# Impact of GC Parameters on The Separation

## Part 5: Choice of Column Temperature

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**In parts 1, 2, 3 and 4 of this series we focused on the selection of stationary phase, column length, ID and the film thickness. Besides the column specific parameters, there are three non-column specific parameters that impact the separation. These are the type of carrier gas, its linear velocity and the temperature of the column. Here we look into the effects of temperature on separations as shown in Figure 1.**

### Oven Temperature

The temperature is a very important parameter to influence separation. As a rule of thumb, for every 15 °C higher or lower, the retention of a column decreases or increases by a factor of 2. That means if the last peak elutes at 100 °C after 10 minutes, it will elute at 5 minutes at 115 °C and at 20 minutes at 85 °C.

Looking at the resolution equation, as seen in Figure 2, temperature will mainly impact the k/k+1 term. When k is low, reducing the temperature will increase this term in a near linear way, which directly impacts the resolution in a linear way.

Figure 3 shows an example of the impact of temperature on retention and separation. Because the k-factor was very low at high temperature, separation is poor. By decreasing oven temperature the k factor increases, which strongly impacts the resolution between the C1-C5 isomers.

Besides a big impact on k, the temperature also impact selectivity (= α factor ), which we will discuss later in this article.

Isothermal separations are always preferred over programmed analysis as they are the most accurate, easy to set up and control. It depends, however, on the range of compounds that have to be separated. If isothermal analysis is not possible a temperature programme is used.

Temperature programmes are typically used when:

- there is a wide range of components to be separated; (volatiles and semi-volatiles)
- the sample contains high boiling material that has to elute from the column
- the sample contains products that impact the retention of the stationary phase (like water on alumina or Molsieve 5A)
- If the sample must be injected

Figure 1

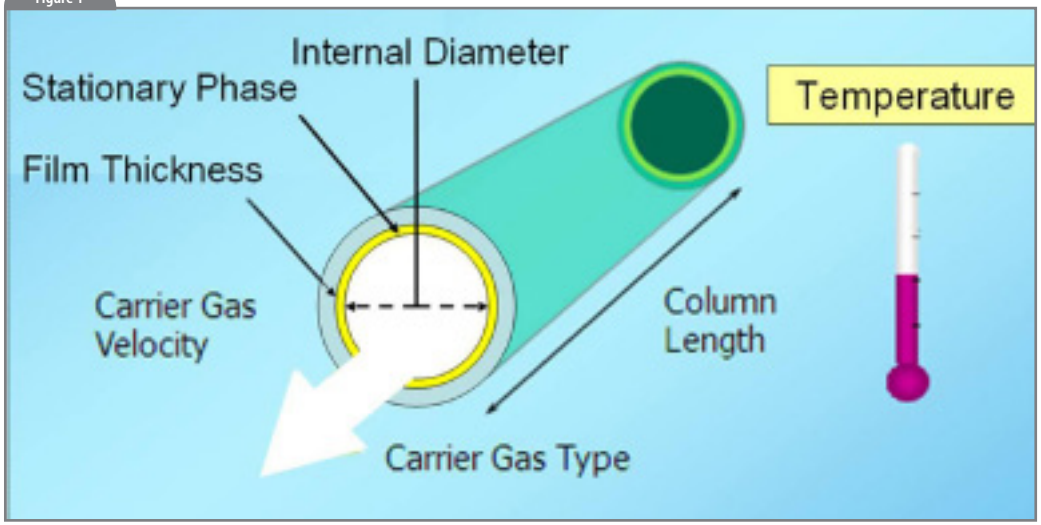


**Figure 1: The 7 main parameters that impact separations in GC: focusing on temperature.**

Figure 2

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

2 1

**Figure 2: Resolution equation: retention factor k is primarily impacted by the temperature.**

at a lower temperature because of focusing reasons required for a narrow injection band. Splitless and on-column techniques require a low starting temperature.

**What is The Optimal Temperature Programme?**

Basically with a temperature programme, the impact of "k" on "R" as shown in Figure 3 must be maximized. This factor will always increase with higher k-values, meaning that theoretically very slow temperature programmes will generate the best possible separation.

The challenge is, that with a very low programme rate, the peaks will become very broad and signal height (sensitivity) reduces. Also analysis time becomes very long. Figure 4 shows an example of a section of a chromatogram of a complex mixture that was analysed on a 30 m x 0.25 mm Rtx-1 column using different programme rates. As can be seen, even with the slowest programme rate of 0.5 °C/min, still some resolution is gained. Analysis times become very long and response will also decrease.

Practically as a rule of thumb, the optimal "practical" programme rate is defined as 10 divided by the dead time in minutes. This value is valid for all the types of carrier gas and can also be used if carrier gases are used at higher linear velocities. Table 1 provides some optimal values related to column dimensions for helium and hydrogen.

**Selectivity Changes due to Temperature**

Many people think that selectivity of the stationary phase is not dependent on temperature but that is not true. Retention indices are always listed at exact temperature conditions because the index will change with temperature. This is not strange, as the different interactions between component and stationary phase, will not change linearly with the temperature.

The result is that:

- Liquid stationary phases will behave MORE POLAR at higher temperatures
- Solid stationary phases will behave LESS POLAR at higher temperatures.

The change of selectivity with temperature is the highest with polar phases. Figure 5 shows an extreme example where benzene is analysed at different temperatures using the high polar Rt-TCEP. If run at 30 °C, benzene elutes before n-undecane, having an RI of 1090. At 110 °C, benzene elutes after dodecane, with an RI of about 1260. If temperature is further increased benzene elutes

Figure 3

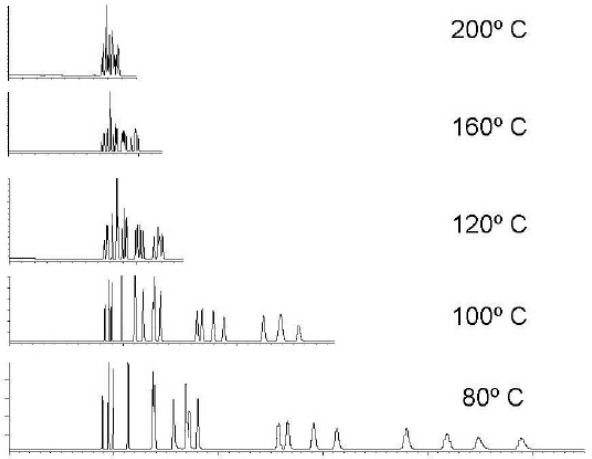


**Figure 3: Impact of temperature on separation of C1-C5 hydrocarbons. Column: 30 m x 0.32 mm Rt AluminaBOND / KCl.**

Figure 4

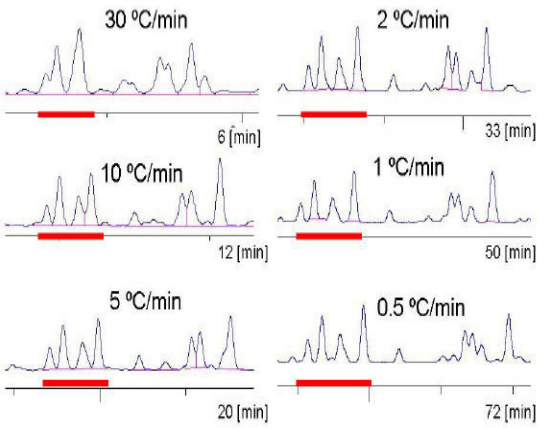


**Figure 4: Separations using different temperature programming using a 30 m x 0.25 mm Rtx-1, df = 0.25 µm; slower programming results in better efficiency but also in longer analysis times and reduced response.**

Table 1

| Column length [m] | Helium | Hydrogen |
|---|---|---|
| 10 | 18 | 33 |
| 15 | 13.5 | 24.5 |
| 20 | 9 | 16 |
| 30 | 6.8 | 12.3 |
| 40 | 4.5 | 8,3 |
| 60 | 3.4 | 6.2 |

**Table 1: Optimal practical temperature programmes for different column dimensions, defined as 10 divided by the dead time in minutes: here using He @ 30 cm/s and $H_2$ @ 55 cm/s.**

Figure 5

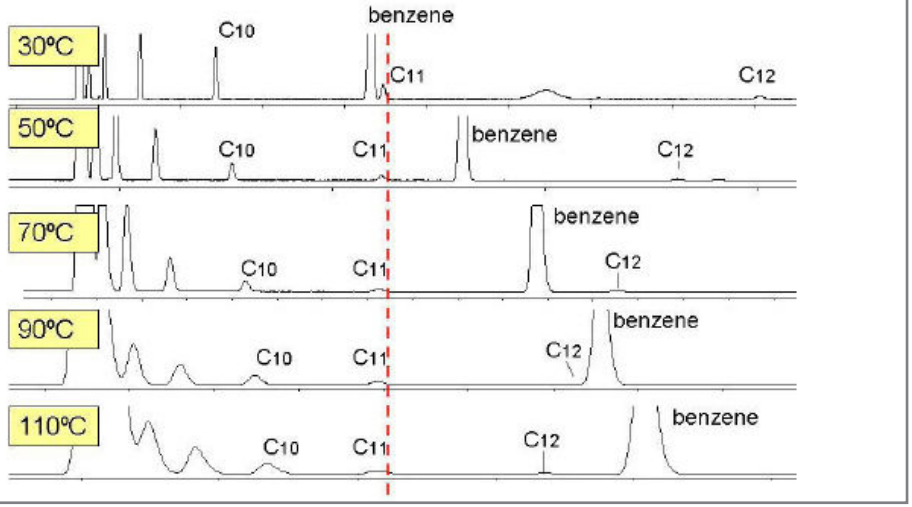


**Figure 5: Analysis of benzene and C8-C13 hydrocarbons on a 60 m x 0.25 mm Rt-TCEP at different temperatures. Note the increase of polarity with increased temperature.**

Figure 6

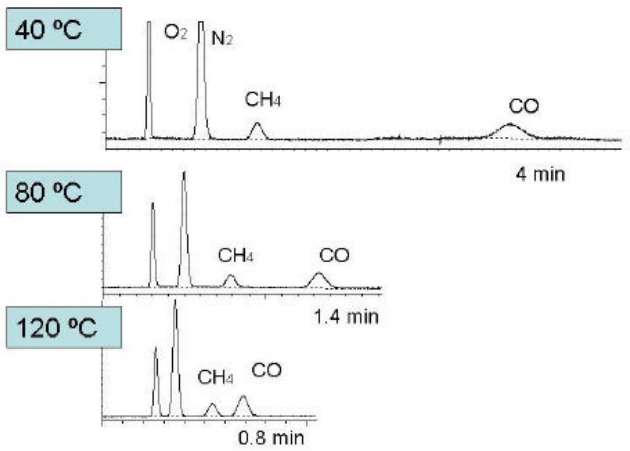


**Figure 6: Gases on a 1 m x 0.53 mm MXT micro-packed at 40, 80 and 120 °C. Note the increase of polarity when operated at lower temperatures.**

Figure 7

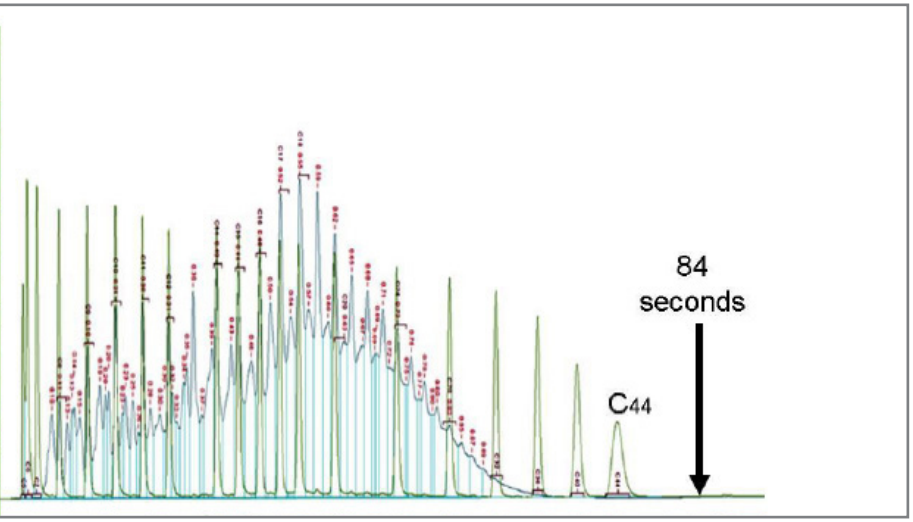


**Figure 7: Fast programming using direct electric heating concept, using an MXT-1 type capillary, built in a Falcon GC, [3, 4].**

after dodecane, with a RI of about 1260. If temperature is further increased Benzene elutes after tri-decane.

Using adsorbents, the selectivity changes in the opposite way. Using alumina, unsaturated hydrocarbons can be positioned at different positions in the chromatogram, see [1]. Figure 6 shows the elution of gases on a Molsieve 5A. Carbon monoxide is retained much stronger at lower temperatures clearly showing that the stationary phase behaves more polar at a reduced temperature [2].

Practically, It is very important that in method development, experiments must be included using different oven temperature programmes.

**Fast Temperature Programming**

The temperature range where most gas chromatographs are used, is between 35 °C and 450 °C. With additional cooling, one can also start sub-ambient. This is not preferred as $CO_2$ or liquefied $N_2$ is required, which adds cost.

The temperature can also be used for very fast separations. Standard gas chromatographs are limited with temperature programme rate. The maximum rate is 30–40 °C/ min. It is important that the "real" oven temperature is as close as possible to the "set" temperature. If this is not realized, there will be non-reproducible retention times. If the oven size is reduced, one can programme faster and keep the real temperature up with the "set" temperature. For different ovens there are oven pillows available to reduce the oven size. This is especially of interest for systems that run at 110/120V.

Another way is to use direct heating, where a heating thread or plate is attached to the column [3]. Such systems can programme with very fast temperature programmes. A practical advantage is that cooling down is also fast, again saving time.

Figure 7 shows a simulated distillation in 84 seconds using a metal capillary that is directly heated. The temperature programme exceeds 300 °C/min to elute C44 in this short time frame.

Note that such systems also have limitations as cutting off sections is not always possible, which makes maintenance more challenging.

Such fast programming solutions are, therefore, perfect for defined samples where the whole sample elutes from the columns.

Figure 8

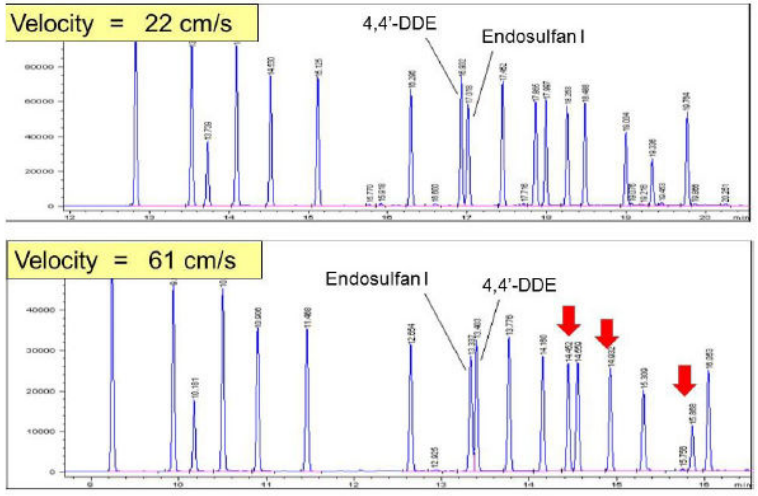


**Figure 8: Impact of linear velocity on separation using a Rtx-CI-Pesticides column. Pesticide mixture run at 22 and 61 cm/s using the same oven temperature program. Because the elution temperatures are different, the chromatograms are different. Even peak reversal is possible as seen here with 4.4-DDE and Endosulfan I.**

Note that with very fast temperature programmes the full efficiency of the column is not utilized as the retention factor k/k+1 in Figure 2 is kept very small.

### Translating Oven Temperature Programme when The Method is Changed

The setting of the correct temperature programme is especially important if an existing method has to be changed. Changes can be related to:

- Moving to a different carrier gas; (higher velocity, cheaper)
- Operating at a higher linear velocity; (higher velocity, to reduce time)
- Changing column dimensions (shorter column, faster analysis)
- Moving from a FID to a vacuum detector (MS).

When the temperature programme is not changed the components will elute at different temperatures, which will result in a different chromatogram. Figure 8 shows an example of how the separations are different when the same programme and column is used at two different linear gas velocities. Peaks move relative from each other and even peak reversal can happen. This happened here for Endosufan I and 4,4'-DDE.

Figure 9

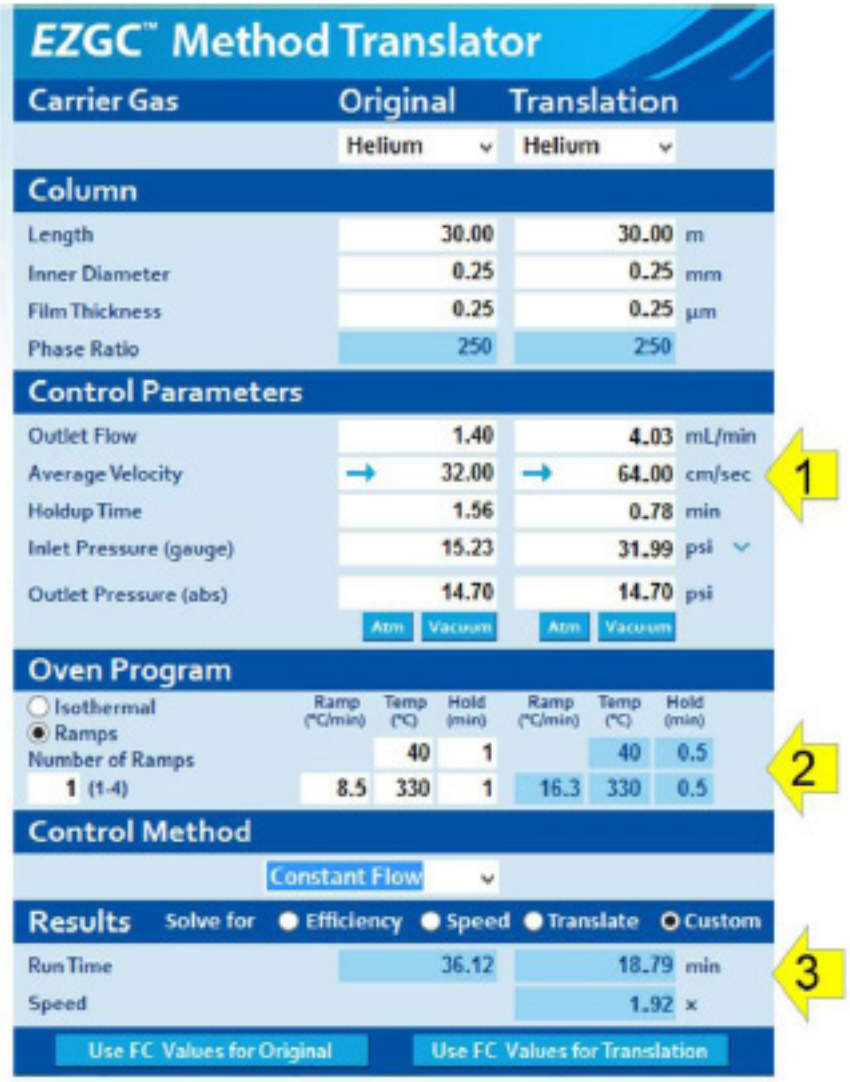


**Figure 9: Snapshot of method calculator [5] that's calculates the programme required to get the same separations. Here the linear velocity of an existing column was increased by a factor of 2. The new oven programme will make sure elution temperatures are the same and the chromatogram will be exactly the same, just 1.92 times faster.**

The same chromatogram will only be obtained if the elution temperatures are similar. To realize this, in all cases listed above, the oven temperature programme needs to be changed.

There are method translation programmes available that will calculate the new programme conditions [5].

Figure 9 gives an example of such a calculation, where the linear velocity of the carrier gas was increased by a factor of two (1). The new temperature programme (2) is calculated. When this programme is used, the elution temperature will be the same and also the chromatogram will be the same as before, but analysis time (3) is reduced by a factor of 1.92.

## References


1. J de Zeeuw, R. Morehead, T.Vezza, and B. Bromps, American Lab, oct 2011,
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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 eight years has served as an international specialist on gas chromatography for Restek in The Netherlands.