

## GC knowledge note # 002

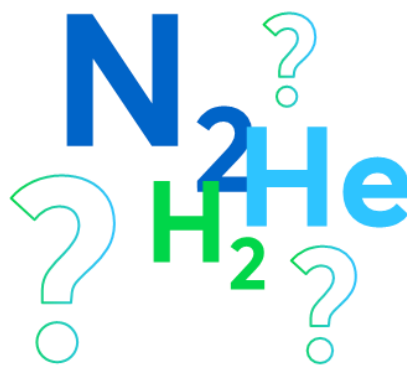
# Carrier gases in capillary GC

### INTRODUCTION

Nitrogen, helium and hydrogen are the three most commonly used carrier gases in modern capillary gas chromatography (GC). Each option has its own properties, advantages and drawbacks, which means that the instrumental parameters must be optimised depending on the carrier gas used, in order to obtain maximum efficiency for the separation.

The role of the carrier gas in GC is to transport analytes as they migrate down the chromatographic column. The carrier gas velocity or flow rate therefore has a clear impact on the speed of the separation obtained, with higher flow rates providing faster separations, albeit with a loss of separation efficiency beyond the optimal value.

The carrier gas diffusivity and viscosity impact the efficiency generated as a function of velocity and it is therefore important to understand the kinetic performance of different carrier gases to select the optimum method conditions. In addition, the use of



hydrogen requires the implementation of certain safety precautions. This technical note discusses the different properties offered by these gases, limitations in their use, along with guidance on how to obtain maximum efficiency for GC separations.

## PROPERTIES OF CARRIER GASES

Perhaps the most important property of the carrier gas is that it should be inert with respect to both the sample being analysed and to the GC capillary column. This ensures that reactive degradation of the column and sample are avoided. Additionally, readily available and inexpensive gas sources of very high purity are required, which has led to the adoption of nitrogen, helium and hydrogen as the three most common carrier gases in GC.

Hydrogen and nitrogen are readily available and comparatively cheap and can also be produced in the lab using gas generators. The use of hydrogen as a carrier gas is sometimes avoided as additional safety precautions are required as hydrogen and air mixtures are combustible at concentrations between 4% and 75% in air.<sup>[1]</sup> Leaks in the GC oven can therefore potentially lead to the build-up of hydrogen and pose a safety risk. Helium has no such safety concerns, but is more limited in supply, has been prone to supply insecurity in recent years and requires extraction, so is therefore more expensive. Gas purity is also important, high grades are required (at least 99.995%), in accordance with instrument specifications. Gas filters and traps should be utilised as an additional measure to ensure gas purity and to help avoid column degradation.

Another consideration for carrier gas selection is detector compatibility. Helium is often the preferred carrier gas for GC-MS applications, although hydrogen can also be used, albeit with the necessary safety precautions. Due to the lower viscosity of hydrogen, additional strain is put on the MS vacuum system and some systems may not be able to generate sufficient vacuum with hydrogen.<sup>[2]</sup> The instrument manufacturer should be consulted before using hydrogen with GC-MS applications.

Unlike liquid chromatography (LC) the carrier gas (analogous to the mobile phase in LC) used in a GC separation has very little impact on the separation selectivity. When running methods with different carrier gases installed on the GC, large changes in the elution order or relative peak spacing will not be observed. However, hydrogen, nitrogen and helium possess very different viscosities, with helium being the most viscous and hydrogen the least.<sup>[3]</sup> As a result, for a method with the same parameters, using helium as a carrier gas (higher viscosity) will create a higher back pressure compared to the same method using hydrogen as the carrier gas (low viscosity), which will have a lower backpressure and higher linear velocity.

## BAND BROADENING IN GC

Another property related to the carrier gas that is highly impactful in GC is solute diffusion in the gaseous phase. Solute diffusion is faster in hydrogen than helium or nitrogen, which has a profound impact upon the optimum carrier gas linear velocity that should be used for each gas. As a chromatographic peak migrates along the column, two competing diffusive effects lead to an overall broadening of the peak. These two effects are dependent on the carrier gas linear velocity, which results in the existence of an optimal velocity for each carrier gas at which maximum efficiency is obtained. This phenomenon is best understood by considering band broadening theory, developed by van Deemter and Golay.<sup>[4, 5]</sup>

The efficiency ( $N$ ) of the column is defined by equation 1, where  $L$  is the column length and  $H$  the theoretical plate height (often referred to as the height equivalent to a theoretical plate,  $HETP$ ). For a fixed column length, lower theoretical plate height values (i.e. narrower peaks) will result in increased separation efficiency. As the plate height increases, increased band broadening occurs, leading to broader peaks and a corresponding decrease in efficiency.

$$N=L/H \quad (1)$$

The van Deemter equation, defined in the 1950's, in its simplified form (equation 2), describes three terms which contribute to band broadening ( $A$ ,  $B$  and  $C$ ) in packed GC columns and relates them to the average carrier gas linear velocity ( $\bar{u}$ ).<sup>[4]</sup>

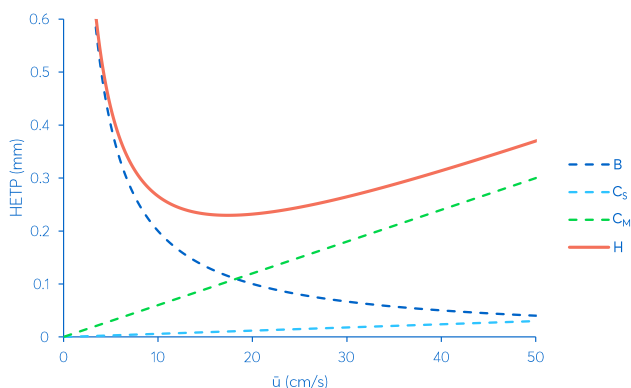
$$H = A + \frac{B}{u} + C \cdot \bar{u} \quad (2)$$

The three terms correspond to the following processes:  $A$  Eddy diffusion,  $B$  longitudinal diffusion and  $C$  mass transfer. In GC separations using open tubular capillary columns, the absence of a packed material within the column means that the  $A$  term is not relevant and equation 1 can be re-written to give equation 3 (often referred to as the Golay equation).<sup>[6, 5]</sup>

$$H = \frac{B}{\bar{u}} + (C_M + C_S) \cdot \bar{u} \quad (3)$$

$C_S$  describes analyte diffusion in the stationary phase and  $C_M$  analyte diffusion in the mobile phase. For capillary columns with thin films, the  $C_M$  term is dominant, whereas in columns with thick stationary phase films, the  $C_S$  term becomes significant.<sup>[7]</sup>

Figure 1 shows a theoretical Golay plot according to equation 3, with the average carrier gas linear velocity plotted on the x-axis and *HETP* plotted on the y-axis. At low linear velocities, longitudinal band broadening (*B* term) heavily impacts the obtainable efficiency and its impact decreases significantly as linear velocity increases. Analyte mass transfer (*C<sub>M</sub>* and *C<sub>S</sub>* terms) however. The composite curve (red) shows that as the carrier gas velocity increases, the *HETP* value decreases until a minimum is reached. This is the velocity at which maximum efficiency for the separation is achieved. As the carrier gas linear velocity increases further, the column efficiency begins to decrease beyond the optimum value.



**Figure 1:** Theoretical composite Golay plot (red) showing the relative contributions from the various terms defined in equation 3 (dashed lines).

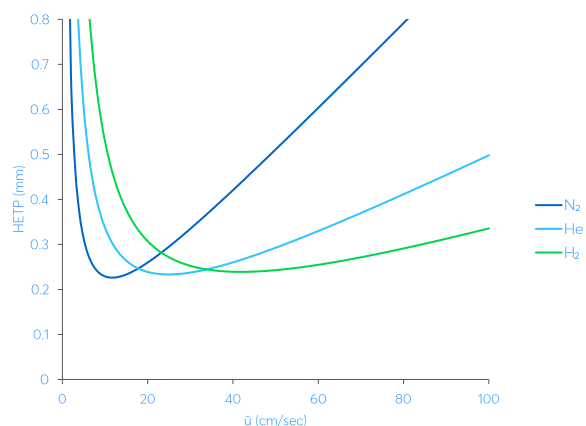
The two dominant terms in capillary GC (*B* and *C<sub>M</sub>*) are dependent on solute diffusion in the carrier gas (*D<sub>M</sub>* is the solute diffusion coefficient), as shown in equations 4 and 5.

$$B = 2D_M \quad (4)$$

$$C_M = \frac{(1+6k+11k^2)r_c^2}{24(1+k)^2D_M} \quad (5)$$

Where *k* is the analyte retention factor and *r<sub>c</sub>* the internal radius of the capillary column. The dependence on solute diffusion means that carrier gases with differing diffusivities will have different optimal velocities, as shown in Figure 2.

Although the lowest *H* minimum is obtained for nitrogen, this is achieved at significantly slower carrier gas velocities than either helium or hydrogen. Therefore, nitrogen will yield the most efficient separations, albeit at



**Figure 2:** Theoretical Golay plots generated using equation 3, showing the *H* vs average linear velocity profiles obtained using different carrier gases; nitrogen, helium and hydrogen. The curves were generated for a 25 m x 0.25 mm ID, 0.25 µm film thickness column and a retention factor of 10.

the expense of significantly longer run times. Efficiency decreases sharply above the optimum velocity for nitrogen, limiting its usability to a relatively narrow range. The minimum plate height for helium is at much higher velocity, whilst that for hydrogen is higher still, meaning that approximately equivalent efficiency will be obtained faster with these two carrier gases. Additionally, the curve for hydrogen in particular, is less steep in the higher velocity region, meaning that even faster carrier gas velocities can be utilised without significantly compromising the separation efficiency. Hydrogen is also the least viscous carrier gas and therefore requires a lower pressure drop over the column to obtain a given flow rate and so operating at higher velocities is more achievable on many GC instruments. For these reasons, hydrogen is clearly the optimal carrier gas when fast, high throughput analysis is required as it provides faster separations/shorter run times, and is typically utilised together with short, narrow bore columns for “Fast GC” separations.

## CONCLUSION

Nitrogen, hydrogen and helium are the three most commonly used carrier gases in capillary gas chromatography. Nitrogen is readily available, safe, can be generated in the lab and provides the highest efficiency separations. However, the maximum efficiency is obtained at low linear velocities, therefore requiring long analysis times. Helium is a widely used and safe

carrier gas option, which provides faster separations than nitrogen. The main drawback of helium is its more limited supply and relatively high cost. Hydrogen clearly generates the fastest separations as the optimum linear velocity, in its respective Golay curve, is much greater than either helium or nitrogen. In addition, the curve is much flatter, meaning that separations can be run at flow rates above the optimum without significantly sacrificing separation efficiency, therefore making hydrogen the ideal choice for fast GC. Combined with economic considerations, laboratories may look to migrate methods from helium to hydrogen to speed up GC separations and boost laboratory productivity. Overall, each has its own particular advantages and disadvantages which must be assessed to determine the most suitable carrier gas for a given application.

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