Impact of GC Parameters on The Separation

Part 6: Choice of Carrier Gas and Linear Velocity

Jaap de Zeeuw, Restek Corporation, Middelburg, The Netherlands.

In part 1-5 of this series we focused on the selection of the column dimensions and stationary phase. We also saw that temperature has a big impact on the chromatography. The last two factors that are somewhat related, are the choice of carrier gas and the setting of linear gas velocity, as shown in Figure 1.

Type of Carrier Gas

In GC there are only a few choices for the carrier gas. The most popular ones are helium, hydrogen and nitrogen. For some specific applications argon is used.

The carrier gas in itself does not impact the separation in GC. This is quite different from LC, where the mobile phase can be modified many ways to enhance selectivity. In GC the choice of carrier gas is defined by a number of factors:

Availability: This may seem an obvious factor, but in recent years, availability for helium has become a bigger challenge. Gases like N_2 and H_2 have no issues at all, as they can even be produced in the lab using generators. Helium cannot be manufactured and must be extracted from a natural resource like natural gas. Because of the insecure supply, labs are looking for alternatives.

Price: each carrier gas also has a cost. Also here helium is a challenge as it's already expensive and expectation is, that the prices will only go up. As a result there is a strong interest in using other types of carrier gas.

Purity: This is an interesting parameter in GC. We always choose the most "pure" carrier gas. You can buy carrier gases with high grade being 99.9999 % pure. You also can buy 99.999 % pure and the price difference is interesting. Some groups buy a less expensive carrier gas and completely rely on the capability of the in-line filters. Bottom line is, that for trace analysis, one needs to optimize the whole system. You need to be assured the carrier gas used to work an expensive GC-MS setup, is clean.

Speed of Analysis: If analysis speed is important, the carrier gas choice will be directed to the gas that delivers shortest analysis time.

Figure 1

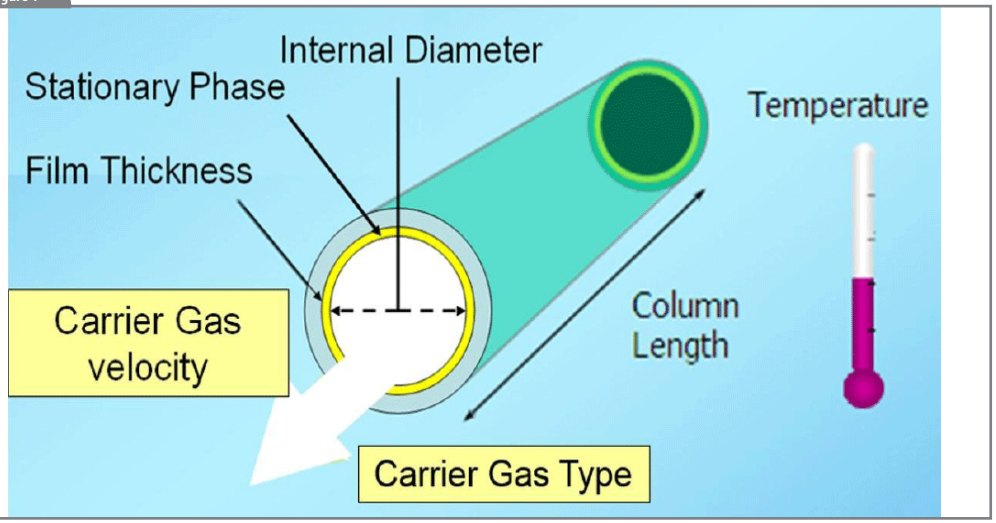

Figure 1: The 7 factors that impact separation in GC: here we focus on carrier gas type and linear velocity.

Figure 2

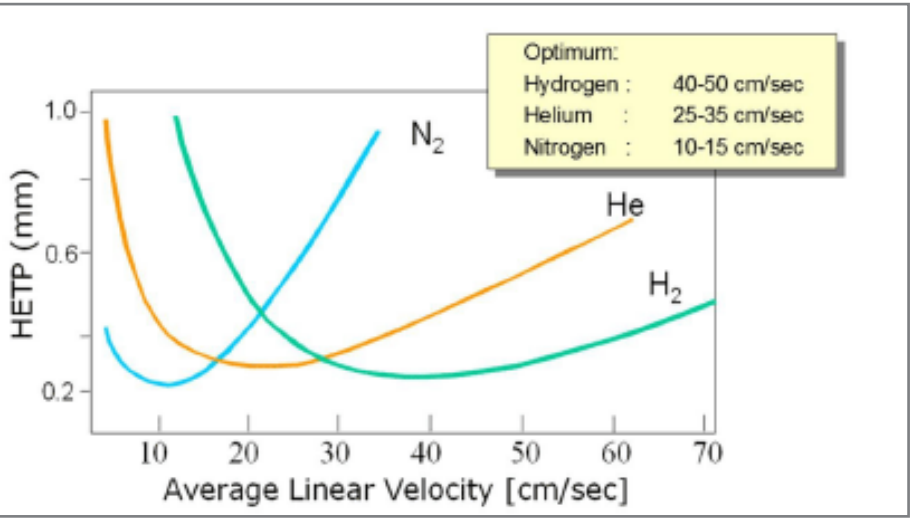

Figure 2: Van Deemter curve for nitrogen, helium and hydrogen.

Without any question, that would be hydrogen. Figure 2 shows the van Deemter curve, where hydrogen has an optimum velocity of about 40-50 cm/s. Once hydrogen is chosen, questions will pop up on safety. How dangerous is hydrogen in reality when used as a carrier gas?

Safety: Here the use of hydrogen raises questions that need to be answered. Using nitrogen or helium, the safety question is not valid, so that's easy. However, if a faster analysis or a different carrier gas is required, one needs to consider the impact.

Sensitivity: For several detectors, it is required to use specific carrier gases because of sensitivity reasons. The TCD will provide highest sensitivity if hydrogen is used as the carrier gas. This is due to the high thermal conductivity of H_2.

If PDD/HID is used, we are restricted to use helium as the carrier gas. In MS helium is also widely used, but also here, hydrogen shows to be promising. Nitrogen and MS usually will result in reduced sensitivity that can be up to a factor 20.

Helium as the Carrier Gas

This is a "neutral" and inert carrier gas and has a lot of nice features. It offers an optimal linear velocity that is 2.5 times higher then nitrogen, allowing fast analysis. It also works nicely in combination with MS techniques, as it has a small mass and very few artifacts can be formed. Mass spectra are predictable and people like that. There is an interest to replace helium, mainly driven by availability and cost. A good substitute is hydrogen, but there are concerns, which will be discussed later.

Helium is a very small molecule and because of the size it has a unique characteristic: One of the unique characteristics is, that it diffuses through the fused silica wall. The speed of diffusion is slow, but if measured, it will take about 48 hours to completely evacuate a helium filled and sealed fused silica column. The driving mechanism is the concentration gradient. This will not happen with hydrogen or another gas as molecules are too "big". The practical impact is, that when a helium filled column is stored, the helium will be replaced by air, and you are actually storing columns under air. Figure 3 shows a simple experiment that shows this effect: A standard Rxi-5Sil MS was filled with helium, and flame-sealed (Figure 3A). After 17 hours, one end was opened and immediately positioned into a solution of black Indian ink. Because

Figure 3

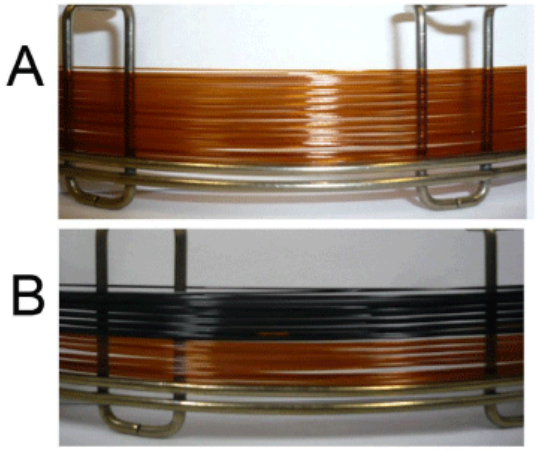

Figure 4

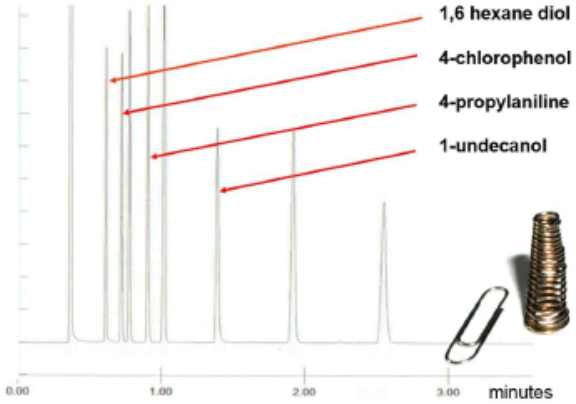

Figure 3: Example of helium diffusion through fused silica. A: column filled with helium and flame sealed. B: after 17 hrs, opening one end under Indian ink. The ink is sucked into the column because there is a vacuum inside the fused silica.

Figure 4: Example of Inertness of MXT tubing. Column: MXT metal, Siltek deactivated, film 0.1 µm 5% phenyl siloxane.

of the vacuum inside the column, the ink is "sucked" into the fused silica, showing the dark bands (Figure 3B. See also [1].)

Helium is a by-product of the exploitation of natural gas. One of the biggest producers of helium in Amarillo, Texas, are cutting down production, which impacts availability and price. Alternate sources will develop, but it will take time. In the Middle East, (Quatar) also natural gas is produced and also here helium is available as a by-product. The question is, when this will be available as a commercial product. Whatever happens, the price of helium will still be a challenge.

Hydrogen

It is correct that hydrogen is explosive, as when hydrogen is discussed we all think about the accident hat happened with the "Hindenburg Zeppelin" [2]. What are the chances a problem develops using hydrogen? In our labs we have been testing millions of GC columns and never saw an issue, so how big is the risk? Hydrogen-air mixtures become explosive if the hydrogen concentration gets above 4%. Hydrogen can enter the oven when the injection connection is not leak tight or when the column breaks. Practically when the column breaks in the middle or at the end, the flow of hydrogen that the column delivers is very small. This is a few mL/min and can never build 4% hydrogen concentration.

The biggest risk is when the column breaks at the inlet. THEN the hydrogen will be released in the oven and a risk can develop.

So, how can we reduce or control that risk? One way is to use a flow-controlled analysis. Flow control will limit the amount of carrier gas. When the column breaks, the system cannot set the desired flows (pressure does not built up), and the system jumps in relative short time in its "stand-by" mode.

One can also increase safety by using metal GC columns. Today's metal (MXT) are very inert and can compete with fused silica for many applications. Figure 4 shows an example of such a non-polar metal column where highly polar compounds such as hexane diol and chlorophenol elute as sharp peaks. If one wants to minimize risk of column breakage, MXT remains a very interesting choice.

Hydrogen as a 1:1 Replacement for Helium

Hydrogen has a higher optimal linear gas velocity. One of the big benefits of using hydrogen is always, that you can reduce analysis time. But… suppose if I do not want to reduce analysis time? You are happy with your method. Can I replace helium for hydrogen with my present method and continue my

Figure 5

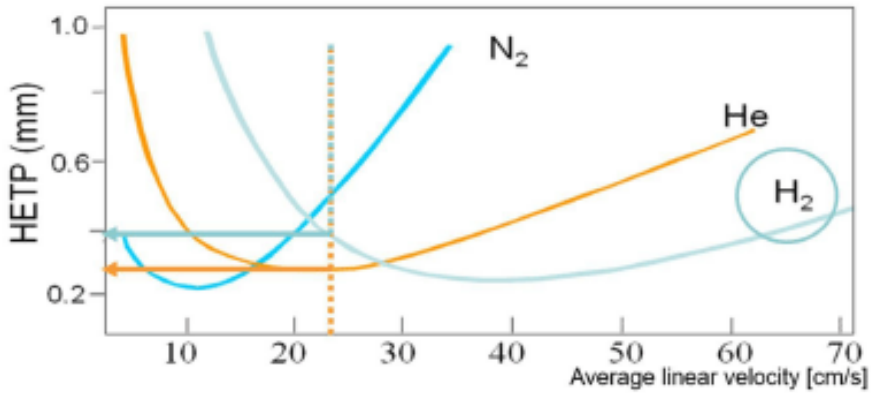

Figure 5: Van Deemter PLOT showing linear velocity and expected loss in efficiency H_2 if operated under "He- optimal velocity. There is a loss of about 20% in HETP.

Figure 6

Gas	Average velocity [cm/s]	Inlet pressure [kPa]	Flow [mL/min]
Helium	30.0	98.16	1.27
Nitrogen	30.0	87.93	1.23
Hydrogen	30.0	43.05	1.02

Figure 6: Inlet pressure and flows for setting linear velocity of 30 cm/s for helium, nitrogen and hydrogen. Note that for setting the same velocity, the H_2 flow is 20% lower then helium.

measurements without changing the method?

This is a very valid question, and the answer is "yes", you can. If you use hydrogen at the SAME linear velocity of helium, you are not working in the optimum and you will lose some efficiency. The loss however, will be very small. To get the same separation, it is important to make the components elute at the same temperature. Practically that means that the average linear gas velocity must be the same.

If hydrogen is used as the carrier gas, the compressibility will be different. That means that inlet pressures have to be corrected for that. One has to be careful using FLOW settings as due to compressibility, linear velocities are quite different. Figure 5 show what is done here. The brown curve is helium and the blue is hydrogen. We are now operating a GC column under approximately the same linear velocity as helium, but using hydrogen. We can expect a loss of efficiency of about 20%. Figure 6 shows the pressure required to set a linear velocity of 30 cm/s using a 30m x 0.25mm Rxi-5Sil MS. For Hydrogen, the flow is only 1.02 mL/min to get 30 cm/s, while for helium, one needs a flow of 1.28 mL/min. for approximately the same linear velocity. This is very important. There is a new method development tool, called the EZ-GC flow calculator, that makes it very easy to calculate the settings, see ref. [3]. Figure 7 shows a snapshot of the flow calculation, using a 30m x 0.25mm capillary. When this flow is used, the temperature programme can be the same and also the analysis time will be comparable.

Figure 8 shows a practical example, where a complex sample of pesticides was analysed using helium AND hydrogen using same linear velocities and same oven conditions. Note that the flow for H_2 was 1.06 mL/min to obtain average velocity of 34 cm/s, while for helium a flow of 1.4 mL/min was required for the same linear velocity. Separation is exactly the same.

Practically it is possible to change to hydrogen, and use the exact same method, as long as the average linear velocities are kept very close. See also ref [4].

Other Risks of using Hydrogen

Hydrogen is also used as burning gas for a FID. If the column breaks near to the detector side, also the H_2 from a FID will enter the GC system. This can be around 15 mL/min. while the detector remains burning. Many people do not realize this and I have not heard anybody making an issue of this.

Also hydrogen is a reducing gas. For example, when analysing for styrene, the temperature of the

Figure 7

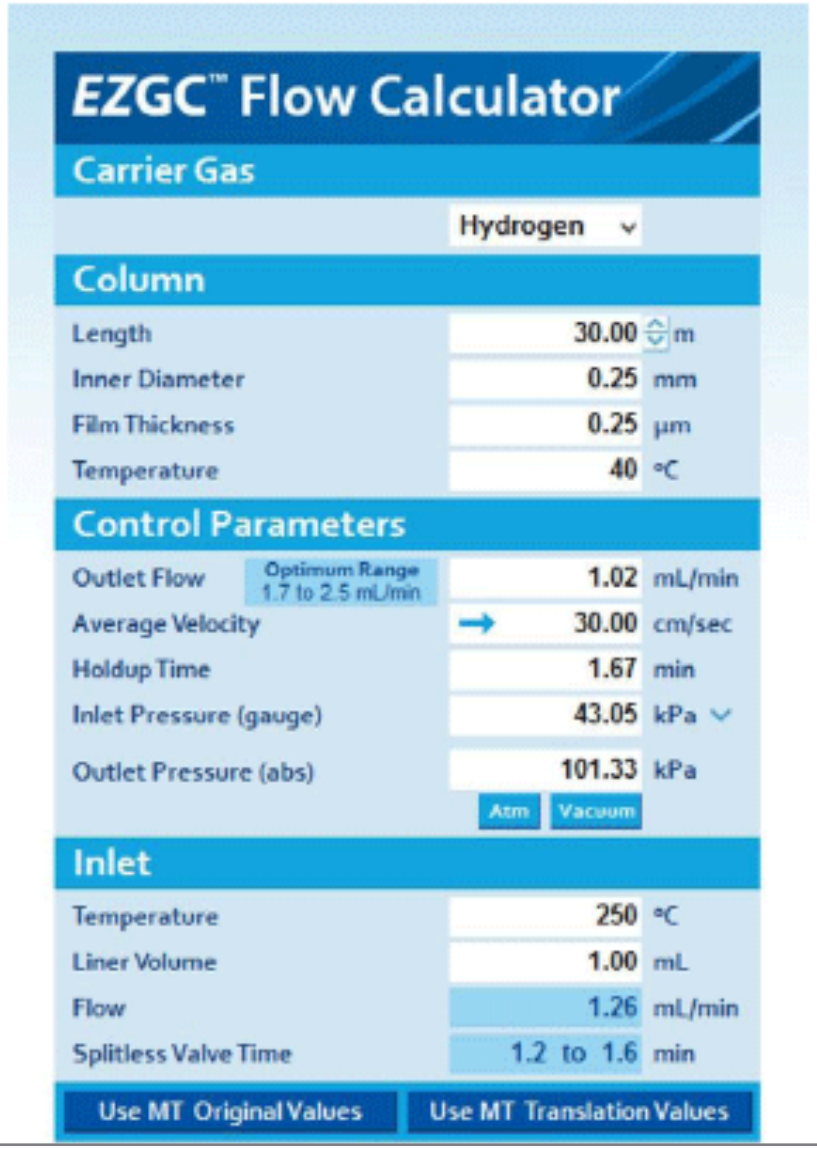

Figure 7: Flow calculation example for a method conversion from helium to hydrogen, aiming for the same 30 cm/s linear velocity. Flow set at 1.02 mLmin for H_2 (helium was 1.27 mL/min). Column 30 m x 0.25 mm, df = 0.25 µm.

Figure 8

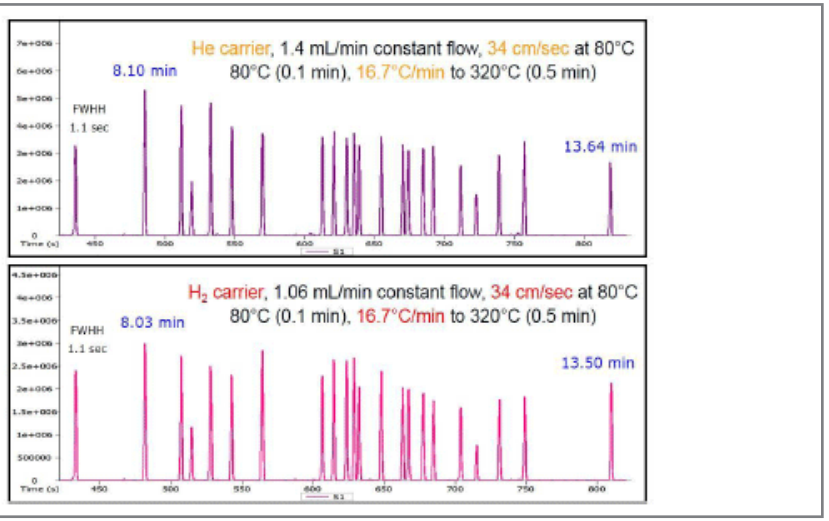

Figure 8: Example of method conversion as proposed in Figure 7. Separation of a pesticide mixture at 34 cm/s using helium and hydrogen, while using the same oven programme. As expected separations and analysis time remain the same; virtually no loss in separation efficiency.

injection port must be kept lower then 150 °C to reduce the formation of ethyl benzene during injection

Nitrogen as the Carrier Gas

Because of all the discussion on using helium and its availability, there is also an increased interest in using nitrogen as the carrier gas. Nitrogen is generally recognized to be a "slow" carrier gas because of its low optimum gas velocity. If nitrogen is used under optimal conditions, the analysis times are 2-2.5 times longer then using helium.

Practically nitrogen can be used for many applications, but it depends on the separation required. If the components are WELL separated, the use of nitrogen usually is not a problem.

Because the selectivity if the phase used is very high, it is possible to keep this separation with less efficient columns.

The PRACTICAL consequences of using a less efficient separation system, one needs to be aware off are as follows:

- Peaks will run into each other faster upon "aging". One must be aware to use more column maintenance

Figure 9

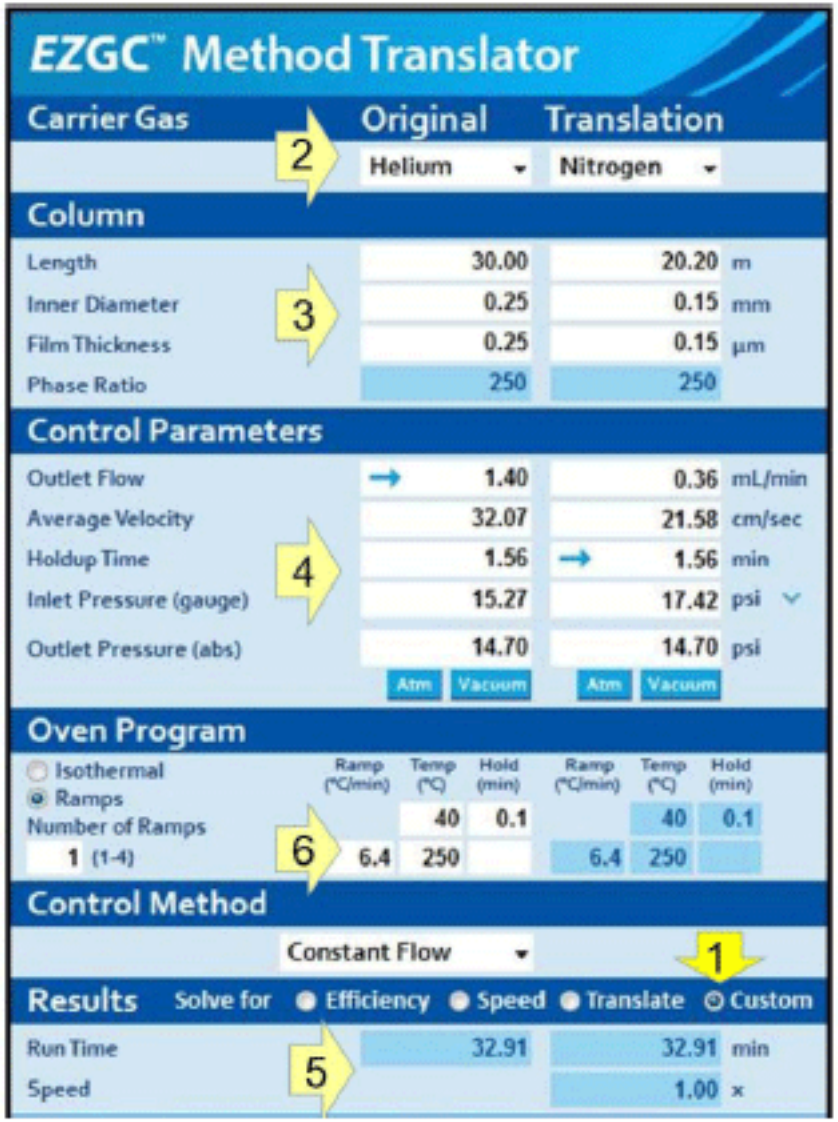

Figure 9: Screen shot of method translation showing the impact on parameters when changing column dimensions from 30m/0.25/0.25 and helium under efficiency optimized flow/velocity, to 20m/0.15/0.15 and using nitrogen. Operating nitrogen at 0.36mL/min shows the same analysis time and the same programming conditions.

Figure 10

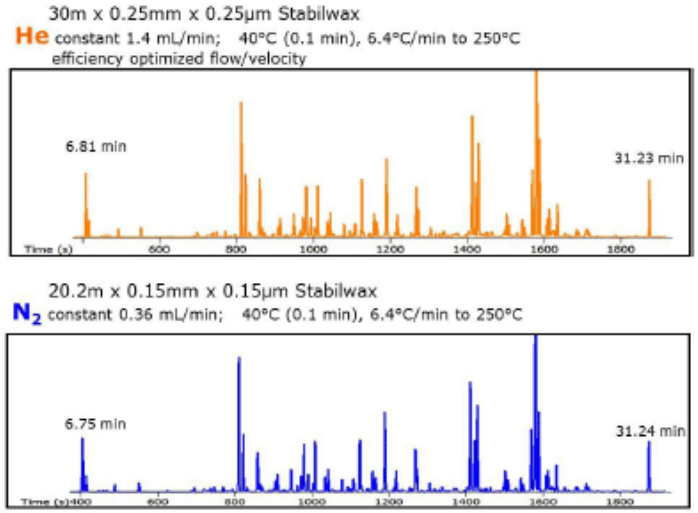

Figure 10: Separation of fragrance mixture on a 30 m x 0.25 mm Stabilwax, 0.25 µm using helium under efficiency-optimized flow/velocity of 1.4 mL/min and on a 20 m x 0.15 mm Stabilwax , 0.15 µm, using nitrogen at 0.36 mL/min. Both chromatograms recorded with similar temperature program. Separation, void- and analysis time are identical.

- Column life time will be shorter. That means that with same column less samples can be analysed. This is a physical reality as a result of using nitrogen. Do not blame the column or manufacturer.

Nitrogen as well as hydrogen can be produced in the lab using nitrogen generators. Make sure that you install purifiers when you plan to use these gases as a "carrier gas" in GC.

A very interesting application of nitrogen as the carrier gas we discovered recently, is to use it in combination with 0.15mm ID columns.

If a 20 m x 0.15 mm column is used instead of a 30 m x 0.25 mm, and helium is replaced by Nitrogen, one can get exact the same separation efficiency and analysis time, as using helium. A snapshot of the translation is shown in Figure 9. The concept was tested practically and worked out very well (see Figure10. For details see [5 and 6].)

The use of N_2 will also benefit the cost of carrier gas as practically the cost of gas consumption may reduce by a factor 20.

Besides costs, there is a practical advantage as when one converts to

N_2, and uses 0.15mm ID columns, the oven temperature programming can be kept the same and even the pressures are in the same magnitude. This simplifies the whole translation a lot. Exact translations can be done using the method translator, see ref. [3].

Limitation is mainly loadability. The 0.15mm columns have 4-5 time slower loadability, meaning for trace analysis, this is a bigger challenge. For all higher level methods, this is a very interesting option.

Saving Carrier Gas

In GC the amount of carrier gas actually used for the separation, is very small.

The biggest chunk of carrier gas is vented via split lines and septum flush lines. If these flows are controlled it is easy "save" carrier gas (and reduce cost).

Today's GC systems have options to save carrier gas, by adjusting the split flow a few seconds after the injection. The injection id is done with a certain split (say 1:100), which means 100 mL/min of carrier gas escapes via the split-vent. Using the gas-saving option, one can reduce that flow to a much smaller value (fe 10 ml/min), and a lot of carrier gas is saved.

References

[1] http://blog.restek.com/?p=568

[2] http://en.wikipedia.org/wiki/Hindenburg_disaster

[3] http://www.restek.com/ezgc-mtfc

[4] http://blog.restek.com/?p=11102

[5] http://blog.restek.com/?p=13831

[6] http://blog.restek.com/?p=13850

Jaap de Zeeuw studied six years of chemistry and graduated in 1979. Jaap has 36 years' experience in GC capillary technology and has developed many PLOT columns as well as bonded-phase columns. He is also the originator of simple concepts for fast GC–MS using a high vacuum inside the capillary column. He has published more than 100 publications in the field of GC on column technology and application. He worked for 27 years for Chrompack/Varian and for the last six years has served as an international specialist on gas chromatography for Restek in The Netherlands.