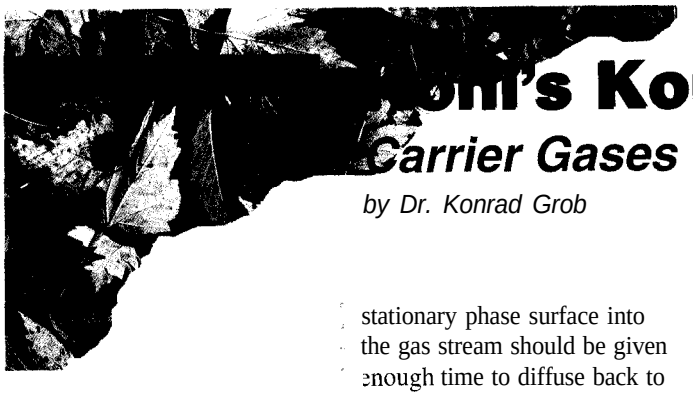


...ni's Korner

Carrier Gases for GC

by Dr. Konrad Grob

Probably more than 90% of the present GC instruments run with helium as carrier gas. Some people use hydrogen or nitrogen, maybe because the first ones are hidden pyromaniacs (some GC ovens actually exploded) and the second still have nitrogen mounted on the instrument from the times they worked with packed columns. These gases serve to produce wind through the column to move our solutes forward. The solute molecules evaporate from the stationary phase surface, i.e. enter the open space of the capillary column, are hit by a carrier gas molecule and start traveling down the tube. After a short distance, however, they touch the sticky surface of the stationary phase and go through another partitioning process. Does the choice of the carrier gas interfere with this? Yes, it does, through its diffusivity and viscosity. You want to know why hydrogen is the best carrier gas?

Diffusivity

Diffusivity provides a measurement for the diffusion speed of a solute vapor in a given gas. For helium and hydrogen, diffusivities are similar, but that of nitrogen is about four times lower (see Table I).

The diffusion speed of the solute in the carrier gas determines the speed of chromatography. A solute molecule evaporating from the stationary phase surface into the gas stream should be given enough time to diffuse back to the stationary phase (Figure 1) before having gone far in order to undergo another partitioning process - it is these contacts which differentiate between different substances, and a large number of contacts are needed to obtain the best separation. We get more of them if the solute diffuses more rapidly and/or when we give it more time, i.e. reduce the gas velocity. However, there is a limit: giving it more time for the diffusion towards the stationary phase (radial diffusion) also provides more time for spreading within the open bore of the column, i.e. band broadening through longitudinal diffusion. This is why there is an optimum gas velocity: it provides a maximum number of contacts with the stationary phase with minimum of band broadening in the gas phase.

This kind of logic applies to all gases. In fact, all carrier gases provide similar separation efficiencies provided conditions are adjusted correspondingly. The time needed is different: since diffusion in hydrogen and helium is much faster than in nitrogen-for (wanted) radial as well as (unavoidable) longitudinal diffusion-GC is 2-3 times faster with the former. If we users of hydrogen wait for one hour, users of nitrogen should wait for 2-3 hours to get the same performance. Nitrogen is for those who own a comfortable arm chair in the lab or who are afraid of the result. Usually users of nitrogen are not really that patient and run their chromatography at similar speed as others using hydrogen and helium. Table II shows what they get. It compares separation efficiencies measured in terms of Trennzahl (TZ) indicating the number of peaks which could be fully separated between two components to be defined, in this case, the alkanes C 13 and C14. At the gas velocities most commonly used with hydrogen (40-60 cm/s), nitrogen produced hardly more than half as many peaks. When using

Table I:

Relevant characteristics of carrier gases'

Carrier gas	Viscosity at 50°C [kg/s m]	Diffusivity (butane, 100°C [m2s])
Hydrogen	9.4	6 10-6
Helium	20.8	5.5 10-6
Nitrogen	18.8	1.5 10-6

Figure 1:

Diffusion of a molecule in the gas phase of the column.

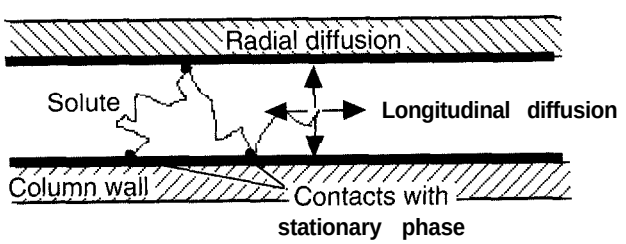


Table II:

Separation efficiencies in terms of separation numbers (Trennzahl, TZ) for the n-alkanes Cl3 and C14 and a12m, 0.25mm ID column coated with a methyl silicone.

Gas velocity	Hydrogen	Nitrogen
50 cm/s	24	13
40 cm/s	**25**	**13**
30 cm/s	23	17
20 cm/s	20	23

hydrogen, the same result could have been obtained from a column roughly 3 times shorter in a third of the time. To give an impression of how the chromatograms look like, an example is shown in Figure 2. At halved velocity, nitrogen provided good performance also.

In this application, nitrogen just requires extra time. However, long retention times also produce low peaks, i.e. poor sensitivity (see **Figure 2).** Additionally, do not try to run triglycerides or other labile compounds with nitrogen as carrier gas: they are largely degraded during the long run time required.

Viscosity

The other difference between the carrier gases concerns the viscosity that determines the inlet pressure required for a given gas velocity. High inlet pressures strongly compress the gas in the column inlet, which causes the problems shortly outlined below. This explains why hydrogen is preferable to helium.
You have certainly seen the h/u curves, also called van Deemter curves, plotting HETP (plate height) against gas velocity. Their peculiarity: the best is at the bottom, i.e. the optimum gas velocity is at the lowest point of the curve; the larger the plate heights, the worse the separation. The curves say that separation is poor when the gas velocity is below the optimum velocity (left of the optimum in Figure 3, the result of excessive longitudinal diffusion) and that it worsens again beyond that optimum (the curve rising at the right, the result of insufficient radial diffusion).

For columns of a given diameter, the optimum velocity is highest when the column is short. This is because inlet pressure is low. For hydrogen or helium, with about the same diffusivity, the optimum is almost the same, i.e. around 40-50 cm/s. Further, the losses in performance upon speeding, i.e. using excessive gas velocity, are relatively small. The longer the column, the higher is the inlet pressure required. This shifts the optimum gas speed to lower values and, as if there were a strict educator behind the chromatographer, speeding is punished more strongly when the velocity must be low anyway. Hence, using a column of doubled length requires more than twice as much run time, because the gas velocity must be lower. In this respect, helium is worse than hydrogen because its viscosity is about twice as high: the higher inlet pressure requires a lower gas velocity and if you do not obey, the punishment is harder.

Figure 2:

Separation of a kerosene fraction using hydrogen or nitrogen as carrier gas at the same average gas velocity (40 cm/sec).

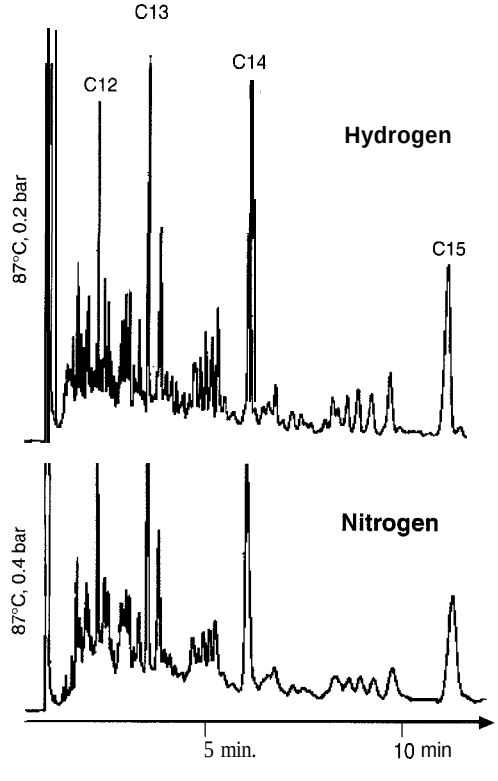
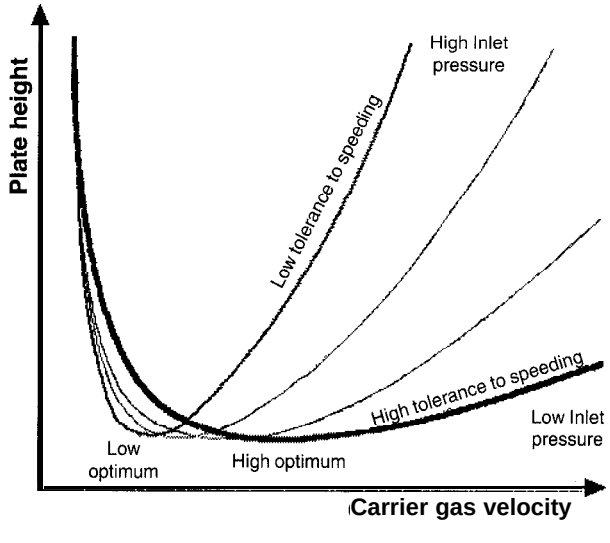


Figure 3:

High inlet pressures cause the optimum gas velocity to be low and the loss in separation efficiency when exceeding this optimum to be high.



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Continued from page 11.

What is the reason for this? If the column head pressure is, e.g., 1 bar, corresponding to 2 bar absolute pressure, the carrier gas in the inlet is compressed to half the volume compared to the column outlet (assuming the latter is at ambient pressure, 1 bar absolute, **Figure 4).** Hence the plug corresponding to 2 ml in the outlet is only 1 ml and is half as long. To displace I ml, half the velocity is required compared to displacing 2 ml at the outlet. Hence optimization must compromize between a low velocity in the inlet and a higher one at the outlet.

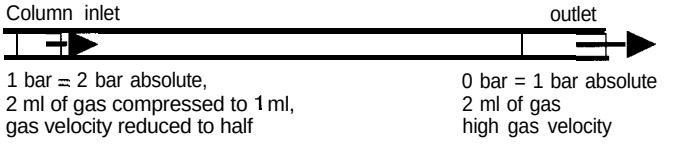
Conclusions are against intuition. From short columns we know that 40-50 cm/s are best. In the last, e.g., 1.5 m of a long column, pressure conditions are the same as in a short column, i.e. the optimum gas velocity and tolerance to speeding must be the same. The problem resulting from the compressibility of the gas is obviously in the inlet of the long column. We are tempted to assume that it is related to the fact that the gas velocity is 20-25 cm/s only and would conclude that a compromize should be chosen between maybe 30 cm/s in the inlet and 70 cm/s in the outlet in order to result in some 50 cm/s as an average. Experiments show that this is wrong: the best average velocity is only 20-25 cm/s. Hence the system wants an even lower velocity in the inlet: about 10 cm/s. And it insists in that: it forces to choose a velocity at the outlet lower than found to be optimum, and if you do not obey to the 10 cm/s in the inlet, punishment is hard. A rapid glance into the above h/u curve shows that 10 cm/s would provide extremely poor performance at the column outlet. Thus the correct conclusion is that optimum velocities are far lower in a compressed gas. This is not really new: GC with vacuum at the outlet, e.g. with GC-MS, is even faster.

Nitrogen has only drawbacks and is not suitable for capillary GC. Helium is as good as hydrogen if inlet pressures are below about 50 kPa. but requires slower GC at higher inlet pressures (for longer columns), the difference being roughly a factor of two when 150-200 kPa must be applied for helium.

The most important argument against the use of hydrogen concerns safety. The next "Korner" will report on how our lab solved that problem.

Figure 4:

Compressibility of the carrier gas causes the gas velocity in the inlet to be lower than in the outlet.



[1]*from Rohrschneider, Ullmanns Enzyklopädie der technischen Chemie, Vol. 5.*

I welcome your feedback. Reach me by e-mail at Koni@orob.oro.

Capillary GC Reference Books

by Dr. Konrad Grob

On-Column Injection in Capillary Gas Chromatography, 2nd Edition

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On-column injections minimize detrimental adsorption and non-linearity problems associated with split/splitless techniques. Grob's text is a must-read treatise for the novice as well as for the experienced chromatographer. Basic technique is explained clearly with excellent schematics.

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Huethig Publishing, Ltd., 1993 • 547~~.
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