Impact of GC Parameters on The Separation

Part I: Choice of the Stationary Phase

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In this series, we will discuss the impact of different parameters on the actual separation. We will do this by discussing how they impact and then explain the impact by some practical examples. In GC there are seven important parameters that we can choose to get a separation. All parameters have an impact and selection of a certain parameter has an impact on the separation.

Strategic column choices can improve lab productivity by assuring that speed and resolution are optimized. While the number of choices available can be challenging to choose from, consideration of the resolution equation variables, Figure 1, being the selectivity factor, retention (capacity) factor and efficiency, simplifies the decision. The most important separation factor to select is the stationary phase. Once the stationary phase has been chosen, physical dimensions (inner diameter, film thickness, length) can be selected based on retention factor and efficiency required. Understanding how the separation factor, retention factors and efficiency influence separations allows analysts to make effective choices and quickly select the best column dimensions for specific separations and techniques.

After the column has been selected there are several non-column related factors that can be adjusted to tune the resolution of the compounds of interest. These non-column factors are oven temperature, carrier gas type and carrier gas velocity. Figure 2 shows the seven major factors that affect chromatographic separation.

Selecting The Stationary Phase

This is the most important decision as the stationary phase defines the selectivity for your components. The 'selectivity' of stationary phases depends on interactions between analyte and stationary phase. These interactions can be based on dipole, hydrogen bridge, van der Waals and steric interactions.

As a rule of thumb, you should use a stationary phase that 'looks like the components that you would like to separate'. This will enhance interaction with target analytes and results in better separations. For example it means that for alcohol separation, a 'Stabilwax' phase is used, and for a hydrocarbon type, the Rtx-1 is used,

Figure 1

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

Figure 1: Resolution equation.

Figure 2

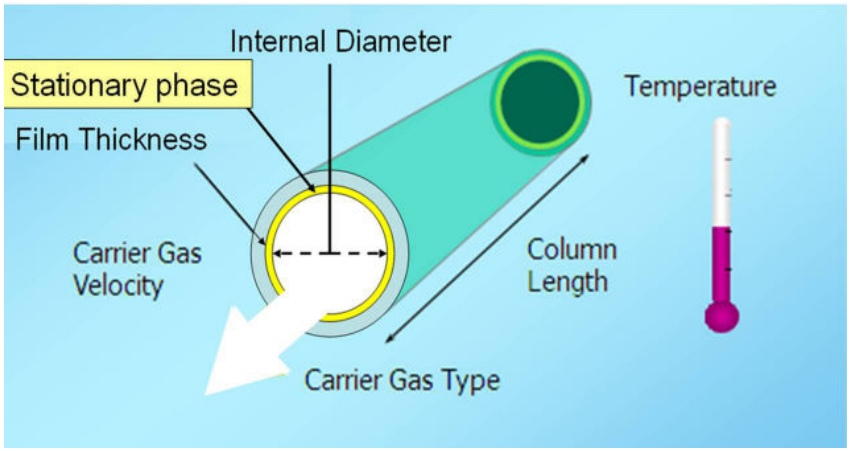

Figure 2: Seven major factors that affect chromatographic resolution. Note: ID = inner diameter, μ = film thickness.

Figure 3

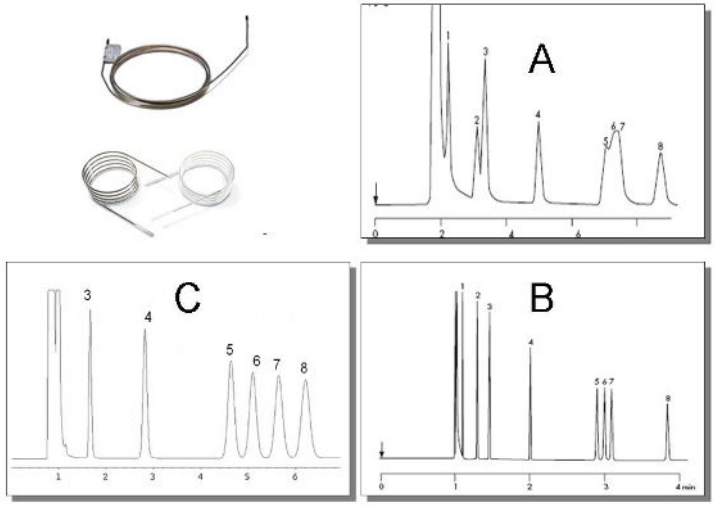

Figure 3: Separation of BTX; A: 2 m x ¼" packed column with 3% PEG; B: 30 m x 0.25 mm capillary, df =0.25 um PEG; C: 2 m, 1/8", 2 mm ID 5% Rt®-1200, 5% Bentone® 34; Peak identification: 3 = benzene, 4 = toluene, 5 = ethylbenzene, 6 = p-xylene, 7 = m-xylene, 8 = o-xylene.

Figure 4

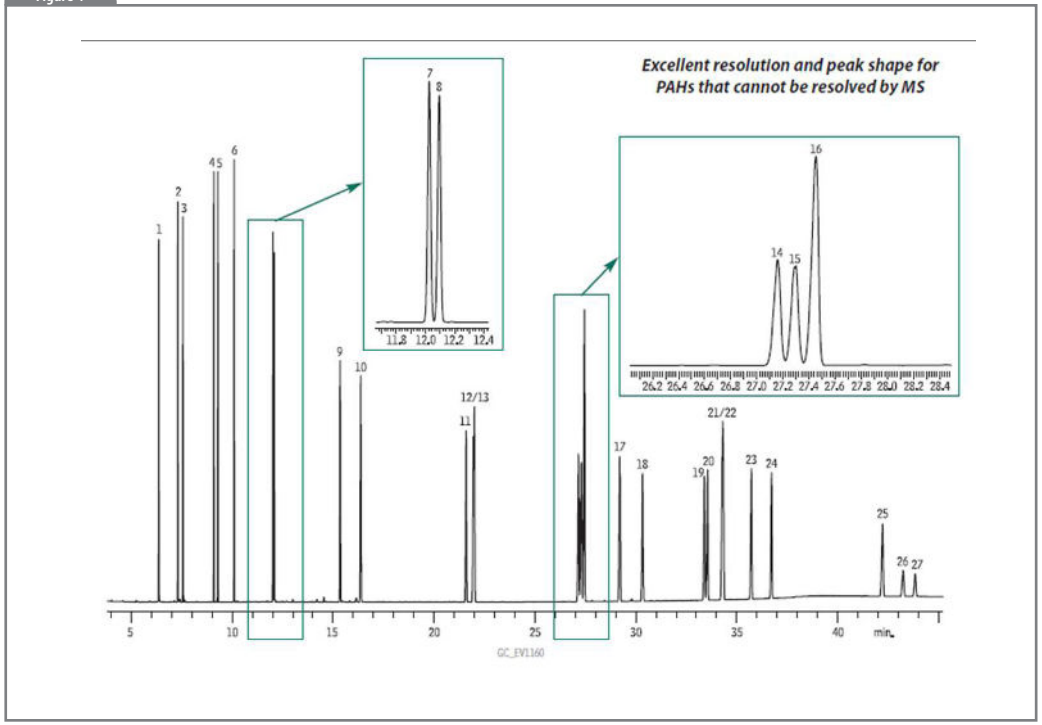

Figure 4: Separation of benzofluoranthenes on Rxi17Sil MS; Full details, see ref. 6.

being 100% polydimethyl siloxane.

So, in what cases will phase selectivity play a critical role?

1. If there are only a limited number of plates available

If efficiency is low, a separation is only obtained if the phase used, is very selective. This is the reason why there are so many stationary phases used with packed column applications. With a packed column, only 5–10,000 plates are available resulting in relative broad peaks. Figure 3 shows the separation of benzene, toluene, ethyl benzene and the three xylenes on different columns. Using a polar PEG type phase the ethyl benzene, meta- and para xylene are not resolved. If a high resolution capillary is used with 100,000 theoretical plates, all components are resolved on a similar type phase, (Figure 3B). Choosing a more selective stationary phase in the packed column, a full base line separation is also obtained (see Figure 3C). Despite developments in capillary GC a large number of applications are still performed with packed columns. If these columns do the analysis in an acceptable time, show stability and deliver the required detection limits, there is no reason to use a capillary

column. Also packed columns have benefitted from developments in capillary technology. Because 1/4/, 1/8 and 1/16" metal tubing could be deactivated using the Siltek processes [1], there is no need anymore for 'glass' packed columns.
There are also 0.53 mm capillary columns that are operated at higher flow-rate. Under these conditions, such columns do not generate a lot of plates, so selectivity becomes even more important.

Selection of the most selective stationary phase is also very important If the analysis time has to be reduced. This will allow a short column and/or high carrier gas velocities to be used, which will generate the shortest analysis times.

2. If components are to be detected by a non-selective detector

A non-selective detector means it detects every component and chromatographic separation is essential. Non-selective detectors such as FID and TCD are very popular as they have linearity of 6–7 decades, are sensitive and relatively low in cost. Components that elute at the same retention time, cannot be quantified individually. Here the stationary phase has to do the separation and selecting the stationary phase becomes very important. The challenge increases when more components are present in the sample. Here it is essential to use the existing information on separations. Table 1 shows some examples of groups of components for which unique selective stationary phases have been developed

3. Using mass spectrometric methods and target components show similar fragmentation

As mass spectrometric detection has become a much more used technique, the selectivity of GC-phases is not always required. By using selective scanning for certain fragments, a mass spectrometer can also be used to separate peaks that co-elute from a GC column.

Even with mass spectroscopy, selectivity is required for separating isobaric compounds. Figure 4 shows the separation of the 3 benzo fluoranthenes, using the Rxi-17Sil MS phase. Only this mid-polar phase can separate the benzofluoranthenes with full baseline resolution. Special selective low-bleed phases have been developed for separating PAH [2], Dioxins [3] and PCB [4]. Also if components have similar degradation products, a bias can occur. For instance If PCBs, dioxins or even hydrocarbons are measured, the fragmentation products in a MS, can be very similar.

For optimal use of mass spectroscopic detection, it is important to use low-bleed and inert GC columns [5]. Despite the separation power of a mass spectrometer, it is always better to have a chromatographic separation first.

Table 1

Permanent gases	Freons/CFC
Separation of CO and CO_2	Blood alcohols
C1-C6 hydrocarbons and isomers	Optical Isomers
C1-C20 hydrocarbons and isomers	Cis/trans FAME
C5-C120 hydrocarbons	USP-467 solvents
Xylenes/substituted benzenes	Biodiesel
Bio-ethanol	Volatile Organic Compounds
Chlorinated pesticides	Sulfur gases
Dioxins, dibenzofurans	Mass spectroscopy
Brominated flame retardants	Oxygenates
PCBs	VOC and semi-VOC acc to EPA
PAHs	

Table 1: Example of applications for which optimized stationary phases are used.

4. When a method needs to be confirmed by chromatography

Besides using mass spectroscopy, chromatography can also be used for a positive identification. The same sample is analysed on two columns with different selectivities. If the retention times of the target analyte on the two columns match with the standard, there is a high level of confidence that the component identification is correct. This is done in chlorinated pesticide analysis (EPA 8081), where special selective phases are developed [7]; Another example is the analysis of blood alcohols. Figure 5 shows the separation of the components of interest on two columns, with optimized selectivities for this type of separation. The elution order of both columns is different due to different selectivity, [8].

5. If selective detection is not 'selective' enough

Selective detection is perfect if the signal is not impacted by other components that may elute together with the target analyte. This effect is called 'quenching'. The signal of a selective detector is always impacted if another component elutes. It depends on the selectivity of the detector if it's a problem or not. For instance, if selectivity of a sulfur specific detector is six magnitudes, it means it will start to show response if the co-eluting peak is a million times higher concentration than the target analyte. This may seem a lot, but in the case of sulfur, amounts of 5–50 ppb of H2S/COS must be quantified in typical

Figure 5

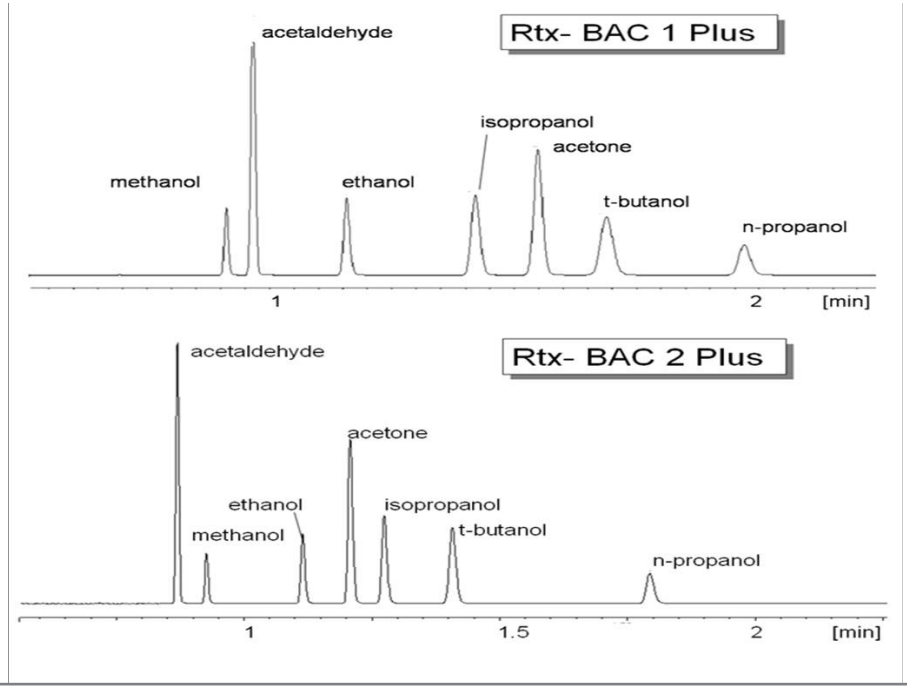

Figure 5: For blood alcohol analysis, conformation is done by analysing the same sample on 2 columns of different selectivity; Full details see ref. 8.

Figure 6

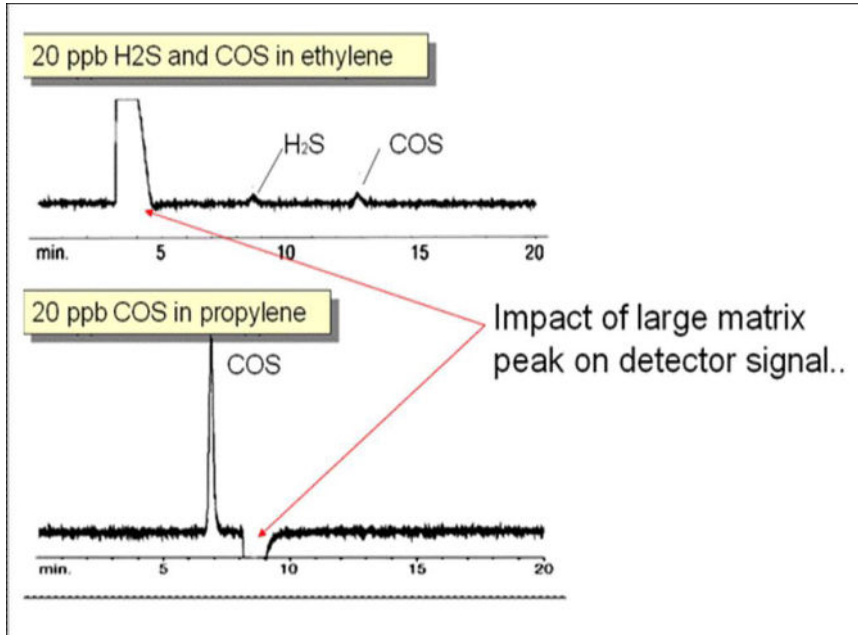

Figure 6: Analysis of ppb levels of COS and H2S in ethylene and propylene, using the Rt XL Sulfur. Even with relative low efficiency, this separation was sufficient to avoid the quenching. Using the PLOT column as referred in [9], even lower sensitivities can be expected.

hydrocarbon streams of ethylene, propylene and propane, see [9]. It is very important that a selective phase is chosen where the matrix peak is not interfering with the trace components to be measured. Figure 6 shows an example of such a selective phase. The H2S and COS are well separated from the main ethylene and propylene peaks. Despite the detector being sulfur-selective, there is still a large signal of the matrix.

6. Multi dimensional separations: column switching

Multi dimensional separations are very powerful but two different selectivities need to be chosen. Usually a non-polar and a polar phase are used. Co-eluting components on the first column, can be easily separated on a second other column which has a different selectivity phase. The transfer is often done with valves but most of the instrument vendors also supply solutions based on Deans/flow switching. The multidimensional separations are still done a lot in process applications and also many analyser configurations are often equipped with packed columns/switching devices. The columns have low plate numbers but because two selectivities are used, a lot of separations can be done. The packed columns are often preferred because of their robustness.

7. Multi dimensional separations: GCxGC

In comprehensive GC, every component is separated in a first long high resolution column, usually 30 m x 0.25 mm, followed in series by a second column, which is about 1–2m long and has a different selectivity. Eluting fractions are focused and re-injected on the second column every 8–15 seconds. To make this work in the most optimal way, the two phases used must have a selectivity that ideally must be orthogonal. As this is not possible, usually in the first dimension a separation on vapour pressure on a non-polar column is performed and on the second a polar phase is used with different interactions and sometimes also with a shape-selectivity. See reference 10 for some typical combinations. This set-up can also be reversed, using a polar first dimension and a non-polar

Figure 7

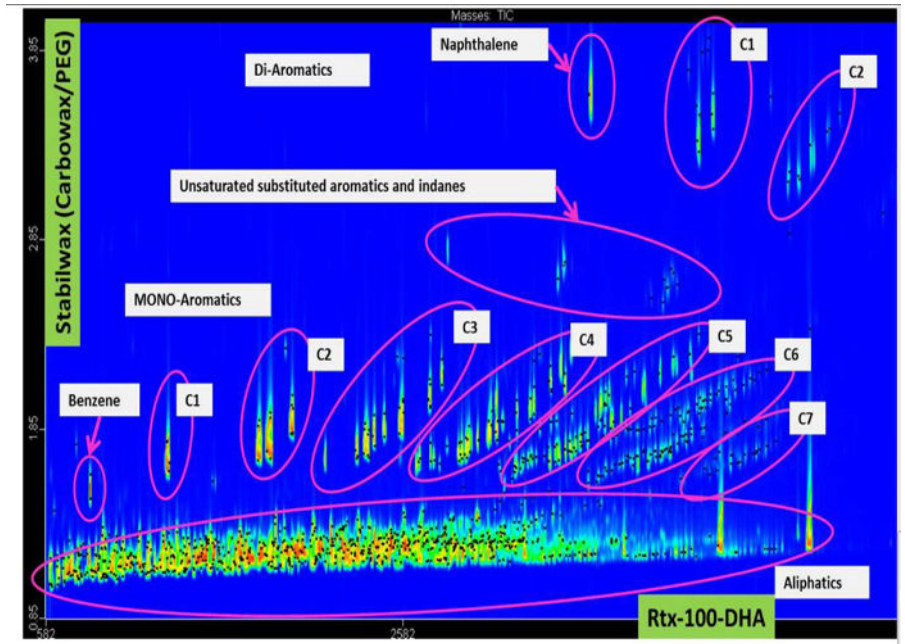

Figure 8

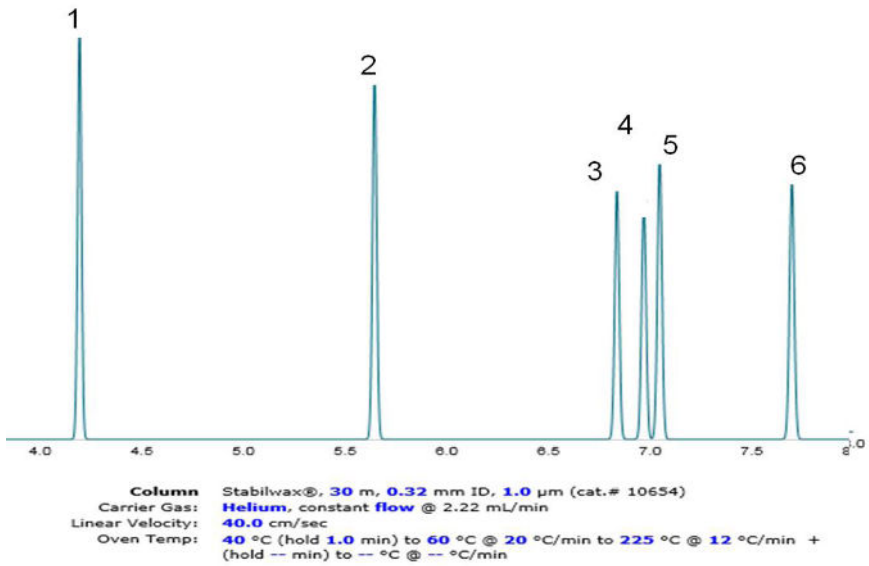

Figure 7: GCxGC separation of fire Debris using a 100m Rtx-DHA first dimension and a Stabilwax for the second dimension column.

Figure 8: Modelated chromatogram for aromatics; 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = meta-xylene; 5 = para-xylene; 6 = ortho-xylene; Full details, see [12].

second dimension. Such set-ups have huge peak capacities as thousands of components can be separated. Figure 7 shows the tremendous separation power of such a GCxGC set-up.

Selectivity of Stationary Phases

The siloxane-based stationary phases are mostly used. The polarity can be changed by incorporating methyl, phenyl, cyanopropyl or trifluoropropyl groups. Such phases show ideal 'liquid' behaviour and have good temperature stability.

Later the development of new generation stationary phases [1], significantly contributed in this field. By stabilization of siloxane polymers using silphenylene as well as surface bonding today's phases can be operated from -60 °C up to 360 °C. Even silphenylene stabilized 50% phenyl type phases have this stability (Figure 4).

Besides the siloxanes, there are also polyethylene glycol type phases, also known as 'wax' phases. Such phases are highly selective for alcohol, aldehydes and aromatic substituted compounds but they do lack temperature stability as they cannot be heated over 260 °C. Despite this, they are still used for a lot of applications. As stated before, for special groups, unique stationary phases are available (see Table 1).

How to Find the Most Selective Phase?

From the structure it remains difficult to predict selectivity. It only gives you a 'general' idea. The best way to choose selectivity is to look at existing separations. Chromatograms are very helpful for that. You can always do a literature search but this takes time and is also expensive. It's easier to use chromatogram databases, which are made available by several GC companies. Such databases can be searched on component name, matrix, group, method and even synonyms. See for example reference 11.

Another interesting development is the availability of chromatogram modeler software that is now also

accessable on-line (see reference 12). Using existing chromatographic measurements as a reference, separations can be predicted. Figure 8 shows an example of the separation of benzene, toluene and xylenes. Reference 13 shows a link to a practical guide.

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Jaap de Zeeuw studied six years of chemistry and graduated in 1979. Jaap has 33 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.