



Impact of GC Parameters on The Separation

Part 4: Choice of Film Thickness

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In part 1, 2 and 3 of this series we focused on the selection of stationary phase, column length and internal diameter. The stationary phase is also deposited as a film or a layer (Figure 1), which is the fourth parameter that we need to understand its impact. The thickness of the layer determines the amount of the stationary phase that is present in the capillary. Retention is directly related to the amount of the stationary phase; thicker films equal more retention. When do we choose thin or thick films and how do they impact the chromatography?. Changing film thickness will impact several parameters: retention, loadability, bleed, efficiency and even inertness.

Film Thickness in Capillary Columns.

Film thickness in capillary columns, is in general between 0.1 and 10 μm for liquid stationary phases such as Rtx-1, 17 and wax. Mostly used are the 0.25 micron films. Thin films are used for the analysis of high boiling materials and thick films for volatiles. If adsorbents are used, we do not talk about films but of layers. Such layers are between 5 and 50 μm in thickness

and are usually built by particles.

It is essential is that the film is distributed homogeneously over the whole column length. If the phase is not distributed as a film anywhere in the column, the efficiency of the column will be compromised, especially with liquid stationary phases. This happens most often in the inlet section when injecting samples. If the film is broken up, stationary

phase may deposit downstream in the column. This can be observed as a kind of droplet (see Figure 2). This will cause peak broadening and activity. That's also why cutting off a section of 10–30 cm from the inlet will often completely restore column efficiency and peak shape: By removing the contamination or sections with distorted film the performance is restored.

How is Film Thickness Measured?

Column length and ID can easily be measured by counting coils and using a microscope. Film thickness can be measured also via a microscope but this would be extremely expensive and will not be very correct as thickness will always depend on where it is measured. Figure 3 shows an example of a SEM picture at 40,000 magnification, showing a 0.20 micron

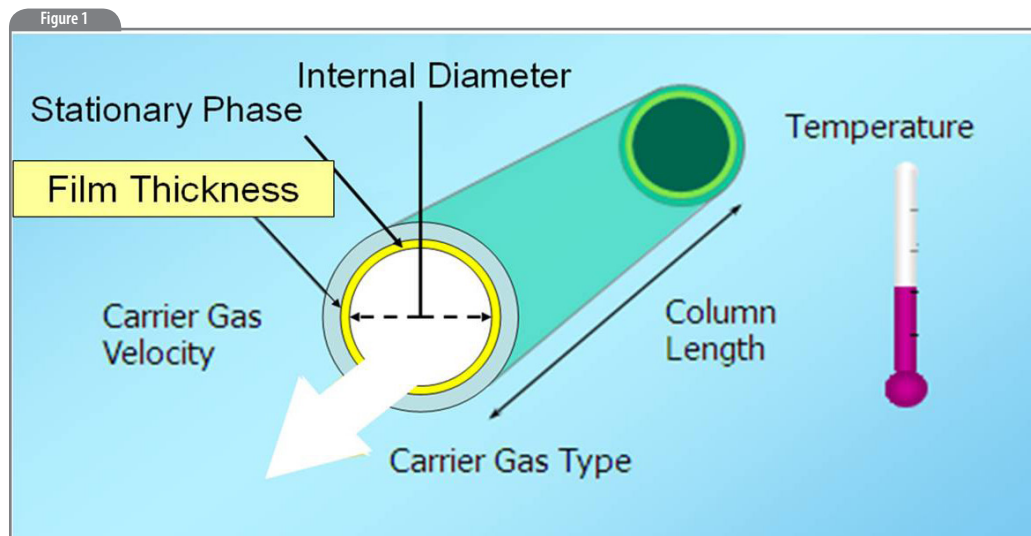


Figure 1: The 7 main parameters that impact separations in GC: focusing on film thickness.

polysiloxane film where the column has on average a 0.25 micron film. There is always some deviation in exact film deposition.

When capillary columns are prepared, some methods allow exact calculation of the film thickness. When static methods are used, the whole column is filled with a solution of the stationary phase. The amount of dissolved polymer is exactly known and with the specific density of the polymer and the volume of the capillary, one can calculate the deposited film.

For polymers that are 100% immobilized, this works well. Some phases cannot be bonded for 100%,

and when columns are rinsed to remove non-bonded polymer, the residual film will be thinner. Here the film has to be calculated.

Calculation of average film thickness can be done using the specific retention volume. This is a fixed value for a certain component at a certain temperature. Using the specific density, the film thickness can be calculated for any column dimension using the formula:

$$df = 0.5 (r \times k) / Vg \times SD$$

where:

df = film thickness in μm ;

r = column radius in μm ;

k = retention factor reference component at test temperature

Vg = specific retention volume for reference component at test temperature in cm^3/g

SD = specific density of phase in g/cm^3

Anomaly:

There is, however, some anomaly between suppliers of GC columns. For example, an exact equivalent film thickness was supplied as was listed by the customer. They asked for a 2.0 micron on 0.53 mm. The column was prepared but did not work. After

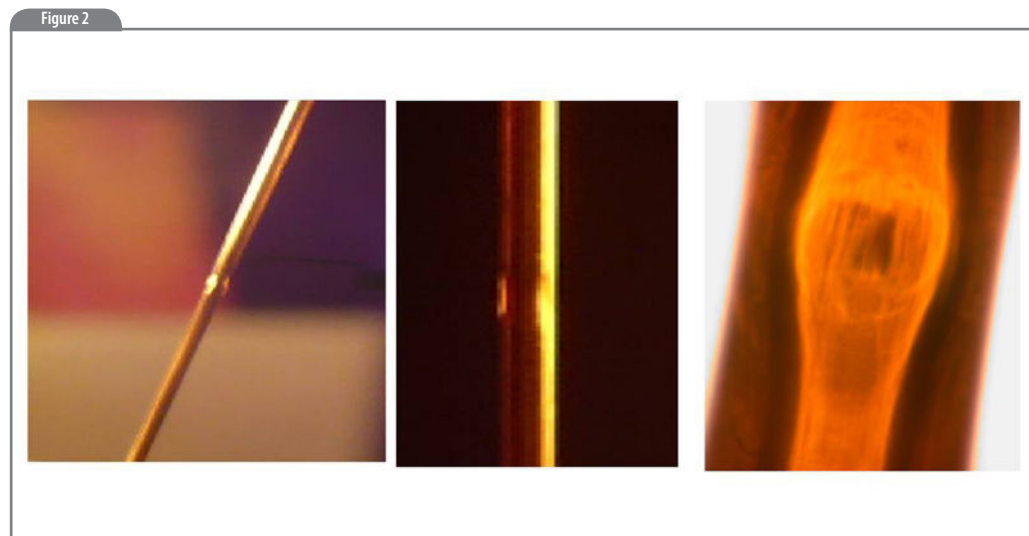


Figure 2: Accumulation of stationary phase resulting in a “droplet” of stationary phase inside the capillary.

testing the original column used by the customer, it showed that this column had a 2.7 micron film, which was in reality a 30% thicker film than was listed on the test report.

We could make the equivalent, but the discussion remains: How is film thickness defined? For some column suppliers there is a history that goes along with that. The problem is, once a “wrong” film is listed in a method because a mistake has been made, what can you do about that? If you supply a “thicker film” that will do the exact separation, it will not be accepted as it does not fit the description, and if you supply exactly the “listed film”, the column will not

Figure 3

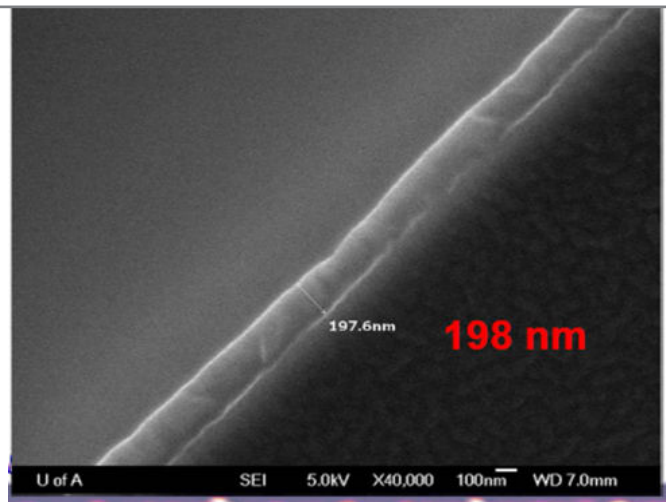


Figure 3: Detail of capillary with an average PDMS film of 0.25 μm ; Courtesy of James Harynuk, University of Alberta, Edmonton, for sharing the picture.

Figure 4

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

↑
1
↑
2

Figure 4: Resolution equation. Two terms are impacted by changing the film thickness.

Figure 5

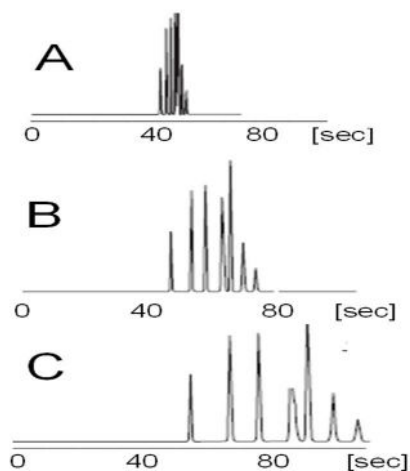


Figure 5: Impact of film thickness on retention. All 30 m x 0.25 mm Rtx-1; A: film = 0.25 μm ; B: film = 0.75 μm , C: film = 1.5 μm .

Figure 6

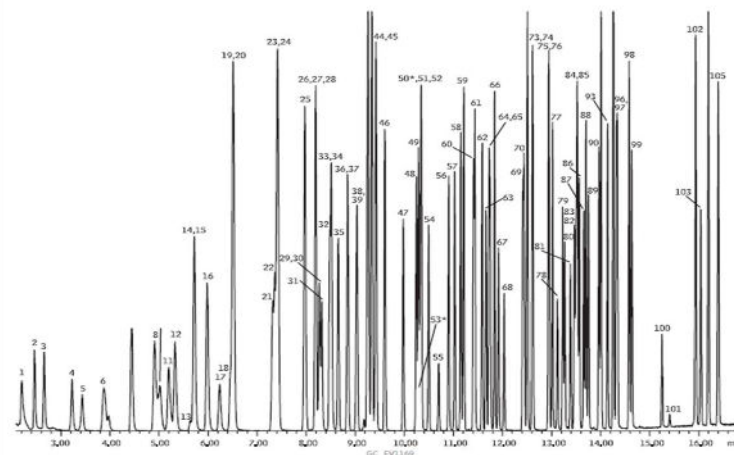


Figure 6: Typical application for VOC using the Rxi®-624Sil MS, 30 m, 0.25 mm ID, 1.40 μm . For conditions and identification (see reference 1).

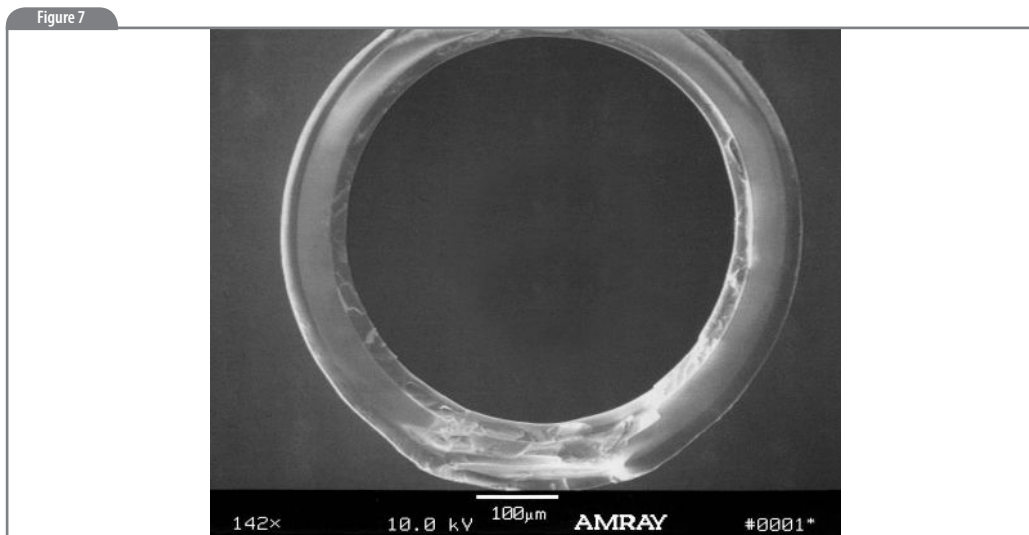


Figure 7: Extreme thick PDMS films of up to 20 μm thickness. Courtesy of John Lipsky, Quadrex Corporation.

do the identical separation, as peaks elute too fast.

Impact of Film Thickness on Retention and Separation

The retention of a capillary is linear dependent on the film thickness. If we look at the resolution equation in Figure 4 the film thickness will influence the resolution in 2 ways:

First on the retention factor “ k ”, the retention factor is linear with the film thickness. Figure 5 shows an isothermal separation where the only change was the film thickness. Increasing film thickness will linearly increase retention factor, which translates in a longer retention time. The section of the resolution equation that incorporates the “ k ”, is

$k/k+1$. This means that at LOW values of k , this factor increases linearly to increase the value of R . This is also seen in Figure 5 where separation significantly improves using a thicker film. As soon as k values become bigger, for example, > 5 , this term becomes very close to 1, meaning the R value will not increase significantly. This is the reason that that higher k (higher retention) will not add anything to resolution.

As a rule of thumb, k should be 4–7. To reduce k values, thinner films can be used and to increase k values, one can choose thicker films.

That’s why for the separation of volatiles, thicker films are always used. The Rxi-624Sil MS phase is very popular, which is a medium polar

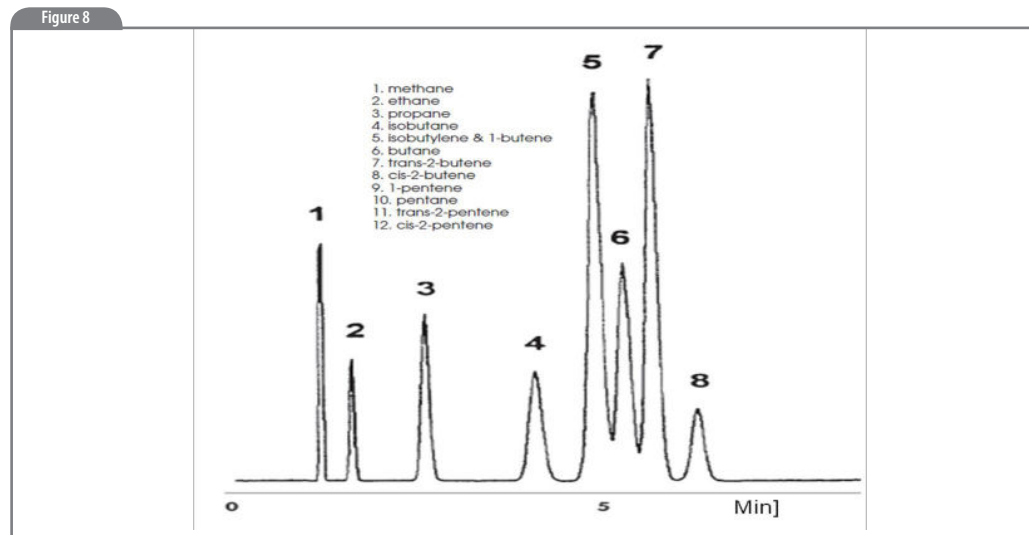


Figure 8: Separation of C1-C5 on a 10 micron PDMS 007-1 PHAT phase film on 30 m x 0.32 mm; For details, see reference 2.

phase, but coated with thick films (see Figure 6). In a 0.25 mm column a 1.4 micron film is used. Such films are also highly efficient.

An alternate way to increase retention is to use PLOT columns. Retention here is, however, based on adsorption, and typically layer thickness is between 5 and 50 micron.

It is possible to increase film thickness of liquid phases to higher values. Quadrex did a great job in making extreme thick layers. Figure 7 shows a PDMS film that is as thick as 20 μm [2]. Such films have high loadability and retention but also rapidly lose their efficiency, due to resistance of mass transfer in the liquid phases. Figure 8 shows a C1-C5 separation on a 10 micron PDMS

phase. Despite even film distribution, the peaks broaden rapidly.

Some Other Points to Consider when Changing Film Thickness

Column bleed is linear with film thickness

Thick-film coated columns will always bleed more. Make sure you use thick film-coated columns not at their highest temperature. If the bleed is too high, you may consider to increase the flow to elute the late eluting compounds at a lower temperature. This can be beneficial because the bleed of most siloxane phases is not dependent on flow. As a result, bleed will be lower if elution temperature is decreased.

Table 1

Film thickness [μm]	Loadability [ng]
0.10	2 – 70
0.25	5 – 200
0.50	15 – 400
1.0	30 – 800
2.0	70 – 2000
5.0	180 – 5000
7.0	250 – 7500

Table 1: Loadability estimation in relation to film thickness for a 0.32mm ID column.

Inertness and robustness increases with increased film thickness

This is for two reasons:

- *Shielding effect:* The thicker film will cover active sites better which reduces their impact
- *Higher elution temperature:* At a higher temperature, adsorption kinetics will be faster, which will improve peak shape.

If a column is selected with a thicker film, and if analysis times need to be similar, the easiest way is to set the initial oven temperature at a higher value. For each factor 2 increase in film, start 15 °C higher. For example if a 0.25 μm film is replaced for a 1.0 μm film, the initial oven temperature is set

30 °C higher. This can only be done if no focusing is required for the setting of the starting temperature. The positive effect on the inertness also helps with robustness/life time. Because activity will be masked more, thicker films will also be preferred from a robustness perspective.

Thicker films will provide highest loadability

Loadability is especially required if high levels have to be analysed. It is not always possible to use splitted injection as both high and low levels of components are present. Often with valve injections (such as are used in analysers) and with direct injection, a thicker film is preferred.

Table 1 gives some indications on the loadability in relation to film thickness. There is a range listed for loadability as it strongly depends on the polarity of the component in relation with the polarity of the stationary phase. For example, 10 ng of a free fatty acid will be overloaded on a 0.25 micron Rtx-1, while on a 0.25 micron Stabilwax, it will provide a perfect symmetrical peak. The upper listed value of loadability for a certain film will already show an overloaded peak with asymmetry factor of approximate 3.0 for a well dissolved component.

References

1. http://www.restek.com/chromatogram/view/GC_EV1169/624Sil
2. Phat films : <http://www.quadrexcorp.com/007-1.html>



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 eight years has served as an international specialist on gas chromatography for Restek in The Netherlands.