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\textsubscript{2} and N\textsubscript{2}

- Best practices for obtaining the same results and minimizing method revalidation
Carrier Gas Decision Tree

Continue using helium, but in a smarter way

- Is the chemist willing to convert to alternative gases?
  - No: He Conservation
  - Yes:
    - Is the Application based on GC or GC/MS?
      - GC:
        - Does the current GC method have excess resolution?
          - No: Consider migration to N₂
          - Yes: Consider migration to H₂
      - GC/MS: GC/MS specific H₂ considerations

Method revalidation not required!
Reducing Helium Use With Conservation

New 7890B Helium Conservation Module

- Automatically switches carrier gas supply to N\textsubscript{2} Standby during idle time

- Integrates into the new 7890B Sleep and Wake function

- Combined with Helium Gas Saver to \textit{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)

- **AUX EPC 1**
  - Nitrogen
  - 70 psig

- **AUX EPC 3**
  - Purge Vent
  - 10 psig
  - 25.2 mL/min N₂

- **AUX EPC 2**
  - Helium
  - 0 psig
  - (< 0.2 mL/min) He

- **Bridge Block**
  - 24.2 mL/min N₂

- **To GC Inlet**
  - Helium OFF, Nitrogen ON at 70 psig
How Does It Work?

Normal Operation Mode (Helium Carrier or Wake Mode)

- **AUX EPC 1**: Nitrogen, 0 psig
- **AUX EPC 3**: Purge, 10 psig
- **AUX EPC 2**: Helium, 80 psig

Helium ON at 80 psig, Nitrogen OFF

To GC Inlet

EPC

24.2 mL/min He

25.2 mL/min He

1 mL/min (out)

(< 0.2 mL/min) N₂

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 N₂ Carrier Sleep Method. GC/FID Analysis

Day 1 - Original He carrier gas run

Day 2 – First He carrier gas run after overnight N₂ sleep method

Day 3 – First He carrier gas run after overnight N₂ sleep method

July 30, 2013
Performance: Pass MS Tune **Within 15min After Switching From N\textsubscript{2} To He As Carrier.** GC/MSD

![Nitrogen Background Graph](image)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>5 mL/min He</th>
<th>Relative to Saturation</th>
<th>2 mL/min He</th>
<th>Relative to Saturation</th>
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<tr>
<td>3</td>
<td>1735168</td>
<td>20.69%</td>
<td>8388096</td>
<td>100.00%</td>
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<tr>
<td>4</td>
<td>1033280</td>
<td>12.32%</td>
<td>4959232</td>
<td>59.12%</td>
</tr>
<tr>
<td>5</td>
<td>590080</td>
<td>7.03%</td>
<td>1618944</td>
<td>19.30%</td>
</tr>
<tr>
<td>6</td>
<td>354112</td>
<td>4.22%</td>
<td>722944</td>
<td>8.62%</td>
</tr>
<tr>
<td>7</td>
<td>228480</td>
<td>2.72%</td>
<td>333696</td>
<td>3.98%</td>
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<tr>
<td>10</td>
<td>56984</td>
<td>0.68%</td>
<td>102576</td>
<td>1.22%</td>
</tr>
<tr>
<td>15</td>
<td>9052</td>
<td>0.11%</td>
<td>17080</td>
<td>0.20%</td>
</tr>
</tbody>
</table>
Helium Savings Calculator – 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

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

- Is the customer willing to convert to alternative gasses?
  - No: He Conservation
  - Yes: GC/MS specific H₂ considerations

- Is the Application based on GC or GC/MS?
  - GC: Does the current GC method have more than enough resolution?
    - No: Consider migration to H₂
    - Yes: Consider migration to N₂
  - GC/MS: Consider migration to H₂
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

$\text{H}_2$ Generator – preferred

- Very clean $\text{H}_2$, >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

$\text{H}_2$ 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_e and its numeric value tells how well two adjacent peaks are separated from each other.

\[ R_e = \sqrt{\frac{N}{4}} \left( \frac{k}{k+1} \right)^{\frac{\alpha-1}{\alpha}} \]

A resolution value of 1.5 tells us that two peaks are baseline separated. The greater (higher) the R_e 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.

\[ t_R' = t_R - t_m \]

\[ n = \frac{5.545}{t_R'} \]

\[ t_R' = \text{Corrected Retention Time.} \]

\[ n = \text{effective theoretical plates.} \]

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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Calculating Efficiency

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

\[
t_R' = t_R - t_m
\]

\[n = \frac{5.545}{W_n} (t_R')^2\]

\[n = \text{effective theoretical plates.}\]

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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 N₂, 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 at 1 mL/min
Constant Flow
(25.4 cm/s)

Nitrogen at 1 mL/min
Constant Flow
(25.8 cm/s)

Good enough resolution
Helium Carrier Gas Alternative

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

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 °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 N₂ makeup

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

1. Istd 1
2. Istd 2
3. Istd 3
4. Istd 4

Chromatogram showing peaks for Istd 1 to 4, with annotations for Glycerol, Monoglycerides, Diglycerides, and triglycerides.
Set the Control Mode: Flow or Holdup Time

Try the same flow or holdup time of the original Helium method
Configure Inlet for Carrier Gas in Chemstation

Select H₂ or N₂
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

Helium
Flow: 3.00 mL/min
P: 7.63 psi
T_r: 0.472 min.
µ: 52.97 cm/s

Hydrogen
Flow: 3.00 mL/min
P: 3.85 psi
T_r: 0.420 min.
µ: 59.50 cm/s

Nitrogen
Flow: 3.00 mL/min
P: 7.09 psi
T_r: 0.464 min.
µ: 53.84 cm/s

mono-C18 unsaturates

23.818 min
23.469 min
23.705 min
Same Holdup Time ($T_r$) Gives Consistent Retention Times Compared to Original Helium Method

- **Helium**
  - Flow: 3.00 mL/min
  - $P$: 7.63 psi
  - $T_r$: 0.472 min.
  - $\mu$: 52.97 cm/s
  - Retention Time: 23.818 min

- **Hydrogen**
  - Flow: 2.64 mL/min
  - $P$: 3.43 psi
  - $T_r$: 0.472 min.
  - $\mu$: 52.97 cm/s
  - Retention Time: 23.862 min

- **Nitrogen**
  - Flow: 2.94 mL/min
  - $P$: 6.98 psi
  - $T_r$: 0.472 min.
  - $\mu$: 52.97 cm/s
  - Retention Time: 23.776 min

- **mono-C18 unsaturates**
**ASTM D6584 - Quantitative Results For Alternative Carrier Gas**

Carrier gas has no effect on reported results

<table>
<thead>
<tr>
<th></th>
<th>Weight Percent</th>
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<tbody>
<tr>
<td></td>
<td>Helium</td>
</tr>
<tr>
<td>Glycerin</td>
<td>0.015</td>
</tr>
<tr>
<td>Monoglycerides</td>
<td>0.226</td>
</tr>
<tr>
<td>Total Glycerin</td>
<td>0.097</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
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<tbody>
<tr>
<td>carrier gas</td>
<td>nitrogen</td>
</tr>
<tr>
<td>Inlet</td>
<td>Split/Splitless</td>
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<tr>
<td>inlet temperature</td>
<td>200 Deg C</td>
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<tr>
<td>TCEP column flow</td>
<td>5 mL/min</td>
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<tr>
<td>split vent flow</td>
<td>70 mL/min</td>
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<td>split ratio</td>
<td>15:1</td>
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<tr>
<td>HP-1 column flow</td>
<td>3 mL/min</td>
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<tr>
<td>FID temperature</td>
<td>250 deg C</td>
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<tr>
<td>oven temperature</td>
<td>60 deg C isothermal</td>
</tr>
<tr>
<td>Run time</td>
<td>16 min</td>
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</tbody>
</table>
Analysis of MtBE and Ethanol in Gasoline using N$_2$ Carrier Gas

- MtBE
- DME(IS) benzene
- Valve reset
- Ethanol
- Aromatic and heavy non-aromatic hydrocarbons

July 30, 2013
### ASTM Precision Specifications

#### D4815 Precision Measures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass %</th>
<th>Spec</th>
<th>Observed</th>
<th>Spec</th>
<th>Observed</th>
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</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.99</td>
<td>0.06</td>
<td>0.01</td>
<td>0.23</td>
<td>0.01</td>
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<tr>
<td>Ethanol</td>
<td>6.63</td>
<td>0.19</td>
<td>0.03</td>
<td>0.68</td>
<td>0.04</td>
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<tr>
<td>MtBE</td>
<td>2.10</td>
<td>0.08</td>
<td>0.01</td>
<td>0.20</td>
<td>0.01</td>
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<tr>
<td>MtBE</td>
<td>11.29</td>
<td>0.19</td>
<td>0.05</td>
<td>0.61</td>
<td>0.08</td>
</tr>
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</table>

#### Accuracy Evaluation

<table>
<thead>
<tr>
<th>Sample</th>
<th>MtBE mass %</th>
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<tr>
<td>known</td>
<td>found</td>
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<tr>
<td>SRM2294 #1</td>
<td>10.97</td>
</tr>
<tr>
<td>SRM2294 #2</td>
<td>10.97</td>
</tr>
<tr>
<td>AccuStd Check</td>
<td>12.00</td>
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</table>
Migration to $\text{H}_2$:  
-- Specific Considerations for GC/MS

- **Is the customer willing to convert to alternative gasses?**
  - **Yes**
    - **Is the Application based on GC or GC/MS?**
      - **GC**
        - **Is the current GC method has more than enough resolution?**
          - **Yes**
            - Consider migration to $\text{N}_2$
          - **No**
            - He Conservation
      - **GC/MS**
        - **Yes**
          - Consider migration to $\text{H}_2$
        - **No**
          - GC/MS specific $\text{H}_2$ considerations

- **No**
  - Consider migration to $\text{N}_2$
H₂: 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

**H₂ isn’t a inert gas**

- Consider full inert flow path
- Use lowest temp possible
- Avoid methylene chloride, carbon disulfide as solvent
H₂: 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 😞
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
H₂ 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

<table>
<thead>
<tr>
<th>NIST Library Match</th>
<th>Helium</th>
<th>Hydrogen</th>
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<tbody>
<tr>
<td>Dichlorvos</td>
<td>924</td>
<td>867</td>
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<tr>
<td>Mevinphos</td>
<td>925</td>
<td>852</td>
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<tr>
<td>Ethalfuralin</td>
<td>927</td>
<td>897</td>
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<tr>
<td>Trifluralin</td>
<td>897</td>
<td>856</td>
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<tr>
<td>Atrazine</td>
<td>914</td>
<td>901</td>
</tr>
<tr>
<td>BHC-gamma (Lindane, gamma HCH)</td>
<td>925</td>
<td>858</td>
</tr>
<tr>
<td>Chlorpyrifos-methyl</td>
<td>922</td>
<td>897</td>
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<tr>
<td>Heptachlor</td>
<td>926</td>
<td>851</td>
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<tr>
<td>Malathion</td>
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<tr>
<td>Chlorpyrifos</td>
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<td>890</td>
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<tr>
<td>DDE, p,p'</td>
<td>934</td>
<td>903</td>
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<tr>
<td>Dieldrin</td>
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<td>903</td>
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<tr>
<td>Hexazinone</td>
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<td>832</td>
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<td>Propargite</td>
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<td>821</td>
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<tr>
<td>Leptophos</td>
<td>884</td>
<td>847</td>
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<tr>
<td>Mirex</td>
<td>903</td>
<td>881</td>
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<tr>
<td>Fenarimol</td>
<td>905</td>
<td>872</td>
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<tr>
<td>Coumaphos</td>
<td>864</td>
<td>804</td>
</tr>
<tr>
<td>Etofenprox (Ethofenprox)</td>
<td>906</td>
<td>842</td>
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</table>
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 5\textsuperscript{th} 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 H₂ and N₂

If you still need a helium alternative:

– 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 GCxGC

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