Ultra-Inert chemistry for Trace Level Analysis

Cikui Liang, Ph.D.

Challenges and Needs of Today's Laboratories

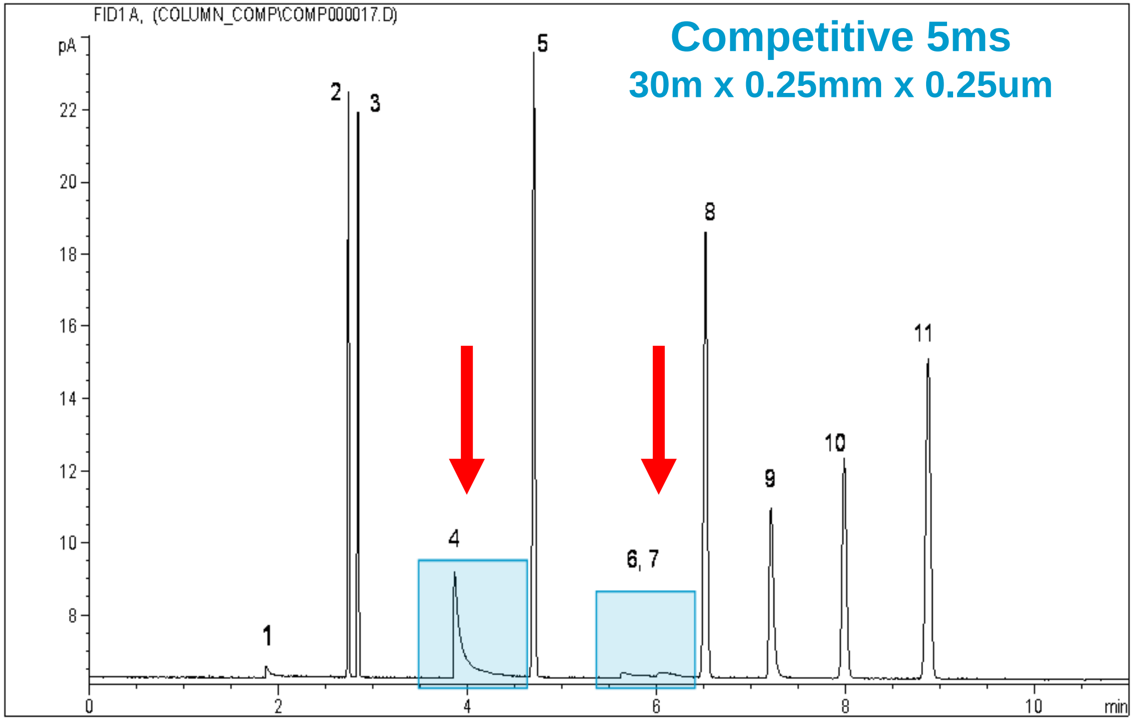
- Challenges
  - Qualification/quantification of trace samples
  - Keep instrument up and running

- Needs
  - Lower detection limits
  - Improved stability in GC or GC/MS system

Lower Detection Limit	
Reduce noise	**Increase signal**
Injection system (septa, liners, connections)	Sample concentration
Carrier gas and detector gases	Sample size
Leaks	Inert injection and detection port sleeves/liner
Temperature setting	Gas velocity or temp program rate
Stationary phase and column bleed	**Column inertness**

What Does Column Activity look like?

column activity → peak tailing and loss of response → reduce sensitivity



1. 1-Propionic acid
2. 1-Octene
3. n-Octane
4 4-Picoline
5. n-Nonane
6. Trimethyl phosphate
7. 1,2-Pentanediol
8. n-Propylbenzene
9. 1-Heptanol
10. 3-Octanone
11. n-Decane

Column activity is the loss of detectable analytes to the GC column through non-ideal chemical reactions and interactions.

How Important Column Inertness to Overall Flow Path 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

What is an Ultra Inert GC Column?

- Not just another column claims better performance
- Not hand picked from standard production based on “exceptional performance”
- New approach to column manufacturing with significantly improved sensitivity and accuracy for trace samples
- Treated with new, proprietary processes for surface treatment and deactivation, resulting in much better peak shape for acidic, basic, and other active compounds
- The deactivated surface coupled with the low-bleed bonded phases lead to much improved analyses and lower detection limits

Test Probes and Column Activity QC Testing

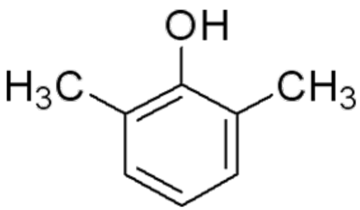
- Test probes are vital to ensure the quality and reproducibility of GC columns
  - Properly deactivated
  - Contain the correct amount of stationary phase
  - consistent column-to-column relative retention time

- Test probes can either highlight or mask the deficiencies of a column
  - An organic acid
  - A base
  - An alcohol
  - Non-active probes (e.g. alkanes)

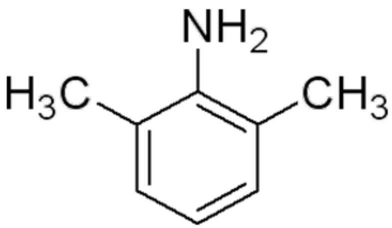
* Peak tailing or loss response of an acid (or base) indicates the column is basic (or acidic).

Agilent Technologies

Weak Probes vs. Strong Probes



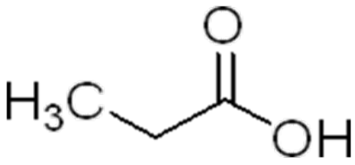
2,6-Dimethylphenol



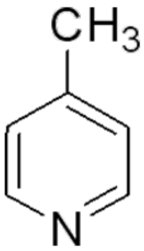
2,6-Dimethylaniline

Weak Probes

Acidic and basic portion of the molecules are shielded by the methyl groups of the 2,6-dimethyl substituted phenyl ring



1-Propionic acid



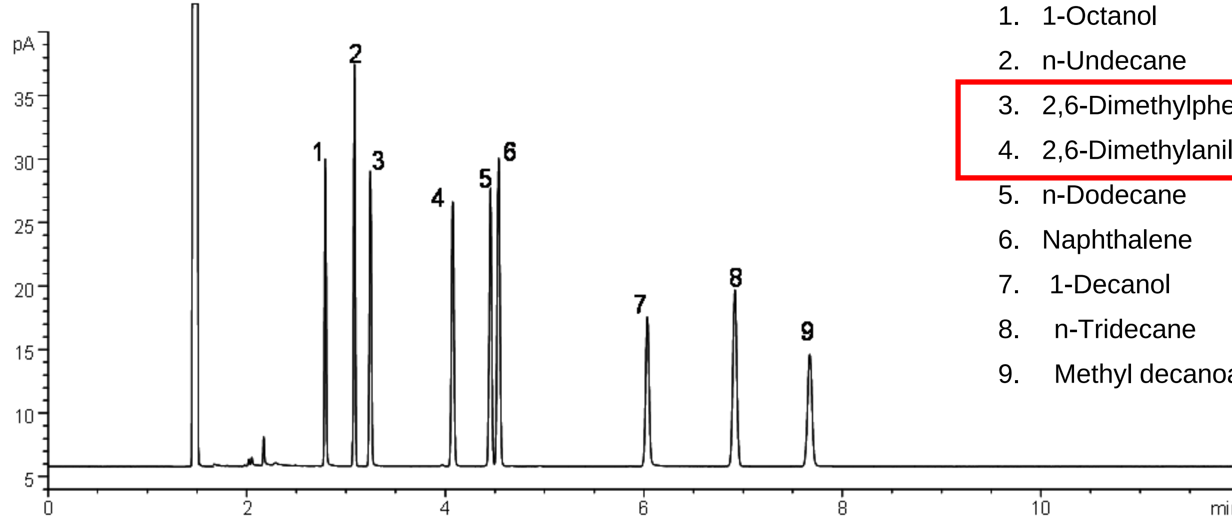
4-Picoline

Strong Probes

Active end of each compound is available to interact with any active sites on the columns

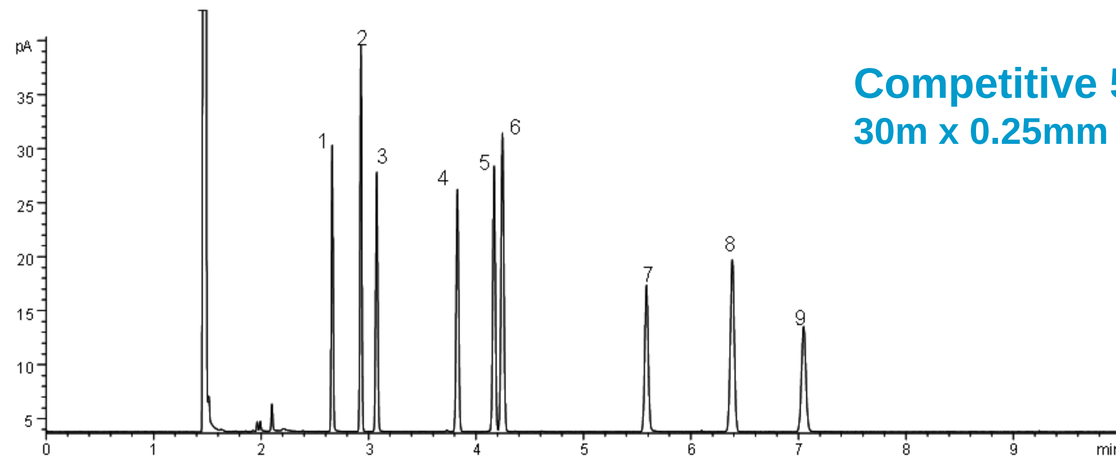
Grob-Type Test Mixture - Not Probative

Agilent J&W DB-5ms Ultra Inert
30m x 0.25mm x 0.25um (P/N 122-5532UI)



1. 1-Octanol
2. n-Undecane
3. 2,6-Dimethylphenol
4. 2,6-Dimethylaniline
5. n-Dodecane
6. Naphthalene
7. 1-Decanol
8. n-Tridecane
9. Methyl decanoate

- Elevated oven temperature at 120°C
- Probes sweep past active sites and can mask solute/column interactions.
- Least probative probes for column activity

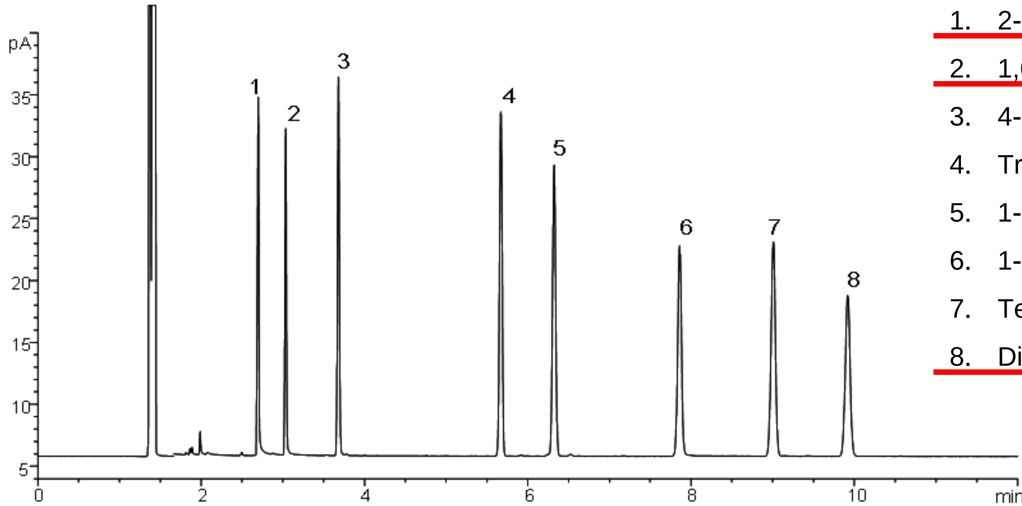


Competitive 5ms column
30m x 0.25mm x 0.25um

Sampler:	Agilent 7683B, 5 µL syringe (Agilent part # 5181-1273), 1.5 µL split injection, 4 ng each component
Carrier:	Hydrogen constant pressure 37 cm/s
Inlet:	Split/splitless; 250 ºC, 1.4 ml/min. column flow, split flow 100 ml/min.
Liner:	Deactivated single taper w glass wool (Agilent part # 5183-4647)
Oven:	120 ºC isothermal
Detection:	FID at 325 ºC, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min. nitrogen makeup

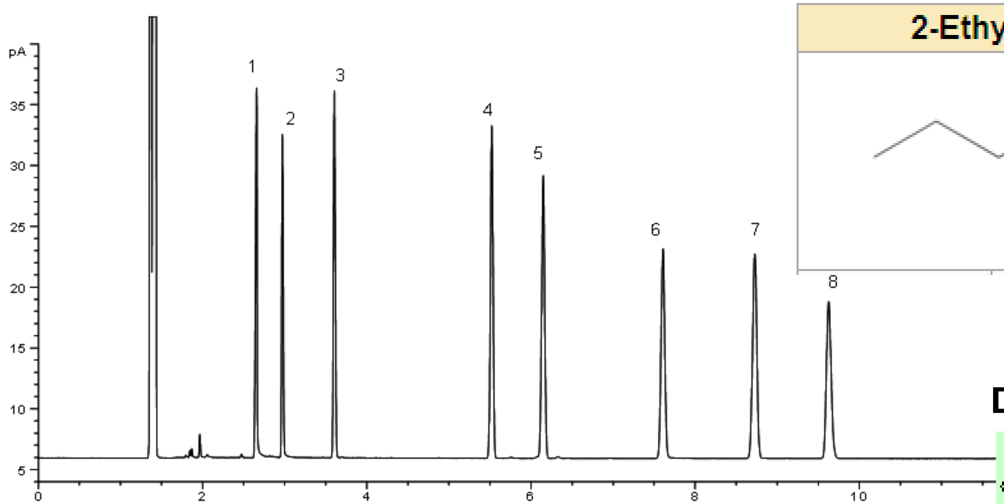
DB-5ms Test Mix – More Probative

Agilent J&W DB-5ms Ultra Inert
30m x 0.25mm x 0.25um
(P/N 122-5532UI)

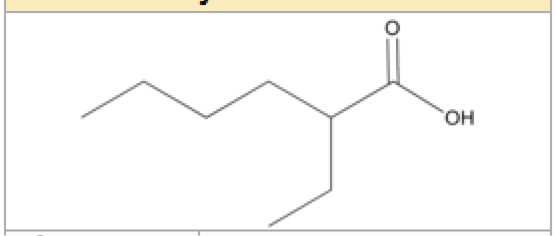


1. 2-Ethylhexanoic acid
2. 1,6-Hexanediol
3. 4-Chlorophenol
4. Tridecane
5. 1-Methylnaphthalene
6. 1-Undecanol
7. Tetradecane
8. Dichlorohexylamine

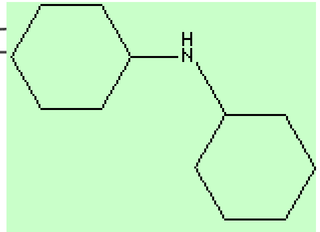
Competitive 5ms column
30m x 0.25mm x 0.25um



2-Ethylhexanoic acid



Dicyclohexylamine

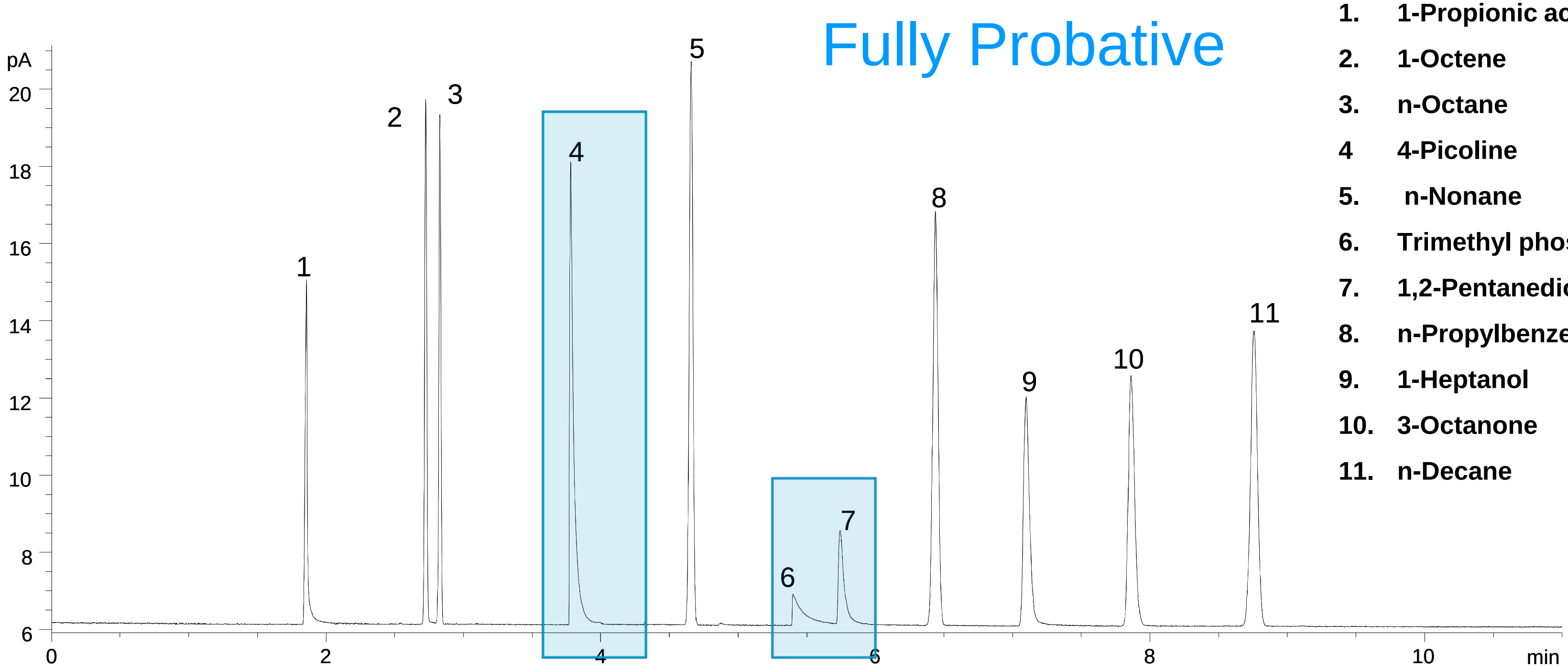


Sampler:	Agilent 7683B, 5 µL syringe (Agilent part # 5181-1273), 1.5 µL split injection, 4 ng each component
Carrier:	Hydrogen constant pressure 38 cm/s
Inlet:	Split/splitless; 250 °C, 1.4 ml/min. column flow, split flow 75 ml/min.
Liner:	Deactivated single taper w glass wool (Agilent part # 5183-4647)
Oven:	125 °C isothermal
Detection:	FID at 320 °C, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min. nitrogen makeup

Ultra Inert Test Probe Mixture – 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

Ultra Inert Test Probe Mixture on a Competitive Column



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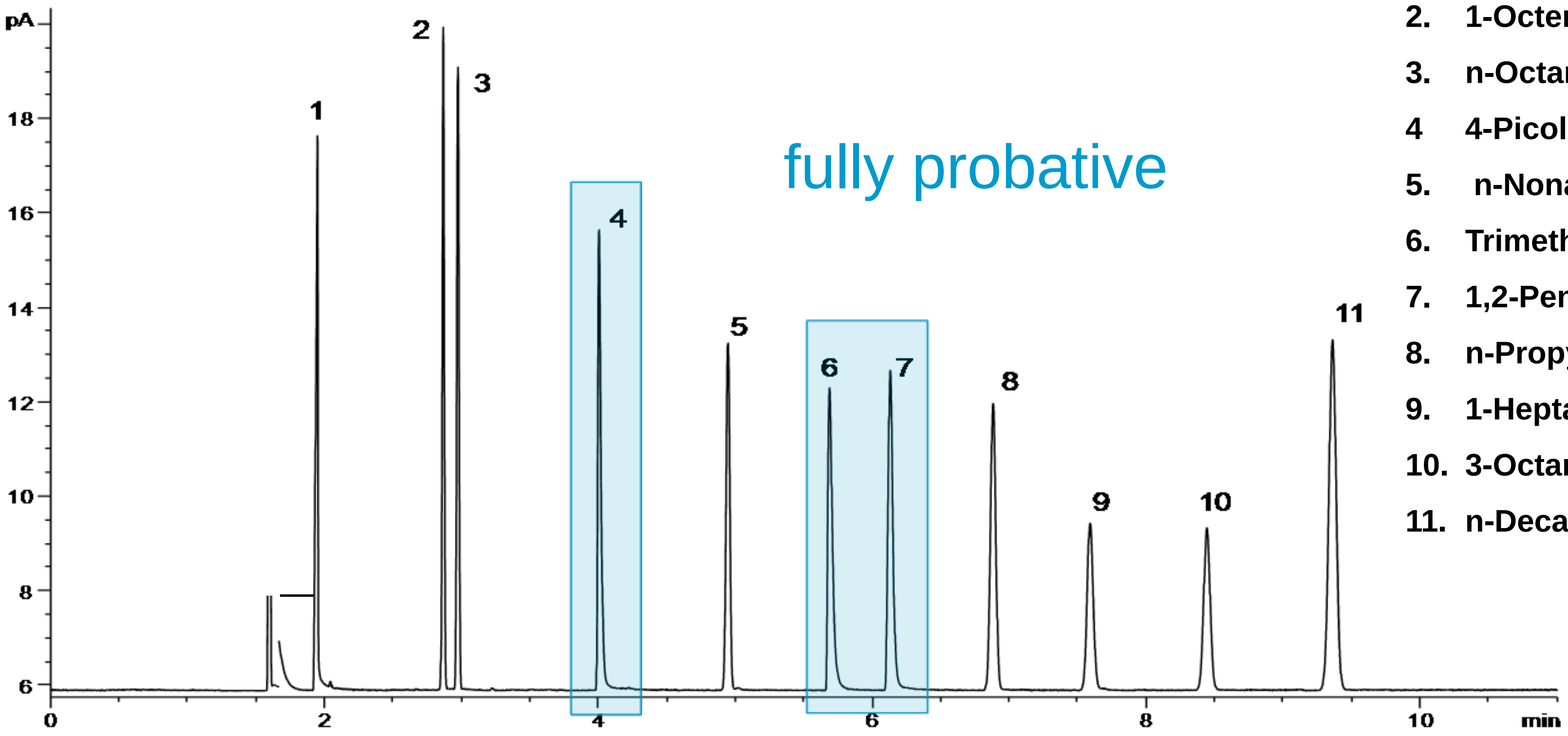
8. n-Propylbenzene
9. 1-Heptanol
10. 3-Octanone
11. n-Decane

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 ºC, 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 ºC isothermal**
Detection:	**FID at 325 ºC, 450 ml/min. air, 40 ml/min. hydrogen, 45 ml/min., nitrogen makeup**

Ultra Inert Test Probe Mixture on an Agilent J&W DB-5ms Ultra Inert column



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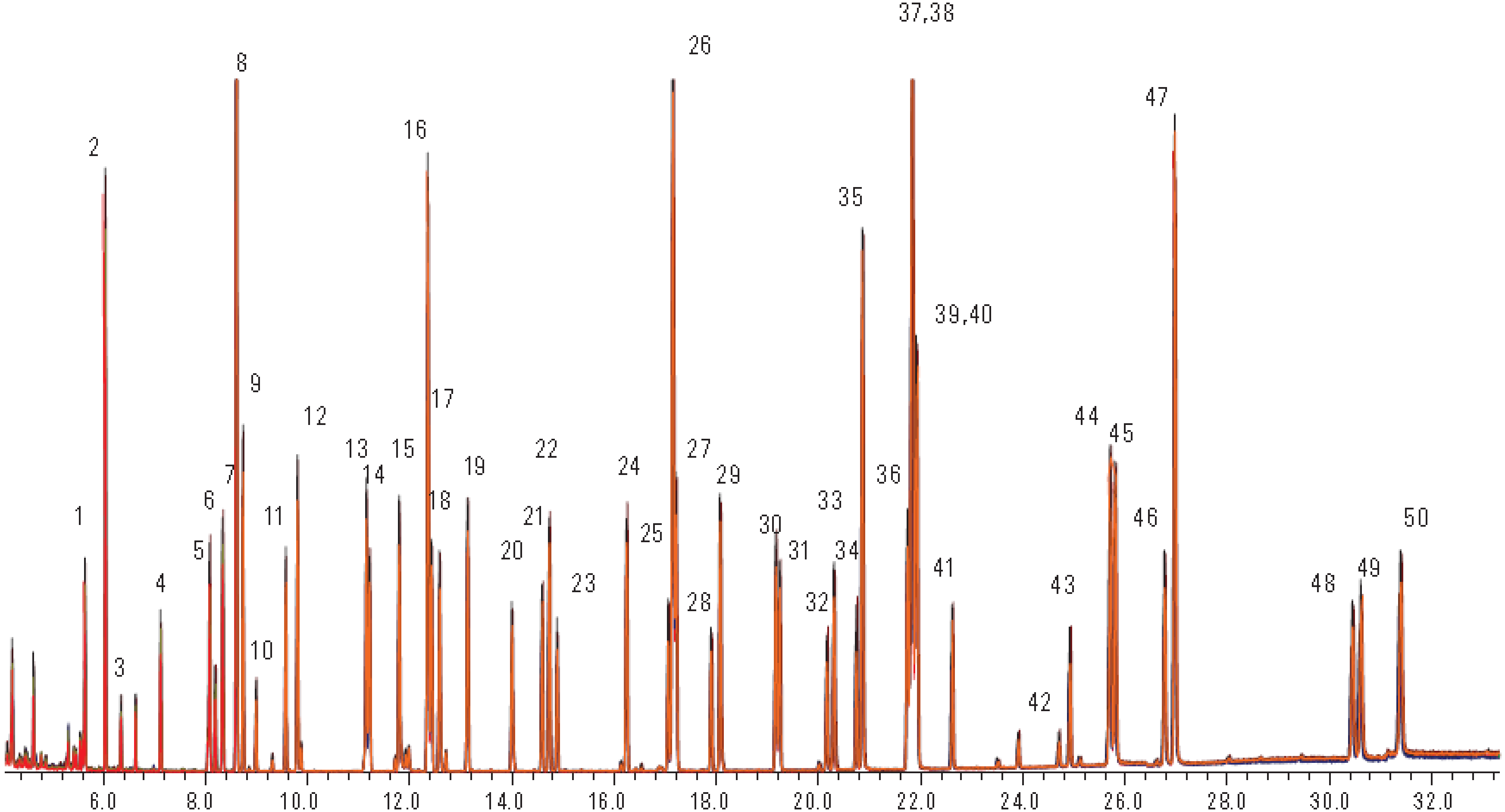
Test Probes – What Do We Learn?

- Test probes can highlight or mask the deficiencies of column activity
- Grob-type mix is not probative for inertness
- DB-5ms text mix is a good test for the 90s
- Ultra Inert test 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

Column Inertness - Proof in
EVERY GC column box – Performance Summary Sheet.

Excellent Inertness and Same Selectivity



10 overlaid TIC for semivolatiles, 2 ng on-column (black-DB-5ms Ultra Inert, red DB-5ms)

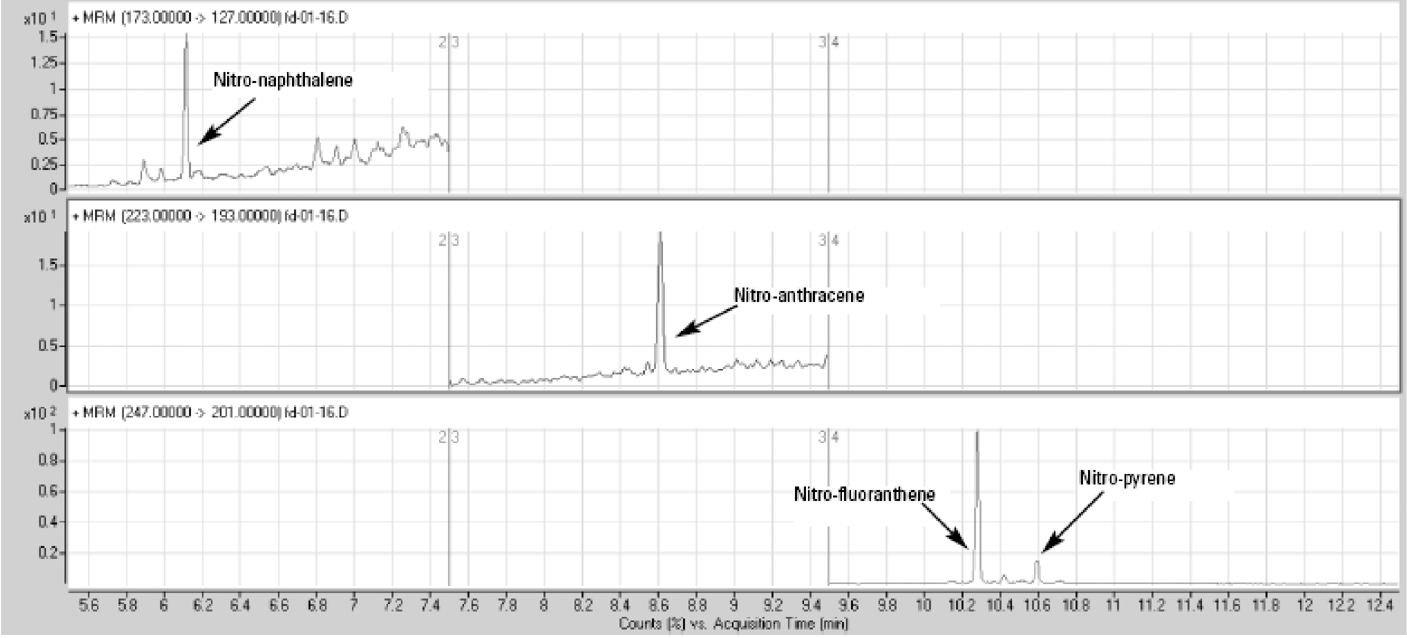
Table 2. Fifty Semivolatile Compound Separation using DB-5 ms and DB-5 ms Ultra Inert Columns

Peak number	Compound	Ava. RT of DB-5 ms (n=5)	Ava. RT of DB-5 ms Ultra inert (n=5)	*RSD% of RT	Rs of DB-5 ms	Rs of DB-5 ms Ultra inert	*m/z*
1	Isophorone	5.647	5.642	0.068	–	–	82
2	1,3 Dimethyl-2-nitrobenzene(SS)	6.047	6.044	0.061	8.4	8.41	134
3	Dichlovos	6.351	6.349	0.059	9.05	9.03	109
4	Hexachlorocyclo-pentadiene	7.129	7.126	0.065	21.58	21.8	237
5	Dimethyl phthalate	8.084	8.087	0.071	23.14	24.1	163
6	2,6-Dinitrotoluene	8.195	8.196	0.074	2.51	2.52	165
7	Acenaphthylene	8.342	8.342	0.080	3.18	3.17	152
8	Acenaphthylene-d10(IS #1)	8.611	8.612	0.076	5.57	5.74	164
9	2-Chlorobiphenyl	8.737	8.739	0.088	2.6	2.74	188
10	2,4-Dinitrotoluene	8.993	8.996	0.085	5.44	5.6	165
11	Diethyl phthalate	9.572	9.579	0.098	12.21	12.35	149
12	Fluorene	9.804	9.808	0.088	4.65	4.6	166
13	2,3-Dichlorobiphenyl	11.153	11.159	0.095	24.87	25.63	222/152
14	Hexachlorobenzene	11.218	11.219	0.090	1.14	1.12	284
15	Pentachlorophenol	11.795	11.798	0.092	9.78	10.07	266
16	Phenanthrene-d10(IS #2)	12.357	12.363	0.088	9.28	9.34	188
17	Phenanthrene	12.426	12.432	0.091	1.16	1.13	178
18	Anthracene	12.585	12.591	0.091	2.66	2.71	178
19	2,4,5-Trichlorobiphenyl	13.133	13.140	0.089	9.27	9.61	256
20	Heptachlor	14.001	14.008	0.090	14.36	14.80	100
21	Di-n-butyl phthalate	14.587	14.600	0.095	9.99	10.14	149
22	2,2',4,4'-Tetrachlorobiphenyl	14.733	14.741	0.085	2.51	2.42	292
23	chlorpyrifos	14.882	14.892	0.088	2.50	2.53	197/97
24	2,2',3',4,6-Pentachlorobiphenyl	16.247	16.255	0.083	22.89	23.28	326
25	Butachlor	17.058	17.070	0.081	13.17	13.74	176/160
26	Pyrene-d10(SS)	17.153	17.163	0.078	1.49	1.41	212
27	Pyrene	17.214	17.223	0.076	0.87	0.91	202
28	p,p'-DDE	17.901	17.913	0.075	11.03	11.34	246
29	2,2',4,4',5,6'-Hexachlorobiphenyl	18.077	18.088	0.074	2.79	2.74	360
30	p,p'-DDD	19.162	19.176	0.075	7.54	7.04	235/165
31	o,p'-DDT	19.235	19.250	0.078	1.17	1.18	235/165
32	Benzyl butyl phthalate	20.157	20.177	0.078	14.76	15.08	149
33	p,p'-DDT	20.301	20.316	0.073	2.39	2.35	235/165
34	bis(2-Ethylhexyl)adipate	20.731	20.755	0.084	7.17	7.25	129
35	Triphenylphosphate (SS)	20.851	20.873	0.082	1.95	1.95	326/325
36	2,2'3,3',4,4'6-Heptachrolobiphenyl	21.737	21.754	0.070	13.80	13.79	394/396
37	Ben[α]anthracene	21.805	21.806	0.033	1.18	1.23	228
38	Chrysene-d12 (IS #3)	21.834	21.835	0.039	0.74	0.75	240
39	2,2',3,3',4,5,6,6'-Octachlorobiphenyl	21.903	21.904	0.036	0.94	1.04	430/428
40	Chrysene	21.928	21.928	0.034	0.80	0.80	228
41	bis(2-Ethylhexyl)phithalate	22.605	22.632	0.081	9.44	10.04	149
42	cis-Permethrine	24.692	24.720	0.077	35.23	36.04	183
43	trans-Permethrin	24.906	24.936	0.080	3.58	3.63	183
44	Benzo[b]fluoranthene	25.704	25.725	0.064	12.10	12.29	252
45	Benzo[k]fluoranthene	25.802	25.824	0.067	1.30	1.40	252
46	Benzo[a]pyrene	26.766	26.789	0.064	12.69	13.60	252
47	Perylene-d12(SS)	26.966	26.991	0.067	2.60	2.74	264
48	Indeno[1,2,3-c,d]pyrene	30.434	30.470	0.077	40.75	40.99	276
49	Dibenz[a,h]anthracene	30.594	30.635	0.086	1.69	1.76	278
50	Benzo[g,h,i]perylene	31.373	31.414	0.088	7.74	8.07	276

*RSD% was calculated by using the retention times for each compound on the DB-5 ms and DB-5 ms Ultra Inert columns.

Nitro-PAHs

Column:	**DB-5ms Ultra Inert 15 m x 0.25 mm x 0.25 µm (Agilent part # 122-5512UI)**
Carrier:	**Helium 43.8 cm/sec constant flow**
Oven:	**70°C (1min) to 310°C at 20°C/min**
Inlet:	**splitness at 250 °C**
MSD:	**7000A Triple Quadrupole GC/MS, ion source at 300°C and Quadrupole at 150°C**



By Frank David (RIC) and Matthew Klee (Agilent)

MRM chromatograms of nitro-PAHs in extract of urban air particulate sample where the concentrations for nitro-naphthalene, nitro-anthracene, nitro-fluranthene, and nitro-pyrene were 21 pg/m3, 10 pg/m3, 77 pg/m3, and 14 pg/m3, respectively.

- Deliver high sensitivity.
- Reliable determination of trace level nitro-PAHs in complex air particulate extract matrices without labor-intensive sample preparation.
- The solutes are selectively detected at pg/uL level, corresponding to pg/m3 in air.

Column Technology for Reliable Trace Analysis

- Column bleed is only half the story in trace analysis.
- Only when a column exhibits **both low bleed** and **low activity** are results reliable.
- Ultra Inert columns set a new industry standard for column inertness QC testing
  - Best columns available for reactive analytes and trace analysis
  - Active analytes adsorbing on the column stops productivity in its tracks.
  - Start with an Ultra Inert Column for guaranteed performance upon installation.