Utilization of Theoretical Efficiency (UTE%)

Coating Efficiency (CE%) is a historical term that compares the measured column efficiency and its theoretical maximum efficiency. It is calculated using **Equation 6**.

UTE% =
$$\left(\frac{H_{actual}}{H_{theoretical}}\right) \times 100$$

Equation 6

Historically, H_{theoretical} was usually so heavily impacted by heterogeneities in the stationary phase film that extra-column contributions to H_{actual} could be ignored (such as injection anomalies, insufficient or misdirected make up gas, mechanical and electronic lag times). Because of improvements to coating efficiency this is no longer the case and H_{actual} is usually more heavily impacted by extra-column contributions than the column itself. Column contributions to H_{actual} become more meaningful with increasing film thickness or polarity, both of which affect stationary phase diffusion. Many authorities prefer the term "utilization of theoretical efficiency," UTE, which take the above factors into account. Typically, UTEs are 85 to 100% for non-polar stationary phases and 60 to 80% for polar phases.

Resolution (R_S)

It is not surprising that the higher the resolution, the less the overlap between two peaks. Separation is only the distance or time between two peak maxima (alpha, α). Resolution takes into consideration both alpha (α) and the width of the peaks. It is calculated using either form of **Equation 7**. Baseline resolution usually occurs at resolution number 1.50; however, there is no visible baseline between the two peaks. Numbers greater than 1.50 indicate there is baseline between the peaks and numbers less than 1.50 indicate there is some degree of co-elution.

$$R = 1.18 \left(\frac{t_{R2} \cdot t_{R1}}{w_{h_1} + w_{h_2}} \right)$$
$$R = 2 \left(\frac{t_{R2} \cdot t_{R1}}{w_{b_1} + w_{b_2}} \right)$$

Equation 7

- t_{B1} = retention time of first peak
- t_{B2} = retention time of second peak
- w_{h1} = peak width at half height (in units of time) of the first peak
- w_{h2} = peak width at half height (in units of time) of the second peak
- w_{b1} = peak width at base (in units of time) of the first peak
- w_{b2} = peak width at base (in units of time) of the second peak

Phase Ratio (β)

A column's Phase Ratio, β , is a dimensionless value calculated using **Equation 8**. If the same stationary phase and column temperature (program or isothermal) are maintained, the change in the phase ratio can be used to calculate the change in a solute's retention. This relationship is expressed by **Equation 9**. The Distribution Constant (K_C) is the ratio of the solute concentration in the stationary phase and mobile phases. The distribution constant is fixed for the same stationary phase, column temperature and solute.

$$\beta = \frac{r}{2d_{f}} \qquad r = \text{column radius (micrometers, } \mu m) \\ d_{f} = \text{film thickness (micrometers, } \mu m)$$

Equation 8

Thus, for a stationary phase and column temperature, the amount and direction of any change in retention upon a change in column diameter or film thickness can be determined. **Equation 9** shows that an increase in the phase ratio results in a corresponding decrease in retention (k) since K_c is a constant. Conversely, a decrease in the phase ratio results in a corresponding increase in retention (k).

$$\frac{c_{s}}{c_{M}} = K_{c}$$

$$K_{c} = k\beta = k\left(\frac{r}{2d_{f}}\right)$$
Equation 9

 c_S = solute concentration in the stationary phase c_M = solute concentration in the mobile phase

Equation 8 shows that the phase ratio decreases with a decrease in diameter or an increase in film thickness. Either of these column changes results in an increase in solute retention. The phase ratio increases with an increase in diameter or a decrease in film thickness. Either of these column changes results in a decrease in solute retention. Sometimes it is desirable to change column diameter or film thickness to obtain a specific effect (increased efficiency), without changing retention. This can be accomplished by proportionate changes in both column diameter and film thickness.

Column Selection Principles

How to narrow your choices, save time, and reduce trial and error.

Selecting the right capillary column for your application can be an uncertain (and sometimes difficult) task. If possible, you should begin by consulting sample applications provided by GC manufacturers and suppliers – or described in published Application Notes.

In addition, the following pages will help you:

- Choose a stationary phase your most critical decision based on factors such as selectivity, polarity, and phenyl content.
- Understand how column diameter influences factors like efficiency, solute retention, head pressure, and carrier gas flow rates.
- Determine which column length will affect solute retention, column head pressure, column bleed – and cost.
- Appreciate the difference between thin-film and thick-film columns with regard to capacity, inertness, bleed, and upper temperature limit.





Column Selection Principles

Selecting the best capillary column for an analysis can be an uncertain and sometimes difficult task. While there are no foolproof techniques, shortcuts, tricks or secrets to column selection, there are some guidelines and concepts that simplify the process. There are four major column parameters to consider: stationary phase, diameter, length, and film thickness.

Selecting Stationary Phases

Choosing the best stationary phase is the most important decision when selecting a capillary column. Unfortunately, it is also the most difficult and ambiguous decision. The most reliable method is to consult the large collection of example applications provided by column manufacturers and suppliers, GC manufacturers and in published literature. While an exact example application may not be available, enough information can usually be obtained to simplify the decision or reduce the number of potential columns. The most difficult situation is when no previous information is available. Stationary phase selection is much easier even if only one chromatogram is available for all or most of the sample compounds.

The concepts of stationary phase selectivity and polarity are very useful when selecting stationary phases. Synonymous use of the terms polarity and selectivity is not accurate, but it is very common. Selectivity is determined by the physicochemical interactions of the solute molecules with the stationary phase. Polarity is determined by the structure of the stationary phase. Polarity does have an effect on separation; however, it is only one of the many stationary phase properties that influence peak separation (see the next section on polarity).

Selectivity can be thought of as the ability of the stationary phase to differentiate between two solute molecules by differences in their chemical or physical properties. Separation is obtained if the interactions between the stationary phase and solutes are different. For liquid or gum stationary phase (polysiloxanes and polyethylene glycols), there are three major interactions: dispersion, dipole, and hydrogen bonding. The following is a simplified and condensed explanation of the interactions for polysiloxane and polyethylene glycol stationary phases.

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Dispersion is the dominant interaction for all polysiloxane and polyethylene glycol stationary phases. Dispersion can be simplified into the concept of volatility. Simply stated, the more volatile a solute, the faster it elutes from the column (i.e., shorter retention time). However, this order can be altered by the effect of solute and stationary phase polarities, and the other interactions. Solute boiling points are sometimes used as a measure of compound volatility. That is, compounds elute in the order of their increasing boiling points. Unfortunately, boiling points cannot be universally applied to the dispersion interactions. Boiling points are fairly valid when dealing with compounds with similar structures, functional groups or homologous series (Figure 1). When dealing with compounds with mixed functional groups, the boiling points simplification often fails (Figure 2). If compound boiling points differ by more than 30°C, they usually can be separated by most stationary phases (there are exceptions). If compound boiling points differ by less than 10°C, the boiling point simplification becomes less certain and more likely to be in error (except for compounds in a homologous series).

Figure 1: Boiling Point Elution Order for Homologous Series

Column: Carrier: Oven:	DB-1, 15 m x 0.25 mm l.D., 0.25 μm Helium at 30 cm/sec 60°C for 1 min, 60-180°C at 20°/min			C ₁₀	c ₁₁	C ₁₂			
		Boiling Point (°C)			C ₁₂	C ₁₄	C ₁₅	C ₁₆	
1. n-Deca	ne (C ₁₀)	174							
2. n-Unde	cane (C ₁₁)	196							
3. n-Dode	cane (C ₁₂)	216							
4. n-Trideo	cane (C_{13})	234					,	ļ	
5. n-Tetrac	decane (C ₁₄)	253		<u>الب اب</u>	<u></u>		<u> </u>		
6. n-Penta	adecane (C ₁₅)	268	U	Z	Tim	4 e (min.)	6	8	
7. n-Hexa	decane (C ₁₆)	287				• ()			

Homologous series of hydrocarbons. The solutes elute in order of their increasing boiling points; however, the peaks are not spaced in proportion to their respective boiling points.

Figure 2: Deviation from Boiling Point Order

Column:	DB-1, 30 m x 0.25	mm I.D., 0.25 µm
---------	-------------------	------------------

UO	olumn: DB-1, 30 m x 0.2	25 mm I.D., 0.25 μm		10	1	2						
		Boiling Points (°C)					4	5	6			
1.	Toluene	111	100% Methyl					1				
2.	Hexanol	157										
3.	Phenol	182										
4.	Decane (C ₁₀)	174				ul						
5.	Naphthalene	219	0	2		4	6	8	10	12	14	16
6.	Dodecane (C ₁₂)	216										

Solutes outside of the homologous series do not elute in the boiling point order.



If the stationary phase is capable of dipole interaction, it enhances its power to separate solutes whose dipole moments are different. Only some stationary phases are able to exploit this interaction. Polyethylene glycols, and cyanopropyl and trifluoropropyl substituted polysiloxanes readily undergo the dipole interactions; methyl or phenyl substituted groups do not undergo a dipole interaction (Table 1). The amount of peak separation for solutes with different dipoles often changes if a stationary phase with a different interaction is used (Figure 3). If the dipole difference between compounds is small, a greater amount of the appropriate group is needed (e.g., a 50% cyanopropylphenyl-methyl polysiloxane instead of a 14% cvanopropylphenyl-methyl polysiloxane). It is difficult to accurately predict the magnitude of the separation change for all of the peaks. Empirical results have shown that dipole interaction stationary phases are well suited for samples containing compounds that have base or central structures to which different groups are attached in various positions. Examples include substituted aromatics, halocarbons, pesticides and drugs.

Table 1: Stationary Phase Interactions							
Functional Group	Dispersion	Dipole	Hydrogen Bonding				
Methyl	Strong	None	None				
Phenyl	Strong	None to Weak	Weak				
Cyanopropyl	Strong	Very Strong	Moderate				
Trifluoropropyl	Strong	Moderate	Weak				
PEG	Strong	Strong	Moderate				

Figure 3: Dipole Interactions



Molecular weight and boiling points are virtually identical for these fatty acid methyl ester (FAME) isomers, with only the dipole interactions due to the hydrogen isomeric positions on the molecules being different. Only strong dipole interactions in the stationary phase can provide chromatographic separation for these types of compounds.



C-18:1 cis and trans isomers on HP-88.

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The hydrogen bonding interaction occurs if there is hydrogen bonding between the solute molecules and the stationary phase. **Table 2** lists the types of compounds that can form hydrogen bonds along with their relative bonding strengths. It is the difference in the strength of the hydrogen bonding that is critical. The same stationary phases that undergo dipole interactions also undergo hydrogen bonding interactions. The amount of peak separation for solutes whose hydrogen bonding potentials differ often changes if a stationary phase with a difference between compounds is small, a great amount of the appropriate group is needed (e.g., a polyethylene glycol instead of a 14% cyanopropylphenyl-methyl polysiloxane). It is difficult to accurately predict the magnitude of the separation change for all of the peaks. Sometimes the desired separation is obtained, but another set of peaks now co-elute with the new stationary phase.

Table 2: Relative Hydrogen Bonding Strengths					
Strength	Compounds				
Strong	Alcohols, carboxylic acids, amines				
Moderate	Aldehydes, esters, ketones				
Weak to None	Hydrocarbons, halocarbons, ethers				

Figure 4: Hydrogen Bonding Interactions



DB-1 does not undergo hydrogen bonding interactions. The change in the elution order of hexanol and phenol with DB-WAX is a combination of the dipole and hydrogen bonding interaction.

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Another stationary phase characteristic that may affect retention in a predictable manner is the phenyl content. In general, the higher the phenyl content of the stationary phase, the higher the retention of aromatic solutes relative to aliphatic solutes. This does not mean that aromatic solutes are more retained (e.g., higher k) by high phenyl content stationary phases, but that aromatic solutes are more retained relative to aliphatic solutes. **Figure 5** shows an example of this retention behavior.

Polarity

Stationary phase polarity is determined by the polarity of the substituted groups and their relative amounts. **Table 3** lists a variety of stationary phases in order of their increasing polarity. Polarity is often erroneously used to select columns or to determine separation characteristics. Stationary phase polarity is only one of many factors that affect retention and separation.

While polarity is not directly related to selectivity, it has pronounced affect on compound retention, thus separation. For compounds of similar volatility, greater retention is obtained for solutes with polarities similar to the stationary phase. In other words, polar compounds are more strongly retained by a polar stationary phase than a less polar stationary phase, and vice versa. This affect can be seen in **Figure 6**. The changes in retention and elution order can be largely attributed to the changes in stationary phase polarity. Changes in the amount of phenyl substitution, and dipole and hydrogen bonding interactions also contribute to the changes; however, it is difficult to assess the magnitude of their individual contributions.

In addition to retention, stationary phase polarity influences other column characteristics. There is a general trend between stationary phase polarity and column lifetime, temperature limits, bleed and efficiency. Column life, temperature limits and efficiency tend to be higher for more non-polar stationary phases. These are general trends and not absolute certainties. Low bleed stationary phases sometimes go against this trend.

N	lon Polarit	y							Mid
DB-1 HP-1 DB-1ms HP-1ms DB-2887 DB-Petro DB-Petro DB-PONA DB-HT Sim Dis DB-1ht Ultra 1	DB-5 HP-5 DB-5ms HP-5ms Semivol DB-5.625 DB-5ht Ultra 2 HP-PASS DB-EVDX	DB-XLB	DB-35 DB-35ms HP-35	HP-Chiral 10β HP-Chiral 20β	DB-17 DB-17ms DB-608 HP-50+ DB-17ht	DB-TPH	DB-502.2 HP-VOC	DB-VRX	DB-1301 DB-624 HP-Fast Residual Solvent

Table 3: Stationary Phase Polarity

Separation and efficiency have to be considered together and not as separate column attributes. Each contributes to peak resolution. When the stationary phase provides adequate resolution between peaks, higher efficiency is not needed. Shorter or larger diameter columns and less than optimal GC conditions can be used in these situations. When resolution is not adequate, there is a need for higher column efficiency.

Figure 5: Phenyl Content Retention 15 m x 0.25 mm I.D., 0.25 µm Column: Toluene 1 Hexanol 50% 3. Phenol Phenyl Decane (C₁₀) 4 DB-1 DB-17 Naphthalene 5. Dodecane (C12) 6. 6 16 10 12 0 2 4 10 12 Λ 8 14 16 8 14 2 6

The aromatics increase in retention relative to the hydrocarbons for the DB-17 columns. DB-17 contains 50% phenyl substitution. DB-1 contains no phenyl substitution.



The alcohols (polar) increase in retention relative to hydrocarbon (non-polar) for the DB-225 column. DB-225 is more polar than DB-1.

Polarity						H	ligh Polari	t y	
DB-1701 DB-1701P CycloSil-β Cyclodex-β	DB-ALC2	DB-225 DB-225 ms HP Blood Alcohol	DB-ALC1	DB-Dioxin	DB-200	DB-210	DB-23	HP-88	DB-WAX DB-WAXetr HP-INNOWax DB-FFAP HP-FFAP DB-WaxFF



Gas-Solid or PLOT Columns

PLOT (Porous Layer Open Tubular) columns are intended for the separation of very volatile solutes (primarily gases) without the need for cryogenic or sub-ambient cooling of the oven. Separations that would require column temperatures below 35°C, even with thick film liquid stationary phase can be obtained at temperatures above 35°C with PLOT columns.

Gas-solid or PLOT column stationary phases are physically different than polysiloxanes and polyethylene glycols. Gas-solid stationary phase are small, porous particles. The particles are stuck to the inner wall of the capillary tubing using a binder or similar means. Solutes are separated based on differences in their adsorption properties. Since the particles are porous, size and shape differentiation occurs also.

GS-Alumina columns are well suited for the separation of C_1 - C_{10} hydrocarbons and small aromatics. The KCl version of the GS-Alumina column changes the retention order for some of the hydrocarbons. The HP-PLOT Q column provides slightly better separation for C_1 - C_3 hydrocarbons, but C_4 and higher hydrocarbons are better separated with a GS-Alumina column. HP-PLOT Q exhibits extremely long retention times and very broad peaks for C_6 and higher hydrocarbons and aromatics. HP-PLOT Q separates sulfur gases from each other and form most light hydrocarbons. HP-PLOT Molesieve is used to separate many noble and permanent gases. GS-GasPro columns combine many of the features of the various other PLOT columns. Light hydrocarbons, inorganic gases and solvents are some of the samples suitable for GS-GasPro.

		Dis	persive				
Shape/S	ize 🚽	(•	Ionic Surfa	ce	
Zb					Abnie/A203		
					SOxyPLOT		
		Dis	persive				
Shape/S	ize 🚽	(•	Ionic Surfa	ce	
Bonded Graphitiz	Porous	s Polymers		Bonded Silic	а		
Molecular S	eves						
		PLOT Colu	ımn Examples				
Zeolite/Molesieve:	HP-PLOT						
Graphitzed Bonded Carbon:	SELOT						
Graphitzed Bonded Carbon: Porous Ploymers:	SB LOT HP-PLOTQ,H P	-PLOTU					
Graphitzed Bonded Carbon: Porous Ploymers: Bonded Silica:	SBELOT HP-PLOTQ,HP SBED	-PLOTU					
Graphitzed Bonded Carbon: Porous Ploymers: Bonded Silica: Alumina/Al ₂ O ₃ :	988LOT HP-PLOTQ,HP 9880 Si-AtnjaG	-PLOTU -Abn K(C H	P-PLOTAI ₂ 0 ₃ K (H	P-PLO	TAI 203"S,H	P-PLOTAI ₂ 0 ₃ "M	

Stationary Phase Selection Summary

- 1. If no information or ideas about which stationary phase to use is available, start with a DB-1 or DB-5.
- 2. Low bleed ("ms") columns are usually more inert and have higher temperature limits.
- 3. Use the least polar stationary phase that provides satisfactory resolution and analysis times. Non-polar stationary phases have superior lifetimes compared to polar phases.
- 4. Use a stationary phase with a polarity similar to that of the solutes. This approach works more times than not; however, the best stationary phase is not always found using this technique.
- 5. If poorly separated solutes possess different dipoles or hydrogen bonding strengths, change to a stationary phase with a different amount (not necessarily more) of the dipole or hydrogen bonding interaction. Other co-elutions may occur upon changing the stationary phase, thus the new stationary phase may not provide better overall resolution.
- 6. If possible, avoid using a stationary phase that contains a functionality that generates a large response with a selective detector. For example, cyanopropyl containing stationary phases exhibit a disproportionately large baseline rise (due to column bleed) with NPDs.
- 7. DB-1 or DB-5, DB-1701, DB-17, and DB-WAX cover the widest range of selectivities with the smallest number columns.
- 8. PLOT columns are used for the analysis of gaseous samples at above ambient column temperatures.

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Table 4: Column Efficiency vs. Diameter

cal Neter

Maximum efficiency for a solute with k=5

Column Diameter

Column diameter has an influence over five parameters of primary concern. They are efficiency, retention, pressure, carrier gas flow rate, and capacity.

Column efficiency (N/m) is inversely proportional to column diameter. The efficiencies listed in **Table 4** show that smaller diameter columns have higher theoretical plates per meter. Resolution is a square root function of the theoretical plate number. Therefore, doubling column efficiency theoretically increases resolution only by 1.41 times (the square root of 2), but closer to 1.2-1.3 times in real practice. Smaller diameter columns are used when peak separation is small and high column efficiency (i.e., narrow peaks) is needed. **Figure 7** shows the difference in resolution for two different diameter columns.

Solute retention is inversely proportional to column diameter, for isothermal temperature conditions. For temperature program conditions, the change is 1/3-1/2 of the isothermal value. Column diameters are rarely selected based on retention. Figure 7 shows the difference in retention for two different diameter columns.

Column head pressure is approximately an inverse squared function of the column radius. For example, a 0.25 mm I.D. column requires about 1.7 times the head pressure of a 0.32 mm I.D. column of the same length (also, carrier gas and temperature). Column head pressures increase or decrease dramatically with changes in column diameter. Column diameters of 0.18 mm I.D. or larger are used for standard GC analysis due to the very high pressures needed for smaller diameter columns. Wider diameter columns, especially shorter ones (e.g., 15 m x 0.32 mm I.D.), are impractical for use in GC/MS systems. The vacuum at the exit of the column greatly reduces the required head pressure, and it is difficult to maintain or control very low head pressures.



Figure 7: Column Diameter – Comparison of Resolution and Retention

At constant pressure, **carrier gas flow rates** increase as column diameters increase. For applications or hardware requiring high flow rates, larger diameter columns are normally used. Headspace and purge & trap systems require higher carrier gas flow rates for proper operation. 0.45 or 0.53 mm I.D. columns are used with these systems so that the higher flow rates can be used. Special considerations must be taken if small diameter columns are used in these types of systems. This includes the use of cryogenic interfaces or ovens, or interfacing through split injectors. Added complexity and /or cost, or sample loss, are involved with these techniques. For applications or hardware requiring low carrier gas flow rates, smaller diameter columns are normally used. GC/MS is the typical system requiring low carrier gas flow rates, and therefore, 0.25 mm I.D. and smaller I.D. columns are used in these applications.

Column capacity increases as the column diameter increases. The actual column capacity also depends on the stationary phase, solute and film thickness. **Table 5** lists typical capacity ranges for a variety of column diameters.

Table 5: Column Capacity in ng									
Film Thickness (µm)		Column Inside Diameter (mm)							
	0.18-0.20	0.25	0.32	0.53					
0.10	20-35	25-50	35-75	50-100					
0.25	35-75	50-100	75-125	100-250					
0.50	75-150	100-200	125-250	250-500					
1.00	150-250	200-300	250-500	500-1000					
3.00		400-600	500-800	1000-2000					
5.00		1000-1500	1200-2000	2000-3000					

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Column Diameter Selection Summary

- Use 0.18-0.25 mm I.D. columns when higher column efficiencies are needed.
 0.18 mm I.D. columns are especially well suited for GC/MS systems with low pumping capacities. Smaller diameter columns have the lowest capacities and require the highest head pressures.
- 2. Use **0.32 mm I.D. columns** when higher sample capacity is needed. They often provide better resolution of earlier eluting solutes for splitless injections or large injection volumes (>2 μ L) than 0.25 mm I.D. columns.
- Use 0.45 mm I.D. columns when only a Megabore direct injector is available and higher column efficiency is desired. Well suited for high carrier gas flow rate situations such as with purge & trap, headspace samplers, and valve injection applications.
- Use 0.53 mm I.D. columns when only a Megabore direct injector is available. Well suited for high carrier gas flow rate situations such as with purge & trap and headspace samplers.
 0.53 mm I.D. columns have the highest sample capacities at constant d_r.

Column Length

Column length influences three parameters of major concern. They are efficiency, retention (analysis time) and carrier gas pressure.

Column efficiency (N) is proportional to column length. Resolution is a square root function of the theoretical plate number. For example, doubling column length (thus efficiency) theoretically increases resolution by only 1.41 times (closer to 1.2-1.3 times in practice). Longer columns are used when peak separation is small and high column efficiency (i.e., narrow peaks) is needed. **Figure 8** shows the difference in resolution for three different lengths.



Column Selection Principles

Solute retention is proportional to column length for isothermal temperature conditions. For temperature program conditions, the change is 1/3-1/2 of the isothermal value. When efficiency is increased by lengthening the column, there is a significant increase in analysis time. **Figure 8** shows the difference in retention for three different lengths.

Column head pressure is nearly proportional to column length. Pressure is usually not an issue unless the column has a very small or large diameter. Long, small diameter columns require extremely high head pressures, and short, wide diameter columns require very low head pressures. Neither situation is very practical and may be a limiting factor. Choice of carrier gas will also have an impact on column pressure.

Column bleed increases as column length increases. Longer columns have more stationary phase, thus more degradation products are produced. The increase in bleed with longer columns is not large and should not be a deterrent to using a longer column when one is necessary.

Column cost is directly related to column length. Doubling column length nearly doubles the price of the column. When efficiency is increased by lengthening the column, there is a significant increase in column cost. When considered in conjunction with the increase in analysis time, lengthening the column should be the last reasonable option for increasing efficiency.

Shorter columns cost more per meter than longer columns. Cutting longer columns into shorter lengths seems like a good method to save money, but it is not recommended. The quality of the smaller pieces cannot be guaranteed and may not be the same as the original, intact column. Theoretically, each piece should provide satisfactory and consistent results. In practice, this does not always occur. The probability of individual piece variation is higher when shorter pieces are cut from the original column. Greater variability between individual pieces is observed as column length, film thickness and stationary phase polarity increases, and column diameter decreases. Finally, there is the increased chance of tubing breakage when rewinding the shorter columns on other cages. Technically, cutting a column into shorter pieces voids the performance warranty.





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Column Length Selection Summary

- 1. Start with 25-30 meter columns when the best length is unknown.
- 10-15 meter columns are well suited for samples containing very well separated solutes or very few solutes. Shorter lengths are used for very small diameter columns to reduce head pressures.
- 50-60 meter columns should be used when resolution is not possible by other means (smaller diameter, different stationary phase, change in column temperature). Best suited for complex samples containing a large number of solutes. Long columns have long analysis times and higher cost.

Column Film Thickness

Column film thickness influences five major parameters: retention, resolution, bleed, inertness and capacity.

For isothermal conditions, solution retention is directly proportional to film thickness. For temperature program conditions, the change is 1/3-1/2 of the isothermal value. Thicker film columns are used to obtain higher retention for very volatile solutes. Volatile solutes normally requiring cryogenic (subambient) cooling with standard film thickness columns can be sufficiently retained at temperatures above 30°C. Changing to a thicker film column has a net effect of providing equal or greater retention at a higher column temperature. Thicker film columns are typically used for volatile compounds like solvents and select gases. Thinner film columns are used to reduce the retention of highly retained solutes. Highly retained solutes can be eluted faster or at a lower temperature. Changing to a thinner film column has the net effect of providing equal or less retention at a lower column temperature. Thinner film columns are typically used for high boiling or molecular weight compounds. **Figure 9** shows the difference in retention for two different film thicknesses.

Solutes with k values less than 2 are very difficult to resolve due to insufficient retention by the column. Changing to a thicker film column results in better resolution since solute retention is increased. The resolution improvement depends on the solute k value for the original column. For solutes with k values of about 5 or less, increasing their retention results in improved resolution. For solute peaks with values of 5-10, increasing their retention provides a small to moderate increase in resolution. For peaks with k values above 10, increasing their retention often results in no resolution improvement and sometimes a loss of resolution. Increasing film thickness to improve the resolution of early eluting peaks may result in a resolution loss for later eluting peaks.