Reducing Pressure on Operational Budgets: Helium Conservation Strategies for GC and GC/MSD

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April 2014
Topics for Today

Minimizing helium use:
• Do a helium use audit and compare it to actual usage
• Identify leaks and other loss areas in the laboratory
• Optimize your analyses to minimize helium consumption

Adapting methods to alternate carriers
• Nitrogen
• Hydrogen
Minimizing Helium Usage

Question: how much helium do you THINK you are using?
- Add up the flows used by all devices consuming helium to get theoretical usage
- Compare theoretical usage to ACTUAL usage
Helium Audit: Add Up All Uses of Helium and Compare It to Actual Usage

Make a spreadsheet of:

- Each instrument or device using helium
- Determine the total flow used by each one:
  - Read the inlet and column flows from the GC interface
  - Make sure to include helium used as detector makeup gas
  - For flows in valve systems that are difficult to measure, just estimate
  - If you have too many GCs, just count them and assume 100 mL/min He for each one. This will give an estimate that is high, but useful as a rough check.
  - For older GCs or other equipment, use a flow meter to measure helium
Read Inlet, Column, and Detector Flows on GC

- For this GC the Purge Flow is 50 mL/min for 2 min, then Gas Saver drops it to 20 mL/min the rest of the time
- The column flow is 1.2 mL/min
- No helium is used as detector makeup gas (we use nitrogen)
We Did a Helium Audit at Agilent Little Falls Site
Example data from parts of our facility

<table>
<thead>
<tr>
<th>Lab</th>
<th>Number of GCs or inlets</th>
<th>avg flow (ml/min)</th>
<th>Total Flow (ml/min)</th>
<th>Liters / day</th>
<th>Liters / day (max)*</th>
<th>Cost/day (minimum)</th>
<th>Cost/day (max)</th>
<th>Floor</th>
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<tbody>
<tr>
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<td>GC area</td>
<td>15</td>
<td>50</td>
<td>750</td>
<td>1080</td>
<td>1620</td>
<td>12.90</td>
<td>19.34</td>
<td>1</td>
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<tr>
<td>COE</td>
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<td>360</td>
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<td>50</td>
<td>850</td>
<td>1224</td>
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<td>65</td>
<td>910</td>
<td>1310.4</td>
<td>1965.6</td>
<td>15.65</td>
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<tr>
<td>SW Validation 2</td>
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<td>750</td>
<td>750</td>
<td>1080</td>
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<td>12.90</td>
<td>19.34</td>
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<td>50</td>
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<td>9.6</td>
<td>13.824</td>
<td>20.736</td>
<td>0.17</td>
<td>0.25</td>
<td>3</td>
</tr>
</tbody>
</table>

**Cost/day** $218.82 $328.23
**Cost/yr** $79,870.03 $119,805.04
Audit Results
Agilent Little Falls Site

For entire facility, based on theoretical total flow of helium used, bill should be about $170,000

Our actual bills were greater than $500,000 per year (!)

Action items:
• Look for leaks
• Raise awareness among users
• Where it makes sense, adjust instrument parameters to reduce helium usage
Leak Detectors

Agilent G3388B Leak Detector

- Allows detection of **helium and hydrogen** to 0.0005 ml/min.
- Detects thermal conductivity differences
- Audible and visual alerts
- Small – about the size of a cell phone
- Recharge using USB to any PC
- Lithium ion battery, > 5 hours of life
- One year warranty from Agilent

Liquid Leak Detector

- Works for all gases
- Good for checking tube fittings
- Must be applied to directly to connection
- Does not find leaks in the area
- Do not use on fittings with vacuum inside
Gas Towers for Instrument Connections
Easy access for leak checking
Infrastructure Plumbing
Not so easy access
Looking For Leaks

Ooh, the meter is climbing

Wow! A big one!
Results of Actions

• Found and fixed many leaks
• Found helium plumbed to industrial device for purging where nitrogen should be used
• Raised awareness among users that reducing helium consumption is important
• Adjusted instruments to use less helium without compromising performance
• **After one year, our helium use dropped by a factor of 2.2**
• A customer, a large chemical company, reported similar results
• Conclusion, do a helium audit
Optimizing Methods To Save Helium
Flows for Split/Splitless and MMI GCs

Total Flow = 50 + 3 + 1.2 + 30 = 84.2

Carrier Gas → Septum Purge → 3 mL/min
Split Flow → 50 mL/min

Column Flow → 1.2 mL/min

Makeup Gas → 30 mL/min

Detector
Change Makeup Gas to Nitrogen
Save 30 mL/min

Total Flow = 50 + 3 + 1.2 = 54.2

Carrier Gas → 3 mL/min
Septum Purge → 3 mL/min
Split Flow → 50 mL/min

Column Flow → 1.2 mL/min
Makeup Gas → 0 mL/min He
30 mL/min N₂

Detector
Use Gas Saver
Save 30 mL/min for All but Injection Time

Carrier Gas → Septum Purge → 3 mL/min
Split Flow → 50 mL/min during inlet purge
20 mL/min all other times

Total Flow during purge after injection = 54.2
Total Flow all other times = 24.2

Column Flow → 1.2 mL/min
Looking at a Single Instrument: My GC/MSD Uses 32 L/day

<table>
<thead>
<tr>
<th>Parameter</th>
<th>No Gas Saver</th>
<th>Gas Saver</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily He Usage (L)</td>
<td>74</td>
<td>32</td>
</tr>
<tr>
<td>He Cylinder Life (days)</td>
<td>109</td>
<td>252</td>
</tr>
</tbody>
</table>

Note that **Gas Saver** offers significant savings with Split/Splitless and MMI inlets.

GC Flow Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>He Carrier Flow (mL/min)</td>
<td>1.2</td>
</tr>
<tr>
<td>He Split flow (mL/min)</td>
<td>50</td>
</tr>
<tr>
<td>Gas Saver Flow (mL/min)</td>
<td>20</td>
</tr>
<tr>
<td>Gas Saver On (min)</td>
<td>2</td>
</tr>
<tr>
<td>Run Time (min.)</td>
<td>20</td>
</tr>
<tr>
<td>Gas Volume in Cylinder (L)</td>
<td>8000</td>
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<tr>
<td>Runs per Day</td>
<td>20</td>
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</tbody>
</table>
Optimizing Split Flow to Lowest Value with MSD

To optimize gas saver, reduce flow stepwise while monitoring m/z 28. Optimal flow is somewhat higher than flow where 28 abundance increases.

- Carrier Gas: 1.2 mL/min
- Septum Purge: 3 mL/min
- Split Flow: 50 mL/min during inlet purge, 10 mL/min optimized

Total Flow during injection = 54.2
Total Flow all other times = 14.2
Minimizing Diffusion of Air Into Inlet
Use Flexible Metal Ferrule to Seal Column in Inlet

- Much easier to install column
- Does not loosen with oven cycling
- Does not diffuse air like graphite
## Helium Usage Comparison

<table>
<thead>
<tr>
<th>Column (mL/min)</th>
<th>Split (mL/min)</th>
<th>Gas Saver (mL/min)</th>
<th>Detector (mL/min)</th>
<th>Runs per Day</th>
<th>Daily He Use (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>50</td>
<td>20</td>
<td>30</td>
<td>20</td>
<td>117</td>
</tr>
<tr>
<td>1.2</td>
<td>50</td>
<td>20</td>
<td>0</td>
<td>20</td>
<td>74</td>
</tr>
<tr>
<td>1.2</td>
<td>50</td>
<td>10</td>
<td>0</td>
<td>20</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>20</td>
<td>0</td>
<td>20</td>
<td>295</td>
</tr>
</tbody>
</table>

20 min run, 2 min gas saver time

By switching detector makeup to nitrogen, using gas saver, and optimizing it to 10 mL/min, **helium usage is reduced by 85%**
Reducing Helium Use Further…

New 7890B Helium Conservation Module

• Automatically switches carrier gas supply to N₂ 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)

AUX EPC 1
Nitrogen
70 psig

AUX EPC 3
Purge Vent
10 psig

AUX EPC 2
Helium
0 psig

25.2 mL/min $N_2$

1.0 mL/min (out)

24.2 mL/min $N_2$

(< 0.2 mL/min) He

Helium OFF, Nitrogen ON at 70 psig

To GC Inlet
EPC
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

Bridge Block

1 mL/min (out)

(> 0.2 mL/min) $\text{N}_2$

25.2 mL/min He

24.2 mL/min He

To GC Inlet
EPC

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 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.M method

Day 3 – First He carrier gas run after overnight N₂ Sleep.M method

April 22, 2014

C&EN Webinar
Performance: Pass MS Tune within 15 min after Switching from N₂ to He as Carrier. GC/MSD

Nitrogen Background

<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>
</tr>
</thead>
<tbody>
<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>
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<tr>
<td>5</td>
<td>590080</td>
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<td>1618944</td>
<td>19.30%</td>
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<td>354112</td>
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<td>333696</td>
<td>3.98%</td>
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<td>10</td>
<td>56984</td>
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<td>102576</td>
<td>1.22%</td>
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<tr>
<td>15</td>
<td>9052</td>
<td>0.11%</td>
<td>17080</td>
<td>0.20%</td>
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</tbody>
</table>
Helium Usage with Helium Conservation Switch

<table>
<thead>
<tr>
<th>Column (mL/min)</th>
<th>Split (mL/min)</th>
<th>Gas Saver (mL/min)</th>
<th>Detector (mL/min)</th>
<th>Runs per Day</th>
<th>Daily He Use (L)</th>
<th>He Cylinder Life (days)</th>
</tr>
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<td>20</td>
<td>0</td>
<td>20</td>
<td>295</td>
<td>43</td>
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</table>

20 min run, 2 min gas saver time

By switching detector makeup to nitrogen, using gas saver, optimizing gas saver, and using the conservation switch, **helium usage is reduced by 95%**
Alternate Carrier Gases
Carrier Gas Decision Tree
Migrating GC methods to nitrogen and hydrogen

- Is the chemist willing to convert to alternative gases?
  - Yes: Consider migration to \( \text{H}_2 \)
  - No: Consider migration to \( \text{N}_2 \)

- Is the Application based on GC or GC/MS?
  - GC: Consider migration to \( \text{N}_2 \)
  - GC/MS: GC/MS specific \( \text{H}_2 \) considerations

- Does the current GC method have more than enough resolution?
  - No: He Conservation
  - Yes: Consider migration to \( \text{N}_2 \)
Use of N\textsubscript{2} as Carrier Gas

Many helium GC methods are 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\textsubscript{2}, especially with PLOT/Micropacked columns
  - Some compounds catalytically reduced in H\textsubscript{2}
- 2-D GC ideally suited to nitrogen
  - Resolution issues solved by using 2 different columns

Potential issues
- Reduced chromatographic resolution at higher flows
- Not suitable for GC/MSD and certain GC detector applications
Van Deemter
Why Nitrogen Gets a Bad Rap for Capillary GC

- \( \text{N}_2 \) actually provides the best efficiency, but at a slower speed
- Many helium methods have too much resolution
  - Lower \( \text{N}_2 \) efficiency at “typical” helium flows can still provide good enough resolution
- Most GC methods now use constant flow
  - \( \text{N}_2 \) 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)

Good enough resolution

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

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

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

Graph showing retention times for Helium, Hydrogen, and Nitrogen.
Use of H\textsubscript{2} as Carrier Gas

Advantages to hydrogen conversion
• Readily available, less expensive, can be generated in lab
• Same or better chromatographic resolution per unit time
• Only alternative to He for GC/MSD
  - Reduces or eliminates source cleaning

Potential issues
• Safety concerns
• Some compounds react/decompose in presence of H\textsubscript{2}
• Not all detectors can be used with H\textsubscript{2}
Introduction: Converting from He to H₂ Carrier Gas

Methods that will generally require less optimization include analytes that are:
- “durable” compounds
- at higher concentrations
- analyzed with split injections
- derivatized

Methods that will generally require more optimization include analytes that are:
- “fragile” compounds
- at trace concentrations

Allow time for necessary updates to SOPs and validation
Designed for Reliability – H₂ Safety

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 Test
   GC and MS designed to contain parts in case of explosion
Hydrogen Sensing Module for 7890 GC Oven

- Complete GC shutdown when 1% H₂ is detected in oven (4% H₂ is LEL)
  - Open flaps, oven vents, turns off ignition sources and puts GC in shutdown state requiring user interaction
- Fully integrated into 7890A+/B GC
- Ability to calibrate on a set schedule or instantly when deemed necessary
  - Ability to print calibration report on demand

For more information:
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

Hydrogen
Flow: 2.64 mL/min
P: 3.43 psi
$T_r$: 0.472 min.
$\mu$: 52.97 cm/s

Nitrogen
Flow: 2.94 mL/min
P: 6.98 psi
$T_r$: 0.472 min.
$\mu$: 52.97 cm/s
First, Listen to Agilent Webinar on Details of Conversion of GC/MSD Method from He to H₂

Go To This URL for recorded webinar:

http://www.agilent.com/chem/heliumupdate

Topics Covered:

• H₂ Safety
• Source of H₂ Carrier and Plumbing
• MS Components Required: Magnet and Draw Out Lens
• Choosing a Column and Method Conditions
• Initial Startup with Hydrogen
• H₂ Conversion Considerations for Success
• Performance Expectations
Inert Flow Path Items Help with H2 Conversion
Reliability, Durability, Speed and Ease of Use
Configuration of Controlled Substance Analyzer

Post column Capillary Flow Technology (PUU) device provides:

A) Column Backflush  
B) No vent column change  
C) Convert from H2 to He with same retention times

220 V Oven With High Speed Oven Insert (Pillow)
Example: Street Heroin
Controlled Substances Analyzer

1. N-Propylamphetamine (ISTD)
2. Benzocaine
3. Caffeine
4. Lidocaine
5. 10,11-Dihydrodibenz(b,f)(1,4)oxazepin-11-one (ISTD)
6. Acetylcodeine
7. 6-Monoacetylmorphine
8. Heroin
9. Papaverine
10. Noscapine
Codeine, H₂ Instrument

Some hydrocodone is formed when codeine is injected.
• About 6% is converted.

TIC: codeine_std.d/data.ms
Summary

• Do a helium audit. You might be amazed at how much He is being wasted
• Review you GC and GC/MS methods to see if there are opportunities to save helium
• Determine if alternate carrier gases can be used for some methods
Helpful Links
Alternate Carrier Gas

Agilent Website for Alternative Carrier Gases


Link to World He Shortage Information:


Agilent 7890B Gas Chromatograph and Related Accessories:

Thank you
Let’s Continue the Conversation

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