Benefits and Considerations of Converting to Hydrogen Carrier Gas

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Many gas chromatography (GC) labs use helium as a carrier gas because it is faster than nitrogen and safer than hydrogen. Unfortunately, helium is a limited natural resource that is becoming much scarcer. The current shortage has severely impacted chromatographers who are finding that helium has become significantly more expensive and is not always available when needed. While helium is abundant in the universe, it is rare on Earth where it is produced by fractional distillation of natural gas.

The United States is a primary producer, but its major reserve, the United States National Helium Reserve (which accounts for approximately 30% of the global supply) is expected to be depleted by 2018 [1]. Other helium supplies are not expected to alleviate the current shortage, so many GC labs are considering moving to hydrogen carrier gas as an alternative. The faster analysis times, lower cost, and unlimited availability of hydrogen make it the best chromatographic choice, but its flammability means implementation must be carefully considered. By using safe, reliable hydrogen generators and understanding how to adapt methods, labs can reap the productivity and cost savings of switching from helium to hydrogen.

Safety Considerations

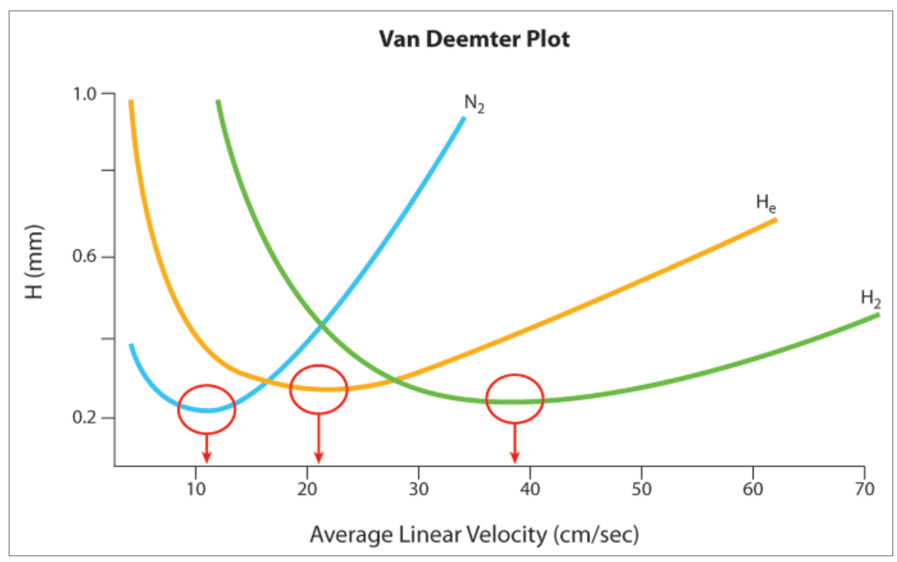
The first concern when switching to hydrogen carrier gas is understanding and managing the safety issues. Fortunately hydrogen generators minimise much of the risk. In contrast to high-pressure gas cylinders, which typically contain 50 L at 200 atm, hydrogen generators generally store only 60 mL at 7 atm or less. This means that although a generator can continually produce hydrogen on demand, the stored quantity is quite small making it a considerably safer choice. In addition, the flow of hydrogen from the generator is controlled and on typical units the maximum flow is approximately 500 mL/min, which is well below the 2 L/min of flow required to reach the lower explosive limit (LEL) for hydrogen in air when released in the oven of an average GC. Generators are also equipped with built-in leak sensors and automatic shut-off features, which turn the unit off if a leak is detected. With soaring helium costs, generators pay for themselves, guarantee a gas supply, and also eliminate the risk posed by keeping high volumes of hydrogen in free-standing, high-pressure gas cylinders.

Another way safety can be improved is by using flow-controlled analysis. In today's GC lab, analysts can choose between pressure and flow controlled analysis. When using hydrogen, flow-controlled operation is the best option as the worst that can happen is the fused silica capillary column breaks at the injection port. With the flow controlled method, only the volume of hydrogen in the inlet and column can be released. This is because the pressure regulator in the injector of an electronic pressure regulation GC will not be able to build pressure, so the system will sense a problem and will automatically enter standby mode. If greater assurances of safety are desired, systems are available that sample the oven air and detect the presence of a different gas (e.g., helium or hydrogen). As a further level of protection, analysts can use metal capillary MXT® columns, which are virtually unbreakable, instead of more fragile fused silica columns. Metal capillary columns are standard for high-temperature applications, such as simulated distillation and biodiesel analysis, but they also perform very well for lower temperature work. While some metal columns may have activity issues, excellent results can be obtained when highly inert, Siltek®-treated columns are used.

Benefits and Application

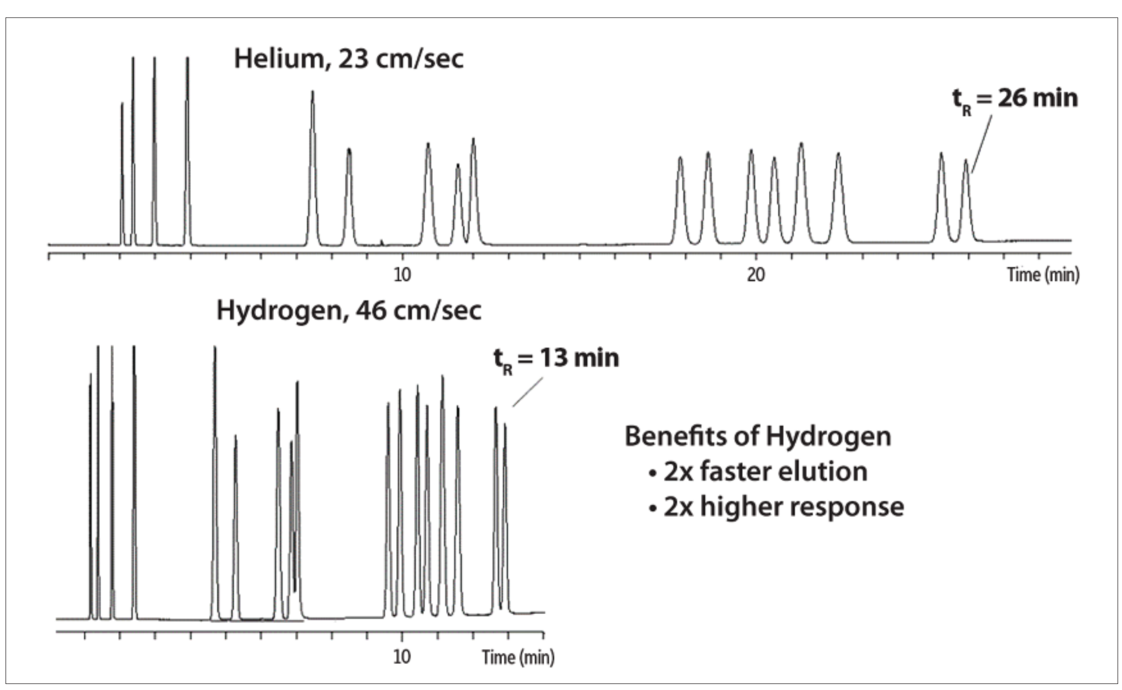
The biggest advantage to using hydrogen as a carrier gas is that it can significantly decrease analysis time. Realistically, analysis times can be reduced by a factor of 1.5 or 2 with only minor losses in separation, which greatly improves throughput and productivity. A quick review of a van Deemter plot for common carrier gases makes this quite clear (Figure 1). Nitrogen offers the greatest efficiency (shortest height equivalent to a theoretical plate), but its maximum efficiency is only obtained when operating at a very slow rate (~10 cm/sec); when linear velocity is increased, efficiency is lost at a dramatic rate. Helium is somewhat less efficient, but offers more reasonable operating rates (~25 cm/sec is optimal and less efficiency is lost at higher rates). However, the best chromatographic performance is seen using hydrogen. Maximum efficiency is comparable to helium, but good results can be obtained across a much wider operating range. Optimal linear velocity when using hydrogen is approximately 40-45 cm/sec; this means analysis times are much faster compared to when using helium, and in many cases results can be obtained in half the time.

Figure 1: Using hydrogen as the carrier gas allows efficient separations to be obtained in half the time compared to when using helium.



The theoretical benefits to productivity when using hydrogen are clear, but let's look at a practical example. Figure 2 shows the analysis of a hydrocarbon mixture in the same GC using helium versus hydrogen. When using hydrogen, twice the linear velocity was used and the components eluted twice as fast with minimal negative impact on efficiency. Peak separations were

Figure 2: Hydrocarbons can be separated in half the time using hydrogen as the carrier gas, significantly improving productivity.



Column: Rt®-Alumina BOND/MAPD; Sample: Hydrocarbon mixture; Injection: Split; Linear velocity: 23 cm/sec (helium), 46 cm/sec (hydrogen); Detector: FID.

maintained and since peaks are twice as narrow, they are also twice as high. This enhances sensitivity and can lead to lower detection limits, but it also allows the injection of smaller sample volumes. The advantages of using hydrogen are clear, but attention must also be given to method conversion prior to implementation.

Adapting methods to hydrogen carrier gas requires some consideration of elution temperature. Changing from helium to hydrogen is relatively simple for isothermal methods; the linear velocity is increased by roughly a factor of two and 50% of the sample volume is injected using the same split ratio. This results in the same sensitivity (peak height). Injecting less sample has the additional benefit of reducing contamination, which in turn reduces the costs and time required for inlet and column maintenance. However, converting temperature-programmed methods is more complex and requires additional changes. If the same peak elution order is desired when using hydrogen, the oven temperature program rate must also be changed or the components will elute at different times and the elution order may change. In order to ensure that the target analytes elute at the same elution temperatures, a change of oven temperature program rate is needed. Roughly, when twice the linear velocity is used, the isothermal times must be cut in half and temperature programs must be multiplied by a factor of two in order to obtain the same separation in half the time. While one can calculate this, there are freeware programs available on the web that are helpful for more complex methods. Or you can use the helpdesk of companies like Restek (support@restek.com) to assist you in determining the new settings.

Summary

As the cost of helium continues to soar and its availability becomes more and more uncertain, many labs using gas chromatography are considering switching to hydrogen carrier gas. Hydrogen can be reliably produced on demand using hydrogen generators, which are safer and more cost-effective than free-standing, high-pressure gas cylinders. In addition, using hydrogen allows efficient separations to be obtained twice as fast compared to helium, which offers clear benefits to sample throughput and overall lab productivity.

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References

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