Electronic Supplementary Material (ESI) for Analyst.
This journal is © The Royal Society of Chemistry 2016

Supporting information for "Manipulating inter pillar gap in pillar array ultra-thin layer planar chromatography platforms"

Nichole A. Crane[a], Nickolay V. Lavrik[b], and Michael J. Sepaniak*[,a]
[a]Department of Chemistry, University of Tennessee, Knoxville, TN, 37996, USA.

[b]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37830, USA.

Table of Contents:

Optimum Flow Rates and Development Distances

	Optimum Velocity (cm/s)		Modeled Distance (cm)		Experimental Distance (cm)	
Morphology	ACN	IPA	ACN	IPA	ACN	IPA
1.9D1.1G	0.32	0.064	0.64	0.41	0.35	0.18
2.2D0.8G	0.44	0.088	0.47	0.33	0.19	0.045
2.5D0.5G	0.71	0.14	0.28	0.17	0.047	0.031
1.2D0.8G	0.44	0.088	0.30	0.19	0.35	0.21

Table 1: Calculated optimum velocities and corresponding development distances for the different pillar arrays.

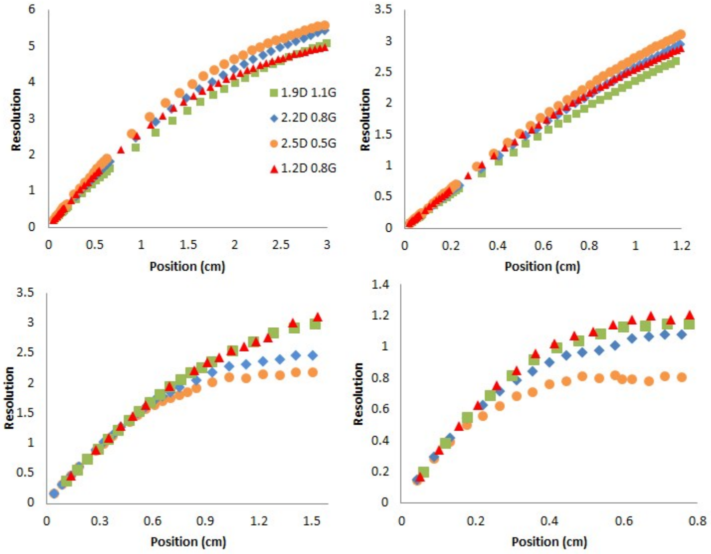

Figure S.I. 1: Computed Resolution with development distance for modeled (a, acetonitrile & b, 2-propanol) and experimental (c, acetonitrile & d, 2-propanol) flow velocities.

Hypothetical Resolution and Calculations

A consequence of reducing velocity as the solvent front moves can be that there are diminishing improvements in resolution as the development proceeds. Resolution calculations are performed using traditional chromatography equations. First considering the van Deemter equation used for these pillar systems and relating it to the variance per unit length (Equation S.I. 1).

$$H = \frac{B}{v} + C_m \cdot v = \frac{\sigma^2}{L} \qquad (1)$$

Using the modeled velocities (Figure 2) and experimental velocities (Figure 3) and the treatment in the text for computing plate height, the instantaneous variance (σ^2) over incremental small displacement of the solvent, Δd, can be determined via Eq S.I. 2. The modeled data corresponds to time increments of 0.01 to 1 second and this translates into distance increments of 0.003 to 0.200 cm depending on the point in the development.

$$\sigma_{inst} = ((\Delta d) \times H)^{1/2} \tag{2}$$

In order to determine resolution the sum of instantaneous variances was performed (Eq. S.I. 3):

$$\sigma_{sum} = (\sigma_{inst1}^{2} + \sigma_{inst2}^{2} + \ldots)^{1/2} \tag{3}$$

Once the σ_{sum} value was found, a couple assumptions are made to compare each individual gapped scenario. We assumed typical retardation factors of 0.9 (R_{f1}) and 0.8 (R_{f2}) for the separation pair. In most of our studies the spot size of analytes are approximately 300 µm. Therefore, the value for σ_{spot} in the resolution equation is 0.0075 cm. The final equation for resolution becomes:

$$Rs = \frac{(R_{f1} - R_{f2}) \times S_f}{4(\sigma_{sum}{}^{2} + \sigma_{spot}{}^{2})^{1/2}} \tag{4}$$

The S_f in this equation corresponds to the distance the solvent front traveled. Figure S.I. 1 provides the calculated Rs with position on the array during the development.

For our modeled systems in the figure, it appears that all the gapped scenarios reach an ideal Rs of 1.5 around 0.50 cm and 0.75 cm of development distance for acetonitrile and 2-propanol, respectively. The poorer performance in terms of Rs for 2-propanol is due to its lower γ'/η ratio, overall slower flow, and hence lower plate height. For each solvent the flows are similar with changing gap size and therefore produce similar Rs versus distance plots.

The most telling observation from the modeled plots is the smaller increases in Rs as the solvent front slows later in the development. For example, if the 2.2D 0.8G acetonitrile case is considered the increase in resolution between positions 0.5 cm to 1.0 cm is 104% but from 2.0 to 2.5 it is only 10.2%. In most cases there is little motivation to develop beyond $S_f = 2.0$ cm. The situation for the experimental data demonstrates the 2.2D 0.8G acetonitrile case as a resolution increase of 62.6% from 0.1 cm to 0.2 cm and an 8.60% increase from 0.6 cm to 0.7 cm. The experimental data concludes that a high vapor pressure mobile phase solvent only needs a development distance of less than 1 cm.

Surface Areas and Volumes of Different Gap Scenarios

Chip Description		$(V_P) * N_P$	$V=\pi r^2 h$	V=l*w*h	$V_C - TV_P$	$(VV/V_C)*100$	$SA=2\pi r*h$	$SA_T=SA*N_P$
Pillar	Gap	Total Pillar Volume (TV_P)	Individual Pillar Volume (V_P) (microns)	Total Chip Volume (V_C)	Void Volume (V_V)	Void Volume (%)	Surface Area/pillar	Surface Area/Chip
1.9	1.1	8.7E+08	45	2.4E+09	1.5E+09	64	96	1.8E+09
2.2	0.8	1.2E+09	61	2.4E+09	1.2E+09	51	110	2.1E+09
2.5	0.5	1.5E+09	79	2.4E+09	8.9E+08	37	130	2.4E+09
1.2	0.8	7.8E+08	18	2.4E+09	1.6E+09	67	60	2.6E+09

Table 2: Calculated surface areas and volumes for the different pillar arrays in µm.

Complete Efficiency and Retention Data

Gap Dimensions	Analyte	Band Width (um)	Plate Height (um)	Retardation Factor	Solvent Front (mm)
1.9D 1.1G	C540A	580 ± 59	2.5 ± 0.6	0.73 ± 0.04	14 ± 0.4
	C120	700 ± 90	2.7 ± 0.6	0.97 ± 0.001	
2.2D 0.8G	C540A	790 ± 110	6.8 ± 1.5	0.64 ± 0.05	11 ± 0.3
	C120	750 ± 88	4.7 ± 1.3	0.86 ± 0.05	
2.5D 0.5G	C540A	560 ± 17	11 ± 1.2	0.57 ± 0.1	6.2 ± 0.1
	C120	610 ± 56	8.1 ± 2.0	0.85 ± 0.07	
1.2D 0.8G	C540A	940 ± 170	7.9 ± 2.8	0.76 ± 0.08	12 ± 1.1
	C120	650 ± 22	2.9 ± 0.1	0.98 ± 0.006	

Table 3: Average separation values (n=3) at 4 minute development corresponding to Figure 4 of manuscript.