

How using Hydrogen Carrier Gas can Alleviate your Helium Supply Woes

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Owing to the worldwide helium shortage, many labs are facing difficulties in maintaining their supply, of one the most commonly used carrier gases for gas chromatography (GC) and as a consequence are facing rapid price increases. Many chromatography labs are therefore looking for alternative carrier gases and for many GC applications, hydrogen provides a good, in some cases better, alternative to helium. The perceived danger of having hydrogen in the lab can be mitigated by using a hydrogen generator which can fulfil the supply requirements of a lab whilst storing a fraction of the volume of gas. This article discusses the reasons behind the helium shortage, what hydrogen offers the chromatographer and illustrates how hydrogen can improve the separation of analytes in a complex mixture of compounds whilst improving sample throughput.

Helium is distilled from natural gas deposits that have collected in the presence of uranium and thorium. These radioactive elements produce helium when they undergo alpha decay and the gas remains trapped along with the natural gas until it is extracted. The presence of helium together with natural gas was first discovered in 1903 in Kansas and since then the physical qualities of helium (inertness, buoyancy, low liquid temperature) have made its use essential in a number of areas in industry and science, as well as it being a mainstay at birthday parties. At levels of 0.3% and above by volume in natural gas deposits, helium is deemed to be worth extracting with some natural gas deposits reported to contain up to 7% helium by volume [1].

In 1925, the United States established the National Helium Reserve (NHR) [2], located in the plains of Texas, and from 1929 the NHR was the world's largest producer of helium, with the Bureau of Mines coordinating extraction and refining programs. Helium was primarily produced and stored for military use and until 1960 the federal government was the sole producer of helium in the United States. In 1960, Congress amended the Helium Act to provide natural gas producers with incentives to extract crude helium and sell it to the government. Much of this helium was stored at the NHR and prices were fixed with a view to cover the costs of the program and to pay off debts. However, post-war federal helium demand was lower than predicted and with private demand far exceeding federal demand, the United States government passed the Helium Privatization Act (HPA) in 1996. The HPA was

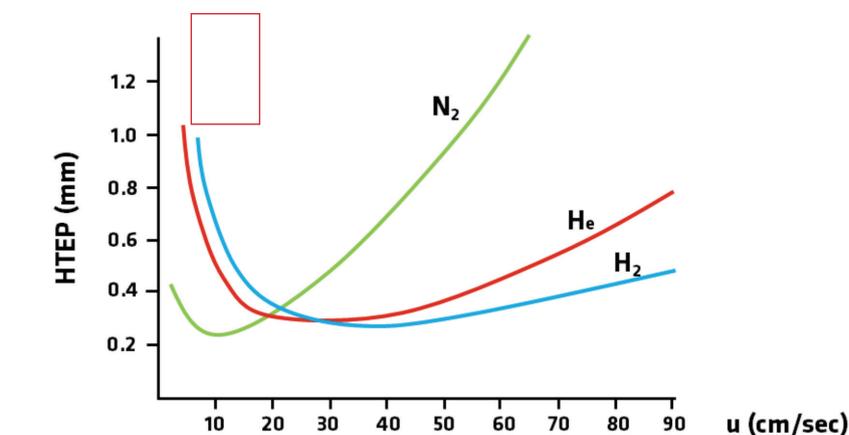


Figure 1 van Deemter curve showing variation of efficiency versus flow rate for helium and hydrogen and nitrogen. This demonstrates how hydrogen can improve the performance of the GC system

an attempt to wipe out the site's \$1.4 billion debt, through selling off all of the national reserves by 2015. Private companies did not move in to refine helium in the quantities expected at the time the bill was passed and the resulting supply problem has prompted other countries to begin extracting helium. Refineries are now producing helium in a number of countries worldwide including Russia, Qatar, Algeria and Australia [1,3].

In 2012 the United States produced an estimated 78% of the world's helium of which around 30% came from the NHR. The shortage of helium has been caused by a number of factors, including worldwide refinery equipment failures and shutdowns [3], with scheduled maintenance in several of the world's natural gas refineries disrupting supply. These factors, coupled with an increasing demand for helium from newly industrialised countries such as China, mean that we are moving even closer to a

worldwide shortage with customers already seeing stark price increases and supply problems as private companies struggle to meet the demand. A look at the figures published by the United States Geological Survey (USGS) shows that while the volume of helium extracted from natural gas fields has remained steady over the past 5 years, consumption from the NHR has steadily increased. In the same period, exports of helium from the United States have risen to 60% of the total [4], and with the NHR rapidly emptying the current situation appears to be unsustainable. Worldwide helium demand far exceeds production and therefore alternatives to helium must be sought for a number of technologies.

The result of the helium shortage has filtered down to the point where even laboratories, who are consuming a fraction of the helium on the market, are affected. Many labs, even those classed as 'preferred customers' are

struggling to source helium and are also seeing increasing prices. The helium shortage has prompted the GC manufacturers to develop systems to reduce helium consumption, such as the Agilent EPC device for the 7890B which allows the system to switch from helium to nitrogen carrier gas when the system is idle and the Thermo Scientific Trace 1300 GC with modified inlet pneumatics which uses nitrogen for all split and purge flows. In addition to gas saving systems, GC and GC-MS manufacturers (Agilent, Bruker, Shimadzu and Thermo) have also developed new systems capable of running on hydrogen and helium.

Hydrogen is already present in a high proportion of GC labs since it is used as a flame gas for FID's. However, many people still have fears about the explosive nature of hydrogen and as a result many laboratories are now prohibited from placing hydrogen cylinders on their premises owing to health and safety restrictions. The safety concerns regarding hydrogen cylinder use mainly involve the total volume of gas contained within a cylinder. A 50 litre cylinder contains around 9,000 litres of pressurised hydrogen which, when rapidly released into a laboratory, could cause an explosion since a volume of 4% hydrogen in air equals the minimum threshold (lower explosion limit) for hydrogen ignition [5]. Rapid release of hydrogen into air can also result in auto-ignition of hydrogen, which is another concern of having hydrogen cylinders in the laboratory environment [6]. In addition to the risk of explosion, variation in the quality of hydrogen from cylinder to cylinder can affect repeatability of analysis, changing cylinders can interrupt GC operation as well as inconveniencing the user. Cylinders are also large and can take up a considerable amount of lab space.

By contrast, gas generators have a relatively small footprint, contain a negligible volume of hydrogen and are able to produce gas on-demand as well as having the capability of simultaneously supplying carrier and flame gas to a number of GCs. The purity of gas produced by a hydrogen generator is often of higher purity than cylinder hydrogen.

In addition to these features, hydrogen generators typically have internal leak detection systems in place that will force the generator to shut down within a certain time-period, forced air ventilation to prevent mixing of hydrogen and oxygen within the generator and an alarm system. These features along with in-oven leak detectors supplied by hydrogen generator suppliers and emergency inlet shut-down features of GCs mean that laboratories should be quickly alerted in the event of a hydrogen leak.

Chromatographers who switch to hydrogen from helium will benefit through improved column separation efficiency over a wider range of flow rates, improved sample throughput

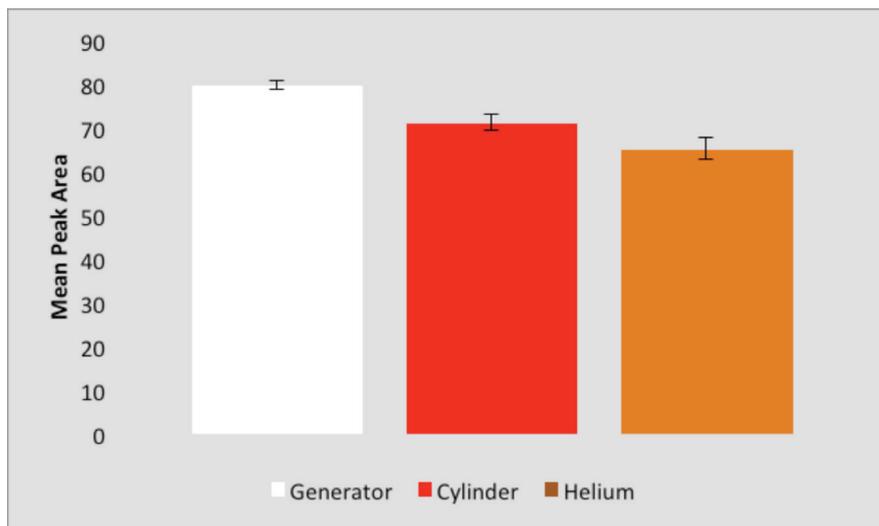


Figure 2. Mean response from 15 repeated injections of Decane (Columns represent mean peak area +/- standard error)

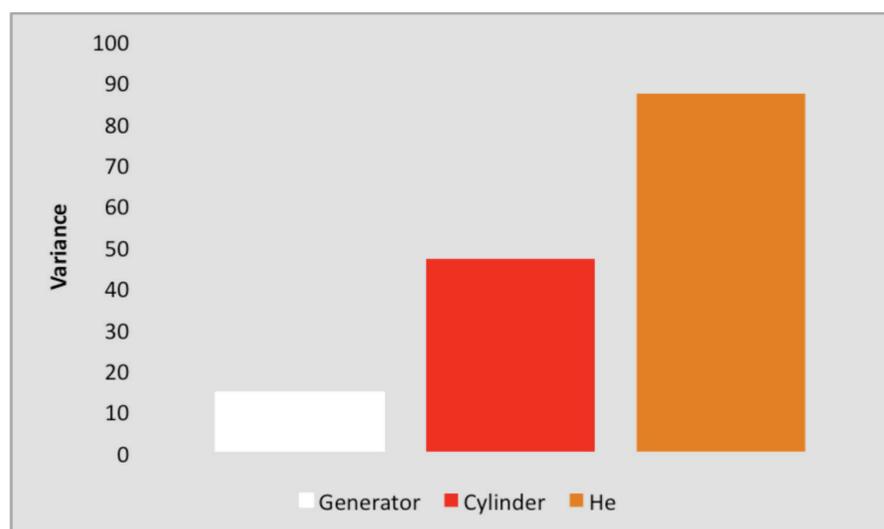


Figure 3. Sample variance of data from 15 repeated injections of Decane using a hydrogen generator, hydrogen cylinder and helium cylinder

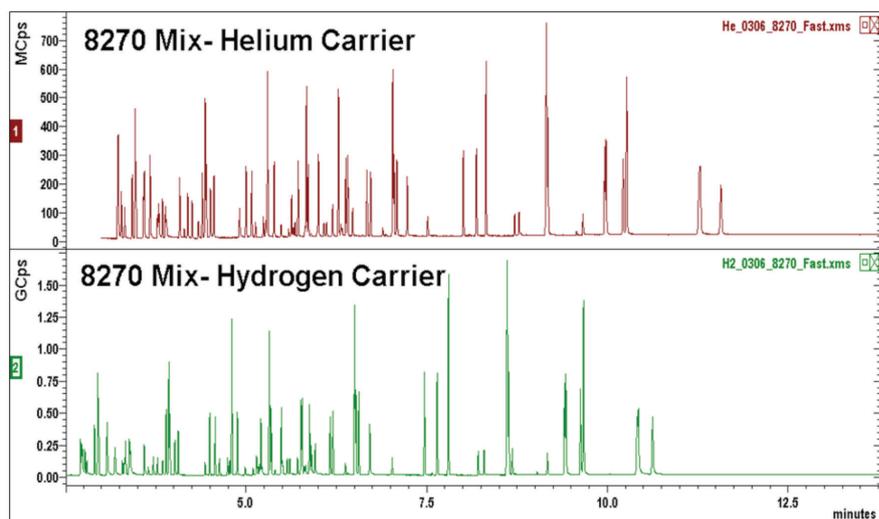


Figure 4. Analysis of a complex mixture using hydrogen and helium carrier gas.

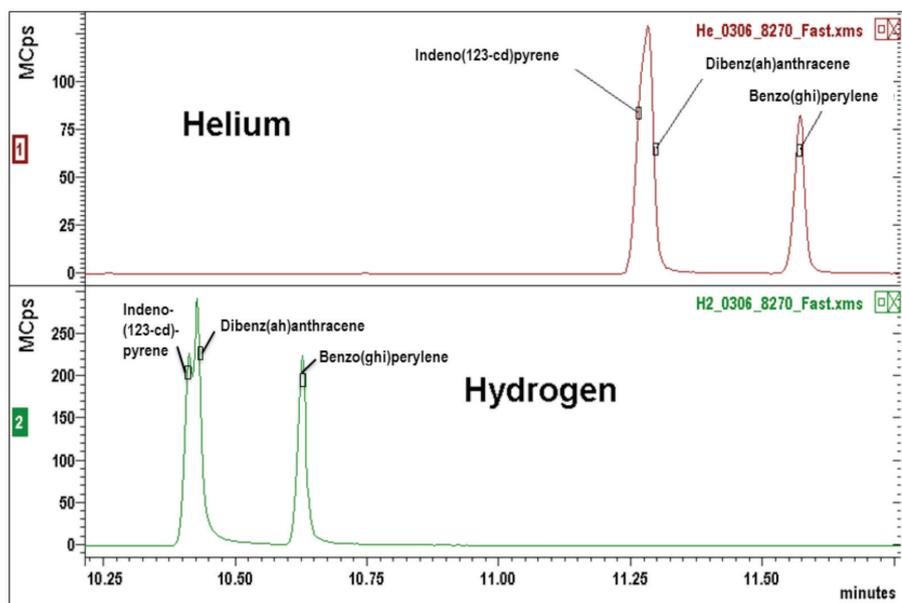


Figure 5. Separation of Indeno(1,2,3-cd)pyrene and Dibenz(ah)anthracene with hydrogen and helium carrier gas.

through shorter run times and should find that using hydrogen is more economical than helium, particularly considering recent helium price increases [7]. Increased sample throughput without resolution loss is a feature of using hydrogen for carrier gas that will particularly appeal to contract labs for which reduced overheads and faster chromatography will increase profits. This is highlighted when looking at the variation of plate height (HETP) observed at differing flow rates with the two gases (Figure 1). Helium has an optimum efficiency at velocities of around 20-30 cm/sec, whereas hydrogen gives optimal performance from around 35-60 cm/sec, but can be used at even higher linear velocities without a great loss of efficiency. If faster analysis is desired, hydrogen can be used in conjunction with smaller diameter, or narrow bore columns which offer faster analysis compared with helium without loss of separation efficiency and similar peak elution[7].

Although hydrogen is the best alternative to helium for carrier gas in the majority of cases, it can react with analytes under certain conditions. Therefore, chromatographers should be careful when using chlorinated solvents with hydrogen carrier gas because of the risk of hydrochloric acid (HCl) formation, which can affect column efficiency through formation of pores in the stationary phase. However, use of the pulsed split injection can ensure fast transfer of analytes onto the column with minimal opportunity for HCl formation in the inlet [8]. In some cases, the reactivity of hydrogen can be used to the advantage of the analyst, particularly in MS applications, where protonation of ion fragments can assist in compound identification[8].

Experimental

Experiments were conducted to investigate the repeatability of results of injections of a decane standard (a component of TPH Mixture 1, Sigma-Aldrich cat. No. 861424-U) and the performance of hydrogen carrier gas produced by a generator with hydrogen and helium from cylinders compared using a GC-FID. Experimental parameters (shown in Table 1) were derived from an existing method using helium carrier gas which was translated using Agilent chemstation software. The flow used for hydrogen carrier gas was double the flow of helium. All other factors eg. column dimensions and oven program were kept the same. Results showed that hydrogen from both generators and cylinders produced consistently larger peak areas than helium (Figure 2). The quantitative difference seen appears to be a consequence of more efficient analyte-stationary phase interaction when using hydrogen carrier gas, although diffusional effects of faster eluting peaks may also have some effect on differences observed in peak area. When looking at the sample variance, results of analysis using carrier gas from a hydrogen generator showed much more uniform results than either cylinder hydrogen or helium (Figure 3). This may be an indication of variation in the quality of gas supplied by cylinders, since both hydrogen and helium from cylinders gave more variable peak area results than gas from the hydrogen generator. This variation may be caused by impurities in the gases from cylinders, whereas the generator produces a uniform quality gas. A second possibility for the variation is that it is because the generator was directly connected to the GC with new, clean tubing, whereas the

hydrogen and helium from cylinders were supplied via longer, existing lengths of tubing where contaminants which are known to build up over time in tubing were responsible for the differences seen?

To further demonstrate the advantages of using hydrogen as a carrier gas, a 0.5 μ L injection of a complex compound mixture containing 76 compounds (Restek Megamix cat. No. 31850) was analysed using the Bruker Scion SQ GC/MS (experimental conditions are shown in Table 2). A comparison of chromatograms obtained using hydrogen and helium show an increased throughput when using hydrogen (Figure 4). Due to the physical properties of helium, increasing linear velocity to increase sample throughput results in a loss of resolution. However, even when running samples with hydrogen at higher linear velocities than with helium, sample resolution can still be improved, with marginally better separation of indeno(1,2,3-cd)pyrene and dibenz(ah)anthracene achieved compared with using helium. These results show that chromatographers can shorten analysis times without seeing a reduction in peak resolution (Figure 5.). This study shows that hydrogen carrier gas produced by a hydrogen generator is suitable for GC/MS analyses with hydrogen carrier gas.

One common fear about using hydrogen for carrier gas in GC/MS applications is that library searches will be affected by differing ion fragmentation patterns and potential reaction between the carrier gas and analytes or solvents. A recent webinar presented by Thermo Scientific assessed library search results using MS data and found that there were no problems with library detection of compounds despite slight changes in relative ion abundances[9].

Summary

The helium shortage has prompted a number of laboratories to switch from helium to hydrogen for carrier gas. This has provided these users with the benefits of reduced cost, superior chromatography and faster throughput. Since it looks unlikely that the availability and price of helium will improve in the near future, the trend towards use of hydrogen looks set to continue.

Acknowledgements

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Experimental

Repeatability Experiment

Table 1. GC conditions used for repeatability experiment

Carrier Gas	Peak Scientific Precision Generator hydrogen	Cylinder hydrogen	Cylinder helium
Carrier Flow	3.6 mL/min	3.6 mL/min	1.6 mL/min
Column	DB-1 (30m x 0.25mm x 0.25µm)	DB-1 (30m x 0.25mm x 0.25µm)	DB-1 (30m x 0.25mm x 0.25µm)
Inlet	Split (50:1)	Split (50:1)	Split (50:1)
Oven			
Oven Initial Temperature	60°C (1 min hold)	60°C (1 min hold)	60°C (1 min hold)
Oven Heating Rate	40°C /min to 280°C	40°C /min to 280°C	40°C /min to 280°C
Run Time	9 min	9 min	16.5 min

Complex Mixture Experiment

Carrier Gas	Peak Scientific Precision Generator hydrogen	Cylinder helium
Carrier Flow	1.0 mL/min	0.8 mL/min
Column	BP-5MS (20m x 0.18mm x 0.18µm)	BP-5MS (20m x 0.18mm x 0.18µm)
Inlet	290°C Pulsed-Split, 0.3 min at 40 psi, 70:1 split	290°C pulsed Split, 0.3 min at 40 psi, 70:1 split
Oven		
Oven Initial Temperature	45°C (1 min hold)	45°C (1.5 min hold)
Oven Heating Rate	30°C /min to 310°C (5 min hold)	20°C /min to 310°C (7.4 min hold)
Run Time	15 min	22 min
MS		
Source	330°C	330°C
Mass range	45-500	45-500
Solvent delay	2 min	2 min
Scan time	120ms	120ms

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