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Selectivity, α

The selectivity of the capillary column is directly related to how the analyte molecule interacts with the stationary phase being considered. If the analyte strongly interacts with the stationary phase, it can be said that strong “intermolecular” forces exist. These intermolecular forces of attraction of the analyte for the stationary phase are a function of the structure of both the analyte molecule and the stationary phase. If these two structures are similar, then these attractive forces for one another are strong. If they are weak, then analyte to stationary phase attraction is weak, and retention is less. Therefore, when selecting a stationary phase, knowledge of the structure of the analytes of interest and the stationary phase is crucial. Table II provides the chemical structure of Restek’s most common stationary phases.

An example of selectivity can be shown using benzene and butanol (both have nearly the same boiling point) eluting through the 5% diphenyl/95% dimethyl polysiloxane stationary phase (Rtx[®]-5/Rtx[®]-5ms). The benzene molecule will dissolve into the stationary phase more readily than the butanol based on the concept that “likes dissolve likes”. Benzene desolvating more readily with the stationary phase results in more interactions with the stationary phase as it elutes through the column. Therefore, the elution of these two compounds on the Rtx[®]-5/Rtx[®]-5ms stationary phase will be butanol eluting first and benzene second.

As methyl groups are replaced by different functionalities such as phenyl or cyanopropyl pendant groups, the selectivity of the column shifts towards compounds that will have a better solubility in the stationary phase. For example the Rtx[®]-200 stationary phase provides high selectivity for analytes containing lone pair electrons, such as halogens, nitrogen, or carbonyl groups. Polyethylene glycol columns, such as the Stabilwax[®] and Rtx[®]-Wax columns are highly selective towards polar compounds such as alcohols. Again using the example above, the butanol will more readily desolvate into the polyethylene glycol stationary phase; therefore, the butanol will have more interaction with the phase and elute after benzene.

Table I lists the Kovats retention indices for the stationary phases in Table II. Assigning a retention index to each probe listed provides a basis for comparing several stationary phases and their relative retention to one another for a set of molecular probes. For example, when Kovats indices are identical on two column phases, then the resulting separations will be identical. If, however, a Kovats value of one probe varies significantly from the value on another phase for the same probe, then the resulting compound elution order will differ. Thus, the Kovats indices are useful for comparing selectivity of different types of compounds among different phases.

Table I Retention indices for Restek phases

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