Party Balloons vs GC/MS- Managing Your Helium Supply

Eric Redman

Vice President of Technical Services

Eurofins Environment Testing America

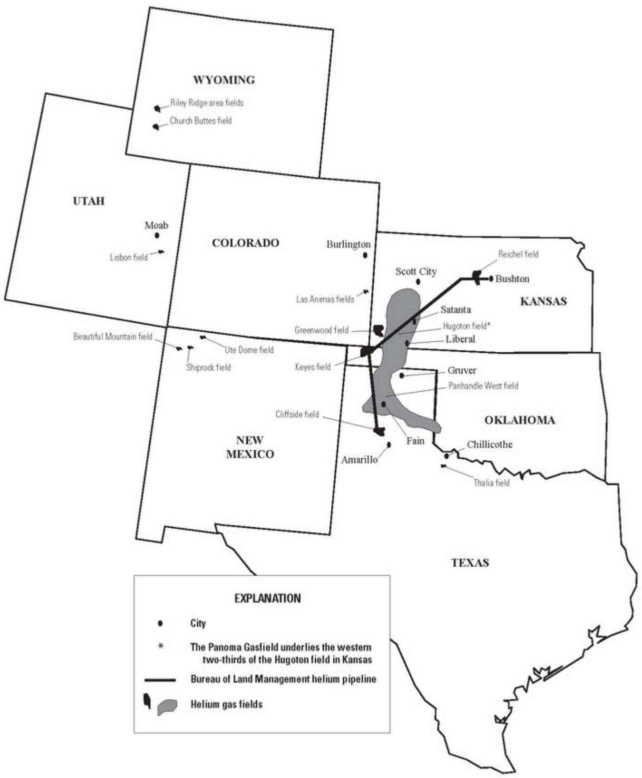
Outline

- Helium as an industrial commodity
  - Supply and demand dynamics
  - Recent impact on environmental labs
  - Future shortages?
- Laboratory management practices
  - Convert to alternative carrier/purge gas (H2, N2)
  - Monitor/optimize Helium usage
  - Assess alternative Helium vendors and supply logistics
- Laboratory case study

Helium- Properties/Characteristics

- Very light elemental gas (0.18g/L)
  - Forms the coldest known liquid (4K)
  - First noble gas in Periodic Table (extremely inert/non-reactive)
  - Least soluble elemental gas (~ 4 ppt)
- Highly abundant in the universe (24% of total mass)
  - Created during the Big Bang
  - Continuously produced by nuclear fusion in stars
- Rare element on Earth
  - Continuously produced by radioactive decay in Earth’s crust
  - Constant diffusion to space yields ~ 5 ppm atmospheric equilibrium

Helium- Production



(USGS)

Created from decay of Uranium and Thorium (He is ~ 8 ppb on average in Earth's crust)

- Trapped in unique geologic formations that prevent diffusive loss. Up to 10% by volume in some deposits.
- Usually obtained as a by-product of natural gas extraction, then distilled/liquefied.

(AEN)

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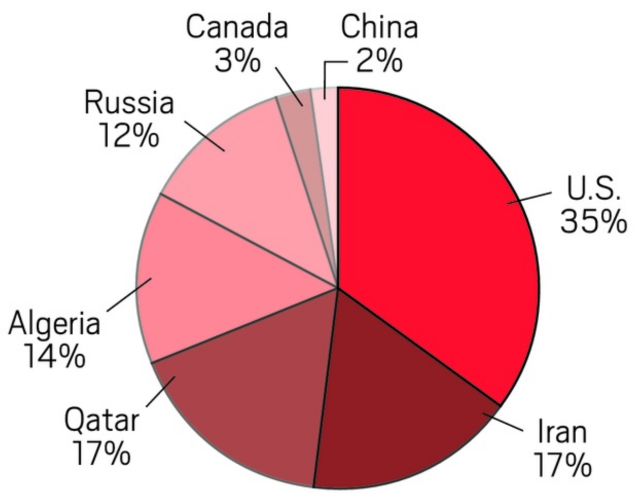
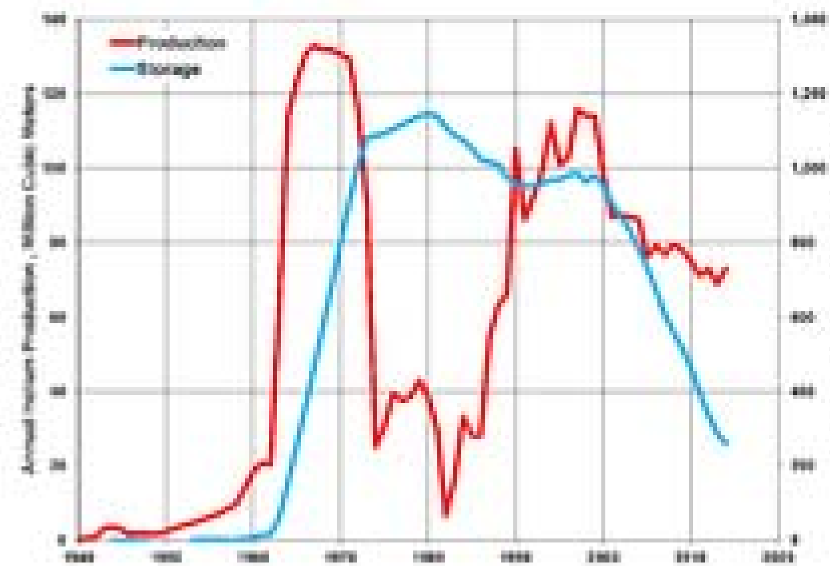
Helium- Supply



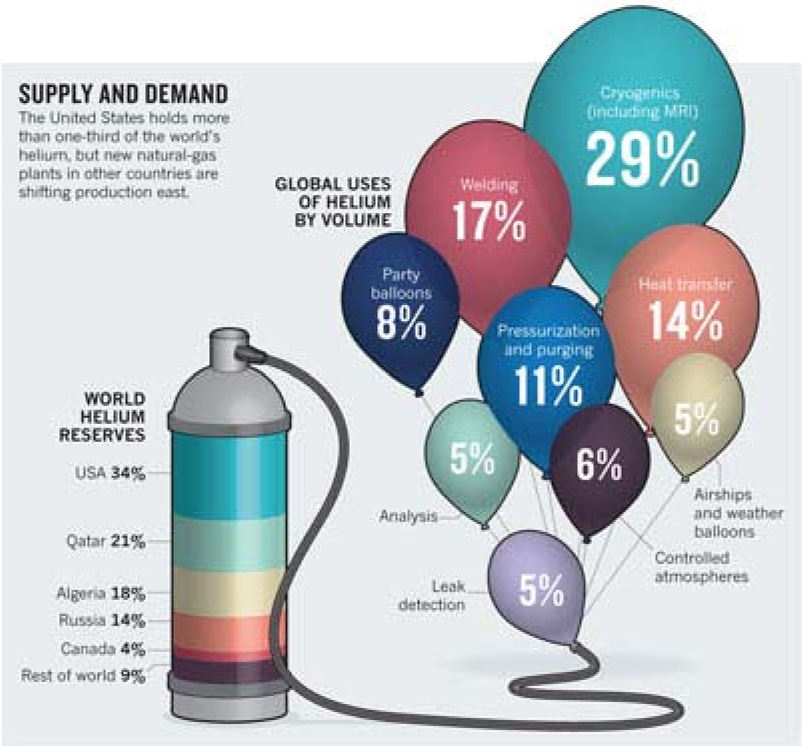
Global helium resources = 59 billion m^3 (C&EN)

- **US has been world's largest producer/supplier**
  - **70-90% of total; 50% from new production, 20-40% from the FHR**
  - **BLM sales from the FHR stabilized pricing for decades, then reversed**
  - **New US production slow to develop, varies with natural gas demand**
  - **New global sources (Qatar, Algeria, Iran, Russia, China) vulnerable to geopolitics, transport constraints**



(USGS)

Helium- Growing Demand



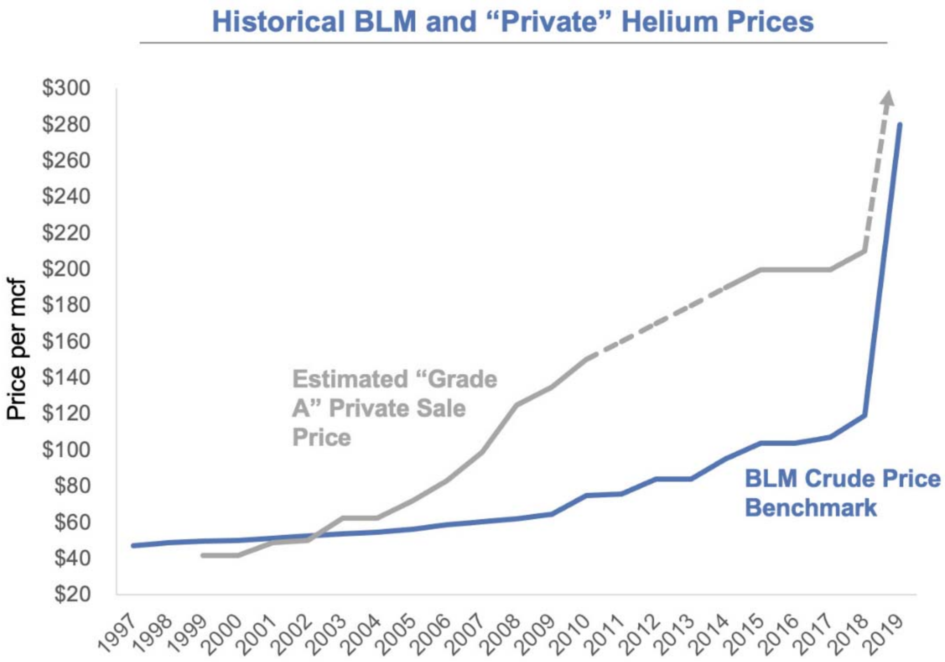
- Largest use as coolant for superconducting magnets (MRI, NMR, sub-atomic research, etc)
- Significant use as pure inert gas for O2-free manufacturing (welding, semiconductor, etc)
- Minor use for party balloons and other LTA apps
- Lab analysis use just 5% of the total

Use in medical imaging and semiconductor industries now driving increased global demand

Helium- Shortages

Increasing demand and unreliable supply has created 3 distinct global shortage events in ~ 2005, ~2012, and ~2018 (Helium 3.0), typically lasting 1-2 years each.

Each event has had adverse impact on environmental laboratory operations, including supply shortfalls and price increases.



Helium- Future Shortages?

Helium 3.0 ended due to Covid pandemic as demand softened temporarily.

A variety of new sources are projected to come on line in the next 10 years.

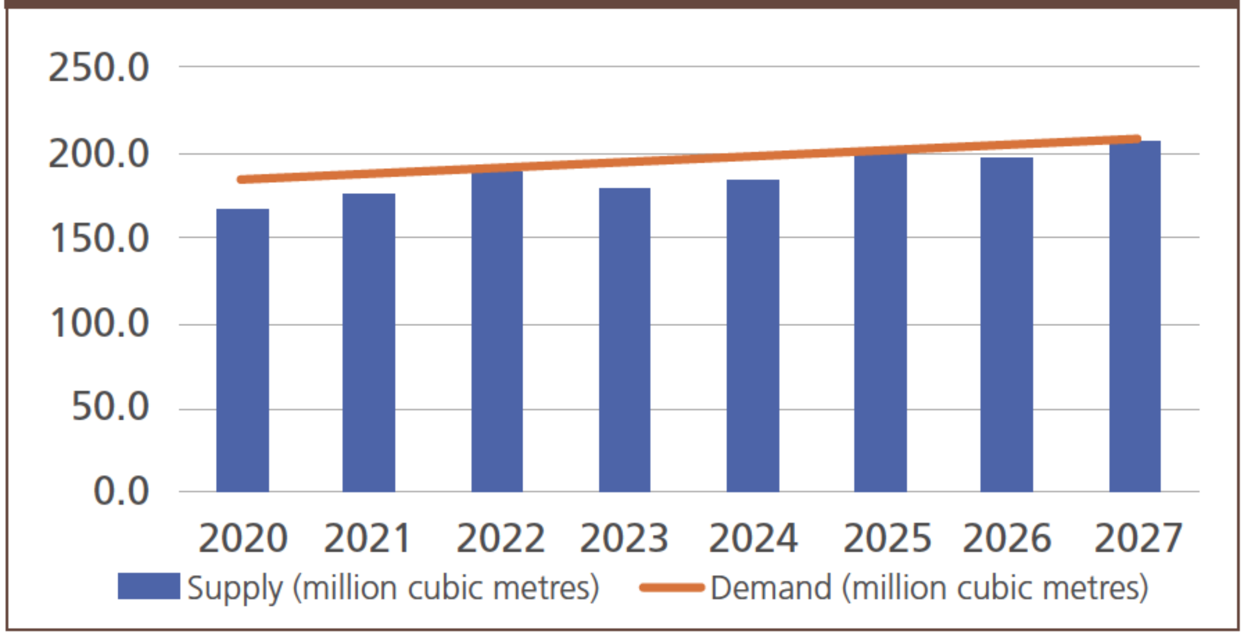
Supply vulnerabilities will exist for several more years; shortages may recur.

Prices are NOT expected to decline.

Environmental lab sector too small to impact overall dynamics.

Conservation in other industries will help.

Figure 3: Helium supply and demand projections 2020–2027 (U.S. Geological Survey, Mineral Commodity Summaries, February 2019, data correct as of 2018) (data adapted from reference 10).

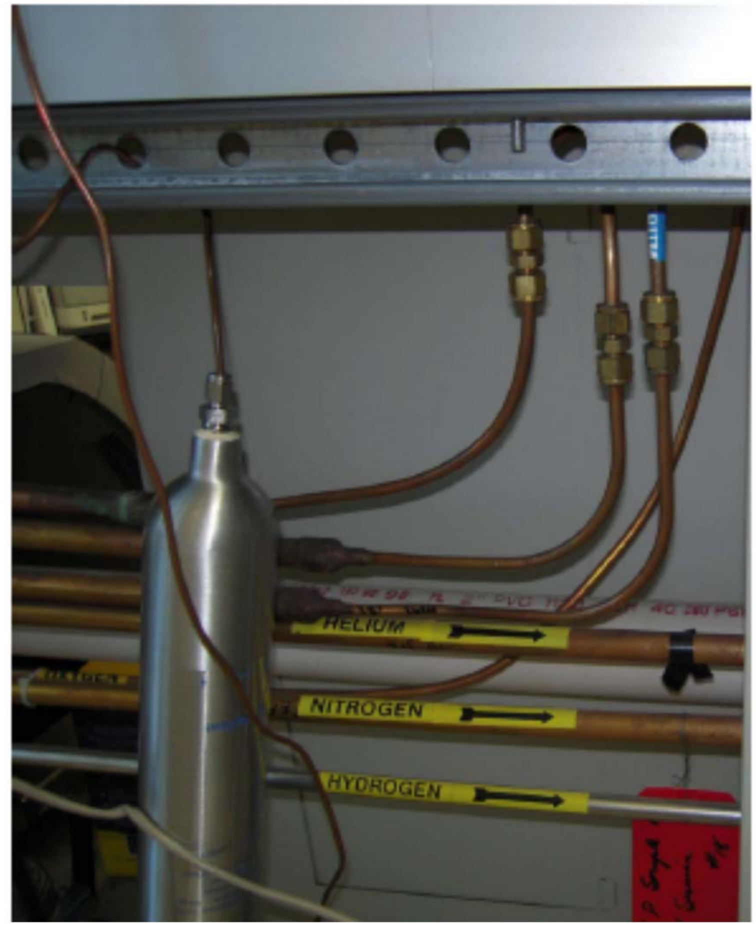


(Chromatography Online)

Laboratory Management Practices

4 simple strategies

1) Assess, review and monitor supply chain and usage.
2) Convert to alternative gases.
3) Implement conservation best practices.
4) Select best available delivery and cost options- go shopping!



Laboratory Management Practices



Supply chain and usage

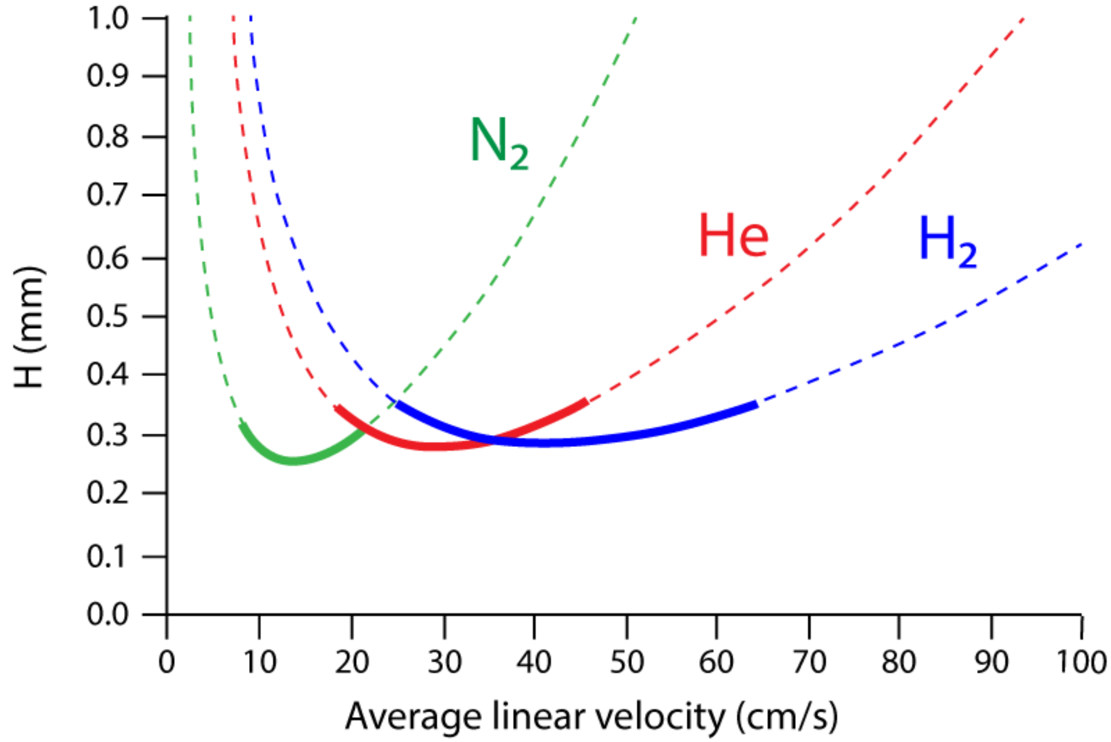
1) Map entire lab, noting all manifolds, valves, unions, caps, and points of use.
2) Determine historical and current usage and refill rates.
3) Calculate expected He consumption for all points of use and compare to actual usage.
4) Perform comprehensive leak checks periodically.
   1. At least annually and when usage anomalies noted.
   2. Not uncommon for leaks to account for 10-20% of total usage.
5) Verify vendor deliveries (full pressure/volume) vs billing.

Convert to alternative gas

When EPA methods were written, Helium was inert, safe, inexpensive and delivered necessary chromatographic performance, and thus became the preferred carrier and purge gas for many GC and GC/MS methods.

But alternatives are possible, most notably H2 and N2.

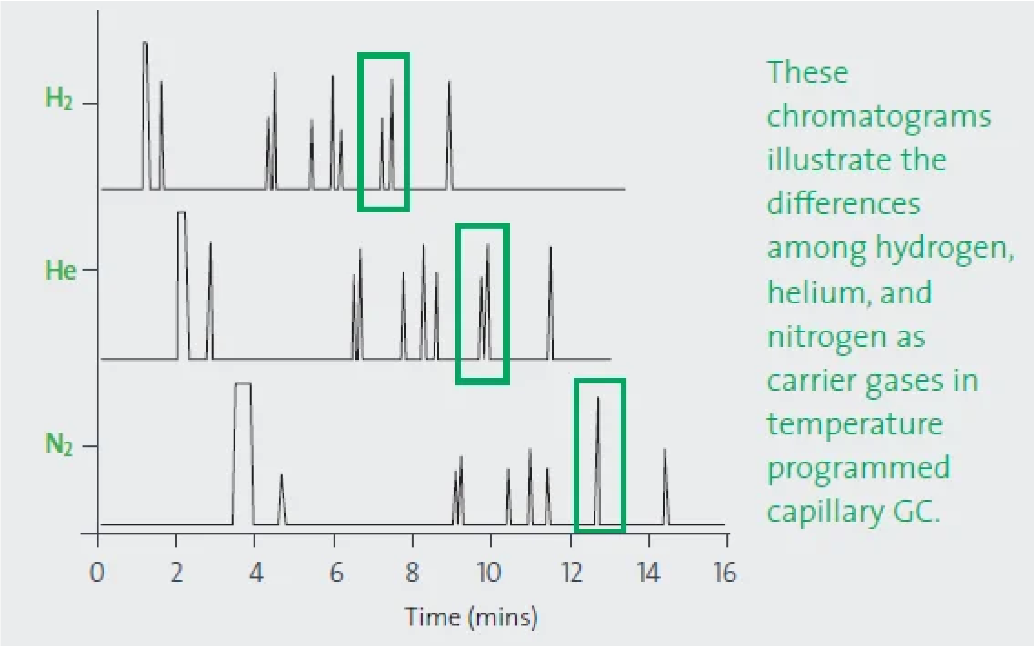
Van Deemter plot- H2 > He > N2



(Chromatography Online)

Alternative gas pros and cons

Chromatography	**H2 > He > N2**
Inertness	**He > N2 > H2**
Availability	**N2 > H2 > He**
Safety	**N2 > He > H2**
MS Ionization	**H2 ~ He > N2**
Purge Efficiency	**He > N2**



(AZoM)

Managing Your Helium Supply- H2 for MS?

Compound Name	Calibration Results							Precision and Accuracy Results (n=10)					
	Hydrogen Carrier				Helium Carrier			Hydrogen Carrier			Helium Carrier		
	Mean RRF	RSD (%)	r	R^2	Mean RRF	RSD (%)	r	Spike (µg/mL)	Mean Rec (%)	RSD (%)	Spike (µg/mL)	Mean Rec (%)	RSD (%)
Compounds with severe deviation in mean response factor or calibration linearity with hydrogen carrier gas – no mass spectral anomalies observed													
2-Nitrophenol	0.04	20	0.995	0.995	0.17	18	0.999	2.0	113	9	2.0	86	4
2-Nitroaniline	0.06	19	0.994	0.998	0.57	23	0.999	2.0	99	20	2.0	77	4
Dimethyl phthalate	0.41	38	0.979	0.998	1.22	6		2.0	101	5	2.0	99	3
2,6-Dinitrotoluene	0.06	40	0.987	0.996	0.25	12		2.0	78	23	2.0	85	4
3-Nitroaniline	0.07	34	0.987	0.996	0.75	17	0.998	2.0	83	14	2.0	64	4
2,4-Dinitrophenol	0.02	36	0.976	0.987	0.12	27	0.997	10	122	11	2.0	48	8
4-Nitrophenol	0.03	28	0.993	0.998	0.34	25	0.998	10	104	18	2.0	45	8
2,4-Dinitrotoluene	0.05	28	0.987	0.997	0.29	15		2.0	75	21	2.0	78	7
Diethyl phthalate	0.38	35	0.972	0.996	1.24	8		2.0	107	5	2.0	98	1
4-Nitroaniline	0.06	18	0.991	0.996	0.35	23	0.999	5.0	70	21	2.0	65	6
2-Methyl-4,6-dinitrophenol	0.03	30	0.987	0.997	0.11	27	0.999	5.0	90	7	2.0	58	10
Di-n-butyl phthalate	0.25	42	0.965	0.999	1.34	7		2.0	107	8	2.0	83	1
Butylbenzyl phthalate	0.11	50	0.994	0.996	0.59	16	0.999	2.0	106	6	2.0	78	3
3,3'-Dichlorobenzidine	0.07	25	0.981	0.999	0.39	13		2.0	109	11	2.0	90	2
Bis(2-ethylhexyl) phthalate	0.14	15			0.83	17	0.999	2.0	125	10	2.0	79	3
Di-n-octyl phthalate	0.43	14			1.53	16	0.999	2.0	131	10	2.0	67	3
Compounds with severe deviation in mean response factor or calibration linearity with hydrogen carrier gas –mass spectral anomalies observed													
Nitrobenzene	0.08	56	0.996	0.996	0.48	10		2.0	97	11	2.0	101	2

(https://www.restek.com/globalassets/images/blog/2013-shimazu-restek-gcms-1303.pdf)

Laboratory Management Practices

Alternative gas conclusions

Modern H_2 generators and GCs address many of the safety and cleanliness issues of H_2, making its use suitable for a broad range of GC methods.

Poor GC and MS source performance make N_2 unsuitable for most GC & GC/MS carrier gas applications, but it can be used as a purge gas in MS VOA applications and carrier gas for methods not dependent on optimal GC resolution (TPH).

H_2 reactivity makes it unsuitable for most MS applications- H2 possible in the future. No viable alternative to He for GC/MS at this juncture.

Conservation best practices

- Turn idle instruments off.
- Fully leverage GC configuration options.
    - 'Gas saver'
    - 'Sleep/wake' modes
    - Split settings/makeup gas
    - Up to 90% savings possible

https://www.agilent.com/cs/library/slidepresentation/Public/GC-GCMS_Users_Meeting_Reducing_Pressure_on_He.pdf

GC Flow Conditions

He Carrier Flow (mL/min):	1.2
He Split flow (mL/min):	50
Gas Saver Flow (mL/min):	20
Gas Saver On (min):	2
Run Time(min.):	20
Gas Volume in Cylinder (L):	8000
Runs per Day:	20

Laboratory Management Case Study



Medium-large Lab S with both conventional and specialty GC and GC/MS. Start with comprehensive mapping and assessment via checklists and spreadsheets

Lab Helium Self-assessment Checklist

- ☐ Map He gas supply lines from source tank(s) to each termination. (Use attached tracking sheet).
- ☐ Create a list of all instrumentation that is supplied with He
- ☐ All fittings leak checked
- ☐ Tank fittings
- ☐ Branch fittings
- ☐ Line valves
- ☐ Instrument connections
- ☐ Instrument internal connections (where accessible)
- ☐ AS valves checked (where accessible)
- ☐ EPC connections checked
- ☐ Inlet weldments checked
- ☐ Line terminations checked
- ☐ Equipment He needs assessed (i.e., can it use H2 of N2?)
- ☐ Gas saver mode on all He instruments
- ☐ Low flow standby methods active on all He instruments
- ☐ P&T converted to N2
- ☐ GC SVOA converted to H2 or N2
- ☐ GC VOA converted to alternate gas (H2 N2 other)
- ☐ Out-of-service instruments shut off and disconnected
- ☐ VOA rinse water reservoirs on N2

Equipment ID	Room	He required?	System Leak Checked?	~ He Usage (ml/min)	Gas Saver active? (Y, N, NA)	Action
GCMSVOA1	VOA	Yes	Yes	20	No	Activate Gas Saver
VOA1 P&T	VOA	No	Yes	40	NA	Convert to N2
Water Res	VOA	No	Yes	<1	NA	Convert to N2
GCMS SVOA 1	SVOA	Yes	Yes	20	Yes	
PCB GC1	SVOA	No	Yes	20	No	Convert to H2
Pest GC1	SVOA	No	Yes	20	No	Convert to H2
Dead leg	SVOA	NA	Yes	0	NA	

Laboratory Management Case Study

At the start of 2019, Lab S was using ~ 205,000 cubic feet of He annually for 32 GC and GC/MS instruments, at cost of ~ $130,000/yr.

- Usage exceeded 1 cyl/mo/inst ROT
- 923 supply line connections checked.
    - 17 minor leaks, 2 major leaks
- 2 GC/ECDs converted to H_2
- 1 GC/FID converted to N_2
- 3 GC/MS VOA converted to N_2 purge
- 3 idle GC/MS systems deactivated
- 18 GC and GC/MS systems fully optimized for He conservation (gas saver, etc)

Laboratory Management Case Study

At the end of 2019, Lab S was using ~ 105,000 cubic feet of He annually for 29 GC and GC/MS instruments, at cost of ~ $66,000/yr. 48% reduction in usage & cost.

Next step is conversion to alternative vendor and supply method (tube trailer in lieu of conventional high pressure cylinders) for an additional 20% cost reduction, in Q4 2021

(Matheson)

Managing Your Helium Supply- What next?

- Expect disruptions and high cost. He supply is complex, dynamic, and vulnerable.

- Continuous reduction in usage (and cost) is still possible
  - Reduction is not difficult
  - Requires management effort
  - Requires staff awareness

- H2 needs to be a viable option for GC/MS methods.
  - Evaluate hardware upgrade costs.
  - Work with clients to accept H2-specific data quality objectives.

(Oklahoma gas well fire, CNN)