Impact of GC Parameters on The Separation

Part 2: Choice of Column Internal Diameter

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In Part 1 of this series we focused on how to select the stationary phase, which is one of the seven important parameters we need to understand (see Figure 1). Once the most interesting stationary phase is selected, the column dimensions must be considered. Here column length, diameter and film thickness are the key parameters. In this article we turn our attention to the column internal diameter and its relevance.

Inside Diameter of Capillary Columns

Where do the different internal diameters of capillary columns come from? When glass capillary columns were used, the standard diameters were 0.25 mm, 0.32 mm and 0.50 mm (Figure 2). The 0.32 mm ID was specifically used for on-column injection as this diameter was required to be entered with a standard on-column needle of 23 gauge (0.23 mm) OD. With fused silica columns we still have the 0.25 and the 0.32 mm. Instead of 0.50 mm, the 0.53 mm was developed. This diameter became the standard. Such diameters could also accommodate a standard 26 gauge (0.41 mm) needle.

Also smaller diameter capillaries have been commercialized. As there was no standardization for some time, capillary columns with different IDs showed up. The ones that are mostly used are: 0.22 mm, 0.20 mm, 0.18 mm, 0.15 mm and 0.10 mm. If you look at the supplier of fused silica tubing, there are even more diameters available [1].

Some Basics on the Impact of the Column Internal Diameter on the Chromatography

Flow-rate

The flow through a typical capillary roughly goes quadratically with the internal diameter. Table 1 shows some optimal flow-rates and linear gas velocities used for different carrier gases and column diameters. Wide bore (0.53 mm ID) columns offer the highest flow-rates and are, therefore, ideal for direct injection using uniliner [2] or valve injection. They are also often used when high loadability is essential. 0.53 mm ID columns have been used as a direct replacement for packed columns using small adaptions to the existing GC configuration [3].

As diameter decreases, the flow also decreases. A 0.10 mm delivers with helium a flow of 0.3 mL/min. This is the outlet flow. On the injection side, where there is a pressure, the flow will be about 0.15 mL/min. This puts a stress on the injection of samples, especially when splitless injection is used. A flow of 0.15 mL/min means

Figure 1

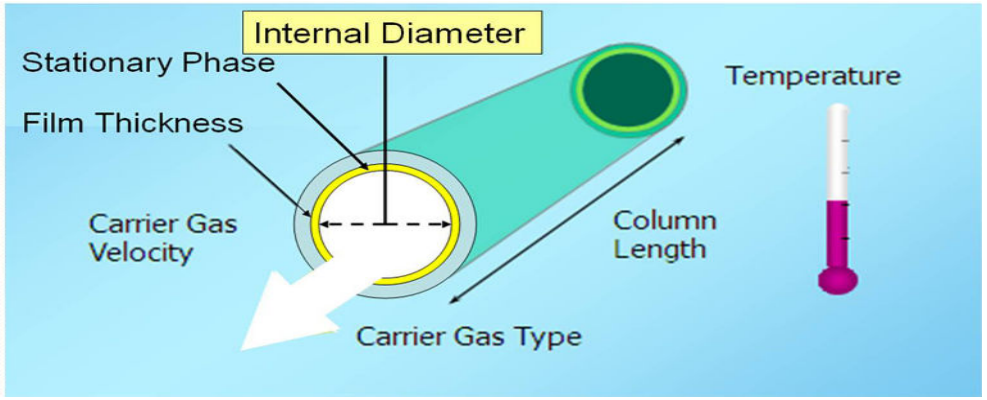

Figure 1: The 7 main parameters that impact separations in GC.

Figure 2

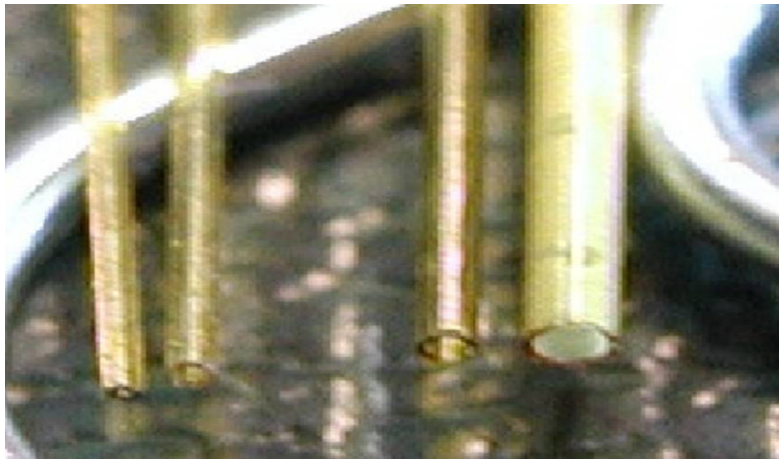

Figure 2: Most popular fused silica column ID used: 0.15mm, 0.25mm, 0.32mm and 0.53mm.

Table 1: Optimal flows / linear velocities vs capillary diameter.*

ID [mm]	Optimum range, linear velocity and flow (40 °C)					
	Nitrogen		Helium		Hydrogen	
	[cm/s]	[mL/min]	[cm/s]	[mL/min]	[cm/s]	[mL/min]
0.100	13-17	0.1-0.15	30-35	0.3-0.34	48-60	0.4-0.6
0.180	12-15	0.2-0.3	27-32	0.6-0.8	44-54	1.0-1.3
0.250	10-13	0.3-0.44	25-30	1.0-1.3	40-50	1.5-2.0
0.320	8-11	0.4-0.55	22-27	1.2-1.6	37-47	2.0-2.7
0.530	6-10	0.7-1.3	20-24	2.6-3.0	35-45	4.7-6.1

* Estimated values for thin-film coated columns with coating efficiencies higher the 80%. When film thickness increases, the optimal velocities and flows will move to lower values. Also for columns that have lower coating efficiencies, the optimum velocities and flows will move to lower values

that for transferring the volume of a 1 mL liner, almost requires 7 minutes. Pressure pulse application is almost mandatory if analysis time is to be optimized.

Separation efficiency and peak width

The plate number increases linearly with a decrease in column diameter. Table 2 shows clearly that for the same nr. of theoretical plates, a shorter column length is required when the internal diameter is reduced. Shorter columns will be faster and are also cheaper. The price to pay is loadability and robustness. Smaller diameter columns will give shortest analysis times but contamination will have a bigger impact on smaller diameter column. This translates in more maintenance and reduced nr. of analysis per column. If the sample contains only volatile materials, the smaller bore columns really show good performance and acceptable life time.

The most general purpose column diameter that is used in industry is the 0.32 mm. This diameter offers a good balance between efficiency and robustness. The 1–2 micron films are particularly preferred.

Pressure

The pressure required for operating smaller diameter columns quickly increases with reduced diameter. Table 3 shows some values for a 15 m column for different carrier gases, all set at the same linear velocity. As with flow, the pressure increases

Table 2: Internal diameter and length needed to produce 100.000 theoretical plates.

ID [mm]	Length for N =100.000 [m]
0.10	10
0.15	15
0.18	18
0.25	25
0.32	32
0.53	53

Table 3: Inlet pressures needed for setting a 30 cm/s velocity using 15 m long capillary; values are for 40 °C, atmospheric outlet.

ID [mm]	Pressure needed for U= 30cm/s [kPa]		
	Nitrogen	Helium	Hydrogen
0.10	306	331	155
0.15	127	137	66
0.18	87	94	46
0.25	44	48	24
0.32	27	29	14
0.53	10	10	5

Figure 3

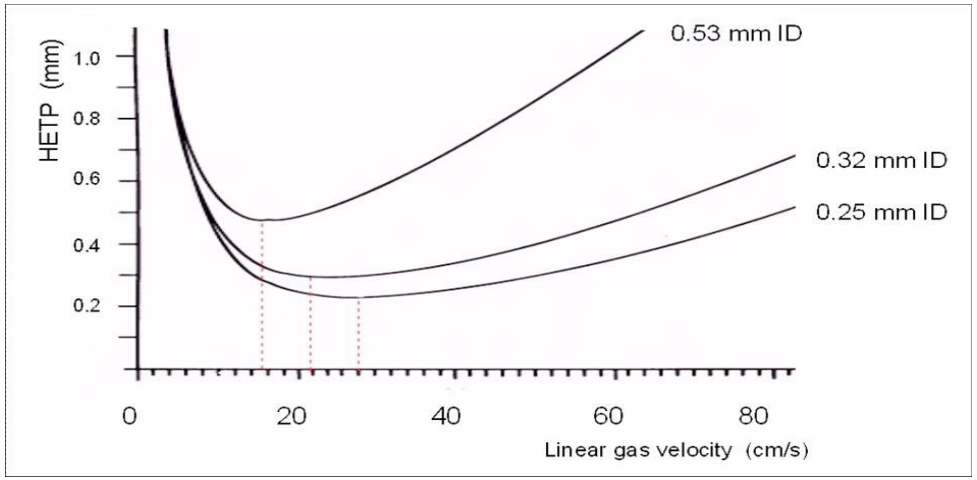

Figure 3: Optimum velocities for helium in 0.53, 0.32 and 0.25 mm ID capillary columns.

Figure 4

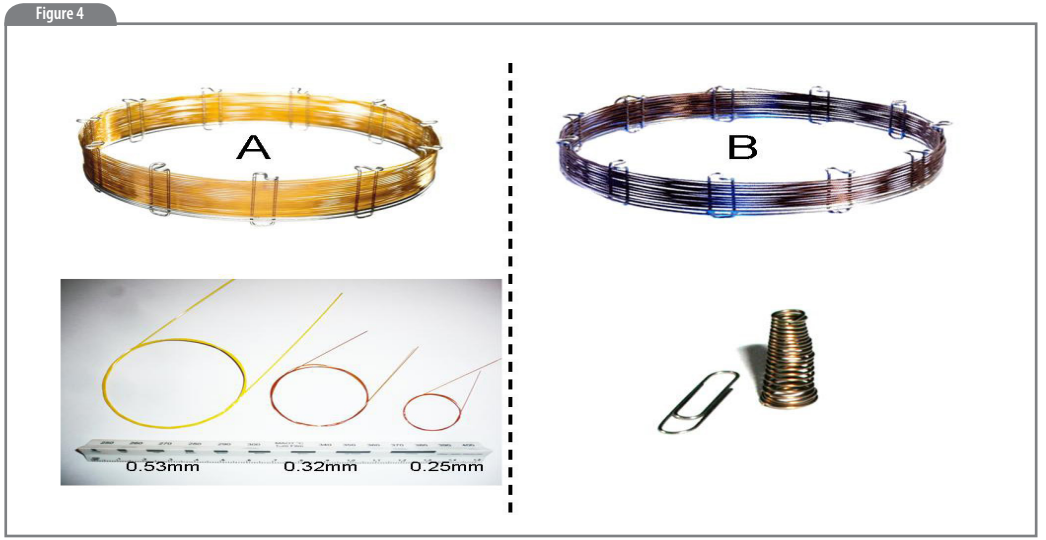

Figure 4: A: Fused silica, coiled at different diameters; B: MXT metal capillary of 0.53mm ID.

quadratically with smaller diameter.

A 0.25 mm needs roughly 4x higher pressure for the same linear velocity then a 0.53 mm. When pressures become very high, there will be a challenge for increased leaks along the needle when injection is done through the septum.

On the positive side, a higher pressure will limit the expansion of sample in the liner, allowing larger injection volumes with a smaller risk of back-flash.

Speed of analysis, optimal gas velocity

As already could be derived from Table 1, if smaller diameter columns are used, the optimum average carrier gas velocity will increase. Figure 3 shows the van Deemter curve for 0.25, 0.32 and 0.53 mm ID columns. For smaller diameter the optimum velocity will be even higher. Besides that a shorter column can be used, it can also be operated at

Figure 5

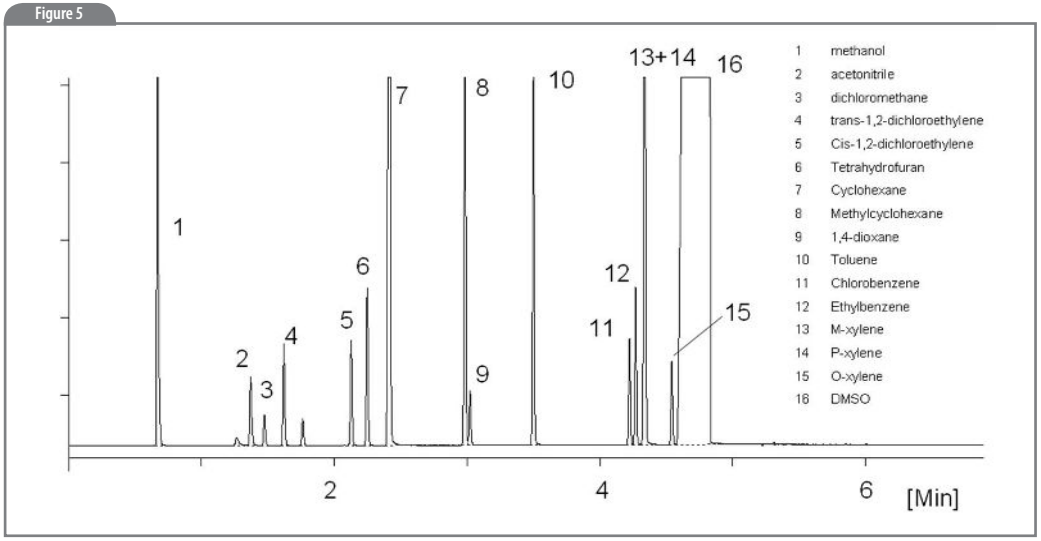

Figure 5: USP residual solvents; Column: 10 m x 0.1 mm Rxi-624Sil MS df = 1.0 µm Oven: 40 °C, 1 min = > 24 °C, 30 °C/min; Carrier: H_2, 220 kPa, 45 cm/s; Injection: Split, 1: 40; Detection: FID.

Figure 6

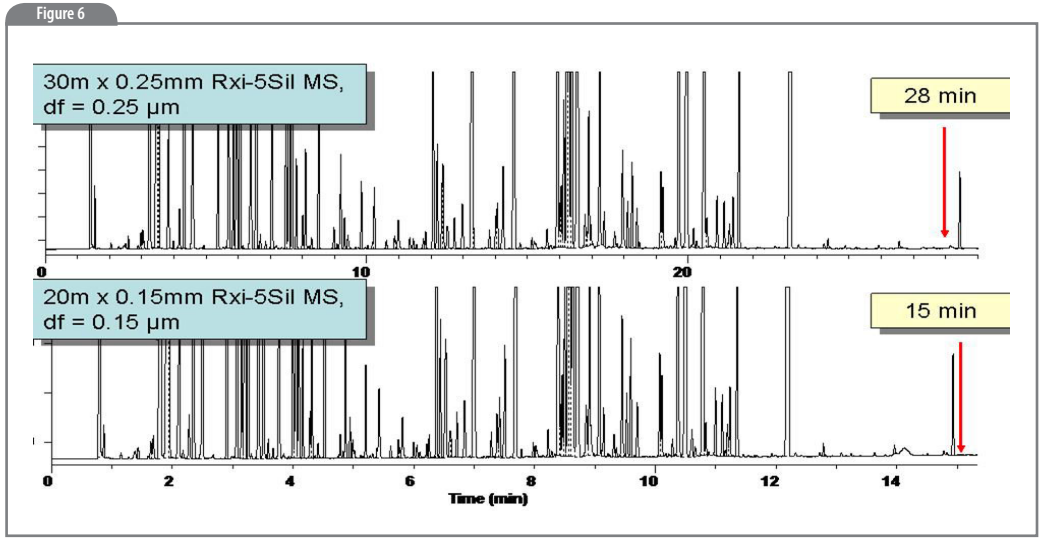

Figure 6: Perfume on a 30 m x 0.25 mm and a 20 m x 0.15 mm Rxi-5Sil MS; details ref. 7.

higher velocities, all ideal for shortest analsyis time.

Loadability

The amount that can be injected on a capillary column is directly related to the amount of stationary phase that is present. In capillaries, this is mainly dependent on diameter and the film thickness. To compensate for reduced loadability, often a thicker film is preferred when using small diameter columns. The 0.53 mm ID columns can be coated with thick films, which make them a very good substitute for a packed column.

Column winding diameter

Fused columns show an increased ring-tension when wound on smaller diameter. If ring tension increases, the risks of column breakage will increase. The ring-tension reduces with column diameter. For example, a 0.53 mm ID column can be wound at a radius of 5 cm, but not smaller. 0.25 mm can be wound down to 2.5 cm. Smaller diameters capillaries can be coiled even smaller. See Figure 4A. The alternative is to use MXT (metal) capillary tubing. Even 0.53mm MXT can be coiled at a 1 cm radius (see Figure 4B.)

Which applications are mainly used for the different column diameters?

Some typical applications for different types of column diameter:

0.10 mm diameter columns

The 0.1mm capillaries are mainly used for applications where speed of analysis is important but efficiency needs to be maintained. They perform well if samples are relatively clean. Operation is challenging as injection needs to be optimized as column flow is very low. Loadability is rather limited and practically such columns need frequent maintenance. One way to compensate for the loadability and increase robustness is to use thicker films. Figure 5 shows an application of residual solvent using a 10 m x 0.1 mm column that was coated with a 1.0 micron film of Rxi-624Sil MS. This is 10 times thicker film than what is typically used. Such films are not commercially available as standard. Also only limited types of stationary phases are available as 0.1 mm capillary.

The 0.1 mm are usually operated with splitted injection, as injection bands must be very narrow. Inlet pressures are relatively high and there is a bigger chance for the development of leaks. Also detector data-collection must be fast as eluting peaks can have a peak width < 1 sec.

At the end, the 0.1 mm is a perfect column from a theoretical point of view, but as soon as practical operation conditions are considered, the 0.1 mm application is limited.

0.15/0.18 mm columns

This diameter is widely used to speed up analysis. The 0.1 mm ID columns had a number of practical challenges that seem not to be a show stopper with the 0.15/0.18 mm ID columns. This type of column can be used in existing instrumentation and allows an analysis time reduction of a

Figure 7

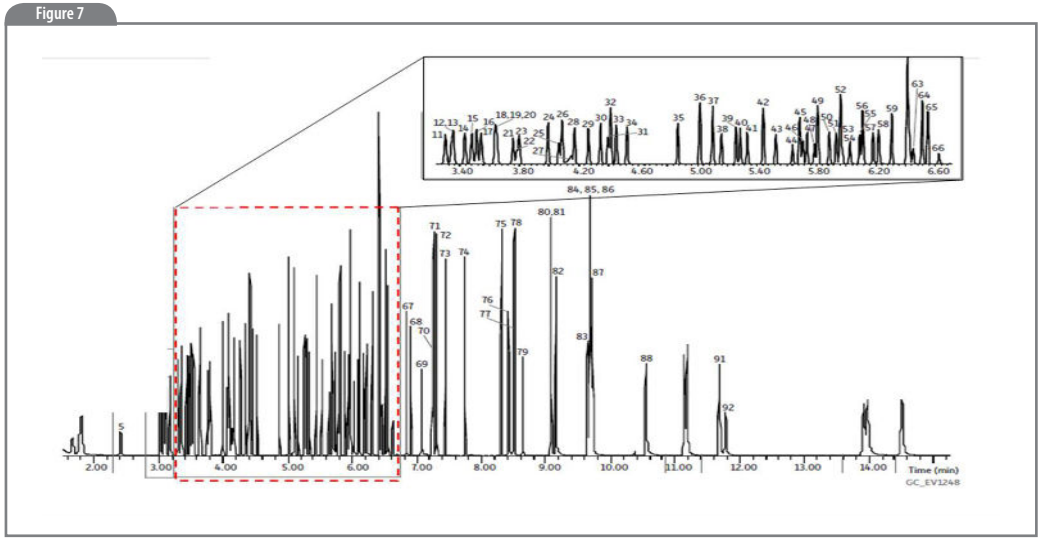

Figure 7: Separation of EPA 8270 semi volatiles using 30 m x 0.25 mm Rxi-5Sil MS (for details see ref. 8).

Figure 8

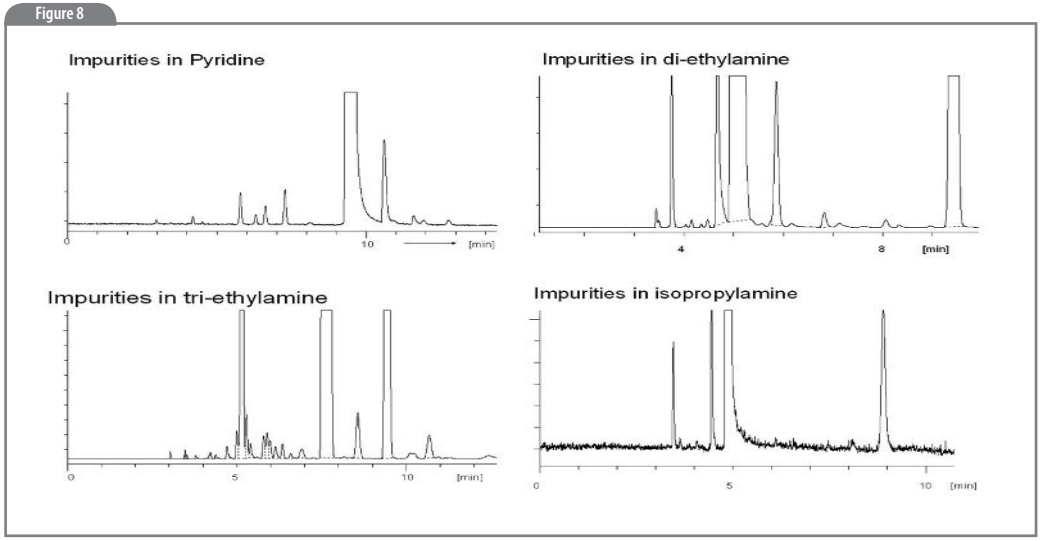

Figure 8: Purity analysis of amine products using Rtx-Volatile amines, 60m x 0,32mm ID allows thick films while maintaining efficiency, which will provide robust application for basic compounds.

minimal factor of 2 if used to replace 0.25/0.32mm ID columns.

For this several articles have been published [4]. Figure 6 shows an example where a 30 m x 0.25 mm is replaced for a 20 m x 0.15 mm. When column dimensions are changed, it is very important to adjust the oven temperature program to secure similar elution temperatures (and the same peak elution order).

Another big advantage of 0.15/0.18 mm columns is that these columns are commercially available with films up to 2 micrometer, resulting in good loadability, high inertness and relatively low bleed. They work very well with MS detection systems. Peak width is not narrower then 1.5 sec allowing enough data points for nearly all MS systems.

This diameter is also recommended to be used for the second dimension separation in GCxGC [5]. It performs better then a 0.1mm as the 0.15 mm is not operated as far from its optimum velocity as a 0.1 mm, and the capacity is higher. Also for 0.15 mm there are also more choices on phase selectivities.

For splitless injections, a pressure pulse is recommended as with a flow of 0.3–0.4 mL/ min(at the inlet), the transfer times in a standard splitless liner become long and solvent effects may not be as effective.

0.25 mm ID columns

This diameter has become the industry standard for split- , splitless and PTV type injection techniques. Flow-rates are 1–2 mL/min, which allows splitless injection times of 20–40 seconds using the standard 4 mm liners. This dimension is also the standard used for vacuum operated detection systems such as the mass spectrometer. In combination with the latest phase technologies, columns can be used up to 360 °C, not only 100% dimethyl siloxanes, but also a range of silphenylene stabilized phases. A 30 m x 0.25 mm offers approximate 120.000 theoretical plates, which translates in high separation power (see example in Figure 7).

The 0.25 mm ID can also be used in longer lengths, generating plate numbers up to 600.000 (150 m columns, ASTM D5501) [6].

0.32 mm ID columns

The 0.32 mm ID capillary was developed primary for using the on-column injection technique. The needles used for on-column, were 0.23 mm OD, which was not suitable to be used for entering 0.25 mm capillaries. On-column is the best injection technique, but it is not the easiest and most robust. The 0.32 mm column did find several other applications. Besides the on-column, the 0.32 mm capillaries can be coated with relative thick-films of stationary phase. For non-polar phases, up to 5 microns can be deposited, resulting in a capillary with high capacity, inertness, efficiency that also offers the option for high flow-rates.

It's a very good diameter if flow programming is considered as initial carrier gas pressure is only 29 psi for helium using a 15 m column (see

Figure 9

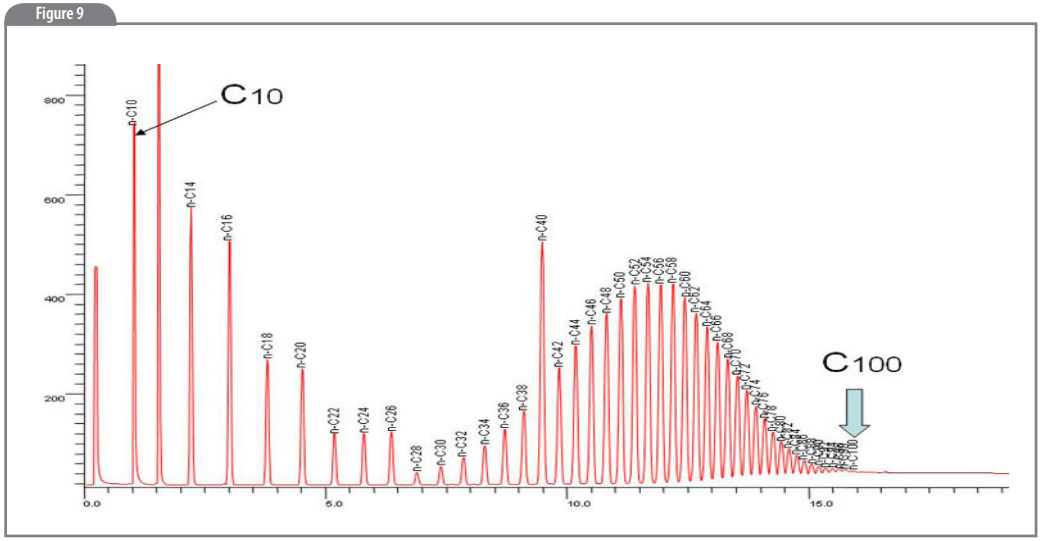

Figure 9: High temperature analysis of hydrocarbons using 0.53 mm ID columns operated under high flow. Details see ref. 9.

Table 3). This can be increased 10-fold to 300 kpa. A 0.25 mm will only increase 6-fold.

The 0.32 mm columns with films up to 1 µm are considered very robust columns and are preferred in many industrial applications where a combination of robustness, inertness and efficiency is required. They also offer a good loadability and are a little easier to work with because of the 0.45 OD. They work very well with all common injection and detection techniques. When MS is used, one needs to be aware that the vacuum pump can deal with the higher flow to maintain vacuum. A 30 m x 0.32 mm needs to be operated at a minimum helium flow of 1.5 mL/min, to maintain a positive pressure in the injection port. Figure 8 shows a typical industrial application using a thick-film 0.32 mm column that was developed for volatile amines.

0.53 mm columns

0.53 mm is the largest internal diameter that is commercially available as a fused silica column. Attempts have been made to use 0.75 mm ID, but the ring tension of the bended fused silica was too big. The 0.53 mm columns will produce relative high flow-rate at moderate pressures.

The first application of the 0.53 mm columns was to have a higher resolution solution in an existing (packed) instrument configuration, [3]. The 0.53 mm column could be coated with thick films and is operated at a flow-rate that was comparable with the packed column. Even under those non-optimal conditions, the 0.53 mm column produced much more theoretical plates than a packed column. The inertness and ease of use, were features that were particularly appreciated. Special (uni)liner configurations were developed that allowed smooth direct injection [2]. This makes them ideally applicable for valve switching applications as are often used in analyser systems.

Such columns were marketed as "Halfmil, NONPAKD, Megabore or Widebore".

The use of high flow-rates was also used in high temperature simdist applications, where 0.53 mm columns are operated under 20 mL/min to elute the heavy boiling fractions (see Figure 9).

Later the 0.53 mm were often used to do gas solid separations with PLOT columns. Often these columns were used with TCD, as for TCD a higher flow-rate was beneficial for sensitivity.

Also when larger injection volumes had to be injected as with headspace techniques, the 0.53 mm ID columns showed useful application.

Lastly 0.53 mm deactivated columns are also widely used as retention gap for on-column injections. This is mainly because injection into a 0.53 mm is easier and the sample plug formed is shorter compared with 0.32 mm ID.

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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.