Impact of GC Parameters on The Separation

Part 3: Choice of Column Length

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

In Part 1 and 2 of this series we focused on selection of stationary phase, and looked at different applications for using different internal diameter. Capillary columns are also available in different length. Here we look at the third parameter: column length as shown in Figure 1. What is the impact of column length on the separation? If length is changed, what do I have to do to get the results that I anticipate?

Capillary Column Length

One of the big advantages of using capillaries is that these can be made very long. It's basically an "open" tube with a very low pressure drop compared with the packed column. This way a lot of plates can be generated.

With the invention of fused silica, very long capillaries could be drawn. Figure 2 shows the wind-up drum of the Restek drawing operation. From a 1 m long tube, approximate 5-6000 m of 0.25 mm ID capillary can be drawn. The drawing is a very exact process, but it allows control on column diameter, strength and surface chemistries.

When I worked at Chrompack, I even made a coated capillary out of a 1300 m piece of tubing. This was rewarded by a certificate for the Guinness book of records. Figure 3 shows the approximate size of this column [1].

Looking at the different vendor programmes, you will find a large variety of column lengths. When columns were introduced, there was a clear difference in length of fused silica capillary columns. In Europe, Chrompack started to market 10, 25 and 50 m length columns. The same happened with SGE in Australia. The US-based companies like J&W, HP, Supelco, Restek all standardized on 15, 30 and 60 m. Once a column is used for a certain method and the method describes a certain column length, the used will always stick to that length. More experienced users will buy a longer column, and cut it to the exact length. This is, however, not common practice.

Impact of Column Length on The Separation

The theoretical plate number or efficiency, is linear with column length. Doubling the length will also double the plate number. The impact of length on separation is not as big as many would anticipate. As shown in Figure 4, the plate number is under the square. That means that by doubling column length, only a factor 1.4 is won in resolution. It also works the other way: reducing column length by a factor of 2, means that only a factor of 1.4 is lost in resolution.

Figure 1

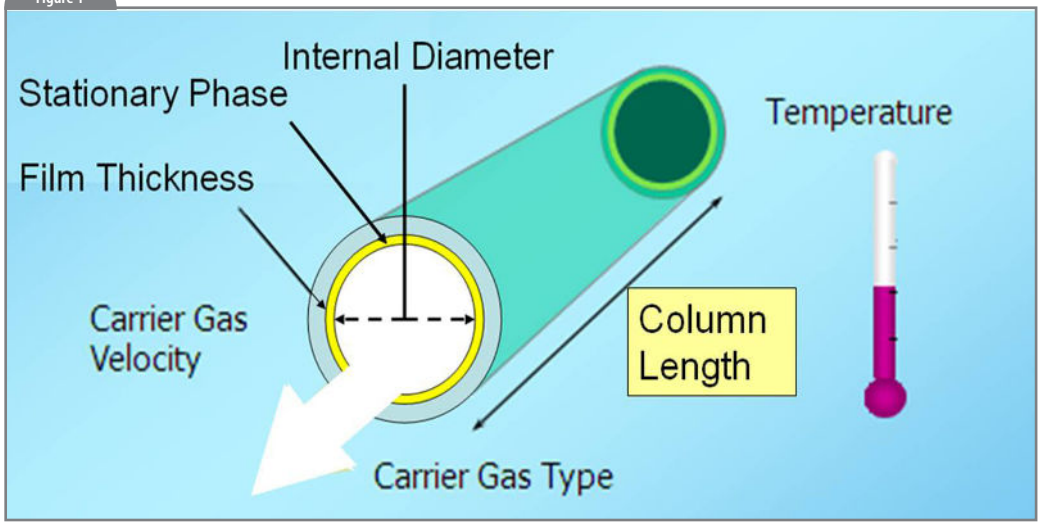

Figure 1: The 7 main parameters that impimpact separations in GC: focusing on length.

Figure 2

Figure 2: Wind-up drum of fused silica drawing tower of Restek: This drum can take up to 7 km of tubing.

Figure 5 shows chromatograms that illustrate the separation for 3 peaks using different column length. A shows the separation on a 30 m, and B is using a 15 m capillary. Peaks are baseline resolved, but analysis time of the 15 m is two times shorter. I always say: "The smarter the chromatographer, the shorter the columns gets". If the most selective stationary phase is chosen, the column length can be very short. The reality is that columns age upon application. Column aging not only means that efficiency may be reduced in time but also that injection band may broaden due to contamination and compromise the separation. For many applications it is preferable to have a little "extra" resolution.

That's why for many applications, a good starting column length is 30 m. It will generate approximate 120.000 theoretical plates when a 0.25 mm is used. Even when the column offers more plates then required, this allows the user also to trim several metres of the inlet and still get the required separations. Practically, if there is enough separation and analysis time is important, one can also run a 30 m capillary at a higher linear velocity.

Use of Very Long Capillary Columns

Very long columns are only required when very complex samples have to be separated. Such applications are for instance ASTM D 6730. This is for detailed hydrocarbon analysis, where >300 compounds have to be separated (see Figure 6). Another application is the cis/trans separation of C18:1 FAME isomers. For this a very high polarity phase (Rtx-2560) is used, which is able to provide the required isomeric FAME-separations. For such separations selectivity must be combined with high efficiency. Alternative solutions may be found in comprehensive 2D-GC, although for cis trans isomers this will not bring a lot.

ASTM D5501 [2] measurement of methanol and ethanol in E-85 biofuels, even recommends a 150 m length capillary. Biofuel(ethanol) is denaturated by adding some gasoline. The methanol, however, elutes just before the isobutane peak, (Figure 7). If low levels have to be analyzed a highly inert 150 m column is required. Note that inertness is key here as when activity is present, the methanol will move into the isobutane, compromising separation. I must say, that I have seen labs where they used 150 m columns in every GC because they wanted to have maximum efficiency. The applications, however, could be done easily on 30 m columns.

Shorter Length Capillary Columns

If selectivity is selected optimal, columns can be very short. Additionally, if efficiency has to be maintained, one can reduce the diameter and generate a lot of theoretical plates with a shorter column. This is what is done in micro

Figure 3

Figure 3: Example of what the world's longest fused silica column looks like.

Figure 5

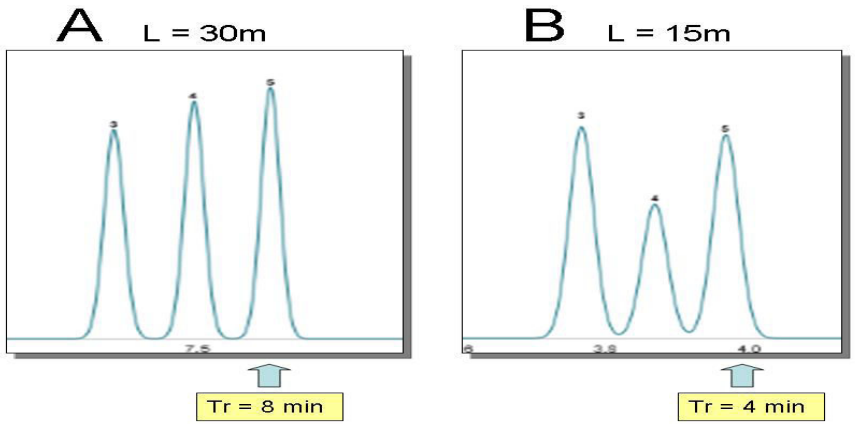

Figure 5: Impact of column length on separation: example A: 30 m and B: 15 m. Still a baseline separation is obtained. The 15 m is 2x faster.

Figure 4

$$R_S = \frac{1}{4} \times \left[\alpha - 1\right] \times \left[\frac{k}{k+1}\right] \times \sqrt{N_{th}}$$

Figure 4: Resolution equation. Plate number is under the square. Impact on R is a square function.

Figure 6

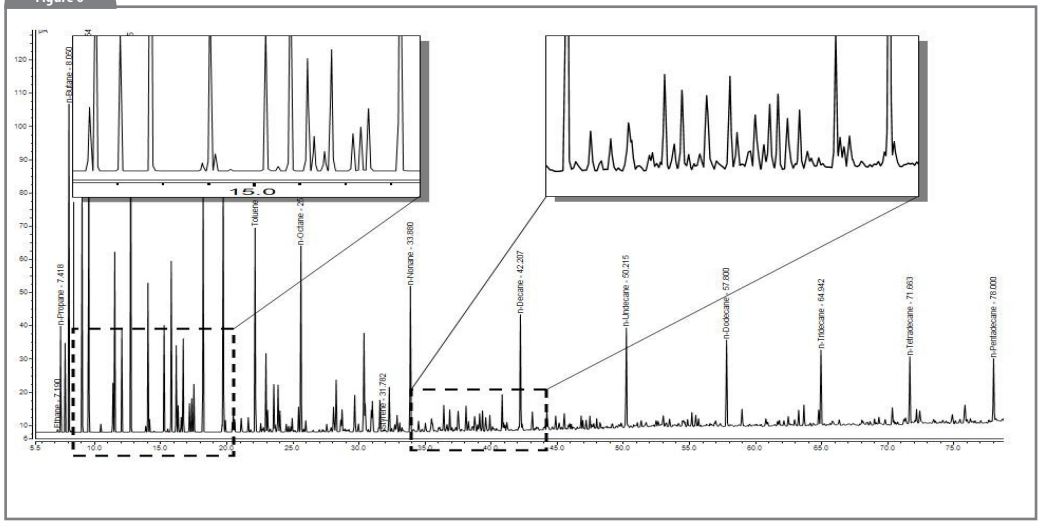

Figure 6: Example of a detailed hydrocarbon analysis using a 100 m x 0.25 mm Rtx-DHA 100.

Figure 7

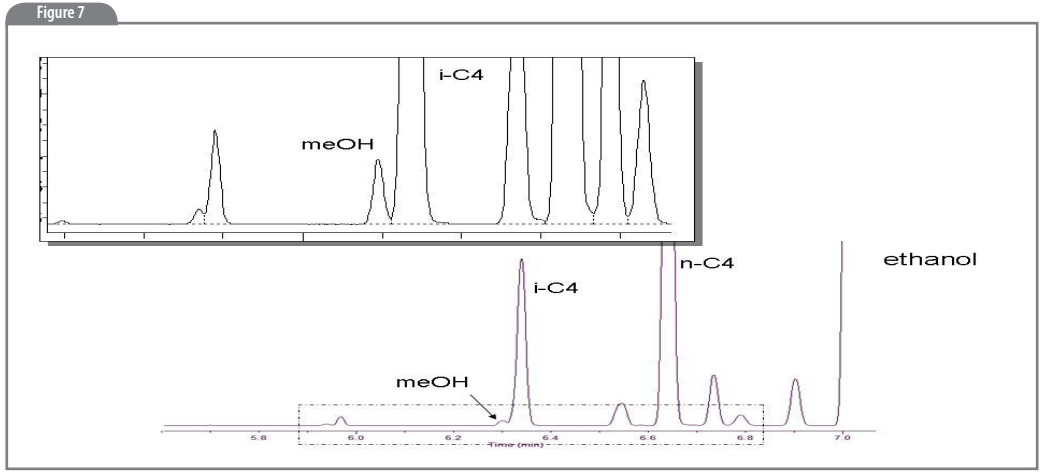

Figure 7: Running E-85 fuel (biofuel) for lower methanol levels using 150 m x 0.25 mm Rtx-DHA-150 df = 1 um; Oven: 60 °C; Zooming in the front end for methanol response.

Figure 8

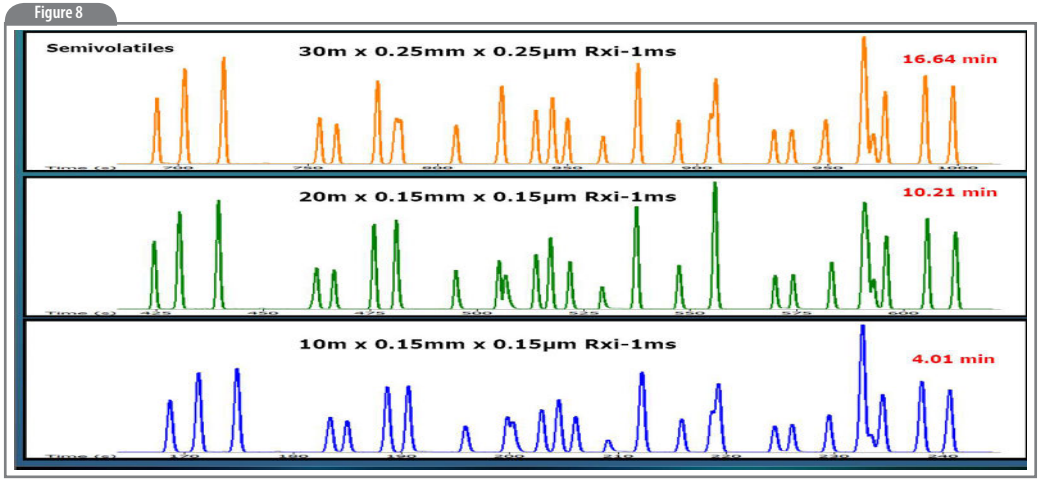

Figure 8: Comparison of separations on different column length: Top: 30 m x 0.25 mm, Middle: 20 m x 0.15 mm, Bottom: 10 m x 0.15 mm. All columns with the same phase and phase ratio.

GC applications. A 10 m x 0.10 mm will generate same efficiency as a 25 m x 0.25 mm. Using shorter columns and smaller diameter, one must deal with the risk of injection errors. That's why in most portable micro-GC applications, chip injection loops are used that can accurately inject nanolitre amounts. [3].

Moreover, short length capillary columns are used where high boiling materials have to be analysed and when efficiency is not very important. In a previous part of this series, we already showed the use of 5 m x 0.53 mm to do hydrocarbon analysis up to C120 [4].

Shorter length columns are a good way to go if one is concerned about analysis time and cost per analysis, however, one must realize that the operation of shorter columns will put more stress on injection quality. Any injection error will show significantly faster on a shorter column.

Figure 8 shows an interesting comparison. The same analysis of semi-volatiles was done using a 30 m x 0 25 mm, a 20 m x 0.15 mm and a 10 m x 0.15 mm. The oven temperature programming conditions were all translated to make sure the components on all the columns elute at the same elution temperature. There is a new EZ-GC method translator available as free-ware. This translator is both, web-operated, see [5], or it can be downloaded as a windows program [5]. It's extremely powerful and easy to use. The first 2 columns have the same number of plates, which also results in the exact same separation. The only difference is the analysis time that is shorter using the 0.15 mm. Moving from a 20 m to a 10 m will again reduce run time but as the diameter is the same, there are also 2x less plates resulting in a decrease of separation. If MS is used this may be acceptable, but for detectors like FID this will not work.

Very Short Capillary Columns

In Comprehensive GC (Real 2 dimensional gas chromatography), a very short capillary is used in the second dimension. Such columns are 1–2 m in length meaning the separations take place within 5–8 seconds. Injection quality is critical, which is only possible using the efficient modulators that are used for this technique. In a normal GC setup, it would be impossible to inject onto such short columns.

References

1. http://blog.restek.com/?p=5402
2. http://www.astm.org/Standards/D5501.htm
3. J. de Zeeuw et al., *Am.Lab.*, Dec 2002, p.26.
4. B. Burger, J Pijpelink; http://www.restek.com/Technical-Resources/Technical-Library/Petroleum-Petrochemical/petro_A022
5. http://www.restek.com/ezgc-mtfc

Jaap de Zeeuw studied six years of chemistry and graduated in 1979. Jaap has 35 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.