DESIGN OF A NEW GAS CHROMATOGRAPHIC COLUMN AND STATIONARY PHASE FOR DIOXIN ANALYSIS USING A NOVEL COMPUTER MODELING TECHNIQUE

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Historically, capillary column stationary phases used for gas chromatographic (GC) separations were synthesized with little regard for the compounds that would ultimately be separated on these columns. Liquid phases were constructed from either polyethylene glycol (PEG, Carbowax®, Stabilwax®, etc.) or polysiloxanes having phenyl, methyl, or cyanopropyl functionality. Chromatography manufacturers and instructors often discuss matching the polarity of the compounds to be separated to the polarity of the stationary phase. Frequently, a "like dissolves like" rationale is used to explain why certain compounds are more strongly retained on certain phases than others when the separation does not follow simple boiling points.

This standard explanation is both misleading and technically inaccurate because there can be significant interactions between the stationary phase and the eluting compounds. Many potential chemical forces can play a role in retention, and the summation of theses forces is known as selectivity. Selectivity of a stationary phase for a certain compound can be caused by hydrogen bonding, dipole-dipole interaction, polarizability, and solubility, as well as a number of other possible interactions. These interactions, when coupled with the boiling point of the compound, are what ultimately lead to retention, and more importantly, to the changes in retention for a group of compounds. For most separations, one or two of these forces will dominate the separation, but rarely is it as simple as matching the polarity of the liquid stationary phase to the compounds to be analyzed.

If each of these forces are not considered in the development and selection of a stationary phase for an analysis, an optimum separation will not be achieved. For many years laboratories have attempted to perform analyses using general purpose columns. These columns are the result of stationary phase design without a specific separation in mind. Therefore, these columns seldom perform the analysis as well as possible, leaving analysts to settle for a less than ideal separation. If separation is compromised by allowing even partial coelution of compounds, quantitation accuracy will be sacrificed.

The science of retention properties has been understood for some time[i], however only in the last few years have computers been able to apply physical chemistry concepts to the prediction of chromatographic retention. Although still in its infancy, we now have the ability to predict retention order, retention time, peak width, and therefore resolution for stationary phases that have yet to be synthesized. This unique approach to the design of new stationary phases at Restek Corporation has yielded application-specific GC columns that can outperform any traditional stationary phase available. This is a result of the stationary phase selectivity being "tuned" to the

compounds being separated. In addition to tuning for the specific separation, other desirable qualities also can be designed during the modeling process; for example, thermal stability, inertness, etc.. The application of this process has yielded a number of capillary column stationary phases which perform better than any of the products available prior to the introduction of these columns. An example of the outcome of process would be the Rtx®-CLPesticides columns, the Rtx®-VMS, Rtx®-VGC, Rtx®-TNT columns, and the Rtx®-5SilMS.

The design of stationary phases can follow one of two methods, depending on whether the analysis of the target compounds can be performed somewhat successfully on pre-existing functionalities. If this is the case, the first step is to analyze all of the target compounds on the functional groups or stationary phases (methyl, phenyl, cyanopropyl, etc.) that would yield unique selectivities for these target compounds. Once this data has been acquired, a multidimensional graph is constructed representing the elution times of the compounds on the various phases. In most cases a linear relationship can be used to connect the individual data points, creating a multidimensional plane that represents retention under any possible combination of these functionalities. Figure 1 shows a portion of such a plot for two functionalities (phases) for several volatile compounds.

Figure 1. Plot of Retention versus Functionality.

Retention time plot for listed volatile compounds:
X axis 1 is the Rtx®-1 column.
X axis 2 is Rtx®-35 column.
Midpoint solution line represents an Rtx®-502.2 column.

Compound	Rtx®-1	Rtx®-502.2	Rtx®-35
1.) Chlorobenzene	17.79	18.57	19.27
2.) 1,1,1,2-Tetrachloroethane	17.78	18.58	19.29
3.) Ethylbenzene	18.26	18.78	19.25
4.) m/p-Xylene	18.48	18.90	19.27
5.) 1-Chloro-2-fluorobenzene	18.16	18.93	19.61
6.) o-Xylene	19.07	19.60	20.07
7.) Styrene	18.93	19.63	20.25
8.) Bromoform	18.58	19.96	21.19

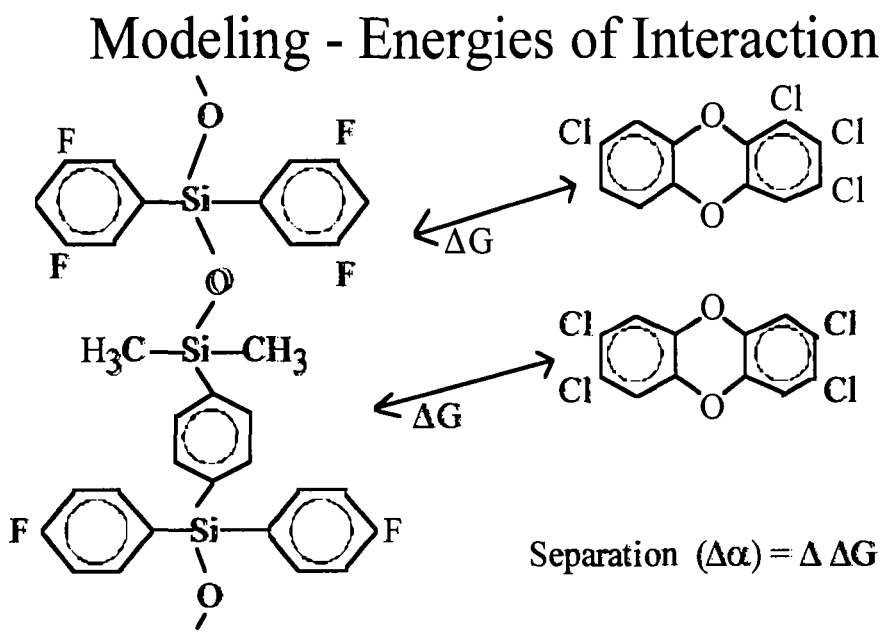
Once the data has been converted to either graphical or numerical format, a solution program determines the location (phase composition) where there are no coelutions and the overall retention time is at a minimum. Figure 1 shows the composition of the Rtx®-502.2column, and the theoretical retention times predicted from a numerical solution. Once this polymer was made, and the retention times were measured, there was almost no error in the predicted retention times versus the actual retention times, thus indicating the solution is valid. It is important to note for the data in Figure 1 that the location where no coelutions occur is not selected. Although Figure 1 only shows this solution for a very limited compound set with only two functionalities, this modeling process has also been applied to multidimensional data (3 to 8 space) with equal success.

The more difficult problem arises when there is no empirical data available, or when no existing single functionality gives desired selectivity for the compounds of interest. This would be the

case in the design of a column to separate the dioxin and furan congeners. While many columns have been used for this analysis, no single column gives desired separation with high thermal stability, low bleed, long lifetime, and separation by chlorination level. Generally most analysts use a 5% diphenyl phase; confirming with a high-cyano phase of some type. There is no column that is ideal, however, and most common functional groups used for stationary phase construction do not give desired selectivity to use the process previously described.

When this case arises, we have developed a second way to predict the separation of compounds on hypothetical phases. Again, recognizing that there is a relationship between a compounds distribution coefficient, and the Gibbs free energy between a solute, and the solvating stationary phase, we can explicitly calculate the resulting separation when this stationary phase is synthesized. This second modeling employs a molecular dynamics calculation of the difference in free energy between the partitioning of the analyte between the stationary phase, and the flowing carrier gas (Figure 2). This technique also allows for testing of many different functionalities, prior to synthesis of the stationary phase, and if the separation is not exact, the data can then be collected to allow modeling by the procedure previously discussed.

Figure 2: Determination of selectivity differences on hypothetical phase for two dioxin congeners



This presentation will address both modeling techniques, as well as demonstrate the success of these procedures.

[1] Giddings, J.C., Unified Separation Science, John Wiley & Sons inc., New York, 1991.