

Improving Capillary SFC Performance with High Volume, High Efficiency Split/Splitless Injection

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Outline of Discussion

- Overview of SFC
- Historical difficulties with capillary SFC
- Split/splitless injection technique
- Comparison with timed split (direct) injection
- Benefits of split/splitless and applications
- Summary



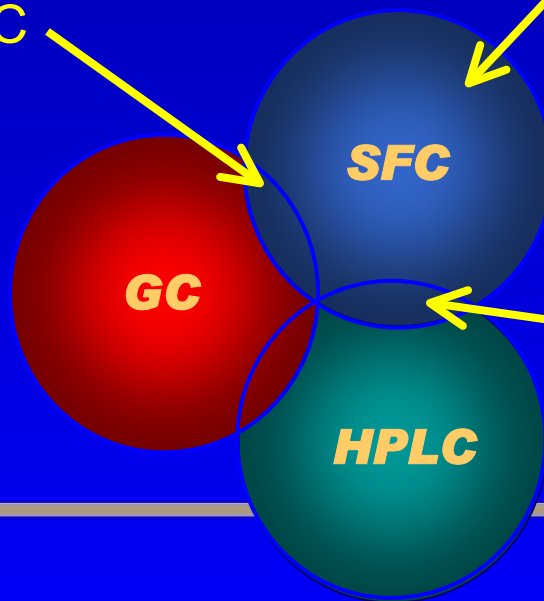
Overview of SFC

- Klesper and Turner first used supercritical fluids as mobile phase in 1962
- SFC's niche in the world of chromatography

Some compounds require derivatization for GC; they do not for SFC

SFC has unique separations for thermally unstable, non-chromophoric, and reactive compounds

SFC has better detector capability and easier method development than HPLC



Problems Associated with SFC

- Difficult technique to use
 - Instrumentation available was difficult to use and not reliable
 - Problems were faced when dealing with supercritical fluids
 - Restriction techniques
 - Injection techniques
- GC and HPLC markets were well established and growing rapidly



Two Approaches to SFC

- GC approach packed or capillary columns with carbon dioxide
 - Developed by Dr. Milton Lee
 - Use of capillary columns patented to BYU and University of Indiana
 - Introduced Model 501 Lee Scientific SFC in 1986
- LC approach packed columns with modified carbon dioxide
 - First commercial SFC instrument introduced by Hewlett Packard in 1982
 - Suprex enters packed column SFC market in 1986



Advantages of using SFC

- Faster method development with SFC than in LC, used density to change mobile phase composition
- Use of the flame ionization detector when using carbon dioxide as the mobile phase
- Supercritical fluids have a higher range of solubility than obtained by GC
- Eliminates derivatization steps
- Better temperature ranges for thermally labile compounds



Current Market

- Petroleum industry has regulated SFC methods for diesel and gasoline testing- packed column
- Pharmaceutical industry uses SFC methods for chiral separations and drug discovery- packed column with modified carbon dioxide
- Capillary column SFC struggles with a few selected niche applications- mainly due to ease of use issues



Split/Splitless Injection Addresses Many Problems Related to Capillary SFC

- Concept originated in 1989 by Dr. Milton Lee and group
- Technique is analogous to Split/Splitless injection practiced in GC



Instrumentation

Selerity Technologies 3100 SFC

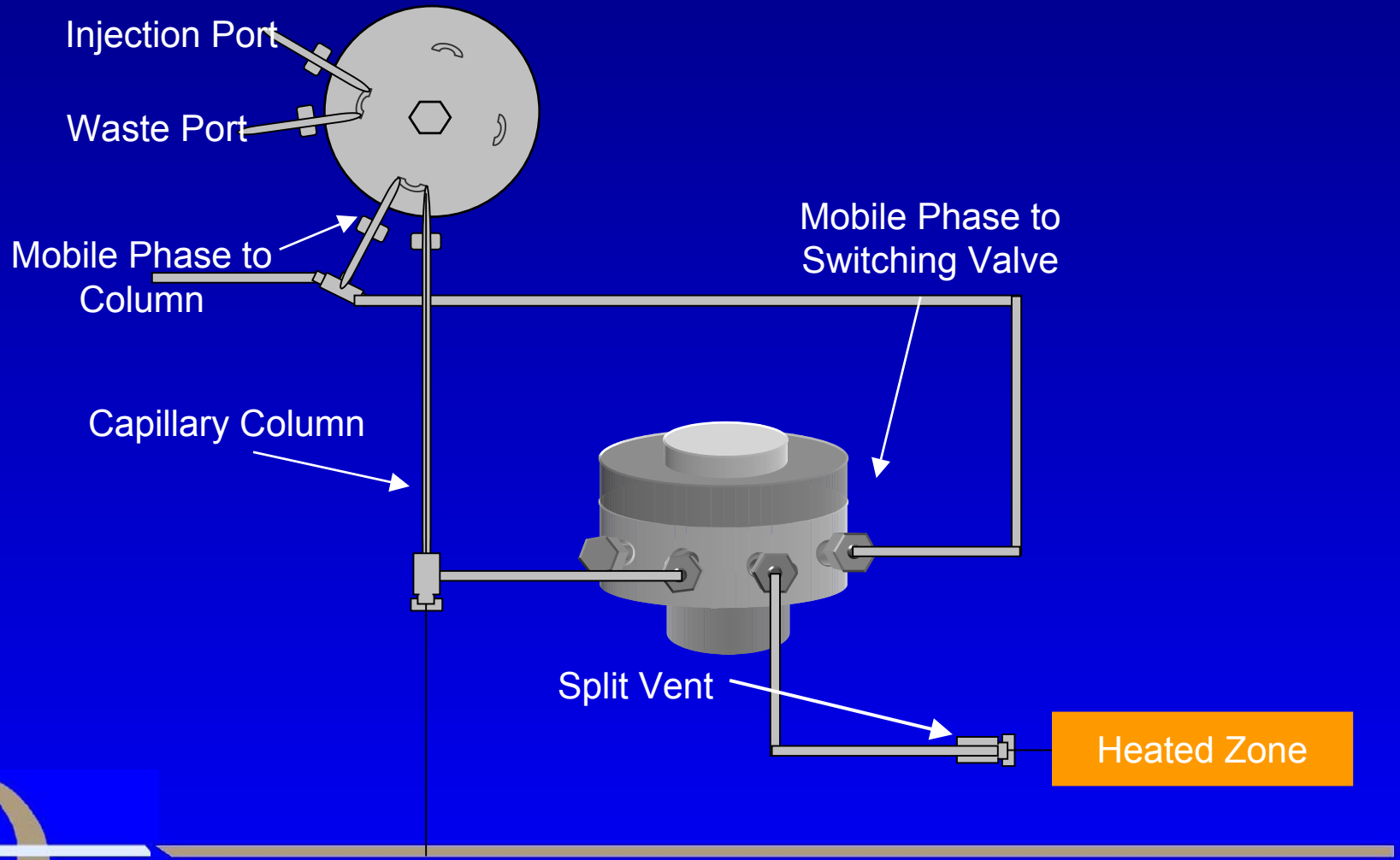


SB-Methyl-100, 50 μ m ID, 5 meters

SB-Biphenyl-30, 50 μ m ID, 5 meters



Diagram of Split/Splitless Injection



Benefits of Split/Splitless Injection for SFC

- Inject the sample onto the column and split off the dead volume
 - Increases sample capacity
 - Improves peak shape and efficiency
 - Decreases solvent effects of early eluting peaks
 - Improves retention time repeatability
 - Improves reproducibility
 - Vary sample concentration by changing the split times

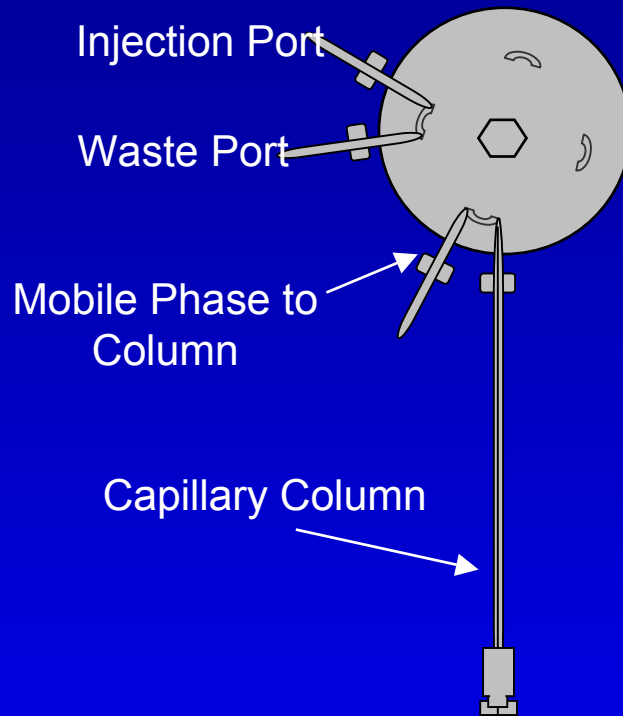


Important Parameters for Technique

- Leak free system
- Equilibrate column conditions before injection
 - Keep split vent open until pump pressure drops back down to starting pressure
 - Open split vent before injection
- Heat the restrictor on split vent

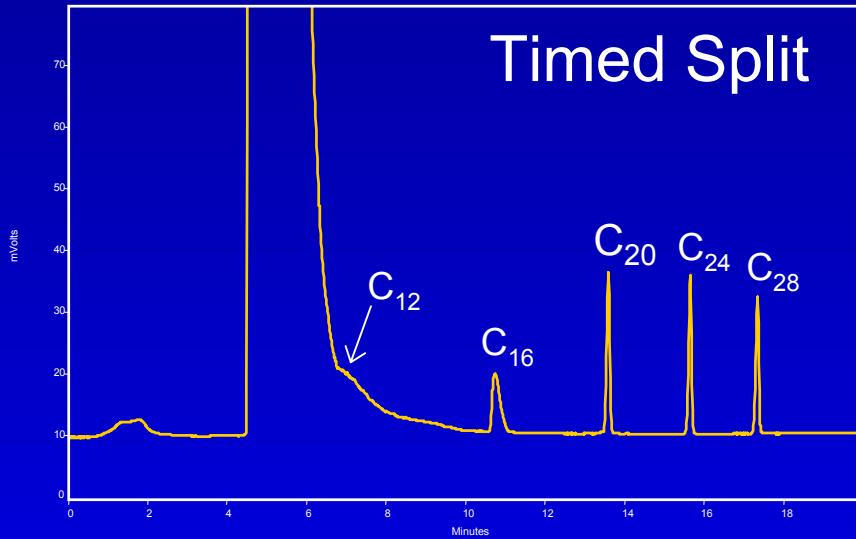


Diagram of Timed Split Injection

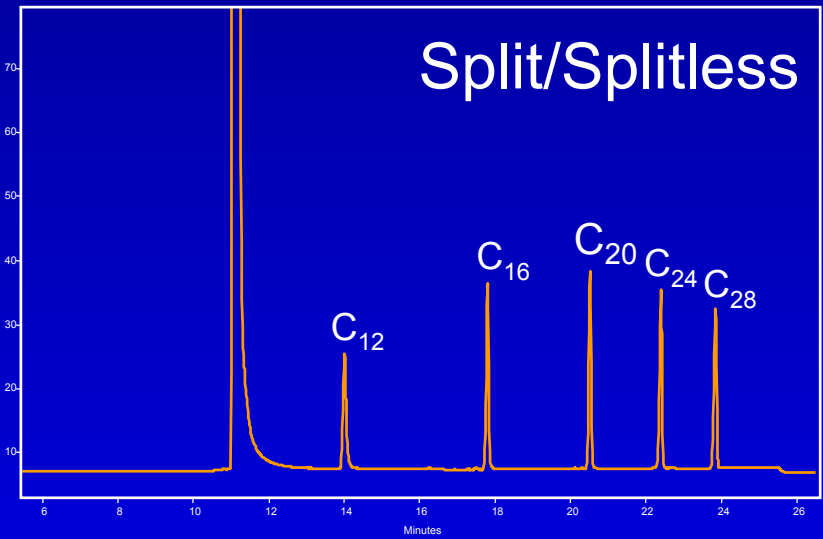


Timed Split vs. Split/Splitless

Hydrocarbon Standard- C_{12} , C_{16} , C_{20} , C_{24} , C_{28}



C_{12} lost in solvent tail



C_{12} sharp peak, resolved from solvent



Calculated %RSD Using Timed Split Technique

Timed Split Injection					
	Area C ₁₂	Area C ₁₆	Area C ₂₀	Area C ₂₄	Area C ₂₈
Run 1	ND	155536	172361	156372	144575
Run 2	ND	173296	185513	168679	156872
Run 3	ND	171031	179241	163979	152768
Run 4	ND	202508	214090	196695	184950
Average		175592.75	187801.25	171431.25	159791.25
STDev		19602.623	18330.427	17589.286	17534.205
%RSD		11.164	9.760	10.260	10.973

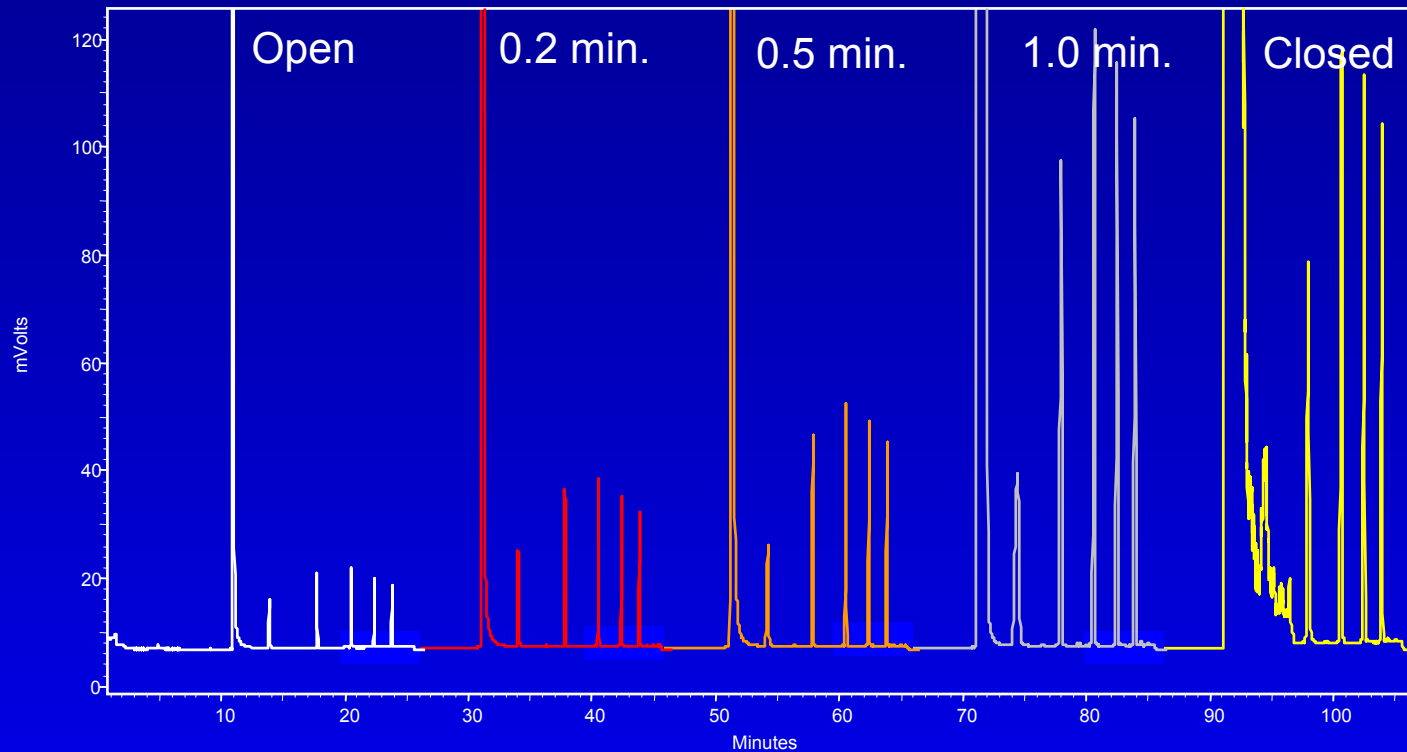


Calculated %RSD Using Split/Splitless Technique

Split/Splitless Injection					
	Area C ₁₂	Area C ₁₆	Area C ₂₀	Area C ₂₄	Area C ₂₈
Run 1	100842	122408	132242	122652	116079
Run 2	107525	130952	141701	130936	123703
Run 3	107441	130817	141007	130566	124207
Run 4	106739	129613	140230	130061	123638
Average	105636.75	128447.50	138795.0	128553.75	121906.75
STDev	3215.866	4071.077	4409.792	3950.8109	3893.480
%RSD	3.044	3.169	3.177	3.073	3.194



Adjust Concentration by Varying Split Vent Open Time

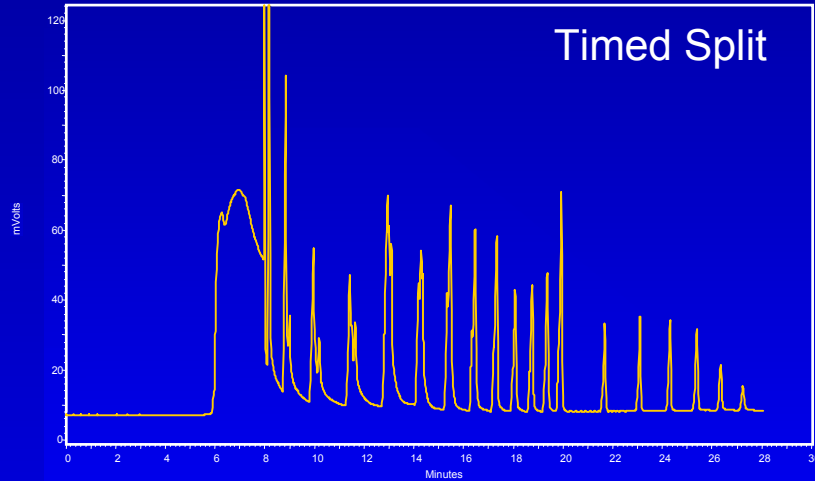


Split/Splitless Injection

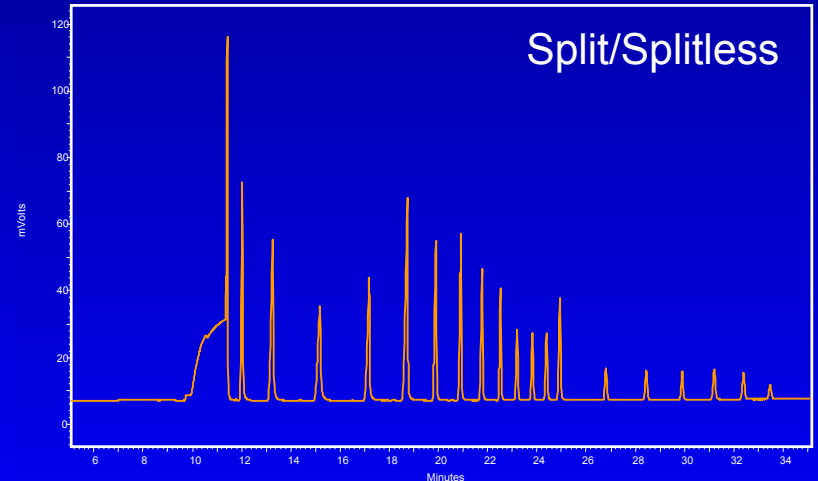


Improves Loadability

Hydrocarbon standard C_5-C_{20} , $C_{24}-C_{44}$ in carbon disulfide



Split peaks

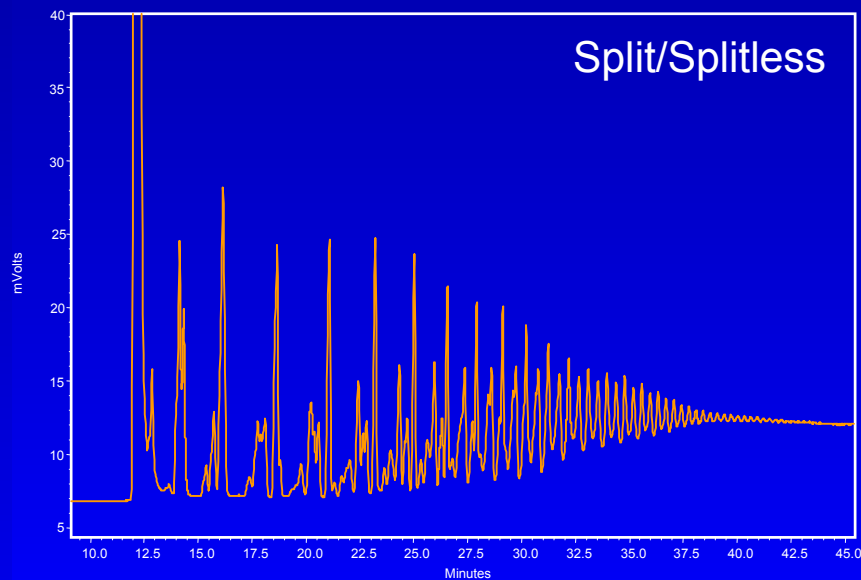
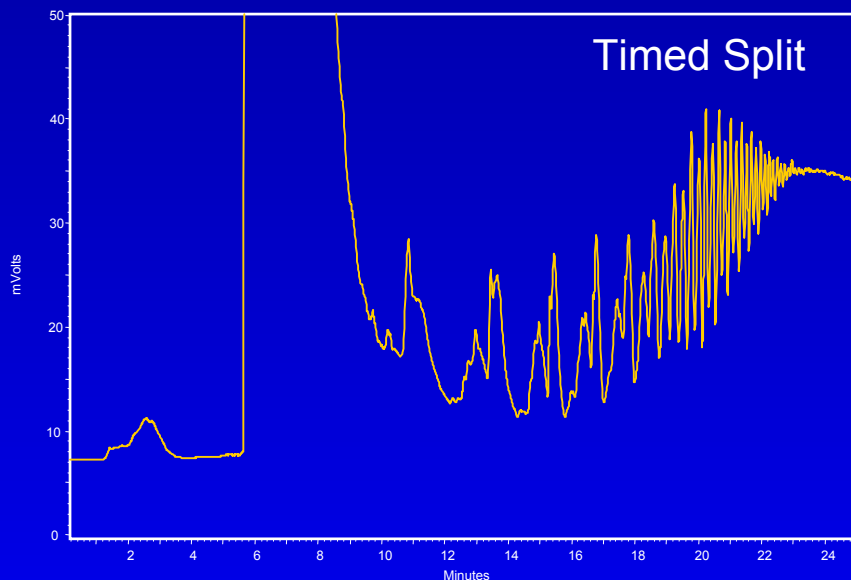


Sharp peaks



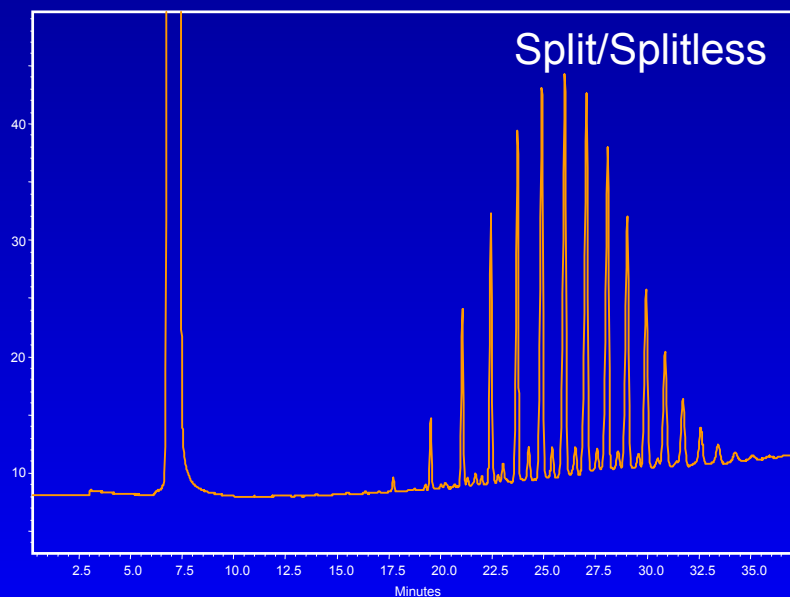
Reduces Solvent Effects from Early Eluting Peaks

Low molecular weight siloxane with tri-functional groups

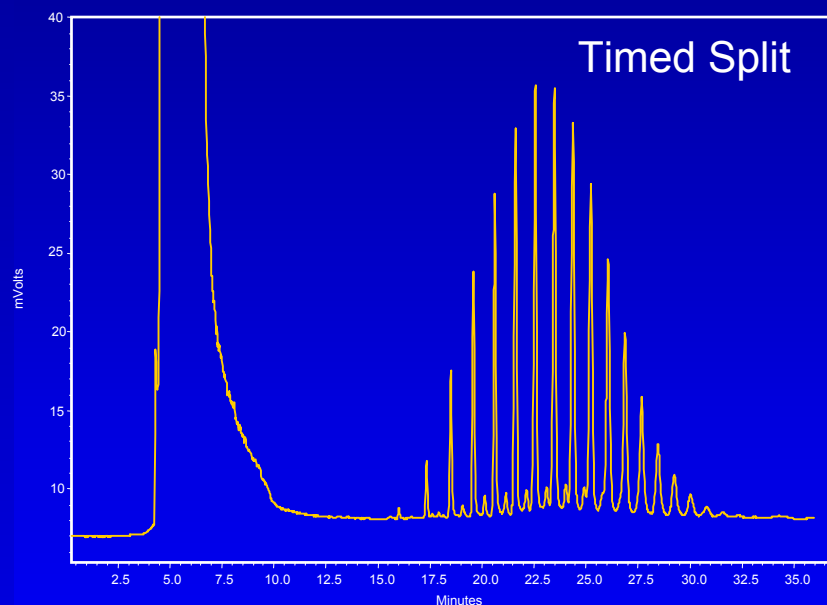


Increases Efficiency

Surfactant (Triton X-100)



10 peaks in Isomeric
distribution



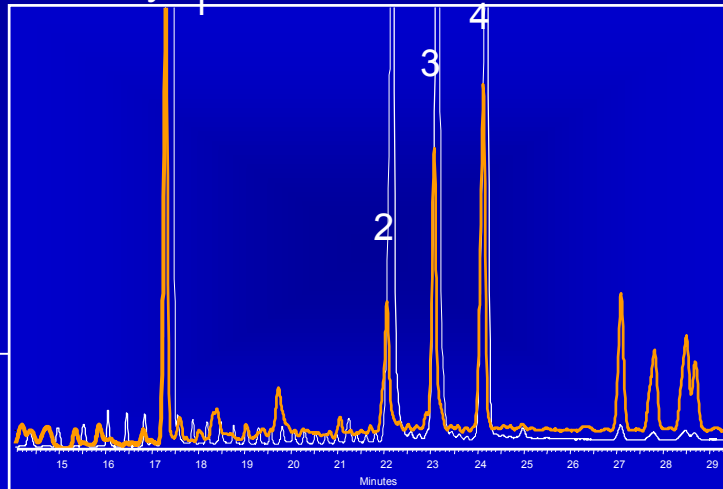
8 peaks in Isomeric
distribution



Improves Retention Time Repeatability

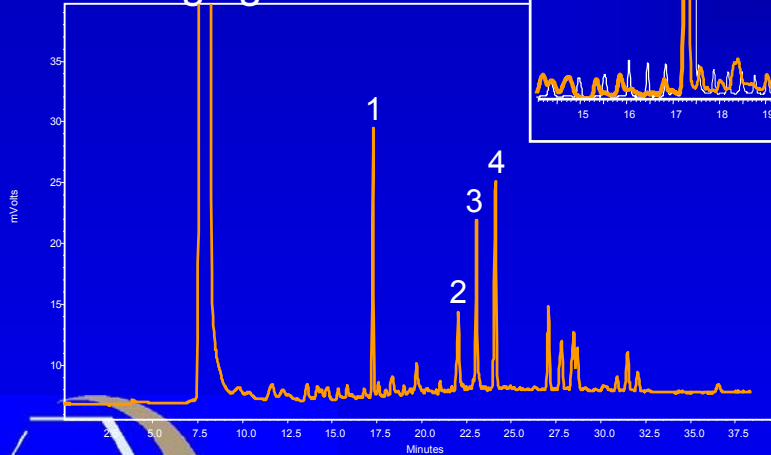
Polymer additives

Overlay 1

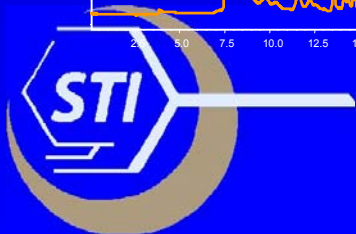
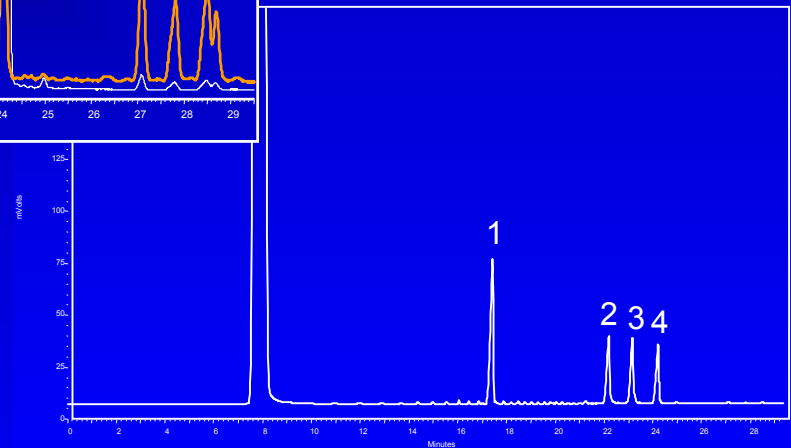


1. n-Eicosane
2. Monopalmitate
3. Monostearate
4. Erucamide

Packaging material

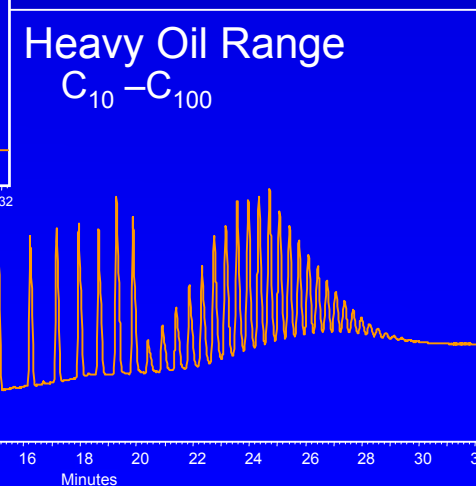
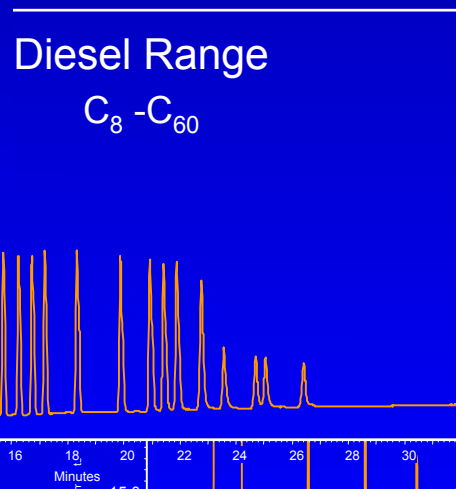
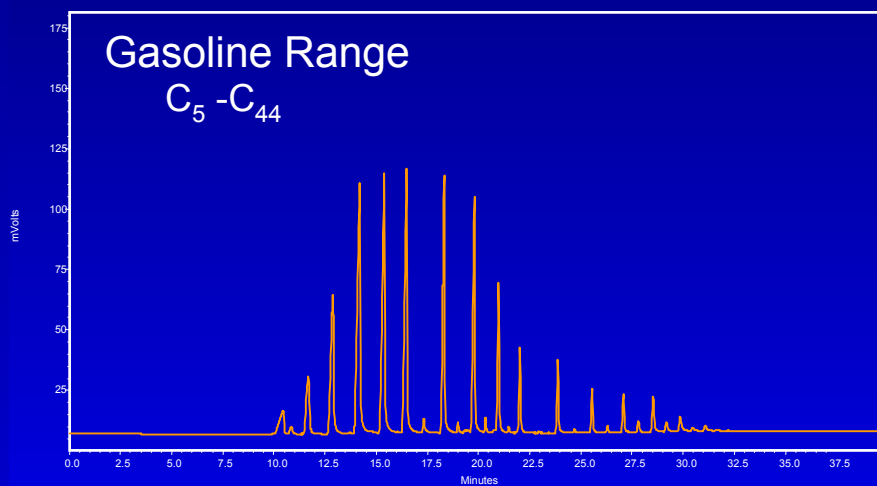


Standards



Extends Molecular Weight Range

Hydrocarbon standard for simulated distillation



Conclusion

- Easy to use
- Adds flexibility to injection
- Loadability
 - Solvent splits off minimizing solvent effects
 - Better sensitivity for early eluting peaks
 - Better efficiency
- Minimize dead volume

