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CAN HYDROGEN GAS GENERATORS REPLACE HELIUM FOR GAS CHROMATOGRAPHY?

OVERCOMING THE OBSTACLES, REAPING THE BENEFITS

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1. Overview

In the face of recurring global helium gas shortages, scientific, medical, industrial, and consumer activities that rely on helium gas have felt the impact. Helium users are facing rising prices, supply chain interruptions, and in some cases, have had to shut-down operations.

With gas chromatography (GC) applications representing only about 1% of global helium use, the GC industry does not wield much market power to secure its helium supply. GC users are sometimes finding themselves at the end of the line compared to major helium applications such as life-saving Magnetic Resonance Imaging (MRI), use as a lifting gas (17%), welding (9%), leak detection, and semiconductor manufacturing (at 5% each), and others.¹

To address these shortages, GC laboratories have begun looking at possible replacement gases and new approaches to help obtain the carrier gases needed to continue their work. One of the most promising options is using the use of gas generators to provide a steady supply of hydrogen gas as a replacement for helium. Although some concerns—and some myths—persist about using hydrogen, it offers multiple benefits and advantages over helium, notably particularly when a gas generator replaces high-pressure gas cylinders.

The safety, convenience, availability, purity, analysis run times, and low cost of hydrogen gas generators can provide an excellent solution for many GC facilities and applications.

In this white paper, we will:

- Outline the challenges of today's helium market and helium's importance for multiple applications, including GC
- Assess the various options to help alleviate helium shortages, such as using replacement gases
- Discuss hydrogen's suitability as a replacement gas, and look at benefits and drawbacks for GC users
- Address the myths around using hydrogen gas in a lab setting, and compare high-pressure gas cyclinders vs. gas generators
- Describe how hydrogen gas generators can be an effective solution to supply GC carrier gas
- Look at key considerations to help you determine if hydrogen gas generation is a good fit for your GC needs, from the standpoint of cost/ROI, convenience, reliability, and sustainability.

¹ <u>Mineral Commodity Summaries 2020</u>. U.S. Geological Survey: Reston Virginia, 2020. DOI 10.3133/mcs2020



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2. The Problem

Helium is an abundant element in the Universe, but it is comparatively rare on Earth. Here, helium is found primarily in underground deposits combined with various other elements. It is an inert gas released over hundreds of millions of years from radioactive elements like thorium and uranium decay.

About 95% of the world's helium supply is currently obtained as part of natural gas processing or liquefied natural gas production.² As natural gas is extracted, it is distilled (fractionalized) and processed through several steps to separate its various components such as nitrogen, methane, and helium.

As a byproduct of natural gas extraction, most of the cost of helium production, including exploration, drilling, and distilling, has been covered by the hydrocarbon industry. There are some underground gas deposits with high helium concentrations but low quantities of hydrocarbon, thus, the cost of extracting helium from these sources has not been economical to date³.

Name	Helium	
Symbol	Не	
Atomic Number	2	
Category	noble gas	
Atomic Weight (kg)	4.002602 (6.68 x 10 ⁻²⁷)	
Atomic Radius (van der Waals)	140 pm	
Electron Configuration	1s ²	
Crystal Structure	close-packed hexagonal	
Physical State at 20°C	gas	
Melting Point	-270°C	
Boiling Point	-269°C	
Specific Gravity	0.138	
Density (g/cm³)	0.000164	
Characteristics	colorless, odorless, non-flammable, inert	
Discovered	1868	

Note: Helium is the second most abundant element in the Universe (23% by volume) and the second lightest (after hydrogen).

Today, the world uses roughly 6.2 billion cubic feet of helium each year⁴, and demand continues to rise. But current usage practices are unsustainable: experts project significant helium supply limitations before the end of this century⁵ unless we undertake new efforts at recycling and develop new supply sources.

2.1. Recurring Helium Shortages & Market Instability

Since 1929, the U.S. has been the world's largest producer of helium.⁶ For decades, the National Helium Reserve (NHR) stored and managed the supply and set prices, with the Bureau of Mines coordinating

² Kornbluth, P., "<u>Helium start-up activity at unprecedented levels.</u>" Gasworld.com, June, 10, 2021. (Accessed September 25, 2021) ³ *Ibid.*

⁴ Greshko, M., "<u>We Discovered Helium 150 Years Ago. Are We Running Out?</u>" National Geographic, August 27, 2018.

⁵ Olafsdottir, A. and Sverdrup, H. "Assessing the Past and Future Sustainability of Global Helium Resources, Extraction, Supply and Use, Using the

Integrated Assessment Model WORLD7." Biophysical Economics and Sustainability Vol 5(6). May 19, 2020. doi 10.1007/s41247-020-00072-5

⁶ "Connor, E., "Helium shortage 2.0 and the alternatives for gas chromatography." SelectScience, Editorial Article August 6, 2021



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extraction and refining programs. It was seen as a strategically important resource for military and defense during both World Wars, during the Cold War, and for the NASA space programs through much of the twentieth century.

Since the 1990s, privatizing helium production and storage led to the ongoing auctioning of the NHR supply, with a final sale set to occur at the end of 2021. As the U.S. hydrocarbon industry has migrated from wells to fracking to extract natural gas, helium is no longer a byproduct. At the same time, countries such as Qatar and Algeria have developed their natural gas and helium production industries (**Figure 1**).

These industry shifts and other market forces have led to several recent periods of helium shortage. The first notable



Figure 1: Construction is underway on South Africa's first liquid helium processing plant, making the country the eighth in the world to produce helium. Image: <u>Regenergen</u>

shortage occurred in 2005-2007, and another in 2011-2013 due to worldwide refinery failures and shutdowns combined with increasing demand from China and other developing nations. Another shortage occurred from 2017 to mid-2020 as Qatar came under a Saudi blockade, producers restricted supply in many regions, and prices increased.

Since then, "the COVID-19 pandemic has further exacerbated issues for labs as global supply chains have been further affected, and supply of oxygen to the medical sector became paramount for gas suppliers. Uncertainty surrounding supply is likely to remain for some time.⁷" Industry experts remain divided about what the future holds, with some predicting continuing periods of worldwide shortages and others remaining optimistic about stabilization in the supply chain.

2.2. Current Supply Outlook

Seeing an opportunity in what has become a volatile market, companies in countries such as Russia, Canada, and Tanzania are looking into the exploration and development of helium processing capabilities (**Figure 1**). For example, relative newcomer Gazprom, the Russian state-owned company, has rapidly become the largest supplier of natural gas to European markets.



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Excavating new production sources can be expensive and time-consuming, however. The lower the concentration of helium in a gas mix, the less efficient and more costly it is to remove, so, not every deposit is a viable source of commercial helium.⁸

Thus far, helium production is still tied to the extraction of natural gas. To uncouple helium and establish more independent production, a new category of helium entrepreneurs is investing in various technologies that could hold promise.⁹ The market is seeing a wave of new helium ventures, although many are still in the early stages and nowhere close to active production.

Relying solely on accessing more underground helium deposits as the answer to solve any future shortages is risky. Even if global deposits hold enough helium theoretically to ensure supply through the end of the 21st century, costs—and therefore prices—are likely to continue rising. Available economic modeling forecasts helium price, currently around US\$15/ton, will reach \$20/ton by the end of this millennium and \$40/ton by 2230.¹⁰

Future shortages and price increases will fall especially hard on "minor" market segments such as GC that do not have much bargaining power. If periods of helium rationing occur, GC would likely be deprioritized in favor of essential medical and other uses.

2.3. Applications at Risk

With applications ranging from medicine to space exploration, helium price, and supply fluctuations can threaten many important human activities (**Figure 2** on page 7). For example:

- **Medicine** Helium is used as a coolant in magnetic resonance imaging (MRI) and nuclear magnetic resonance imaging machines, important diagnostic tools for non-invasive scans to detect cancer and other organ and tissue damage. Helium also helps with certain lung/respiratory treatments.
- Weather Prediction Helium helps weather balloons reach the stratosphere, where they collect valuable temperature, humidity, air pressure, and wind speed data that are used by meteorologists for forecasting and research.
- **Physics** As with MRI machines in medicine, helium helps cool the magnets used in other applications. For example, physicists at the forefront of atomic research use particle accelerators that rely on helium to operate superconducting magnets.
- **Computers & Networking** Superconducting bits are also essential to advanced quantum computers currently under development. Similarly, helium helps cool and protect the fragile fiber optic cables that connect internet users around the globe.
- **Maintenance** Helium is useful for detecting leaks in the hull of ships, in HVAC systems, and as a tracer gas for leak detection in many vacuum-sealed systems.

⁸ Witsill, F., "Global helium shortage is a growing threat to graduation parties and scientific research." Detroit Free Press, May 8, 2019.

 ⁹ Brumfiel, J., "<u>The World is Constantly Running Out of Helium. Here's Why It Matters.</u>" National Public Radio, Short Wave, November 8, 2019. ¹⁰
¹⁰ Olafsdottir, A. and Sverdrup, H. "Assessing the Past and Future Sustainability of Global Helium Resources, Extraction, Supply and Use, Using the Integrated Assessment Model WORLD7." *Biophysical Economics and Sustainability* Vol 5(6). May 19, 2020. <u>doi 10.1007/s41247-020-00072-5</u>



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- **Space Exploration** Helium is used to pressurize the fuel tanks of liquid-fueled rockets. It's also important for satellite instruments and in the aerospace industry for supersonic wind tunnels.
- **Consumer Applications** While party balloons are probably the most widely known use of helium outside of industrial and scientific circles, they represent only about 15% of global helium usage annually.¹¹ Additionally, helium-neon gas lasers are used for scanning barcodes at grocery store check stands.

With its extremely low boiling point, helium in the liquid state is the world's best coolant. Its small molecule size also makes it particularly useful for certain types of leak detection. Due to these and other physical properties of helium, there are some applications where there is no substitute. For these users, a reliable supply of the gas is "mission critical."

2.4. Helium for Gas Chromatography

GC applications fall under the "analysis & laboratory" market segment (shown in **Figure 2** on page 7), but they represent only about 1% of the global helium users. Historically, most gas chromatography labs have used helium as a carrier gas, with hydrogen, nitrogen, and argon also sometimes used.

In a laboratory environment, a carrier gas transports a sample to be analyzed (analyte) through a column into a detector, where the sample is then analyzed. For GC, two important considerations for selecting a carrier gas include speed and purity. As carrier gas constantly flows into the detector, high-purity gas of at least 99.995% needs to be used to reduce baseline noise that could obscure separation analysis results.

Helium offers the advantages of safety (non-reactive, non-combustible) with a relatively wide optimum linear velocity range, providing a moderate analysis speed. Other gases could be used for many GC applications, but for decades the low price, satisfactory performance, and accessibility of helium dampened interest in alternative solutions.

¹¹ "<u>Are Balloons Using Up All the Helium?</u>" BalloonFacts.org (Retrieved October 29, 2021).



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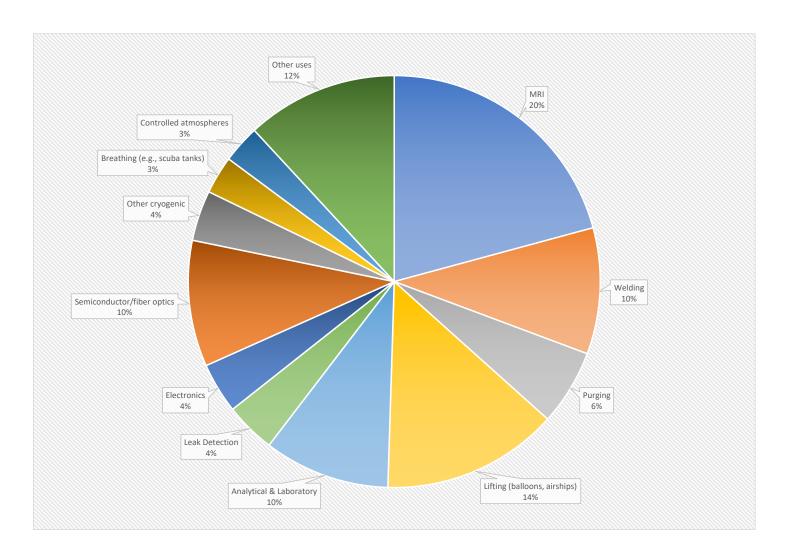


Figure 2: Uses of helium by application. Gas chromatography is one small part of the "Analysis & Laboratory" segment, which accounts for just about 1% of the total helium market. (Note: Percentages shown are approximate, representing the 2019-2020 period. They do not total 100% due to rounding and compiling data from multiple sources, including USGS Mineral Commodity Summaries, Edison, and others).



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3. Potential Helium Supply Options

Simply increasing the extraction and processing of helium is not a perfect solution to address global supply needs, other options need to be considered, including recovery and recycling or using replacement gases for applications where that is feasible. For GC, gases such as nitrogen, hydrogen, and argon are possible replacements. These various options are discussed below.

3.1. Helium Recovery and Recycling

Recycling helium might sound like a straightforward solution to current and future shortages, but it is not so simple. Currently, only a tiny percentage of helium is recaptured and recycled. The largest barrier to recycling is the cost, which can be prohibitive for smaller users. The up-front capital investment starts at around US\$100K for even a small lab facility to implement recycling, and often costs several million dollars for larger facilities.

As a result, recycling tends to be found only in industry settings, large universities, and national labs."¹² For a hospital with a US\$1-3 million MRI system whose magnetic coils can be severely damaged ("quenched") by any interruption in helium supercooling, the investment in helium recycling infrastructure might make sense. Some experts suggest that any facilities using more than 30,000 liters of helium per year should consider installing small-scale helium reliquifiers.

A typical GC application might use as much as 150 cubic feet of helium per year¹³ (if running 24 x 7 x 365), equivalent to around one cylinder per month. For large MRI facilities, recycling might be an economically viable option, but the costs of recycling (plus the space, labor, and cost requirements to install, use, and maintain recycling equipment) is still out of reach for GC operators.

3.2. Replacement Gas Considerations

The availability and low price of helium for decades made it the default carrier gas for a majority of GC applications. But the more recent market and supply volatility has forced GC users to look at other gases as a replacement option. Hydrogen, nitrogen, and argon are all potential options for carrier gas and detector gas, depending on the application and specific user requirements.

Nitrogen (N_2) – some users are looking at nitrogen as a replacement makeup gas. It is readily available (nitrogen comprises 79.1% of Earth's atmosphere), relatively inexpensive, and inert. Two nitrogen atoms make up the molecule (N_2) , giving it similar properties to a noble gas.

For Flame Ionization Detector (FID) gas chromatography applications, nitrogen improves the shape of the flame, which enhances the sensitivity of the analysis. However, nitrogen must be used at slower flow rates to achieve adequate resolution between peaks. Its disadvantages include a narrow optimum linear velocity range and a low optimum linear velocity that requires more analysis time.

¹² "Helium should be recycled." *Nature* 547, 6. July 6, 2017. DOI: <u>10.1038/547006a</u>

¹³ Kandle, F., and Bartram, R., "Choosing Conversation Over Conversion: The Great Helium Debate." American Laboratory, May 23, 2013.



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Argon (Ar) – is the third most common gas in the atmosphere after nitrogen and oxygen, although it makes up less than one percent of the atmosphere (roughly 0.9%). It is a noble gas and completely inert, nonreactive with every other substance. Commercially, it is produced only as a byproduct of industrial air separation, thus supply is limited, and the cost is comparatively high.

Argon has a relatively high density so it can be effective for purging applications. It also offers good performance for arc welding and window insulation where its low thermal conductivity is an advantage. It has been used to replace helium as a coolant for photovoltaic panels, for example. But in most GC applications it is typically less ideal than the alternatives.

Hydrogen (H_2) – Hydrogen offers multiple advantages for gas chromatography. It has a higher optimal linear velocity and can be operated at higher flow rates. Analytes elute earlier with hydrogen than with helium, which speeds up analysis times, thus increasing sample throughput while still maintaining high sample quality.

Name	Hydrogen	
Symbol	Н	
Atomic Number	1	
Category	diatomic non-metal	
Atomic Weight (kg)	1.007829	
Atomic Radius (van der Waals)	120 pm	
Electron Configuration	1s ²	
Crystal Structure	hexagonal	
Physical State at 20°C	gas	
Melting Point (H ₂)	-259.16°C	
Boiling Point (H ₂)	-252.897°C	
Specific Gravity	0.0696	
Density (g/cm³)	0.000082	
Characteristics	colorless, odorless, high velocity and heat con- ductivity, flammable	
Discovered	1766	

Note: Hydrogen is the most abundant element in the universe (75% by volume) and the lightest.

On the downside, hydrogen does pose a fire and explosion risk if mishandled. The risks can be easily mitigated, however. The potential downside of hydrogen is a slightly increased risk: it is a flammable gas that requires some precautions to ensure safe use.

Hydrogen's lower explosive limit (LEL) is 4.1% concentration in air. Because of its lightness, hydrogen rises and dissipates quickly. Even in a small laboratory, the large volume of air compared to the relatively low rate of helium production or consumption during typical GC analysis means the danger of reaching the LEL is quite low. Installation of hydrogen gas detectors can further mitigate the risk.

3.3. Comparing Helium and Hydrogen for GC

For many applications, using hydrogen in place of helium is a viable solution. The two gases are equally compatible with the range of materials used for GC equipment and supplies, including both metals (aluminum, brass, copper, and stainless steel) and polymers/plastics (e.g., PA, PTFE, PCTFE, PVDF, and PFA).



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Hydrogen can improve GC throughput and results: it provides a faster elution and analysis time than helium and generates sharper peak shapes. Adapting current GC methods to hydrogen carrier gas may require some adjustment of elution temperatures. "For those researchers who value time and increased sensitivity, hydrogen is a smart alternative. Further, given that helium is a limited resource and much more expensive than hydrogen, many labs are switching to hydrogen carrier gas."¹⁴

While helium can only be obtained by purchasing gas canisters from a supplier, hydrogen can be easily produced onsite at a laboratory facility in virtually unlimited supply. Hydrogen is industrially produced from the steam reforming of natural gas. Using a gas generator, high-purity hydrogen can also be produced by simple electrolysis of deionized water, per the formula: $2H_2O \rightarrow 2H_2 + O_2$

	HELIUM	HYDROGEN
Atomic Number	2, noble gas	1, non-metal
Reactivity	Inert	Reactive
Toxicity	Non-toxic	Non-toxic
Properties	Lowest boiling point: 268.9°C Liquid at ultra-cool temperature	Low atomic mass: 1.007825 g.mol-1 Low boiling point (l/c): -252.8°C
Molecule Size	0.118 nm (van der Waals radius)	0.12 nm (van der Waals radius)
Thermal Conductivity (W/m K)	0.146	0.161
Viscosity (µPa s)	18.6	8.4
Density (kg/m³)	0.169	0.0852
Reactivity	Very inert, will not react with analytes	Reactive under some circumstances
Flammability	Non-flammable	Can form explosive mixture with air at >4% concentration
Sustainable	Non-replenishable resource	Easily generated from deionized water
Separation Time	Time-efficient separations	Mose time-efficient separations
Cost	Increasingly costly	Affordable, especially via in-house gas generator
Supply Mode	High-pressure gas cylinders	High-pressure gas cylinders or gas generators

Comparing Helium and Hydrogen Characteristics and Suitability for GC Applications¹⁵

 ¹⁴ "<u>Hydrogen vs. Helium for Gas Chromatography.</u>" Infographic published in Taking Care of Business, Lab Manager vol. 14, no. 1, February, 2019.
¹⁵ Ibid.



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There are a few limitations, however; hydrogen gas is not a one-size-fits-all solution. There are some applications that require helium, thus substituting hydrogen or another gas is not possible. For example, in cryogenic applications, or with a helium ionisation detector (HID), which is "a very specific type of detector that can analyse volatile inorganics in very low ppm levels and it relies on the specific properties of helium to function. Hydrogen also cannot be used when analysing unsaturated or aromatic hydrocarbon solvents, because it is a reactive gas that could possibly hydrogenate these samples and thereby distort the analytical results."¹⁶

Hydrogen does make a suitable carrier gas with most detector types: Thermo Conductivity Detector (TCD), Flame Ionisation Detector (FID), Flame Photometric Detector (FPD), Photo Ionisation Detector (PID). Hydrogen can also replace helium for Mass Selective Detector (MSD) in some cases with careful adaptation. The only hydrogen replacement exception is with a Discharge Ionisation Detector, which requires helium as the carrier gas.

3.4. Van Deemter Curves

The van Deemter curve function is useful to compare the carrier efficiencies of different gases. Band broadening, or separation, refers to when molecules spread out within a chromatography column, enabling analysis. The van Deemter curve is based on an equation for a hyperbolic function that shows the point where peak separation occurs. The use of different carrier gases can affect the separation time due to their velocity.

The curve (**Figure 3** on page 12) plots plate height (H) compared to the linear velocity of the gases. Hydrogen can be used at a higher flow rate than either helium or nitrogen—its viscosity increases more slowly with temperature—thus has higher velocities. A higher linear velocity reduces sample throughput time (**Figure 4** on page 13), increasing the efficiency of laboratory operations.

¹⁶ Stephen Harrison, Global Head of Specialty Gases and Specialty Equipment, Linde, as quoted in "Hot Topic: Helium: Economising world usage." *Gasworld* (Gasworld.com), Issue 96, May 1, 2013.



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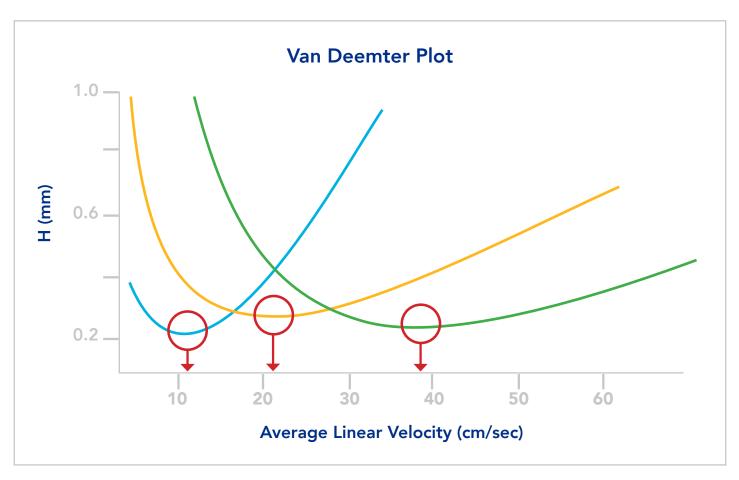


Figure 3: Using hydrogen as the carrier gas allows efficient separations to be obtained in half the time compared to using helium.

3.5. Chromatogram Results

A chromatogram is one output of the gas chromatography process. It is a two-dimensional plot of all of the components of the compound being tested and the respective concentrations of each in the mixture. The peaks on the graph show concentration of individual elements and having some distance between the peaks shows that components were effectively separated during analysis, required for the most accurate measurement. Ideally, a carrier gas helps ensure that chromatogram results have narrow peaks and clear separation. Using hydrogen as a carrier gas has shown excellent chromatogram results (**Figure 4** on page 13).

¹⁶ Stephen Harrison, Global Head of Specialty Gases and Specialty Equipment, Linde, as quoted in "Hot Topic: Helium: Economising world usage." *Gasworld* (Gasworld.com), Issue 96, May 1, 2013.



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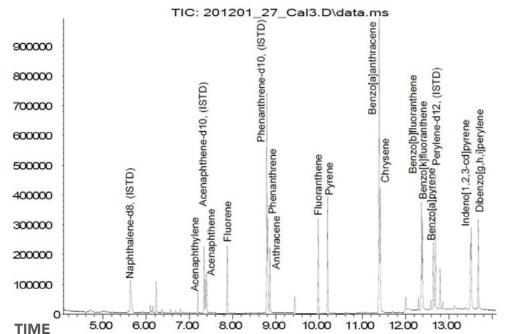
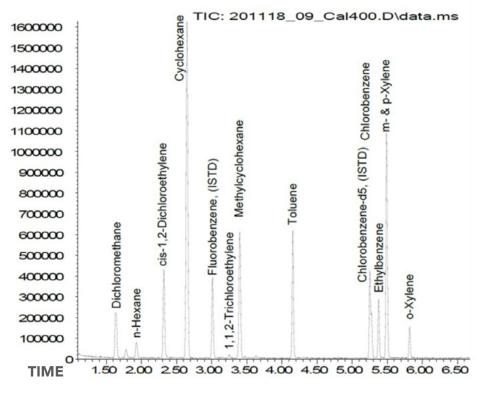


Figure 4: Using hydrogen as a carrier gas yields good GC results, with strong peaks and clear peak separation evident in the chromatograms. Top: analysis example of polycyclic aromatic hydrocarbons (PAHs) in water.¹⁷ Bottom: analysis example of residual solvents and organic volatile impurities (OVIs) in pharmacueticals.¹⁸

ABUNDANCE



¹⁷ Turner, D., Stokes, R., and Morgan, G., "Evaluation of hydrogen as a carrier gas in the analysis of polyaromatic hydrocarbons in water by liquid/liquid extraction – large volume injection – gas chromatographjy – masspectrometry (LLE-LVI=GC-MS). White paper published by VICI AG International, DATE.

¹⁸ Turner, D., Stokes, R., and Morgan, G., "Evaluation of hydrogen as a carrier gas in the analysis of residual solvents in pharmaceuticals by HS_GS-MS. White paper published by VICI AG International, DATE.



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4. The Solution: Hydrogen Gas Generators

For a variety of reasons, transitioning to using hydrogen gas can be an excellent solution for GC laboratories. The Van Deemter curves illustrate the wide range over which high efficiency is obtained, making hydrogen the best carrier gas for samples containing compounds that elute over a wide temperature range. In particular, hydrogen gas generators offer all of the benefits of hydrogen with added safety, convenience, and cost advantages, discussed below.

4.1. Generators vs. High-Pressure Cylinders

One disadvantage of helium is that it is only available in high-pressure cylinders, which presents the safety risks inherent in any gas that is contained under pressure should the cylinders become overheated or punctured. Even inert gases such as helium and nitrogen can explode under pressure when exposed to heat.

Cylinders are inconvenient to store and move. It is also necessary for users to monitor the amount of gas in the cylinder to ensure empty cylinders are replaced in time to avoid interrupting analysis or other helium-dependent operations. Hydrogen gas generators can provide a continuous supply of gas without interruption.

Additionally, using gas canisters can often require long tubing lines with hookups at the end of lab benches or even in another room (**Figure 5**). These long lines mean a larger volume of gas under pressure, with the



Figure 5: Typical high-pressure gas cylinders of nitrogen, helium, and oxygen (air zero) with gas pressure meters and regulators attached to piping lines that lead into a chemistry laboratory.

attendant risks of a leak or line break that vents gas into the lab. Venting wastes expensive gas, and risks ruining analysis or breaking columns in the GC oven.

By contrast, gas generators are small and can be placed close to GC systems, requiring minimal length of tubing. They produce and store only a small volume of gas (typically less than 1 liter at a time)¹⁹ and have automatic sensors and shut-off valves to prevent leaks.

Converting to a hydrogen gas generator for GC carrier gas confers multiple benefits and advantages in terms of:

• Safety

Convenience

- Availability
 - Purity

- Faster Analysis Times
- Lower Cost

¹⁹ "Connor, E., "Helium shortage 2.0 and the alternatives for gas chromatography." SelectScience, Editorial Article August 6, 2021.



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4.2. Safety

Gas generators present a much safer option than using high-pressure cylinders. Even when hydrogen gas is used, the safety benefits are significant, and the risks are much lower than they have often been portrayed. First, using gas generators eliminates the risk of personnel injuries that can occur while lifting or moving heavy gas canisters, or if a canister is dropped.

The risk of leak, fire, or explosion is also much lower with a generator than with high-pressure gas cylinders. When working with cylinders, laboratory staff must be alert for any signs of leaks or damage on the cylinder or tubing. Having a large volume of high-pressure gas on the premises introduces a constant state of risk.

With a hydrogen generator, however, labs can minimize these risks by generating only the amount of hydrogen gas required at one time and storing only small volumes. A cylinder typically contains 8,000 liters of gas under pressure. Hydrogen generators generally store <50 mL, dramatically reducing the potential harm in the unlikely event of a leak.

The flow of hydrogen from the generator is carefully controlled: typically, the maximum flow is approximately 500 mL/min, which is well below the 2 L/min of flow required to reach the LEL for hydrogen in the air when it is released in an average GC oven. To further reduce any risks, gas generators are also equipped with built-in leak sensors and automatic shut-off features.

Safety can be further improved by using flow-controlled analysis. Using hydrogen for flow-controlled operation means only the volume of gas in the inlet and column can be released; the worst that can happen is the fused silica capillary column breaks at the injection port.

The instrument's Electronic Pressure Control (EPC) in the inlet will sense any leakage problem and will automatically switch to standby mode. Additional safety steps can include choice of different types of columns or placing a hydrogen sensor in the GC oven.

4.3. Convenience

Using helium canisters means inconvenient interruptions in GC analysis every time a canister empties and needs to be replaced. Canisters require personnel time and labor for purchasing, receiving, transferring, inventorying, monitoring usage, and switching out used canisters. Finally, canisters are also large and unwieldy objects that require ample storage space that is safe from overheating.

Working with an in-house hydrogen generator, on the other hand, is a more reliable, inexpensive, and convenient way of obtaining carrier gas. With a hydrogen generator, labs can produce their own high-purity carrier gas supply without having to depend on cylinder deliveries. Gas generation also protects the organization from market price fluctuations. Once installed, a hydrogen generator stays in your lab, eliminating all the logistical hassles. Their small equipment footprint also takes up minimal space in the lab. No air compressors or other equipment is required.

4.4. Availability

For labs relying on helium, potential supply chain disruption can cause delays in sample analysis and operational issues. But even the small interruption of needing to change out high-pressure cylinders can delay



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analyses and create general disruption of day-to-day workflow. With a gas generator, laboratories have access to a constant 24 x 7 supply of hydrogen gas. There is no danger of running out midway through an analysis.

4.5. Purity

The purity of commercially supplied gases can vary slightly from one canister to the next. Even if the supply is always within stated tolerance ranges, the slightest differences in purity can impact sensitive analysis results. Even with a perfectly pure canister gas, contaminants can be introduced into the flow from piping joints, sealants, or micro-leaks. By comparison, a hydrogen gas generator from VICI DBS produces >99.99996% pure hydrogen gas, consistently.

4.6. Faster Analysis Times

The biggest advantage of using hydrogen as a carrier gas is that it can significantly decrease analysis time. Realistically, analysis times can be reduced by a factor of 1.5 or 2 with only minor losses in separation, which greatly improves both throughput and productivity—in many cases results can be obtained in half the time.

4.7. Lower Cost

As helium prices increase due to limited supply, switching to affordable hydrogen offers immediate savings. Further by producing hydrogen with a gas generator, labs can eliminate the indirect costs associated with purchasing, transporting, and storing gas canisters.

Using a helium gas generator also simplifies budgeting: price fluctuations in the volatile commercial helium market are no longer a concern. Carrier gas expenses are constant and predictable—and minimal.

4.8. Environmentally Friendly

Helium is a non-renewable resource that must be extracted from underground reserves typically using hydrocarbon-fueled equipment, and at a cost of ecosystem degradation and pollution. Commerical hydrogen canisters are most commonly produced using the energy-intensive process of steam reformation methane. Once processed, these cylinder gases are transported to the end-user by trucks that typically burn petroleum fuel.

By contrast, a hydrogen generator is delivered only once for installation. Eliminating canister deliveries reduces the overall carbon footprint of a facility. Now, only a modest amount of electrical power is needed to produce renewable hydrogen gas from deionized water, with no harmful byproducts.



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Dispelling The Myths About Hydrogen Gas for Chromatography ²⁰

Myth: Hydrogen is too dangerous.

Facts:

- Hydrogen is lighter than air, rising quickly (45 miles/hr) and dissipating quickly in the large air volume of a laboratory.
- Many GC labs are already using hydrogen for various purposes (e.g., FID detectors).
- Hydrogen generators produce gas on-demand, storing only a small amount at a time—typically <100 ml of hydrogen—at low pressure. By contrast, a typical canister contains 50 L under high pressure at 200 atm.
- Flow rates from a hydrogen generator are controlled and remain far below the LEL for hydrogen (4.1% in air) when released in the oven of an average GC.
- Hydrogen generators are equipped with built-in leak detection sensors that shut down the system automatically in the event of a leak.

Myth: It's difficult to transition from helium to hydrogen.

Facts:

- Many GC methods will not have to be redeveloped to use hydrogen. Some GC method redevelopment may be required for more complex chromatograms.
- To help ease the carrier gas transition, method development software is widely available
- Labs that use regulated methods may believe they are constrained from making any changes. However, it is worth consulting the regulating agency—many new, approved methods are available for using hydrogen as a carrier gas.

Myth: Hydrogen is too reactive for most GC applications

Facts:

Some GC users have concerns about hydrogen as it is a reducing agent that can promote hydrogenation. However...

- Hydrogenation occurs only at high temperatures and pressures when a metallic catalyst is present (e.g., nickel, platinum, or palladium). These conditions can be easily avoided.
- Using commonly available open tubular fused silica columns can prevent hydrogenation conditions.
- Taking some precautions when using nickel or alumina (Al2O3) columns is recommended.

²⁰ "<u>Hydrogen vs. Helium for Gas Chromatography.</u>" Infographic published in *Taking Care of Business*, Lab Manager vol. 14, no. 1, February, 2019.



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5. The ROI of Hydrogen Gas Generators

Replacing helium gas cylinders with hydrogen gas generators offers most users a clear cost advantage with a medium-and-long-term return on investment (ROI) many times over. Consider the following factors for your facility:

- How many helium cylinders are used per month or per year? At roughly US\$300-\$450 each, costs can add up quickly.
- How much is spent on replacement filters, maintenance, and safety inspections per year?
- Add to that the costs of delivery, handling, and installation.

Using just 2 hydrogen cylinders per month can quickly add up to nearly \$10,000 per year in direct costs. This doesn't even factor in internal/indirect costs such as labor and storage space.

In comparison, converting your GC lab to a hydrogen gas generator requires a one-time investment in the equipment, installation, and some basic conversion steps. At the high end, this can cost \$15,000 but is often less. But thereafter, very little additional outlay is required. Based on these rough numbers, a hydrogen generator from VICI DBS can easily pay for itself after just 2-3 years of use. It then provides many years of additional cost savings compared to the \$15K annual outlay that helium gas cylinders would have required. Recreate this calculation for your own facility to see the expected ROI (likely many multiples) and the low total cost of ownership you might expect (**Figure 6**).

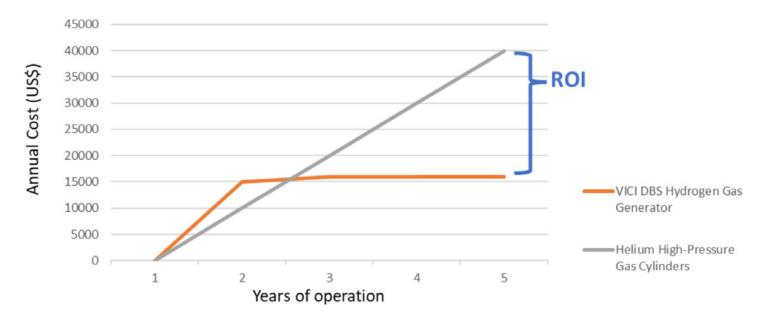


Figure 6: An example scenario for a GC lab that currently uses two helium cylinders per month. Switching to a hydrogen gas generator, including all installation, conversion, and ongoing operating costs, pays for itself in less than 3 years, and from then on generates an ROI year after year.



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6. Advantages of VICI DBS Generators

A key reason that GC customers are adopting VICI DBS gas generators is the innovative technology we employ—from our proprietary hollow-fiber nitrogen-generating membranes to the use of titanium to ensure the highest levels of hydrogen purity.

The optimized design of VICI DBS hydrogen generators takes deionized water and separates the hydrogen through electrolysis. It is then purified using a unique GLS (gas liquid separator) and a subsequent high-efficiency proton-exchange membrane (PEM). For ultra-high-purity hydrogen, a state-of-the-art heater-less dryer is used.

VICI DBS nitrogen, hydrogen, and other gas generators provide safe, consistent, and reliable performance. The range of our analytical hydrogen gas generator product line (**Figure 7**) also extends our innovative solutions and approach to other applications such as TOC and FT-IR. VICI DBS also offers N2 and zero air generators.

Advantages of VICI DBS helium generators include:

- Small quantity of gas ensures safety less than 50 ml internal volume
- Can be operated continuously 24/7 with automatic flow compensation
- Dual H2 or H2+air configuration offers flexibility, saves space, and saves cost as no additional equipment is required
- Simple to maintain with no tools or caustics required and no system downtime needed
- Configurable to meet the needs of your lab, in benchtop, station, rack-mounted or tower styles with varying dimensions.
- Set up multiple generators in parallel to increase flow rate.



Figure 7: The range of hydrogen generators from VICI DBS includes (left to right) <u>Standard</u> for benchtop use, <u>Rack</u>, which mounts to a 19" rack, <u>Station</u>, which fits underneath, and supports the weight of a GC, and the space-saving <u>Tower</u>.



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7. Conclusion

In recent decades, the helium market has become destabilized with price fluctuations and periodic shortages. These changes have presented difficulties for gas chromatography operators, causing many to start looking for alternative carrier gas supply options.

Hydrogen offers multiple advantages for GC users. The Van Deemter curves illustrate the wide range over which high efficiency is obtained, making hydrogen the best carrier gas for samples containing compounds that elute over a wide temperature range. For many applications, hydrogen can be a superior option, although the safety of high-pressure hydrogen cylinders can still be a concern.

Analytical gas generators offer clear improvements in the areas of safety, purity, convenience, and cost compared to high-pressure gas cylinders. With recent innovations and advancements in gas generator technology and performance, there is little reason to continue using high-pressure gas cylinders with instruments such as GC-FID and LC/MS.

The process of converting a laboratory from helium to primarily hydrogen is well established and not overly complex or expensive. Many GC users have already experienced the benefits of performance improvement and lower costs that VICI DBS hydrogen gas generators offer.

Is a Hydrogen Generator Right for Your Gas Chromatography Lab

To evaluate a switch to hydrogen generation, consider the following questions:

- 1. Does your application require helium or is hydrogen a potential substitute?
- 2. How much is your organization spending each year on helium cylinders and how much have these costs increased in the last 5-7 years?
- 3. Has your supply of helium ever been interrupted? If so, what was the effect of the interruption on lost analysis time, downtime costs, and lost revenue?
- 4. How much square footage of your facility is currently dedicated to helium cylinder storage? How many labor hours are used for monitoring, replacement, and shipping/receiving of cylinders?
- 5. Has your facility ever experienced a safety accident due to high-pressure gas cylinders (such as damage to building or equipment, injuries to staff)? If so, how much did the incident(s) cost the organization?
- 6. Any other safety or security considerations due to having outside delivery personnel access to your facility?
- 7. To migrate from helium to hydrogen, consider any new equipment or supplies that will be required, such as columns, tubing, venting, and leak detection.
- 8. If analysis speed could be increased by 20-25% without any loss in quality, how valuable would that be in terms of decreased labor hours and/or increase revenue?

To learn more or discuss how a hydrogen generator can improve your analysis times, provide better purity, consistency, safety, and convenience, while lowering your costs, contact VICI DBS today.