Semivolatile Analysis

Frank L. Dorman, Chris English, and Gary Stidsen

Semivolatile Compounds

1. N-nitrosodimethylamine	28. 2-nitrophenol	55. acenaphthylene	81. anthracene
2. pyridine	29. benzoic acid	56. 3-nitroaniline	82. di-n-butylphthalate
3. methyl methanesulfonate	30. bis(2-chloroethoxy)methane	57. acenaphthene-d10	83. 4-nitroquinoline-1-oxide
4. 2-fluorophenol	31. 2,4-dichlorophenol	58. acenaphthene	84. isodrin
5. ethyl methanesulfonate	32. 1,2,4-trichlorobenzene	59. 2,4-dinitrophenol	85. fluoranthene
6. phenol-d6	33. naphthalene-d8	60. 4-nitrophenol	86. benzidine
7. phenol	34. naphthalene	61. pentachlorobenzene	87. pyrene
8. aniline	35. 2,6-dichlorophenol	62. 2,4-dinitrotoluene	88. aromite
9. bis(2-chloroethyl)ether	36. 4-chloroaniline	63. dibenzofuran	89. p-terphenyl-d14
10. 2-chlorophenol	37. hexachloropropene	64. 2,3,4,6-tetrachlorophenol	90. chlorbenzilate
11. 3-chlorophenol	38. hexachlorobutadiene	65. diethyl phthalate	91. butyl benzyl phthalate
12. 1,3-dichlorobenzene	39 4-chloro-3-methylphenol	66. 4-chlorophenyl phenyl ether	92. kepone
13. 1,4-dichlorobenzene-d4	40. isosafrole	67. fluorene	93. bis(2-ethylhexyl)phthalate
14. 1,4-dichlorobenzene	41. 2-methylnaphthalene	68. 4-nitroaniline	94. 3,3'-dichlorobenzidine
15. benzyl alcohol	42. 1-methylnaphthalene	69. 4,6-dinitro-2-methylphenol	95. benzo(a)anthracene
16. 1,2-dichlorobenzene-d4	43. hexachlorocyclopentadiene	70. diphenylamine	96. chrysene-d12
17. 1,2-dichlorobenzene	44. 1,2,4,5-tetrachlorobenzene	71. azobenzene	97. chrysene
18. 2-methylphenol	45. 2,4,6-trichlorophenol	72. 2,4,6-tribromophenol	98. di-n-octyl phthalate
19. bis(2-chloroisopropyl)ether	46. 2,4,5-trichlorophenol	73. phenacetin	99. benzo(b)fluoranthene
20. 4-methylphenol/3-methylphenol	47. 2-fluorobiphenyl	74. 4-bromophenyl phenyl ether	100. benzo(k)fluoranthene
21. N-nitroso-di-n-propylamine	48. safrole	75. hexachlorobenzene	101. benzo(a)pyrene
22. acetophenone	49. 2-chloronaphthalene	76. pentachlorophenol	102. perylene-d12
23. hexachloroethane	50. 2-nitroaniline	77. pentachloronitrobenzene	103. 3-methylcholanthrene
24. nitrobenzene-d5	51. 1,4-naphthoquinone	78. dinoseb	104. indeno(1,2,3-cd)pyrene
25. nitrobenzene	52. dimethylphthalate	79. phenanthrene-d10	105. dibenzo(a,h)anthracene
26. isophorone	53. 1,3-dinitrobenzene	80. phenanthrene	106. benzo(ghi)perylene
27. 2,4-dimethylphenol	54. 2,6-dinitrotoluene		

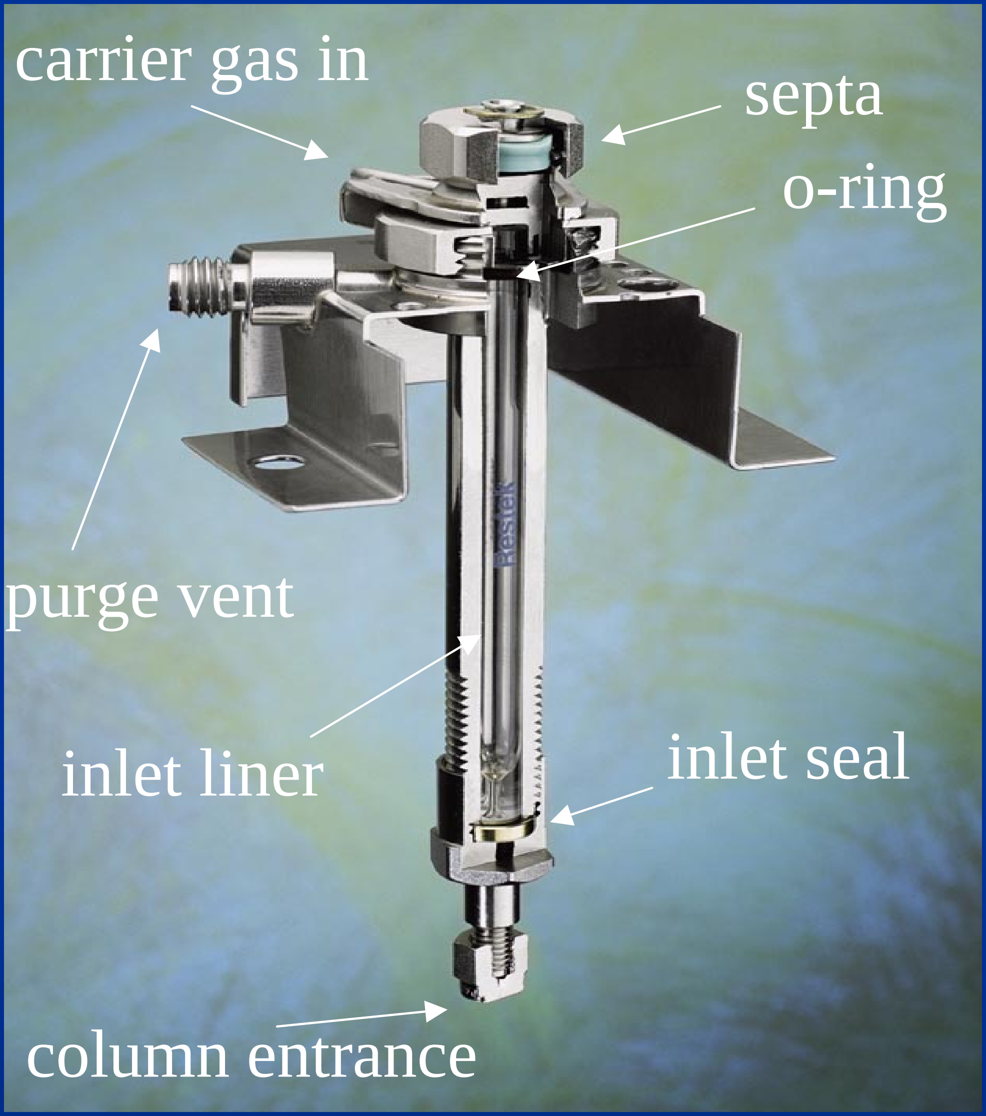
Semivolatile Analysis

- Injection techniques
  - Split/splitless
    - Gooseneck liners
    - Drilled Uniliner
  - Deactivation
- Analysis
  - Instrument conditions

Split/Splitless Injection

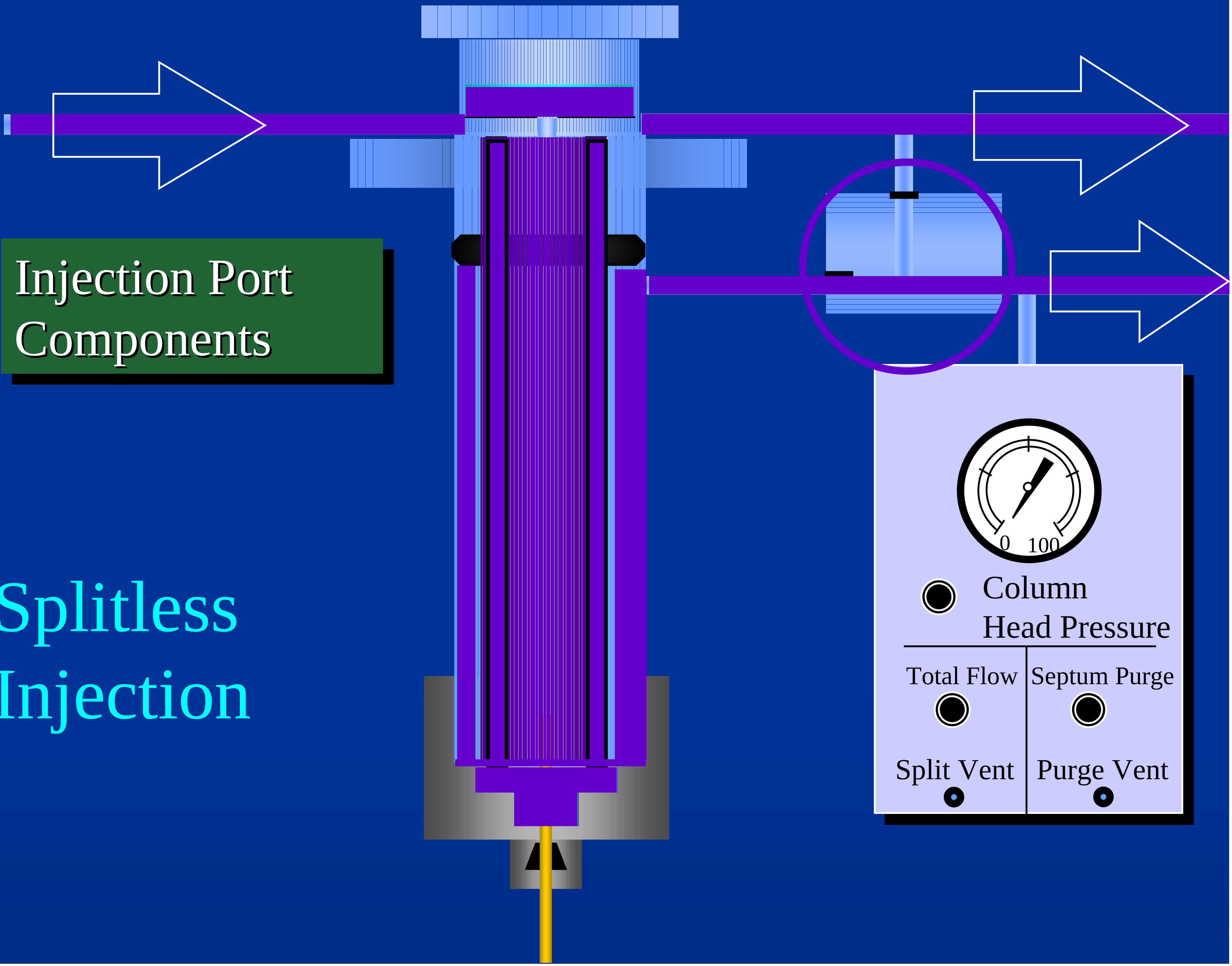
- Important aspects of injector
  - Flow pattern
  - Hold time
  - Sample Vaporization
  - Liners
  - Activity
    - Acidic and basic compounds

Split/Splitless Injection Port



Injection Port Components

Splitless Injection



Factors Affecting Splitless Injection

1. Hold Times

Column ID (mm)	Column Flow Rate (cc/min.) He	Approx. Hold Time
0.18	0.3	3 min
0.25	0.7	1.5 min
0.32	1.2	45 sec
0.53	2.6	30 sec

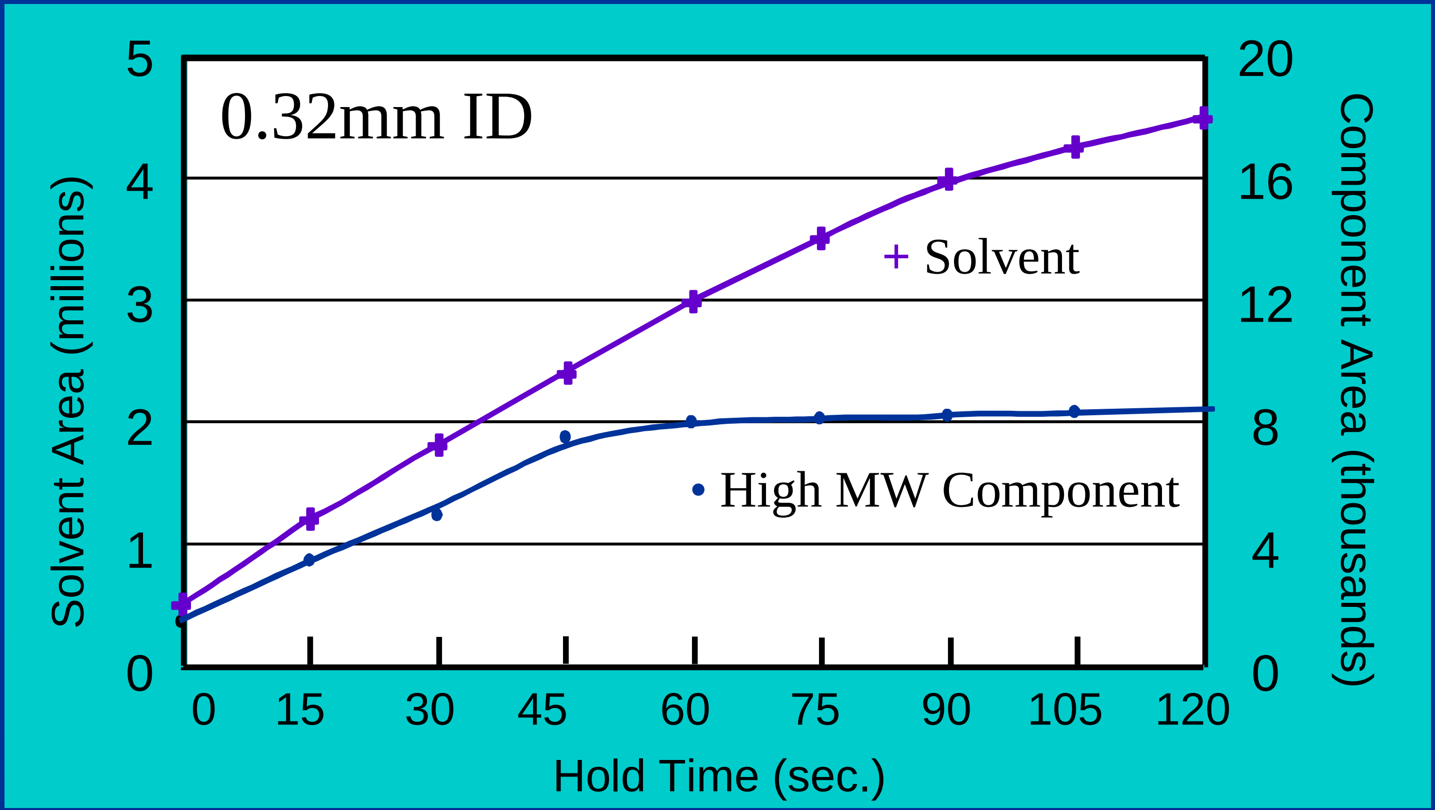
Determine this empirically

Determine this empirically

Note: based on a 2µL injection volume of CH_2Cl_2 = 0.8 mL sample expansion value @ 250°C & 10 psig.

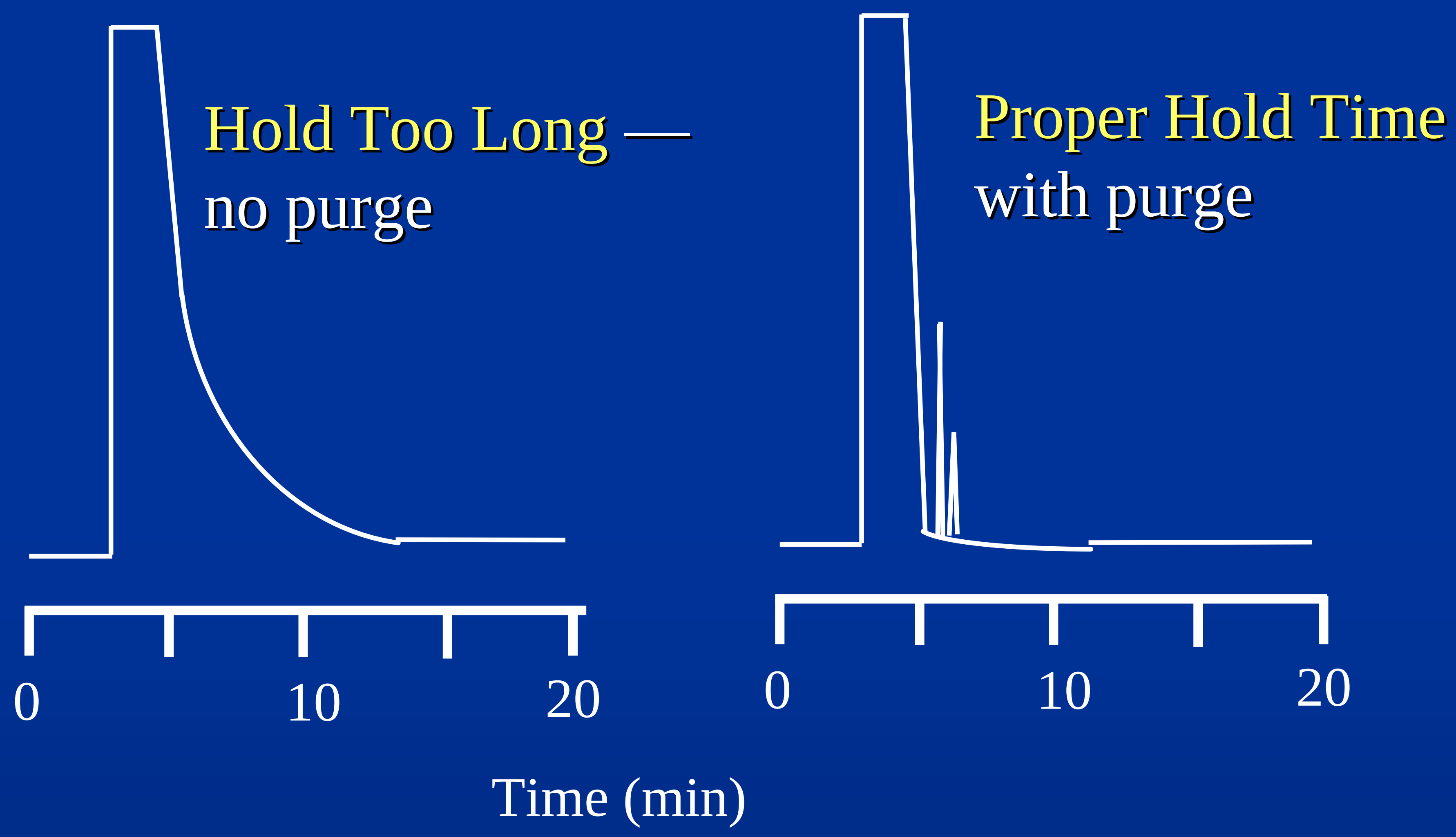
Factors Affecting Splitless Injection

1. Hold Time Optimization



Factors Affecting Splitless Injection

1. Hold Times



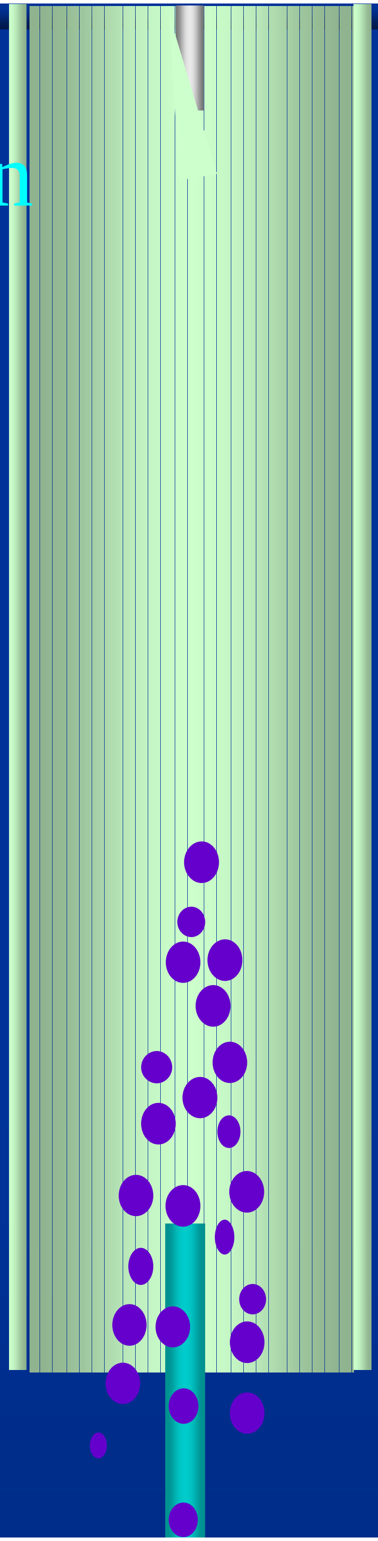
Factors Affecting Splitless Injection

3. Sample Vaporization

Fast Autosampler :

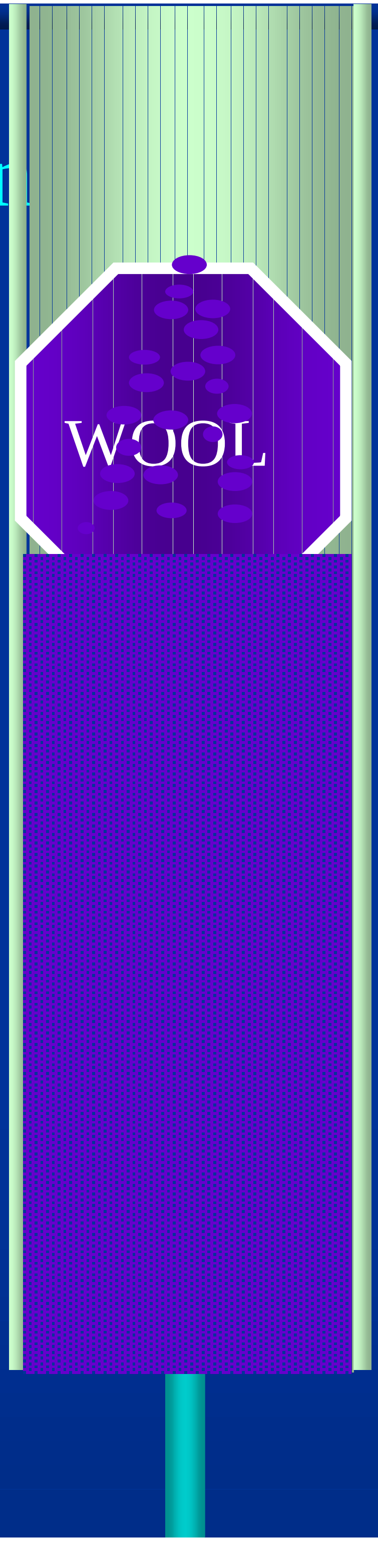
Incomplete vaporization

<u>Aerosols</u> or droplets reach the column instead of vapors



Factors Affecting Splitless Injection

3. Sample Vaporization



Fast Autosampler :

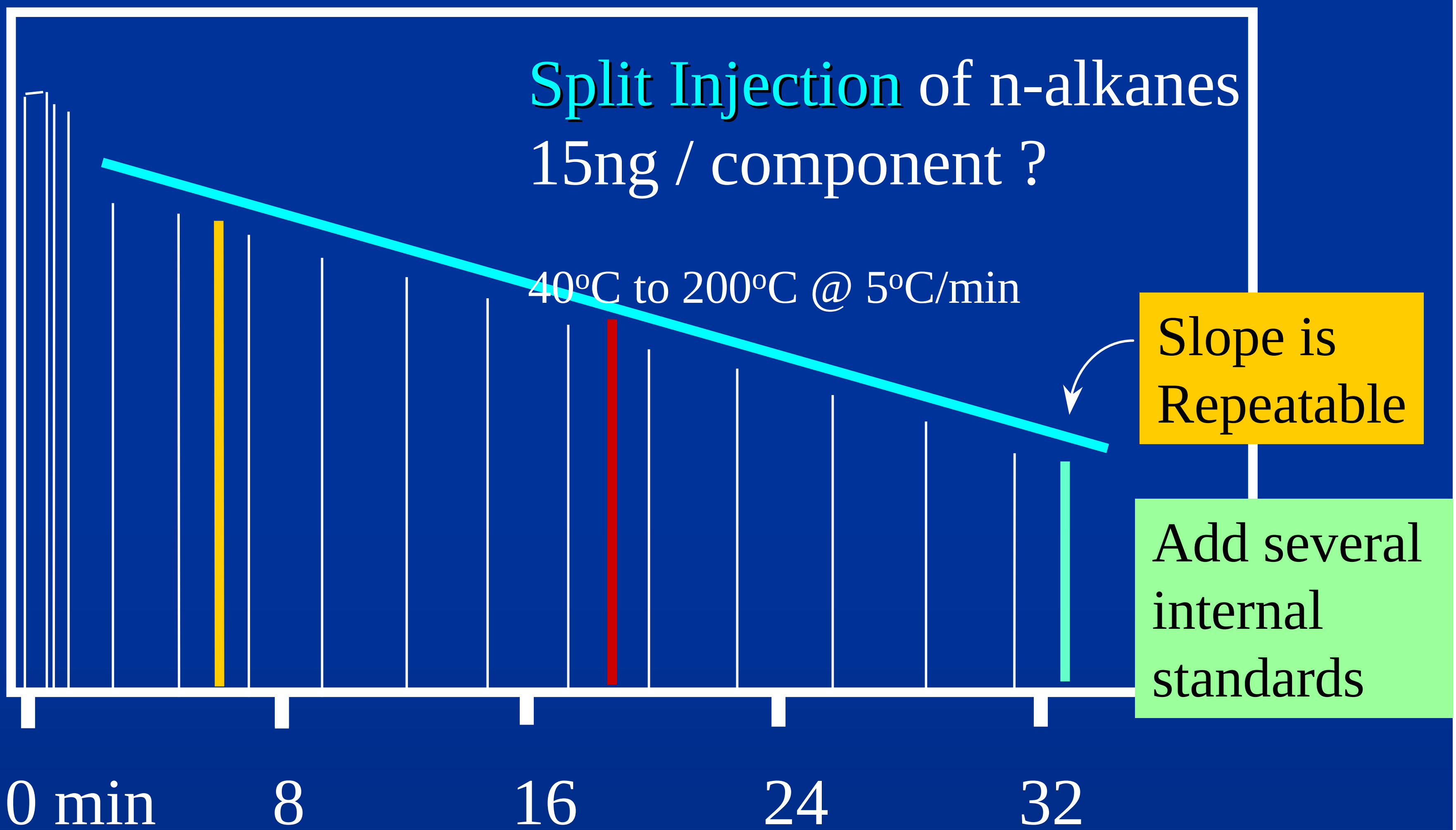
Pack with wool or CarboFrit™

STOPS AEROSOLS COMPLETELY

II. Splitter Discrimination

Molecular Weight Discrimination

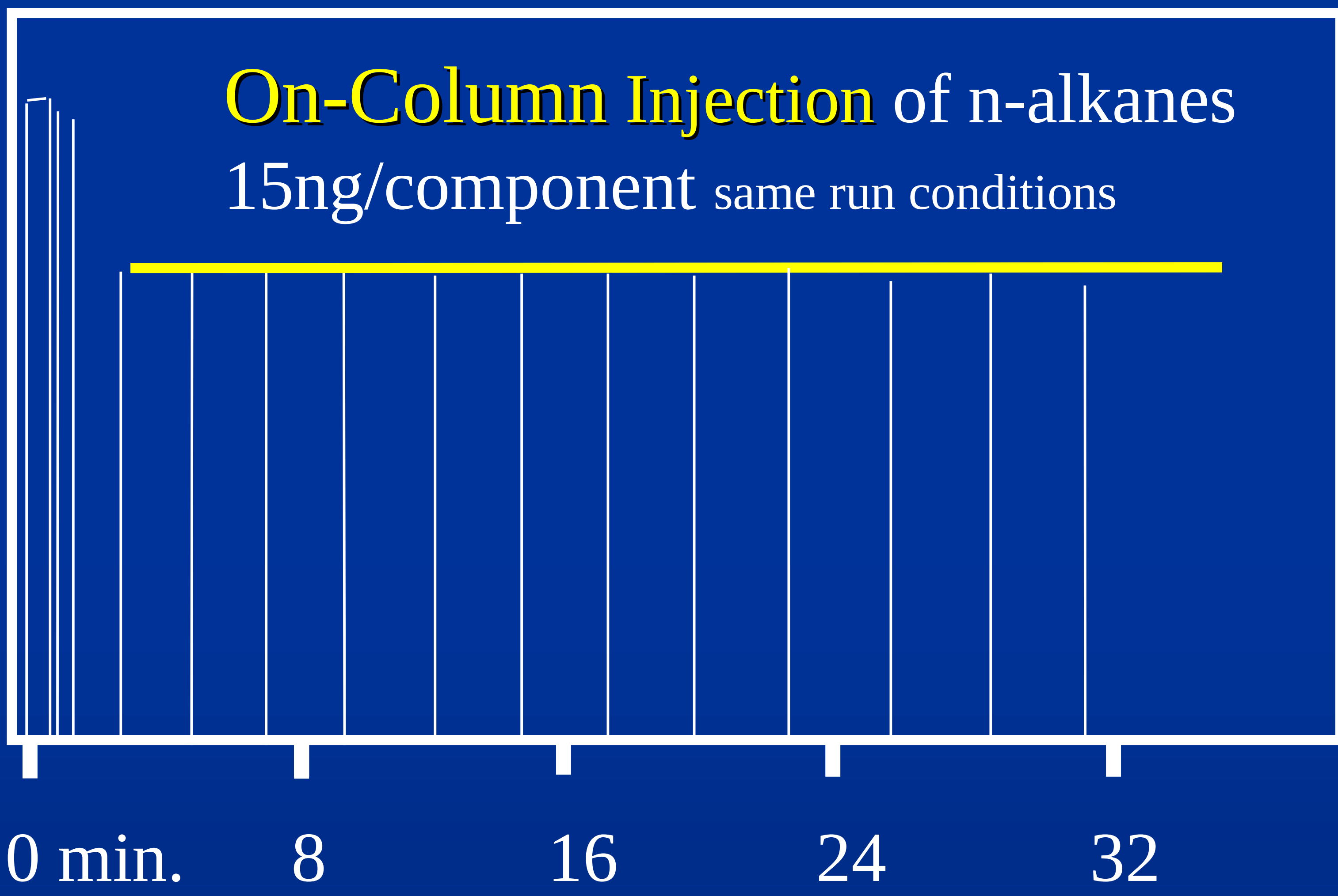
Rtx-1: 30m, 0.32mm ID, 0.25µm



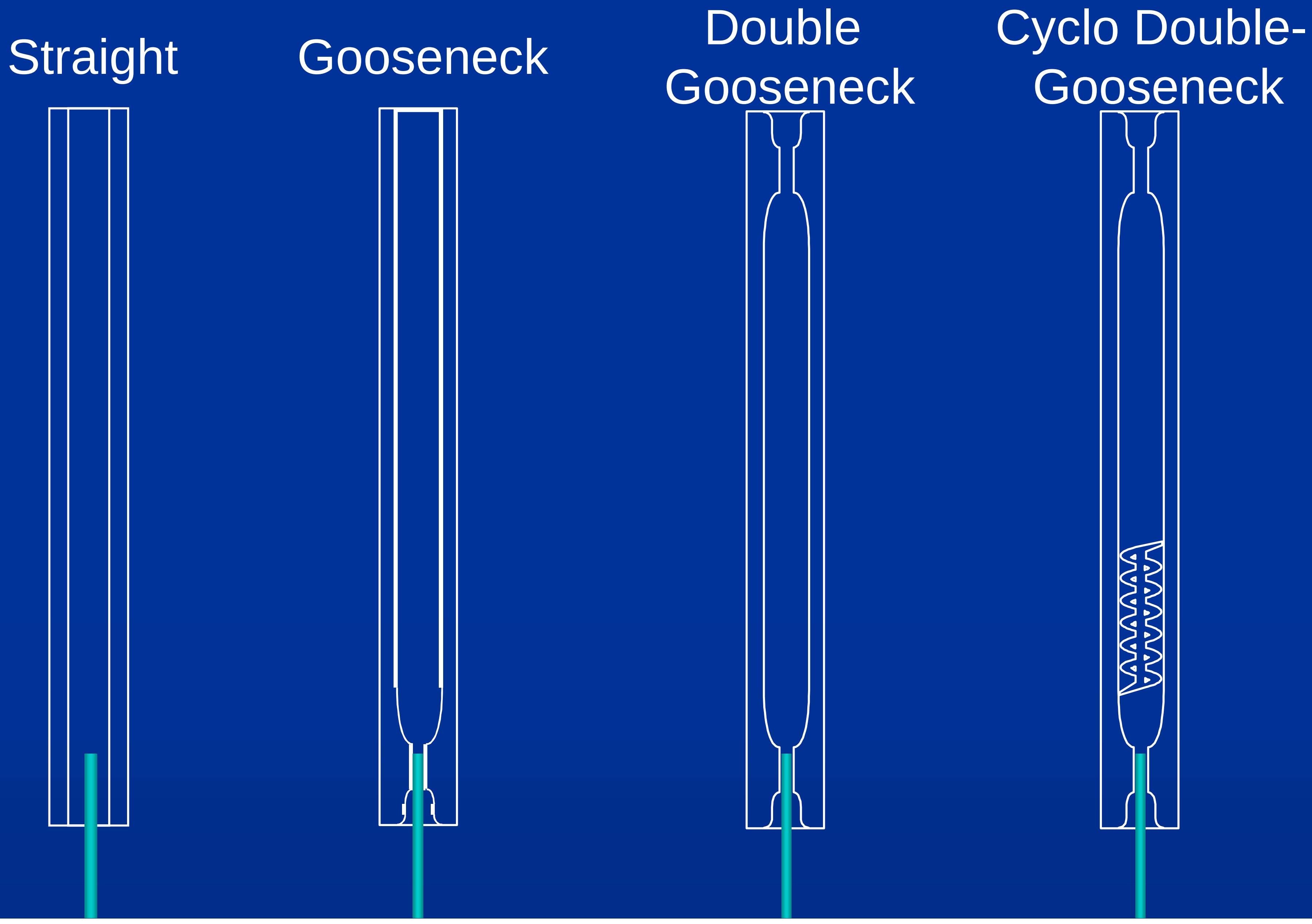
II. Splitter Discrimination

No Molecular Weight Discrimination

Rtx-1: 30m, 0.32mm ID, 0.25µm



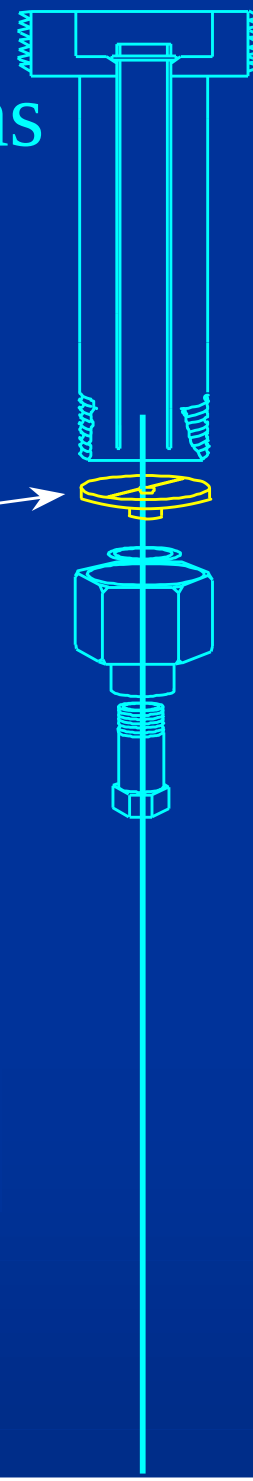
Splitless Liner Designs



Splitless Injection — Other Considerations

Sample Breakdown

Double gooseneck inlet sleeves minimize the catalytic effects of the hot metal parts at the base of splitless inlets.



Sleeve Type	endrin breakdown clean disk	endrin breakdown dirty disk
Splitless with Wool	6.0%	12.8%
Gooseneck	2.0%	2.4%

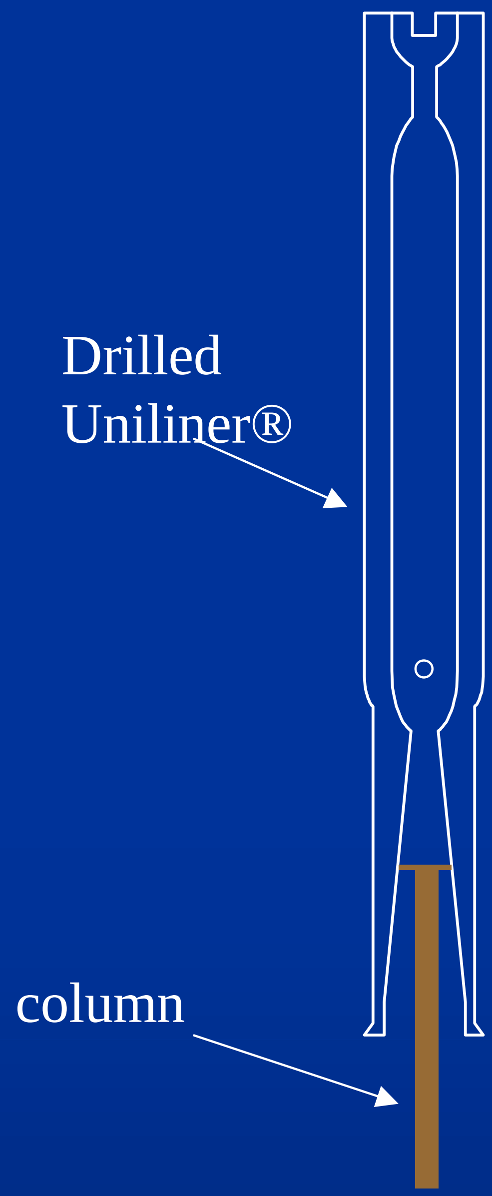
Vespel® Ring Inlet Seals
Types of Surface Treatments

Split/splitless Injection using the Drilled Uniliner

- For trace analysis
- Inlet sleeve has a press-fit connection with column at bottom of sleeve
- More inert sample pathway
- Helps eliminate injection port discrimination

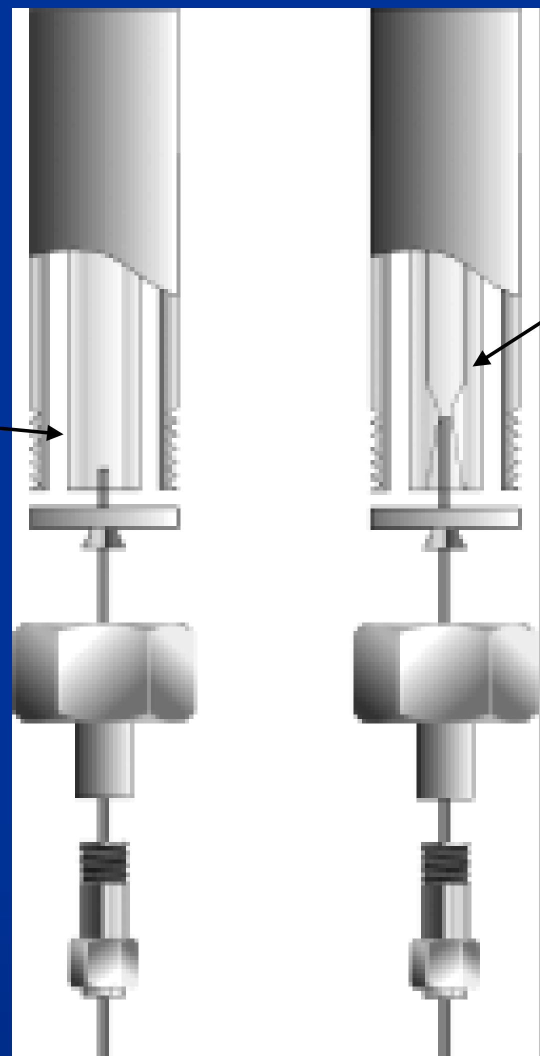
Drilled Uniliner

- Allows DI and Splitless injection methods
- Minimizes injection port discrimination
- Reduces loss of active compounds for more accurate results



Installing the Drilled Uniliner

Remove
the split
or
splitless
sleeve



Install a Direct
Injection sleeve

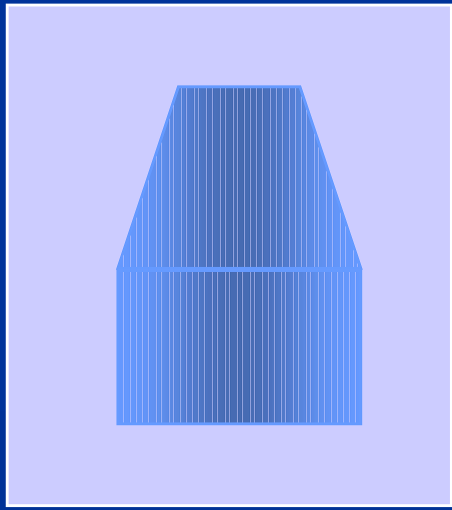
Press-fit
connection

Direct Injection Mode

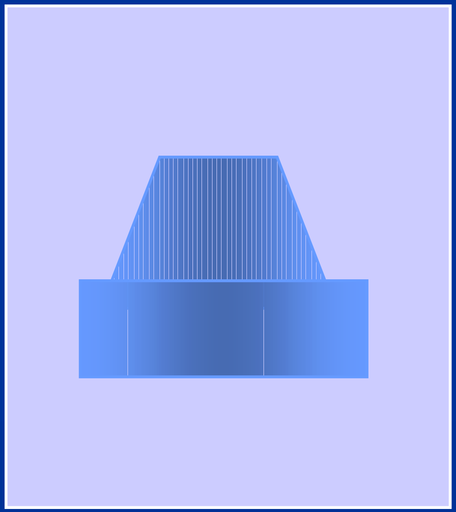
Making the proper press-fit connection

1. Pre-seat or pre-crush new ferrules

New Ferrule



Pre-seated Ferrule

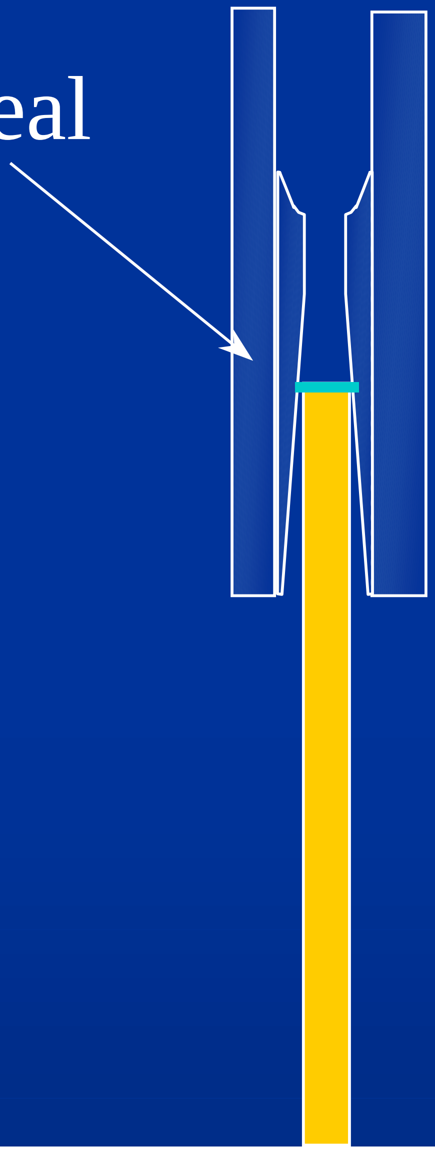


Direct Injection Mode

Making the proper press-fit connection

2. Install column into press-fit seal

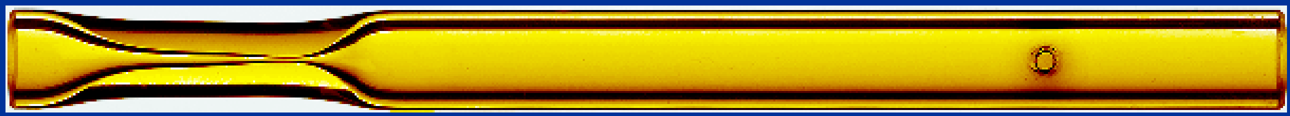
3. Tighten column nut



Drilled Uniliners

4mm
IP deactivated

4mm
Siltek deactivated



2mm
Siltek deactivated

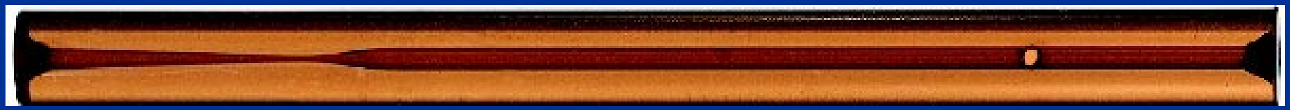


Figure 5 – Injection port discrimination: Comparing the single gooseneck liner under constant flow and pressure pulsed conditions.

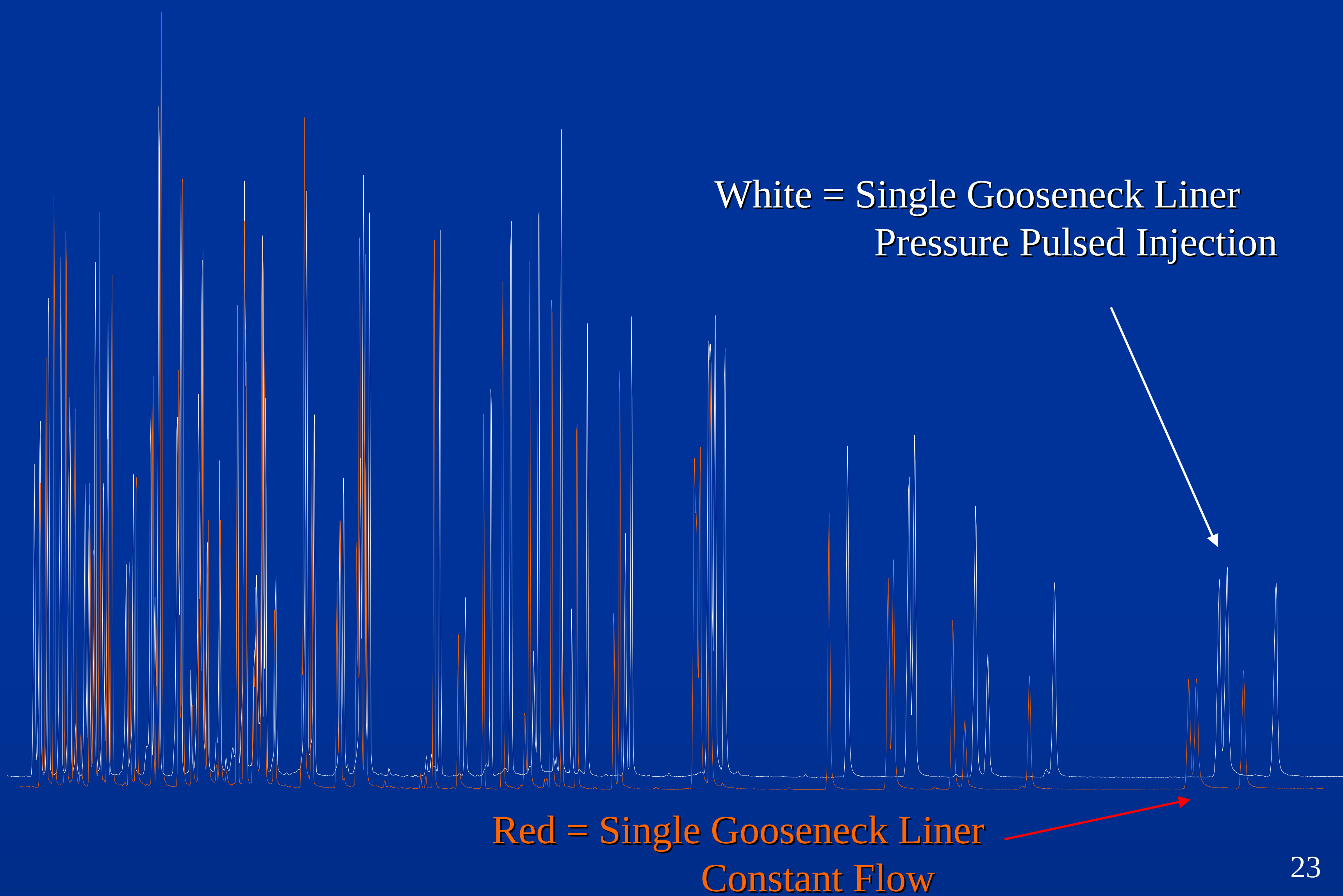
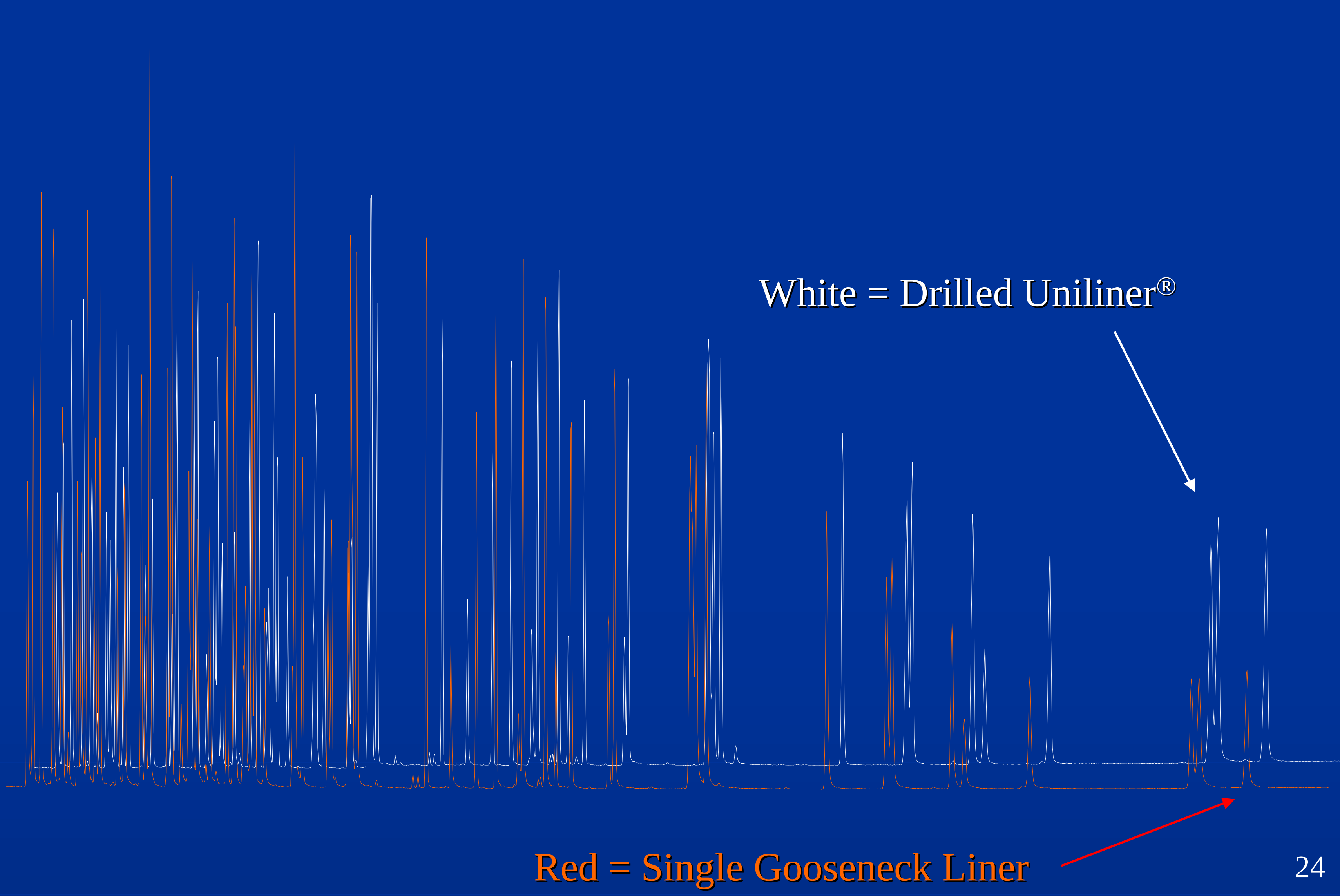


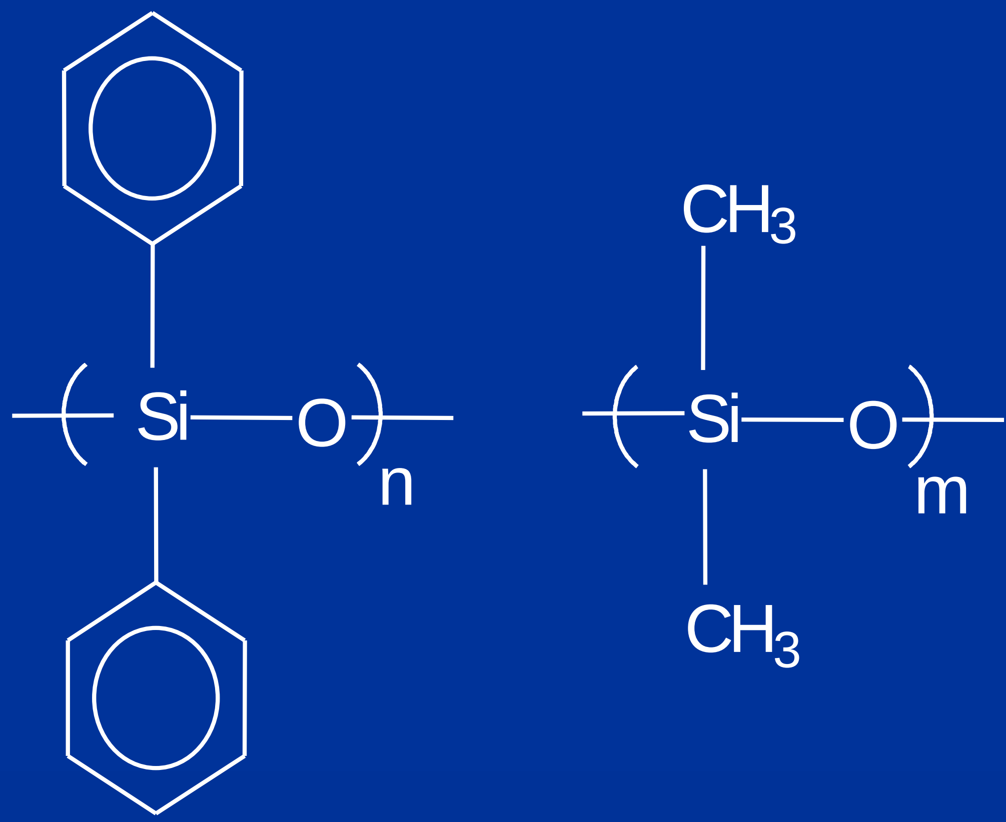
Figure 6 - Injection port discrimination: Comparing the single gooseneck liner to the Drilled Uniliner ®, both under constant flow conditions.



Comparison of Deactivations

- Deactivated Drilled Uniliner®
  - IP, Siltek™, and base procedure
- Run sequence
  - 7 reps at 4 ppm
    - Show largest difference in RRF due to active sites
  - Calibration curve
    - 4, 10, 16, 24, 32, and 80 ppm
    - ISTD at 8 ppm

Polymeric Deactivation



n or m = 3-6

Modification of the Fused Silica Surface

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

Guard Column Bleed Comparison at 330C

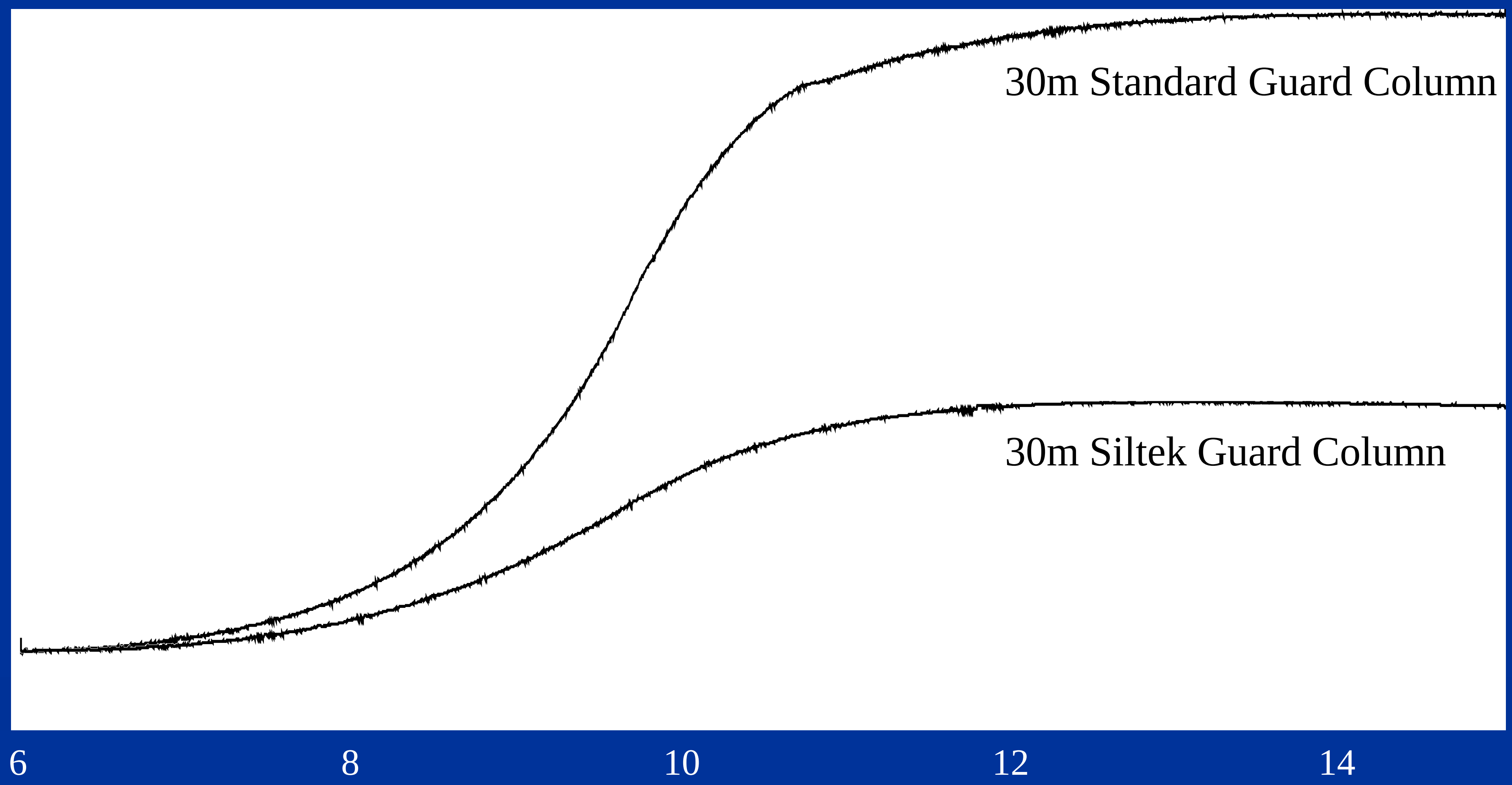
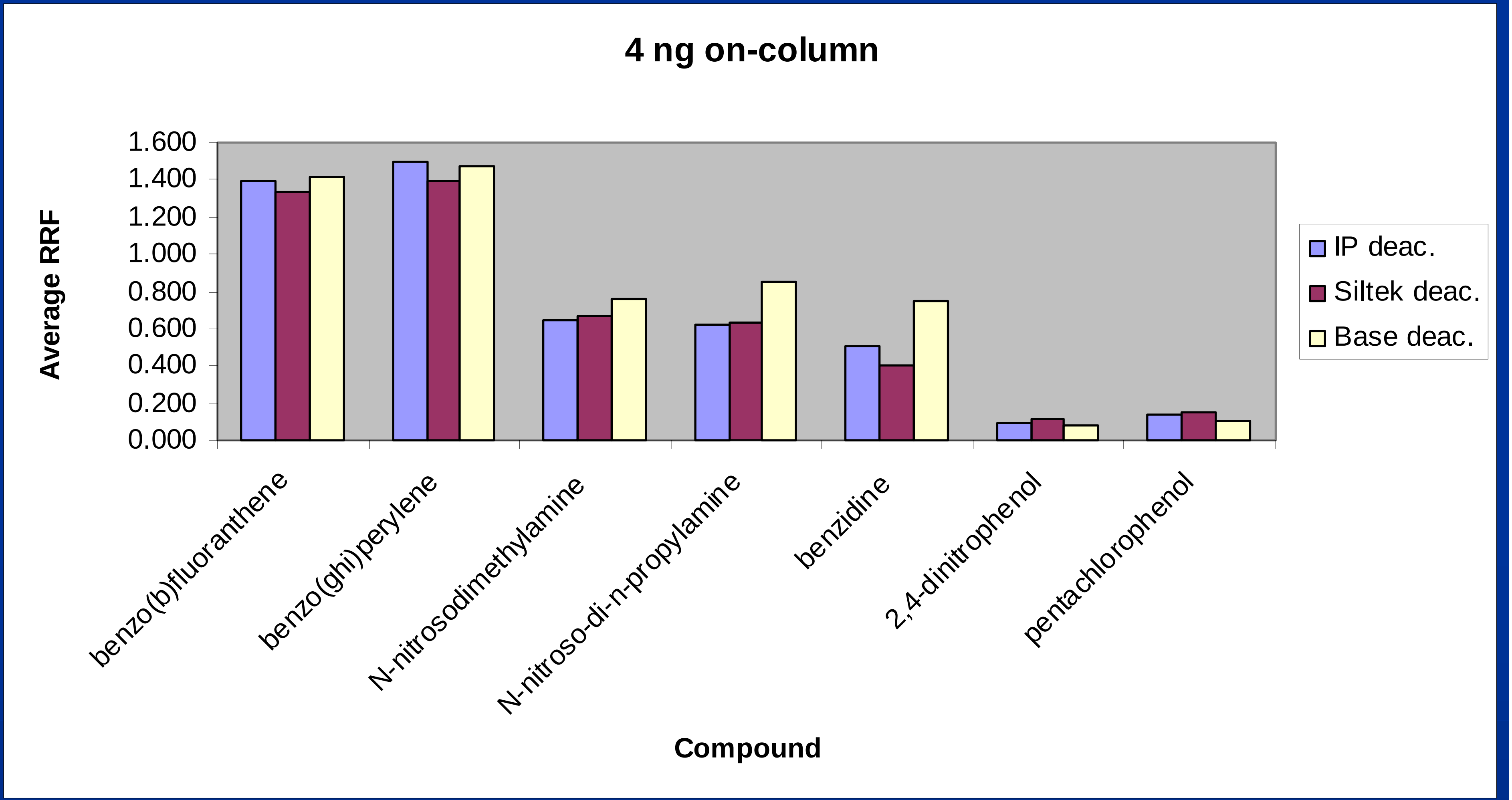


Figure 8

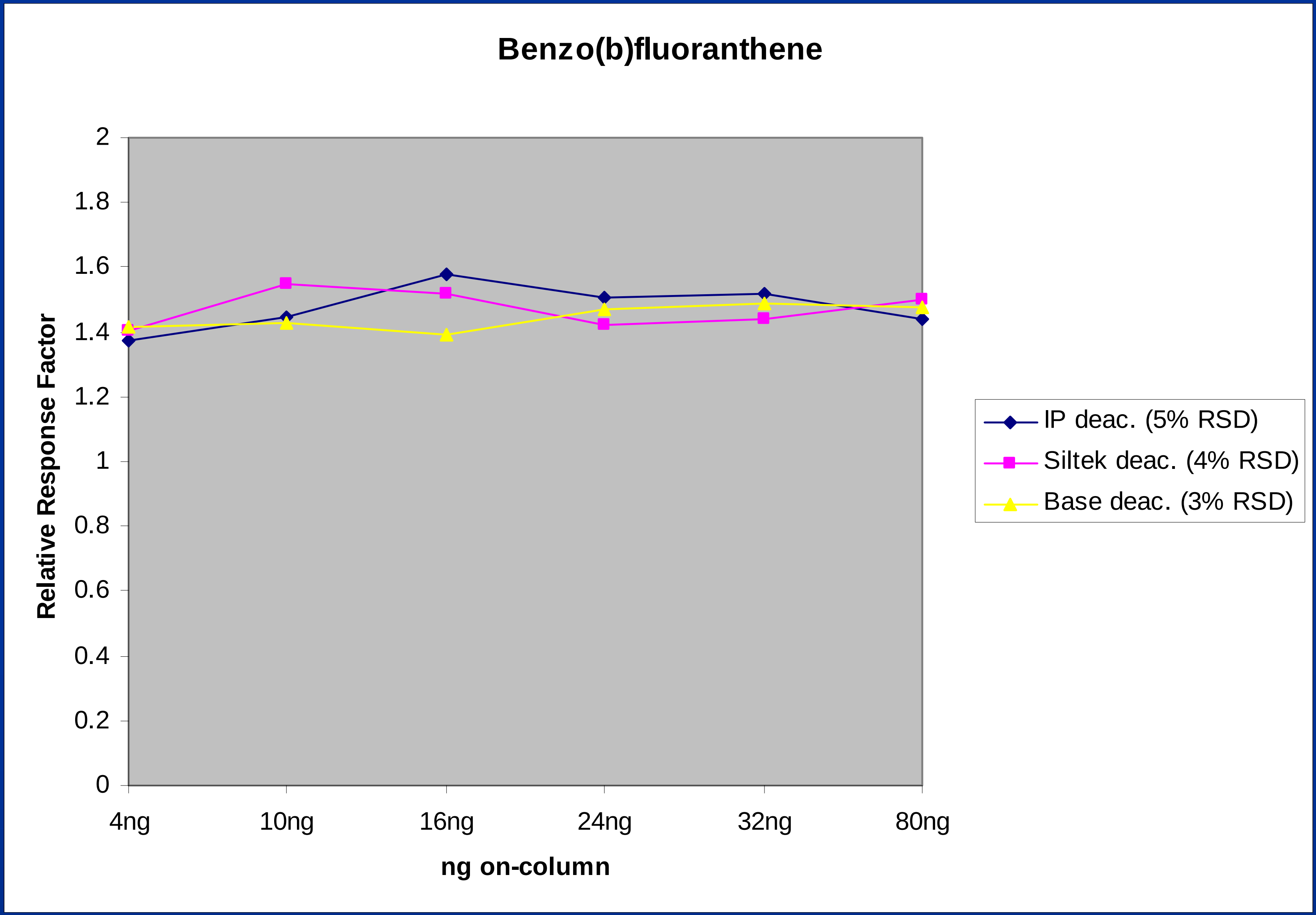
Liner Deactivation
Average RRF from 4ppm Standards



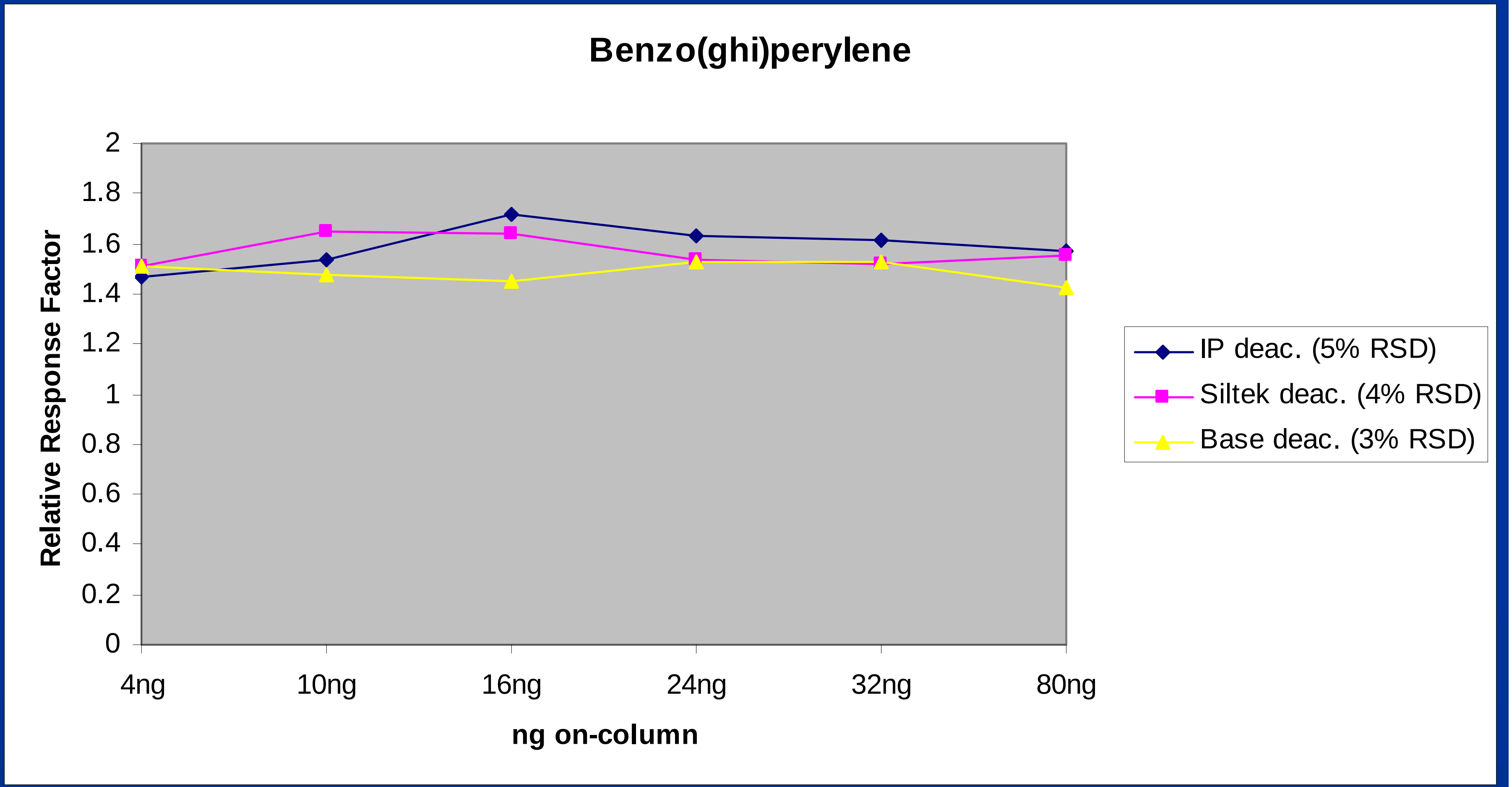
Affects of Deactivation on Linearity

- Response factors of 4ppm standard gave a good indication of the activity of the liner surfaces.
- What are the affects of deactivation on linearity?

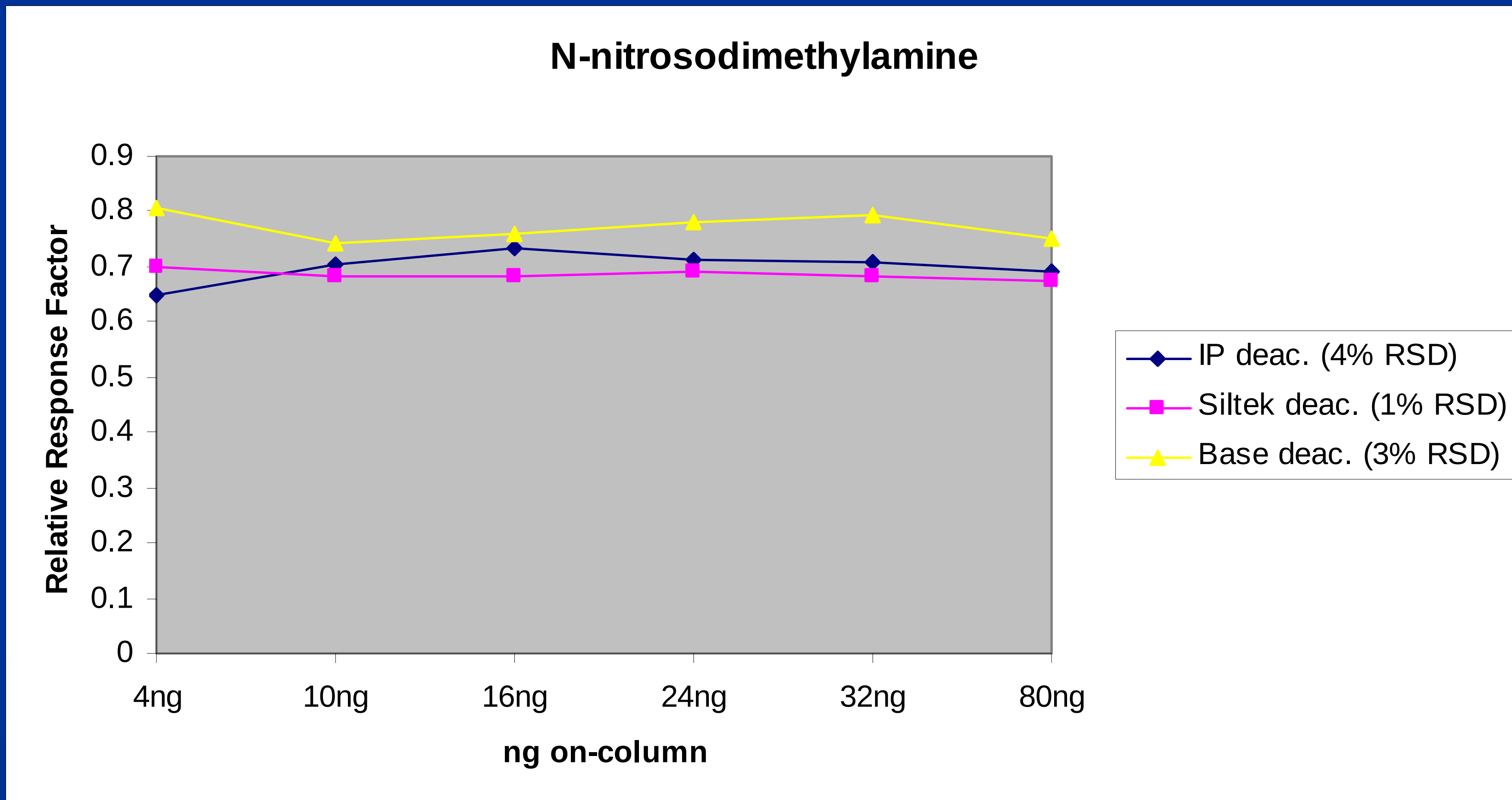
Affects of Deactivation on Linearity



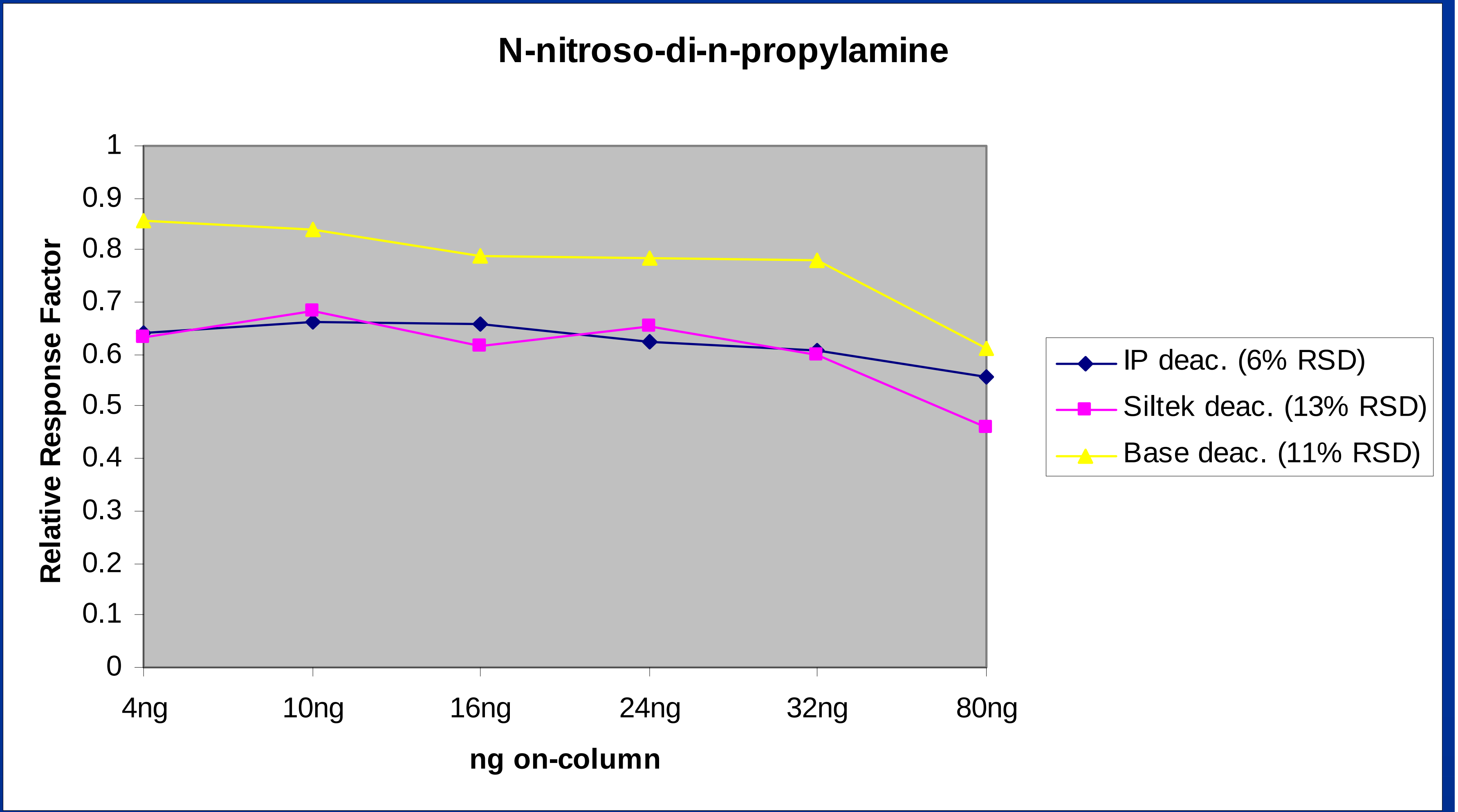
Affects of Deactivation on Linearity



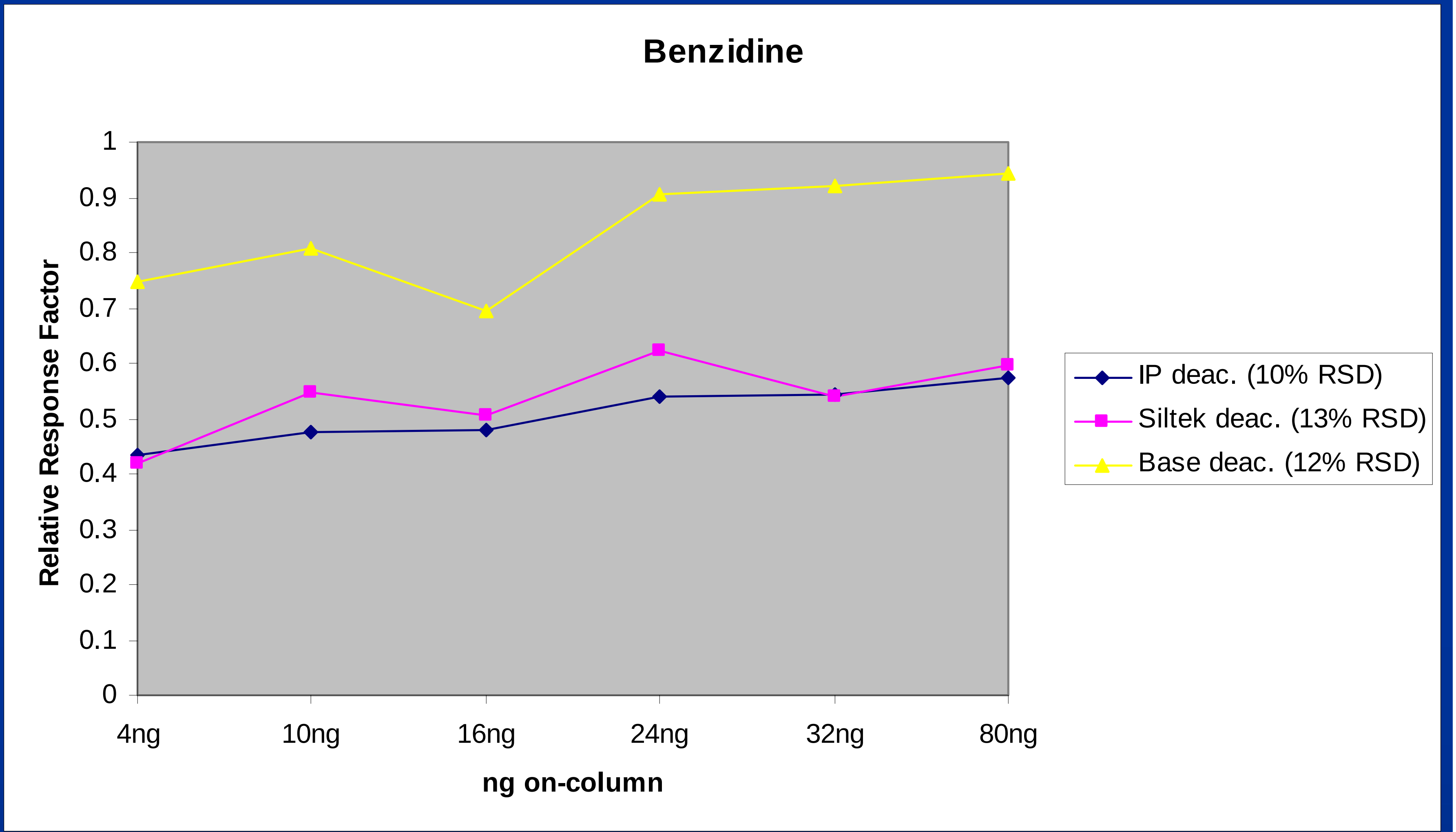
Affects of Deactivation on Linearity



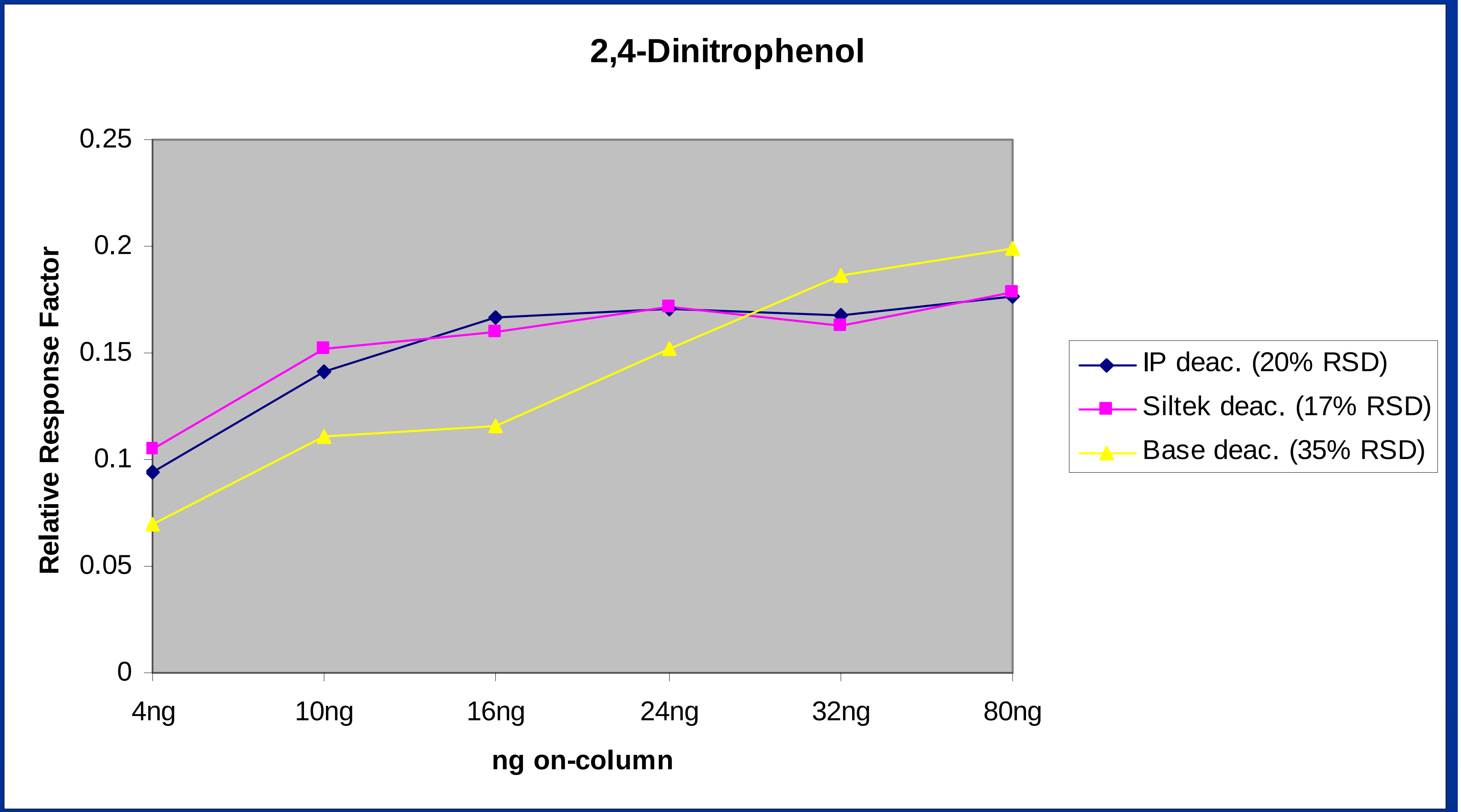
Affects of Deactivation on Linearity



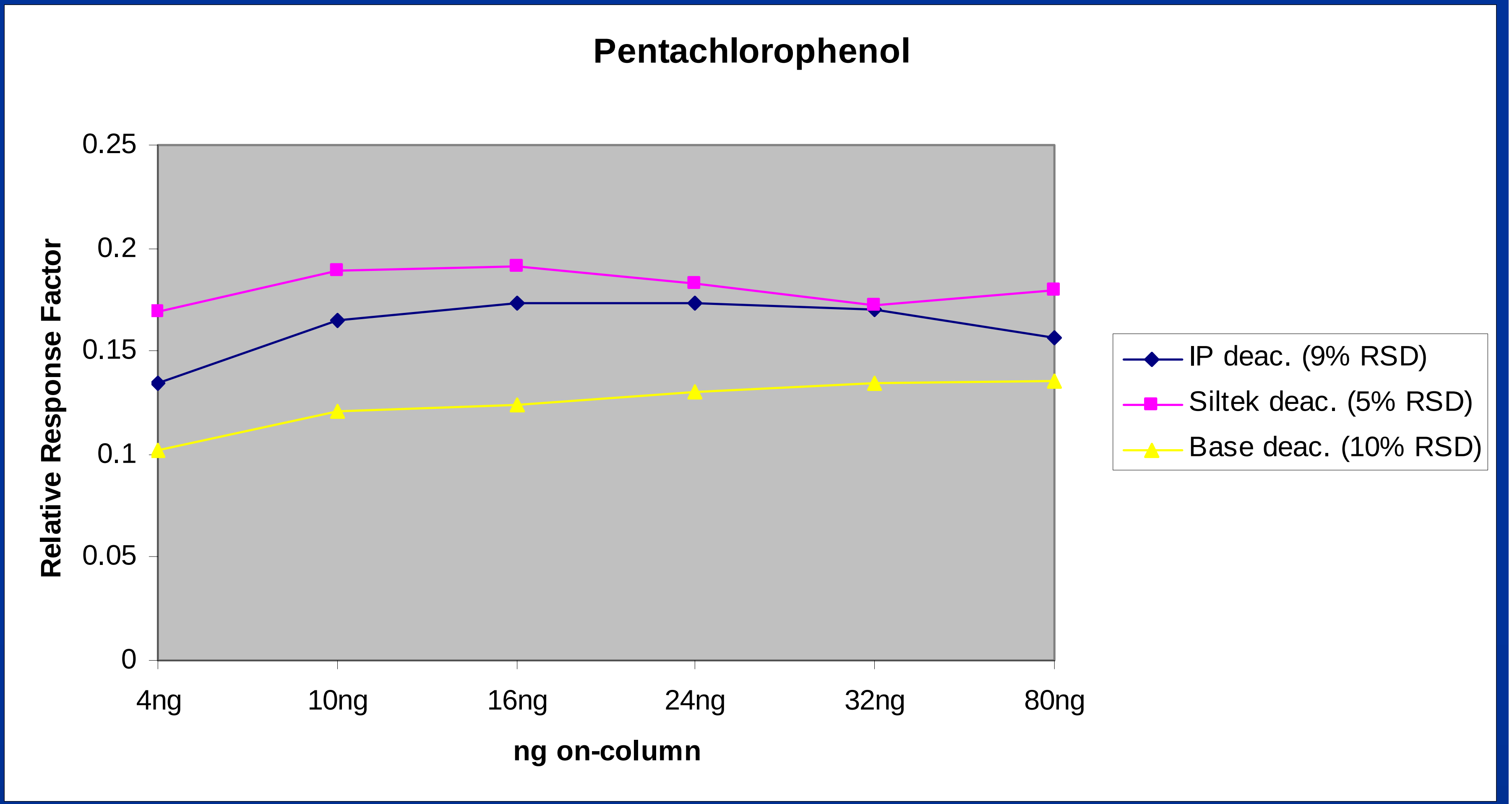
Affects of Deactivation on Linearity



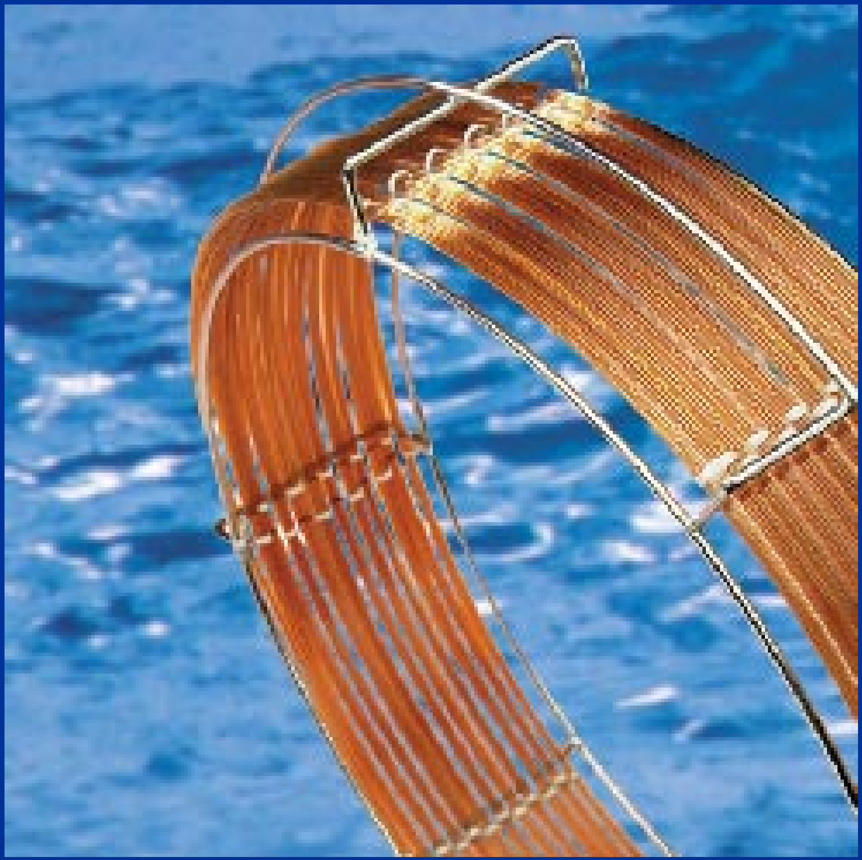
Affects of Deactivation on Linearity



Affects of Deactivation on Linearity



Column Selection



- Low bleed
- Separation of critical compounds

Instrument Analysis

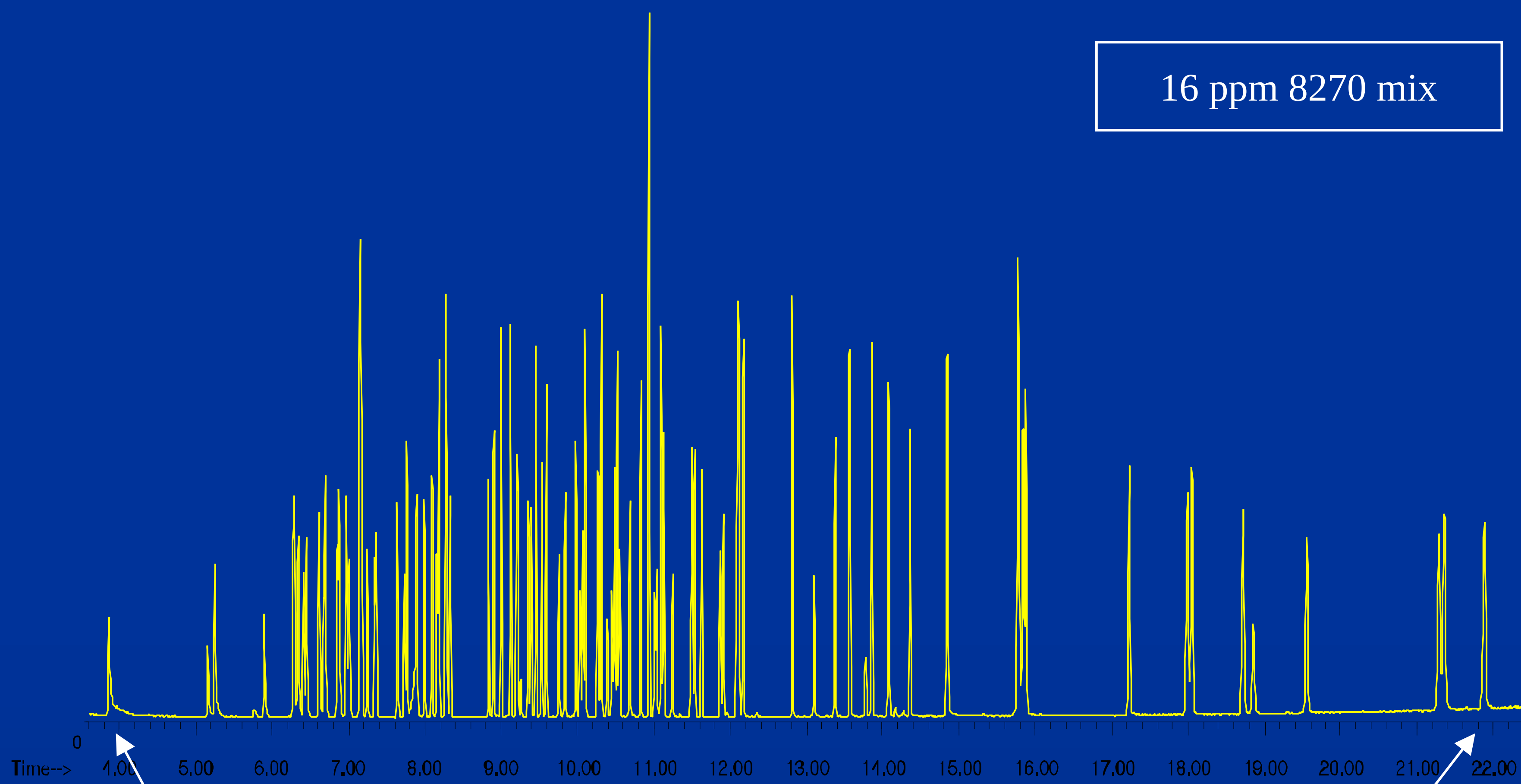
- Flow rate
  - Constant flow @ 1 ml/min
- Temperature program
  - initial hold time
    - helps resolve early eluting compounds
    - elute compounds on ramp rate vs isothermal
    - fast ramp rate through non-critical areas
- Column dimensions
  - Lower concentration standards allow for the use of a thinner film column.
  - Will utilize the 30m x 0.25mm ID, 0.25um film

Determined Run Conditions

- Constant flow rate @ 1.0 ml/min
- Injection port temperature: 300 C
- MS transfer temperature: 280 C
- Temperature program:
  - 35 C (2 min)
  - 20 C/min
  - 260 C (0 min)
  - 6 C/min
  - 330 C (1 min)

Rtx-5Sil MS
(30m x 0.25mm ID, 0.25um film)

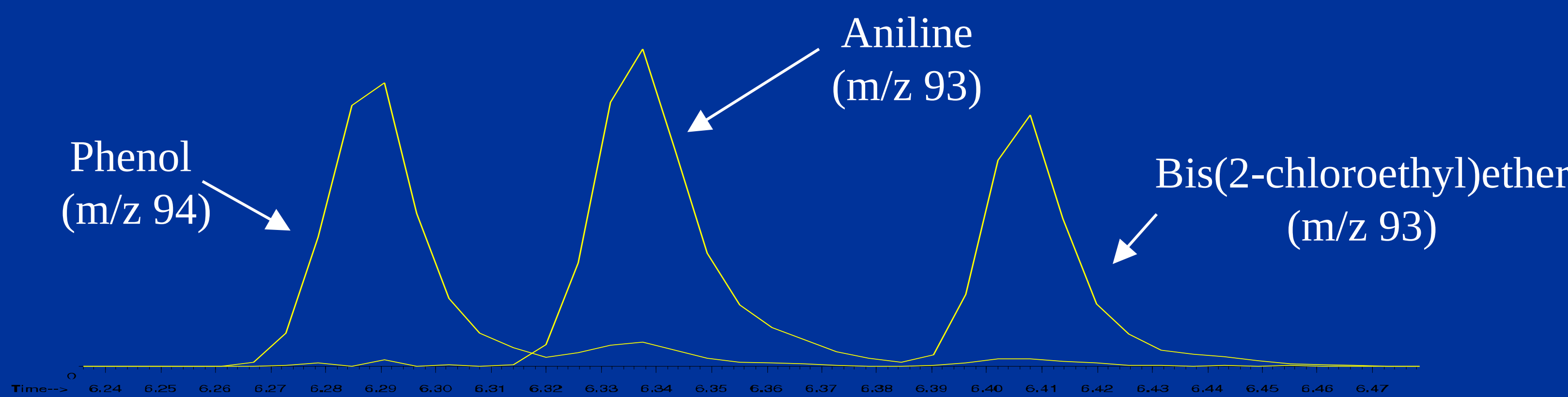
16 ppm 8270 mix

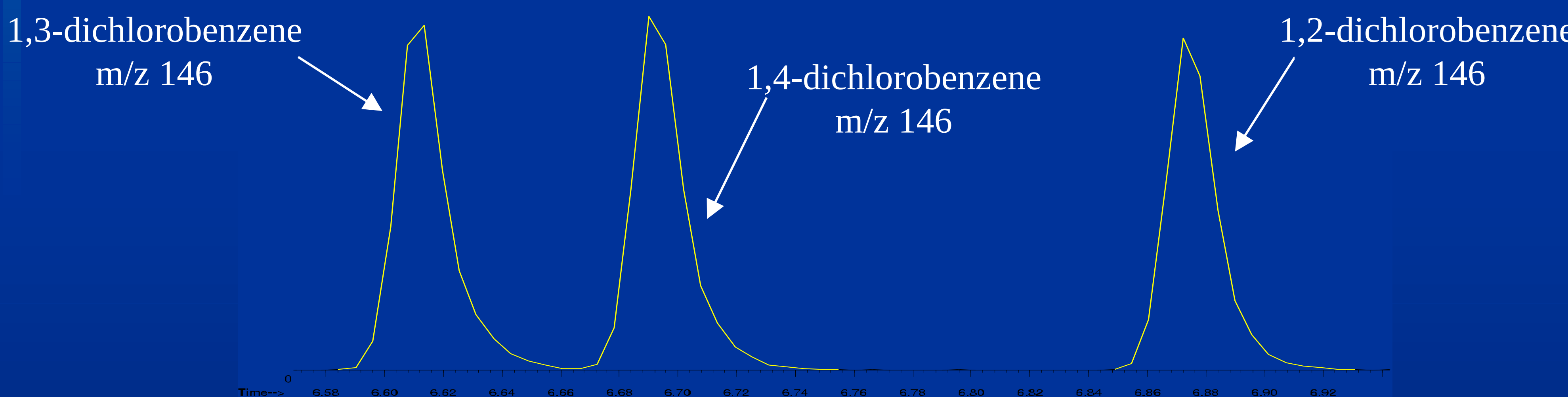


N-nitrosodimethylamine
& pyridine

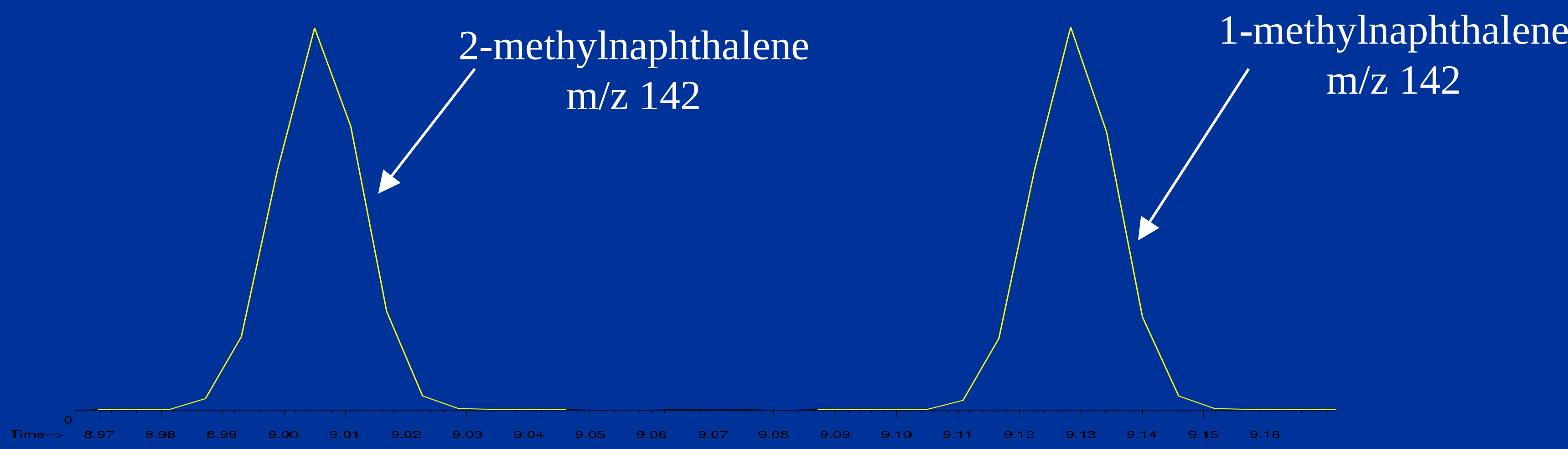
benzo(g,h,i)perylene

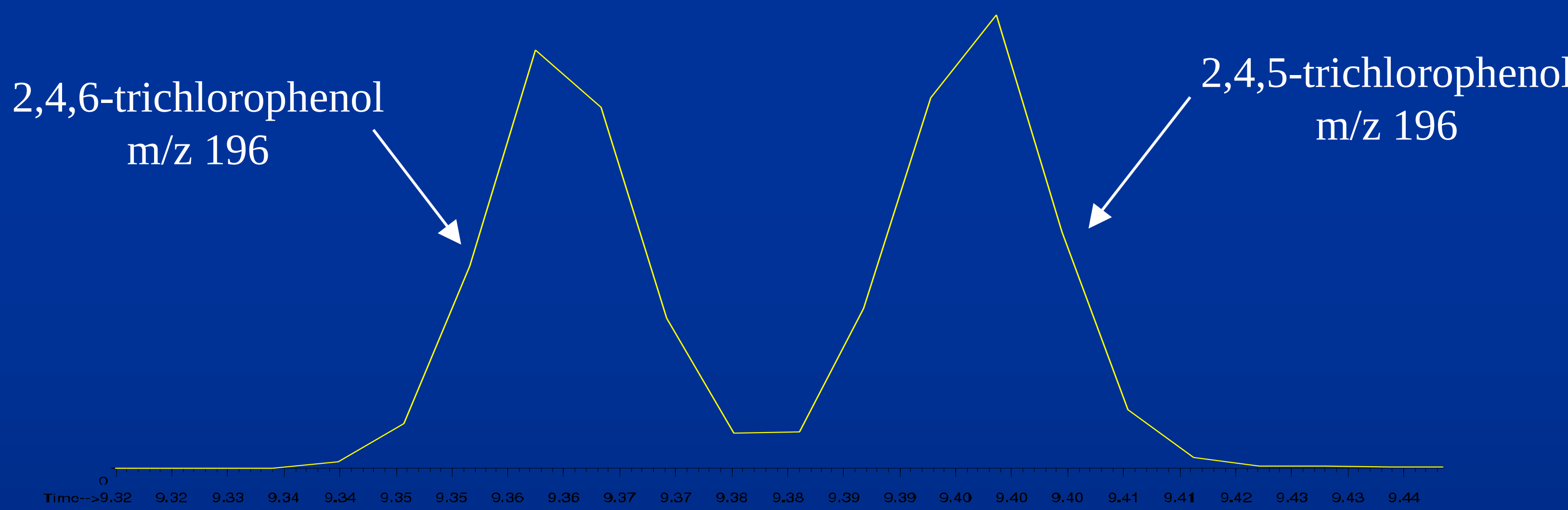
Separation of Critical Pairs
Rtx-5Sil MS (30m x 0.25mm, 0.25um film)



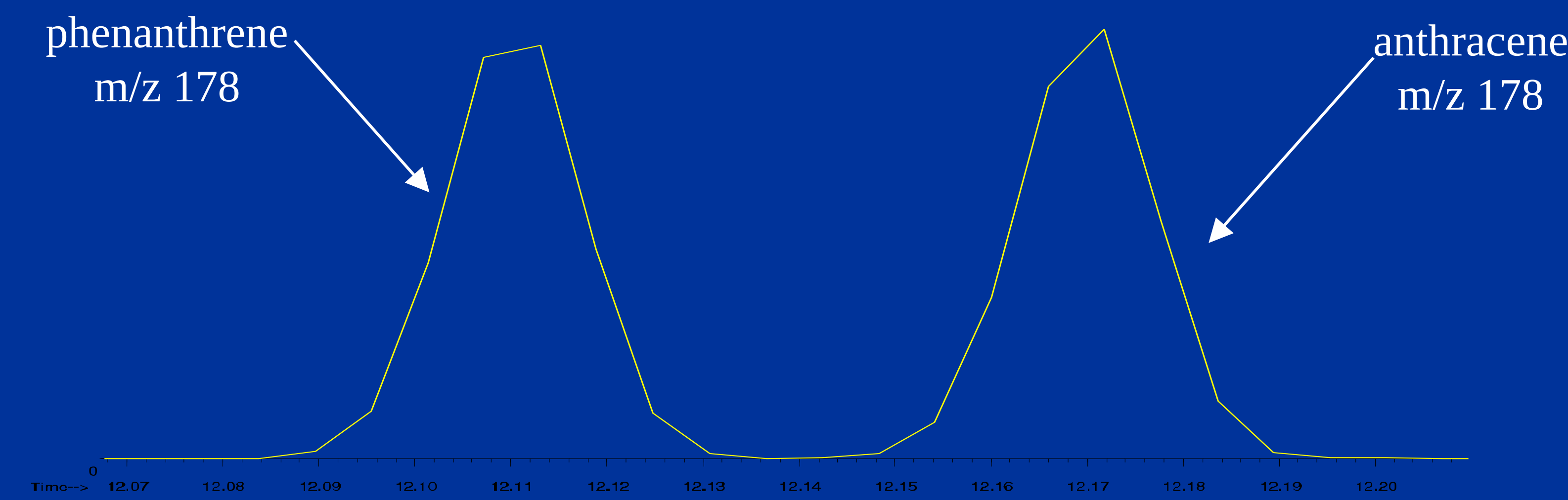


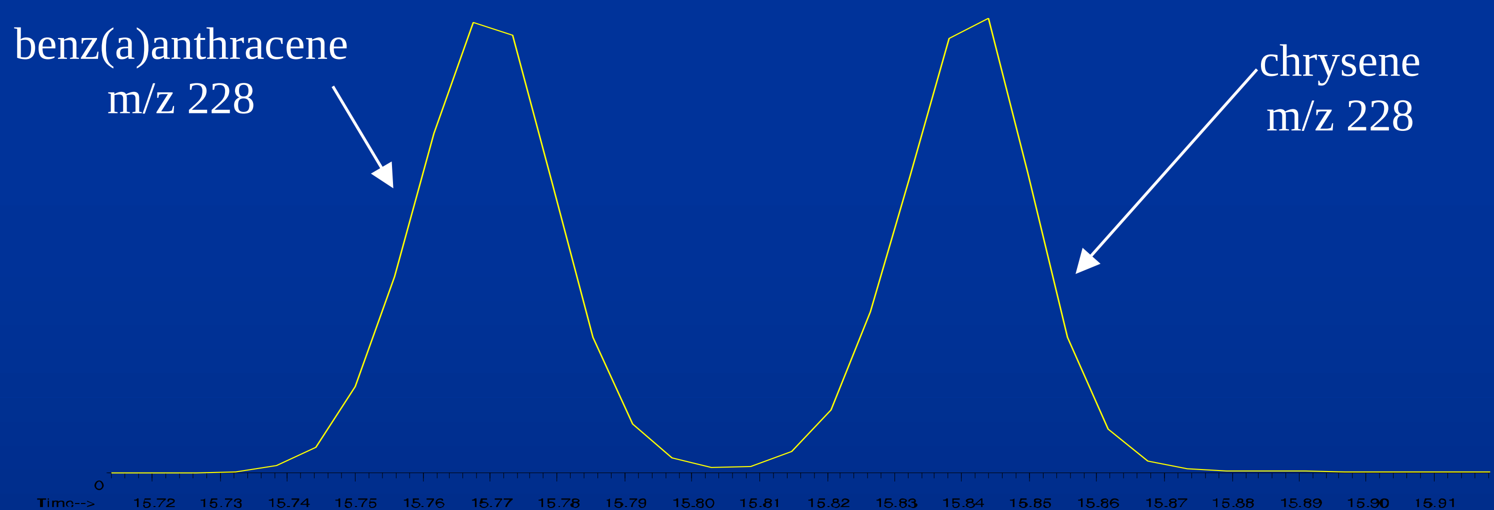
Separation of Critical Pairs
Rtx-5Sil MS (30m x 0.25mm, 0.25um film)



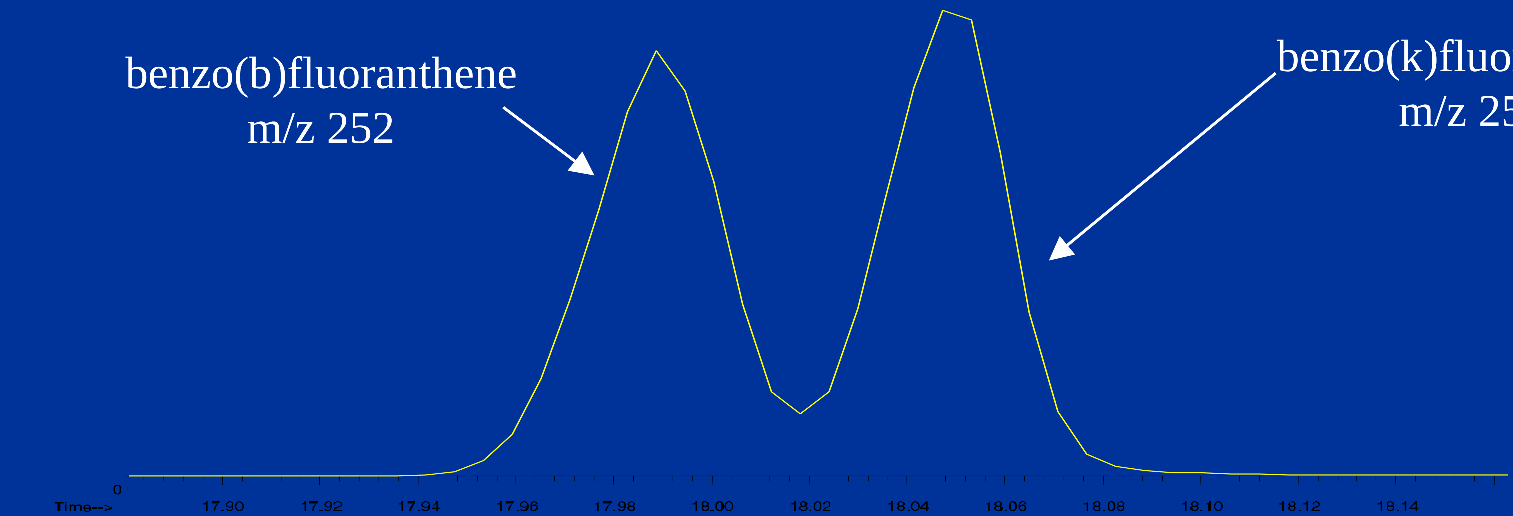


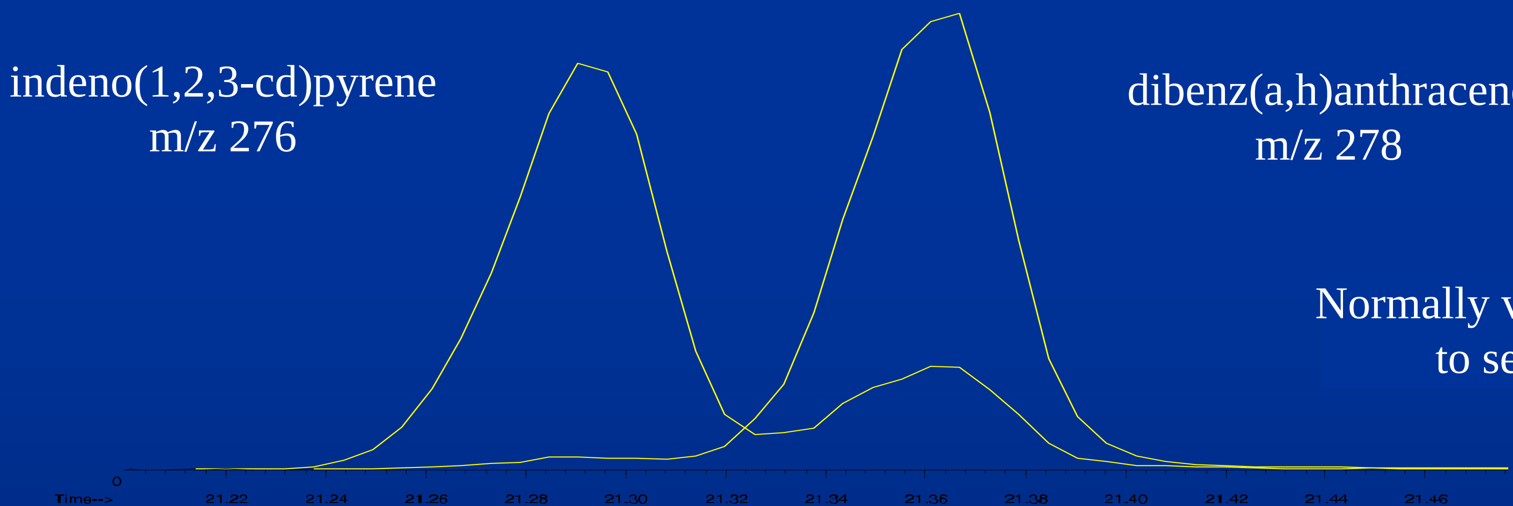
Separation of Critical Pairs
Rtx-5Sil MS (30m x 0.25mm, 0.25um film)





Separation of Critical Pairs
Rtx-5Sil MS (30m x 0.25mm, 0.25um film)





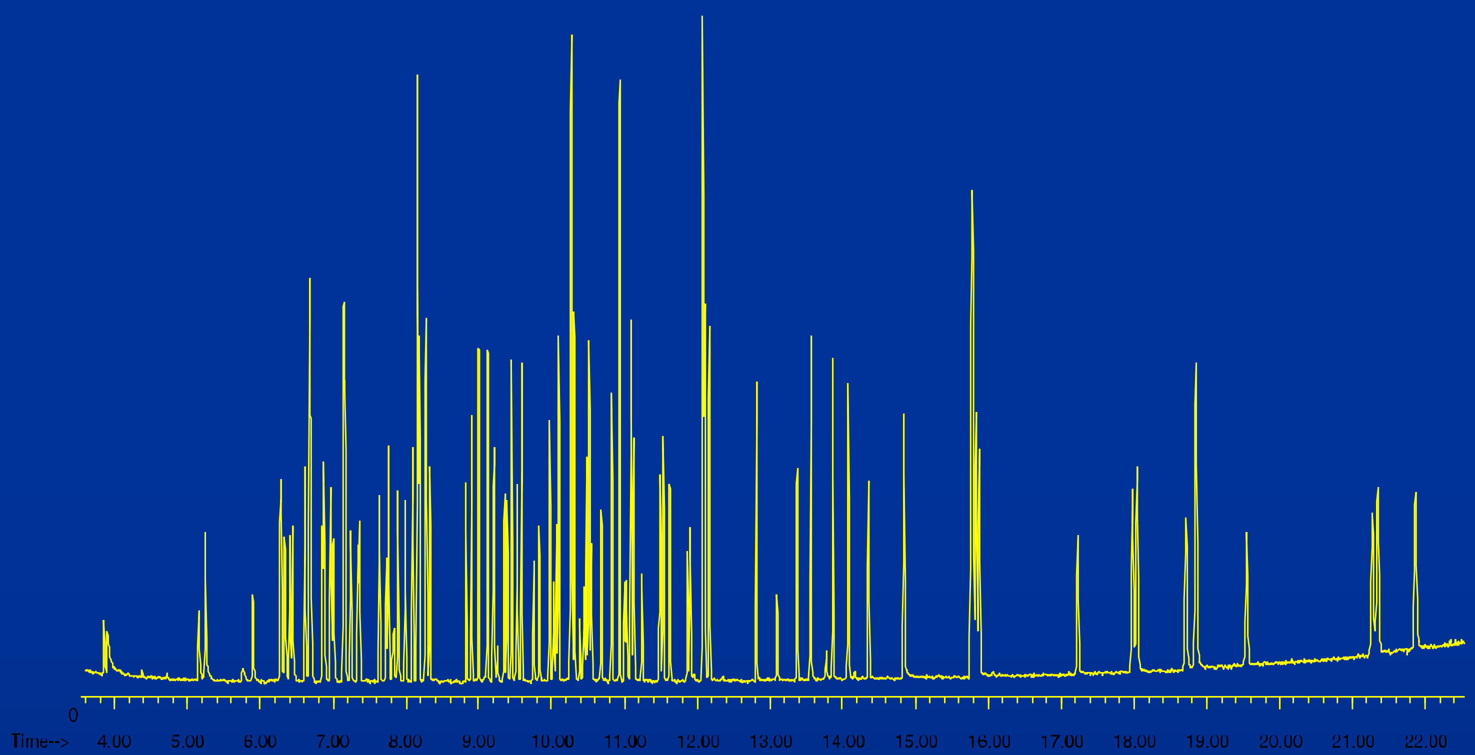
Normally very difficult
to separate

Instrument Calibration

- Calibration curve
  - 1/5 concentration level of 8270 recommendation
  - 4, 10, 16, 24, and 32 ppm standard
  - 8 ppm internal standard concentration
- 1 uL injection
- Analysis performed on HP(Agilent) 6890 w/ 5973 MS

4 ppm 8270 Calibration Standard

- Excellent signal to noise for 4 ng on-column injection
- Low column bleed
- Elimination of injection port discrimination



Rtx-5Sil MS (30m x 0.25mm ID, 0.25 um film)

Linearity from Calibration Sequence

Compound	RT	ISTD	m/z	4ppm RF	10ppm RF	16ppm RF	24ppm RF	32ppm RF	ave RRF	5 point %RSD	4 point %RSD (w/o 4ppm)
N-nitrosodimethylamine	3.79	1	74	0.724	0.736	0.775	0.742	0.748	0.745	3%	2%
pyridine	3.80	1	79	1.055	0.951	1.058	0.967	1.004	1.007	5%	5%
aniline	6.28	1	93	1.777	1.773	1.962	1.933	1.946	1.878	5%	5%
N-nitroso-di-n-propylamine	7.12	1	169	0.776	0.746	0.801	0.740	0.770	0.767	3%	4%
benzoic acid	7.84	2	122	0.148	0.193	0.201	0.203	0.228	0.195	15%	7%
2,4-dichlorophenol	7.94	2	162	0.215	0.248	0.240	0.249	0.259	0.242	7%	3%
hexachlorocyclopentadiene	9.14	3	237	0.283	0.310	0.323	0.333	0.357	0.321	9%	6%
3-nitroanaline	10.21	3	138	0.323	0.318	0.343	0.339	0.348	0.334	4%	4%
acenaphthene	10.26	3	152	0.637	0.618	0.634	0.610	0.641	0.628	2%	2%
2,4-dinitrophenol	10.34	3	184	0.110	0.139	0.156	0.155	0.169	0.146	16%	8%
4-nitrophenol	10.41	3	109	0.162	0.168	0.185	0.187	0.202	0.181	9%	7%
azobenzene	11.07	3	77	1.387	1.446	1.436	1.369	1.414	1.410	2%	2%
nitrosodiphenylamine	11.04	4	169	0.718	0.698	0.723	0.771	0.738	0.729	4%	4%
pentachlorophenol	11.81	4	266	0.094	0.122	0.132	0.132	0.146	0.125	15%	7%
benzidine	13.72	5	184	0.213	0.178	0.188	0.206	0.269	0.211	17%	19%
benzo(b)fluoranthene	17.88	6	252	1.344	1.448	1.504	1.506	1.628	1.486	7%	5%
benzo(ghi)perylene	21.76	6	276	1.341	1.428	1.492	1.488	1.593	1.468	6%	5%
ISTD											
1,4-dichlorobenzene-d4	6.62	1	152								
naphthalene-d8	8.10	2	136								
acenaphthene-d10	10.22	3	164								
phenanthrene-d10	12.02	4	188								
chrysene-d12	15.70	5	240								
perylene-d12	18.73	6	264								

Conclusion

- Drilled Uniliner results in a more inert sample pathway and eliminates injection port discrimination
- Utilization of a thin film column helps reduce analysis time