The Importance of a Deactivation in Achieving Inert and Stable High Resolution Gas Chromatography Capillary Columns

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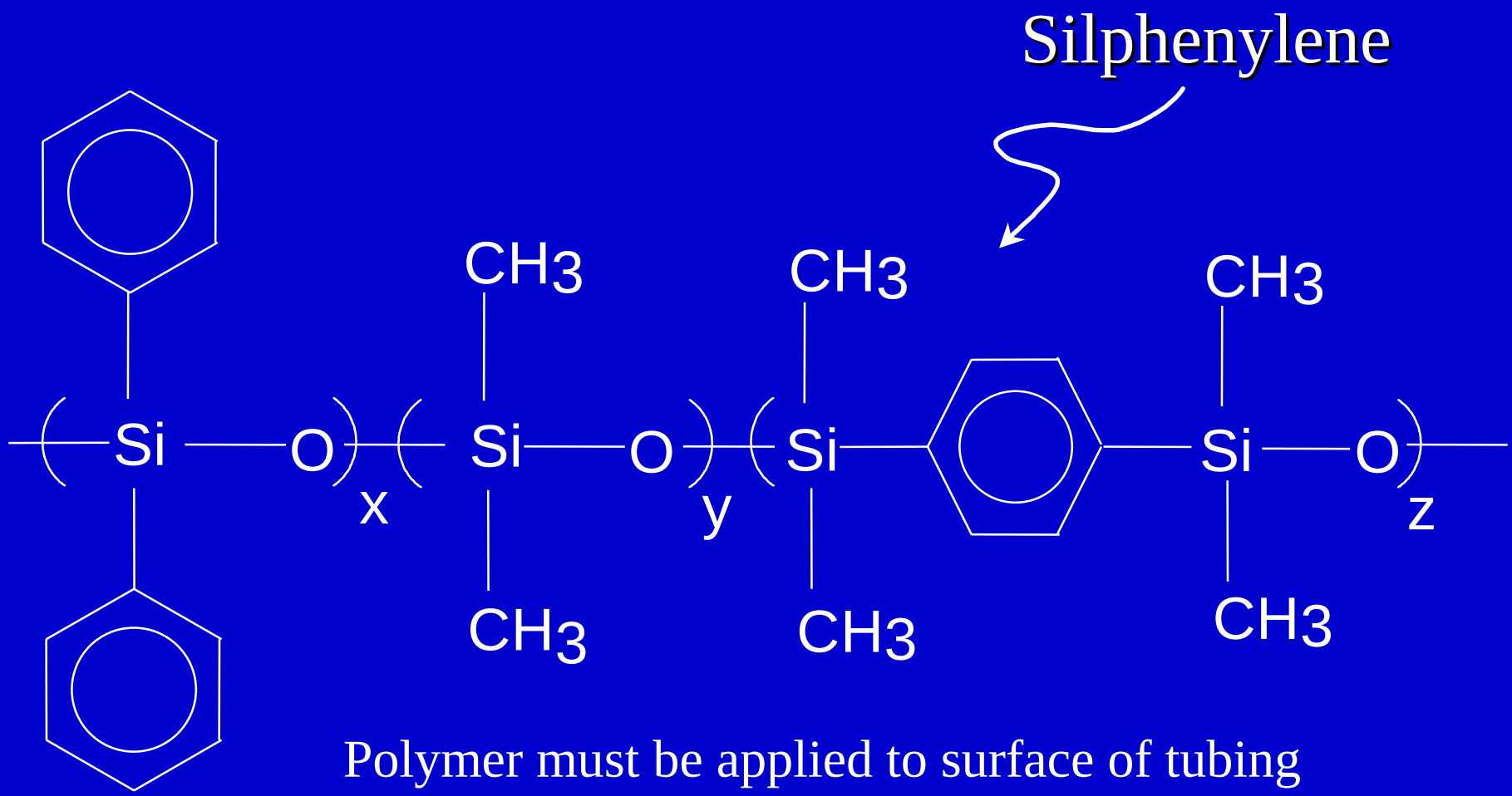
Investigate Deactivation Chemistries for Demanding Applications

- USEPA method 8270 and Appendix 9
  - Laboratories investigating lower limits of detection
  - Dinitrophenols
  - Anilines
  - Halogenated Phenols
  - Endrin (8081)
  - Greater resolution for faster analyses
- Using Rtx-5Sil MS capillary column
  - 30M X 0.25 mm i.d. X 0.5 um d.f.

Rtx-5Sil MS Stationary Phase

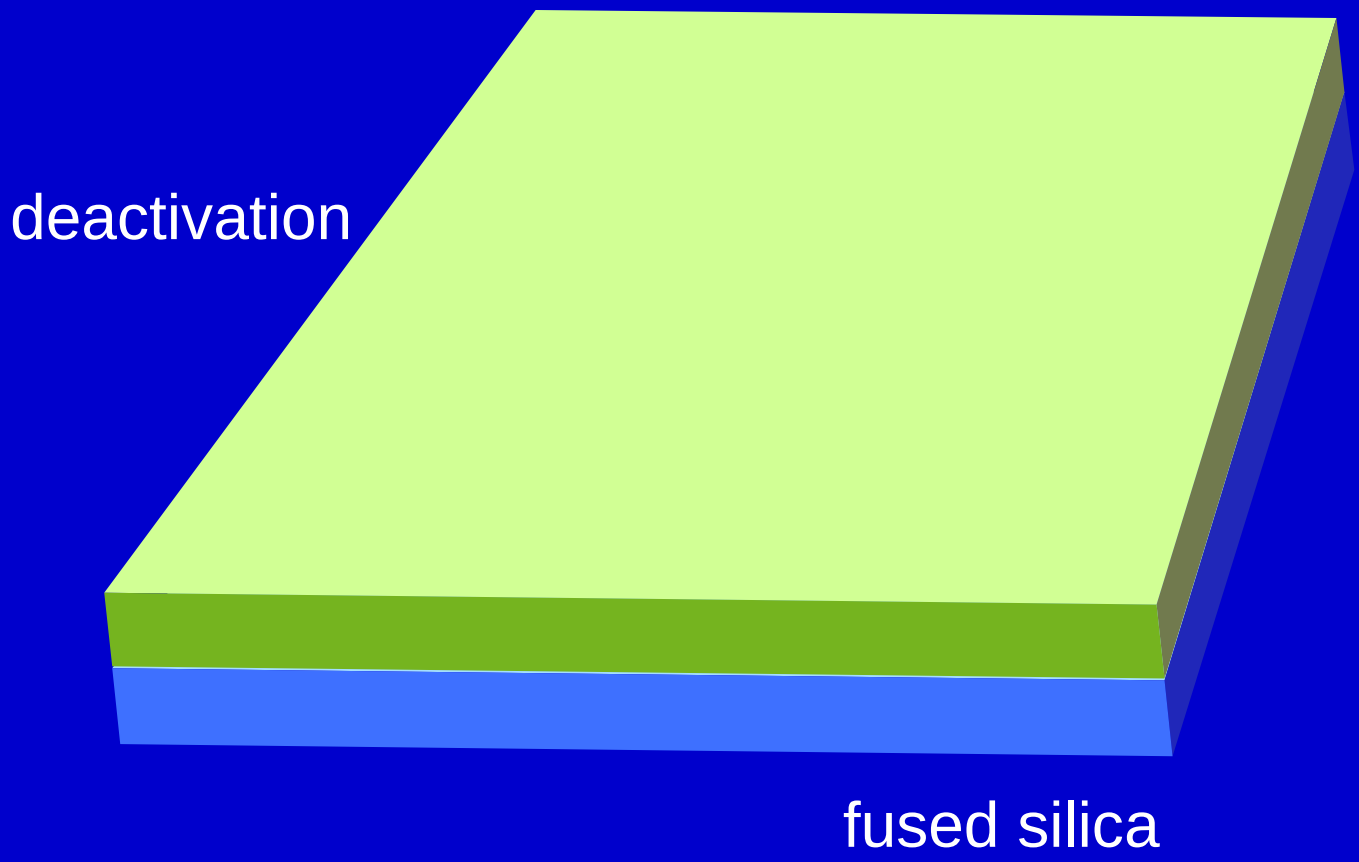


Polymer must be applied to surface of tubing

Why Deactivate?

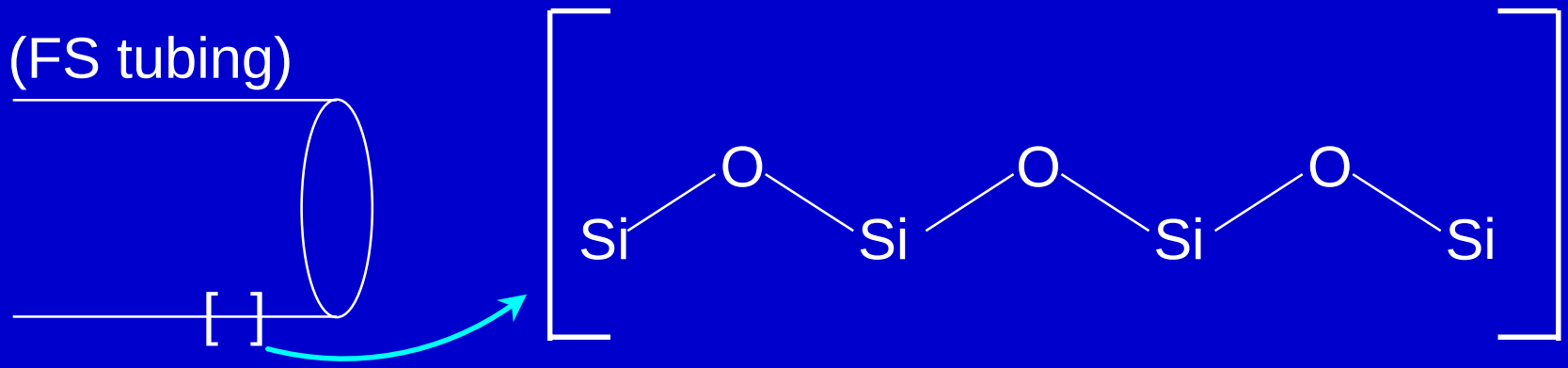
- “Bare” Fused Silica tubing is reactive
  - Surface silanols are acidic
    - Inertness to reactive compounds
  - Many compounds “See” the surface of the tubing
- Batch-to-batch variability
- Some Polymers do not wet surface
  - Need to match surface tension of polymer and tubing
    - Lowers bleed
    - Improves efficiency

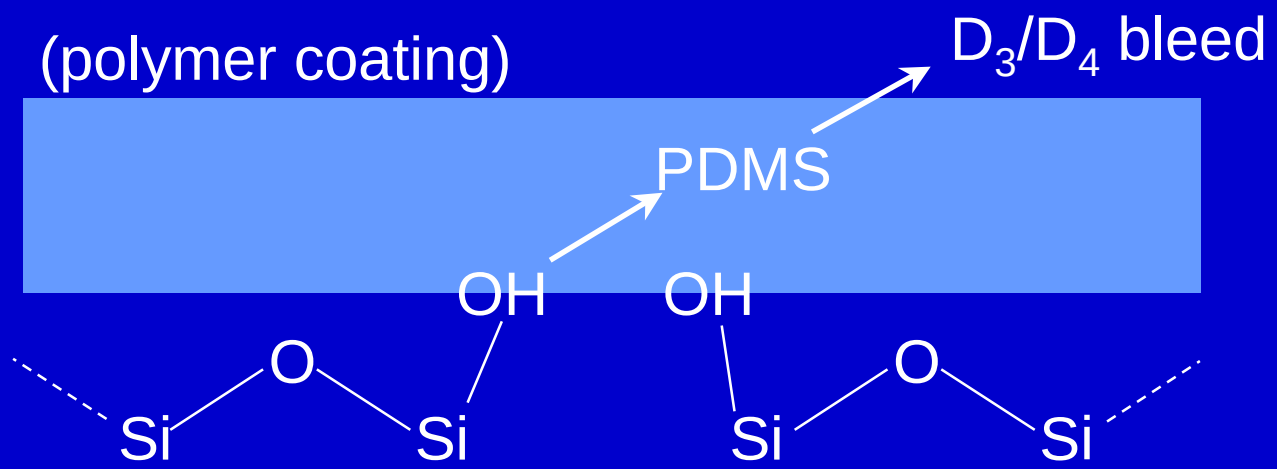
Origins of Bleed...



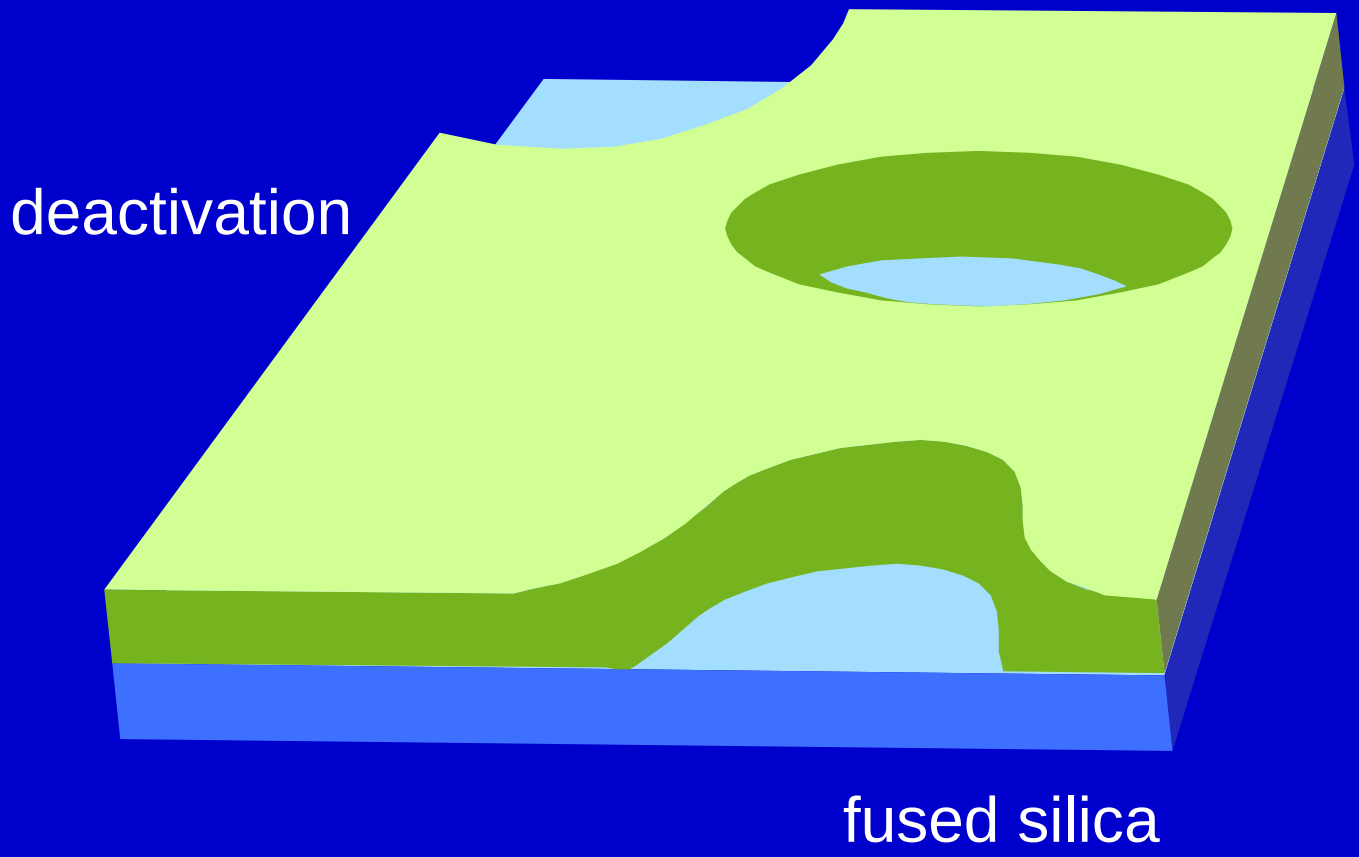
Origins of Bleed…

- Oligomers that are “created” in a column’s lifetime

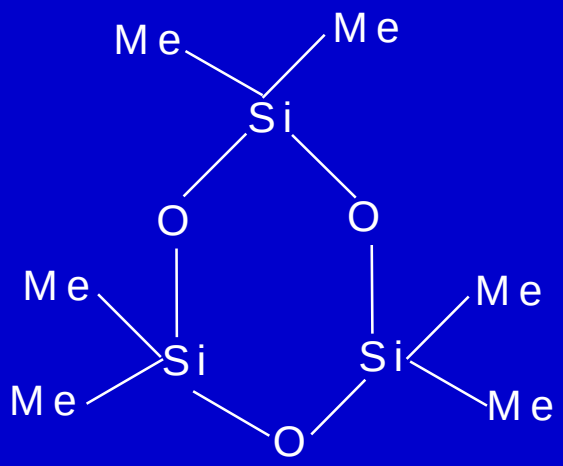




Origin of Bleed… as well as Poor Efficiency

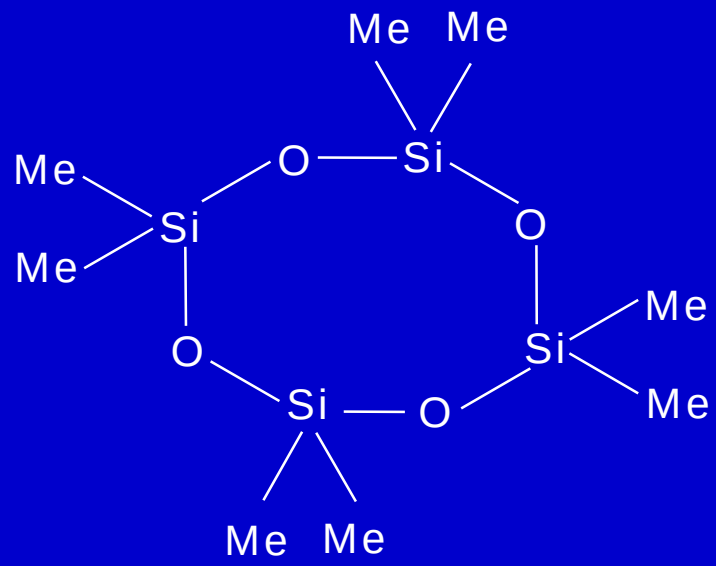


Typical Chemical Structure



D_3

m/z = 207



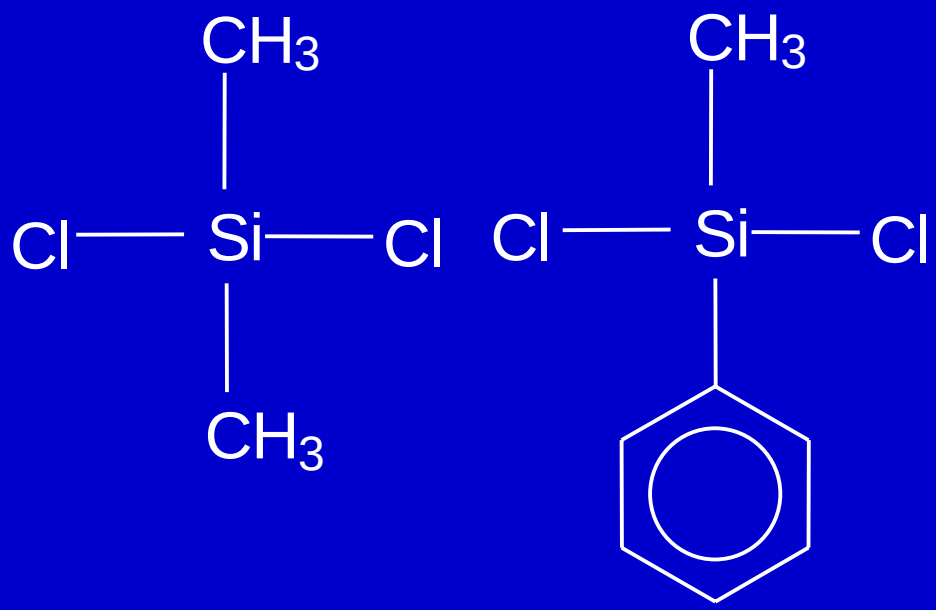
D_4

m/z = 281

Types of Deactivation Chemistries

- "Pinpoint" deactivation
  - Chloro-silanes
  - Disilazanes
    - Linear
    - Functionalized
- Polymeric deactivation
  - "IP" deactivation
- Surface modification
  - Siltek

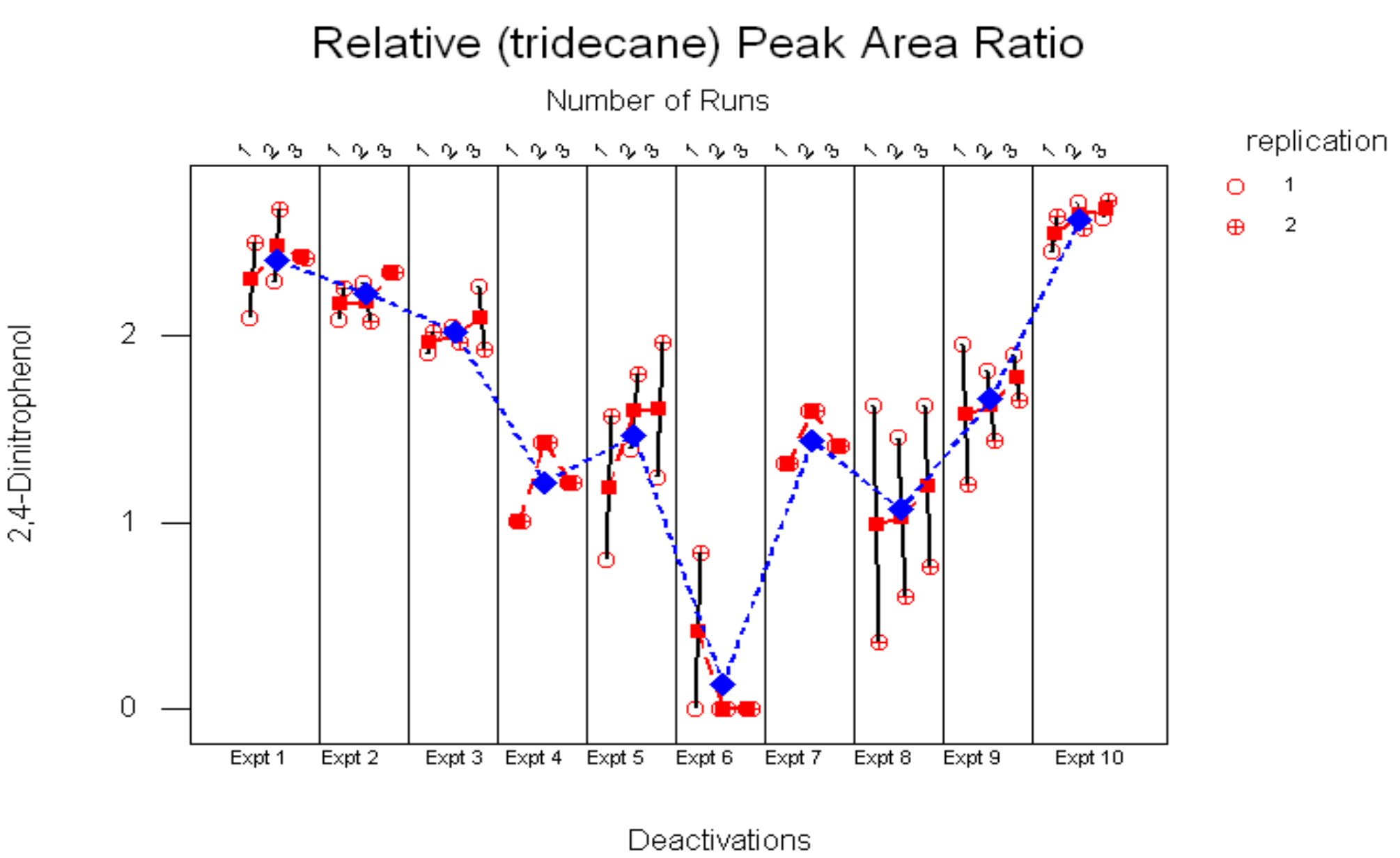
Chlorosilane Deactivation



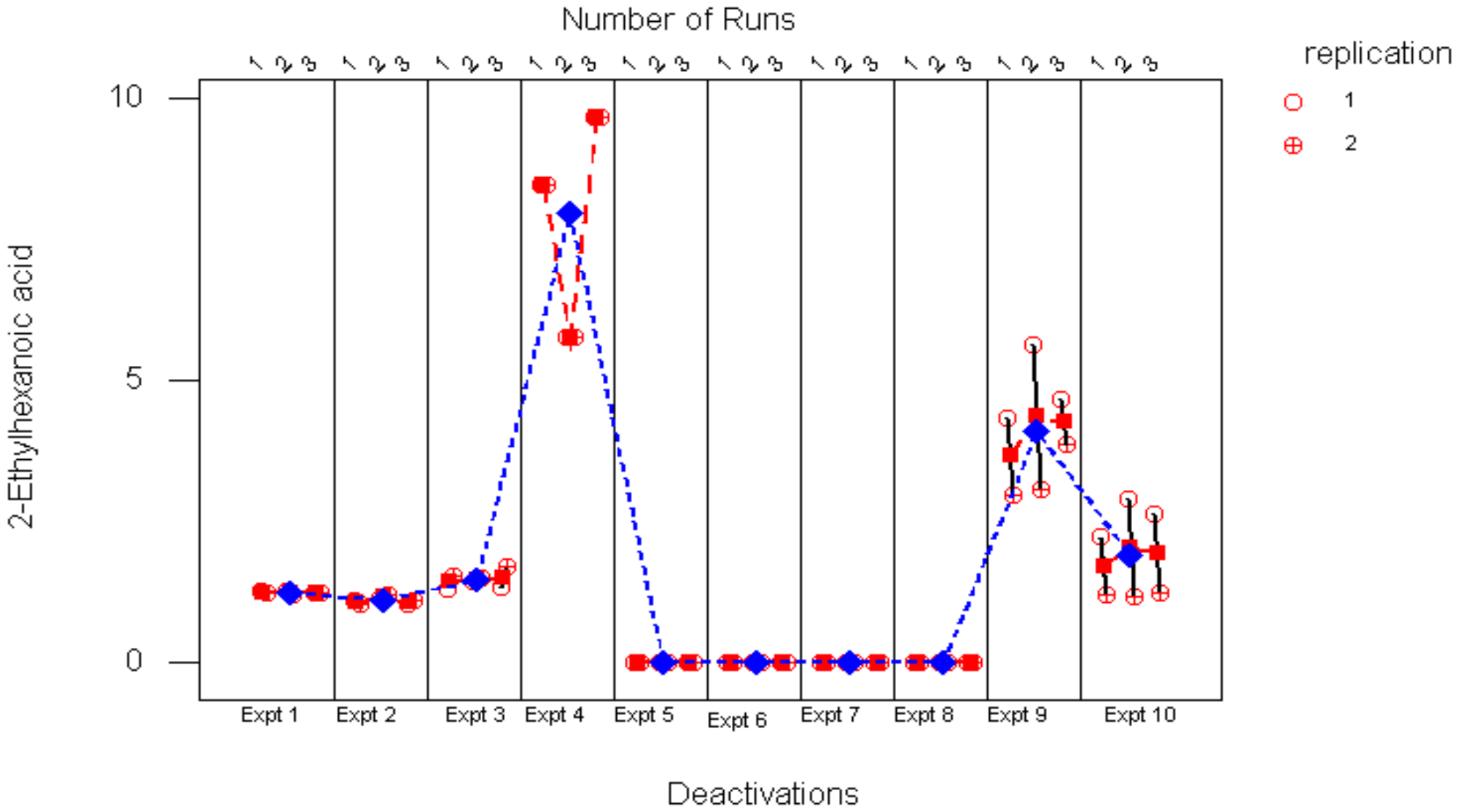
Adds to silanol group by HCl elimination, then polymer can be applied

Deactivation Chemistries Investigated

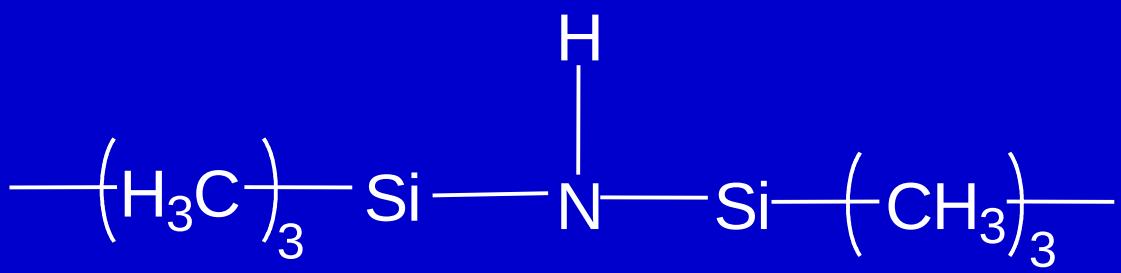
1. The first three experimental deactivations are slightly to moderately acidic.
2. The Fourth one is a competitor
3. The following four (5-8) are slightly to moderately basic
4. Experiment 9 is Siltek
5. The last experiment is Restek’s IP deactivation


Relative (tridecane) Peak Area Ratio
Number of Runs
1 2 3
replication
1
2
2,4-Dinitrophenol
0
1
2
Expt 1
Expt 2
Expt 3
Expt 4
Expt 5
Expt 6
Expt 7
Expt 8
Expt 9
Expt 10
Deactivations

Tailing Factor



Linear Disilazane

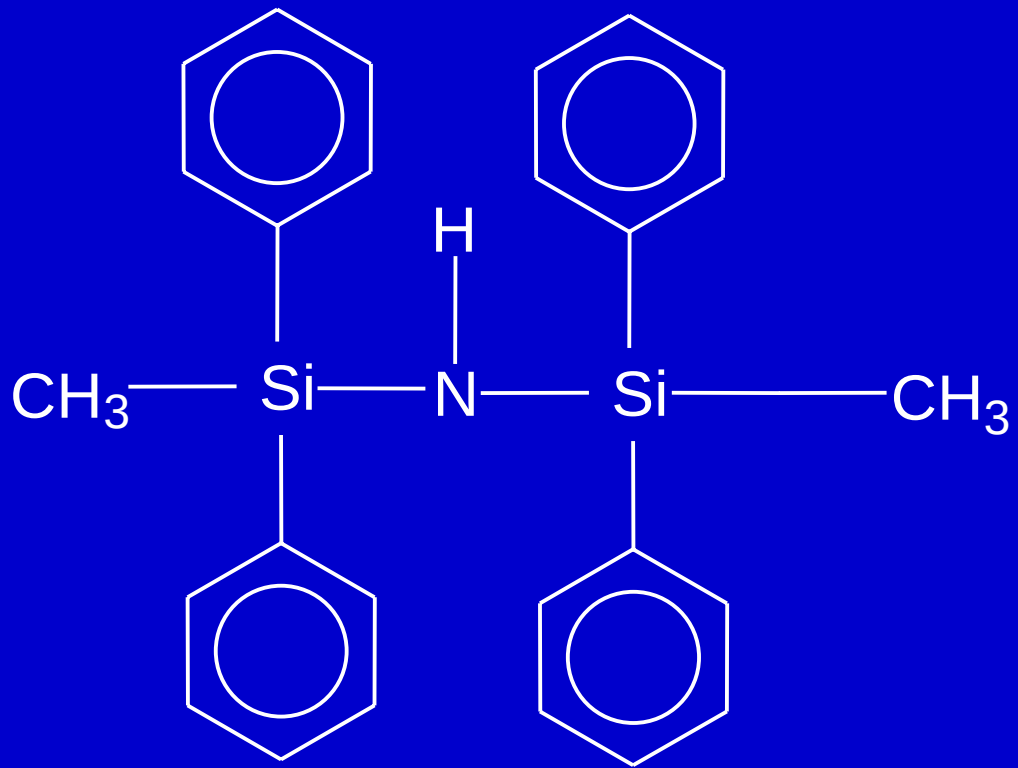


Hexamethyldisilazane

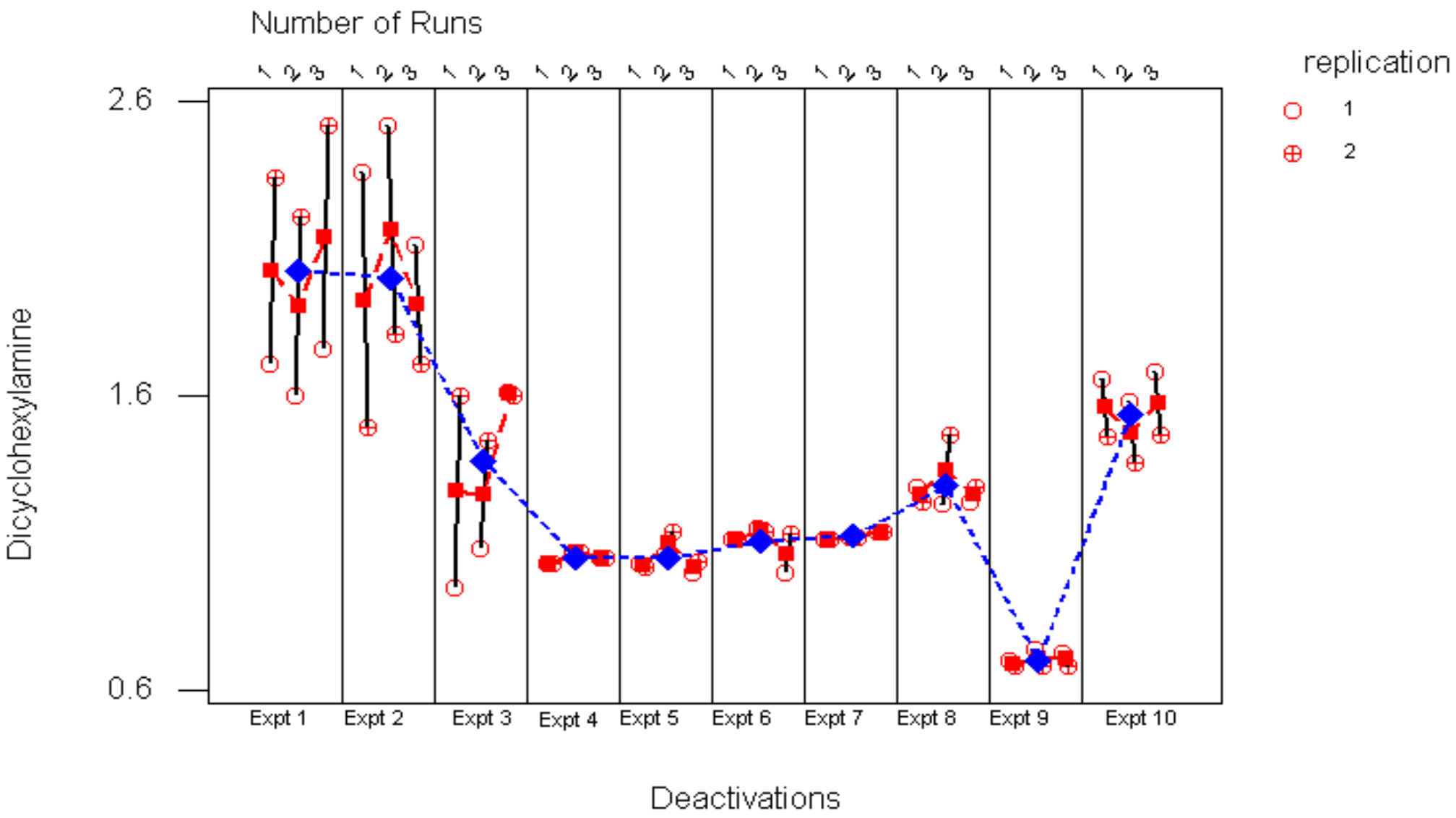
Will result in a basic surface due to presence of amine groups

Functionalized silazane

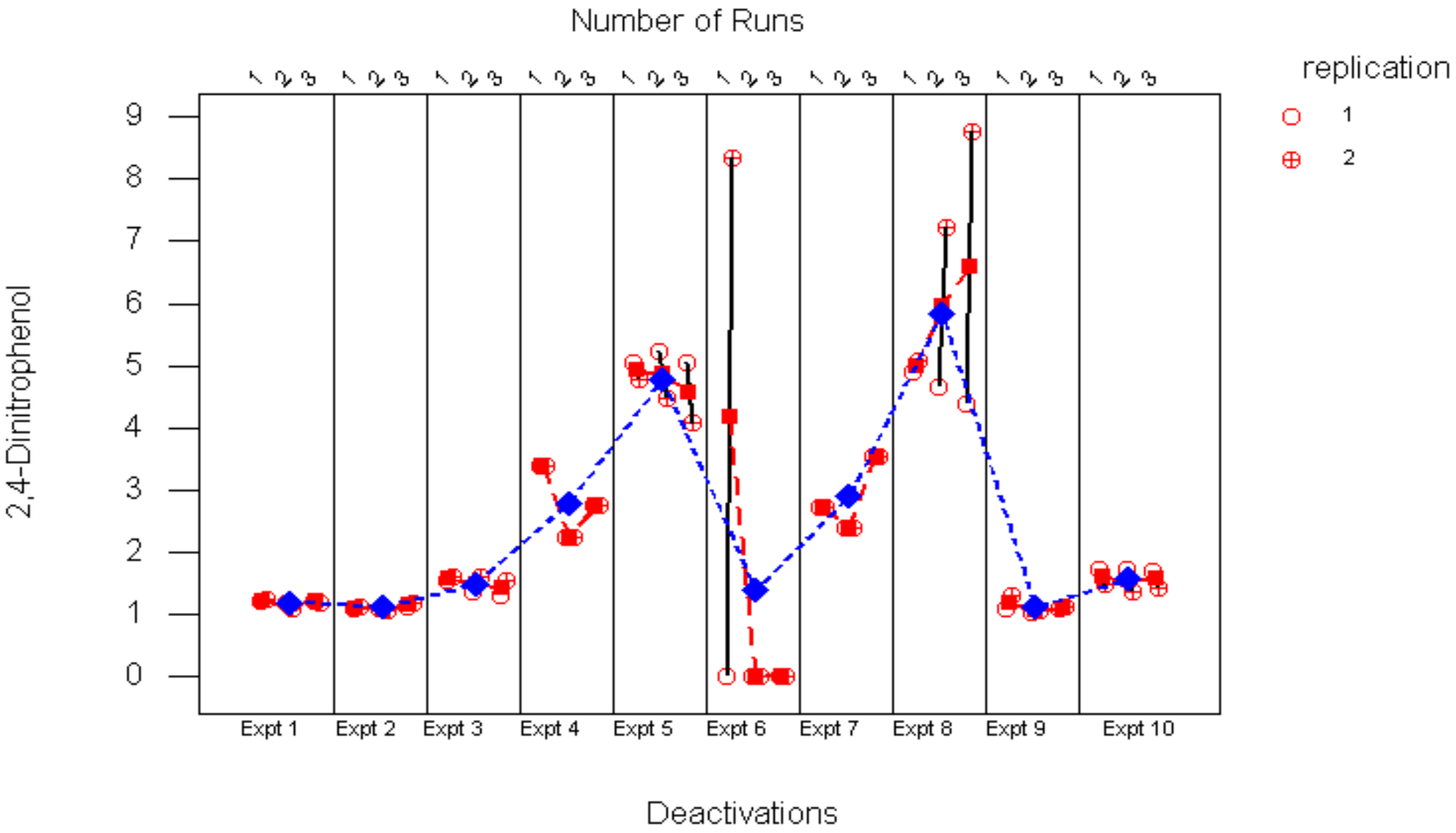
Tetraphenyldimethyldisilazane



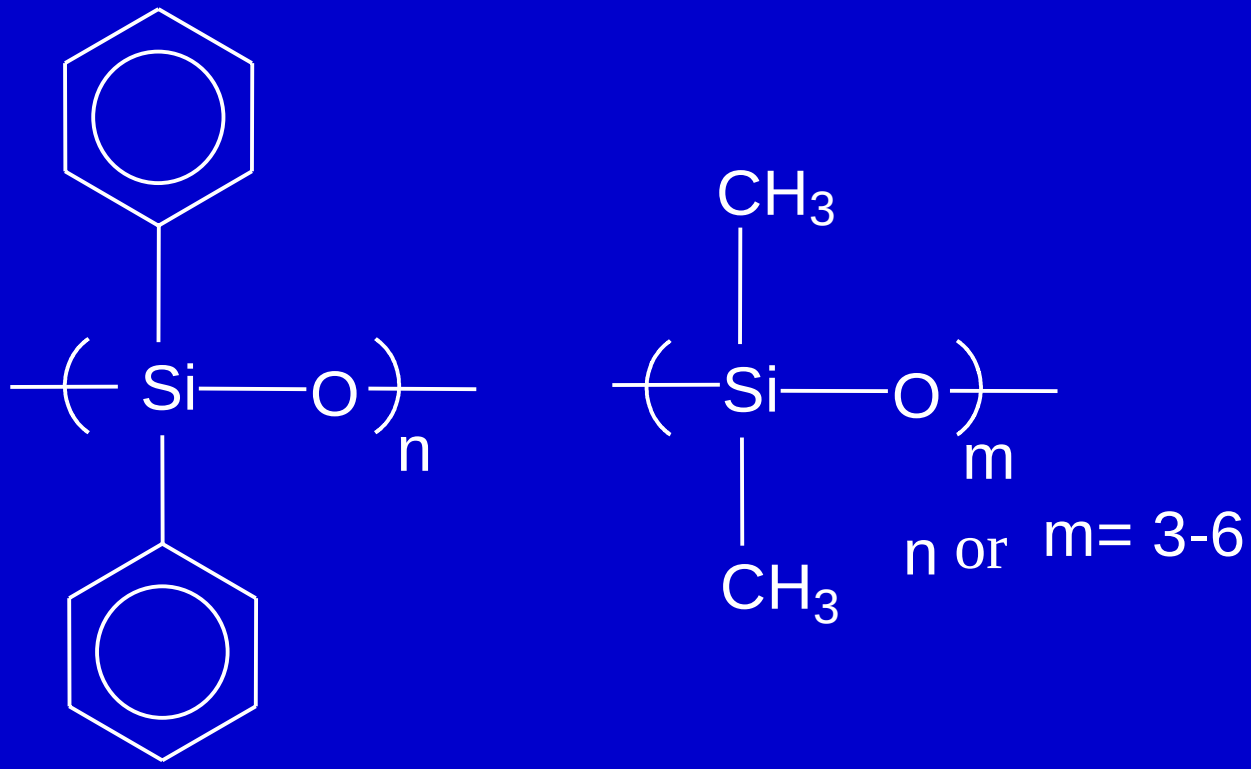
Tailing Factor



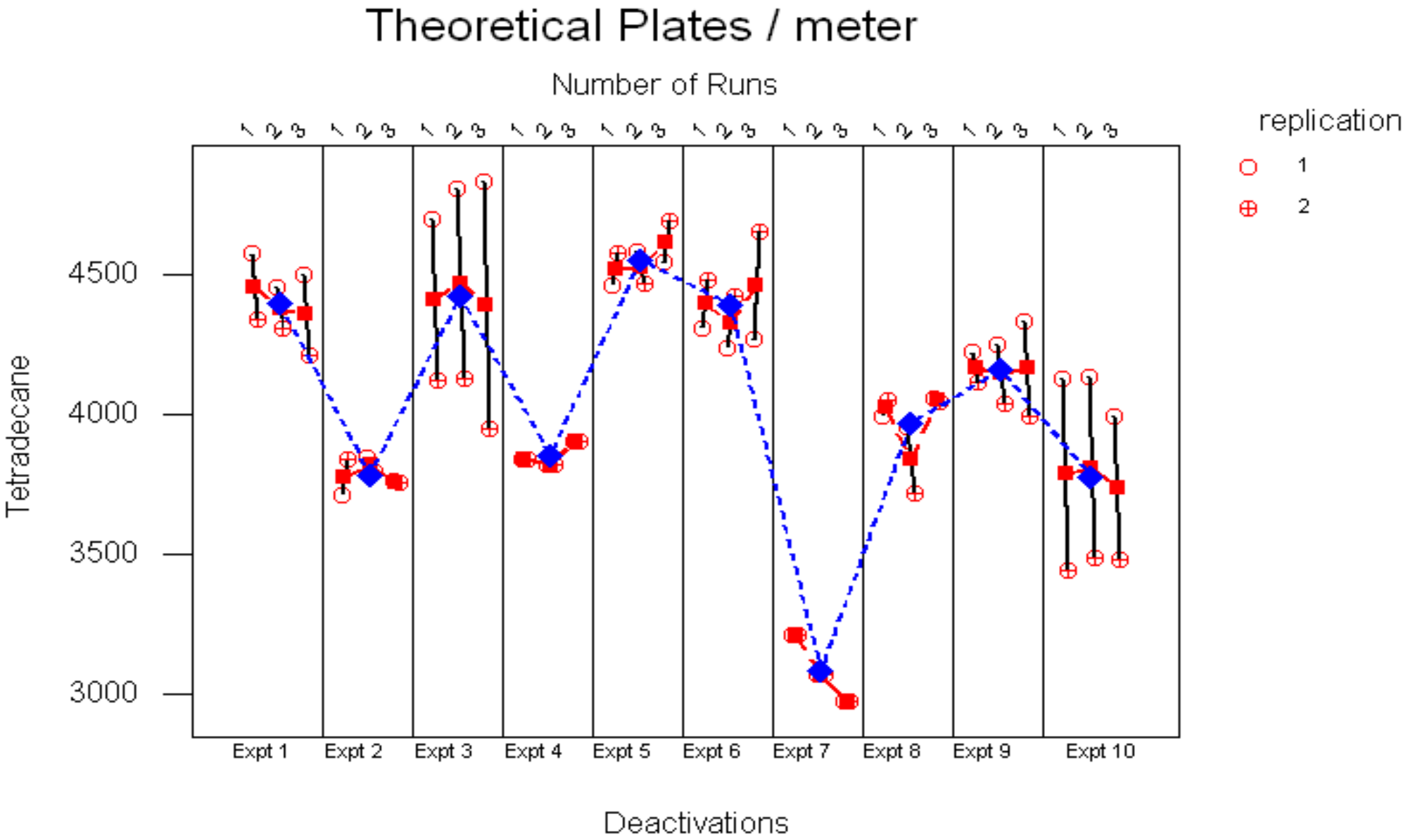
Tailing Factor

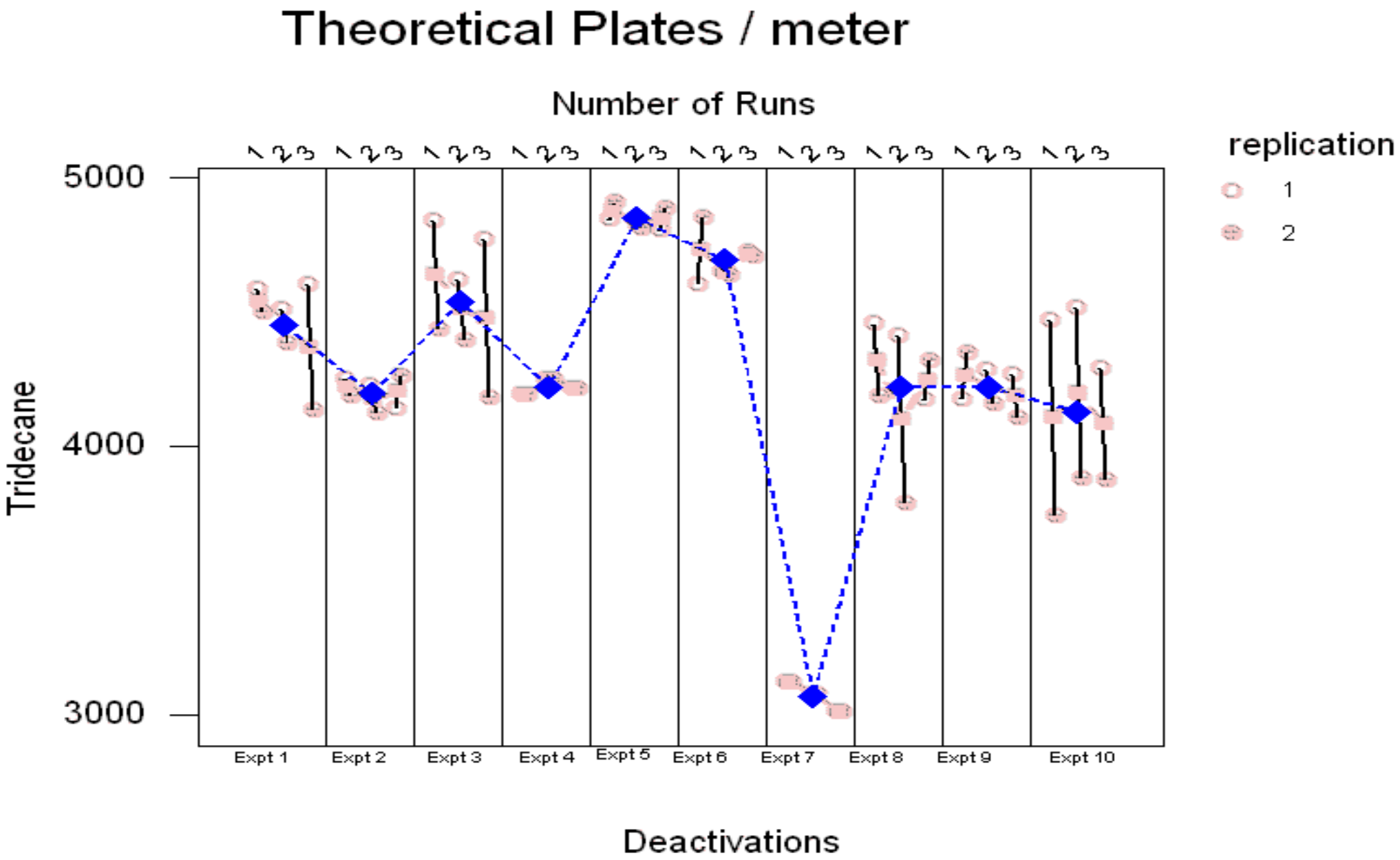


Polymeric Deactivation



May “cover” unreacted silanols


Theoretical Plates / meter
Number of Runs
replication
1
2
Tetradecane
4500
4000
3500
3000
Expt 1
Expt 2
Expt 3
Expt 4
Expt 5
Expt 6
Expt 7
Expt 8
Expt 9
Expt 10
Deactivations


Theoretical Plates / meter
Number of Runs
1 2 3
5000
4000
3000
Tridecane
Expt 1
Expt 2
Expt 3
Expt 4
Expt 5
Expt 6
Expt 7
Expt 8
Expt 9
Expt 10
Deactivations
replication
1
2

Modification of the Fused Silica Surface

- Siltek™ is a deposition process, unlike silazane or silicone deactivation which modifies the surface of the silica tubing.

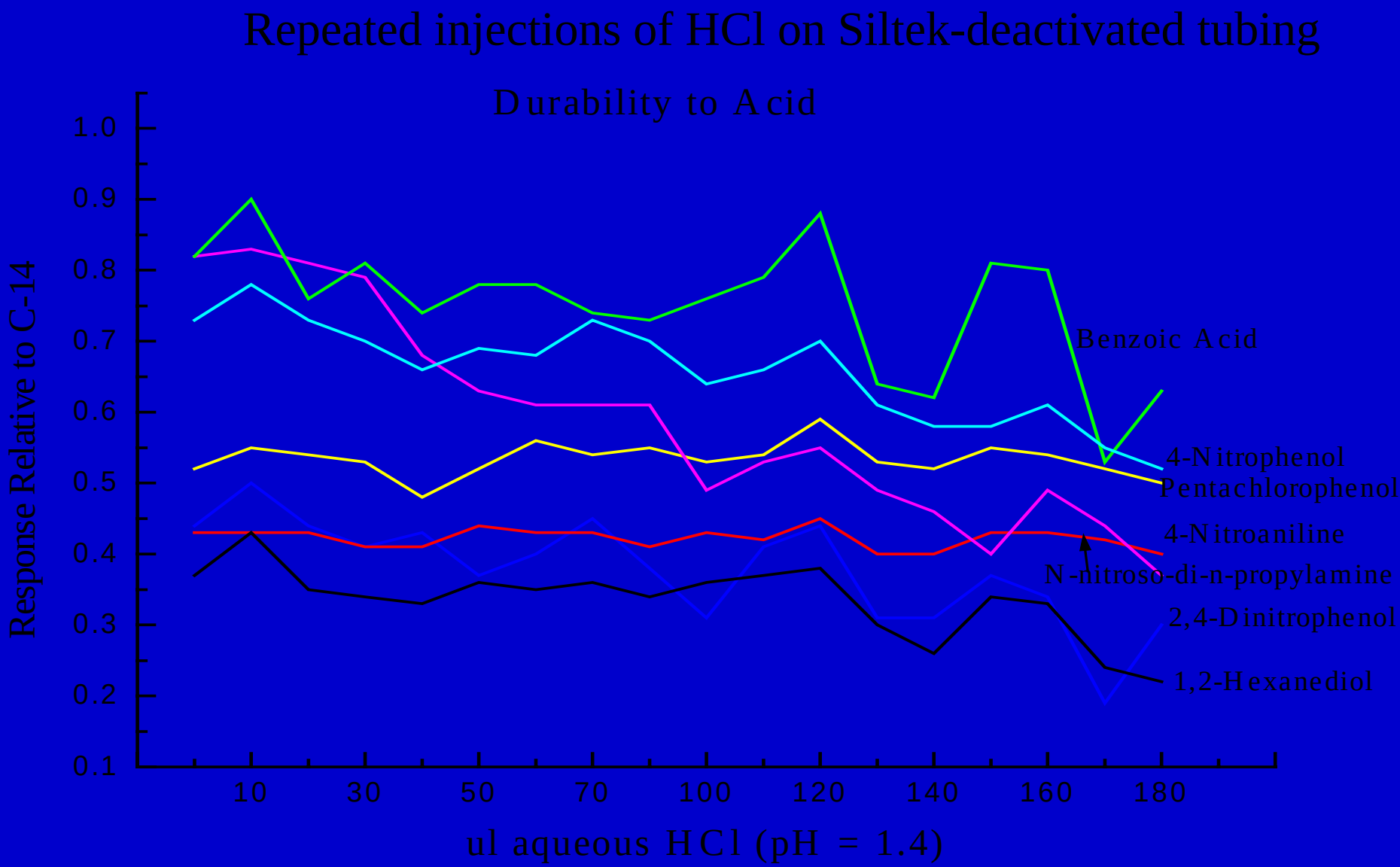

Repeated injections of HCl on Siltek-deactivated tubing
Durability to Acid
Response Relative to C-14
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10
30
50
70
100
120
140
160
180
ul aqueous HCl (pH = 1.4)
Benzoic Acid
4-Nitrophenol
Pentachlorophenol
4-Nitroaniline
N-nitroso-di-n-propylamine
2,4-Dinitrophenol
1,2-Hexanediol

Figure 6

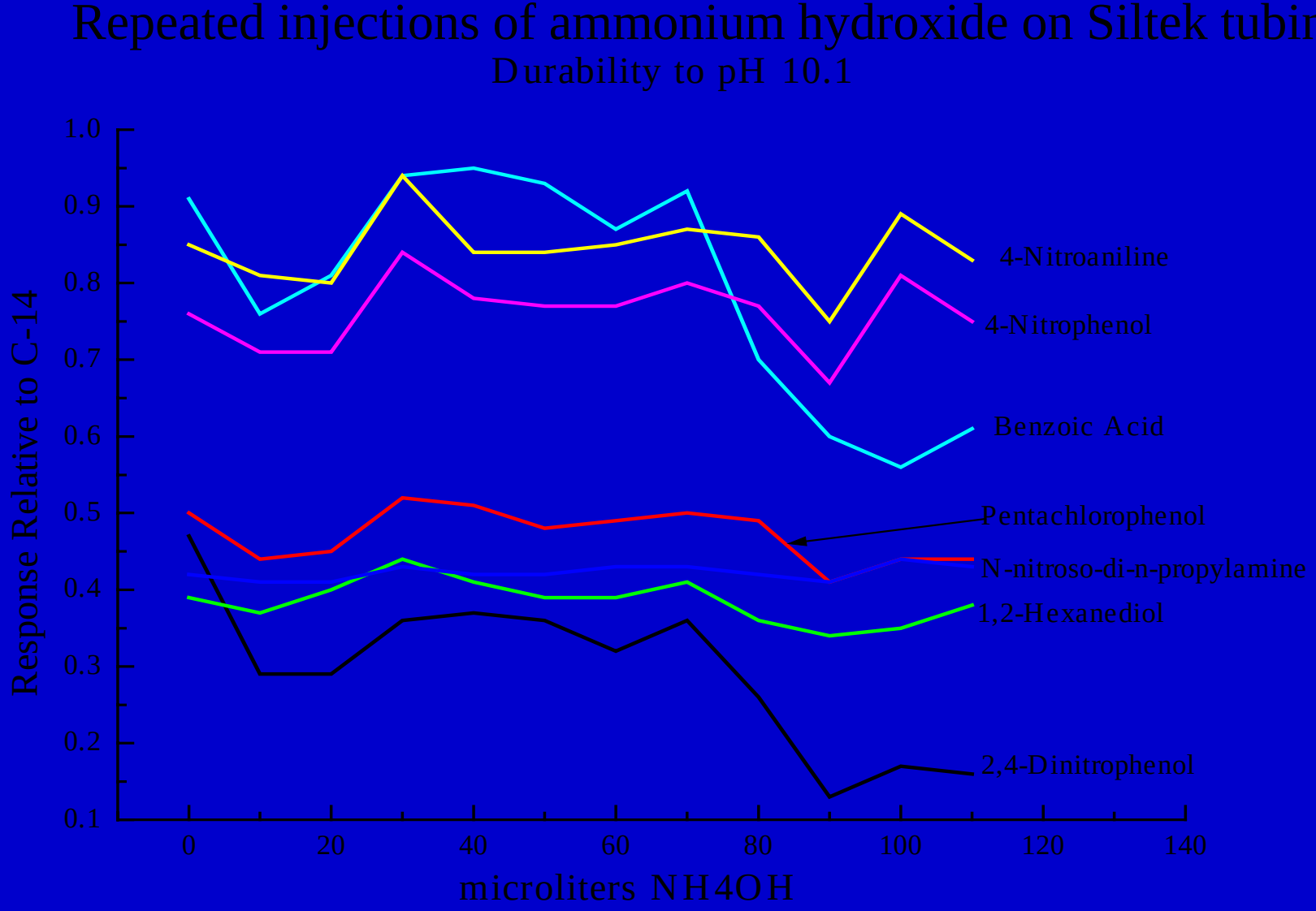

Repeated injections of ammonium hydroxide on Siltek tubing
Durability to pH 10.1
Response Relative to C-14
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
120
140
microliters NH4OH
4-Nitroaniline
4-Nitrophenol
Benzoic Acid
Pentachlorophenol
N-nitroso-di-n-propylamine
1,2-Hexanediol
2,4-Dinitrophenol

Figure 7

Guard Column Bleed Comparison at 330C

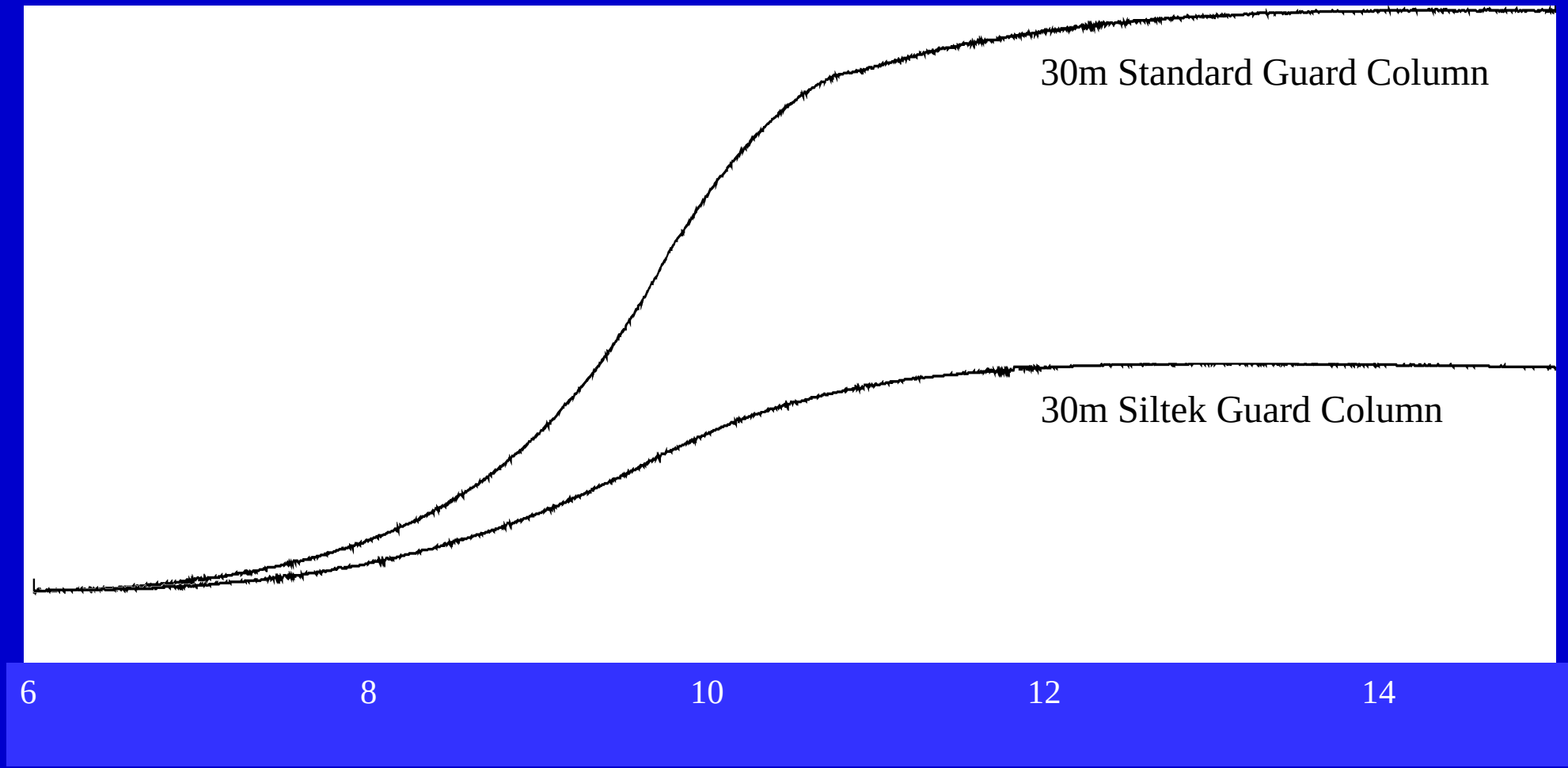
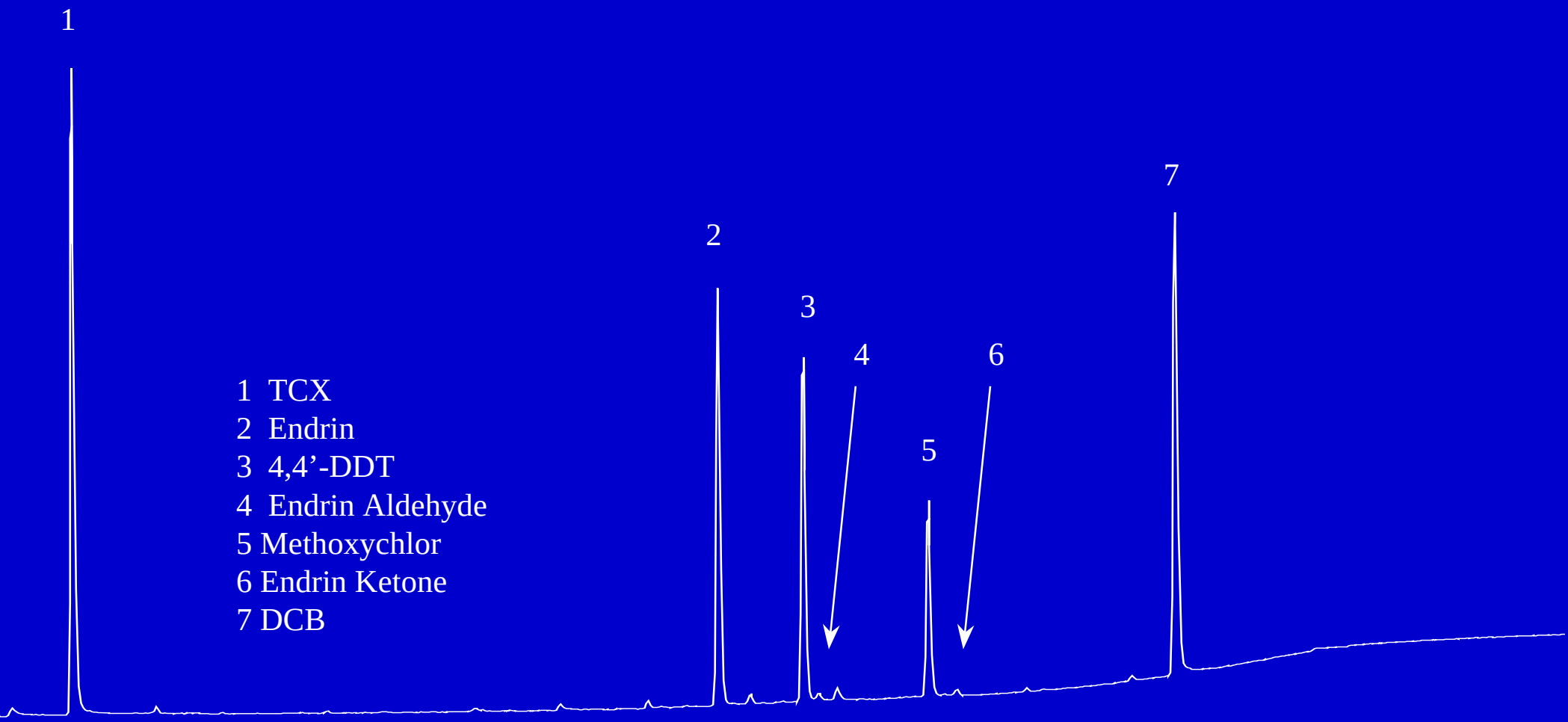


Figure 8

Endrin Breakdown on a Siltek Deactivated Uniliner measures 1%



Concentration On-Column: 50 PPB
Rtx-CLPesticides2; 30m X 0.53mm X 0.42 um, Cat. # 11340
Direct Injection into a Siltek-Deactivated Uniliner @ 250C; Detector: 300
Oven: 120C (1 minute), 9/min to 300 (10 minute)
Helium Carrier @ 39 cm/sec

Figure 3

Figure 2. Average Response Factors for key semivolatile components:

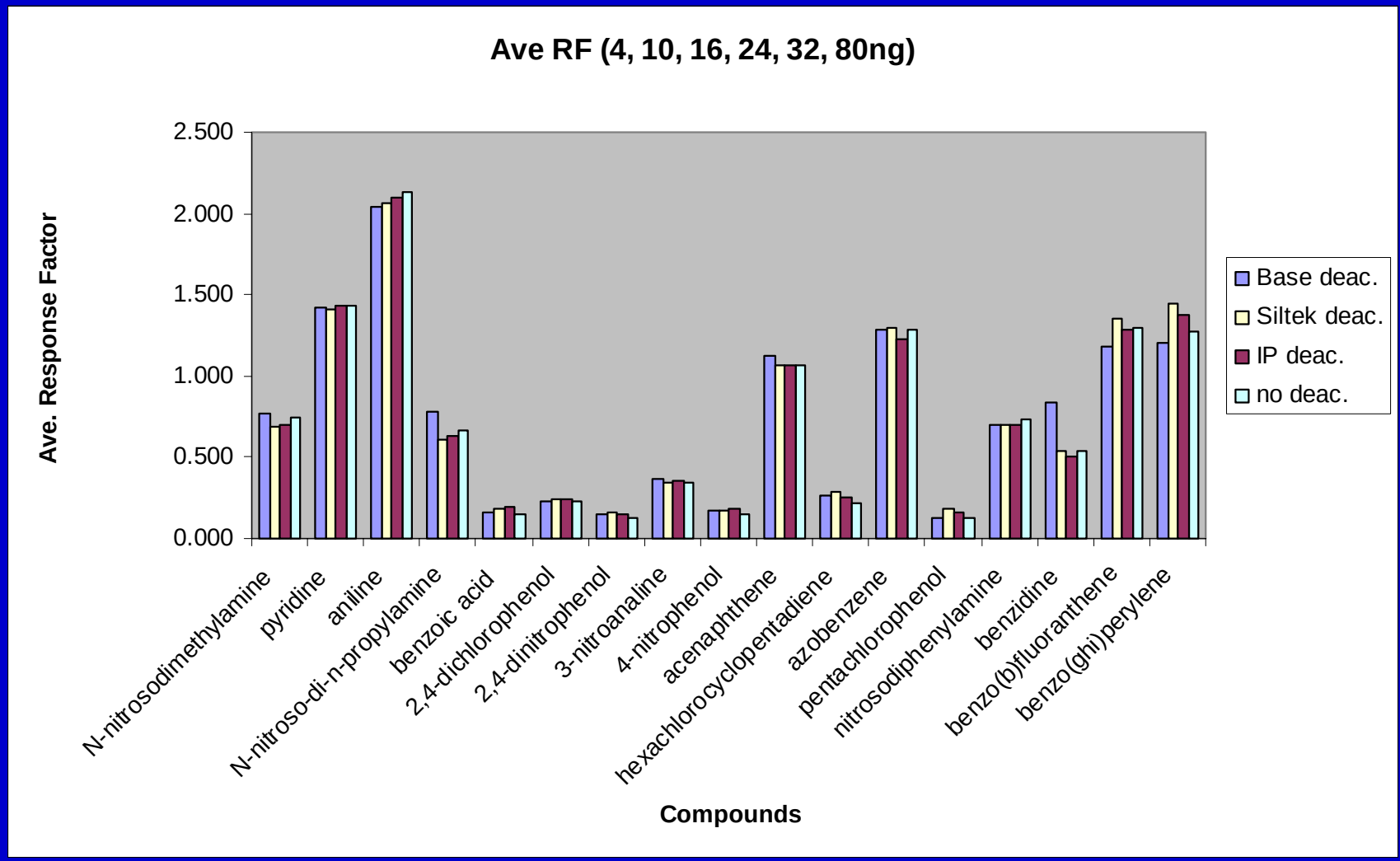


Figure 3. Average Response Factors for key semivolatile components at 4ng on column:

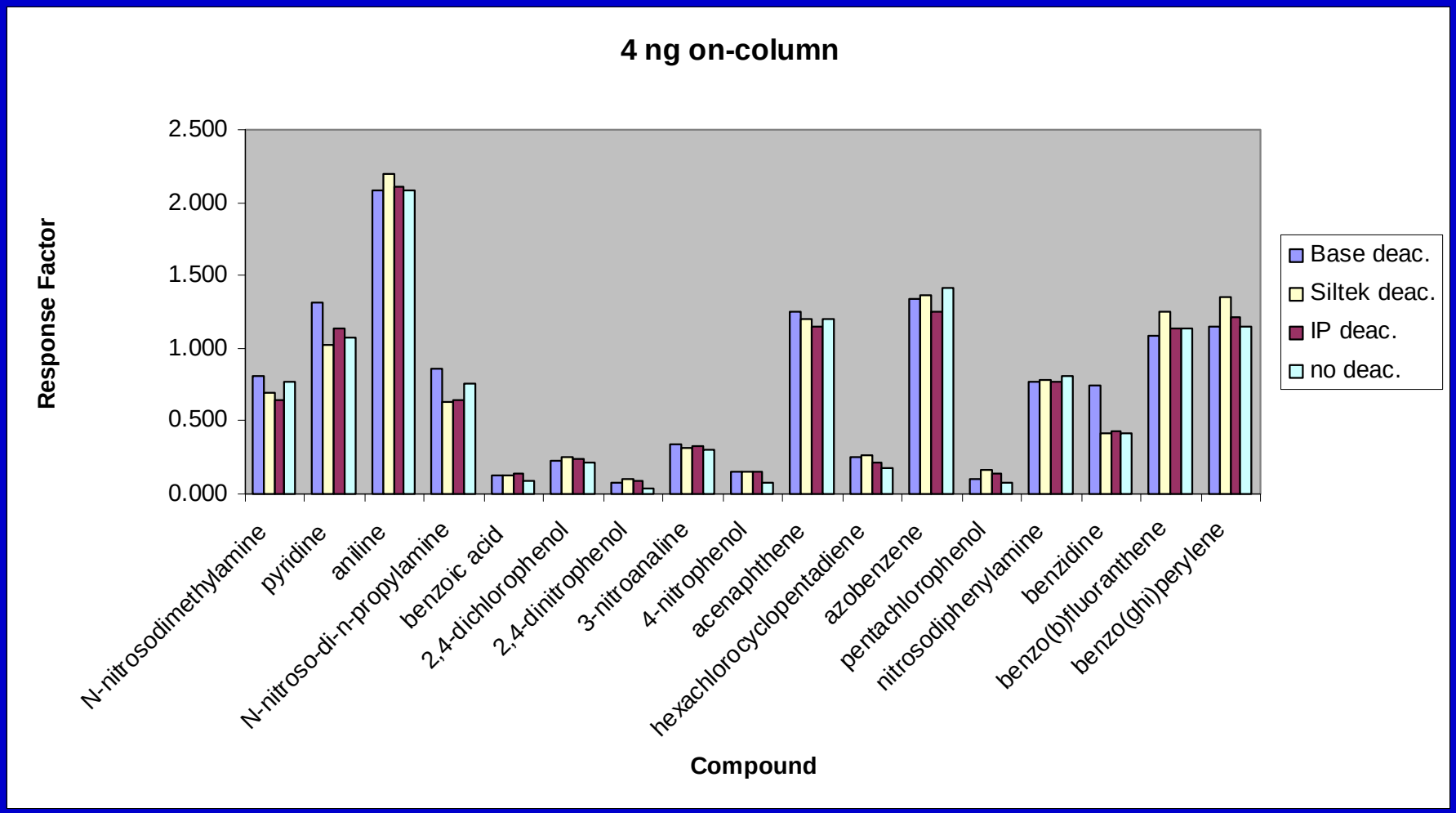
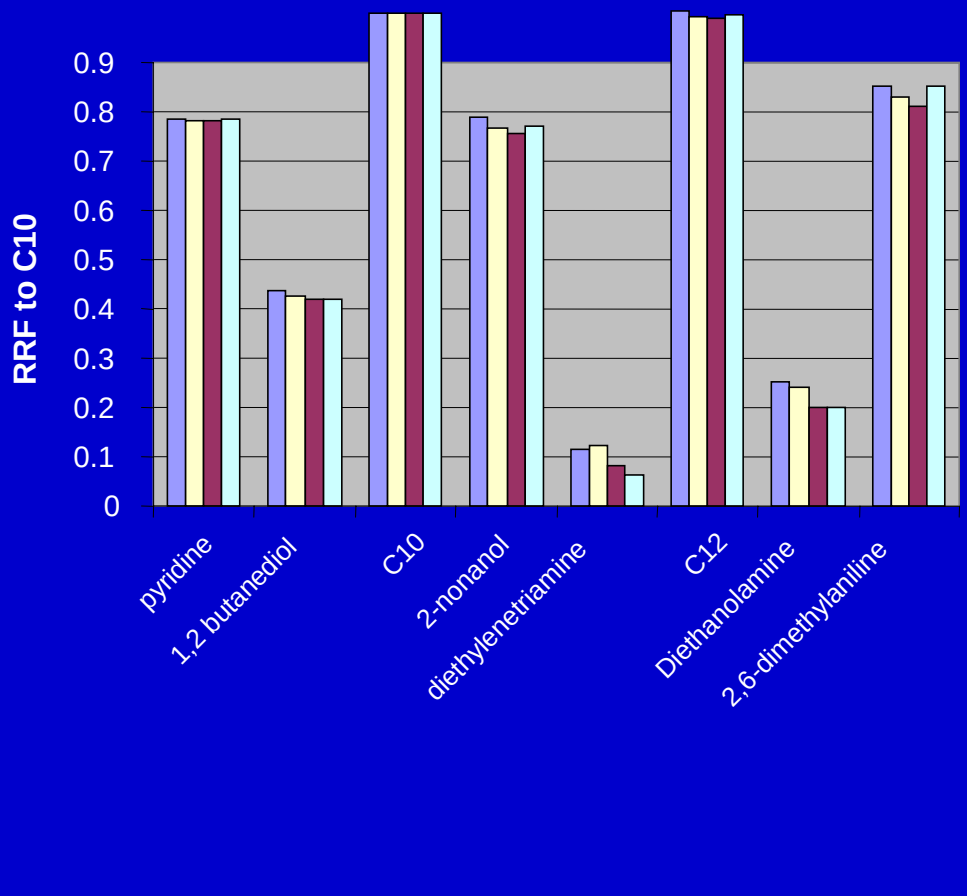


Figure 5A-B. Results for Amine Evaluation, Injections 2-6

A. Average Response Factors for Injections 2-6



B. %RSD for Injections 2-6

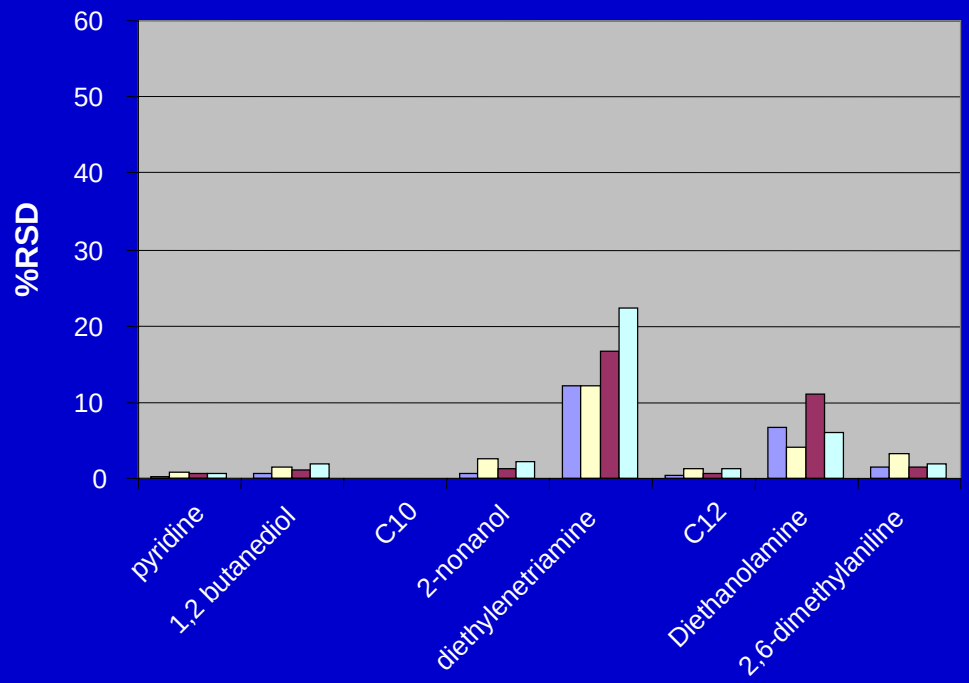
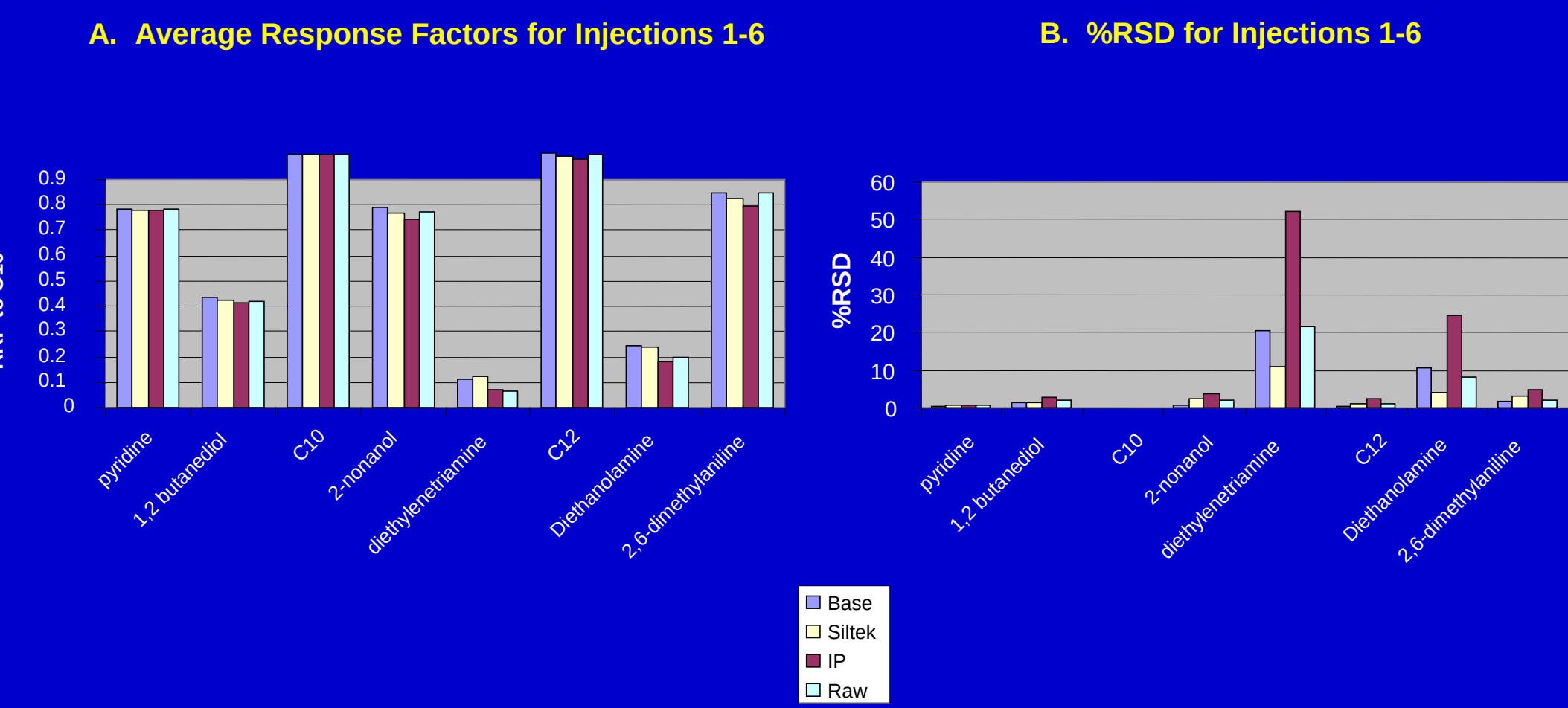


Figure 6A-B. Results for Amine Evaluation, Injections 1-6



				C14					
	diol	nitrosamin	benzacid	counts (k)	DNP	NP	nitroanil	PCP	Carbazole
Competitor 1	0.464	0.471	0.929	24	0.336	0.749	0.907	0.380	1.572
	0.480	0.484	0.992	30	0.364	0.899	1.033	0.381	1.760
ave	0.472	0.478	0.961	27	0.350	0.824	0.970	0.381	1.666
%diff	3.4	2.8	6.8	25.0	8.3	20.0	13.9	0.3	12.0
Competitor 2	0.339	0.539	0.000	31	0.000	0.695	0.994	0.098	1.748
	0.357	0.509	0.000	32	0.001	0.704	0.958	0.143	1.703
ave	0.348	0.524	0.000	32	0.001	0.700	0.976	0.121	1.726
%diff	5.3	-5.6	na	3.2	na	1.3	-3.6	45.9	-2.6
Restek IP	0.482	0.545	1.053	31	0.398	0.88	1.007	0.507	1.816
	0.489	0.517	1.081	34	0.449	0.853	0.997	0.488	1.72
ave	0.486	0.531	1.067	33	0.424	0.867	1.002	0.498	1.768
%diff	1.5	-5.1	2.7	9.7	12.8	-3.1	-1.0	-3.7	-5.3
Siltek	0.497	0.493	1.004	31	0.434	0.860	0.951	0.458	1.739
	0.502	0.496	1.028	32	0.487	0.903	1.011	0.516	1.859
ave	0.500	0.495	1.016	32	0.461	0.882	0.981	0.487	1.799
%diff	1.0	0.6	2.4	3.2	12.2	5.0	6.3	12.7	6.9

Summary of Deactivation Data

- Deactivation chemistry plays a critical role in column inertness and efficiency
- “specific” deactivations (amine) useful for niche applications
- “IP” polymeric deactivation is generally more widely applicable than silazane chemistries
- Siltek appears to be the optimum deactivation for the phases tested so far…