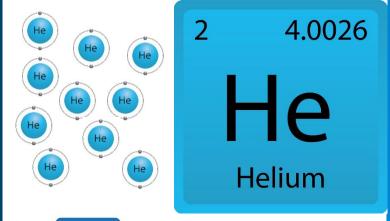
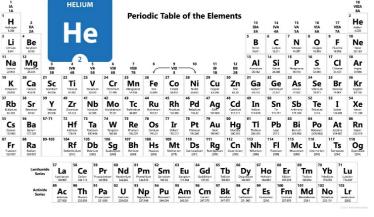
How to Combat the Helium Shortage: Making the Switch from Helium to Hydrogen or Nitrogen Carrier Gas

Mark Sinnott
Application Engineer
December 5th 2019









Market Situation

The world of He supply is not reliable, prices are increasing and customers are seeking alternative carrier gases

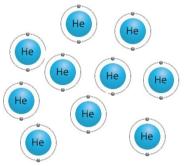




Researchers have a need to find suitable alternatives to either eliminate or reduce He consumption

Industries That Use Helium







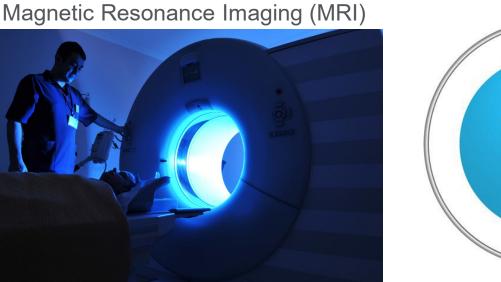
4.0026 He Helium

Boiling point -269 °C/4.2 K

Research

Nuclear Magnetic Resonance spectroscopy (NMR)

Gas chromatography









December 9, 2019

Healthcare

Webinar Outline

Use of Gas Saver

Carrier gas decision tree

Decision making guide to fit your carrier gas requirements

Helium conservation

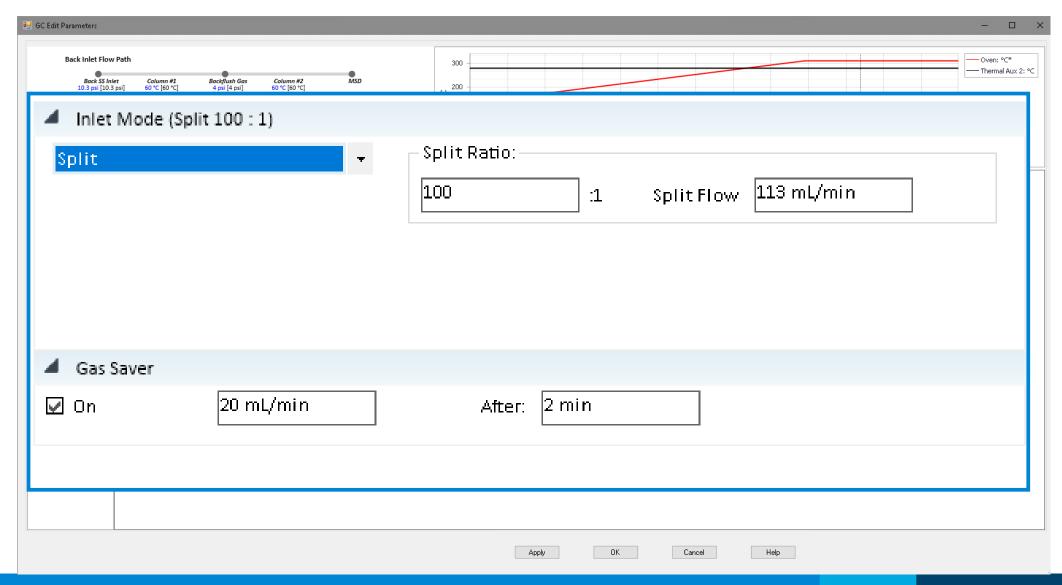
- Smarter helium use with new hardware/software tools
- No need to revalidate existing GC methods

Migrating existing helium GC methods to H₂ or N₂

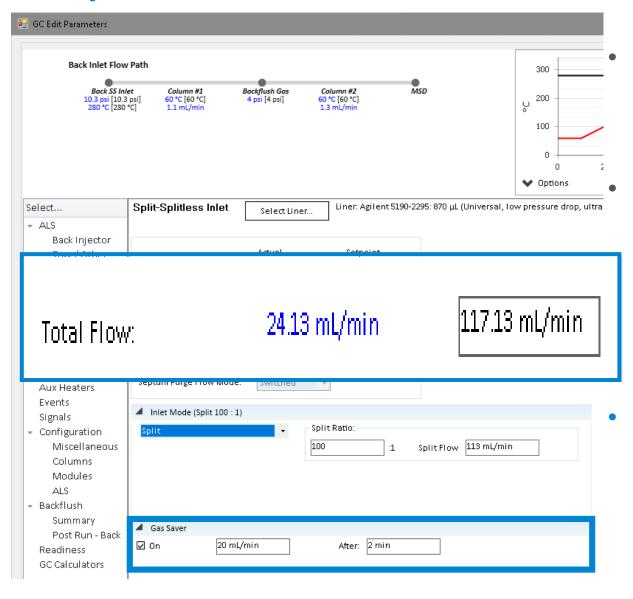
Best practices to obtain the same results and minimize method revalidation

Cautions about making the switch to Hydrogen for MSD systems

Have You Ever Noticed the Gas Saver Section of the Inlet Method Editor?



Why Would I Want to Use Gas Saver?



When enabled, GC automatically runs Gas Saver

Beneficial when using split mode

Gas Saver mode turns on after injection

Turns off during the prep run and injection duration

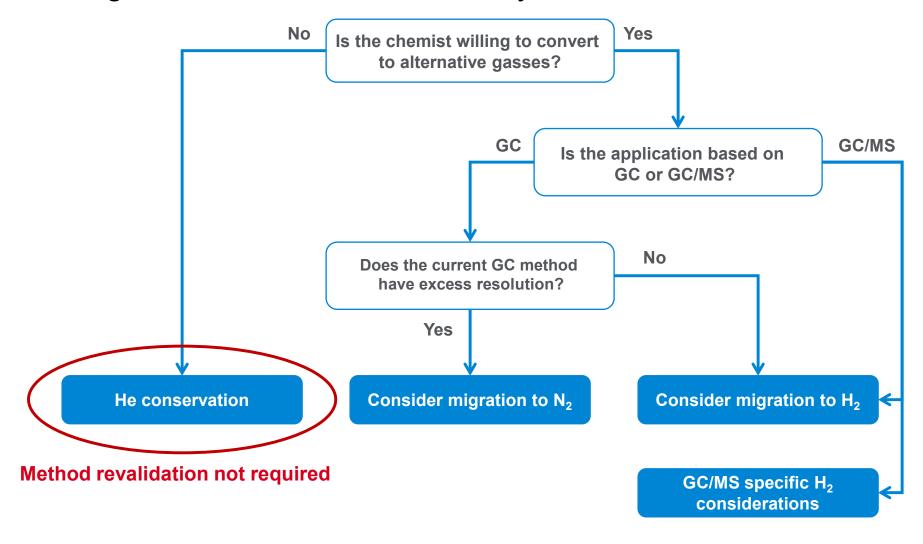
Lowers carrier gas use to save helium (or other carrier gas) and cut costs

Suggested parameters

- Flow No lower than 15 mL/min
 Recommended: ~20 mL/min
- Time ~2 to 5 minutes

Carrier Gas Decision Tree

Continue using helium, but in a smarter way



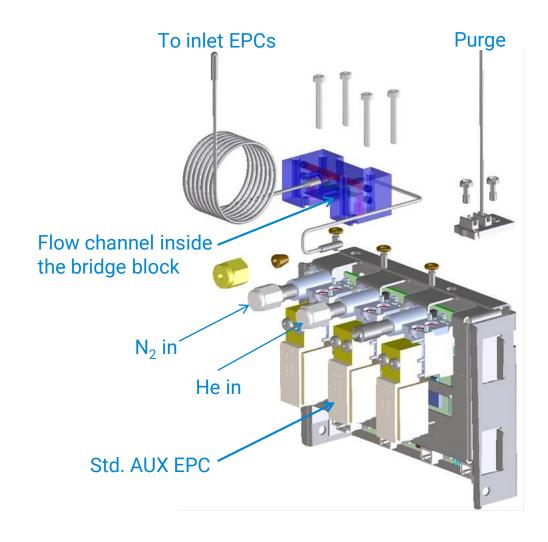
Reducing Helium Use With Conservation

Programmable helium conservation module (available for Agilent 7890B, 8860, 8890 GC systems)

- Automatically switches carrier gas supply to N₂ standby during idle time
- Integrates into the Sleep and Wake function of the GC
- Combined with Helium Gas Saver to greatly reduce helium consumption
- Better alternative to just "shutting off the GC"
 - No system contamination with ambient air exposure
 - Faster restart of heated zones

Helium Conservation Module

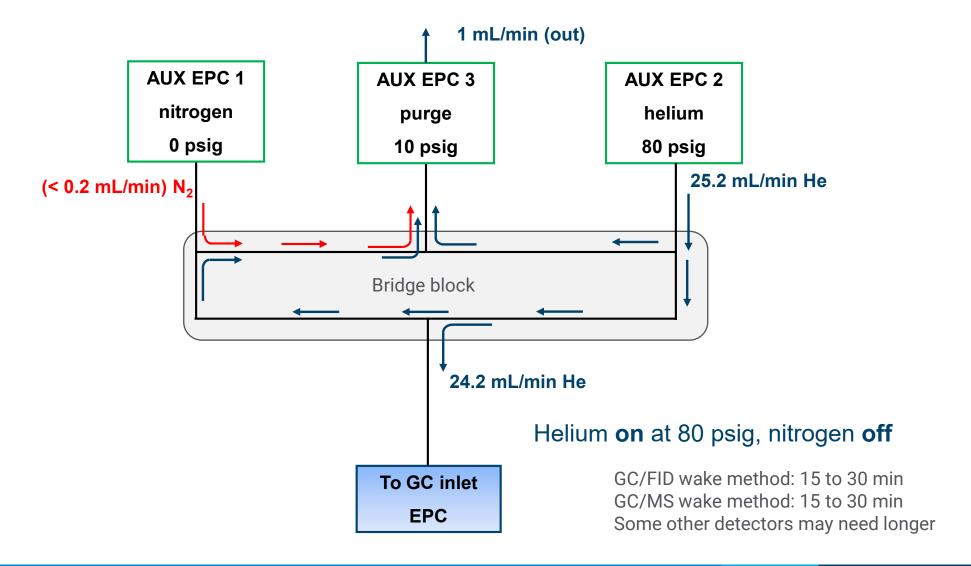
Seamlessly integrated onto GC hardware and software



- Built on 5th generation EPC
- Fully controlled by Agilent data systems
- Purge channel prevents cross contamination of gases
- Precise pressure control between tank and GC
- Switch between gases within 15 to 30 min for most detectors

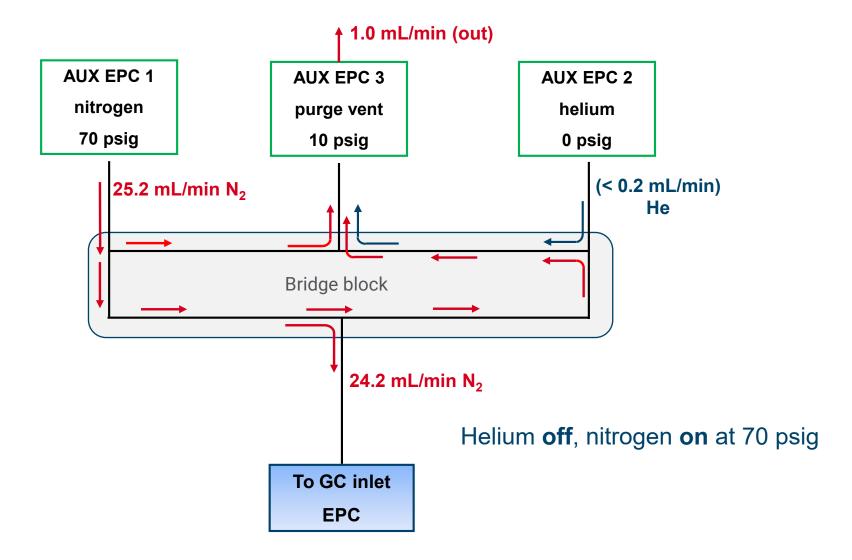
How Does It Work?

Normal operation mode (helium carrier or wake mode)



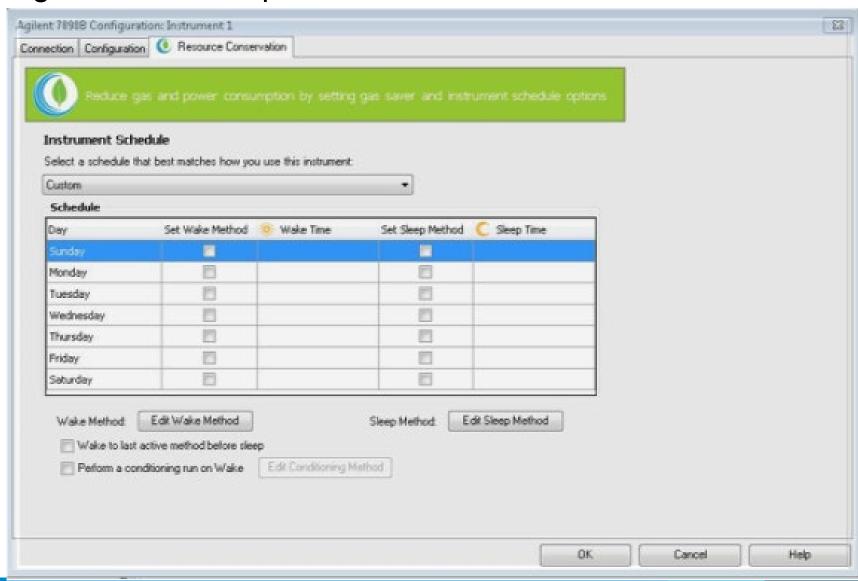
How Does It Work?

Helium savings mode (nitrogen carrier, or sleep mode)

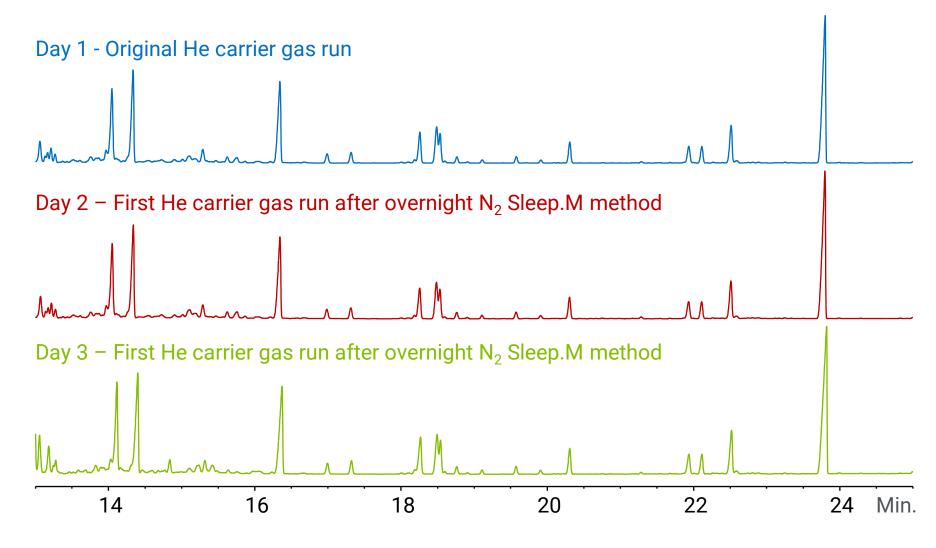


How It Works: Configuring Sleep/Wake Operation

Simple, straight forward setup



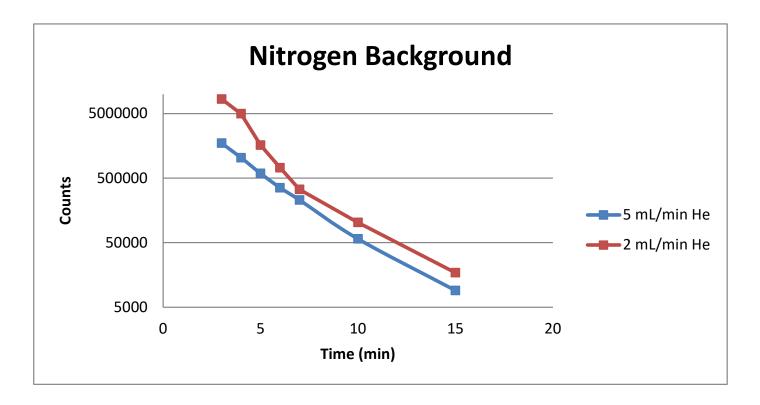
Performance: GC/FID Analysis



No change in chromatography after N₂ carrier Sleep method.

Performance: MS Tune

Passes Within 15min After Switching From N_2 to He As Carrier. GC/MSD



		Counts of N		
		Relative to		Relative to
Time (min)	5 mL/min He	Saturation	2 mL/min He	Saturation
3	1735168	20.69%	8388096	100.00%
4	1033280	12.32%	4959232	59.12%
5	590080	7.03%	1618944	19.30%
6	354112	4.22%	722944	8.62%
7	228480	2.72%	333696	3.98%
10	56984	0.68%	102576	1.22%
15	9052	0.11%	17080	0.20%

Helium Savings-Single GC Channel

Extend helium supply and lower cost using conservation techniques



Method: ASTM D4815 - Ethanol in Gasoline Column: PDMS 30m x 0.53mm x 2.65um

GC Flow Conditions

CO I IOW CONGINONO	
He Carrier Flow (mL/min):	8
He Split flow (mL/min):	70
Gas Saver Flow (mL/min):	20
Gas Saver On (min):	3
Run Time(min.):	20
Gas Volume in Cylinder (L):	8000
Runs per Day:	30
He Cylinder Cost (\$):	300
N2 Cylinder Cost (\$):	60

Parameter	No Conservation	Helium Conservation
Daily He Usage (L)	112	21
He Cylinder Life (days)	71	376
Daily N ₂ Usage (L)	0	24
N ₂ Cylinder Life (days)	0	340
Yearly He Cost (\$)	\$1,537	\$292
Yearly N2 Cost (\$)	\$0	\$64

Example

- ASTM Method D4815
 - Widely used to measure ethanol in gasoline
 - Helium cylinder last two months under normal operation
- Helium conservation
 - Helium cylinder life extended to 12 months
 - 4x yearly gas costs per year

Yearly Total Gas Cost

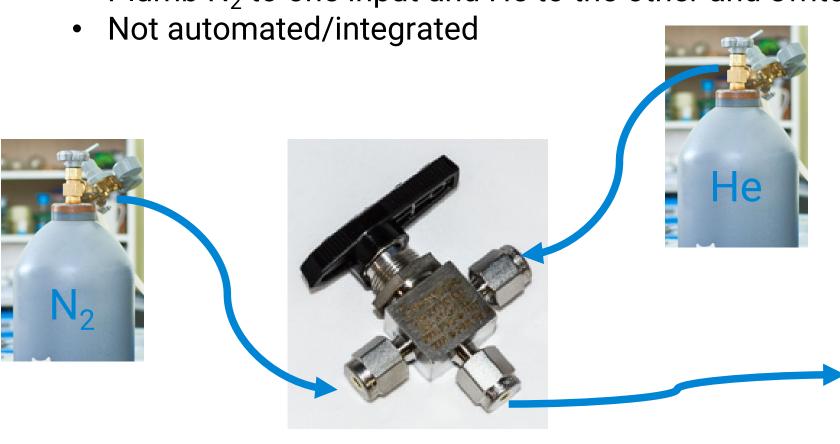
\$1,537

\$356

Alternative for Older Systems (or Non-Agilent Systems)

Use of a 3-way stream selection valve to manually switch between N₂/He

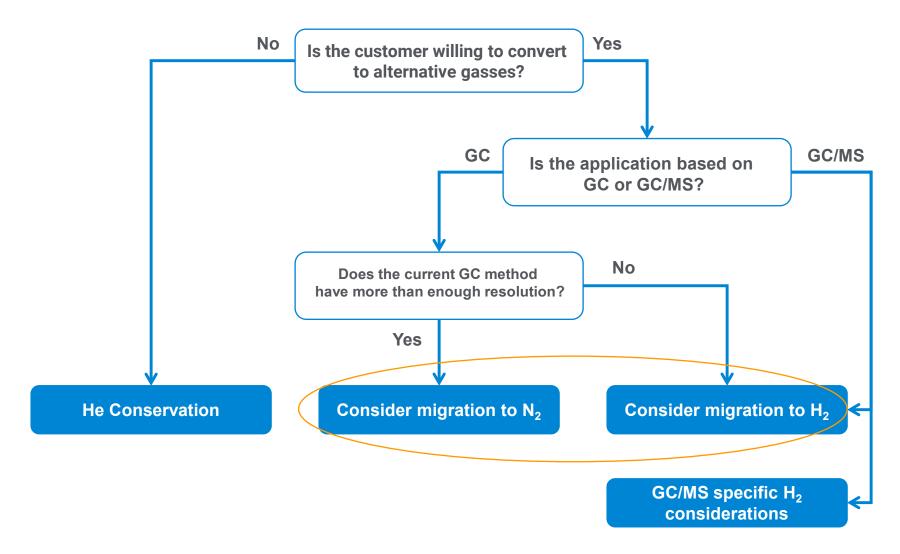
Plumb N₂ to one input and He to the other and switch valve as needed





Carrier Gas Decision Tree

Migrating GC methods to nitrogen and hydrogen



Safety Considerations for Hydrogen Migration

GC and GC/MS: Both offer H₂ enabled features

Read Hydrogen safety guide!!

https://www.agilent.com/cs/library/usermanuals/public/Hydrogen.pdf

Safety Shutdown

When gas pressure set points are not met, the valve and heater are shut off to prevent explosion

Flow Limiting Frit

If valve fails in open position, inlet frit limits the flow

Oven ON/OFF Sequence

Fan purges the oven before turning on heater to remove any collected H₂

Explosion "ready"

GC and MS designed to contain parts in case of explosion

i.e. Spring in GC door

H₂ sensor available

Considerations for Hydrogen Gas Sources

H₂ generator – preferred

- Very clean H₂, >99.9999% available
- Consistent purity
- Built-in safety features
- Make sure to buy a good generator with a low spec for water and oxygen
- Parker's H-MD are used at Agilent sites

H₂ cylinder

- Consider Gas Clean filter
- Possible to add safety device



Considerations for Hydrogen Gas Plumbing

Tubing

- Use chromatographic quality stainless steel tubing (recommended)
- Do not use old tubing (H₂ is known as scrubbing agent)
- Especially don't use old copper tubing (brittleness is a safety concern)

Venting

Connect split vent and septum purge vent to exhaust

Leak checking

Recommend G3388B leak detector



Use N₂ As Carrier Gas

Many HPI methods suited to nitrogen

- Readily available and less expensive gas
- No safety concerns
- Suitable for simple routine analysis (with sufficient resolution)
- More inert than H₂, especially with PLOT/micropacked columns
 - Some compounds catalytically reduced in H₂
- 2-D GC ideally suited to nitrogen
 - Resolution issues solved using two different columns

Potential issues

- Reduced chromatographic resolution at higher flows
- Not suitable for GC/MSD and certain GC detector applications



Helium Carrier Gas Alternatives

Important theoretical considerations relating to peak efficiency

We would like to know the actual

time the component spends in

^{tR} = corrected retention time.

n = effective theoretical

plates.

the stationary phase.

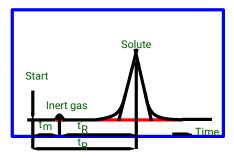
Sharp, narrow peaks in a chromatogram is an indication of a high efficiency GC column.

- Remember that efficiency is represented mathematically by the symbol "N" called Theoretical Plates, and that the larger N is, the better the resolving power of the column (i.e., higher resolution).
- Resolution is described mathematically by the symbol R_s and its numeric value tells how well two adjacent peaks are separated from each other.

$$R_s = \frac{\sqrt{N}}{4} \left(\frac{k}{k+1} \right) \left(\frac{\alpha-1}{\alpha} \right)$$

A <u>resolution value of 1.5</u> tells us that two peaks are <u>baseline separated</u>. The greater (higher) the R_s value, the more separation that has been achieved.

Calculating efficiency



Let's relate "n" to the length of the column.

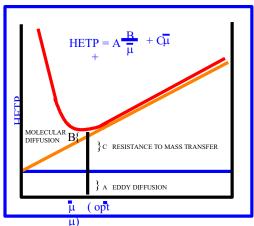
Plates per meter (N) = $\frac{n}{l}$

Plates per meter (N) = $\frac{1}{L}$ or

Height equivalent to a theoretical plate (HETP) $= \frac{L}{n}$

Thus, the more efficient the column, the bigger the "N" the smaller the "HETP".

Efficiency and carrier gas linear velocity



Efficiency is a function of the carrier gas linear velocity or flow rate.

The minimum of the curve represents the smallest HETP (or largest plates per meter) and thus the best efficiency. "A" term is not present for capillary columns.

- Plot of HETP versus linear velocity is know as the Van Deemter plot.
- The linear velocity value at the minimum of the curve is the optimum value for achieving the best efficiency.

Helium Carrier Gas Alternatives

Let's make this easy

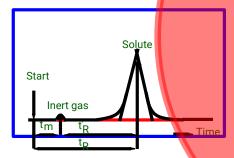
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A <u>resolution value of 1.5</u> tells us that two peaks are <u>baseline separated</u>. The greater (higher) the R_s value, the more separation that has been achieved.

Calculating efficiency



We would like to know the actual time the component spends in the stationary phase

$$t = t_R - t_m$$
 $n = \left(\frac{t_R}{W_h}\right)^2$

tR = corrected retention time.

n = effective theoretical

plates.

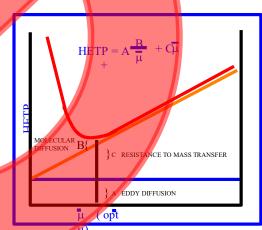
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Efficiency and carrier gas linear velocity



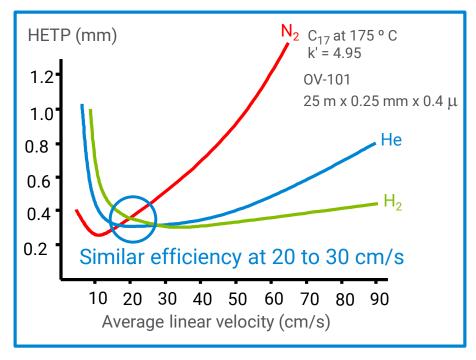
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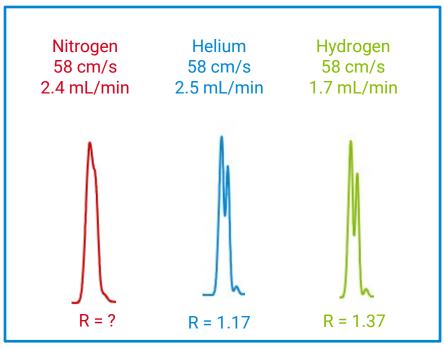
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- Plot of HETP versus linear velocity is know as the Van
 Deemter plot.
- The linear velocity value at the minimum of the curve is the optimum value for achieving the best efficiency.

Van Deemter

Why nitrogen gets a bad reputation for capillary GC





- N₂ actually provides the best efficiency, but at a slower speed
- Most helium methods have too much resolution
 - Lower N₂ efficiency at higher flows can still provide "good enough" resolution
- Most GC methods now use constant flow
 - N₂ efficiency losses with temperature programming are not as severe

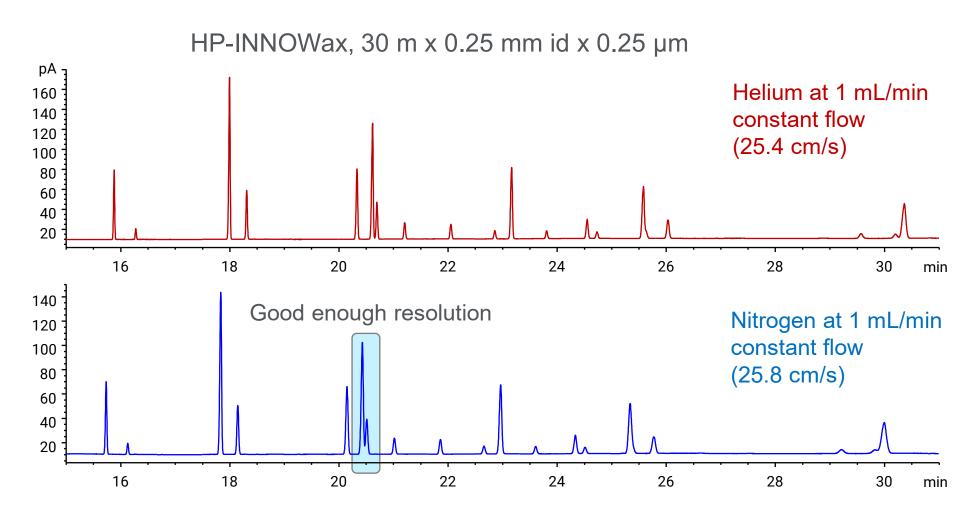
Helium Carrier Gas Alternatives

Let's make this easy

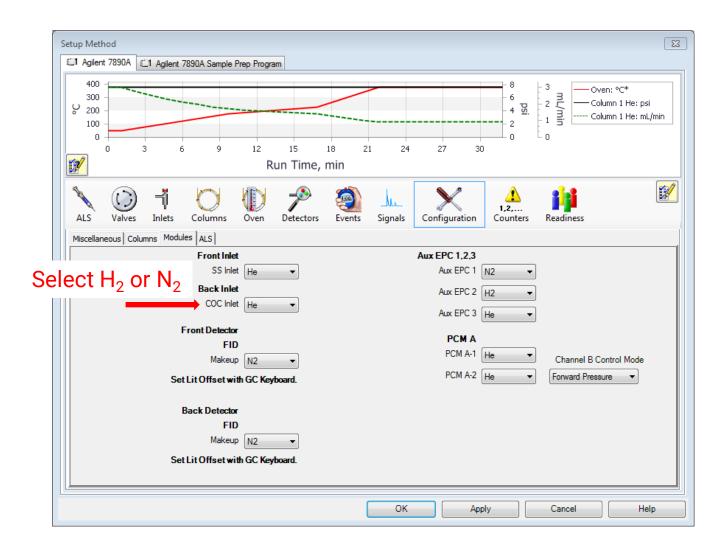
- Goal: Change carrier gas while keeping other method conditions the same
 - Use the same column
 - Use the same oven program
 - Adjust column flow or holdup time to:
 - Maintain same peak elution order
 - Maintain same peak retention times (or as close as possible)
- Easier method revalidation using this approach
 - Minimal changes to timed integration events
 - Minimal changes to peak identification table
- For N₂, test resolution of key components
 - Adjust GC conditions (temperature, flow) if needed

Many Helium GC Have Excess Resolution

EN14103 – GC analysis of FAME content in biodiesel



Configure Inlet for Carrier Gas in ChemStation

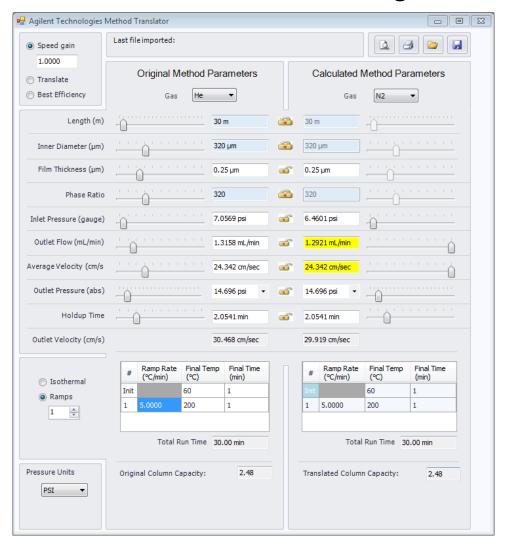


How Do I Build a New Method for Use with H₂ or N₂ Carrier?



New Windows 7 Method Translation Calculator

Another useful tool for carrier gas calculations



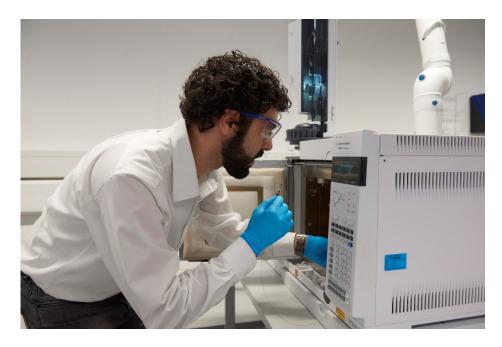
- Flexible tool helps convert existing helium methods to alternative carrier
- Built into the new OpenLab CDS software
- Can also run as Windows 7 program
- Download from the Agilent Helium Update page:

www.agilent.com/chem/heliumupdate

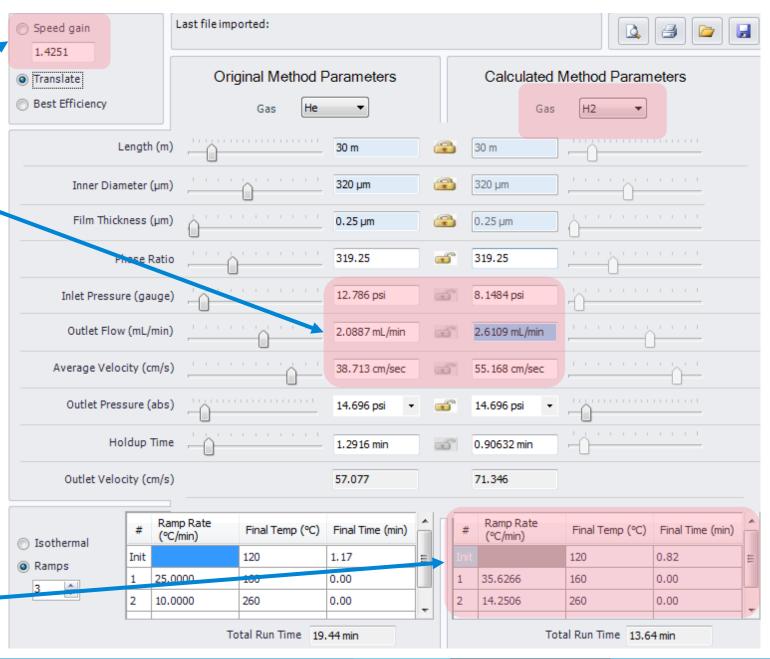


Same Column, Hydrogen Carrier Gas Speed gain

New pressure/flow/velocity



New temperature program



Method Translation Software

Switch from He to H₂ or N₂ carrier gas

Same column and gas type but faster velocities

Different column dimensions

Combination of all of the above

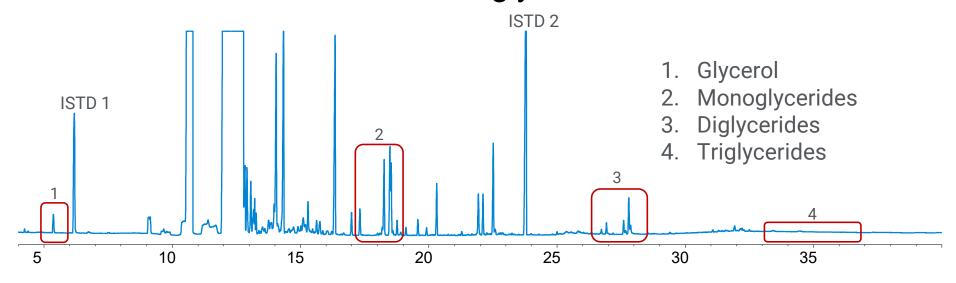
Link to software download:

https://www.agilent.com/en-us/support/gas-chromatography/gcmethodtranslation?searchTermRedirect=gc%20method%20translation%20sotware



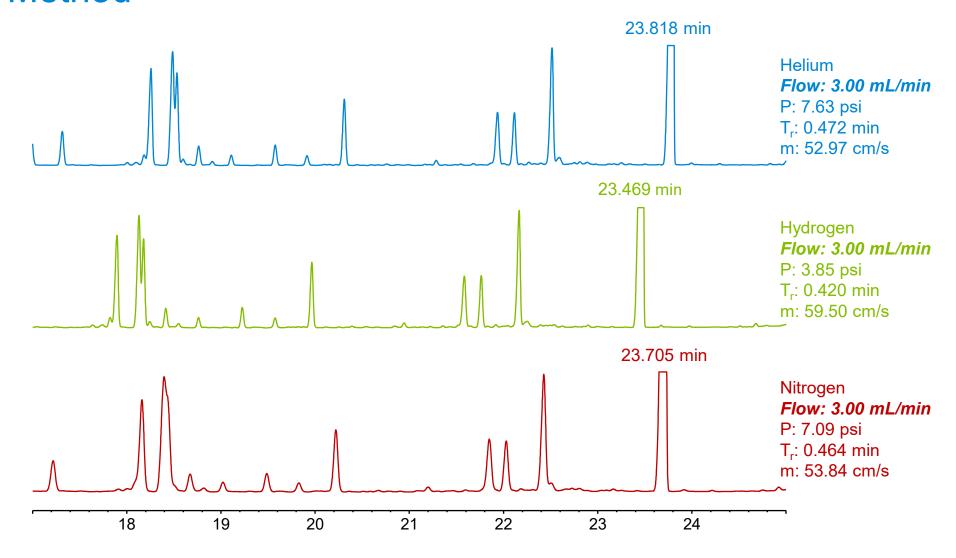
Helium Carrier Gas Alternative

Test Case: ASTM D6584 for free and total glycerin in biodiesel



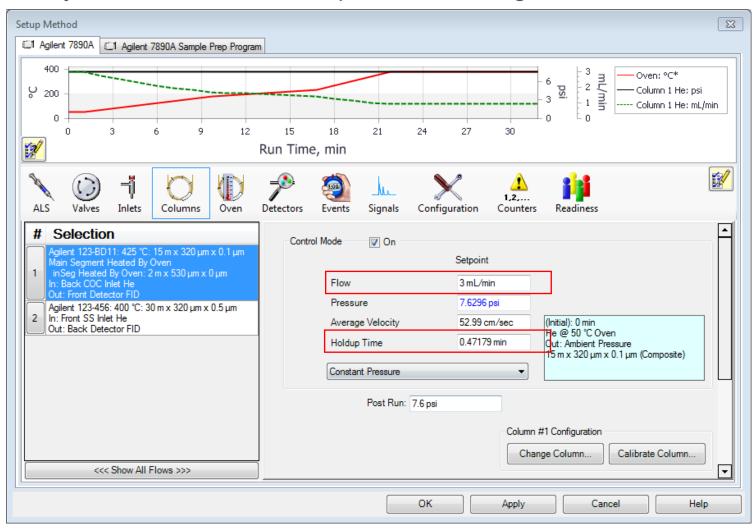
COC inlet:	Oven track mode	
Precolumn:	Ultimetal 2 m x 0.53 mm id	
Column:	Ultimetal DB5HT, 15 m x 0.32 mm id x 0.1 df	
Column flow:	Helium at 3.0 mL/min (50 °C)	
Column pressure:	7.63 psi constant pressure mode	
Initial column temp:	50 °C for 1 min	
Oven ramp 1:	15 °C/min to 180 °C	
Oven ramp 2:	7 °C/min to 230 °C	
Oven ramp 3:	30 °C/min to 380 °C, hold 10 min	
Detector:	FID with 25 mL/min N ₂ makeup	

Wider Retention Time Variation Using the Same Flow as the Original Helium Method

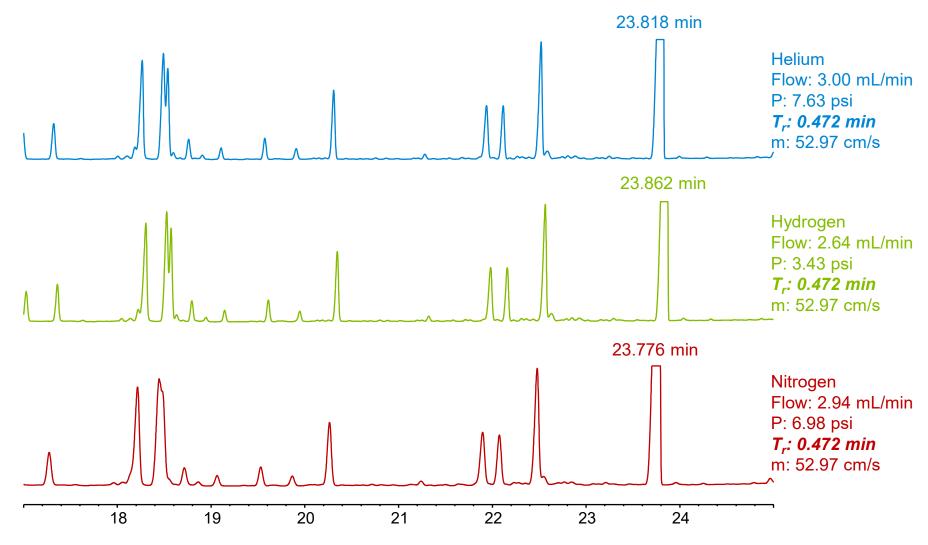


Set the Control Mode: Flow or Holdup Time

Try the same flow or holdup time of the original helium method

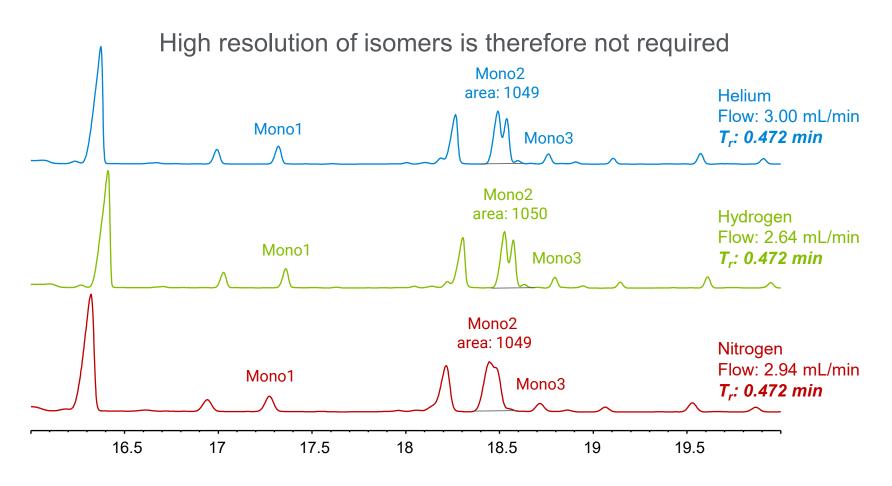


Same Holdup Time (T_r) Gives Consistent Retention Times Compared to Original Helium Method



Monoglyceride Resolution "Good Enough" Using Nitrogen Carrier

All monoglycerides are summed for final reporting



ASTM D6584 - Quantitative Results for Alternative Carrier Gas

Carrier gas has no effect on reported results

	Weight Percent			
	Helium	Hydrogen	Nitrogen	
Glycerin	0.015	0.014	0.013	
Monoglycerides	0.226	0.216	0.223	
Total glycerin	0.097	0.095	0.098	

Analysis of Oxygenates and Aromatics in Gasoline Using 2-D Gas Chromatography

ASTM Method D4815 – Oxygenated additives

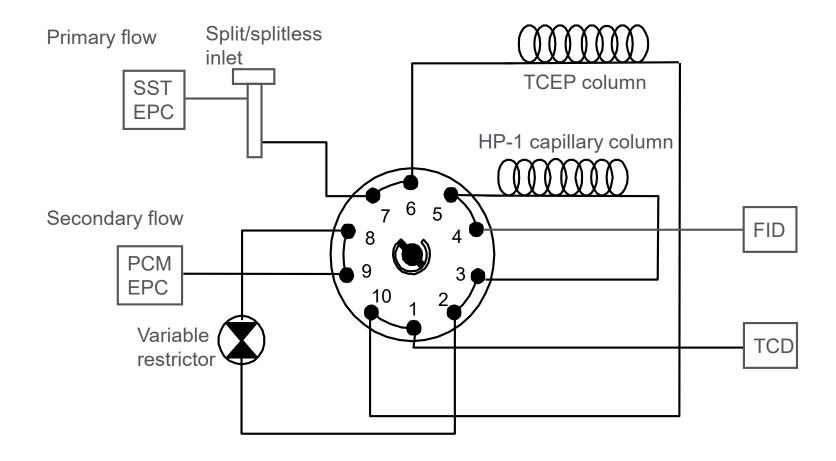
- Ethers and alcohols from 0.1 wt% to 15 wt%
- Usually only one or two additives in a sample

Preliminary separation removes light hydrocarbons from sample

- Polar TCEP micropacked columns retain ethers and alcohols
- Back flush TCEP* column to nonpolar capillary column (HP-1) to complete analysis

* TCEP = 1,2,3-tris(2-cyanoethoxy)propane

Configuration and Operation for D4815 and D5580

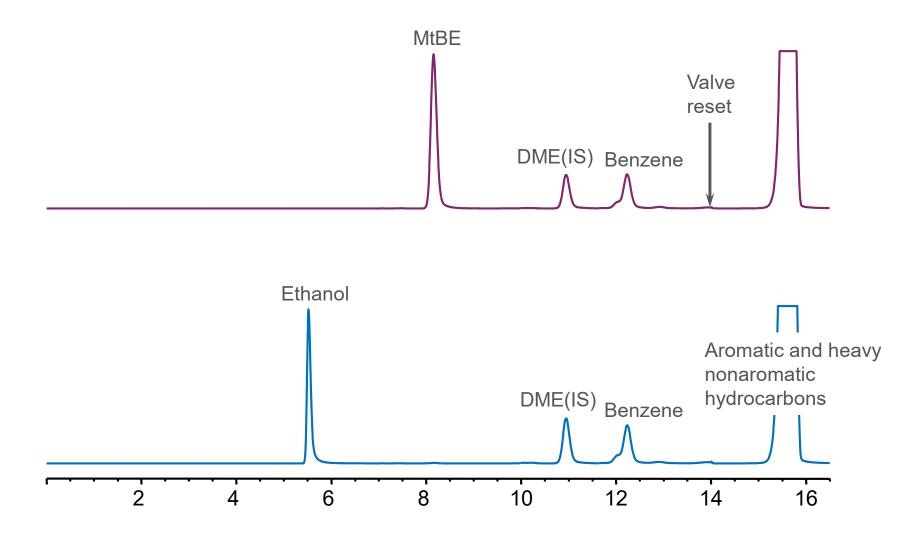


Instrument Conditions

Use nitrogen carrier gas with original ASTM GC flow conditions

Method D4815					
Carrier gas	Nitrogen				
Inlet	Split/splitless				
Inlet Temperature	200 °C				
Inlet pressure	9 PSI (constant P)				
TCEP column flow	5 mL/min				
Split ratio	15:1				
Split flow	70 mL/min				
PCM pressure program	13 PSI for 14 min 99 PSI/min to 40 PSI				
HP-1 column flow	3 mL/min				
FID Temperature	250 °C				
Oven Temperature	80 °C Isothermal				
Run time	16 minutes				

Analysis of MtBE and Ethanol in Gasoline Using N₂ Carrier Gas



ASTM Precision Specifications

D4815 precision measures

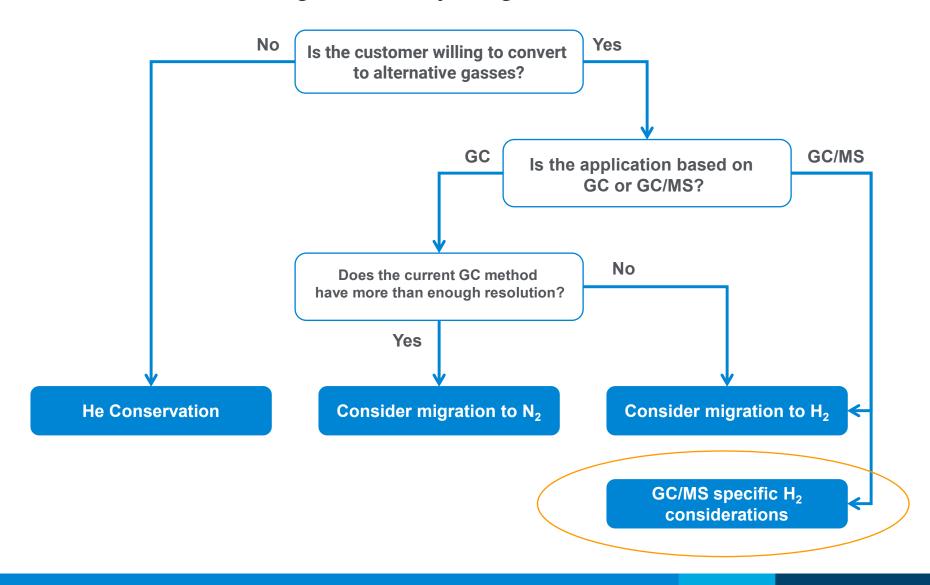
		Repeatability		Reproducibility	
Compound	Mass %	Spec	Observed	Spec	Observed
Ethanol	0.99	0.06	0.01	0.23	0.01
Ethanol	6.63	0.19	0.03	0.68	0.04
MtBE	2.10	0.08	0.01	0.20	0.01
MtBE	11.29	0.19	0.05	0.61	0.08

Accuracy evaluation

	MtBE mass %		
Sample	known	found	
SRM2294 #1	10.97	10.61	
SRM2294 #2	10.97	10.60	
AccuStd Check	12.00	11.81	

Carrier Gas Decision Tree

Migrating GC methods to nitrogen and hydrogen



MSD systems: Do not Switch from He to H₂ unless absolutely necessary

- Hydrogen is a very reactive gas!
- You <u>WILL</u> experience a noisy/elevated background that can be persistent (days/weeks)
- Chemical reactions happen in the inlet, column, and sometimes the source that can change your results.
- EVERY analyte in EVERY matrix in EVERY method will need to be validated using hydrogen to make sure there are no chemical reaction problems.
- Looking for untargeted unknowns is problematic due to the possibility of reactivity.
- Library search match quality will be impacted.
- Tuning results will be different than with helium. Some tunes, notably BFB and DFTPP, may not pass
- First, try all helium conservation measures instead of switching to H2.

*There are no published performance specifications for any current Agilent GCMS system using hydrogen carrier gas.



MSD: Converting from He to H₂ Carrier Gas

- Many GC/MS users are considering changing from helium to hydrogen
- carrier gas due to price/availability problems with helium.
 - Read Chemical and Engineering News July 16, 2012 (Page 32-34)
- It is important to recognize the differences with using hydrogen carrier. Time should be allotted for adapting the method, optimization, and resolving potential problems. Areas that will need attention include:
 - choice of supply of H₂
 - GC/MSD hardware changes
 - choosing new chromatographic conditions
 - potential reduction in signal-to-noise ratio (2-5x or more) due to higher noise
 - changes in spectra and abundance ratios for some compounds
 - activity and reactivity with some analytes

*There are no published performance specifications for any current Agilent GCMS system using hydrogen carrier gas.



GC/MS Migration to H₂ Carrier Gas

Recent C&EN webinar discussion points

- Read Hydrogen safety guide before proceeding!
 - https://www.agilent.com/cs/library/usermanuals/public/Hydrogen.pdf
- System setup
 - H₂ safety, H₂ source, gas connection, system clean up
- Method migration
 - Method transfer SW, method migration consideration, revalidation
- GC/MS analytical performance expectation
 - Sensitivity impact, MS spectrum impact, analyte compatibility
- For more details
 - C&EN webinar on October 9, 2012
 - Recorder session: http://cen.acs.org/media/webinar/agilent_100912.html

Summary: Helium Conservation Benefits

Seamless integration

No need to revalidate existing GC methods
Fully integrated with Agilent 7890B and CDS (OpenLab, Mustang, MassHunter)
Carrier gas ID and setpoints are a part of the method for compliance and transfer
Easily implemented using new Agilent Sleep/Wake functions

Greater reliability

Based on proven 5th generation AUX EPC Agilent 7890/8890 provides warning if setpoints are not reached For hydrogen users, nitrogen substitution when not running GC

Greater performance

Purge channel prevents cross contamination of gases
Delivers more stable gas pressure control from the tank regulator to the inlet EPC module

Acts as an intermediate pressure regulator from the tank to inlet EPC to ensure greater analytical precision

Summary – Migration to H₂ and N₂

- Don't forget about Gas Saver
- Be especially cautious when migrating to H₂ with an MSD system
- For resolution critical methods, H₂ offer the best alternative
 - Agilent GC and GC/MS systems have many built-in safety features
- For many GC applications, N₂ offers a cheap, easy alternative without any safety worries
 - Many existing helium methods have too much resolution
 - N₂ can be used without changing any of the existing GC conditions
 - Keep the holdup time the same as the original method
 - −2-D methods have high resolution built in, so N₂ is ideally suited as a carrier gas
 - Valve-based or Deans switch (not GC x GC flow modulation)
- For more information on Helium Carrier Gas

www.agilent.com/chem/heliumupdate

Contact Agilent Chemistries and Supplies Technical Support



1-800-227-9770 option 3, option 3:

Option 1 for GC and GC/MS columns and supplies

Option 2 for LC and LC/MS columns and supplies

Option 3 for sample preparation products, filtration, and QuEChERS

Option 4 for spectroscopy supplies

Available in the USA 8-5 all time zones



gc-column-support@agilent.com



spp-support@agilent.com

spectro-supplies-support@agilent.com

