Low Bleed Stationary Phases for Gas Chromatography

Advantages of Low Bleed Phase

Lower bleed compared to standard phases

Better signal to noise (sensitivity)

Higher upper temperature - shorter run times

Lower detector maintenance

Improved spectral purity

Potential for longer column life

Stationary Phase Bleed

Normal degradation of the stationary phase

All columns exhibit some bleed

WHAT IS A BLEED PROBLEM?

An abnormal elevated baseline at high temperature

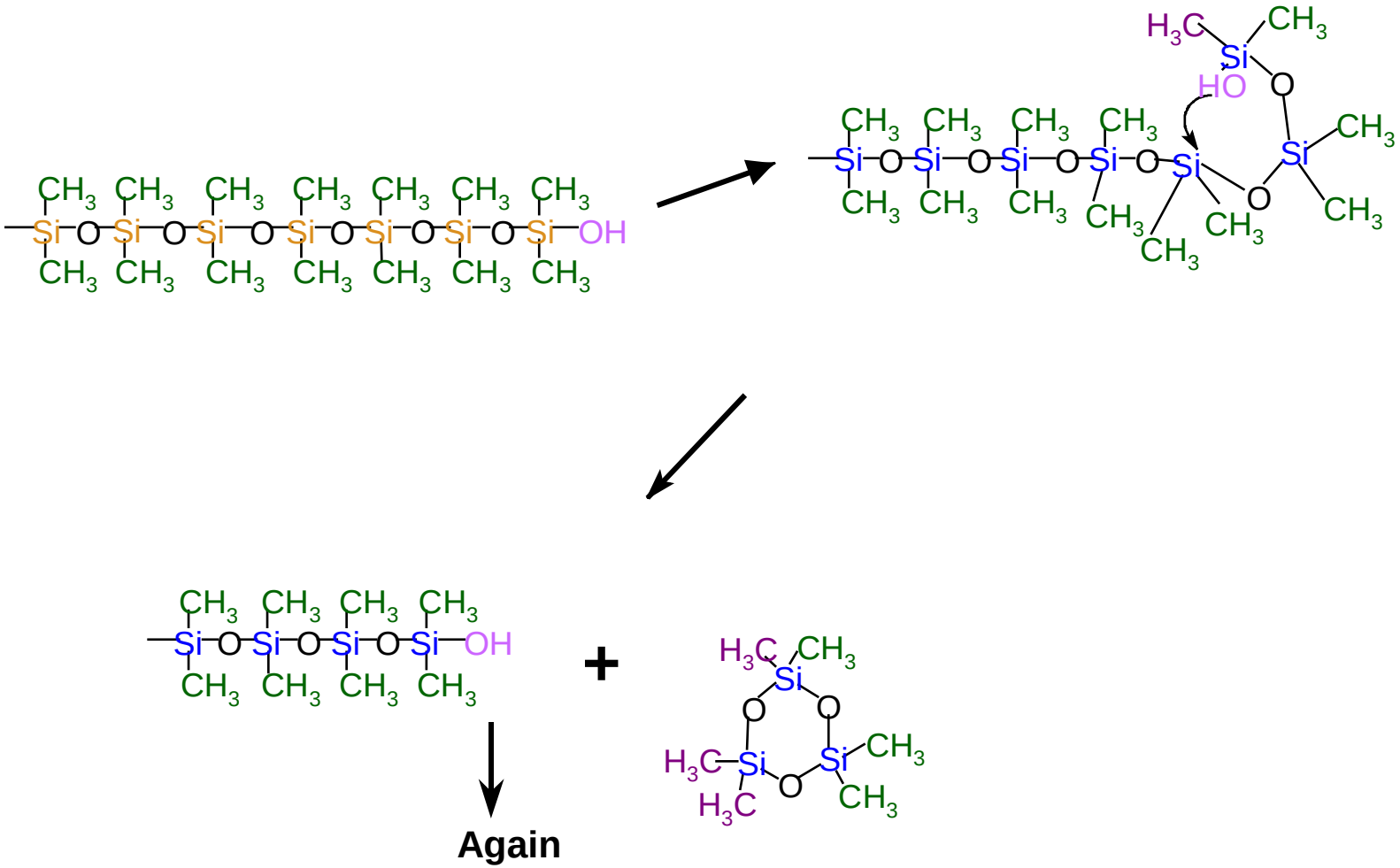
IT IS NOT

A high baseline at low temperature

Wandering or drifting baseline at any temperature

Discrete peaks

Stationary Phase Bleed Mechanism



“ms” Phase and Column Criteria

Higher upper temperature limit

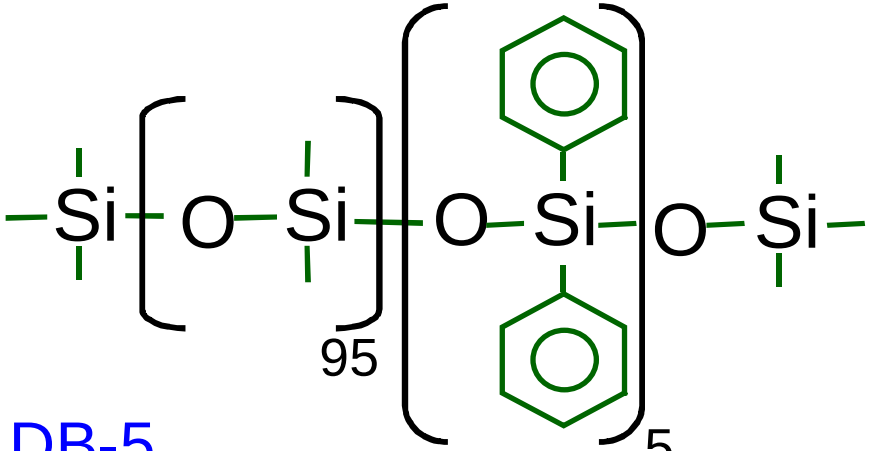
Lower bleed than columns with “equivalent” phase

Superior inertness to acidic and basic compounds

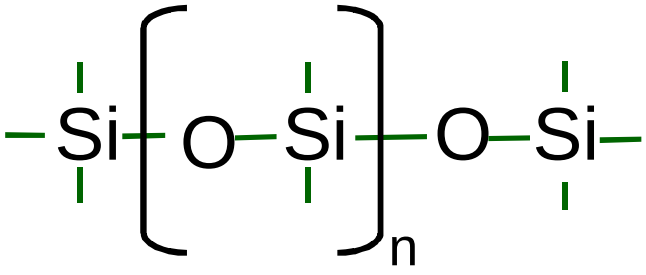
Analogous phase selectivity

Capillary GC Phase Development

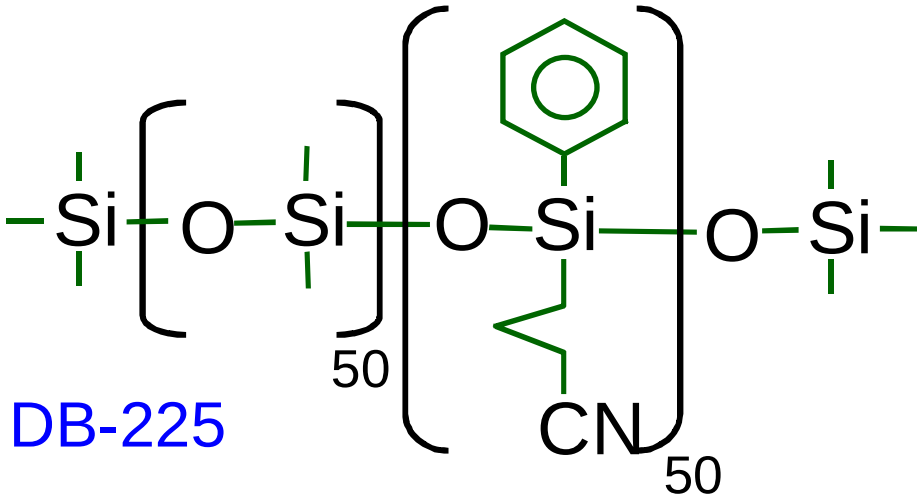
Early Phases



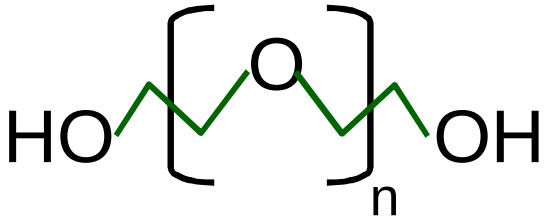
DB-5



DB-1



DB-225



DB-WAX

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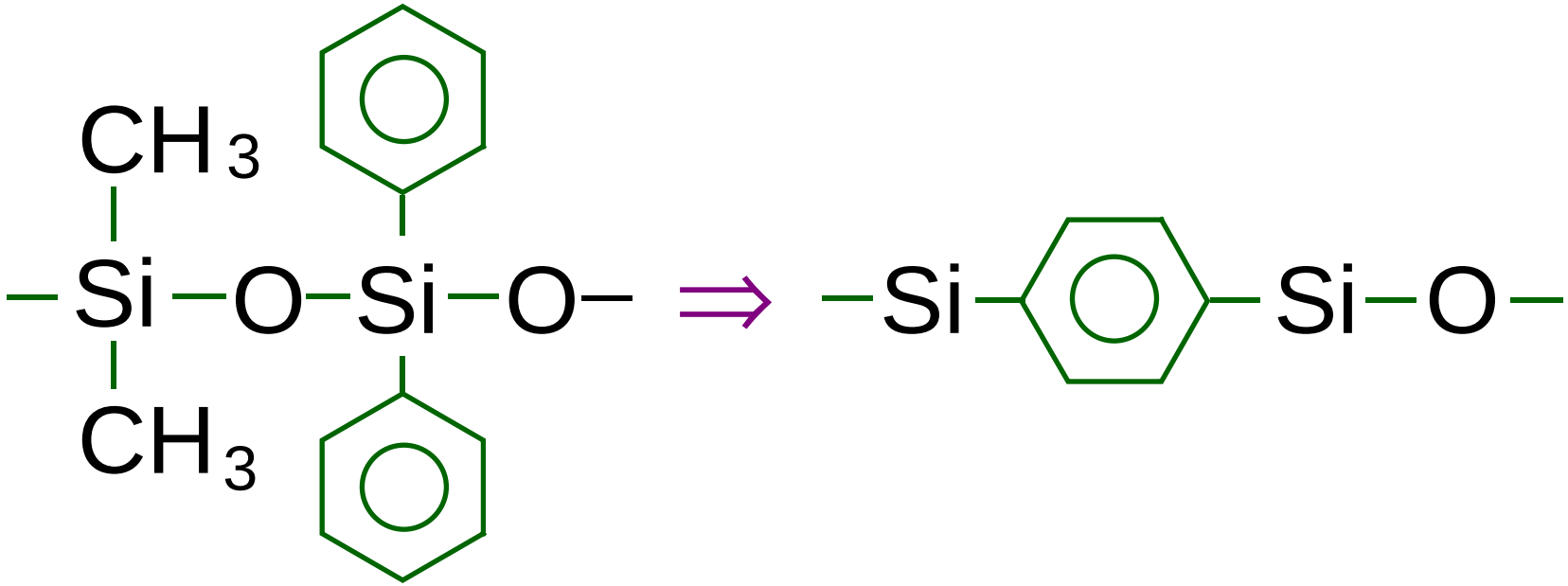
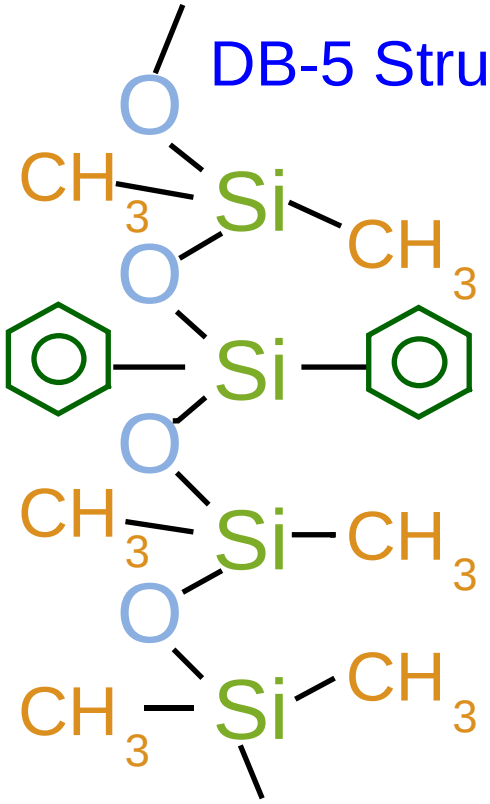
Phenylene Polymer Chemistry



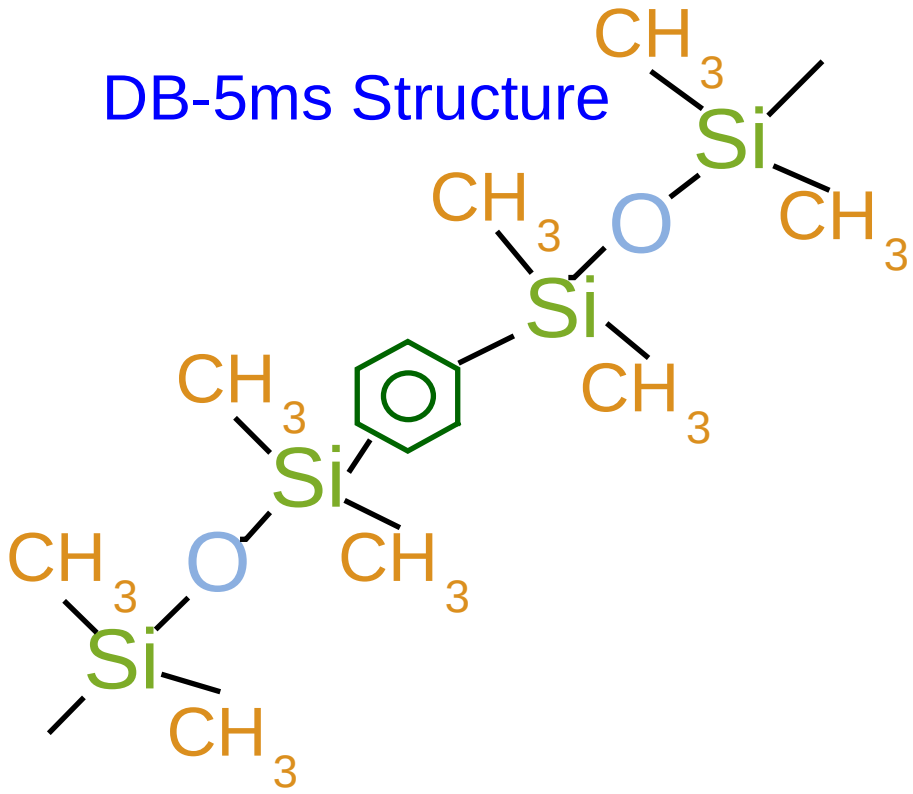
- **Better thermal stability**
- **Lower bleed**

DB-5MS Structure

DB-5 Structure



DB-5ms Structure



DB-5
5% Phenyl

DB-5ms
1.Increased stability
2.Different selectivity
3.Optimized to match DB-5

Types of Low Bleed Columns

Phases tailored to “mimic” currently existing polymers

New phases unrelated to any previously existing polymers

Optimized polymerization chemistry and manufacturing processes

Low Bleed Success Stories

"5% Phenyl"

DB-5ms	BPX5
HP-5TA	CP-Sil8CB/MS
HP-5ms	007-5ms
Rtx-5ms	MDN-5ms

"35% Phenyl"

"50% Phenyl"

"Other" Low Bleed

DB-XLB

HT5,HT8

"50% Cyanopropyl-phenyl"

Low Bleed Family

1ms - siloxane 360 MAOT

5ms - arylene

Next generation arylene:

XLB, 17ms, 35ms, 225ms

ion trap tested:

DB-5ms ITD

DB-XLB ITD

Phase Selectivity

Many “backbone stiffening” substitutes give analogous “phenyl like” characteristics

But

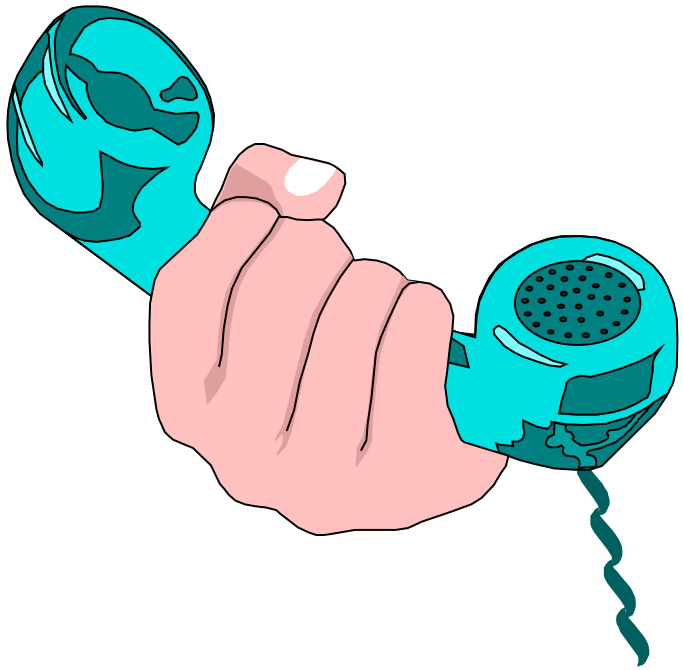
not so for 100% Dimethylpolysiloxane

Break Number 1

For Questions and Answers

Press *1 on Your Phone to

Ask a Question



Early Attempts at “100% DMPS”
Low Bleed Column

Column	Delta Bleed (pA)
DB-1	5.0
Cyclohexyl	5.0
Butyl	20
Ethyl	40
Butenyl	40

All columns: 30 m x 0.25 mm I.D., 0.25 µm
Conditions: 135°C to 320°C

Retention Indices for Low Density Alkane Substitutions

Undecanol and Acenaphthylene

Column	Undecanol	Acenaphthylene
DB-1	1355.10	1424.62
Cyclohexyl	1344.55	1436.77
Butane	1349.85	1427.19
Butenyl	1356.34	1432.80
Ethyl	1356.41	1433.30

All columns: 30 m x 0.25 mm I.D., 0.25 µm
Conditions: H_2 carrier, Split 100:1, Isothermal 135°C

Retention Indicies for “Low Arylene” Substitutes

Column	3,5-DMP	1-Nitrohexane	1,4-DIIPB	1-Nonanol	2-Decanone
DB-1	952.4	1009.4	1152.1	1156.9	1169.3
Mfg B	966.1	1015.1	1157.3	1161.1	1174.1
Mfg C	958.7	1015.0	1157.0	1161.0	1173.0

% “Phenyl” Substitution
Based on Average RI Values

Mfg B	**1.4% phenyl equivalent**
Mfg C	**1.0% phenyl equivalent**

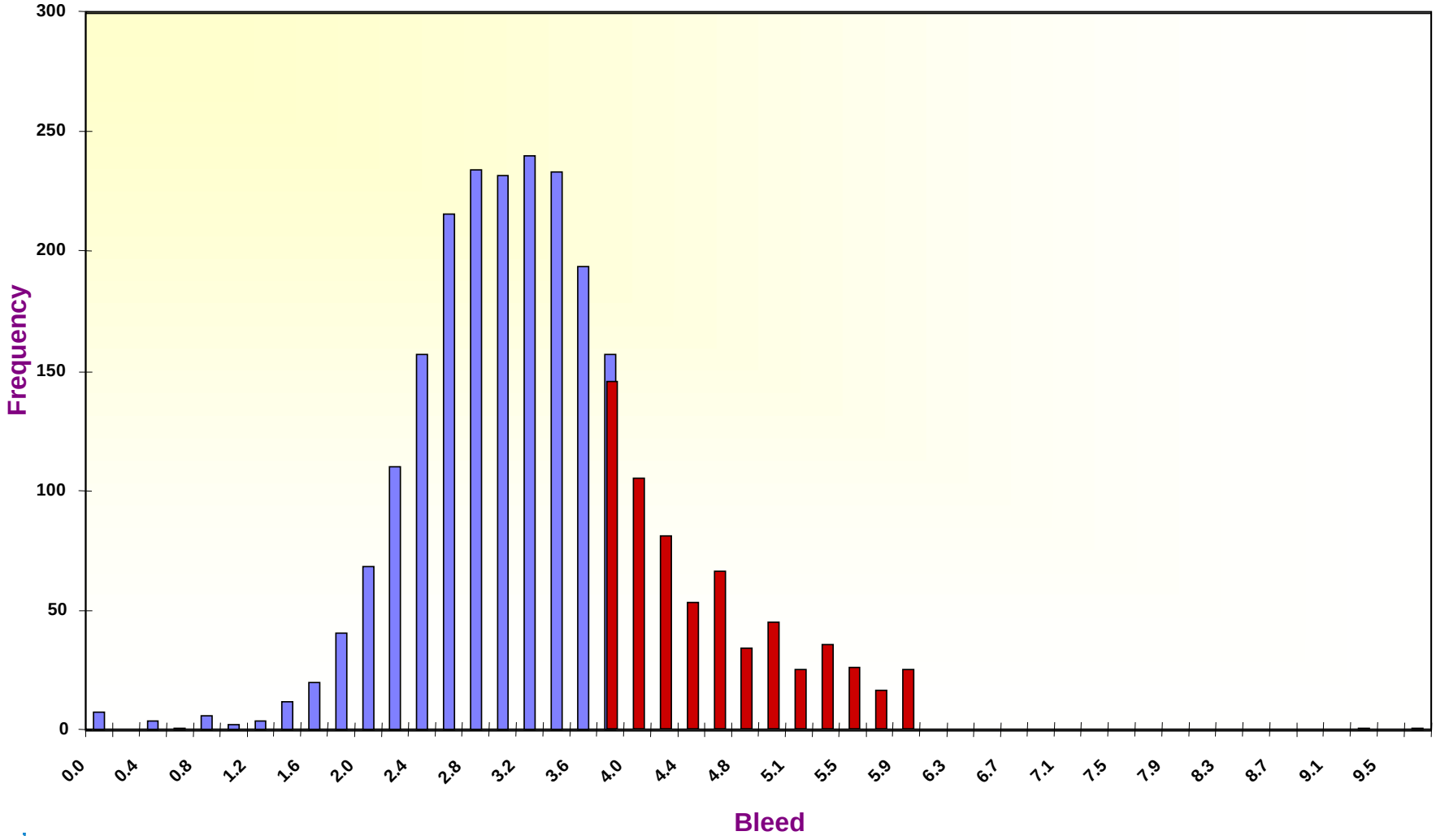
Optimizing an Already Robust Phase

Changes to fused silica surface prior to polymerization

Changes to polymerization chemistry

Changes to chemical manifolds used to process columns

Column Bleed Histogram for 100% DMPS Columns



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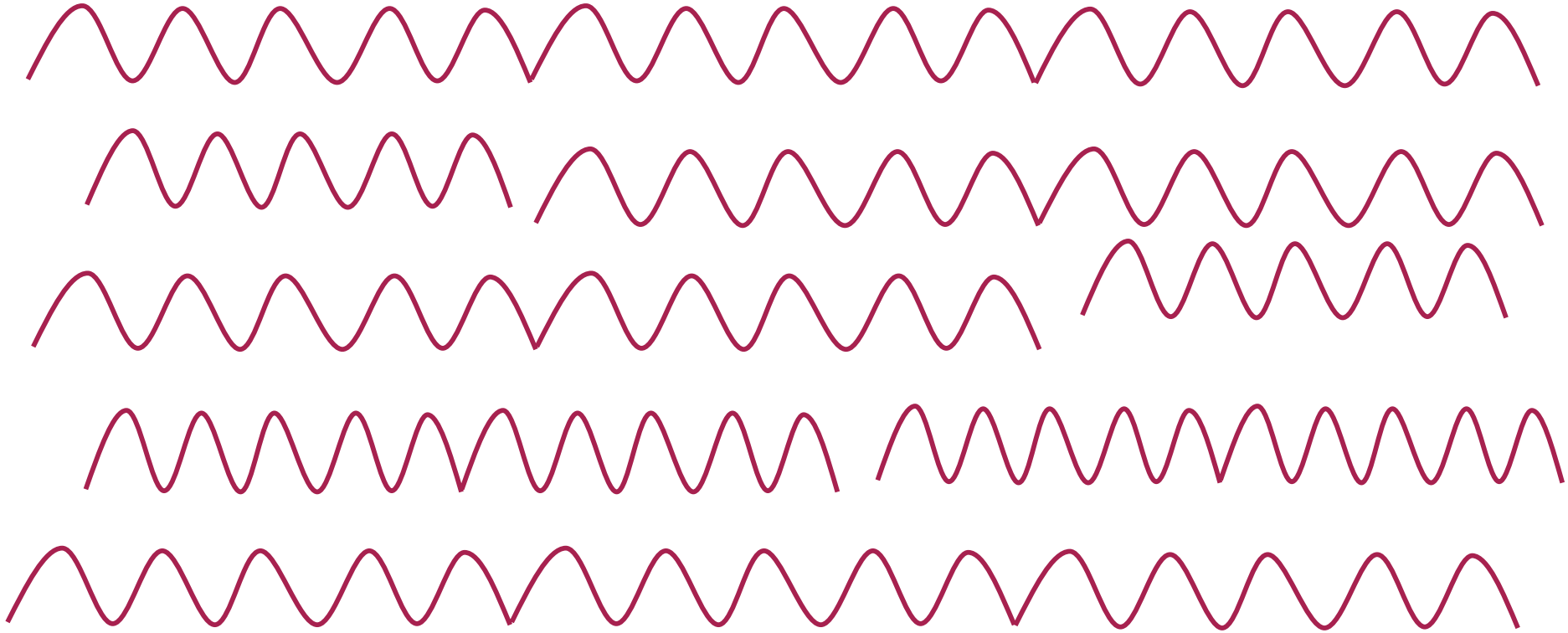
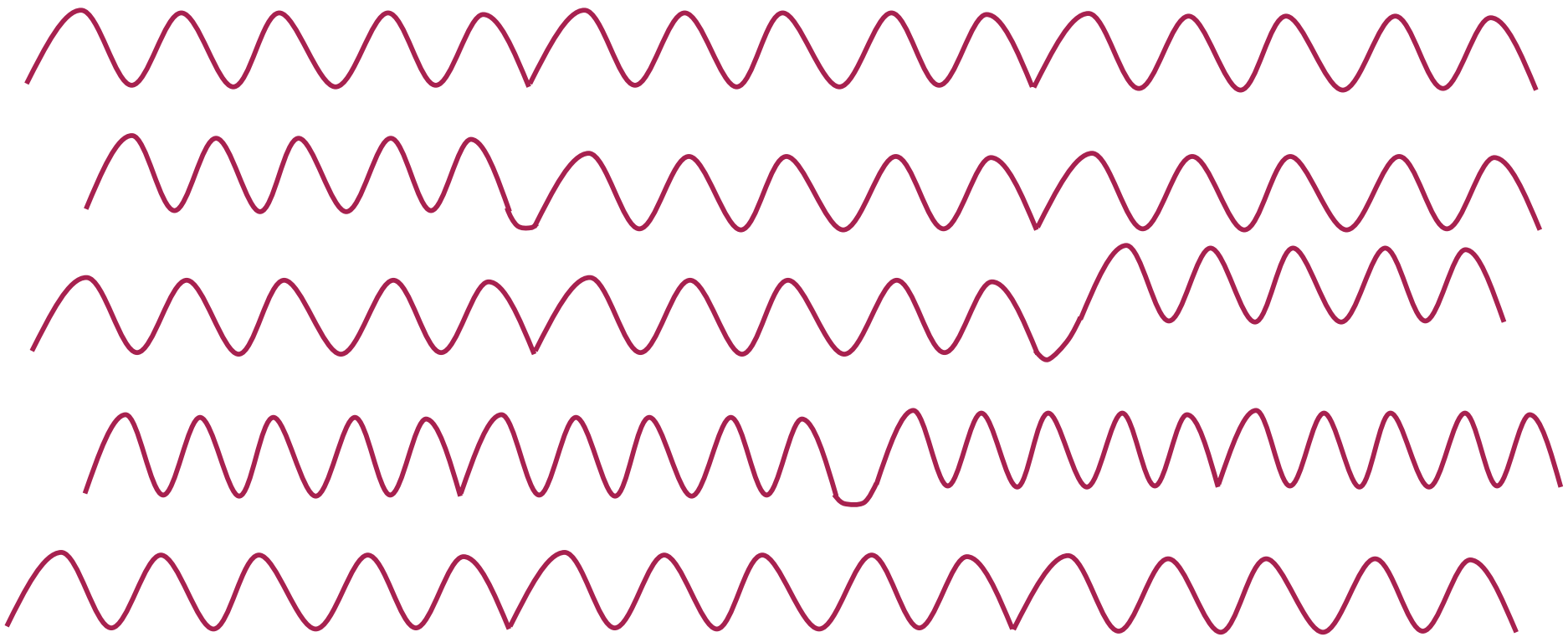
Molecular Weight Distribution and Bleed in DMPS Columns



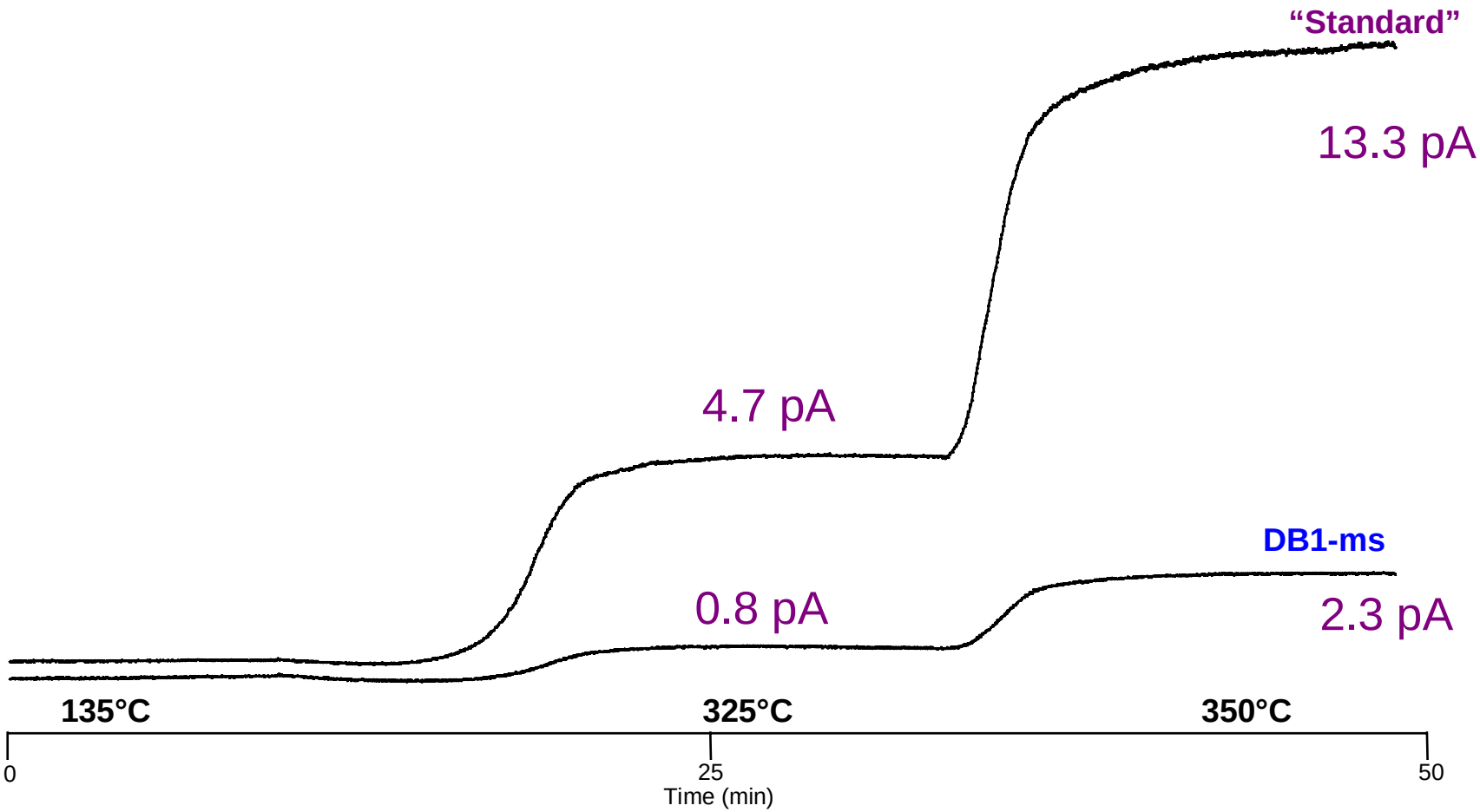
DMPS chains of inconsistent lengths

Molecular Weight Distribution and Bleed in DMPS Columns



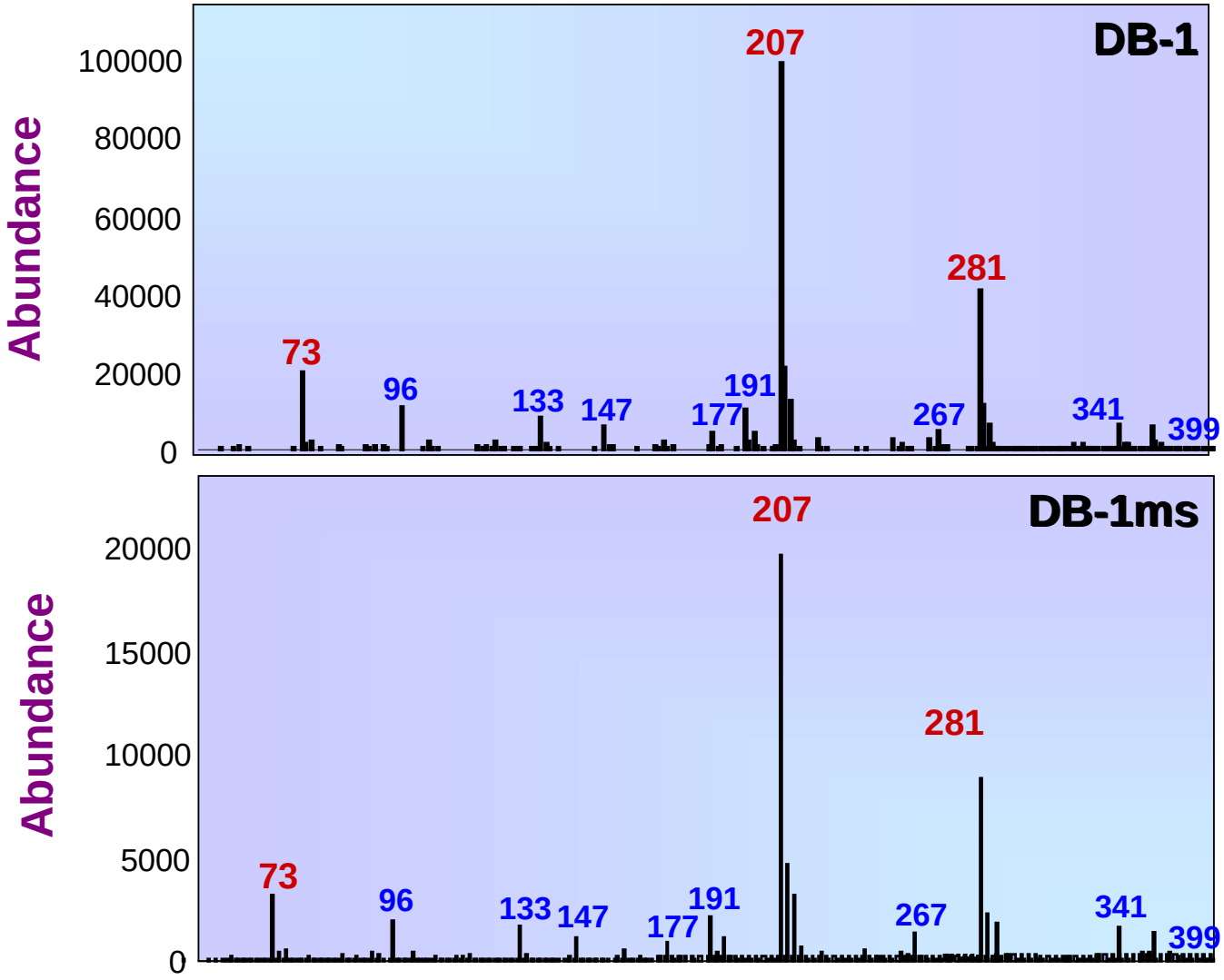
DMPS chains of ***consistent*** lengths

Relative Improvements in Bleed for Standard versus Low Bleed DMPS



Columns: 30 m x 0.25 mm I.D., 0.25 µm film

Mass Spectral Comparison of DB-1 and DB-1ms



Columns: 30 m x 0.25 mm I.D., 0.25 µm film, Oven Temperature 325°C

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Retention Indices Comparison

Retention indices at 90°C

Compound	DB-,1	DB-1ms
3,5-Dimethylpyridine	952.4	954.0
1-Nitrohexane	1009.4	1009.7
1,4-Diisopropylbenzene	1152.1	1152.7
1-Nonanol	1156.9	1157.2
2-Decanone	1169.3	1169.7

Columns: 30 m x 0.25 mm I.D., 0.25 µm film

Comparison of Selectivity

Columns: 30 m x 0.25 mm I.D., 0.25 µm

Carrier: Helium at 42 cm/sec, measured at 40°C

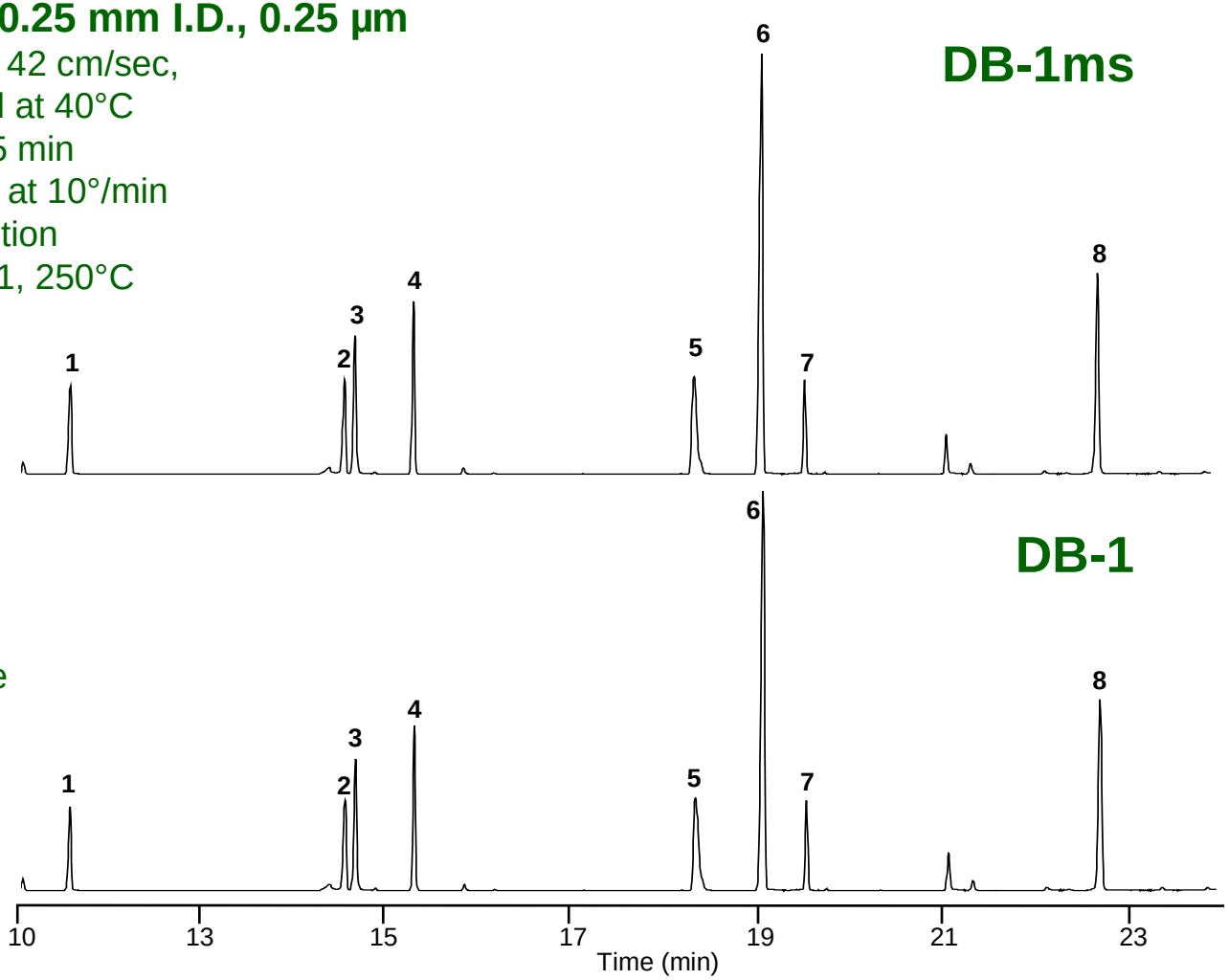
Oven: 40°C for 5 min
40-200°C at 10°/min

Injector: 1 µL injection
Split 100:1, 250°C

Detector: MSD

Compound List

1. Benzyl alcohol
2. 3-Nitrotoluene
3. 4-Chlorophenol
4. Hexachlorobutadiene
5. Dicyclohexylamine
6. Acenaphthene
7. Pentadecane
8. Phenanthrene

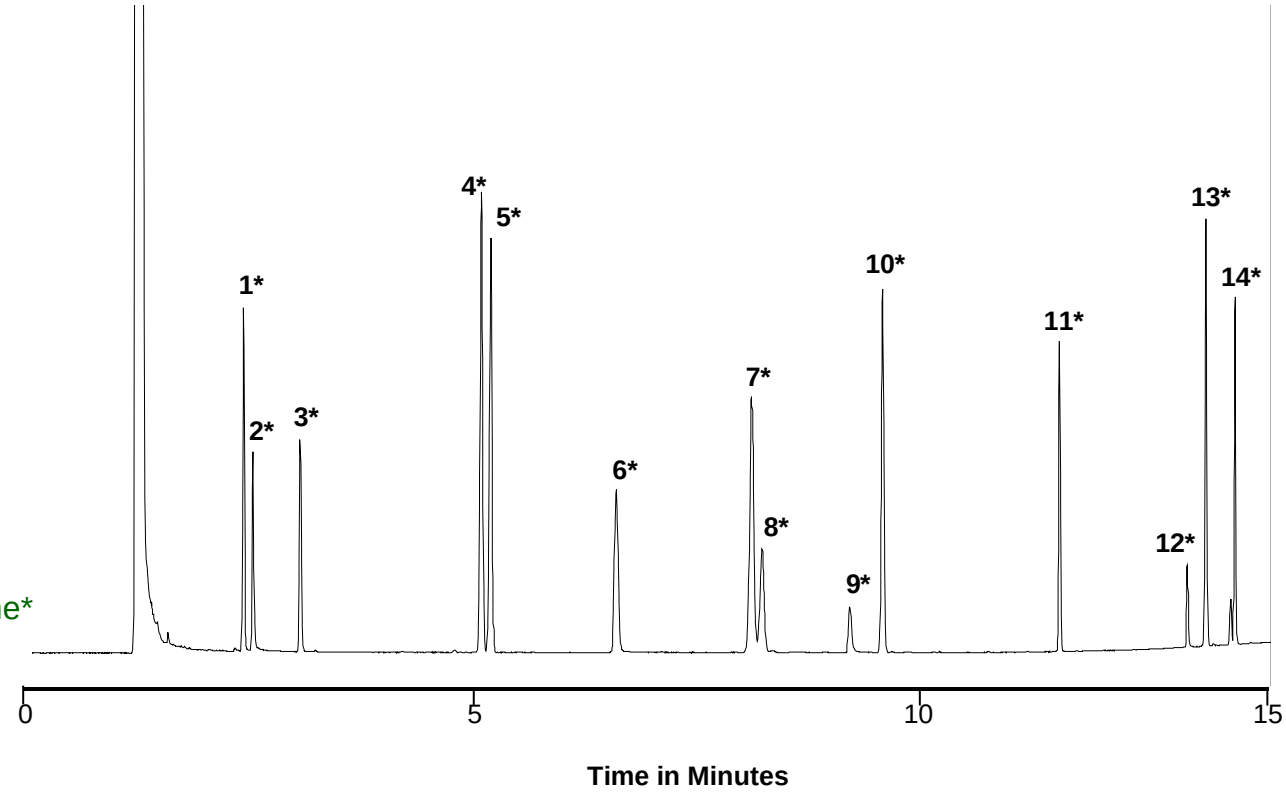


Inertness Testing on DB-1ms

Column: **DB-1ms**
30 m x 0.25 mm I.D., 0.25 µm
J&W P/N: **122-0132**
Carrier: Hydrogen at 39.8 cm/sec, measured at 125°C
Oven: 125°C for 8.5 min
125-265°C at 20°/min
Injector: Split 1:50, 250°C
Detector: FID, 300°C

1. 2-Ethylhexanoic acid*
2. 1,6-Hexanediol*
3. 4-Chlorophenol*
4. 1-Methylnaphthalene
5. Tridecane
6. 1-Undecanol
7. Tetradecane
8. Dicyclohexylamine*
9. 2,4-Dinitrophenol*
10. Acenaphthene
11. N-Nitrosodiphenylamine*
12. Pentachlorophenol*
13. Phenanthrene
14. Carbazole

*** Active Analytes**



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GS-CarbonPLOT

Proprietary carbon-layer phase

Very high retention

High upper temperature limit (360ºC)

“Bonded” phase -- cannot generate particles

Good for CO_2, light hydrocarbons, etc.

Not affected by water in samples

Low bleed (for a PLOT column)

GS-GasPro

Proprietary “silica-based” phase

Very inert column for reactive compounds

“Bonded” phase; cannot generate particles

Excellent for MSD and valve systems

Low-bleed (for a PLOT column)

Not affected by water in samples

Currently only available in 0.32 mm I.D.

GS-GasPro

Applications include:

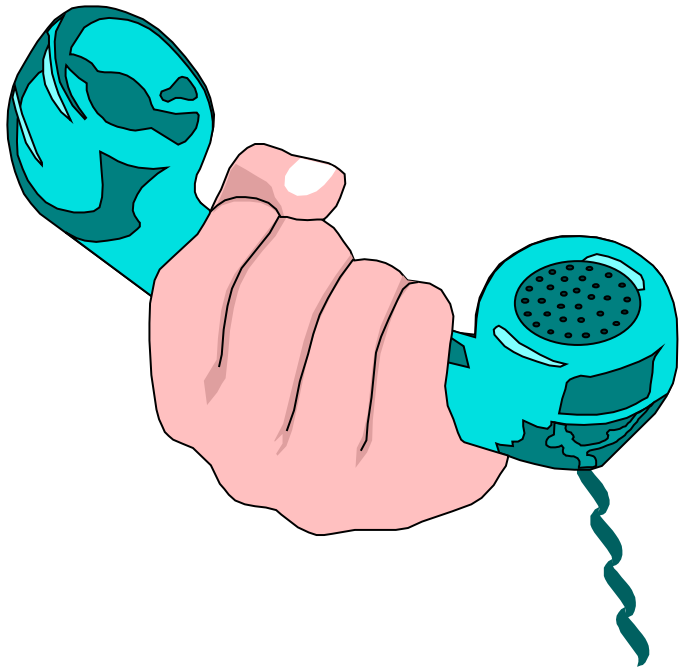
- **Hydrocarbons (C_1 to C_{10})**
- **CO_2**
- **Sulfur gases**
- **Freons**
- **Hydrides**
- **Permanent gases (-80ºC oven)**

Break Number 2

For Questions and Answers

Press *1 on Your Phone to

Ask a Question



Applications

Controlled Substances & Related Samples

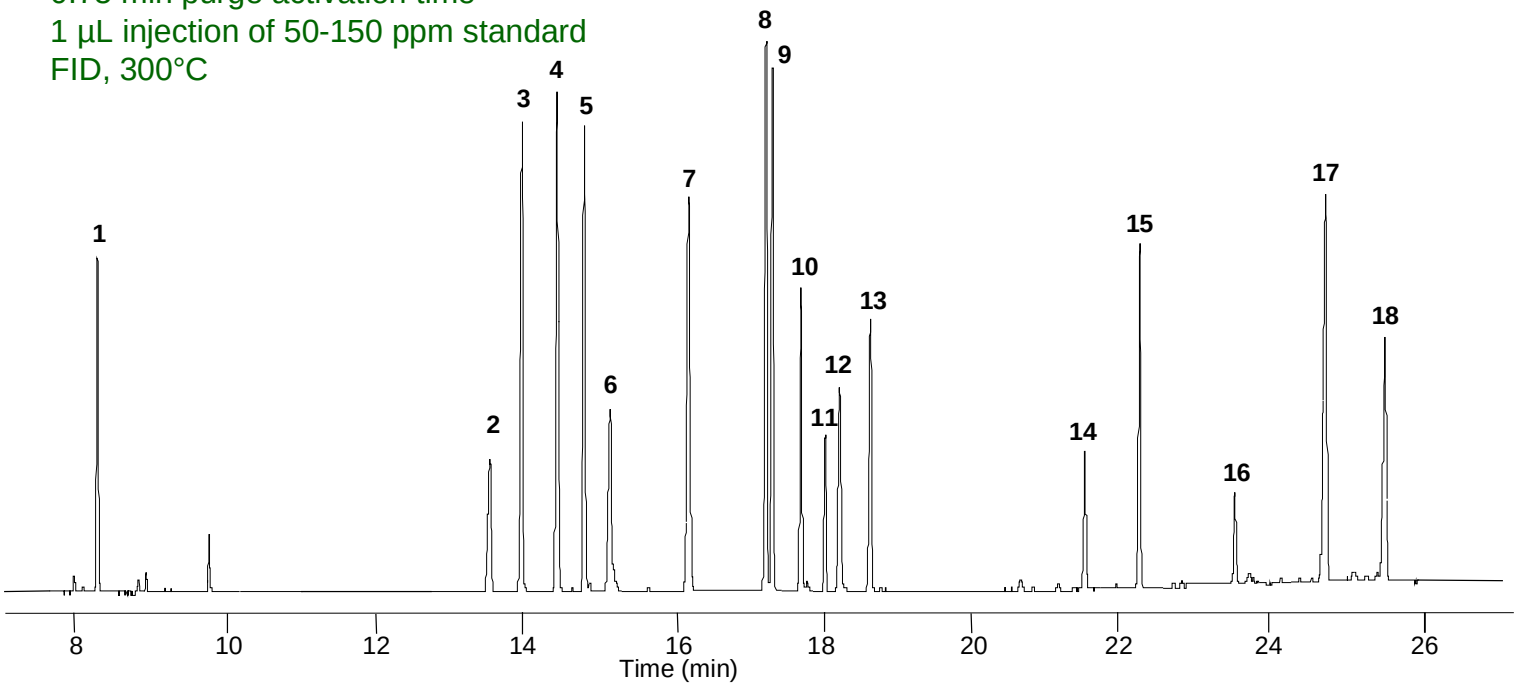
GC/MS is the preferred means of identification

Ideal for trace level analysis -
greater signal-to-noise ratios
and lower detection limits

Drugs

Column: **DB-1ms**
30 m x 0.25 mm I.D., 0.25 µm
J&W P/N: **122-0132**
Carrier: Helium at 40 cm/sec, measured at 50°C
Oven: 50°C for 1 min
50-125°C at 25°/min
125-325°C at 10°/min
325° for 5 min
Injector: Cold Splitless using Optic II injector
50-250°C at 10°/sec,
0.75 min purge activation time
Sample: 1 µL injection of 50-150 ppm standard
Detector: FID, 300°C

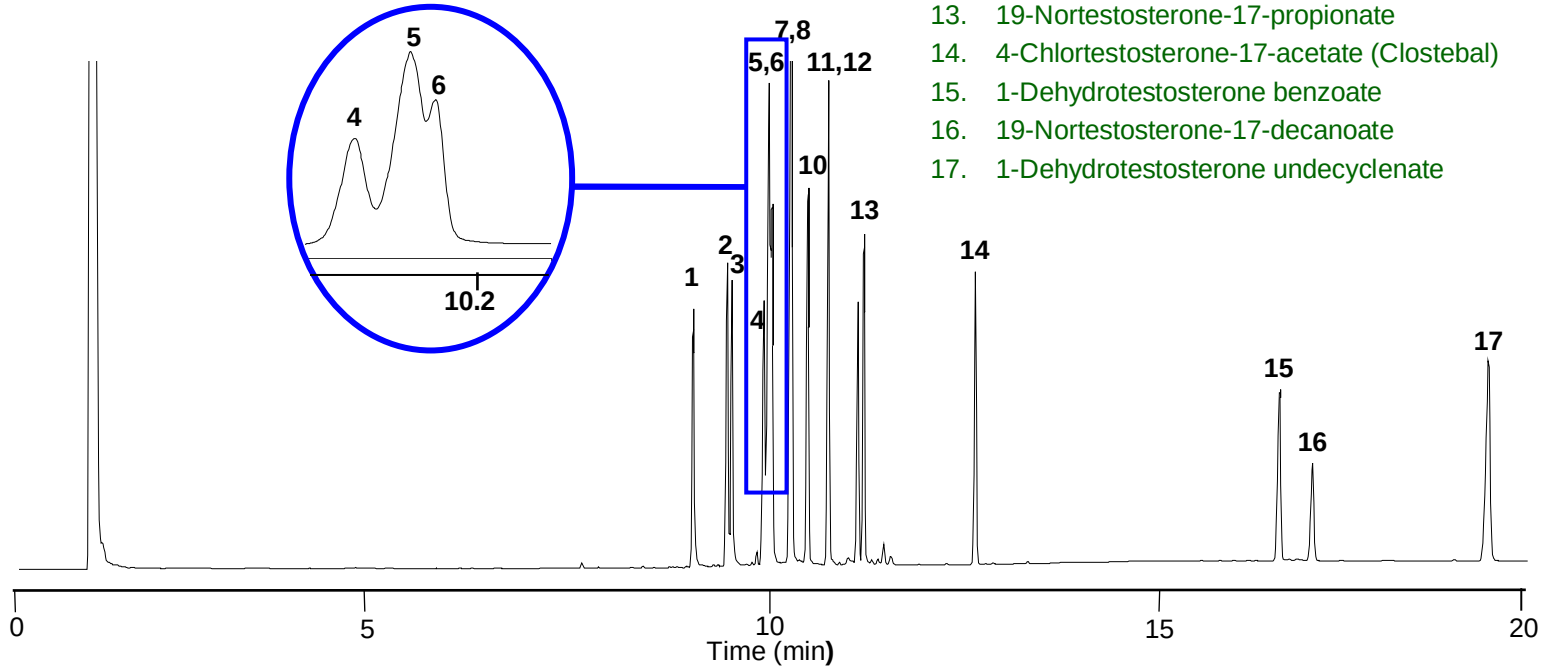
1. Nicotine
2. Caffeine
3. Glutethimide
4. Lidocaine
5. PCP
6. Phenobarbital
7. Methadone primary metabolite
8. Methaqualone
9. Methadone
10. Cocaine
11. Desipramine
12. Carbazepine
13. Trimipramine
14. Heroin
15. Fentanyl
16. Ibogaine
17. Triazolam
18. LSD



Anabolic Steroids

Column: **DB-1ms**
30 m x 0.25 mm I.D., 0.25 µm
J&W P/N: **122-0132**
Carrier: Helium at 40 cm/sec, measured at 180°C
Oven: 180-320°C at 10°/min
320° for 4 min
Injector: Split 1:40,
Sample: 2 µL of 0.125 µg/µL each in Methanol
Detector: FID, Nitrogen makeup gas at 30 mL/min

1. Dehydroisoandrosterone (Prasterone)
2. 5α-Androstan-17α-ol-3-one (Stanolone)
3. 19-Nortestosterone (Nandrolone)
4. Mesterolone
5. 17α-epi-testosterone
6. Testosterone
7. 1-Dehydrotestosterone (Boldenone)
8. 17α-Methyltestosterone
9. 1-Dehysro-17α-methyltestosterone (Methandrostenolone)
10. Norethandrolone
11. 1-Dehydrotestosterone acetate
12. Oxymetholone
13. 19-Nortestosterone-17-propionate
14. 4-Chlortestosterone-17-acetate (Clostebal)
15. 1-Dehydrotestosterone benzoate
16. 19-Nortestosterone-17-decanoate
17. 1-Dehydrotestosterone undecyclenate



C743

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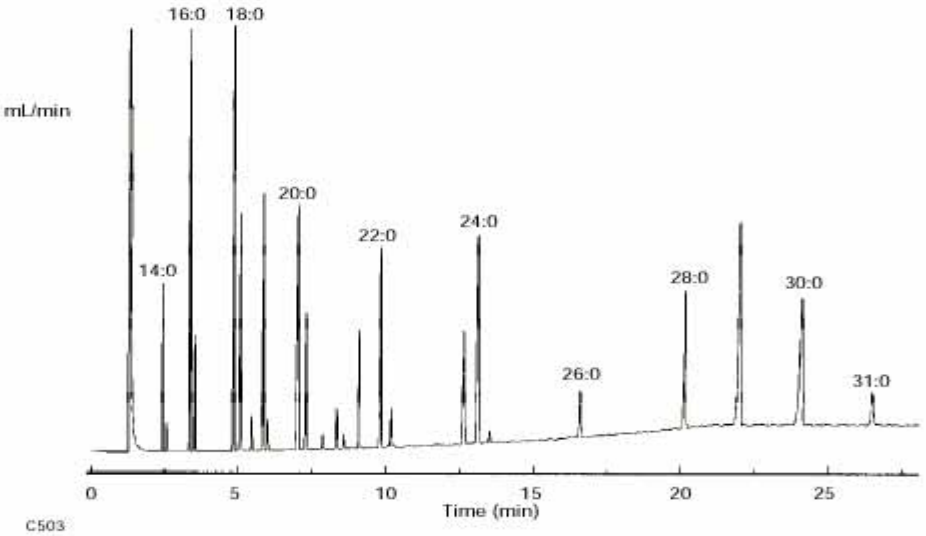
Dial 1-816-650-0621 for e-Seminar Audio

Increased upper temperature limit extends analyses to run less volatile compounds, and reduces run times through higher final temperature

DB-225ms
Lower Bleed - Higher MAOT

FAMEs

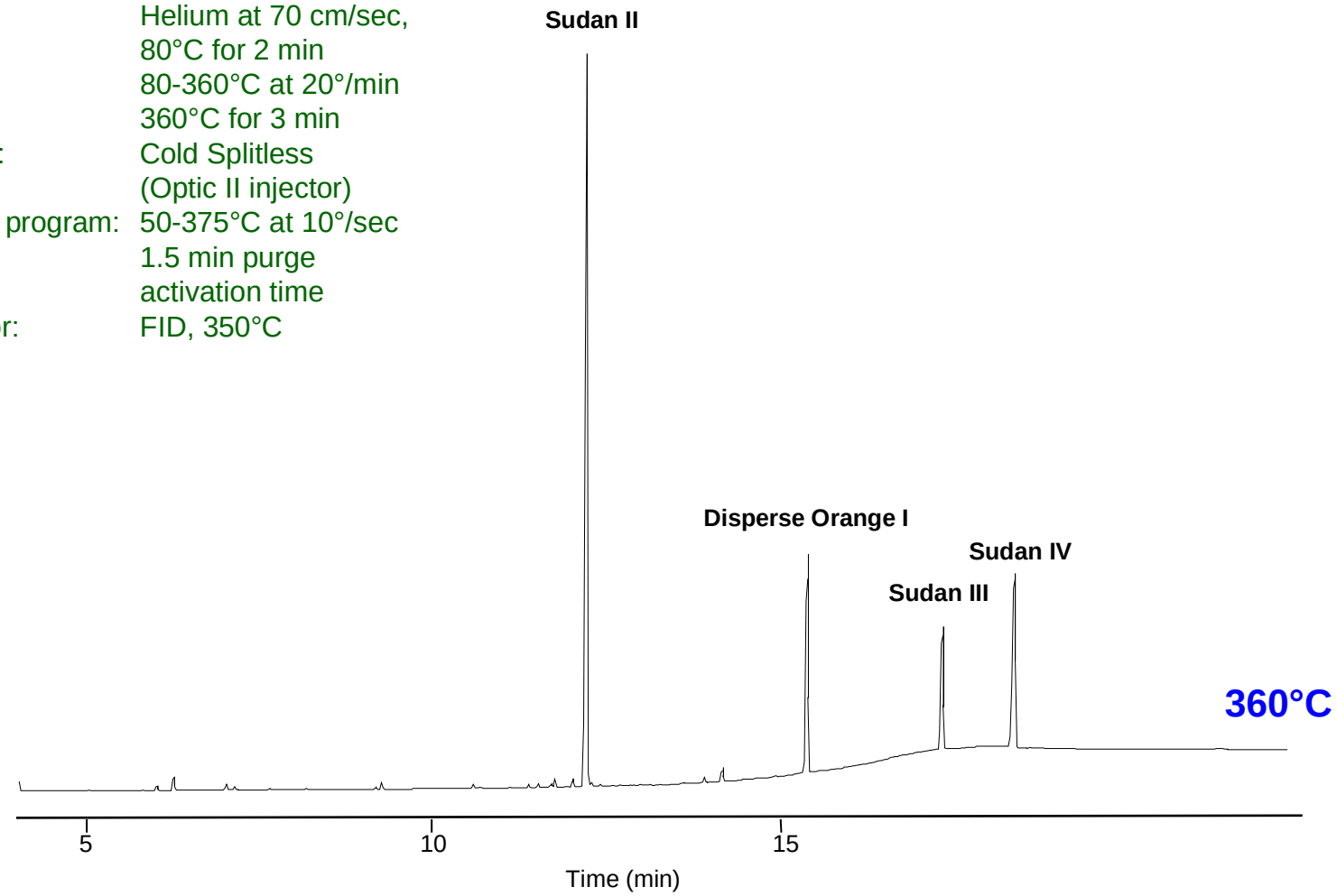
Column:	**DB-225ms**
	30 m x 0.25 mm I.D., 0.25 µm
J&W P/N:	**122-2932**
Carrier:	Hydrogen at 40 cm/sec
Oven:	200°C for 1 min
	200-260°C at 3°/min
Injector:	Split 1:50, 250°C
Detector:	FID
	Nitrogen make-up gas at 30 mL/min



The higher isothermal upper temperature limit of DB-225ms (260°C vs. 220°C for DB-225) allows the elution of higher molecular weight FAMEs (above 24:0) while maintaining a reasonable run time.

AZO Dyes

Column:	**DB-1ms**
	30 m x 0.25 mm I.D., 0.25 µm
J&W P/N:	**122-0132**
Carrier:	Helium at 70 cm/sec,
Oven:	80°C for 2 min
	80-360°C at 20°/min
	360°C for 3 min
Injector:	Cold Splitless
	(Optic II injector)
Injector program:	50-375°C at 10°/sec
	1.5 min purge
	activation time
Detector:	FID, 350°C

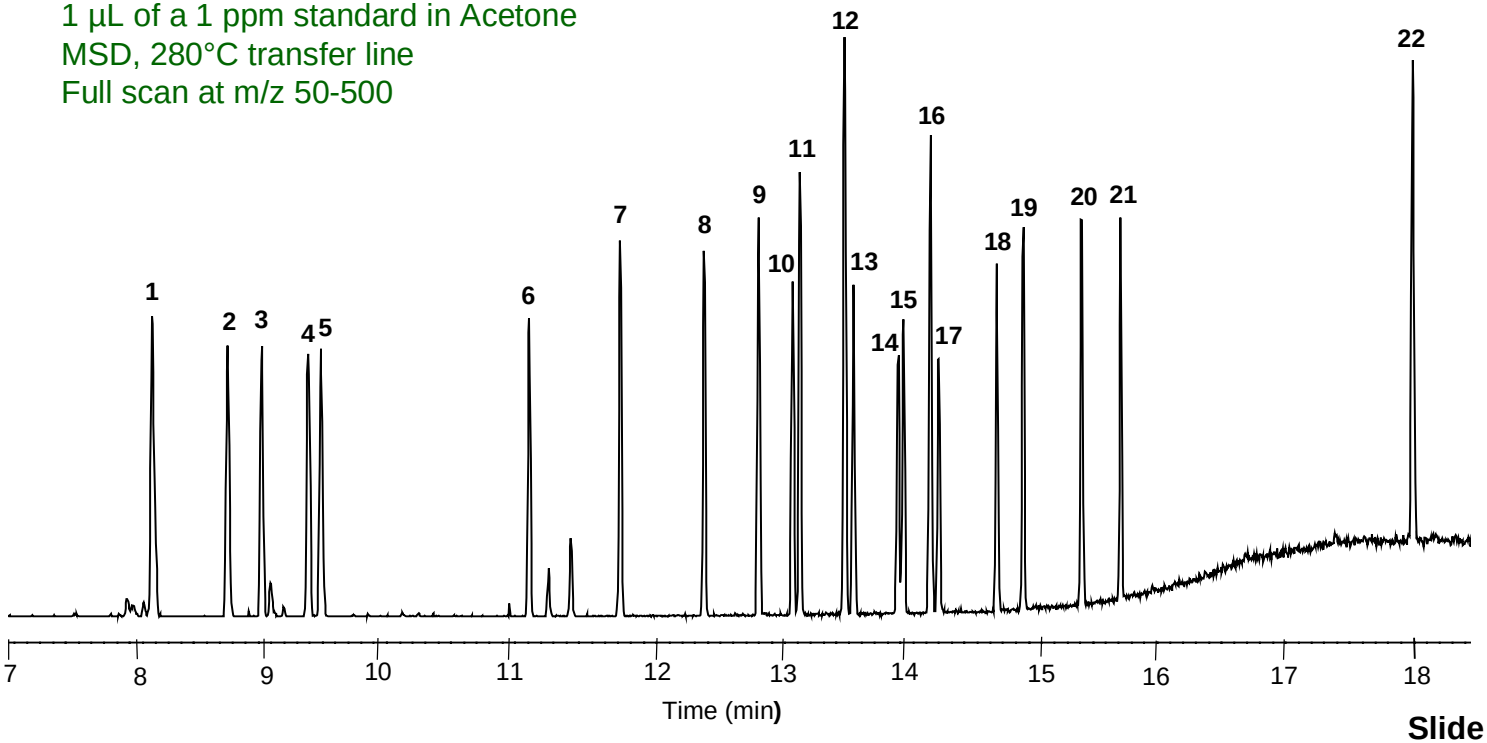


Greater inertness allows analysis of active and difficult to analyze compounds

CLP Pesticides

Column:	**DB-1ms**
	30 m x 0.25 mm I.D., 0.25 µm
J&W P/N:	**122-0132**
Carrier:	Helium at 45 cm/sec, constant flow mode
Oven:	110°C for 0.5 min 110-250°C at 10°/min 250-300°C at 25°/min 300°C for 2 min
Injector:	Splitless, 250°C 0.5 min purge activation time
Sample:	1 µL of a 1 ppm standard in Acetone
Detector:	MSD, 280°C transfer line Full scan at m/z 50-500

1. 2,4,5,6-Tetrachloro-m-xylene (IS)
2. α-BHC
3. β-BHC
4. γ-BHC
5. δ-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide
9. γ-Chlordane
10. Endosulfan I
11. α-Chlordane
12. 4,4´-DDE
13. Dieldrin
14. Endrin
15. Endosulfan II
16. 4,4´-DDD
17. Endrin aldehyde
18. Endosulfan aldehyde
19. 4,4´-DDT
20. Endrin ketone
21. Methoxychlor
22. Decachlorobiphenyl (IS)



C758

Organochlorine Pesticides (EPA Method 8081A)

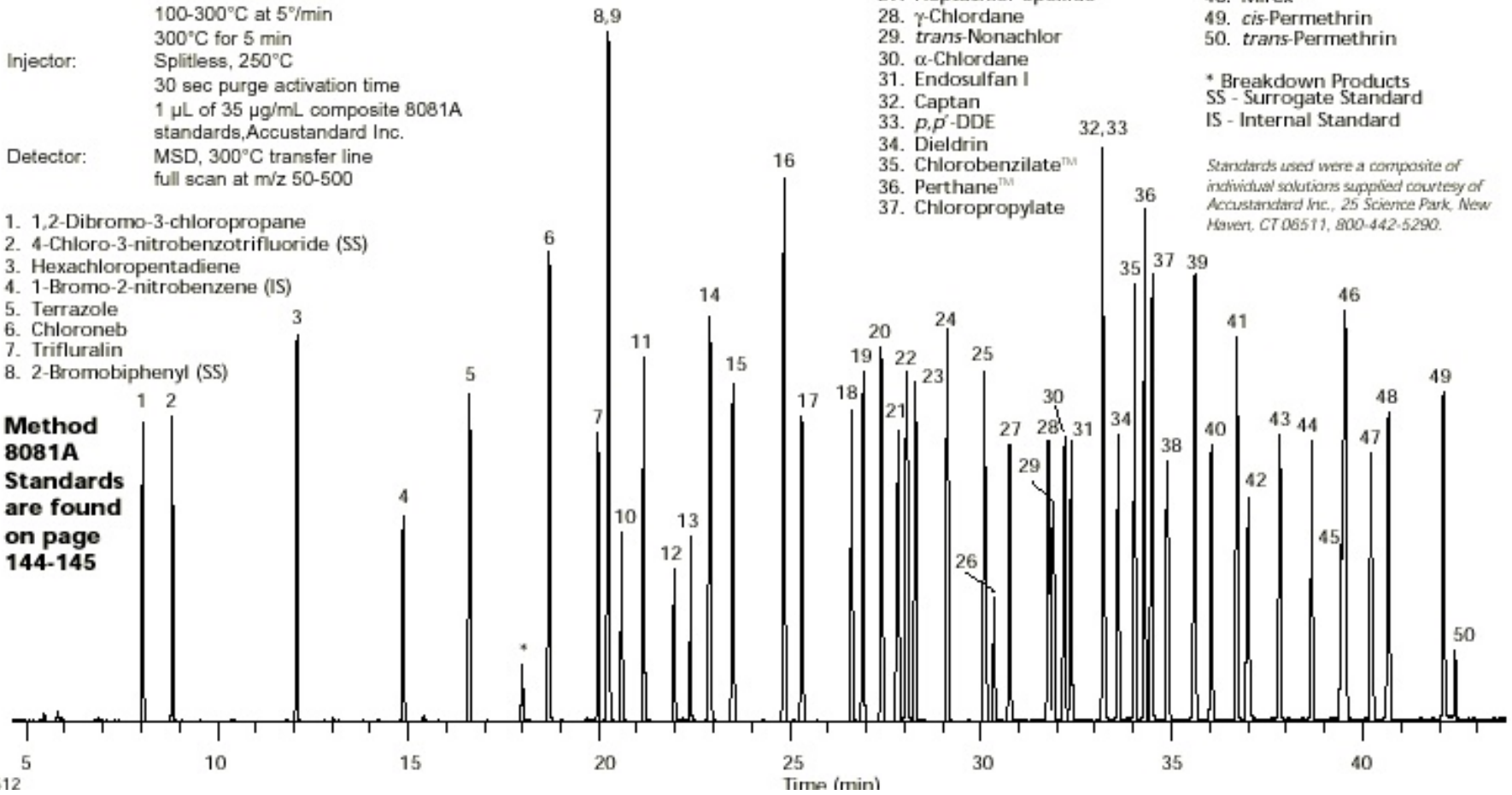
Column:	**DB-35ms**
	30 m x 0.25 mm I.D., 0.25 µm
J&W P/N:	**122-3832**
Carrier:	Helium at 35 cm/sec, measured at 50°C
Oven:	50°C for 1 min 50-100°C at 25°/min 100-300°C at 5°/min 300°C for 5 min
Injector:	Splitless, 250°C 30 sec purge activation time 1 µL of 35 µg/mL composite 8081A standards,Accustandard Inc.
Detector:	MSD, 300°C transfer line full scan at m/z 50-500

1. 1,2-Dibromo-3-chloropropane
2. 4-Chloro-3-nitrobenzotrifluoride (SS)
3. Hexachloropentadiene
4. 1-Bromo-2-nitrobenzene (IS)
5. Terrazole
6. Chloroneb
7. Trifluralin
8. 2-Bromobiphenyl (SS)
9. Tetrachloro-m-xylene (SS)
10. α, α-Dibromo-m-xylene
11. Propachlor
12. Di-allate A
13. Di-allate B
14. Hexachlorobenzene
15. α-BHC
16. Pentachloronitrobenzene (IS)
17. γ-BHC
18. β-BHC
19. Heptachlor
20. Alachlor
21. δ-BHC
22. Chlorothalonil
23. Aldrin
24. Dacthal™
25. Isodrin
26. Kelthane
27. Heptachlor epoxide
28. γ-Chlordane
29. *trans*-Nonachlor
30. α-Chlordane
31. Endosulfan I
32. Captan
33. *p,p'*-DDE
34. Dieldrin
35. Chlorobenzilate™
36. Perthane™
37. Chloropropylate
38. Endrin
39. *p,p'*-DDD
40. Endosulfan II
41. *p,p'*-DDT
42. Endrin aldehyde
43. Endosulfan sulfate
44. Dibutylchlorendate (SS)
45. Captafol
46. Methoxychlor
47. Endrin ketone
48. Mirex™
49. *cis*-Permethrin
50. *trans*-Permethrin

* Breakdown Products
SS - Surrogate Standard
IS - Internal Standard

Standards used were a composite of individual solutions supplied courtesy of Accustandard Inc., 25 Science Park, New Haven, CT 06511, 800-442-5290.

Method 8081A Standards are found on page 144-145



C512

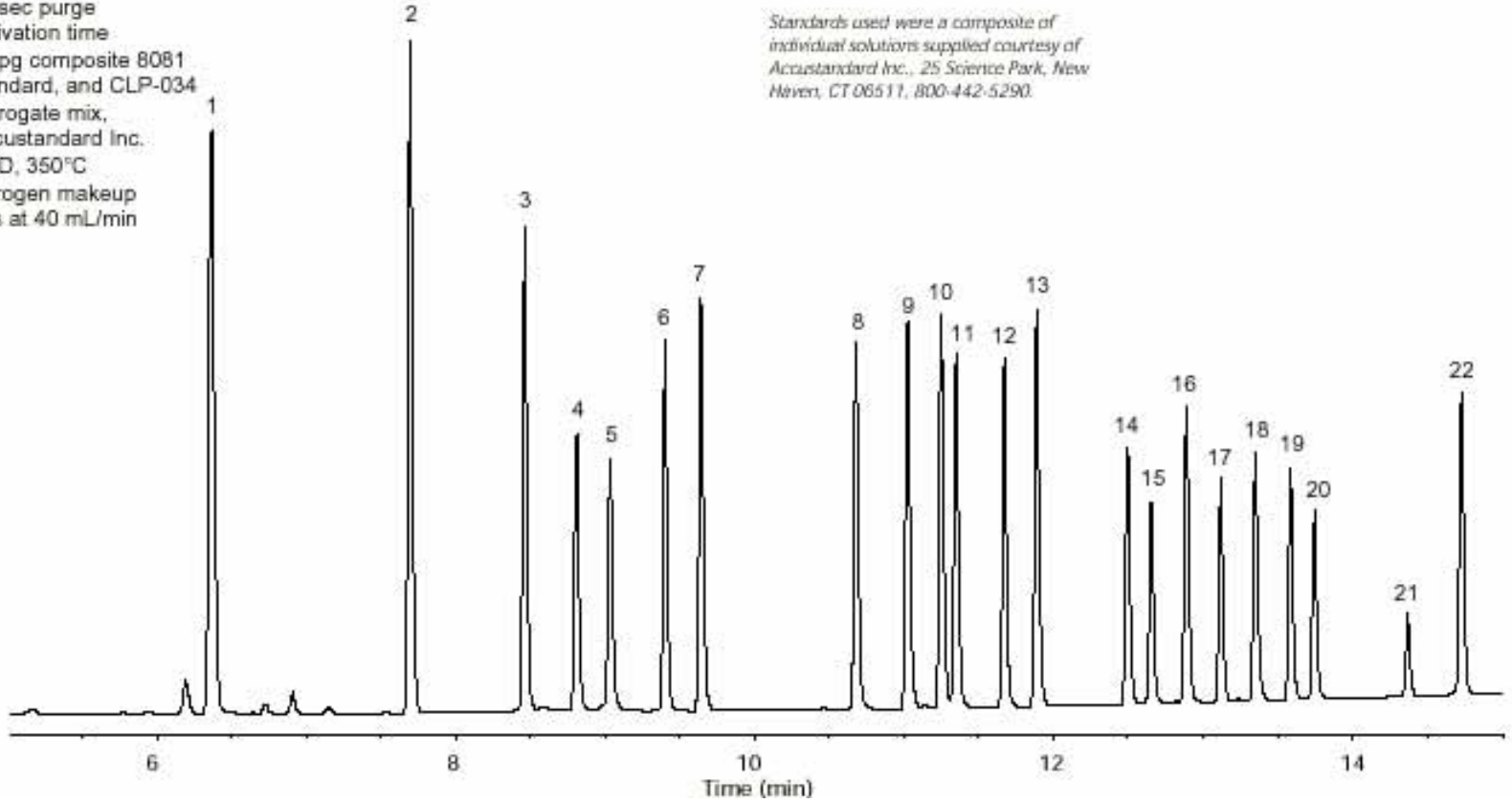
CLP Pesticides

Column: **DB-17ms**
30 m x 0.25 mm I.D., 0.25 µm
J&W P/N: **122-4732**
Carrier: Helium at 45 cm/sec, measured at 110°C
Oven: 110°C for 0.5 min
110-150°C at 25°/min
150-260°C at 12°/min
260-320°C at 15°/min
320°C for 2 min
Injector: Splitless, 250°C
30 sec purge activation time
50 pg composite 8081 standard, and CLP-034 surrogate mix, Accustandard Inc.
Detector: ECD, 350°C
Nitrogen makeup gas at 40 mL/min

1. Tetrachloro-m-xylene (SS)
2. α-BHC
3. γ-BHC
4. β-BHC
5. Heptachlor
6. δ-BHC
7. Aldrin
8. Heptachlor epoxide
9. γ-Chlordane
10. α-Chlordane
11. Endosulfan I
12. *p, p'*-DDE
13. Dieldrin
14. Endrin
15. *p, p'*-DDD
16. Endosulfan II
17. *p, p'*-DDT
18. Endrin aldehyde
19. Endosulfan sulfate
20. Dibutylchlorendate (SS)
21. Methoxychlor
22. Endrin ketone

SS - Surrogate Standard

Standards used were a composite of individual solutions supplied courtesy of Accustandard Inc., 25 Science Park, New Haven, CT 06511, 800-442-5290.

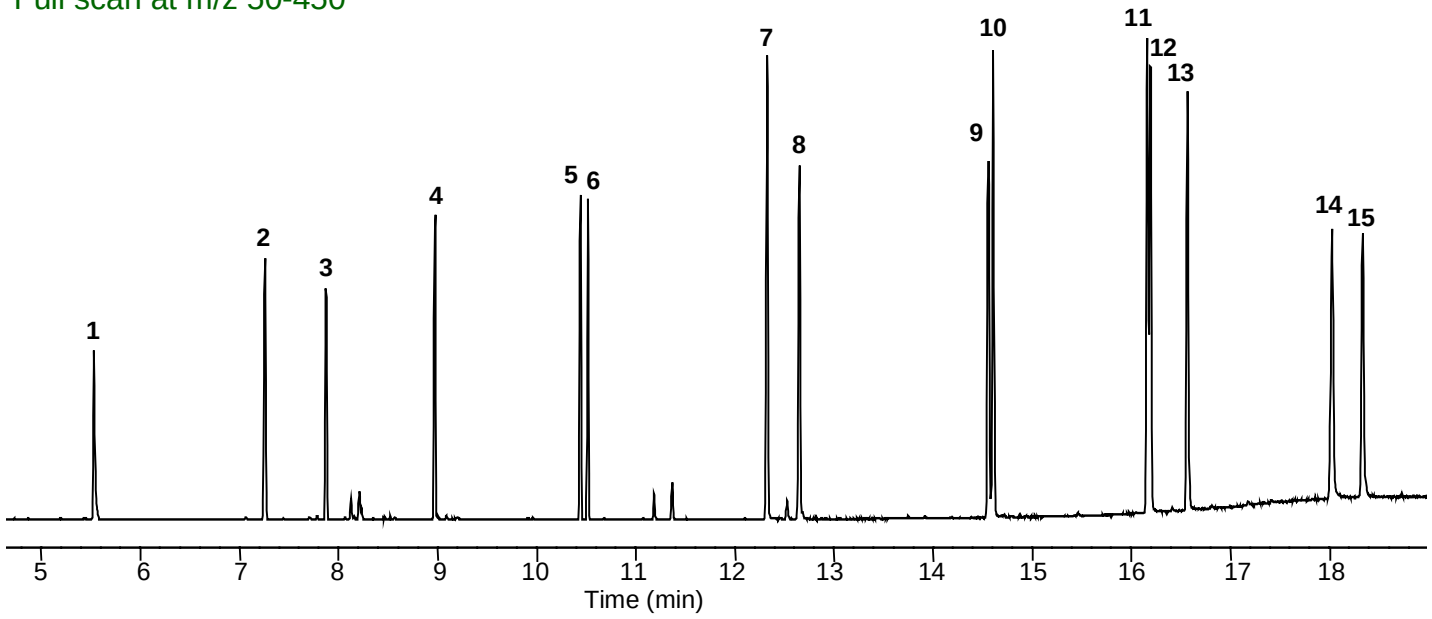


C510

PAHs

Column:	**DB-1ms**
	30 m x 0.25 mm I.D., 0.25 µm
J&W P/N:	**122-0132**
Carrier:	Helium at 40 cm/sec, constant flow mode
Oven:	80°C for 1 min 80-325°C at 15°/min 325°C at 2°/min
Injector:	Splitless, 300°C 0.8 min purge activation time
Sample:	1 µL of a 5 ppm standard in Toluene
Detector:	MSD, 325°C transfer line Full scan at m/z 50-450

1. Naphthalene
2. Acenaphthene
3. Acenaphthylene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(a)anthracene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Dibenz(a,h)anthracene
15. Benzo(g,h,l)perylene



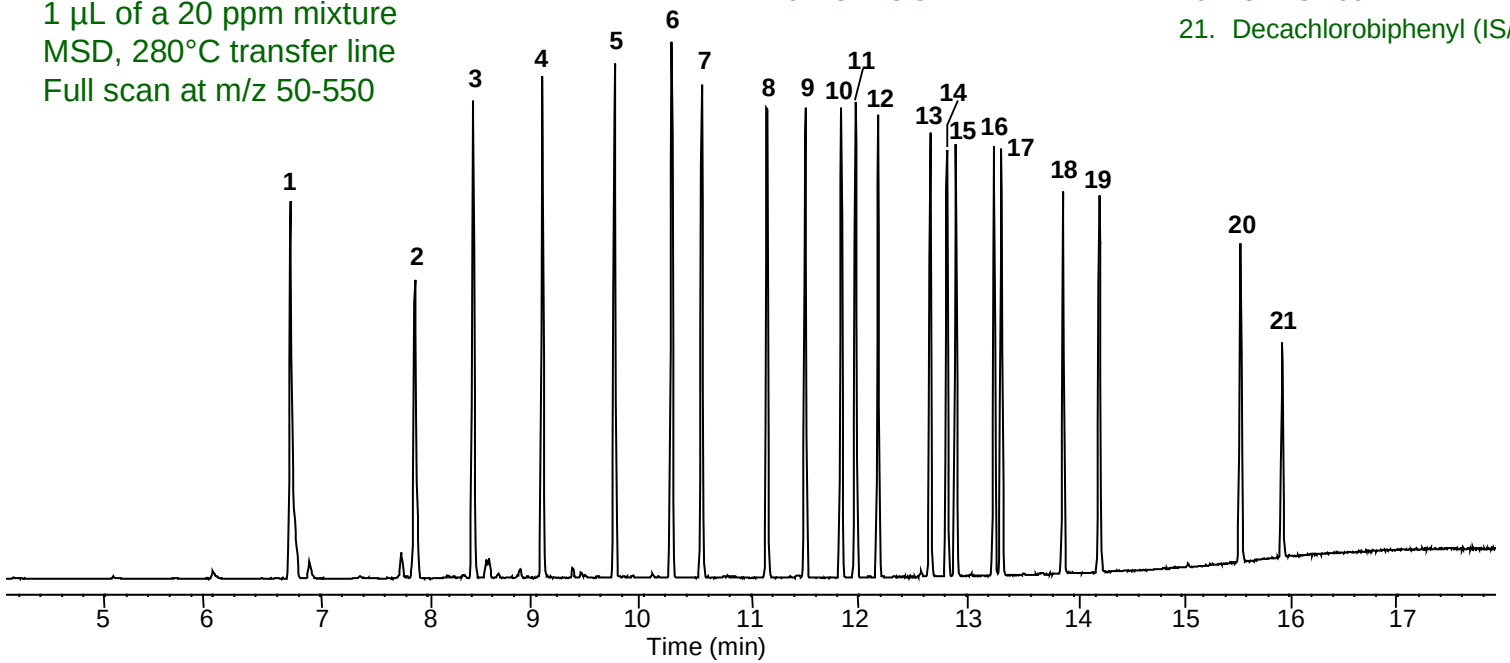
C757

EPA Method 8082 PCB Congeners

Column: **DB-1ms**
30 m x 0.25 mm I.D., 0.25 µm
J&W P/N: **122-0132**
Carrier: Helium at 46 cm/sec, measured at 100°C, constant pressure mode
Oven: 100°C for 0.8 min
100-325°C at 15°/min
325°C at 2°/min
Injector: Splitless, 275°C
0.8 min purge activation time
Sample: 1 µL of a 20 ppm mixture
Detector: MSD, 280°C transfer line
Full scan at m/z 50-550

(PCB congeners are listed by their IUPAC numbers)

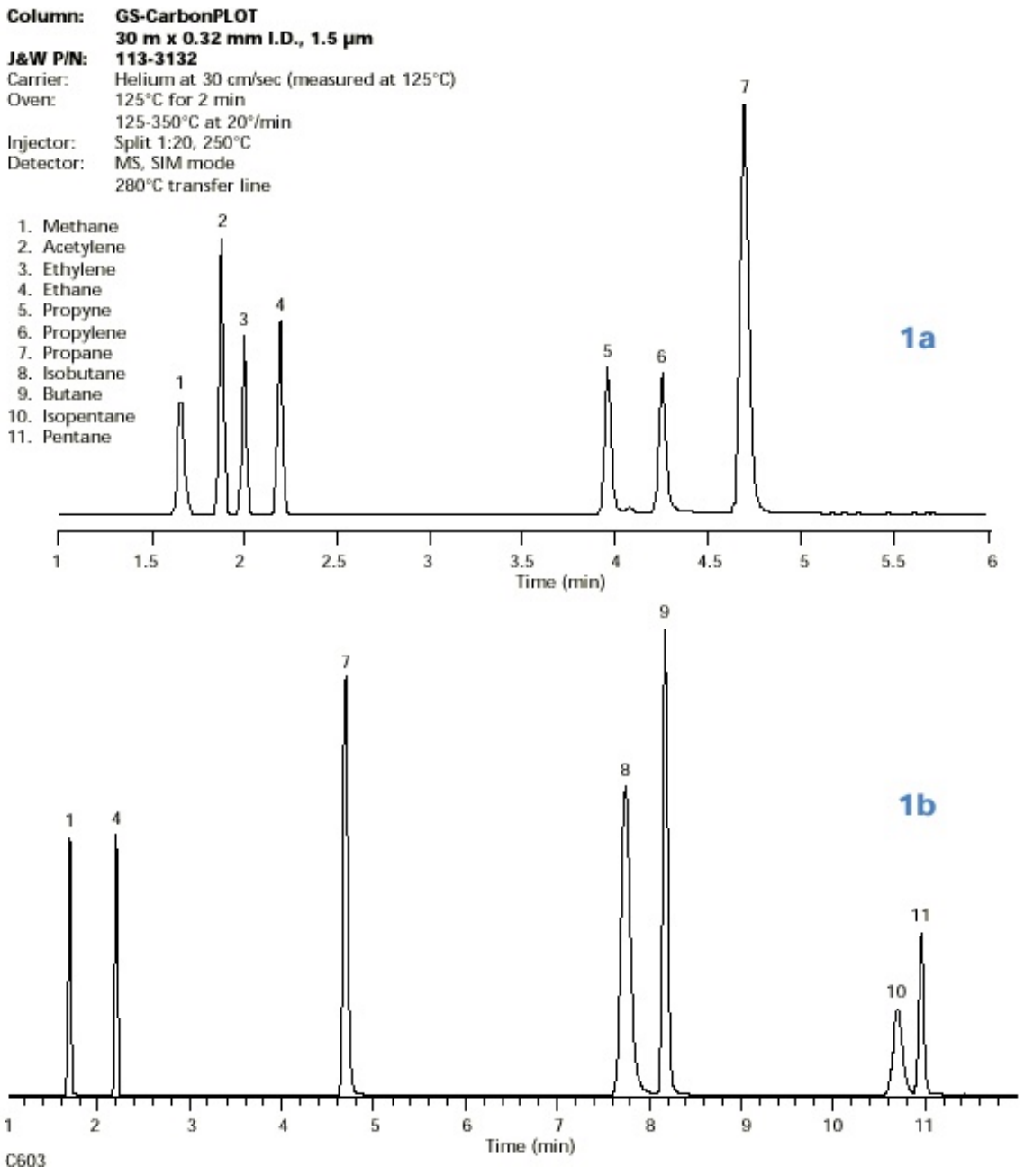
1. IUPAC 1
2. Tetrachloro-m-xylene (IS/SS)
3. IUPAC 5
4. IUPAC 18
5. IUPAC 31
6. IUPAC 52
7. IUPAC 44
8. IUPAC 66
9. IUPAC 101
10. IUPAC 87
11. IUPAC 110
12. IUPAC 151
13. IUPAC 153
14. IUPAC 141
15. IUPAC 137
16. IUPAC 187
17. IUPAC 183
18. IUPAC 180
19. IUPAC 170
20. IUPAC 206
21. Decachlorobiphenyl (IS/SS)



C761

Dial 1-816-650-0621 for e-Seminar Audio

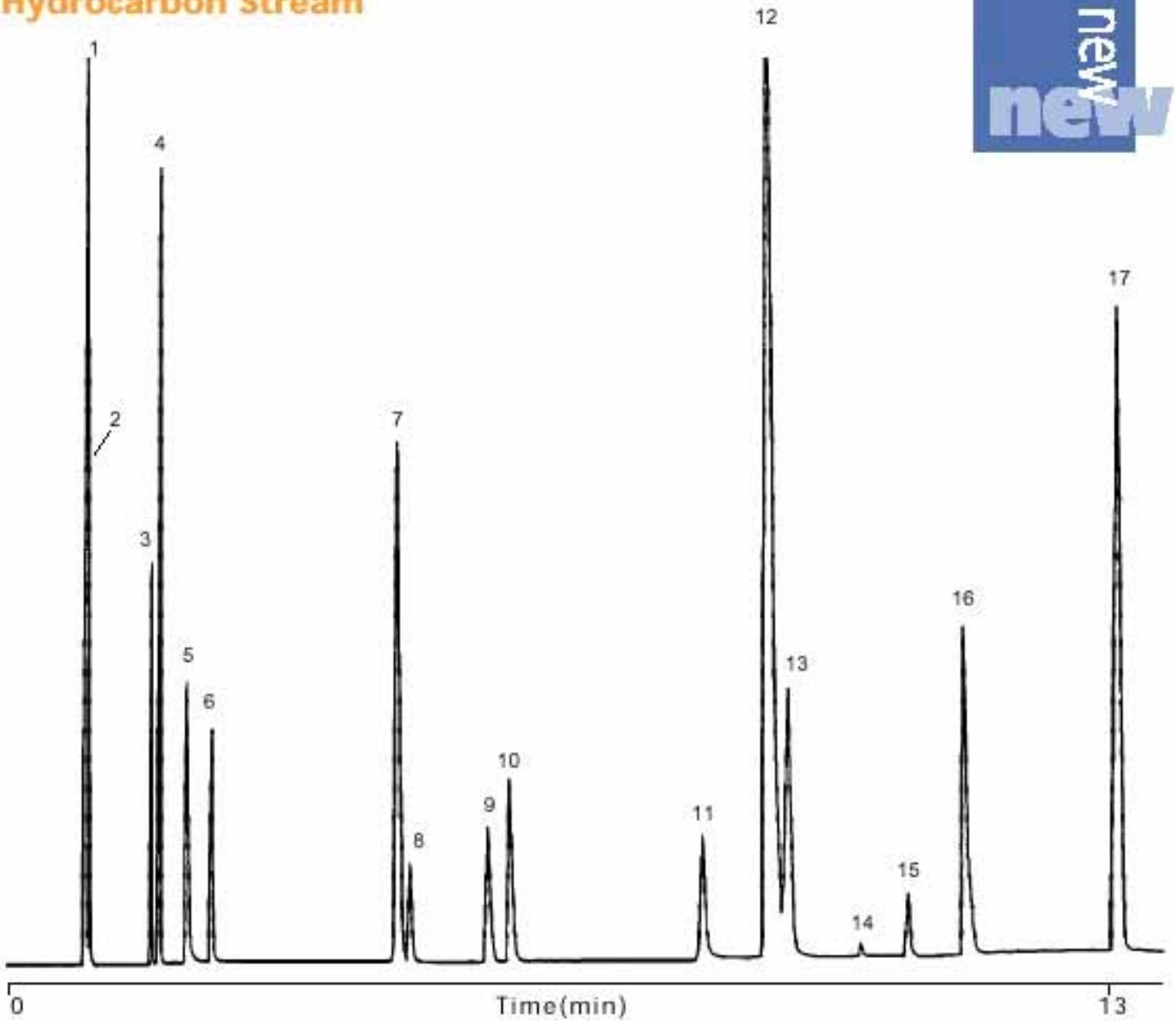
“MS”-grade PLOT columns allow analysis of permanent gases and other highly volatile compounds


Column: GS-CarbonPLOT
30 m x 0.32 mm I.D., 1.5 µm
J&W P/N: 113-3132
Carrier: Helium at 30 cm/sec (measured at 125°C)
Oven: 125°C for 2 min
125-350°C at 20°/min
Injector: Split 1:20, 250°C
Detector: MS, SIM mode
280°C transfer line
1. Methane
2. Acetylene
3. Ethylene
4. Ethane
5. Propyne
6. Propylene
7. Propane
8. Isobutane
9. Butane
10. Isopentane
11. Pentane
1a
1b
Time (min)
Time (min)
C603

Sulfur Gases in Light Hydrocarbon Stream

Column: **GS-GasPro**
30 m x 0.32 mm I.D.
J&W P/N: **113-4332**
Carrier: Helium at 53 cm/sec
Oven: 25°C for 4 min
25 - 200°C at 10°/min
200°C Hold
Injector: 200 µL
Detector: TCD

1. Nitrogen
2. Methane
3. Ethane
4. CO_2
5. SF_6
6. Ethylene
7. COS
8. Acetylene
9. Propane
10. H_2S
11. Ethylene oxide/cyclopropane
12. Propylene
13. Propadiene
14. Isobutane
15. Butane
16. SO_2
17. Methyl acetylene



C579

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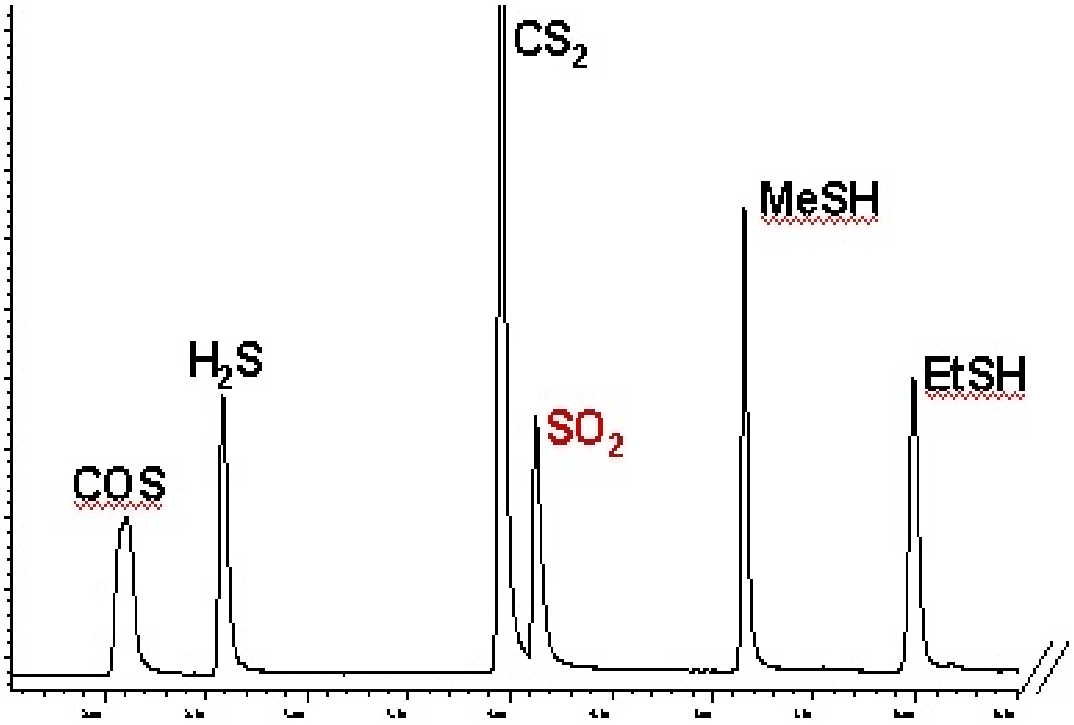
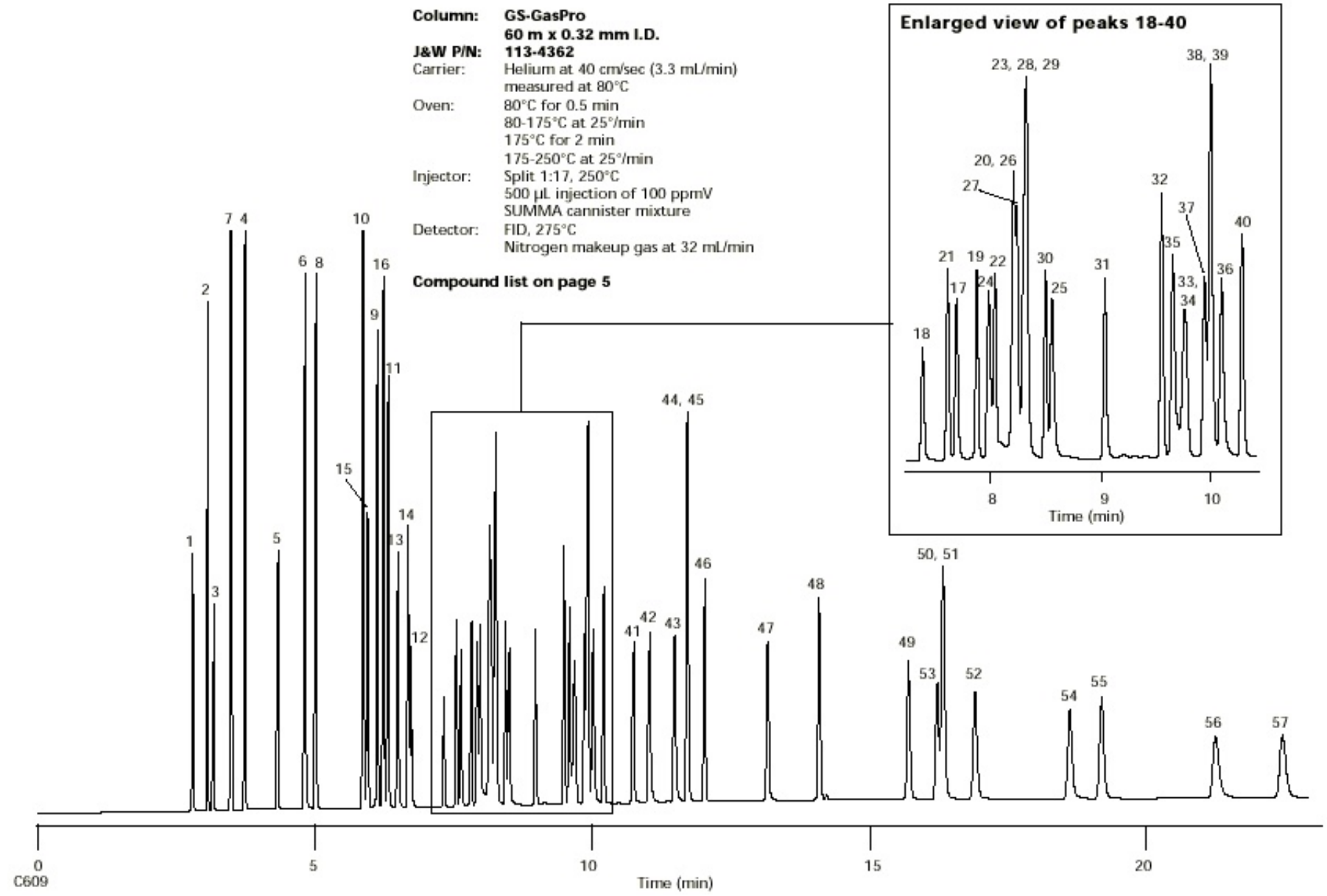
Dial 1-816-650-0621 for e-Seminar Audio

Column: **GS-GasPro**
5 m x 0.32 mm I.D.
Injector: Gas sample valve, 1.0 mL fixed sample loop
Detector: Sievers SCD, reaction tube 800°C
Carrier: Helium, 39 cm/sec at 0°C (determined by T_R of COS)
Oven: 0°C for 1 min, 30° / min to 160°C, hold at 160°C for 4 min,
50° / min to 260°C, hold at 260°C for 5 min



SO_2 = 100 ppbV
others = 89 ppbV



Agilent Technologies

Dial 1-816-650-0621 for e-Seminar Audio

Summary

Low bleed columns are available in a wide range of selectivities, including DB-1ms that provides virtually identical retention to 100% DMPS, and PLOT columns with remarkably low bleed.

Wrap-up E-Seminar Questions

Thank you for attending Agilent e-Seminars. Our e-Seminar schedule is expanding every week. Please check our website frequently at:

www.agilent.com