

## 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 non-polar 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, are polar and are highly selective towards polar compounds such as alcohols.

## Table 2

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

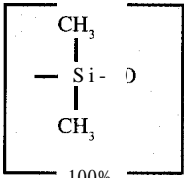
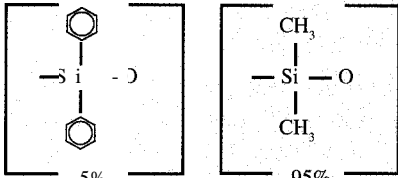
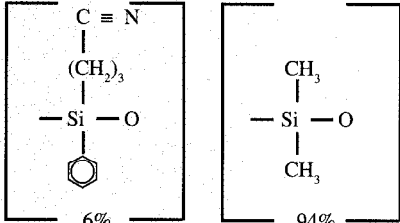
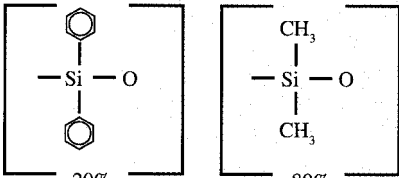
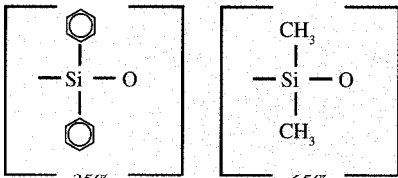
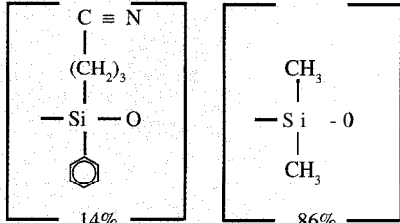
<p>Rtx/MXT-1 100% dimethyl polysiloxane</p>  <p>100%</p> <p><b>Polarity:</b> non-polar <b>Uses:</b> solvents, petroleum products, pharmaceutical samples, waxes</p>	<p>Rtx/MXT/XTI-5 5% diphenyl - 95% dimethyl polysiloxane</p>  <p>5%      95%</p> <p><b>Polarity:</b> non-polar <b>Uses:</b> flavors, environmental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

Table I (cont.) Table I, listing column phase structures, is continued on page 38.

**Table I** (cont.) Table I, listing column phase structures continued from page 38.

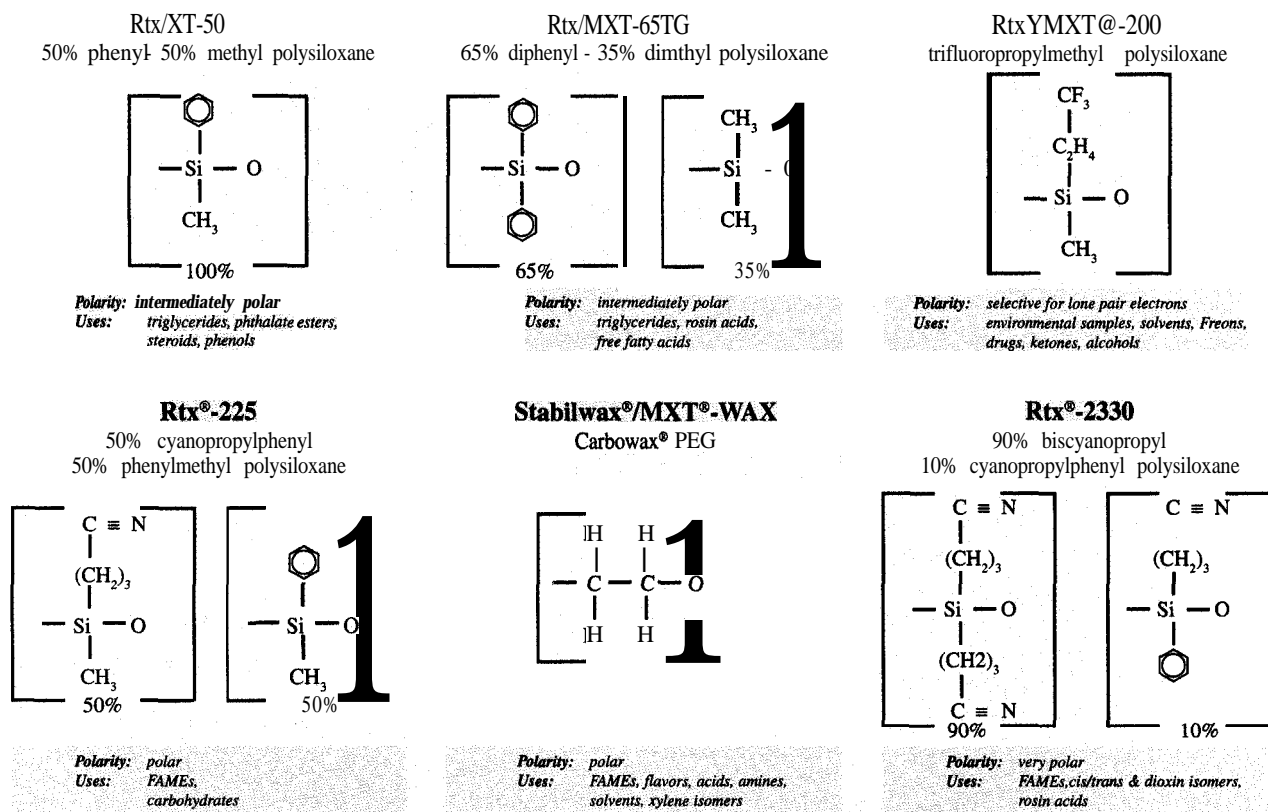
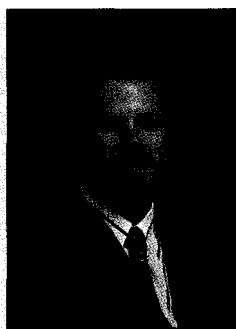


Table II shows retention indices for the stationary phases shown in Table I. Retention indices are mathematical derivations indicating the elution point of a probe with respect to two hydrocarbons. For example, if the retention index for benzene was 650, then it would elute halfway between C6 (RI=600)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

□ Table 11

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	
	963	1158	998	1230



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## □ 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, 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 MSD because of the limited flow at optimum linear velocity.

□ **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 filmed 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 common dimensions of columns. Similar values indicate similar elution for different IDs.

- **Table IV**

*Common beta Values*

Column ID	0.10um	0.25um	0.50um	1.00um	1.50um	3.00um	5.00um
0.18mm	450	180	90	45	30	15	9
0.25mm	625	250	125	63	42	21	13
0.32mm	so0	320		80	53	27	16
0.53mm	1325	530	265	128	88	43	27

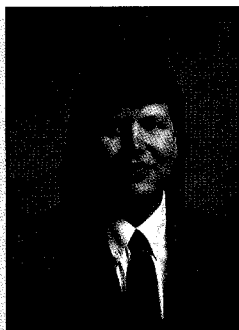


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The following chromatograms show a sample containing low boiling compounds analyzed on a 0.25, 1.0, and 5.0 $\mu$ m column with all other variables held constant. Notice that the 0.25 $\mu$ m column does not resolve butanol from benzene (peaks 1 &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

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#### Film Thickness Effects

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

