Using Computer Modeling to Predict and Optimize Separations for Comprehensive 2-Dimensional Gas Chromatography

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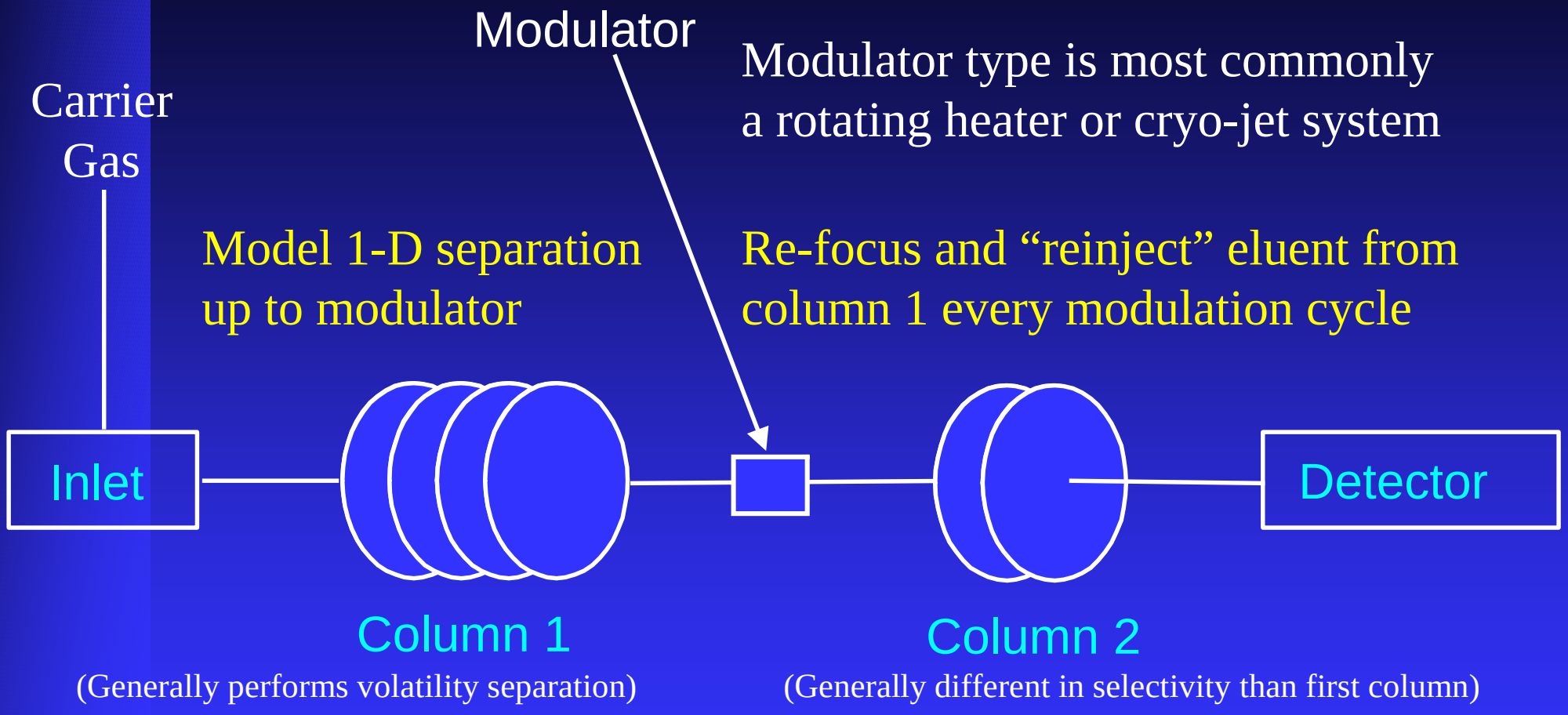
Comprehensive 2D-GC System



Why do we need to model GCxGC Separations?

- Optimization is much more difficult
  - Changes in oven programming, modulation time, offset temperatures, etc… have a more complex impact on separations
- "Translation" from GC-GC-TOFMS for method development to GCxGC-FID or GCxGC-ECD for more routine analysis
- Choice of best column ensemble is not as obvious

Optimization/Modeling of Separations

- Several approaches have been used for conventional separations
- Allows prediction of optimal conditions for a users column (Pro EZ-GC)
- Allows prediction of optimal stationary phase chemistry and conditions (*Anal. Chem.* **74**(9), 2133-2138 2002)
- Can these be applied to Comprehensive 2-D separations?

1-D Modeling

General Equation for Resolution:

$$R = 1/4\sqrt{L / h}\ x\ (k / k+1)\ x\ (\alpha\text{-}1 / \alpha)$$

Selectivity Factor (α) – addressed by stationary phase modeling

not commonly done by end user

Capacity Factor (k), and Column Factor – addressed by physical modeling

can be simultaneous with, or independent of stationary phase modeling

Stationary Phase Optimization

- Window diagramming
- Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
- Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition **AND** column dimensions
  - Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX, Rtx-OPPesticides2, Customer-specific columns
- Computer prediction of solute/stationary phase interactions for new polymer designs

Achieving Analyte Separation

Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha-1 / \alpha)$$

Capacity Factor

$$k = (t_R - t_0) / t_0$$

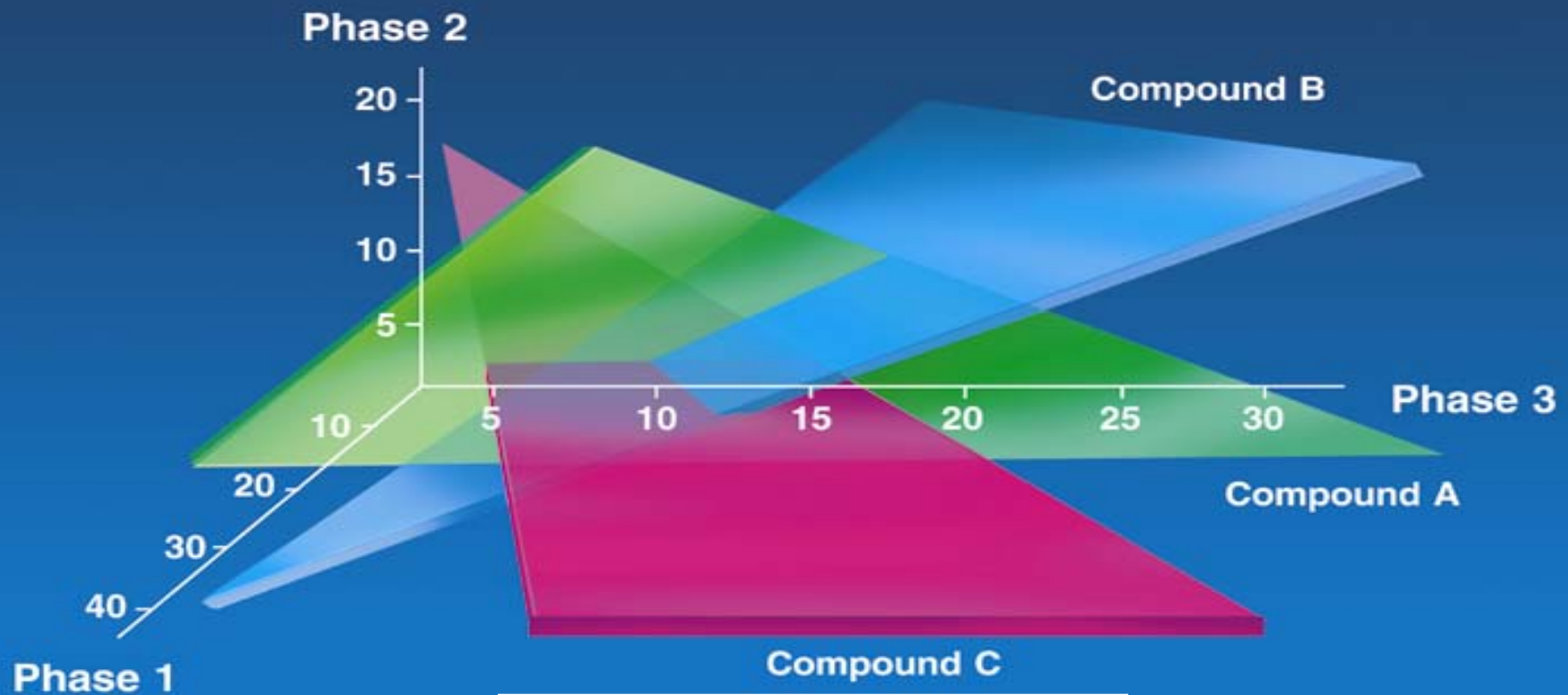
Selectivity

$$\alpha = k_2 / k_1$$

Thermodynamics:

$$\Delta G = \Delta H - T\Delta S \qquad \Delta G = -RT \ln K_D$$

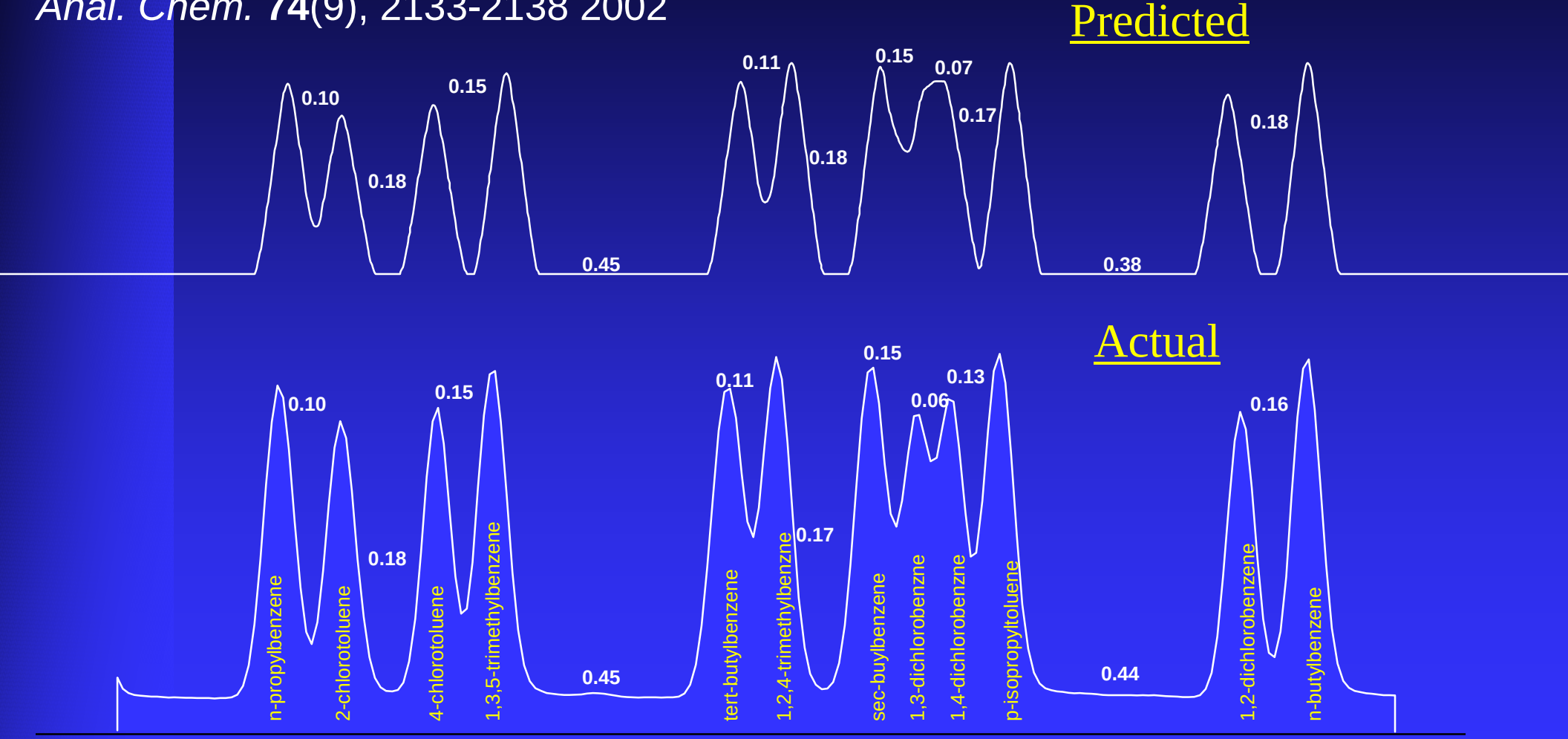
3-Space Selectivity Model for 3 Compounds



Surface= $\mathcal{F}\Delta H\Delta S$

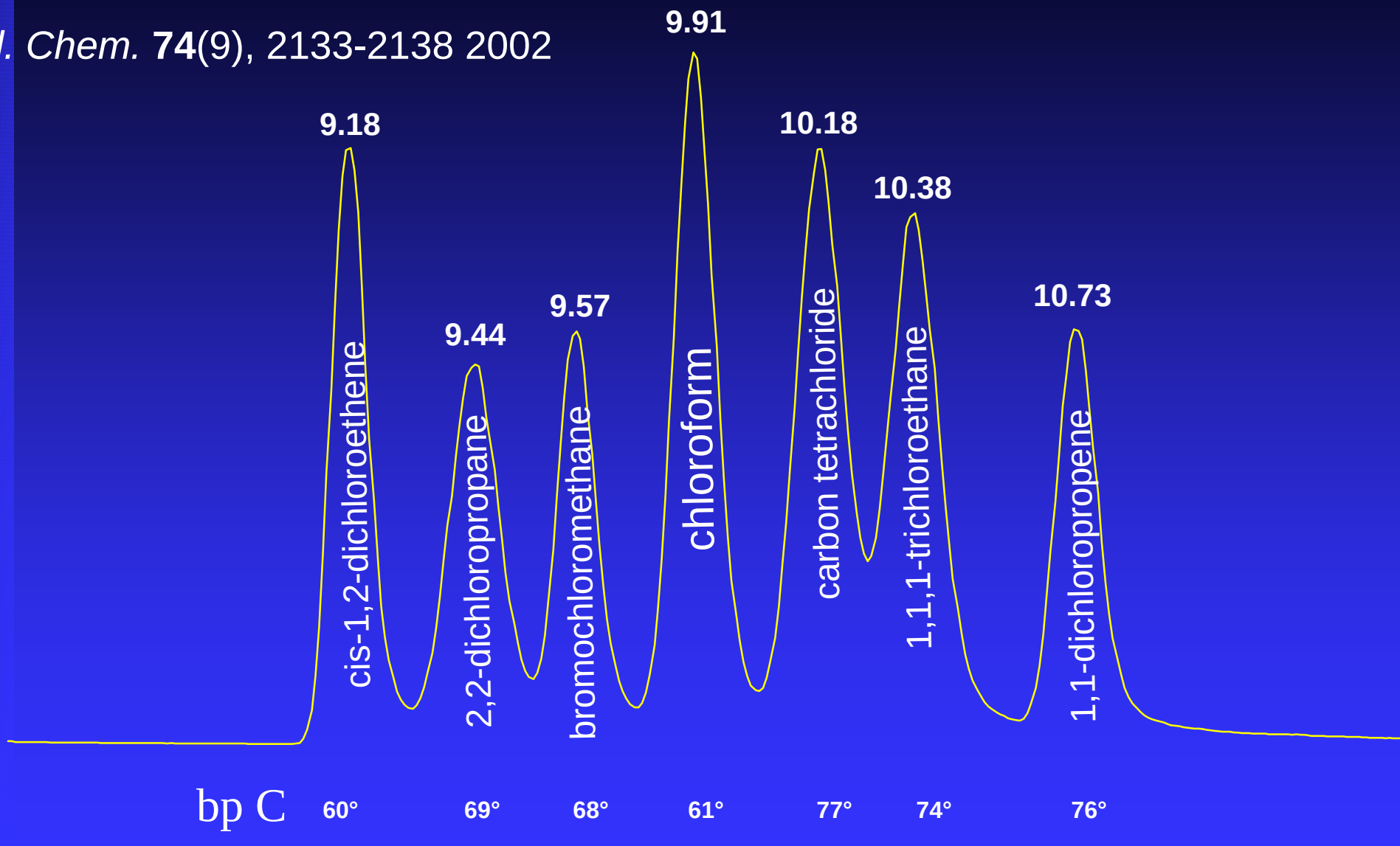
Volatiles Analysis: Predicted vs. Actual 4 Dimensional Phase

Anal. Chem. **74**(9), 2133-2138 2002



Volatiles Analysis: Rtx®-VGC

Anal. Chem. **74**(9), 2133-2138 2002



Simultaneous 2-D Modeling
---or---
Why 2D is not 2X 1D GC

1.) Calculation of the pressure at the modulation point

not as straight forward during a “desorption”

2.) Not a normal “injection” onto second column

there may be a selective retention of analyte in the phase at the modulation point

3.) There is no “buffer volume” at the modulation point, or a pressure controller to adjust for any pressure surges

at 1 atm a liquid expands 1000X as it vaporizes

Input Data

- Compounds of interest analyzed in 1-D mode on each stationary phase of interest at two different temperatures or temperature programs
- A separate ΔH and ΔS are calculated for each compound on each stationary phase independent of physical parameters
- Separation is modeled on conditions of 1st column
- Eleuent is re-focused (peak width is re-calculated) and injected onto 2nd column
- Final elution from second column is reported as a function of both 1st and 2nd dimension – tabular report

Grob Test Mixture

As numbered on 2D Chromatogram

- 1.) 2,3-butanediol
- 2.) decane
- 3.) undecane
- 4.) 1-octanol
- 5.) 1-nonanol
- 6.) 2-ethylhexanoic acid
- 7.) 2,6-dimethylphenol
- 8.) 2,6-dimethylaniline
- 9.) C10 FAME
- 10.) C11 FAME
- 11.) dicyclohexylamine
- 12.) C12 FAME

Pressure at Modulation Point

$$p_m^2 = \frac{\pi}{16R}\left(\frac{p_{icol1}^2 a_2 + p_{ocol2}^2 a_1}{a_1 + a_2}\right)$$

$$a_1 = \frac{\eta_1 T_1 L_1}{r_1^4} \text{ and } a_2 = \frac{\eta_2 T_2 L_2}{r_2^4}$$

Partition Coefficient of Component i in Stationary Phase i

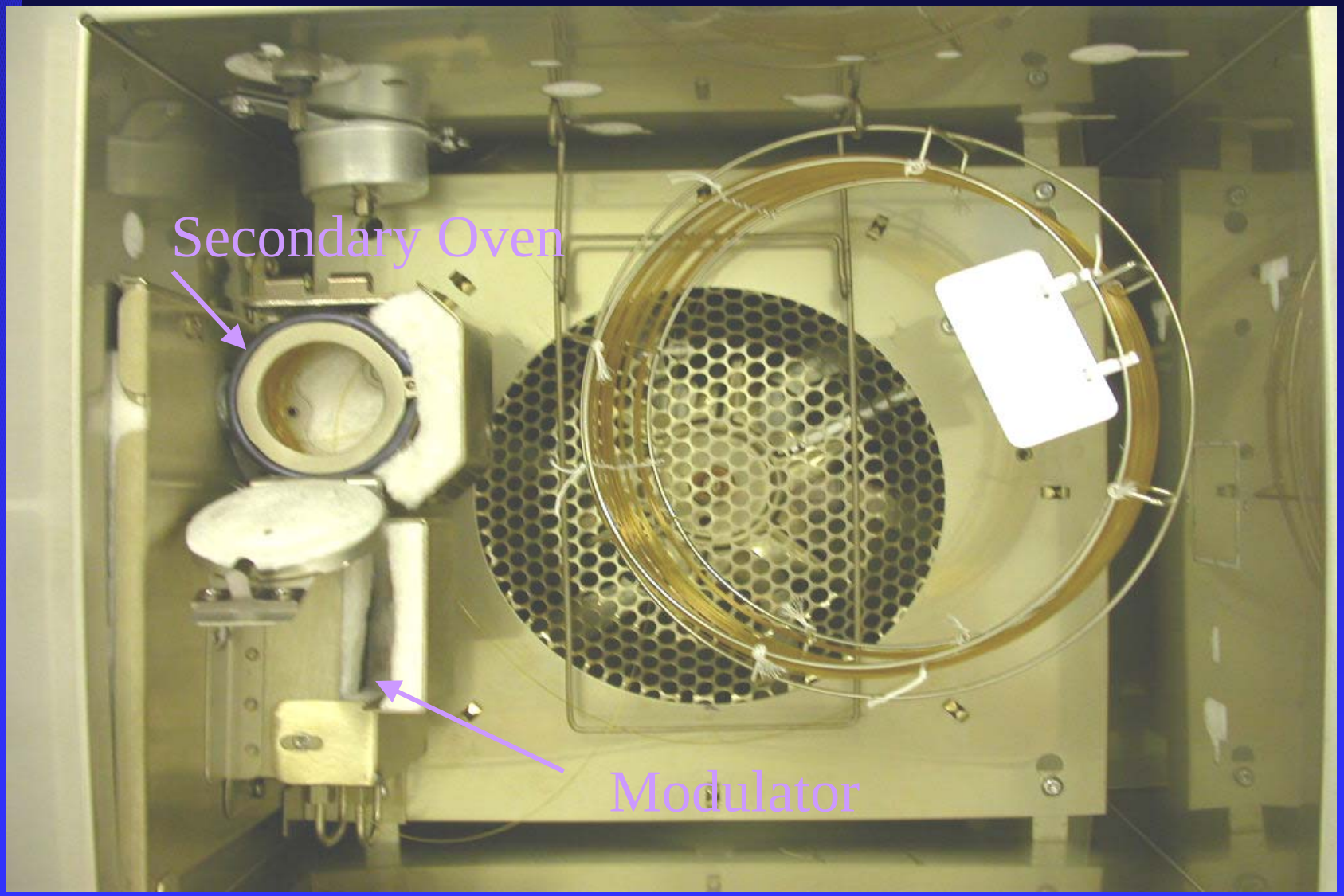
$$K_i = e^{-(\Delta H_i - T\Delta S_i)/RT}$$

Retention ratio as a function of stationary phase composition

$$\Re = \frac{1}{1 + \beta \sum_{i=1}^{N} X_i K_i}$$

LECO GCxGC-FID

Modulator and Secondary Oven



Run Conditions

Primary Oven	
Initial Temp (*C)	40
Hold Time (min)	0.2
Ramp (*C/min)	17
Final Temp (*C)	200
Hold Time (min)	1
Modulator	
Temp Offset (*C)	30
Mod. Time (sec)	3
Hot Pulse (sec)	0.4

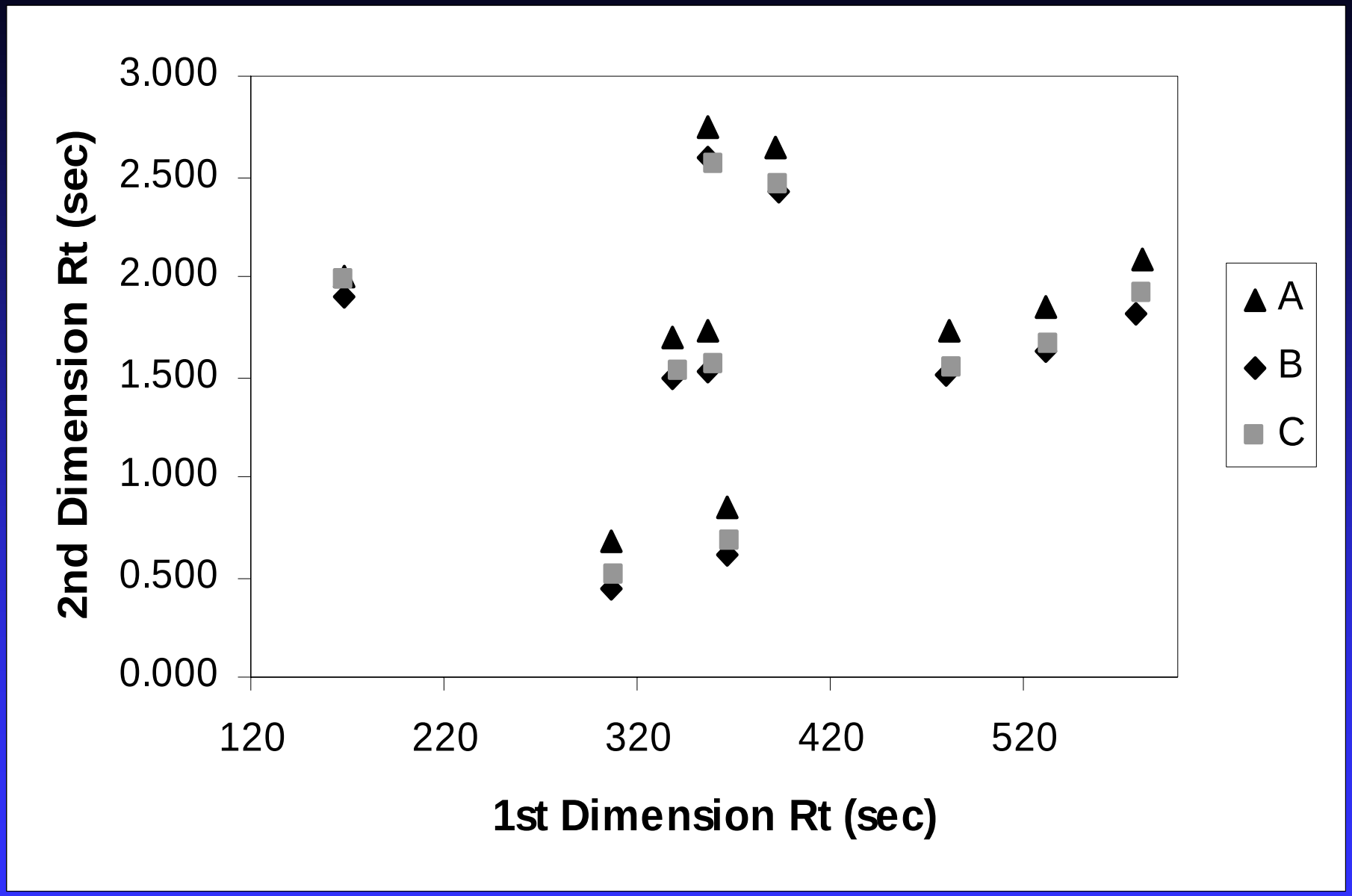
2nd Oven	
Temp Offset (*C)	10
GC Conditions	
Constant Pressure	20 psi
Split Ratio	10:1
Inlet Temp	250*C
Detector Temp	250*C

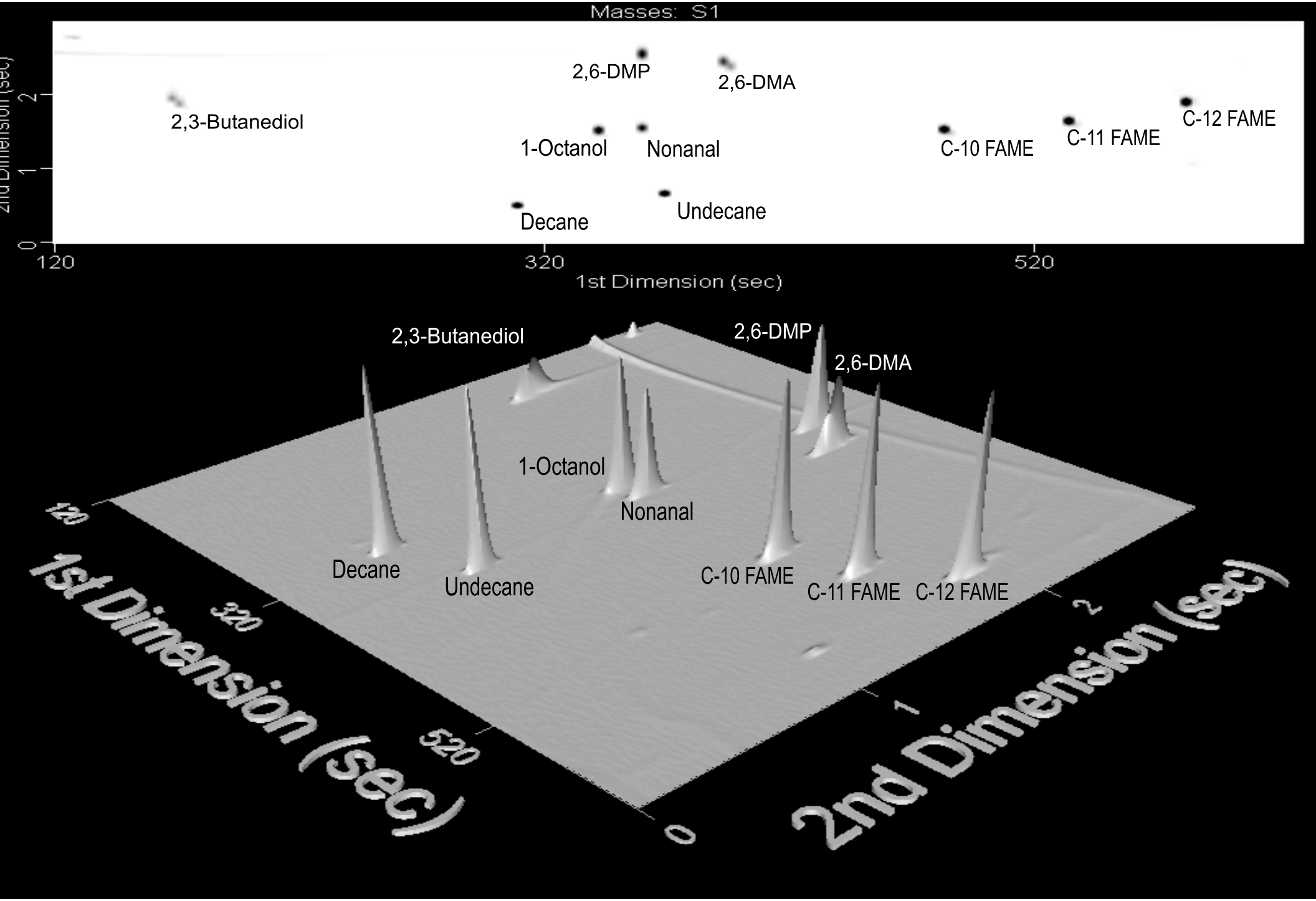
Effect of Modulation Location

- Selective desorption out of stationary phase during modulation cycle
- Tested three configurations:
  - A - Modulation on end of first column
  - B - Modulation on start of second column
  - C - Modulation on intermediate transfer line

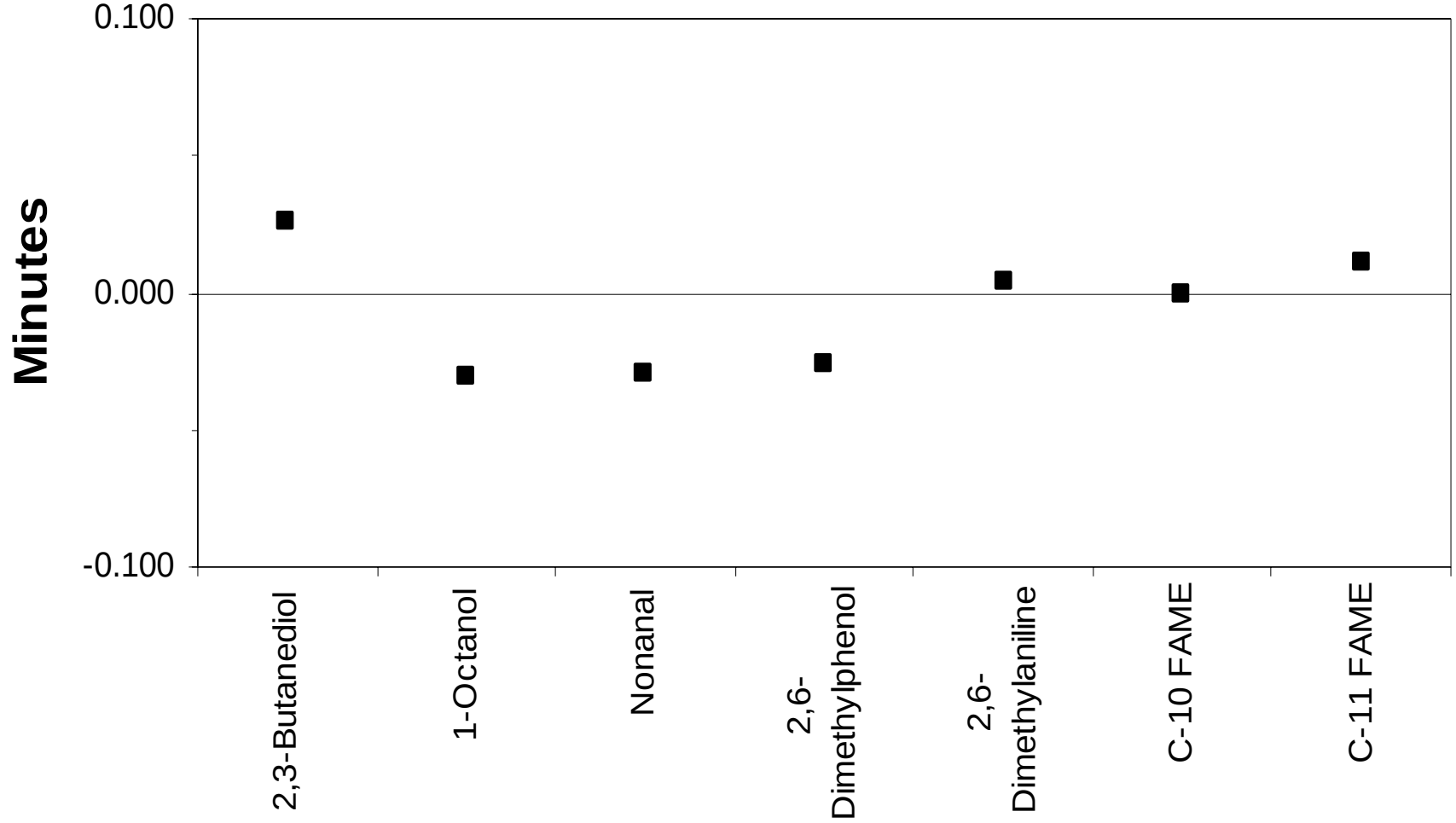
1st Dim Rt	End of 1st A	Beg of 2nd B	Guard Col C
2,3-Butanediol	168	168	168
Decane	306	306	309
1-Octanol	339	339	342
Nonanal	357	357	360
2,6-Dimethylphenol	357	357	360
Undecane	366	366	369
2,6-Dimethylaniline	391	393	393
C-10 FAME	481	480	483
C-11 FAME	532	531	534
C-12 FAME	581	579	582

2nd Dim Rt	End of 1st A	Beg of 2nd B	Guard Col C
2,3-Butanediol	1.995	1.905	1.980
Decane	0.678	0.445	0.515
1-Octanol	1.688	1.500	1.533
Nonanal	1.733	1.530	1.568
2,6-Dimethylphenol	2.743	2.588	2.563
Undecane	0.852	0.610	0.680
2,6-Dimethylaniline	2.642	2.420	2.460
C-10 FAME	1.725	1.508	1.540
C-11 FAME	1.845	1.635	1.658
C-12 FAME	2.083	1.818	1.913

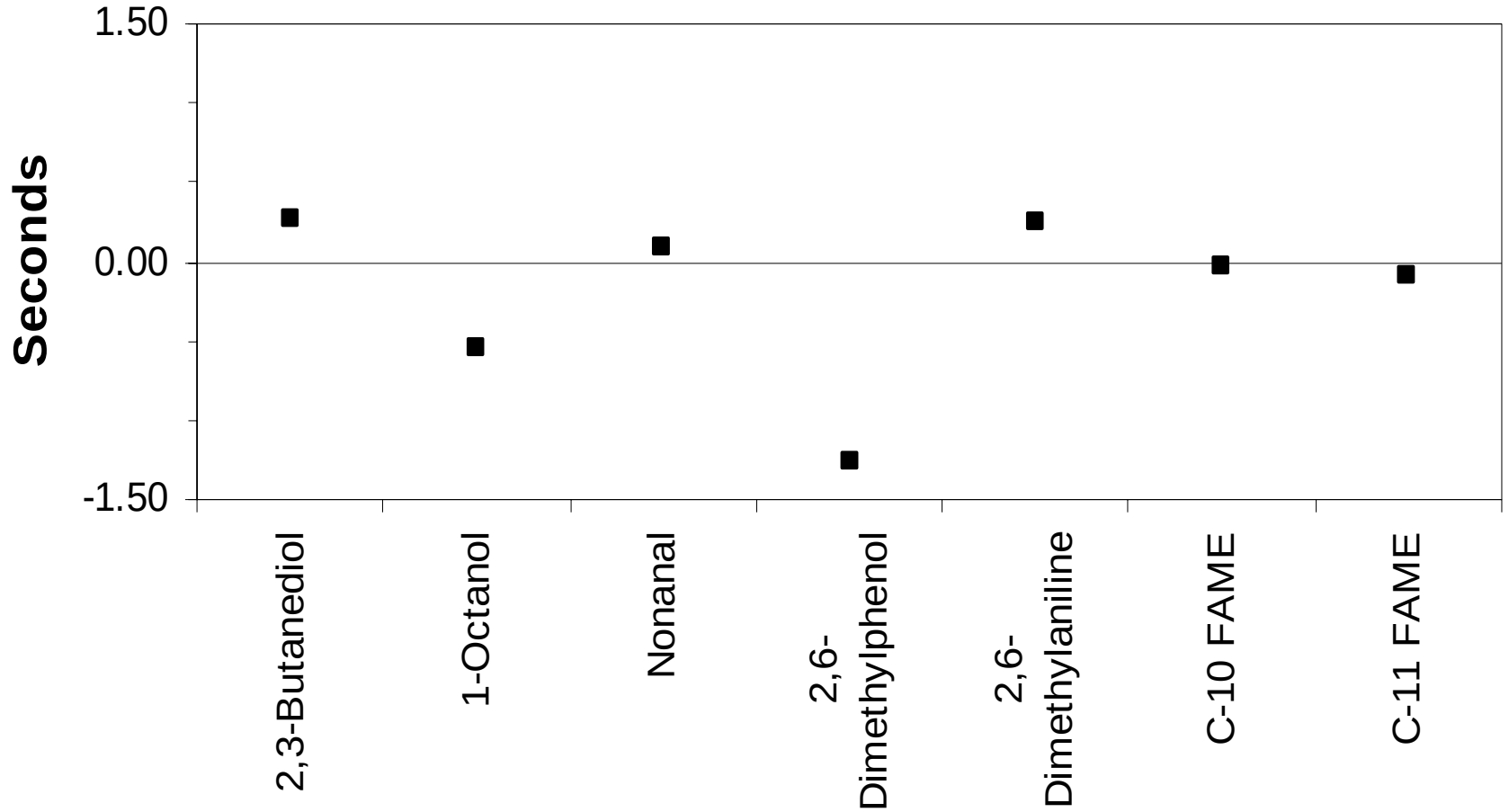

3.000
2.500
2.000
1.500
1.000
0.500
0.000
2nd Dimension Rt (sec)
120
220
320
420
520
1st Dimension Rt (sec)
A
B
C


Masses: S1
2,6-DMP
2,6-DMA
2,3-Butanediol
C-12 FAME
C-11 FAME
1-Octanol
Nonanal
C-10 FAME
Undecane
Decane
0
1
2
120
320
520
1st Dimension (sec)
2,3-Butanediol
2,6-DMP
2,6-DMA
1-Octanol
Nonanal
Decane
Undecane
C-10 FAME
C-11 FAME
C-12 FAME
1st Dimension (sec)
2nd Dimension (sec)

Predicted – Experimental Retention Times, Arrival to Modulation point



Predicted – Experimental Retention Times, Second Dimension Separation



Comparison 2nd Dim Rt	(All times in sec) CASPD avg total (sec)	CASPD Calc 2nd Rt	# Slices (from CASPD)
2,3-Butanediol	5.257	2.2565	1
1-Octanol	3.988	0.9879	1
Nonanal	4.653	1.6531	1
2,6-Dimethylphenol	4.305	1.3047	1
2,6-Dimethylaniline	5.705	2.7054	1
C-10 FAME	4.517	1.5167	1
C-11 FAME	4.578	1.5776	1

	Guard Col C	Adj. C Total 2nd Rt	CASPD - Adj. C (sec)
2,3-Butanediol	1.980	4.980	0.277
1-Octanol	1.533	4.533	-0.545
Nonanal	1.568	4.568	0.086
2,6-Dimethylphenol	2.563	5.563	-1.258
2,6-Dimethylaniline	2.460	5.460	0.245
C-10 FAME	1.540	4.540	-0.023
C-11 FAME	1.658	4.658	-0.080

Summary

- Modeling procedure appears successful
  - Some refinement is necessary
- Modeling optimization software can save large amount of R&D time for column ensemble development
- Translation between TOFMS and FID/ECD work ongoing
- Simplification of CASPD2D procedures ongoing
- Work submitted to Journal of Chromatography A

Acknowledgements

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  - Financial Support