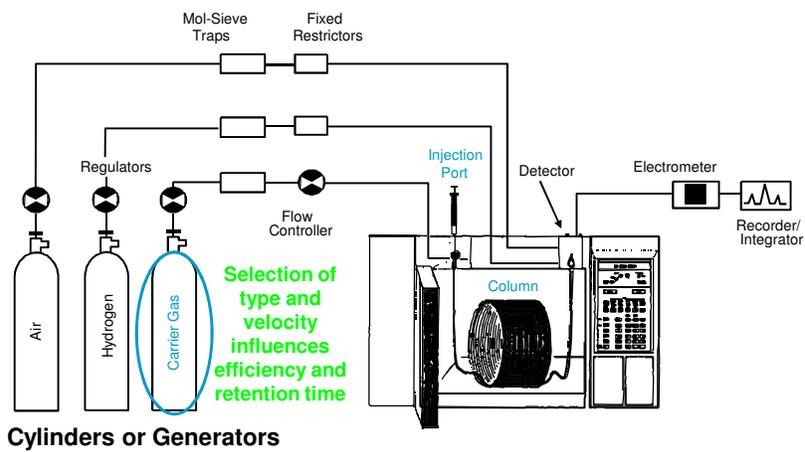


Carrier Gas Considerations and Utilizing the EPC

Typical Gas Chromatographic System



Carrier Gas

Affects resolution and retention time

Optimal range of velocities

Too low or high results in loss of resolution

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

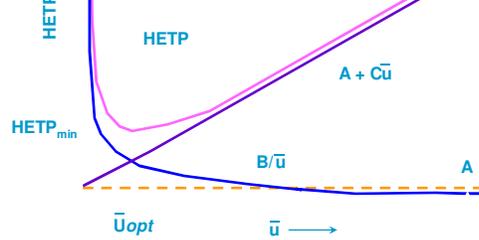
B = Longitudinal diffusion term

C = Mass transfer term

van Deemter Curves

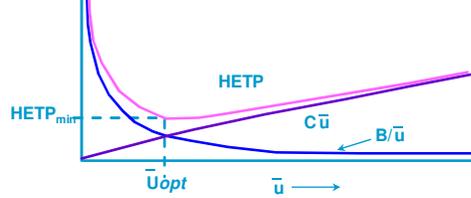
Packed Columns

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

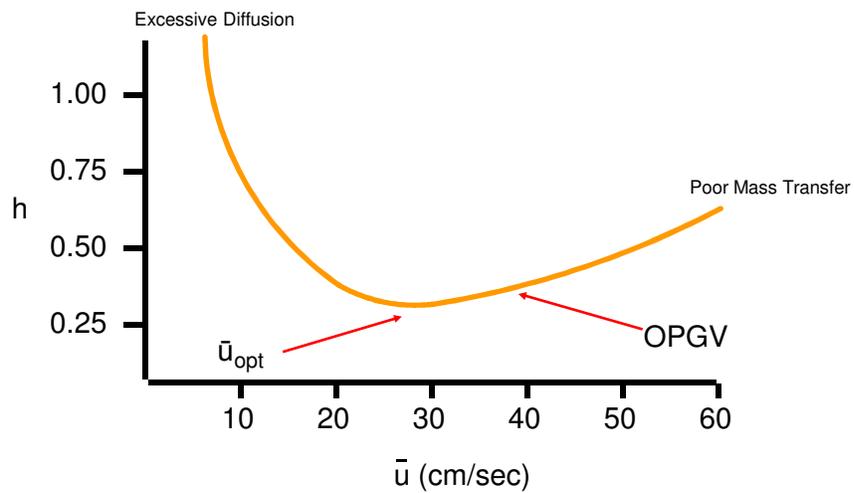


Open-Tubular Column

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



van Deemter Curve



\bar{u}_{opt} and OPGV

\bar{u}_{opt} : Optimum gas velocity (slowest velocity!)
Maximum efficiency

OPGV: Optimum *practical* gas velocity
Maximum efficiency per unit time
(1.5 to 2) X \bar{u}_{opt}

Best \bar{u} = Balance resolution and analysis time

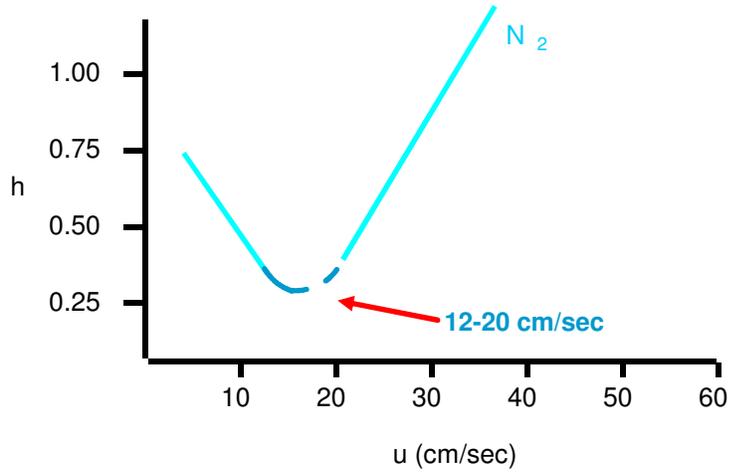
Diffusion Constants for Dodecane @ 150°C

Nitrogen = 0.15 cm²/sec

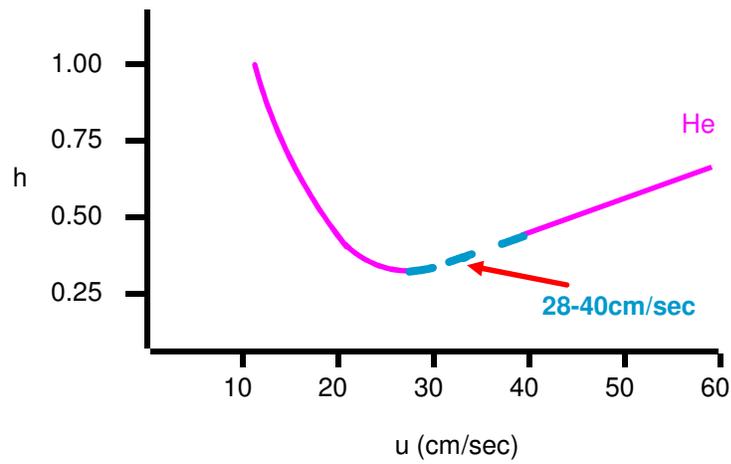
Helium = 0.4 cm²/sec

Hydrogen = 0.6 cm²/sec

van Deemter Curve Nitrogen

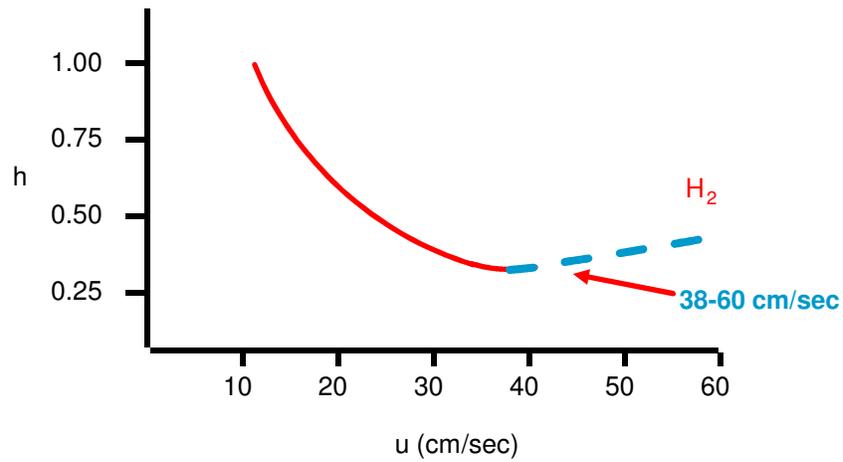


van Deemter Curve Helium



van Deemter Curve

Hydrogen



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Agilent Technologies

Carrier Gas Selection

Carrier Gas - Hydrogen Comments

Hydrogen is extremely diffusive in air

Difficult to reach explosive level of ~4 %

Most GC's flow regulated with safety shutdown

Spring loaded/Explosion ready doors

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Agilent Technologies

Carrier Gas Selection

Hydrogen as Carrier – Contamination?

Contamination of GC flow modules and lines.

Hydrogen acts as a scrubber.

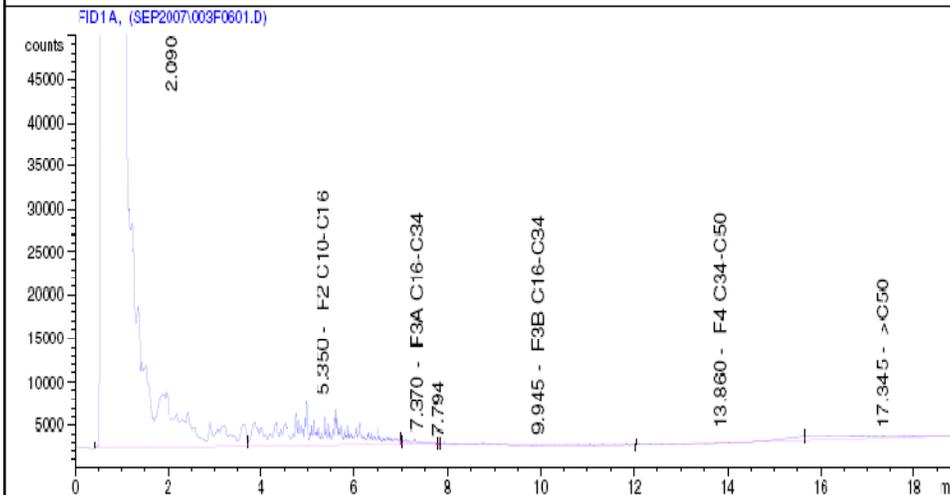
On the MS this typically looks like Hydrocarbon contamination

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.

Contamination?! – scrubbing or vapor volume



Hydrogen as Carrier – MS and Lower Pressures

Hydrogen is more difficult for the MS vacuum system to pump away as compared to Helium.

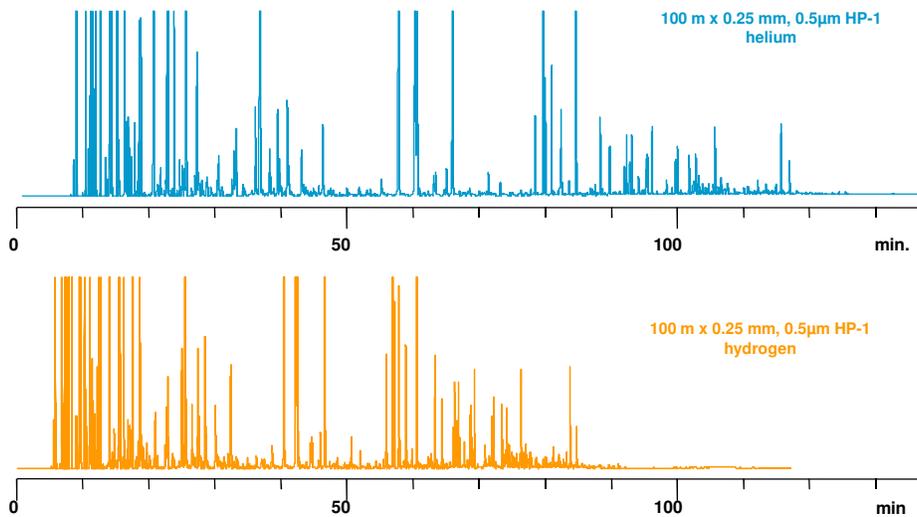
Be careful not to get to a “negative” head pressure situation. (pulling instead of pushing flow is not good).

Trace level work on the MS requires low flow rates.

Must use smaller ID columns so you don't have higher flow rates. (length plays a role as well)

0.18mm ID or smaller is ideal for trace level MS work when using Hydrogen.

Fast DHA Analysis – 33% Faster with Hydrogen



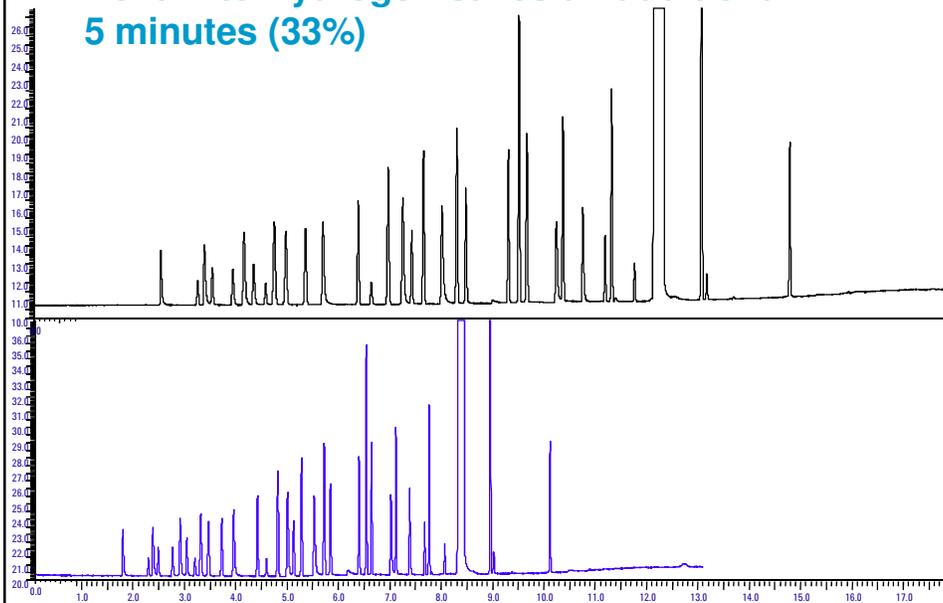
Solvents in Drugs

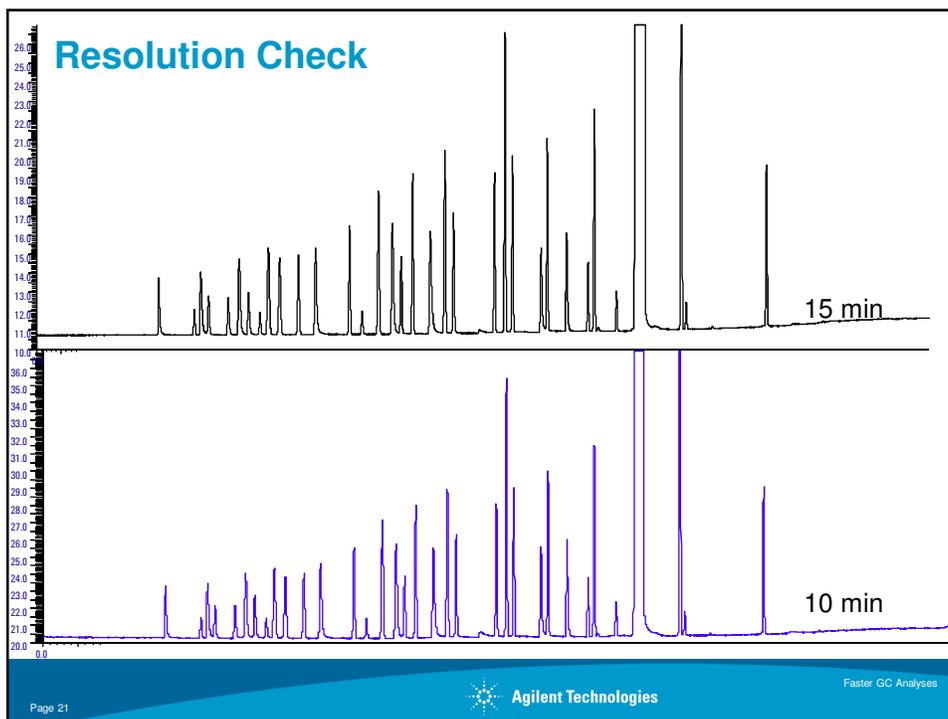
GC Method Translation

Criterion: Translate Only Best Efficiency Fast Analysis None **Speed gain: 1.45889**

	Original Method	Translated Method				
Column						
Length, m	30	<input type="checkbox"/> 30				
Internal Diameter, μm	250	<input type="checkbox"/> 250.0				
Film						
Thickness, μm	1.4	<input checked="" type="radio"/> 1.4				
Phase Ratio	44.64	<input type="radio"/> 44.64				
Carrier Gas	Helium	<input checked="" type="checkbox"/> Hydrogen				
Enter one Setpoint						
Head Pressure, psi	16.382	10.571				
Flow Rate, mL/min	1.5	1.8750				
Outlet Velocity, cm/sec	54.71	68.39				
Average Velocity, cm/sec	33.69	49.15				
Hold-up Time, min	1.48406	1.01725				
Outlet Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696				
Ambient Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696				
Oven Temperature 1-ramp Program						
	Ramp Rate	Final Temp.	Final Time	Ramp Rate	Final Temp.	Final Time
	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min
Initial		40	3.84		40	2.632
Ramp 1	13.01	200	1.87	18.980	200	1.282
Sample Information	None					

Helium to Hydrogen saves an additional 5 minutes (33%)





Volatile Chlorinated Solvents on a Megabore

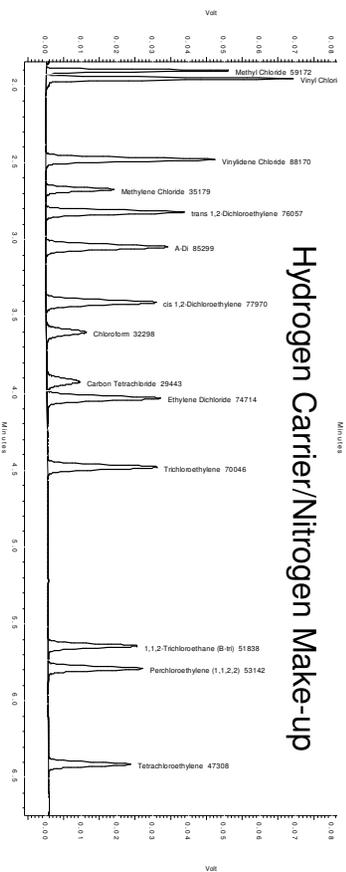
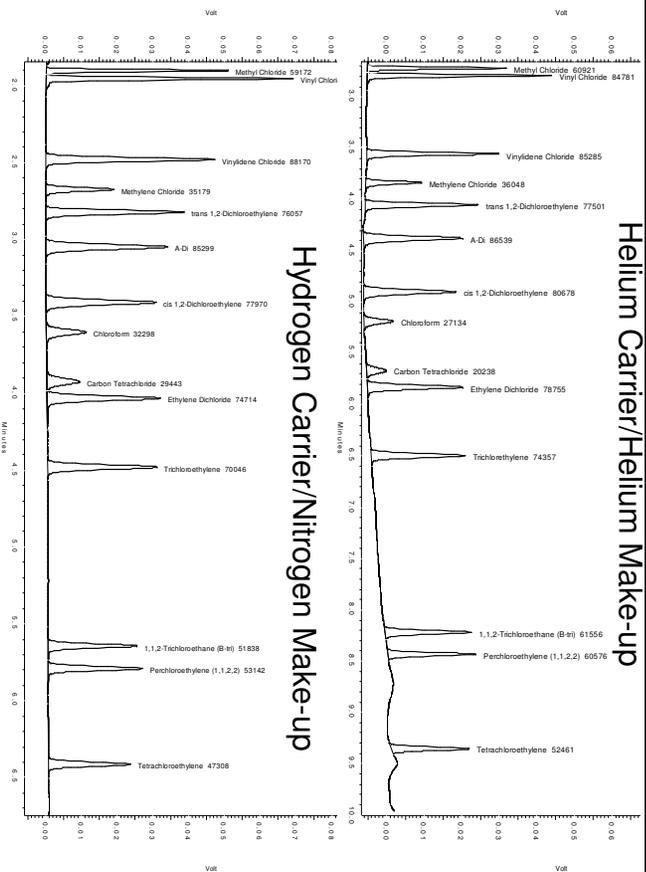
GC Method Translation - CH233.MXD

Criterion: Translate Only Best Efficiency Fast Analysis None Speed gain: 1.45977

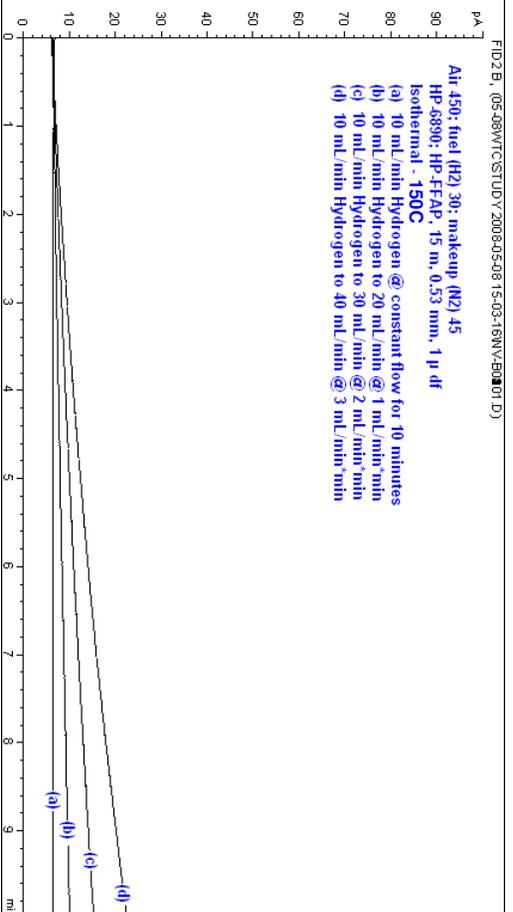
	Original Method	Translated Method	
Column			
Length, m	75.0	<input checked="" type="checkbox"/> 75.0	
Internal Diameter, μm	530	<input checked="" type="checkbox"/> 530	
Film		<input type="checkbox"/> Unlock	
Thickness, μm	3	<input checked="" type="radio"/> 3	
Phase Ratio	44.17	<input type="radio"/> 44.17	
Carrier Gas	Helium	<input type="checkbox"/> Hydrogen	
Enter one Setpoint			
Head Pressure, psi	16.5174	10.669	
Flow Rate, mL/min	10.0000	12.5000	
Outlet Velocity, cm/sec	91.54	114.43	
Average Velocity, cm/sec	56.18	82.01	
Hold-up Time, min	2.22489	1.52414	
Outlet Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696	
Ambient Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696	
Oven Temperature 2-ramp Program			
	Ramp Rate	Final Temp.	Final Time
	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min
Initial	80	5	
Ramp 1	20	180	00.000
Ramp 2			
	29.195	180	0.000
Sample Information None			

Carrier Gas Selection

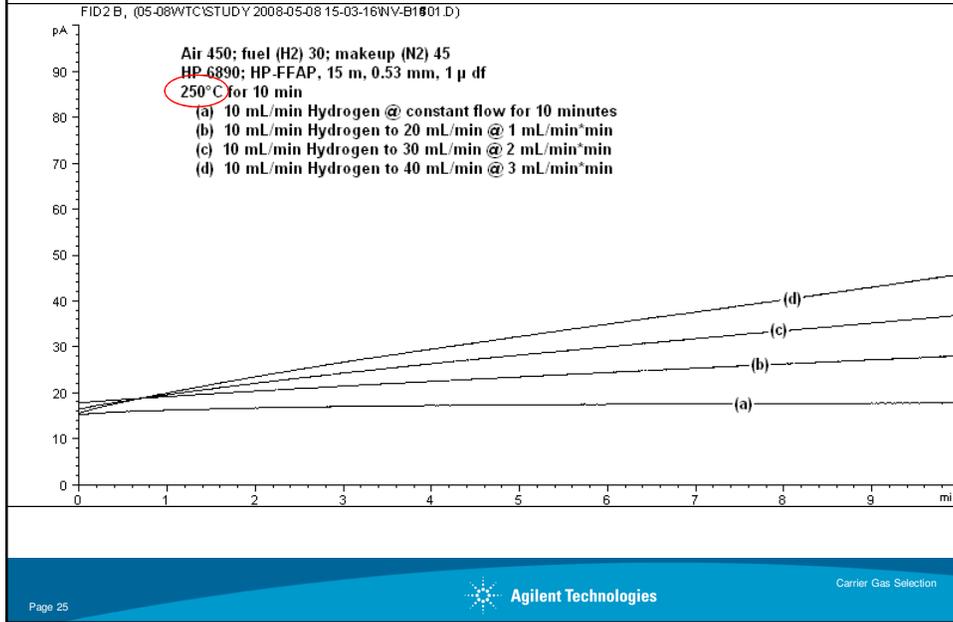
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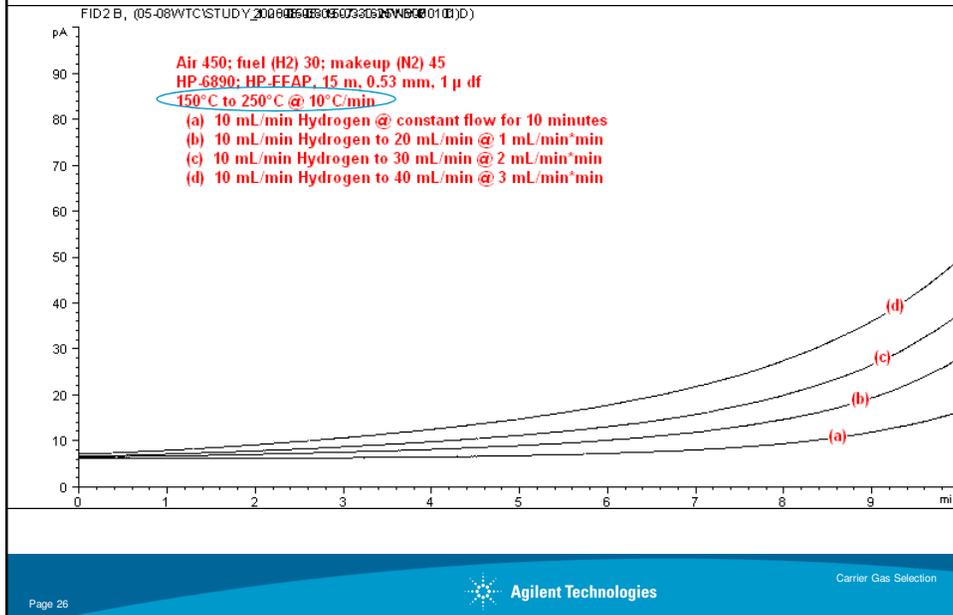
Megabore with Hydrogen Carrier - could give a baseline rise as the total H2 increases



Isothermal column bleed and Hydrogen increase

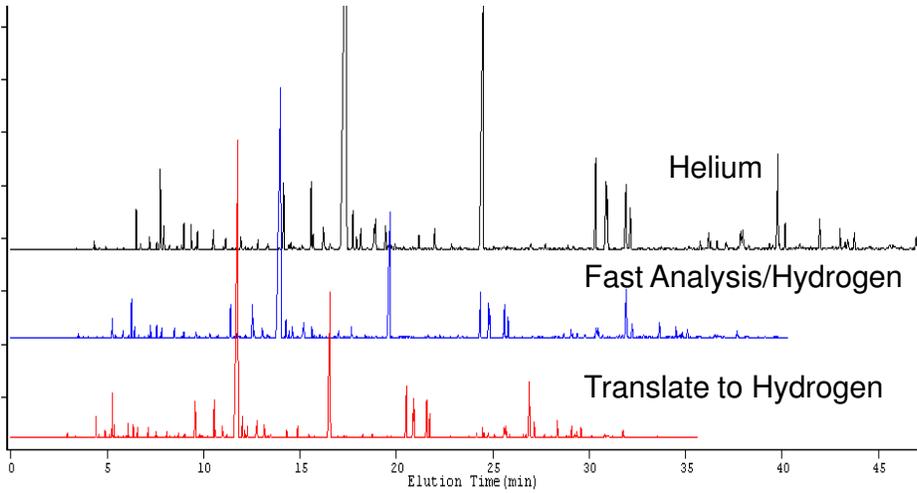


Temperature program column bleed with increasing Hydrogen



Steam Cracked Naphtha

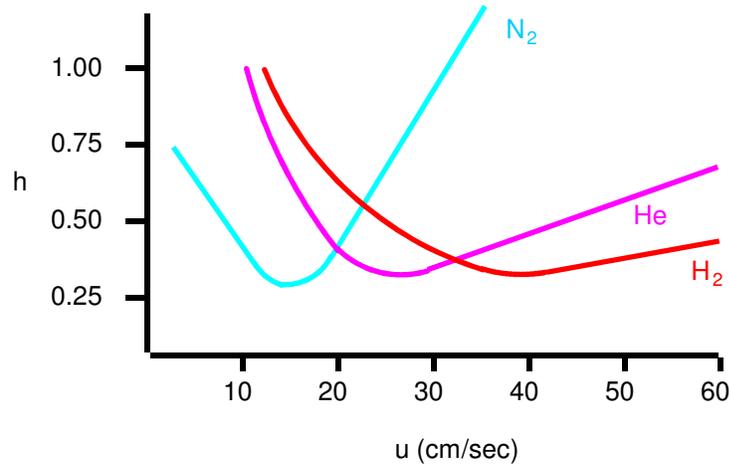
DB-1, 60m x 0.32mm x 0.25um



Steam Cracked Naphtha

GC Method Translation - NONE.MXD			
Criterion:	Translate Only	Best Efficiency	Fast Analysis
Speed gain:			1.23431
Original Method	Translated Method	Translated Method	Translated Method
Column Length, m	60.00	<input checked="" type="checkbox"/> 60.00	<input checked="" type="checkbox"/> 60.00
Internal Diameter, μ m	320.0	<input checked="" type="checkbox"/> 320.0	<input checked="" type="checkbox"/> 320.0
Film Thickness, μ m	0.250	<input type="checkbox"/> Unlock <input checked="" type="radio"/> 0.250	<input type="checkbox"/> Unlock <input checked="" type="radio"/> 0.250
Phase Ratio	320.0	<input type="radio"/> 320.0	<input type="radio"/> 320.0
Carrier Gas	Helium	<input type="checkbox"/> Hydrogen	<input type="checkbox"/> Hydrogen
Enter one Setpoint			
Head Pressure, psi	17.189	9.313	11.122
Flow Rate, mL/min	3.2000	3.2000	4.0000
Outlet Velocity, cm/sec	56.48	56.48	70.60
Average Velocity, cm/sec	34.09	42.08	49.97
Hold-up Time, min	2.93327	2.37645	2.00136
Outlet Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696	<input type="checkbox"/> 14.696
Ambient Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696	<input type="checkbox"/> 14.696
Oven Temperature	1-ramp Program		
	Initial Ramp 1		
	Ramp Rate	Final Temp.	Final Time
	$^{\circ}$ C/min	$^{\circ}$ C	min
	3.000	-20.00	5.000
	3.703	250.00	16.203
	4.397	250.00	13.646
Sample Information	None		

van Deemter Curves



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Agilent Technologies

Carrier Gas Selection

Carrier Gas Comparison

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

Agilent Technologies

Carrier Gas Selection

Carrier Gas - Selection Summary

Hydrogen is best especially for wide k range analyses

Helium is acceptable

Nitrogen is not recommended

Carrier Gas

Properties

Expands to fill the space it occupies

Expands with increase in temperature

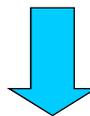
Viscosity increases with temperature

Compressible

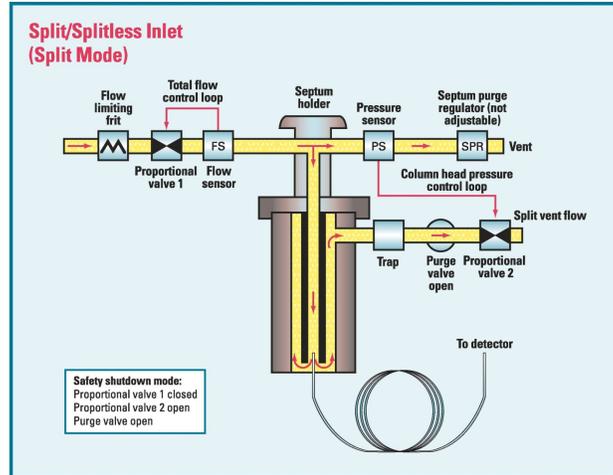
THEREFORE:

Flow increases as it goes down the length of the column

AND At Constant Pressure:

T  \bar{u} 

EPC To The Rescue!



BENEFITS OF EPC

Reliability and Reproducibility of set-points

(ambient temperature and pressure compensation)

Choice of constant flow versus constant pressure

Ability to **Pulse** flow during injection to buffer expansion and increase speed of transfer and amount on column

Flow ramping available to reduce time at the end of the analysis or during **Bake Out**

EPC CAUTIONS

Things to be aware of

EPC doesn't measure flow or velocity, they are calculated, THEREFORE...

Dimensions of the column, length and especially internal diameter, must be entered precisely or an errant velocity will result.

The Poiseuille Equation

Affects Of Column Radius And Length

$$F = \left(\frac{\pi r^4}{16 \eta L} \right) \left(\frac{(p_i^2 - p_o^2)}{p_o} \right)$$

Volumetric flow is a quadratic to the fourth power function of radius

Linear velocity is a squared function of radius

Length has less of an impact

EPC for Split/Splitless Pulsed Injection

Pressure Pulse contains sample expansion and transfers analytes to the column faster.

Pulsed Split

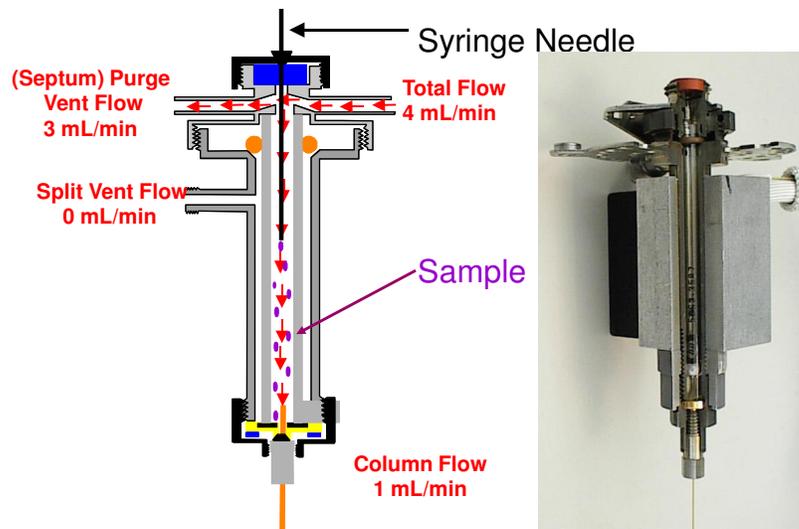
- the most volatile components and solvent effected most
- faster sample transfer not as critical since it's already fast

Pulsed Splitless

- sample containment more critical than in split injection
- much sharper peaks than in traditional splitless injection

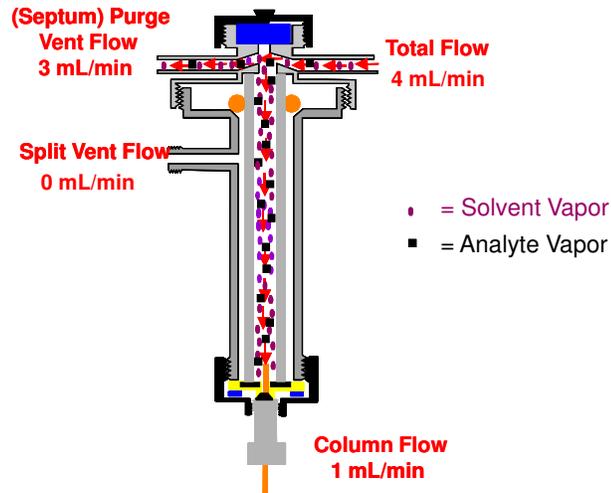
Splitless Injection

Sample Injection



Splitless Injection

Injection Overload = Backflash

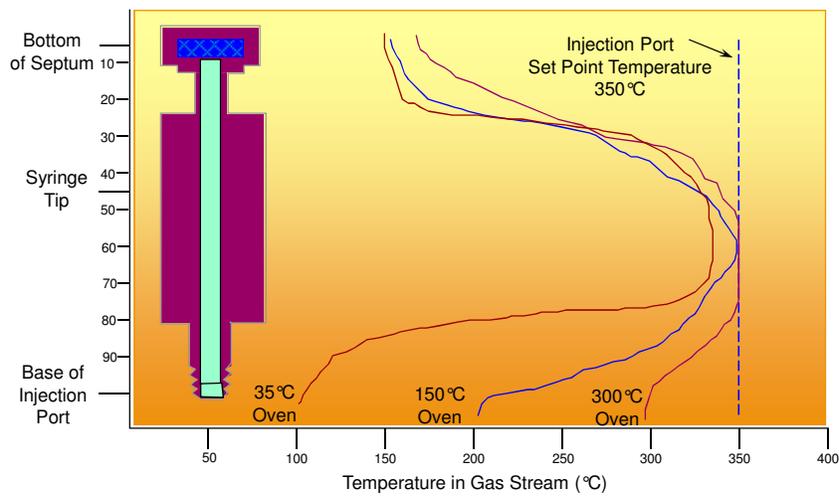


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Carrier Gas Selection

Temperature Profile of a Typical Vaporization Injector vs Oven Temperature



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Carrier Gas Selection

Solvent Expansion Equation

$$\text{Solvent Vapor Volume} = 22,400 \times A \times B \times C \times I$$

A = solvent density/solvent molecular weight

B = $15 / (15 + \text{column headpressure [in psi]})$

C = $(\text{Injection Port Temperature}[\text{°C}] + 273) / 273$

I = liquid injection volume [μL]

Example

1 μL of water injected at 250 °C under 15 psi headpressure

$$22,400 \times 1/18 \times 15/30 \times 523/273 \times 1 = 1,192 \mu\text{L vapor}$$

Pressure Flow Calculator & Solvent Vapor Volume Calculator



Pressure Flow Calculator

Column Pressure/Flow Calculator

Column Parameters

Length (m): 80.0

i.d. (mm): 0.320

Temp (C): 100

Carrier Gas Parameters

Inlet Pressure (gauge): 10.0

Outlet Flow (mL/min): 1.66

Average Velocity (cm/s): 31.4

Outlet Pressure (Absolute): 14.7

1 Atm Vacuum Other

Split Ratio

Split vent flow: 0.0

Split Ratio(vent flow/col flow): :1

Holdup time

1.59 minutes

Inlet

Inlet Temperature (C): 175

Inlet Flow (mL/min): 1.62

Carrier gas

Helium (Opt. Vel. range: 20 40)

Pressure Units: KPa psi bar

Buttons: Help, Plot..., Print, OK

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Agilent Technologies

Carrier Gas Selection

Solvent Vapor Volume Calculator

Solvent Vapor Volume Calculator

Approximate vapor volume(ul): 1021 ul

Overload: 103%

Injection Volume (ul): 1.0

Inlet Temp (C): 175

Inlet Pressure: 14.6

Pressure Units: KPa psi bar

Solvent Properties

Water

Boiling Pt (C): 100

Denisty (g/cm3): 0.998

Mol'wt. (amu): 18.02

Injection Liner Volume (ul): 990

19251-60540 strait

Capacity limits (%): 75 100

Buttons: Print, Help, OK

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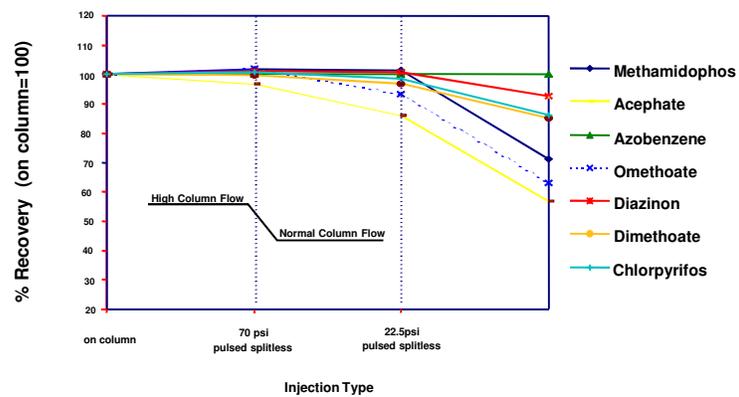
Carrier Gas Selection

Minimizing Backflash

- Large volume liner
- Small injection volume
- Low expansion solvent
- Low injector temperature
- High carrier gas flow rates (EPC?)
- High head pressures (EPC?)

Benefits of the Pulsed Splitless Mode

% Recovery of Each Labile Pesticide Relative to Cool On-Column injection



Select Pulsed Splitless Mode in Inlets

Instrument | Edit | Inlets: (6890)

■ Oven Temp

Temperature (°C)

Time (min.)

Plot...

Injector Valves **Inlets** Columns Oven Detectors Signals Aux Runtime Options

Front: EPC Split-Splitless Inlet

Mode: Splitless Gas: He

On	Actual	Setpoint
<input type="checkbox"/>		250
<input checked="" type="checkbox"/>	8.81	
<input checked="" type="checkbox"/>	53.6	

Purge Flow to Split Vent: 50.0 mL/min @ 2.00 min

GasSaver 20.0 mL/min @ 2.00 min

Front

Apply

OK

Cancel

Help

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Agilent Technologies

Carrier Gas Selection

Check the Splitless Pressure

Instrument | Edit | Columns: (6890)

■ Oven Temp

Temperature (°C)

Time (min.)

Plot...

Injector Valves Inlets **Columns** Oven Detectors Signals Aux Runtime Options

Column: 1 Mode: Const Flow

Inlet: Front

Detector: MSD

Outlet psi: Vacuum

He Flow

Setpoint	Actual
Pressure: 8.81	psi
Flow: 1.0	mL/min
Average Velocity: 37	cm/sec

Installed Column

Change...

Manufacturer's Specifications

Model No: Agilent 19091T-433 280°C Max
 HP-1301 6% Cyanopropyl Phenyl Methyl
 Capillary: 30.0 m x 250 µm x 0.25 µm nominal

Flow	ml/min ²	ml/min	Hold min	Run Time
Initial		1.0	0.00	10.00
Ramp 1	0.00	0.0	0.00	
Ramp 2	0.00	0.0	0.00	
Ramp 3	0.00	0.0	0.00	
Post Run			0.00	10.00

Apply

OK

Cancel

Help

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Agilent Technologies

Carrier Gas Selection

Double or Triple the Pressure for ~1 sec less than the Purge Activation Time

Instrument | Edit | Inlets: (6890)

■ Oven Temp

Temperature (°C)

Time (min.)

Plot...

Injector Valves Inlets Columns Oven Detectors Signals Aux Runtime Options

Front: EPC Split-Splitless Inlet

Mode: Pulsed Splitless Gas: He

On	Actual	Setpoint
<input checked="" type="checkbox"/> Heater, °C		250
<input checked="" type="checkbox"/> Pressure, psi		8.81
<input checked="" type="checkbox"/> Total Flow, mL/min		53.6

Injection Pulse Pressure: 18.0 psi until 0.47 min

Purge Flow to Split Vent: 50.0 mL/min @ 0.50 min

GasSaver 20.0 mL/min @ 2.00 min

Front

Apply

OK

Cancel

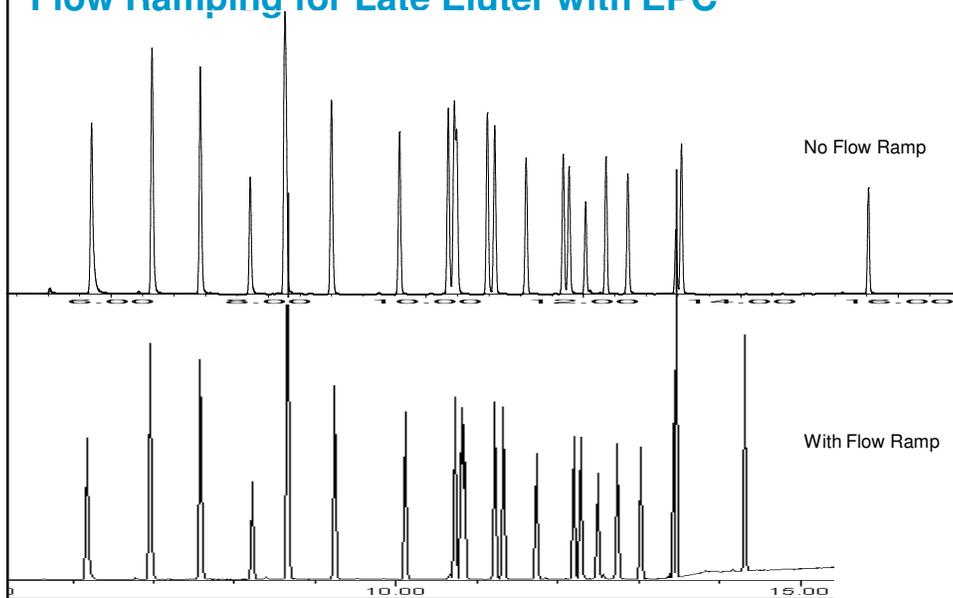
Help

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Carrier Gas Selection

Flow Ramping for Late Eluter with EPC

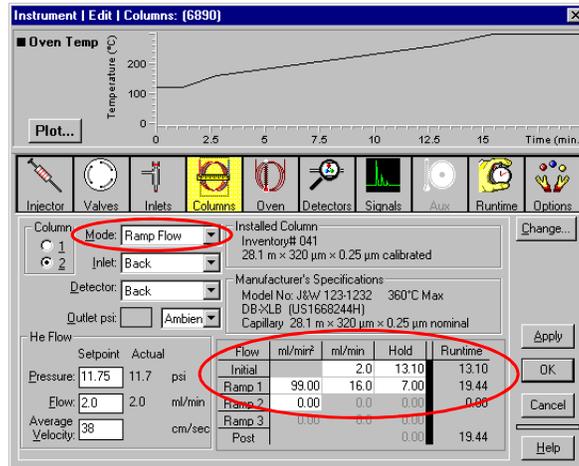


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Carrier Gas Selection

EPC Flow Ramping for Late Eluters and Faster Bake Outs



Using Method Translator for Calculating Pressure Needed for a Given Flow at a Given Temperature

GC Method Translation

Criterion: Translate Only Best Efficiency Fast Analysis None Speed gain: 0.62368

	Original Method	Translated Method
Column		
Length, m	30	40.00
Internal Diameter, µm	320	100.0
Film		
Thickness, µm	0.25	0.078
Phase Ratio	320.0	320.0
Carrier Gas	Helium	Hydrogen
Enter one Setpoint		
Head Pressure, psi	78.265	441.653
Flow Rate, mL/min	16	6.2500
Outlet Velocity, cm/sec	661.71	2646.83
Average Velocity, cm/sec	153.60	127.73
Hold-up Time, min	0.325528	0.521946
Outlet Pressure (absolute), psi	14.696	14.696
Ambient Pressure (absolute), psi	14.696	14.696
Oven Temperature Isothermal, °C	320	320
Sample Information	None	

Using Chemstation for Calculating Pressure Needed for a Given Flow at a Given Temperature

Instrument | Edit | Oven: (6890)

Temperature (°C) vs. Time (min.) plot showing a ramp from 200°C to 300°C.

Oven Ramp	°C/min	Next °C	Hold min.	Run Time
Initial		200	2.00	2.00
Ramp 1	20.00	230	0.00	6.50
Ramp 2	0.00	240	0.00	
Ramp 3	0.00	270	0.00	
Ramp 4	0.00	0	0.00	
Ramp 5	0.00	0	0.00	
Ramp 6	0.00	0	0.00	
Post Run		0	0.00	6.50

Instrument | Edit | Columns: (6890)

Temperature (°C) vs. Time (min.) plot showing a ramp from 200°C to 300°C.

Flow	ml/min?	ml/min	Hold min.	Run Time
Initial		16.0	13.10	6.50
Ramp 1	99.00	16.0	0.00	6.50
Ramp 2	0.00	0.0	0.00	
Ramp 3	0.00	0.0	0.00	
Post Run		0.00	0.00	6.50

Conclusions

Carrier Gases have an optimum range of velocities
 -Too low or high results in loss of resolution

Hydrogen is the best carrier gas for high velocity work
 -Can be used safely in 6890/7890
 -Lighter molecule than Helium
 -Lower pressure considerations

EPC gives the ability to change flow reproducibly
 -Pulsed Injection (efficiency, backflash)
 -Flow Programming (bake out, late eluters)