Addressing the World Helium Shortage For Gas Chromatography

Helium Conservation and Converting GC Methods to Nitrogen and Hydrogen Carrier Gas

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Presentation Outline

Carrier Gas Decision Tree

- Decision making guide to fit your carrier gas requirements

Helium Conservation

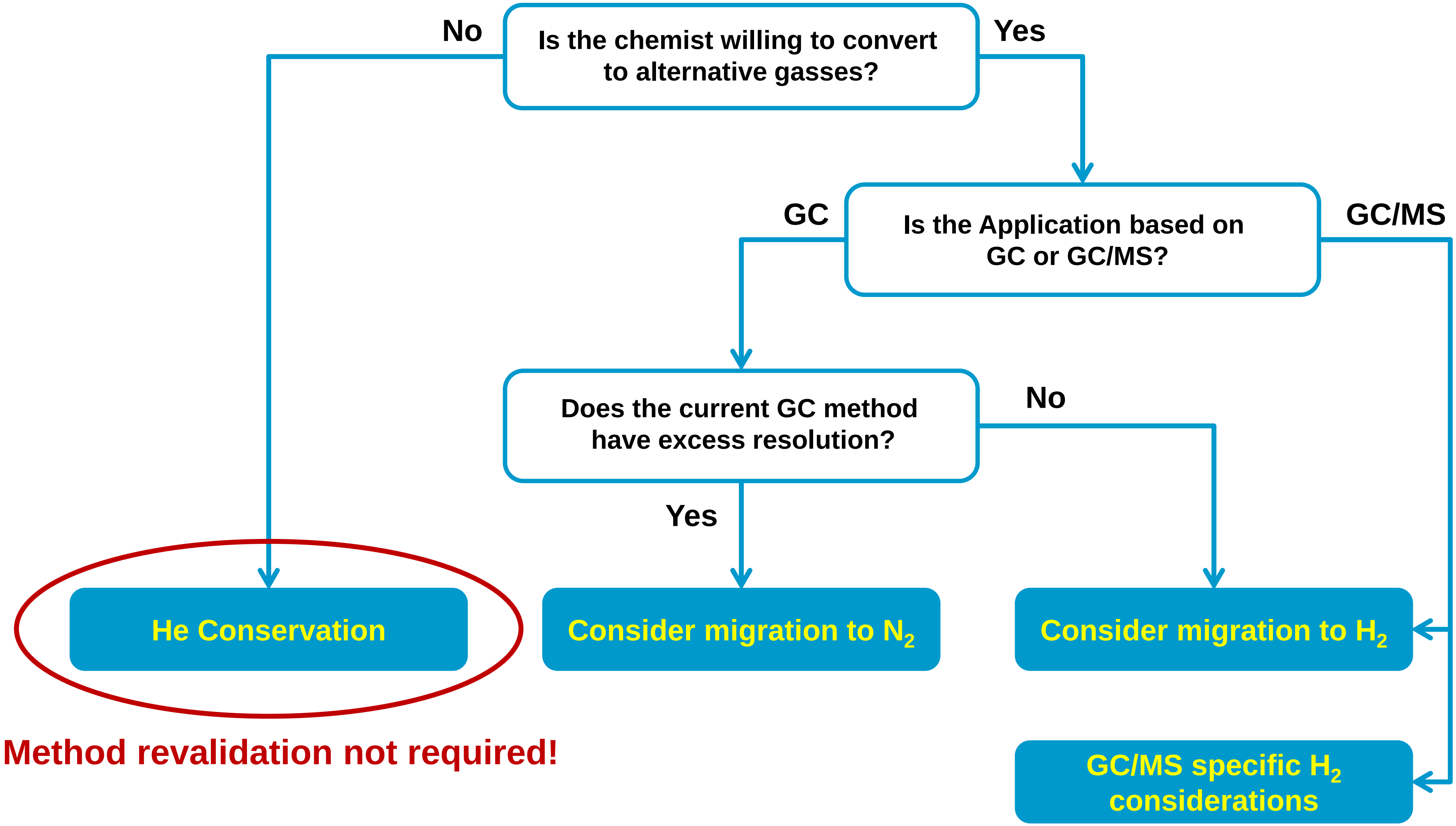
- Smarter helium use with new hardware/software tools
- No need to revalidate existing GC methods

Migrating Existing Helium GC Methods to H_2 and N_2

- Best practices for obtaining the same results and minimizing method revalidation

Carrier Gas Decision Tree

Continue using helium, but in a smarter way



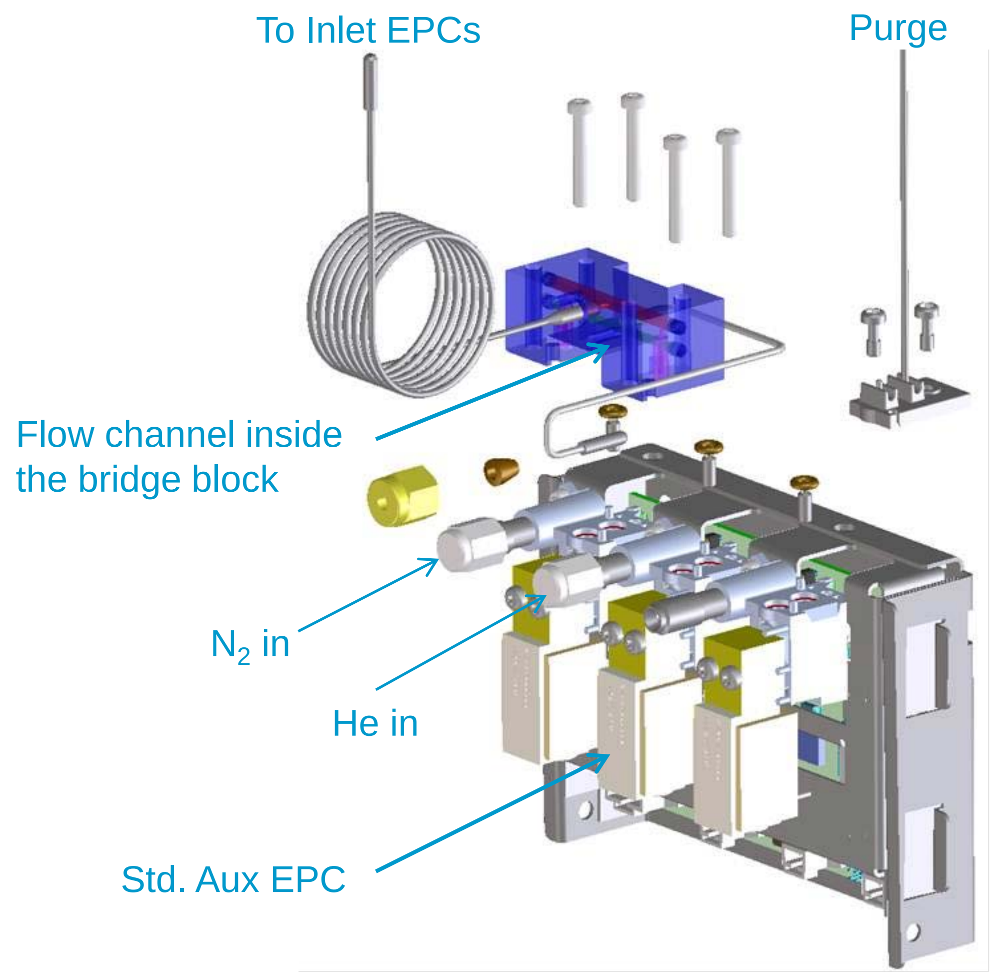
Reducing Helium Use With Conservation

New 7890B Helium Conservation Module

- **Automatically switches carrier gas supply to N_2 Standby during idle time**
- **Integrates into the new 7890B Sleep and Wake function**
- **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 re-start of heated zones**

Helium Conservation Module

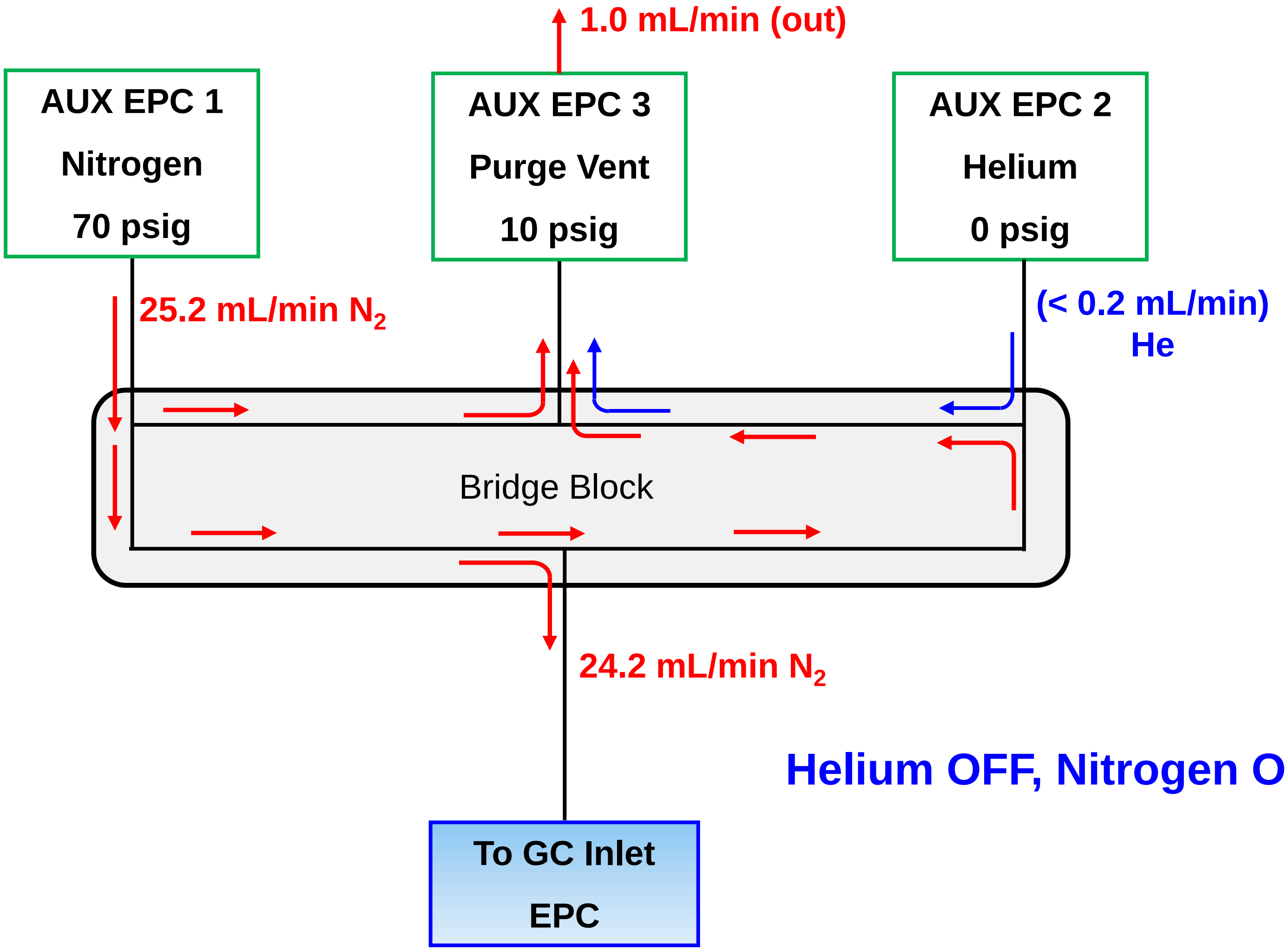
Seamlessly integrated onto 7890 GC hardware and software



- 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 15-30 min for most detectors

How Does It Work?

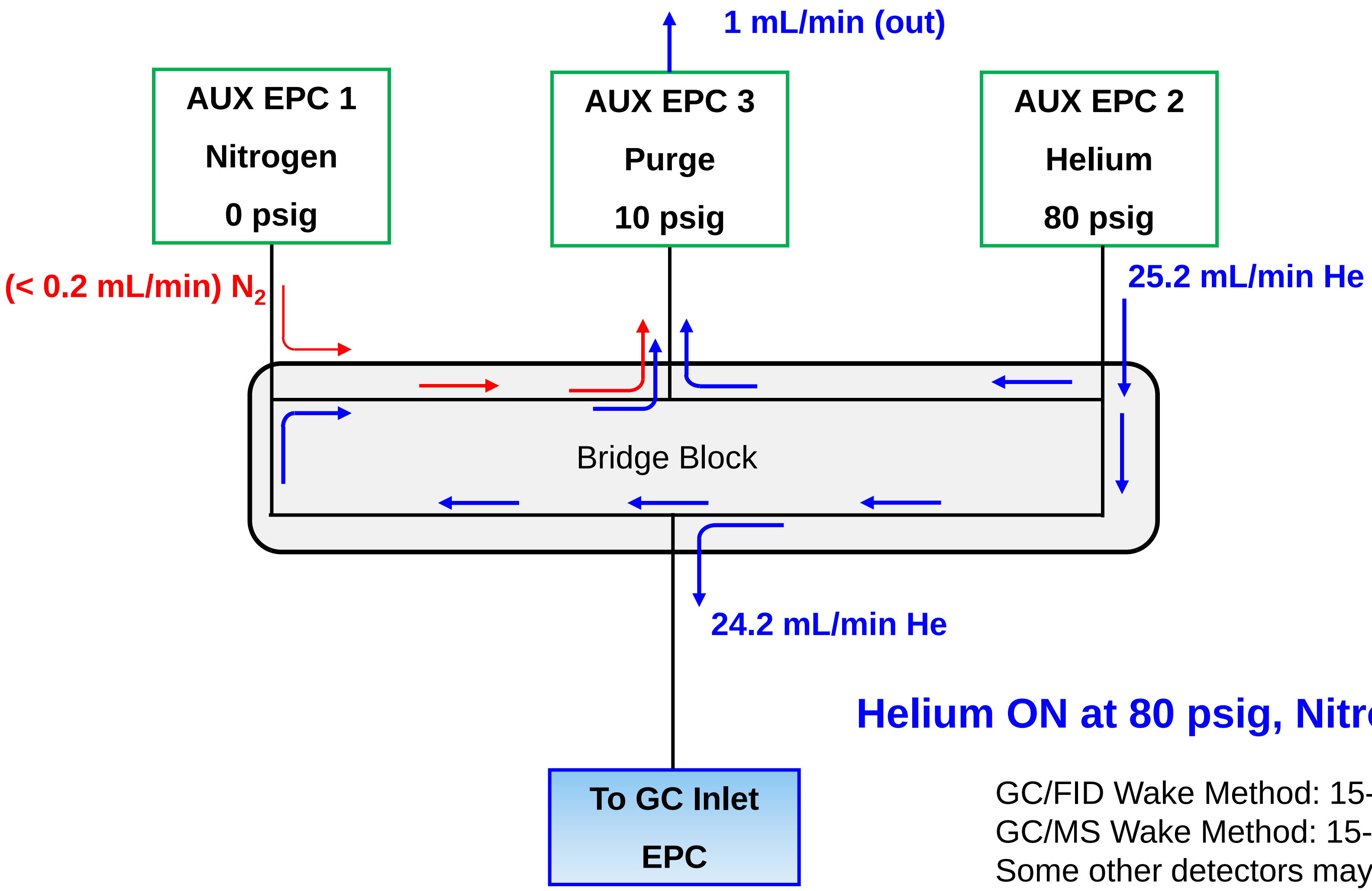
Helium Savings Mode (Nitrogen Carrier, or Sleep Mode)



Helium OFF, Nitrogen ON at 70 psig

How Does It Work?

Normal Operation Mode (Helium Carrier or Wake Mode)

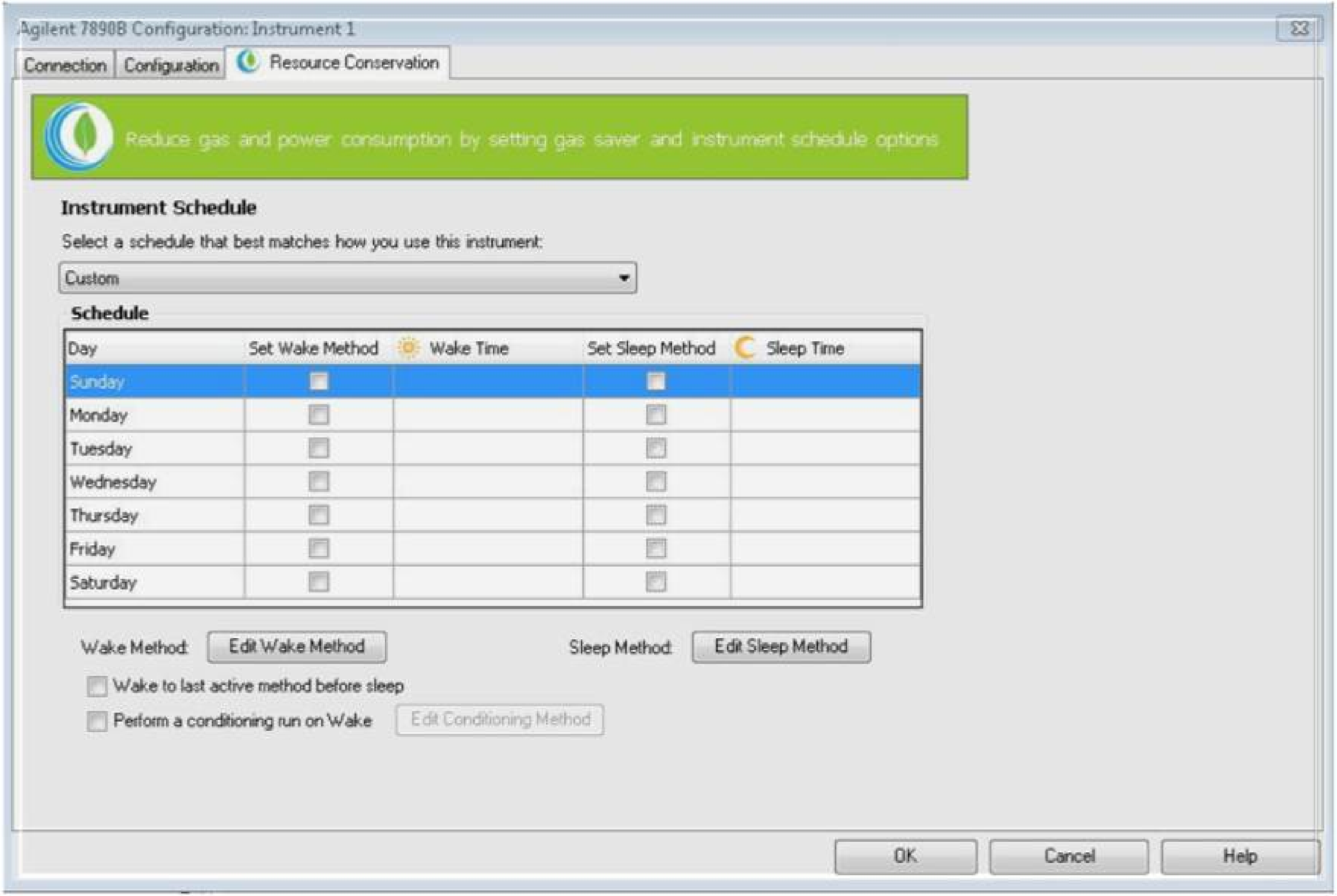


Helium ON at 80 psig, Nitrogen OFF

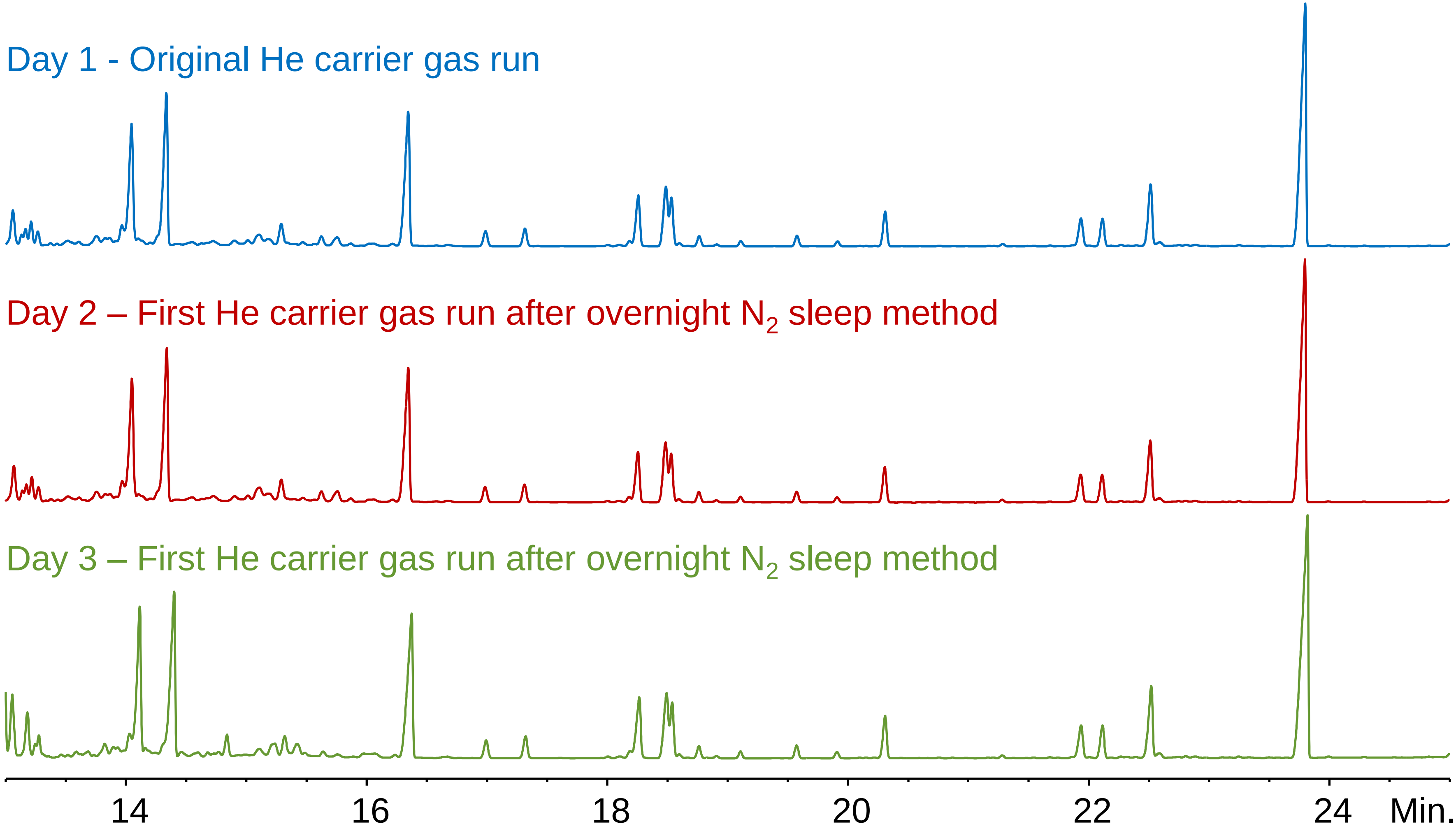
GC/FID Wake Method: 15-30 Min
GC/MS Wake Method: 15-30 Min
Some other detectors may need longer

How It Works: Configuring Sleep/Wake Operation

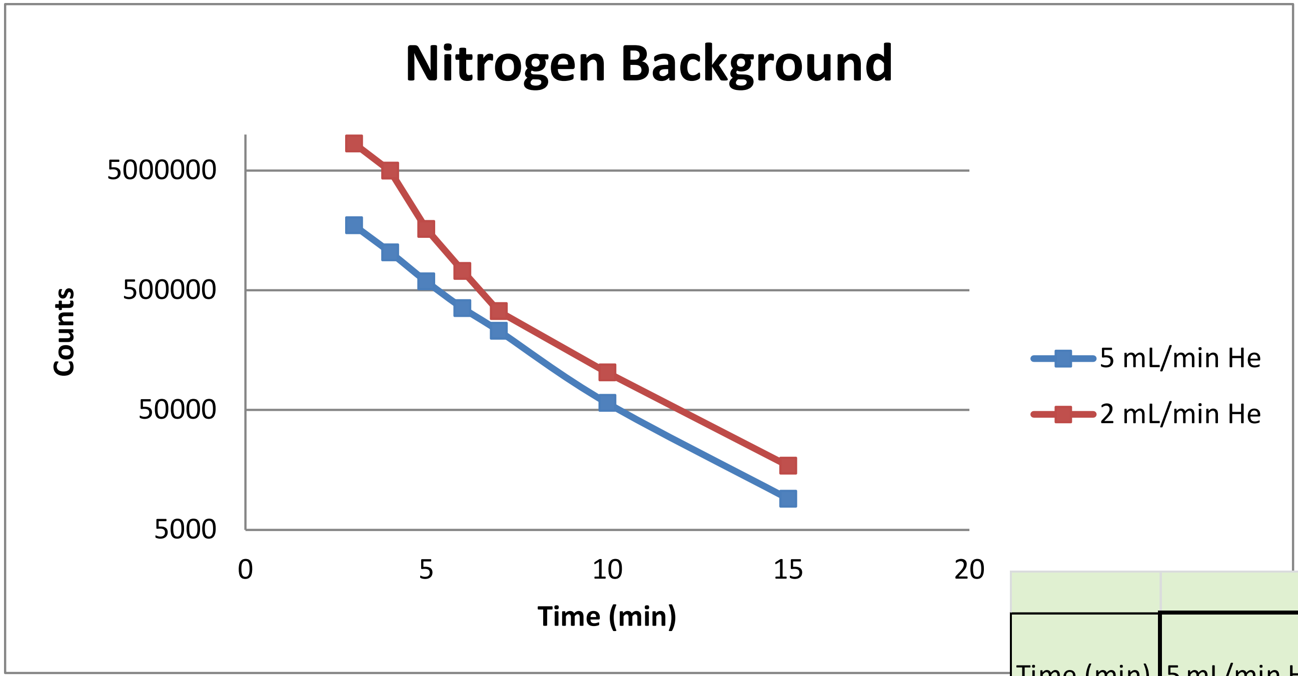
Simple, Straight Forward Setup



Performance: No Change in Chromatography After N_2 Carrier Sleep Method. GC/FID Analysis



Performance: Pass MS Tune Within 15min After Switching From N_2 To He As Carrier. GC/MSD



	Counts of Nitrogen Ion			
Time (min)	5 mL/min He	Relative to Saturation	2 mL/min He	Relative to 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 Calculator – Single GC Channel

Extend helium supply and lower cost using conservation techniques

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Method: ASTM D4815 - Ethanol in Gasoline

Column: PDMS 30m x 0.53mm x 2.65um

GC Flow Conditions

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

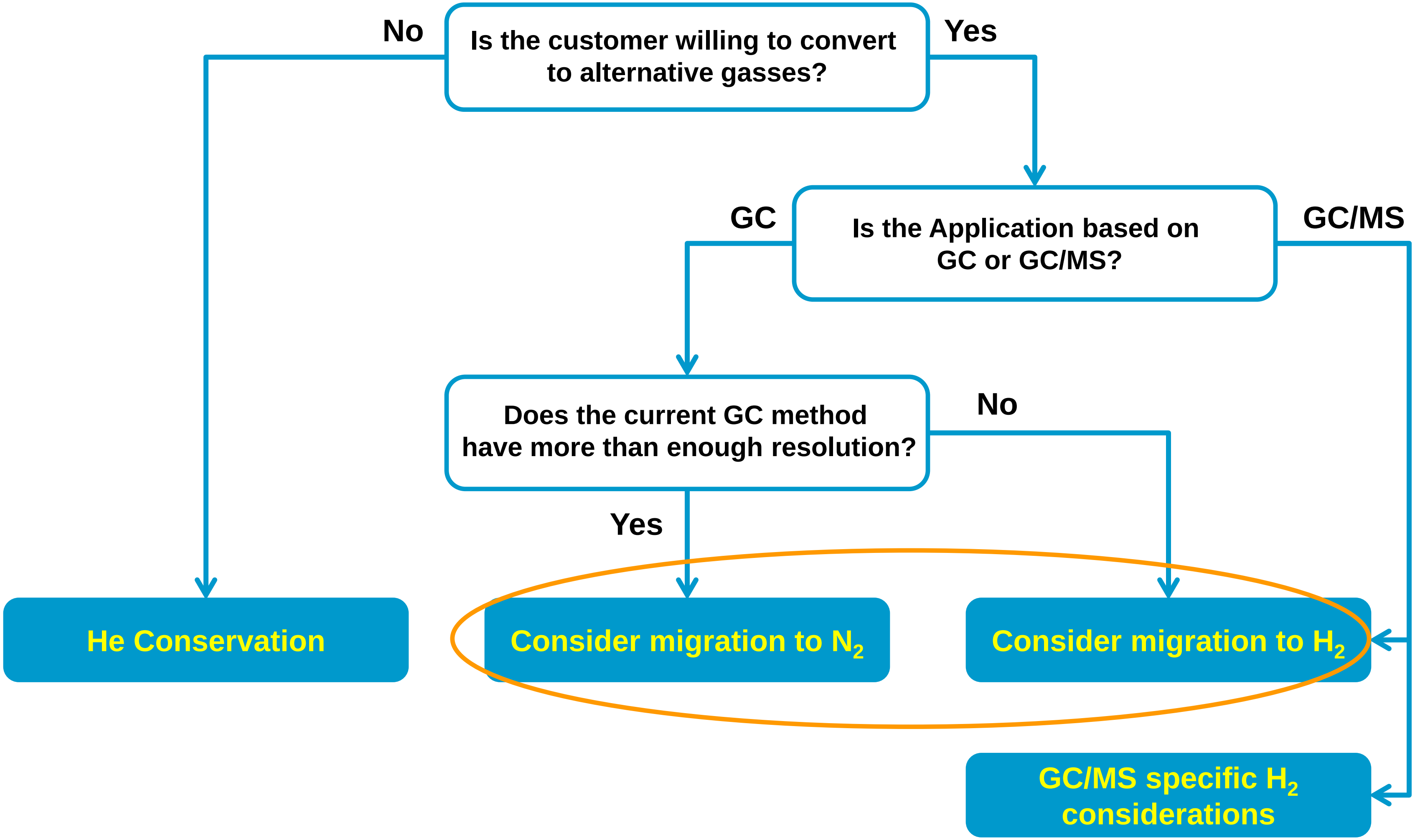
Parameter	No Conservation	Helium Conservation
Daily He Usage (L)	112	21
He Cylinder Life (days)	**71**	**376**
Daily N_2 Usage (L)	0	24
N_2 Cylinder Life (days)	0	340
Yearly He Cost ($)	$1,537	$292
Yearly N2 Cost ($)	$0	$64
Yearly Total Gas Cost ($)	**$1,537**	**$356**

Example

- ASTM Method D4815
  - Widely used to measure ethanol in gasoline
  - Helium cylinder last 2 months under normal operation
- Helium Conservation
  - Helium cylinder life extended to 12 months
  - 4x yearly gas costs per year

Carrier Gas Decision Tree

Migrating GC methods to nitrogen and hydrogen



Safety Considerations for Hydrogen Migration

GC, GC/MS: Both offer H_2 enabled features

- Agilent H_2 safety letter and safety manuals available
- GC levels of safety design
  - Safety Shutdown
  - Flow Limiting Frit
  - Oven ON/OFF Sequence
- Newer version 6890, 7890 GC and 5773, 5975 MSD offer greater safety than older versions of GC and GC/MSD
- Plumbing Considerations
  - Use chromatographic quality stainless steel tubing
  - Do not use old tubing (H_2 is known as scrubbing agent)
  - Especially don't use old copper tubing (brittleness is a safety concern)

Source of Hydrogen

H_2 Generator – preferred

- Very clean H_2, >99.9999% available
- More consistent purity
- Built-in safety considerations
- Make sure to buy a good one with a low spec for water and oxygen
- Parker's H-MD are used in LFS and SCS

H_2 Cylinder

- Consider gas clean filter
- Possible to add safety device

Use N_2 as carrier gas

Many helium GC methods suited to nitrogen conversion

- Readily available and less expensive gas
- No safety concerns
- Suitable for simple routine analysis (with sufficient resolution)
- More inert than H_2, especially with PLOT/Micropacked columns
  - Some compounds catalytically reduced in H_2
- Most helium GC methods have too much resolution
  - lower column efficiency with N_2 won't affect results
- 2-D GC ideally suited to nitrogen
  - column combinations designed to solve specific resolution problems

Potential issues

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

Helium Carrier Gas Alternatives

Important Theoretical Considerations Relating To Peak Efficiency

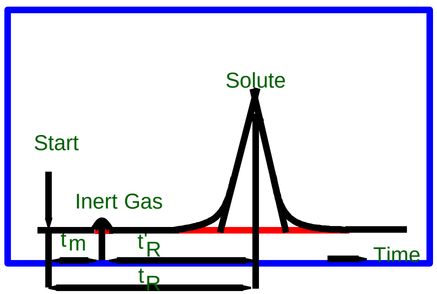
Sharp, narrow peaks in a chromatogram is an indication of a high **efficiency** GC column.

- 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 resolution value of 1.5 tells us that two peaks are baseline separated. 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.

$t_R' = t_R - t_m$ $\quad n = 5.545 \left(\frac{t_R'}{W_h}\right)^2$

t_R' = Corrected Retention Time.

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

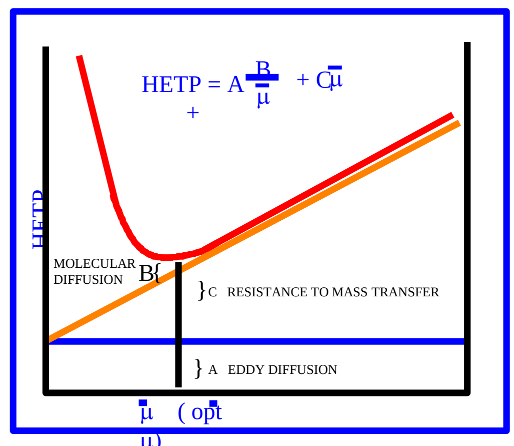
n = effective theoretical plates.

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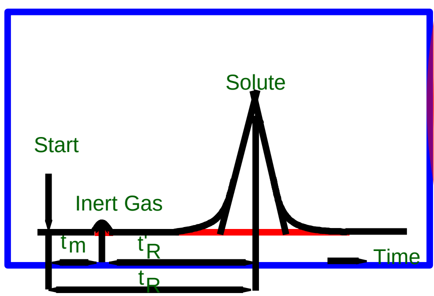

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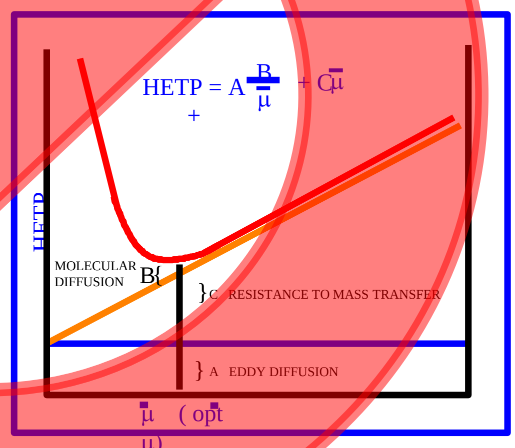

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Helium Carrier Gas Alternatives
Let's Make This Easy

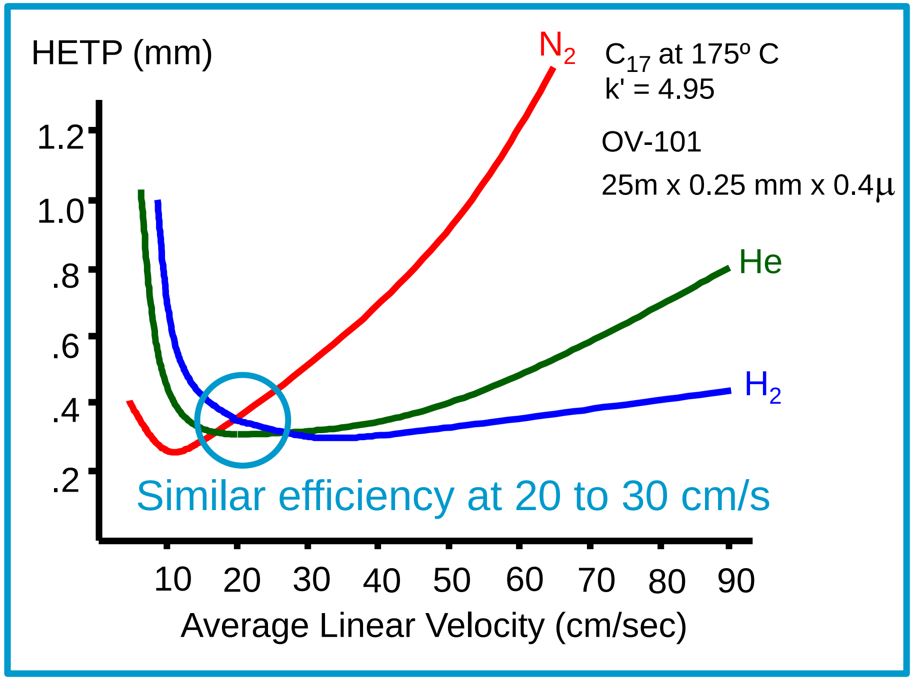
- Goal: change carrier gas while keeping other method conditions the same
  - use the same column
  - use the same oven program
  - adjust column flow or holdup time to:
    - maintain same peak elution order
    - maintain same peak retention times (or as close as possible)

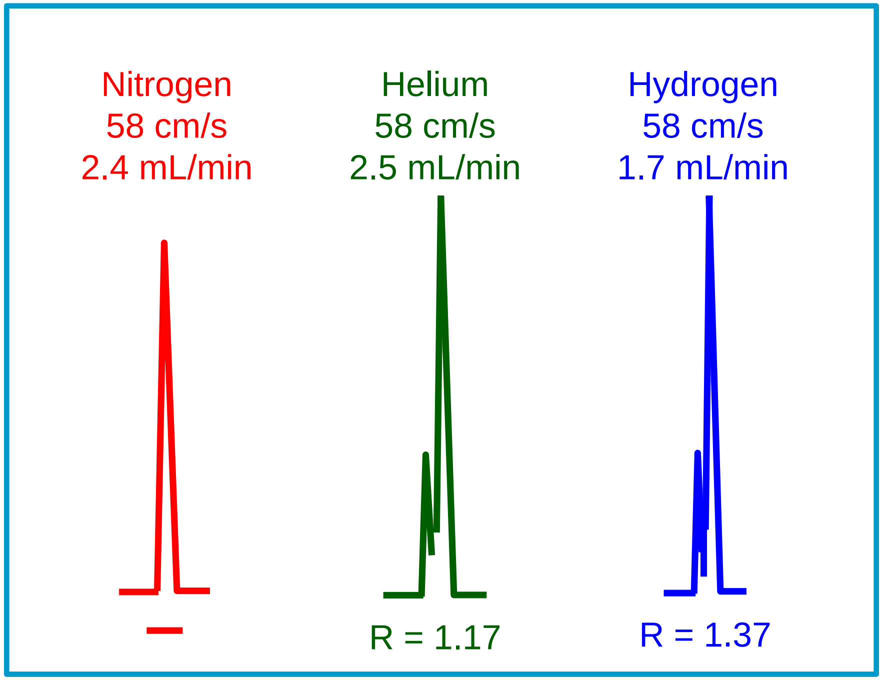
- Easier method revalidation using this approach
  - minimal changes to timed integration events
  - minimal changes to peak identification table

- For N_2, test resolution of key components
  - adjust GC conditions (temp, flow) if needed

- Use tools built into the Agilent Chemstation to guide us through the process

The Tyranny of Van Deemter
Why Nitrogen Gets a Bad Rap for Capillary GC



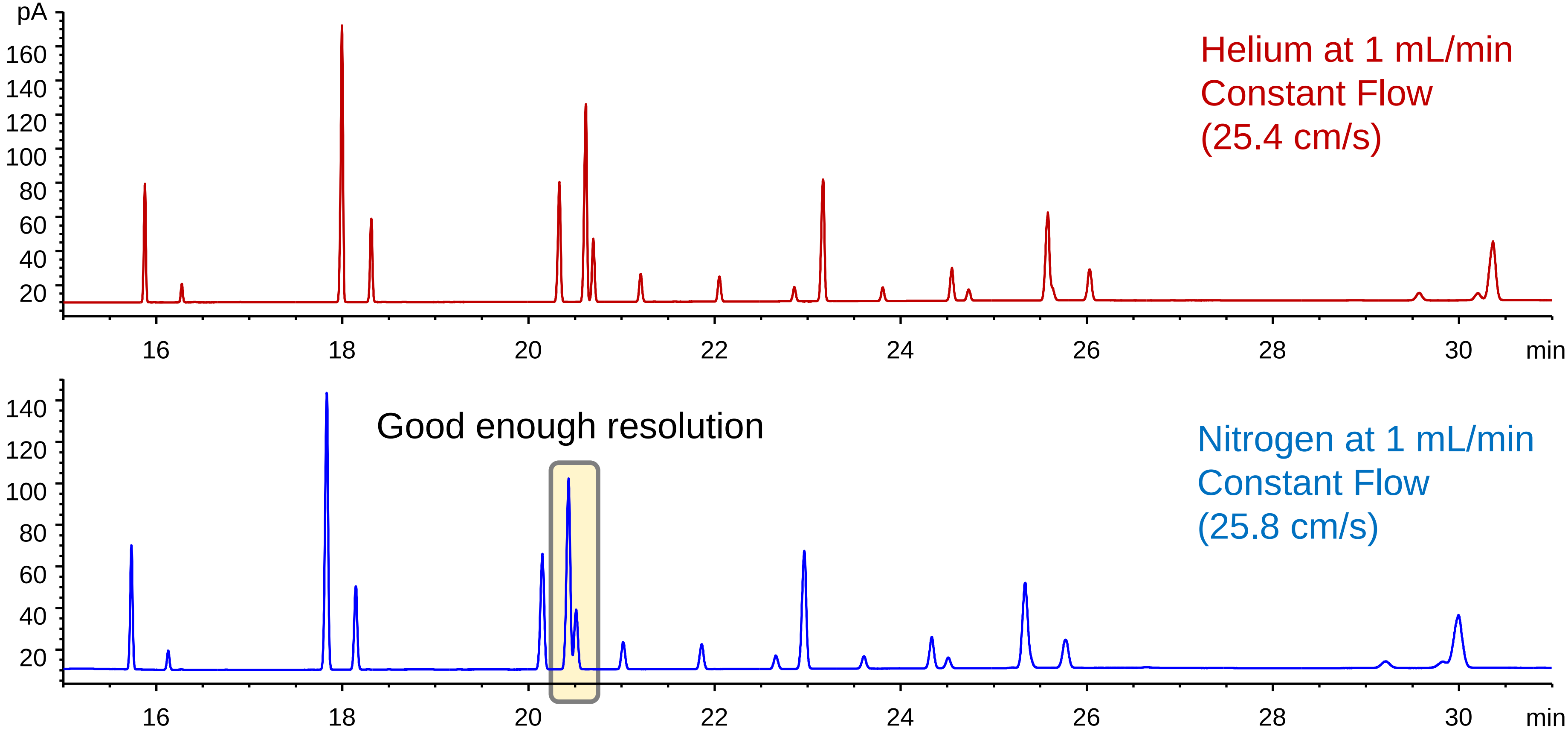


- N_2 actually provides the best efficiency, but at a slower speed
- Most helium GC methods have too much resolution
  - Lower N_2 efficiency at "typical" helium flows can still provide good enough resolution
- Most GC methods now use constant flow
  - Efficiency losses with temp programming are not as severe

Many Helium GC Have Excess Resolution

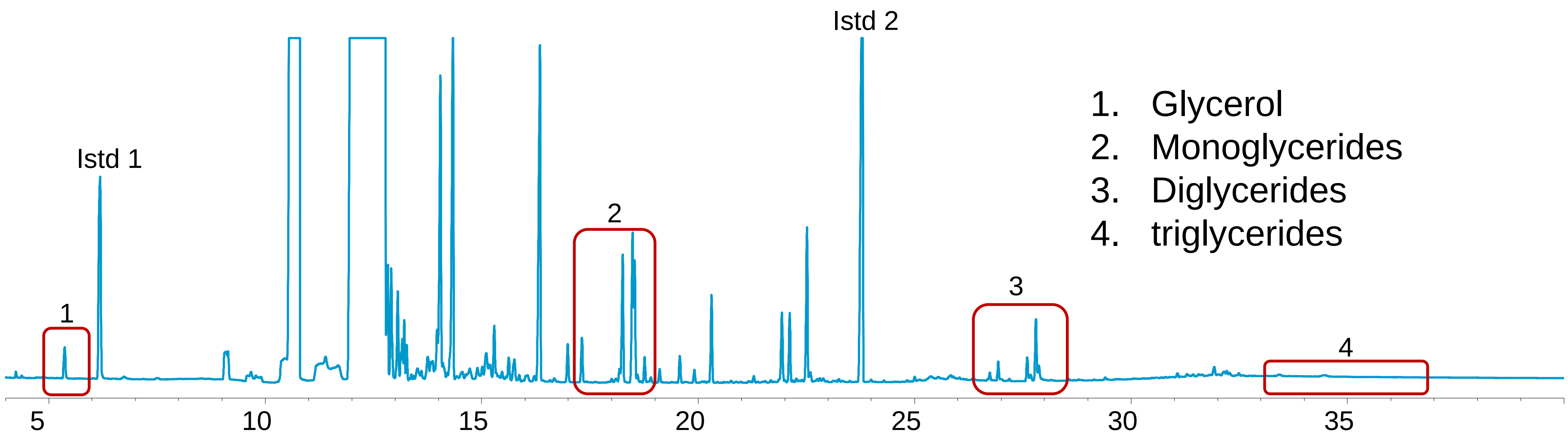
EN14103 – GC Analysis of FAME content in biodiesel

HP-INNOWax, 30m x 0.25mm ID x 0.25 um



Helium Carrier Gas Alternative

Test Case 1: ASTM D6584 for Free and Total Glycerin in Biodiesel

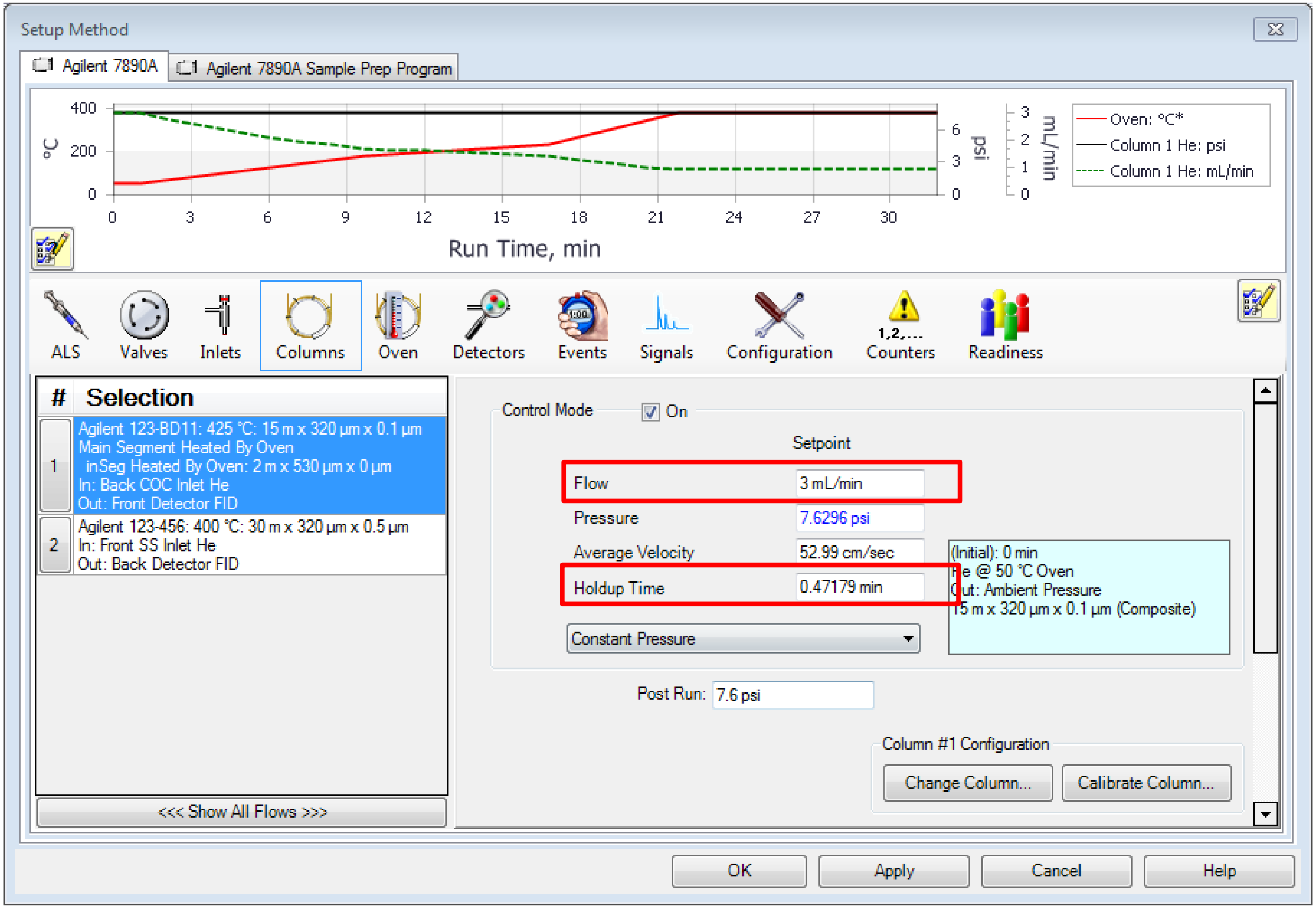


1. Glycerol
2. Monoglycerides
3. Diglycerides
4. triglycerides

COC Inlet:	Oven Track Mode
Pre-column:	Ultimetal 2m x 0.53mm ID
Column:	Ultimetal DB5HT, 15m x 0.32mm ID x 0.1 df
Column Flow:	Helium at 3.0 mL/min (50 deg C)
Column Pressure:	7.63 psi constant pressure mode
Initial Column Temp:	50 ^{o}C for 1 min.
Oven Ramp 1:	15 ^{o}C/min to 180 ^{o}C
Oven Ramp 2:	7 ^{o}C/min to 230 ^{o}C
Oven Ramp 3:	30 ^{o}C/min to 380 ^{o}C, hold 10 min.
Detector:	FID with 25 mL/min N_2 makeup

Set the Control Mode: Flow or Holdup Time

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



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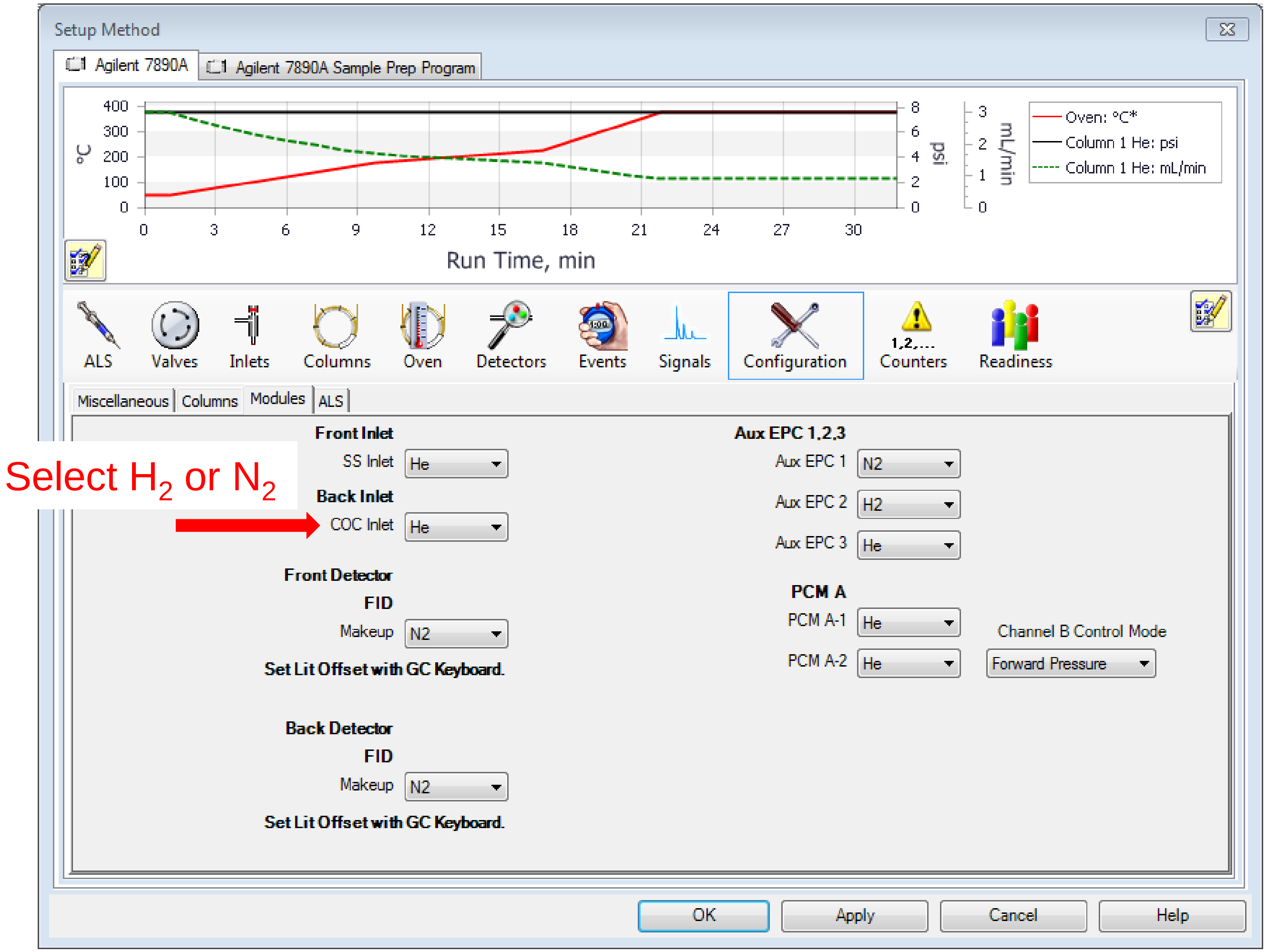
Configure Inlet for Carrier Gas in Chemstation



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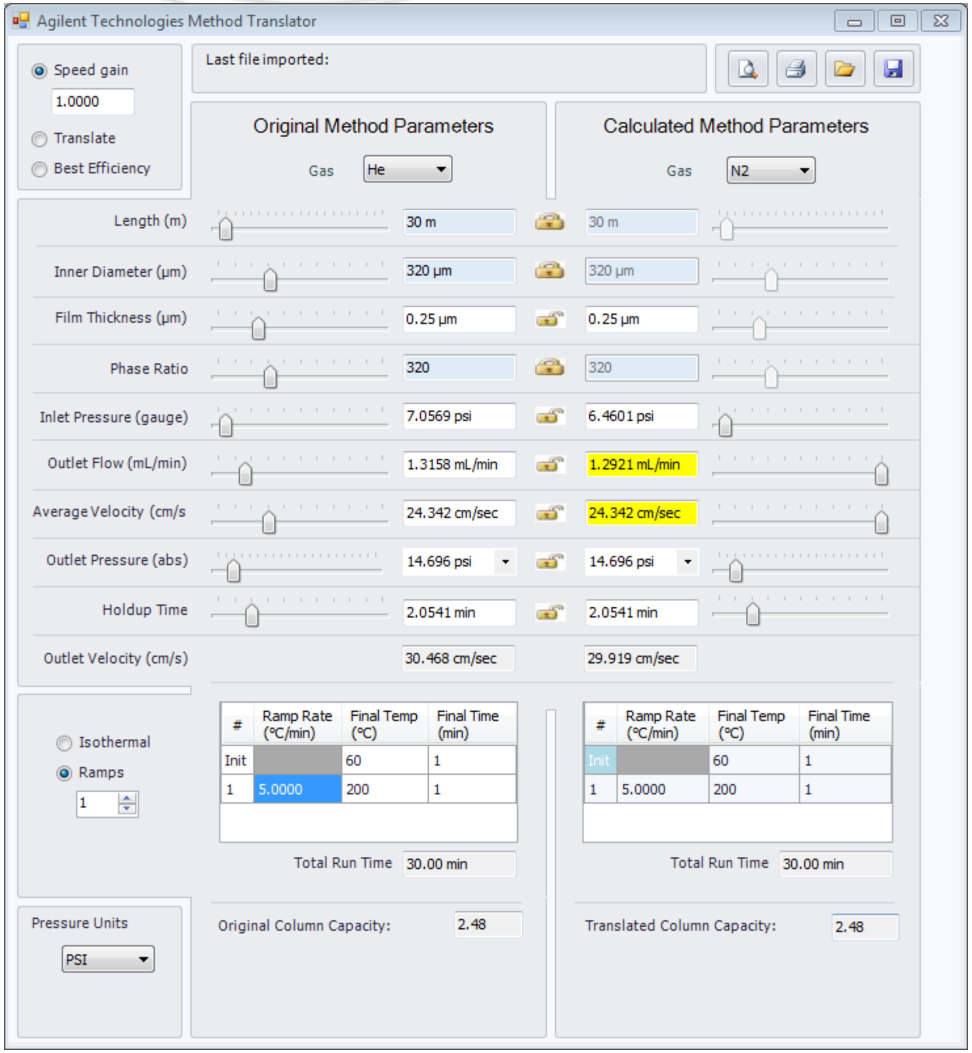
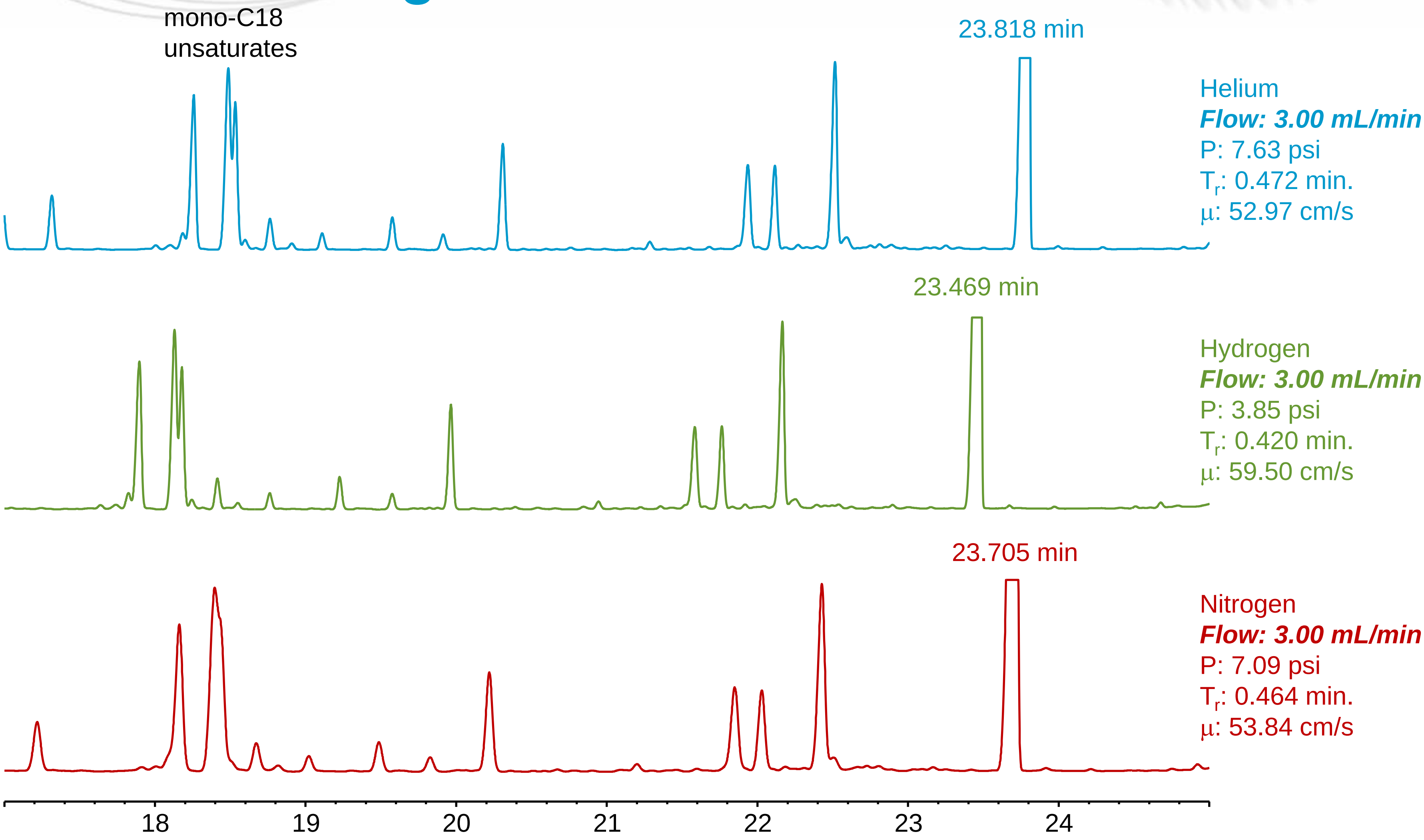
New Windows 7 Method Translation Calculator
Another useful tool for carrier gas calculations

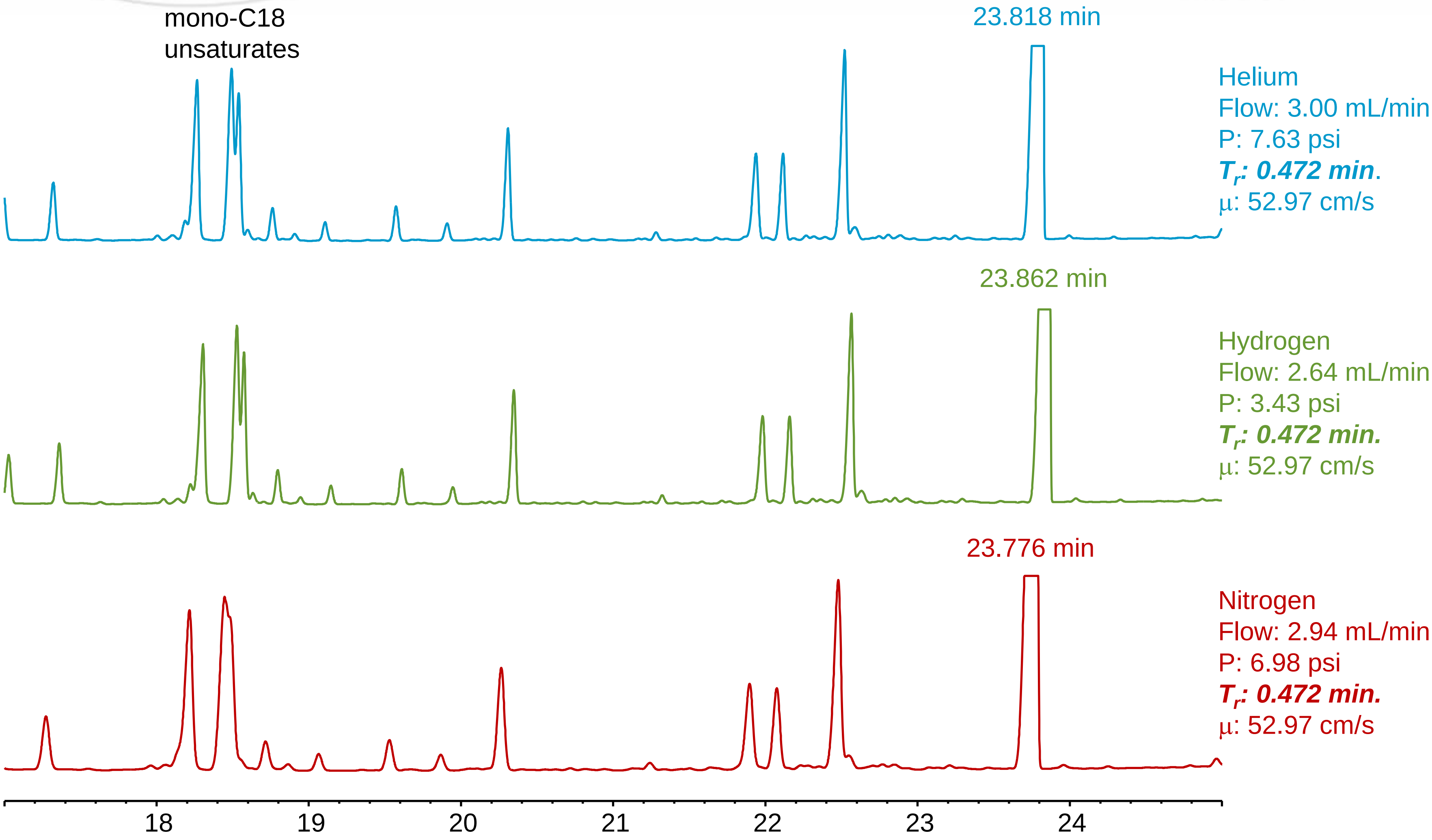


- Flexible tool helps convert existing helium methods to alternative carrier
- Built into the New OpenLAB CDS Software
- Can also run as Windows 7 program
- Download from the Agilent Helium Update Page: www.agilent.com/chem/heliumupdate

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



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



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**

Test Case 2: Analysis of Oxygenates 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

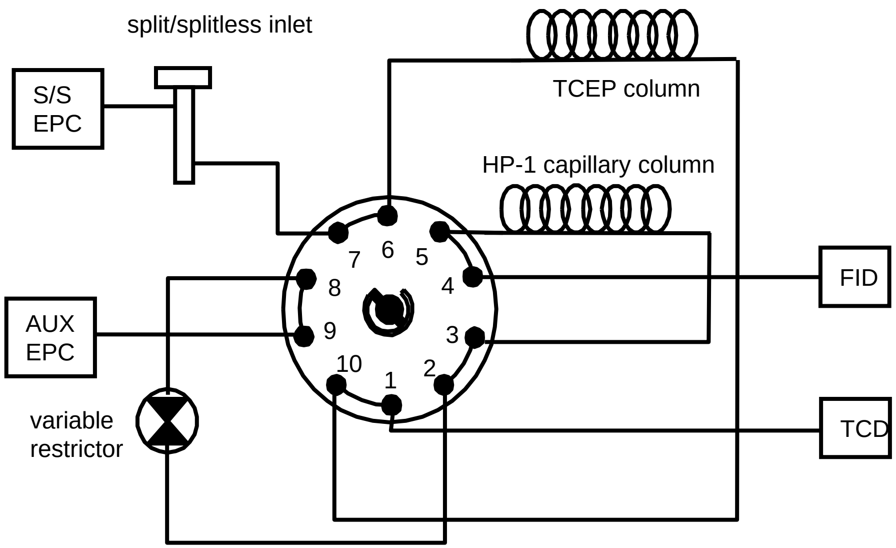
Preliminary separation removes light hydrocarbons from sample

- Polar TCEP micro-packed columns retains ethers and alcohols
- Back flush TCEP column to non-polar capillary column (HP-1) to complete analysis

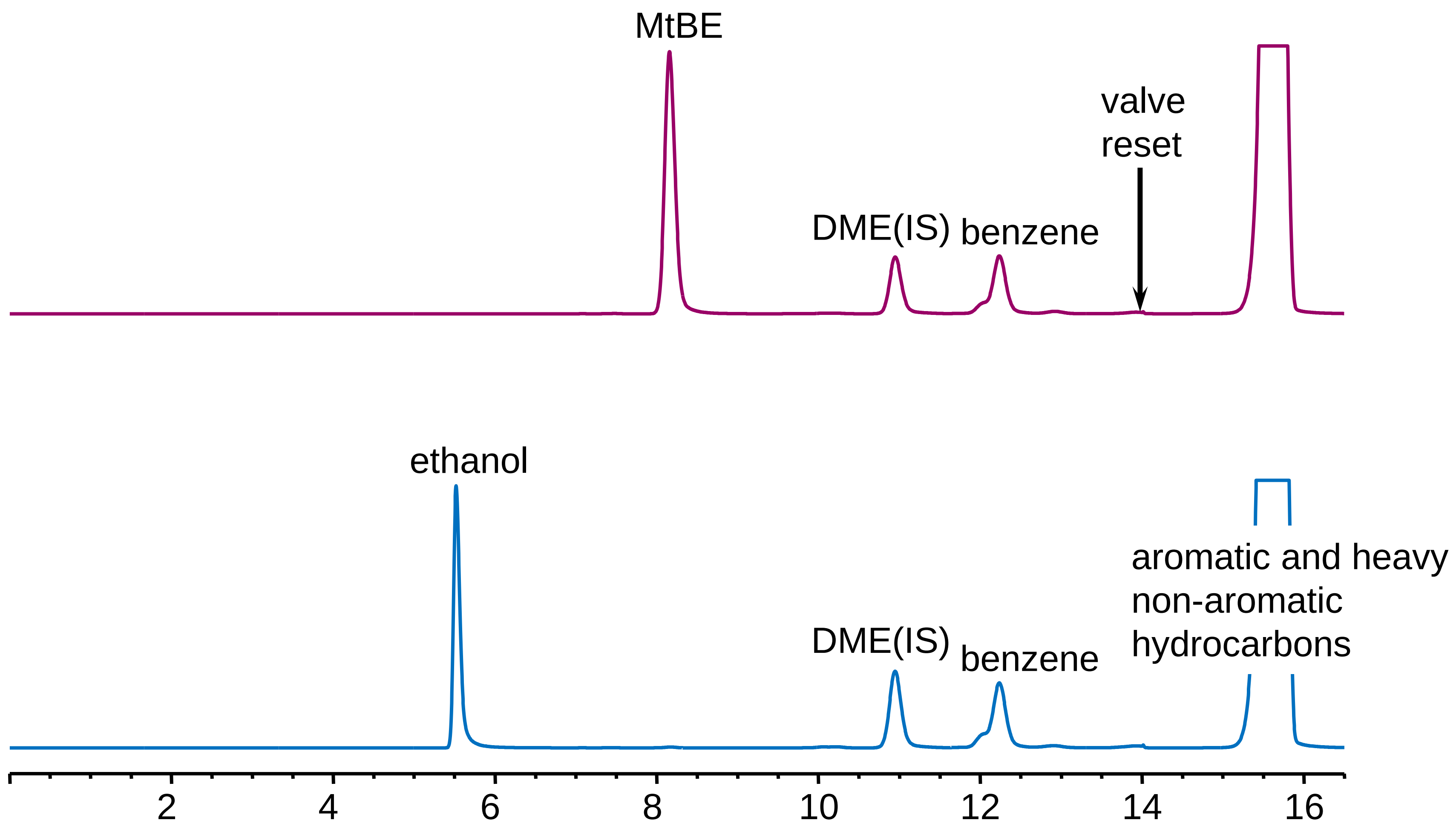
Configuration and Operation for D4815

Nitrogen carrier gas using original ASTM GC flows conditions

	D4815 Method
carrier gas	**nitrogen**
Inlet	Split/Splitless
inlet temperature	200 Deg C
TCEP column flow	**5 mL/min**
split vent flow	**70 mL/min**
split ratio	15:1
HP-1 column flow	**3 mL/min**
FID temperature	250 deg C
oven temperature	60 deg C isothermal
Run time	16 min



Analysis of MtBE and Ethanol in Gasoline using N_2 Carrier Gas



ASTM Precision Specifications

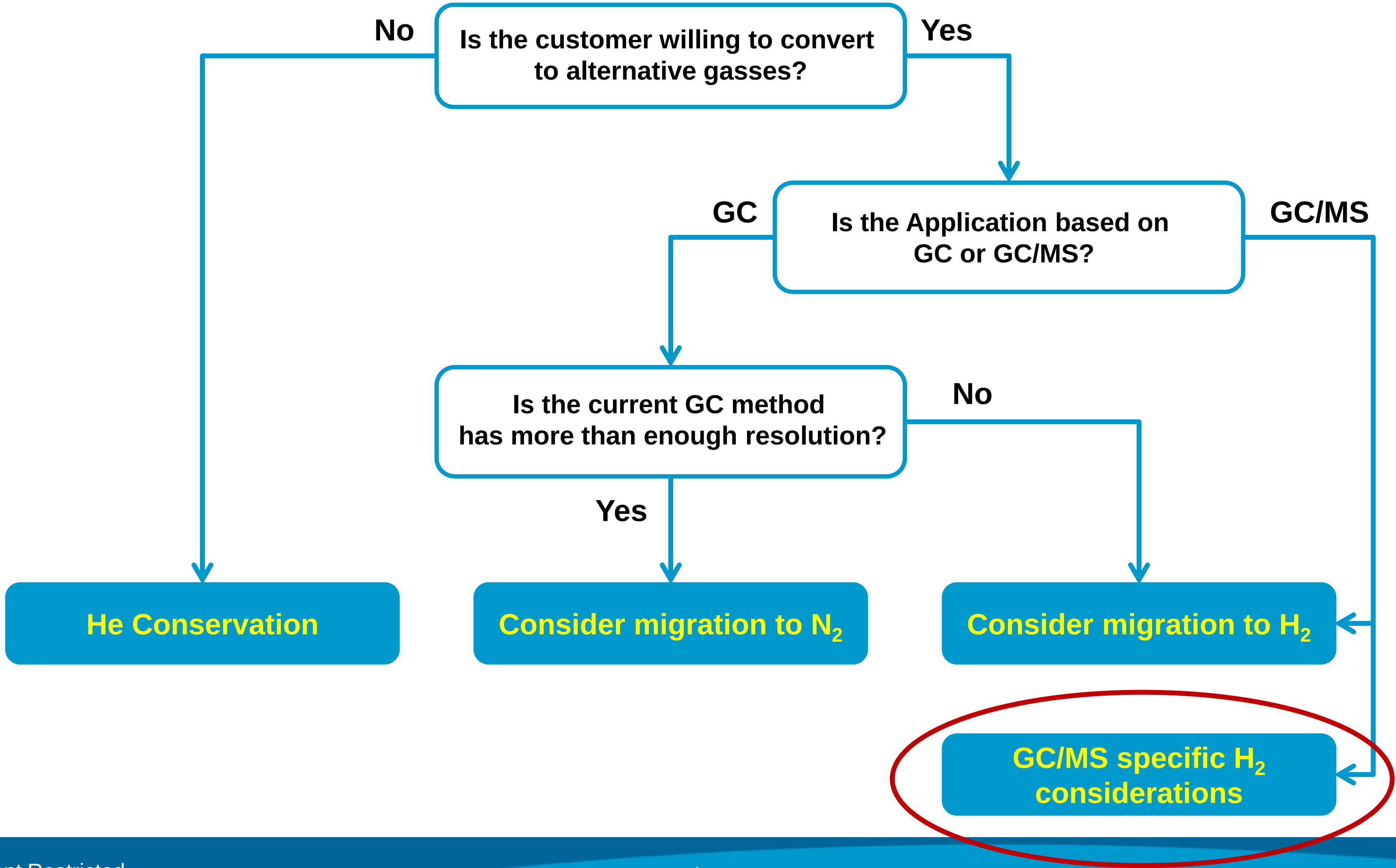
D4815 Precision Measures

		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

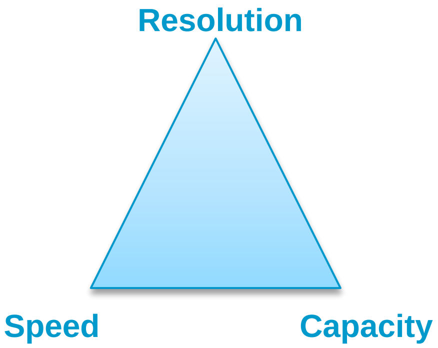
Migration to H_2:
-- Specific Considerations for GC/MS



H_2: Chromatographic Method Migration

Be aware:

- Consider flow limitation due to MSD pumping capacity
- Ensure >35 cm/sec flow rate (see Van Deemter Curves)
- Keeping similar peak elution order
- Consider column sample capacity



H_2 isn't a inert gas

- Consider full inert flow path
- Use lowest temp possible
- Avoid methylene chloride, carbon disulfide as solvent

H_2: Additional HW modification on GC/MS

Check Magnetic (5975 only)

- Ensure SN is printed on it
- Call CE if not

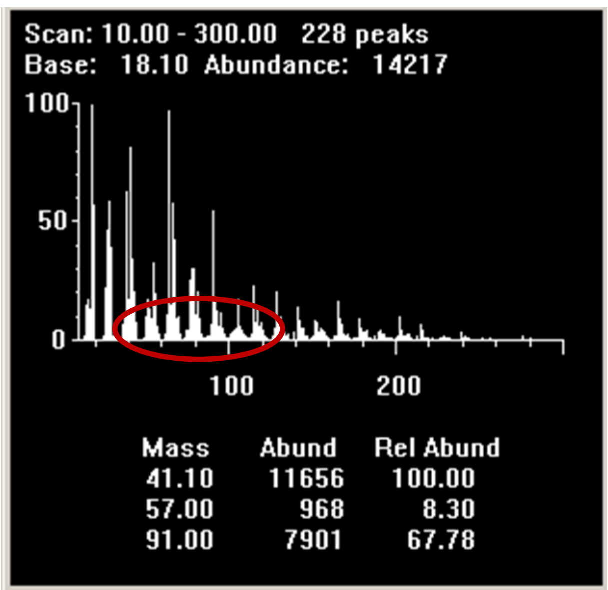
Use H2 optimized draw out lens

- PN: G2589-20045

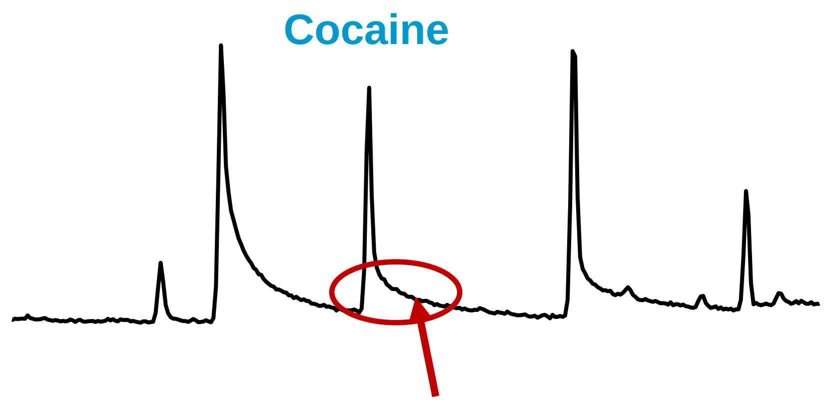
H_2 for GC/MS: Initial Setup

When start: customer should expect

- High background that looks like hydrocarbons ☹
- Reduced signal to noise (worse MDL) ☹
- Significant tailing for many compounds ☹



Mass	Abund	Rel Abund
41.10	11656	100.00
57.00	968	8.30
91.00	7901	67.78



spectrum changes
over tailed peak profile

H_2 for GC/MS: Initial Setup

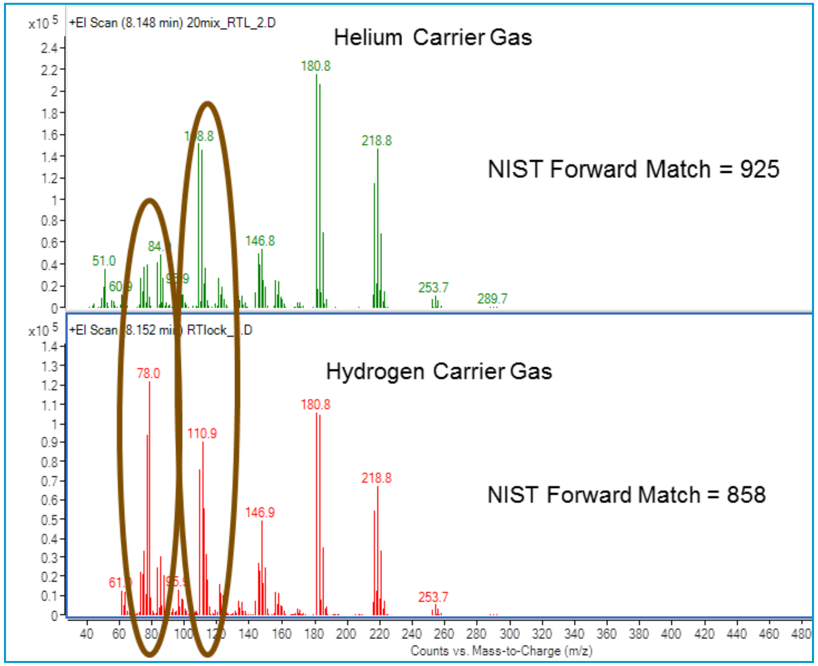
Overnight system clean up:

- After setup, purging and pump down
- Set the source to max temp for your source
- Reduce the EMV to 800V
- Leave the FILAMENT ON overnight.
- System will be cleaned in the morning
- Make a run with matrix to check
- Ready to go

H_2 for GC/MS: Analytical Result Expectations

- **Sensitivity reduction: 2 – 5 times**
- **Trace conc. "reactive" compounds (e.g. flavor) may lost**
- **Possible spectrum infidelity**
  - **Observed ion ratio change for some compounds**
  - **Extra/missing ions, but often time not qualifier ions**

Lindane



	NIST Library Match	
	Helium	Hydrogen
Dichlorvos	924	867
Mevinphos	925	852
Ethalfluralin	927	897
Trifluralin	897	856
Atrazine	914	901
BHC-gamma (Lindane, gamma HCH)	925	858
Chlorpyrifos-methyl	922	897
Heptachlor	926	851
Malathion	916	836
Chlorpyrifos	901	890
DDE, p,p'-	934	903
Dieldrin	926	903
Hexazinone	901	832
Propargite	851	821
Leptophos	884	847
Mirex	903	881
Fenarimol	905	872
Coumaphos	864	804
Etofenprox (Ethofenprox)	906	842

Summary: Helium Conservation Benefits

- **Seamless integration**
  - No need to revalidate existing GC methods
  - Fully integrated with 7890B and CDS (OpenLAB, Mustang, Mass Hunter)
  - Carrier gas ID and set points 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
  - 7890 provides warning if set points 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 H_2 and N_2

If you still need a helium alternative:

– For resolution critical methods, H_2 offer the best alternative

  – Agilent GC and GC/MS systems have many built-in safety features

– For many GC applications, N_2 offers a cheap, easy alternative without any safety worries

- Many existing helium methods have too much resolution
- N_2 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 N_2 is ideally suited as a carrier gas
  – Valve-based or Deans switch, not GCxGC

– For more information on Helium Carrier Gas www.agilent.com/chem/heliumupdate