Changing from Helium to Nitrogen and Maintaining the Separation Efficiency in the Same Analysis Time

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For several reasons, there is interest in replacing helium with a different carrier gas in gas chromatography. Hydrogen is the obvious choice but there is a concern on safety and reactivity. It is also possible to use nitrogen but this is often not considered because it has a low optimal flow and velocity. Here we will show that it is possible to replace helium for nitrogen as the carrier gas while separation, peak elution order, analysis time, response and even oven temperature conditions can be kept the same.

Summary
By using method translation and chromatogram modelling it became clear that the loss of efficiency using nitrogen could be perfectly compensated by using a smaller ID capillary of a shorter length. By replacing a 30 m x 0.25 mm column for a 20 m x 0.15 mm column, it is demonstrated that separations under nitrogen are almost exactly the same as obtained with helium, in the same analysis time, while using exactly the same conditions for oven programming. Even the inlet pressures are very close.

The only price that has to be paid is a loss in loadability, which means that this concept will not work for every application but for many it will. Besides the guaranteed availability, using nitrogen offers a big advantage in the cost and consumption volume of carrier gas, meaning cost per analysis will also benefit.

Carrier Gases
In gas chromatography there are mainly three carrier gases used: nitrogen, helium and hydrogen. Figure 1 shows the van Deemter plots, showing the column efficiency versus the linear gas velocity (one can also use flow here). Nitrogen is considered a slow carrier gas with an optimum of 11–13 cm/sec. Helium is about 2 times faster and hydrogen is the fastest gas. Because of concerns of safety and reactivity, hydrogen is often avoided and helium is the preferred carrier gas. Also there are several detection systems that prefer helium because of the detection principle. Think here about the mass spectrometer and the pulse discharge based detectors.(PDD, HID, BID).

Hydrogen
Hydrogen is an interesting alternative and has a number of advantages [1]:

- It has a high optimal linear velocity, allowing analysis time to

Figure 1

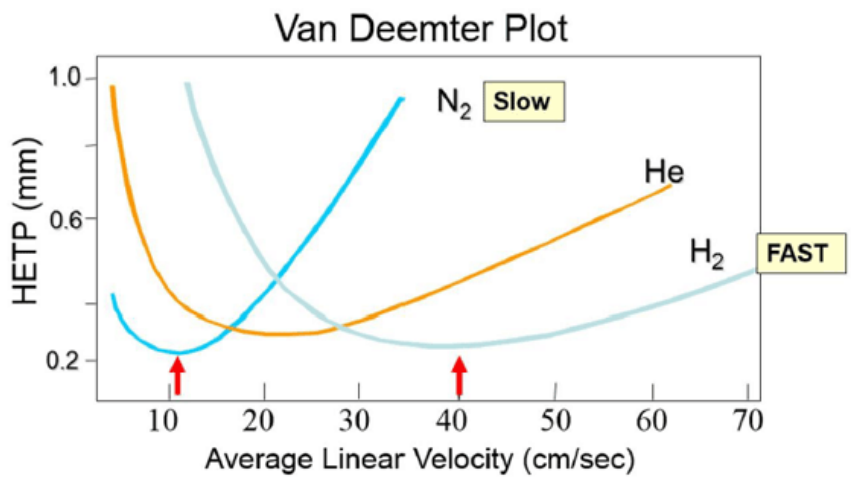


Figure 1: Van Deemter curves for nitrogen, helium and hydrogen.

Figure 2

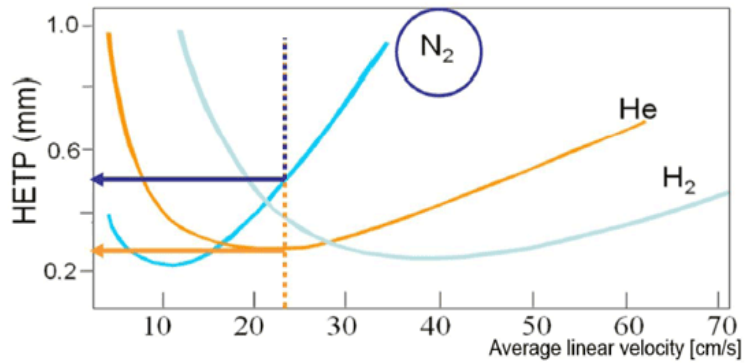


Figure 2: Van Deemter curves showing HETP loss when nitrogen is used under the optimal velocity of helium.

be shortened by a factor of 1.7

- It is widely available, cheap and can be produced in the lab using a generator
- Because of the speed, peaks are narrower and needs less sample for the same signal, benefitting the life time of liner and column.

You can even use hydrogen at the same velocity as helium and get the same chromatography: see [2]. Here also the same temperatare programme can be used. The challenges using hydrogen mostly concern safety. Despite all kinds of precautions that are already in place, many labs do not want to use hydrogen. Reactivity also remains a concern. When combined with hot inlets, components can hydrogenate.

Figure 3 shows the separation of pesticides using N_2 at higher linear velocity. This was possible, because the stationary phase used offered very high selectivity and some loss of efficiency could be afforded.

Using Nitrogen at The Speed of Helium

If nitrogen is operated under optimal flow conditions, analysis time will be 2–2.5 times longer and this will not be appreciated. Nitrogen can also be used at the same velocity as helium. Figure 2 shows what we can expect using the van Deemter curve. Because of the higher speed, there is a loss of theoretical plates of about a factor 2. You can use the same oven conditions as used for helium. The chromatogram will be the same but only peaks are a little broader and about 30% lower in intensity.

For separations that are good enough this can be an interesting approach. The practical implication one has to realize, are:

- Because peaks are broader, the peaks will merge faster upon column ageing. That means that the number of analyses that can be done under these conditions will be smaller. You will have to use more columns and cost per analysis will increase.
- For the same reason the maintenance intervals will be shorter.
- Peaks are lower in intensity, so there is a sensitivity loss.

Figure 3 shows the separation of pesticides using N_2 at higher linear velocity. This was possible, because the stationary phase used offered very high selectivity and some loss of efficiency could be afforded.

Using Nitrogen and Compensation for The Loss of Efficiency Using a Different Diameter Capillary

It has been known for a long time that analysis time can be shortened

Figure 3

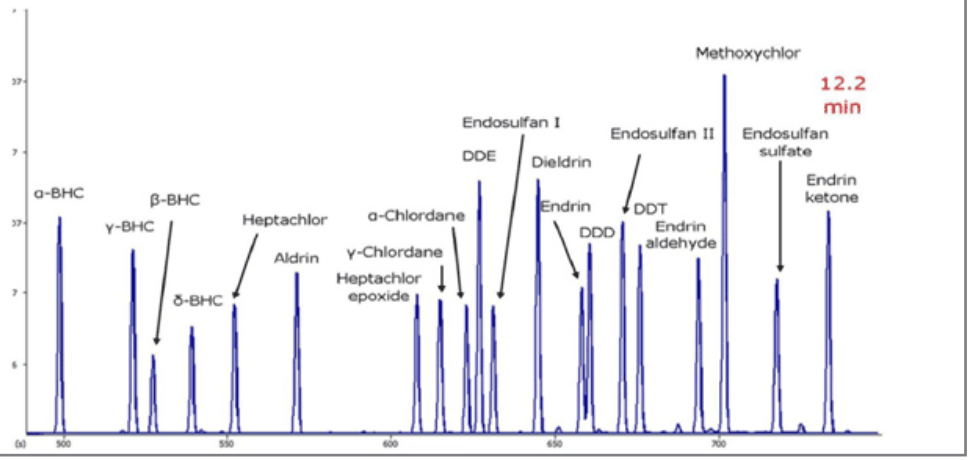
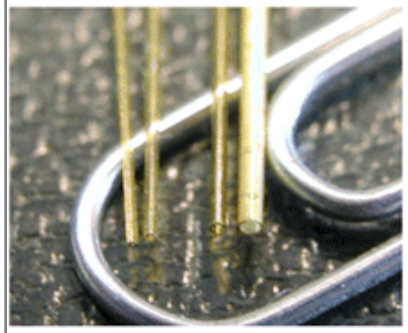


Figure 3: Example of using nitrogen at higher velocity. Pesticides on Rtx-CI-Pesticides. Because this phase is very selective, the loss of efficiency due to operation under nitrogen will not be a problem.

Figure 4



60 m x 0.53 mm => 120.000 plates

30 m x 0.25 mm => 120.000 plates

20 m x 0.15 mm => 120.000 plates

Figure 4: Relation of column diameter and plate number.

using a smaller diameter capillary [3]. The same separation can be obtained using a shorter length column. Figure 4 shows a series combination of column diameters and length required for 120.000 plates. It is clear that shorter columns will provide faster separations.

Practically 0.15 mm columns have proven to be very effective and can be coated with different phases with phase ratios to match the capillaries that are available in 0.25 and 0.32 mm columns.

What makes this exercise especially interesting is that the optimum flow/velocity also increases when internal diameters are reduced (see Figure 5). 0.15mm columns can be operated at relatively higher linear velocity and this is what we will use. The figure shows helium as carrier gas but with nitrogen the increase of optimum will also be comparable.

In this experiment a 30 m x 0.25 mm capillary with 0.25 um film operated under helium was substituted for a 20 m x 0.15 mm capillary with a 0.15 um film, which was operated under nitrogen. The stationary phase and phase ratio was kept the same. The method translator[4], that was recently made available by Restek, will be used to calculate conditions.

Figure 6 shows a snapshot of the data obtained using the EZ-GC method translation. As this is a custom calculation the translation is done in a "custom" mode.

1. Shows the custom option
2. Shows the carrier gas selection
3. Column dimensions, original 0.25 m and the new 0.15 mm
4. Hold up times are set at a SIMILAR value (gas velocity for nitrogen will be higher then optimal)
5. To check the analysis time, these values should be similar: exact same run time
6. Shows the temperature programme, which will also be exactly the same.

We see that when the hold-up times are matched, the exact SAME temperature programme can also be used and the result is that the analysis time will also be exactly the same. Also note that the pressures required for nitrogen are just a little higher then the pressure required for helium. The big question is: how much resolution is sacrificed when this exercise is done? Running nitrogen at a higher velocity will cost efficiency. Also what is the benefit of using the SAME temperature programme?

Using the Same Temperature Programme

Normally when changing column dimension or linear gas velocity, the temperature programme has to be adjusted to obtain the same separations and peak sequence. If the temperature programme is NOT adjusted the components will elute at different temperatures and

Figure 5

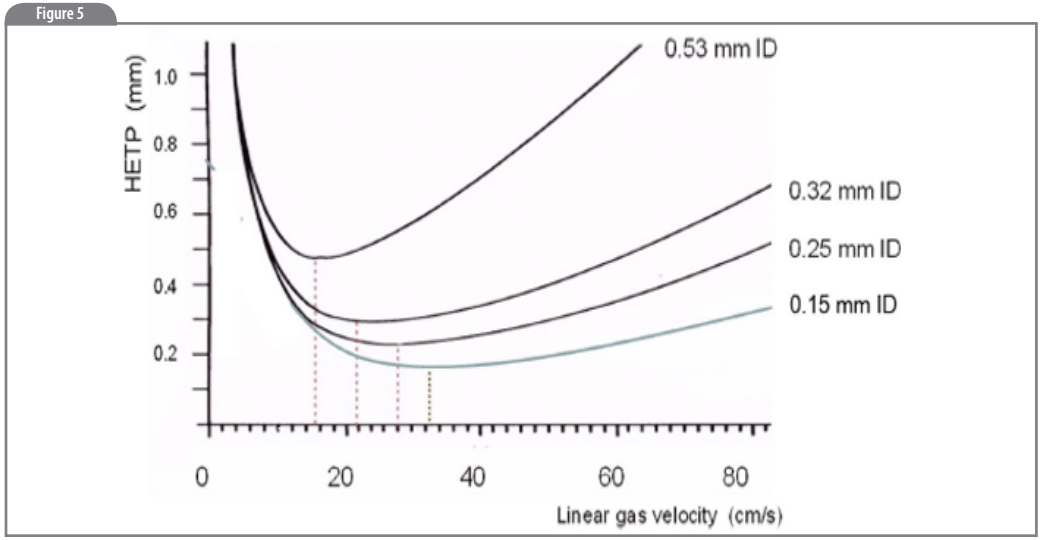


Figure 5: Van Deemter plots for helium and different diameter capillary columns. Optimum velocities move to the higher values with decreasing ID.

Figure 6

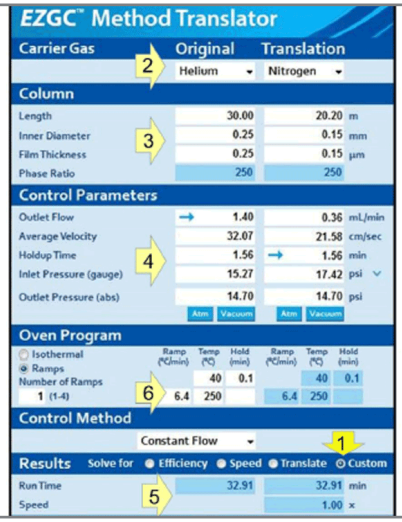


Figure 6: Screen shot of method translation showing the impact on parameters when changing column dimensions from 30m/0.25/0.25 and helium under efficiency optimized flow/velocity, to 20m/0.15/0.15 and using nitrogen. Operating nitrogen at 0.36mL/min shows the same analysis time and the same programming conditions. Numbers are explained in the text.

the separations can become worse and even peak swapping can occur. Figure 7 shows an example of a complex mixture using the similar column under different conditions, where elution temperatures are changed. As can be seen, just by having around 15 degrees different elution temperatures, the elution profile and separations completely change. Several areas (in red) show different separations, even peak reversal will happen. To prevent this, it is important that when flow, carrier gas or column dimensions are changed, the oven temperature programmes must be changed also. The goal is to have the same elution temperatures of all compounds. If elution temperatures are similar, the chromatogram will be similar.

In our exercise here, when using nitrogen, the void time was adjusted using a smaller ID column and this way it is possible to use the SAME temperature programme. This automatically means that peaks elute at the same temperature and the chromatogram obtained will be very similar and it also happens in the same time frame.

The loss in efficiency using nitrogen at higher speed is a concern but as shown in Figure 5, the optimum for nitrogen will move to a higher value, using 0.15 mm ID.

Practical Experiment

In order to proof the concept, a 30 m x 0.25 mm Stabilwax column with a film of 0.25 µm and a 20 m x 0.15 mm with a film of 0.15 µm were compared using helium and nitrogen as the carrier gas. The sample chosen was a perfume containing many components of different chemical nature. The analysis was initially done under helium using the 30/0.25/0.25 using the efficiency-optimize flow/velocity (1.40 mL/min) and after this the 0.15 mm ID column was installed and operated under the conditions as calculated with the method translator (see Figure 6). To match the void times, a flow of 0.36 mL/min was required. As expected, the translator calculated the same programming conditions and also the same retention time.

Figure 8 shows the chromatograms that were obtained. Separations are exactly the same and are achieved in exactly the same analysis time.

Figure 9 shows an expansion and also in detail exactly the same separations are obtained using nitrogen as the carrier gas.

The same comparison was also done using the speed-optimized flow. This is basically a velocity that is approximately 30% higher then the "efficiency-optimized flow/velocity". For helium using the 30 m/0.25/0.25

Figure 7

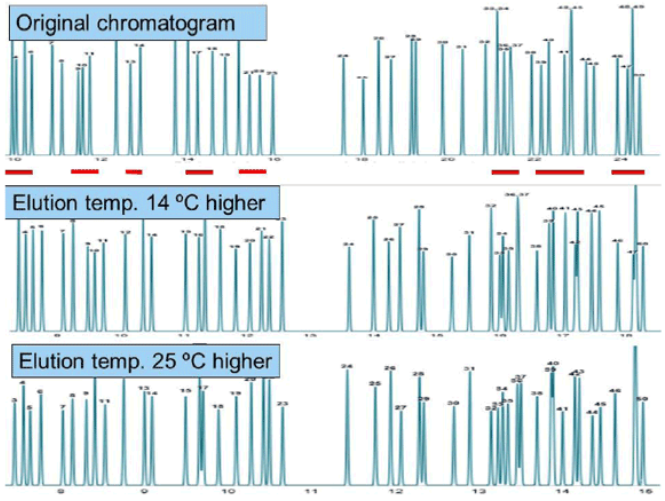


Figure 7: Impact of elution temperature on separation. The same components analysed on the same column using different oven temperature programming conditions. Separation strongly depends on the elution temperature. Look specifically at underlined sections.

Figure 8

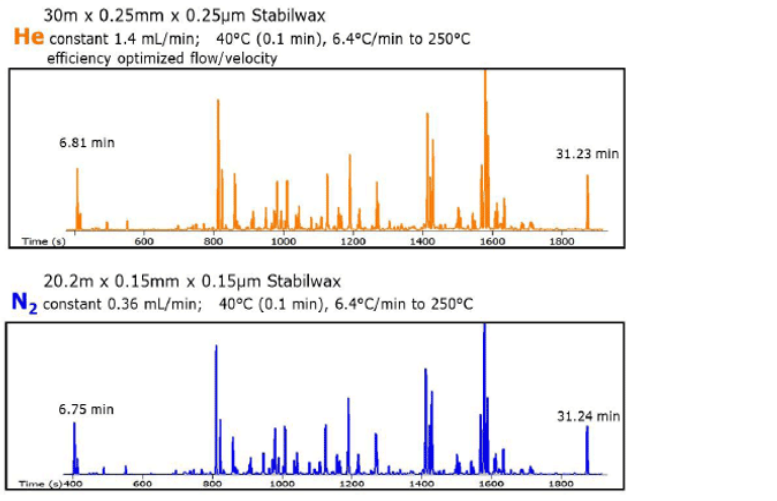


Figure 8: Separation of fragrance mixture on a 30 m x 0.25 mm Stabilwax, 0.25 µm using helium under efficiency-optimized flow/velocity of 1.4 mL/min and on a 20 m x 0.15 mm Stabilwax, 0.15 µm, using nitrogen at 0.36 mL/min. Both chromatograms recorded with similar temperature programme. Separation, void- and analysis time are identical.

this was 2.0 mL/min. The translated flow using nitrogen for the same void time was 0.52 mL/min (see Figure 10).

Operation under the "speed optimized flow" will cost some separation efficiency. With regards to the analysis time, the column is operated deliberately outside its optimum. For nitrogen the loss of efficiency is usually bigger because of the slope of the right side.

As can be seen in Figures 11 and 12, even at the speed optimized flow for helium, the higher translated flow using nitrogen provides exactly the same separation. This was also to be expected as the slope of the van Deemter curve for smaller bore columns is also decreasing (see Figure 5). Besides the efficiency optimized flow, also for speed optimized flow, the void time, the analysis time and temperature programming conditions are similar resulting in the same separations.

Here it was tested using a polar, Stabilwax coated column. As the selectivity of polar phases is impacted more by temperature than non-polar phases (such as Rxi-1ms, Rxi-5ms, Rxi-XLB, etc), this exercise will work even better for non-polar phases. See also [5].

Summary of features obtained using 0.15mm columns under nitrogen:

- Separations are identical
- Analysis time is the same
- No change in oven temperature programme
- Pressure required for nitrogen is just a little higher
- Nitrogen is always available
- Price advantage for nitrogen and volume used
- 0.15mm columns have same OD as 0.25 mm: can use the same ferrules
- 0.15mm columns have proven to work for many years and can be manufactured with different phase technologies

Limitations

This conversion will only work if the 0.15 mm columns used have a comparable efficiency to the larger diameter capillary columns. Because of the smaller diameter the loadability will be 4–5 times less. When very low levels need to be measured this will be a challenge. Also the column flow of 0.15 mm ID columns is about 4 times smaller, which means that for splitless injection, the injection time must be longer or a pressure pulse must be used.

Figure 9

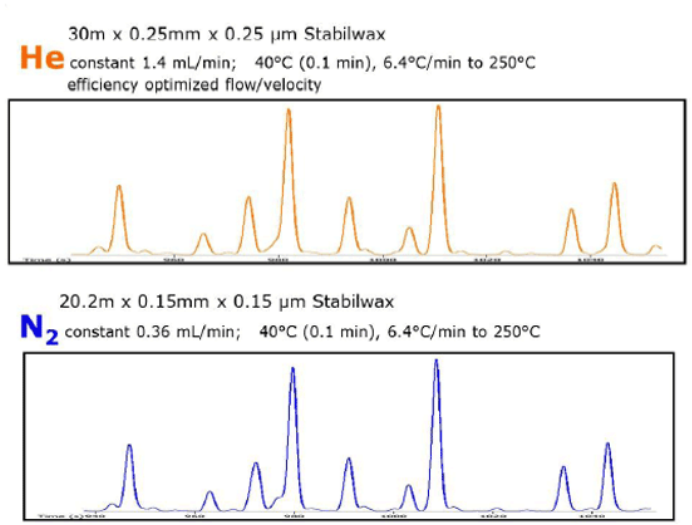


Figure 9: Detail of separation shown in Figure 8 again showing the same separation.

Figure 10

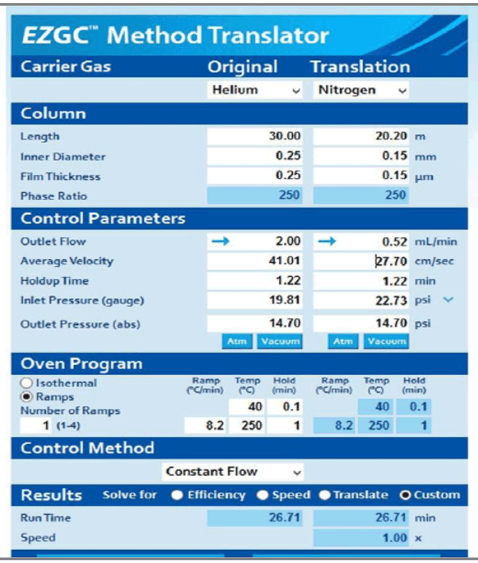


Figure 10: Screen shot of method translation showing the impact on parameters when changing column dimensions from 30m/0.25/0.25 and helium under speed optimized flow/velocity, to 20m/0.15/0.15 and using nitrogen. Operating nitrogen at 0.52 mL/min shows the same analysis time and the same programming conditions.

Figure 11

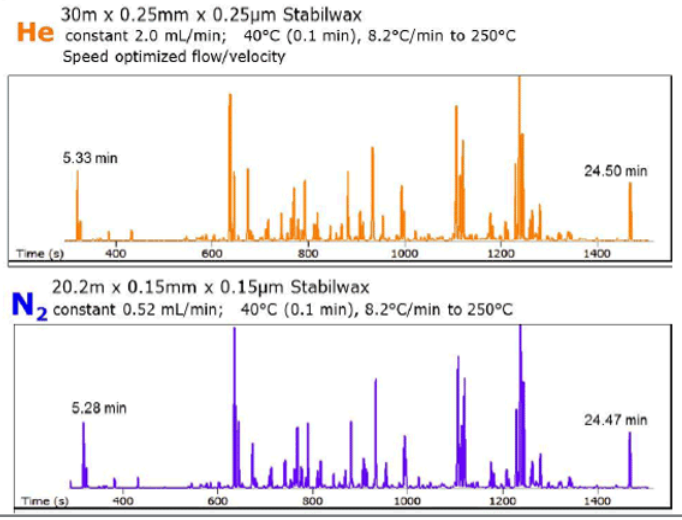


Figure 11: Separation of fragrance mixture on a 30 m x 0.25 mm Stabilwax, 0.25 µm using helium under speed-optimized flow/velocity of 2.0 mL/min and on a 20 m x 0.15 mm Stabilwax, 0.15 µm, using nitrogen at 0.52 mL/min. Both chromatograms recorded with similar temperature programme. Separation, void- and analysis time are identical.

Figure 12

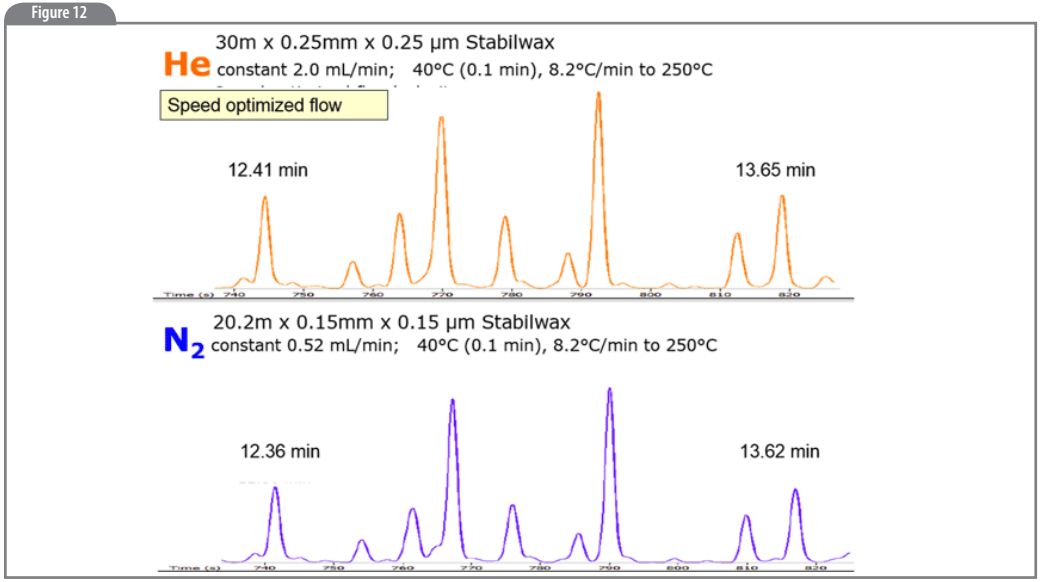


Figure 12: Detail of separation shown in Figure 11.

Conclusion

It is demonstrated that by using a 20 m x 0.15 mm column instead of a 30 m x 0.25 mm, it is possible to convert existing methods using helium as carrier gas, to nitrogen while maintaining the separation as well as the analysis time. Also the temperature programming can be kept the same. The inlet pressure for nitrogen is a little higher.

This allows many methods to be converted to nitrogen and the supply of this carrier gas is guaranteed. Additionally, nitrogen is significantly cheaper, meaning cost per analysis will also benefit. The setting of conditions has been made very easy using the method translator. The use of the method translator allowed us to calculate the predictions of this concept. The practical experiments proved that it worked.

Acknowledgement

Special thanks to Jack Cochran, Restek USA, who took his weekend time off to generate the data that demonstrates that this concept really works.

References

[1] J. de Zeeuw, Chromatography Today, Nov/Dec 2012, p.24-27

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

[3] J. de Zeeuw, Petro on line, june/july 2013, p.30-31

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

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

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.