

Column Considerations for Optimizing Semi-Volatiles Analysis (and Sample Flow Path Inertness)

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Semi-Volatiles Analysis has 2 Main Problems

HELP = high end linearity problem

- response rolls off at higher concentrations, that is RFs are lower than they should be at higher concentrations. Usually good responders with a simple spectrum such as phthalates and PAHs

★ LEAP = low end **activity** problem

- system chews up 1 - 3? 5? 10? ng of certain analytes. RFs are lower than they should be at lower concentrations for active compounds especially nitrophenols.

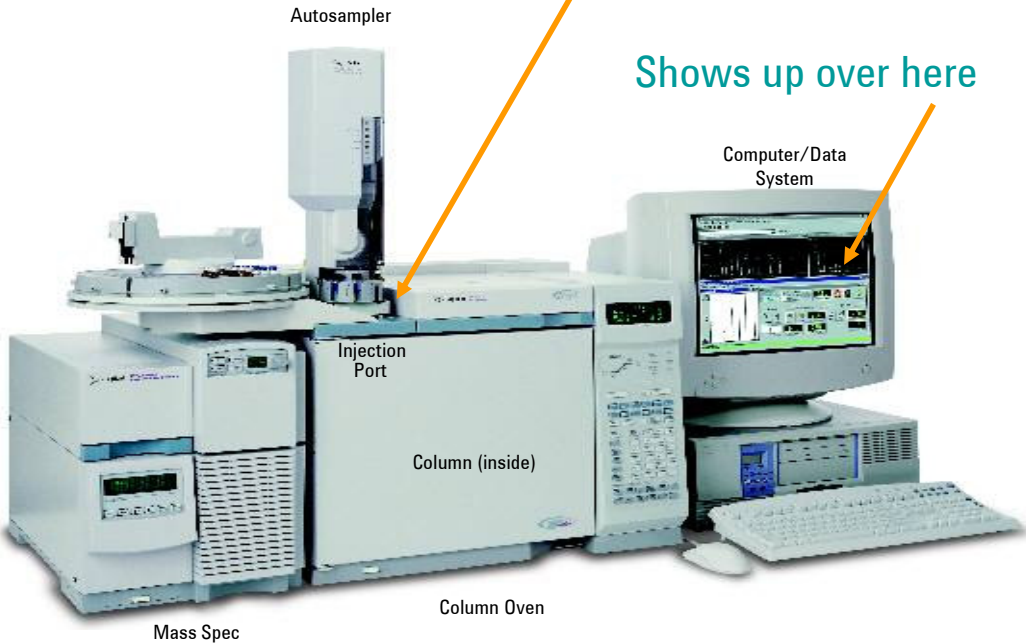
– 2,4-dinitrophenol is the worst

(range 160-5 ng/uL chosen for 8270)

GC System Inertness What do we mean?

What goes in here

Shows up over here



GC Flow Path Surface Areas

	l (cm)	d (cm)	pi	Surface Area (cm ²)
Liner	7	0.2	3.142	4.4
Seal	0.4	0.8	3.142	1.0
Column	3000	0.025	3.142	235.6



Splitless Inlet Liners Tested



3587

3316

3315

80730

80700

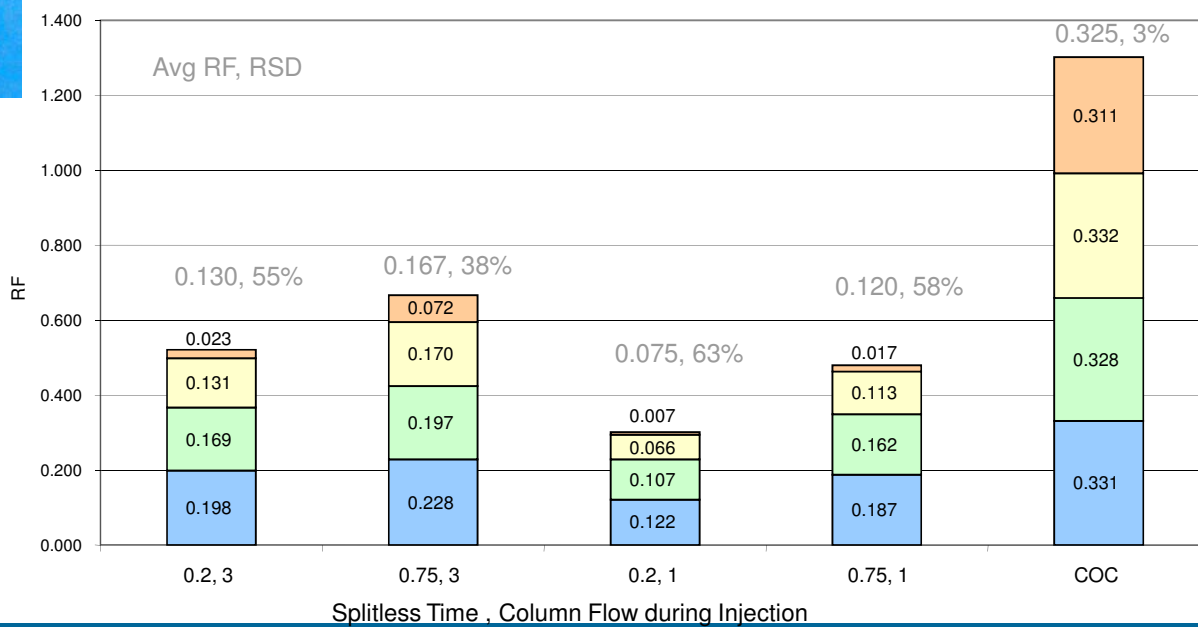
Hole
for
EPC

3587 - 4 sets of Inlet Conditions

Single taper
with wool

2,4-Dinitrophenol RFs

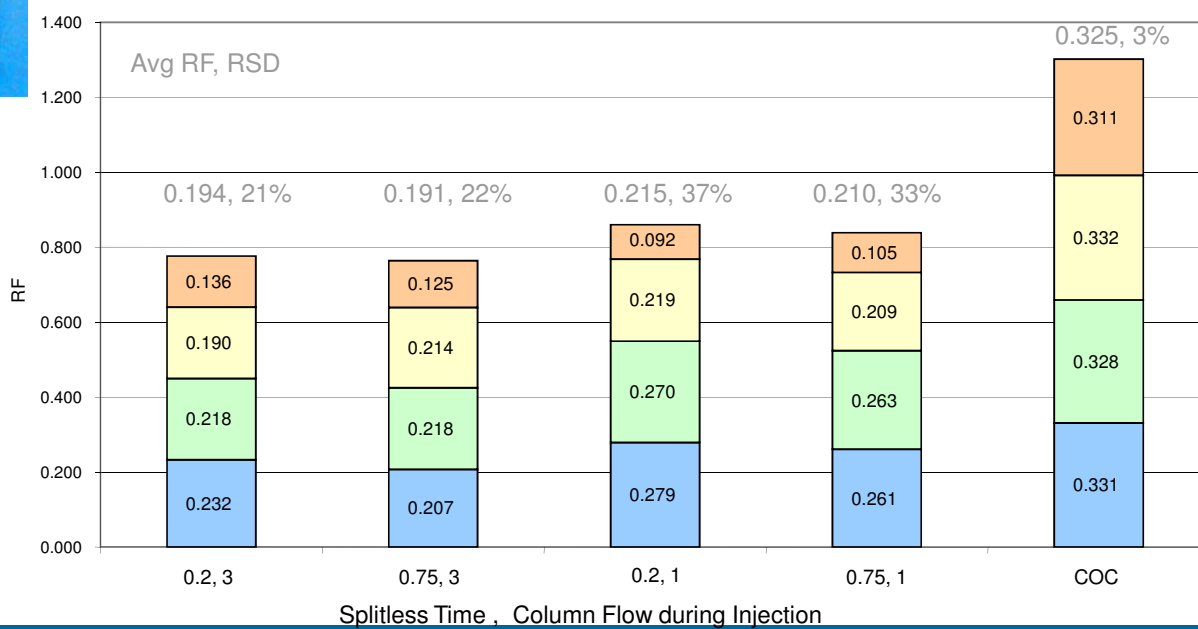
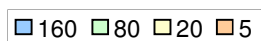
■ 160 ■ 80 ■ 20 ■ 5



3316 - 4 sets of Inlet Conditions

Single taper
no wool

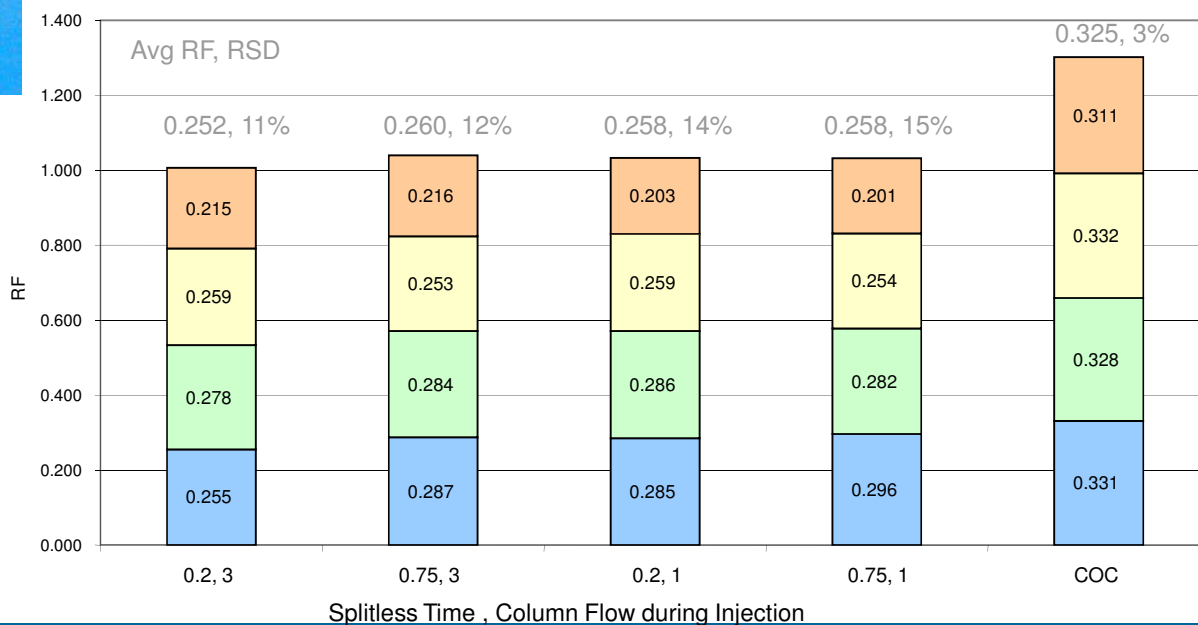
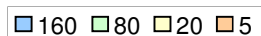
2,4-Dinitrophenol RFs



3315 - 4 sets of Inlet Conditions

Dual taper no wool

2,4-Dinitrophenol RFs

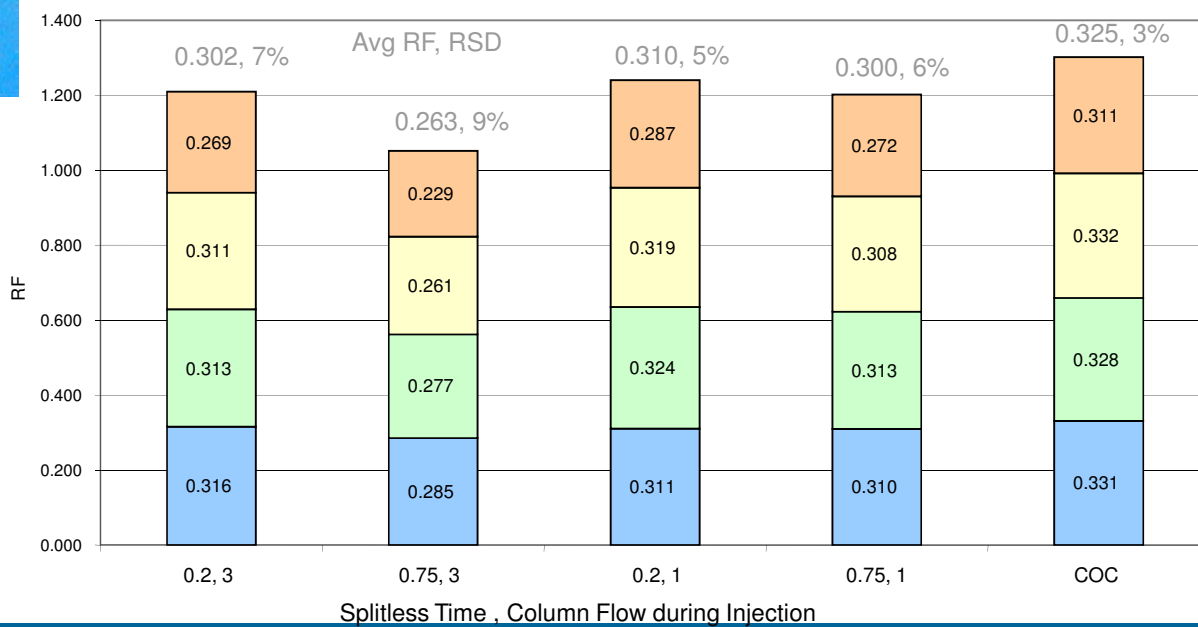


80730 - 4 sets of Inlet Conditions

Single taper
direct connect

2,4-Dinitrophenol RFs

160 80 20 5



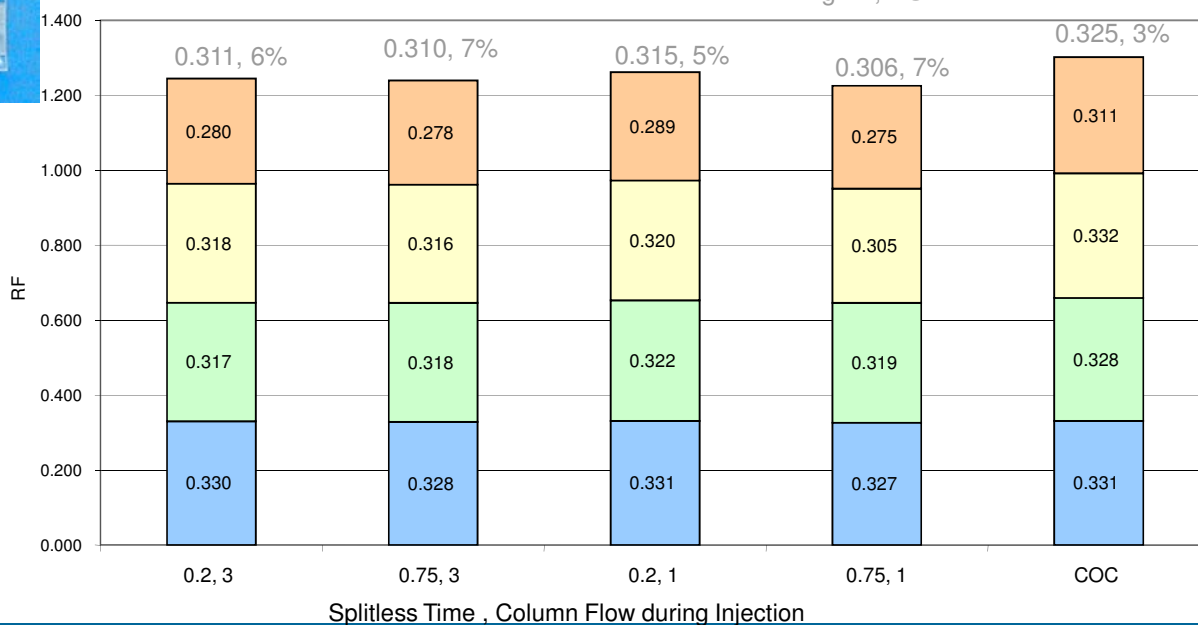
80700 - 4 sets of Inlet Conditions

Dual taper
direct connect

2,4-Dinitrophenol RFs

■ 160 ■ 80 ■ 20 ■ 5

Avg RF, RSD



Splitless Inlet Liners-Results

3587 Single taper with glass wool

- worst performance for active compounds

3316 Single taper (open top)

- add a wisp of wool for dirty samples

3315 Dual taper (closed top)

- works well but you can't add wool

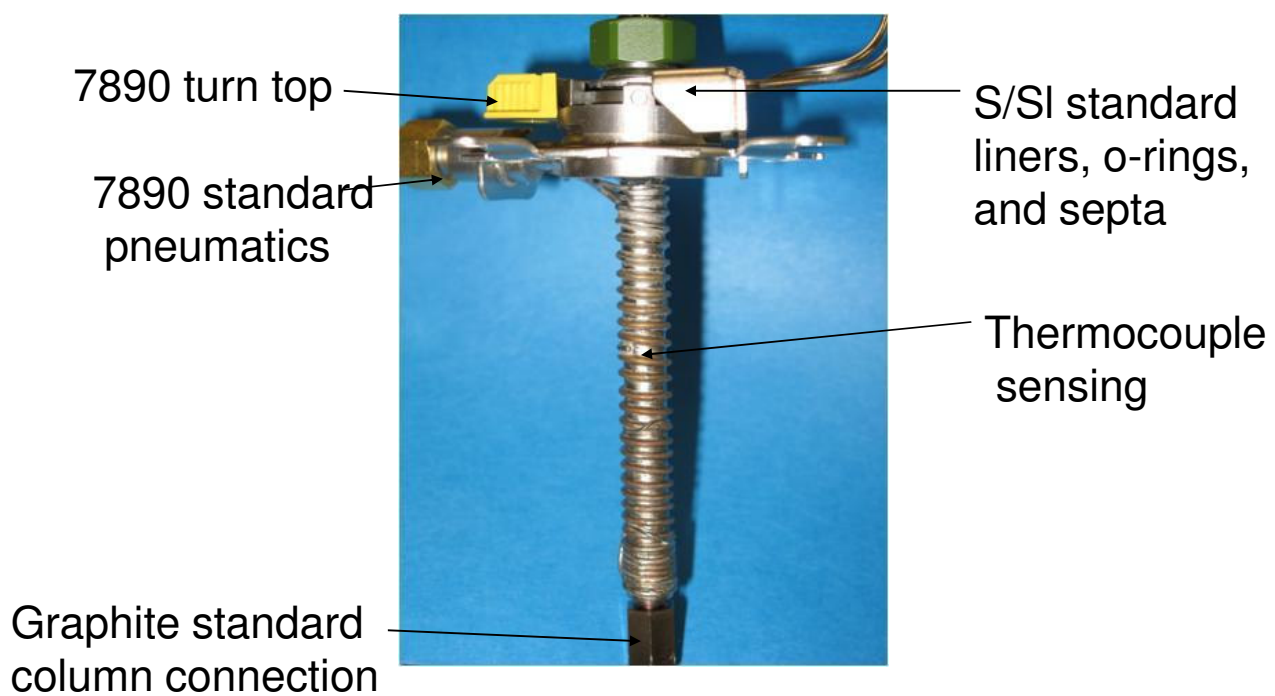
80730 & 80700 Direct connect

- show the best performance

Ultra Inert Liner - soon to be released

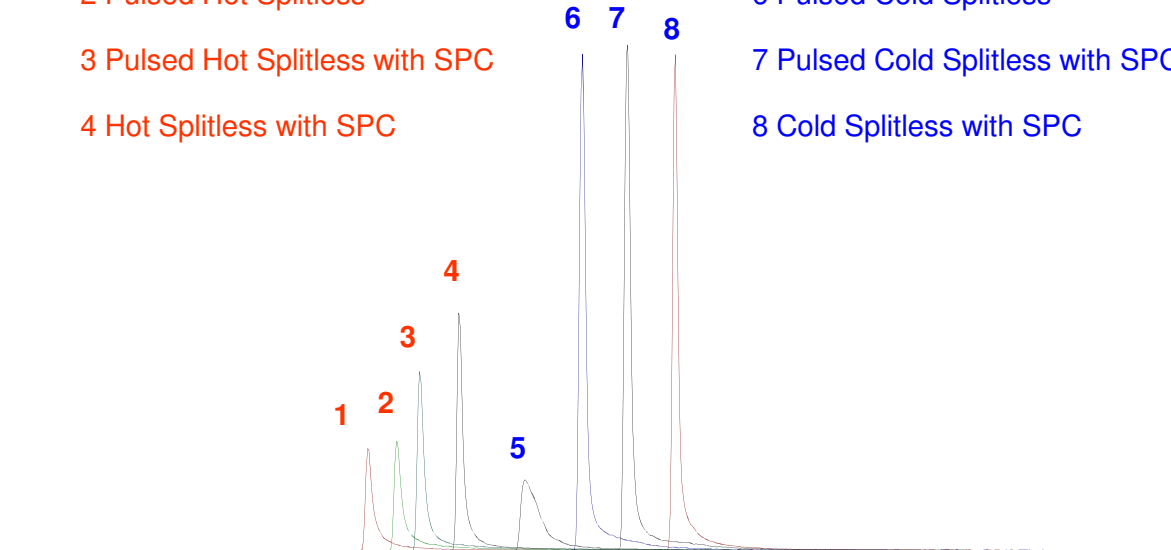
best performance yet!

MMI Design



MMI , N-nitrosodimethylamine, earliest eluter at 3.83 min

- 1 Hot Splitless
- 2 Pulsed Hot Splitless
- 3 Pulsed Hot Splitless with SPC
- 4 Hot Splitless with SPC
- 5 Cold Splitless
- 6 Pulsed Cold Splitless
- 7 Pulsed Cold Splitless with SPC
- 8 Cold Splitless with SPC



Data intentionally offset on y-axis

MMI , Pentachlorophenol, 10.8 min

1 Hot Splitless

2 Pulsed Hot Splitless

3 Pulsed Hot Splitless with SPC

4 Hot Splitless with SPC

6,7

5 Cold Splitless

6 Pulsed Cold Splitless

7 Pulsed Cold Splitless with SPC

8 Cold Splitless with SPC

8

5

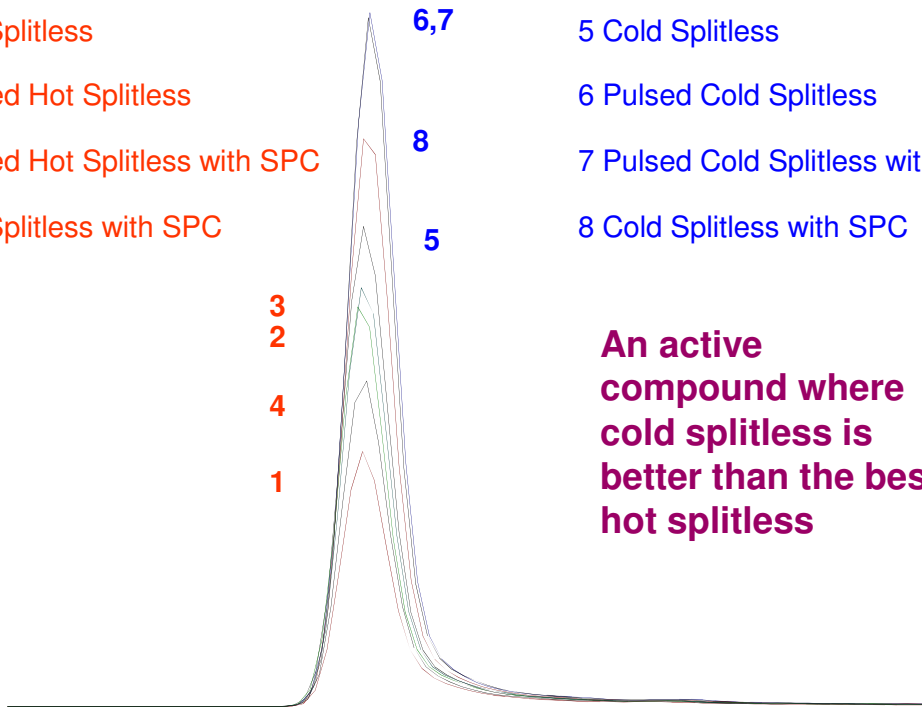
3

2

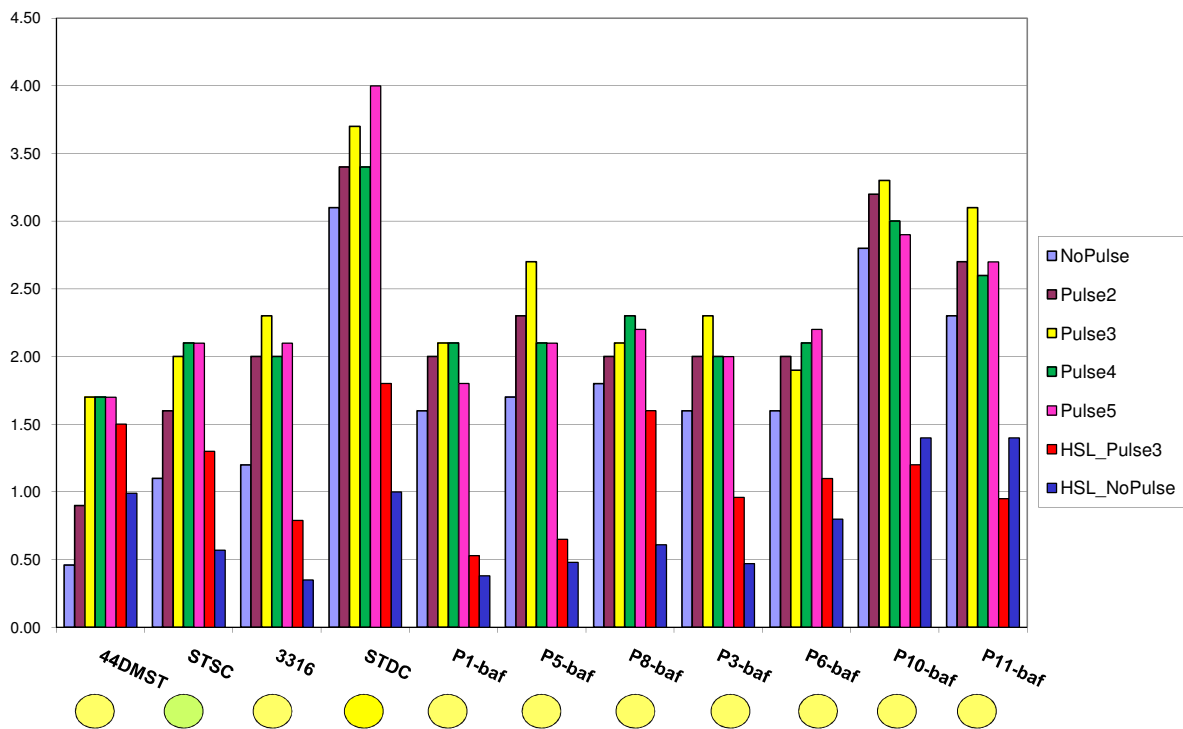
4

1

An active compound where cold splitless is better than the best hot splitless



PCP response (y-axis), 11 liners (x-axis), 5 CSL and 2 HSL methods



The 7 prototypes all look similar for cold splitless, 10 & 11 tighter ?

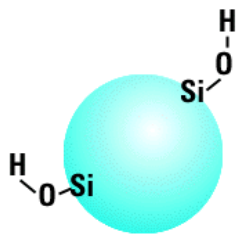
How important is Column Inertness to overall Inertness?

GC Flow Path Surface Areas

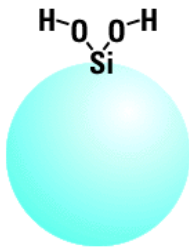
	l (cm)	d (cm)	pi	Surface Area (cm ²)
Liner	7	0.2	3.142	4.4
Seal	0.4	0.8	3.142	1.0
Column	3000	0.025	3.142	235.6

Where does column activity come from?

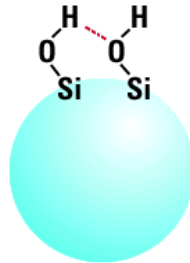
- Isolated



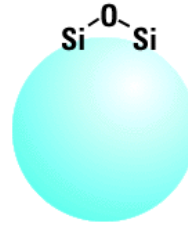
- Geminal



- Vicinal



- Siloxane

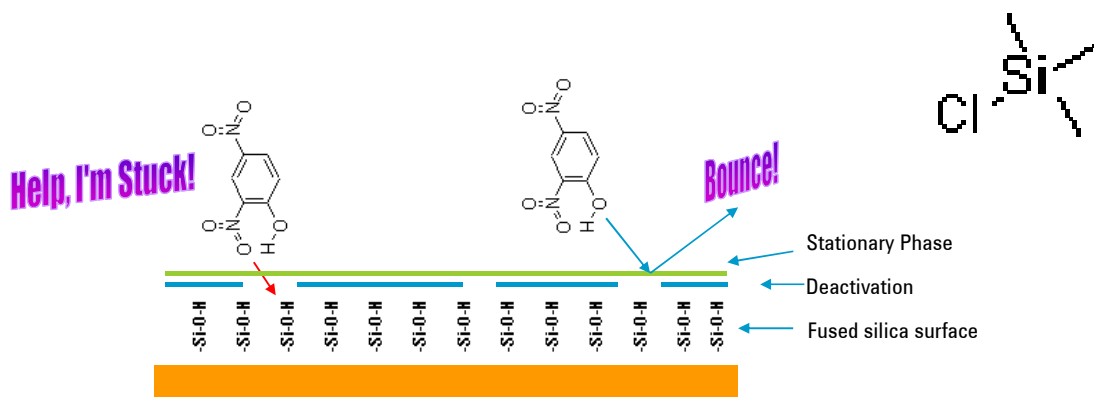


- Sterically difficult to “cap” all of them—estimates 40-65% capped with traditional deactivation.
- Non-traditional sources such as trace impurities in starting materials and manufacturing lines.

The Past: Traditional Deactivations

Dichlorodimethylsilane, various silazanes, etc... “endcaps”

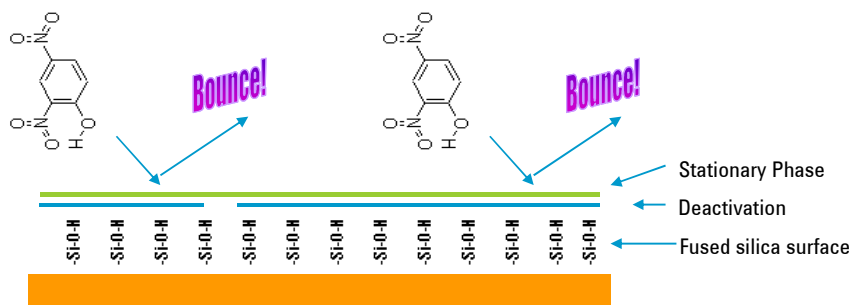
Traditional deactivation has gaps in surface coverage due to bulky TMS type moieties, and tight fused silica lattice, and is somewhat inert and chemically resistant.



The Present: DB-5ms and HP-5ms Engineered Deactivations

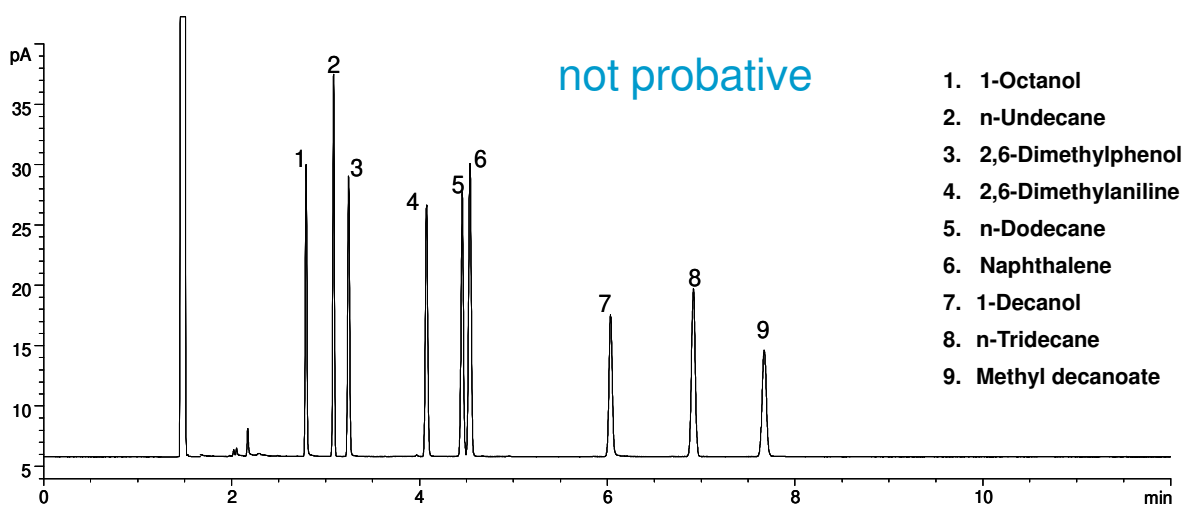
Polymeric Deactivation Technology

“Binds” at multiple points with many silanols



“Blankets” sterically hindered active silanols, fewer silanols

Grob-type Test Mix Results on a DB-5ms Ultra Inert



Sampler: Agilent 7683B, 5 μ L syringe (Agilent part # 5181-1273), 1.0 μ L split injection, 4 ng each component

Carrier: Hydrogen constant pressure 37 cm/s

Inlet: Split/splitless; 250 $^{\circ}$ C, 1.4 ml/min. column flow, split flow 140 ml/min.

Liner: Deactivated single taper w glass wool (Agilent part # 5183-4647)

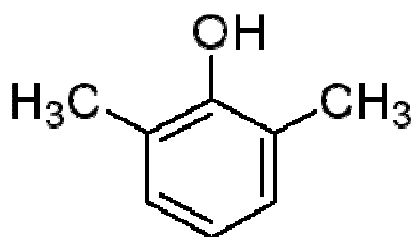
Oven: 120 $^{\circ}$ C isothermal

Detection: FID at 325 $^{\circ}$ C, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min. nitrogen makeup

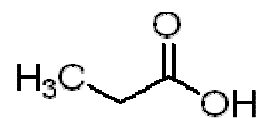
Weak Probes

versus

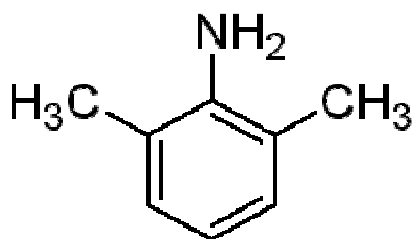
Strong Probes



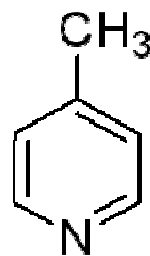
2,6-Dimethylphenol



1-Propionic acid

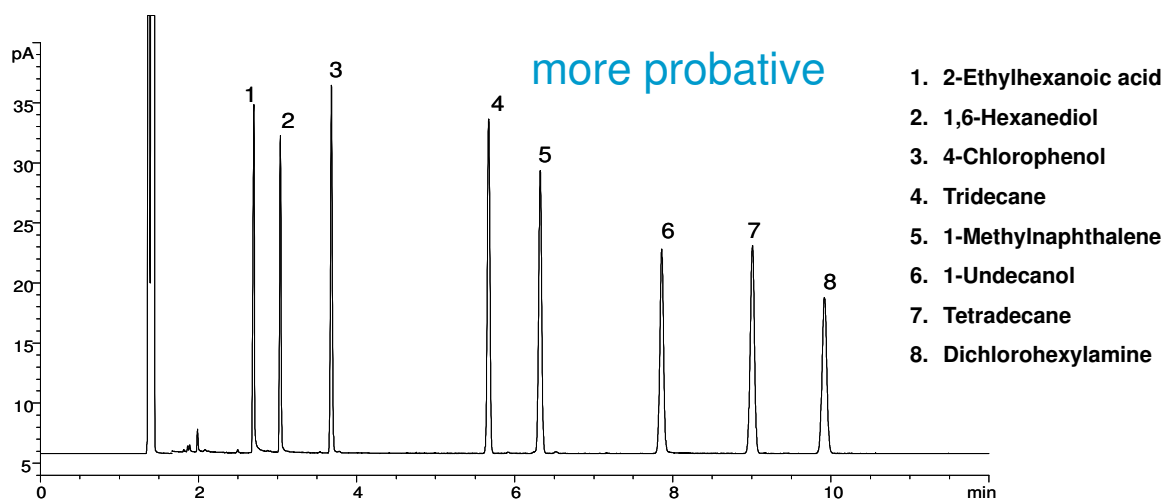


2,6-Dimethylaniline



4-Picoline

DB-5ms Mix (1990's) on DB-5ms Ultra Inert



Sampler: Agilent 7683B, 5 μ L syringe (Agilent part # 5181-1273), 1.0 μ L split injection, 4 ng each component

Carrier: Hydrogen constant pressure 38 cm/s

Inlet: Split/splitless; 250 $^{\circ}$ C, 1.4 ml/min. column flow, split flow 100 ml/min.

Liner: Deactivated single taper w glass wool (Agilent part # 5183-4647)

Oven: 125 $^{\circ}$ C isothermal

Detection: FID at 320 $^{\circ}$ C, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min. nitrogen makeup

Ultra Inert Test Mix – QC Testing for Today’s Demanding Applications

Probe	(ng on column)	Column functional test
1. 1-Propionic acid	1.0	Basicity
2. 1-Octene	0.5	Polarity
3. n-Octane	0.5	Hydrocarbon marker
4. 4-Picoline	1.0	Acidity
5. n-Nonane	1.0	Hydrocarbon marker
6. Trimethyl phosphate	1.0	Acidity
7. 1,2-Pentanediol	1.0	Silanol
8. n-Propylbenzene	1.0	Hydrocarbon marker
9. 1-Heptanol	1.0	Silanol
10. 3-Octanone	1.0	Polarity
11. n-Decane	1.0	Hydrocarbon marker

- Carefully selected very demanding test probes for in-depth evaluation of column inertness
- Test temperature 65 °C (isothermal), well below that normally used in conventional tests

Sampler: Agilent 7683B, 0.5 µL syringe (Agilent part # 5188-5246), 0.02 µL split injection

Carrier: Hydrogen constant pressure, 38 cm/s

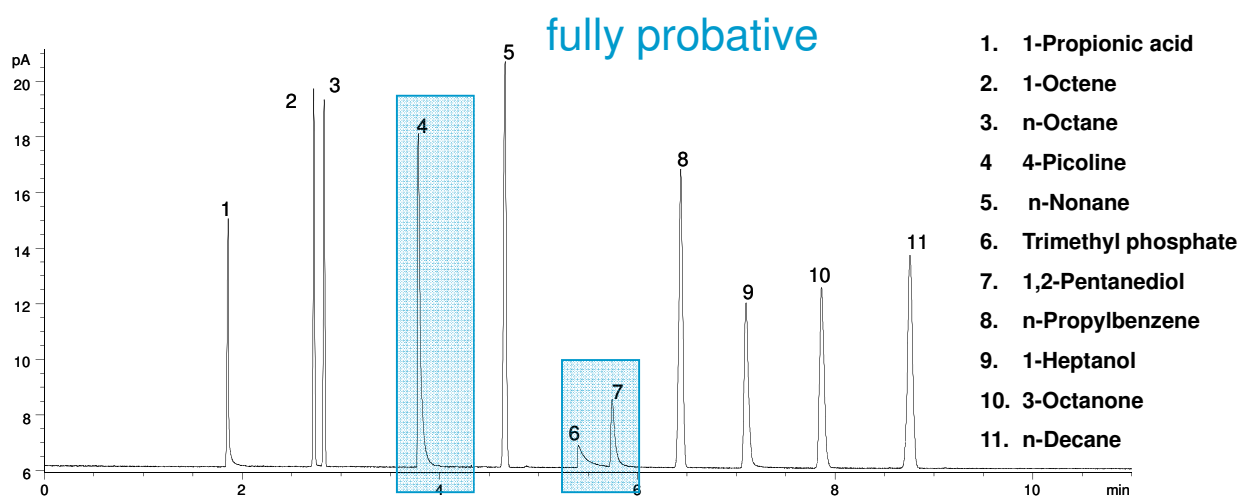
Inlet: Split/splitless; 250 °C, 1.4 ml/min. column flow, split flow 900 ml/min., gas saver flow 75 ml/min. on at 2.0 min.

Liner: Deactivated single taper w glass wool (Agilent part # 5183-4647)

Oven: 65 °C isothermal

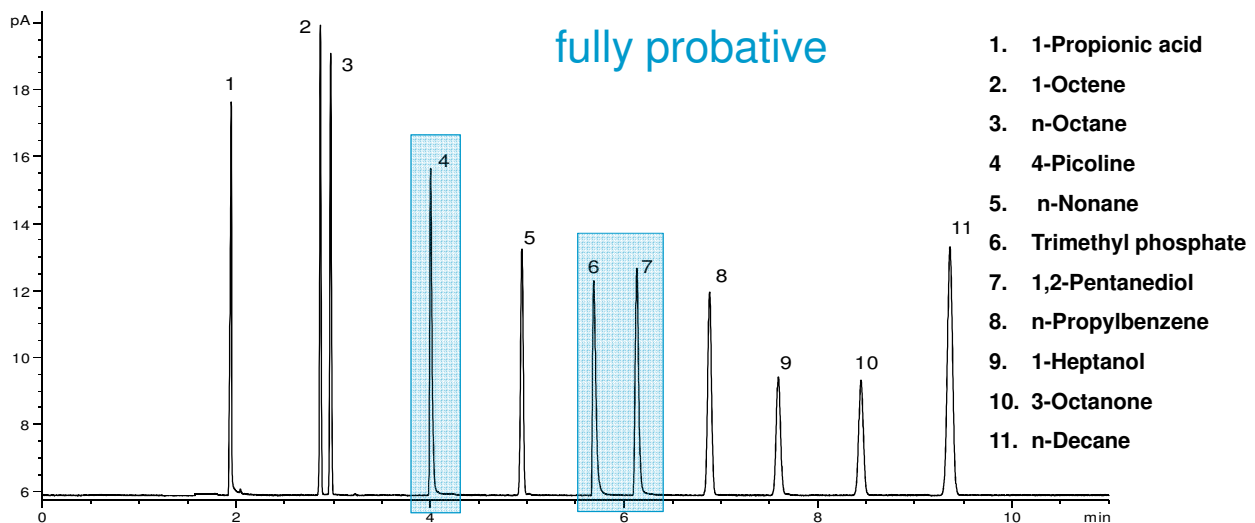
Detection: FID at 325 °C, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min., nitrogen makeup

Ultra Inert Mix on a Brand R “Premium” Column



Sampler: Agilent 7683B, 0.5 μ L syringe (Agilent part # 5188-5246), 0.02 μ L split injection
Carrier: Hydrogen constant pressure, 38 cm/s
Inlet: Split/splitless; 250 $^{\circ}$ C, 1.4 ml/min. column flow, split flow 900 ml/min., gas saver flow 75 ml/min. on at 2.0 min.
Liner: Deactivated single taper w glass wool (Agilent part # 5183-4647)
Oven: 65 $^{\circ}$ C isothermal
Detection: FID at 325 $^{\circ}$ C, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min., nitrogen makeup

Ultra Inert Mix on Agilent J&W DB-5ms Ultra Inert



Sampler: Agilent 7683B, 0.5 μ L syringe (Agilent part # 5188-5246), 0.02 μ L split injection

Carrier: Hydrogen constant pressure, 38 cm/s

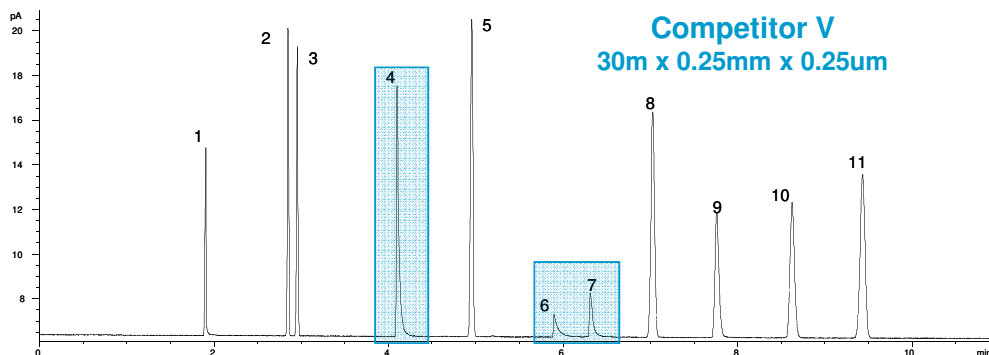
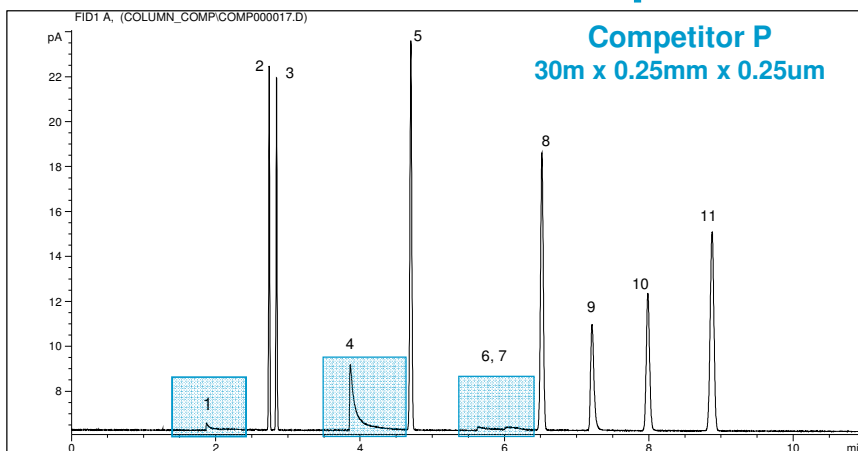
Inlet: Split/splitless; 250 $^{\circ}$ C, 1.4 ml/min. column flow, split flow 900 ml/min., gas saver flow 75 ml/min. on at 2.0 min.

Liner: Deactivated single taper w glass wool (Agilent part # 5183-4647)

Oven: 65 $^{\circ}$ C isothermal

Detection: FID at 325 $^{\circ}$ C, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min., nitrogen makeup

Ultra Inert Mix on Other Competitor Columns



Test Mix Observations

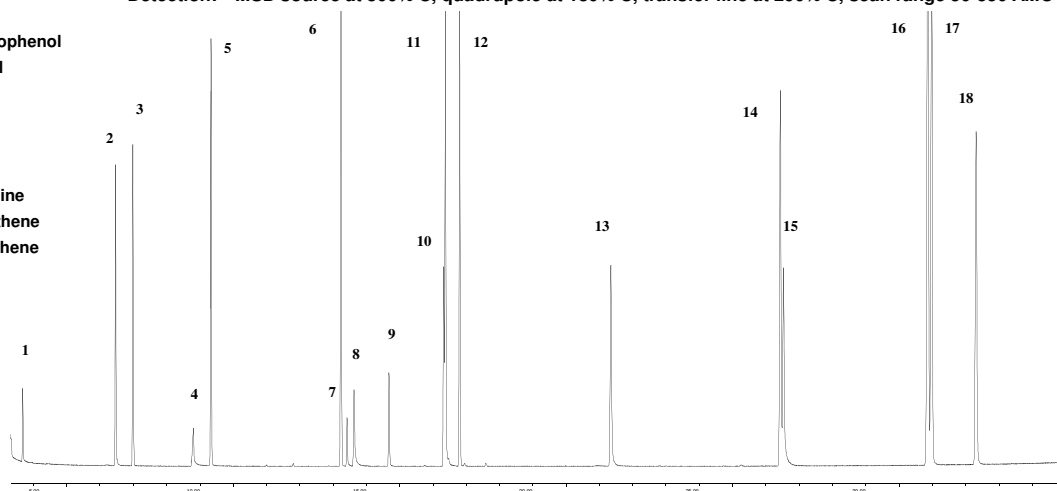
- Grob's style mix not probative for inertness
- DB-5ms test mix good test for the 90s
- Ultra Inert Mix probes inertness and differentiates an excellent column from a mediocre one
- Well designed test mix uncovers potential adsorption of acid and base analytes and raises the bar in inertness QC

Semi Volatiles Application: DB-5ms Ultra Inert 30m x 0.25mm x 0.25µm column

Short Mix = low to high boilers and active analytes

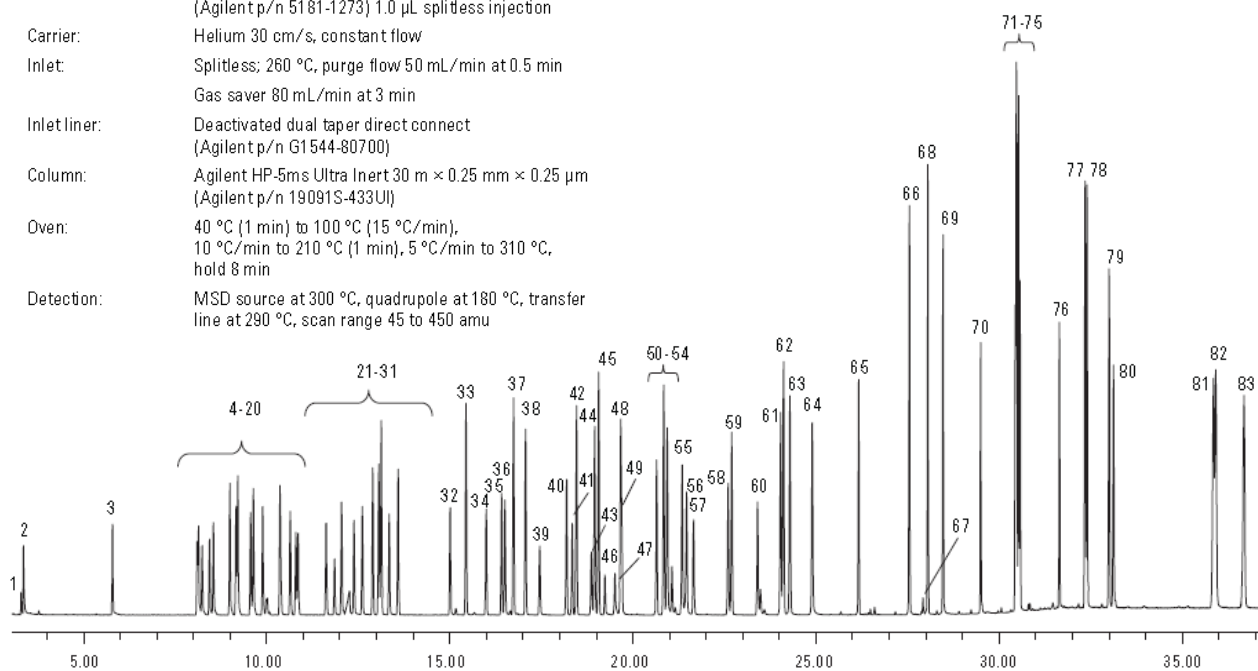
1. N-nitrosodimethylamine
2. Aniline
3. 1,4 dichlorobenzene-D4
4. Benzoic acid
5. Naphthalene-D8
6. Acenaphthene-D10
7. 2,4-dinitrophenol
8. 4-nitrophenol
9. 2-methyl-4,6-dinitrophenol
10. pentachlorophenol
11. 4-aminobiphenyl
12. Penanthrene-D10
13. Benzidine
14. Chrysene-D12
15. 3,3'-dichlorobenzidine
16. Benzo [b] fluoroanthene
17. Benzo [k] fluoroanthene
18. Perylene-D12

GC : Agilent 6890N/5975B MSD
Sampler : Agilent 7683B, 5.0 µL syringe (Agilent part # 5188-5246), 1.0 µL splitless injection, 5 ng on column
Carrier: Helium constant flow 30 cm/s
Inlet: Split/splitless; 260% C, 53.7 ml/min. total flow, purge flow 50 ml/min. on at 0.5 min., gas saver off
Inlet Liner: Deactivated single taper w glass wool (Agilent part # 5183-4647)
Column: Agilent J &W DB-5ms Ultra Inert 30m x 0.25mm x 0.25µm (Agilent part # 122-5532UI)
Oven: 40% C (1 min) to 100°C (15% C/min), 10% C to 210% C (1 min), 5% C/min. to 310% C (8 min)
Detection: MSD source at 300% C, quadrupole at 180% C, transfer line at 290% C, scan range 50-550 AMU



8270 “Large Mix” 5 ng on column (83 Compounds)

GC: Agilent 6890N/5975B MSD
Sampler: Agilent 7683B, 5.0- μ L syringe
(Agilent p/n 5181-1273) 1.0 μ L splitless injection
Carrier: Helium 30 cm/s, constant flow
Inlet: Splitless; 260 °C, purge flow 50 mL/min at 0.5 min
Gas saver 80 mL/min at 3 min
Inlet liner: Deactivated dual taper direct connect
(Agilent p/n G1544-80700)
Column: Agilent HP-5ms Ultra Inert 30 m \times 0.25 mm \times 0.25 μ m
(Agilent p/n 19091S-433U)
Oven: 40 °C (1 min) to 100 °C (15 °C/min),
10 °C/min to 210 °C (1 min), 5 °C/min to 310 °C,
hold 8 min
Detection: MSD source at 300 °C, quadrupole at 180 °C, transfer
line at 290 °C, scan range 45 to 450 amu



Compound List (83)

1. n-Nitrosodimethylamine
2. Pyridine
3. 2-Fluorophenol
4. Phenol-d5
5. Phenol
6. Aniline
7. Bis(2-chloroethyl)ether
8. 2-Chlorophenol
9. 1,3-Dichlorobenzene
10. 1,4-Dichlorobenzene-D4
11. 1,4-Dichlorobenzene
12. Benzyl alcohol
13. 1,2-Dichlorobenzene
14. o-Cresol
15. Bis(2-chloroisopropyl)ether
16. p-Cresol
17. n-Nitroso-di-n-propylamine
18. Hexachloroethane
19. Nitrobenzene-d5
20. Nitrobenzene
21. Isophorone
22. 2-Nitrophenol
23. 2,4-Dimethylphenol
24. Benzoic acid
25. Bis(2-chloroethoxy)methane
26. 2,4-Dichlorophenol
27. 1,2,4-Trichlorobenzene
28. Naphthalene-d8
29. Naphthalene
30. 4-Chloroaniline
31. Hexachlorobutadiene
32. 4-Chloro-3-methylphenol
33. 2-Methylnaphthalene
34. Hexachlorocyclopentadiene
35. 2,4,6-Trichlorophenol
36. 2,4,5-Trichlorophenol
37. 2-Fluorobiphenyl
38. 2-Chloronaphthalene
39. 2-Nitroaniline
40. Dimethyl phthalate
41. 2,6-Dinitrotoluene
42. Acenaphthylene
43. 3-Nitroaniline
44. Acenaphthene-d10
45. Acenaphthene
46. 2,4-Dinitrophenol
47. 4-Nitrophenol
48. Dibenzofuran
49. 2,4-Dinitrotoluene
50. Diethyl phthalate
51. Fluorene
52. 4-Chlorophenyl phenyl ether
53. 4-Nitroaniline
54. 2-Me-4,6-dinitrophenol
55. n-Nitrosodiphenylamine
56. Azobenzene
57. 2,4,6-Tribromophenol
58. 4-Bromophenyl phenyl ether
59. Hexachlorobenzene
60. Pentachlorophenol
61. Phenanthrene-d10
62. Phenanthrene
63. Anthracene
64. Carbazole
65. Dibutylphthalate
66. Fluoranthene
67. Benzidine
68. Pyrene
69. p-Terphenyl-d14
70. Benzyl butyl phthalate
71. 3,3-Dichlorobenzidine
72. Benzo[a]anthracene
73. Chrysene-D12
74. Chrysene
75. Bis(2-ethylhexyl)phthalate
76. Di-n-octyl phthalate
77. Benzo[b]fluoranthene
78. Benzo[k]fluoranthene
79. Benzo[a]pyrene
80. Perylene-d12
81. Indeno[1,2,3,cd]pyrene
82. Dibenzo[a,h]anthracene
83. Benzo[g,h,i]perylene

Semivolatiles Prone to Peak Tailing (App. Note 5990-3416EN)

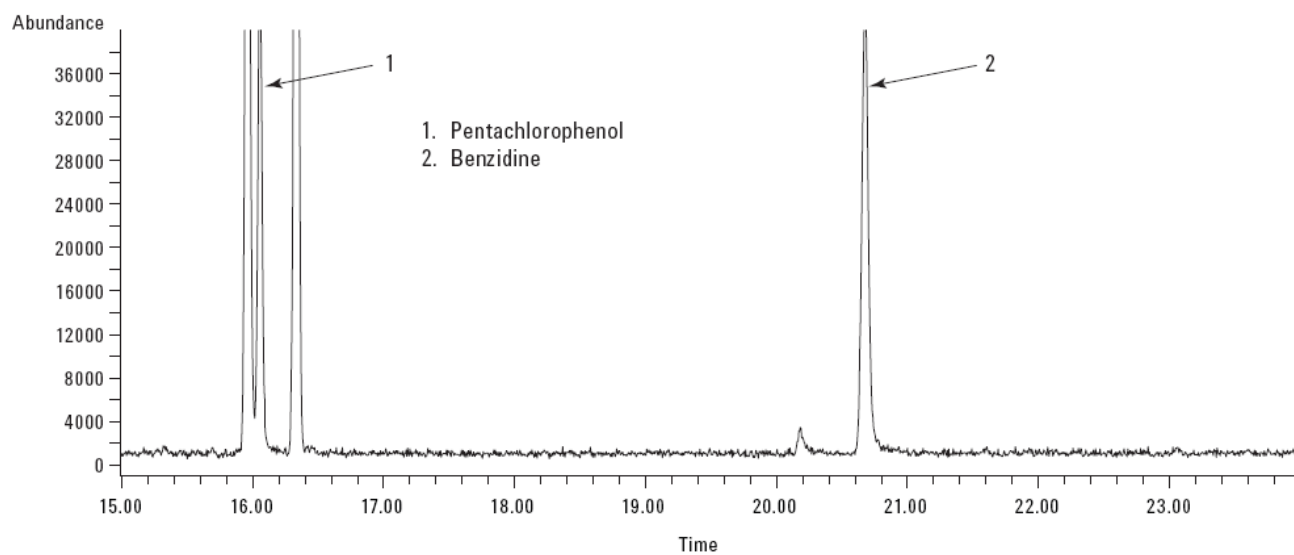


Figure 2. Enlarged section of the total ion chromatogram for a 1- μ L injection of 1.0 μ g/mL EPA 8270 short mix standard. The peaks of interest noted in the figure are two semivolatiles that are prone to peak tailing. Chromatographic conditions are listed in Table 1.

Semivolatiles Prone to Peak Tailing (App. Note 5990-3416EN)

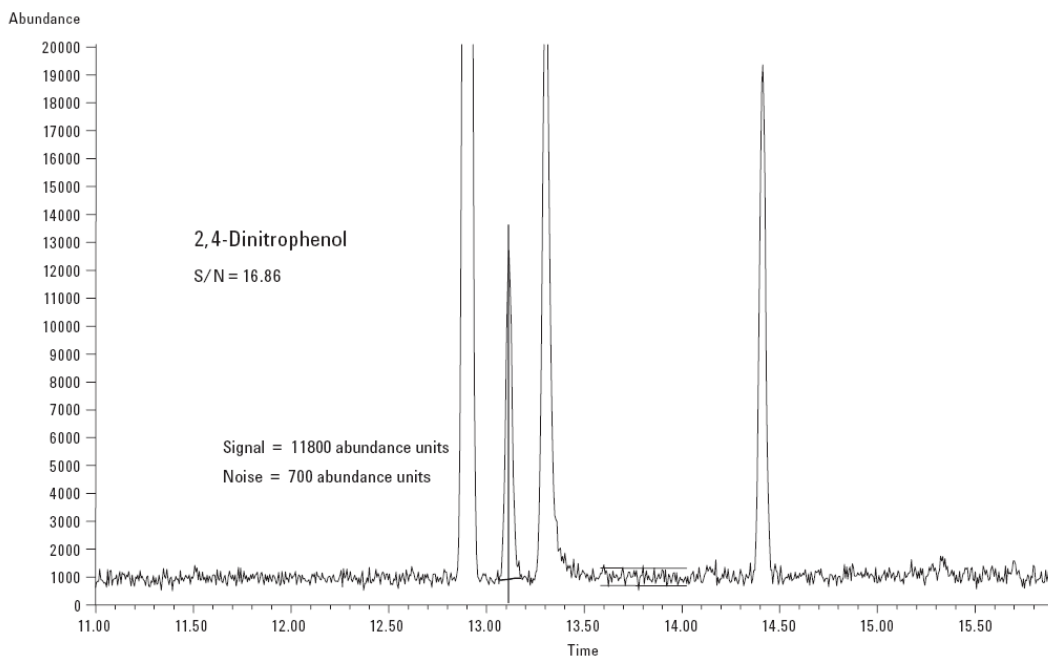
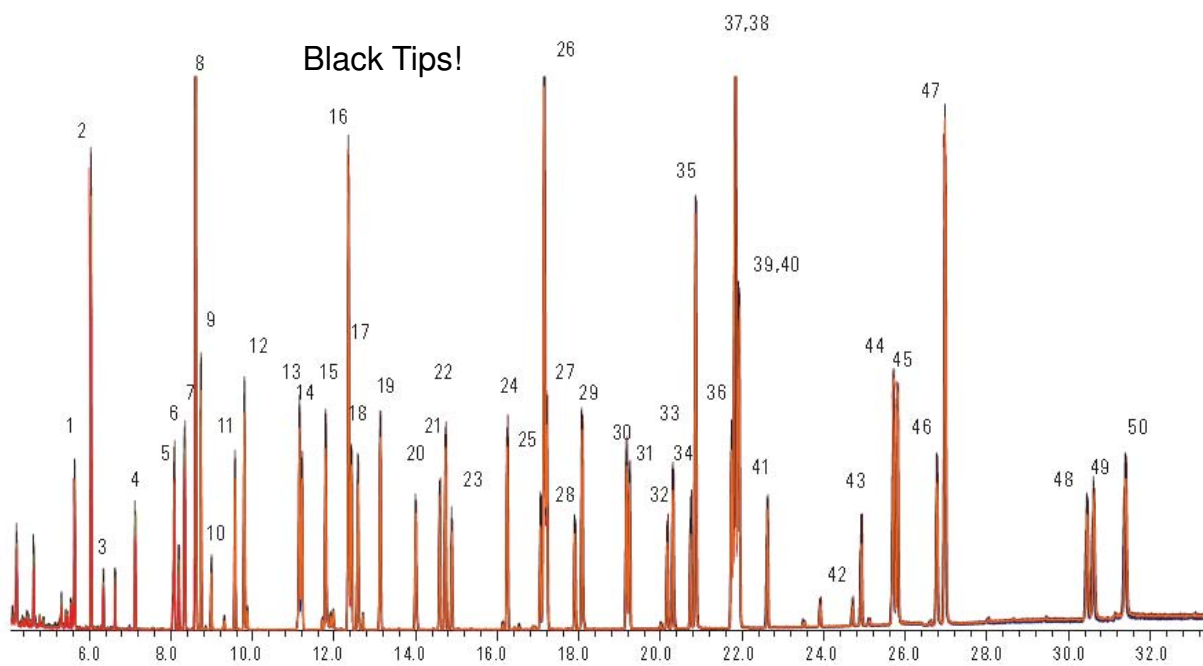


Figure 4. Enlarged section of the total ion chromatogram (scan mode) for a 1- μ L injection of 1 μ g/mL EPA Method 8270 short mix standard on an Agilent J&W HP-5ms Ultra Inert 30 m \times 0.25 mm \times 0.25 μ m capillary GC column (p/n 19091S-433U). The peak in the figure is 2,4-dinitrophenol, one of the more demanding semivolatiles. This injection represents an on-column loading of 1 ng per component. Chromatographic conditions are listed in Table 1.

Excellent Inertness and Same Selectivity



Resolution

$$R_s = \frac{\sqrt{N}}{4} \left(\frac{k}{k+1} \right) \left(\frac{\alpha-1}{\alpha} \right)$$

Efficiency	$N = f(\text{gas}, L, r_c)$	L = Length
Retention	$k = f(T, d_f, r_c)$	r_c = column radius
Selectivity	$\alpha = f(T, \text{phase})$	d_f = film thickness
		T = temperature

Resolution

$$R_s = \frac{\sqrt{N}}{4} \left(\frac{k}{k+1} \right) \left(\frac{\alpha-1}{\alpha} \right)$$

Efficiency

$$N = f(\text{gas}, L, r_c)$$

L = Length

Retention

$$k = f(T, d_f, r_c)$$

r_c = column radius

Selectivity

$$\alpha = f(T, \text{phase})$$

d_f = film thickness

T = temperature

Column Diameter

Capillary Columns

I.D. (mm)	Common Name
0.53	Megabore
0.45	High speed Megabore
0.32	Widebore
0.20-0.25	Narrowbore
0.18	Minibore (Now HE Columns)
0.10	Microbore
0.05	“Nanobore”




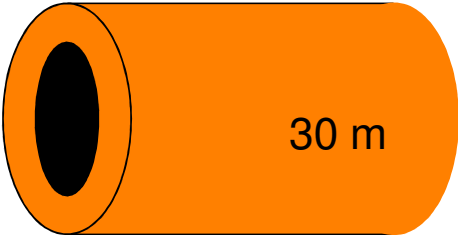
This is getting “bore-ing”

Column Diameter - Theoretical Efficiency

	I.D. (mm)	n/m	
 5 m	0.05	23,160	N ~ 112,000
 10 m	0.10	11,980	N ~ 112,000
 20 m	0.18	6,660	
 30 m	0.20	5830	N ~ 112,000
	0.25	4630	
	0.32	3760	N ~ 112,000
	0.45	2840	
	0.53	2060	




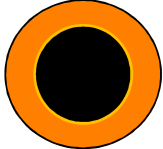

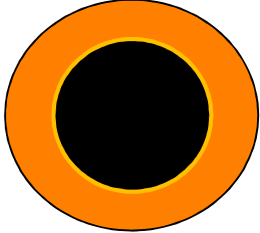
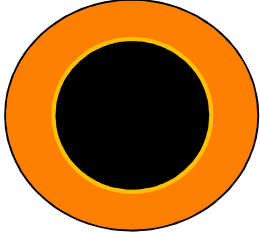
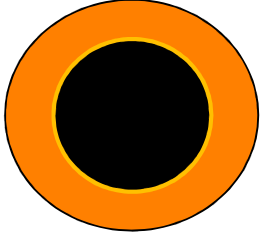
k = 5

Column Diameter - Theoretical Efficiency

	I.D. (mm)	n/m	
 5 m	0.05	23,160	
 10 m	0.10	11,980	
 20 m	0.18	6,660	N ~ 140,000
	0.20	5830	
 30 m	0.25	4630	N ~ 140,000
	0.32	3760	
	0.45	2840	
	0.53	2060	

k = 5

Column Diameter and Capacity

	I.D. (mm)	Capacity (ng)
	0.05	1-2
	0.10	6-13
	0.18	25-55
	0.20	35-70
	0.25	80-160
	0.32	110-220
	0.45	600-800
	0.53	1000-2000

Like Polarity
Phase/Solute
0.25 μm film thickness

Method Translation Software - FREE

GC Method Translation

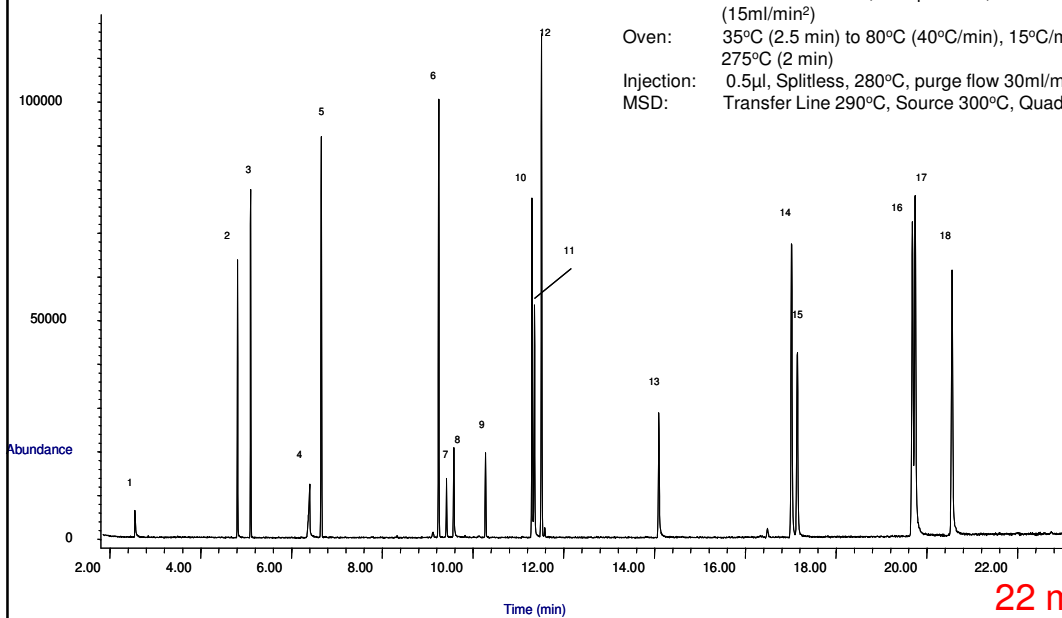
Criterion: Translate Only Best Efficiency Fast Analysis None **Speed gain: 1.55885**

	Original Method	Translated Method																										
Column																												
Length, m	30	20																										
Internal Diameter, μm	250.0	180																										
Film																												
Thickness, μm	0.250	<input type="radio"/> Unlock 0.180																										
Phase Ratio	250.0	<input checked="" type="radio"/> 250.0																										
Carrier Gas	Helium	Helium																										
Enter one Setpoint																												
Head Pressure, psi	0.563	5.698																										
Flow Rate, mLn/min	0.4833	0.3480																										
Outlet Velocity, cm/sec	Very large	Very large																										
Average Velocity, cm/sec	25.00	25.98																										
Hold-up Time, min	2.00000	1.28300																										
Outlet Pressure (absolute), psi	0	<input checked="" type="checkbox"/> 0																										
Ambient Pressure (absolute), psi	14.696	<input type="checkbox"/> 14.696																										
Oven Temperature 1-ramp Program																												
	<table border="1"> <thead> <tr> <th>Ramp Rate</th> <th>Final Temp.</th> <th>Final Time</th> </tr> <tr> <th>$^{\circ}\text{C}/\text{min}$</th> <th>$^{\circ}\text{C}$</th> <th>min</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td>40</td> <td>1</td> </tr> <tr> <td>Ramp 1</td> <td>5</td> <td>290</td> <td>0</td> </tr> </tbody> </table>	Ramp Rate	Final Temp.	Final Time	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min	Initial	40	1	Ramp 1	5	290	0	<table border="1"> <thead> <tr> <th>Ramp Rate</th> <th>Final Temp.</th> <th>Final Time</th> </tr> <tr> <th>$^{\circ}\text{C}/\text{min}$</th> <th>$^{\circ}\text{C}$</th> <th>min</th> </tr> </thead> <tbody> <tr> <td>Initial</td> <td>40</td> <td>0.642</td> </tr> <tr> <td>Ramp 1</td> <td>7.794</td> <td>290</td> <td>0.000</td> </tr> </tbody> </table>	Ramp Rate	Final Temp.	Final Time	$^{\circ}\text{C}/\text{min}$	$^{\circ}\text{C}$	min	Initial	40	0.642	Ramp 1	7.794	290	0.000
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Ramp 1	7.794	290	0.000																									
Sample Information	None																											

Semi volatiles Application:

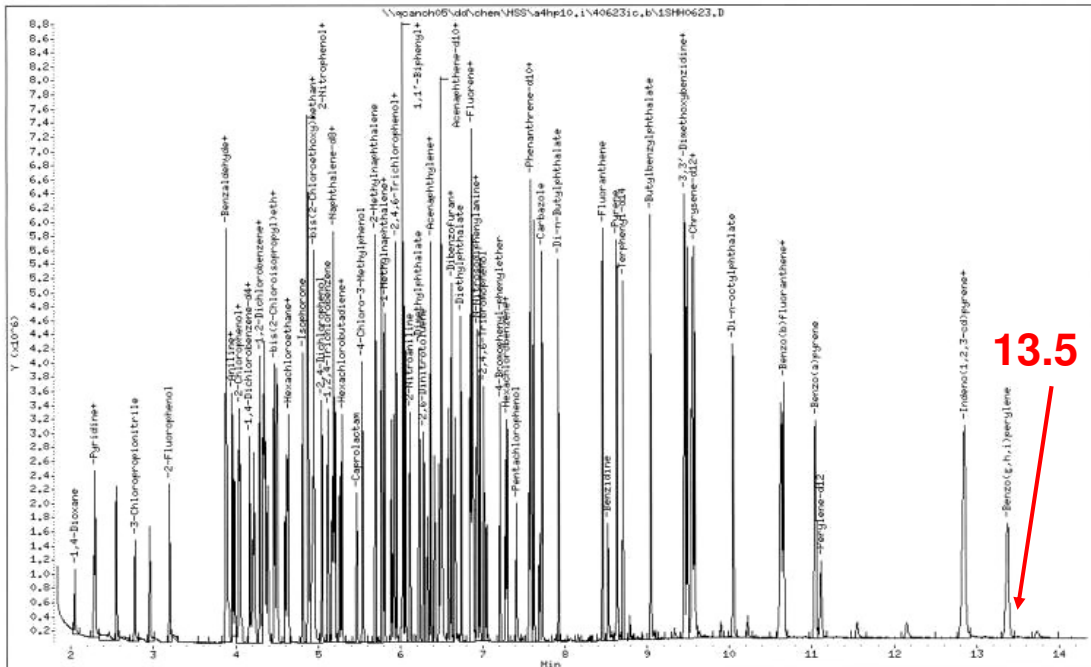
HP-5ms Ultra Inert 20m x 0.18 mm x 0.18 μ m column

Sample: 0.5 ng on column loading of Short Mix components with ISTD
Column: Agilent J & W HP-5ms Ultra Inert 20m 0.18mm 0.18 μ m
Carrier: Helium 37cm/sec, Ramped flow; 0.7ml/min (0.1min) to 1.3ml/min (15ml/min²)
Oven: 35°C (2.5 min) to 80°C (40°C/min), 15°C/min to 200°C, 8°C/min to 275°C (2 min)
Injection: 0.5 μ l, Splitless, 280°C, purge flow 30ml/min at 0.75 min
MSD: Transfer Line 290°C, Source 300°C, Quad 180°C



1. n-Nitrosodimethylamine
2. Aniline
3. 1,4-Dichlorobenzene-d4
4. Benzoic Acid
5. Naphthalene-d8
6. Acenaphthene-d10
7. 2,4-Dinitrophenol
8. 4-Nitrophenol
9. 2-Me-4,6-dinitrophenol
10. 4-Aminobiphenyl
11. Pentachlorophenol
12. Phenanthrene-d10
13. Benzidine
14. Chrysene-d12
15. 3,3'-Dichlorobenzidine
16. Benzo[b]fluoranthene
17. Benzo[k]fluoranthene
18. Perylene-d12

Fast 8270 Semivolatile Analysis 20m x 0.18mm ID x 0.36um, DB-5.625 (same sel. as DB-5msUI)



(App. Note 5989-1510EN)



Fastest Experimental Conditions

DB-5.625, 20 m x 0.18 mm ID, 0.36 μm

Temperature and Flow Programmed

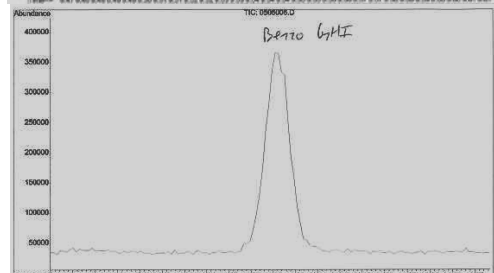
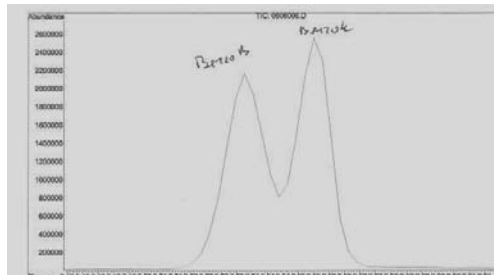
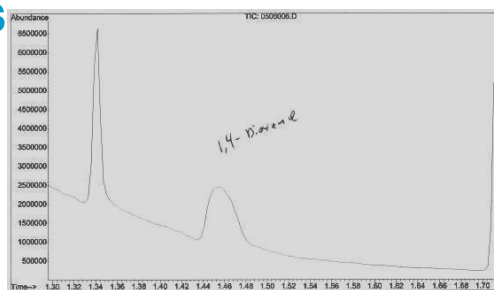
1.45 min First Solvent

9.5 min Benzo [b] fluoranthene

11.1 min Benzo[g,h,i]perylene

11.5 min GC Run,

16.25-16.5 min cycle time



Conclusions

For reliable semi-volatiles analysis inertness is a must.

The entire sample flow path plays a role in inertness.

Liner and moreover GC Column choice is critical.

Dimensions can affect speed but also capacity.

Non-volatile residue buildup is still a problem. (backflush?)