

Stationary Phase Selectivity

When Purchasing a new column, the most important consideration is the stationary phase. There are many different interactions that occur between the analytes and the functional groups of the stationary phase. These interactions contribute more to the overall results of the analysis than any other factor in the column. That is why it is important to understand as much about your column and sample as possible.

Table I shows the chemical structure of most common stationary phases. Changes in selectivity can be observed by using a column with different functional groups as well as increasing the percentage of substitution of those functional groups. The non-polar Rtx'-1 phase will preferentially retain non-polar compounds compared to polar compounds such as alcohols. As non-polar methyl units are substituted with polar functionalities such as phenyl and cyanopropyl units, the selectivity of the column shifts towards more polar compounds. In turn, non-polar compounds are retained less as there are less overall methyl units for the nonpolar compounds to interact with. The Rtx'-200 stationary phase contains trifluoropropyl units which provide high selectivity for analytes containing lone pair electrons, such as nitro and carbonyl groups. Polyethylene glycol columns, such as Stabilwax and Rtx''/MXT-WAX columns, are polar and are highly selective towards polar compounds such as alcohols.

Table I

Comparison of structures, polarities, properties, and uses for each capillary column phase listed in order of increasing polarity.

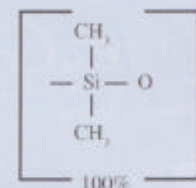

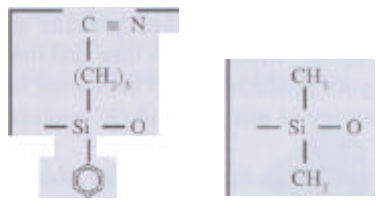


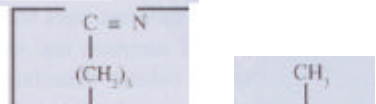
<p>Rtx[®]/MXT[®]-1 100% dimethyl polysiloxane</p>  <p>100%</p> <p>Polarity: non-polar Uses: solvents, petroleum products, pharmaceutical samples, waxes</p>	<p>Rtx[®]/MXT[®]/XTI[®]-5 5% diphenyl - 95% dimethyl polysiloxane</p>  <p>5% 95%</p> <p>Polarity: non-polar Uses: flavors, environmental samples, aromatic hydrocarbons</p>	<p>Rtx[®]/MXT[®]-1301, Rtx[®]/MXT[®]-624 6% cyanopropylphenyl 94% dimethyl polysiloxane</p>  <p>6% 94%</p> <p>Polarity: slightly polar Uses: volatile compounds, insecticide solvents in pharmaceutical prep</p>
<p>Rtx[®]/MXT[®]-20 20% diphenyl - 80% dimethyl polysiloxane</p>  <p>20% 80%</p> <p>Polarity: slightly polar Uses: volatile compounds, alcohols</p>	<p>Rtx[®]/MXT[®]-35 35% diphenyl - 65% dimethyl polysiloxane</p>  <p>35% 65%</p> <p>Polarity: intermediately polar Uses: pesticides, Aroclor[®] samples, amines, nitrogen containing herbicides</p>	<p>Rtx[®]/MXT[®]-1701 14% cyanopropylphenyl 86% dimethyl polysiloxane</p>  <p>14% 86%</p> <p>Polarity: intermediately polar Uses: pesticides, Aroclor[®] samples, alcohols, oxygenates</p>

Table I, listing column phase structures, is continued on page 7. (cont.)

Table I, listing column phase structures, continued from page 6.

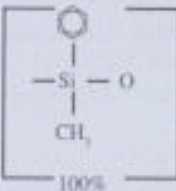
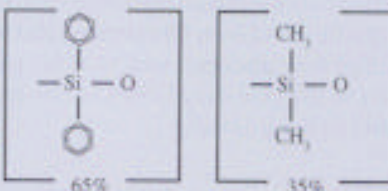
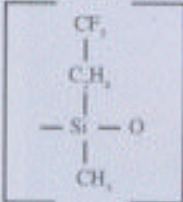
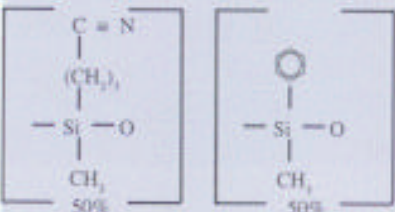
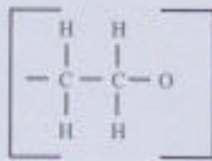
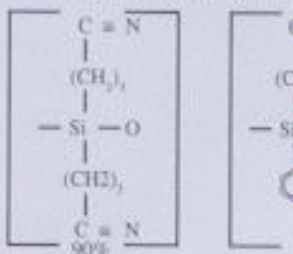
<p>Rtx[®]/MXT[®]-50 50% phenyl - 50% methyl polysiloxane</p>  <p>100%</p> <p>Polarity: <i>intermediately polar</i> Uses: <i>triglycerides, phthalate esters, steroids, phenols</i></p>	<p>Rtx[®]/MXT[®]-65TG 65% diphenyl - 35% dimethyl polysiloxane</p>  <p>65% 35%</p> <p>Polarity: <i>intermediately polar</i> Uses: <i>triglycerides, acetic acids, free fatty acids</i></p>	<p>Rtx[®]/MXT[®]-200 trifluoropropylmethyl polysiloxane</p>  <p>Polarity: <i>selective for lone pair electron</i> Uses: <i>environmental samples, active samples, drugs, ketones, alcohols</i></p>
<p>Rtx[®]-225 50% cyanopropylphenyl 50% phenylmethyl polysiloxane</p>  <p>50% 50%</p> <p>Polarity: <i>polar</i> Uses: <i>FAMEs, carbohydrates</i></p>	<p>Stabilwax[®]/MXT[®]-WAX Carbowax[®] PEG</p>  <p>Polarity: <i>polar</i> Uses: <i>FAMEs, flavors, acids, amines, solvents, xylene isomers</i></p>	<p>Rtx[®]-2330 90% biscyanopropyl 10% cyanopropylphenyl polysiloxane</p>  <p>90% 10%</p> <p>Polarity: <i>very polar</i> Uses: <i>FAMEs, ketones & diols, mono acids</i></p>

Table 11 shows retention indices for the stationary phases shown in Table I. Retention indices are mathematical derivations indicating the elution point of a probe with respect to two hydrocarbons. For example, if the retention index for benzene was 650, then it would elute halfway between C6 (RI=600) and C7 (RI=700),

EI Table II

The retention indices for each phase illustrate the differences in selectivity for a variety of compounds.

Phase	Benzene	Butanol	Pentanone	Nitropropane
Rtx [®] /MXT [®] -1	651	651	667	705
Rtx [®] /MXT [®] -5/ XTI [®] -5/Rtx [®] -5MS	667	667	689	743
Rtx [®] /MXT [®] -1301/624	689	729	739	816
Rtx [®] /MXT [®] -20	711	704	740	820
Rtx [®] /MXT [®] -35	746	733	773	867
Rtx [®] /MXT [®] -1701	721	778	784	881
Rtx [®] /MXT [®] -50	778	769	813	921
Rtx [®] /MXT [®] -65TG	794	779	825	938
Rtx [®] /MXT [®] -200	738	758	884	980
Rtx [®] -225	847	937	958	958
Stabilwax [®] /MXT [®] -WAX	963	1158	998	1230

Internal Diameter (ID)

When selecting an internal diameter, sample concentration and instrumentation must be considered. If the concentration of the sample exceeds the column's capacity, then loss of resolution, poor reproducibility, and peak distortion will result. Table III shows typical column characteristics. Note the limited capacity of narrow bore columns (0.18mm ID <50ng) versus the high capacity of 0.53mm ID columns (2000ng). Also, 0.53mm ID columns are recommended in high flow situations, such as with a purge-and-trap unit. Conversely, narrow bore columns can be installed directly into a mass spectrometry detector because of the limited flow at optimum linear velocity.

Table III Film thickness directly effects phase ratio (P) which is an important consideration when changing internal diameter. When internal diameter increases, film thickness (W) must increase in order to provide the similar resolution and retention. Table IV shows P values for common dimensions of columns. Similar values indicate similar elution for different IDs.

Table 111 Typical Column Characteristics

	Column ID			
	0.18mm	0.25mm	0.32mm	0.53mm
Helium (flow: 20cm/sec.)	0.3cc/min.	0.7cc/min.	1.2cc/min.	2.6cc/min.
Hydrogen (flow: 40cm/sec.)	0.6cc/min.	1.4cc/min.	2.4cc/min.	2.6cc/min.
Sample Capacity	<50ng	50–100ng	400–500ng	1000–2000ng
Trenzahl Values	40	30	25	15
Theoretical Plates/Meter	5300	3300	2700	1600
Effective Plates/Meter	3900	2500	2100	1200

Film Thickness

Film thickness has a direct effect on the retention and elution temperature for each sample compound. Thicker films retain compounds longer by maximizing the amount of time the compounds spend in the stationary phase. Thinner films retain compounds less by minimizing the amount of time the compounds spend in the stationary phase. Therefore, very volatile compounds should be analyzed on thick-film columns to increase the time the compounds spend in the column and allow them to separate. High molecular weight compounds, such as triglycerides, must be analyzed on a thin film column. This minimizes the amount of time the analytes stay in the column and provide low bleed at elevated temperatures, which are required when analyzing high molecular weight compounds.

Film thickness directly effects phase ratio (beta) which is an important consideration when changing internal diameter. When internal diameter increases, film thickness (df) must increase in order to provide the similar resolution and retention. Table IV shows beta values for column dimensions of columns. Similar values indicate similar elution for different IDs.

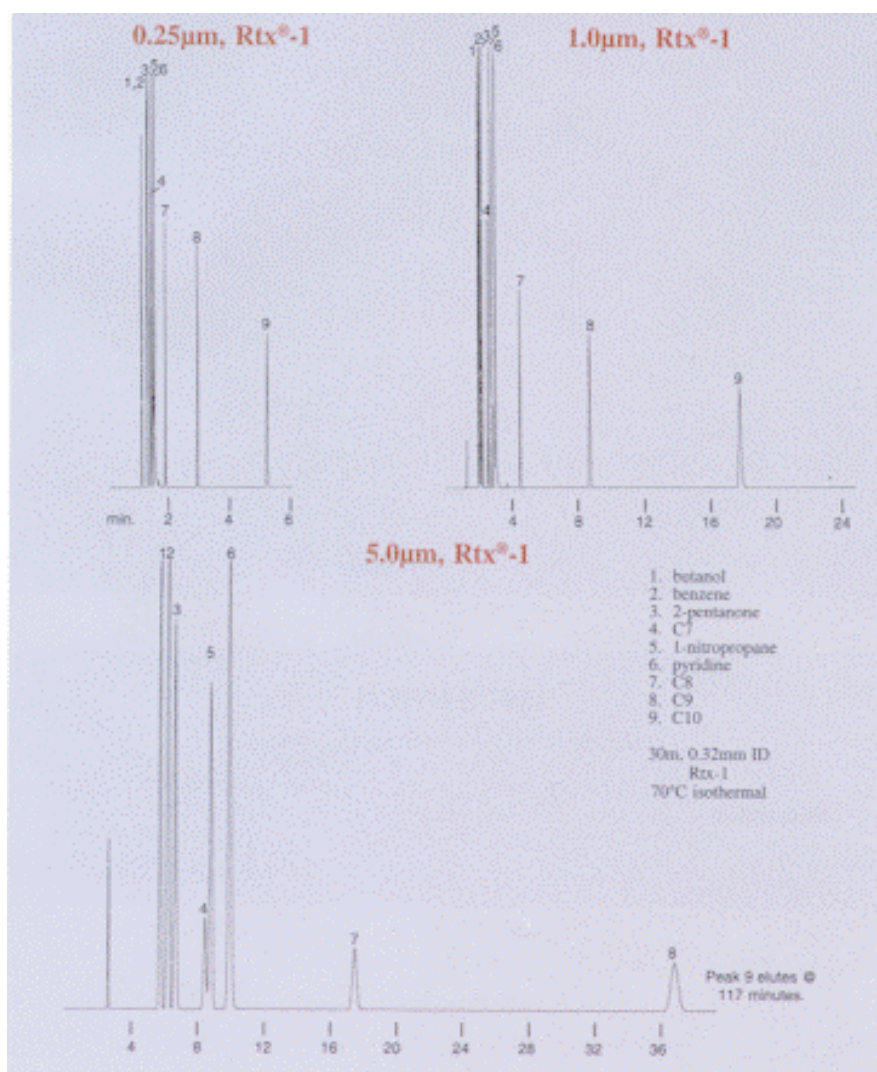
Table IV Common "beta" values

Column ID	df	0.10µm	0.25µm	0.50µm	1.00µm	1.50µm	3.00µm	5.00µm
0.18mm		450	180	90	45	30	15	9
0.25mm		625	250	125	63	42	21	13
0.32mm		800	320	160	80	53	27	16
0.53mm		1325	530	265	128	88	43	27

The following chromatograms show a sample containing low boiling compounds analyzed on a 0.25, 1.0, and 5.0um film column, with all other variables held constant. Notice that the 0.25um column does not resolve butanol from benzene (peaks 1 & 2). The 1.0um column provides about 80% resolution of this pair. Note that the retention times of the compounds eluting on the 0.25um column more than double compared to the 1.0um column. Now, compare the 5.0um to the 0.25 and 1.0um columns. The resolution between butanol and benzene (peaks 1 & 2) is not any better than the 1.0um column, and the retention times have increased six times over the 0.25um. For this particular sample, the 1.0um column is best. The resolution is better on the 1.0um column than on the 0.25um column, and the 5.0um column does not offer any additional improvements over the 1.0um column. If our true interest was in resolving the compounds prior to butanol (peak 1), then the 5.0um column would be the preferred film thickness.

Film Thickness Effects

A sample containing low boiling components shows the differences in resolution between 0.25, 1.0, and 5.0um film columns. The 1.0um offers better resolution than the 0.25um, and the 5.0um does not offer any further improvements over the 1.0um. column for compounds eluting after C6.



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GC Columns

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Length

Longer columns provide more resolving power, increase analysis times, and cost more. Often an analyst must determine whether the amount of resolution increase is worth the extra time and expense. The benefits of using longer columns differ depending on whether isothermal or temperature programmed analyses are being performed.

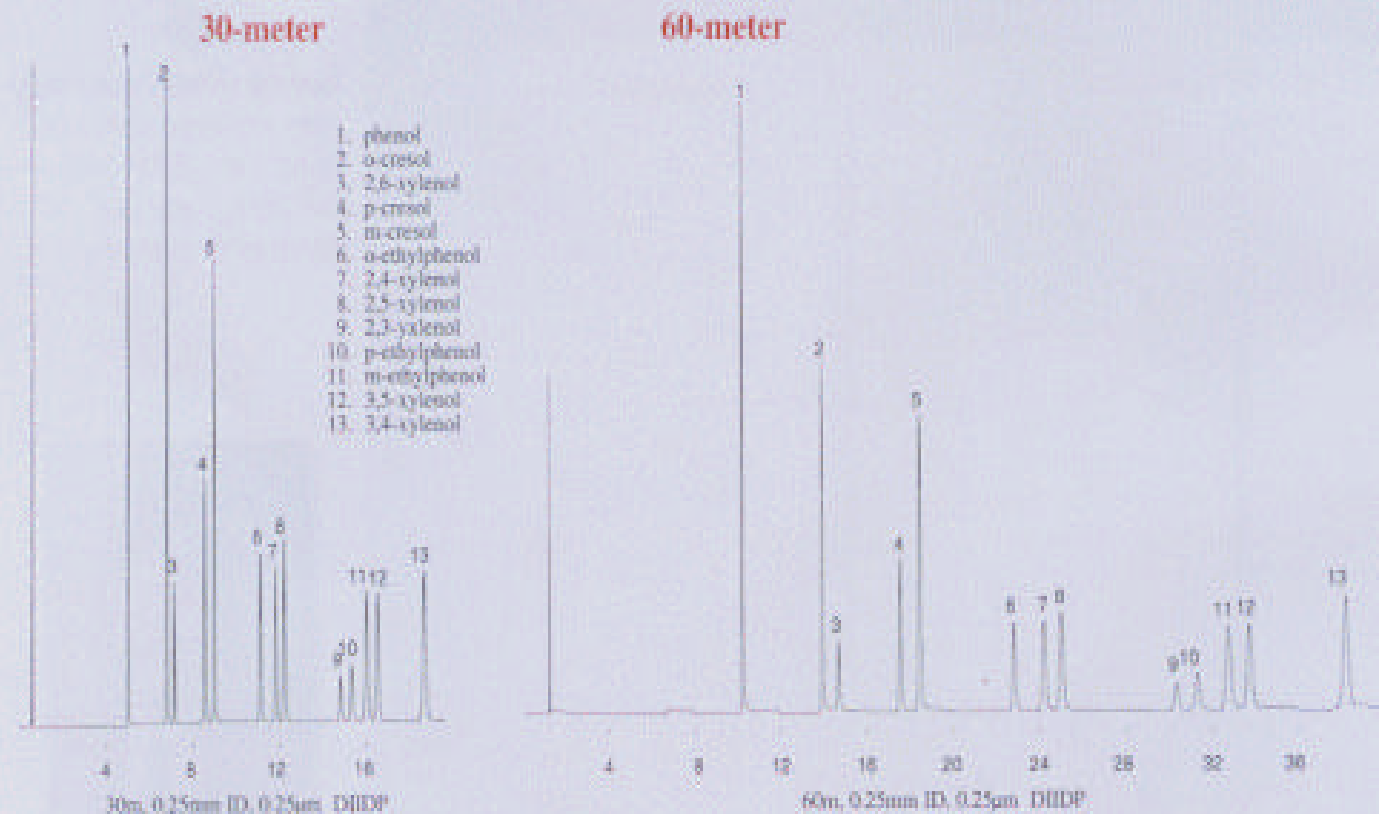
For an isothermal analysis, retention time is dependent on length of the column. If the column length is doubled, the analysis time will double as well. However, the increase in resolution is only approximately 40%, because resolution is calculated using the square root of the length.

Isothermal Analysis

When using a 60-meter column in an isothermal analysis, the resolution increases but the analysis time is approximately double that of the 30-meter column

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When using a 60-meter column in an isothermal analysis, the resolution increases but the analysis time is approximately double that of the 30-meter column.



LENGTH EFFECTS

Length affects resolution and speed of analysis.

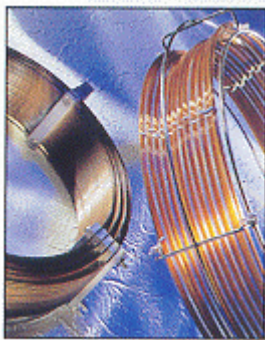
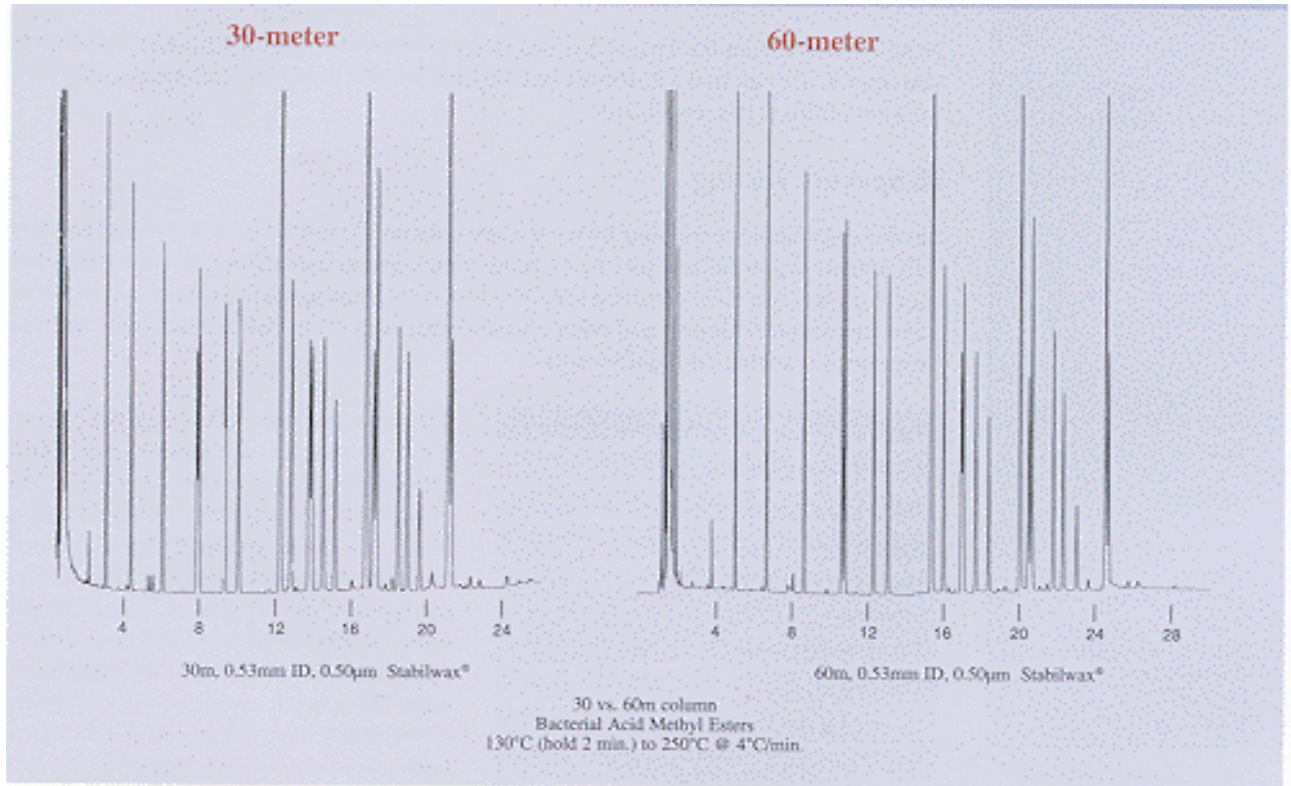
$$\text{Resolution} = \frac{1}{4} \sqrt{\frac{L}{h}} \times \frac{k}{k+1} \times \frac{\alpha-1}{\alpha}$$

L = length
h = HETP
k = capacity factor
α = selectivity

In the case of temperature programmed analyses, retention times are more dependant on temperature than column length. The increase in resolution is the same as an isothermal run, but there is only a marginal increase in analysis time

Temperature Programmed Analyses

When using temperature programming, 60-meter columns provide better resolution than 30-meter columns



Installing a Column

See elsewhere on OUR Website for basic instructions and in-depth troubleshooting “/Capillary Installation Guide”