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**Separation Science Application Note**

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# High-Speed Analysis of Pesticides Using Application-Specific Chromatographic Columns and Time of Flight Mass Spectrometry

Frank L. Dorman, Eric J. Reiner, and  
Jack Cochran

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# Advantages of Fast GC

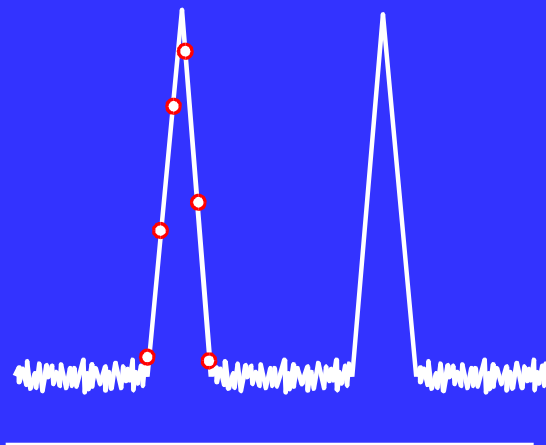
- Shorter Column lengths, faster ramp rates
  - Increased sample throughput
- Smaller column I.d., faster ramp rates
  - Narrower peak width
  - More plates/meter
  - Lower carrier flow rates
  - Higher column head pressures

# Disadvantages of Fast GC

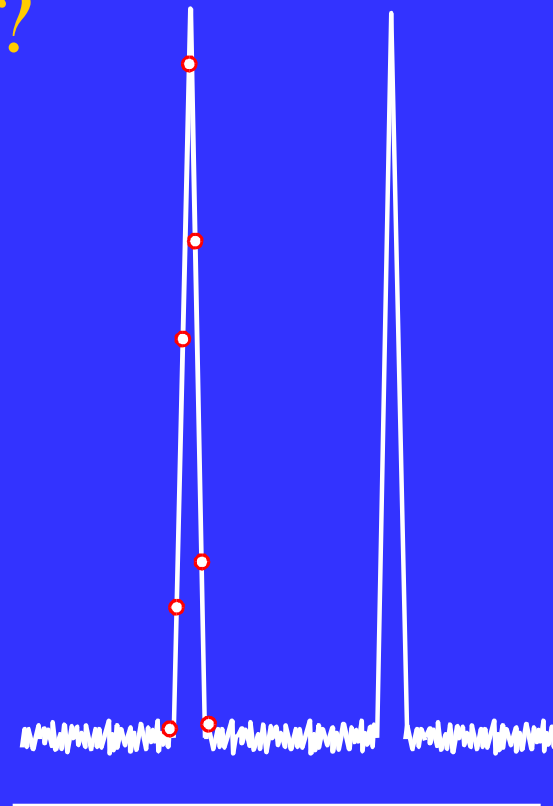
- Smaller column IDs
  - Lower column capacity – can require injection modification, and extract cleanup
- Narrower peak width
  - Places demands on detection systems
- Fast GC has not been accepted as much as academic literature would imply, mainly due to limitations of detection systems



How many data points are necessary to correctly characterize a chromatographic peak?

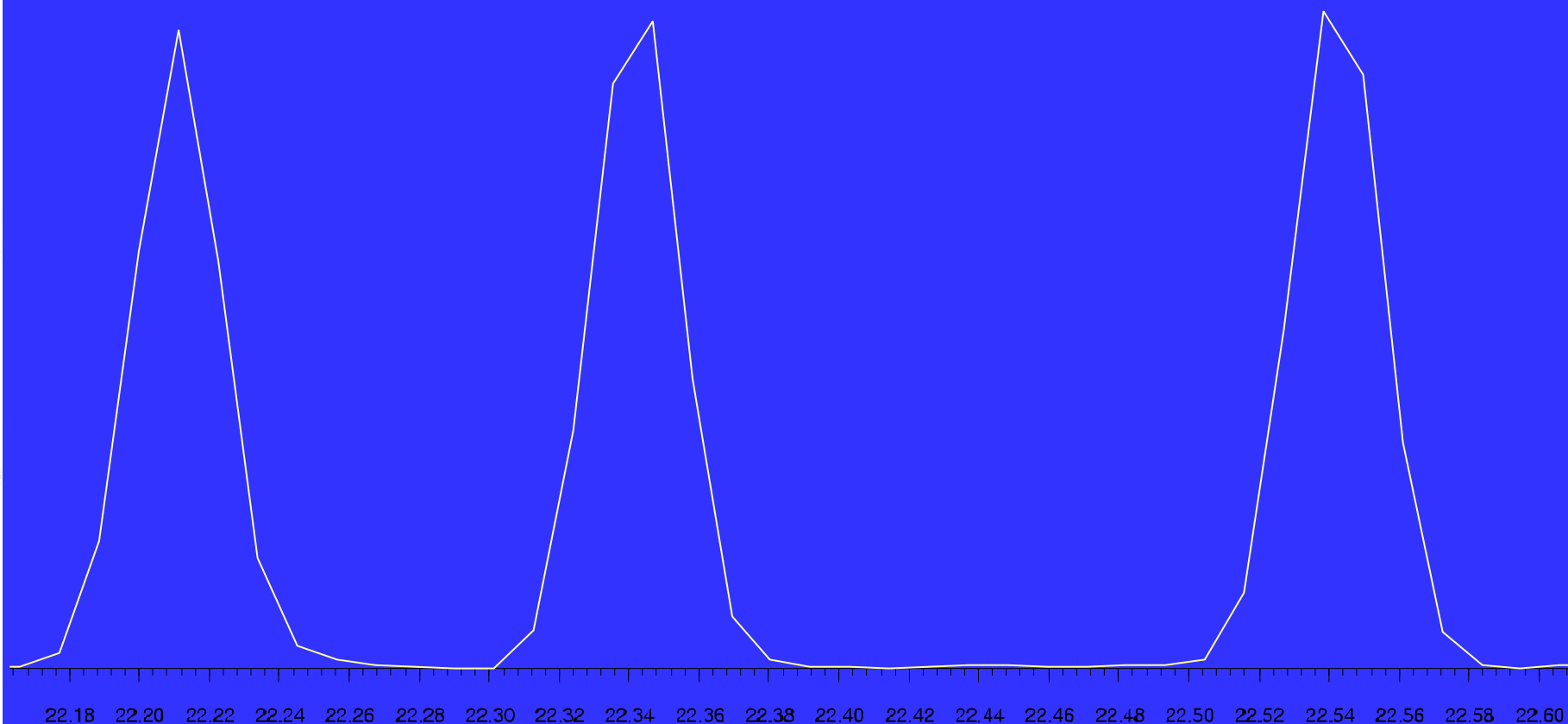


Minutes

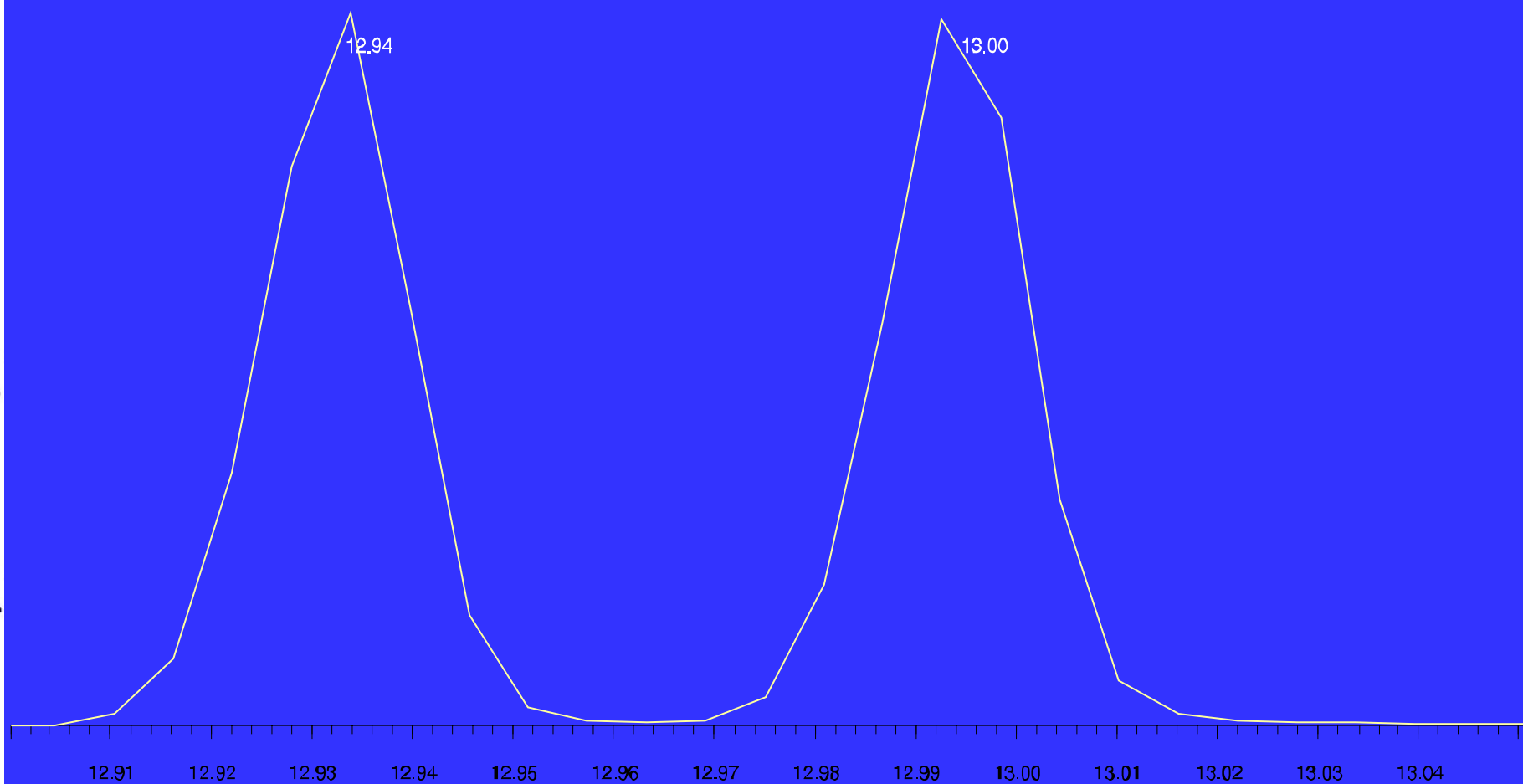


Seconds

# Sampling Frequency Limitations of Quadrupoles and Ion Traps Can Cause Peak Biasing



# Peak Biasing...

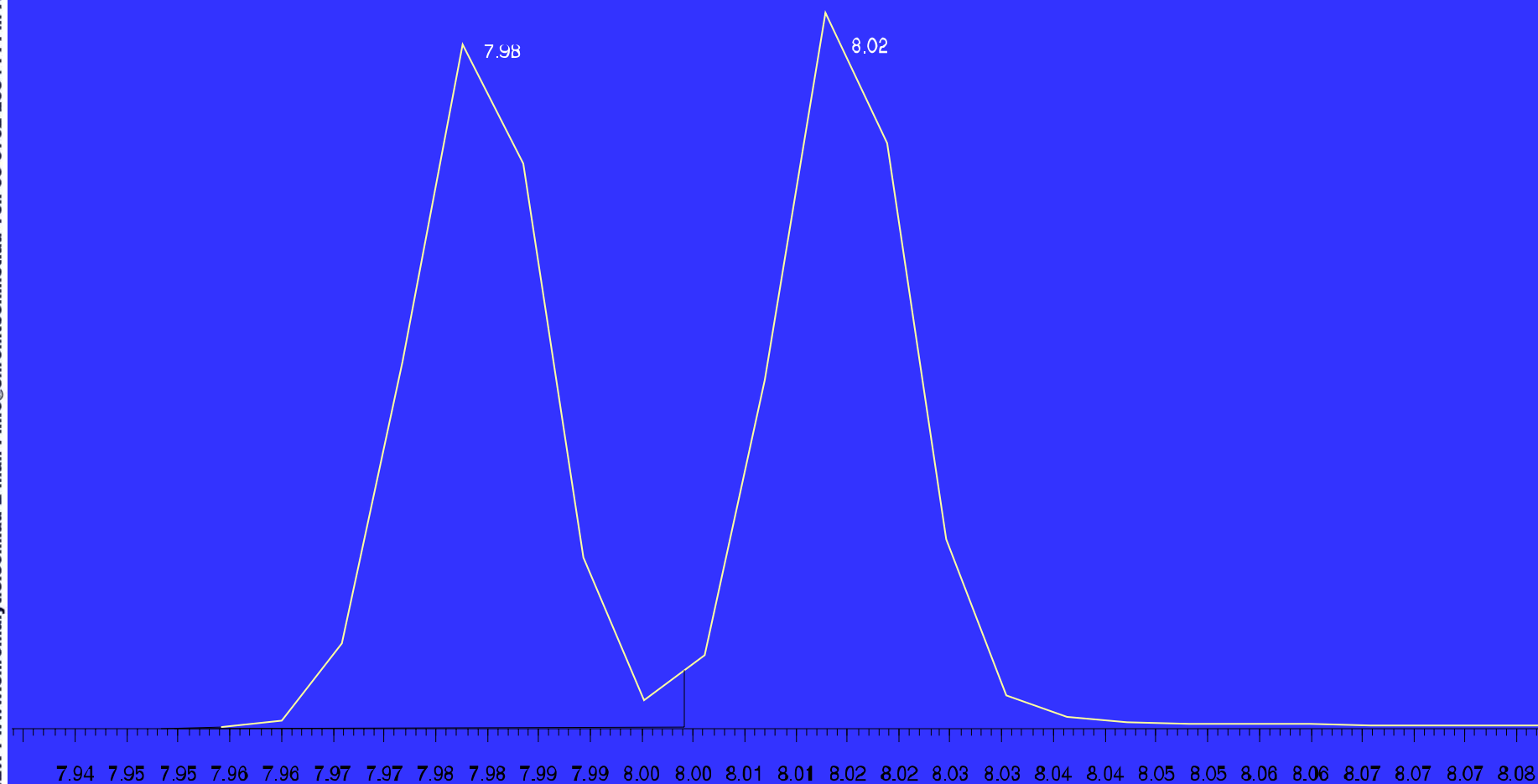


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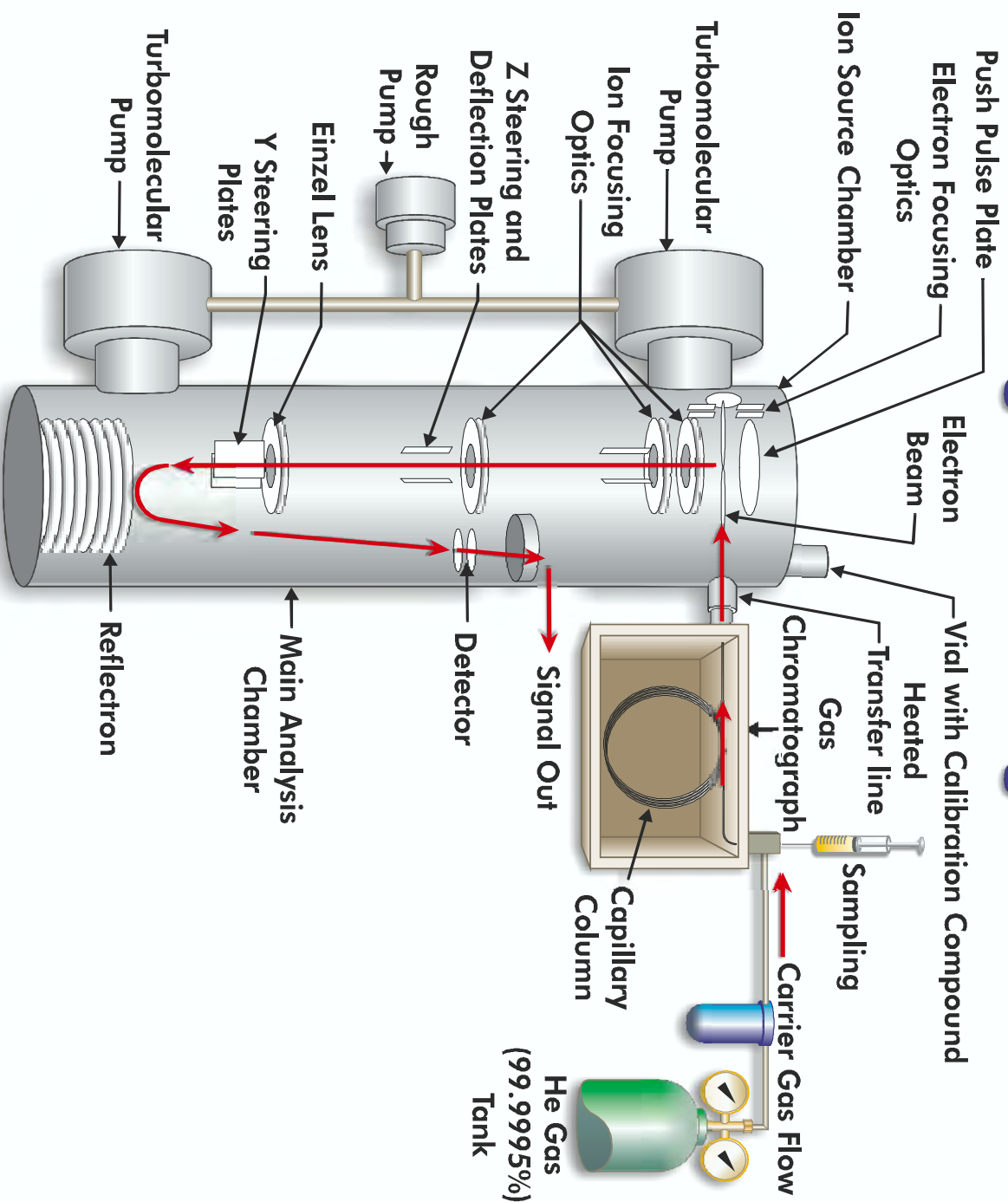
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# Peak Biasing...



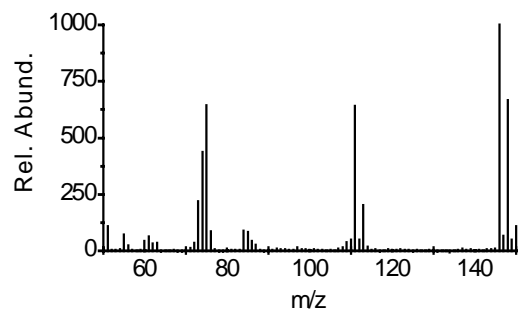
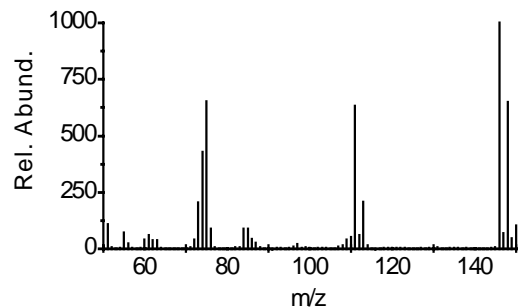
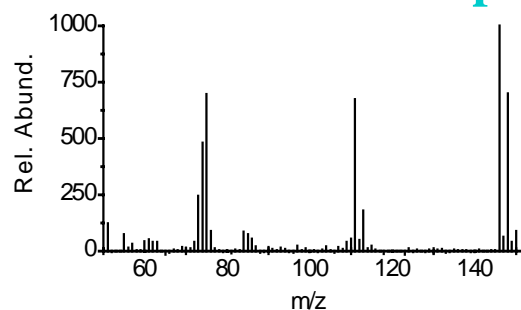
# Pegasus II Diagram



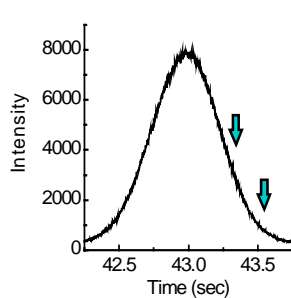
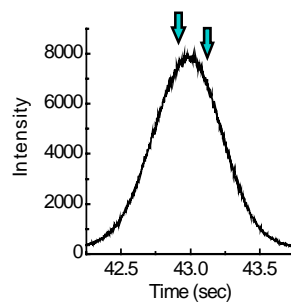
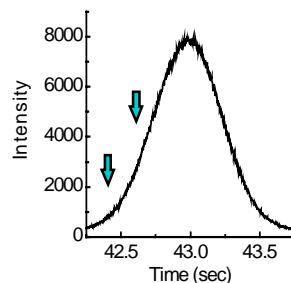
# Spectra - TOF vs. Scanning MS

TOF Ion Ratios Vary Less Than 1% Across the Peak

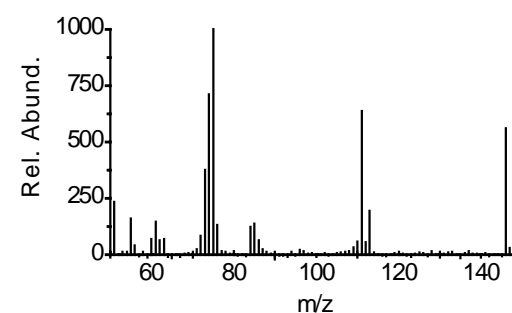
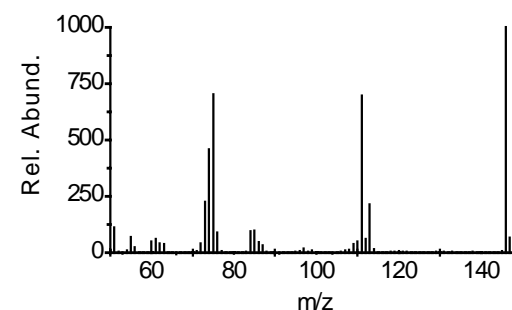
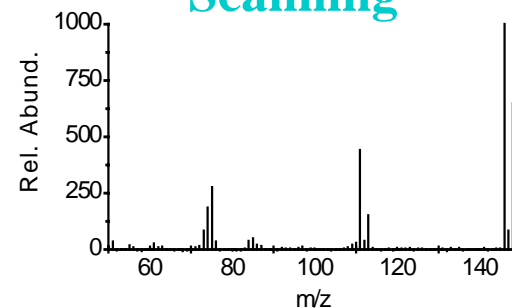
## Simultaneous Sampling



## GC Peak



## Scanning

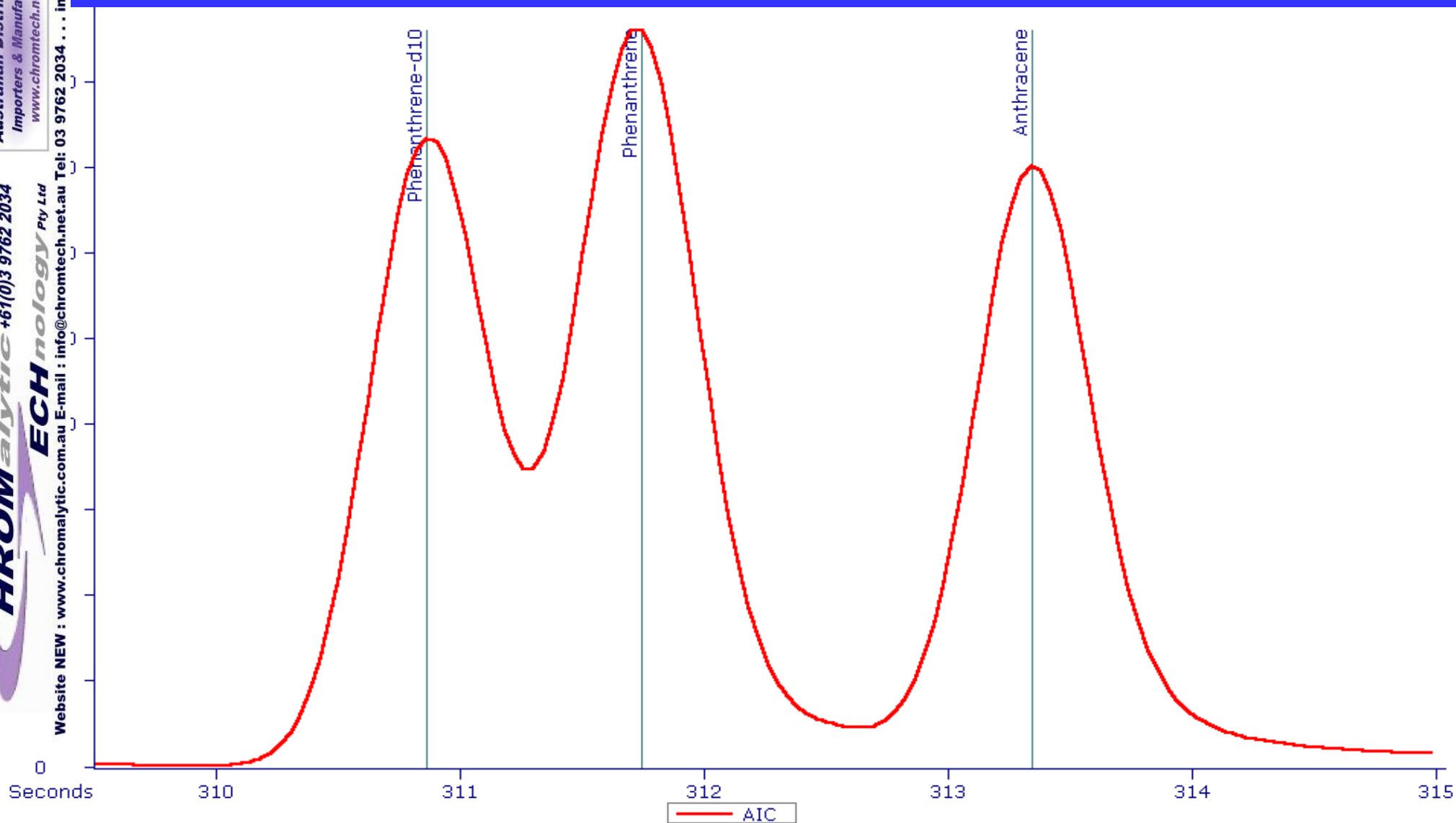


# PAH Standard – AIC

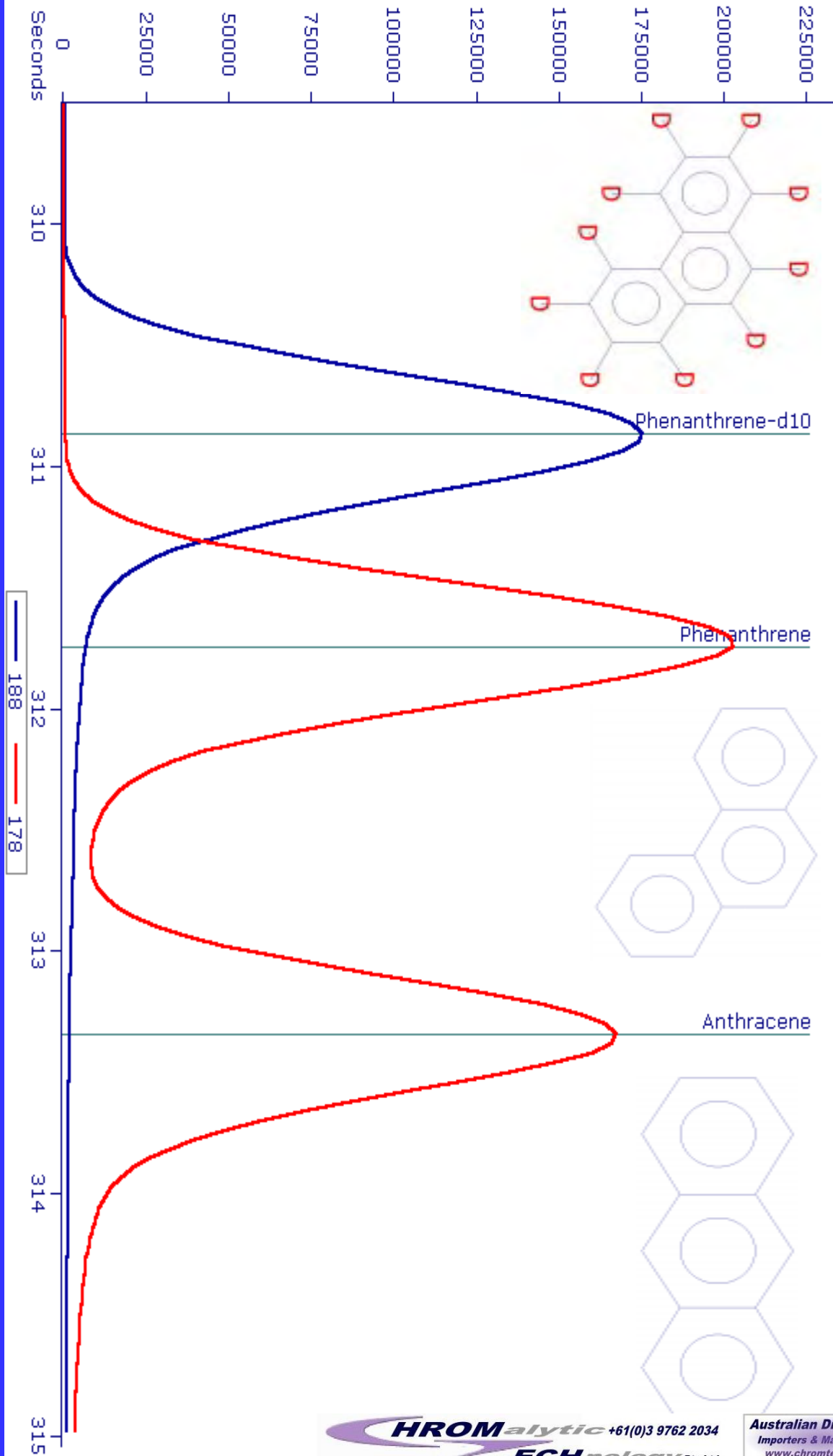
## D10-Phenanthrene, Phenanthrene, Anthracene

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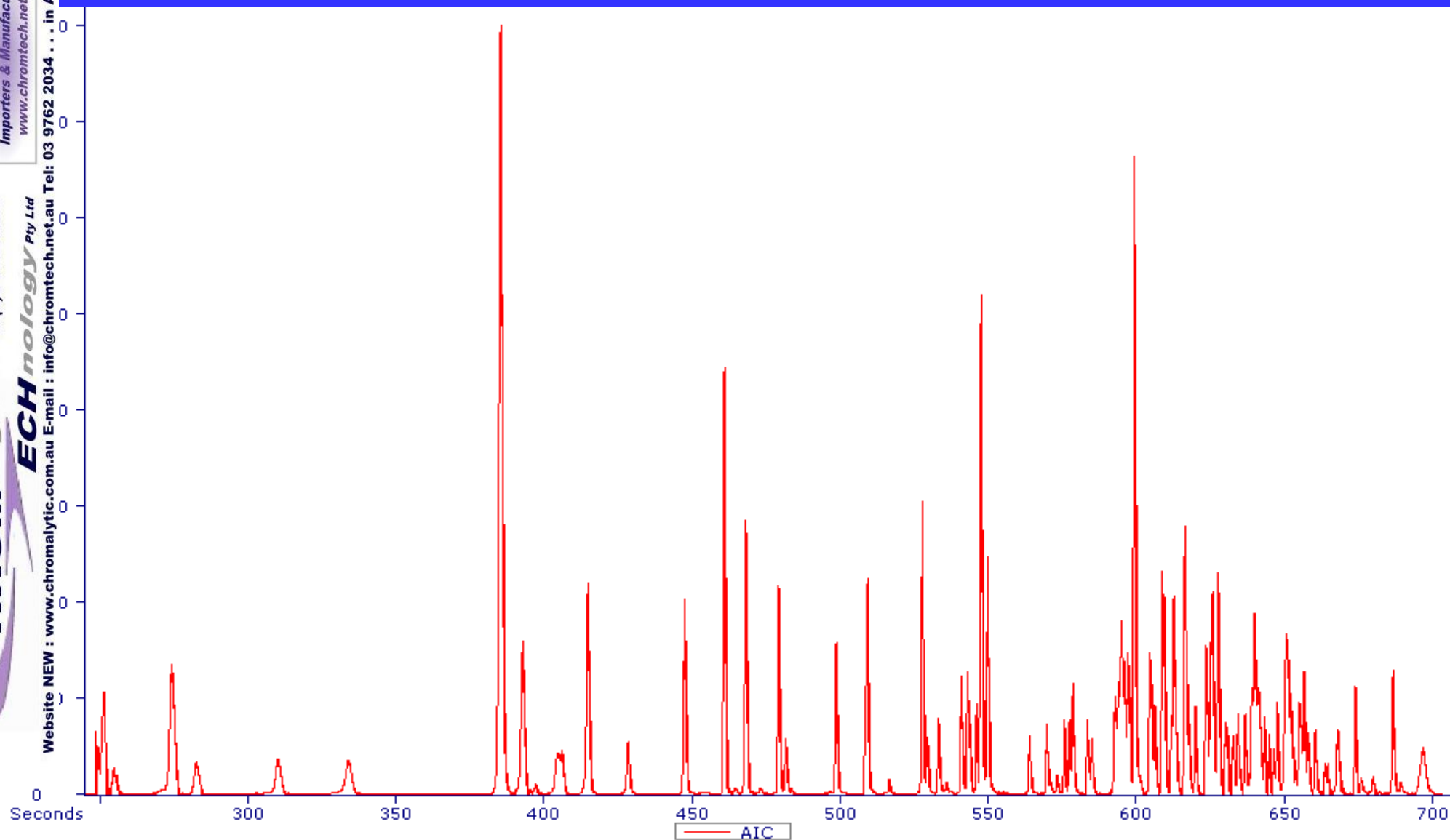
Peak #	Name	R.T.	Similarity	Reverse	Hit #	UniqueMass	S/N	Area	Library	CAS	Formula	Weight
6	Anthracene-d10	310.86	934	934	1	188	5993.3	2966200	MAINLIB	1719-06-8	C14D10	1 <sup>00</sup>
7	Phenanthrene	311.74	982	982	1	178	4412.7	3178700	MAINLIB	85-01-8	C14H10	1
8	Anthracene	313.34	977	977	1	178	3777.0	2847500	MAINLIB	120-12-7	C14H10	1





# Sample D-0998

## Analytical Ion Chromatogram (AIC)



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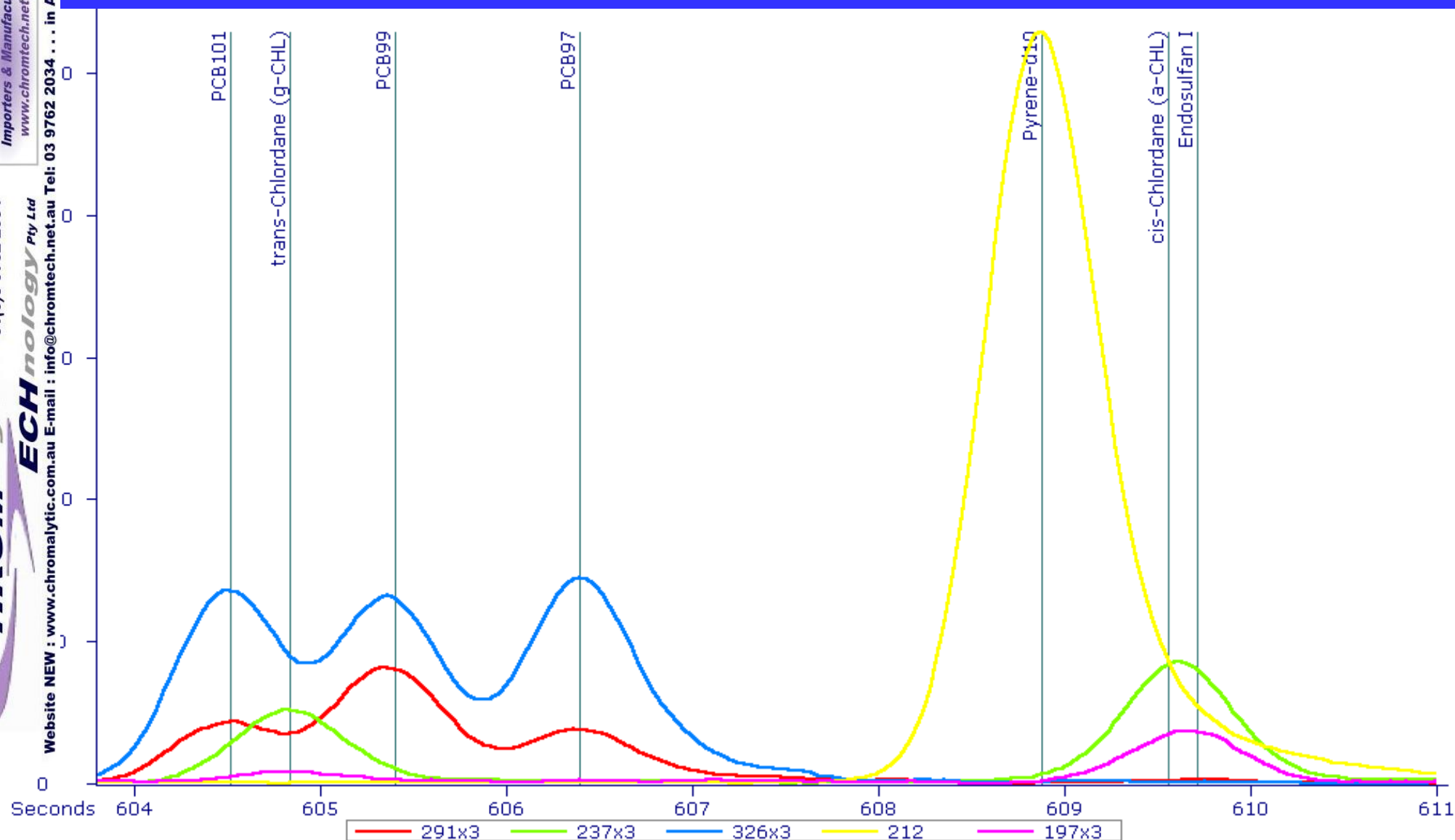
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# Sample D-0998

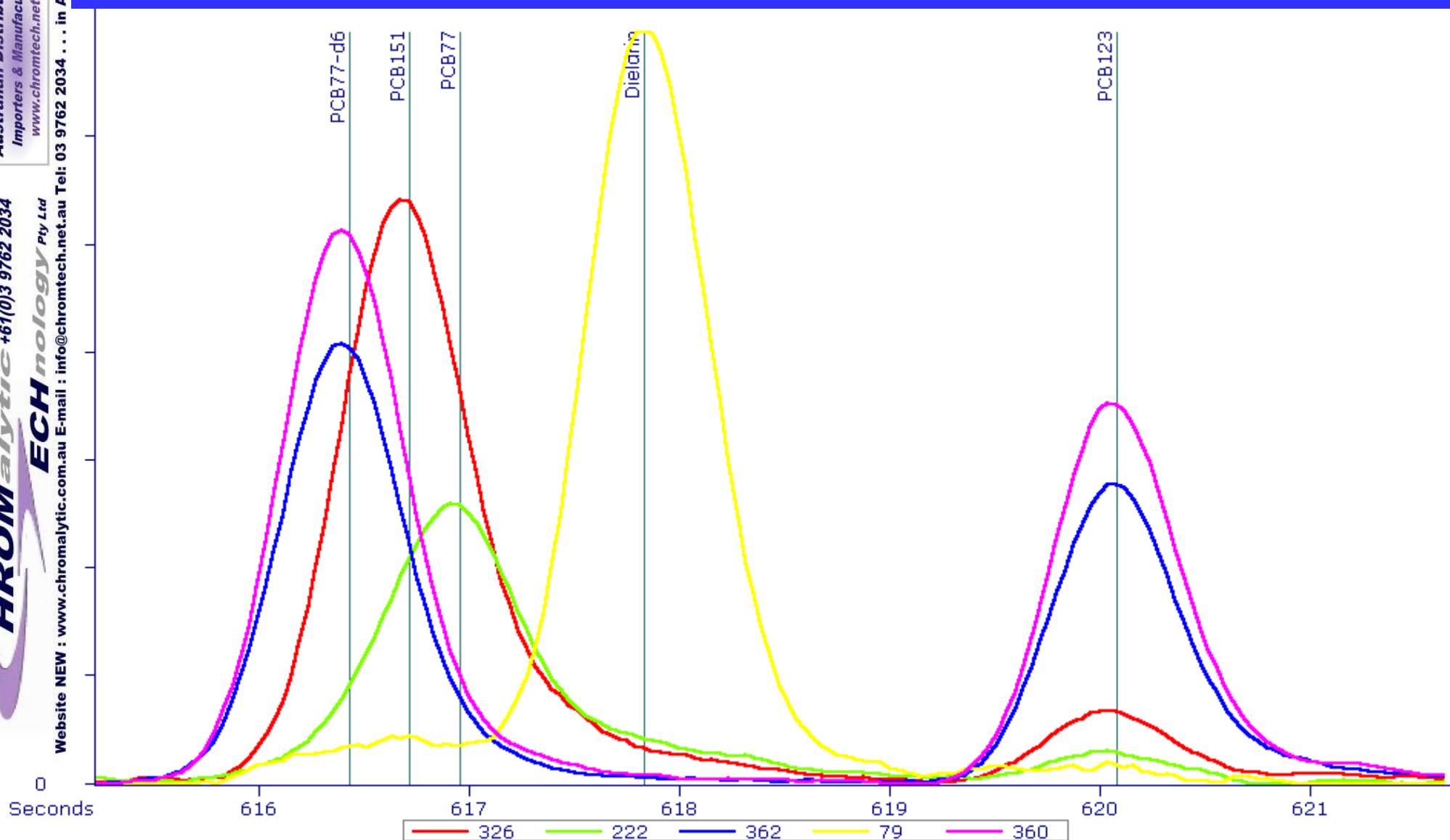
## PCB77-d6, PCB151, PCB77, Dieldrin, PCB123

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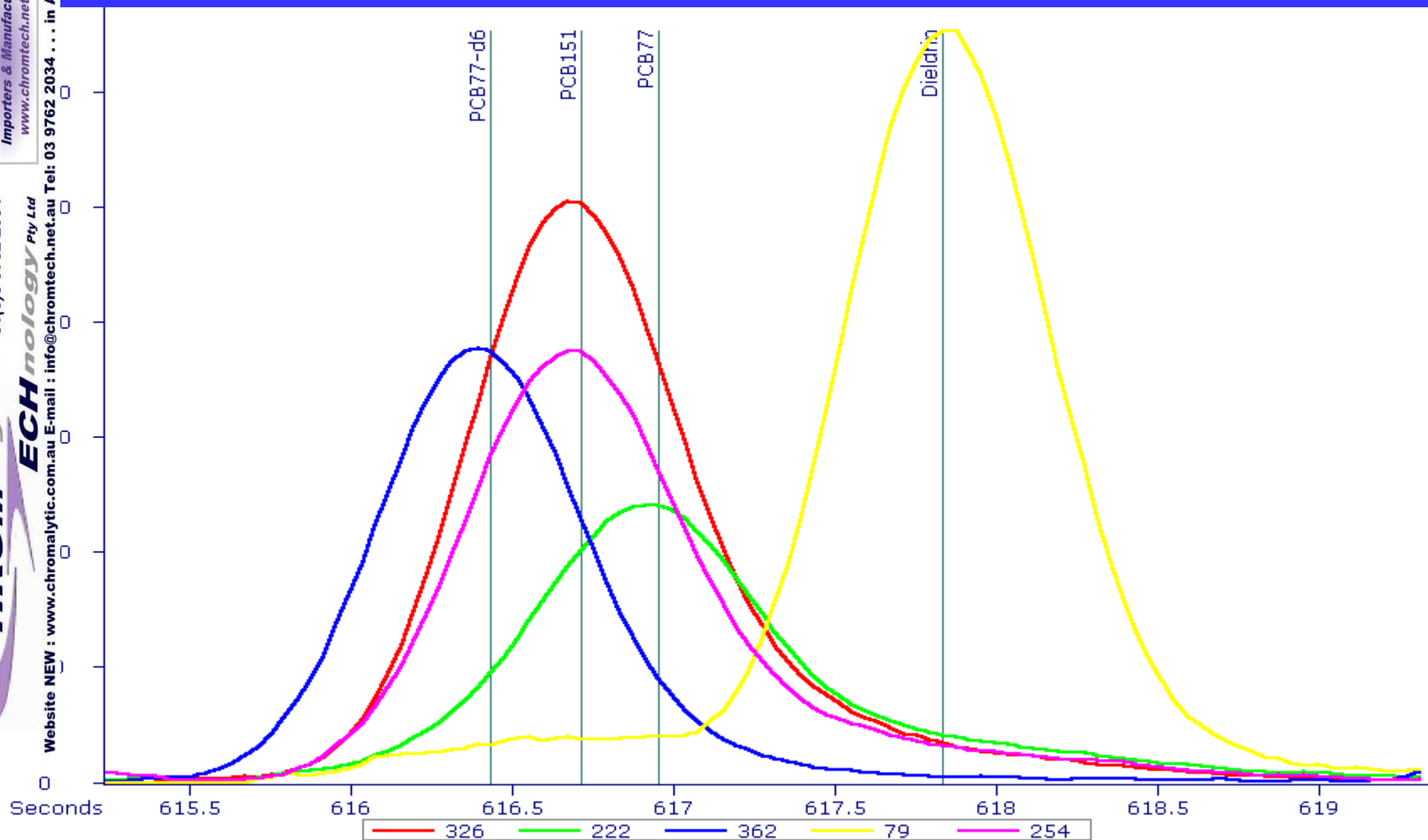
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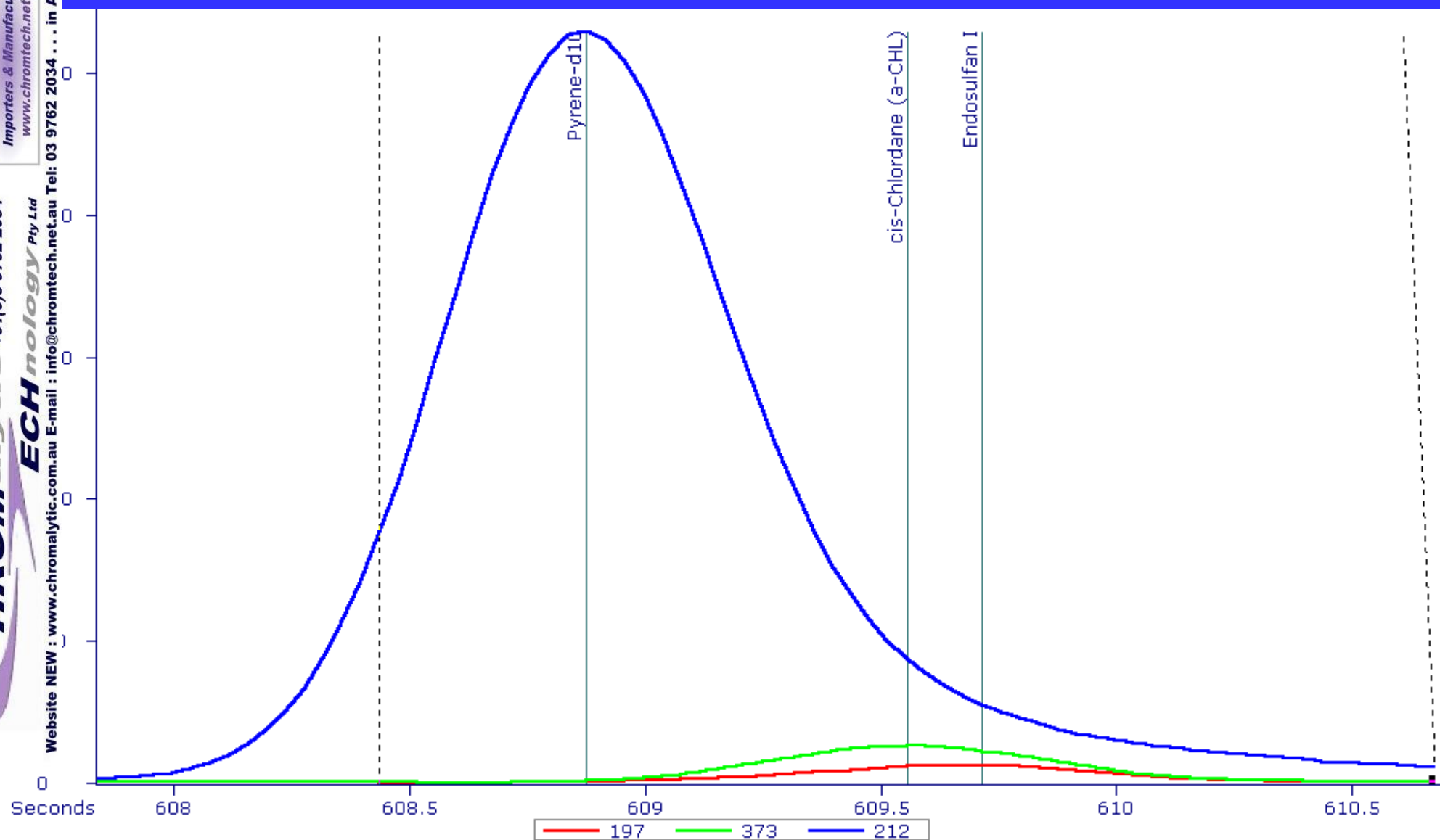
# Sample D-0998

## Analytical Ion Chromatogram (AIC)



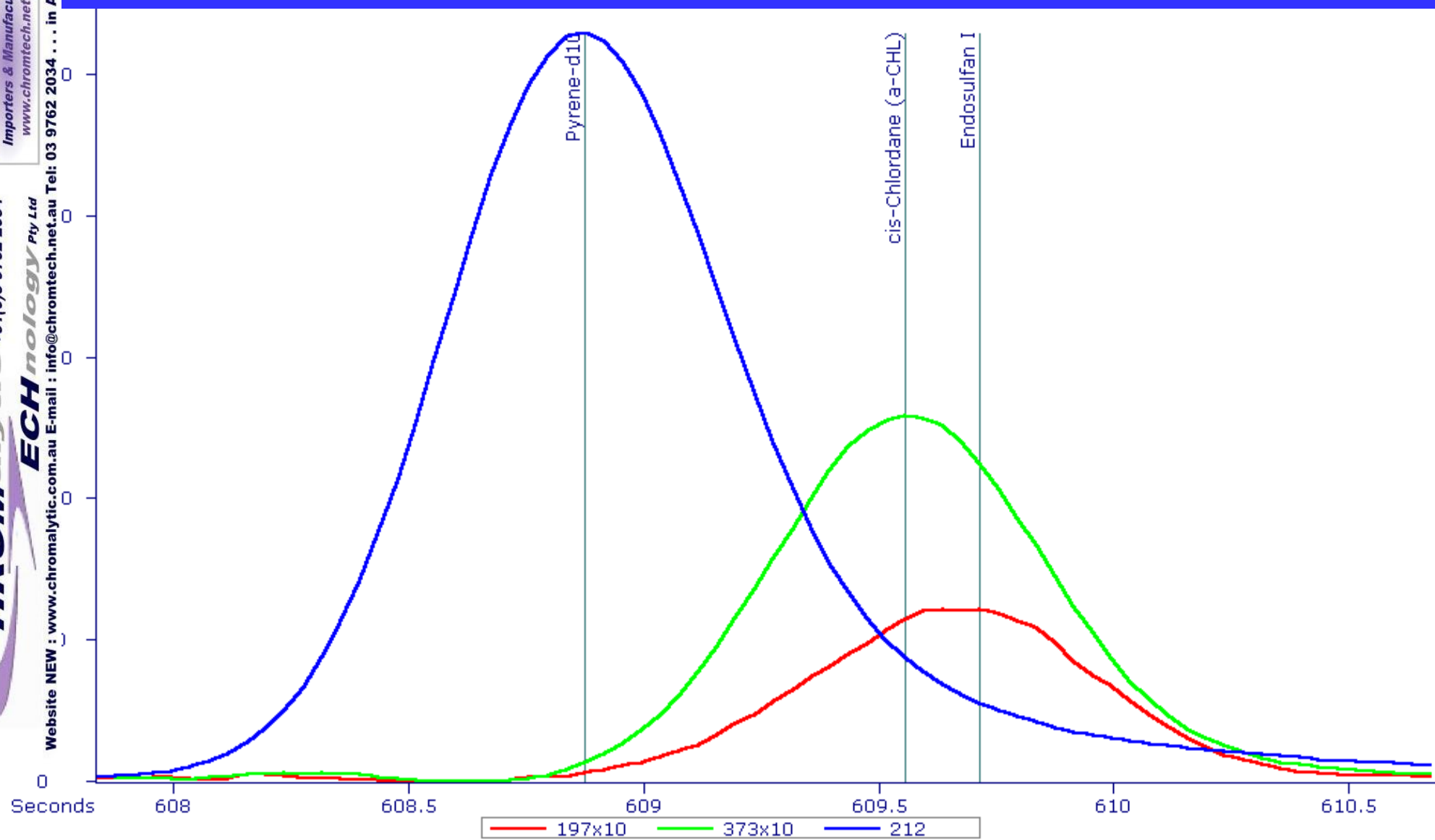
# Sample D-0998

## Pyrene-d10, $\alpha$ -CHL, Endosulfan I



# Sample D-0998

## Pyrene-d10, $\alpha$ -CHL, Endosulfan I

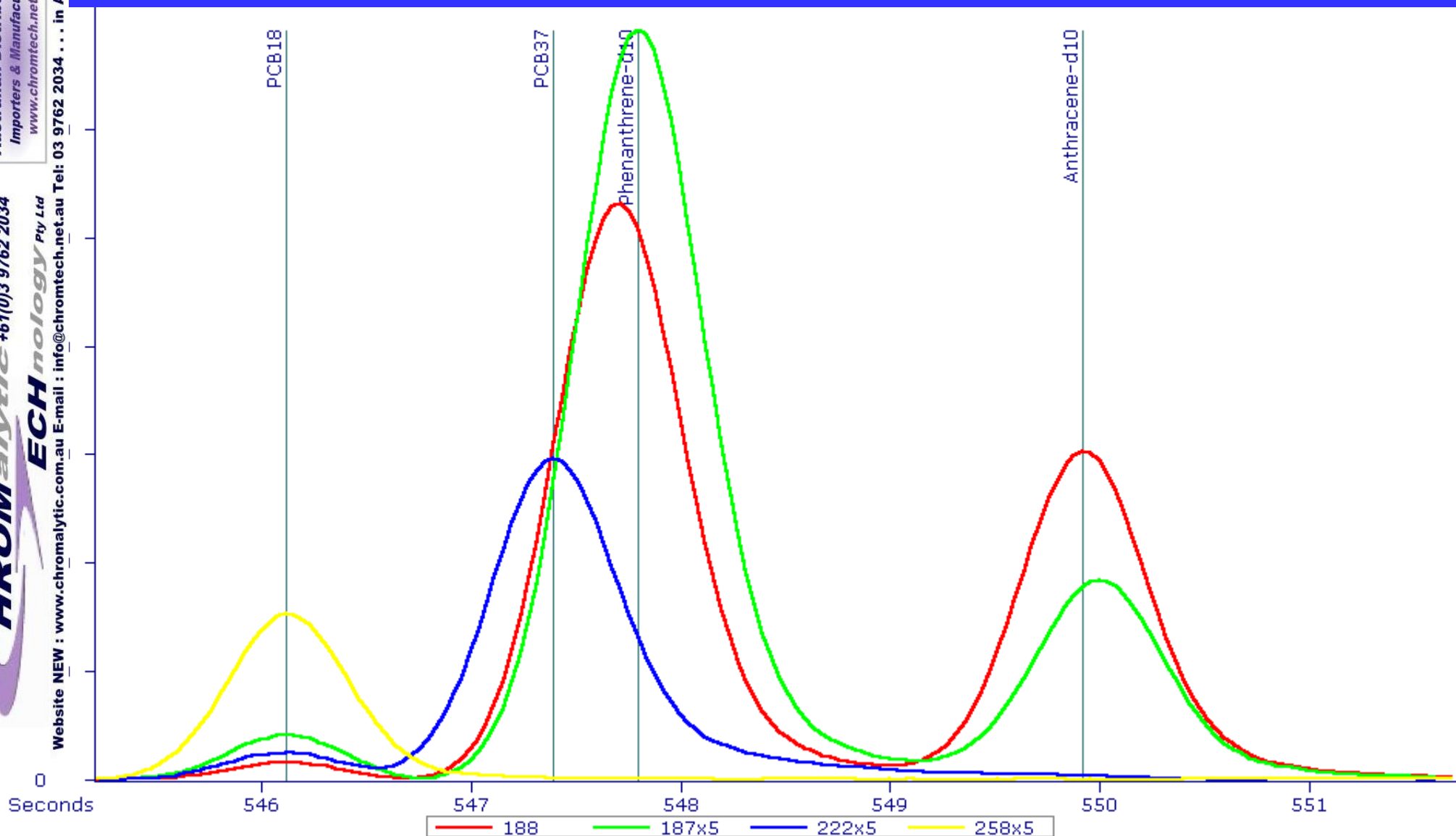


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## Sample D-0998

### PCB18, PCB37, Phenanthrene-D10, Anthracene-D10

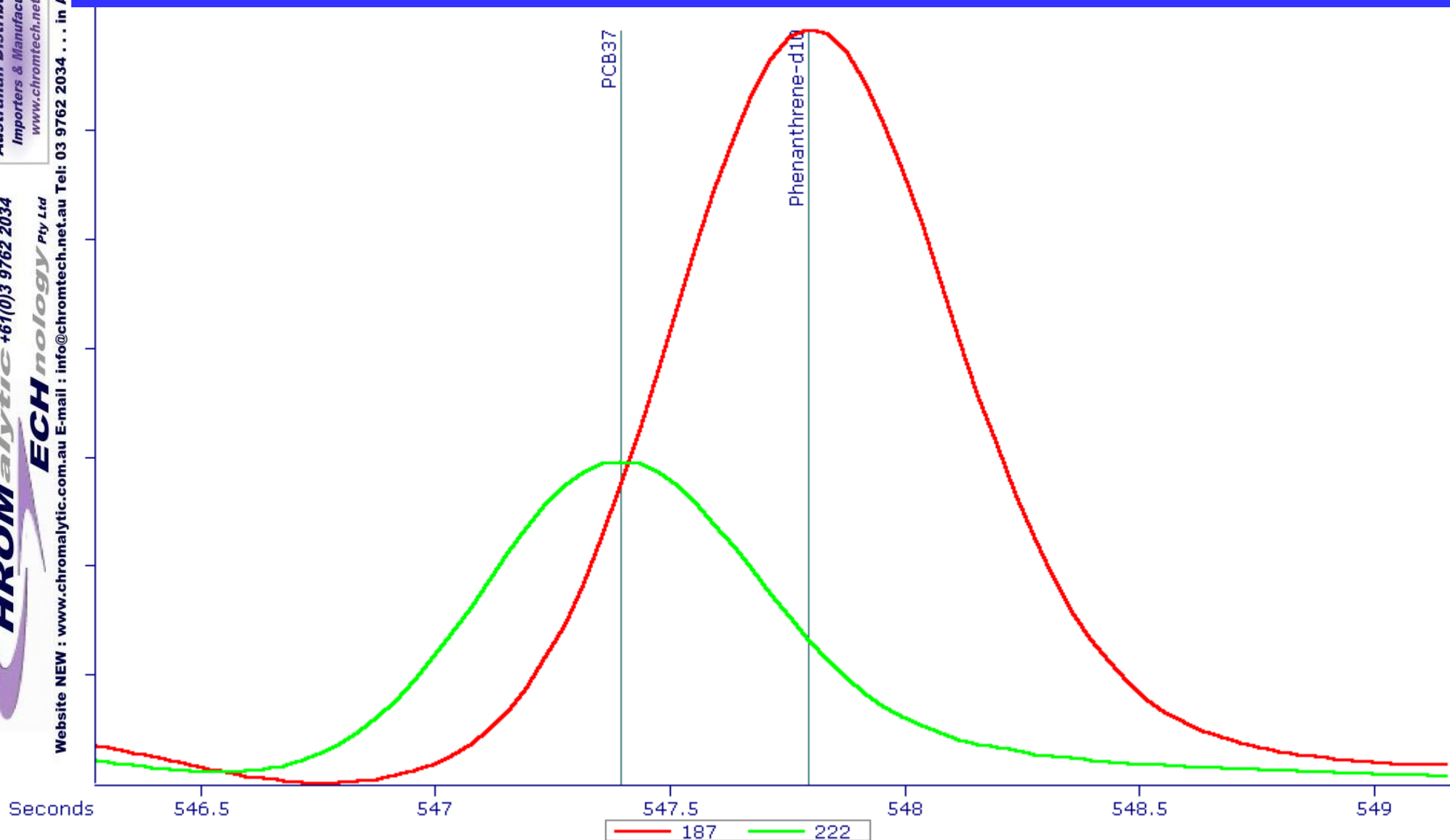


# Sample D-0998

## PCB37, Phenanthrene-d10

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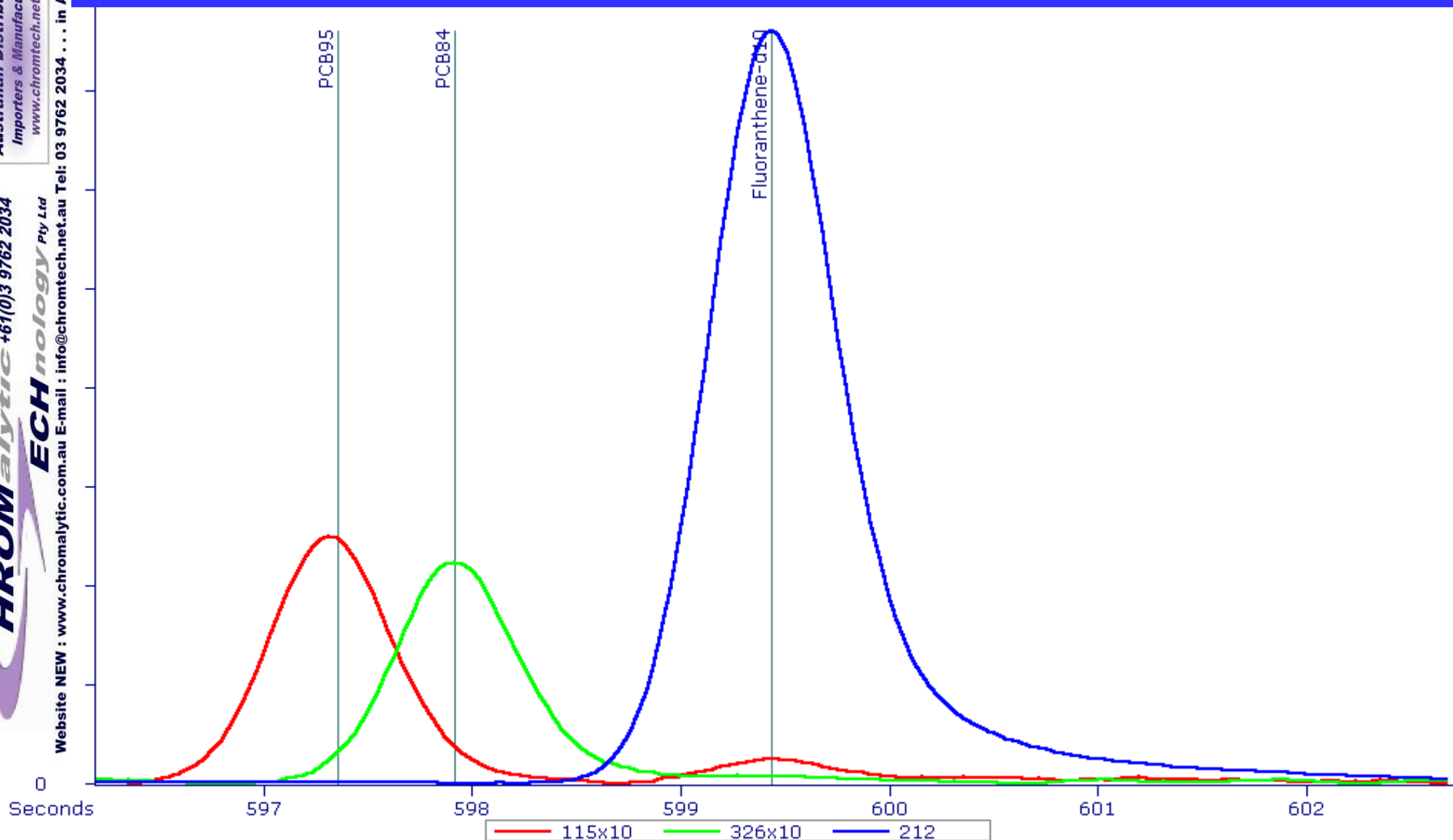


# Sample D-0998

## PCB95, PCB84, Fluoranthene-d10

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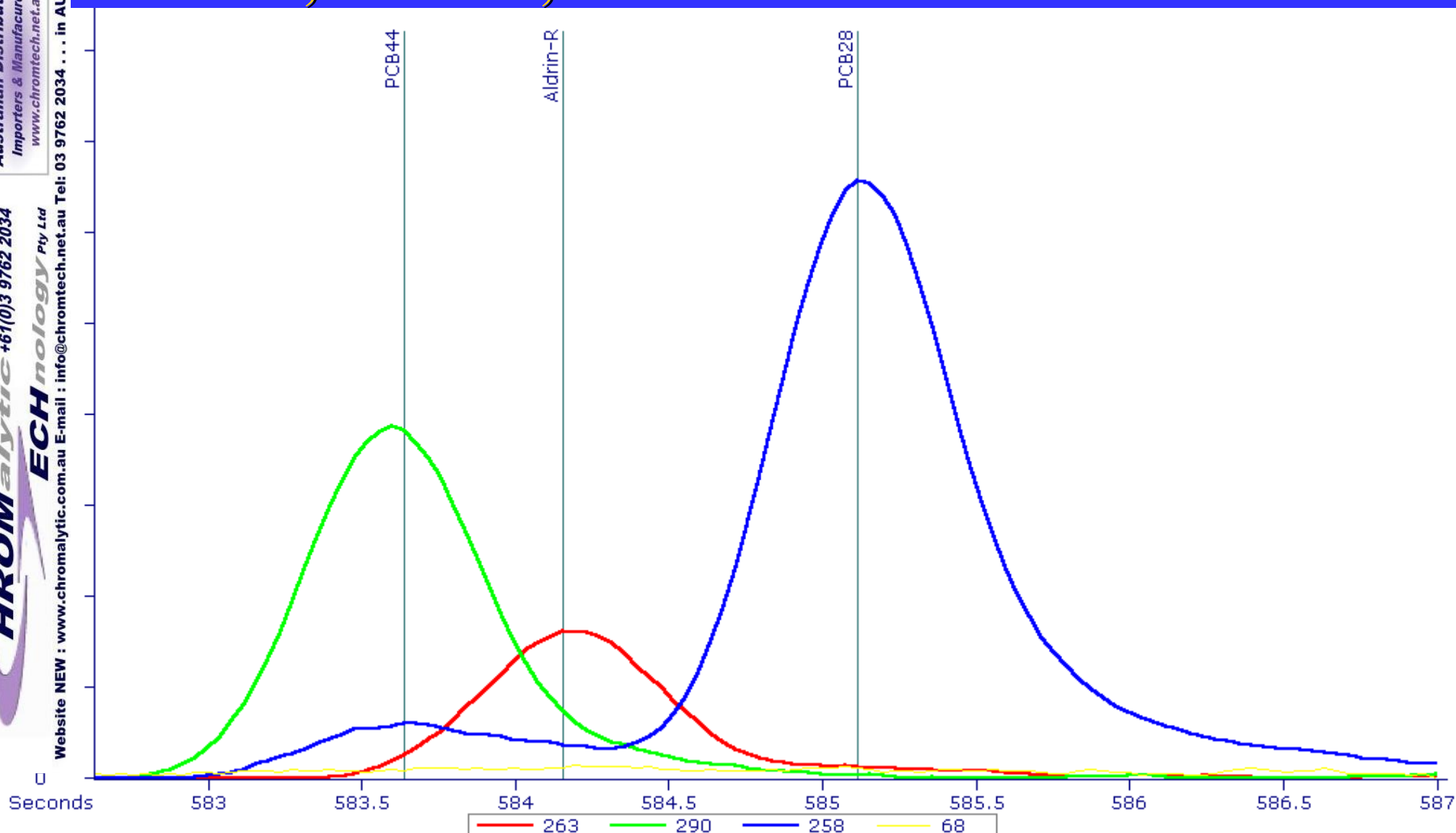
# Sample D-0998

## PCB44, Aldrin-R, PCB28

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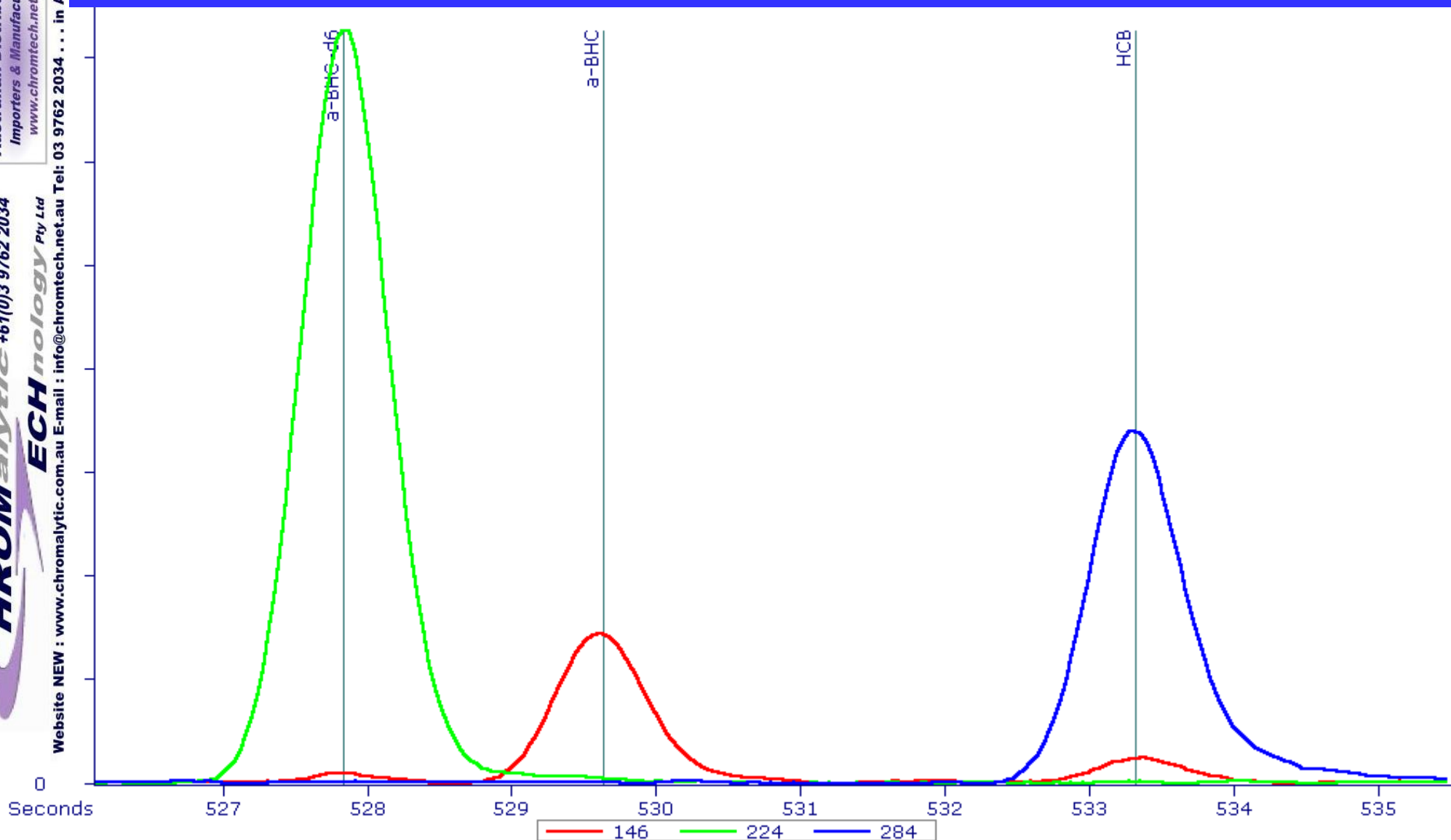


# Sample D-0998

## $\alpha$ -BHC-d6, $\alpha$ -BHC, HCB

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# Equations and Terms

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha - 1 / \alpha)$$

## Capacity Factor

$$k = t_R - t_0 / t_0$$

## Selectivity

$$\alpha = k_2 / k_1$$

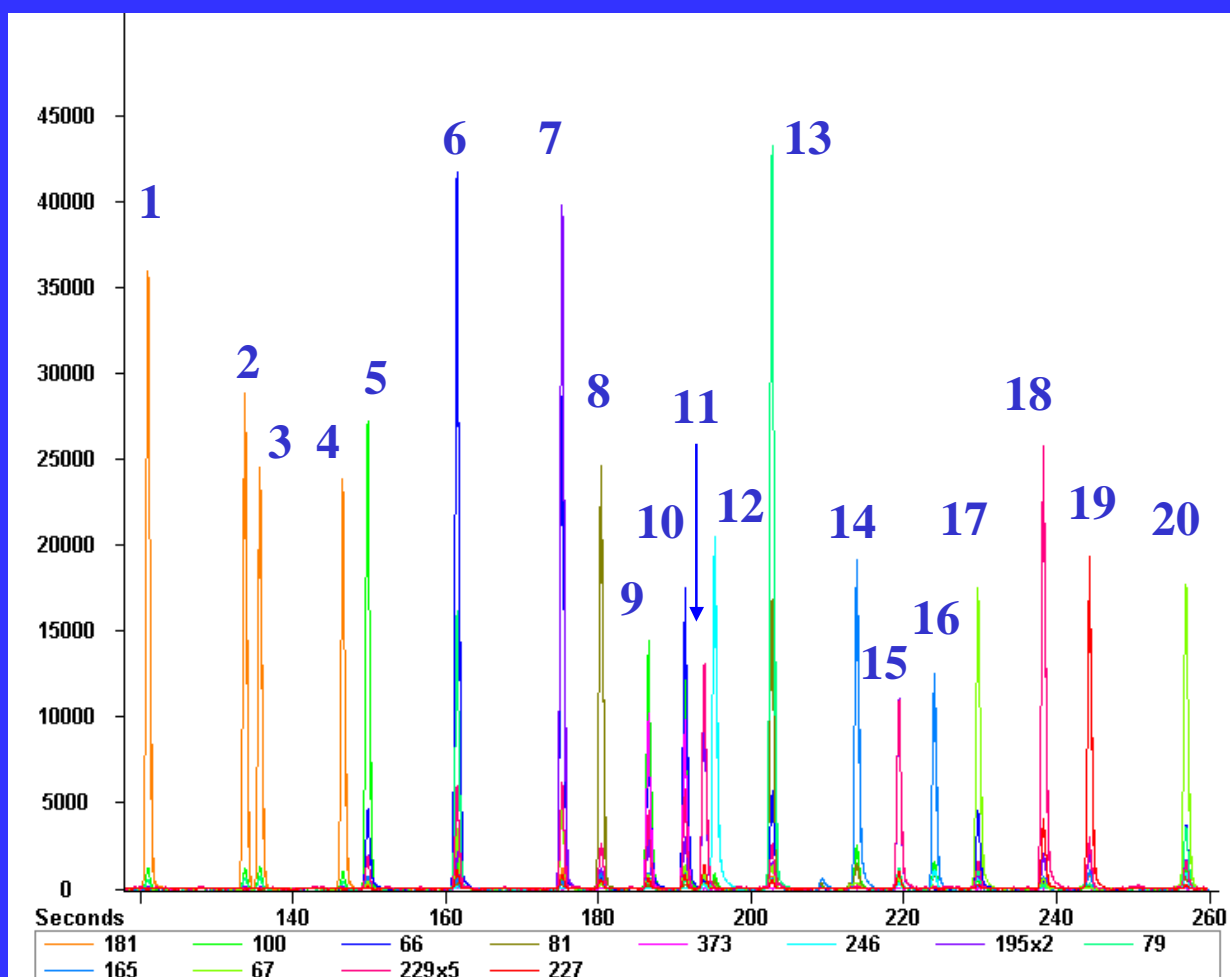
# Coupling Tuned-Selectivity Phases to TOF-MS

- Do not need to rely as much on deconvolution procedures
- May be especially important for compounds with similar mass spectra
- More easily understood by auditors, and regulatory agencies?

# Fast GC/TOFMS of OCPs on CLPII

LECO Pegasus II GC/TOFMS

1. Alpha-BHC
2. Gamma-BHC
3. Beta-BHC
4. Delta-BHC
5. Heptachlor
6. Aldrin
7. Isodrin
8. Heptachlor epoxide
9. Gamma-Chlordane
10. Alpha-Chlordane
11. 4,4'-DDE
12. Endosulfan I
13. Dieldrin
14. 4,4'-DDD
15. Endosulfan II
16. 4,4'-DDT
17. Endrin aldehyde
18. Endosulfan sulfate
19. Methoxychlor
20. Endrin Ketone



Baseline resolution in less than 4.5 minutes!

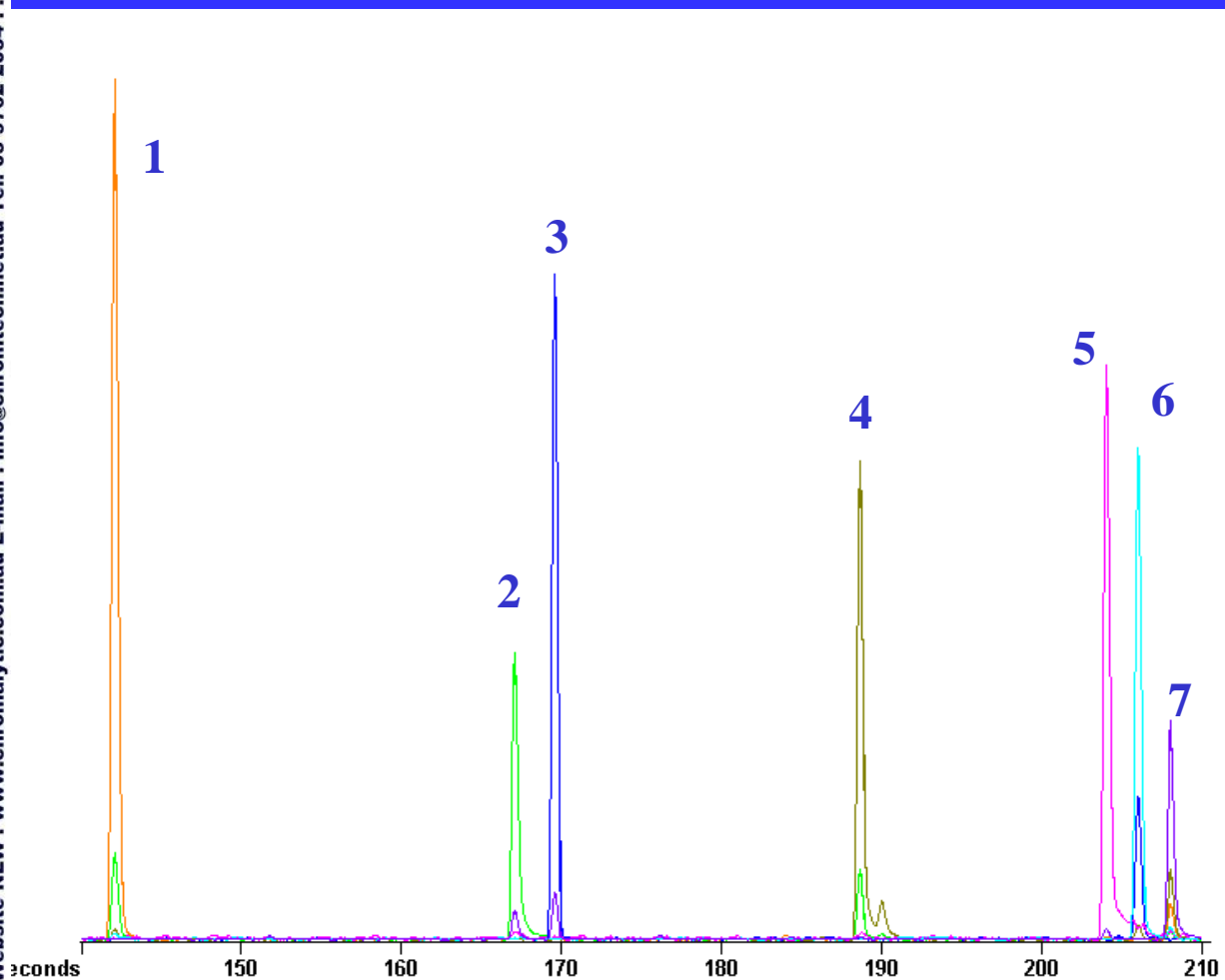
# Fast GC/TOFMS of OC/OPPs on CLPII

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1. 1,2-Dibromo-3-chloropropane
2. Dichlorvos
3. Hexachlorocyclopentadiene
4. Mevinphos
5. Demeton O
6. TEPP
7. Ethoprop

# Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

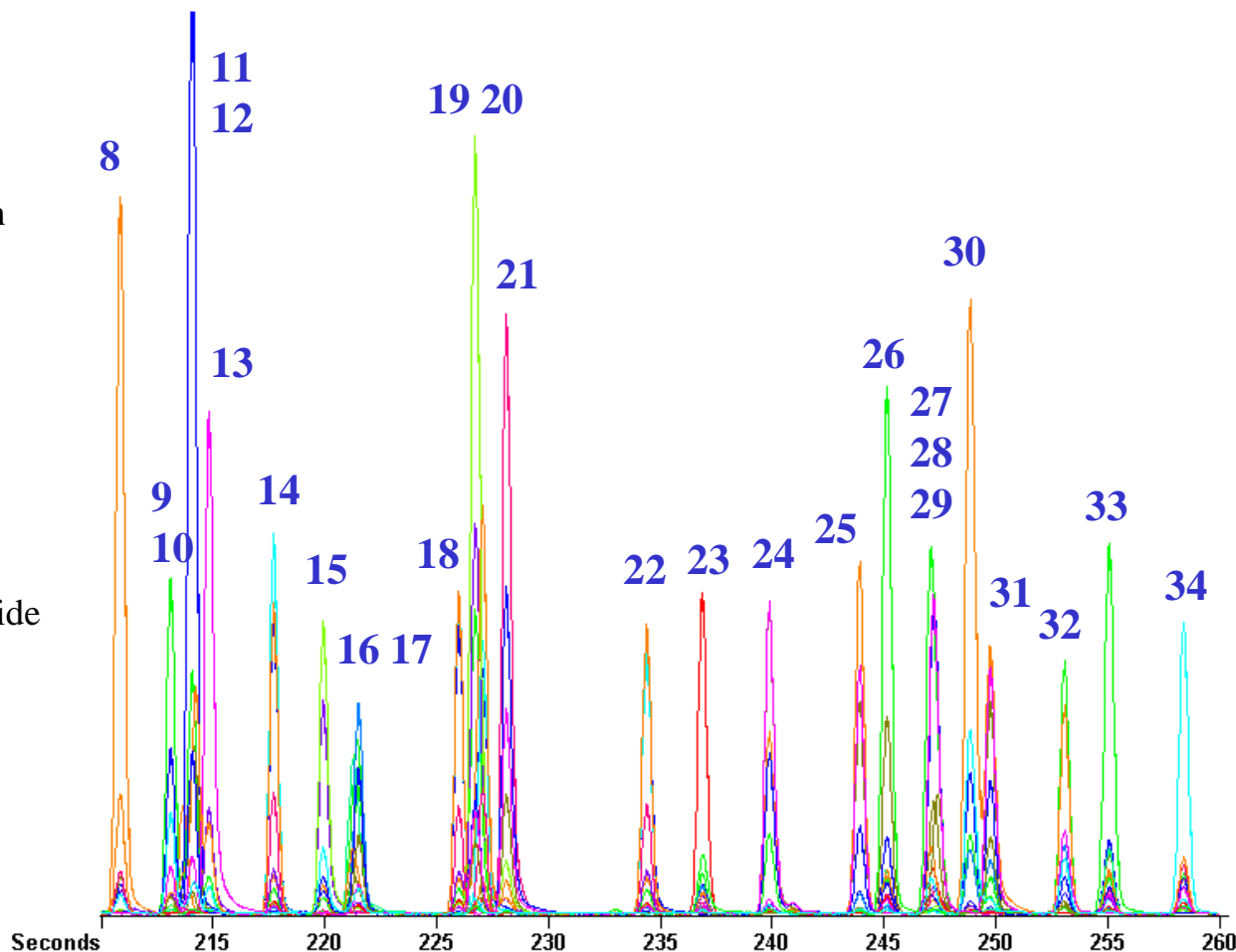
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- |                   |     |                    |
|-------------------|-----|--------------------|
| trans-Diallate    | 22. | Delta-BHC          |
| Sulfotepp         | 23. | Heptachlor         |
| cis-Diallate      | 24. | Ronnel             |
| Phorate           | 25. | Methyl parathion   |
| Daled             | 26. | Aldrin             |
| Hexachlorobenzene | 27. | Chlorpyrifos       |
| Alpha-BHC         | 28. | Malathion          |
| Demeton S         | 29. | Merphos            |
| Monocrotophos     | 30. | Trichloronate      |
| Diazinon          | 31. | Fenthion           |
| Gamma-BHC         | 32. | Parathion          |
| Disulfoton        | 33. | Isodrin            |
| Beta-BHC          | 34. | Heptachlor epoxide |
| Dimethoate        |     |                    |

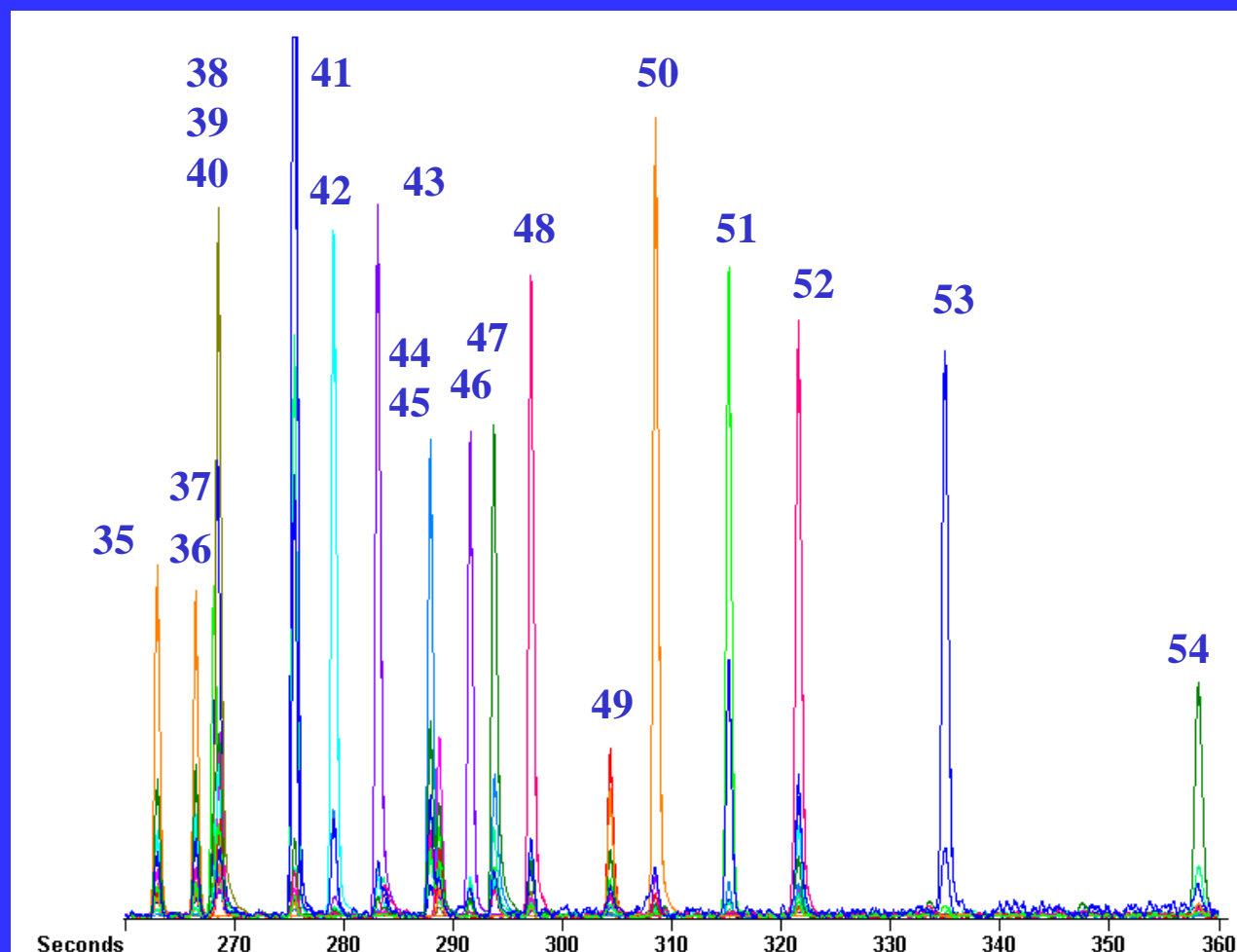




# Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

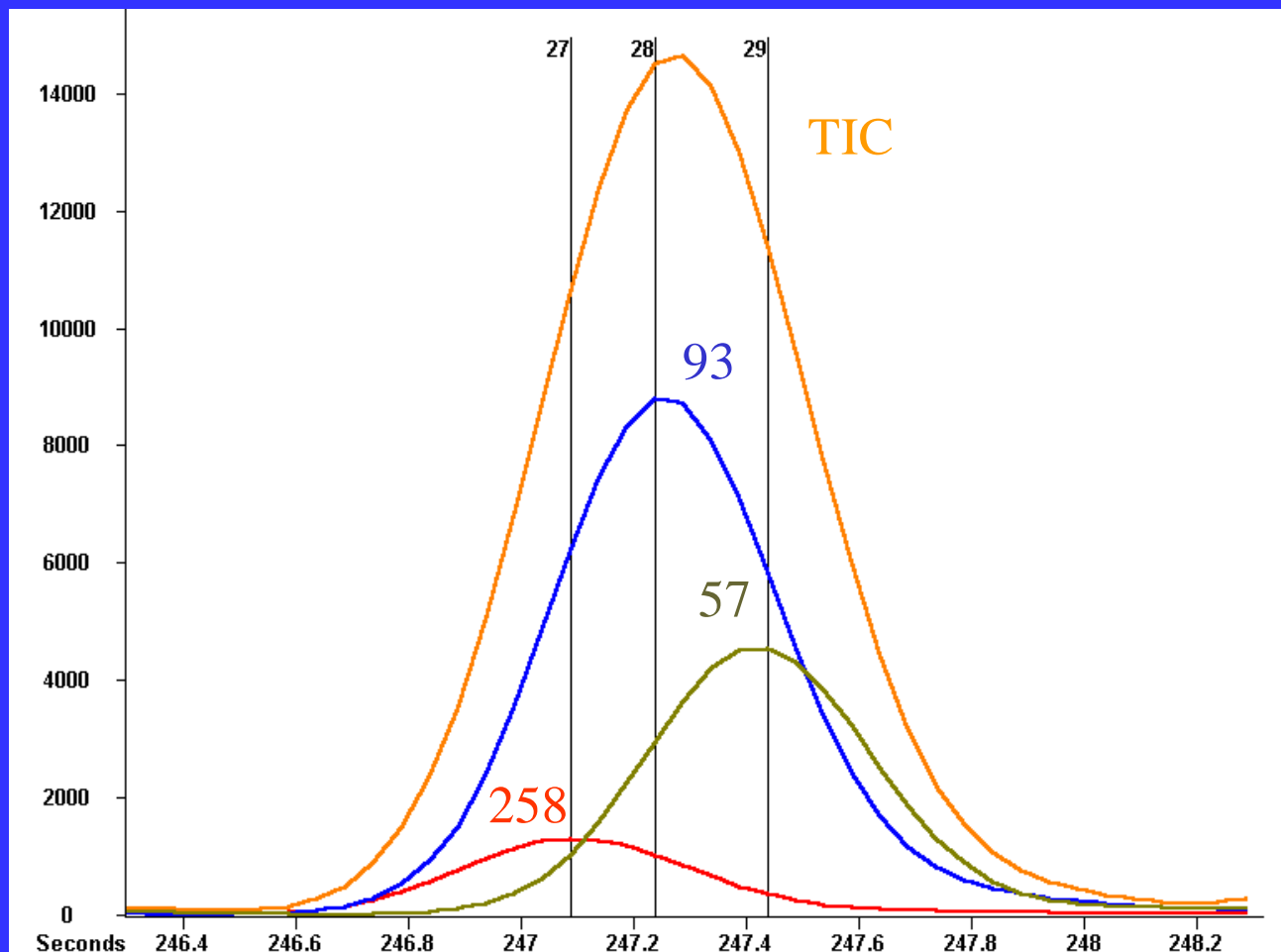
- 35. Gamma-Chlordane
- 36. Alpha-Chlordane
- 37. Tokuthion
- 38. Stirofos
- 39. 4,4'-DDE
- 40. Endosulfan I
- 41. Dieldrin
- 42. Chlorobenzilate
- 43. 4,4'-DDD
- 44. Sulprofos
- 45. Endosulfan II
- 46. 4,4'-DDT
- 47. Fensulfothion
- 48. Endrin aldehyde
- 49. Endosulfan sulfate
- 50. Methoxychlor
- 51. EPN
- 52. Endrin ketone
- 53. Azinphos methyl
- 54. Coumaphos



54 compounds in 6 minutes!

# Automatic Peak Find Using TOFMS

LECO Pegasus II GC/TOFMS



Three compounds located in a one-second wide peak.

27. Chlorpyrifos

28. Malathion

29. Merphos

The acquisition rate of  
TOFMS allows location  
of unique masses and  
subsequent deconvolution  
of mass spectra.

spectra/second

# Summary

- TOF-MS has “scan” speed required to accurately characterize peaks eluting from fast GC methods.
- Deconvolution procedures are further enhanced when some chromatographic separation is possible.
- Coupling tuned-selectivity phases with TOF-MS can lead to very powerful separation tool.

# Acknowledgements

- Eric J. Reiner  
Ministry of the Environment - Ontario, Canada
- Jack Cochran  
Leco Corporation - Las Vegas

*For more information...*

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# Fast Analysis of Semi-Volatile Compounds: US EPA Method 8270

Gary Stidsen and Frank Dorman  
Jarl Snider

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# Product Definition

Design a GC analysis for 8270 that increases laboratory sample throughput by:

- Decreasing analysis time
- Resolution of key analytes
- Utilizing run parameters that can be used for current mass specs including HP59XX.
- 106 compounds including internal standards and surrogates plus 30 chlorinated and organophosphorus pesticides

# Classes of Compounds

## 8270 Calibration Mix #1

benzoic acid  
4-chloro-3-methylphenol  
2-chlorophenol  
2,4-dichlorophenol  
2,6-dichlorophenol  
2,4-dimethylphenol  
4,6-dinitro-2-methylphenol  
2,4-dinitrophenol  
dinozeb  
2-methylphenol

3-methylphenol  
4-methylphenol  
2-nitrophenol  
4-nitrophenol  
pentachlorophenol  
phenol  
2,3,4,6-tetrachlorophenol  
2,4,5-trichlorophenol  
2,4,6-trichlorophenol

## 8270 Calibration Mix #2

aniline  
benzidine  
4-chloroaniline  
3,3'-dichlorobenzidine  
diphenylamine  
2-nitroaniline

3-nitroaniline  
4-nitroaniline  
N-nitrosodimethylamine  
N-nitrosodi-n-propylamine  
pyridine

# Classes of Compounds

## 8270 Calibration Mix #3

aramite

bis (2-chloroethyl) ether

bis (2-chloroethoxy) methane

bis (2-chloroisopropyl) ether

4-bromophenyl phenyl ether

chlorobenzilate

2-chloronaphthalene

4-chlorophenyl phenyl ether

1,2-dichlorobenzene

1,3-dichlorobenzene

1,4-dichlorobenzene

1,3-dinitrobenzene

hexachlorobenzene

hexachlorobutadiene

hexachlorocyclopentadiene

hexachloroethane

hexachloropropene

isodrin

kepone

pentachlorobenzene

pentachloronitrobenzene

1,2,4,5-tetrachlorobenzene

1,2,4-trichlorobenzene



# Classes of Compounds

## 8270 Calibration Mix #4

acetophenone  
azobenzene  
benzyl alcohol  
bis (2-ethylhexyl) phthalate  
butyl benzyl phthalate  
dibenzofuran  
diethyl phthalate  
dimethyl phthalate  
di-n-butyl phthalate  
di-n-octyl phthalate  
2,4-dinitrotoluene

2,6-dinitrotoluene  
ethyl methanesulfonate  
isophorone  
isosafrole (cis & trans)  
methyl methanesulfonate  
1,4-naphthoquinone  
nitrobenzene  
4-nitroquinoline-1-oxide  
phenacetin  
safrole

# Classes of Compounds

## 8270 Calibration Mix #5

acenaphthene  
acenaphthylene  
anthracene  
benzo(a)pyrene  
benzo(ghi)perylene  
benzo(a)anthracene  
benzo(b)fluoranthene  
benzo(k)fluoranthene  
chrysene  
dibenz(a,h)anthracene

fluoranthene  
fluorene  
ideno(1,2,3-cd)pyrene  
1-methylnaphthalene  
naphthalene  
3-methylcholanthrene  
2-methylnaphthalene  
phenanthrene  
pyrene

# Classes of Compounds

## 8270 Calibration Mix #6

diallate (cis & trans)  
dimethoate  
disulfoton  
famphur  
methyl parathion

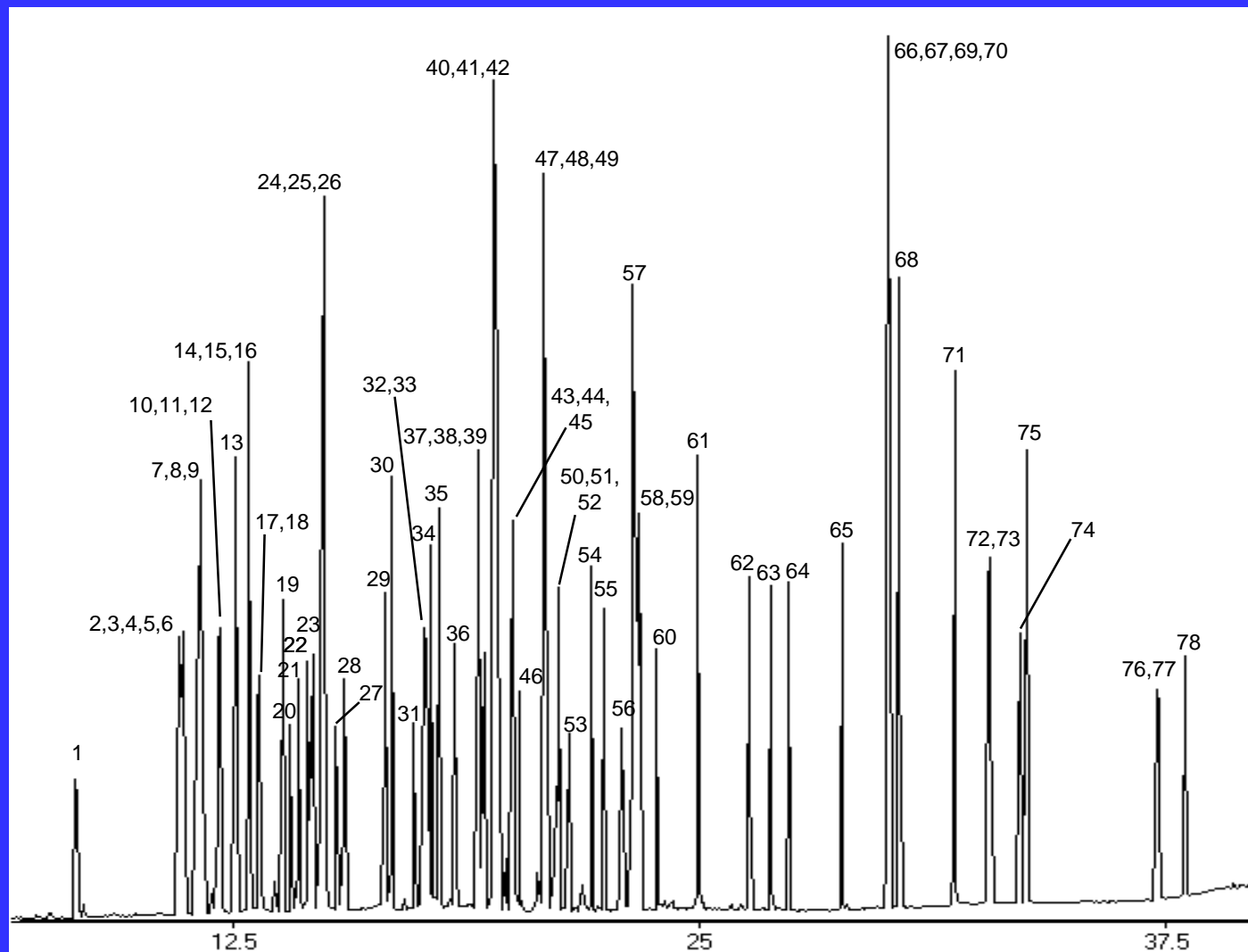
parathion  
phorate  
pronamide  
thionazine  
0,0,0-triethyl phosphorothioate

## Organochlorine Pesticide Mix AB #1

aldrin  
a-BHC  
a-chlordane  
b-BHC  
4,4'-DDD  
4,4'-DDE  
4,4'-DDT  
d-BHC  
dieldrin  
endosulfan I

endosulfan II  
endosulfan sulfate  
endrin  
endrin aldehyde  
endrin ketone  
g-BHC (lindane)  
g-chlordane  
heptachlor  
heptachlor epoxide (B)  
methoxychlor

# Current Analysis



# Analysis Conditions

30m, 0.25mm ID, 0.50 $\mu$ m Rtx-5MS (cat.# 12638)  
2 $\mu$ L splitless injection. On-column concentration: 20ng.

**Oven temp.:** 40°C (hold 2 min.) to 300°C @  
10°C/min. (hold 4 min.), to 330°C  
@ 10°C/min. (hold 10 min.).

**Inj. / det. temp.:** 280°C / 300°C

**Det. type:** MS

**Carrier gas:** helium

**Linear velocity:** 32 cm/sec. set @ 40°C

**Ionization:** EI

**Splitless hold:** 0.5 min.

**Scan Range:** 35-500AMU

# Peak Identification

- |                                   |                                |                                 |
|-----------------------------------|--------------------------------|---------------------------------|
| 1. 2-fluorophenol (Surr)          | 27. 4-chloroaniline            | 53. 2,4,6-tribromophenol (Surr) |
| 2. phenol-d5 (Surr)               | 28. hexachlorobutadiene        | 54. 4-bromophenyl-phenylether   |
| 3. phenol                         | 29. 4-chloro-3-methylphenol    | 55. hexachlorobenzene           |
| 4. bis(2-chloroethyl)ether        | 30. 2-methylnaphthalene        | 56. pentachlorophenol           |
| 5. 2-chlorophenol-d4 (Surr)       | 31. hexachlorocyclopentadiene  | 57. phenanthrene-d10 (IS)       |
| 6. 2-chlorophenol                 | 32. 2,4,6-trichlorophenol      | 58. phenanthrene                |
| 7. 1,3-dichlorobenzene            | 33. 2,4,5-trichlorophenol      | 59. anthracene                  |
| 8. 1,4-dichlorobenzene-d4 (IS)    | 34. 2-fluorobiphenyl (Surr)    | 60. carbazole                   |
| 9. 1,4-dichlorobenzene            | 35. 2-chloronaphthalene        | 61. di-n-butylphthalate         |
| 10. 1,2-dichlorobenzene-d4 (Surr) | 36. 2-nitroaniline             | 62. fluoranthene                |
| 11. 1,2-dichlorobenzene           | 37. dimethylphthalate          | 63. pyrene                      |
| 12. 2-methylphenol                | 38. acenaphthylene             | 64. terphenyl-d14 (Surr)        |
| 13. 2,2'-oxybis-(1-chloropropane) | 39. 2,6-dinitrotoluene         | 65. butylbenzylphthalate        |
| 14. 4-methylphenol                | 40. 3-nitroaniline             | 66. 3,3-dichlorobenzidine       |
| 15. N-nitroso-di-n-propylamine    | 41. acenaphthene-d10 (IS)      | 67. benzo(a)anthracene          |
| 16. hexachloroethane              | 42. acenaphthene               | 68. bis(2-ethylhexyl)phthalate  |
| 17. nitrobenzene-d5 (Surr)        | 43. 2,4-dinitrophenol          | 69. chrysene-d12 (IS)           |
| 18. nitrobenzene                  | 44. 4-nitrophenol              | 70. chrysene                    |
| 19. isophorone                    | 45. dibenzofuran               | 71. di-n-octylphthalate         |
| 20. 2-nitrophenol                 | 46. 2,4-dinitrotoluene         | 72. benzo(b)fluoranthene        |
| 21. 2,4-dimethylphenol            | 47. diethylphthalate           | 73. benzo(k)fluoranthene        |
| 22. bis(2-chloroethoxy)methane    | • Fluorene                     | 74. benzo(a)pyrene              |
| 23. 2,4-dichlorophenol            | • 4-chlorophenyl-phenylether   | 75. perylene-d12 (IS)           |
| • 1,2,4-trichlorobenzene          | 50. 4-nitroaniline             | 76. indeno(1,2,3-cd)pyrene      |
| 25. naphthalene-d8 (IS)           | 51. 4,6-dinitro-2-methylphenol | 77. dibenzo(a,h)anthracene      |
| 26. naphthalene                   | 52. N-nitrosodiphenylamine     | • benzo(g,h,i)perylene          |

# Fast Analysis Concerns

- Flow rate considerations for diffusion pumps (<1.3 mL/min)
- Closely eluting compounds w/same quantitation ions
  - phenol / aniline / bis(2-chloroethyl)ether
  - 1,3- & 1,4-dichlorobenzene
  - 2- & 1-methylnaphthalene
  - 2,4,6- & 2,4,5-trichlorobenzenes
  - phenanthrene / anthracene
  - benz(a)anthracene / chrysene
  - benzo(b)fluoranthrene / benzo(k)fluoranthrene

# Reducing Analysis Time

- Important criteria to reducing run times
  - initial hold time
    - resolve early eluting compounds
  - eluting compounds on ramp rate vs isothermal
  - fast ramp rate through non critical areas



# Initial Work

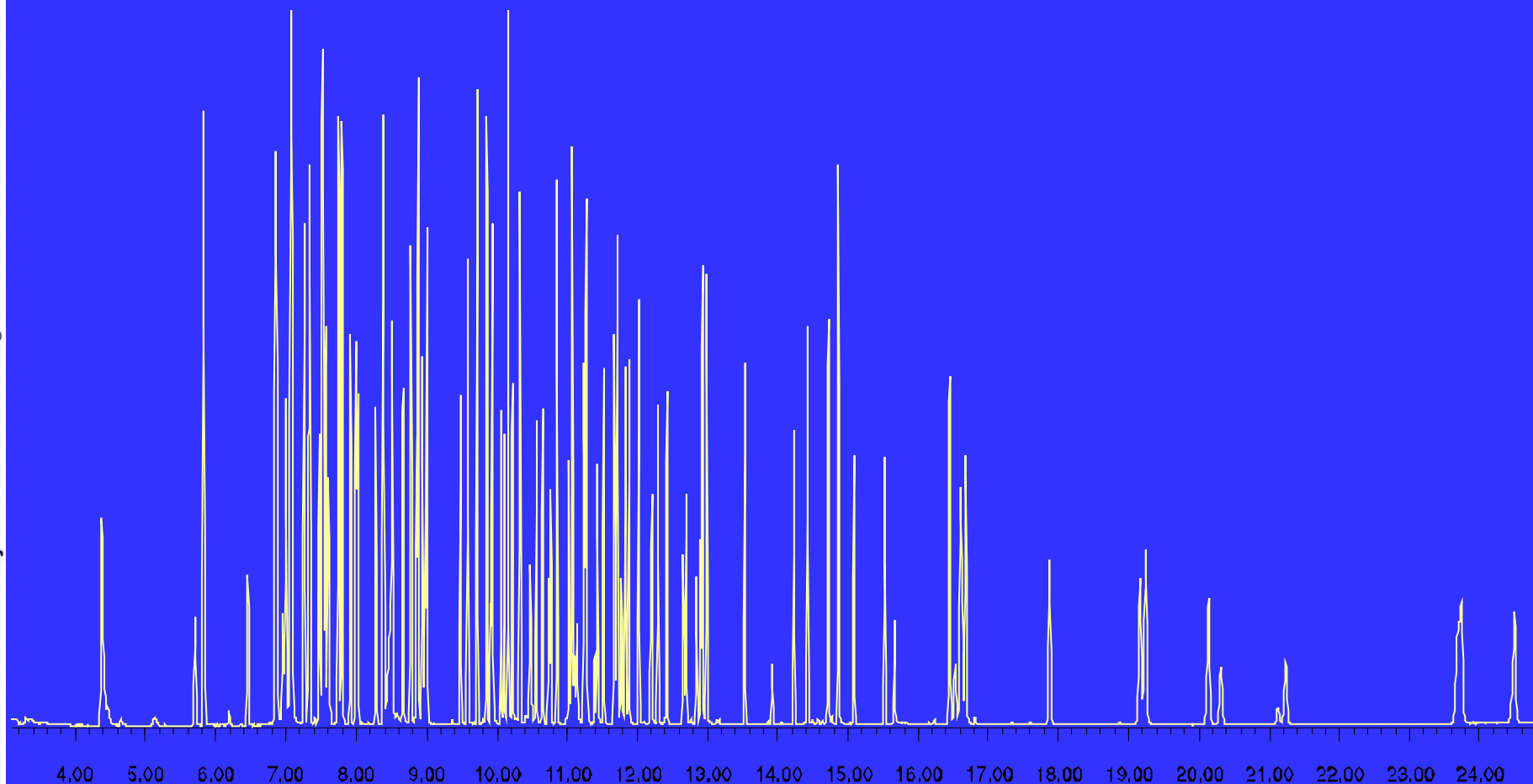
- Constant flow
- Maximize ramp rate
  - Start out with fast ramp rate and work backwards
  - Adjust oven temperature program so all compounds after initial hold elute on ramp rate
- Overload of high standard
  - Testing performed with 160ng due to potential overload causing coelution of closely eluting compounds

# Resulting Run Conditions

- Constant flow rate @ 1.0 mL/min
- Temperature program:
  - 40°C (2 min)
  - 20°C/min
  - 290°C (0 min)
  - 2°C/min
  - 303°C (0 min)
  - 6°C/min
  - 330°C (1 min)

# Rtx-5Sil MS

(30m x 0.25mm ID, 0.5 $\mu$ m film)



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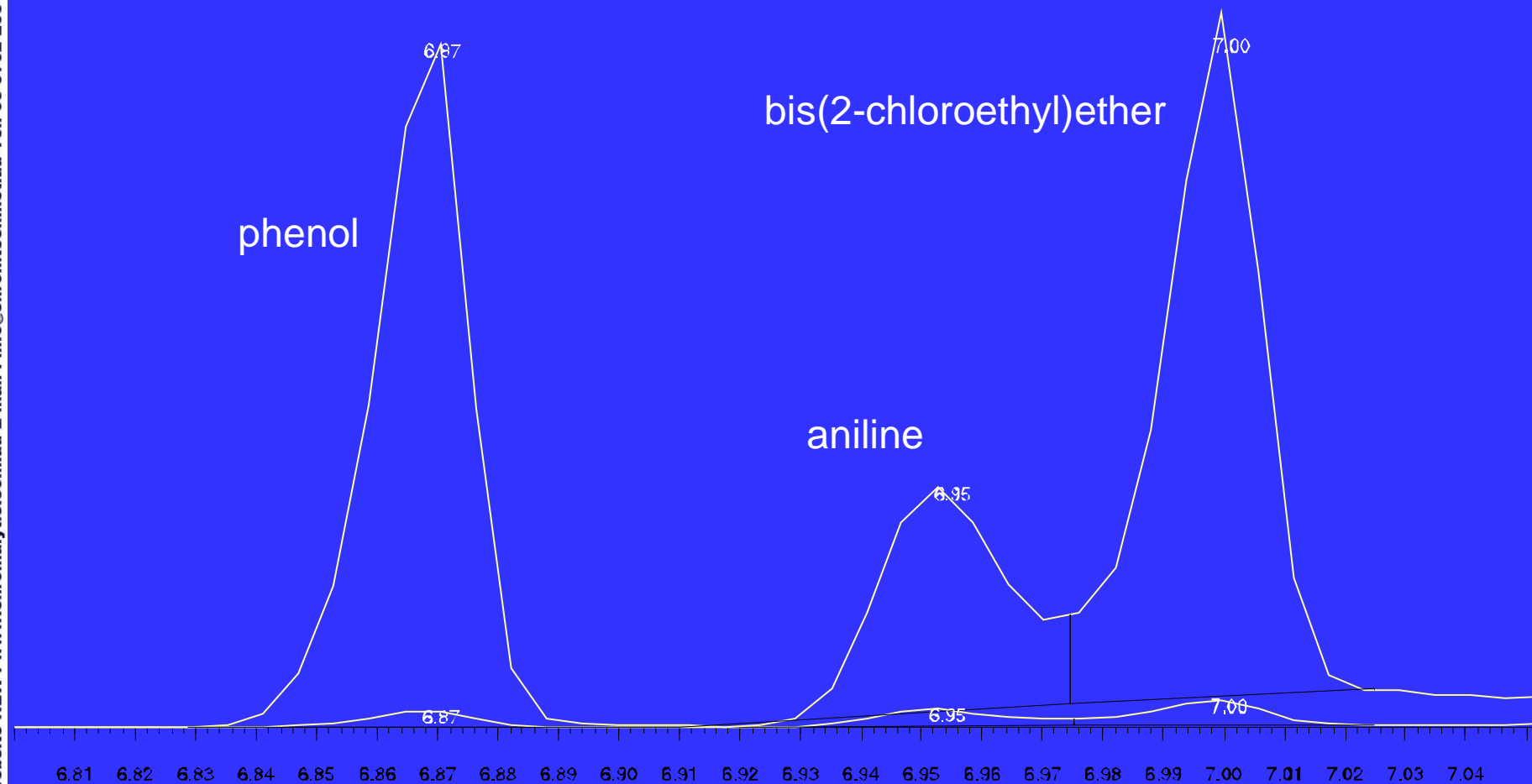
Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA

**CHROM**alytic +61(0)3 9762 2034

**ECH**nology Pty Ltd

# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5 $\mu$ m film)



# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5µm film)

1,3-dichlorobenzene

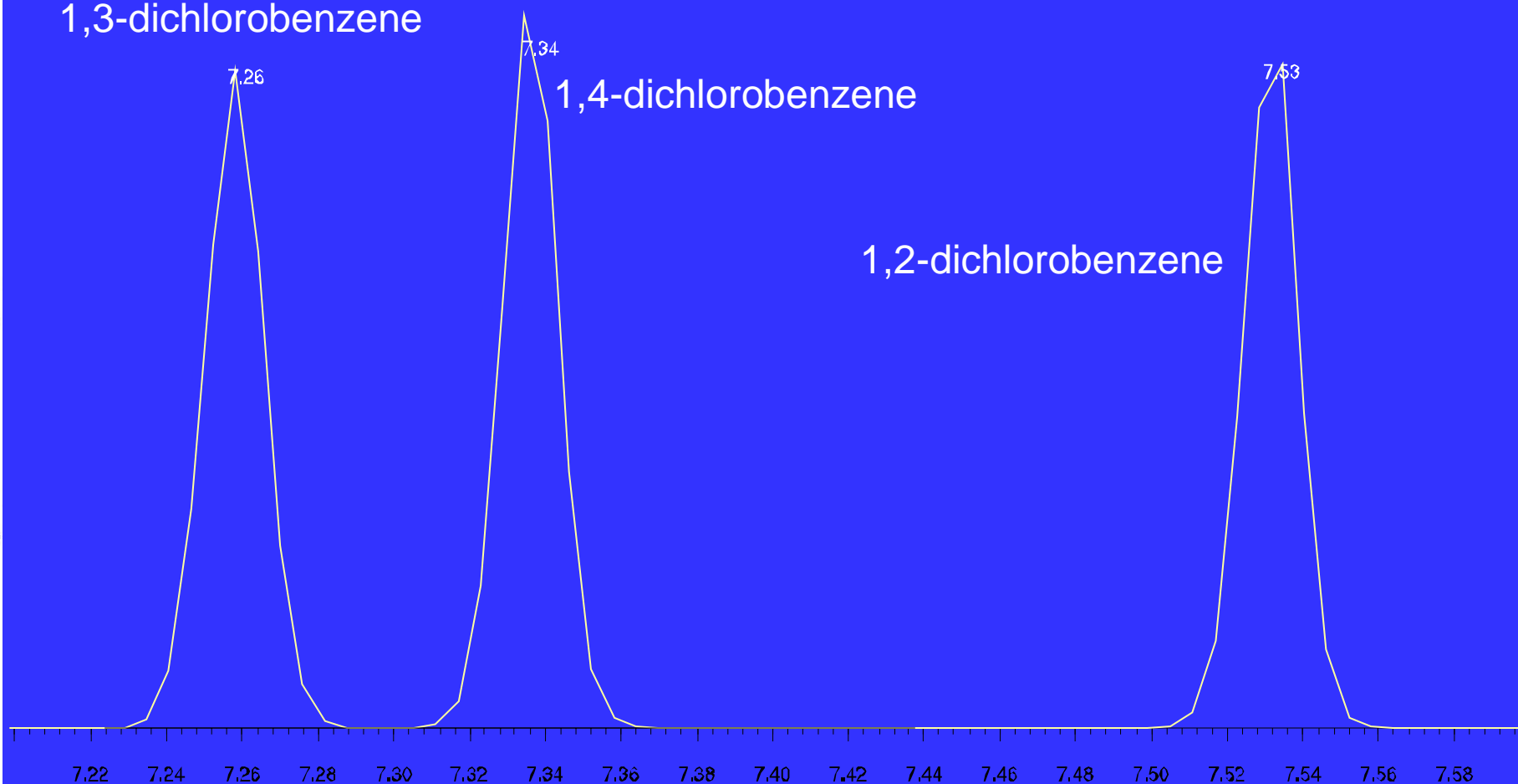
7.26

7.34

1,4-dichlorobenzene

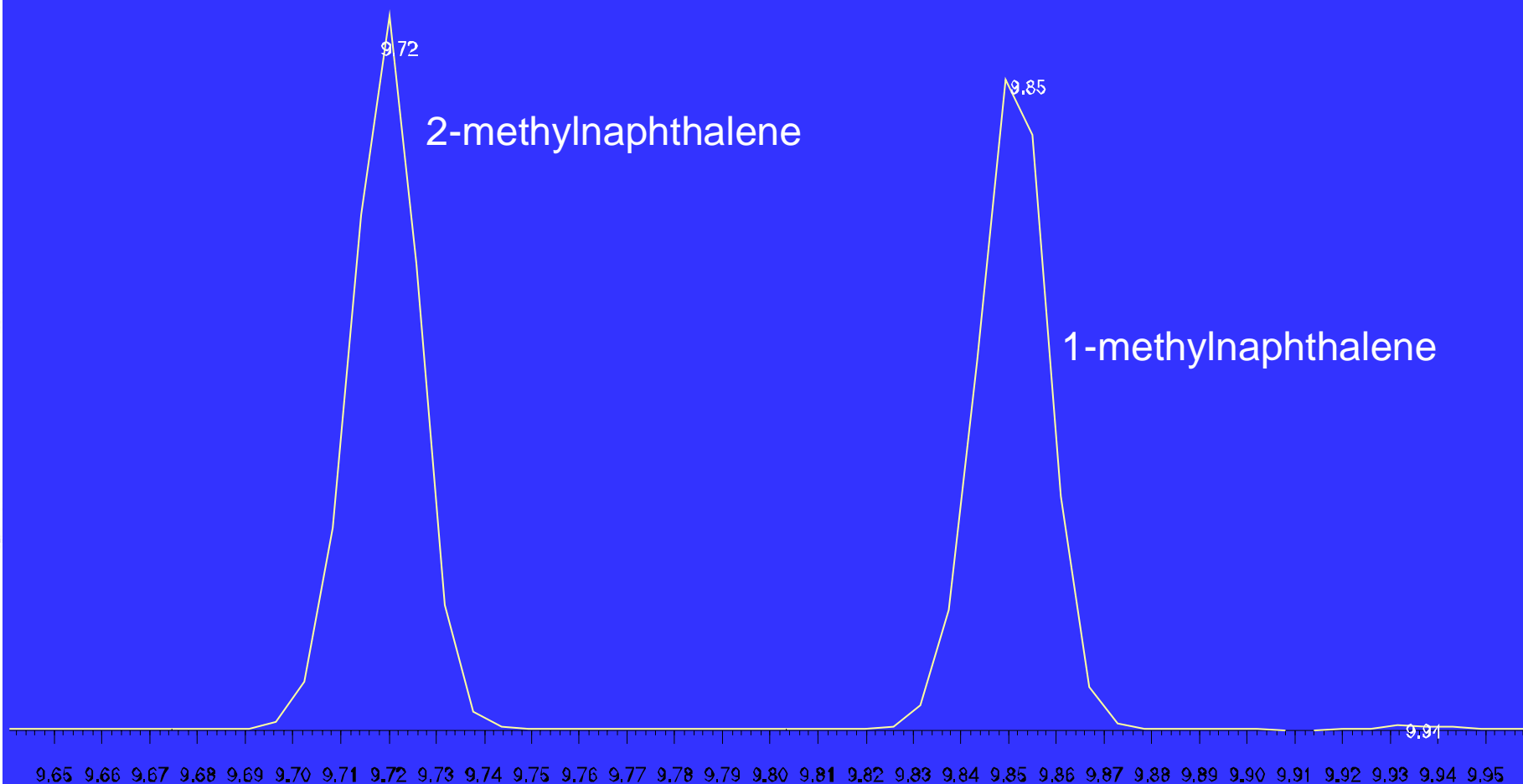
7.53

1,2-dichlorobenzene



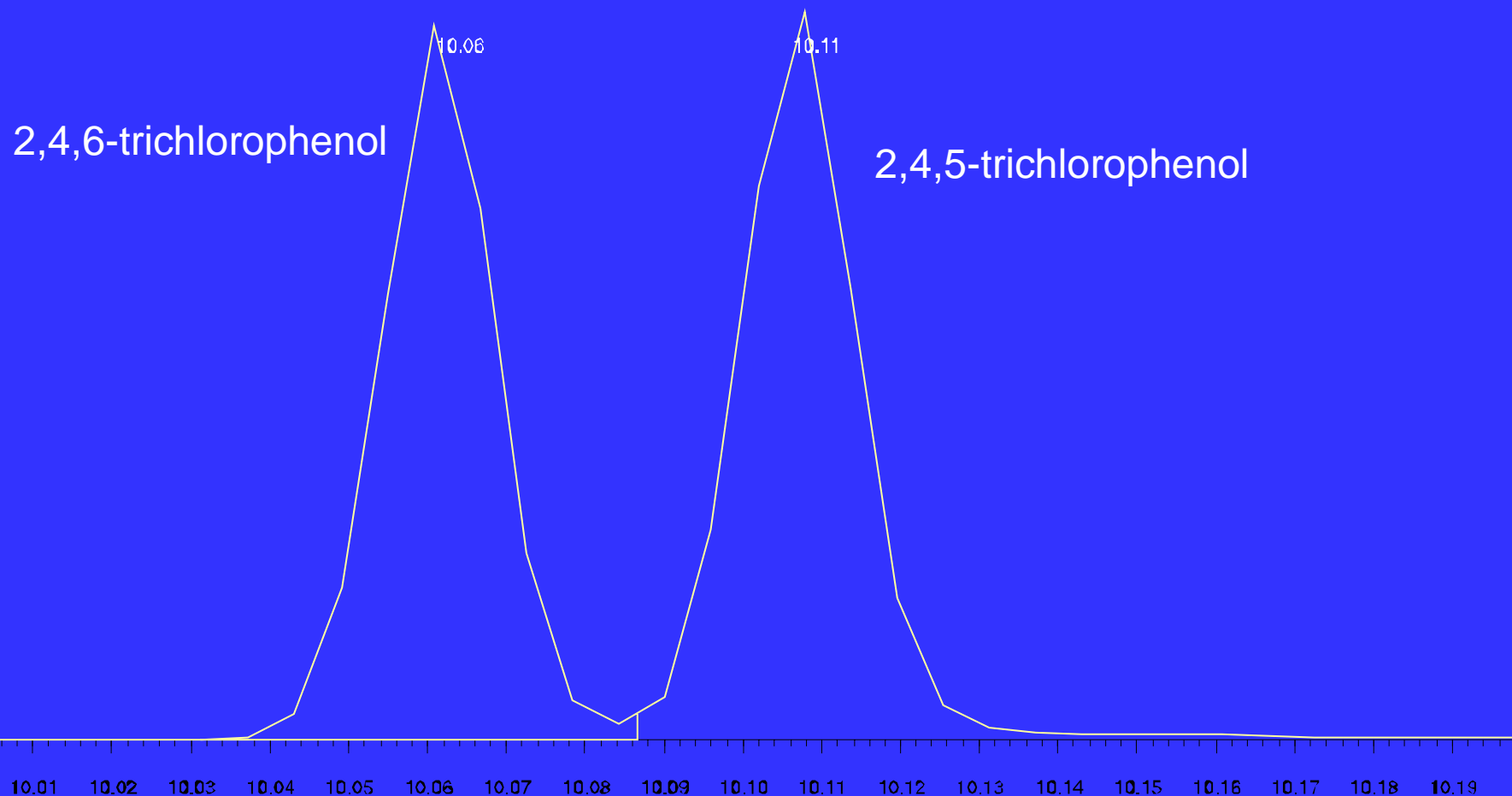
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5µm film)



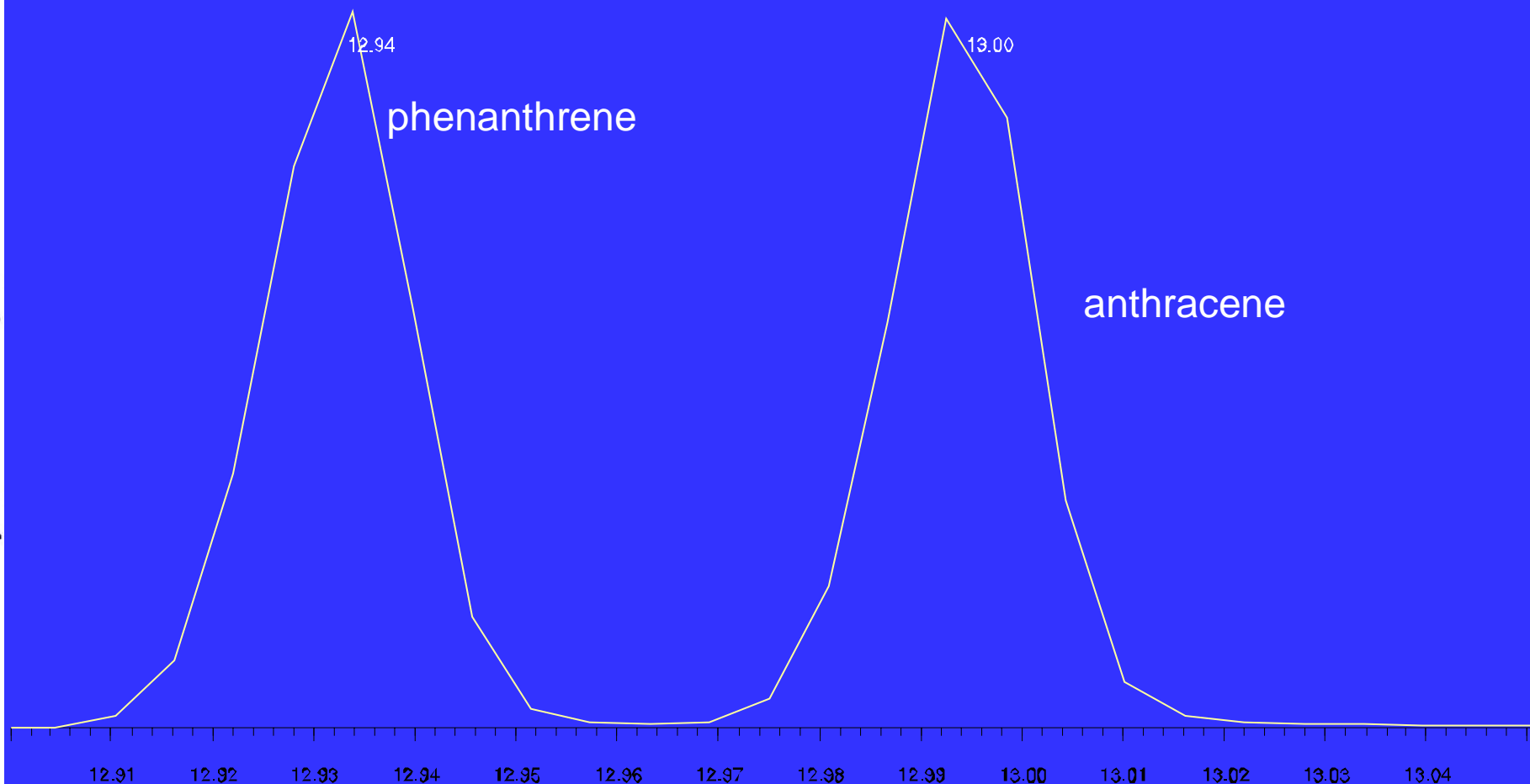
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5 $\mu$ m film)



# Separation of Critical Pairs

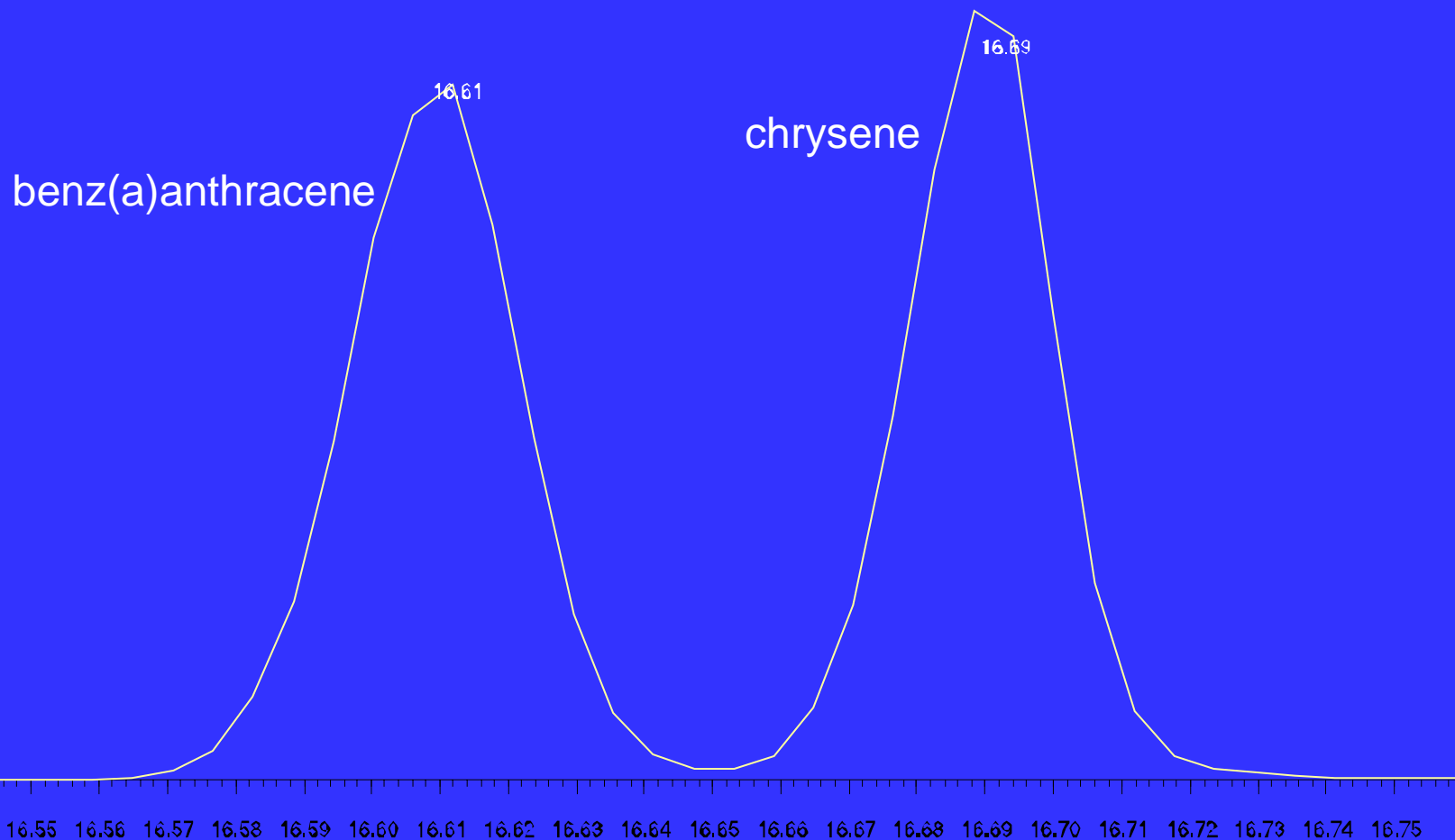
## Rtx-5Sil MS (30m x 0.25mm, 0.5µm film)





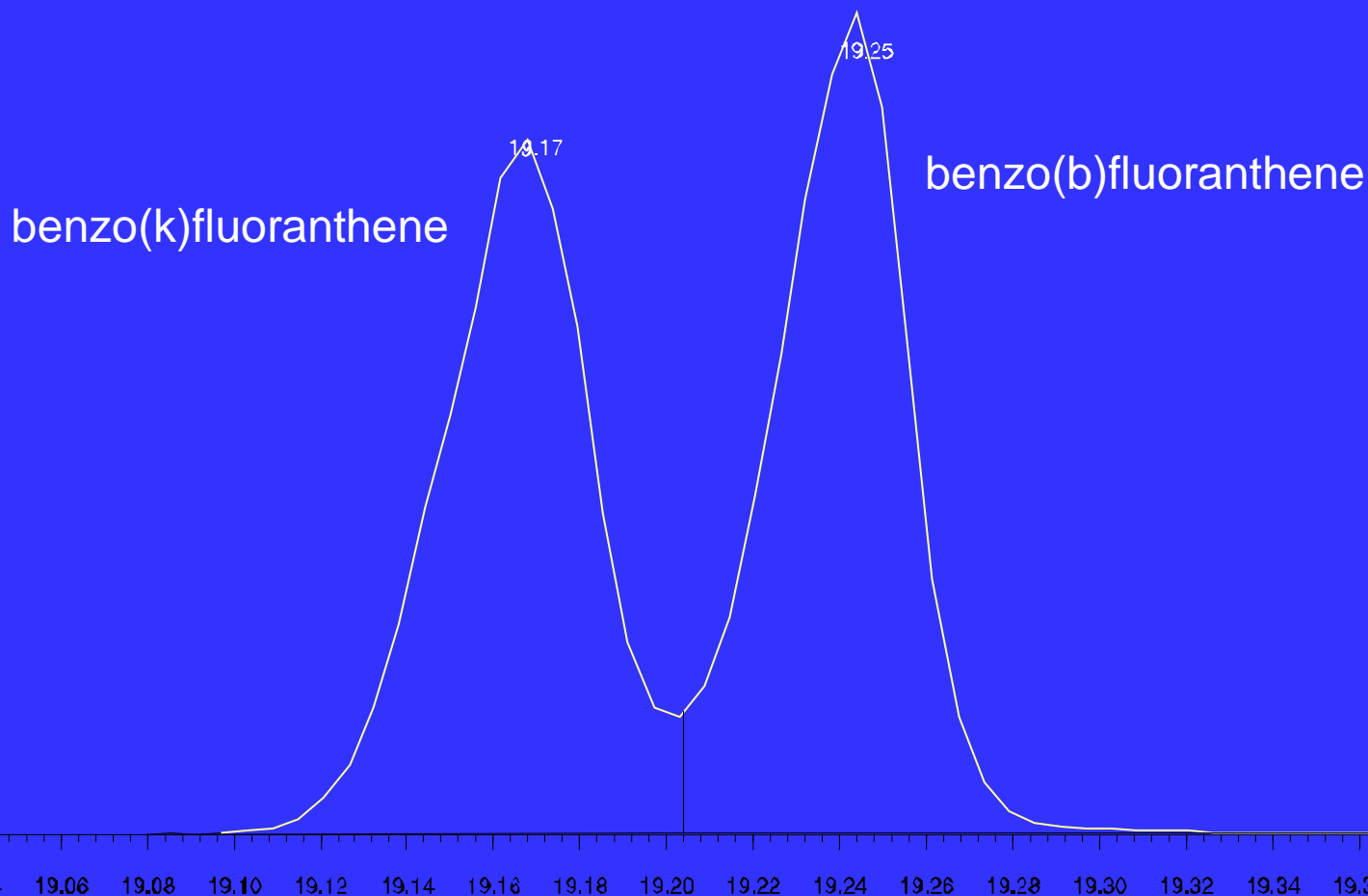
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5 $\mu$ m film)



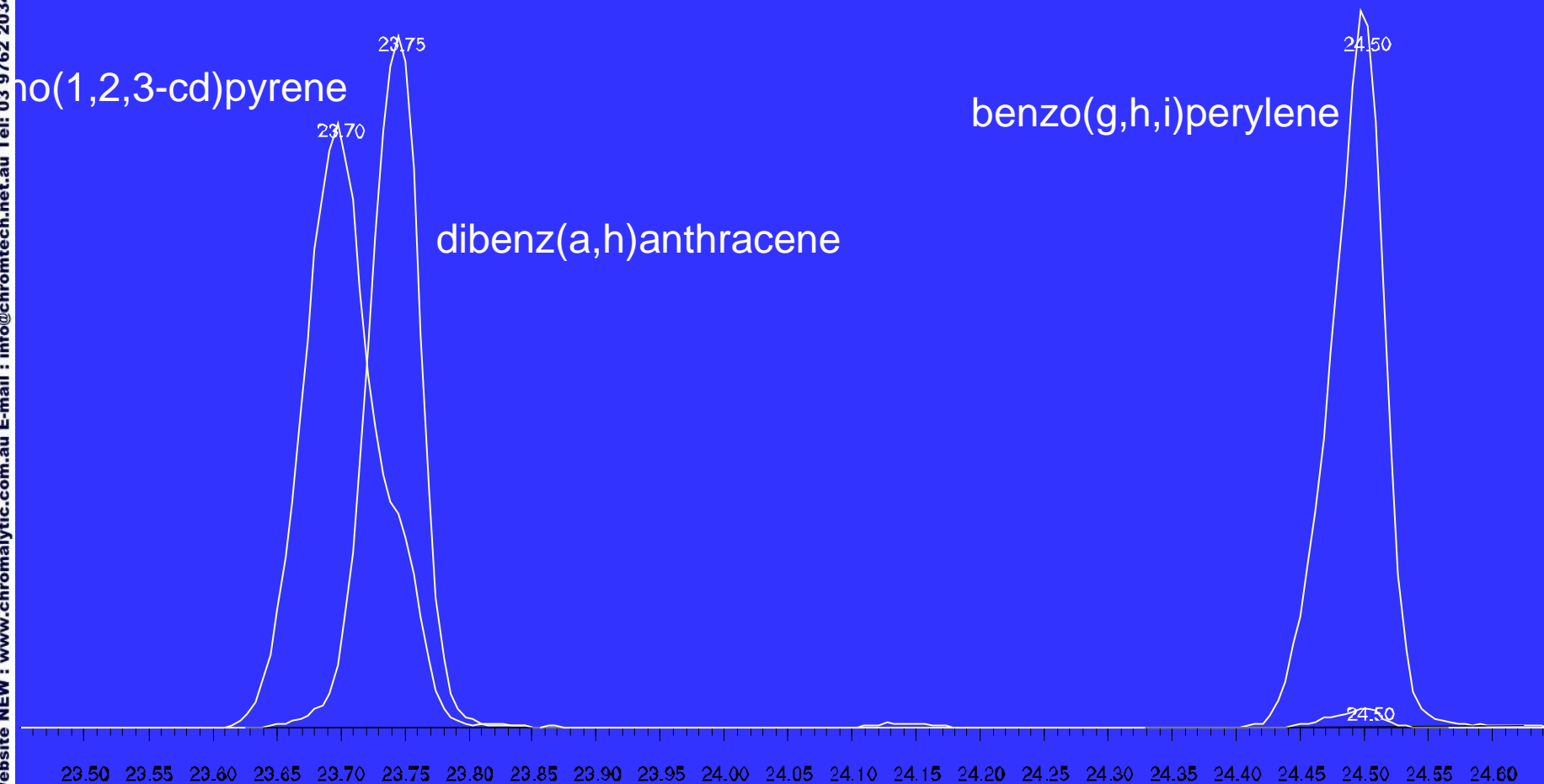
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5 $\mu$ m film)



# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.5 $\mu$ m film)

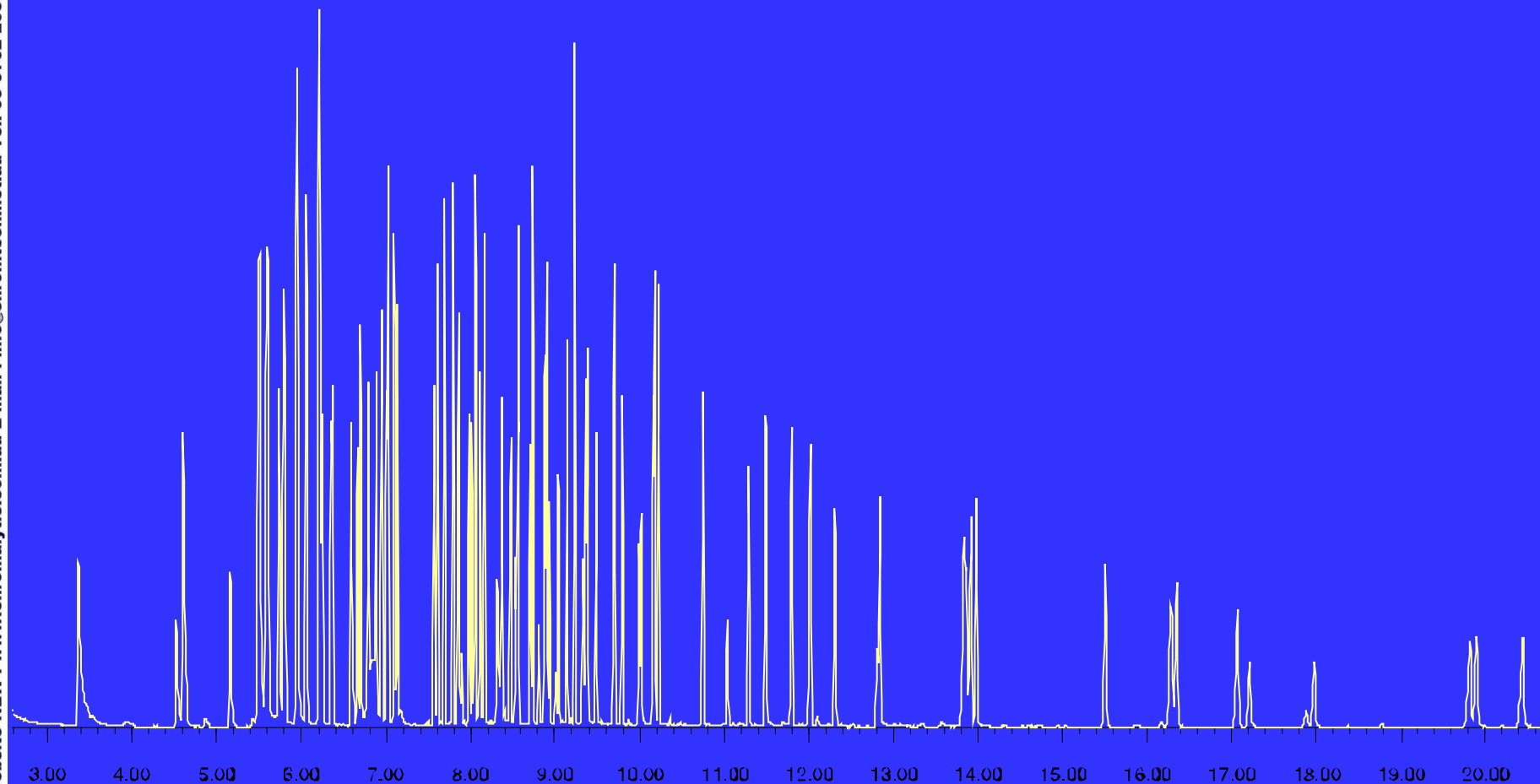


# Can We Go Faster?

- Thinner film columns
- Shorter columns
- Smaller ID

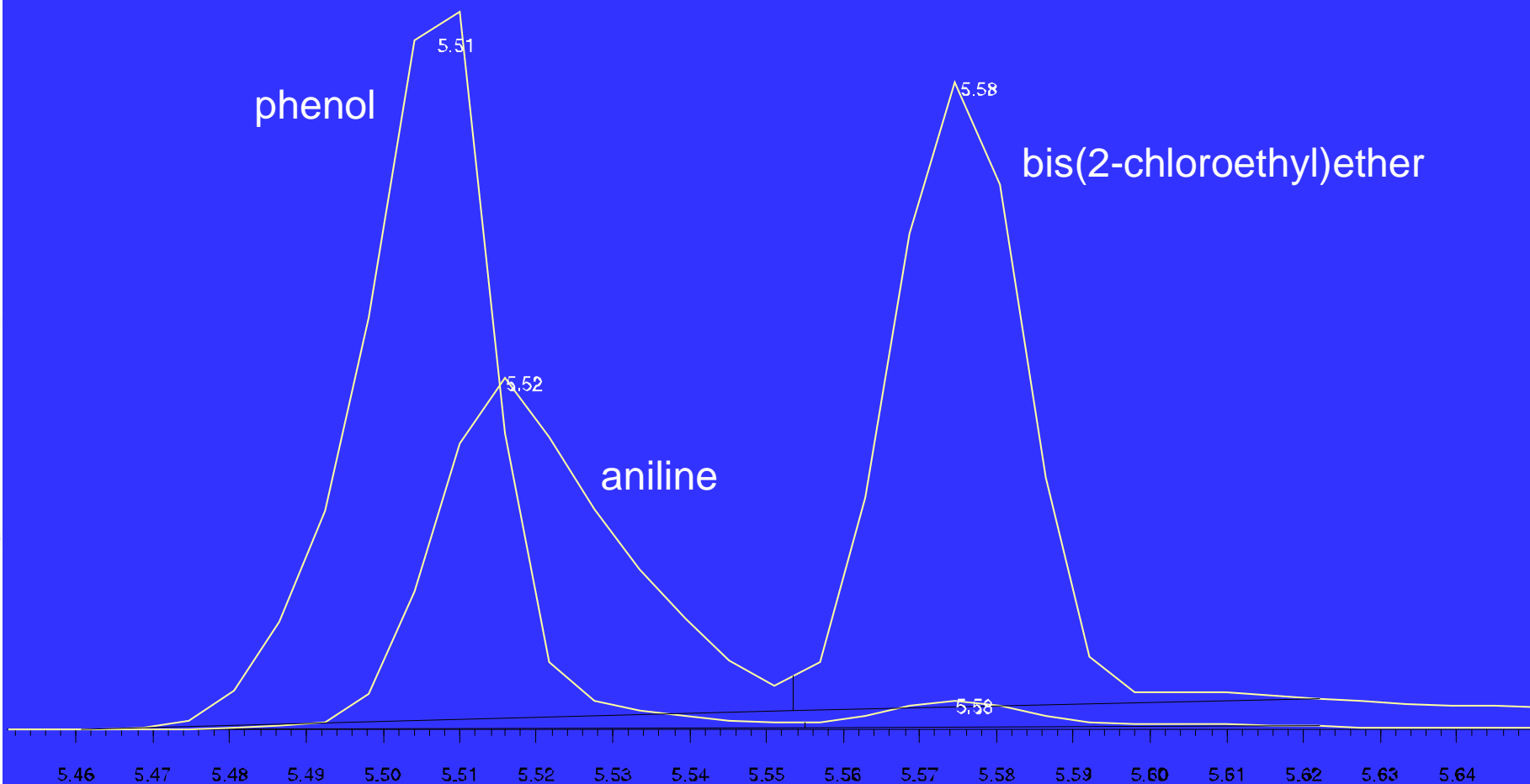
# Rtx-5Sil MS

(30m x 0.25mm ID, 0.25 $\mu$ m film)



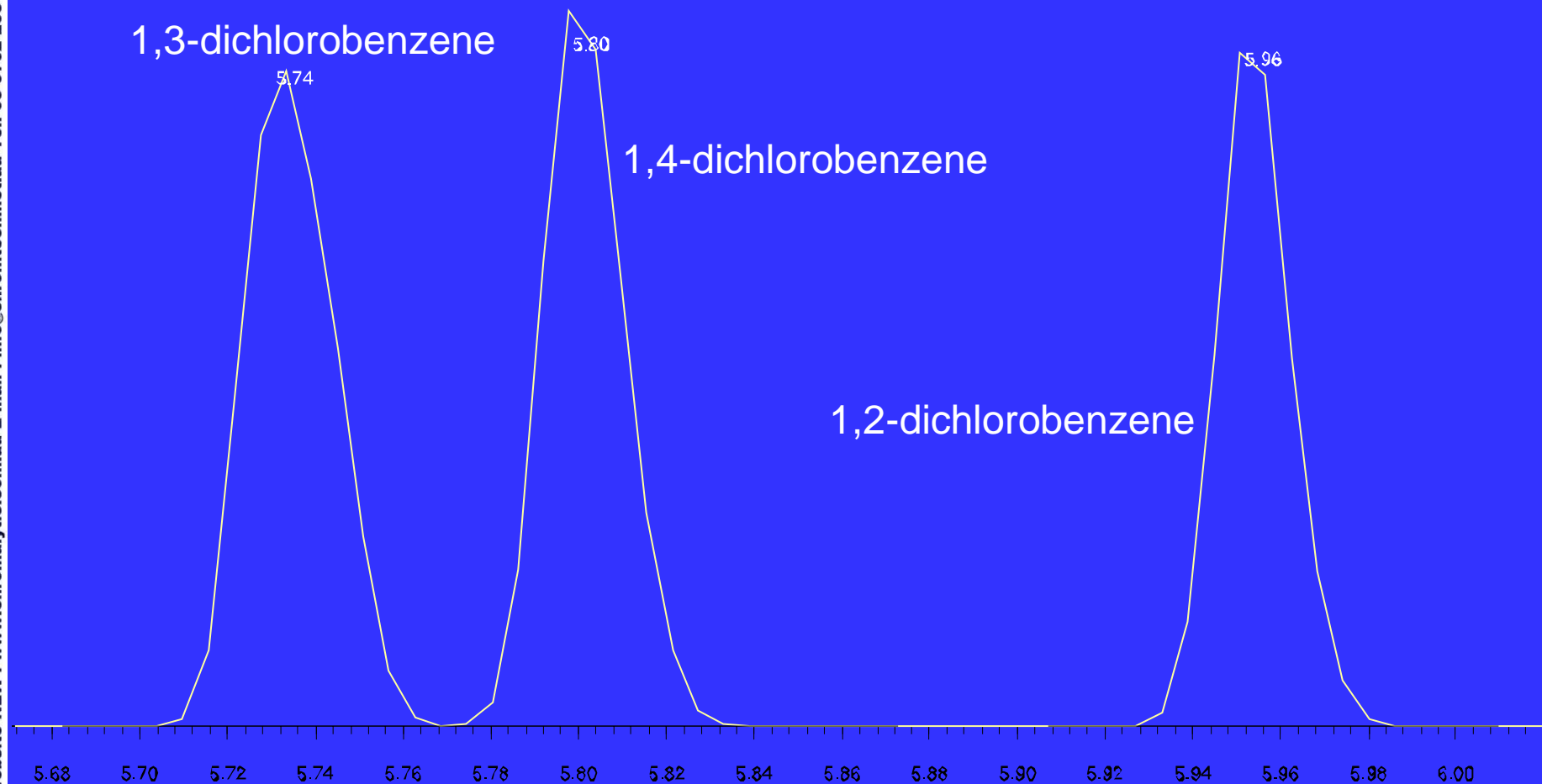
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25 $\mu$ m film)



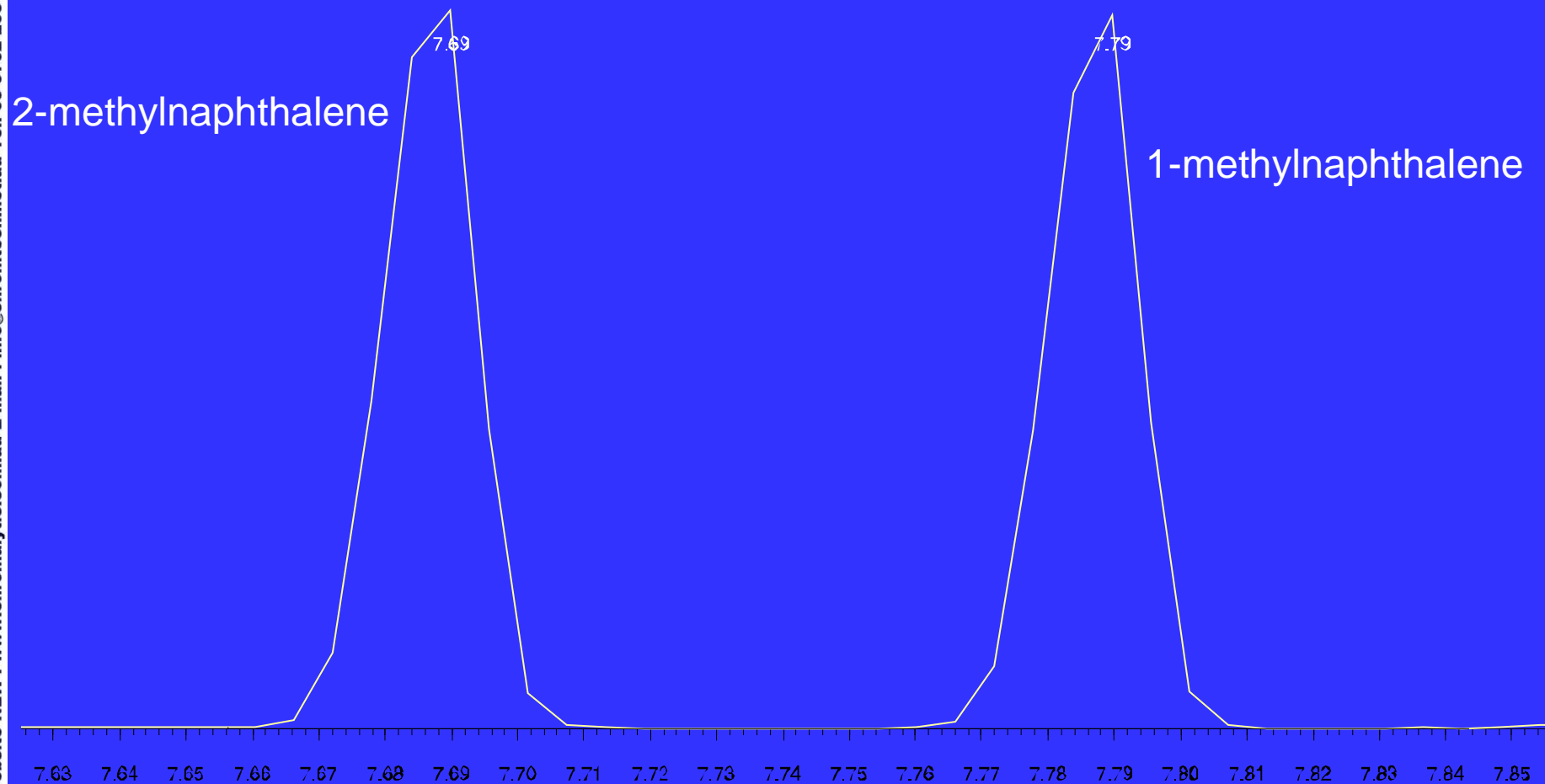
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25µm film)



# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25 $\mu$ m film)





# Separation of Critical Pairs

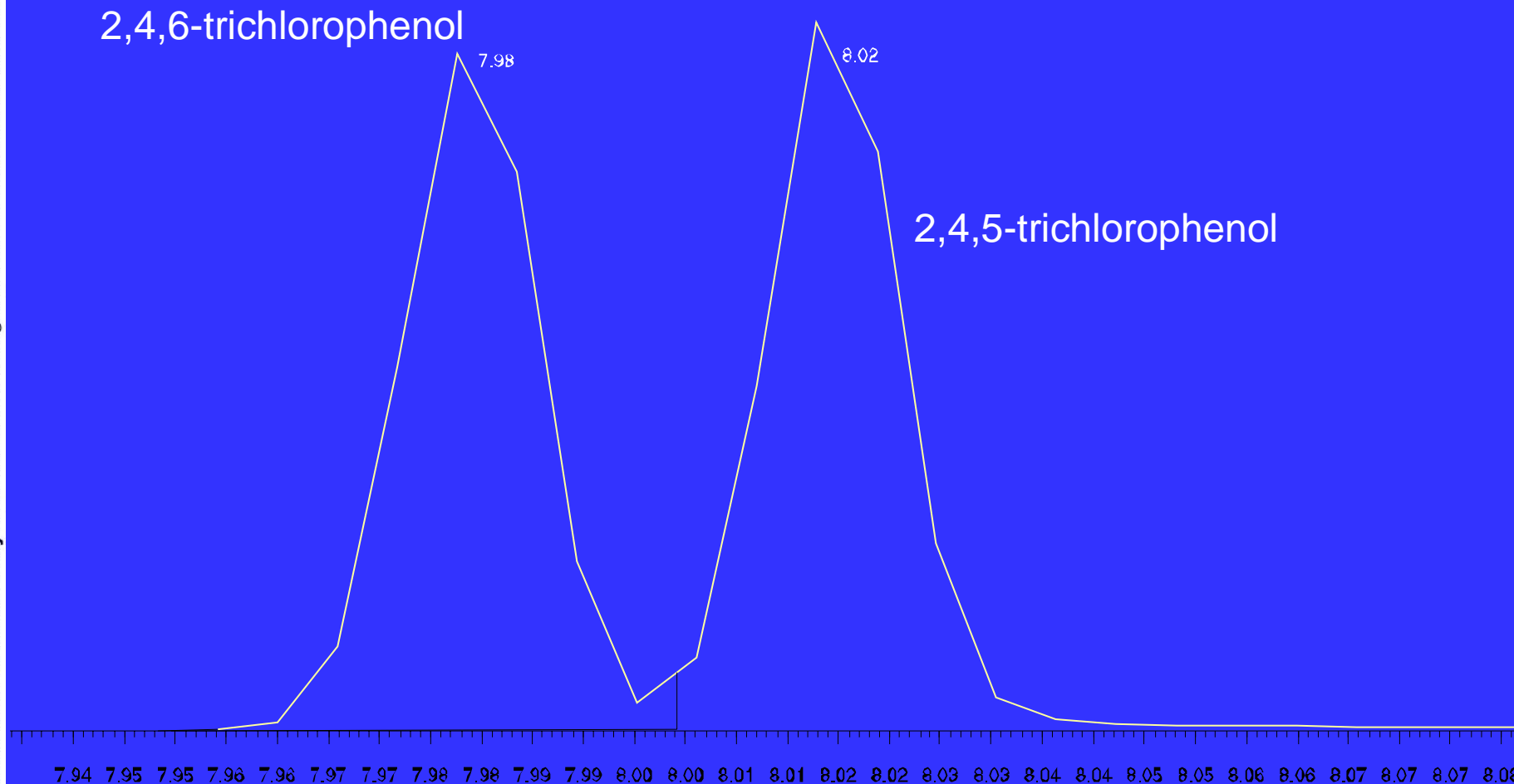
## Rtx-5Sil MS (30m x 0.25mm, 0.25 $\mu$ m film)

2,4,6-trichlorophenol

7.98

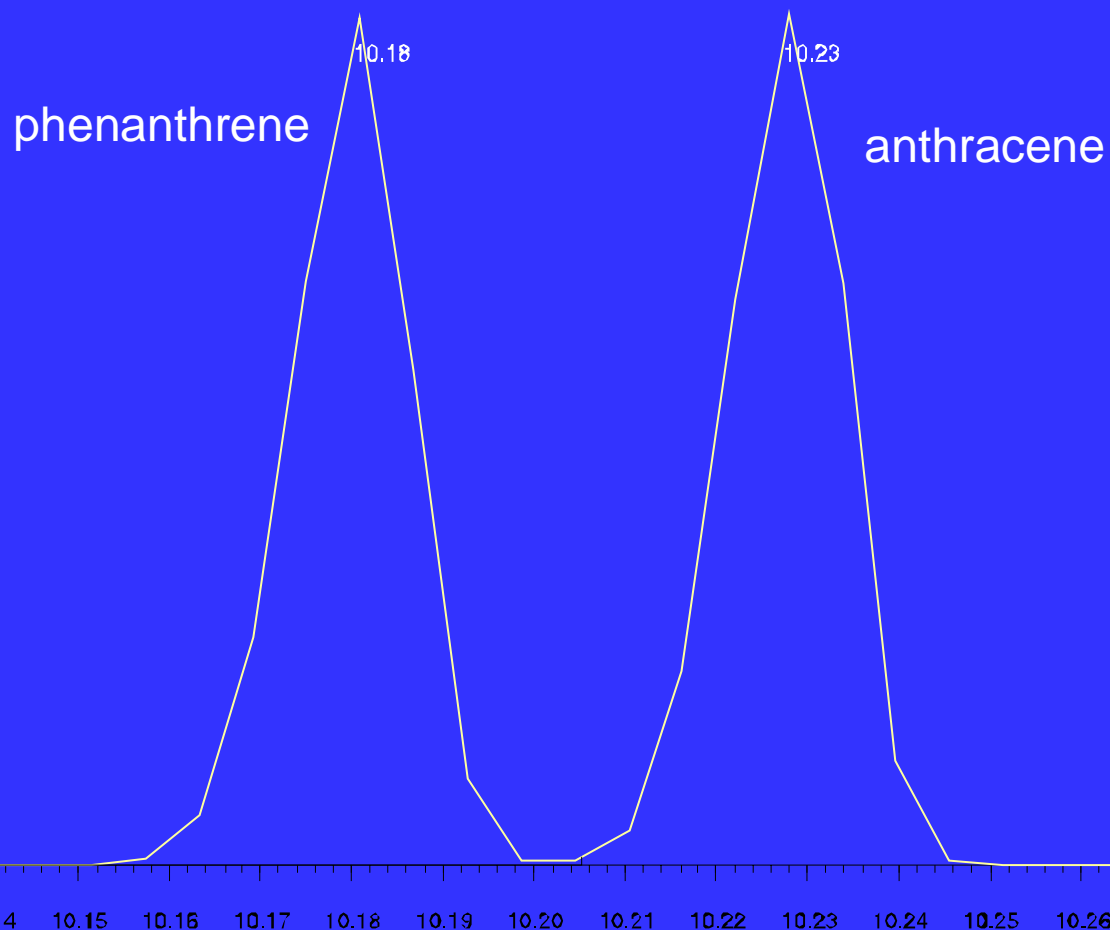
8.02

2,4,5-trichlorophenol



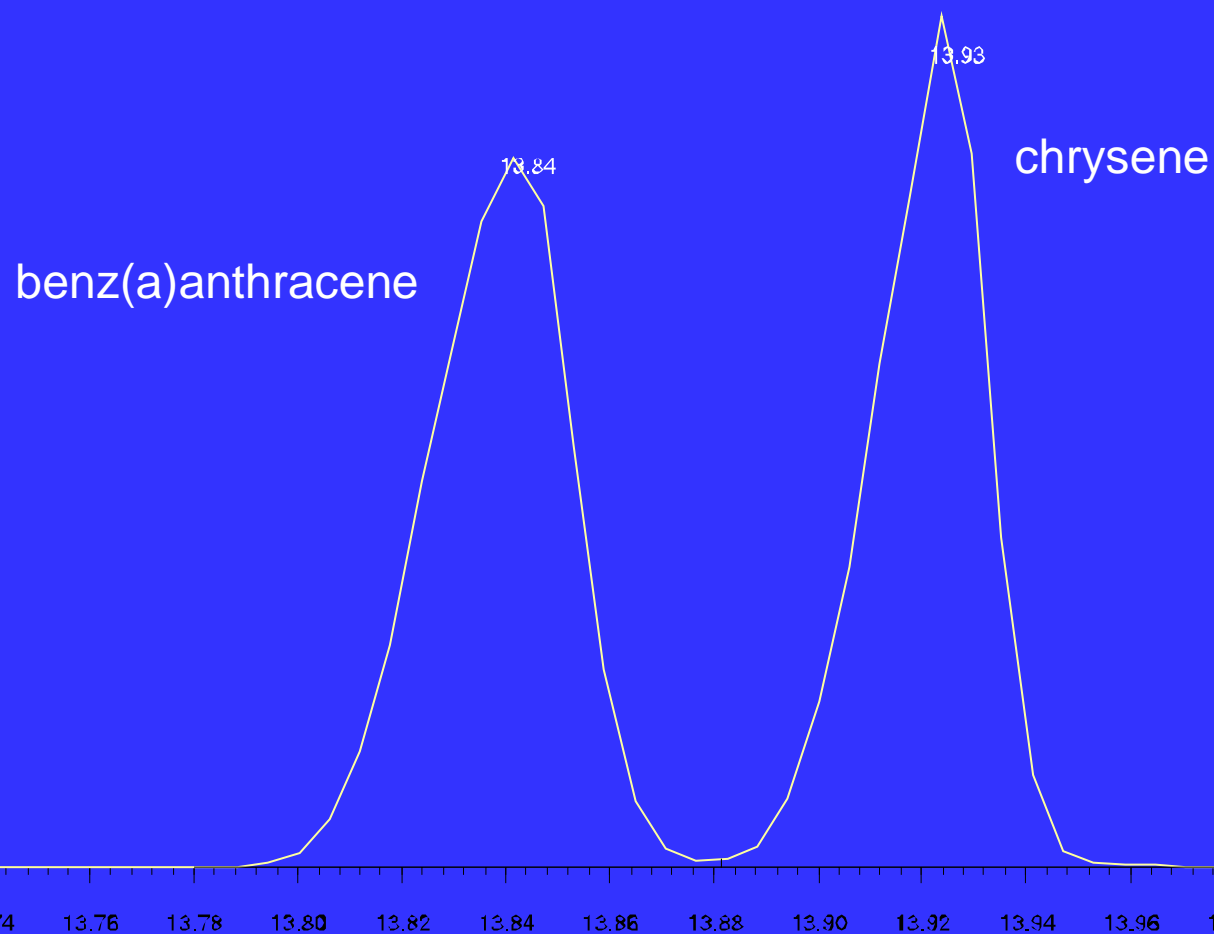
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25 $\mu$ m film)



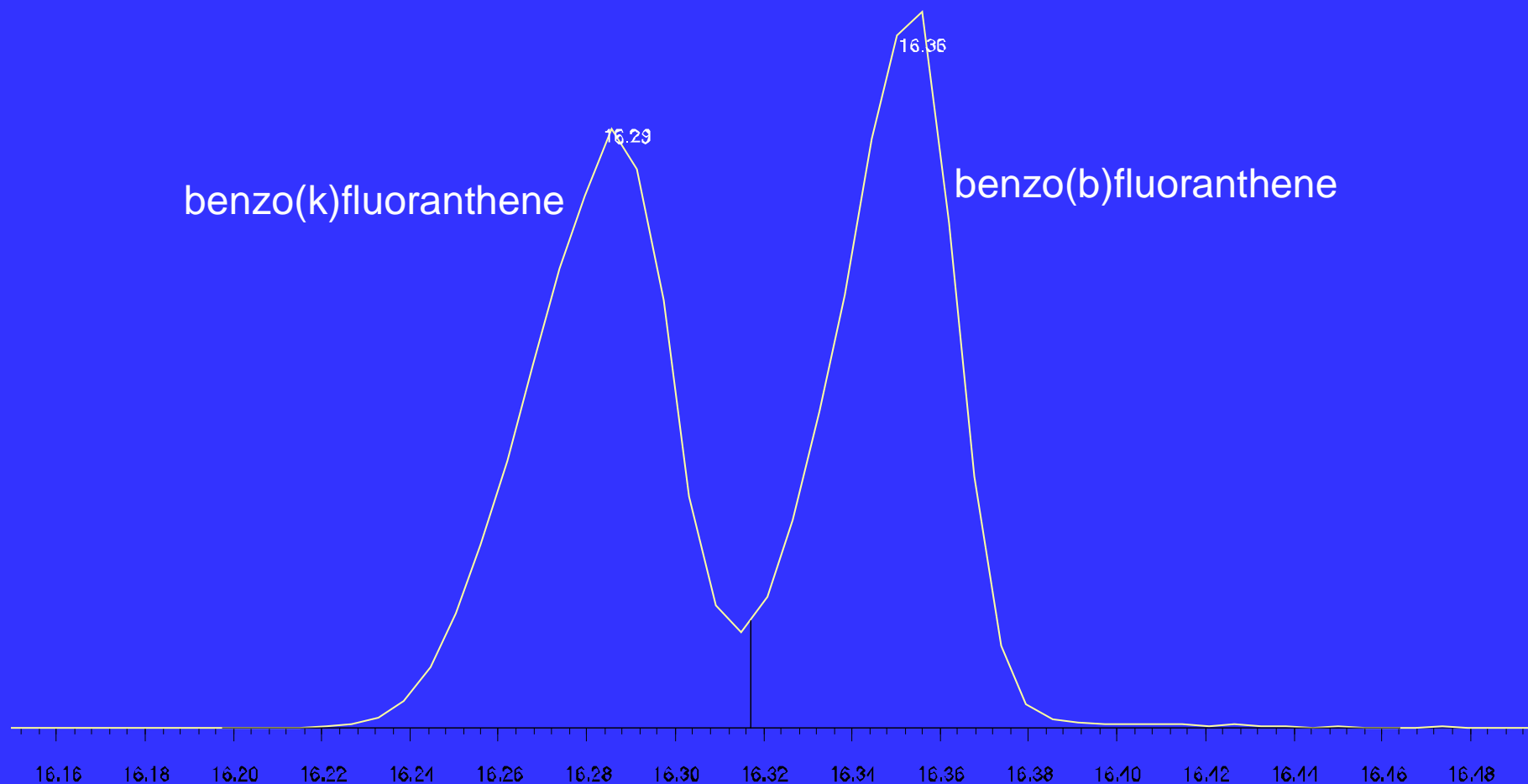
# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25 $\mu$ m film)



# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25 $\mu$ m film)



# Separation of Critical Pairs

## Rtx-5Sil MS (30m x 0.25mm, 0.25µm film)

benzo(1,2,3-cd)pyrene

19.82

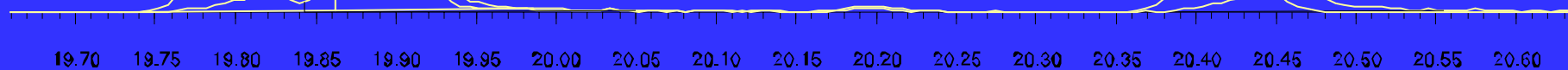
19.91

dibenz(a,h)anthracene

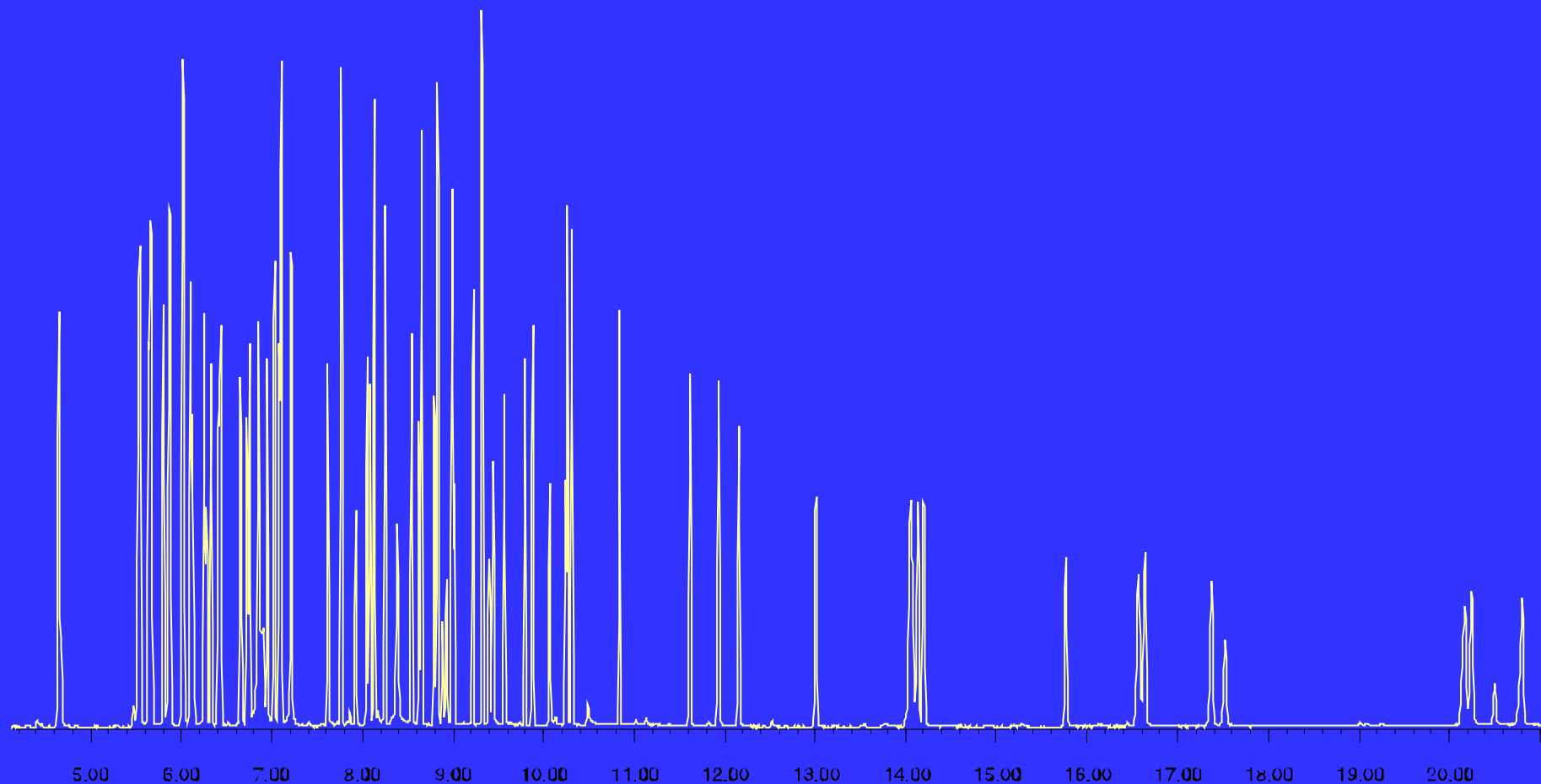
19.91

benzo(g,h,i)perylene

20.45



# Rtx-5 MS Chromatogram (30m x 0.25 mm ID, 0.25 $\mu$ m film)



## Conclusion

- Faster analysis can be accomplished for 8270
- Keep compounds eluting on the temperature program ramp rate
- Faster elution of PAHs helps with column capacity due to lower k value

# The Analysis of Semi-Volatiles with Various Inlet Liner Deactivations

Gary Stidsen, Frank Dorman and  
David Smith

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# GC Inlet Liner Deactivation is Critical for Demanding Analyses

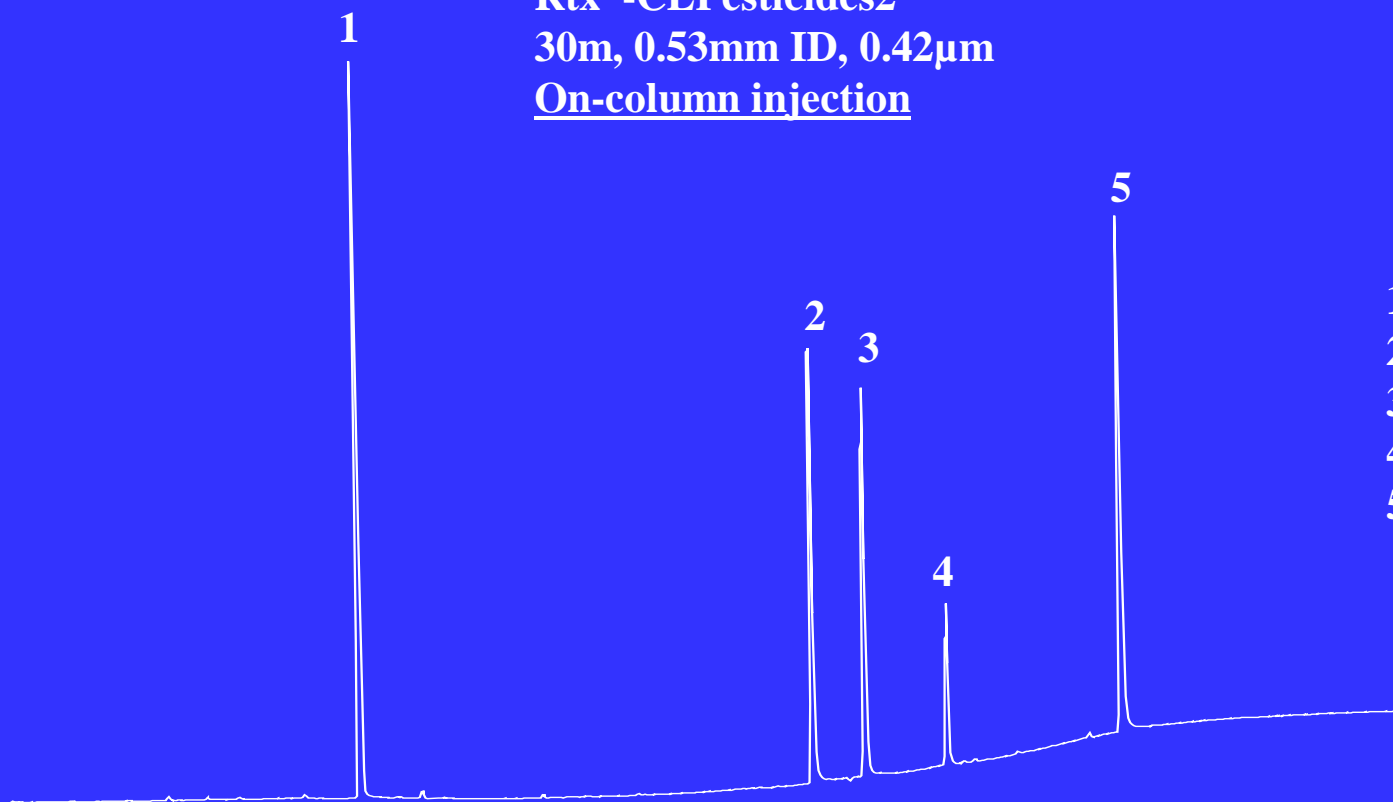
- Chlorinated pesticides
- Amines (basic compounds)
- Environmental semi-volatiles

# Criteria for Evaluating Inlet Liner Performance

- Breakdown of endrin and DDT
- Linear response for acids and bases
- Short conditioning times and low bleed
- Thermal stability
- Resistance to sample degradation

# Pesticide Breakdown, On-Column

Rtx<sup>®</sup>-CLPesticides2  
30m, 0.53mm ID, 0.42µm  
On-column injection



1. TCX
2. endrin
3. 4,4'-DDT
4. methoxychlor
5. DCB

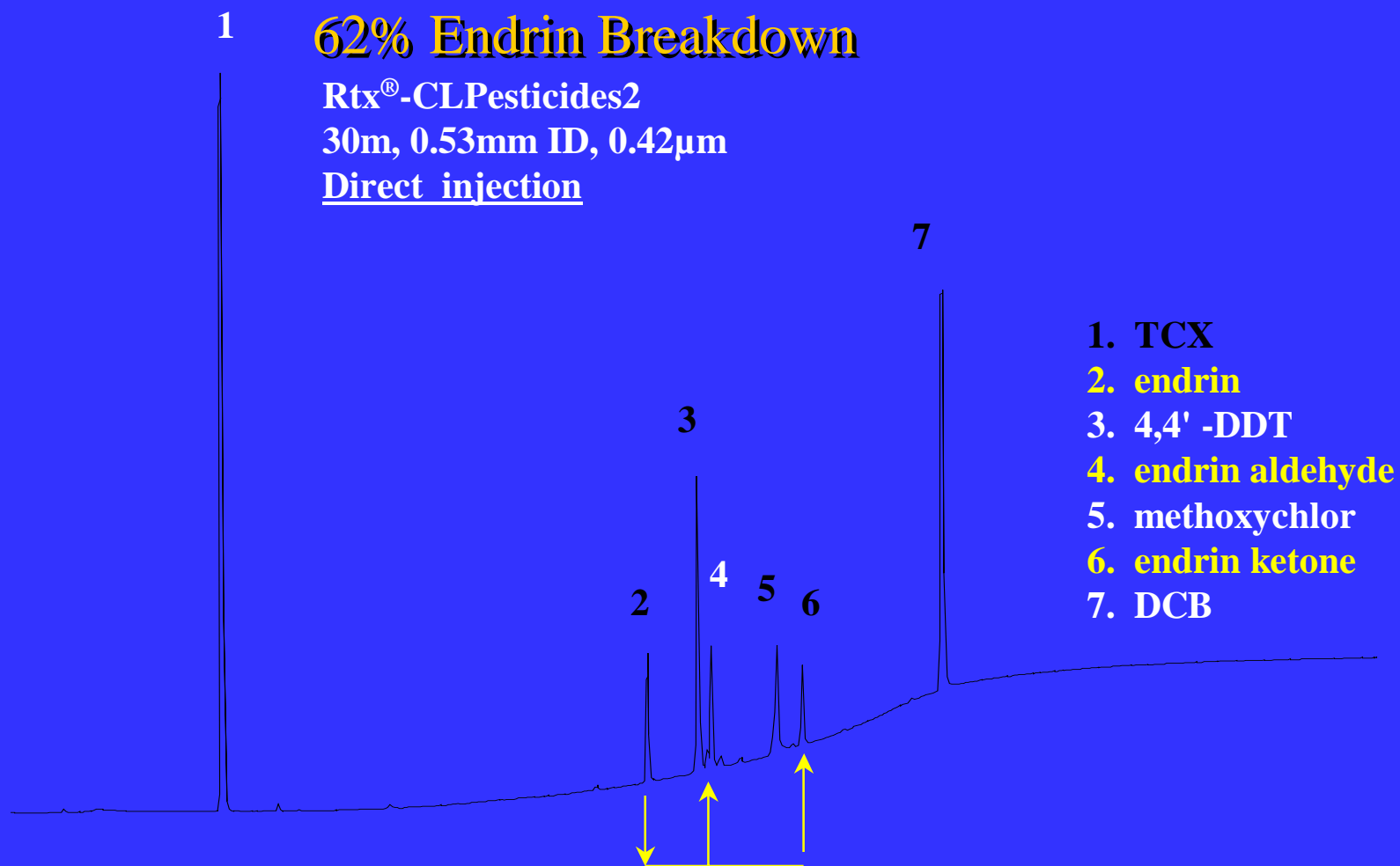
# Raw Glass Inlet Liner

## 62% Endrin Breakdown

Rtx<sup>®</sup>-CLPesticides2

30m, 0.53mm ID, 0.42µm

Direct injection



1. TCX
2. endrin
3. 4,4' -DDT
4. endrin aldehyde
5. methoxychlor
6. endrin ketone
7. DCB

# Types of Liner Deactivation Chemistry

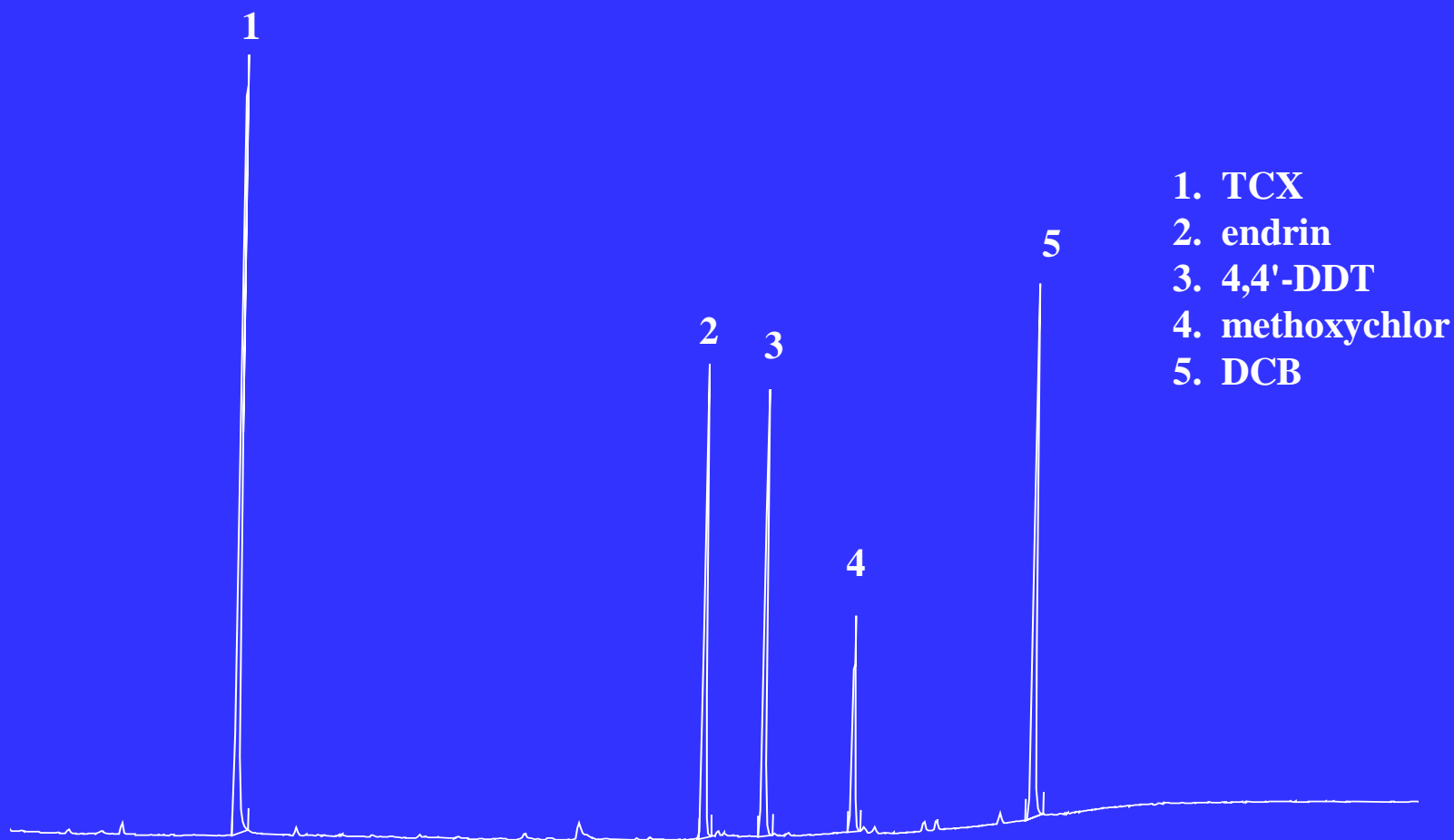
- Pinpoint
- Polymeric
- Base or amine
- Siltek™ Deactivation

# Siltek™ Deactivation

- Inertness for acids, bases, neutrals, pesticides (developed for pesticides analysis)
- Low bleed
- Thermal stability
- Durability (acids, bases, water)
- Regeneration (solvent sonication: explosives analysis and customer feedback)
- Developing Siltek II for SemiVols+

# Siltek™ Inertness

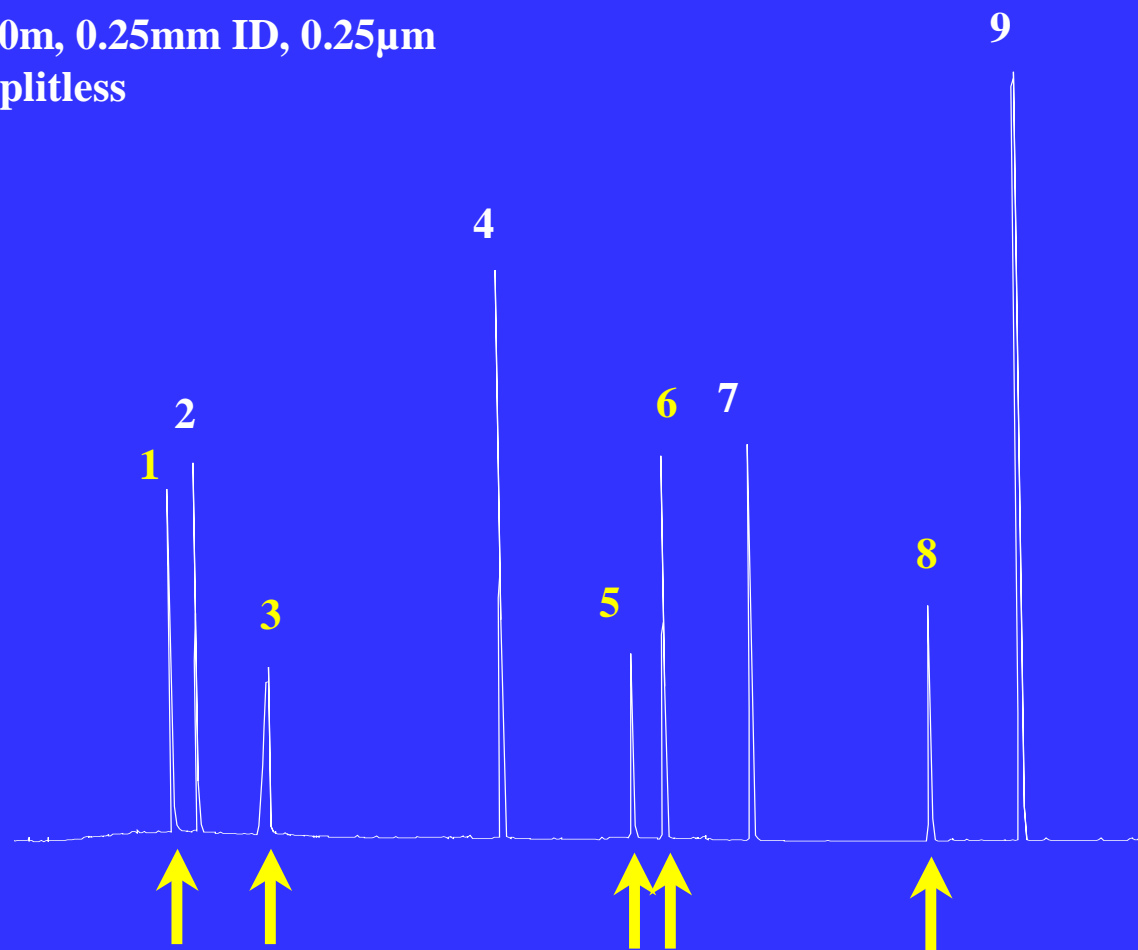
## 1.5% Endrin Breakdown



1. TCX
2. endrin
3. 4,4'-DDT
4. methoxychlor
5. DCB

# Acid Response Splitless XTI Injection

Rtx<sup>®</sup>-5  
30m, 0.25mm ID, 0.25µm  
Splitless

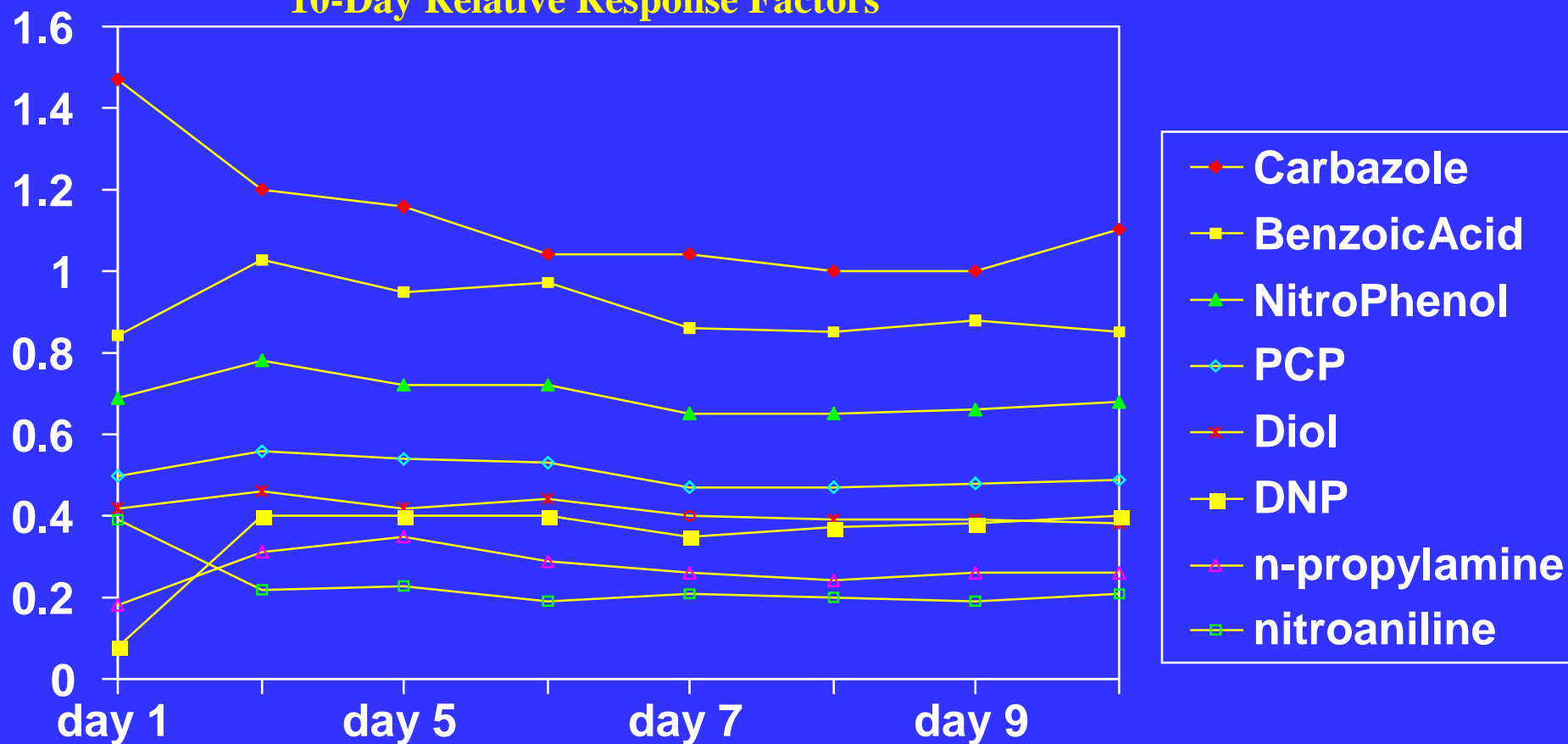


1. 1,2-hexanediol
2. nitro-di-n-propylamine
3. benzoic acid
4. C14
5. 2,4-dinitrophenol
6. nitrophenol
7. nitroaniline
8. pentachlorophenol
9. carbazole



# Thermal Stability at 330°C

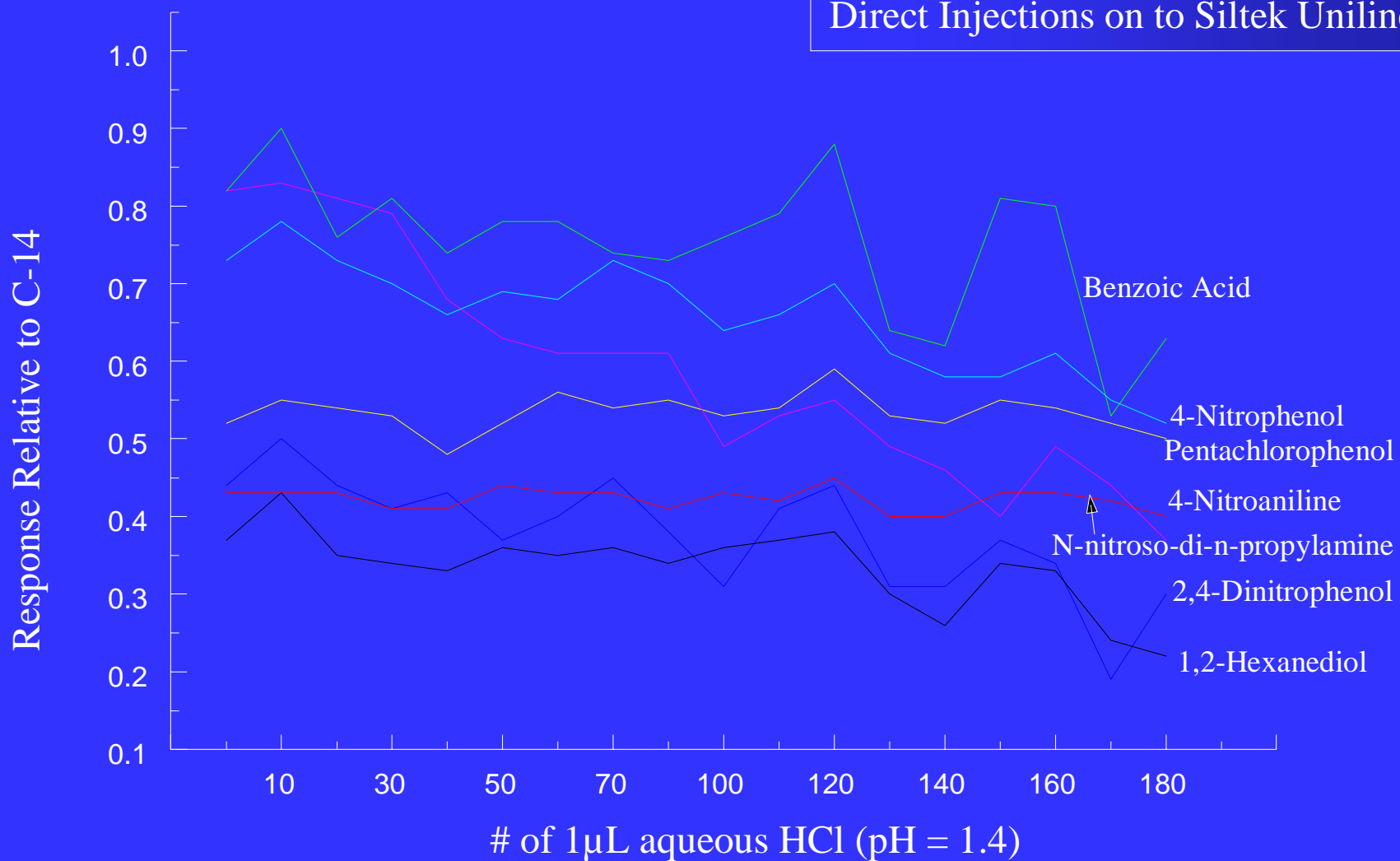
## 10-Day Relative Response Factors



XTI-5, 30m, 0.25mm ID, 0.5 $\mu$ m, splitless Siltek™ liner; Inj.: 330°C; Det.: 330°C;  
Oven temp.: 40°C (hold 2 min.) to 190°C @ 6°C/min to 330°C @ 30°C/min. (hold 10 min.)

# Siltek Sleeve Resistance to Acidic Matrix

Direct Injections on to Siltek Uniliner



# Siltek Sleeve Resistance to Basic Matrix

Direct Injections on to Siltek Unlined



# of 1 µL NH<sub>4</sub>OH (pH = 10.1)

# Chromatographic System

- Agilent 6890 GC
- Agilent 5973 GC/MS
- Restek Rtx-5Sil MS 30m x 0.28mm x 0.5um
- Constant flow rate @ 1.0 mL/min
- Temperature program:
  - 40°C (2 min); 20°C/min to 290°C (0 min); 2°C/min to 303°C (0 min); 6°C/min to 330°C (1 min)
- Splitless hold time 0.4min
- Single gooseneck 4mm ID liners

# Classes of Compounds

## 8270 Calibration Mix #1

benzoic acid	3-methylphenol
4-chloro-3-methylphenol	4-methylphenol
2-chlorophenol	2-nitrophenol
2,4-dichlorophenol	4-nitrophenol
2,6-dichlorophenol	pentachlorophenol
2,4-dimethylphenol	phenol
4,6-dinitro-2-methylphenol	2,3,4,6-tetrachlorophenol
2,4-dinitrophenol	2,4,5-trichlorophenol
dinoseb	2,4,6-trichlorophenol
2-methylphenol	

## 8270 Calibration Mix #2

aniline	3-nitroaniline
benzidine	4-nitroaniline
4-chloroaniline	N-nitrosodimethylamine
3,3'-dichlorobenzidine	N-nitrosodi-n-propylamine
diphenylamine	pyridine
2-nitroaniline	

# Classes of Compounds

## 8270 Calibration Mix #3

aramite

bis (2-chloroethyl) ether

bis (2-chloroethoxy) methane

bis (2-chloroisopropyl) ether

4-bromophenyl phenyl ether

chlorobenzilate

2-chloronaphthalene

4-chlorophenyl phenyl ether

1,2-dichlorobenzene

1,3-dichlorobenzene

1,4-dichlorobenzene

1,3-dinitrobenzene

hexachlorobenzene

hexachlorobutadiene

hexachlorocyclopentadiene

hexachloroethane

hexachloropropene

isodrin

kepone

pentachlorobenzene

pentachloronitrobenzene

1,2,4,5-tetrachlorobenzene

1,2,4-trichlorobenzene

# Classes of Compounds

## 8270 Calibration Mix #4

acetophenone  
azobenzene  
benzyl alcohol  
bis (2-ethylhexyl) phthalate  
butyl benzyl phthalate  
dibenzofuran  
diethyl phthalate  
dimethyl phthalate  
di-n-butyl phthalate  
di-n-octyl phthalate  
2,4-dinitrotoluene

2,6-dinitrotoluene  
ethyl methanesulfonate  
isophorone  
isosafrole (cis & trans)  
methyl methanesulfonate  
1,4-naphthoquinone  
nitrobenzene  
4-nitroquinoline-1-oxide  
phenacetin  
safrole

# Classes of Compounds

## 8270 Calibration Mix #5

acenaphthene  
acenaphthylene  
anthracene  
benzo(a)pyrene  
benzo(ghi)perylene  
benzo(a)anthracene  
benzo(b)fluoranthene  
benzo(k)fluoranthene  
chrysene  
dibenz(a,h)anthracene

fluoranthene  
fluorene  
ideno(1,2,3-cd)pyrene  
1-methylnaphthalene  
naphthalene  
3-methylcholanthrene  
2-methylnaphthalene  
phenanthrene  
pyrene



# Classes of Compounds

## 8270 Calibration Mix #6

diallate (cis & trans)  
dimethoate  
disulfoton  
famphur  
methyl parathion

parathion  
phorate  
pronamide  
thionazine  
0,0,0-triethyl phosphorothioate

## Organochlorine Pesticide Mix AB #1

aldrin  
a-BHC  
a-chlordane  
b-BHC  
4,4'-DDD  
4,4'-DDE  
4,4'-DDT  
d-BHC  
dieldrin  
endosulfan I

endosulfan II  
endosulfan sulfate  
endrin  
endrin aldehyde  
endrin ketone  
g-BHC (lindane)  
g-chlordane  
heptachlor  
heptachlor epoxide (B)  
methoxychlor

# Criteria for Trace Analysis

## EPA Method 8270C

- Linearity of response relative to ISTD 20 - 160ng/ $\mu$ L
- Minimum relative response factor (RRF) and % relative standard deviation (RSD)

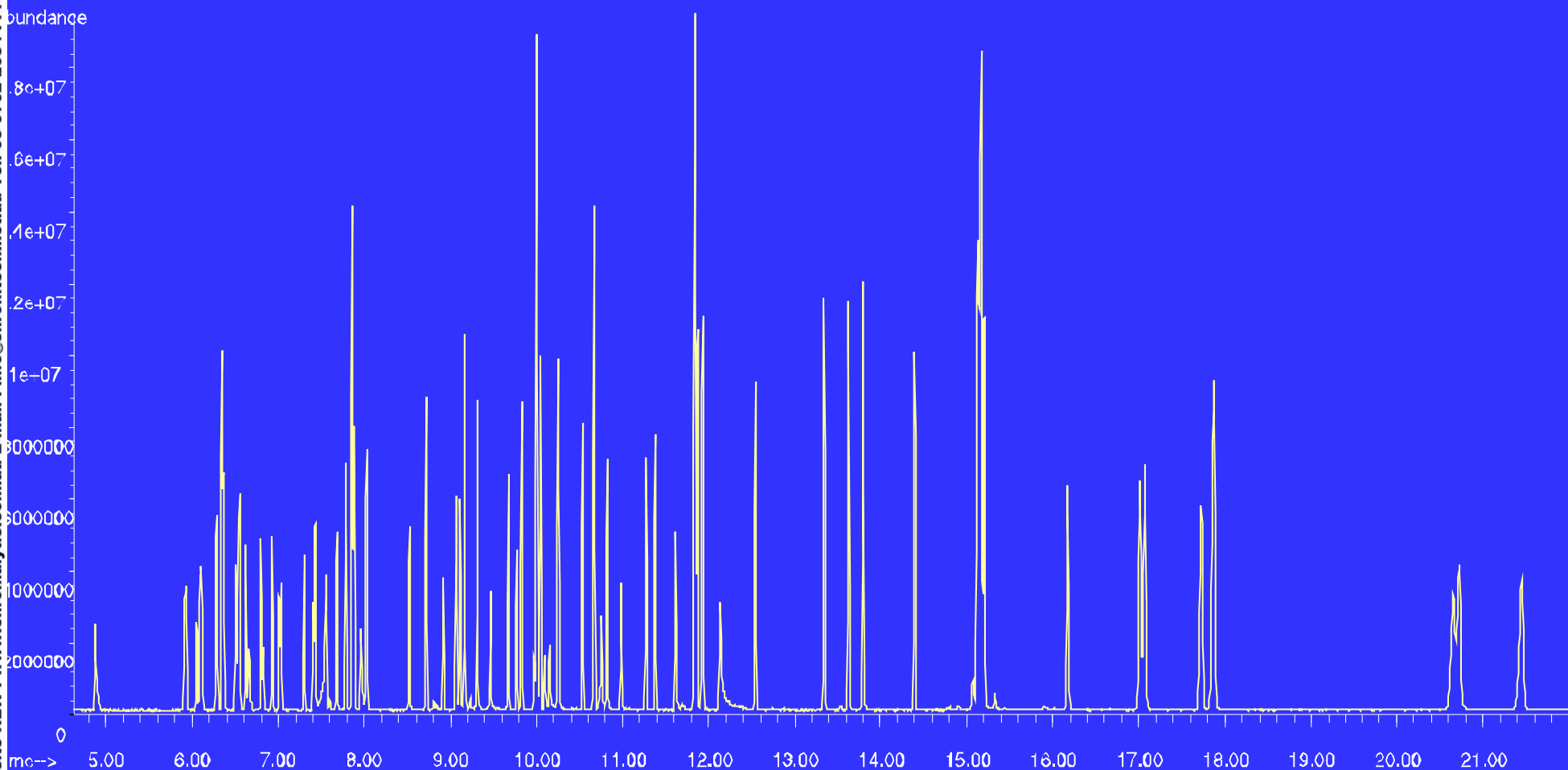
	Min. RRF	Min. %RSD
2,4-dinitrophenol	0.050	15
4-nitrophenol	0.050	15
N-nitroso-di-n-propylamine	0.050	15
hexachlorocyclopentadiene	0.050	15

# Sample Chromatogram

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Importers & Manufacturers  
[www.chromtech.net.au](http://www.chromtech.net.au)

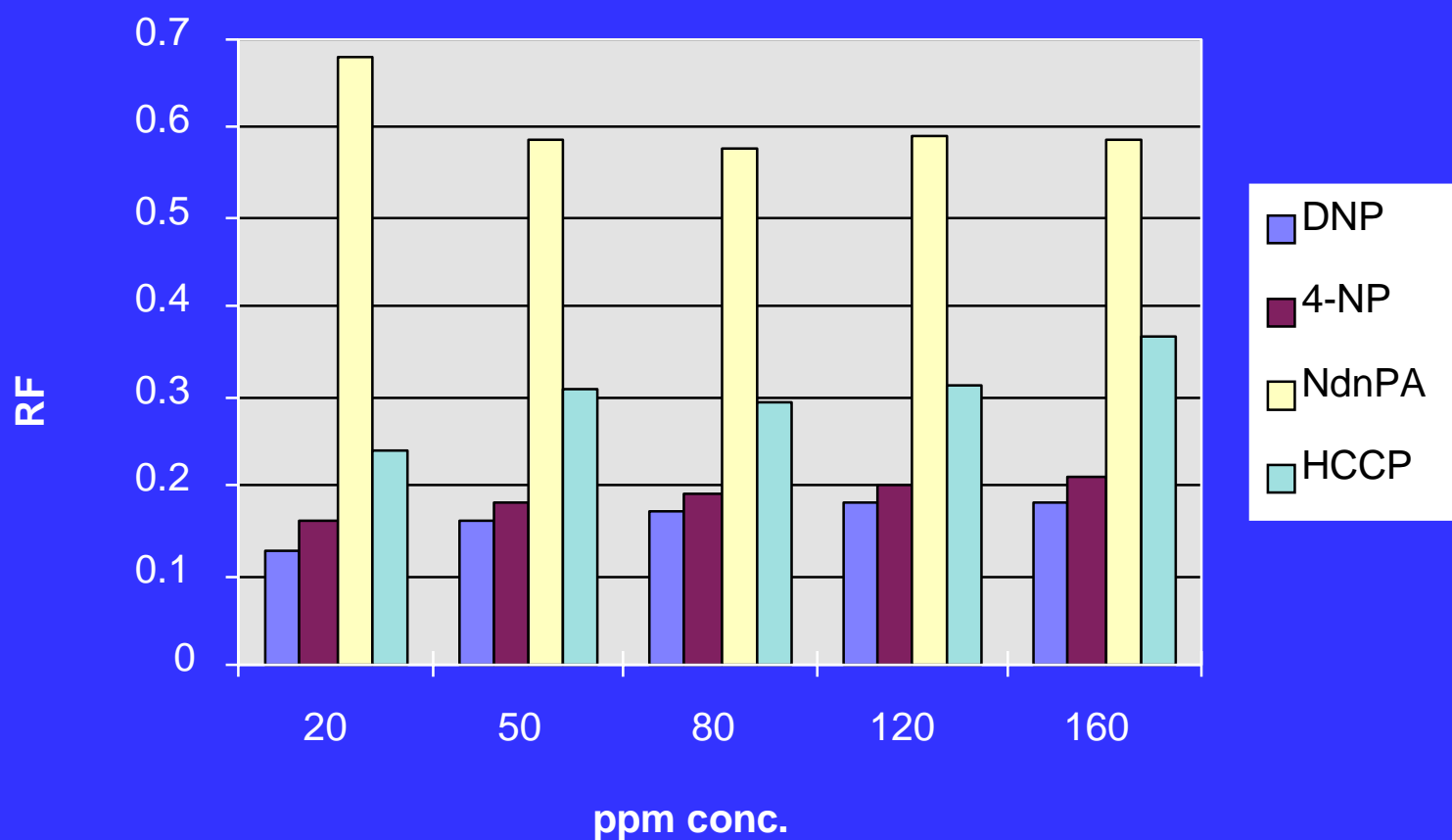
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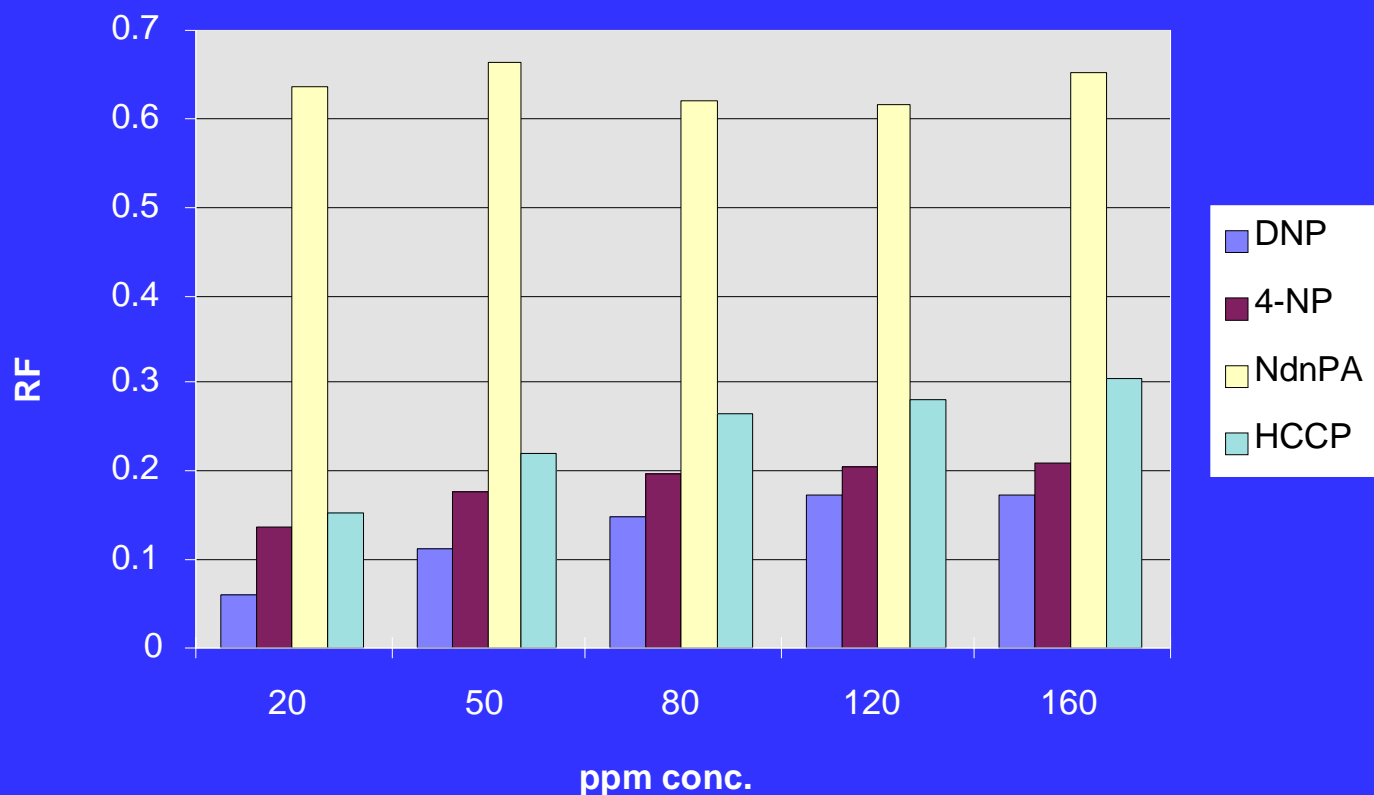
# Standard Liner Response

Response Factors for SPCCs



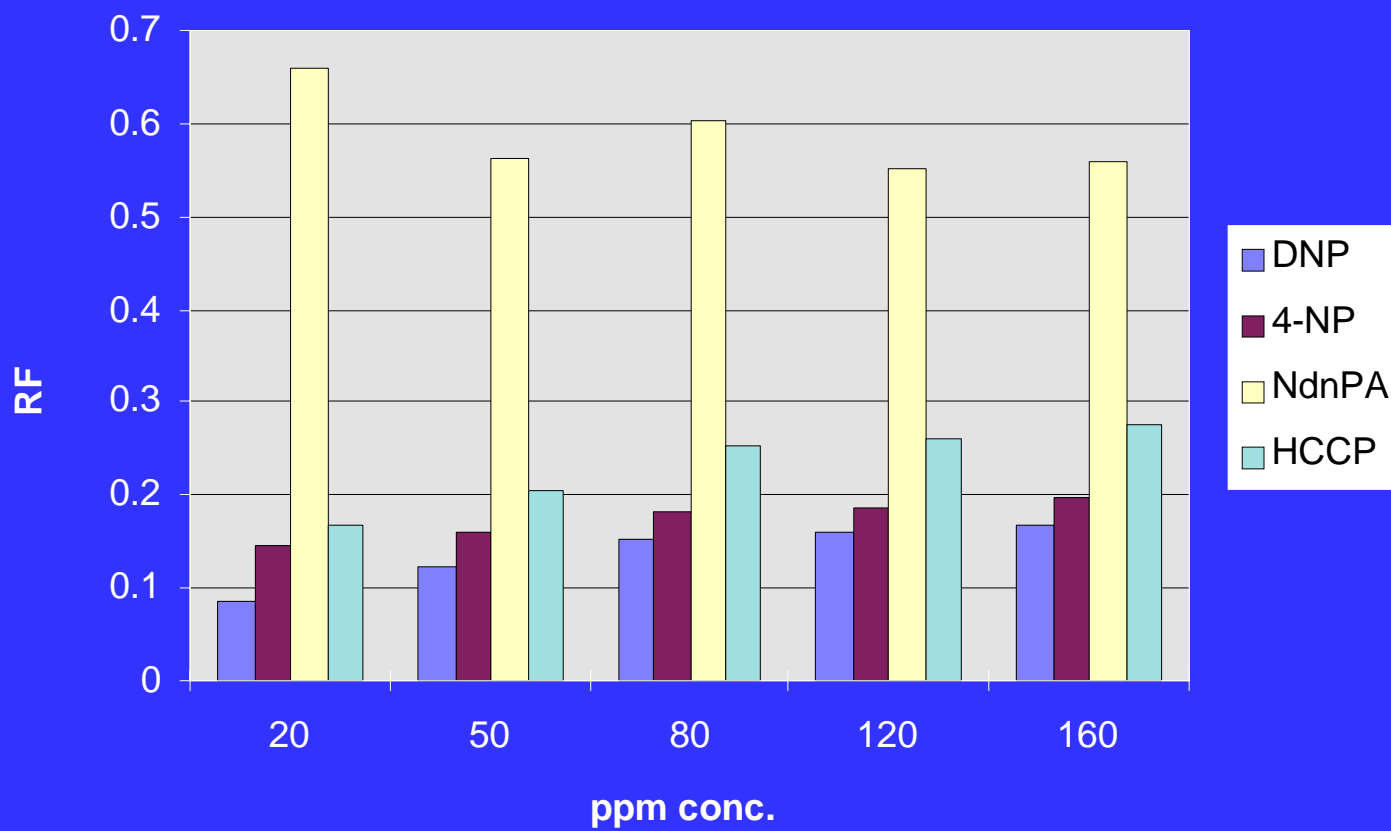
# Standard Siltek Liner Response

Response Factors for SPCCs



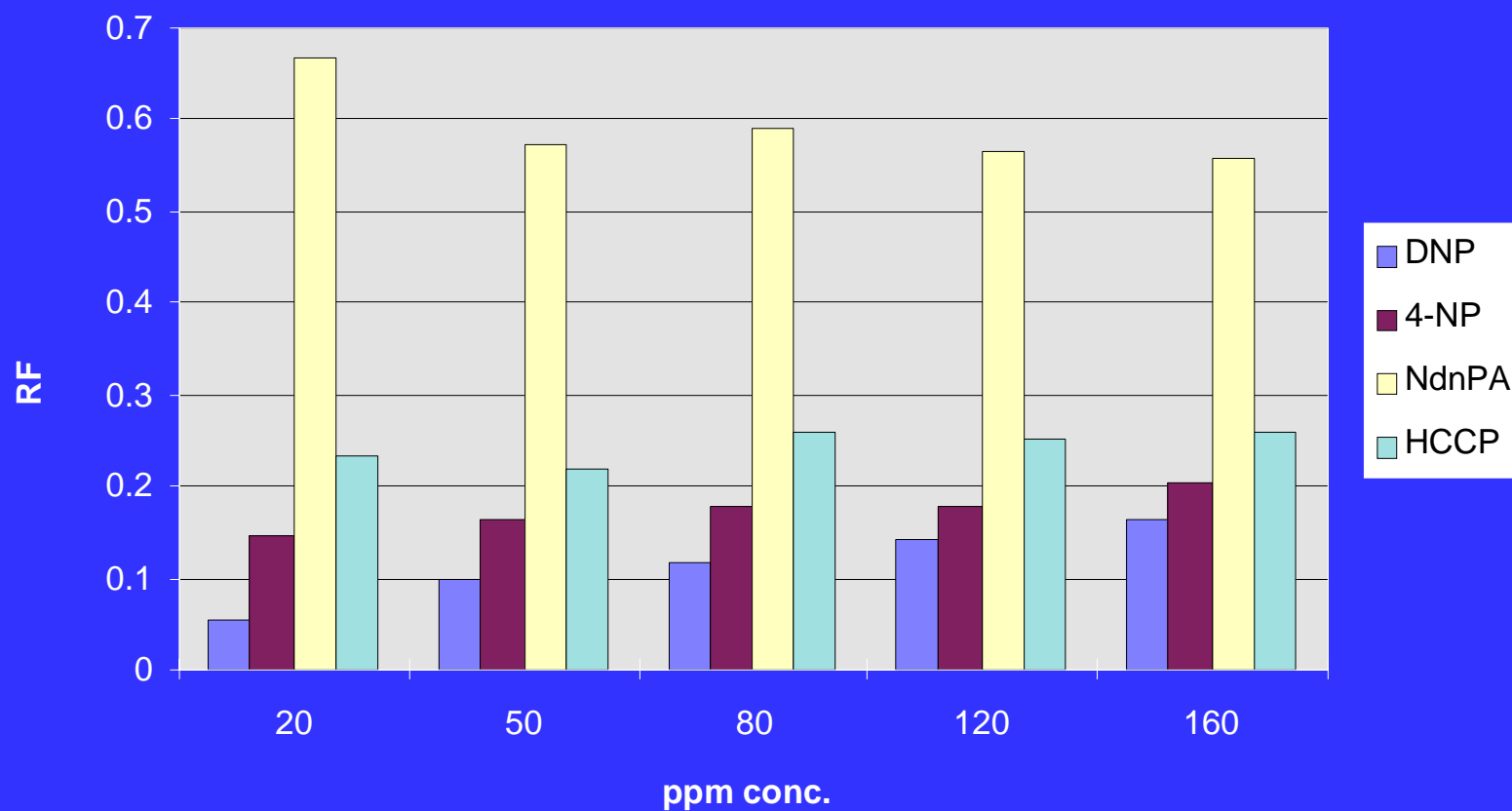
# Experimental Siltek-A Response

Response Factors for SPCCs



# Experimental Siltek-B Response

Response Factors for SPCCs



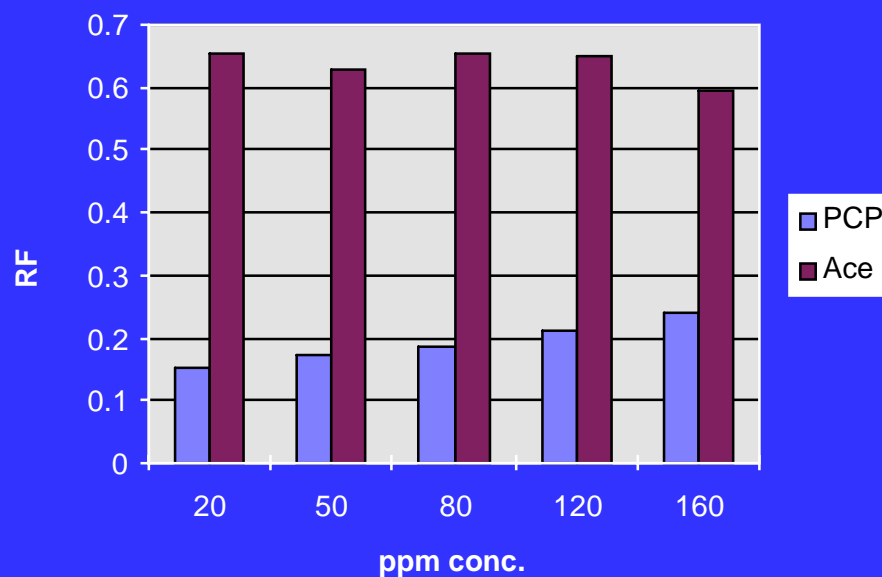
# Relative Standard Deviation Comparison

	Standard	Siltek	Siltek A	Siltek B
DNP	13.6	35.1	24.7	36.1
4-NP	9.0	16.2	12.4	12.1
NdnPA	7.0	3.2	7.6	7.6
HCCP	14.8	24.5	19.1	7.4



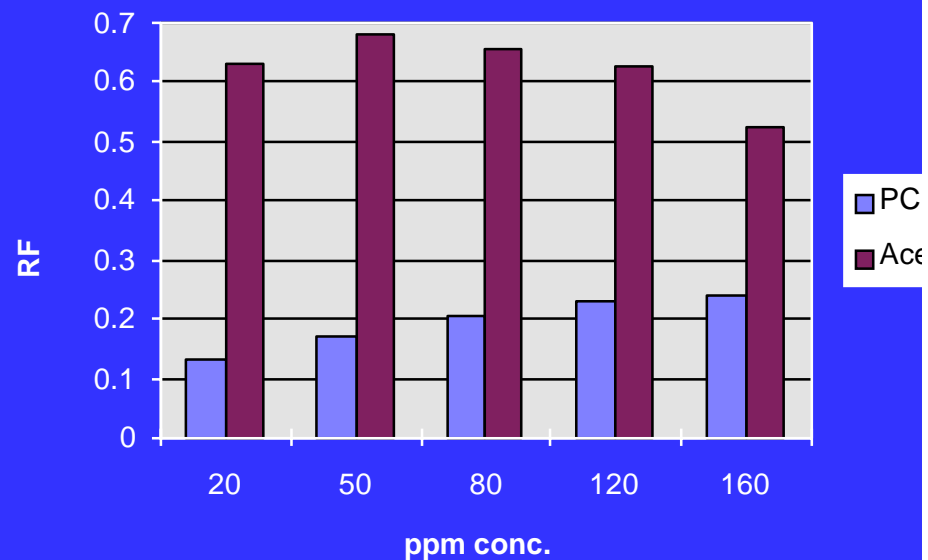
# Results of Other Test Probes - Standard Liner and Siltek Liner

Response Factors



Standard

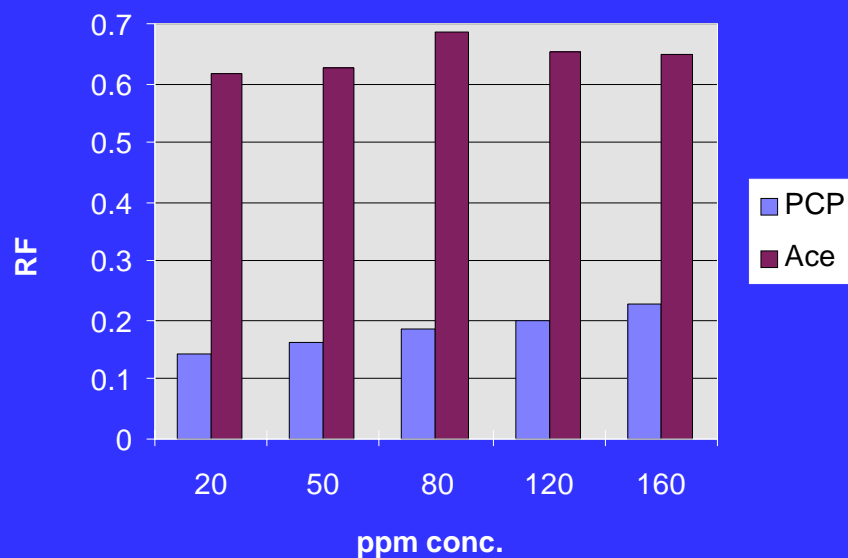
Response Factors



Siltek

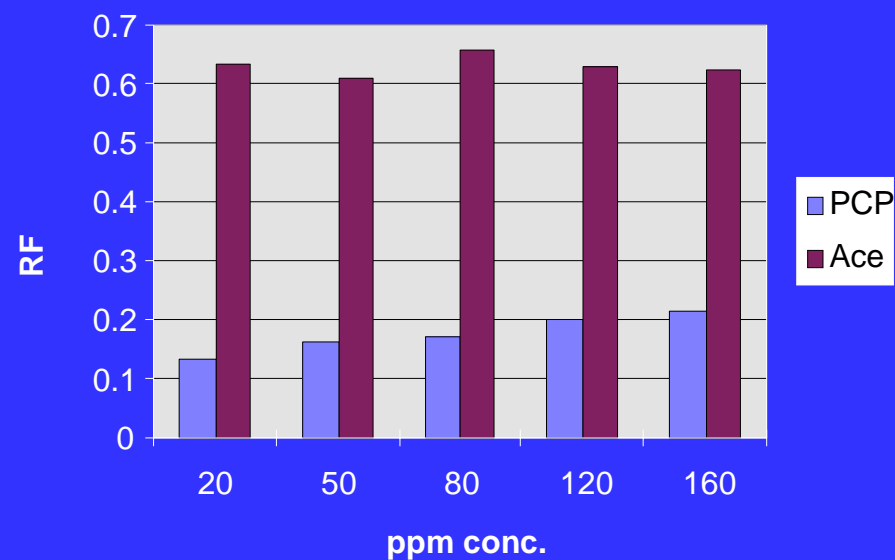
# Results of Other Test Probes - Siltek A & B

Response Factors



Siltek A

Response Factors



Siltek B

# Other Test Probes: RSDs

	Standard	Siltek	Siltek A	Siltek B
PCP	17.8	22.3	18.0	17.9
Acenaphthylene	4.0	9.7	4.3	2.8

# Conclusions

- Current Siltek™ products allow a wide variety of analyses, except at acidic and basic extremes
  - standard liners for acidic (i.e., semivolts)
  - base-deactivated for amines (ethanolamines)
  - Siltek for pesticides, explosives, sulfurs, volatiles, petrochemical, high temp., caustic, etc.
- Progressing on Siltek II which will also allow highly efficient Semi-Volatile analyses
- Future - Siltek III to include amines (i.e., one surface for all analyses)

# Improved Phases for the GC Analysis of Chlorinated and Organophosphorus Pesticides

Frank Dorman, Lydia Nolan, and Gary Stidsen

Restek Corporation

110 Benner Circle

Bellefonte, PA 16823

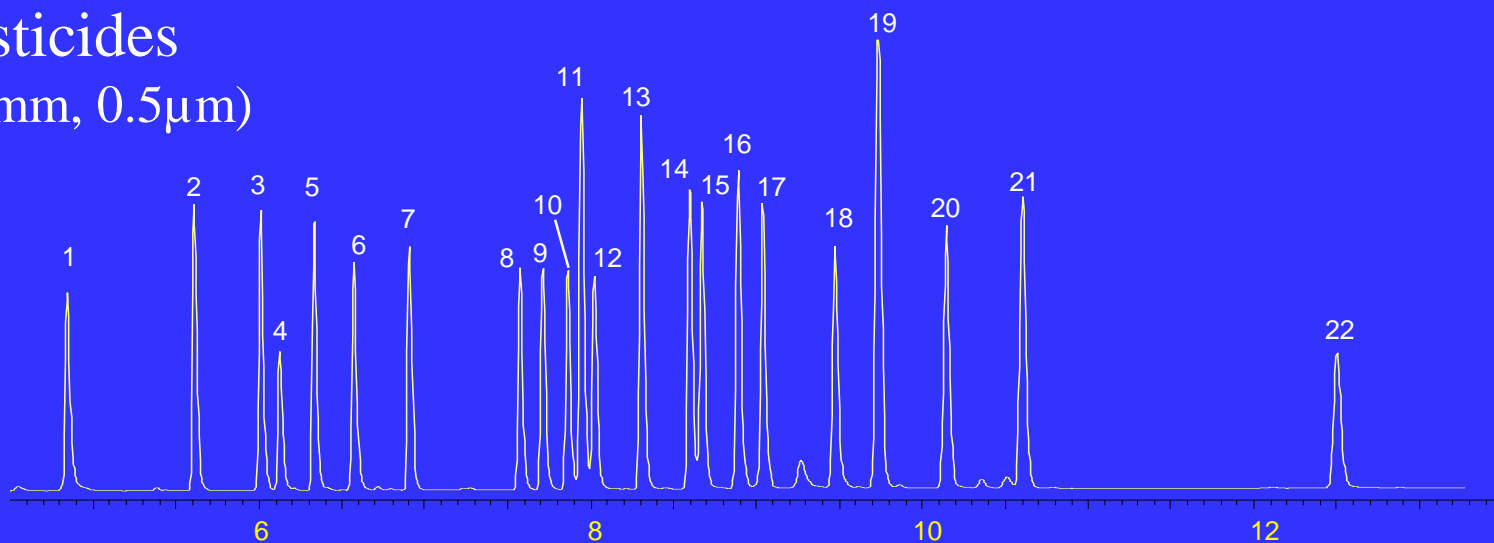
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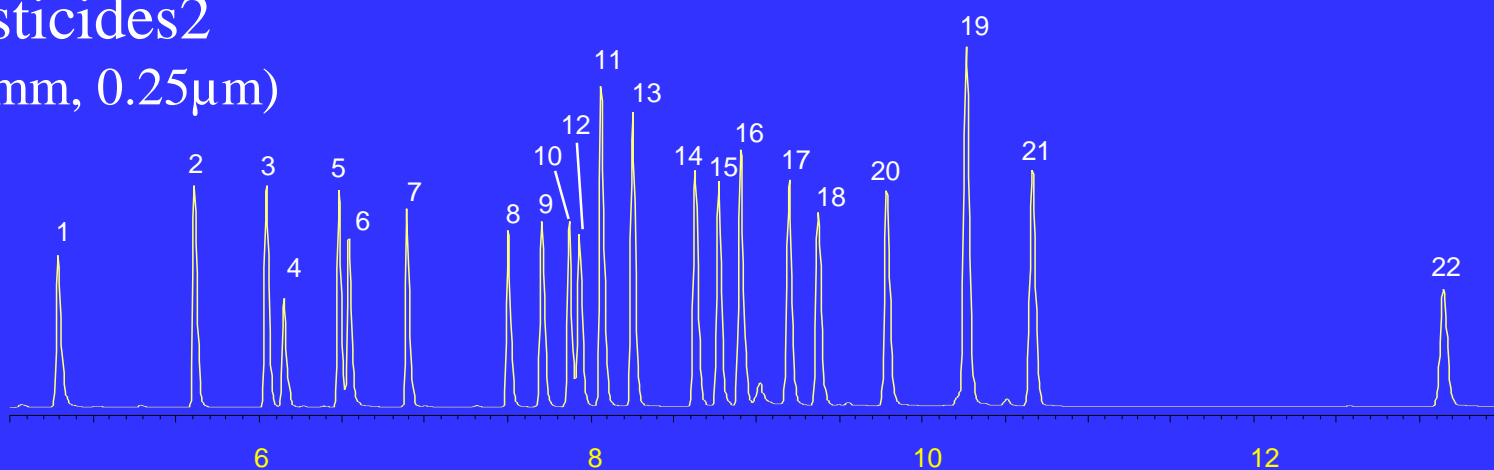
# Chlorinated Pesticides

## Fast Runs

Rtx-CLPesticides  
(30m x 0.32mm, 0.5 $\mu$ m)



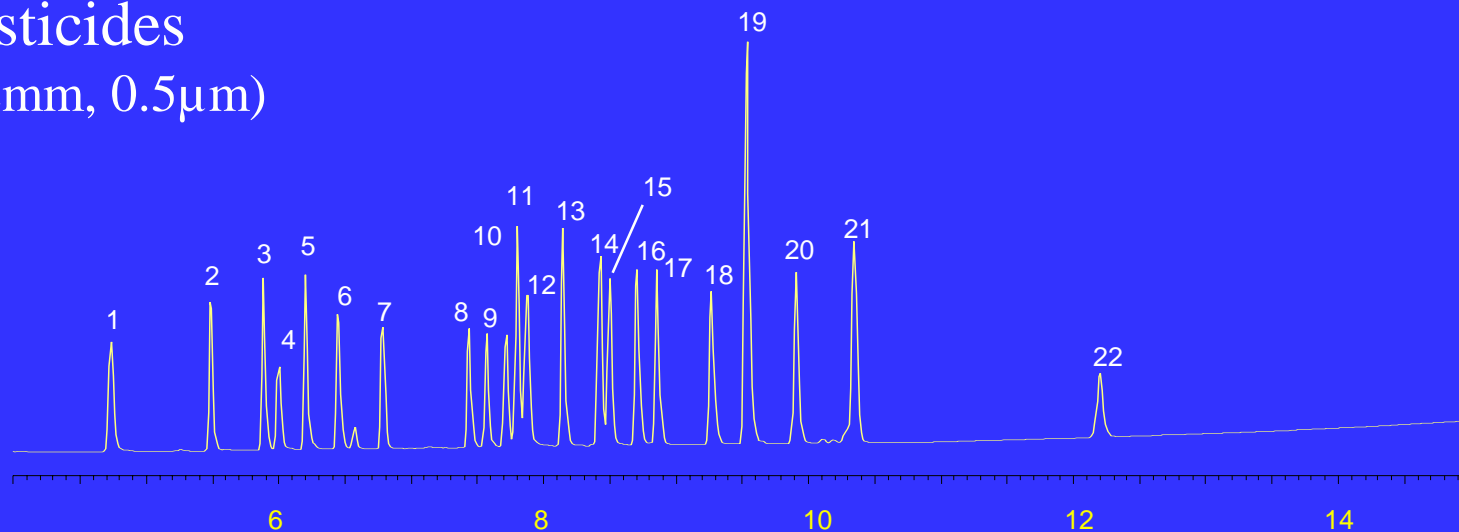
Rtx-CLPesticides2  
(30m x 0.32mm, 0.25 $\mu$ m)



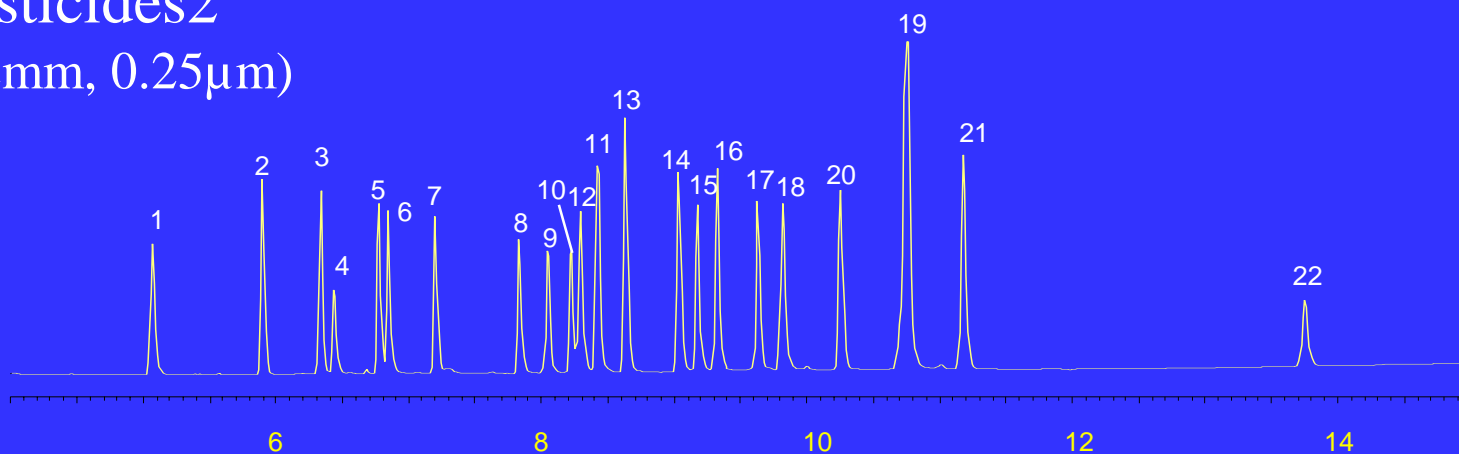
# Chlorinated Pesticides

## Siltek Deactivation

Stx-CLPesticides  
(30m x 0.32mm, 0.5 $\mu$ m)



Stx-CLPesticides2  
(30m x 0.32mm, 0.25 $\mu$ m)



# Chlorinated Pesticides

## Analytical conditions

GC oven: 120°C(1min) up at 20°C /min to 245°C,  
up at 6°C /min to 310°C

Injector: 220°C, splitless, 1min purge off hold,  
4mm single gooseneck Siltek sleeve

Detector: 310°C, Agilent ECD

Column: Stx-CLPesticides on Siltek, cat# 11544

30m x 0.32mmID, 0.5µm

Rtx-CLPesticides, cat# 11139

30m x 0.32mmID, 0.5µm

Column: Stx-CLPesticides 2 on Siltek, cat# 11444

30m x 0.32ID, 0.25µm

Rtx-CLPesticides 2, cat#11324

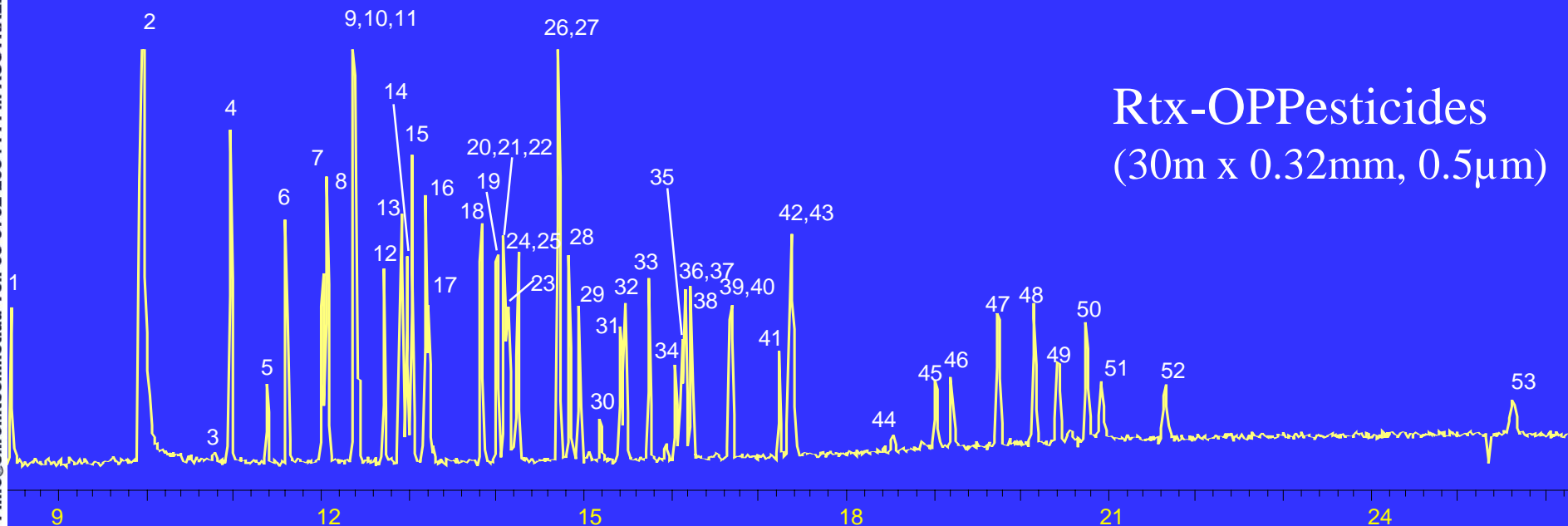
30m x 0.32mmID, 0.25µm

RT#	Analyte
1	2,4,5,6 tetrachloro-m-xylene - surrogate
2	alpha-BHC
3	gamma-BHC
4	beta-BHC
5	delta-BHC
6	heptachlor
7	aldrin
8	heptachlor epoxide
9	gamma-chlordane
10	alpha-chlordane
11	4,4' DDE
12	endosulfan I
13	dieldrin
14	endrin
15	4,4' DDD
16	endosulfan II
17	4,4' DDT
18	endrin aldehyde
19	methoxychlor
20	endosulfan sulfate
21	endrin ketone
22	decachlorobiphenyl - surrogate

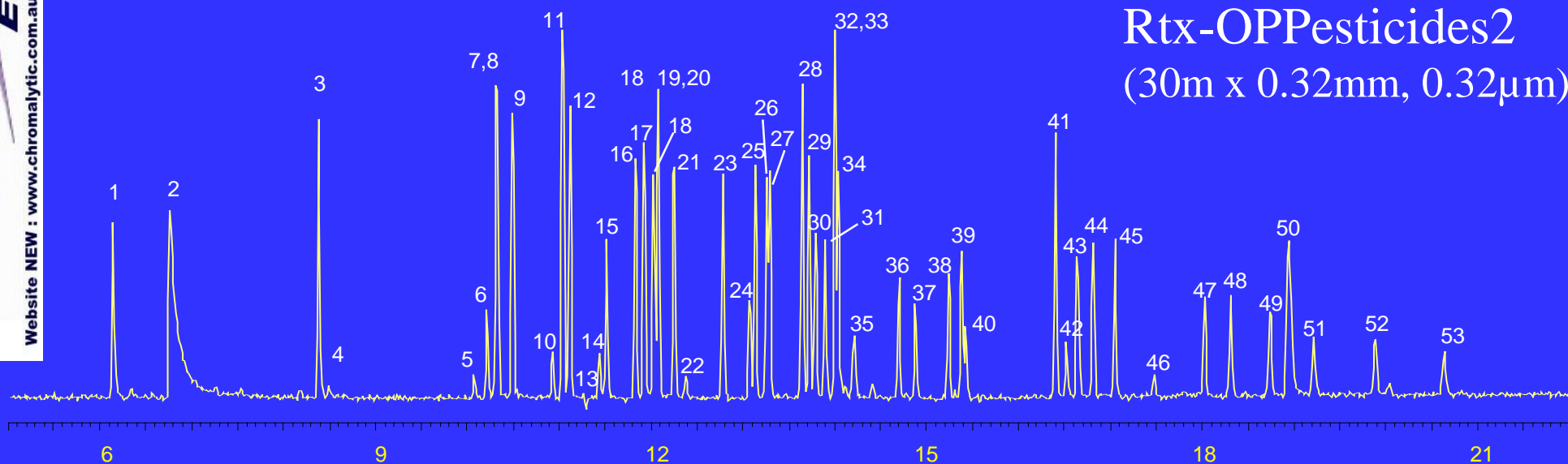


# Organophosphorus Pesticides

Rtx-OPPesticides  
(30m x 0.32mm, 0.5 $\mu$ m)



Rtx-OPPesticides2  
(30m x 0.32mm, 0.32 $\mu$ m)



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# Organophosphorus Pesticides Retention Comparison

GC oven:

80°C(0.5min)up12°C/min to  
280°C(15min)

Injector: 200°C splitless, purge  
off time 1min, 4mm single  
gooseneck Siltek sleeve

Detector: Agilent FPD 250°C  
DT @80c=1.44min, helium  
carrier

Columns:

RTX-OPPesticides, cat# 11239  
30m x 0.32ID, 0.5um

RTX-OPPesticides2, cat# 11241  
30m x 0.32ID, 0.32um

RT#	Analyte - RTX-OPP2	Analyte - RTX-OPP
1	dichlorvos	dichlorvos
2	hexamethylphosphoramide	hexamethylphosphoramide
3	mevinphos	trichlorfon
4	trichlorfon	mevinphos
5	TEPP	demeton-o
6	demeton-o	thionazin
7	tributyl phosphate -surrog	ethoprop
8	thionazin	phorate
9	ethoprop	tributyl phosphate -surrog
10	naled	sulfotepp
11	sulfotepp	naled
12	phorate	diazinon
13	dicrotophos	terbufos
14	monocrotophos	TEPP
15	demeton-s	fonophos
16	terbufos	dioxathion
17	dimethoate	disulfoton
18	diazinon	demeton-s

# Organophosphorus Pesticides Retention Comparison

RT#	Analyte - RTX-OPP2	Analyte - RTX-OPP
19	dioxathion	dichlorofenthion
20	fonophos	chlorpyrifos methyl
21	disulfoton	dimethoate
22	phosphamidon isomer	monocrotophos
23	dichlorofenthion	dicrotophos
24	phosphamidon	merphos
25	chlorpyrifos methyl	ronnel
26	parathion-methyl	chlorpyrifos
27	ronnel	aspon
28	aspon	fenthion
29	fenitrothion	trichloronate
30	malathion	phosphamidon isomer
31	chlorpyrifos	malathion
32	parathion-ethyl	parathion-methyl
33	trichloronate	fenitrothion
34	fenthion	tokuthion
35	merphos	phosphamidon
36	chlorfenvinphos	merphos oxone

# Organophosphorus Pesticides Retention Comparison

RT#	Analyte - RTX-OPP2	Analyte - RTX-OPP
37	crotoxyphos	chlorfenvinphos
38	stirofos	parathion-ethyl
39	tokuthion	crotoxyphos
40	merphos oxone	stirofos
41	ethion	bolstar
42	fensulfothion	carbophenothion
43	bolstar	ethion
44	carbophenothion	triphenyl phosphate -surrogate
45	famphur	leptophos
46	triphenyl phosphate -surrogate	fensulfothion
47	EPN	tri-o-cresyl phosphate
48	phosmet	EPN
49	leptophos	phosmet
50	tri-o-cresyl phosphate	famphur
51	azinphos-methyl	azinphos-methyl
52	azinphos-ethyl	azinphos-ethyl
53	coumaphos	coumaphos

# Organophosphorus Pesticides: MS Data

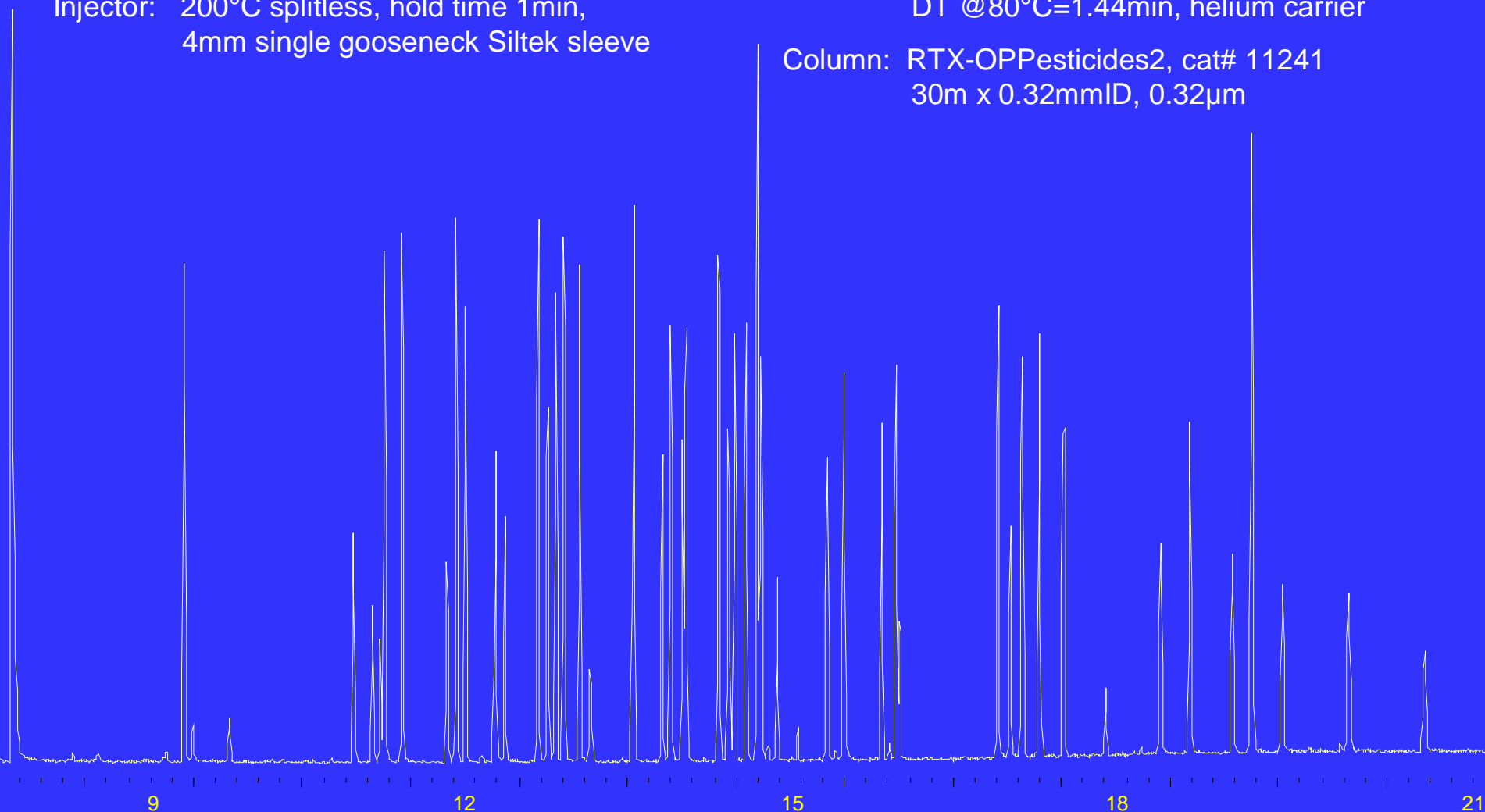
GC oven: 80°C (0.5min) up 12°C/min to  
280°C (15min)

Injector: 200°C splitless, hold time 1min,  
4mm single gooseneck Siltek sleeve

Detector: Agilent 5971A MSD  
full scan 50-550AMU

DT @80°C=1.44min, helium carrier

Column: RTX-OPPesticides2, cat# 11241  
30m x 0.32mmID, 0.32µm

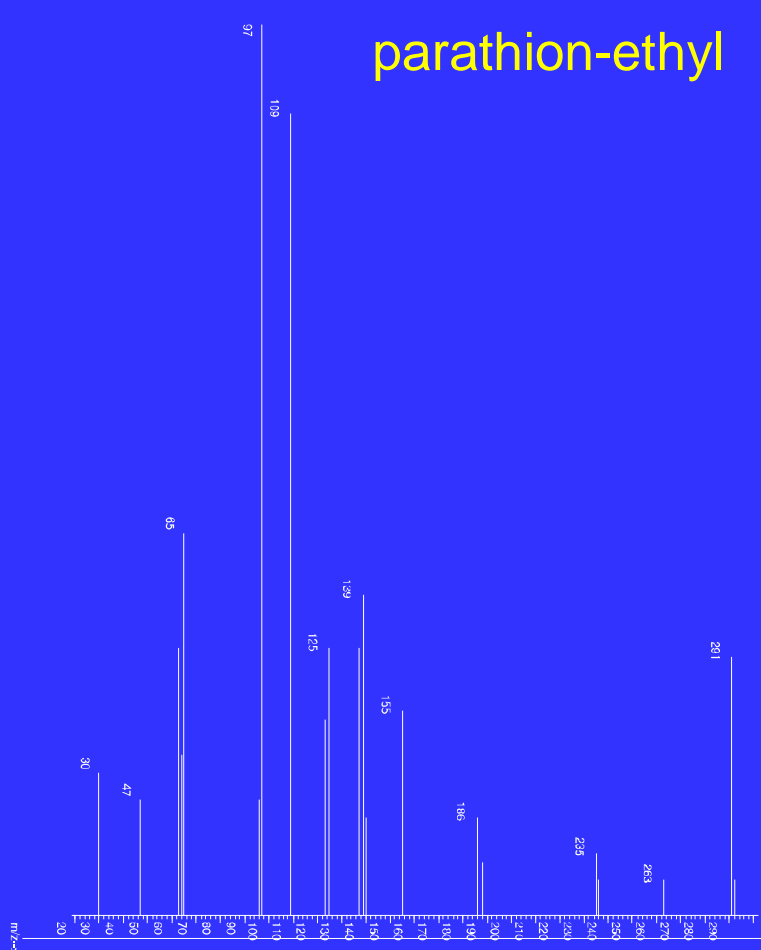


# Organophosphorus Pesticides

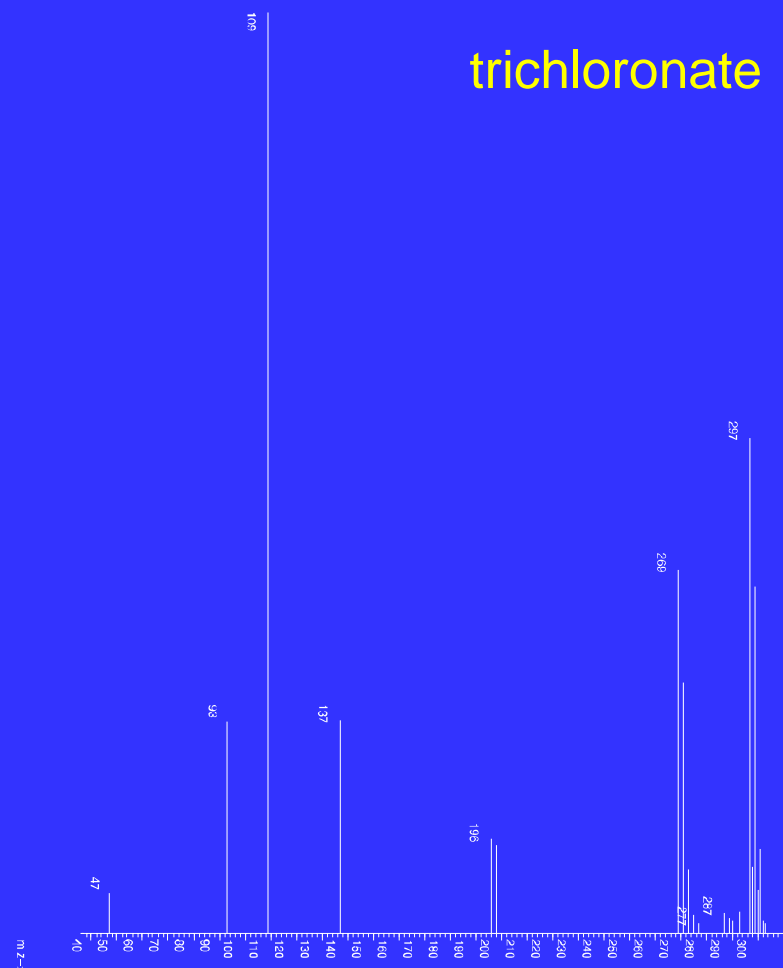
## MS Spectra

Rtx-OPPesticides2  
(30m x 0.32mm, 0.32 $\mu$ m)

parathion-ethyl



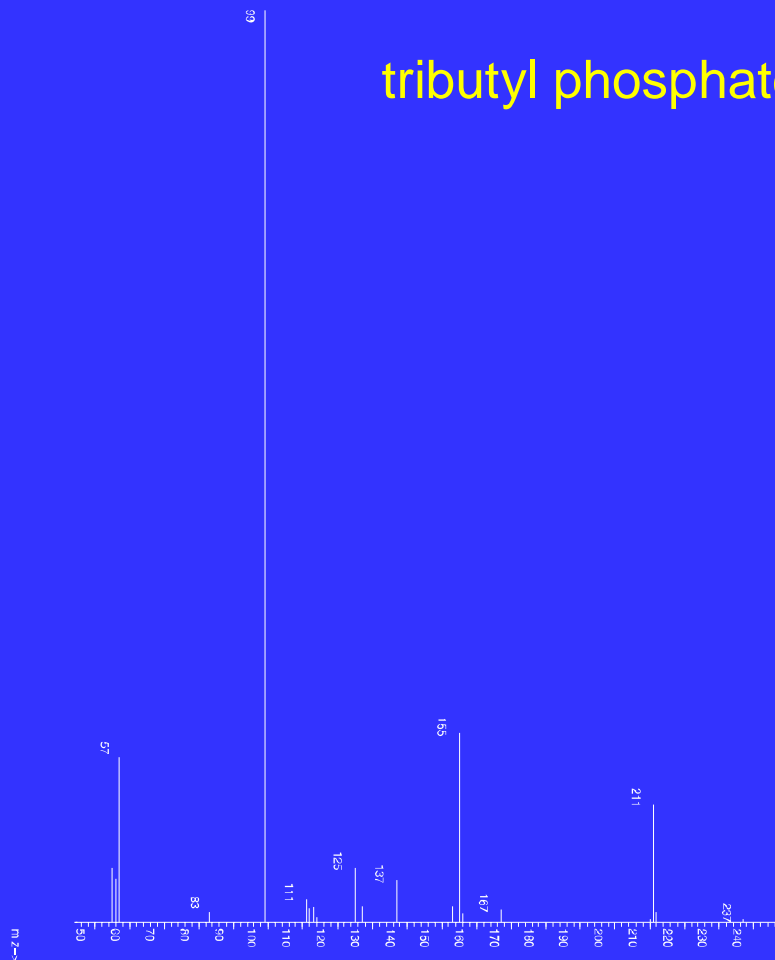
trichloronate



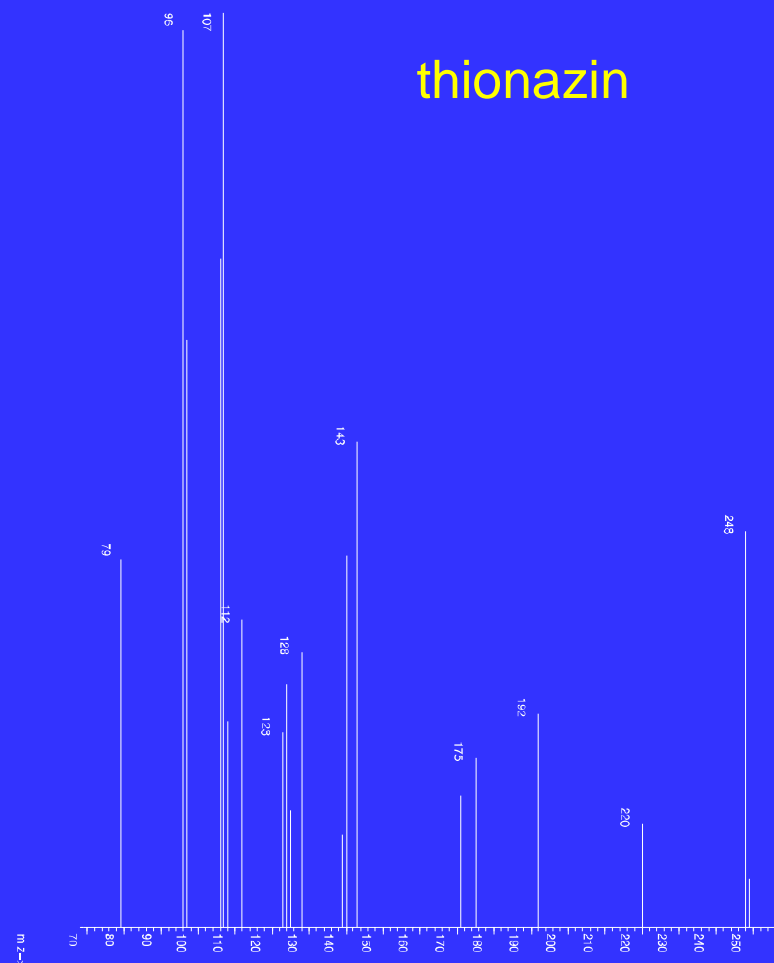
# Organophosphorus Pesticides MS Spectra

Rtx-OPPesticides2  
(30m x 0.32mm, 0.32 $\mu$ m)

tributyl phosphate



thionazin



# Organochlorine Pesticides

- Chromatographic resolution of USEPA 8081 compounds
- Rtx-CLPesticides and Rtx-CLPesticides2 columns
- Dual column configuration
- Low bleed
- High inertness
- Faster analysis times

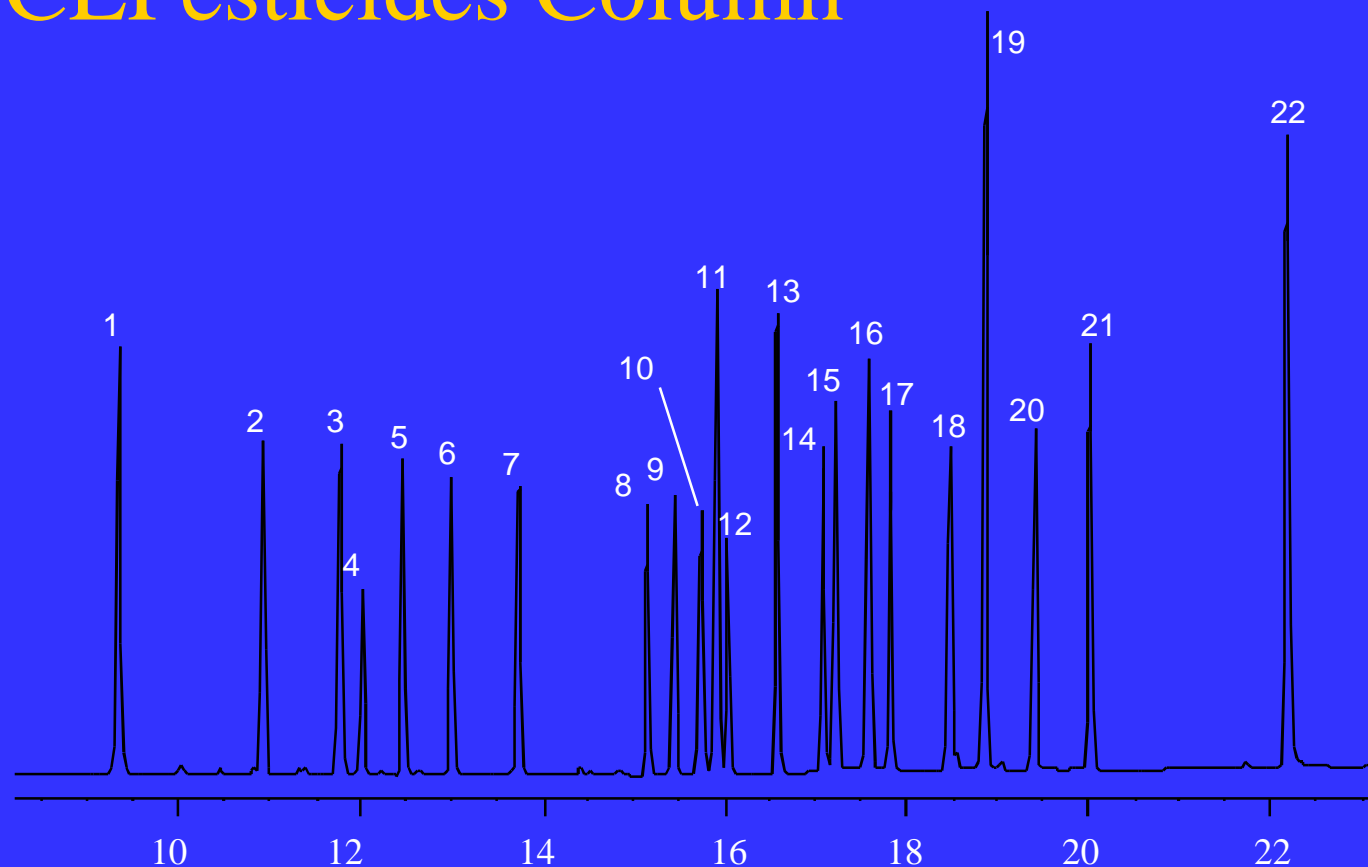


# Chlorinated Pesticides

- 1 2,4,5,6-tetrachloro-m-xylene
- 2 alpha BHC
- 3 gamma BHC
- 4 beta BHC
- 5 delta BHC
- 6 heptachlor
- 7 aldrin
- 8 heptachlor epoxide
- 9 gamma chlordane
- 10 alpha chlordane
- 11 4,4'-DDE

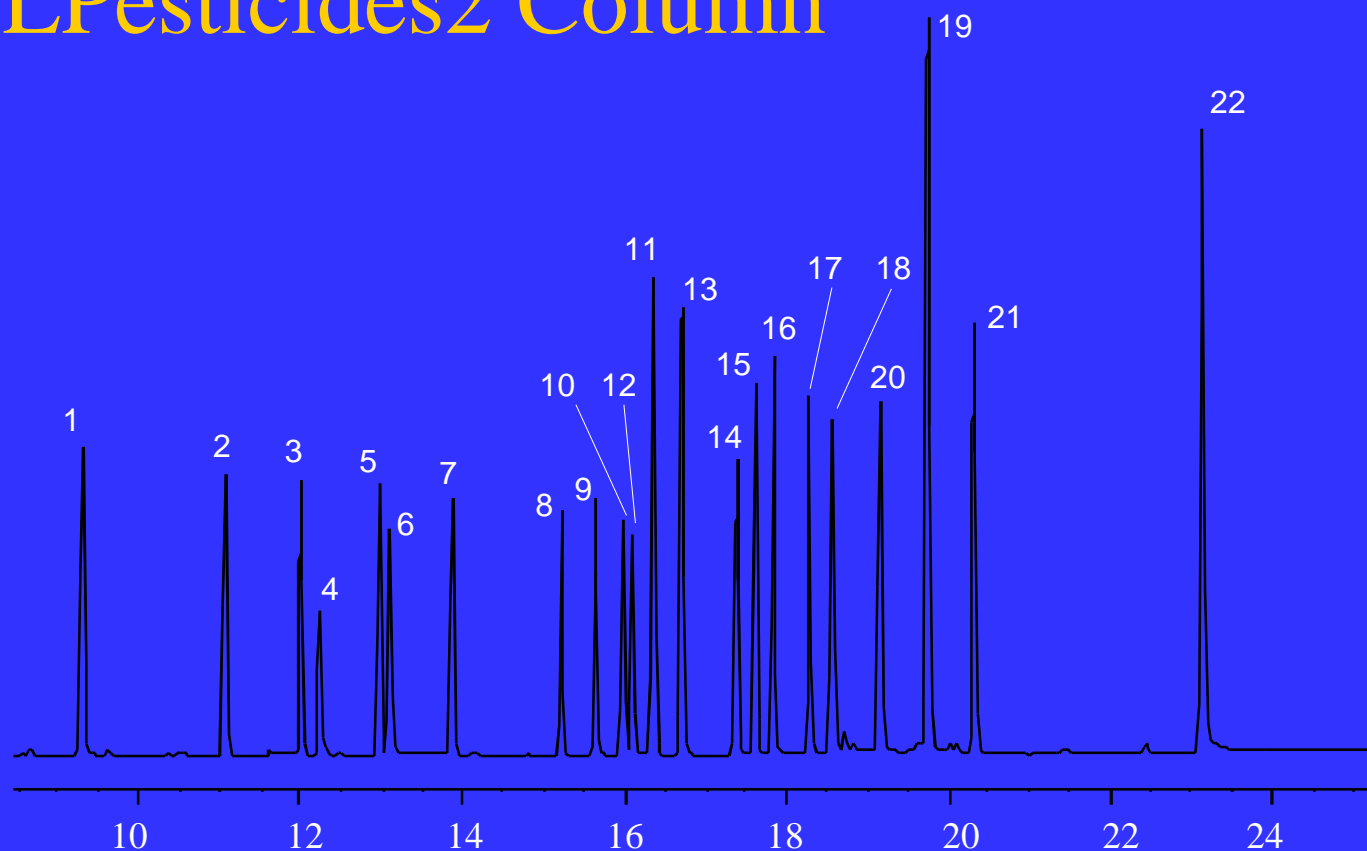
- 12 endosulfan I
- 13 dieldrin
- 14 endrin
- 15 4,4'-DDD
- 16 endosulfan II
- 17 4,4'-DDT
- 18 endrin aldehyde
- 19 methoxychlor
- 20 endosulfan sulfate
- 21 endrin ketone
- 22 decachlorobiphenyl

# Rtx<sup>®</sup>-CLPesticides Column



30m, 0.32mm ID, 0.5 $\mu$ m, Rtx<sup>®</sup>-CLPesticides; EPA 8081 list, direct injection, Uniliner<sup>®</sup> liner (cat. #20335). Oven temp.: 120°C (hold 1 min.) to 300°C @ 9°C/min. (hold 10 min.); Inj. temp.: 200°C; Dead time: 1.797; Head pressure: 5.0psi (constant); Flow rate: 2.1mL/min. at 120°C.

# Rtx<sup>®</sup>-CLPesticides2 Column



30m, 0.32mm ID, 0.25 $\mu$ m Rtx<sup>®</sup>-CLPesticides2; EPA 8081 list, direct Uniliner<sup>®</sup> sleeve (cat. #20335). Oven temp.: 120°C (hold 1 min.) to 300°C @ 9°C/min. (hold 10 min.); Inj. temp.: 200°C; Dead time: 1.797; Head pressure: 5.0psi (constant); Flow rate: 2.1mL/min. @ 120°C.

# Siltek Deactivation

- Surface modification, not deactivation layer
  - Does not attach to existing silanol groups
- Higher level of inertness for Endrin
- More resistant to acid or base attack
  - Stays inert for longer time
- More easily cleaned
  - Solvent rinsing usually acceptable

# Requirements of Organophosphorus Column

- Chromatographic separation of USEPA 8141 compounds
- Companion column to Rtx-OPPesticides
- 20 minute total run time
- Also compatible with GC/MS analysis
  - Low Bleed
  - Resolution of compounds with similar spectra

## “Old Days of GC”

- Chromatography has become a “history lesson” rather than a science
- Applications compromised to fit existing columns and stationary phases
- Most phases not designed with any application in mind
- Marketing based on “subtle” differences

# Future of GC

- Columns and stationary phases designed around applications
- Potential for specific phase and column for an individual separation
- Marketing based on real differences
- Requires understanding and ability to model of analyte-phase interactions

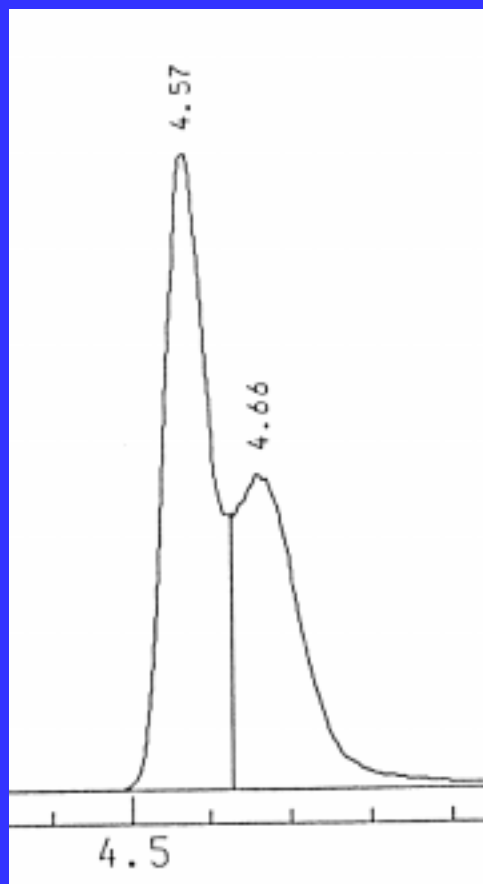
# Stationary Phase Optimization Techniques

- Window diagramming
- Computer simulation of  $R_t$  and  $W_{1/2}$  (ezGC™)
- Computer prediction of optimized stationary phase composition and column dimensions
- Computer prediction of solute/stationary phase interactions for new polymer designs



# How Resolution Affects Quantitation

## VRX phase



### Results of Resolution Tests @ 20ppb

<i>MeCl<sub>2</sub> &amp; Freon 113</i>	<i>Rep 1</i>	<i>19.85</i>	<i>18.48</i>
	<i>Rep 2</i>	<i>19.29</i>	<i>18.48</i>
	<i>Rep 3</i>	<i>19.36</i>	<i>18.52</i>
<i>Methylene Chloride</i>	<i>Rep 1</i>	<i>21.48</i>	
	<i>Rep 2</i>	<i>20.79</i>	
	<i>Rep 3</i>	<i>20.95</i>	
<i>Freon 113</i>	<i>Rep 1</i>		<i>16.3</i>
	<i>Rep 2</i>		<i>16.46</i>
	<i>Rep 3</i>		<i>16.25</i>

# Achieving Analyte Separation

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha - 1 / \alpha)$$

## Capacity Factor

$$k = (t_R - t_0) / t_0$$

## Selectivity

$$\alpha = k_2 / k_1$$

## Thermodynamics:

$$\Delta G = \Delta H - T\Delta S \quad \Delta G = RT \ln K_D$$

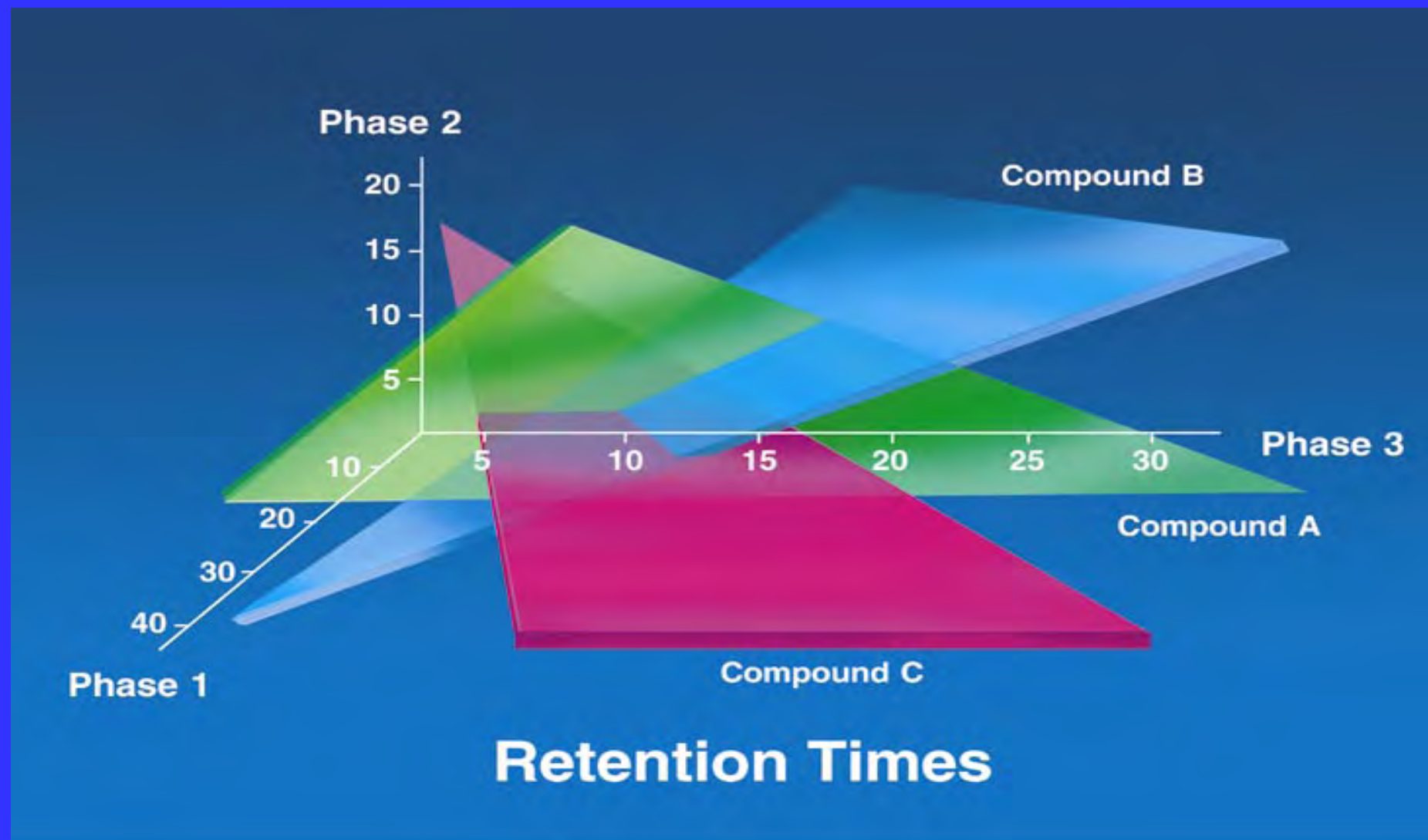
# Stationary Phase Optimization

- Window diagramming
- Computer simulation of  $R_t$  and  $W_{1/2}$  (ezGC)
- Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition AND column dimensions
  - Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX, Rtx-OPPesticides2, Customer-specific columns
- Computer prediction of solute/stationary phase interactions for new polymer designs

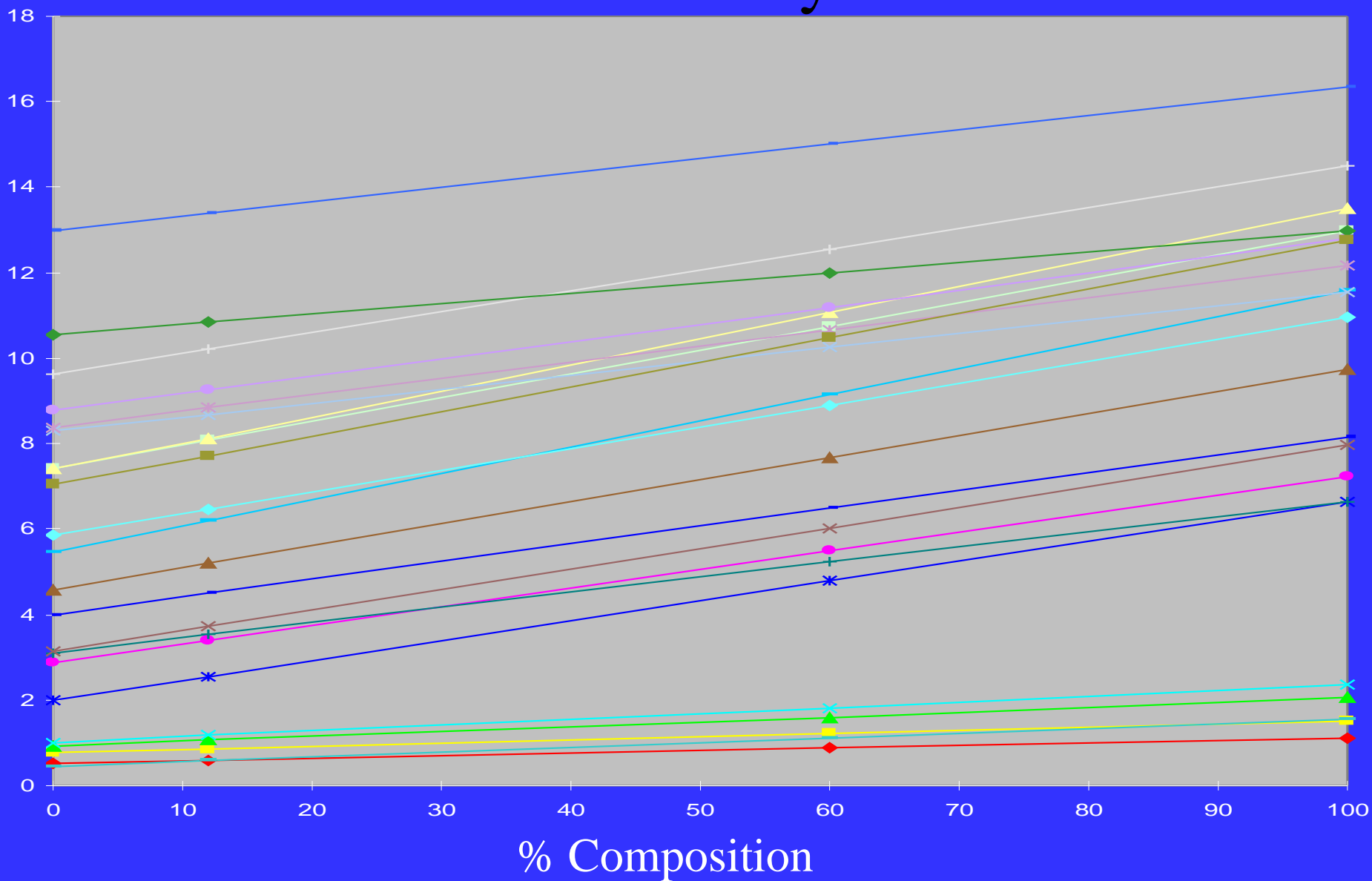
# Process for Rtx-OPPesticides2 Column

- Acquire data for target compounds under two temperature programs for functionalities displaying selectivity
- Computer Assisted Stationary Phase Design (CASPD)
  - Calculate  $\Delta H$  and  $\Delta S$  for each compound
  - Working in Retention Index, perform optimization of Selectivity and Dimensions
- Synthesize and coat column

# 3-Space Selectivity Model for 3 Compounds



# End-on View of Selectivity Model



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# Compounds 1 – 25 of 53 OP Pesticides

Target Compound	Predicted Rt	Actual Rt	Difference (min)
dichlorvos	4.08	4.05	-0.03
HMPA	4.70	4.70	0.00
mevinphos	6.43	6.34	-0.09
trichlorfon	6.44	6.43	-0.01
TEPP	8.20	8.40	0.20
demeton-o	8.46	8.52	0.06
thionazin	8.58	8.52	-0.06
TBP	8.60	8.52	-0.08
ethoprop	8.84	8.74	-0.10
naled	9.34	9.32	-0.02
sulfotepp	9.42	9.56	0.14
phorate	9.53	9.56	0.03
dicrotophos	9.61	9.59	-0.02
monocrotophos	9.70	9.62	-0.08
demeton-s	9.80	9.62	-0.18
terbufos	10.44	10.32	-0.12
dimethoate	10.67	10.62	-0.05
dioxathion	10.78	10.77	-0.01
fonophos	10.91	10.79	-0.11
diazinon	10.93	10.90	-0.04
disulfoton	11.13	11.09	-0.03
phosph isomer	11.19	11.16	-0.04
dichlorofenthion	11.38	11.37	-0.01
chlorpyrifos methyl	11.94	12.03	0.09
phosphamidon	12.14	12.03	-0.11



# Summary

- Rtx-CLPesticides and Rtx-CLPesticides2 columns utilizing Siltek™ deactivation provide ultimate separation of organochlorine pesticides.
- Rtx-OPPesticides and Rtx-OPPesticides2 columns are optimal dual column pair for USEPA 8141.
- Rtx-OPPesticides2 column best for separation of organophosphorous pesticides by GC/MS.



# Reversed Phase HPLC of Polar Compounds

Terrence S. Reid and C. Vernon Bartlett  
Restek Corporation  
110 Benner Circle, Bellefonte, PA 16823 USA

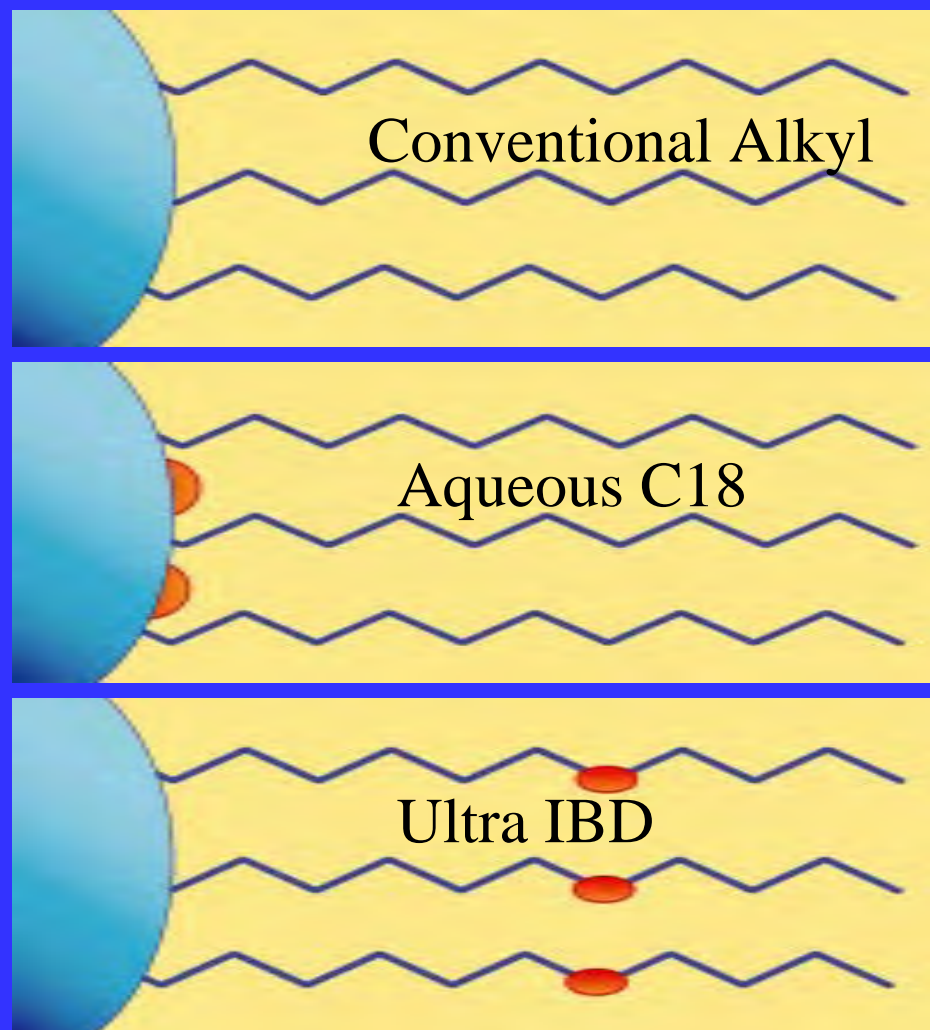
Restek Corporation  
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# Abstract

Many polar compounds are difficult to retain using conventional reversed phase columns, even with little or no organic solvent in the mobile phase. The Ultra Aqueous C18 and Ultra IBD columns were designed to provide enhanced retention and selectivity for highly polar compounds in the reversed phase mode, as well as compatibility with highly aqueous mobile phases. The unique features of these columns are demonstrated in the analyses of nutraceuticals, pesticides, and carboxylic acids.

# Figure 1. Stationary Phases



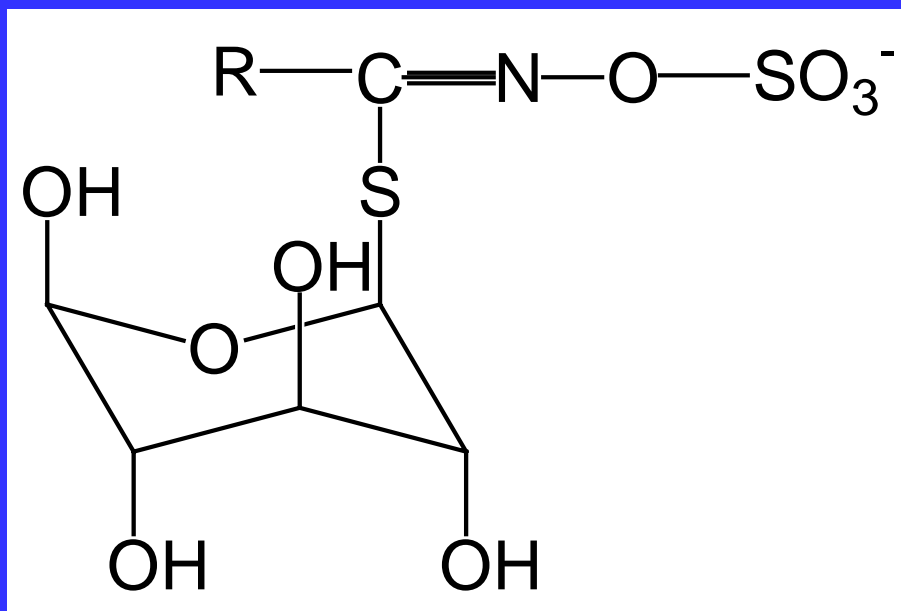
The Aqueous C18 and Ultra IBD stationary phases have secondary polar functionalities that enhance the retention of polar compounds, eliminate retention loss caused by chain folding (even in 100% aqueous mobile phase), and, in some cases, provide unique selectivity.

# Nutraceuticals

Glucosinolates are contained in a number of edible plants. The consumption of these compounds is associated with a significantly reduced risk for a variety of malignant cancers. Glucosinolates are precursors of isothiocyanates, including sulforaphane (4-methylsulfinylbutyl isothiocyanate), which regulate mammalian enzymes of xenobiotic metabolism.

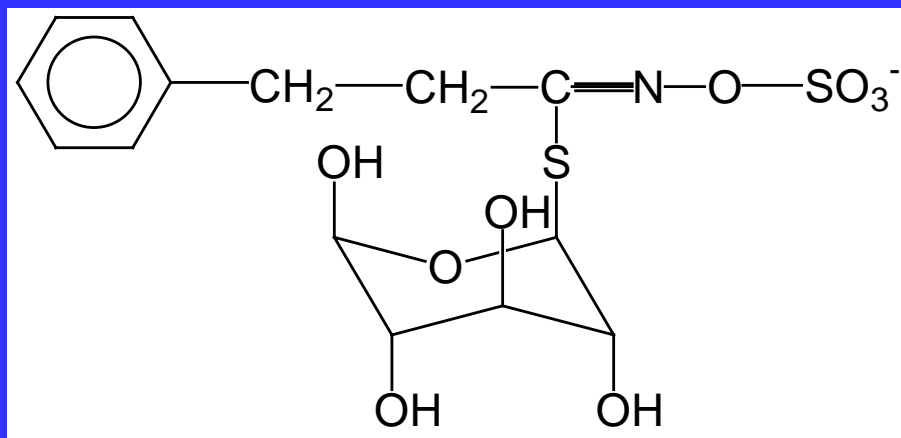
Fahey, J.W, et al, Proc. Nat. Acad. Sci. USA, Vol. 94, pp. 10367-10372, Sept. 1997.

## Figure 2. Glucosinolates



Glucosinolates are  $\beta$ -thioglucoside N-hydroxysulfates having this general structure.

## Figure 3. Phenethyl Glucosinolate



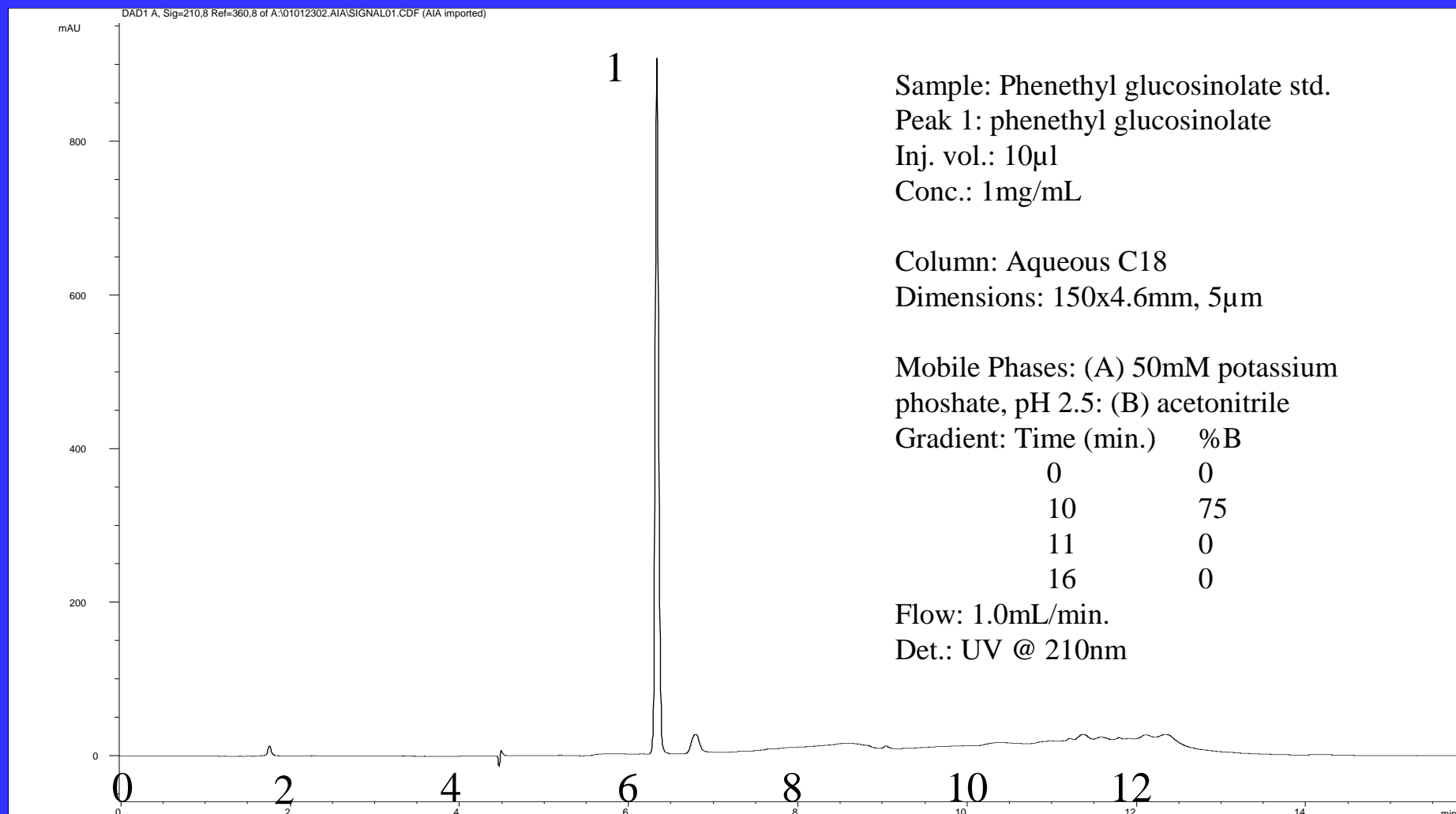
Phenethyl glucosinolate (gluconasturtiin) is one of the numerous glucosinolates widely distributed in cruciferous vegetables, and was used as a marker for glucosinolates in this study.



# Glucosinolates

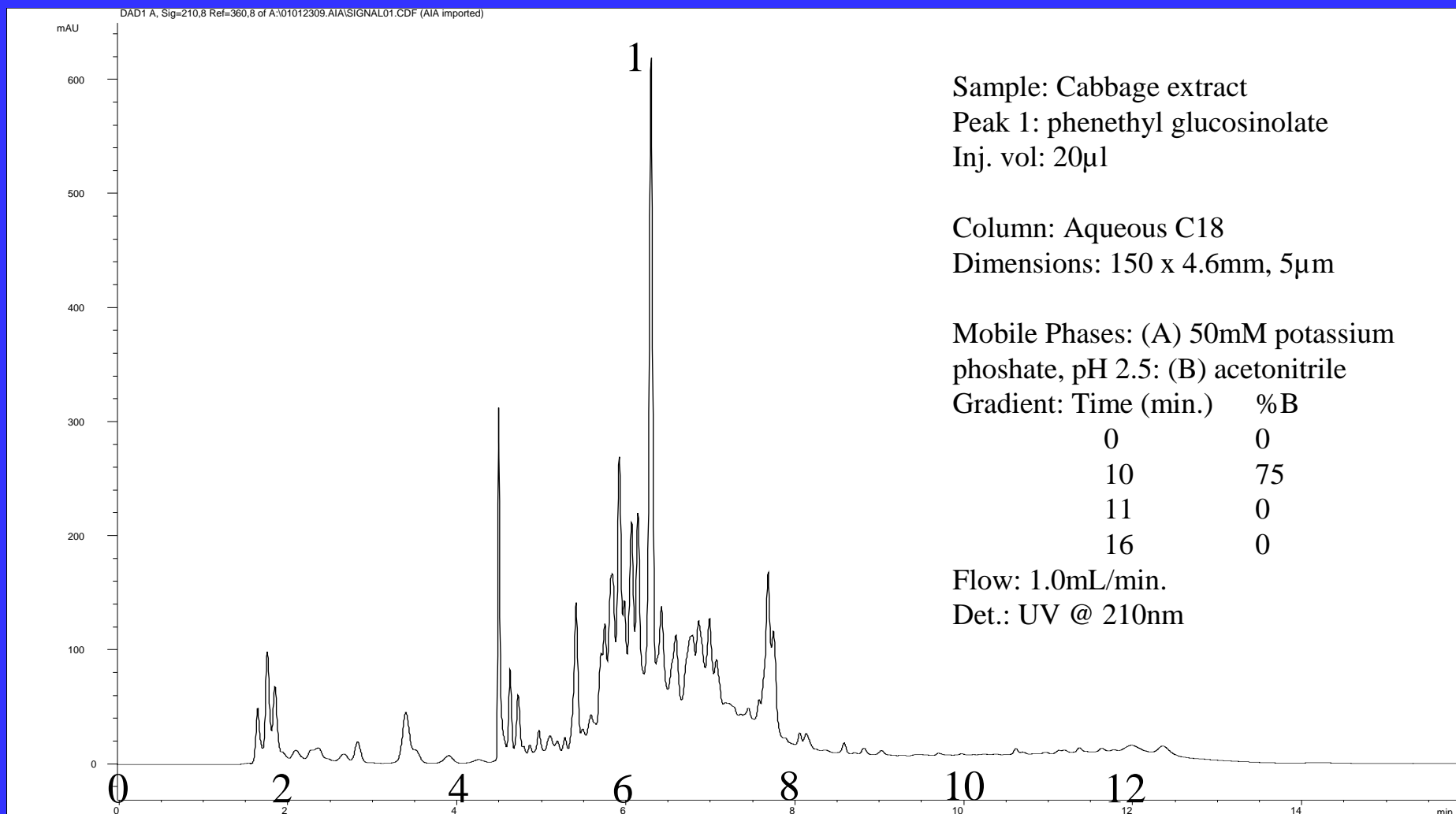
Figure 4 shows the analysis of the phenethyl glucosinolate standard using the Aqueous C18 column. Extracts of cabbage and watercress were analyzed using the same conditions, as shown in Figures 5 and 6. Gradient elution from 0 to 75% acetonitrile was used to retain and elute analytes with a wide range of polarities.

# Figure 4. Phenethyl Glucosinolate Standard

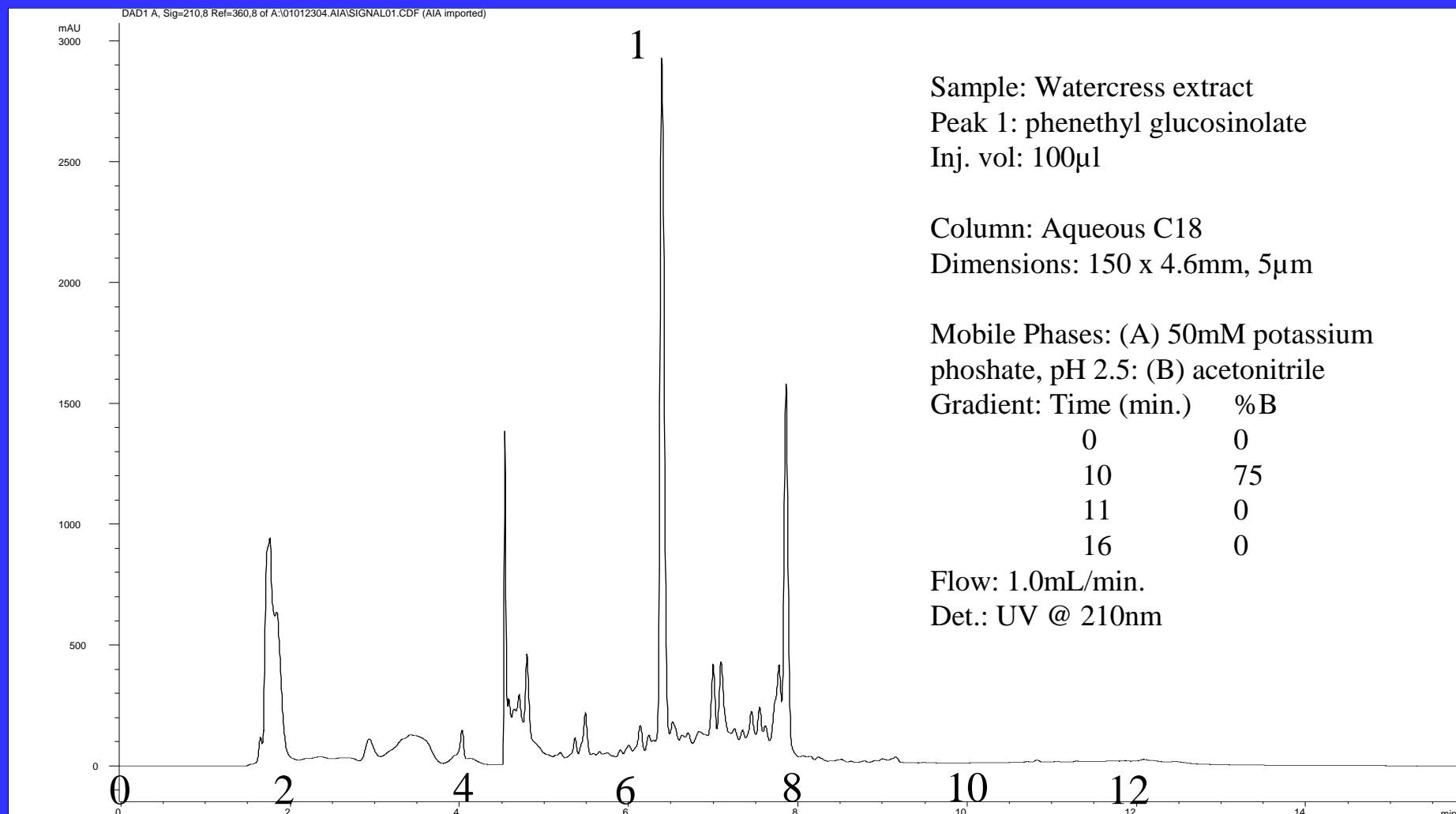




# Figure 5. Cabbage Extract



# Figure 6. Watercress Extract

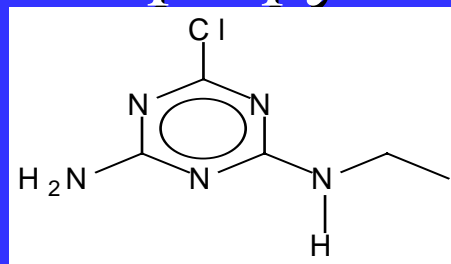


# Pesticides

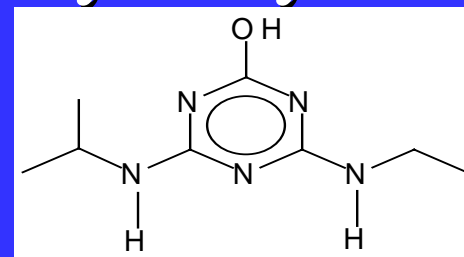
The unique selectivity of the Ultra IBD column was used to develop a two-column method for analyzing a mixture of the 17 triazine, phenylurea, and carbamate pesticides and metabolites shown in Figure 7. Figure 8 shows the separation on the Ultra C18 column in which 15 of the 17 compounds are resolved. Figure 9 shows that an Ultra IBD column with the same conditions also resolves 15 out of 17 compounds, but the pesticides that coelute on the C18 are well resolved, as indicated by the arrows.

# Figure 7A. Pesticides: 17-Component Mixture

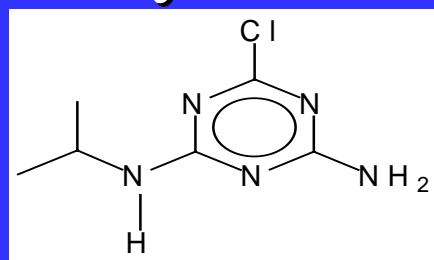
1. Desisopropylatrazine



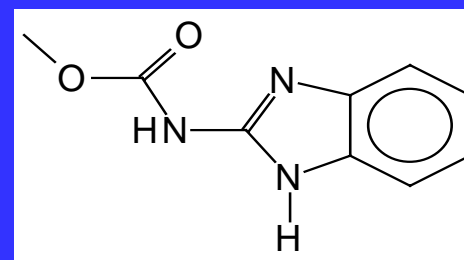
2. Hydroxyatrazine



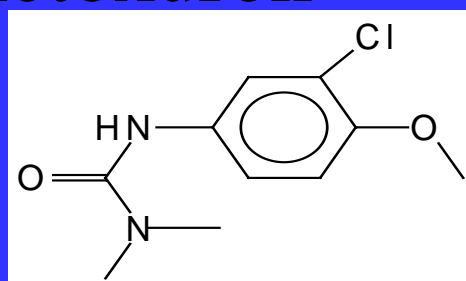
3. Desethylatrazine



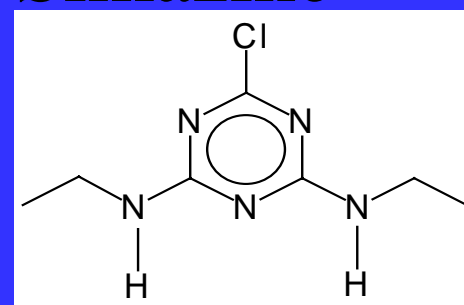
4. Carbendazim



5. Metoxuron

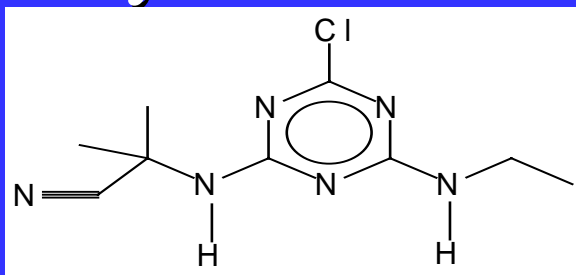


6. Simazine

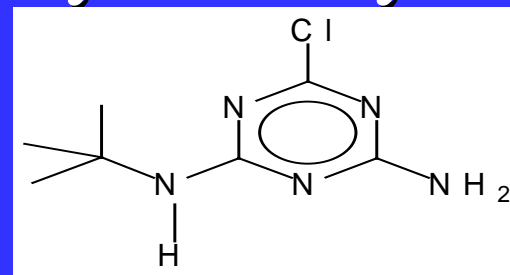


# Figure 7B. Pesticides: 17-Component Mixture

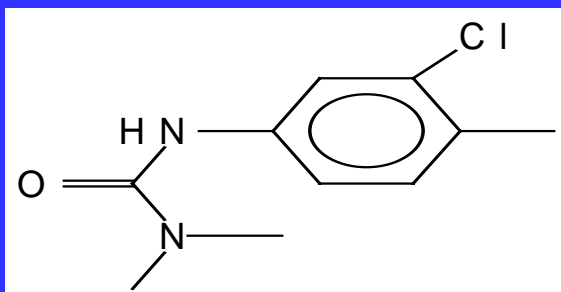
7. Cyanazine



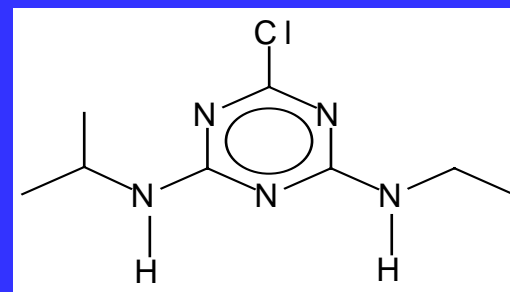
8. Desethylterbuthylazine



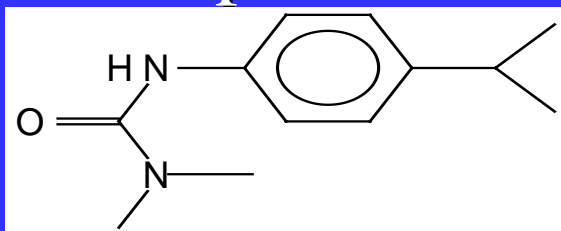
9. Chlortoluron



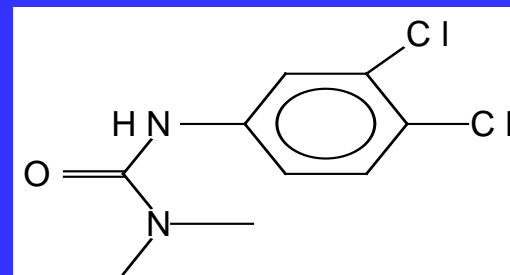
10. Atrazine



11. Isoproturon

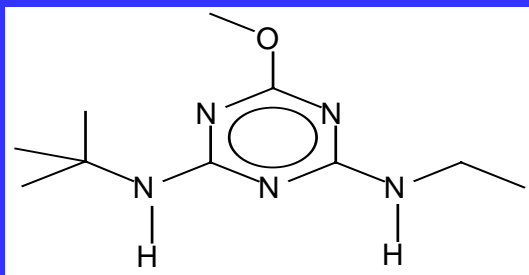


12. Diuron

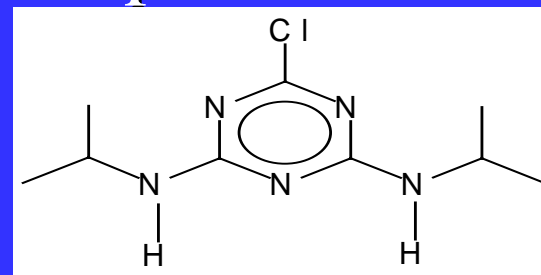


# Figure 7C. Pesticides: 17-Component Mixture

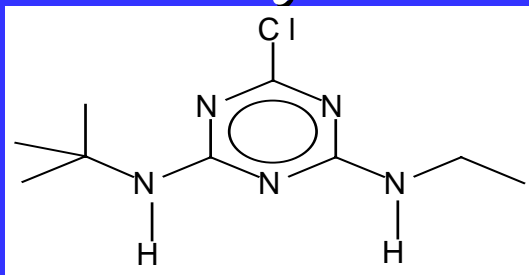
13. Terbumeton



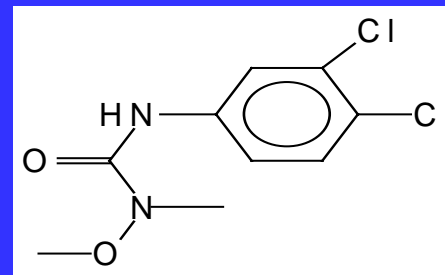
14. Propazine



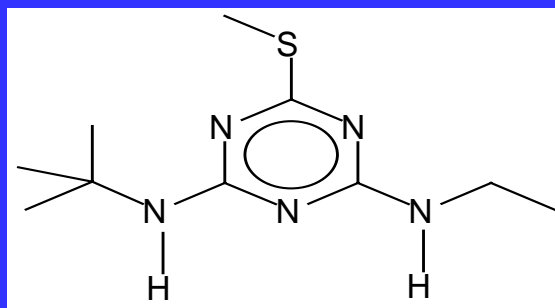
15. Terbutylazine



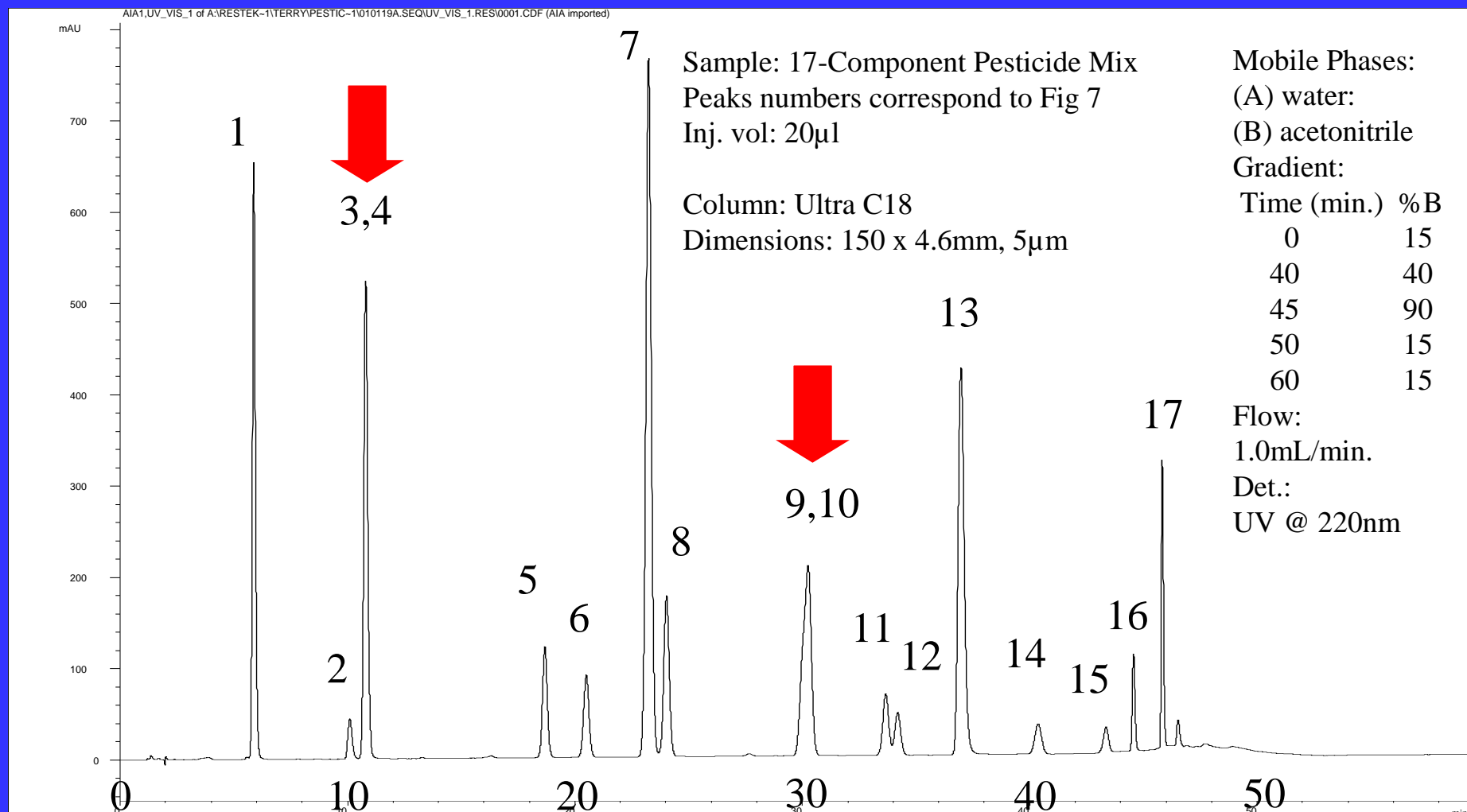
16. Linuron



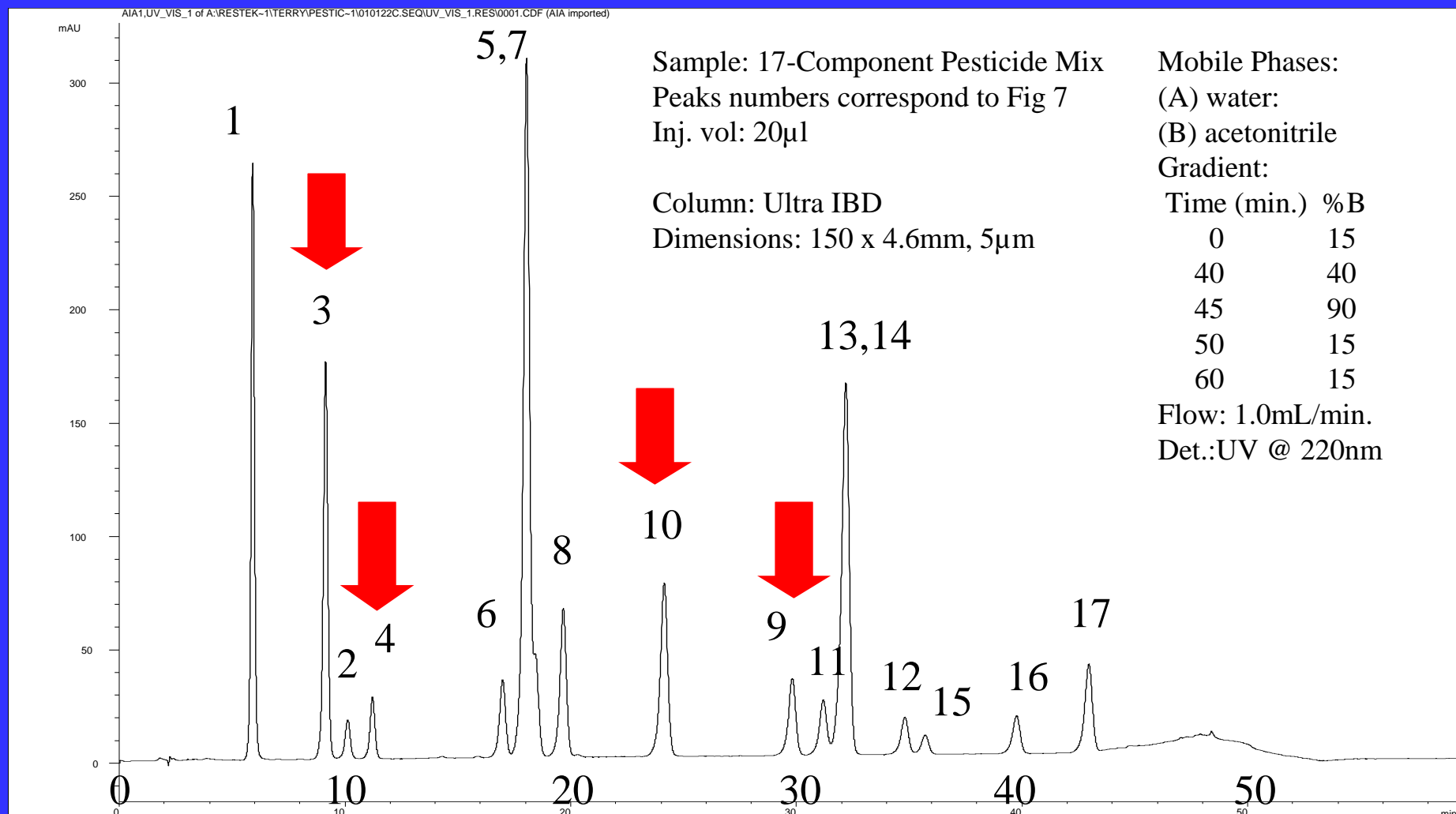
17. Terbutryn



# Figure 8. Pesticides on Ultra C18 Column



# Figure 9. Pesticides on Ultra IBD Column



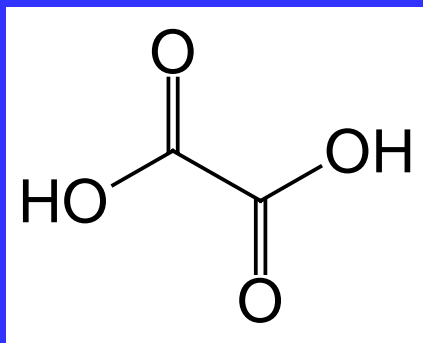


# Carboxylic Acids

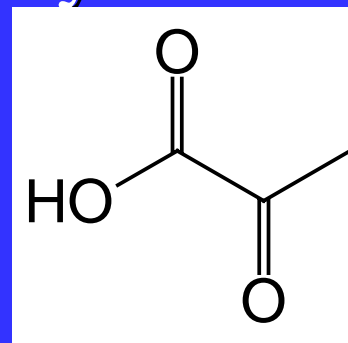
Small carboxylic acids can be difficult to retain by reversed phase HPLC, often requiring a highly aqueous mobile phase. Highly aqueous mobile phases are problematic for many C18 columns, leading to retention loss that is attributed to chain folding. The Aqueous C18 column was designed to enhance retention of polar compounds and to provide stable retention, even with completely aqueous mobile phases.

# Figure 10. Carboxylic Acids

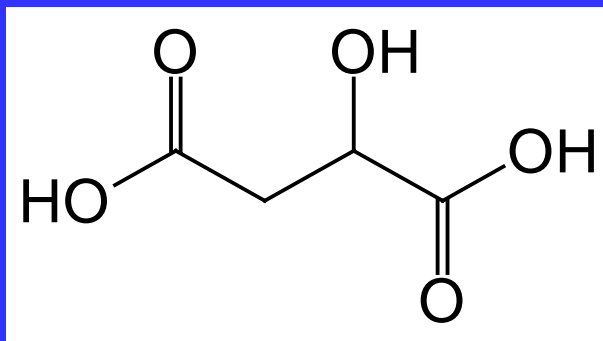
## 1. Oxalic acid



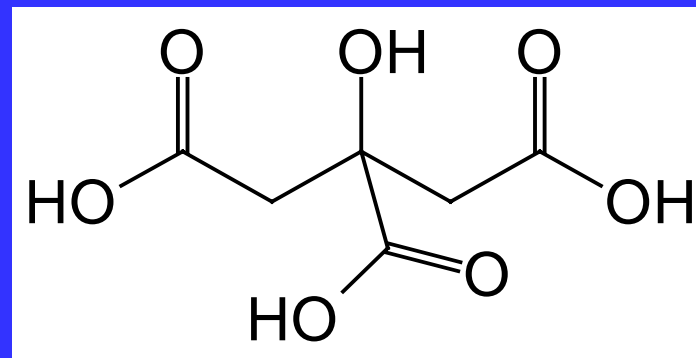
## 2. Pyruvic acid



## 3. Malic acid



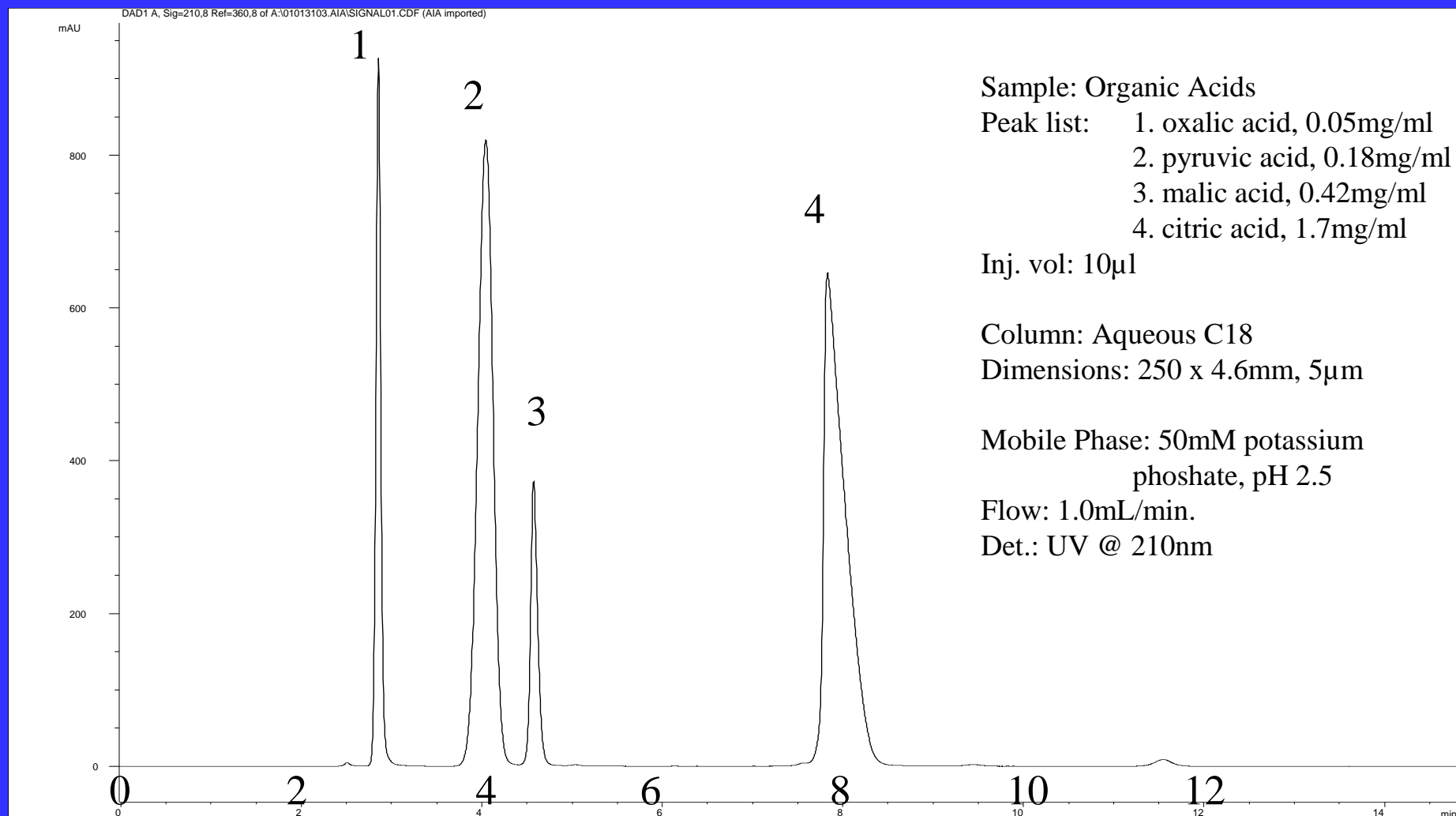
## 4. Citric acid



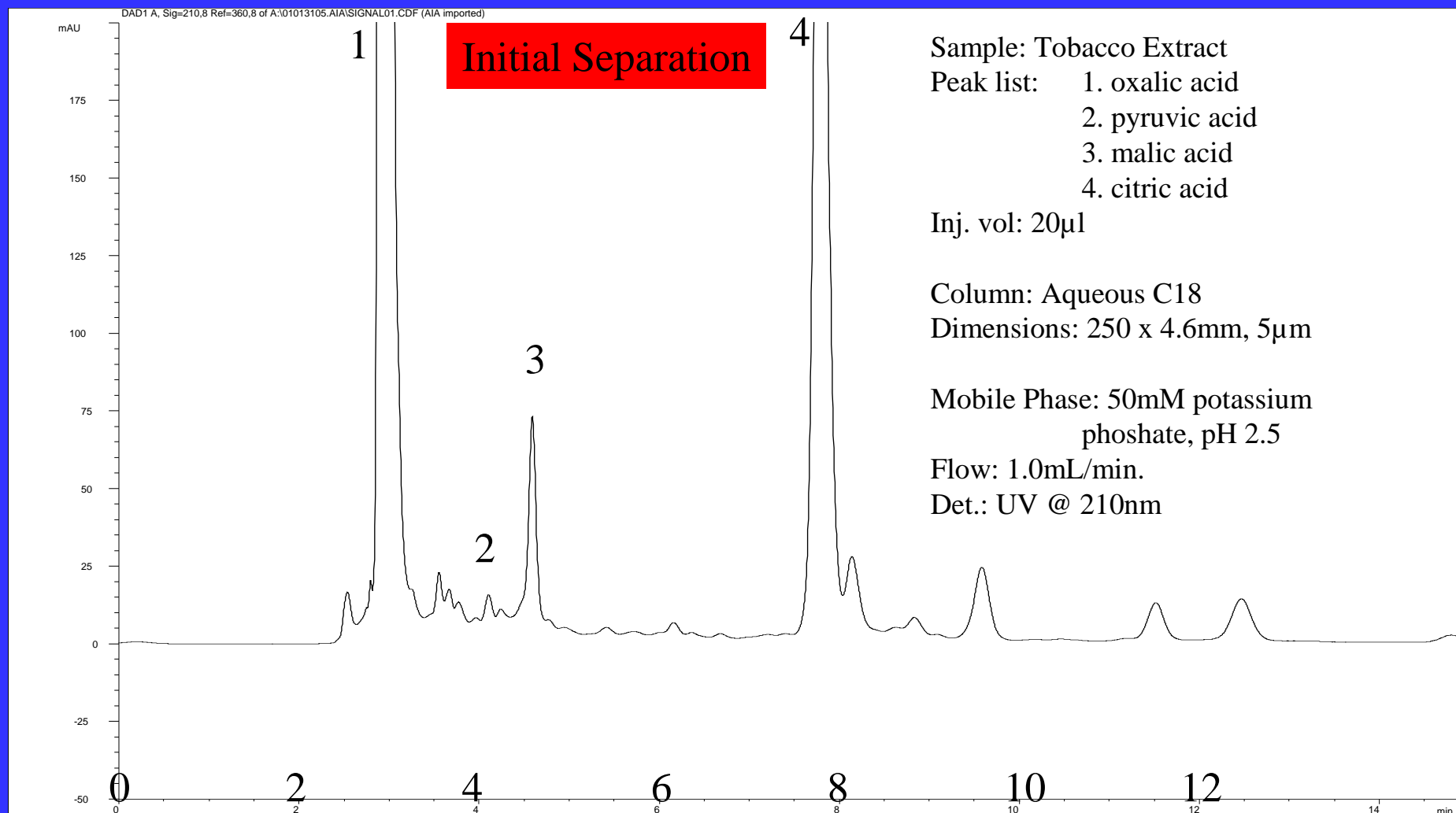
## Carboxylic Acids (Cont.)

Figure 10 shows four small carboxylic acids that were analyzed using the Aqueous C18 column and a completely aqueous mobile phase. Figure 11 shows the resolution of a mixture of standards and Figure 12 shows the analysis of a tobacco extract. The stability of the Aqueous C18 column is demonstrated in Figure 13, which shows the reproducible separation of the same sample as in Figure 12 after 168 injections.

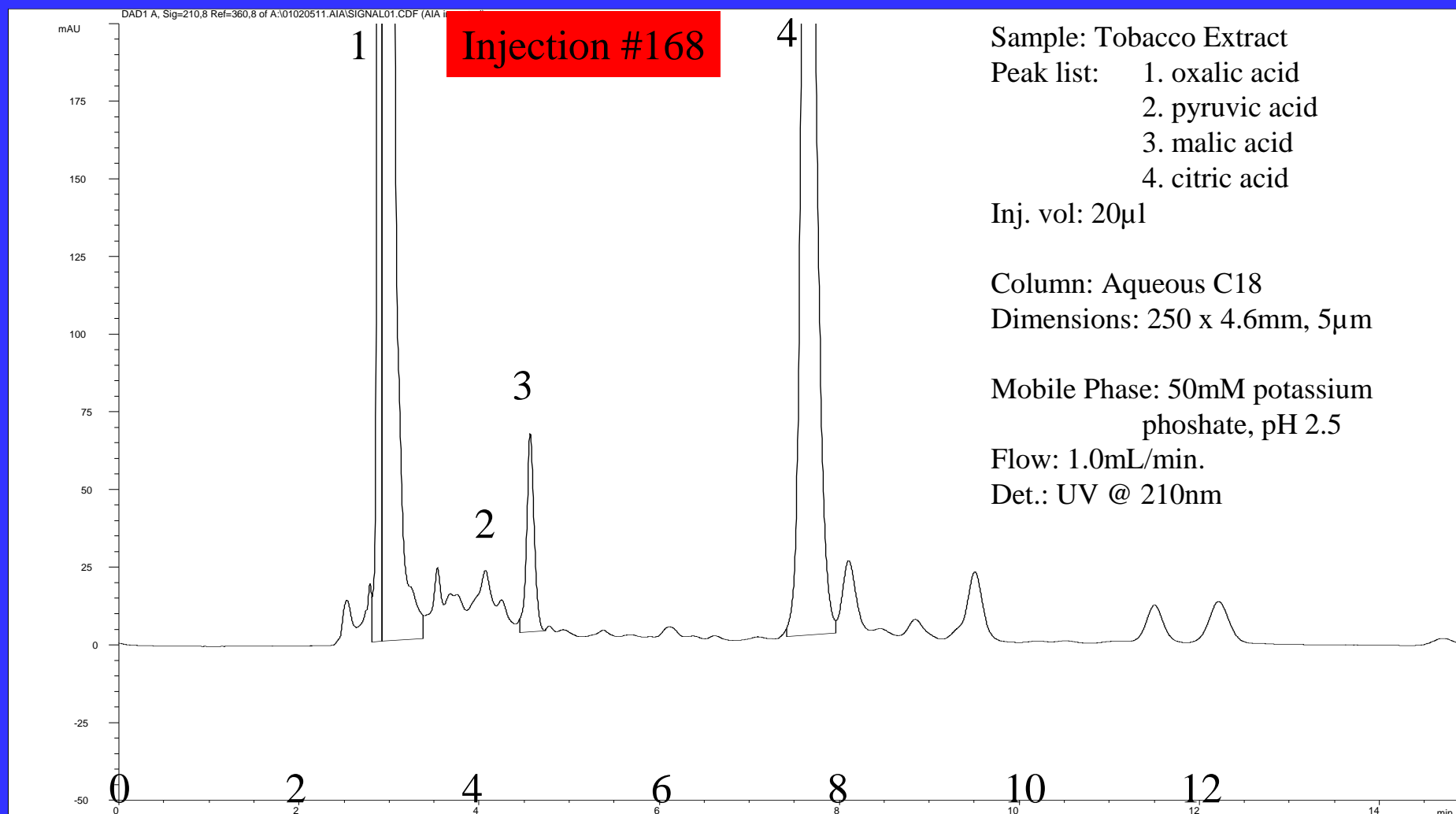
# Figure 11. Carboxylic Acids on Aqueous C18 Column



# Figure 12. Tobacco Extract on Aqueous C18 Column



# Figure 13. Stability of Aqueous C18 Column



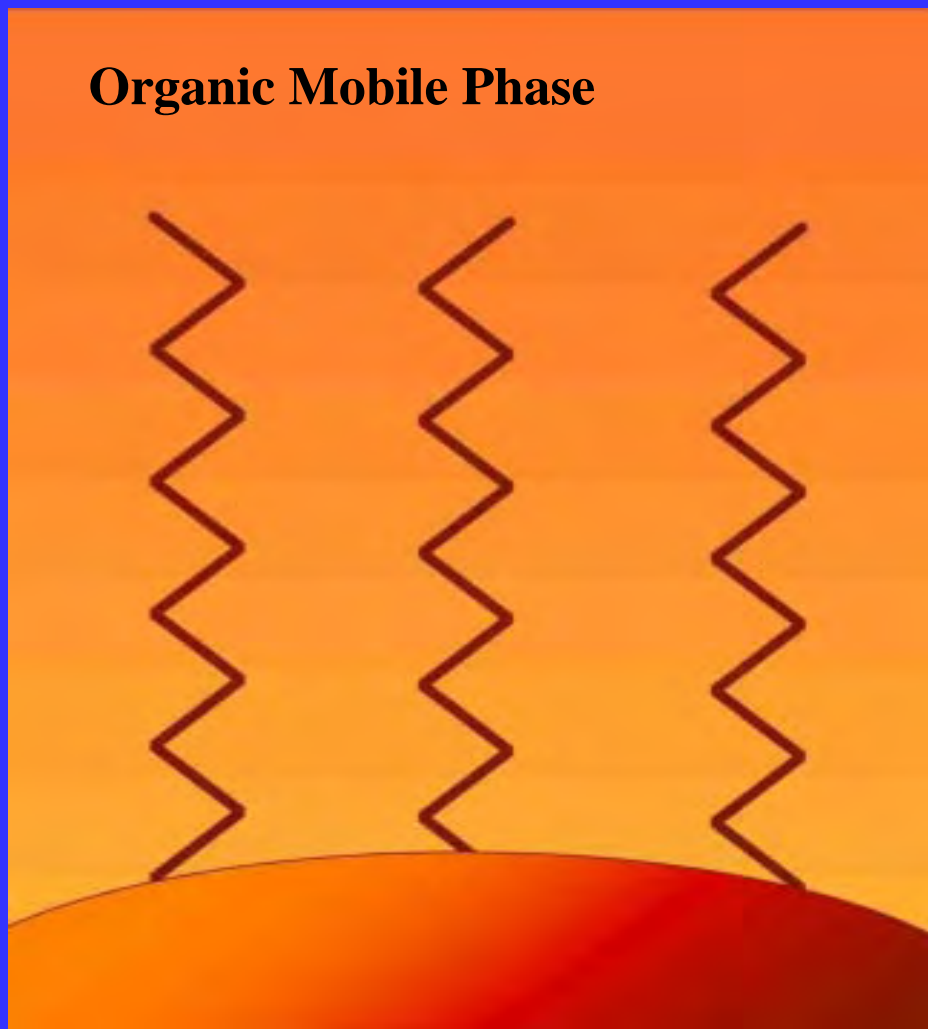
# Chain Folding

Figure 14 depicts how highly aqueous mobile phases can cause chain folding with conventional C18 columns. Chain folding can result in a total loss of retention as shown in Figure 15. Exposure to completely aqueous mobile phases at ambient pressure (no flow) accelerates the chain folding process. Figure 16 demonstrates that the Aqueous C18 column provides reproducible retention, even when stored in completely aqueous mobile phase at ambient pressure for extended periods.

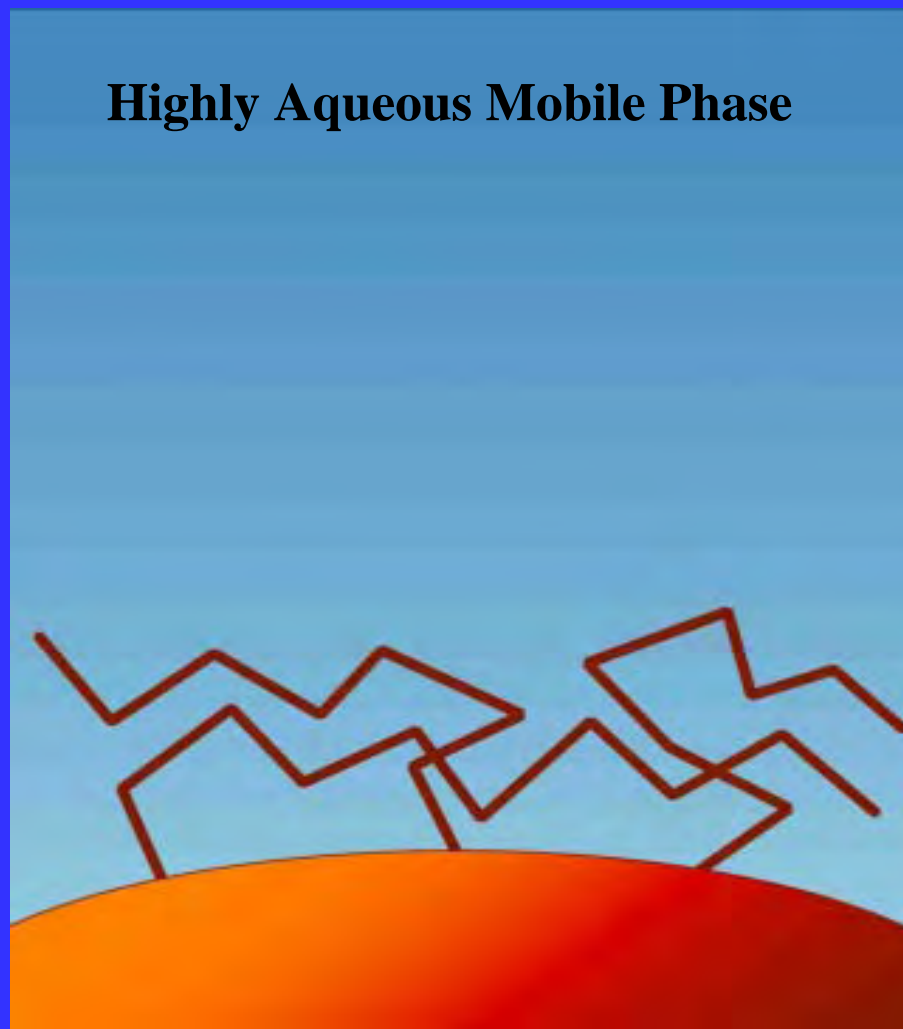


# Figure 14. Chain Folding (Conventional C18)

**Organic Mobile Phase**

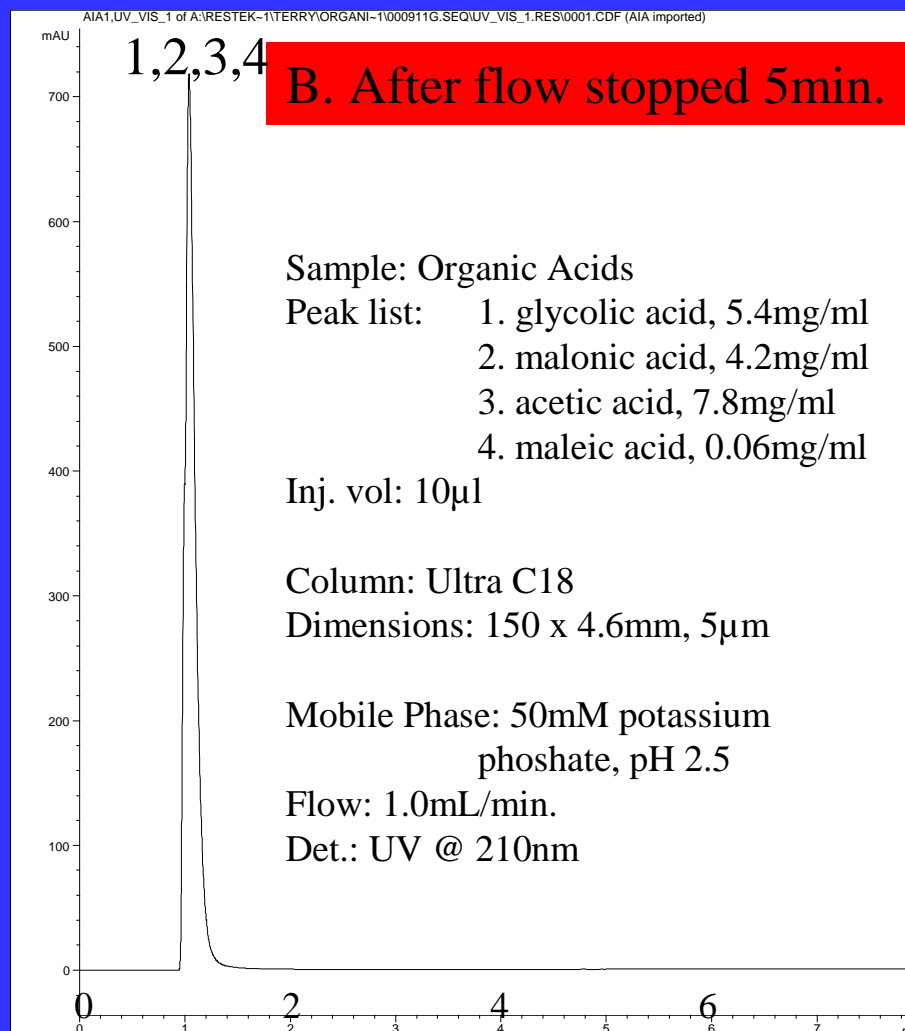
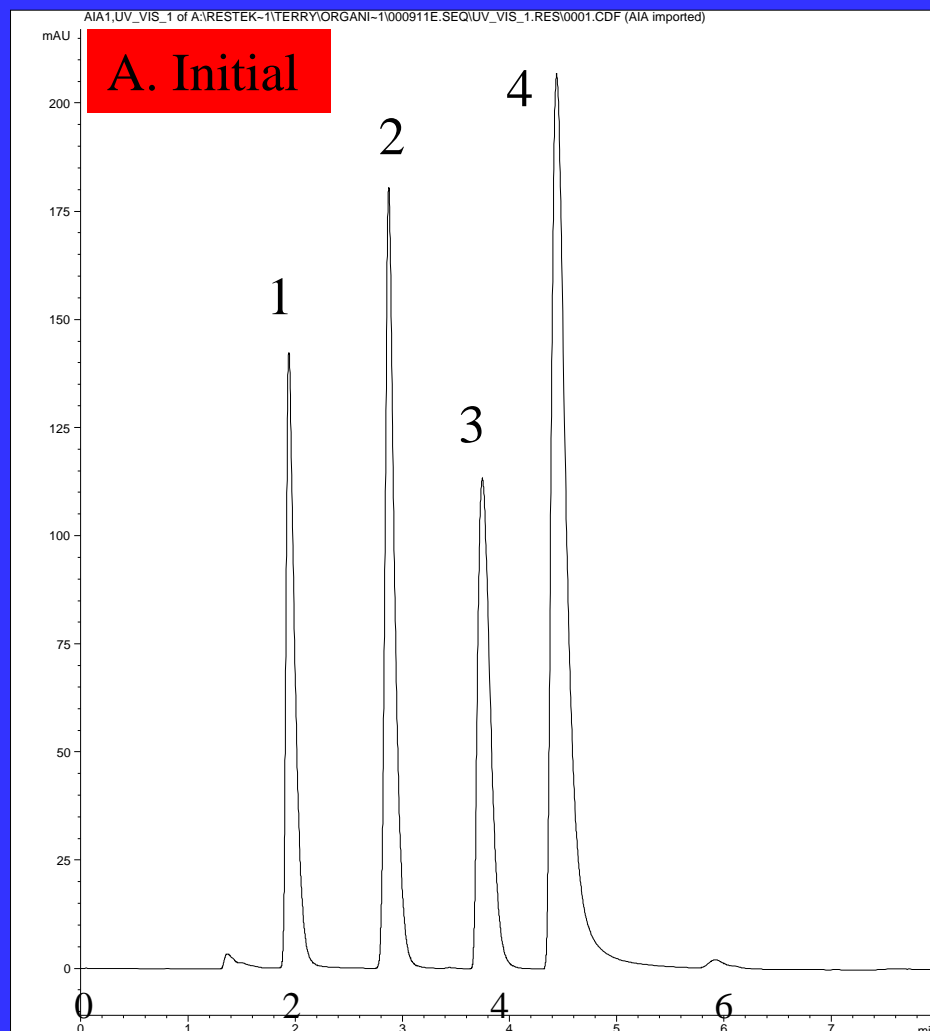


**Highly Aqueous Mobile Phase**

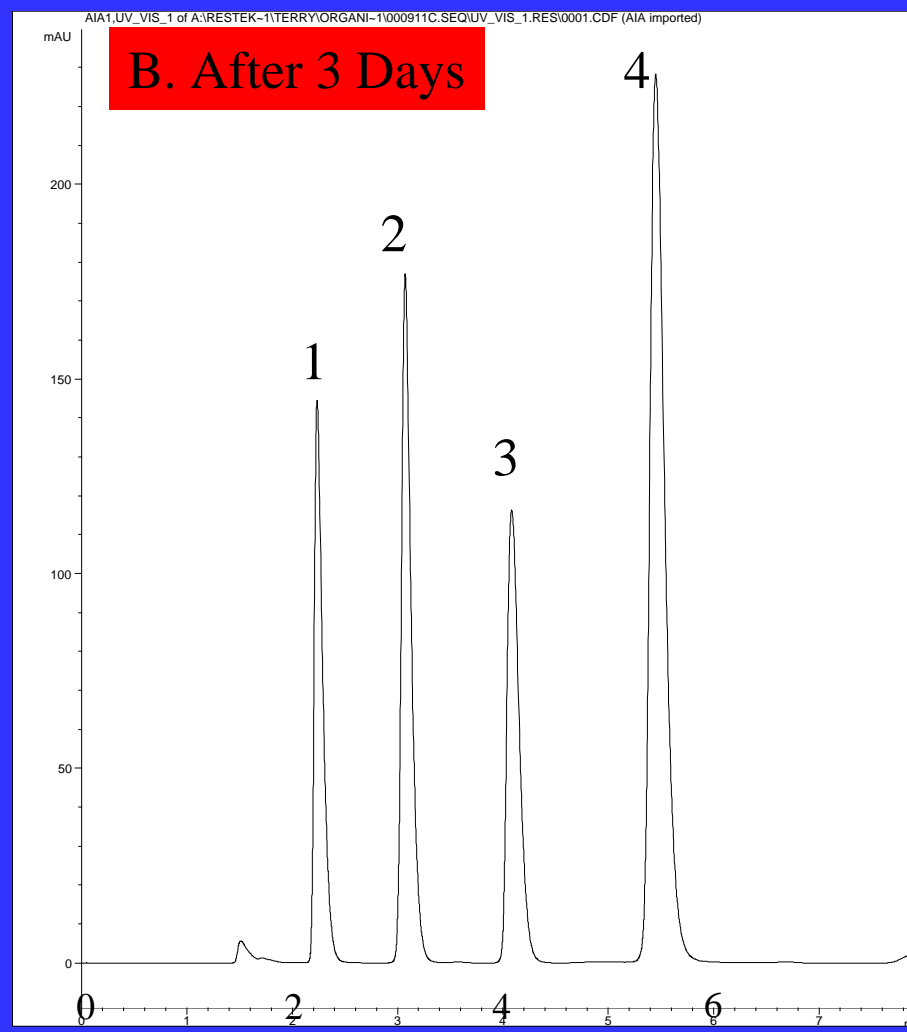
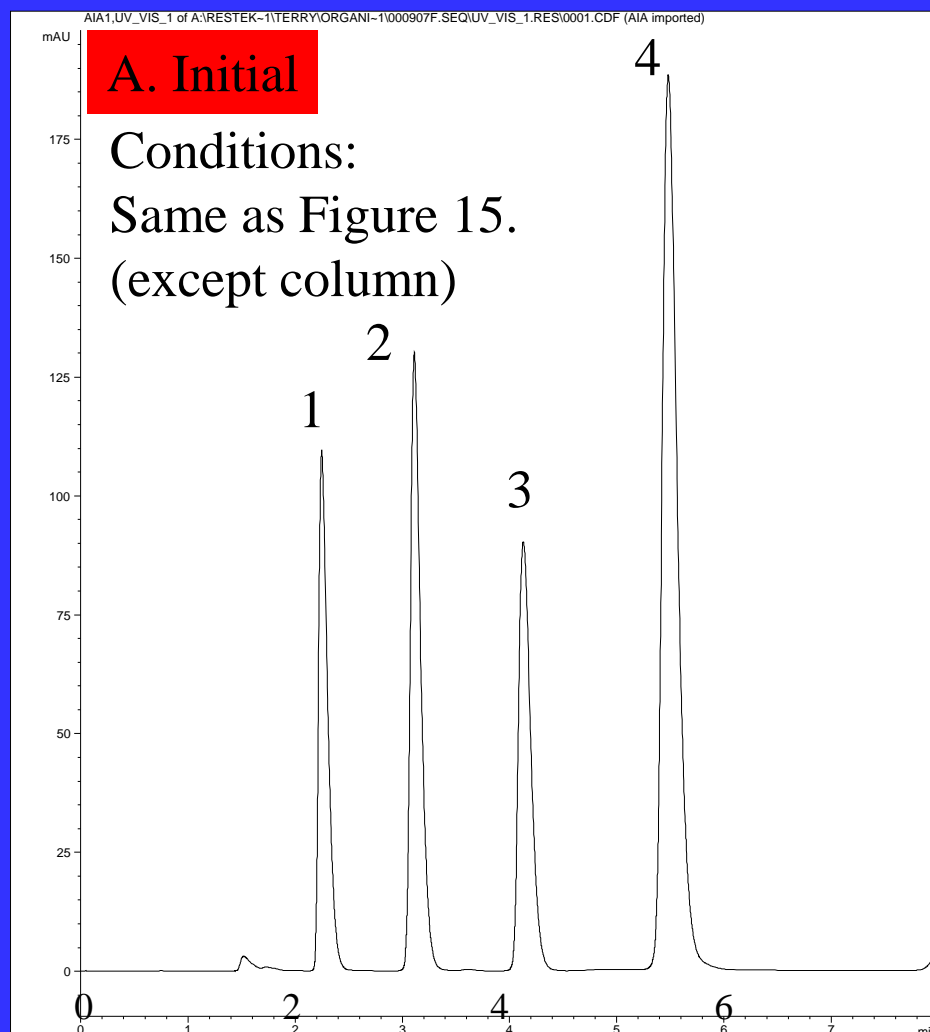




# Figure 15. Chain Folding with Conventional C18



# Figure 16. Stability of Aqueous C18 Column



# Conclusions

The secondary polar character of the Aqueous C18 and Ultra IBD columns provide enhanced retention of polar compounds, stable retention in totally aqueous mobile phases, and unique selectivity.

The characteristics of the Aqueous C18 and Ultra IBD columns can be advantageous for analyzing a wide range of polar compounds, including nutraceuticals, pesticides, and carboxylic acids.

# Acknowledgement

The phenethyl glucosinolate standard and extracts of cabbage and watercress were generously provided by Dr. Gerard Engelen-Eigles, University of Minnesota, Horticulture Department.

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## Extraction and Analysis of Explosives Following US EPA Method 8095

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# Abstract

The standard environmental test method for nitroaromatic, nitramine, and nitroester analysis has been US EPA method 8330<sup>1</sup>. This method uses HPLC separation and detection by ultra-violet absorption. Analysts have been interested in a GC method that overcomes the disadvantages of the HPLC method, including high solvent usage, multiple co-elutions, and long run times.

US EPA method 8095<sup>2</sup> has been written as a GC/ECD alternative to method 8330. This GC/ECD method was developed at the U.S. Army Cold Regions Research and Engineering Laboratory<sup>3</sup>. Method 8095 includes all of the method 8330 target compounds plus 3,5-dinitroaniline, nitroglycerine, and PETN.

Restek has designed two new stationary phases, Rtx<sup>®</sup>-TNT and Rtx<sup>®</sup>-TNT 2 columns, specifically for method 8095. The TNT columns provide better resolution and higher thermal stability than any of the columns currently recommended in Method 8095. The Rtx<sup>®</sup>-TNT, primary column and Rtx<sup>®</sup>-TNT 2, confirmational column, operate under identical GC oven temperature programs, allowing simultaneous dual-column confirmational analysis of all 16 nitroaromatic compounds.

# Explosives Analysis by Gas Chromatography Using Method 8095

- GC more common than HPLC in environmental laboratories
- Selective detection using ECD
- Direct flash injection of ACN extract
- Simultaneous dual-column analysis

# Explosives Target Compound List

## Method 8095

1. nitrobenzene
2. 2-nitrotoluene
3. 3-nitrotoluene
4. 4-nitrotoluene
5. nitroglycerine
6. 1,3-dinitrobenzene
7. 2,6-dinitrotoluene
8. 2,4-dinitrotoluene
9. 1,3,5-trinitrobenzene
10. trinitrotoluene
11. PETN
12. RDX
13. 4-amino-2,6-dinitrotoluene
14. 3,5-dinitroaniline
15. 2-amino-4,6-dinitrotoluene
16. tetryl
17. HMX



# Sample Extraction and Preparation

## Water Samples

- A main difference in sample preparation for GC is that the samples are not diluted 1:1 with reagent water prior to being injected, as is the case for HPLC samples
- Method 8095 requires solid phase extraction (SPE) disks or cartridges to extract analytes of interest from water samples, such as described in EPA 3535A<sup>2</sup>. The extraction is performed using SDB/RPS-type disks or RDX type cartridges. Please note that method 8095 does not use the acetonitrile/salting out extraction procedure as described in method 8330.
- The use of SPE for explosives extraction requires extra drying time after the sample is loaded. Most explosive compounds have low water solubility, so the extra drying time helps their recovery into the acetonitrile elution solvent, and reduces the water content in the injected sample. Safety considerations prevent explosive extracts from further concentration by Kuderna-Danish concentrators. The extra drying time, when using SPE, leads to drier extracts which reduce the need for recalibration and maintenance when using water-sensitive electron capture detectors.

# Sample Extraction and Preparation Soil Samples

- In Method 8095, analytes of interest are extracted from soil and sediment samples using the same acetonitrile extraction with ultra-sonication procedure as described in Method 8330. Samples are air-dried at room temperature or cooler to a constant weight. Then the samples are screened with a colorimetric test, such as EPA Method 8515, to determine if they contain too much explosive residue to be safely ground with a mortar and pestle. If the sample contains less than 1% explosive residue, generally it is considered safe to be ground with a mortar and pestle. Two grams of the finely ground soil are extracted using 10 milliliters of acetonitrile in a cooled ultra-sonication bath for 18 hours. The acetonitrile extracts are then dried and filtered before analysis.
- A main difference in sample preparation for GC is that the samples are not diluted 1:1 with reagent water prior to being injected, as is the case for HPLC samples

# Injection Modes

## Cool On-column Injection

- While few laboratories routinely use cool on-column injection ports because of the perception of high maintenance, it has several advantages over direct injection for the analysis of explosives. These advantages include complete sample transfer into the column via a highly inert pathway and reduced peak width.
- For those with more questions about on-column injection ports, Jack Cochran, LECO Corporation, will be presenting a talk on on-column injection ports and explosives analysis.

Tuesday Morning, Room 261, 8:30 AM, (428)

**New Tools for the Analysis of Explosives: An On-column Injection Liner for a PTV Inlet, Two TNT GC Columns, and a Gas Chromatograph/Time-of-Flight Mass Spectrometer.**

# Injection Modes

## Direct Flash Injections

- Most laboratories will analyze explosive samples by direct injection. Many direct injection parameters need to be optimized for successful analysis of these compounds. The injection port temperature must be determined carefully to provide good response for the thermally labile compounds, such as nitroglycerine and PETN, and sufficient vaporization for the high boiling compounds, such as HMX. For most analyses, an injection port temperature between 250 – 275 °C is best.
- Restek offers a unique Siltek deactivated sleeve to meet the needs of explosive analysis by direct injection. The internal diameter of the sleeve was reduced from the typical 4mm ID to a new 1mm ID. This reduction of dead volume in the injection port reduces peak broadening. Initial results with Siltek indicate improved reproducibility and better inertness to explosive residues than standard deactivations. Most sample residue can be solvent rinsed off of Siltek, allowing the sleeve to be reused without the need for re-deactivation.

# Carrier Gas Flow

- Explosive analysis by GC works best when using very high carrier gas flows. While low-boiling compounds (e.g., nitrotoluenes) could be analyzed well at normal carrier gas flow rates, the high boiling compounds (e.g., HMX) are best analyzed with carrier gas flow rates five to seven times the normal linear velocity.
- Most laboratories will find a column head pressure of 2 to 3 psi is optimum for this analysis. This should provide a linear velocity of 100 to 140 cm/second, or a flow of 12 – 17 ml/min..

# Oven Temperature Programming and Solvent Focusing

- While Method 8095 recommends an initial oven temperature of 100 °C, Restek discovered improved solvent focusing and decreased peak widths by using an initial oven temperature of 80 °C with acetonitrile injections. This improvement was seen with both cool on-column and direct injections.

# Columns Recommended in Method 8095

- EPA 8095 lists the DB<sup>®</sup>-1 (100 % dimethylpolysiloxane) and the HP<sup>®</sup>-5 (5% diphenyl 95% dimethylpolysiloxane) as possible primary columns.
- The DB<sup>®</sup>-1 completely co-elutes RDX and PETN.
- The HP<sup>®</sup>-5 resolves RDX and PETN but usually co-elutes 4-amino-2,6-dinitrotoluene and 3,5-dinitroaniline.
- The Rtx<sup>®</sup>-TNT is much better than the DB-1 since RDX/PETN is a critical separation.
- EPA 8095 list the Rtx<sup>®</sup>-200 (trifluoropropyl methyl polysiloxane) and the Rtx<sup>®</sup>-225 ( 50% cyanopropyl methyl 50% phenyl methyl polysiloxane) as the possible confirmational columns.
- The Rtx<sup>®</sup>-200 is significantly more retentive than any of the primary columns. HMX is usually not detected. RDX and 2-amino-4,6-dinitrotoluene co-elute. Nitroglycerin and 2,6-dinitrotoluene co-elute.
- The Rtx<sup>®</sup>-225 has poor thermal stability. The column is only stable to 260 °C. This column is also too retentive. ECD bleed levels are also an issue with cyano containing polymers.
- The Rtx<sup>®</sup>-TNT2 is better than any of the confirmational columns since all compounds can be detected with the the Rtx<sup>®</sup>-TNT in a simultaneous dual-column run.



# Gas Chromatography Column Design Criteria for the Rtx<sup>®</sup>-TNT and Rtx<sup>®</sup>-TNT2

- Short Column, Wide-bore, Standard  $d_f$
- Analysis Time < 20 min
- Low Bleed with ECD
- Critical Resolution
- Column Inertness
- Dual Column Analysis Capability

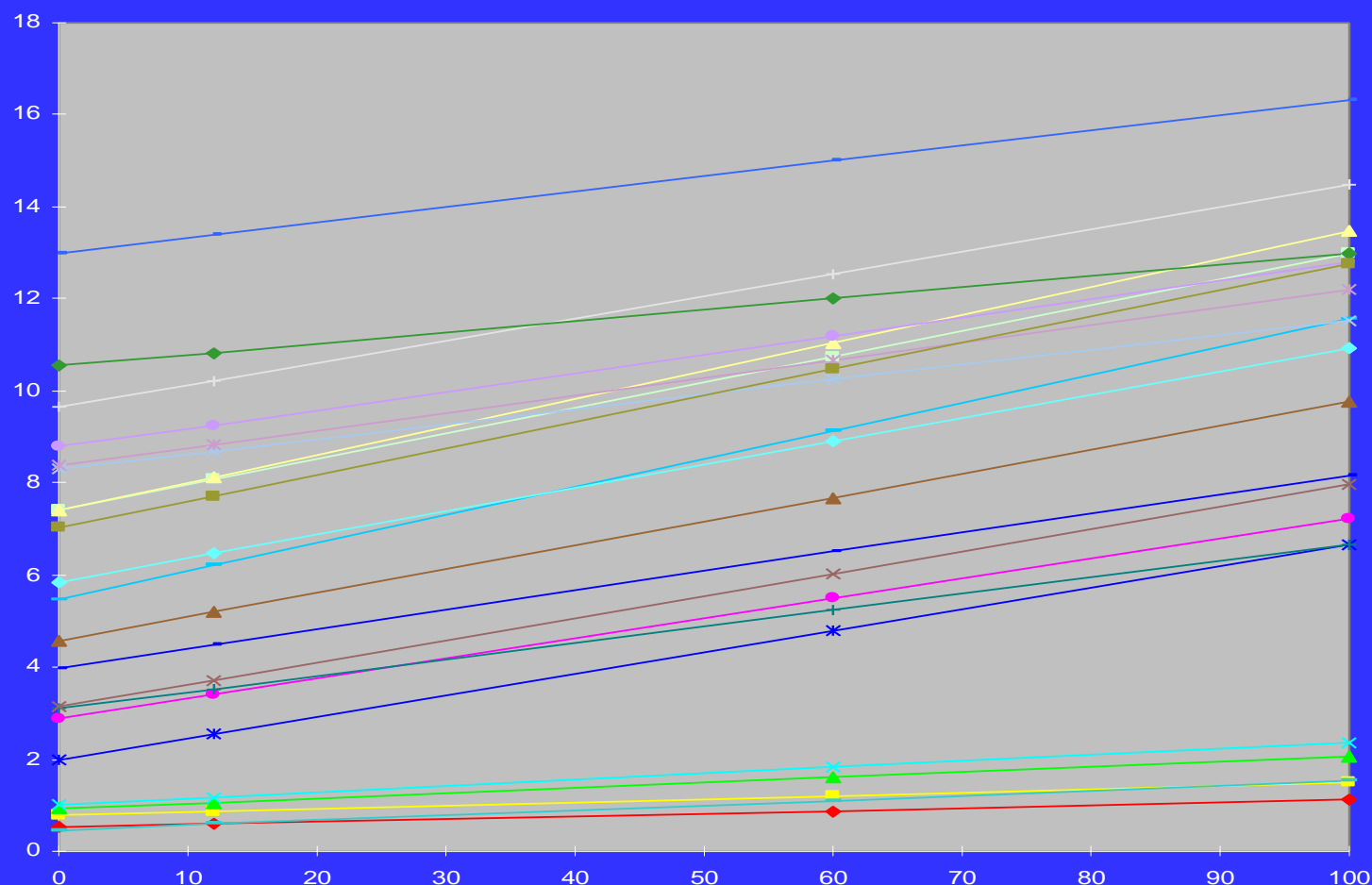




# Stationary Phase Optimization

- Window Diagramming
- Computer Simulation of Retention Time
- Computer Prediction of Optimized Stationary Phase Composition and Column Dimensions

# Window Diagramming and Computer Assisted Stationary Phase Development

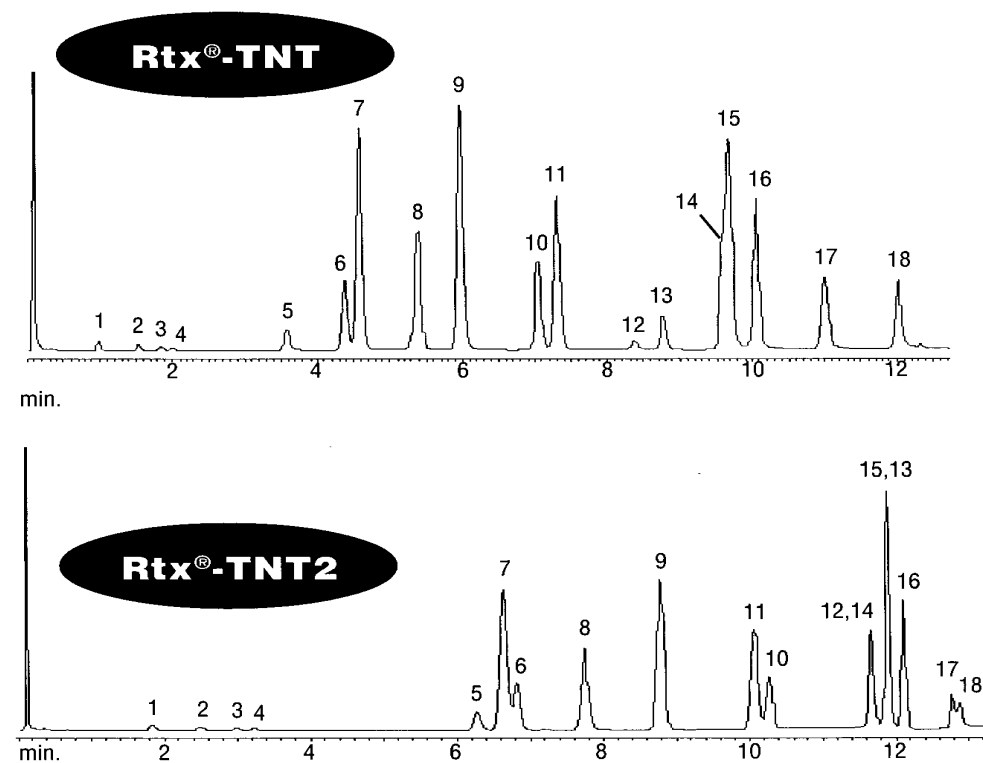


# 6 m x 0.53 mm Restek Rtx-TNT Columns

## Direct Injection

- 1 Nitrobenzene
- 2 2-Nitrotoluene
- 3 3-Nitrotoluene
- 4 4-Nitrotoluene
- 5 Nitroglycerin
- 6 1,3-Dinitrobenzene
- 7 2,6-Dinitrotoluene
- 8 2,4-Dinitrotoluene
- 9 3,4-Dinitrotoluene
- 10 1,3,5-Trinitrobenzene
- 11 TNT
- 12 PETN
- 13 RDX
- 14 4-Amino-2,6-dinitrotoluene
- 15 3,5-Dinitroaniline
- 16 2-Amino-4,6-dinitrotoluene
- 17 Tetryl
- 18 HMX

*Rtx®-TNT and Rtx®-TNT2 columns provide the best resolution of nitroaromatic explosive compounds in under 13 minutes.*



6m, 0.53mm ID, 1.50µm Rtx ® -TNT (cat. #12998)

6m, 0.53mm ID, 1.50µm Rtx ® -TNT2 (cat. #12999).

Direct injection using a 1mm Siltek™ Uniliner® (cat. #21052-214.1).

On-column conc.: 200-1000pg for each compound. 8095 Calibration

Mix A (cat.# 31607), 8095 Calibration Mix B (cat.# 31608), and 3,4-dinitrotoluene (cat.#31452).

Oven temp.: 80°C (hold 1 min.) to 180°C @ 10°C/min. to 300°C @ 30°C/min. (hold 3 min.);

Inj. temp.: 250°C; Det.: ECD @ 330°C with anode purge;

Dead time: 4.4 sec.; Head pressure:

He @ 3psi (20.7 KPa);

Flow rate: He @ 17mL/min. @ 80°C.

# Analytical Reference Materials

- Obtaining pure, neat compounds for the preparation of calibration standards can be very difficult. Some of these compounds are not available commercially at a high enough purity for accurate analytical results. These materials can contain desensitizing agents, such as beeswax, water, plasticizers, or other manufacturing by-products. Many commercially available explosives are shipped wet and must be dried carefully before solution preparation.
- To ensure the highest quality explosive standards, Restek chemists carefully purified or synthesized all of the compounds listed in Method 8095. All compounds used to prepare these standards have 98% purity or higher. Multiple analytical techniques, including GC, HPLC, GC/MS, FTIR, and DSC, are used to verify raw material purity.

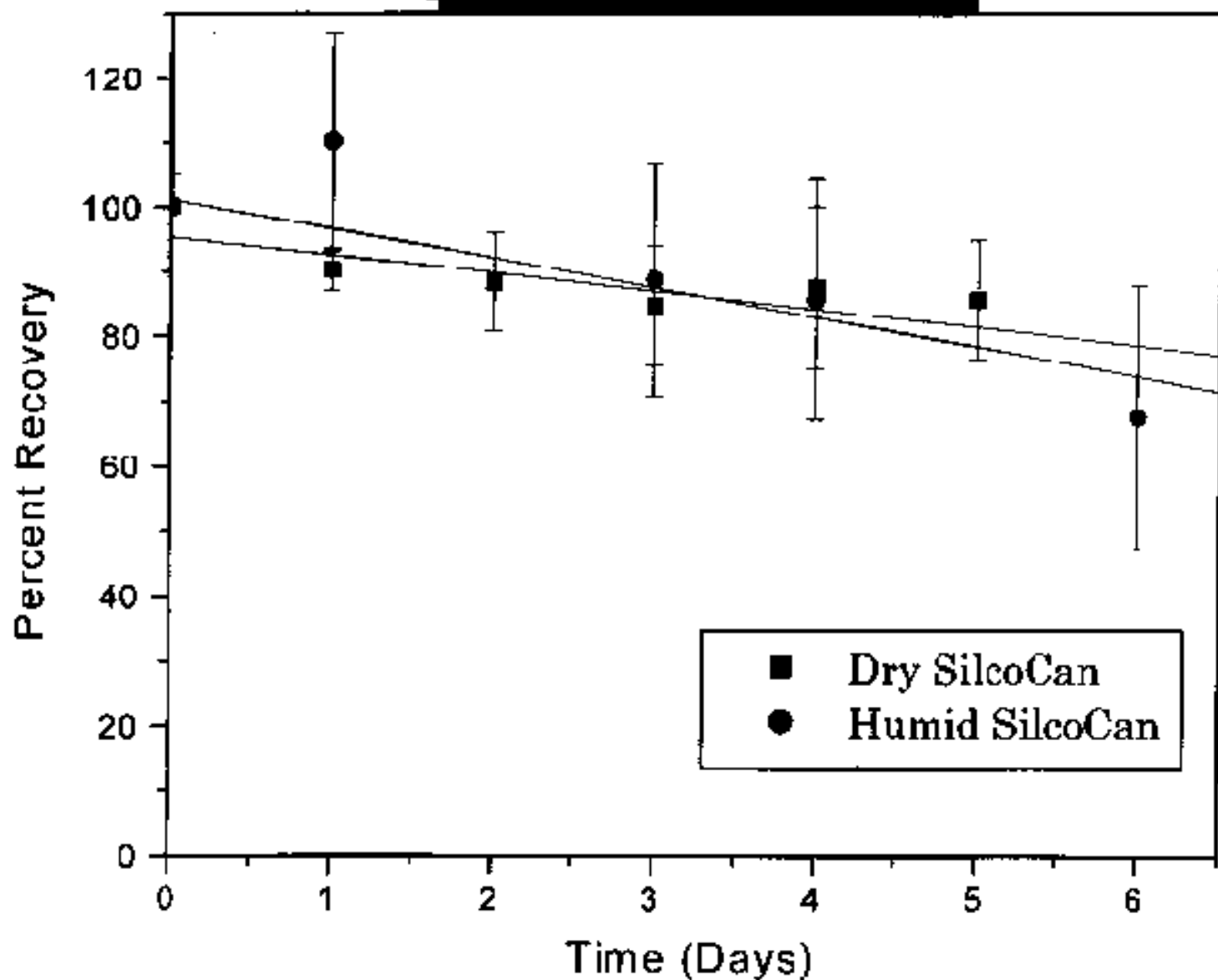
# Conclusions

- Using GC/ECD for explosives analysis as per Method 8095 is now an excellent alternative to HPLC analysis. Careful consideration of sample extraction, preparation, and analytical techniques will ensure successful analysis of the explosives. Restek has optimized the column stationary phases and dimensions, injection technique, and analytical reference materials to help achieve the best resolution of nitroaromatic compounds in the fastest analysis time.

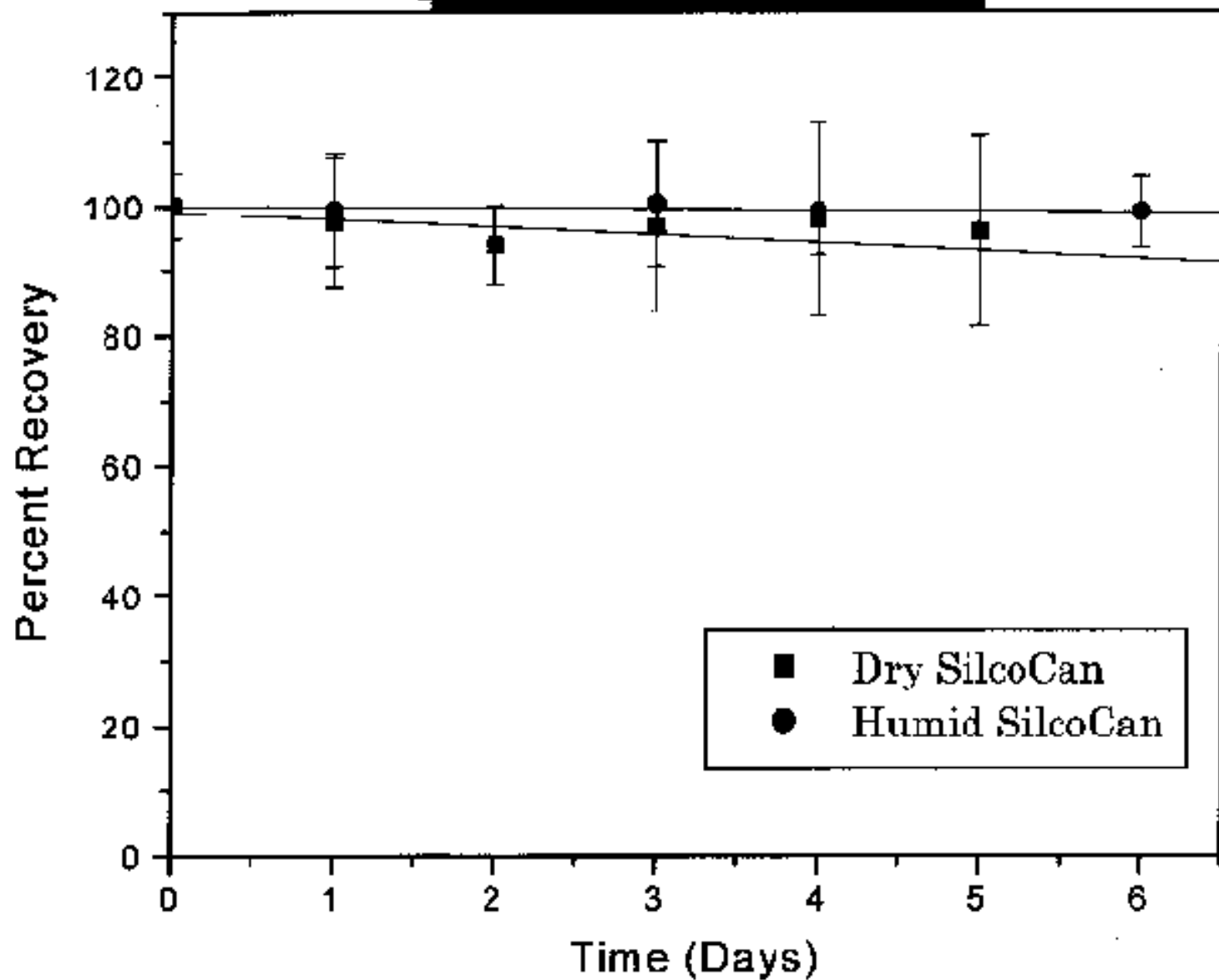
# References

- 1. US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846 Update III, Office of Solid Waste, Washington, DC, 1997.
- 2. US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Proposed Draft Update IVB, Office of Solid Waste, Washington, DC, 1999.
- 3. M. E. Walsh, T. Ranney. "Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water Using Solid-Phase Extraction and Gas Chromatography-Electron Capture Detection: Comparison with High-Performance Liquid Chromatography." *Journal of Chromatographic Science*, Vol. 36, pp. 406–416, August 1998.

H<sub>2</sub>S Stability in SilcoCans  
Humid *versus* Dry

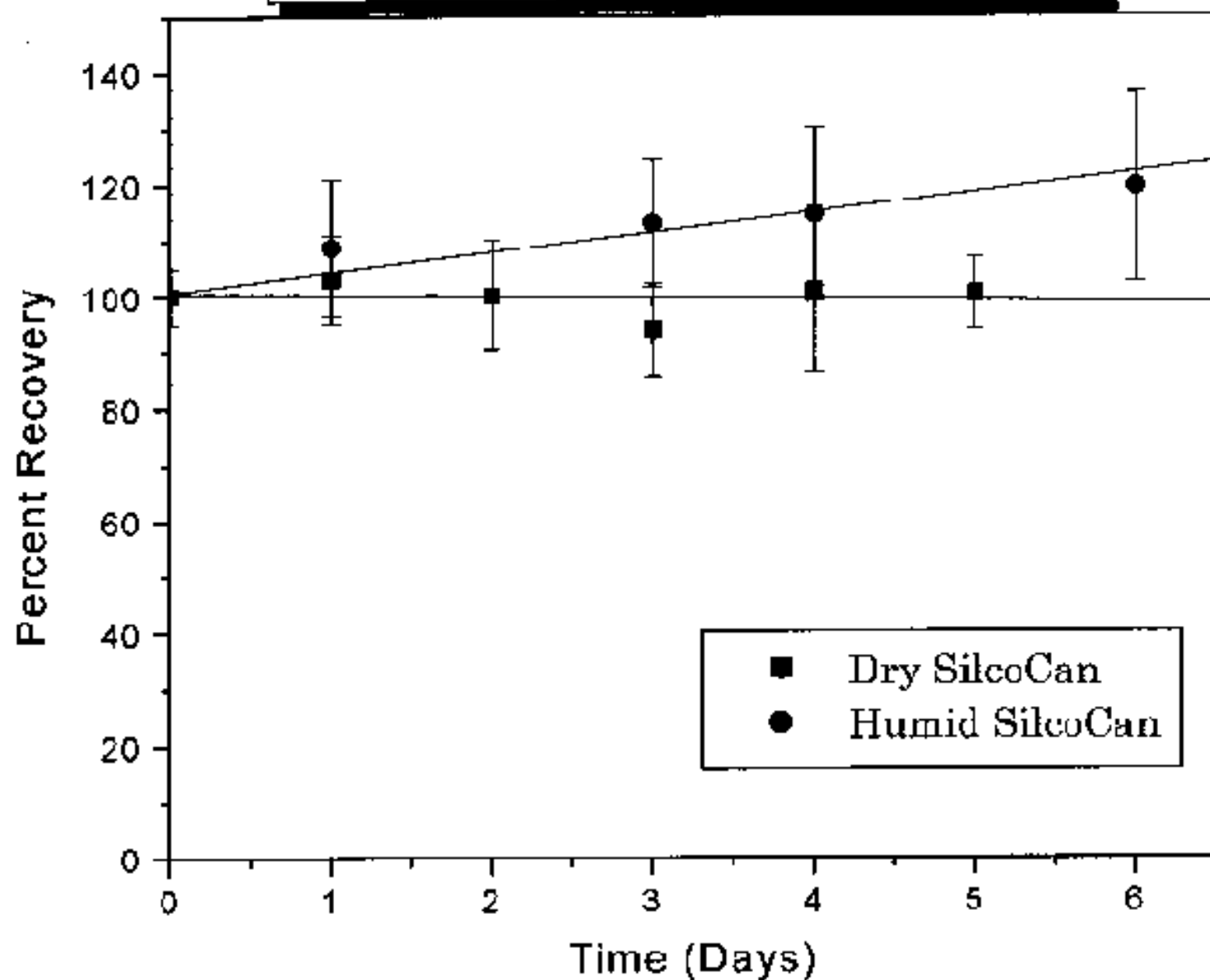


COS Stability in SilcoCans  
Humid *versus* Dry

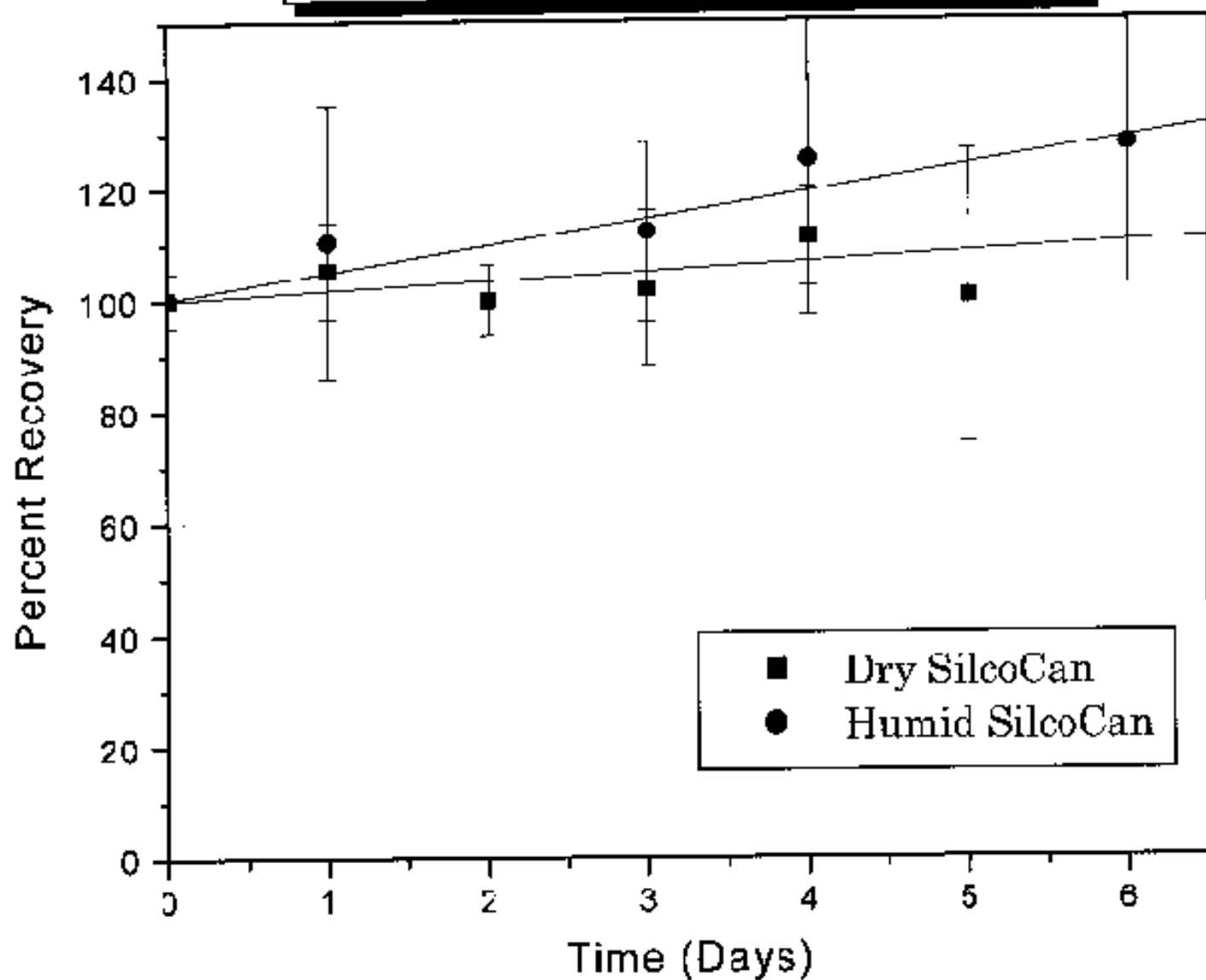




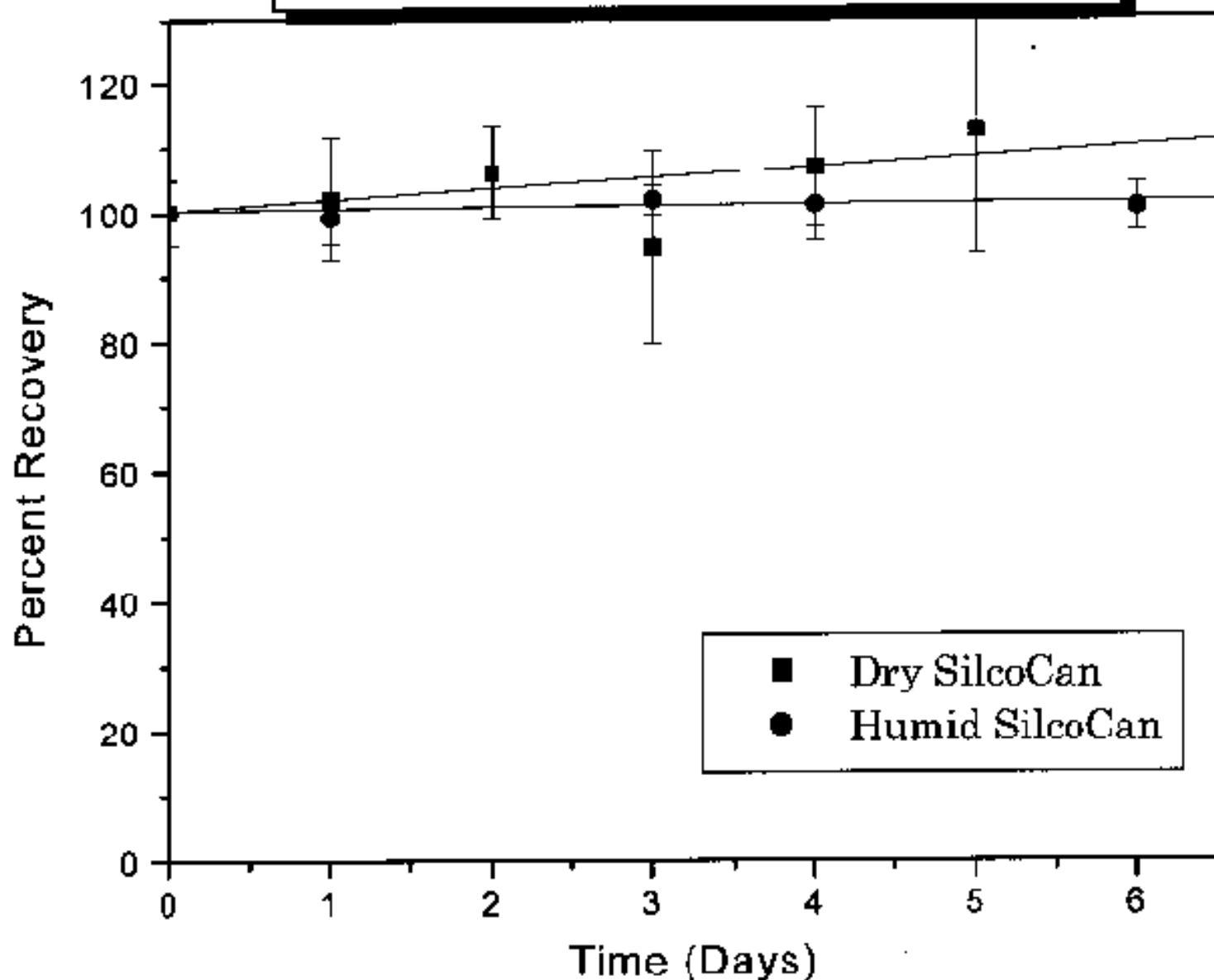
Methyl Mercaptan Stability in SilcoCans  
Humid *versus* Dry



Ethyl Mercaptan Stability in SilcoCans  
Humid *versus* Dry



Dimethyl Disulfide Stability in SilcoCans  
Humid *versus* Dry



## Conclusion

This study investigated the stability of very low level sulfur VOCs (1-20ppbv) in SilcoCan™ and electropolished canisters, using both dry nitrogen and humid conditions. The electropolished canisters exhibit degradation of reactive sulfurs VOCs such as H<sub>2</sub>S and methyl mercaptan and ethyl mercaptan. Both dry and humidified 11ppbv sulfur VOCs exhibited virtually no breakdown or reactivity in SilcoCan™ canisters after 6 days of storage.

## References

1. Quang Tran, You-Zhi Tang; Stability of Reduced Sulphur Compounds in whole Air Samplers, 1994 AWMA/EPA International Symposium of Measurement of Toxic and Related Air Pollutants.
2. Hoyt, Steven; Longacre, Vivian; and Stroupe, Michael; Measurement of Oxygenated Hydrocarbons and Reduced Sulfur Gases by Full Scan GC/MS: EPA TO-14; *Sampling and Analysis of Airborne Pollutants*, Eric Winegar, Lawrence Keith.
3. Parmar, Sucha; Kitto, Andrew; Ugarova, Luda: A Study of "Holding Times" for Sulfur Compounds in Restek SilcoCan Canister, 1996 AWMA/EPA International Symposium of Measurement of Toxic and Related Air Pollutants.
4. Method TO-14A, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography; *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. Jan 1997

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## Stability of Semi-Volatile Compounds in US EPA Method 8270 and Appendix IX Analytical Reference Materials

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fax (814)353-1309

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# Abstract

EPA method 8270 and Appendix IX contain over 150 commonly analyzed semi-volatile pollutants. The compounds include PAH's, chlorinated hydrocarbons, aldehydes, ketones, nitrosamines, phenols, anilines and benzidines. Preparing stable analytical reference materials for this extensive compound list is not trivial. Poorly formulated mixtures will give compound interaction over time in the flame sealed ampule that ultimately misrepresents the originally prepared target concentration leading to poor calibration data quality.

Data will be presented on the stability of many different semi-volatile analytical reference materials formulations. Incompatible compounds and their proposed reactions and products will be described. The role of solvent purity and specifications in good long term reference material will also be described.

# Purpose

The purpose of this work was to identify the most commonly analyzed EPA 8270 and Appendix IX compounds and formulate these into a minimum number of stable, easily handled calibration stock mixtures.

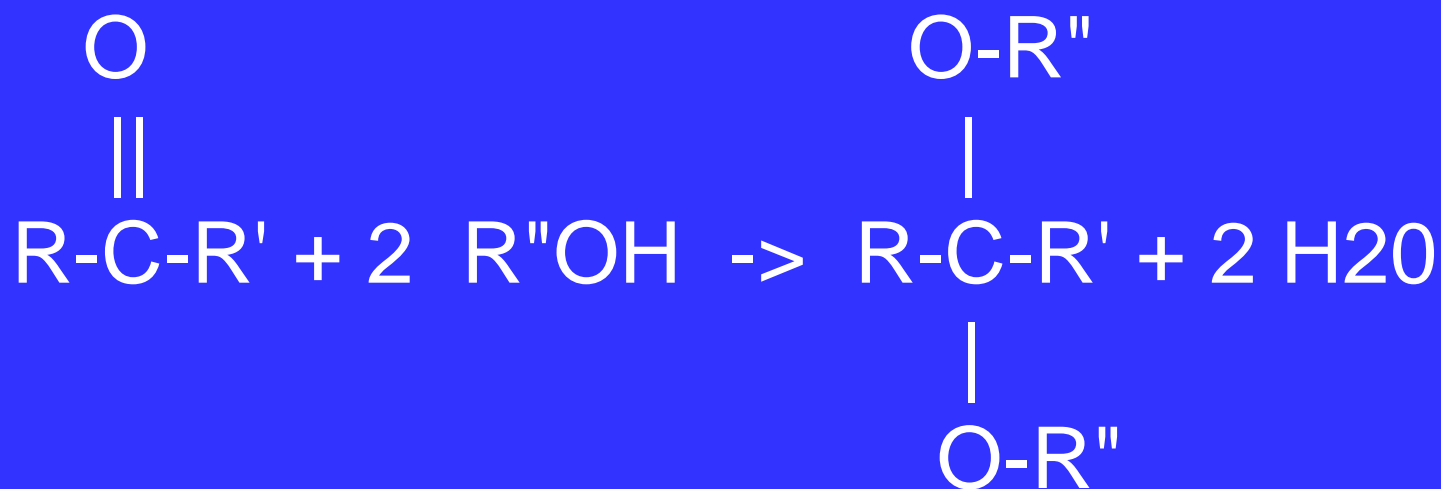
# Acid / Base Reactions

- Acids, such as phenols and benzoic acid will react with bases, such as anilines, benzidines, and nitrosamines. Most calibration standards prepared with these compounds together will only be usable for only about one week. These incompatible compounds were kept separate to ensure maximum shelf life of the ampulated stock solutions.
- Low response, tailing peaks, or complete loss of these compounds are signs of acid / base reactions in your calibration standards.



# Ketone Addition Reaction with Alcohols

- Most ketones will form hemi-acetals and acetals in the presence of alcohols. The general reaction is as follows:



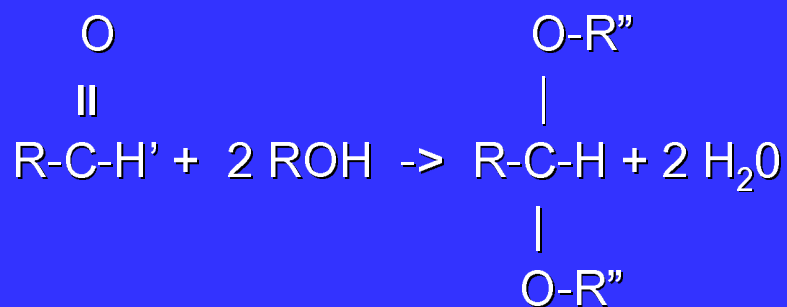
This reaction may be catalyzed by either acid or base

# PAH Reactions in the Presence of Hexachlorocyclopentadiene and Hexachlorobutadiene

- PAHs have been known to spontaneously chlorinate in the presence hexachlorocyclopentadiene and hexachlorobutadiene. The reaction is a substitution reaction with chlorine for hydrogen on the PAH. The exact mechanism has not been determined at this time. No loss of hexachlorocyclopentadiene nor hexachlorobutadiene is seen in this reaction.
- The reaction is believed to be caused by free chlorine or chlorine radicals in certain lots of hexachlorocyclopentadiene and hexachlorobutadiene.
- Purification of hexachlorocyclopentadiene and hexachlorobutadiene by distillation prevents this reaction.

# Aldehyde Adduct formation in the presence of alcohols

- Aldehydes will form adducts in the presence of alcohols. An example is benzaldehyde in the presence of methanol. This reaction may take place immediately or slowly over several months.
- Most brands and grades of methylene chloride contain methanol added at a concentration of about 500ppm as a stabilizer. This may or may not be listed on the bottle label. Methylene chloride can be quickly screened for added methanol by GC/FID on a non-polar column, such as the Rtx-5.
- The methylene chloride used for this study was amylene stabilized and contained no methanol.



This reaction may be catalyzed by either acid or base

# Chlorinated Triazine Herbicides

- Chlorinated triazine herbicides will substitute chlorine for OH or OR in the presence of water or alcohol.
- This reaction is catalyzed by light or acid.
- The reaction is very fast once started since the reaction product HCl is a catalyst.

Chlorinated Triazines include:

Atrazine

Cyanazine

Cyprozone

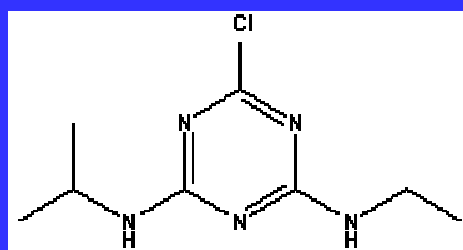
Procyazine

Propazine

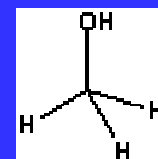
Simazine

Terbuthylazine

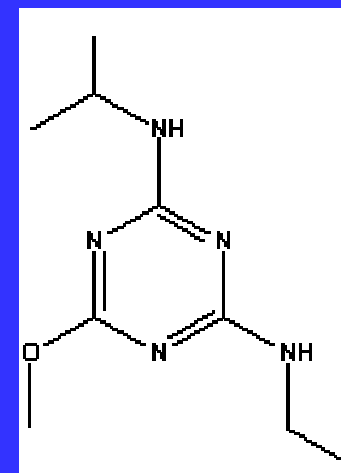
Trietazine



+



→



+



# Stability Testing

- Stability testing was based on flame sealed ampules stored at 4°C or –18°C under real-time conditions.
- Stored solutions were compared by GC/MS to newly prepared solutions.
- A stored solution was determined to be unusable if there was more than 5% difference in response for any one analyte.

# Final Phenols Calibration Mixture

2,3,4,6-Tetrachlorophenol  
2,4,5-trichlorophenol  
2,4,6-Trichlorophenol  
2,4-Dichlorophenol  
2,4-Dimethylphenol  
2,4-Dinitrophenol  
2,6-Dichlorophenol  
2-Chlorophenol  
2-Methylphenol (o-cresol)  
2-Nitrophenol  
3-Methylphenol (m-cresol)  
4,6-Dinitro-2-methylphenol  
4-Chloro-3-methylphenol  
4-Methylphenol (p-cresol)

4-Nitrophenol  
Benzoic acid  
Dinoseb  
Pentachlorophenol  
Phenol

2000 ppm each in methylene chloride

This mixture is currently stable for 37 months at 4°C

# Final Anilines / Nitrosamines Mixture #1

2-Nitroaniline  
3,3'-dichlorobenzidine  
3-Nitroaniline  
4-Chloroaniline  
4-Nitroaniline  
Aniline  
Benzidine  
N-Nitrosodi-n-propylamine  
N-Nitrosodimethylamine  
Pyridine

2000 µg/ml in methylene chloride

This mixture is currently stable for 18 months at –18°C.

# Final Chlorinated Compounds Mix

1,2,4,5-Tetrachlorobenzene  
1,2,4-trichlorobenzene  
1,2-dichlorobenzene  
1,3-Dichlorobenzene  
1,3-Dinitrobenzene  
1,4-Dichlorobenzene  
2-Chloronaphthalene  
4-Bromophenyl phenyl ether  
4-Chlorophenyl phenyl ether  
Bis(2-chloroethoxy)methane  
Bis(2-chloroethyl) ether  
bis(2-chloroisopropyl)ether [2,2'-  
oxybis-(1-chloropropane)]  
Chlorobenzilate  
Hexachlorobenzene

Hexachlorobutadiene  
Hexachlorocyclopentadiene  
Hexachloroethane  
Hexachloropropene  
Isodrin  
Kepone  
Pentachlorobenzene  
Pentachloronitrobenzene  
Aramite

2000 ppm each in methylene chloride

This mixture is currently stable for 12 months at  $-18^{\circ}\text{C}$ . More stability testing is in progress.



# Final Neutral Compound Mixture

1,3,5-Trinitrobenzene

1,4-Naphthoquinone

2,4-Dinitrotoluene

2,6-Dinitrotoluene

4-Nitroquinoline-1-oxide

Acetophenone

azobenzene

Benzyl alcohol

Bis(2-ethylhexyl)phthalate

Butyl benzyl phthalate

Di-n-butyl phthalate

DI-n-octyl phthalate

Dibenzofuran

Diethyl phthalate

Dimethyl phthalate

Ethyl methanesulfonate

Isophorone

Isosafrole (cis & trans)

Methyl methanesulfonate

Nitrobenzene

Phenacetin

Safrole

2000 ppm each in methylene chloride

This mixture is currently stable for 24 months at  $-18^{\circ}\text{C}$ . More Stability testing is in progress.

# Final PAH Mixture

1-methylnaphthalene  
2-Methylnaphthalene  
3-Methylcholanthrene  
Acenaphthene  
Acenaphthylene  
Anthracene  
Benz(a) anthracene  
Benzo(a) pyrene  
Benzo(b) fluoranthene  
Benzo(g,h,i) perylene  
Benzo(k) fluoranthene  
Chrysene  
Dibenz(a,h) anthracene  
Fluoranthene  
Fluorene  
Ideno(1,2,3-cd) pyrene  
Naphthalene  
phenanthrene  
Pyrene

2000 ppm each in methylene chloride

This mixture is currently stable for 37 months at 4°C.

# Final Organophosphorus Mixture

0,0,0-Triethyl phosphorothioate

Diallate (cis or trans)

Dimethoate

Disulfoton

Famphur

Methyl parathion

Parathion

Phorate

Pronamide

Thionazine

2000 ppm each in methylene chloride

This mixture is currently stable for 11 months at 4°C.

# Final Organochlorine Pesticide Mixture

4,4'-DDD  
4,4'-DDE  
4,4'-DDT  
Aldrin  
alpha-BHC  
Alpha-chlordane  
beta-BHC  
delta-BHC  
Dieldrin  
Endosulfan I  
Endosulfan II  
Endosulfan sulfate  
Endrin  
Endrin aldehyde  
Endrin ketone  
gamma-BHC (Lindane)  
Gamma-chlordane  
Heptachlor  
Heptachlor epoxide  
Methoxychlor

200 ppm each in 1:1: hexane/toluene

Currently stable for 37+ months at 4°C.

# Final Anilines / Nitrosamines Mix #2

1,4-Phenylenediamine  
1-Naphthylamine  
2-Acetylaminofluorene  
2-Naphthylamine  
2-Picoline  
3,3'-Dimethylbenzidine  
4-Aminobiphenyl  
5-Nitro-o-toluidine  
a,a,-Dimethylphenethylamine (free base)  
Methapyrilene (free base)  
N-Nitrosodibutylamine  
N-Nitrosodiethylamine  
N-Nitrosomethylethylamine  
N-Nitrosomorpholine  
N-Nitrosopiperidine  
N-Nitrosopyrrolidine  
o-Toluidine  
p-Dimethylaminoazobenzene

This mixture is currently stable for 18 months at  $-18^{\circ}\text{C}$ .

2000 ppm each in methylene chloride

# Conclusions

- Stable stock calibration mixtures can be prepared by carefully considering potential chemical interactions between target analytes, impurities, solvents, and solvent stabilizers.
- Solvents must be carefully chosen and screened to obtain good shelf life of stock solutions.
- Stock solution storage plays a role in shelf life. Amber glass ampules will prevent reactions caused by light. While refrigerator storage is generally recommended for semivolatile standards, freezer storage will improve stability for certain mixtures, especially anilines and benzidines.



# New Capillary Gas Chromatographic Columns for the Analysis of Dioxins, Furans, and PCBs

Frank L. Dorman, Eric J. Reiner, and  
Karen MacPherson

Restek Corporation • [www.restekcorp.com](http://www.restekcorp.com)

# Abstract

The analyses of Dioxins, Furans, and PCBs are generally performed using at least 2 different methods, and if data for the co-planar PCBs is required a third method is often utilized. This can mean that for 1 sample it may be necessary to perform a dual-column ECD method for the non-coplanar PCBs, high resolution mass spec analysis for the dioxins and furans, and either mass spec or another ECD analysis for the co-planar PCBs. Additionally common methodologies for these analyses can result in 1-hour long chromatographic separations, and different sample preparation procedures may also be required.

This investigation describes the preliminary data in the attempt to consolidate all of these analyses plus the toxaphene and PAH analyses into a single high resolution GC/MS separation.



# Experimental

## C/MS

l separations using Agilent 6890 GC coupled to a Micromass Ultima HRMS @10,000RP; **Injection port:** 280°C; **Carrier gas:** He or H<sub>2</sub>

## Columns

**M:** 0.10mm ID, 0.10µm Rtx<sup>®</sup>-5MS (Restek Corp.); **Column head pressure:** 100psi; **Oven program:** 100°C (hold 1 min.) to 0°C @ 100°C/min. to 235°C @ 13°C/min. to 300°C @ 27°C/min. (hold 4 min.); **Injection volume:** 0.2µL.

**M:** 0.18mm ID, 0.18 µm Rtx<sup>®</sup>-5MS (Restek Corp.); **Column head pressure:** 61psi.; **Oven program:** 100°C (hold 0.62 n.) to 200°C @ 64.5°C/min. to 235°C @ 4.8°C/min. (hold 6.2 min.) to 300°C @ 9.7°C/min (hold 5.6 min); **Injection volume:** 1.0µL.

## Extract Preparation

tracts are prepared similar to the US EPA Method 8290, but the extracts are further cleaned using carbon SPE. This method ows for the collection of two sample extract fractions: one containing the non-coplanar PCBs, and the other containing the planar PCBs, dioxins, furans, and PAHs.

# Separation Requirements

## Dioxins and Furans

Chromatographic resolution and analysis times are dependant on column dimensions (length, i.d., phase thickness). The table below summarizes a number of column options for the analysis of dioxins/furans. The conventional 60M 5% diphenyl column assigned a relative analysis time of 1. Experimentally it has been determined that 175,000 plates are required to obtain the necessary separation of 2,3,7,8-TCDD from its nearest neighbors (1,2,3,7/1,2,3,8-TCDD unresolved pair eluting before, and 1,2,3,9-TCDD eluting after). This criterion can be easily met on both the 40M, and the 60M columns, however, the analysis can be completed in nearly ½ of the time on the 40M column. The 20M column is also capable of meeting these requirements about ¼ of the time, however, there is little room for trimming the column when the column performance begins to deteriorate with use. For the dioxin and furan analysis, therefore, a 40M column was selected for this work.

## PCBs

In order to minimize the number of ions that must be simultaneously monitored, it is desirable to elute the bulk of the PCB compounds prior to the elution of the dioxin and furan compounds. This can be accomplished by injecting the non-coplanar PCB fraction into a 20M column that is parallel to the 40M column used for the separation of the dioxin/furan fraction.

## Column Configuration

Columns are installed in parallel into an MS ion source, with PCB fraction being injected onto the 20M column, and the dioxin/furan fraction being injected onto the 40M column. Resulting analysis time is less than a single fraction on the conventional 60M column.

# Analysis

Sample chromatograms are shown for the separation of several PCBs and dioxins by chlorination level. PCB data for the analysis of two reference materials (sediment and biota) are summarized in the tables below. This method was also evaluated on three different extracts, soil, biota, and air versus the conventional separation on the 60M column. This data appears as a comparison of the “fast” method to the “conventional” method in the table.

## *Analysis of PCB Congener Reference Sediment EC-3*

PCB Congener	Expected Value ng/g	N	Average Value
18	9.0 +/- 4.7	8	9.2
28	18.6 +/- 8.6	8	14.7
52	35.6 +/- 12.9	8	28.9
105	13.1 +/- 4.3	8	18.9
118	28.5 +/- 5.4	8	28.6
138	25.2 +/- 6.3	8	26.0
153	24.2 +/- 4.1	8	22.6
170	8.9 +/- 1.3	8	9.6
180	15.4 +/- 6.6	8	13.7

Extract	Compound	Conventional GC/HRMS (60M)	Fast GC/HRMS (40M)
Soil	2,3,7,8-T <sub>4</sub> CDD	2.2 ppt	2.3 ppt
Fish	2,3,7,8-T <sub>4</sub> CDD	14 ppt	13 ppt
Air	1,2,3,7,8-P <sub>5</sub> CDD	0.093 pg/M <sup>3</sup>	0.093 pg/M <sup>3</sup>

# Summary

This presentation describes the initial attempt at method consolidation and throughput increase from a parallel-dual-column separation using GC-HRMS for the analysis of PCBs, Dioxins, Furans, and PAHs. The authors are continuing to refine this method, but initial results are very promising. This method should allow for the combining of several different analytical methods to a single instrument, with a total analysis time of less than 30 minutes.

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*For reprints, please leave card in envelope*

# Acknowledgements

**Eric J. Reiner, Ph.D.**, Ministry of the Environment—Ontario, Canada

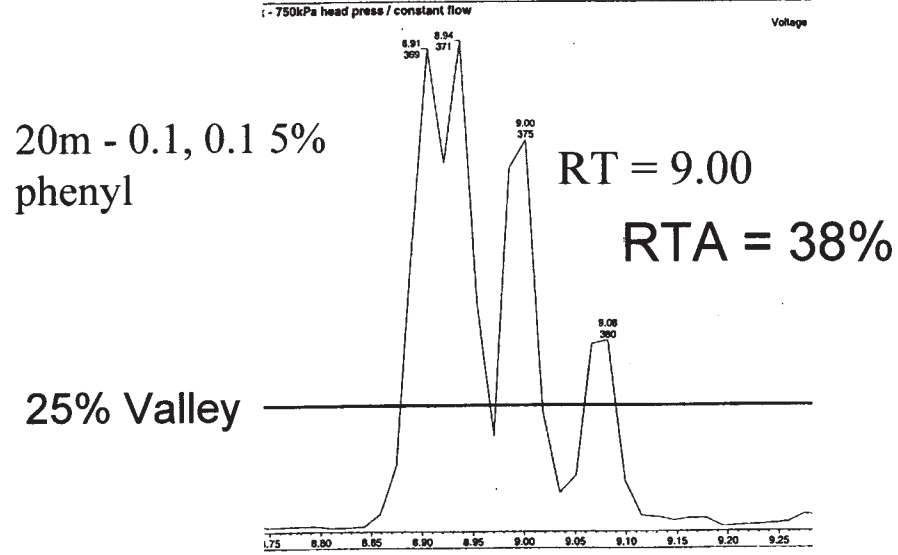
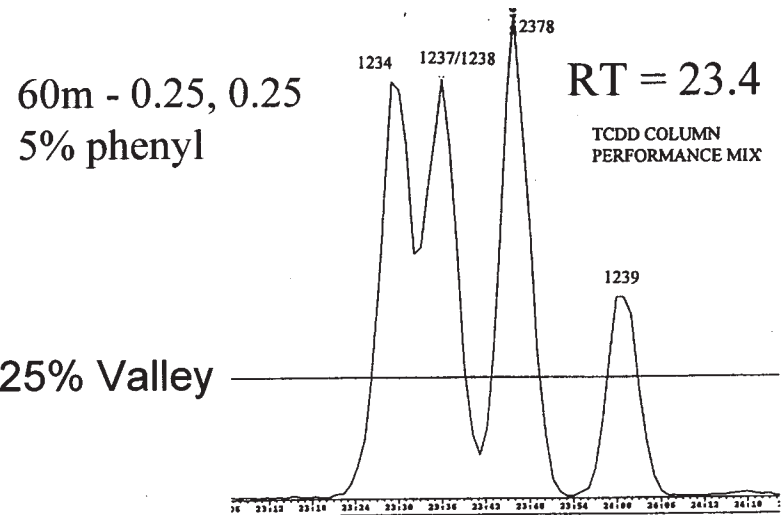
**Karen McPherson**, Ministry of the Environment—Ontario, Canada

# PCB Congener Analysis of NRC CARP-1 Reference Fish

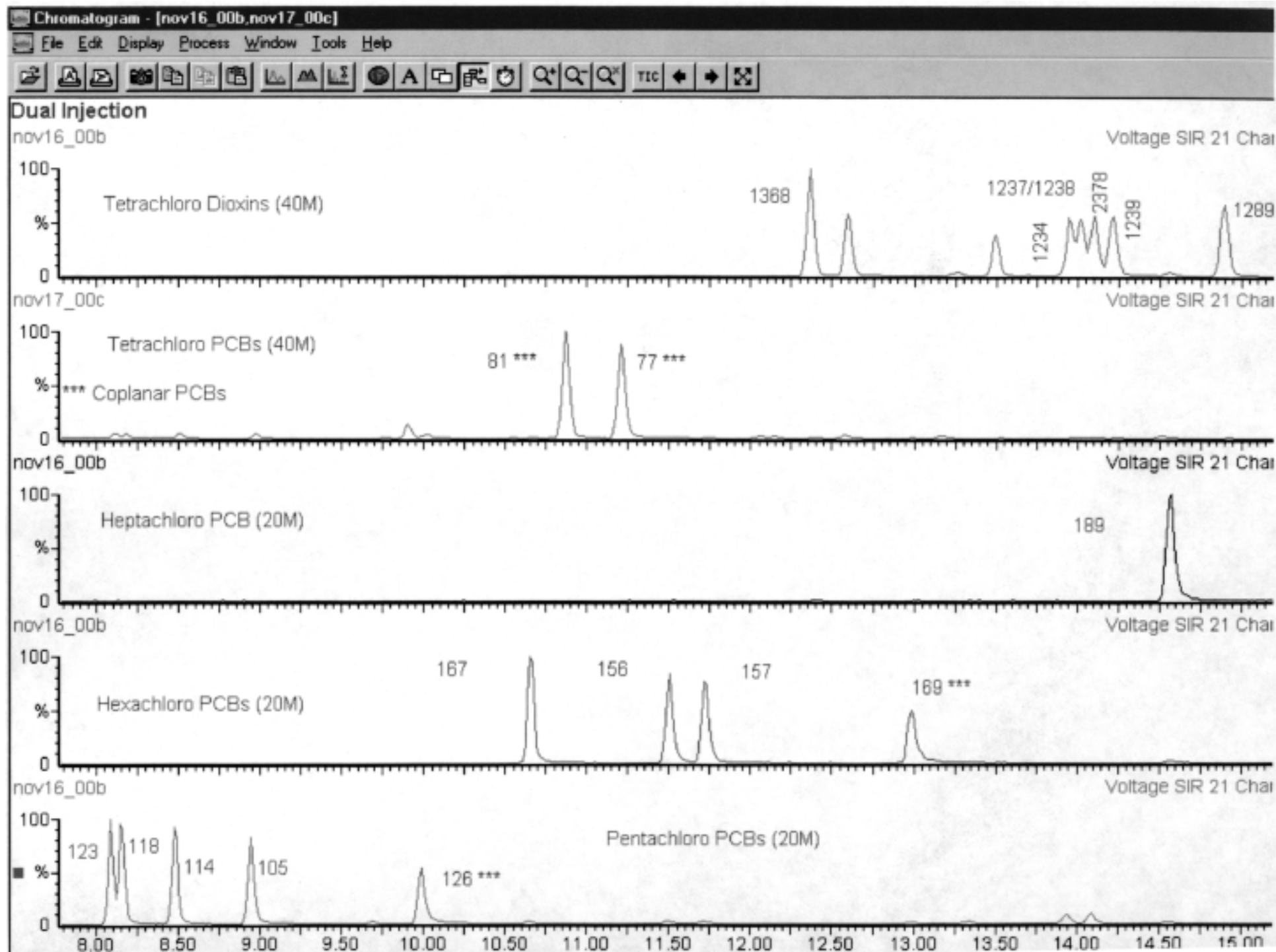
PCB CONGENER	CERTIFIED VALUE (ng/g)	N	AVERAGE
52	124 $\pm$ 32	3	141
101	124 $\pm$ 37	3	131
105	54 $\pm$ 24	3	51
118	132 $\pm$ 60	3	126
138	102 $\pm$ 23	3	102
153	83 $\pm$ 39	3	96
170	22 $\pm$ 8	3	22
180	46 $\pm$ 14	3	48
187	36 $\pm$ 16	3	39

# Column Comparison: Dioxin

Column Length (m)	20	60	40
i.d. (mm)	0.1	0.25	0.18
Film Thickness (μm)	0.1	0.25	0.18
Theoretical Plates/m	8,600	3,300	5,300
Total Plates	172,000	198,000	212,000
Effective Plates (TCDD)	176,000	230,000	285,000
Relative Efficiency	0.93	1	1.03
Relative Anal. Time	0.33	1	0.55









# Stationary Phase Selection for Nucleotides and Nucleosides Using High Performance Liquid Chromatography

Terrence S. Reid and Keith J. Duff

Restek Corporation

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# Abstract

Mixtures of nucleotides, nucleosides and their respective purine or pyrimidine bases are difficult to analyze by reversed phase high performance liquid chromatography (RP HPLC). These compounds cover a wide range of polarities and functionalities, from the acidic nucleotides to the basic purines and pyrimidines, making it very difficult to retain and resolve all of them with conventional alkyl stationary phases. Traditional HPLC analyses of these compounds often use a combination of reversed phase- ion pairing (RP-IP) and/or ion exchange (IEX) mode.

# Abstract (cont.)

Nucleotides are often analyzed by anion exchange while nucleosides are sometimes analyzed by cation exchange modes. These methods are not compatible with all the solutes in these mixtures and lack ruggedness.

This study is important in demonstrating that all three classes of compounds (nucleotides, nucleosides, bases) can be analyzed by RP-HPLC using one column and the same simple isocratic mobile phase. This provides greater convenience, reproducibility and ruggedness in developing methods for these mixtures.

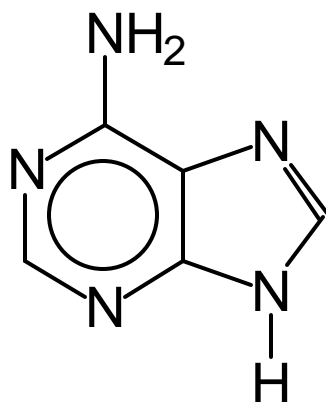
# Abstract (cont.)

By using a unique, intrinsically base deactivated stationary phase (Ultra IBD), simple RP-HPLC conditions were identified which resolve any common purine or pyrimidine base from its related ribonucleoside and mono-, di- and triphosphate nucleotides.

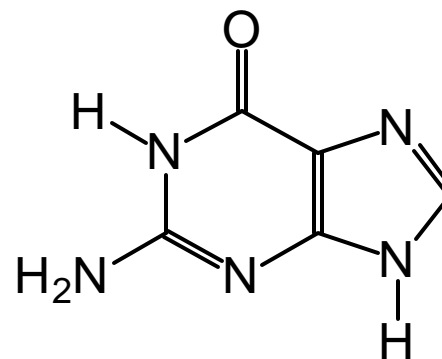
# Introduction

A nucleoside consists of a nitrogenous base linked to a pentose (sugar). A nucleotide is composed of a nucleoside plus one or more phosphate groups. The nitrogenous bases of nucleosides and nucleotides are either purines or pyrimidines. Figure 1 shows the structures of the major purines (adenine, guanine) and pyrimidines (cytosine, uracil, thymine). Figure 2 shows the structures of four common ribonucleosides in which a base is linked to ribose. Figure 3 shows the structures of three important nucleotides, ATP, ADP, and AMP, which are composed of the nucleoside adenosine plus three, two and one phosphate group(s), respectively.

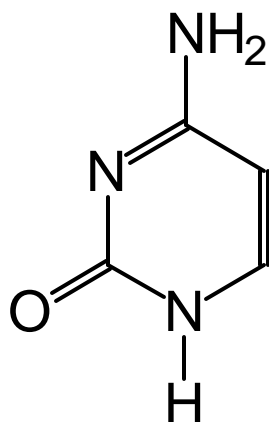
Figure 1. Purine and Pyrimidine Bases



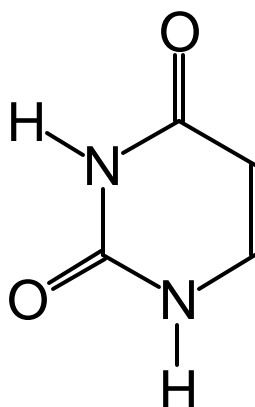
Adenine



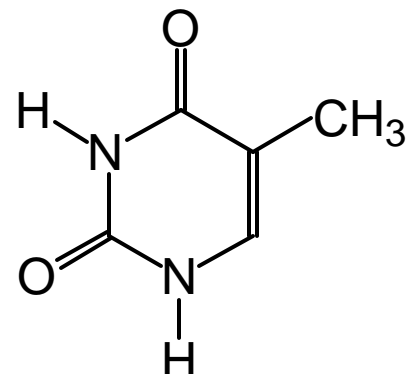
Guanine



Cytosine



Uracil



Thymine

Figure 2. Nucleosides

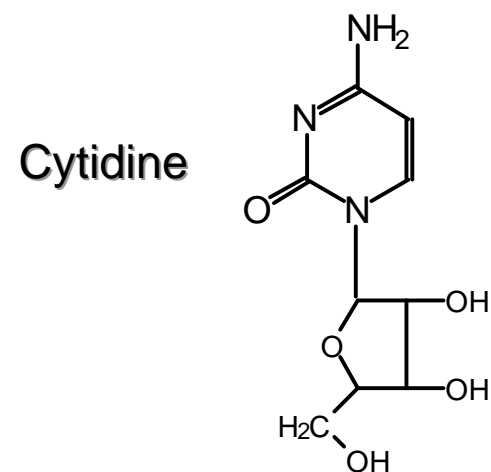
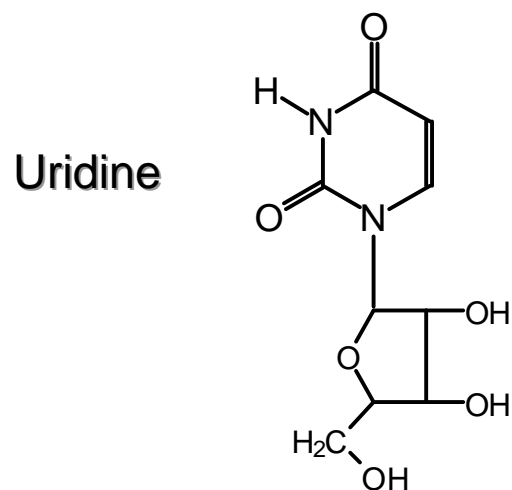
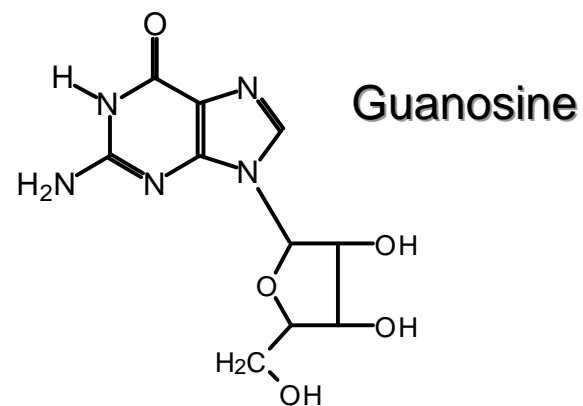
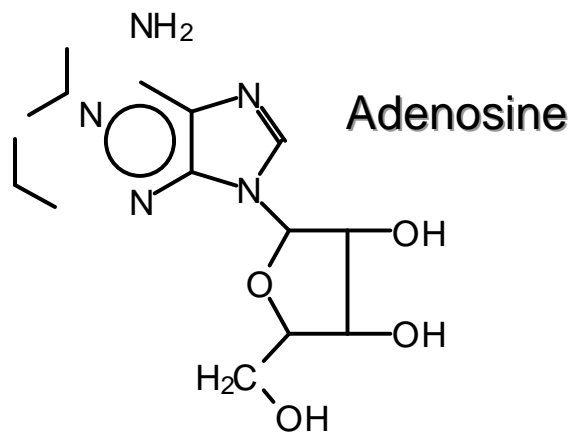
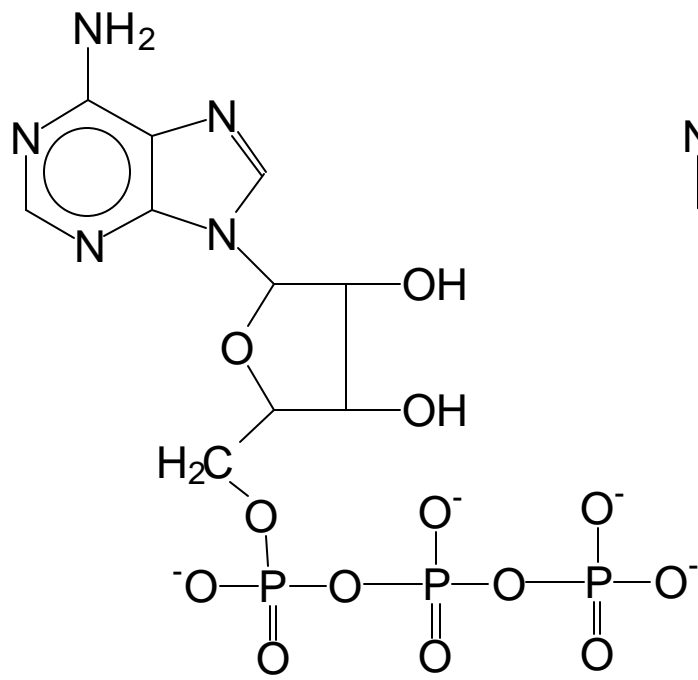
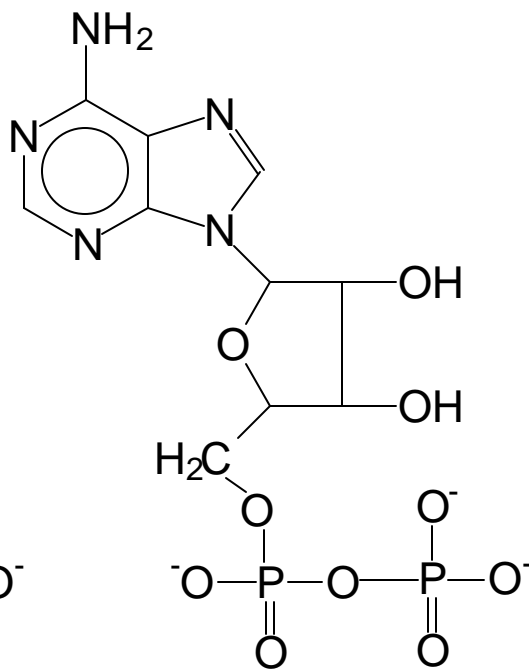


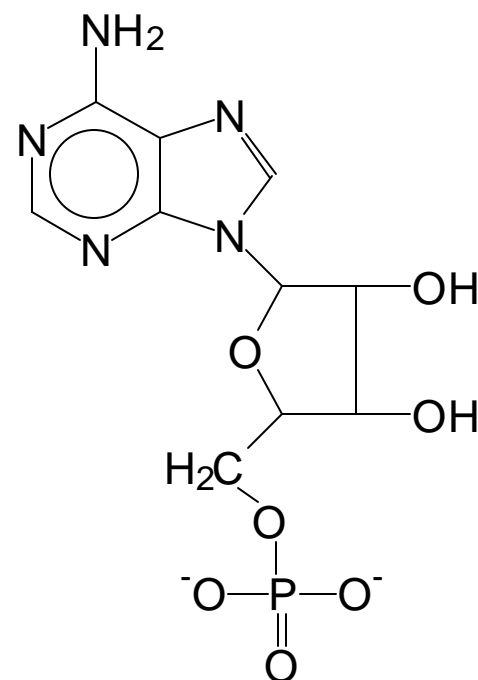
Figure 3. Nucleotides



5'-ATP



5'-ADP



5'-AMP



# Introduction (cont.)

The Ultra IBD (intrinsically base-deactivated) column is particularly effective for retaining and resolving complex mixtures of nucleotides, nucleosides, and purine and pyrimidine bases. The unique stationary phase of the Ultra IBD is composed of a polar group within, or intrinsic to, an alkyl chain. The polar group gives extra retention for many polar analytes as well as unique selectivity, a very high level of base deactivation, and compatibility with highly aqueous mobile phases. The Ultra IBD is ideal for LC/MS because it can often resolve acidic, basic, zwitterionic and/or neutral compounds in a single analysis using simple mobile phases.

# HPLC Conditions

- Column: Ultra IBD, 150x4.6mm, 5um (Restek Corporation)
- Instrument: HP 1100
- Mobile Phase: 97.5:2.5 (v/v) 20mM Ammonium acetate, pH 5.8: MeOH
- Flow Rate: 1.0 mL/min
- Detection: UV 260nm
- Temperature: 35°C
- Injection Volume: 20µl

# HPLC Conditions (cont.)

Samples: Mixtures of standards dissolved in 20mM Ammonium acetate, pH 5.8. Concentrations of individual components were approximately 80-360  $\mu\text{g/mL}$  for the five component mixtures and approximately 40-160  $\mu\text{g/mL}$  for the 11 component mixture.

All nucleotides had the phosphates linked to the C5 hydroxyl of ribose (ie. 5'-ATP).

# Results

Figures 4 through 8 each show a separation of one of the major purines or pyrimidines from its respective ribonucleoside and mono-, di-, and triphosphate nucleotide. Note that each of these separations was achieved using the same conditions and that in each case the order of elution is triphosphate, diphosphate, then monophosphate nucleotide, followed by the base, and lastly the nucleoside. There are slight “shoulders” on the peaks for GDP (Figure 5), TTP (Figure 7), and UMP (Figure 8). These were present in the GDP, TTP, and UMP standards, respectively and were presumed to be impurities or degradation products.

Figure 4. Adenine Family

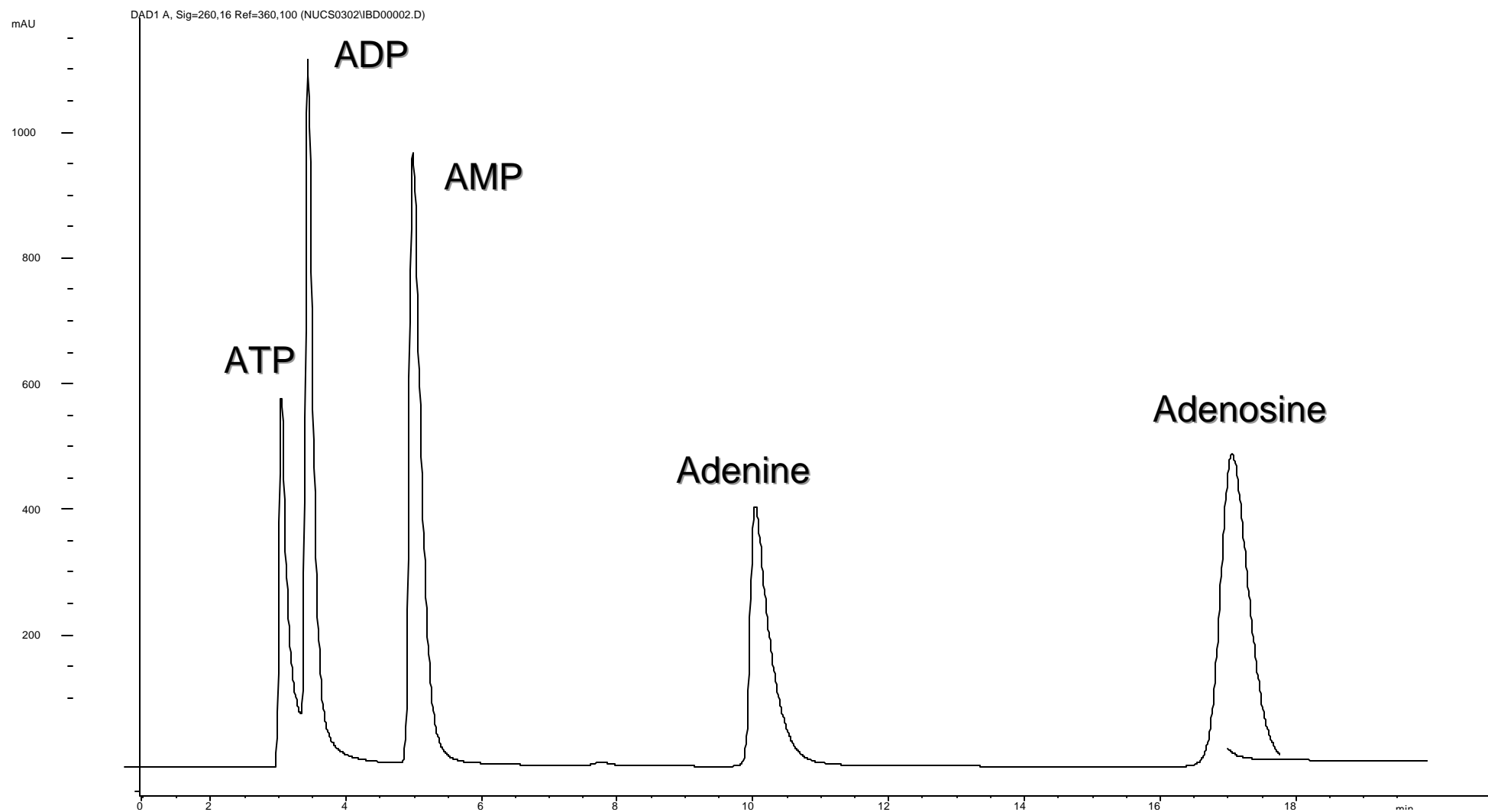


Figure 5. Guanine Family

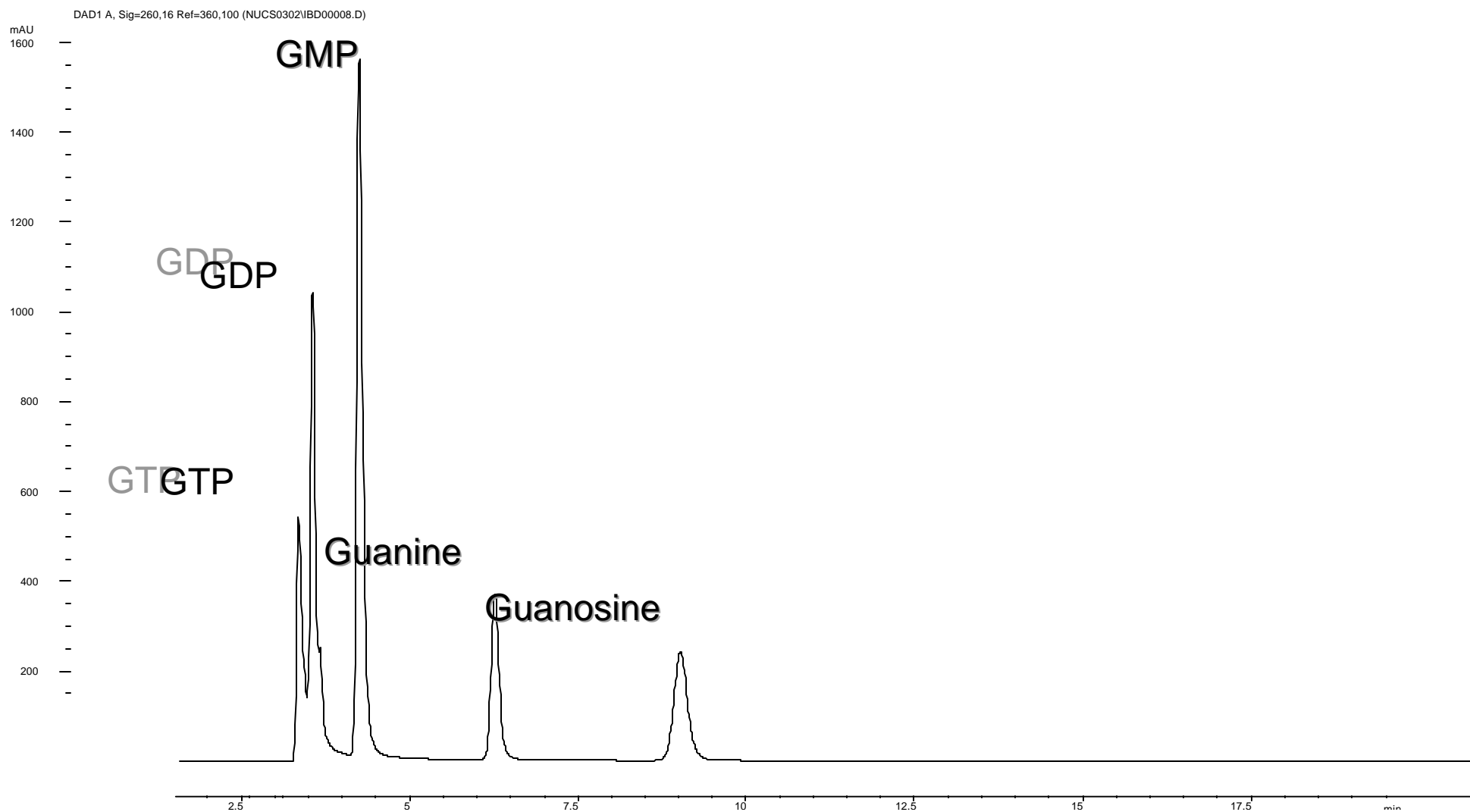


Figure 6. Cytosine Family

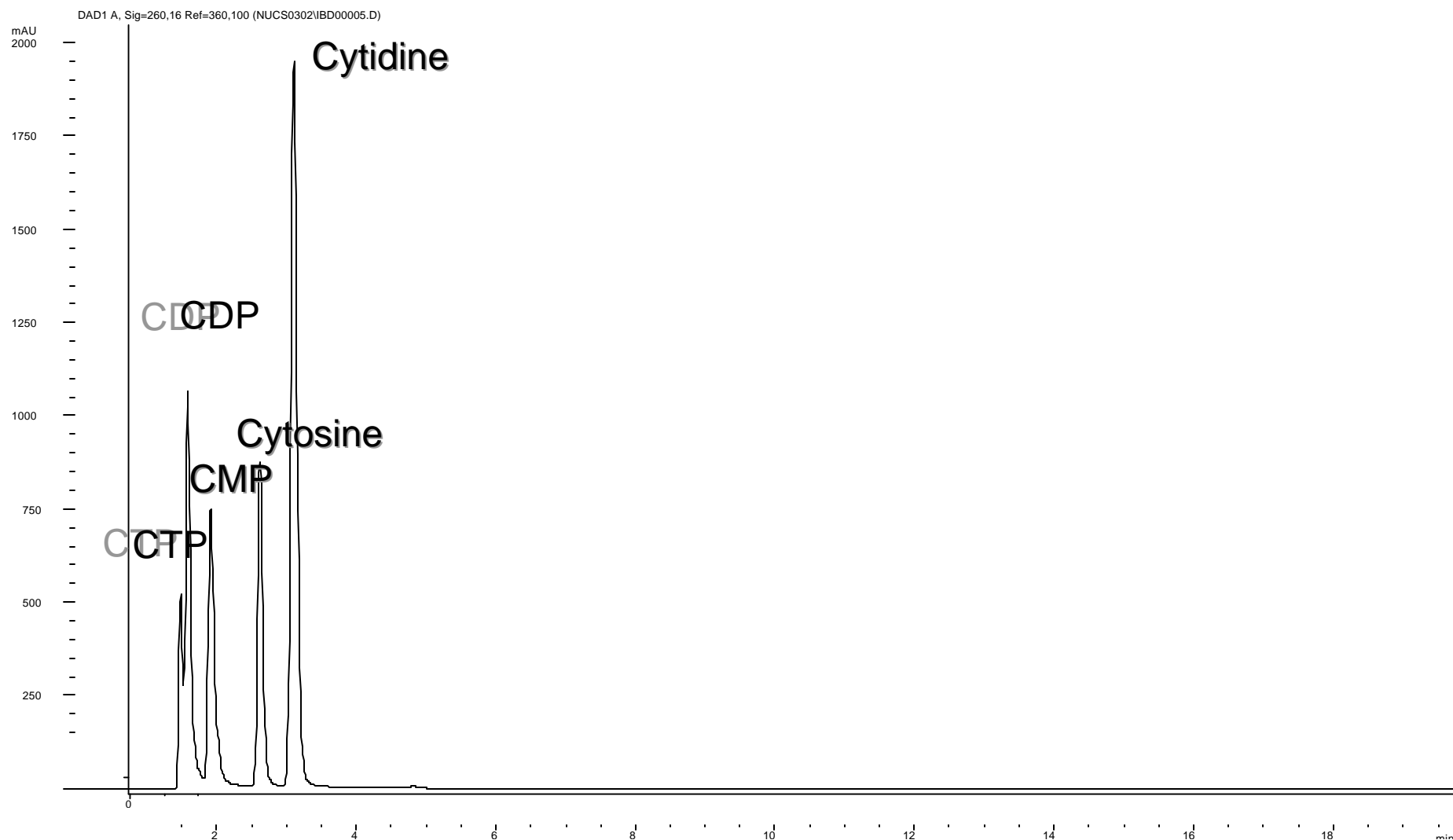
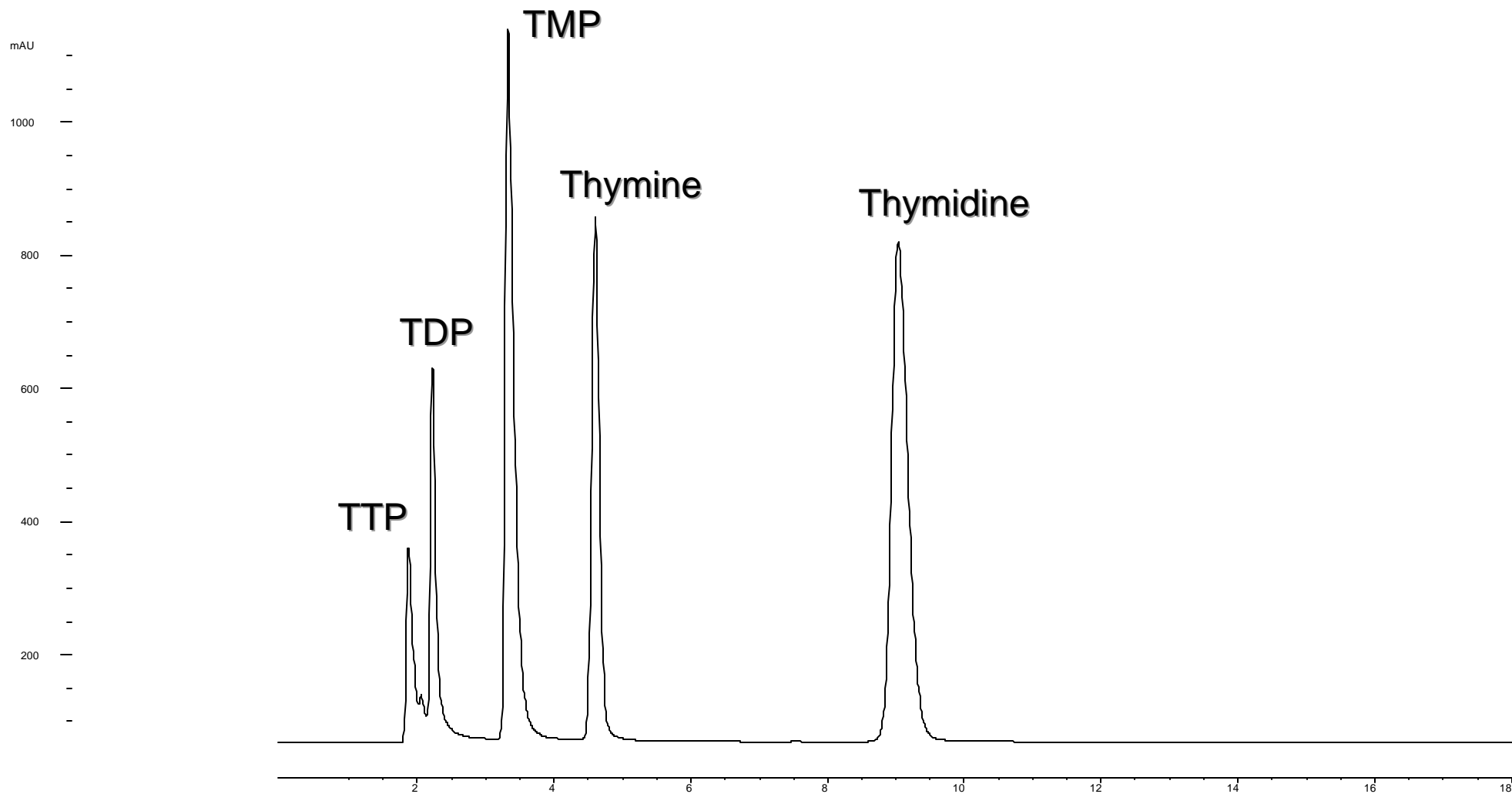


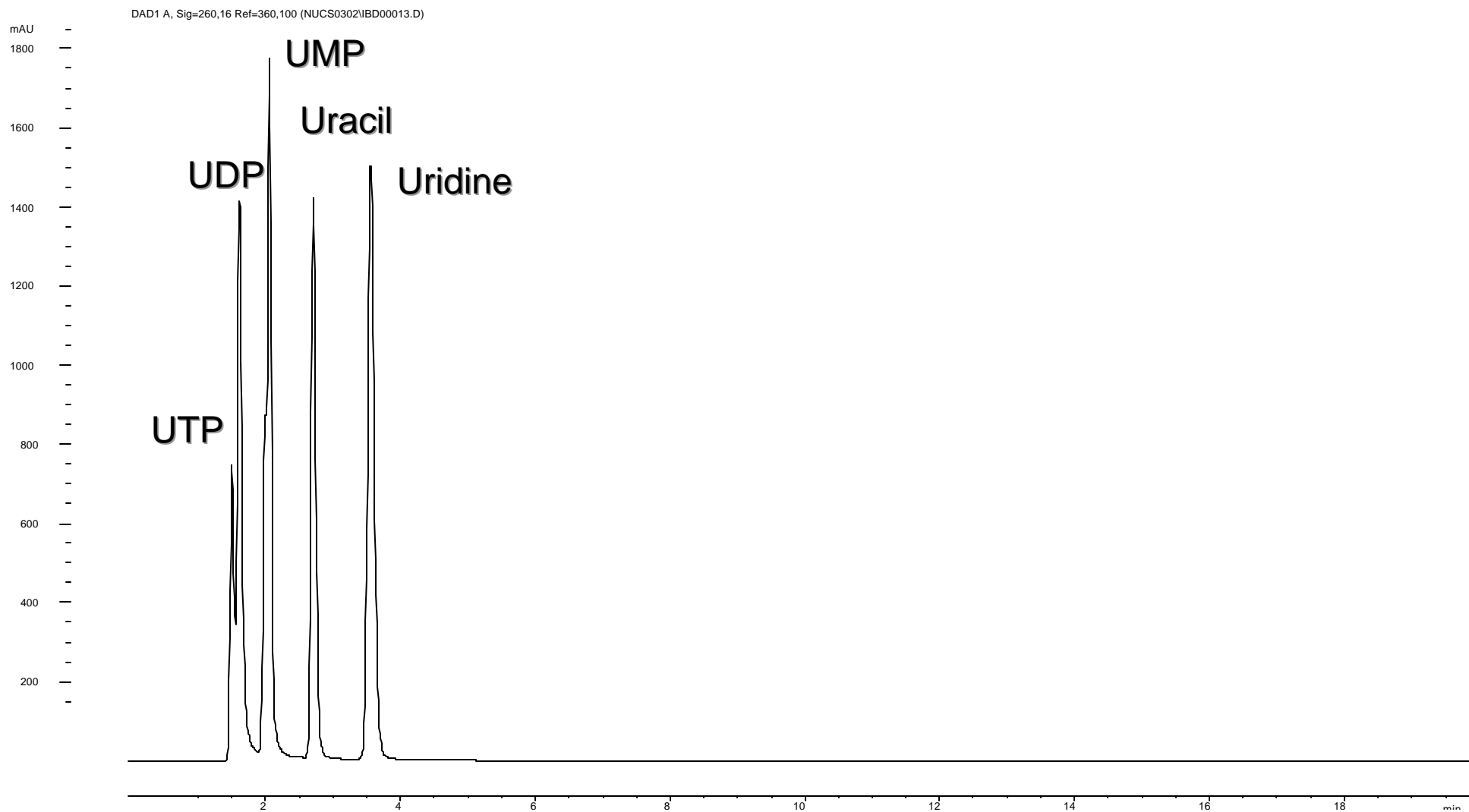
Figure 7. Thymine Family

DAD1 A, Sig=260,16 Ref=360,100 (NUCS0302\IBD00011.D)





# Figure 8. Uracil Family



## Results (cont.)

Table 1 lists the typical retention times obtained for all 25 of the compounds separated in Figures 4 – 8. While not all 25 compounds can be resolved in a single run, it would be possible to analyze all of these compounds using these chromatographic conditions with MS or MS/MS detection. Note that the mobile phase is compatible with MS detection, as all of its components are volatile. Figure 9 shows the resolution of a mixture of 11 various nucleotides, nucleosides, and bases.

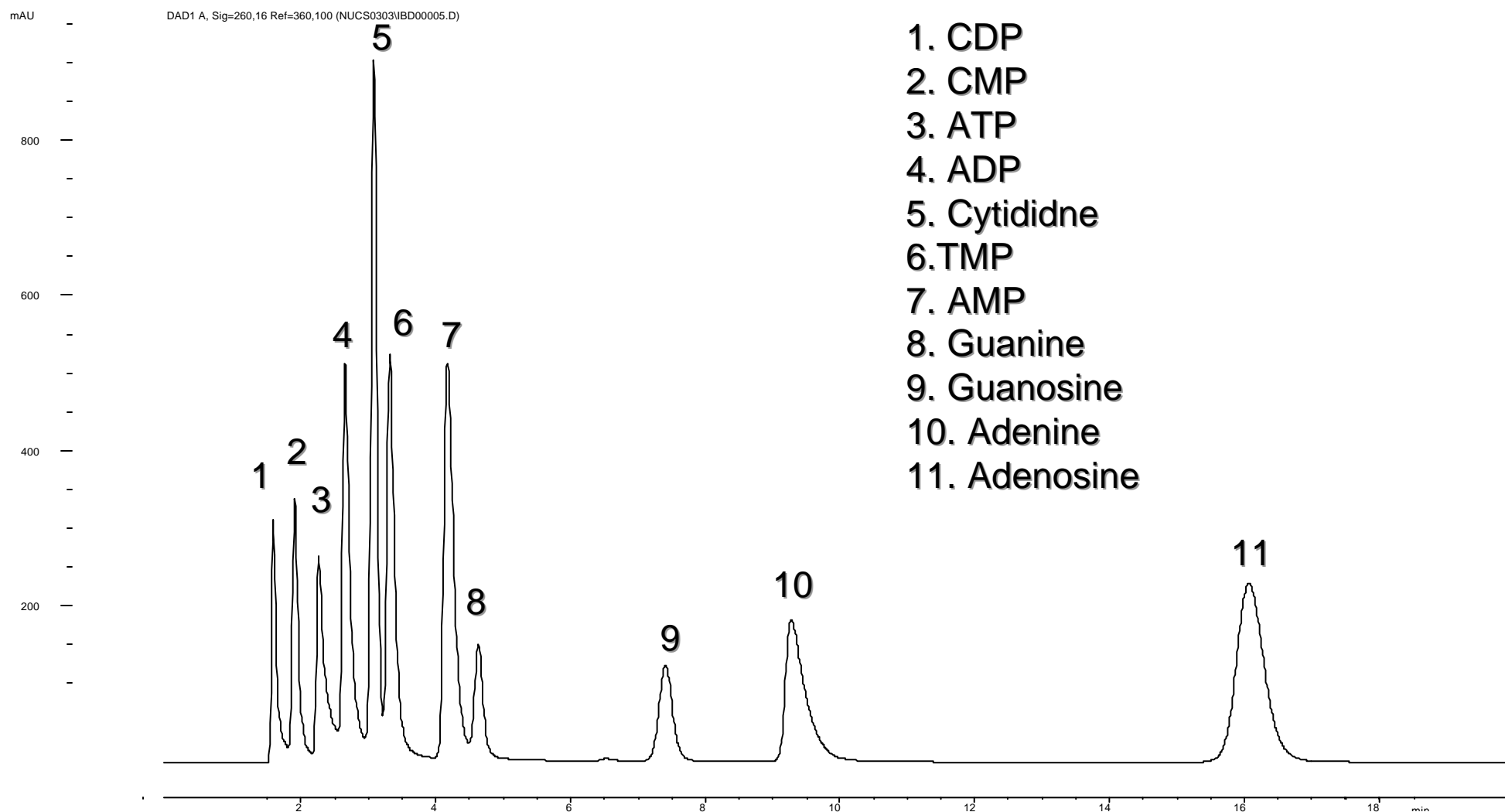
Table 1. Typical Retention Times For Common Nucleotides, Nucleosides, and Purine and Pyrimidine Bases.

<u>Compound</u>	<u>Ret.(min)</u>	<u>Compound</u>	<u>Ret.(min)</u>
CTP	1.5	TDP	2.2
UTP	1.5	ATP	2.3
CDP	1.6	GMP	2.6
UDP	1.6	Cytosine	2.6
GTP	1.7	ADP	2.7
TTP	1.8	Uracil	2.7
CMP	1.9	Cytidine	3.1
GDP	1.9	TMP	3.3
UMP	2.0	Uridine	3.6

Table 1. Typical Retention Times For Common Nucleotides, Nucleosides, and Purine and Pyrimidine Bases (Cont.).

<u>Compound</u>	<u>Ret.(min)</u>
AMP	4.2
Guanine	4.6
Thymine	4.6
Guanosine	7.4
Thymidine	9.0
Adenine	9.3
Adenosine	16.2

Figure 9. Eleven Component Mixture of Nucleotides, Nucleosides, and Related Bases



# Conclusions

The unique stationary phase of the Ultra IBD column can retain and resolve mixtures of nucleotides, nucleosides, and purine and pyrimidine bases by RP HPLC, using isocratic elution with a simple, volatile mobile phase. A single set of chromatographic conditions was identified which can resolve any of the common purine or pyrimidine bases from its respective ribonucleoside and mono-, di-, and triphosphate nucleotides. Future work will focus on MS detection.

# The Analysis of Marine Oil Based FAMEs by Capillary Gas Chromatography

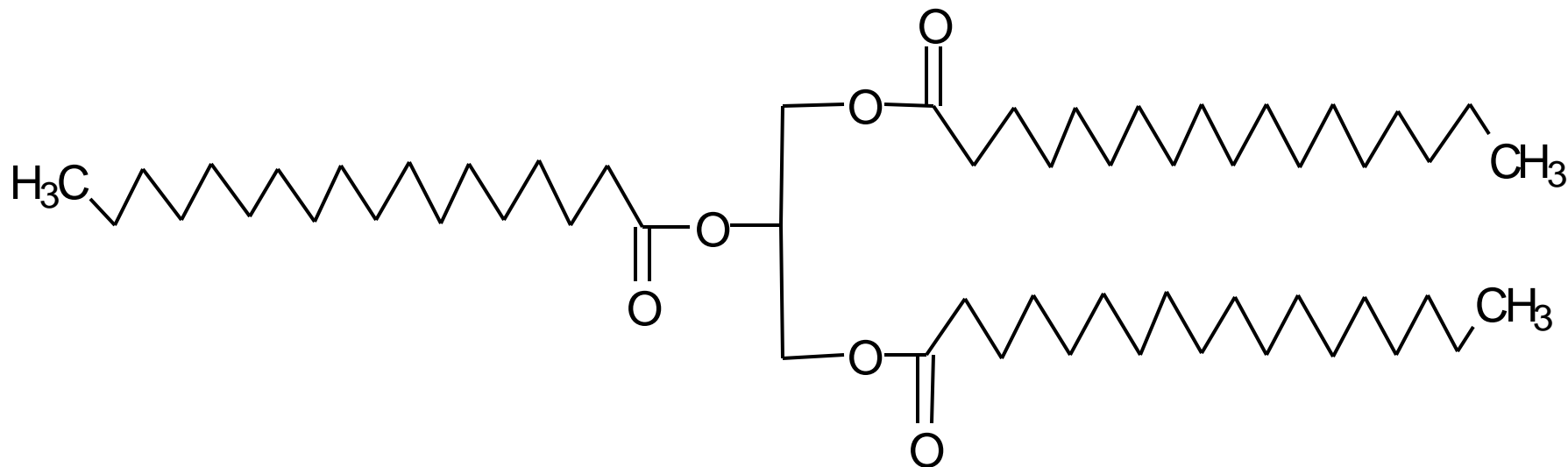
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Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA



# Food Lipids: Acylglycerols

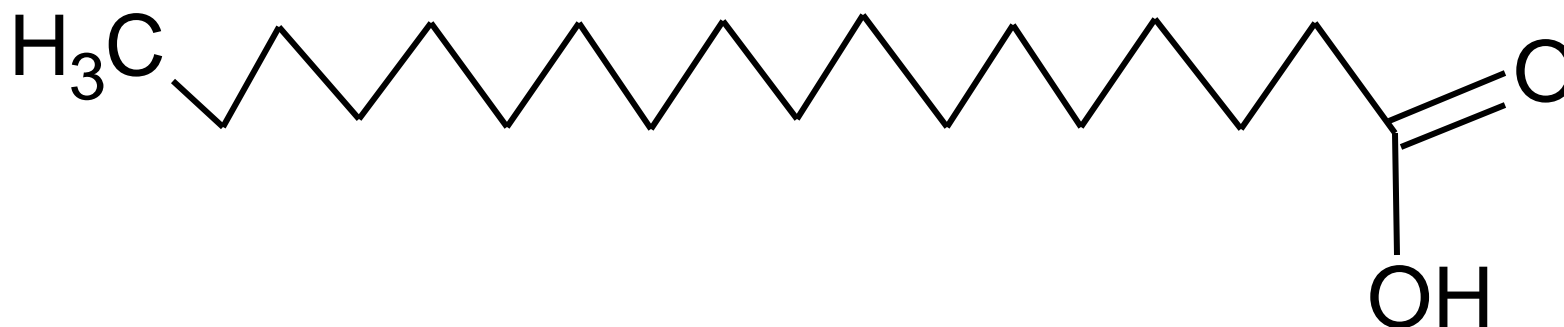


Tristearin or glycerol tristearate

Neutral fats: mono-, di-, or triesters of glycerol with fatty acids



# Food Lipids: Free Fatty Acids



Three fatty acids are contained in a triglyceride

- Saturated  $\approx$  no double bonds in the carbon chain
- Unsaturated  $\approx$  one or more double bonds in the chain
- *Cis* or *trans* possible around the double bond
- $\omega 3 \approx$  double bond is on 3<sup>rd</sup> carbon from the methyl end

# Typical Fatty Acid Compositions

Fatty Acid	Corn Oil	Soy Oil	Olive Oil	Peanut	Lard
<b>C14:0</b>			Trace	Trace	3
<b>C14:1</b>					Trace
<b>C16:0</b>	13	11	14	6	29
<b>C16:1</b>			2	Trace	3
<b>C18:0</b>	4	4	2	5	14
<b>C18:1</b>	29	25	64	61	38
<b>C18:2</b>	54	51	16	22	11
<b>C18:3</b>		9			Trace
<b>C20:0</b>	Trace	Trace	Trace	2	Trace
<b>C20:1</b>					Trace
<b>C20:2</b>					Trace
<b>C22:0</b>	Trace	Trace		3	

# Marine/Fish Oil Fatty Acids

Fatty Acid	Herring	Cod	Trout
C14:0	6.4	1.4	2.7
C16:0	12.7	19.6	20.9
C16:1	8.8	3.5	3.9
C18:0	0.9	3.8	8.3
C18:1	12.7	13.8	18.4
C18:2 <sub>w</sub> 6	1.1	0.7	7.3
C18:3 <sub>w</sub> 3	0.6	0.1	1.6
C18:4 <sub>w</sub> 3	1.7	0.4	3.2
C20:1	14.1	3.0	ND
C20:4 <sub>w</sub> 6	0.3	2.5	1.7
C20:5 <sub>w</sub> 3	8.4	17.0	5.8
C22:1	20.8	1.0	ND
C22:5 <sub>w</sub> 3	0.8	1.3	Trace
C22:6 <sub>w</sub> 3	4.9	29.8	7.0

From: deMan, Principles of Food Chemistry

# Nutraceuticals & Functional Foods

- Naturally derived, biologically active compounds
- Health benefit
- Consumed in various forms
  - ◆ Dietary supplement
  - ◆ Functional food or ingredient
- Regulation is still unclear

# Nutraceutical Products

## Marine/Fish Oils

- Rich in Polyunsaturated Fats
  - ◆  $\omega$ -3 fatty acids: potential health benefit
  - ◆ PUFAs can oxidize more readily
- Consumed as Fish or in Capsule Form
  - ◆ Enrichment of PUFAs possible in capsules
- Fatty Acid Composition Monitored by GC
  - ◆ Levels of DHA, EPA
- Lipid Class Separations by LC

# Marine Oil FAME Analysis

## Preparation of the FAMEs

- Standard Methods
  - ◆ AOCS Ce 1b-89
  - ◆ European Pharmacopeia 2001:1352
- Saponification with NaOH or KOH
- Methylation
  - ◆  $\text{BF}_3/\text{MeOH}$  or  $\text{BCl}_3/\text{MeOH}$
- Extraction
  - ◆ Add saturated salt solution
  - ◆ Extract into isooctane

# Marine Oil FAME Analysis

## Standard GC Conditions

- Analytical Column
  - ◆ FAMEWAX™, 30m x 0.32mm x 0.25µm
- Oven Program
  - ◆ 100°C to 210°C at 8°C/min, 30 min hold
- Flow Rate
  - ◆ Hydrogen @ 1 mL/min
- Injector
  - ◆ 250°C, 100:1 split
- FID @ 250°C (or MSD)

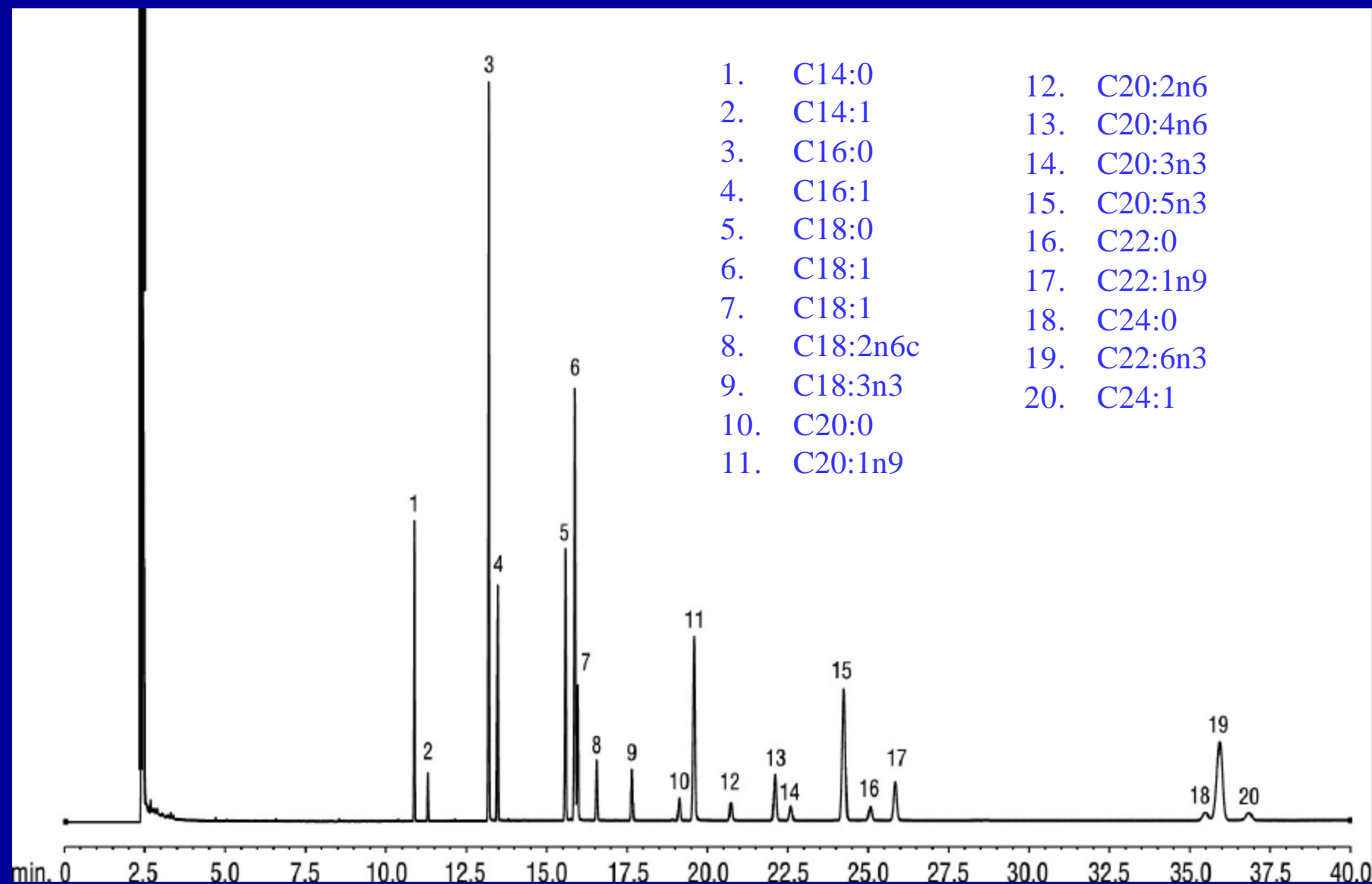
# Marine Oil FAMEs - Standard

**HRomalytic**  
Australian Distributors  
Importers & Manufacturers  
www.chromtech.net.au

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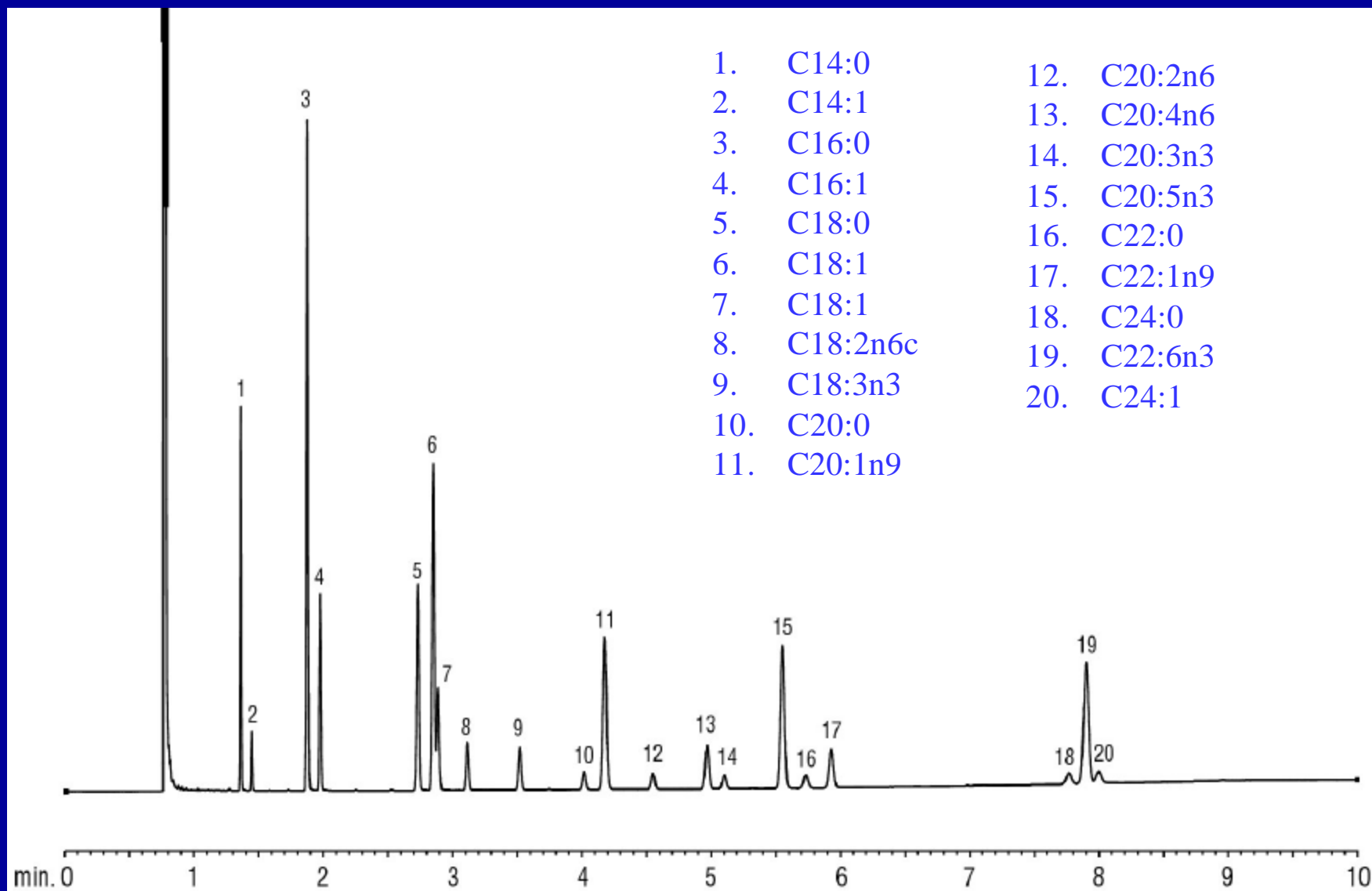
**ECHnology** Pty Ltd

Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034 . . . in AUSTRALIA





# Marine Oil FAMEs - Standard



# Marine Oil FAME Analysis

## Fast vs. Slow GC Programs

### ■ Oven Program

SLOW: 100°C to 210°C at 8°C/min, 30 min hold

FAST: 195°C to 240°C at 5°C/min, 1 min hold

### ■ Flow Rate

SLOW: Hydrogen @ 1 mL/min

FAST: Hydrogen @ 3 mL/min

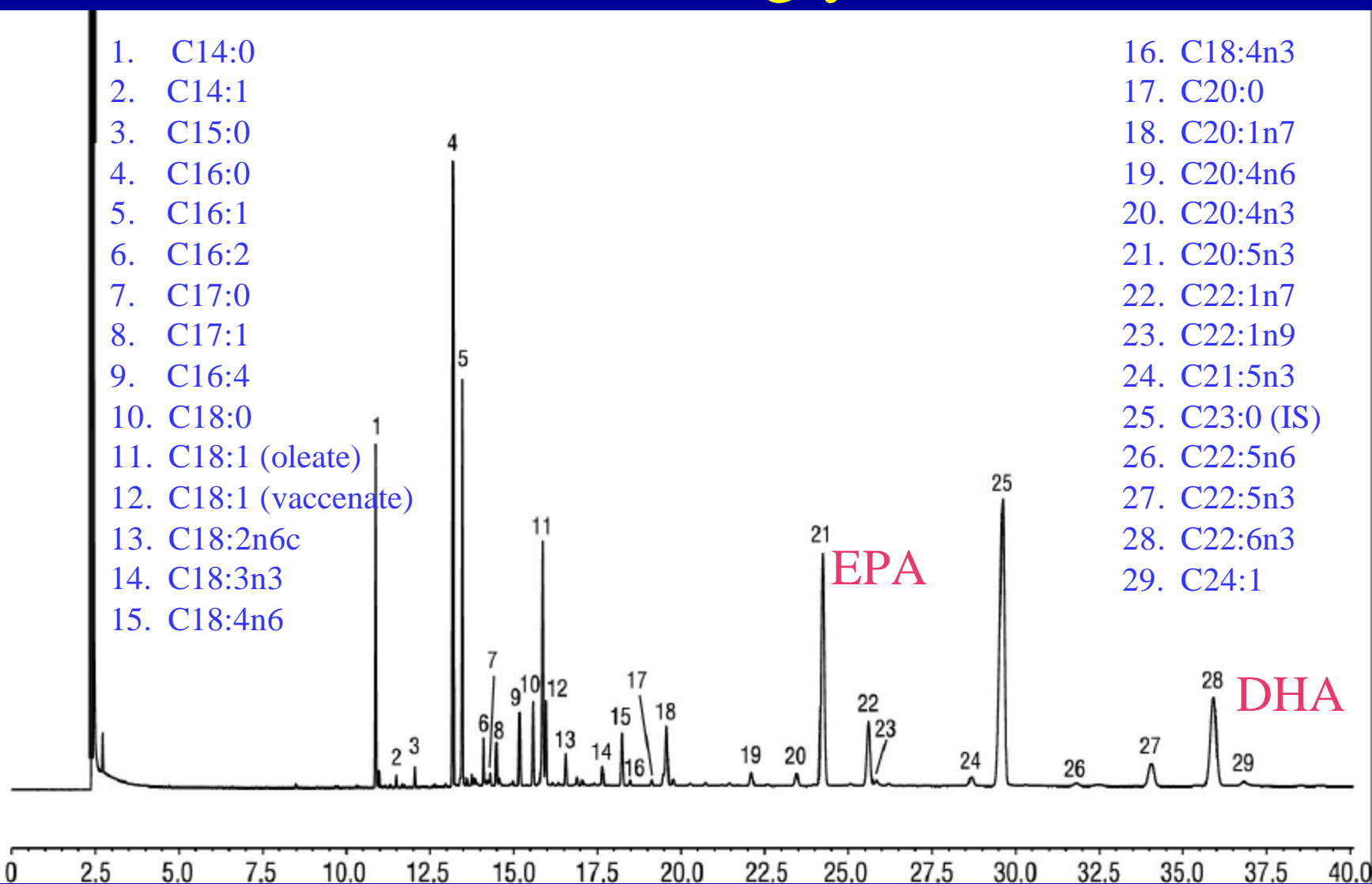
### ■ Injector

SLOW: 100:1 split

FAST: 300:1 split

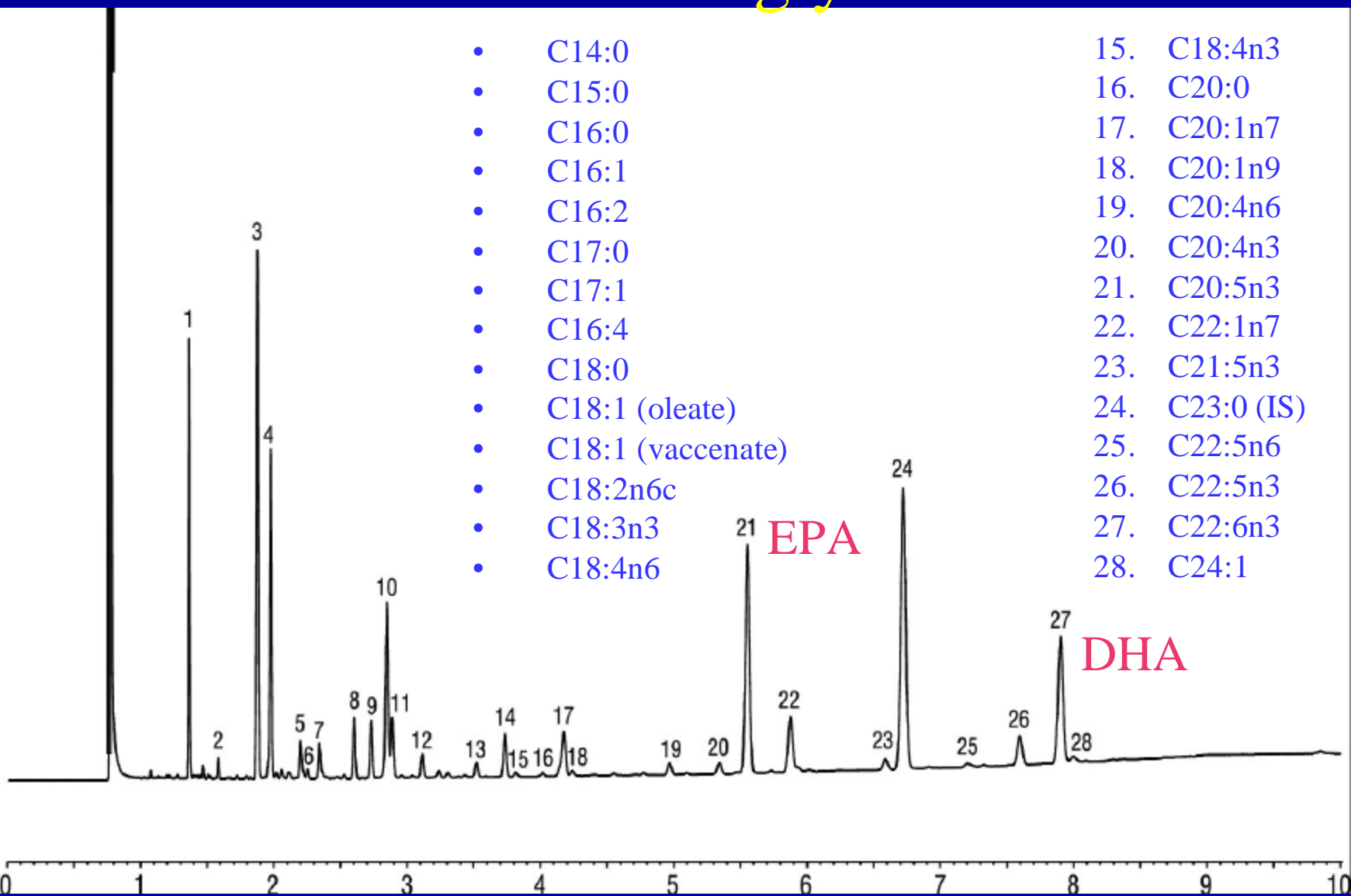
# Marine Oil FAMES – Slow Program

## 18% EPA/12% DHA Triglycerides



# Marine Oil FAMES – Fast Program

## 18% EPA/12% DHA Triglycerides



# Validation Study

## 18/12 Triglyceride Capsule

<b>SLOW GC PROGRAM</b>		<b>FAST GC PROGRAM</b>			
<b>mg of EPA</b>	<b>mg of DHA</b>	<b>mg of EPA</b>	<b>mg of DHA</b>	<b>% Difference</b>	
				<b>EPA</b>	<b>DHA</b>
191.87	128.93	192.38	129.66	0.26	0.57
190.97	127.81	191.54	128.45	0.30	0.51
190.64	128.16	192.65	129.24	1.06	0.84
190.44	128.46	192.07	128.66	0.86	0.16
191.36	128.49	191.45	129.37	0.05	0.68
190.52	128.81	192.61	129.92	1.10	0.86
172.40	110.22	172.26	108.98	0.08	1.12
			<b>AVERAGE--&gt;</b>	<b>0.53</b>	<b>0.68</b>

*Data courtesy of Dave Waddell, Ocean Nutrition Canada*

# Summary of Validation Study:

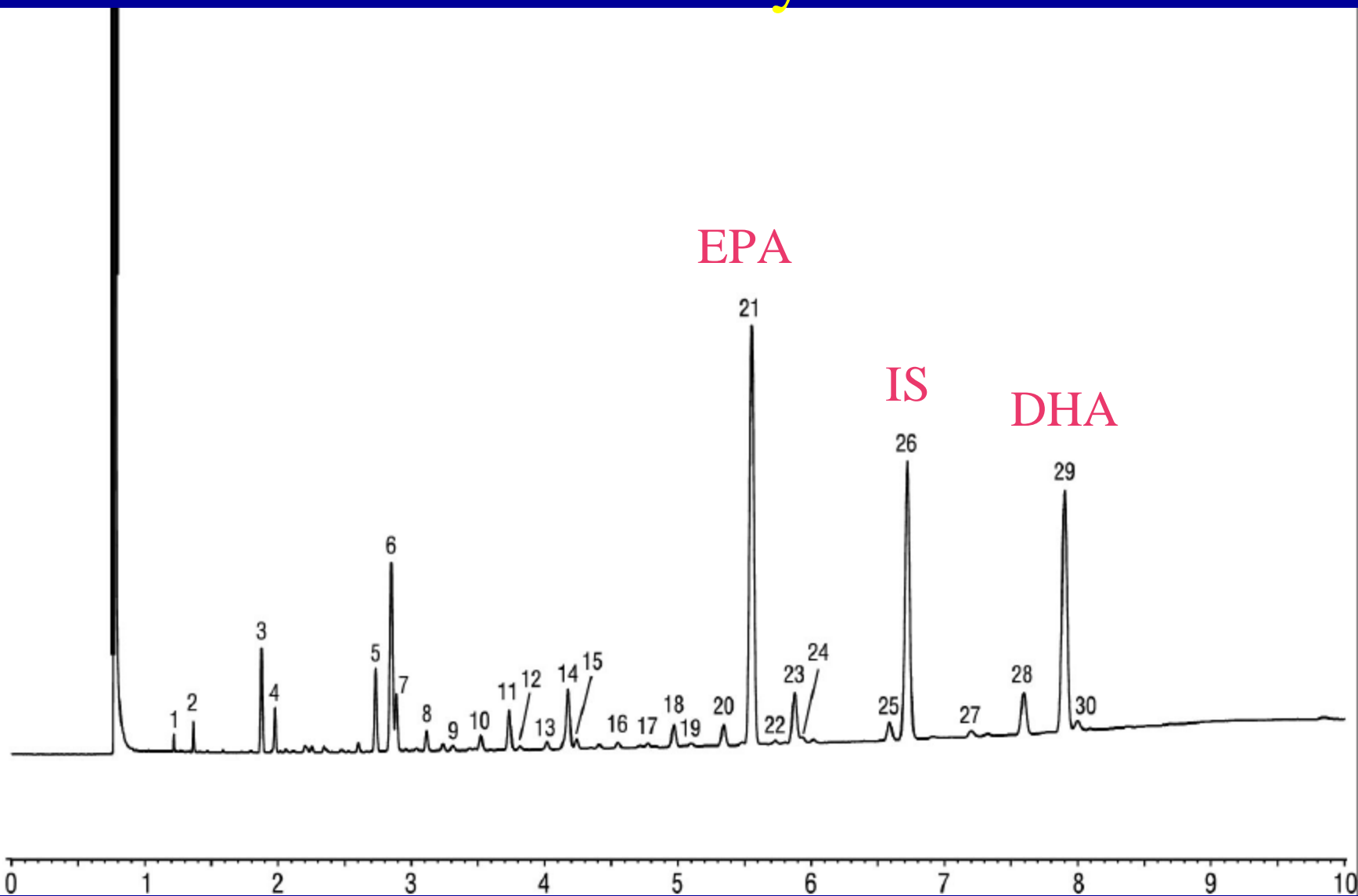
## Slow vs. Fast GC Programs

Product	% Difference EPA	% Difference DHA
18 EPA/12 DHA Triglyceride	0.53	0.68
30 EPA/12 DHA Ethyl Ester	0.56	0.61
40 EPA/20 DHA Triglyceride	0.53	0.52
High EPA Triglyceride	0.20	0.38

*Data courtesy of Dave Waddell, Ocean Nutrition Canada*

# Marine Oil FAMEs – Sample

## 30% EPA/20% DHA Ethyl Esters



# Summary of Marine Oil FAME Analysis

- Preparation of the Methyl Esters
  - ◆ AOCS vs. European Pharmacopeia
- Column Selection
  - ◆ PEG vs. high cyano phases
  - ◆ Column configuration
- GC Program Optimization
  - ◆ Oven program and linear velocity
  - ◆ 40+ minute run to under 10 minutes!
  - ◆ Excellent agreement between methods



# Advantages of Using Highly Retentive Phases in LC/MS Development

Keith J. Duff, David S. Bell,  
C. Vernon Bartlett  
Restek Corp., Bellefonte, PA  
Shane R. Needham  
Pfizer Inc, Groton, CT

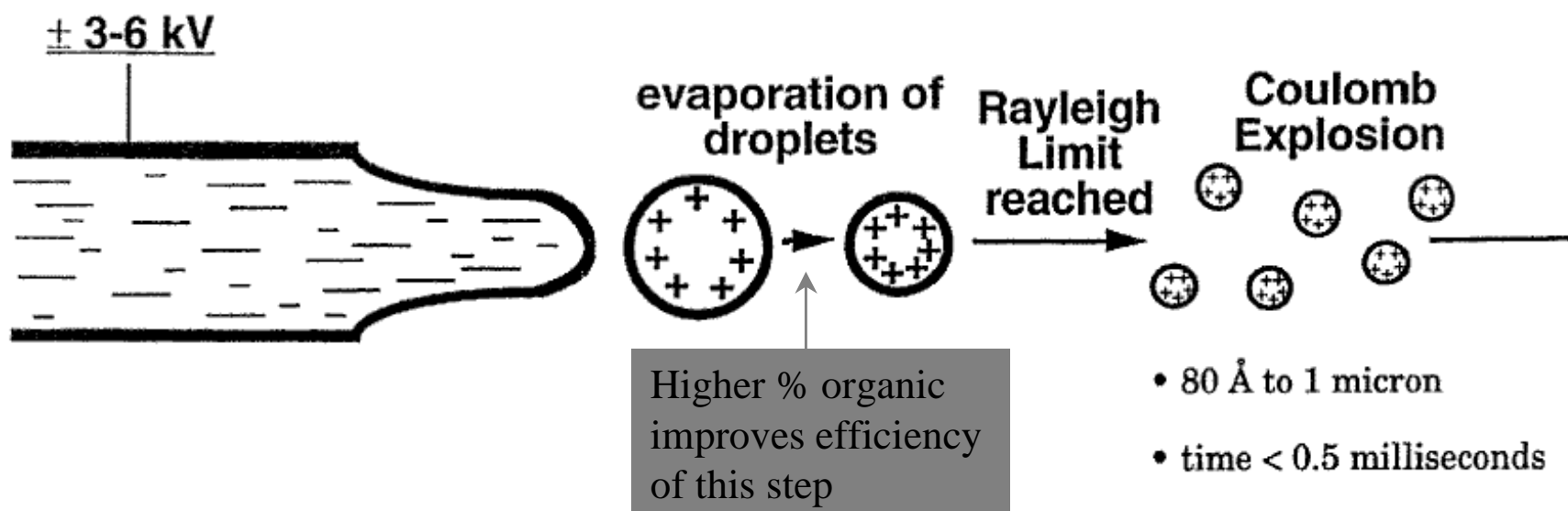
# Introduction

- Electrospray ionization (ESI) requires evaporation of the mobile phase (M.P.) leaving the analyte ions in the gas phase.
- The higher the organic content in the M.P., the more efficient the evaporation process.
- This added efficiency translates into greater signal in the mass spectrometer.

# State-of-the-Art LC/MS Columns

- New LC/MS packings have been developed that can be used with very high organic content in the M.P.
- This can results in an order of magnitude improvement in LC/MS sensitivity.
- Also provides fast LC/MS analyses.

New phases enable the use of more % organic in the mobile phase. This, in turn, allows for more efficient ESI desolvation/ionization, which yields higher LC/MS sensitivity.



Five novel phases were developed for optimum LC/MS performance and sensitivity:

*ANALYTE TYPE*

Neutral

Acidic/Amino Acids

Basic (1<sup>st</sup> Generation)  
(2<sup>nd</sup> Generation)

Combination - all types

*NEW PHASE*

Allure<sup>R</sup> C18

Allure<sup>R</sup> Acidix

Allure<sup>R</sup> Basix

Allure<sup>R</sup> PFPP

Ultra IBD

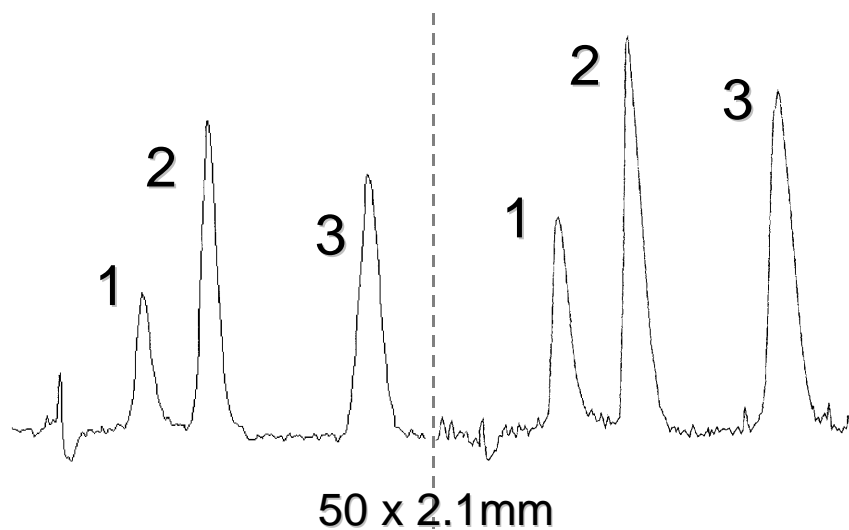
# Allure™ C18 VS. Conventional C18 Phase - Neutral Steroids

Conventional C18  
12%C

H<sub>2</sub>O:MeOH (40:60)

Allure™ C18  
27%C

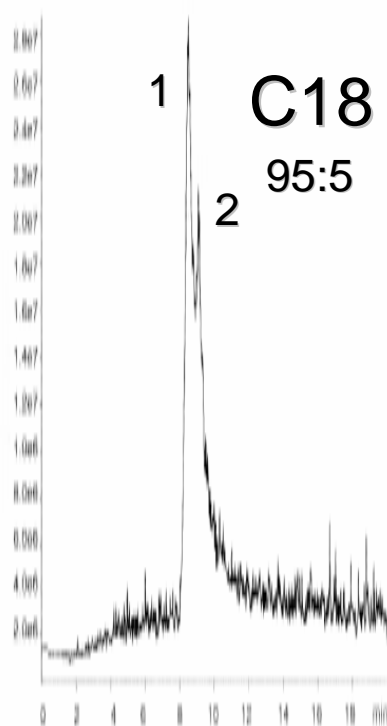
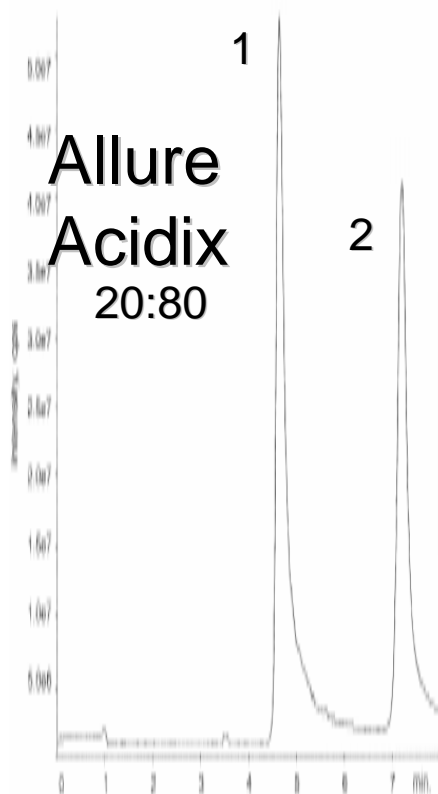
H<sub>2</sub>O:MeOH (33:67)



Data courtesy of Shane Needham, Pfizer Inc

- Higher C load allows use of 12% more organic; Results in a 26% increase in LC/MS sensitivity
- 1. Deoxycorticosterone (DCC) Acetate, 2. DCC Glucoside, 3. DCC; 0.4mL/min; Pos. ion ESI-TOF

# Allure™ Acidix - New Acidic Analyte Packing



1. Salicylic Acid, 2. Aspirin

Polar stationary phase:

- Allows increased % organic in M.P.
- Increases signal:noise
- Improves selectivity/resolution
- Improves peak shape
- 150 x 4.6mm; 20mM  $\text{NH}_4\text{HCO}_2$ , pH 4.5:ACN (v/v); 1mL/min; Neg. ion ESI



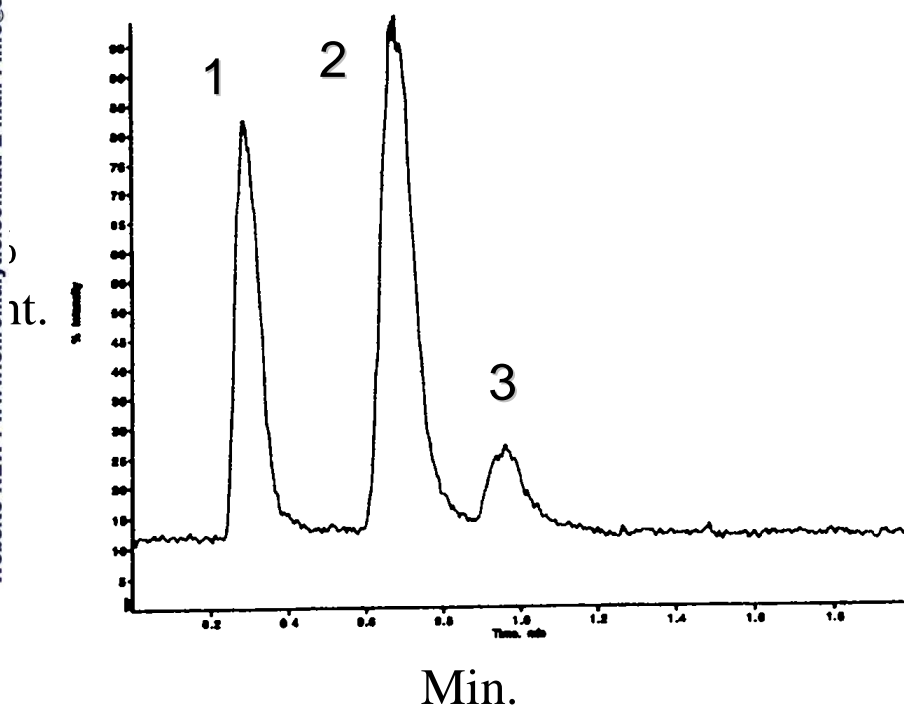
# Allure™ Acidix - Underivatized Amino Acid Separation

Column: Allure Acidix

Sample: 1. homocysteine thiolactone, 2. homocysteine, 3. homocystine

Mobile Phase: water, pH 3 (HCOOH):  
ACN (40:60 v/v).

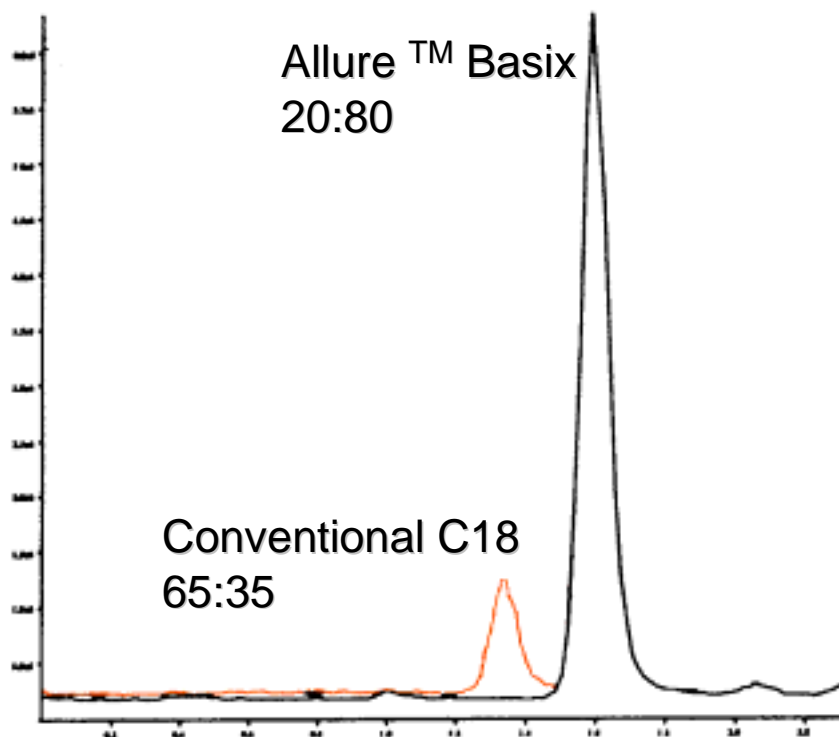
- Excellent peak shape under mild M.P. conditions.
- No derivatization necessary.
- Enables monitoring reaction pathways with minimal experimental interferences.





# Allure™ Basix - 1st Generation Basic Analyte Packing

## Amitriptyline



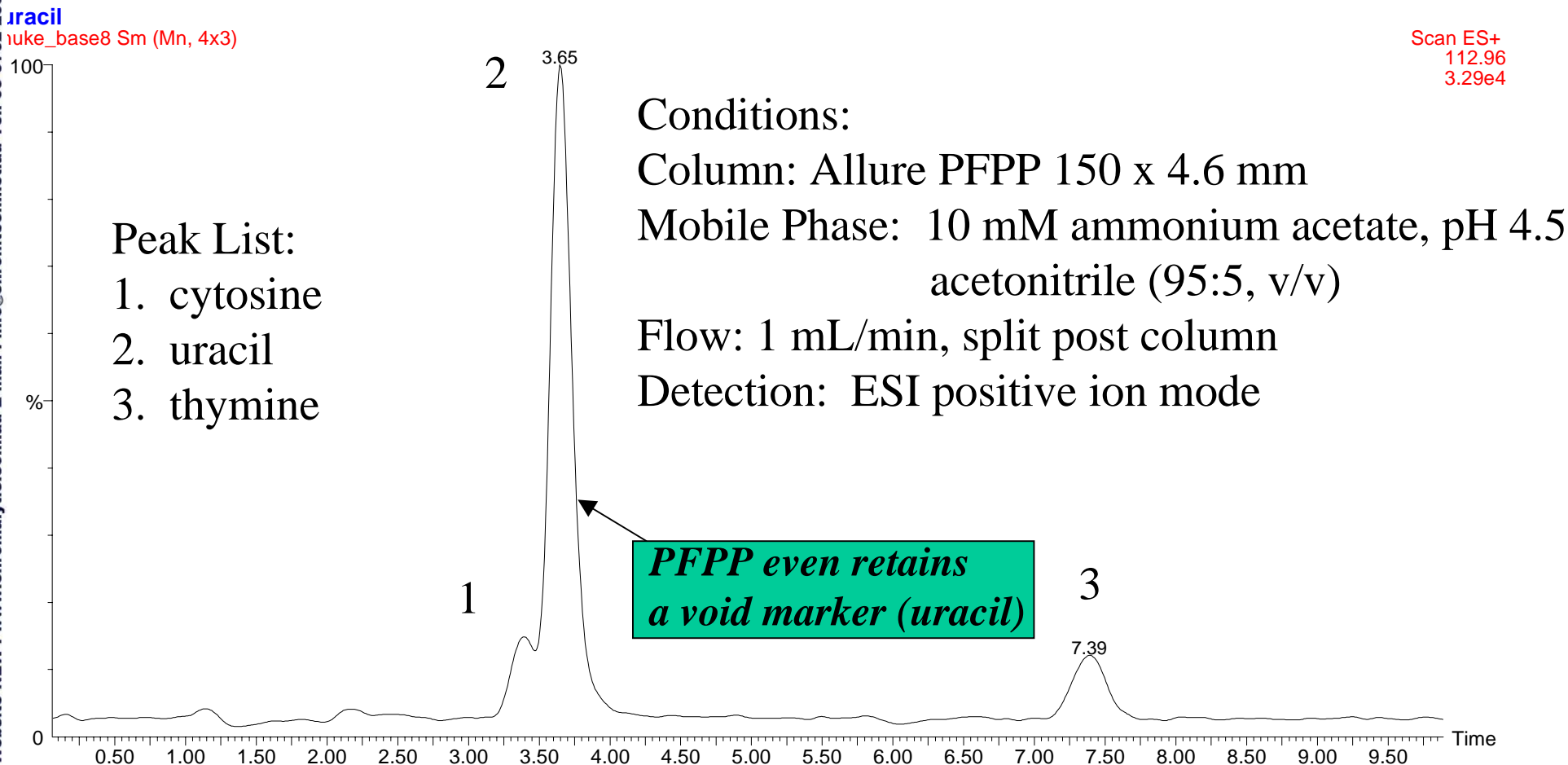
- Designed to use for basic compounds.
- Adjusted % organic (in 5mM Am. Acet., pH=4.5 M.P.) from 35% (conven. C18) to 80% (Basix) for same  $k'$ .
- Signal-to-noise increase: 243%

# Allure™ PFPP - 2nd Generation

## Basic Analyte Packing

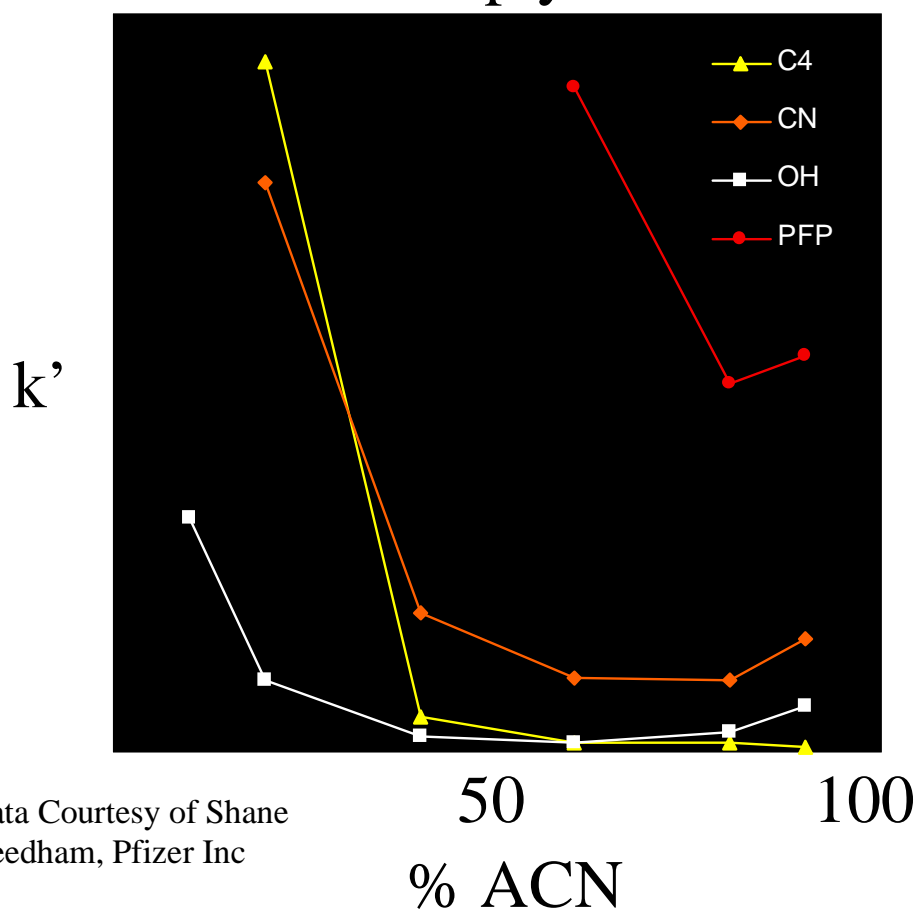
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# Allure™ PFPP - Uses Highest % Organic for Basic Analytes

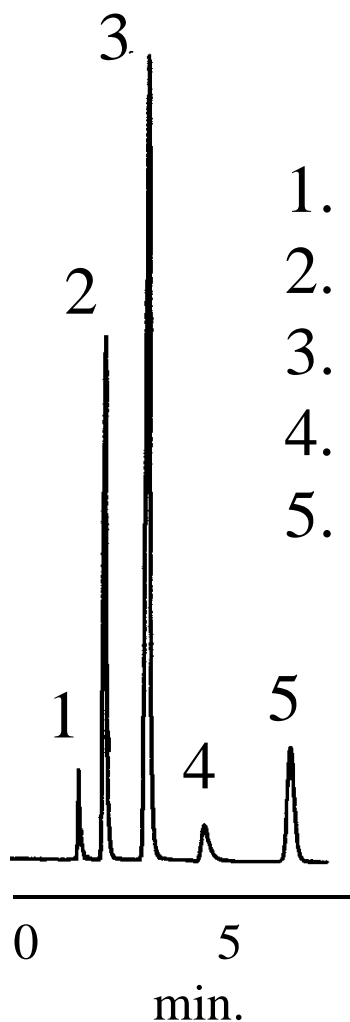
## Amitriptyline



- PFPP allows the use of much more organic in M.P. to give the same amount of retention of conventional phases.
- This allows increased sensitivity in LC/MS, LC/IR, and LC/ELSD of 600% or more.
- 5mM  $\text{NH}_4\text{OAc}$ , pH 4.5:ACN; 30 x 2.1mm; 0.4mL/min

Data Courtesy of Shane  
Needham, Pfizer Inc

# Ultra IBD - Separates Acid/Basic Mixtures



1. Lidocaine
2. Chlorpheniramine
3. Doxepin
4. Maleic Acid
5. Benzoic Acid

- Good peak shape for both acids and bases.
- Unique selectivity compared to C18 phases.
- M.P.: 65:35 - 50mM KH<sub>2</sub>PO<sub>4</sub>, pH 3:ACN  
Flow: 1mL/min
- Detection: 254nm

# Conclusion

- New LC/MS packings have been developed that enable the use of higher % organic content in the mobile phase.
- These packings typically provide up to an order of magnitude increase in sensitivity.
- The proper column choice is easily made, *a priori*, based on the pK<sub>a</sub> of the analyte.

# A Low Bleed, High Temperature Polydimethylsiloxane Liquid Phase for Simulated Distillation



# Introduction

- ASTM Method D 6352-98 is used for the determination of the boiling range distribution of petroleum distillate fractions.
- The method specifies the use of a short, wide bore, thin film capillary column.
- The upper temperature of the analysis is set at 400°C.

# Column Design

- Method criteria: 5 m x 0.53mm ID x 0.10um
- Stainless steel tubing
- Treated with Sulfinert process
- A high temperature, non-polar stationary phase was developed that was able to withstand 430°C while producing minimal bleed.
- Matching the McReynolds requirements of the method.



# Experimental Design

- A lifetime study was performed by repetitively injecting a standard mixture designed for ASTM D2887 calibration.
- A Polywax 1000 sample was injected and resolution between C50 and C52 was calculated according to the method.
- Record kept of the retention time for C52 and the bleed at 430°C over the course of the experiment.
- Repeated until the column resolution fell below ASTM D6352-98 specifications.

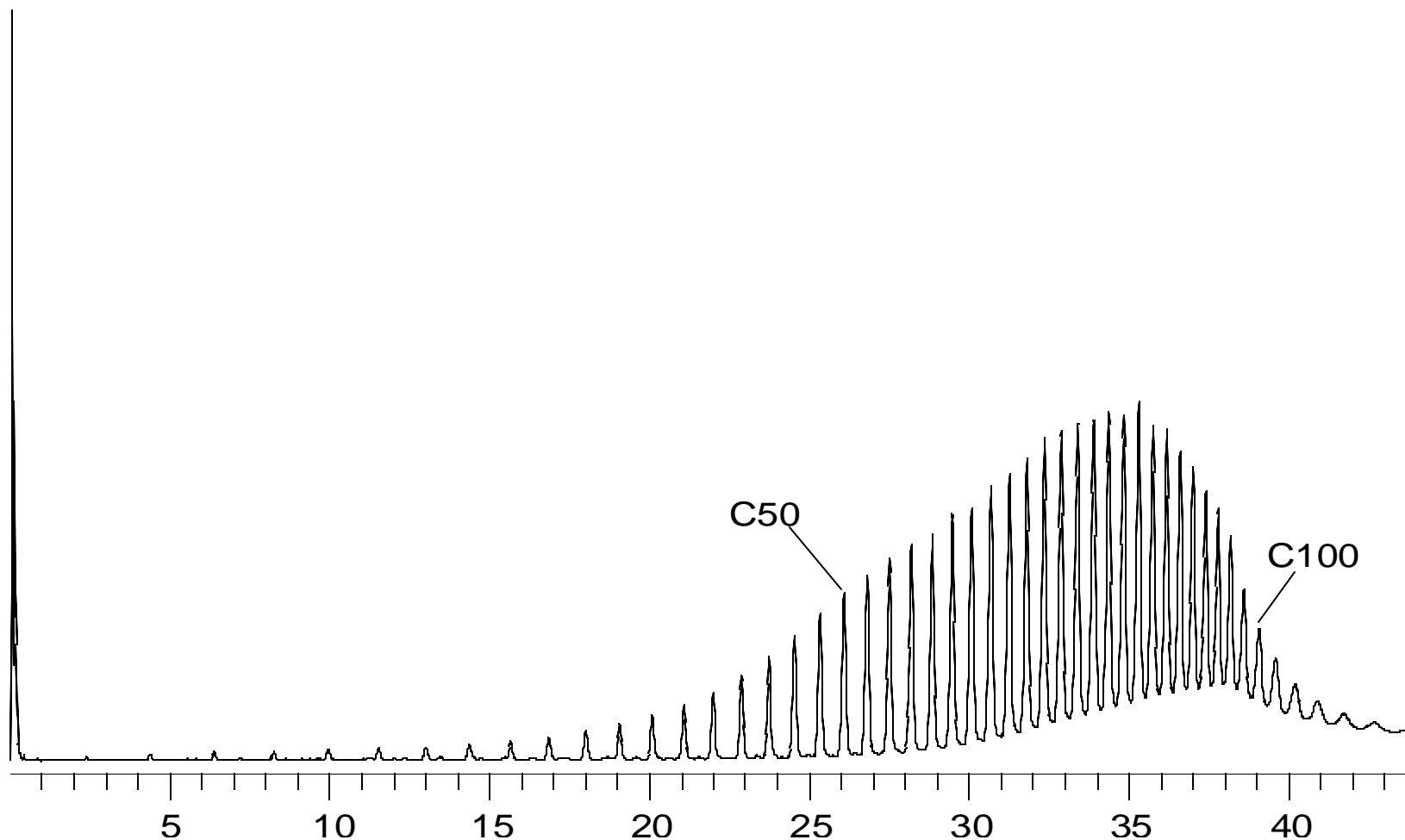
# GC Conditions

- D2887 sample
  - 40°C to 430°C at 70°C/minute
  - Hold at 430°C for 10 minutes
- Polywax 1000 sample
  - 50°C to 430°C at 10°C/ minute
  - Hold at 430°C for 6 minutes
- Carrier Gas – Helium, 1.8psi (14ml/min)
- Sample – 0.2uL, 2% sample in Carbon Disulfide
- Cold On Column Injection with Oven Tracking

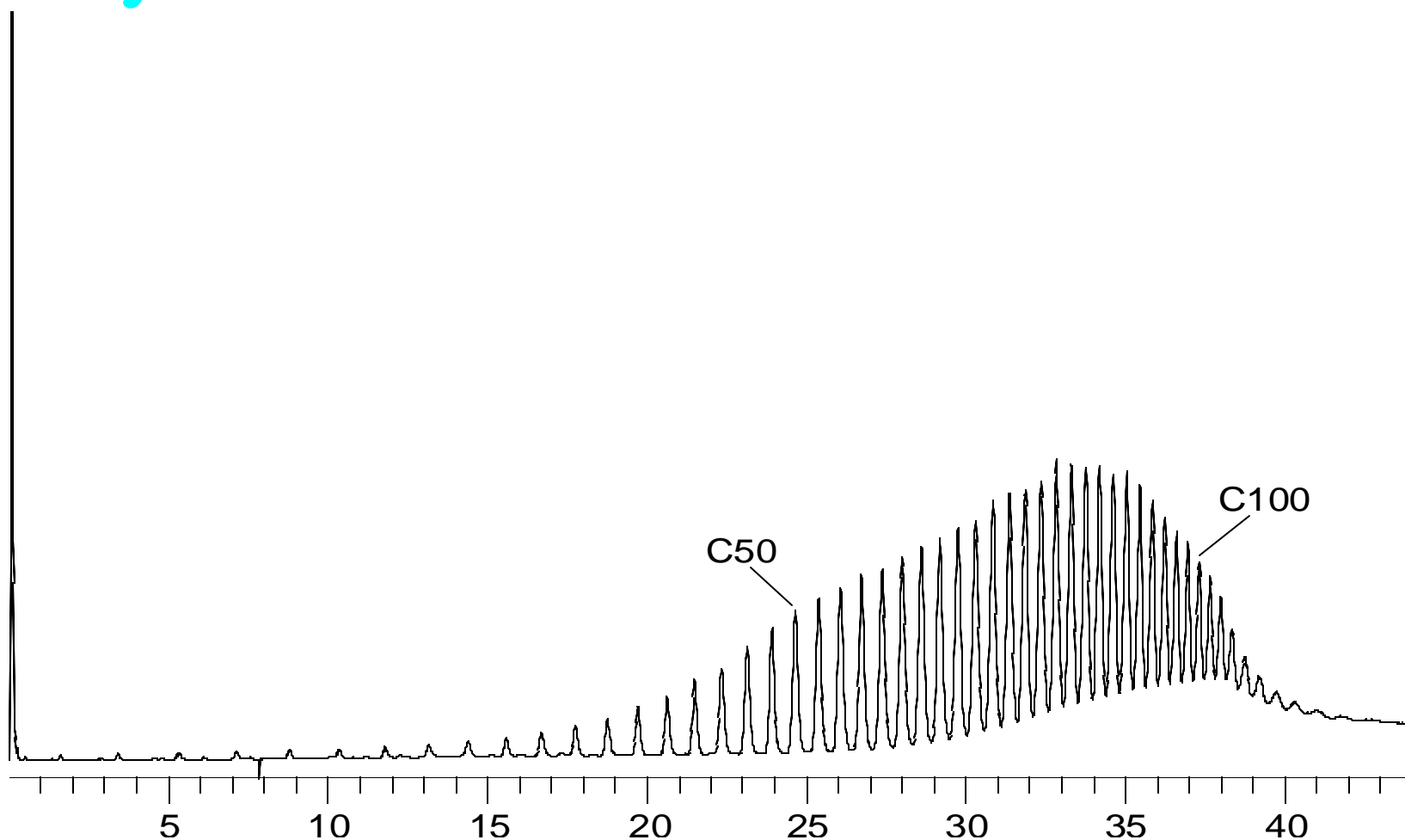
# Results

- Column demonstrated consistent performance for 400 analyses at temperatures 30° higher than method specifications.
- Column resolution for C50/C52 did not fall below the specifications of the method until approximately 350 injections.

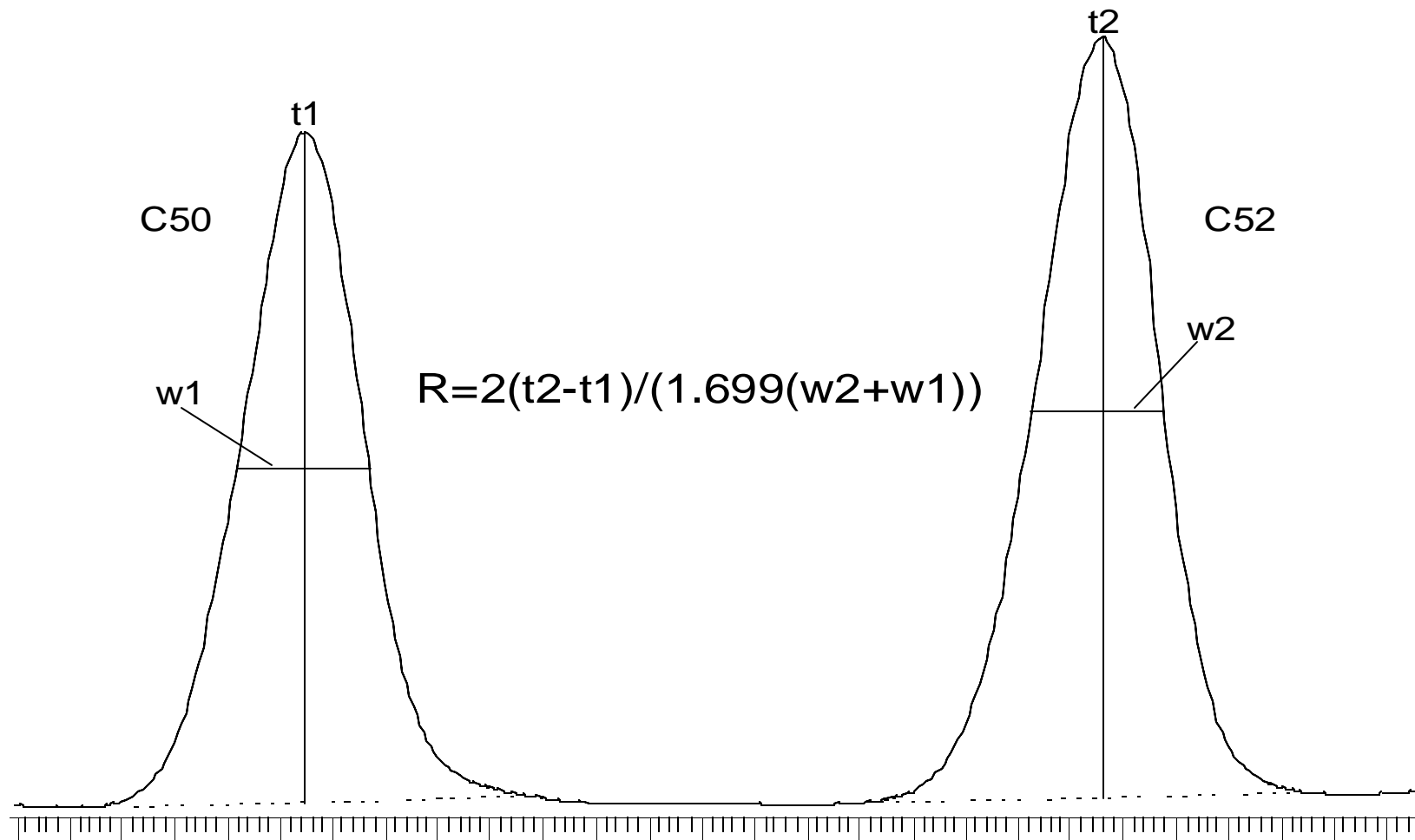
# Polywax 1000 – Run #1



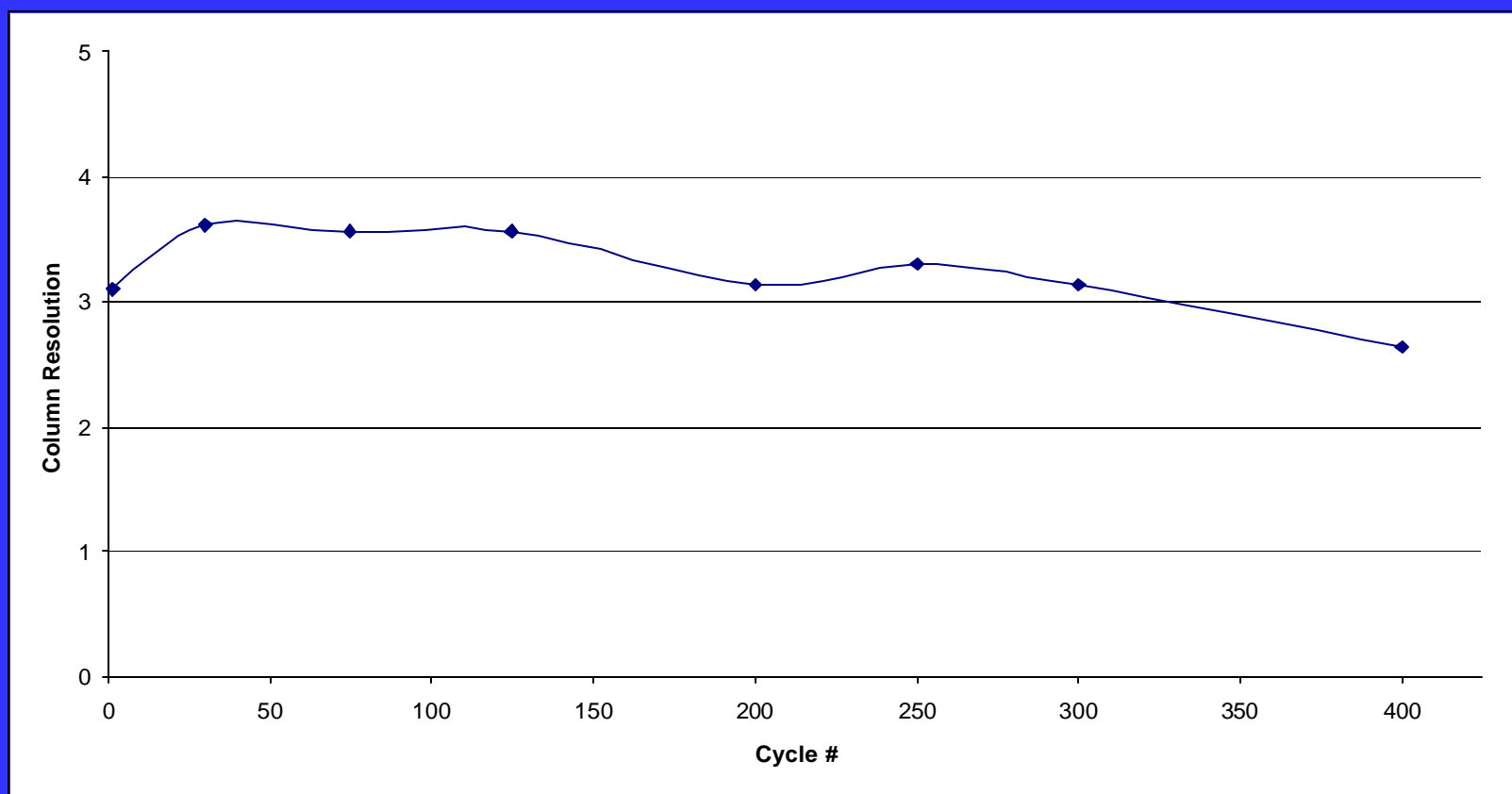
# Polywax 1000 – Run #400



# C50 / C52 Resolution – Run #1



# C50 / C52 Resolution

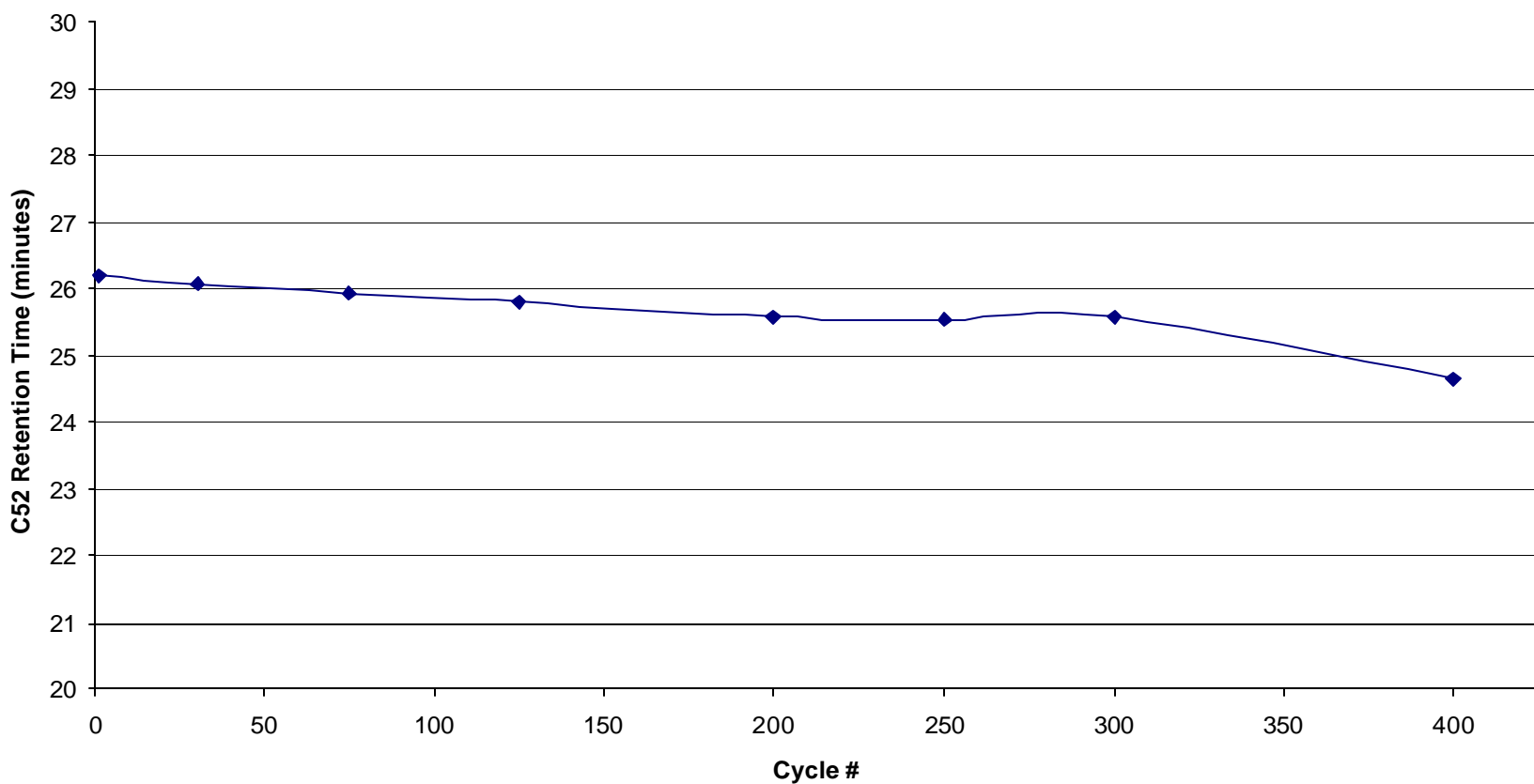


# Column Stability

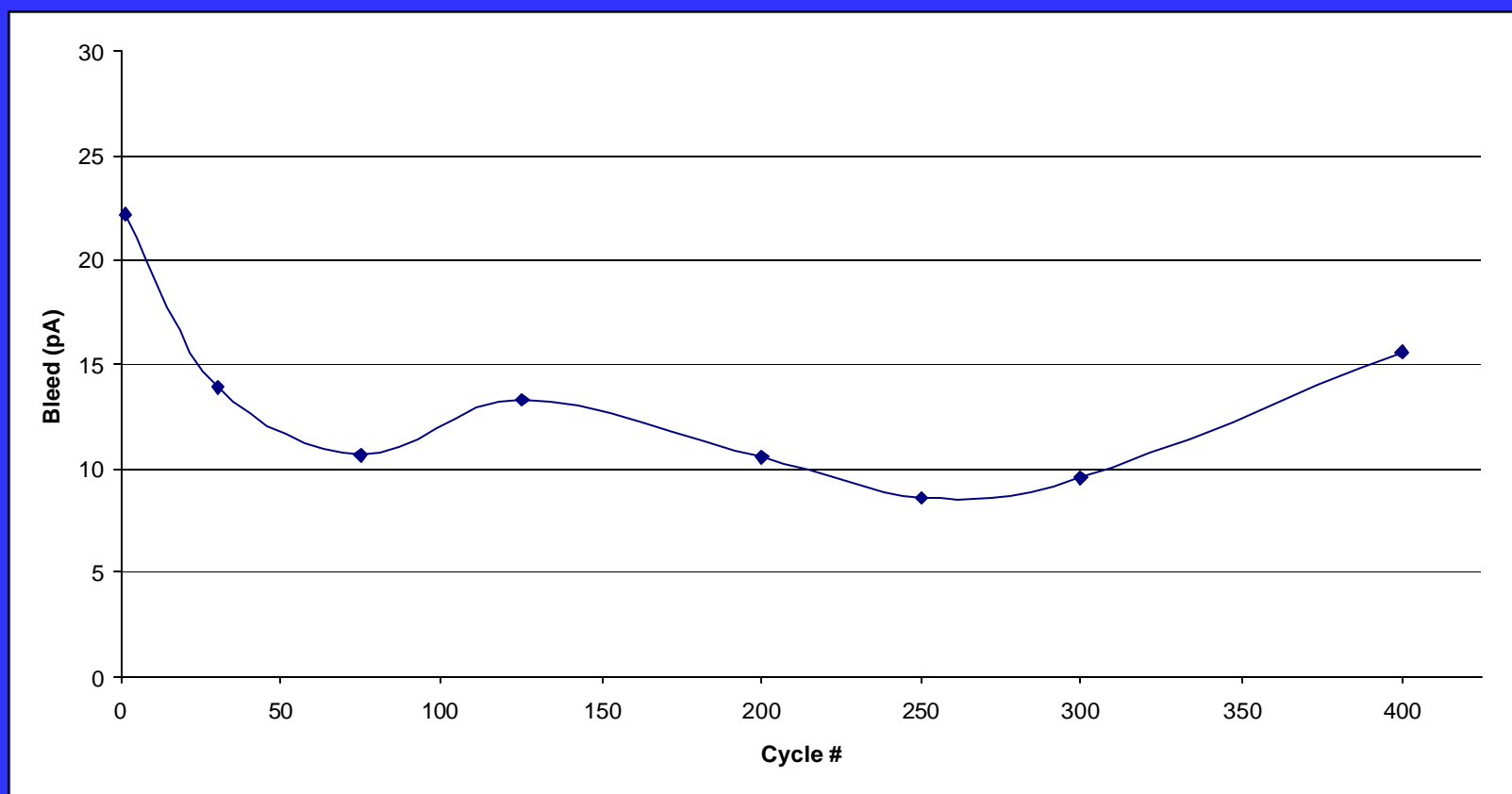
- C52 retention time was monitored to ensure that significant amounts of stationary phase were not being lost due to thermal cycling.
- After 400 injections the retention time of C52 moved approximately 1.4 minutes.
- Column bleed at 430°C was monitored to ensure that the phase had not undergone significant thermal decomposition.
- Bleed values were consistently low and did not interfere with the analysis.



# C52 Retention Time Stability



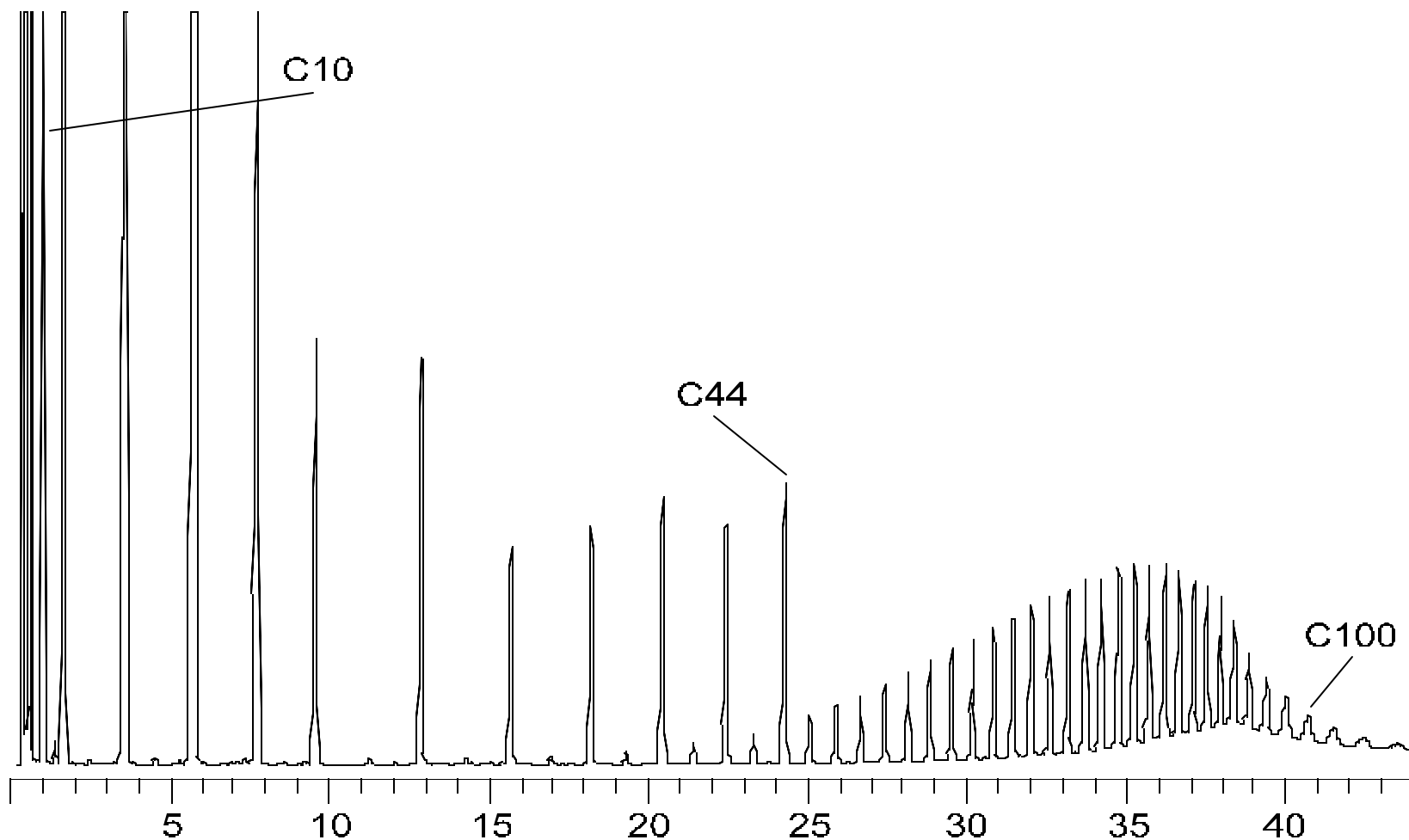
# Column Bleed Stability



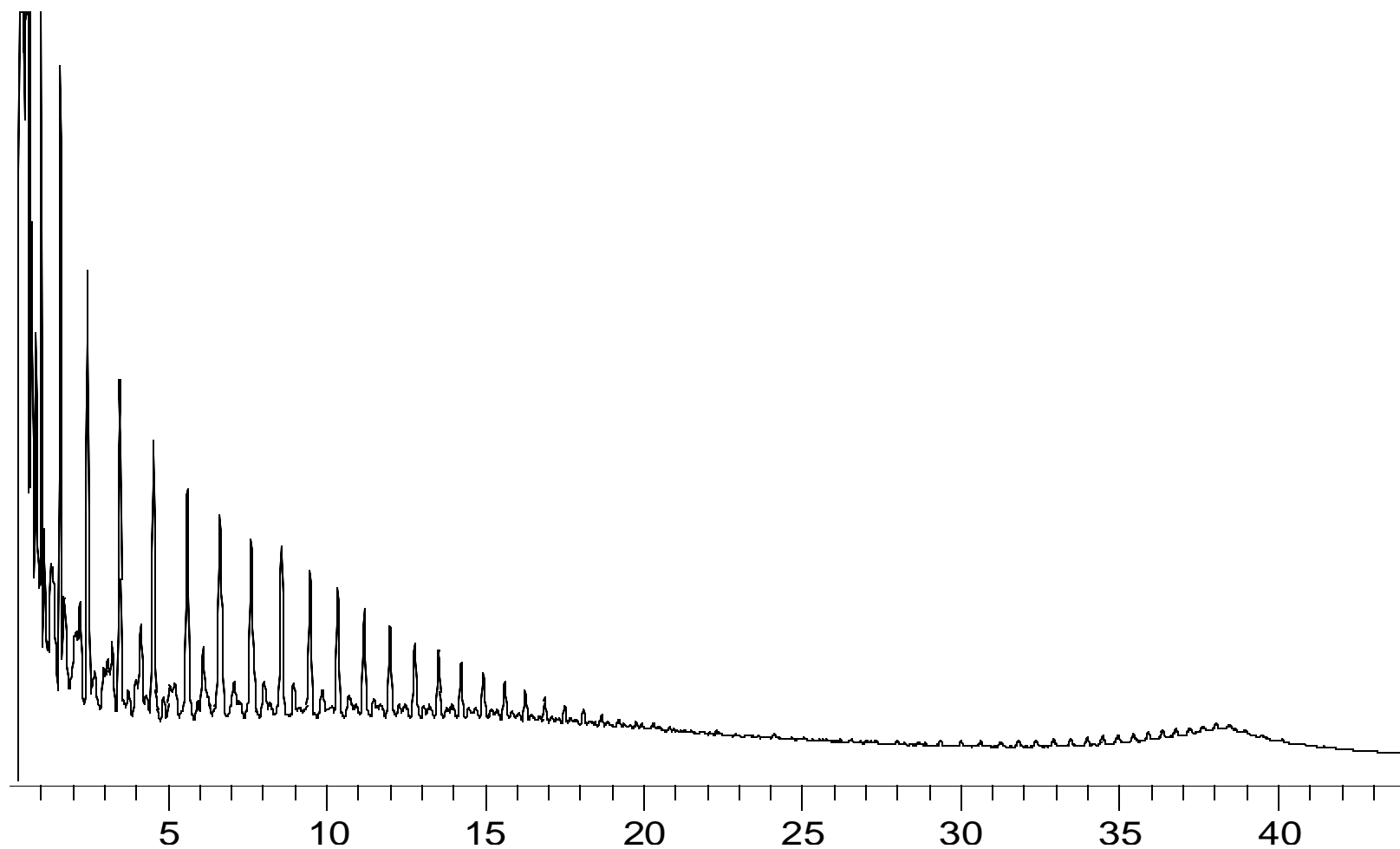
# Column Performance after 400 Cycles

- After 400 cycles to 430°C, a Polywax 1000 sample gave a column resolution value of 2.7
- A mixed sample of the D2887 standard and Polywax 1000 was injected to calibrate the column for C10 through C100.
- A diluted sample of Pennsylvania light crude oil was then analyzed and compared to the calibration mixture.
- Adequate resolution of the hydrocarbons in the crude oil sample was obtained even though the column was below the minimum resolution criteria of the method.

# C10 to C100 Calibration



# Pennsylvania Light Crude Oil



# Summary

- The MXT-1HT column demonstrates superior performance compared to columns made from fused silica or aluminum clad tubing.
- When combined with a high temperature, non-polar stationary phase, the column was able to withstand 400 cycles at 430°C.
- Column demonstrated low bleed and adequate separating efficiency to resolve hydrocarbons in a crude oil sample.

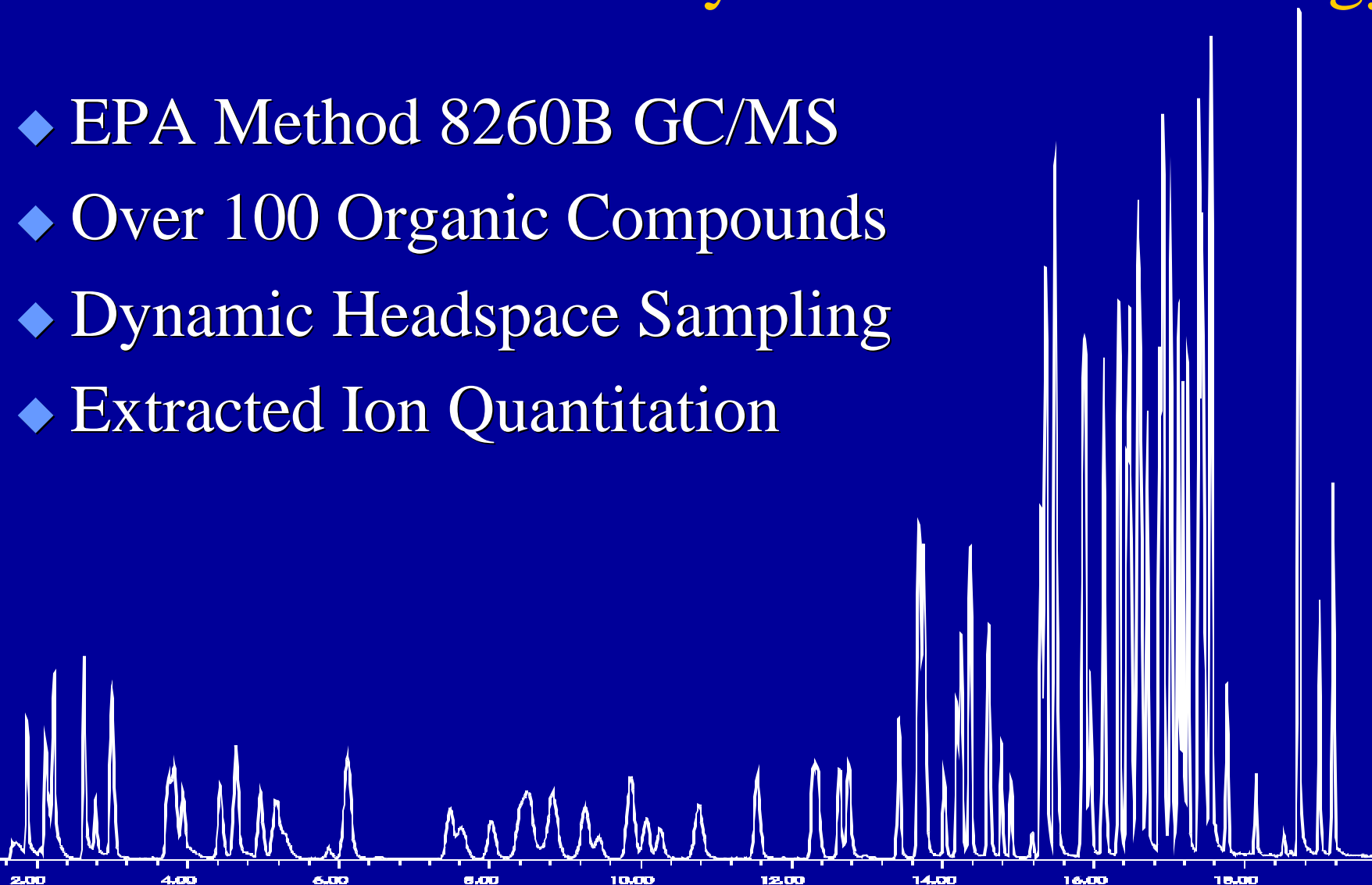
# Analysis of Volatile Organic Compounds by Purge and Trap using GC/MS and a unique Stationary Phase

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# GC/MS Volatiles Analysis EPA Methodology

- ◆ EPA Method 8260B GC/MS
- ◆ Over 100 Organic Compounds
- ◆ Dynamic Headspace Sampling
- ◆ Extracted Ion Quantitation





# Dynamic Headspace Sampling – Purge & Trap

- ◆ Purge & Trap increases sensitivity compared to other introduction methods
- ◆ However, purging analytes from the sample to the trap, then desorbing the trap, can result in broad peaks for the most volatile compounds.
- ◆ Column design needs to take into account the early eluting peak shapes and isomeric pairs (ex. Chlorotoluenes, dichlorobenzenes).

# Column Design Criteria

- ◆ Analysis Time
- ◆ Low Bleed
- ◆ Critical Resolution
- ◆ No Cryofocusing
- ◆ GC/MS Compatible
- ◆ Computer Aided Stationary Phase Design (CASPD) can help achieve these criteria

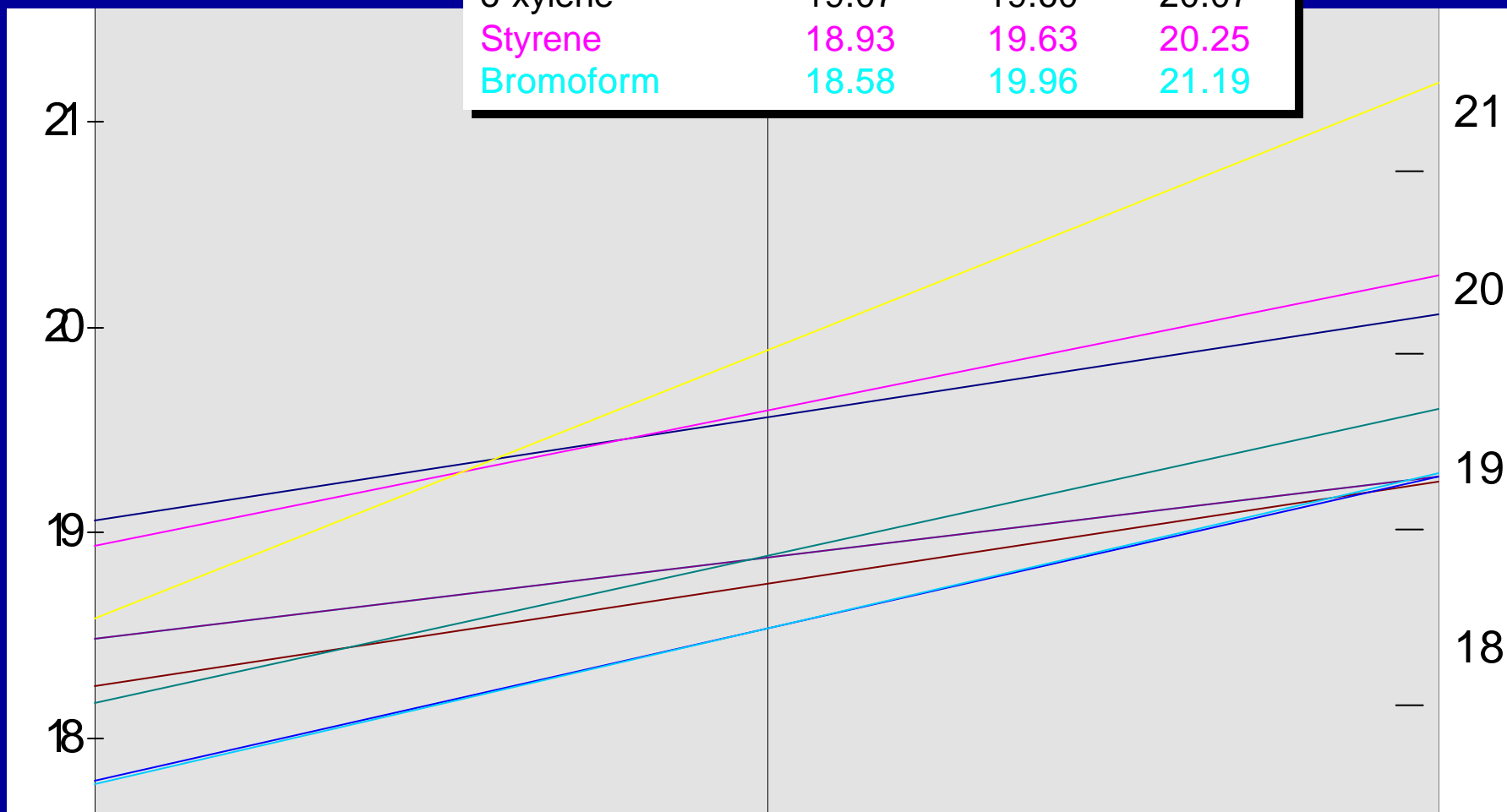


# Computer Aided Stationary Phase Design

- ◆ Phase modeling involves comparing analyte retention times collected on different stationary phases.
- ◆ This data can be used to predict the optimum resolution of compounds with different phase combinations.
- ◆ For example, Rtx-1 and Rtx-35 can be modeled to predict a composition for the Rtx-502.2 stationary phase.

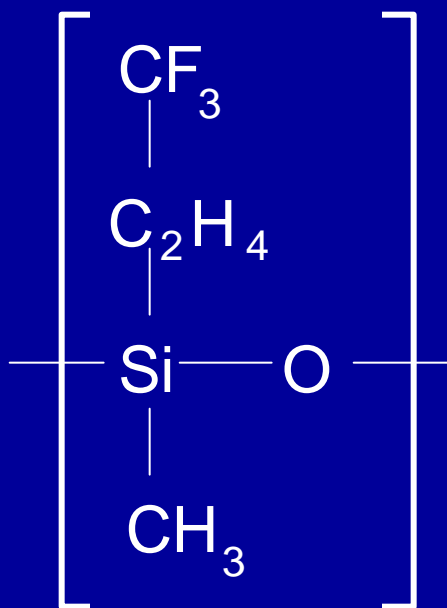
# Modeling

	Rtx-1	Rtx-502	Rtx-35
Chlorobenzene	17.79	18.57	19.27
1112te ethane	17.78	18.58	19.29
E benzene	18.26	18.78	19.25
m/p-xylene	18.48	18.90	19.27
o-ClF benzene	18.16	18.93	19.61
o-xylene	19.07	19.60	20.07
Styrene	18.93	19.63	20.25
Bromoform	18.58	19.96	21.19

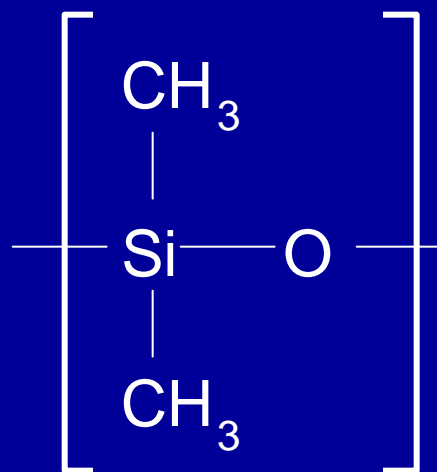


# Stationary Phases Used for Modeling

trifluoropropylmethyl  
polysiloxane

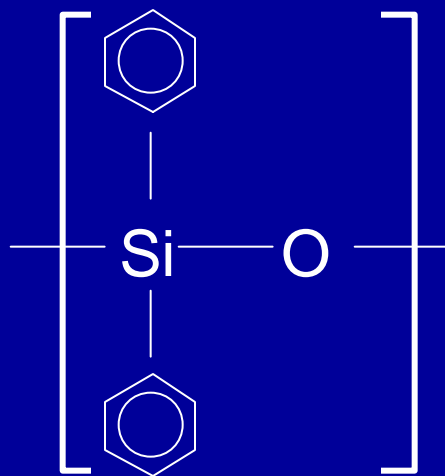


dimethyl  
polysiloxane

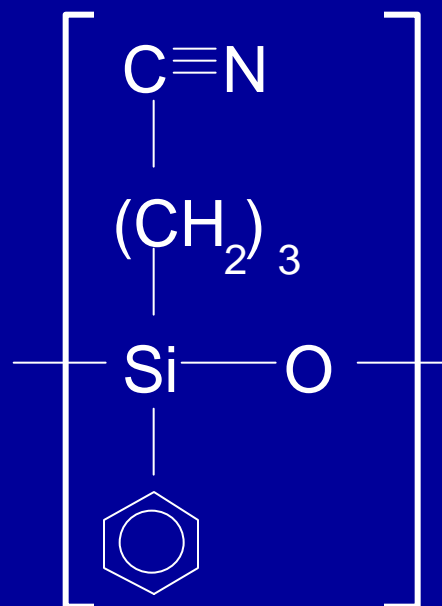


# Stationary Phases Used for Modeling

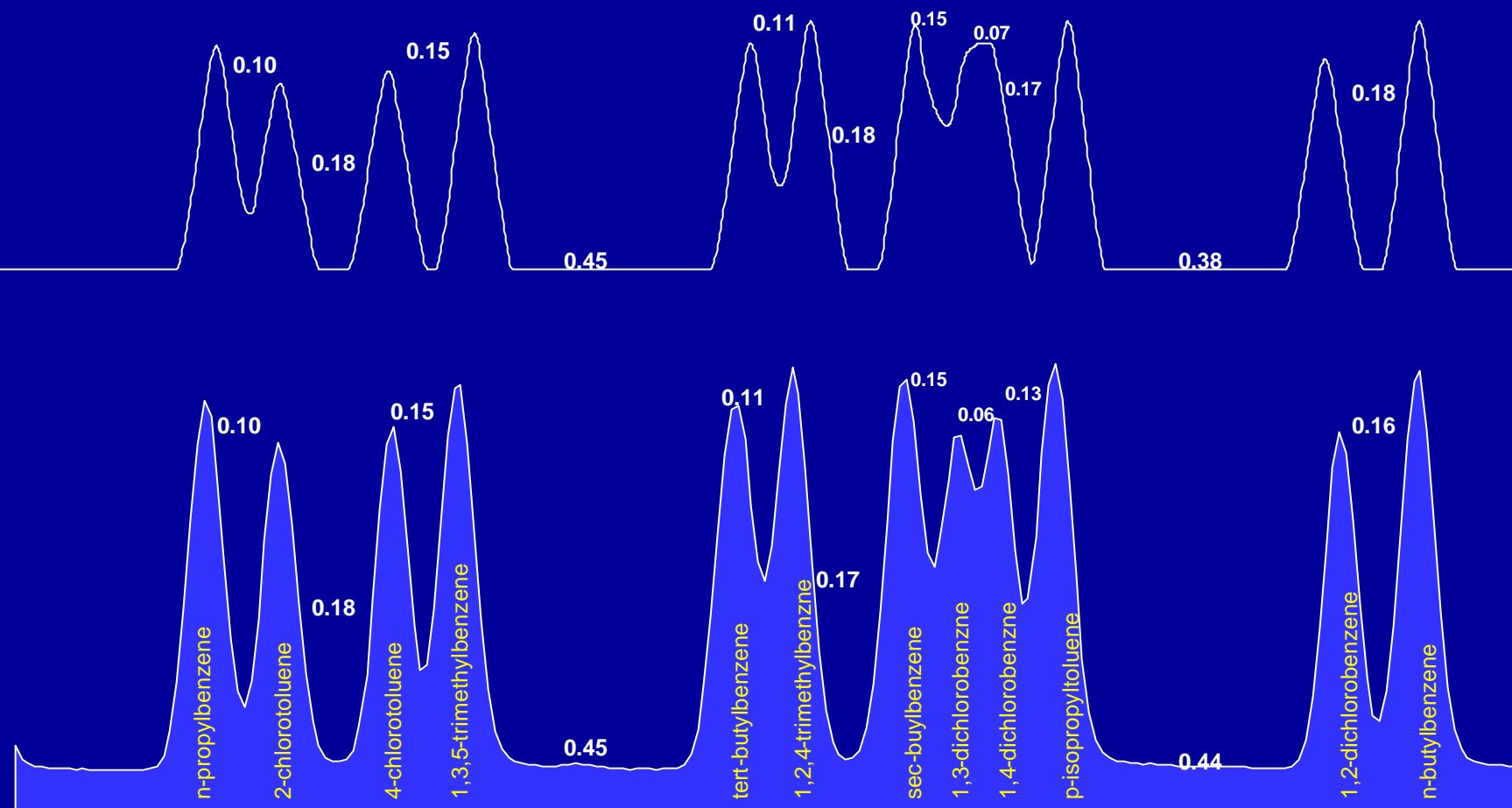
diphenyl  
polysiloxane



cyanopropylphenyl  
polysiloxane



# Predicted vs. Actual Using a 4 Dimensional Phase



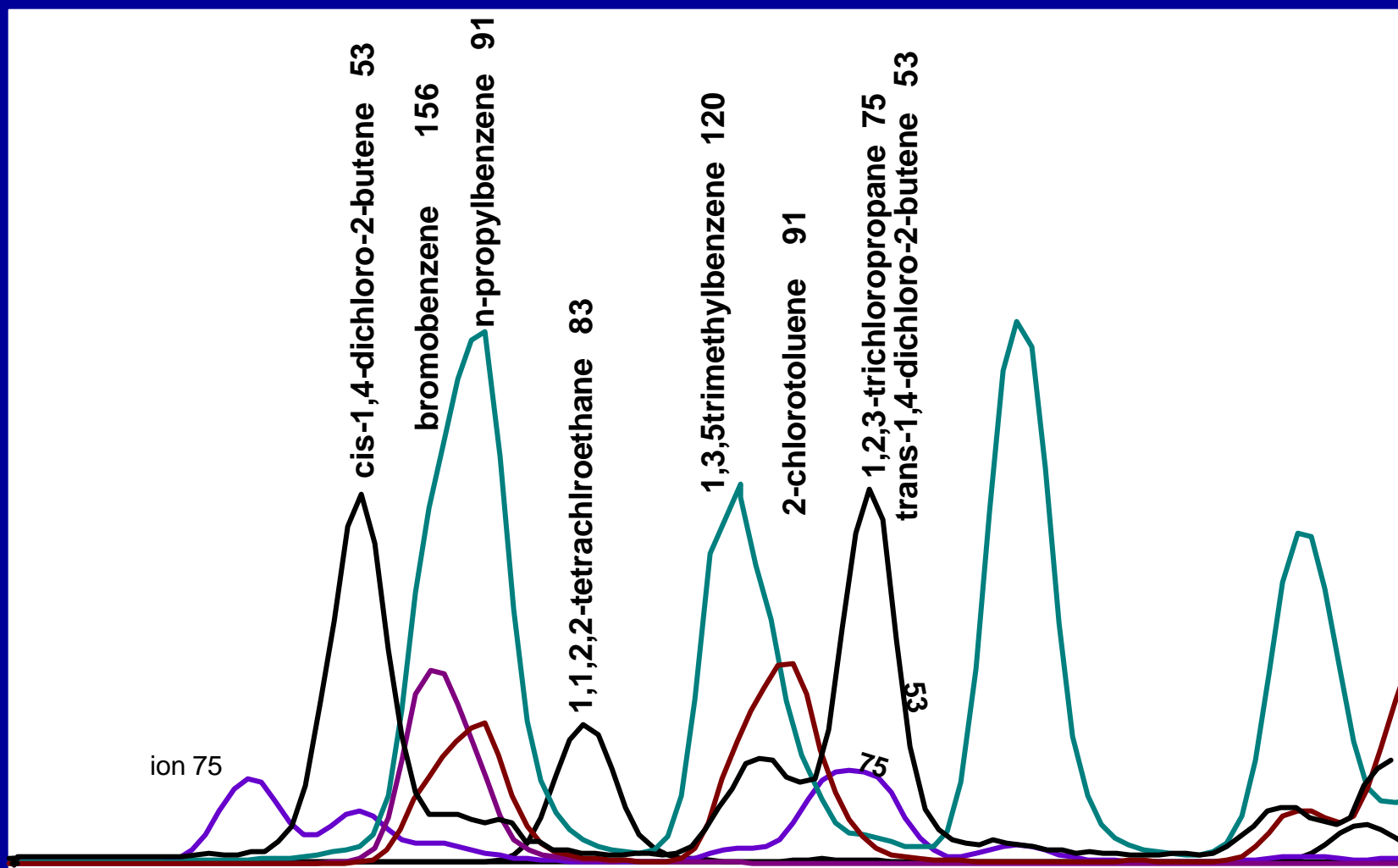
# Rtx-VMS

- ◆ Stationary Phase created using CASPD and optimized for GC/MS.
- ◆ Resolution and bleed levels were evaluated across a range of column dimensions and run conditions for maximum versatility.



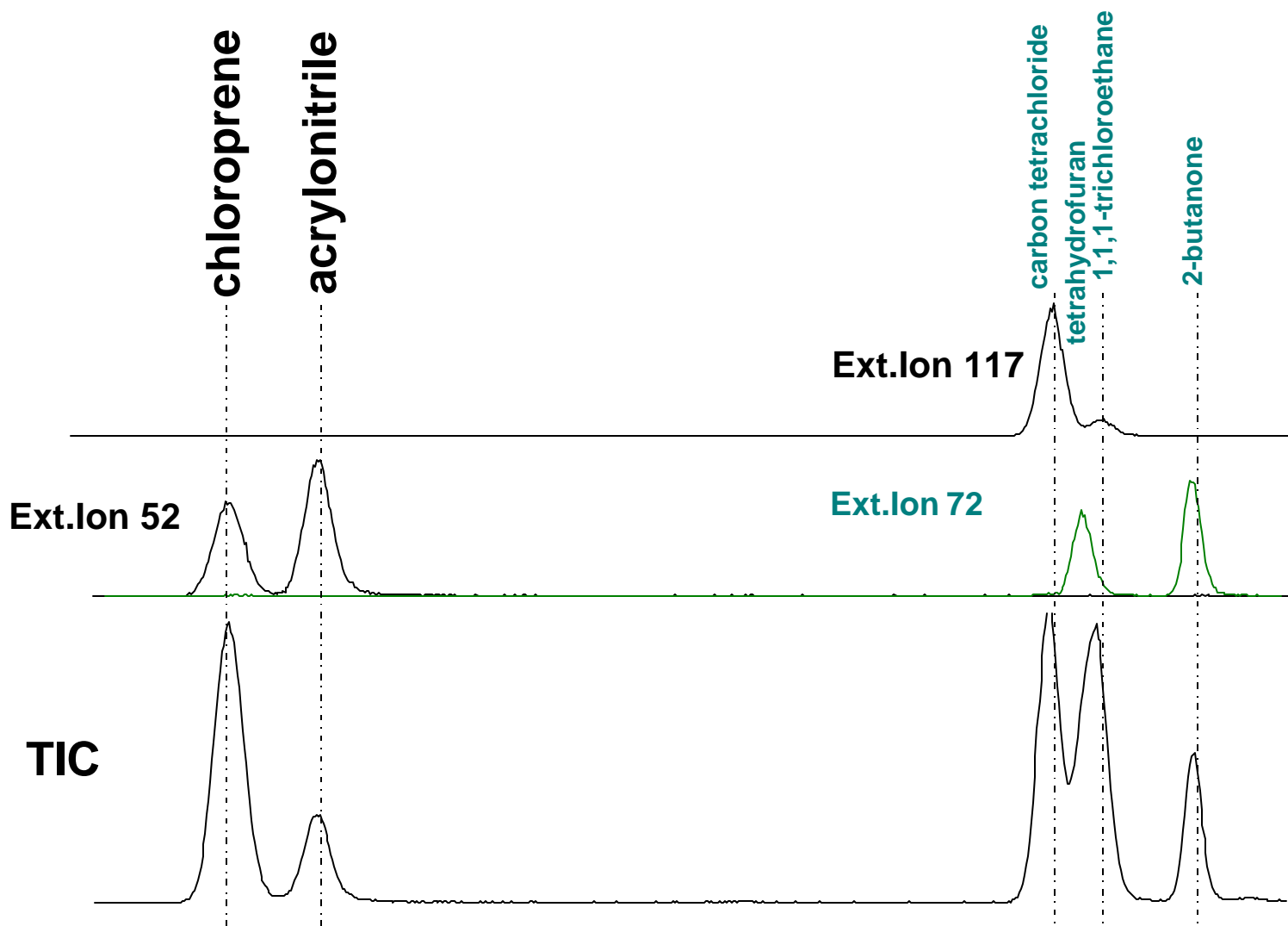
# Rtx<sup>®</sup>-VMS

# Extracted Ion



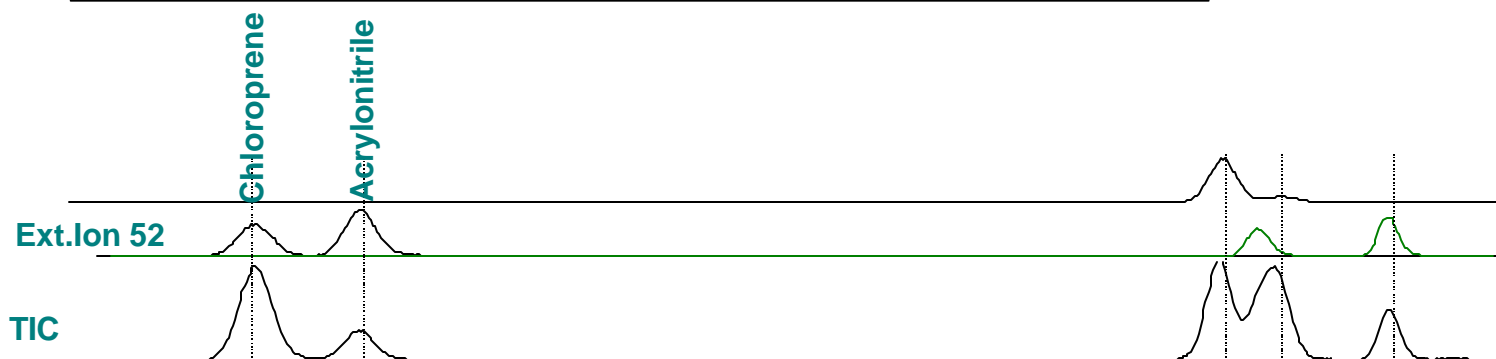
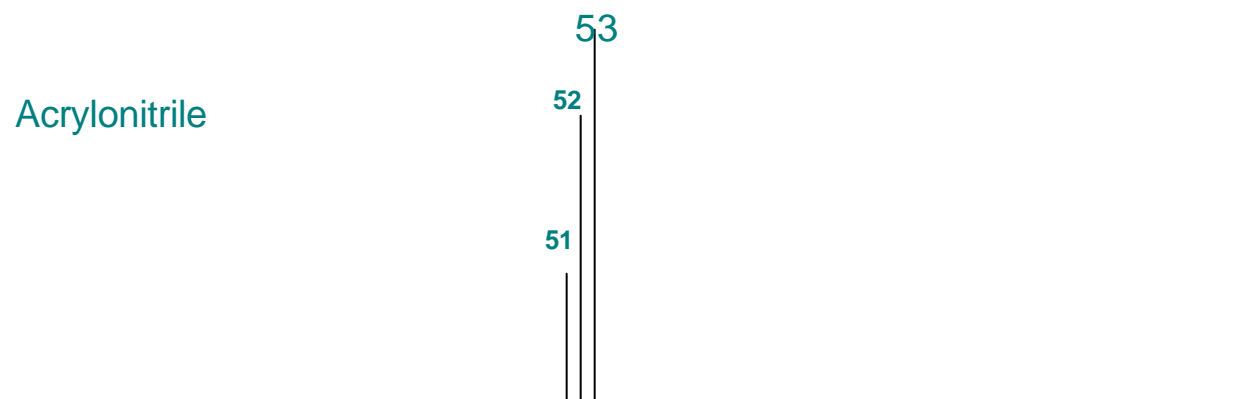
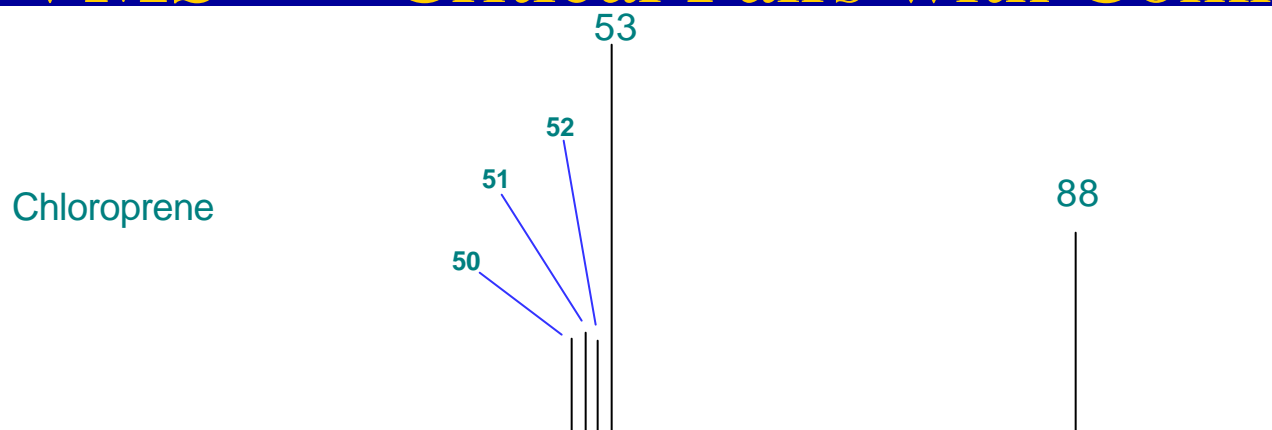
# Rtx<sup>®</sup>-VMS

## Critical Pairs with Common Ions



# Rtx<sup>®</sup>-VMS

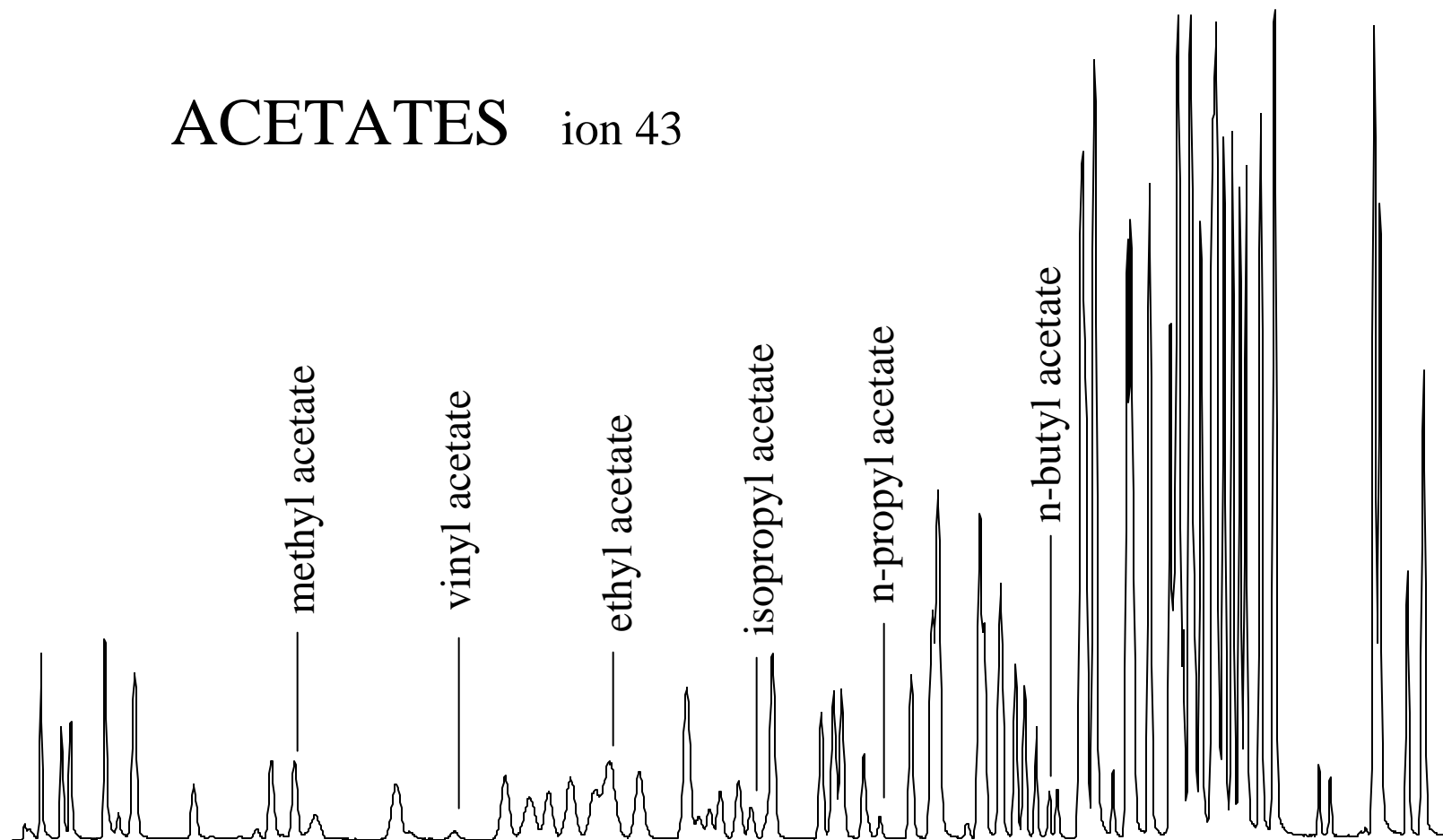
# Critical Pairs with Common Ions



Rtx<sup>®</sup>-VMS

Volatiles GC/MS Column

ACETATES ion 43



Time-->

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**ECH**nology Pty Ltd

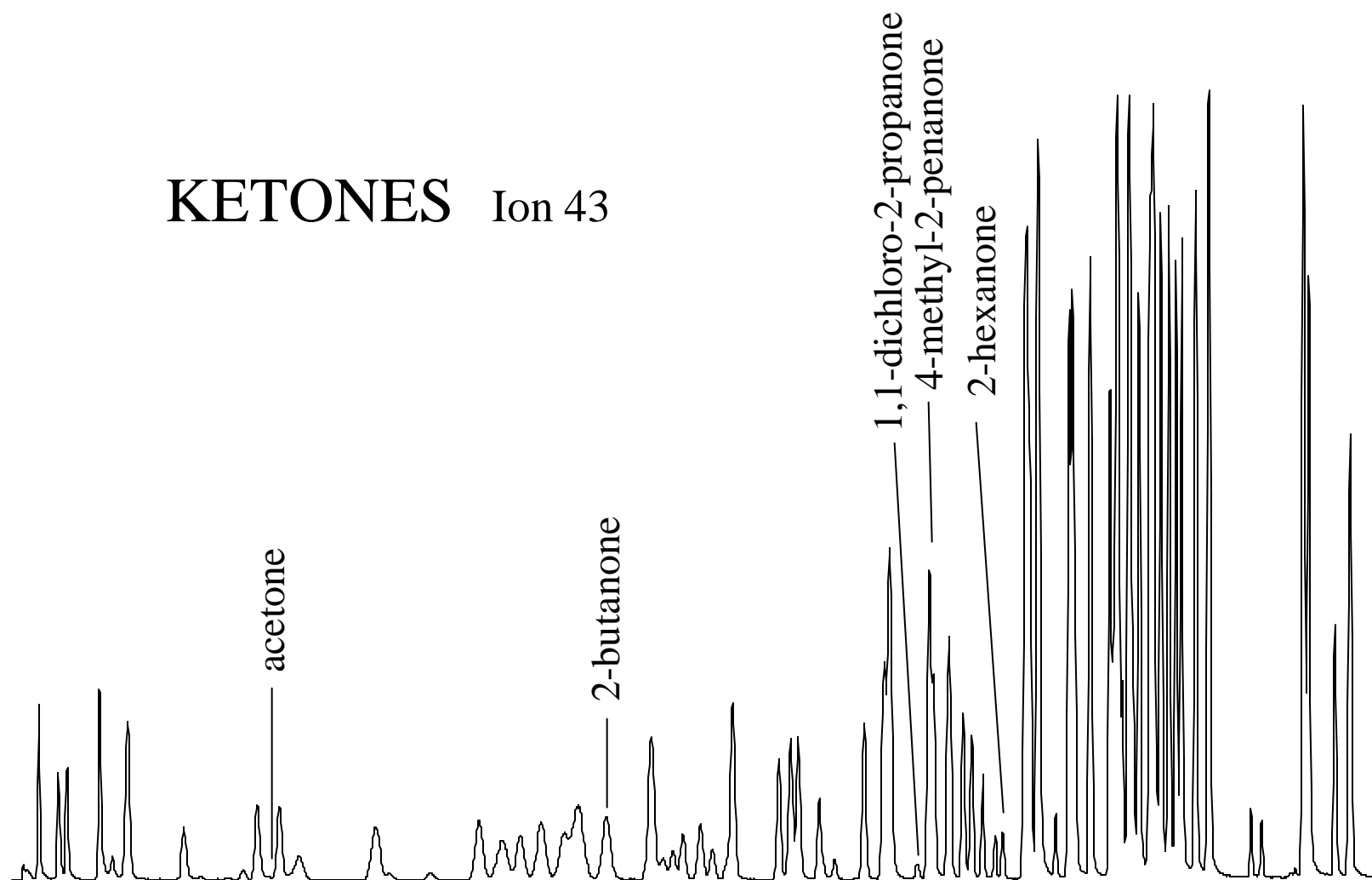
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# Rtx<sup>®</sup>-VMS

# Volatiles GC/MS Column

## KETONES Ion 43



Time-->

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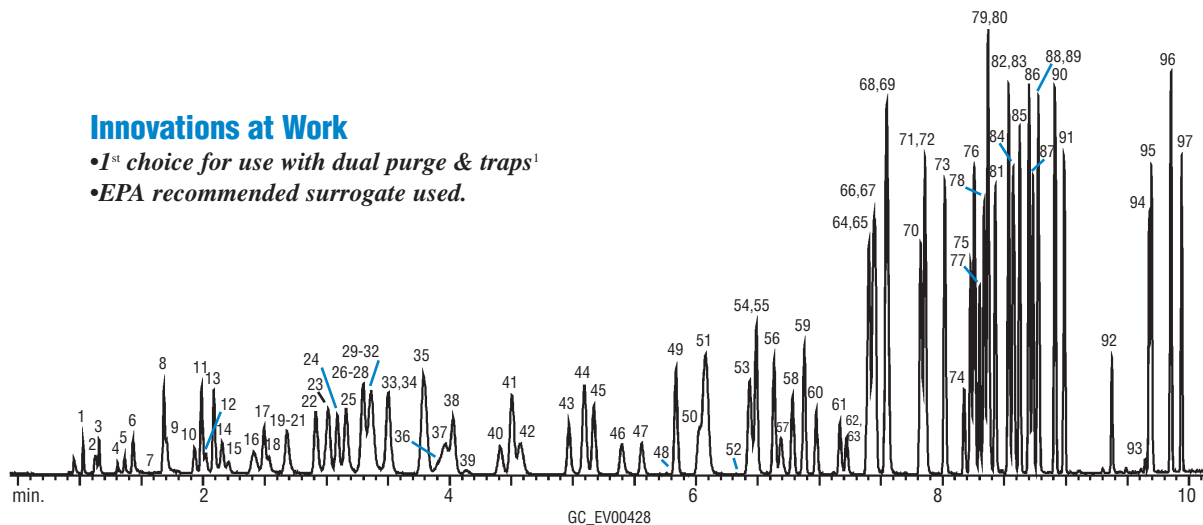
## Column Variations for GC/MS – 0.18mm ID

- ◆ 0.18mm ID columns are attractive due to increased efficiency and resolution enhancements
- ◆ An Rtx-VMS 20m x 0.18mm x 1.0um column gives excellent resolution of EPA 8260B components in 10 minutes without cryogenic cooling
- ◆ Desorb flow rate set at 40ml/min for 1 min
- ◆ Column flow rate optimized at 1 ml/min

**Volatile Organics**  
**EPA Method 8260B**  
**Rtx®-VMS**

**Innovations at Work**

- 1<sup>st</sup> choice for use with dual purge & traps<sup>1</sup>
- EPA recommended surrogate used.



20m, 0.18 mm ID, 1.00µm Rtx®-VMS (cat.# 49914)  
 Compounds in at 10ppb in 5mL of RO water  
 unless otherwise noted, ketones in at 2.5X  
 Concentrator: Tekmar LSC-3100 Purge and Trap  
 Trap: Vocab 3000 (type K)  
 Purge: 11 min. @ 40mL/min. @ ambient temperature  
 Dry purge: 1 min. @ 40mL/min.  
 Desorb preheat: 245°C  
 Desorb: 250°C for 2 min., Flow 40mL/min.  
 Bake: 260°C for 8 min.  
 Interface: transfer line 0.53mm ID Silcosteel® tubing  
 1:40 split at injection port. 1mm ID sleeve.  
 Oven temp.: 50°C (hold 4 min.) to 100°C @ 18°C/min. (hold 0 min.)  
 to 230°C @ 40°C/min. (hold 3 min.)  
 Carrier gas: helium @ ~1.0mL/min. constant flow  
 Adjust dichlorodifluoromethane to a retention time of 1.03 min. @ 50°C.  
 Detector: HP 5973 MSD  
 Scan range: 35-300amu

- |   |                                     |                                       |                                 |
|---|-------------------------------------|---------------------------------------|---------------------------------|
| 1. dichlorodifluoromethane              | 26. ethyl acetate                   | 51. toluene                           | 76. <i>n</i> -propylbenzene     |
| 2. chloromethane                        | 27. carbon tetrachloride            | 52. pyridine (250ppb)                 | 77. 1,1,2,2-tetrachloroethane   |
| 3. vinyl chloride                       | 28. methyl acrylate                 | 53. tetrachloroethene                 | 78. 2-chlorotoluene             |
| 4. bromomethane                         | 29. propargyl alcohol (500ppb)      | 54. 4-methyl-2-pentanone              | 79. 1,3,5-trimethylbenzene      |
| 5. chloroethane                         | 30. dibromofluoromethane (SMC)      | 55. <i>trans</i> -1,3-dichloropropene | 80. 1,2,3-trichloropropane      |
| 6. trichlorofluoromethane               | 31. tetrahydrofuran                 | 56. 1,1,2-trichloroethane             | 81. 4-chlorotoluene             |
| 7. ethanol (2500ppb)                    | 32. 1,1,1-trichloroethane           | 57. ethyl methacrylate                | 82. <i>tert</i> -butylbenzene   |
| 8. 1,1-dichloroethene                   | 33. 2-butanone                      | 58. dibromochloromethane              | 83. pentachloroethane           |
| 9. carbon disulfide (40ppb)             | 34. 1,1-dichloropropene             | 59. 1,3-dichloropropane               | 84. 1,2,4-trimethylbenzene      |
| 10. allyl chloride                      | 35. benzene                         | 60. 1,2-dibromoethane                 | 85. <i>sec</i> -butylbenzene    |
| 11. methylene chloride                  | 36. pentafluorobenzene (IS)         | 61. <i>n</i> -butyl acetate           | 86. <i>p</i> -isopropyltoluene  |
| 12. acetone                             | 37. <i>tert</i> -amyl-methyl ether  | 62. 2-hexanone                        | 87. 1,3-dichlorobenzene         |
| 13. <i>trans</i> -1,2-dichloroethene    | 38. 1,2-dichloroethane              | 63. 2-picoline (250ppb)               | 88. 1,4-dichlorobenzene-d4 (IS) |
| 14. methyl <i>tert</i> -butyl ether     | 39. isobutyl alcohol (500ppb)       | 64. chlorobenzene-D5 (IS)             | 89. 1,4-dichlorobenzene         |
| 15. <i>tert</i> -butyl alcohol (100ppb) | 40. isopropyl acetate               | 65. chlorobenzene                     | 90. <i>n</i> -butylbenzene      |
| 16. diisopropyl ether                   | 41. trichloroethene                 | 66. ethylbenzene                      | 91. 1,2-dichlorobenzene         |
| 17. 1,1-dichloroethane                  | 42. 1,4-difluorobenzene (SMC)       | 67. 1,1,1,2-tetrachloroethane         | 92. 1,2-dibromo-3-chloropropane |
| 18. acrylonitrile                       | 43. dibromomethane                  | 68. <i>m</i> -xylene                  | 93. nitrobenzene (250ppb)       |
| 19. vinyl acetate                       | 44. 1,2-dichloropropane             | 69. <i>p</i> -xylene                  | 94. hexachlorobutadiene         |
| 20. allyl alcohol (250ppb)              | 45. bromodichloromethane            | 70. <i>o</i> -xylene                  | 95. 1,2,4-trichlorobenzene      |
| 21. ethyl- <i>tert</i> -butyl ether     | 46. methyl methacrylate             | 71. styrene                           | 96. naphthalene                 |
| 22. <i>cis</i> -1,2-dichloroethene      | 47. <i>n</i> -propyl acetate        | 72. bromoform                         | 97. 1,2,3-trichlorobenzene      |
| 23. 2,2-dichloropropane                 | 48. 2-chloroethanol (2500ppb)       | 73. isopropylbenzene                  |                                 |
| 24. bromochloromethane                  | 49. <i>cis</i> -1,3-dichloropropene | 74. 4-bromo-1-fluorobenzene (SMC)     |                                 |
| 25. chloroform                          | 50. toluene-d8(SMC)                 | 75. bromobenzene                      |                                 |

<sup>1</sup>A.L. Hilling and G. Smith, *Environmental Testing & Analysis*, 10(3), 15-19, 2001.

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## Column Variations – 0.25mm ID

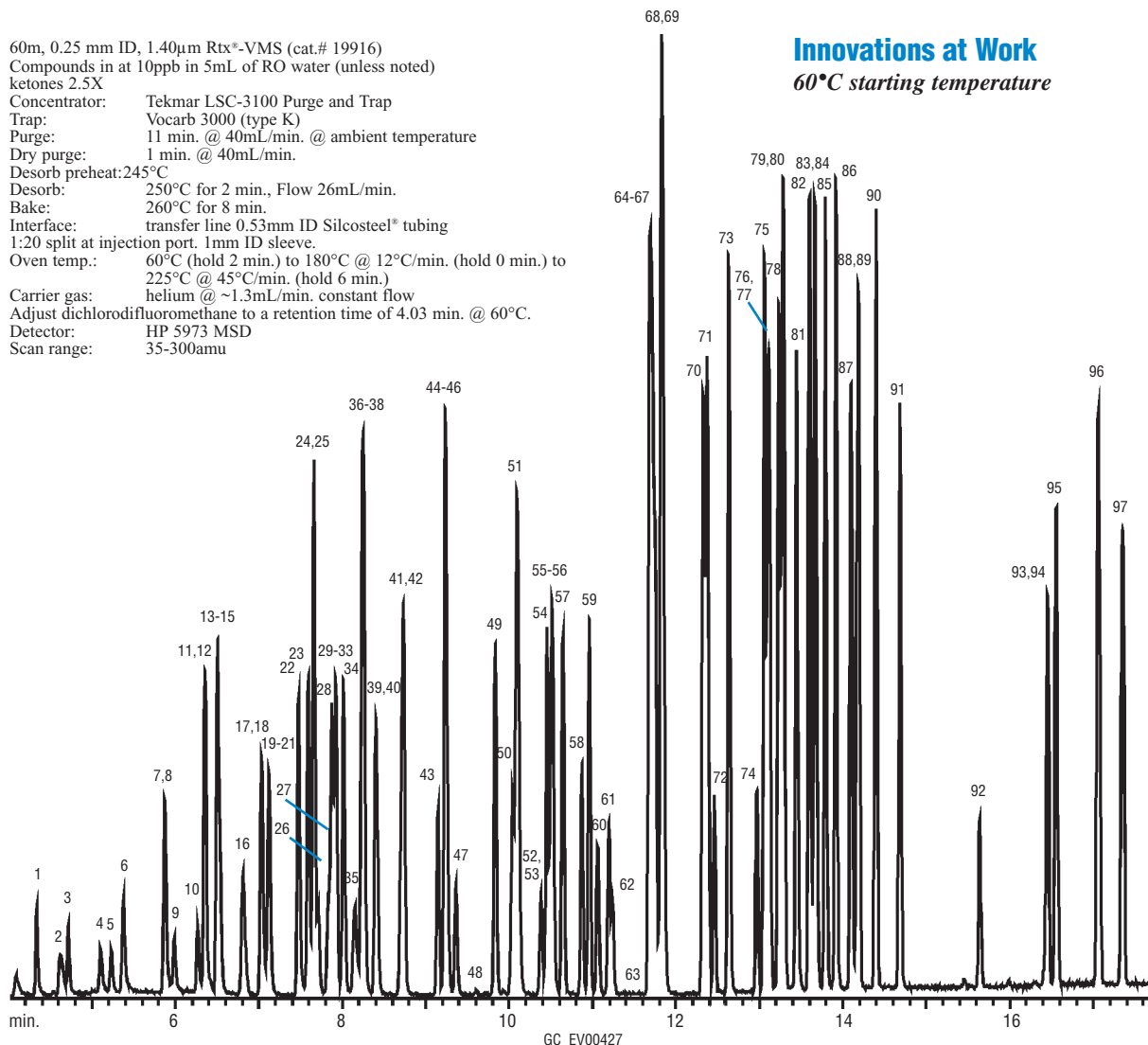
- ◆ Rtx-VMS 60m x 0.25mm x 1.4um column
- ◆ 60°C starting temperature
- ◆ 20:1 split injection
- ◆ Constant Flow @ 1.3 ml/min.
- ◆ 97 components in EPA 8260B in 18 minutes



# **Volatile Organics** **EPA Method 8260B** **Rtx®-VMS**

60m, 0.25 mm ID, 1.40µm Rtx®-VMS (cat.# 19916)  
 Compounds in at 10ppb in 5mL of RO water (unless noted)  
 ketones 2.5X  
 Concentrator: Tekmar LSC-3100 Purge and Trap  
 Trap: Vocab 3000 (type K)  
 Purge: 11 min. @ 40mL/min. @ ambient temperature  
 Dry purge: 1 min. @ 40mL/min.  
 Desorb preheat: 245°C  
 Desorb: 250°C for 2 min., Flow 26mL/min.  
 Bake: 260°C for 8 min.  
 Interface: transfer line 0.53mm ID Silcosteel® tubing  
 1:20 split at injection port. 1mm ID sleeve.  
 Oven temp.: 60°C (hold 2 min.) to 180°C @ 12°C/min. (hold 0 min.) to 225°C @ 45°C/min. (hold 6 min.)  
 Carrier gas: helium @ ~1.3mL/min. constant flow  
 Adjust dichlorodifluoromethane to a retention time of 4.03 min. @ 60°C.  
 Detector: HP 5973 MSD  
 Scan range: 35-300amu

**Innovations at Work**  
 60°C starting temperature



- |                                 |                                |                                   |                                 |
|---------------------------------|--------------------------------|-----------------------------------|---------------------------------|
| 1. dichlorodifluoromethane      | 26. ethyl acetate              | 51. toluene                       | 76. 1,1,2,2-tetrachloroethane   |
| 2. chloromethane                | 27. methyl acrylate            | 52. 4-methyl-2-pentanone          | 77. bromobenzene                |
| 3. vinyl chloride               | 28. propargyl alcohol (500ppb) | 53. pyridine (250ppb)             | 78. 1,3,5-trimethylbenzene      |
| 4. bromomethane                 | 29. dibromofluoromethane (SMC) | 54. trans-1,3-dichloropropene     | 79. 2-chlorotoluene             |
| 5. chloroethane                 | 30. tetrahydrofuran            | 55. ethyl methacrylate            | 80. 1,2,3-trichloropropane      |
| 6. trichlorofluoromethane       | 31. carbon tetrachloride       | 56. tetrachloroethene             | 81. 4-chlorotoluene             |
| 7. ethanol (2500ppb)            | 32. 2-butanone                 | 57. 1,1,2-trichloroethane         | 82. tert-butylbenzene           |
| 8. 1,1-dichloroethene           | 33. 1,1,1-trichloroethane      | 58. dibromochloromethane          | 83. 1,2,4-trimethylbenzene      |
| 9. carbon disulfide (40ppb)     | 34. 1,1-dichloropropene        | 59. 1,3-dichloropropane           | 84. pentachloroethane           |
| 10. allyl chloride              | 35. pentafluorobenzene (IS)    | 60. n-butyl acetate               | 85. sec-butylbenzene            |
| 11. methylene chloride          | 36. tert-amyl methyl ether     | 61. 1,2-dibromoethane             | 86. p-isopropyltoluene          |
| 12. acetone                     | 37. benzene                    | 62. 2-hexanone                    | 87. 1,3-dichlorobenzene         |
| 13. trans-1,2-dichloroethene    | 38. isobutyl alcohol (500ppb)  | 63. 2-picoline (250ppb)           | 88. 1,4-dichlorobenzene-d4 (IS) |
| 14. tert-butyl alcohol (100ppb) | 39. 1,2-dichloroethane         | 64. ethylbenzene                  | 89. 1,4-dichlorobenzene         |
| 15. methyl tert-butyl ether     | 40. isopropyl acetate          | 65. chlorobenzene-D5 (IS)         | 90. n-butylbenzene              |
| 16. diisopropyl ether           | 41. 1,4-difluorobenzene (SMC)  | 66. chlorobenzene                 | 91. 1,2-dichlorobenzene         |
| 17. 1,1-dichloroethane          | 42. trichloroethene            | 67. 1,1,1,2-tetrachloroethane     | 92. 1,2-dibromo-3-chloropropane |
| 18. acrylonitrile               | 43. dibromomethane             | 68. m-xylene                      | 93. nitrobenzene (250ppb)       |
| 19. vinyl acetate*              | 44. bromodichloromethane       | 69. p-xylene                      | 94. hexachlorobutadiene         |
| 20. allyl alcohol (250ppb)      | 45. 1,2-dichloropropane        | 70. o-xylene                      | 95. 1,2,4-trichlorobenzene      |
| 21. ethyl-tert-butyl ether*     | 46. methyl methacrylate        | 71. styrene                       | 96. naphthalene                 |
| 22. cis-1,2-dichloroethene      | 47. n-propyl acetate           | 72. bromoform                     | 97. 1,2,3-trichlorobenzene      |
| 23. 2,2-dichloropropane         | 48. 2-chloroethanol (2500ppb)  | 73. isopropylbenzene              |                                 |
| 24. bromochloromethane          | 49. cis-1,3-dichloropropene    | 74. 4-bromo-1-fluorobenzene (SMC) |                                 |
| 25. chloroform                  | 50. toluene-d8 (SMC)           | 75. n-propylbenzene               |                                 |

\*These compounds can be resolved using a lower starting temperature.

# EPA Method 8240

- ◆ Developed to monitor 73 compounds in hazardous waste
- ◆ Rtx-VMS 30m x 0.25mm x 1.4um is a good choice for this shorter list
- ◆ Analysis times of 14 minutes

# **Volatile Organics** **EPA Method 8240 (8260 Short List)** **Rtx®-VMS**

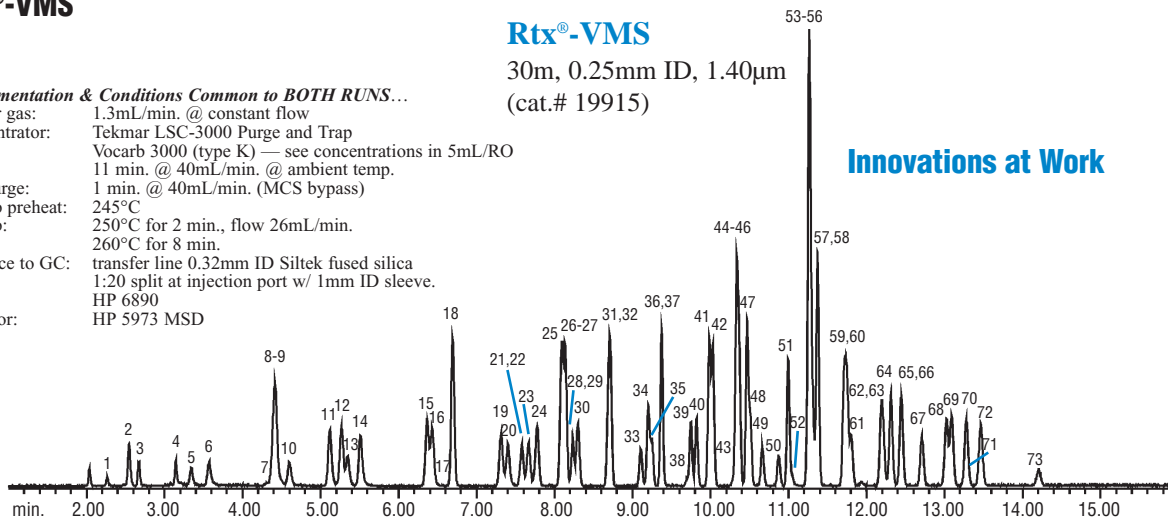
## **Instrumentation & Conditions Common to BOTH RUNS...**

Carrier gas: 1.3mL/min. @ constant flow  
 Concentrator: Tekmar LSC-3000 Purge and Trap  
 Trap: Vocab 3000 (type K) — see concentrations in 5mL/RO  
 Purge: 11 min. @ 40mL/min. @ ambient temp.  
 Dry purge: 1 min. @ 40mL/min. (MCS bypass)  
 Desorb preheat: 245°C  
 Desorb: 250°C for 2 min., flow 26mL/min.  
 Bake: 260°C for 8 min.  
 Interface to GC: transfer line 0.32mm ID Siltek fused silica  
 1:20 split at injection port w/ 1mm ID sleeve.  
 GC: HP 6890  
 Detector: HP 5973 MSD

## **Rtx®-VMS**

30m, 0.25mm ID, 1.40µm  
 (cat.# 19915)

**Innovations at Work**

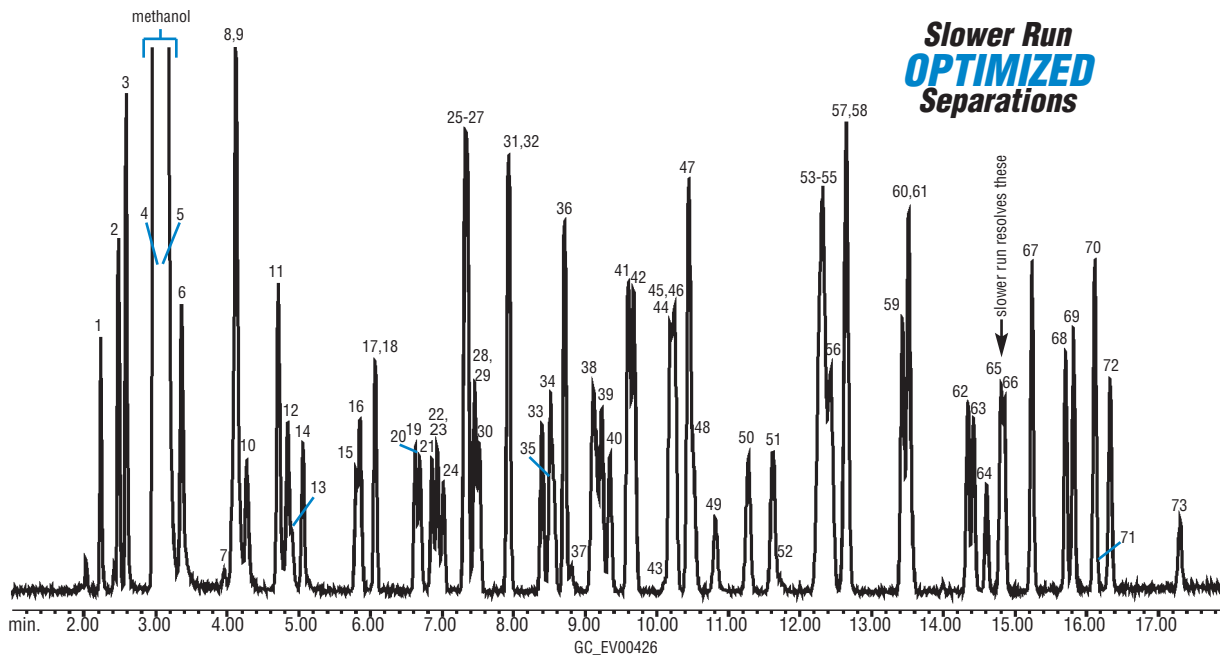


## **Top chromatogram:**

Oven temp.: 40°C (hold 4 min.) to 90°C @ 16°C/min. (no hold)  
 to 210°C @ 32°C/min. (hold 5 min.)  
 Adjust dichlorodifluoromethane to a retention time of 2.27 min. @ 40°C.  
 MS Scan Range: 35-300amu  
 compound concentrations, by mix: (in 5mL of RO water)  
 Compounds at 100ppb (cat.# 30213, 30004, 30006, 30011, 30042)  
 Alcohols at 1ppm (cat.# 30214) except 2Cl ethanol at 10ppm.  
 vinyl acetate at 500ppb (cat.#30216)  
 8240 Nitrile Mix at 200ppb (cat.# 30215)  
 8240 Mix 1A at 300ppb (cat.# 30217)  
 8240 Mix 2A at 500ppb (cat.# 30218)

## **Bottom chromatogram:**

Oven temp.: 45°C (hold 4 min.) to 110°C @ 19°C/min. (hold 5 min.)  
 to 220°C @ 32°C/min. (hold 5 min.)  
 Adjust dichlorodifluoromethane to 2.23 min. @ 45°C.  
 MS Scan Range: 29-260amu, for 2Cl ethanol response  
 compound concentrations, by mix: (in 5mL of RO water)  
 Compounds at 100ppb (cat.# 30213, 30004, 30006, 30011, 30042)  
 Alcohols at 1ppm (cat.# 30214) (see MS scan)  
 vinyl acetate at 100ppb (cat.# 30216)  
 8240 Nitrile Mix at 400ppb (cat.# 30215)  
 8240 Mix 1A at 300ppb (cat.# 30217)  
 8240 Mix 2A at 500ppb (cat.# 30218)



**Slower Run  
 OPTIMIZED  
 Separations**

1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. ethanol
8. 1,1-dichloroethene
9. carbon disulfide
10. iodomethane
11. allyl chloride
12. methylene chloride
13. acetone
14. *trans*-1,2-dichloroethene
15. 1,1-dichloroethane

16. acrylonitrile
17. allyl alcohol
18. vinyl acetate
19. bromochloromethane
20. chloroform
21. carbon tetrachloride
22. propargyl alcohol
23. 1,1,1-trichloroethane
24. 2-butanone
25. benzene
26. propionitrile
27. methacrylonitrile
28. 1,2-dichloroethane-d4
29. isobutyl alcohol
30. 1,2-dichloroethane

31. trichloroethene
32. 1,4-difluorobenzene
33. dibromomethane
34. 1,2-dichloropropane
35. bromodichloromethane
36. methyl methacrylate
37. 1,4-dioxane
38. 2-chloroethanol
39. 2-chloroethyl vinyl ether
40. *cis*-1,3-dichloropropene
41. toluene-d8
42. toluene
43. pyridine
44. 4-methyl-2-pentanone
45. tetrachloroethene

46. *trans*-1,3-dichloropropene
47. ethyl methacrylate
48. 1,1,2-trichloroethane
49. dibromochloromethane
50. 1,2-dibromoethane
51. 2-hexanone
52. 2-picoline
53. chlorobenzene-D5
54. ethylbenzene
55. chlorobenzene
56. 1,1,1,2-tetrachloroethane
57. *m*-xylene
58. *p*-xylene
59. *o*-xylene
60. styrene

61. bromoform
62. 4-bromo-1-fluorobenzene
63. *cis*-1,4-dichloro-2-butene
64. 1,1,2,2-tetrachloroethane
65. 1,2,3-trichloropropane
66. *trans*-1,4-dichloro-2-butene
67. pentachloroethane
68. 1,3-dichlorobenzene
69. 1,4-dichlorobenzene
70. benzyl chloride
71. malononitrile
72. 1,2-dichlorobenzene
73. 1,2-dibromo-3-chloropropane

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# EPA Method 624

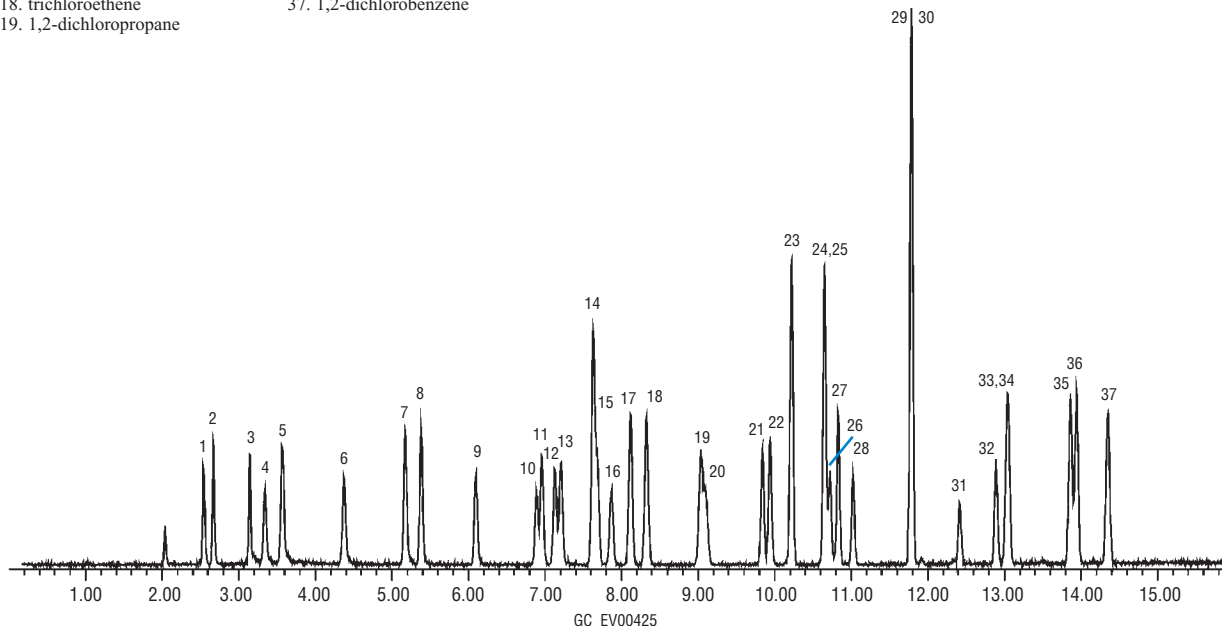
- ◆ 37 aromatic and halogenated compounds in wastewater
- ◆ Previously used packed columns, but can be performed with many different capillary column dimensions
- ◆ Rtx-VMS 30m x 0.25mm x 1.4um gives separation in less than 15 minutes, starting at 40°C

# EPA Method 624 Rtx®-VMS

- |                                     |                                       |
|-------------------------------------|---------------------------------------|
| 1. chloromethane                    | 20. bromodichloromethane              |
| 2. vinyl chloride                   | 21. 2-chloroethyl vinyl ether         |
| 3. bromomethane                     | 22. <i>cis</i> -1,3-dichloropropene   |
| 4. chloroethane                     | 23. toluene                           |
| 5. trichlorofluoromethane           | 24. tetrachloroethene                 |
| 6. 1,1-dichloroethene               | 25. <i>trans</i> -1,3-dichloropropene |
| 7. methylene chloride               | 26. 2-bromo-1-chloropropane           |
| 8. <i>trans</i> -1,2-dichloroethene | 27. 1,1,2-trichloroethane             |
| 9. 1,1-dichloroethane               | 28. dibromochloromethane              |
| 10. bromochloromethane              | 29. ethylbenzene                      |
| 11. chloroform                      | 30. chlorobenzene                     |
| 12. carbon tetrachloride            | 31. bromoform                         |
| 13. 1,1,1-trichloroethane           | 32. 4-bromofluorobenzene              |
| 14. benzene                         | 33. 1,4-dichlorobutane                |
| 15. pentafluorobenzene              | 34. 1,1,2,2-tetrachloroethane         |
| 16. 1,2-dichloroethane              | 35. 1,3-dichlorobenzene               |
| 17. fluorobenzene                   | 36. 1,4-dichlorobenzene               |
| 18. trichloroethene                 | 37. 1,2-dichlorobenzene               |
| 19. 1,2-dichloropropane             |                                       |

30m, 0.25mm ID, 1.40µm Rtx®-VMS (cat#19915)  
 Conc.: 20 ppb in 5mL of RO water  
 Concentrator: Tekmar LSC-3000 Purge and Trap  
 Trap: Vocarb 3000 (type K)  
 Purge: 11 min. @ 40mL/min. @ ambient temperature.  
 Dry purge: 1 min. @ 40mL/min. (MCS bypassed using Silcosteel® tubing)

Desorb preheat: 245°C  
 Desorb: 250°C for 2 min. , Flow 10mL/min.  
 Bake: 260°C for 8 min.  
 GC Interface: 1:10 split at injection port. 1mm ID sleeve.  
 GC: HP 6890  
 Oven temp.: 40°C (hold 4 min.) to 95°C @ 24°C/min. (hold 3 min.), to 210°C @ 40°C/min. (hold 6 min.)  
 Carrier gas: helium @ ~1mL/min. constant flow  
 Adjust dichlorodifluoromethane to a retention time of 2.54 min. @ 40°C  
 Detector: HP 5973 MSD  
 Scan range: 25-300amu



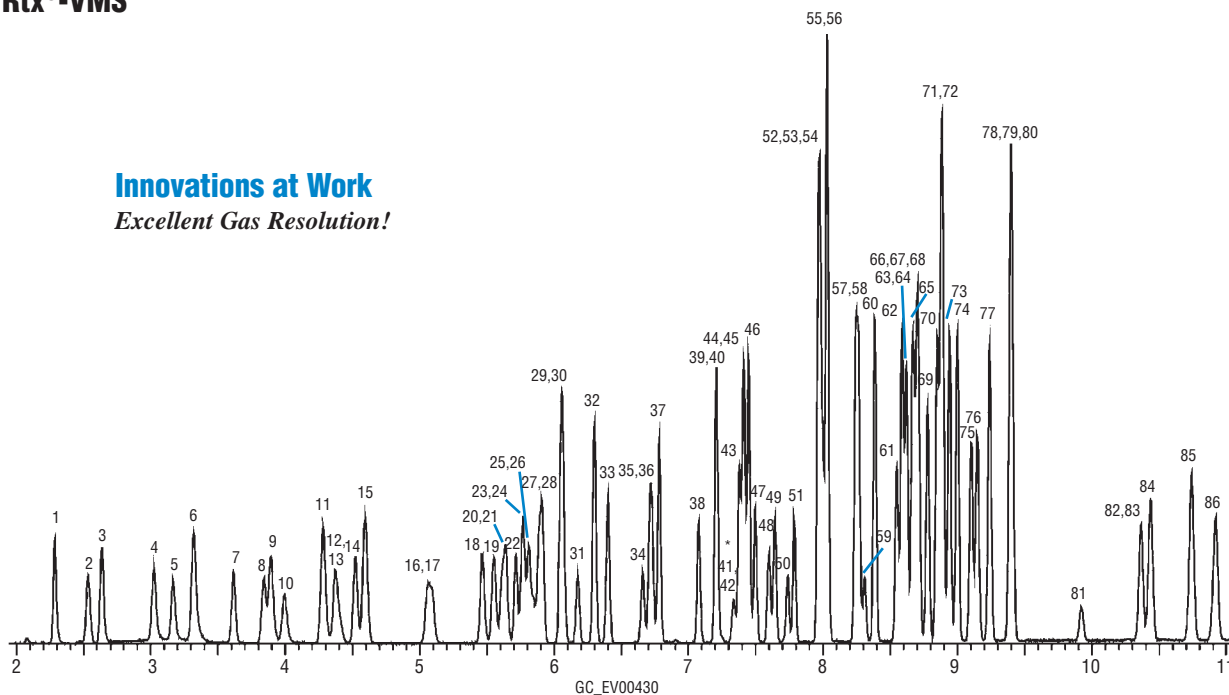
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## EPA Method 524.2 revision IV

- ◆ Monitors 84 compounds in drinking water
- ◆ Rtx-VMS overcomes closely eluting pairs found on other phases (ex. “624”) such as 1,1-dichloro-2-propanone/4-methyl-2-pentanone and methyl acrylate/propionitrile
- ◆ Rtx-VMS 30m x 0.25mm x 1.4um performs the analysis in less than 11 minutes
- ◆ Only difficult pair on the Rtx-VMS is 2-nitropropane/ 1,1-dichloro-2-propanone which share ion 43

# EPA Method 524.2, Revision 4 Rtx®-VMS

**Innovations at Work**  
*Excellent Gas Resolution!*



30m, 0.25mm ID, 1.4µm Rtx®-VMS (cat.# 19915)  
Carrier gas: helium @ ~1.3mL/min. constant flow  
Adjust dichlorodifluoromethane to a retention time of 2.29 min. @ 45°  
Concentrator: Tekmar LSC-3000 Purge and Trap  
Oven temp.: 45°C (hold 2 min.) to 85°C @ 14°C/min. to 210°C @ 40°C/min. (hold 4 min.)  
GC: HP 6890 Series II  
Trap: Vocab 3000  
Purge: 11 min. @ 40mL/min.  
Dry purge: 1 min. @ 40mL/min. (MCS bypassed)  
Desorb preheat: 245°C  
Desorb: 250°C for 2 min.  
Bake: 260°C for 8 min.  
Interface: 1:10 split in port  
Transfer line: 5m, 0.32mm ID Siltek™ tubing (cat.# 10027)  
Detector: HP 5973 MSD  
Scan range: 35-300amu

Standards:  
20ppb in 5mL of RO water (unless otherwise noted); ketones at 40ppb.  
502.2 Cal Mix #1 (cat.# 30042)  
502.2 Cal2000 MegaMix™ (cat.# 30431)  
524 Cal Mix 7A & 7B (cat.# 30202)  
524 Cal Mix #8 (cat.# 30203)  
524 IS/SS Mix (cat.# 30201)

- |                                      |                                     |                                       |   |
|--------------------------------------|-------------------------------------|---------------------------------------|---|
| 1. dichlorodifluoromethane           | 23. carbon tetrachloride            | 45. <i>trans</i> -1,3-dichloropropene | 67. 1,2,3-trichloropropane              |
| 2. chloromethane                     | 24. tetrahydrofuran (40ppb)         | 46. ethyl methacrylate                | 68. <i>trans</i> -1,4-dichloro-2-butene |
| 3. vinyl chloride                    | 25. 1,1,1-trichloroethane           | 47. 1,1,2-trichloroethane             | 69. 4-chlorotoluene                     |
| 4. bromomethane                      | 26. 2-butanone                      | 48. dibromochloromethane              | 70. <i>tert</i> -butylbenzene           |
| 5. chloroethane                      | 27. 1,1-dichloropropene             | 49. 1,3-dichloropropane               | 71. 1,2,4-trimethylbenzene              |
| 6. trichlorofluoromethane            | 28. 1-chlorobutane                  | 50. 1,2-dibromoethane                 | 72. pentachloroethane                   |
| 7. diethyl ether                     | 29. benzene                         | 51. 2-hexanone                        | 73. <i>sec</i> -butylbenzene            |
| 8. 1,1-dichloroethane                | 30. propionitrile                   | 52. ethylbenzene                      | 74. <i>p</i> -isopropyltoluene          |
| 9. carbon disulfide (40ppb)          | 31. 1,2-dichloroethane              | 53. chlorobenzene                     | 75. 1,3-dichlorobenzene                 |
| 10. iodomethane (40ppb)              | 32. fluorobenzene                   | 54. 1,1,1,2-tetrachloroethane         | 76. 1,4-dichlorobenzene                 |
| 11. allyl chloride                   | 33. trichloroethene                 | 55. <i>m</i> -xylene                  | 77. <i>n</i> -butylbenzene              |
| 12. methylene chloride               | 34. dibromomethane                  | 56. <i>p</i> -xylene                  | 78. hexachloroethane                    |
| 13. acetone                          | 35. 1,2-dichloropropane             | 57. <i>o</i> -xylene                  | 79. 1,2-dichlorobenzene-d4              |
| 14. <i>trans</i> -1,2-dichloroethane | 36. bromodichloromethane            | 58. styrene                           | 80. 1,2-dichlorobenzene                 |
| 15. methyl <i>tert</i> -butyl ether  | 37. methyl methacrylate             | 59. bromoform                         | 81. 1,2-dibromo-3-chloropropane         |
| 16. 1,1-dichloroethane               | 38. <i>cis</i> -1,3-dichloropropene | 60. isopropylbenzene                  | 82. nitrobenzene                        |
| 17. acrylonitrile                    | 39. toluene                         | 61. 4-bromofluorobenzene              | 83. hexachlorobutadiene                 |
| 18. <i>cis</i> -1,2-dichloroethane   | 40. chloroacetonitrile              | 62. <i>n</i> -propylbenzene           | 84. 1,2,4-trichlorobenzene              |
| 19. 2,2-dichloropropane              | 41. 2-nitropropane*                 | 63. bromobenzene                      | 85. naphthalene                         |
| 20. bromochloromethane               | 42. 1,1-dichloropropanone*          | 64. 1,1,2,2-tetrachloroethane         | 86. 1,2,3-trichlorobenzene              |
| 21. chloroform                       | 43. 4-methyl-2-pentanone            | 65. 1,3,5-trimethylbenzene            |   |
| 22. methyl acrylate                  | 44. tetrachloroethene               | 66. 2-chlorotoluene                   |   |

\*These peaks (41 and 42) share a quantitation ion (43)

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# Conclusions

- ◆ Computer modeling can be used to optimize phase development, column dimensions and run conditions
- ◆ Column dimensions to interface with the GC/MS is a matter of customer preference
- ◆ Analysis of 100 + compounds typically use longer columns for better resolution and higher starting temperatures
- ◆ Rtx-VMS has excellent selectivity and rapid cycle time for all commonly used EPA GC/MS volatile methods



# For More Information...

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# Selecting an LC/MS Interface

Becky Wittrig, Ph.D.  
RESTEK CORPORATION



# LC/MS Interfaces

- I. Background of LC/MS
  - I. Historical Perspective
  - II. Reasons for use
- II. Interfaces
  - I. Transport devices
  - II. Particle Beam
  - III. Thermospray
  - IV. Atmospheric Pressure Interfaces



# Historical Perspective

- Goldstein – 1886
  - Existence of positively charged particles
- Wein – 1898
  - Positively charged ions can be deflected in electrical and magnetic fields
- J.J. Thomson – 1913
  - Demonstrated isotopes of Neon
  - “Father of mass spectrometry”
- First GC-MS interface - 1960's

# Historical Perspective

- First LC-MS interface developed - 1969
  - 1  $\mu$ L/min flow into an EI source
- Transport devices applied to LC/MS - 1970's
  - Loss of volatile components
  - Thermally-reactive compound losses
- Thermospray (TSI) gains popularity - 1983
  - 1.0 – 1.5 mL/min
  - Mobile phases consist primarily of an aqueous buffer

# Historical Perspective

## Atmospheric Pressure Interfaces (API)

- Early 1990's (commercialization)
- Now most common interface
- Electrospray (ESI)
  - Initial interfaces required lower flows (1-5 uL/min)
  - Able to produce multiply-charged molecules
- Atmospheric Pressure Chemical Ionization
  - Similar to Thermospray
  - "Solvent-mediated" ionization

# Why Use Mass Spectrometry?

- Spectral resolution is possible
  - Chromatographic coelutions
- Compound identification from spectral data
  - Mass spectrum is very dependant on the ionization
  - Limited availability of LC/MS libraries
- High degree of specificity

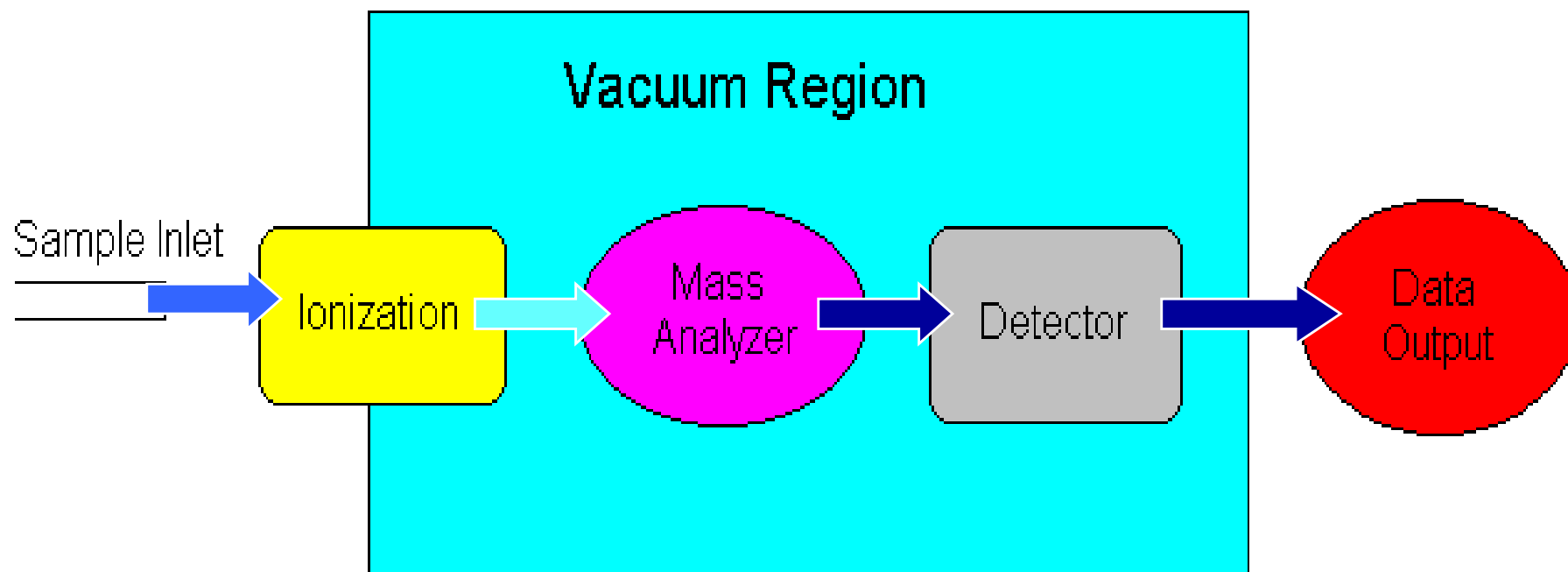
# LC/MS Interfaces

- I. Background of LC/MS
  - I. Historical Perspective
  - II. Reasons for use
- II. Interfaces
  - I. Transport devices
  - II. Particle Beam
  - III. Thermospray
  - IV. Atmospheric Pressure Interfaces





# Components of an MS Detector



Ions  
Made

Ions  
Selected

Ions  
Detected

# LC/MS Systems Interfaces

## Analyzers

- Transport Devices
- Particle Beam
- Thermospray
- Atmospheric Pressure
  - Electrospray
  - APCI
- Others

- Quadrupoles
- Ion Trap
- MS<sup>n</sup>
- High Resolution
- Time-of-Flight (TOF)
- Others

# Ion Sources

- Analytes must be charged (ions)
  - Needed to separate and detect
- Where ionization occurs
  - In the interface
  - In a separate ion source
- Types of ionization
  - “Hard” - considerable fragmentation
  - “Soft” - molecular ion is main product
- Ions can be positive or negative

# Requirements of LC/MS Interfaces

- Elimination of the mobile phase
  - Most difficult step
  - Can use splitters
  - Volatilized solvent vapor removed under vacuum
- Often where ionization occurs
- Vacuum required by mass analyzers

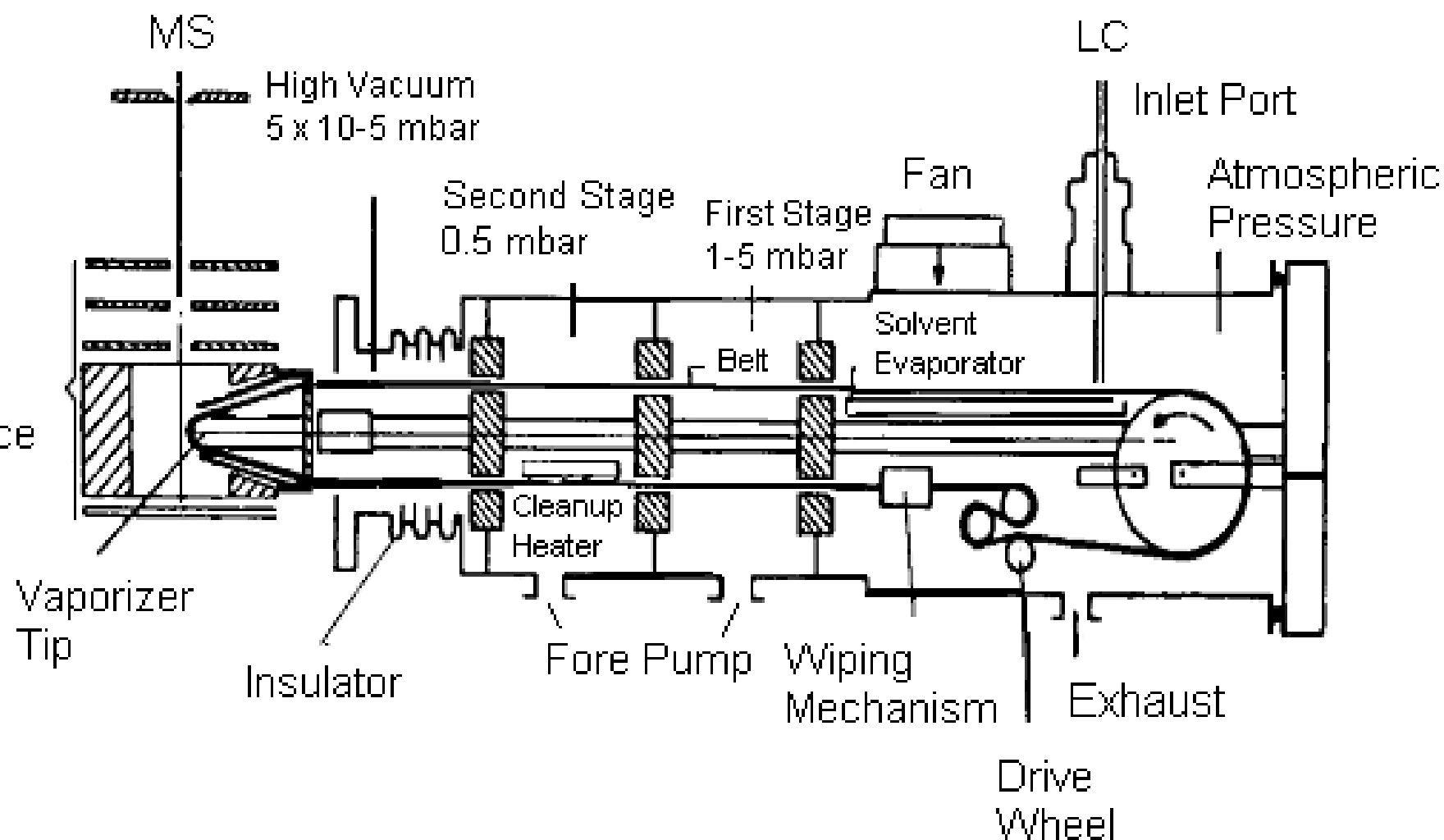
# Challenges in Interfacing LC to MS

- Flow Rate Concerns
  - Differential pumping can only handle 2  $\mu\text{L}/\text{min}$  of water
  - For maximum sensitivity, want to use all of the eluent
- Use of Buffers and Additives
  - Non-volatile buffers a concern
  - Some additives suppress ionization
- Wide Range of Analytes
  - Many are nonvolatile, thermally labile

# Transport Devices

- One of the first commercial interfaces
- Sample deposited onto a moving belt or wire
- Sample passes through multiple vacuum zones
  - Solvent elimination
- Sample is desorbed into source using heat
  - Electron impact ionization
- Belt/wire cycles back

# Moving Belt Interface



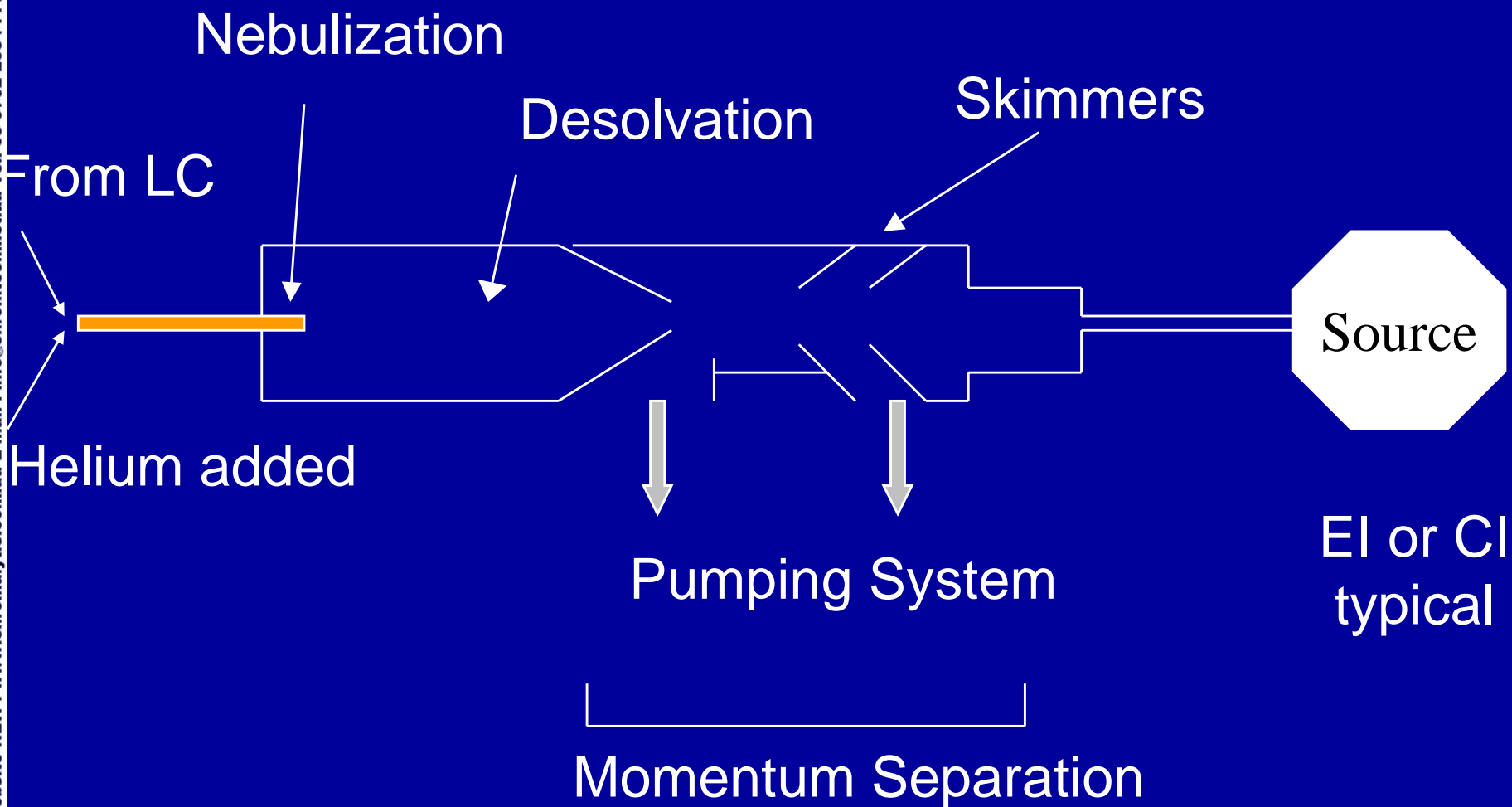
From: Niessen

# Particle Beam Interface

- Column effluent is nebulized
  - Pneumatic or thermospray nebulization
- Desolvation chamber is under a moderate vacuum
- A momentum separator is used for analyte enrichment
  - High MW compounds favored
- Analytes into the EI or CI source as small particles
  - Evaporative collisions with the walls

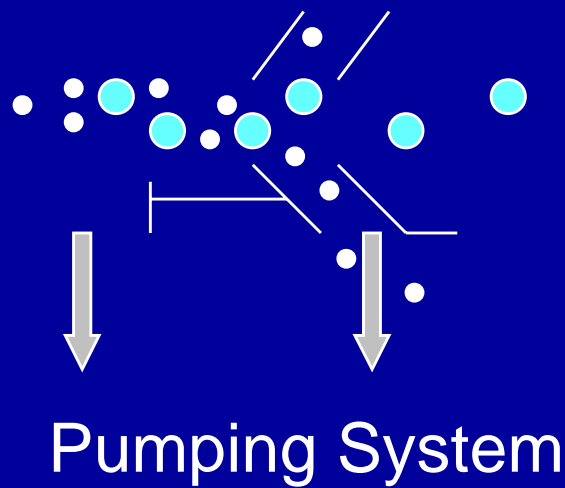


# Particle Beam Interface



# Analyte Enrichment in PB Interfaces

- Analyte Ion
- Solvent

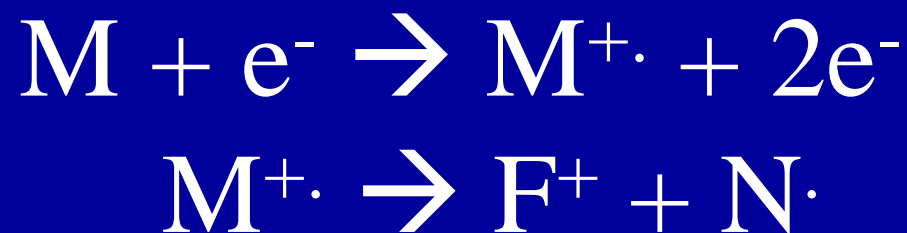


Analyte enrichment with a molecular beam approach

Heavier molecules are in the core of the vapor jet and are sampled through the skimmer

# Electron Impact Ionization

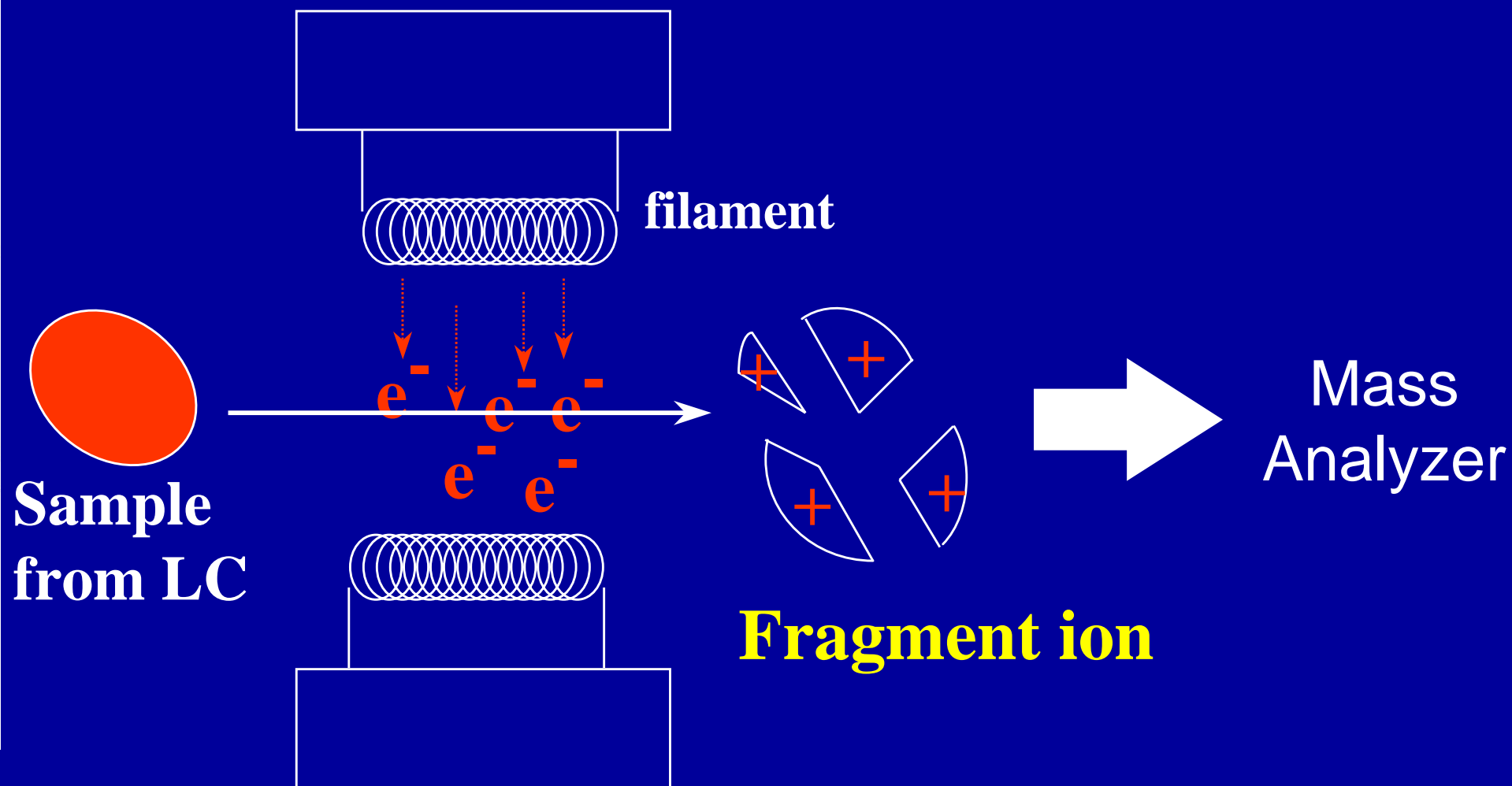
- LC interfaces with the ion source
- Electrons are “boiled” from a hot wire (filament), and accelerated (70eV)
- As electrons pass neutral molecules, they may remove outer shell electrons



# Electron Impact Ionization

- Produces positively charged ions
- Fragmentation is generally significant for most molecules – “hard ionization”
  - Masses of these fragments is the information used in interpretation
- Efficiency of ionization is  $1/10^5$ 
  - Bulk of molecules are removed by vacuum pump – Use Traps

# Electron Impact Ionization (EI)



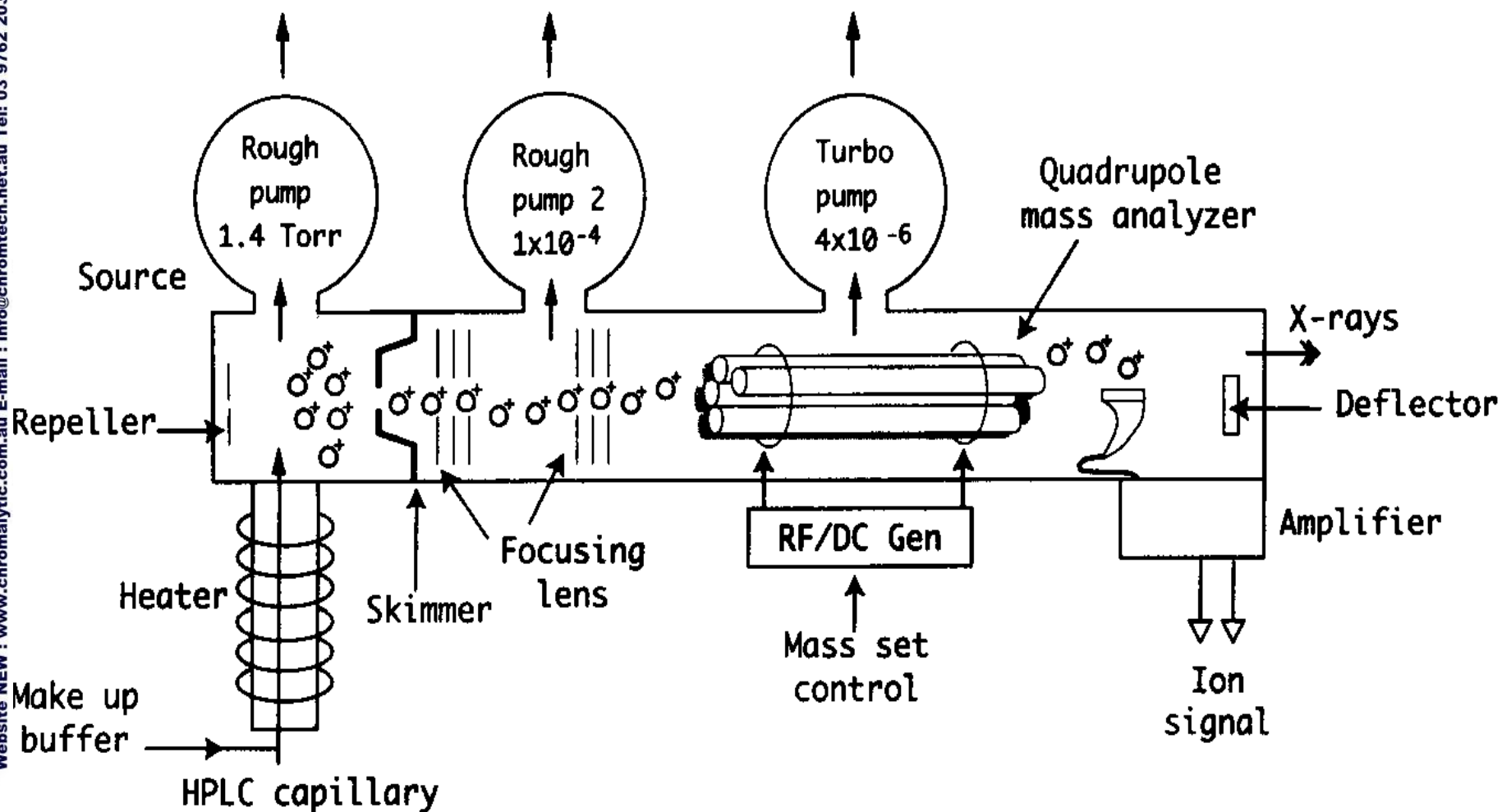
# Thermospray Interface

- Nebulization of the eluent from a heated transfer tube
- Uses a “reagent gas”
  - Mobile phase buffer
  - Added buffer solution
  - Similar spectra to GC/MS CI
- Reagent gas is ionized
  - Volatilization
  - EI with high energy electrons
- Charge transfer to the analyte(s)

# Thermospray Interface

- Effectively replaced transport systems
- Ionization in a medium pressure environment
  - Approx. 1000 Pa or 0.01 atm
- Inlet flows of 1 to 2 mL/min
  - Can use standard LC column flows
- Positive and negative ions are possible
- Temperature optimization is critical
  - Maintain gas phase

# Thermospray LC/MS System

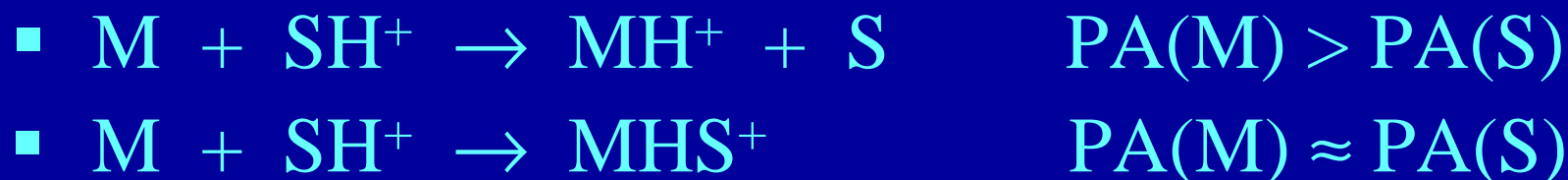


From: McMaster and McMaster

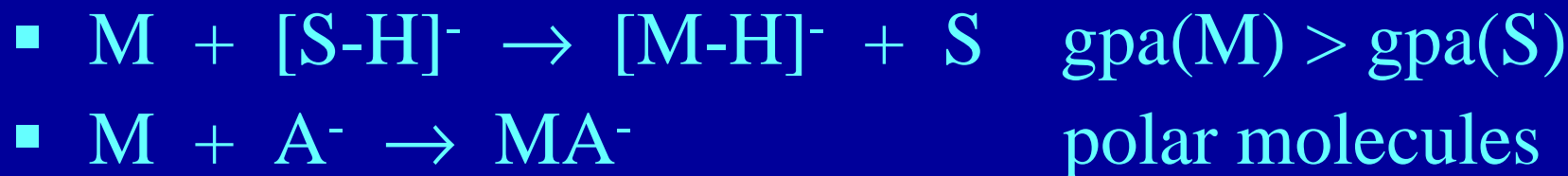


# Thermospray Ionization

- Positive Ion Mode



- Negative Ion Mode



$gpa$  = gas phase acidity

# Typical Proton Affinities

Compound	Proton Affinity
Water	723
Methanol	773
Acetonitrile	797
Ethers, esters, ketones	630-670
PAHs	710-800
Carboxylic Acids	<800
Alcohols	750-840
Peptides	880-1000

From: Niessen

# Thermospray Modes of Operation

- Solvent-Mediated CI
  - Typical mobile phase: MeOH or MeCN + 0.1M NH<sub>4</sub>OAc
  - Ionization by ion evaporation (pre-formed ions) or ion-molecule reactions
- Discharge or Filament On Mode
  - High energy electrons (0.5-1 keV) ionize the reagent gas
  - Ion-molecule reactions

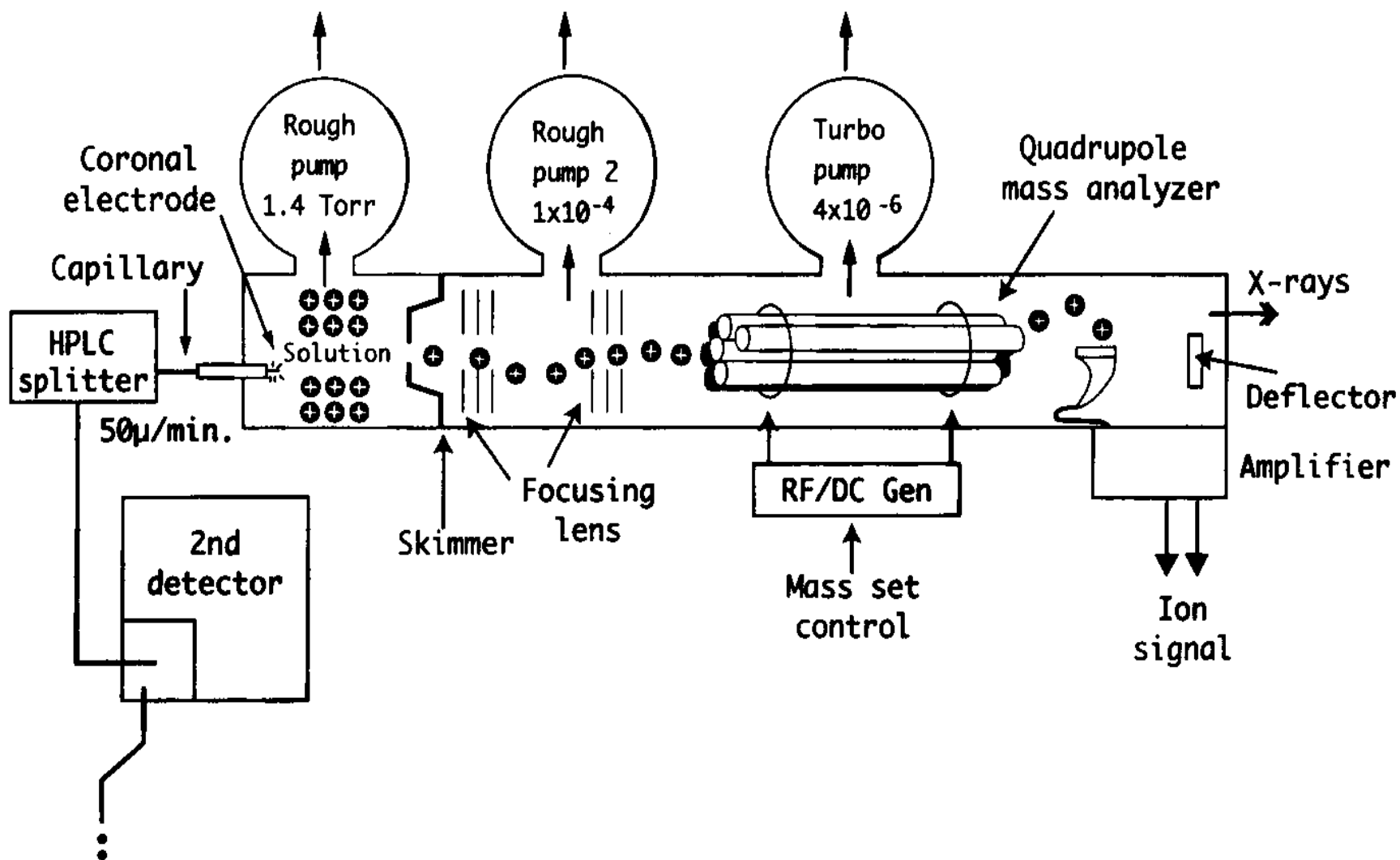
# Electrospray Interface

- High electric potential applied to eluent from transfer capillary
  - Atmospheric pressure
  - Droplet formation
  - Ionization in the solution phase
- Orthogonal sampling of ions
  - Reduces contamination of the sampling orifice
  - Z-Spray devices

# Electrospray Interface

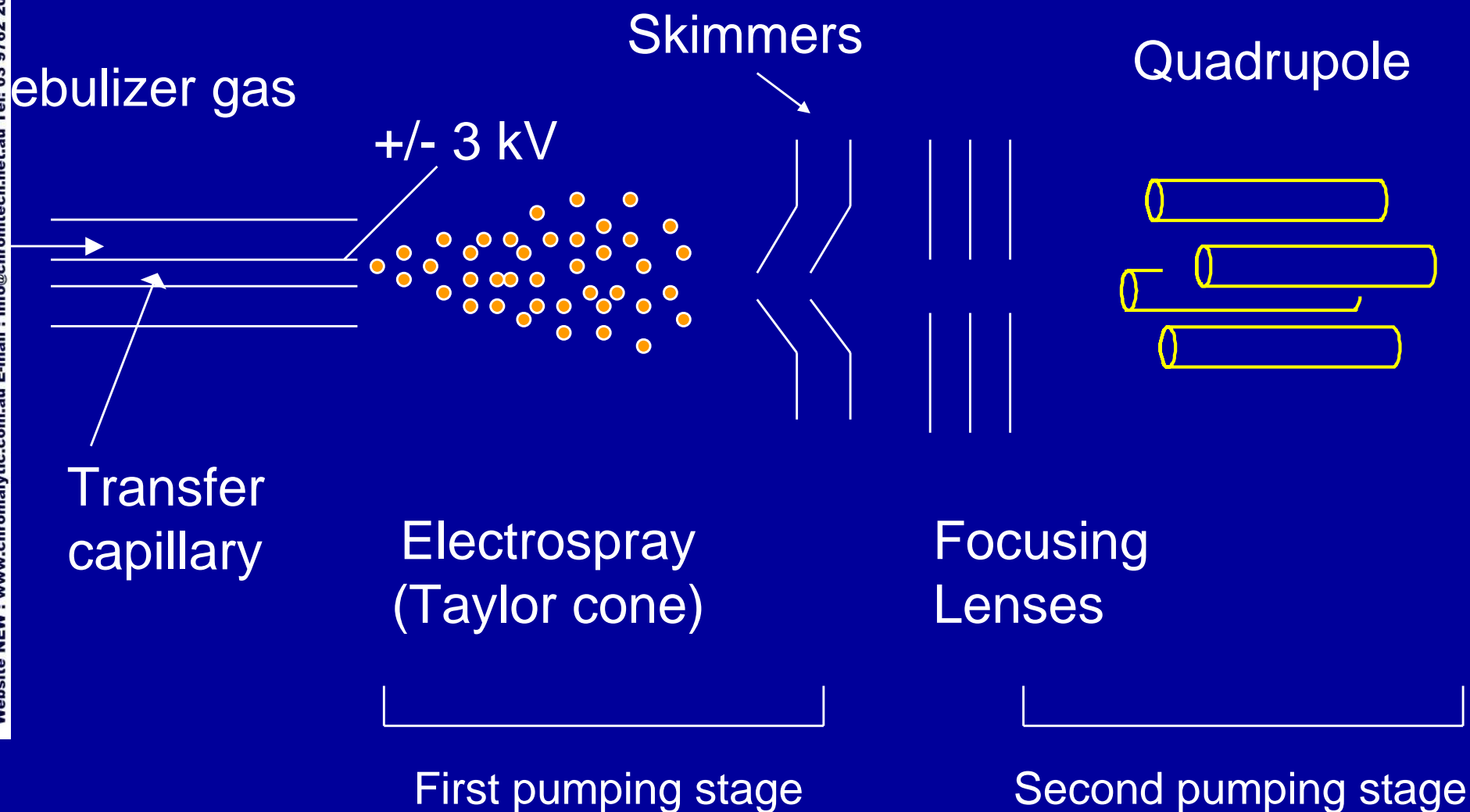
- Higher flows now possible
  - Pneumatic + thermal nebulizers
- Applicable to volatile and nonvolatile analytes
  - Need to be ionizable
- Can create multiply-charged ions
  - Allows for analysis of large molecules

# Electrospray LC/MS System

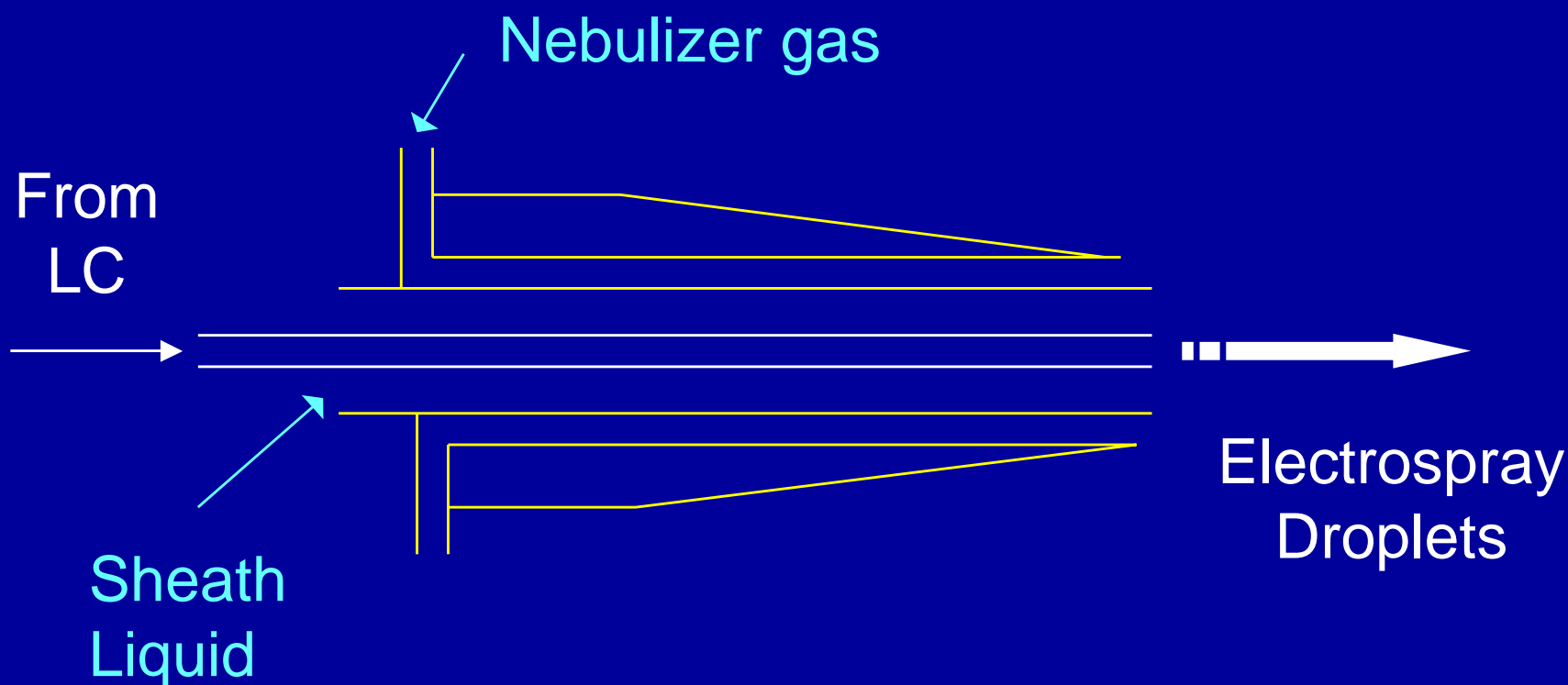


From: McMaster and McMaster

# Electrospray Interface



# Electrospray Needle Design



Example of an electrospray needle design (coaxial flow)

The nebulizer gas disrupts the liquid surface so that small droplets are formed and then dispersed by the gas

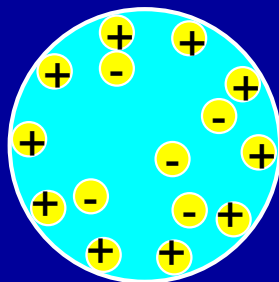


# Theory of API Electrospray

Charged Droplets



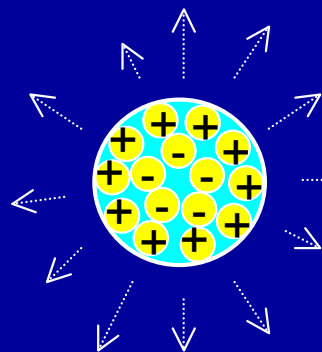
Analyte Ions



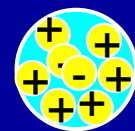
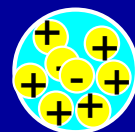
Evaporation



**Rayleigh  
Limit  
Reached**



**Coulomb Explosions**



Solvent Ion Clusters  
Salts/Ion pairs  
Neutrals



Solvent Ion Cluster



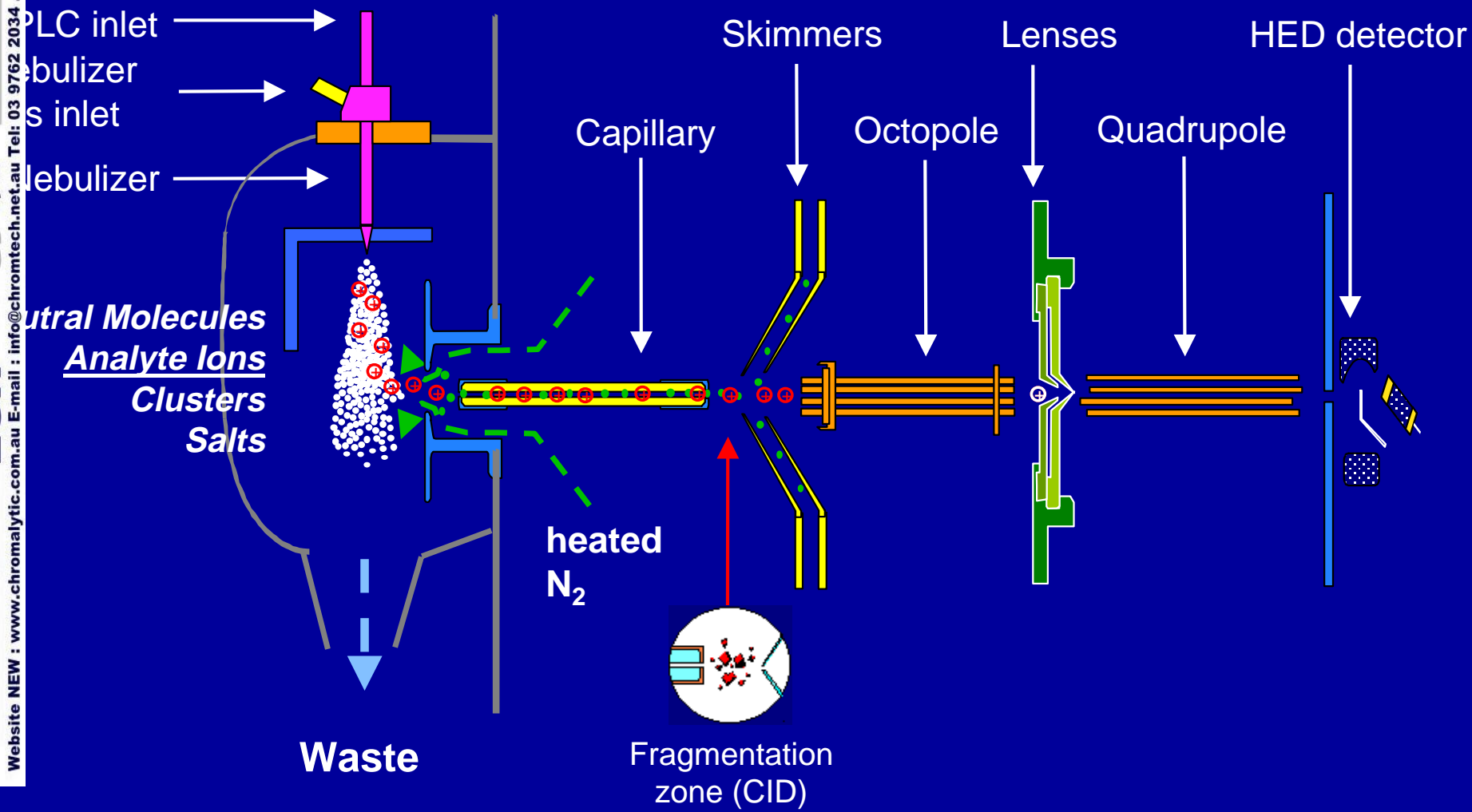
Analyte Ion

*Courtesy of Agilent Technologies*

# Agilent 1100 LC/MSD Electrospray

Australian Distributors  
Importers & Manufacturers  
www.chromtech.net.au

Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034  
HROMalytic Pty Ltd  
ECH nology Pty Ltd



Courtesy of Agilent Technologies

# Electrospray Interface

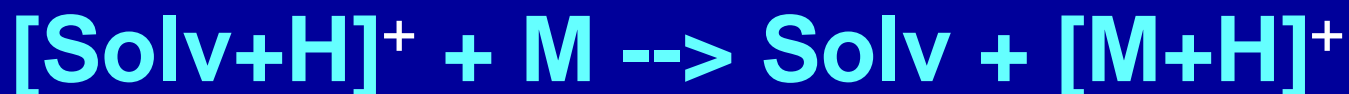
- Best vaporization with higher % organic and lower flow rates
- Cluster ion formation possible
  - Solvent clusters
  - Analyte/salt clusters
- Salts and sample impurities can affect the response
  - TFA causes signal suppression
  - TFA anion masks the analyte ion

# APCI Interface

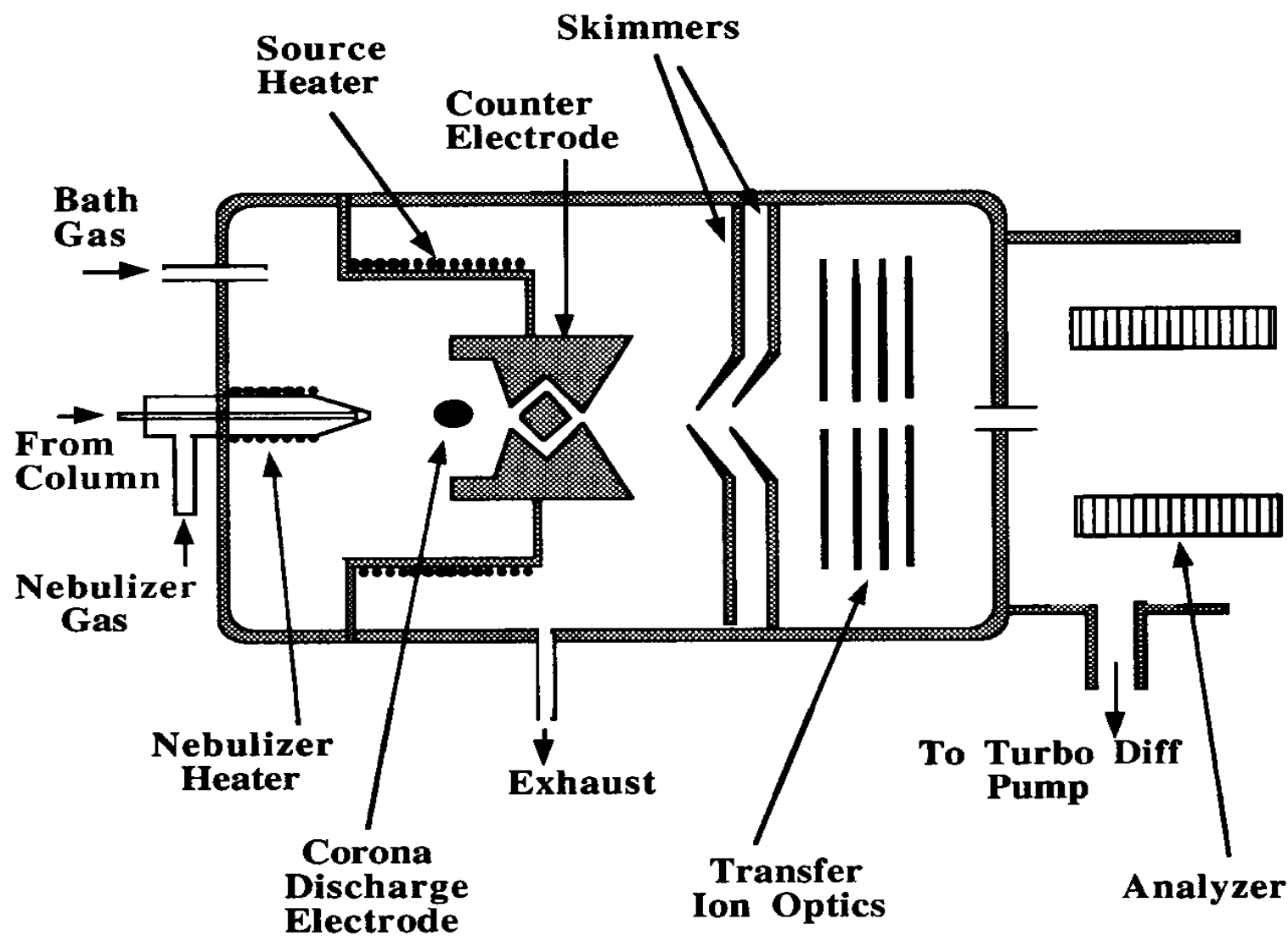
- Atmospheric Pressure Chemical Ionization
- Initially investigated in 1974
  - Popular in late 1980's
- Uses an API (ESI) source
- Column effluent nebulized into heated vaporizer tube
- Solvent vapor acts as a reagent gas
  - Charge transfer to the analytes
- Can be very sensitive

# APCI Interface

- Results in a chemical ionization spectrum  $[M+H]^+$  or  $[M-H]^-$
- Products depend on equilibrium (concentration) conditions
- Analytes must have sufficient proton affinities
- May be simplest interface to operate
- Liquid flow rates of 0.2-2.0 mL/min

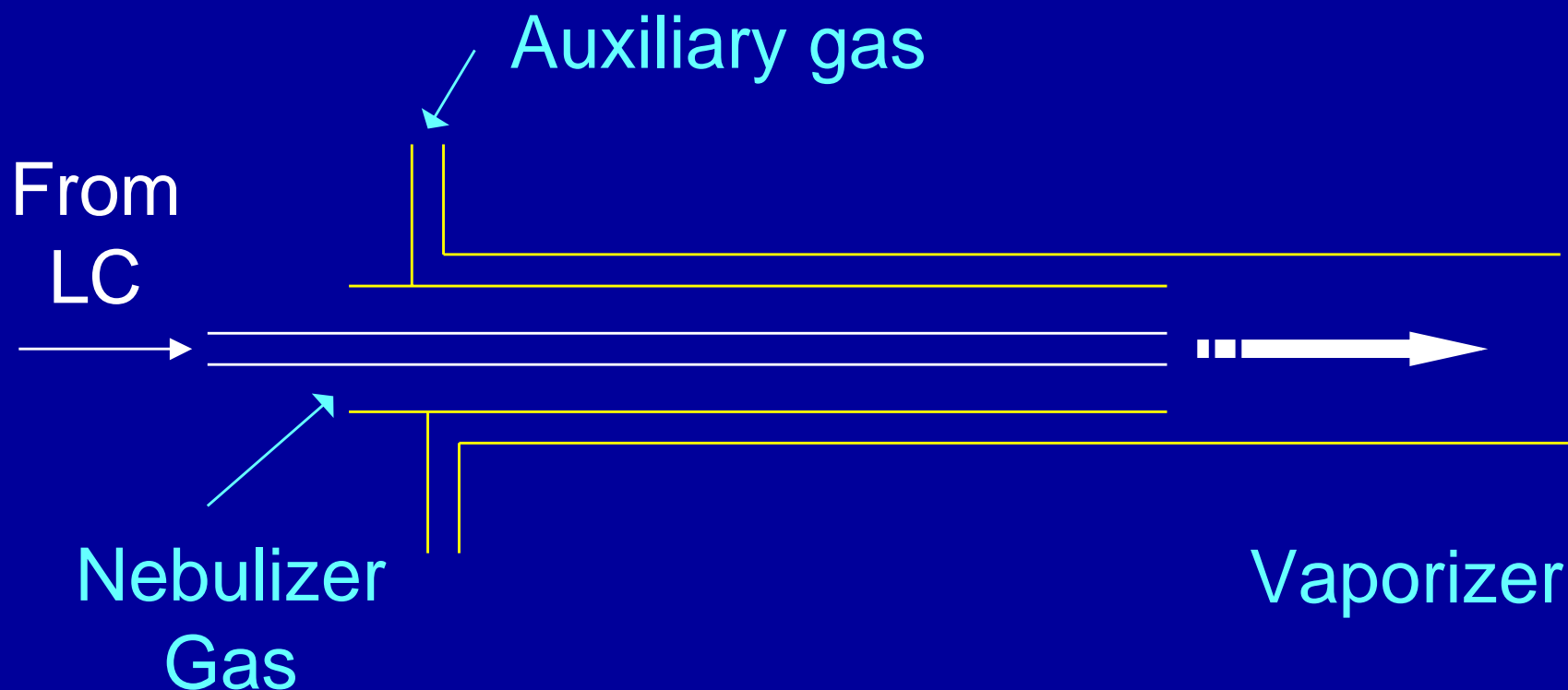


# APCI Interface



From: Scott

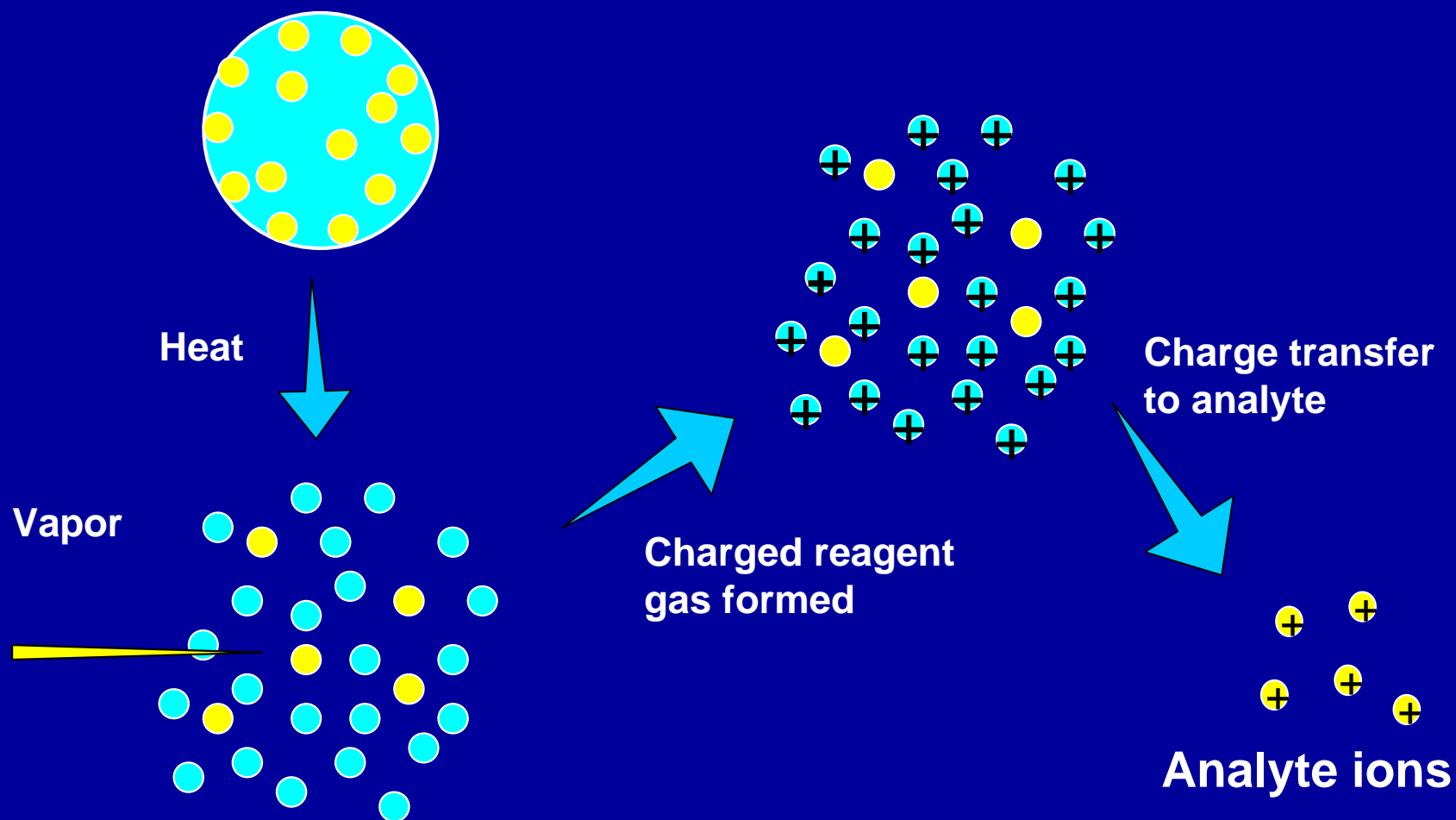
# APCI Probe (Heated)



The vaporizer tube temperature is optimized for complete transfer to the vapor state

# Theory of APCI

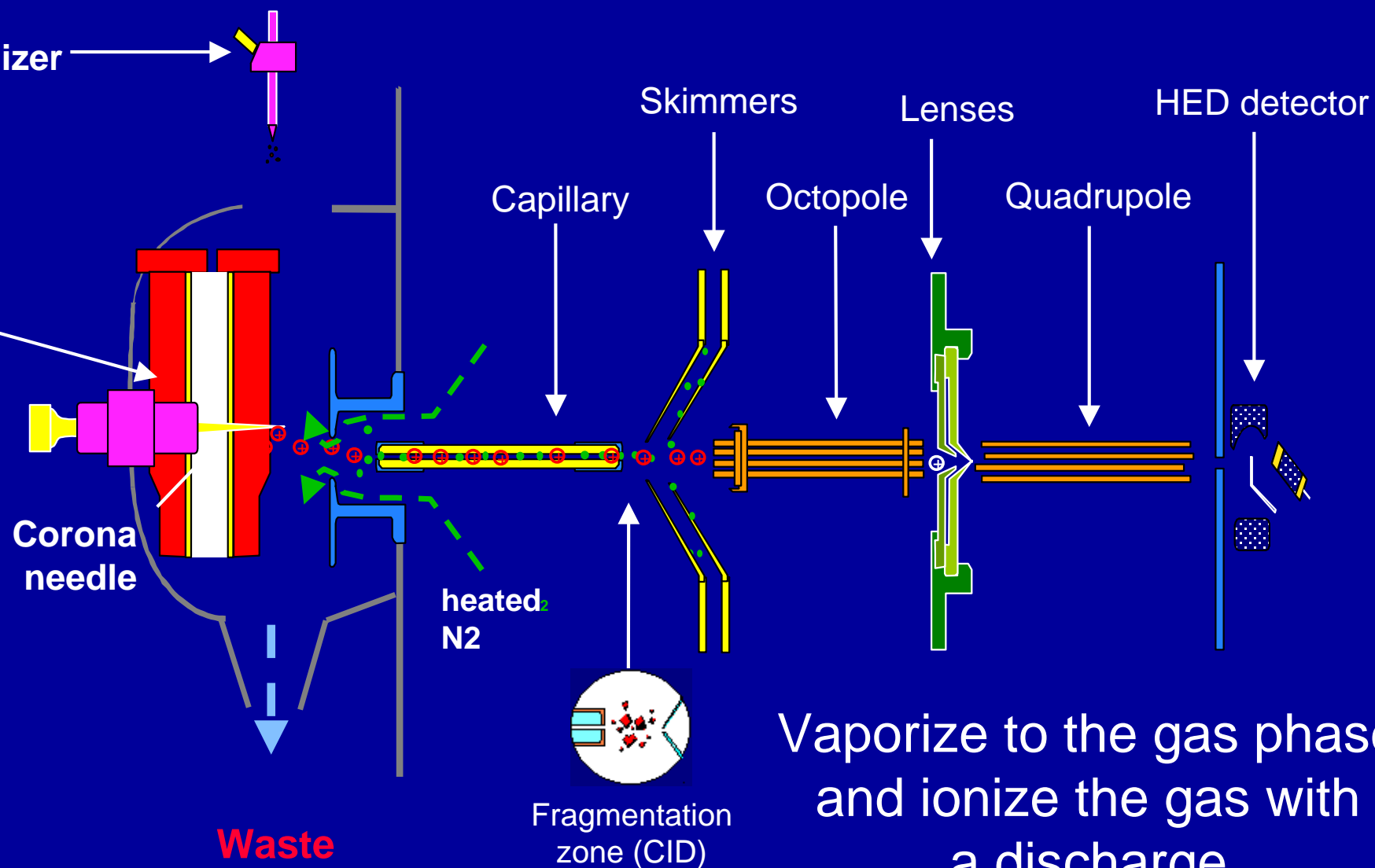
Analyte containing aerosol



*Courtesy of Agilent Technologies*



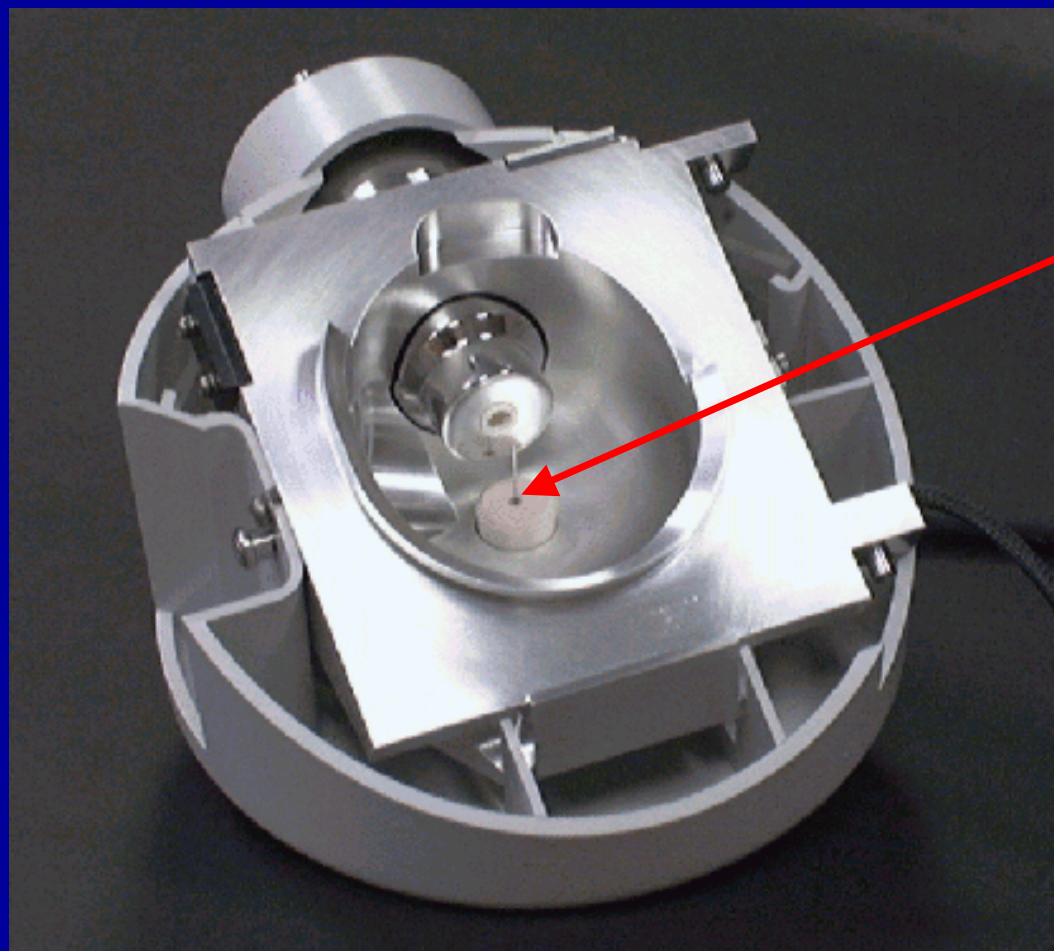
# Agilent 1100 LC/MSD - APCI



Vaporize to the gas phase  
and ionize the gas with  
a discharge

Courtesy of Agilent Technologies

# Agilent 1100 LC/MSD APCI Ion Source



Corona Needle

Vaporize into the gas phase and ionize the gas with a discharge

*Courtesy of Agilent Technologies*

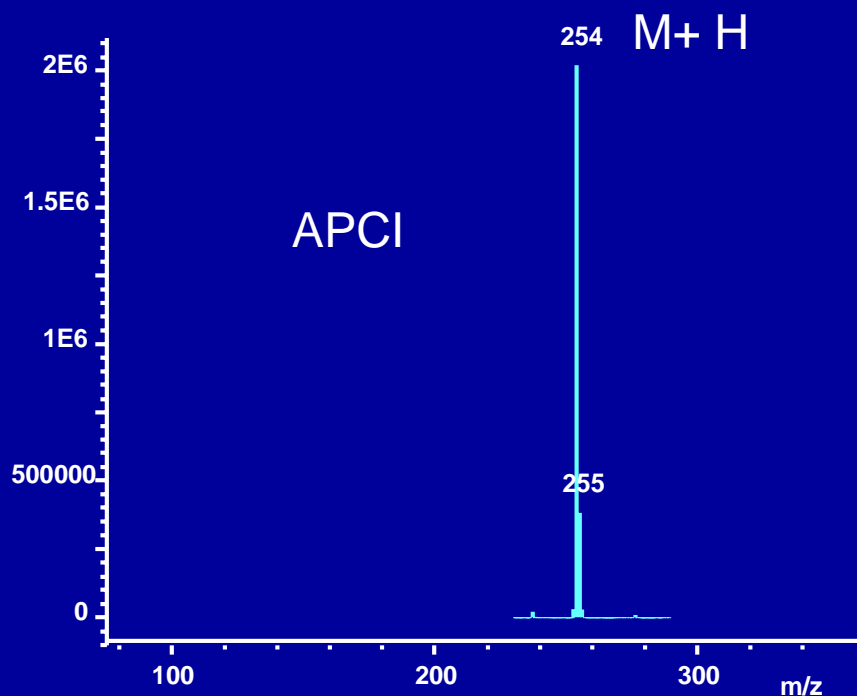
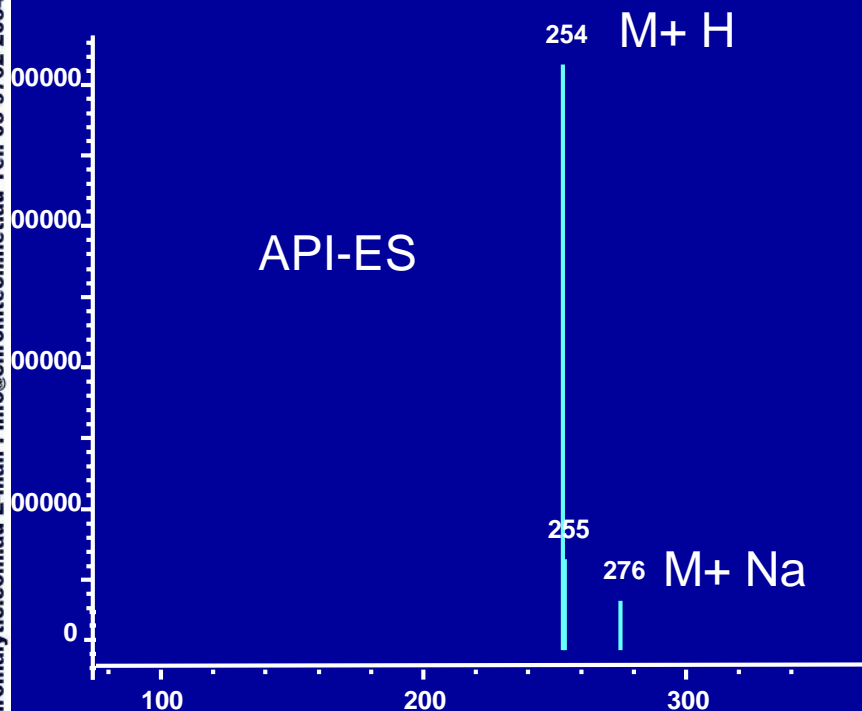


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Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA

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**ECH**nology Pty Ltd

# API-ES vs. APCI for Triamterene



Comparison of the mass spectra typical of  
Electrospray vs. APCI

# Optimizing Mobile Phases for API-MS

- Ion-Pair Agent Alternatives
  - Use highly bases-deactivated silica columns
  - Use low pH (3-4) to reduce tailing
  - Use columns that retain based on polar interactions (e.g. CN, IBD)
- Using Ion-Pair Reagents
  - Use low amounts (<0.02%)
  - Use post-column addition to negate the effect of the ion-pair agent

# Sample Considerations for LC/MS

## The Analyte Must Have Ionizable Groups

- Amines
- Carboxylic Acids
- Ketones, Aldehydes

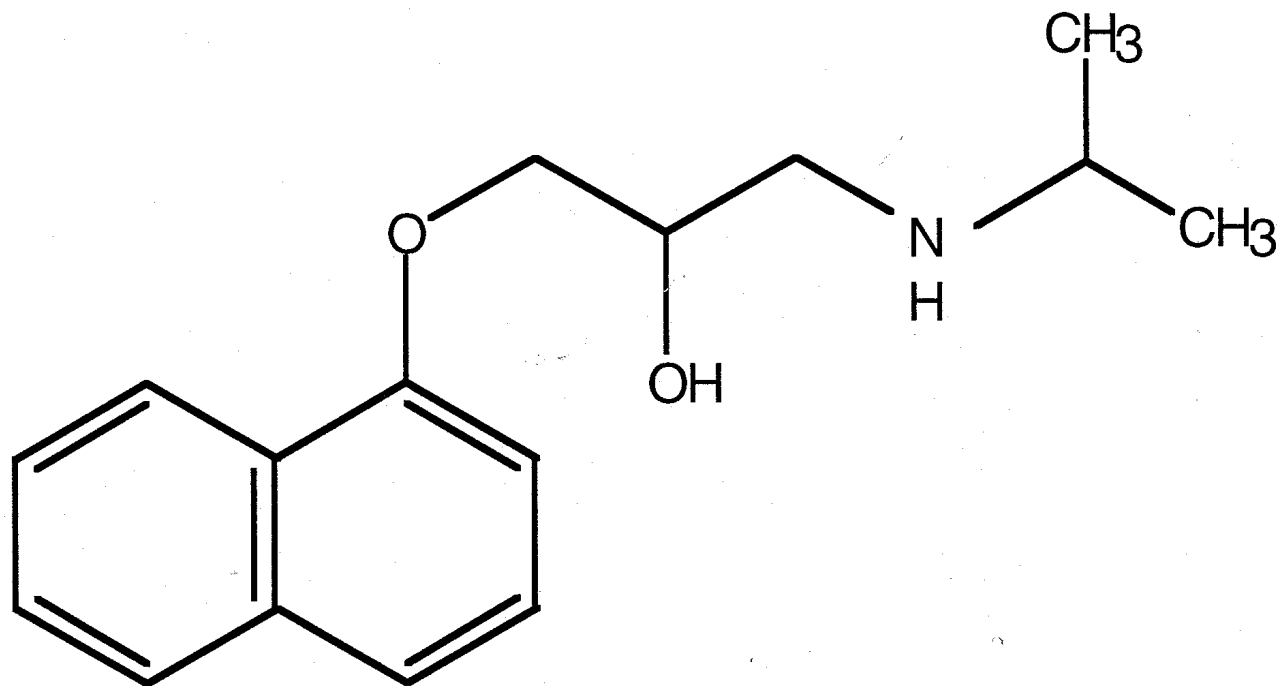
## For Best Sensitivity, Work at a pH Where the Analyte is Ionized

- Neutral to basic pH (7-9) for acids
- Acidic pH (3-4) for bases

# Sample Considerations

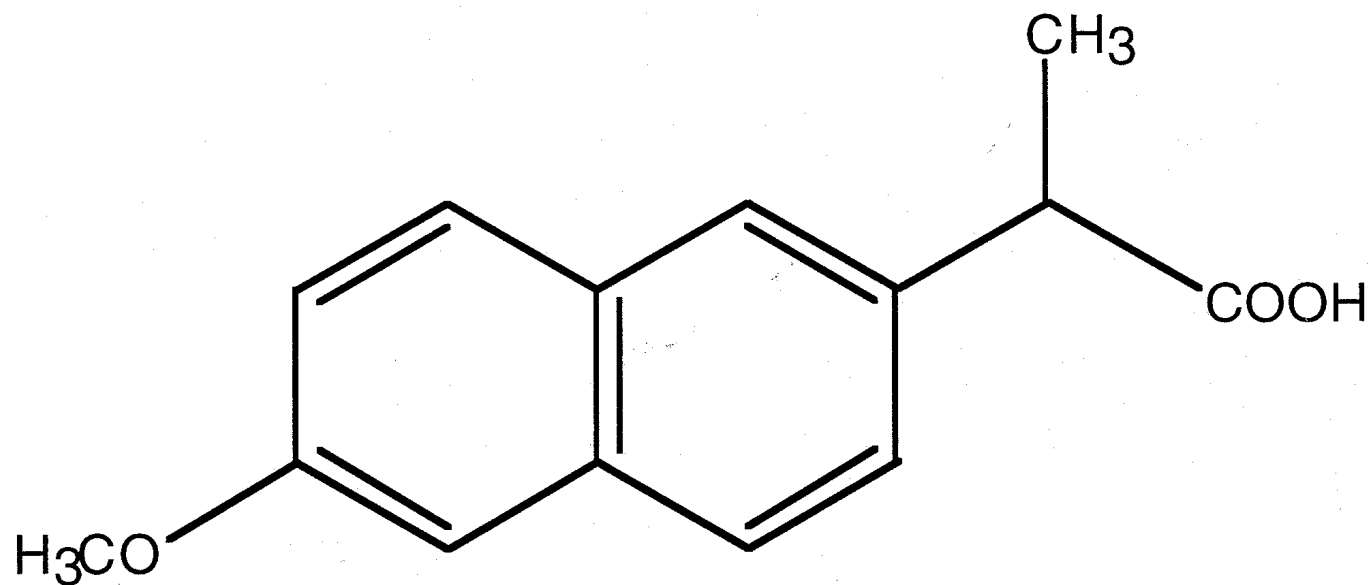
- Positive Ion Mode
  - Analyte =  $(M+H)^+$
- Negative Ion Mode
  - Analyte =  $(M-H)^-$

# Basic Compound – Sensitive in Positive Ion Mode



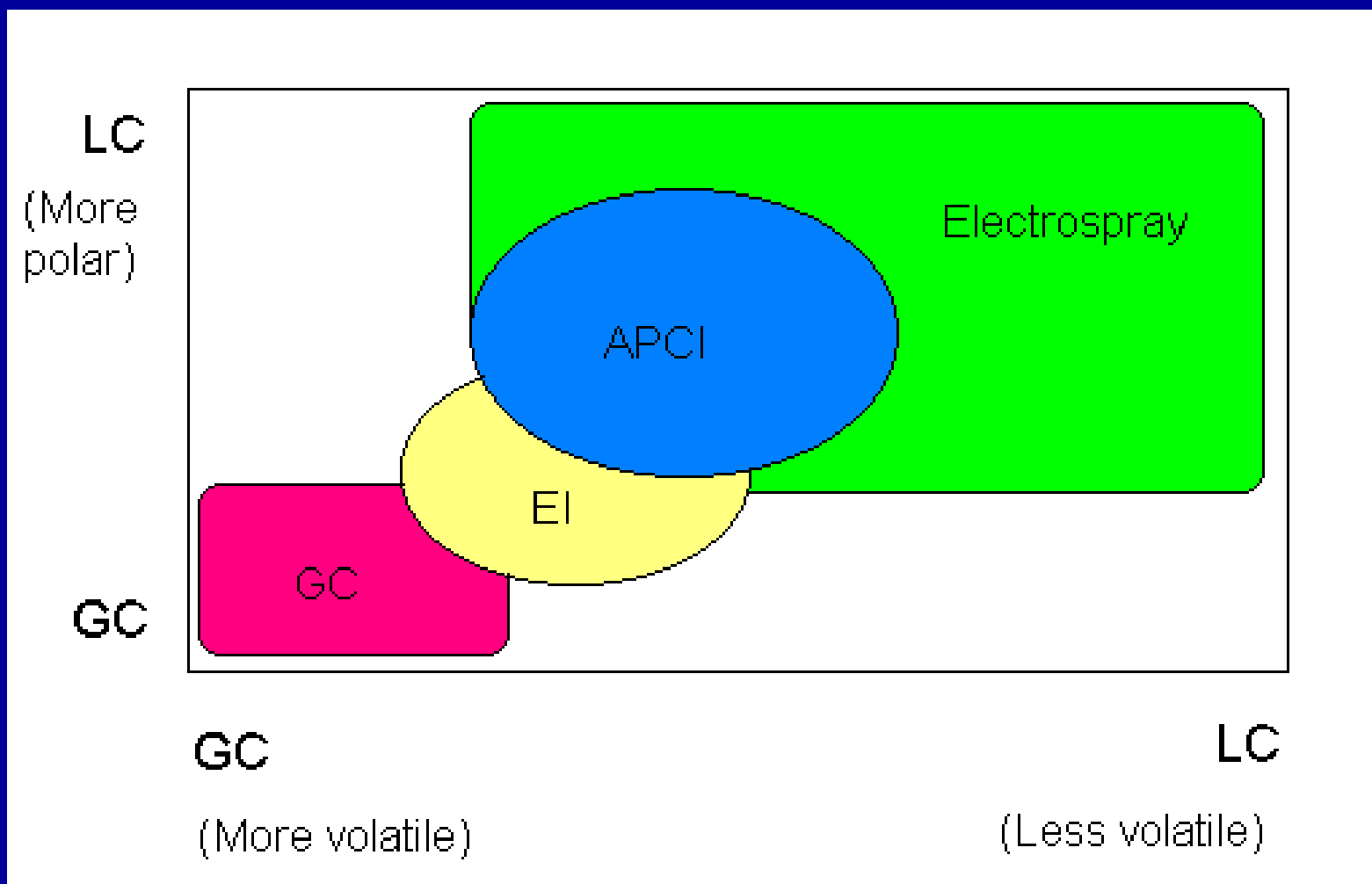


# Acidic Compound – Sensitive in Negative Ion Mode





# Selecting an Interface



“Advances in LC/MS”, Waters Corporation, Milford, MA.

# Electron Ionization (EI)

- Analytes Suitable for EI
  - Small molecules with rings and double bonds
  - Compounds that would need derivatization for GC/MS
  - Pesticides, PAHs, natural products
- Compound Identifications
  - Fragmentation is possible
- Poor Detection Limits
- Will Not Tolerate Non-Volatile Buffers

# Comparison of API vs. EI

- Atmospheric Pressure Ionization (API)

- MW confirmation
- Good for fragile compounds
- Able to fragment in the source
- Low (ppb) LODs in SIM mode

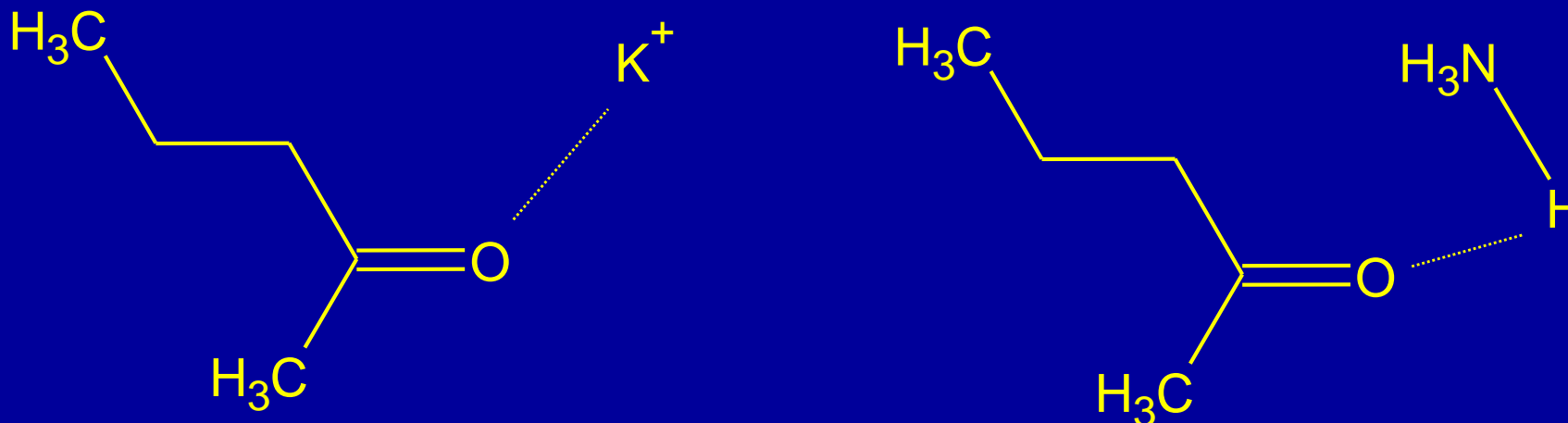
- Electron Ionization (EI)

- Ionization occurs in a vacuum
- Standard libraries are available
- Classical EI spectra (similar to GC/MS)
- Higher LODs (ppm to high ppb)

# Atmospheric Pressure Ionization (API)

- Electrospray Ionization (ESI) Uses Solution Phase Ionization
- Atmospheric Pressure Ionization (APCI) Uses Gas Phase Ionization
- Products are  $[M+H]^+$  and  $[M-H]^-$ , adducts
- Suitable for Analyzing Drugs, Small Molecules, Dyes, Peptides
- Good Sensitivity
- Thermal Degradation is Possible (APCI)

# Adduct Formation with API



Adducts can form between polar molecules and sample or solvent components. For example, adducts with  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $MeOH$ ,  $MeCN$ , and  $H_2O$  are common.

# Electrospray Ionization

- + Good molecular weight information, including high MW compounds
- + Can be used for volatiles, nonvolatiles, ionic/polar compounds
- + Good sensitivity
- Need relatively low flow rates
- Need to be able to form ions in solution
- Limited structural information
- Problems with high aqueous and buffer solutions

# Atmospheric Pressure Chemical Ionization

- + Gives molecular weight information
- + Easy to use, rugged
- + Can use higher LC flow rates (up to 2 mL/min)
- Thermal degradation can occur
- Limited structural information
- Not appropriate for higher MW (e.g., >1000 Da)

# MALDI

- Matrix-assisted laser desorption/ionization
  - Sample is deposited on a target and co-crystallized with a solid matrix (dihydroxybenzoic acid)
  - Desorption/ionization occurs using a laser such as Nd-YAG (266nm,  $v^4$ )
  - Energy transferred to matrix, then analyte
  - Useful in excess of 200kDa (biomacromolecules)



# Fast Atom Bombardment (FAB)

- Cf-FAB = Continuous Flow FAB
- Column eluent mixes with a matrix (glycerol)
- Eluent + matrix deposited on a target
- Analyte film hit with fast atoms or ions
- Only low flow rates used

# Acknowledgements

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Charlie Schmidt - Thermo Instruments

Agilent Technologies

Liquid Chromatography-Mass Spectrometry, Marcel Dekker, New York, NY, W.M.A. Niessen ed. 1999

Chromatographic Detectors, Marcel Dekker, New York, NY, Raymond P.W. Scott ed. 1996

GC/MS A Practical Users Guide, Marvin C McMaster and Christopher McMaster, Wiley-VCH, New York, NY 1988

# Gas Chromatographic Analysis of Polybrominated Diphenyl Ethers Using a Novel GC Column and Direct Flash Injection

Frank L. Dorman, Chris English, Karen MacPherson, and Eric Reiner

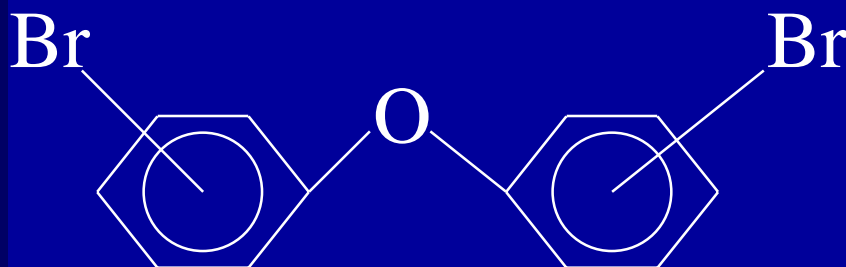
Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



## Brominated Diphenylether Flame Retardants:

- Products based on penta-, octa-, and decaBDE are commercially used as flame retardants.
- Global production of DeBDE is approximately 40,000 tons/year.
- Heavily used for furniture treatment and electronics in USA, Japan, and Europe
- May form PBDDs and PBDFs when combusted, and toxicity is estimated to be similar to PCDDs and PCDFs

# Polybrominated Diphenylethers



## Br 1-10

- Named similarly to PCB congeners (BDE 1-209)  
J. High Resolut Chromatogr **15**:260
- Human exposure via the food chain is 0.2 – 0.7 mg/day  
Organohalogen Compounds **35**:411
- Listed as Endocrine Disruptors  
Environ Health Perspect **101**:378

# Common Amenable Methods of Analysis

- High-resolution mass spectrometric detection
  - Additional specificity may improve sensitivity in complex matrices
  - Many dioxin labs are also interested in PBDE's
- Electron capture detection
  - More common to most labs
  - Lower cost
- Others not investigated yet
  - GC-NCI-MS
  - HPLC-MS

# Prior Reported Analyses

- GC-HRMS

- Difficulty eluting nona's and decaBDE due to high molecular weight
- On-column injection required to minimize molecular weight discrimination
  - May require more maintenance and cleaner sample extracts than hot flash techniques.
- Column bleed levels hurt sensitivity of higher bromination level congeners
- Often done using two columns:
  - Longer column to separate lower bromination level congeners
  - Short column to analyze nona and decaBDE's



# Prior Methods of Analysis

- Decision made if deca (and possibly nona and octa) are desired.
  - Higher molecular weight congeners are either analyzed separately, or not at all.
  - Higher molecular weight congeners are allowed to “ghost” out on “standard” column (5% diphenyl)
  - If interested in BDE 209, longer run times are common
- Loss of higher molecular weight congeners is generally due to injection technique



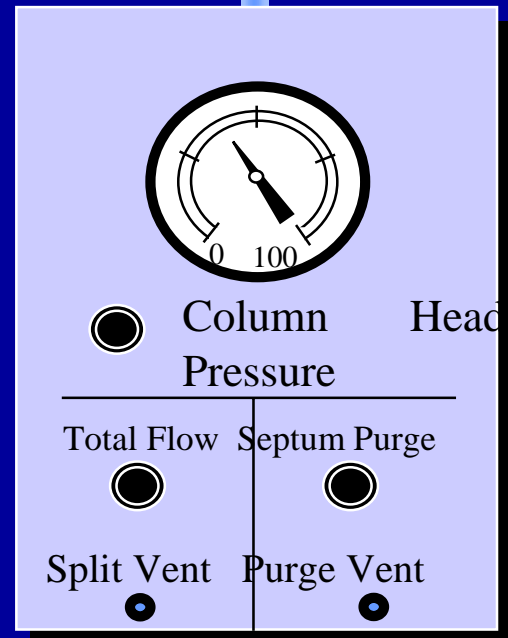
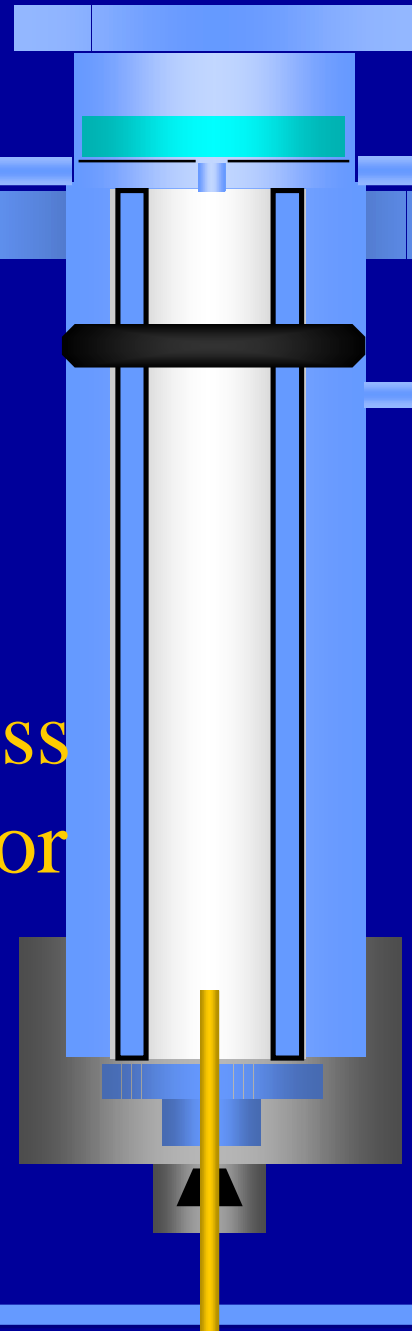
## Analytical Needs:

- Need injection technique which does not have discrimination issues like splitless
- Extracts may contain high levels of contamination, and not all labs will want to thoroughly clean the extracts
- High temperature stationary phase and column that has necessary selectivity, and low bleed levels

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Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034 . . . in AUSTRALIA

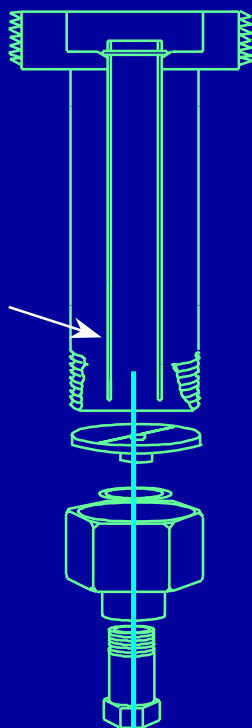
# HP 5890 Splitless Capillary Injector



restek www.restekcorp.com

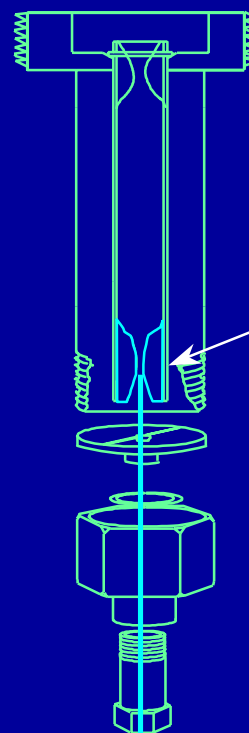
# Convert Split or Splitless Inlets to Direct Injection Mode

Remove the split or splitless sleeve



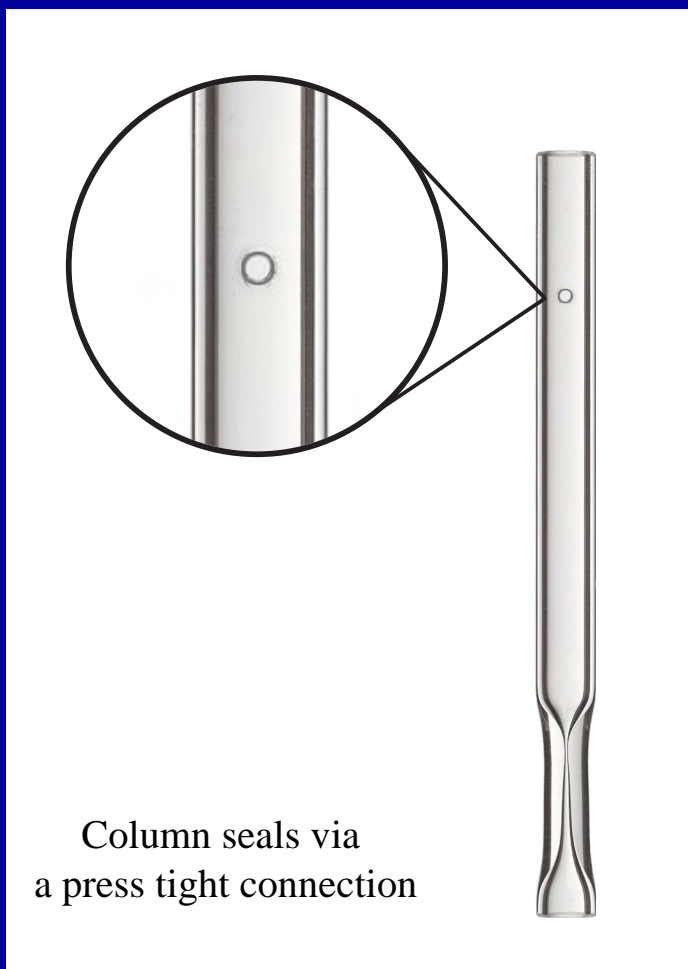
Install a Direct Injection sleeve

Press-fit connection



restek [www.restekcorp.com](http://www.restekcorp.com)

## Uniliner w/ Hole



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

Column seals via  
a press tight connection

# Rtx-500 Capillary GC Column

- Carborane-stabilized stationary phase
  - Maximum temperature of 380 C in “standard high-temperature” tubing
  - Maximum temperature of 440 C in passivated metal columns (Mxt-500)
- Extremely low bleed levels
  - Surpasses phenyl/methyl phases, and silphenylene stationary phases
- Common dimensions available

# Wellington Laboratories BDE Mix-C

4-bromodiphenyl ether (3)	250	141,115
2,4-Dibromodiphenyl ether (7)	168	328,139
4,4'-dibromodiphenyl ether (15)	328	168,221
2,2',4-tribromodiphenyl ether (17)	248	408,406
2,4,4'-tribromodiphenyl ether (28)	406	248,246
2,2',4,5'-tetrabromodiphenyl ether (49)	326	486,328,324
2,3',4',6-tetrabromodiphenyl ether (71)	326	486,324,328
2,2',4,4'-tetrabromodiphenyl ether (47)	326	486,328,324
2,3',4,4'-tetrabromodiphenyl ether (66)	326	486,328,324
3,3',4,4'-tetrabromodiphenyl ether (77)	326	486,328,324
2,2',4,4',6-pentabromodiphenyl ether (100)	406	564,566
2,3',4,4',6-pentabromodiphenyl ether (119)	404	406,564
2,2',4,4',5-pentabromodiphenyl ether (99)	406	564,566
2,2',3,4,4'-pentabromodiphenyl ether (85)	406	564,566
3,3',4,4',5-pentabromodiphenyl ether (126)	566	564,568,406
2,2',4,4',5,6'-hexabromodiphenyl ether (154)	484	644,486
2,2',4,4',5,5'-hexabromodiphenyl ether (153)	644	484,486,482
2,2',3,4,4',5'-hexabromodiphenyl ether (138)	642	484
2,2',3,4,4',5',6-heptabromodiphenyl ether (183)	722	564
decabromodiphenyl ether (209)	956	

# Baseline separation of Tri, Tetra, Penta, Hexa, Hepta, and DecaBDE's congeners in 44 minutes!

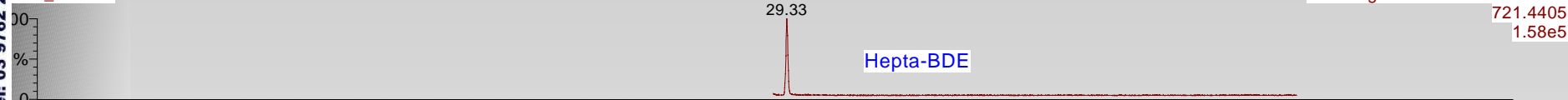
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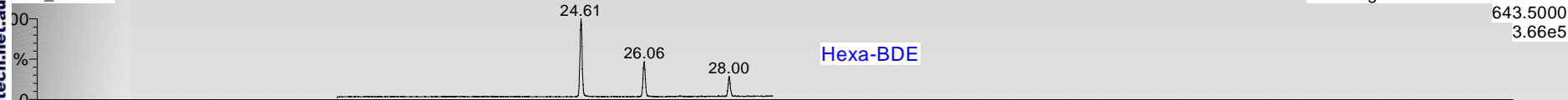
le209 13C  
:b04\_02bde2



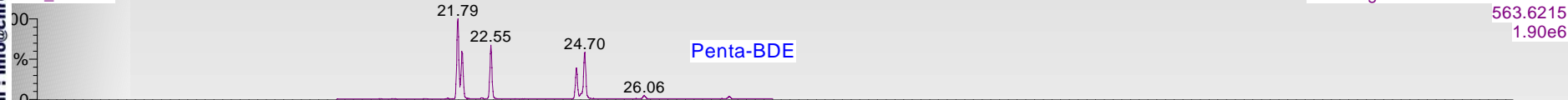
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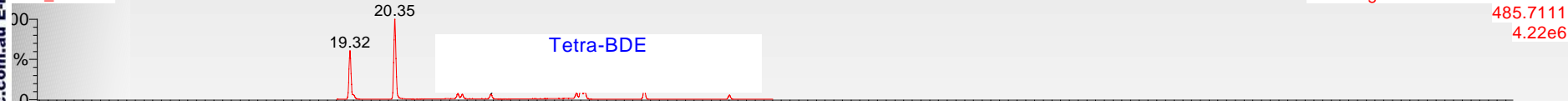
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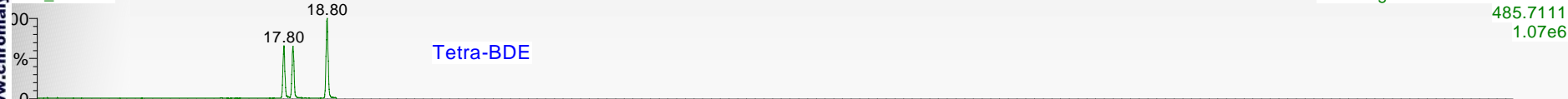
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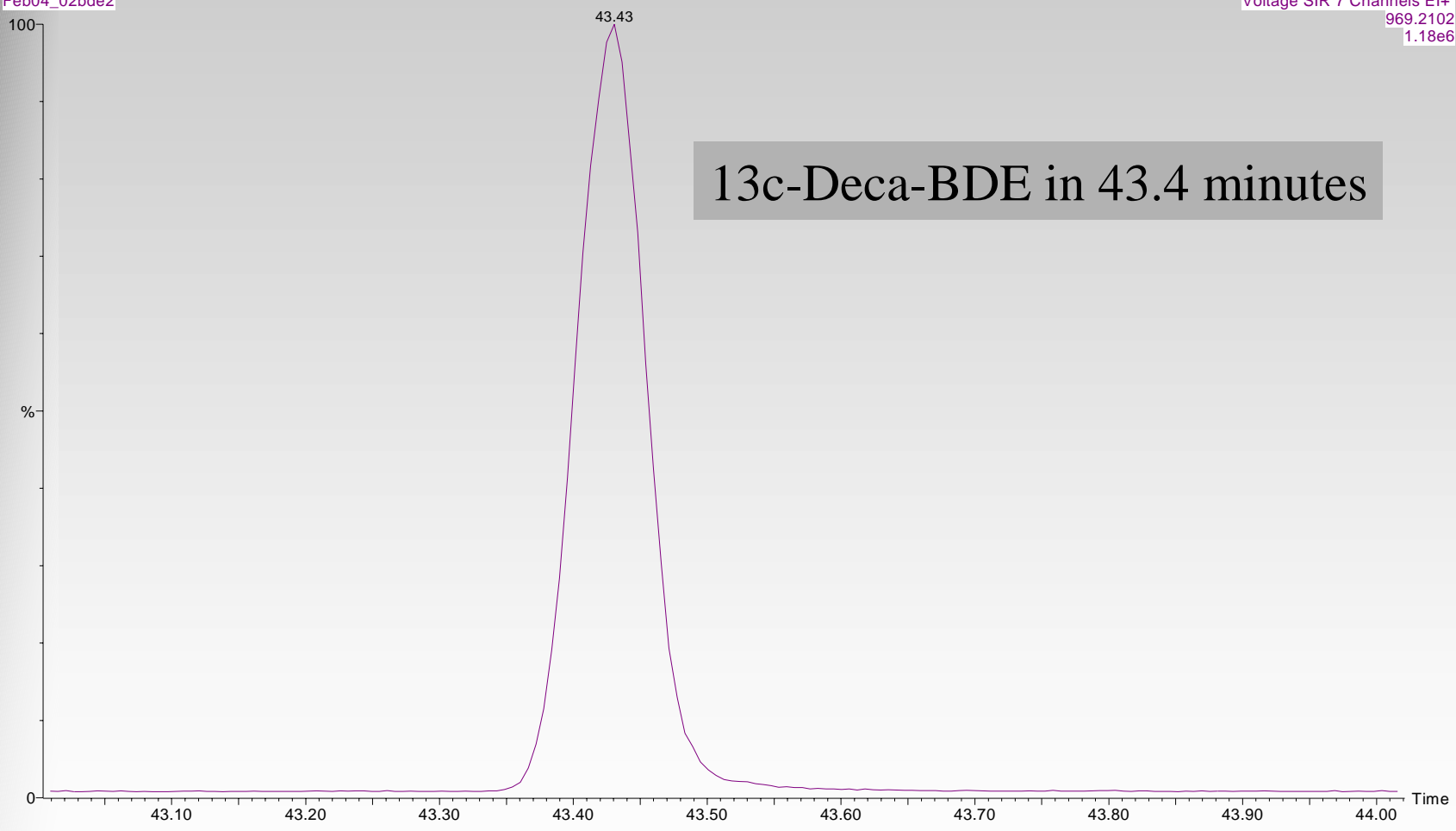
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bde209 13C  
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Voltage SIR 7 Channels EI+  
969.2102  
1.18e6



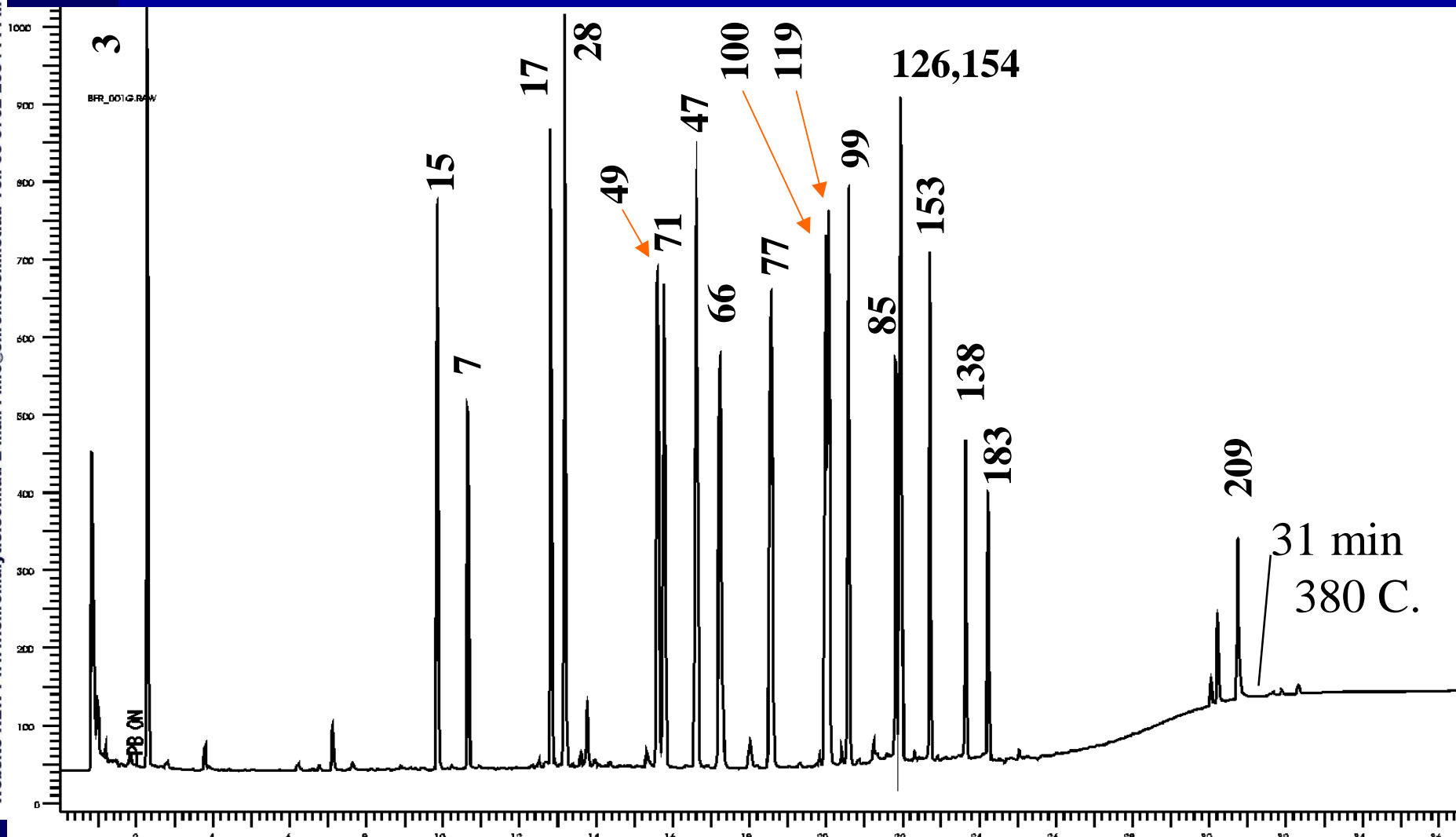


BROMINATED FLAME RETARDANT GC PROGRAM				
INSTRUMENT CONFIGURATION				
Micromass Autospec-UltimaNT (High Resolution Mass Spectro				
Source Temperature = 300°C				
GC CONDITIONS (HP 6890 +)				
Constant flow @ 1.5mL/min				
Injector Temp. 300°C				
Temp. Ramp Temp. Hold Time				
Start Temp. 100 1 min				
10 110 0.64				
80 180 0				
5 350 23				
TOTAL RUN TIME = 60.51				
**NB: DecaBDE (last elutor) elutes at ~43 min.				

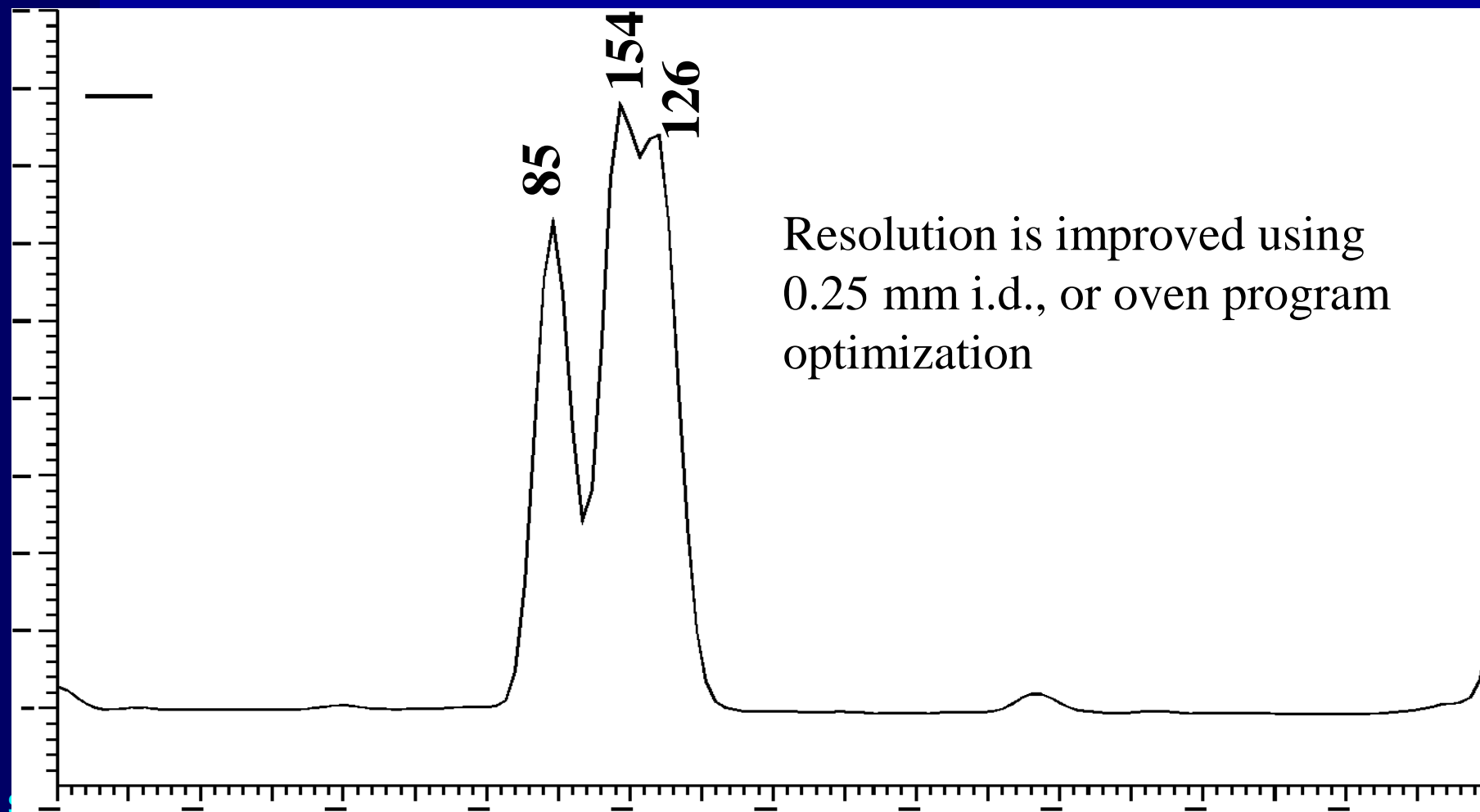
# GC-ECD Analysis

- Electron capture detector is common to many laboratories
- Compounds have excellent response by ECD
- Higher flow rates may allow for more rapid separation using larger-diameter columns
- Instrumentation less expensive than HRMS
- Instrumentation is also field portable

# Wellington Laboratories BDE Mix-C

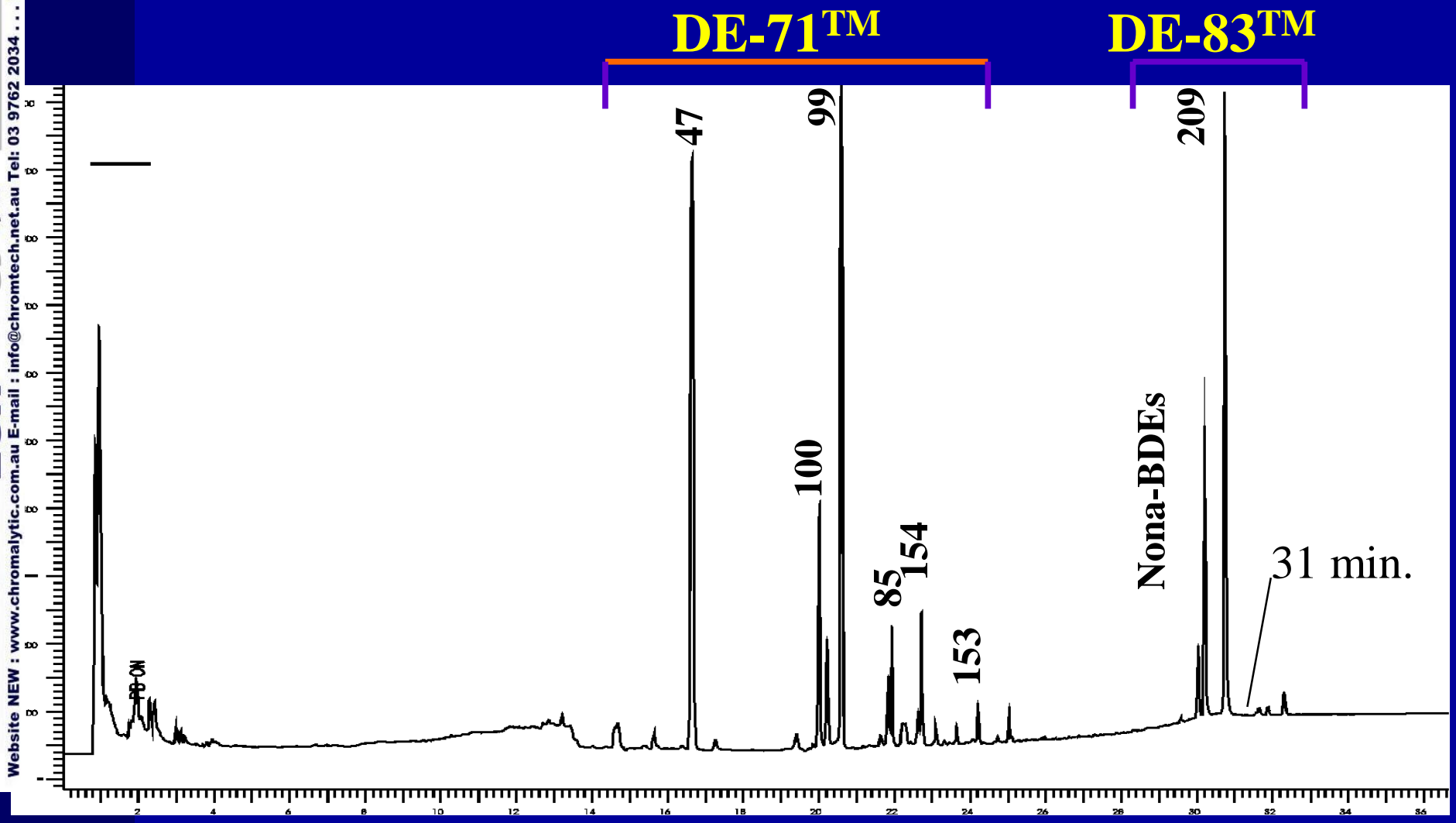


# 0.53 mm i.d. column partially resolves BDE 154 and 126 under these conditions



Resolution is improved using  
0.25 mm i.d., or oven program  
optimization

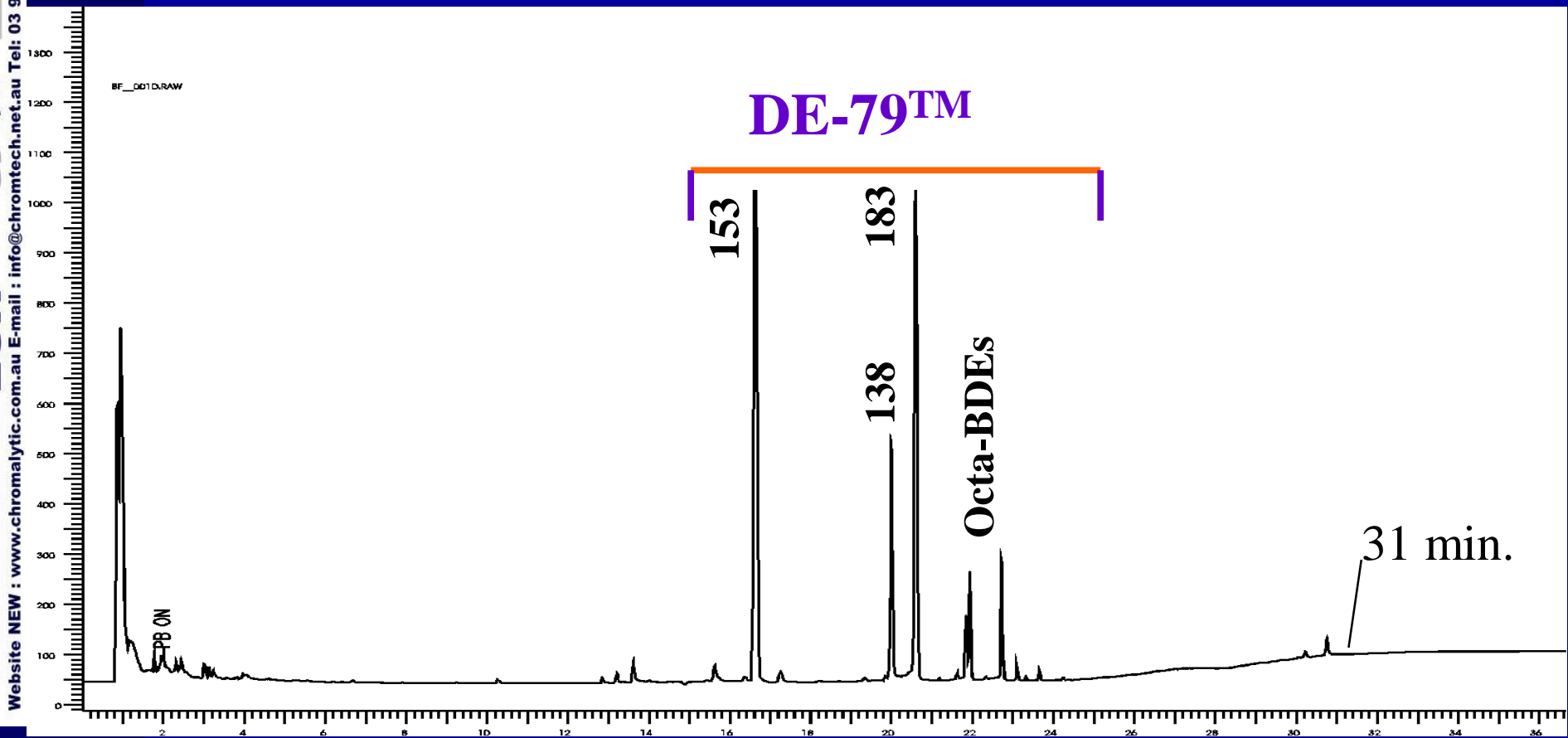
# Commercially Available PBDE Mixes



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# Commercially Available PBDE Mixes



# Conditions

**Column:** Rtx-500 30m x 0.53mm x 0.15 Ser# 233548  
**Flows:** Hydrogen 7.69ml/min (66.7cm/sec) @ 100°C  
**Dead Time:** MeCl2 Headspace 0.76min @ 100°C  
**Oven:** 100(1) 15/260(5) 15/380 (15) ~ 40 min runtime  
**Standards:** Wellington Laboratory BDE-Mix C  
1ul injection 30pg on column.  
**Injection:** Drilled Press-Tight Uniliner.

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# Acknowledgements

- Reference materials courtesy of Wellington Laboratories – Guelph, Ontario
- Dr. Eric Reiner and Karen MacPherson of the Ontario Ministry of the Environment – Etobicoke, Ontario provided the HRMS analyses, and guidance.



# The Design of High Temperature Metal Capillary Gas Chromatography Column Based on Polydimethylsiloxane

Dinesh V. Patwardhan Ph. D., Barry Burger,  
Rick Morehead, Jarl Snider, Kristi Sellers,  
Chris Cox

Restek Corporation  
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# Outline

Background

Column Bleed

Column Selectivity

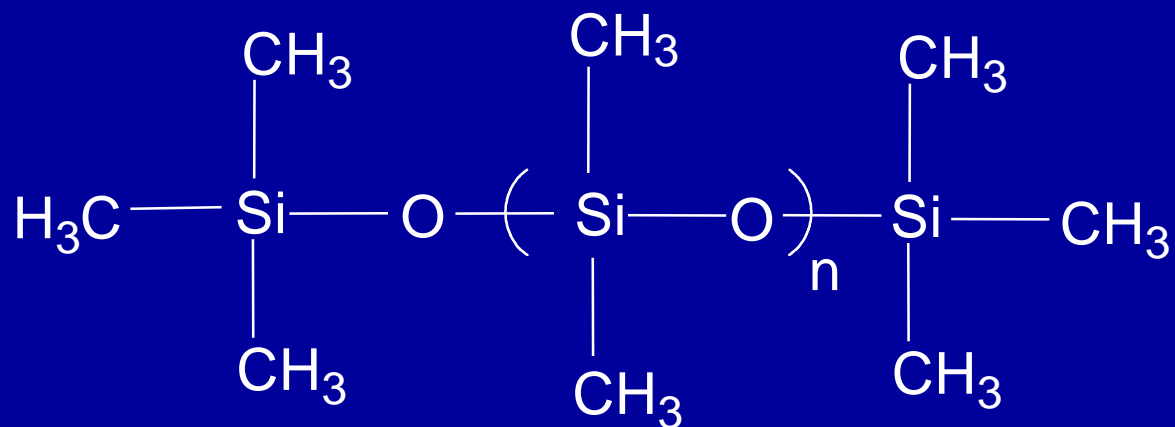
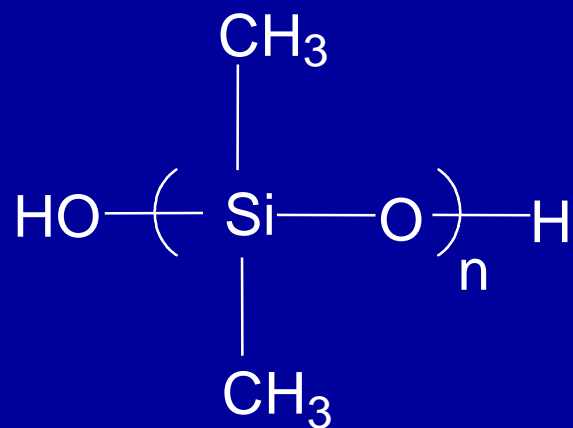
Unique Attributes of High Temperature Column

Applications

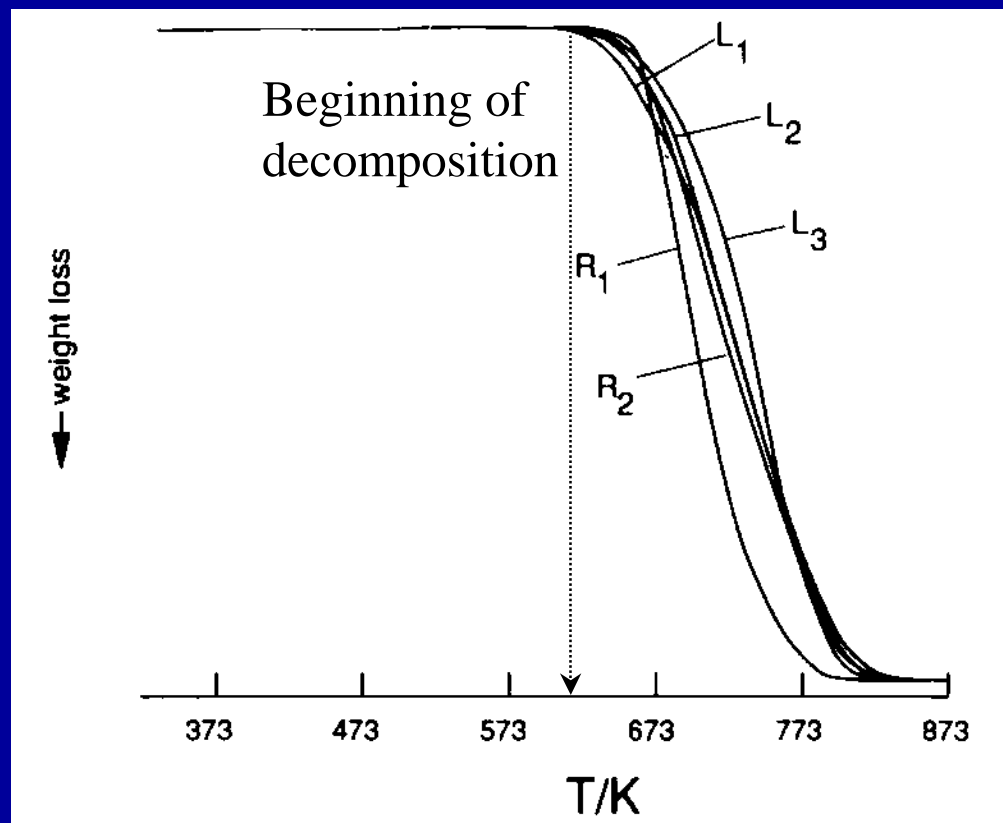
Conclusions

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# Polydimethylsiloxane



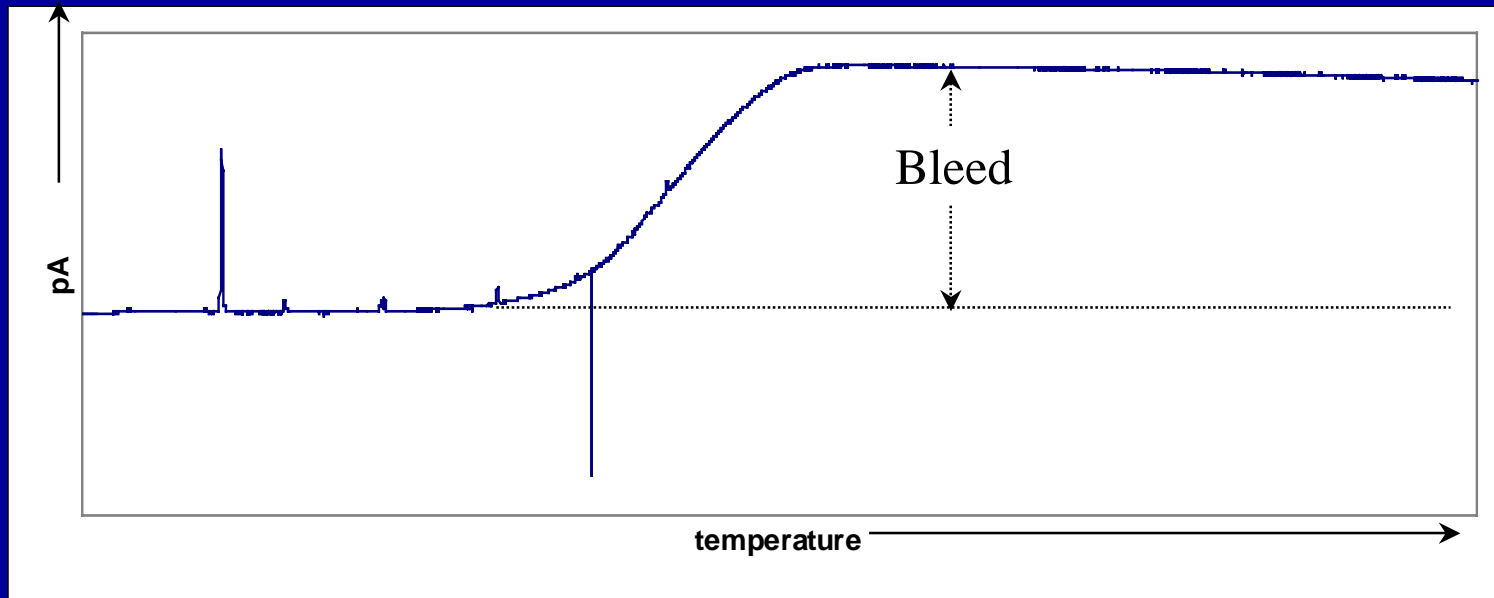
# Thermal Stability of PDMS



Adapted from Siloxane Polymers, ed. Clarson & Semlyen, 1993.

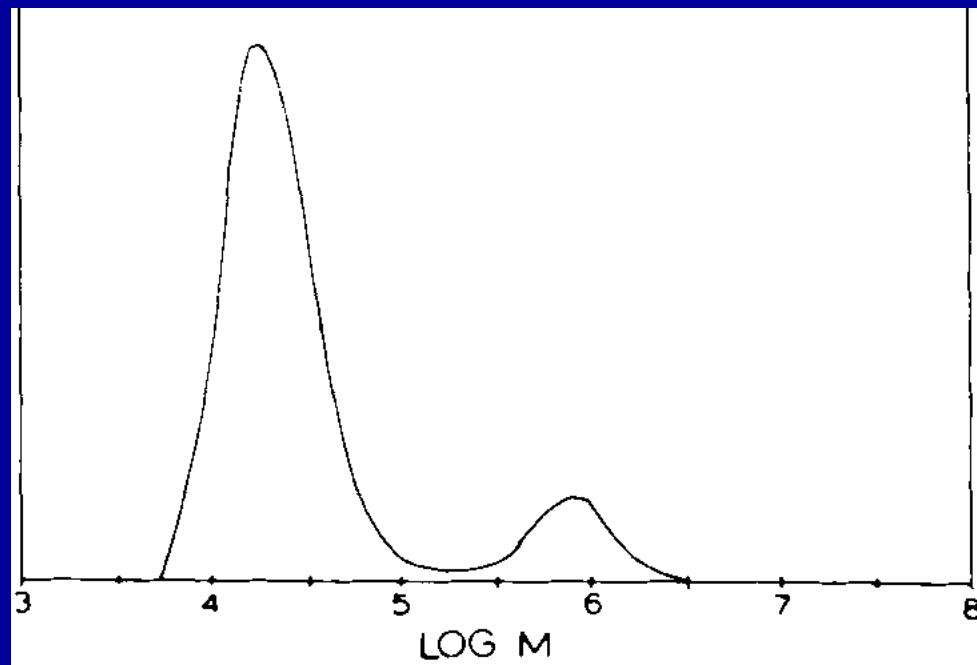
# Bleed

- Chromatography of silicone “bleed” from the gas chromatography column under temperature programming



# Origin of Bleed...

- Polymer Synthesis



Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.

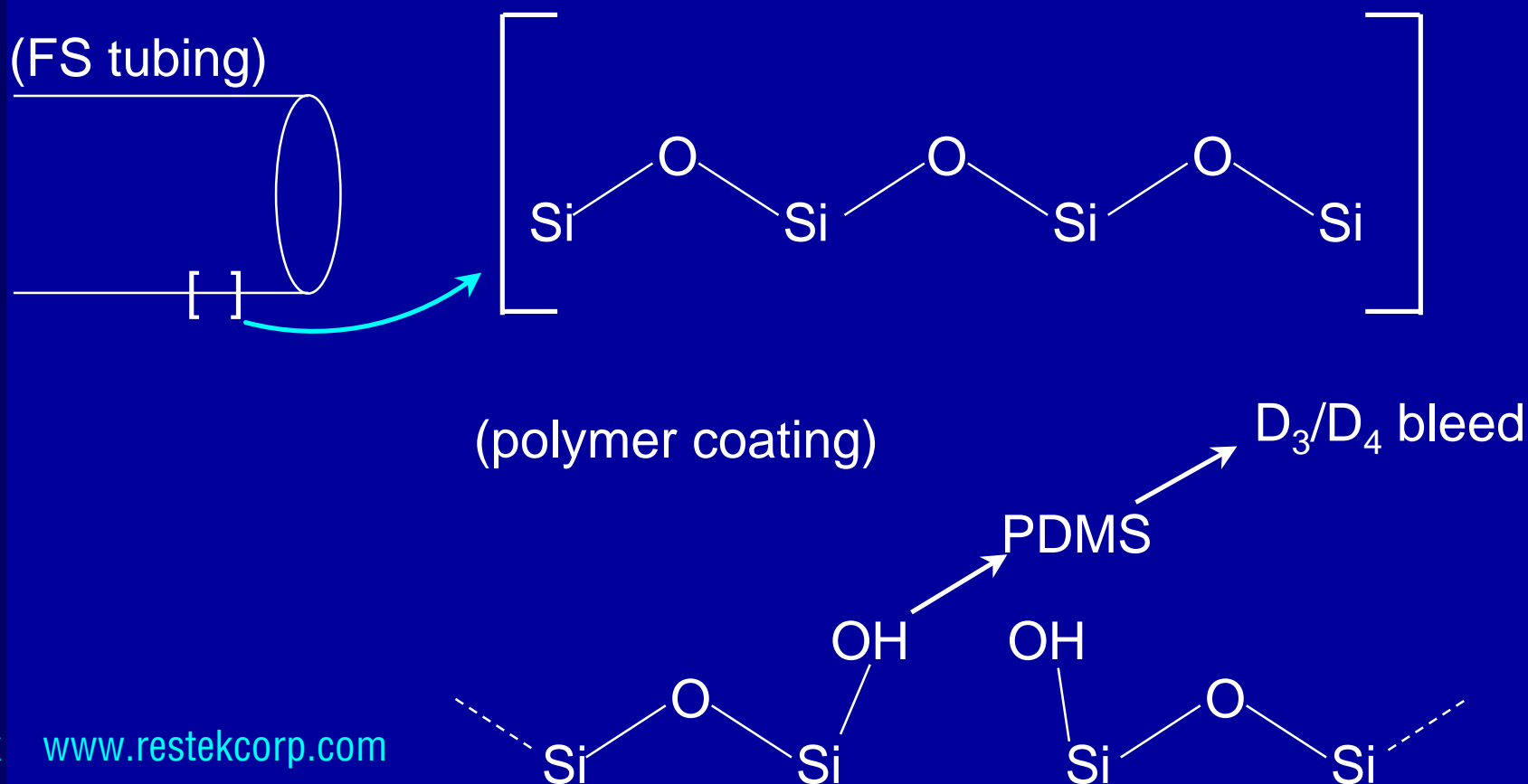
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# Polymer Synthesis

- Silicone Polymers can be synthesized using well known catalysts (KOH, HCl) under equilibration polymerization conditions.
- We use newer, more advanced catalysts, better synthetic techniques.

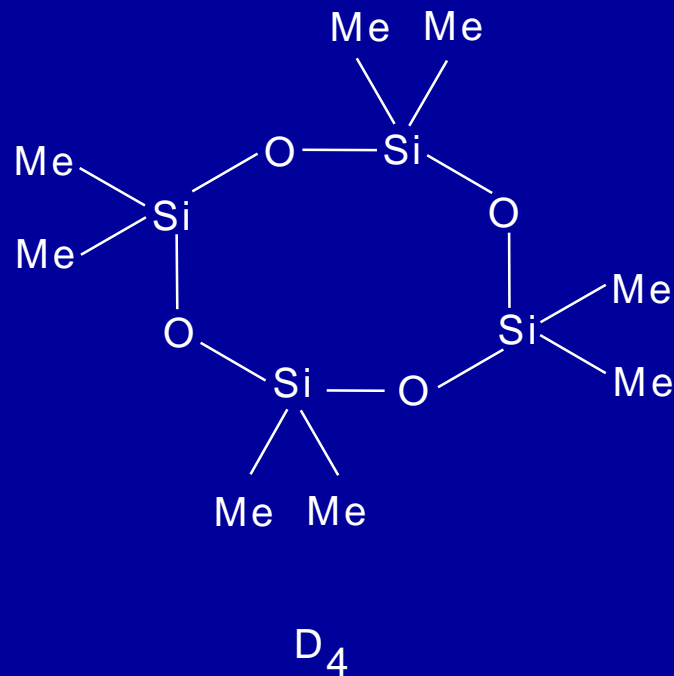
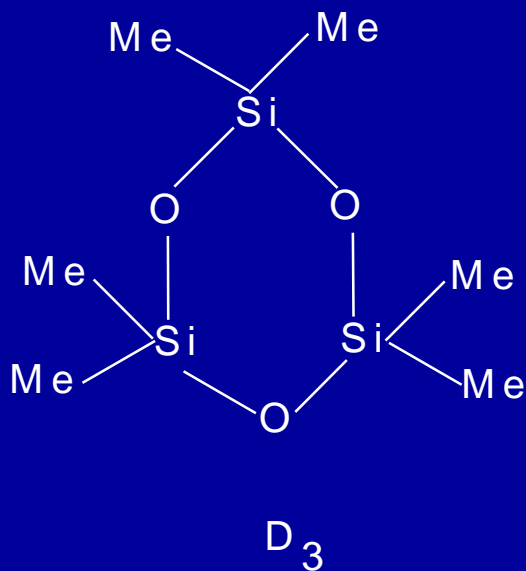
# Origin of Bleed...

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



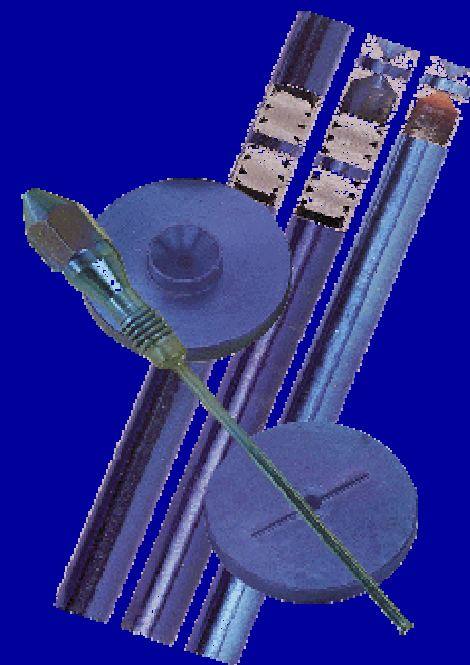


# Typical Chemical Structure of Bleed

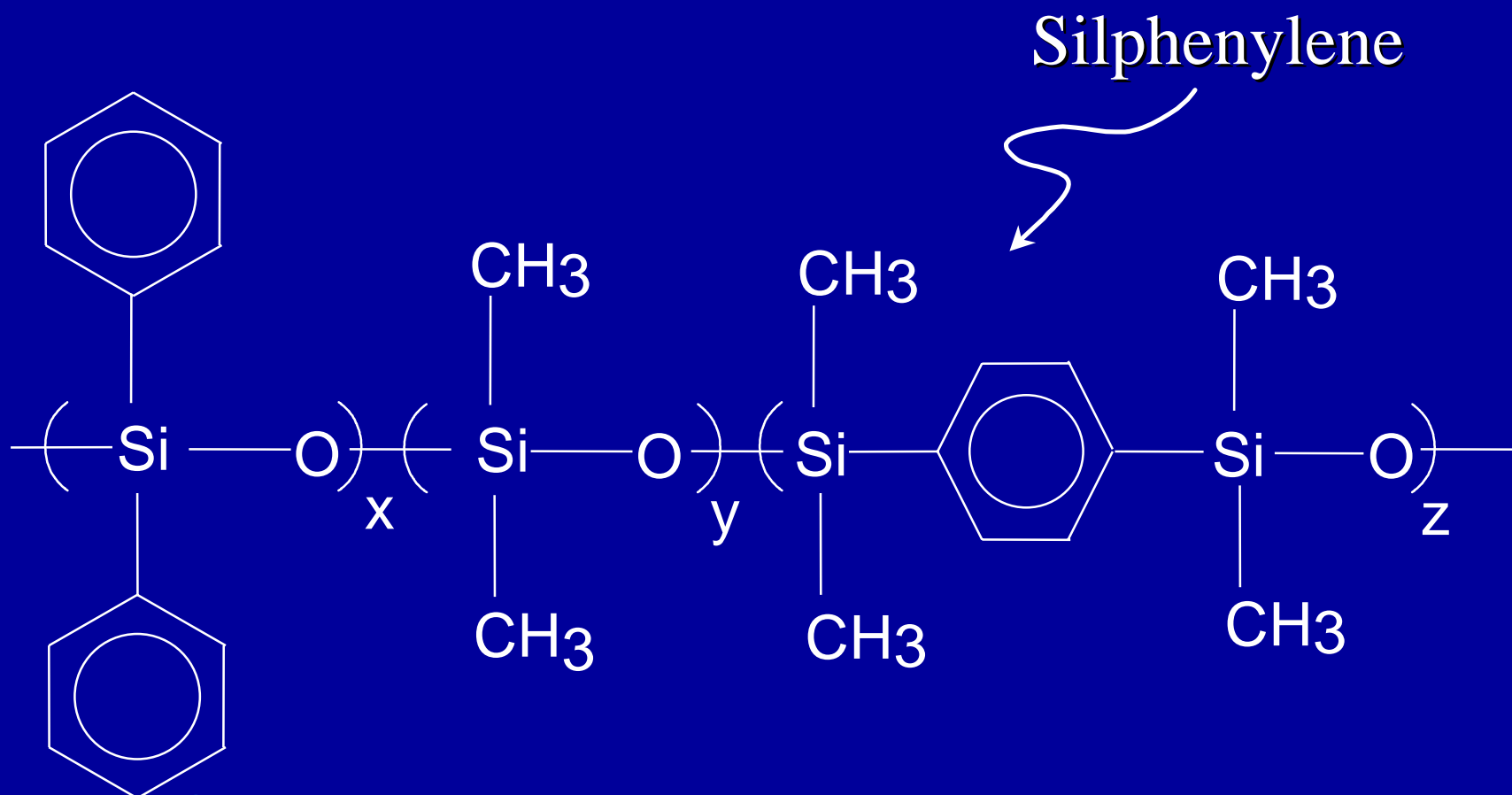


# Deactivation of Metal Columns

- We are using an advanced deactivation called Siltek™. It is a deposition process, unlike silazane or silicone deactivation.

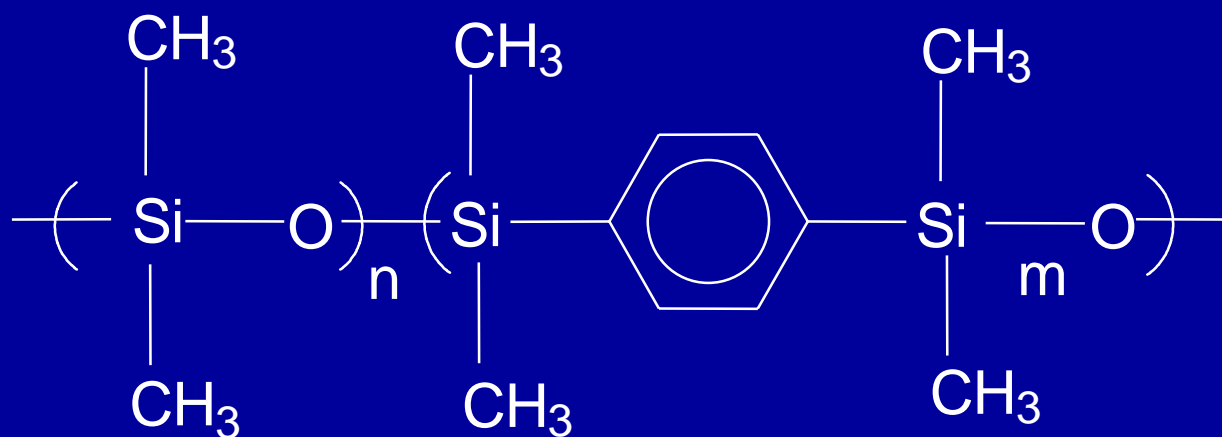


# Enhancement of Thermal Stability by Using “Additives”



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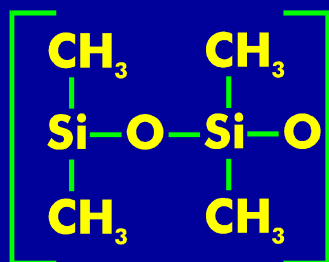
## Additives...



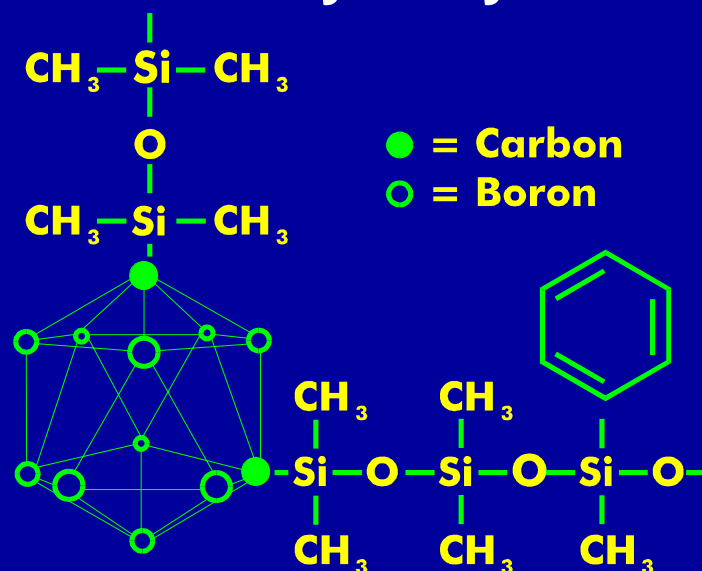
- A column with true Polydimethylsiloxane selectivity cannot be obtained by having silphenylene in the backbone.

# Stationary Phases for High Temperature Simulated Distillation

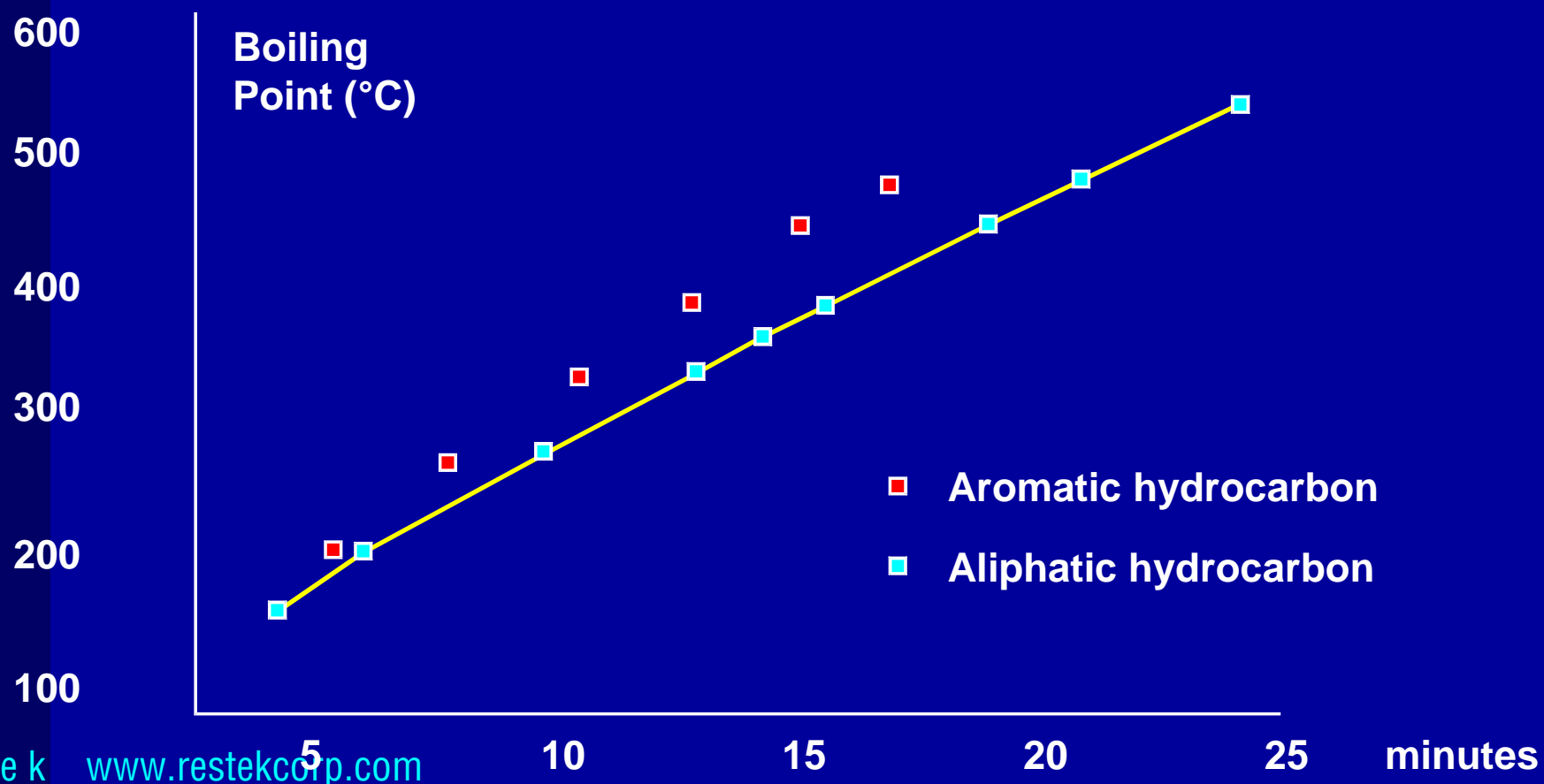
## Dimethyl Polysiloxane



## Carborane Dimethyl Polysiloxane

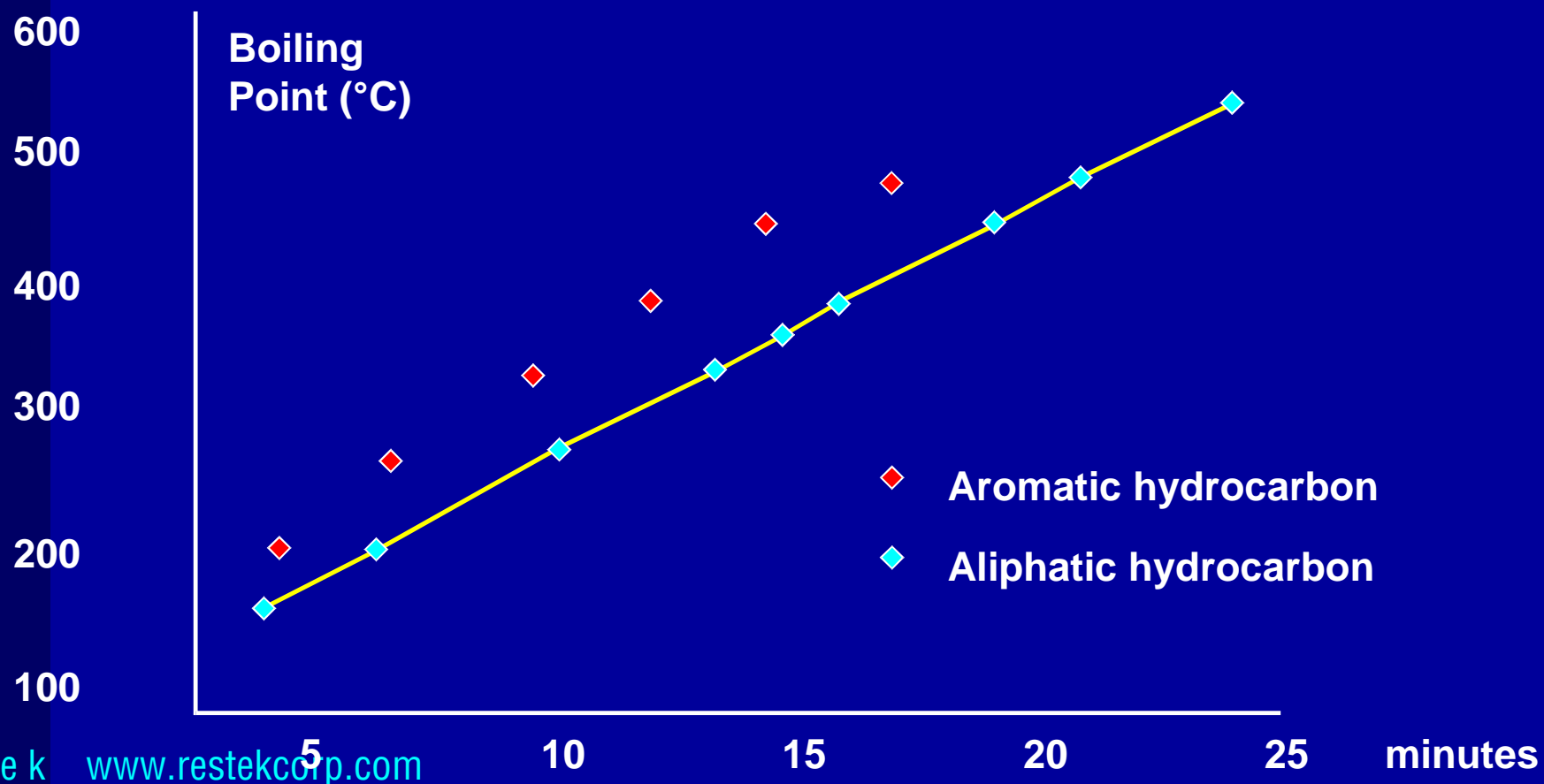


# Retention According to BP methyl silicone



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# Retention According to BP carborane



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# Effect of Stationary Phase on Calculated BP

<u>Aromatic</u> <u>Hydrocarbon</u>	<u>Published BP<sup>1</sup></u> <u>(°C)</u>	<u>Calculated BP</u>		
		<u>Rtx-1</u>	<u>UCW-982</u>	<u>OV-101</u>
benzene	80	81.3	82	80.3
p-xylene	139	138.6	140.2	137.7
naphthalene	218	204.6	206.9	204.3
acenaphthalene	280	252.7	255.6	252.2
anthracene	342	304.1	307.2	303.4
chrysene	447	385.6	389.2	384.9
dibenzo(a,h)anthracene	524	452.3	455.7	450.4



# Published vs Calculated BP for Aromatics

Compound	Published BP (°C)	Calculated BP	
		Dimethyl <u>Polysiloxane</u>	Carborane Dimethyl <u>Polysiloxane</u>
naphthalene	217	201	180
acenaphthalene	279	249	222
phenanthrene	340	300	275
anthracene	340	302	277
pyrene	393	342	321
chrysene	448	382	363
benzo-a-pyrene	477	414	410

# High Temperature Simulated Distillation

- ASTM Method D 6352-98 is used for the determination of the boiling range distribution of petroleum distillate fractions.
- The method specifies the use of a short, wide bore, thin film capillary column.
- The upper temperature of the analysis is set at 400°C.

# Column Design

- Method criteria: 5 m x 0.53mm ID x 0.10um
- Stainless steel tubing
- Treated with Siltek Deactivation
- A high temperature, non-polar stationary phase was developed that was able to withstand 430°C while producing minimal bleed.
- Matching the McReynolds requirements of the method.

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# Experimental Design

- A lifetime study was performed by repetitively injecting a standard mixture designed for ASTM D2887 calibration.
- A Polywax 1000 sample was injected and resolution between C50 and C52 was calculated according to the method.
- Record kept of the retention time for C52 and the bleed at 430°C over the course of the experiment.
- Repeated until the column resolution fell below ASTM D6352-98 specifications.

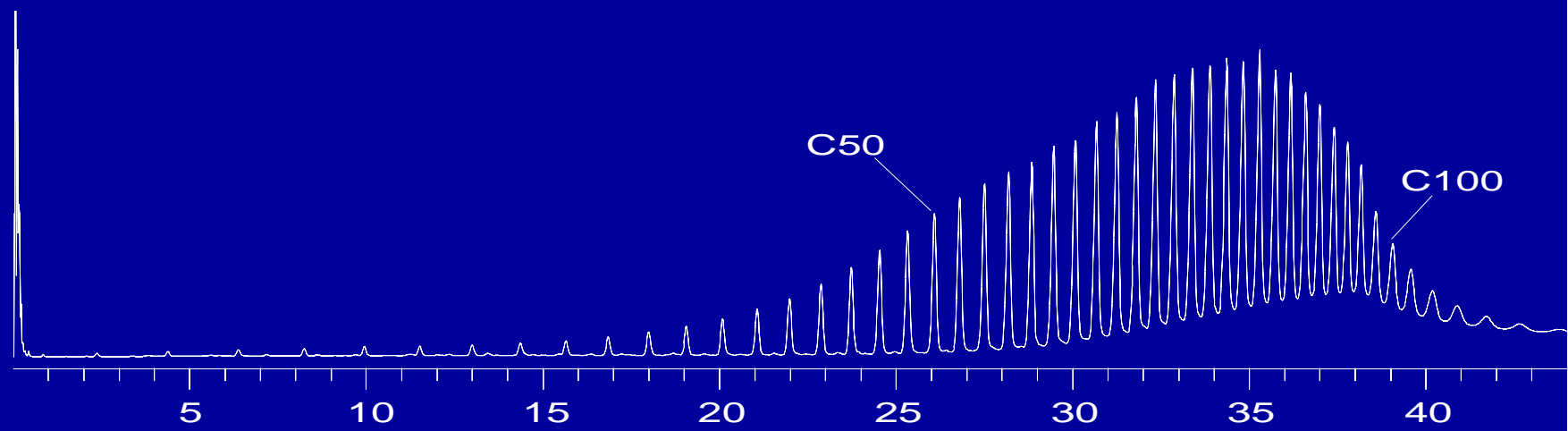
## GC Conditions

- D2887 sample
  - 40°C to 430°C at 70°C/minute
  - Hold at 430°C for 10 minutes
- Polywax 1000 sample
  - 50°C to 430°C at 10°C/ minute
  - Hold at 430°C for 6 minutes
- Carrier Gas – Helium, 1.8psi (14ml/min)
- Sample – 0.2uL, 2% sample in Carbon Disulfide
- Cold On Column Injection with Oven Tracking

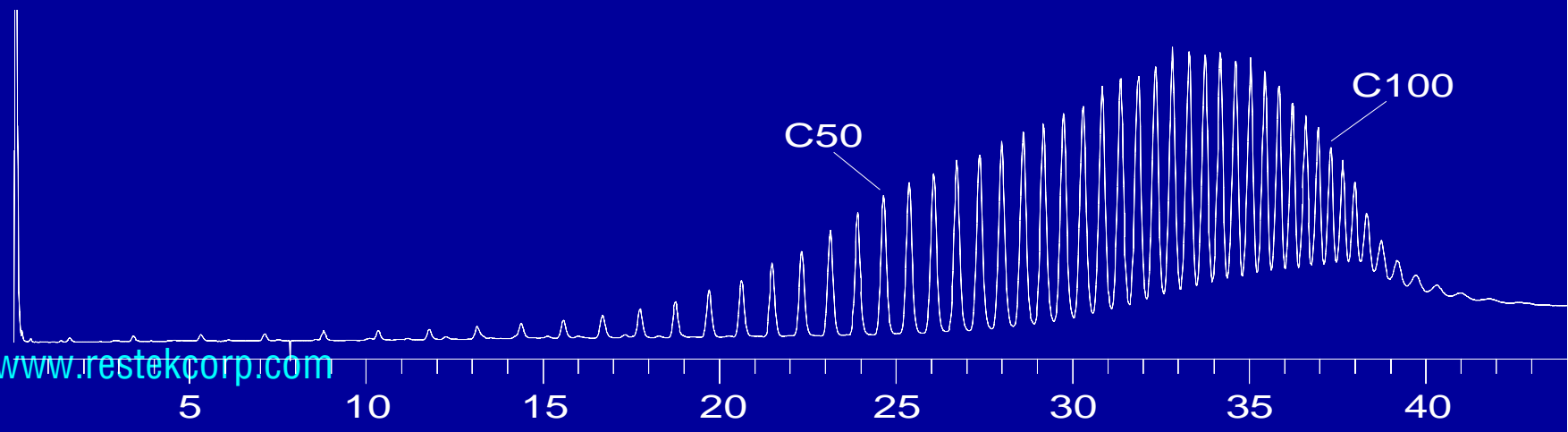
## Results

- Column demonstrated consistent performance for 400 analyses at temperatures 30° higher than method specifications.
- Column resolution for C50/C52 did not fall below the specifications of the method until approximately 350 injections.

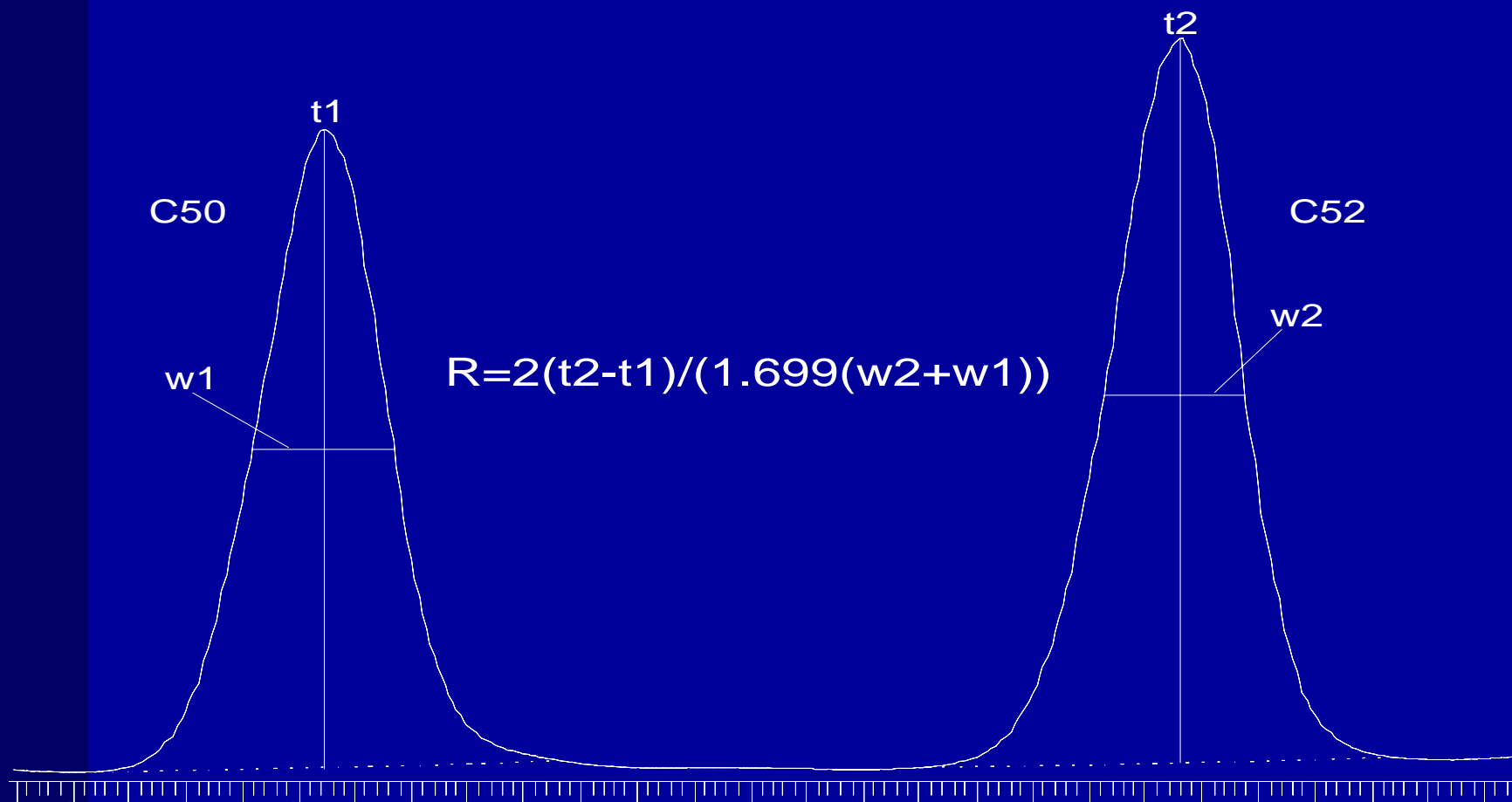
# Polywax 1000 – Run #1



# Polywax 1000 – Run #400



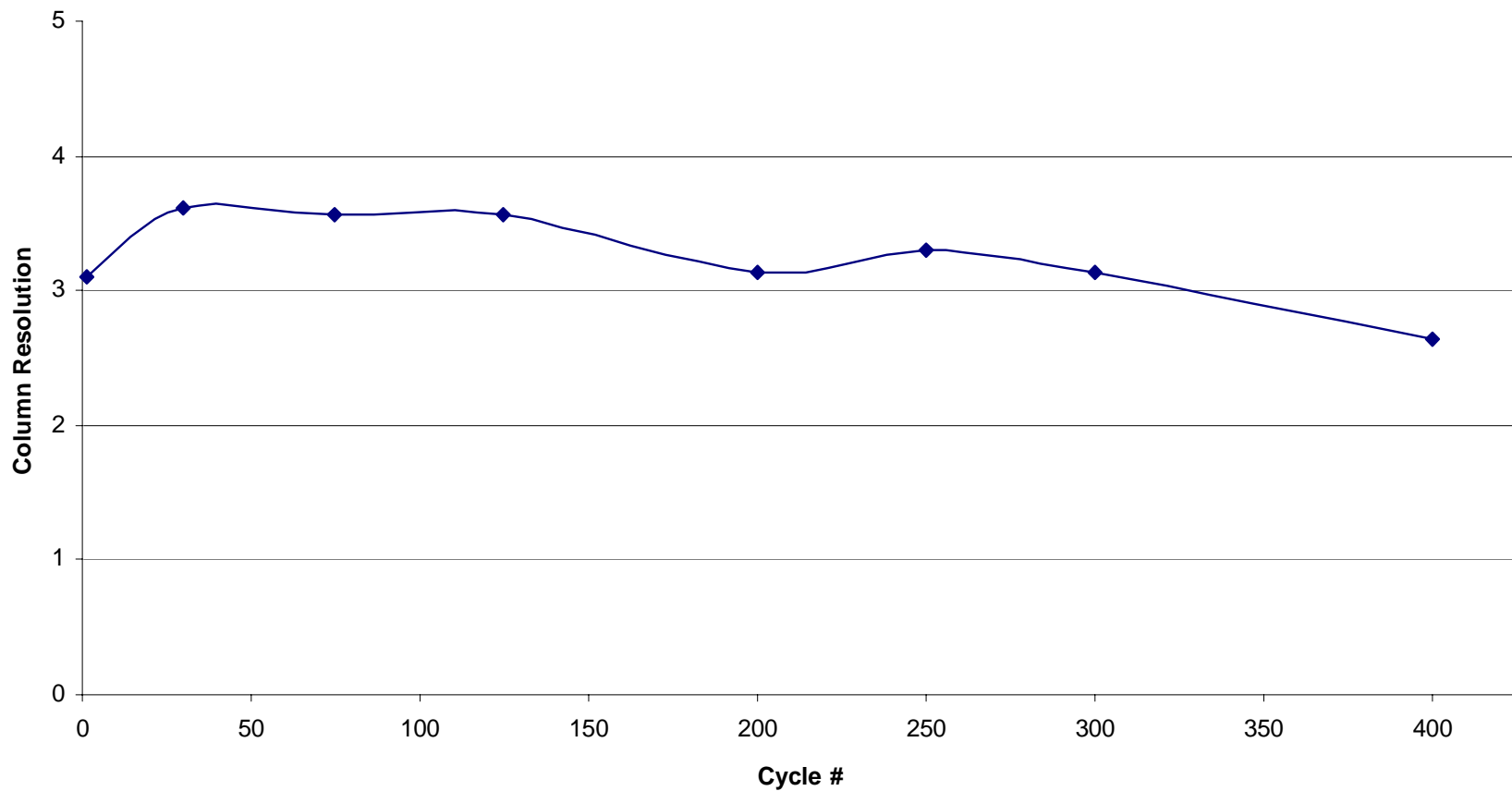
# C50 / C52 Resolution – Run #1



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# C50 / C52 Resolution

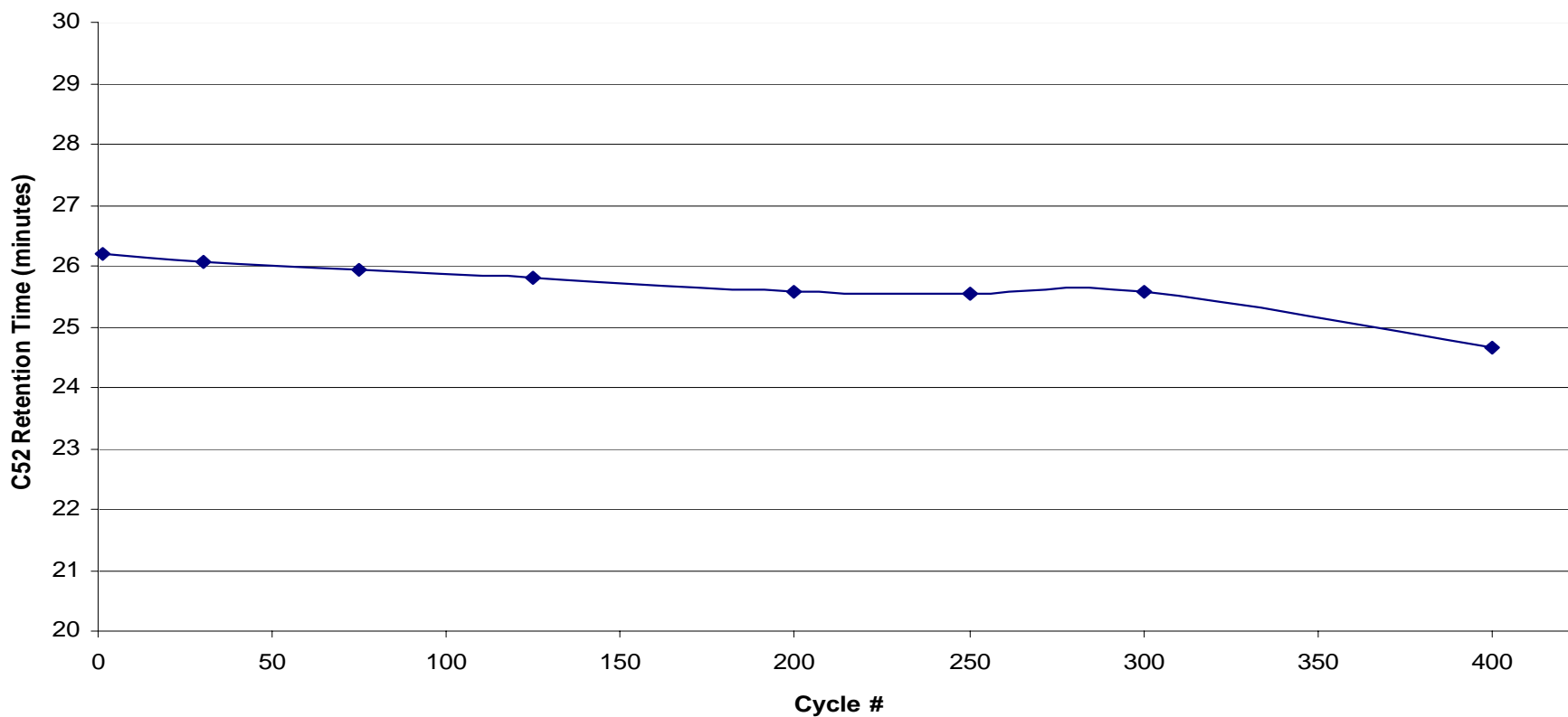


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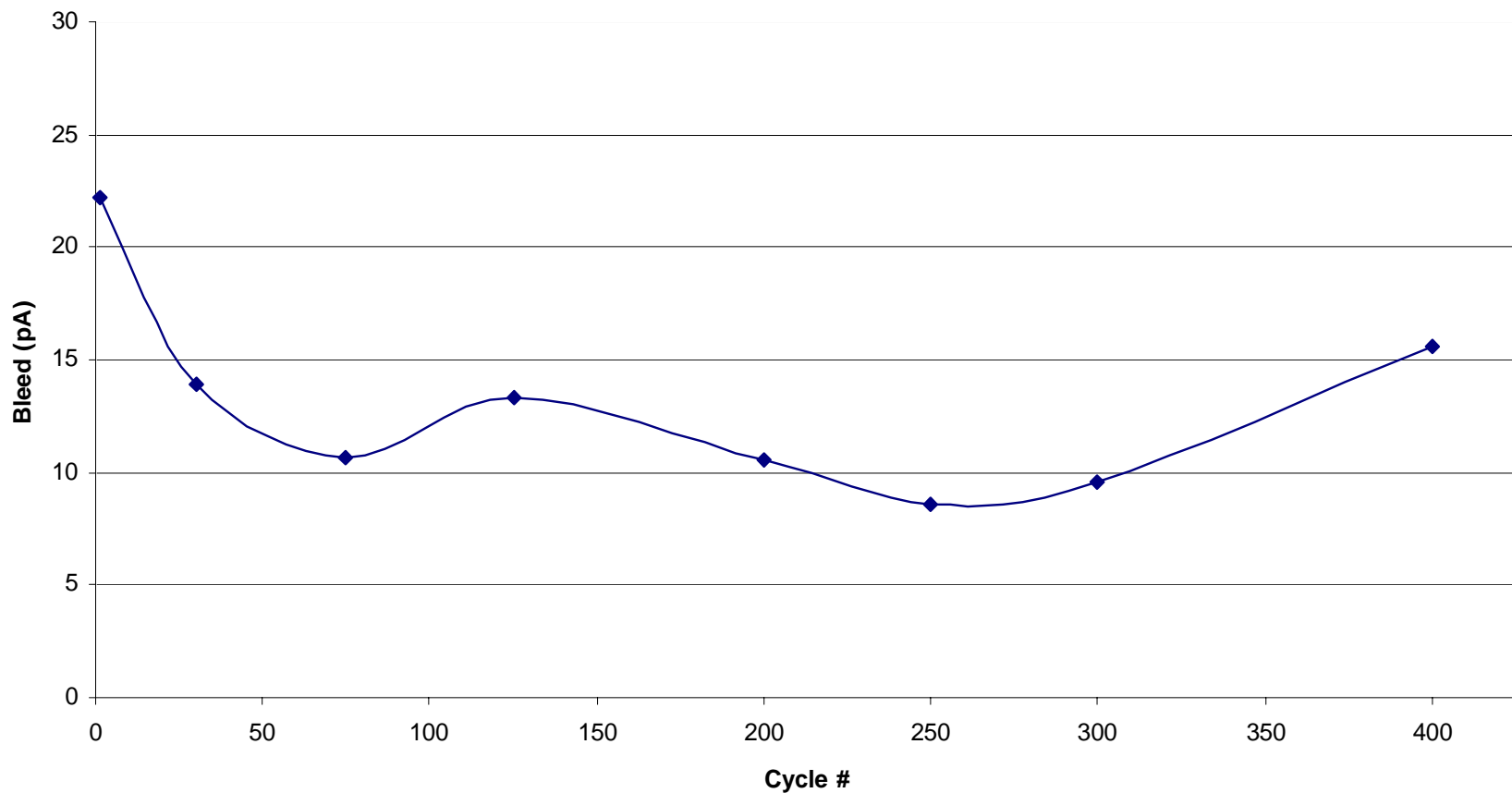
## Column Stability

- C52 retention time was monitored to ensure that significant amounts of stationary phase were not being lost due to thermal cycling.
- After 400 injections the retention time of C52 moved approximately 1.4 minutes.
- Column bleed at 430°C was monitored to ensure that the phase had not undergone significant thermal decomposition.
- Bleed values were consistently low and did not interfere with the analysis.

# C52 Retention Time Stability



# Column Bleed Stability



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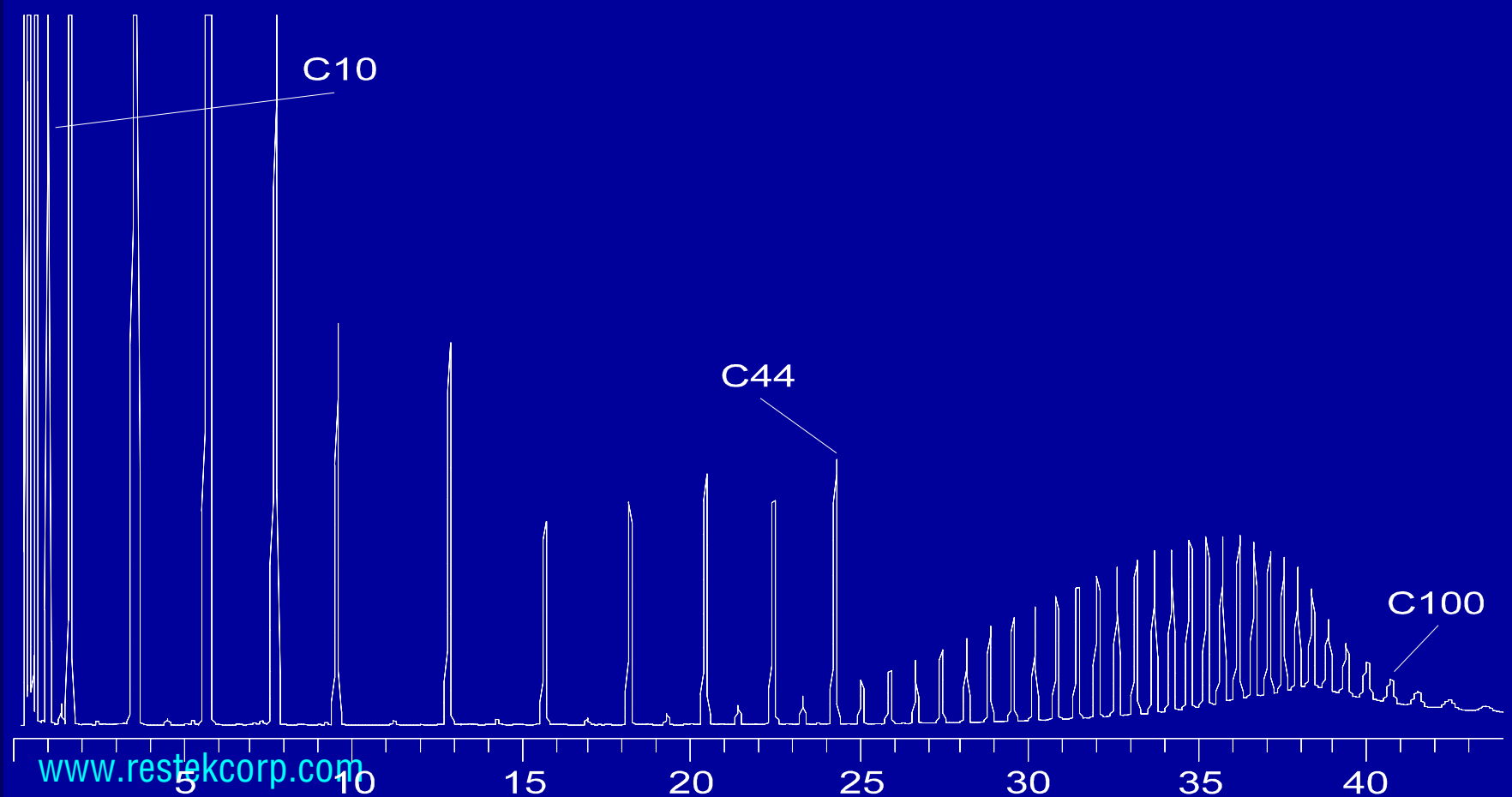
# Column Performance after 400 Cycles

- After 400 cycles to 430°C, a Polywax 1000 sample gave a column resolution value of 2.7
- A mixed sample of the D2887 standard and Polywax 1000 was injected to calibrate the column for C10 through C100.
- A diluted sample of Pennsylvania light crude oil was then analyzed and compared to the calibration mixture.
- Adequate resolution of the hydrocarbons in the crude oil sample was obtained even though the column was below the minimum resolution criteria of the method.

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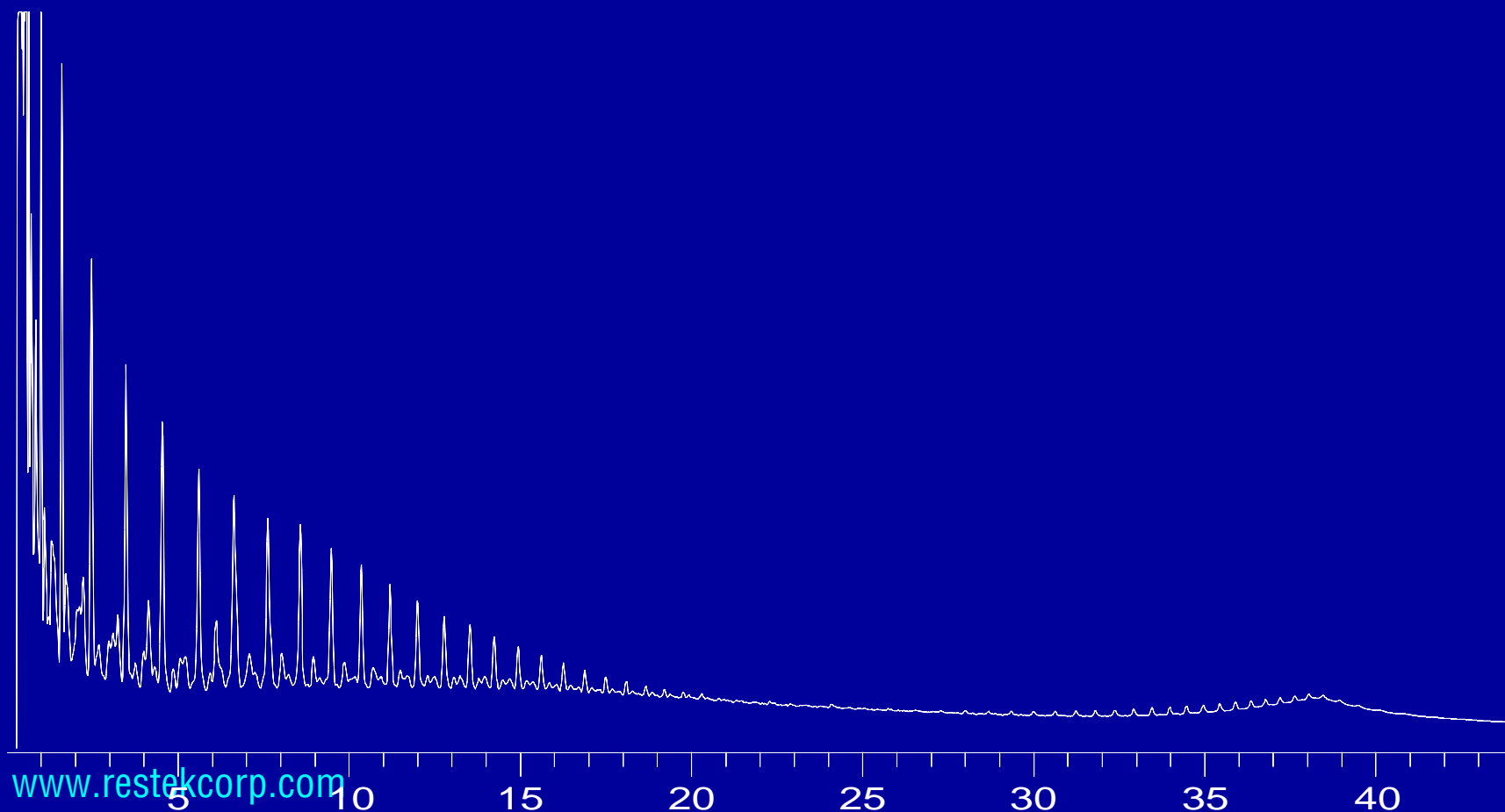
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# C10 to C100 Calibration



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# Pennsylvania Light Crude Oil



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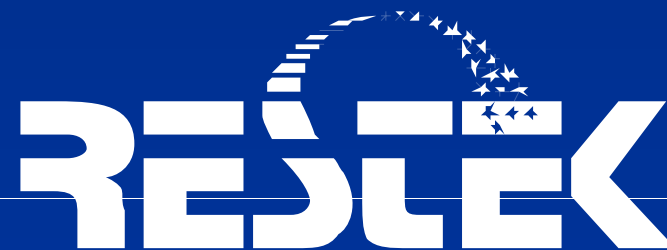
## Summary

- The MXT-1HT column demonstrates superior performance due to Siltek Deactivation and our in-house polymer synthesis.
- The MXT-1HT has the selectivity of polydimethylsiloxane.
- Able to withstand 400 cycles at 430°C and still retain good column efficiency and low bleed.
- Column demonstrated low bleed and adequate separating efficiency to resolve hydrocarbons in a crude oil sample.



# Chlorinated Pesticides and PCB Analysis

Frank L. Dorman, Chris English, and  
Gary Stidsen



# Target Compounds

- 20-40 Individual Chlorinated Pesticides
  - Examples: BHC, DDT, Endrin, Methoxychlor
- Chlorinated Pesticide Mixtures
  - Chlordane, Toxaphene
- 9 PCB Aroclor® mixtures: 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268

# Pesticide & PCB Analysis

- Injection techniques
  - Split/splitless
    - Gooseneck liners
    - Drilled Uniliner
- Analysis
  - Dual column
- Electron capture detectors

# Split/Splitless Injection

- Important aspects of injector
  - Flow pattern
  - Hold time
  - Sample Vaporization
  - Liners
  - Activity
    - Endrin/DDT breakdown

# Split/Splitless Injection Port



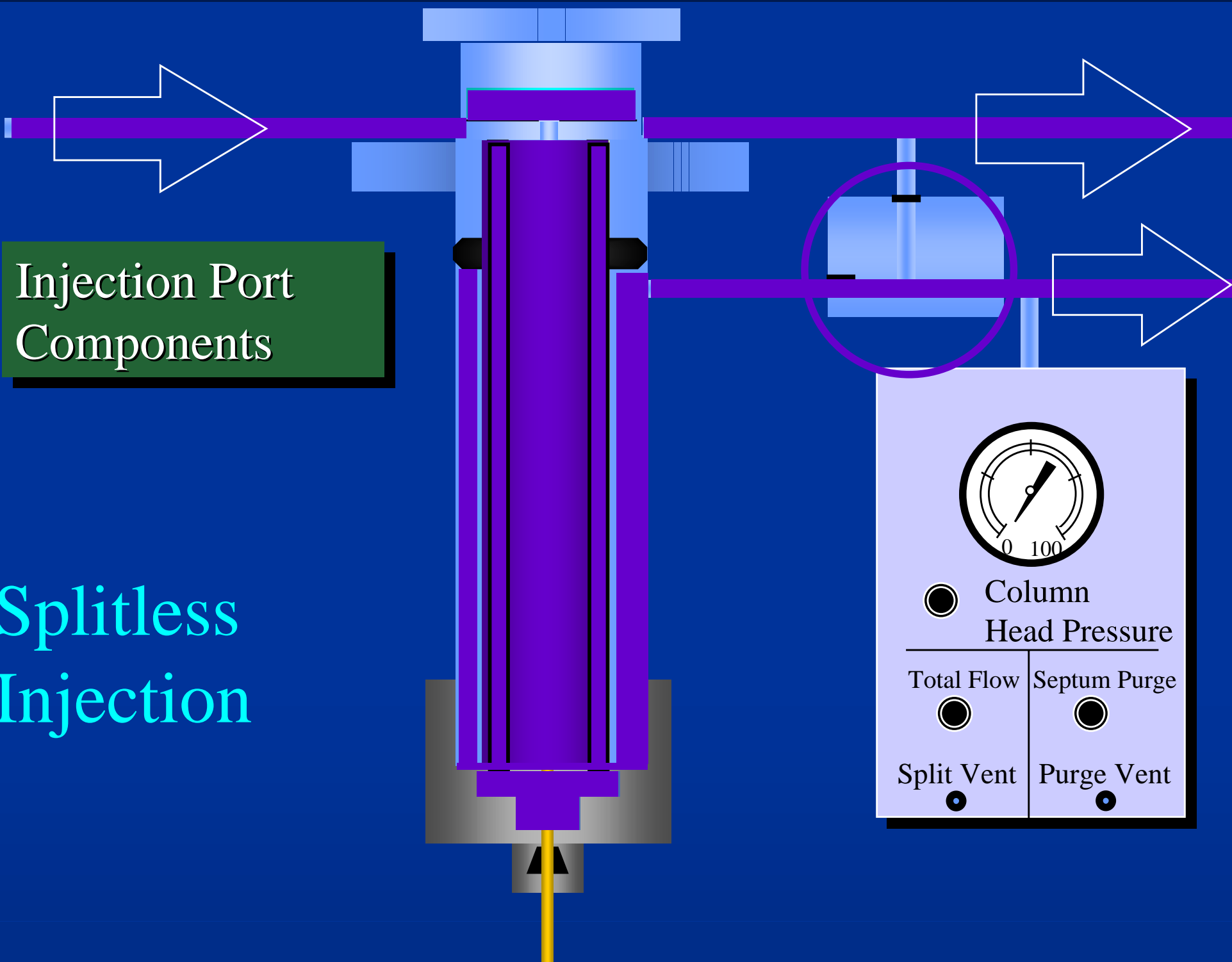
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# Injection Port Components

## Splitless Injection



# Factors Affecting Splitless Injection

## 1. Hold Times

Column ID (mm)	Column Flow Rate (cc/min.)	Approx. Hold Time
	He	
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

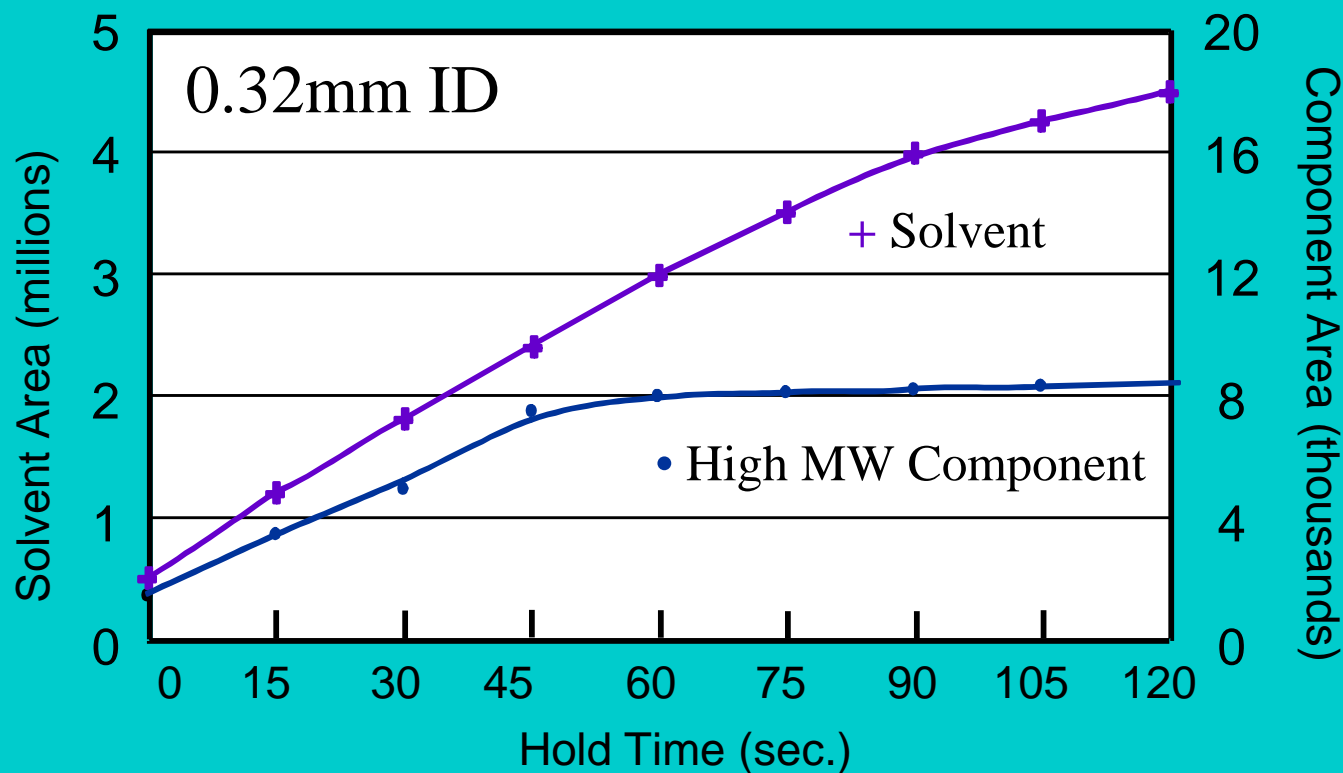
*Determine  
this  
empirically*

Note: based on a 2 $\mu$ L injection volume of CH<sub>2</sub>Cl<sub>2</sub> = 0.8 mL sample expansion value @ 250°C & 10 psig.



# Factors Affecting Splitless Injection

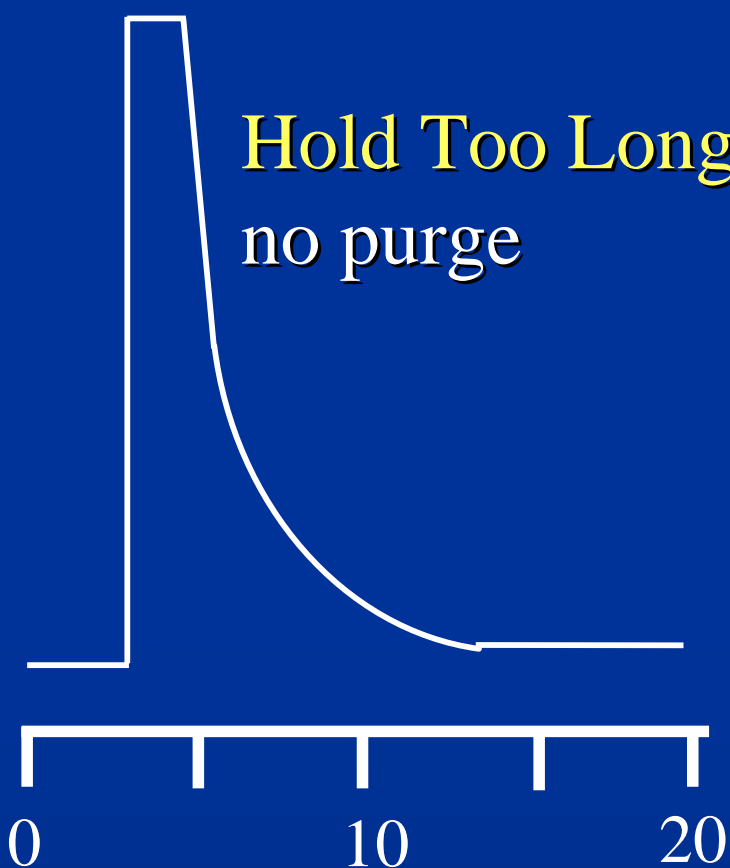
## 1. Hold Time Optimization



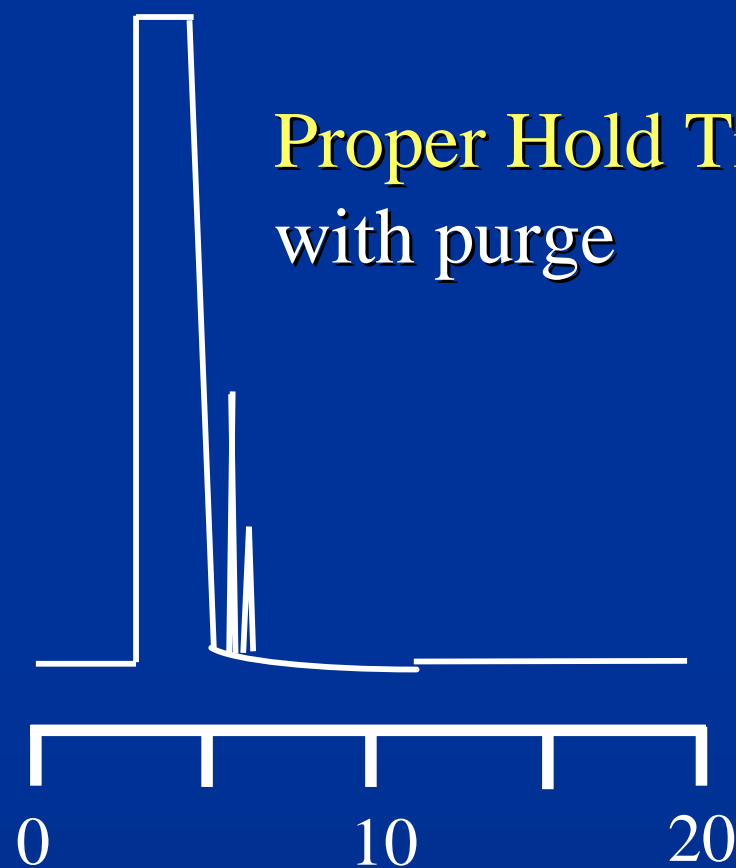


# Factors Affecting Splitless Injection

## 1. Hold Times



Hold Too Long —  
no purge



Proper Hold Time  
with purge

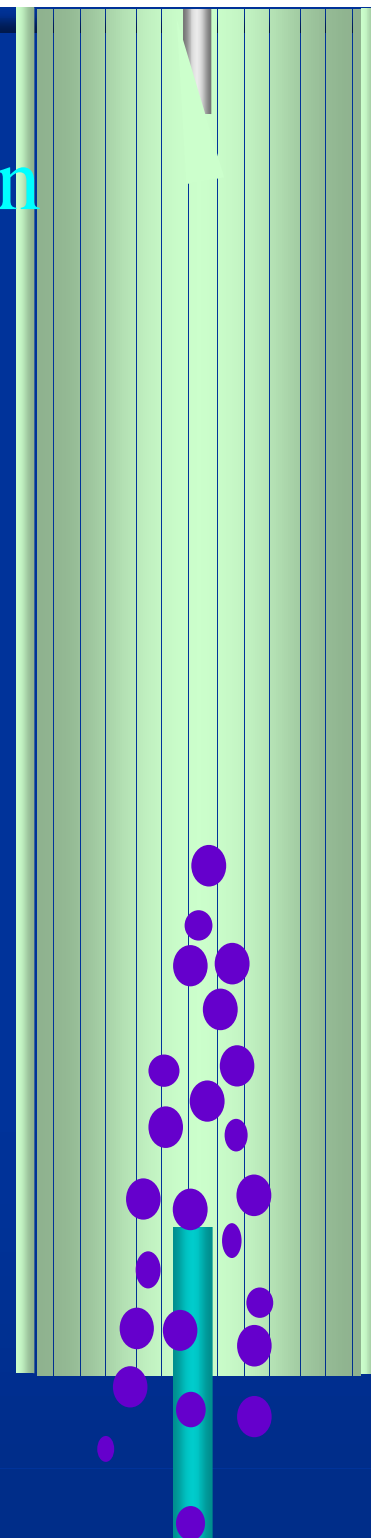
Time (min)

# Factors Affecting Splitless Injection

## 3. Sample Vaporization

Fast Autosampler :  
Incomplete vaporization

Aerosols or droplets reach the  
column instead of vapors



# Factors Affecting Splitless Injection

## 3. Sample Vaporization

Fast Autosampler :

Pack with wool or CarboFrit™

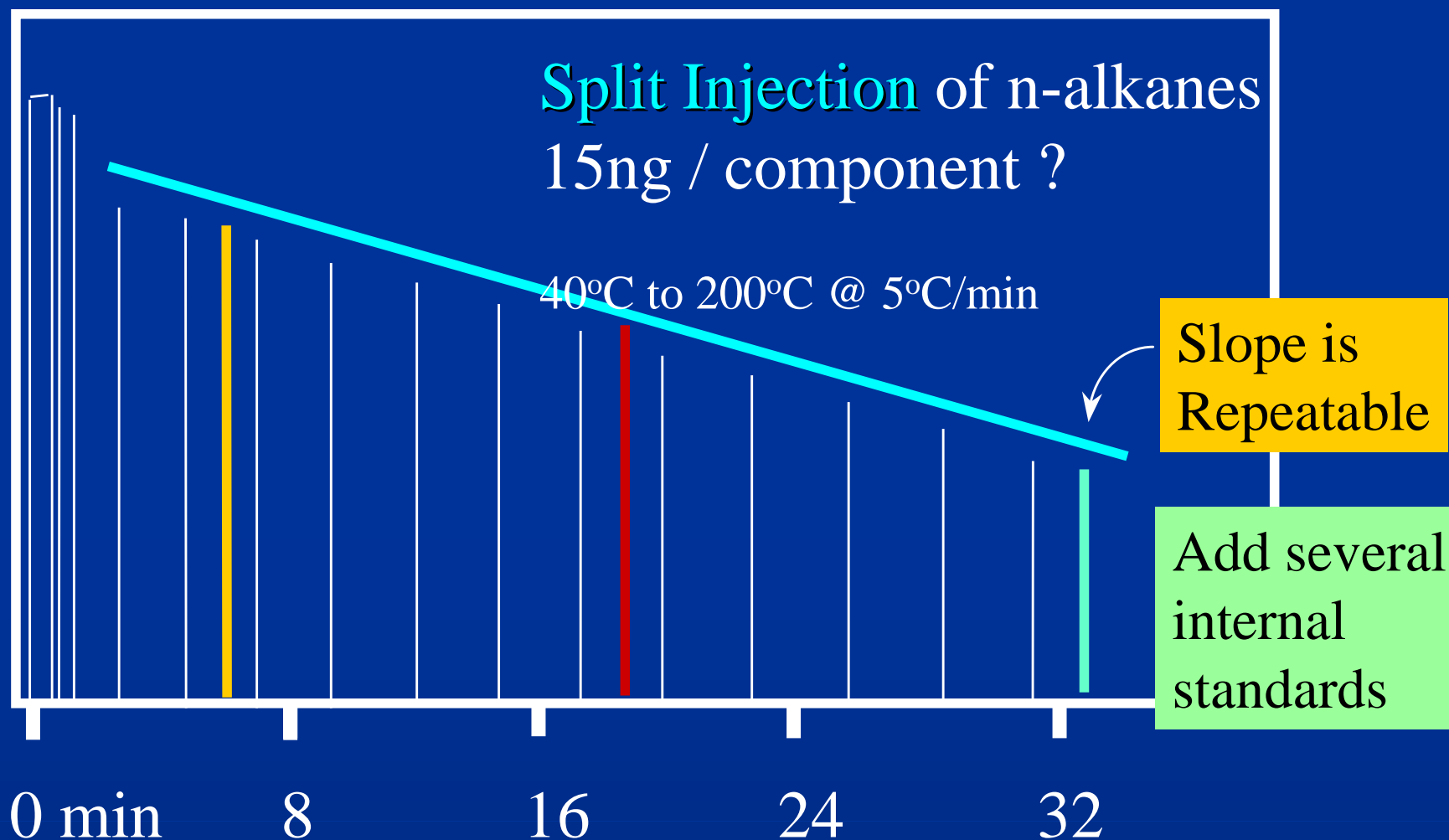
STOPS AEROSOLS COMPLETELY



WOOL

## II. Splitter Discrimination Molecular Weight Discrimination

Rtx-1: 30m, 0.32mm ID, 0.25 $\mu$ m

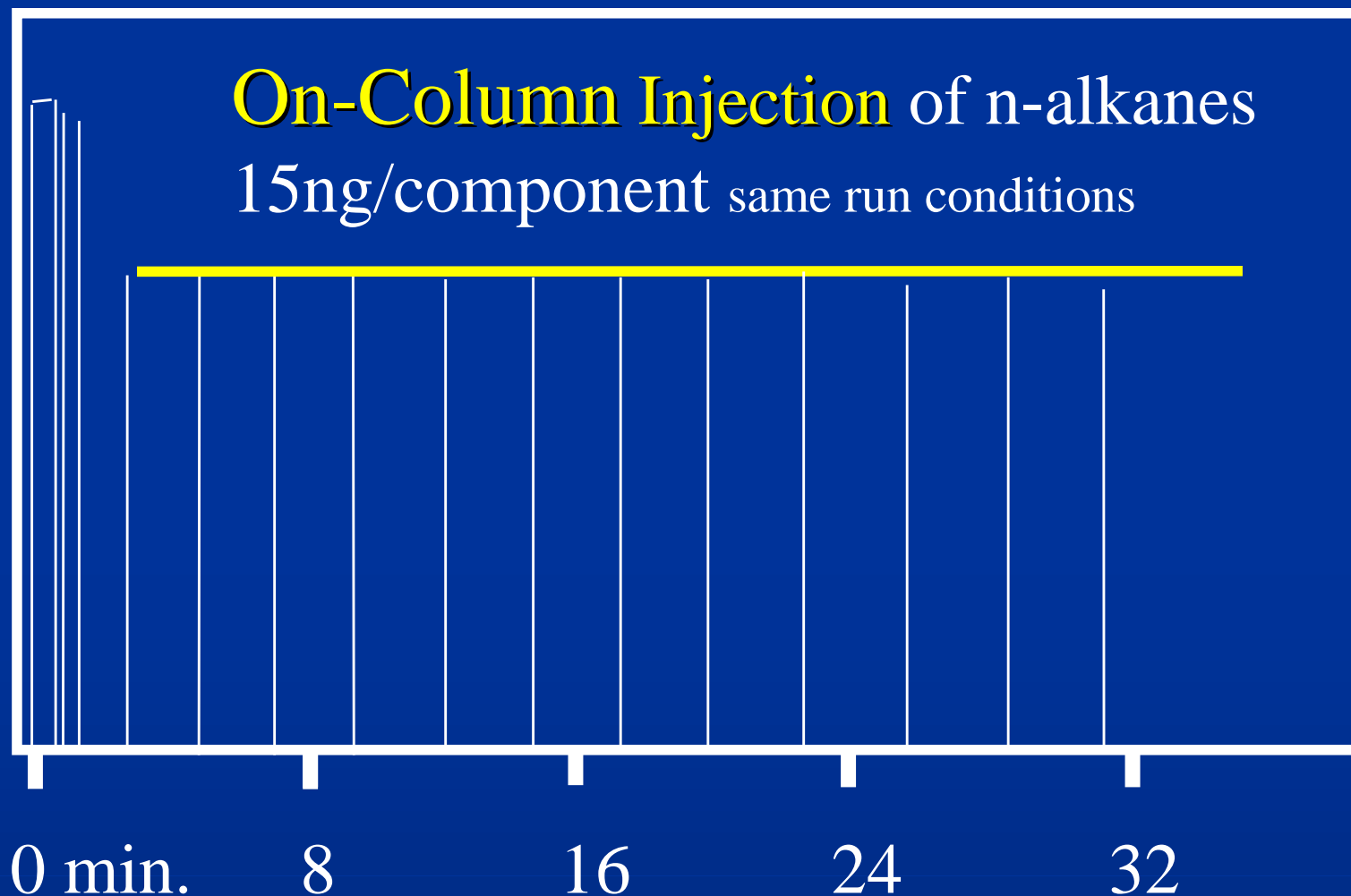


## II. Splitter Discrimination

### No Molecular Weight Discrimination

Rtx-1: 30m, 0.32mm ID, 0.25 $\mu$ m

**On-Column Injection** of n-alkanes  
15ng/component same run conditions



# Splitless Liner Designs

Straight



Gooseneck



Double  
Gooseneck



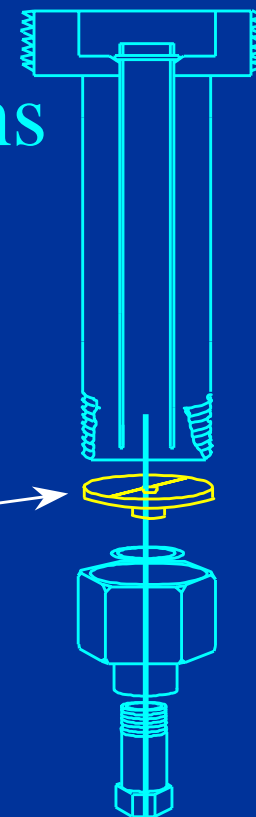
Cyclo Double-  
Gooseneck



# 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	dirty disk
Splitless with Wool	6.0%	12.8%
Gooseneck	2.0%	2.4%

# Vespel® Ring Inlet Seals

## Types of Surface Treatments

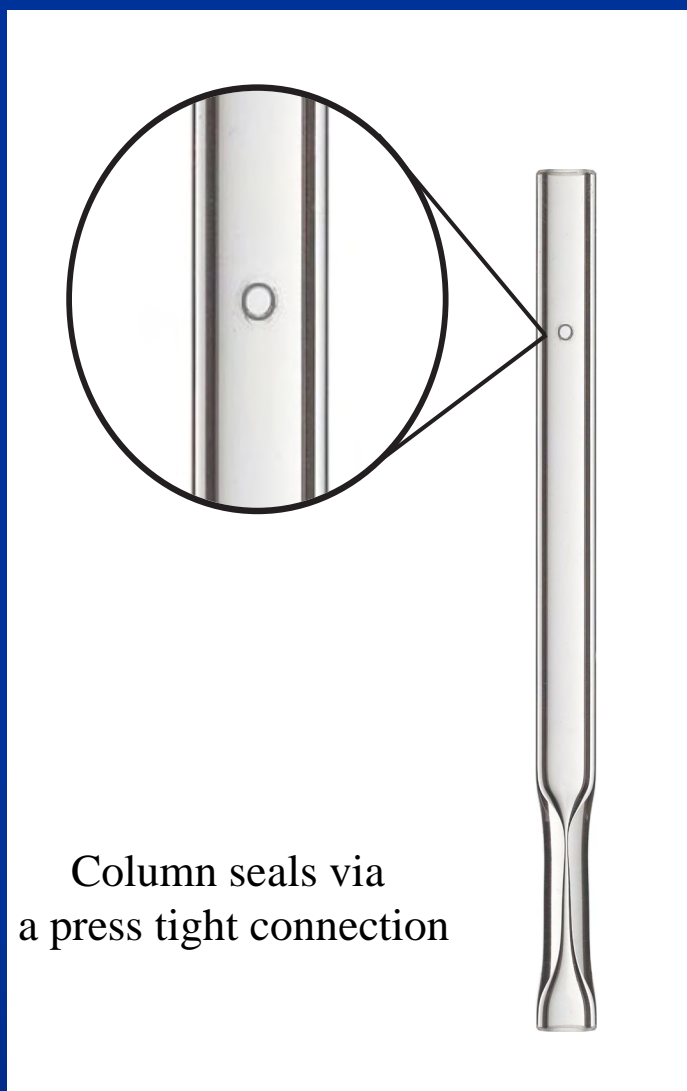




# Split/splitless Injection using Drilled Uniliner

- 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

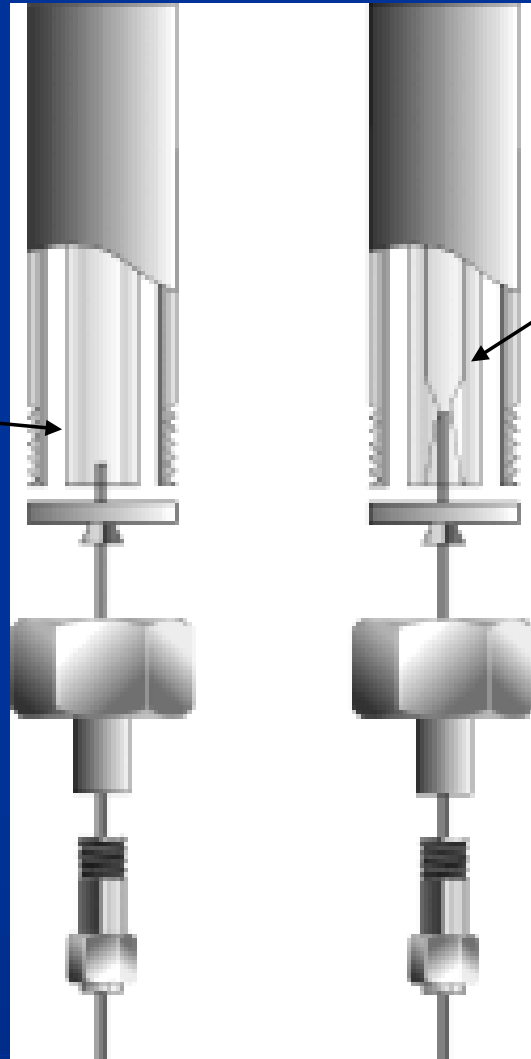
# Drilled Uniliner



- 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

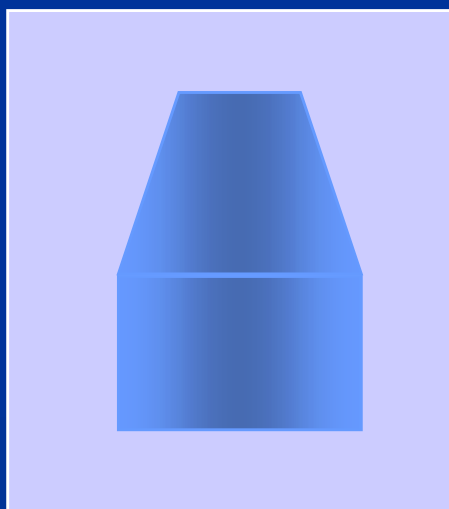
Press-fit  
connection

# Direct Injection Mode

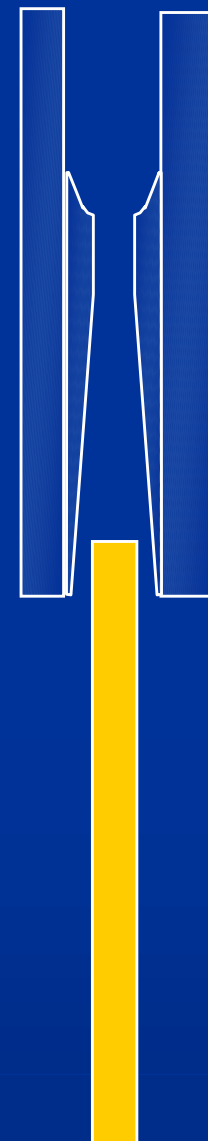
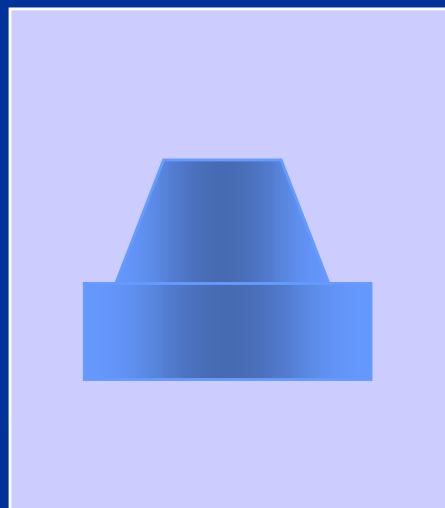
## Making the proper press-fit connection

### 1. Pre-seat or pre-crush new ferrules

New Ferrule



Pre-seated Ferrule

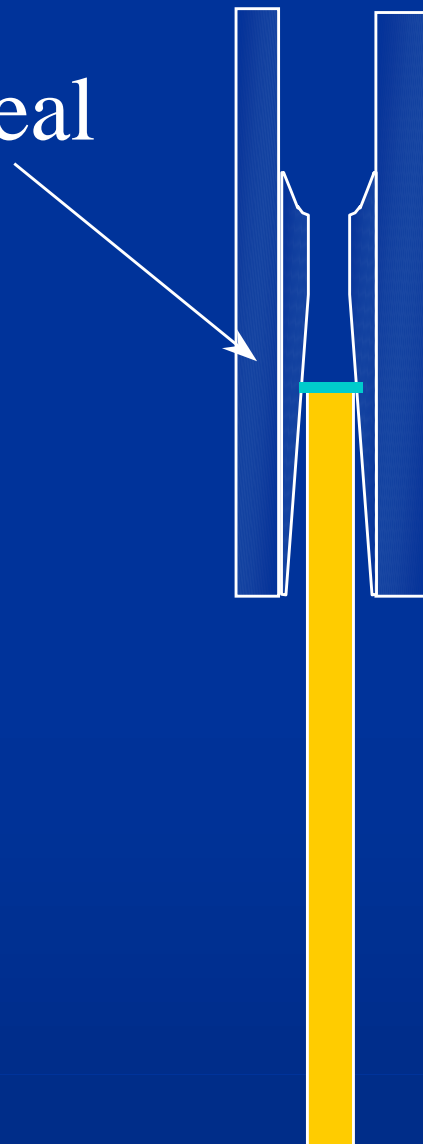


# Direct Injection Mode

## Making the proper press-fit connection

2. Install column into press-fit seal

3. Tighten column nut



# Direct Injection Liners



Open-top  
Uniliner®  
w/ wool



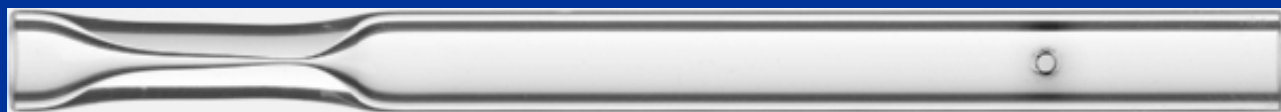
Cyclo  
Uniliner®



Standard  
Uniliner®

# Drilled Uniliners

4mm  
IP deactivated



4mm  
Siltek deactivated



2mm  
Siltek deactivated

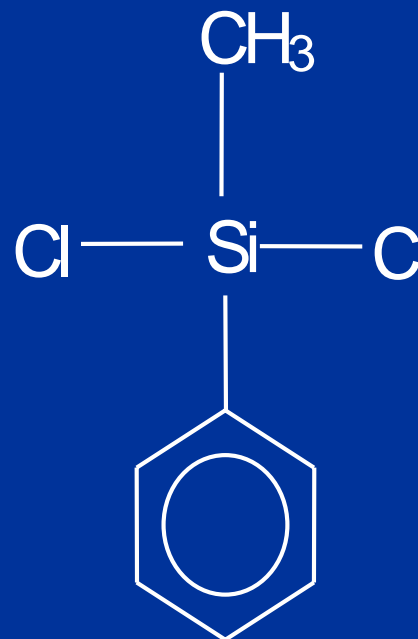
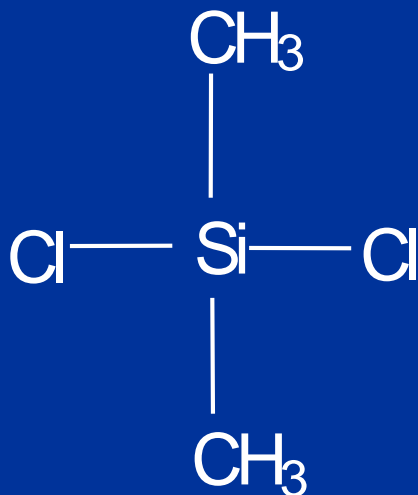


# Inlet Liner Deactivation

- “Pinpoint” deactivation
  - Chloro-silanes
- Polymeric deactivation
  - “IP” deactivation
- Surface modification
  - Siltek

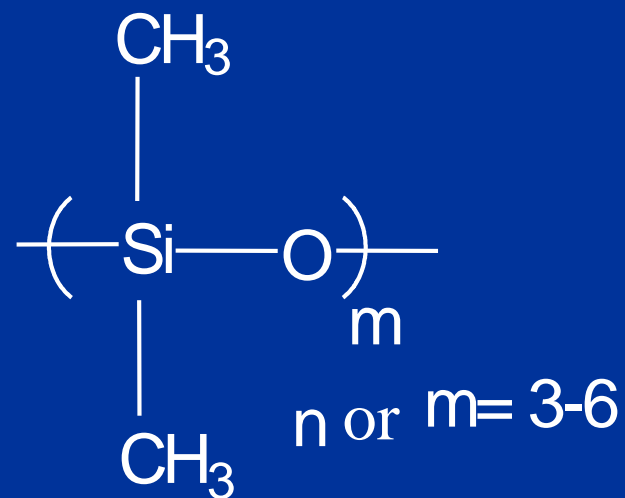
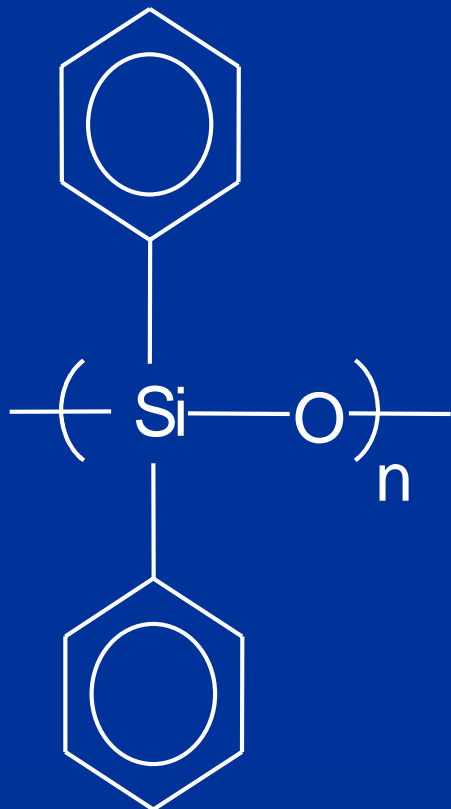


# Chlorosilane Deactivation



Adds to silanol group by HCl elimination

# Polymeric Deactivation



May “cover” unreacted silanols

# 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

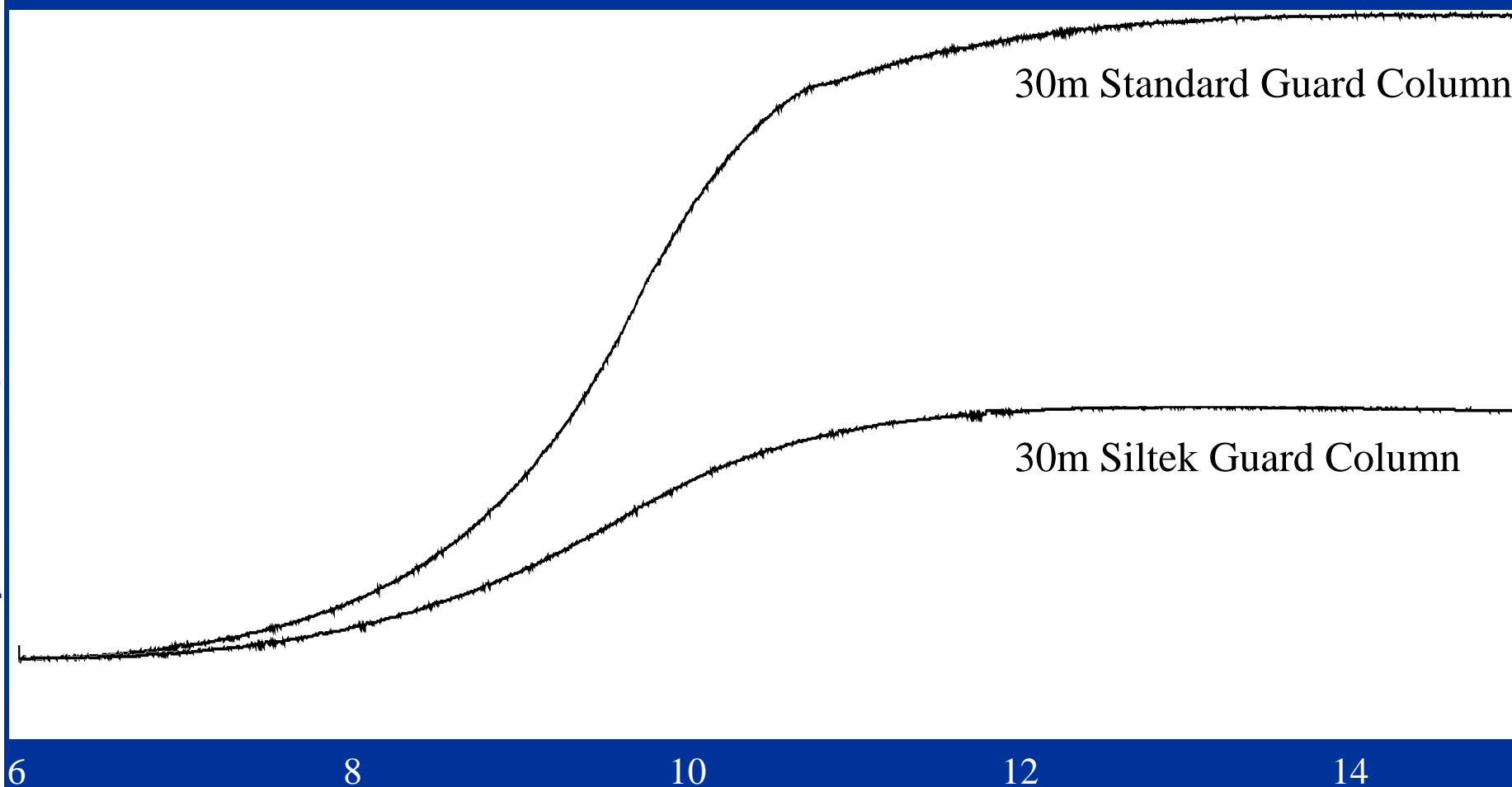


Figure 8

# Endrin and 4,4'DDT Breakdown

- Endrin breaks down to Endrin Aldehyde and Endrin Ketone
  - Active sites, septa particles, carrier gas contamination
- 4,4'-DDT breaks down to 4,4'-DDD and 4,4'-DDE
  - Dirty injection port – oils, nonvolatile material

# Column Selection - Dual Column Analysis



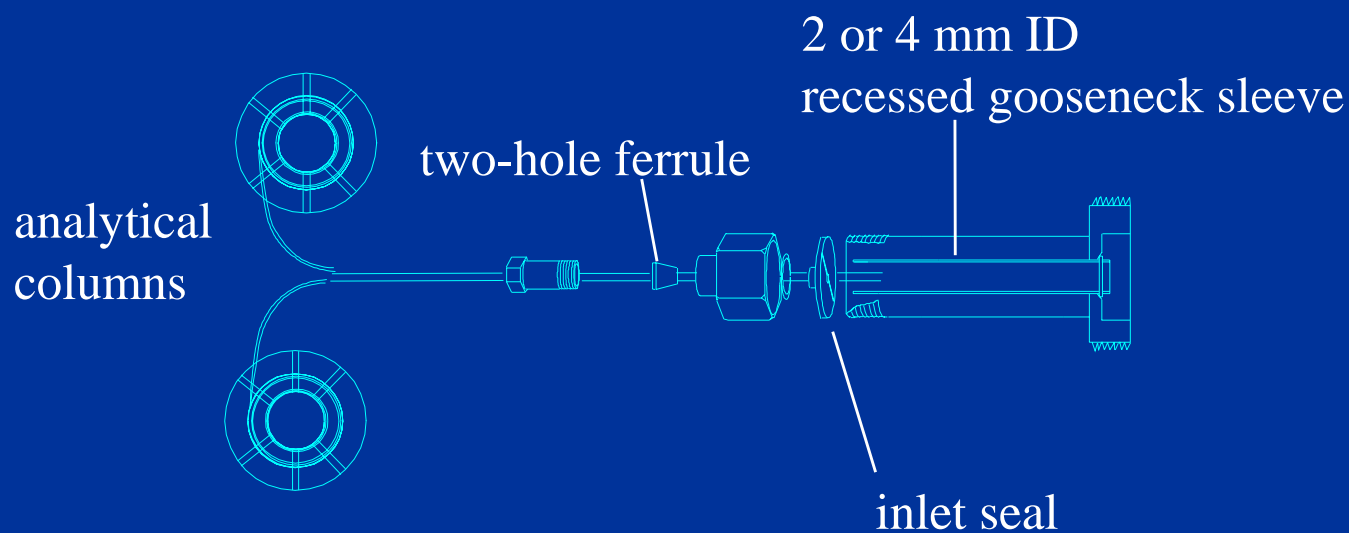
- Utilizes columns of different selectivity
- Changes elution order and retention times for components
- Improves qualitative reliability
- Can be done simultaneously to increase sample throughput

# Typical Column Pairings

- Rtx-5 and Rtx-50
  - Good resolution, runs typically greater than 25 minutes
- Rtx-1701 and Rtx-35
  - Good resolution, activity problems on 1701 polymer, runs typically greater than 25 minutes
- Rtx-CLP1 and Rtx-CLP2
  - Best resolution and run times less than 15 minutes
- Dimensions
  - Length: 15, 30, or 60 meter
  - ID: 0.10mm - 0.53mm
  - Film thickness varies

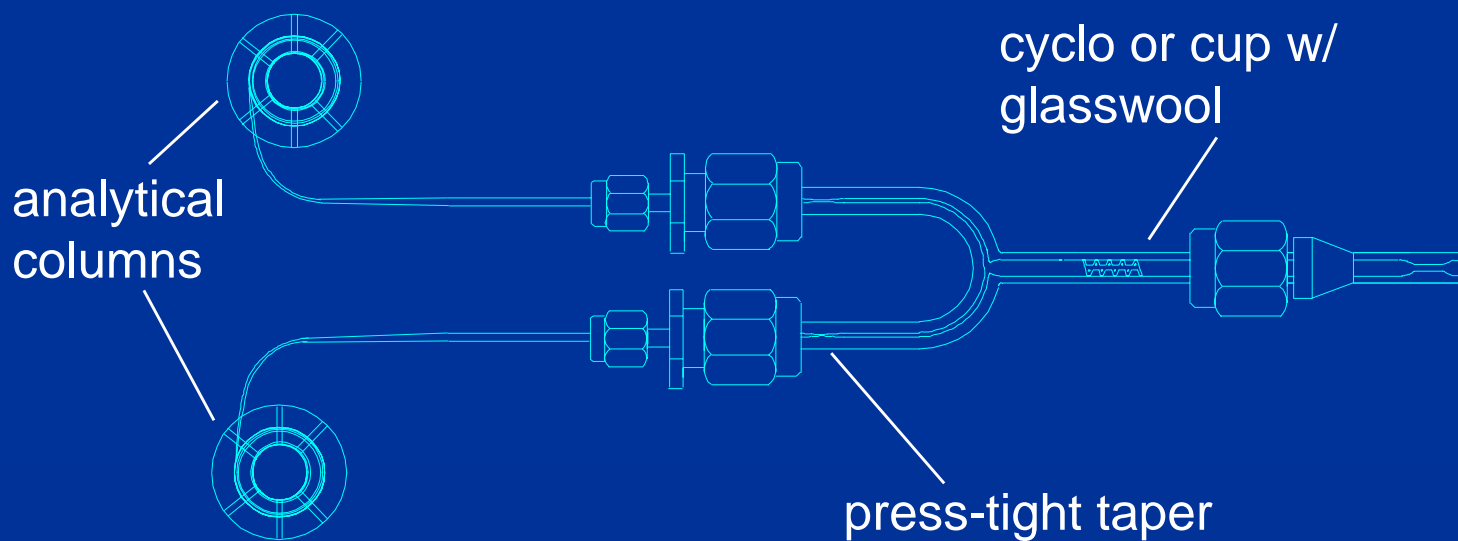


# Dual Column Fitting With a Two-Hole Ferrule for Split Inlets

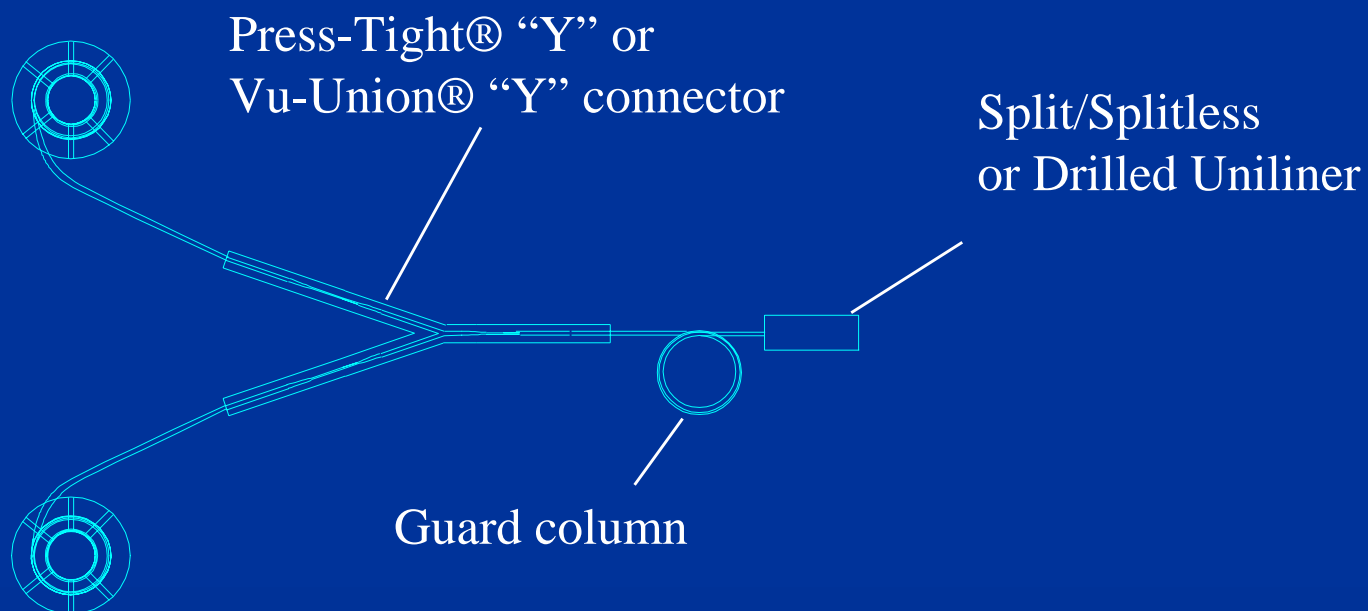




# Dual Column "T"



# Dual Column Injection



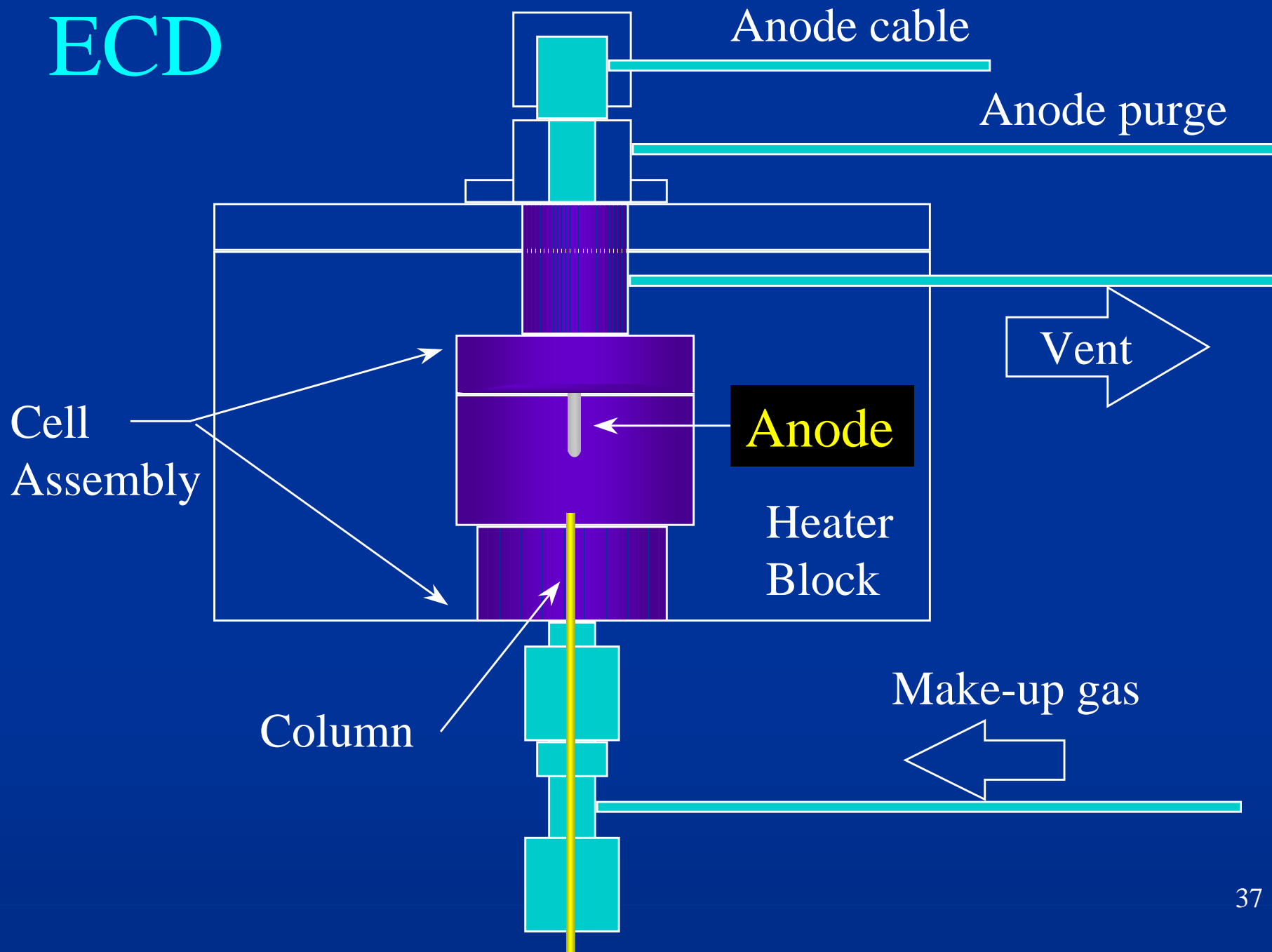
# ECD – General Information

- Type
  - Selective, concentration-dependent, non-destructive
- Response
  - Electronegative substituents (halogens, nitro groups, organometallic compounds)
- Published Linear Dynamic Range -  $10^4$
- Minimum Detectability
  - 0.5pg on column for g-BHC
- Typical Applications
  - Chlorinated pesticides, PCBs, and herbicides

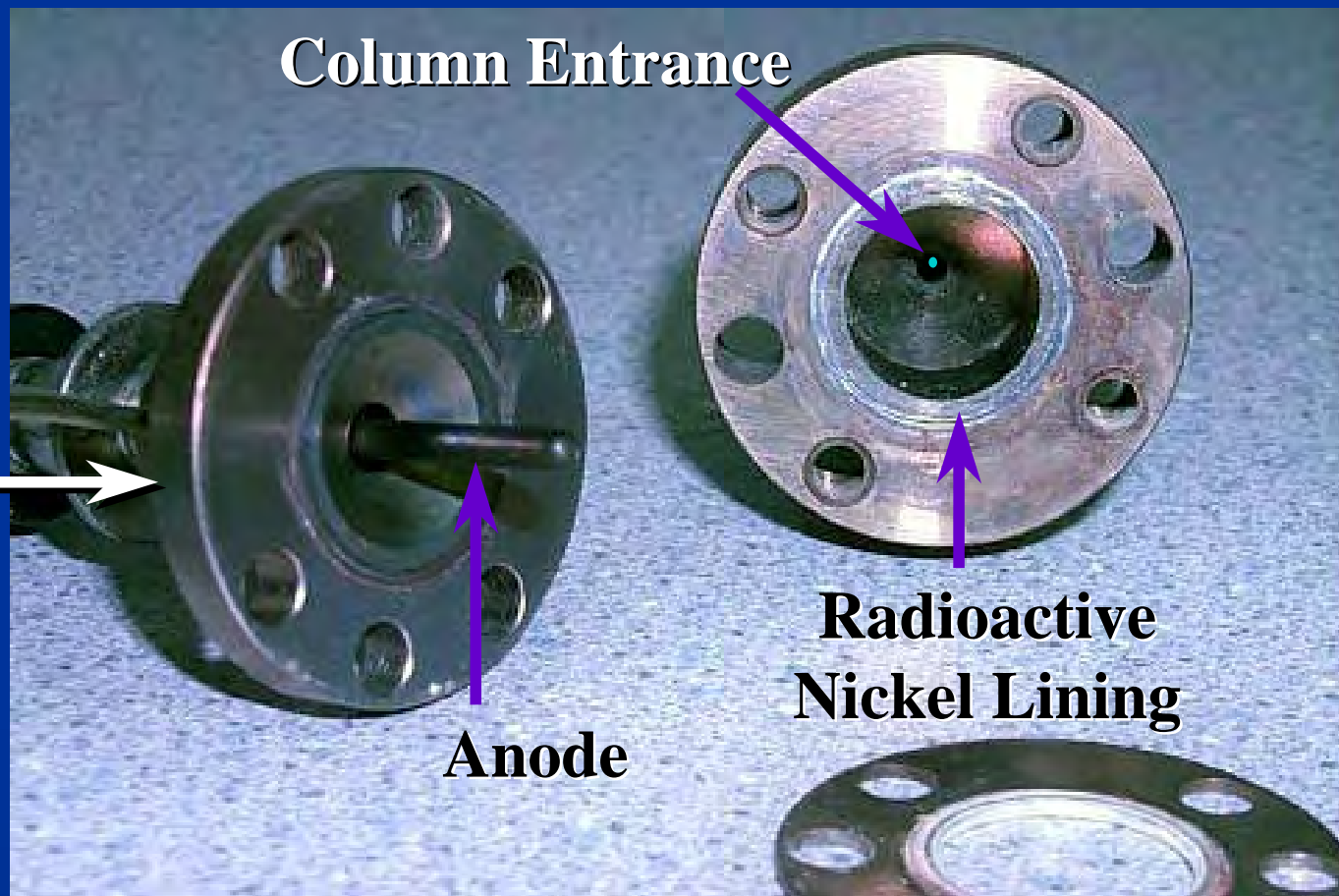
# ECD Response Relative to Hydrocarbons

Compound	ECD Response
Hydrocarbons	1
Ethers, esters	10
Aliphatic alcohols, ketones, amines, -Cl, -F compounds	100
-Br, -Cl <sub>2</sub> , & -F <sub>2</sub> compounds	1,000
Anhydrides & -Cl <sub>3</sub> compounds	10,000
-I, -Br <sub>2</sub> , poly-Cl, & poly-F compounds	100,000
-I <sub>2</sub> , -Br <sub>3</sub> , poly-Cl, & poly-F compounds	1,000,000

# ECD



# ECD – Cell Disassembly



Do not disassemble without proper permit.

# ECD

## Rtx-CLPesticides2

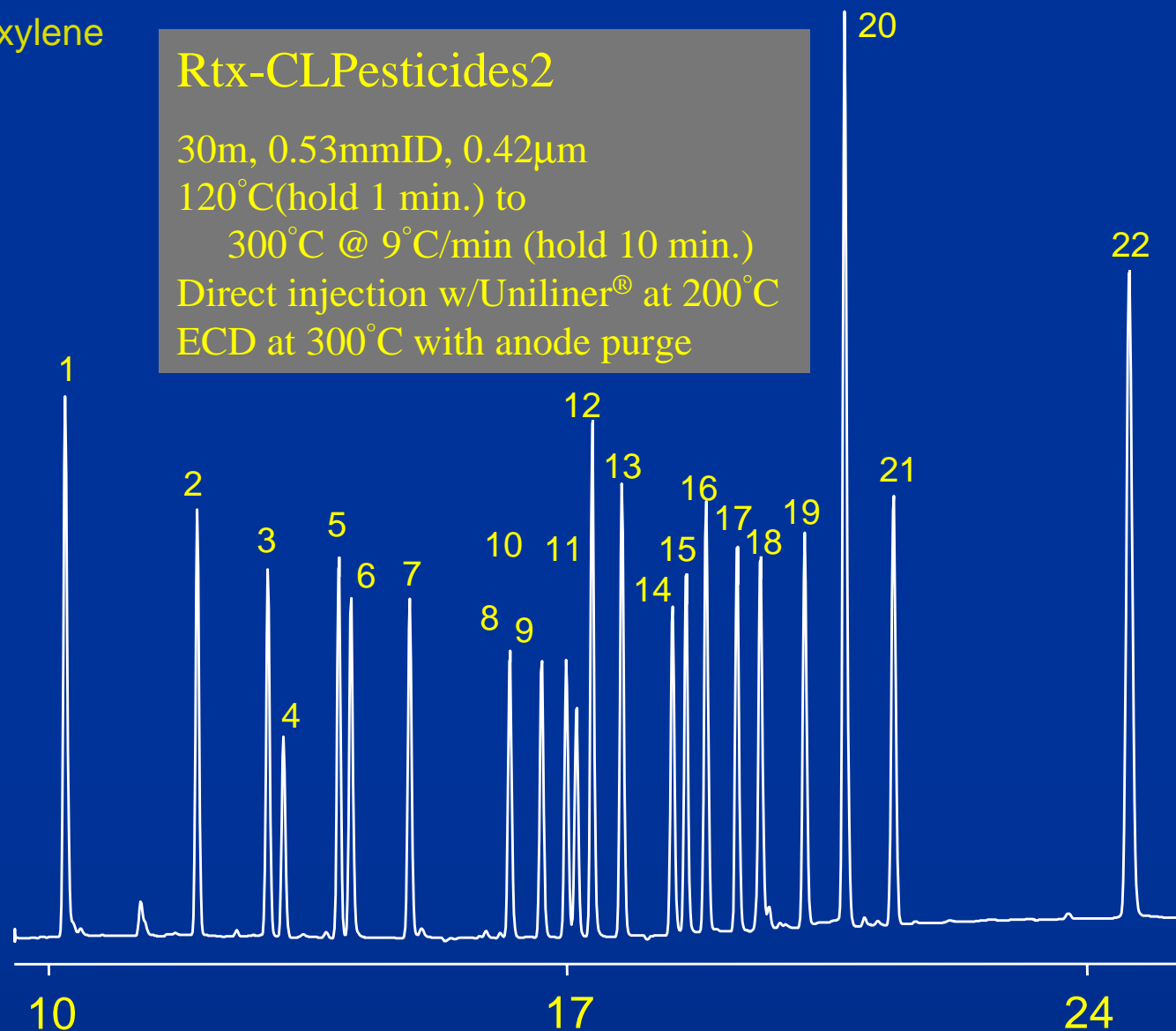
30m, 0.53mmID, 0.42µm

120°C(hold 1 min.) to

300°C @ 9°C/min (hold 10 min.)

Direct injection w/Uniliner® at 200°C

ECD at 300°C with anode purge



16-160pg on-column concentration

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



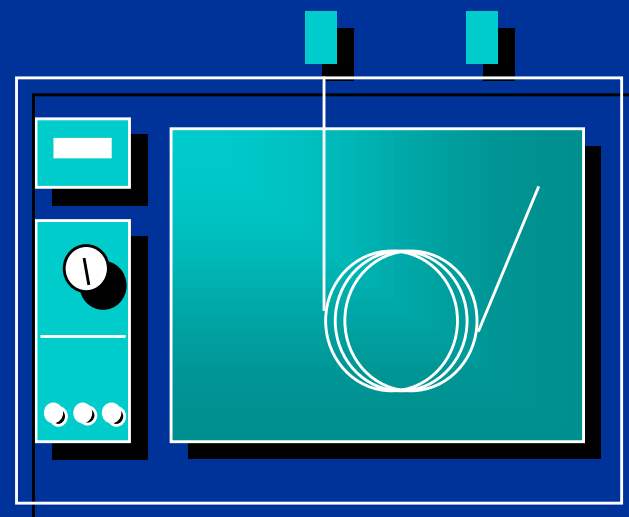
# ECD Operating Briefs

- Nitrogen or argon/methane (95/5) make-up gas
- Oxygen and water free systems:
  - Produce stable baseline
  - Increase lifetime of radioactive foil
  - Require a molecular sieve “S” trap, oxygen trap, or a triple filter



# ECD Operating Briefs

- Precondition column out of the (cooled) detector
- ECDs are very sensitive to bleed



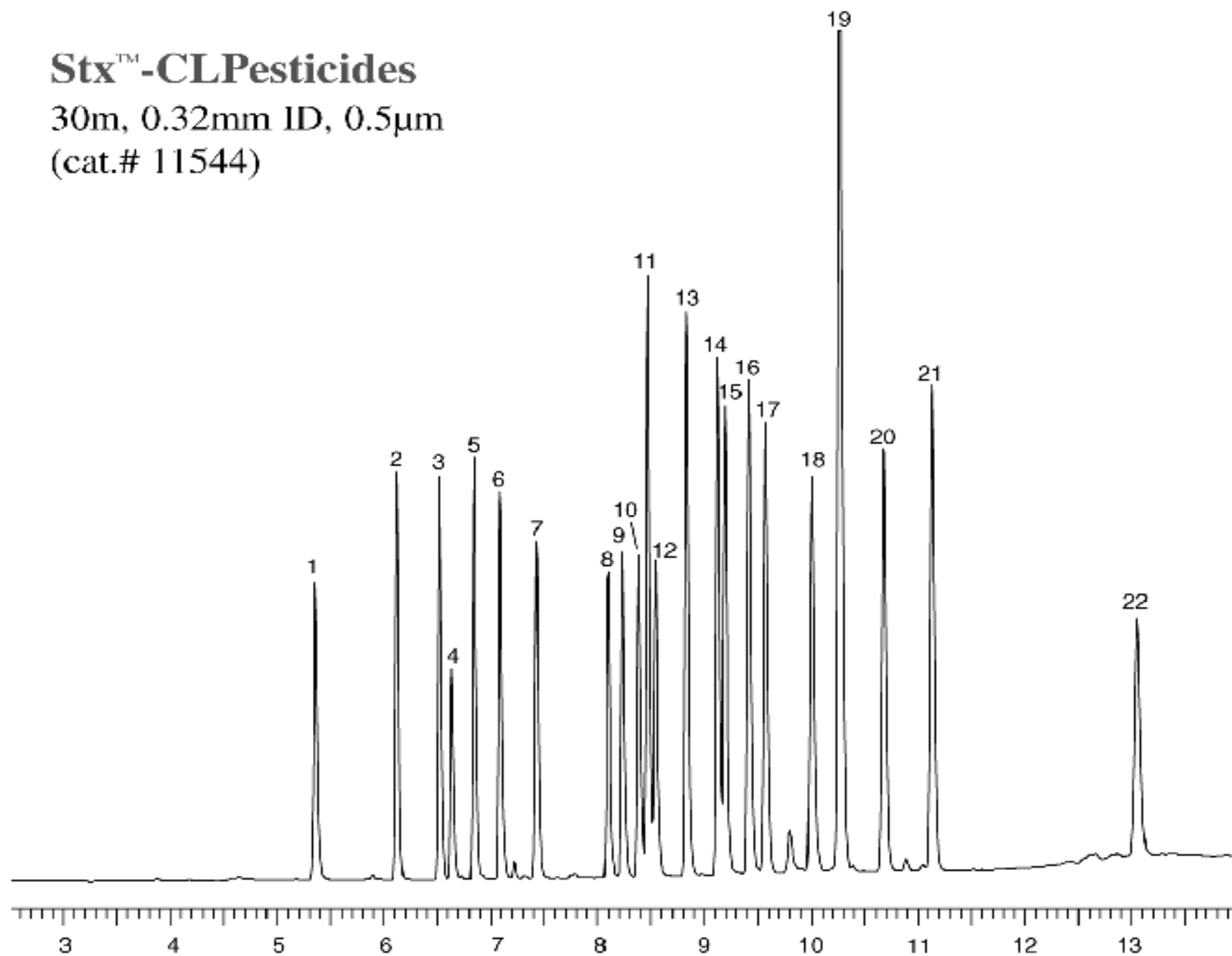
Note: This is a non-destructive detector. Vent or trap toxic eluents during analyses!

# ECD Maintenance

- Change traps regularly to prevent oxygen and moisture contamination
- Clean anode w/ aluminum oxide powder
- Thermal conditioning - refer to instrument manufacturer's procedure
- Wipe test
- Refoil detector cell

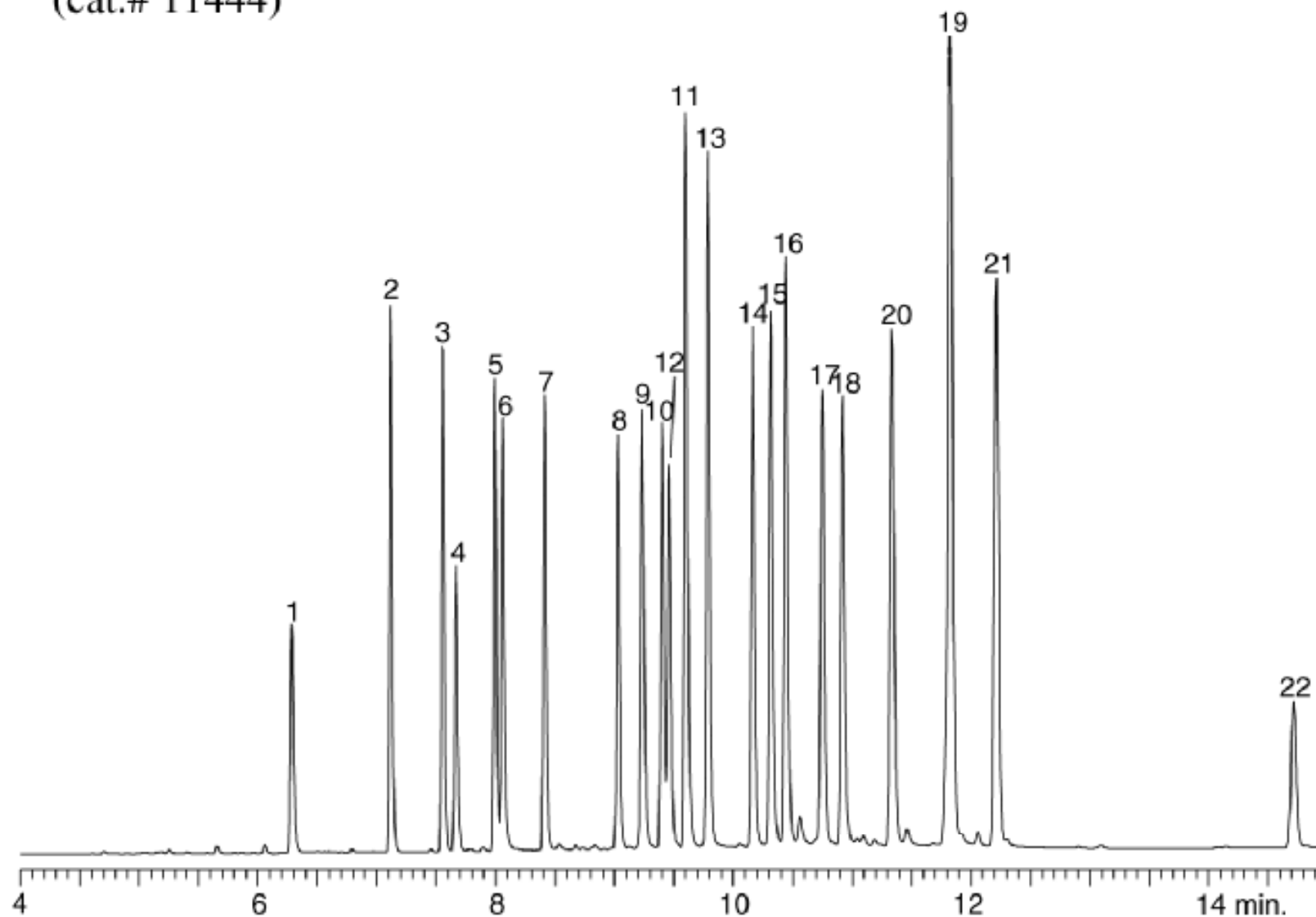
# Stx™-CLPesticides

30m, 0.32mm ID, 0.5µm  
 (cat.# 11544)



## Stx™-CLPesticides2

30m, 0.32mm ID, 0.25µm  
 (cat.# 11444)



# Peak Table and GC Conditions for Fast Analysis

- |                                      |                             |
|--------------------------------------|-----------------------------|
| 1. 2,4,5,6 tetrachloro-m-xylene (SS) | 12. endosulfan I            |
| 2. a-BHC                             | 13. dieldrin                |
| 3. g-BHC                             | 14. endrin                  |
| 4. b-BHC                             | 15. 4,4'-DDD                |
| 5. d-BHC                             | 16. endosulfan II           |
| 6. heptachlor                        | 17. 4,4'-DDT                |
| 7. aldrin                            | 18. endrin aldehyde         |
| 8. heptachlor epoxide                | 19. methoxychlor            |
| 9. g-chlordane                       | 20. endosulfan sulfate      |
| 10. a-chlordane                      | 21. endrin ketone           |
| 11. 4,4'-DDE                         | 22. decachlorobiphenyl (SS) |

Oven temp.: 110°C (hold 1 min.) to 245°C @ 20°C/min. to 300°C @ 6°C/min.

Inj. & det. temp.: 210°C / 310°C

Carrier gas: helium

Dead time: 0.8min. @ 120°C

Inlet liner: Siltek(tm) Drilled Uniliner® liner (cat.# 21055-214.5)

Inj.: 1µL direct injection of 20/40/200ng/mL std. concentration in hexane

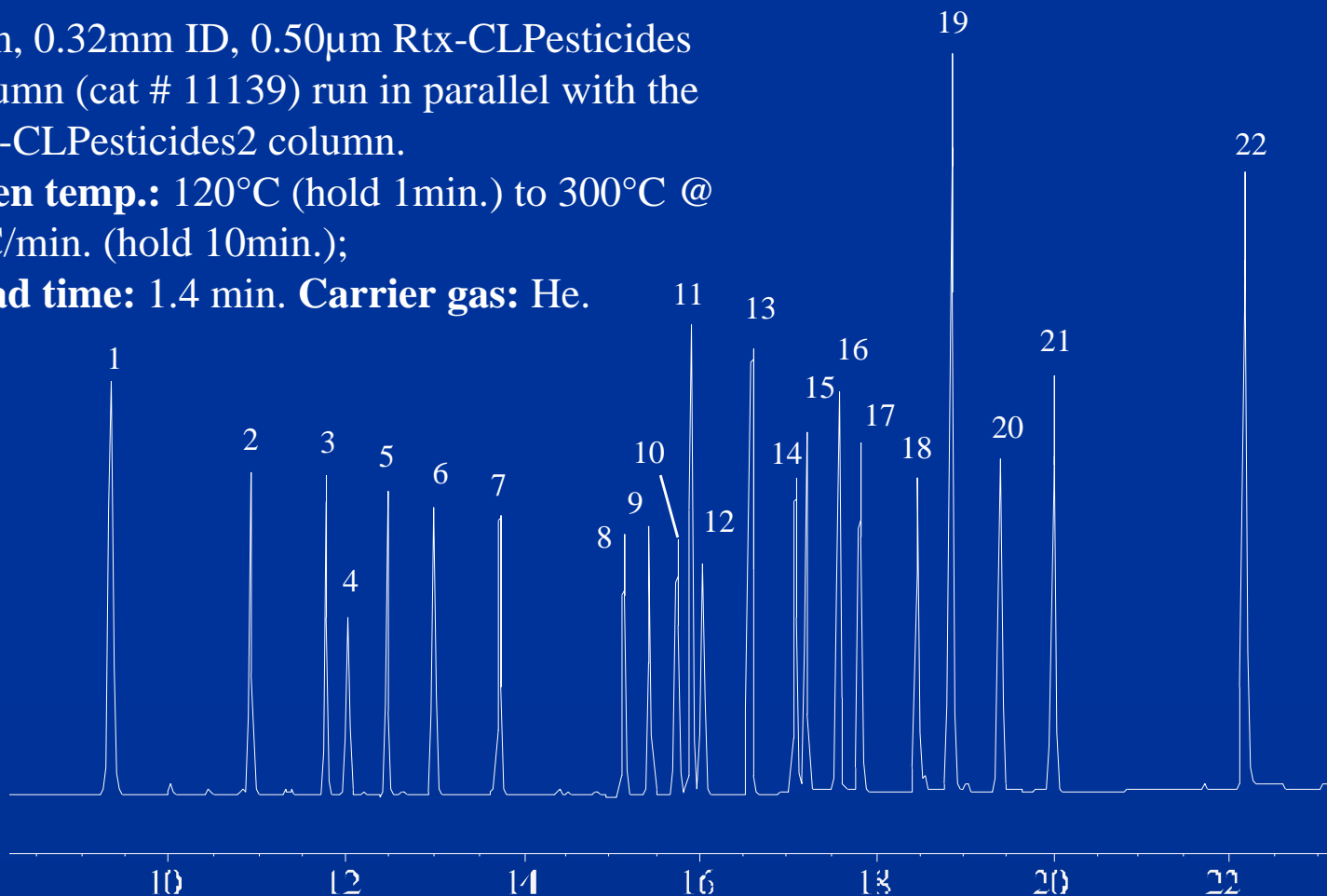
Make-up gas: nitrogen

# Rtx-CLPesticides

30m, 0.32mm ID, 0.50 $\mu$ m Rtx-CLPesticides column (cat # 11139) run in parallel with the Rtx-CLPesticides2 column.

**Oven temp.:** 120°C (hold 1min.) to 300°C @ 9°C/min. (hold 10min.);

**Dead time:** 1.4 min. **Carrier gas:** He.

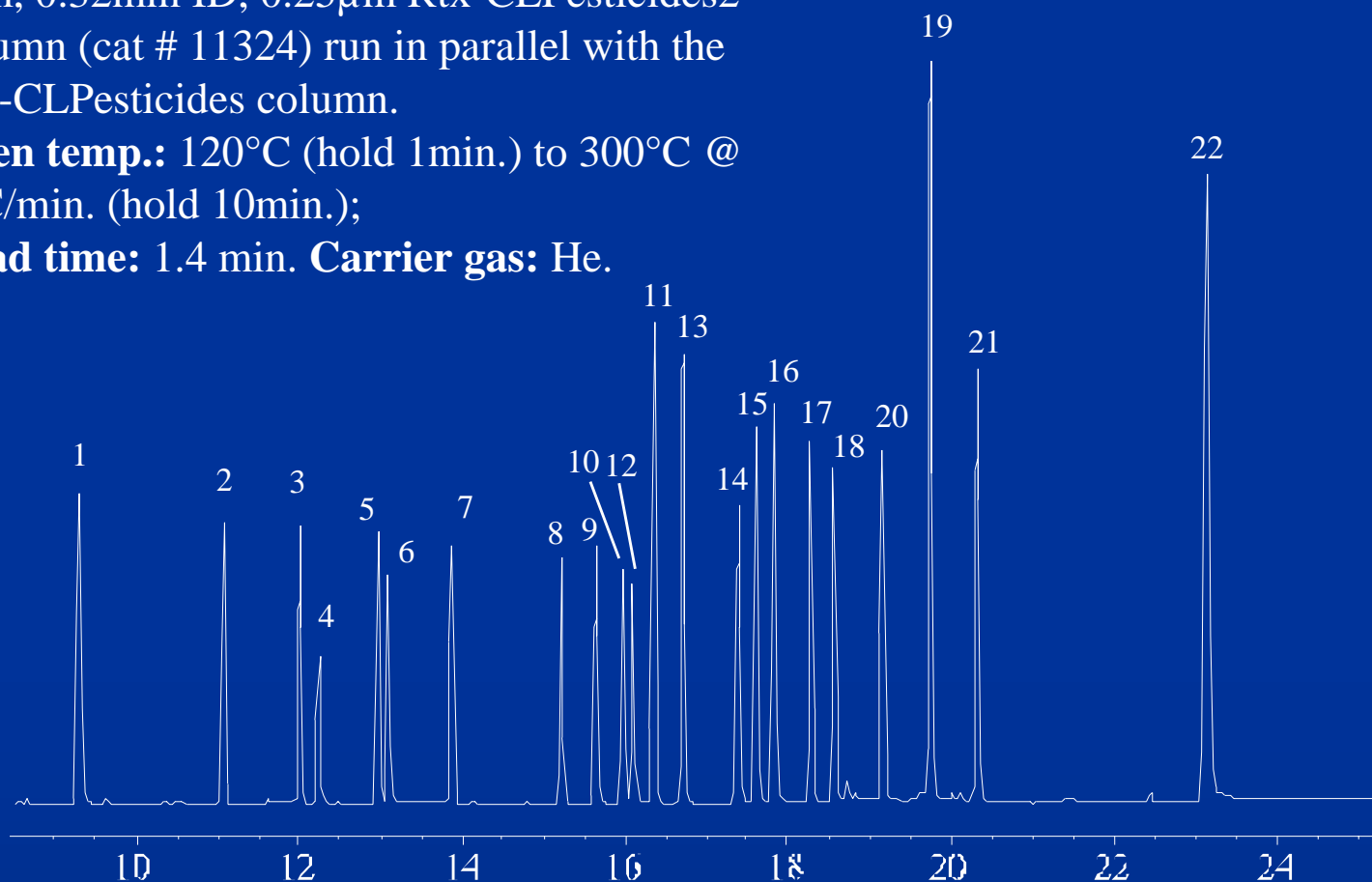


# Rtx-CLPesticides2

30m, 0.32mm ID, 0.25 $\mu$ m Rtx-CLPesticides2 column (cat # 11324) run in parallel with the Rtx-CLPesticides column.

**Oven temp.:** 120°C (hold 1min.) to 300°C @ 9°C/min. (hold 10min.);

**Dead time:** 1.4 min. **Carrier gas:** He.



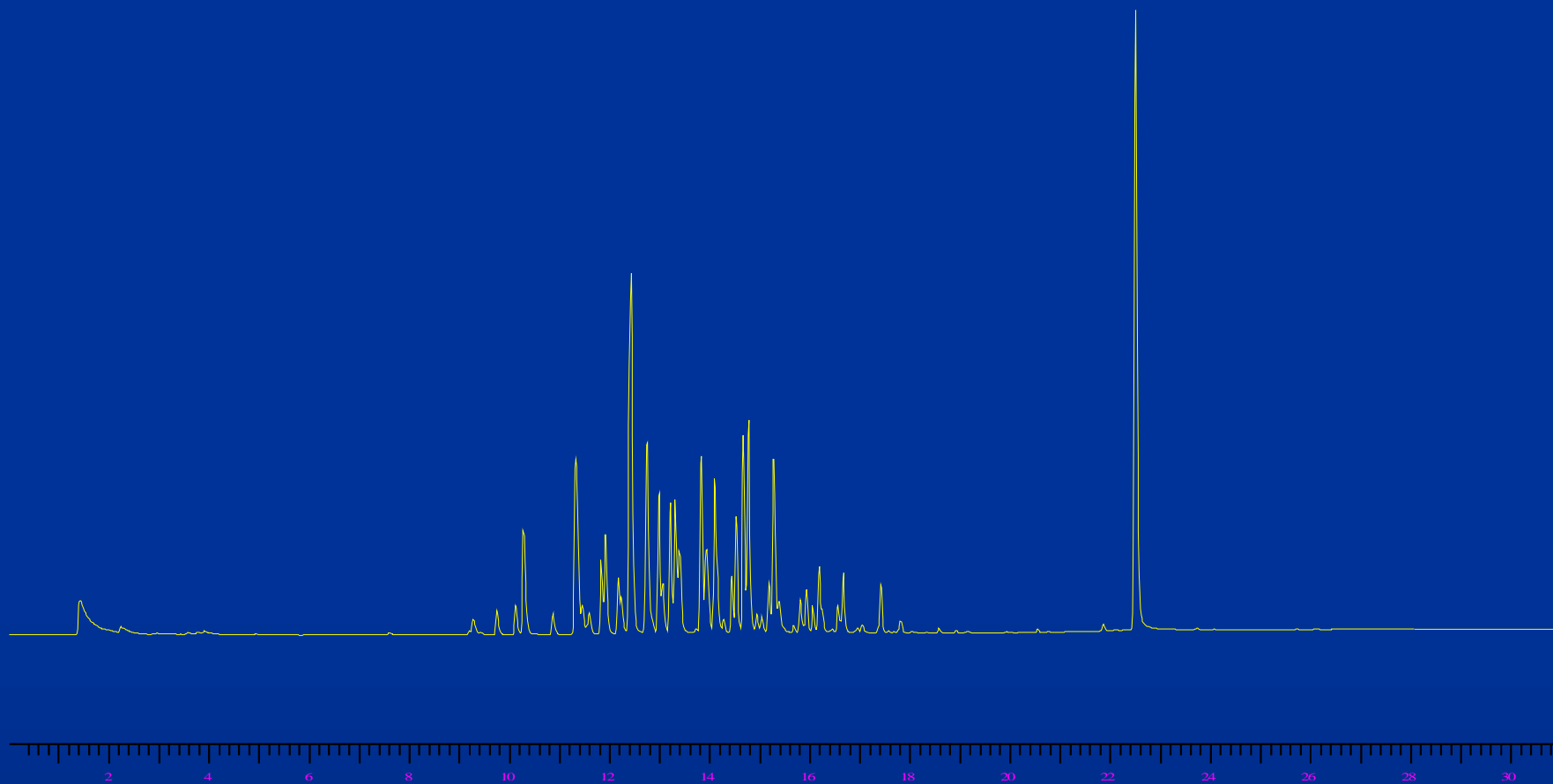
# EPA Method 8080 Pesticides

1. 2,4,5,6-tetrachloro-m-xylene
2.  $\alpha$ -BHC
3.  $\gamma$ -BHC
4.  $\beta$ -BHC
5.  $\delta$ -BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9.  $\gamma$ -chlordane
10.  $\alpha$ -chlordane
11. 4,4'-DDE
12. endosulfan I
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endosulfan II
17. 4,4'-DDT
18. endrin aldehyde
19. methoxychlor
20. endosulfan sulfate
21. endrin ketone
22. decachlorobiphenyl

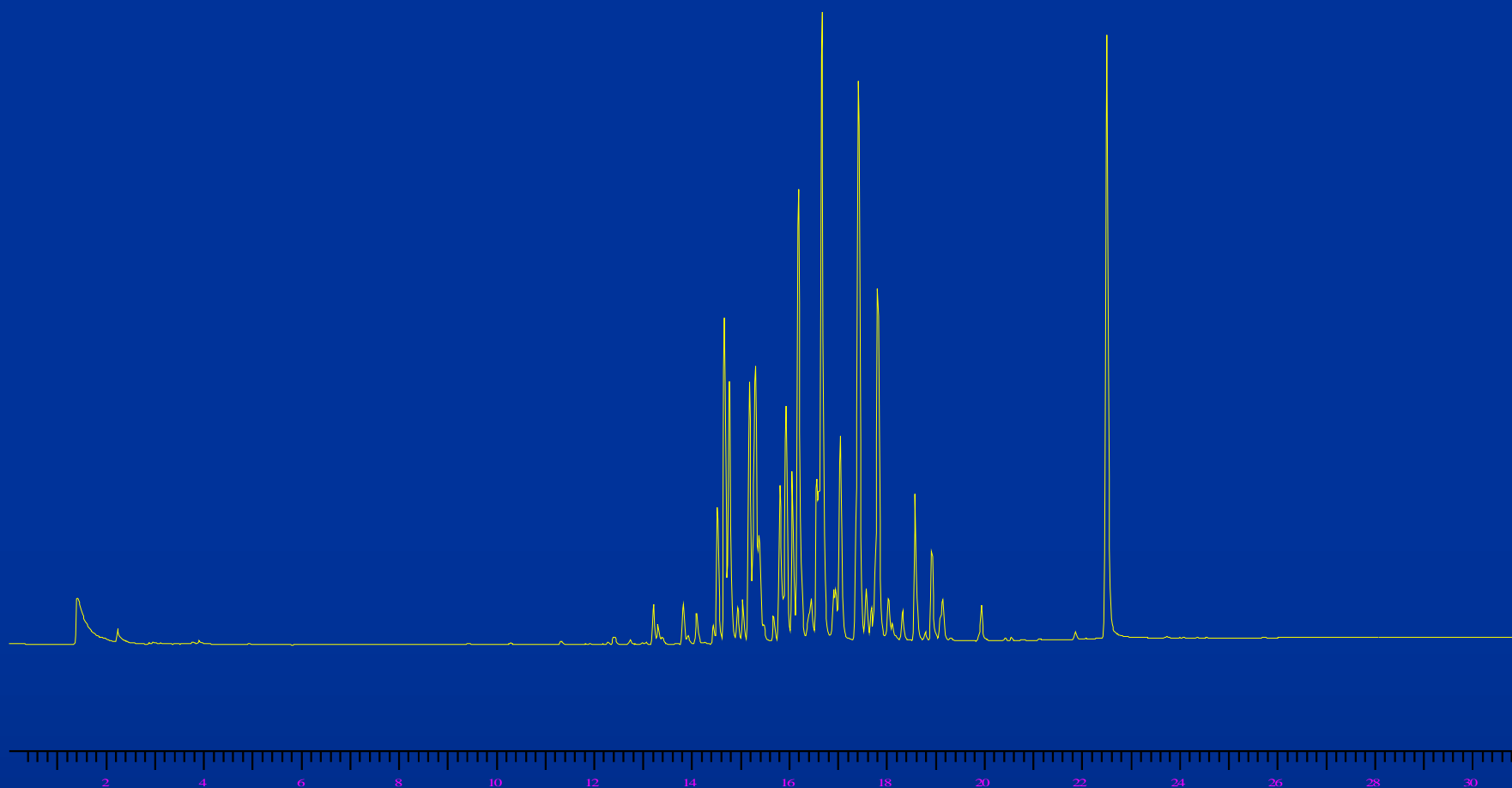
*Lit. #59547 — 8081A*



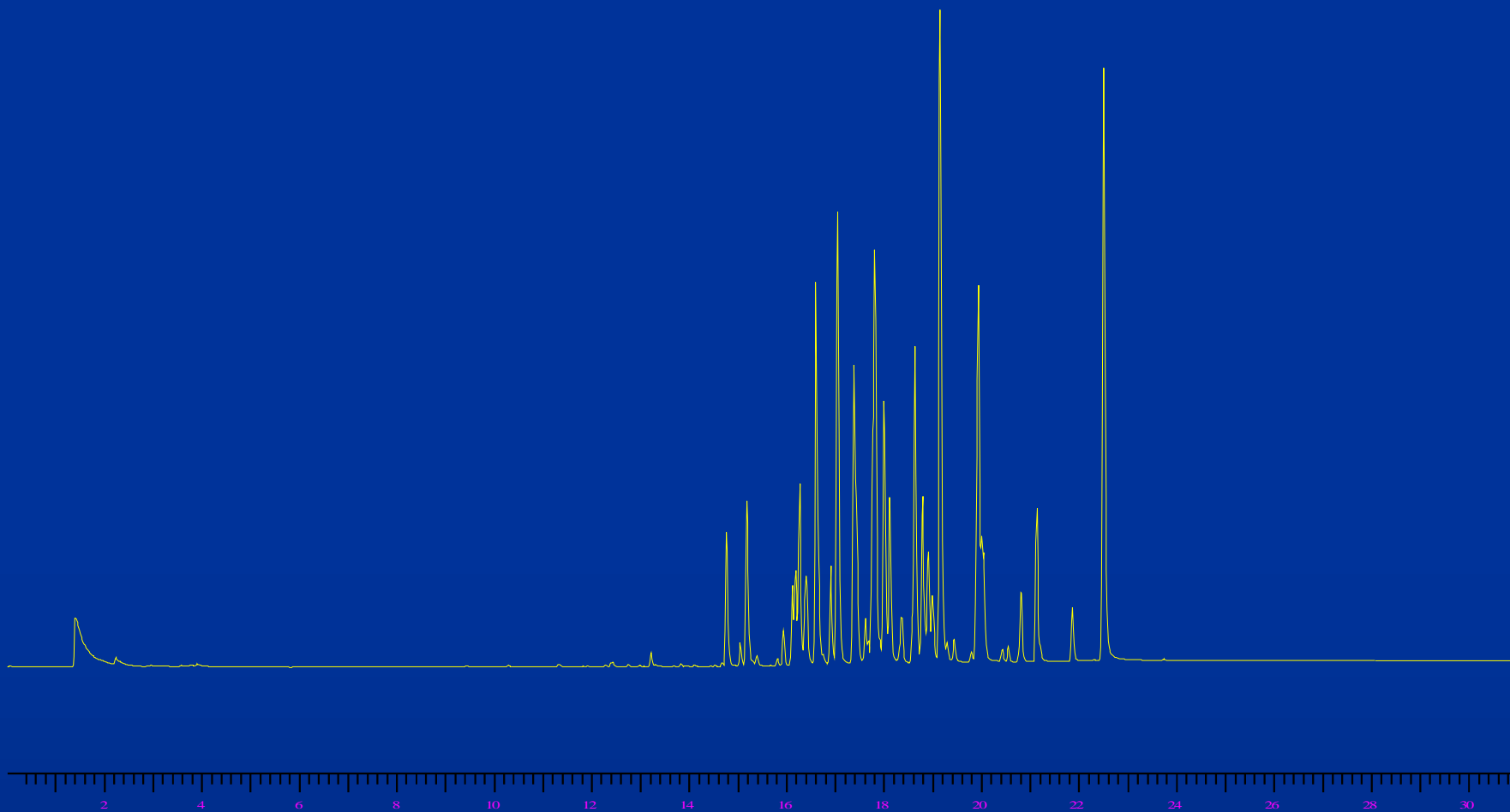
# Aroclor 1242



# Aroclor 1254



# Aroclor 1260



# Summary: Chlorinated Pesticides

- Clean-up suggested to remove matrix interferences
- Dual column setup suggested with one injection port
- Rtx®-CLPesticides & Rtx®-CLPesticides2 columns

# Introducing New Functionalities in Liquid Stationary Phases in GC Columns for Confirming Organic Volatile Impurity Testing in Pharmaceutical Products.

CHRISTOPHER M. ENGLISH,  
CHRISTOPHER S. COX, FRANK L.  
DORMAN, & DINESH PATWARDHAN.

# Abstract

One of the most common GC testing methods used by pharmaceutical laboratories is the analysis of organic volatile impurities (OVIs) in finished pharmaceutical products. There are many challenges in performing OVI analyses. The most commonly used capillary GC stationary phases for OVI analysis of regulated solvents are the G27 (5% diphenyl/95%dimethyl polysiloxane) and G43 (6%cyanopropyl phenyl/94%dimethyl polysiloxane) columns. However, other stationary phases must be employed depending on the specific solvents used in the manufacturing process of a pharmaceutical compound.

Often the OVIs are low-boiling, low molecular weight compounds that are difficult to retain and resolve on capillary stationary phases. Thick stationary films (3.0 $\mu$ m and 5.0 $\mu$ m) often are used to achieve required separations at a sacrifice in analysis time and the inability to use high temperature operating temperatures. Restek is developing a new stationary phase for confirming OVIs, that will resolve and elute unregulated compounds from regulated solvents.

Retention time information on seventy-six of the most common solvents will be presented on three stationary phases. Chromatograms of these common solvents will be presented to show the utility of these phases for the OVI analysis. This data will also be used to design a new column that will attempt to resolve all 76 compounds.



# Background

Residual solvents in pharmaceuticals are defined as volatile organic chemicals that are used or produced in the manufacture of drug substances or excipients, or in the preparation of drug products. The solvents are not completely removed by practical manufacturing techniques. Since there is no known therapeutic benefit from residual solvents, all residual solvents should be removed to the extent possible to meet product specifications, good manufacturing practices or other quality based requirements.

# USP Compound Classes

These solvents can be characterized by toxicity  
in three classes as follows:

Class I – have unacceptable toxicities and should be avoided.

Class II—less severe, should be avoided if possible.

Class III—less toxic and should be used when possible.

Solvents –not classified, or isomers of analytes listed above.

# USP Changes Address Challenging Separations

USP made changes in 1997 to overcome the difficulties resulting from unregulated solvents coeluting with regulated solvents and thereby causing over-representation of their concentration. These changes allow FID methods, GC/MS or a second validated column to be used. Restek is currently developing a new stationary phase, which is designed to be a confirmation column to phases such as G43 & G27.

# Analysis of Common Solvents Using Two Columns

The following conditions apply to both chromatograms shown (Rtx-G27 & Rtx-VGC), the only deviation from these parameters is the film thickness of the Rtx-VGC, which is 3.0 microns. The chromatograms are headspace injections of 24 common residual solvents for pharmaceutical processing. Prepared to equal about 500ppm in the bulk pharmaceutical. The Rtx-C would make a suitable confirmation column to the G27 phase for this compound set, but a column specifically engineered for these compounds could be used for a variety of methods and provide better resolution.

# USP <467> Common solvents

**Method I:** G27 30m x 0.53mm x 5.0 df , w/ 5m PM guard

**Inj:** Headspace at 500ppm in bulk pharm. 2:1 split

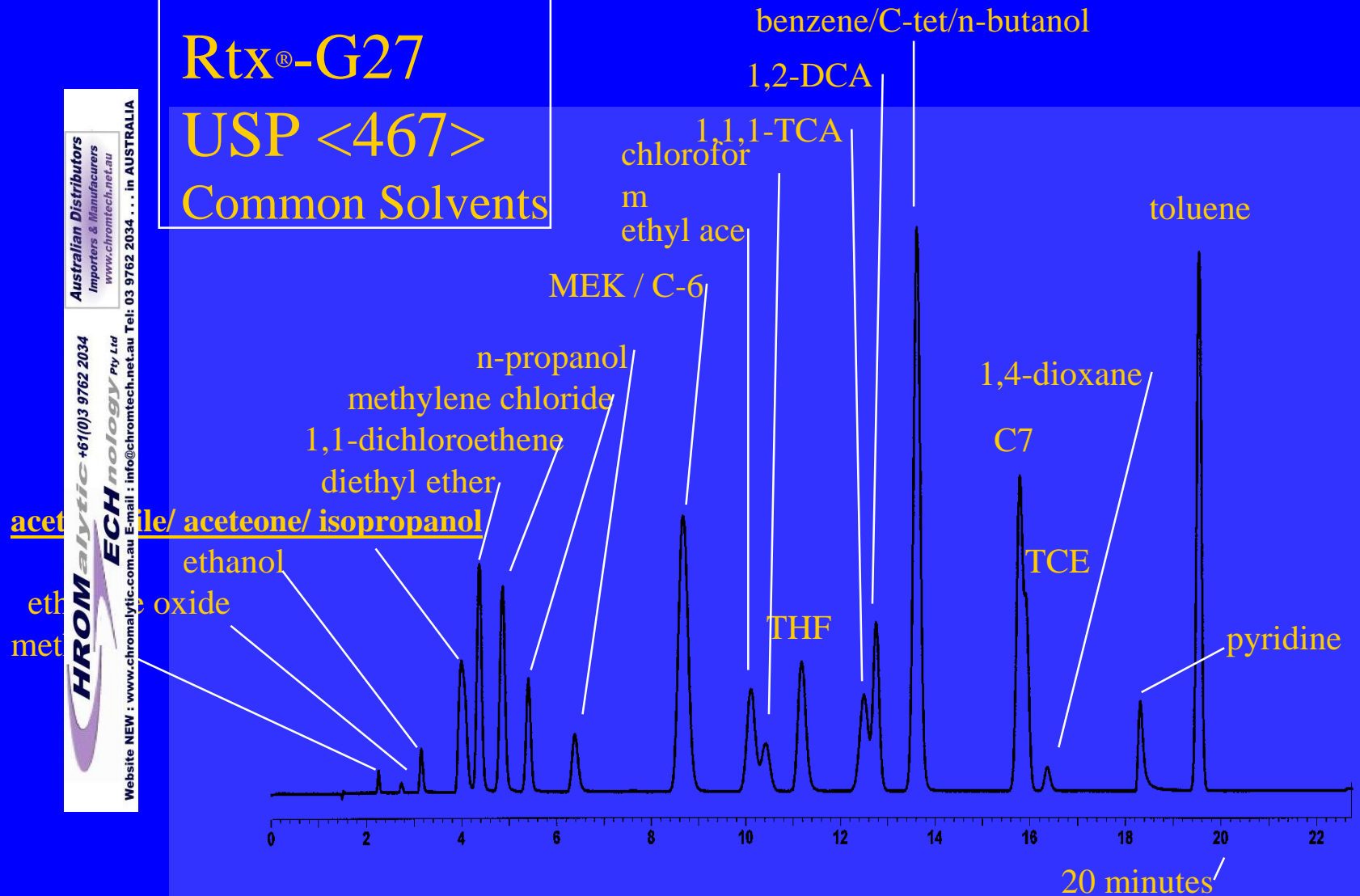
**Oven Temp:** 35(10)5/100 (0) 25/240(5)

**Detector:** FID, 260°C,  $1 \times 10^{-11}$  AFS

**Carrier:** helium, 4.1psi const, 35cm/sec @ 35°C

samples shaken and heated at 90°C for 15 minutes, 1mL headspace injection.

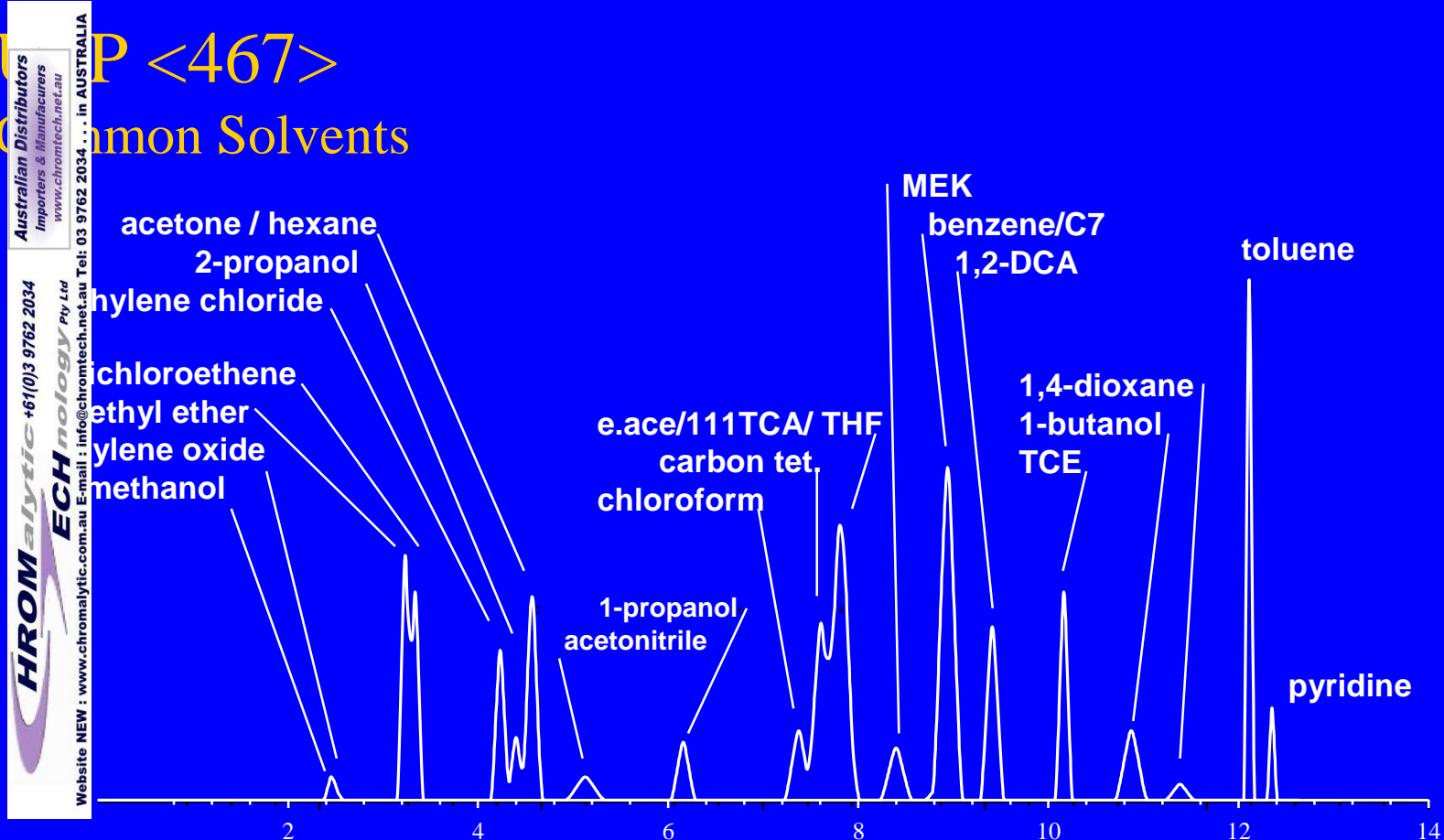
# Rtx®-G27 USP <467> Common Solvents



# Rtx®-VGC

## UP <467>

### Common Solvents



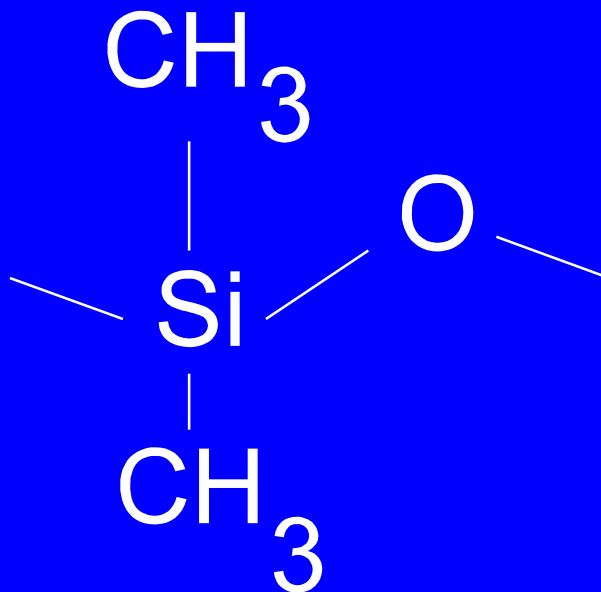
# Chromatograms of the 76 Solvents Using the Rtx-1, Rtx-200 and an Experimental Fluorinated Polymer.

The three chromatograms are run under the exact same conditions. These analytes can be modeled allowing predictions of retention time under any set of conditions, such as, column diameter, column length, film thickness, temperature, detector considerations, injection techniques, and flow. This allows subsets of the compound list to be resolved using specific conditions. Contact Restek for more information.



# Stationary Phases Used for Modeling

## Dimethyl-polysiloxane

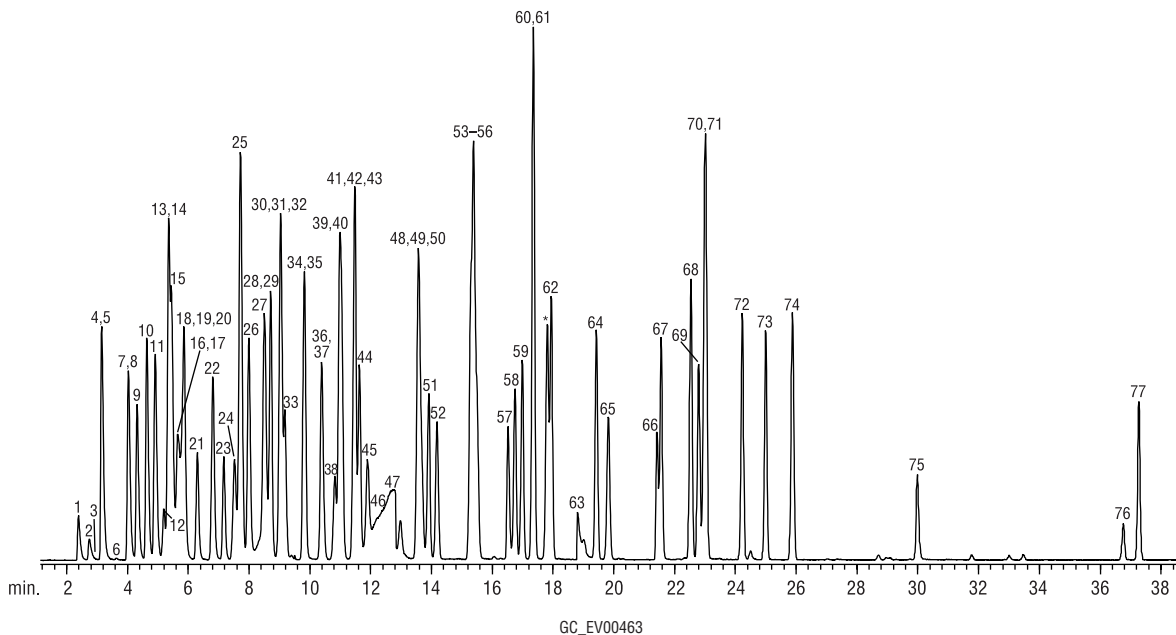


Rtx-1

# Rtx-1

VI methods allow for GC/MS confirmational analysis to identify complex chromatograms. GC/MS compound identification errors are common since ketones & acetates share parent ions (43). Alkanes & alkenes also present challenges since these compounds contain the 57 ion. The chromatogram shown illustrates the problems with non-polar phase with this compound list. Polar compound such as ethylene glycol have poor solubility in the dimethyl-polysiloxane phase resulting in poor sensitivity & linearity. The alcohols are retained less relative to the non-polar analytes.

# USP Solvents Rtx®-1



Rtx®-1 60m, 0.53mm, 3.00µm (cat.# 10188)  
 Sample: solvents  
 Conc.: solventless mixture ~1.3% each\*  
 Sample size: needle vapor  
 Inj.: split, 250°C  
 Septa purge: 5mL/min.  
 Split vent flow: 100mL/min. ~1:13 split  
 Carrier: helium  
 Head pressure: 11.0psi constant pressure  
 Linear velocity: 45.6 cm/sec @ 35°C  
 Det: Mass Selective  
 Scan range: 10amu to 260amu  
 MS interface: open split interface ~1:7 split  
 Oven temp.: 35°C (hold 4 min.) to 250°C @ 4°/min.

1. formaldehyde  
 2. water  
 3. chloromethane  
 4. methanol  
 5. acetaldehyde  
 6. ethylene oxide  
 7. chloroethane  
 8. ethanol  
 9. acetonitrile  
 10. acetone  
 11. 2-propanol  
 12. 2-chloropropane  
 13. diethylether  
 14. pentane  
 15. ethyl formate  
 16. formic acid  
 17. methylal  
 18. 1,1-dichloroethene  
 19. methyl acetate  
 20. methylene chloride

21. nitromethane  
 22. 1-propanol  
 23. *trans*-1,2-dichloroethene  
 24. methyl *tert*-butyl ether  
 25. 2-methylpentane (spiked at 9%)  
 26. 2-butanone (MEK)  
 27. 2-butanol  
 28. *cis*-1,2-dichloroethene  
 29. acetic acid  
 30. isopropyl ether  
 31. ethyl acetate  
 32. hexane  
 33. chloroform  
 34. tetrahydrofuran  
 35. 2-methoxyethanol  
 36. 1,2-dichloroethane  
 37. methyl cyclopentane  
 38. 1,1,1-trichloroethane  
 39. 1,2-dimethoxyethane  
 40. methyl isopropyl ketone

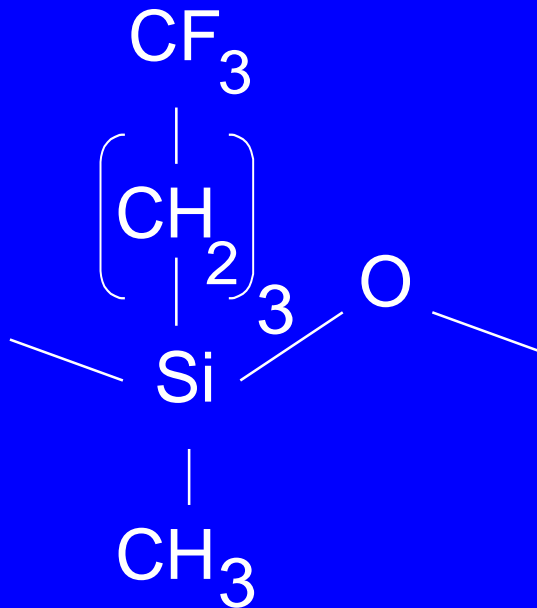
41. 2,2-dimethoxypropane  
 42. isopropyl acetate  
 43. 1-butanol  
 44. benzene  
 45. carbon tetrachloride  
 46. ethylene glycol  
 47. formamide  
 48. 1,4-dioxane  
 49. trichloroethene  
 50. isooctane  
 51. 2-ethoxyethanol  
 52. *n*-heptane (C7)  
 53. isoamyl alcohol  
 54. hexanone (MIBK)  
 55. pyridine  
 56. methyl cyclohexane  
 57. dimethyl formamide (DMF)  
 58. 1,1,2-trichloroethane  
 59. 1-pentanol  
 60. isobutyl acetate

61. toluene  
 62. 2-hexanone (MBK)  
 63. dimethyl sulfoxide  
 64. butyl acetate  
 65. 1,1-diethoxypropane  
 66. N,N-dimethylacetamide  
 67. chlorobenzene  
 68. ethylbenzene  
 69. isoamyl acetate  
 70. *p*-xylene  
 71. *m*-xylene  
 72. *o*-xylene  
 73. anisole  
 74. isopropylbenzene (cumene)  
 75. 1-methyl-2-pyrrolidinone  
 76. sulfolane  
 77. 1,2,3,4-tetrahydronaphthalene

\*paraldehyde

# Trifluoropropyl-methyl

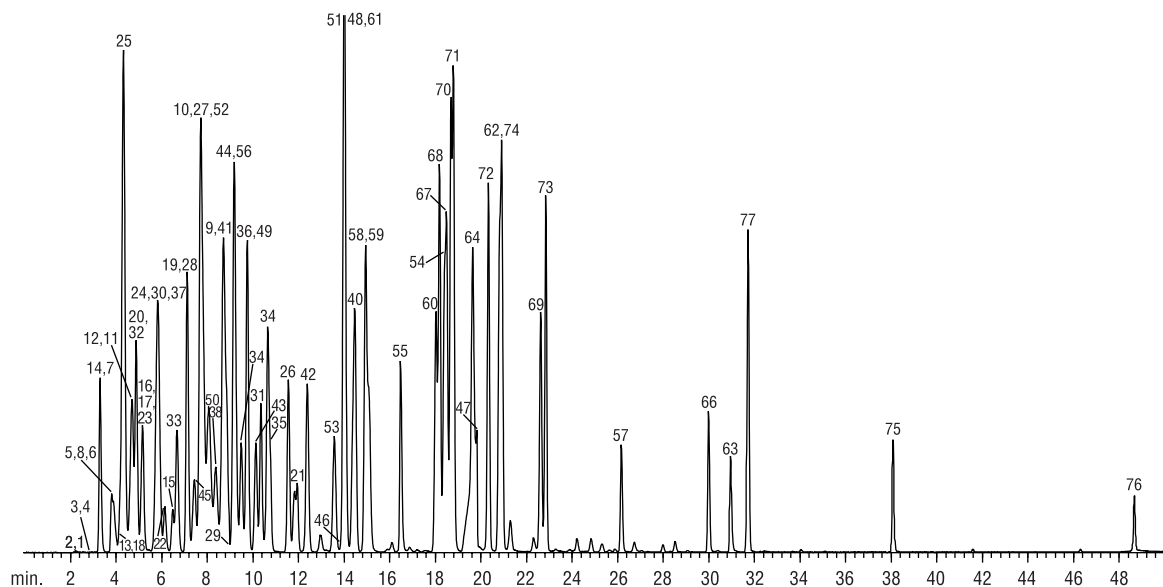
Rtx-200



## Rtx-200

Like the Rtx-1 the Rtx-200 column is low bleed and is offered in thick films (3.0 micron). It has better peak shapes for glycols and other polar analytes. The Rtx-200 still lacks the “polarity” necessary to better retain compounds, such as alcohols, ketones and glycols. A phase that can withstand higher temperatures and yet have wax-like characteristics would allow for better retention.

# USP Solvents Rtx®-200

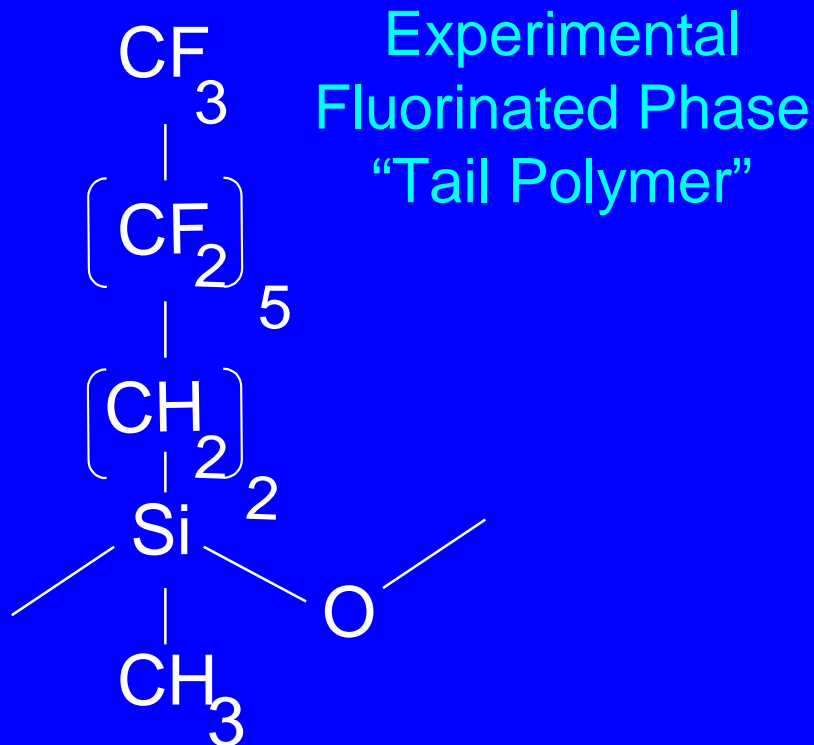


GC\_EV00464

Rtx®-200 60m, 0.53mm, 3.00µm (cat.# 15088)  
 Sample: solvents  
 Conc.: solventless mixture ~1.3% each\*  
 Sample size: needle vapor  
 Inj.: split, 250°C  
 Septa purge: 5mL/min.  
 Split vent flow: 100mL/min. ~1:13 split  
 Carrier: helium  
 Head pressure: 11.0psi constant pressure  
 Linear velocity: 45.6 cm/sec @ 35°C  
 Det: Mass Selective  
 Scan range: 10amu to 260amu  
 MS interface: open split interface ~1:7 split  
 Oven temp.: 35°C (hold 4 min.) to 250°C @ 4°/min.

- |                        |                                      |                              |                                   |
|------------------------|--------------------------------------|------------------------------|-----------------------------------|
| 1. formaldehyde        | 21. nitromethane                     | 41. 2,2-dimethoxypropane     | 61. toluene                       |
| 2. water               | 22. 1-propanol                       | 42. isopropyl acetate        | 62. 2-hexanone (MBK)              |
| 3. chloromethane       | 23. <i>trans</i> -1,2-dichloroethene | 43. 1-butanol                | 63. dimethyl sulfoxide            |
| 4. methanol            | 24. methyl <i>tert</i> -butyl ether  | 44. benzene                  | 64. butyl acetate                 |
| 5. acetaldehyde        | 25. 2-methylpentane (spiked at 9%)   | 45. carbon tetrachloride     | 65. 1,1-diethoxypropane           |
| 6. ethylene oxide      | 26. 2-butanone (MEK)                 | 46. ethylene glycol          | 66. N,N-dimethylacetamide         |
| 7. chloroethane        | 27. 2-butanol                        | 47. formamide                | 67. chlorobenzene                 |
| 8. ethanol             | 28. <i>cis</i> -1,2-dichloroethene   | 48. 1,4-dioxane              | 68. ethylbenzene                  |
| 9. acetonitrile        | 29. acetic acid                      | 49. trichloroethene          | 69. isoamyl acetate               |
| 10. acetone            | 30. isopropyl ether                  | 50. isooctane                | 70. <i>p</i> -xylene              |
| 11. 2-propanol         | 31. ethyl acetate                    | 51. 2-ethoxyethanol          | 71. <i>m</i> -xylene              |
| 12. 2-chloropropane    | 32. hexane                           | 52. <i>n</i> -heptane (C7)   | 72. <i>o</i> -xylene              |
| 13. diethylether       | 33. chloroform                       | 53. isoamyl alcohol          | 73. anisole                       |
| 14. pentane            | 34. tetrahydrofuran                  | 54. hexanone (MIBK)          | 74. isopropylbenzene (cumene)     |
| 15. ethyl formate      | 35. 2-methoxyethanol                 | 55. pyridine                 | 75. 1-methyl-2-pyrrolidinone      |
| 16. formic acid        | 36. 1,2-dichloroethane               | 56. methyl cyclohexane       | 76. sulfolane                     |
| 17. methylal           | 37. methyl cyclopentane              | 57. dimethyl formamide (DMF) | 77. 1,2,3,4-tetrahydronaphthalene |
| 18. 1,1-dichloroethene | 38. 1,1,1-trichloroethane            | 58. 1,1,2-trichloroethane    |                                   |
| 19. methyl acetate     | 39. 1,2-dimethoxyethane              | 59. 1-pentanol               |                                   |
| 20. methylene chloride | 40. methyl isopropyl ketone          | 60. isobutyl acetate         |                                   |

# Tridecafluoro-1,1,2,2-tetrahydrooctyl-methyl

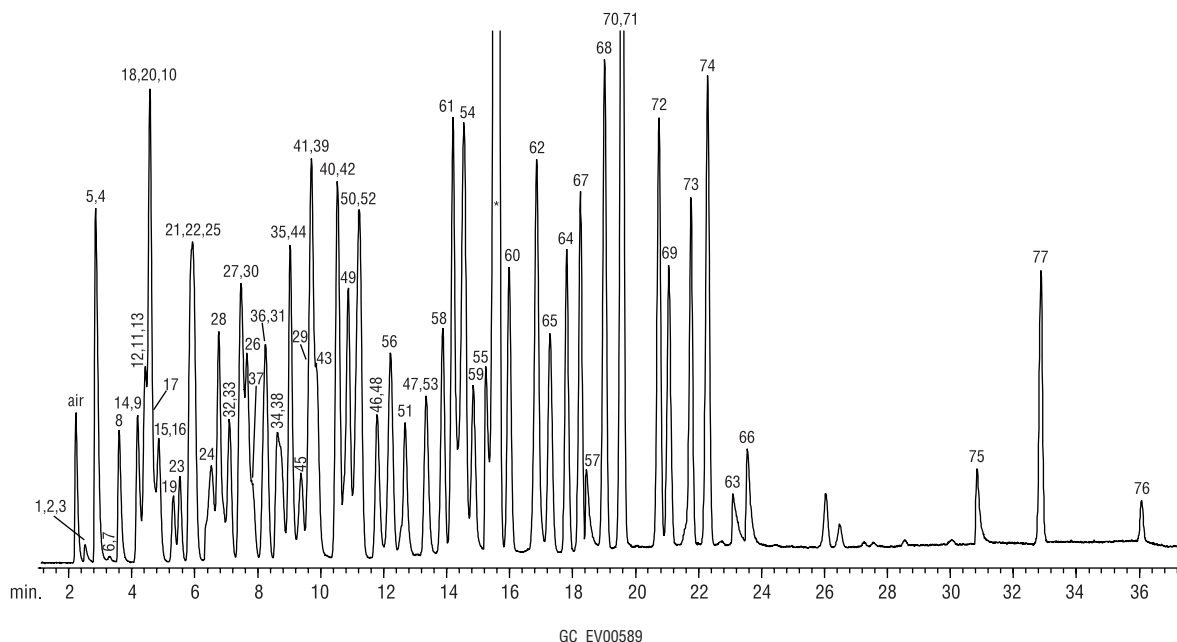


# Experimental “Tail” Polymer

This is one of a series of experimental columns currently under investigation. Understandably, this polymer has similar characteristics to the Rtx-200. Direct comparisons, which maintain equal amounts of fluorine atoms, indicate that nitrogen containing compounds & ketones have less retention on this phase than the trifluoropropyl phase. This can also be seen in the chromatograms shown.



## USP Solvents Experimental Fluorinated Polymer "Tail"



Experimental Fluorinated Polymer "Tail" 60m, 0.53mm, 3.00µm

Sample: solvents  
Conc.: solventless mixture ~1.3% each\*  
Sample size: needle vapor  
Inj.: split, 250°C  
Septa purge: 5mL/min.  
Split vent flow: 100mL/min. ~1:13 split  
Carrier: helium  
Head pressure: 11.0psi constant pressure  
Linear velocity: 45.6 cm/sec @ 35°C  
Det: Mass Selective  
Scan range: 10amu to 260amu  
MS interface: open split interface ~1:7 split  
Oven temp.: 35°C (hold 4 min.) to 250°C @ 4°/min.

1. formaldehyde  
2. water  
3. chloromethane  
4. methanol  
5. acetaldehyde  
6. ethylene oxide  
7. chloroethane  
8. ethanol  
9. acetonitrile  
10. acetone  
11. 2-propanol  
12. 2-chloropropane  
13. diethylether  
14. pentane  
15. ethyl formate  
16. formic acid  
17. methylal  
18. 1,1-dichloroethene  
19. methyl acetate  
20. methylene chloride

21. nitromethane  
22. 1-propanol  
23. *trans*-1,2-dichloroethene  
24. methyl *tert*-butyl ether  
25. 2-methylpentane (spiked at 9%)  
26. 2-butanone (MEK)  
27. 2-butanol  
28. *cis*-1,2-dichloroethene  
29. acetic acid  
30. isopropyl ether  
31. ethyl acetate  
32. hexane  
33. chloroform  
34. tetrahydrofuran  
35. 2-methoxyethanol  
36. 1,2-dichloroethane  
37. methyl cyclopentane  
38. 1,1,1-trichloroethane  
39. 1,2-dimethoxyethane  
40. methyl isopropyl ketone

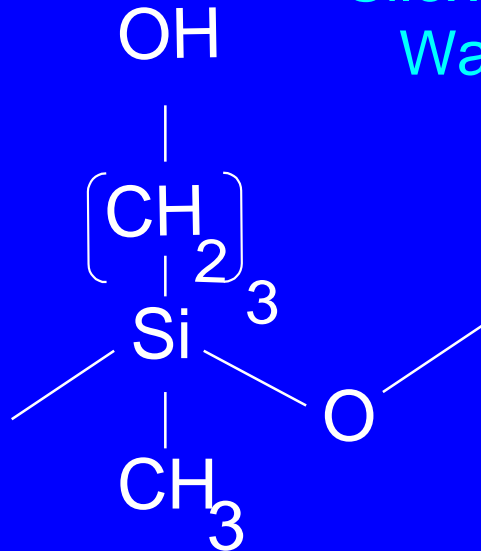
41. 2,2-dimethoxypropane  
42. isopropyl acetate  
43. 1-butanol  
44. benzene  
45. carbon tetrachloride  
46. ethylene glycol  
47. formamide  
48. 1,4-dioxane  
49. trichloroethene  
50. isooctane  
51. 2-ethoxyethanol  
52. *n*-heptane (C7)  
53. isoamyl alcohol  
54. hexanone (MIBK)  
55. pyridine  
56. methyl cyclohexane  
57. dimethyl formamide (DMF)  
58. 1,1,2-trichloroethane  
59. 1-pentanol  
60. isobutyl acetate

61. toluene  
62. 2-hexanone (MBK)  
63. dimethyl sulfoxide  
64. butyl acetate  
65. 1,1-diethoxypropane  
66. N,N-dimethylacetamide  
67. chlorobenzene  
68. ethylbenzene  
69. isoamyl acetate  
70. *p*-xylene  
71. *m*-xylene  
72. *o*-xylene  
73. anisole  
74. isopropylbenzene (cumene)  
75. 1-methyl-2-pyrrolidinone  
76. sulfolane  
77. 1,2,3,4-tetrahydronaphthalene

\*paraldehyde

# 1-hydroxypropyl-methyl

Experimental  
Siloxane-based  
Wax Phase



# Experimental Siloxane-Based Wax Phase

Years ago Restek attempted to fill the gap in polarity between polyethylene-glycol phases and bonded siloxane-based polymers by mixing the two phases together. The effects gave poor retention of complex compound mixtures, such as the ones presented in the chromatograms, but suffered many other problems. The bleed was high and the selectivity of these phases changed over time since the polyethylene-glycol bled at a higher rate than the dimethylpolysiloxane. These phases do not mix well, which compromised the coating efficiency of the column. Development of a bonded siloxane wax-like phase could solve these problems and aid in the development of a successful solution to the OVI column.

# New OVI Column

Restek is developing a stationary phase that will resolve the Class I compounds from the Class II & III analytes at the concentrations required by the USP. The second goal is to resolve the Class II from the Class III, as well as added solvents and their isomers. Conventional polysiloxanes will not meet the design criteria.

# For More Information...

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Restek Corporation  
110 Benner Circle  
Bellefonte, PA 16823  
(800) 356-1688

# HPLC Stationary Phase Selection for Environmental Analysis

C. Vernon Bartlett, Terrence S. Reid and  
Rahul D. Patil  
Restek Corporation  
110 Benner Circle, Bellefonte, PA 16823 USA

# Abstract

This study compares the selectivity of various stationary phases for environmental analysis, including pesticides, explosives, carbamates, and PAH's. Key stationary phase variables are identified and strategies for phase selection are provided.

# Introduction

There are several variables to consider in HPLC column selection, but the most critical one is the stationary phase. Stationary phases can be broadly classified by the primary ligand such as octadecyl (C18), octyl (C8), cyano, and phenyl. However there are many other variables that can play a critical role in selectivity such as ligand density and degree of polymeric character.



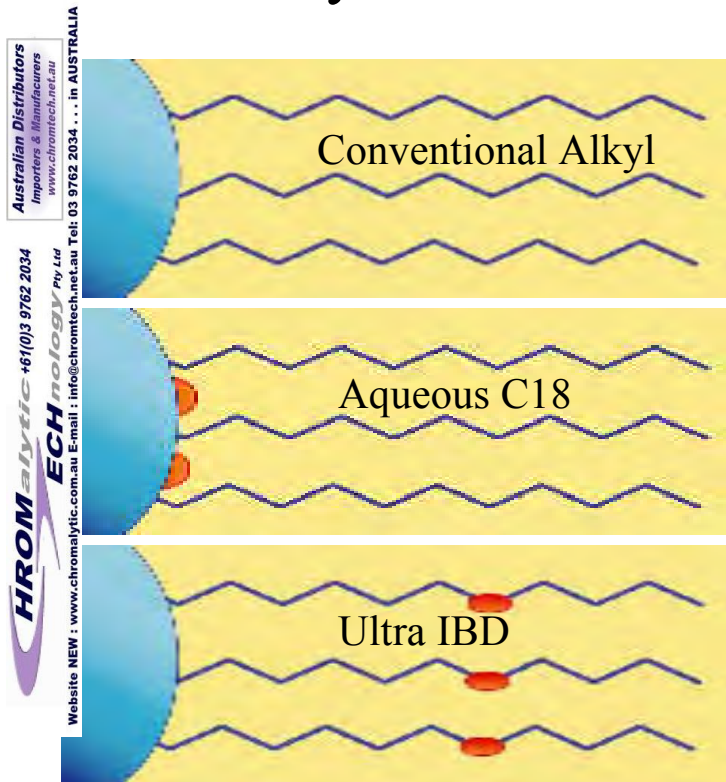
# Introduction

In addition to the common alkyl, phenyl, and cyano stationary phases, there are many newer stationary phases with more complex chemistries.

Many of these are based on alkyl chains with some secondary functionality added to aid selectivity.

Another approach for adjustment of selectivity is to use more than one stationary phase (i.e multiple columns) with complimentary selectivity in order to achieve better resolution with difficult separations.

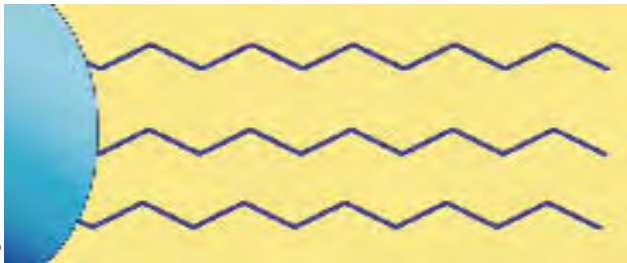
# Stationary Phases



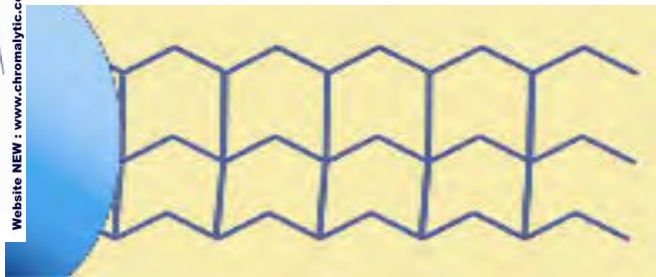
The Aqueous C18 and Ultra IBD stationary phases have secondary polar functionalities that enhance the retention of polar compounds, eliminate retention loss caused by chain folding (even in 100% aqueous mobile phase), and, in some cases, provide unique selectivity.

# Stationary Phases

Conventional Alkyl



Cross-linked Alkyl



Alkyl phases can be cross-linked to enhance structural integrity against folding. Also, the correct degree of polymeric character of a cross-linked alkyl phase is essential to enhancing selectivity for PAH separations.

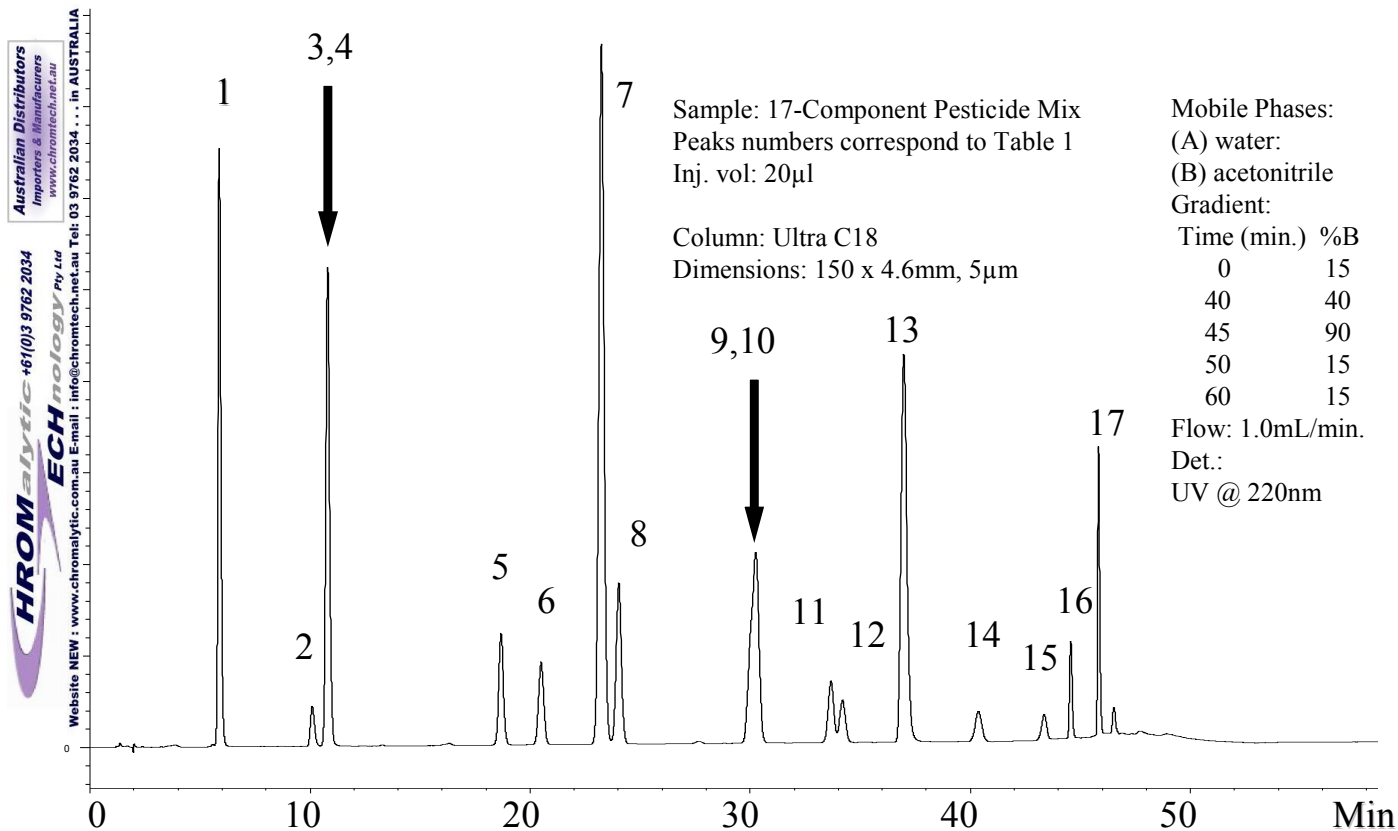
# Pesticides

The unique selectivity of the Ultra IBD column was used to develop a two-column method for analyzing mixture of the 17 triazine, phenyl urea, and carbamate pesticides and metabolites listed on Table . On the Ultra C18 column, 15 of the 17 compounds are resolved. An Ultra IBD column with the same conditions also resolves 15 of the 17 compounds, but the pesticides that co-elute on the C18 are well resolved, as indicated by the arrows.

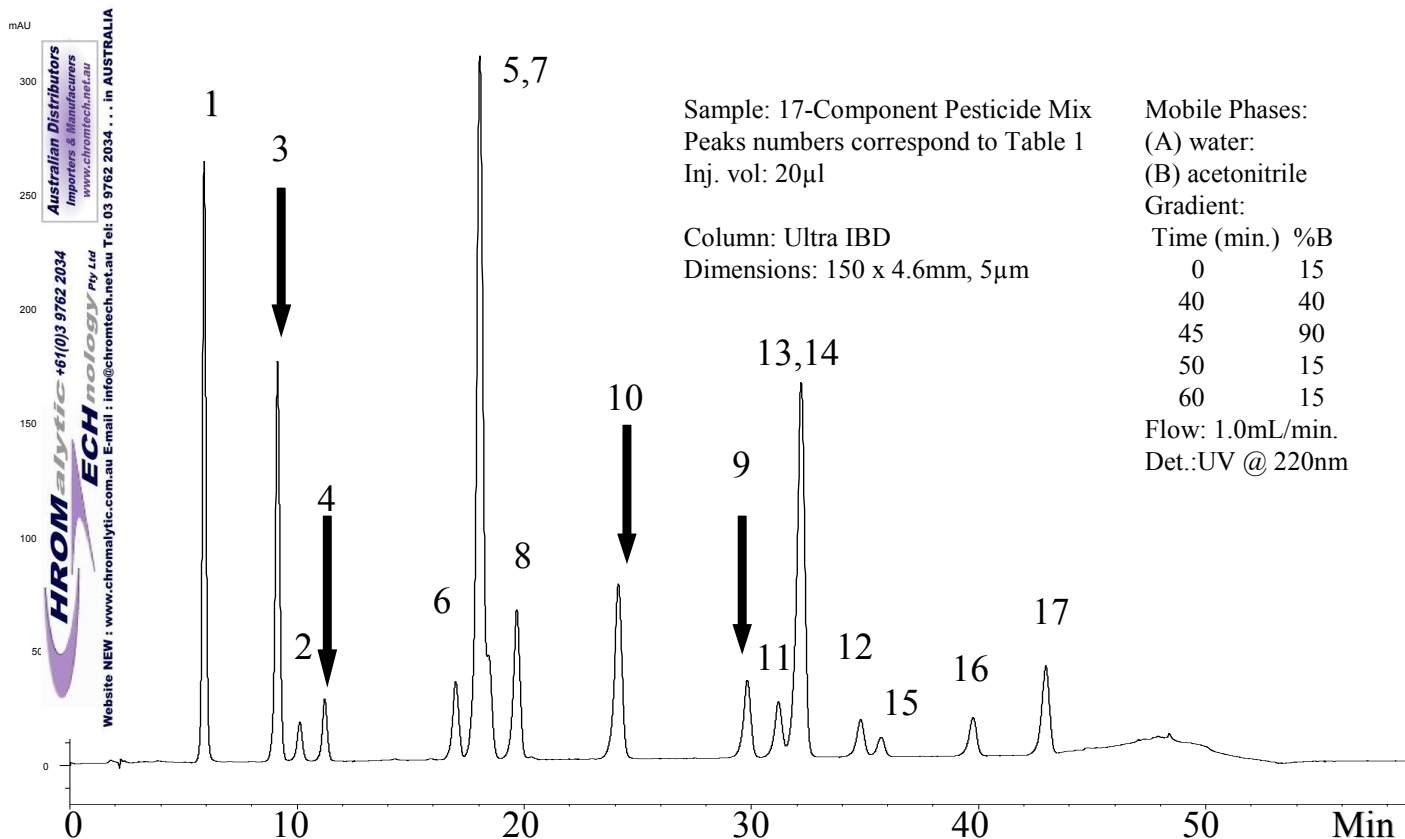
# Table 1. Pesticides: 17-Component Mixture

- |                          |                   |
|--------------------------|-------------------|
| 1. Desisopropylatrazine  | 9. Chlortoluron   |
| 2. Hydroxyatrazine       | 10. Atrazine      |
| 3. Desethylatrazine      | 11. Isoproturon   |
| 4. Carbendazim           | 12. Diuron        |
| 5. Metoxuron             | 13. Terbumeton    |
| 6. Simazine              | 14. Propazine     |
| 7. Cyanazine             | 15. Terbutylazine |
| 8. Desethylterbutylazine | 16. Linuron       |
|                          | 17. Terbutryn     |

# Pesticides on Ultra C18 Column



# Pesticides on Ultra IBD Column



# Explosives

Typically EPA 8330 explosives are run using complimentary columns of CN and C18 phases.

By placing a 5 $\mu$ m, 20mm x 4.0 mm ID Pinnacle II Cyano guard column in front of the 5 $\mu$ m, 25cm x 4.6 mm Pinnacle II C18, the co-eluting peaks tetryl and nitrobenzene can be separated.

This enhanced separation takes advantage of the high selectivity for tetryl and nitrobenzene on the CN column.

Due to the high selectivity, only a 20mm length CN column is needed to increase resolution.



# EPA 8330 Explosives Method Conditions

**Mobile Phase: 50: 50 Water:Methanol**

**Flow Rate: 1.5 mL/min**

**Temperature: 27.0 °C**

**Detection: UV @ 254 nm**

**Injection volume: 3 µL**

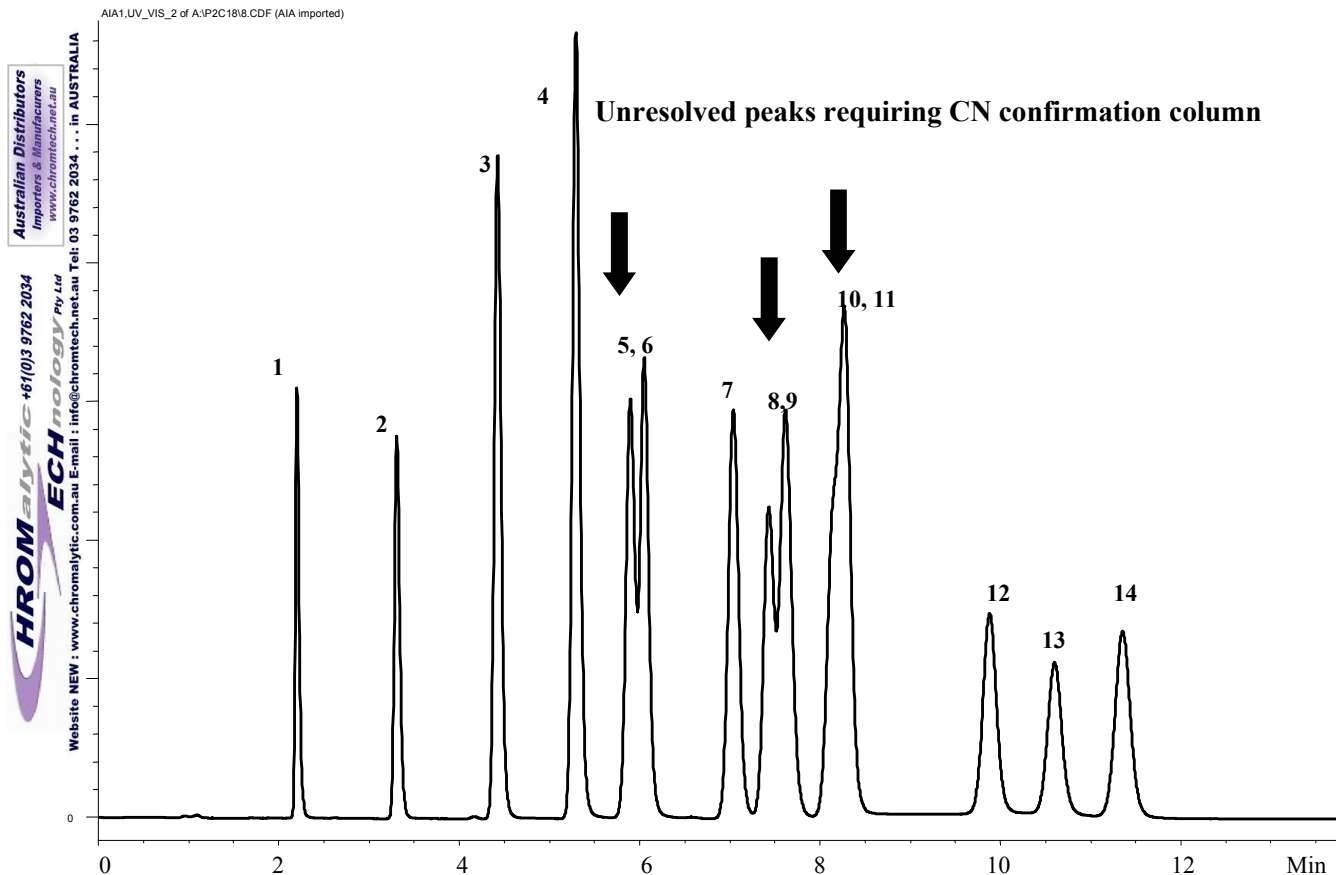
**Concentration: 500 µg/mL each component**

**Sample Diluent: Acetonitrile**

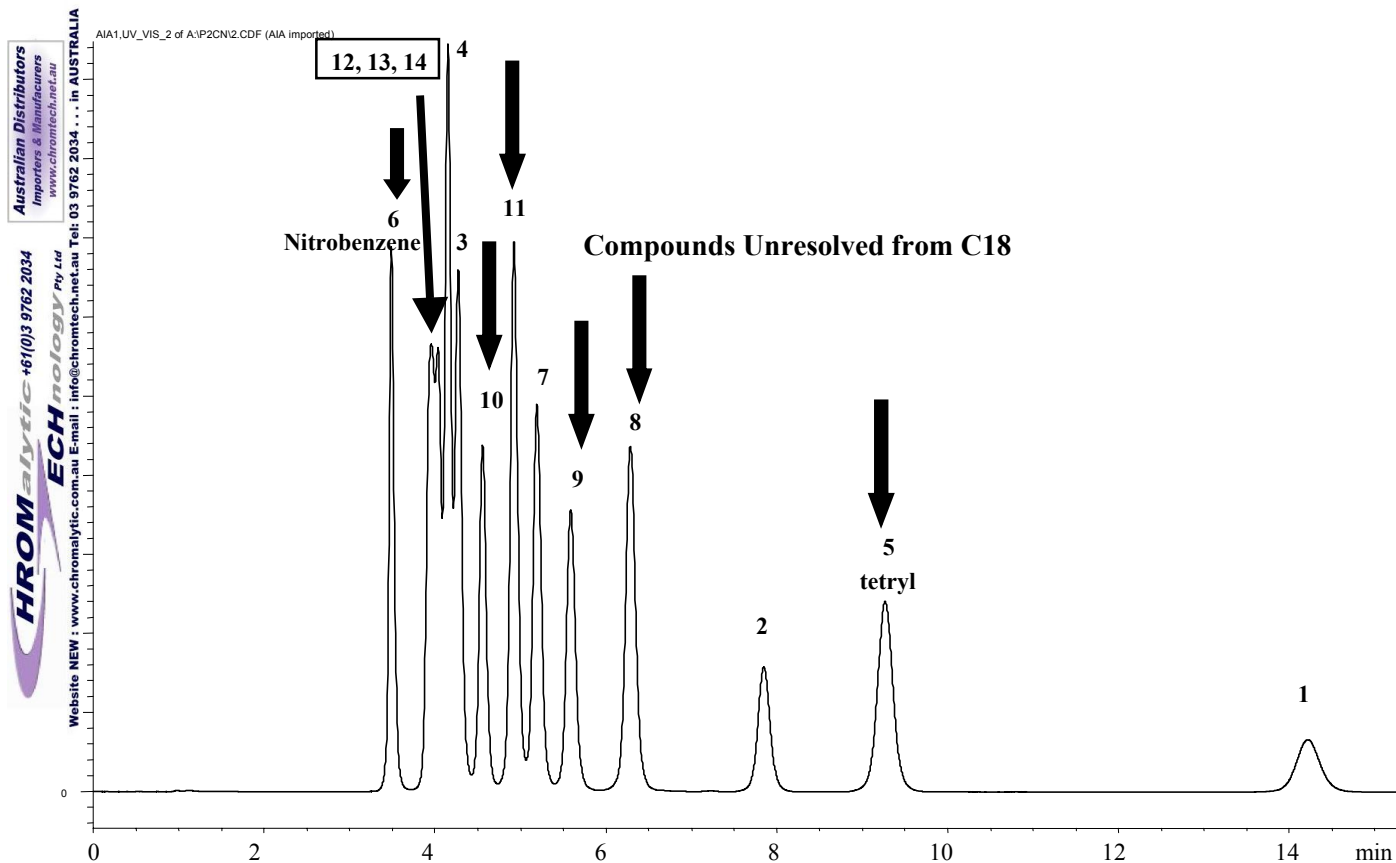
## **Peak List:**

- |                          |                               |
|--------------------------|-------------------------------|
| 1. HMX                   | 8. 2-Amino-4,6-dinitrotoluene |
| 2. RDX                   | 9. 4-Amino-2,6-dinitrotoluene |
| 3. 1,3,5-Trinitrobenzene | 10. 2,6-Dinitrotoluene        |
| 4. 1,3-Dinitrobenzene    | 11. 2,4-Dinitrotoluene        |
| 5. Tetryl                | 12. 2-Nitrotoluene            |
| 6. Nitrobenzene          | 13. 4-Nitrotoluene            |
| 7. 2,4,6-Trinitrotoluene | 14. 3-Nitrotoluene            |

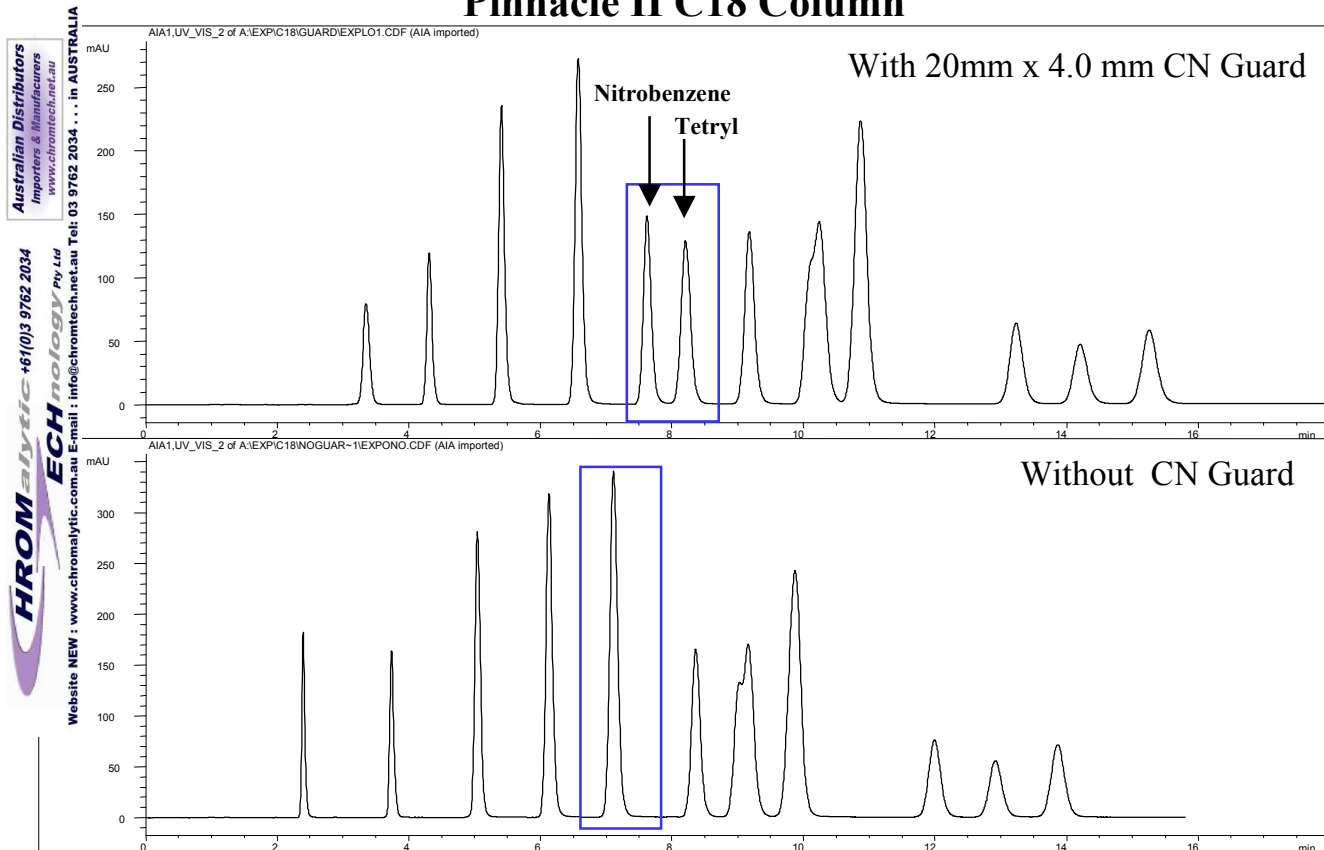
# Explosives Separation on Pinnacle II C18, 25cm x 4.6mm, 5um



# Explosives Separation Pinnacle II CN, 25cm x 4.6mm, 5um



# Explosives Co-elution Resolved Using Pinnacle II CN Guard with Pinnacle II C18 Column



# Carbamates

For EPA Method 8318 (Carbamates), the Pinnacle carbamate column provides an excellent separation in under 40 minutes. This column separates analytes based on their hydrophobicity.

Retention times can be shortened and greater selectivity obtained by taking direct advantage of polar differences as well as hydrophobicity with the Ultra IBD column.

Other columns as the experimental carbamate obtain higher selectivity toward related analytes through alterations of the ligand to promote shape selectivity.

# Pinnacle Carbamate Column – Reference Separation

Applications Note: LC\_0192

## Carbamate Pesticides on Pinnacle Carbamate

### List:

- 1 Carb sulfonide
- 2 Carb sulfone
- 3 Carb
- 4 Carb
- 5 Carb
- 6 Carb
- 7 Carb
- 8 Carb
- 9 Carb
- 10 Carb
- 11 Carb

Column: Pinnacle Carbamate

Catalog#: 9173575

Dimensions: 250 x 4.6mm

Particle size: 5µm

Pore size: 120Å

Solvent A: Water

Solvent B: Methanol

Gradient Program:

20-68% B; 0-20 min.

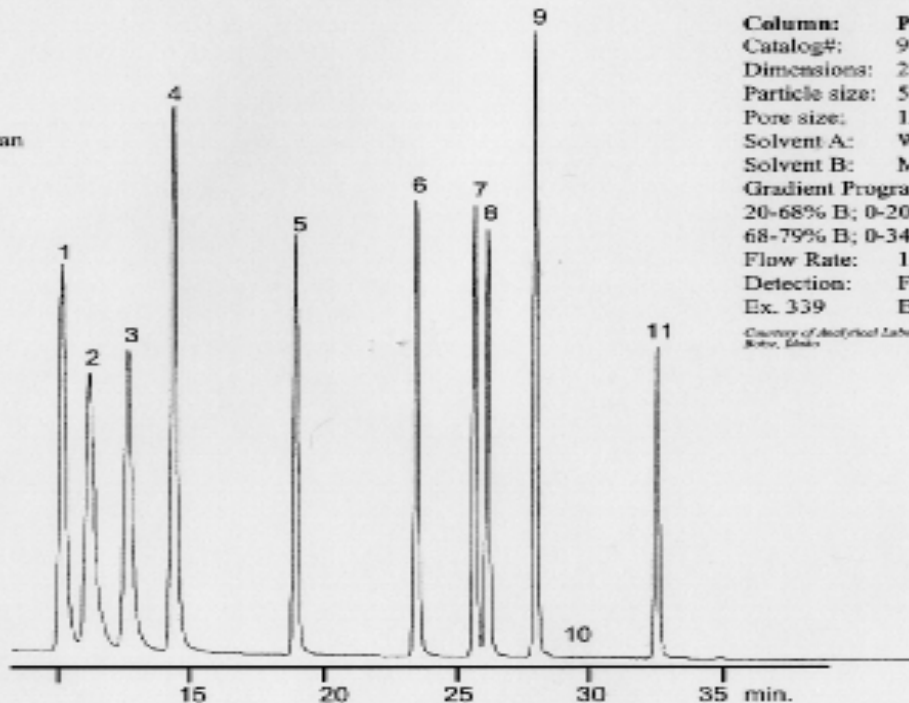
68-79% B; 0-34 min.

Flow Rate: 1.0mL/min

Detection: Fluorescence

Ex. 339 Em. 445nm

Courtesy of Analytical Laboratories, Inc.  
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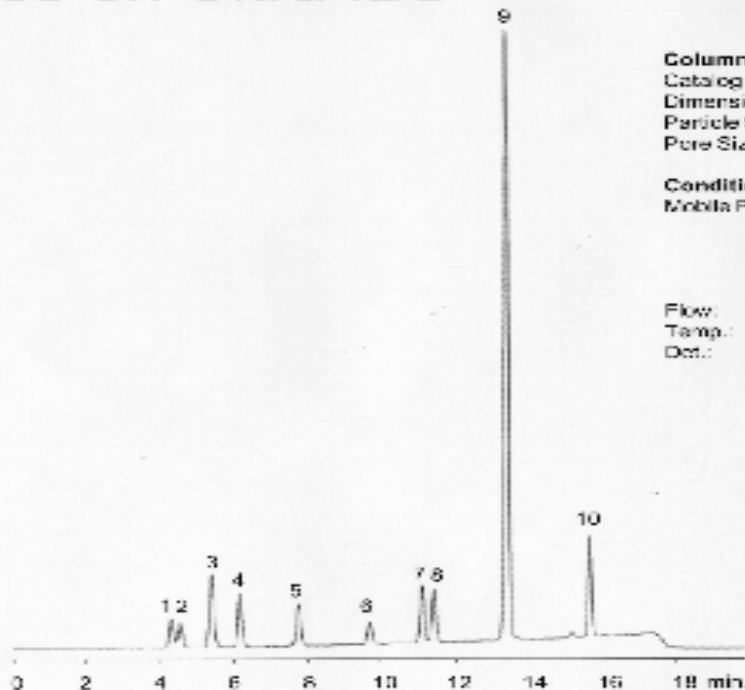
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1182

5 $\mu$ L  
1 mg/mL  
each component  
Methanol

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Conditions:	
Mobile Phase:	Gradient
	A: Water
	B: Methanol
	Initial: 80% A, 20% B
	15 min: 20% B, 80% B
Flow:	1.0mL/min
Temp:	ambient
Detection:	UV @ 230nm



# EPA Method 8318 (Carbamates) on Experimental Column

## Degradation products are more easily observed.

Callibr: 1. ak  
2. ak  
3. ck  
4. m  
5. 3-4  
6. ak  
7. pn  
8. ck  
9. ck  
10. m  
19. un  
Degradat  
A. ak  
B. ck  
C. 3-4  
D. pn  
E. ck  
F. ck  
G. m  
H. 3-4  
I. 3-4  
J. m  
K. m

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Peak List:  
1. Oxide?  
2. Oxide?  
3. Oxide?  
4. m  
5. 3-4  
6. ak  
7. pn  
8. ck  
9. ck  
10. m  
19. un  
Degradat  
A. ak  
B. ck  
C. 3-4  
D. pn  
E. ck  
F. ck  
G. m  
H. 3-4  
I. 3-4  
J. m  
K. m

present in degraded Standard.

Products of:  
A. ak  
B. ck  
C. 3-4  
D. pn  
E. ck  
F. ck  
G. m  
H. 3-4  
I. 3-4  
J. m  
K. m

**Sample:**  
Riesek EPA 531.1 Carbamate calibration standard  
catalog# 32273.  
Standard components diluted to 40 µg/mL in water before  
injection.

Inj.: 15 µL  
Conc.: 40 µg/mL  
Solvent: water:methanol (50:50)

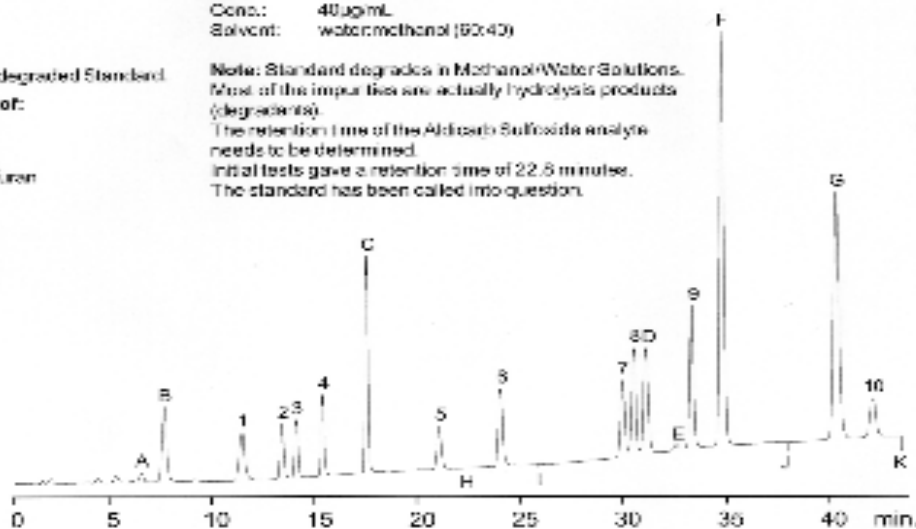
**Note:** Standard degrades in Methanol/Water Solutions.  
Most of the impurities are actually hydrolysis products  
(degradents).  
The retention time of the Aldicarb Sulfoxide analyte  
needs to be determined.  
Initial tests gave a retention time of 22.6 minutes.  
The standard has been called into question.

**Column:**  
Catalog#: Custom  
Dimensions: 150mm x 4.8mm  
Particle Size: 5 µm  
Pore Size: 200 Å

**Conditions:**  
Flow: 1.2 mL/min  
Temp.: 30°C  
Det.: UV @ 210nm

**Mobile Phase:** Gradient  
A: water  
B: methanol

Time (minutes)	%B
0.00	5.0
10.00	10.0
15.00	25.0
25.00	35.0
32.00	40.0
50.00	60.0





# Polyaromatic Hydrocarbons

EPA Methods require the analysis of 16 Polyaromatic hydrocarbons (PAH's). Ordinary nonomerically bonded C18 stationary phases do not resolve all 16 PAH's. C18 phases with the proper degree of polymeric structure (cross-linking) have the shape selectivity to resolve all 16 PAH's

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# PAH Selectivity Test Probe

A simple isocratic test using a three component PAH test mix has been shown to be an excellent test probe for comparing the relative degree polymeric character of C18 stationary phases<sup>1</sup>. This test can accurately predict the ability of C18 phases to resolve all 16 PAH's.

1. Sander, L.C. and Wise, S.A., Synthesis and Characterization of Polymeric C18 Stationary Phases For Liquid Chromatography, *Anal. Chem.*, **56**, pp.504-510, (1984).

# PAH Selectivity Test

Column Dimensions: 150 x 3.2mm, 5 $\mu$ m

Mobile Phase: 85/15 acetonitrile/water

Flow rate: 1.0 ml/min

Temp.: 25C

Detection: UV 254nm

Sample: 10 $\mu$ l NIST SRM 869a containing:

benzo(a)pyrene (BaP),

1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN), and

phenanthro[3,4-c]phenanthrene (PhPh)

# Results of PAH Selectivity Test

Column

Alpha (TBN/BaP)

Exp.PAH#1

0.93

Exp.PAH#2

0.62

Exp.PAH#3

0.56

Exp.PAH#4

0.85

The lower the alpha value, the greater the polymeric character of the cross-linked C18 phase.

# 16 Component PAH Test

Column Dimensions: 150 x 3.2mm, 5 $\mu$ m

Mobile Phases: (A) water, (B) acetonitrile

Gradient: 40%B to 100% B in 30min,

Hold 100%B for 10min.

Flow rate: 1.0 ml/min

Temp.: 25C

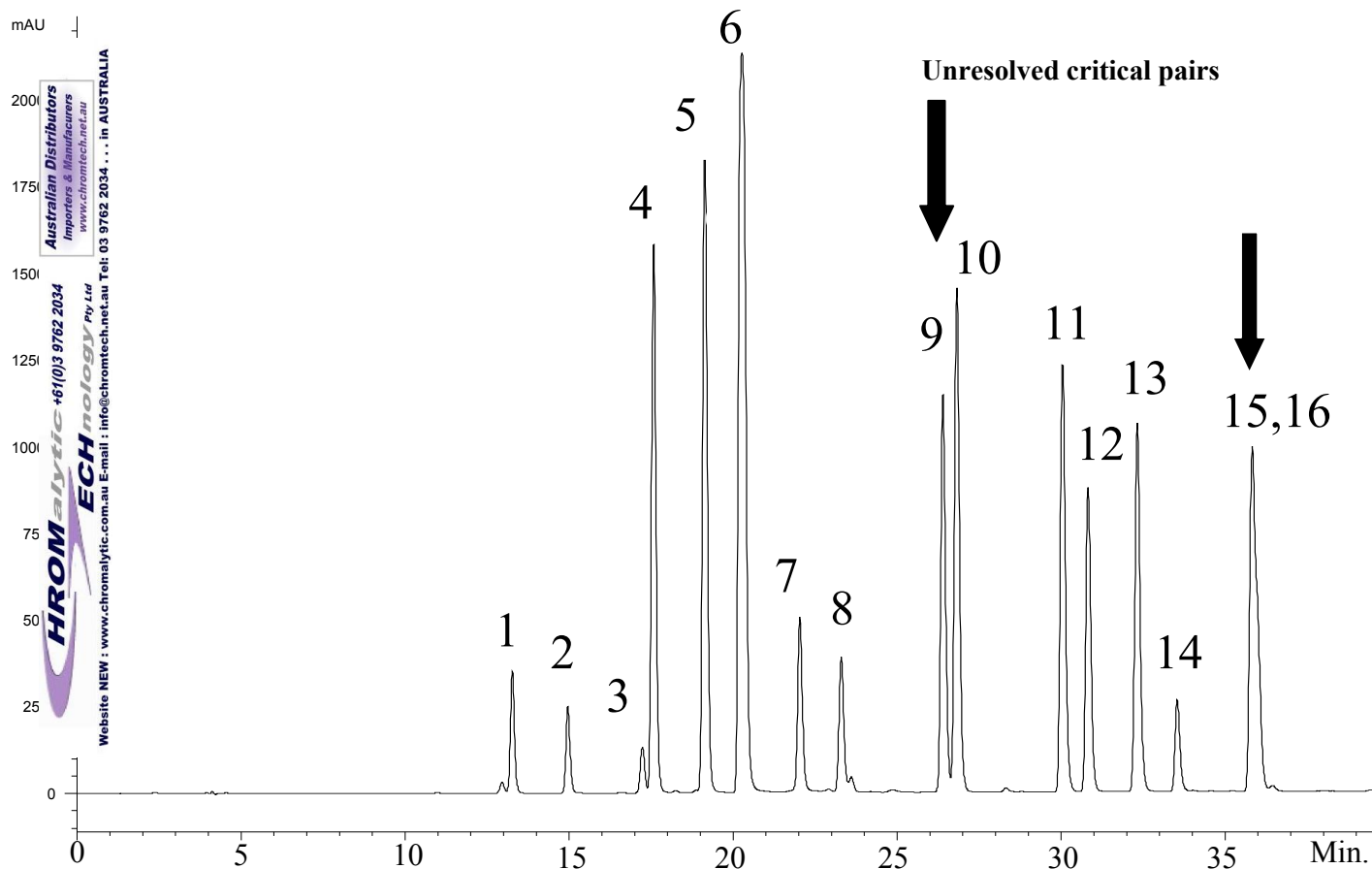
Detection: UV 254nm

# 16 Component PAH Test (Cont.)

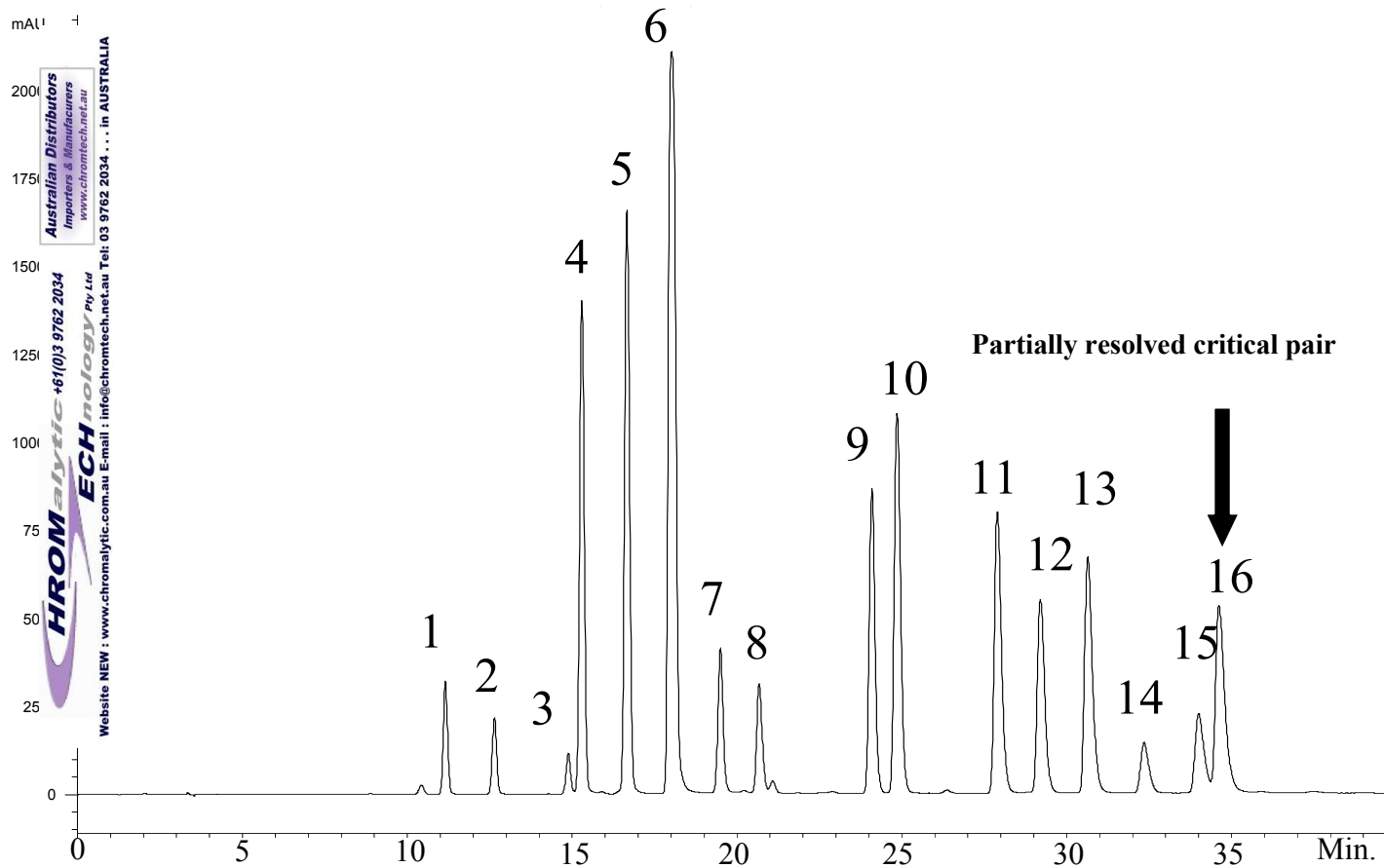
Sample: 5 $\mu$ L Restek 610 PAH Calibration Mix A  
Peak List:

- |                   |                             |
|-------------------|-----------------------------|
| 1. Naphthalene    | 9. Benzo(a)anthracene       |
| 2. Acenaphthylene | 10. Chrysene                |
| 3. Acenaphthene   | 11. Benzo(b)fluoranthene    |
| 4. Fluorene       | 12. Benzo(k)fluoranthene    |
| 5. Phenanthrene   | 13. Benzo(a)pyrene          |
| 6. Anthracene     | 14. Dibenzo(a,h)anthracene  |
| 7. Fluoranthene   | 15. Benzo(g,h,i)perylene    |
| 8. Pyrene         | 16. Indeno(1,2,3-c,d)pyrene |

# Exp. PAH #1 - One co-elution

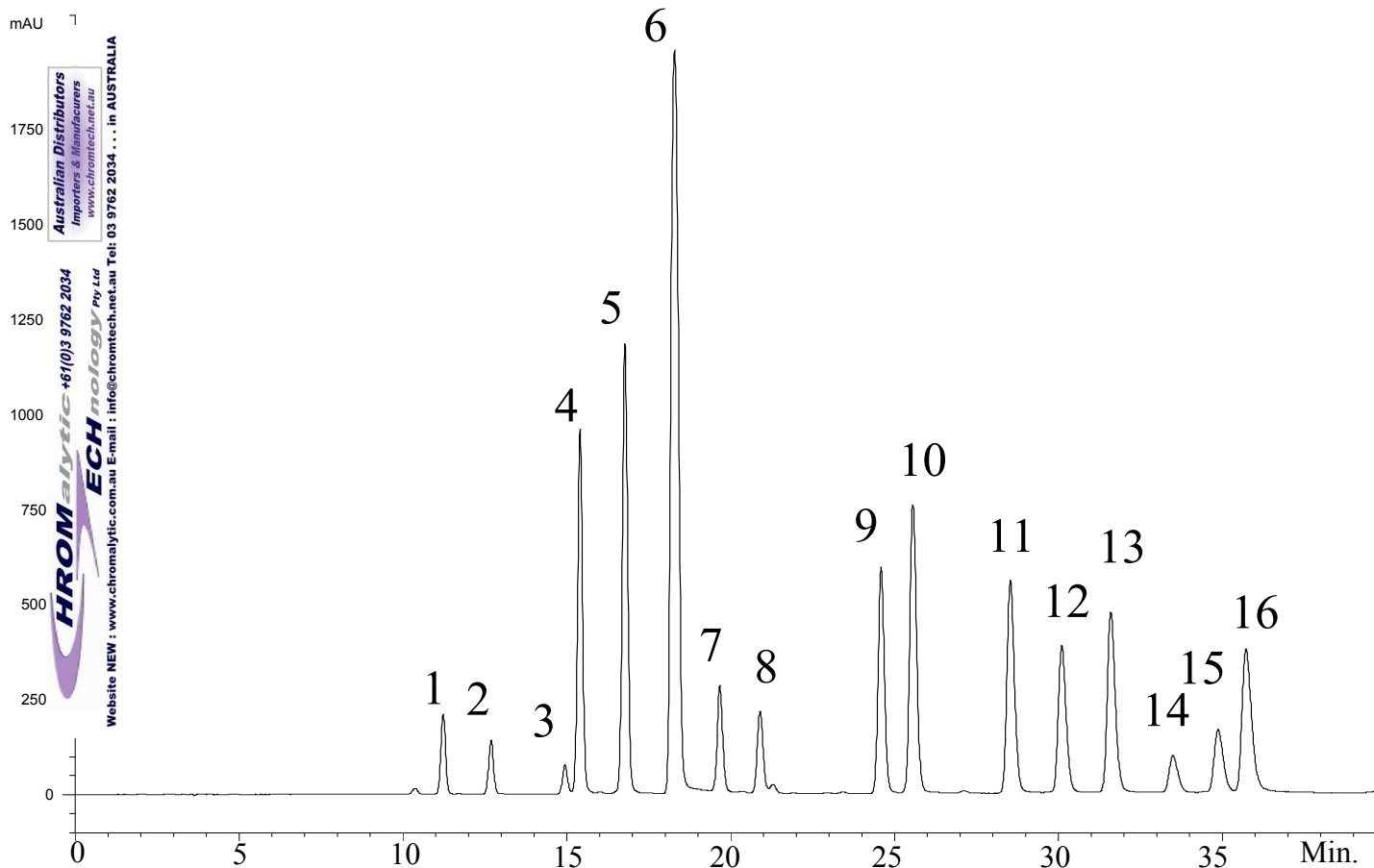


# Exp. PAH#2 - All 16 PAH's resolved

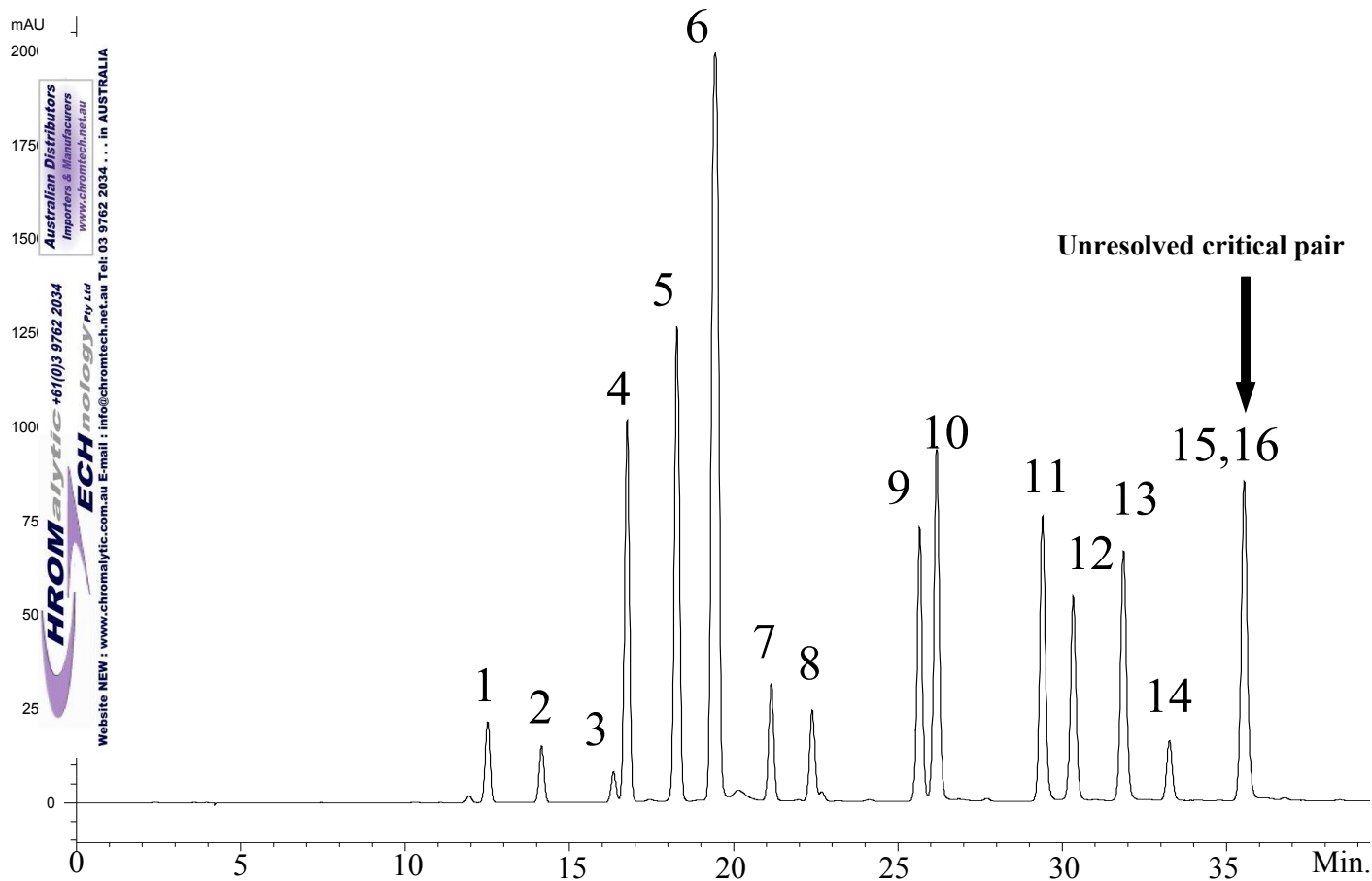




# Exp. PAH#3 - Best Separation - All 16 PAH's baseline resolved



# Exp. PAH#4 - One Co-elution



# Conclusions

- Using alternative stationary phases can give complimentary selectivity to confirm analytes unresolved by standard alkyl phases.
- Phases with high and complimentary selectivity can be used within a guard cartridge to enhance critical pair separations.
- Taking advantage of mixed mode interactions can substantially decreases analysis time.
- Controlling polymeric character of an alkyl stationary phase is critical to achieving shape selectivity of PAH analytes.

# Evaluation of Stationary Phases for the Analysis of Volatiles by US EPA Methods 8260 & 524.2.

CHRISTOPHER M. ENGLISH,

FRANK L. DORMAN, DINESH V. PATWARDHAN  
& MARK LAWRENCE.

# Abstract

There are many columns that are currently used for the analysis of volatile environmental pollutants by GC/MS. Most of the stationary phases that are offered have adequate selectivity, bleed and inertness for the most common methods. Problems occur when starting temperatures & oven ramp rates are increased. Laboratories that increase runtimes without carefully checking the mass-spectra of each coeluting analyte may compromise data integrity.

This paper will compare four common stationary phases to a new volatile-mass / spec phase for separation of isomeric pairs using high oven starting temperatures and a rapid final oven ramp rate. Other common analytes that share ions will also be presented.

# Introduction

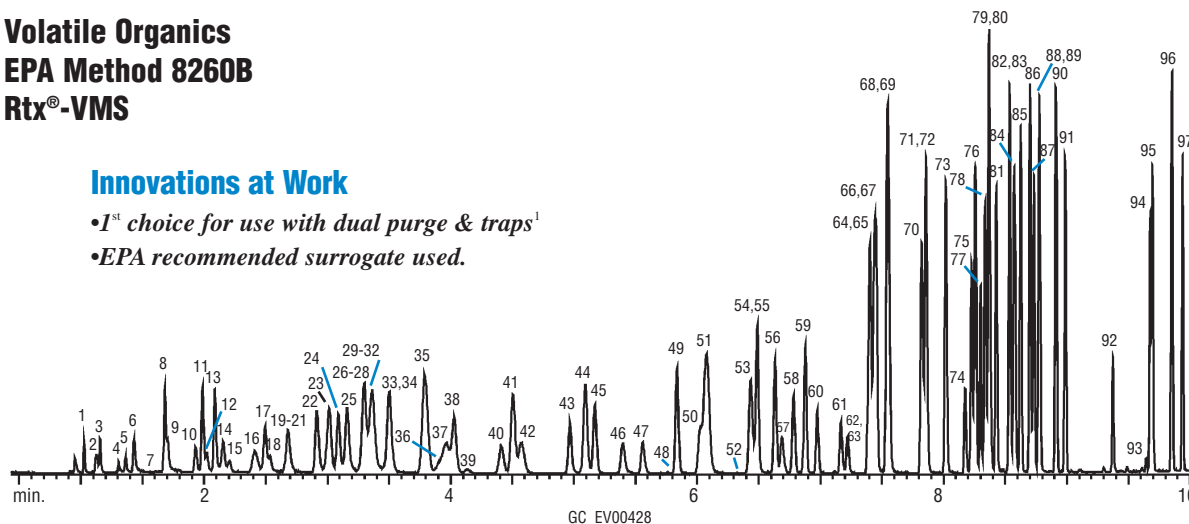
Chromatographic and purge & trap cycle times have been the limiting factor for volatile analysis for many years. With the advent of interfacing two purge & trap concentrators onto one GC/MS, analysts are now interested in columns with sub-ten-minute runtimes.

The Rtx-VMS chromatogram shown below spectrally resolves all of the target compounds in under 10 minutes. Faster runtimes are possible by substituting chlorobenzene-D5 with an alternate internal standard. This solution works for the VMS phase but will not work for other phases since the resolution of isomers is compromised. This paper will compare other phases run under these conditions for separation of isomeric pairs.

# Volatile Organics EPA Method 8260B Rtx®-VMS

## Innovations at Work

- 1<sup>st</sup> choice for use with dual purge & traps<sup>1</sup>
- EPA recommended surrogate used.



GC\_EV00428  
 20m, 0.18 mm ID, 1.00µm Rtx®-VMS (cat.# 49914)  
 Compounds in at 10ppb in 5mL of RO water  
 unless otherwise noted, ketones in at 2.5X  
 Concentrator: Tekmar LSC-3100 Purge and Trap  
 Trap: Vocab 3000 (type K)  
 Purge: 11 min. @ 40mL/min. @ ambient temperature  
 Dry purge: 1 min. @ 40mL/min.  
 Desorb preheat: 245°C  
 Desorb: 250°C for 2 min., Flow 40mL/min.  
 Bake: 260°C for 8 min.  
 Interface: transfer line 0.53mm ID Silcosteel® tubing  
 1:40 split at injection port. 1mm ID sleeve.  
 Oven temp.: 50°C (hold 4 min.) to 100°C @ 18°C/min. (hold 0 min.)  
 to 230°C @ 40°C/min. (hold 3 min.)  
 Carrier gas: helium @ ~1.0mL/min. constant flow  
 Adjust dichlorodifluoromethane to a retention time of 1.03 min. @  
 50°C (M, 29 [Degree] C Trademark) C.  
 Detector: HP 5973 MSD  
 Scan range: 35-300amu

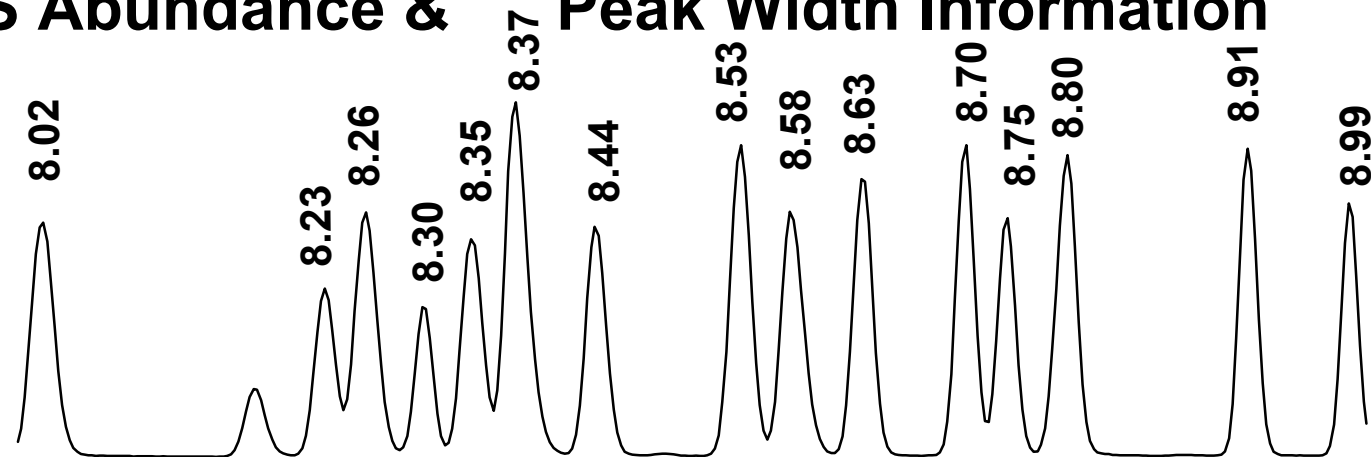
- |   |                                     |                                       |                                 |
|---|-------------------------------------|---------------------------------------|---------------------------------|
| 1. dichlorodifluoromethane              | 26. ethyl acetate                   | 51. toluene                           | 76. <i>n</i> -propylbenzene     |
| 2. chloromethane                        | 27. carbon tetrachloride            | 52. pyridine (250ppb)                 | 77. 1,1,2,2-tetrachloroethane   |
| 3. vinyl chloride                       | 28. methyl acrylate                 | 53. tetrachloroethene                 | 78. 2-chlorotoluene             |
| 4. bromomethane                         | 29. propargyl alcohol (500ppb)      | 54. 4-methyl-2-pentanone              | 79. 1,3,5-trimethylbenzene      |
| 5. chloroethane                         | 30. dibromofluoromethane (SMC)      | 55. <i>trans</i> -1,3-dichloropropene | 80. 1,2,3-trichloropropane      |
| 6. trichlorofluoromethane               | 31. tetrahydrofuran                 | 56. 1,1,2-trichloroethane             | 81. 4-chlorotoluene             |
| 7. ethanol (2500ppb)                    | 32. 1,1,1-trichloroethane           | 57. ethyl methacrylate                | 82. <i>tert</i> -butylbenzene   |
| 8. 1,1-dichloroethene                   | 33. 2-butanone                      | 58. dibromochloromethane              | 83. pentachloroethane           |
| 9. carbon disulfide (40ppb)             | 34. 1,1-dichloropropene             | 59. 1,3-dichloropropane               | 84. 1,2,4-trimethylbenzene      |
| 10. allyl chloride                      | 35. benzene                         | 60. 1,2-dibromoethane                 | 85. <i>sec</i> -butylbenzene    |
| 11. methylene chloride                  | 36. pentafluorobenzene (IS)         | 61. <i>n</i> -butyl acetate           | 86. <i>p</i> -isopropyltoluene  |
| 12. acetone                             | 37. <i>tert</i> -amyl-methyl ether  | 62. 2-hexanone                        | 87. 1,3-dichlorobenzene         |
| 13. <i>trans</i> -1,2-dichloroethene    | 38. 1,2-dichloroethane              | 63. 2-picoline (250ppb)               | 88. 1,4-dichlorobenzene-d4 (IS) |
| 14. methyl <i>tert</i> -butyl ether     | 39. isobutyl alcohol (500ppb)       | 64. chlorobenzene-D5 (IS)             | 89. 1,4-dichlorobenzene         |
| 15. <i>tert</i> -butyl alcohol (100ppb) | 40. isopropyl acetate               | 65. chlorobenzene                     | 90. <i>n</i> -butylbenzene      |
| 16. diisopropyl ether                   | 41. trichloroethene                 | 66. ethylbenzene                      | 91. 1,2-dichlorobenzene         |
| 17. 1,1-dichloroethane                  | 42. 1,4-difluorobenzene (SMC)       | 67. 1,1,1,2-tetrachloroethane         | 92. 1,2-dibromo-3-chloropropane |
| 18. acrylonitrile                       | 43. dibromomethane                  | 68. <i>m</i> -xylene                  | 93. nitrobenzene (250ppb)       |
| 19. vinyl acetate                       | 44. 1,2-dichloropropane             | 69. <i>p</i> -xylene                  | 94. hexachlorobutadiene         |
| 20. allyl alcohol (250ppb)              | 45. bromodichloromethane            | 70. <i>o</i> -xylene                  | 95. 1,2,4-trichlorobenzene      |
| 21. ethyl- <i>tert</i> -butyl ether     | 46. methyl methacrylate             | 71. styrene                           | 96. naphthalene                 |
| 22. <i>cis</i> -1,2-dichloroethene      | 47. <i>n</i> -propyl acetate        | 72. bromoform                         | 97. 1,2,3-trichlorobenzene      |
| 23. 2,2-dichloropropane                 | 48. 2-chloroethanol (2500ppb)       | 73. isopropylbenzene                  |                                 |
| 24. bromochloromethane                  | 49. <i>cis</i> -1,3-dichloropropene | 74. 4-bromo-1-fluorobenzene (SMC)     |                                 |
| 25. chloroform                          | 50. toluene-d8(SMC)                 | 75. bromobenzene                      |                                 |

## Rtx-VMS Abundance & Peak Width Information

The EZ-GC<sup>®</sup> computer program allows up to 100 compounds to be modeled on a single stationary phase under varying GC conditions & column dimensions with an excellent level of both precision and accuracy. Retention time, abundance, and peak width were loaded into EZ-GC<sup>®</sup>. The abundance and peak width values were determined from the Rtx-VMS chromatogram which was run using an HP5973 GC/MS system (see GC\_EV00428 for specific conditions).



# Rtx-VMS Abundance & Peak Width Information



Rtx-VMS Compounds Examined	RT (min.)	Peak Wi	MS Abundance (x 1000)
isopropylbenzene	8.02	0.045	440
bromobenzene	8.23	0.058	340
n-propylbenzene	8.26	0.055	460
1,1,2,2-tetrachloroethane	8.30	0.05	290
2-chlorotoluene	8.35	0.04	400
1,3,5-trimethylbenzene	8.37	0.045	440
1,2,3-trichloropropane	8.37	0.06	180
4-chlorotoluene	8.44	0.04	400
tert-butylbenzene	8.53	0.05	550
1,2,4-trimethylbenzene	8.58	0.055	440
sec-butylbenzene	8.63	0.045	525
p-isopropyltoluene	8.70	0.055	545
1,3-dichlorobenzene	8.75	0.04	460
1,4-dichlorobenzene	8.80	0.04	475
n-butylbenzene	8.91	0.055	501
1,2-dichlorobenzene	8.99	0.04	475

**Peak Widths &  
Abundance  
Determined from  
Purge and Trap  
Analysis.**

# Rtx-VMS Model versus Actual Analysis

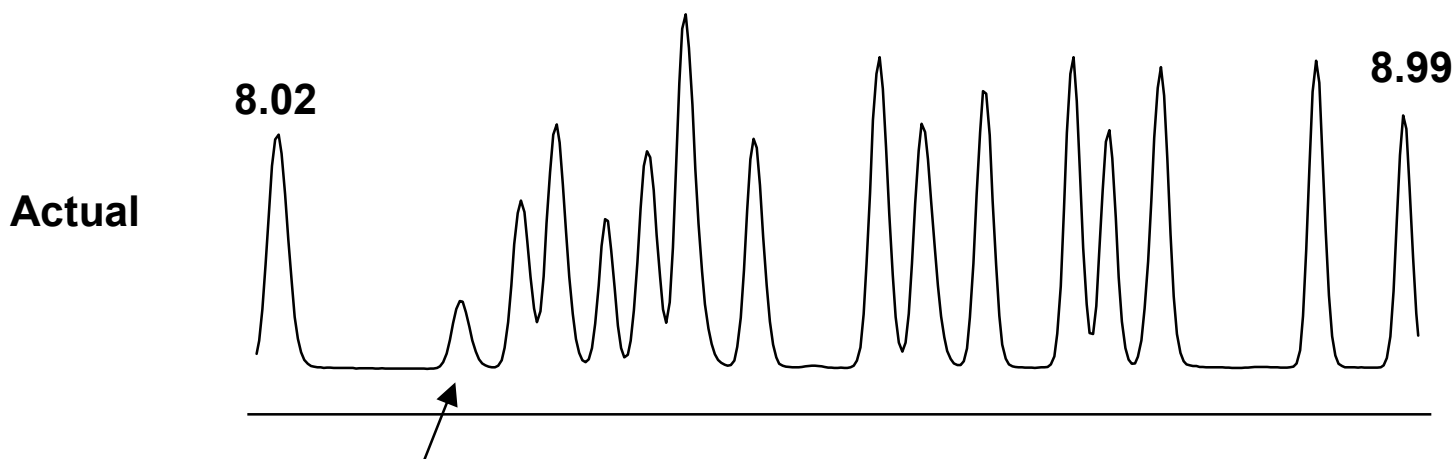
Using retention time indices specific to each of the stationary phases in combination with the abundance values & peak widths values from the VMS phase; model chromatograms were produced. Since column efficiency may change with each stationary phase – only differences in retention time will be examined. The abundance and peak width information was loaded into the program to produce sample chromatograms as a visual aid only.

The first step in the column comparison was to determine the effectiveness of EZ-GC<sup>®</sup> by comparing our known VMS chromatogram with a model. Retention times were collected for these compounds under fast and slow conditions and were entered into EZ-GC<sup>®</sup>. The application chromatogram was modeled using this fast/slow data. The diagram below shows the difference between the actual chromatogram and the model to be 0.01 minutes.

# Rtx-VMS Model versus Actual Analysis

**Rtx-VMS 20 m x 0.180 mm x 1.0  $\mu$ m**

**50°C (4) @ 18°C/min to 100°C @ 40°C/min to 230°C (1) Flow : ~ 1.0 ml/min**



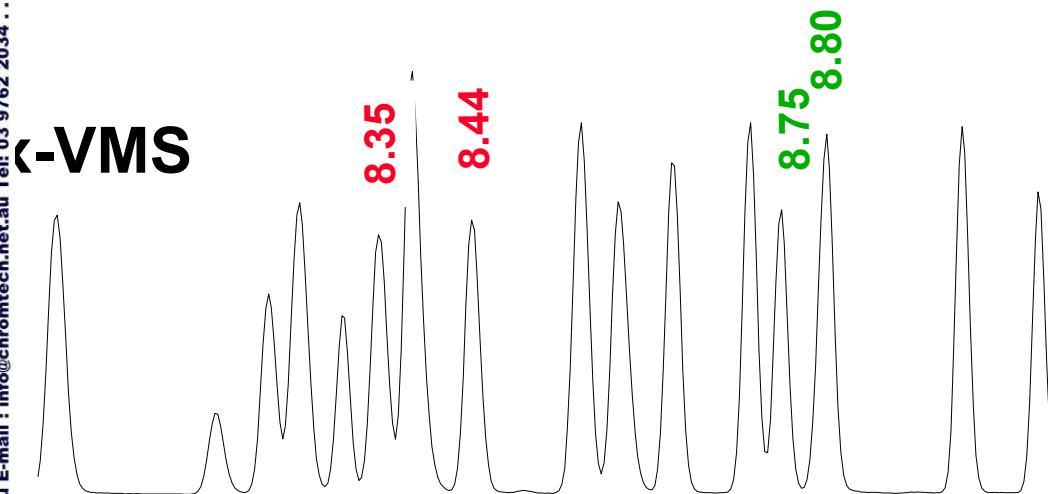
## Rtx-VMS Compared to the Rtx-624

The change in retention between the chlorotoluenes modeled on the VMS & 624 phases is 0.03 minute, which in reality, constitutes a significant difference since this data is produced with a 20m x 0.18mm ID column with a 40°C/minute oven ramp rate. A faster final oven ramp rate is possible using the VMS phase since these compounds are well separated. Using a 60m x 0.53mm ID x 3.0df column for a direct comparison the difference between these phases is 0.9 minute. The 624 phase is suitable for fast dual-purge & trap applications. Analytes that share ions and coelute on the 624 phase and are resolved by the VMS include: ether/ethanol, vinyl acetate/ethyl-tert-butyl-ether & t-butyl alcohol/methyl-tert-butyl-ether. Several of these compounds require a lower starting oven temperature (35°C) using the VMS phase which is not shown in this application.

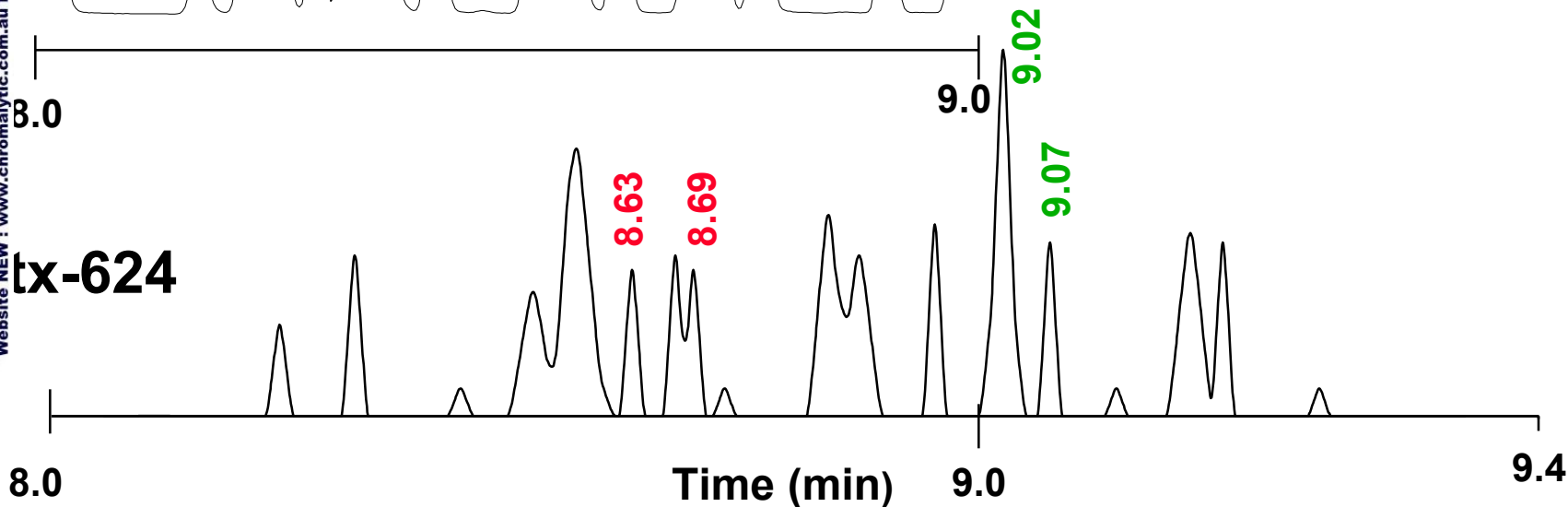
# Rtx-VMS Compared to the Rtx-624

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	Rtx-VMS	Rtx-624
2-Cl-toluene	8.35	8.63
4-Cl-toluene	8.44	8.69
RT diff.	0.09	0.06
1,3-DCB	8.75	9.02
1,4-DCB	8.80	9.07
RT diff.	0.05	0.05



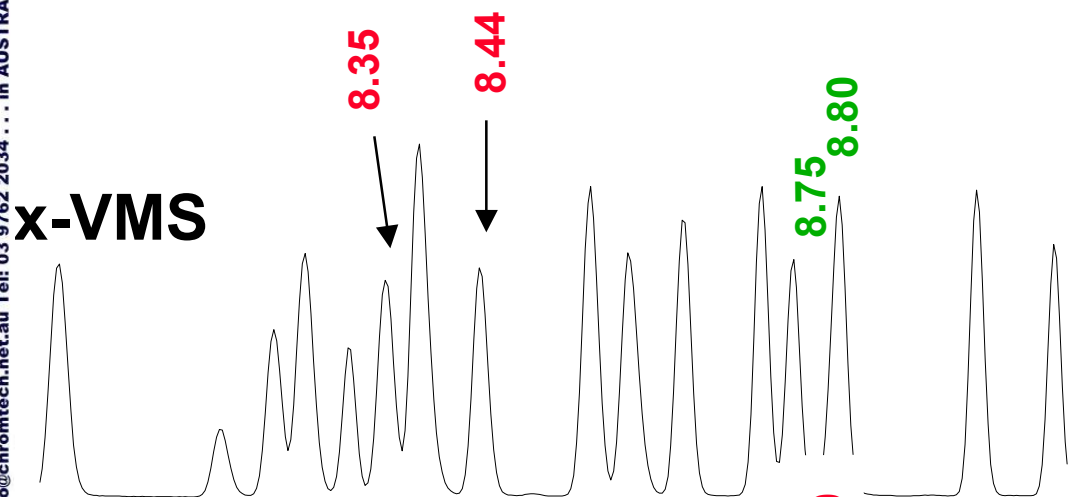
## Rtx-VMS Compared to the Rtx-502.2

The Rtx-502.2 is a cross-bonded diphenyl-methyl containing polysiloxane, which is particularly resistive to oxidative breakdown and exhibits lower bleed compared to the cyanopropyl-phenyl polysiloxanes (624phase). The disadvantage is the difficult resolution between bromomethane and chloroethane. Although our model indicates partial resolution between the chlorotoluenes under these run-conditions, linearity is effected over the concentration range. Slower final oven ramp rates will resolve these isomers, but it will sacrifice runtime.

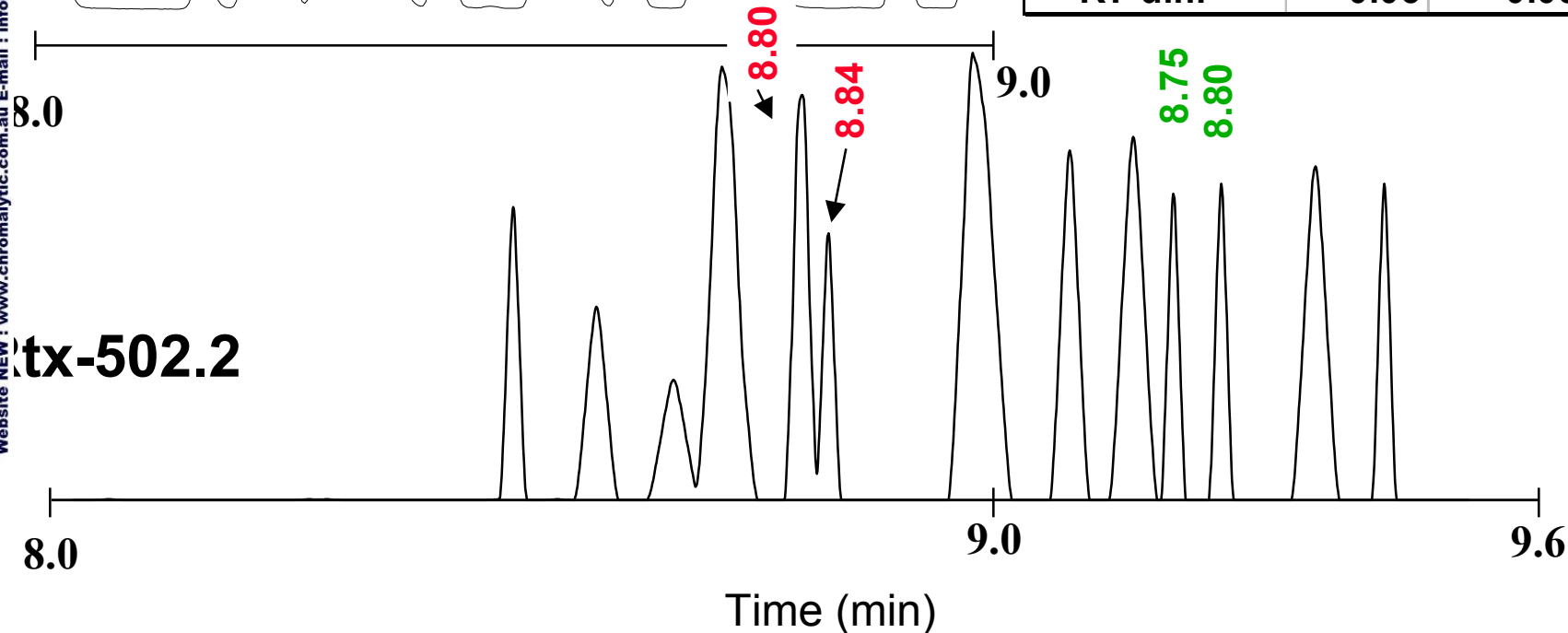
# Rtx-VMS Compared to the Rtx-502.2

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	Rtx-VMS	Rtx-502.2
2-Cl-toluene	8.35	8.80
4-Cl-toluene	8.44	8.84
RT diff.	0.09	0.04
1,3-DCB	8.75	9.21
1,4-DCB	8.80	9.26
RT diff.	0.05	0.05



# Rtx-VMS Compared to the Rtx-VRX

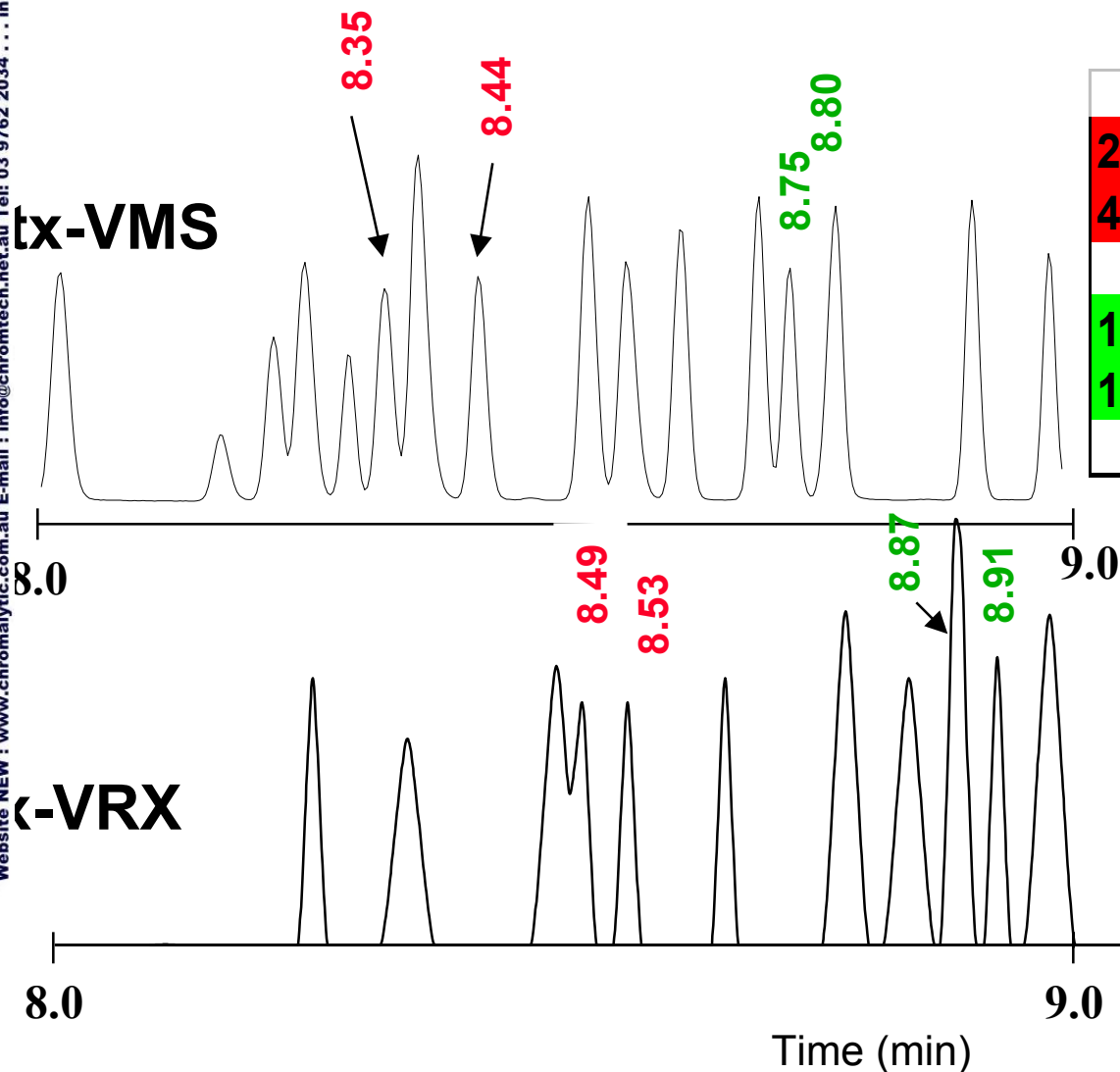
The Rtx-VRX incorporates a low percentage of pentafluorobenzylpropyl- polysiloxane, which gives this column similar characteristics to an Rtx-1, only it resolves close eluting GC pairs such as 2,2-dichloropropane & chloroform. It is possible to do fast dual purge and trap applications using this phase as long as the recommended EPA internal standard, chlorobenzene-d5 is substituted with another compound. As shown in the direct comparison the Rtx-VMS does out-perform the VRX stationary phase for this application.



# Rtx-VMS Compared to the Rtx-VRX

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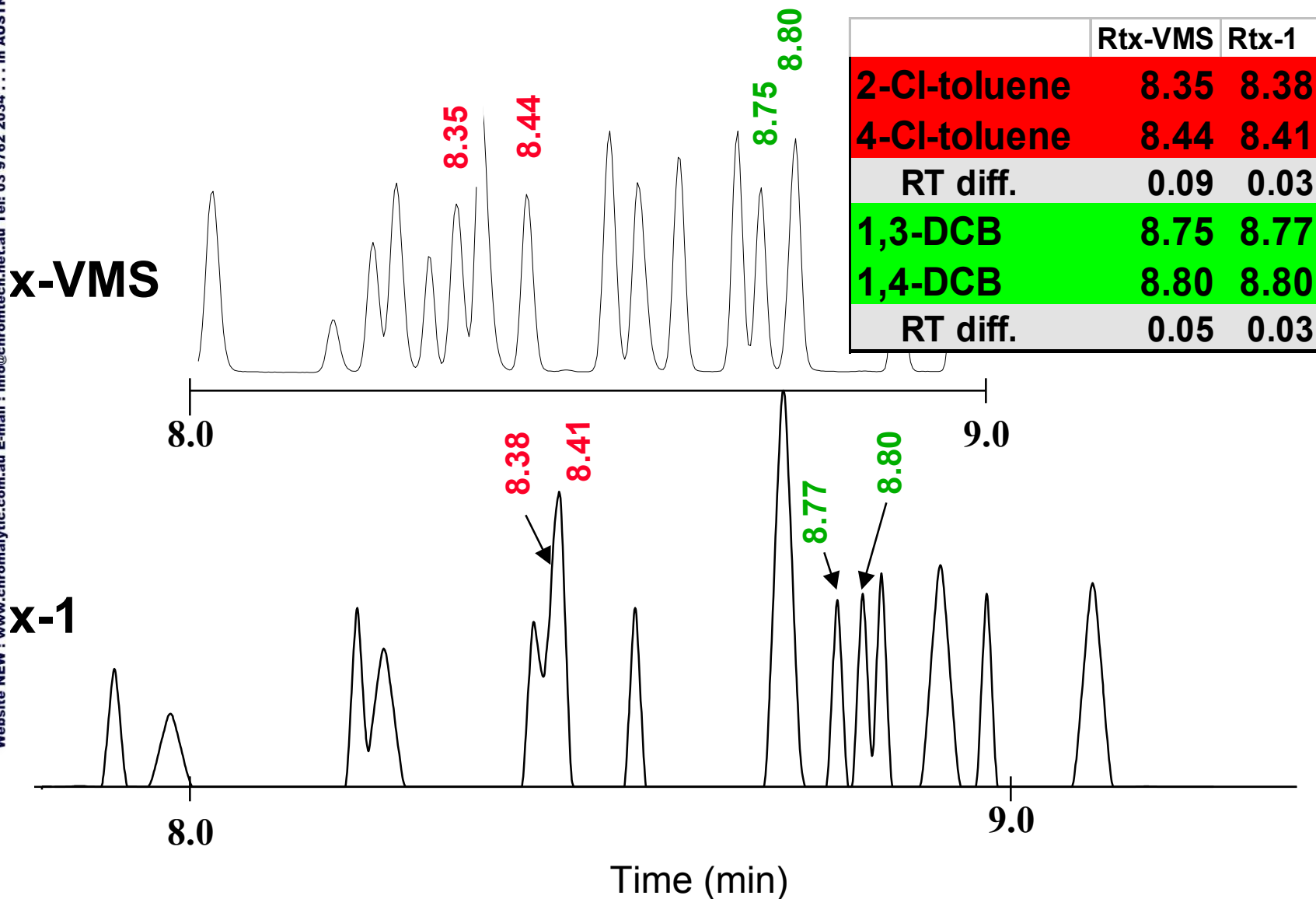


	Rtx-VMS	Rtx-VRX
2-Cl-toluene	8.35	8.49
4-Cl-toluene	8.44	8.53
RT diff.	0.09	0.04
1,3-DCB	8.75	8.87
1,4-DCB	8.80	8.91
RT diff.	0.05	0.04

# Rtx-VMS Compared to the Rtx-1

Although the 100% dimethyl-polysiloxane (Rtx-1) polymer is unchallenged for air analysis, this phase does not perform well for fast purge and trap analysis. Like the VRX phase chlorobenzene-d5 & 1,1,1,2-tetrachloroethane are poorly resolved as are the isomers shown.

# Rtx-VMS Compared to the Rtx-1



The VMS phase has the best resolution of isomeric pairs and other target compounds for US EPA Method 8260B.

# Rtx-VMS – Best Resolution of Isomeric Pairs.

<b><u>COMPOUND</u></b>	<b>Shared Ions</b>	<b>Rtx-VMS</b>	<b>Rtx-624</b>	<b>Rtx-502.2</b>	<b>Rtx-VRX</b>	<b>Rtx-1</b>
chlorobenzene-d5	117	7.34	7.62	7.90	7.34	7.25
1,1,2-tetrachloroethane	117	7.42	7.70	7.93	7.39	7.24
RT diff.		0.08	0.08	0.07	0.04	0.01
chlorotoluene	126,91	8.35	8.63	8.80	8.49	8.38
chlorotoluene	126,91	8.44	8.69	8.84	8.53	8.41
RT diff.		0.09	0.06	0.04	0.04	0.03
3-dichlorobenzene	146	8.75	9.02	9.21	8.87	8.77
4-dichlorobenzene	146	8.80	9.07	9.26	8.91	8.80
RT diff.		0.05	0.05	0.05	0.04	0.03

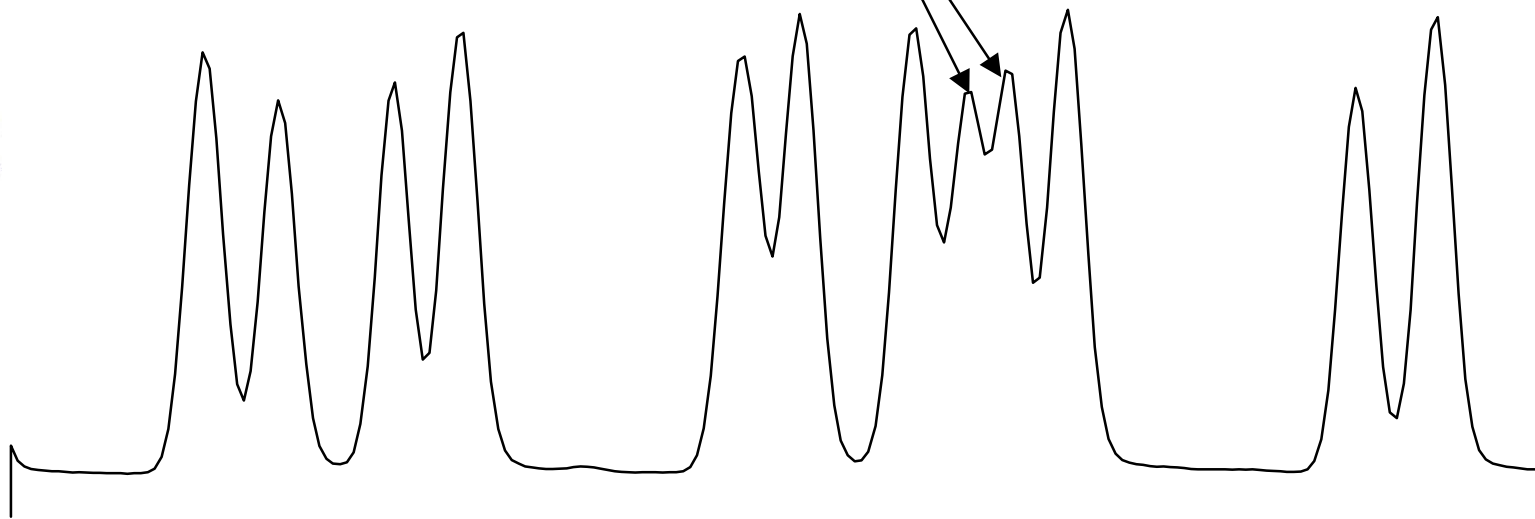
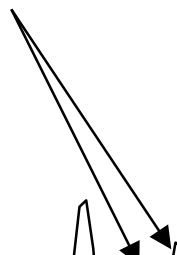
# A Candidate for Volatile Applications Fails for Resolution of the DCBs.

One of our attempts to build a column suitable for fast volatile analysis met all of the design criteria except for the resolution between the dichlorobenzenes.

# Experimental Fluorinated Phase

A Candidate for Volatile Applications Fails for Resolution of the DCBs.

1,3 & 1,4 Dichlorobenzenes



# Experimental Fluorinated Phase

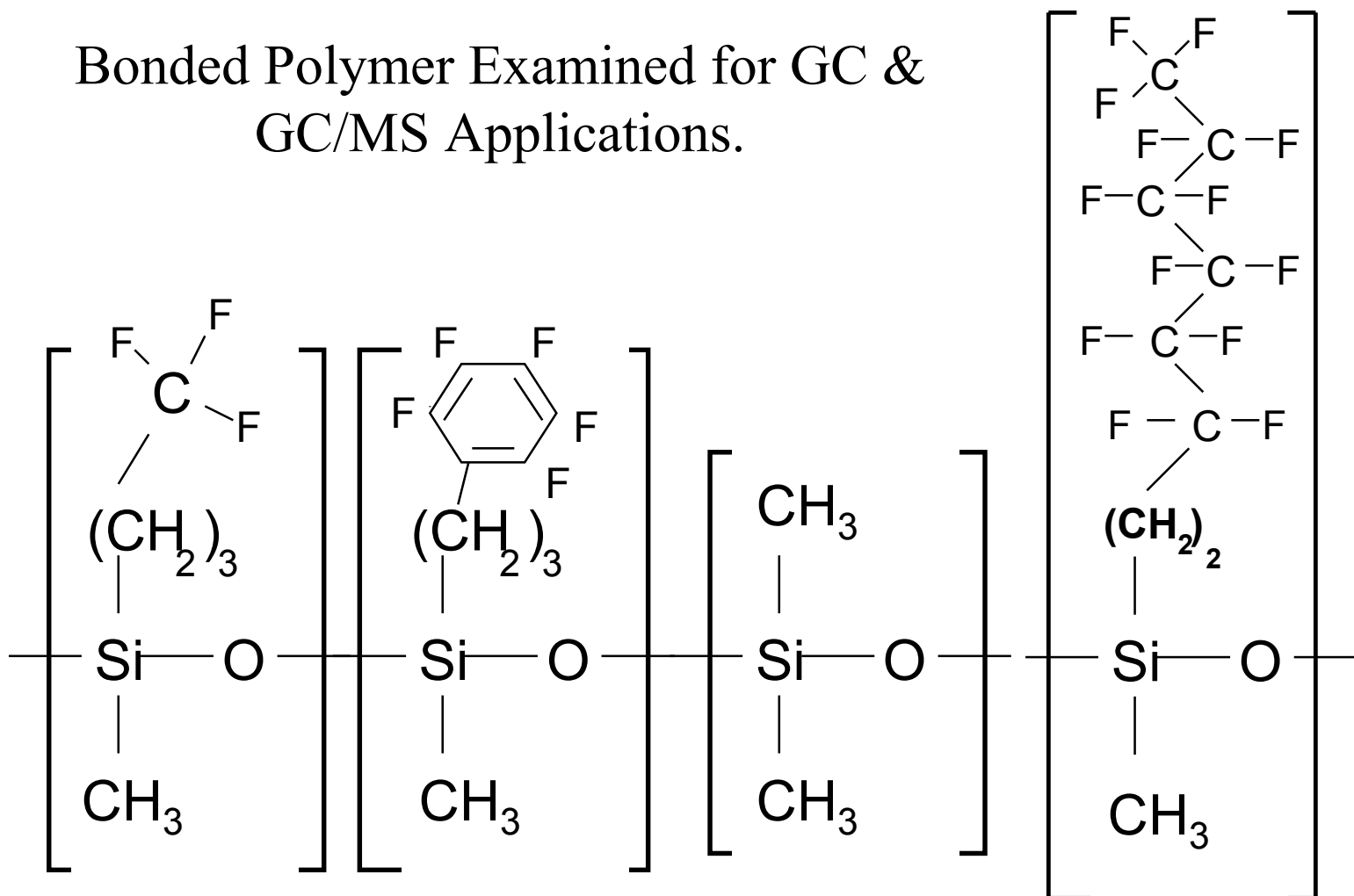
## Bonded Polymer Examined for Volatile Applications.

This phase was built based on predictions of separation. The separation criteria was met on all accounts except for the dichlorobenzenes. The first step in designing a new column is to start with functionalities that the target analytes are soluble in. The better the solubility between the analyte and the phase the better the chances of resolving these compounds.



# Experimental Fluorinated Phase

Bonded Polymer Examined for GC & GC/MS Applications.



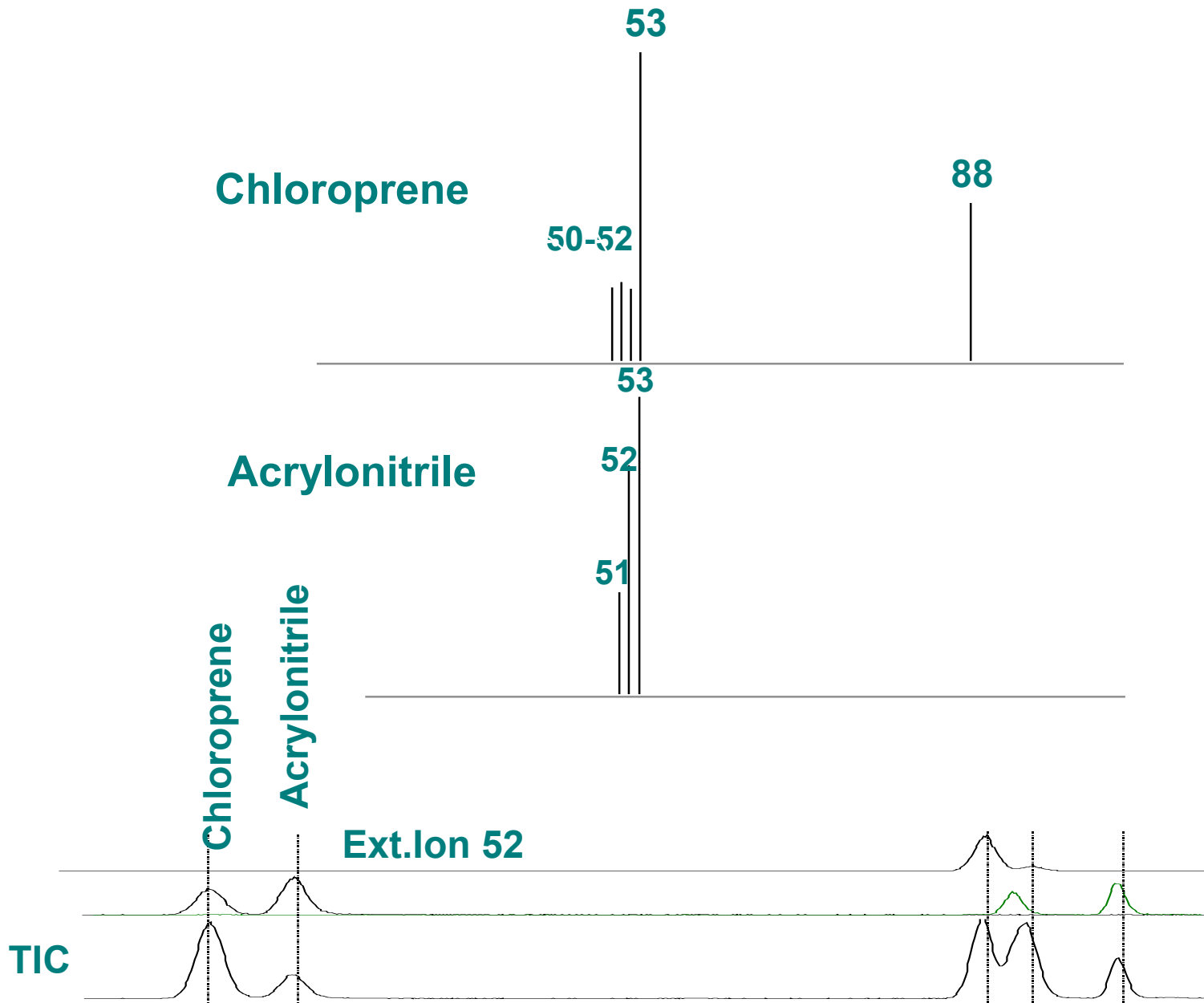
# Rtx-VMS Column Meets Design Criteria

The successful polymer known as the VMS phase not only met the resolution criteria for the isomeric pairs but also exceeded separations of critical pairs. The percentage of functionality was adjusted to resolve chloroprene and acrylonitrile.

# Rtx<sup>®</sup>-VMS Critical Pairs with Common Ions

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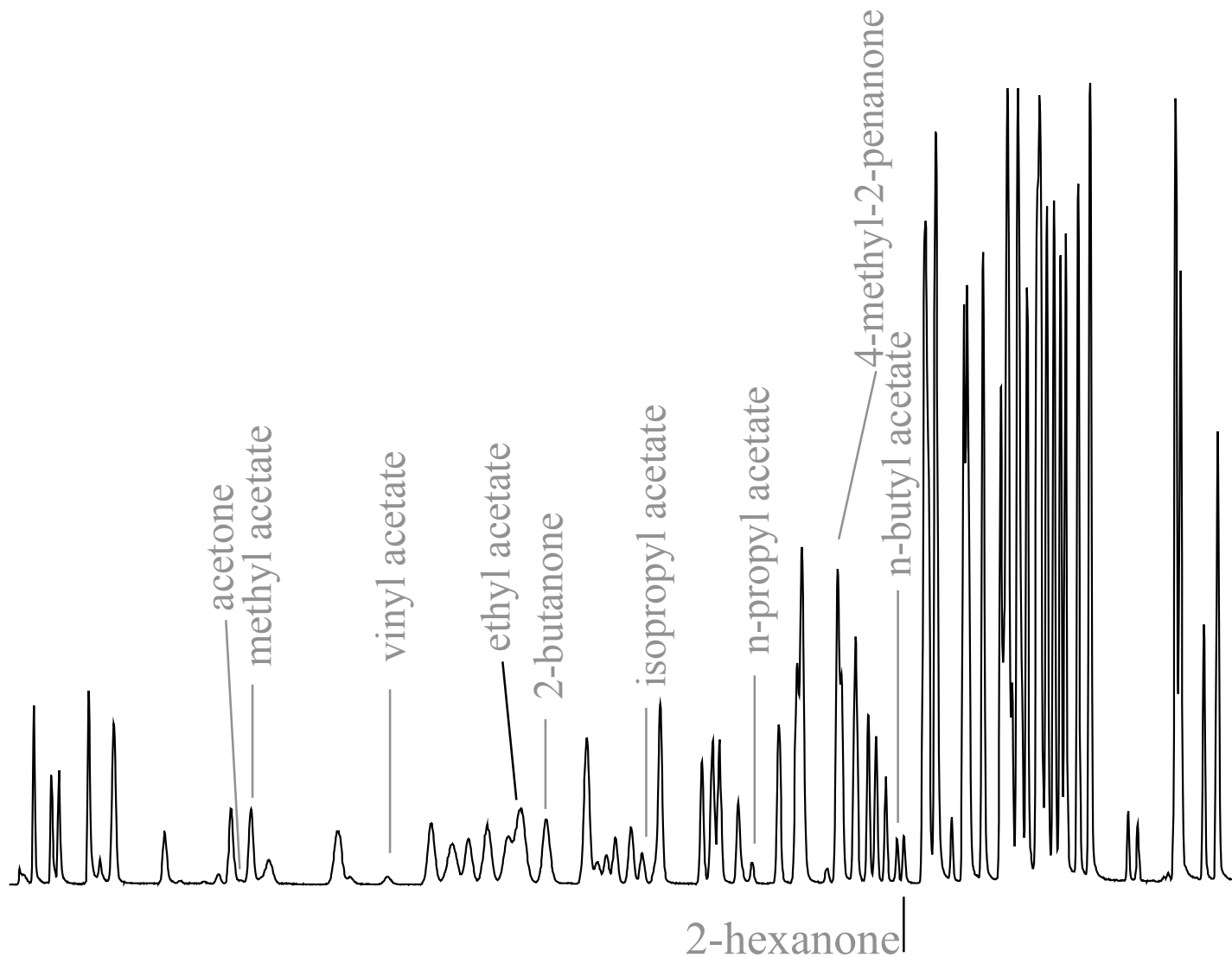


# Rtx-VMS Resolution of Acetates & Ketones.

Since the acetates and ketones share the spectral ion 43 its important that these analytes are resolve. The diagram shows the elution of the most commonly analyzed acetates and ketones.

# Acetates & Ketones Share ion 43

Time-->



## Rtx-VMS Designed for EPA Method 8260B

The Rtx-VMS column was designed to address the increasing number of analytes listed in EPA Method 8260B, and also is a good choice for separating compounds listed in EPA Method 524.2, revision IV. The major difference between the Rtx-VMS phase and others such as the “624,” “502.2,” and “VRX” is its overall selectivity and the distance between isomeric pairs like 2/4-chlorotoluene. A faster final oven ramp rate is possible because these compounds elute farther apart on the Rtx-VMS phase, preventing a partial coelutions that would interfere with quantitation. Using the EPA-suggested surrogates the analysis time is under 10 minutes making this the clear choice for fast GC applications.

# For More Information...

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# Characterization of Amorphous Silica Supports for Reversed Phase HPLC

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# Abstract

We have measured physical characteristics and metals content for a variety of silicas and chromatographically compared their relative levels of base deactivation after bonding monomeric alkyl stationary phases to them. Some aggressive base deactivation procedures significantly altered the characteristics of the silica, particularly pore size and surface area. Some base deactivated silica can provide superior chromatography for peak shape over type B materials. This study attempts to correlate the physical and chemical properties of different silica varieties with their level of base deactivation.

# Introduction

- Reversed Phase HPLC columns are manufactured from a wide range of silicas that vary in many chemical and physical properties. Differences in the properties of the underlying silica may have a major influence on the resulting chromatographic properties of the finished column. Important physical properties include particle size distribution, pore size distribution, pore volume, and the surface area. An important chemical property is the concentration of metals.

# Introduction

- The first generation of HPLC silica was type A made from inorganic sols. The second generation includes base deactivated silica prepared by various chemical treatments of type A silica to remove surface metals. Metal impurities in silica are commonly known to have a detrimental effect on peak shape of basic analytes. It has been theorized that at least some of the improvement in base deactivation obtained following chemical removal of metals may be due to the resulting physical changes of the silica (i.e. pore shaping).

# Introduction

- The latest and third generation of silica is high purity, Type B silica, synthesized from an organic sol. Type B silica contains extremely low concentrations of metals and has a major advantage over earlier generations of silica for some applications.

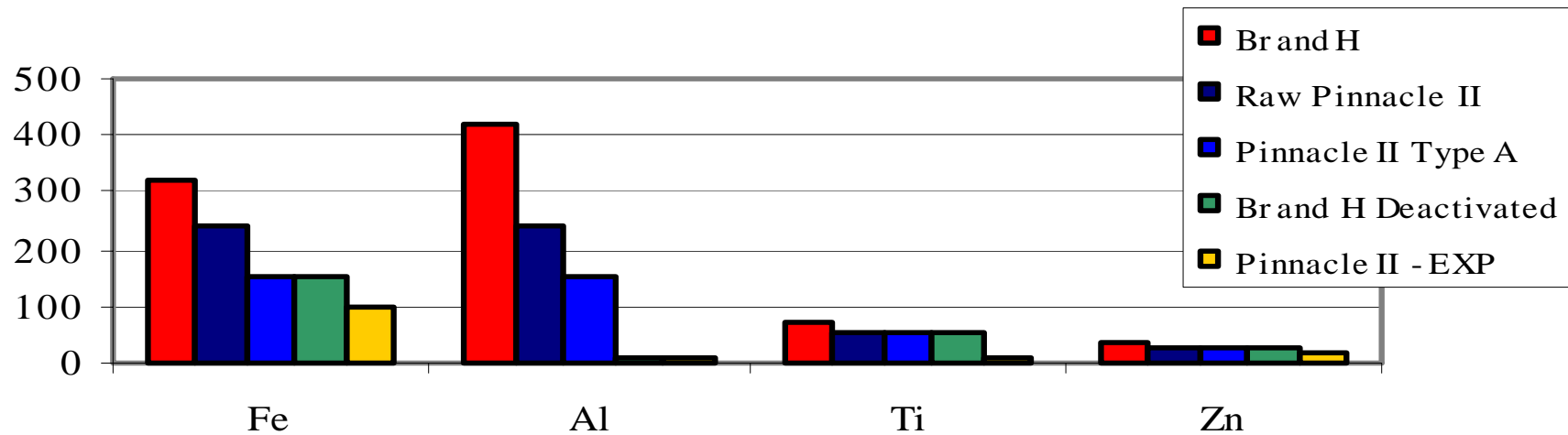
# Measured Silica Properties

- Metals Content (ppm)
- Mean particle size and distribution ( $\mu\text{m}$ )
- Total pore volume ( $\text{ml/g}$ ) with average pore size ( $\text{\AA}$ ) and distribution
- Mean surface area ( $\text{m}^2/\text{g}$ )

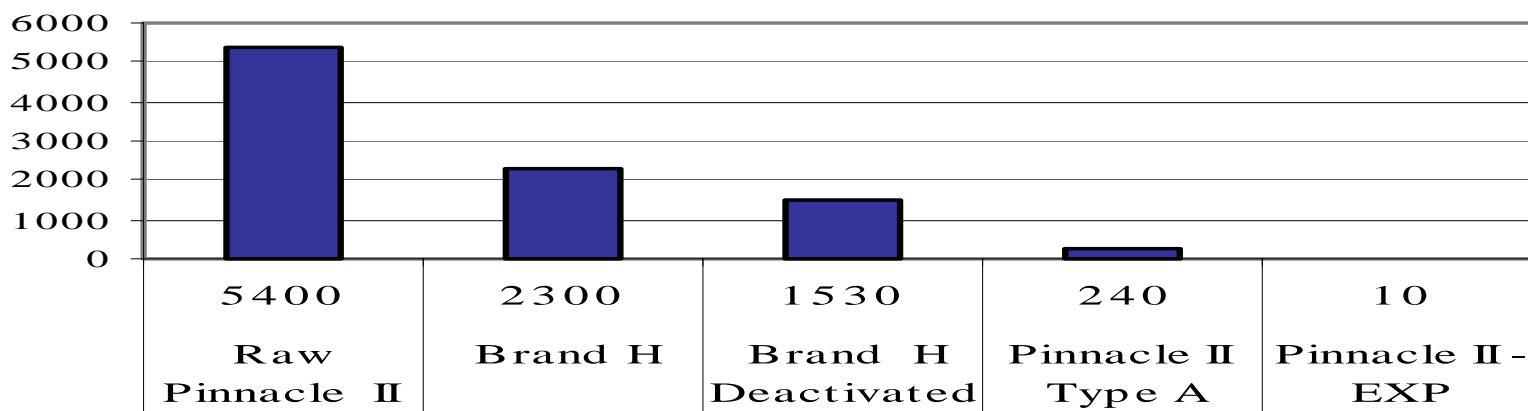
# Silica Metals Content

- Silica derived from inorganic sources (Type A) must undergo metals removal procedures to create usable materials for HPLC chromatography.
- Refined metal removal processes using the type A silica can create a base deactivated silica.
- Type B silica is derived from “metal free” organic sols. Metals content is due to post-particle contamination.
- Certain processes can produce a base deactivated silica that rival type B for metals content.

## Metals content of silica derived from Inorganic Sols

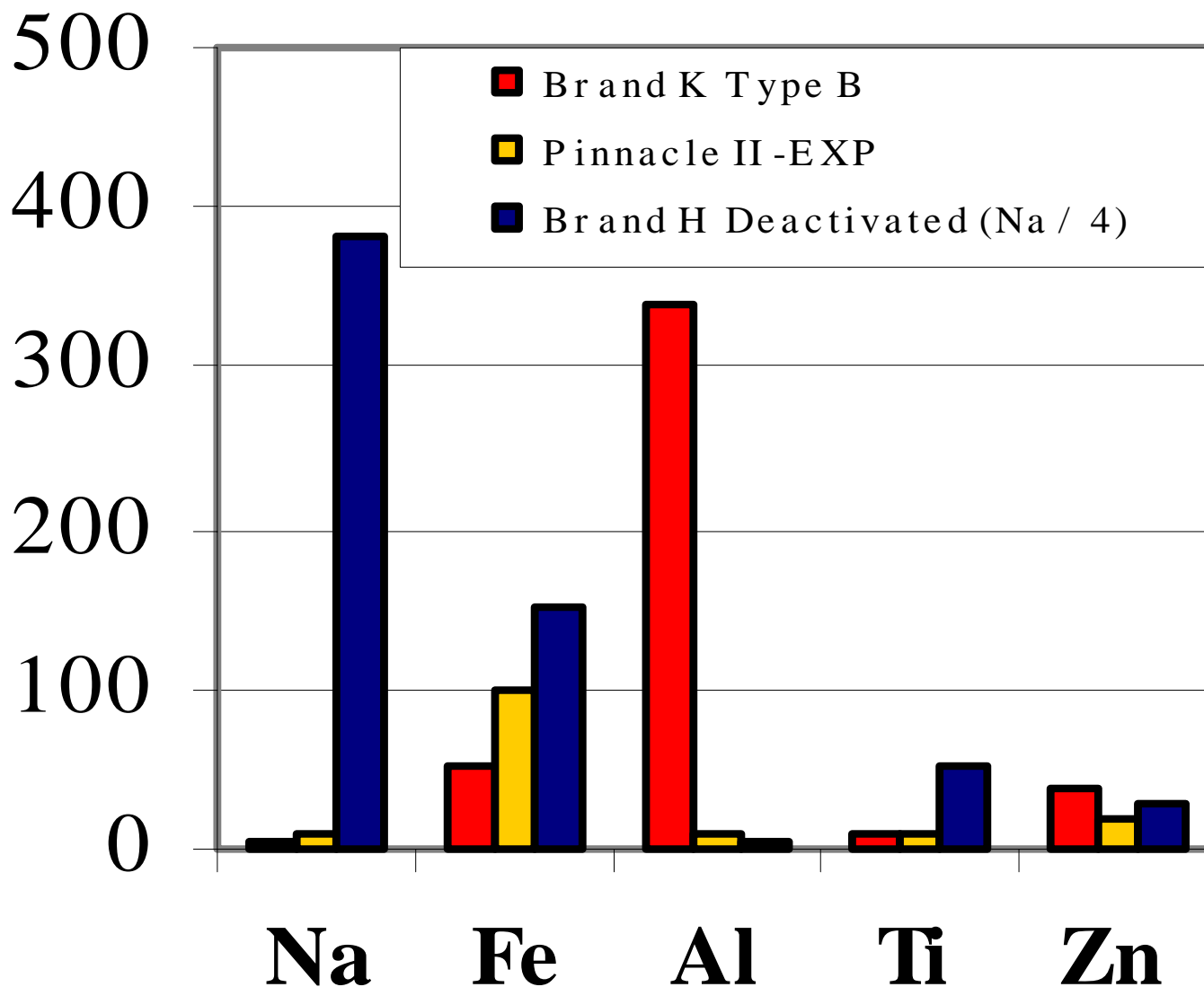


## Sodium Content



Raw, Type A, and Base Deactivated Materials

# Base Deactivated Silica vs Type B Silica





# Pyridine/Phenol Test for Base Deactivation

Column Dimensions: 150x4.6mm, 5 $\mu$ m

Mobile Phase: 80/20 20mm K<sub>x</sub>PO<sub>4</sub>, pH 7.0/Acetonitrile

Flow rate: 1ml/min

Detector: UV @ 254 nm

Injection volume: 5 $\mu$ l

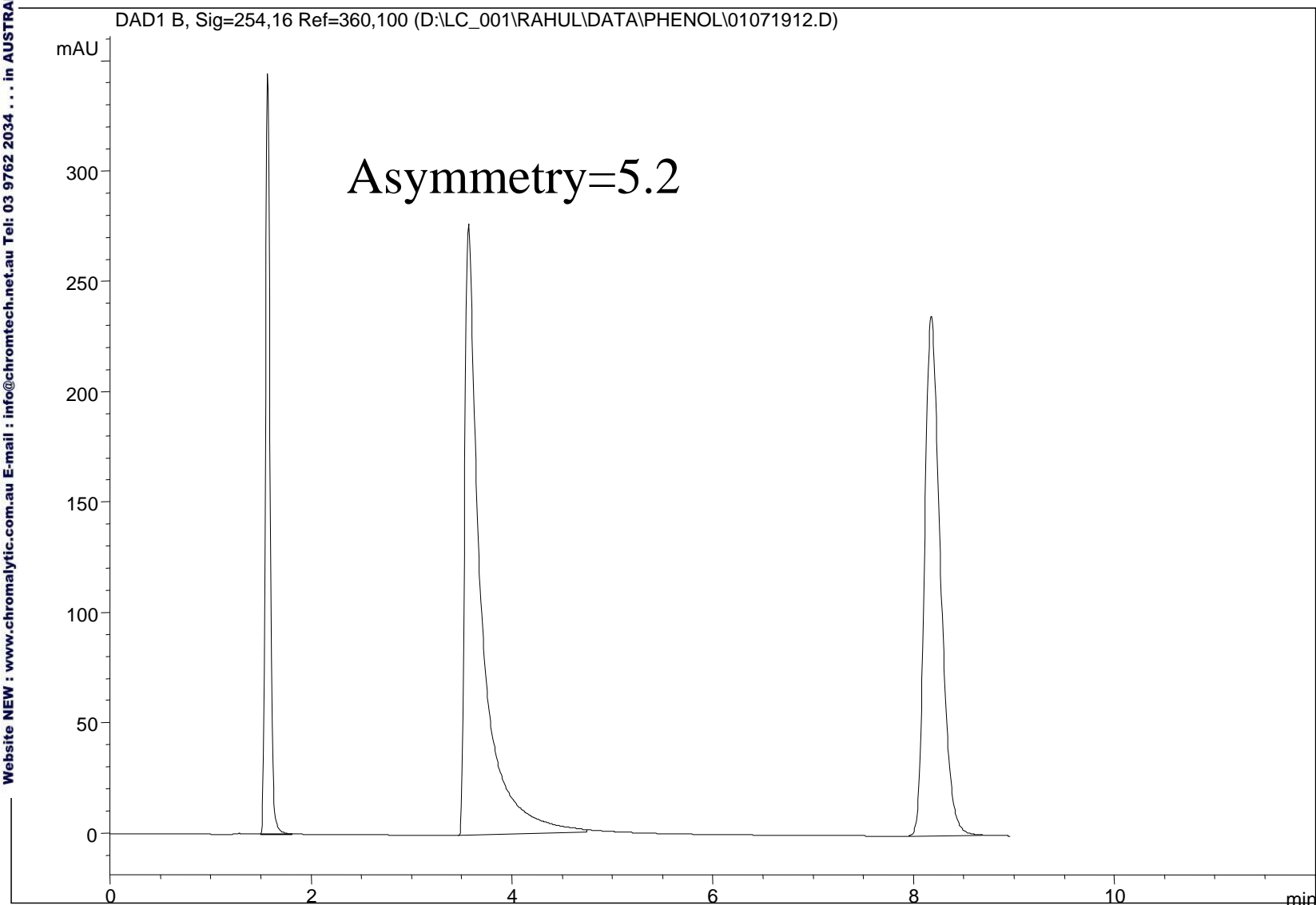
Peaks: 1. Uracil  
2. Pyridine  
3. Phenol

# Type A with C18 Bonding

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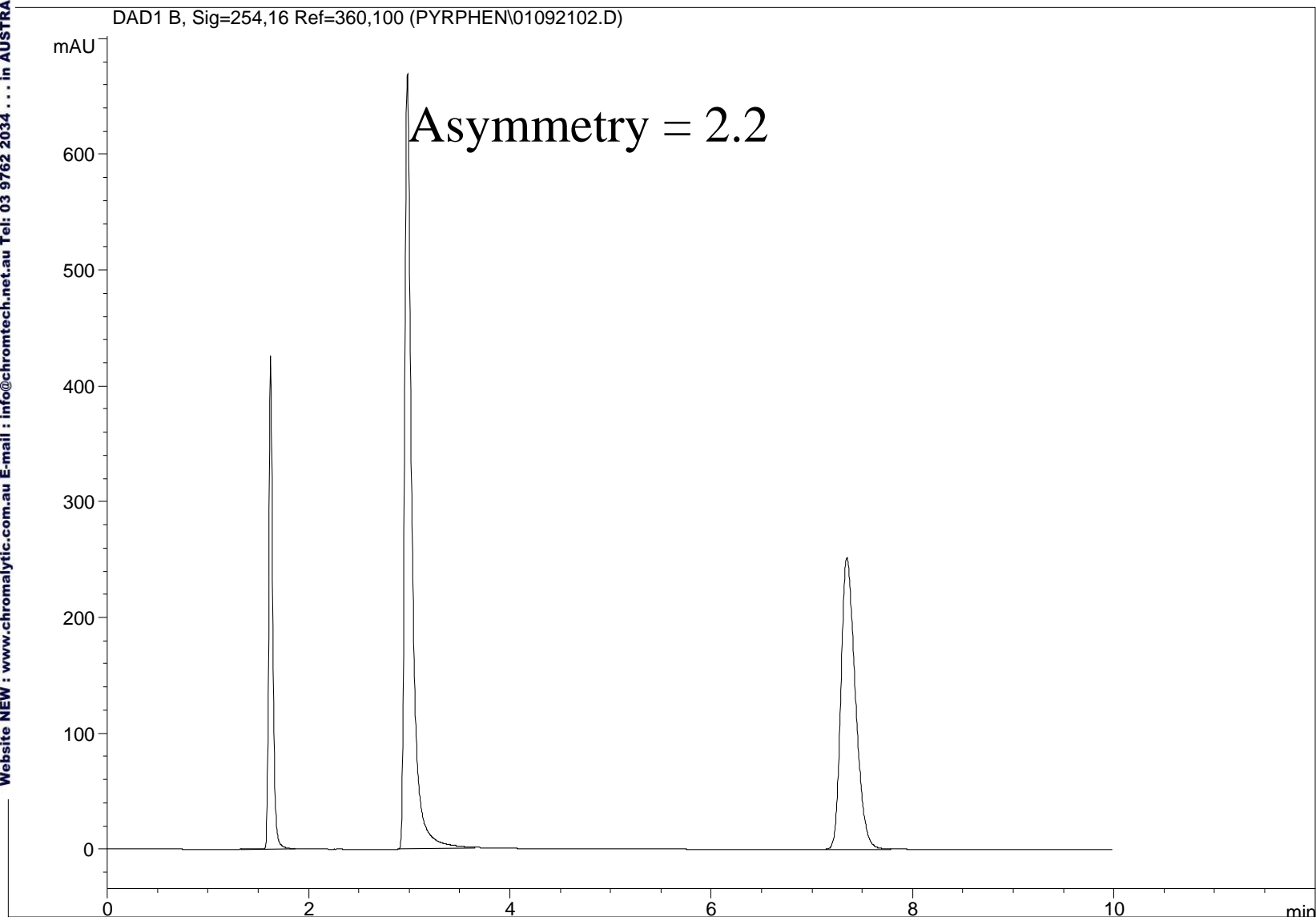
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# Brand H – Deactivated with C18 Bonding

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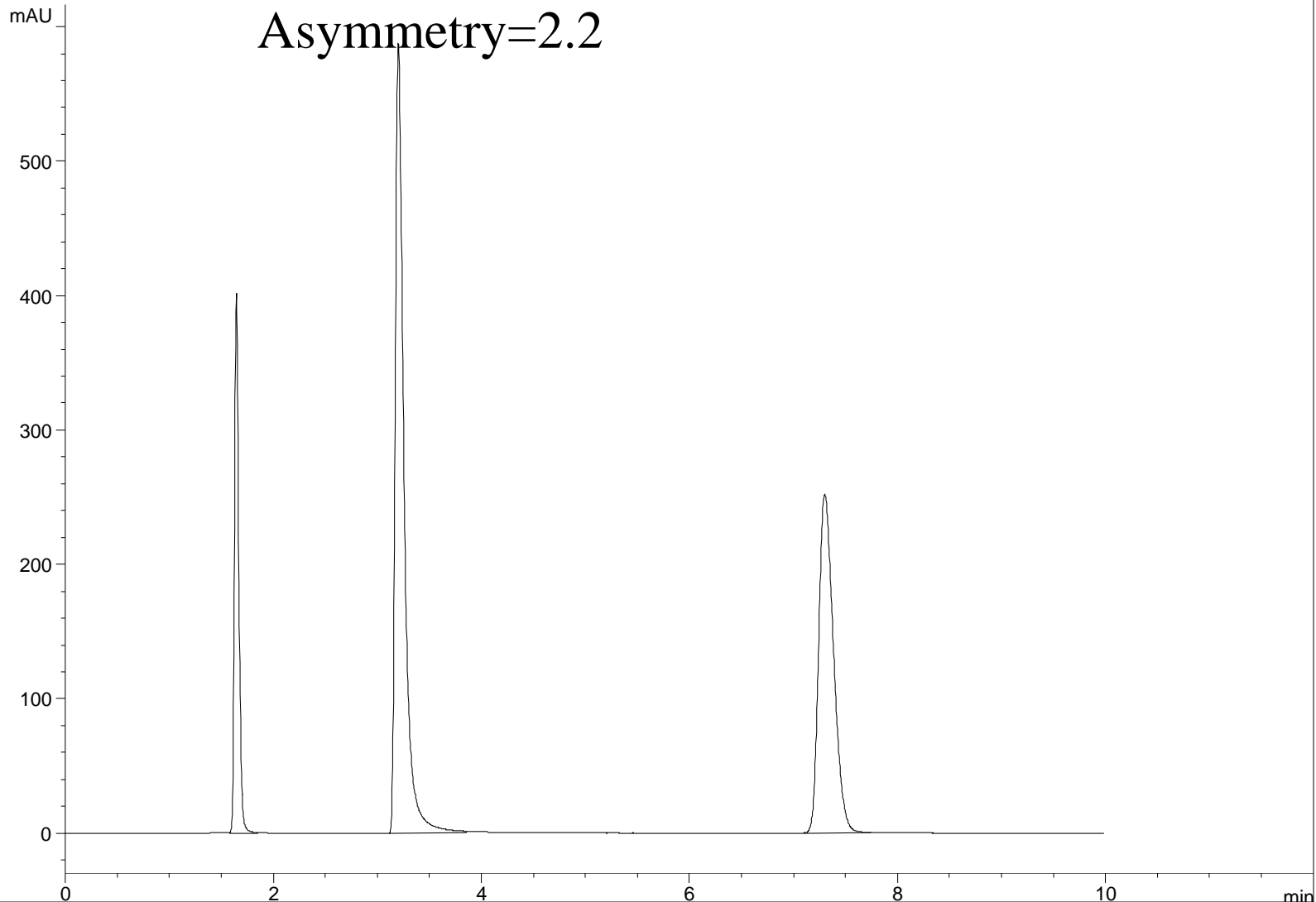
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# Pinnacle II-Exp with C18 Bonding

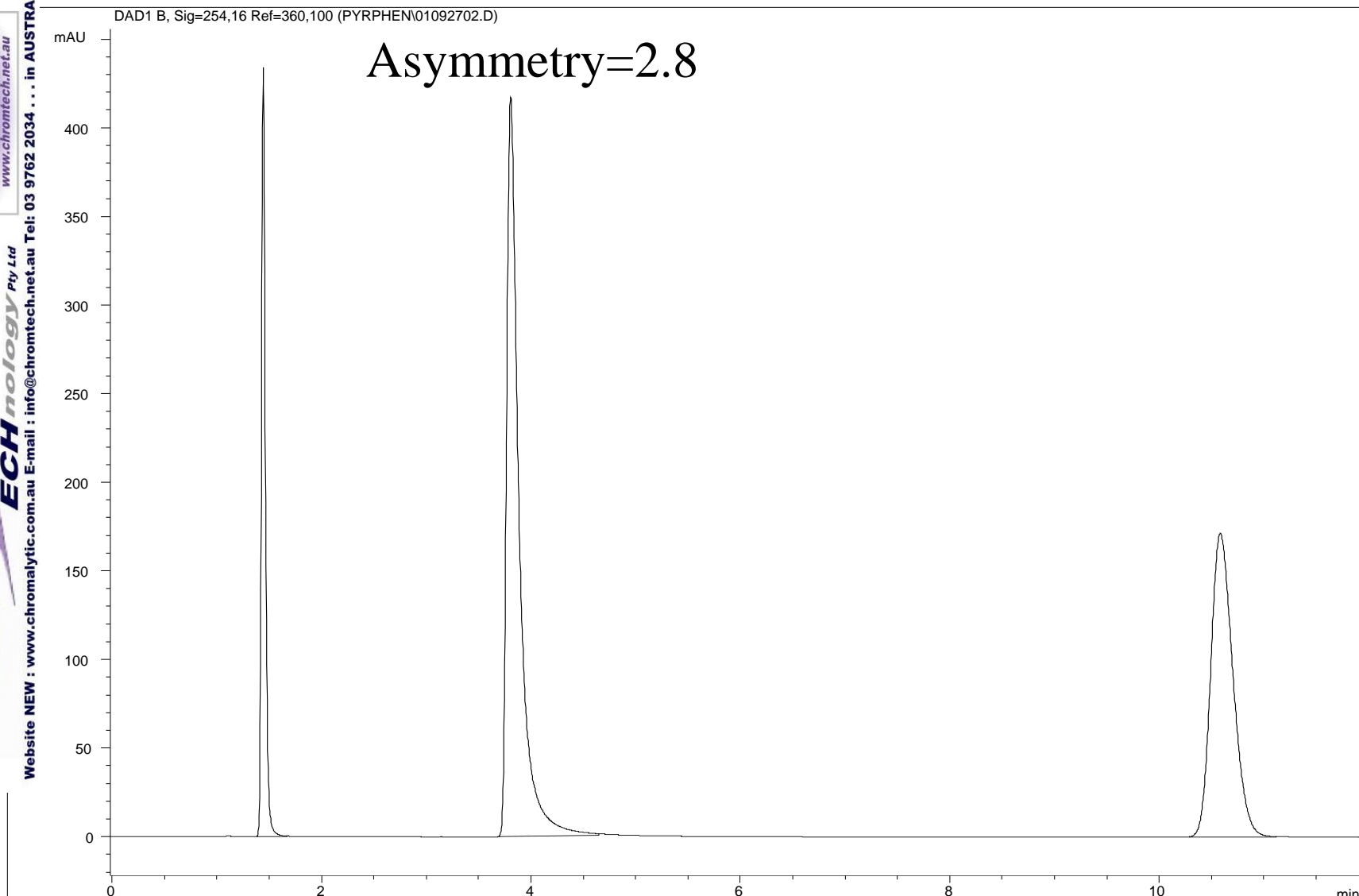
DAD1 B, Sig=254,16 Ref=360,100 (PYRPHEN01092604.D)

Asymmetry=2.2



# Brand K – Type B with C18 Bonding

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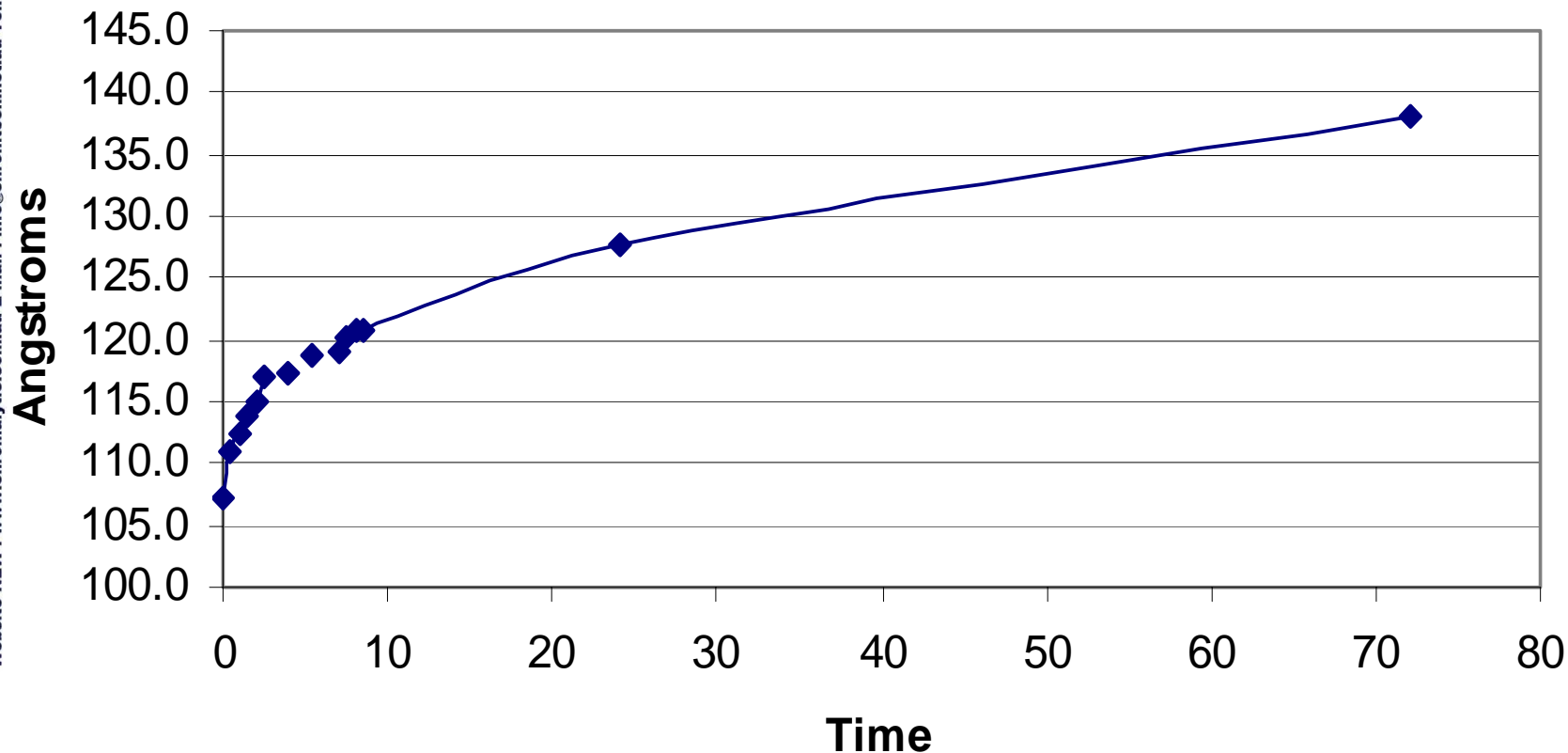


# Base Deactivation Treatments

- Over time the metal extraction treatments enlarge the pore size of the silica.
- An increase in the pore size creates an increase in the pore volume. This increases the void volume.
- As pore size increases for the silica particle surface area decreases.
- The loss in surface area reduces the maximum amount of phase that can be placed onto the silica surface relative to the parent material.
- Treatment and synthesis routes also effect the surface of the particle.

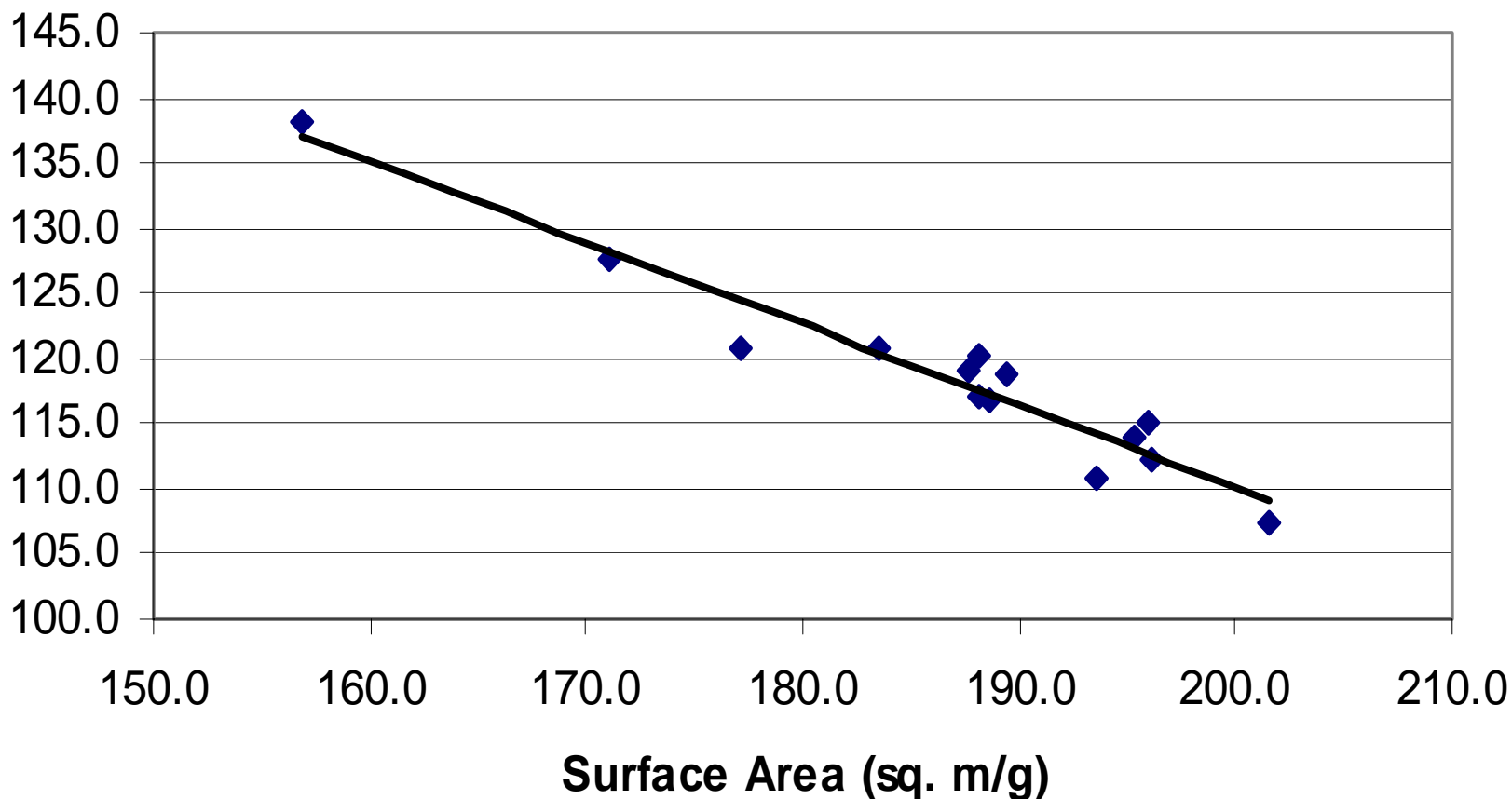
# Base Deactivation Treatments

## Mean Pore Size Increase vs Time



# Base Deactivation Treatments

## Mean Pore Size vs Surface Area



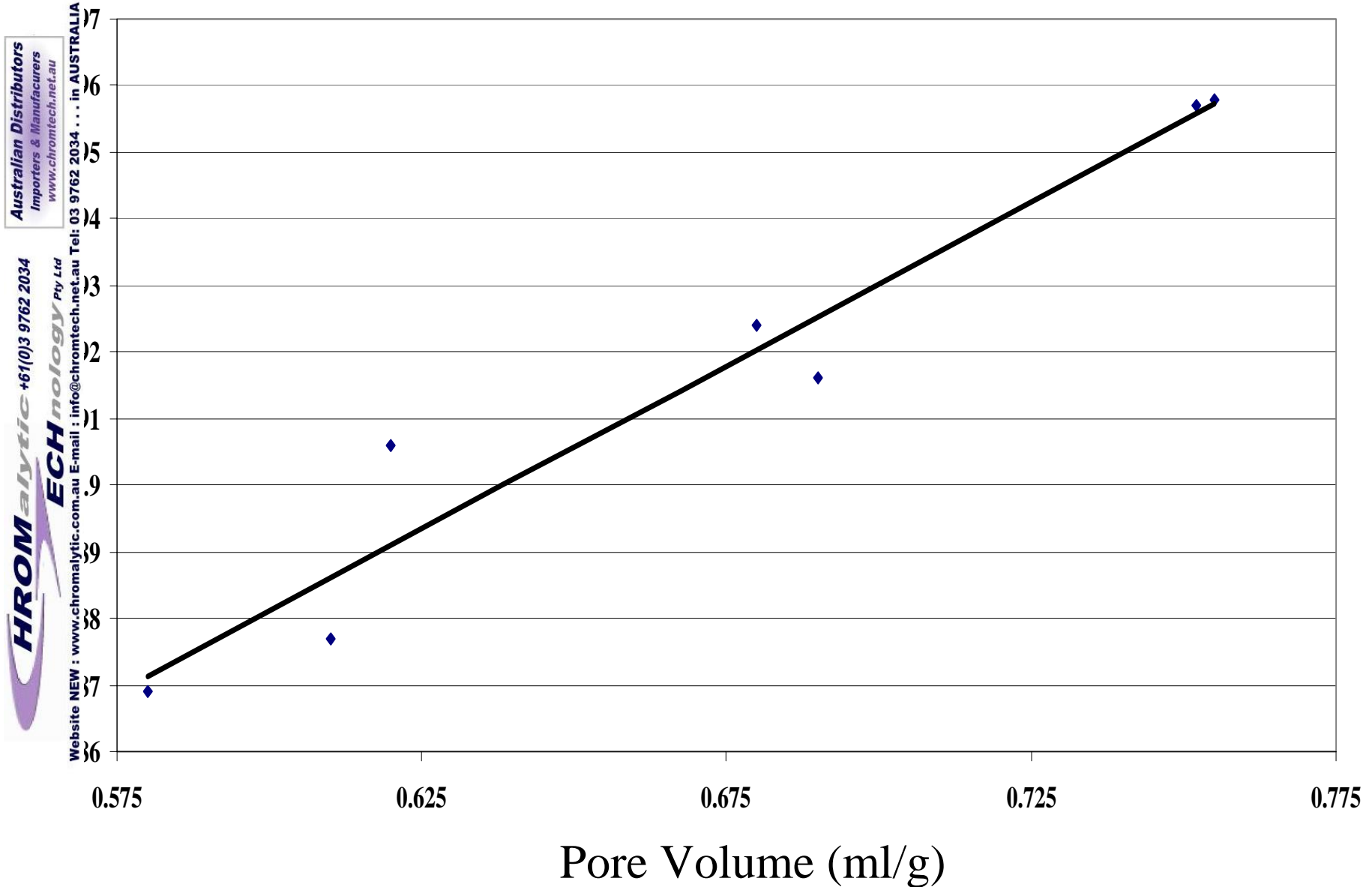


# Silica Pore Volume vs Retention

- As the pore volume of a silica particle increases, the surface area decreases.
- Increased pore volume creates a linear increase in  $V_o$ . Unretained components take longer to elute from the column.
- An increase in pore volume will decrease  $k'$  though the retention of retained components may appear to be the same.

# Pore Volume vs Void Time

$$y = 0.4915x + 1.5862$$
$$R^2 = 0.9434$$



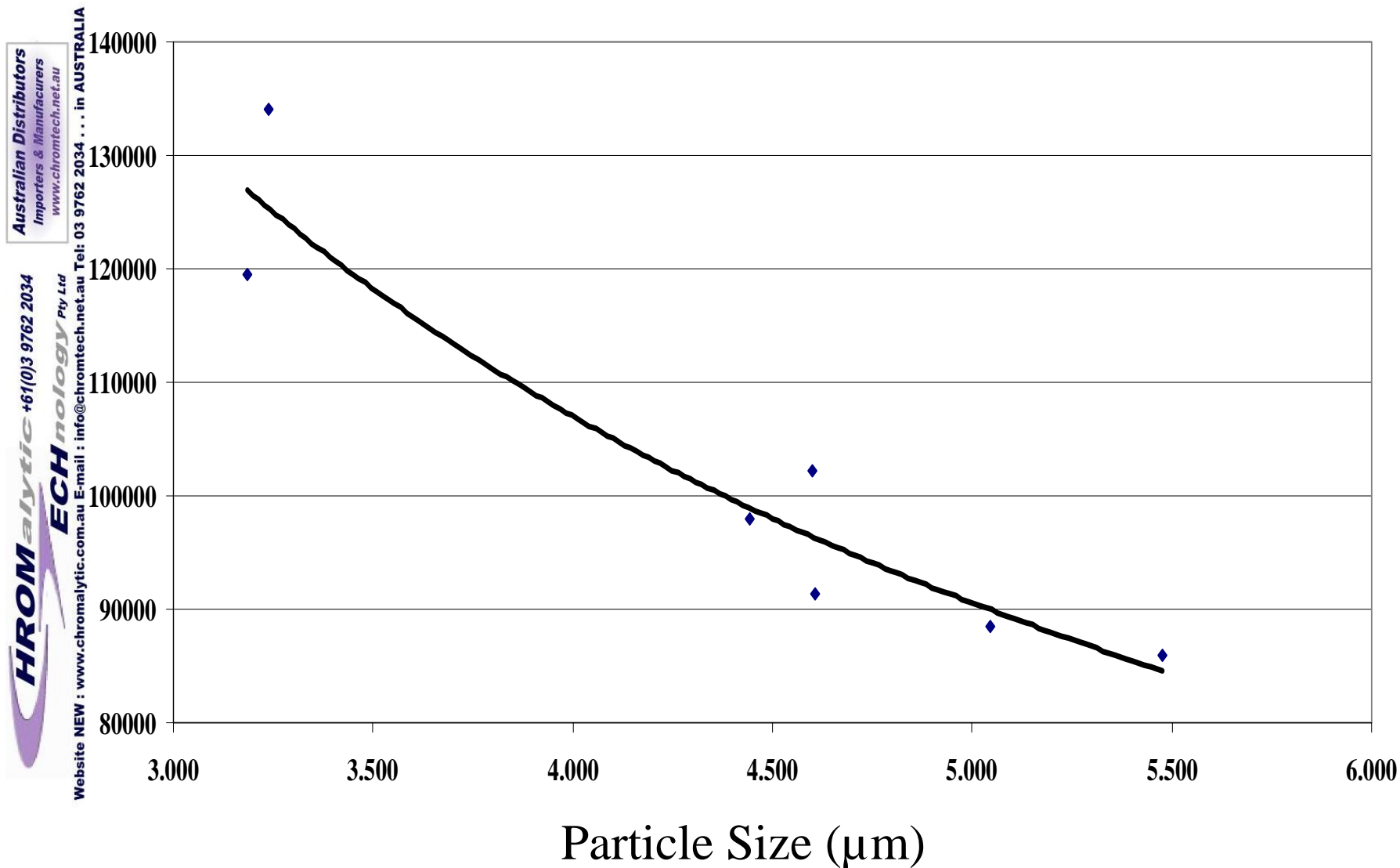
# Particle Size and Distribution

- Silica for analytical chromatography is typically available in 3, 5, and 10  $\mu\text{m}$  particles sizes.
- The mean of these particle sizes and the distribution ranges vary between manufactures.
- The smaller the particle size the higher the number of theoretical plates a column can produce.
- Typically columns produced with smaller particles give greater theoretical plates at the cost of higher pressures.
- When using silica of the same pore volume, smaller particles produce a linear increase in  $k'$ .

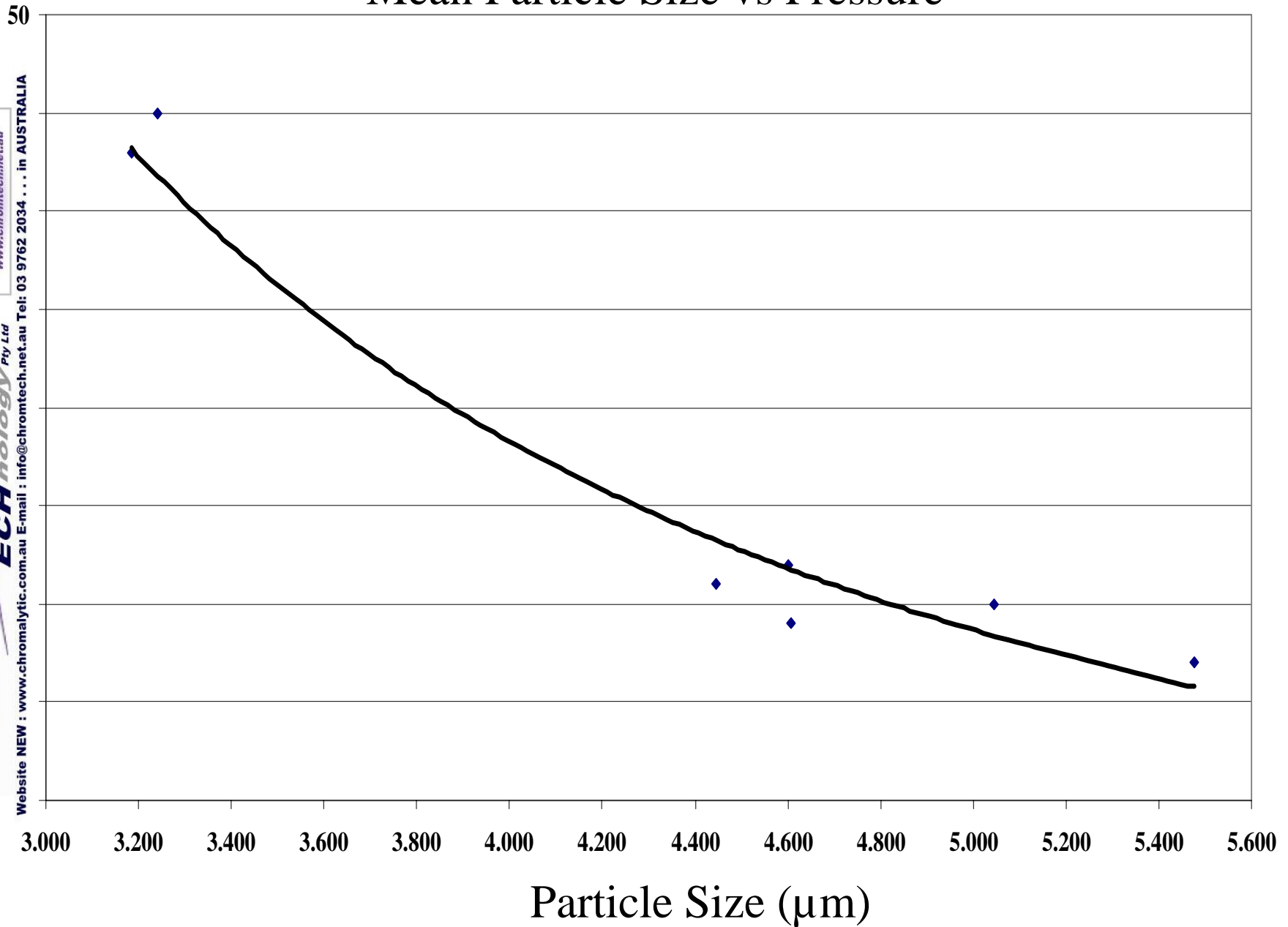
# Particle Size and Distribution

- Typically a 3  $\mu\text{m}$  particle can produce 135,000 plates/meter while a 5 $\mu\text{m}$  particle can produce 85,000 plates/meter minimum.
- The pressure increases exponentially when a smaller particle size is used.

# Theoretical Plates/Meter vs Particle Size



# Mean Particle Size vs Pressure



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# Mean Particle Diameter vs k'

1.86

$$y = -0.2146x + 2.8015$$

$$R^2 = 0.9986$$

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4.4

4.5

4.6

4.7

4.8

4.9

5

5.1

Mean Particle Diameter ( $\mu\text{m}$ )

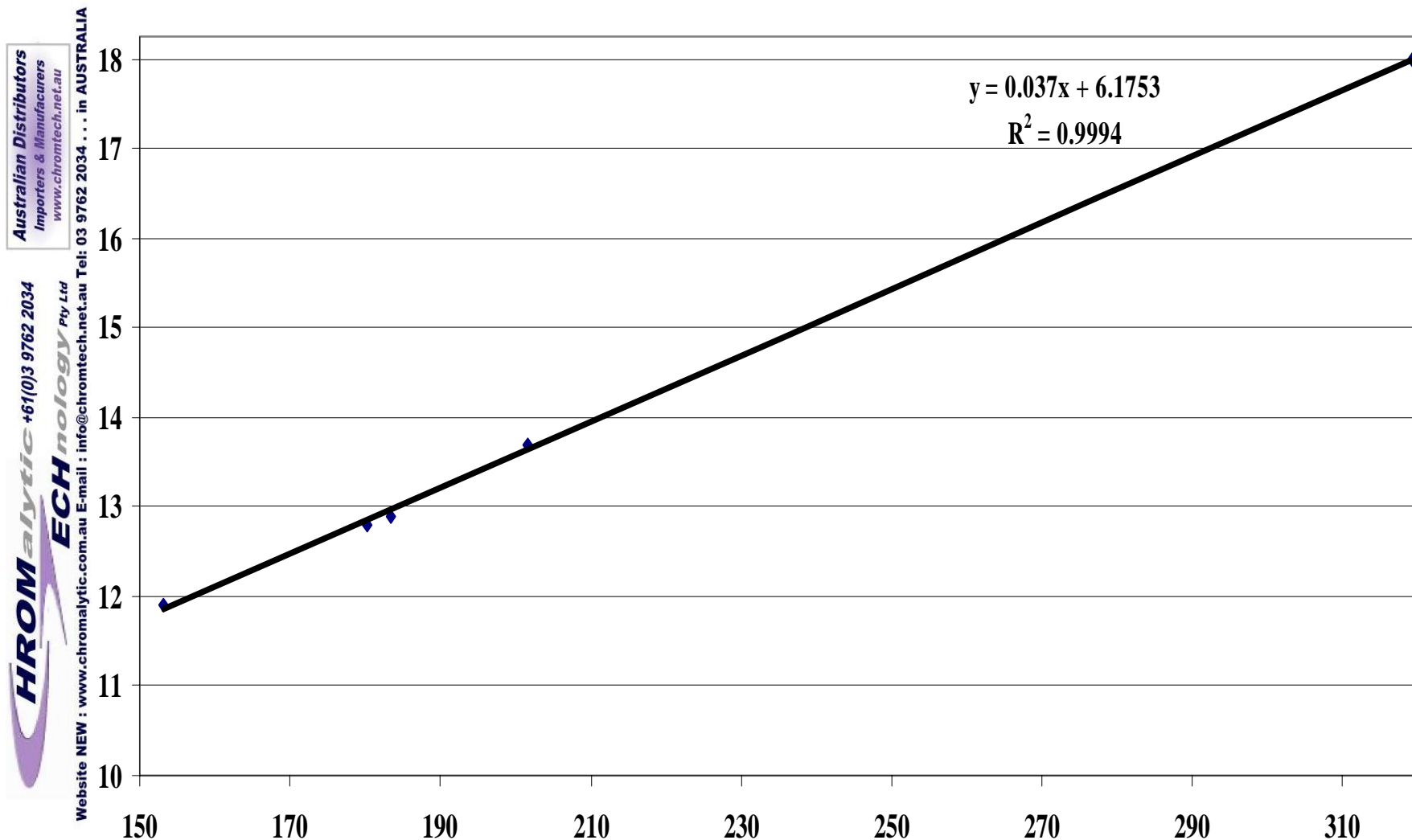
k

# Silica Surface Area

- The surface area of the silica is one of the factors limiting carbon loading of a particular phase (as C18).
- The lower the surface area, the lower the carbon load. Carbon load is directly proportional to surface area if bonding technique provides consistent surface coverage.
- Increases/Losses in carbon load will cause a shift in the  $k'$  of analytes.



# Silica Surface Area vs Maximum C-18 Loading



Silica Surface Area (Sq.m/g)

# Conclusions

- No two silica support lots are exactly the same.
- Variations may be great from manufacturer to manufacturer.
- Simply recommending a column to perform a legacy separation based on phase type (C-8, C-18, etc) is not enough.
- These factors are very important when selecting alternate columns for methods under development or making substitutions.
  - Particle Surface Area
  - Particle Pore Volume
  - Mean particle size and Distribution
  - Mean Particle Pore Size
  - Metals content

# Conclusions

- Some base deactivated silicas can provide better peak shape than type B materials.
- Base deactivated silica typically has lower surface area than type B. This results in a lower carbon load for the material.
- To find a phase that will give similar retention characteristics, carbon loading and surface area must be compared.

# Acknowledgments

- The authors wish to thank:  
Randall R. Romesberg, Larry Peters, and Bob King for their support in carrying out experiments and manufacturing columns to produce data for this presentation.

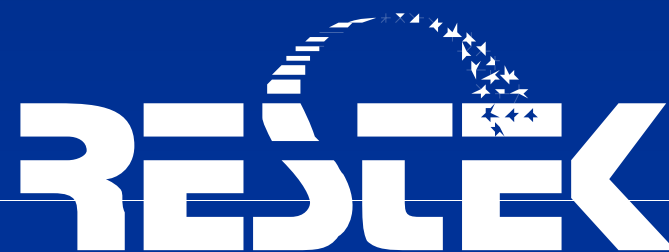
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# Semivolatile Analysis

Frank L. Dorman, Chris English, and  
Gary Stidsen



# Semivolatile Compounds

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



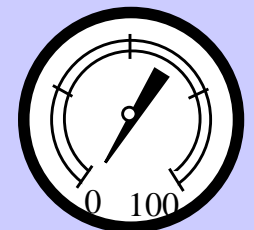
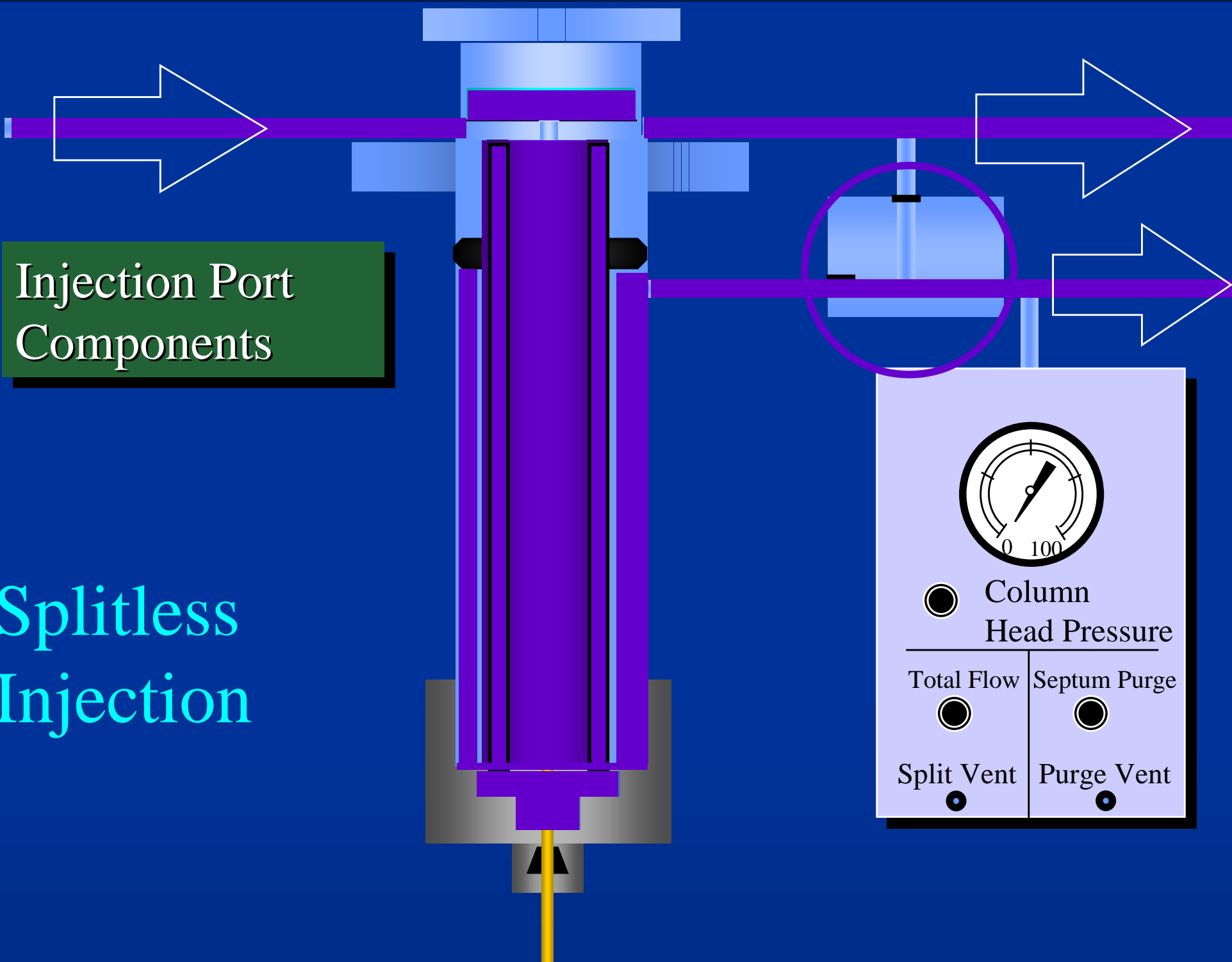
Australian Distributors  
Importers & Manufacturers  
www.chromtech.net.au

**HR**OMalytic +61(0)3 9762 2034  
**ECH**nology Pty Ltd

Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034 . . . in AUSTRALIA

# Injection Port Components

## Splitless Injection



- Column Head Pressure
- Total Flow
- Septum Purge
- Split Vent
- Purge Vent

# Factors Affecting Splitless Injection

## 1. Hold Times

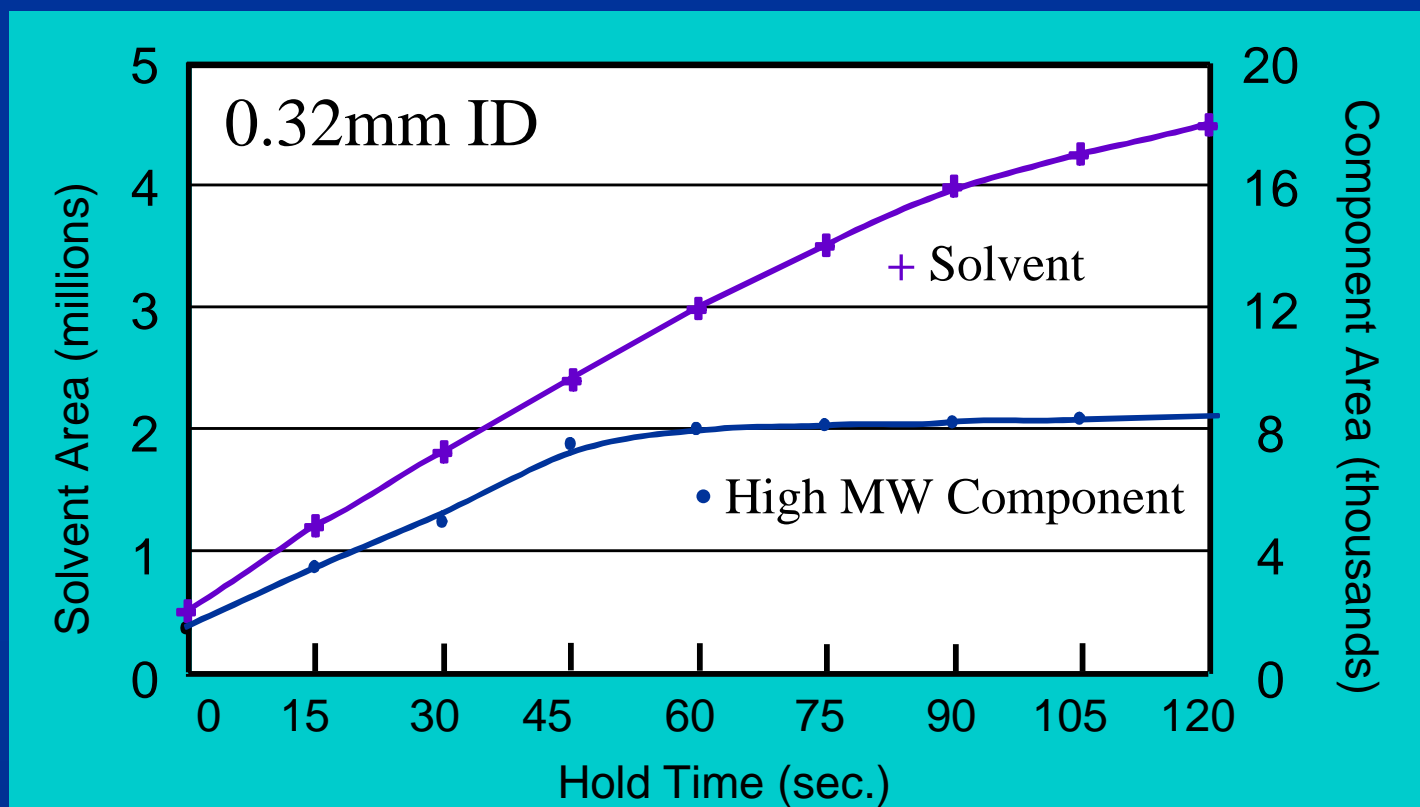
Column ID (mm)	Column Flow Rate (cc/min.)	Approx. Hold Time
	He	
0.18	0.3	3 min
0.25	0.7	1.5 min
0.32	1.2	45 sec
0.53	2.6	30 sec

*Determine  
this  
empirically*

Note: based on a 2 $\mu$ L injection volume of CH<sub>2</sub>Cl<sub>2</sub> = 0.8 mL sample expansion value @ 250°C & 10 psig.

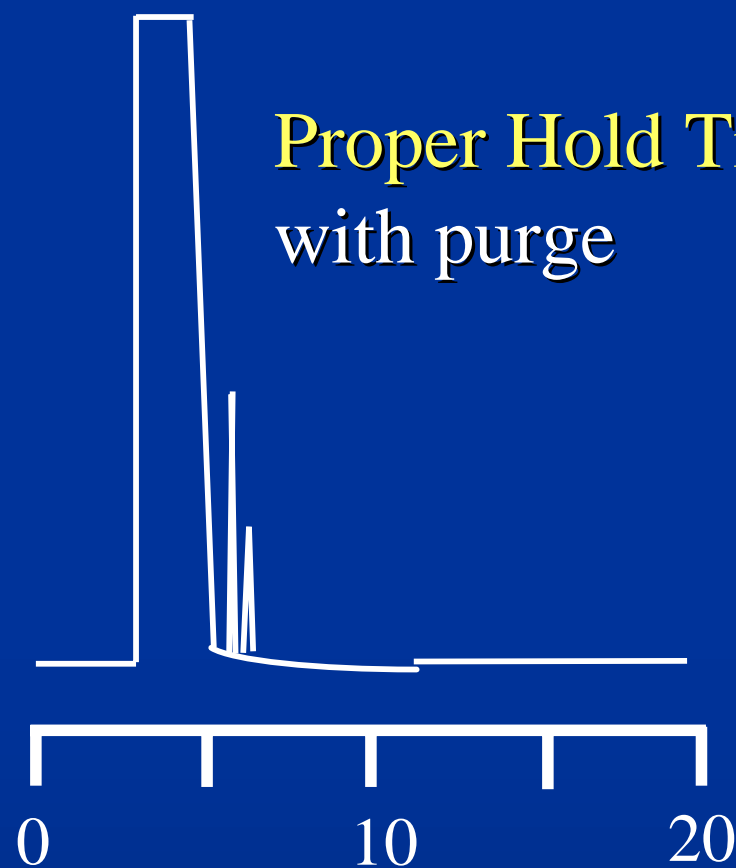
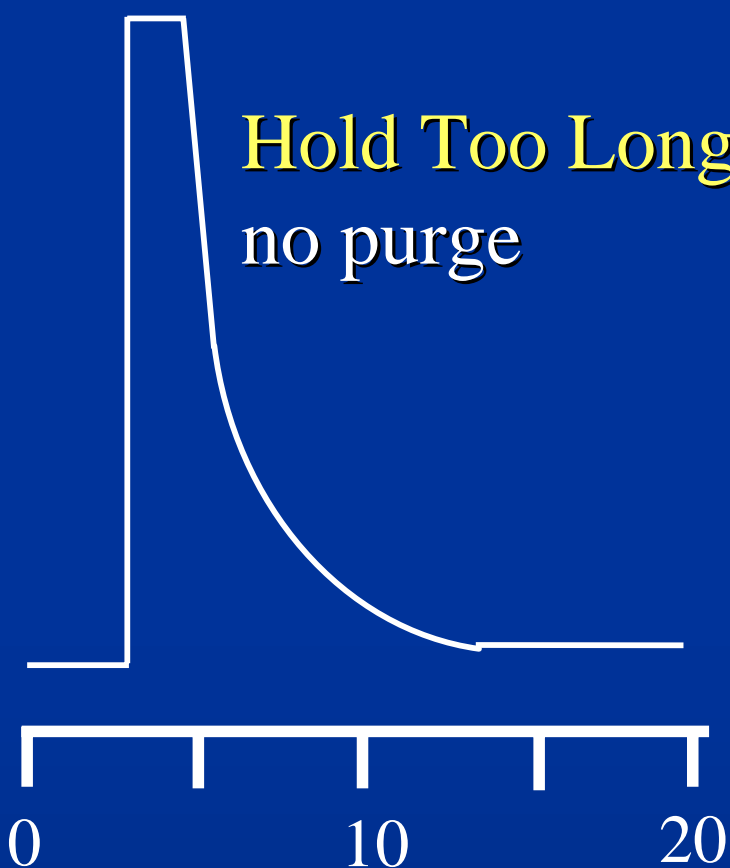
# Factors Affecting Splitless Injection

## 1. Hold Time Optimization



# Factors Affecting Splitless Injection

## 1. Hold Times



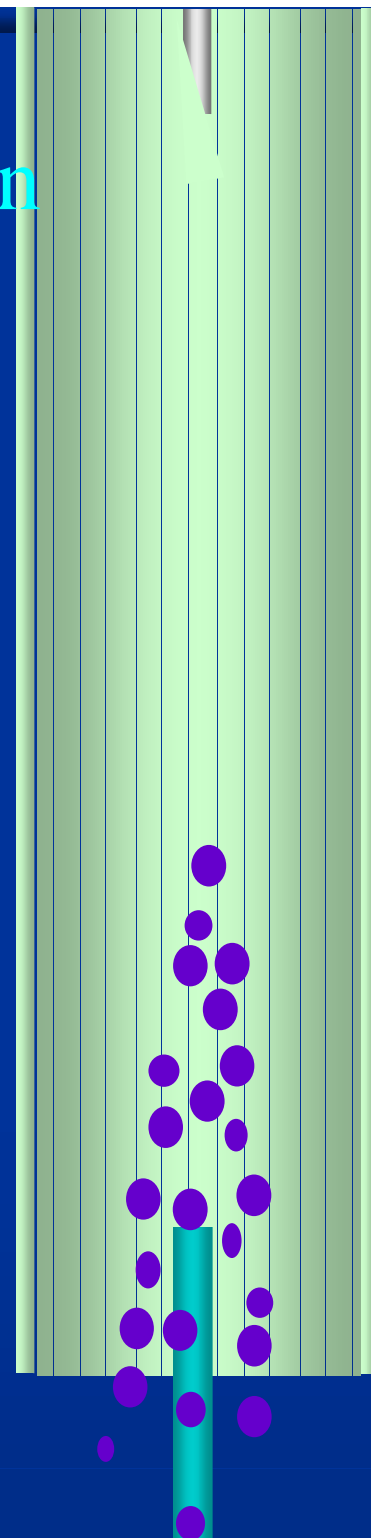
Time (min)

# Factors Affecting Splitless Injection

## 3. Sample Vaporization

Fast Autosampler :  
Incomplete vaporization

Aerosols or droplets reach the  
column instead of vapors



# Factors Affecting Splitless Injection

## 3. Sample Vaporization

Fast Autosampler :

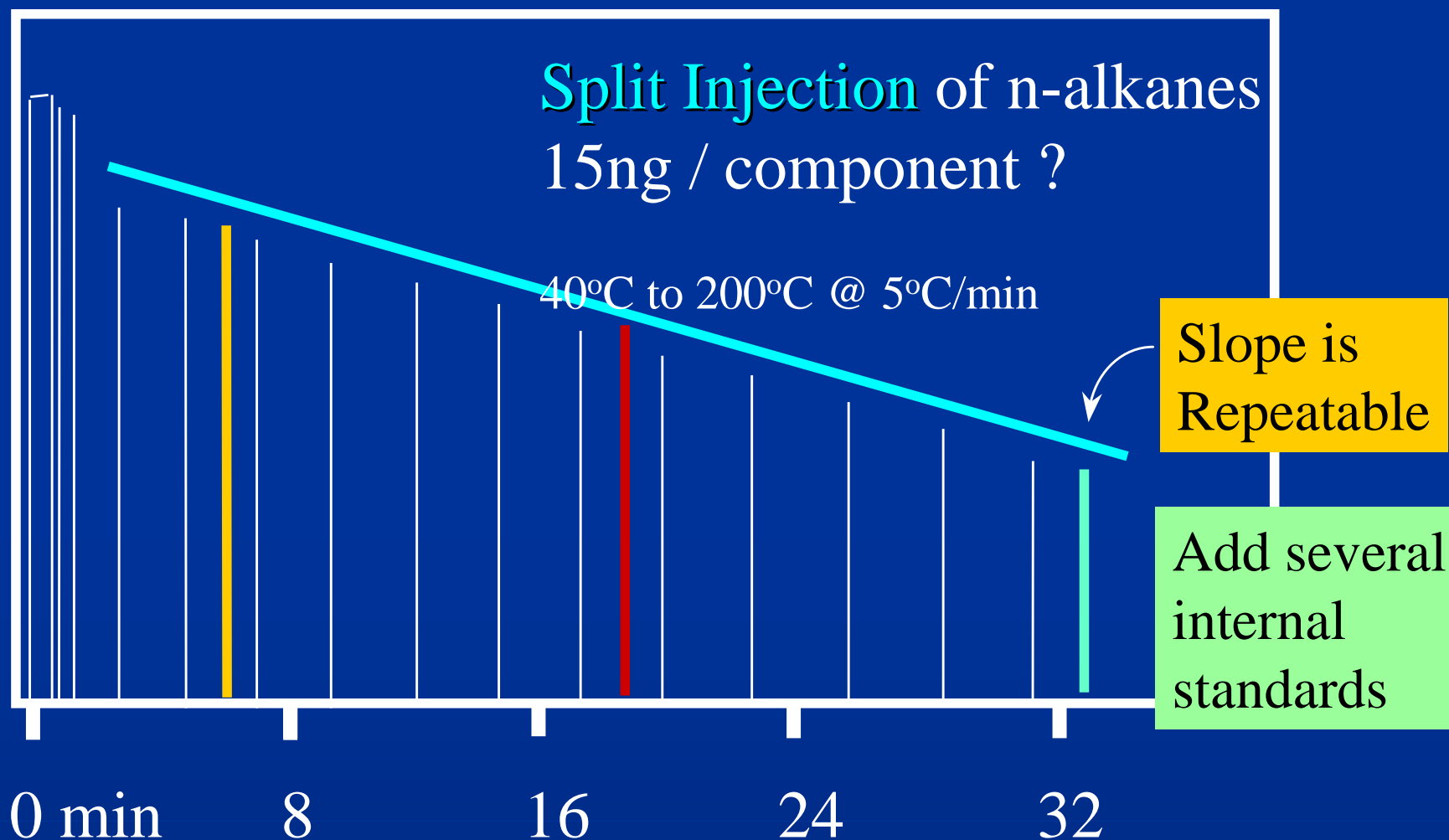
Pack with wool or CarboFrit™

STOPS AEROSOLS COMPLETELY



## II. Splitter Discrimination Molecular Weight Discrimination

Rtx-1: 30m, 0.32mm ID, 0.25 $\mu$ m



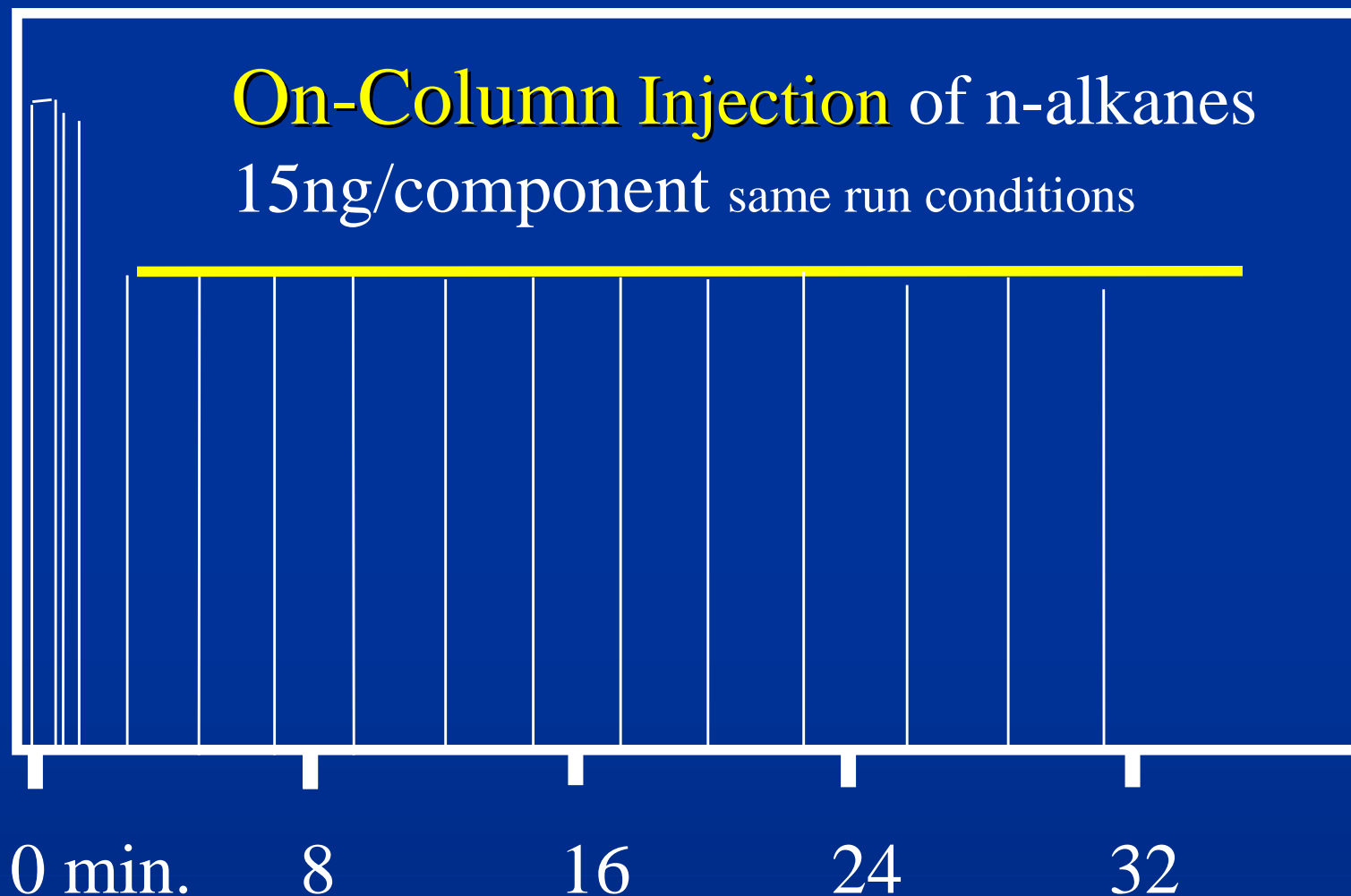


## II. Splitter Discrimination

### No Molecular Weight Discrimination

Rtx-1: 30m, 0.32mm ID, 0.25 $\mu$ m

**On-Column Injection** of n-alkanes  
15ng/component same run conditions



# Splitless Liner Designs

Straight



Gooseneck



Double  
Gooseneck



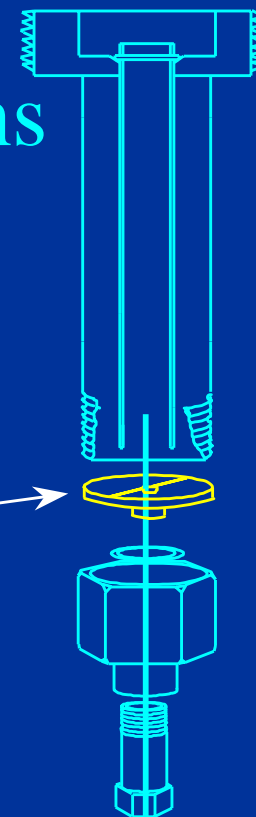
Cyclo Double-  
Gooseneck



# 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	dirty disk
Splitless with Wool	6.0%	12.8%
Gooseneck	2.0%	2.4%

# Vespel® Ring Inlet Seals

## Types of Surface Treatments



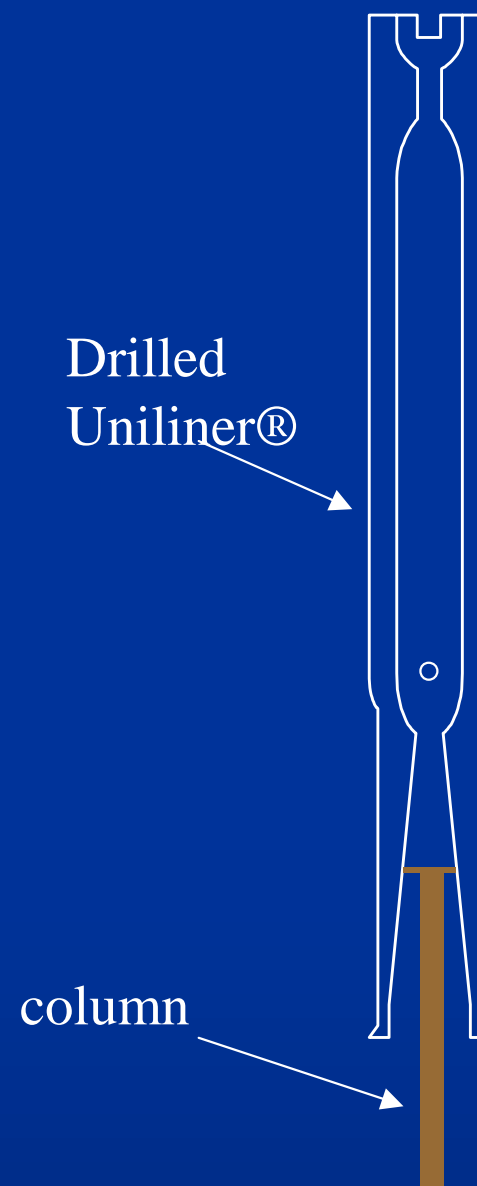
**CHROM**alytic +61(0)3 9762 2034  
**ECH**nology Pty Ltd  
Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA  
Australian Distributors  
Importers & Manufacturers  
[www.chromtech.net.au](http://www.chromtech.net.au)

# 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

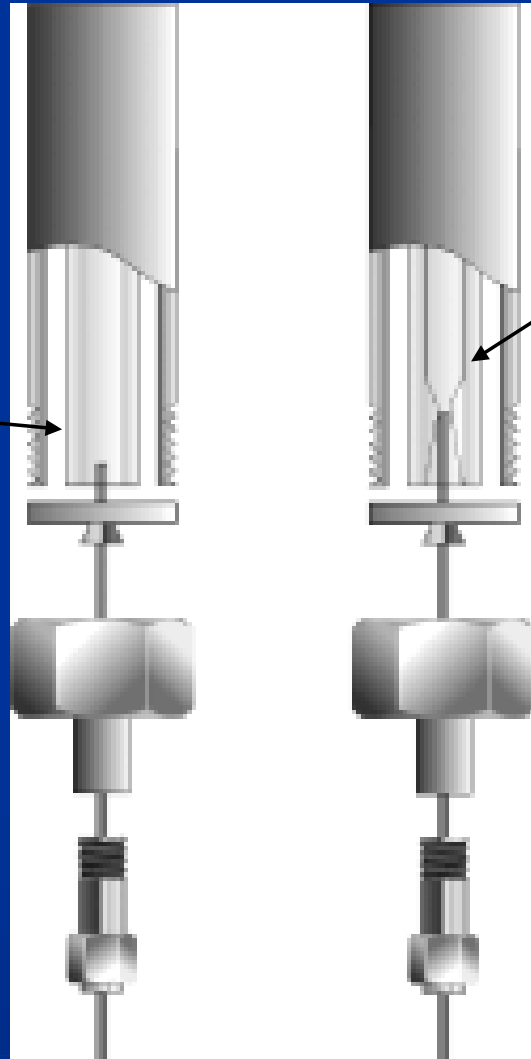
# Drilled Uniliner

- 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

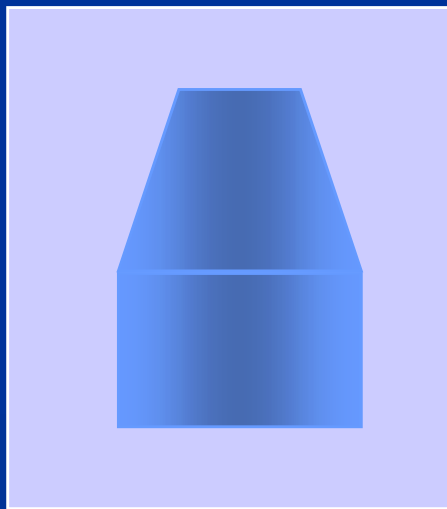
Press-fit  
connection

# Direct Injection Mode

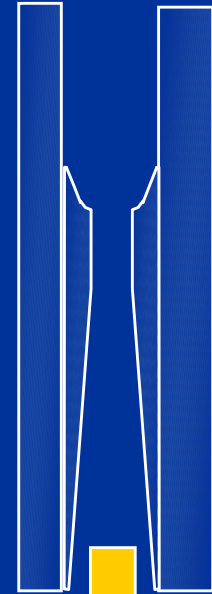
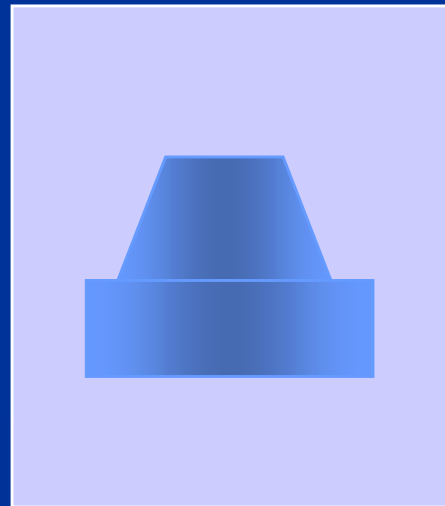
## Making the proper press-fit connection

### 1. Pre-seat or pre-crush new ferrules

New Ferrule



Pre-seated Ferrule



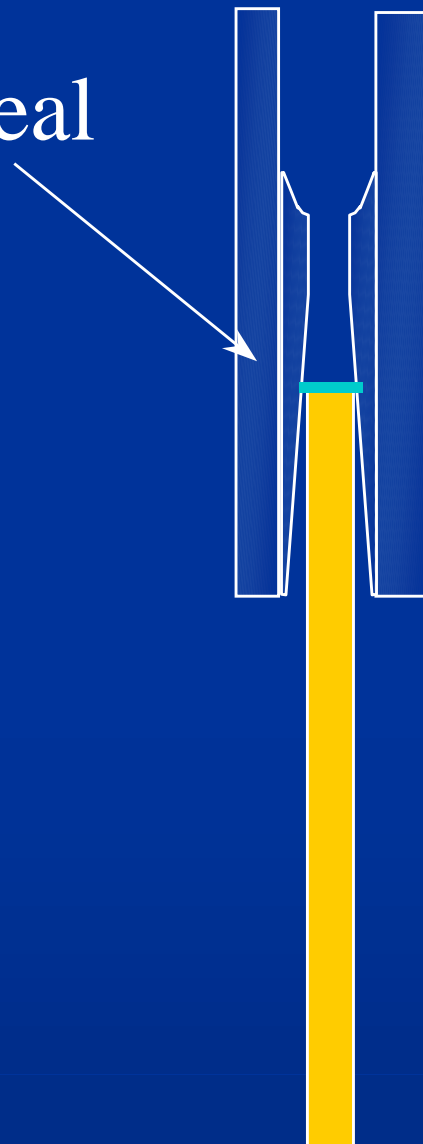


# Direct Injection Mode

## 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.

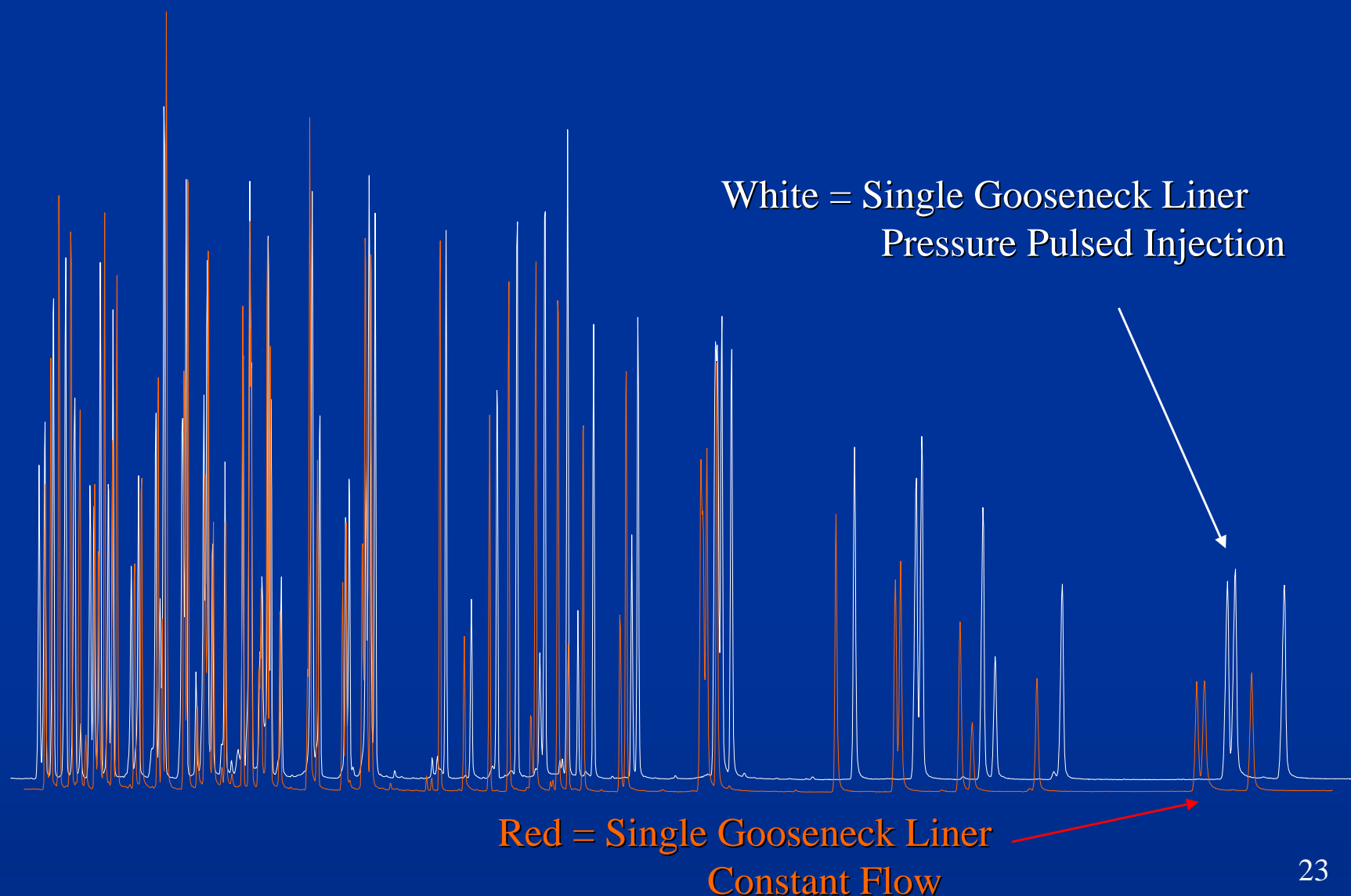
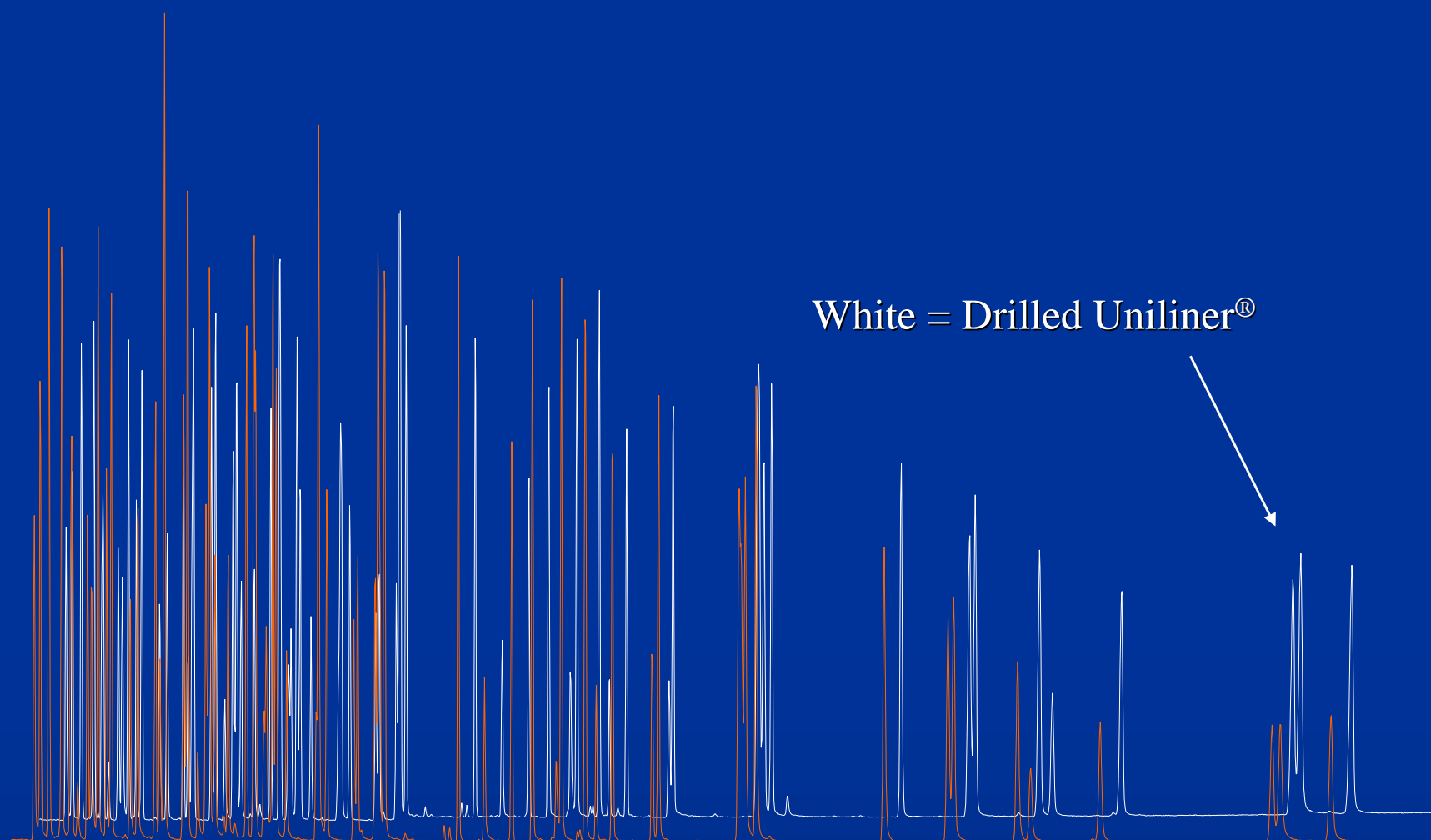


Figure 6 - Injection port discrimination: Comparing the single gooseneck liner to the Drilled Uniliner<sup>®</sup>, both under constant flow conditions.



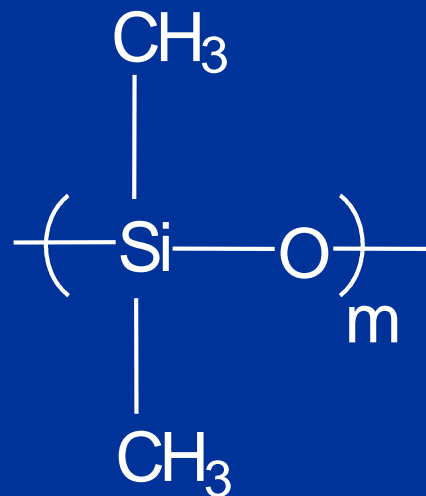
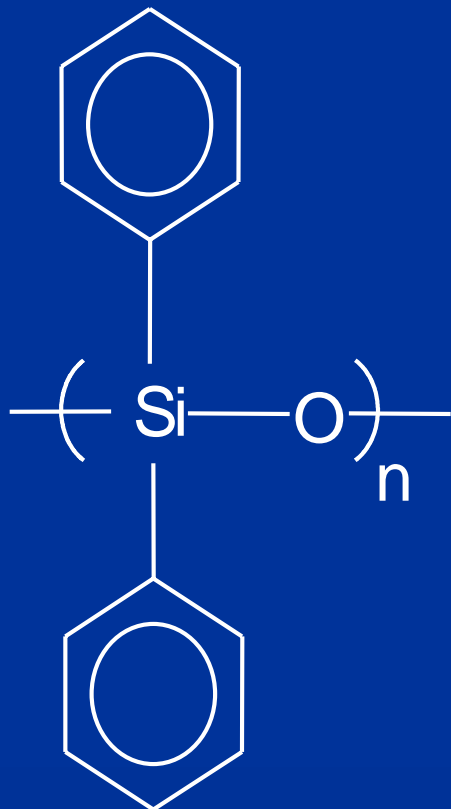
White = Drilled Uniliner<sup>®</sup>

Red = Single Gooseneck Liner

# 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

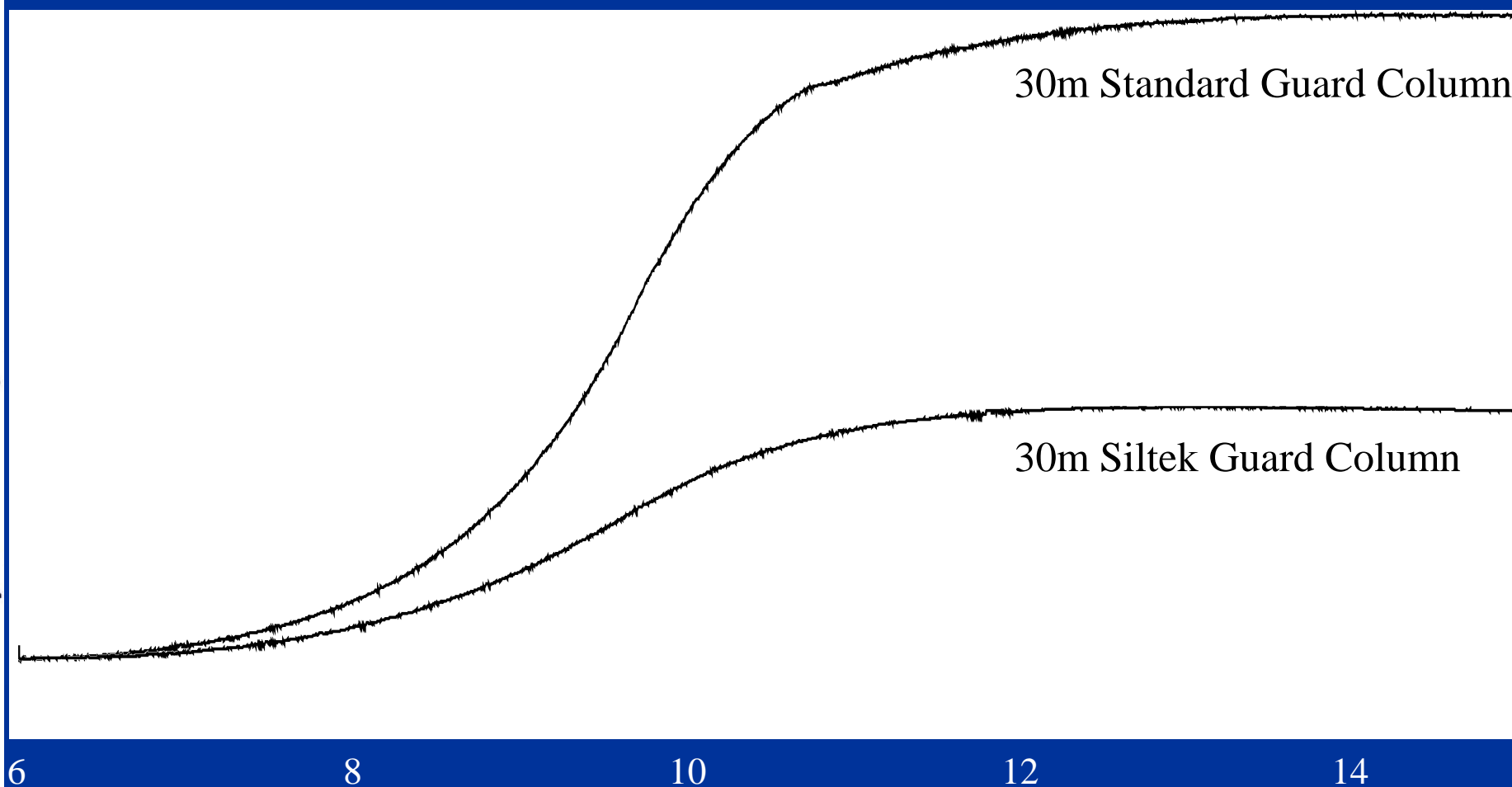
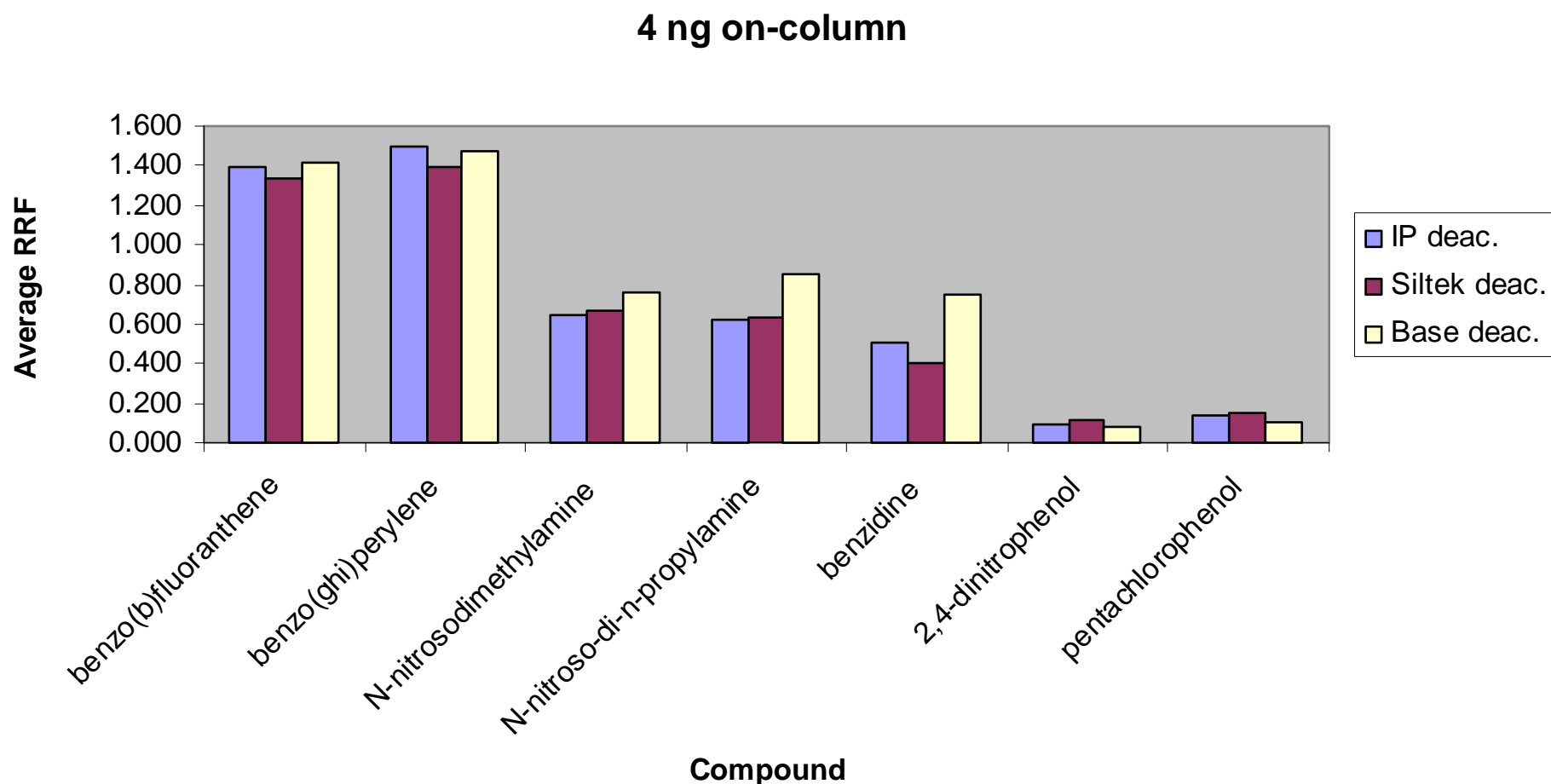


Figure 8



# Liner Deactivation

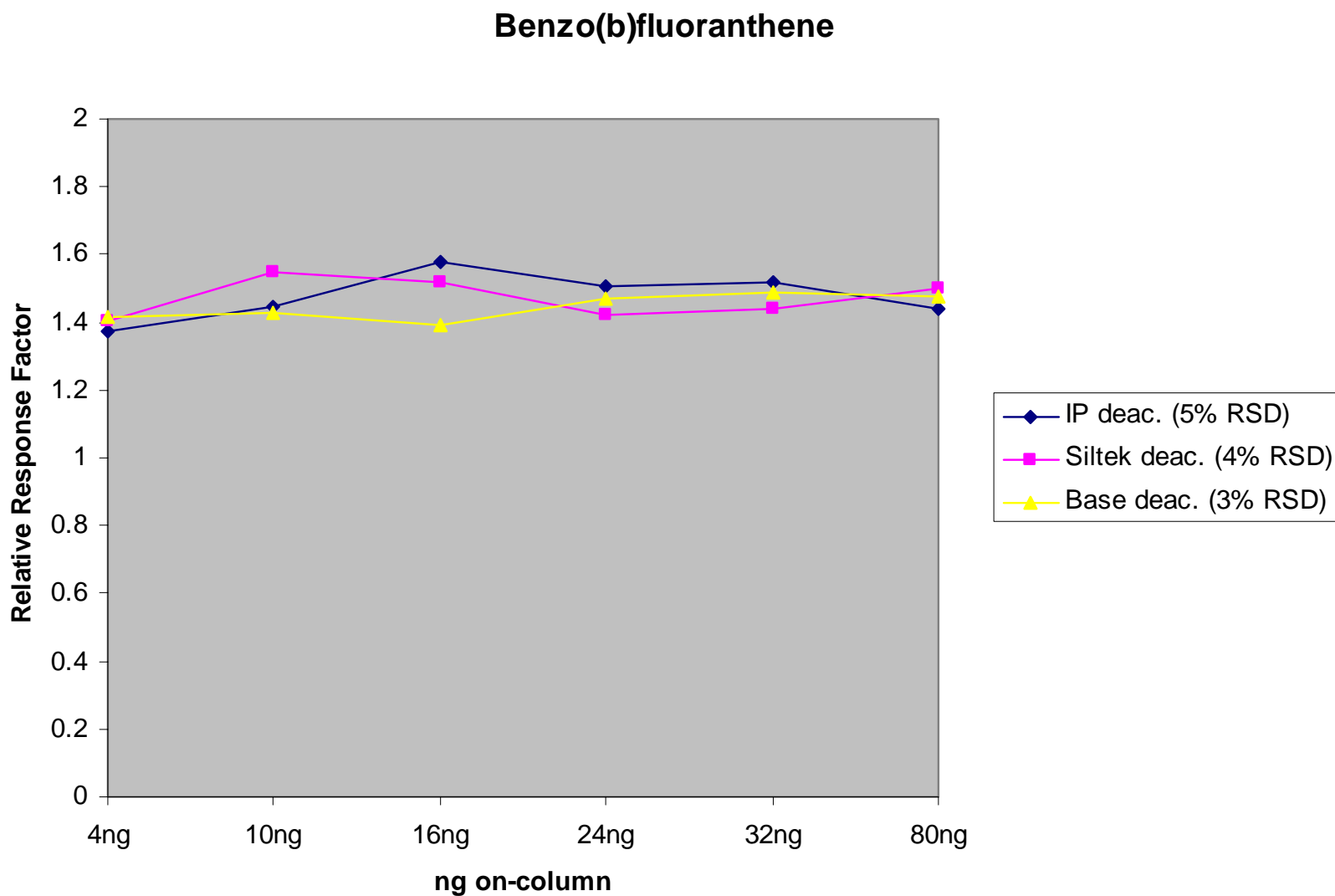
## Average RRF from 4ppm Standards



# Affects of Deactivation on Linearity

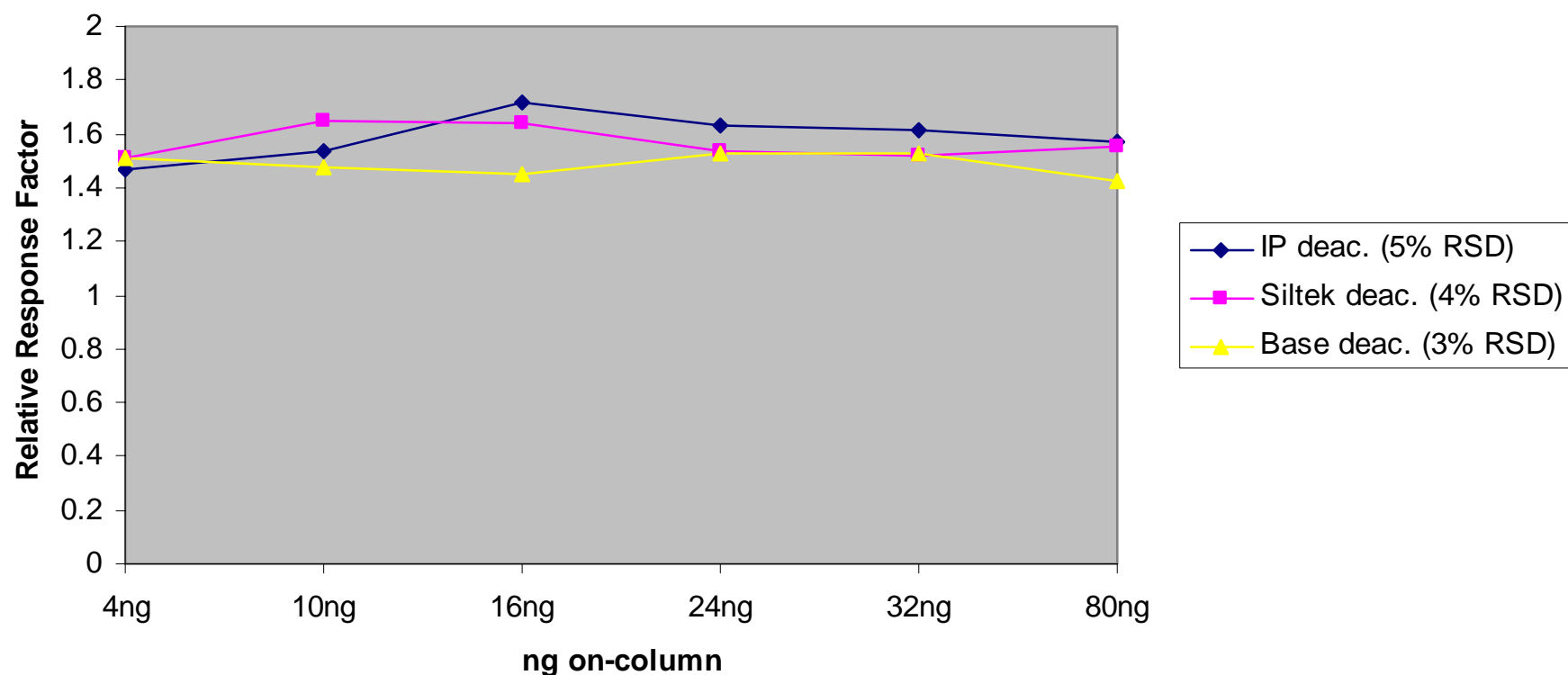
- Response factors of 4ppm standard gave a good indication of the activity of the liner surfaces.
- What are the affects of deactivation on linearity?

# Affects of Deactivation on Linearity

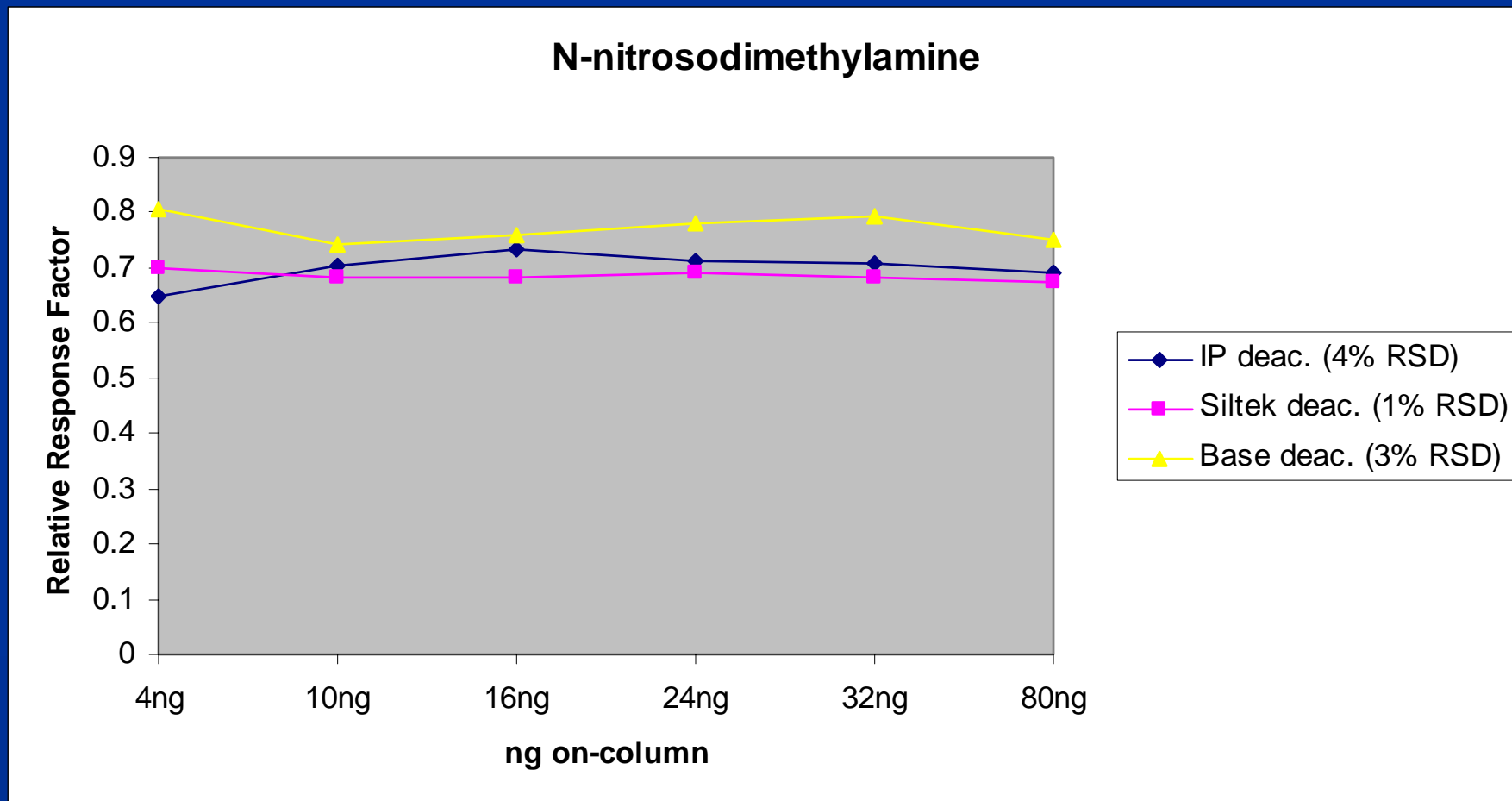


# Affects of Deactivation on Linearity

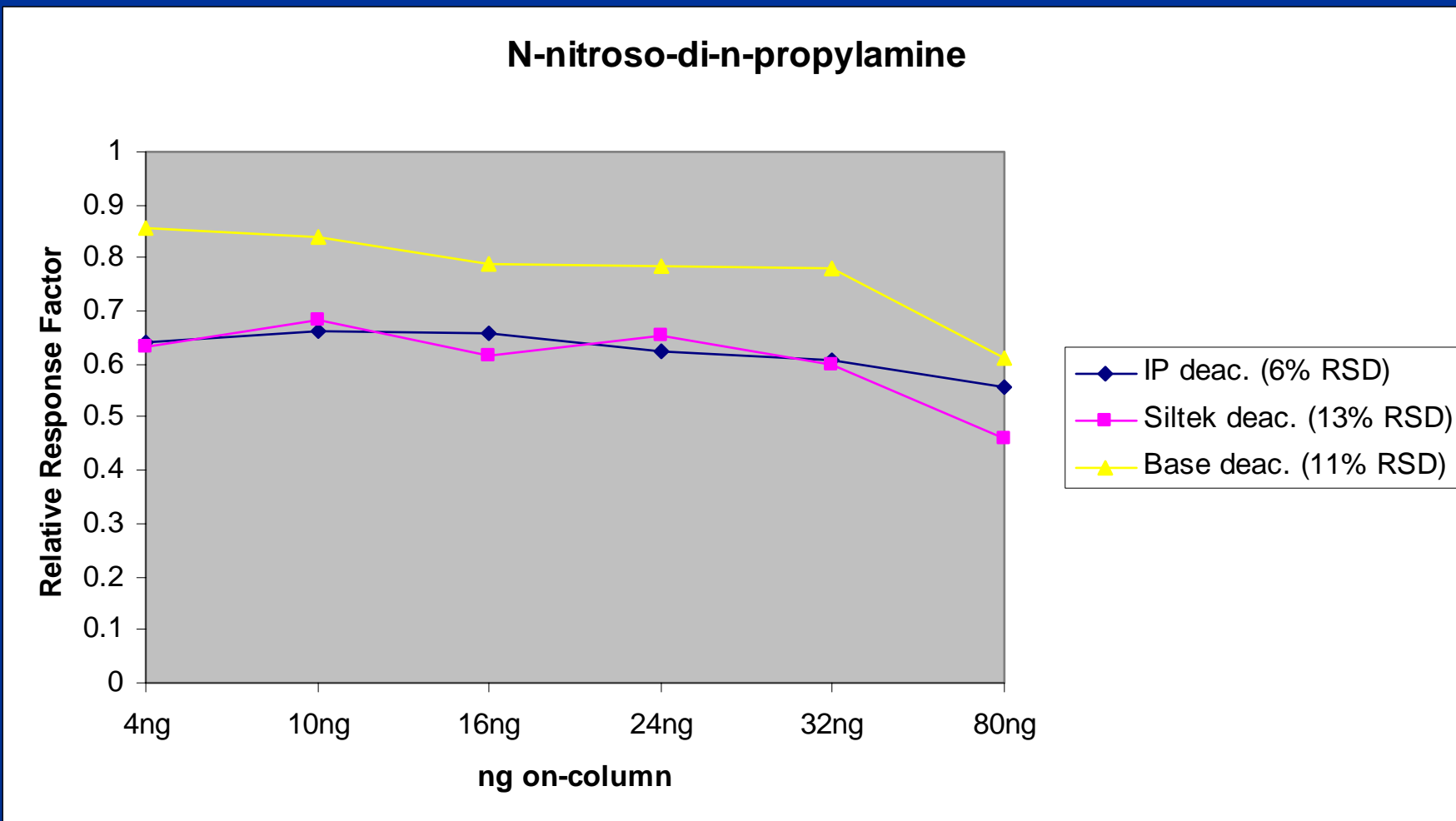
Benzo(ghi)perylene



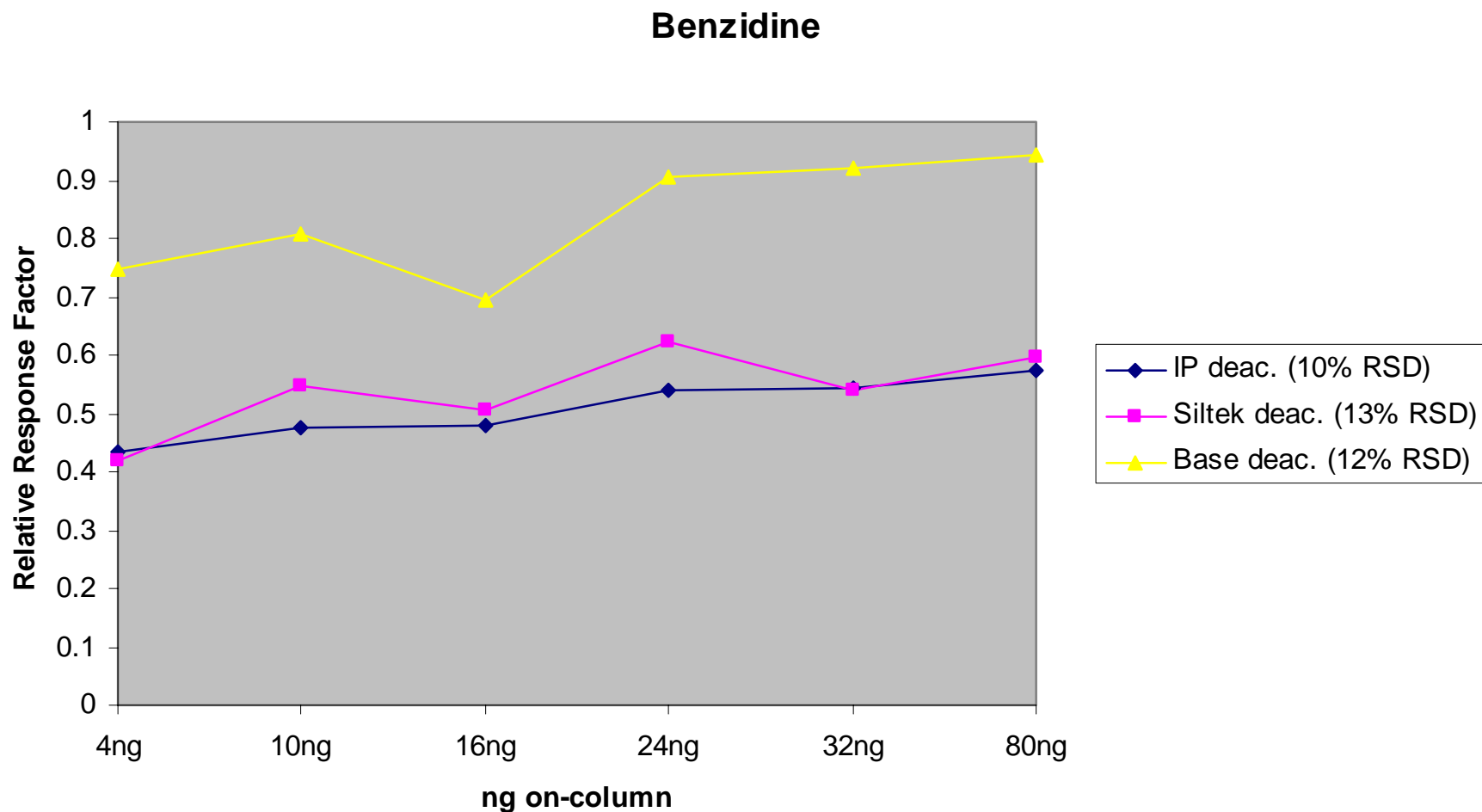
# Affects of Deactivation on Linearity



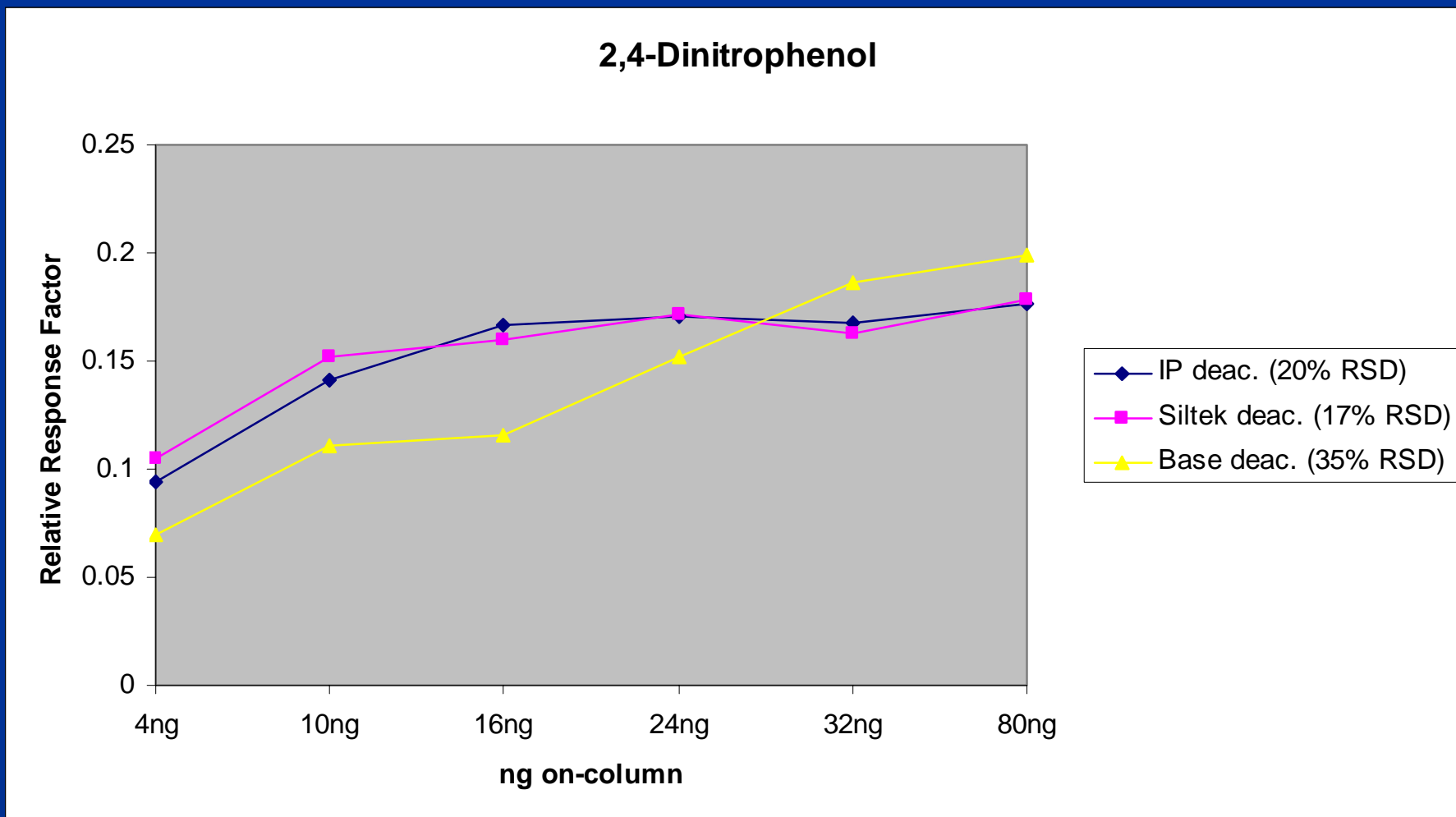
# Affects of Deactivation on Linearity



# Affects of Deactivation on Linearity

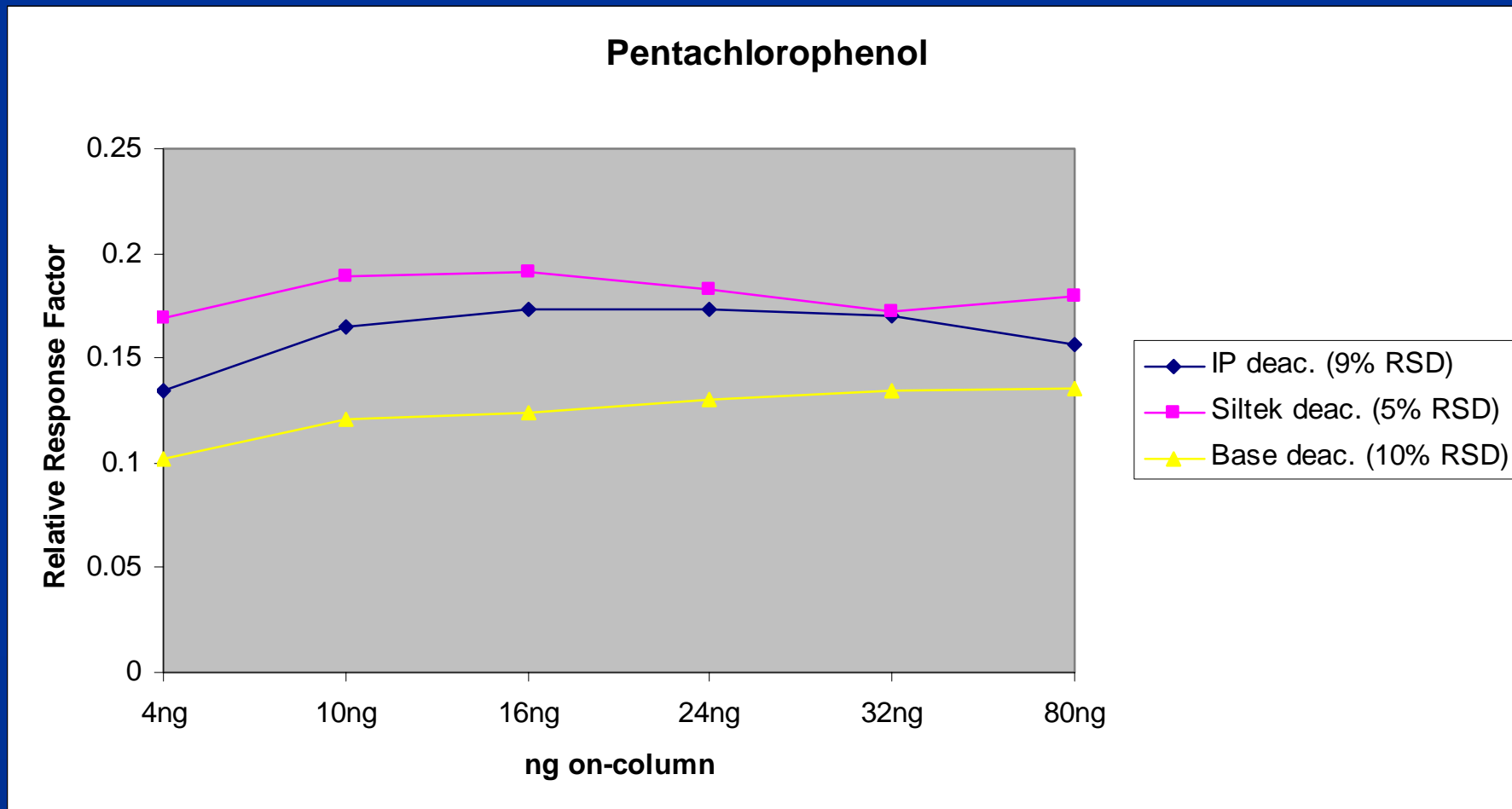


# Affects of Deactivation on Linearity

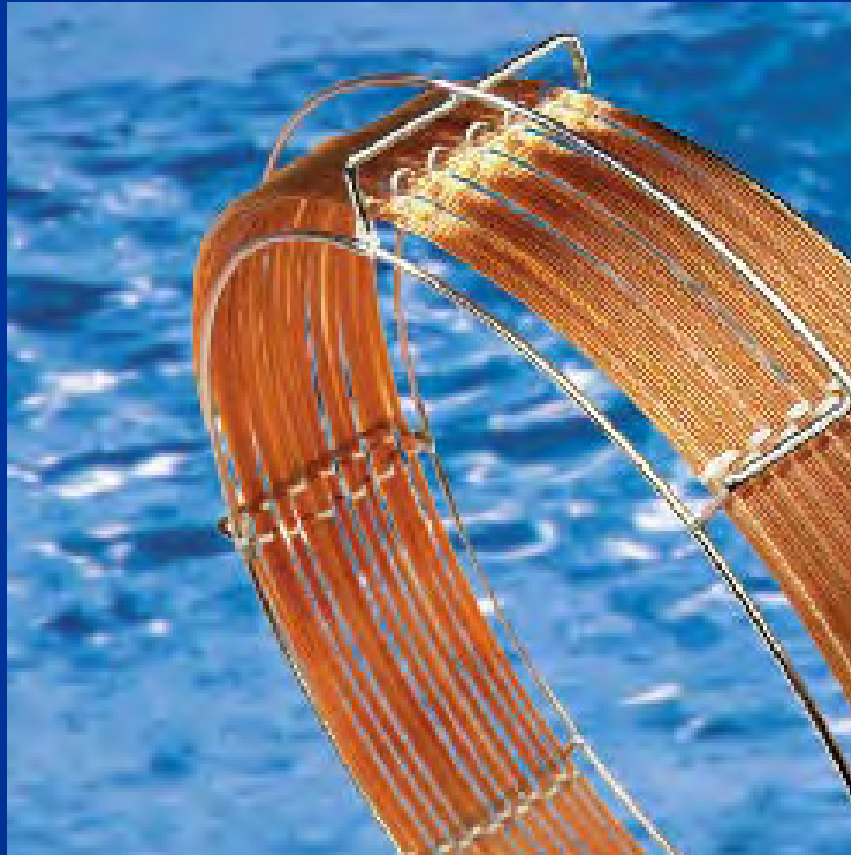




# Affects of Deactivation on Linearity



# 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

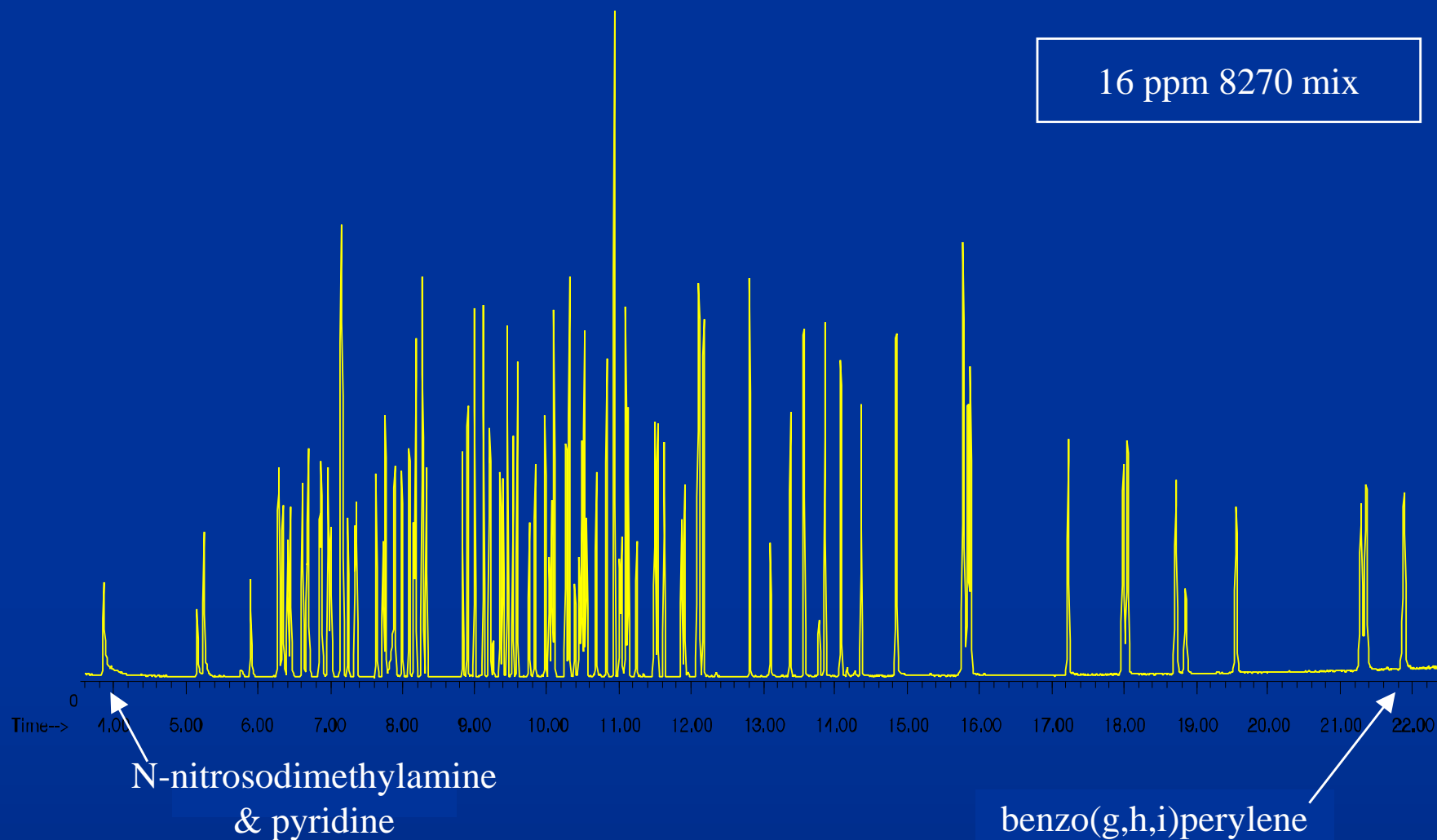
# Determined Run Conditions

- 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-5Si1 MS

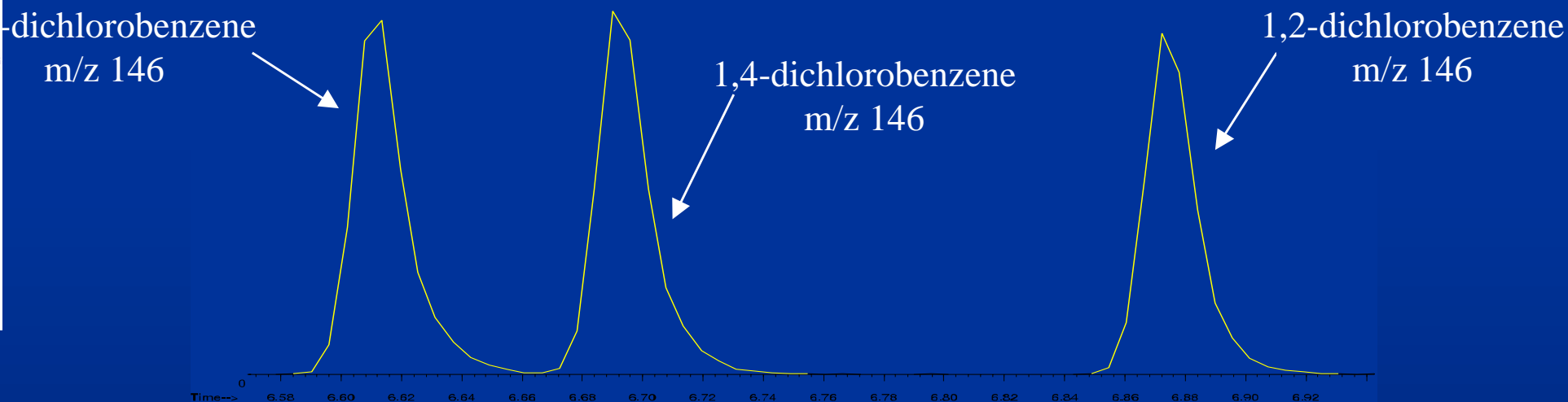
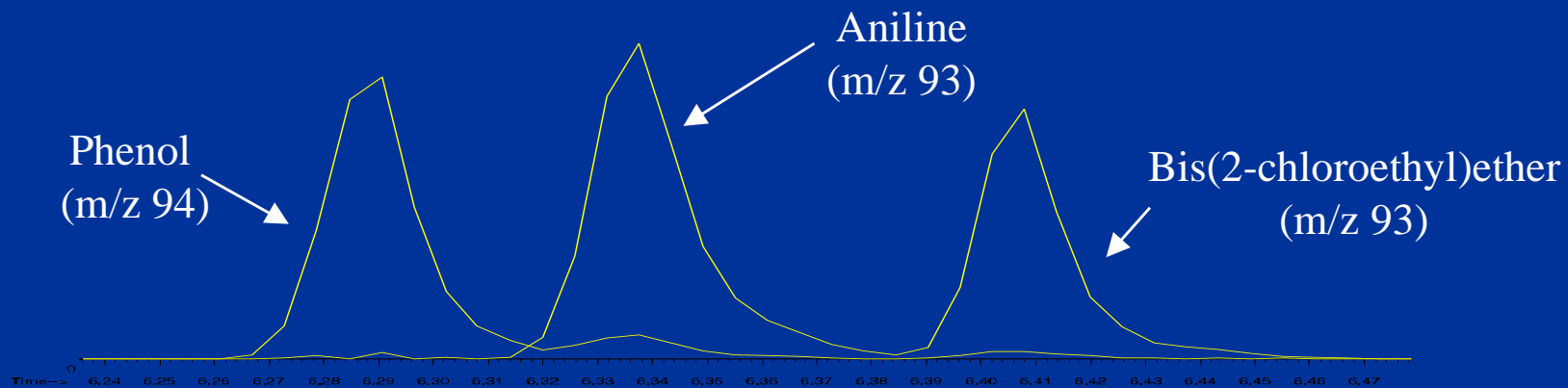
(30m x 0.25mm ID, 0.25um film)

16 ppm 8270 mix



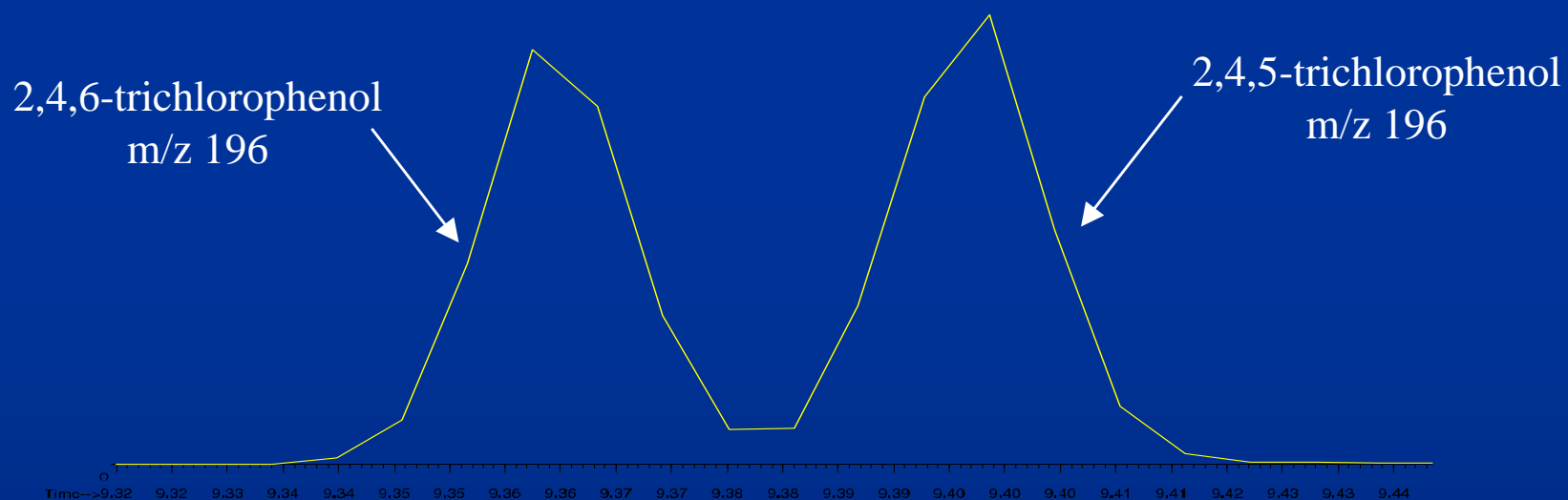
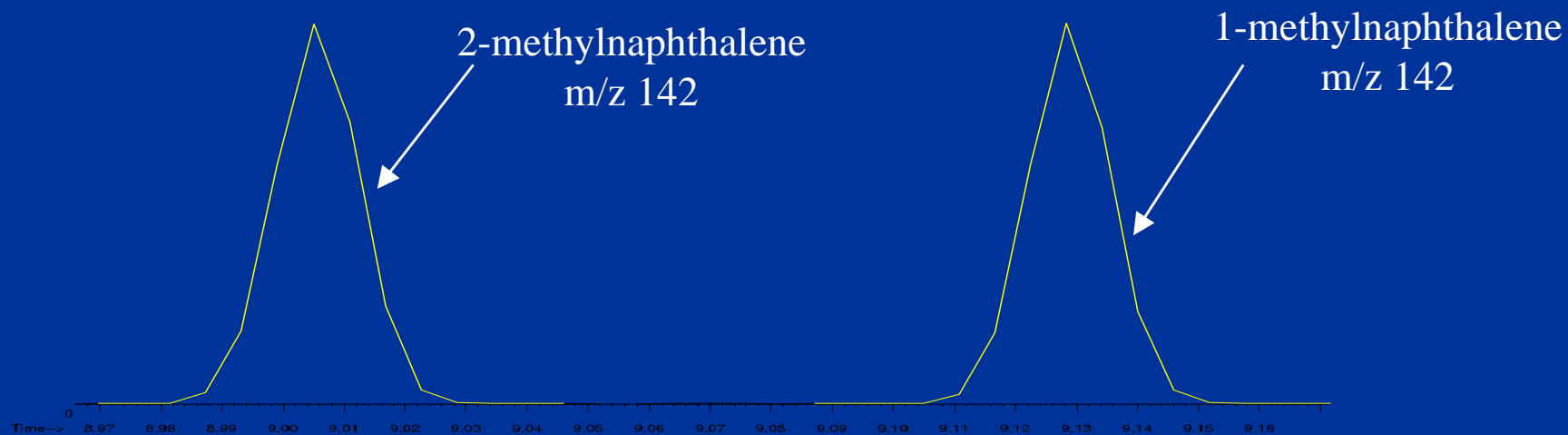
# Separation of Critical Pairs

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



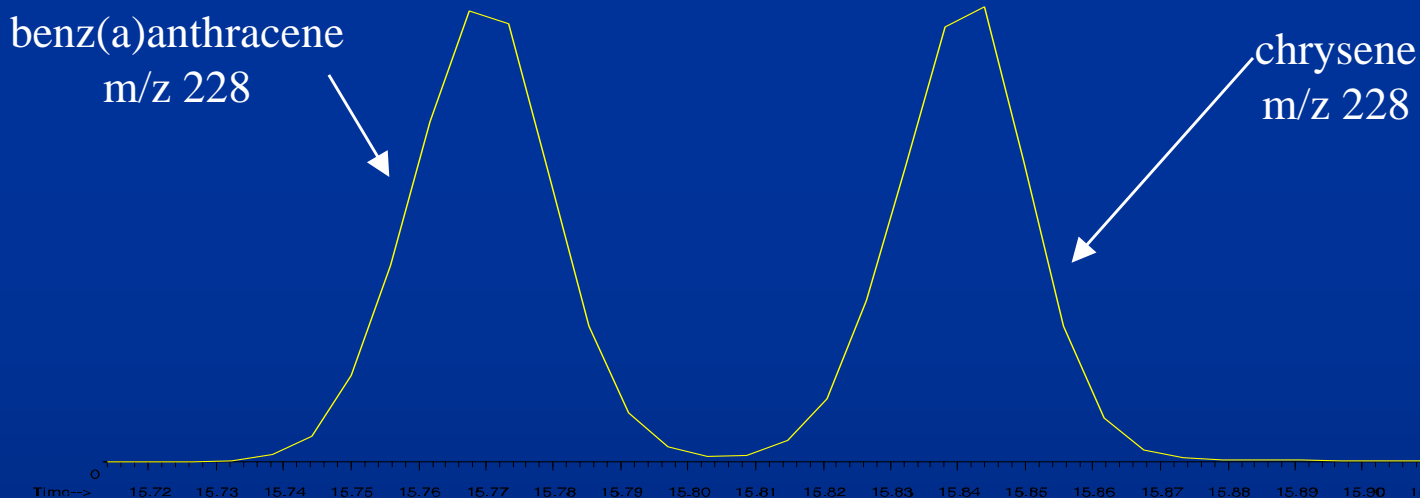
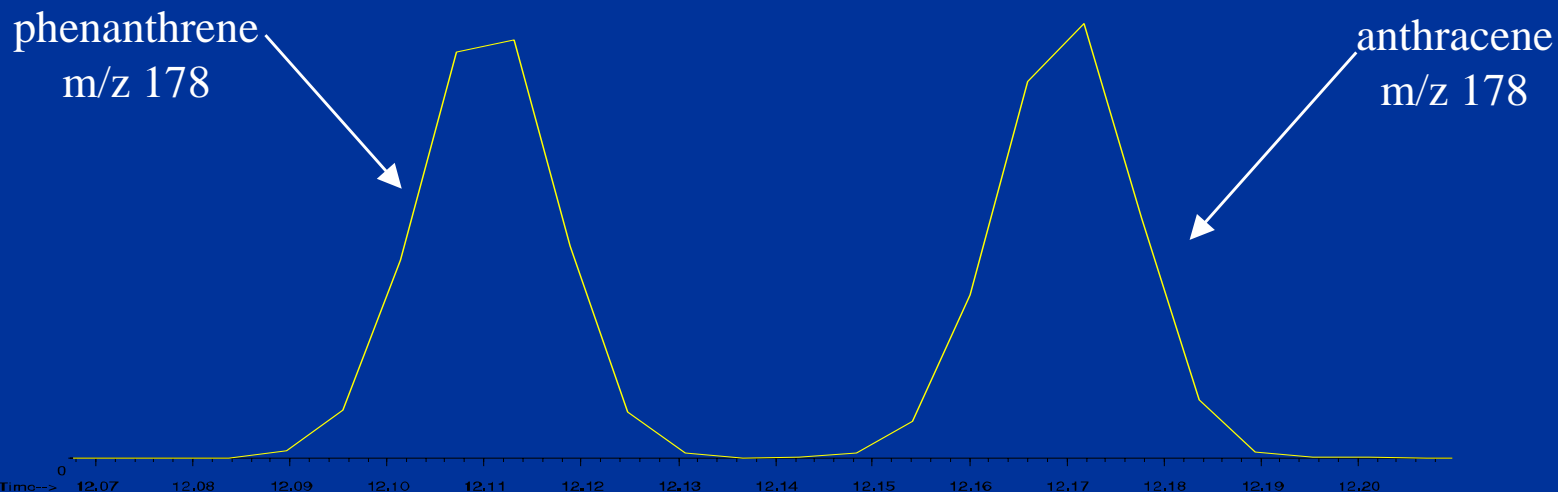
# Separation of Critical Pairs

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



# Separation of Critical Pairs

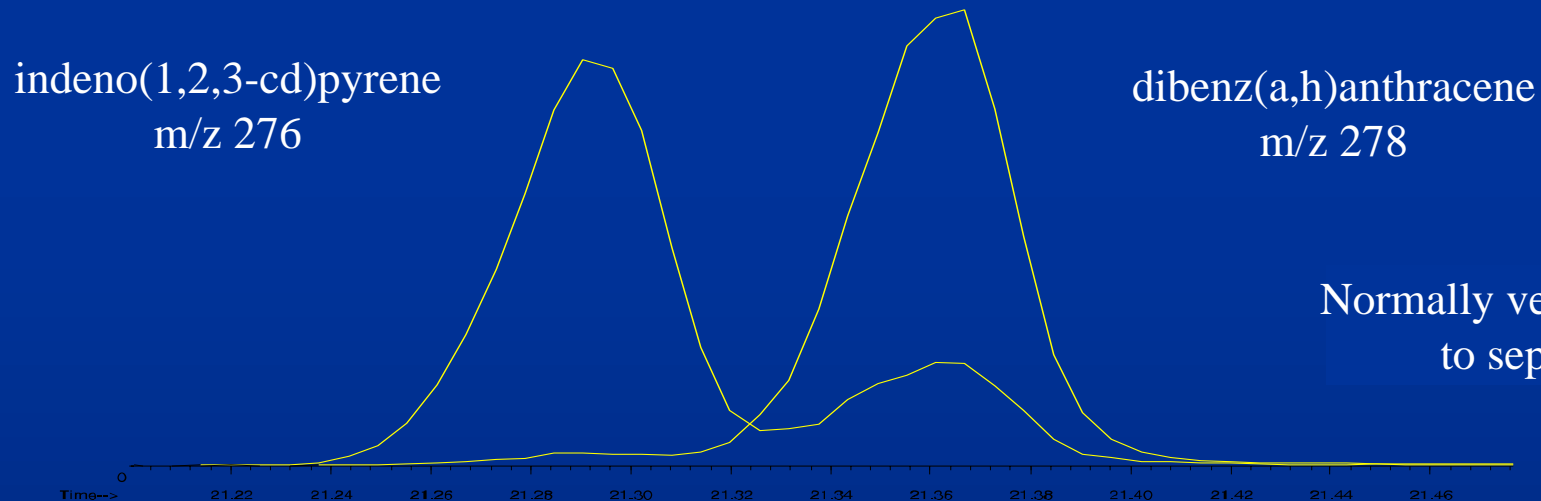
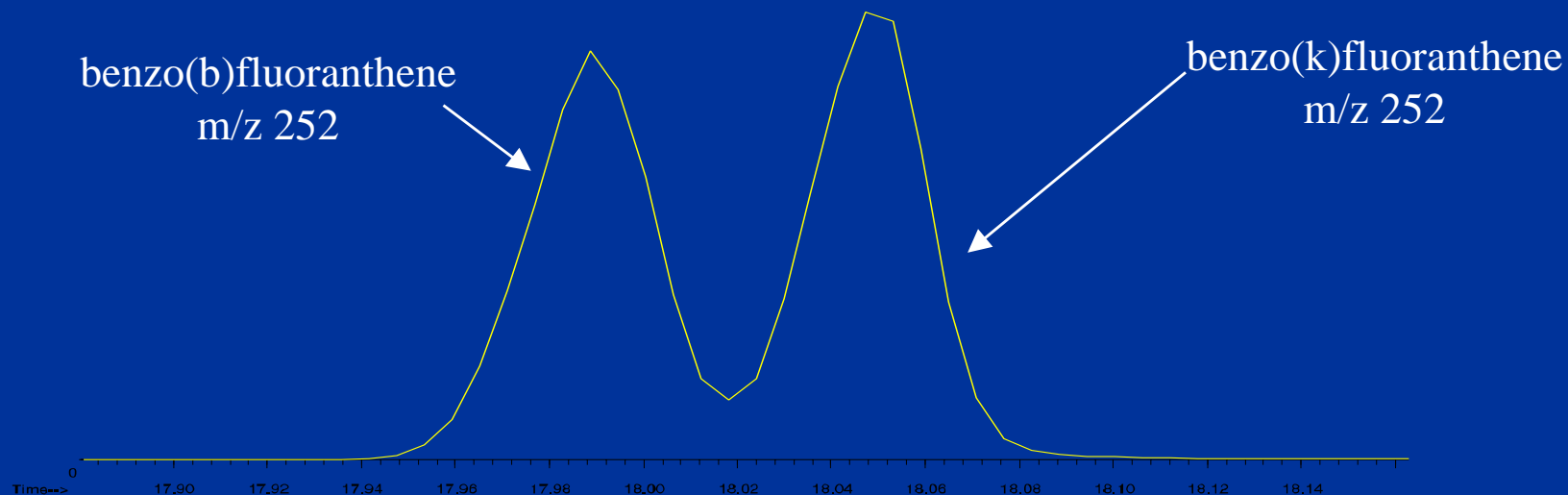
## Rtx-5Sil MS (30m x 0.25mm, 0.25um film)





# Separation of Critical Pairs

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



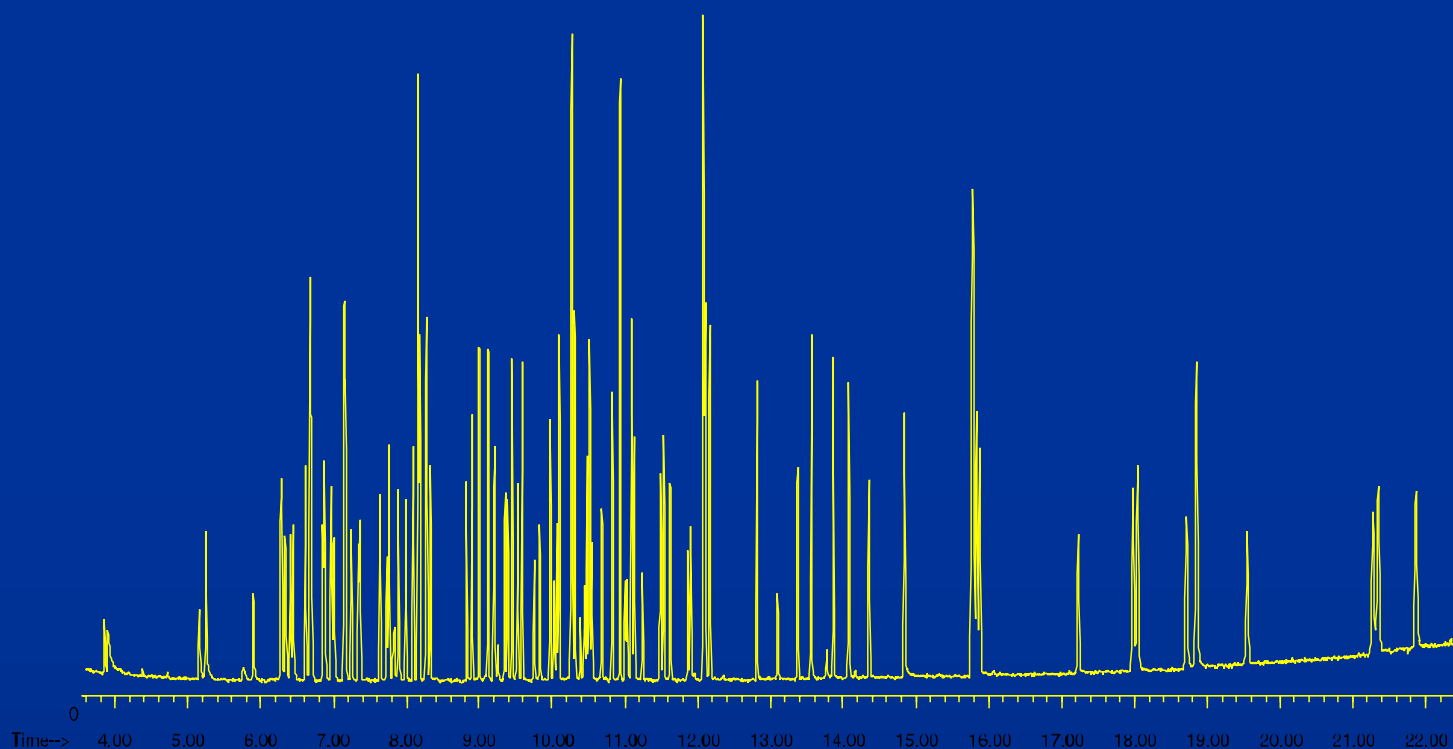
Normally very difficult  
to separate

# 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)<sub>47</sub>

# Linearity from Calibration Sequence

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

# High-Speed Gas Chromatographic Analysis of Chlorinated Pesticides Using a Tandem Column Ensemble and Stop-Flow Modulation

Frank L. Dorman, Rebecca Wittrig, Chris M. English, Gary B. Stidsen, Tincuta Veriotti, and Richard D. Sacks

# Stop-Flow GC: Improved Resolution with Fast Analysis Times

- I. The Stop-Flow GC System
- II. Advantages of Stop-Flow GC
- III. Applications
  - A. Chlorinated Pesticides
  - B. Residual Solvents

# Desires of GC Analysts

- Higher Sample Throughput
  - Lowers cost/sample
  - Increases sample capacity
  - Fewer instruments to accomplish same workload
- Better Resolution
  - Can allow for shorter run times
  - Improves quantitation
  - Can allow for analysis of very complex matrices



# Methods to Improve Speed and/or Resolution

## Tuning Stationary Phase Selectivity

- Design column to achieve specific separation
- Users can send retention data for optimization

## Physical Parameter Optimization

- Pro ezGC™ Software allows user optimization

## Hardware Modification

- GC Racer allows increased temperature ramp rates with (common) existing instrumentation

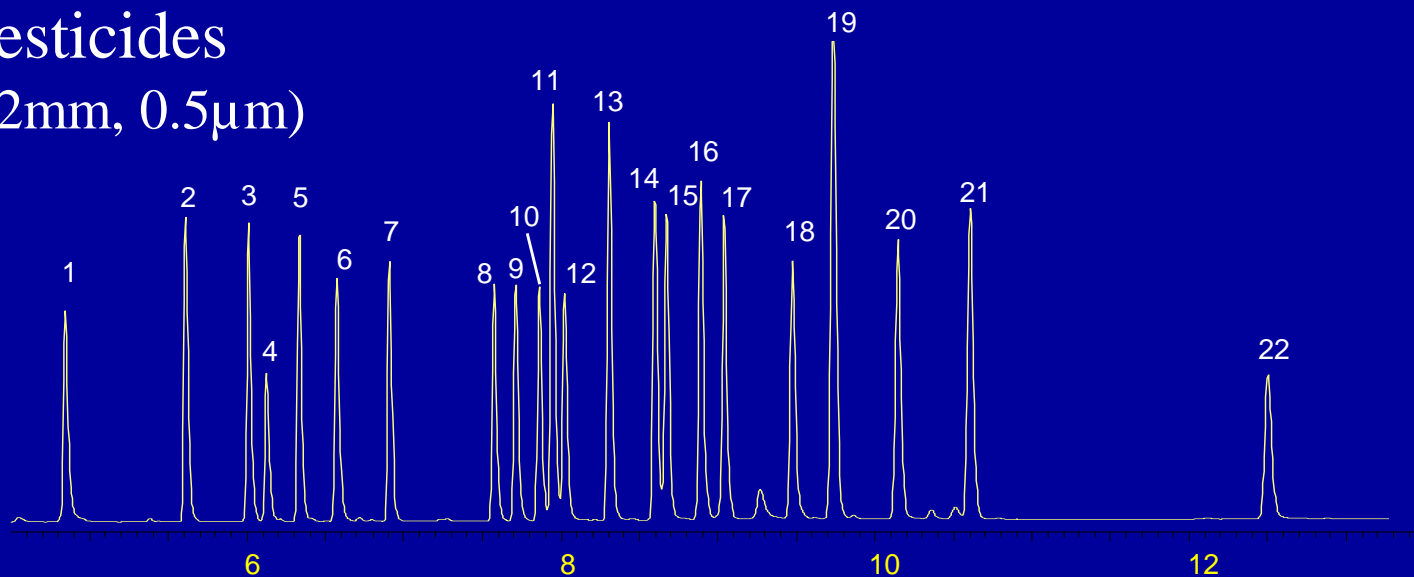
# Methods to Improve Speed and/or Resolution

- Fast GC/Flash GC
  - Short, narrow i.d. columns
  - Ballistic heating (resistive, microwave)
- Multicolumn GC
  - Bertsch, Guichon, Giddings
- Comprehensive 2D-GC
  - Begun by John Phillips – Southern Illinois Univ.
- Stop-Flow GC
  - Richard Sacks – Univ. of Michigan

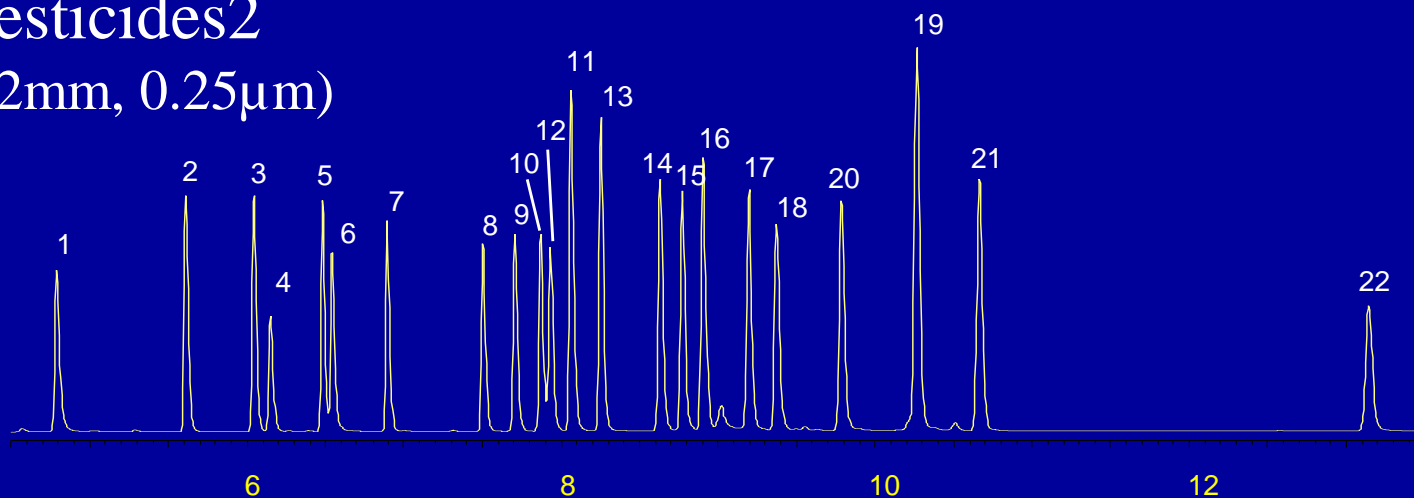
# Chlorinated Pesticides

## Fast Runs

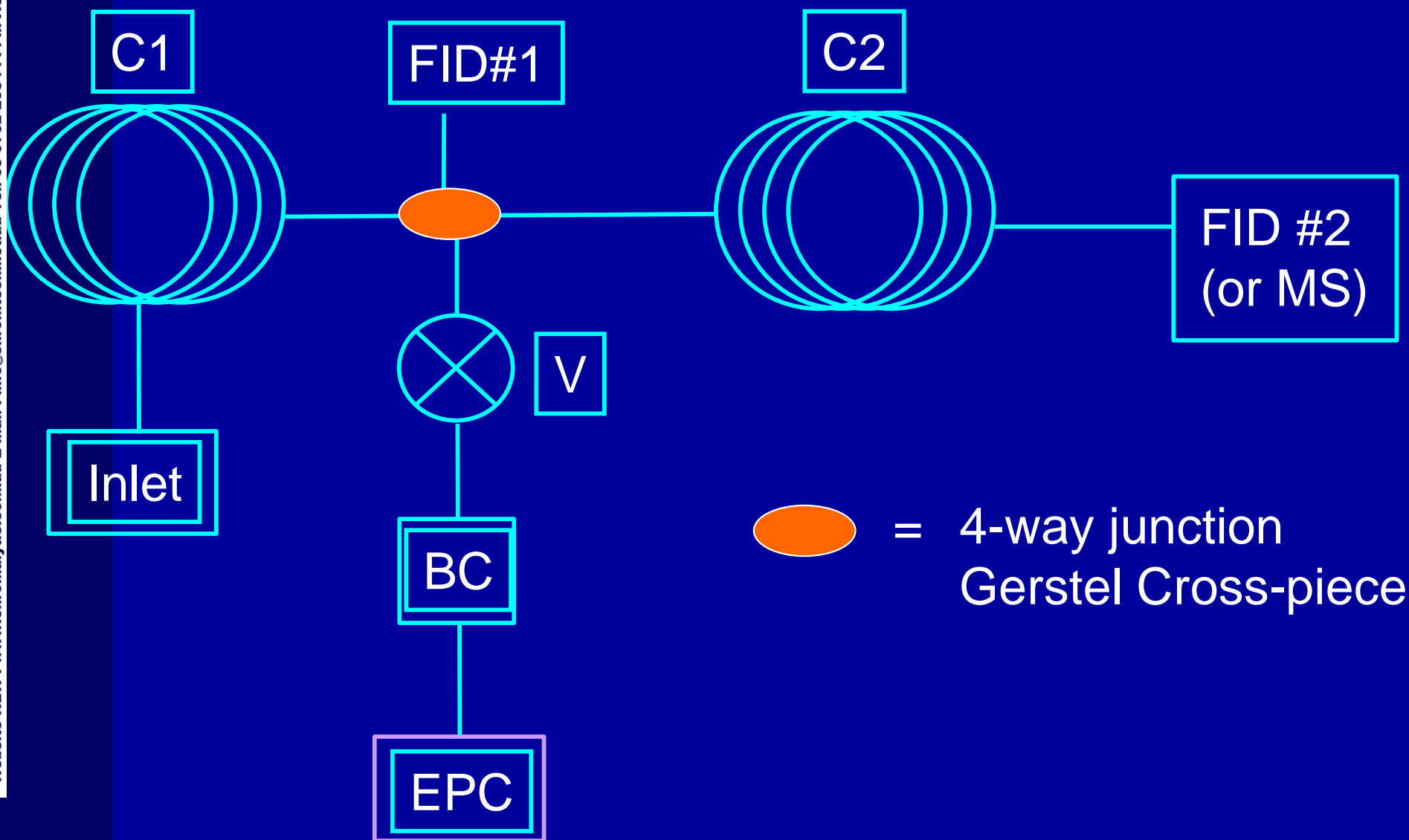
Rtx-CLPesticides  
(30m x 0.32mm, 0.5 $\mu$ m)



Rtx-CLPesticides2  
(30m x 0.32mm, 0.25 $\mu$ m)

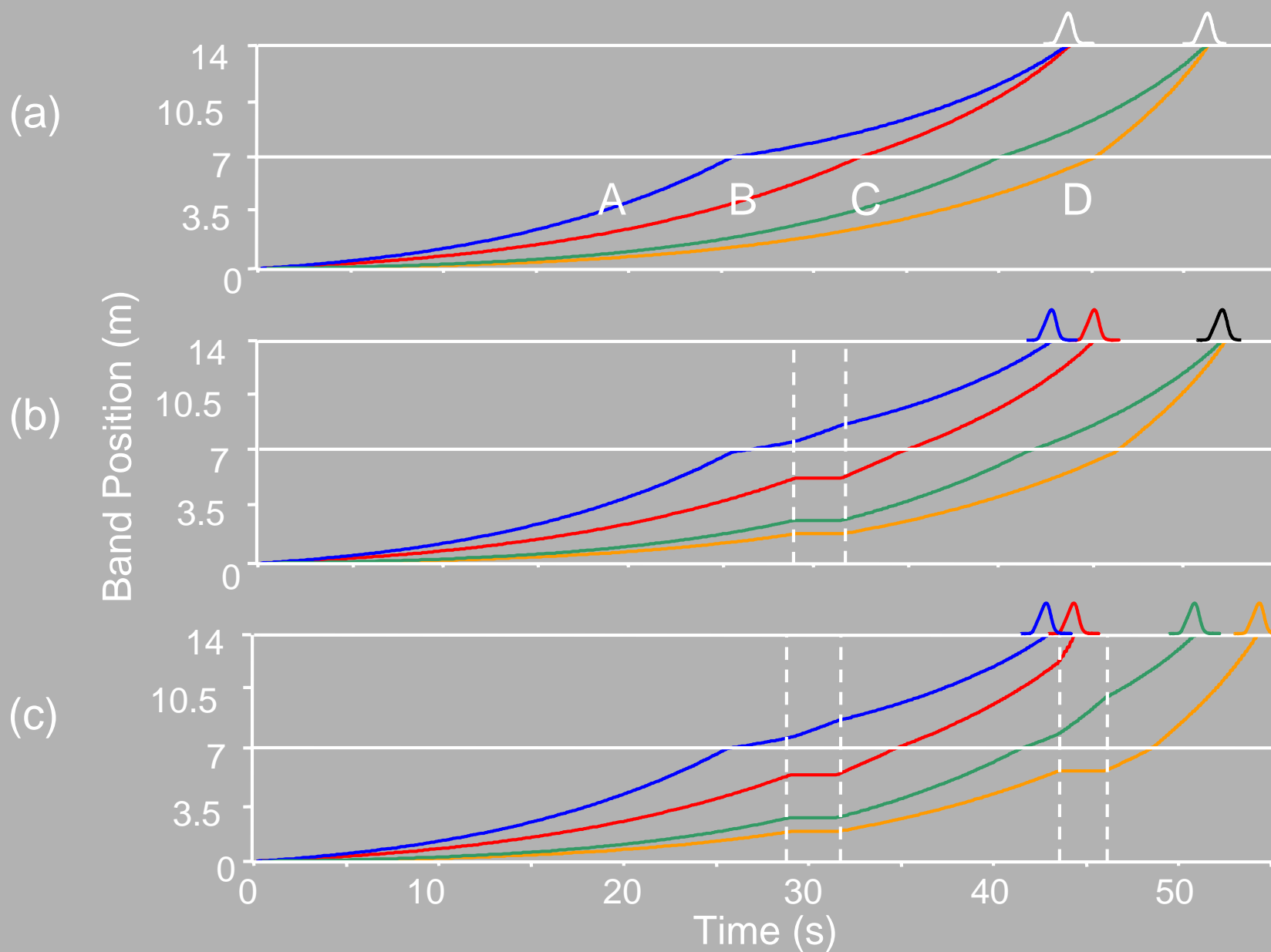


# Stop Flow GC System: Sacks, et. al.\*



\*Richard Sacks, University of Michigan

# Stop Flow System: Pressure Tunable Selectivity



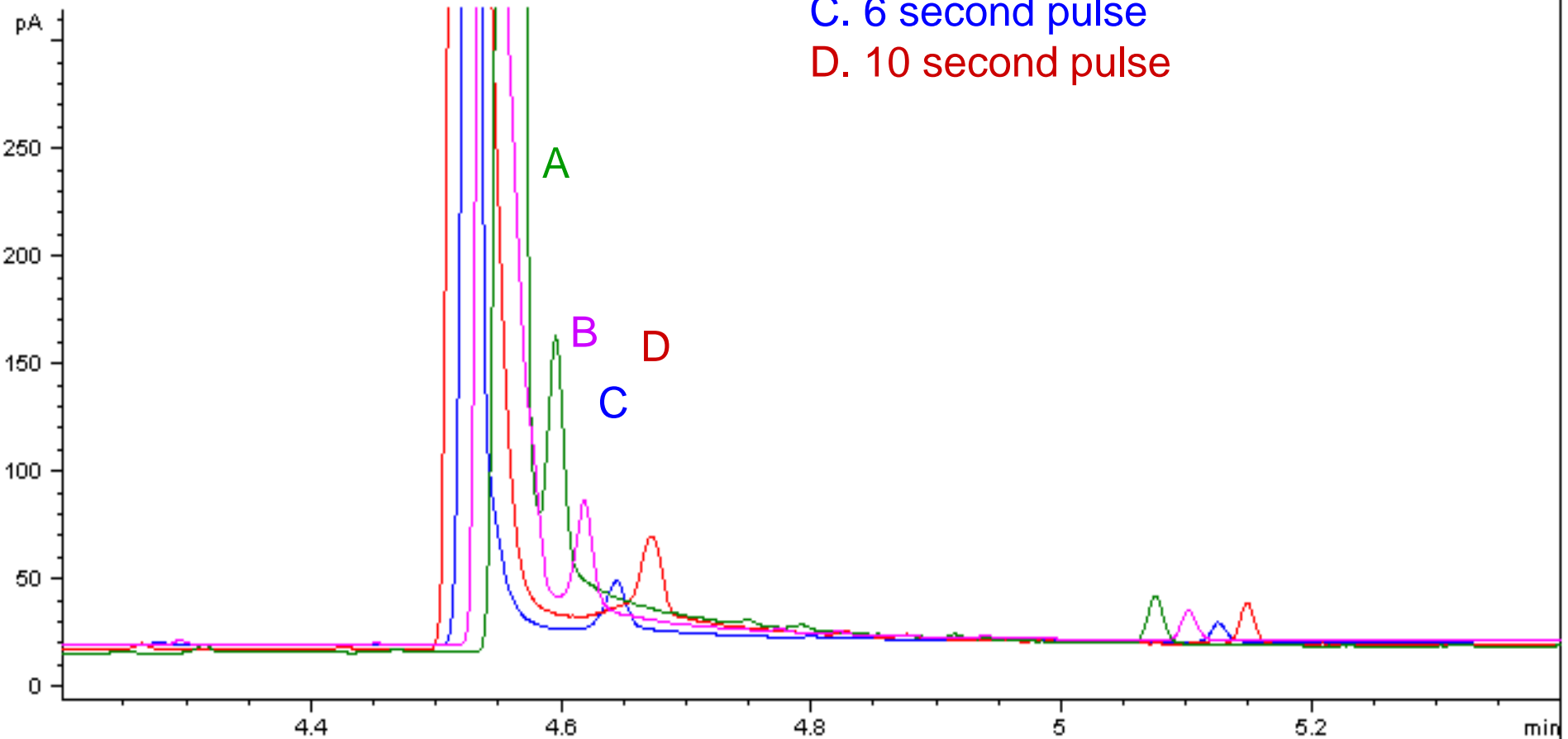
# Advantages of Stop-Flow GC

- Minimal Hardware Modifications
- Dual-Column System
  - Standard dimension GC columns
- Flexibility
  - Ability to “tune” the selectivity of a separation
- Controlled by GC's Current Software

# Separation of Limonene and Eucalyptol

## Increasing Stop-flow Pulse Lengths

- A. No stop-flow pulse
- B. 2 second pulse
- C. 6 second pulse
- D. 10 second pulse



# Application: Chlorinated Pesticides

- Environmental testing industry
  - EPA methods 8081, 508, and 608
  - High volume tests
- Importance of rapid, accurate assays
  - Application-specific stationary phases
  - Best run times around 13 minutes



# Chlorinated Pesticides

1	Aldrin	11	Dieldrin
2	$\alpha$ -BHC	12	Endosulfan I
3	$\beta$ -BHC	13	Endosulfan II
4	$\delta$ -BHC	14	Endosulfan sulfate
5	$\gamma$ -BHC (lindane)	15	Endrin
6	$\alpha$ -Chlordane	16	Endrin aldehyde
7	$\gamma$ -Chlordane	17	Endrin ketone
8	4,4'-DDD	18	Heptachlor
9	4,4'-DDE	19	Heptachlor epoxide
10	4,4'-DDT	20	Methoxychlor

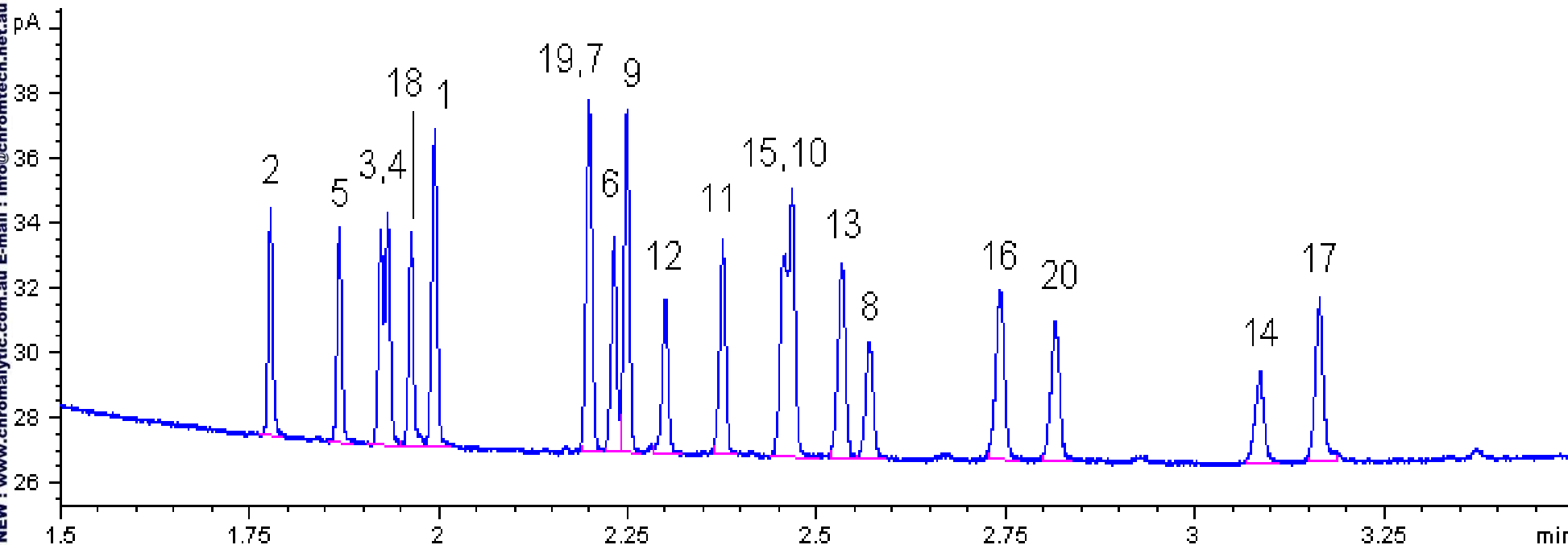
# Chlorinated Pesticides

## After column #1 (Rtx-200)

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# Chlorinated Pesticides

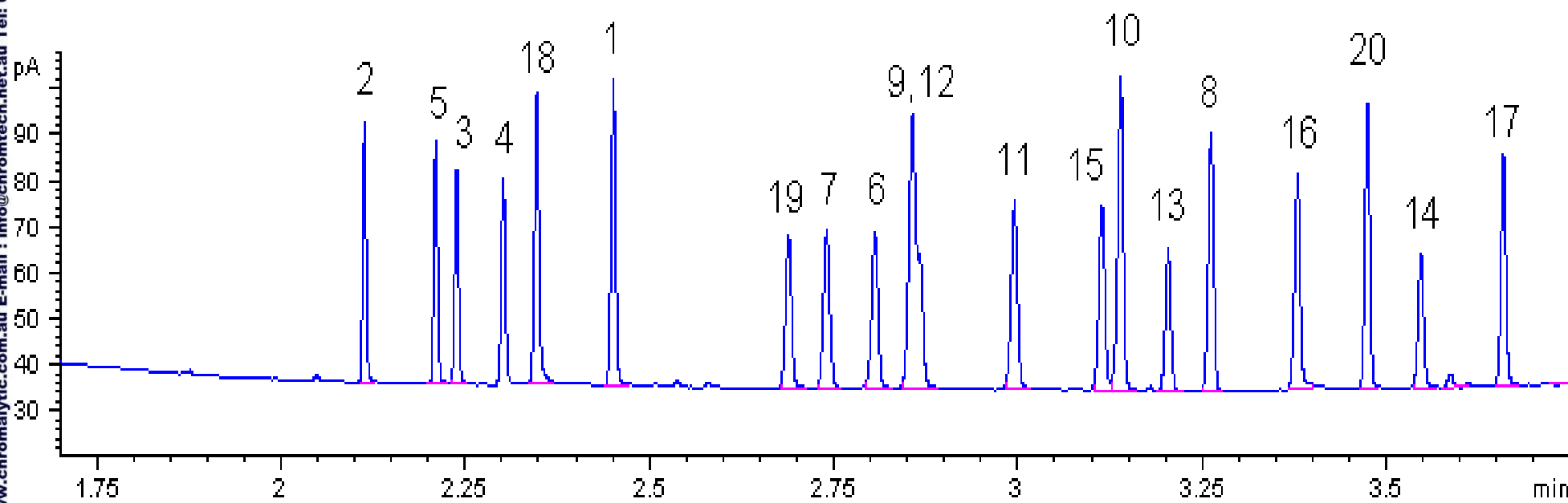
## After column #2 (Rtx-5)

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## Chlorinated Pesticides: Run Conditions

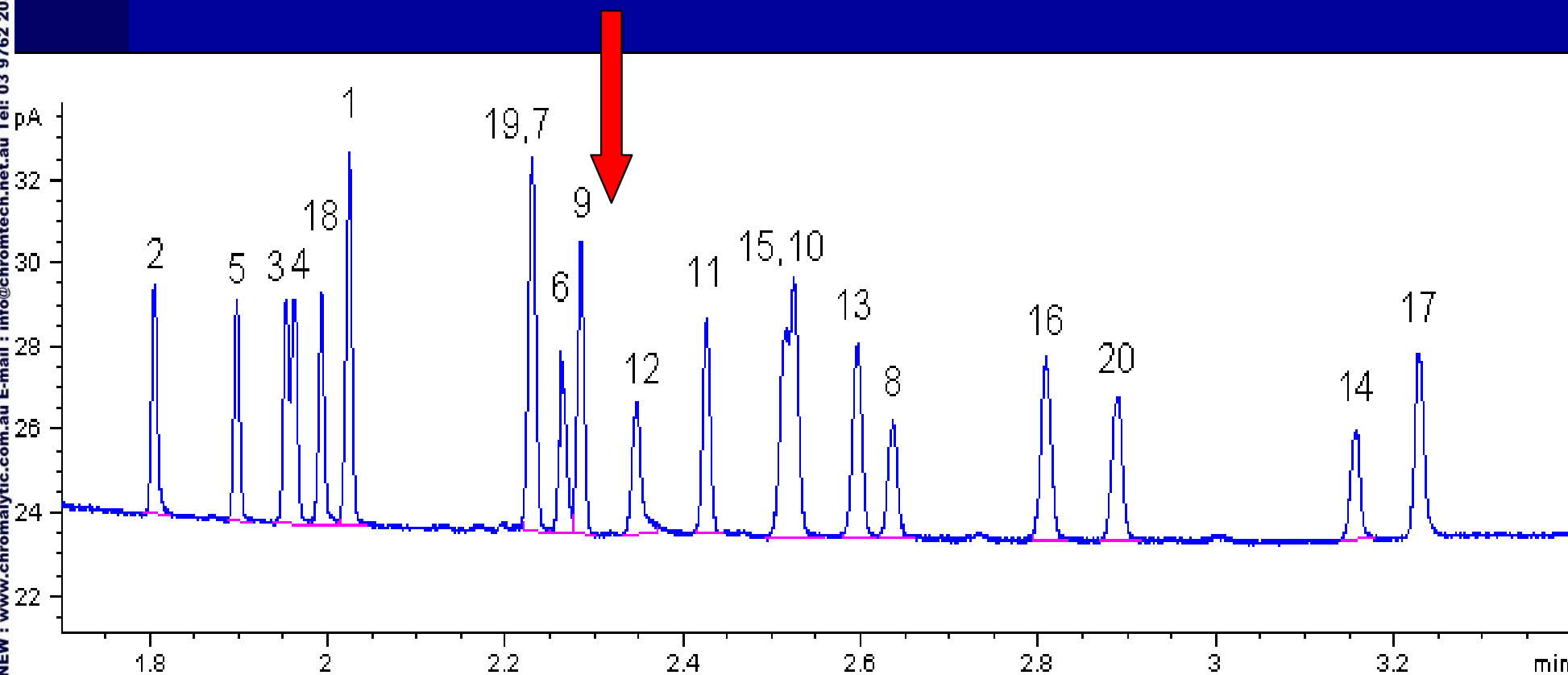
	<b><i>Fast Procedure</i></b>
Analytical Columns	Rtx-200 10m x 0.18mm, 0.2µm Rtx-5 10m x 0.18mm, 0.18µm
Oven Program	60°C (0.4 min. hold) to 220°C at 100°C/min., to 235°C at 15°C/min., to 300°C at 120°C/min., 0.5 min. hold
Inlet Pressure	45 psig
Injector	300°C
Injection	0.2-0.5 µL splitless 0.25min hold time
Detectors	Dual FIDs @ 300°C

# Chlorinated Pesticides

Showing location of the stop-flow pulse

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# Chlorinated Pesticides

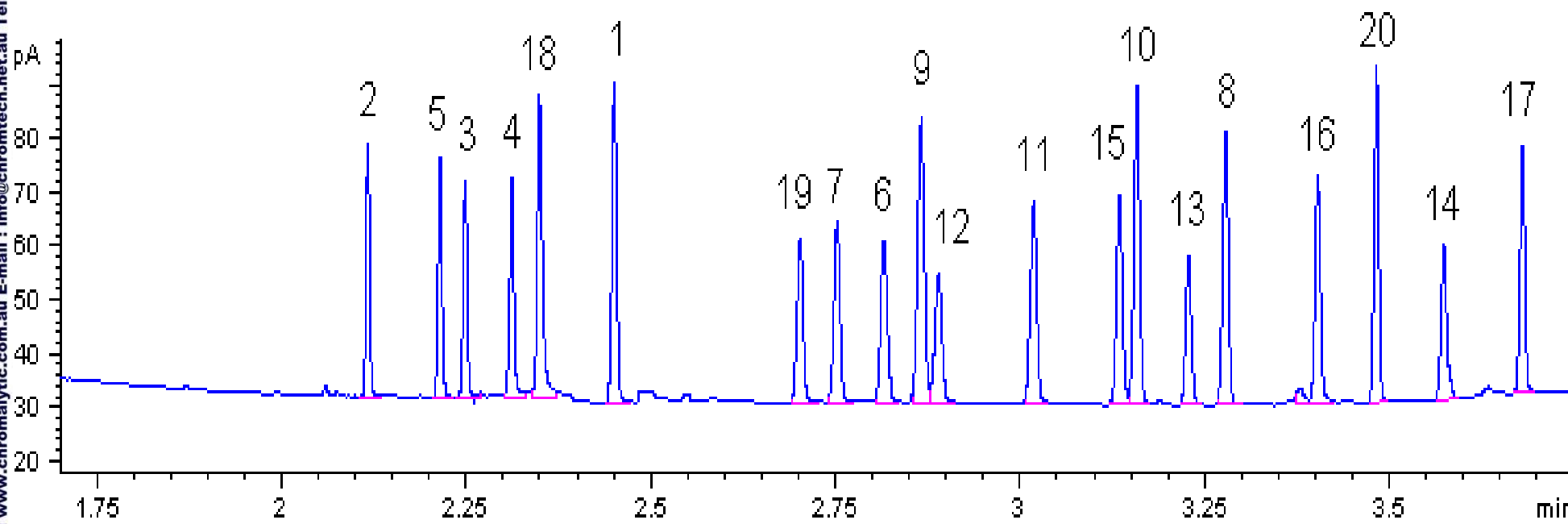
## With 1 stop-flow pulse

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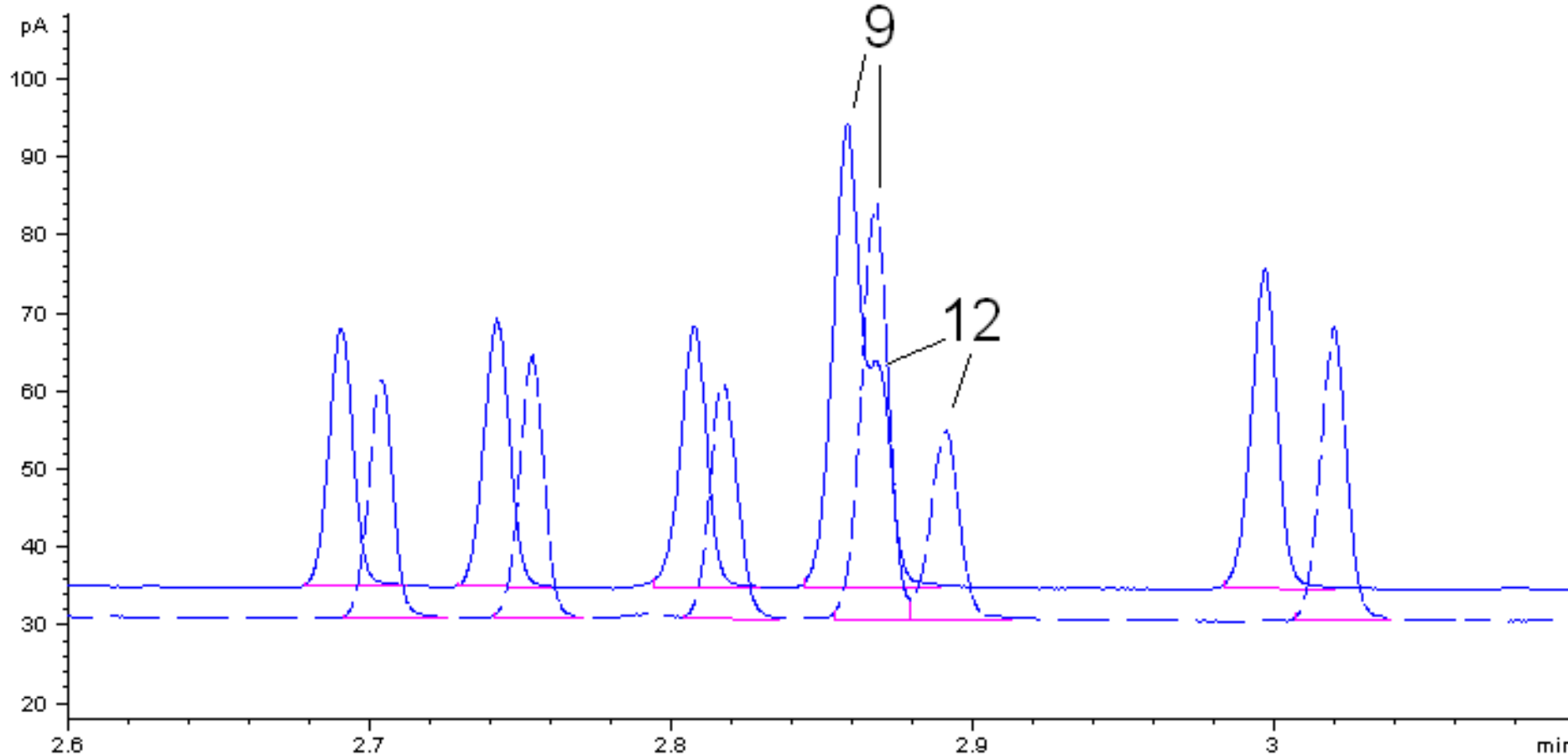
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# Chlorinated Pesticides

## With 1 stop-flow pulse



# Stop-Flow GC

- Stop-Flow allows the analyst to add “space” between specific peaks
  - Improved use of chromatographic “real estate”
  - Permits time-compressed GC runs using faster oven temperature ramps



# GC Racer

- Interfaces to existing GC's
- Operates using existing GC control
  - No software or firmware
- Allows for maximum ramp rates up to 440°C
- Can allow for 2-5 times speed enhancement for most methods

# GC Racer



**GC Racer Heater Installed in an Agilent 5890**

# GC Racer



GC Racer Installed on an Agilent 5890

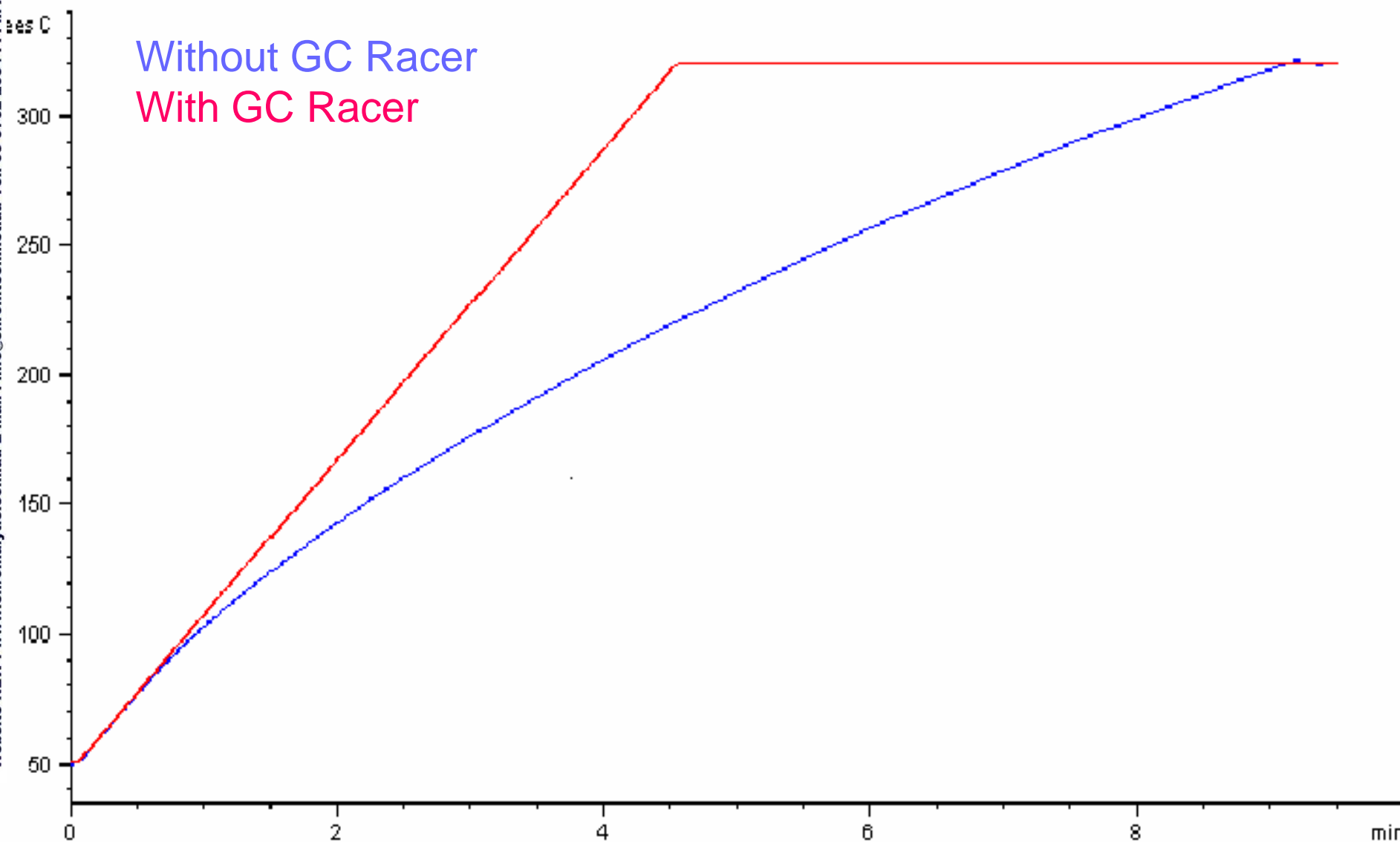
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# Agilent 6890 GC, temperature program of 60°C/min.

Without GC Racer  
With GC Racer

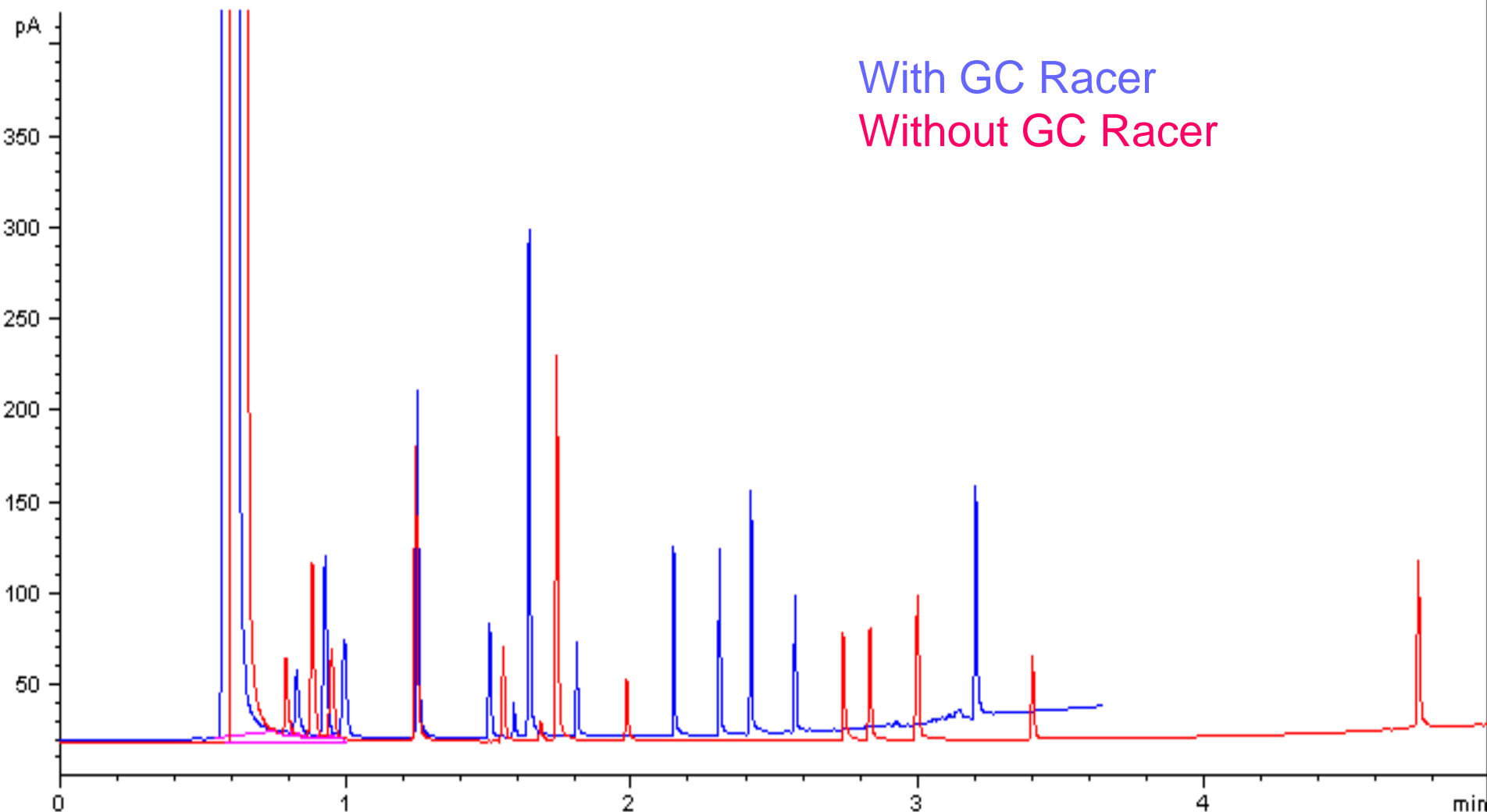


# Volatile Compounds, with and without the GC Racer

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# Application: Residual Solvents

- Pharmaceutical Formulations
- Guidelines for Testing
  - International Conference on Harmonization
  - European Pharmacopoeia
- Compound Lists Vary
  - Over 60 compounds of regulatory interest
  - Classes based on toxicities
  - Resolution of large lists on a single stationary phase can be extremely difficult



# Class I & II Residual Solvents

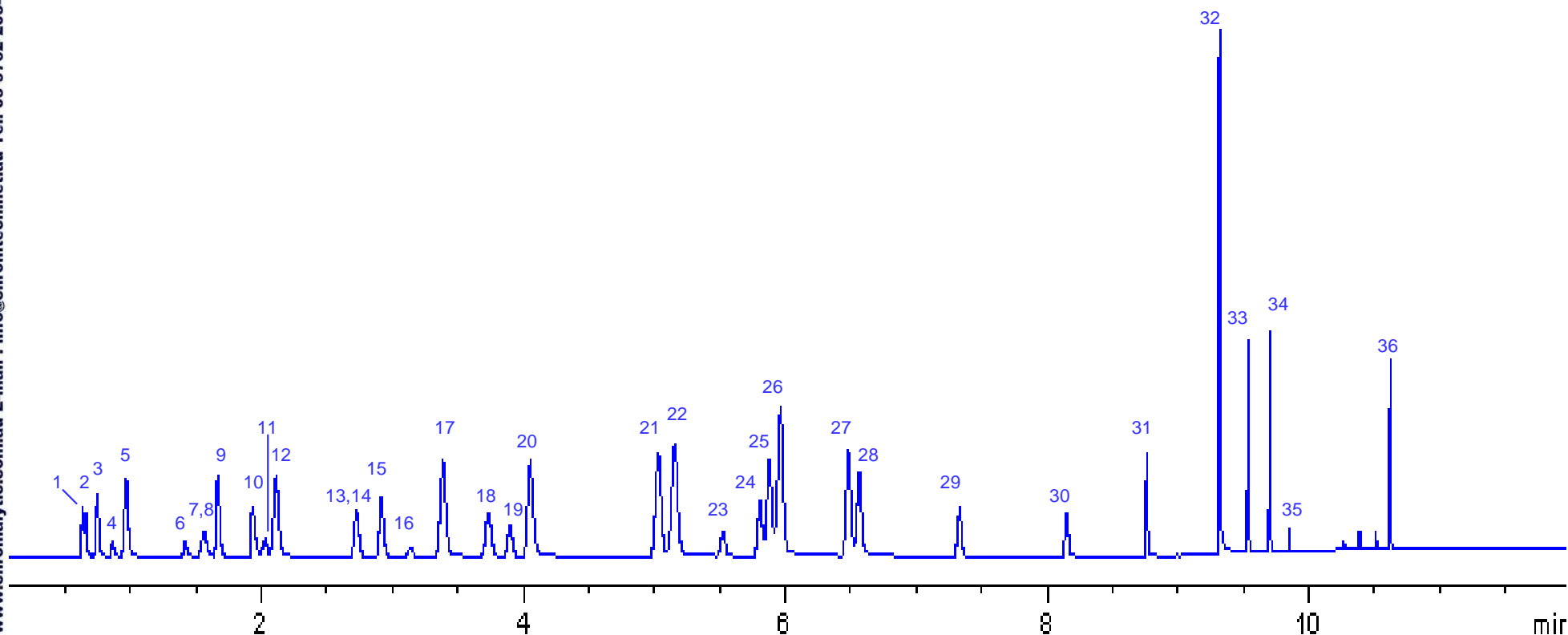
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Peak #	Compound	Peak #	Compound
1	2-methylpentane	19	1,2-dichloroethane (1,2-DCA)
2	hexane	20	2-hexanone (MBK)
3	methyl cyclopentane	21	p-xylene
4	1,1-dichloroethene (1,1-DCE)	22	m-xylene
5	methyl cyclohexane	23	nitromethane
6	<i>trans</i> -1,2-dichloroethene	24	2-methoxyethanol
7	carbon tetrachloride (CCl <sub>4</sub> )	25	pyridine
8	1,1,1-trichloroethane (1,1,1-TCA)	26	o-xylene
9	methanol	27	chlorobenzene
10	1,2-dimethoxyethane	28	2-ethoxyethanol
11	methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	29	1,1,2-trichloroethane (1,1,2-TCA)
12	benzene	30	dimethyl formamide (DMF)
13	<i>cis</i> -1,2-dichloroethene	31	N,N-dimethylacetamide (DMA)
14	trichloroethene (TCE)	32	1,2,3,4-tetrahydronaphthalene (THN)
15	acetonitrile (MeCN)	33	ethylene glycol (EG)
16	chloroform	34	1-methyl-2-pyrrolidinone (1-MP)
17	toluene	35	formamide
18	1,4-dioxane	36	sulfolone

## Fast Run Conditions: 1<sup>st</sup> FID

After Rtx-Stabilwax, 15m x 0.25mm x 0.5 $\mu$ m





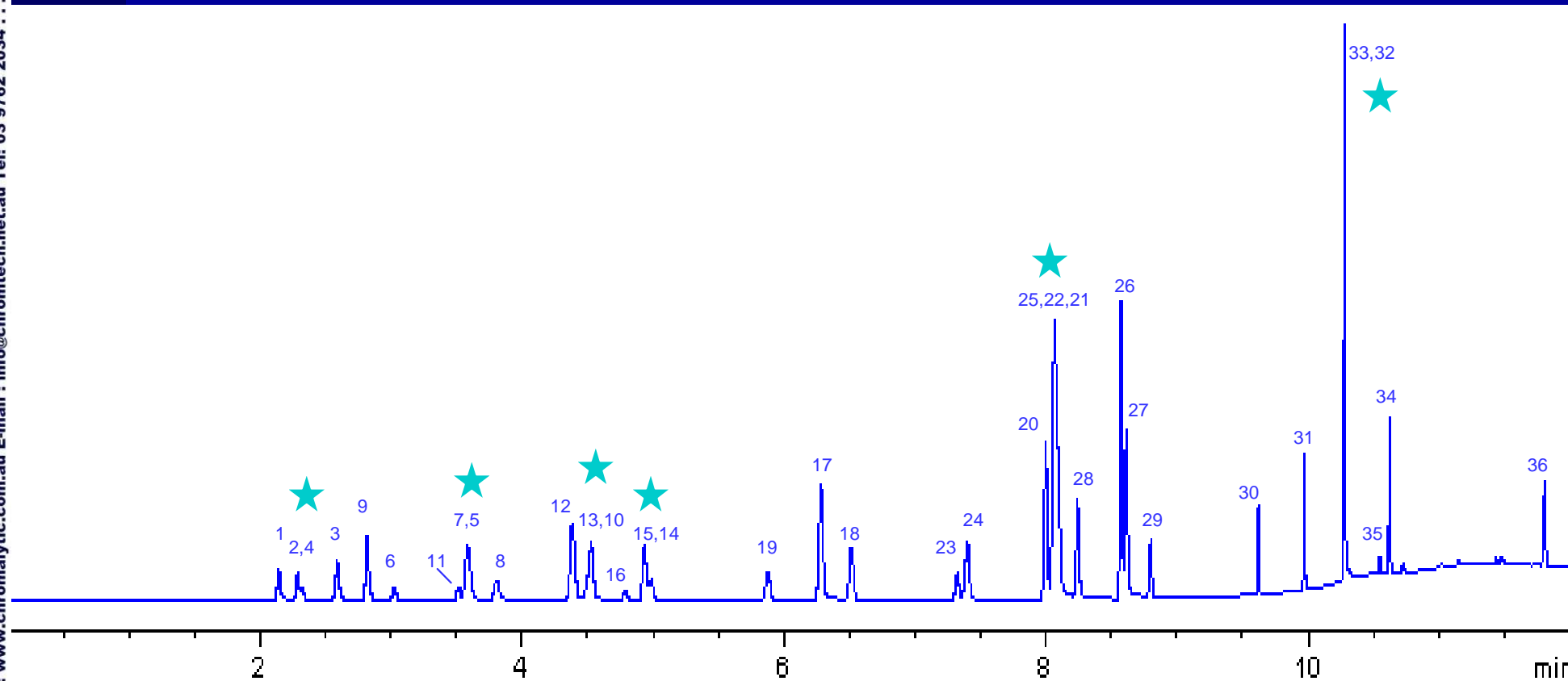
# Fast Run Conditions: 2<sup>nd</sup> FID

After Rtx-Stabilwax + Rtx-200 (30m x 0.25mm x 1.0 $\mu$ m)

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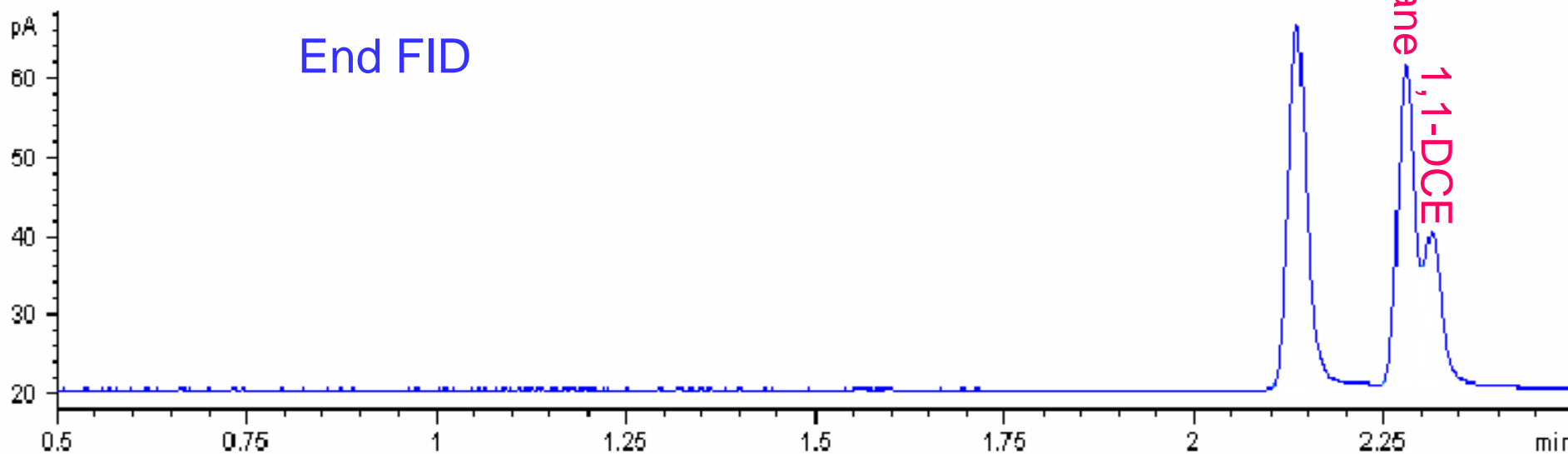


## Residual Solvents: Run Conditions

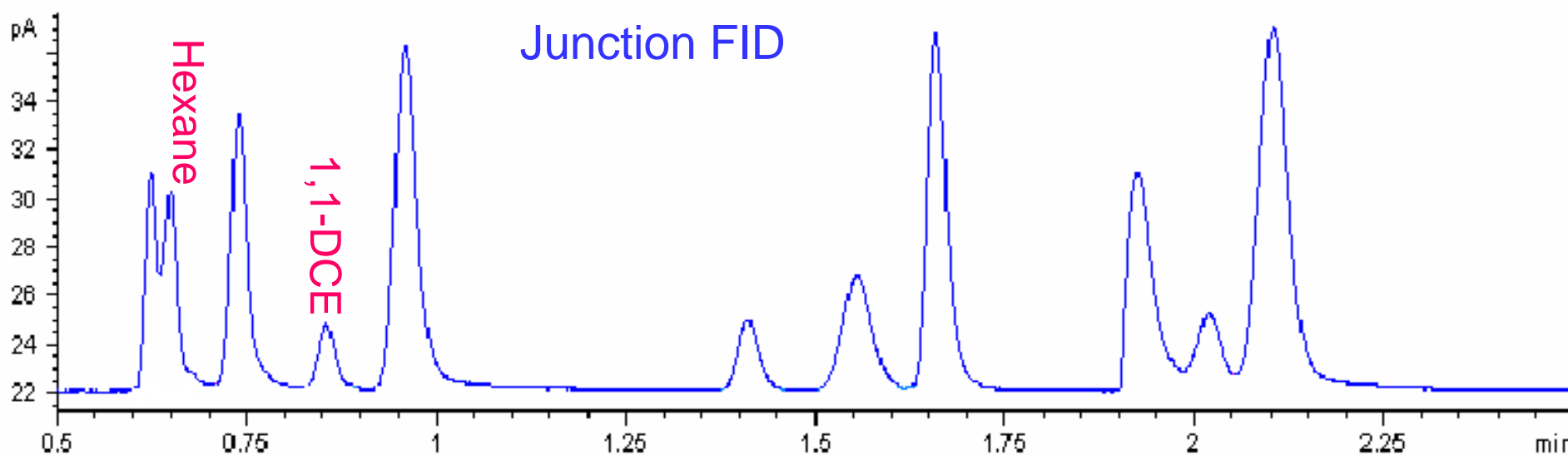
	<b><i>Standard Procedure</i></b>	<b><i>Fast Procedure</i></b>
Analytical Columns	Stabilwax 15m x 0.25mm, 0.5µm Rtx-200 30m x 0.25mm, 1µm	Stabilwax 15m x 0.25mm, 0.5µm Rtx-200 30m x 0.25mm, 1µm
Oven Program	40°C (6 min. hold) to 100°C at 4°C/min., to 220°C at 15°C/min., 5 min. hold	40°C (1 min. hold) to 65°C at 6°C/min., to 100°C at 12°C/min., to 250°C at 70°C/min., 1.8 min. hold
Column Flow	1.5 mL/min. constant flow	2.5 mL/min. to 9.5 min. 3.5 mL/min. at 10 min.
Injector	230°C	230°C
Injection	0.2 µL HS, 200:1 split	0.2 µL HS, 200:1 split
Detectors	Dual FIDs @ 250°C	Dual FIDs @ 250°C

## Class I & II Residual Solvents: No Pulses

End FID



Junction FID



## Residual Solvents: Pulse @ 44 sec.

End FID

Hexane  
1,1-DCE

Junction FID

4s

Hexane

1,1-DCE

# Residual Solvents: No Pulses

End FID

CH<sub>2</sub>Cl<sub>2</sub>

CCl<sub>4</sub> + methylcyclohexane

1,1,1-TCA

methylcyclohexane

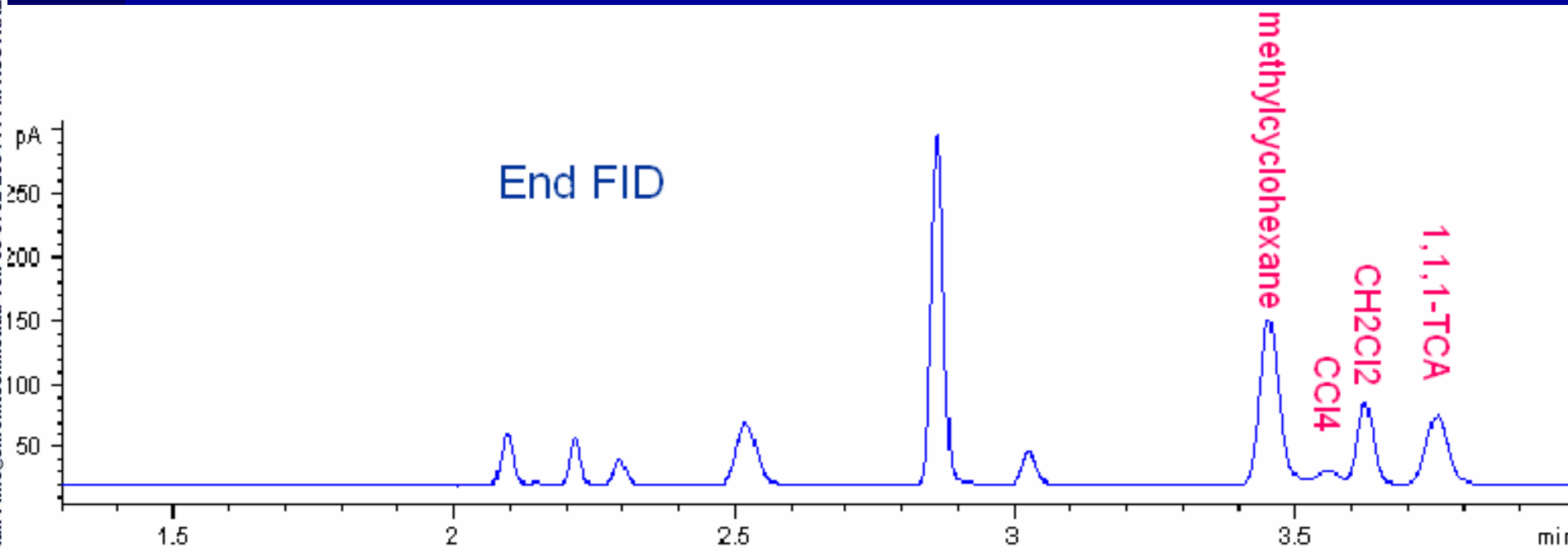
Junction FID

CCl<sub>4</sub> + 1,1,1-TCA

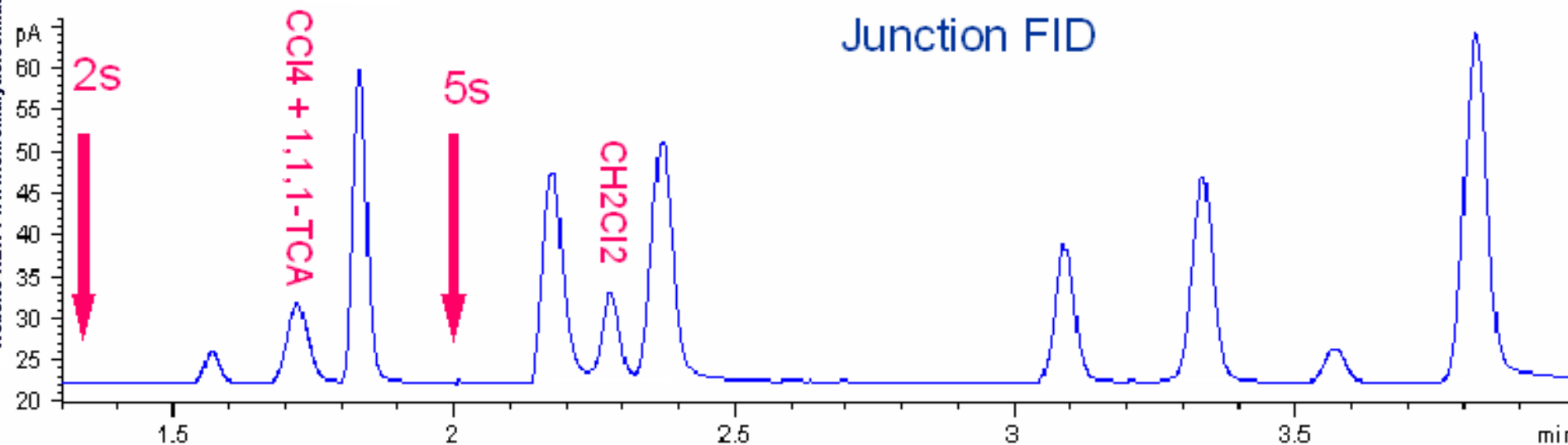
CH<sub>2</sub>Cl<sub>2</sub>

## Residual Solvents: Pulses @ 72 & 120 sec.

End FID



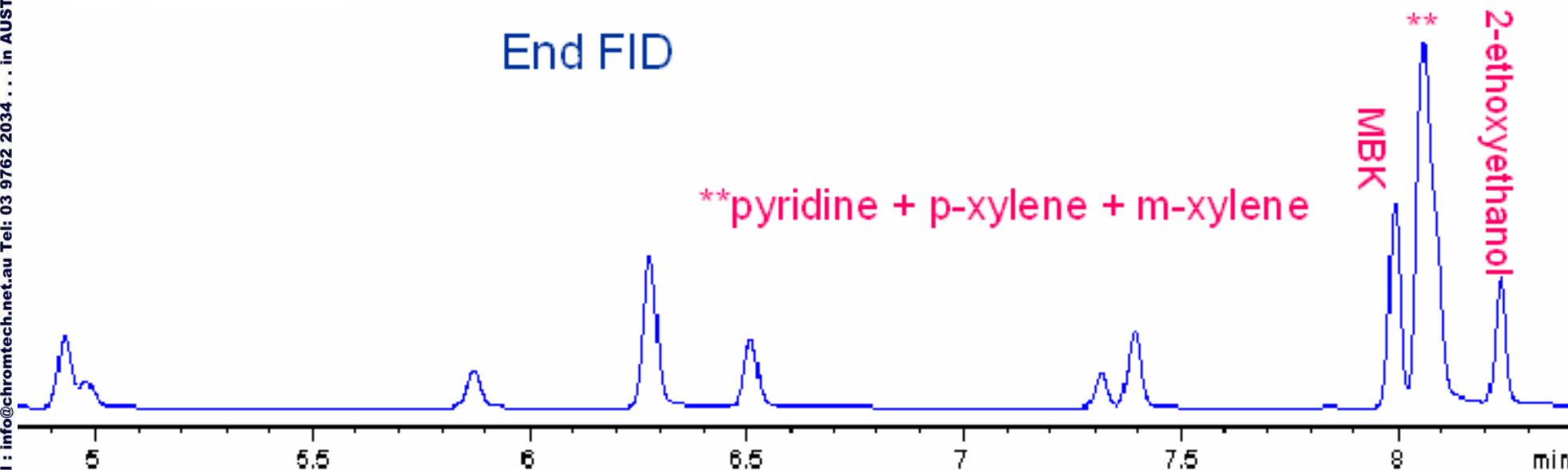
Junction FID



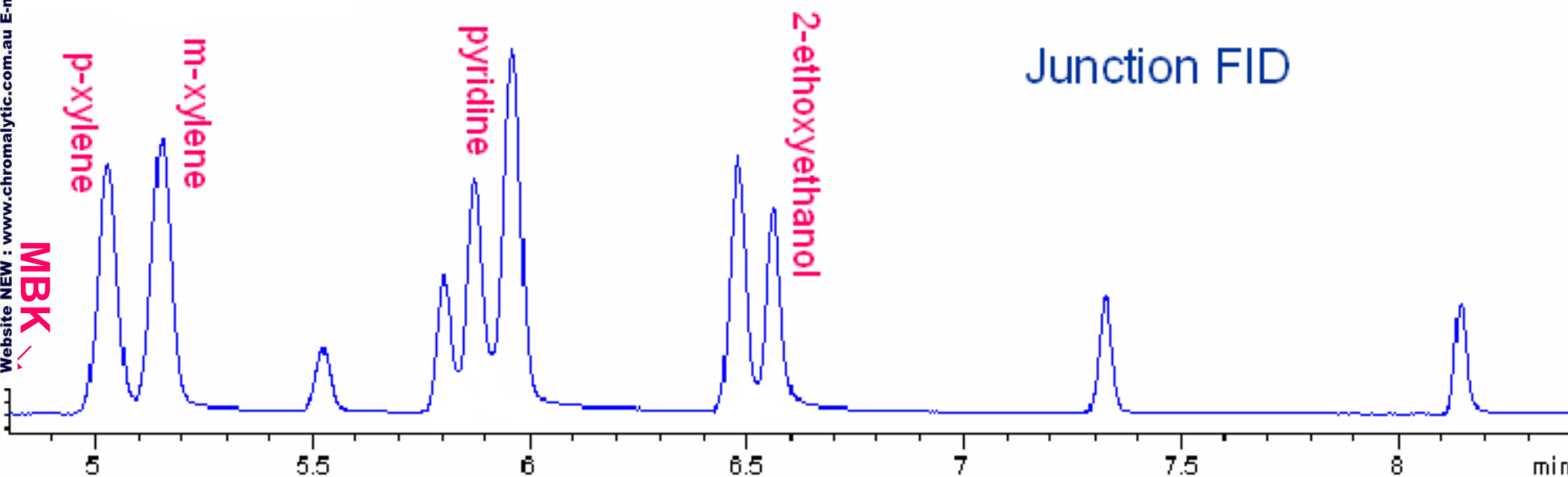
# Residual Solvents: No Pulses

End FID

\*\*pyridine + p-xylene + m-xylene  
MBK  
\*\*  
2-ethoxyethanol

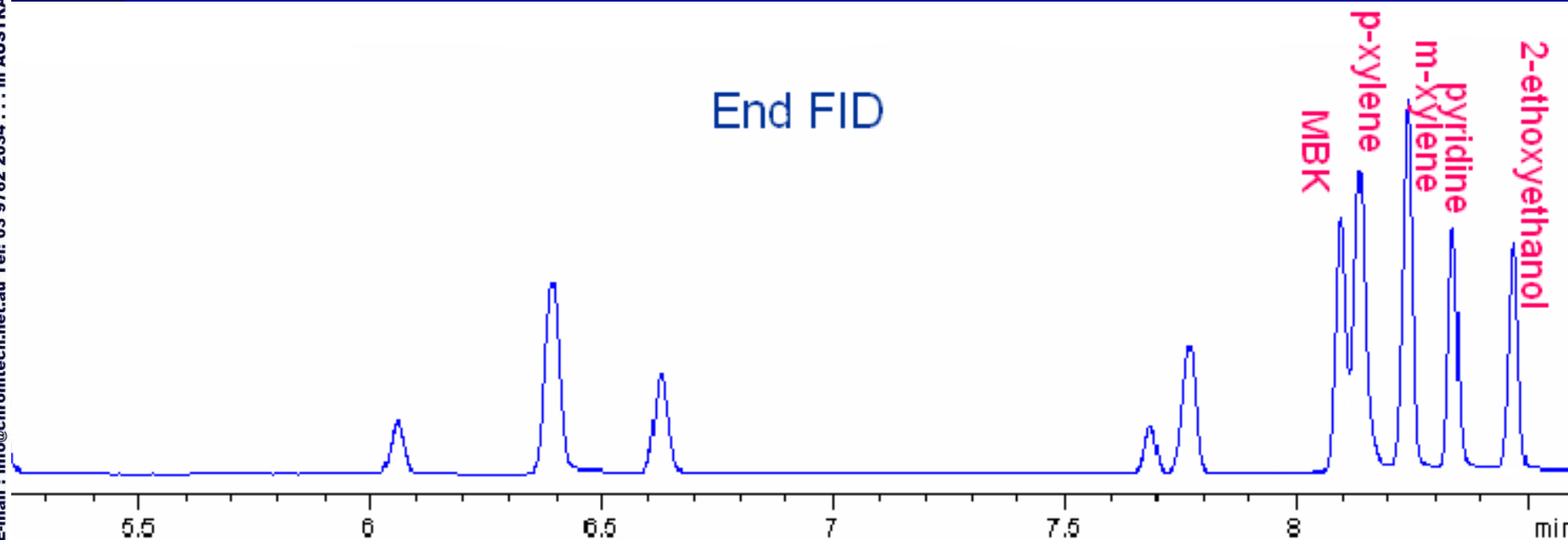


Junction FID

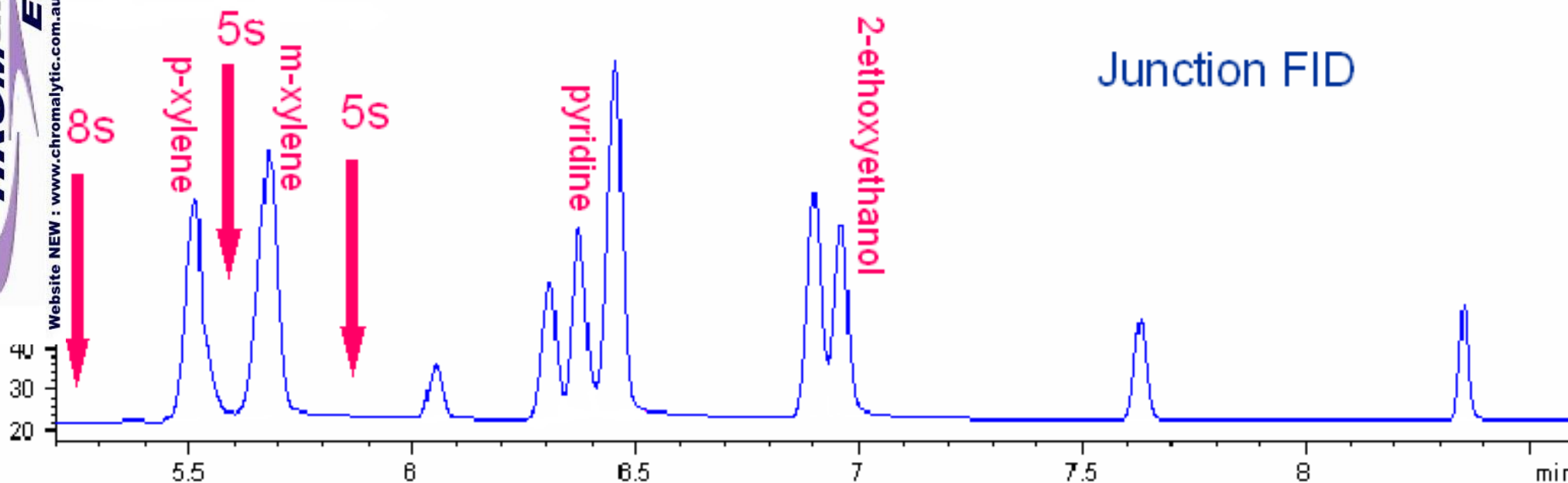


## Residual Solvents: Pulses @ 290, 330, & 346 sec.

End FID



Junction FID



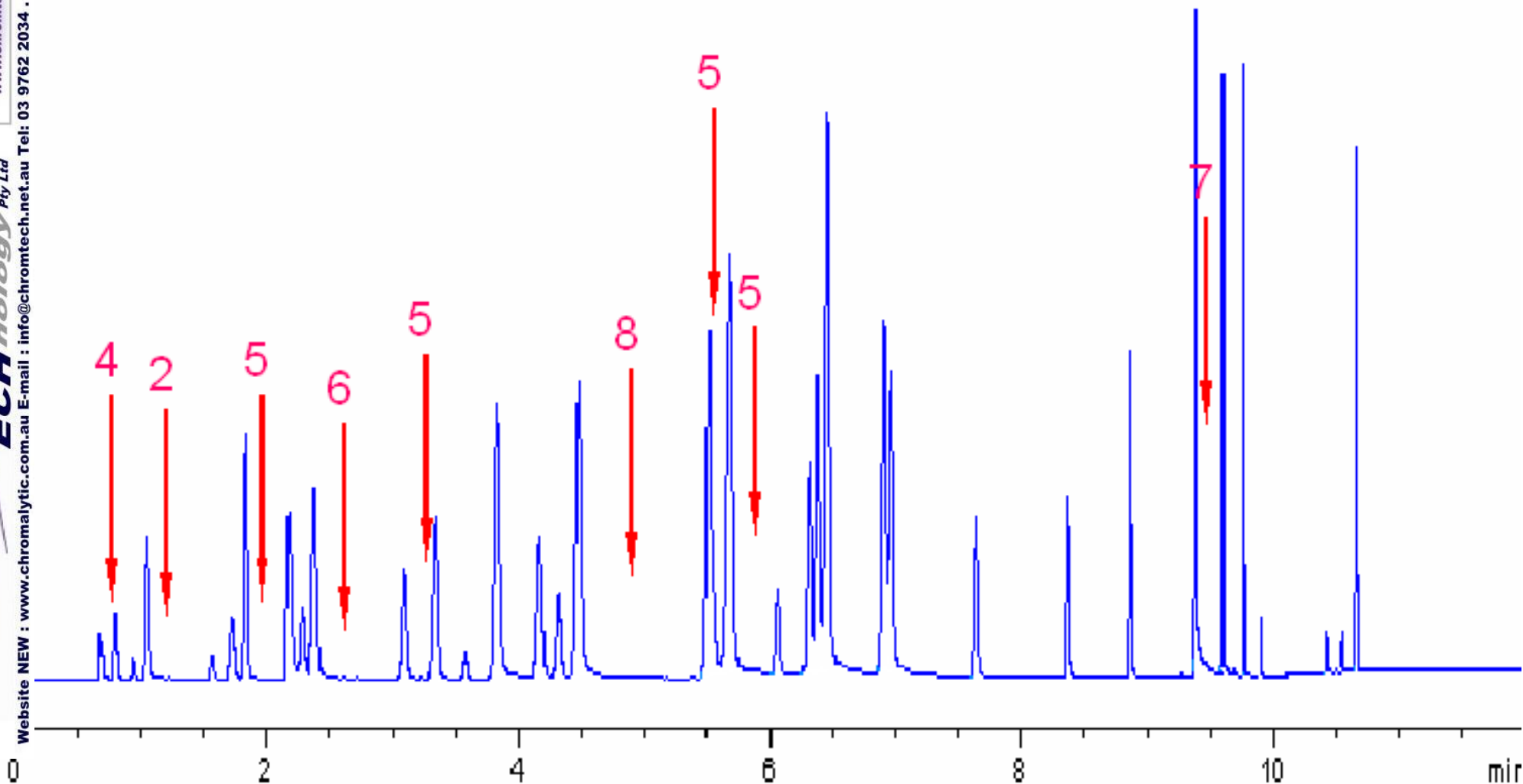


# Class I & II OVI: Total of 9 Pulses at the Junction

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# Class I & II OVI: Total of 9 Pulses *at the End Detector – all 36 resolved*

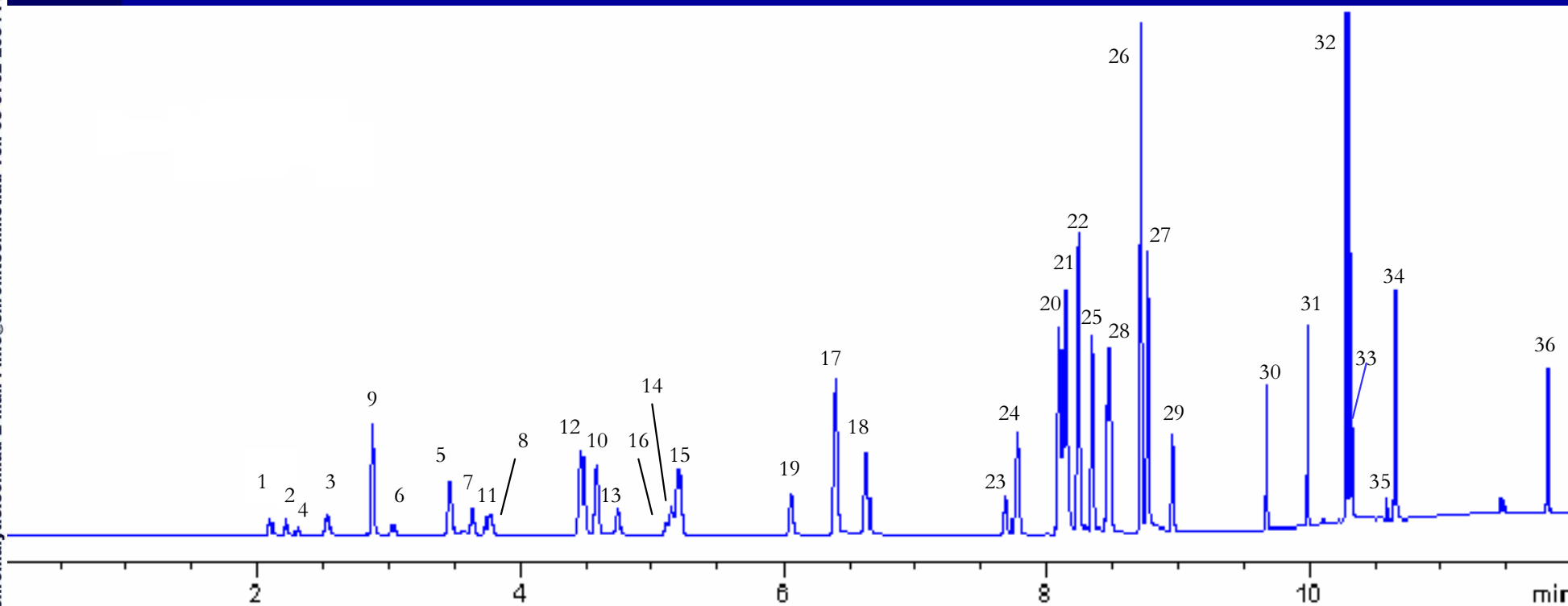
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# Summary of Stop-Flow GC

- Ability to “Tune” the Selectivity
- Flexibility
  - Standard dimension columns
  - Can vary the pulse sequences
- Significant Improvements in Analysis Times Possible
  - Fast oven programs, high flow rates

# HPLC Method Development

Becky Wittrig, Ph.D.  
RESTEK CORPORATION



# HPLC Method Development

- I. Method Development Strategy
- II. Selecting a Detector
- III. Selecting the Separation Mode
- IV. Mobile Phase and pH
- V. Optimization Based on the Resolution Equation

# Overview of Method Development Strategy

- Define method goals
- Establish sample prep procedure
- Select detector
- Select mode of separation
  - Column and mobile phase
- Perform preliminary separations
- Optimize conditions
- Calibrate and validate

# Define Method Goals

- What is known about the sample?
- What level of detection is required?
- Are standards available?
- How fast does the analysis need to be?
- How much resolution is required?

# What is Known About the Sample?

- Chemical structure(s)
- Acidic/Basic, pKa
- Molecular weight
- Stability (light and solvents)
- Solubility
- Concentration
- Matrix



# Sample Prep Options

- Filtration
- Centrifugation
- Solvent extraction
- Solid Phase Extraction (SPE)
- Supercritical Fluid Extraction (SFE)
- Preparative Chromatography
- Column Switching
- Derivatization

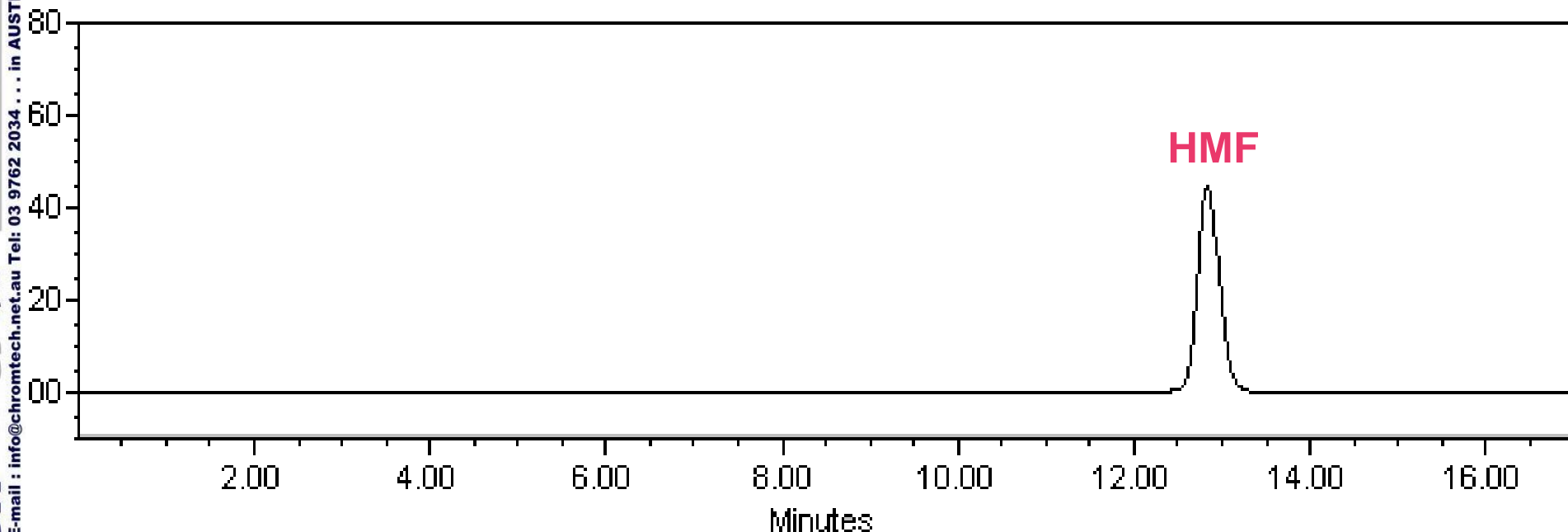
# Sample Prep Guidelines

- Minimum sample purity required:
  - Free of particulates
  - Completely soluble in mobile phase
- Start with minimal sample prep
  - Filtration is often sufficient
- Additional sample prep needs may be identified during preliminary separations

# Sample Prep: HMF Standard by HPLC

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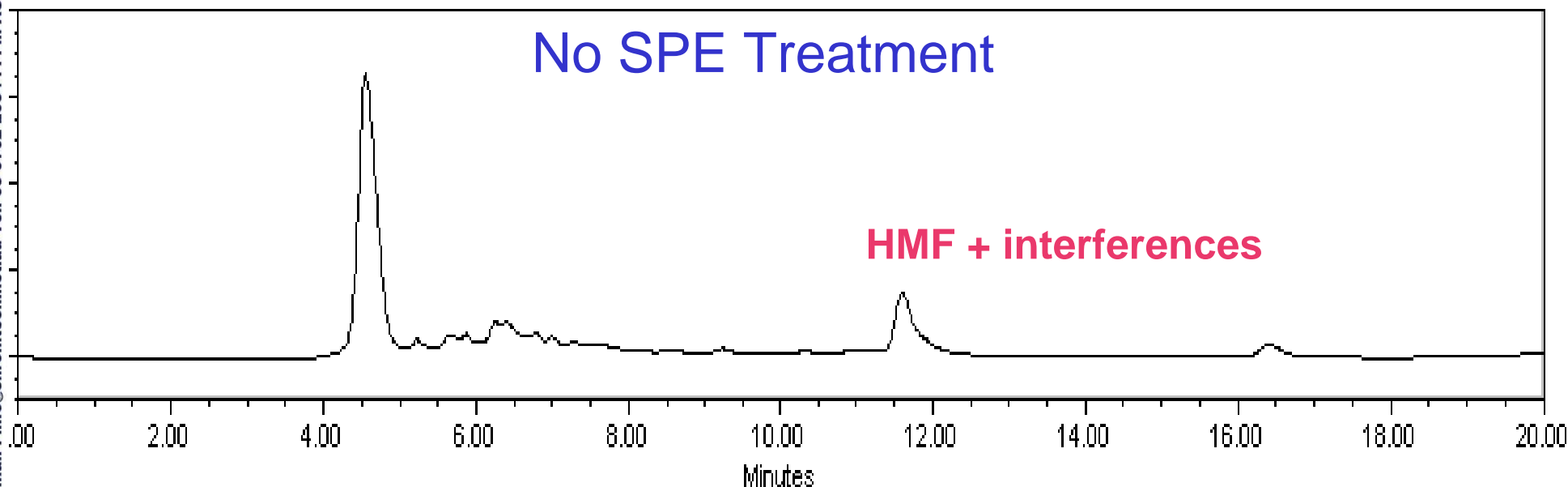


Column: Ultra C18 (Restek Corp.), 250 mm x 4.6 mm, 5  $\mu$ m  
Mobile Phase A: 90:10 water:methanol, 10 mM ammonium formate  
Mobile Phase B: 10:90 water:methanol, 10 mM ammonium formate  
Gradient: 0-5 min at 100% A, to 100% B at 10 min, 10 min. hold  
Flow: 0.5 mL/min.  
Temperature: ambient  
Detector: UV @ 280 nm  
Injection Volume: 10  $\mu$ L

# Sample Prep: HMF in Grape Juice by HPLC

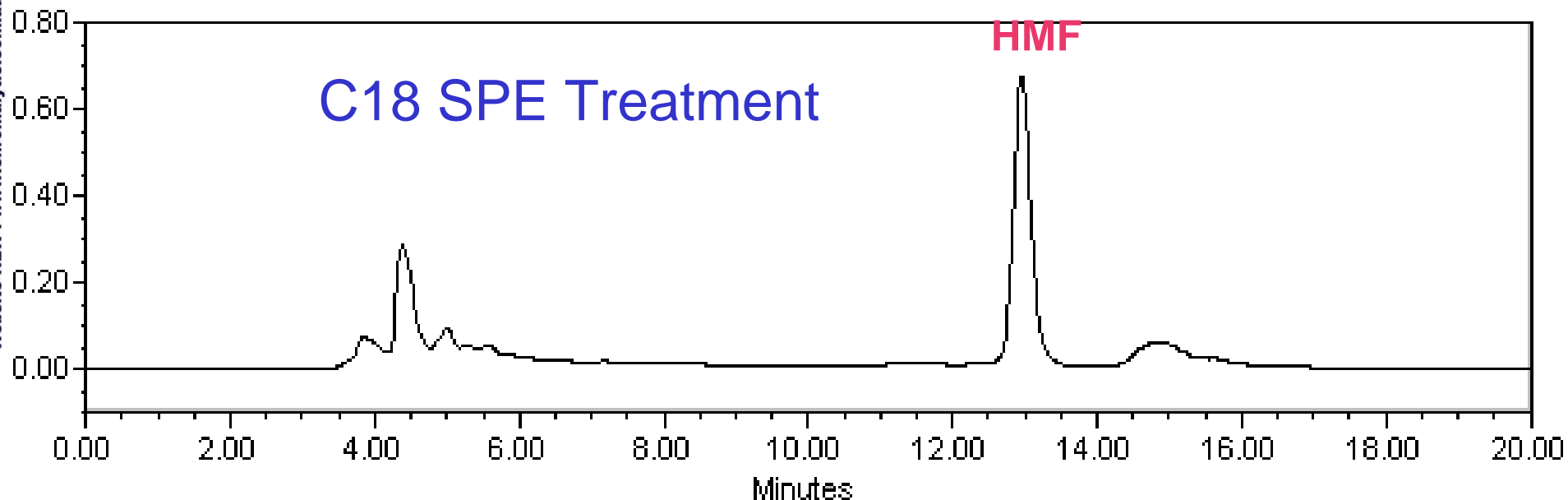
No SPE Treatment

HMF + interferences



C18 SPE Treatment

HMF



# Detector Selection: Types

- Ultraviolet/Visible Absorbance (UV/Vis)
- Mass Spectrometer (MS)
- Refractive Index (RI)
- Evaporative Light Scattering (ELS)
- Fluorescence (FL)
- Electrochemical (EC)

# Detector Selection

- Selection is Based on:
  - Chemical nature of analytes and potential interferences
  - Limit of detection required
  - Availability and/or cost of detector

# Detector Selection: UV/Vis

- Requirement: analyte must absorb more light than sample matrix at some wavelength
- Most widely used
- Most compounds absorb at low UV
- Diode Array Detector (DAD) can monitor multiple wavelengths simultaneously

# Detector Selection: UV/Vis

<u>Chromophore</u>	<u>Formula</u>	<u><math>\lambda_{\text{max}}</math> (nm)</u>
Amine	$-\text{NH}_2$	195
Ethylene	$-\text{C}=\text{C}-$	190
Ketone	$\text{RR}'\text{C}=\text{O}$	195
Ester	$\text{ROC}=\text{O}$	205
Aldehyde	$\text{RHC}=\text{O}$	210
Carboxyl	$\text{COOH}$	200-210
Nitro	$\text{NO}_2$	310
Phenyl	$-\text{C}_6\text{H}_5$	202,255
Naphthyl		220,275



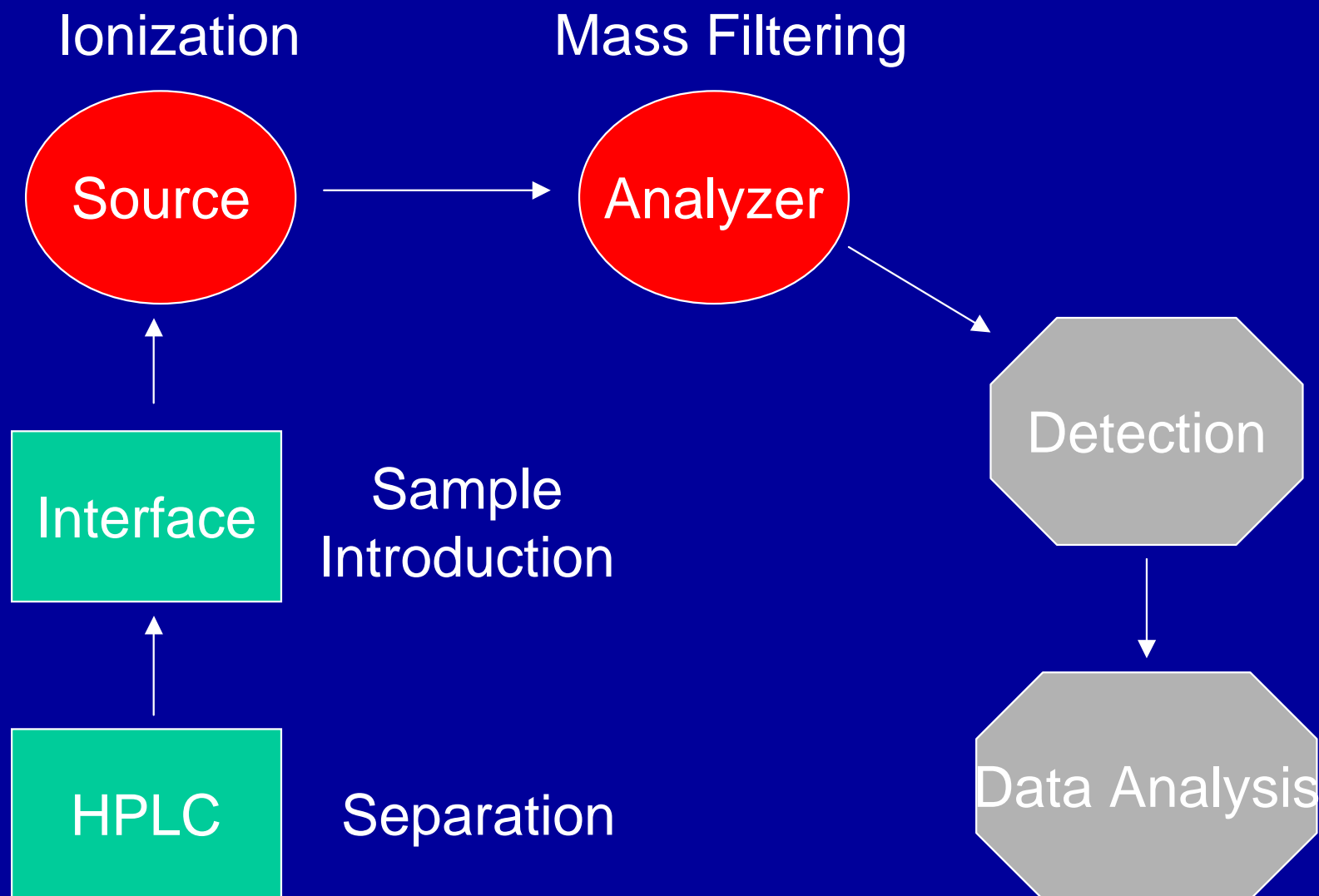
# Detector Selection: UV/Vis

- Choose detection wavelength that maximizes sensitivity and specificity
- Solvents used may cause slight shifts in  $UV_{max}$  from published values (2-5 nm)
  - Check absorbance of analyte in mobile phase
- Mobile phase solvents have UV cutoff points
  - Operating below cutoff point will:
    - Reduce sensitivity
    - Add to baseline noise

# Detector Selection: Mass Spectrometer

- Requirement: analyte must be ionizable
- Rapidly growing in popularity
- Positive identification of analyte
- Can discriminate between co-eluting peaks in selected ion mode
  - Reduces resolution required
- For best sensitivity, work at pH where analytes are ionized
  - Neutral to basic pH (7-9) for acids
  - Acidic pH (3-4) for bases

# Detector Selection: Mass Spectrometer



# Detector Selection: Refractive Index

- Monitors difference in the refractive index of the sample cell vs. the reference cell
- Non-selective
- Concentration dependent
- Sensitivity is typically 100x-1000x less than a UV/Vis detector
- Cannot be used with gradients (without special modifications)

# Detector Selection: Light Scattering ELSD

- Detector is mass dependent and non-selective
- Ideal for:
  - ◆ High molecular weight compounds
  - ◆ Sugars and less volatile acids
- Amount of light scattering is related to the molecular mass of the analyte
- Can be used with gradient systems
- Solvents should be volatile for best results

# Advances in Instrumentation Light Scattering Detectors

## 3 distinct processes:

- Nebulization of the mobile phase
- Evaporation of the mobile phase
- Light scattering by analyte particles

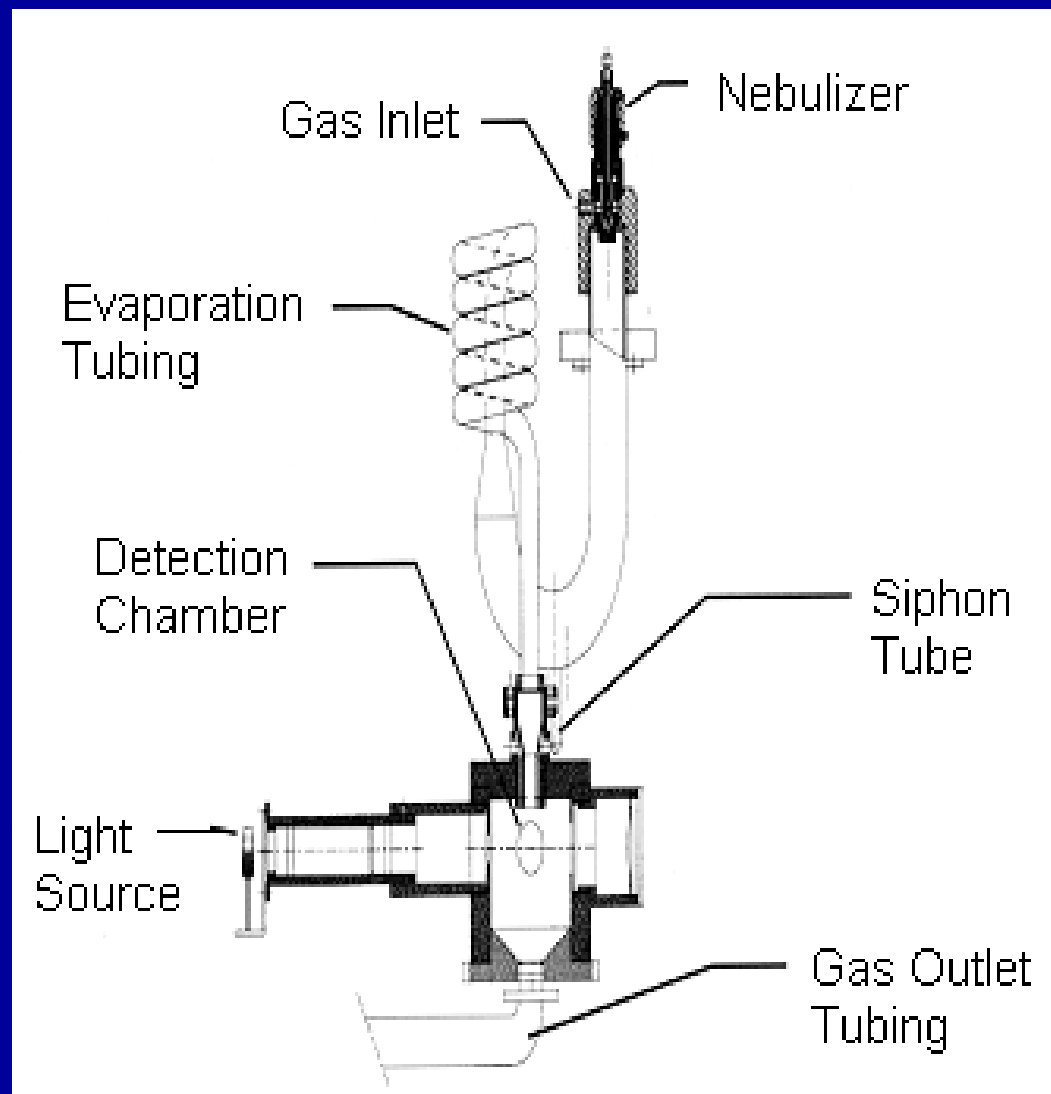


Diagram courtesy of ESA, Inc.

# Detector Selection: Fluorescence

- Analyte must fluoresce
- Excite at one wavelength, measure the emission at a longer wavelength
- Up to 1000x more sensitive than UV/Vis
- High specificity
- Concentration dependent
- Operation similar to a UV/Vis detector

# Detector Selection: Electrochemical

- Requirement: Analytes can be oxidized or reduced by an electrical current
- More sensitive than fluorescence
- Not as selective as fluorescence (typically)
- Not compatible with gradient elution



# Detector Selection: Approximate LODs

■ EC	$10^{-12}$
■ MS	$10^{-11}$
■ FL	$10^{-11}$
■ UV	$10^{-10}$
■ RI	$10^{-7}$
■ ELS	$10^{-7}$

# Selecting the Mode of Separation

- Sample solubility

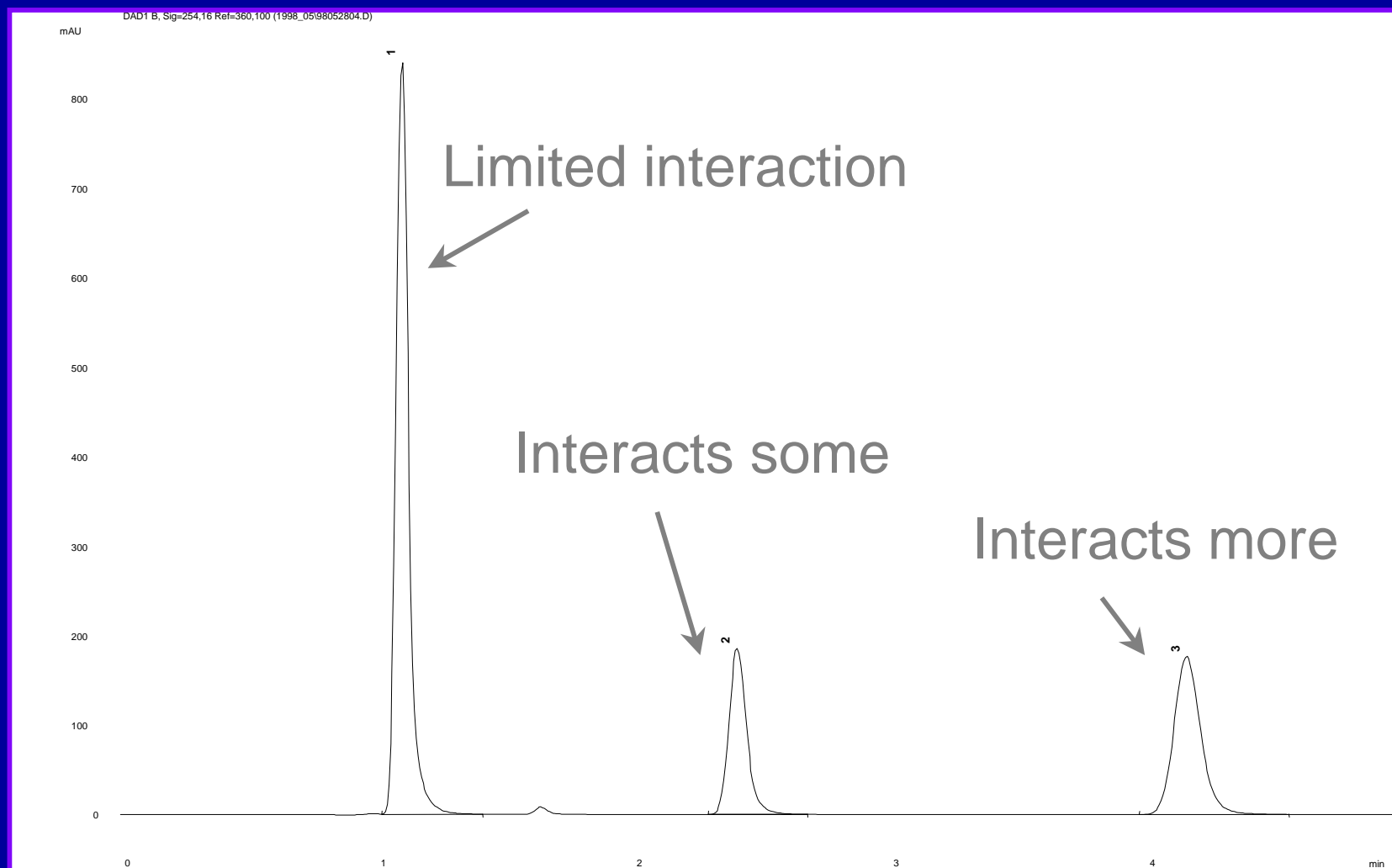
- How do analytes of interest differ from other compounds in sample?

- Reversed phase is the most frequently used mode

# Mode Selection : Reversed Phase

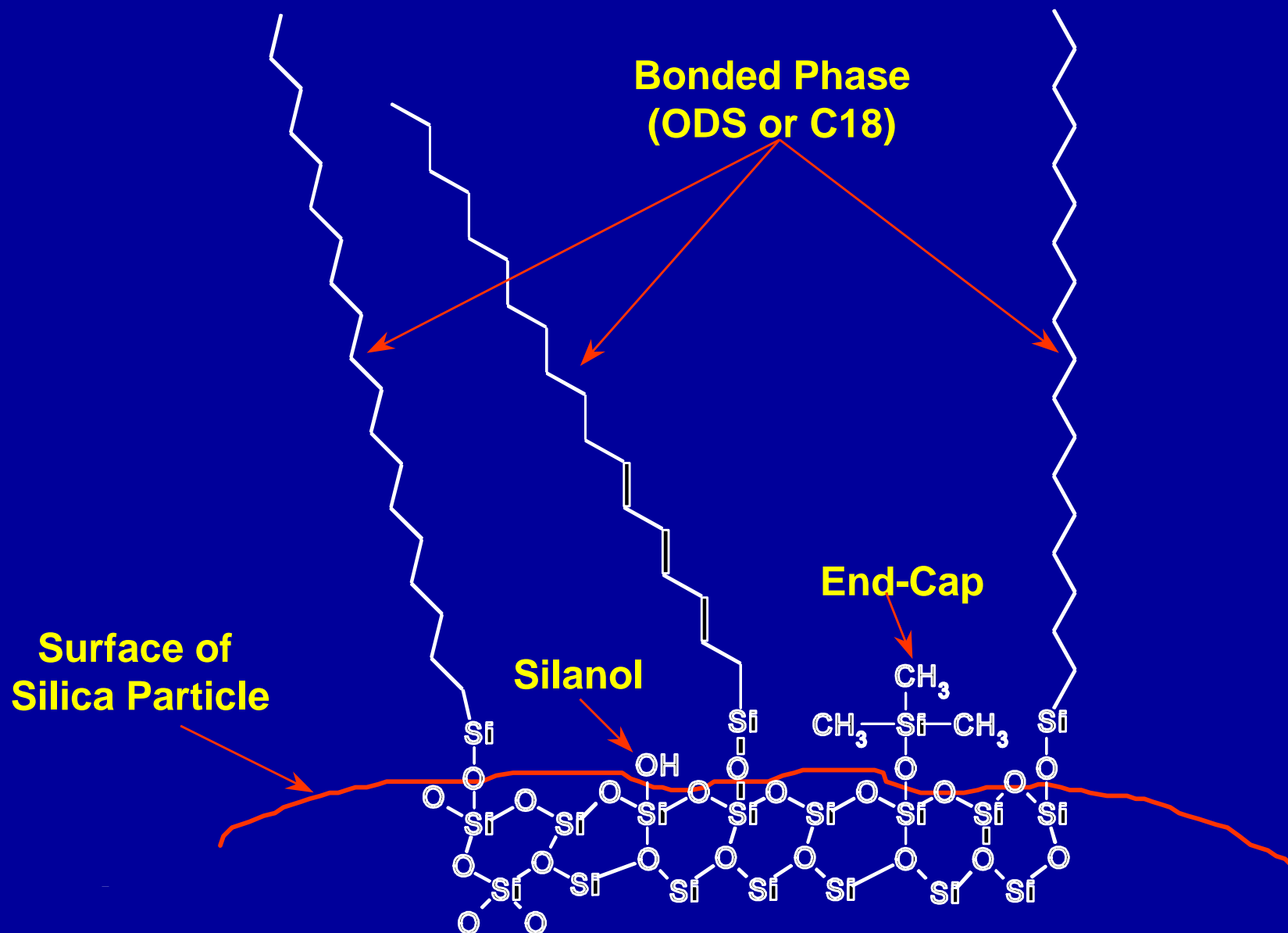
- Mobile phase is polar
- Stationary phase is less polar
- Major distinction between analytes is their hydrophobicity
- The sample should be soluble in water or a polar organic solvent (i.e. methanol)
- Examples are C18 (ODS), C8 (Octyl), Phenyl, Butyl, and Methyl

# Mode Selection : Reversed Phase Nonionic Compounds



Hydrophilic  $\longrightarrow$  Hydrophobic

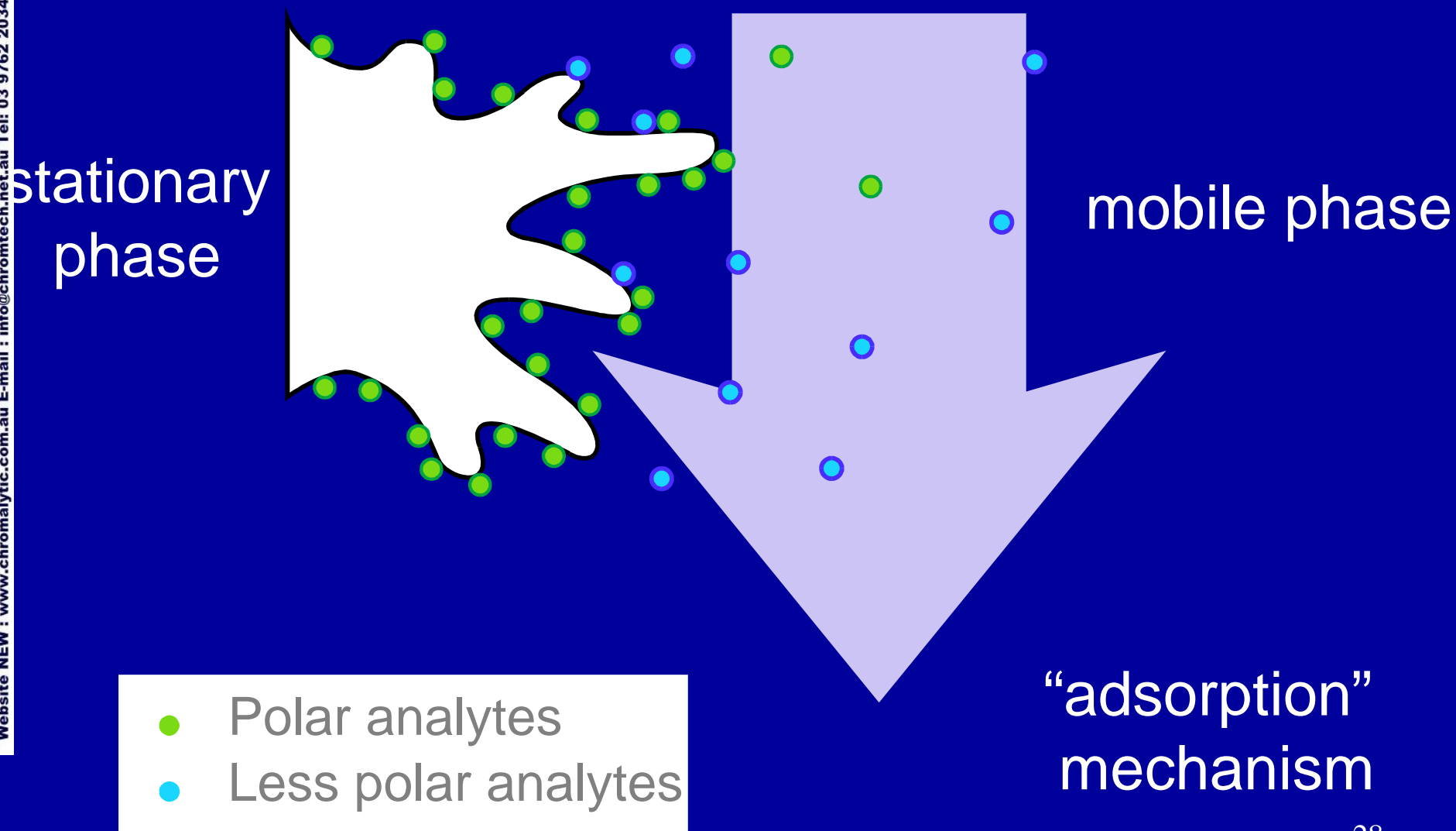
# Reversed Phase: The Bonded Phase Surface



# Mode Selection : Normal Phase

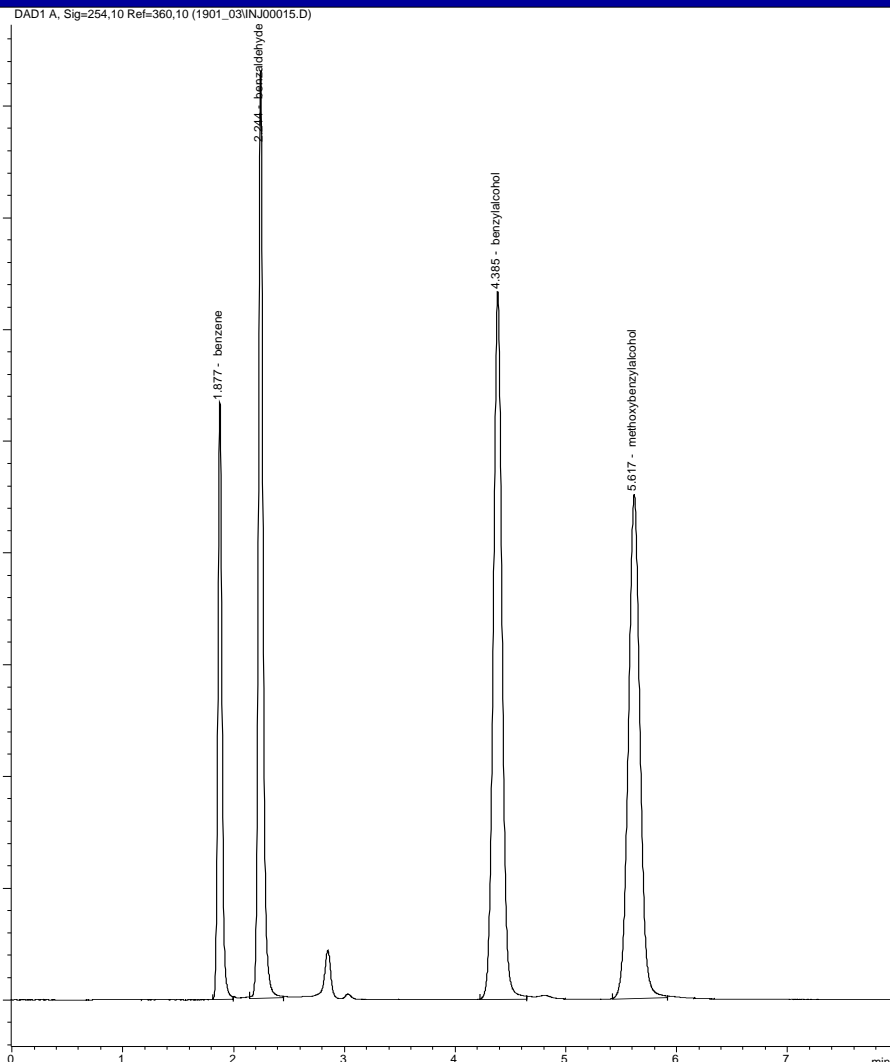
- Mobile phase is non-polar while stationary phase is more polar
- When a major distinction between analytes is NOT their hydrophobicity
- Sample should be soluble in a hydrophobic solvent such as hexane
- Mobile phase is a weak to moderate solvent for the sample
- Examples are Silica, Cyano, Amino and Diol

# Normal Phase Mode of Separation



# Normal Phase Test Mix

## Pinnacle II Silica Column



Peak list:

1. benzene
2. benzylaldehyde
3. benzylalcohol
4. methoxybenzylalcohol

Column: Pinnacle II Si,  
150x4.6mm, 5 $\mu$ m

Mobile phase: 96% hexane:4% IPA

Flow: 1.0 ml/min

Temp.: ambient

Det.: UV @ 254



# Mode Selection : Ion Exchange

When analytes are ionic or potentially ionic

Mobile phase is typically an aqueous buffer

Mobile phase strength is a function of ionic strength

pH is critical

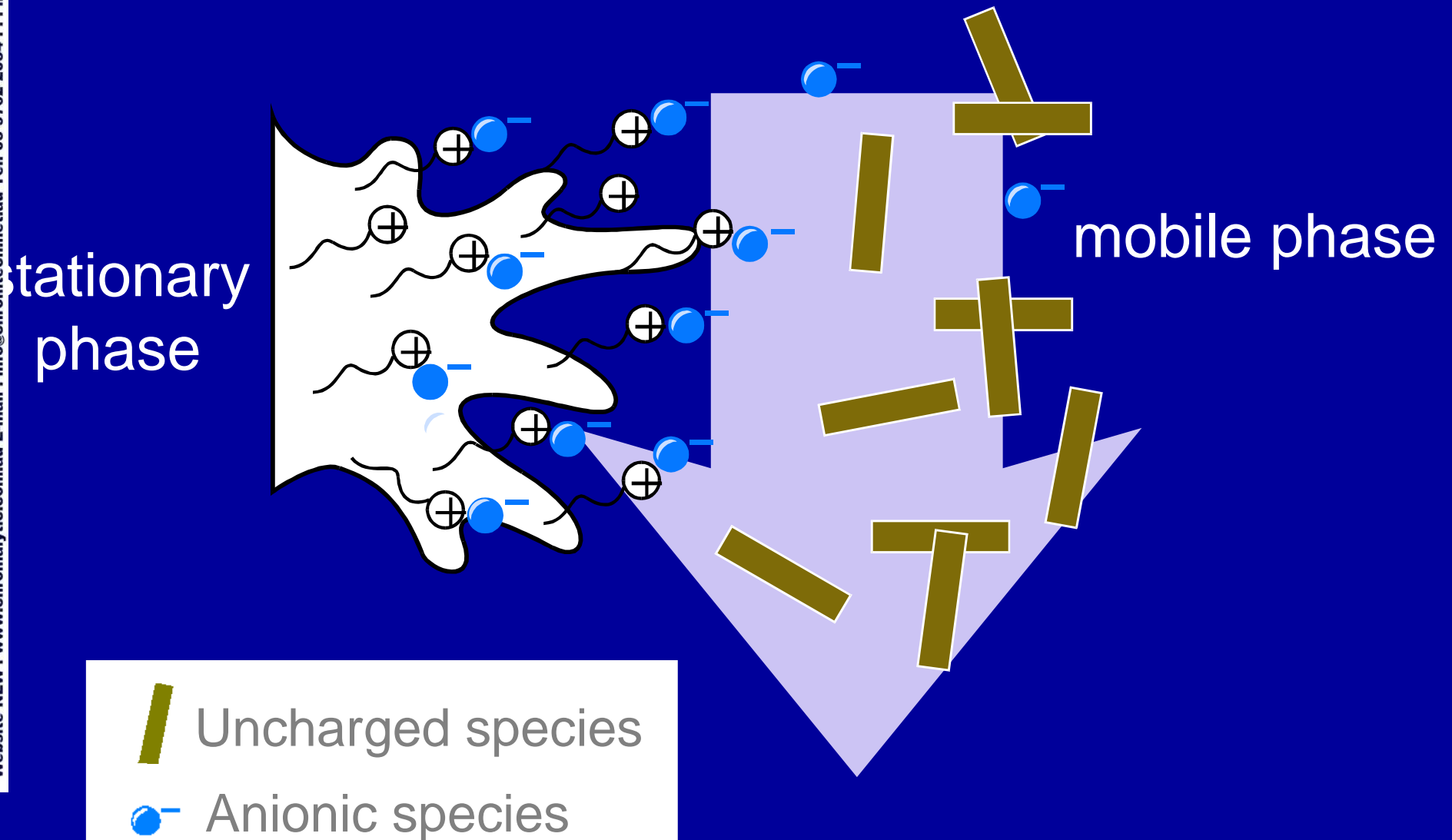
SAX is Strong Anion Exchange (WAX = Weak)

SCX is Strong Cation Exchange (WCX = Weak)

Examples

- Inorganic Cations and Anions, Organic Acids and Bases, Amino Acids, Nucleotides, Catecholamines, Peptides, Antibiotics

# Mode Selection : Ion Exchange



# Mode Selection: Reversed Phase Ion-Pair

- When analytes are ionic or potentially ionic
- Mobile phase is composed of a buffer, an ion-pair reagent and a polar organic solvent
- Typical ion-pair reagents include
  - Alkyl sulfonates (heptane sulfonic acid, octane sulfonic acid) for bases
  - Quaternary amines (tetrabutylammonium chloride) for acids

# Mode Selection: Size Exclusion

- Major distinction between the analytes in the mixture is their hydrodynamic volume
- Generally for molecular weights  $> 2000$
- Want to avoid partitioning
- The mobile phase should be a strong solvent for the sample
- Aqueous SEC is called Gel Filtration
  - Proteins and other biomolecules
- Organic SEC is called Gel Permeation (GPC)
  - Polymers

# Why Is Reversed Phase the Most Popular Mode?

- Large proportion of analytes are water soluble
- Wide range of stable stationary phases available
  - used to alter retention and selectivity
- Simple mobile phases work for many applications (i.e. water:acetonitrile)
- Selectivity can be altered by changing the mobile phase

# General Rules for Mobile Phase Selection

- In partition chromatography, the mobile phase should be a moderate to poor solvent for the samples
  - Produce a capacity factor of 1 to 10 (2 to 5)
- For ion exchange and size exclusion the mobile phase should be a strong solvent for the sample
- The use of *additives or modifiers* can enhance a separation
  - Improving peak shape
  - Altering selectivity

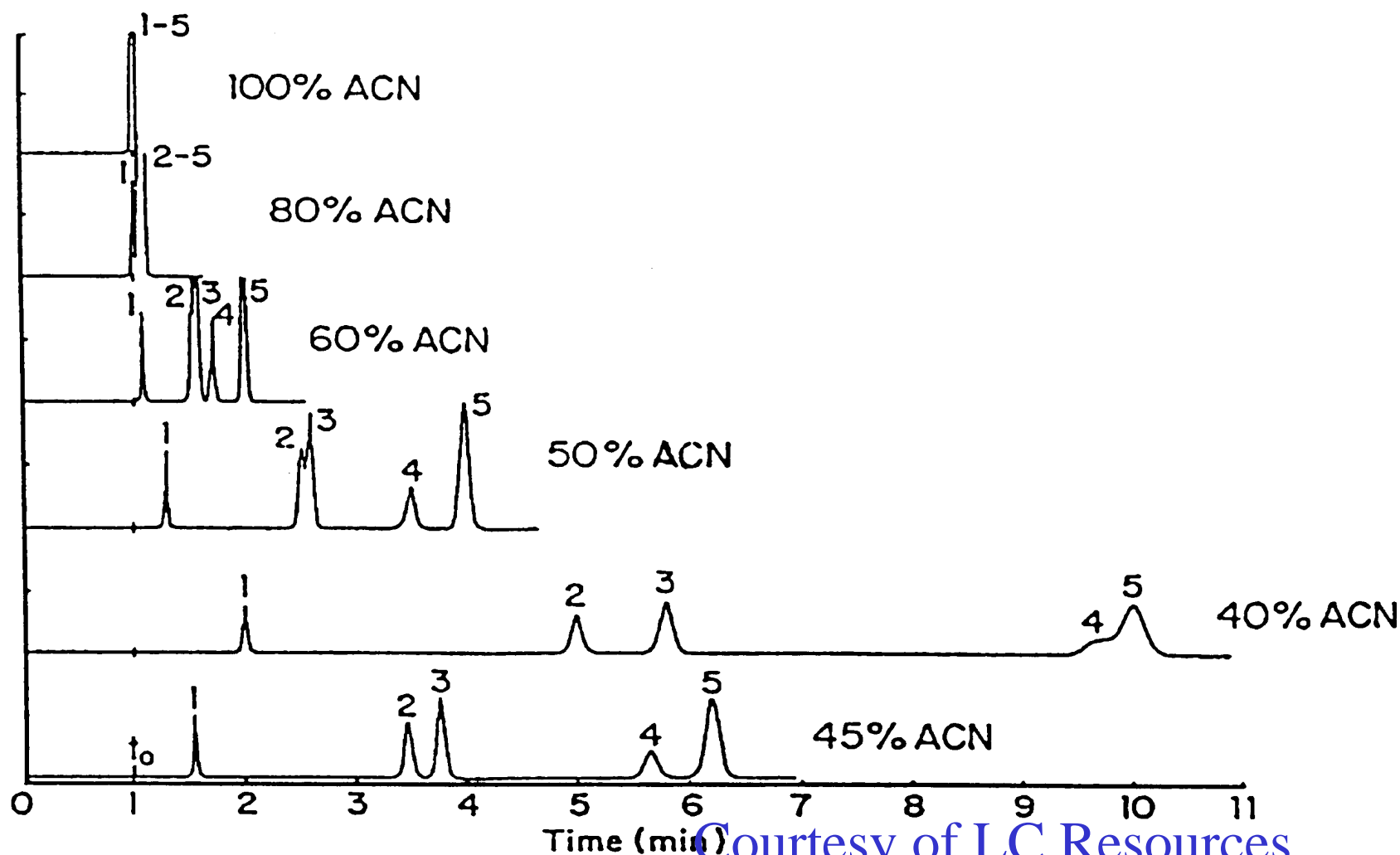
# Mobile Phase Selection: Organic Solvent

- Water miscible
- Low viscosity
- Low UV cut-off
- Unreactive
- Most commonly used:
  - Acetonitrile
  - Methanol
  - Tetrahydrofuran (THF)

# Mobile Phase Selection

## Adjusting Retention with %B

### Effect of Solvent Strength on Band Spacing



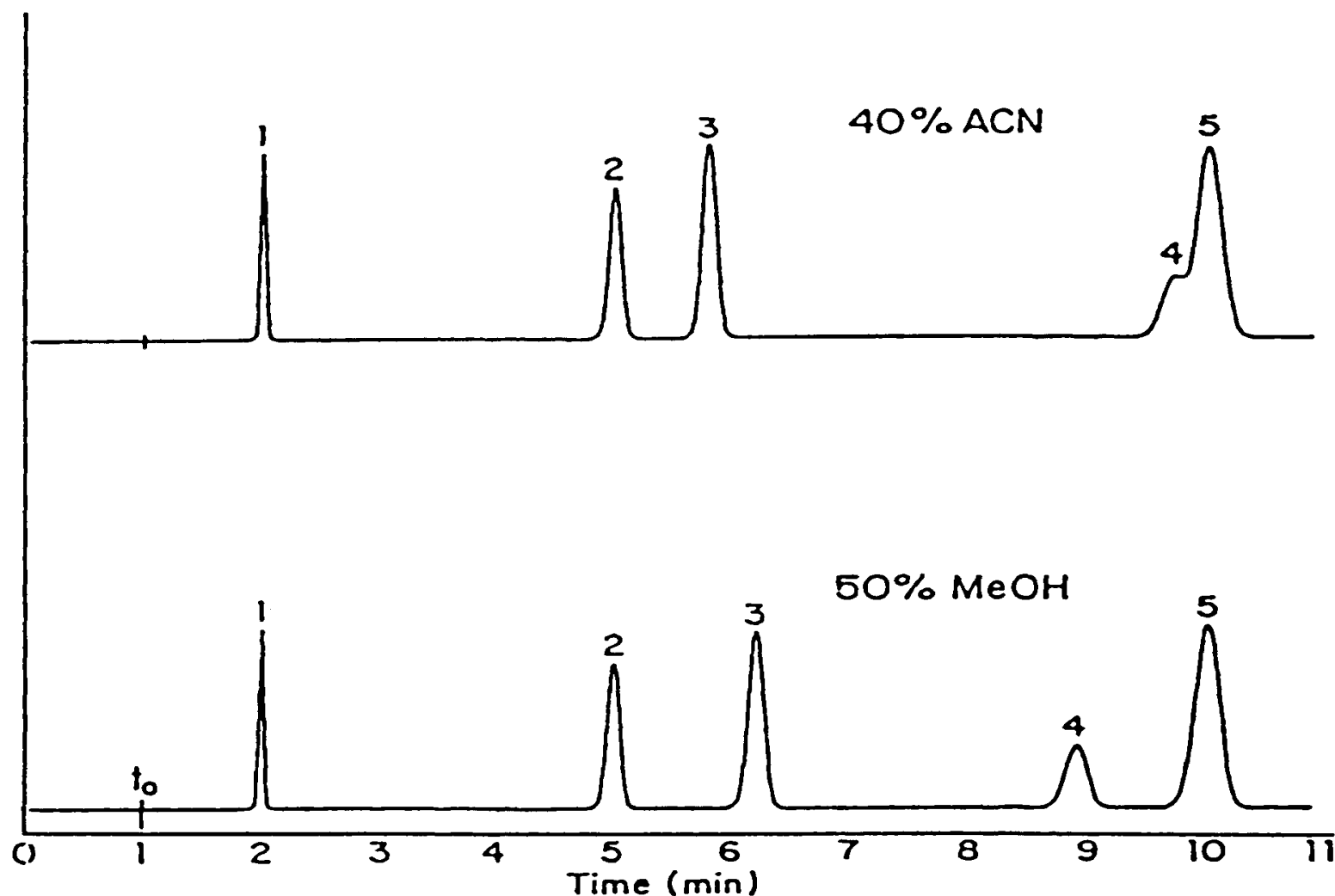
Courtesy of LC Resources



# Mobile Phase Selection

## Changing the Selectivity

### Effect of Solvent Type on Band Spacing



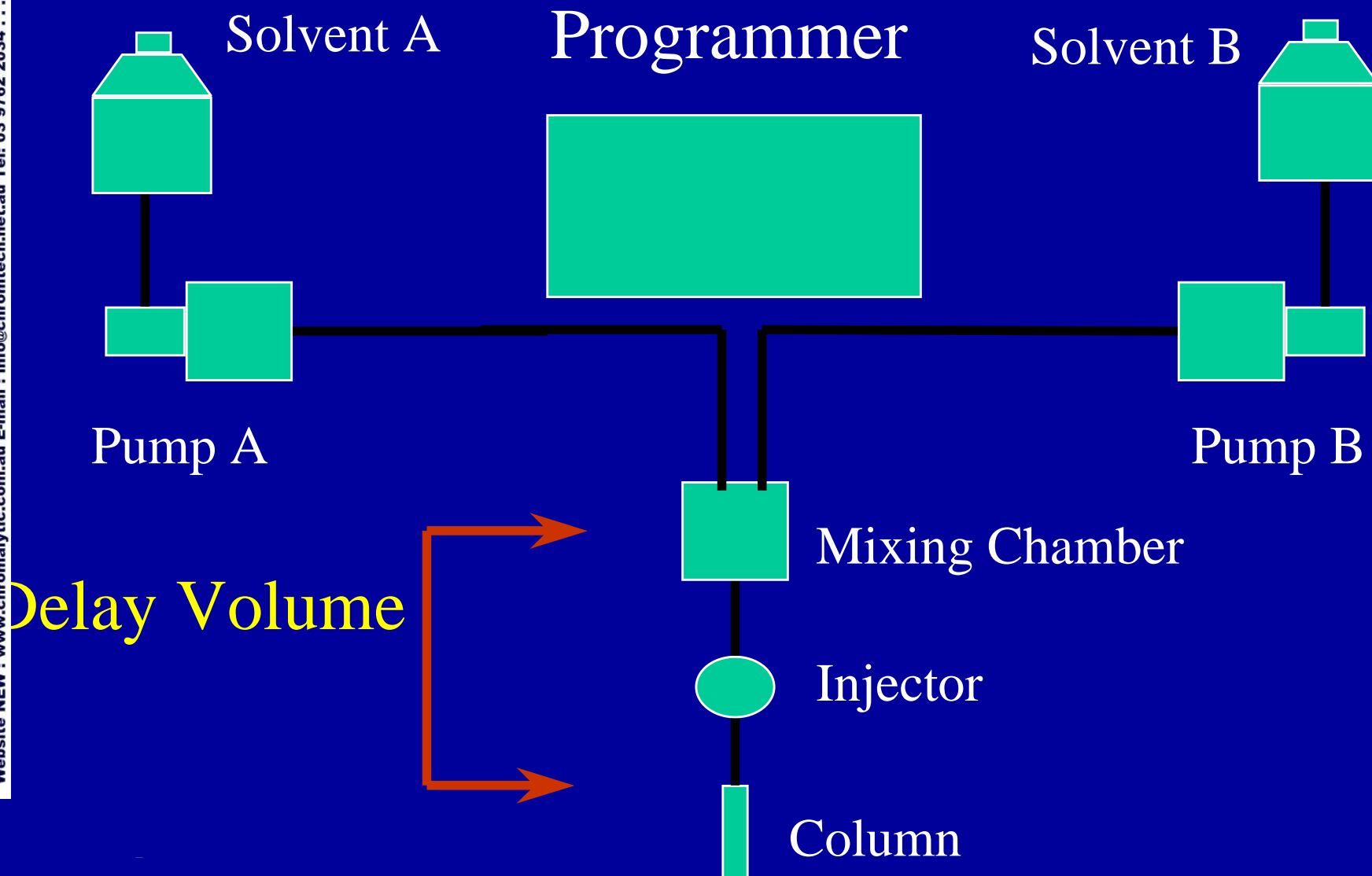
# What if a single mobile phase (isocratic) will not elute all analytes in the desired $k'$ range?

- Use gradient elution
- Mobile phase strength changes over time
- Weak mobile phase early in the gradient
  - $k' > 2$  for weakly retained analytes
- Strong mobile phase later in the gradient
  - $k' < 10$  for strongly retained analytes
- Initial scouting run
  - Use to estimate %organic for an appropriate elution
  - Elutes all strongly-retained compounds

# Disadvantages Of Gradient Elution

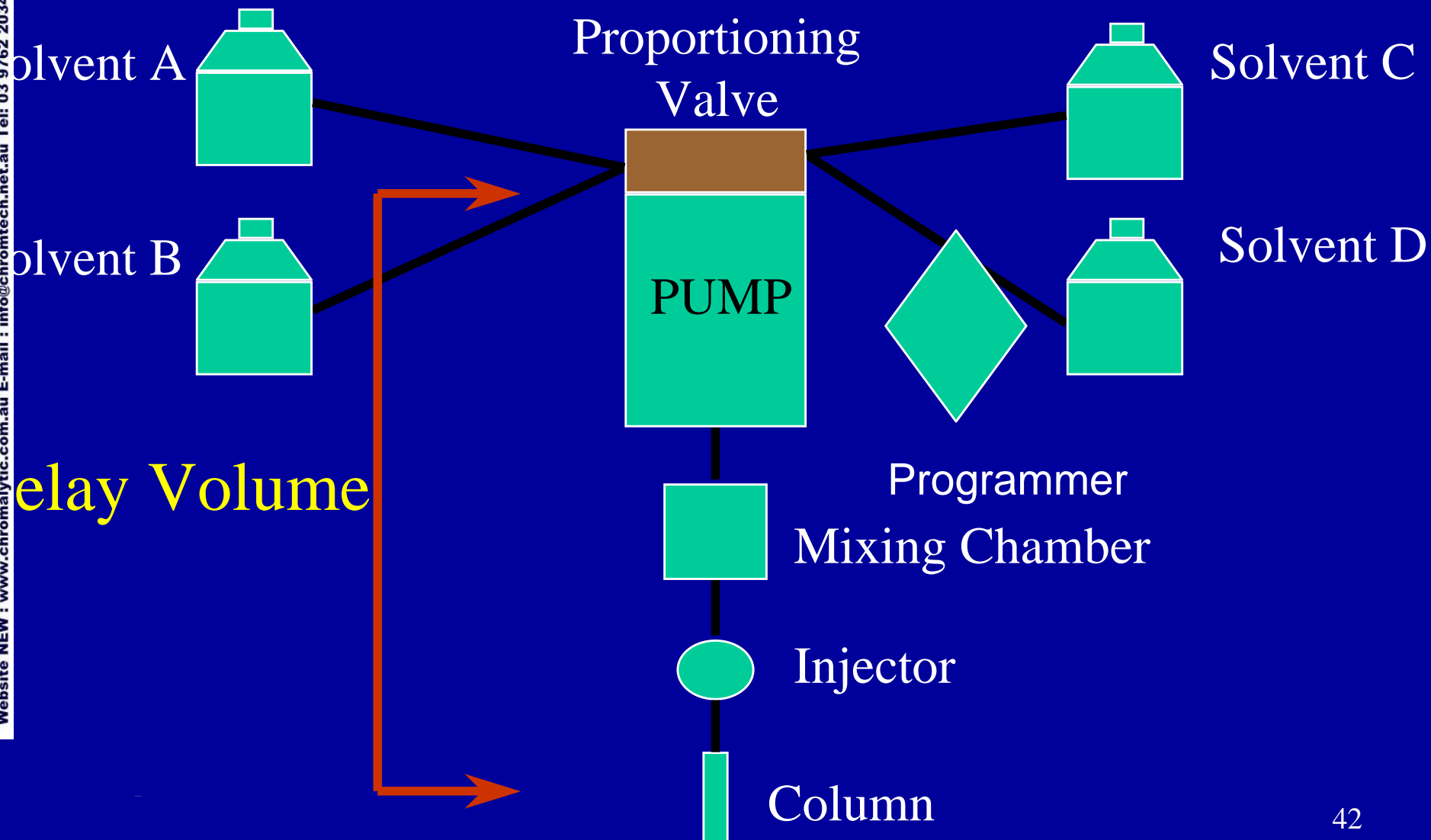
- Column re-equilibration required after every analysis
- Requires a pump with at least two-solvent capability
- Not compatible with some forms of detection (RI, EC)
- More variables to control for reproducibility
- Delay volume becomes important
  - Volume of mobile phase contained in the HPLC system between pump(s) and column

# High Pressure Gradient System



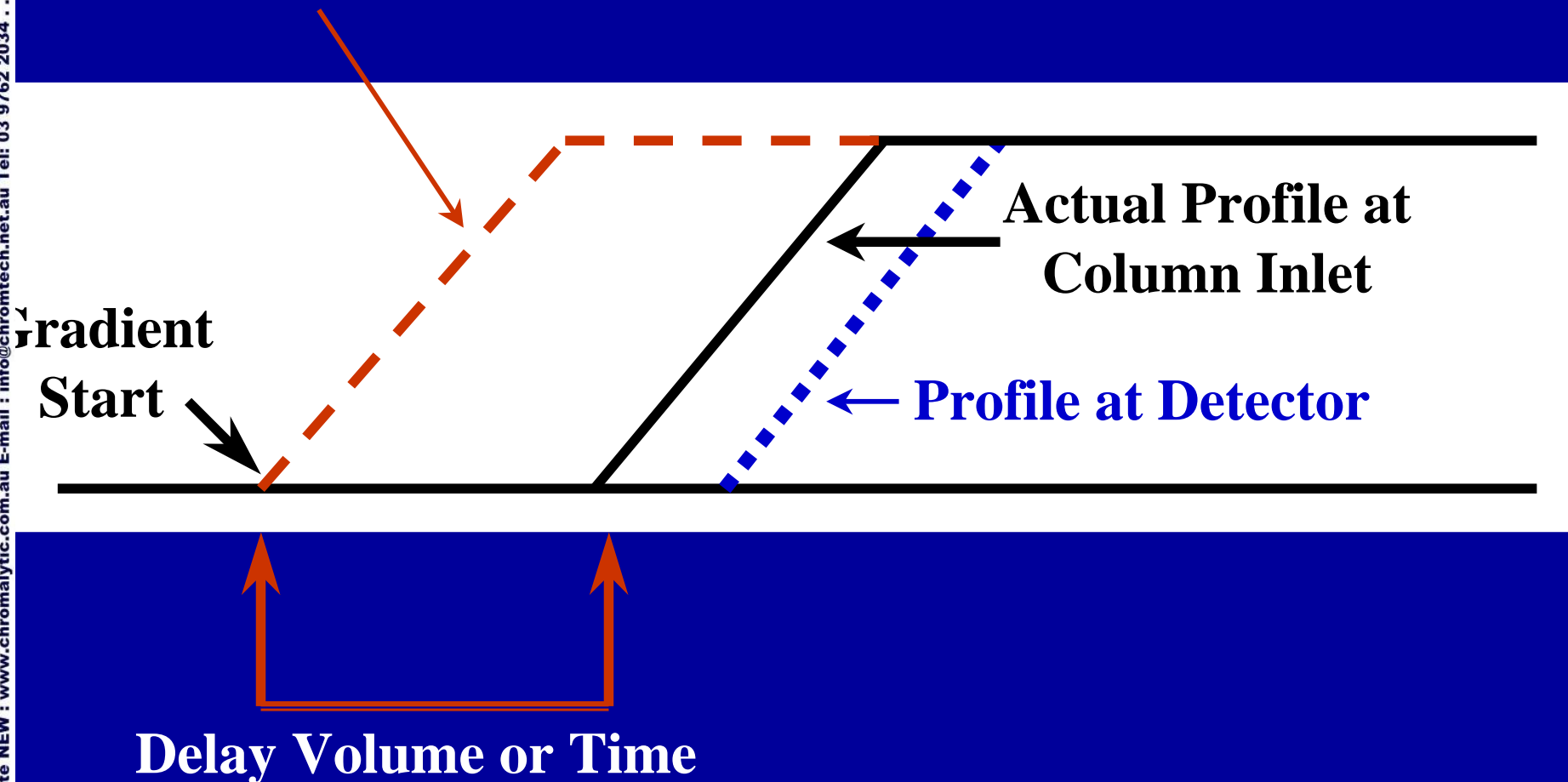
# Low Pressure Gradient System

## Quaternary



# Gradient Profile

## Electronic Profile



Measure using (A) methanol or water, (B) A + 1% acetone  
Step gradient from 100%A to 100%B, UV @ 265nm

# Gradient Variables

- Solvent selection and mobile phase composition
- Gradient shape
- Gradient steepness
- Duration and position of isocratic conditions
- Pressure and flow

# Tips for a Successful Gradient Run

- Keep it as simple as possible
- Be aware that delay volumes will vary from instrument to instrument
- Make sure post run equilibration time is adequate to return column to initial conditions
- Pre-mix mobile phase modifiers
- Pre-mix solvents with poor miscibility
- Avoid ion-pair gradients



# Mobile Phase Selection

## pKa and Mobile Phase pH

pH is an important consideration in method development  
At a pH close to the pKa, peak distortion results  
Partial dissociation of a weak acid or base into its  
conjugate form



Dissociation of a weak acid

$$\text{pH} = \text{pK} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Henderson-Hasselbalch Equation

# Buffers for Reverse Phase HPLC

pH Range	Buffer	UV cutoff (nm)
1.1 - 3.1 6.2 - 8.2 11.3 - 13.3	phosphate	210
2.1 - 4.1 3.7 - 5.7 4.4 - 6.4	citrate	250
3.8 - 5.8	acetate	230
7.3 - 9.3	tris(hydroxymethyl) aminomethane	220
8.2 - 10.2	borate	210

# Mobile Phase Selection

## Incorrect pH for Tetracyclines

- The pKa for tetracyclines is ~3.3
- At pH 3, the form of the analyte is in a ratio of 2:1 weak acid to conjugate base

$$\log \frac{[A^-]}{[HA]} = \text{pH} - \text{pK}$$

$$\log \frac{[A^-]}{[HA]} = 3 - 3.3 = -0.3$$

$$\frac{[A^-]}{[HA]} = 0.5$$

# Tetracyclines at pH 3

## Peak List:

1. Oxytetracycline
2. Tetracycline
3. Demeclocycline
4. Chlortetracycline
5. Doxycycline

## Conditions:

Column: Pinnacle ODS Amine

Dimensions: 150 x 4.6 mm

Particle Size: 5  $\mu$ m

Pore Size: 120A

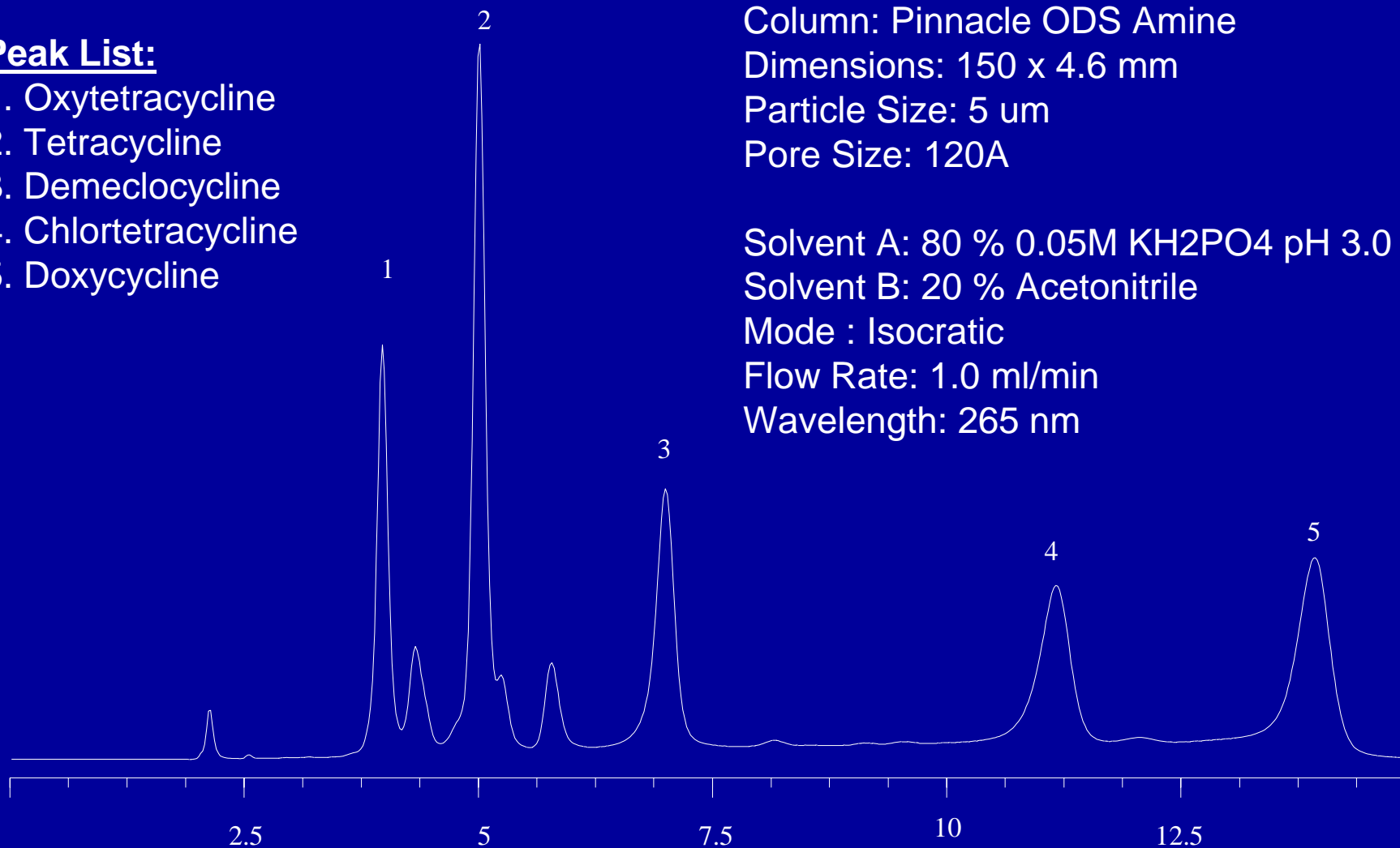
Solvent A: 80 % 0.05M  $\text{KH}_2\text{PO}_4$  pH 3.0

Solvent B: 20 % Acetonitrile

Mode : Isocratic

Flow Rate: 1.0 ml/min

Wavelength: 265 nm



# Tetracyclines at pH 2

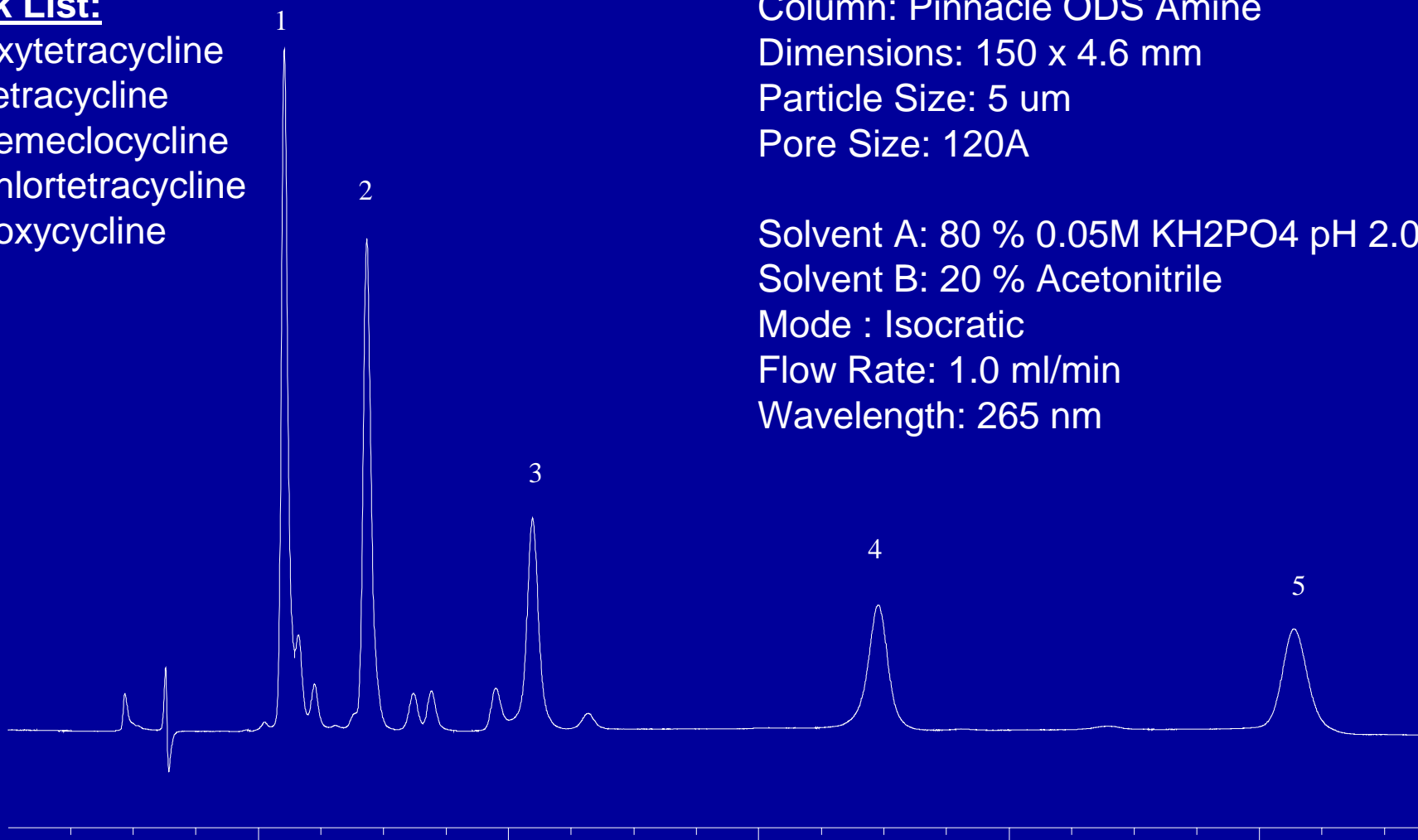
## Peak List:

Oxytetracycline  
Tetracycline  
Demeclocycline  
Chlortetracycline  
Doxycycline

## Conditions:

Column: Pinnacle ODS Amine  
Dimensions: 150 x 4.6 mm  
Particle Size: 5  $\mu$ m  
Pore Size: 120A

Solvent A: 80 % 0.05M  $\text{KH}_2\text{PO}_4$  pH 2.0  
Solvent B: 20 % Acetonitrile  
Mode : Isocratic  
Flow Rate: 1.0 ml/min  
Wavelength: 265 nm



# The Resolution Equation

- The ultimate goal of chromatography is to resolve two or more compounds into separate peaks.
- Resolution ( $R_s$ ) is defined by the distance between two peaks relative to the widths of the peaks

$$R = \Delta t_r / W$$

# The Resolution Equation

$$R = \frac{1}{4} \left( \frac{\alpha - 1}{\alpha} \right) (\sqrt{N}) \left( \frac{\kappa'}{1 + \kappa'} \right)$$

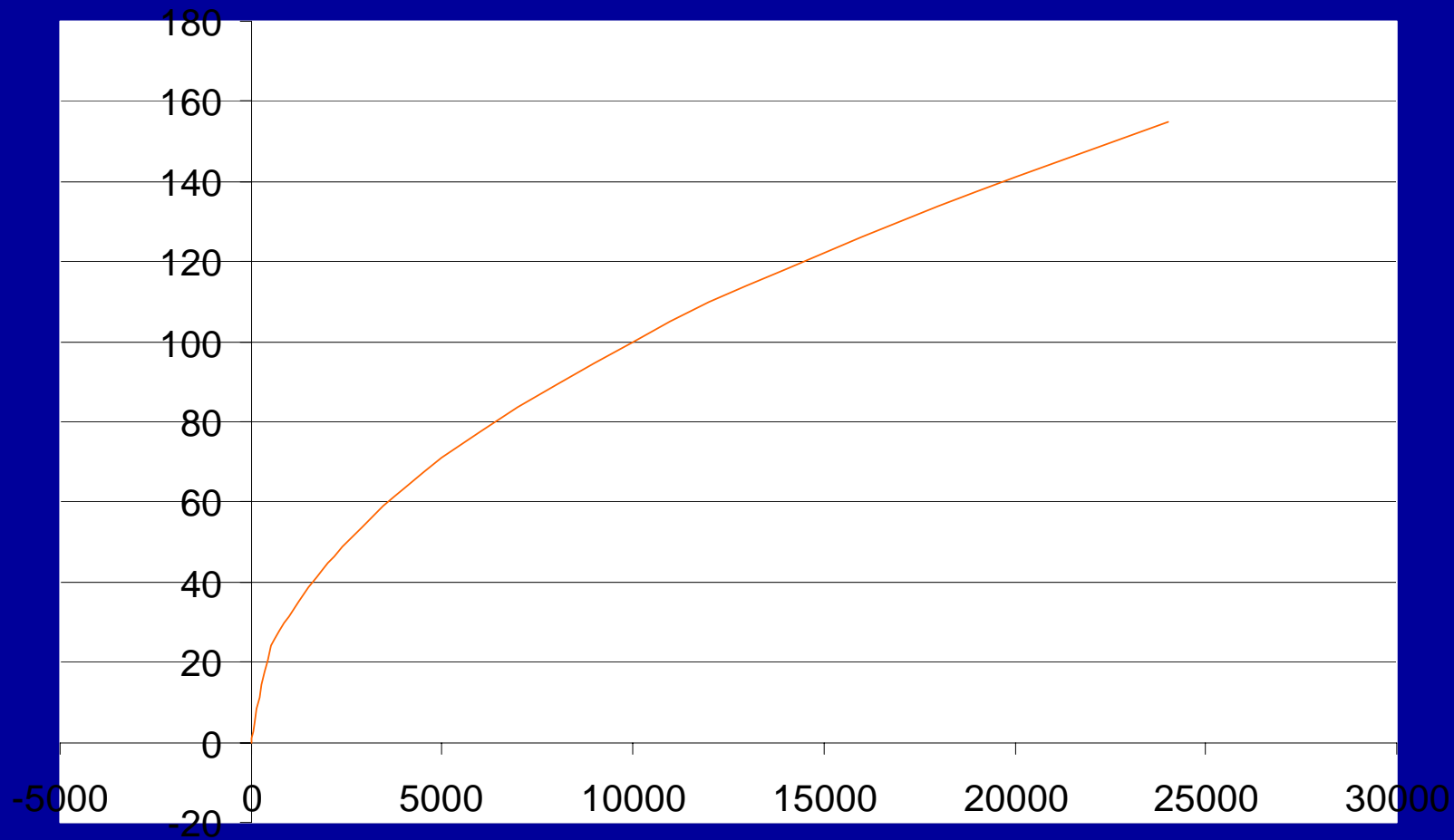
Selectivity

Efficiency

Capacity

# Effect of N on Resolution

R



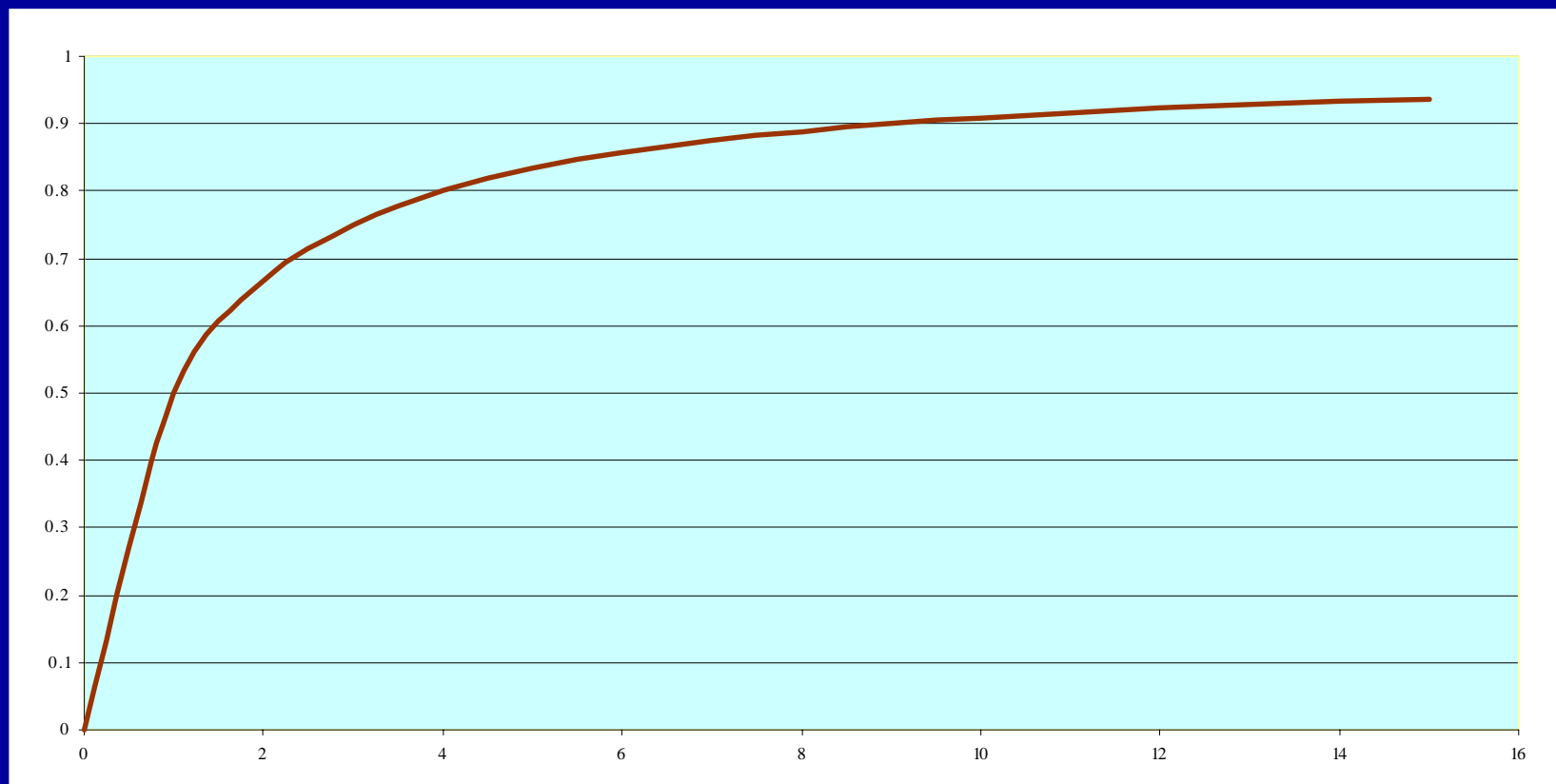


# Effect of N on Resolution

- Resolution is proportional to square root of N
  - To double resolution, N would have to increase by a factor of 4
- N can be increased with longer column or smaller particle size
  - $R \propto \sqrt{N}$
  - $N \propto \text{column length}$
  - $N \propto 1/\text{particle diameter}$
  - Limited by column pressure

# Effect of $k'$ on Resolution

R



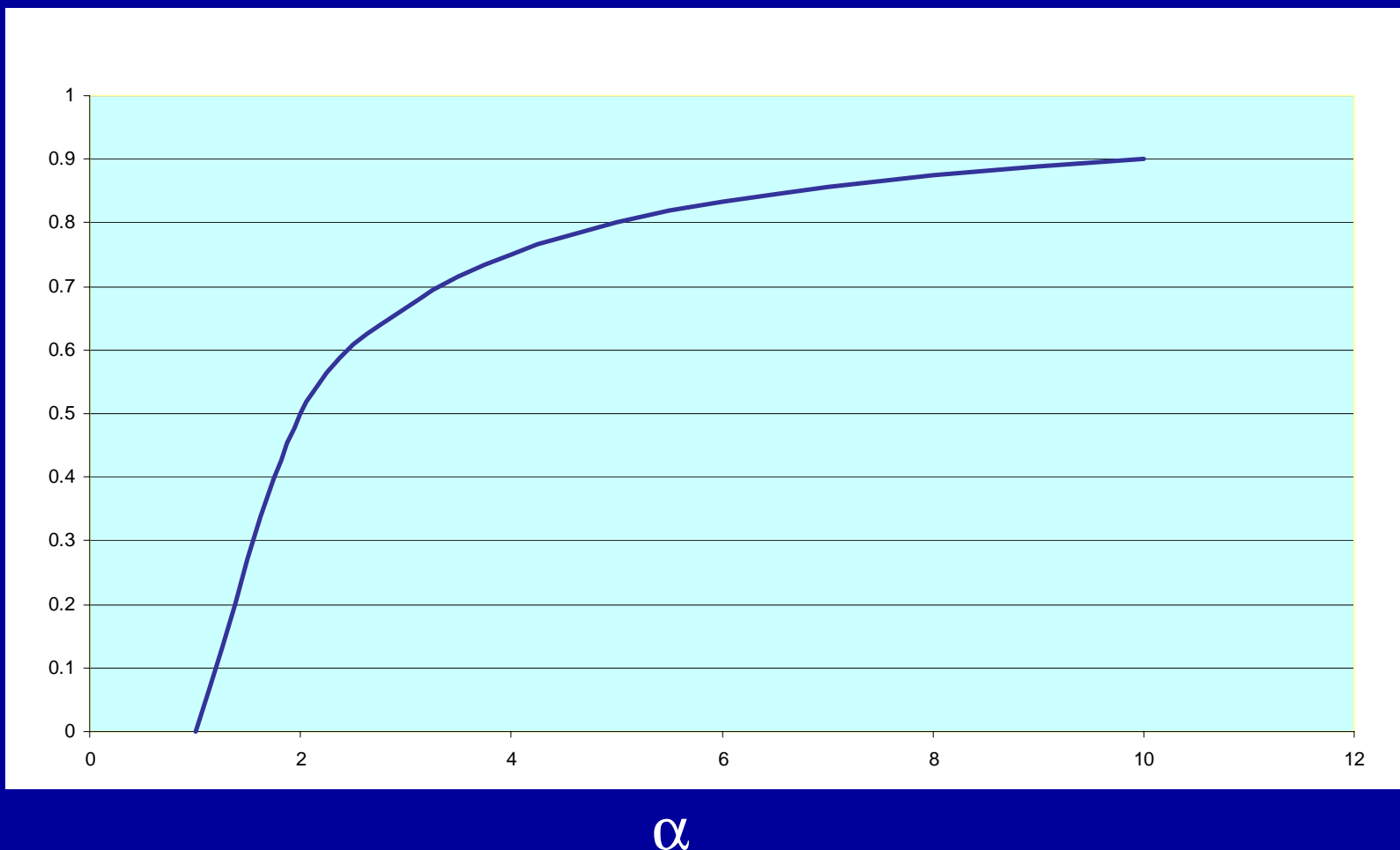
$k'$

# Effect of $k'$ on Resolution

- Practical limitation on how much  $R$  can be increased by changing  $k'$
- Increasing  $k'$  has increasingly smaller benefit to  $R$ , especially at  $k' > 5$
- Increasing  $k'$  comes at cost of greater analysis time
- $k'$  is changed by altering mobile phase strength

# Effect of $\alpha$ on Resolution

R



$\alpha$

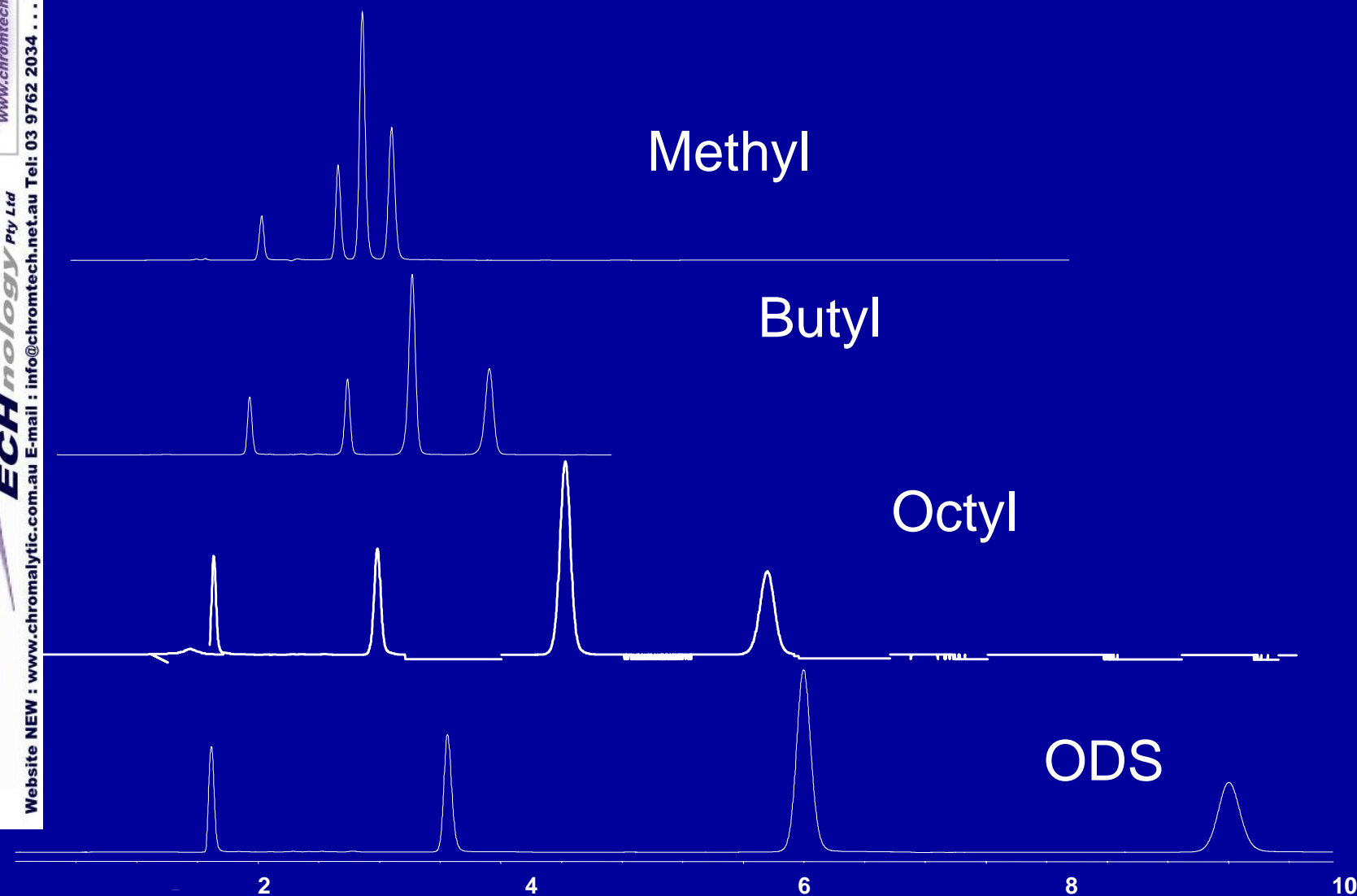
# Effect of $\alpha$ on Resolution

- Changing  $\alpha$  is the most effective way to increase resolution
- $\alpha$  can be altered over wide range without sacrificing time or higher pressure
- Adjust  $\alpha$  by changing stationary phase or mobile phase solvents

# Method Development Based on the Resolution Equation

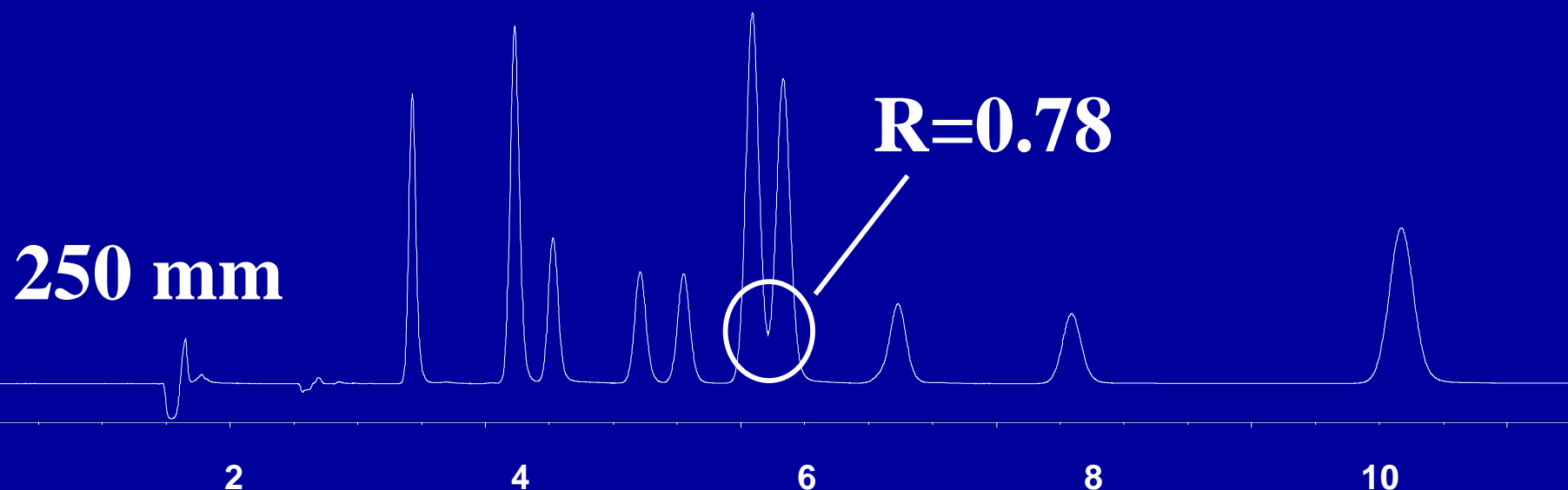
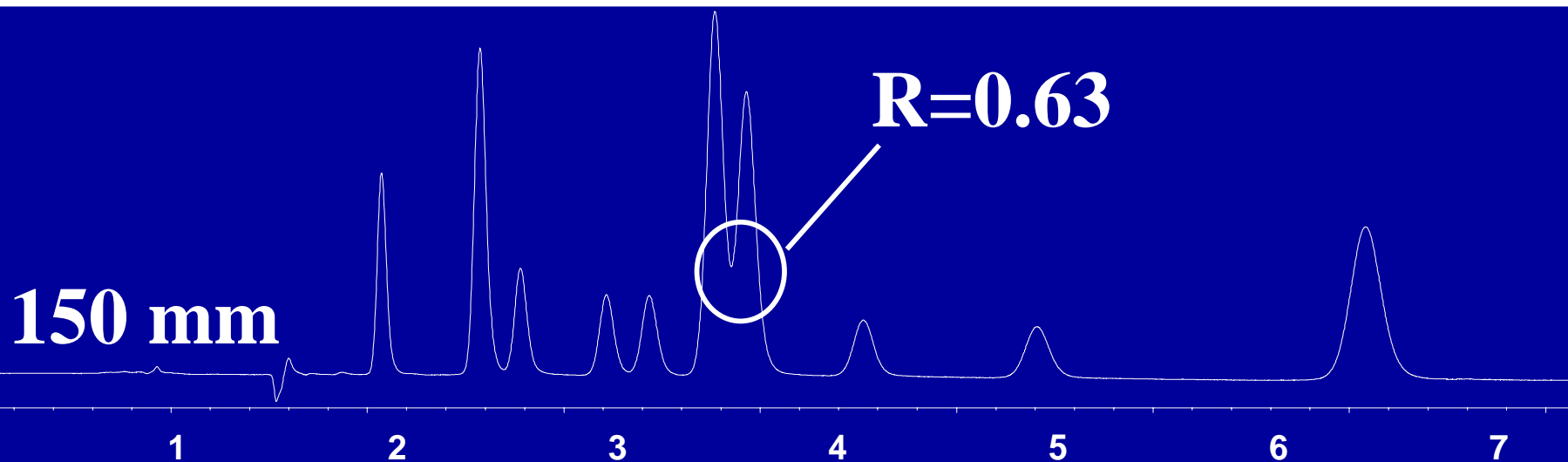
1. Adjust  $k'$  to optimum range (~2-5)
2. If not close to desired resolution, adjust selectivity by changing either mobile phase or stationary phase
  - Return to step 1
3. If close to desired resolution, increase  $N$  by increasing column length or decreasing particle size

# Stationary Phase Type ( $\alpha$ )



# Barbiturates

## 150 mm vs 250 mm Length





# Triazines

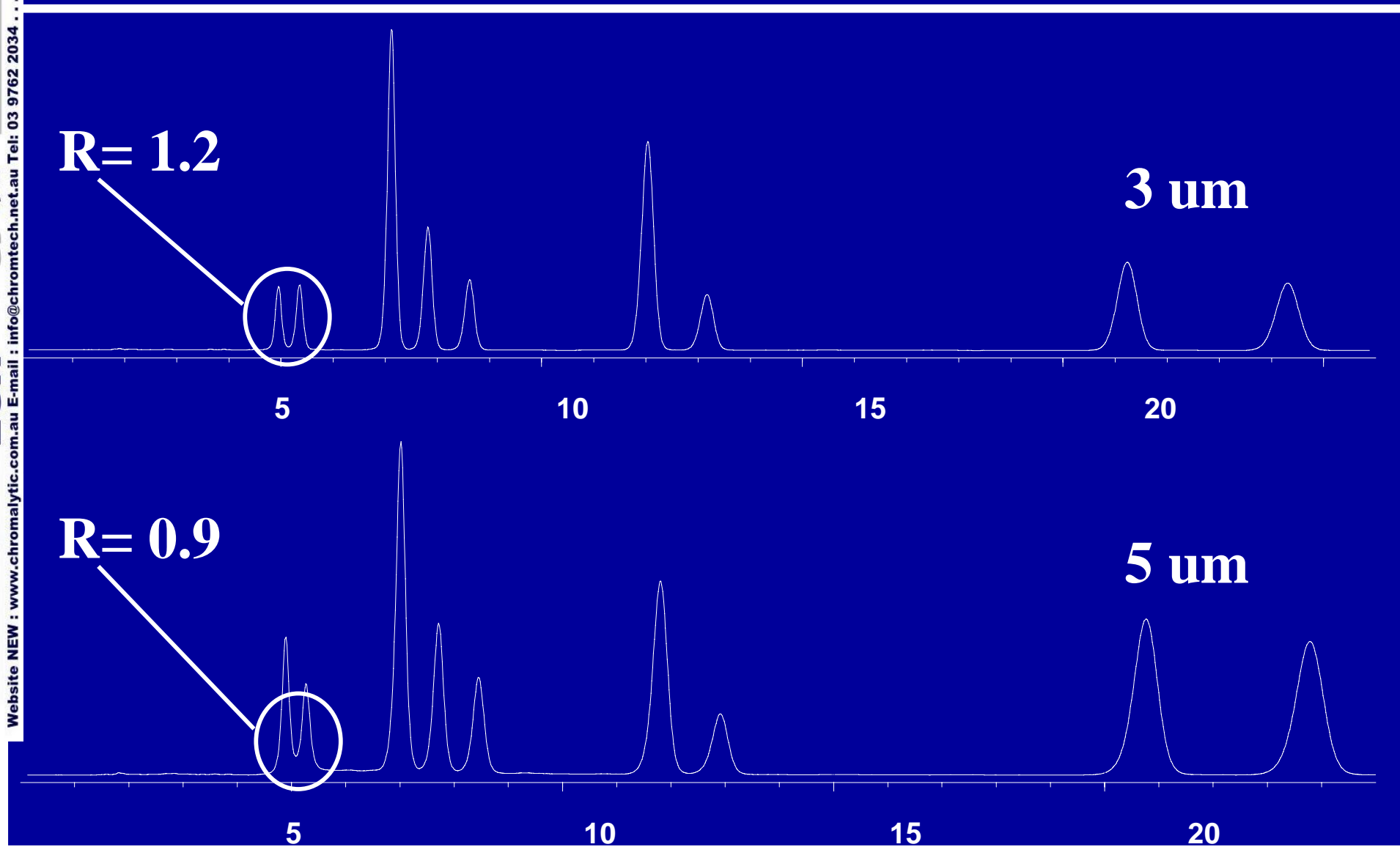
## 3 um vs 5 um dp

$R = 1.2$

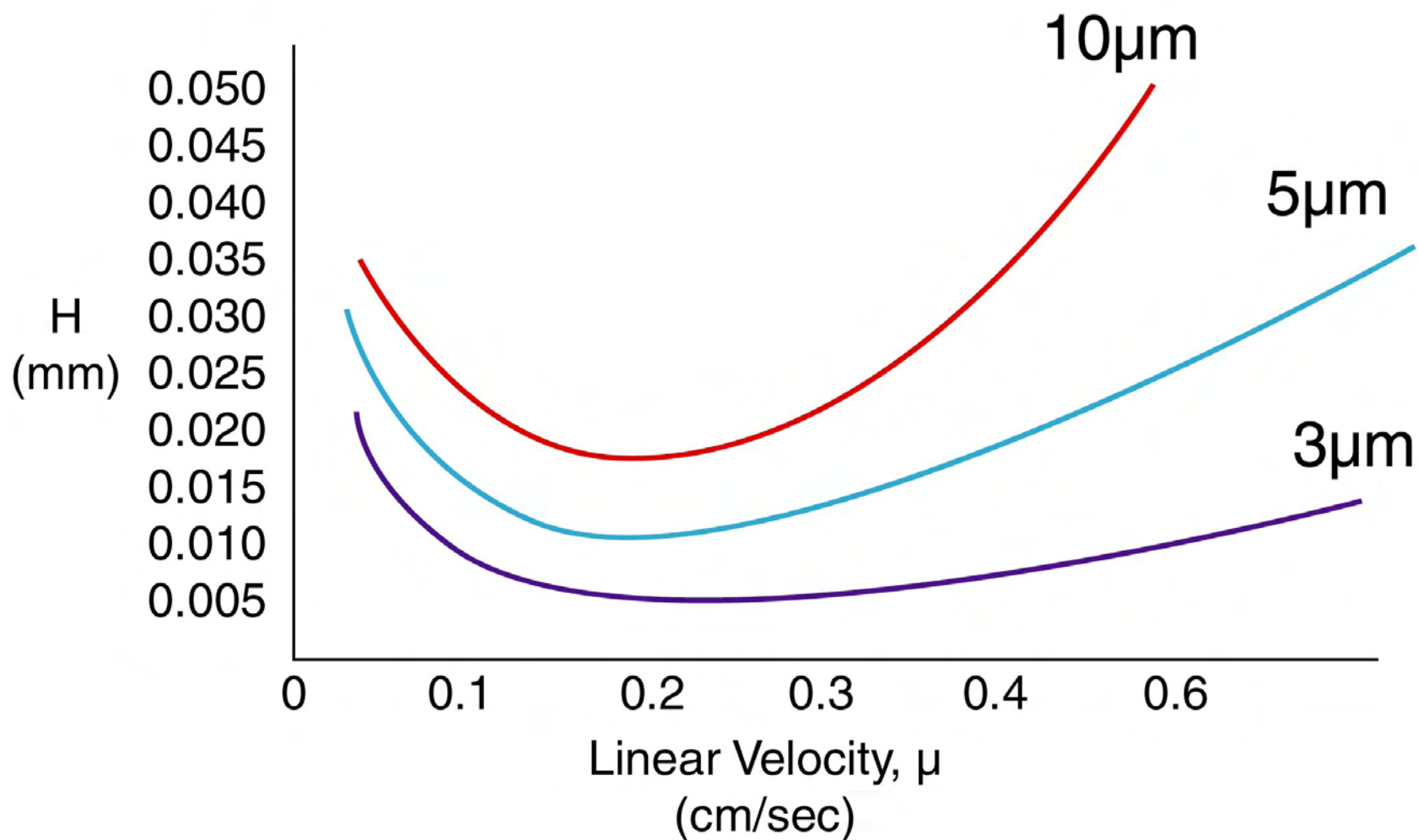
3 um

$R = 0.9$

5 um



# Van Deemter Plot



# Approximate Optimum Flow Rate

Column ID (mm)	Flow Rate (mL/min)	
	<u>3<math>\mu</math>m</u>	<u>5<math>\mu</math>m</u>
1.0	0.075	0.050
2.1	0.300	0.200
3.2	0.750	0.500
4.6	1.5	1.0

# Temperature Control

- Slightly above ambient temperature (i.e. 30°C) to maximize temperature stability
- Temperature affects retention and in some cases selectivity
- Increasing temperature can decrease pressure by reducing mobile phase viscosity
- Maximum recommended temperature for most columns is 80°C

# HPLC Method Validation

- Ensure that the method will provide similar results over a long period of time in other labs
- Challenge the method to determine the limits of allowed variability for each method parameter
- International Council on Harmonization (ICH)
  - Guidelines for the validation of analytical methods
  - Applied universally by all agencies and all analytical methods

# ICH Method Development Parameters

- Precision
- Accuracy
- Limit of Detection
- Limit of Quantitation
- Specificity
- Linearity
- Range
- Robustness
- System Suitability

# Summary of Method Development

- Define goals
- Gather information
- Select mode
- Adjust  $k'$
- Adjust  $\alpha$
- Optimize N if needed
- Know when to quit

# Liquid Injection Techniques

- Flash Vaporization
  - Split injection
  - Splitless injection
  - Direct - Uniliner w/Hole



# Flash Vaporization - Split Injection

## Advantages:

- Easy to use
- Easy to automate
- Ideal for dirty samples

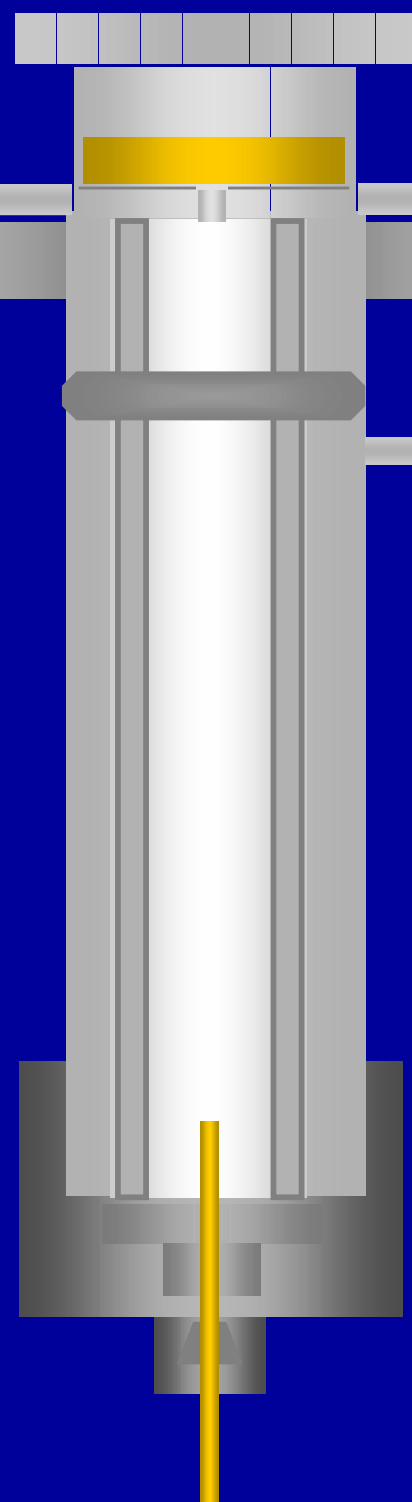
## Disadvantages:

- Sample degradation
- Backflash
- Discrimination
- Not a trace technique



# Injection Port Components

## Flash Vaporization Split Injection



☐ Column Head Pressure

Total Flow

☐

Split Vent

☐

Septum Purge

☐

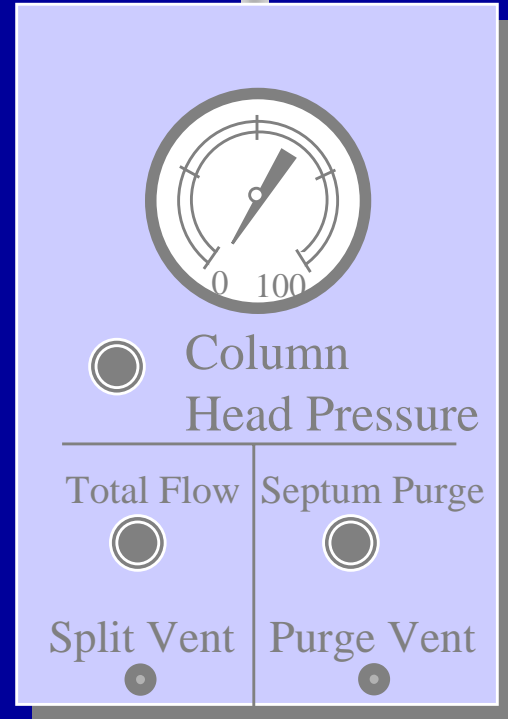
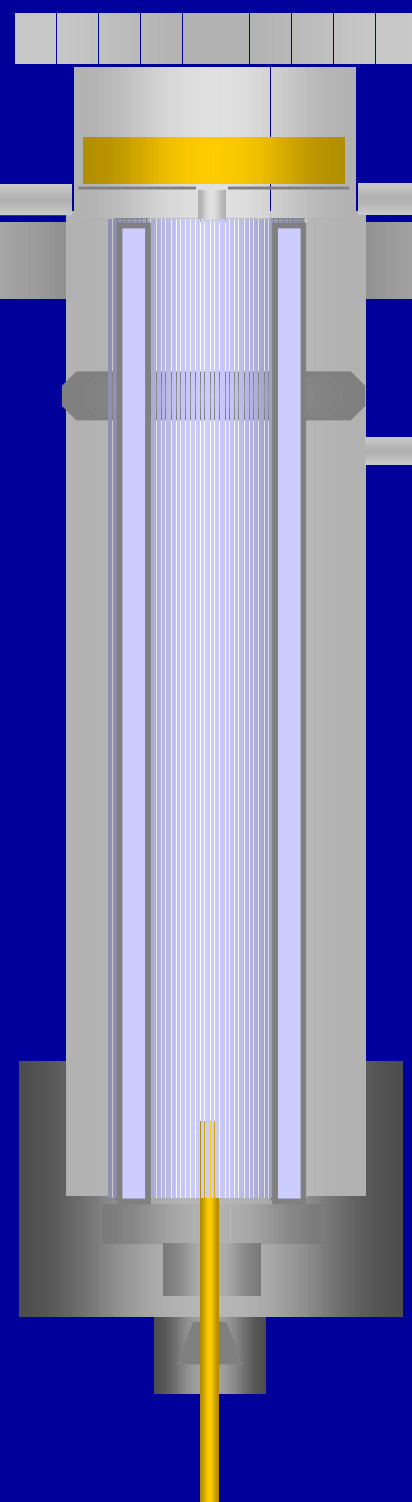
Purge Vent

☐

# Injection Port Components

Liner or 'Sleeve'

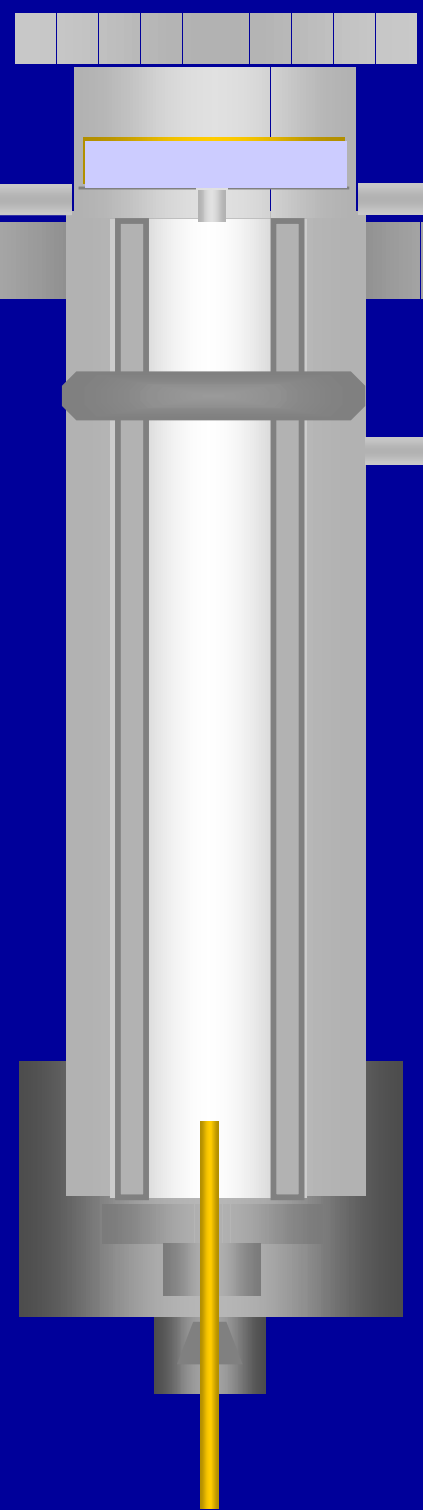
Flash  
Vaporization  
Split Injection



# Injection Port Components

Septum

Flash  
Vaporization  
Split Injection



☐ Column Head Pressure

Total Flow

☐

Split Vent

☐

Septum Purge

☐

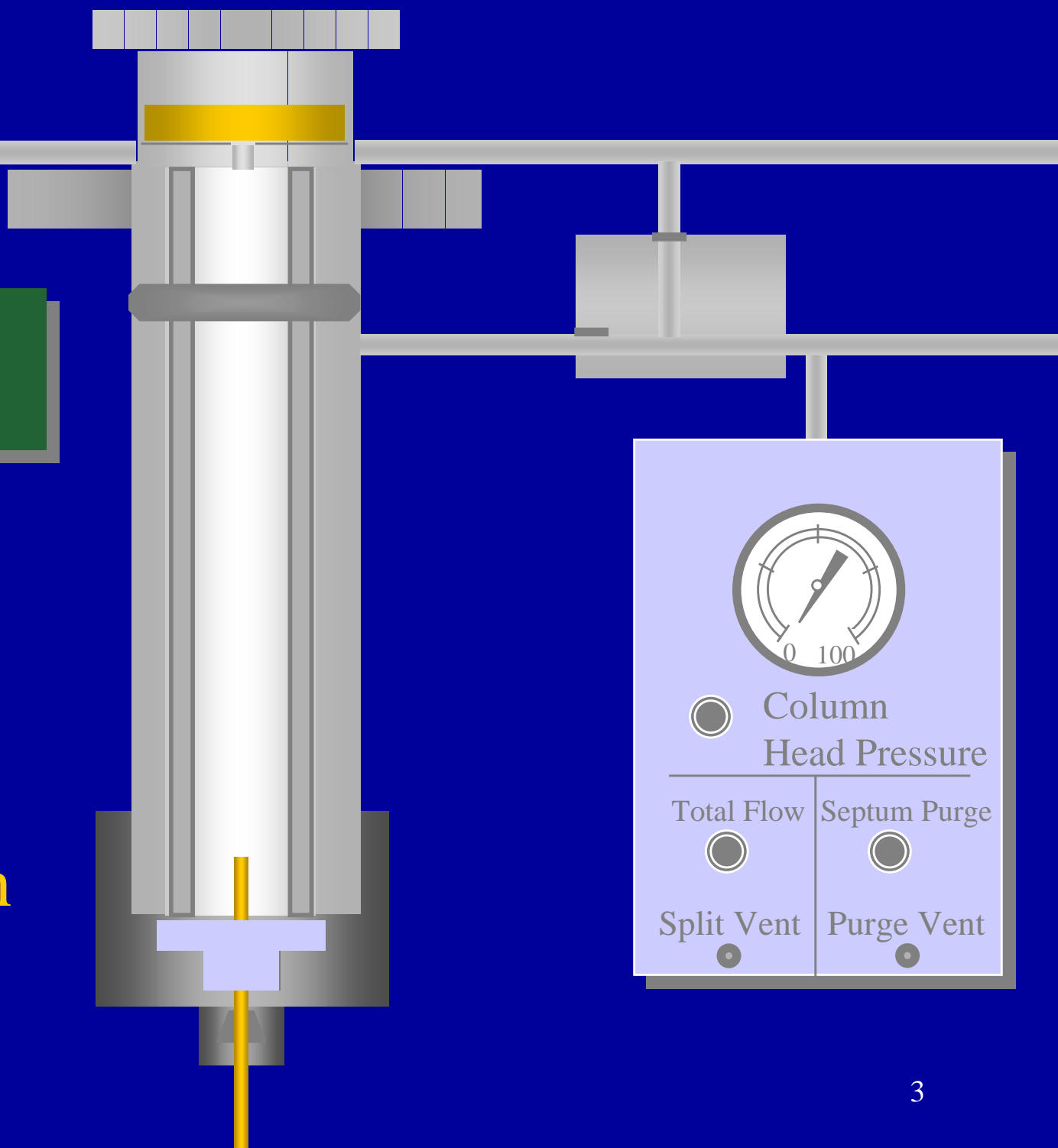
Purge Vent

☐

# Injection Port Components

Inlet Seal

Flash  
Vaporization  
Split Injection



0 100

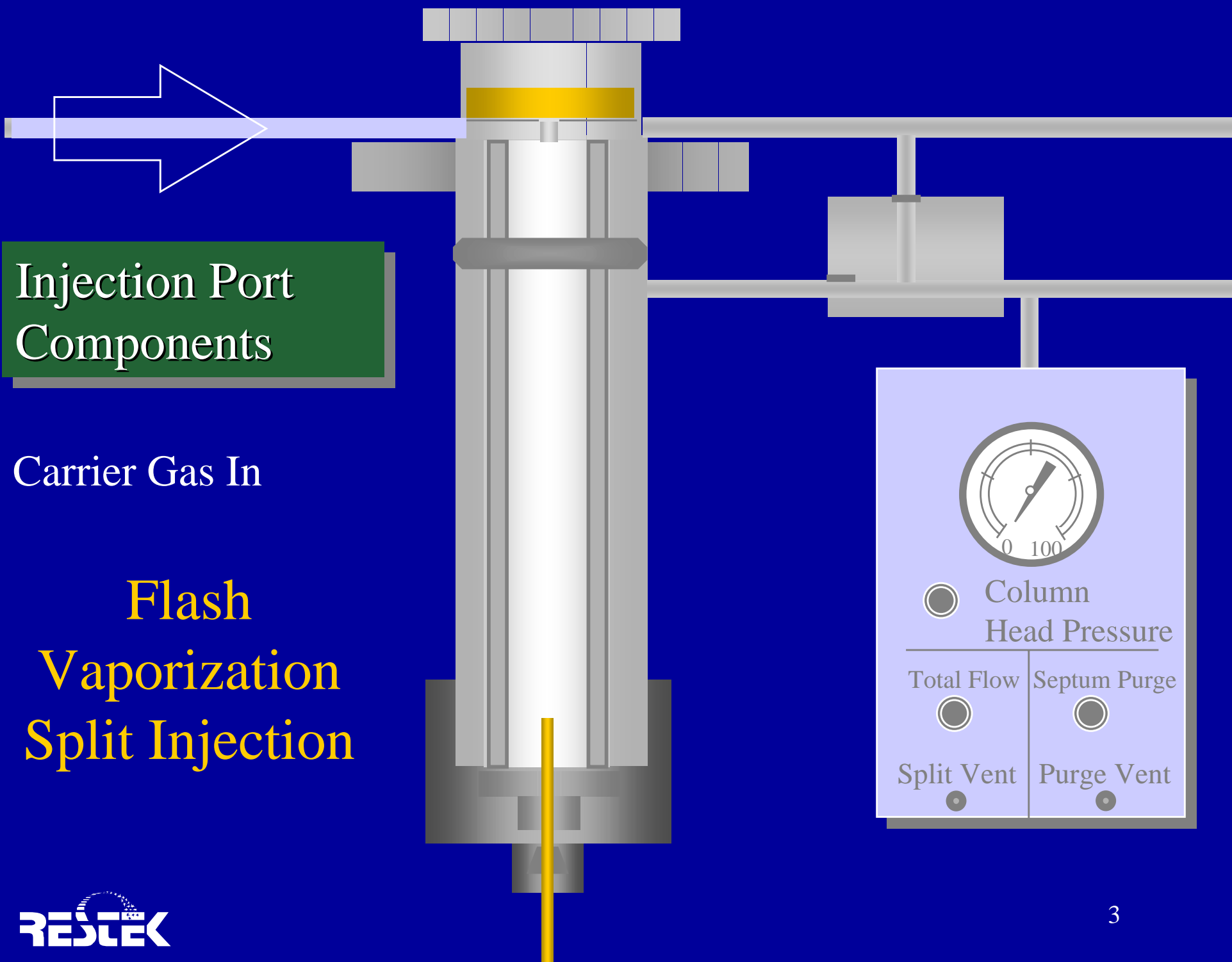
Column  
Head Pressure

Total Flow	Septum Purge
Split Vent	Purge Vent

# Injection Port Components

Carrier Gas In

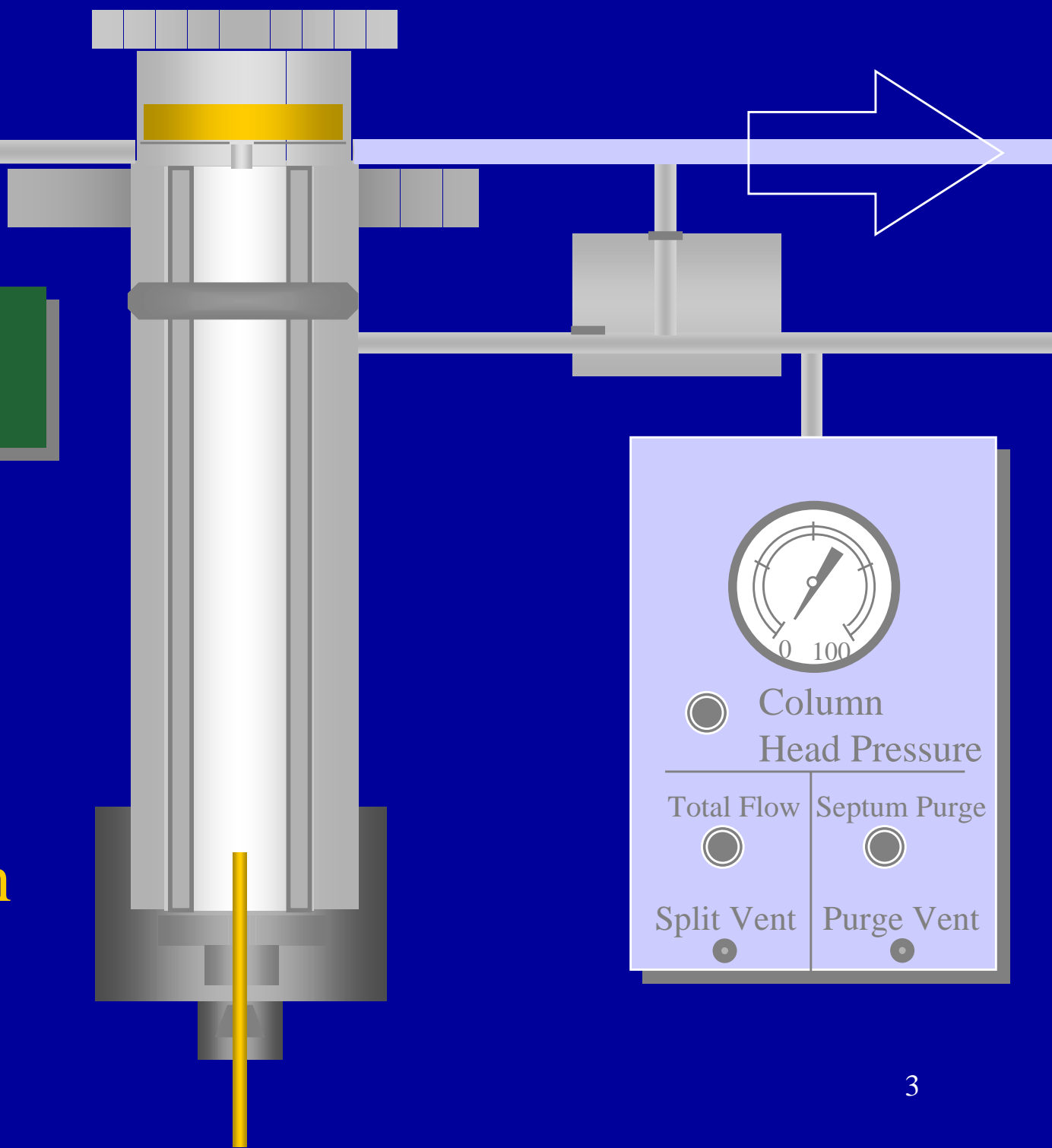
Flash  
Vaporization  
Split Injection



# Injection Port Components

Septum purge

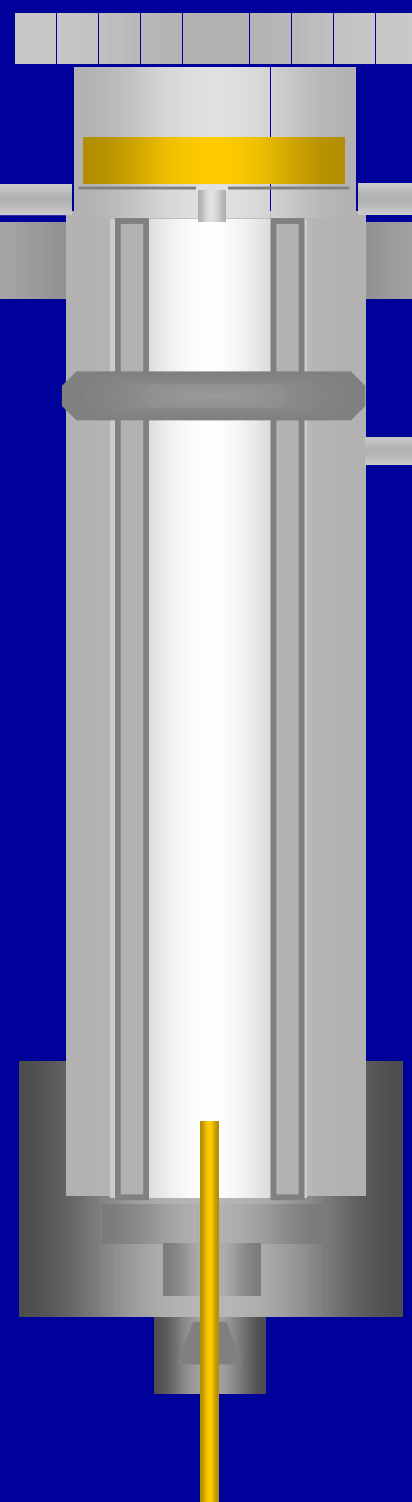
Flash  
Vaporization  
Split Injection



# Injection Port Components

Solenoid Valve

Flash  
Vaporization  
Split Injection



☐ Column Head Pressure

Total Flow

☐

Split Vent

☐

Septum Purge

☐

Purge Vent

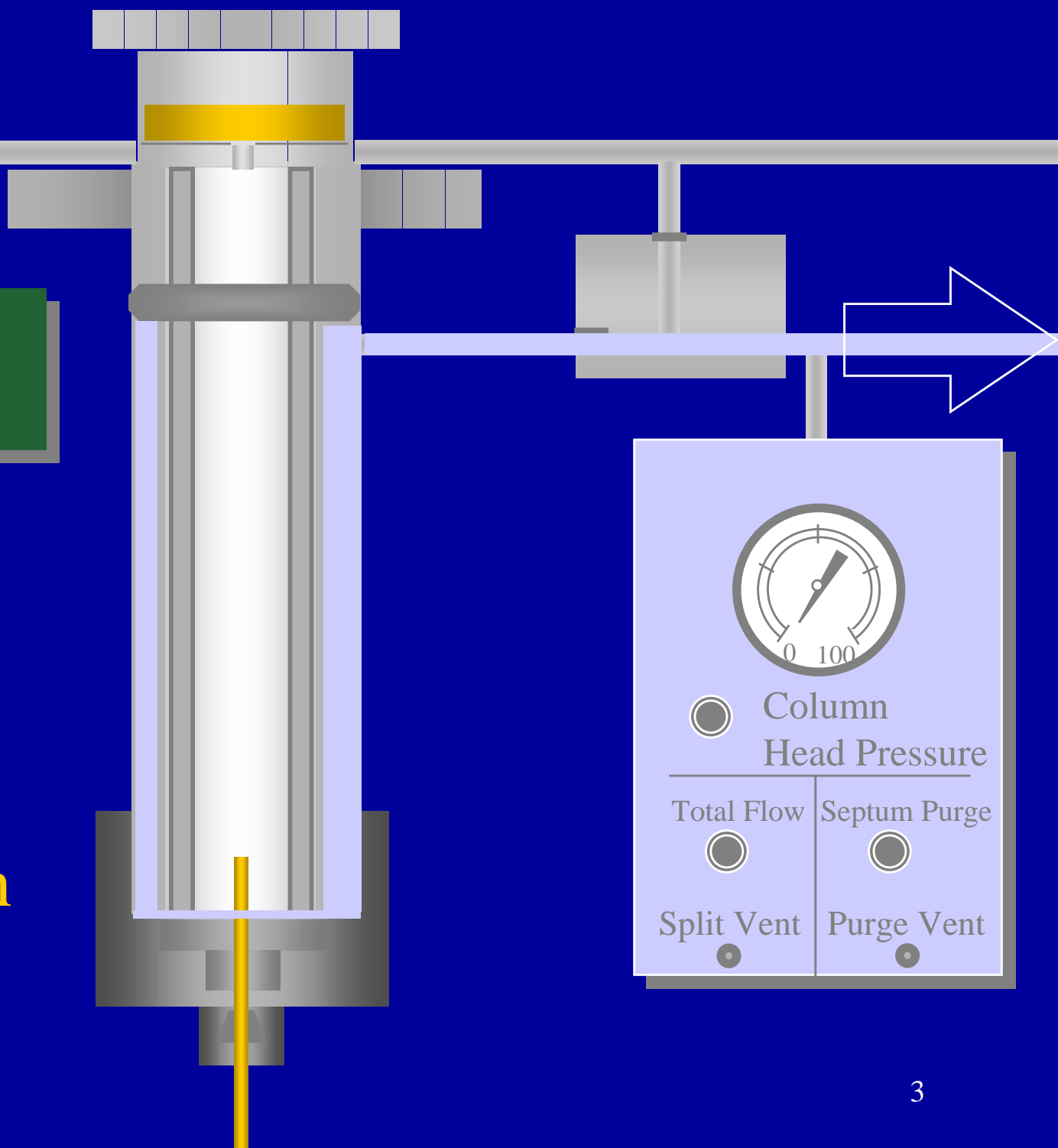
☐



# Injection Port Components

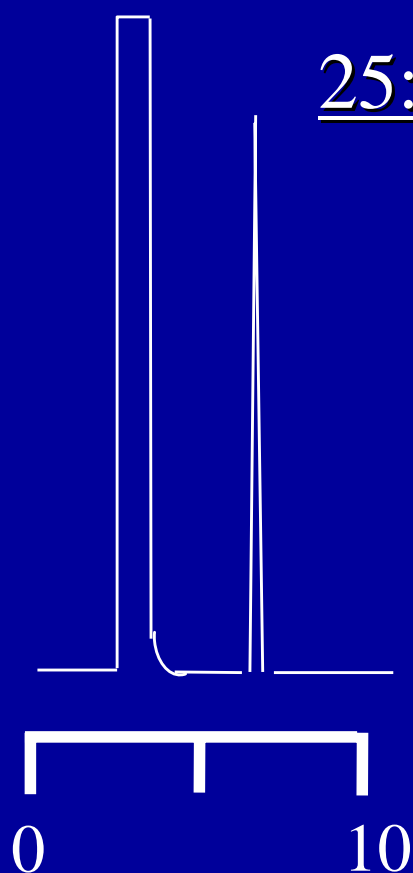
To Split Vent

Flash  
Vaporization  
Split Injection

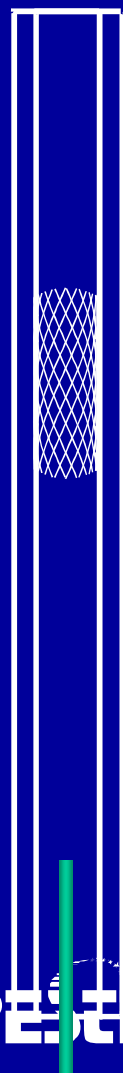


# Flash Vaporization - Split Injection

Increasing the split ratio decreases the peak area,  
if all other variables are equal.



# Split Injection Liner Designs



Split with wool  
or CarboFrit™

Use only a  
small amount  
of wool



Laminar Cup

Excellent  
vaporization,  
expensive



Cycloplitter®

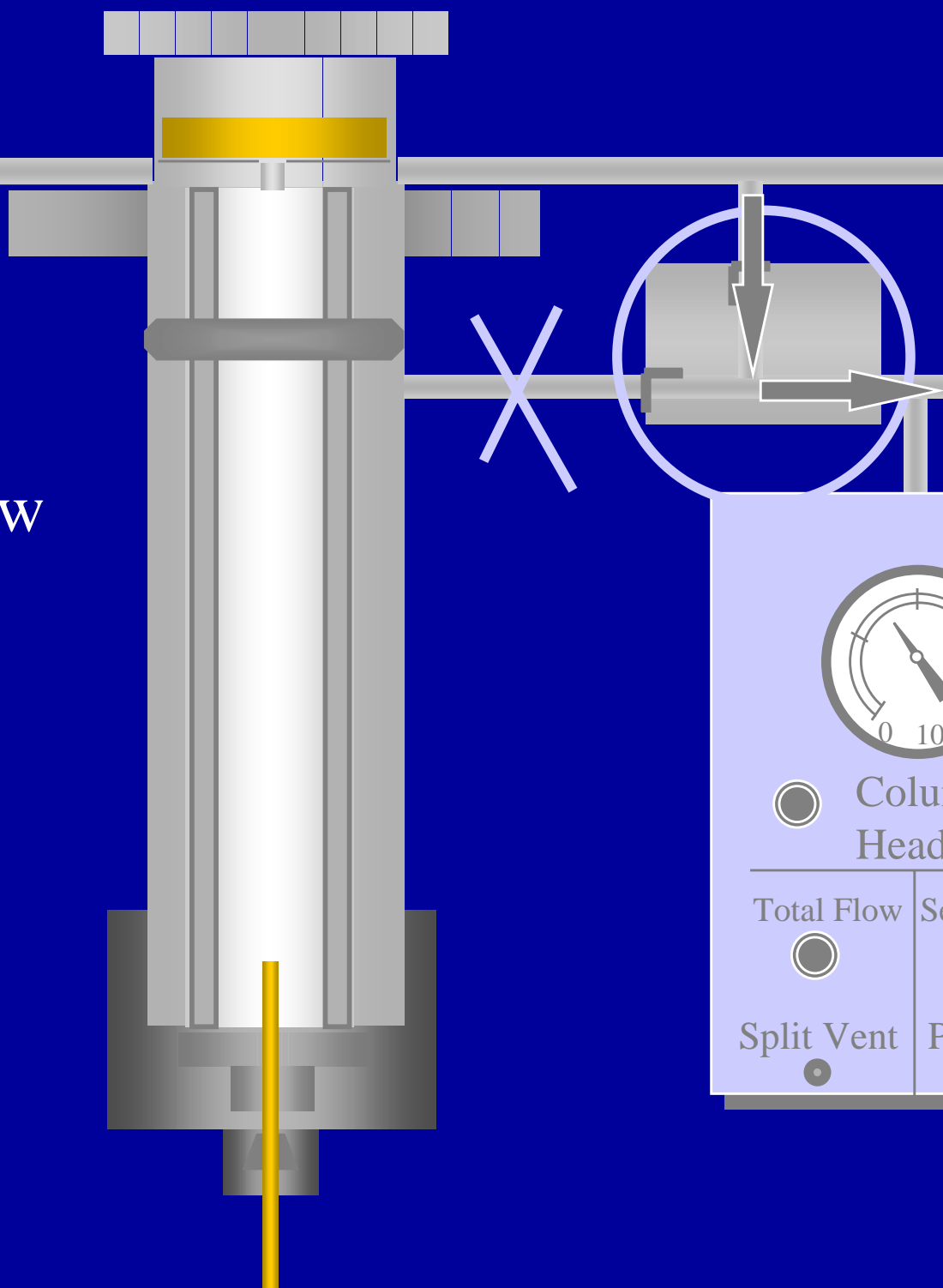
Keeps  
contamination  
out of column

# Flash Vaporization - Splitless Injection

- Used for trace analysis
- Mode of operation of a split injector
- Slow sample transfer to column
  - Long contact time with the liner promotes vaporization
  - Long initial sample bandwidth, so solvent focusing is important
  - Requires careful optimization

Solenoid valve  
controls the flow

# Splitless Injection



0 100

Column  
Head Pressure

Total Flow	Septum Purge
Split Vent	Purge Vent

# Splitless Injection Characteristics

- Slow sample velocity through liner
- Long residence time can lead to compound breakdown
  - Injection port inertness is critical
- Requires careful optimization
  - Oven temperature, solvent type, liner volume, solenoid hold time...

# Splitless Injection

## Factors Affecting Performance

- Hold time
- Solvent focusing:
  - Solvent boiling point
  - Solvent polarity
- Incomplete sample vaporization due to rapid auto injection
- Surface deactivation

# Factors Affecting Splitless Injection Hold Times

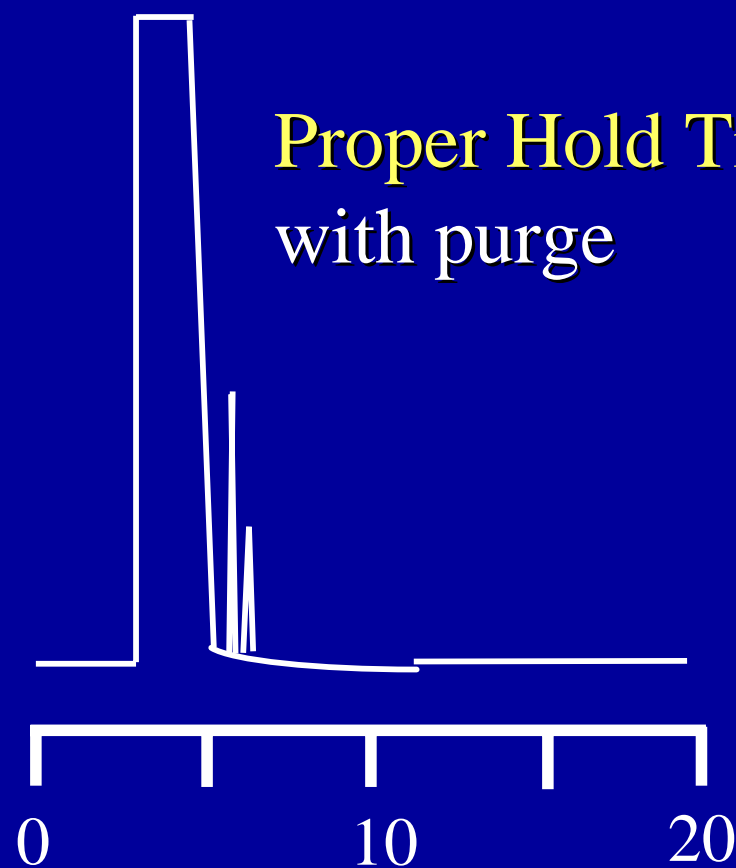
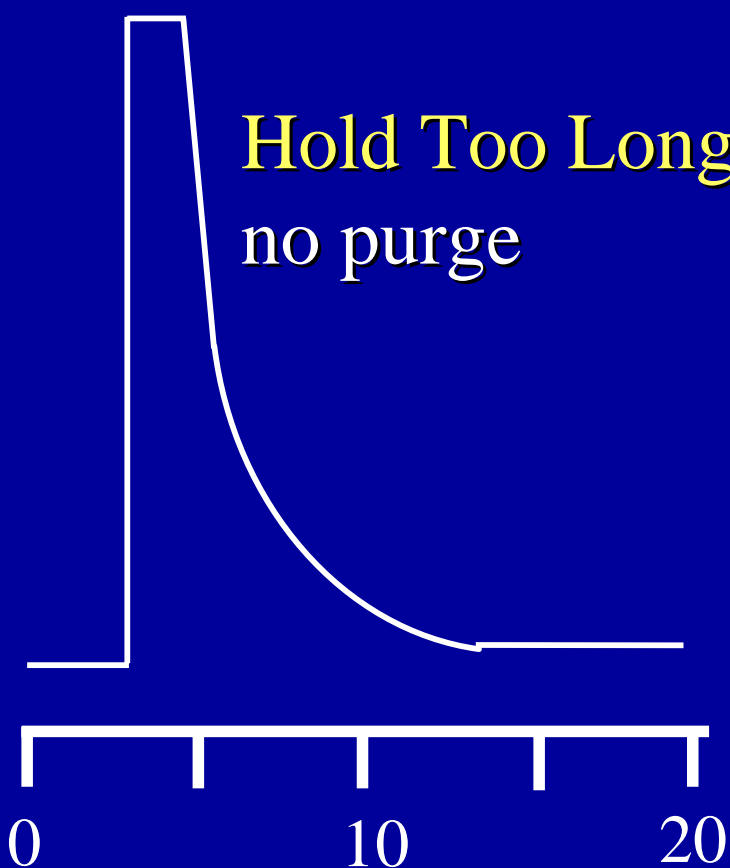
Column ID (mm)	Column Flow Rate (cc/min.) He	Approx. Hold Time
0.18	0.3	3 min
0.25	0.7	1.5 min
0.32	1.2	45 sec
0.53	2.6	30 sec

Determine  
empirically

Note: based on a 2 $\mu$ L injection volume of CH<sub>2</sub>Cl<sub>2</sub> = 0.8 mL sample expansion value @ 250°C & 10 psig.



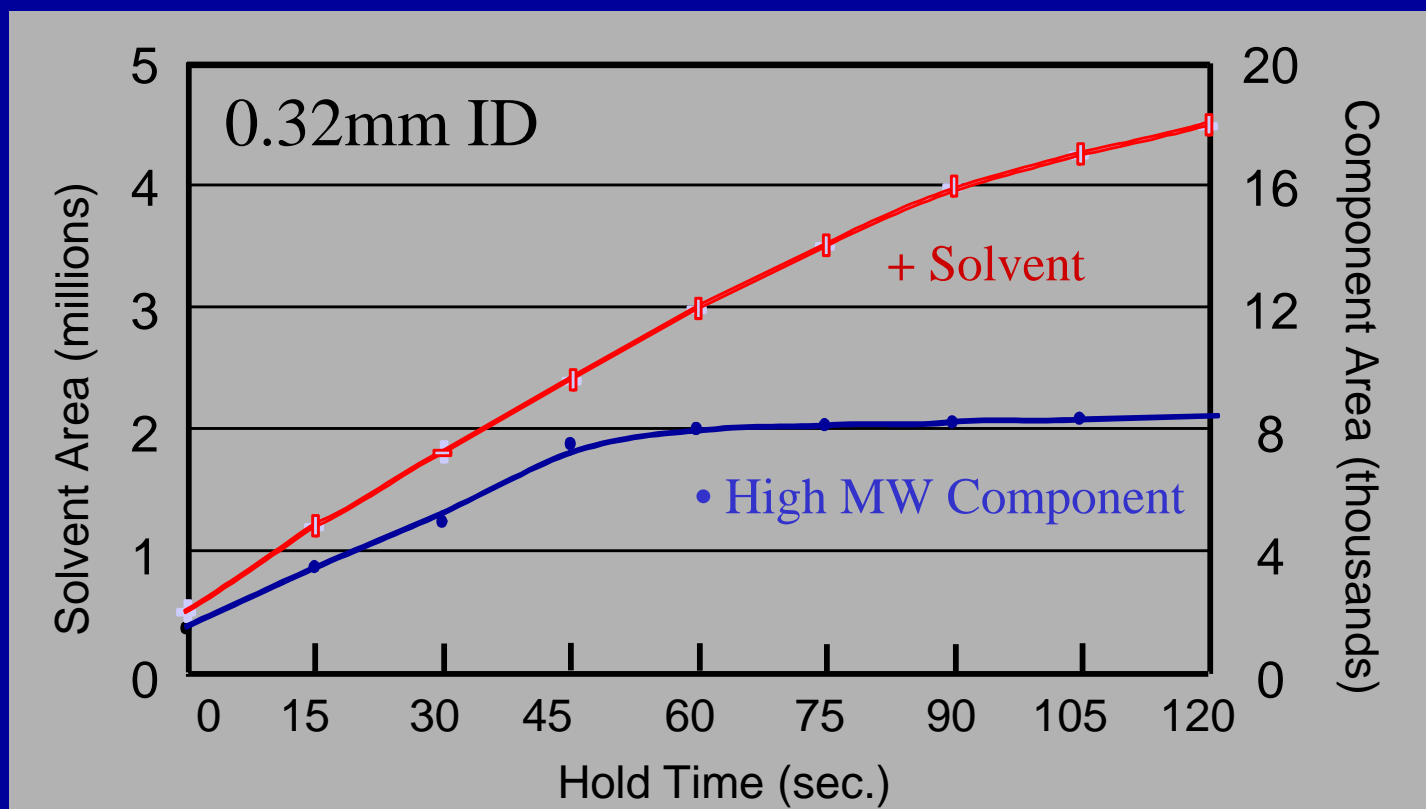
# Factors Affecting Splitless Injection Hold Times



Time (min)

# Factors Affecting Splitless Injection

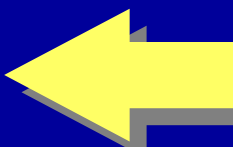
## Hold Time Optimization



# Factors Affecting Splitless Injection

## Solvent Focusing, cont'd

	(°C)
pentane	36
methylene chloride	40
acetone	56
chloroform	62
methanol	64.5
hexane	69
1,1,1 trichloroethane	74.1
ethyl acetate	77
ethanol	78.3

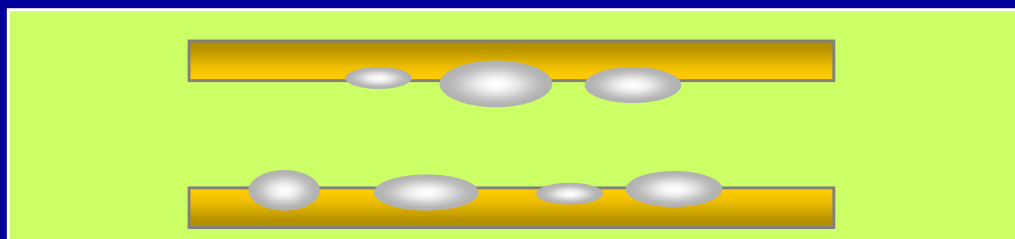


Subambient cooling will improve chromatography

Note: When the first component has a much higher bp than the solvent, you may inject above the bp of the solvent (Analyte Focusing, e.g., analysis of chlorinated pesticides)

# Solvent Focusing

## Solvent Polarity, cont'd



Mismatched Polarity:

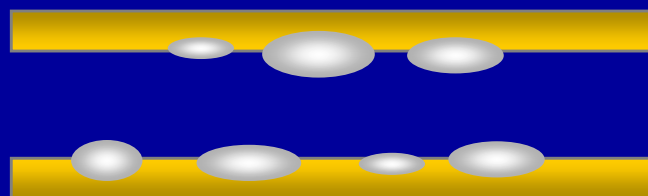
The solvent will bead or puddle, causing non-uniform analyte focusing and split peaks



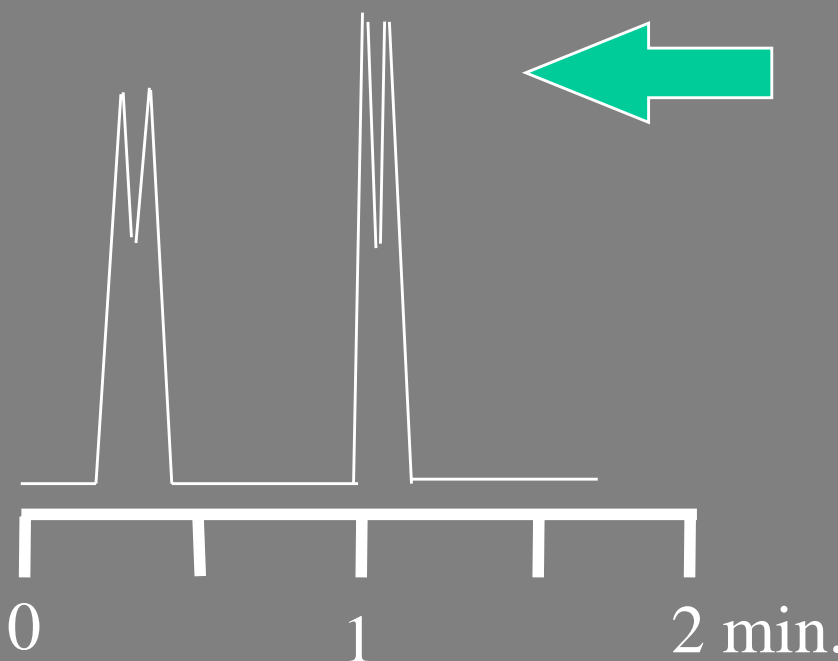
Polarity Match:

The solvent wets the stationary phase

# Solvent Focusing Solvent Polarity



Beading causes  
non-uniform analyte  
focusing



Split Peaks

# Splitless Liner Designs

Straight



Gooseneck



Double  
Gooseneck



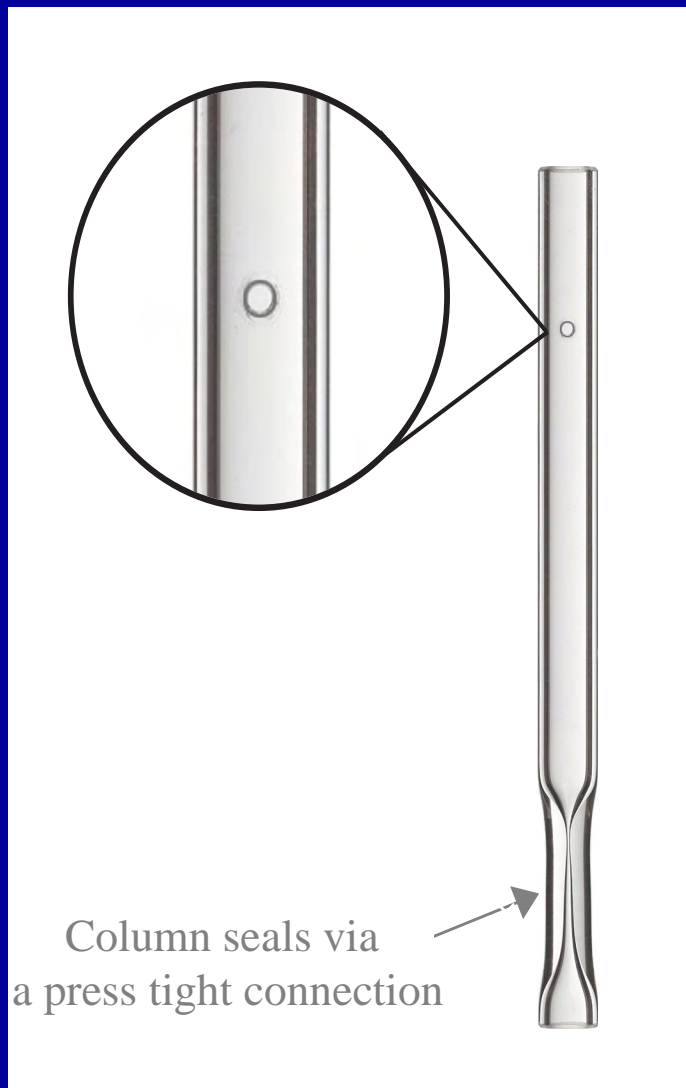
Cyclo Double-  
Gooseneck



# 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 w/ Hole

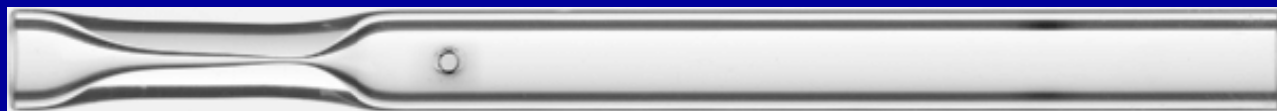


- Allows DI and Splitless injection methods
- Minimizes injection port discrimination
- Reduces loss of active compounds for more accurate results
- Hole can be placed on bottom or top of liner (each has benefits)



# Drilled Uniliners

4mm  
IP deactivated



4mm  
Siltek deactivated



2mm  
Siltek deactivated



# Injection Port Liner Drilled Uniliner w/ hole

The Uniliner with a hole is a unique liner that can be used for both direct and splitless injection. The column is connected at the bottom of the liner, eliminating any sample contact with metal below the liner. In order for the carrier gas to be routed through the split vent, a hole has been placed on the side of the liner. This hole allows the carrier gas to be vented through the split vent line during the split operation of the injection port.

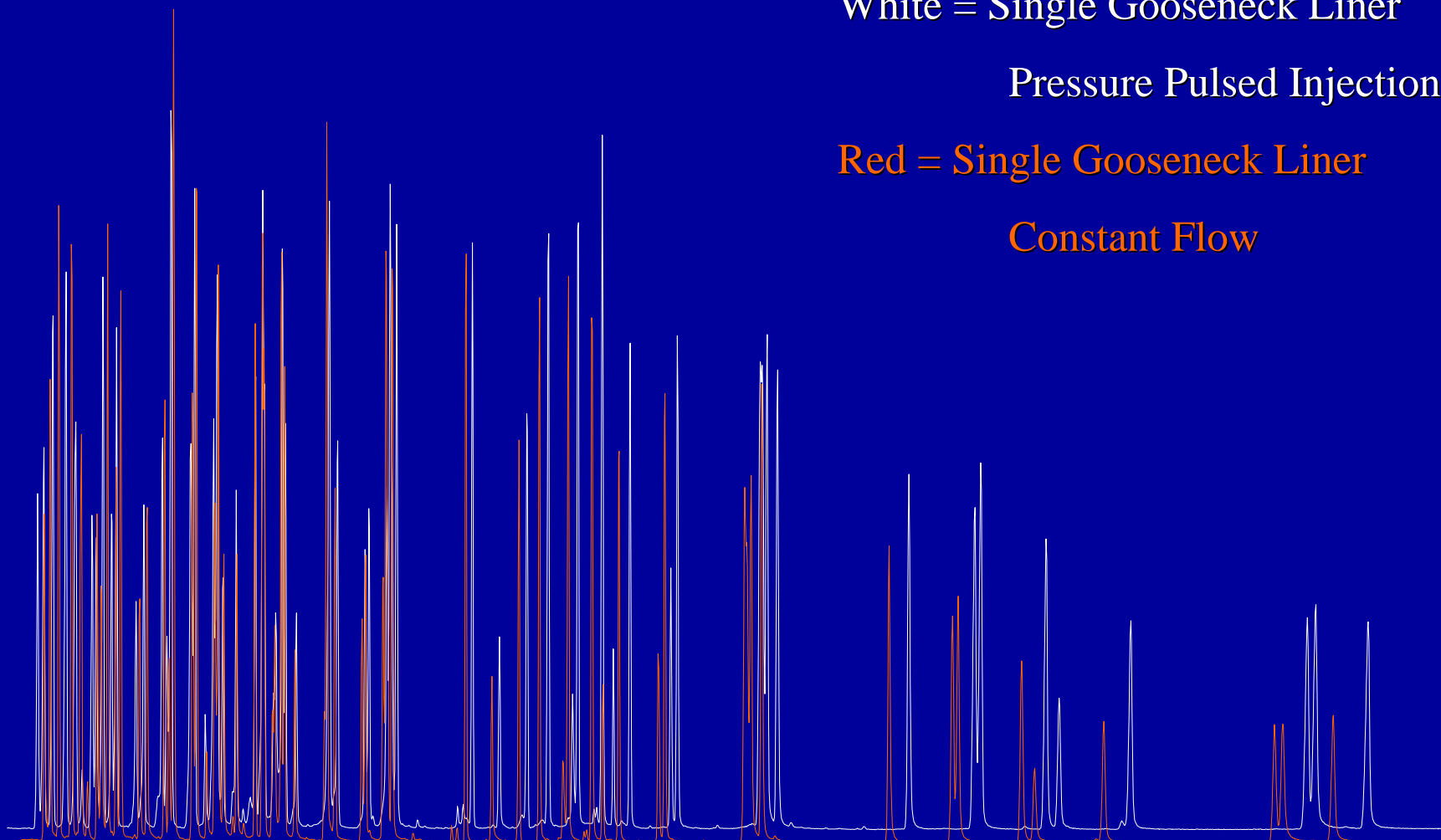
# Injection Port Liner Drilled Uniliner w/ hole

There are two styles of Drilled Uniliner<sup>®</sup> liners, one with a hole near the top, and a second with a hole near the bottom of the liner. The choice of liner is dependent on how closely the first compound elutes to the solvent peak. If the first compound elutes near the solvent peak, as in Method 8270, the drilled Uniliner<sup>®</sup> with the hole at the bottom of the liner should be used. This allows all the solvent to be flushed out of the entire inlet liner, reducing any solvent tailing, which could interfere with the first eluting compounds. The drilled Uniliner<sup>®</sup> with the hole near the top of the liner works well when the first compounds elute away from the solvent peak as in ethylene glycol in water, or chlorinated pesticide analysis.

The Drilled Uniliner<sup>®</sup> also helps eliminate injection port discrimination for the late eluting PAHs. This is shown in figures 5A and 5B. Figure 5A shows the difference between a pressure pulsed injection versus constant flow for the single gooseneck liner. Figure 5B shows the difference between the Drilled Uniliner<sup>®</sup> and single gooseneck liner under constant flow condition. The Drilled Uniliner<sup>®</sup> exhibits the least amount of injection port discrimination.

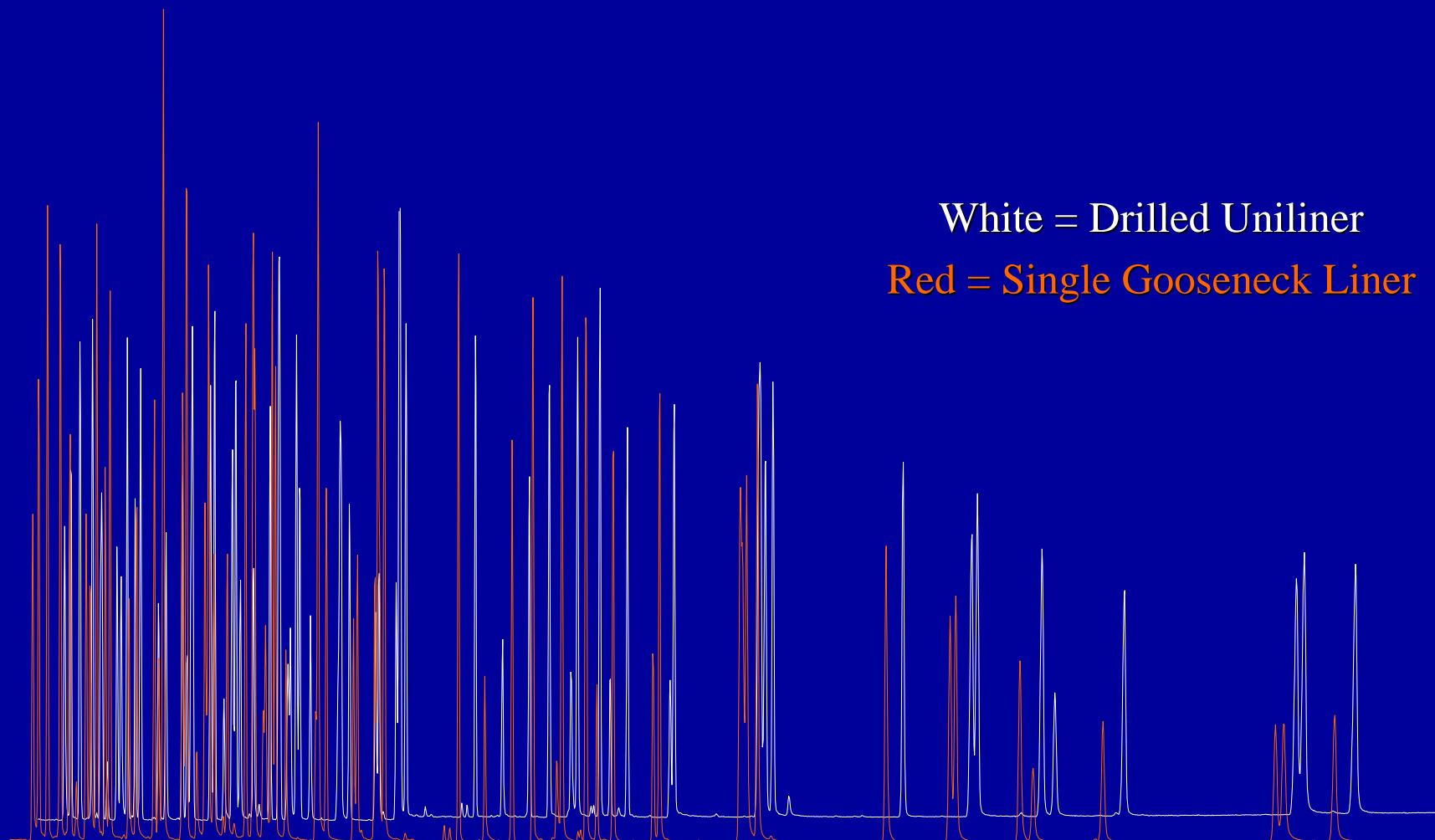
## Figure 5a - Single Gooseneck Liner (Constant Flow vs Pressure Pulsed Injection)

White = Single Gooseneck Liner  
Pressure Pulsed Injection  
Red = Single Gooseneck Liner  
Constant Flow



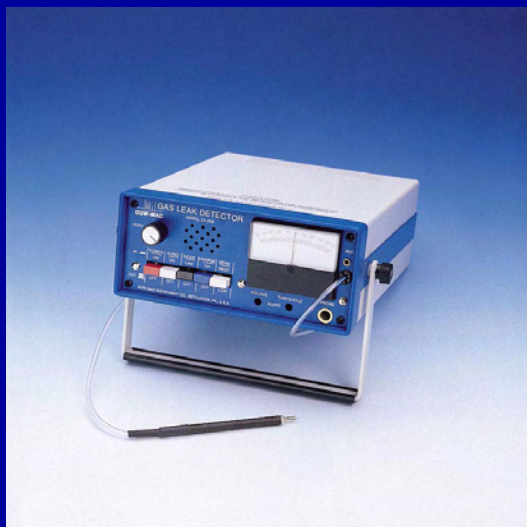
## Figure 5b - Single Gooseneck vs Drilled Uniliner® Sleeve (Constant Flow)

White = Drilled Uniliner  
Red = Single Gooseneck Liner





# Leak Detectors



# Optimizing the Analysis of Volatile Organic Compounds by Purge and Trap.

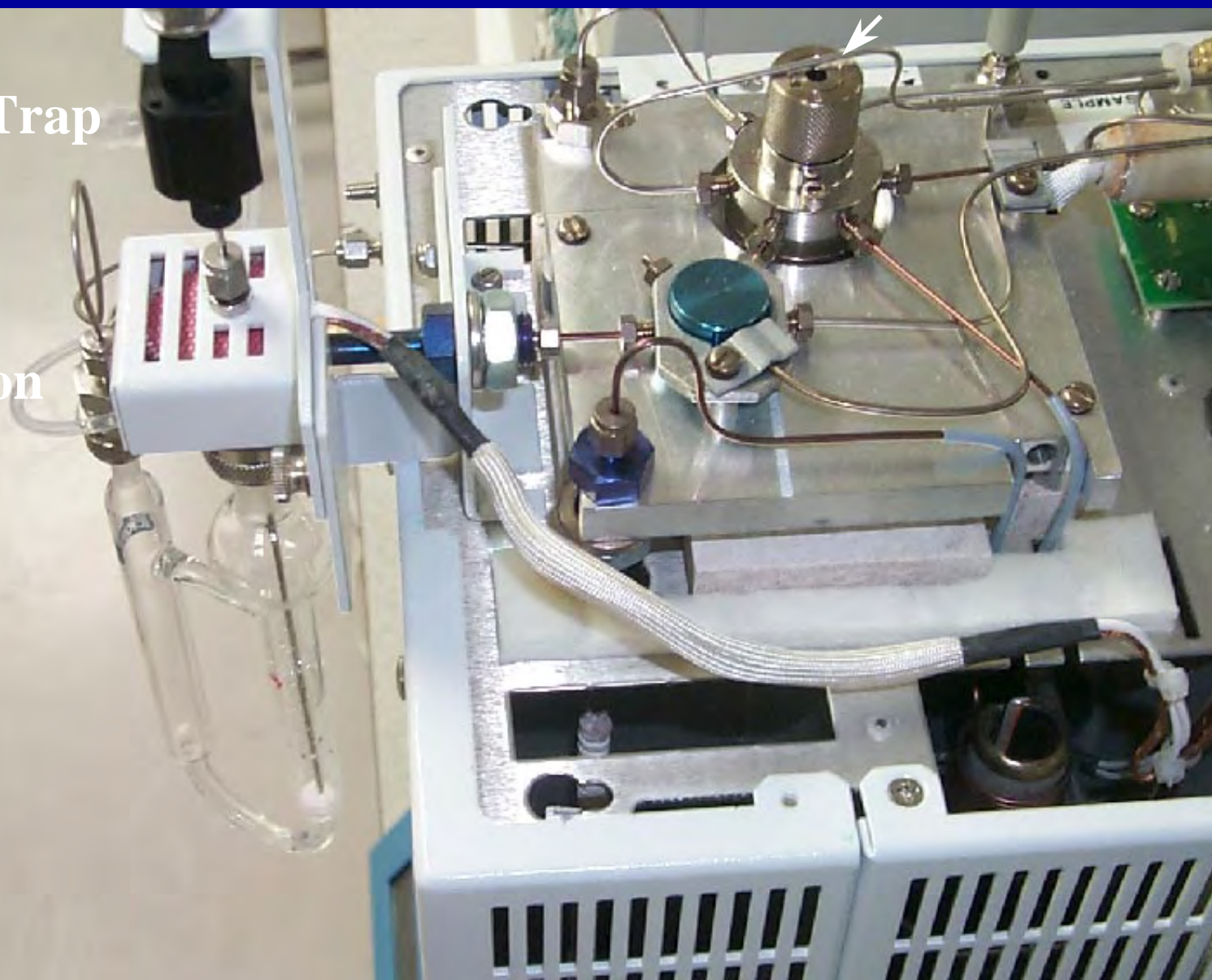
## USEPA Method 8260

# EPA Method 8260B

Purge and Trap

GC

MS Detection



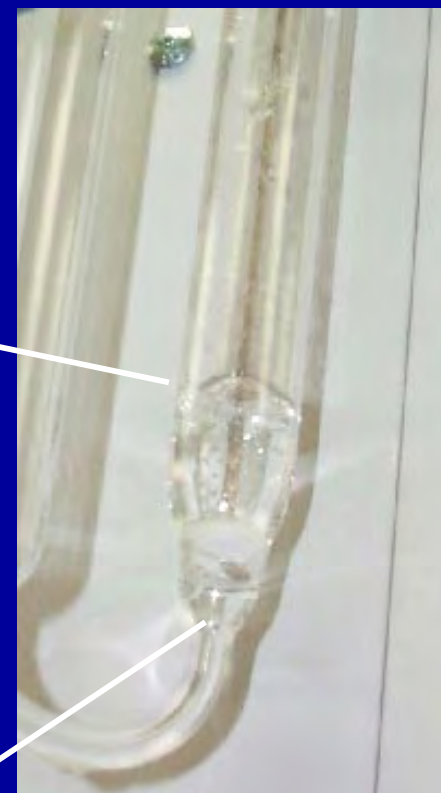
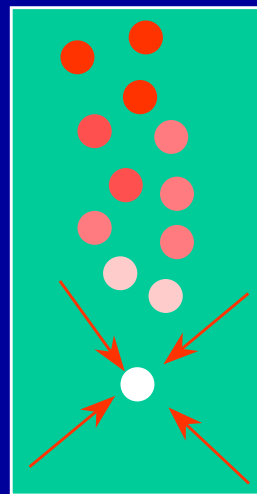


# Optimizing P&T for 8260

- Purge
- Dry Purge
- Desorb Preheat
- Desorb
- Bake
- Traps



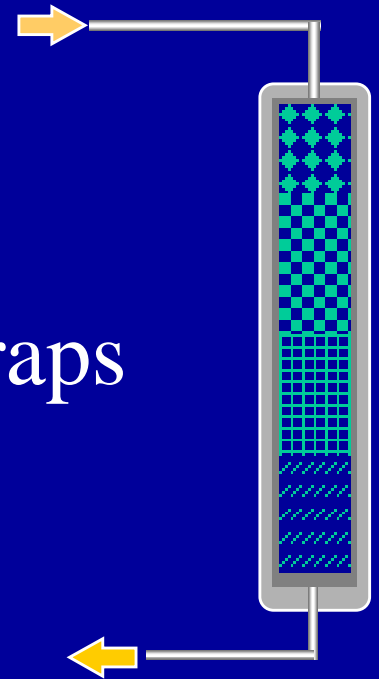
# Purge



- EPA SW-846 Suggests 11 min. purge @ 40m/min  
Heated purge allows less purge time  
Always purge at/or below 40ml/min.

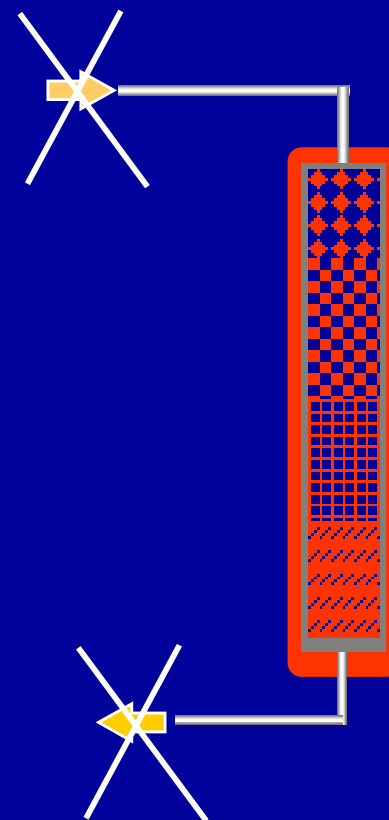
# Dry Purge

- Avoid using if possible
  - Does not work with hydrophilic traps
  - Broadens the gases
  - Increases P&T Cycle Time



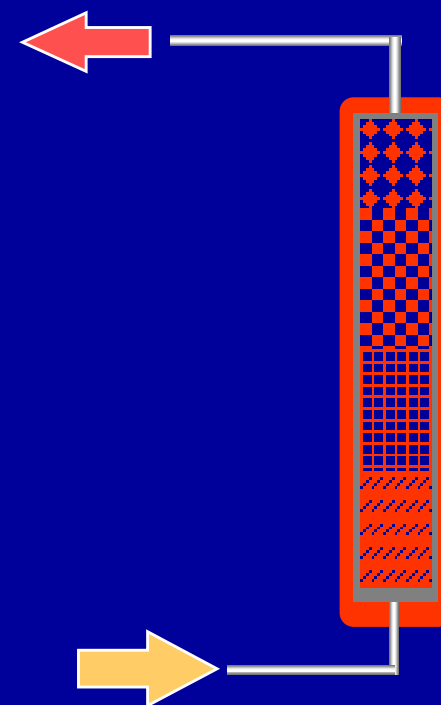
# Desorb Preheat

- Trap is heated without flow.
- Typical temp: 5° below desorb temp.
- Minimizes retention on trap.



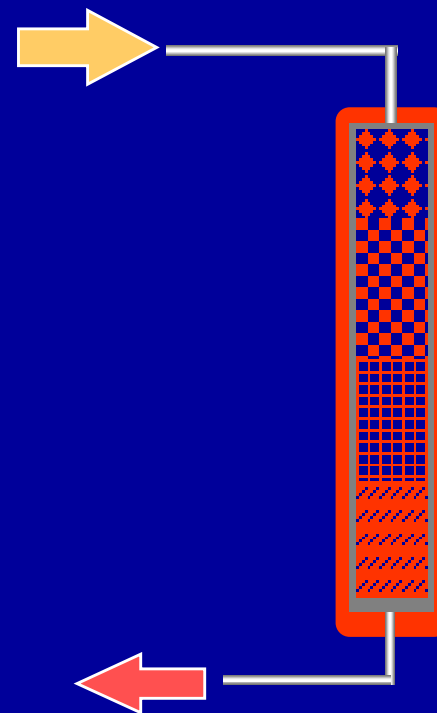
# Desorb

- Trap is backflushed into column.
- Typical time: 2-4min.  
O.I. ~1min.  
Tekmar ~ 2 min.
- Typical flow: 10-80 mL/min.  
> 20ml/min best performance
- Typical temp: 180° - 250°C

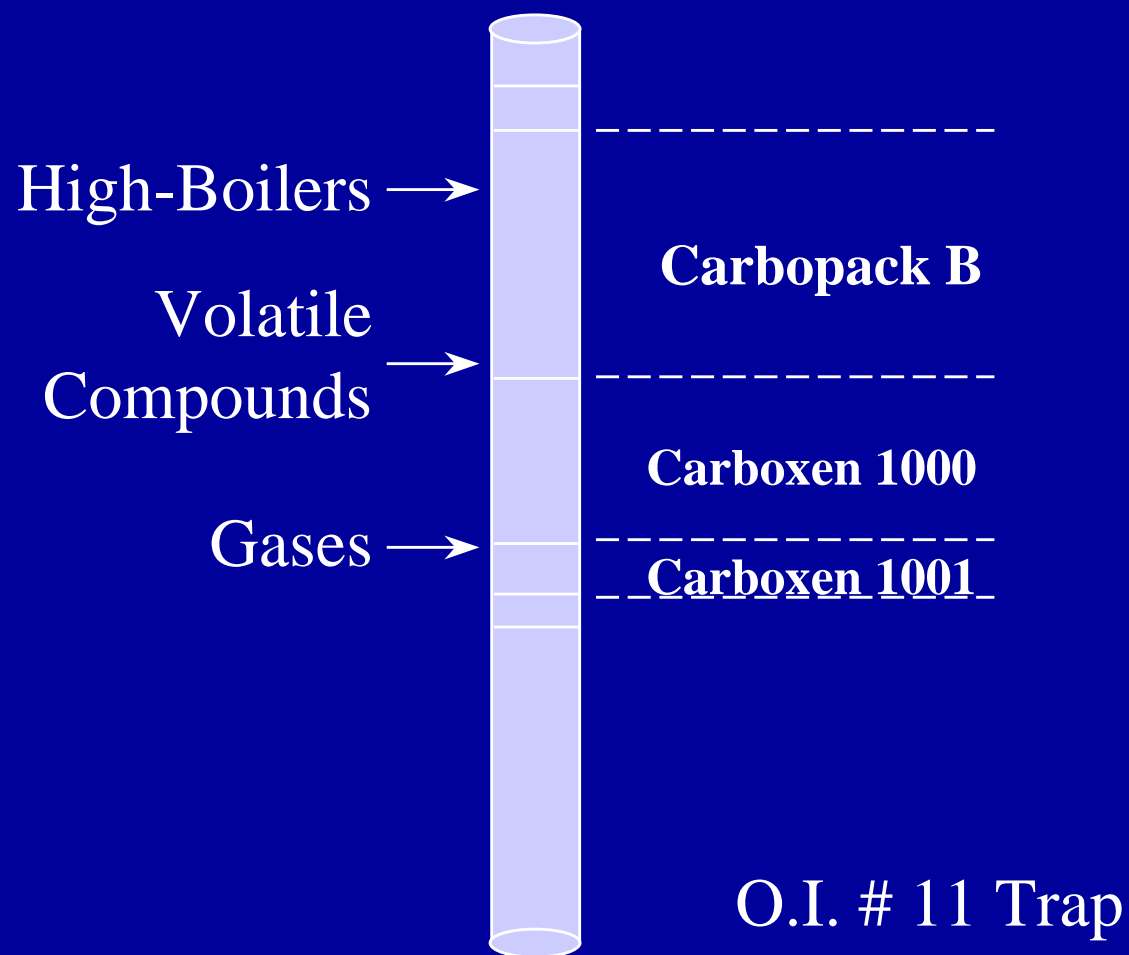


# Bake

- Trap is baked clean with flow
- Typical time: 8 minutes
- Adjust bake using Naphthalene
- Typical temp: 5-10 above desorb
- Do not overheat adsorbents



# Vocarb<sup>®</sup> 3000 Type “K”



# Vocarb<sup>®</sup> 3000 Type “K”

- Pros

Low H<sub>2</sub>O, Meoh & CO<sub>2</sub> retention

Excellent gas retention

Polar/Non-polars

- Cons

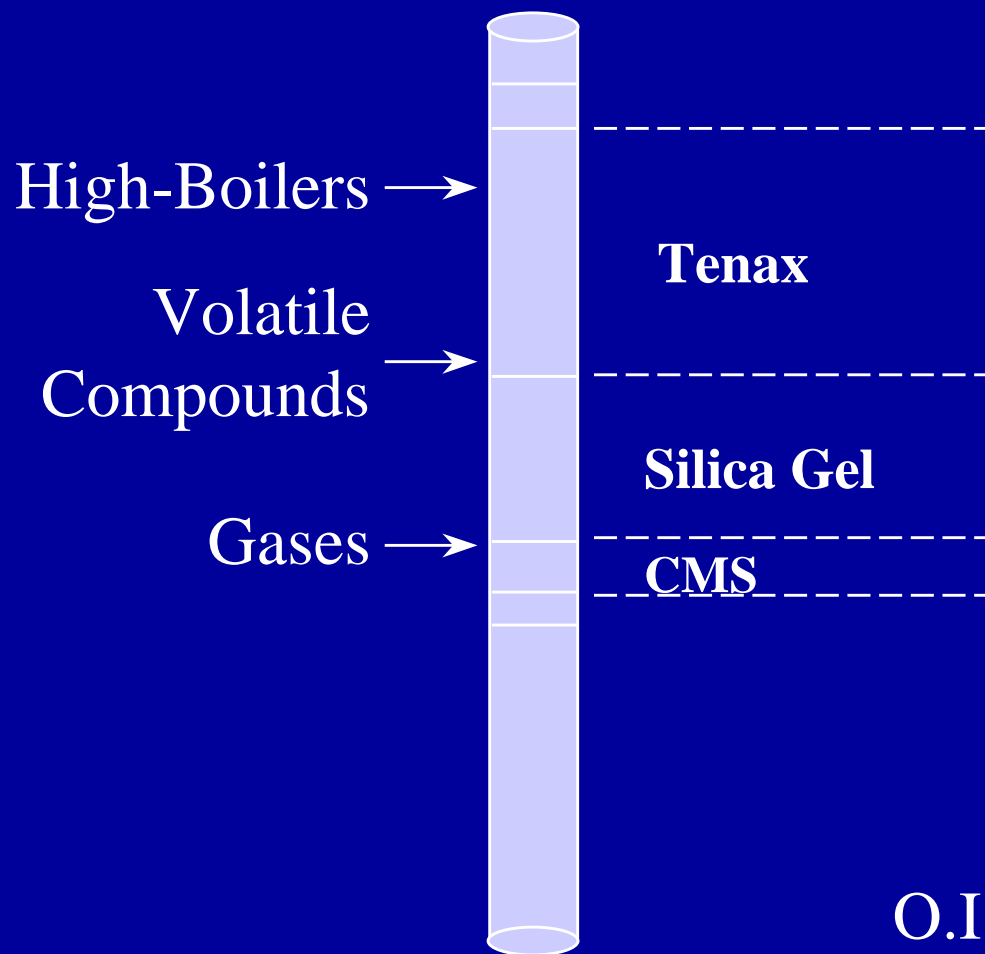
Variability from trap to trap

Trap breakdown/contamination

\* Suggested for Tekmar Purge & Traps



# Tenax<sup>®</sup>/silica gel/CMS



O.I #10 Trap

# Tenax<sup>®</sup>/silica gel/CMS

- Pros
  - Excellent recoveries of polars
  - Broad range of analytes
  - Very consistent
- Cons
  - CO<sub>2</sub> retention
  - Requires use of moisture control system

\* Suggested for O.I. Purge and Traps.

# Common Types Of Traps

Type of Trap	Dry Purge	Temp: MAX
Tenax	Yes	220°C
Tenax\Silica Gel	No	220°C
Tenax\Silica\Charcoal	No	220°C
OV-1\Tenax\ Silica\Charcoal	No	230°C
OV-1\Tenax\Silica	No	220°C
OV-1\Tenax	Yes	220°C
Carbopack B\ Carbosieve S-III	Yes	260°C
Vocarb 4000 (4 beds)	Yes	270°C
Vocarb 3000 (3 beds)	Yes	270°C

# Purge & Trap Connection Through the Injection Port

- Connect transfer line to carrier gas line on GC
- Pro: manual injections
- Con: dead volume (overcome with high flows)
- Use 1mm sleeve

# Narrow Bore GC Systems

- Desorb at 10-80mL/min. and split desorb flow to decrease column flow
- Injection port splitting lowers amount of sample on column
- Purge larger volume (25mL) to increase sensitivity
- 0.18 to 0.25mm ID columns
- Improved resolution

# Injection Port Connection Setup

## Step #1 -- cut injection port lines.

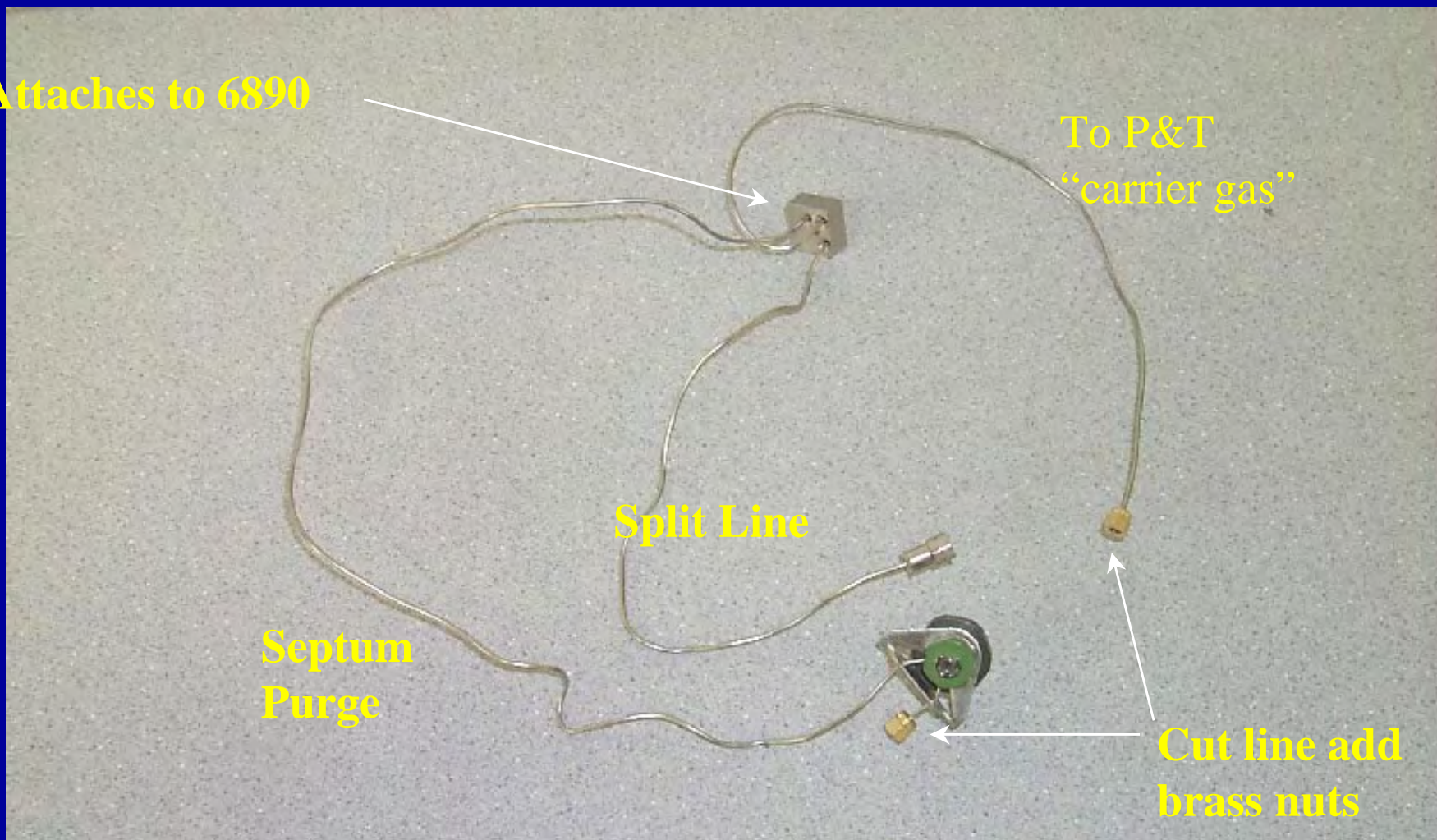
Attaches to 6890

To P&T  
"carrier gas"

Split Line

Septum  
Purge

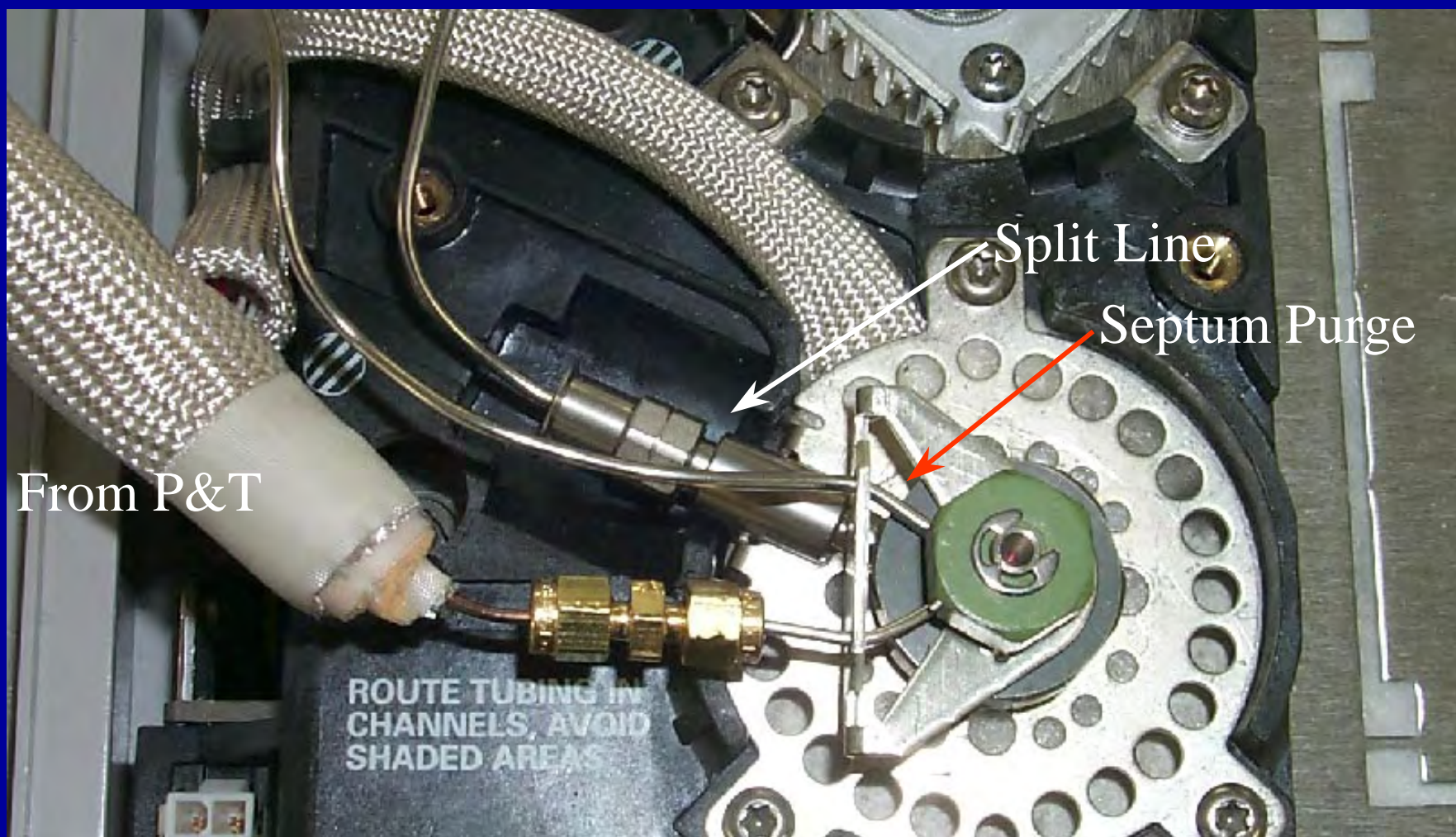
Cut line add  
brass nuts





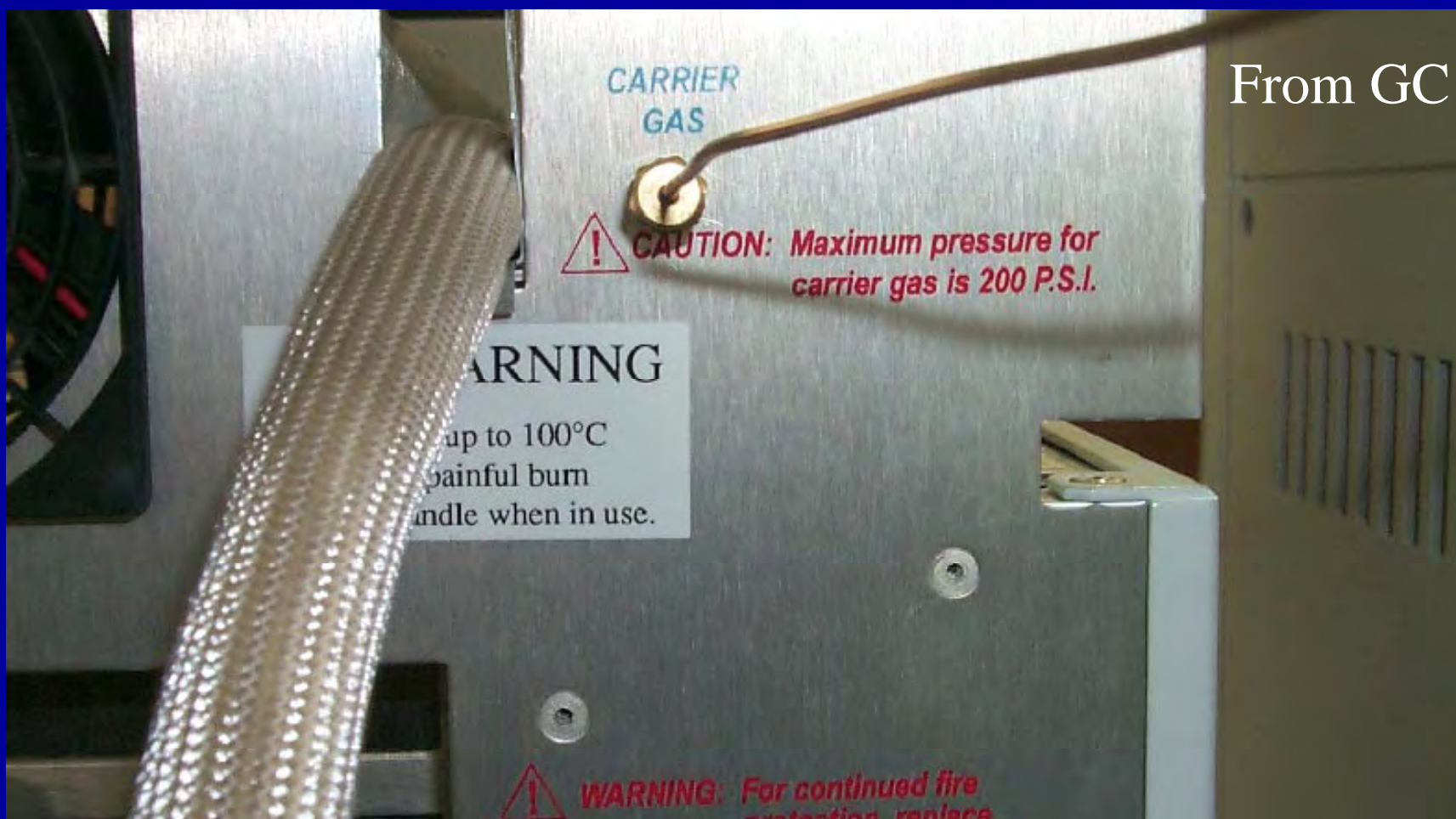
# Injection Port Connection Setup

## Step #2 - install lines



# Injection Port Connection Setup

## Step #3 -gas lines to P&T



From GC



# GC/MS Detectors

- Quadrapole
- Ion Trap



# Tuning GC/MS System

- Tune with PFTBA (FC 43)
- Check tune with BFB 50ng solution
- Must pass criteria

# Tuning Objectives

- Maximize all abundances
- Optimize high mass
- Adjust peak width
- Adjust mass assignments

# Ion Abundance Criteria: For 4-Bromofluorobenzene (BFB)

Mass	Relative Abundance Criteria
50	15-40% of mass 95
75	30-80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5-9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 176

# GC/MS

## Electron Multiplier

- After Market K&M, ETP 10X more sensitive
- Increase Signal & Noise
- Increase voltage decreases lifetime
- Use at lowest sens. to achieve DL

# Compound Class & Fragmentation Ions

- Aldehydes, Amides, Amines 44,58,72,59,30
- Aliphatic Hydrocarbons 43, 57, 71, 85, 99
- Alkylbenzenes 104, 91
- Aromatics (HC) 39, 50, 51, 52, 63, 65, 76, 77, 91
- Ethers 31,45, 59, 73
- Fluorine Containing 50, 69
- Methacrylates 41, 69
- Methyl Ketones 43, 58
- Oxygen Containing 31,45,59,73
- Sulfur Containing 47,61
- Unsaturated Hydrocarbons 41, 55, 69

# Contamination and Its Ions

- Silcon 73, 147, 207, 221, 281, 355, 429, 503
- Rough Vacuum Pump Oil 55-57, 61-67, 81-85, 95-99
- Diffusion Pump Oil 77, 115, 141, 168, 223, 260, 446
- Plasticizers 149, 223, 278

# GC/MS Tips

- Use air/water scan for leaks in system
- Monitor 69 area from tune to tune
- Watch source pressure –
  - Leaks
  - Flows
  - Troubleshoot vacuum pump



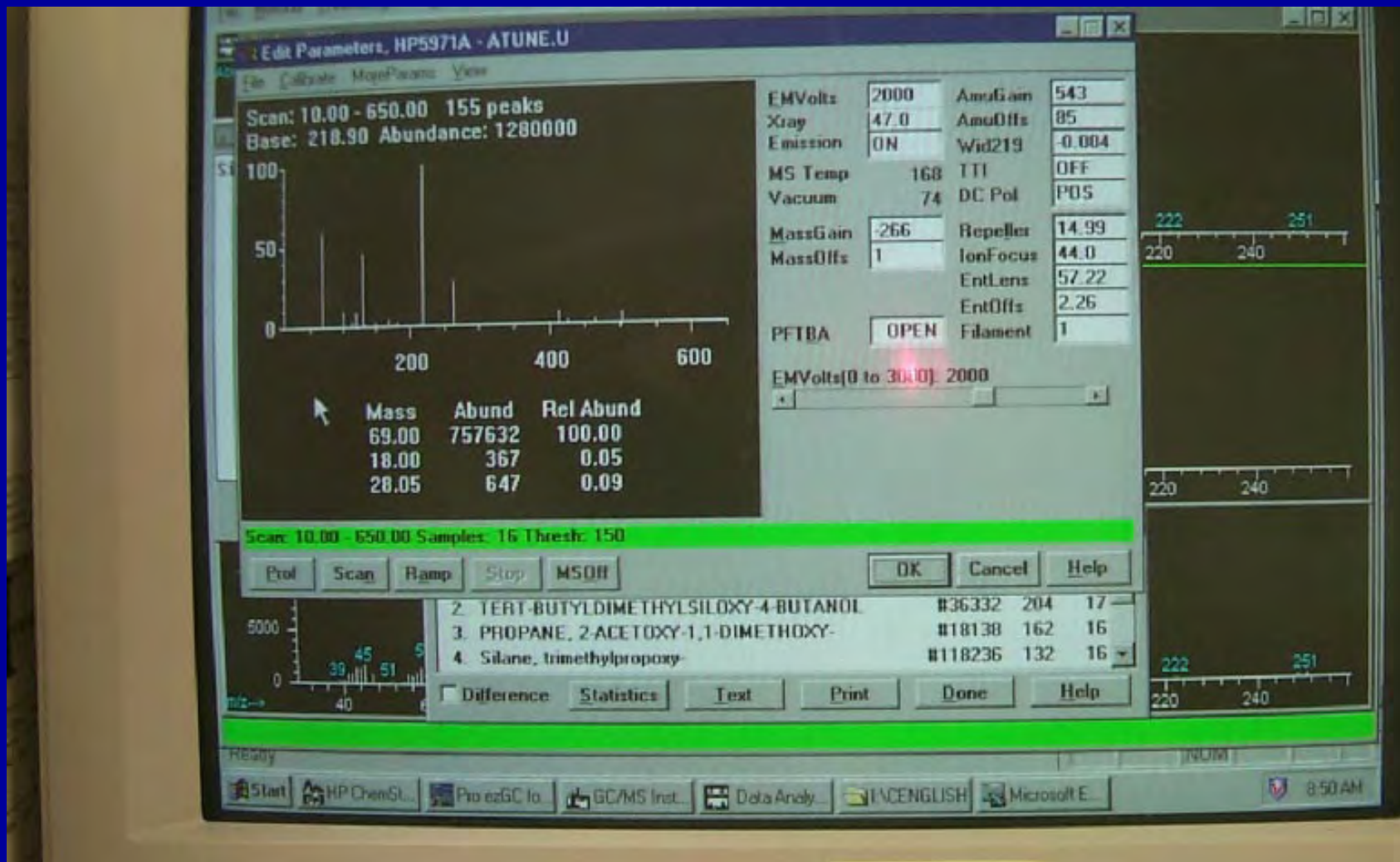
# Air Water Checks

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# Mass Spectroscopy Troubleshooting

- Leaks-
  - air/water
  - methanol & scan for mass 31
  - check source pressure

*Lit. #59887 — VOA Guide*

# Compound-Specific Sensitivity Problems and Their Causes

- Leaks
  - Dichlorodifluoromethane
  - Chloromethane
  - Vinyl Chloride
  - Bromomethane
  - Chloroethane

# Compound-Specific Sensitivity Problems and Their Causes

- Active Sites
  - Bromoform, Bromomethane
  - 2-Chloroethyl Vinyl Ether
  - Chloroethane
  - 1,1,1-Trichloroethane
  - 1,1,2,2-Tetrachloroethane
  - Ketones

# Causes of Ghost Peaks

- Carryover
- Impurities in the gas supply
- Contamination
- Trap breakdown

# Calibration

- Multipoint calibrations diluted in purge & trap grade methanol
- Careful with volatile loss (store standards in freezer)
- Monitor response of standards (especially gases)

# Common Problems

- Water
- Reduced sensitivity
- Sample contamination (ghost peaks)
- Broad peaks and/or tailing peaks



# Advances in Surface Passivation Techniques used for the Analysis of Sulfur Species in the Petrochemical and Refining Industries

Gary Barone, Marty Higgins,  
David A. Smith  
Restek Corporation



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# Outline

- Options
- Coating process
- Performance data
- Effect of moisture on coated surface
- Other Applications

# Options

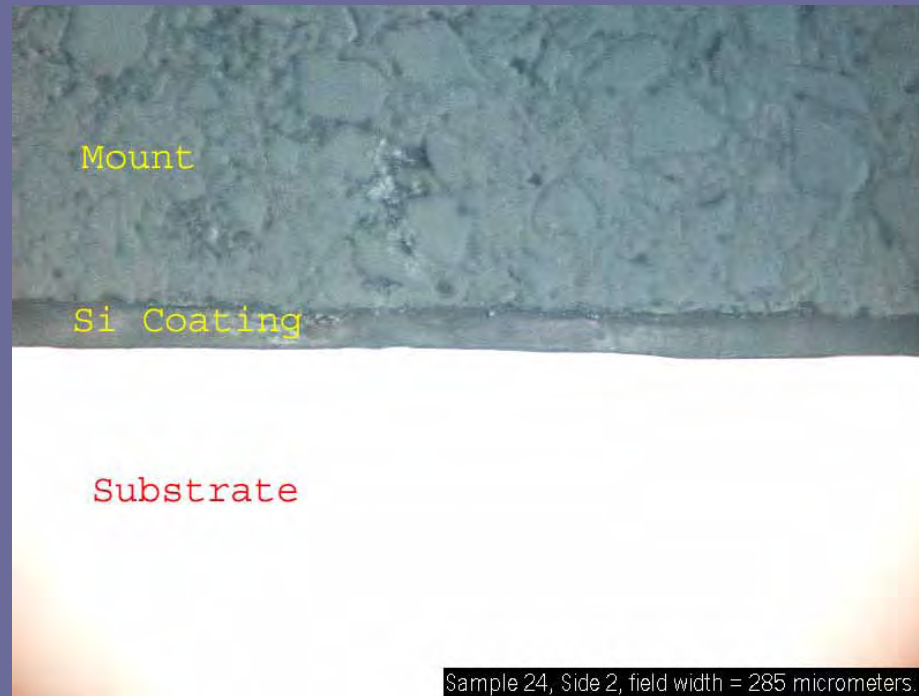
- Stainless steel (welded / raw)
- Electropolished stainless steel
- Coated stainless steel (CVD)
- Functionalized coated stainless steel

# Chemical Vapor Deposition Process

- Thermal decomposition of silanes
- Amorphous silicon deposition
- Functionalization of surface if desired
- Process
  - Clean (caustic surfactant; ultrasonic)
  - Vacuum
  - 400°C
  - Applied in vessel or oven chamber
- Total 3D coverage, not line-of-sight
- High volume (size dependent)



# Coating Cross Section



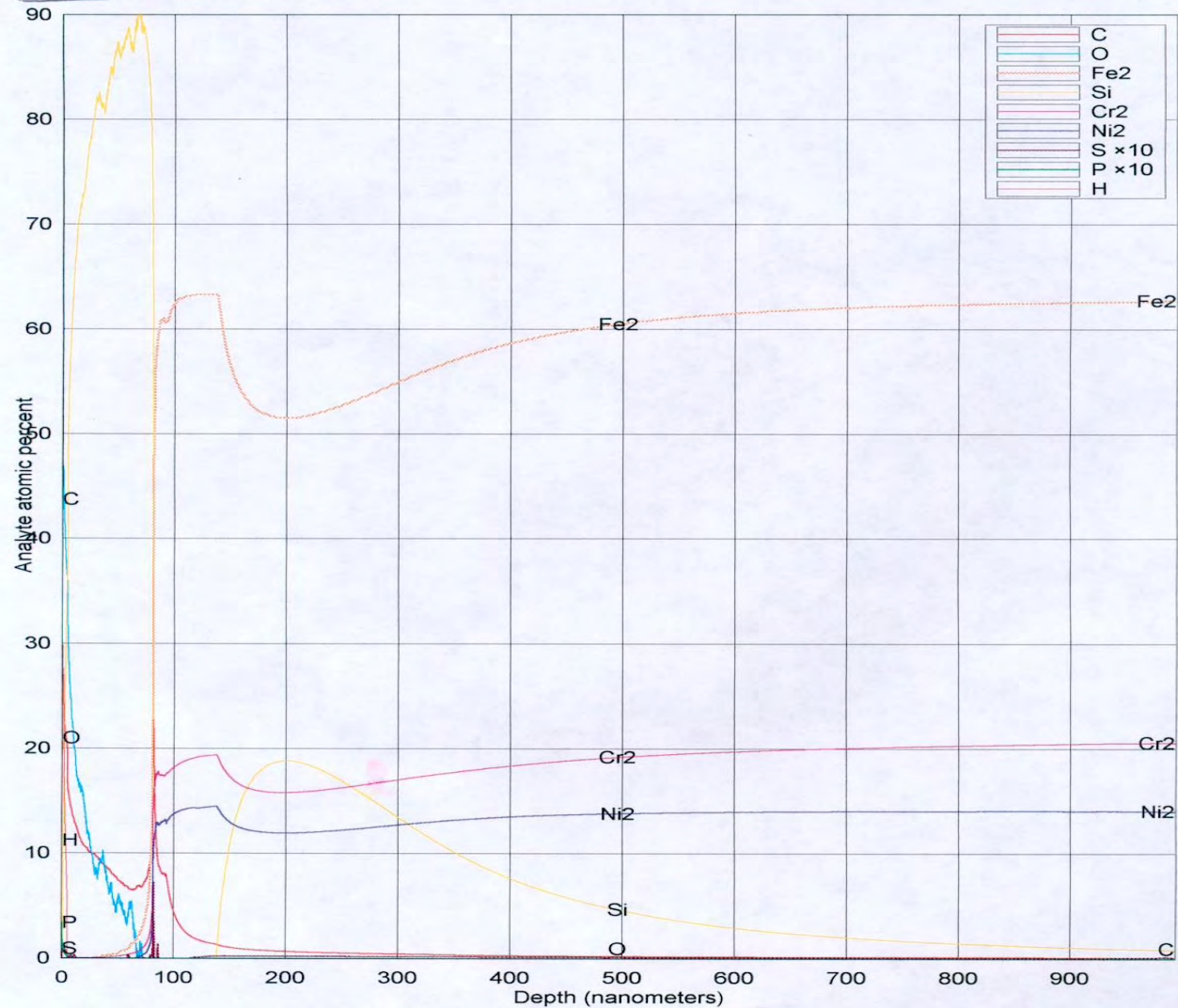
Sample 24, Side 2, field width = 285 micrometers.

# GD-OES Depth Profile

Quantitative Depth Profile  
Operator: JC  
Notes:

Swagelok

CR-360.2 - Analyzed 04/28/04 10:06:37

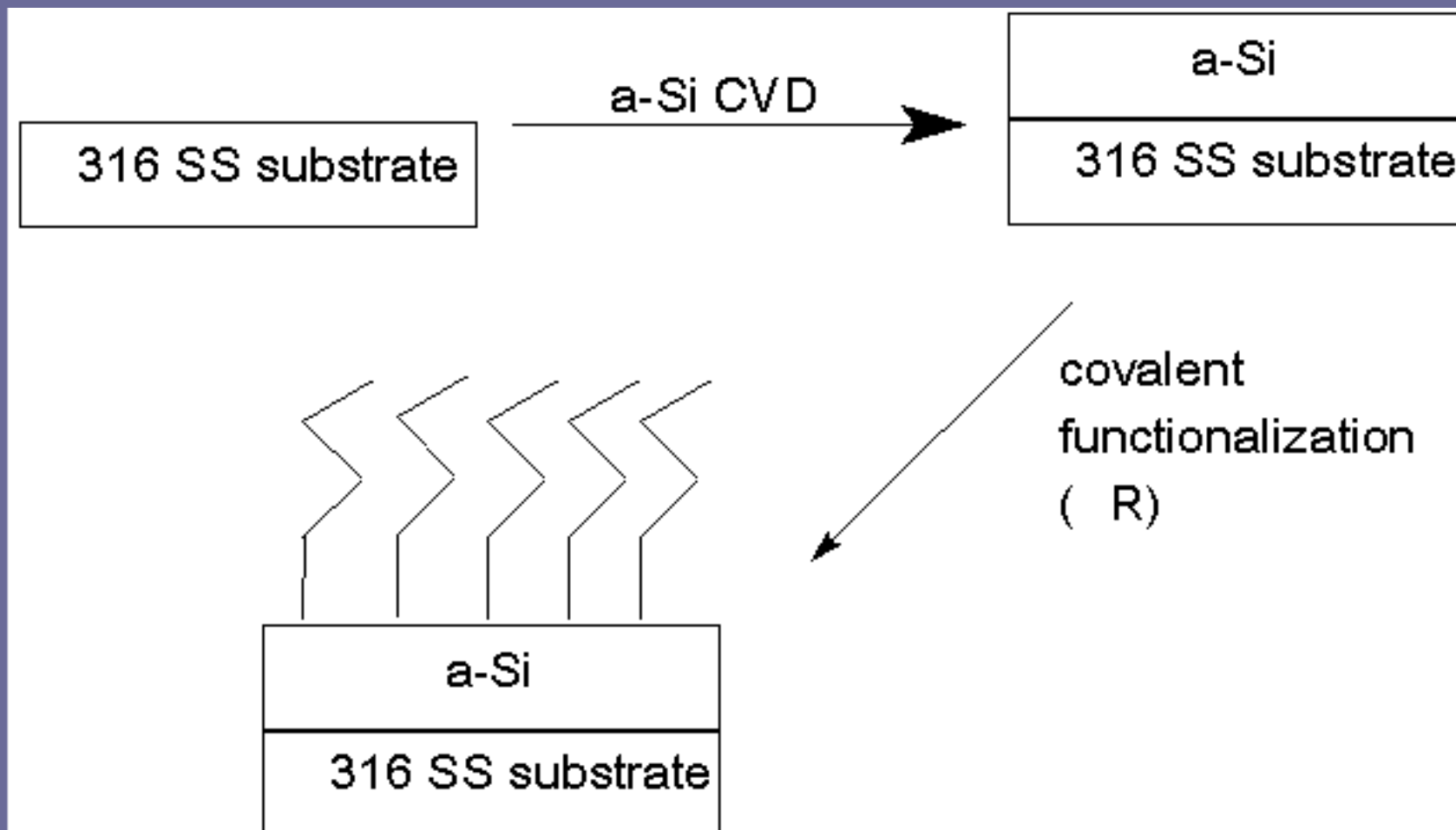




# Secondary Enhancements

- Amorphous silicon deposition
  - Up to 20um in depth
  - Multiple layers to eliminate pin-holes
  - Enhances corrosion resistance
- Additional organic functionalization possible
  - Decrease of pin-holes
  - Improving surface inertness

# Patented Functionalization



# Coating Appearances





# Common Coated Components

- Sampling Systems
- Transfer Tubing
- Valving
- Particle Filters
- Tube Fittings and Adaptors
- Sample Cylinders; Outage Tubes
- Analyzer components
- Continuous Emission Monitoring (CEM) equipment

# Inertness: Amorphous Silicon and Surface-Functionalized Amorphous Silicon

- Both coatings are based on Chemical Vapor Deposition process. Similar physical properties
- Amorphous silicon
  - recommended if level of active compounds is 10-50 ppm or higher
- Functionalized
  - ideal for extremely low-level, <1ppb and up, transfer and storage of active compounds

# Inertness

- Application: Reduce activity of substrate (i.e., stainless steel) to minimize adsorption of compounds
- Coated system products deliver better reproducibility and accuracy by reducing hold-up of active compounds

# Current Applications

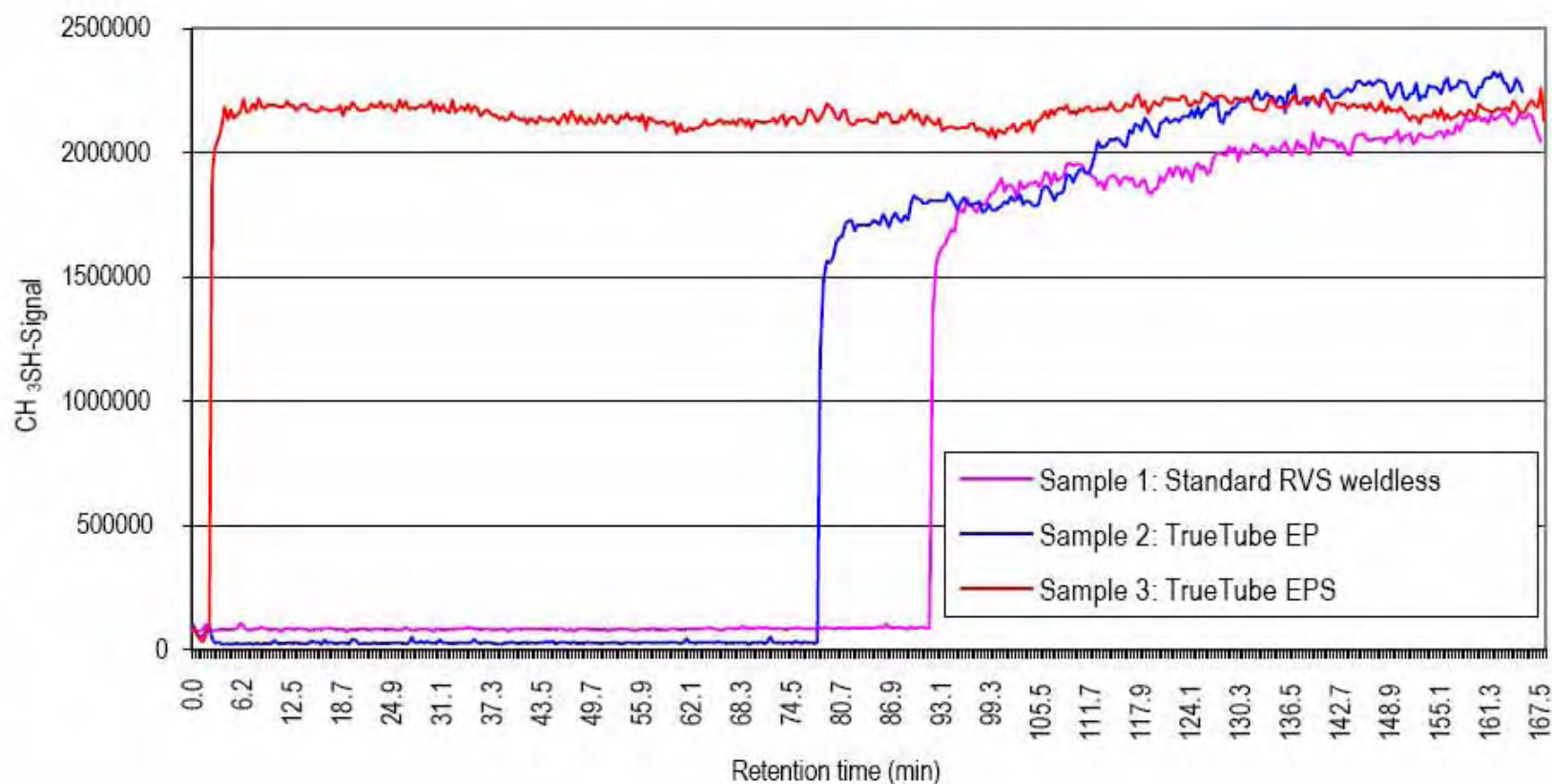
- Sulfurs: Application areas
  - Natural Gas; LPG
  - Ethylene; Propylene
  - Fuel Cells
  - Petrochemical process Streams
  - Beverage Grade CO<sub>2</sub> (Soda/Beer)
  - Flavor (Wine/Beer)

# Flow-through data

- 100' 1/8" x .020" tubing
  - Standard weldless 316L
  - Electropolished 316L
  - a-silicon coated EP 316L
- 0.5ppmv methylmercaptan in He
- SCD detection
- Data courtesy of Shell Research Technology Centre, Amsterdam

# Effectiveness of coated transfer systems to reduce hold-up: Methyl Mercaptan

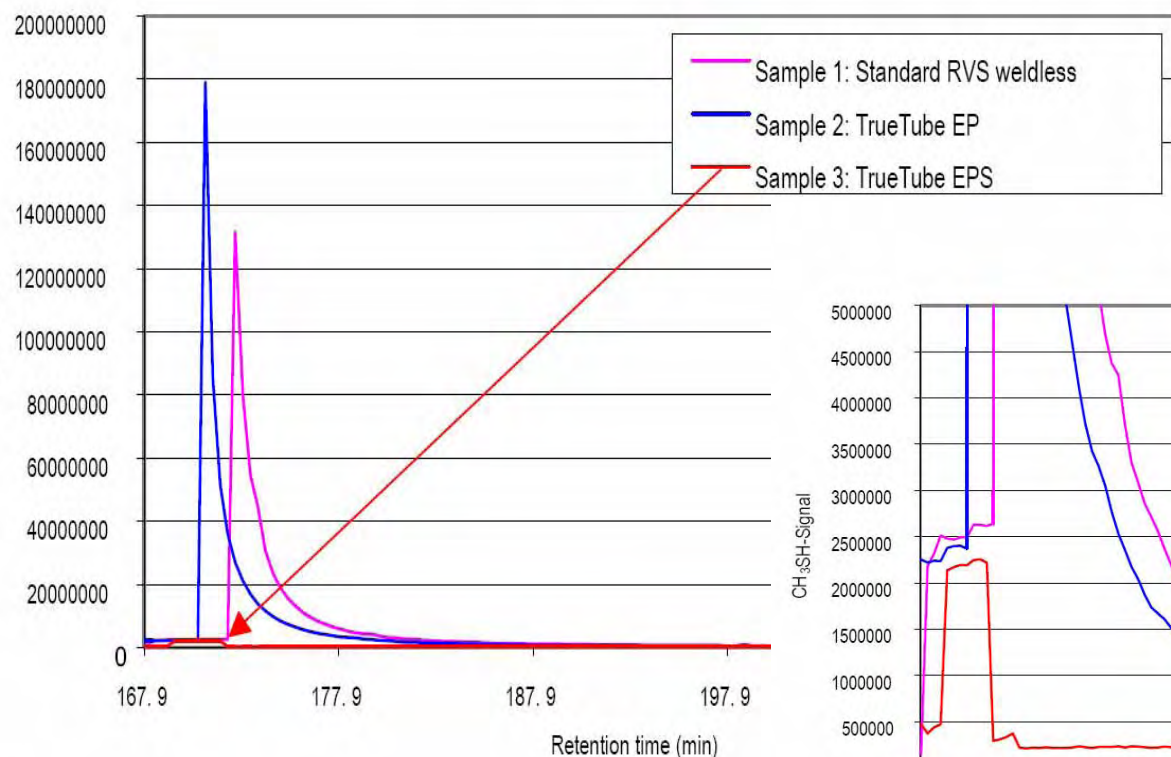
Adsorption of CH<sub>3</sub>SH on different tubings



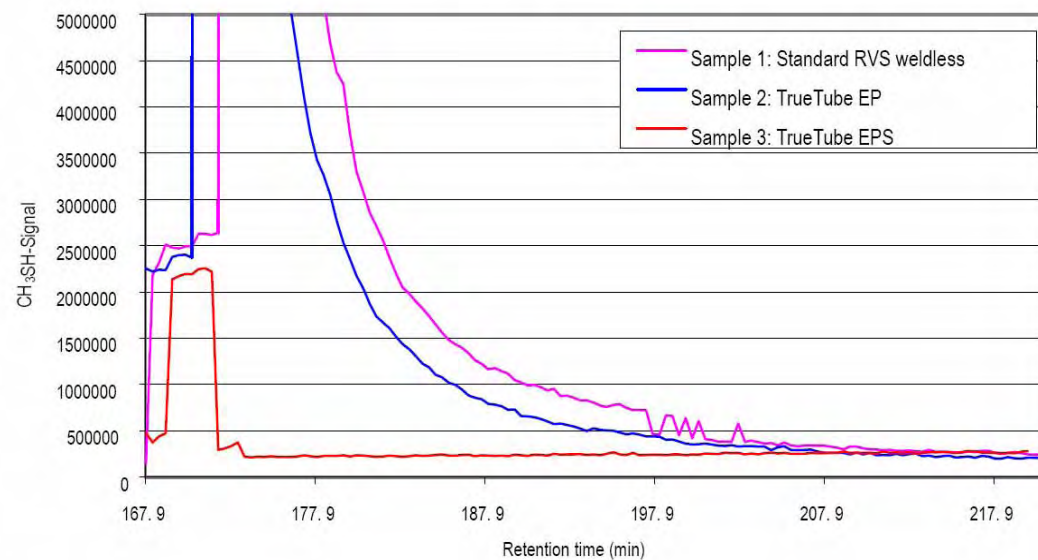


# Inert surface eliminates “memory” effect common with transfer of active compounds

Desorption of CH<sub>3</sub>SH on different tubings



Desorption of CH<sub>3</sub>SH on different tubings

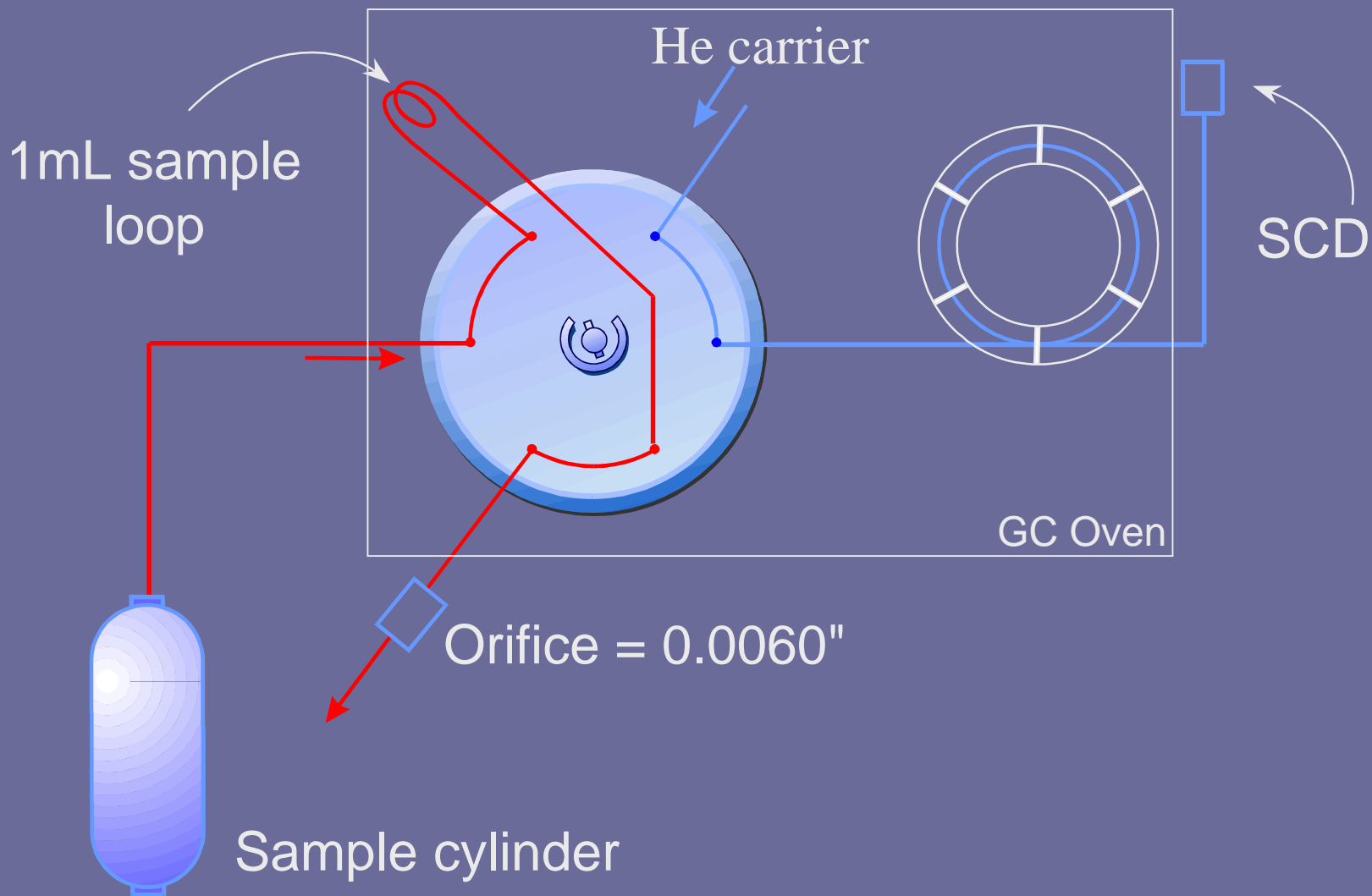


# Testing System for Sulfur Gas Storage & Transfer

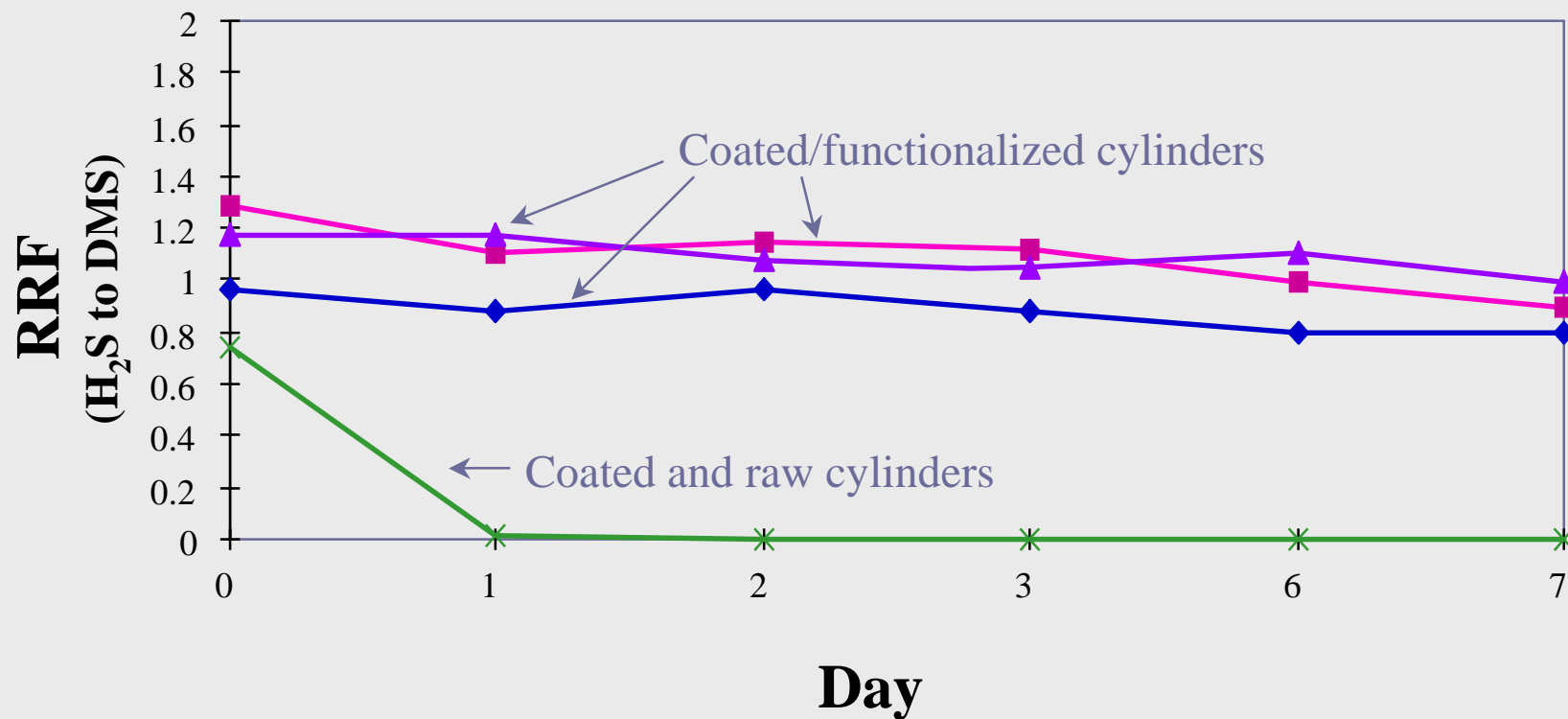
- Coated/uncoated sample cylinders and sample valves
- Coated sampling system (transfer line, sampling valve, 1ml sample loop)
- 48hr (minimum) containment of dry sample
- 55ppbv reference standard
- Dimethyl sulfide internal standard



# Complete Sulfur Analysis System



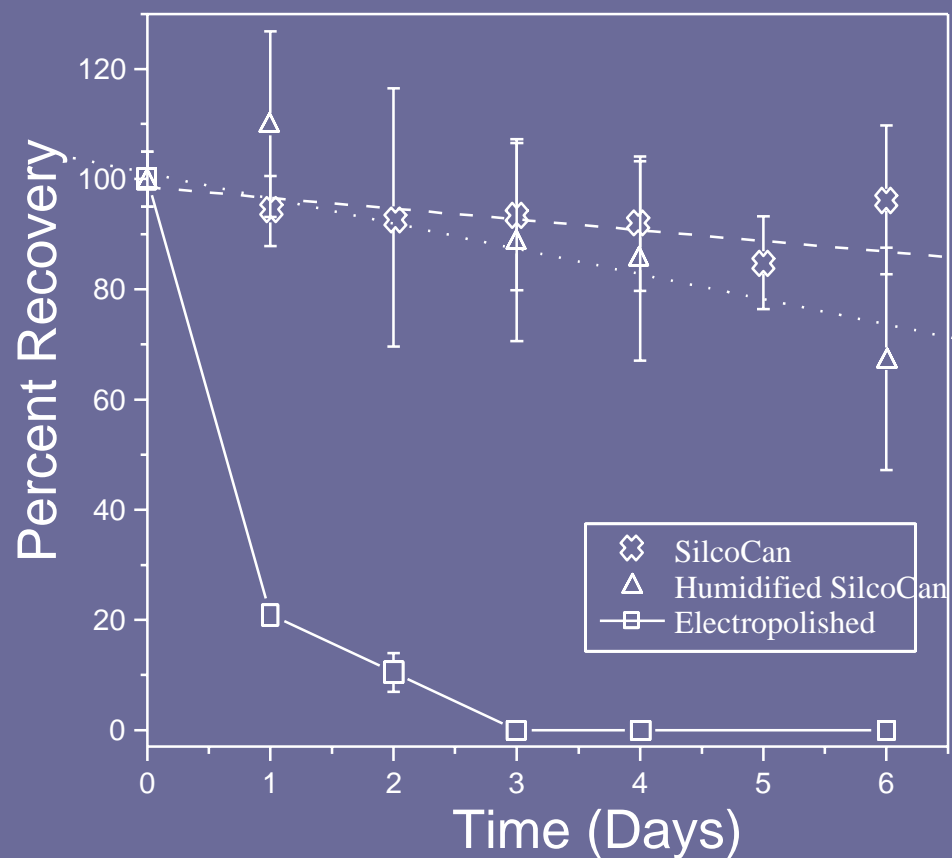
# 17ppbv H<sub>2</sub>S Containment in 500ml Cylinders



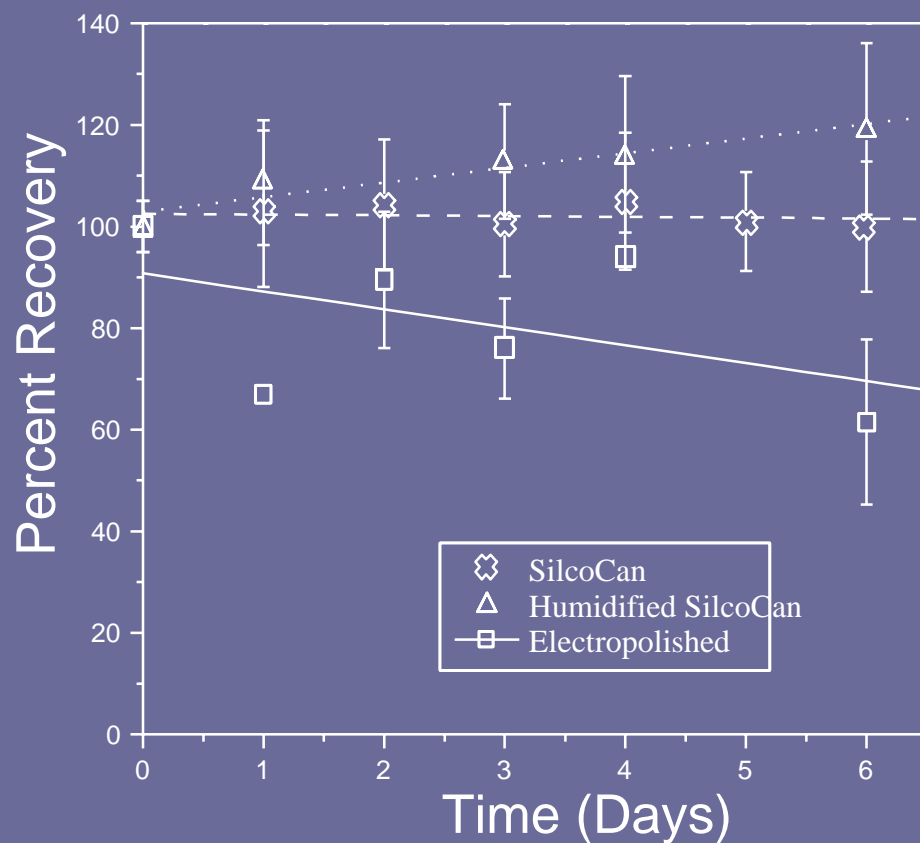
# Stability Study Test

- 11ppbv
- 6 days stability study
- Reference std is at 55ppbv
- Dimethyl sulfide as internal standard
- Coated Sampling Cans (n=18)
- Humidified (rh=50%) Coated Sampling Cans (n=5)
- Electropolished Cans (n=2)

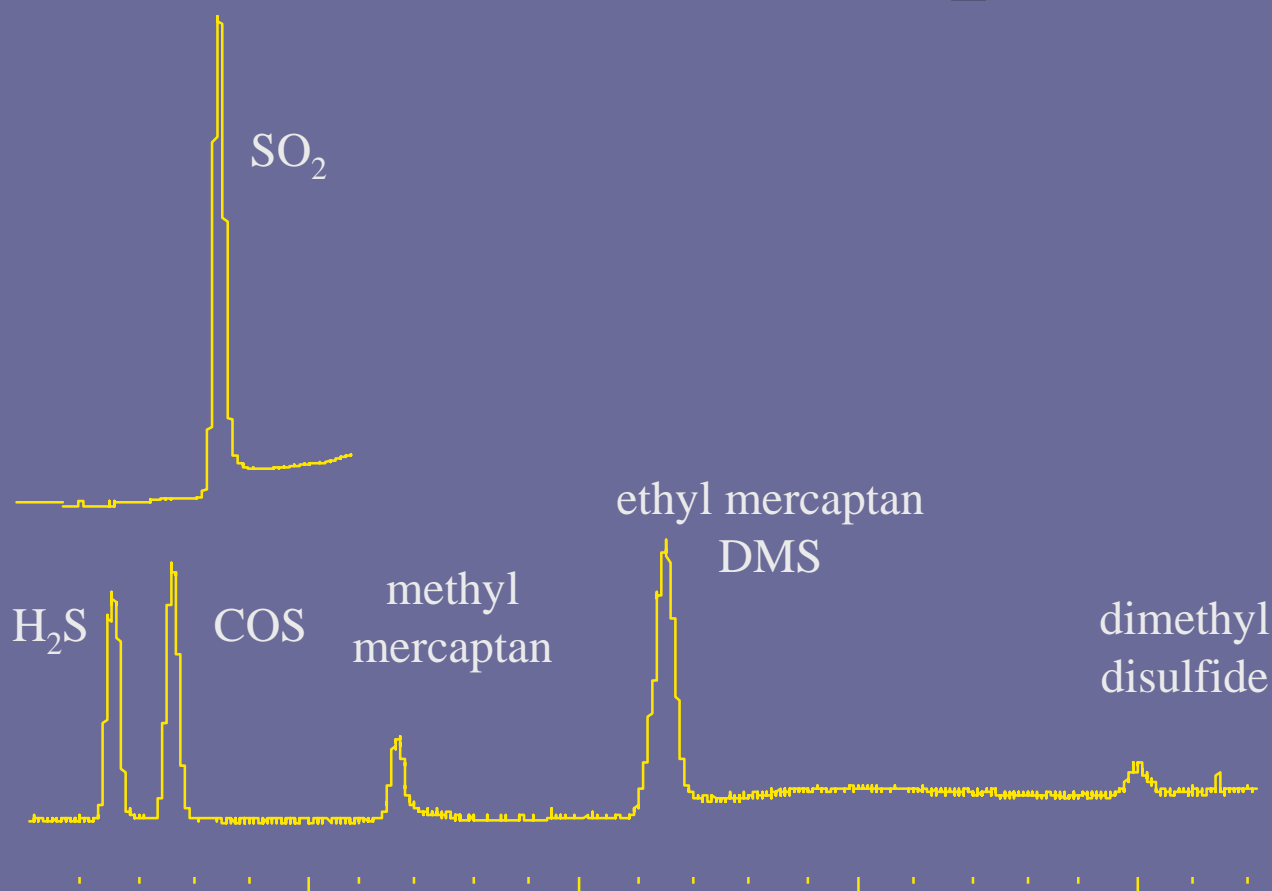
# H<sub>2</sub>S at 11ppbv in 6l Air Sampling Cans



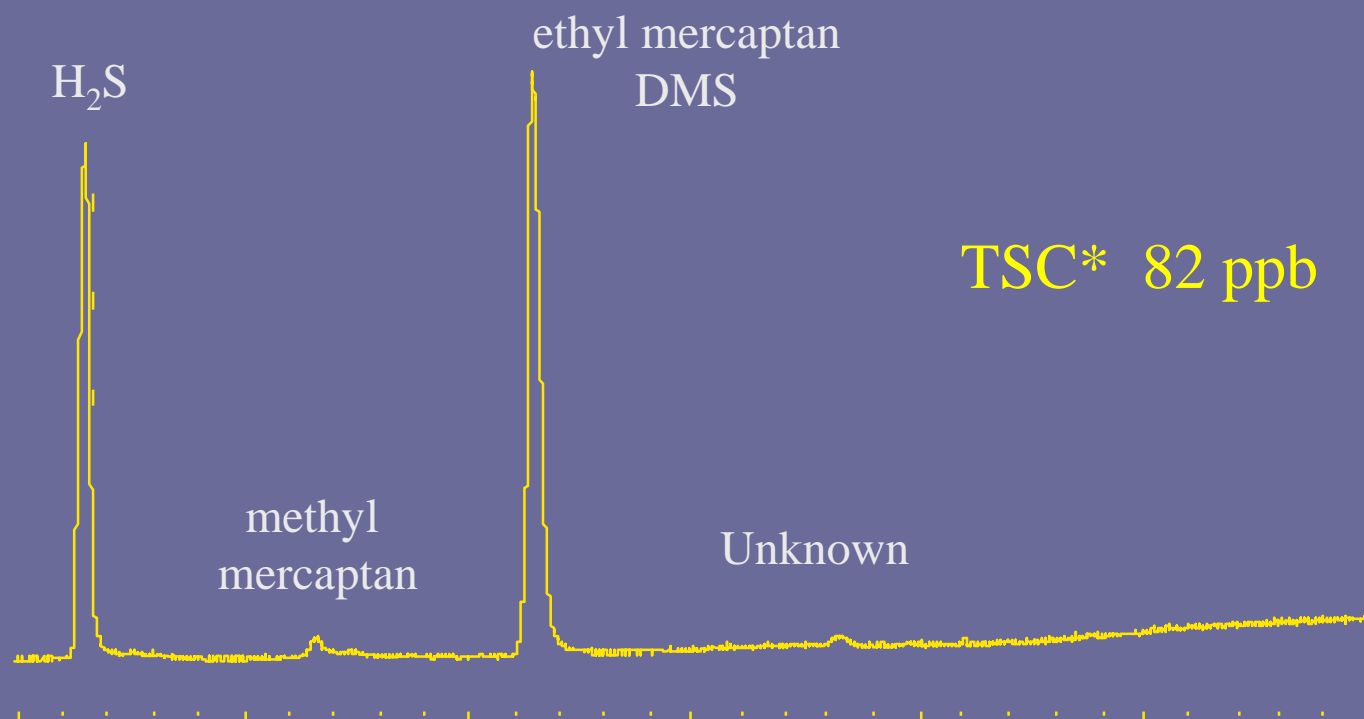
# Methyl Mercaptan at 11ppbv in 6l Air Sampling Cans



# Other Applications: Transfer of 20ppb sulfur standard spiked in beverage grade CO<sub>2</sub>



# Quality testing of beer using coated system



# Effect of moisture

- Coatings decrease adsorption of water, hydrophobic
- Leads to quicker removal of moisture through sampling lines
- Components less susceptible to corrosion
- Faster cycle times and increased accuracy with less moisture hold-up in tubing
- Several coatings and surfaces available



# Moisture Data

- 1ppm moisture, 0.35slpm
- Amount of time to equilibrate a 1ppm moisture sample through 100 feet of dry tubing:
  - Commercial Seamless 316L tubing:
    - 180 minutes (96% equilibrated)
  - Electropolished Seamless 316L tubing:
    - 60 minutes (98% equilibrated)
  - a-silicon coated e-polished seamless 316L tubing
    - 30 minutes (98% equilibrated)

# Moisture Data (cont)

- Time to dry 100' tubing wetted with 1ppm of moisture when connected to a dry purge
  - Commercial Seamless 316L tubing:
    - 175 minutes
  - Electropolished Seamless 316L tubing:
    - 65 minutes
  - a-silicon coated e-polished seamless 316L tubing
    - 35 minutes

# Additional Benefits of a-silicon layer

- Corrosion Resistant. a-silicon layer improves corrosion resistance in
  - Acidic environments
  - Marine environments
- Anti-Coking. Coating barrier eliminates catalytic effect of substrate.
- Ultra-High-Vacuum (UHV). Reduces outgassing of vacuum components.

# Corrosion Resistance

- Stainless steel surfaces susceptible to attack from hydrochloric acid, sulfuric acid and nitric acid
- Is it possible to Enhance Corrosion resistance by deposition of an amorphous silicon layer?
- Silicon is insoluble in hydrochloric acid, sulfuric acid and nitric acid

# Benefits

- To extend lifetimes of equipment exposed to corrosive environments and/or process streams
- Protection of high value equipment in corrosive environments

# Known Applications

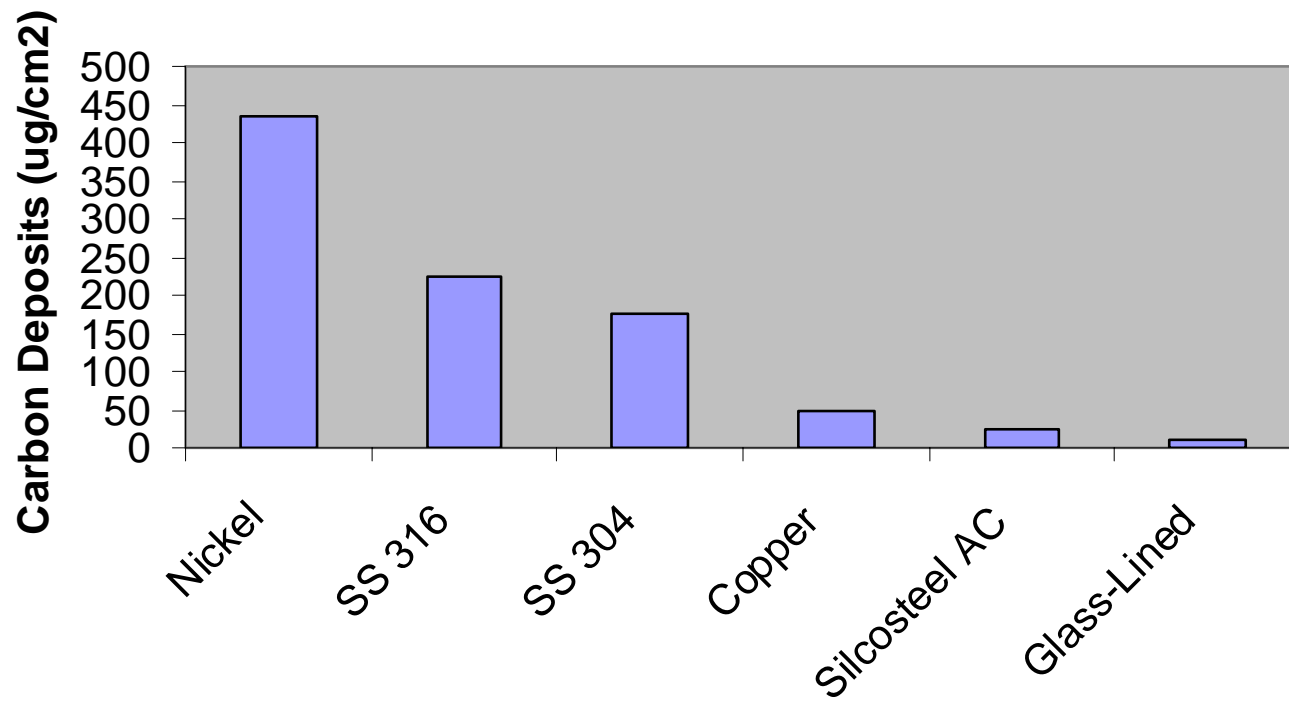
- Enhancing corrosion resistance in Marine environments
- Process streams containing HCl
- Protection of Continuous Emissions Monitoring Equipment (Nitric and Sulfuric acid)
- Use in Automotive Exhaust test equipment (Nitric and Sulfuric acid)

# Anti-Coking

- In applications of heated hydrocarbon transfer, carbon deposits can form
- Carbon deposits are catalyzed by nickel, sulfur and carbon in steel lattice
- The functionalized  $\alpha$ -silicon coating produces a barrier that eliminates catalytic carbon buildup

# Anti-Coking Data

**Carbon Deposits from JP-8 Fuel on Various Types of Tubing**



- Semih Eser; PSU Prof. Fuel Sciences
- 8x improvement over raw 316L



# Ultra-High Vacuum applications

- a-silicon layer releases moisture from surface more readily in vacuum
- Layer acts as a boundry to reduce outgassing of hydrocarbons and moisture from coated components used in vacuum systems
- Reduced outgassing rate by 14x @10 hrs of pumping
- Consistently outperforms cleaned parts
- Eliminates bakeout
- Faster pump down
- Lower base pressure with smaller pumps

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# Conclusions/Future

- Continual process improvement and new product development
  - Hardness
  - Improved corrosion resistance
  - Customized surfaces
- Develop Corrosion data comparing coating on different substrates
  - Enhancement of Carbon Steel
  - Protection of high nickel alloys
  - Value of coating in marine environments
  - Application of coating to valves & fasteners

# Acknowledgements

- Swagelok® Company
- O'Brien Corporation
- Haritec Scientific & Engineering Support
- Shell Research and Technology Centre
- Matco Associates

# Improved Sensitivity and Analysis Time for Semivolatile Organic Compounds Using GC-TOFMS : Can This Analysis Really be Performed in Less Than 10- Minutes?

**Frank Dorman, Gary Stidsen, Chris English,  
Michael Wittrig**

**Restek Corporation, Bellefonte, PA**

**Jack Cochran**

**LECO Corporation, Las Vegas, NV**

# Desires of GC Analysts

- Higher Sample Throughput
  - Lowers cost/sample
  - Increases sample capacity
  - Fewer instruments to accomplish same workload
- Better Resolution
  - Can allow for shorter run times
  - Improves quantitation
  - Can allow for analysis of very complex matrices

# USEPA Method 8270

## ■ GC-MS, Full Scan

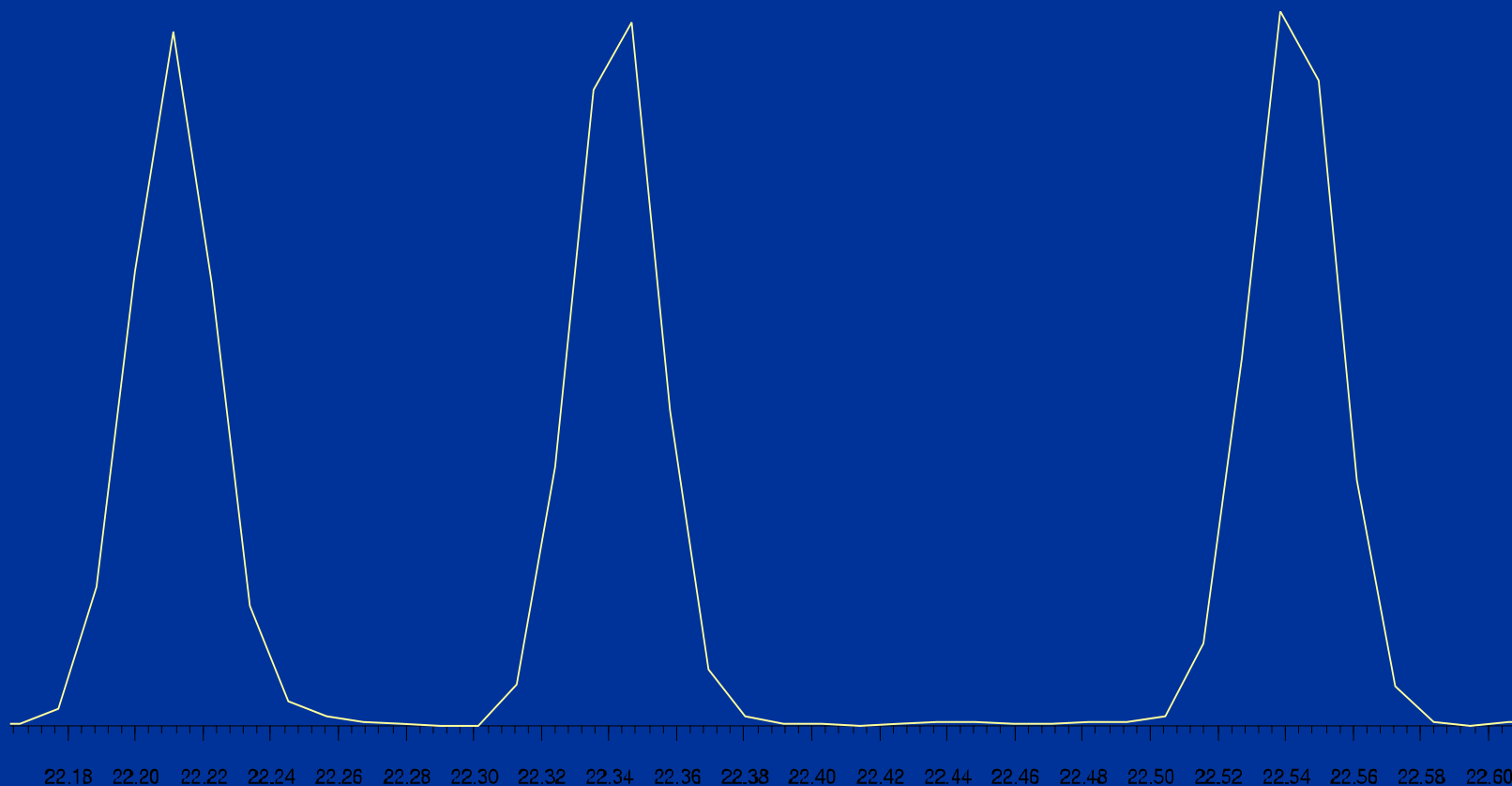
- 6 to 7 data points across peak is minimum recommendation
- 20 to 25 minute analysis time is practical limitation if using “conventional” MSD’s
- 20 to 160 ng calibrations – will overload most columns suitable for the analysis
- Extracts may have high concentration of co-extractable compounds
- Instrumentally intensive – routine maintenance



# How Many data points are enough to characterize a peak?



# Sampling Frequency Limitations of Quads and Ion Traps Can Cause Peak Biasing



# If we want to approach the 10-minute analysis time range, we will need to change something...

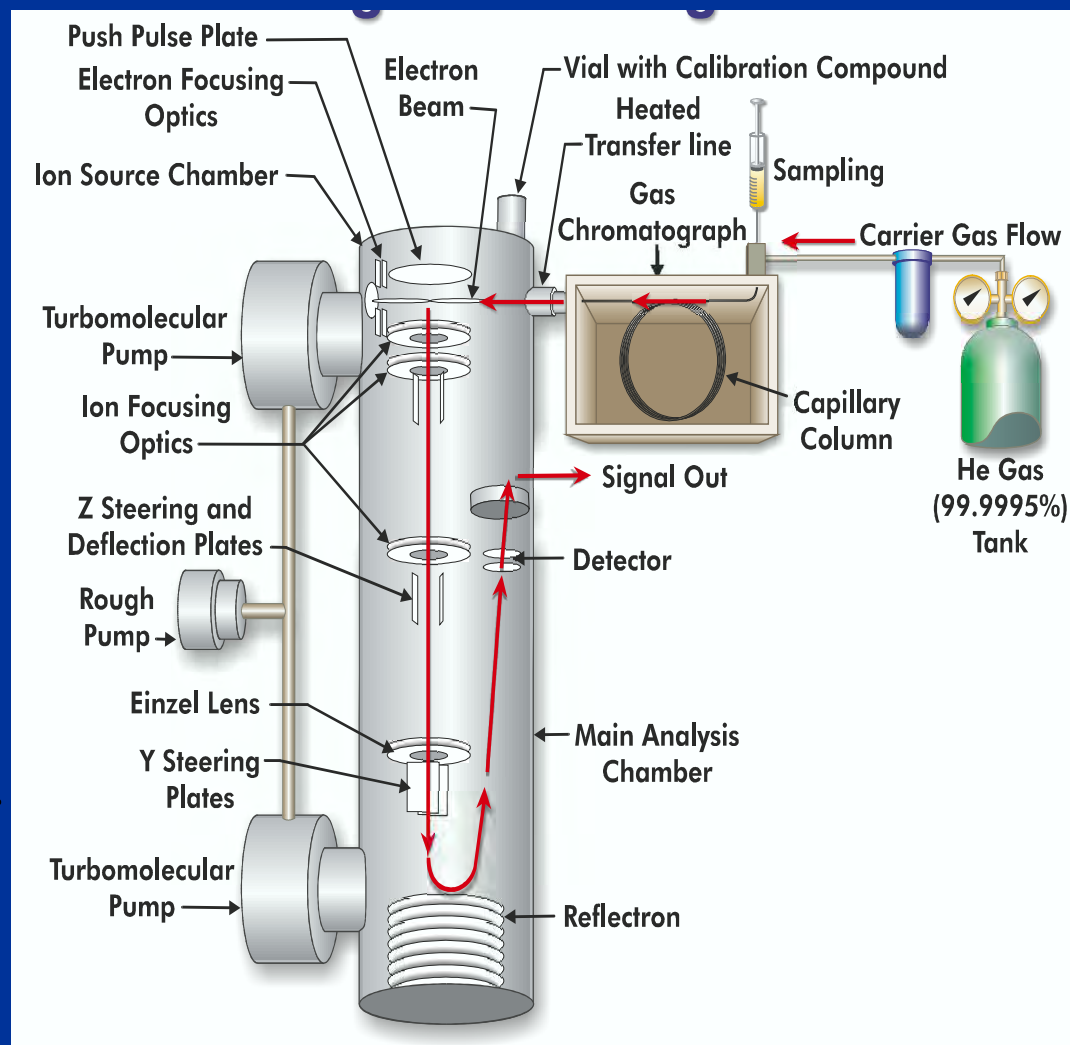
- Scan rate?
  - Most are running as fast as possible
- Scan Range
  - Not practical
- Time-of-Flight MS?
  - Can't sacrifice sensitivity, or calibration range
  - Can't add significant amount of maintenance
  - Feasible???

# Major Benefits of TOFMS

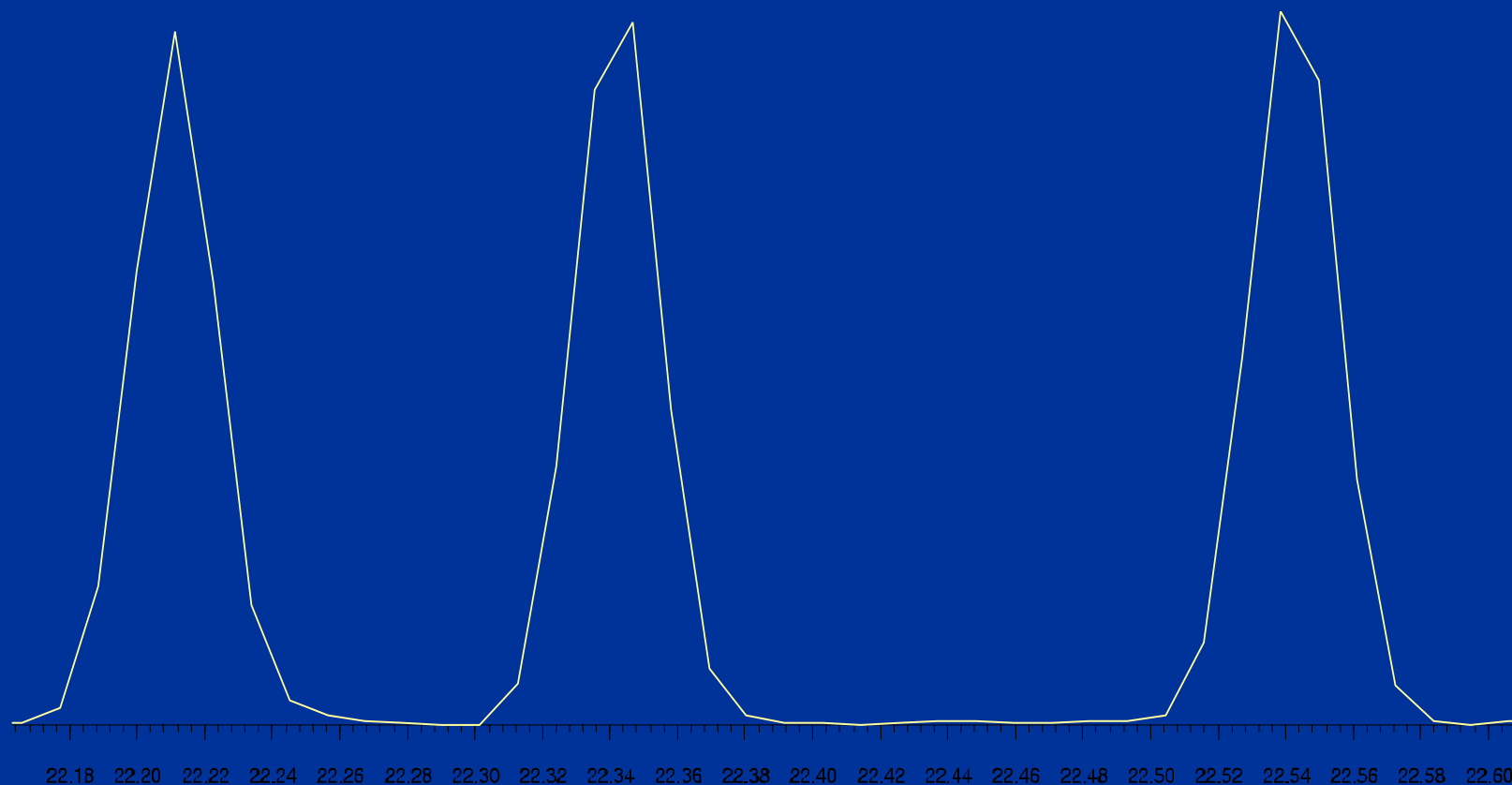
- Full mass spectrum acquired
- Full mass range sensitivity
  - Low pg range for most compounds
- Fast acquisition rates
  - Up to hundreds of spectra/sec
  - Defines narrow peaks from fast GC techniques
- Automated peak find
  - Find compounds buried beneath matrix
  - Locate non-target compounds
- Spectral deconvolution
  - Produce quality mass spectra from coeluting peaks
  - Library search deconvoluted spectra

# LECO Pegasus III GC-TOFMS

- Make ions
- Pulse them down a flight tube
- Arrival at detector is by time-of-flight
  - Low mass = faster
  - High mass = slower
- Detect ions



# Sampling Frequency Limitations of Quads and Ion Traps Can Cause Peak Biasing



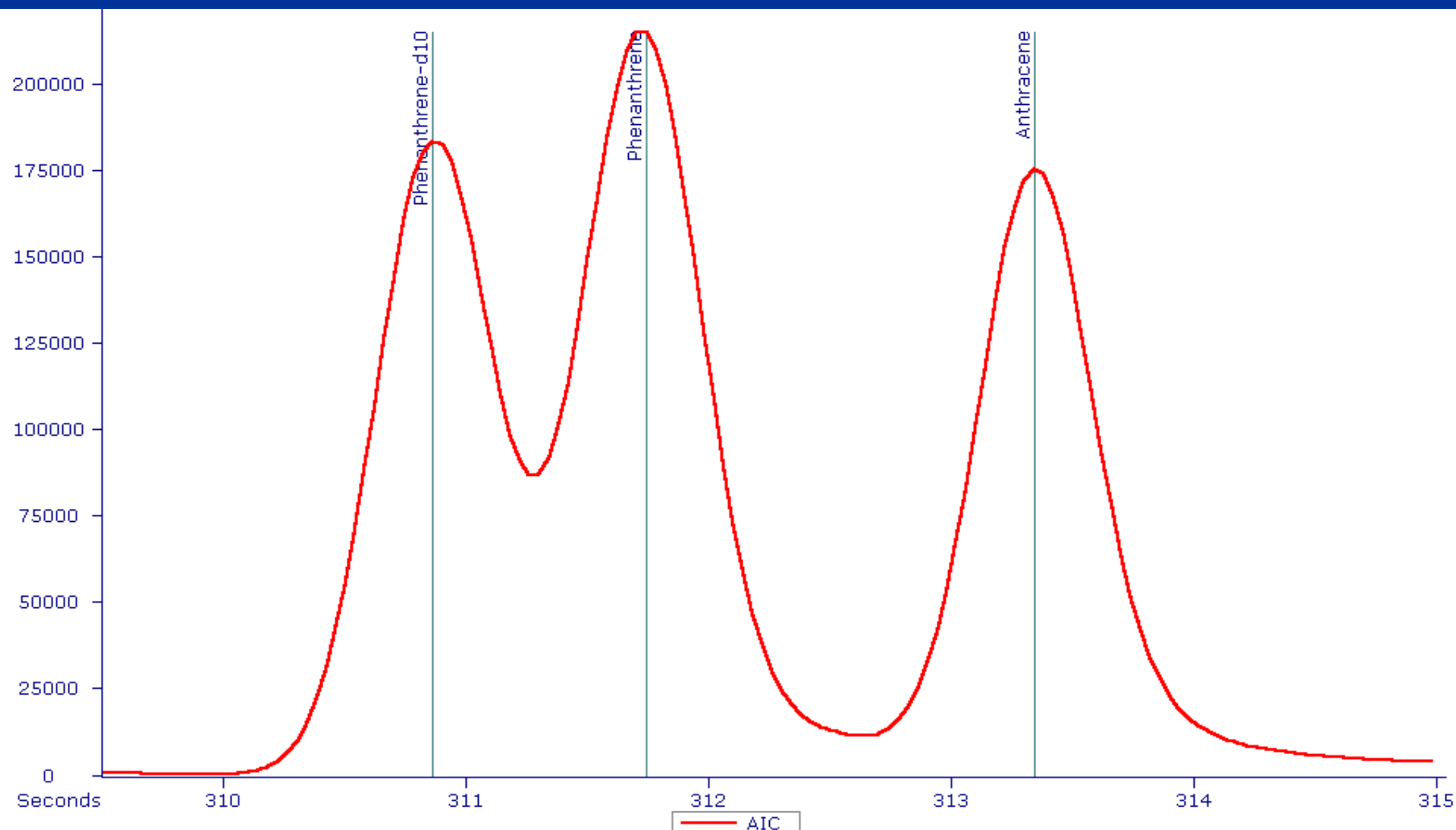
# PAH Standard – TIC

## Phenanthrene-D10, Phenanthrene, Anthracene

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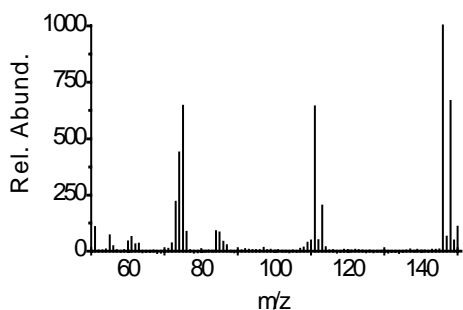
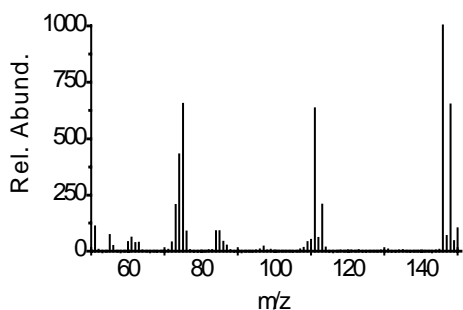
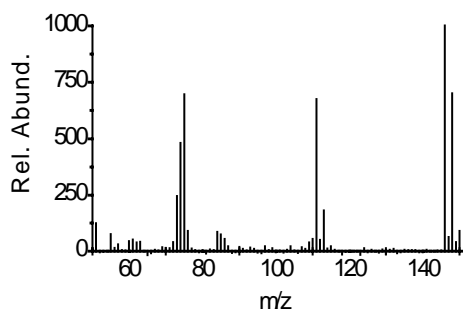
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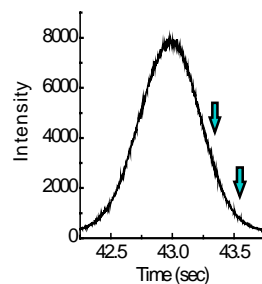
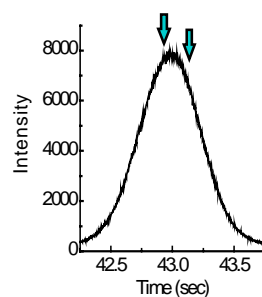
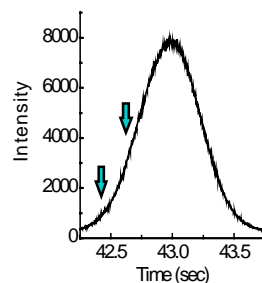


# Spectral Reproducibility

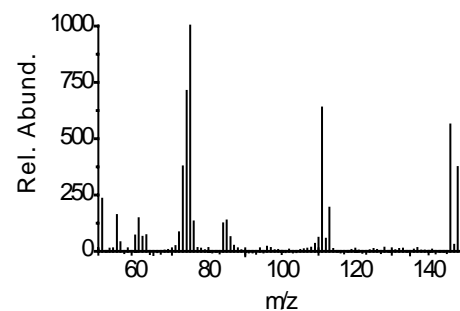
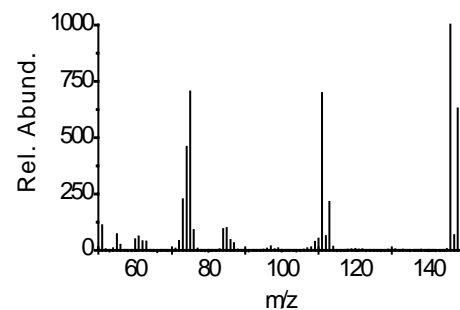
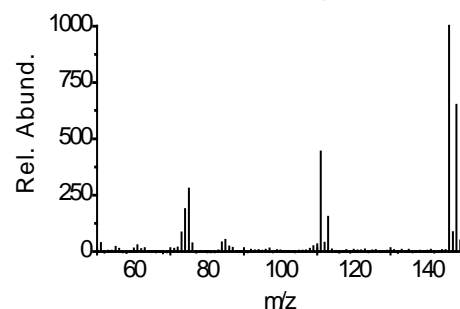
TOFMS



GC Peak



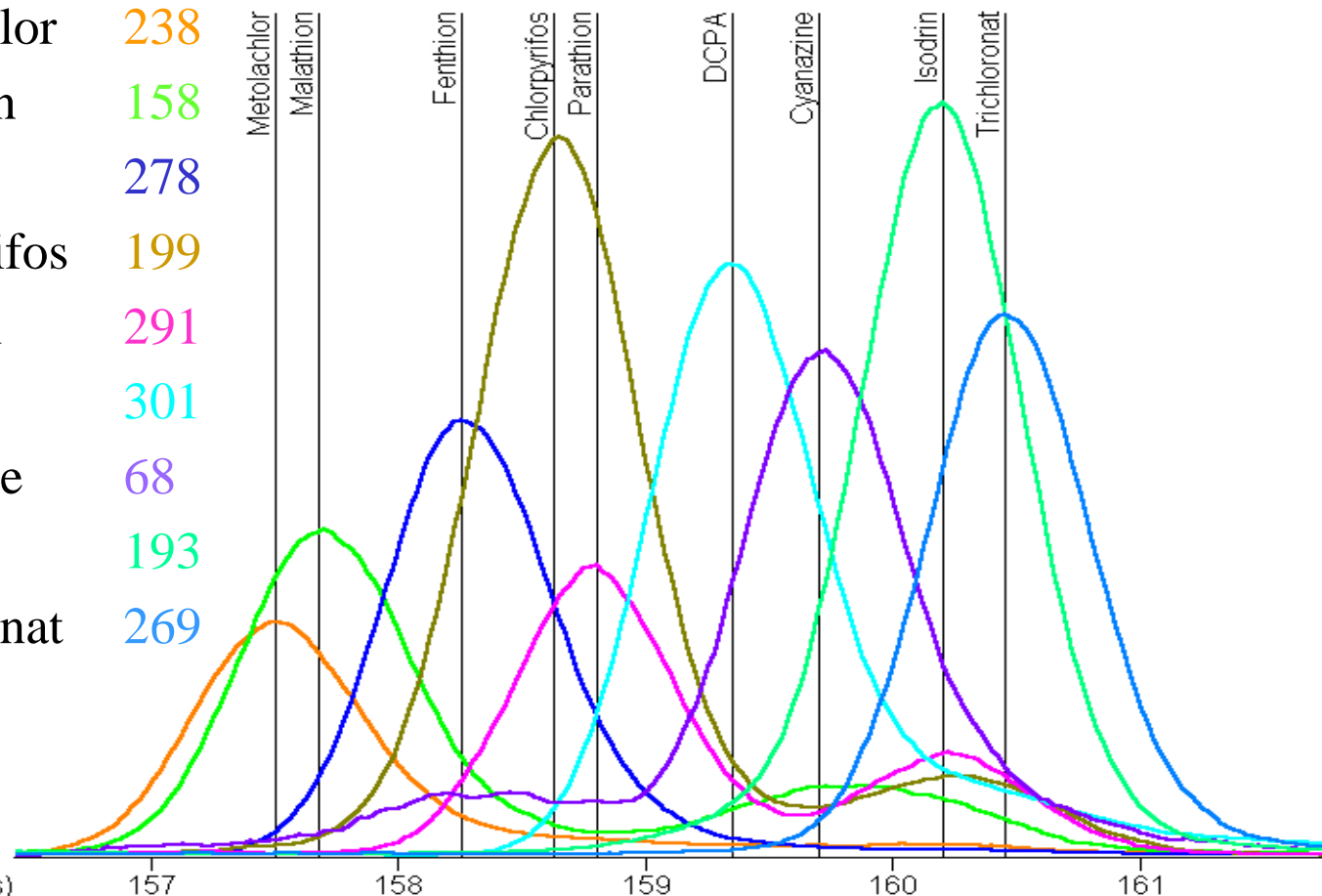
Scanning MS





# Peak Find at 40 Spectra/sec

Metolachlor	238
Malathion	158
Fenthion	278
Chlorpyrifos	199
Parathion	291
DCPA	301
Cyanazine	68
Isodrin	193
Trichloronat	269



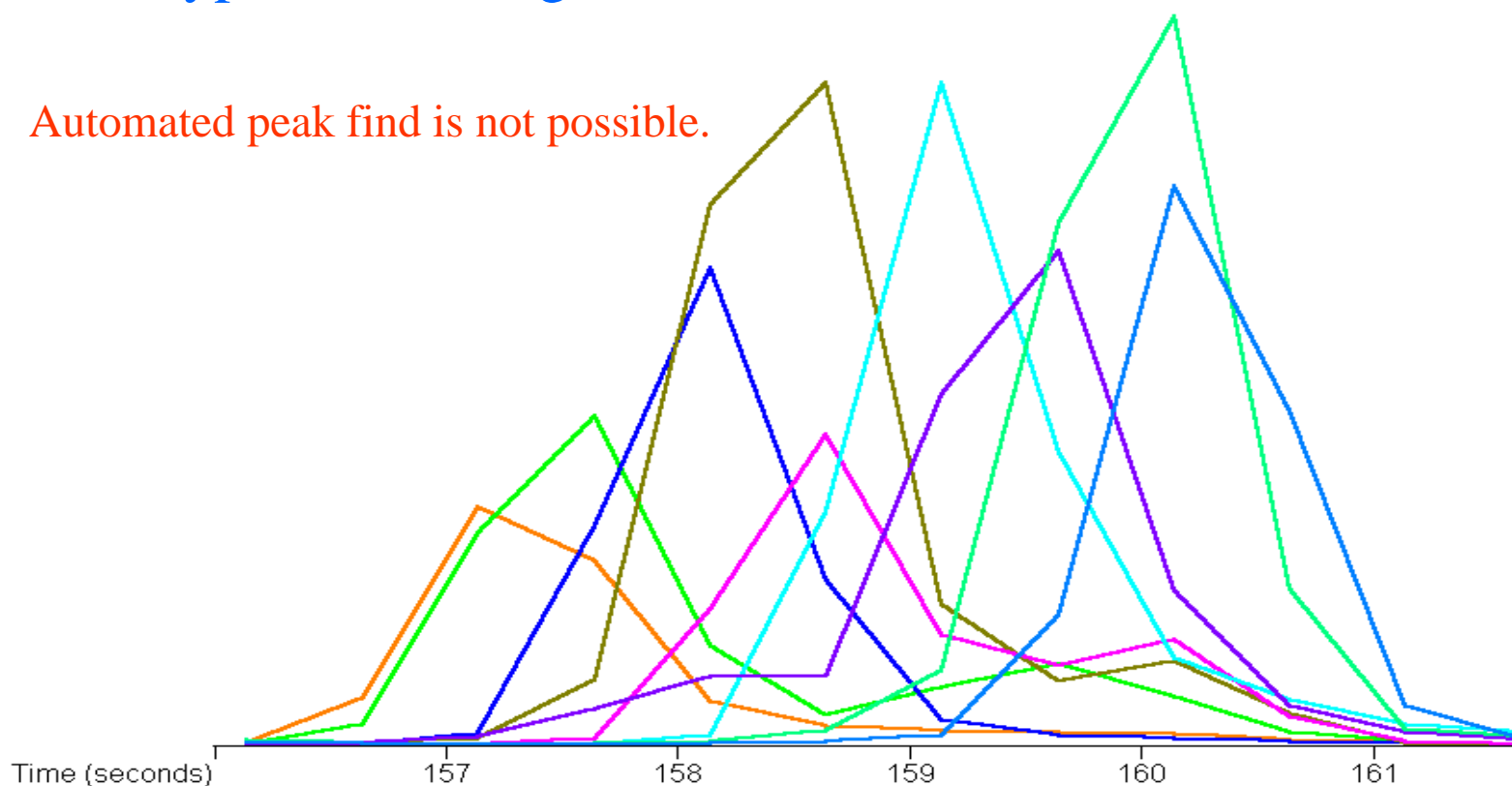
9 peaks located.



# 2 Spectra/sec

Typical scanning instrument rate

Automated peak find is not possible.



# 8270 Experiment

- Silarylene-based, Rtx-5Sil MS GC column
  - Low bleed, high Tmax
- Split Injection
  - Sharper Peaks, narrower peak width
  - Better sample handling for contaminated samples
- TOFMS
  - Record full scan data at necessary rate
- Analyze “real” samples and compare to “accepted values”
  - Technique needs to be equivalent, at a minimum for acceptance by environmental community

# GC Conditions

## ■ Split injection

- 4mm Restek Siltek liner with Siltek wool
- One microliter at 250°C
- Split ratio 50:1
- 10m x 0.18mm x 0.18µm Restek Rtx-5SilMS column
- Constant flow helium, 2 mL/minute

## ■ GC oven program

- 40°C (0.1 min), 30°/min to 340°(0 min)
- 25 sec solvent delay
- Total run time: 10 min

# GC Column Selection

- Short and narrow bore for rapid analysis
  - 10m x 0.18mm x 0.18 $\mu$ m Rtx-5SilMS
  - 2 mL/min He = ~130 cm/sec linear velocity
- Maximum operating temperature of 340°C
  - Necessary when fast oven programming is used so all compounds elute on ramp
  - Low bleed means low background to MS
- High degree of inertness
  - Analyzing many active compounds, including acids and bases

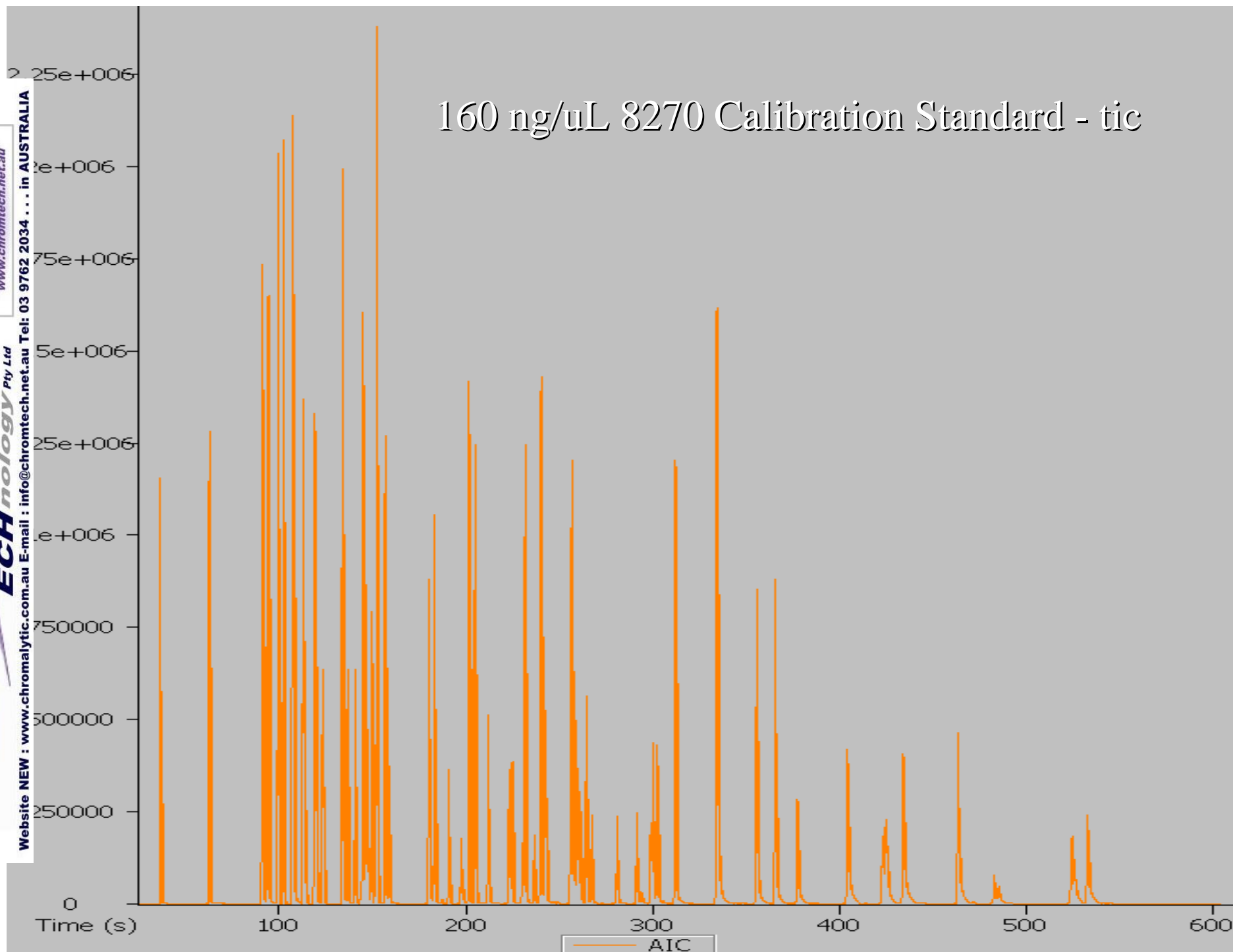
# TOFMS Conditions LECO Pegasus III

- Source temperature: 250°C
- Electron ionization: 70 eV
- Stored mass range: 35 to 500 u
- Acquisition rate: 20 spectra/sec

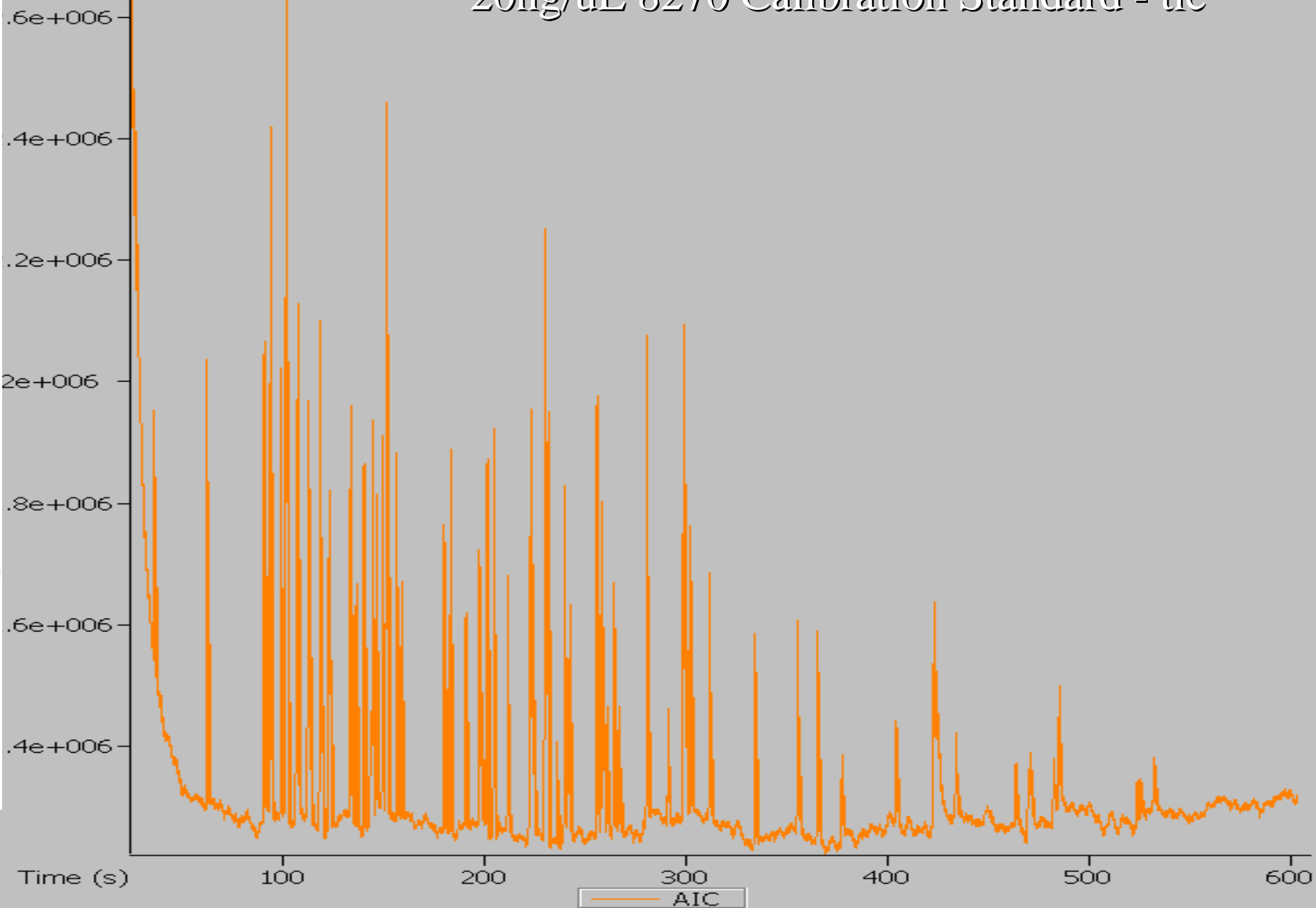
# Calibration

- 20 to 160 ng/uL
  - At 50:1 split ratio
- Can we go even lower?
  - Go as far as reasonably possible until we have linearity or sensitivity issues...
  - 8270, and 525 in 1 run?

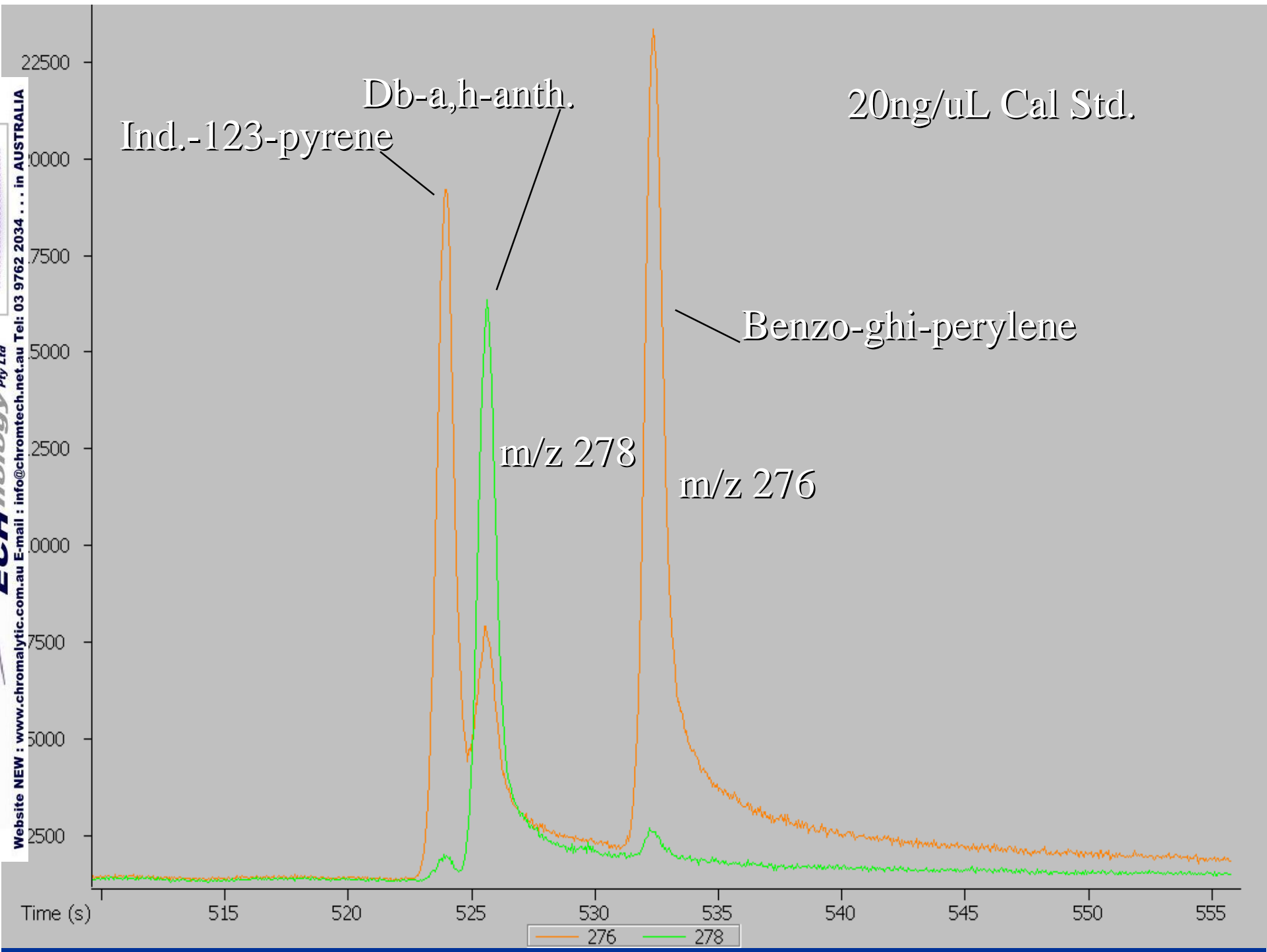
# 160 ng/uL 8270 Calibration Standard - tic

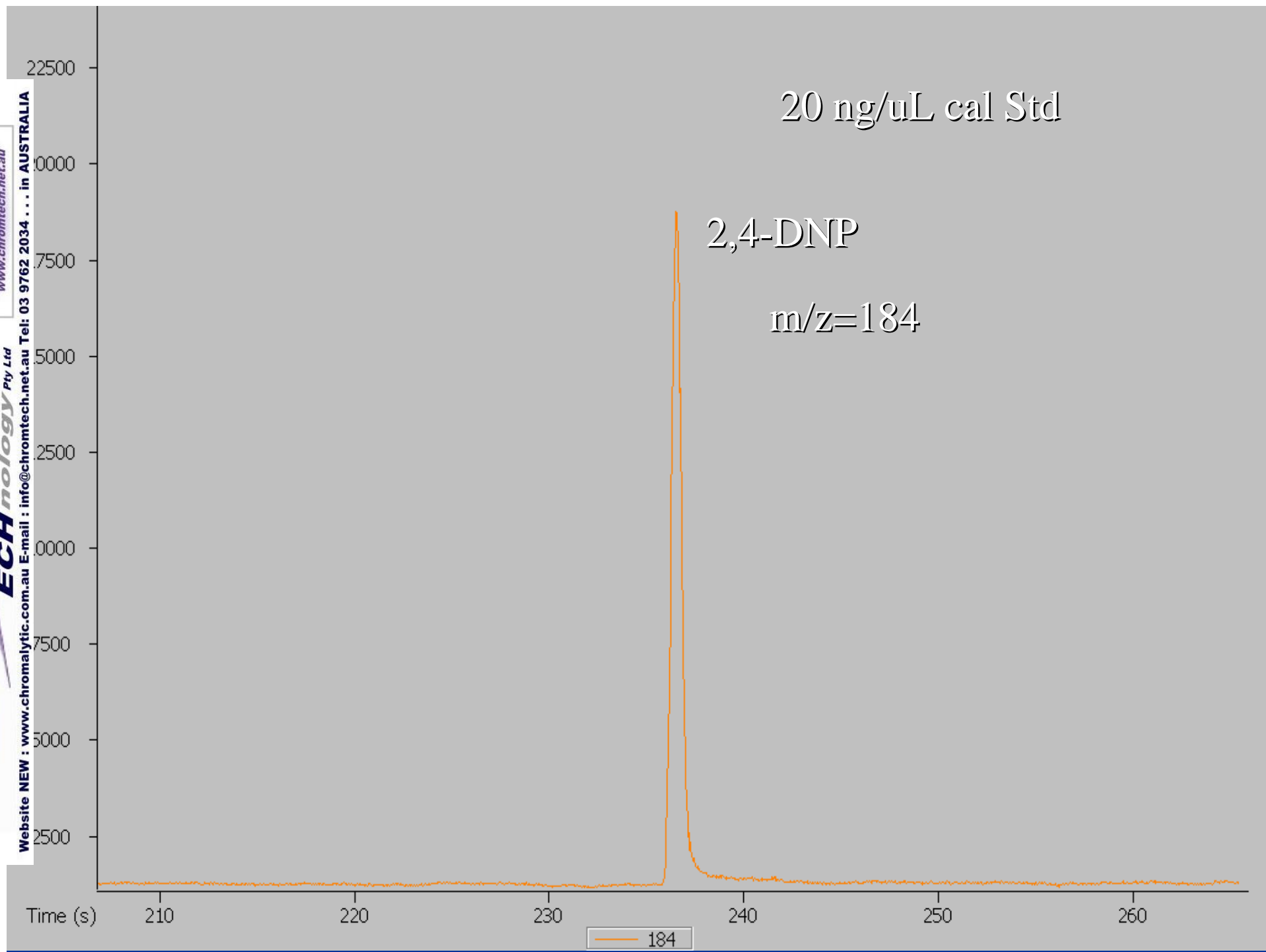


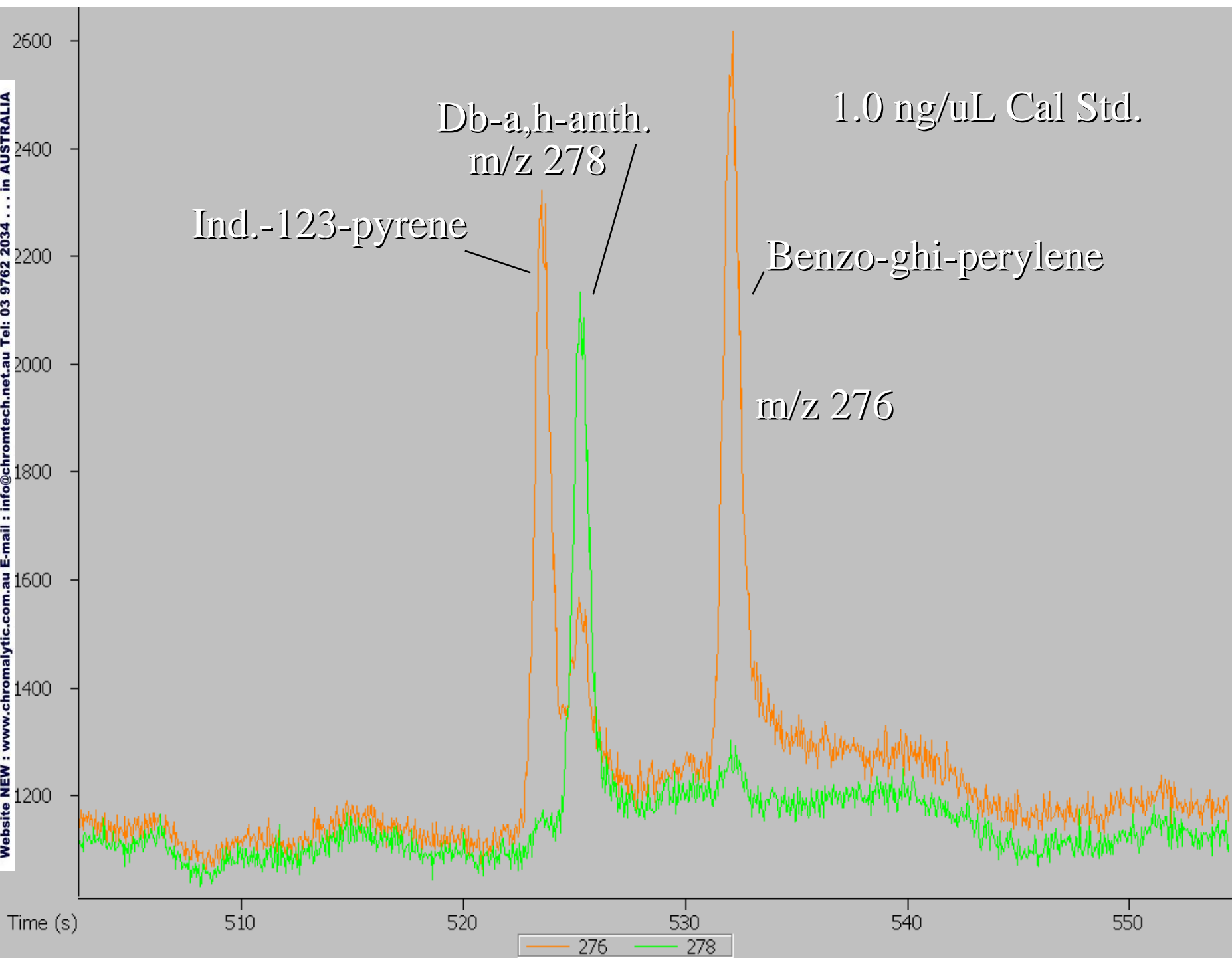
## 20ng/uL 8270 Calibration Standard - tic

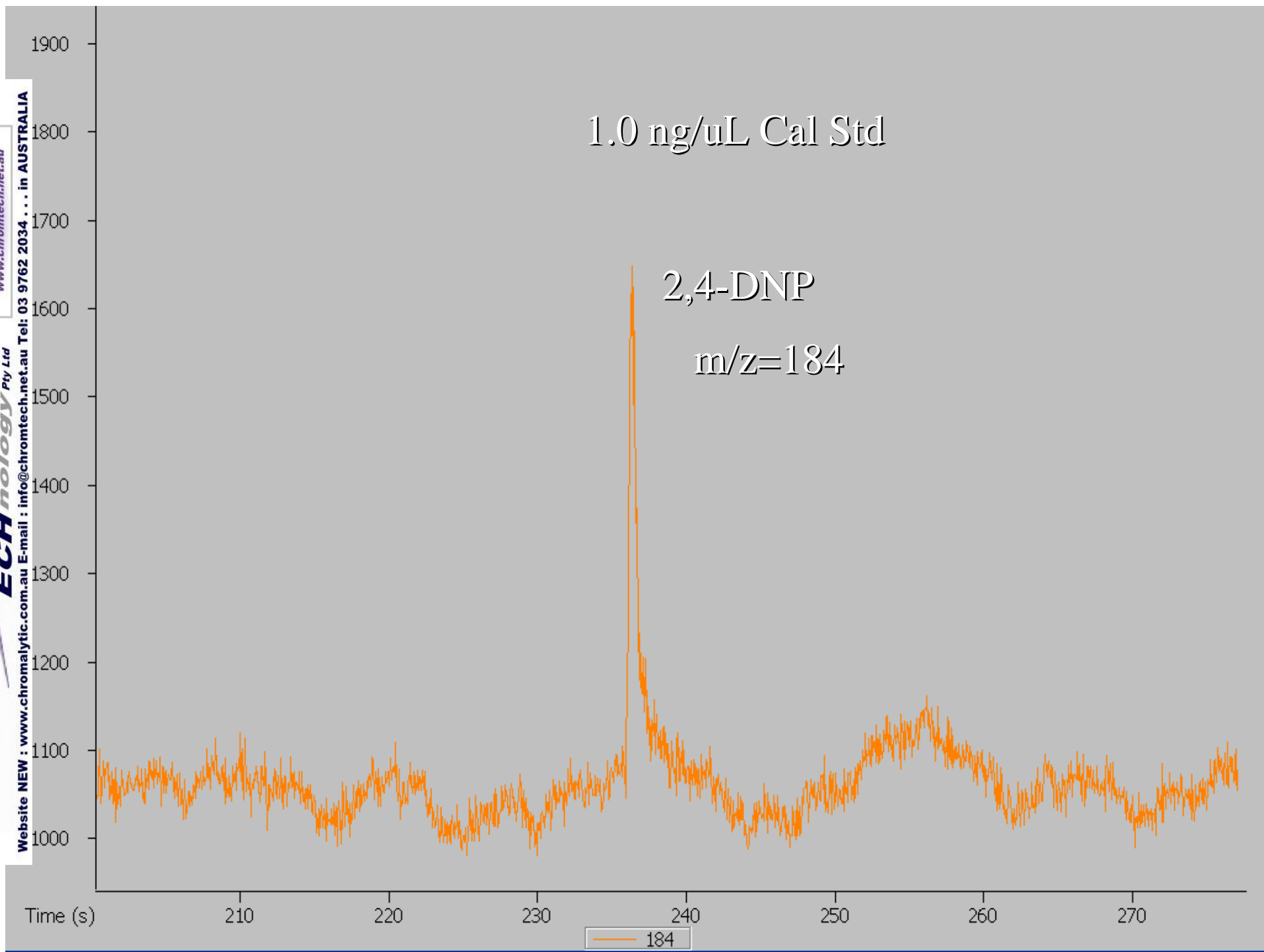


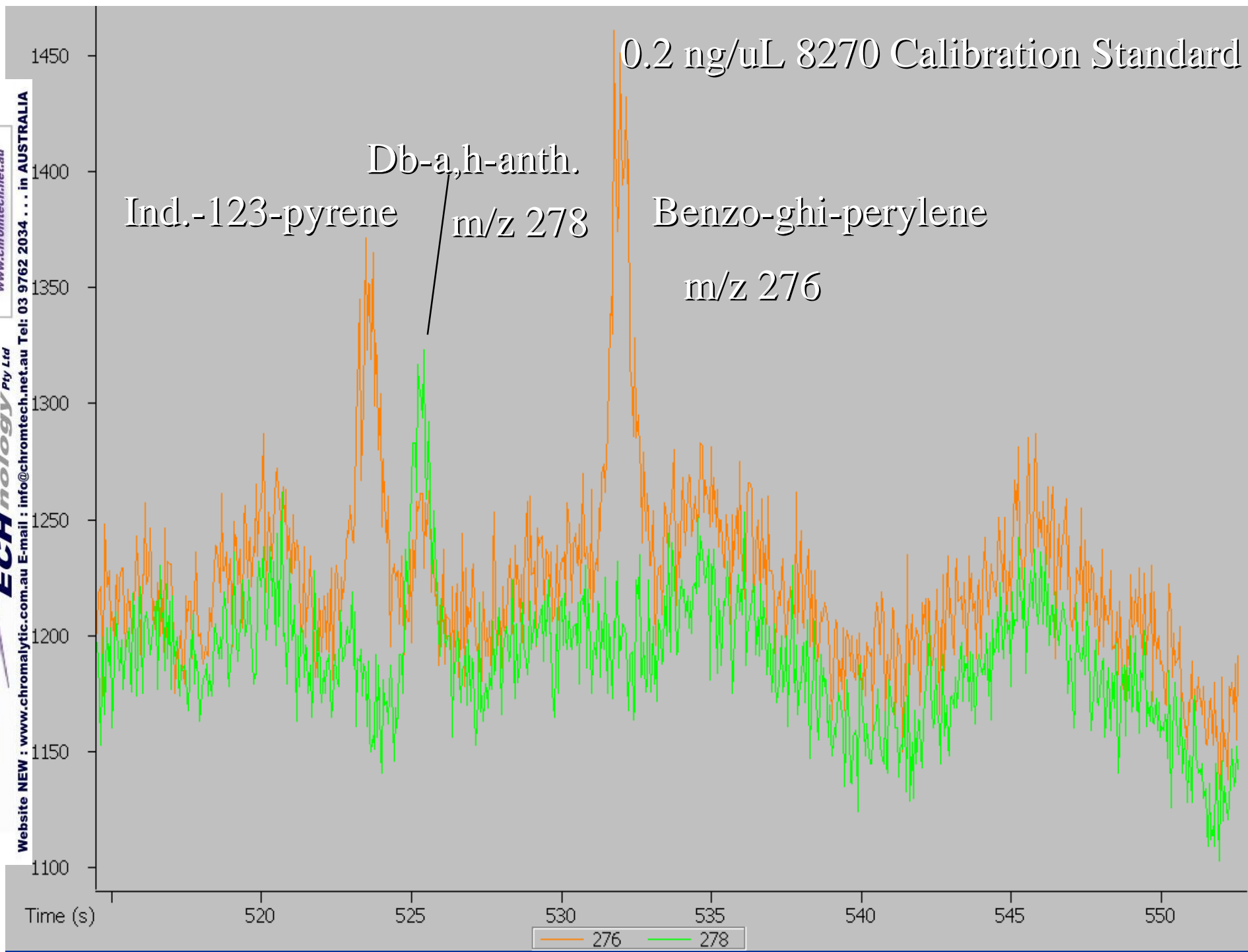




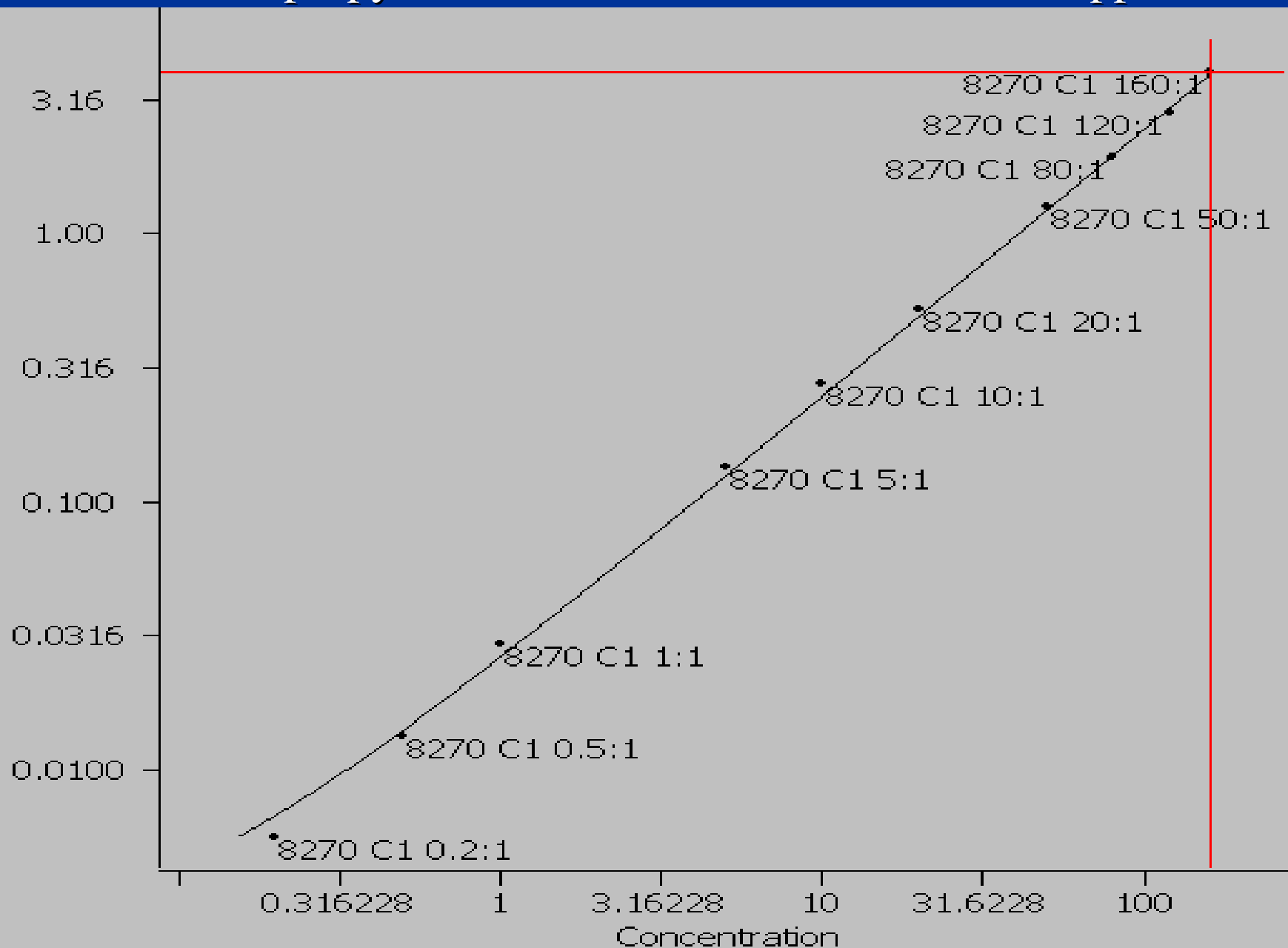








# N-nitrosodipropylamine Calibration Curve 0.2 to 160 ppm



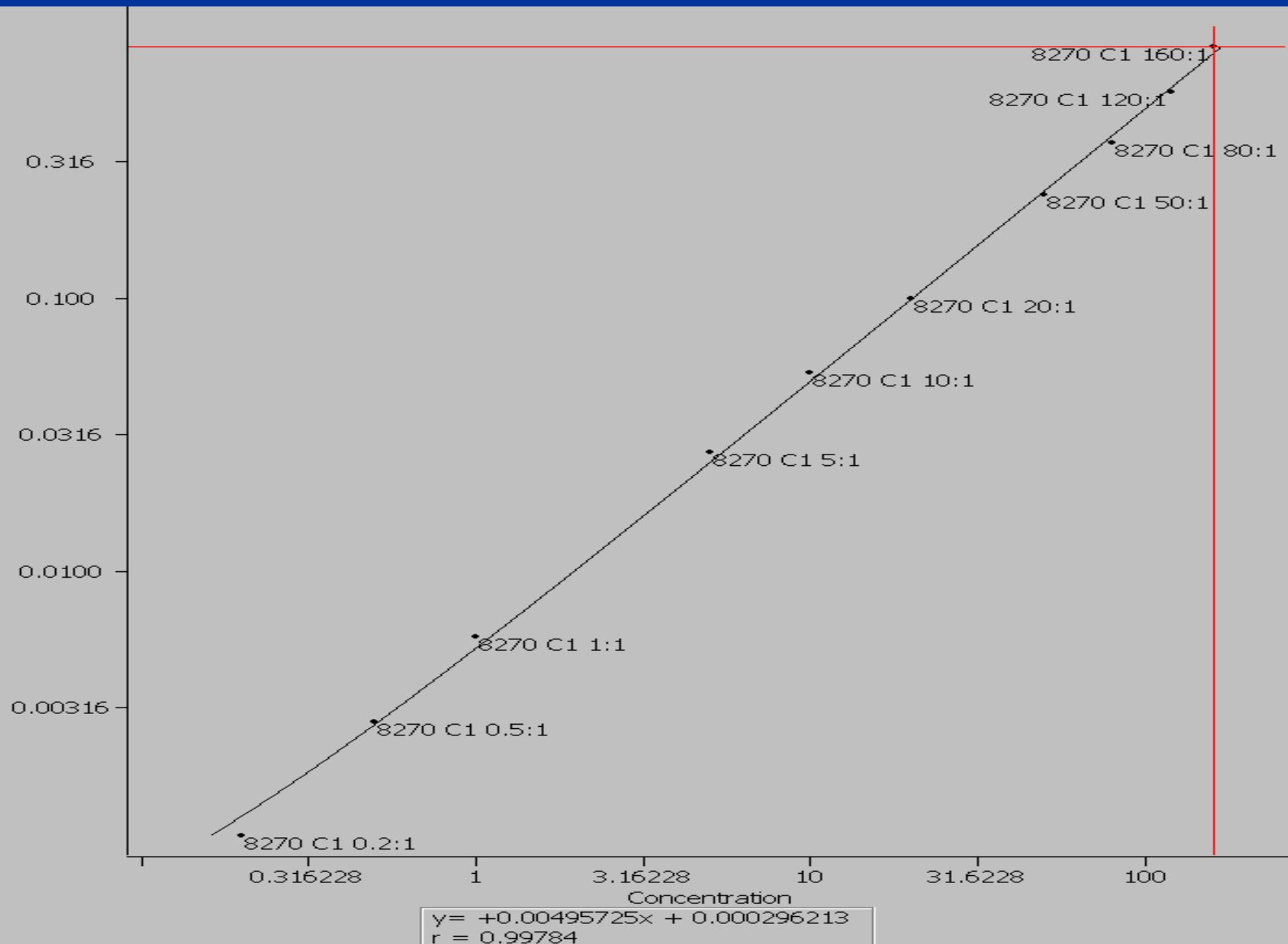
$$y = +0.0247311x + 0.00190052$$
$$r = 0.99916$$

# Hexachlorobutadiene Calibration Curve 0.2 to 160 ng/uL

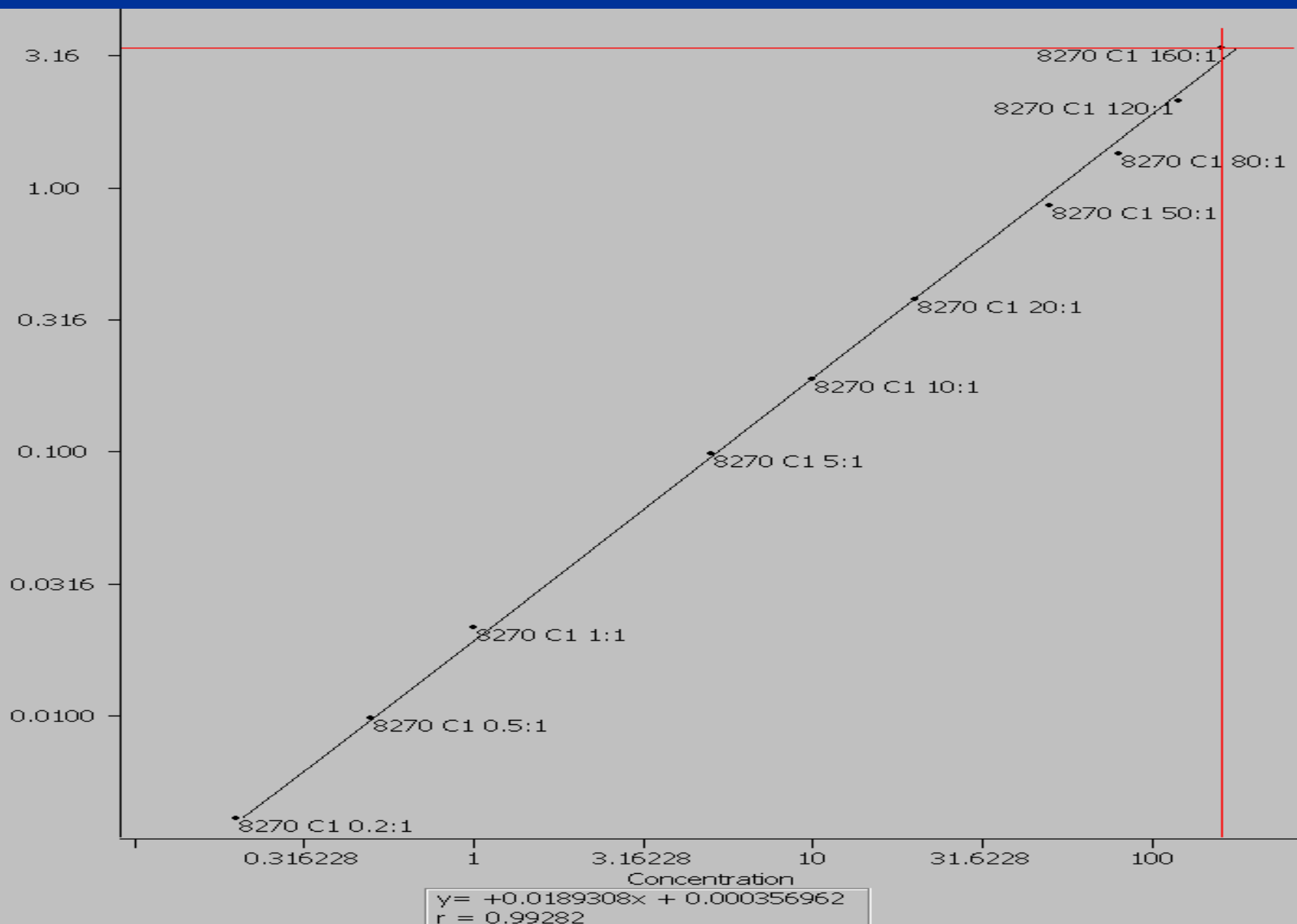
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# Indeno-1,2,3-cd pyrene Calibration Curve 0.2 – 160 ng.uL





## Calibration: 0.2 – 160 ng/uL

Analyte	Name	RF	% RSD RF
1	N-nitrosodimethylamine	1.0355	8.2945
2	2-Fluorophenol	1.2680	7.6450
3	Phenol-d6	.3376	6.7295
4	Phenol	1.7126	8.1128
5	2-Chlorophenol-d4	1.2784	8.7205
6	Bis(2-chloroethyl) ether	1.7656	10.312
7	2-Chlorophenol	1.3272	8.3891
8	1,3-Dichlorobenzene	1.4816	8.8188
10	1,4-Dichlorobenzene	1.5300	9.3936
12	1,2-Dichlorobenzene	1.4162	9.8743
13	Benzyl alcohol	0.62129	5.4928
14	2-Methylphenol	1.0014	7.5679
15	Bis(2-Chloroisopropyl) ether	4.0564	10.865
16	N-nitrosodipropylamine	1.0531	6.8509
17	4-Methylphenol	1.3962	7.6146
18	Hexachloroethane	0.63759	6.3153
20	Nitrobenzene	0.79893	5.7447

## Calibration: 0.2 – 160 ng/uL

Analyte	Name	RF	% RSD RF
25	2,4-Dichlorophenol	0.45040	5.4932
26	Benzoic acid	0.28141	6.0157
27	1,2,4-Trichlorobenzene	0.50528	6.2814
30	4-Chloroaniline	0.76842	5.8820
31	Hexachlorobutadiene	0.20824	7.2981
32	4-Chloro-3-methyl phenol	0.52651	4.2807
33	2-Methylnaphthalene	0.77941	7.0069
34	Hexachlorocyclopentadiene	0.58097	4.9004
35	2,4,6-Trichlorophenol	0.65494	6.3512
36	2,4,5-Trichlorophenol	0.75073	4.2657
37	2-Fluorobiphenyl	2.0950	8.7763
38	2-Chloronaphthalene	2.3569	7.4887
39	2-Nitroaniline	1.2166	3.4748
40	Dimethyl phthalate	2.4481	5.8420
41	Acenaphthylene	3.3182	8.2350
42	2,6-Dinitrotoluene	0.54913	5.3293
44	3-Nitroaniline	0.68362	11.639
45	Acenaphthene	1.7045	8.1745
46	2,4-Dinitrophenol	0.25791	8.7682

## Calibration: 0.2 – 160 ng/uL

Analyte	Name	RF	% RSD RF
47	Dibenzofuran	2.7990	8.3769
48	4-Nitrophenol	0.56334	7.9127
49	2,4-Dinitrotoluene	0.75561	7.4913
50	Fluorene	1.9027	6.7142
51	Diethyl phthalate	2.7242	5.1845
52	4-Chlorophenyl phenyl ether	0.96773	6.5160
53	4-Nitroaniline	0.68371	11.678
54	4,6-Dinitro-2-methylphenol	0.17243	12.039
55	N-Nitrosodiphenylamine	0.74167	5.7546
56	2,4,6-Tribromophenol	0.16120	6.6840
59	Pentachlorophenol	0.17331	7.8475
61	Phenanthrene	1.5889	9.3179
62	Anthracene	1.6295	5.2792
63	Carbazole	1.4902	4.5625
64	Dibutyl phthalate	2.3977	4.8314
65	Fluoranthene	1.3318	4.1521
66	Pyrene	2.8087	14.550
68	Butyl benzyl phthalate	1.3279	9.5554

# Data Comparison

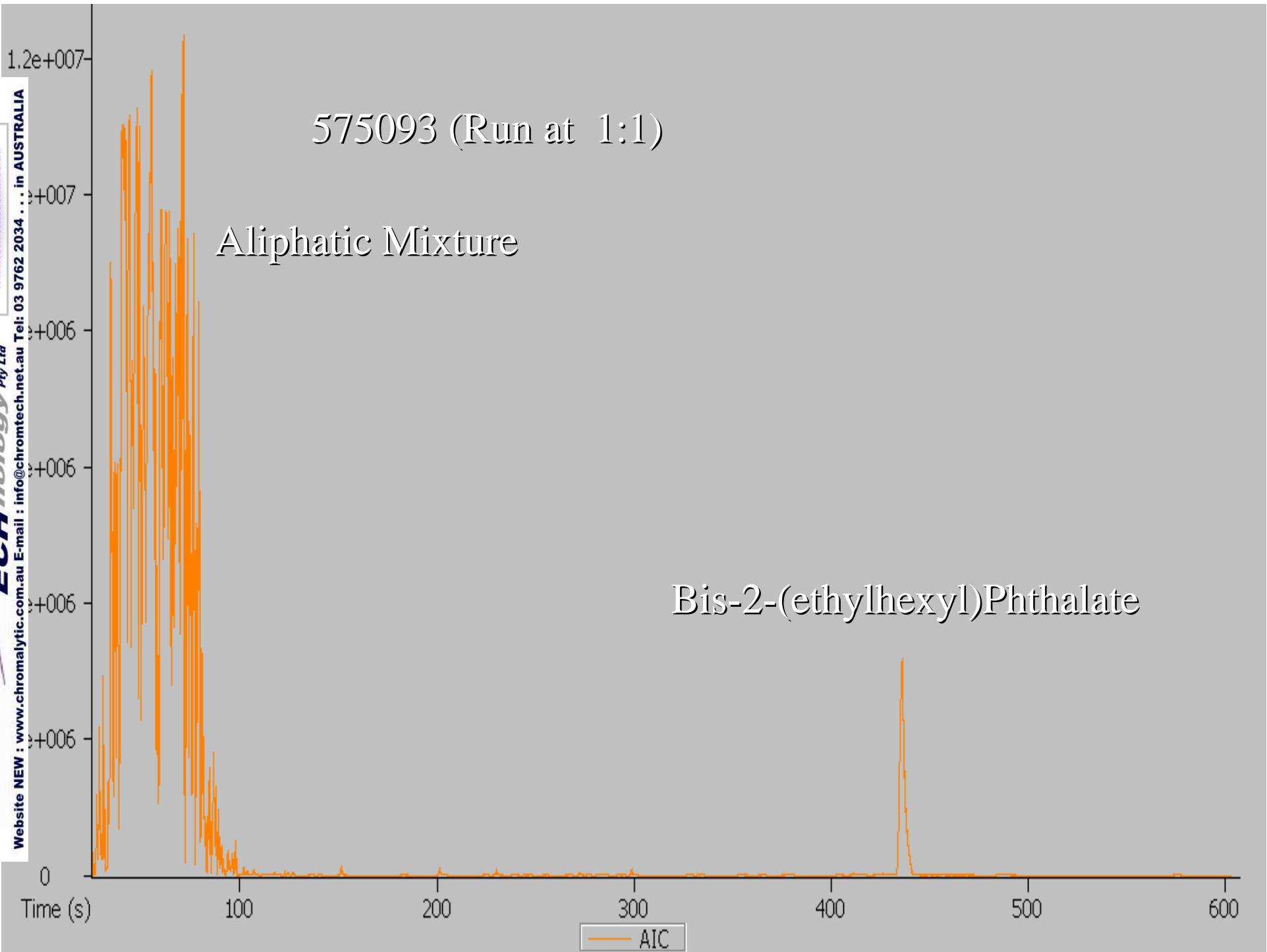
15 samples analyzed, ranging from  
extraction blanks and LCS's to  
highly contaminated soils

# K5LCS

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
N-nitrosodimethylamine	35.15	28	-25.5
2-Fluorophenol	78.94	77	-2.5
Phenol-d6	76.99	78	1.3
Phenol	43.18	34	-27.0
2-Chlorophenol-d4	81.98	78	-5.1
Bis(2-chloroethyl) ether	38.91	34	-14.4
2-Chlorophenol	37.81	33	-14.6
1,3-Dichlorobenzene	35.01	31	-12.9
1,4-Dichlorobenzene	35.42	30	-18.1
1,2-Dichlorobenzene-d4	55.47	56	0.9
1,2-Dichlorobenzene	34.99	30	-16.6
Benzyl alcohol	35.91	35	-2.6
2-Methylphenol	34.18	35	2.3
Bis(2-Chloroisopropyl) ether	37.34	34	-9.8
N-nitrosodipropylamine	28.72	33	13.0

575095

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
2-Fluorophenol	65.61	67.95	3.4
Phenol-d6	62.26	70.2	11.3
2-Chlorophenol-d4	66.53	67.46	1.4
1,2-Dichlorobenzene-d4	45.11	46.97	4.0
2-Methylphenol	1.33	1.4	5.0
4-Methylphenol	1.19	1.3	8.5
Nitrobenzene-d5	43.77	46.94	6.8
2-Fluorobiphenyl	40.11	37.16	-7.9
2,4,6-Tribromophenol	48.67	47.38	-2.7
p-Terphenyl-d14	0.42	0.38	-10.5
Bis(2-ethylhexyl) phthalate	1.67	4.8	65.2





# 575093 D1

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
2-Fluorophenol	0	32	100.0
Phenol-d6	64.83	34	-90.7
2-Chlorophenol-d4	68.25	35	-95.0
1,2-Dichlorobenzene-d4	36.39	27	-34.8
Nitrobenzene-d5	32.14	20	-60.7
2-Fluorobiphenyl	34.81	24	-45.0
Bis(2-ethylhexyl) phthalate	6500	4025	-61.5



# 575093MS

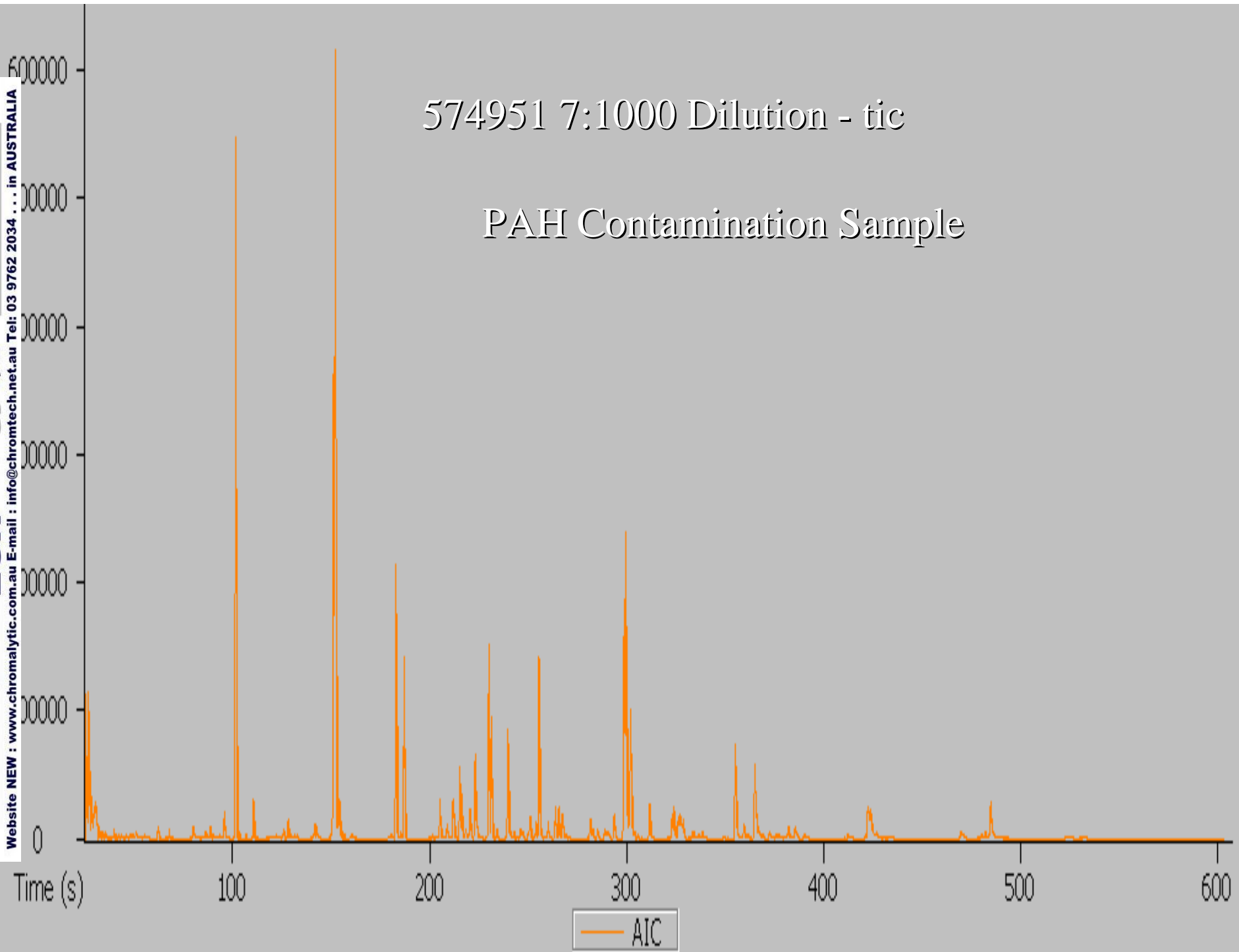
Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
N-nitrosodimethylamine	93.81	40.1	-133.9
2-Fluorophenol	ND	ND	
Phenol-d6	96.83	62.1	-55.9
Phenol	52.97	16.03	-230.4
2-Chlorophenol-d4	60.64	64.98	6.7
Bis(2-chloroethyl) ether	29.48	28.47	-3.5
2-Chlorophenol	30.12	30.47	1.1
1,3-Dichlorobenzene	28.48	25.53	-11.6
1,4-Dichlorobenzene	29.19	26.04	-12.1
1,2-Dichlorobenzene-d4	42.89	45.5	5.7
1,2-Dichlorobenzene	29.5	25.54	-15.5
Benzyl alcohol	26.46	29.91	11.5
2-Methylphenol	29.24	29.58	1.1
Bis(2-Chloroisopropyl) ether	30.1	26.73	-12.6
N-nitrosodipropylamine	19.92	28.06	29.0

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574951 7:1000 Dilution - tic

PAH Contamination Sample



574951

Target Compound	TOF Concentration at DF=142.9	Corrected Concentration	STL Value	% Difference TOF -vs- STL
2-Fluorophenol	0.43	61.4	49.25	-24.8
Phenol-d6	0.46	65.7	ND	
2-Chlorophenol-d4	0.43	61.4	55.42	-10.9
1,2-Dichlorobenzene-d4	0.27	38.6	73.14	47.2
Nitrobenzene-d5	0.32	45.7	ND	
Naphthalene	53.61	7660.9	6560	-16.8
2-Methylnaphthalene	16.84	2406.4	2378	-1.2
2-Fluorobiphenyl	0.31	44.3	68.99	35.8
Acenaphthylene	7.45	1064.6	861	-23.6
Acenaphthene	8.75	1250.4	1148	-8.9
Dibenzofuran	10.7	1529.0	1312	-16.5
Fluorene	13.64	1949.2	1681	-16.0
2,4,6-Tribromophenol	0.61	87.2	42.82	-103.6
Phenanthrene	33.72	4818.6	4510	-6.8

# 574951 - continued

Target Compound	TOF Concentration at DF=142.9	Corrected Concentration	STL Value	% Difference TOF -vs- STL
Anthracene	15.12	2160.6	2132	-1.3
Carbazole	4.3	614.5	ND	
Fluoranthene	17.28	2469.3	2501	1.3
Pyrene	15.27	2182.1	1845	-18.3
-Terphenyl-d14	0.27	38.6	76.88	49.8
Benzo[a]anthracene	8.29	1184.6	1066	-11.1
Chrysene	5.65	807.4	943	14.4
Bis(2-ethylhexyl) phthalate	0.34	48.6	ND	
Benzo[b]fluoranthene	6.17	881.7	533	-65.4
Benzo[k]fluoranthene	1.82	260.1	697	62.7
Benzo[a]pyrene	3.55	507.3	738	31.3
Indeno[123-cd]pyrene	2.4	343.0	254	-35.0
Dibenz[ah]anthracene	0.69	98.6	127	22.4
Benzo[ghi]perylene	1.42	202.9	221	8.2

# Did we pass?

- Data are comparable
  - Very few values are outside the accepted error range
- Data processing time is similar
  - Spectral quality from TOFMS is generally more accurate, and automatic
- Analysis time goals were met
- Calibration passes all USEPA method requirements (8270, OLM, 625, 525, etc...)
- Sensitivity improvement by 10 to 20 fold
  - Even using split injection

# Conclusions

- Fast GC-TOFMS
  - Quantification of actual samples similar to “accepted” technique
    - » Analysis time improved versus conventional GC-MS
    - » Sensitivity Improvement
  - Analysis times of less than 10 minutes are possible
  - Low pg sensitivity with full mass spectrum
  - Automated data handling
- Rtx-5Sil MS column performed very well
  - Inertness, even at low concentrations, was excellent
  - Met all separation needs
- Fast GC-TOFMS should have little downtime
  - Split injection
  - Inert, high temperature stable GC column
  - No mass spectrometer source cleaning
- Complete data comparison is available

# Methods of Analysis of Polychlorinated Biphenyl Congeners Using an Application-Specific Capillary GC Column

Frank L. Dorman, Gary B. Stidsen, Chris M. English and Lydia Nolan

Restek Corporation, Bellefonte, PA

Jack Cochran

LECO Corporation, Las Vegas, NV



# 209 Possible PCB Congeners

- 7 Indicator Congeners (European):
  - 28,52,101,118,138,153,180
  - Indicate presence/absence of PCB's
- 12 Most Toxic Congeners (WHO):
  - 77,81,126,169
  - 105, 114, 118, 123, 156, 157, 167, 189
  - Have Dioxin-like behavior
- 136 Congeners in Aroclor Products
  - Frame, et. al. (Fresenius J. Anal .Chem. 357, 714-22)
  - Add 126, 81, 169, and 209
- 140 Congeners should satisfy almost everyone



# Analytical Techniques

## ● GC-MS

### ■ Pros:

- Allows for spectral separation of coeluting congeners of different chlorination level
- Single column
- Common instrumentation in many laboratories

### ■ Cons:

- Moderate sensitivity

# Analytical Techniques

## ● GC-ECD

### ■ Pros:

- High Sensitivity
- Simplest instrumentation
- Common instrumentation in many laboratories

### ■ Cons:

- Dual column system usually necessary
- Must have chromatographic separation

# Analytical Techniques

## ● GCxGC-TOFMS (GCxGC – ECD)

### ■ Pros:

- Allows for spectral separation of coeluting congeners of different chlorination level
- Sensitivity improvement –vs- GC-MS
- Increase in peak capacity for chromatographic separation

### ■ Cons:

- Instrumentally more complex
- Commercial instrumentation only recently available

# Which GC Column?

- Identification of all 209 available on many phases
- **Rtx-PCB** column designed for this analysis
  - Greatest number of resolved congeners
  - High thermal stability
- Rtx-XLB column good for GC-MS
- Rtx-1, 5, CLPesticides, CLPesticides2, **440**, Dioxin2, 500, 35, 1301, etc...

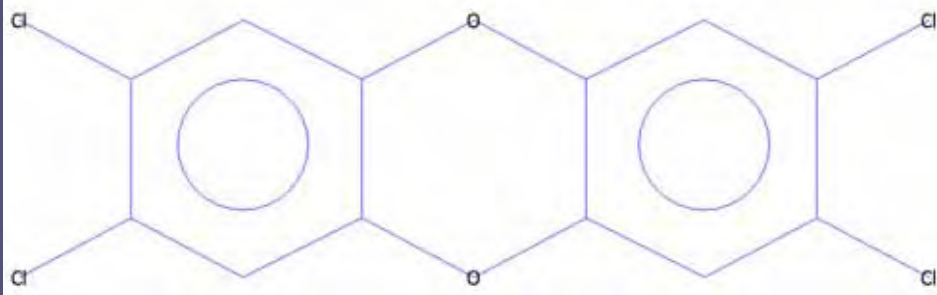
# Dioxin-like PCBs

PCB#	Cl#	Cl Pos.		PCB#	Cl#	Cl Pos.
77	4	34-34		156	6	2345-34
81	4	345-4		157	6	234-345
				167	6	245-345
105	5	234-34		169	6	345-345
114	5	2345-4				
118	5	245-34		189	7	2345-345
123	5	345-24				
126	5	345-34				

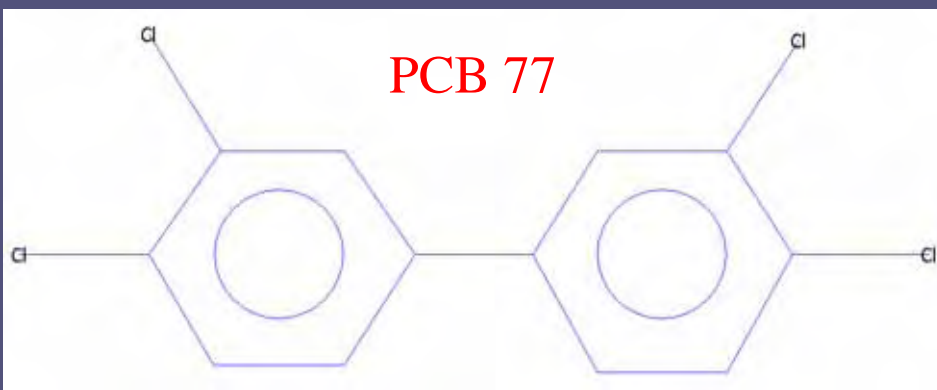
World Health Organization, non- and mono-ortho substituted

# Toxicity of PCBs

2378-TCDD



PCB 77

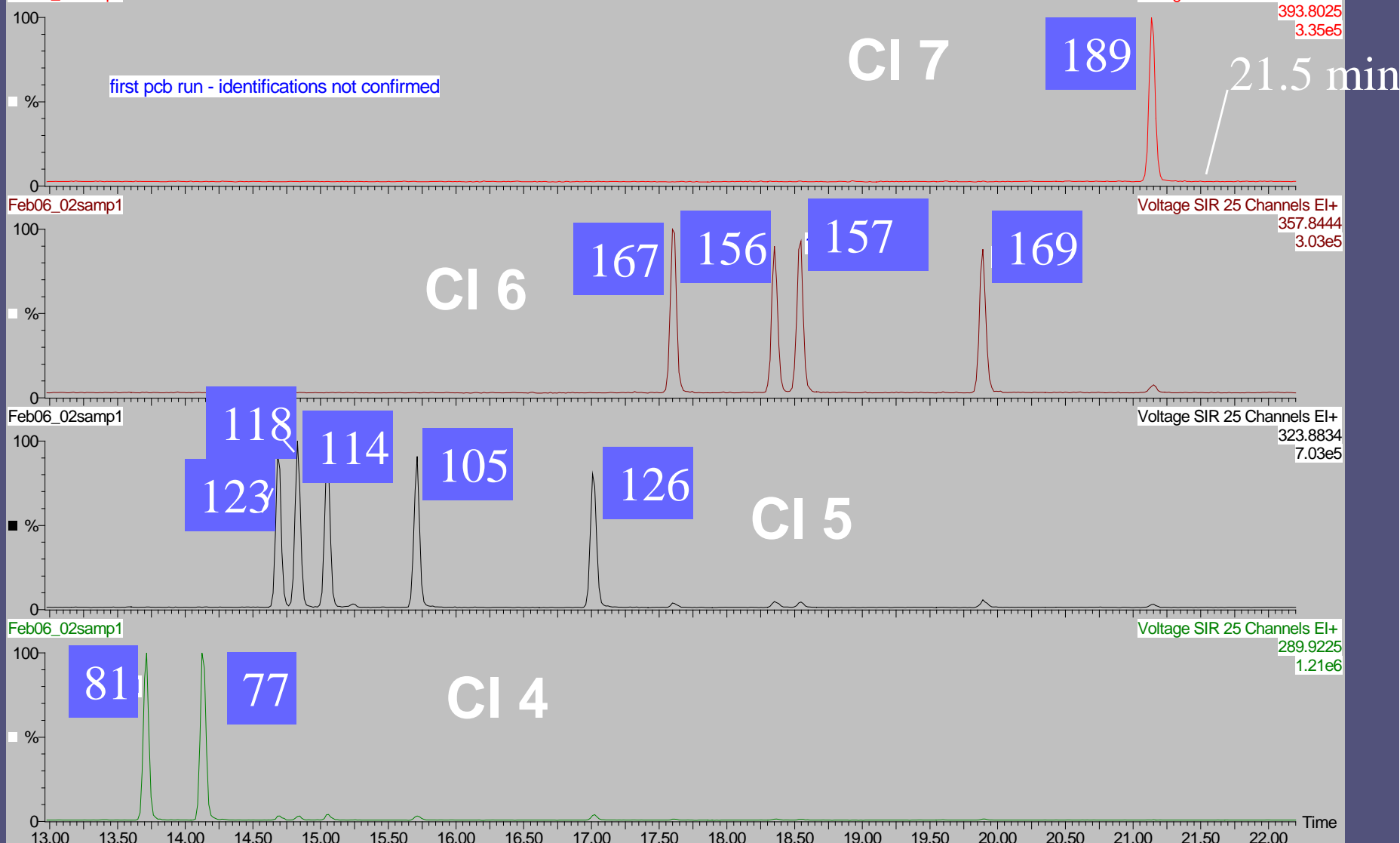


- Planar shape
- Fit in a 3x10Å rectangle
- Chlorines on the corners
- Binds with Ah receptor, like dioxins
- Toxicity Equivalency Factors
  - 2378-TCDD = 1.0
  - PCB 77 = 0.0001
  - PCB 126 = 0.1
  - PCB 169 = 0.01

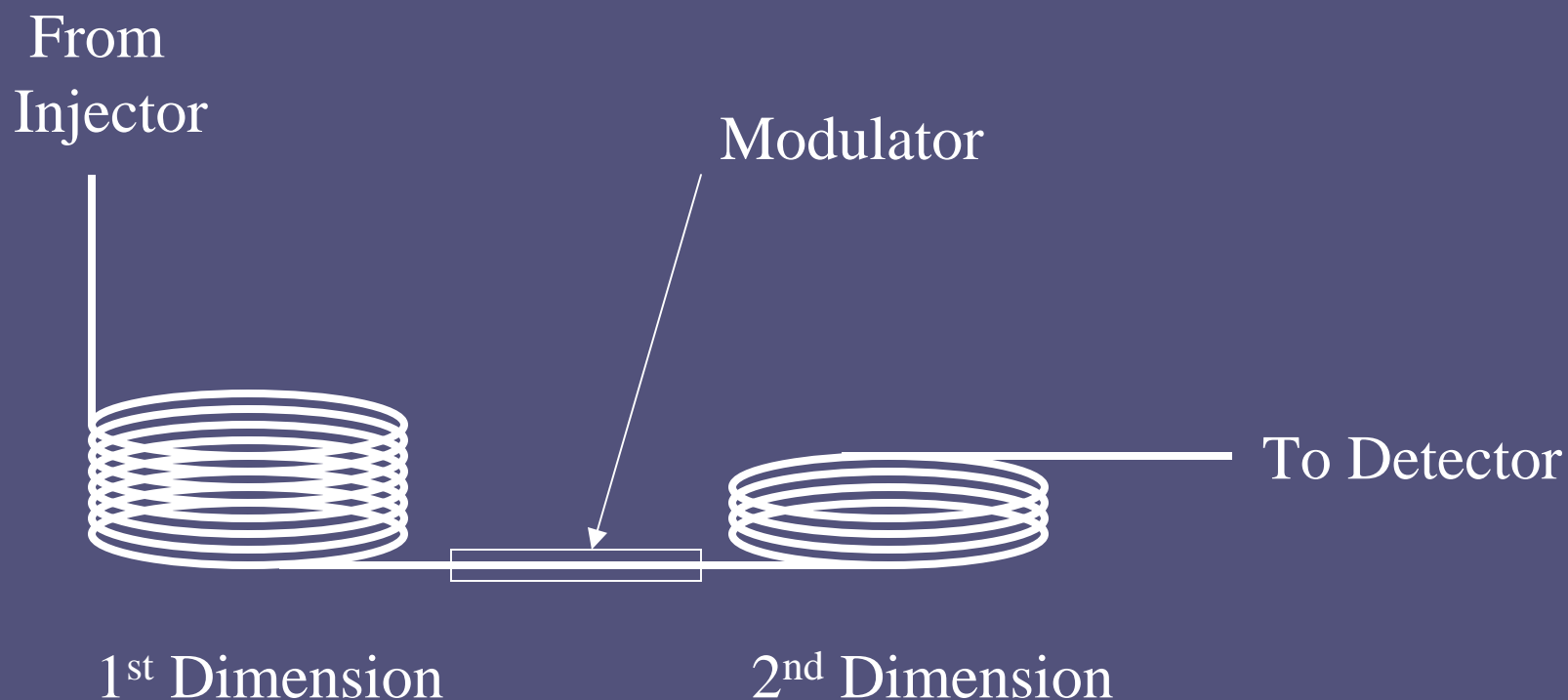
# Toxic PCB Congeners (Carbon Cleanup)

dlp-cs5 on htc

Feb06\_02samp1



# GCxGC Schematic



Two independent separation mechanisms



# GCxGC Setup

- Primary column (1<sup>st</sup> dimension)
  - Longer, wider bore, thicker film
  - Non-polar
- Modulator
  - Thermal in nature
  - Concentrates effluent from primary column
  - “Injects” this effluent onto secondary column
- Secondary column (2<sup>nd</sup> dimension)
  - Very short, narrow bore, thinner film
  - Polar or selective

# GCxGC Column

- Integral column – No press fit
  - 50m x 0.18mm x 0.18 $\mu$ m Rtx-1
  - 5m x 0.18mm x 0.10 $\mu$ m Rtx-PCB
  - Installed so that all 5m of Rtx-PCB was past modulator and in a secondary oven
- Constant flow He at 1.5 mL/min
- Splitless injection
  - 1  $\mu$ L
  - 250°C
  - Purge time 60 sec

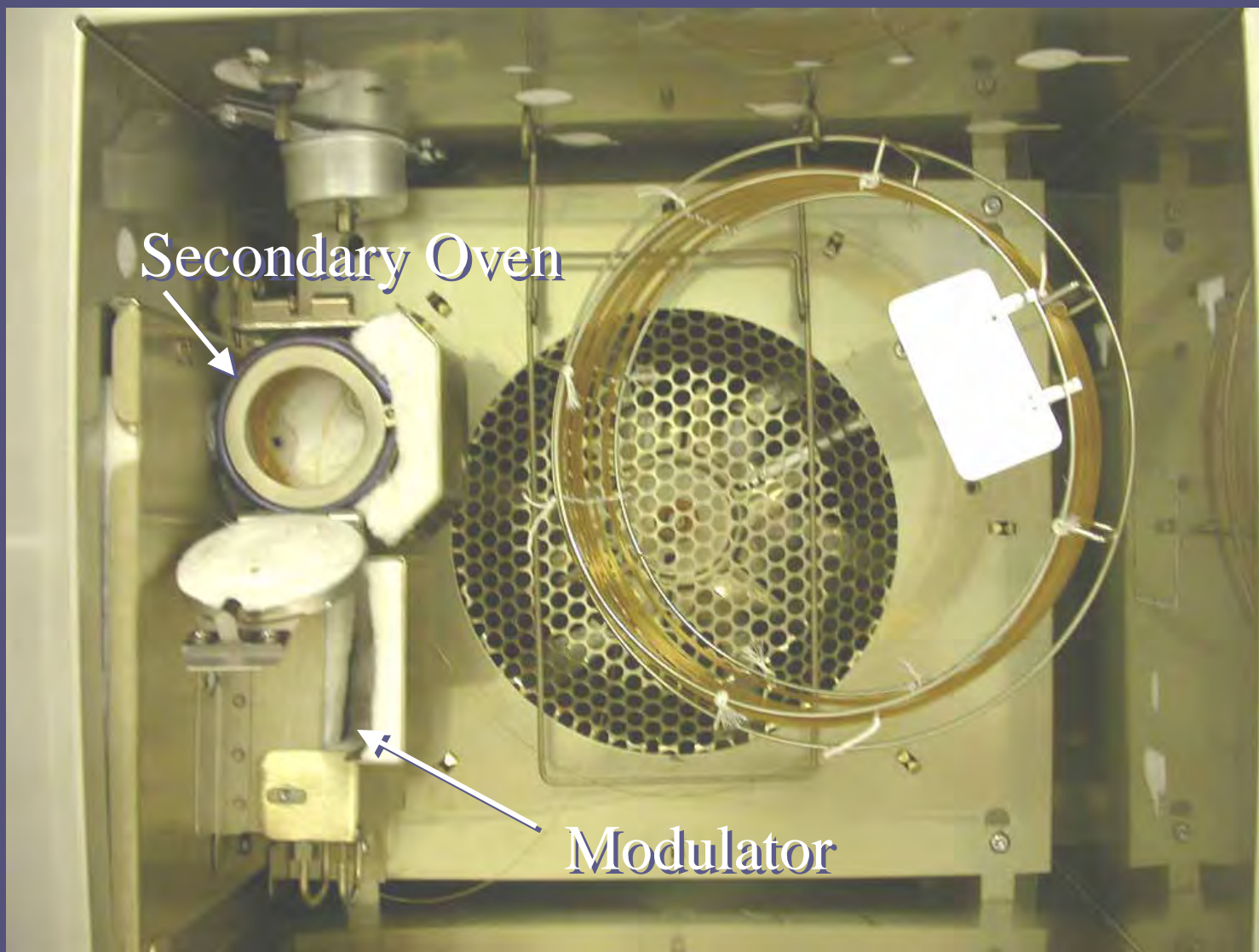
# GCxGC Conditions

- Primary oven
  - 120°C (1 min), 5°/min to 330°
- Modulator (quad jet)\*
  - Temperature offset: 40°C
  - Modulation time: 2 sec
- Secondary oven
  - 140°C (1 min), 5°/min to 350°

Run time = 43 min

\*Built by LECO under license from Zoex Corporation

# Modulator and Secondary Oven

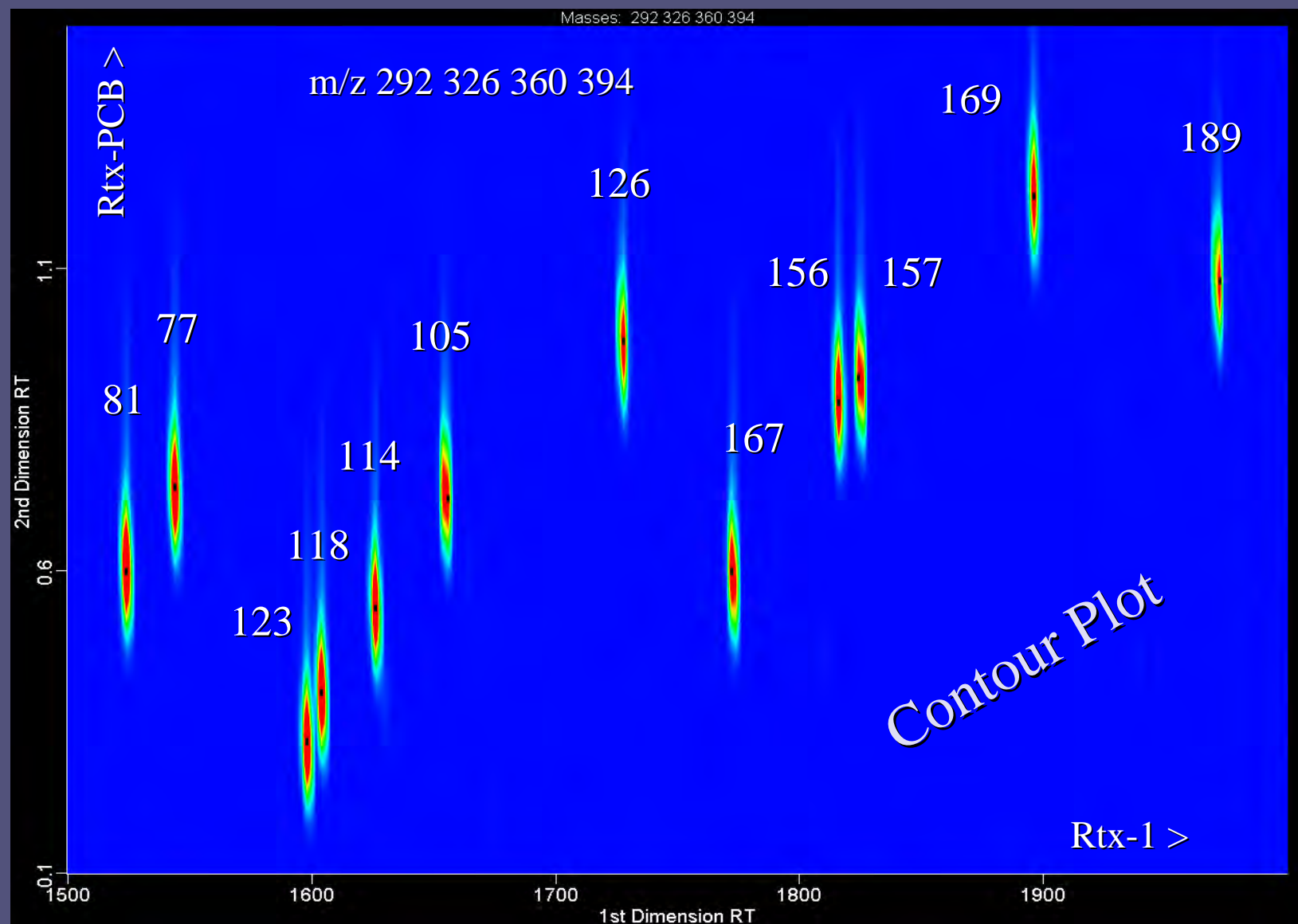


# TOFMS Conditions LECO Pegasus 4D

- Source temperature: 225°C
- Electron ionization: 70 eV
- Stored mass range: 120 to 520 u
- Acquisition rate: 50 spectra/sec

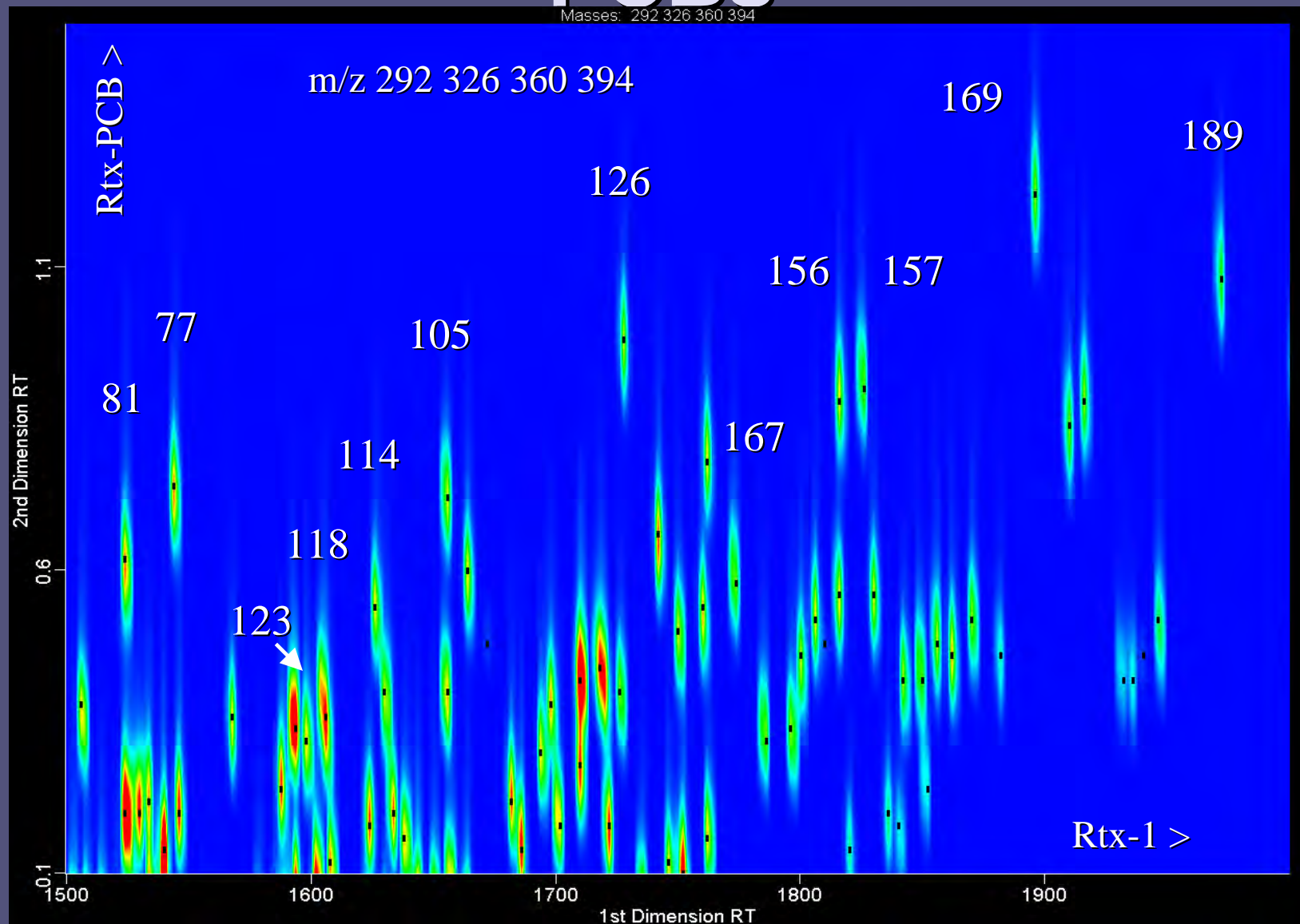


# Dioxin-like PCBs



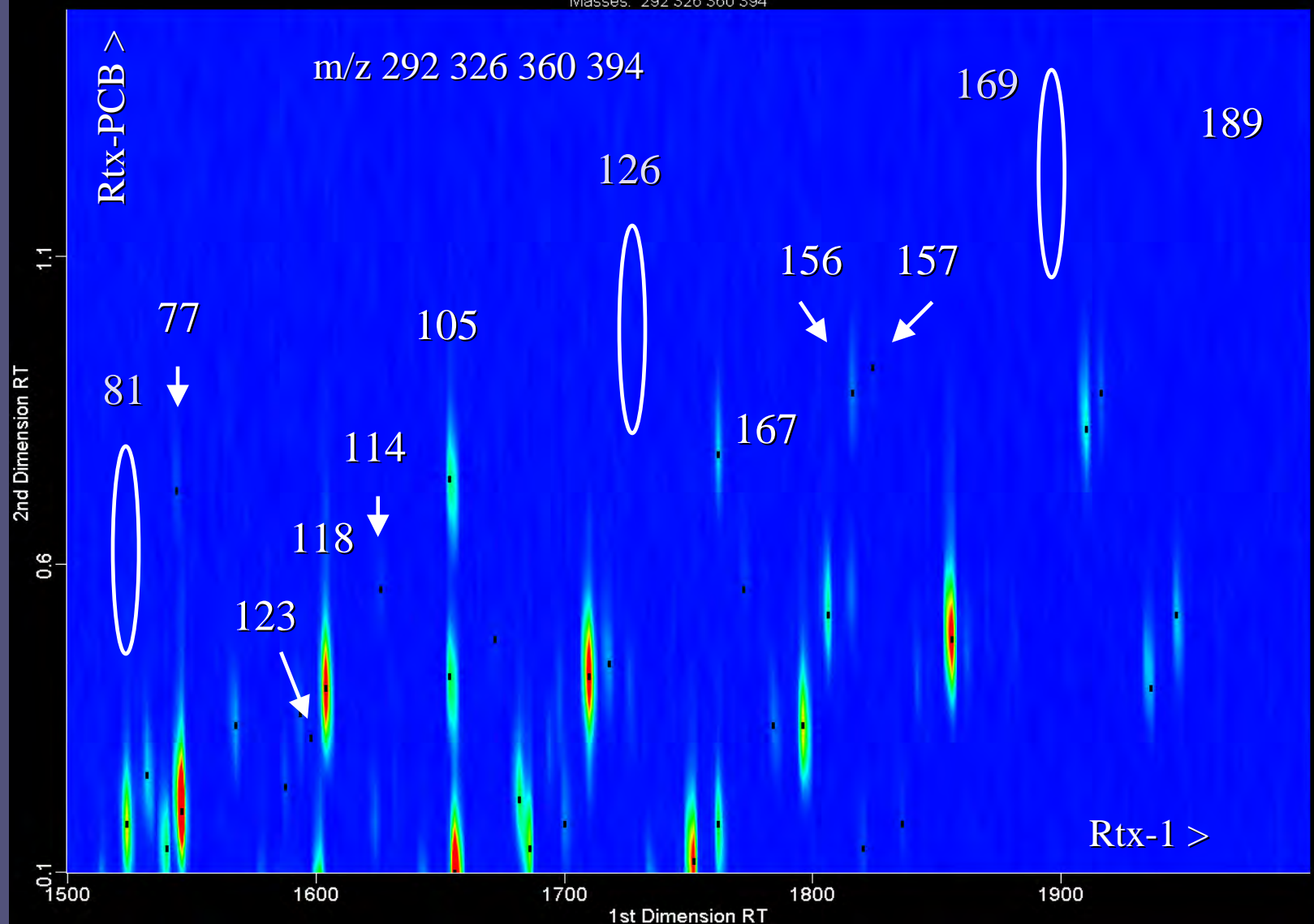
# Dioxin-like PCBs vs. Other PCBs

Masses: 292 326 360 394



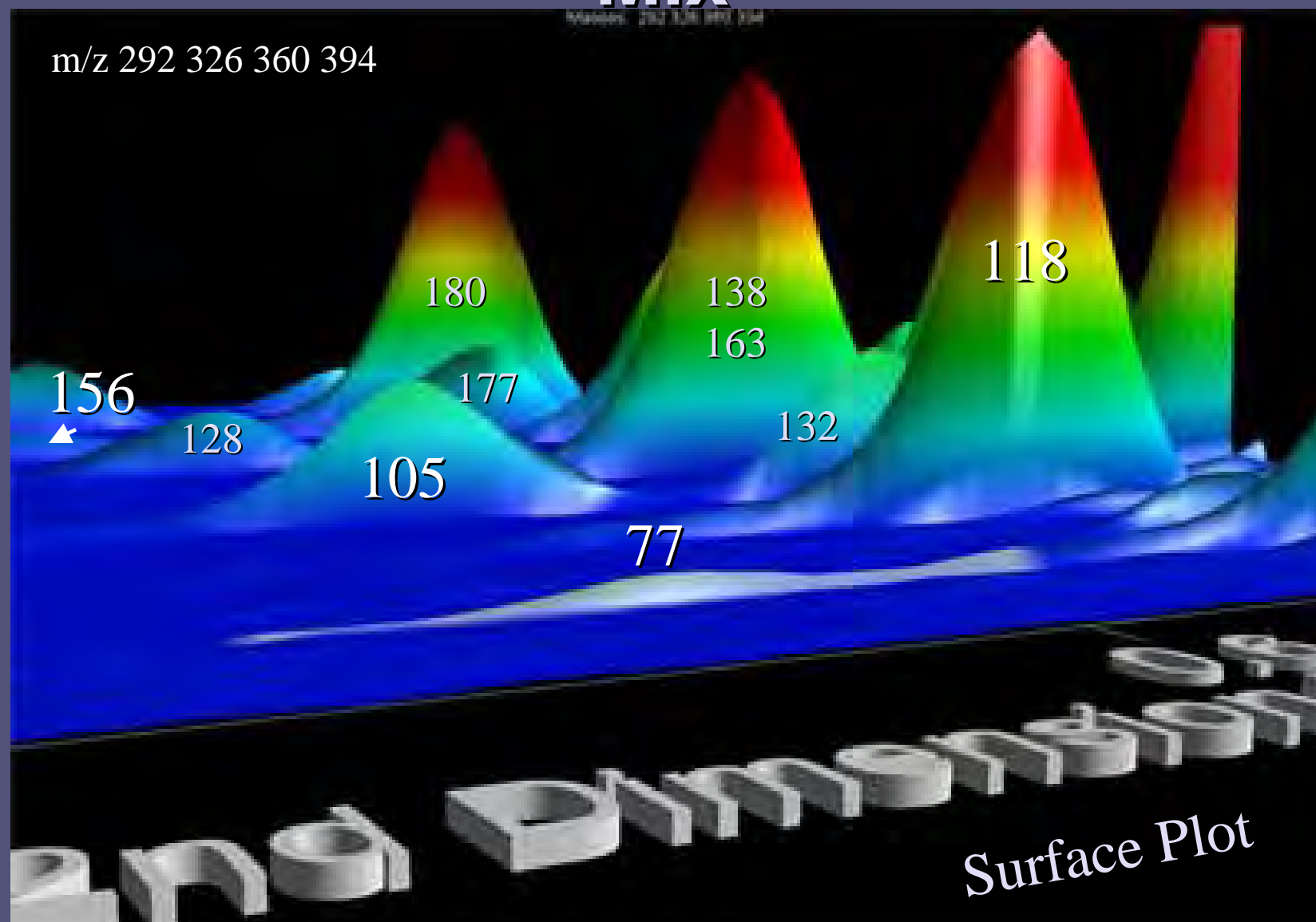
# Dioxin-like PCBs in an Aroclor Mix

Masses: 292 326 360 394

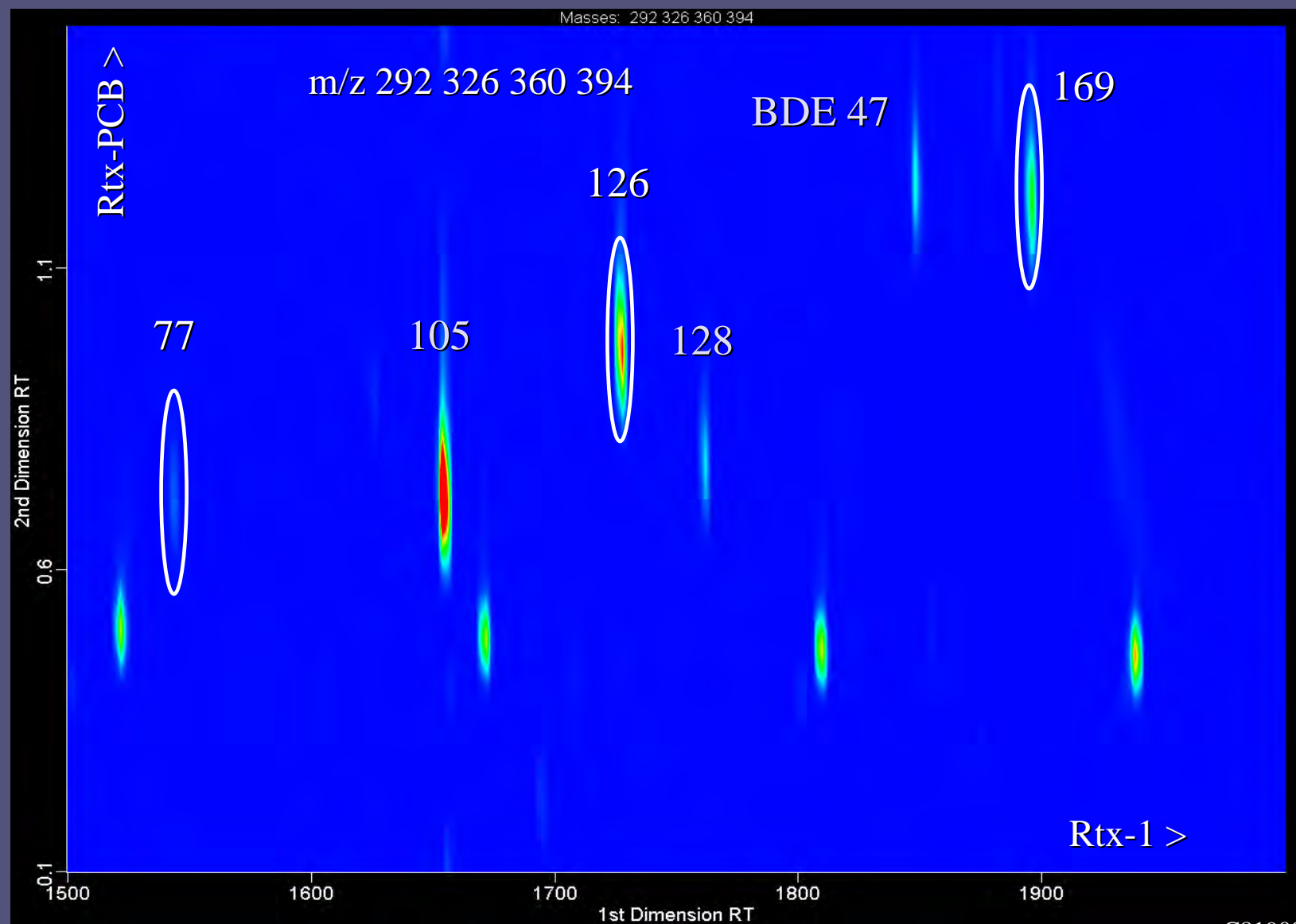




# Dioxin-like PCBs in an Aroclor Mix

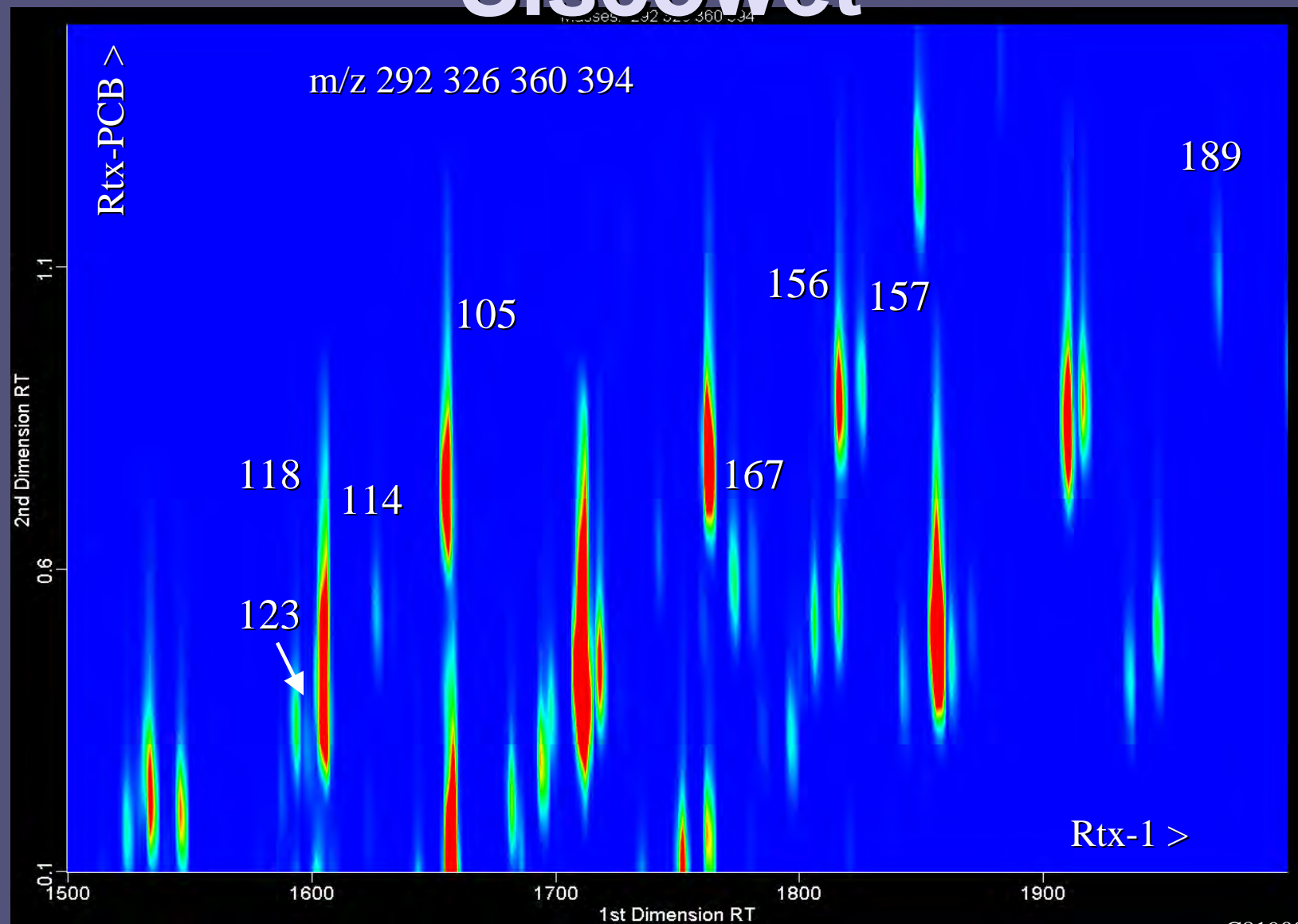


# Non-ortho PCBs in Siscowet



C81900-0019

# Mono-ortho PCBs in Siscowet



C81900-0019

# Non-ortho PCBs in Siscowet

PCB		HR	TOF		HR	TOF		HR	TOF
77		170	170		140	150		640	630
81		22	24		30	31		83	84
126		610	570		1200	1100		1700	1400
169		250	270		550	490		470	440

- Results in pg/g for three different Siscowet from Lake Superior
- Based on extracted amount and final extract volume:
  - 20 pg/g = ~2.5 pg/μL
  - 200 pg/g = ~25 pg/μL

# Conclusions

- GCxGC-TOFMS is a viable way to determine dioxin-like PCBs in fish
  - Sensitive: modulation enhances detection
  - Selective: 2<sup>nd</sup> dimension separations
- Full mass spectra provide powerful confirmations
- Peak find and spectral deconvolution enable location, identification, and quantification (?) of other environmentally significant compounds

# GC-TOFMS Analysis of Indicator Polychlorinated Biphenyls

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# Experiment

- Determine retention times for all **209 PCBs** on a new low-bleed capillary column
  - Analyze individual congener standards
  - Hexachlorobenzene for relative retention times
- Analyze mix of Aroclors 1221:1242:1254:1262
  - 1:2:2:2 ratio
  - Show chromatogram with congeners labeled
- GC-MS results obtained using a time-of-flight mass spectrometer to allow for possible spectral deconvolution

# GC-TOFMS Conditions

## ● Gas Chromatography

- One microliter splitless 250°C, 60 sec valve
- 60 m x 0.18 mm x 0.18 µm **Restek Rtx-PCB** column
  - Constant flow helium, 1.5 mL/minute
  - 70°C (1 min), 50°/min to 120°, 3°/min to **360°** (1 min)

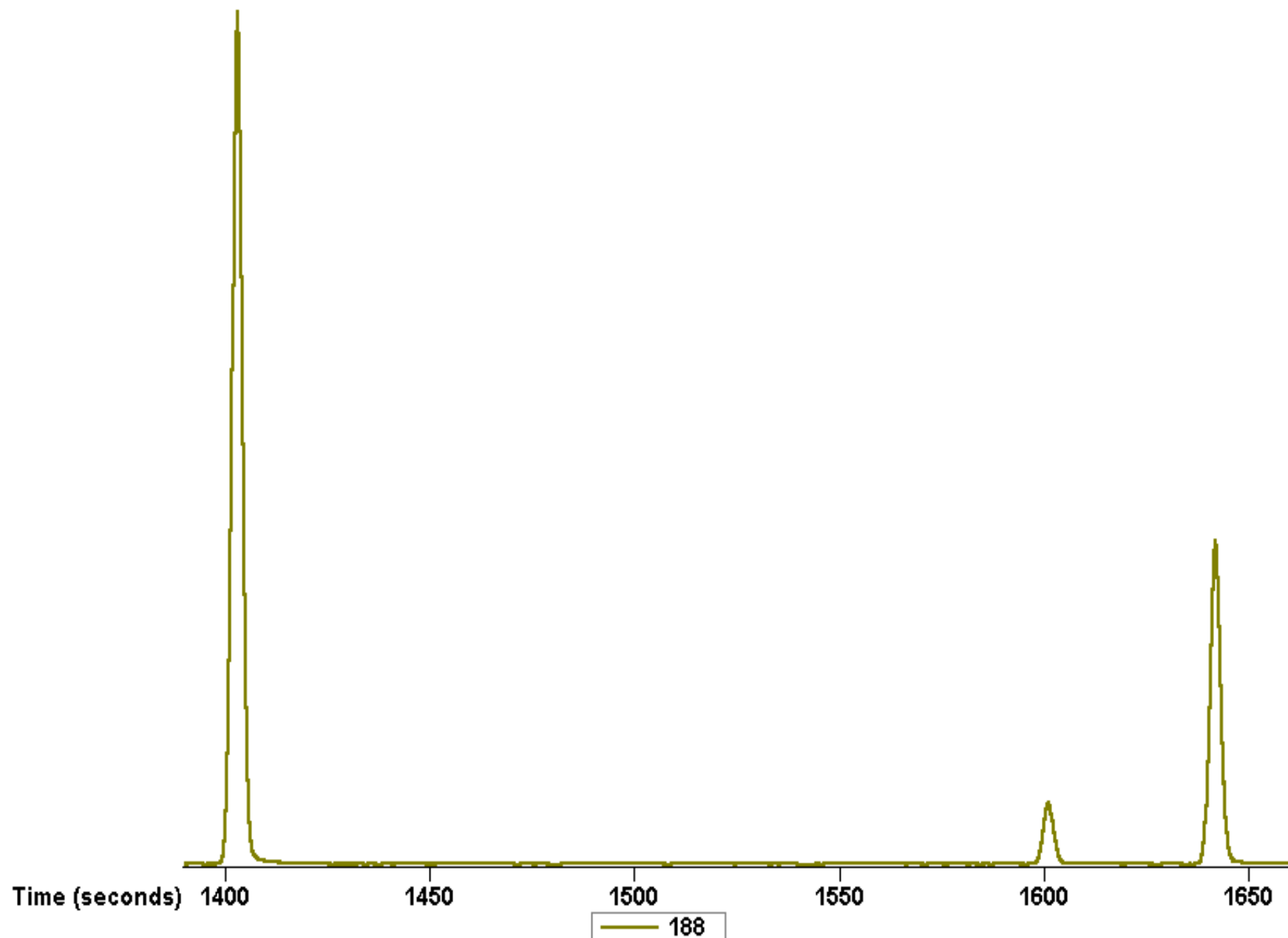
## ● Mass Spectrometry **LECO Pegasus III**

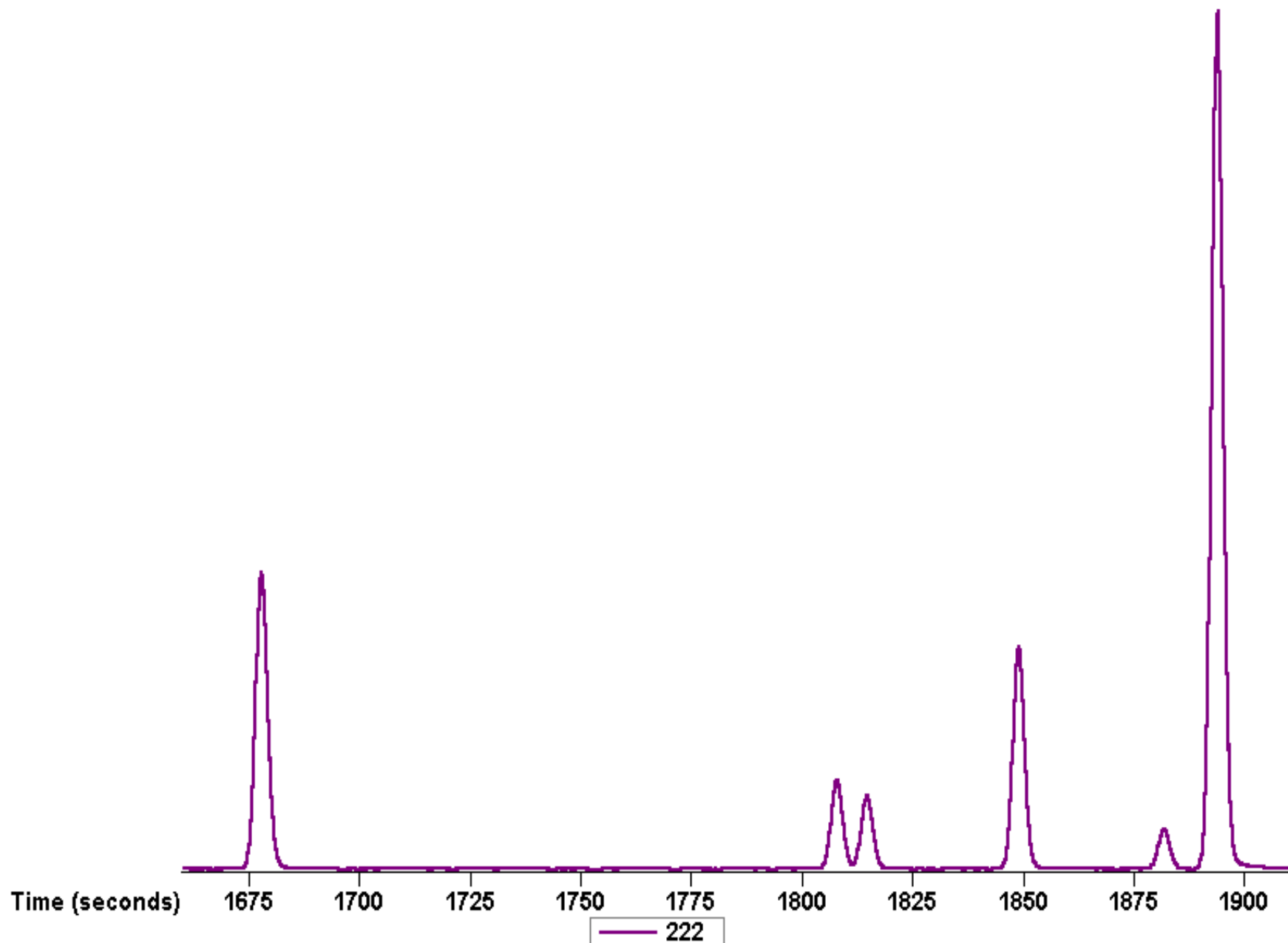
- Source temperature: 225°C
- Electron ionization: 70 eV
- Stored mass range: 120 to 520 u
- Acquisition rate: 5 spectra/sec

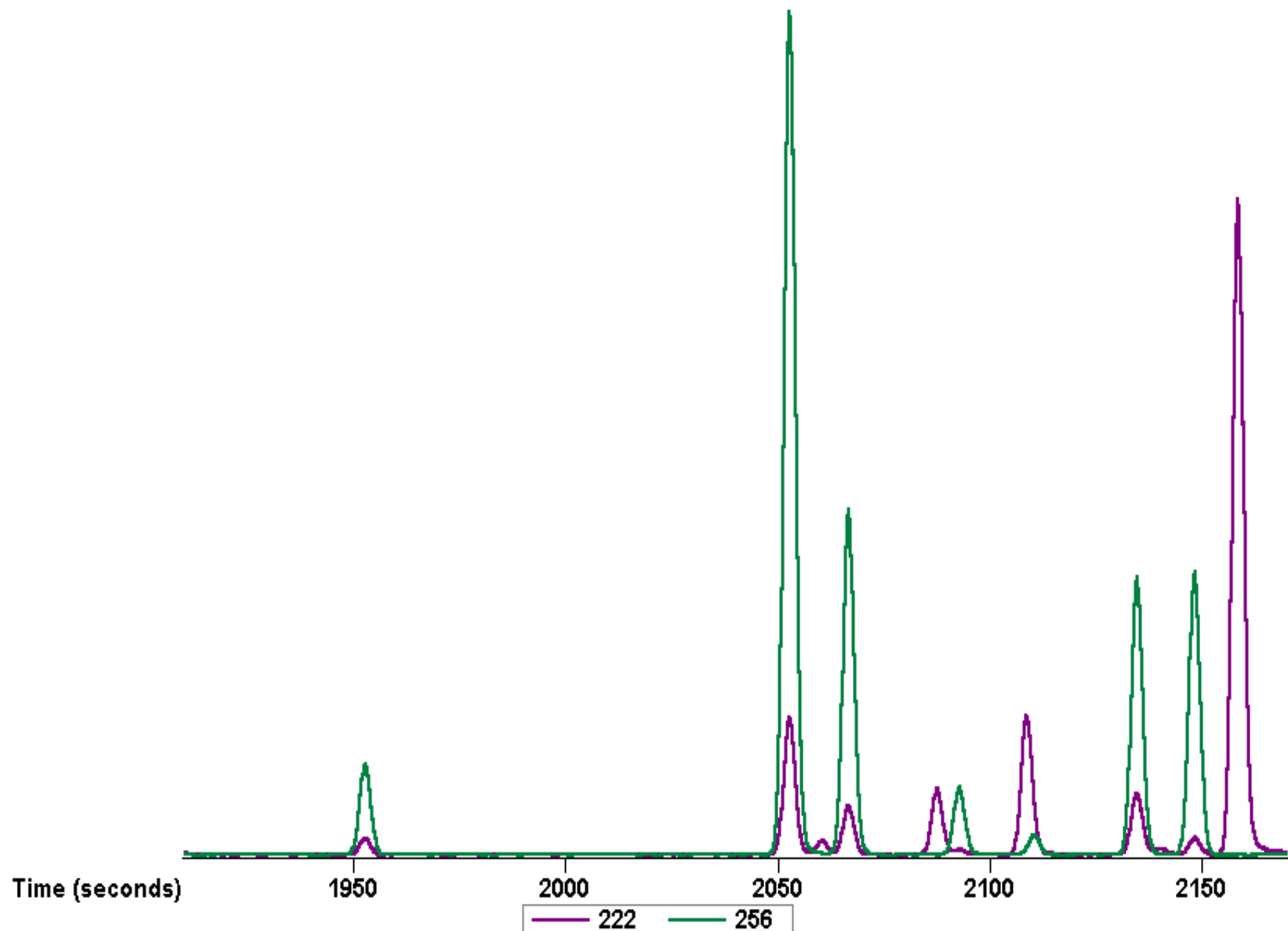


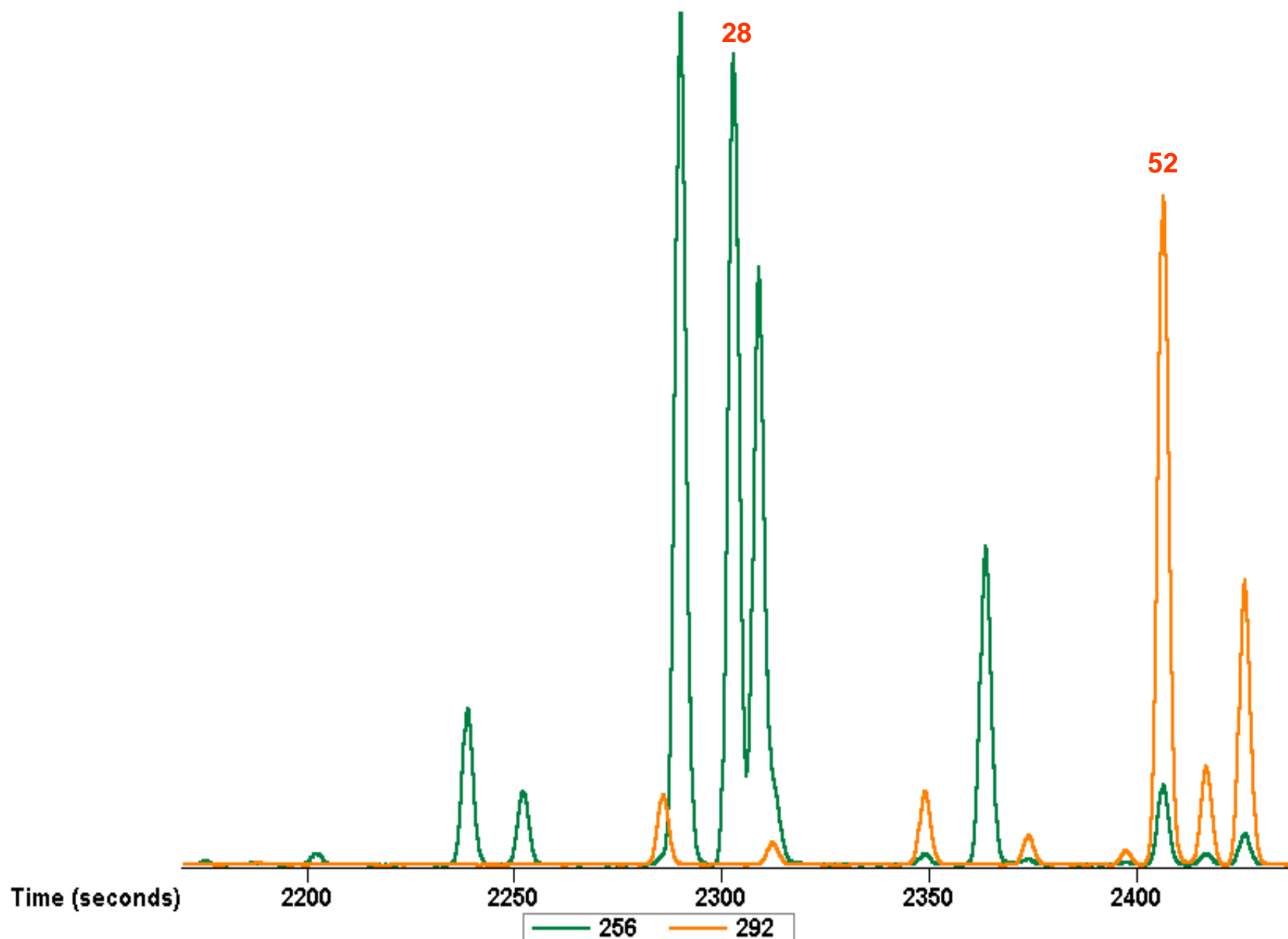
# Aroclor Mix Chromatogram

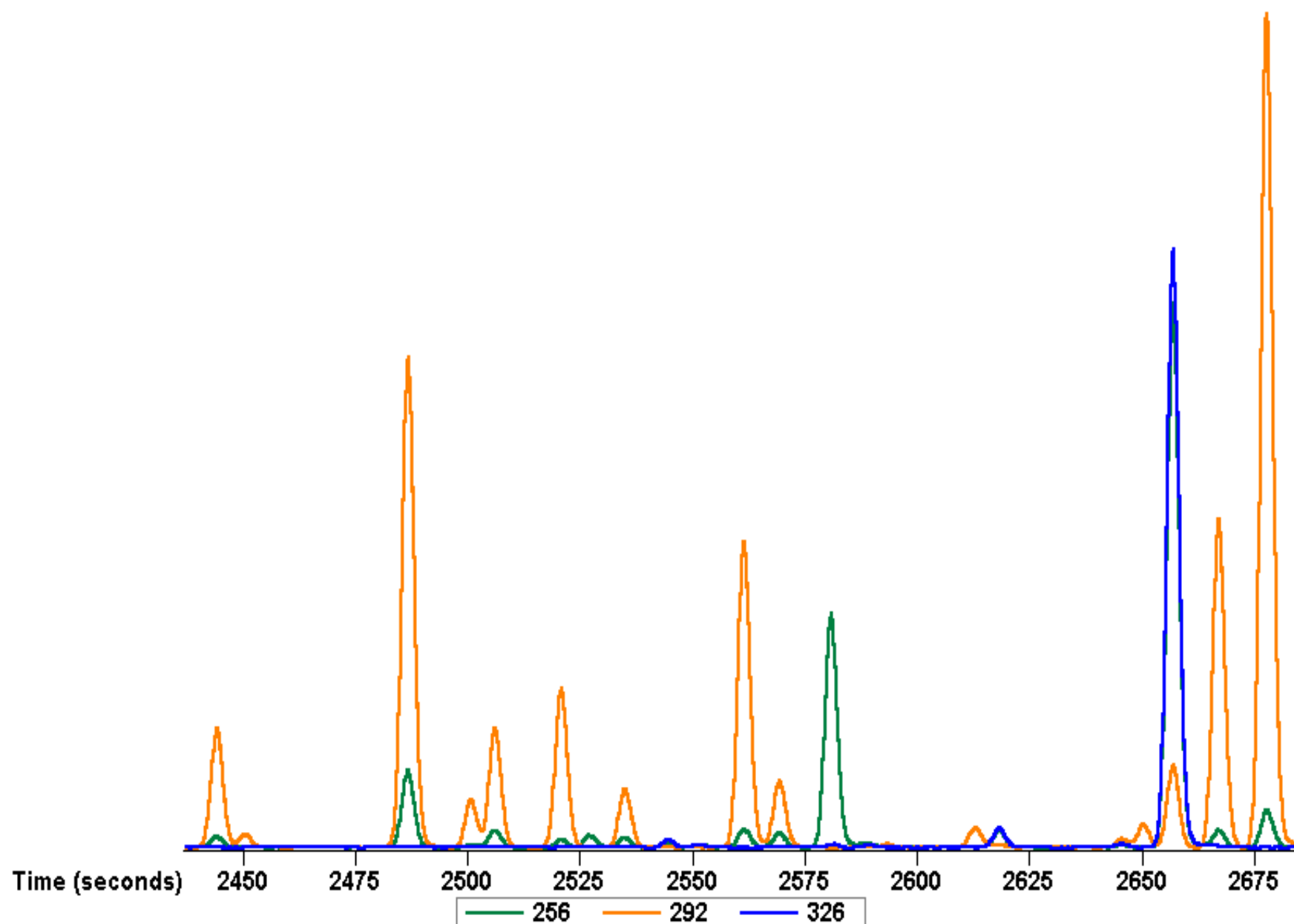
- Overlaid ion chromatograms are plotted
  - For example, hexachlorobiphenyl is 360
  - Peaks are labeled with congener numbers
    - Text size and format is only for space and not meant to indicate anything about PCBs, except:
      - **European indicator congeners** are in **red**
- Chromatograms are not to one scale
  - Each panel is adjusted so most of the PCB peaks can be seen

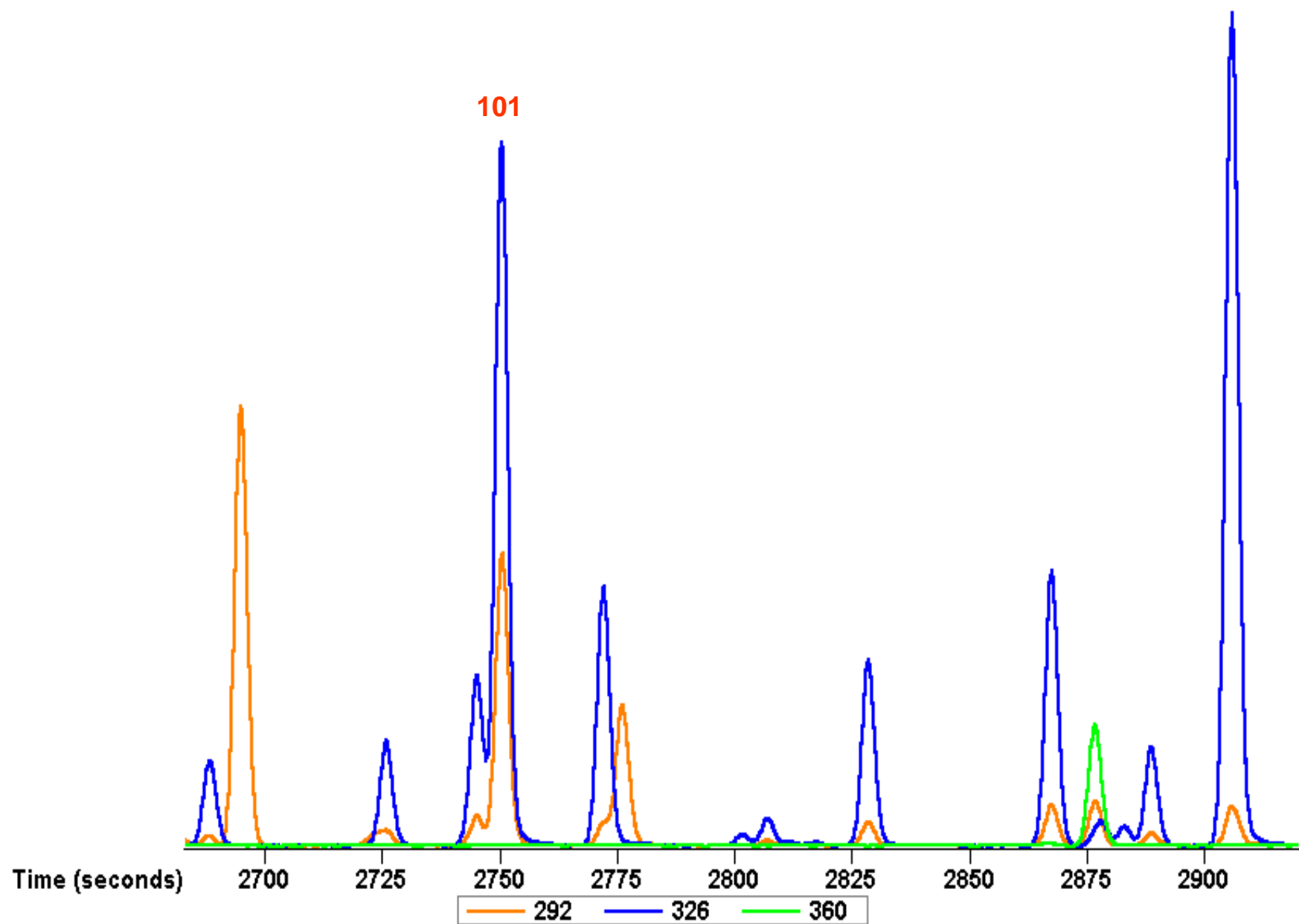


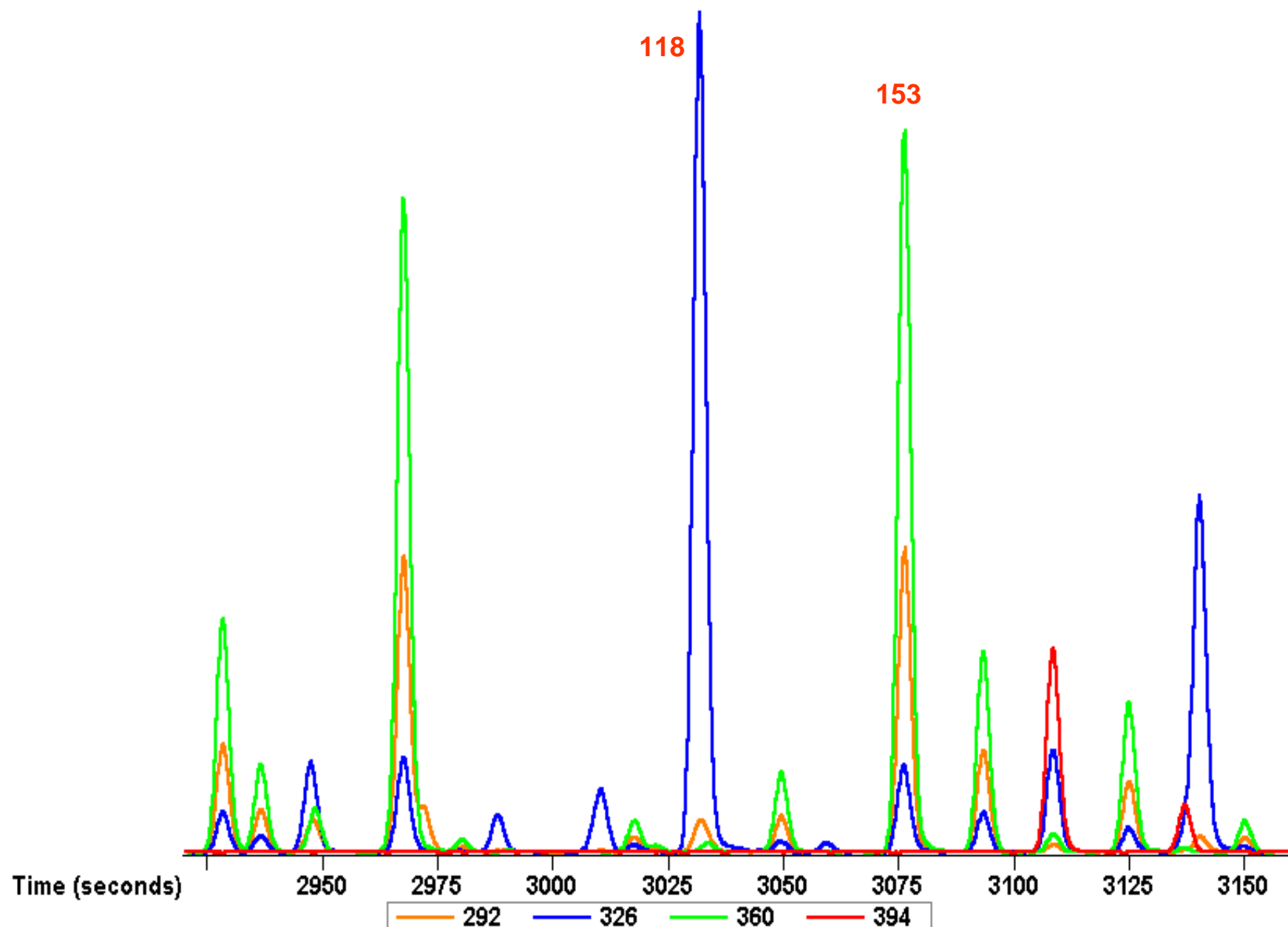




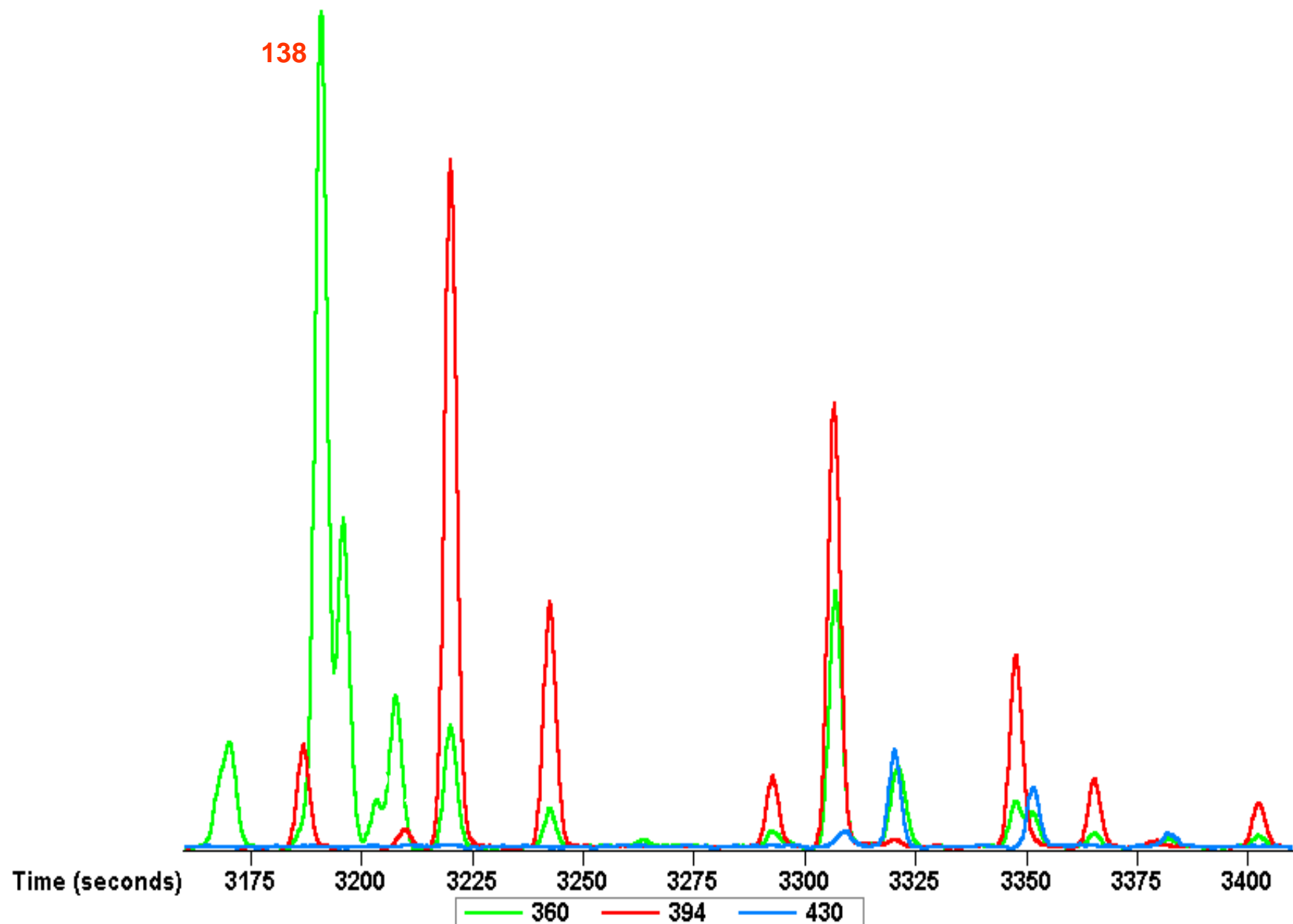


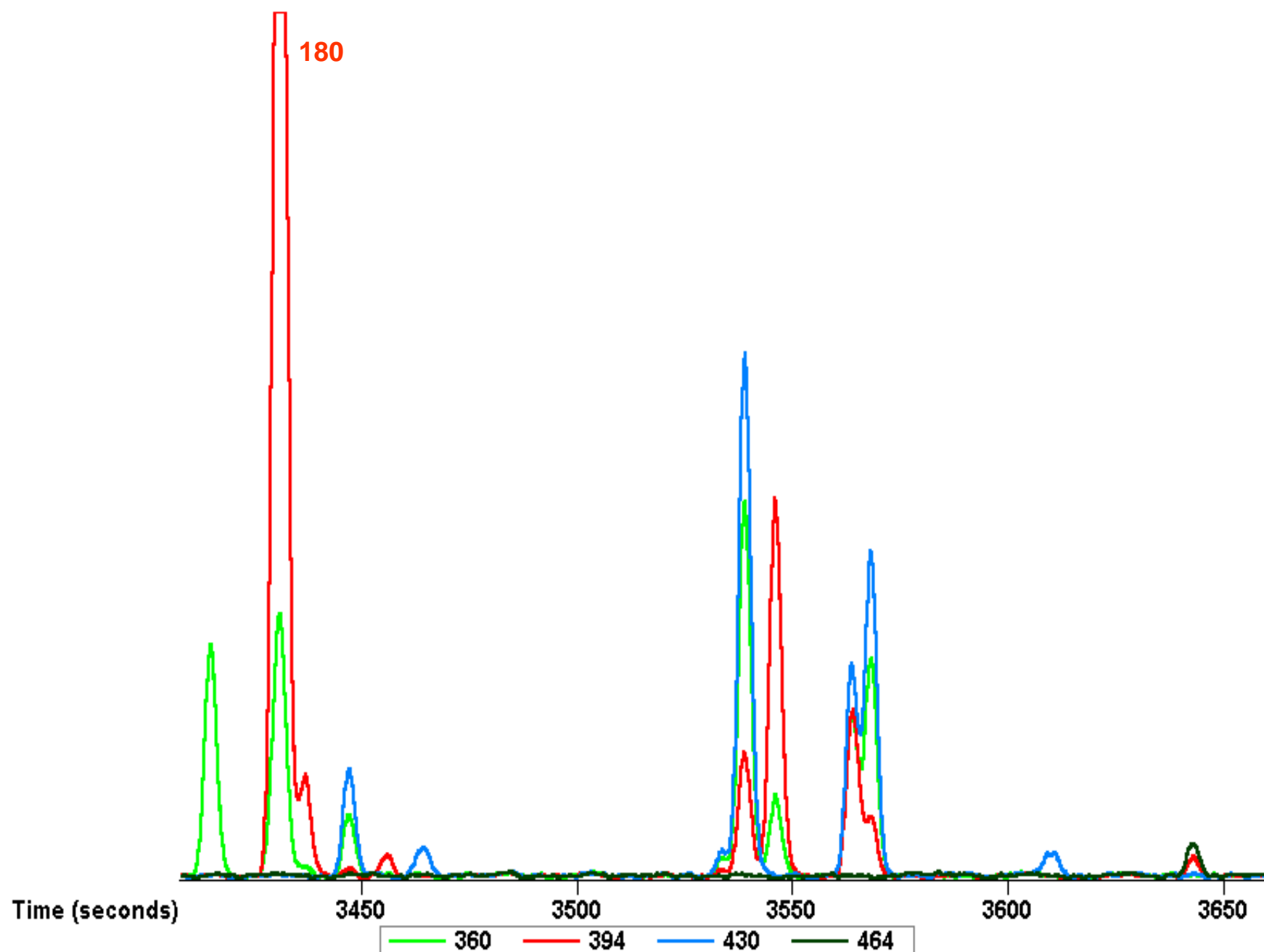


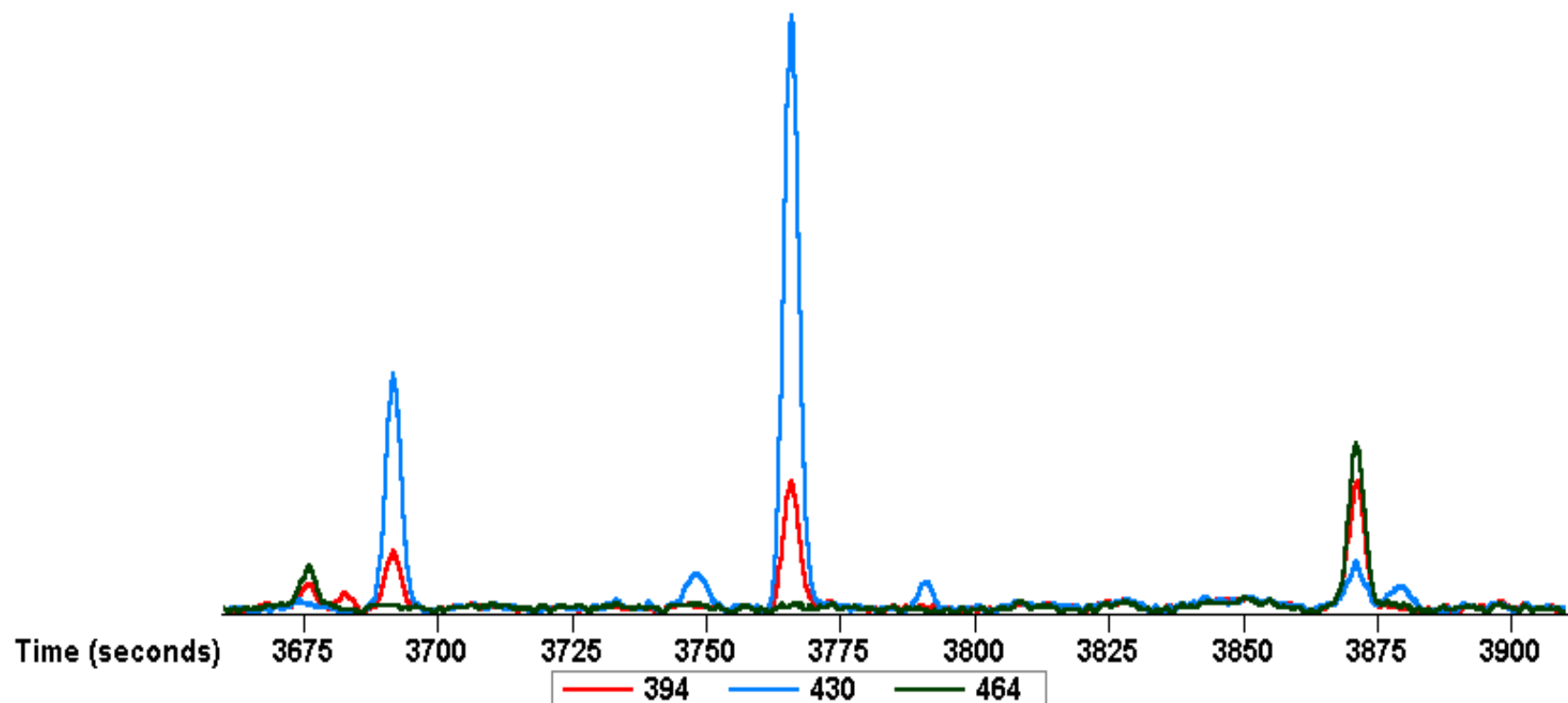






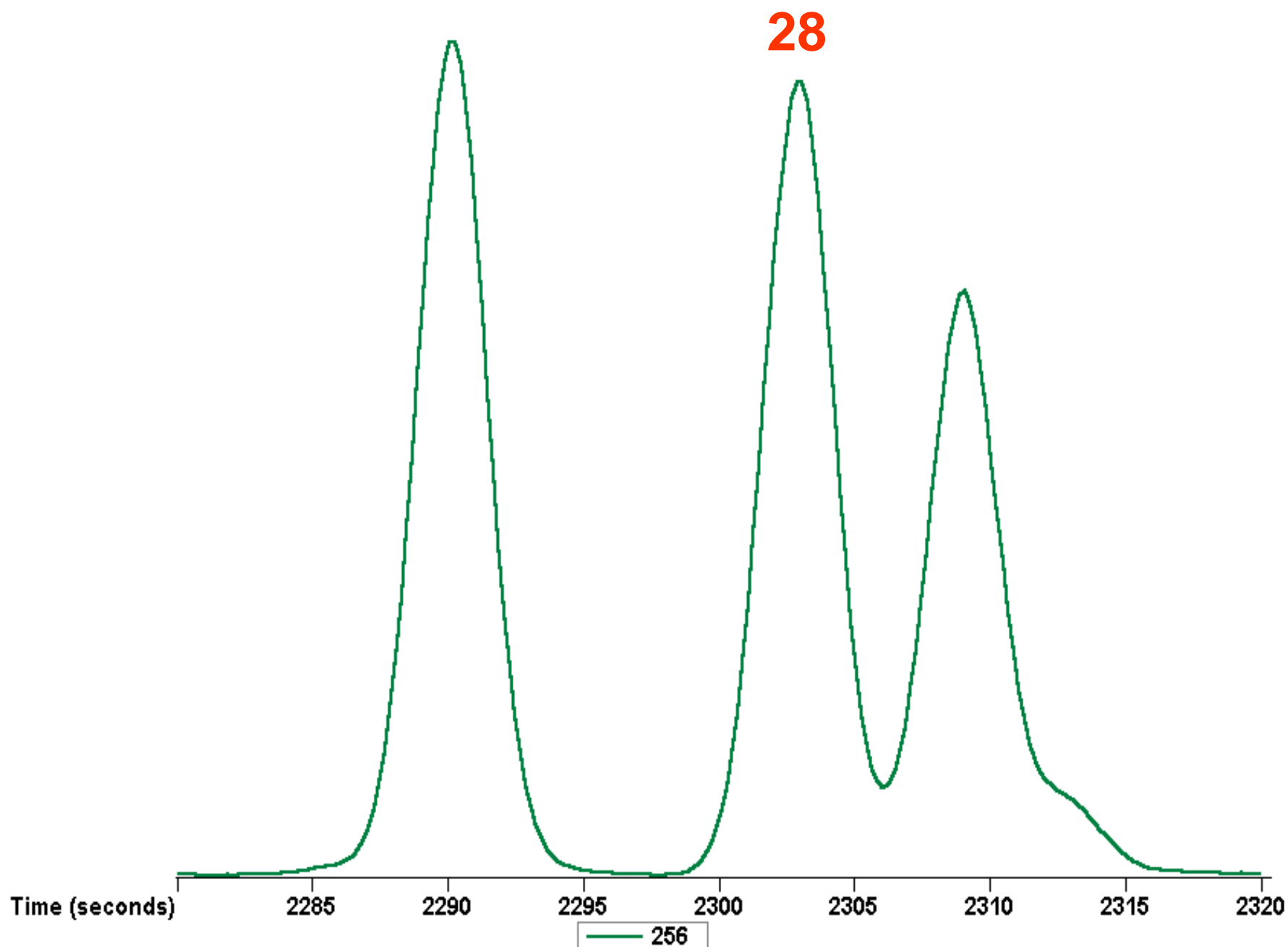


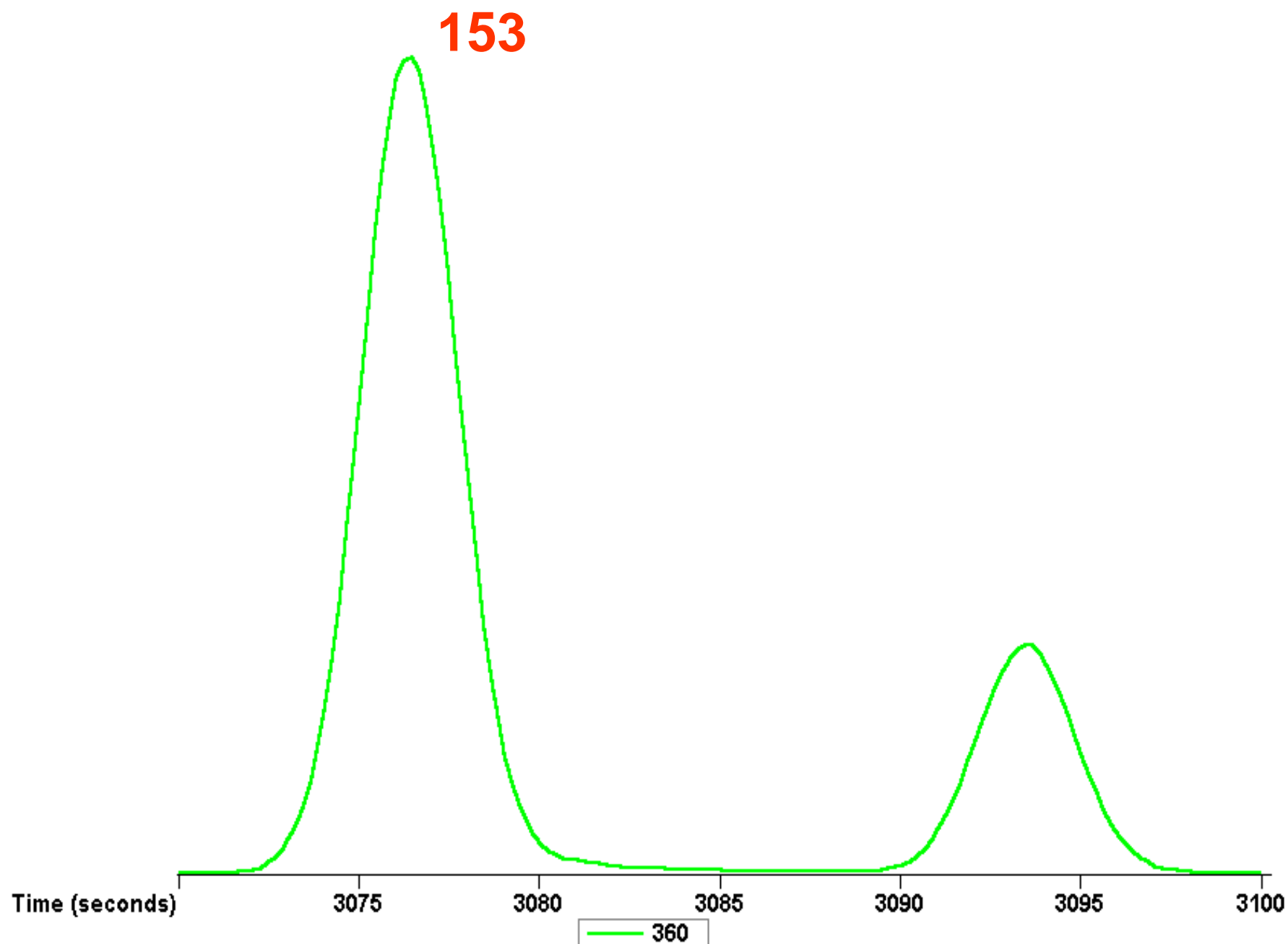


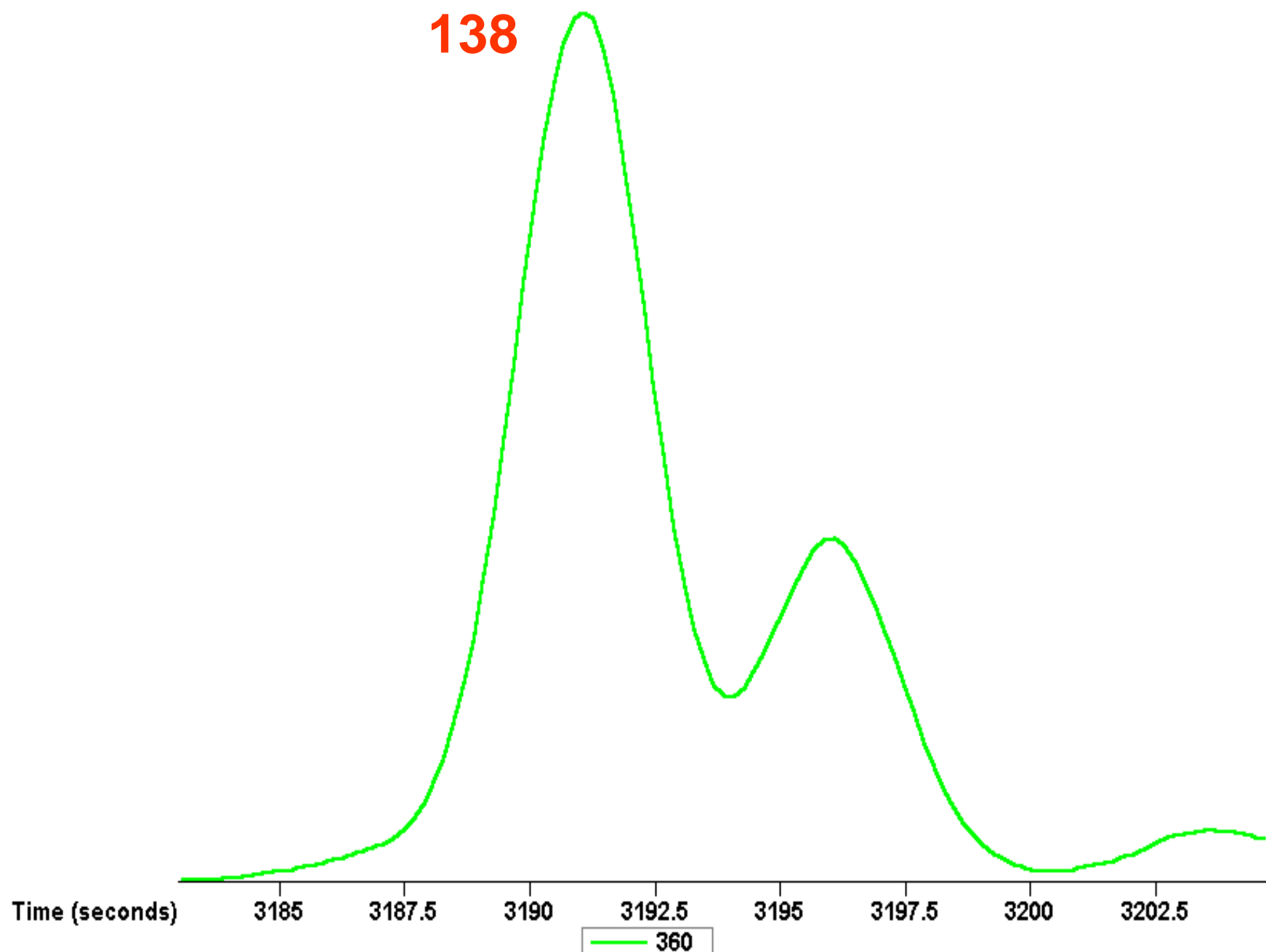


# Important Congener Separations

- European indicator PCBs
- May coelute on 5% phenyl methylsilicone and other column phases







# Conclusions

- Greater than 140 Aroclor PCBs can be determined with the new column and mass spectrometry
- The seven European indicator PCBs can be determined individually
- Spectral deconvolution available with TOFMS allows qualitative identification for coeluting PCBs

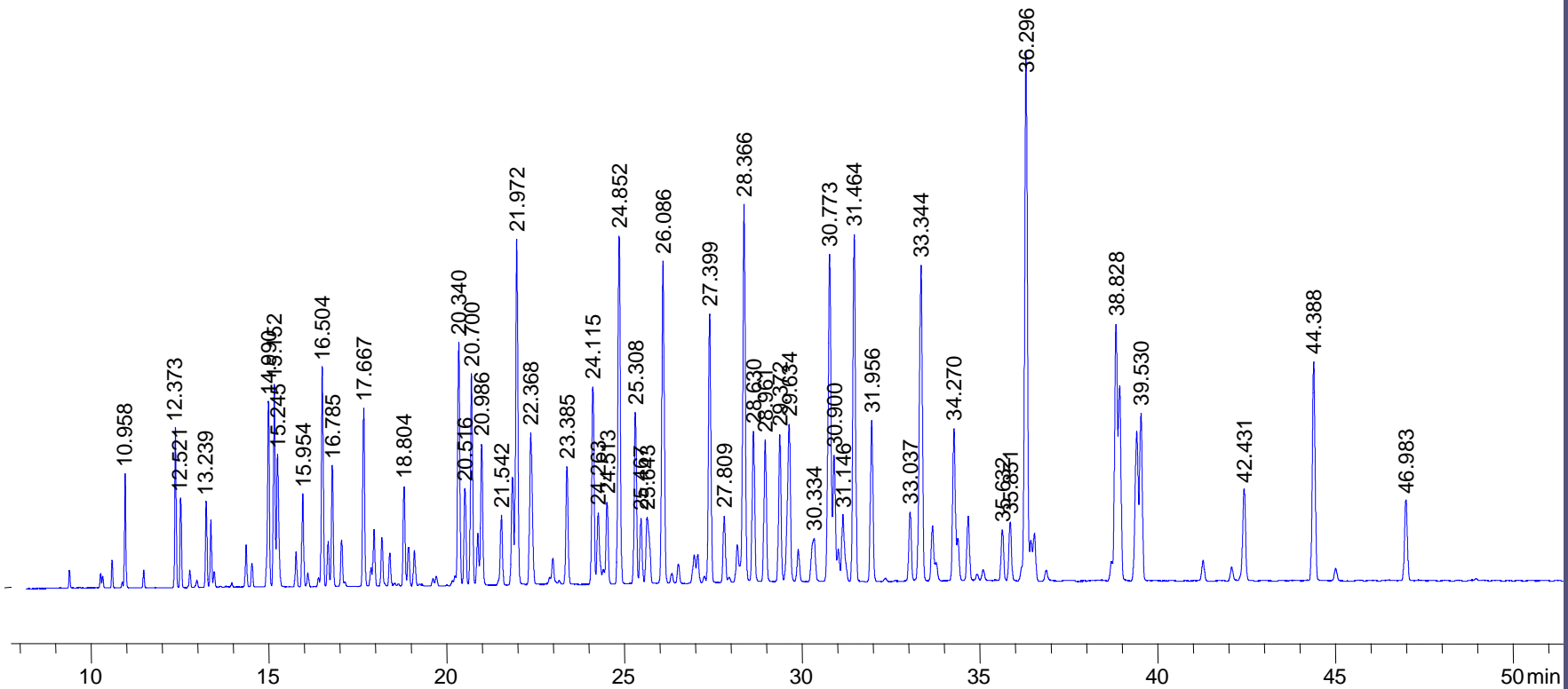


# GC-ECD Analysis

- Columns should be “complementary”
  - As many congeners resolved as possible
  - Different coelutions (nothing will resolve all 140 environmentally-significant congeners)
  - Similar thermal properties
  - Operation under same temperature and pressure programs

# Rtx-PCB

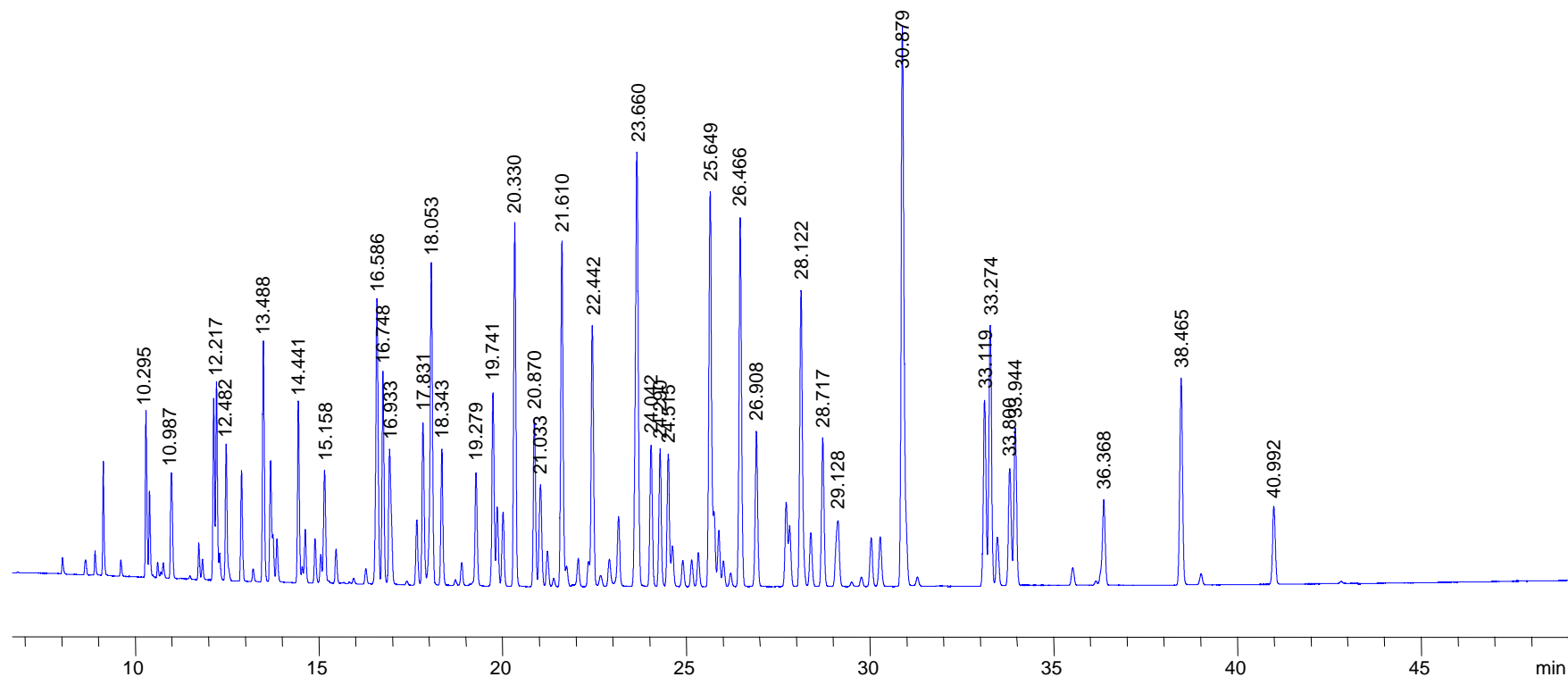
(40m x 0.18mm, 0.18um film)



300ppb Aroclor 1242, 1254, 1262  
100°C(1 min) 20°C/min 200°C(0 min)  
2°C/min 320°C(1 min)

# Rtx-440

(40m x 0.18mm, 0.18um film)



300ppb Aroclor 1242, 1254, 1262  
 100°C(1 min) 20°C/min 200°C(0 min)  
 2°C/min 320°C(1 min)

# Quantitation of Congeners

Rule#1: If compound elutes as single on both columns report lower value

	<u>Rtx-PCB</u>	<u>Rtx-440</u>
Peak	PCB 28	PCB 28

# Quantitation of Congeners

Rule#2: If compound elutes as single on one column and multiple congeners on the second report the single column result if confirms on second column

	<u>Rtx-PCB</u>	<u>Rtx-440</u>
Peak	PCB 53 + 31	PCB 31

# Quantitation of Congeners

Rule #3: If there are complicating coelutions on both columns calculate the results using normalized responses (ex. PCB 136)

	<u>Rtx-PCB</u>	<u>Rtx-440</u>
Peak	PCB 136 + 117	PCB 115 + 136
	PCB 115	

# Quantitation of Congeners

Rule #3 continued:

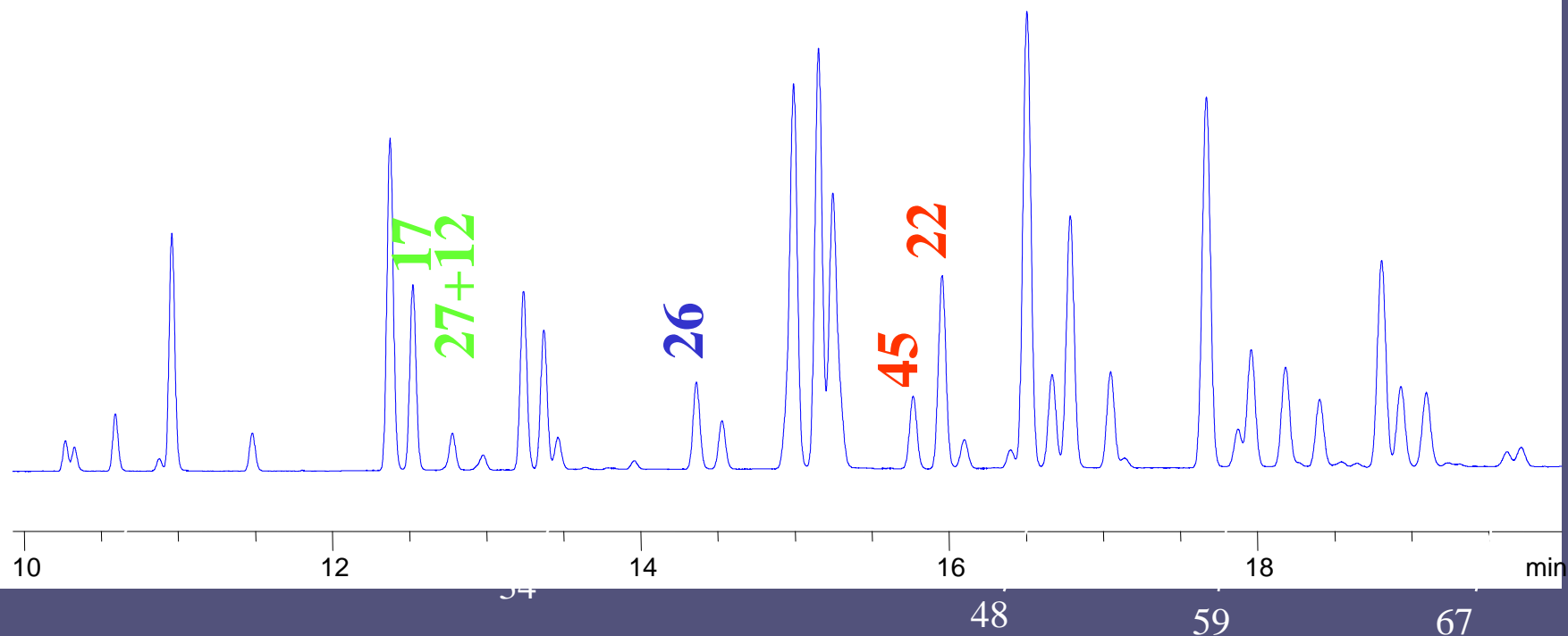
PCB 136 Concentration =

$$\left( [\text{PCB 115+136}] \times \frac{(\text{RF115} + \text{RF136})}{2 \times \text{RF115}} - [\text{PCB 115}] \right) \frac{\text{RF115}}{\text{RF136}}$$

RF = response factor of congener on ECD

# Rtx-PCB

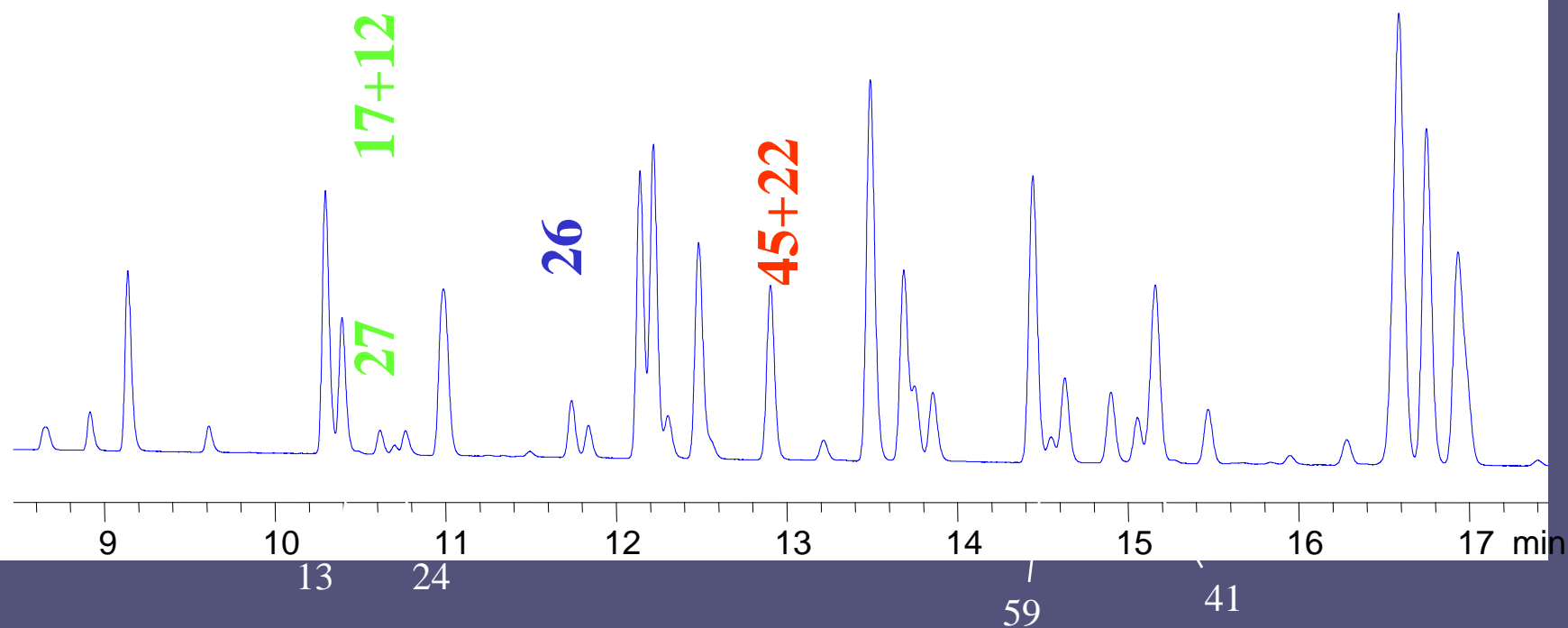
(40m x 0.18mm, 0.18um film)





# Rtx-440

(40m x 0.18mm, 0.18um film)



# PCB Congener Separation

50 72 19

141

Rtx-440

Rtx-PCB

Case

PCB#

s or m

PCB#

s or m

1

2

3

1

s

1

s

1

3

s

3

s

1

4

m

4

m

1

4+10 reported together

5

m

5

s

1

6

s

6

s

1

7

m

7

s

1

8

m

8

s

1

9

m

9

s

1

10

m

10

m

1

4+10 reported together

12

m

12

m

1

ok

13

s

13

m

1

15

s

15

s

1

16

m

16

s

1

17

m

17

s

1

18

s

18

s

1

19

s

19

s

1

20

m

20

m

1

33+20 reported together

22

m

22

s

1

# GC-ECD Summary

- Rtx-PCB and Rtx-440 Combination
  - Quantification of the 141 PCB congeners possible using the 3-case quantification system
  - High thermal stability
  - Good choice for dual column operation

# Overall Conclusions

- GC-MS analysis with Rtx-PCB column
  - European indicator unbiased
  - WHO-12 with carbon cleanup
- GCxGC-TOFMS
  - TOFMS has acquisition speed necessary to characterize the narrow peaks
  - WHO-12 resolved from non-toxic without carbon cleanup
- Dual-Column GC-ECD
  - Also successful, with high sensitivity
  - All congeners of significance can be quantified

# Improved Sensitivity with Simplified HPLC Analysis and Sample Preparation of Paraquat/Diquat

C.Vernon Bartlett, Bruce Albright,  
Lydia Nolan and Rebecca Wittrig

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823



# Introduction

Paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride,  $C_{12}H_{14}N_2Cl_2$ , Figure 1), and diquat (1,1'-ethylene-2,2'-bipyridilium dibromide,  $C_{12}H_{12}N_2Br_2$ , Figure 1), are non-selective contact herbicides widely used in agriculture to control broadleaf and grassy weeds (use of paraquat is restricted in the United States). Highly charged dual quaternary amines, they are readily soluble in water. They also are highly toxic, and ingestion of either compound can have serious effects, as they can alter reduction-oxidation activities in biological systems.

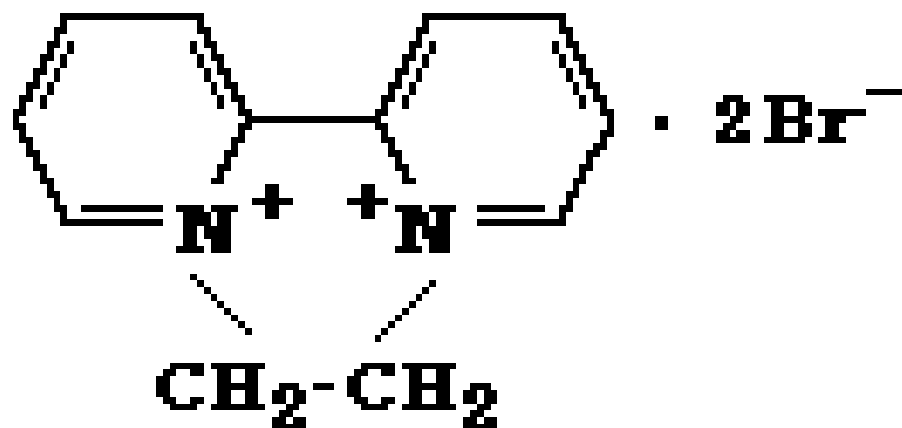
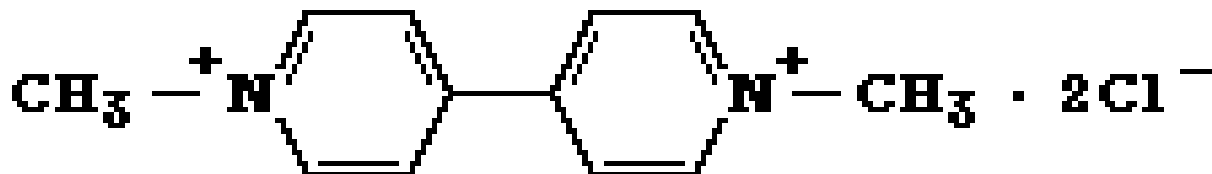
The highly charged herbicides are difficult to retain by standard reversed phase HPLC, thus ion pairing reversed phase methods such as US EPA Method 549 were developed. New materials and techniques now allow simplification, better detection, recovery, and throughput for these analytes. We have developed a simple, effective analysis for paraquat and diquat, based on a new HPLC column and a unique mobile phase. This analysis can be performed on a conventional HPLC system with a UV detector. The separation makes use of a different analytical property – chaotropism: an ability to disrupt the structure of water and thereby alter the interactions among analyte, mobile phase, and stationary phase. In this case, the object is to promote the solubility of the highly polar analytes in a non-polar substrate (the stationary phase).

# Introduction, ctd.

Unlike ion pairing techniques, this new approach requires only water, the charge dispersion reagent, and acetonitrile to accomplish the separation. For highest sensitivity, we monitored for paraquat at 257nm and for diquat at 308nm. Using the HPLC column and these new conditions, the detection limit is 6 ppb for either herbicide – a detectable amount of 0.12 nanograms on column. This analytical sensitivity is enhanced five-fold when accompanied by a new simple SPE sample preparation method. The SPE method allows sampling up to 1 liter of water, with greater than 97% recovery efficiency for samples using reagent water.

Figure 1. Chemical structures of paraquat and diquat

paraquat dichloride CAS# 1910-42-5



diquat dibromide CAS# 85-00-7



# Column Selection

Because highly charged paraquat and diquat are poorly retained on an alkyl stationary phase, any standard reversed phase HPLC technique that relies solely on the hydrophobicity of the column and the strength of the mobile phase likely will fail to achieve a separation. If changing the hydrophobicity of the stationary phase is ineffective, the next choice is to lower the relative hydrophilicity of the mobile phase. We have developed a simple, effective analysis for paraquat and diquat, based on a new HPLC column and a unique mobile phase. This analysis can be performed on a conventional HPLC system using a UV detector.

The separation makes use of a different analytical property – chaotropism: an ability to disrupt the ability of water to solvate ions and thereby alter the charged interactions among the analyte, the mobile phase, and the stationary phase. In this case, by dispersing the analyte's charge, the solubility of the highly polar analyte upon a non-polar substrate (the stationary phase) can be enhanced. The analyte's retention is then enhanced because it remains longer upon the absorbed solvent layer (acetonitrile) present on the stationary phase.

The packing for the new column is manufactured from type B silica, to ensure proper selectivity and analyte retention, and to minimize interactions between the analytes and residual silanols and metal ions on the packing particles, which can lead to tailing and unwanted / unpredictable retention.

# Column Selection, ctd.

The reagent used in the mobile phase alters the chemical nature of the analyte as perceived by the column and mobile phase. This reagent reduces the ability of water to solvate the analytes and hydrogen bond with them, essentially forcing the charged complexes to remain longer in the absorbed solvent layer of the stationary phase, and thus improve the retention.

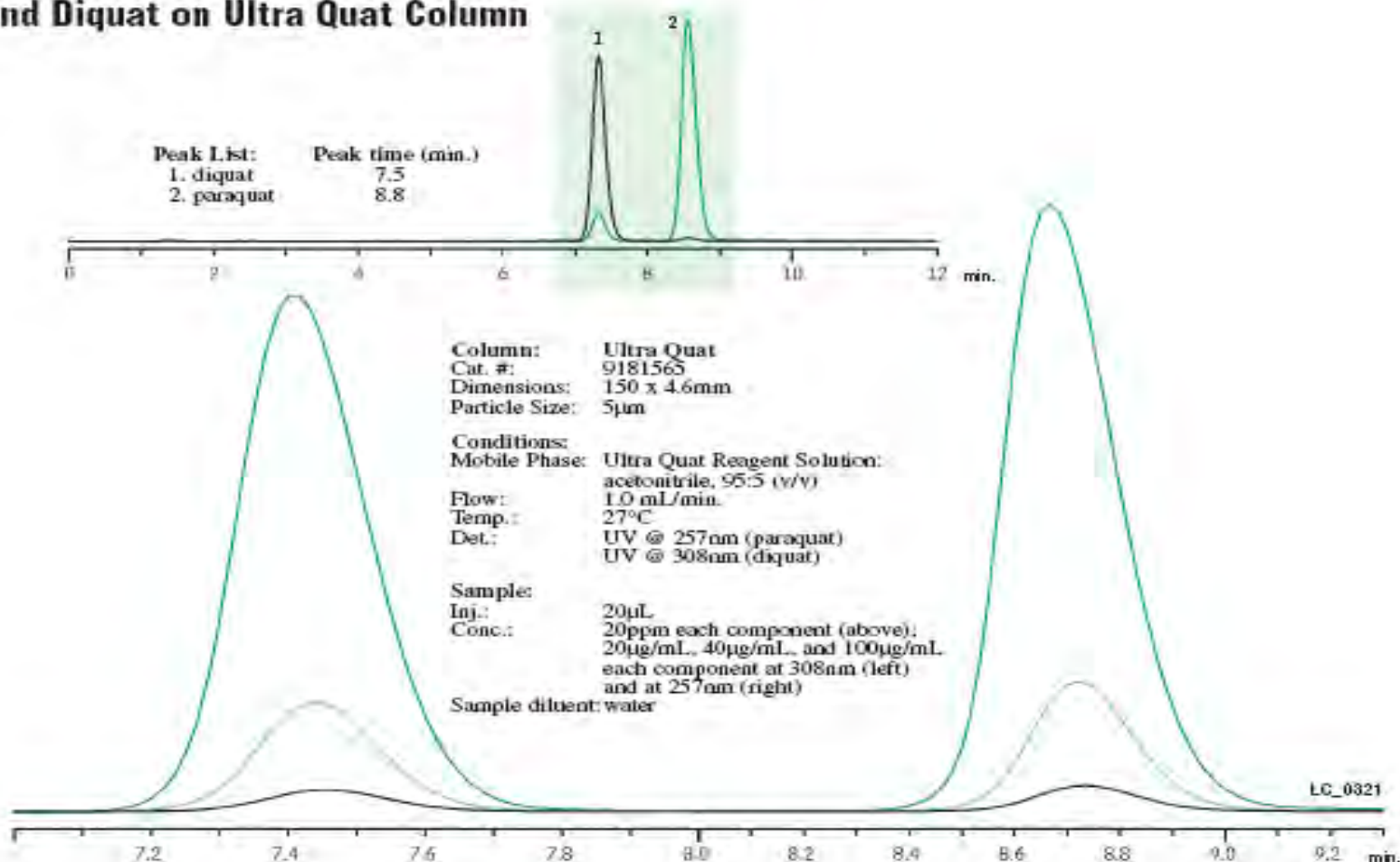
- The use of solvents as acetonitrile allow for dispersive interactions with the chaotropic anions.
- Solvents/reagents that are capable of hydrogen bonding interactions as methanol should be avoided as they may cause ghost peaks or lead to total retention loss in this analysis.
- The chaotropic agents are inorganic anionic salts added to the aqueous portion of the mobile phase. <sup>1</sup>

Table I. Chromatographic conditions for Analyzing Paraquat and Diquat by HPLC-UV.

<b>HPLC Column</b>	Ultra Quat, 150x4.6mm, 5 $\mu$ m (100Å)
<b>Mobile Phase</b>	A: 549.2 (modified) Mobile Phase Modifier solution, cat# 32441, 20 ml to 1000 ml of water B: acetonitrile
<b>Isocratic</b>	95% A : 5%B
<b>Flow Rate</b>	1.0 mL/min
<b>Detection</b>	UV @ 257nm Paraquat UV @ 308nm Diquat
<b>Injection</b>	20 $\mu$ L
<b>Concentration</b>	10 ppm each or as indicated

Figure 2. EPA 549.2 (modified), using an Ultra Quat column and the conditions in Table I.

### Paraquat and Diquat on Ultra Quat Column



Restek Corporation 110 Benner Circle Bellefonte, PA 16823  
 814-353-1300 • 800-356-1688 • Fax: 814-353-1309 • www.restekcorp.com

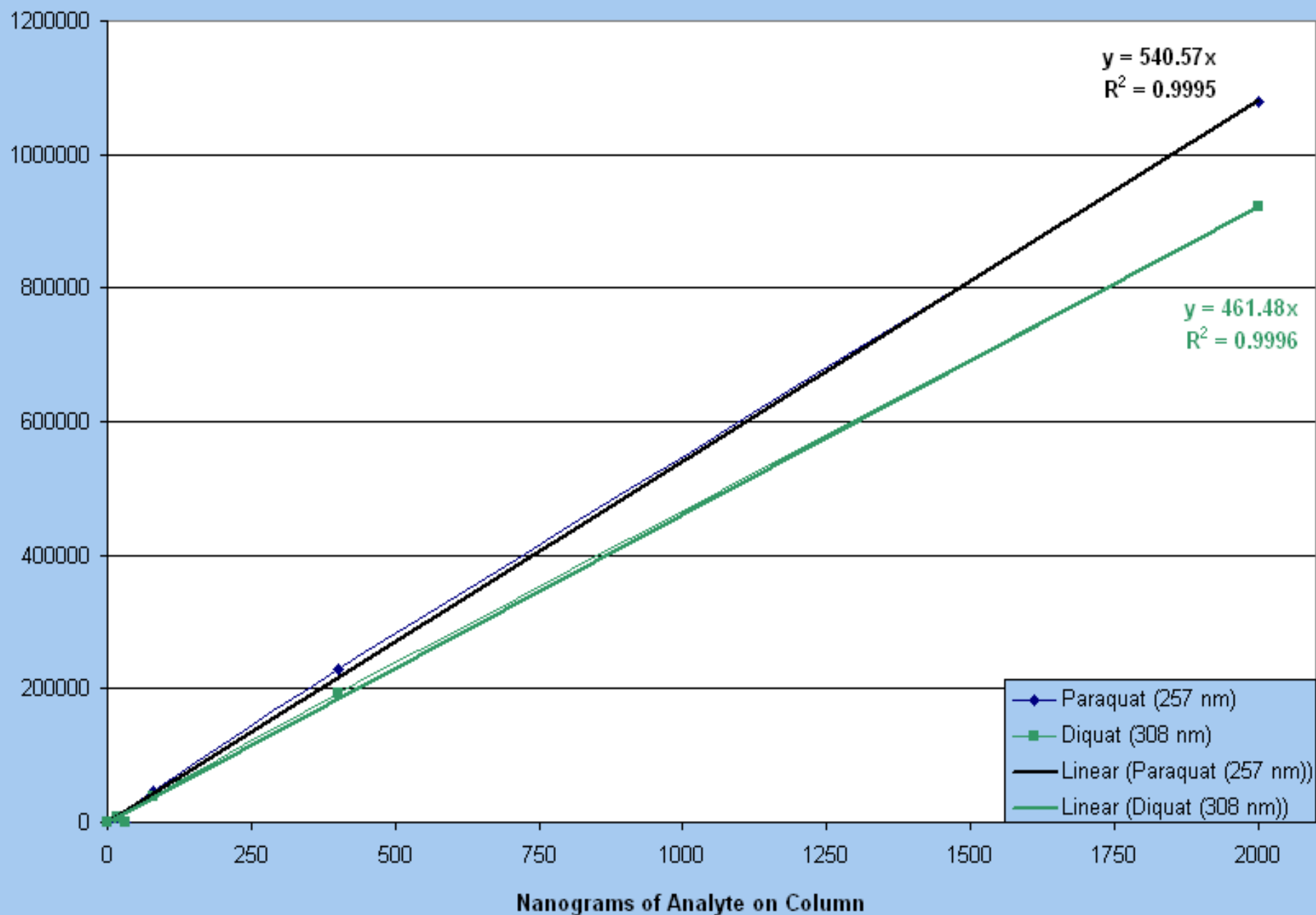
# Table II. Approximate detection/quantification limits for Paraquat/Diquat using Simplified HPLC UV method

On column limit of detection  
(LOD): 0.12 ng

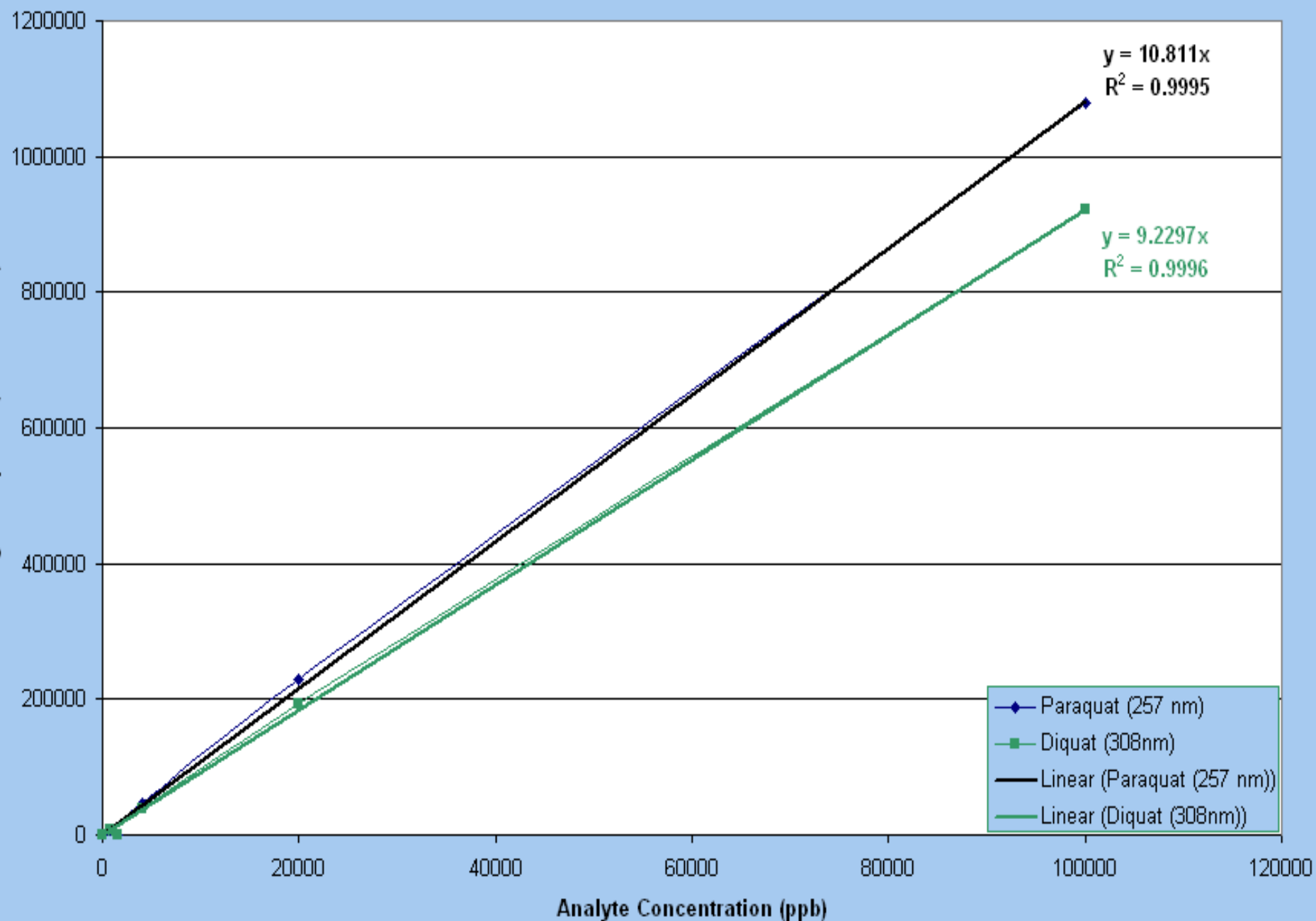
On column limit of quantification  
(LOQ): 0.4 ng

Sample Volume (mL)	Injection Volume (μL)	Limit of Detection (ppb)	Limit of Quantification (ppb)
1	20	6	20
100	20	0.06	0.2
250	20	0.024	0.08
1000	20	0.006	0.02
1	100	1.2	4
100	100	0.012	0.04
250	100	0.0048	0.016
1000	100	0.0012	0.004
1	200	0.6	2
100	200	0.006	0.02
250	200	0.0024	0.008
1000	200	0.0006	0.002

## Response of Analytes vs Column Loading at 20 microliters



## Analyte Response vs Concentration





## Solid Phase Extraction (EPA 549.2 Modification)

To meet the required detection limits for these herbicides, a concentration step is necessary. Solid phase extraction (SPE) can be used to extract the herbicides from a water matrix, before elution with an aqueous acidic solution. Several types of phases were tested for this application, including both strong (propyl and benzyl- types) and weak ion exchangers. We found that a weak cation exchanger gave the best overall recoveries.

The modified extraction method does not require the use of an SPE alkyl C8 phase with ion pairing agents. Ion pair agents have detrimental effects upon sensitivity and resolution using the modified HPLC method.

Analytical conditions are given in Table I, the details of the extraction method are summarized in Table III and recovery results are listed in Table IV. When using a 1L sample size and 6mL tube size, sampling rates of up to 25mL/min were possible and still resulted in excellent recovery efficiency. The 1L sample for these studies had a concentration of 50ppb each herbicide and required no pH adjustment before extraction (extracts were done at neutral pH).



Table III. Conditions for the modified SPE extraction of Paraquat and Diquat.

SPE tube	6mL, 500mg Ultra Quat SPE
Tube conditioning	1. 4mL acetonitrile 2. 4mL deionized water
Sample	1L sample water
Sample flow rate	Sample passed through tube at 20-25mL/min flow rate
Wash	Inner surface of tube rinsed with small amount of deionized water
Dry	Tube dried for less than 30 seconds

Table IIIa. Conditions for the SPE extraction, ctd.

Extraction	<ol style="list-style-type: none"><li>1. 1 x 2mL acidic elution solution*; allow to soak into bed for up to 1 minute; follow with 2 x 2mL more solution.</li><li>2. Pass solutions through bed at a slow, drop wise rate into prepared collection vessels.#</li><li>3. Neutralize samples with 5-7uL of ammonium hydroxide (check using pH paper) and correct final volume to 5mL before analysis.</li></ol> <p>* 1mL 85% H<sub>3</sub>PO<sub>4</sub> diluted to 1liter with deionized HPLC grade water (0.1% solution)</p> <p># collection and analytical vessels must be deactivated before use</p>
------------	---

Table IV. Recoveries of Paraquat and Diquat after Solid Phase Extraction.

Analyte	% Recovery 1L sample	%RSD n=5
paraquat	97.2	5.4
diquat	100.3	5.6

All samples were collected in glassware that was deactivated using 20% DMDCS in toluene, following label directions.

Samples for analysis were prepared and stored in Silcote CL7 deactivated autosampler vials. Polypropylene vials and inserts also may be used.

# Conclusions

Polar paraquat and diquat can't be separated on a C8 HPLC column without adding ion pair modifier to the mobile phase. USEPA Method 549.2 sometimes does not provide optimum resolution but does allow detection to 0.14ng on column. To overcome these limitations, we have developed a mobile phase modifier for rapid (11 minutes), complete ( $R > 4.0$ ) resolution of paraquat and diquat, with detection to 0.12ng on column with a linearity range of 6.4 ppb to 100,000 ppb for sample analysis within a single system.

In addition, the sample preparation method presented here, using solid phase extraction, resulted in a two hundred fold analyte concentration, with accurate (greater than 97%), reproducible (% RSD < 6) recoveries from one liter water samples. The SPE tube is a weak cation exchanger optimized for this extraction method. This new simple HPLC mobile phase and SPE sample preparation eliminate complicated analytical systems and improve overall method detection limits.

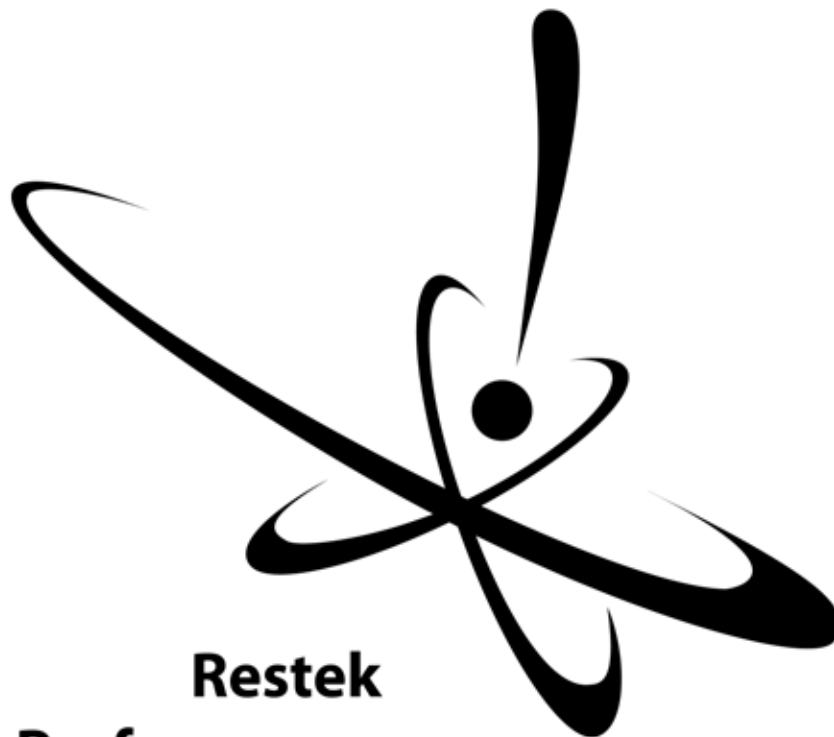
# Acknowledgements

- <sup>1</sup> ***Influence of inorganic mobile phase additives on the retention, efficiency and peak symmetry of protonated basic compounds in reversed phase liquid chromatography***; Journal of Chromatography A, 1049 (2004) 63-73; Li Pan, Rosario LoBrutto, Yuri V. Kazakevich, Richard Thompson.

# Evaluation of Coatings and Alloys to Extend the Lifetime of Equipment Used in Corrosive Environments

Gary Barone; David Smith; Marty Higgins,  
Restek Corporation, Bellefonte, PA

# Logo



**Restek  
Performance  
Coatings**

# Introduction

In acidic environments it is critical to engineer solutions to account for the depreciation of equipment caused by corrosion. Current commercial solutions that address corrosion are specialized alloys and coating

Coatings often are employed as acid-resistant barriers between the corrosive environment and equipment.

This presentation evaluates the performance of a silicon based coating in corrosive environments. Comparisons are made to non-coated stainless steel alloys.



# Experimental

The following ASTM methods were run to evaluate the performance of coated and non-coated materials in corrosive environments:

- Pitting and crevice corrosion (ASTM G 48, Method B)
- 1000 Salt Spray Testing (ASTM B 117)
- Condensing Humidity Testing (ASTM D 4585)
- Cyclic Polarization Electrochemical Corrosion Testing (ASTM G 61)

Experiments conducted by Matco Associates (Pittsburgh, PA).

# Results and Discussion

## ASTM G48, Method B

### Crevice Corrosion

Results from the pitting and crevice corrosion testing revealed that the silicon coated 316L stainless steel experienced no crevice corrosion and only slight pitting (figure 1a)

The bare 316L stainless steel coupons experienced severe crevice corrosion and pitting corrosion (figure 1b)

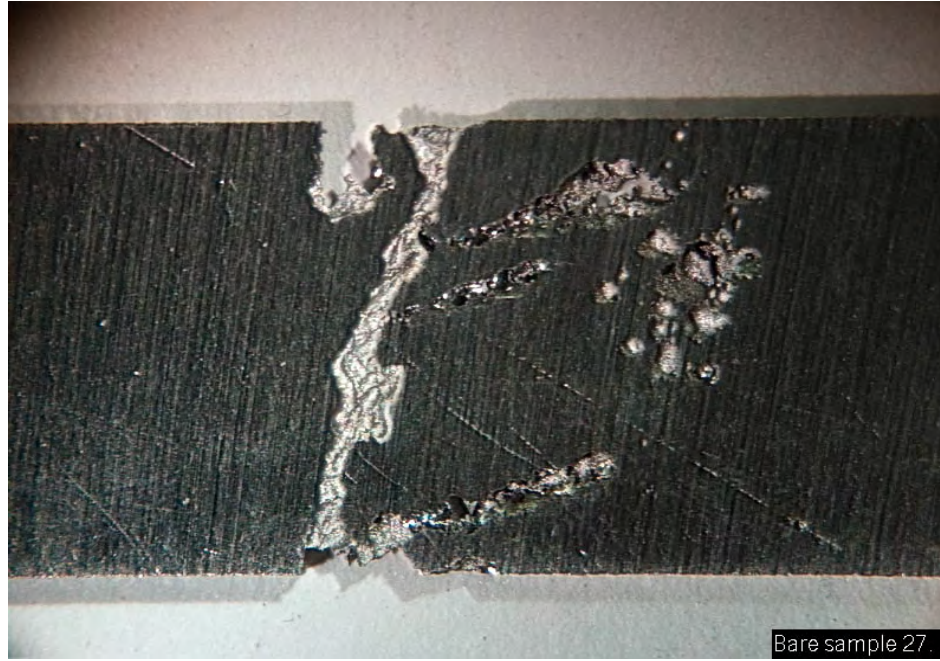
Table 1 summarizes weight loss resulting from exposure to the 6% w/w ferric chloride solution required by this method.

Elimination of crevice corrosion is an important step in reducing equipment depreciation in corrosive environments.

# Figure 1a



# Figure 1b



Bare sample 27.

# Table 1

- |  |   |
|--|---|
| <ul style="list-style-type: none"><li>• Weight Loss:<br/>Silcosteel®-CR treated<br/>316L stainless steel<br/>coupons</li></ul>                               | <ul style="list-style-type: none"><li>• Weight Loss:<br/>Bare 316L stainless<br/>steel coupon</li></ul>   |
| <ul style="list-style-type: none"><li>• Sample 1: 19 g/m<sup>2</sup></li><li>• Sample 2: 25 g/m<sup>2</sup></li><li>• Sample 3: 25 g/m<sup>2</sup></li></ul> | <ul style="list-style-type: none"><li>• Sample 1: 231 g/m<sup>2</sup></li><li>• Sample 2: 209 g/m<sup>2</sup></li><li>• Sample 3: 228 g/m<sup>2</sup></li></ul> |



# Results and Discussion

## ASTM B 117

### Salt Spray

The 1000 hour salt spray exposure did not have any effect on the silicon coated 316L stainless steel samples (figure 2a)

The bare 316L stainless steel samples exhibited light surface rusting but no signs of pitting (figure 2b)

Results of this study indicate the potential application of Silcosteel<sup>®</sup>-CR to enhance product lifetime and reduce equipment maintenance in marine environments.



Figure 2a

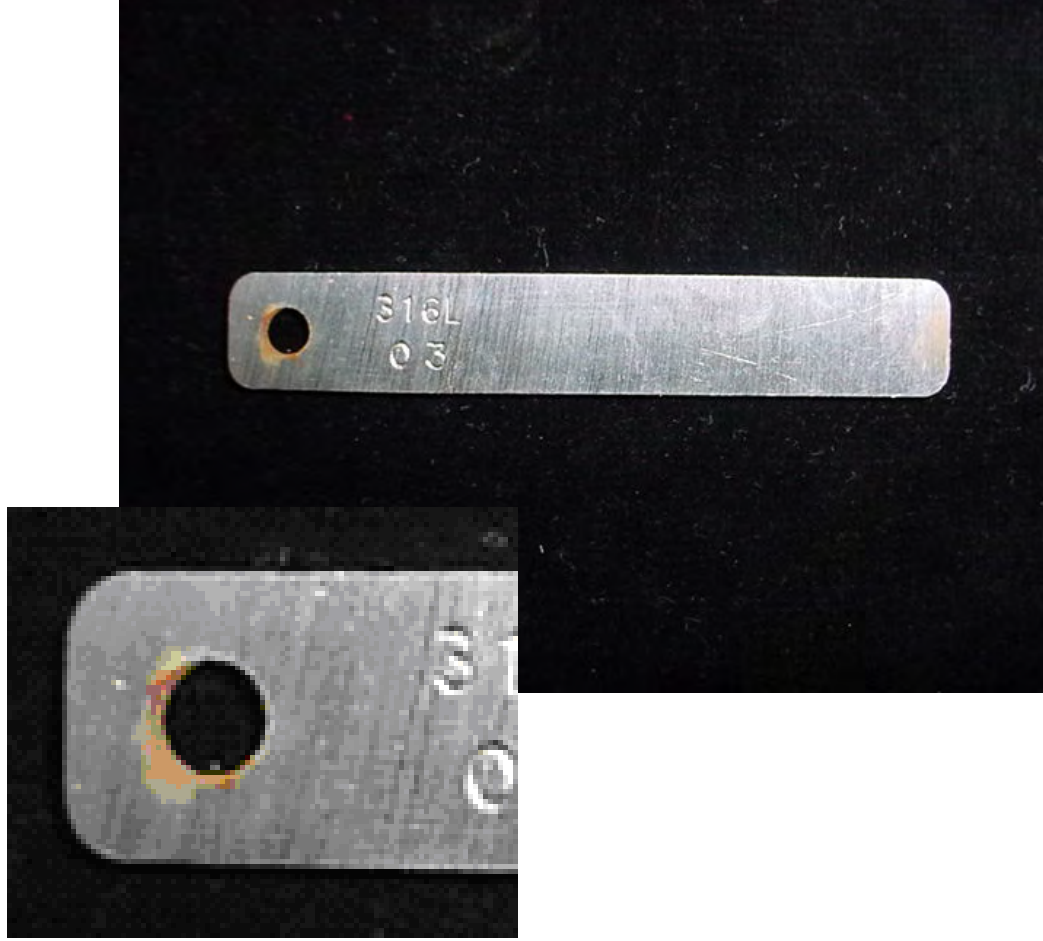


Figure 2b



# Results and Discussion

## ASTM D 4585

### Condensing Humidity

Exposure to condensing humidity had no effect on the silicon coated 316L stainless steel coupon (figure 3a) and produced only a slight oxide layer on the bare 316L stainless steel coupon (figure 3b).

This testing proved the stability of the Silcosteel<sup>®</sup>-CR coating in an environment designed to simulate outdoor applications of the coatings.

# Figure 3a





Figure 3b

# Results and Discussion

## ASTM G 61

### Cyclic Polarization

Cyclic Polarization Electrochemical Corrosion Testing to evaluate the pitting potential.

Pitting Potential  $E_b$ , in millivolts, determined in a 3000ppm Cl-containing neutral solution:

- Silicon coated coupon: 1460mv
- Bare coupon: 370mv

Pitting potential,  $E_b$ , in millivolts, determined in a 3000ppm Cl-containing acidic solution (1N H<sub>2</sub>SO<sub>4</sub>)

- Silicon coated coupon: 927mv
- Bare coupon: 370mv

The increased energy required to generate pitting is the barrier towards corrosion supplied by the Silcosteel<sup>®</sup>-CR treatment.

# Conclusion

Use of a silicon overlay coating dramatically improves the corrosion resistance of stainless steel components.

Improved resistance to attack acts to prolong components life and offer an alternative to expensive alloy solutions to corrosion.

The amorphous silicon coating, Silcosteel<sup>®</sup>-CR, has proven to extend resistance in marine exposure environments, chloride environments and is rugged and durable enough to withstand atmospheric exposure.

# High Vacuum Applications of Silicon-Based Coatings on Stainless Steel

Gary A. Barone, David A. Smith, Marty Higgins:  
Restek Corporation, Bellefonte, PA

Bruce R.F. Kendall:  
Elvac Associates, Bellefonte, PA

# Introduction

Ultra-High Vacuum (UHV) environments of  $10^{-7}$  Torr or lower and high vacuum environment of  $10^{-5}$  Torr or lower are critical for many instruments and semi-conductor manufacturing processes. Under these vacuum conditions, steel and aluminum components outgas large quantities of water,  $\text{CO}_2$ ,  $\text{CO}$ , and other contaminant molecules. Large pumping systems and extensive bake-out treatments are required to remove these materials in order to attain and maintain low vacuum environments. This research investigates the use of an amorphous silicon coating to reduce outgassing of components in high vacuum and UHV environments.



# Theoretical Basis

- Outgassing rate (F) in monolayers per sec:

$$F = [\exp (-E/RT)]/t'$$

$t'$  = period of oscillation of molecule perp. To surface, ca.  $10^{-13}$  sec

$E$  = energy of desorption (Kcal/g mol)

$R$  = gas constant

source: Roth, A. Vacuum Technology, Elsevier Science Publishers, Amsterdam 2<sup>nd</sup> ed., p. 177.

- Experimental design allows us to isolate and directly compare outgassing rates with increasing temperature. By applying heat, the outgassing rates are exponentially increased for the purpose of timely data collection. These comparisons with experimental controls directly illustrate the difference incurred by the applied coatings



# System

- Turbo pump for base pressures to  $10^{-8}$  Torr
  - pumping rate between gauge and pump: 12.5 l/sec (pump alone: 360 l/sec)
  - system vent with dry  $N_2$  between thermal cycles
- Ion pump for base pressures to  $10^{-10}$  Torr
  - pumping rate between gauge and pump: 11.7 l/sec (pump alone: 400 l/sec)
  - system under constant vacuum
- Baffle systems used to ensure identical conductance pathways
  - no line-of-site between samples

# System

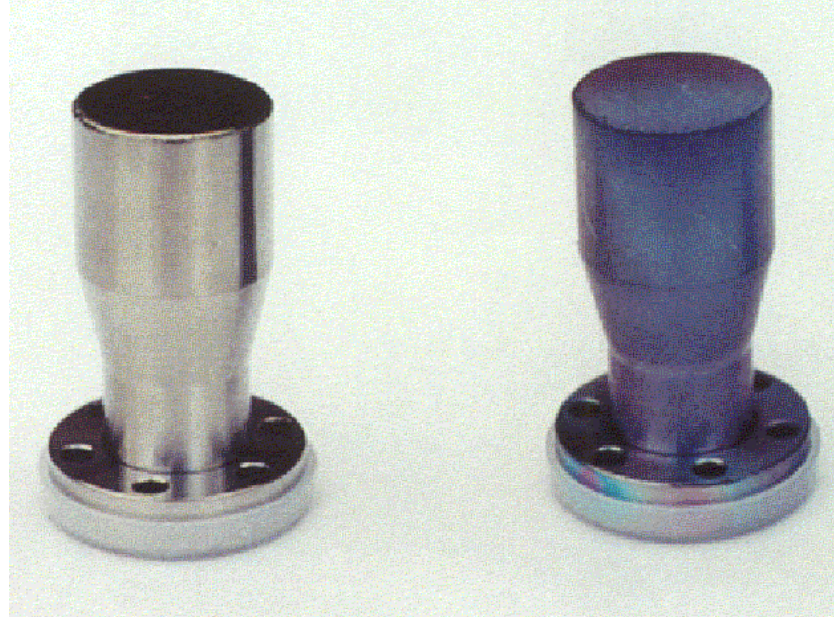
- Cleaning of all components as follows:
  - Ultrasonic cleaning of all components in aqueous caustic surfactant.
  - Heat to 400°C in inert atmosphere
  - Vacuum at 400°C
- Silcosteel® coatings (amorphous silicon) applied to components, after previous cleaning process, to reduce outgassing. Coating process:
  - CVD process
  - Entire surface coverage
  - Manipulation of coating process parameters reduce outgassing
- Figure 1 is a photograph of a non-coated and coated component used in one of the studies.

# Experimental

Both the “HEAT CLEANED” only and Silcosteel®-UHV treated components were attached to an ion pump system. The systems was then pumped down to an initial base pressure. Several variants of coating were studied to understand the impact of coating composition and depth.

The “HEAT CLEANED” only and Silcosteel®-UHV treated components were individually heated, and the resultant pressure increase was a measured effect of materials outgassing from the substrate into the vacuum environment

# Figure 1



# Results and Discussion

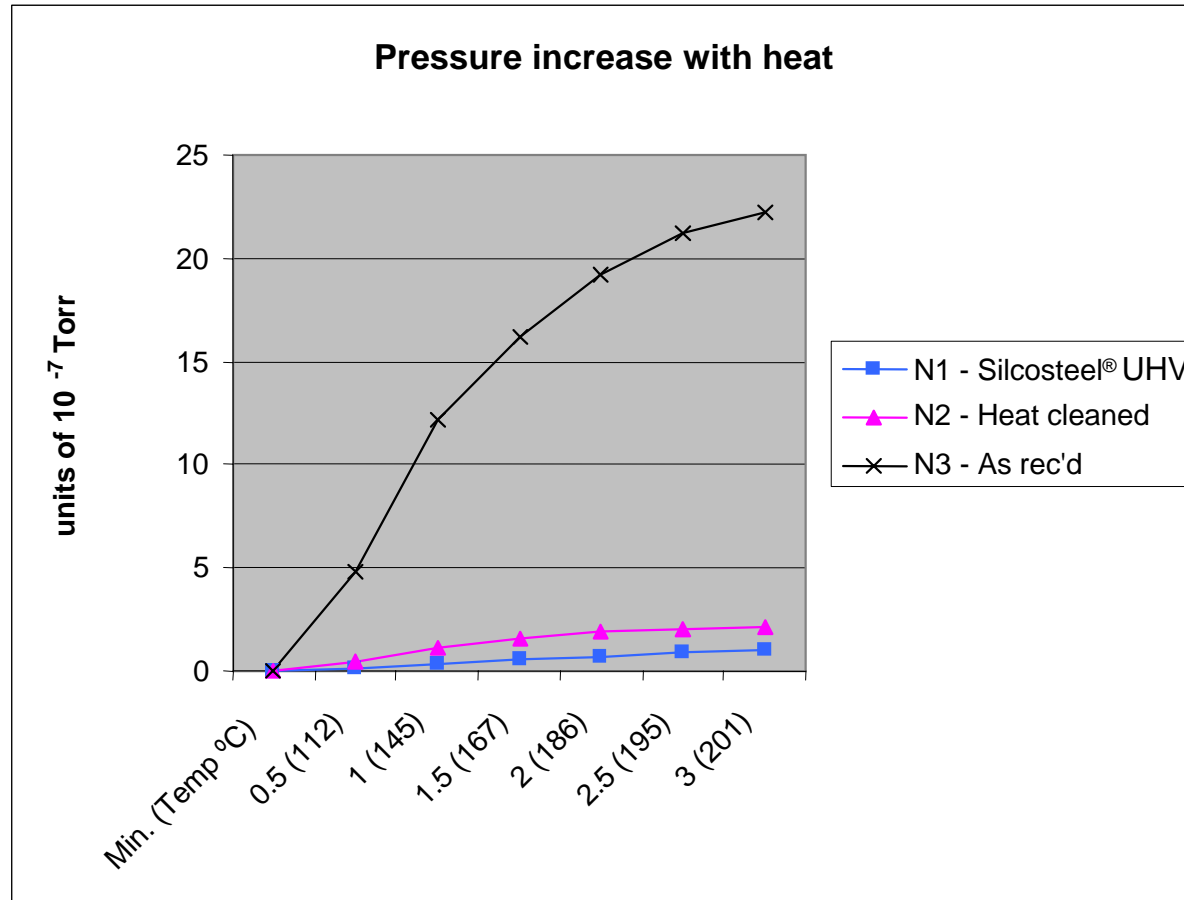
## INITIAL PUMPDOWN RESULTS ( $10^{-7}$ Torr)

Figure 2 charts the pressure increase vs. time/temperature as a result of heating the vacuum components. Base pressure was  $10^{-7}$  Torr and the system was under vacuum for 10 hours.

The vacuum components that were used as received from the manufacturer demonstrated a large amount of outgassing causing a large pressure increase. It was impractical to study these components at any lower levels of base pressure due to immense outgassing.

The heat treated and coated components both exhibited little pressure increase in the  $10^{-7}$  environment with heating

# Figure 2



# Results and Discussion

## EXTENDED VACUUM STUDY ( $10^{-9}$ Torr)

Figures 3,4 and 5 demonstrate pressure increase of vacuum components exposed to heating after extended time under pumpdown

Figure 3, data after 8 days of pumpdown

Figure 4, data after 41 days of pumpdown

Figure 5, data after 156 days of pumpdown

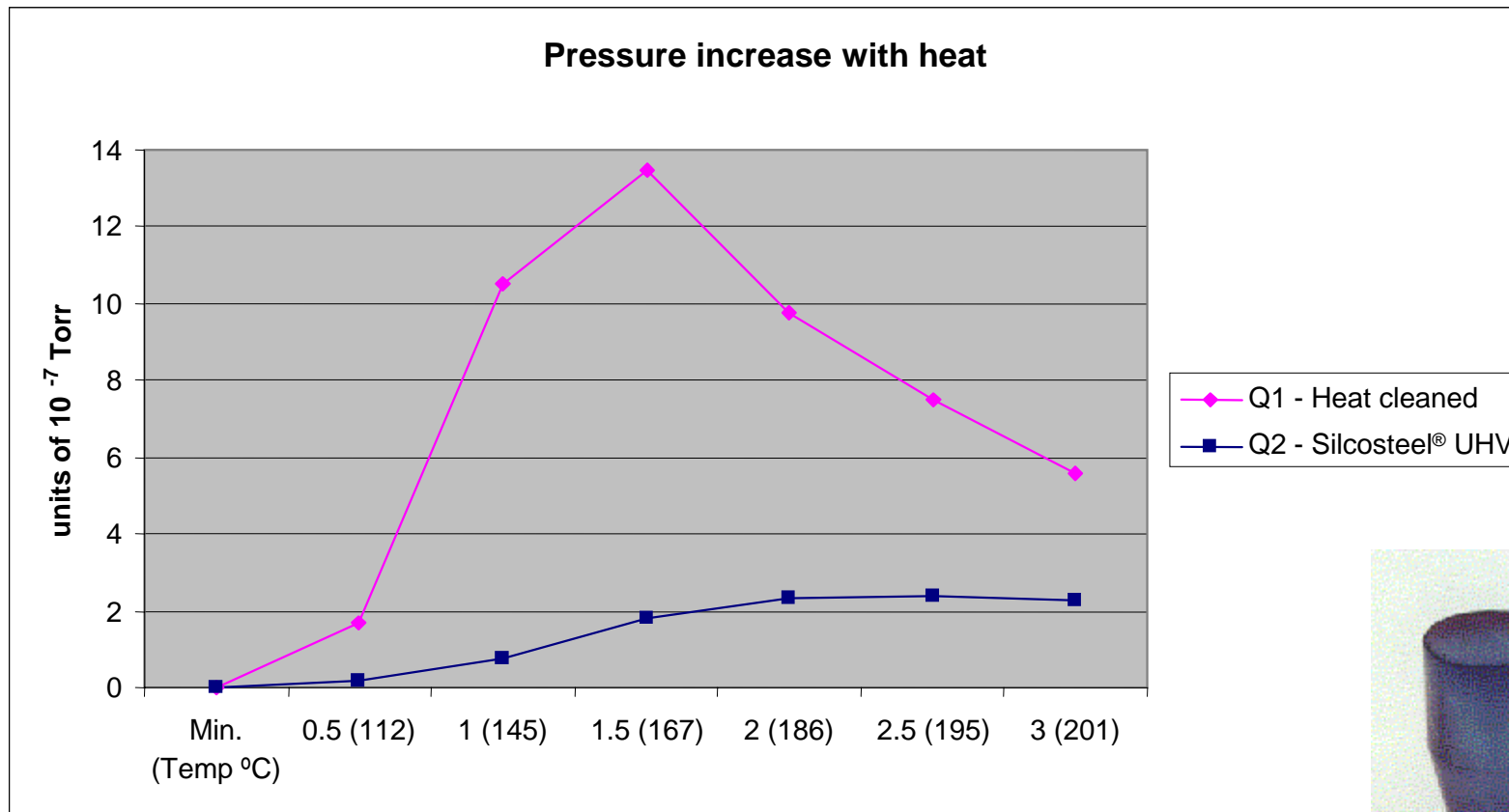
Ion pump used with base pressure of  $1 \times 10^{-9}$  Torr

Amorphous silicon components continued to experience a lesser degree of outgassing material even after long periods of time under vacuum.

NOTE: Magnitude of Y-axis in each figure diminishing as better vacuum is achieved in the test system and overall outgassing of components decreases

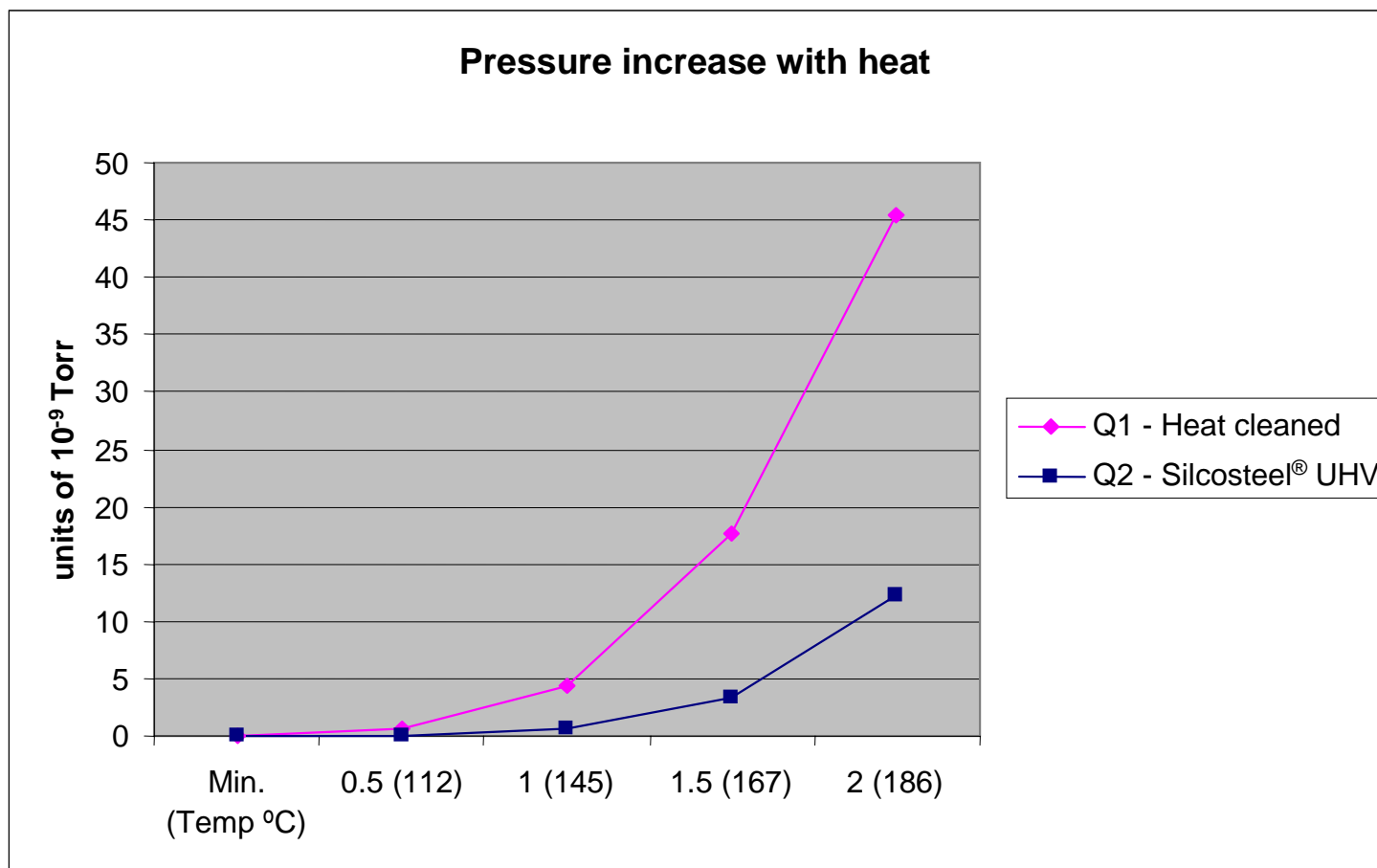


# Figure 3

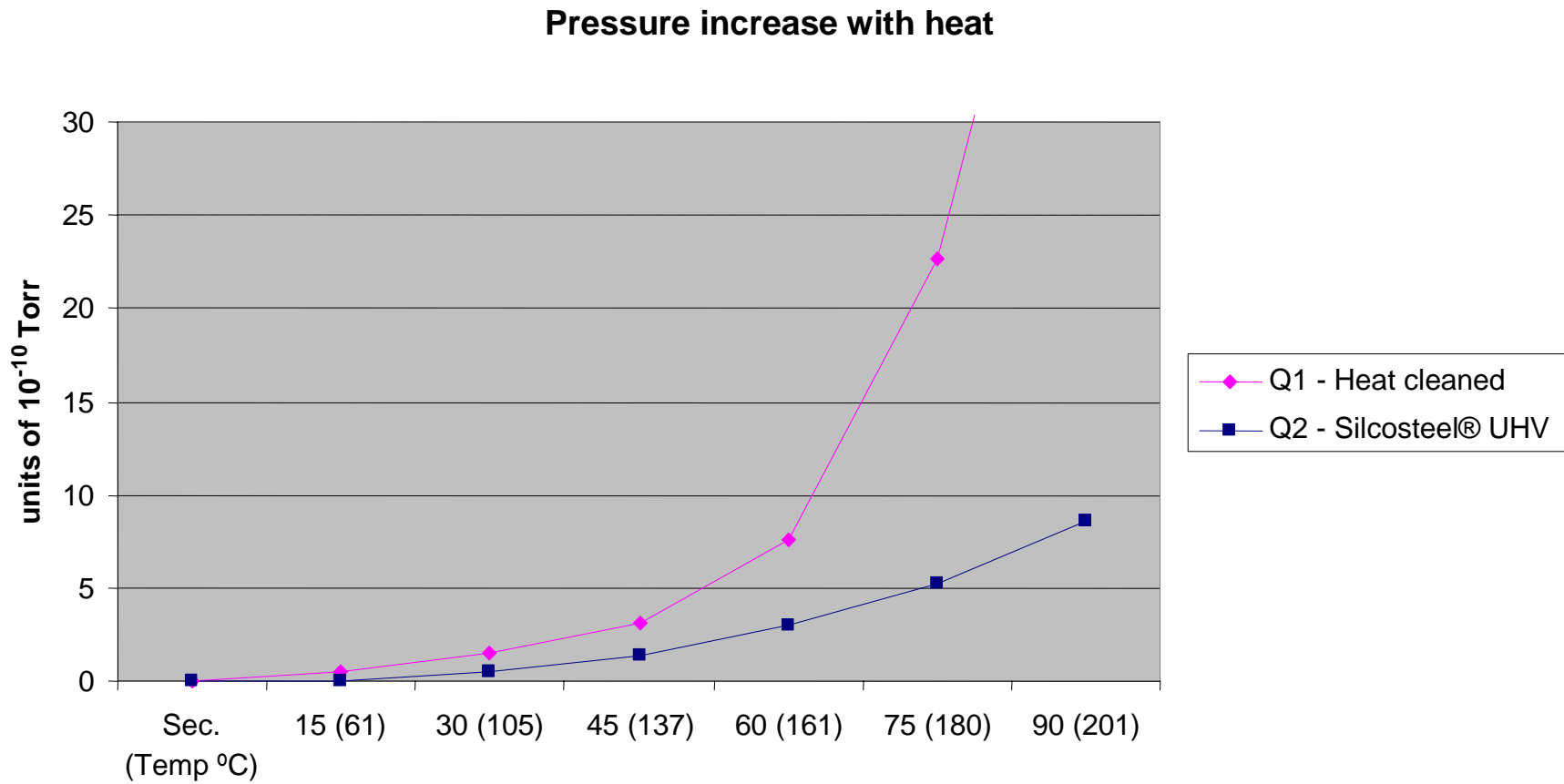




# Figure 4



# Figure 5



# Conclusions

This studied has illustrated the need for pre-treatment of vacuum components prior to installation and use. Vacuum components as received from the manufacture outgas greatly. As such, use in high vacuum and UHV vacuum environments is impractical.

The use of a caustic cleaning system and aggressive heating in an inert/vacuum condition reduces outgassing of new vacuum components by orders of magnitude.

This study also demonstrated the advantage of using an amorphous silicon coating (Silcosteel-UHV) to reduce outgassing of vacuum components.

The coatings act as a barrier, trapping volatile materials such as carbon monoxide, carbon dioxide and water. As such, these volatile materials are kept from entering the vacuum environment

# Acknowledgements

- Televac, for supplying test samples for this study

# Fingerprint Identification of Cocaine Adulterants by GC and LC

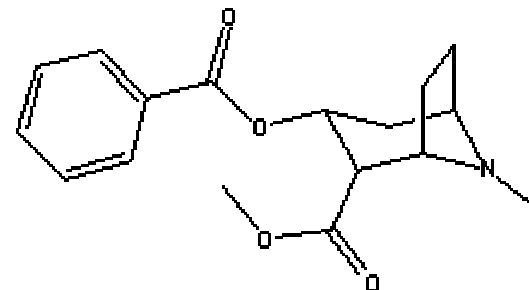
Tim Herring, Kristi Sellers and Rick Morehead

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823



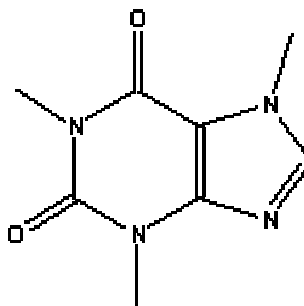
# Introduction

Cocaine



Illicit cocaine is commonly “cut” with adulterants or diluents that mimic the stimulant or local anesthetic effects of cocaine. Incorporating these additives into cocaine increases the volume or weight of product available for sale, which results in increased profits for drug dealers. Because illicit cocaine composition can be specific to a dealer, adulterant and diluent identification of seized cocaine is critical in determining the possible routes of distribution and sales.

Caffeine



Both Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) can be used to identify cocaine adulterants such as sugars, anesthetics, analgesics and stimulants. Several different detection systems can be used to obtain identification and quantitative information.

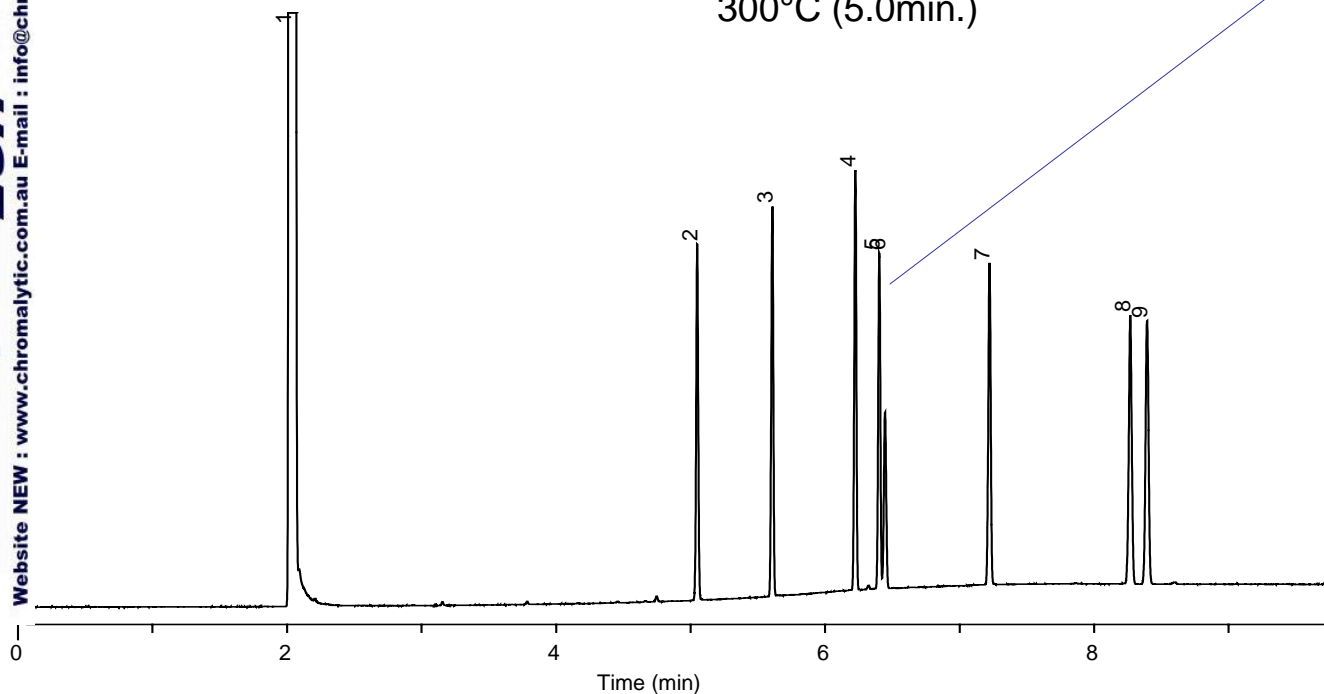
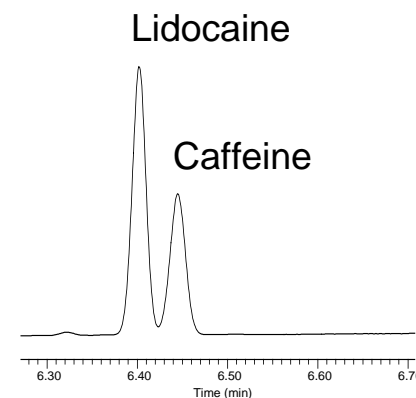
Gas chromatography is the most common analytical technique used for the analysis of all of the adulterants found in cocaine with exception of sugars. Although sugars can be derivatized for analysis by GC, they are more easily detected using HPLC.

Detection of adulterants found in cocaine after separation by GC can be performed using FID (Flame Ionization Detection), NPD (Nitrogen Phosphorus Detection) and MS (Mass Spectrometry) detectors. Although FID and NPD provide good sensitivity for identifying and quantitating adulterants found in cocaine (see Chromatogram #1), GC/MS is the most widely accepted detection method. GC/MS data is not only very sensitive, but also provides positive identification of the adulterants based on mass spectral information. MS data can be used as confirming evidence in a court of law.

# Cocaine Adulterants by GC/FID

## Chromatogram #1

**GC Column:** Rtx-440 30m, 0.25mmID, 0.50um (Part# 12938)  
**GC:** Agilent 6890  
**Injector:** Split, 10:1, 250°C  
**Injection Amt.:** 1.0ul, sample 100ppm each in Methanol  
**Inlet Liner:** Laminar Cup Splitter  
**Flow Rate:** 1.0 ml/min  
**Carrier Gas:** Helium  
**Detector Temp.:** 300°C  
**Temp. Program:** 150°C (0 min.), 25°C/min. to 300°C (5.0min.)



### Peak List:

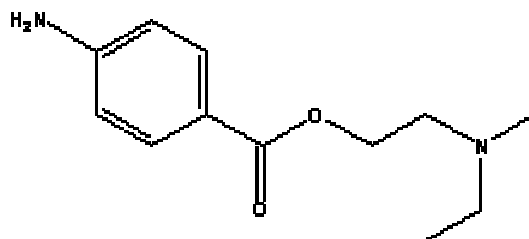
2. Benzocaine
3. Phenacetin
4. Prilocaine
5. Lidocaine
6. Caffeine
7. Procaine
8. Cocaine
9. Tetracaine



A second, less common, chromatographic method for identification of the adulterants and diluents in cocaine is High Performance Liquid Chromatography (HPLC). UV detection, either fixed or variable wavelength, is the most common detection mode. If sugars, such as lactose, are present, Refractive Index (RI) detection must be used since sugars have little or no UV absorbance(see Chromatogram #2).

Both types of detection methodology provide reproducible retention times, adequate peak identification and good quantitation. HPLC/MS is an alternative technique for analyzing adulterants in cocaine. HPLC/MS can also give confirming spectral data similar to GC/MS. However, reliable HPLC/MS methodology is still under development.

Procaine



# Sugars by HPLC/RI

## Chromatogram #2

**Column:** Pinnacle II Amino, 3um, 150 X 4.6mm  
(Part# 9217365)

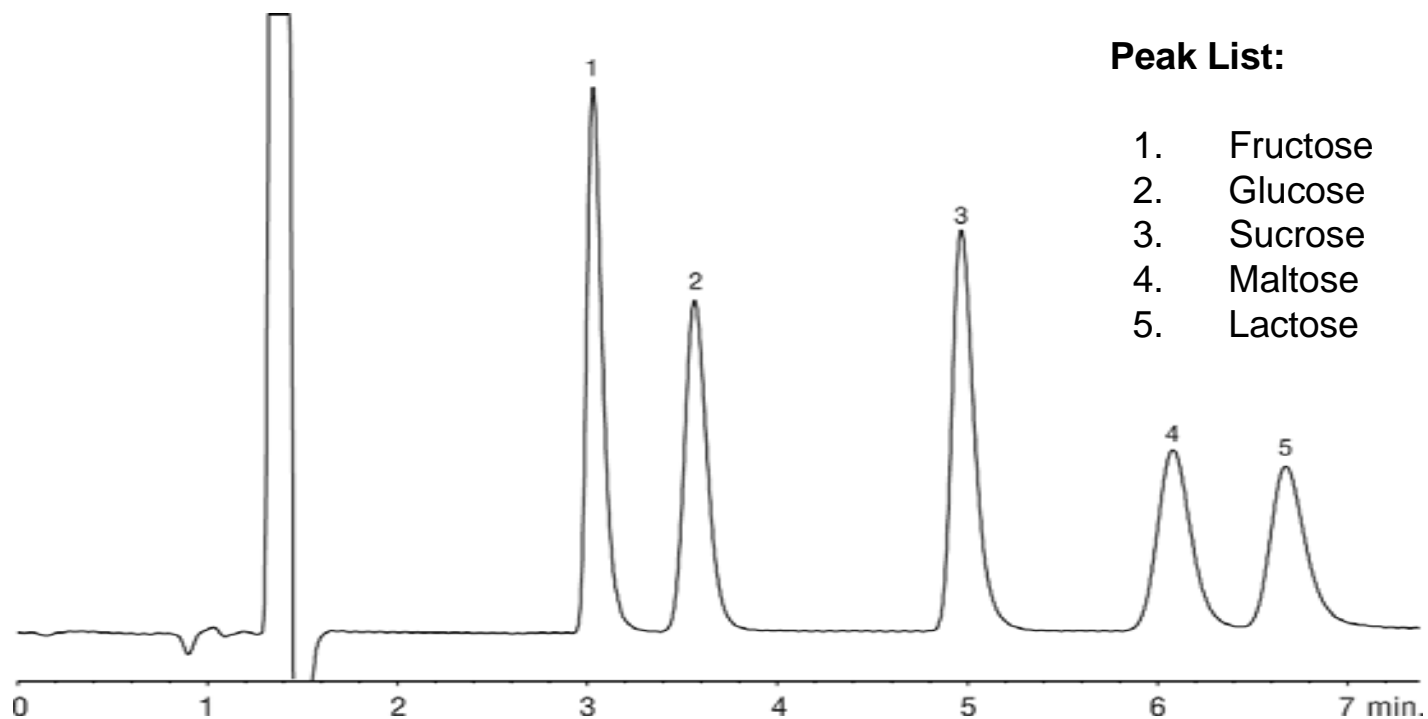
**Mobile Phase:** Water:Acetonitrile, 25:75

**Flow Rate:** 1.5ml/min.

**Column Temp.:** 35°C

**Detector:** RI @ 35°C

**Injection Amt.:** 5ul



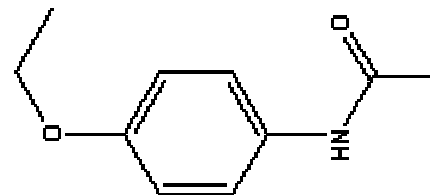
### Peak List:

### Conc. (ug/ml)

1.	Fructose	2.0
2.	Glucose	2.1
3.	Sucrose	4.0
4.	Maltose	4.5
5.	Lactose	4.4

# Experimental

Phenacetin



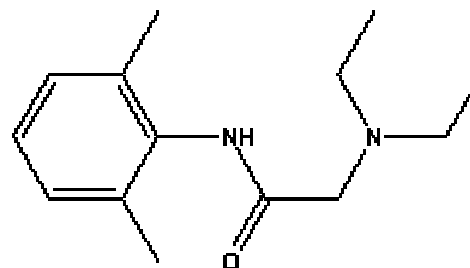
For the purposes of this study, GC/MS, and HPLC/UV-Vis data was obtained and analyzed. Mock samples of illicit cocaine were prepared using a variety of adulterants and diluents. Stimulants including caffeine, local anesthetics such as lidocaine, and over the counter analgesics like phenacetin, were added to cocaine hydrochloride in varying concentrations. A simple “dilute and shoot” sample preparation scheme was used to dissolve the samples before analysis. High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) methods were developed for identifying each adulterant or diluent added to cocaine. Method development focused on maximizing the resolution of all of the compounds in the study while minimizing the total analysis time in order to increase sample throughput.

# Cocaine Adulterants by GC/MS

## Run Conditions #1

<b>GC Column:</b>	Rtx-440 30m, 0.25mmID, 0.25um fused silica capillary column (Part# 12923)
<b>GC/MS:</b>	Agilent 6890 w/5973 MS & 7683 Autosampler
<b>Injector:</b>	Split, 10:1, 250°C
<b>Injection Amt.:</b>	1.0ul, Sample in Methanol
<b>Inlet Liner:</b>	Laminar Cup Splitter
<b>Flow Rate:</b>	1.0 ml/min
<b>Carrier Gas:</b>	Helium
<b>Transfer Line:</b>	180°C
<b>Solvent Delay:</b>	5 min.
<b>Scan Range:</b>	35-550
<b>Tune:</b>	PFTBA
<b>Temperature Program:</b>	150°C (0 min.), 25°C/min. to 275°C (0 min.), 15°C/min. to 300°C (5.0 min.)

Lidocaine

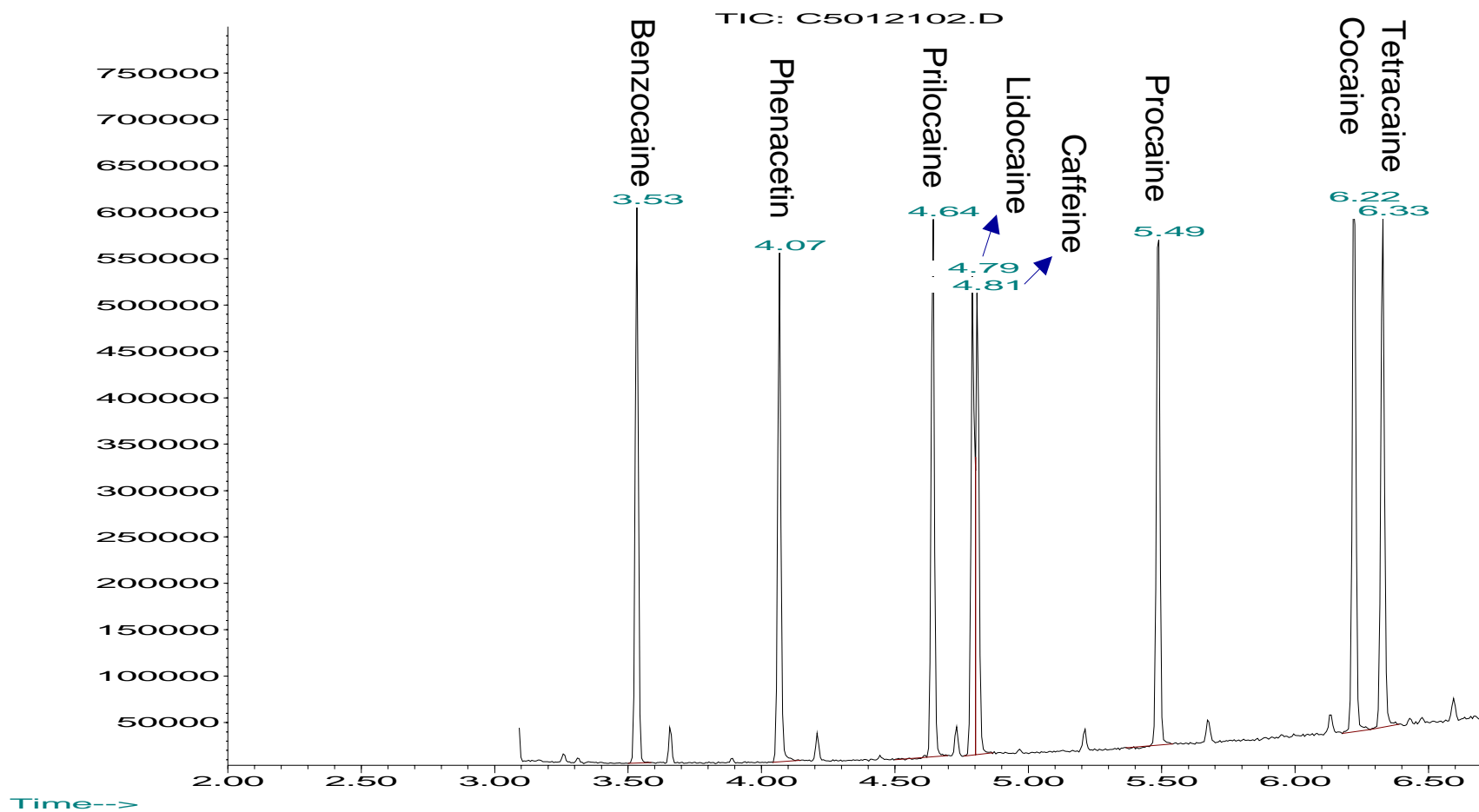


Several different adulterants were added to cocaine in equal amounts. The on-column concentrations of all of the compounds were 10ng each. GC/MS run conditions were optimized to give the maximum separation and the shortest analysis time. (See Run Conditions #1). Total analysis time was 6.5 minutes. All compounds were baseline resolved with the exception of caffeine and lidocaine; They were resolved by approximately 25% (see TIC #1). However, since they have very different mass spectra, extracted ion analysis could be performed resulting in positive identification of each compound. Lidocaine has a distinctive mass fragment of 86m/z and caffeine has a distinctive mass fragment of 194m/z (see MS #1 & MS #2).

# Cocaine & Adulterants by GC/MS

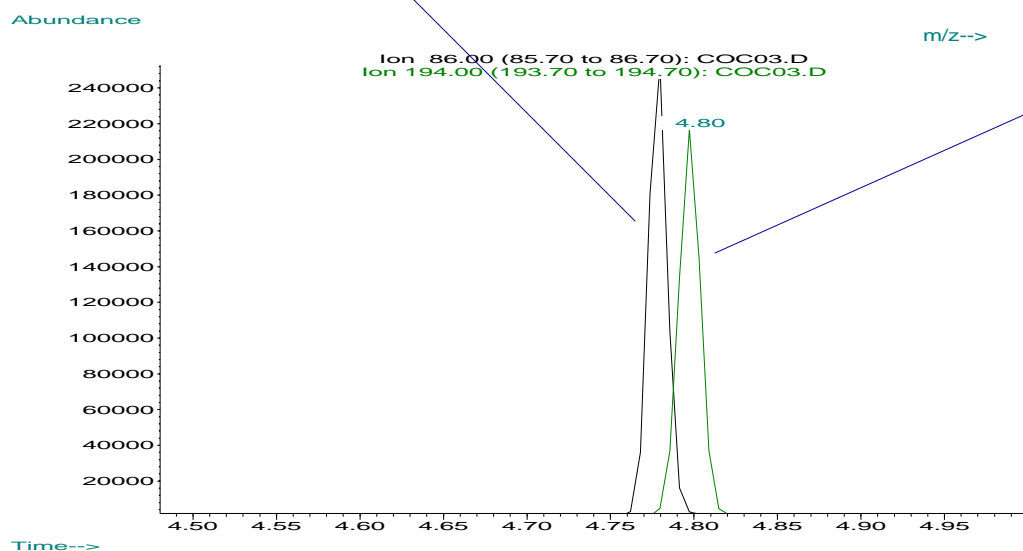
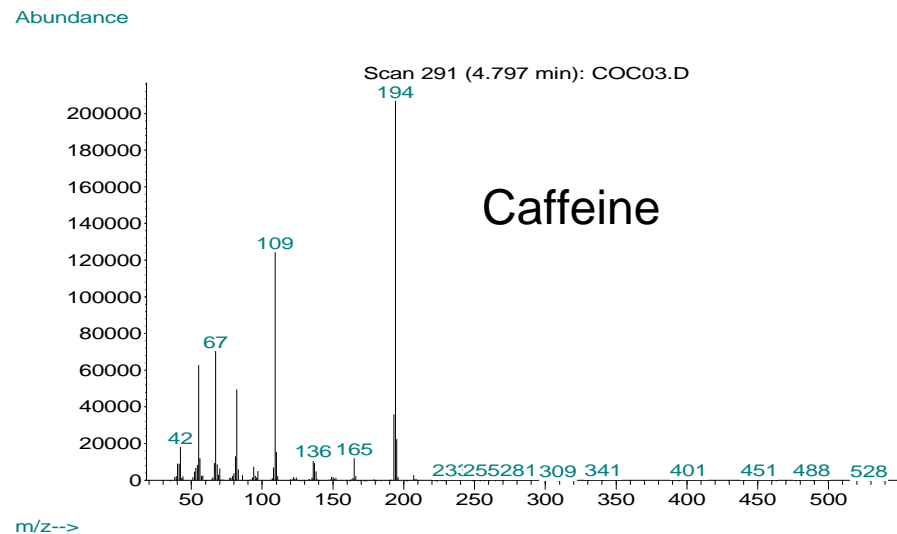
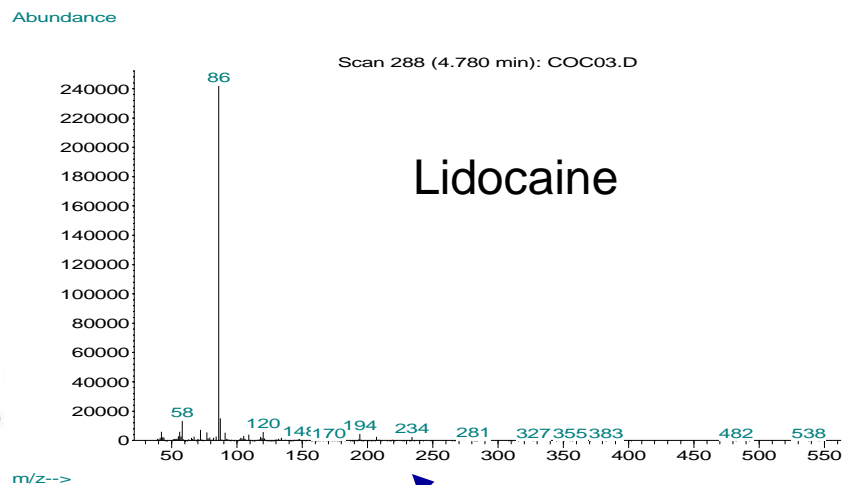
## TIC #1

Abundance



# Cocaine & Adulterants by GC/MS

## TIC, EI & Mass Spectrum of Caffeine & Lidocaine, MS #1 & MS #2

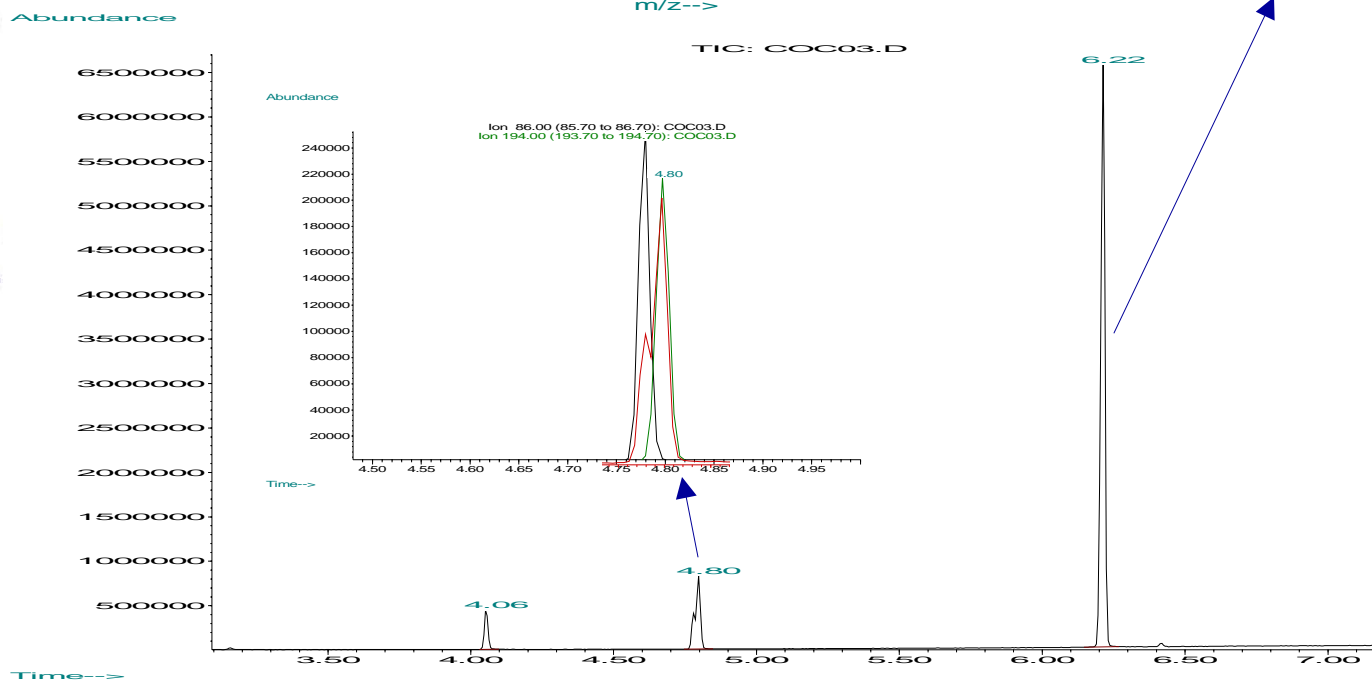
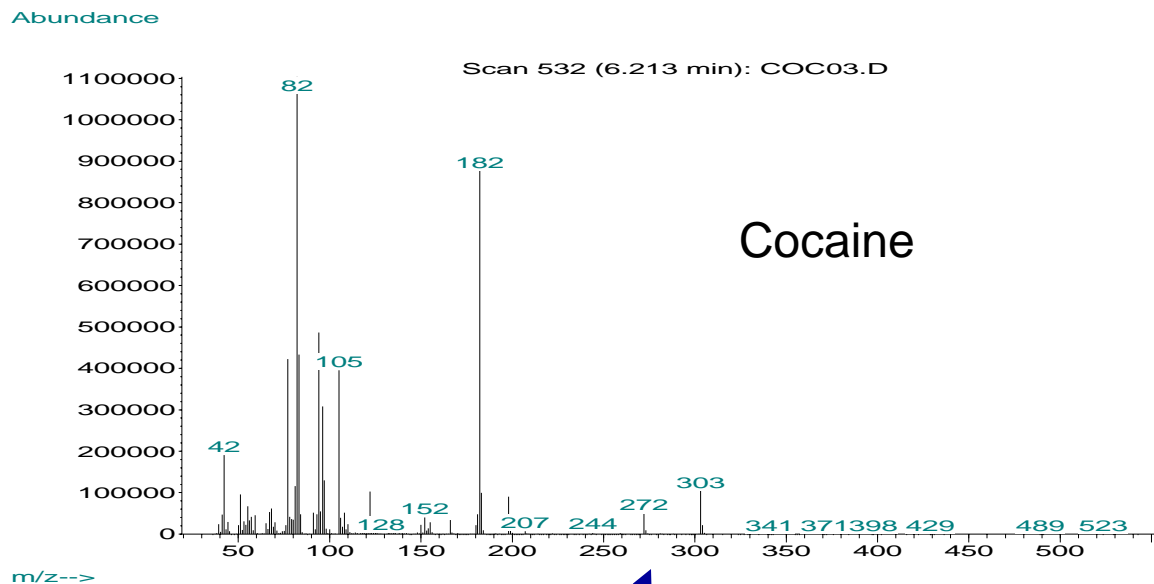


A mock sample containing 80% cocaine, 10% caffeine, 5% lidocaine and 5% phenacetin was prepared and analyzed to compare the separation of caffeine and lidocaine at lower concentrations. The on-column concentrations of the caffeine and lidocaine were 1.0 & 0.5 ng, respectively. At lower concentrations, only 10% resolution was obtained. Extracted ion analysis not only provided absolute identification, but also allowed for proper integration (quantitation) of each compound. (See TIC #2). Total analysis time was again 6.5 minutes.



# Cocaine & Adulterants by GC/MS

## TIC #2 of Mock Sample, EI & Mass Spectrum of Cocaine

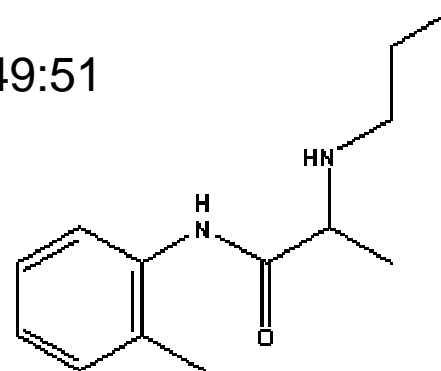


# Cocaine & Adulterants by HPLC/UV-Vis

## Run conditions #2

<b>HPLC Column:</b>	Ultra C18 5um, 150 X 4.6mm LC column (Part #9174565)
<b>HPLC/UV-Vis:</b>	Dionex HPLC with Gena 50 Autosampler
<b>Column Temperature:</b>	40°C
<b>Flow Rate:</b>	0.50ml/min
<b>Sample Solvent:</b>	Mobile Phase
<b>Injection Amt.:</b>	20ul
<b>UV-Vis Wavelength:</b>	234nm
<b>Mobile Phase:</b>	0.1% Formic Acid: Methanol, 49:51
<b>Program:</b>	Isocratic

Prilocaine



For HPLC analysis, several different adulterants were also added to the cocaine standard in equal amounts. The on-column concentrations of all of the compounds were 100ng each. HPLC/UV-Vis run conditions were optimized to give the maximum separation and the shortest analysis time. (See Run Conditions #2). Total analysis time was 8.0 minutes. All compounds were baseline resolved with the exception of prilocaine and lidocaine; They were resolved by approximately 10% (see Table #1). Since they have almost identical retention times, positive identification of each compound becomes very difficult as does accurate quantitation if both compounds are present in the sample.

**Table #1. Cocaine & Adulterant Retention Times.**

**Ultra C18**

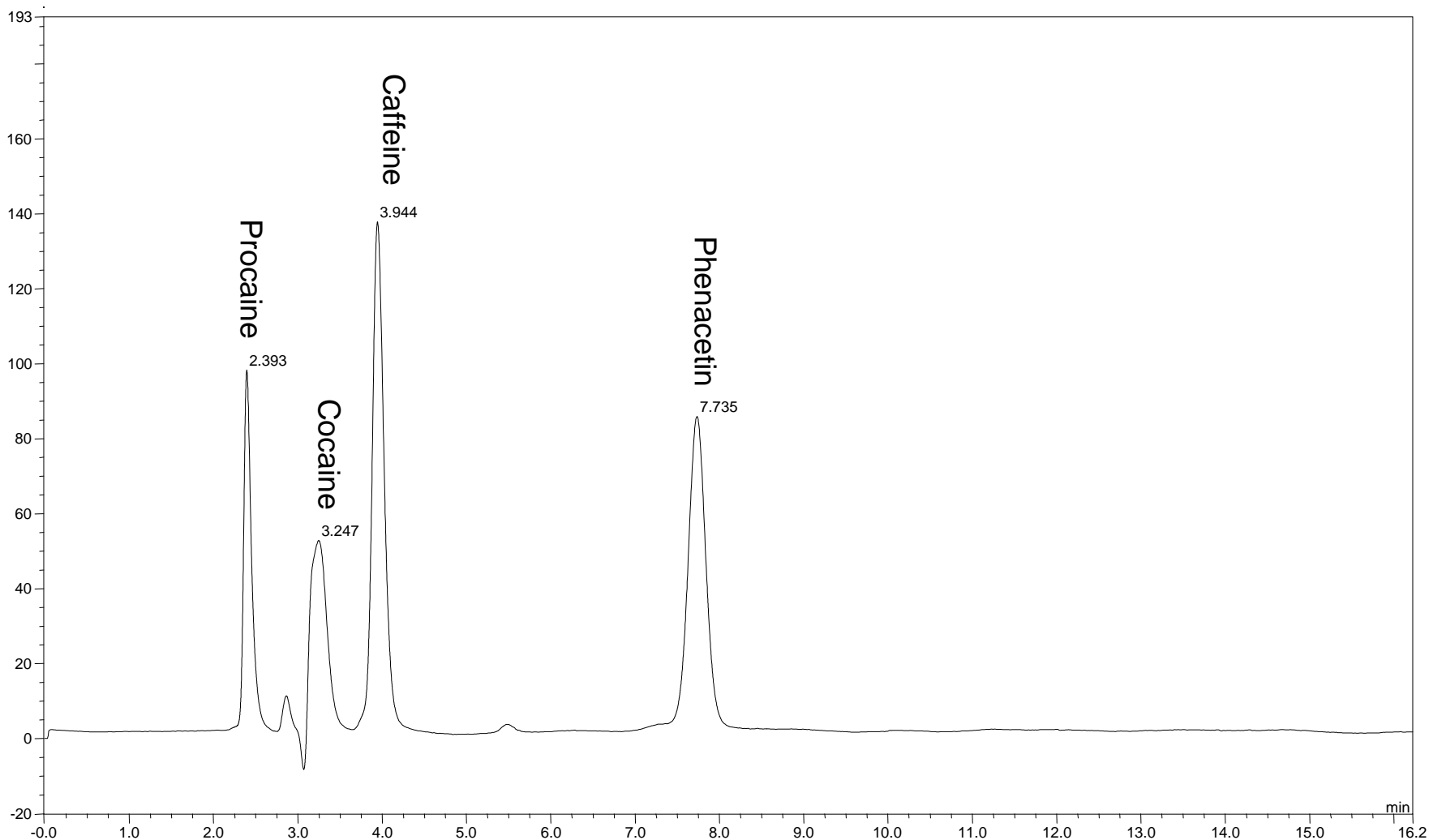
Compound	RT (min.)
Procaine	2.39
Prilocaine	2.75
Lidocaine	2.78
Cocaine	3.25
Caffeine	3.94
Tetracaine	4.63
Phenacetin	7.74
Benzocaine	8.01

Several different HPLC Stationary phases were evaluated to check for improved separation of the prilocaine and lidocaine. Phases such as Allure Basix, Allure C18, Allure PFP, Ultra Cyano, Ultra IBD, Ultra Amino and Pinnacle II Amino showed either no retention of all eight compounds (cocaine and the adulterants) or no separation of the prilocaine and lidocaine.

A mock sample containing 65% cocaine, 16% caffeine, 10% procaine and 10% phenacetin was prepared and analyzed on the Ultra C18 column. The on-column concentrations of the cocaine, caffeine, procaine and phenacetin were 133, 33, 20 and 20ng, respectively. The Ultra C18 stationary phase gave the best retention and the greatest resolution of all of the compounds considered in this study. (See Table #1 and Chromatogram #3). Total analysis time was again 8.0 minutes.

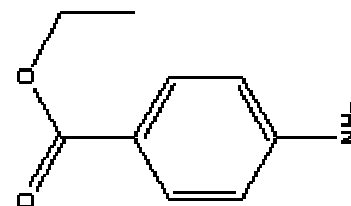
# Cocaine & Adulterants by HPLC/UV-Vis

## Chromatogram #3; Mock Sample at 234nm



# Conclusions

Benzocaine



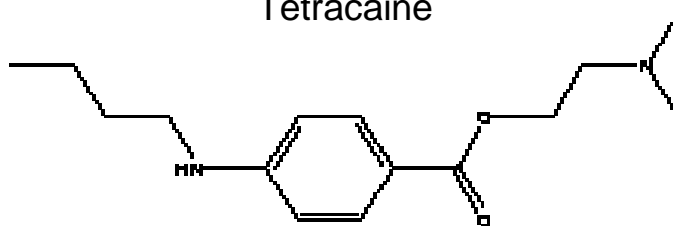
“Fingerprint” identification of mock cocaine samples could be achieved through the identification of the type and number of additives. Since GC/MS provides adequate semiquantitative information regarding the concentration of each additive relative to the cocaine concentration and the most undisputable identification of a substance (both retention time and mass spectrum data), it is the preferred chromatographic method for analyzing cocaine and cocaine adulterants. Sugars, of course, must be analyzed by HPLC using an RI detector.

Future method development work should be conducted in HPLC/MS to allow analysts the flexibility of using either GC/MS or HPLC/MS as their method of choice. Mobile phase and column choice will be critical parameters to optimize for this method.

# References

1. Handbook of Forensic Drug Analysis, Frederick P. Smith, 2005
2. Forensic and Clinical Applications of Solid Phase Extraction, Telepchak, August and Chaney, 2004
3. Determination of Cocaine and Metabolites in Urine Using Electrospray LC/MS by Slawson, Shaw and Hughes, 2000

Tetracaine



# Using Computer Modeling for the Development of Gas Chromatographic Stationary Phases and Columns

Frank L. Dorman, Paul D. Schettler, and  
Chris English

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)





## “Old Days of GC”

- Chromatography has become a “history lesson” rather than a science
- Applications compromised to fit existing columns and stationary phases
- Most phases not designed with any application in mind
- Marketing based on “subtle” differences

# Future of GC

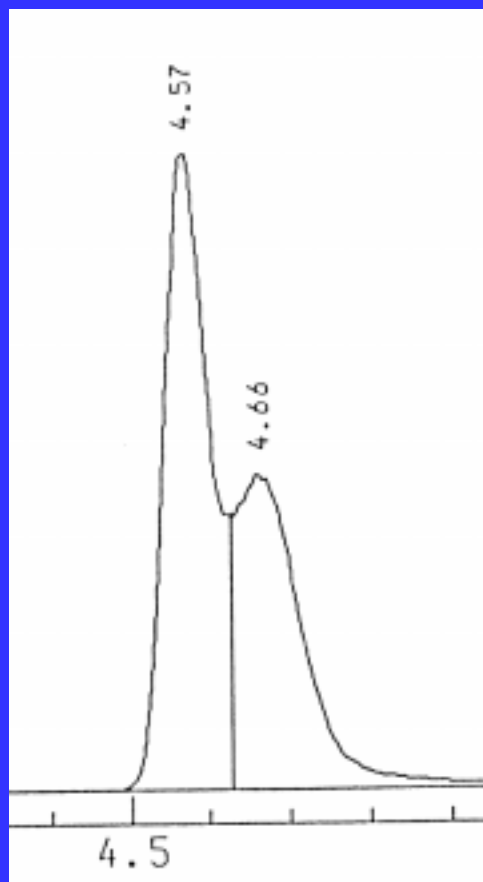
- Columns and stationary phases designed around applications
- Potential for specific phase and column for an individual separation
- Marketing based on real differences
- Requires understanding of analyte-phase interactions
- Can this be done economically?

# Stationary Phase Optimization Techniques

- Window diagramming
- Computer simulation of  $R_t$  and  $W_{1/2}$  (ezGC™)
- Computer prediction of optimized stationary phase composition and column dimensions
- Computer prediction of solute/stationary phase interactions for new polymer designs

# How Resolution Affects Quantitation

## VRX phase



### Results of Resolution Tests @ 20ppb

<i>MeCl<sub>2</sub> &amp; Freon 113</i>	<i>Rep 1</i>	<i>19.85</i>	<i>18.48</i>
	<i>Rep 2</i>	<i>19.29</i>	<i>18.48</i>
	<i>Rep 3</i>	<i>19.36</i>	<i>18.52</i>
<i>Methylene Chloride</i>	<i>Rep 1</i>	<i>21.48</i>	
	<i>Rep 2</i>	<i>20.79</i>	
	<i>Rep 3</i>	<i>20.95</i>	
<i>Freon 113</i>	<i>Rep 1</i>		<i>16.3</i>
	<i>Rep 2</i>		<i>16.46</i>
	<i>Rep 3</i>		<i>16.25</i>

# Equations and Terms

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha - 1 / \alpha)$$

## Capacity Factor

$$k = t_R - t_0 / t_0$$

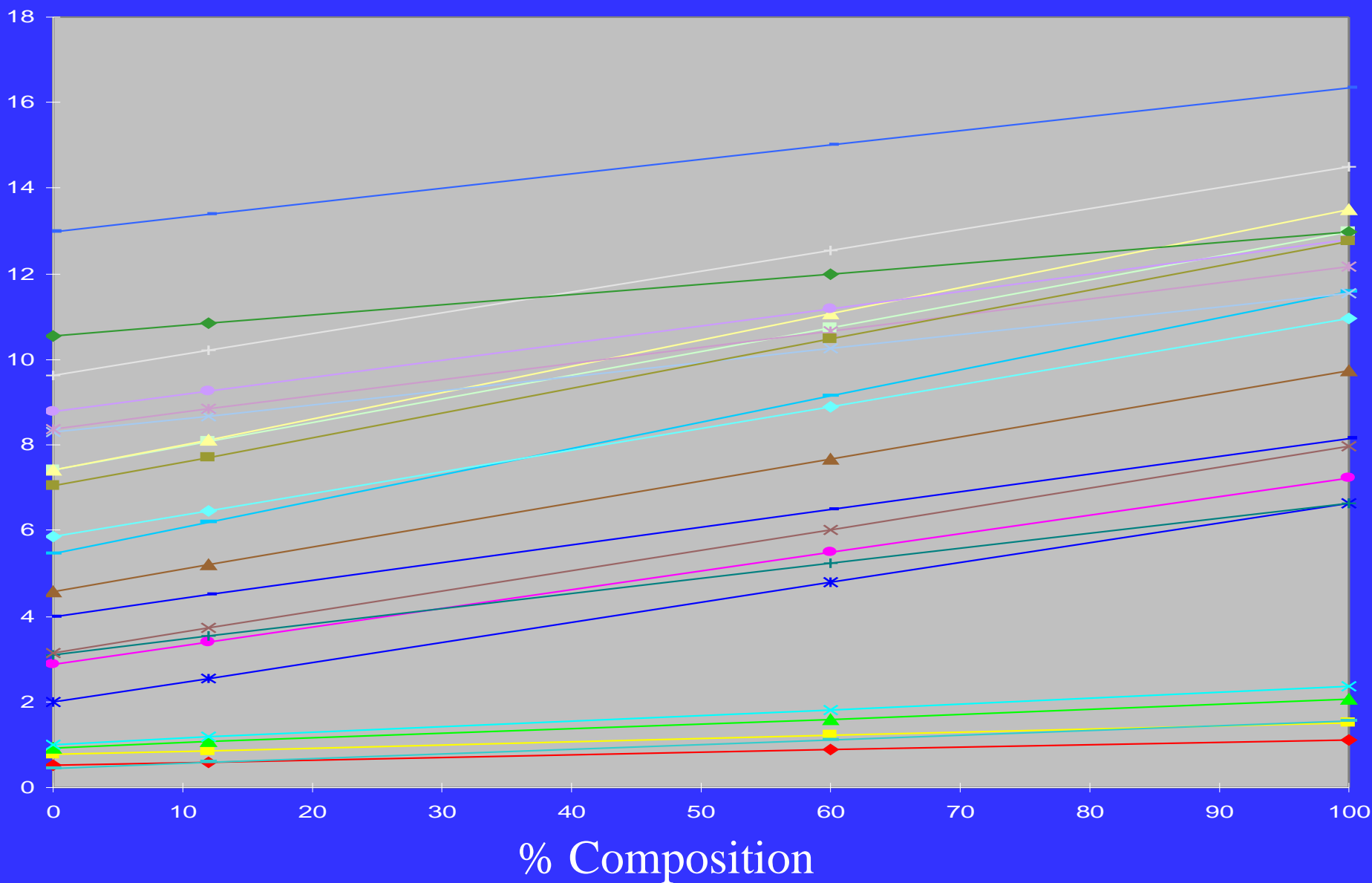
## Selectivity

$$\alpha = k_2 / k_1$$

# Stationary Phase Optimization

- Window diagramming (Rtx-502.2)
- Computer simulation of selectivity, independent of  $R_t$  and  $W_{1/2}$  (ezGC<sup>TM</sup>)
  - Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx-TNT, Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

# “Window Diagram” Model



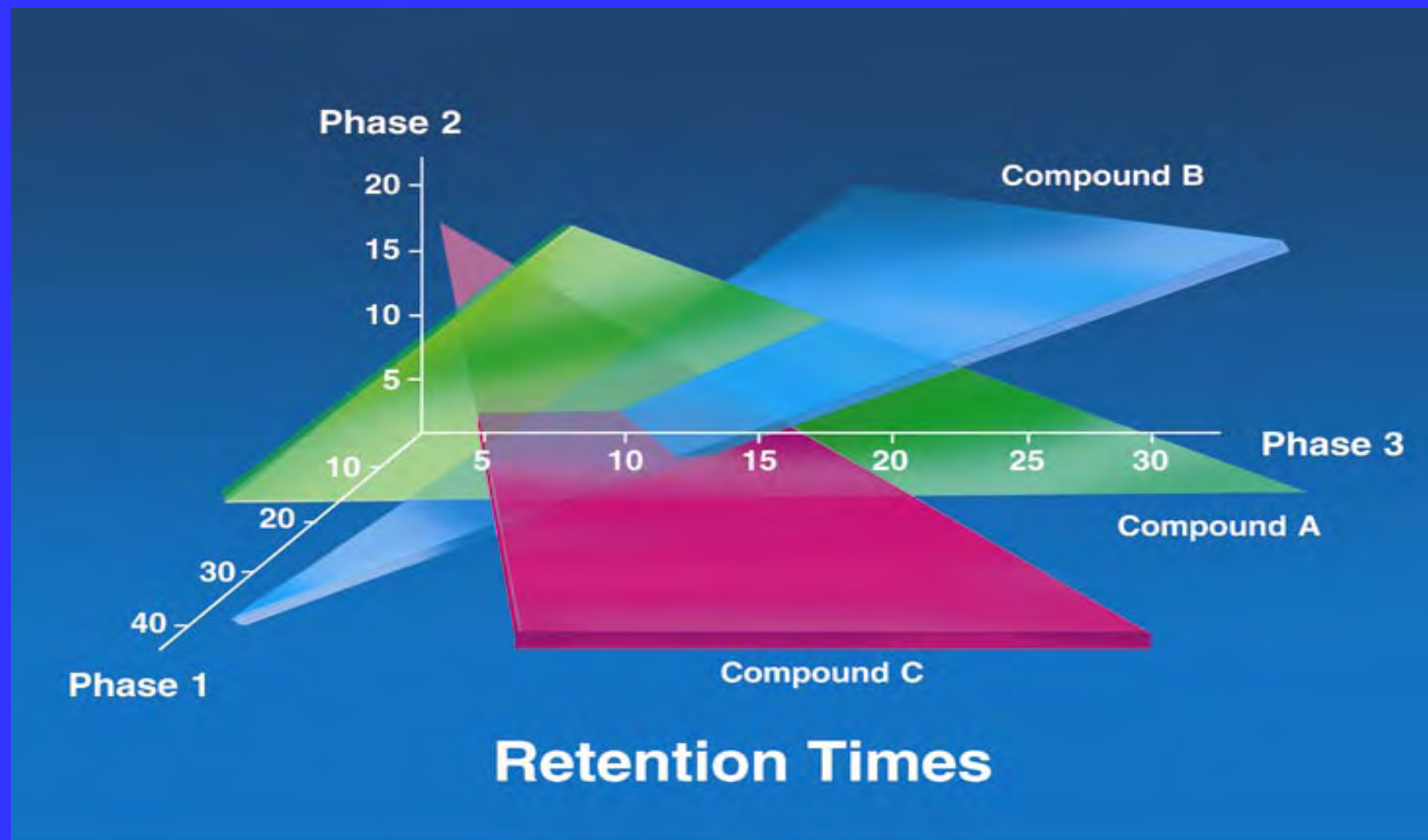
% Composition

# Stationary Phase Optimization

- Window diagramming
- Computer simulation of  $R_t$  and  $W_{1/2}$  (ezGC)
  - Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx®-CLPesticides, Rtx-CLPesticides2, Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs



# 3-Space Selectivity Model for 3 Compounds



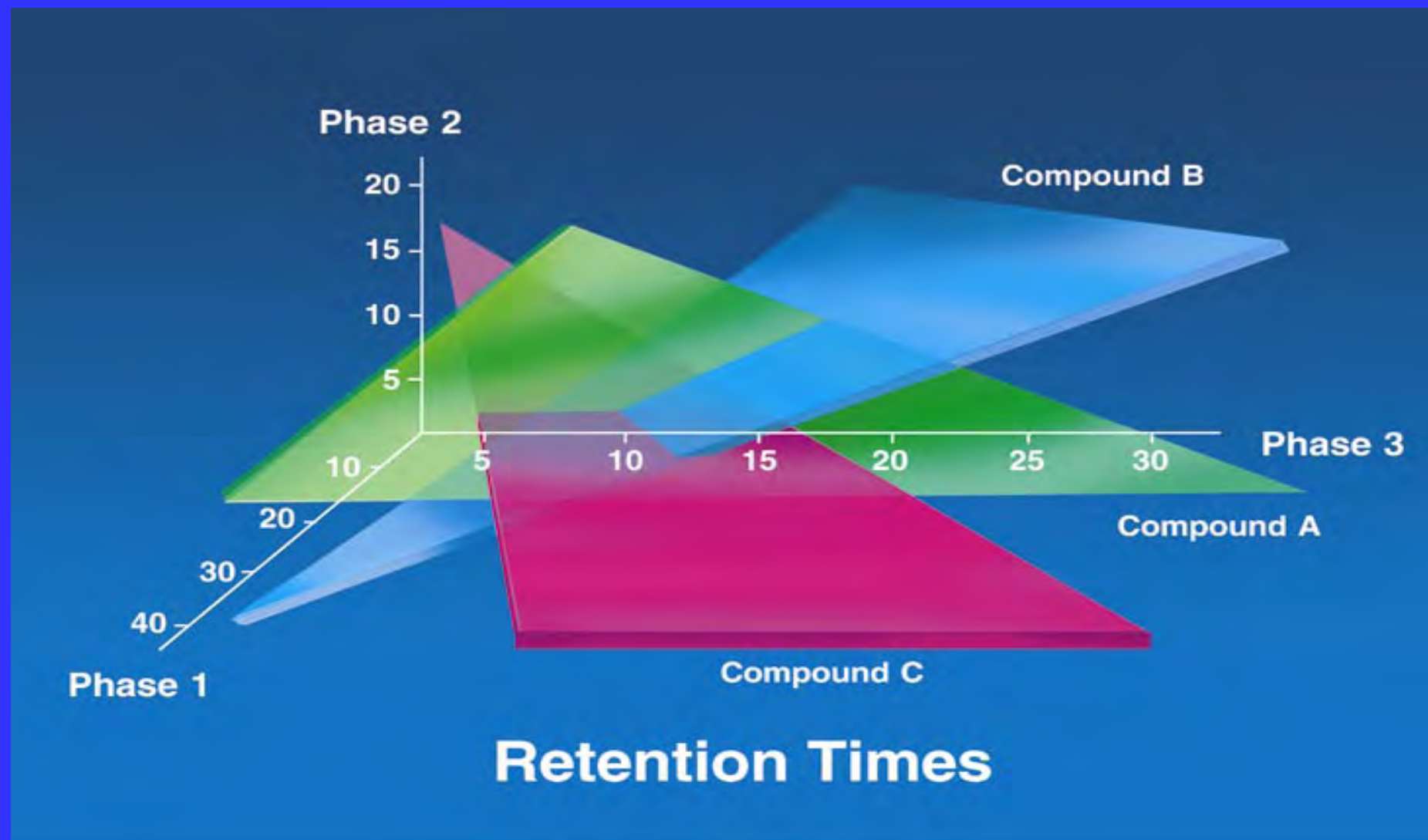
# Stationary Phase Optimization

- Window diagramming
- Computer simulation of  $R_t$  and  $W_{1/2}$  (ezGC)
- Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition AND column dimensions
  - Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX, Rtx-OPPesticides2, Customer-specific columns
- Computer prediction of solute/stationary phase interactions for new polymer designs

# Process for Rtx-OPPesticides2 Column

- Acquire data for target compounds under two temperature programs for functionalities displaying selectivity
- Computer Assisted Stationary Phase Design (CASPD)
  - Calculate  $\Delta H$  and  $\Delta S$  for each compound
  - Working in Retention Index, perform optimization of Selectivity and Dimensions
- Synthesize and coat column

# 3-Space Selectivity Model for 3 Compounds



# Compounds 1 – 25 of 53 OP Pesticides

Target Compound	Predicted Rt	Actual Rt	Difference (min)
dichlorvos	4.08	4.05	-0.03
HMPA	4.70	4.70	0.00
mevinphos	6.43	6.34	-0.09
trichlorfon	6.44	6.43	-0.01
TEPP	8.20	8.40	0.20
demeton-o	8.46	8.52	0.06
thionazin	8.58	8.52	-0.06
TBP	8.60	8.52	-0.08
ethoprop	8.84	8.74	-0.10
naled	9.34	9.32	-0.02
sulfotepp	9.42	9.56	0.14
phorate	9.53	9.56	0.03
dicrotophos	9.61	9.59	-0.02
monocrotophos	9.70	9.62	-0.08
demeton-s	9.80	9.62	-0.18
terbufos	10.44	10.32	-0.12
dimethoate	10.67	10.62	-0.05
dioxathion	10.78	10.77	-0.01
fonophos	10.91	10.79	-0.11
diazinon	10.93	10.90	-0.04
disulfoton	11.13	11.09	-0.03
phosph isomer	11.19	11.16	-0.04
dichlorofenthion	11.38	11.37	-0.01
chlorpyrifos methyl	11.94	12.03	0.09
phosphamidon	12.14	12.03	-0.11



# Individual Custom Column?

- Customer contacted us about custom column for separation of volatile silanes and hydrocarbons
- Customer provided data on Rtx-1 Rtx-35, and Rtx-200 under two different temperature programs
- Data was input to CASPD, and phase was successfully predicted and developed

# CASPD 2.2 Output Table

**Australian Distributors**  
Importers & Manufacturers  
www.chromtech.net.au

**CHROM**alytic +61(0)3 9762 2034  
ECHnology Pty Ltd  
Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034 . . . in AUSTRALIA

	# failures	# rel fails	run time(m	L(m)	d0 (mm)	fd(um)	pi (psig)	po (psia)	td (sec)	T-td(C)	T Prog #	Funct. A	Funct. B
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1847	0.8153
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1845	0.8155
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1843	0.8157
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1843	0.8157
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1841	0.8159
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1841	0.8159
	0	0	31.67	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1839	0.8161
	0	0	31.70	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1550	0.8450
	0	0	31.70	90	0.32	1.8	15	14.7	529.1	35.0	4	0.1550	0.8450
	1	1	31.65	90	0.32	1.8	15	14.7	529.1	35.0	4	0.2102	0.7898
	3	3	31.78	90	0.32	1.8	15	14.7	529.1	35.0	4	0.0659	0.9341

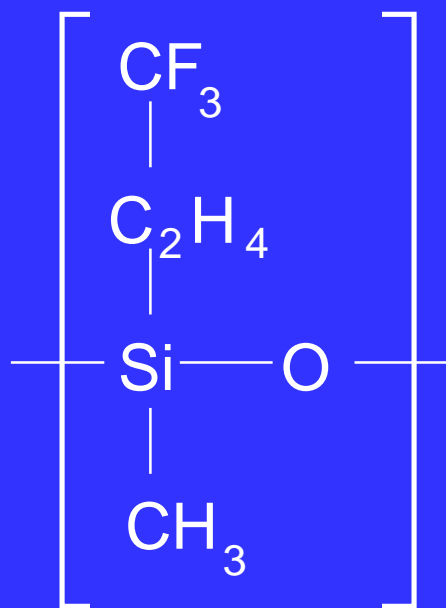
# What If No Selective Functionality Can be Found?

- Accept less than ideal separation
  - Effect on quantitation and/or run time
- Use “old method” of trial and error
  - Slow, and inefficient
  - No guarantee that solution will be found
- Test functionalities electronically
  - Unproven technique
  - CPU intensive
  - Fast

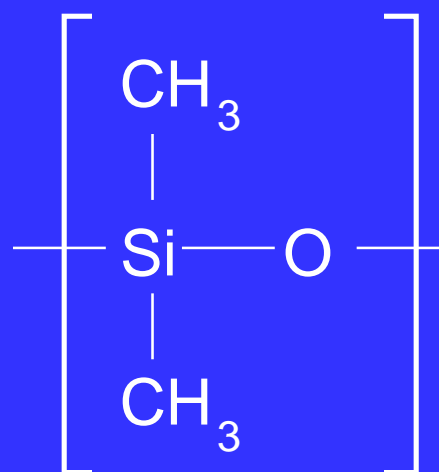


# Conventional Stationary Phases Used for Capillary GC

trifluoropropylmethyl  
polysiloxane

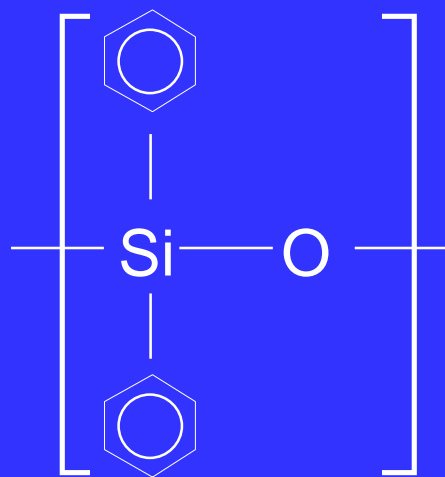


dimethyl  
polysiloxane

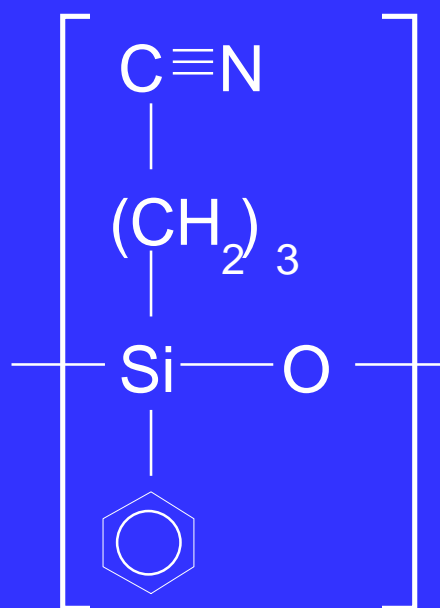


# Conventional Stationary Phases Used for Capillary GC

diphenyl  
polysiloxane



cyanopropylphenyl  
polysiloxane

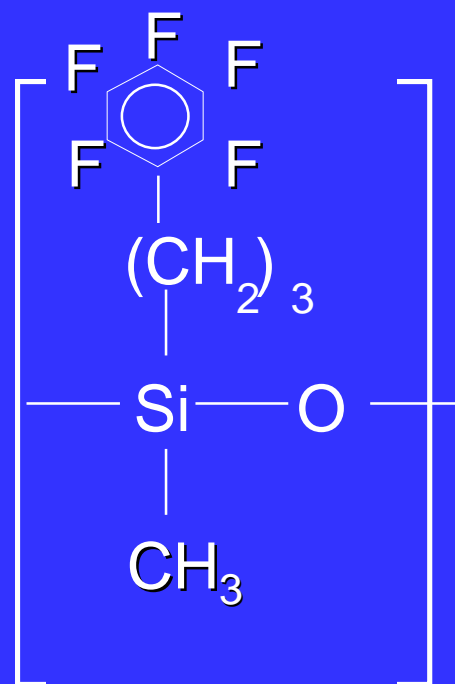


# Alternative Stationary Phases Used for Capillary GC

biphenyl  
polysiloxane

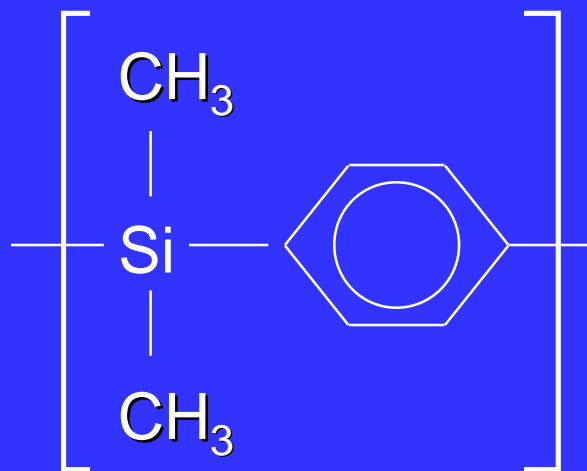


pentafluorophenyl  
polysiloxane

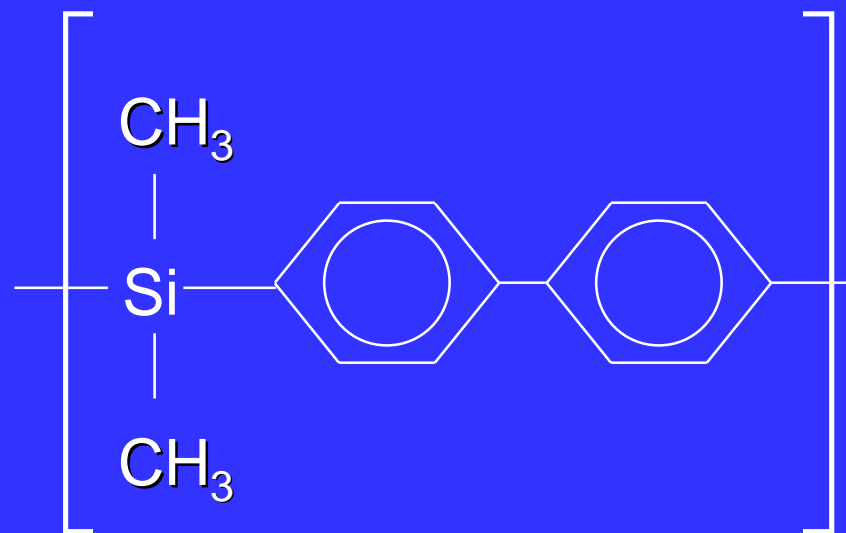


# Alternative Stationary Phases Used for Capillary GC

Silarylene



Silbiarylene



# Stationary Phase Optimization

- Window diagramming
- Computer simulation of  $R_t$  and  $W_{1/2}$  (ezGC)
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx®-CLPesticides Rtx-CLPesticides2, Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

# Achieving Analyte Separation

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha-1 / \alpha)$$

## Capacity Factor

$$k = (t_R - t_0) / t_0$$

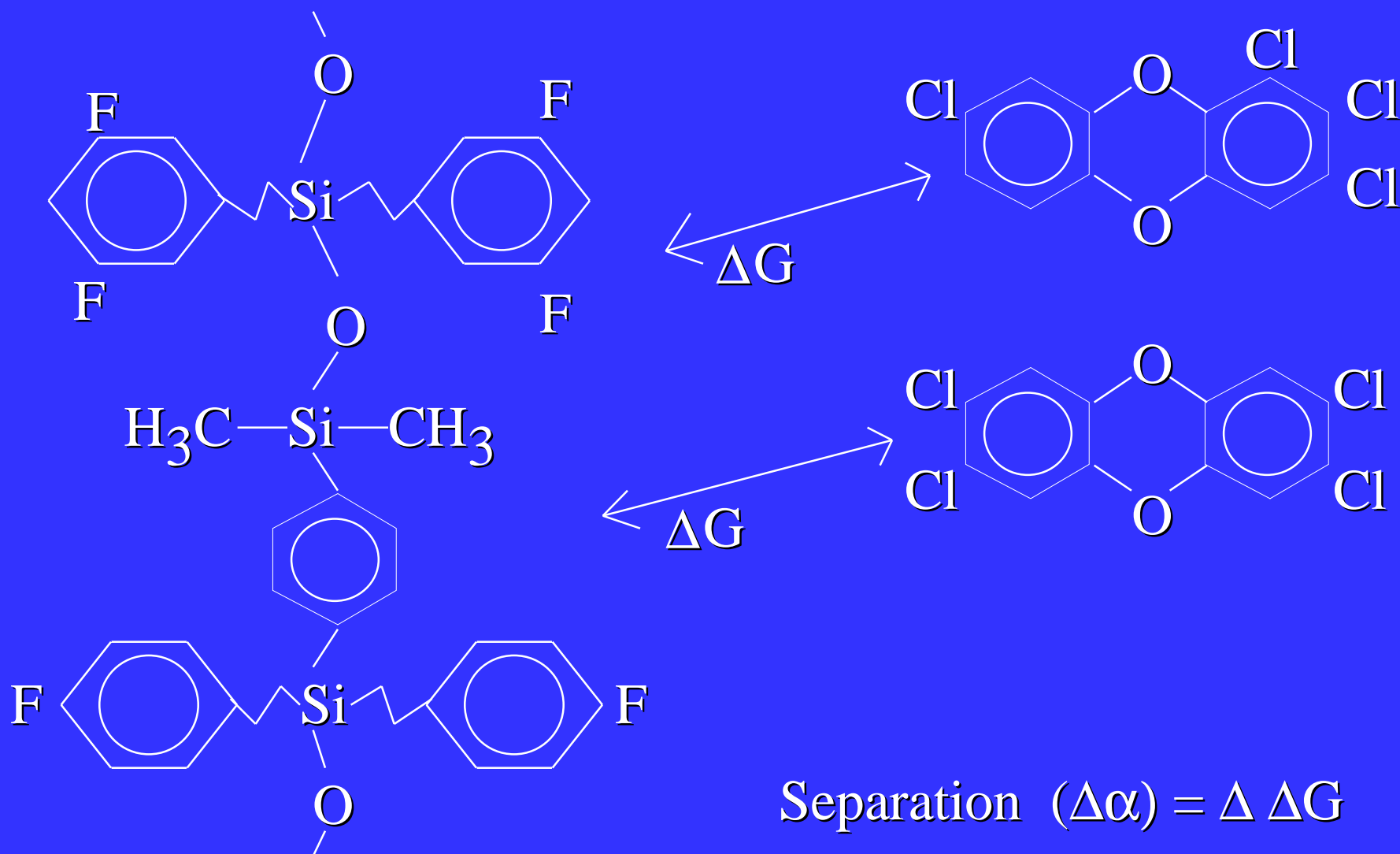
## Selectivity

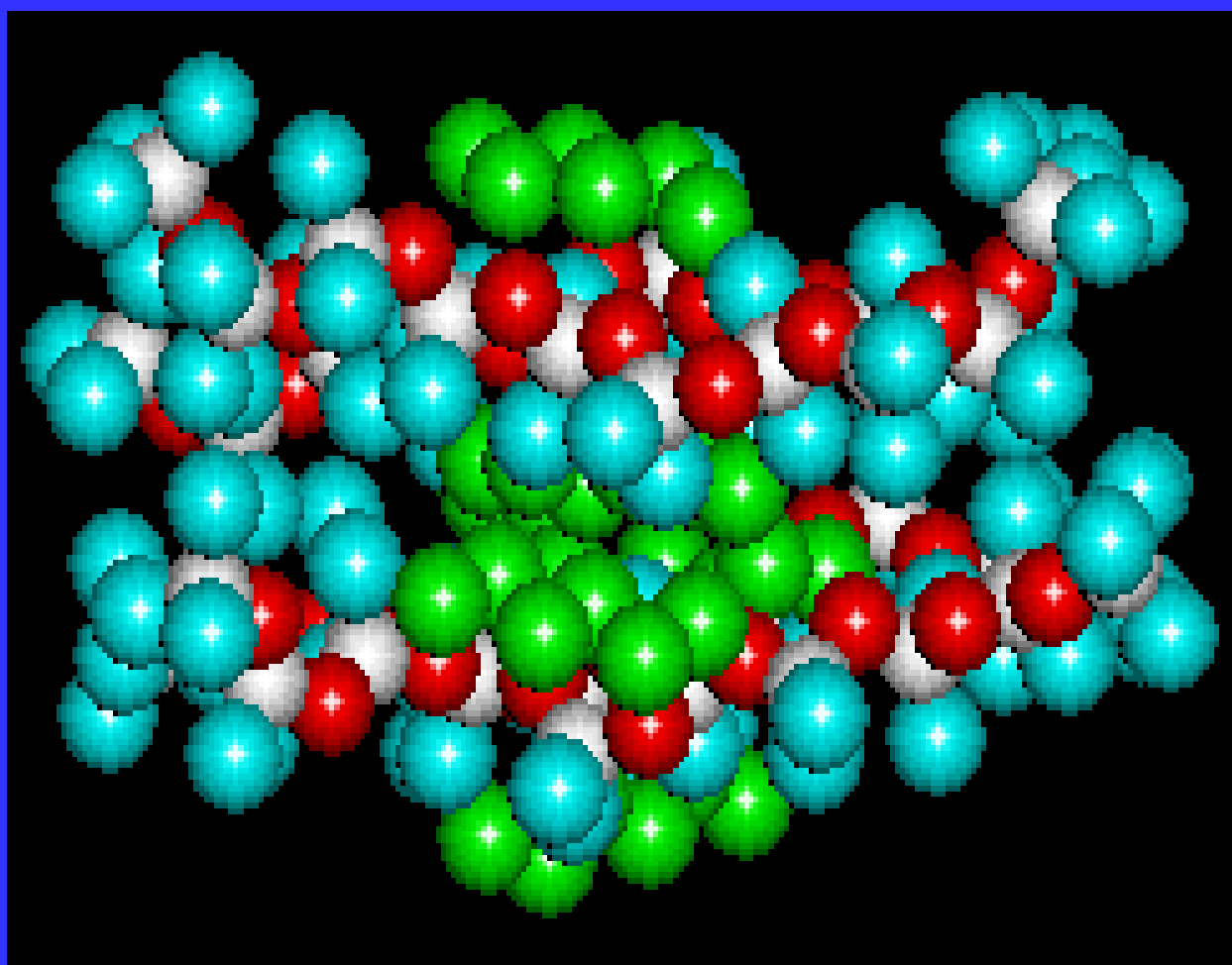
$$\alpha = k_2 / k_1$$

## Thermodynamics:

$$\Delta G = \Delta H - T\Delta S \quad \Delta G = RT \ln K_D$$

# Modeling - Energies of Interaction







# Summary

- Column optimization program complete
- Allowed for 10 new phases over last three years
- Individual customer columns possible:
  - Cost of polymer synthesis (1-5 K\$ typical) – one time fee
  - Custom column cost
- Development of program to electronically “test” possible future functionalities underway

# The Design of High Temperature Capillary Gas Chromatography Columns Based on Polydimethylsiloxane

Jarl Snider, D. J. Hotnisky, Kristi Sellers,  
Dinesh V. Patwardhan Ph. D.

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# Outline

Background

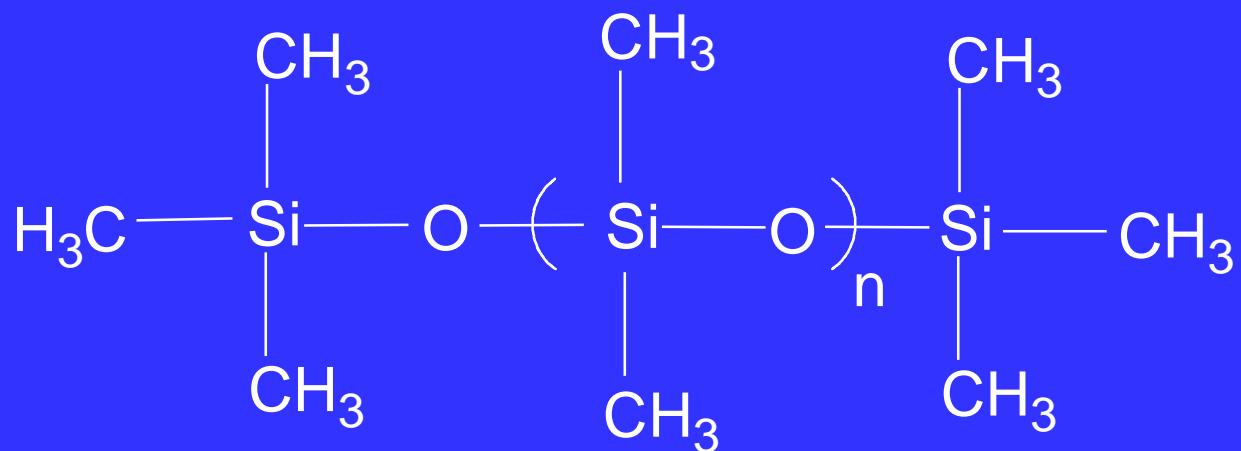
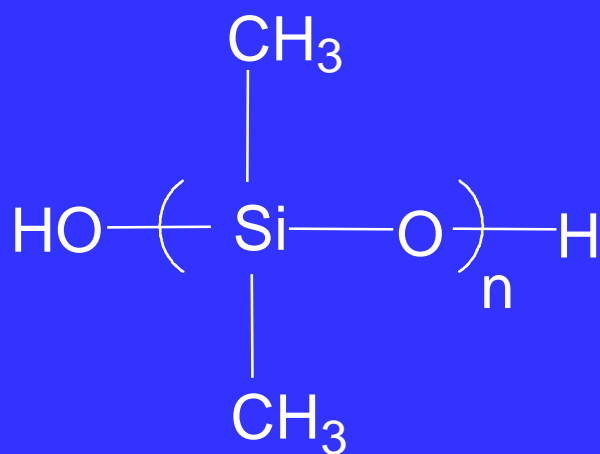
Definition of Terminology

Unique Attributes of High Temperature Column

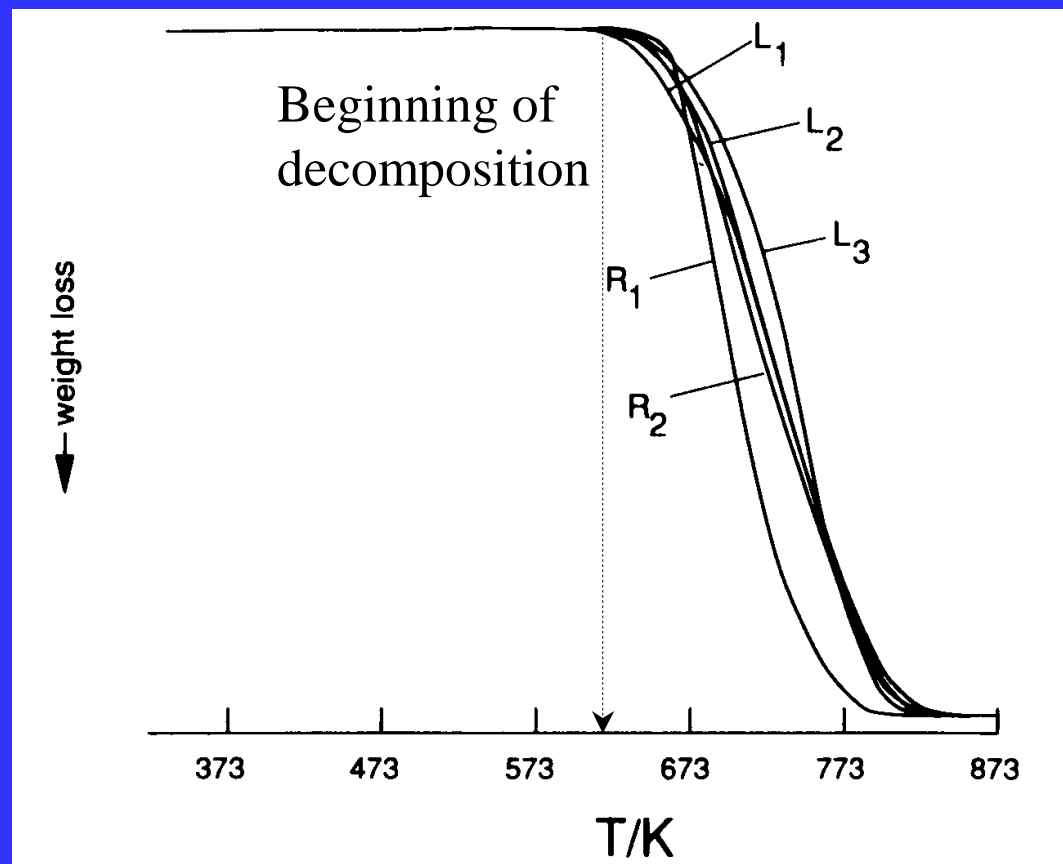
Applications

Conclusions

# Polydimethylsiloxane



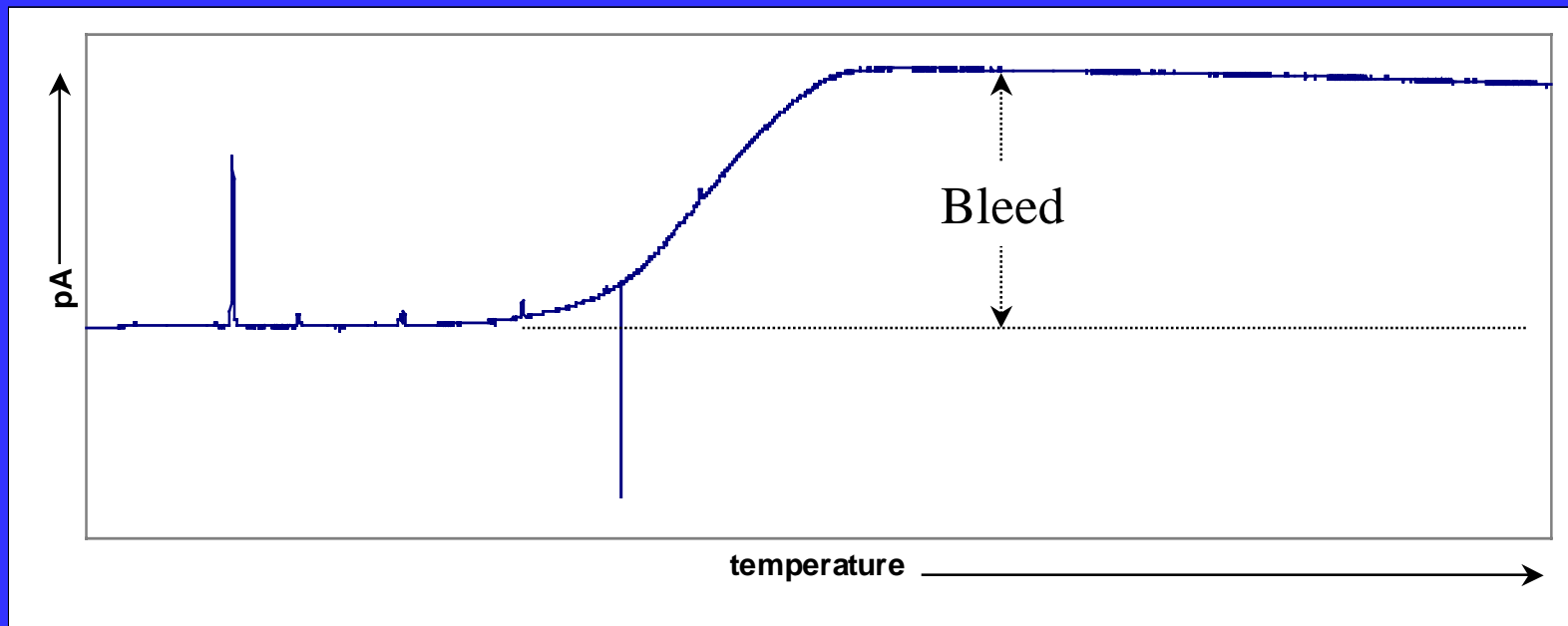
# Thermal Stability of PDMS



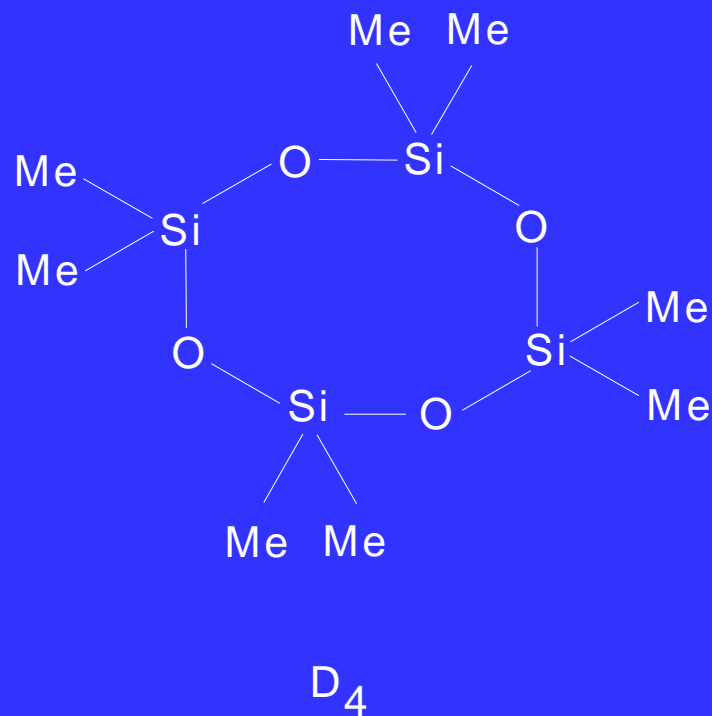
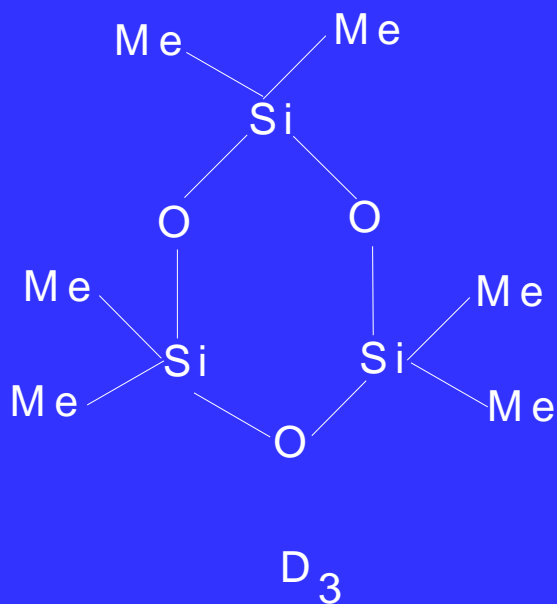
Adapted from Siloxane Polymers, ed. Clarson & Semlyen, 1993.

# Bleed

- Chromatography of “loose” silicones from the column



# Typical Chemical Structure of Bleed



# Challenge

- Since the decomposition temperature for PDMS is 343°C, it is a challenge to make a column that is stable and has low bleed at 380°C.

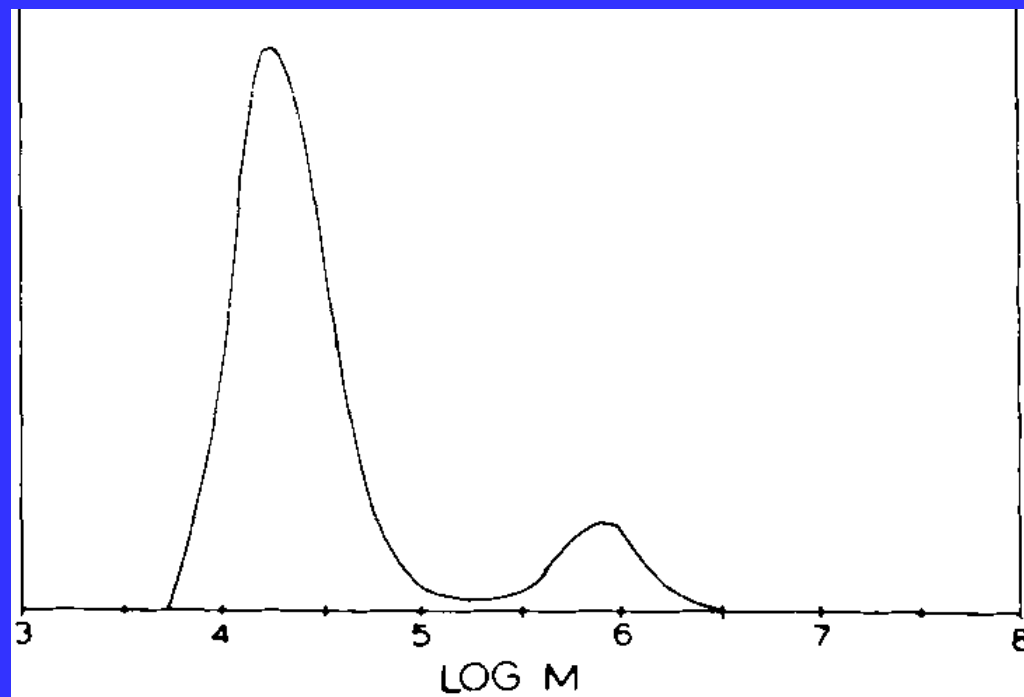


# Origin of Bleed

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

# Origin of Bleed...

- Polymer Synthesis



Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.

# Polymer Synthesis

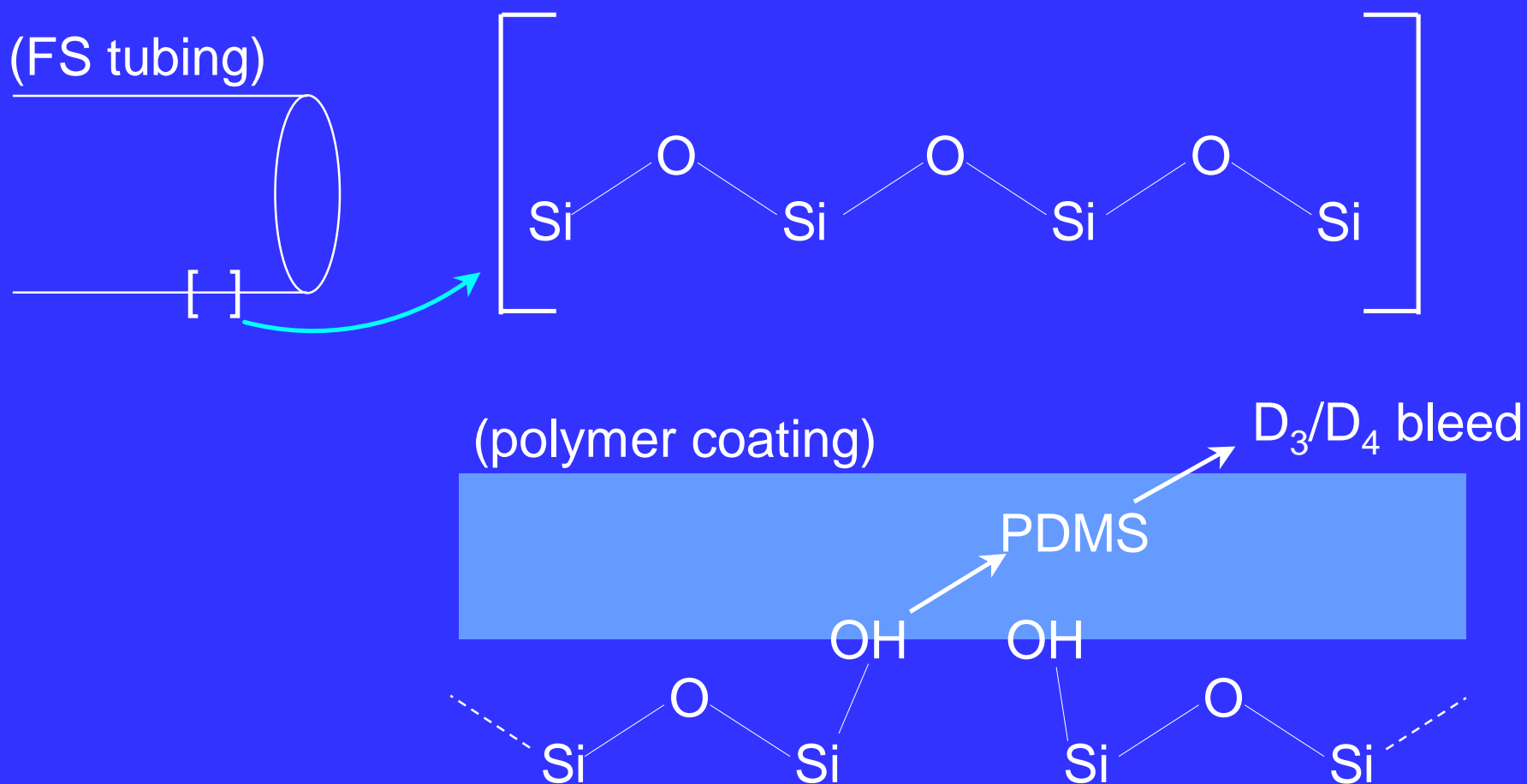
- Silicone Polymers can be synthesized using well known catalysts (KOH, HCl) under equilibration polymerization conditions.
- We use newer, more advanced catalysts, better synthetic techniques.

# Origin of Bleed...

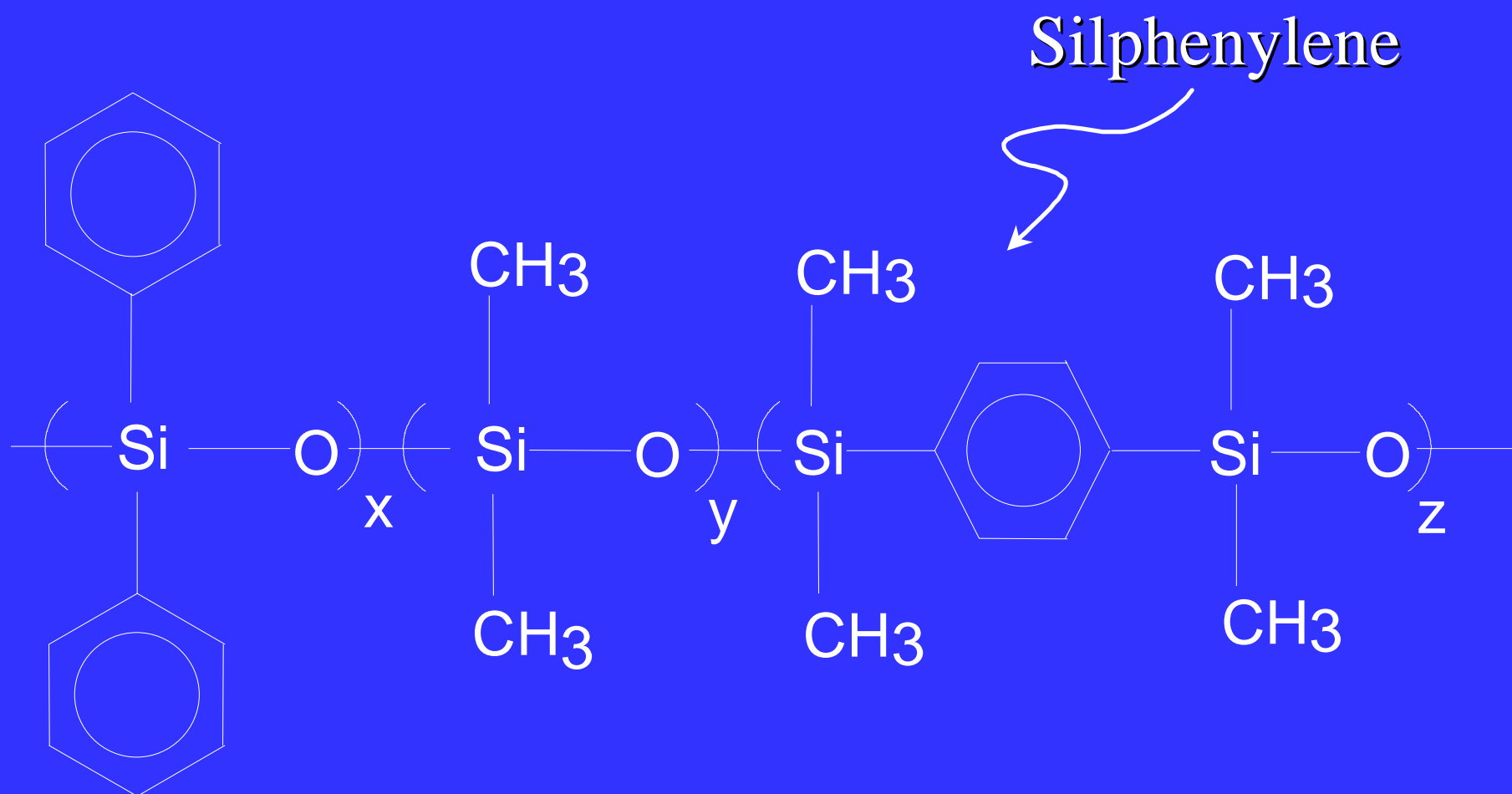
- Polymer Synthesis
- Oligomers that are “created” in a column’s lifetime

# Origin of Bleed...

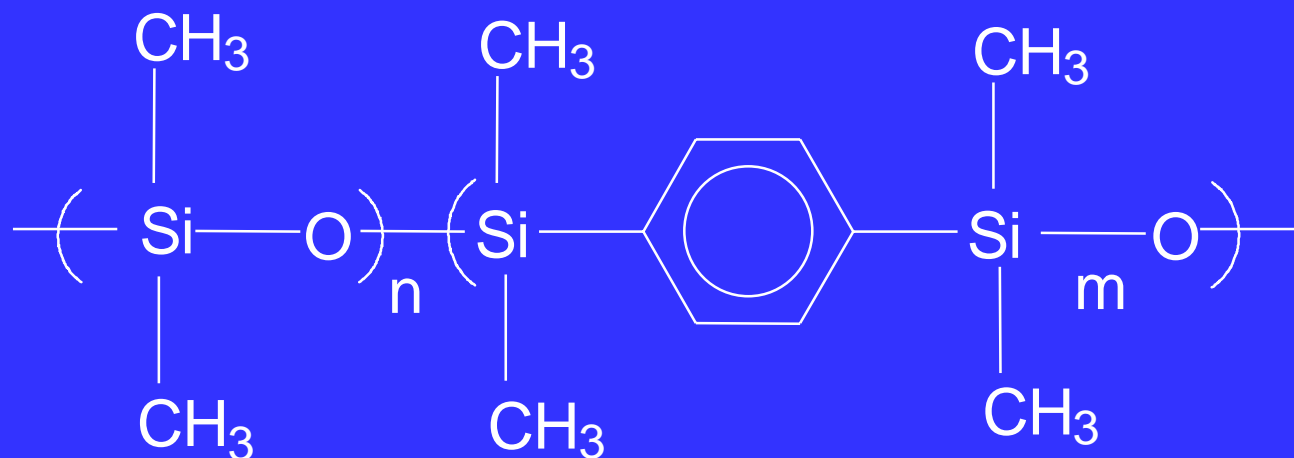
- Oligomers that are “created” in a column’s lifetime



# Enhancement of Thermal Stability by Using “Additives”



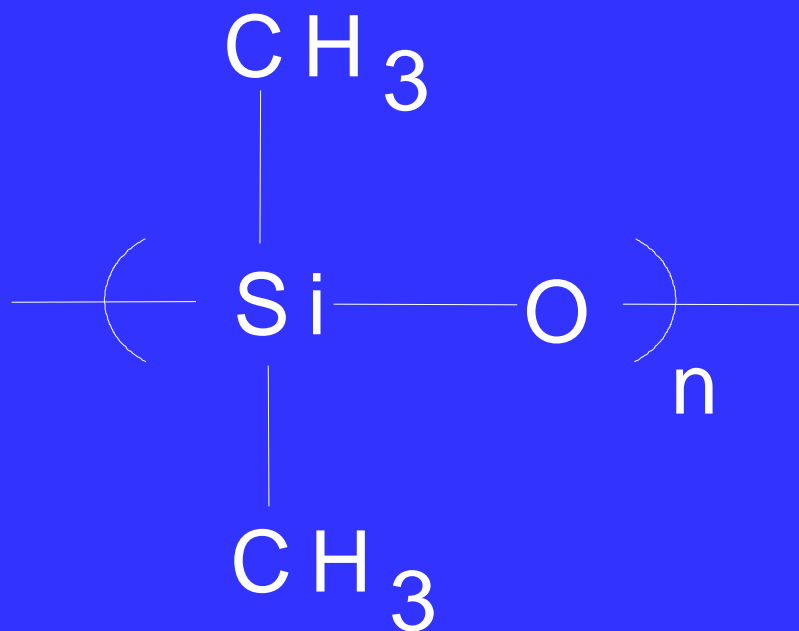
## Additives...



- A column with true “One” selectivity cannot be obtained by having silphenylene in the backbone.

# Stx™-1 HT

- The polymer or the phase is PDMS.

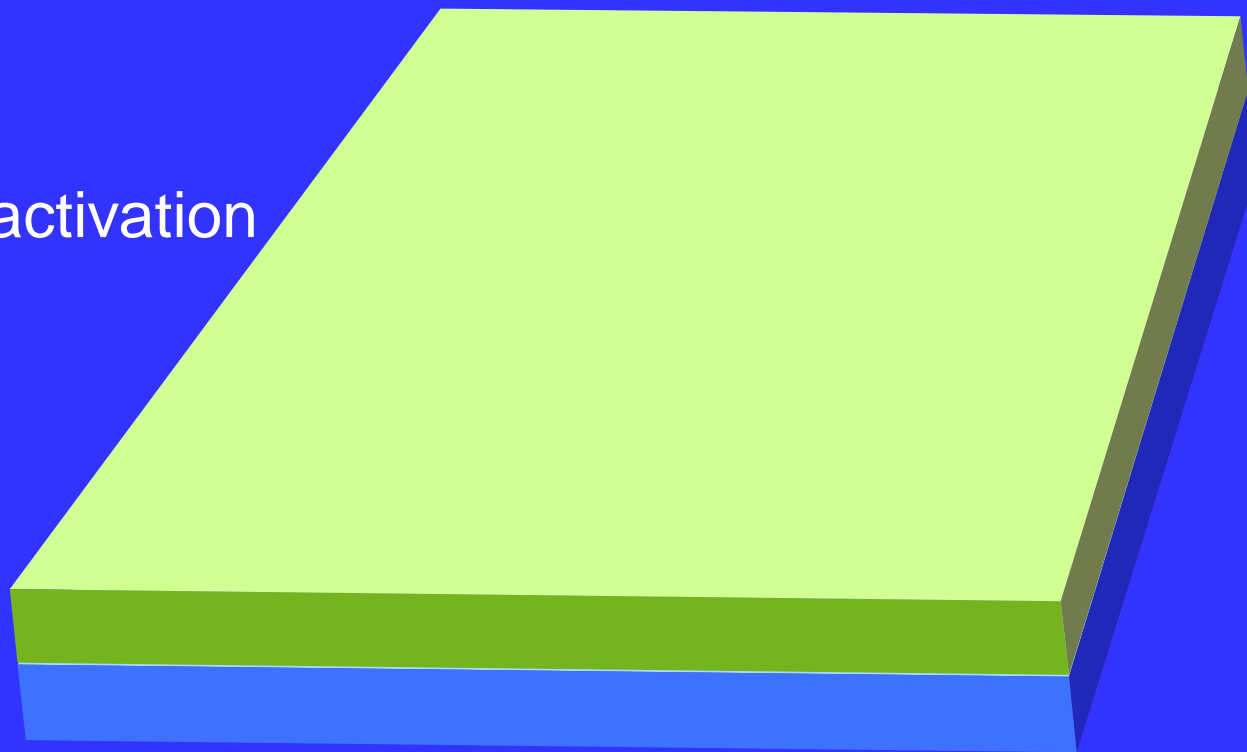




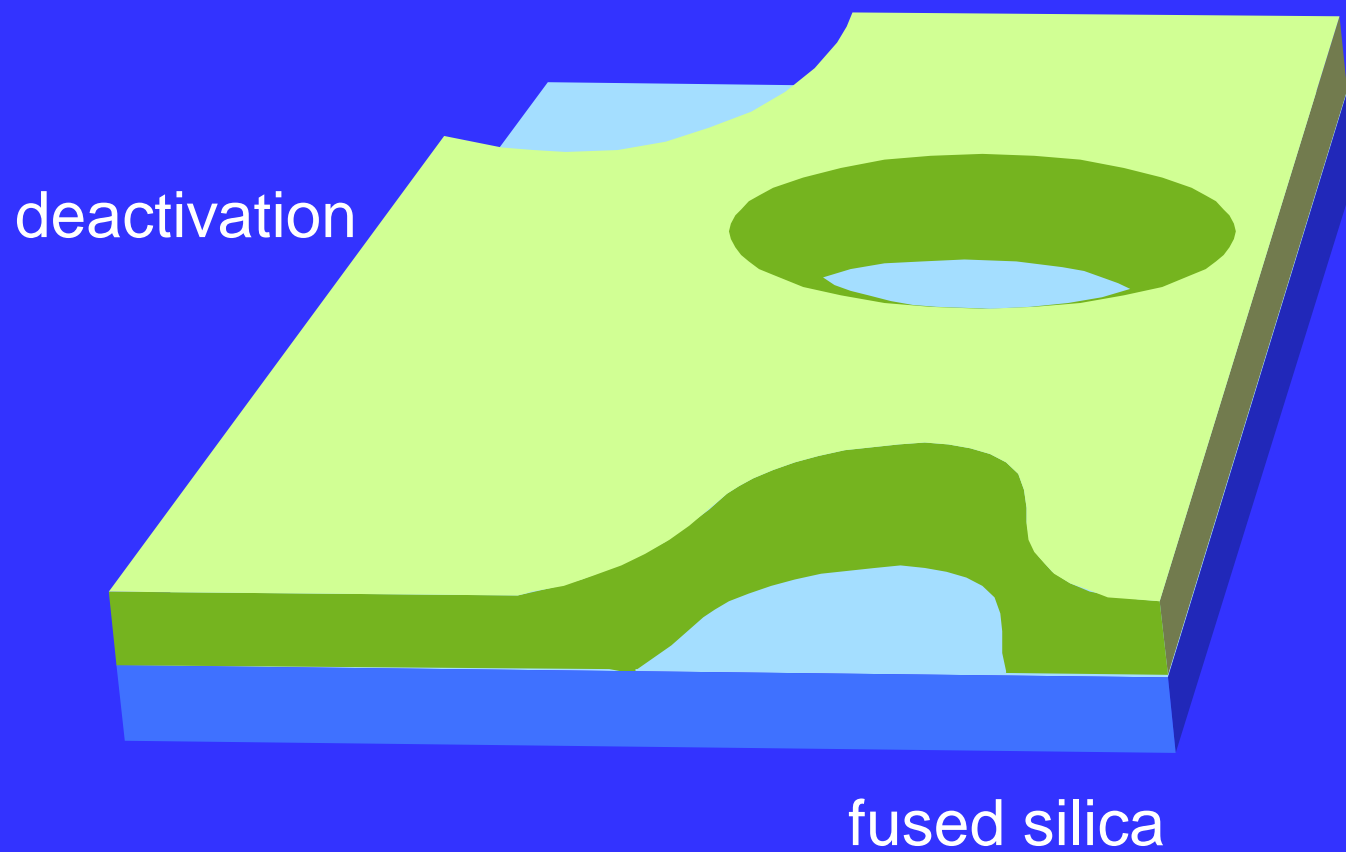
# Origin of Bleed...

deactivation

fused silica



# Origin of Bleed...

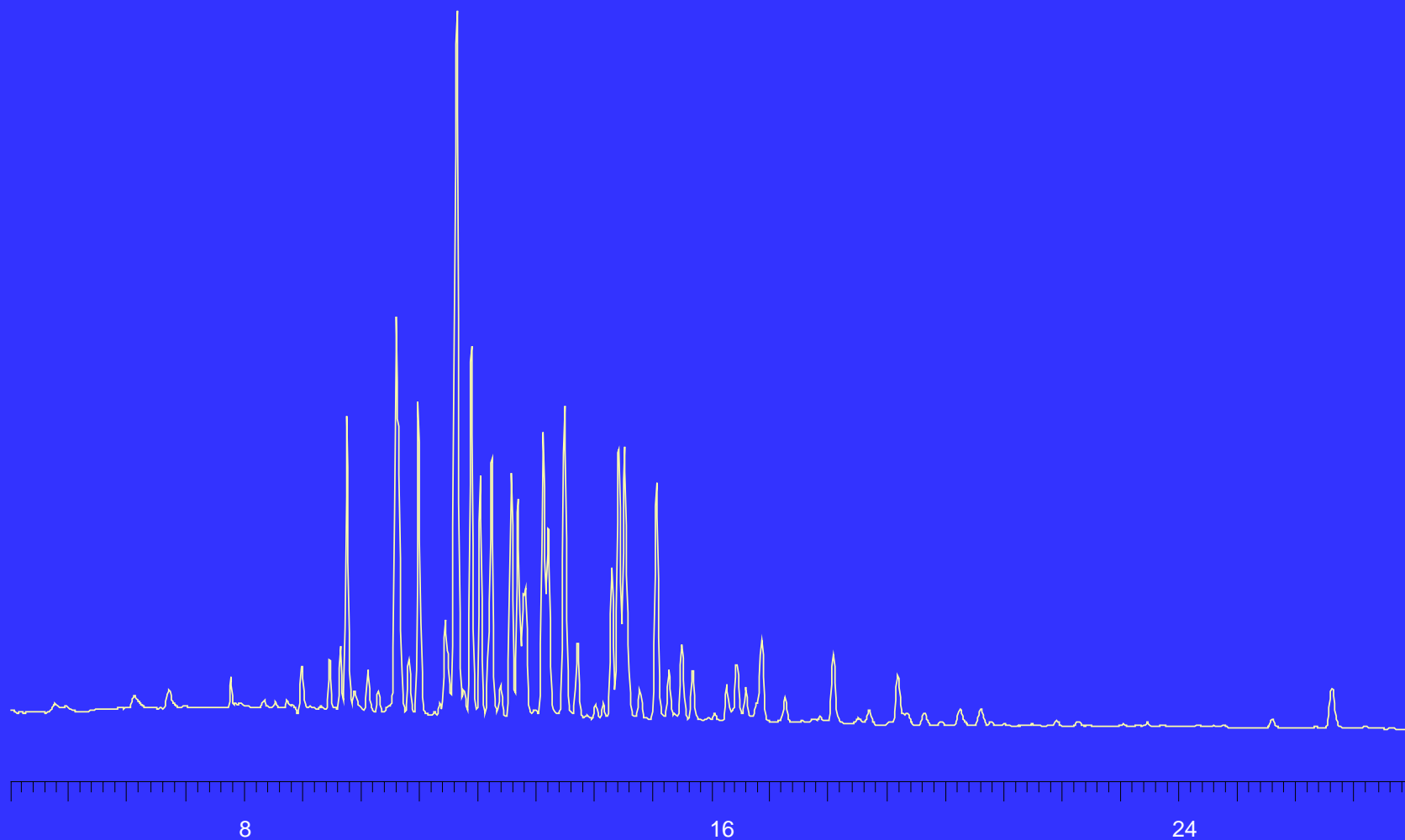


# Deactivation of the Fused Silica Surface

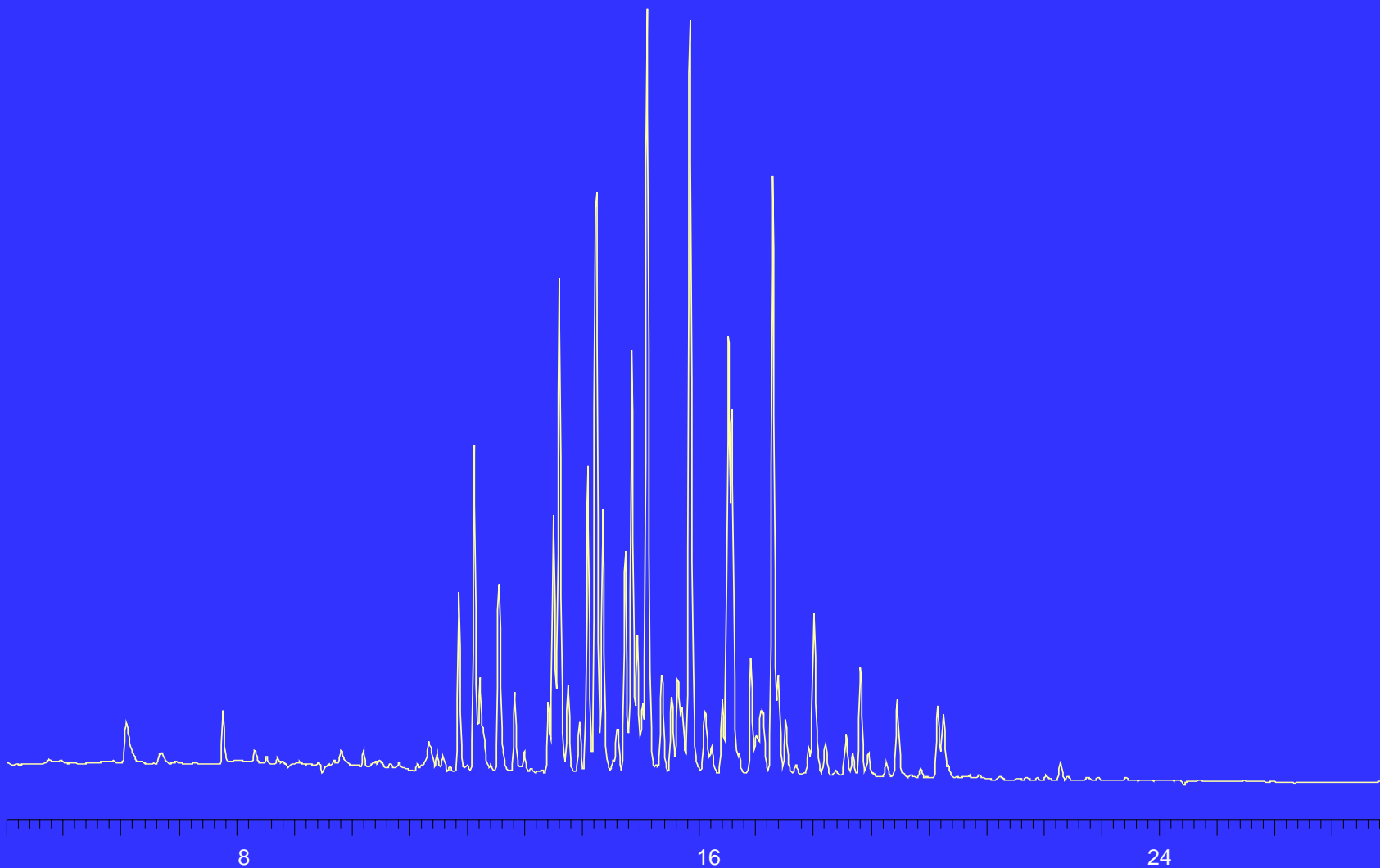
- We are using an advanced deactivation called Siltek™. It is a deposition process, unlike silazane or silicone deactivation.



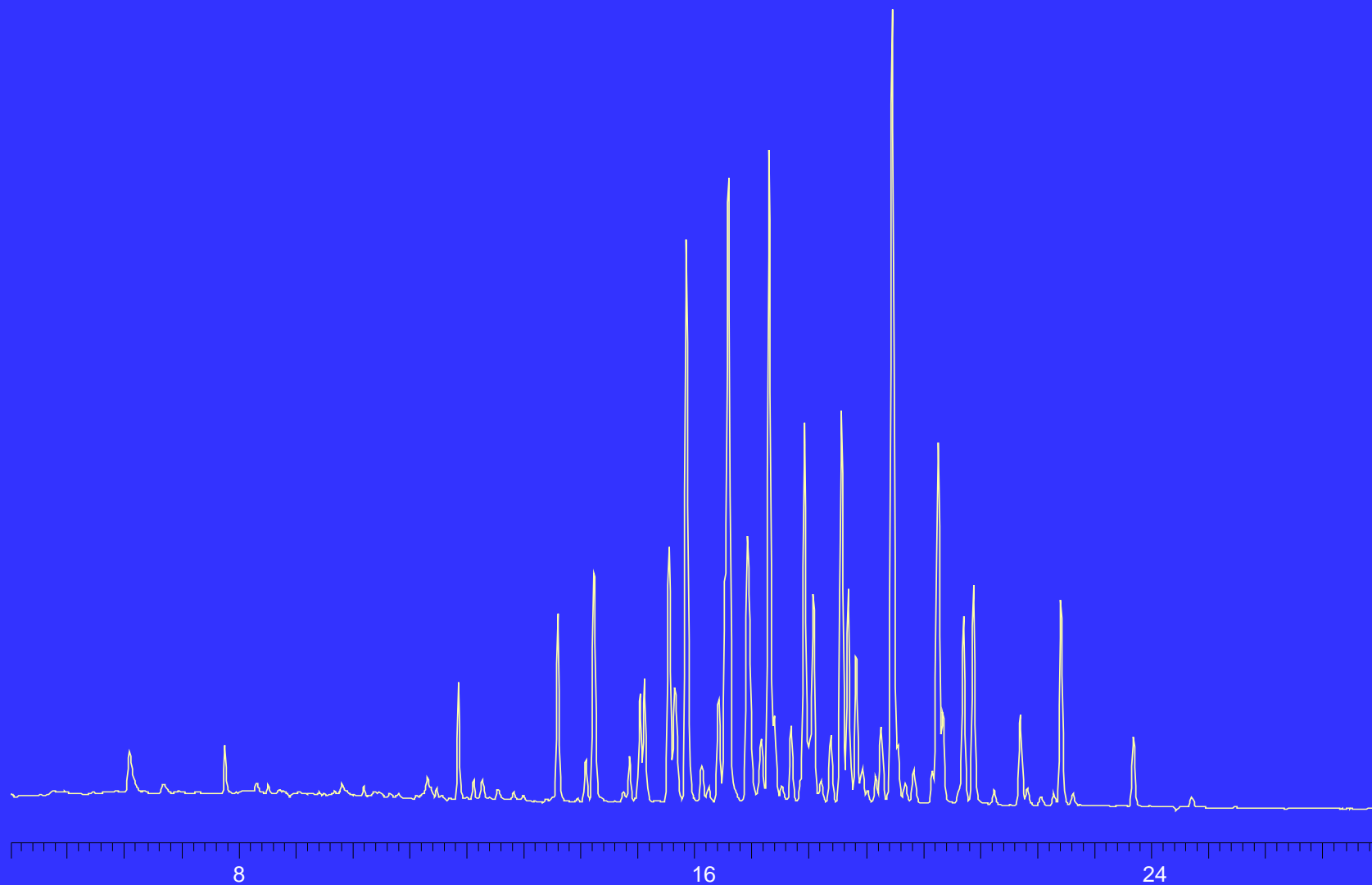
# Aroclor<sup>®</sup> 1242



# Aroclor<sup>®</sup> 1254



# Aroclor<sup>®</sup> 1260



# Aroclor<sup>®</sup> Run Conditions

Column: Stx-HT1  
Serial #: 215041  
Description: 30m, 0.32mmID, 0.10µm  
Sample: Aroclor Solutions  
Part #32009, 32011, 32012

Concentration: 400ppb

Solvent: Hexane  
Sample Size: 1.0µL

Instrument: HP5890  
Injector: Splitless/275°C

Splitless Hold Time: 1.0min.  
Split Vent Flow: 40cc/min.  
Septa Purge: 5cc/min.  
Carrier Gas: Helium  
Head Pressure: 8.5psi  
Column Flow Rate: 1.9cc/min.  
Linear Velocity: 31cm/sec.  
Detector: ECD/310C  
Make up Gas Flow: 40cc/min.  
  
Temp. Program: 75°C(1.0min.) 15°C/min.  
to 150°C(0) 5°C/min.  
300°C(10min.)

# PCB Congeners

Column: Stx-HT1  
Serial #: 215041  
Description: 30m, 0.32mmID, 0.10µm

Sample: PCB Congener Standard #2  
Part #32294

Concentration: 100ng  
Solvent: Iso-Octane  
Sample Size: 1.0µL

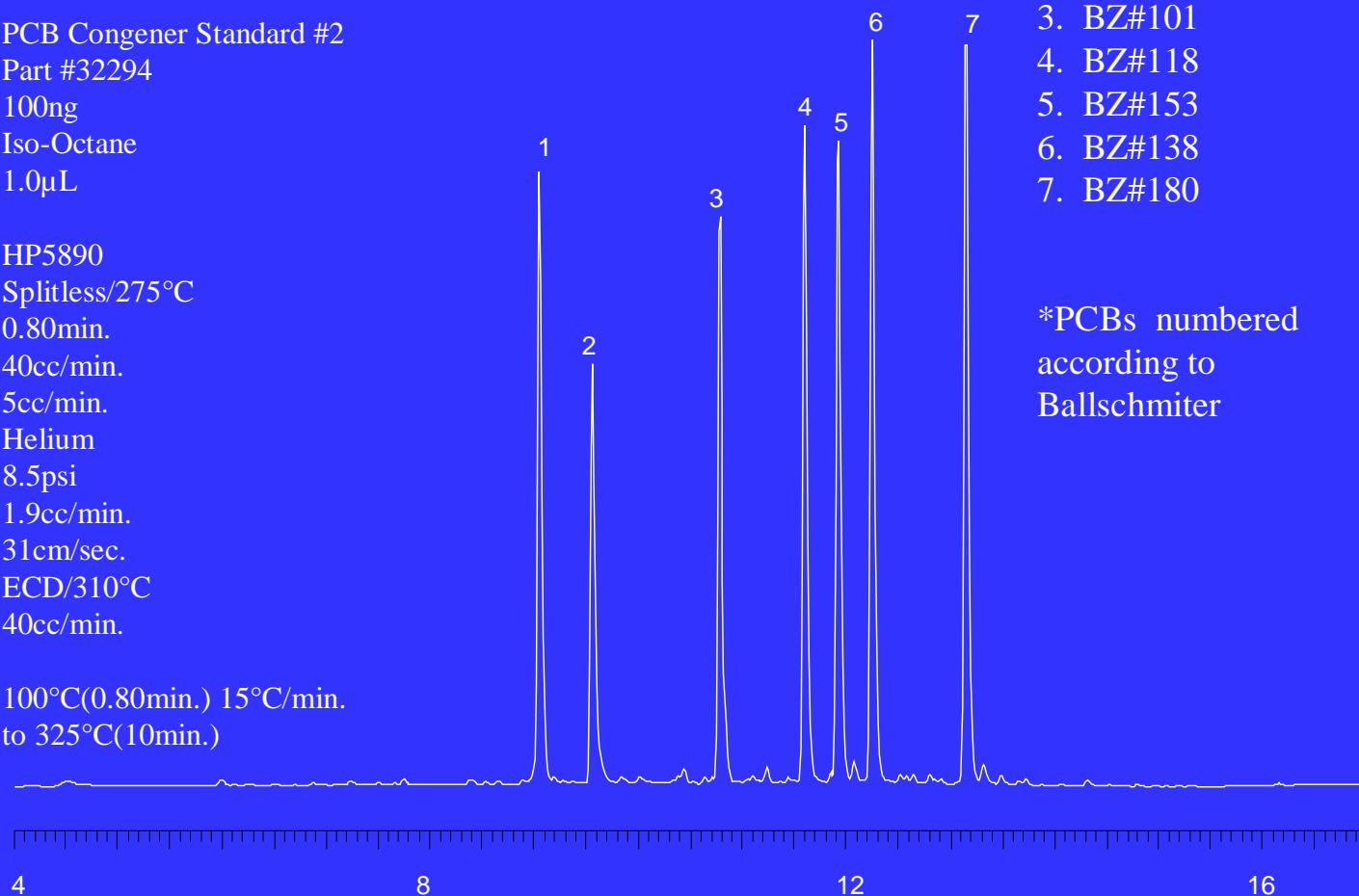
Instrument: HP5890  
Injector: Splitless/275°C  
Splitless Hold Time: 0.80min.  
Split Vent Flow: 40cc/min.  
Septa Purge: 5cc/min.  
Carrier Gas: Helium  
Head Pressure: 8.5psi  
Column Flow Rate: 1.9cc/min.  
Linear Velocity: 31cm/sec.  
Detector: ECD/310°C  
Make up Gas Flow: 40cc/min.

Temp. Program: 100°C(0.80min.) 15°C/min.  
to 325°C(10min.)

Elution Order:

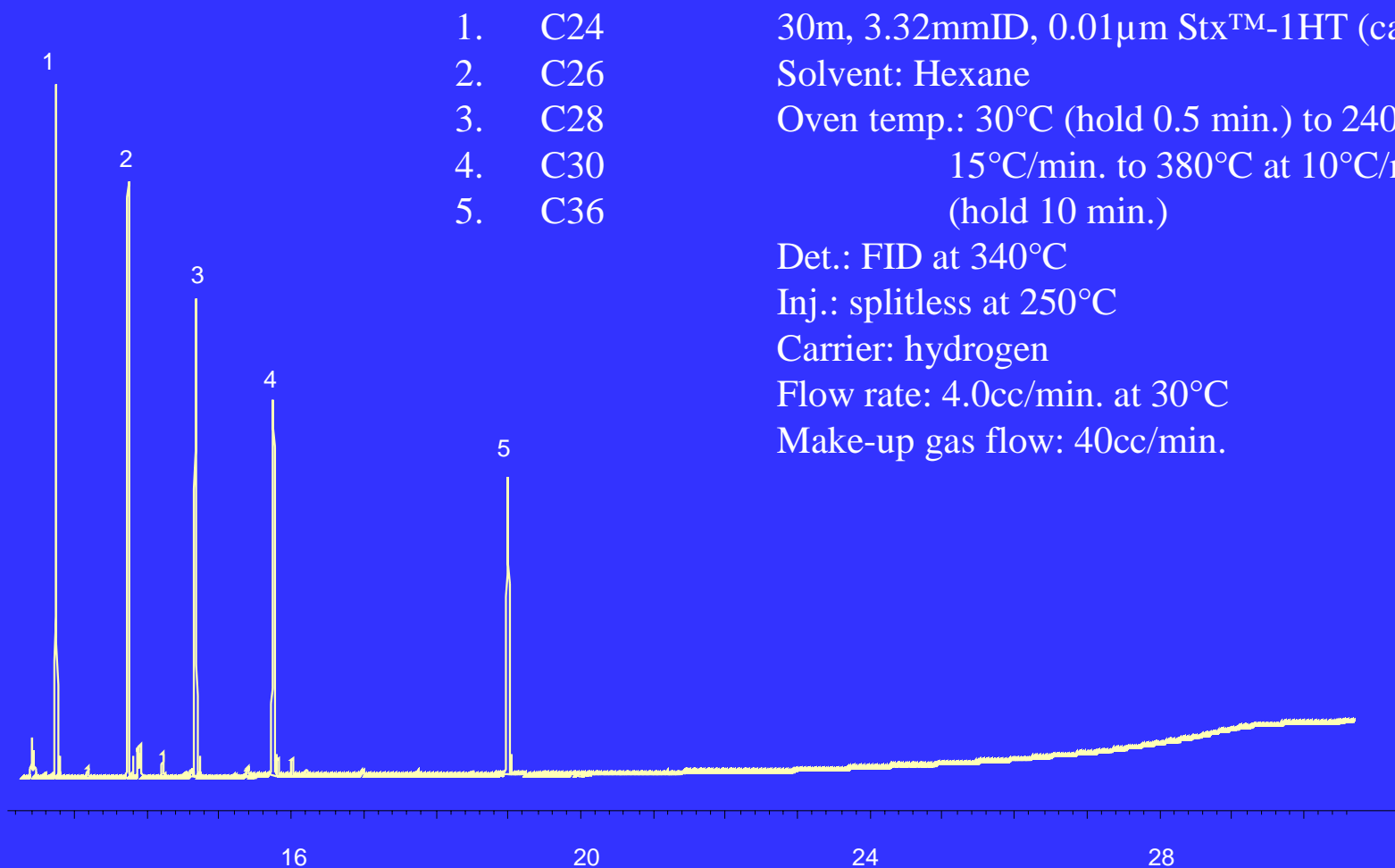
1. BZ#28
2. BZ#52
3. BZ#101
4. BZ#118
5. BZ#153
6. BZ#138
7. BZ#180

\*PCBs numbered  
according to  
Ballschmiter

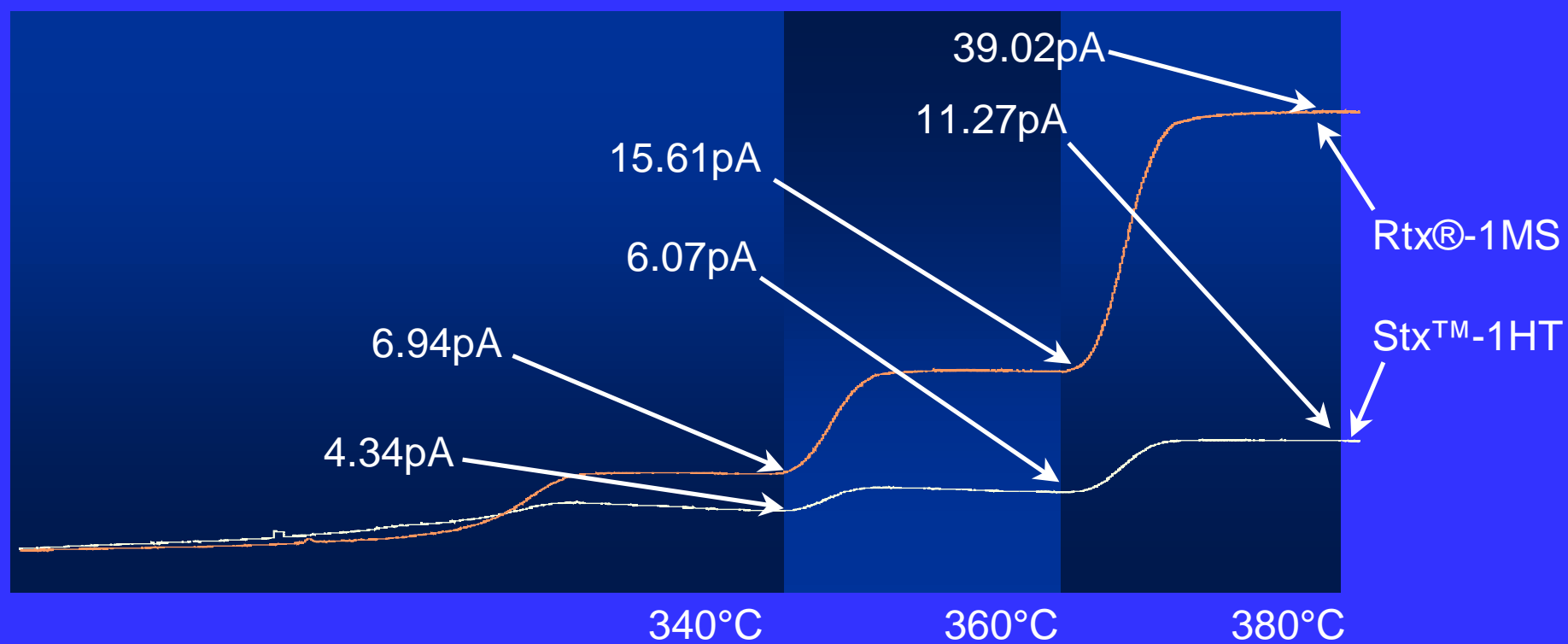




# 10ppm Aliphatics



# Bleed Comparison



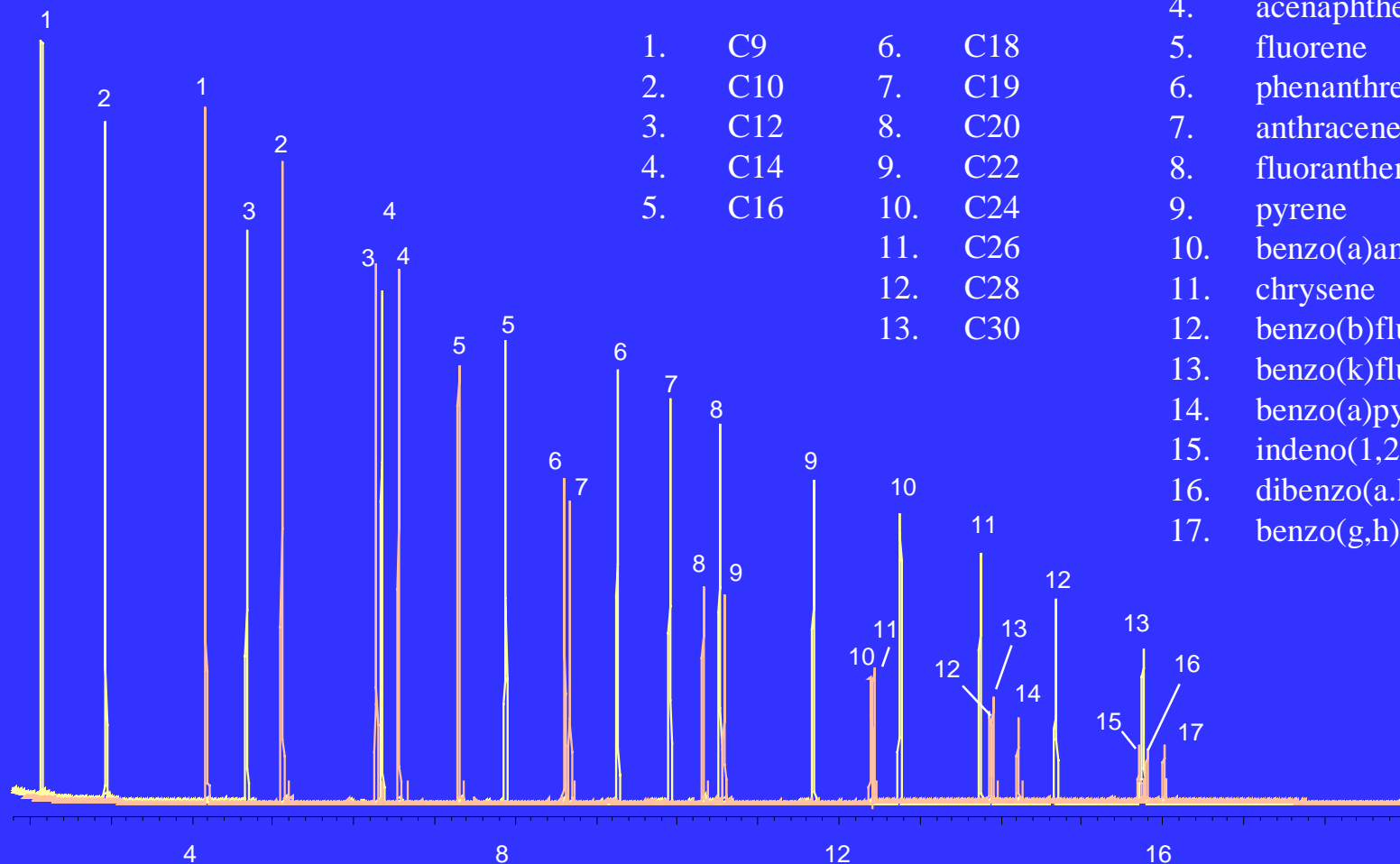
# 50ppm Hydrocarbons

## Aromatic Hydrocarbons:

1. naphthalene
2. 2-methylnaphthalene
3. acenaphthylene
4. acenaphthene
5. fluorene
6. phenanthrene
7. anthracene
8. fluoranthene
9. pyrene
10. benzo(a)anthracene
11. chrysene
12. benzo(b)fluoranthene
13. benzo(k)fluoranthene
14. benzo(a)pyrene
15. indeno(1,2,3-cd)pyrene
16. dibenzo(a,h)anthracene
17. benzo(g,h)perylene

## Aliphatic hydrocarbons:

- |        |         |
|--------|---------|
| 1. C9  | 6. C18  |
| 2. C10 | 7. C19  |
| 3. C12 | 8. C20  |
| 4. C14 | 9. C22  |
| 5. C16 | 10. C24 |
|        | 11. C26 |
|        | 12. C28 |
|        | 13. C30 |



# Analysis Conditions

30m, 3.32mmID, 0.01 $\mu$ m Stx™-1HT (cat.# 11709)

Oven temp.: 30°C (hold 0.5 min.) to 240°C at  
15°C/min. to 380°C at 10°C/min.  
(hold 10 min.)

Det.: FID at 340°C

Inj.: splitless at 250°C

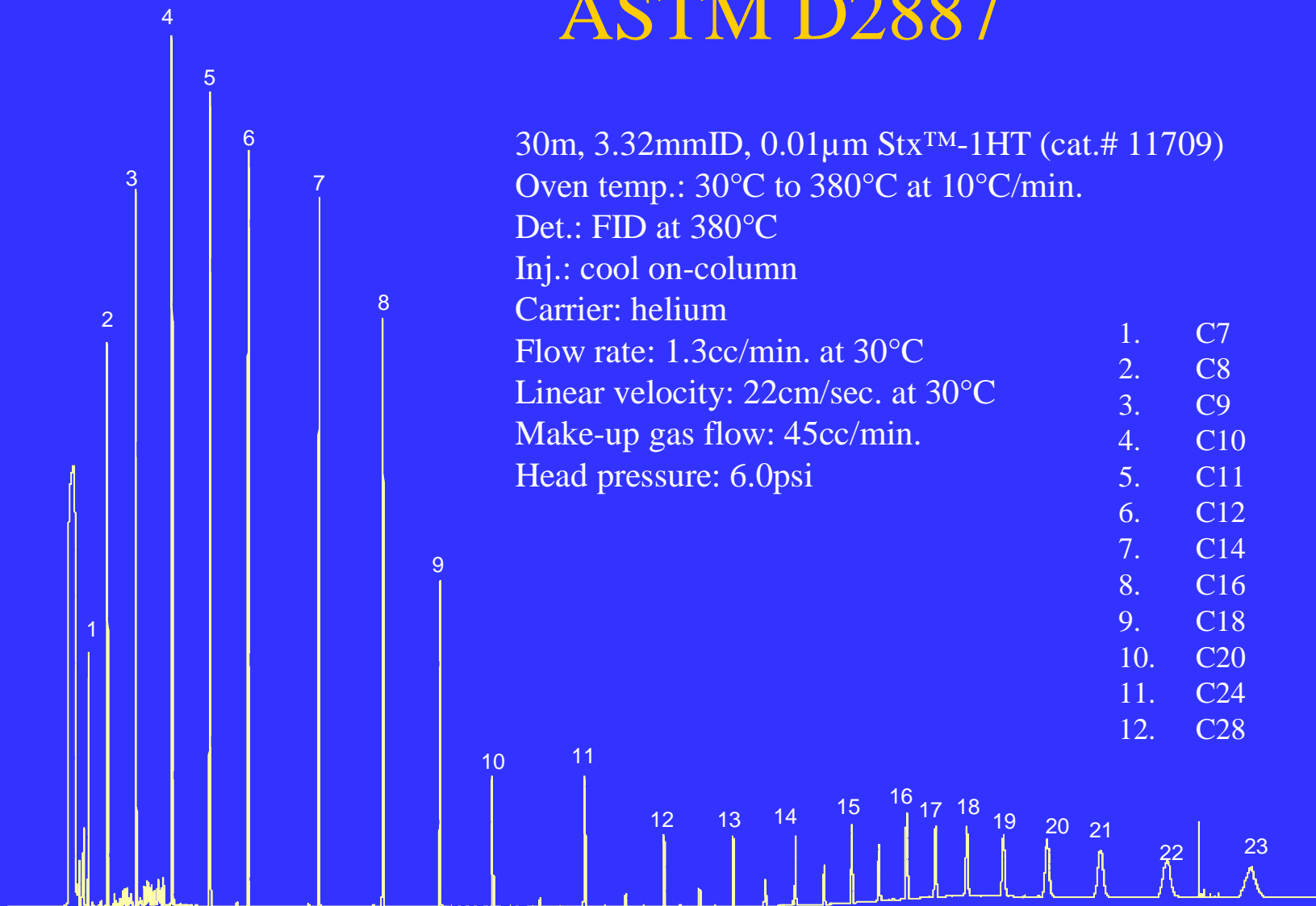
Carrier: hydrogen

Flow rate: 4.0cc/min. at 30°C

Make-up gas flow: 40cc/min.

1.0 $\mu$ L injections of MA EPH Aliphatic Hydrocarbon  
standard (cat.# 31459, solvent: hexane) & MA EPH  
Aromatic Hydrocarbon standard (cat.# 31458, solvent:  
methylene chloride) @ 50ppm concentration.

# ASTM D2887



30m, 3.32mmID, 0.01 $\mu$ m Stx™-1HT (cat.# 11709)

Oven temp.: 30°C to 380°C at 10°C/min.

Det.: FID at 380°C

Inj.: cool on-column

Carrier: helium

Flow rate: 1.3cc/min. at 30°C

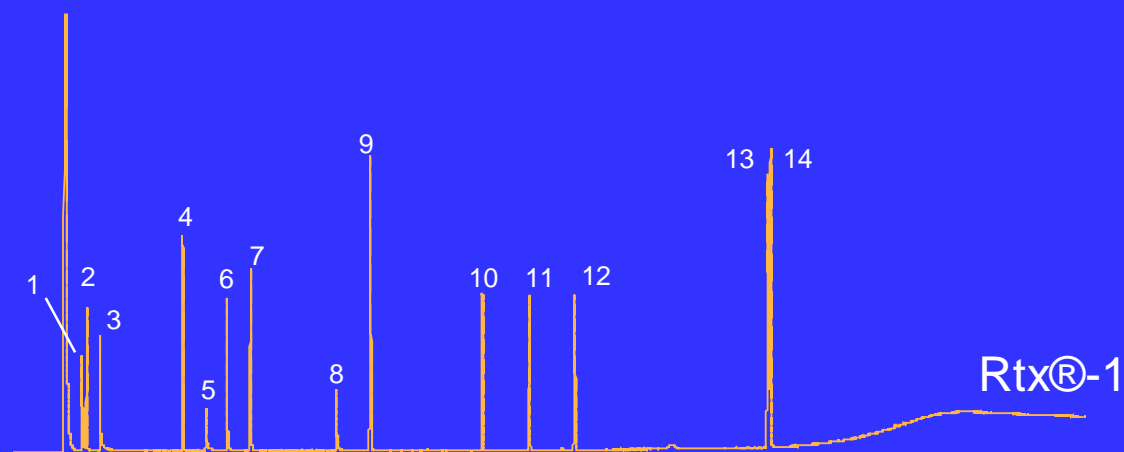
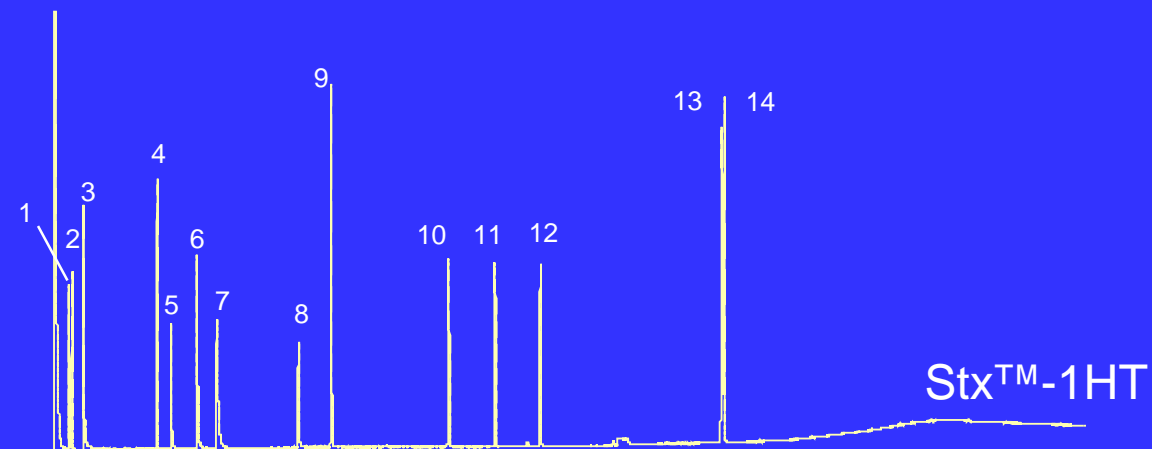
Linear velocity: 22cm/sec. at 30°C

Make-up gas flow: 45cc/min.

Head pressure: 6.0psi

1.	C7	13.	C32
2.	C8	14.	C36
3.	C9	15.	C40
4.	C10	16.	C44
5.	C11	17.	C46
6.	C12	18.	C48
7.	C14	19.	C50
8.	C16	20.	C52
9.	C18	21.	C54
10.	C20	22.	C56
11.	C24	23.	C58
12.	C28		

# XTI Mix on Rtx-1 & Stx-1HT



1. 1,2-hexanediol
2. nitro-di-N-propylamine
3. benzoic acid
4. C14
5. 2,4-dinitrophenol
6. nitrophenol
7. nitroaniline
8. pentachlorophenol
9. carbazole
10. C20
11. C21
12. C22
13. benzo(b)fluoranthene
14. benzo(k)fluoranthene

# Summary

- Definitions
- The design of low bleed & stable column system was discussed
- Several applications were shown

# A New Stationary Phase for Confirming Organic Volatile Impurity Testing in Pharmaceutical Products

Chris M. English, Christopher Cox,  
Frank L. Dorman, & Dinesh Patwardhan

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)





# GC Analysis of OVI by USP <467>

- Method I: G27 30m x 0.53mm x 5.0 df
  - Direct Aqueous
- Method IV: G43 30m x 0.53mm x 3.0 df
  - Static Headspace
- Method V: G43 30m x 0.53mm x 3.0 df
  - Direct Aqueous
- Method VI: choice of 9 columns, depending on monograph

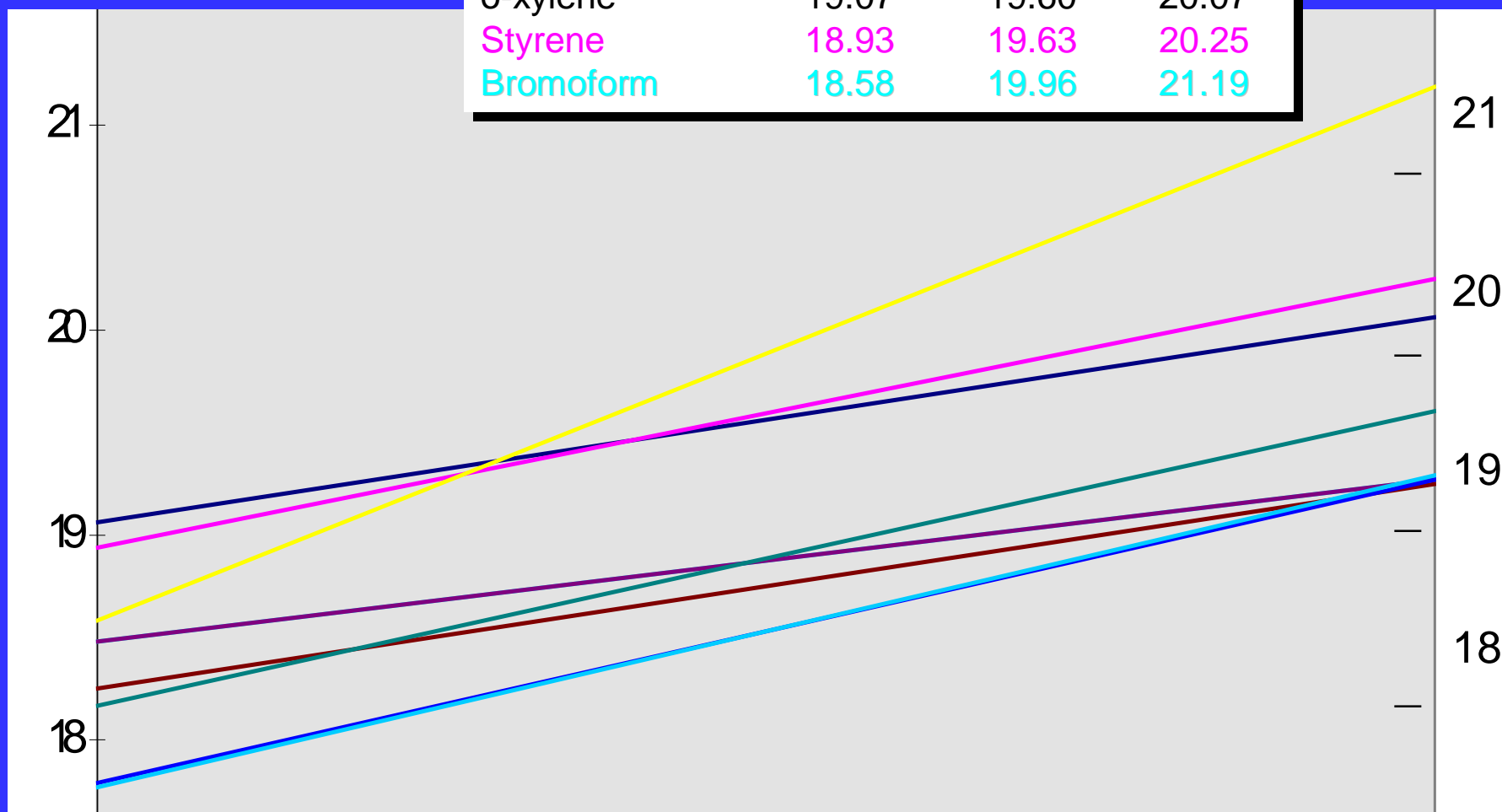
# Confirmation Column Criteria

- Change in selectivity
  - Low bleed
  - Critical resolution
  - FID or MS detection
- 
- Column Design



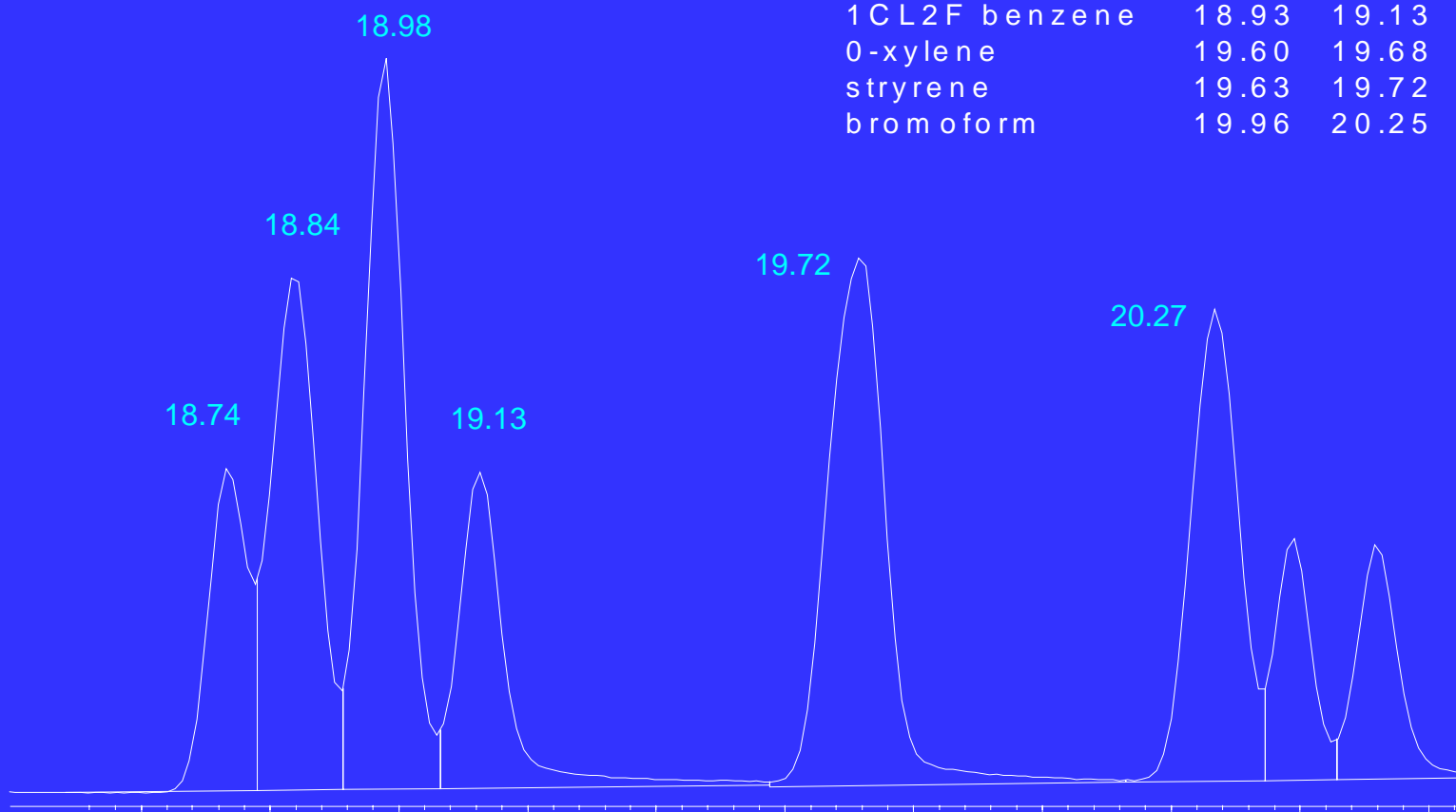
# Modeling

	Rtx-1	Rtx-502	Rtx-35
Chlorobenzene	17.79	18.57	19.27
1112te ethane	17.78	18.58	19.29
E benzene	18.26	18.78	19.25
m/p-xylene	18.48	18.90	19.27
o-ClF benzene	18.16	18.93	19.61
o-xylene	19.07	19.60	20.07
Styrene	18.93	19.63	20.25
Bromoform	18.58	19.96	21.19



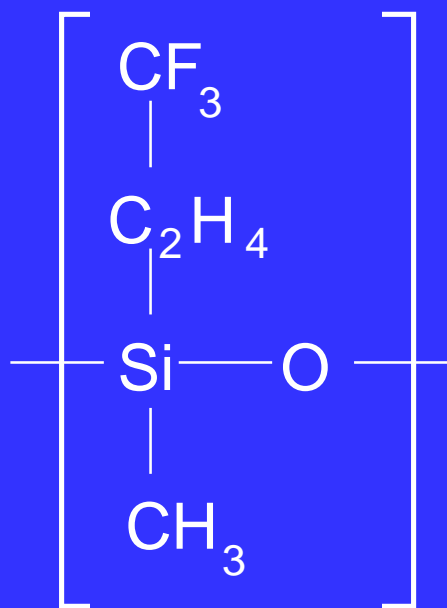
# Predicted vs. Actual Retention Times

	pred	actual	differ
Chlorobenzene	18.57	18.74	-0.17
1,1,1,2-tetraethane	18.58	18.75	-0.17
Ebenzene	18.78	18.84	-0.06
m/p-xylene	18.90	18.98	-0.08
1,1,2,2-tetrafluorobenzene	18.93	19.13	-0.20
o-xylene	19.60	19.68	-0.08
styrene	19.63	19.72	-0.09
bromoform	19.96	20.25	-0.29

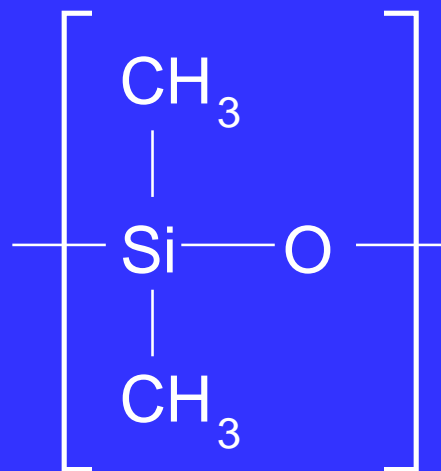


# Stationary Phases Used for Modeling

trifluoropropylmethyl  
polysiloxane

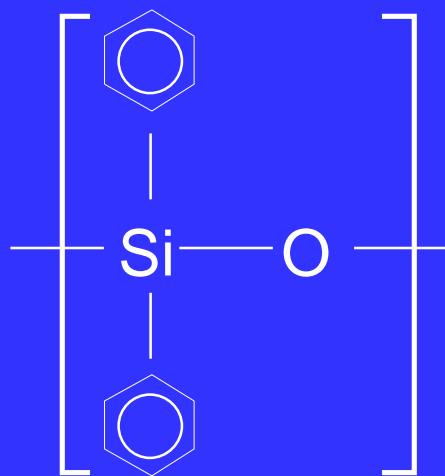


dimethyl  
polysiloxane

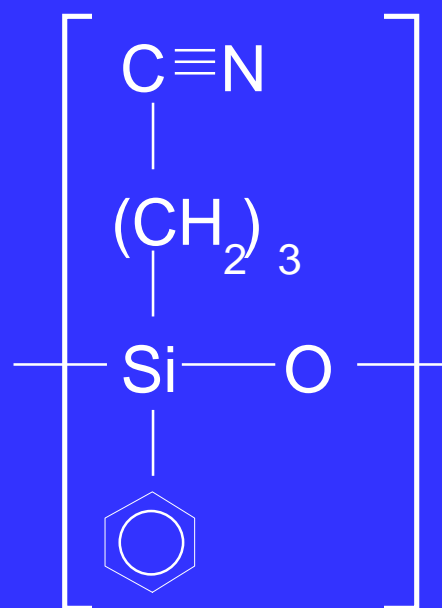


# Stationary Phases Used for Modeling

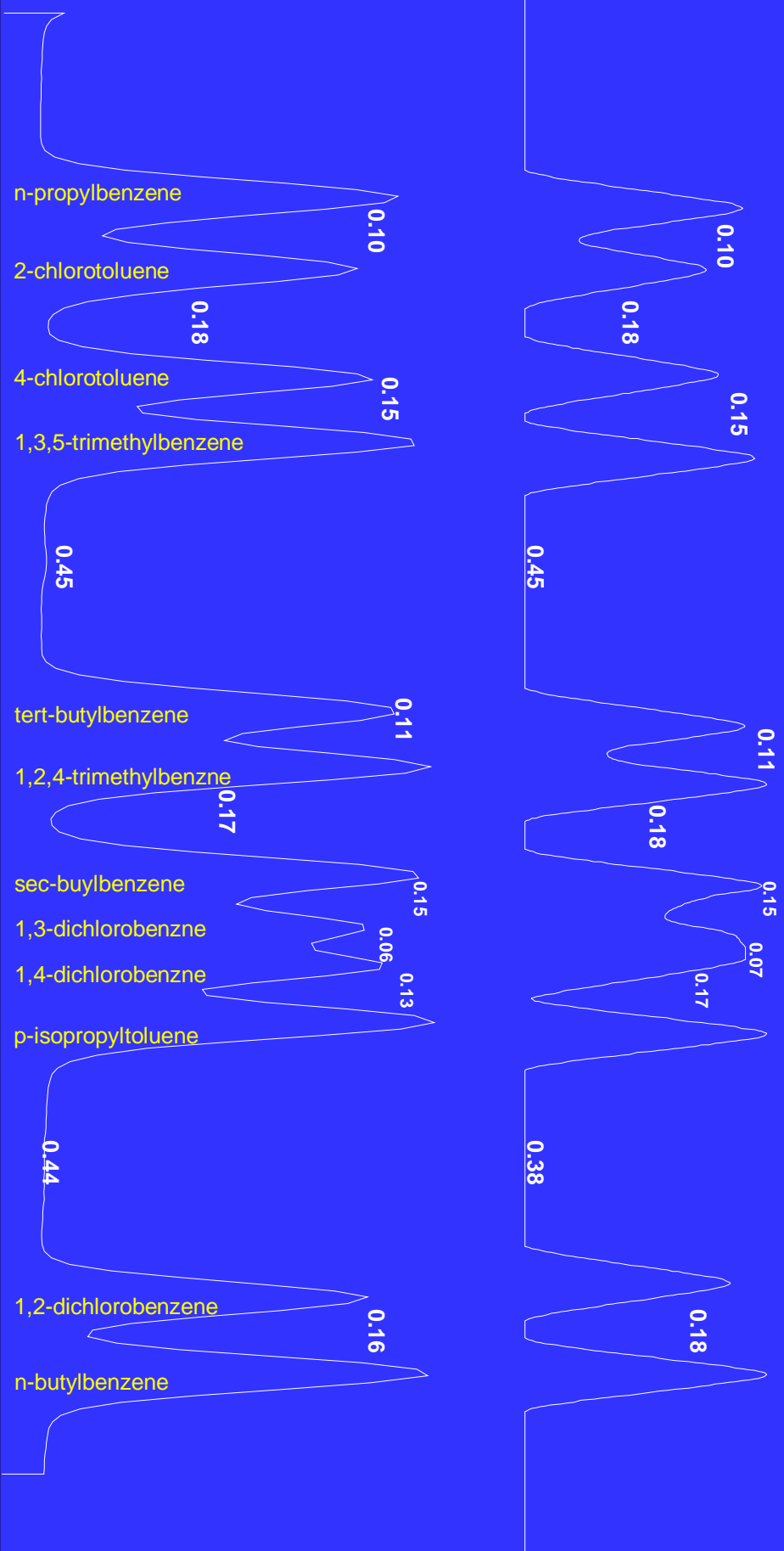
diphenyl  
polysiloxane



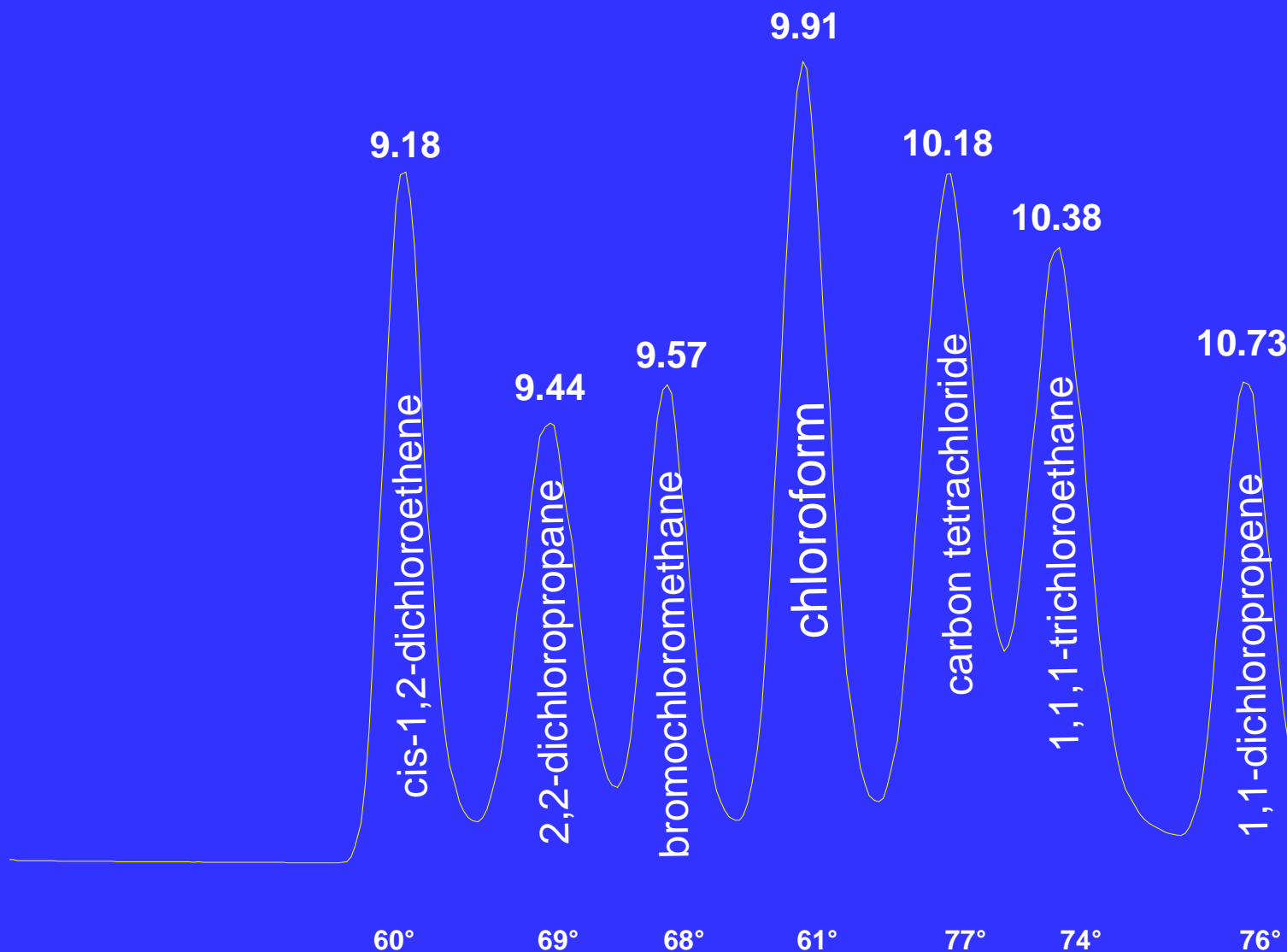
cyanopropylphenyl  
polysiloxane



# Predicted vs. Actual 4 Dimensional Phase



# Actual Phase - Rtx<sup>®</sup>-VGC





# USP <467> Method I

Method I: G27 30m x 0.53mm x 5.0µm df, w/5m PM guard

Inj: Direct Aqueous, 1/10 dilution, 70°C, 1µL

Oven Temp: 35(5)8/175 (0) 35/260

Detector: FID, 260°C,  $1 \times 10^{-12}$  AFS

Carrier: helium, 4.1psi const., 35cm/sec @ 35°C

methylene chloride	600ppm
chloroform	60ppm
benzene	2ppm
trichloroethylene	80ppm
1,4-dioxane	380ppm

# Rtx®-VGC USP <467> Method I



# USP <467> Method IV

**Method IV:** G43 30m x 0.53mm x 3.0µm df

**Inj:** 100µL cat#36007 in 5mL water, 1g sodium sulphate in 20mL headspace vial

**Oven Temp:** 40(20)35/240(20)

**Detector:** FID, 260°C,  $1.25 \times 10^{-11}$  AFS

**Carrier:** helium, 3.5psi const., 35cm/sec @ 40°C

**Split Ratio:** 2:1

**Concentrator:** ThermoQuest HS2000 Headspace Autosampler Vial 80°C, 60 min. shaker on

# USP <467> Method IV

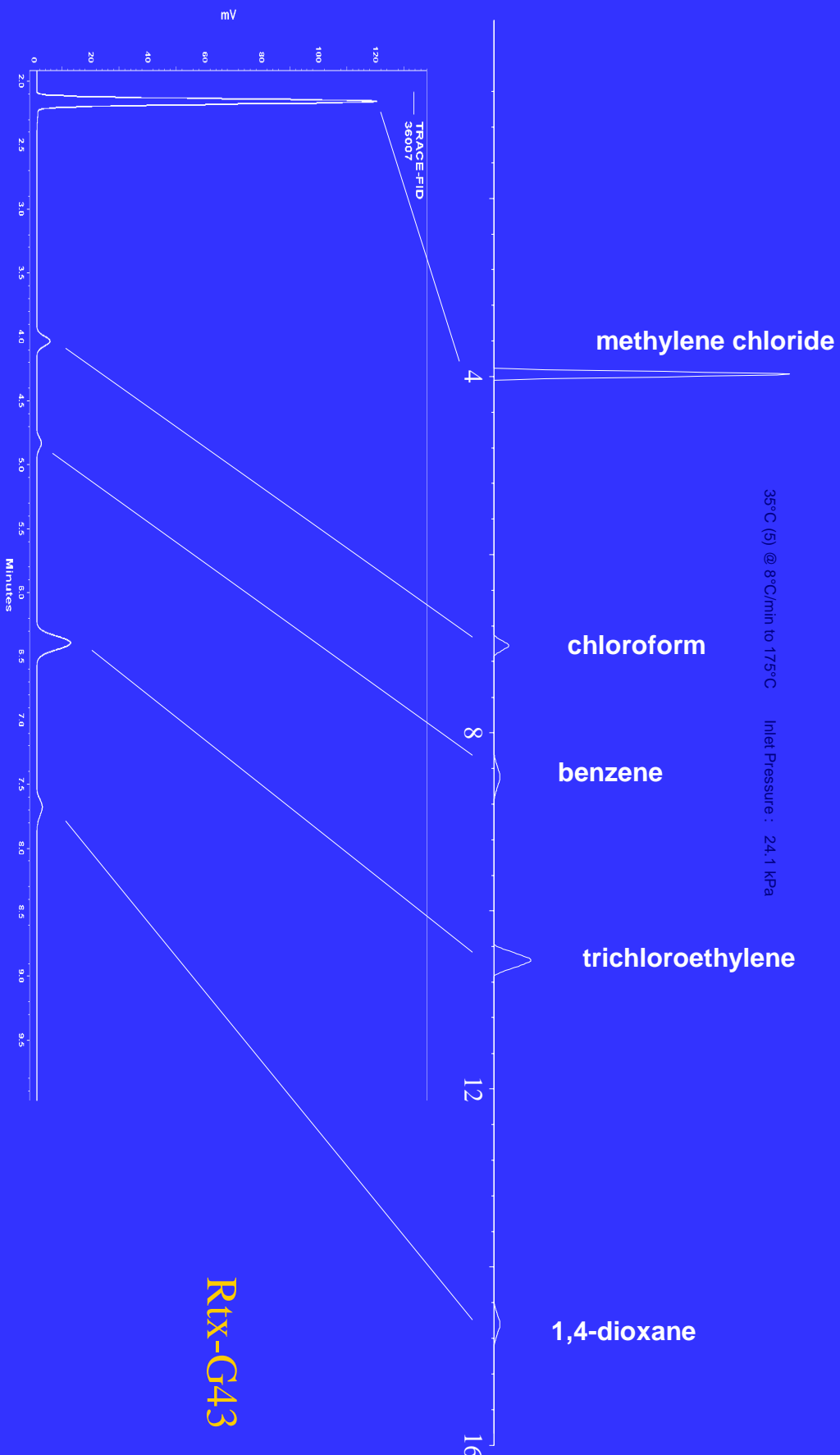
USP <467> Calibration Mix #5 (cat# 3007)

Prepared in dimethylsulfoxide, 1mL/ampul

methylene chloride	600ppm
chloroform	60ppm
benzene	2ppm
trichloroethylene	80ppm
1,4-dioxane	380ppm

# Rtx®-VGC

## USP <467> Method IV



Rtx-G43

# USP <467> Method V

Method V: G43 30m x 0.53mm x 5.0µm df, w/5m PM guard

Inj: Direct Aqueous, 1/10 dilution, 70°C, 1µL

Oven Temp: 40(20)35/240(10)

Detector: FID, 260°C,  $1 \times 10^{-12}$  AFS

Carrier: helium, 4.1psi const., 35cm/sec @ 35°C

# USP <467> Method V

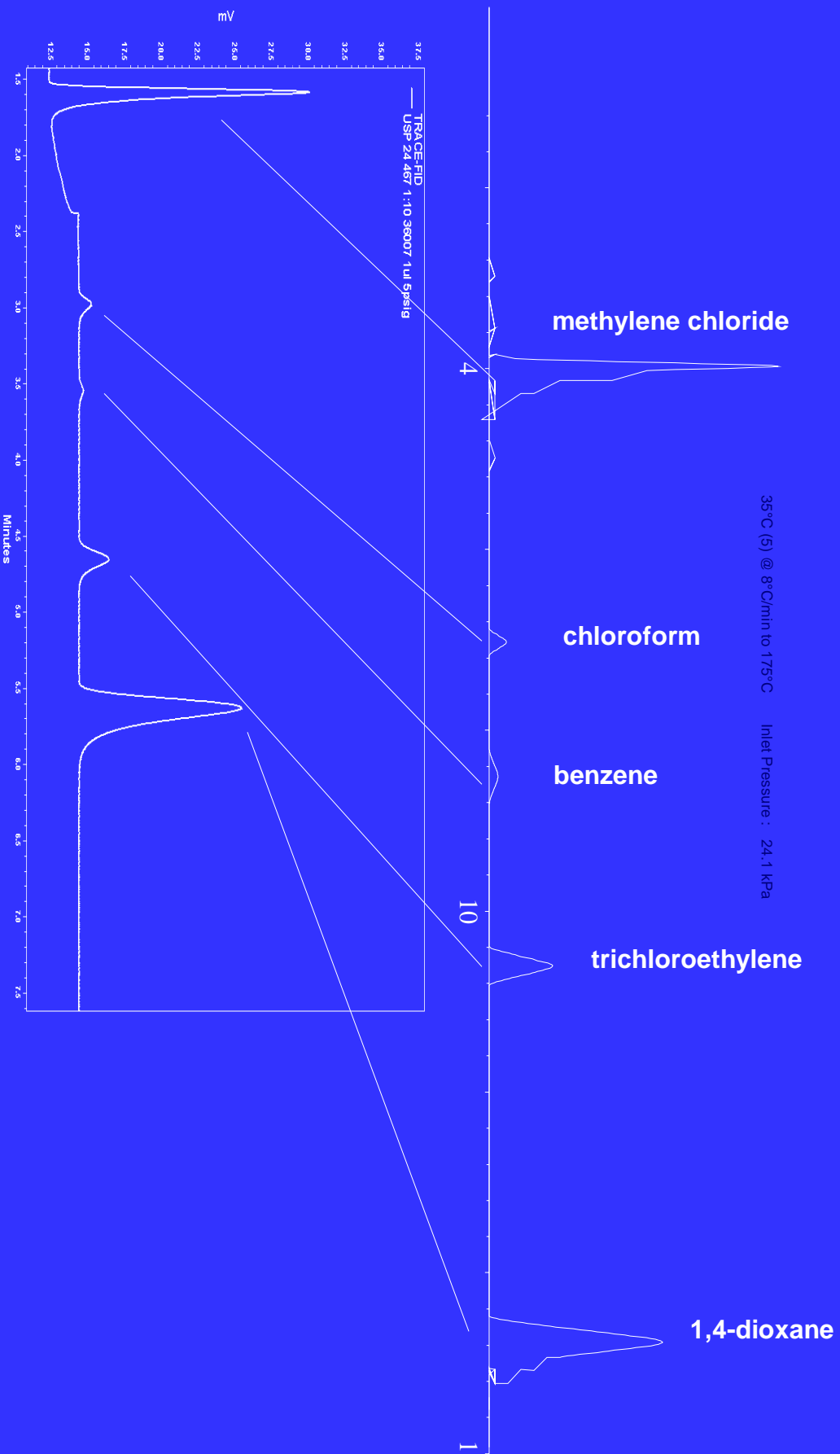
USP <467> Calibration Mix #5 (cat# 3007)

Prepared in dimethylsulfoxide, 1mL/ampul

methylene chloride	600ppm
chloroform	60ppm
benzene	2ppm
trichloroethylene	80ppm
1,4-dioxane	380ppm

# Rtx®-VGC

## USP <467> Method V





# USP <467> Common solvents

Method I: G27 30m x 0.53mm x 5.0 $\mu$ m df, w/5m PM guard

Inj: Headspace at 500ppm in bulk pharm. 2:1 split

Oven Temp: 35(10)5/100 (0) 25/240(5)

Detector: FID, 260°C,  $1 \times 10^{-11}$  AFS

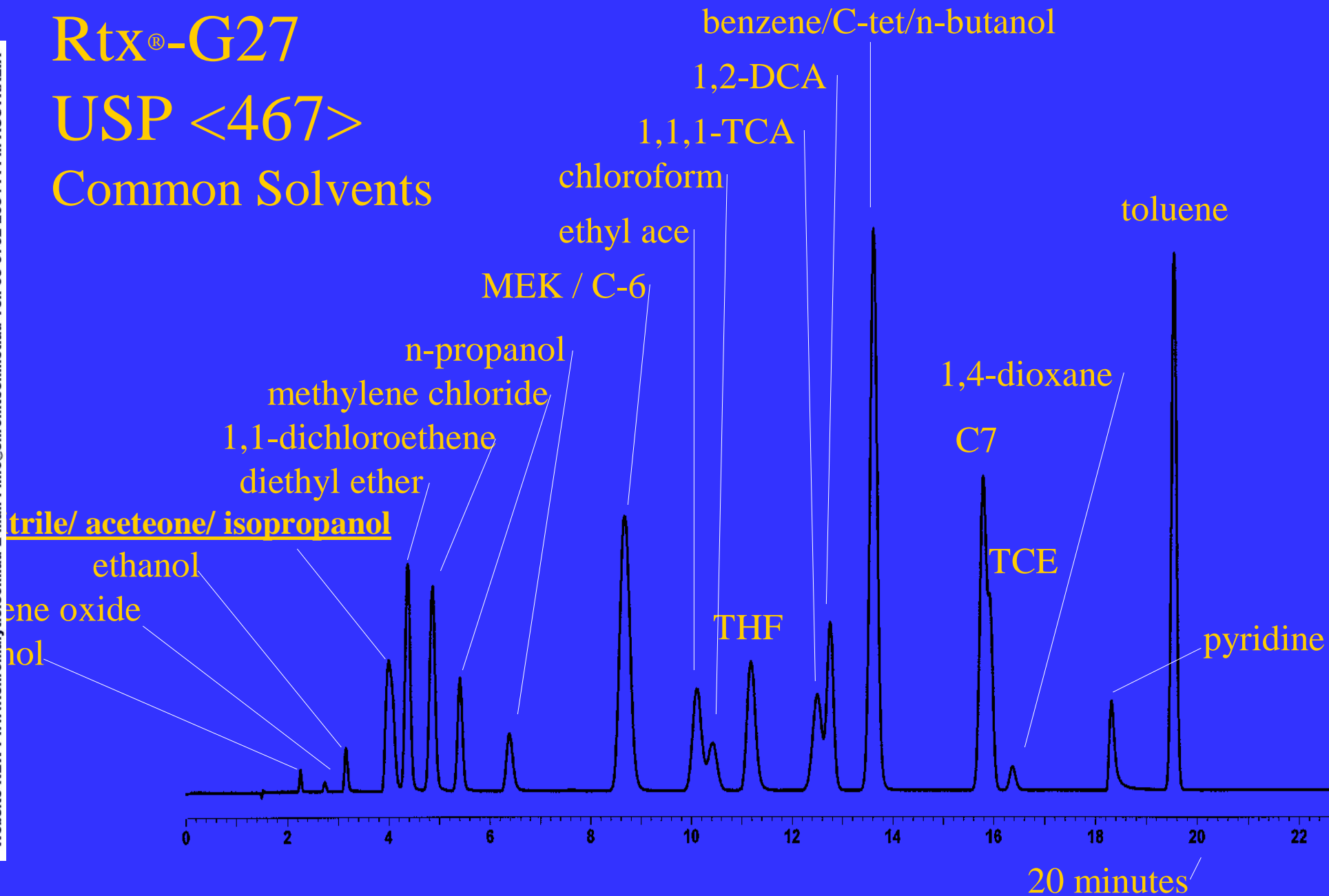
Carrier: helium, 4.1psi const., 35cm/sec @ 35°C

Samples shaken and heated at 90°C for 15 minutes, 1mL headspace injection.

# Rtx®-G27

## USP <467>

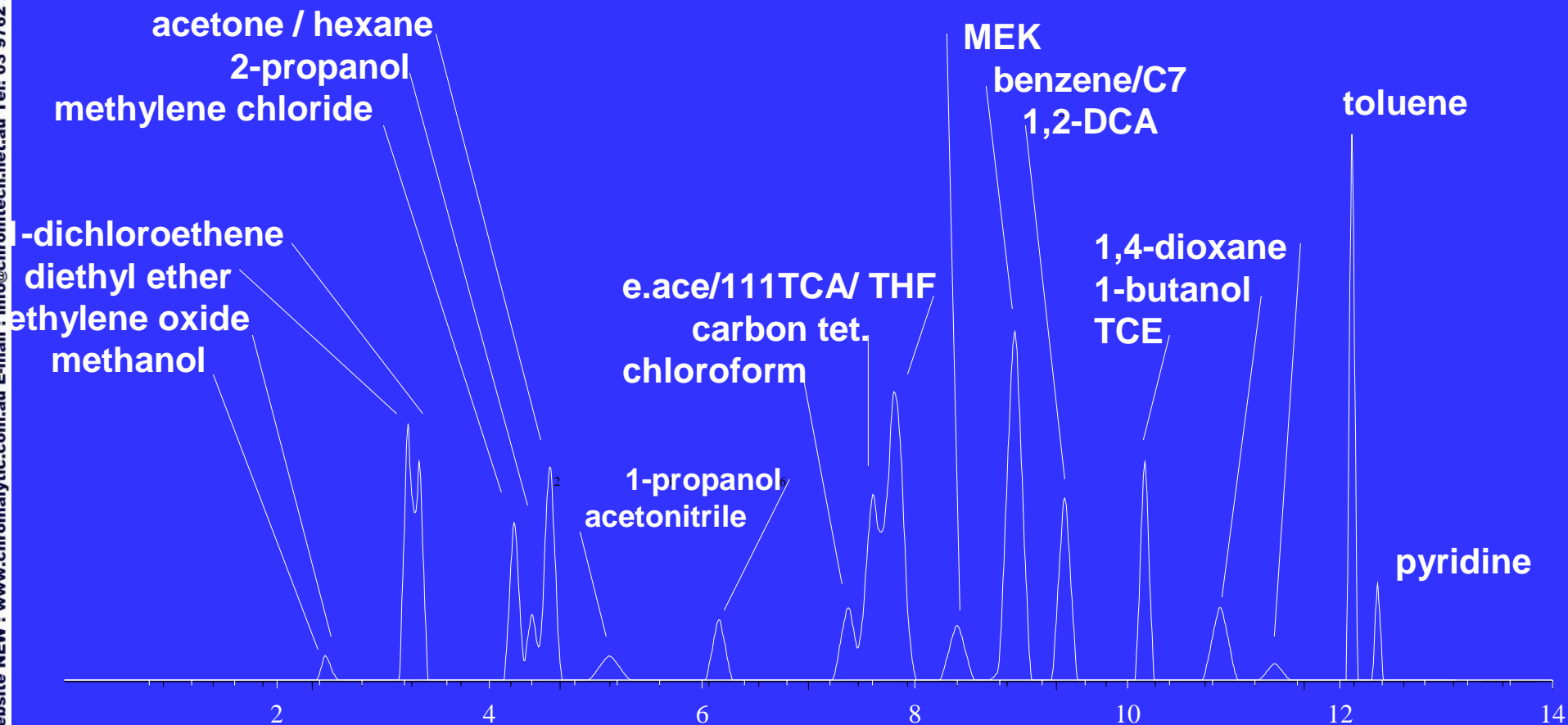
### Common Solvents



20 minutes

# Rtx®-VGC

## USP <467> Common Solvents



# Rtx<sup>®</sup>-VGC

- New stationary phase
- Unique selectivity
- Low bleed
- Confirm G27, G43



# Conclusions

- First in a series of application-specific columns
- Define customer needs
- Computer modeling
- Stationary phase predictions
- Resolution of critical compounds
- Most stable polymer functionalities

# For More Information...

Author e-mail: [cenglish@restekcorp.com](mailto:cenglish@restekcorp.com)

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110 Benner Circle  
Bellefonte, PA 16823  
(800) 356-1688

# Annular Denuder Coatings for the Collection of Organic Vapor Phase During PM<sub>2.5</sub> Sampling

David M. Shelow,  
Jingzhen Xu, PhD

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



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**ECH**nology Pty Ltd  
Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au)

# Particulate Matter (PM)

- Size – 0.005 to 50 $\mu\text{m}$ 
  - PM10
    - Coarse 2.5 $\mu\text{m}$  – 10 $\mu\text{m}$
    - PM2.5 fine fraction
    - Ultrafine 1 $\mu\text{m}$
- Mass
  - 2 to 200 $\mu\text{g}/\text{m}^3$
- Composition
  - $\text{SO}_4$ ,  $\text{NH}_3$ ,  $\text{NO}_3$ , EC/OC, PAH



# Particulate Matter Sources

- Coarse - PM10
  - Dust, sea salts, vehicles, combustion products
- Fine – PM2.5
  - Vehicles emissions, oil & coal utility, wood fuel, biomass burning
- Primary Emissions
  - Transportation, fuel combustion, road dust, construction
- Secondary Aerosol Formulation
  - Sulfates, nitrates, organic particulates from VOCs

# Problems Associated With PM

- Health effects
  - Inhalables (PM10) – the larger particles get trapped in bronchial tubes of upper respiratory tract
  - Respirables (PM2.5) – the smaller the particle the deeper into the lungs it can penetrate
  - Possible linkage to chronic bronchitis and asthma

# Need for Speciation

- Characterization of metals, ions, and carbon constituents
- Air quality modeling analysis
- Aiding in health studies
- Understanding the effects of atmospheric constituents
- Aid in monitoring network design by USEPA

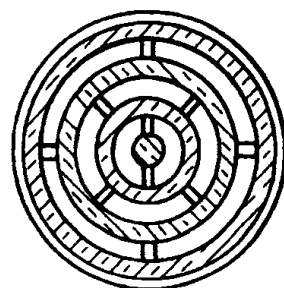
# Analytical Speciation Methodology for PM

- Analytical Method
- Gravimetric
- Ion Chromatography
- Thermal/Optical Method-NIOSH 5040
- EDXRF, ICP, AA
- Analyte
- Total Mass
- SO<sub>4</sub>, Cl, NH<sub>4</sub>, NO<sub>3</sub>
- EC/OC
- S, Al, Si, Ti, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Ba, Pb, metals

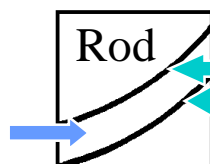
# Denuder Technology

- Denuder Types
  - Single channel or multi channel denuders
  - Glass, metal, ceramic
  - Annular – typically 1mm annulus
  - Honeycomb
- Coated
- Many times placed in series
- Extracted for the analysis
- Can be recoated and reused
- Often used as a “scrubber”

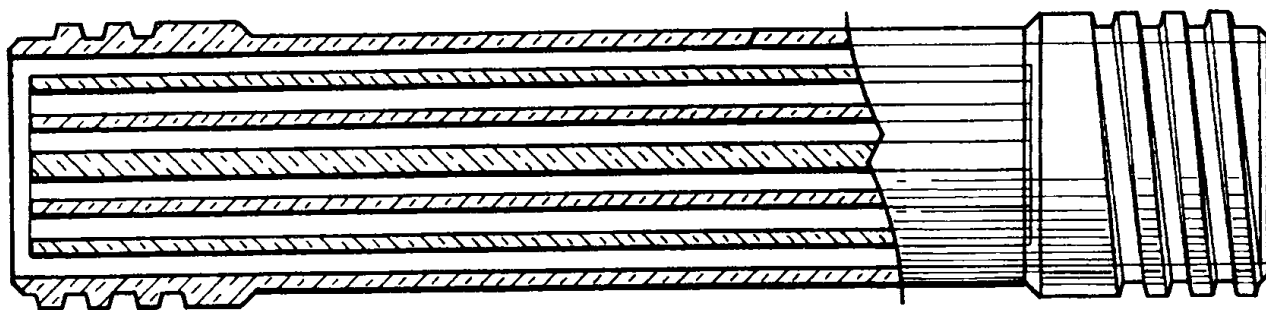
# Multi Channel Annular Denuder



Annulus

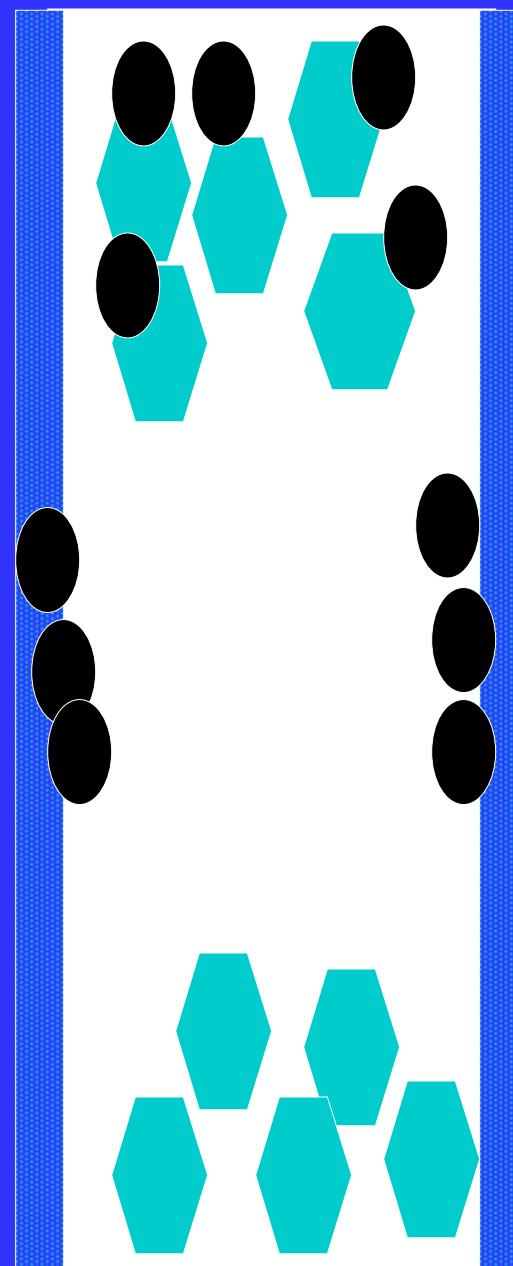


Adsorbent coating



# How Denuders Work

- The vapor phase of the particulate is adsorbed onto the adsorbent material coated on the walls of the denuder.
- Stripped particulate is collected downstream.
- Denuder is solvent rinsed to extract vapor phase.





# Denuder Types





# Denuder Types cont.



# Common Denuder Coatings

- Coating

- Citric acid

- $\text{Na}_2\text{CO}_3$

- $\text{MgO}$

- XAD-4

- Analytes

- $\text{NH}_3$

- $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$

- Nitric acid scrubber

- SVOCs-PAH

# Organic PM2.5 Speciation

- Vapor phase of particulate is denuded from particle. Vapor phase has a higher partitioning coefficient.
- Partitions in adsorbent coated on walls
- Can be extracted and analyzed
- For semi-volatiles technology not fully developed
- PAHs commonly extracted using XAD-4

# XAD-4 Physical Characteristics

- Styrene divinylbenzene copolymer
- High surface area – 780m<sup>2</sup>/g
- Average pore size 50Å

# Denuder XAD-4 Coating Requirements

- Milled to 1-2 $\mu$ m
- Soxhlet extraction cleaned
- Vacuum oven dried
- Crosslinking agents added prior to coating
- Uniform deposition
  - Ensure laminar flow
  - Decrease turbulence
  - Affect efficiency of sampling
- Sample capacity

# XAD-4 Denuder Coating

- Dr. Lara Gundel at LBNL has developed a procedure for coating glass annular denuders with XAD-4.
- Slurry of XAD-4 in Hexane
- Fill denuder, roll or invert, remove, dry, weigh, repeat 10 times
- US Patent 5,763,360
- Licensing agreement

# Comparison of Gundel/Restek Coatings

- XAD-4
- 52mm x 285mm 8 Channel denuders
- LBL denuders coated by Dr. Lara Gundel
- Restek coated using a 1 step coating procedure, vacuum oven dried
- Samples taken at Houston EPA Supersite September 2000
- 2 denuders in series



Sample collected during Texas Air Quality Study 2000 at LaPorte, Collection period - September 10,2000 from 00:00 to 11:30 AM				
	[] ng/m <sup>3</sup>			
LBL denuders	front denuder		back denu	front/total
Name	1st wash	2nd wash	1st wash	lbl
phenol	12	0	16	43%
Naphthalene	11	0	23	32%
nC12	9	0	0	100%
nC13	10	0	0	100%
1-methyl naphthalene	12	0	0	100%
2-Methyl naphthalene	6	0	1	89%
Biphenyl	2	0	0	100%
Dimethyl naphthalene	2	0	0	100%
acenaphthene	3	0	0	100%
Dibenzofuran	4	0	0	100%
nC16	4	0	0	100%
fluorene	4	0	0	100%
nC17	4	0	0	93%
phenanthrene	8	0	0	100%
anthracene	8	0	0	96%
nC19	1	0	0	100%
nC20	1	0	0	100%
fluoranthene	2	0	0	100%
nC21	1	0	0	100%
pyrene	0	0	0	100%

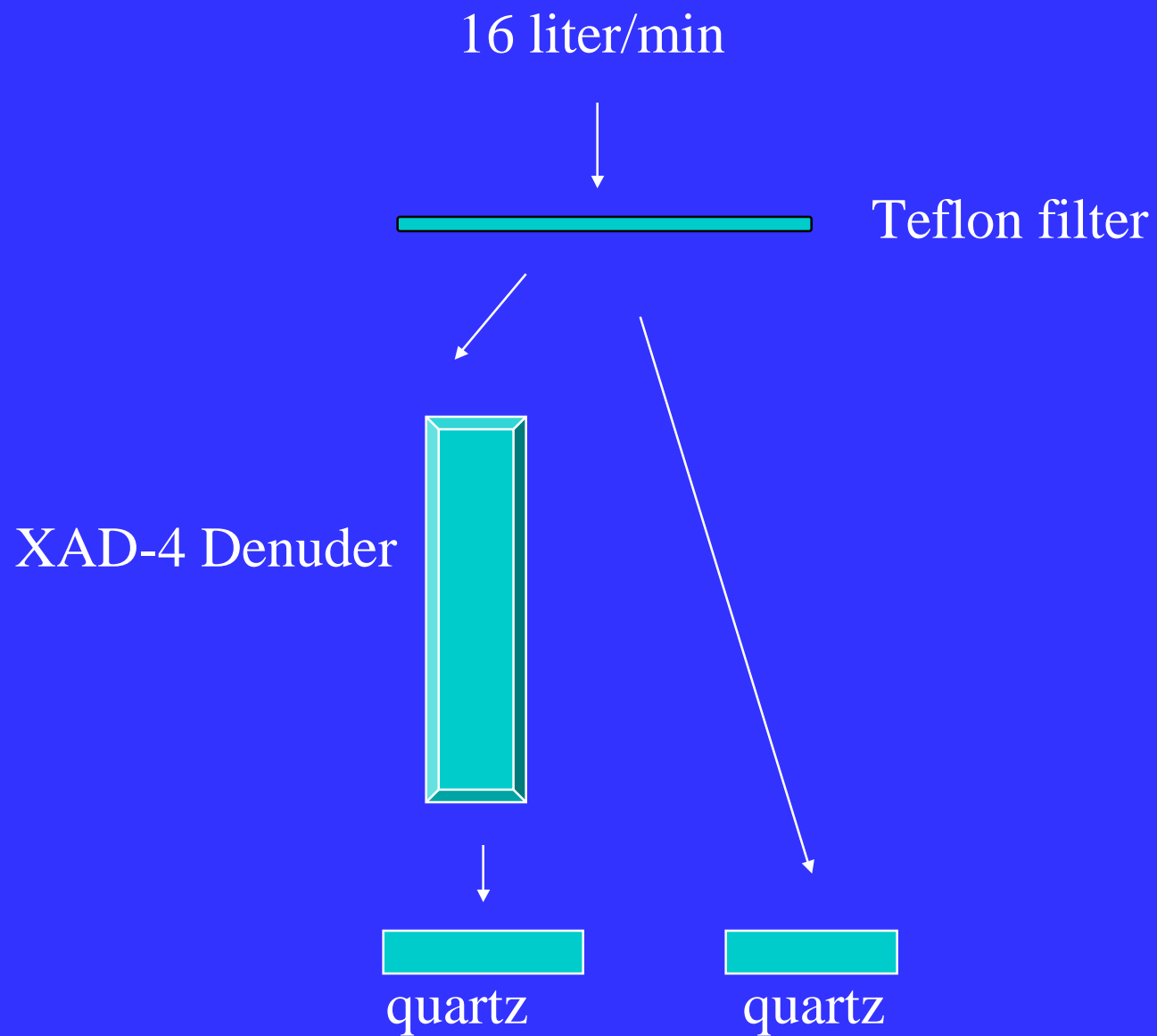


	[] ng/m^3			
Restek denuders	front denuder		back denu	front/total
Name	1st wash	2nd wash	1st wash	
phenol	25	0	25	49%
Naphthalene	23	0	25	49%
nC12	9	0	0	100%
nC13	10	0	0	100%
1-methyl naphthalene	15	0	0	100%
2-Methyl naphthalene	8	0	0	100%
Biphenyl	2	0	0	100%
Dimethyl naphthalene	2	0	0	100%
acenaphthene	4	0	0	100%
Dibenzofuran	4	0	0	100%
nC16	4	0	0	100%
fluorene	4	0	0	100%
nC17	5	0	0	100%
phenanthrene	7	0	0	100%
anthracene	7	0	0	100%
nC19	1	0	0	100%
nC20	1	0	0	100%
fluoranthene	1	0	0	100%
nC21	1	0	0	100%
pyrene	0	0	0	100%

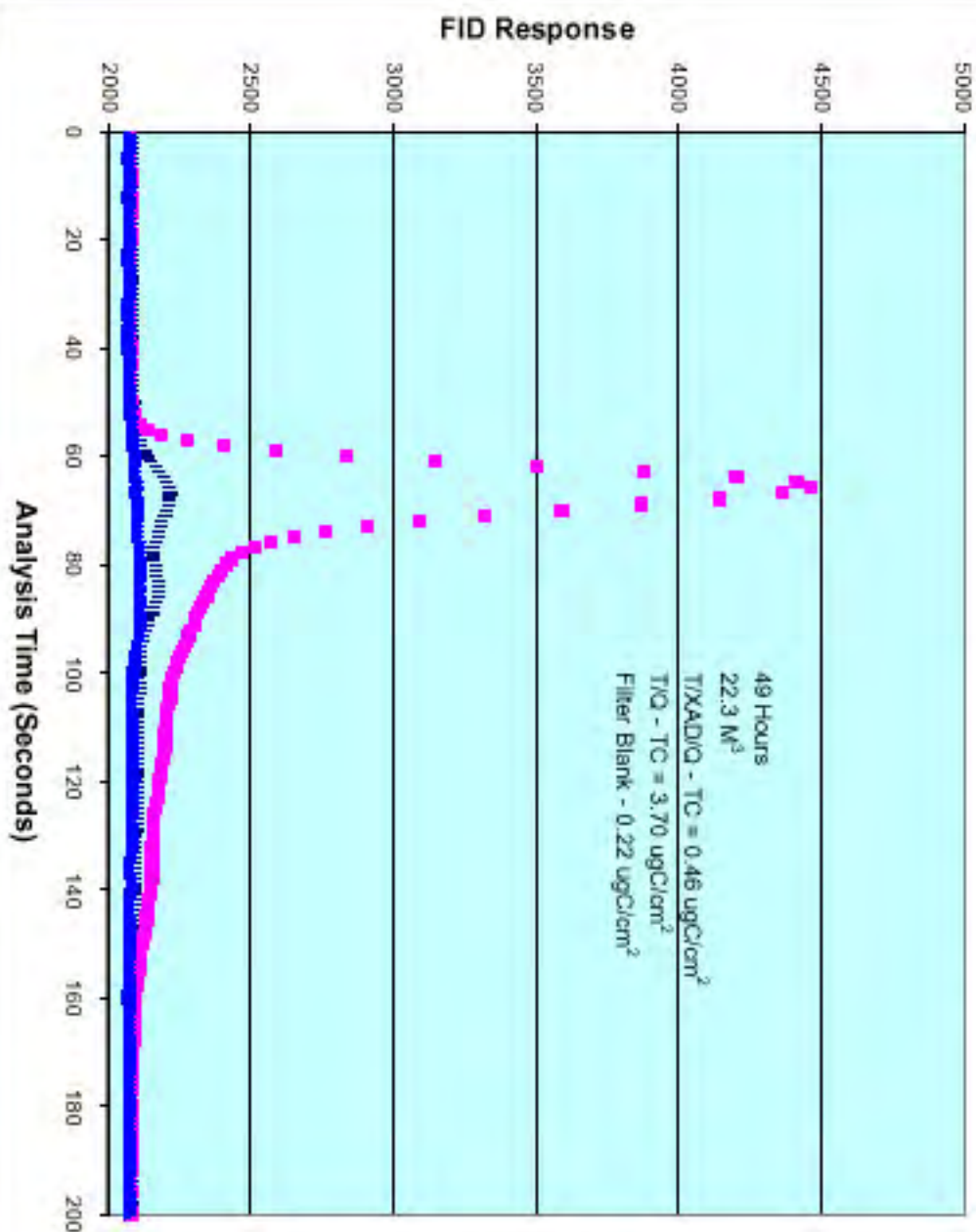
Comparison of Front Denuder % recovery		
Name	LBL	Restek
phenol	43%	49%
Naphthalene	32%	49%
nC12	100%	100%
nC13	100%	100%
1-methyl naphthalene	100%	100%
2-Methyl naphthalene	89%	100%
Biphenyl	100%	100%
Dimethyl naphthalene	100%	100%
acenaphthene	100%	100%
Dibenzofuran	100%	100%
nC16	100%	100%
fluorene	100%	100%
nC17	93%	100%
phenanthrene	100%	100%
anthracene	96%	100%
nC19	100%	100%
nC20	100%	100%
fluoranthene	100%	100%
nC21	100%	100%
pyrene	100%	100%

# XAD-4 As an Organic Scrubber

- XAD-4 coated on metal denuder
- Total carbon test on quartz filter
- NIOSH 5040 method
- Sunset Labs Instrument Thermal Optical Analyzer



## TC Analysis On Quartz



| Teflon/XAD Front  
 ■ Teflon Front Only  
 ▲ Filter Blank



# Future Research

- Non-particulate coating
  - Non-particulate porous film
  - Elimination of carbon artifact for TC
  - Eliminate particles bias
  - Ability to dope for selectivity
- Carbon coating
  - Great organic scrubber

# Photo of Non-Particulate Coated Denuder



# Conclusion

- Denuders technology has become an important part of PM2.5 speciation.
- XAD-4 is currently being evaluated for organic speciation such as PAHs.
- More research is needed to find more selective coatings for organic speciation of classes of compounds.



# Acknowledgements

- Len Stockburger, PhD, USEPA
- Dr. Lara Gundel, PhD, LBNL
- Dave Smith, PhD, Sunset Labs
- Technology possible by Licensing agreement # L-99-1278 between Restek and Lawrence Berkeley National Laboratory

# Improved Phases for the GC Analysis of Organophosphorus Pesticides

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# Abstract

Organophosphorus pesticide (OPP) analysis is common in agricultural analytical laboratories. With the decline of organochlorine pesticide use, OPPs have become increasingly popular as the active ingredients in insecticides. In addition, they are used in termite treatments, lawn and garden sprays, indoor insect sprays and baits, and in pet flea collars and sprays. Testing of agricultural products is required because of potential health risks associated with these compounds.

The gas chromatographic (GC) analysis of OPPs is demanding because some of the compounds are light and temperature sensitive. In addition, specialty detectors (e.g. the nitrogen phosphorus detector or flame photometric detector) and dual-column analyses are required in OPP methods in order to obtain low-level detection and identification. This presentation will discuss a primary and confirmational column set developed for the analysis of OPPs. The phases were developed using a proprietary phase modeling software program, which aids in the optimization of the phase chemistry, film thickness, and column dimensions.

# Developing an Organophosphorus Column

In developing a GC column for organophosphorus pesticide analysis, the column should be capable of separating USEPA 8141 compounds, serve as a companion column to columns such as the Rtx-OPPesticides, and have a total run time of 20 minutes or less. In addition, it should be compatible with GC/MS analysis (i.e. low bleed, and able to chromatographically resolve compounds with similar spectra).

Traditional column selection has involved asking a “senior” person in the laboratory, consulting a column manufacturer’s applications section, matching the polarity of the column to the compounds of interest or trying to force the separation onto an existing phase. Conversely, modern column selection involves columns and stationary phases that are designed around applications. Specific phases and columns can be developed for a target separation. This approach requires an understanding of and the ability to model analyte-phase interactions.

# Stationary Phase Optimization

Stationary phase optimization can be achieved through window diagramming or by computer simulation of the retention time,  $R_t$ , and peak width at half height,  $W_{1/2}$ . Simulation programs such as ezGC have been applied in the development of phases such as the Rtx®-CLPesticides and Rtx-CLPesticides2.

The next step in polymer development involves the computer prediction of optimized stationary phase composition and column dimensions. This approach uses computer prediction of solute/stationary phase interactions to aid in the design of new polymers. Columns such as the Rtx-TNT, Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX, and Rtx-OPPesticides2 were developed using this approach.

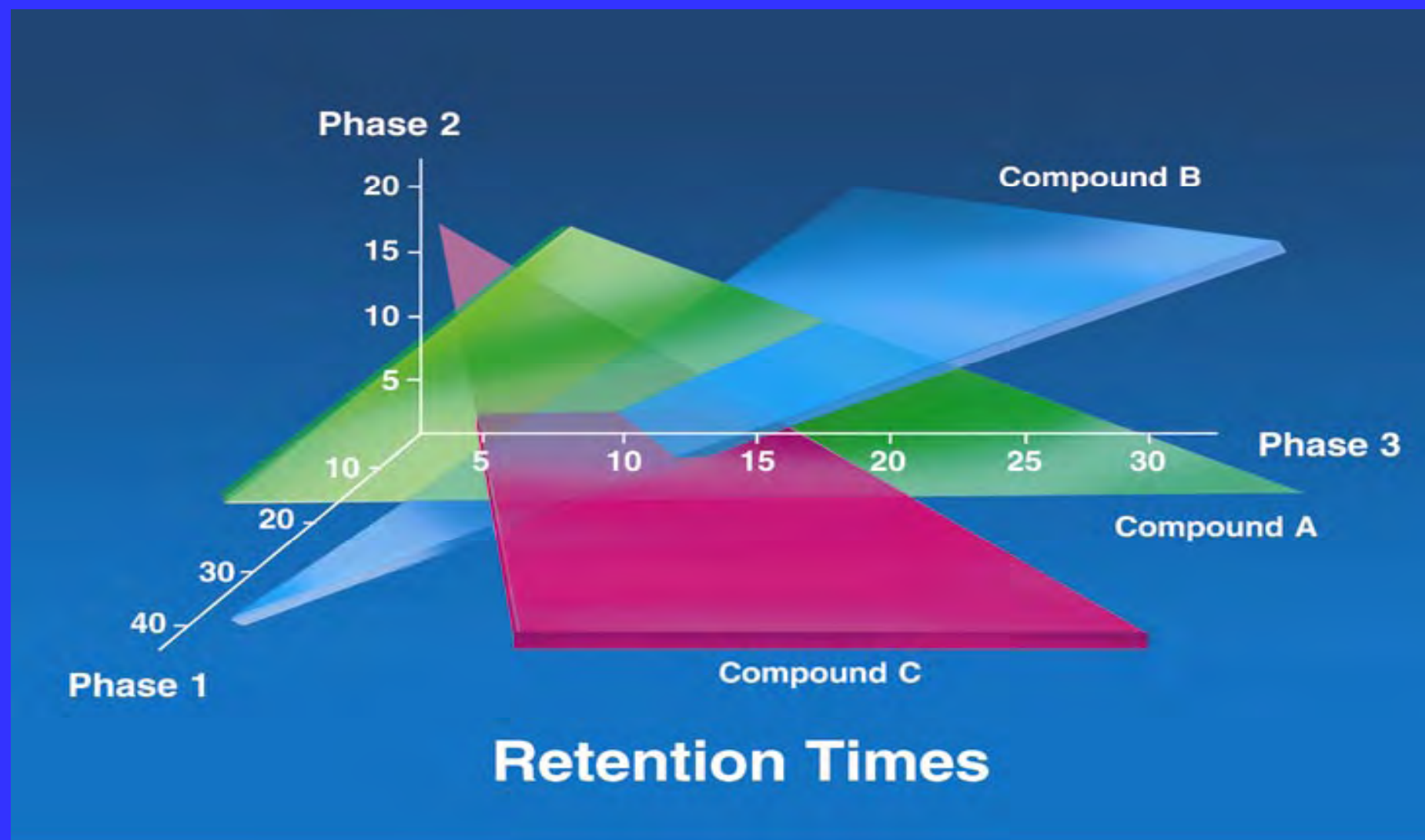


# Development of the Rtx-OPPesticides2 Column

In the development of the Rtx-OPPesticides2 column, data was first acquired for target compounds under two temperature programs. Columns with functionalities that displayed selectivity for these compounds were used. Computer Assisted Stationary Phase Design (CASPD) was used to calculate  $\Delta H$  and  $\Delta S$  for each compound. By working in Retention Index, the phase and dimensions could be optimized for the target separation. The stationary phase can then be synthesized and the column coated at the appropriate phase thickness.

Below is a simple 3-D model depicting a polymer composition for 3 compounds. This is a simplified model describing the 53 compounds which were modeled for the Rtx-OPPesticides2 column.

# 3-Space Selectivity Model for 3 Compounds



# CASPD Modeling Results

The modeling software output includes not only the predicted phase composition but also predicted retention times and run conditions. The following table shows the comparison of the modeled results to the experimental results for the column made from the predicted polymer.

As indicated, the compounds eluted within 0.2 minutes of the CASPD prediction. The accuracy of the software benefits both R&D and Innovations chemists involved in new product development. Instead of making various polymers with different percentages of functional groups, computer modeling can be performed to generate polymer formulations that result in optimal resolution in short analytical run times.



# Comparison of Predicted vs Actual Retention Times of OP Pesticides

Target Compound	Predicted Rt	Actual Rt	Difference (m in)
dichlorvos	4.08	4.05	-0.03
H M P A	4.70	4.70	0.00
mevinphos	6.43	6.34	-0.09
trichlorfon	6.44	6.43	-0.01
TE P P	8.20	8.40	0.20
demeton-o	8.46	8.52	0.06
thionazin	8.58	8.52	-0.06
T B P	8.60	8.52	-0.08
ethoprop	8.84	8.74	-0.10
naled	9.34	9.32	-0.02
sulfotepp	9.42	9.56	0.14
phorate	9.53	9.56	0.03
dicrotophos	9.61	9.59	-0.02
monocrotophos	9.70	9.62	-0.08
demeton-s	9.80	9.62	-0.18
terbufos	10.44	10.32	-0.12
dimethoate	10.67	10.62	-0.05
dioxathion	10.78	10.77	-0.01
fonophos	10.91	10.79	-0.11
diazinon	10.93	10.90	-0.04
disulfoton	11.13	11.09	-0.03
phosph isomer	11.19	11.16	-0.04
dichlorofenthion	11.38	11.37	-0.01
chlorpyrifos methyl	11.94	12.03	0.09
phosphamidon	12.14	12.03	-0.11

# Analysis OP Pesticides by FPD

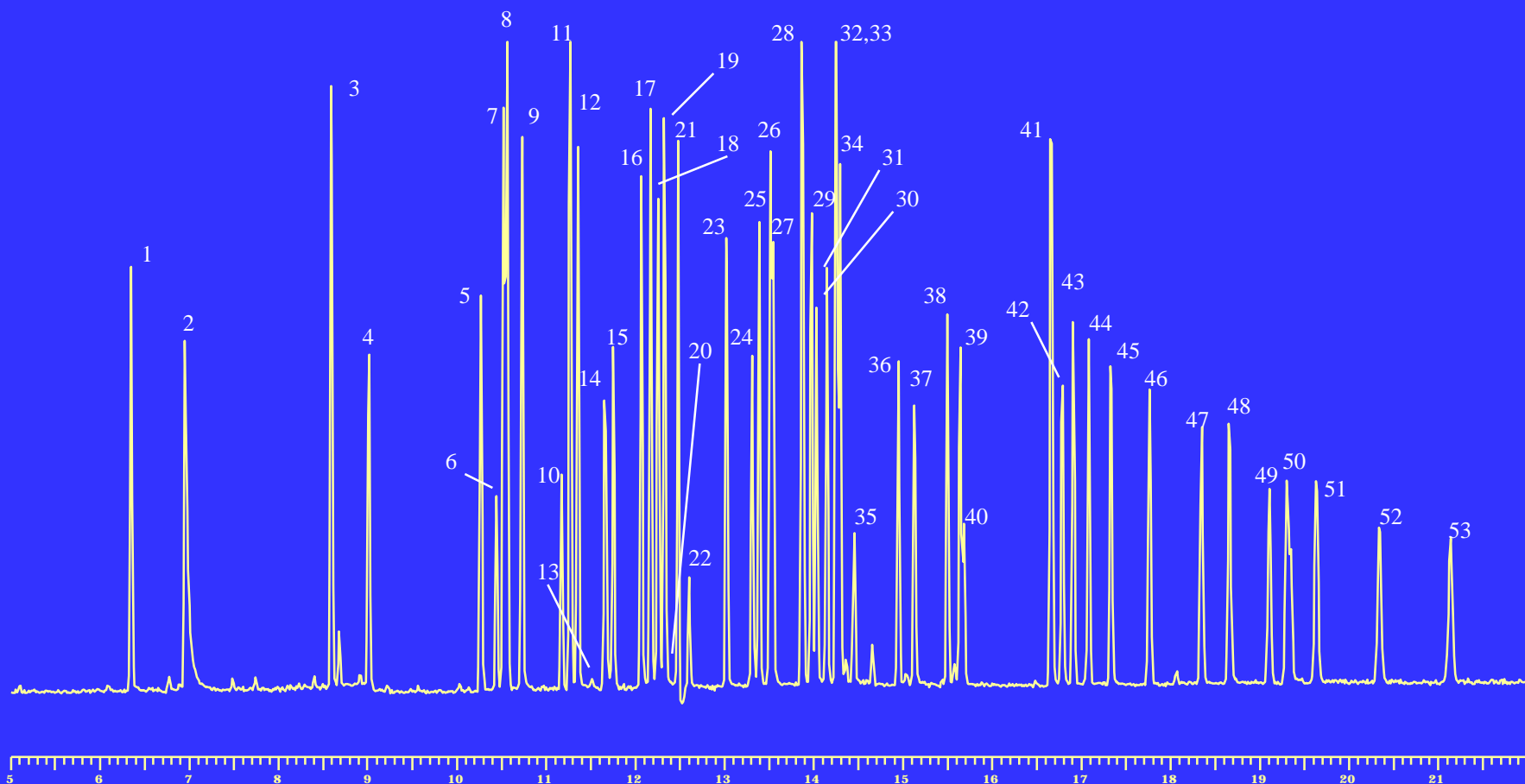
The analysis of organophosphorus pesticides requires a primary and secondary column for positively identified compounds using selective detectors.

The Rtx-OPPesticides2 column is an excellent choice for the primary column, resolving all 53 compounds except for one pair within 22 minutes.

The Rtx-OPPesticides column is a good choice for a second column offering the fewest number of coelutions in the short analysis time of 22 minutes, under the same run conditions as the Rtx-OPPesticides2 column.

Following are the chromatographic results of 53 organophosphorus compounds run under optimized conditions for the Rtx-OPPesticides2 column.

# Rtx-OPPesticides2 column (30m x 0.32mm ID, 0.5um film)

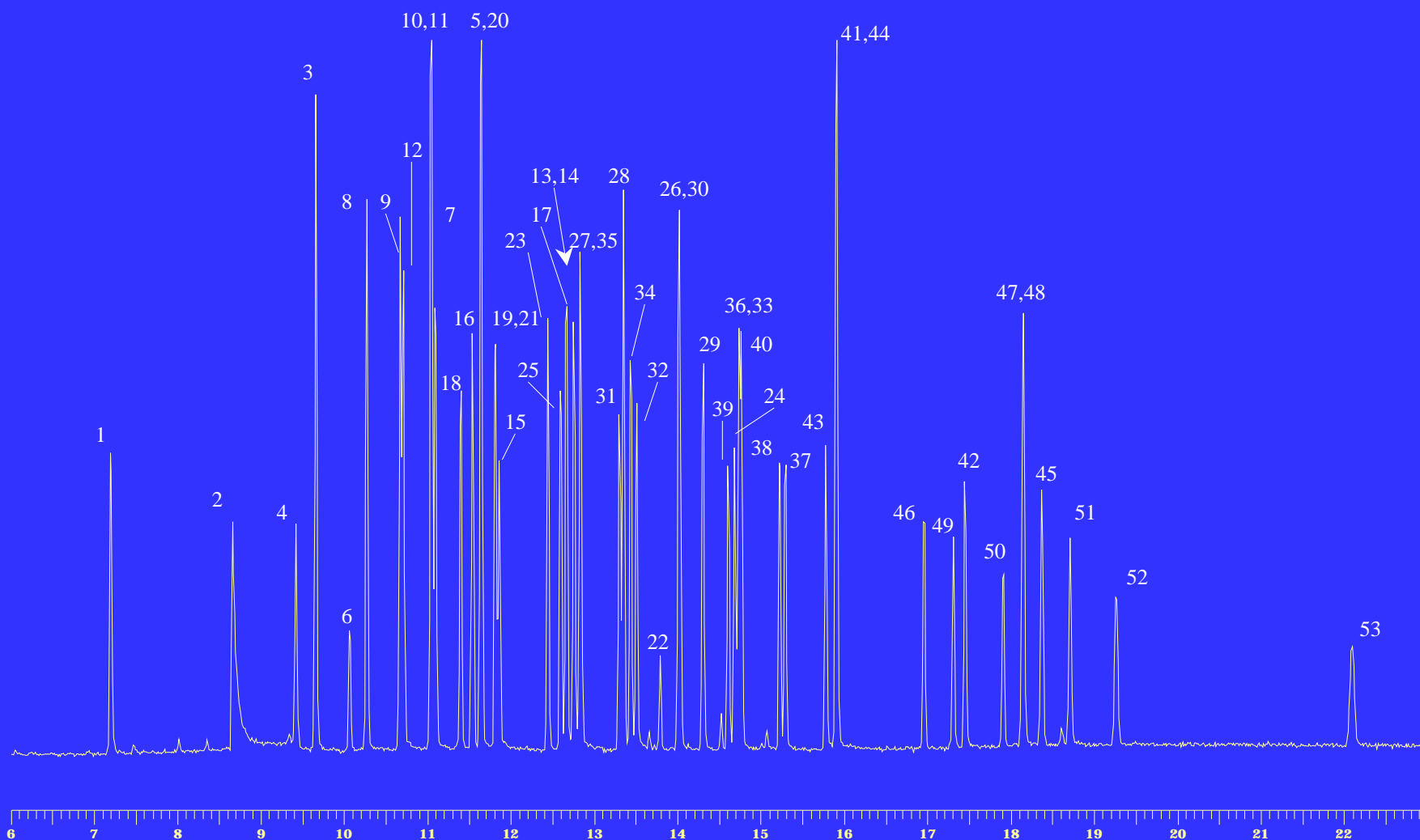


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# Rtx-OPPesticides column (30m x 0.32mm ID, 0.5um film)



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# Organophosphorus Pesticides by FPD

## Peak IDs

PK#	Compound	PK#	Compound	PK#	Compound
1	dichlorvos	20	fonophos	38	stirofos
2	hexamethylphosphoramide	21	disulfoton	39	tokuthion
3	mevinphos	22	phosphamidon isomer (breakdown product)	40	merphos oxon (breakdown product)
4	trichlorfon	23	dichlorofenthion	41	ethion
5	TEPP	24	phosphamidon	42	fensulfothion
6	demeton-o	25	chlorpyrifos methyl	43	bolstar
7	tributyl phosphate (SS)	26	parathion-methyl	44	carbophenothion
8	thionazin	27	ronnel	45	famphur
9	ethoprop	28	aspon	46	triphenyl phosphate (SS)
10	naled	29	fenitrothion	47	EPN
11	sulfotepp	30	malathion	48	phosmet
12	phorate	31	chlorpyrifos	49	leptophos
13	dicrotophos	32	trichloronate	50	tri-o-cresyl phosphate
14	monocrotophos	33	parathion-ethyl	51	azinphos-methyl
15	demeton-s	34	fenthion	52	azinphos-ethyl
16	terbufos	35	merphos	53	coumaphos
17	dimethoate	36	chlorfenvinphos		
18	diazinon	37	crotoxyphos		
19	dioxathion				

# Organophosphorus Pesticides by FPD Run Conditions

GC oven: 80°C(0.5min)@12°C/min to 280°C(10min)

Injector: 200°C splitless, purge off time 1min,

4mm single gooseneck Siltek sleeve

Detector: Agilent FPD 250°C

DT @80C = 0.98min for the Rtx-OPPesticides

= 1.03min for the Rtx-OPPesticides2

Carrier gas: helium

Columns:

RTX-OPPesticides, cat# 11239 30m x 0.32mm ID, 0.5um film

RTX-OPPesticides2, cat# 11241 30m x 0.32mm ID, 0.32um film

Standard Conc.: 100 ng/ml



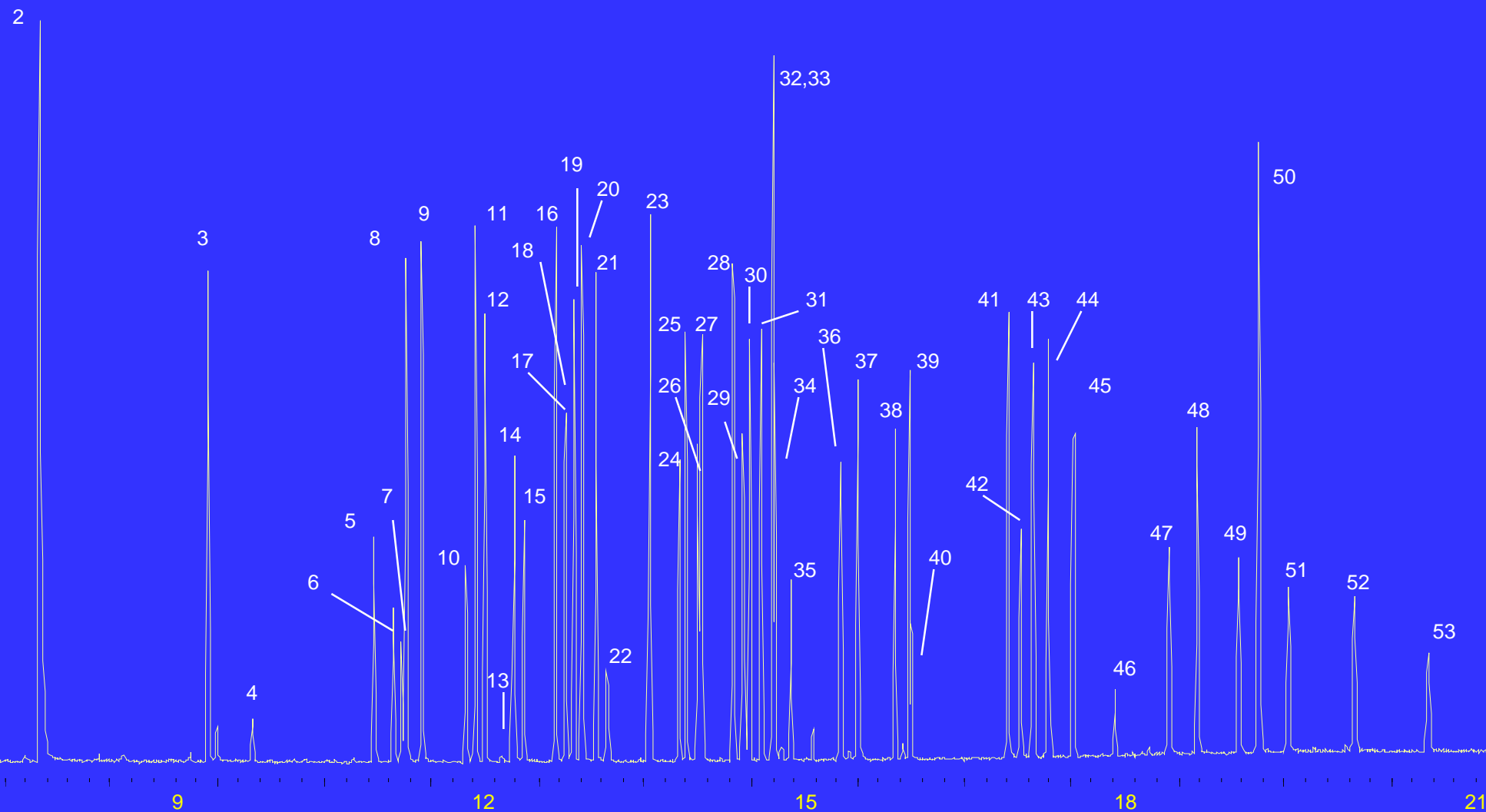
# Analysis OP Pesticides by GC/MS

Polymers designed for selective detectors, like the NPD or FPD, must maximize resolution between analytes for identification and quantitation. Due to the high selectivity for the modeled compounds, these columns are also a good choice for GC/MS analysis. Although MS detectors can be used for resolving compounds that chromatographically coelute, it is best to minimize coelutions.

The Rtx-OPPesticides2 column is optimized for resolution of all 53 OP Pesticides and is made with a low bleed polymer. This makes the column an excellent choice for GC/MS analysis of organophosphorus pesticides. The following chromatogram shows an analysis time of <21 minutes and only 2 pairs of coeluting compounds. These coeluting compounds have different mass spectra, allowing them to be identified and quantitated.

# GC/MS analysis using Rtx-OPPesticides2 column 30m x 0.25mmID, 0.25um film

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# Compound List for Rtx-OPPesticides2 GC/MS

Oven: 80°C (0.5min) @ 12°C/min to  
280°C (15min)

Injector: 225°C splitless, hold time 1min,  
4mm single gooseneck Siltek sleeve

Detector: Agilent 5971A MSD  
full scan 50-550AMU

DT @80°C=1.44min, helium carrier

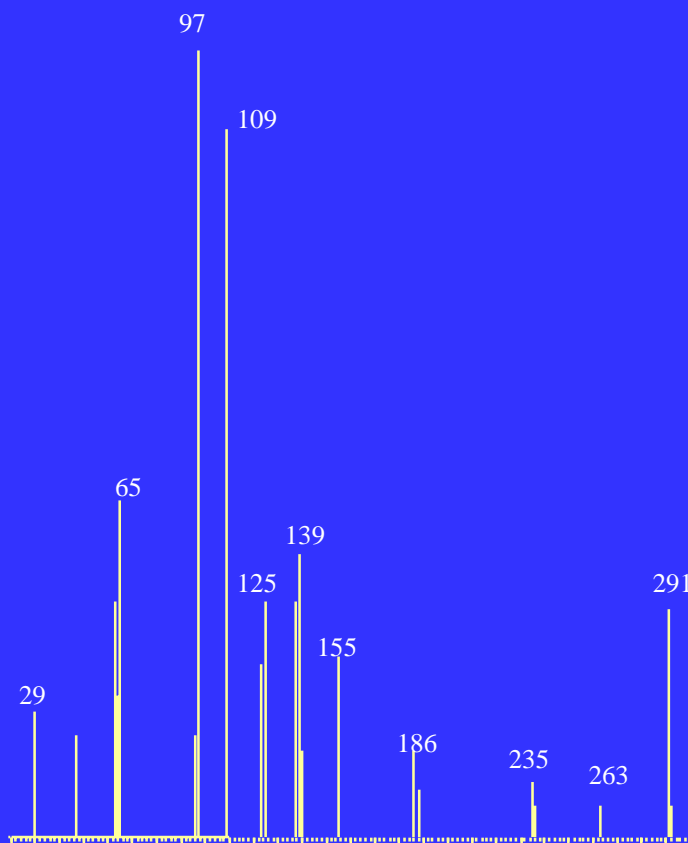
Column: Rtx-OPPesticides2, cat# 11243  
30m x 0.25mmID, 0.25µm

cpd #	compound	RT		cpd#	compound	RT
1	dichlorvos	6.81		28	aspon	13.85
2	HMPA	7.33		29	fenitrothion	13.94
3	mevinphos	8.92		30	malathion	13.99
4	trichlorfon	9.33		31	chlorpyrifos	14.10
5	TEPP	10.48		32	parathion-ethyl	14.20
6	demeton-o	10.66		33	trichloronate	14.20
7	thionazin	10.77		34	fenthion	14.24
8	TBP	10.73		35	merphos	14.39
9	ethoprop	10.93		36	chlorfenvinphos	14.85
10	naled	11.34		37	crotoxyphos	15.00
11	sulfotepp	11.43		38	stirofos	15.35
12	phorate	11.51		39	tokuthion	15.48
13	dicrotophos			40	merphos oxid prod	15.52
14	monocrotophos	11.79		41	ethion	16.42
15	demeton-s	11.88		42	fensulfothion	16.53
16	terbufos	12.18		43	bolstar	16.65
17	dimethoate	12.27		44	carbophenothion	16.80
18	diazinon	12.34		45	famphur	17.03
19	dioxathion			46	TPP	17.41
20	fonophos	12.42		47	EPN	17.92
21	disulfoton	12.57		48	phosmet	18.19
22	phosph isomer	12.67		49	leptophos	18.58
23	dichlorofenthion	13.06		50	TOCP	18.76
24	phosphamidon	13.33		51	azinphos-methyl	19.04
25	chlorpyrifos methyl	13.40		52	azinphos-ethyl	19.66
26	parathion-methyl	13.52		53	coumaphos	20.35
27	ronnel	13.55				

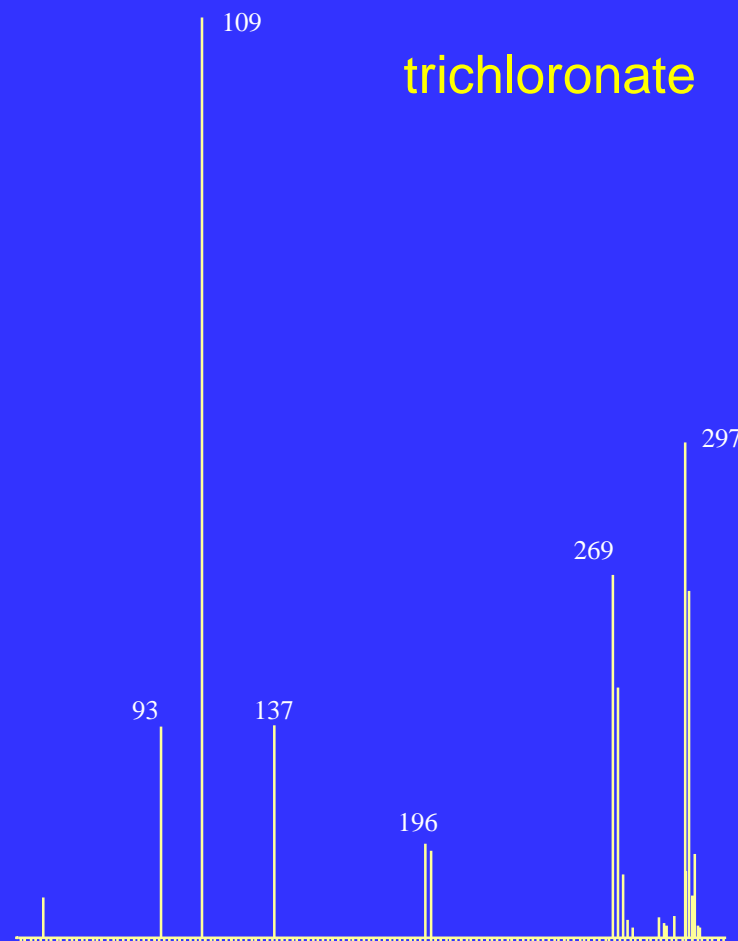
# Organophosphorus Pesticides MS Spectra

Rtx-OPPesticides2  
(30m x 0.25mm, 0.25 $\mu$ m)

parathion-ethyl

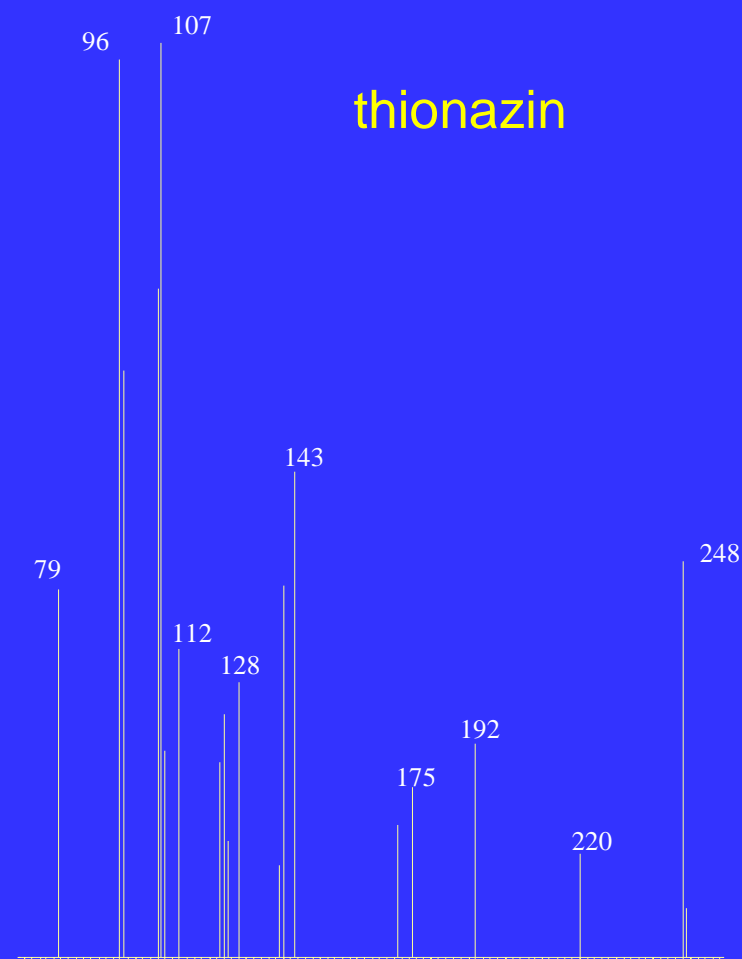
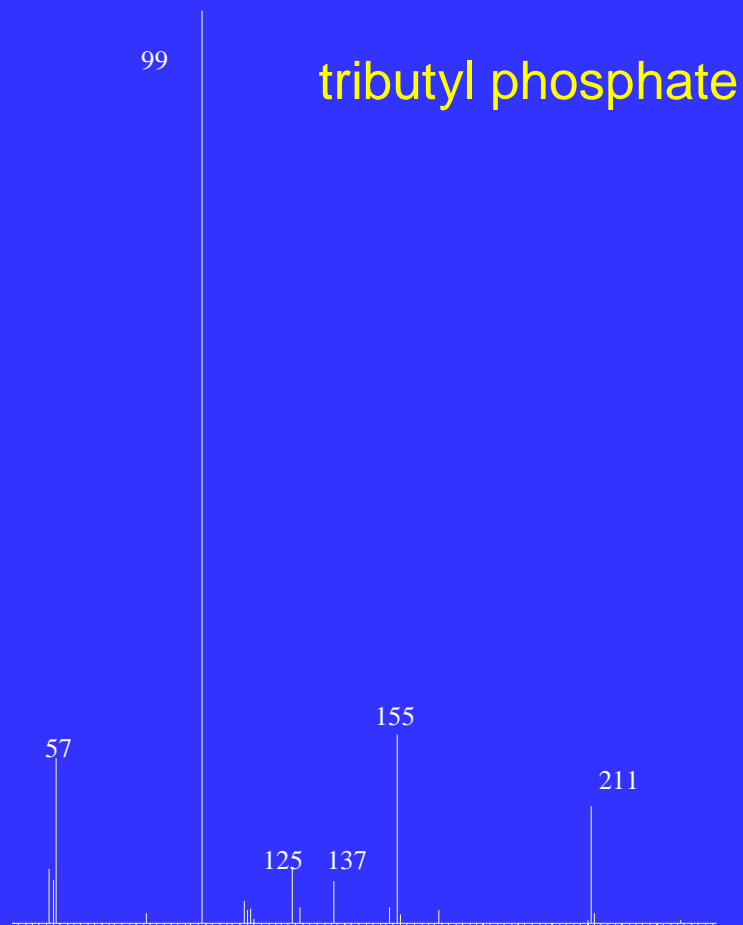


trichloronate



# Organophosphorus Pesticides MS Spectra

Rtx-OPPesticides2  
(30m x 0.25mm, 0.25 $\mu$ m)



# Summary

- The Rtx-OPPesticides and Rtx-OPPesticides2 columns are the optimal dual column pair for USEPA 8141A.
- The Rtx-OPPesticides2 column provides the best separation of organophosphorus pesticides by GC/MS due to the low bleed of this phase and separation of compounds with similar spectra.
- Using computer assisted stationary phase development, the phases have been optimized for these separations, resulting in faster analysis times.

# The Analysis of Trace Level Sulfurs in Beverage Grade CO<sub>2</sub>

Barry Burger, David Smith  
Restek Corp.  
110 Benner Circle  
Bellefonte, Pa. 16823

# Project Objective

- Develop a robust micro-packed column for the analysis of trace level sulfurs in CO<sub>2</sub> with the following critical characteristics:
  - Thermal stability (310°C)
  - Inert (sub ppb levels)
  - Low bleed (< 20pa @ 310°C)
  - High sample capacity (15,000 ng)
  - Rapid analysis
  - Column longevity

# Porous Polymer Column Optimization

- Porous polymer surface modification for the maximum degree of inertness
- Particle classification resulting in a tighter sample bandwidth
- Must resolve SO<sub>2</sub> from all other target sulfur compounds (TSC)

# Column tubing considerations

- Low ID RMS value resulting in increased theoretical plates/efficiency
- Sulfinert deactivation resulting in state-of-the-art inertness
- Flexibility, easily installs in any GC
- Unreactive to sulfurs @ 20 ppbv levels



# Advantages of the Packed Sulfinert™ column

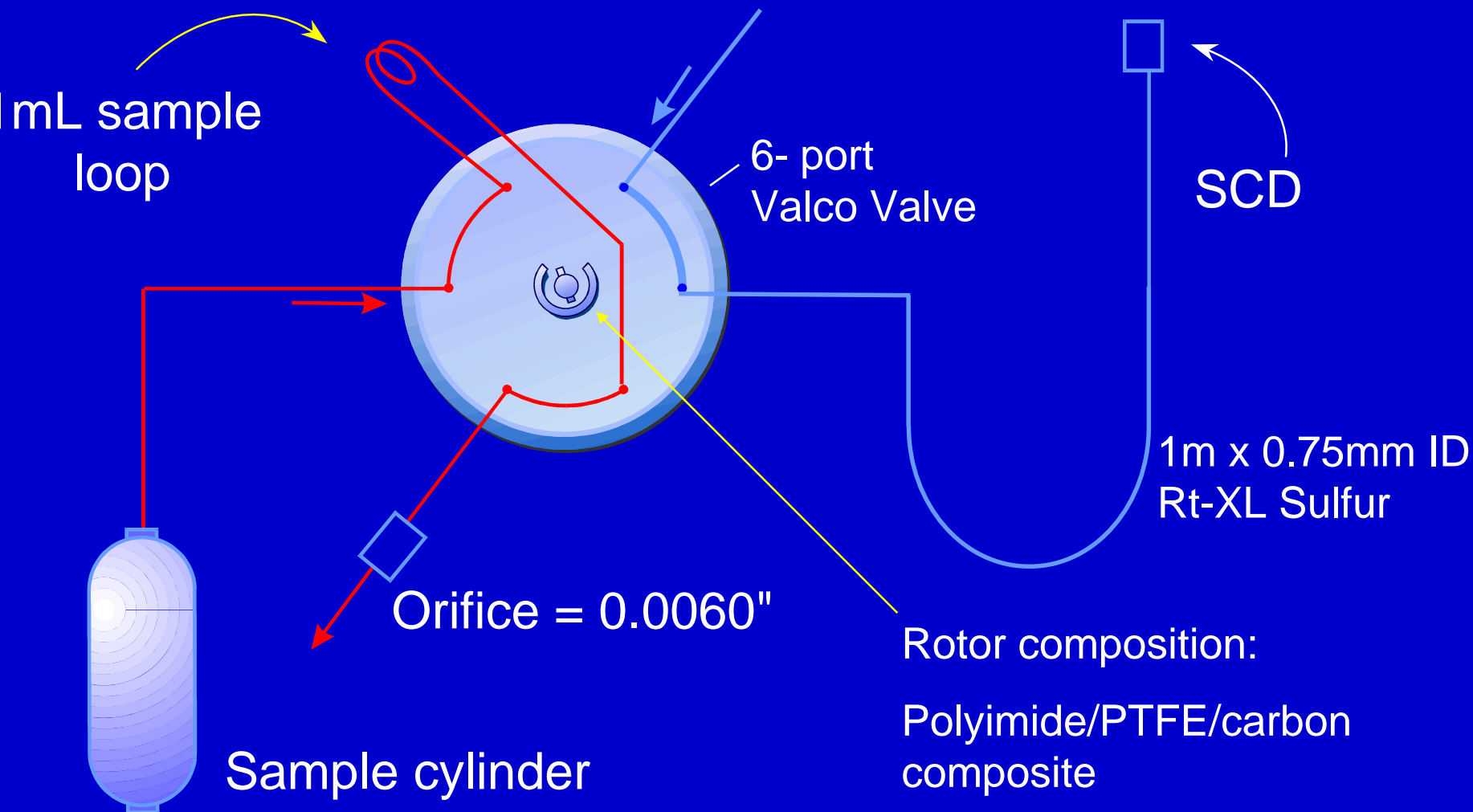
- No cryogenic oven cooling required
- Highly breakable glass column eliminated
- Critical resolution of SO<sub>2</sub>, H<sub>2</sub>S & COS
- Column has the flexibility to be installed in any model GC
- Cost effective

# GC system requirements

- Detection limit of  $< 0.02$  ppm for SO<sub>2</sub> plus the other TSC
- Method of detection: SCD, HECD, FPD or PFPD detector
- All wetted sample pathways Sulfinert™ passivated for maximum inertness

# Sulfinert™-Treated Inlet System

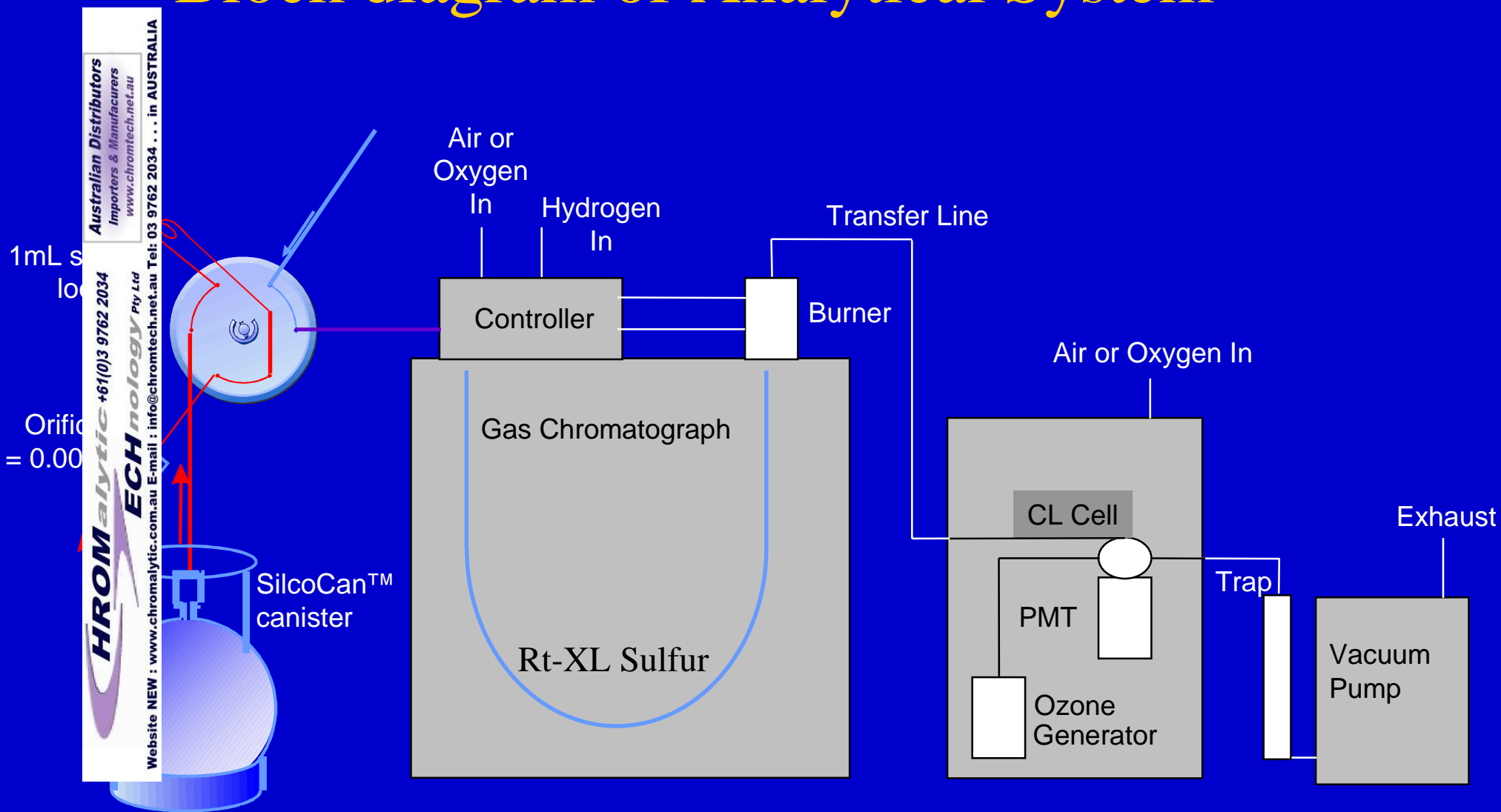
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# Chromatographic Parameters for the Rt-XL Sulfur Column

- 1 meter x 0.75mm ID micro-packed column with Sulfinert™ deactivation
- 10mL/min. helium
- 60°C > 260°C @ 15°C/min. > hold 10 min.
- GC/SCD (Sievers) Detection

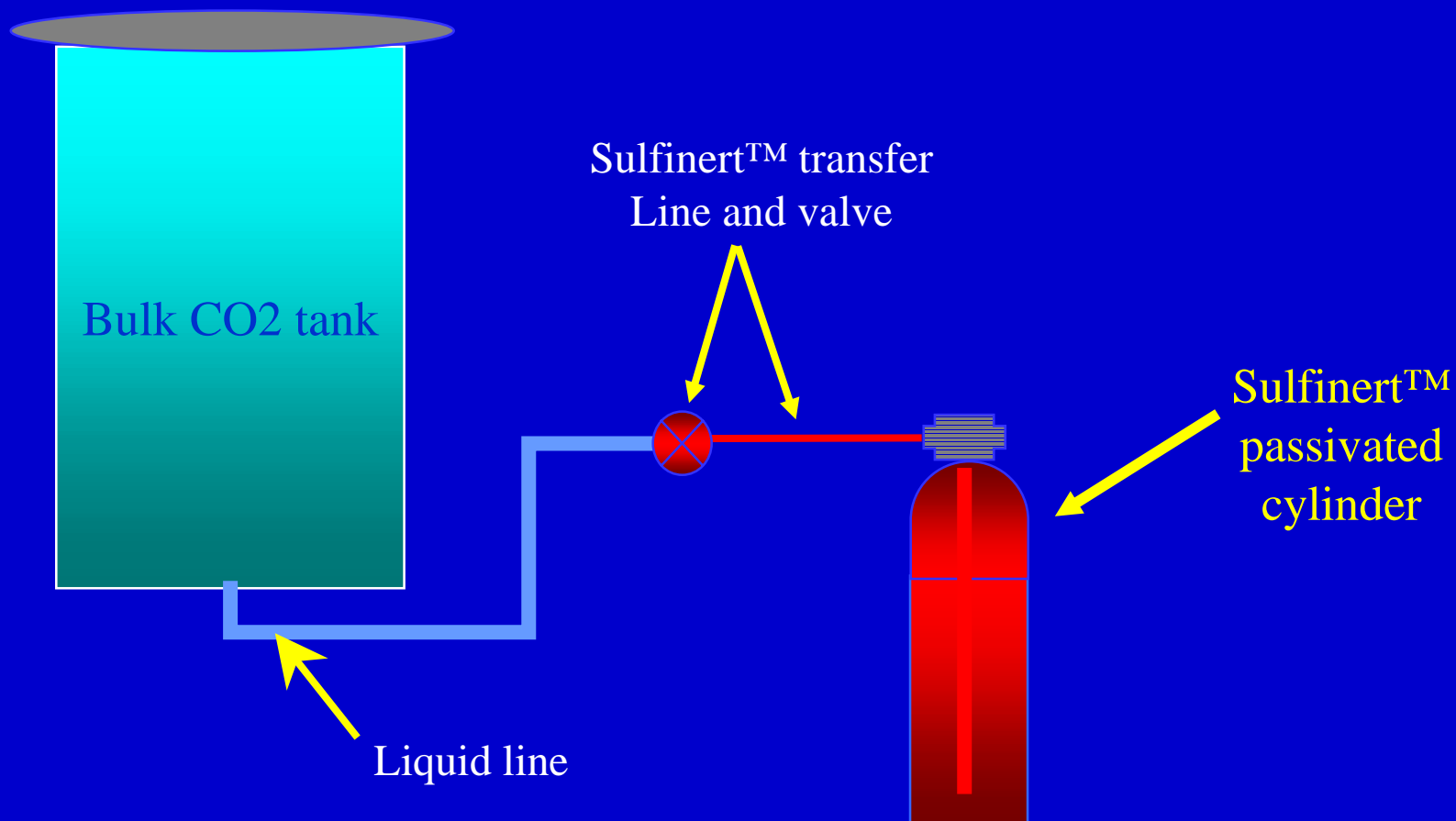
# Block diagram of Analytical System



# Sampling system integrity for CO<sub>2</sub> liquid sample acquisition

- Passivated vessel to collect the liquid CO<sub>2</sub>, conforming to the International Society of Beverage Technologists (ISBT) procedure 1.0
- Connections between the bulk CO<sub>2</sub> and the sample vessel must be passivated to prevent adsorption of the sulfur compounds
- What are the options, and how are the ISBT criteria adhered to?

# Sample Acquisition System



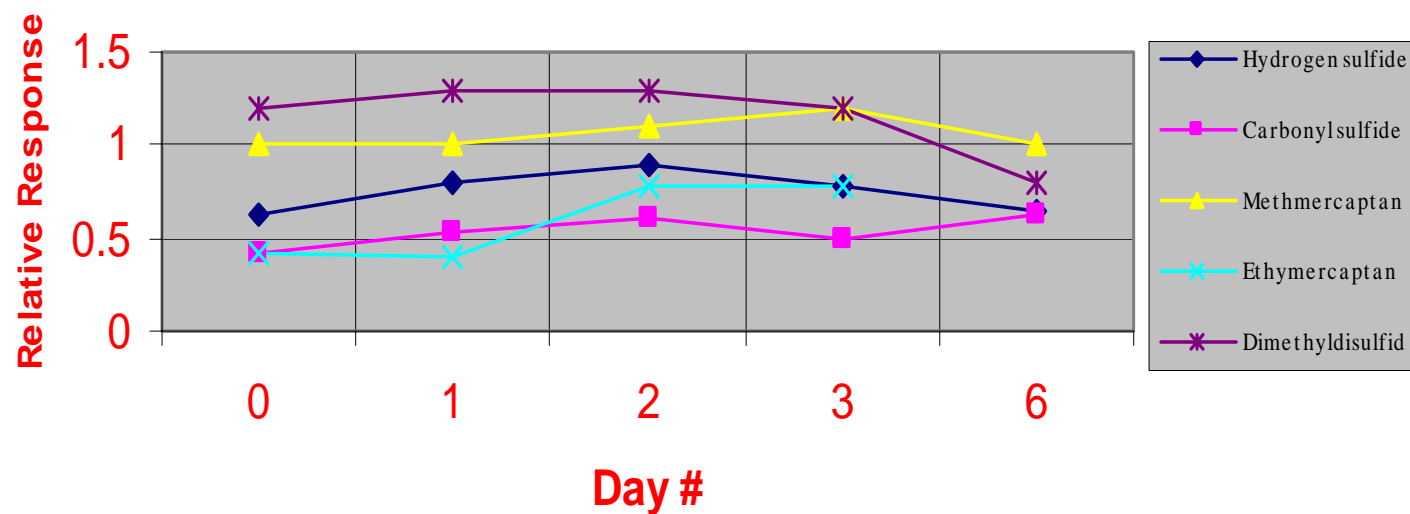
# Sulfinert™ Vessel Inertness

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## Sulfur Stability @ 1.5ppbv





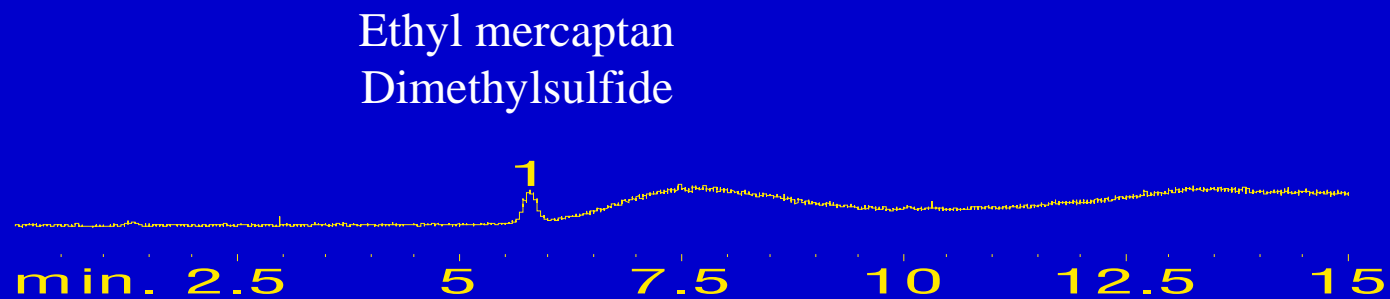
# Response Factors @ 1.5ppbv

		Day 0	Day 1	Day 2	Day 3	Day 6		
		RRF/DMS	RRF/DMS	RRF/DMS	RRF/DMS	RRF/DMS		% RSD
Hydrogen Sulfide		0.62	0.9	0.85	0.77	0.7		14.6
Carbonyl Sulfide		0.42	0.53	0.6	0.5	0.62		15.07
Methyl Mercaptan		1	1	1.1	1.2	1		8.43
Ethyl Mercaptan		0.42	0.39	0.77	0.77	0.35		39.15
Dimethyldisulfide		1.2	1.3	1.3	1.2	0.8		17.87

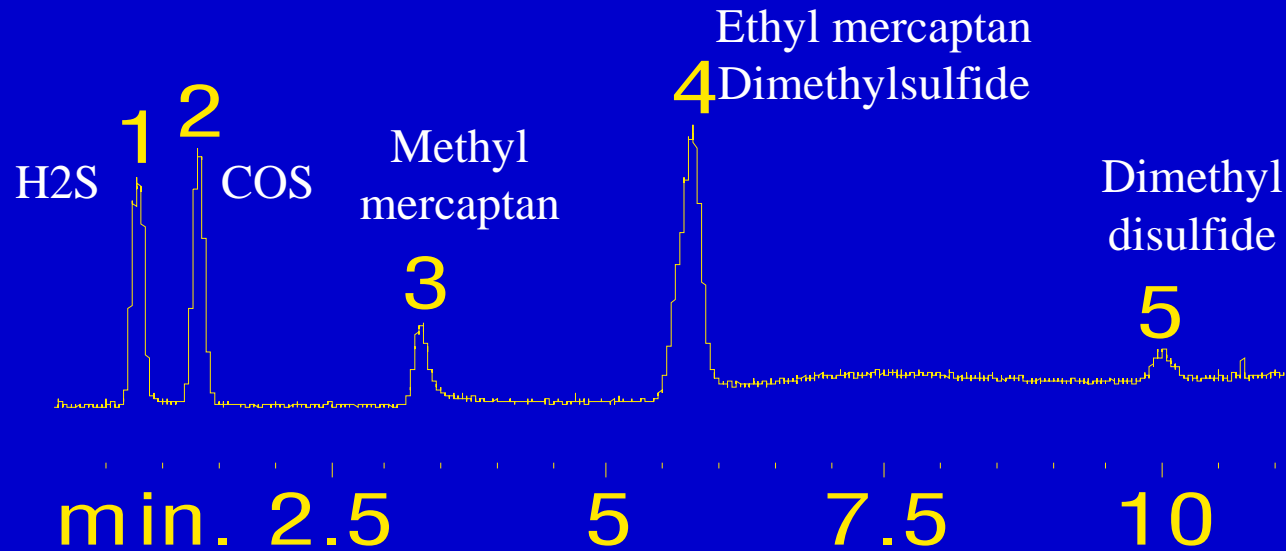
# Beverage Sampling Data

- Beverage grade CO<sub>2</sub> blank
- 20ppb sulfur standard in beverage grade CO<sub>2</sub>
- 20 ppb SO<sub>2</sub> in beverage grade CO<sub>2</sub> standard
- Headspace analysis of beer
- Analysis of a hard lemon alcoholic beverage
- Analysis of a top brand of cola

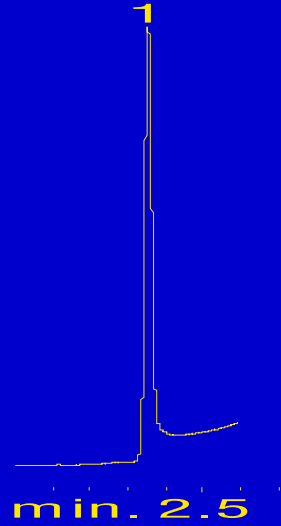
# Beverage Grade CO<sub>2</sub> blank



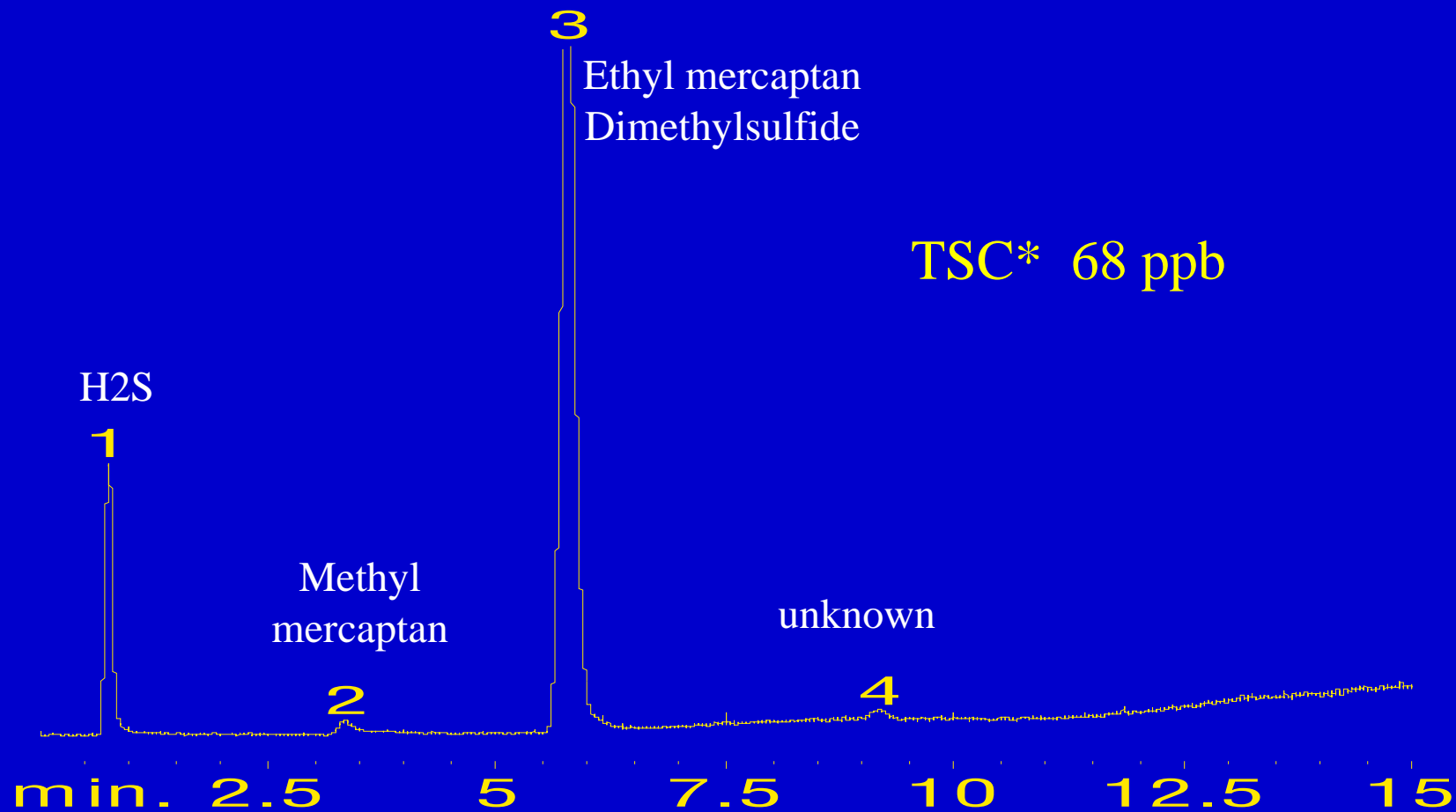
# 20 ppb Sulfur Standard in Beverage Grade CO<sub>2</sub>



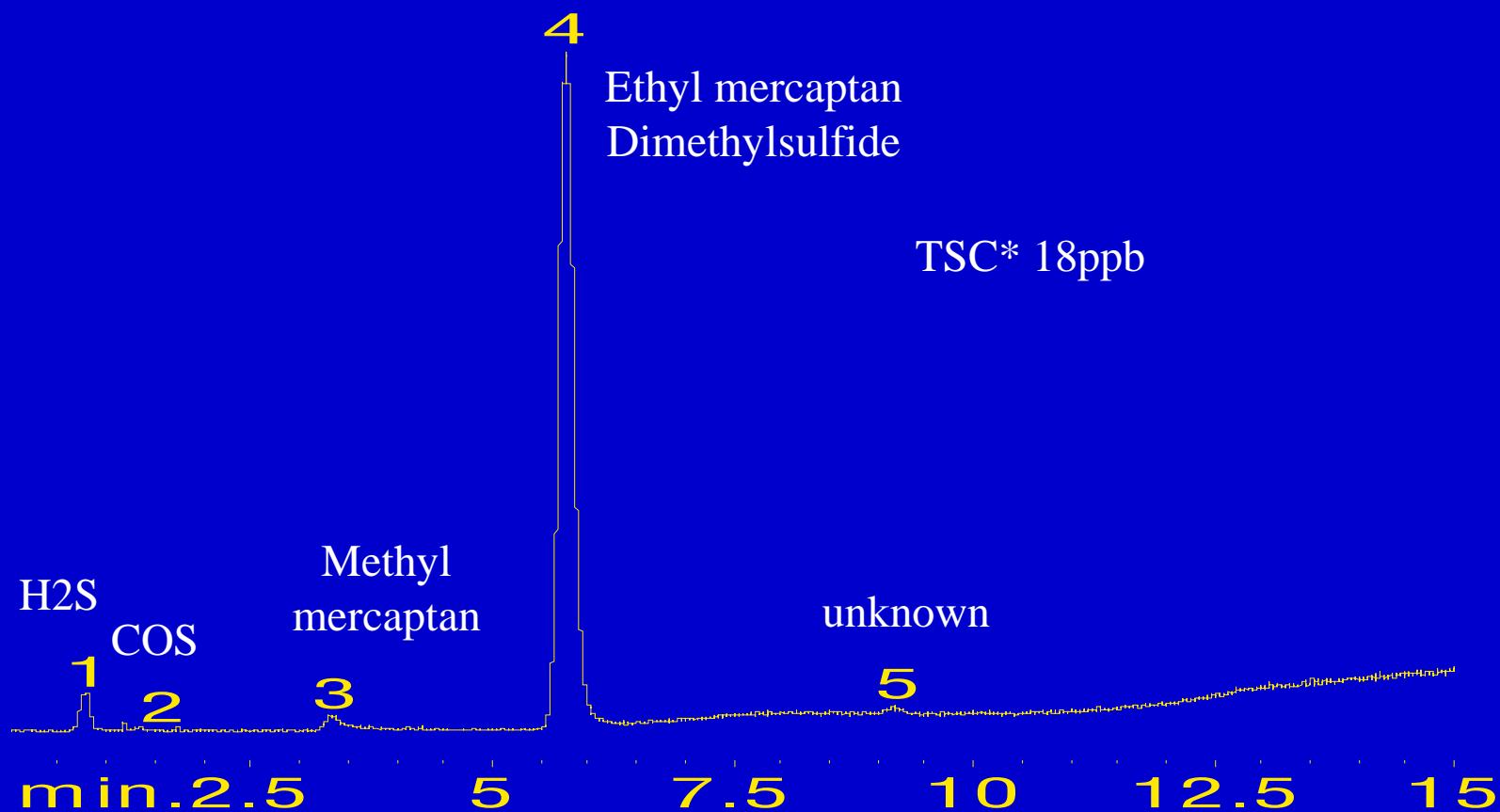
# 20 ppb SO<sub>2</sub> in CO<sub>2</sub> Standard



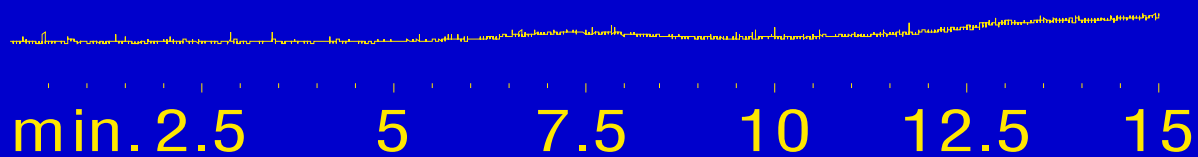
# Brand "F" Beer Headspace Sample



# Hard Lemon Beverage Headspace Sample



# Top Brand Cola    Headspace Sample





# Conclusion

- The Rt-XL Sulfur micro-packed column is a robust, low cost, rapid turn-around analytical tool for ppb level analysis of sulfur compounds.
- Sulfinert™ treatment for steel surfaces is unsurpassed for low-level ppb containment and transfer of highly reactive sulfur compounds.

# Acknowledgements

- Seivers Instrument Inc. for their cooperation.
- Lou D'agostaro of DCG Partnership 1 Ltd. of Pearland Texas for supplying us with the sulfur standards.

*For More Information:*

Author e-mail: [Barry@restekcorp.com](mailto:Barry@restekcorp.com)

Restek Corporation  
110 Benner Circle  
Bellefonte, PA 16823  
(800) 356-1688

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

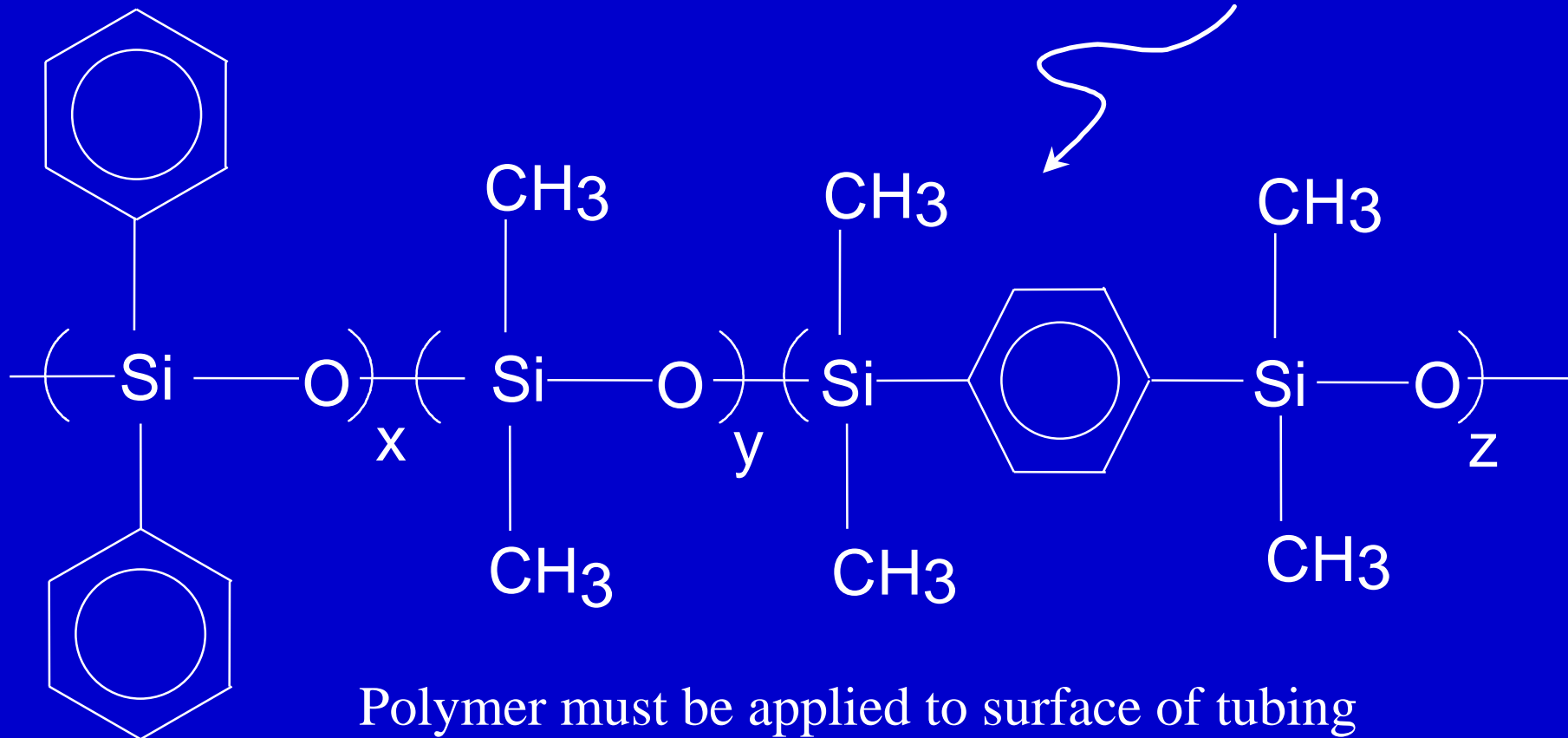
Frank L. Dorman, Dinesh V. Patwardhan ,  
Christopher S. Cox, David A. Smith, and  
Kristi Sellers

# 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

Silphenylene



Polymer must be applied to surface of tubing

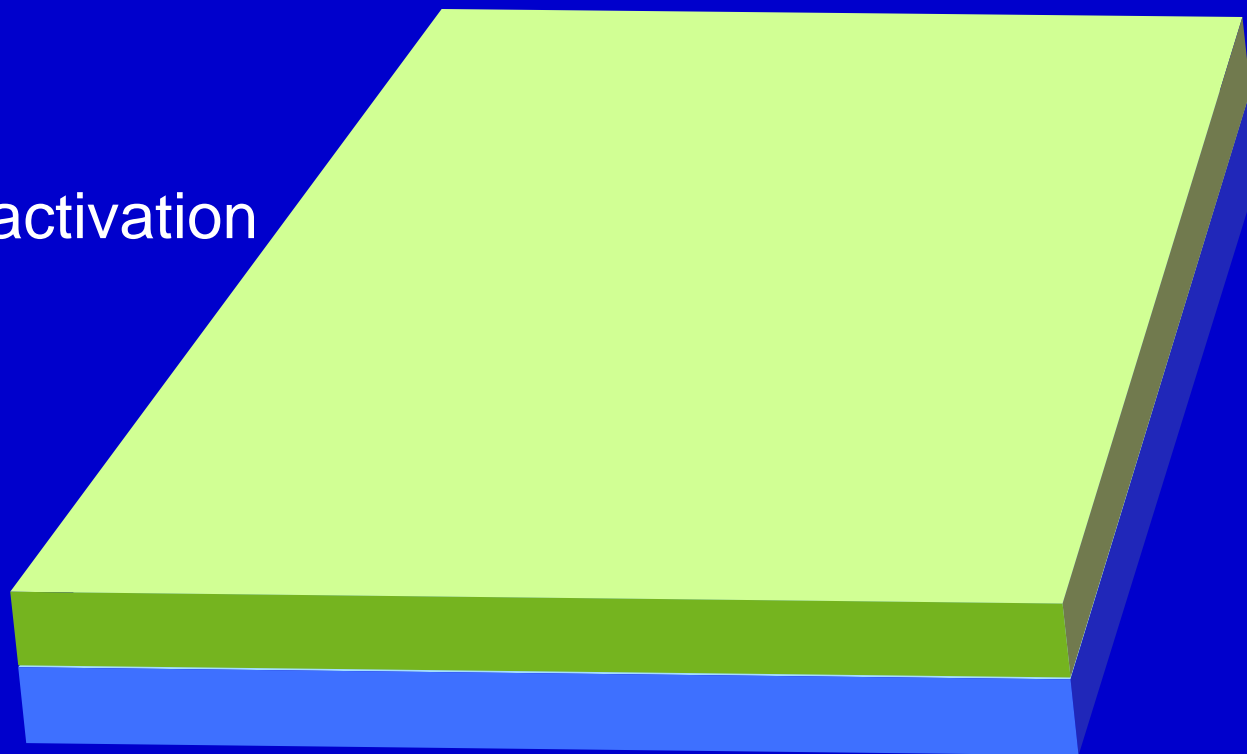
# Why Deactivate?

- “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...

deactivation

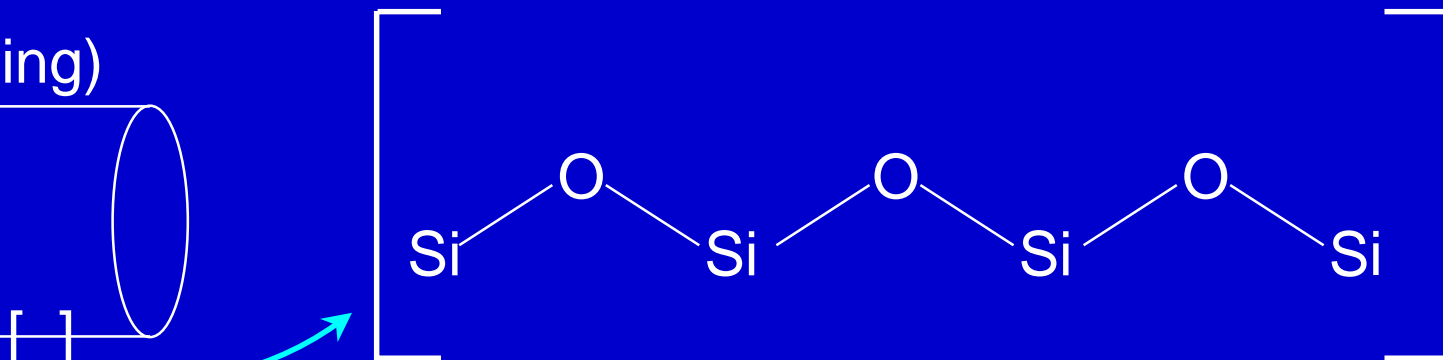
fused silica



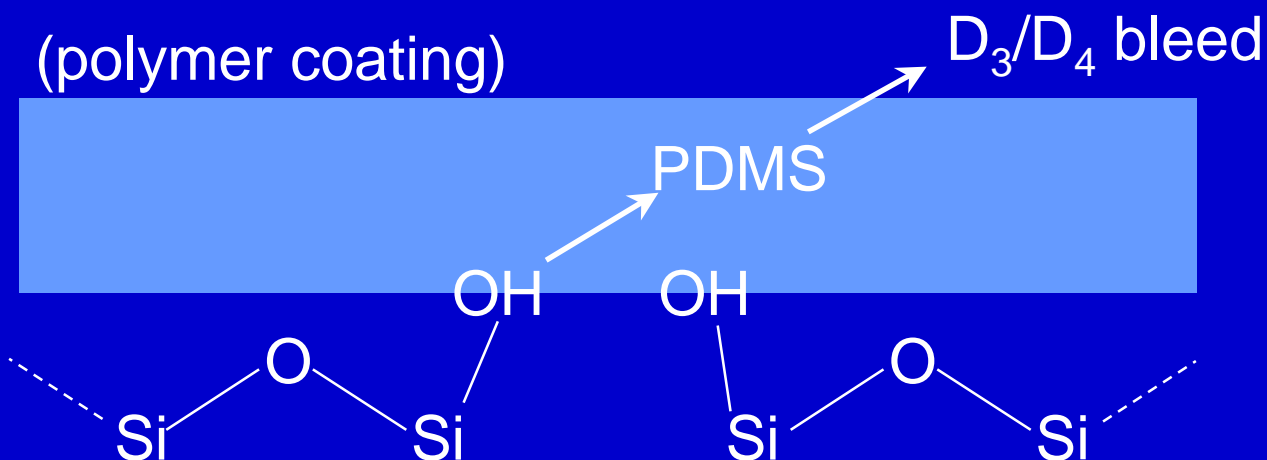
# Origins of Bleed...

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

(FS tubing)



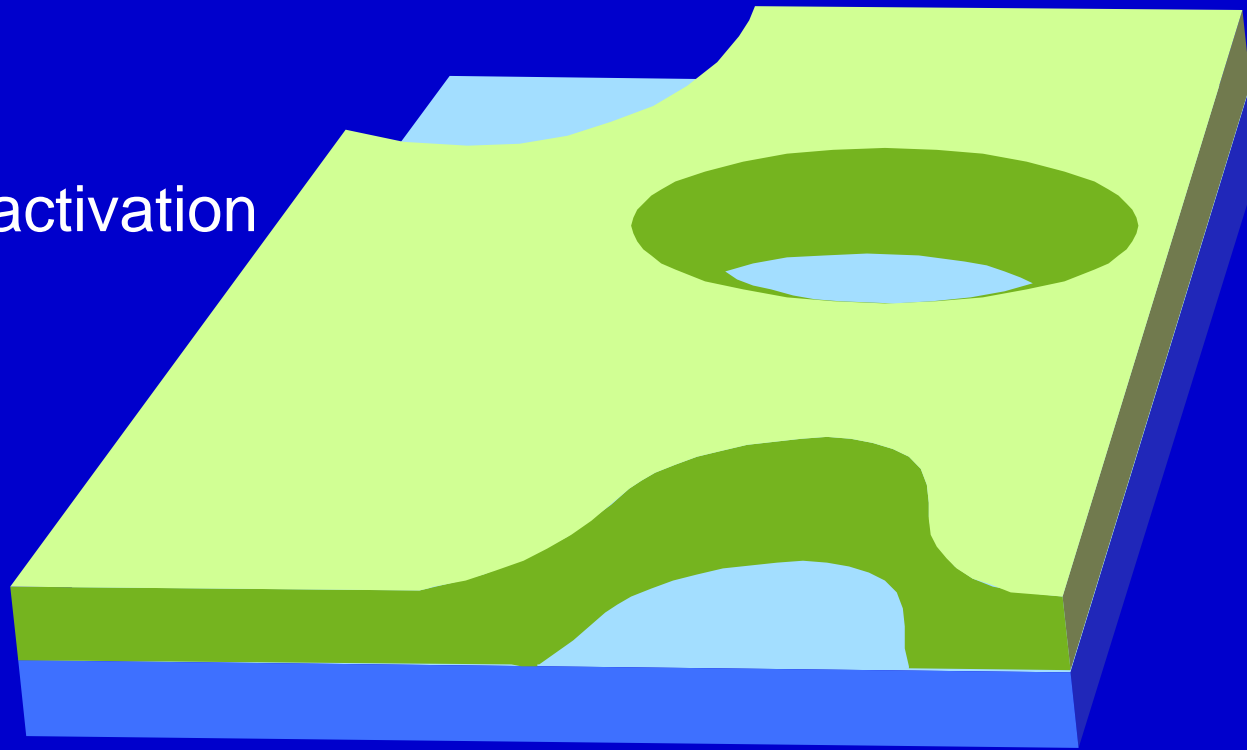
(polymer coating)





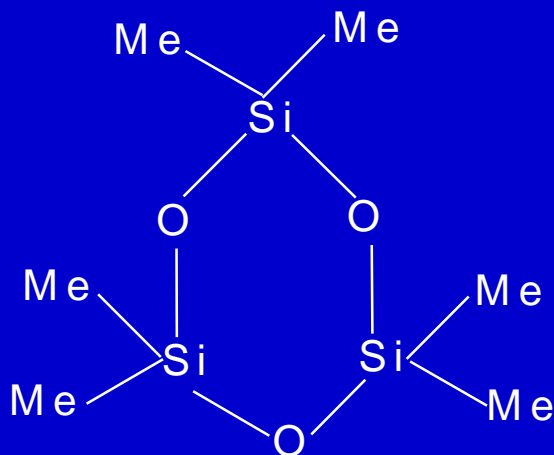
# Origin of Bleed... as well as Poor Efficiency

deactivation



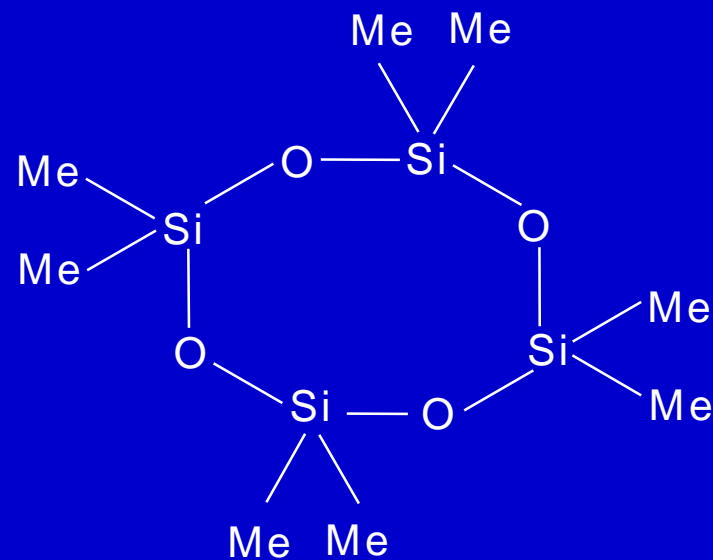
fused silica

# Typical Chemical Structure



$D_3$

$m/z = 207$



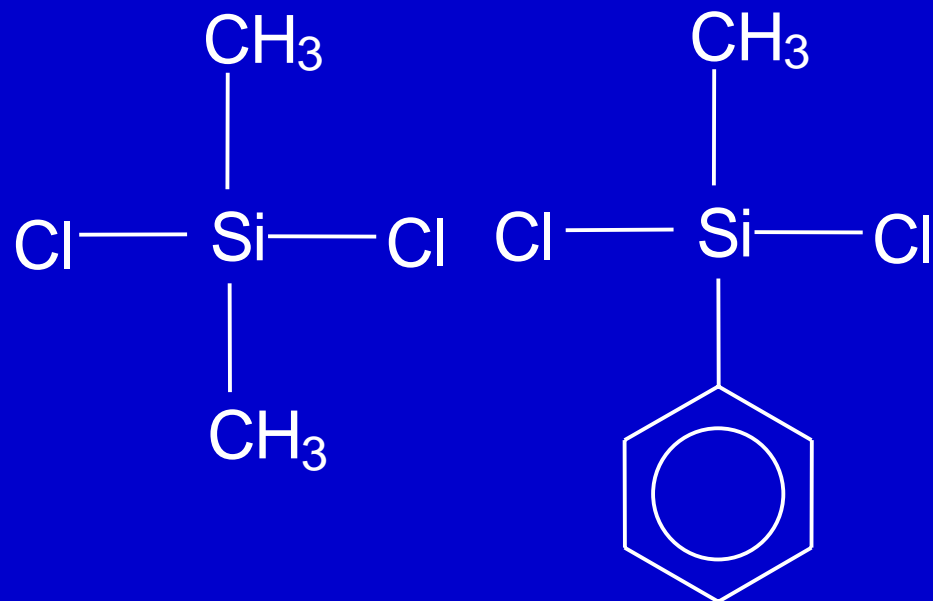
$D_4$

$m/z = 281$

# 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

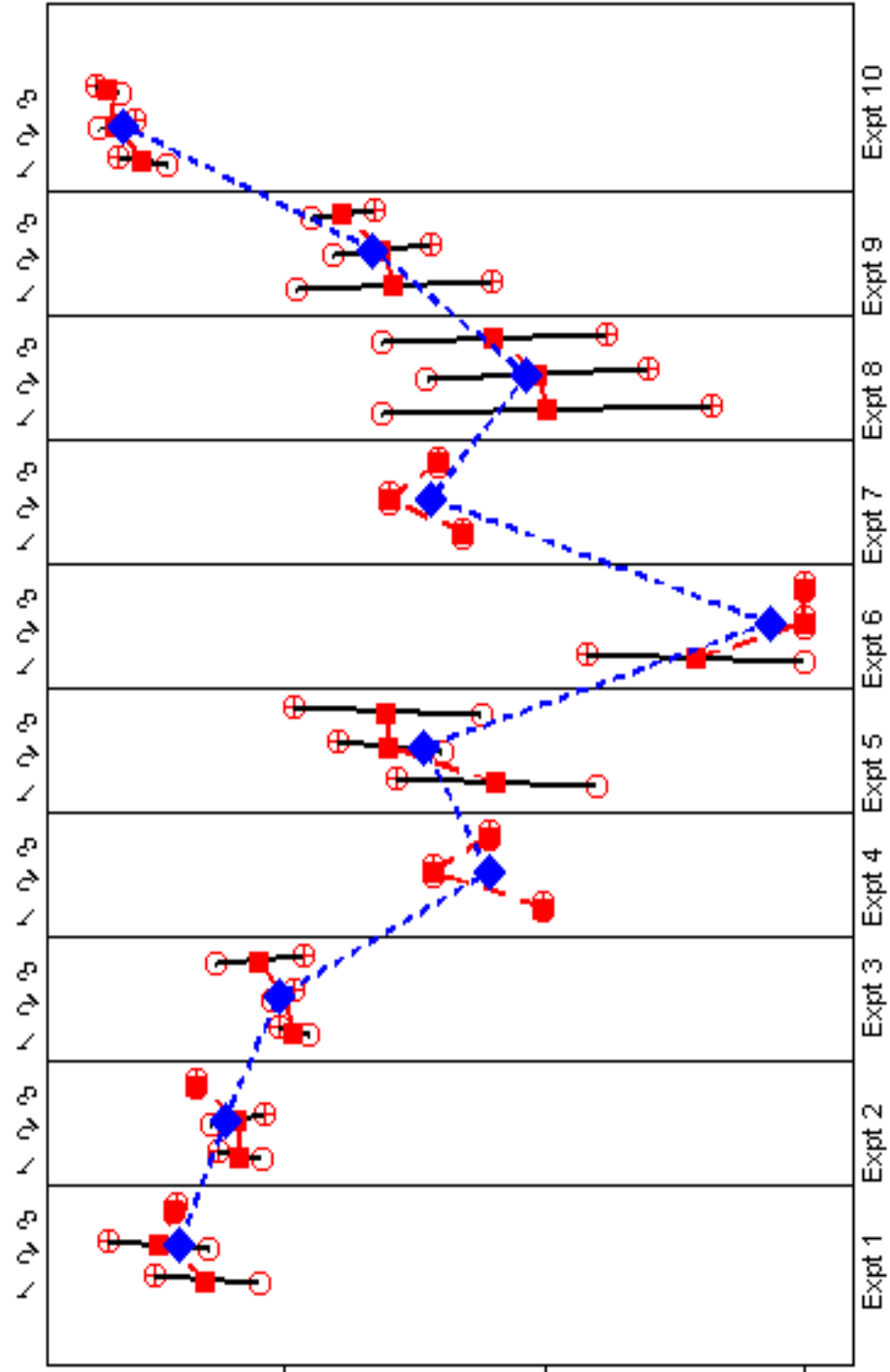
# Deactivation Chemistries Investigated

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

replication  
1  
2

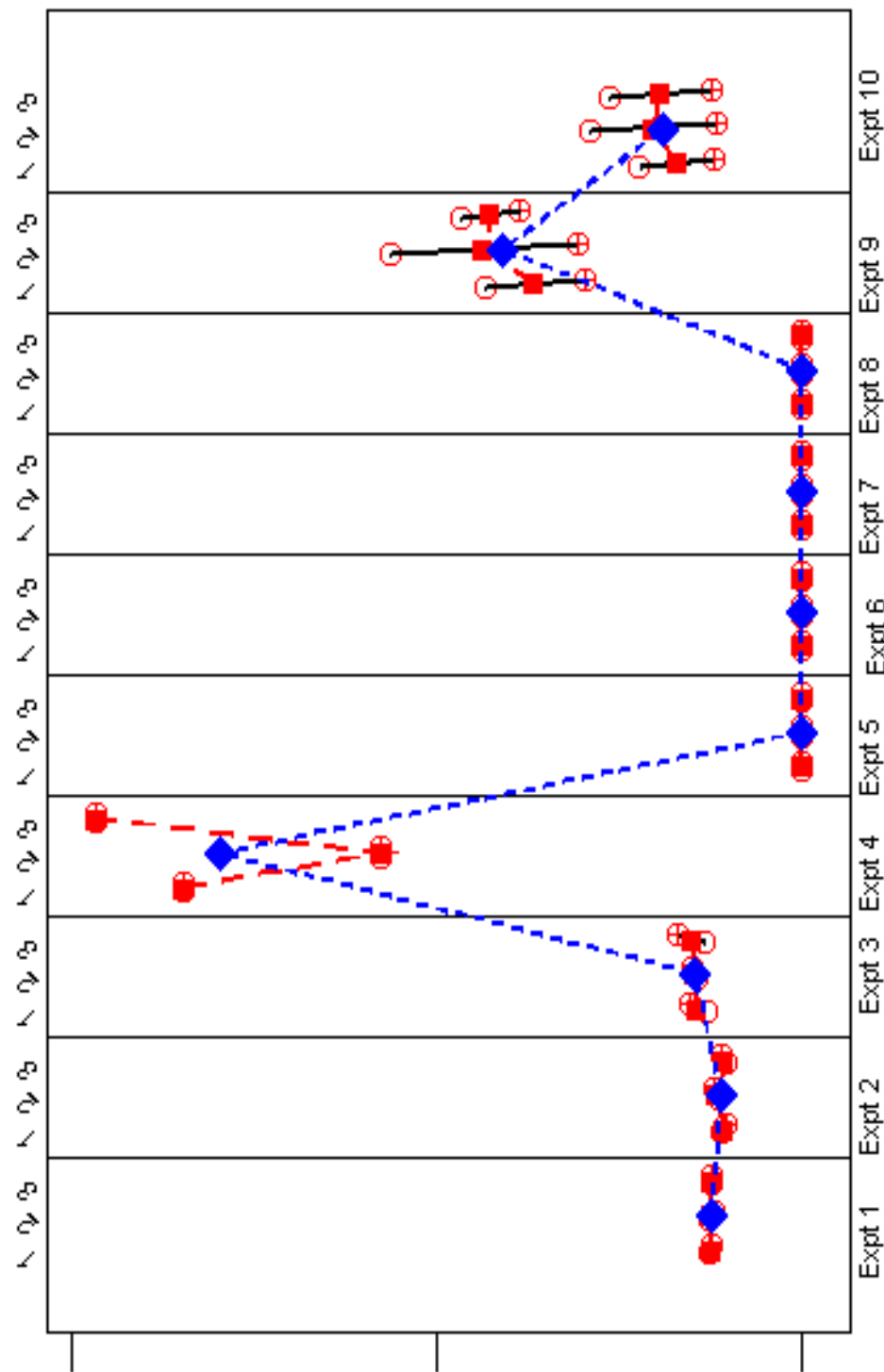


Deactivations

# Tailing Factor

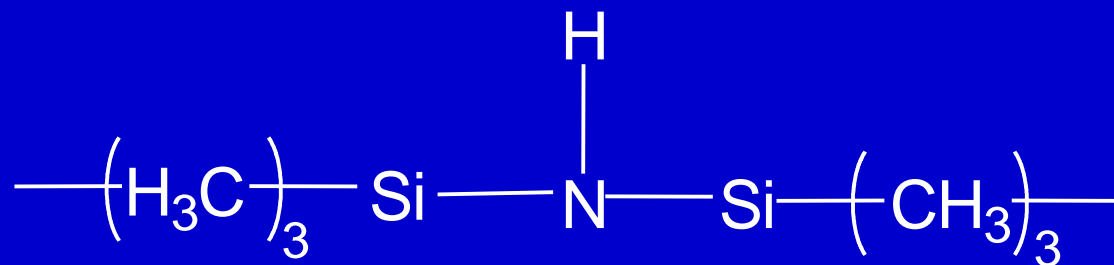
Number of Runs

replication  
1  
2



Deactivations

## Linear Disilazane



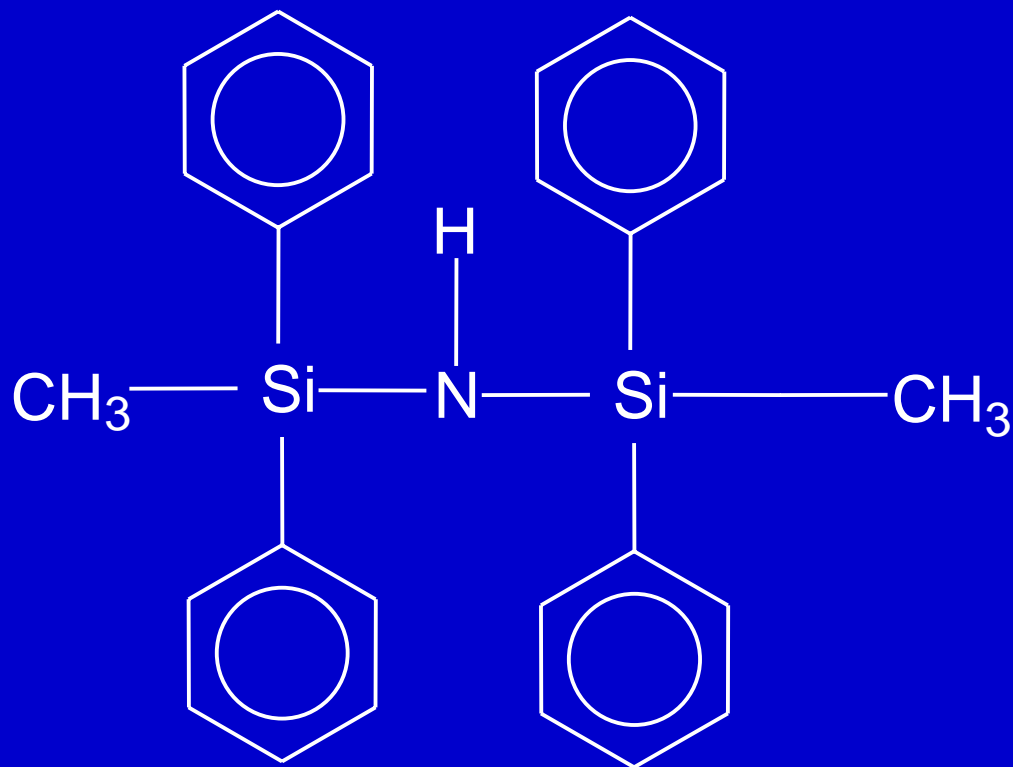
## Hexamethyldisilazane

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

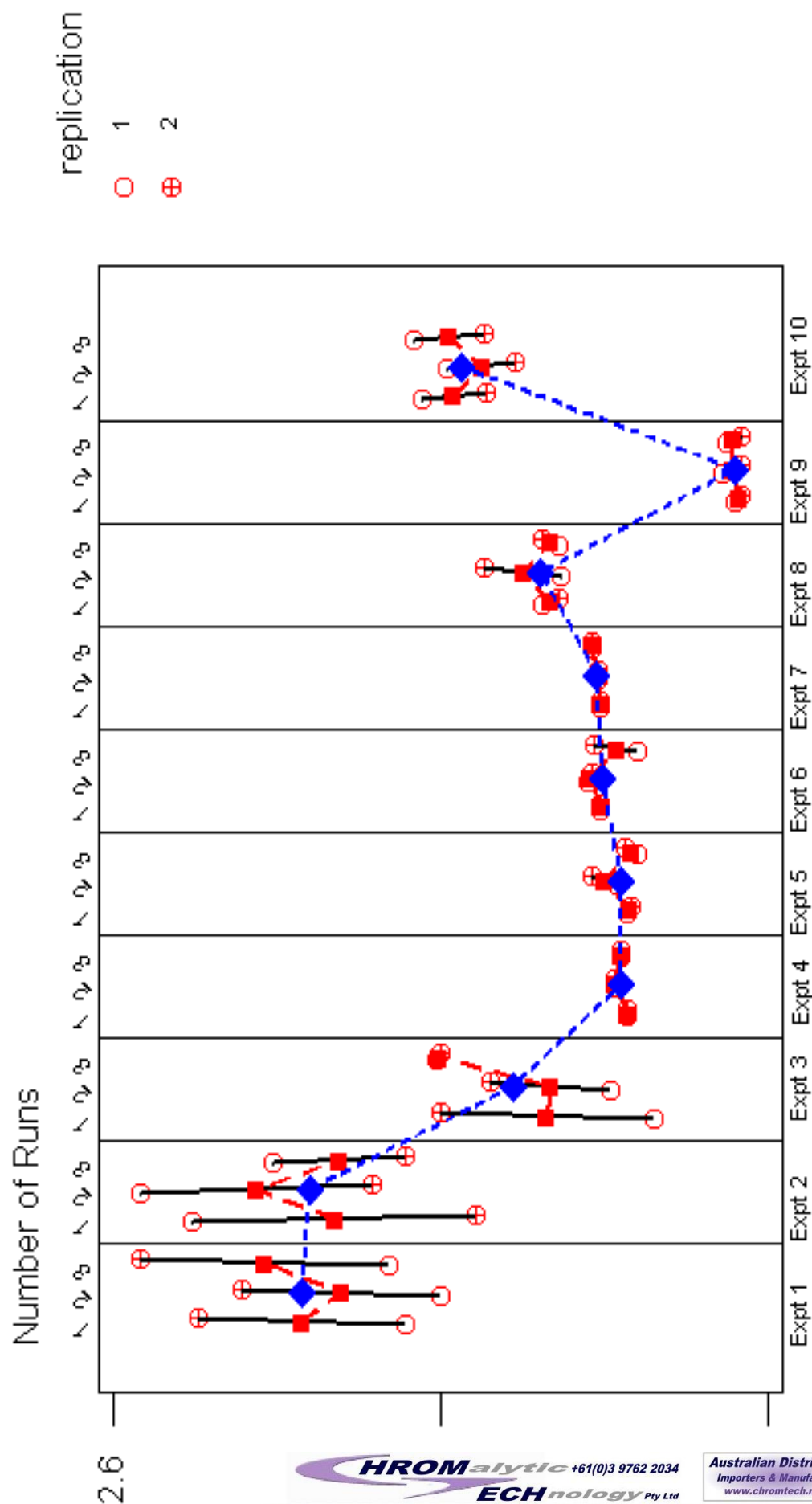


# Functionalized silazane

## Tetraphenyldimethyldisilazane



# Tailing Factor

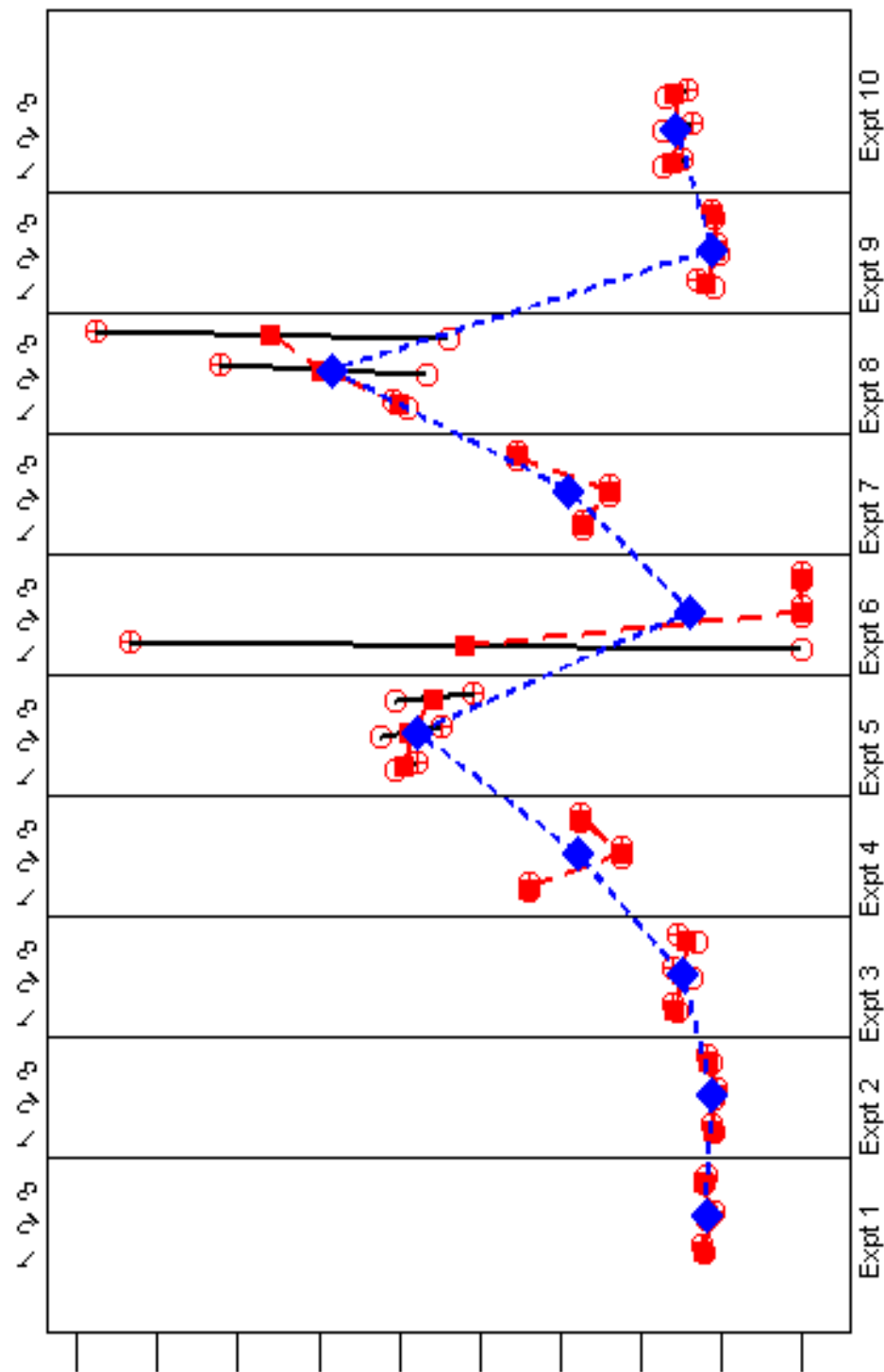


Deactivations

# Tailing Factor

Number of Runs

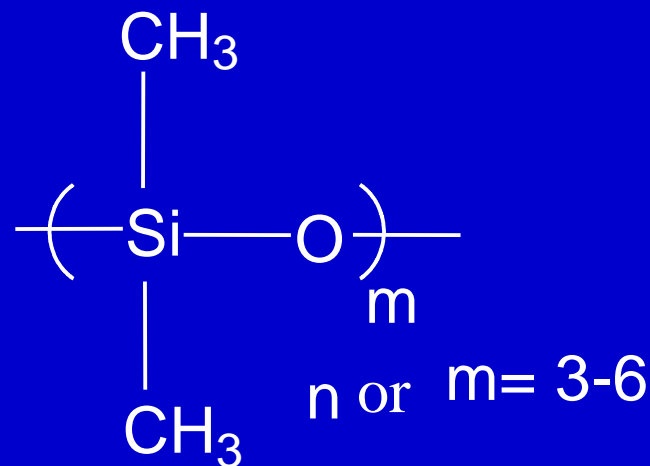
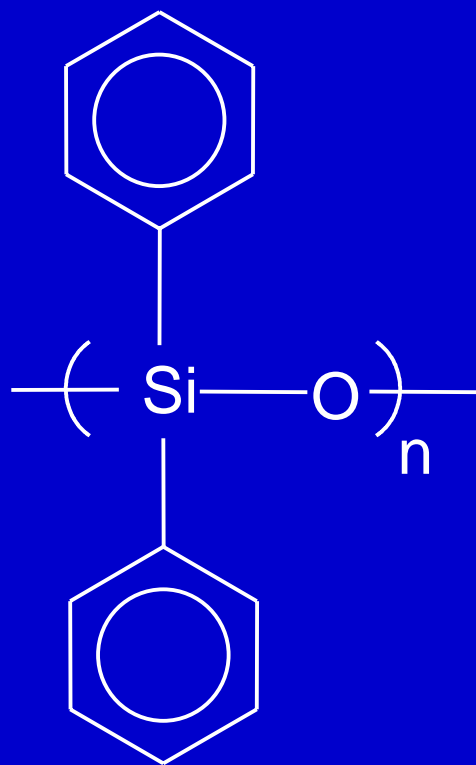
replication  
1  
2



Deactivations

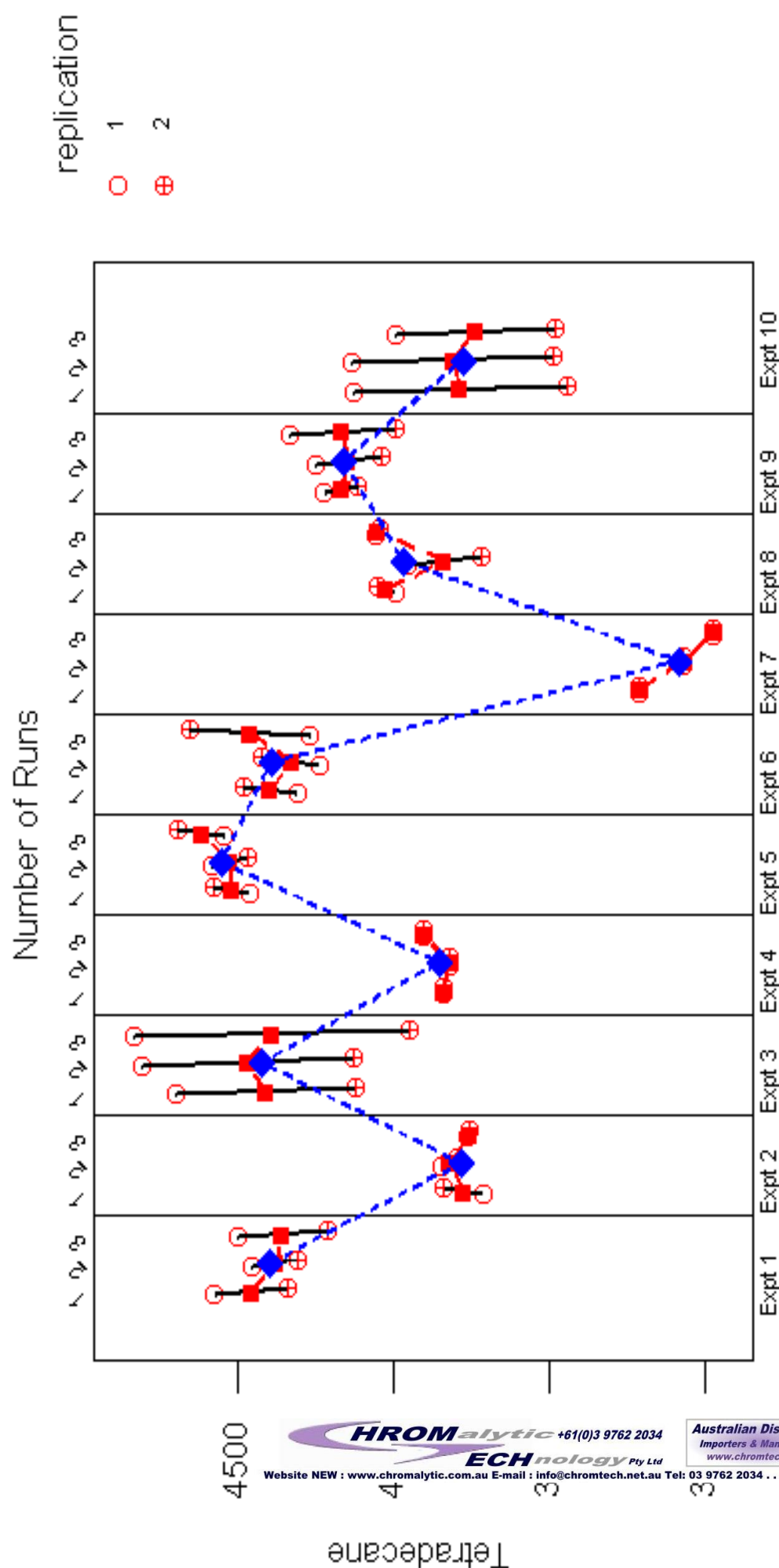
2,4-Dinitrophenol

# Polymeric Deactivation



May “cover” unreacted silanols

# Theoretical Plates / meter



Deactivations

4500

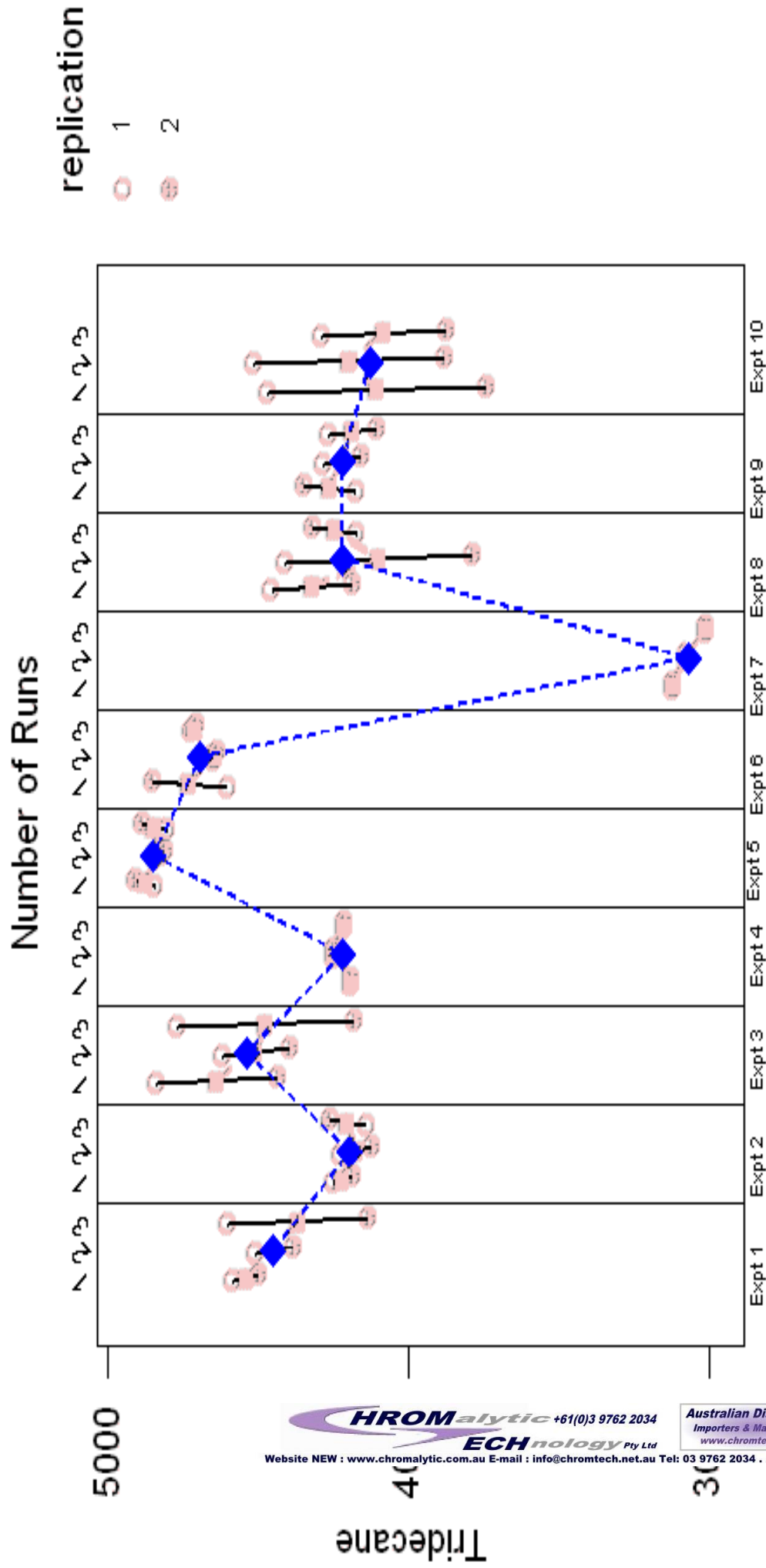
4

Tetradeccane

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# Theoretical Plates / meter



Deactivations

# 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

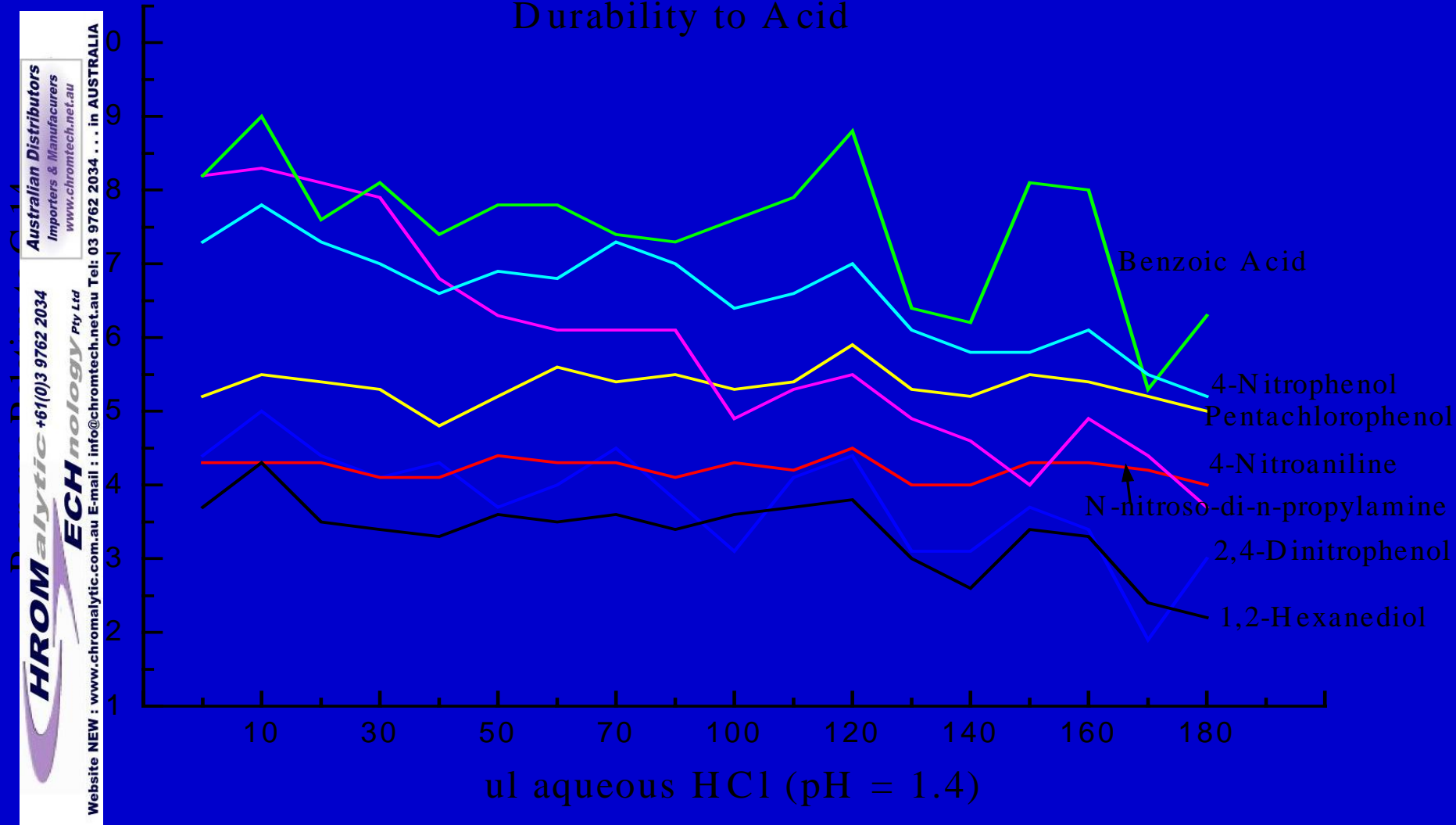


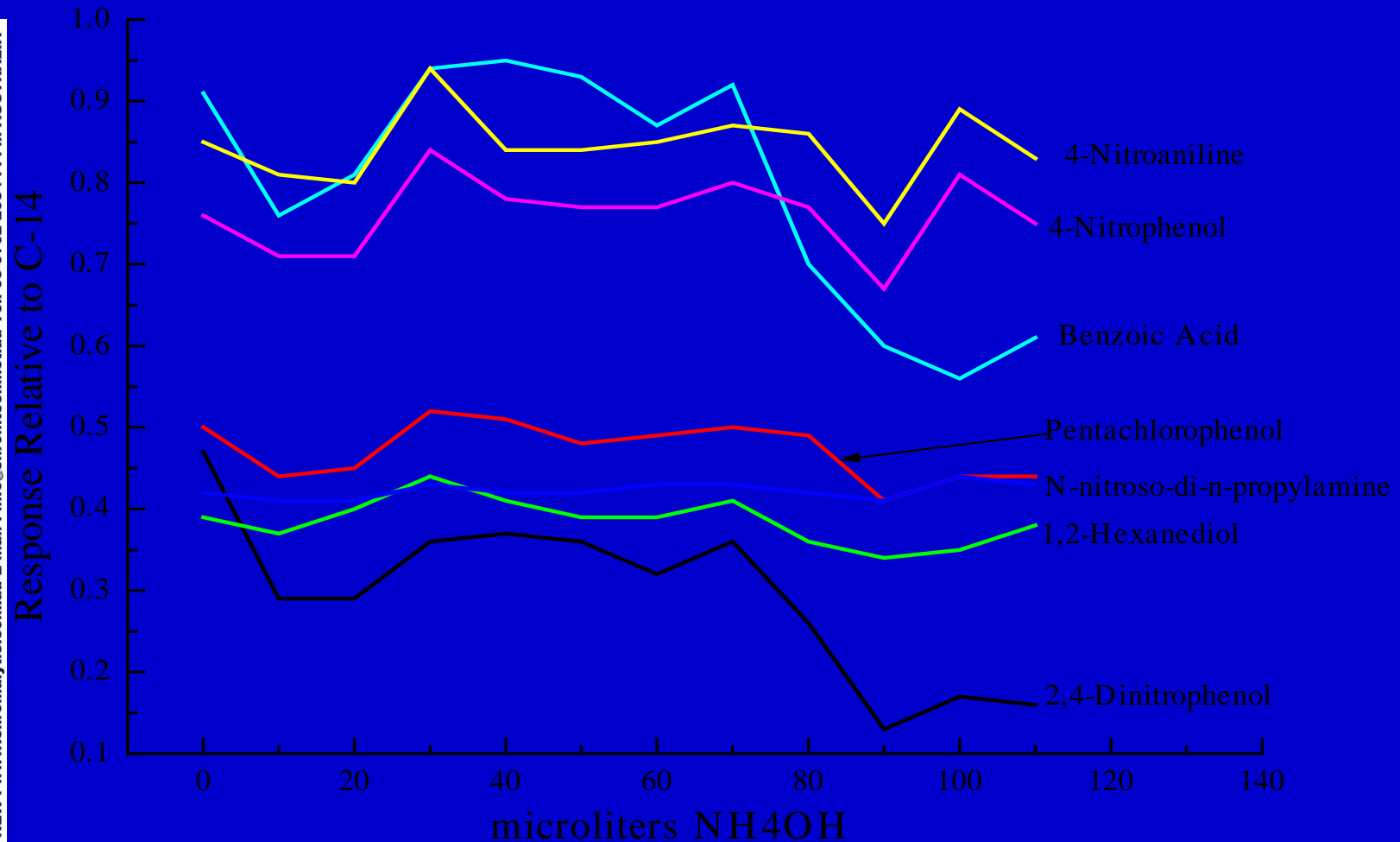
Figure 6



# Repeated injections of ammonium hydroxide on Siltek tubing

## Durability to pH 10.1

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**Figure 7**

# Guard Column Bleed Comparison at 330C

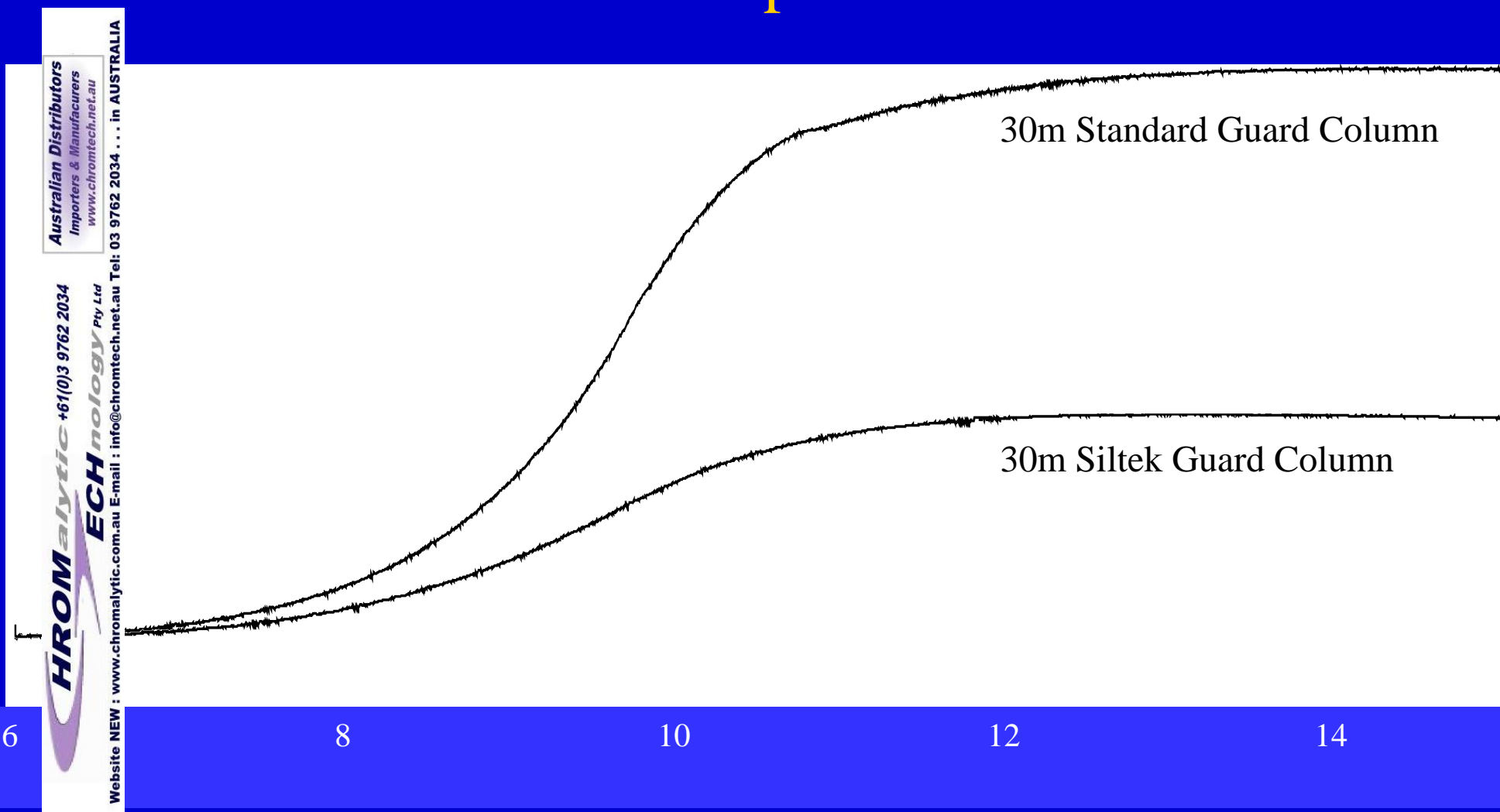
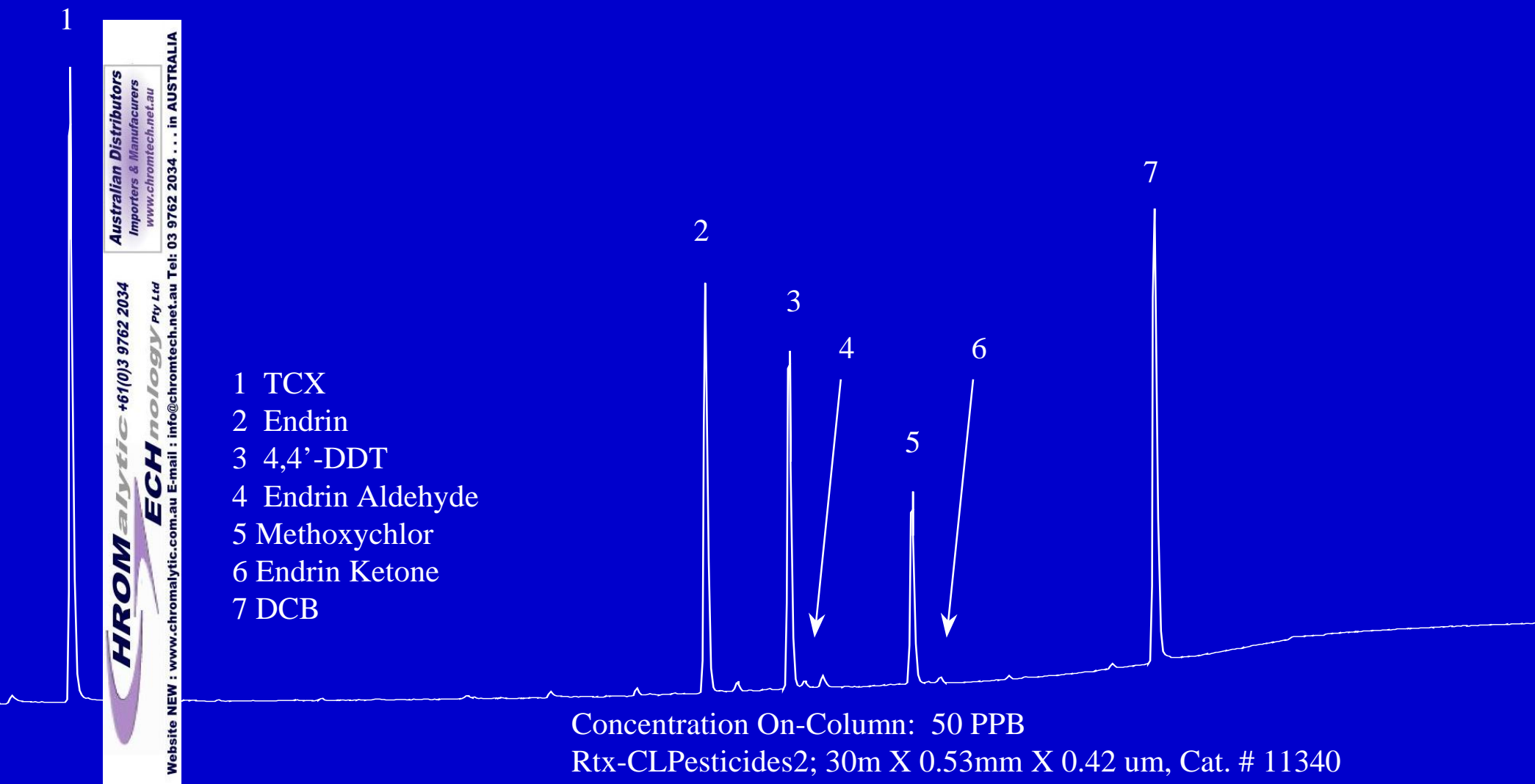


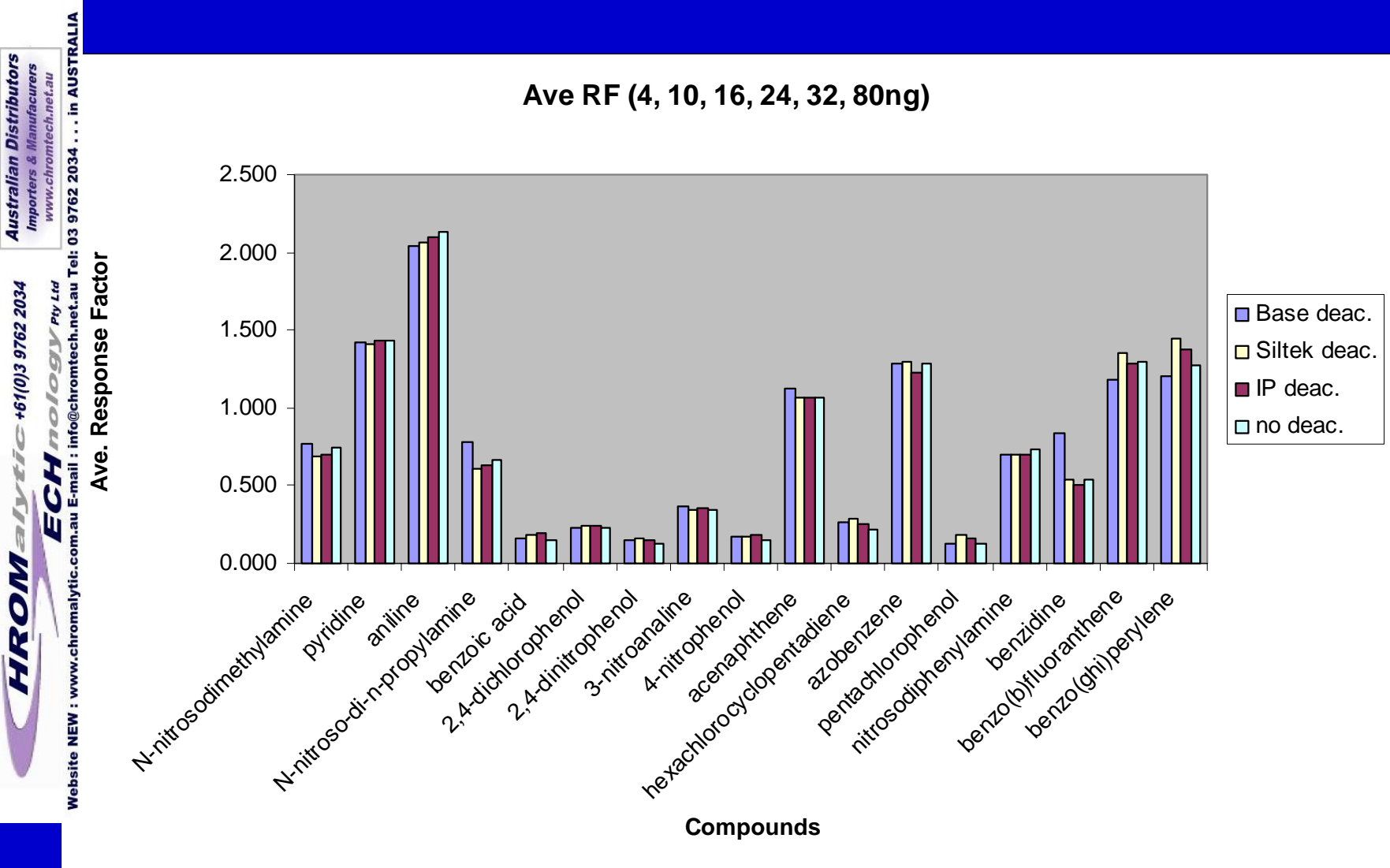
Figure 8

# Endrin Breakdown on a Siltek Deactivated Uniliner measures 1%



**Figure 3**

**Figure 2. Average Response Factors for key semivolatile components:**



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

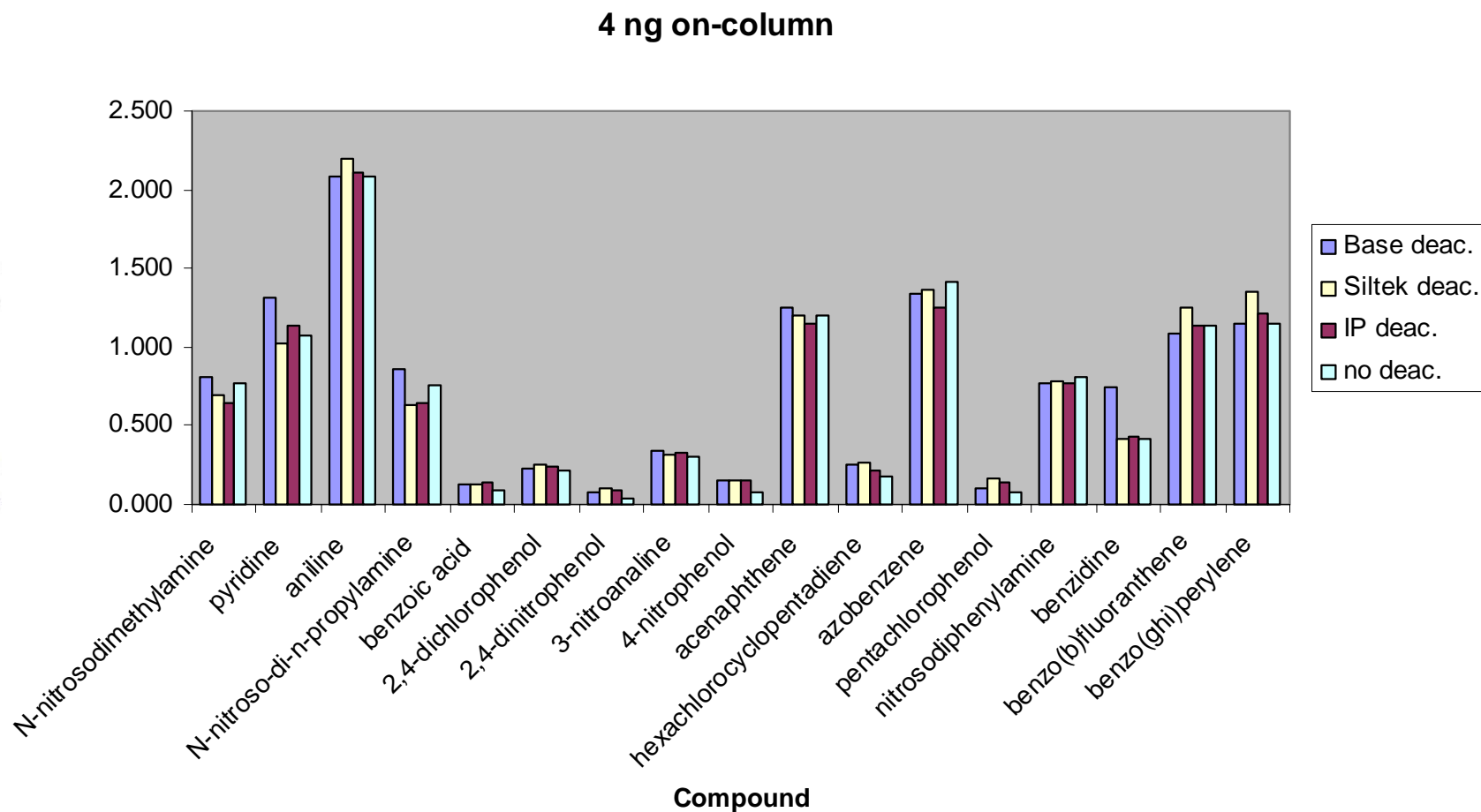
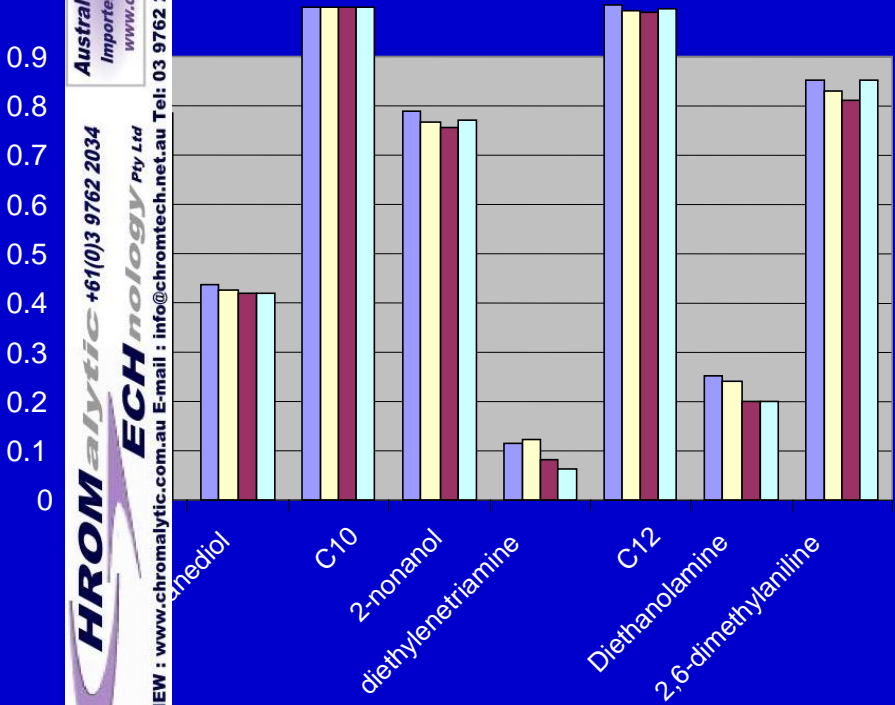
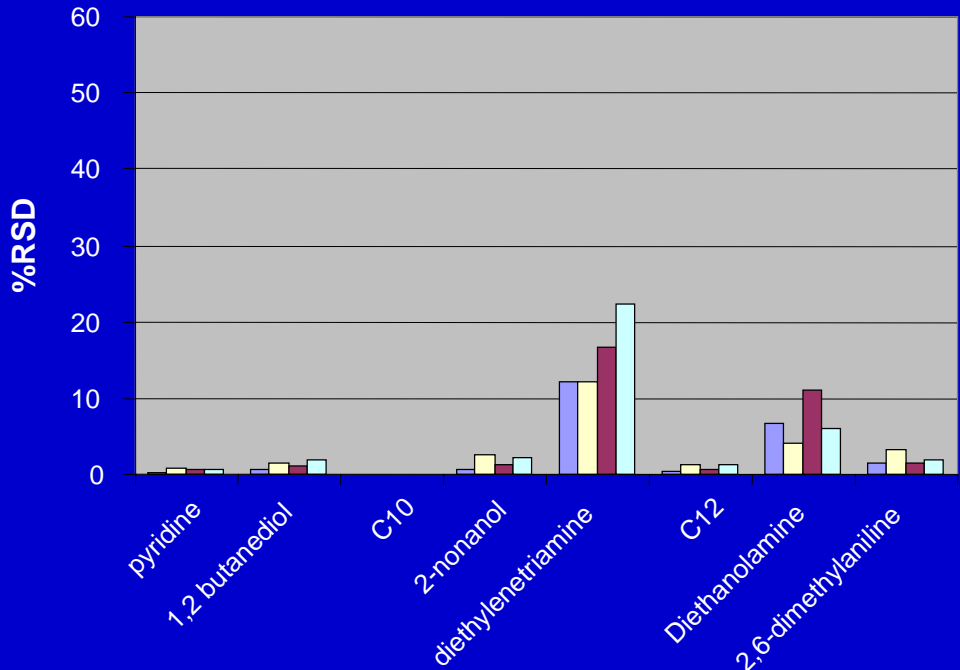


Figure 5A-B. Results for Amine Evaluation, Injections 2-6

A. Large Response Factors for Injections 2-6

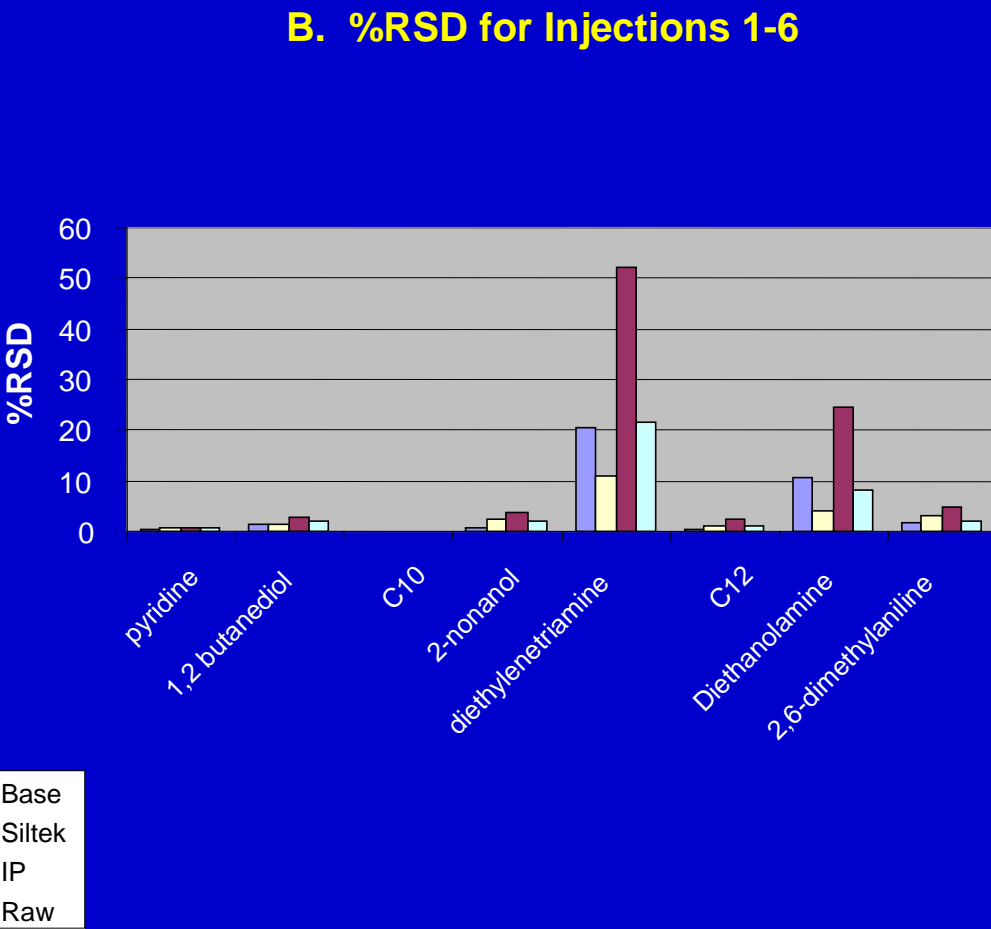
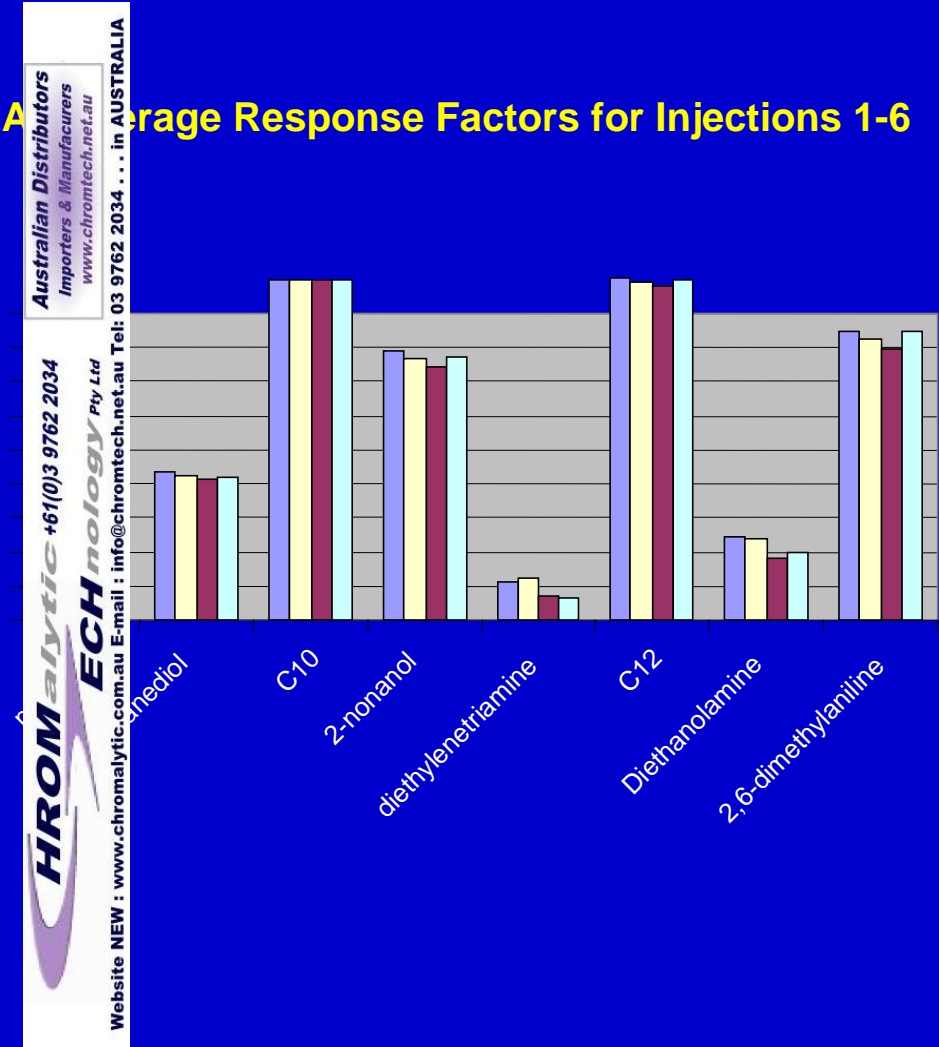


B. %RSD for Injections 2-6



Base  
Siltek  
IP  
Raw

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



				C14					
	diol	nitrosamin	benzacid	counts (k)	DNP	NP	nitroanil	PCP	Carbazole
petitor 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
petitor 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
ek 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
	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...

# Low Cost Solution for Accelerating Gas Chromatographic Separations

Frank L. Dorman, Stephen J. MacDonald,  
Gary Barone, Mike Goss, and Brad Rightnour

# Desires of GC Analysts

- Higher Sample Throughput
  - Lowers cost/sample
  - Increases sample capacity
  - Fewer instruments to accomplish same workload
- Better Resolution
  - Can allow for shorter run times
  - Improves quantitation
  - Can allow for analysis of very complex matrices

# Methods to Improve Speed and/or Resolution “high-end” technology

- Fast GC/Flash GC
  - Short, narrow I.d. columns
  - Ballistic heating (resistive, microwave)
- Multicolumn GC
  - Bertsch, Guichon, Giddings
- Comprehensive 2D-GC
  - Begun by John Phillips – Southern Illinois Univ.
- Stop-Flow GC
  - Richard Sacks – Univ. of Michigan

# Methods to Improve Speed and/or Resolution “lower-end” technology

- Tuning Stationary Phase Selectivity
  - Design column to achieve specific separation
  - Users can send retention data for optimization
- Physical Parameter Optimization
  - Pro EZ-GC Software allows user optimization
- Hardware Modification
  - GC Racer allows common existing instrumentation to achieve increased temperature ramp rates

# “Fast” GC Techniques

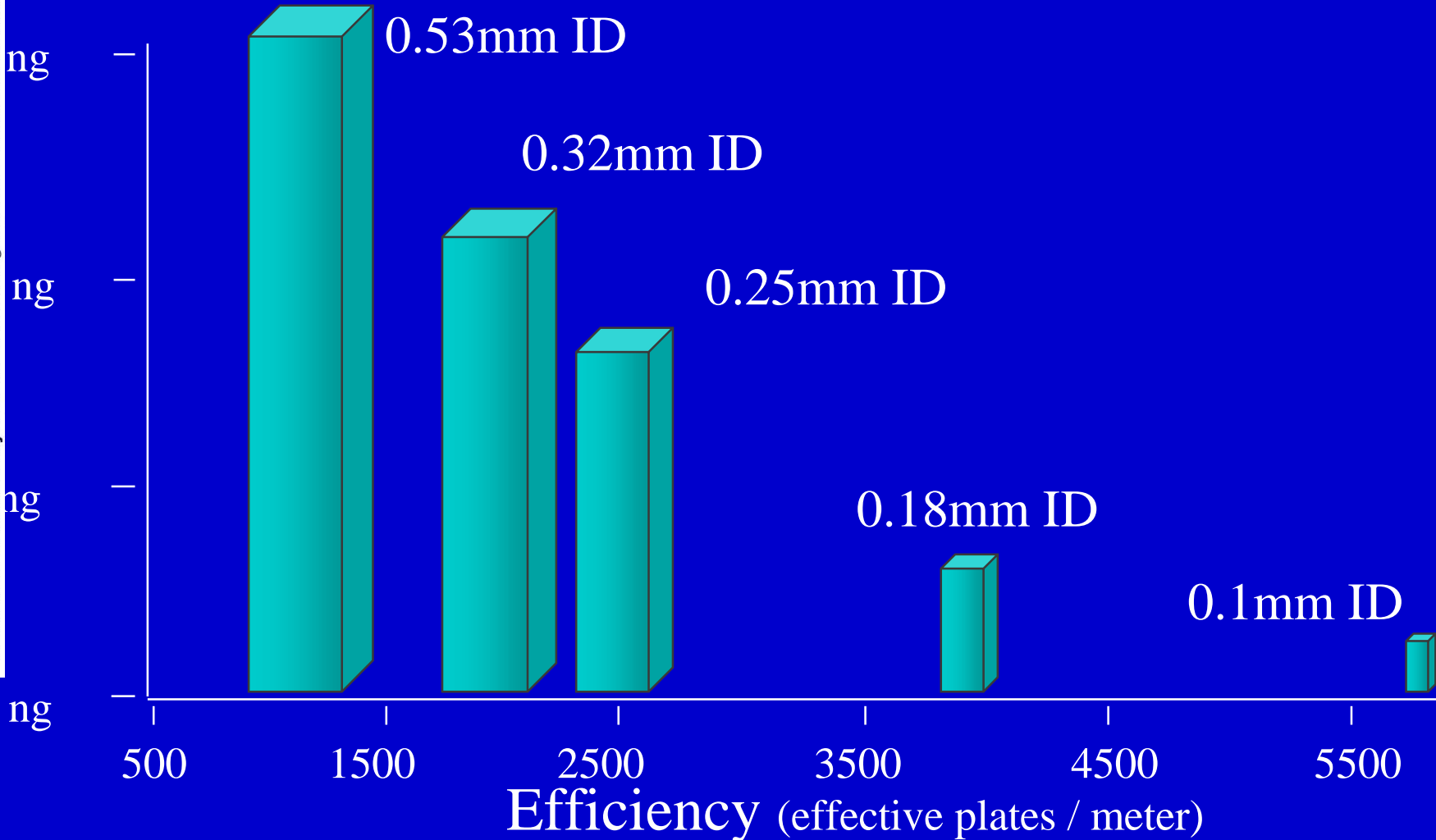
- How fast is fast?
  - 100°C/min., 100°C/sec.?
- How fast is necessary?
  - Partially depends on column dimensions
- Does the technique require different columns?
  - “caged” columns for resistive heating
  - Microwave heated columns
  - Narrow-bore columns

Capacity

# Column Selection

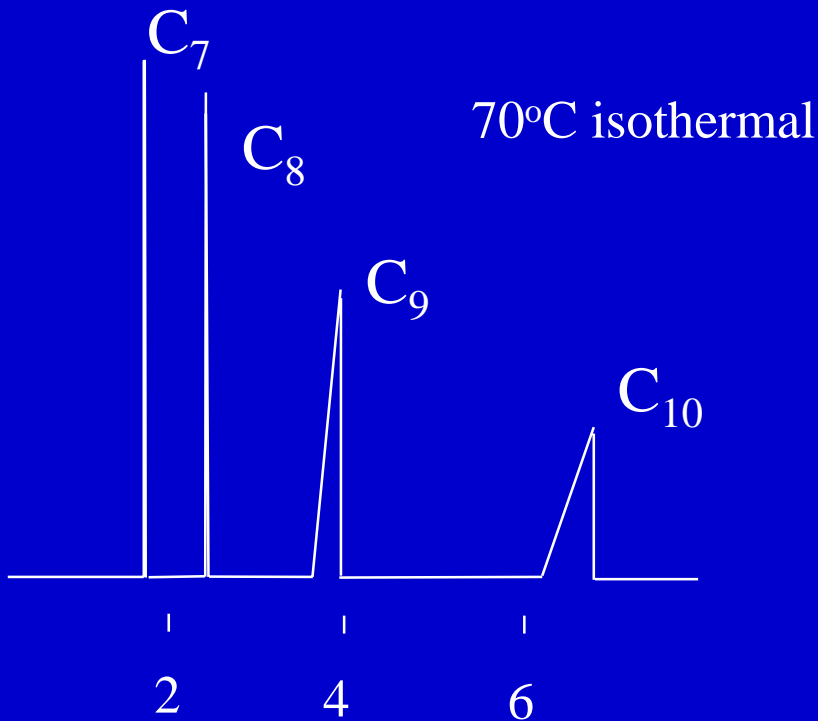
## Typical Column Capacity vs. Efficiency

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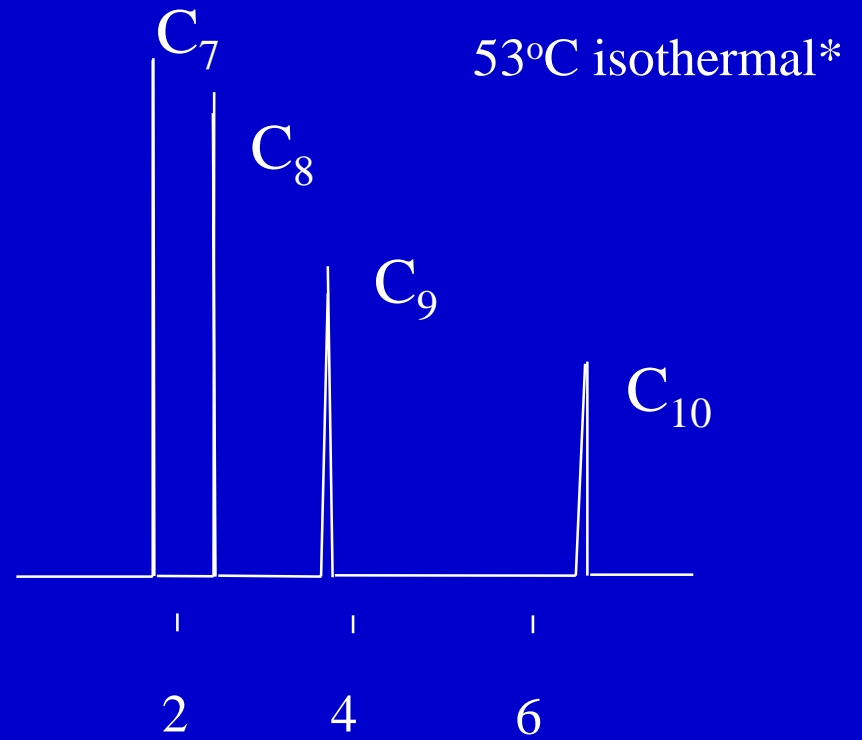


# Effect of ID on Capacity

Rt : 15m, 0.25mm ID, 0.25 $\mu$ m



15m, 0.53mm ID, 0.25 $\mu$ m

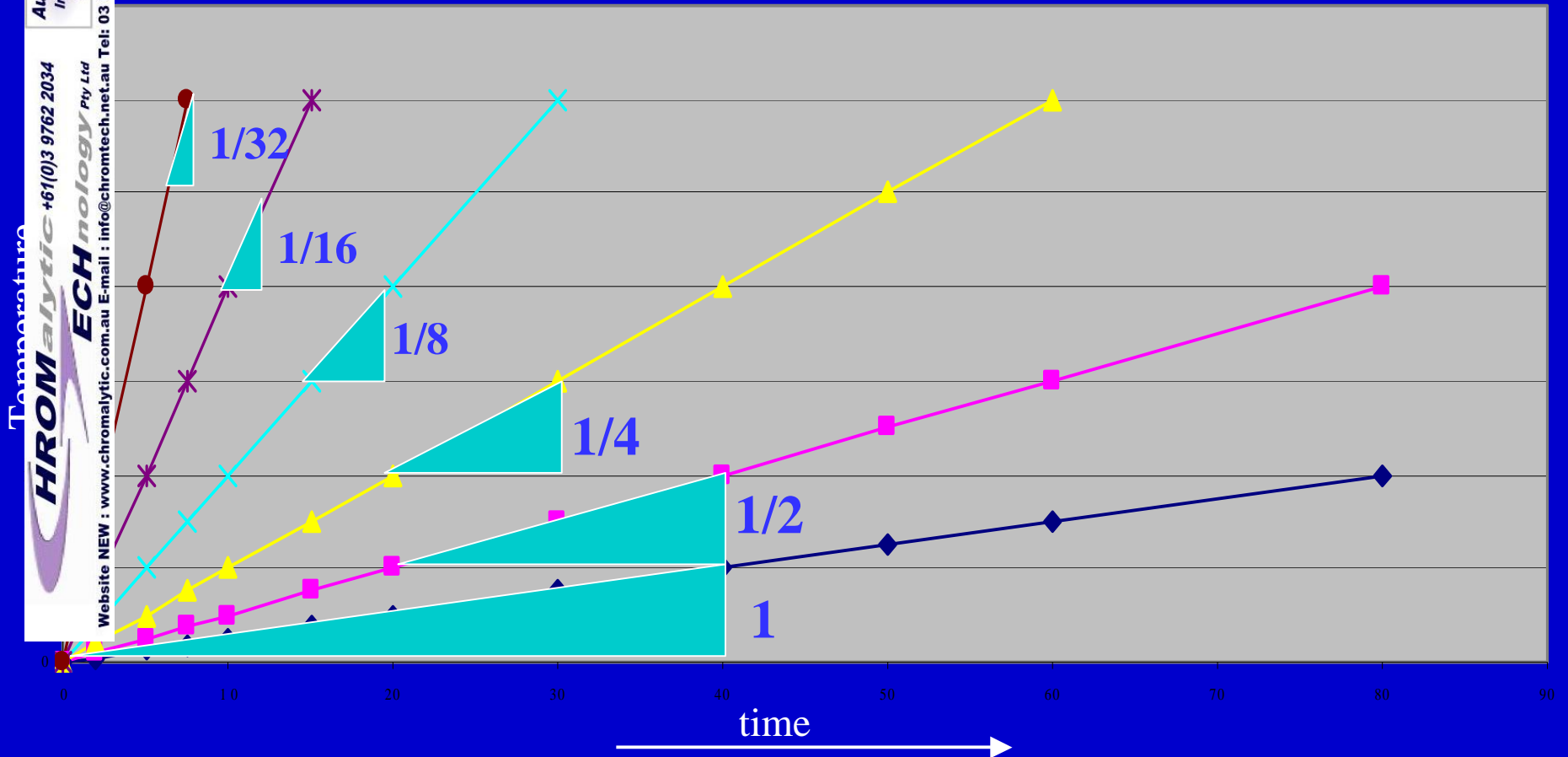


\* run at different temperatures to keep k values similar



# Effect of Temperature Programming Rate on Number of Theoretical Plates:

Area of the triangle Represents relative number of  
theoretical plates at different heating rates.



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# GC Racer

- Interfaces to existing GCs
  - 5890 A model available
  - 5890 Series 2 model available
  - 6890 model ready in April
  - Others to follow
- Operates using existing GC control
  - No software or firmware
- Allows for maximum ramp rates up to 440°C
- Can allow for 2-5 times speed enhancement for most methods



**GC Racer Heater Installed in an Agilent 5890**



**GC Racer Installed on an Agilent 5890**

## Versatility of HSGC Techniques

HSGC Technique	GC Racer	Flash	Micro Bore	Others
<u>Quality Factor</u>				
Injectors	All	Split/splitless	Most	?
Guard Columns	Yes	No	Yes	Yes
Retention Gap	Yes	No	Yes	Yes
Columns	All	5 or 10 m	< 0.1 mm i.d.	Small i.d. <sup>(1)</sup>
Sample Capacity	Full Range	Med - Low	Low	??
Temp Programming	Yes	Yes	Yes	Yes
Detectors	All	Most	All	?
EPC	Yes	No	High Pressure	All
RT Locking	Yes	No	Yes	Yes
Validation	None	Required	None	Required

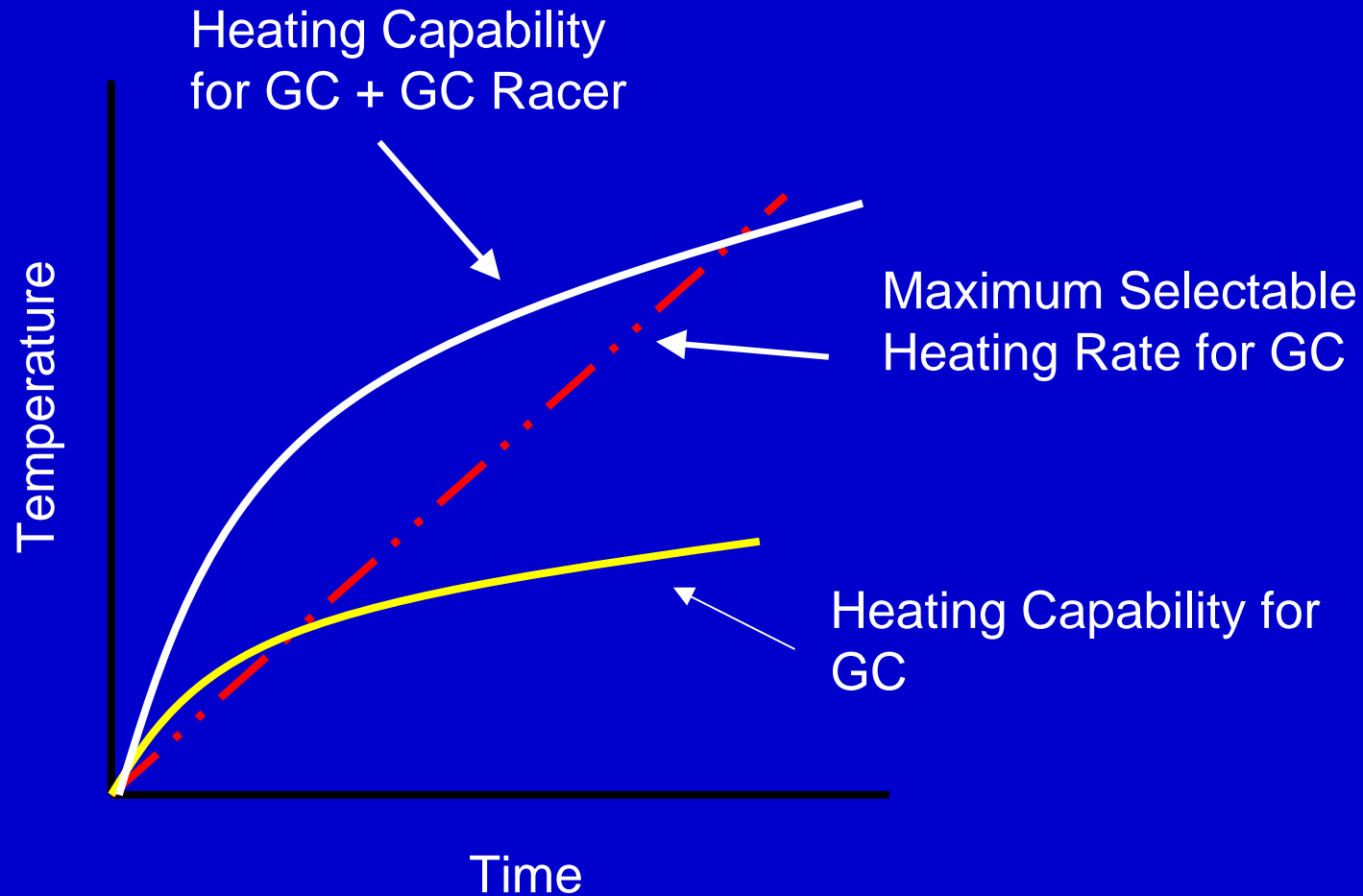


## Simplicity of HSGC Techniques

HSGC Technique	GC Racer	Flash	Micro Bore	Others
<u>Simplicity Factor</u>				
Installation	User	Professional	Not	Professional ?
Column changing	Plug and Play		Applicable	
Column Purchase	Standard	Specialized	Standard	Standard?
User Training	Any Source	Sole Source	Any Source	?
Software	None	Yes	None	Yes
Bench space	None	Yes	None	Yes
Reduced Operational Requirements	No	Yes	No	??

## Affordability of HSGC Techniques

GC Technique	GC Racer	Flash	Micro Bore	Others
<u>Detector</u>				?
Purchase Price	3,800	20,000	400	
Installation Cost	0	3,000	0	
Maintenance Cost	0	??	0	
Training Cost	0	included in installation cost	0	
Number of Columns	GC dependent (1 – 4)	1	1	



**GC Racer: Allows use of fast heating rates throughout entire temperature range**



## Versatility of Zip GC Racer

### Versatility Factor

Injectors	All	S/SS, Direct, PTV, SPME, 3 <sup>RD</sup> Party
Columns	All	Every size, every manufacturer, every length -
Guard Columns	Yes	Fused silica, metal, packed.
Retention Gap	Yes	
Sample Capacity		From microbore to packed column capacity
Temperature Programming		HP 5890: 60 °C/min up to 400 °C.
Detectors	Full Range	FID, MSD, FPD, PID, TCD, HID, ... every make, model, manufacturer.
EPC	All	original EPC and third party EPC accessories
RT Locking	Yes	Seamless addition to existing system
	Yes	

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# Simplicity of Zip GC Racer

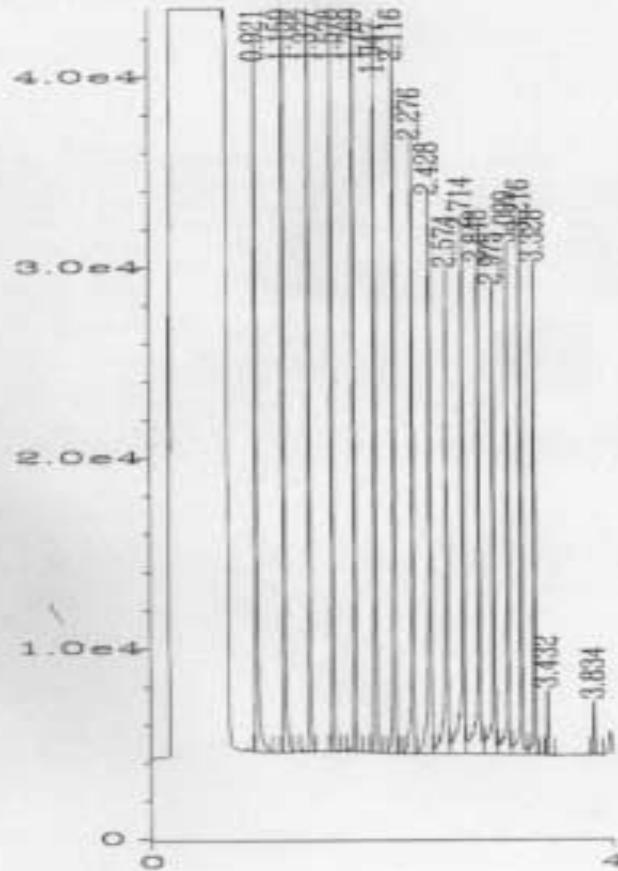
## Simplicity Factor

Installation	Simple; 3 plug in connections. Plug and Play
Column changing	Standard method, no special columns, interfaces, or tools.
Column Purchase	User continues to buy from vendor of choice.
User Training	None
Software	None
Bench space	None
Reduced Operational Requirements	None

**Ruggedness of Zip GC Racer**

The Zip GC Racer is based on the same heating technology used by GC manufacturers for the past 40+ years. Most GCs go to the junkyard without ever having oven failures. MTBF for GC heaters is a long, long, very long time.

Alpha Site	U Mass			
Beta Sites			Woods Hole Environmental Group	Restek Corp
Host GC	HP 5890 Series II		HP 5890	HP 5890
Application	Tenn/Miss DRO		Extractable HC	SimDis PCB's
Comments	Blew a few fuses – nobody got hurt.			
Problems encountered	Typical Design Issues		None	None



# Area Percent Report

=====  
 a File Name : C:\HPCHEM\1\DATA\MARCH19\001F0403.D  
 Operator : SteveMac  
 Instrument : ANALYZER1  
 Sample Name : Tenn/Miss DRO  
 Run Time Bar Code:  
 Acquired on : 21 Oct 00 11:26 AM  
 Report Created on: 24 Oct 00 06:03 PM  
 Page Number : 1  
 Vial Number : 1  
 Injection Number : 3  
 Sequence Line : 4  
 Instrument Method: TENNDR0.MTH  
 Analysis Method : TENNDR0.MTH  
 =====

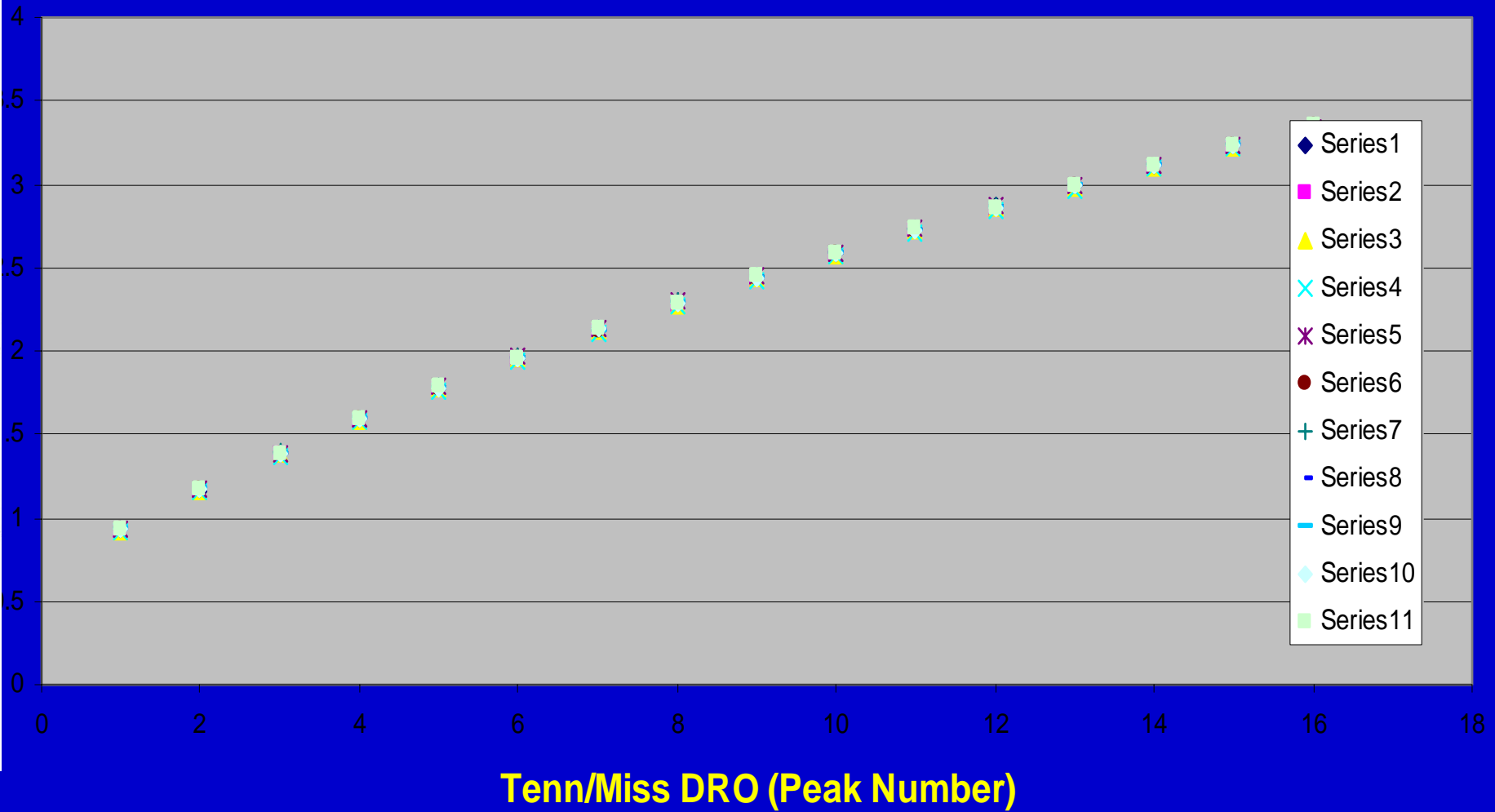
Sig. 1 in C:\HPCHEM\1\DATA\MARCH19\001F0403.D

pk#	Ret Time	Area	Height	Type	Width	Area %
1	0.921	34658	37521	BB	0.028	7.1855
2	1.159	35141	41700	BB	0.021	7.2856
3	1.377	34297	47435	BB	0.024	7.1106
4	1.578	30035	43098	BB	0.018	6.2270
5	1.769	32638	38410	BB	0.020	6.7665
6	1.947	31864	39014	BB	0.022	6.6961
7	2.116	34325	39851	BB	0.019	7.1164
8	2.276	30390	30619	BV	0.038	6.3006
9	2.428	33151	29803	VV	0.019	6.8729
10	2.574	27481	25768	VV	0.022	5.6975
11	2.714	30435	28265	VV	0.020	6.3099
12	2.848	27168	25436	VV	0.020	5.6325
13	2.975	24715	24750	VV	0.017	5.1240
14	3.099	23861	26293	VV	0.021	4.9469
15	3.216	25866	26421	VV	0.015	5.3626
16	3.328	21451	25677	VB	0.025	4.4473
17	3.432	2475	3450	BB	0.017	0.5130
18	3.834	2388	2889	BB	0.021	0.4951

## Tenn/Miss DRO Mix with GC Racer

Temp Program: 50°C (0.33 min hold), 70°C/min to 300°C, hold 0.1 min

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# Polywax 1000

- Polyethylene (even numbers) with average molecular weight of 1000 daltons
- Requires high temperature for elution of homologous series
- Good candidate for faster technique

# MXT-1HT Polywax 1000 C<sub>10</sub>-C<sub>100</sub>

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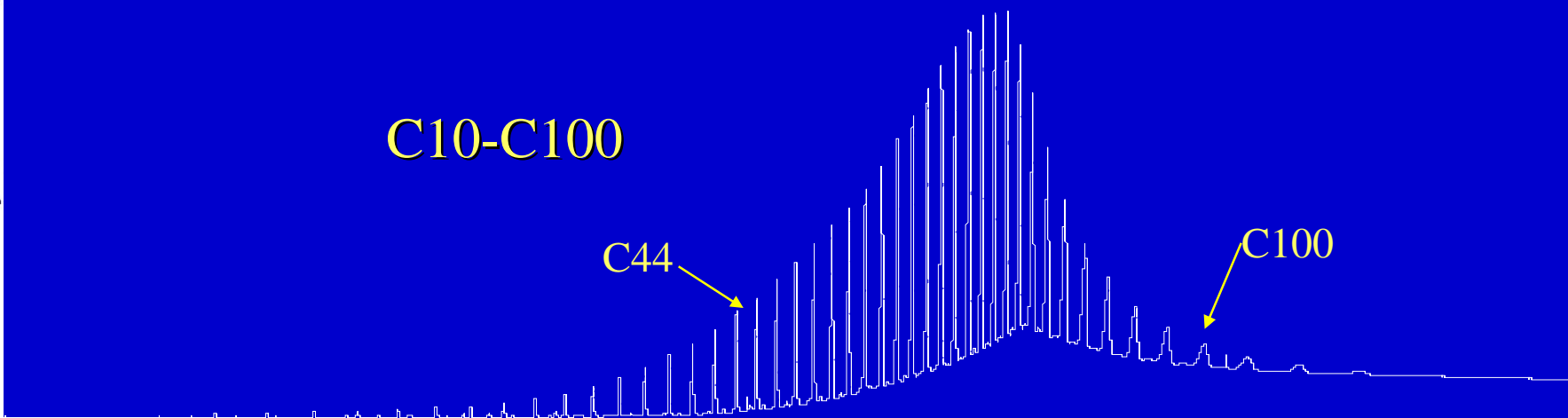
40c > 430c > @ 10/min. hold 20

C<sub>10</sub>-C<sub>100</sub>

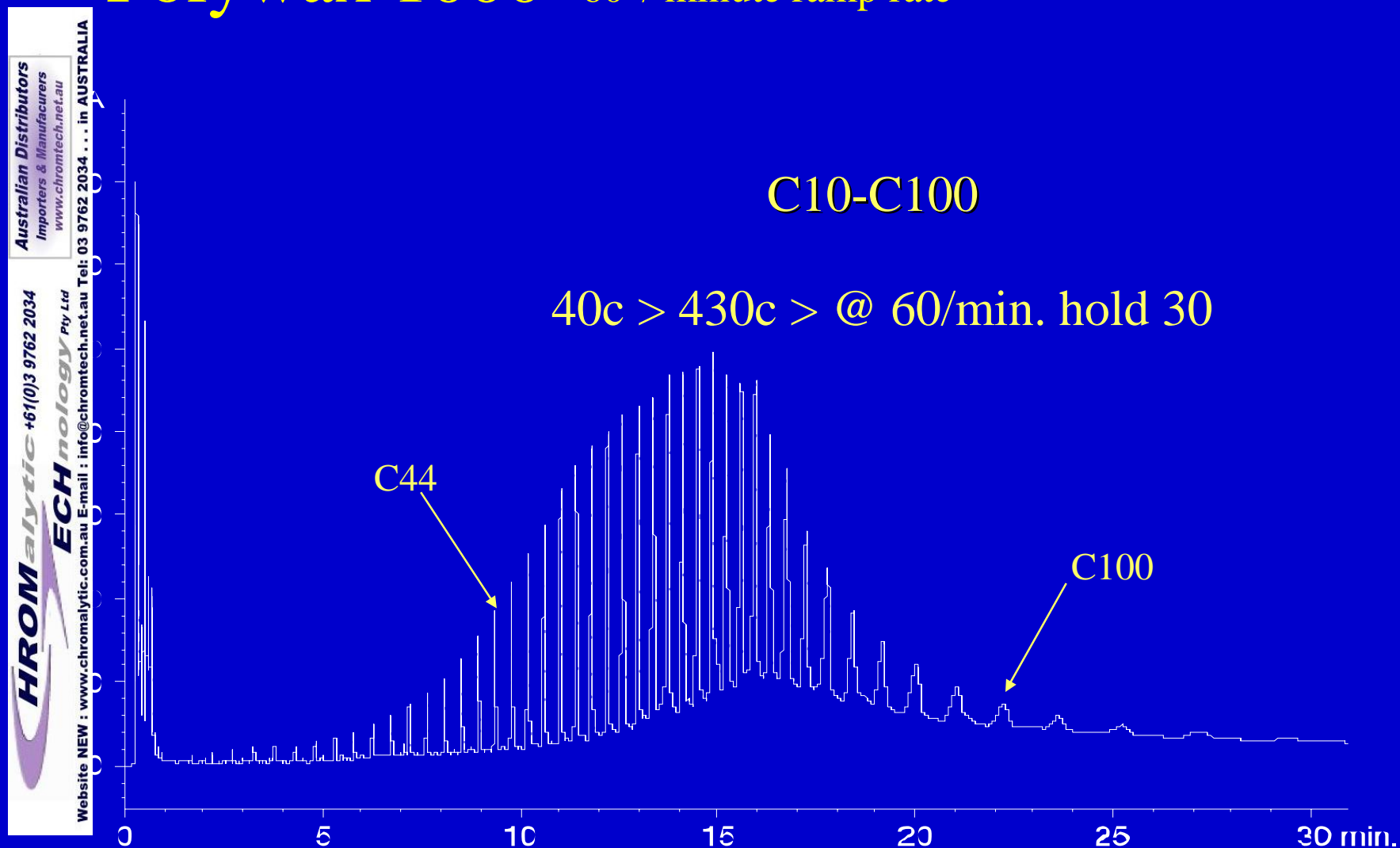
C<sub>44</sub>

C<sub>100</sub>

0 10 20 30 40 50 min.



# Polywax 1000 $60^{\circ}\text{C}/\text{minute}$ ramp rate



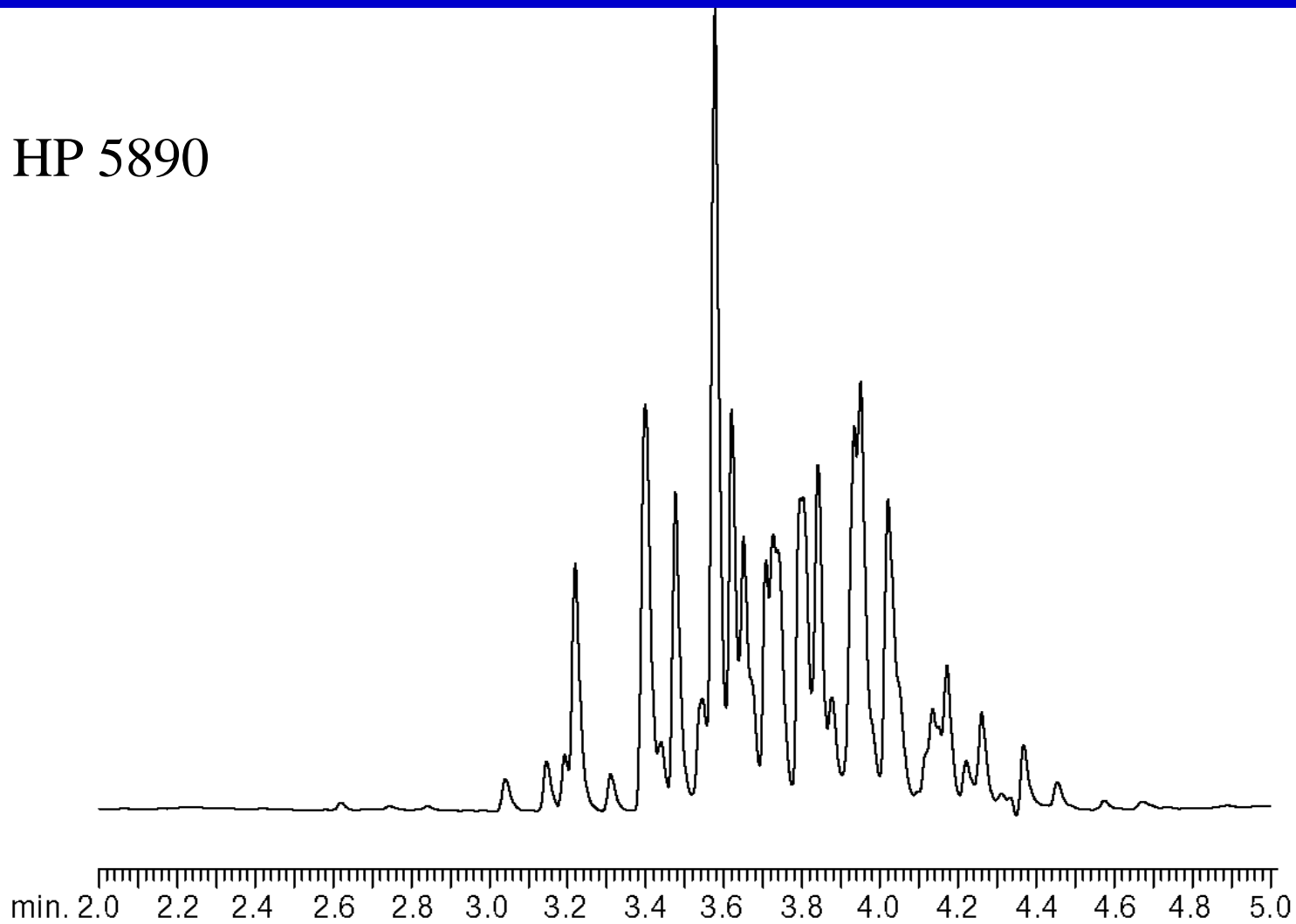


# PCB Aroclors

- Screening or analysis of PCB Aroclors can be performed quickly since complete separation is not a factor
- One of the most common tests required at remediation sites or for waste oil disposal
- Good candidate for accelerated separation

Rtx-5 15 M X 0.32 mm I.d. X 0.50  $\mu$ m d.f.

HP 5890



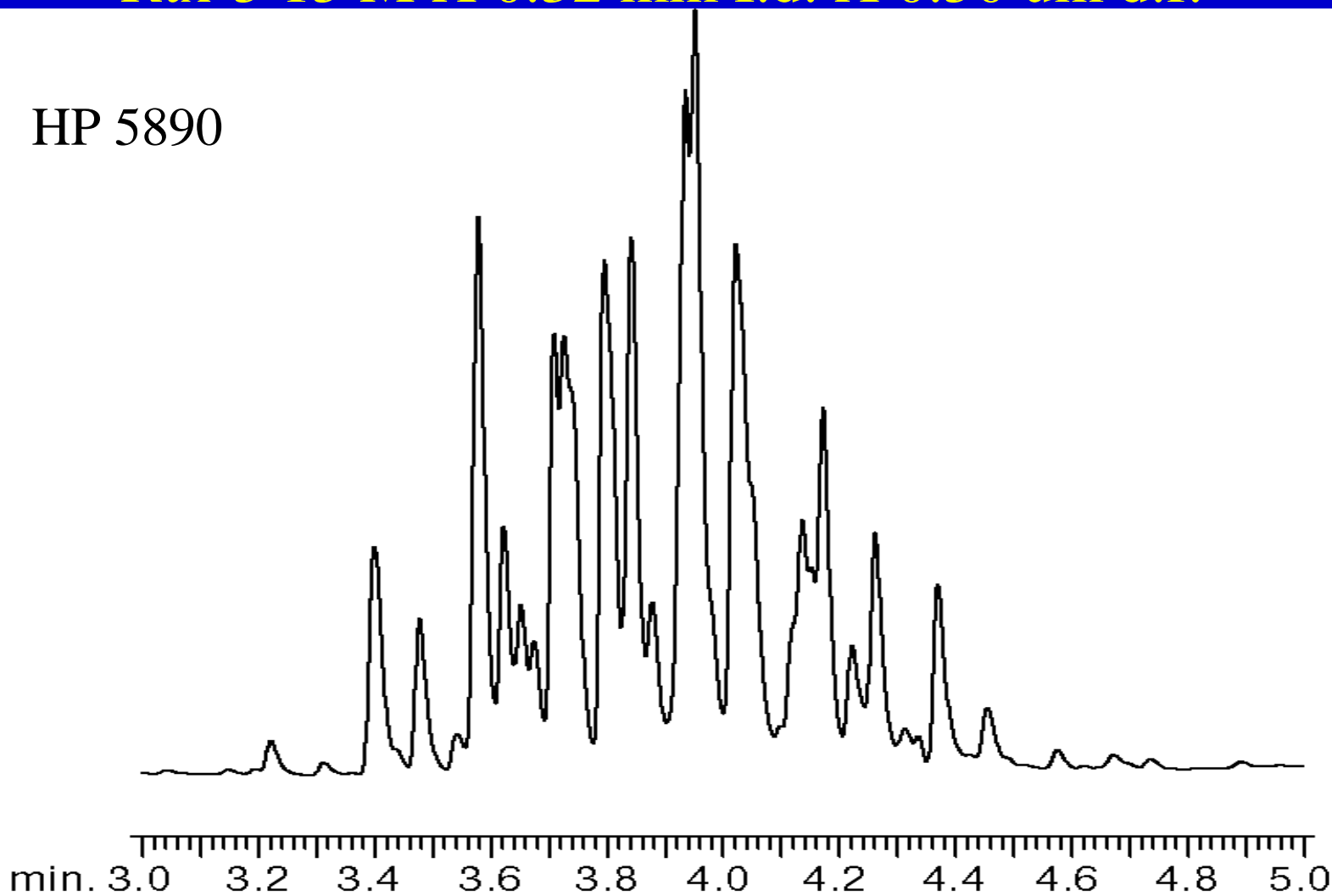
Aroclor 1242 with Zip Racer 110 C (Hold 1 min) to  
300 C at 60C/min (hold 5 min)

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Rtx-5 15 M X 0.32 mm I.d. X 0.50  $\mu$ m d.f.

HP 5890



Aroclor 1248 with Zip Racer 110 C (Hold 1 min) to 300 C at  
60C/min (hold 5 min)

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Rtx-5 15 M X 0.32 mm I.d. X 0.50  $\mu$ m d.f.

HP 5890

min. 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0

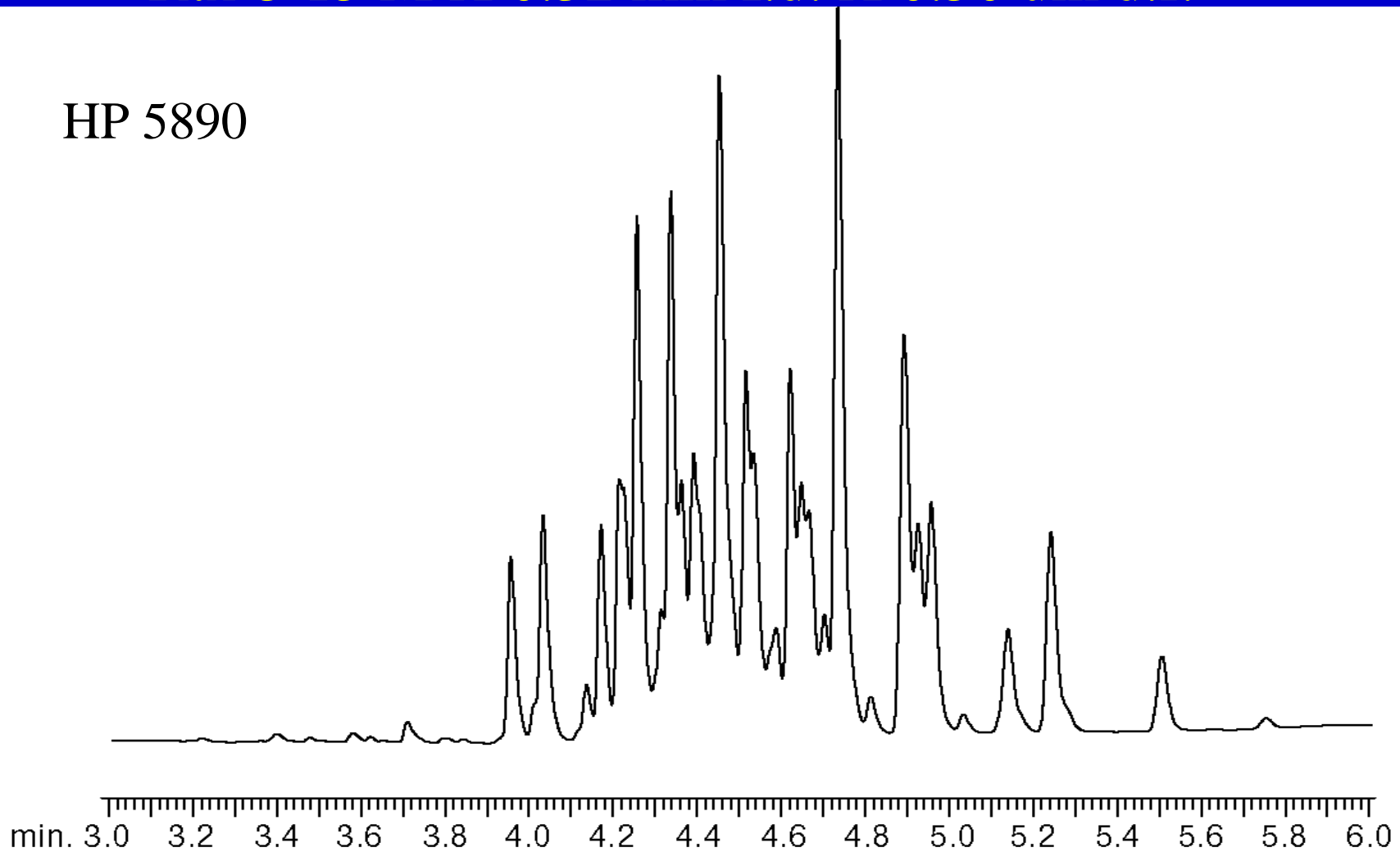
Aroclor 1254 with Zip Racer 110 C (Hold 1 min) to 300 C at 60C/min (hold 5 min)

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Rtx-5 15 M X 0.32 mm I.d. X 0.50  $\mu$ m d.f.

HP 5890



Aroclor 1260 with Zip Racer 110 C (Hold 1 min) to 300 C at  
60C/min (hold 5 min)

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## Affordability of Zip GC Racer

Purchase Price	Small fraction of the cost of existing technology.			
Installation Cost	User installed in less than 30 min.			
Maintenance Cost	No Preventative Maintenance Required			
Training Cost	None			
Number of Columns	No Training Required			
	GC dependent; 1 or 2			

# Summary

## For the Routine User:

- GC Racer is simple to install
- No training necessary
- Allows improvement in oven ramp rates
  - Many methods can benefit
- No re-qualification necessary
- No software to learn
- Uses existing GC instrumentation

# Review of Liner Selection Criteria for Gas Chromatographic Analysis

Gary B. Stidsen, Michael A. Goss,  
Brad R. Rightnour, and Gary A. Barone,



# Project Objective

The objective is to investigate the effects of intermediate polarity, Siltek™, and base deactivation, and liner geometry for the analysis of neutral, acidic, and basic compounds in EPA Method 8270.

# Overview

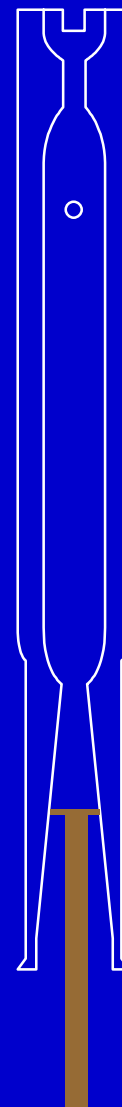
- Compare inlet liner deactivations
  - Intermediate Polarity, Siltek™, Base
- Effects of liner geometry
  - Single gooseneck, Drilled Uniliner®, double gooseneck, Cycloliner
    - Injection conditions
      - Constant flow
      - Pressure pulse

# Inlet Sleeve Deactivation

- Standard Intermediate Polarity (IP)
  - Polymeric deactivation
- Siltek™ Deactivation
  - Chemical vapor deposition
- Base deactivation
  - Deactivation leaves a basic character to the glass surface

# Experimental Conditions

- Rtx<sup>®</sup>-5Sil MS
  - 30m x 0.25mm ID, 0.25um film
- Drilled Uniliner<sup>®</sup>
  - Eliminate metal contact in injection port
- Standard concentration
  - 4, 10, 16, 24, 32, 80 ng/μl
  - ISTD at 8 ng/μl
- 1μl injections, 0.4 min. purge time
- Injection port temp. at 300°C
- HP 6890 w/5973 GC/MS
- 35°C (2 min.) 20°C/min. 260° (0 min.)  
6°C/min. 330° (1 min.)

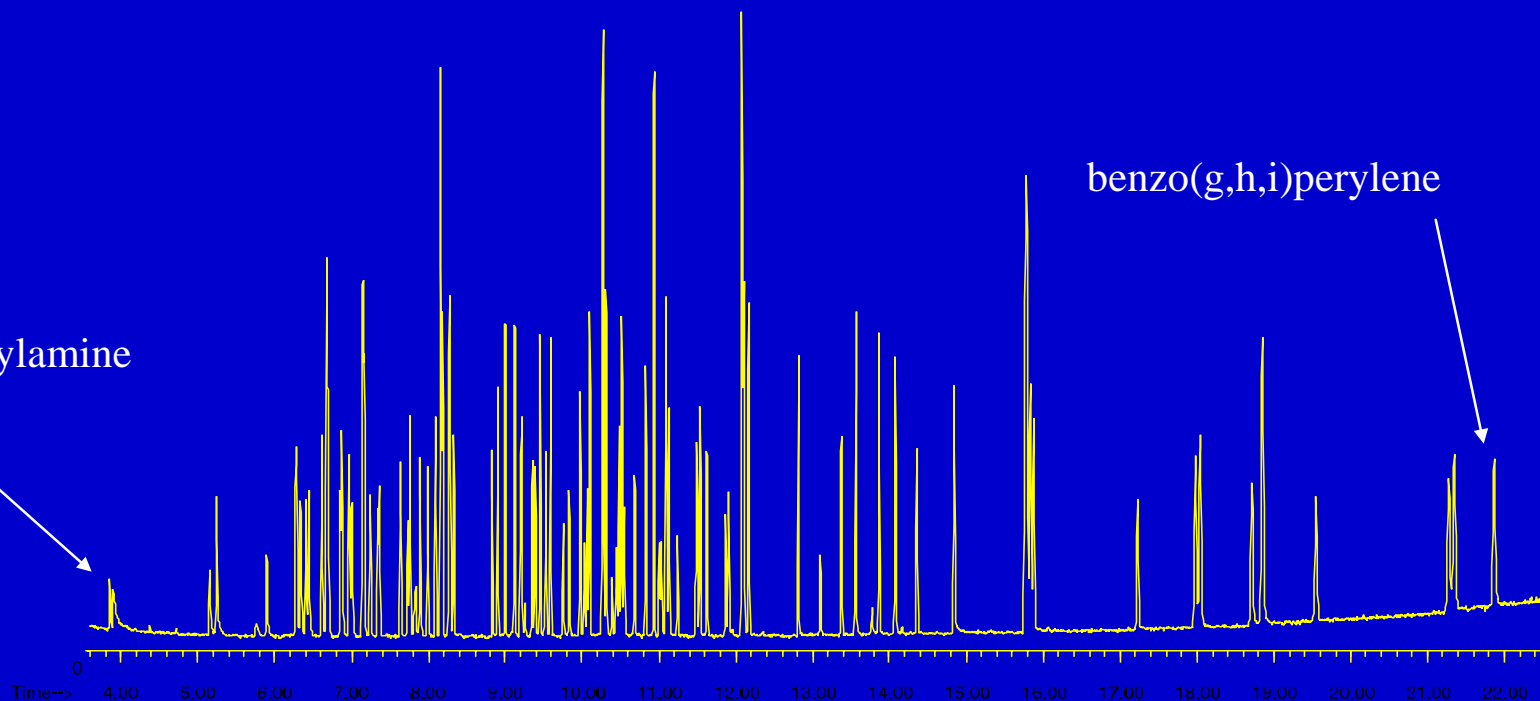


# Compound List

- Standard mix: 104 compound mix of US EPA 8270 list including ISTD
- Compounds used for comparisons:
  - Neutral compounds
    - Benzo(b)fluoranthene
    - Benzo(ghi)perylene
  - Acidic compounds
    - 2,4-dinitrophenol
    - Pentachlorophenol
  - Basic compounds
    - N-nitrosodimethyl amine
    - N-nitroso-di-n-propyl amine
    - Benzidine

# 4ppm 8270 Calibration Standard

- Excellent signal-to-noise for 4ng on-column injection
- Low column bleed



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# Comparison of Deactivations

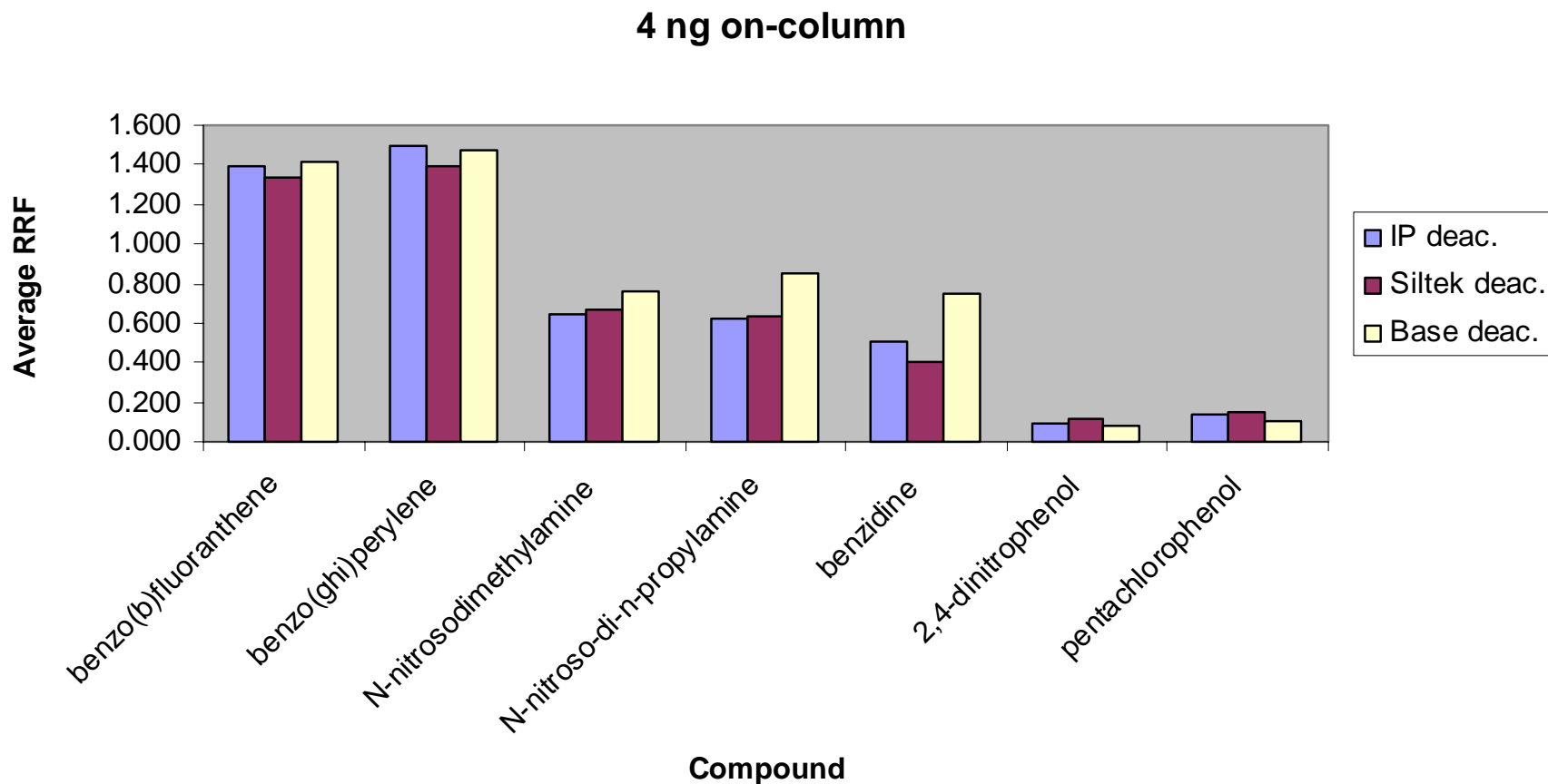
- Deactivated Drilled Uniliner®
  - IP, Siltek™, and base procedure
- Run sequence
  - 7 reps at 4ppm
    - Show largest difference in RRF due to active sites
  - Calibration curve
    - 4, 10, 16, 24, 32, and 80 ppm
    - ISTD at 8ppm

# Liner Deactivation

## Average RRF from 4ppm Standards

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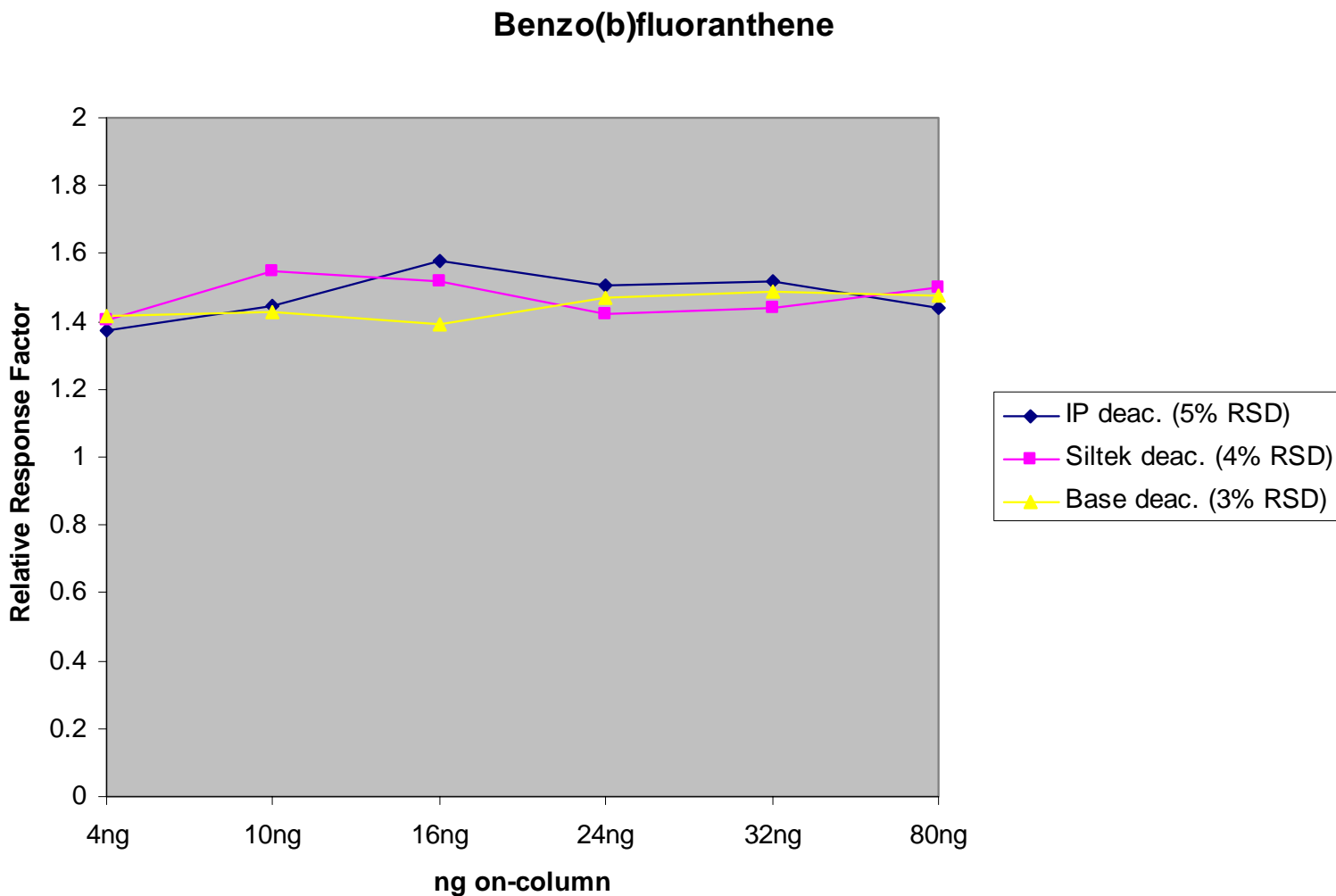




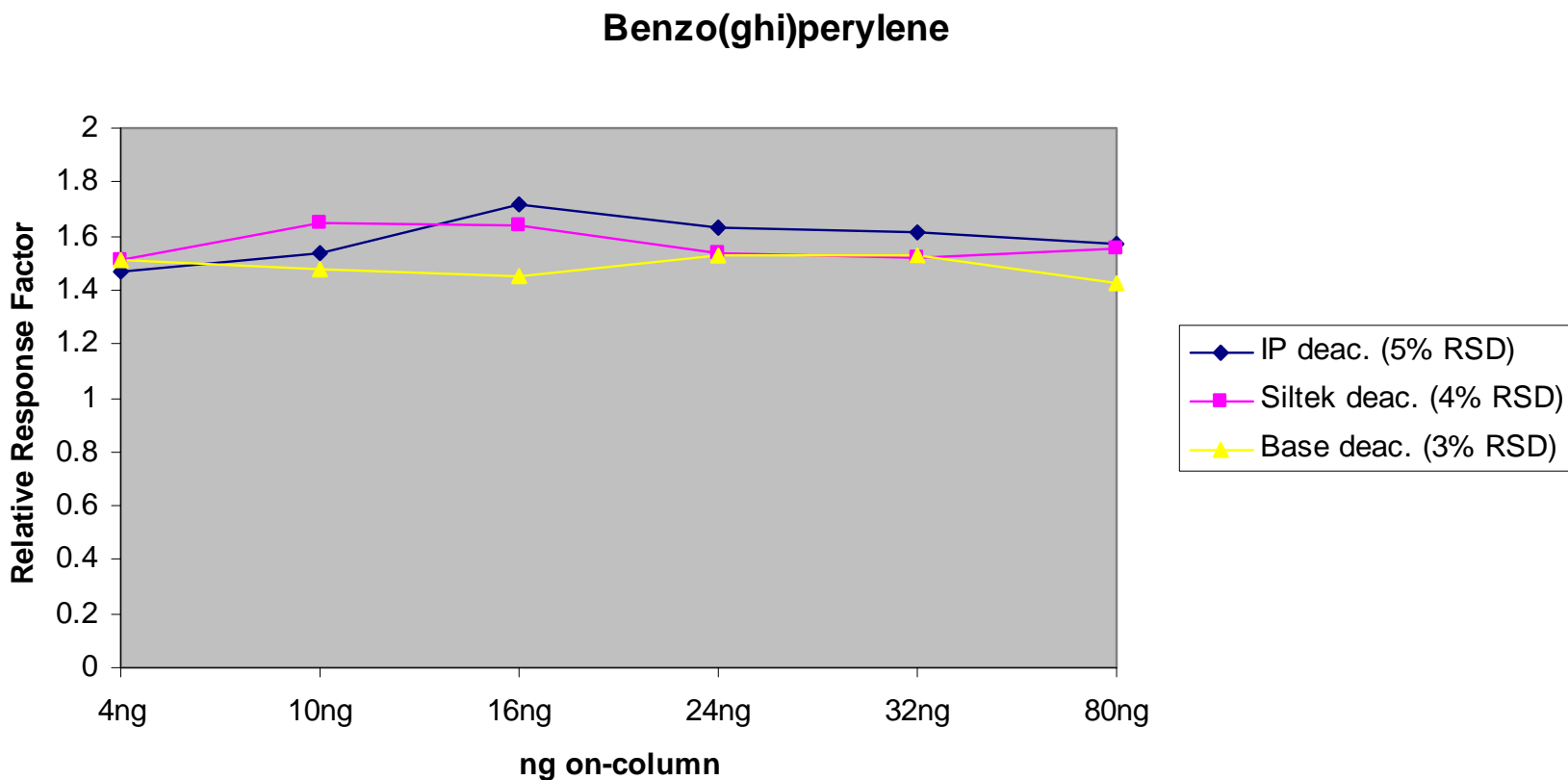
# Effects of Deactivation on Linearity

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

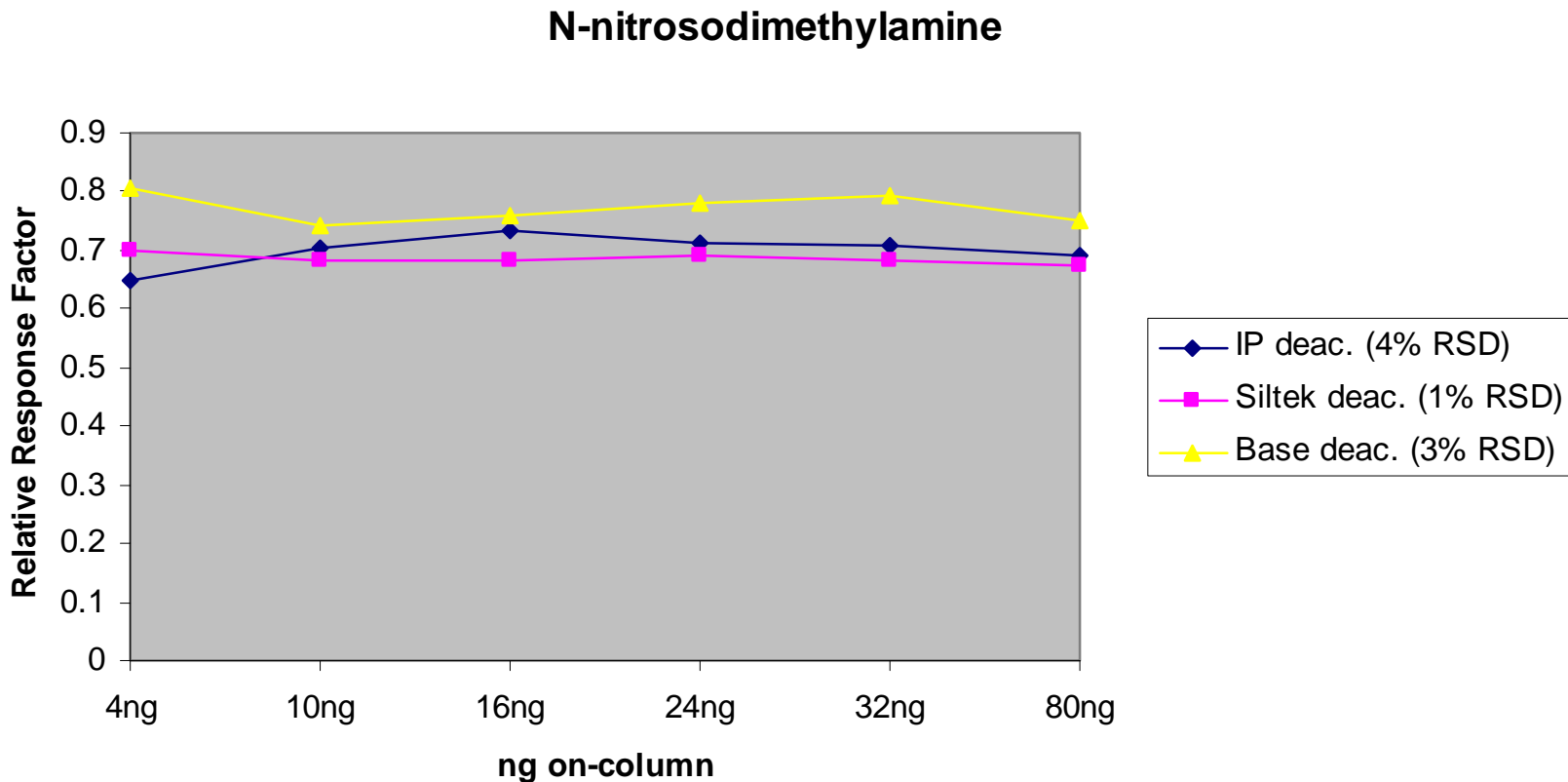
# Effects of Deactivation on Linearity



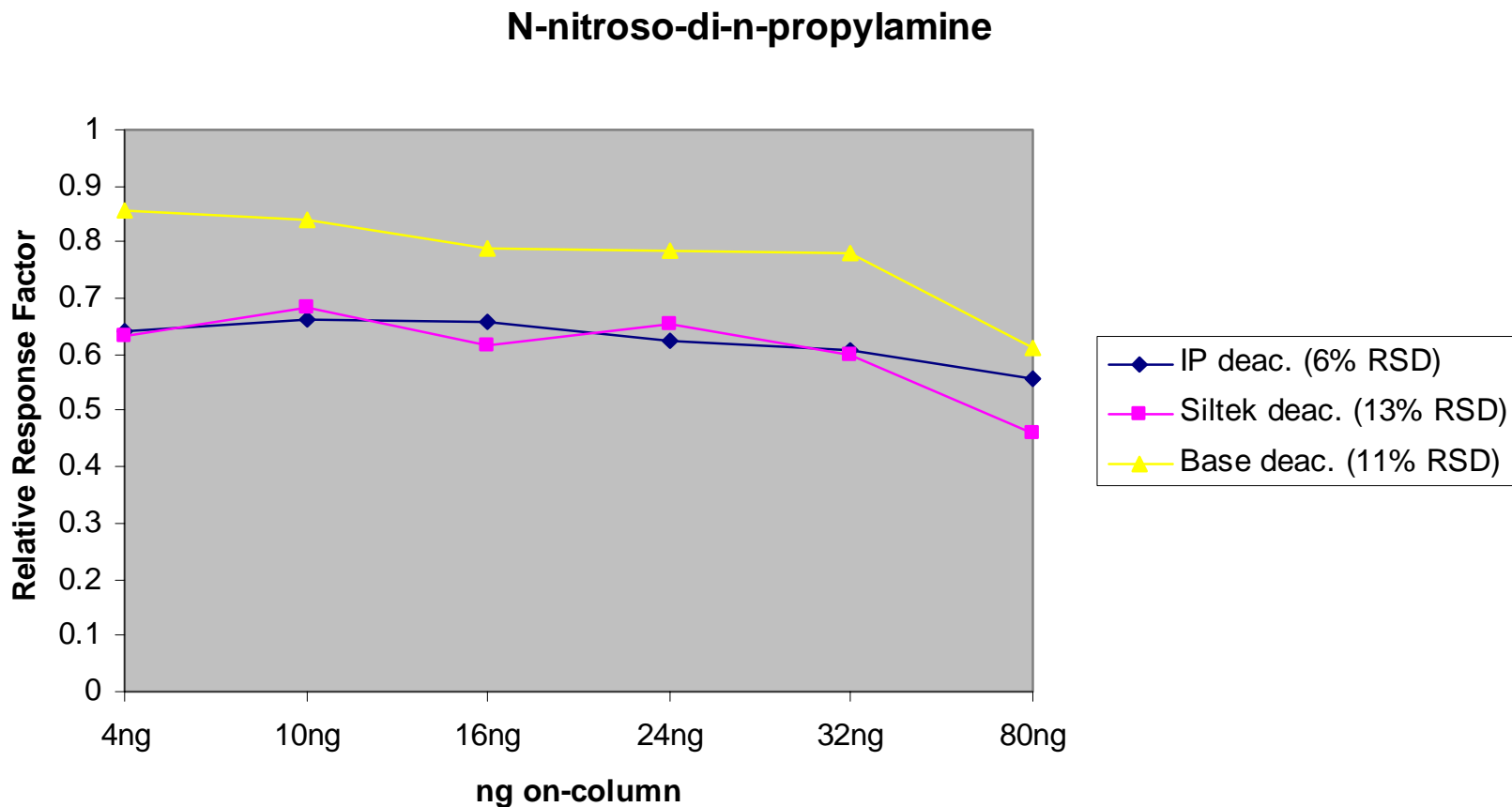
# Effects of Deactivation on Linearity



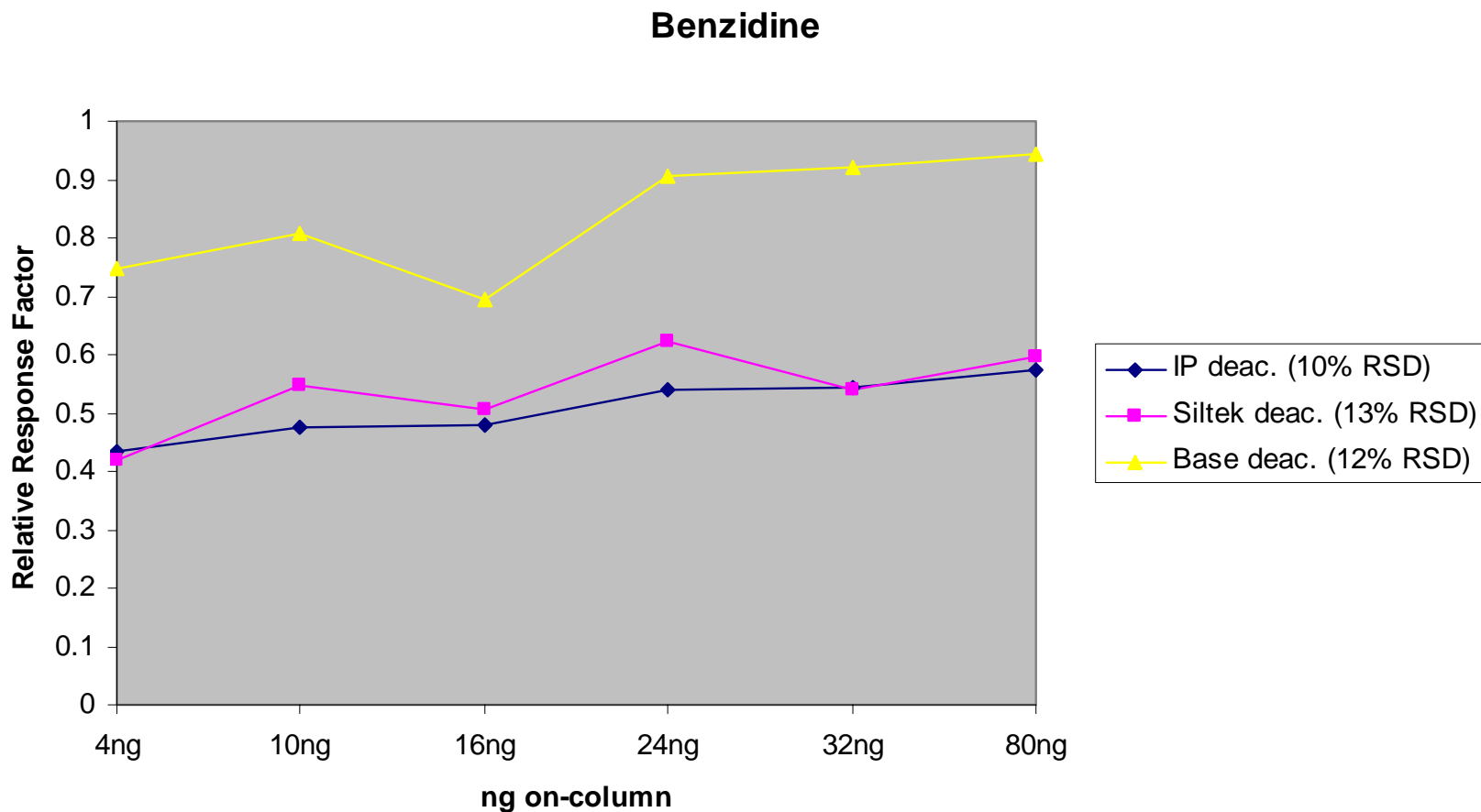
# Effects of Deactivation on Linearity



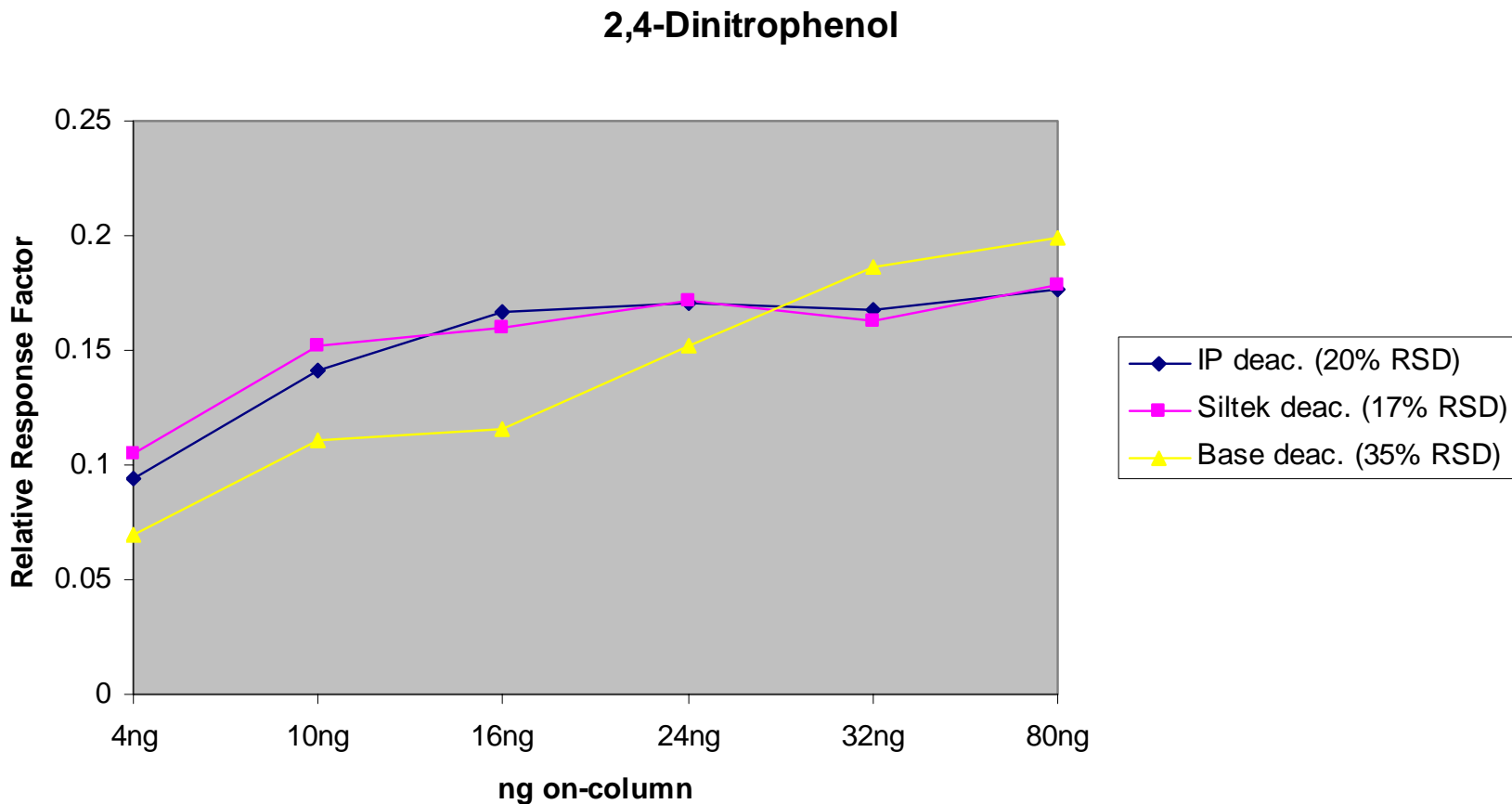
# Effects of Deactivation on Linearity



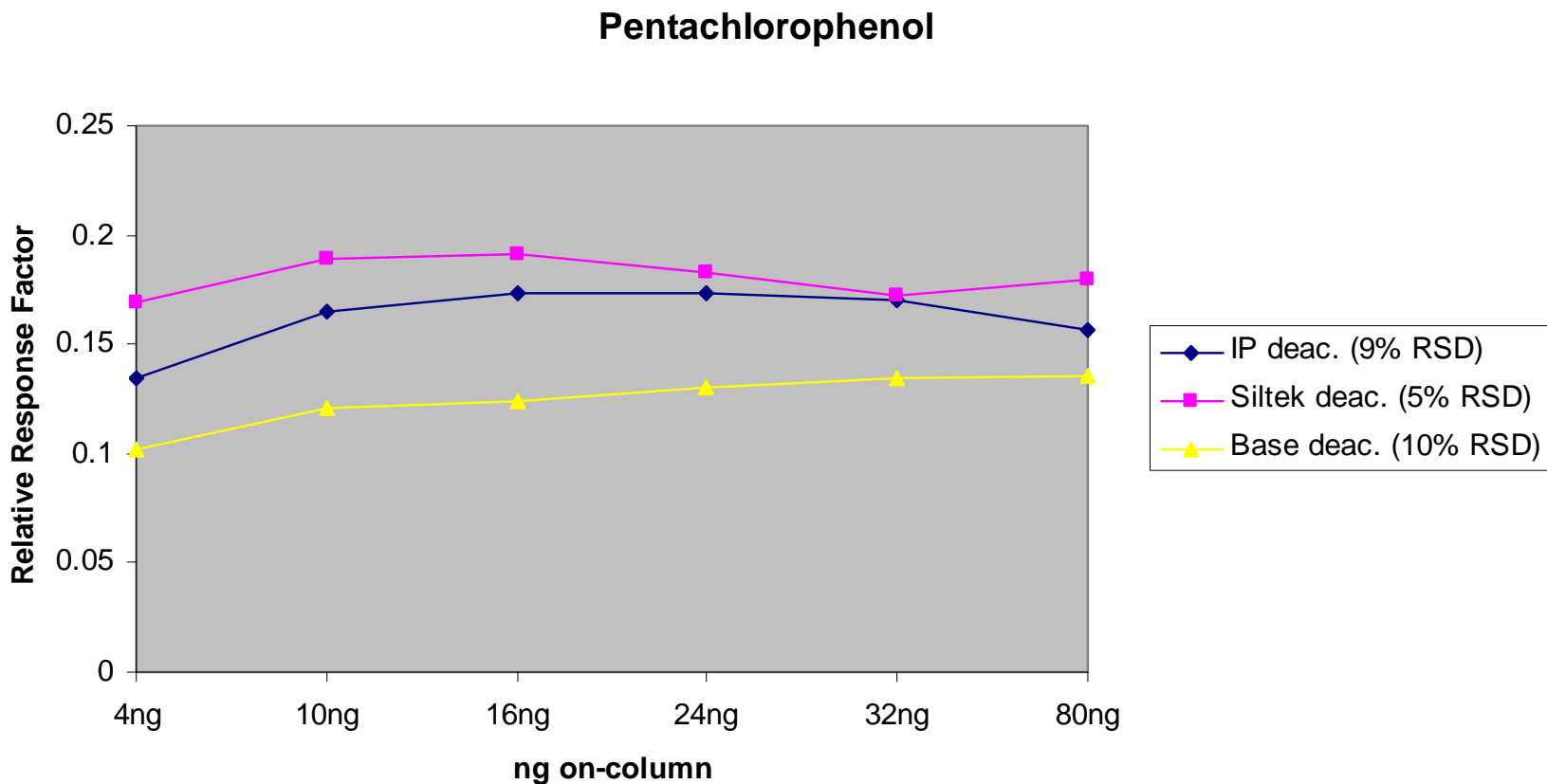
# Effects of Deactivation on Linearity



# Effects of Deactivation on Linearity



# Effects of Deactivation on Linearity





# Summary of Deactivation

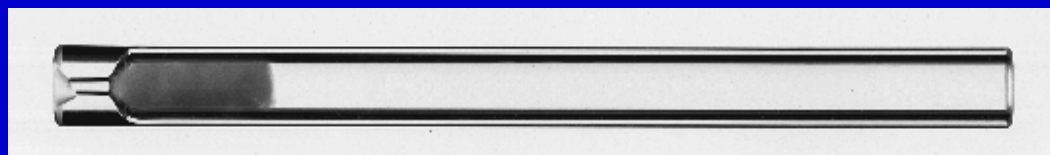
- The combination of response factors and linearity give a good picture of the effects of liner activity.
- Base deactivation results in low phenol compound response and variable linearity.
- IP and Siltek™ both exhibited acceptable response factors and linearity.

# Liner Geometry

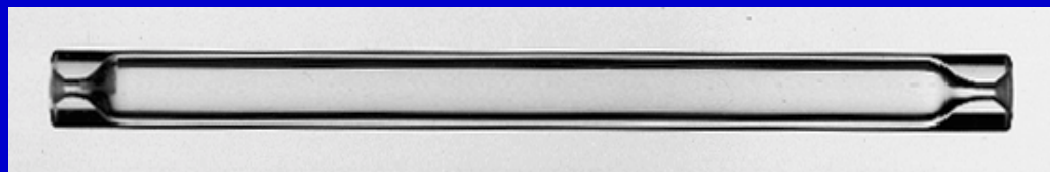
- Purpose
  - Vaporize sample prior to column
  - Shield sample from active metal parts of the injection port
- Problems
  - Need surface area and time to help vaporize sample
  - Opening at both ends of liner allows vapor cloud to expand out of glass liner, exposing sample to active sites

# Liner Geometry

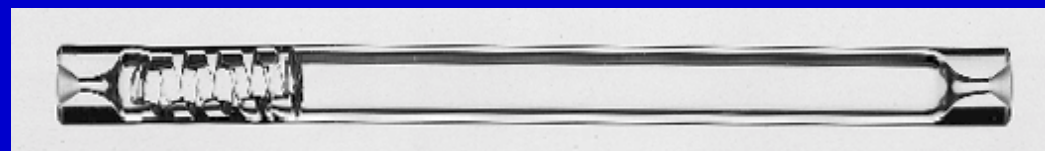
Single Gooseneck



Double-Gooseneck



Cyclo Double  
Gooseneck



Drilled Uniliner



# Experimental Conditions for Liner Geometry

- Same conditions as deactivation study
  - Did not optimize conditions for each liner.
- 2 injection conditions
  - 1mL/min. constant flow (CF)
  - Pressure pulse (PP)
    - 30psig for 0.5 min., then constant flow at 1mL/min.
- Run sequence
  - 4, 10, 16, 24, 32, and 80ppm

# Results of Liner Geometry

- Visual chromatographic differences
- Compare relative response factors (RRF) for different liner geometries
  - Pressure pulse versus constant flow
  - Average over 6 point curve
- Compare differences in linearity (%RSD)
  - Pressure pulse versus constant flow
  - Average over 6 point curve

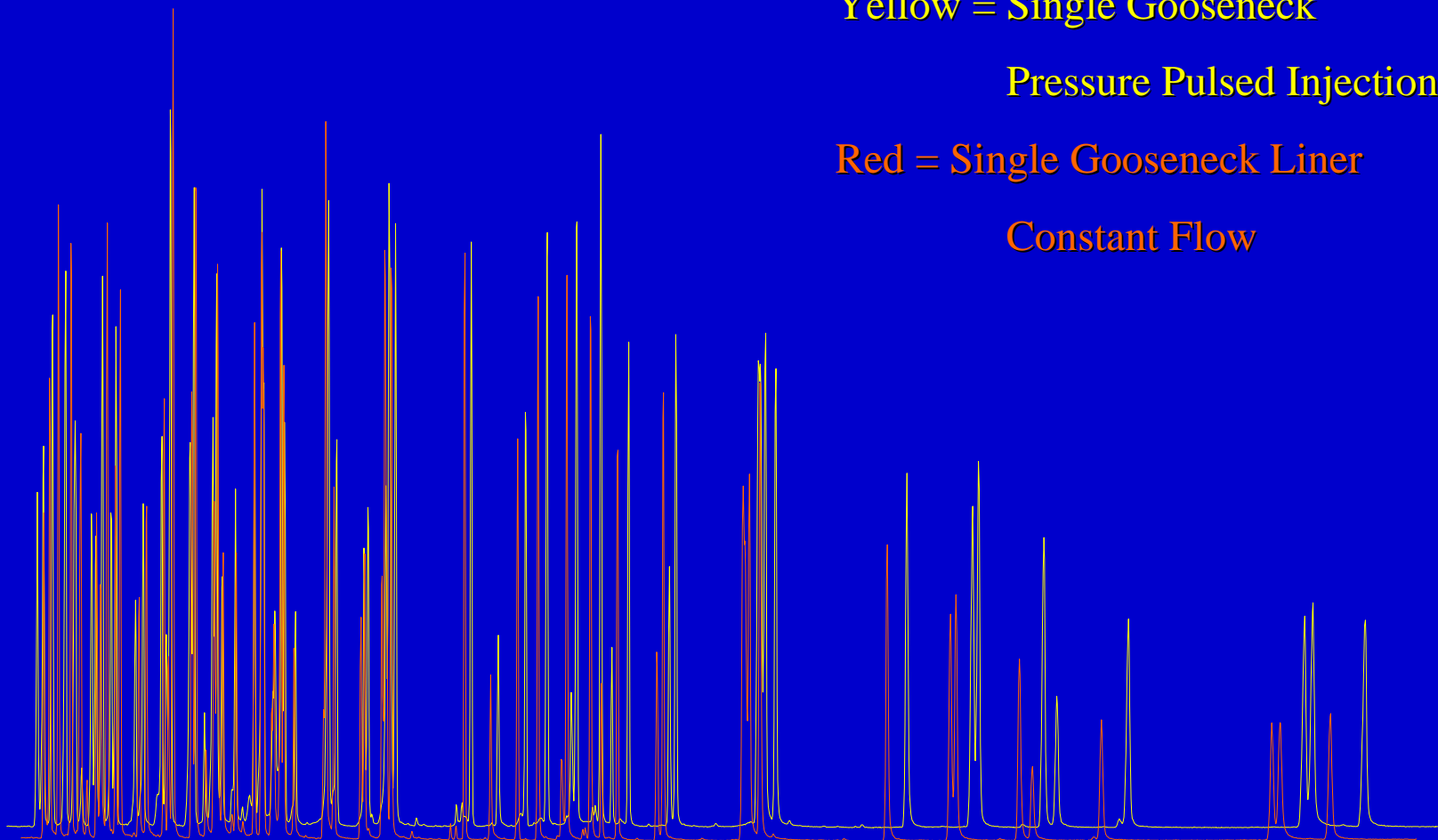
# Single Gooseneck Liner (Constant Flow vs Pressure Pulsed Injection)

Yellow = Single Gooseneck

Pressure Pulsed Injection

Red = Single Gooseneck Liner

Constant Flow

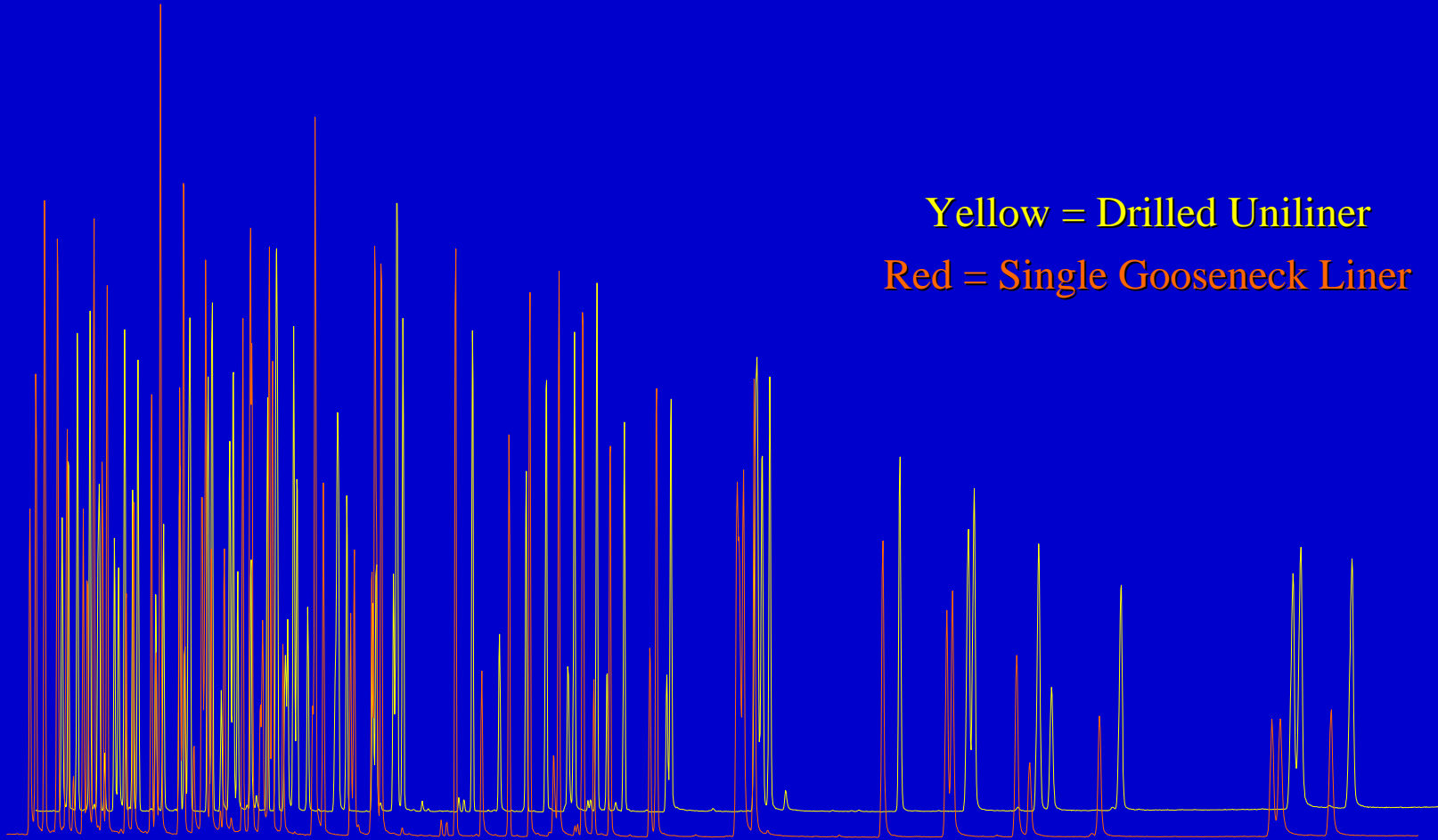


# Single Gooseneck vs Drilled Uniliner<sup>®</sup> Sleeve (Constant Flow)

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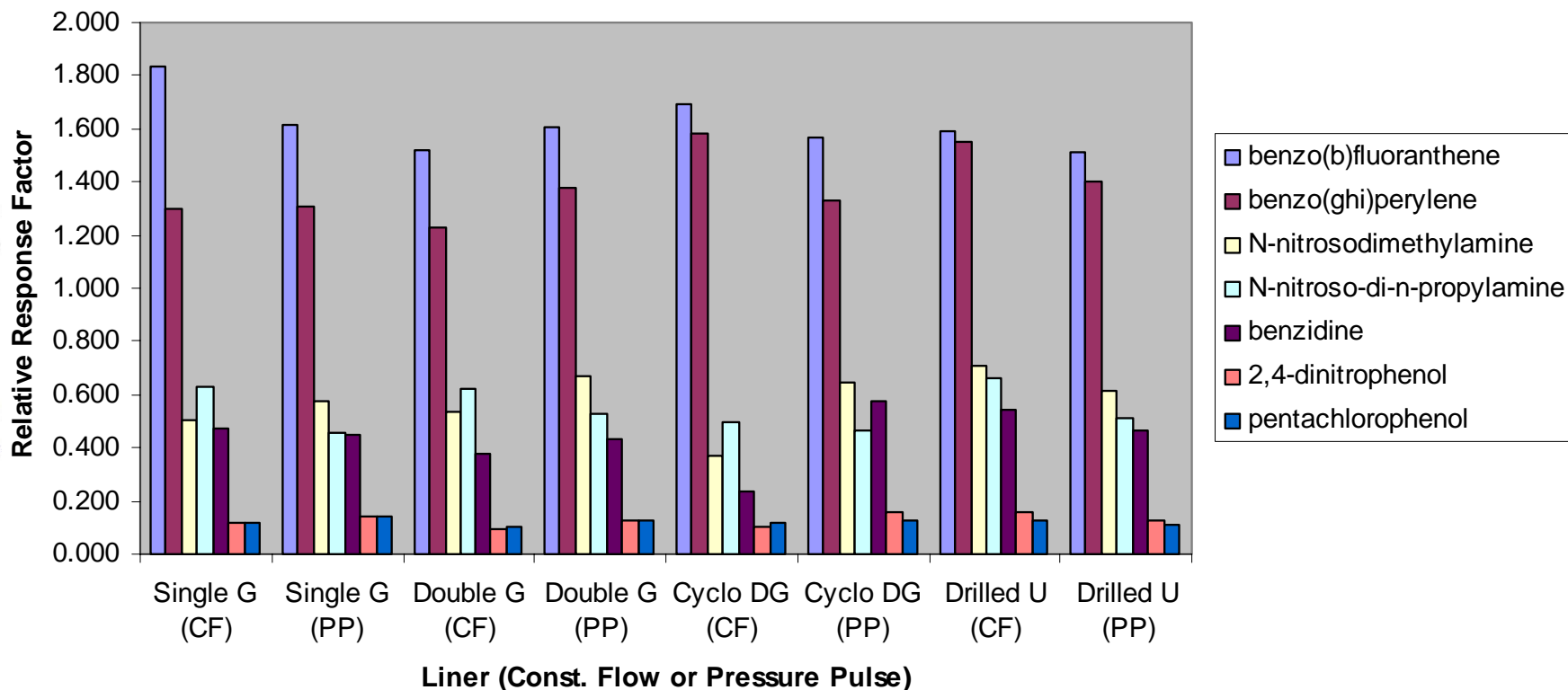
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Yellow = Drilled Uniliner  
Red = Single Gooseneck Liner

# Average RRF of 6 Point Curves

## Liner Geometry Average RRF

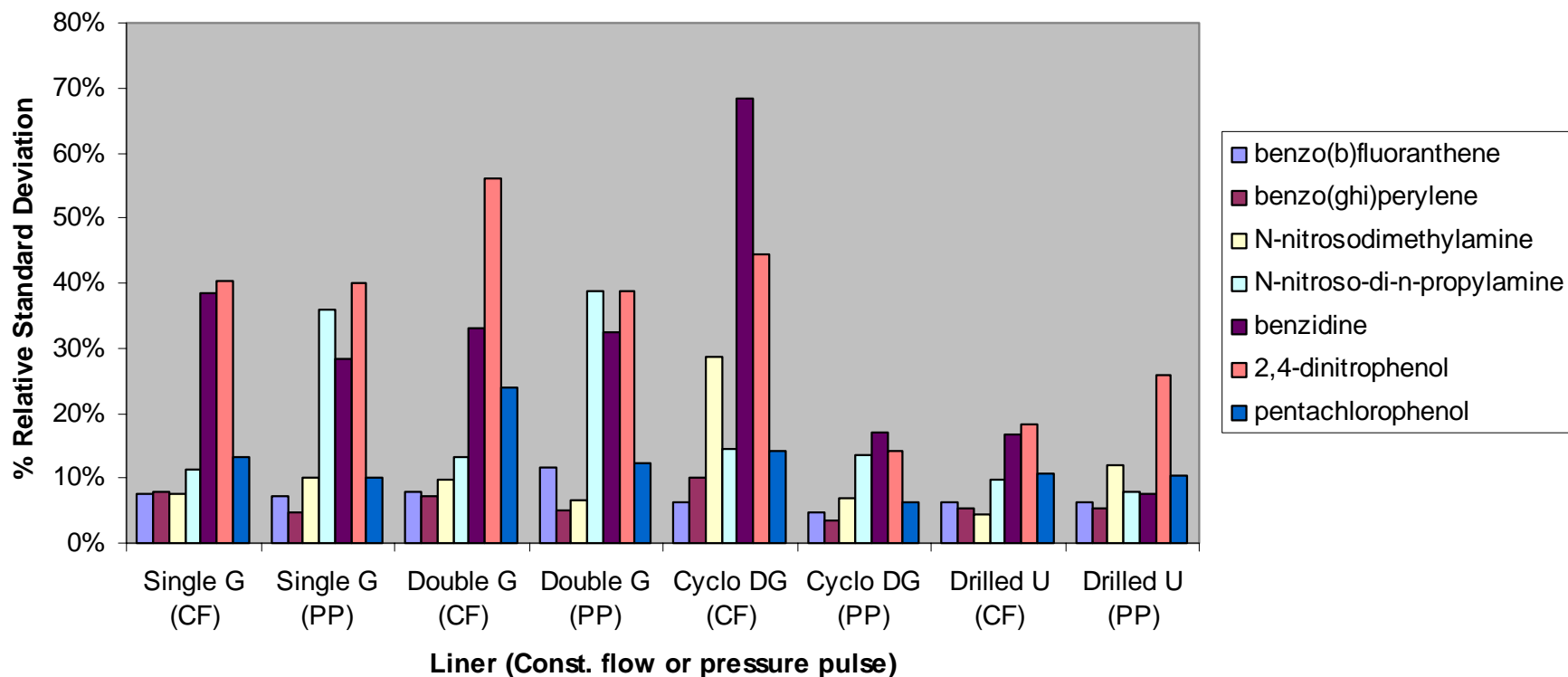


Note: Higher is better



# Linearity Results from 6 Point Curves

%RSD of Different Liner Geometries



Note: Lower is better

# Summary

- IP and Siltek™ deactivation are comparable for running method 8270.
- Pressure pulsing does improve the response of active compounds.
- Drilled Uniliner® appears to give the best overall results under constant flow conditions.

# Future Work

- Continue comparison of experimental deactivations being designed
- Continue work with liner geometry

# Prediction of Chromatographic Selectivity, Retention Times, and Peak Widths for New Capillary Stationary Phases and Columns

Frank L. Dorman, Paul D. Schettler, and  
Chris English

# How is GC Learned/Used?

- GC thought of, and often taught as “Separation by boiling point”
- Where mobile and stationary phases “do chemistry” in HPLC, in GC column dimensions and temperature program are typically adjusted
- GC applications are not usually optimized, and separations are compromised to fit existing columns and stationary phases
- Most phases not designed with any application in mind, and common phases are similar in selectivity (-1s & -5s)

# Needs for Difficult GC Separations:

- Stationary phase selectivity should be optimized for particular separation, to maximize resolution and minimize run time
- Column dimensions should be matched to analytical requirements (flow, capacity, etc.)
- Current offerings of stationary phases and functionalities are limited
- Selection of phase and column, and optimization of separations needs to be easy for end user

# General Equation for Resolution:

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha - 1 / \alpha)$$

Selectivity Factor ( $\alpha$ ) – addressed by  
stationary phase modeling  
not commonly done by end user

Capacity Factor ( $k$ ), and Column Factor –  
addressed by physical modeling  
can be simultaneous with, or independent of  
stationary phase modeling

# Stationary Phase Optimization Techniques

- Empirical Modeling:
  - Window diagramming approach
  - Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
  - Computer prediction of optimized stationary phase composition and column dimensions, with specific resolution factors (times and peak widths)
- Molecular Modeling:
  - Computer prediction of solute/stationary phase interactions for new polymer designs



# Stationary Phase Optimization

- Window diagramming (Rtx-502.2)
- Computer simulation of selectivity, independent of column dimensions (ezGC™)
  - Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx-TNT, Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

# Window Diagrams

- Maier and Karpathy ('60s):
  - Demonstrated that mixing phases together could yield unique selectivity for packed column applications
- Laub and Purnell ('70s)
  - Mixed phase packed column applications
- Jennings et al ('80s)
  - Packed column applications, and capillary work based on lengths of dissimilar columns
  - DB<sup>TM</sup>-1301 developed using DB<sup>TM</sup>-1 and DB<sup>TM</sup>-1701

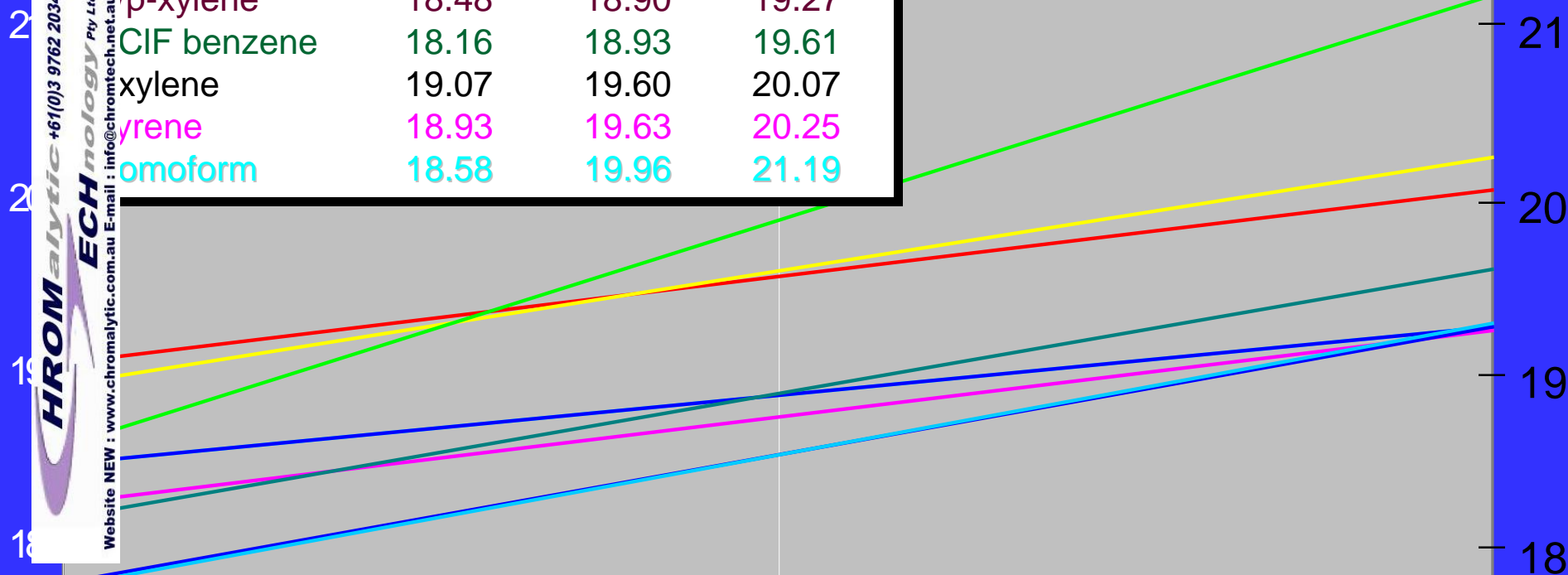
# Window Diagramming

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	Rtx <sup>®</sup> -1	Rtx <sup>®</sup> -502	Rtx <sup>®</sup> -35
Chlorobenzene	17.79	18.57	19.27
1,2-dichloroethane	17.78	18.58	19.29
Benzene	18.26	18.78	19.25
m/p-xylene	18.48	18.90	19.27
Chlorobenzene	18.16	18.93	19.61
o-xylene	19.07	19.60	20.07
p-xylene	18.93	19.63	20.25
1,1-dichloroethane	18.58	19.96	21.19



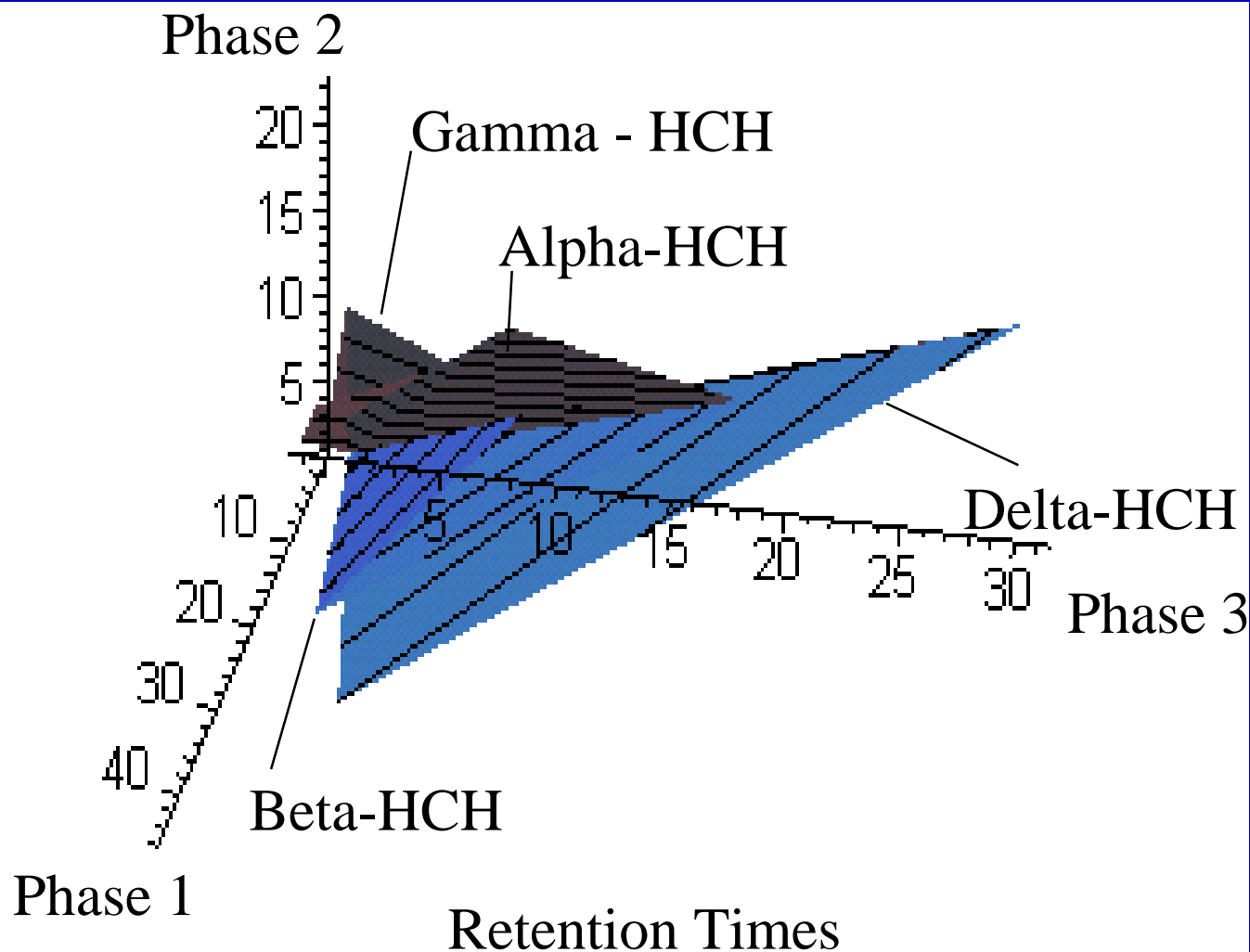
# Stationary Phase Optimization

- Window diagramming
- Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
  - Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx®-CLPesticides, Rtx-CLPesticides2, Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

# Computer simulation of phase selectivity, independent of column dimensions (ezGC™)

- “Fix” Run Conditions
- Input data is normalized for column and program parameters
- Search for optimum solution by varying the stationary phase composition
- Program tracks up to 8 dimensions of phase functionalities
- No solution requires separate re-optimization of input data

# 3-Space Selectivity Surface for 4 Pesticide Compounds



# Rtx<sup>®</sup>-CLPesticides Column Benefits

- Baseline resolution of all 22 compounds
- < 25 minute analysis time
- Available in all common dimensions
  - 0.18, 0.25, 0.32 and 0.53mm ODs
- Very low electron capture detector (ECD) bleed levels
- High thermal stability
  - 330°C maximum temperature

# Confirmation Column?

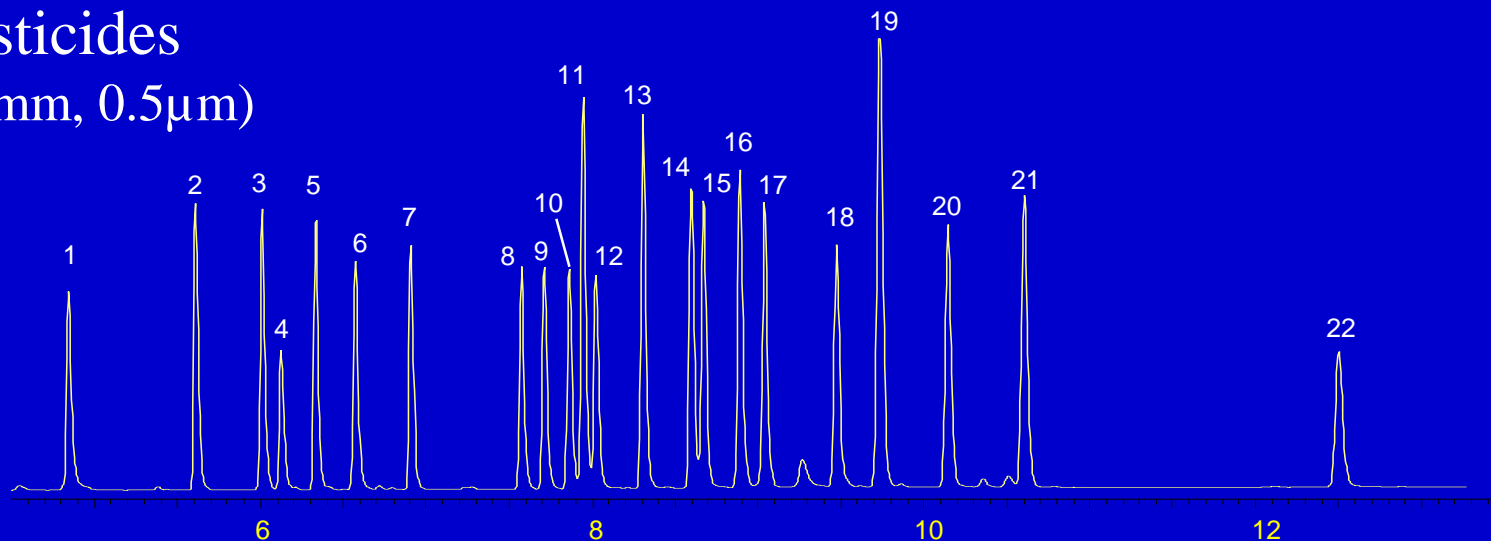
- Requirements
  - Same analysis conditions as primary column
  - Different elution order
  - Baseline resolution desirable
  - High thermal stability and inertness
  - Similar analysis times
- Rtx<sup>®</sup>-CLPesticides2 column meets requirements



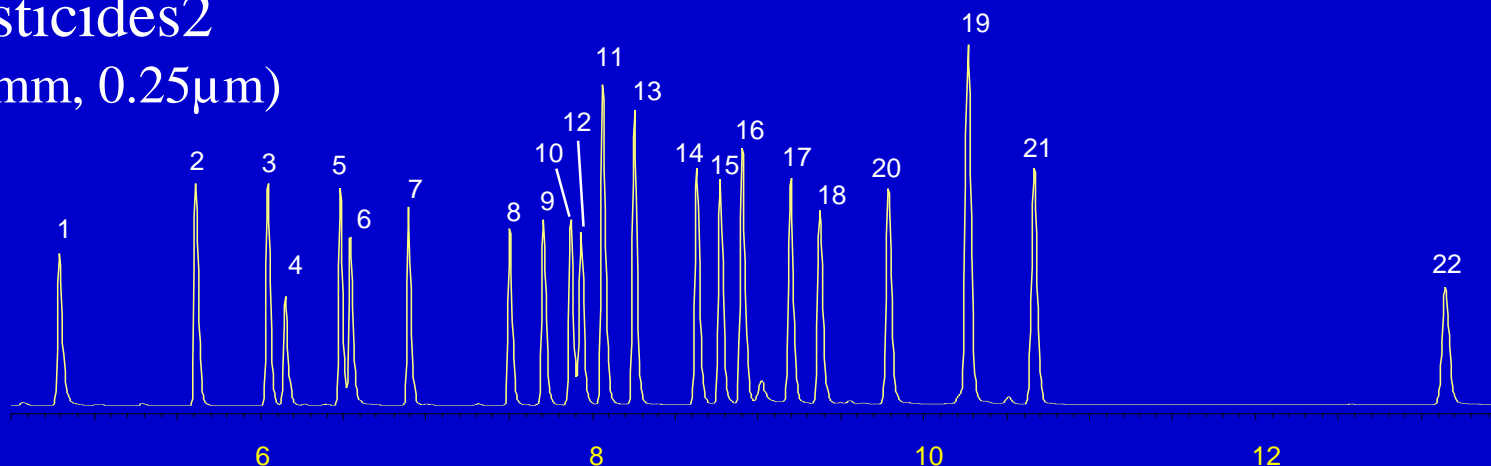
# Chlorinated Pesticides

## Fast Runs

Rtx-CLPesticides  
(30m x 0.32mm, 0.5 $\mu$ m)



Rtx-CLPesticides2  
(30m x 0.32mm, 0.25 $\mu$ m)



# Chlorinated Pesticides

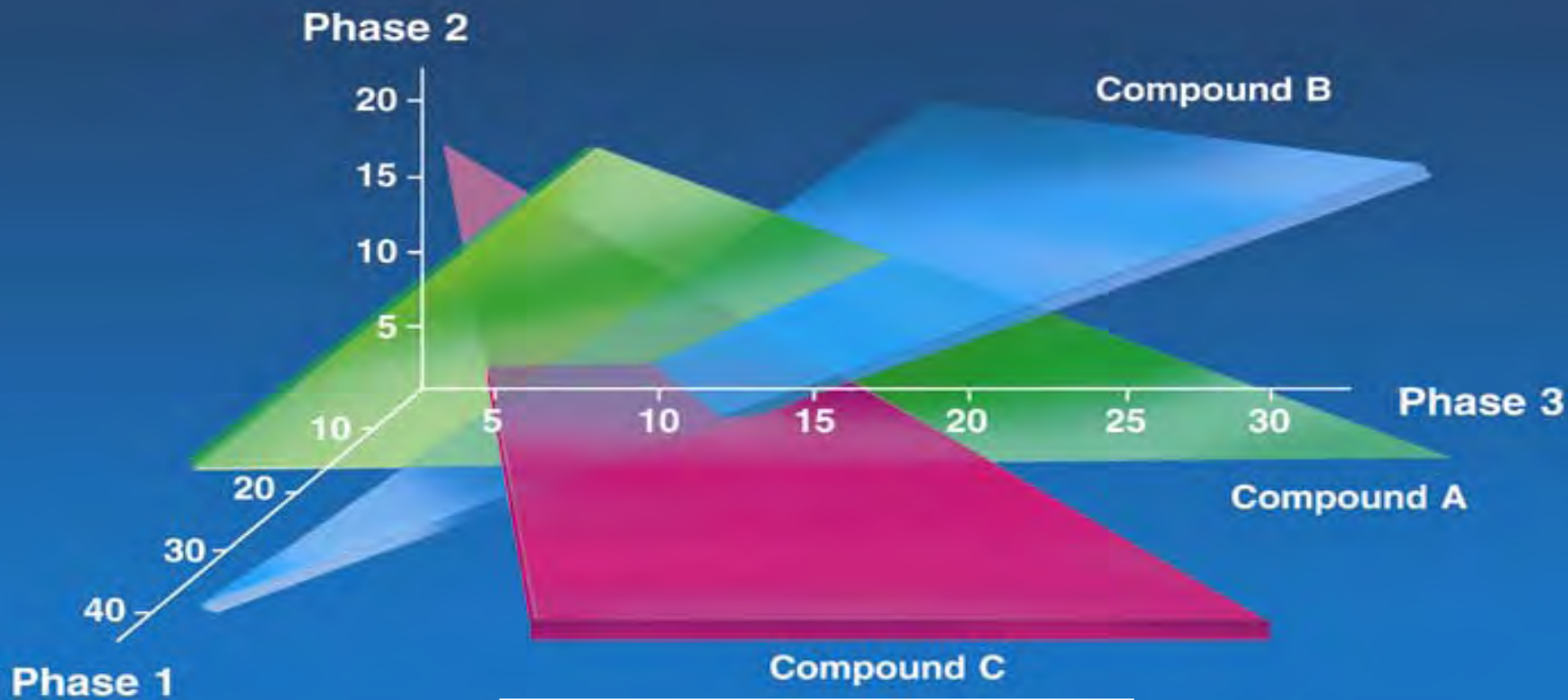
- 1 2,4,5,6-tetrachloro-m-xylene
- 2 alpha BHC
- 3 gamma BHC
- 4 beta BHC
- 5 delta BHC
- 6 heptachlor
- 7 aldrin
- 8 heptachlor epoxide
- 9 gamma chlordane
- 10 alpha chlordane
- 11 4,4' -DDE

- 12 endosulfan I
- 13 dieldrin
- 14 endrin
- 15 4,4' -DDD
- 16 endosulfan II
- 17 4,4' -DDT
- 18 endrin aldehyde
- 19 methoxychlor
- 20 endosulfan sulfate
- 21 endrin ketone
- 22 decachlorobiphenyl

# Stationary Phase Optimization

- Window diagramming
- Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
- Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition AND column dimensions
  - Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX, Rtx-OPPesticides2, Customer-specific columns
- Computer prediction of solute/stationary phase interactions for new polymer designs

# 3-Space Selectivity Model for 3 Compounds



$$\text{Surface} = F \Delta H \Delta S$$

# Explosives Analysis by HRGC

- ◆ HRGC more common than HPLC
- ◆ Selective detection using ECD
- ◆ Direct flash injection of ACN extract
- ◆ Simultaneous dual column analysis

# Explosives Target List EPA 8095

- 1 EGDN
- 2 nitrobenzene
- 3 2-nitrotoluene
- 4 3-nitrotoluene
- 5 4-nitrotoluene
- 6 nitroglycerine coelutes with 2,6-dinitrotoluene on Rtx-200
- 7 1,3-dinitrobenzene
- 8 2,6-dinitrotoluene co-elutes with nitroglycerine on Rtx-200
- 9 1,2-dinitrobenzene (surrogate)
- 10 2,4-dinitrotoluene
- 11 3,4-dinitrotoluene (internal standard)
- 12 1,3,5-trinitrobenzene
- 13 trinitrotoluene
- 14 picric acid
- 15 PETN co-elutes with RDX on Rtx-1, co-elutes with 2-amino-4,6-dinitrotoluene on Rtx-200
- 16 RDX co-elutes with PETN on Rtx-1
- 17 4-amino-2,6-dinitrotoluene co-elutes with 3,5-dinitroaniline on Rtx-5
- 18 3,5-dinitroaniline co-elutes with 4-amino-2,6-dinitrotoluene on Rtx-5
- 19 2-amino-4,6-dinitrotoluene co-elutes with PETN on Rtx-200
- 20 tetryl
- 21 nitroguanidine
- 22 HMX does not elute as a peak when the run time is longer than 20 minutes

# Design Criteria

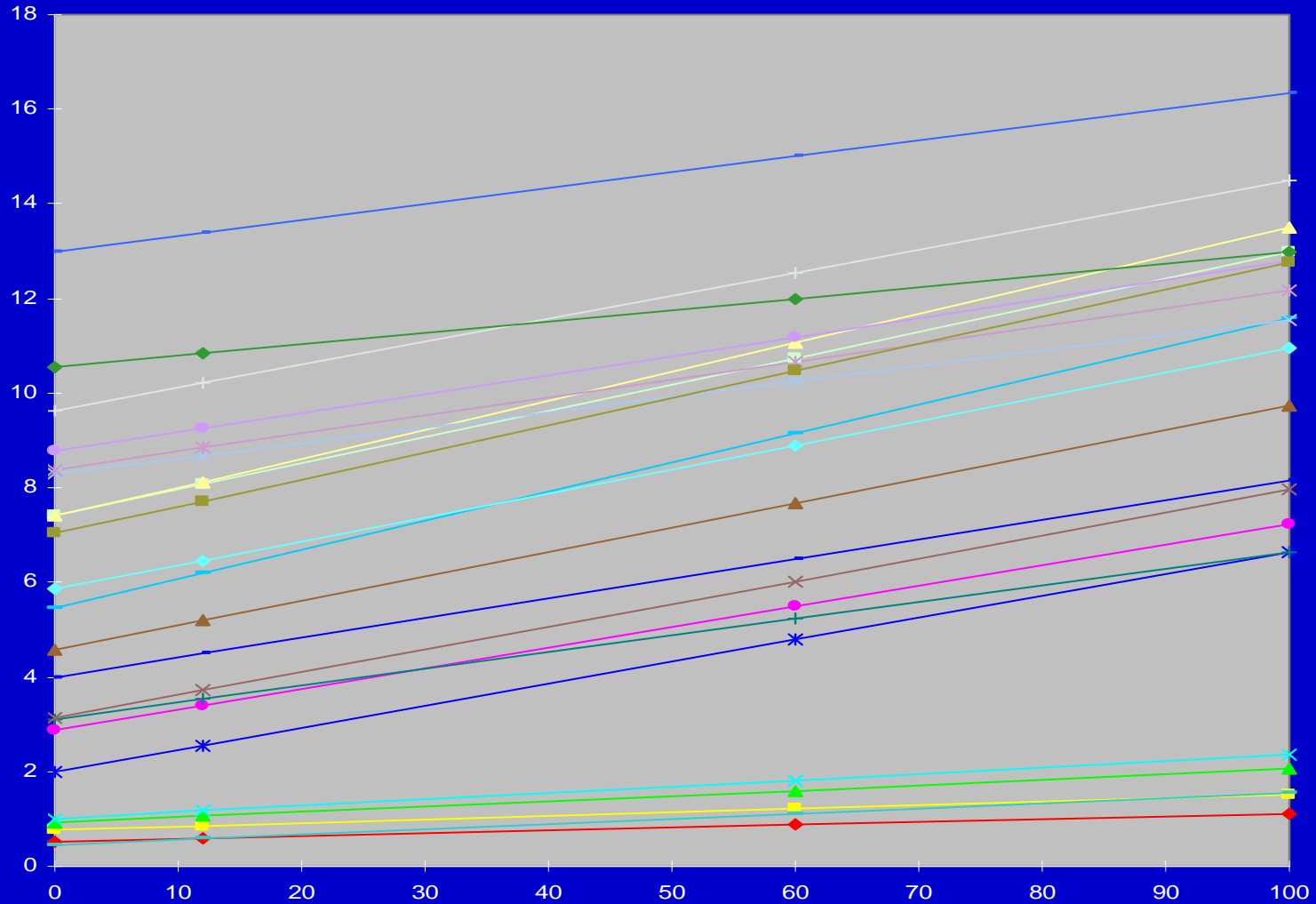
- Short Column, Wide-bore, Standard  $d_f$ , High  $\mu$
- Analysis Time < 20 min.
- Low Bleed with ECD
- Baseline Resolution
- Column Inertness





# Modeling for Explosives

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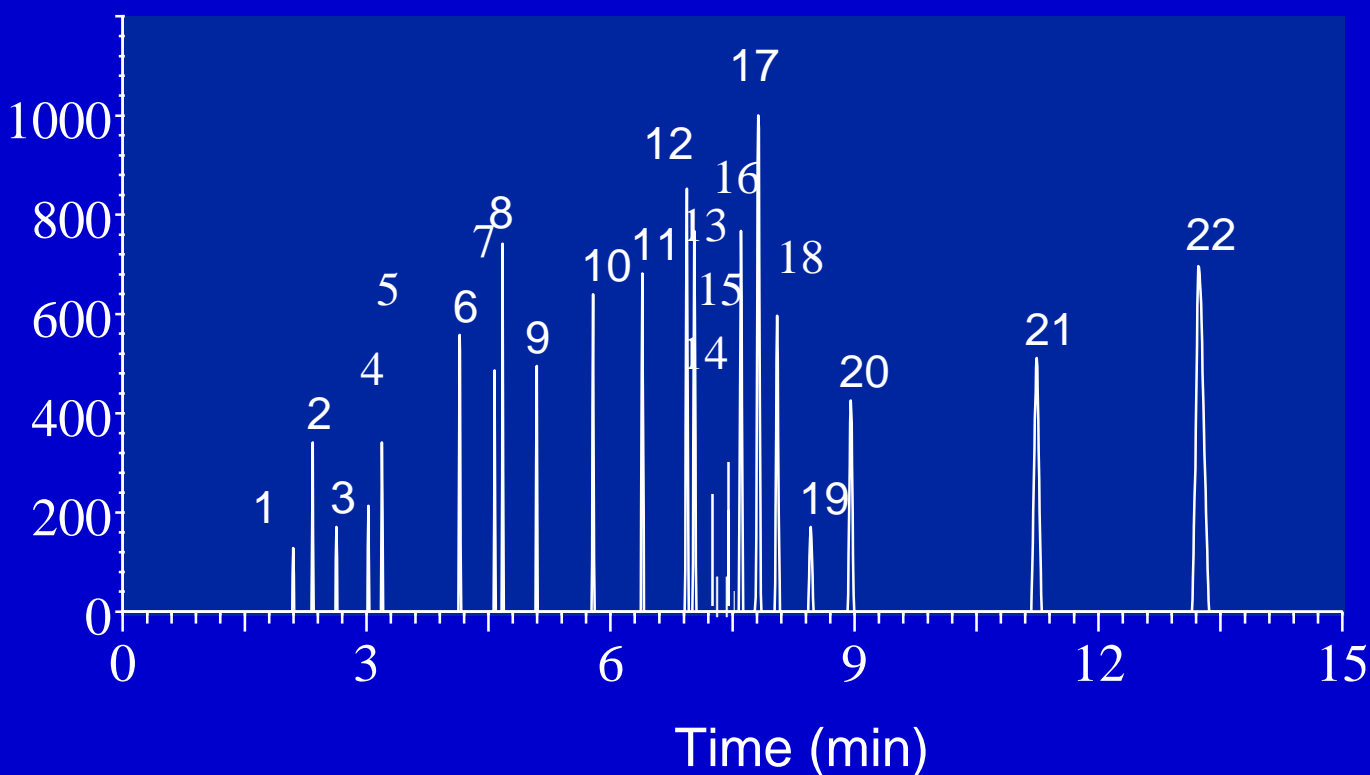




# First Optimization Rtx-TNT

Rtx-TNT1 6 m x 0.53 mm x 1.5  $\mu$ m Direct Inj 250C ECD 300C He@10mls/min.

100°C 2min.to 200°C @ 10°C/min to 250°C @ 20°C/min.(10)

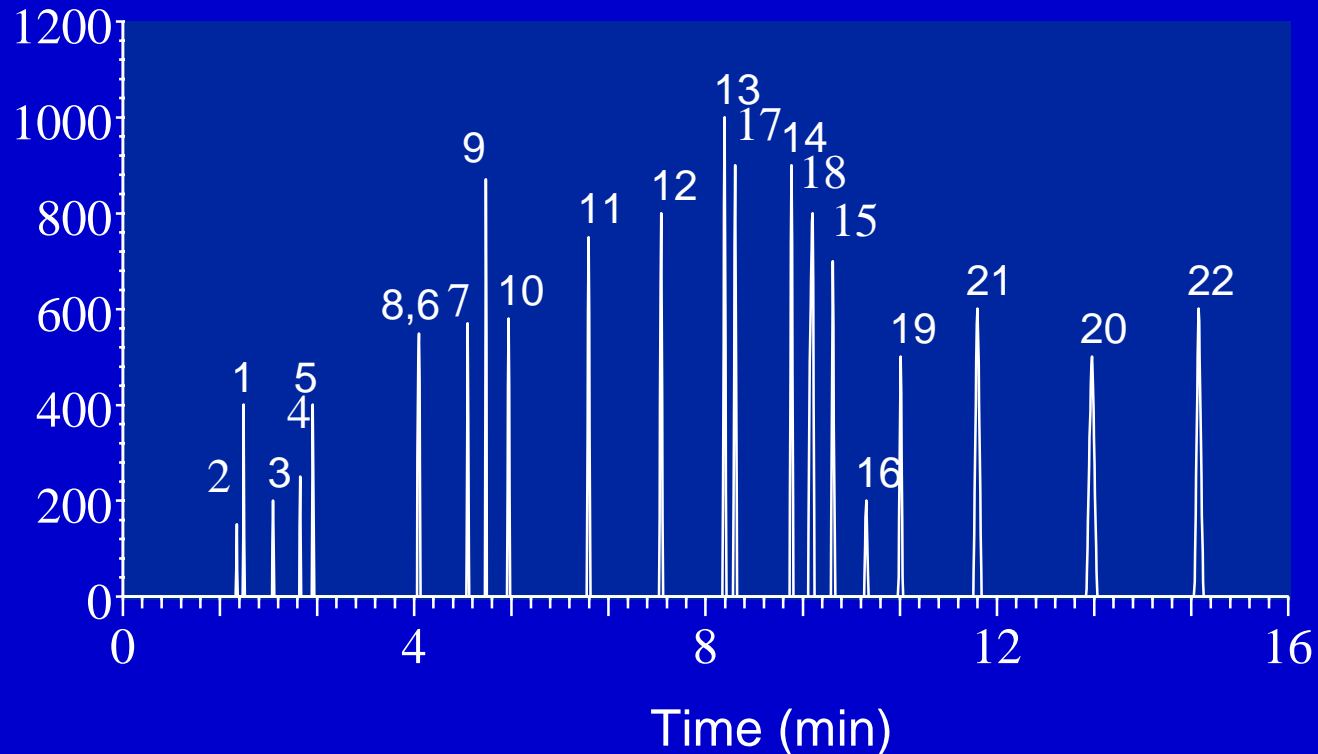


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# Second Optimization Rtx-TNT2

**Rtx-TNT2** 6 m x 0.53 mm x 1.5  $\mu$ m Direct Inj 250C ECD 300C He@10mls/min.  
 100°C 2 min. to 200° C @ 10°C/min to 250°C @200°C/min. (10)

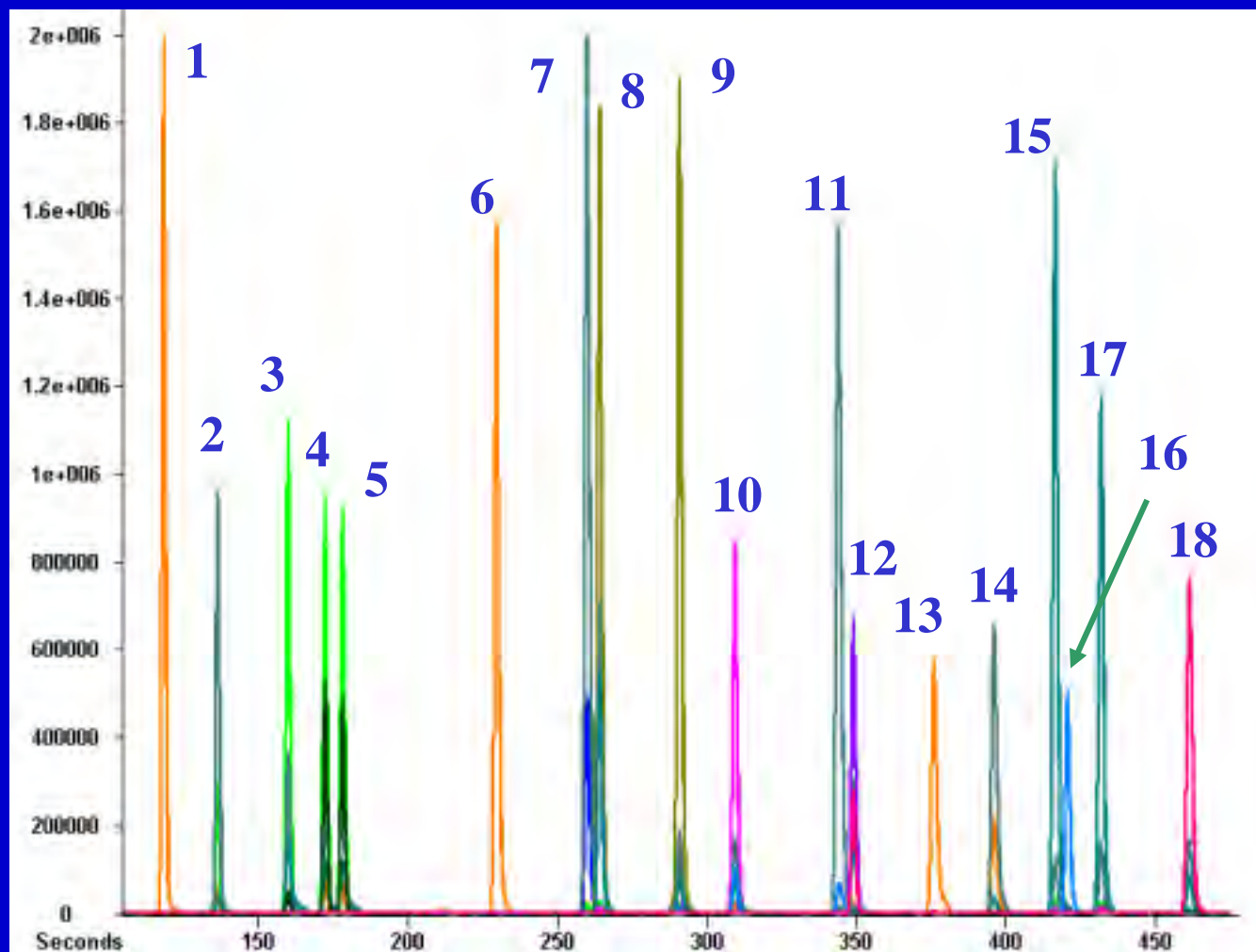


# On-Column Injection Rtx-TNT

1. ethylene glycol dinitrate
2. benzene
3. toluene
4. toluene
5. toluene
6. glycerin
7. nitrobenzene
8. nitrotoluene
9. nitrotoluene
10. nitrotoluene
11. Trinitrobenzene
12. N
13. N
14. N
15. 2-amino-2,6-dinitrotoluene
16. nitroaniline
17. 2-amino-4,6-dinitrotoluene
18. N

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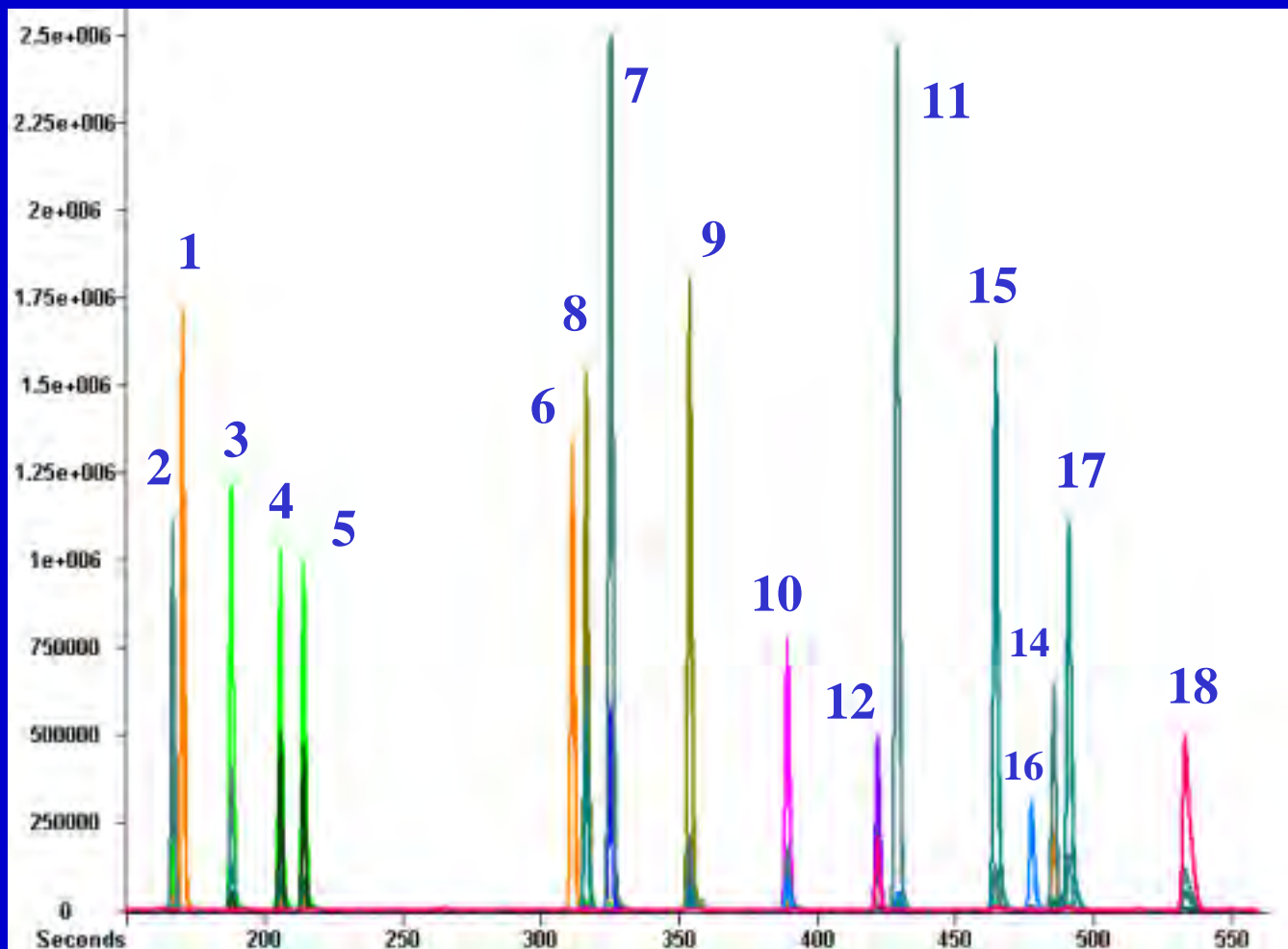
Less than 8 minutes!

# On-Column Injection Rtx-TNT2

1. ethylene glycol dinitrate
2. benzene
3. toluene
4. toluene
5. toluene
6. glycerin
7. dinitrobenzene
8. dinitrotoluene
9. dinitrotoluene
10. dinitrotoluene
11. Trinitrobenzene
12. 2,4-dinitrophenol
13. 2,6-dinitrophenol
14. 2,4,6-trinitrophenol
15. 2-amino-2,6-dinitrotoluene
16. dinitroaniline
17. 2-amino-4,6-dinitrotoluene
18. 2,4,6-trinitroaniline

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9 minutes.



PETN is thermally degraded.

# What If No Selective Functionality Can be Found?

- Accept less than ideal separation
  - Effect on quantitation and/or run time
- Use “old method” of trial and error
  - Slow, and inefficient
  - No guarantee that solution will be found
- Test functionalities electronically
  - Unproven technique for GC applicaiton
  - CPU intensive
  - Faster than trial and error

# Stationary Phase Optimization

- Window diagramming
- Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx®-CLPesticides Rtx-CLPesticides2, Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

# Computer Modeling: 2 Approaches

- Molecular Dynamics Approach:
  - Molecules are treated as harmonic oscillators, and forces of interaction are minimized to determine orientation.
- Quantum Mechanical Approach:
  - Wave functions are calculated, and molecular orbital structure is determined.
- Two techniques are complementary



# Achieving Analyte Separation

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha - 1 / \alpha)$$

## Capacity Factor

$$k = (t_R - t_0) / t_0$$

## Selectivity

$$\alpha = k_2 / k_1$$

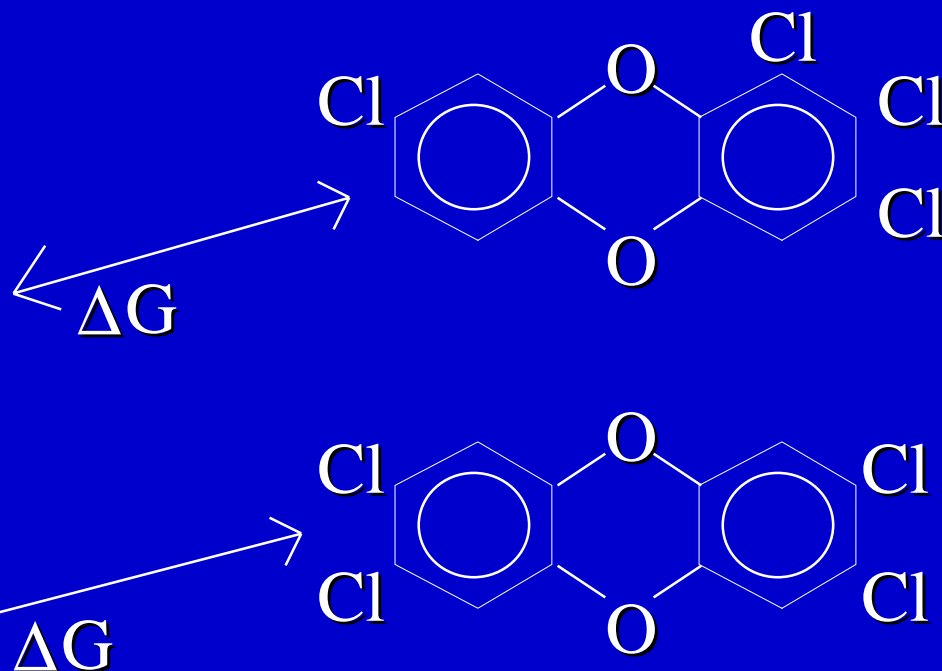
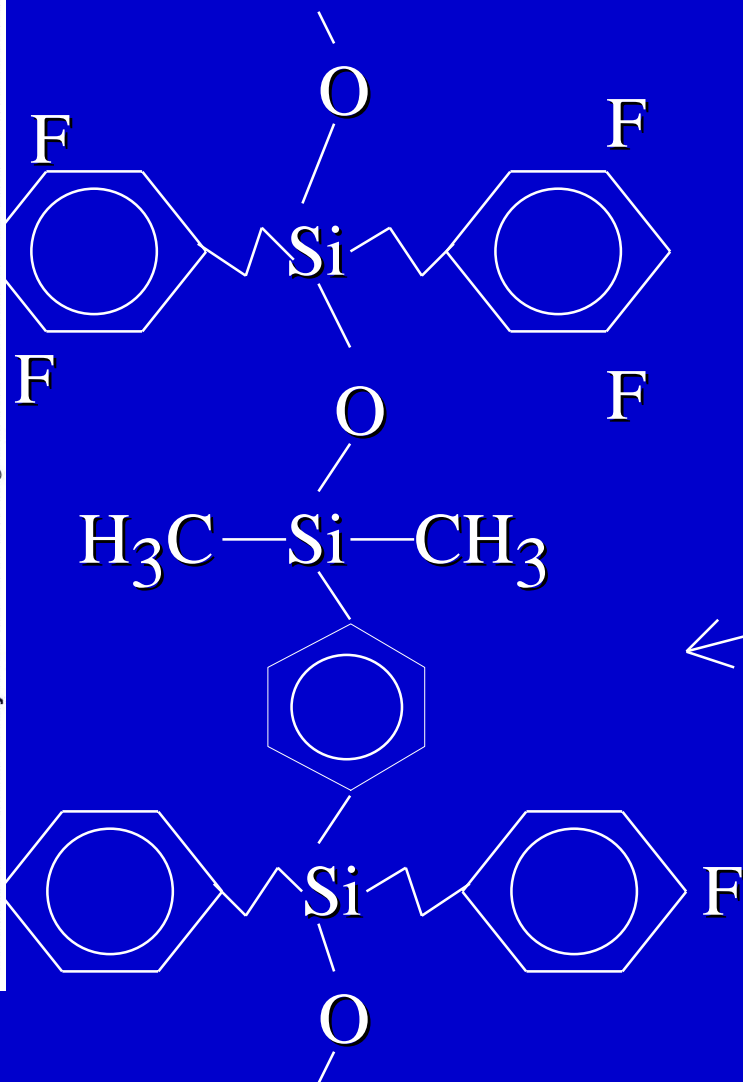
## Thermodynamics:

$$\Delta G = \Delta H - T\Delta S$$

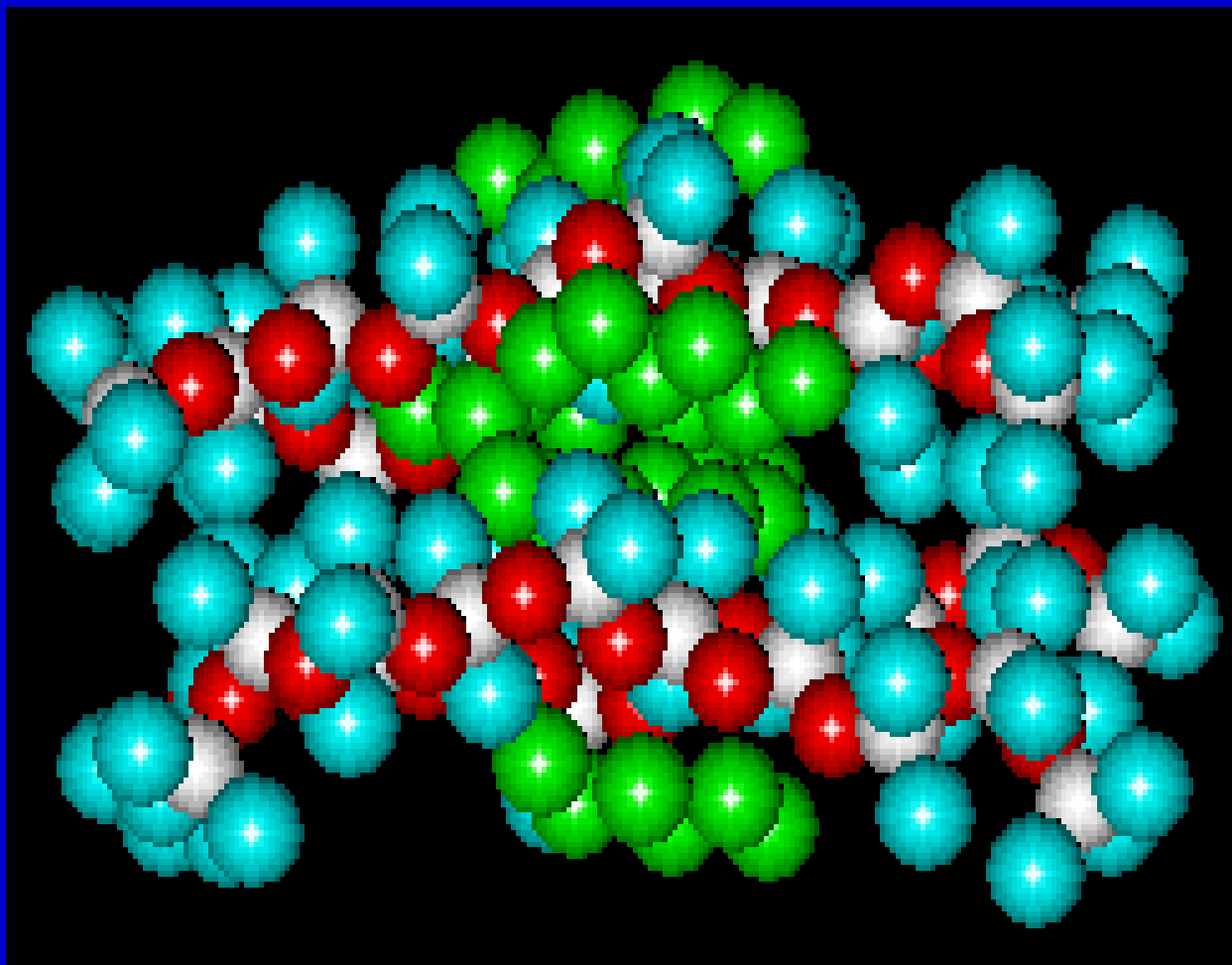
$$\Delta G = -RT \ln K_D$$



# Modeling - Energies of Interaction



Separation ( $\Delta\alpha$ ) =  $\Delta \Delta G$



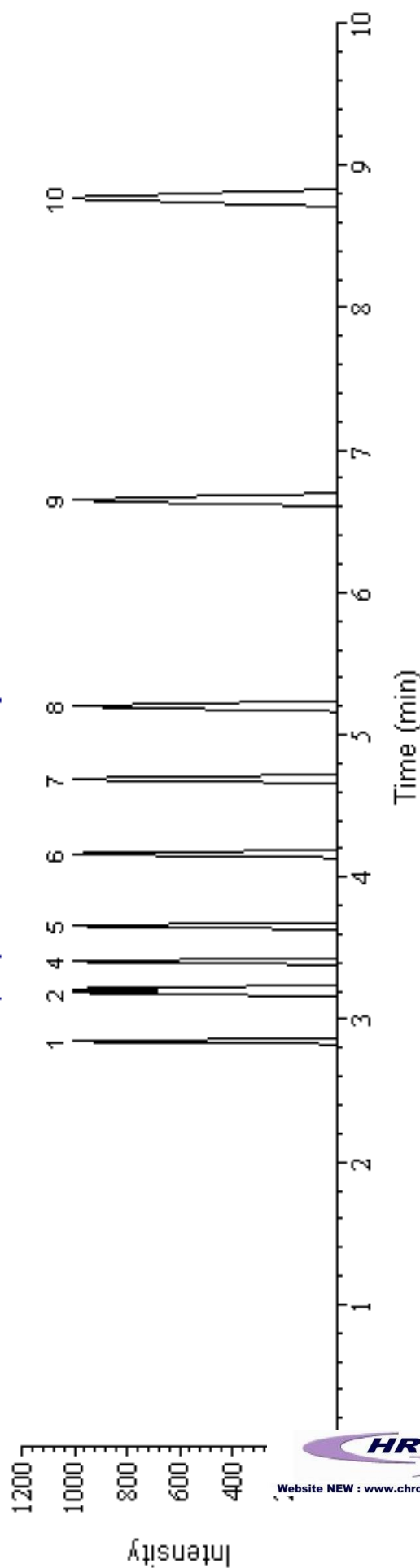
# Molecular Modeling Results:

- Initial attempts were not successful
- Evaluated different force fields – AMBER
- Modified calculations based on work of A.Z. Panagiotopoulos
- Demeton-O on PDMS phase:
  - Observed  $\Delta G = -1.14E4$  J/mol
  - Calculated  $\Delta G = -1.13E4$  J/mol

# Physical Parameter Optimization

- Chromatographers need ability to optimize separations to make most efficient possible use of time
  - Aids column choice
  - Excellent teaching tool
  - Allows for run-time and separation optimization for common compounds, or specific user compounds

Solution 1- Rbx-1 30 m x 0.320 mm x 1.0 µm  
70°C (10) Linear Velocity: 20.00 cm/sec



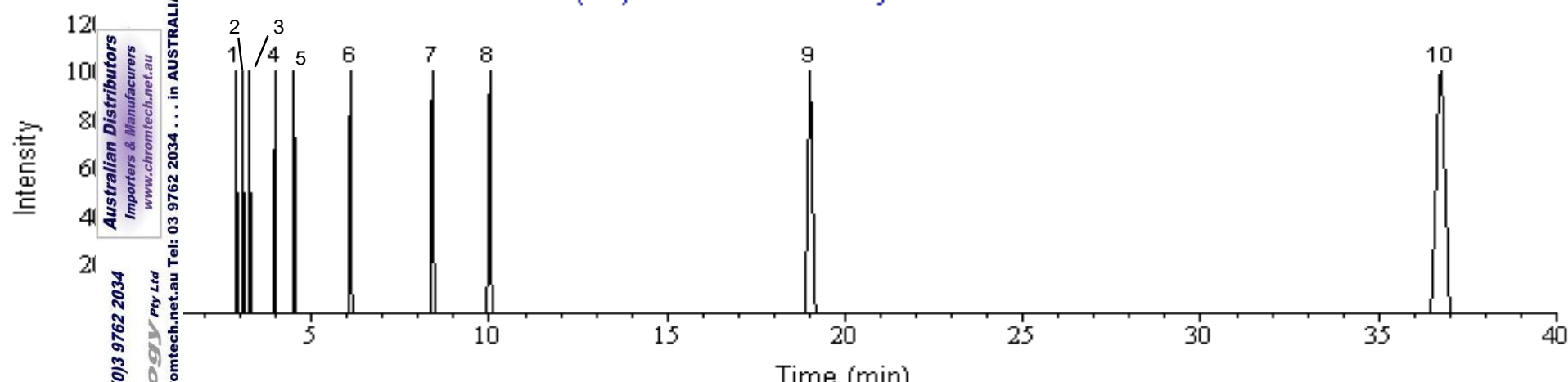
Solution

bular

#	Co	ent Name	tR (min)	Width (min)	Rs
1.	acet		2.843	0.0417	8.10
2.	1-pr	ol	3.183	0.0466	0.65*
3.	pent		3.214	0.0471	0.65*
4.	meth	hylketone (MEK)	3.407	0.0499	4.06
5.	hexa		3.654	0.0535	4.93
6.	1-bu		4.162	0.0610	8.57
7.	3-pe	one	4.688	0.0687	7.36
8.	hept		5.197	0.0761	7.36
9.	1-pe	ol	6.650	0.0974	18.94
10.	octa		8.770	0.128	21.60

\* &lt; Minimum Resolution

Solution 1 - 10 out of 10 components resolved &gt;= 4.00

Solution 1- StabilWax 30 m x 0.320 mm x 1.0 µm  
70°C (41) Linear Velocity: 20.00 cm/sec

Solution 1

#	Component Name	tR (min)	Width (min)	Rs
1.	hexane	2.882	0.0422	4.48
2.	pentane	3.072	0.0450	4.00
3.	heptane	3.254	0.0477	4.00
4.	octane	3.960	0.0580	9.10
5.	acetone	4.492	0.0658	9.10
6.	methyl ketone	6.079	0.0890	23.94
7.	3-pentanone	8.386	0.123	12.95
8.	1-propanol	9.988	0.146	12.95
9.	1-butanol	19.011	0.278	61.23
10.	1-pentanol	36.737	0.538	63.20

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# What about my compounds?

- User libraries are easy to create
  - Compounds analyzed using two different temperature programs
  - Must measure dead times for column
  - Input directly or via spreadsheet
- Two runs necessary to determine optimum set of physical parameters for compound list

# For the Routine User:

- Pro EZ-GC is relatively simple to operate
- Allows rapid selection of optimal program
  - Flow rates, carrier types and temperatures
- Transportable from PC to PC
- Low cost
- Can aid in column choice for common analyses
- Excellent teaching tool



# Summary

- Stationary Phase Modeling:
  - Allowed for 10 new commercially-available phases over last three years
  - Individual customer columns can be cost effective
  - Most important factor for resolution is choosing a highly selective stationary phase
- Physical Modeling:
  - Pro ezGC reintroduced for operation under current operating systems. Low cost, and allows for physical optimization.

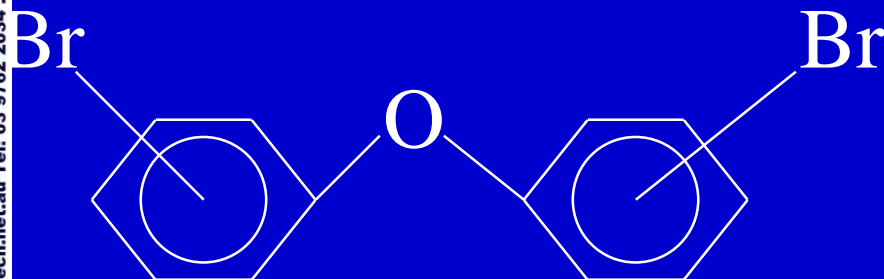
# Gas Chromatographic Analysis of Polybromonated Diphenyl Ethers Using a Novel GC Column

Frank L. Dorman, Chris English, Karen MacPherson, and Eric Reiner

# Brominated Flame Retardants:

- Products based on penta-, octa-, and decaBDE are commercially used as flame retardants
- Global production of DeBDE is approximately 40,000 tons/year
- Heavily used for furniture treatment and electronics in USA, Japan, and Europe
- May form PBDDs and PBDFs when combusted, and toxicity is estimated to be similar to PCDDs and PCDFs

# Polybrominated Diphenylethers



## Br 1-10

- Named similarly to PCB congeners (BDE 1-209)  
J. High Resolut Chromatogr **15**:260
- Human exposure via the food chain is 0.2 – 0.7 mg/day  
Organohalogen Compounds **35**:411
- Listed as Endocrine Disruptors  
Environ Health Perspect **101**:378

# Methods of Analysis

- Electron capture detection
  - Lower cost
  - More common to most labs
- High-resolution mass spectrometric detection
  - Additional specificity may improve sensitivity
  - Many dioxin labs are also interested in PBDEs
- Others not investigated
  - GC-NCI-MS
  - HPLC-MS

# Prior Analyses

- GC-HRMS
  - Difficulty eluting nona's and decaBDE due to high molecular weight
  - Column bleed levels hurt sensitivity of higher bromination levels
  - Often done using two columns:
    - Longer column to separate lower bromination level congeners
    - Short column to analyze nona and decaBDEs

# Prior Methods of Analysis

- Decision made if deca (and possible nona and octa) are desired
  - Higher molecular weight congeners are either analyzed separately, or not at all
  - Higher molecular weight congeners are allowed to “ghost” out on “standard” column (5% diphenyl)
- Loss of higher molecular weight congeners is also due to injection technique

# Convert Split or Splitless Inlets to Direct Injection

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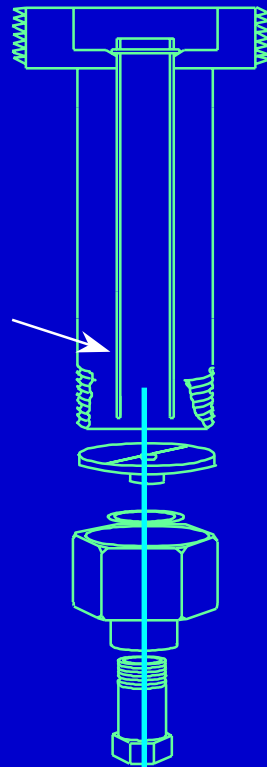
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Always keep

split vent

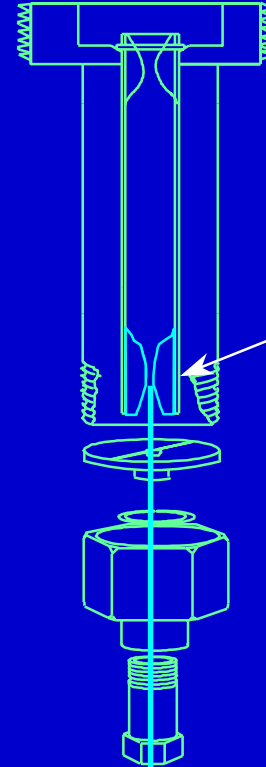
page off

Remove  
the split  
or  
splitless  
sleeve



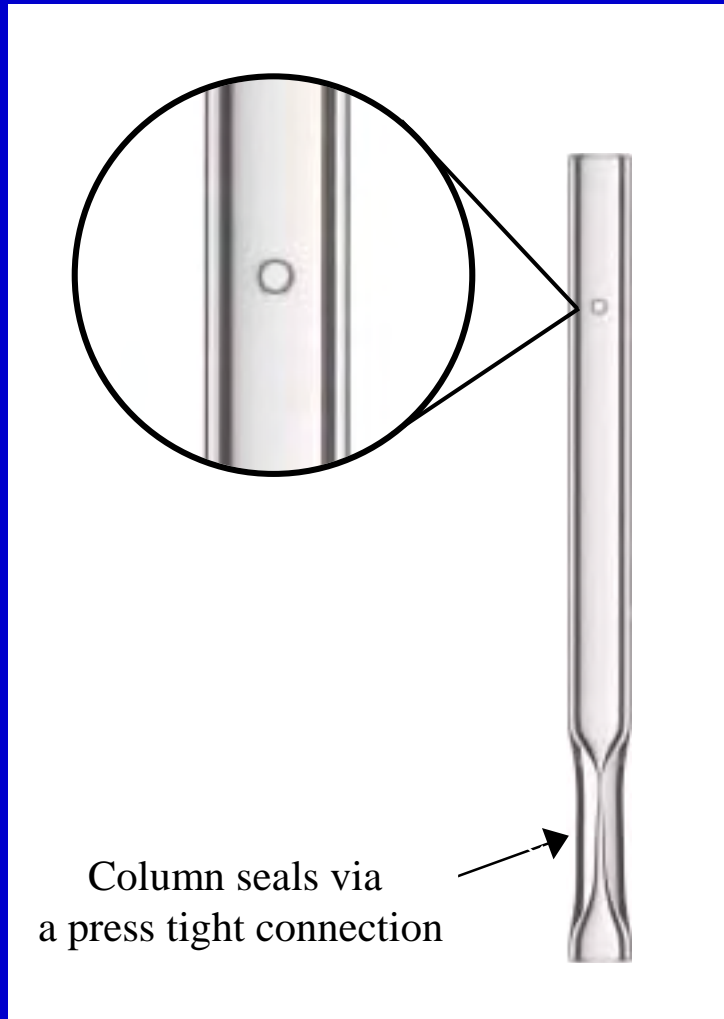
Install a Direct  
Injection sleeve

Press-fit  
connection





# Uniliner w/ Hole



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

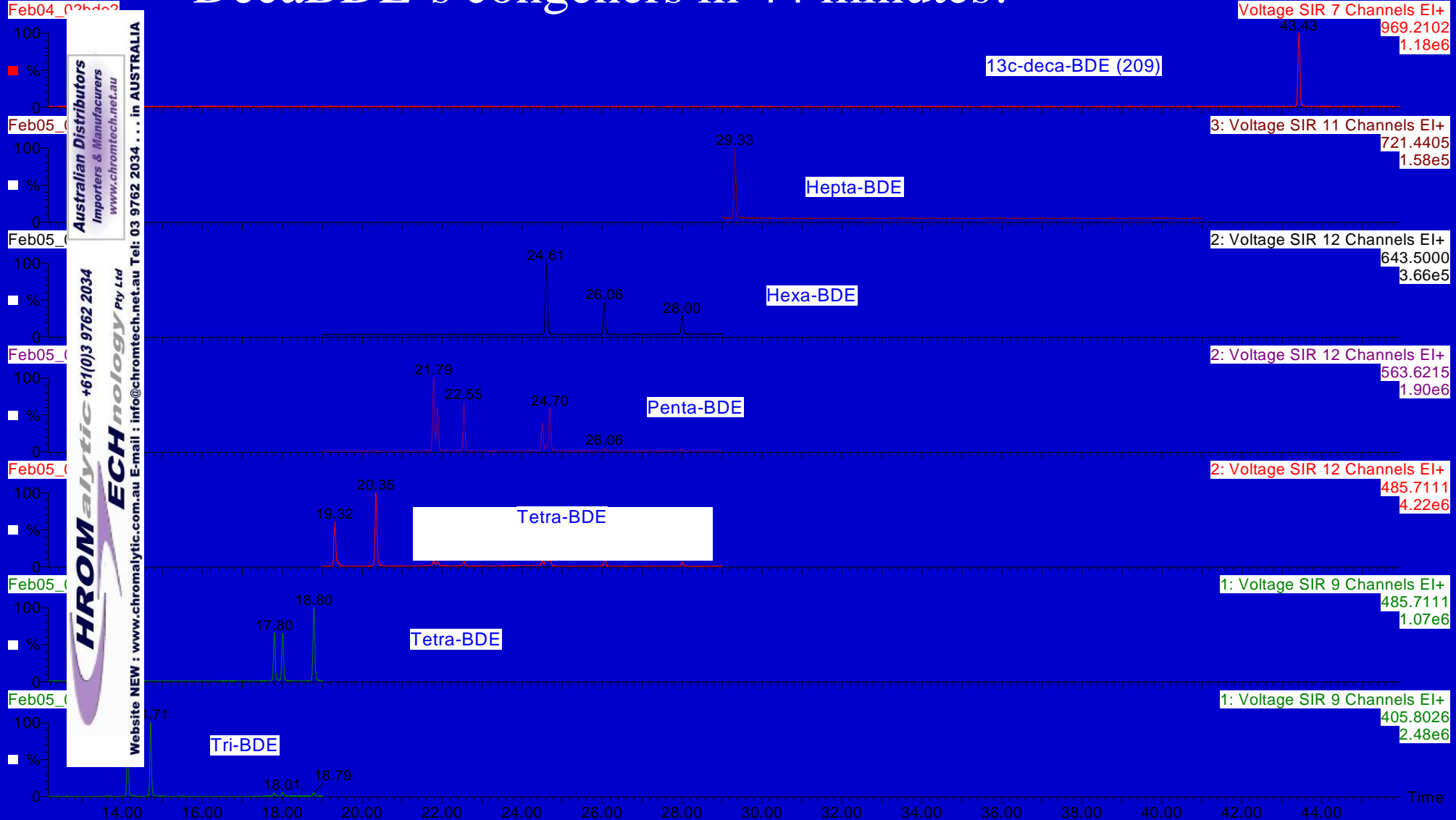
# Rtx-500 Capillary GC Column

- Carborane-stabilized stationary phase
  - Maximum temperature of 380°C in “standard high-temperature” tubing
  - Maximum temperature of 440°C in passivated metal columns (Mxt-500)
- Extremely low bleed levels
  - Surpasses phenyl/methyl phases, and silphenylene stationary phases
- Common dimensions available

# Wellington Laboratories BDE Mix-C

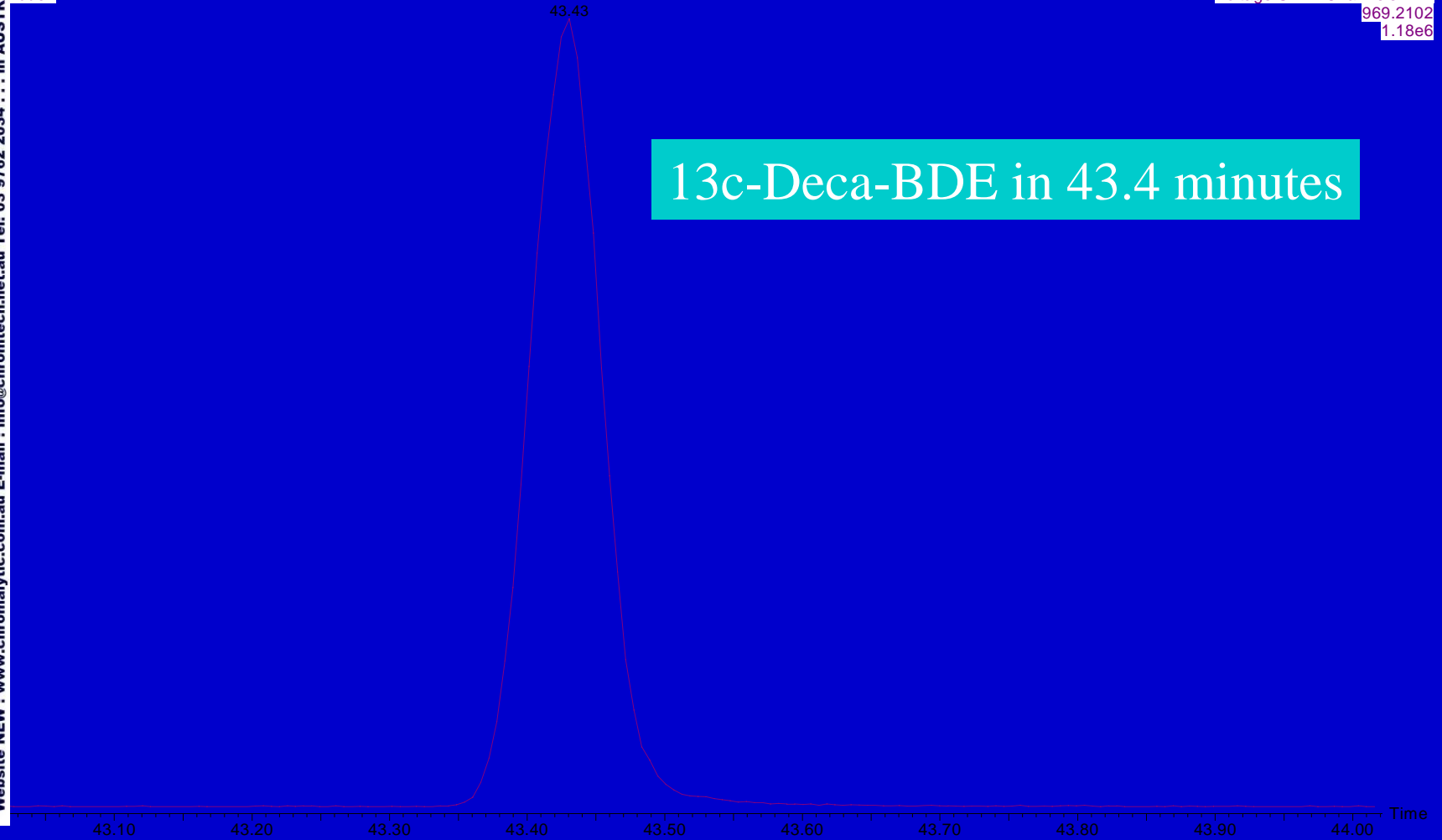
<b>CHROMALYTIC</b> <b>ANALYTICAL</b> <b>TECHNOLOGY</b> <b>Pty Ltd</b> Website NEW : <a href="http://www.chromalytic.com.au">www.chromalytic.com.au</a> E-mail : <a href="mailto:info@chromotech.net.au">info@chromotech.net.au</a> Tel: 03 9762 2034 +61(0)3 9762 2034 Australian Distributors Importers & Manufacturers <a href="http://www.chromotech.net.au">www.chromotech.net.au</a>	monobromodiphenyl ether (3)	250	141,115
	1,2-dibromodiphenyl ether (7)	168	328,139
	1,3-dibromodiphenyl ether (15)	328	168,221
	1,4-tribromodiphenyl ether (17)	248	408,406
	1,2,3-tribromodiphenyl ether (28)	406	248,246
	1,2,4,5-tetrabromodiphenyl ether (49)	326	486,328,324
	1,2,4,6-tetrabromodiphenyl ether (71)	326	486,324,328
	1,3,4,4'-tetrabromodiphenyl ether (47)	326	486,328,324
	1,3,4,4'-tetrabromodiphenyl ether (66)	326	486,328,324
	1,3,4,4'-tetrabromodiphenyl ether (77)	326	486,328,324
	1,2,3,4,4',6-pentabromodiphenyl ether (100)	406	564,566
	1,2,3,4,4',6-pentabromodiphenyl ether (119)	404	406,564
	1,2,3,4,4',5-pentabromodiphenyl ether (99)	406	564,566
	1,2,3,4,4',5-pentabromodiphenyl ether (85)	406	564,566
	1,2,3,4,4',5-pentabromodiphenyl ether (126)	566	564,568,406
	1,2,3,4,4',5,6'-hexabromodiphenyl ether (154)	484	644,486
	1,2,3,4,4',5,5'-hexabromodiphenyl ether (153)	644	484,486,482
	1,2,2',3,4,4',5'-hexabromodiphenyl ether (138)	642	484
	2,2',3,4,4',5',6-heptabromodiphenyl ether (183)	722	564
	decabromodiphenyl ether (209)	956	

## 1.18e6



13C  
2bde2

Voltage SIR 7 Channels EI+  
969.2102  
1.18e6



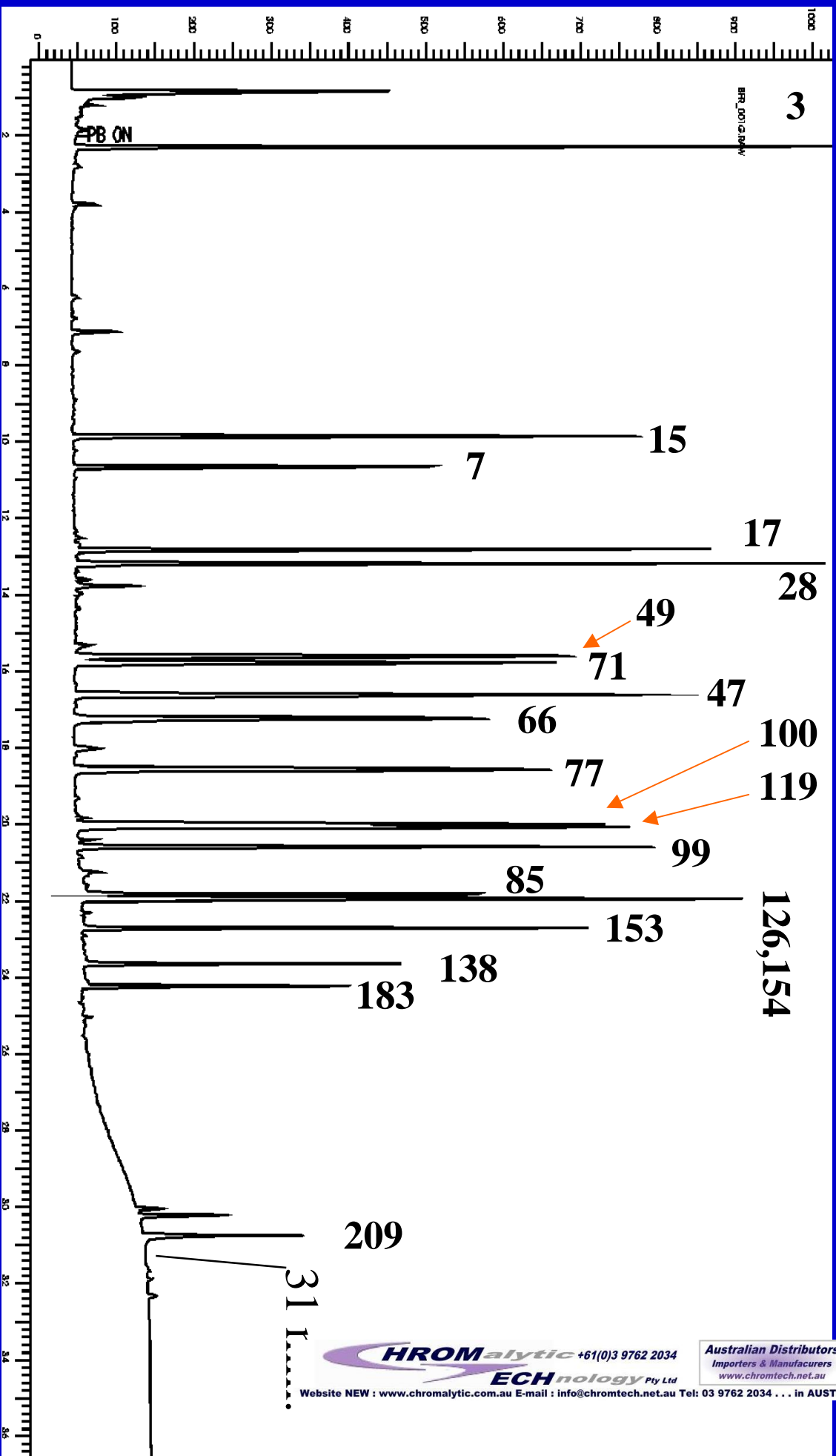
13c-Deca-BDE in 43.4 minutes

	<b>BROMINATED FLAME RETARDANT GC PROGRAM</b>				
	<b>INSTRUMENT CONFIGURATION</b>				
	Micromass Autospec-UltimaNT (High Resolution Mass Spectro				
	Source Temperature = <b>300°C</b>				
	<b>GC CONDITIONS</b>		<b>(HP 6890 +)</b>		
		<b>Constant flow @ 1.5mL/min</b>			
		<b>Injector Temp.</b>	<b>300°C</b>		
		<b>Temp. Ramp</b>	<b>Temp.</b>	<b>Hold Time</b>	
		Start Temp.	100	1 min	
		10	110	0.64	
		80	180	0	
		5	350	23	
		<b>TOTAL RUN TIME =</b>		<b>60.51</b>	
		<b>**NB: DecaBDE (last elutor) elutes at ~43 min.</b>			

# GC-ECD Analysis

- Electron capture detector is common to many laboratories
- Compounds have excellent response by ECD
- Higher flow rates may allow for more rapid separation using larger-diameter columns
- Instrumentation less expensive than HRMS
- Instrumentation is also field portable

# Wellington Laboratories BDE Mix-C



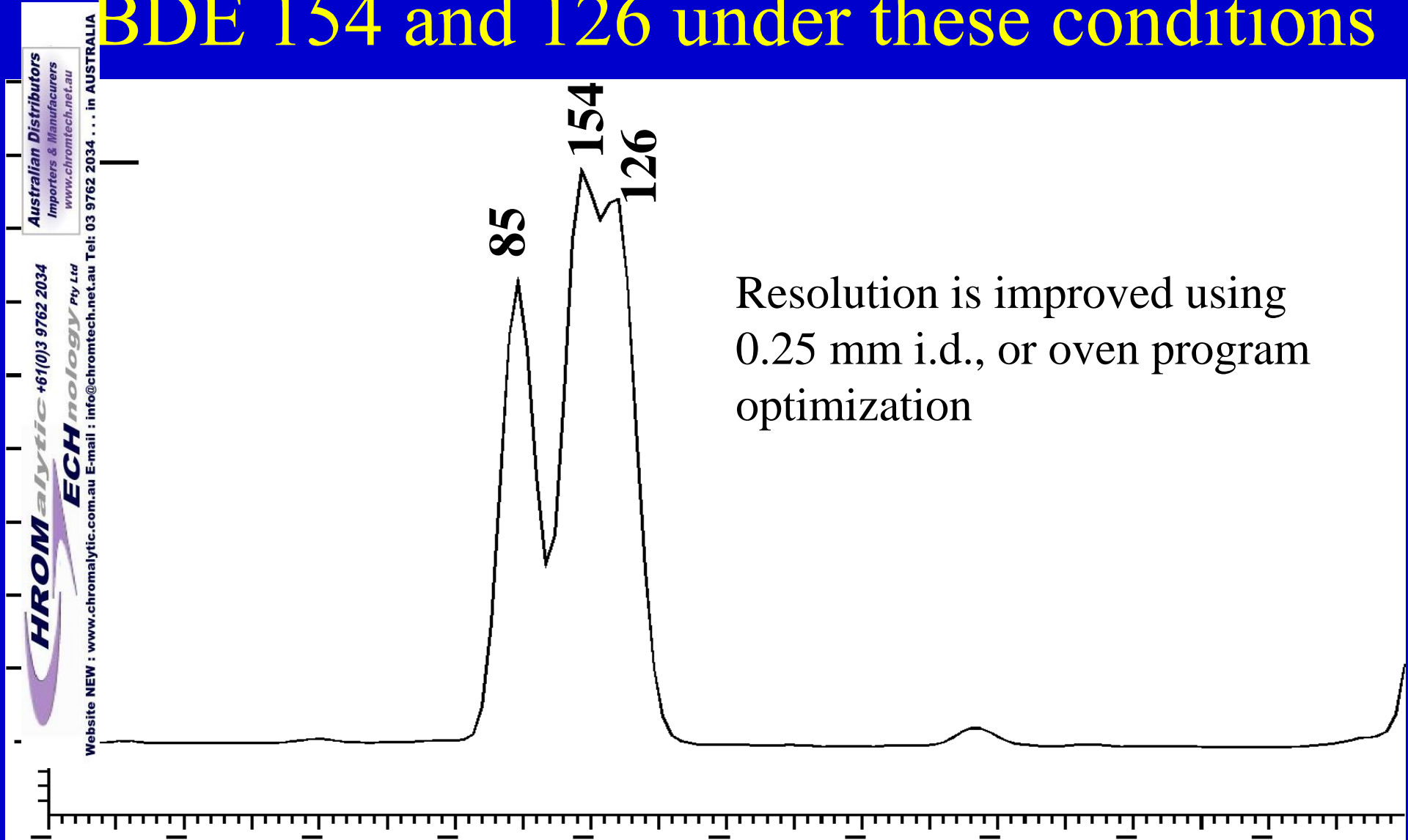
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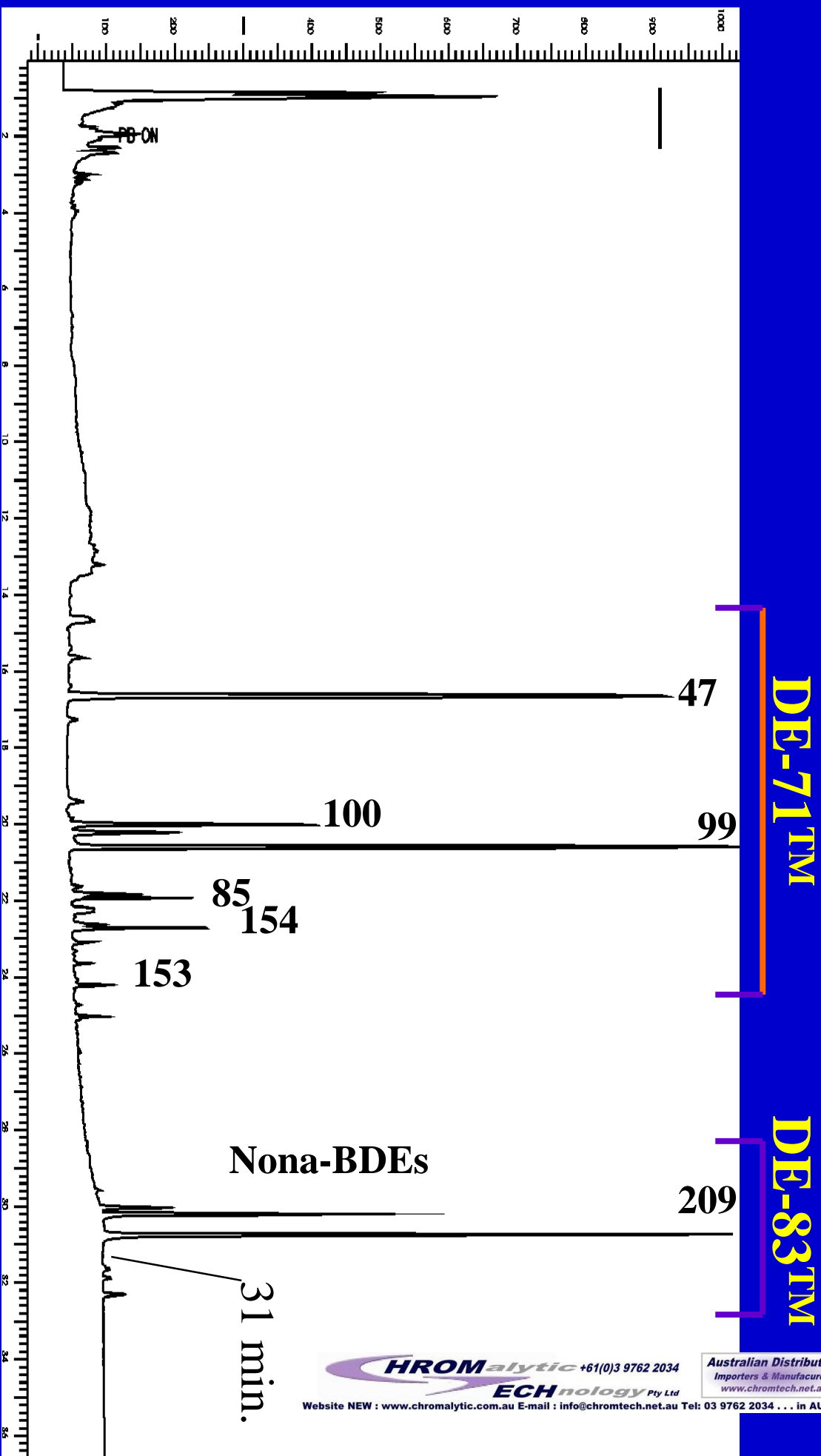
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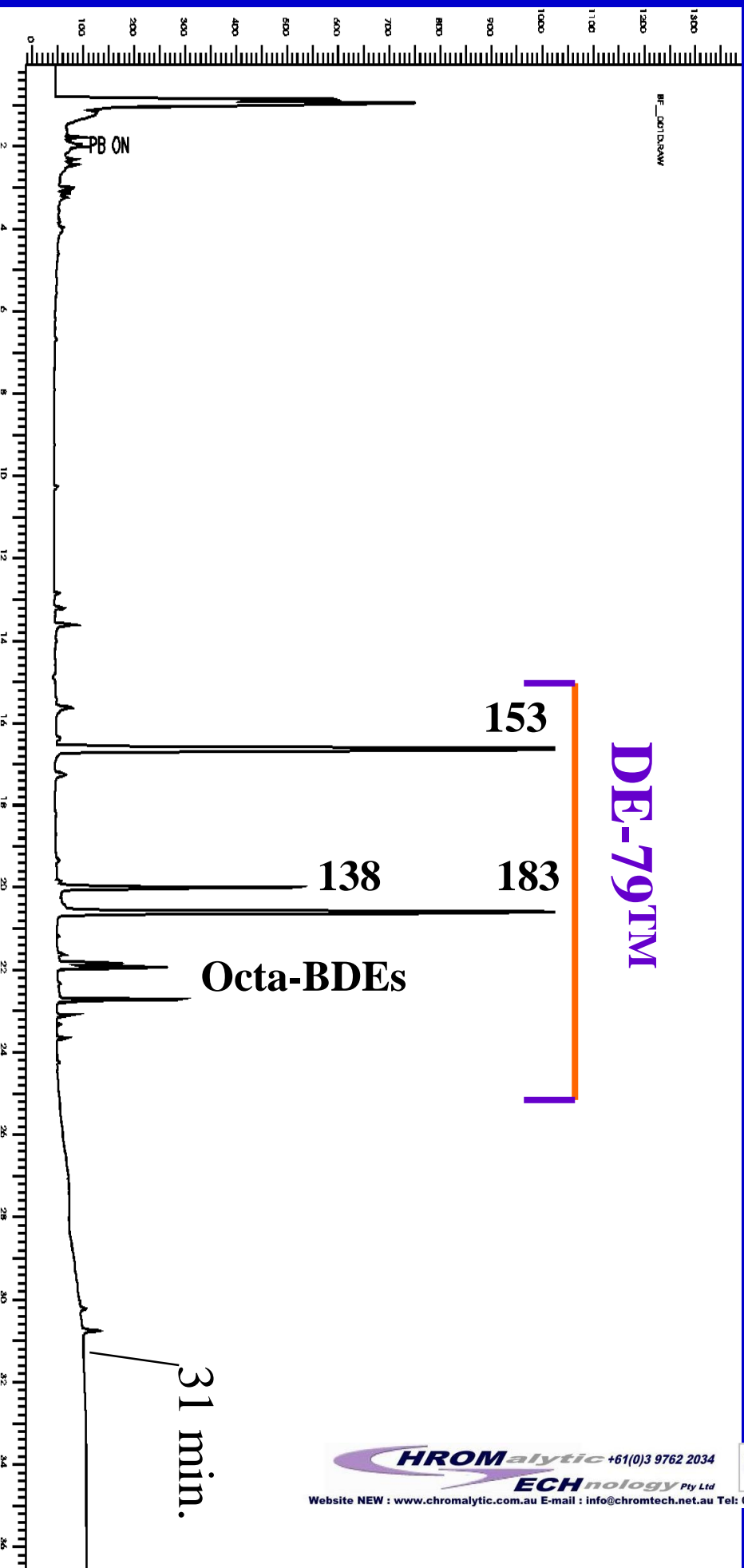
# 0.53 mm i.d. column partially resolves BDE 154 and 126 under these conditions



# Commercially Available PBDE Mixes



# Commercially Available PBDE Mixes



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# Conditions

**Column:** Rtx-500 30m x 0.53mm x 0.15 Ser# 233548  
**Flow:** Hydrogen 7.69ml/min (66.7cm/sec) @ 100°C  
**Detector:** MeCl<sub>2</sub> Headspace 0.76min @ 100°C  
**Injection:** 100(1) 15/260(5) 15/380 (15) ~ 40 min runtime  
**Standards:** Wellington Laboratory BDE-Mix C  
1ul injection 30pg on column  
**Injection:** Drilled Press-Tight Uniliner

# Other Uses of Rtx-500 Columns

## • PCB Congener Analysis

- Separation of World Health Organization 12 toxic congeners
- Investigating use for larger lists of PCB Congeners

## • PBB and PCBB Congeners

- Similar separations to PCBs with higher temperature requirements

## • PCDDs/PCDFs

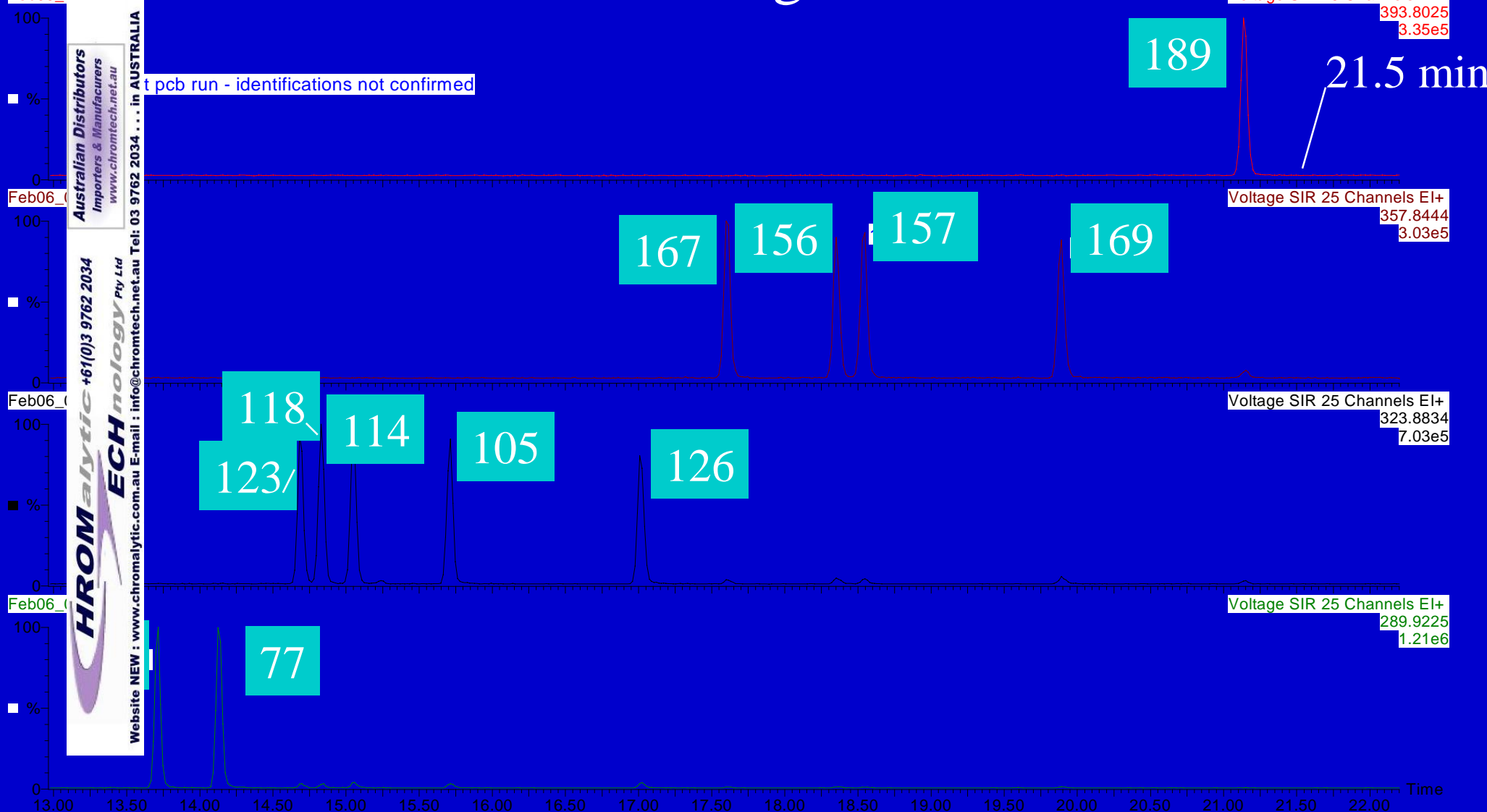
- Currently under investigation

## • PBDDs/PBDFs

- ?

## dlp-cs5 on htc

Feb06\_02samp1



# Summary

- Rtx-500 Capillary GC Column
  - Consolidated PBDE analysis to a single column with excellent separation and reasonable run time
  - Extremely low-bleed polymer improves sensitivity of late-eluting compounds
  - Completely resolves all toxic PCB congeners
  - Very robust stationary phase which will not exhibit selectivity changes
  - Maximum thermal stability 380°C in fused silica, 440°C in passivated metal columns

# Acknowledgements

- Reference materials courtesy of Wellington Laboratories – Guelph, Ontario
- Dr. Eric Reiner and Karen MacPherson of the Ontario Ministry of the Environment – Etobicoke, Ontario provided the HRMS analyses, and guidance.



# Abstract

- The analysis of polychlorinated biphenyls (PCB's) by GC can be a very challenging analysis. Numerous researchers have demonstrated various separations on the common commercially available GC stationary phases, but all of these have had limitations when it comes to the separation of all 209 possible PCB congeners. While it may be argued that the complete separation of all 209 possible congeners is not necessary, separation of the environmentally significant and the toxic congeners is important.
- The separation requirements for the analysis of PCB congeners differ considerably depending on the type of detector used. Separation needs when using a mass spectrometer are different then when using standard GC detectors.
- This presentation will discuss the separation needs for PCB congeners when using a mass spectrometer, and demonstrate an improved separation of PCB congeners, using a new capillary stationary phase developed for this purpose.

# Experiment

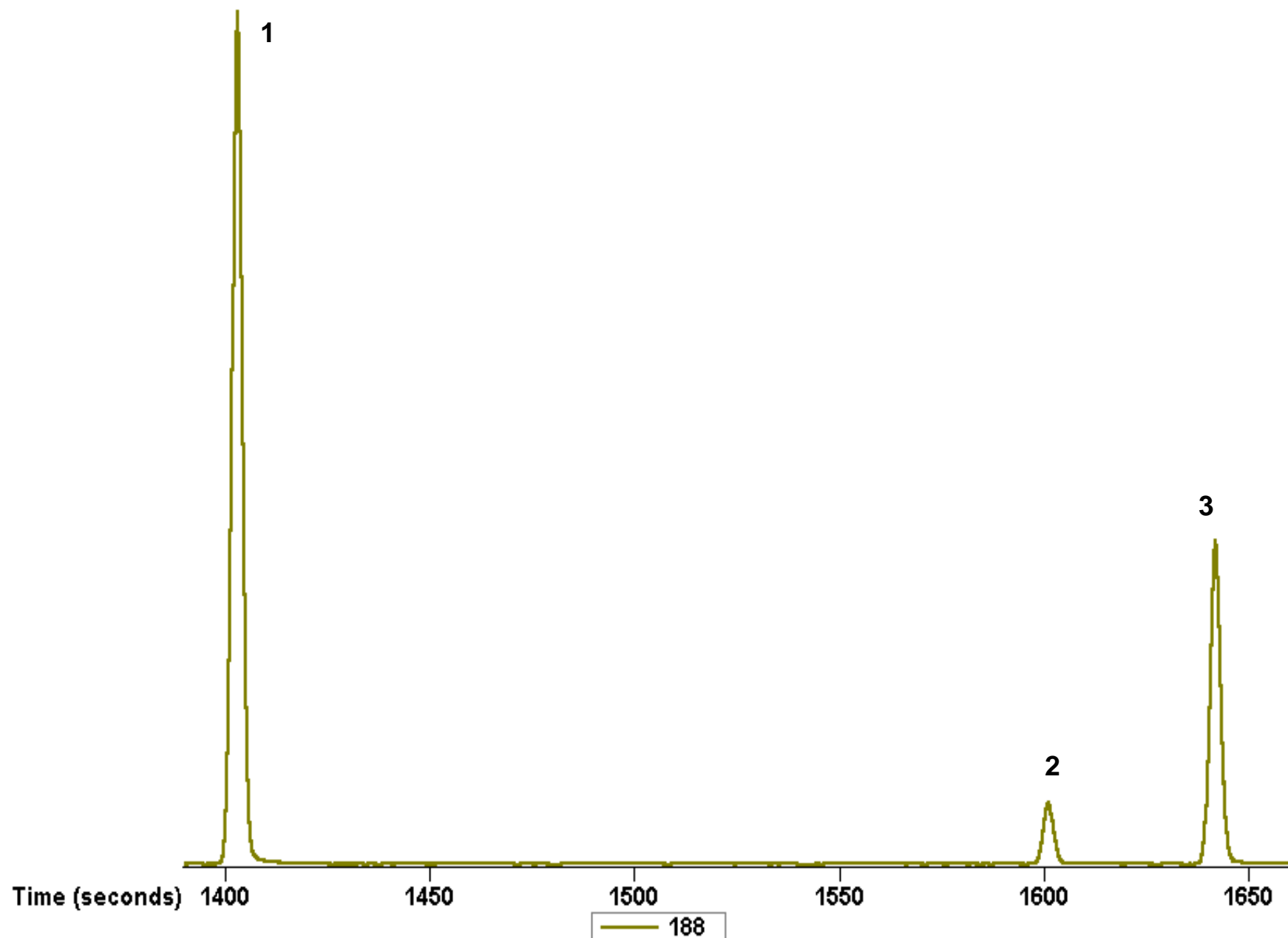
- Determine retention times for all **209 PCBs** on a new low-bleed capillary column
  - AccuStandard 9 mixtures
  - Hexachlorobenzene for relative retention times
- Analyze mix of Aroclors 1221:1242:1254:1262
  - 1:2:2:2 ratio
  - Show chromatogram with congeners labeled
- GC-MS results obtained using a time-of-flight mass spectrometer to allow for possible spectral deconvolution

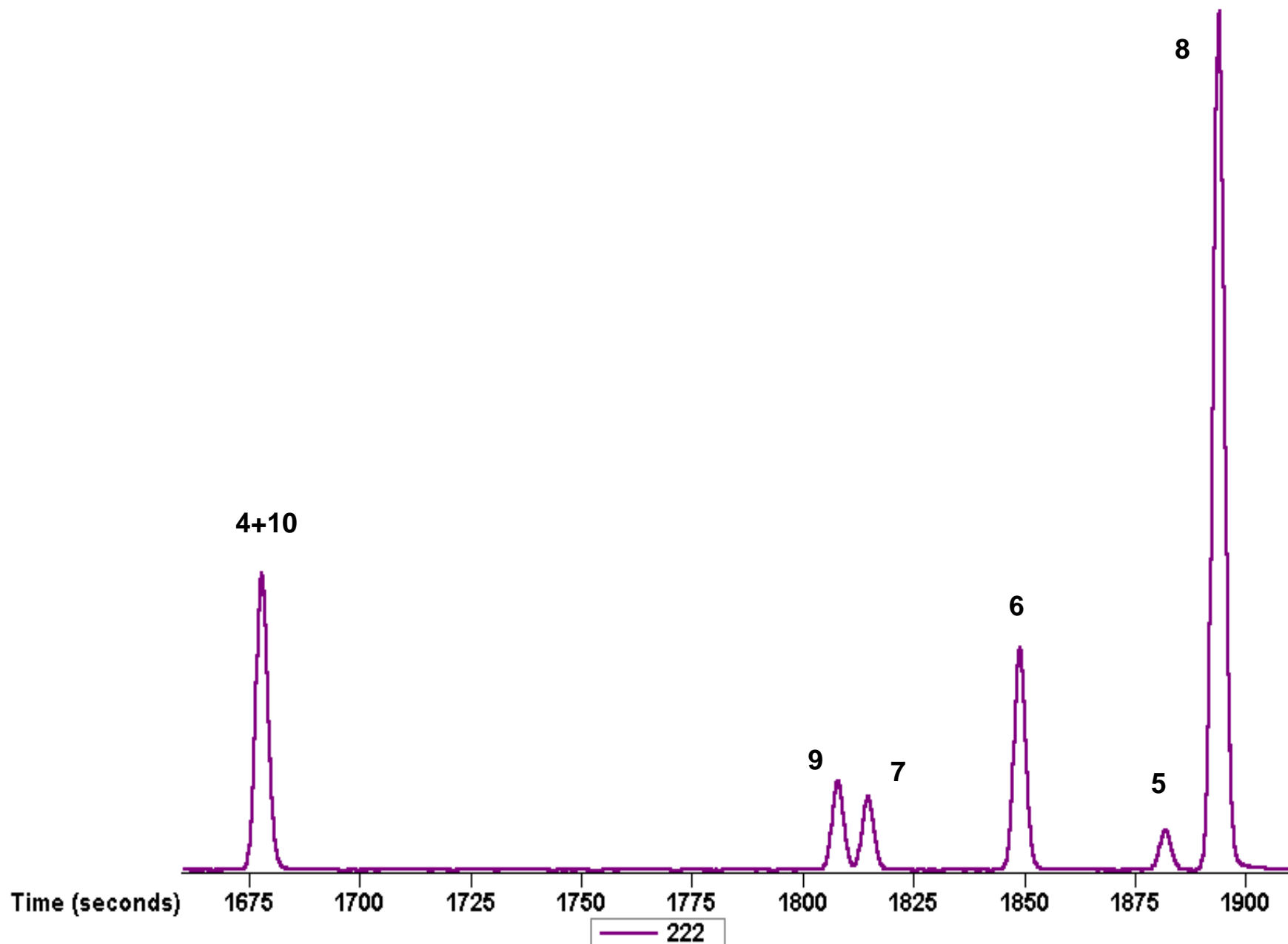
# GC-TOFMS Conditions

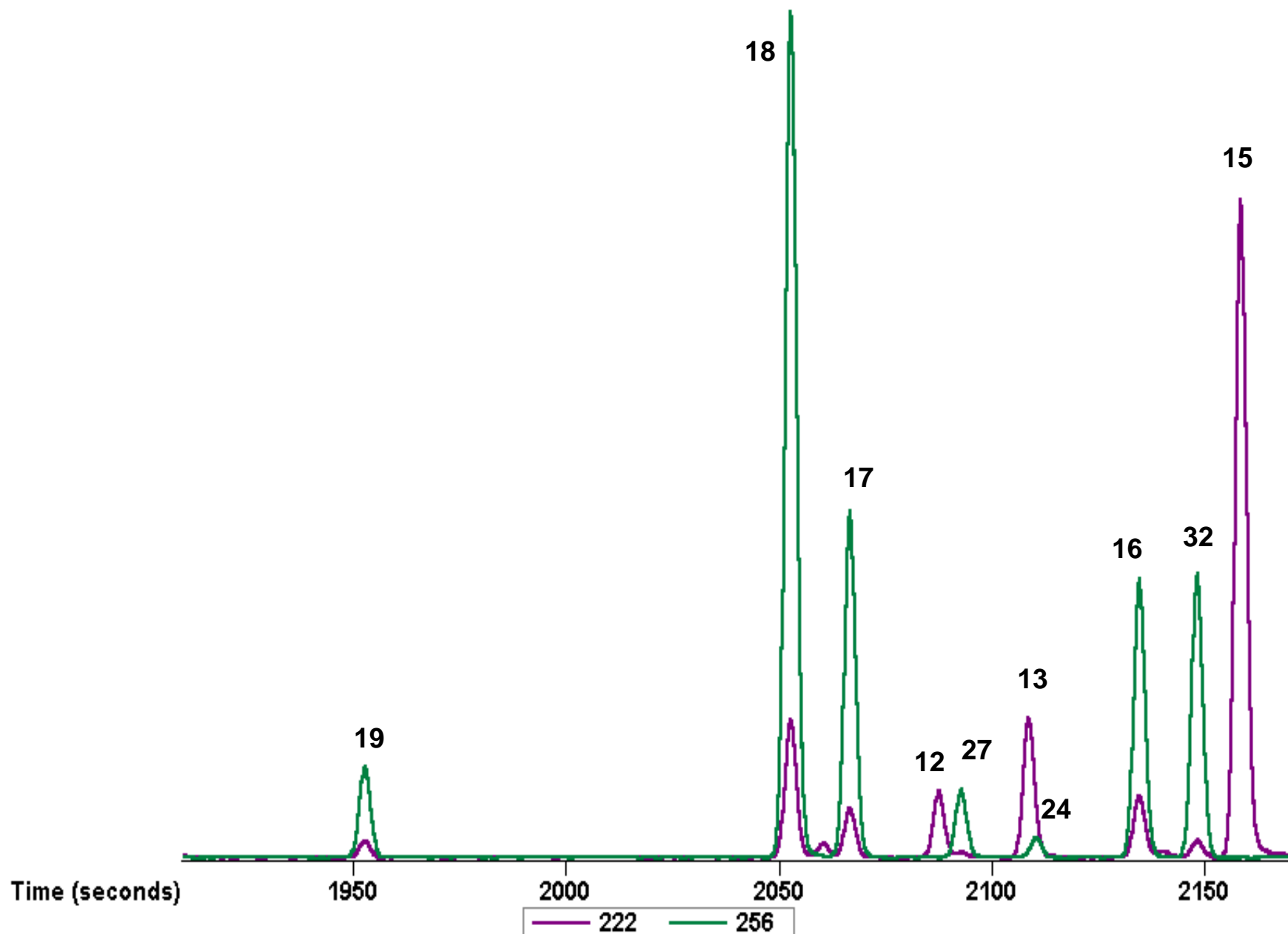
- Gas Chromatography
  - One microliter splitless 250°C, 60 sec valve
  - 60 m x 0.18 mm x 0.18 µm **Restek Rtx-PCB** column
    - Constant flow helium, 1.5 mL/minute
    - 70°C (1 min), 50°/min to 120°, 3°/min to **360°** (1 min)
- Mass Spectrometry **LECO Pegasus III**
  - Source temperature: 225°C
  - Electron ionization: 70 eV
  - Stored mass range: 120 to 520 u
  - Acquisition rate: 5 spectra/sec

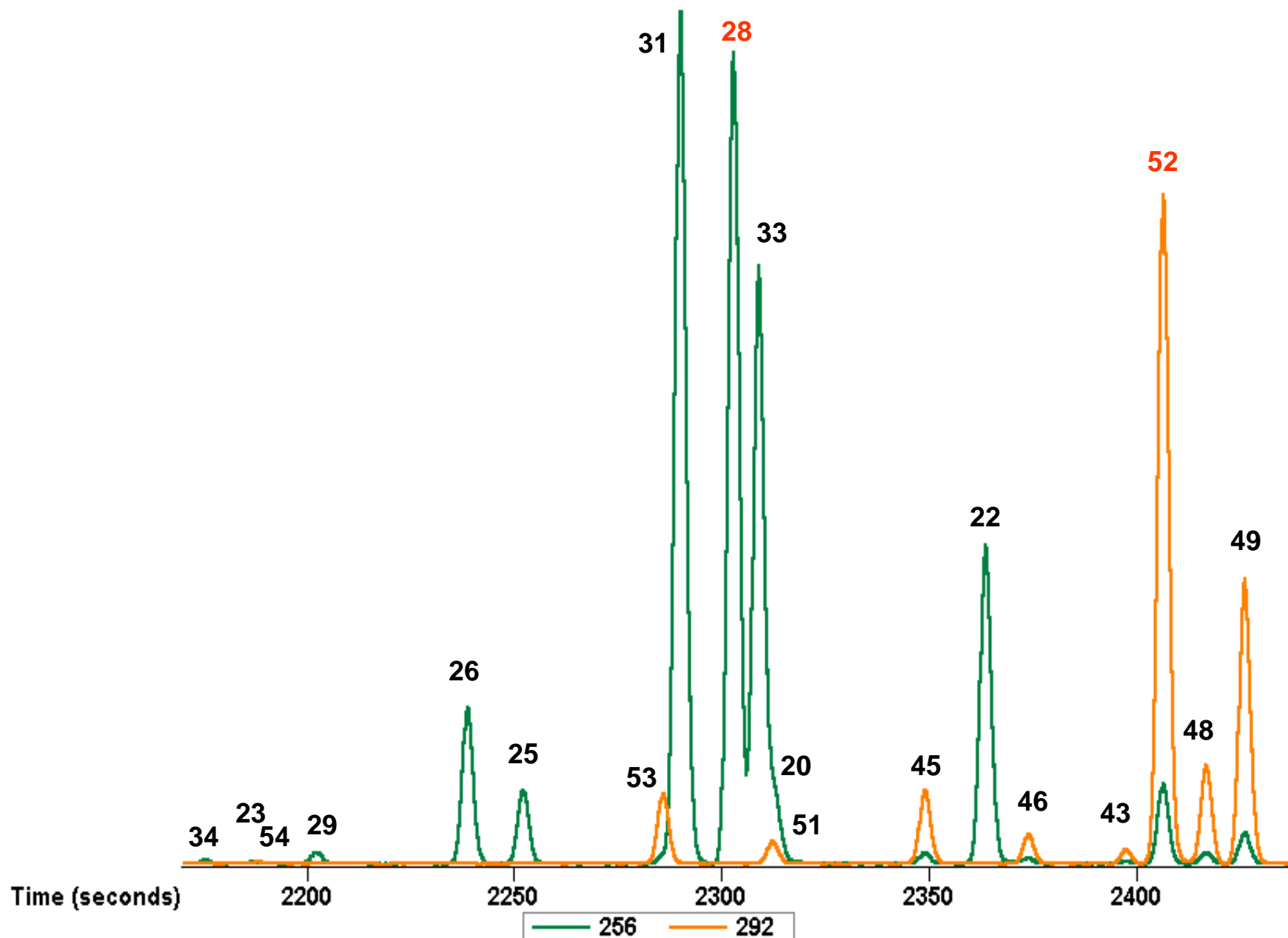
# Aroclor Mix Chromatogram

- Overlaid ion chromatograms are plotted
  - For example, hexachlorobiphenyl is 360
  - Peaks are labeled with congener numbers
    - Text size and format is only for space and not meant to indicate anything about PCBs, except:
    - European indicator congeners are in red
- Chromatograms are not to one scale
  - Each panel is adjusted so most of the PCB peaks can be seen

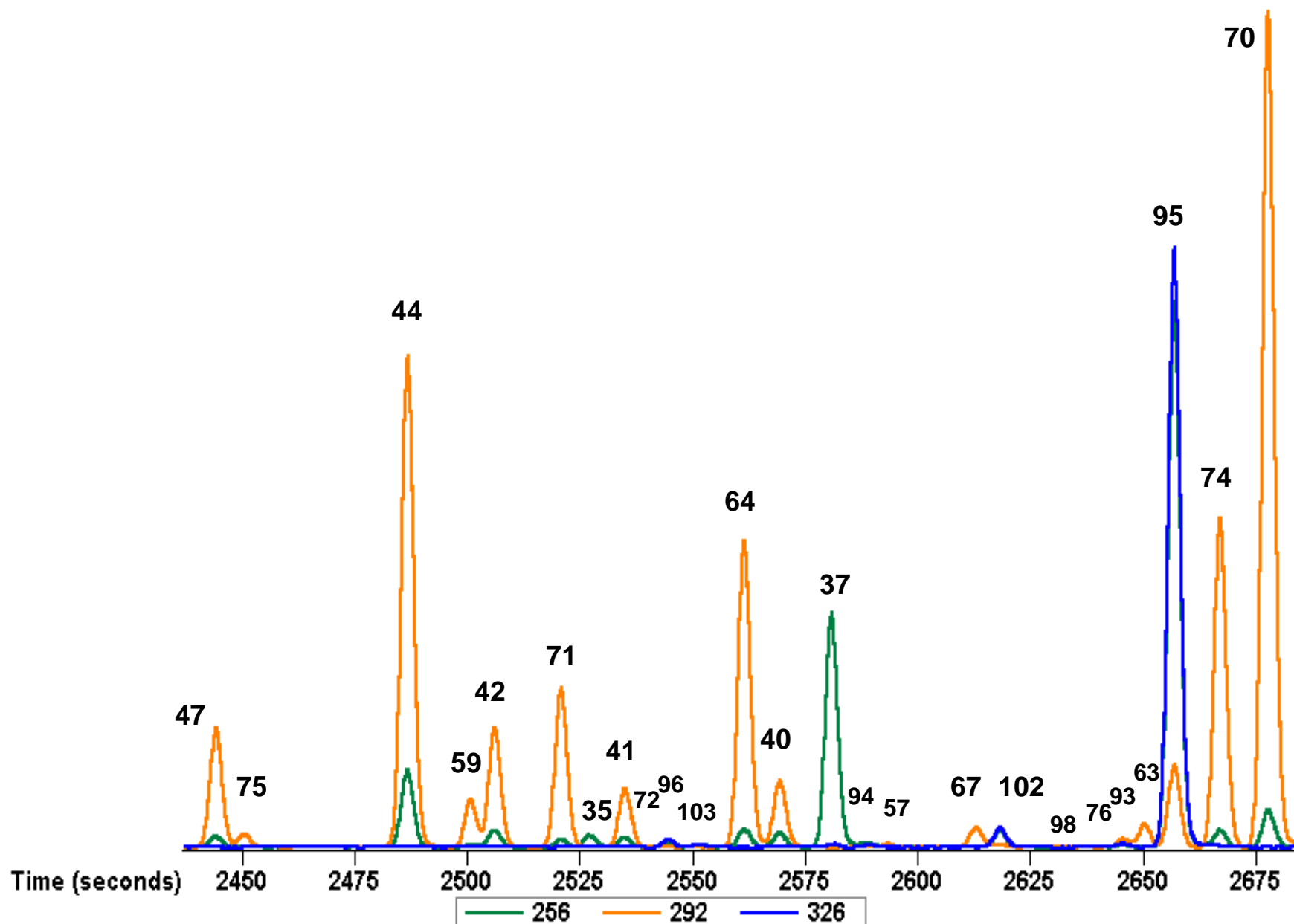


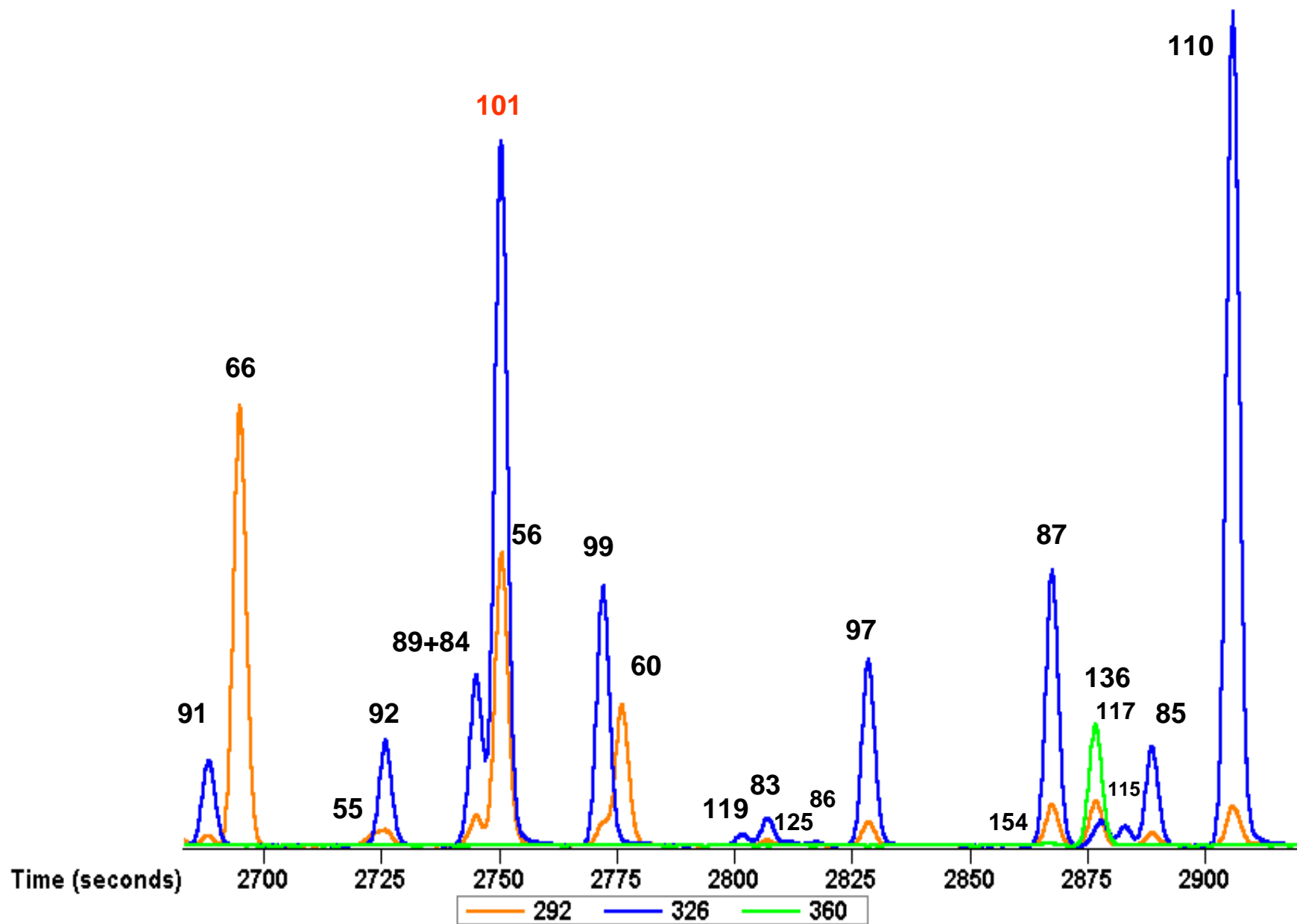


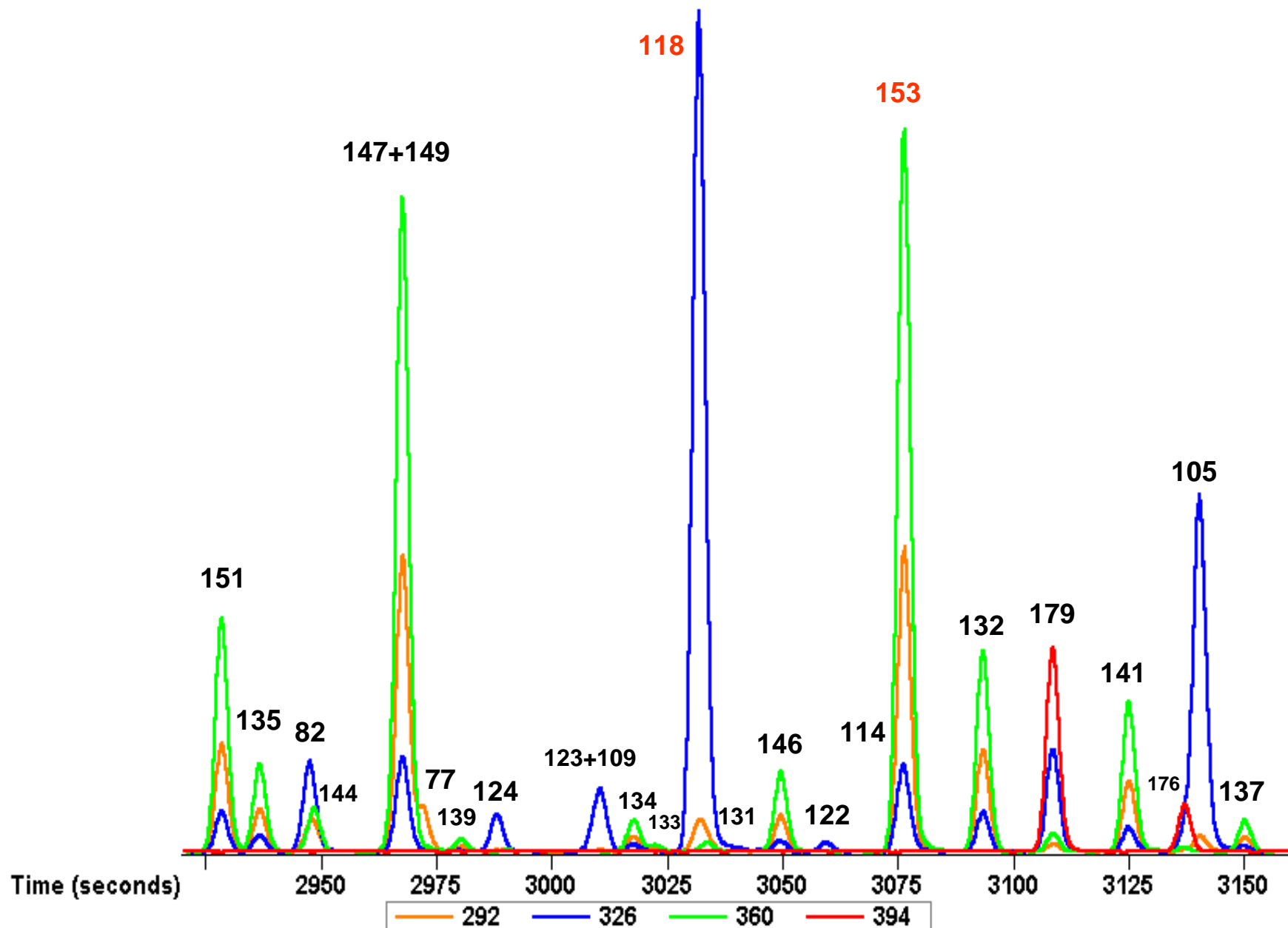


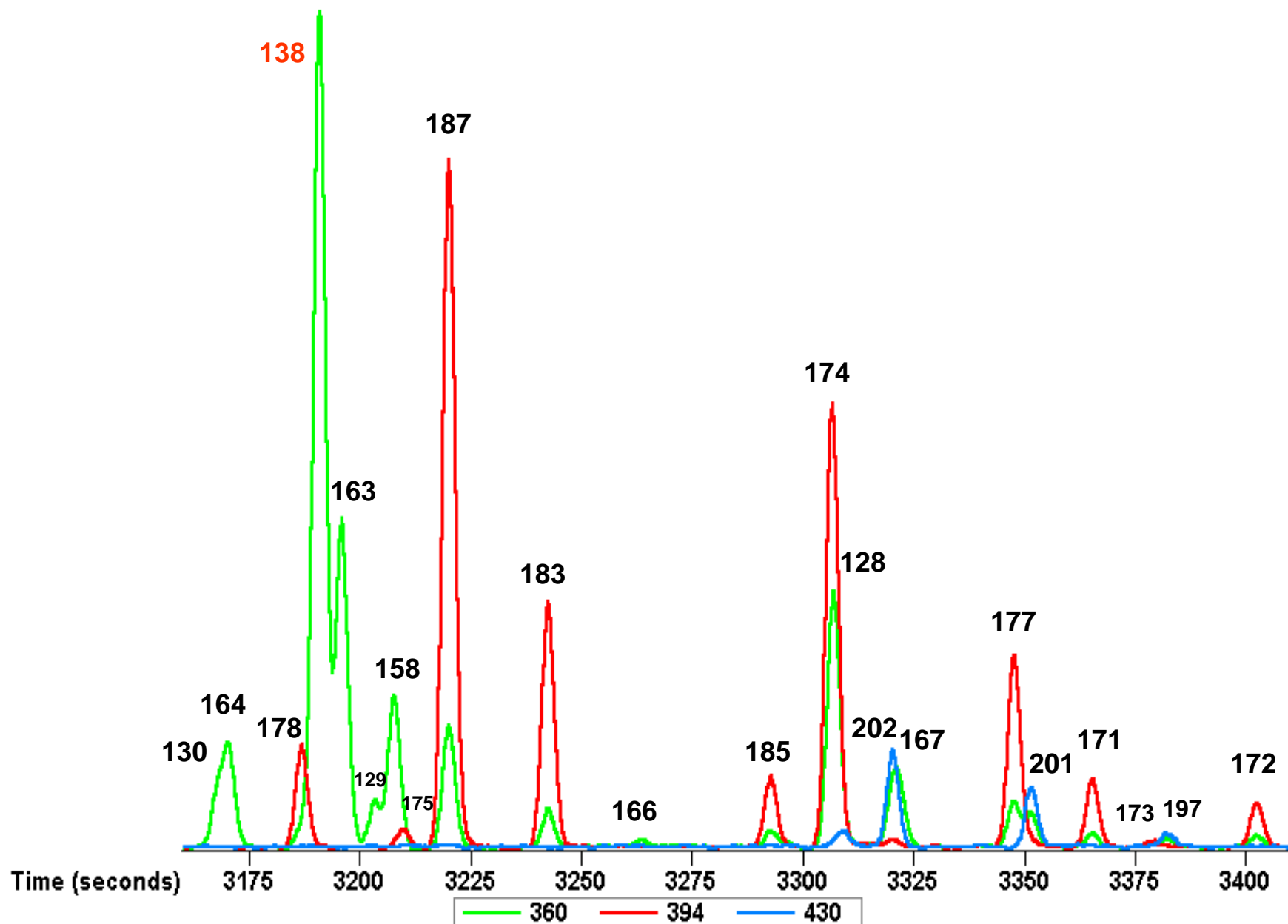


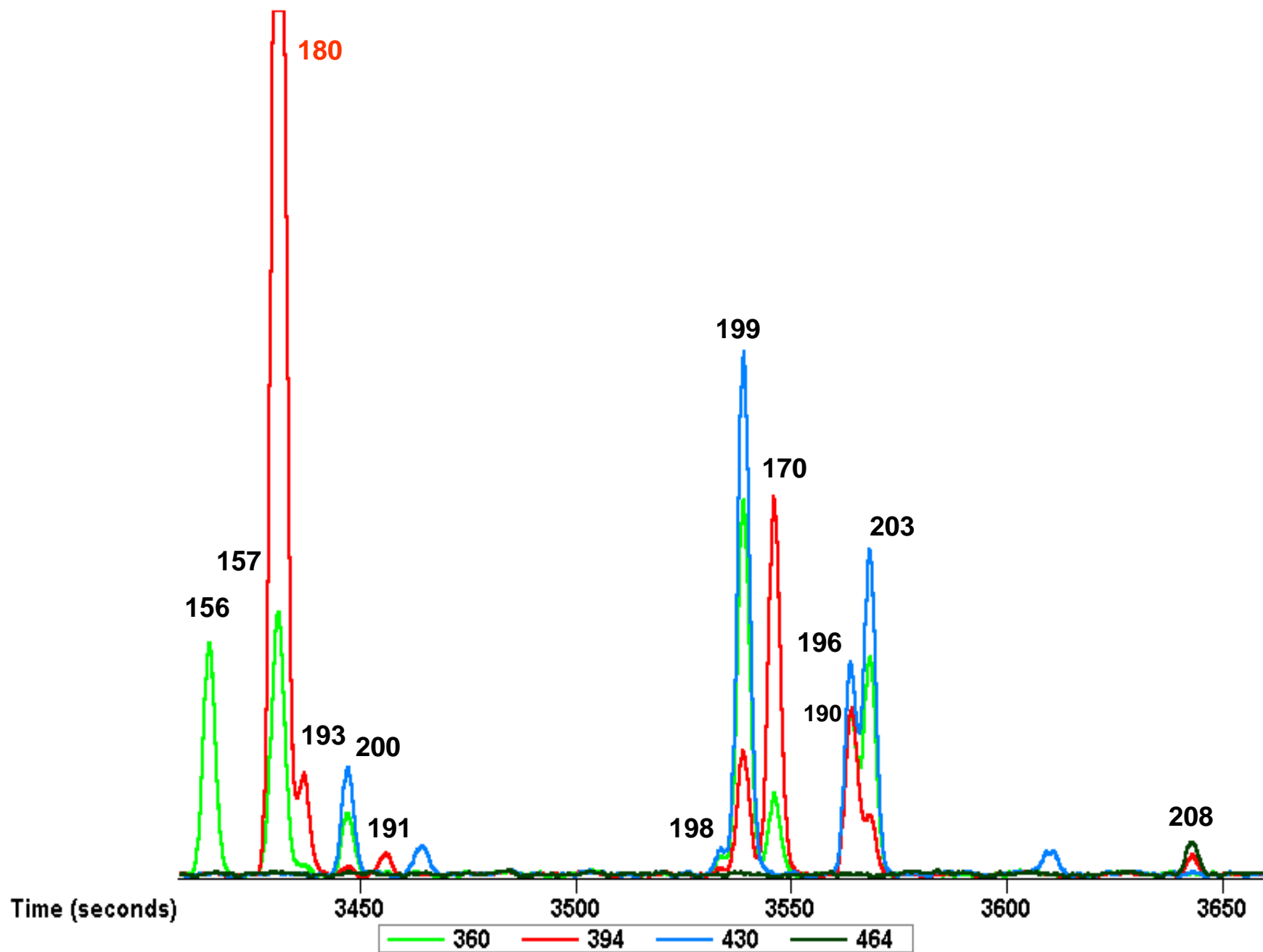


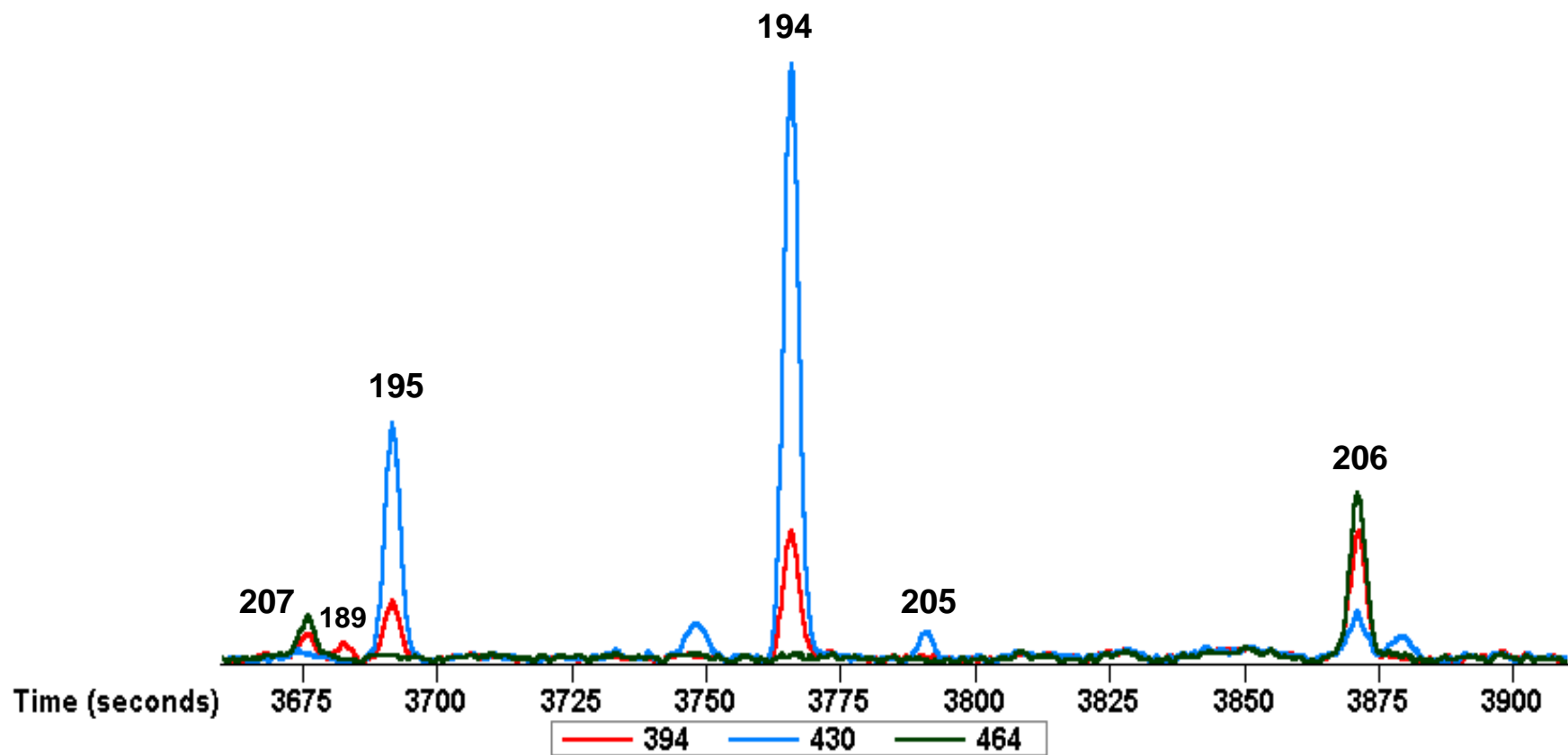






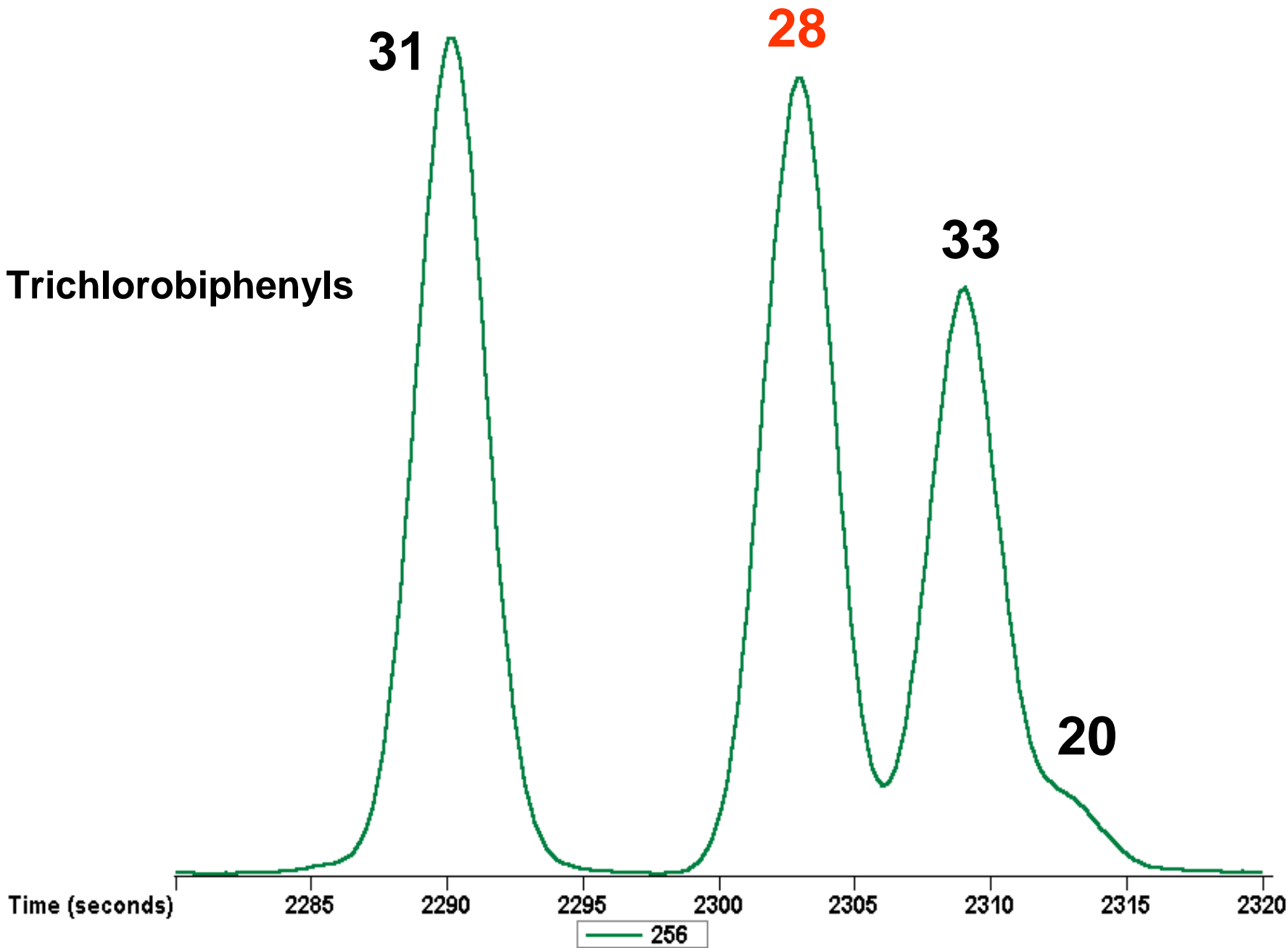




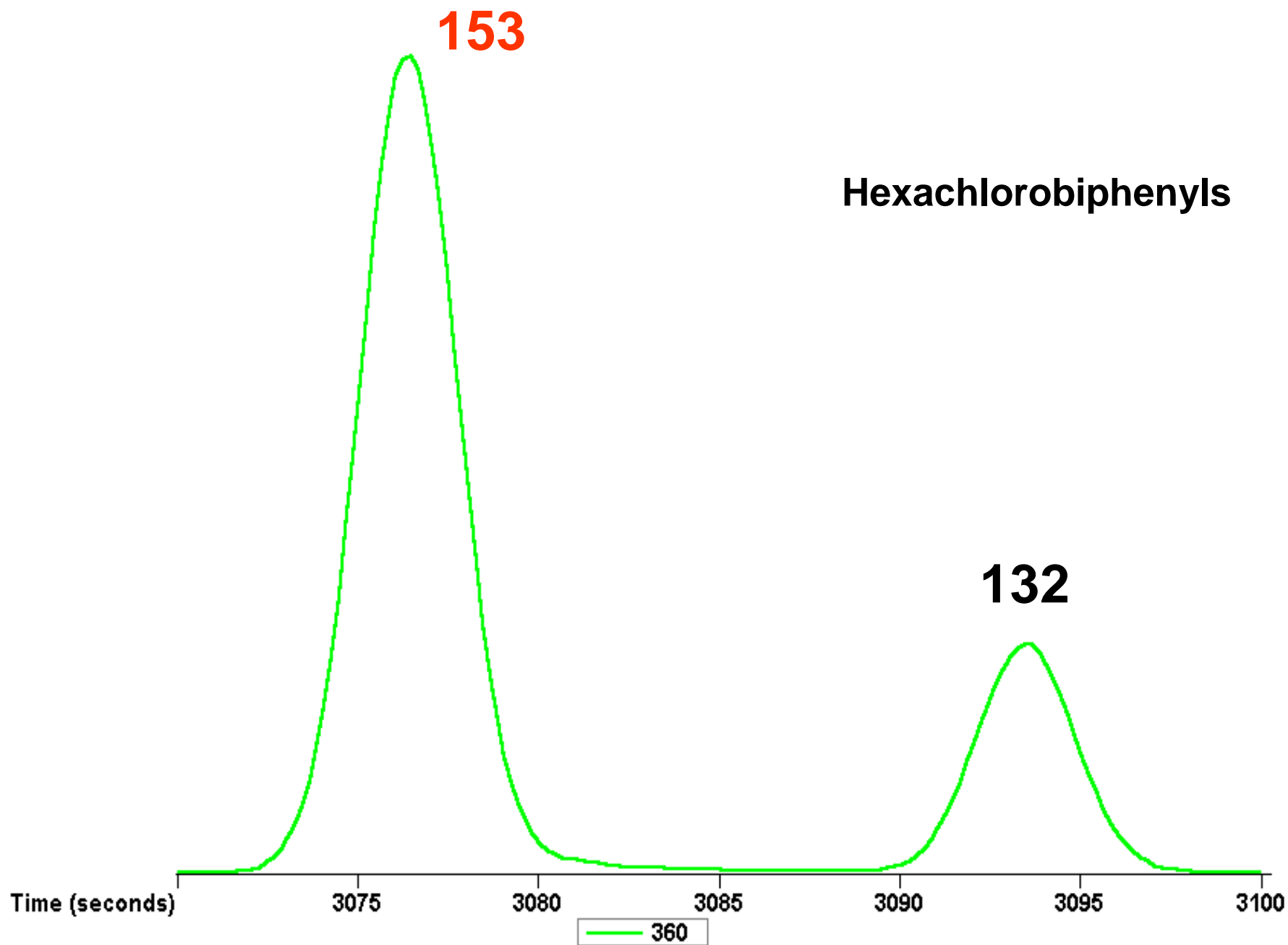


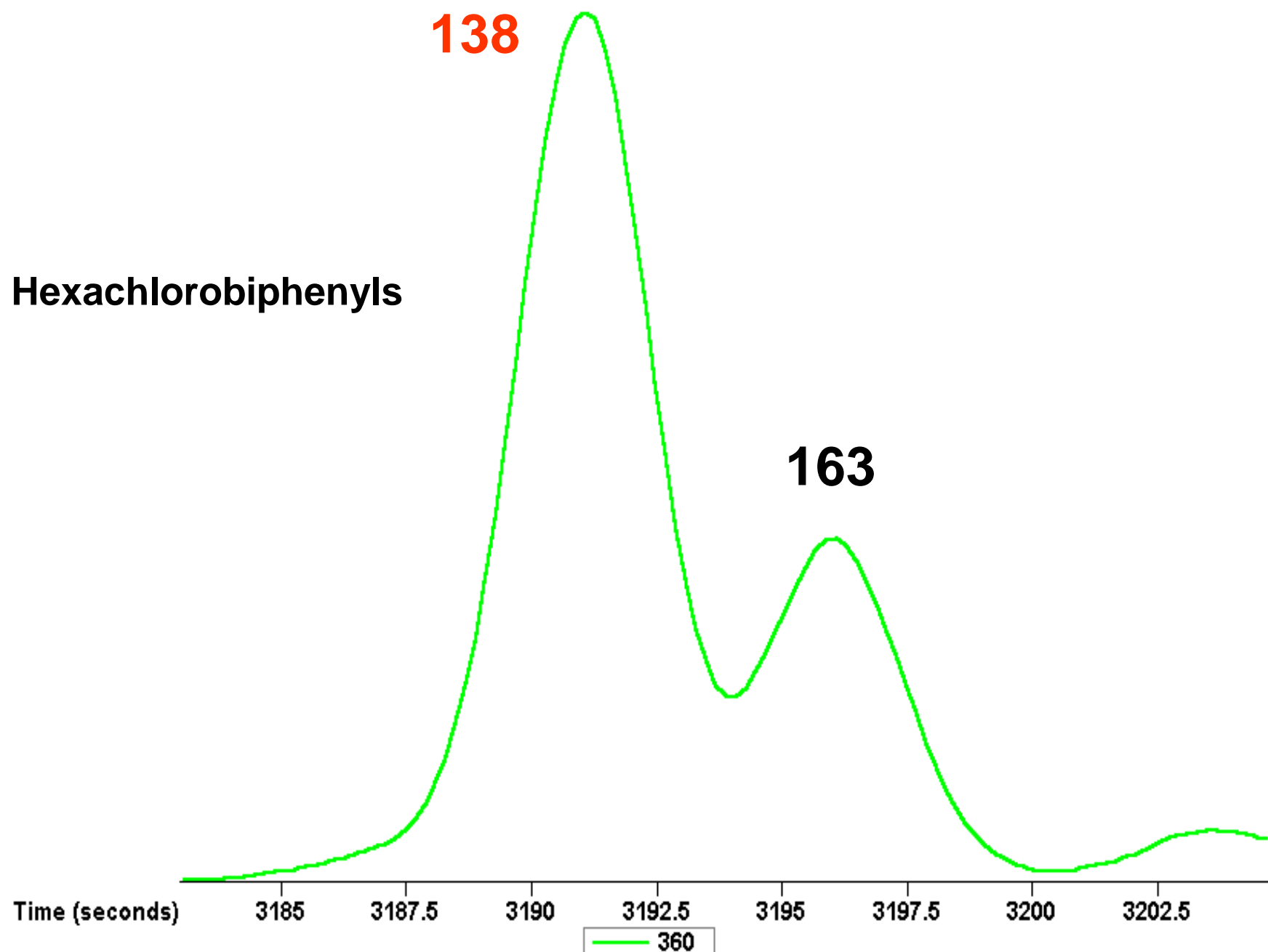
# Important Congener Separations

- European indicator PCBs
- May coelute on 5% phenyl methylsilicone and other column phases









# Table Key

- Congener classification according to their significance in Aroclors 1242, 1254, or 1260
  - **Bold Underline**: Congener > 1.0 Wt%
  - **Bold**: Congener 0.05 to 1.0 Wt%
  - *Italics*: Trace or undetected congener
- Congener naming according to Guitart et al. by chlorine positions
  - 107: 234-35
  - 108: 2346-3
  - 109: 235-34
  - 199: 2345-2356
  - 200: 23456-236
  - 201: 2346-2356
- RRT is relative retention time
- Coelutions of significance where MS won't help are

PCB#	CI#	RT (sec)	RT (min)	RRT
<b>1</b>	1	1403.3	23.39	0.7206
<b>2</b>	1	1601.3	26.69	0.8222
<b>3</b>	1	1642.1	27.37	0.8432
<b>4</b>	2	1678.1	27.97	0.8617
<b>10</b>	2	1679.7	28.00	0.8625
<b>9</b>	2	1808.3	30.14	0.9285
<b>7</b>	2	1815.3	30.26	0.9321
<b>6</b>	2	1849.3	30.82	0.9496
<b>5</b>	2	1882.3	31.37	0.9665
<b>8</b>	2	1894.3	31.57	0.9727
<b>19</b>	3	1953.3	32.55	1.0030
<b>14</b>	2	1963.3	32.72	1.0079
<b>30</b>	3	1993.5	33.22	1.0236
<b>18</b>	3	2053.3	34.22	1.0543
<b>11</b>	2	2061.1	34.35	1.0582
<b>17</b>	3	2067.3	34.46	1.0615
<b>12</b>	2	2088.1	34.80	1.0721
<b>27</b>	3	2093.3	34.89	1.0748
<b>13</b>	2	2109.3	35.15	1.0829
<b>24</b>	3	2110.9	35.18	1.0839

PCB#	CI#	RT (sec)	RT (min)	RRT
<u>16</u>	3	2135.1	35.58	1.0963
<u>32</u>	3	2148.7	35.81	1.1033
<u>15</u>	2	2158.9	35.98	1.1084
<u>34</u>	3	2176.1	36.27	1.1173
23	3	2187.3	36.45	1.1234
54	4	2188.9	36.48	1.1237
<u>29</u>	3	2202.7	36.71	1.1309
50	4	2237.1	37.28	1.1486
<u>26</u>	3	2239.3	37.32	1.1498
<u>25</u>	3	2252.7	37.54	1.1567
<u>53</u>	4	2286.5	38.11	1.1738
<u>31</u>	3	2290.7	38.18	1.1762
<u>28</u>	3	2303.5	38.39	1.1828
<u>33</u>	3	2309.5	38.49	1.1858
<u>51</u>	4	2312.9	38.55	1.1874
21	3	2312.7	38.54	1.1874
<u>20</u>	3	2313.3	38.56	1.1877
<u>45</u>	4	2349.5	39.16	1.2064
<u>22</u>	3	2364.3	39.40	1.2140
73	4	2374.3	39.57	1.2189

PCB#	CI#	RT (sec)	RT (min)	RRT
<b>46</b>	4	2374.5	39.58	1.2193
69	4	2391.5	39.86	1.2279
<b>43</b>	4	2397.7	39.96	1.2312
36	3	2398.9	39.98	1.2317
<b>52</b>	4	2406.9	40.11	1.2359
<b>48</b>	4	2417.3	40.29	1.2412
<b>49</b>	4	2426.5	40.44	1.2458
104	5	2440.3	40.67	1.2529
<b>47</b>	4	2444.7	40.75	1.2552
65	4	2448.5	40.81	1.2571
<b>75</b>	4	2451.3	40.85	1.2584
62	4	2450.7	40.84	1.2586
39	3	2452.9	40.88	1.2598
38	3	2461.3	41.02	1.2637
<b>44</b>	4	2487.3	41.45	1.2772
<b>59</b>	4	2501.3	41.69	1.2842
<b>42</b>	4	2506.7	41.78	1.2870
71	4	2521.5	42.02	1.2947
35	3	2527.9	42.13	1.2978
41	4	2535.7	42.26	1.3020

PCB#	CI#	RT (sec)	RT (min)	RRT
72	4	2542.1	42.37	1.3052
96	5	2545.1	42.42	1.3067
103	5	2552.3	42.54	1.3105
68	4	2560.5	42.67	1.3150
<b>64</b>	4	2561.9	42.70	1.3153
<b>40</b>	4	2569.9	42.83	1.3195
<b>37</b>	3	2581.3	43.02	1.3254
100	5	2581.9	43.03	1.3255
94	5	2589.1	43.15	1.3297
57	4	2594.1	43.23	1.3319
<b>67</b>	4	2613.5	43.56	1.3420
58	4	2614.7	43.58	1.3426
<b>102</b>	5	2618.9	43.65	1.3446
61	4	2635.9	43.93	1.3533
98	5	2637.9	43.96	1.3544
93	5	2646.1	44.10	1.3586
76	4	2646.1	44.10	1.3587
<b>63</b>	4	2650.9	44.18	1.3610
121	5	2653.9	44.23	1.3630
<b>95</b>	5	2657.5	44.29	1.3646

PCB#	CI#	RT (sec)	RT (min)	RRT
88	5	2658.9	44.31	1.3656
<u>74</u>	4	2667.9	44.46	1.3699
155	6	2675.7	44.59	1.3742
<u>70</u>	4	2678.3	44.64	1.3752
<u>91</u>	5	2688.7	44.81	1.3805
<u>66</u>	4	2695.7	44.93	1.3842
80	4	2709.7	45.16	1.3917
55	4	2723.3	45.39	1.3984
<u>92</u>	5	2726.5	45.44	1.3999
<u>89</u>	5	2743.7	45.73	1.4087
<u>84</u>	5	2745.9	45.77	1.4100
<u>101</u>	5	2750.9	45.85	1.4124
90	5	2751.5	45.86	1.4125
<u>56</u>	4	2751.5	45.86	1.4128
113	5	2757.3	45.95	1.4157
<u>99</u>	5	2772.9	46.21	1.4238
150	5	2776.1	46.27	1.4258
<u>60</u>	4	2776.7	46.28	1.4258
152	6	2798.9	46.65	1.4370
119	5	2802.3	46.71	1.4388



PCB#	CI#	RT (sec)	RT (min)	RRT
83	5	2807.5	46.79	1.4416
125	5	2811.3	46.85	1.4438
112	5	2812.1	46.87	1.4440
86	5	2817.7	46.96	1.4467
108	5	2821.5	47.02	1.4488
145	6	2825.9	47.10	1.4509
<u>97</u>	5	2828.9	47.15	1.4524
148	6	2835.5	47.26	1.4563
79	4	2841.9	47.36	1.4591
116	5	2855.5	47.59	1.4665
154	6	2867.7	47.79	1.4722
<u>87</u>	5	2868.3	47.80	1.4728
78	4	2870.3	47.84	1.4737
111	5	2871.1	47.85	1.4746
<u>136</u>	6	2877.3	47.96	1.4773
117	5	2878.9	47.98	1.4780
115	5	2883.5	48.06	1.4806
<u>85</u>	5	2889.1	48.15	1.4833
120	5	2895.7	48.26	1.4869
<u>110</u>	5	2906.7	48.44	1.4925

PCB#	CI#	RT (sec)	RT (min)	RRT
81	4	2927.7	48.79	1.5030
<b>151</b>	6	2929.1	48.82	1.5039
<b>135</b>	6	2937.3	48.96	1.5082
<b>82</b>	5	2948.3	49.14	1.5139
<b>144</b>	6	2949.1	49.15	1.5142
<b>147</b>	6	2966.3	49.44	1.5231
<b>149</b>	6	2968.3	49.47	1.5241
<b>77</b>	4	2972.3	49.54	1.5261
140	6	2980.3	49.67	1.5306
<b>139</b>	6	2981.3	49.69	1.5307
<b>124</b>	5	2988.9	49.81	1.5344
143	6	2990.5	49.84	1.5359
107	5	3005.3	50.09	1.5430
<b>123</b>	5	3009.5	50.16	1.5452
<b>109</b>	5	3011.3	50.19	1.5462
188	7	3011.5	50.19	1.5467
<b>134</b>	6	3018.5	50.31	1.5498
106	5	3018.9	50.31	1.5500
<b>133</b>	6	3023.1	50.38	1.5521
142	6	3027.5	50.46	1.5549

PCB#	CI#	RT (sec)	RT (min)	RRT
<b>118</b>	5	3032.5	50.54	1.5570
<b>131</b>	6	3034.3	50.57	1.5580
<b>184</b>	7	3040.7	50.68	1.5612
<b>165</b>	6	3044.1	50.73	1.5628
<b>146</b>	6	3050.3	50.84	1.5663
<b>122</b>	5	3060.1	51.00	1.5710
<b>161</b>	6	3060.3	51.00	1.5712
<b>168</b>	6	3072.5	51.21	1.5780
<b>114</b>	5	3076.1	51.27	1.5794
<b>153</b>	6	3077.1	51.28	1.5800
<b>132</b>	6	3094.1	51.57	1.5887
<b>179</b>	7	3109.3	51.82	1.5966
<b>141</b>	6	3125.7	52.10	1.6050
<b>176</b>	7	3137.5	52.29	1.6109
<b>105</b>	5	3140.9	52.35	1.6126
<b>137</b>	6	3150.7	52.51	1.6177
<b>186</b>	7	3157.1	52.62	1.6211
<b>127</b>	5	3157.7	52.63	1.6212
<b>130</b>	6	3168.7	52.81	1.6267
<b>164</b>	6	3171.1	52.85	1.6283

PCB#	CI#	RT (sec)	RT (min)	RRT
<u>178</u>	7	3187.7	53.13	1.6368
<u>138</u>	6	3191.7	53.19	1.6389
<u>163</u>	6	3196.7	53.28	1.6411
160	6	3198.9	53.31	1.6429
<u>129</u>	6	3203.9	53.40	1.6450
<u>158</u>	6	3208.5	53.48	1.6473
182	7	3209.7	53.49	1.6480
<u>175</u>	7	3210.5	53.51	1.6482
<u>187</u>	7	3221.1	53.68	1.6540
<u>183</u>	7	3243.3	54.06	1.6654
<u>166</u>	6	3264.1	54.40	1.6759
159	6	3277.3	54.62	1.6828
126	5	3290.3	54.84	1.6893
<u>185</u>	7	3293.3	54.89	1.6909
162	6	3295.9	54.93	1.6927
<u>128</u>	6	3307.9	55.13	1.6984
<u>174</u>	7	3307.7	55.13	1.6984
<u>202</u>	8	3321.1	55.35	1.7050
<u>167</u>	6	3322.7	55.38	1.7060
181	7	3328.9	55.48	1.7091

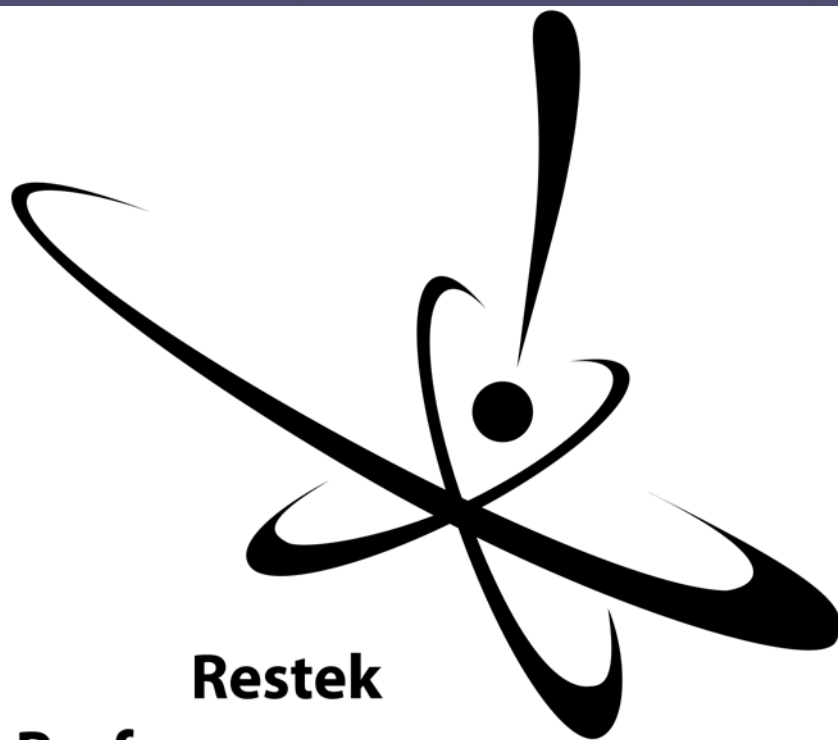
PCB#	CI#	RT (sec)	RT (min)	RRT
<u>177</u>	7	3348.5	55.81	1.7194
<u>201</u>	8	3352.3	55.87	1.7210
<u>204</u>	8	3353.9	55.90	1.7220
<u>171</u>	7	3366.1	56.10	1.7284
<u>173</u>	7	3379.7	56.33	1.7354
<u>197</u>	8	3383.1	56.39	1.7371
<u>172</u>	7	3403.1	56.72	1.7474
<u>192</u>	7	3414.7	56.91	1.7534
<u>156</u>	6	3415.3	56.92	1.7535
<u>157</u>	6	3430.1	57.17	1.7611
<u>180</u>	7	3432.1	57.20	1.7623
<u>193</u>	7	3437.5	57.29	1.7651
<u>200</u>	8	3447.7	57.46	1.7700
<u>191</u>	7	3456.5	57.61	1.7747
<u>198</u>	8	3534.3	58.90	1.8148
<u>199</u>	8	3539.9	59.00	1.8177
<u>170</u>	7	3546.9	59.12	1.8212
<u>190</u>	7	3564.7	59.41	1.8302
<u>196</u>	8	3564.7	59.41	1.8304
<u>203</u>	8	3569.3	59.49	1.8328

PCB#	CI#	RT (sec)	RT (min)	RRT
169	6	3583.5	59.72	1.8399
<b>208</b>	9	3643.7	60.73	1.8708
207	9	3676.5	61.28	1.8876
<b>189</b>	7	3683.3	61.39	1.8911
<b>195</b>	8	3692.9	61.55	1.8962
<b>194</b>	8	3766.9	62.78	1.9342
<b>205</b>	8	3791.5	63.19	1.9468
<b>206</b>	9	3872.3	64.54	1.9884
209	10	3952.9	65.88	2.0295

# Conclusions

- Greater than 140 Aroclor PCBs can be determined with the new column and mass spectrometry
- The seven European indicator PCBs can be determined individually
- Spectral deconvolution available with TOFMS allows qualitative identification for coeluting PCBs

# Restek Corporation Performance Coatings



**Restek  
Performance  
Coatings**

**Australian Distributors**  
Importers & Manufacturers  
[www.chromtech.net.au](http://www.chromtech.net.au)

**HRM**alytic +61(0)3 9762 2034  
**ECH**nology Pty Ltd

Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA



# Restek Corporation Background

- Established in 1985 as gas chromatography supplies company
- Currently \$25M+ annual revenue, double-digit growth 16 of 18 years
  - GC columns and consumables
  - Chemical standards
  - LC columns and consumables
  - Air analysis canisters and supplies
  - Performance Coatings Division



# Performance Coatings Background

- Began with tubing in 1987
- Stand-alone parts in 1993
- Initial goal to impart the inertness of glass on a steel surface (Silcosteel®)
- New surfaces in 1997 expanded applicability and performance (Siltek™)
- Patent protection
- Concerted development effort launched in 2002

# What can we coat?

- Tubing:
  - 0.004" to 0.5" ID
  - 2000+ ft. continuous lengths
- Complex geometry parts (inside and out)
  - Fittings, valves, frits, custom parts
  - Largest vessel: 1' ID x 4' cylinder w/ 10" opening
- Substrates
  - Stainless steels, steels, alloys, glass, ceramics

# What can't we coat?

- Nickel (most high-performance alloys will coat)
- Aluminum\*
- Copper
- Brass
- Gold, Silver-plated components
- Magnesium
- Elastomers

\*heat-dependent

# Basic Manufacturing Process

- Receive items
- Document – digital, customer contact
- Clean
  - Standard: caustic ultrasonic bath, 2 systems
  - Custom: solvation via other means
- Process
  - Vacuum
  - 400°C
  - Chemical vapor deposition, silicon-based
- Clean
- Document – digital, customer contact
- Pack, ship

# Application Areas

- Analytical (passivation): Silcosteel<sup>®</sup>, Siltek<sup>™</sup>, Sulfinert<sup>™</sup>
  - Transfer lines
  - Instrumentation parts
  - GC consumables
- Anti-Coking: Silcosteel<sup>®</sup>-AC
- Anti-Corrosion: Silcosteel<sup>®</sup>-CR
- Ultra-High Vacuum: Silcosteel<sup>®</sup>-UHV





Coating Appearances:

Silcosteel<sup>®</sup>

Sulfinert<sup>™</sup>

Siltek<sup>™</sup>

# Coating Appearances (cont.)

**Australian Distributors**  
Importers & Manufacturers  
[www.chromtech.net.au](http://www.chromtech.net.au)

Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA

**HRM**alytic +61(0)3 9762 2034  
**ECH**nology Pty Ltd





# New Process Oven



**Australian Distributors**  
Importers & Manufacturers  
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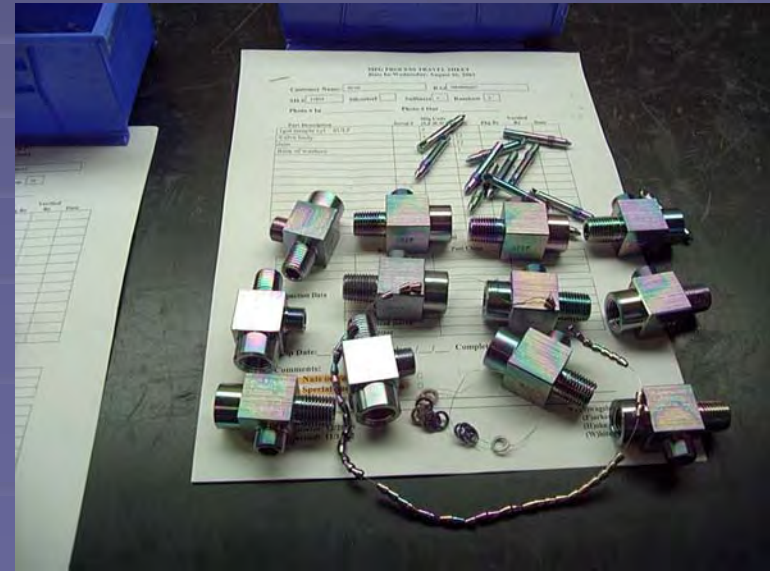
Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au) Tel: 03 9762 2034 . . . in AUSTRALIA

# More Parts

**Australian Distributors**  
**Importers & Manufacturers**  
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**ECH**nology Pty Ltd

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# Inertness

- Application: Reduce activity of substrate (ie., stainless steel) to minimize adsorption of compounds
- Coated system products deliver better reproducibility and accuracy by reducing hold-up of active compounds
- List of some active compounds: Hydrogen Sulfide, Nitrous Oxides, Mercury, Alcohols, Aldehydes, Ketones, etc.,.

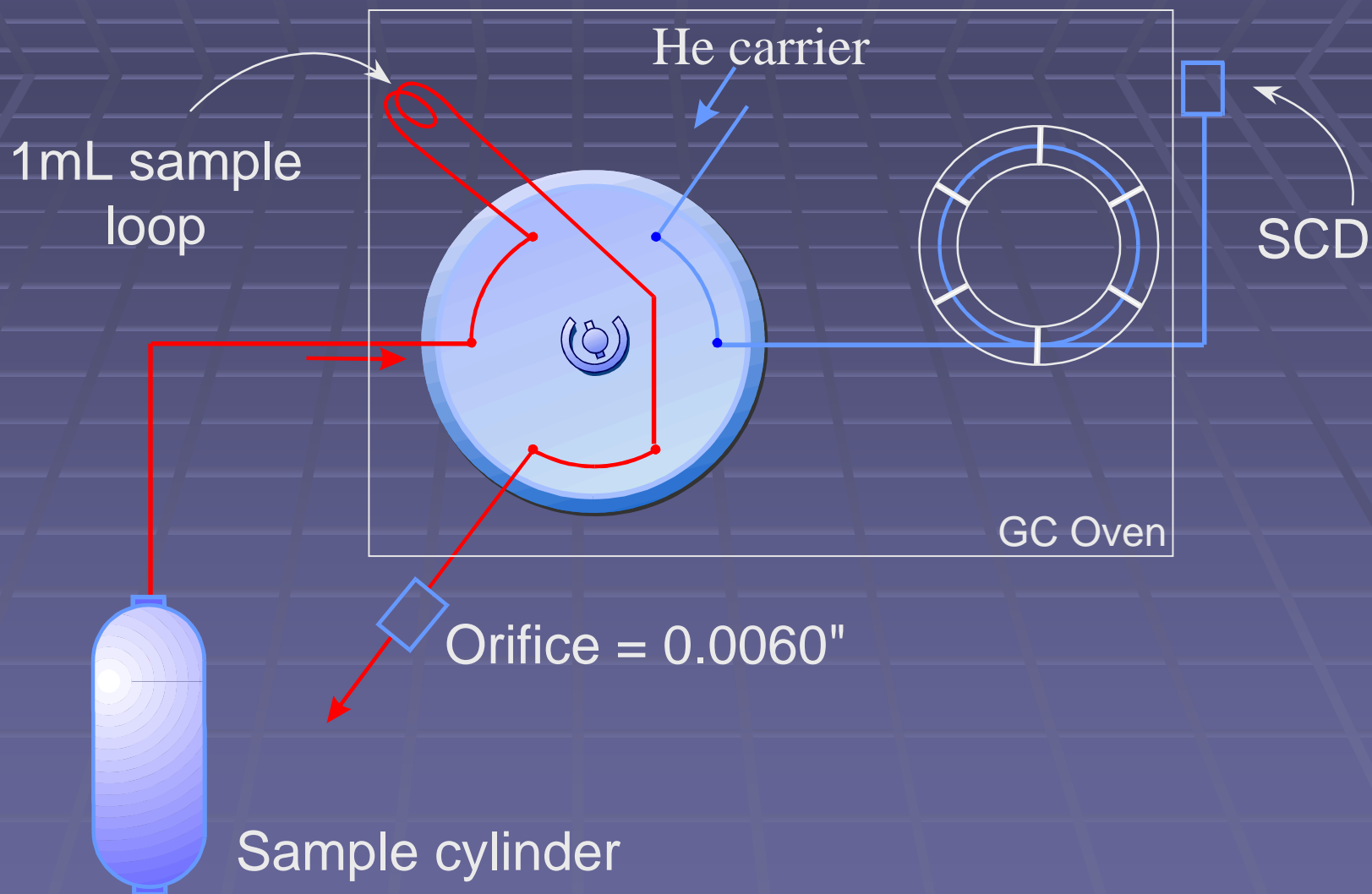
# Project Objective

- To create passivation processes for stainless steel and glass surfaces which will allow the analysis of low-ppbv sulfur gases
  - Chromatographic sampling system
  - Containment vessels (high pressure vessels and air sampling canisters)

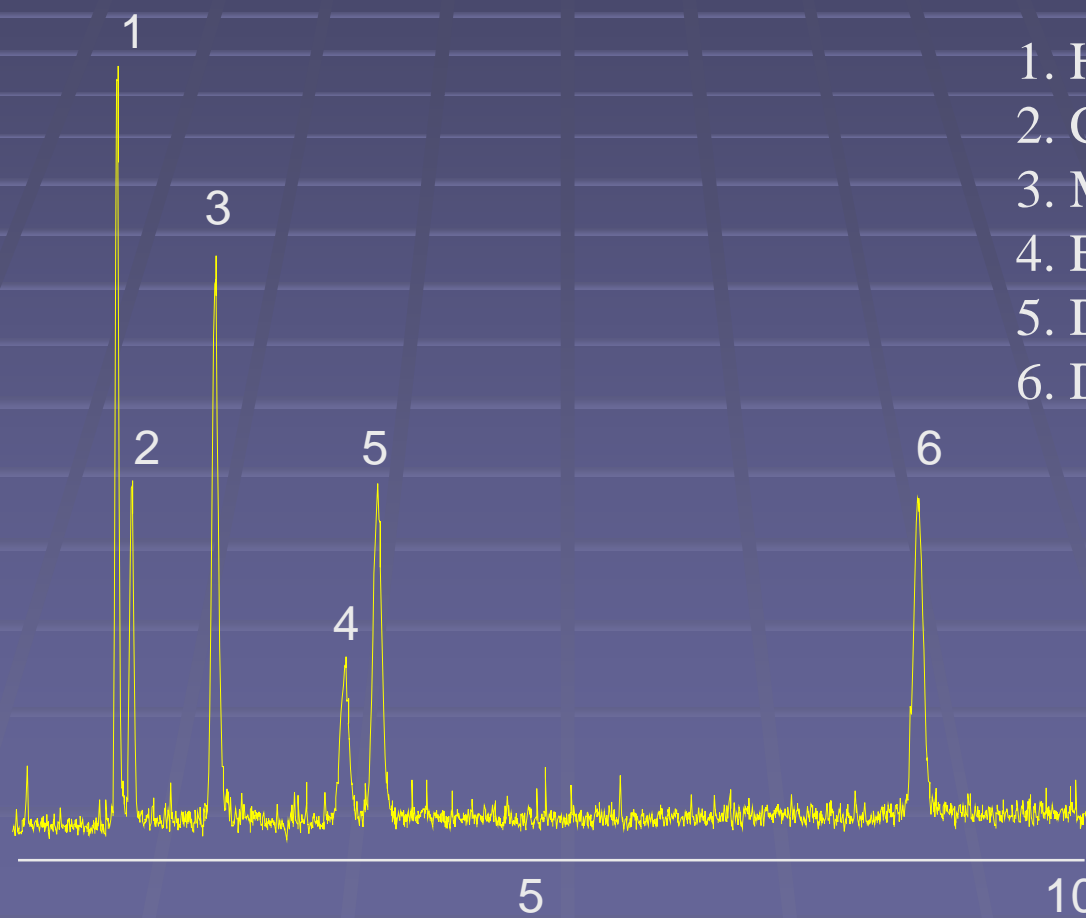
# Testing System for Sulfur Gas Storage & Transfer

- Sulfinert™-deactivated sample cylinders with Sulfinert™ sample valves
- Sulfinert™-deactivated sampling system (transfer line, sampling valve, 1ml sample loop)
- 48hr (minimum) containment of dry sample
- 55ppbv reference standard
- Dimethyl sulfide internal standard

# Complete Sulfur Analysis System



# 11ppbv Sulfur Standard



1. H<sub>2</sub>S
2. COS
3. Methyl Mercaptan
4. Ethyl Mercaptan
5. Dimethyl Sulfide
6. Dimethyl Disulfide

Rtx-1 60m x 0.53mm, 7.0 $\mu$ m

# List of Sulfur Compounds

Compound Name	Formula	Conc (ppmv)	Conc (ppbv)	Conc as S (ppbv)
hydrogen sulfide	H <sub>2</sub> S	105	11.51	10.83
carbonyl sulfide	COS	98	10.74	5.73
methyl mercaptan	CH <sub>3</sub> SH	101	11.07	7.38
ethyl mercaptan	CH <sub>3</sub> CH <sub>2</sub> SH	101	11.07	5.71
dimethylsulfide	CH <sub>3</sub> SCH <sub>3</sub>	99	10.85	6.81
dimethyl disulfide	CH <sub>3</sub> SSCH <sub>3</sub>	100	10.96	7.46

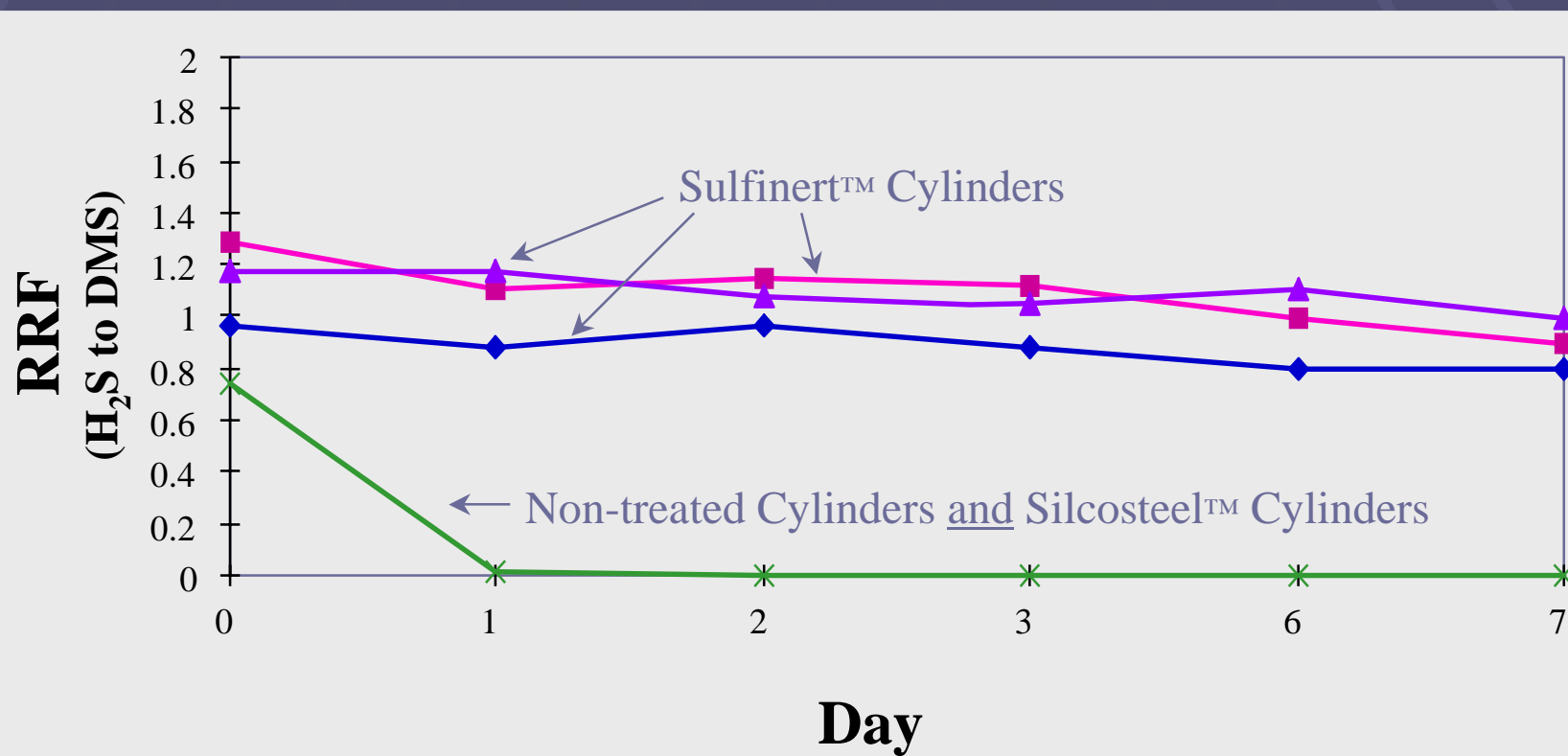


# System Repeatability

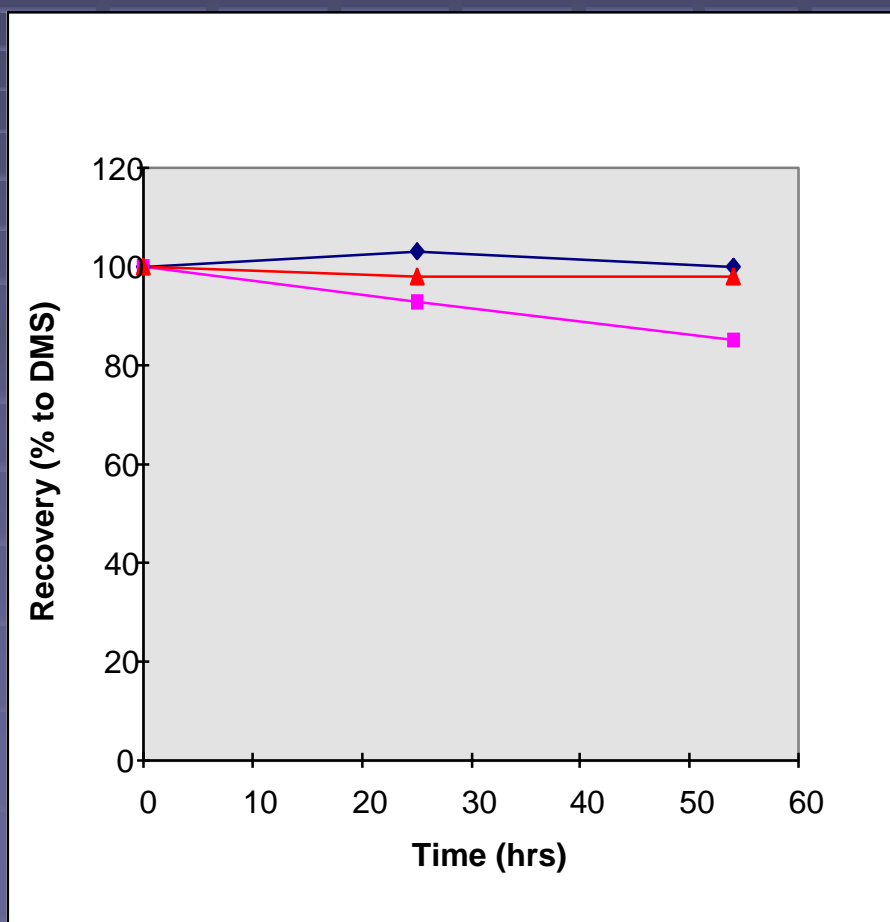
Compound Name	%RSD
hydrogen sulfide	2.2
carbonyl sulfide	4.2
methyl mercaptan	2.0
ethyl mercaptan	8.7
dimethylsulfide	3.3
dimethyl disulfide	9.2

n=7

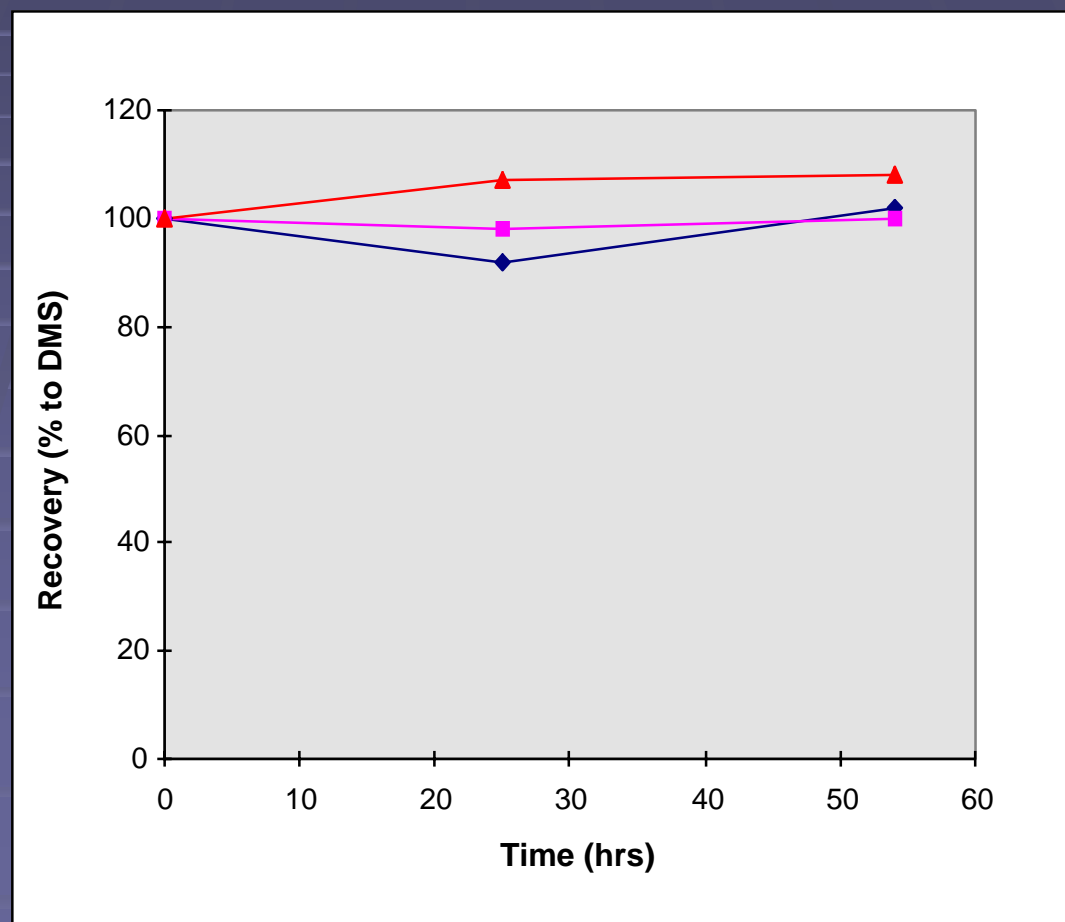
# 17ppbv H<sub>2</sub>S Containment in 500ml Cylinders



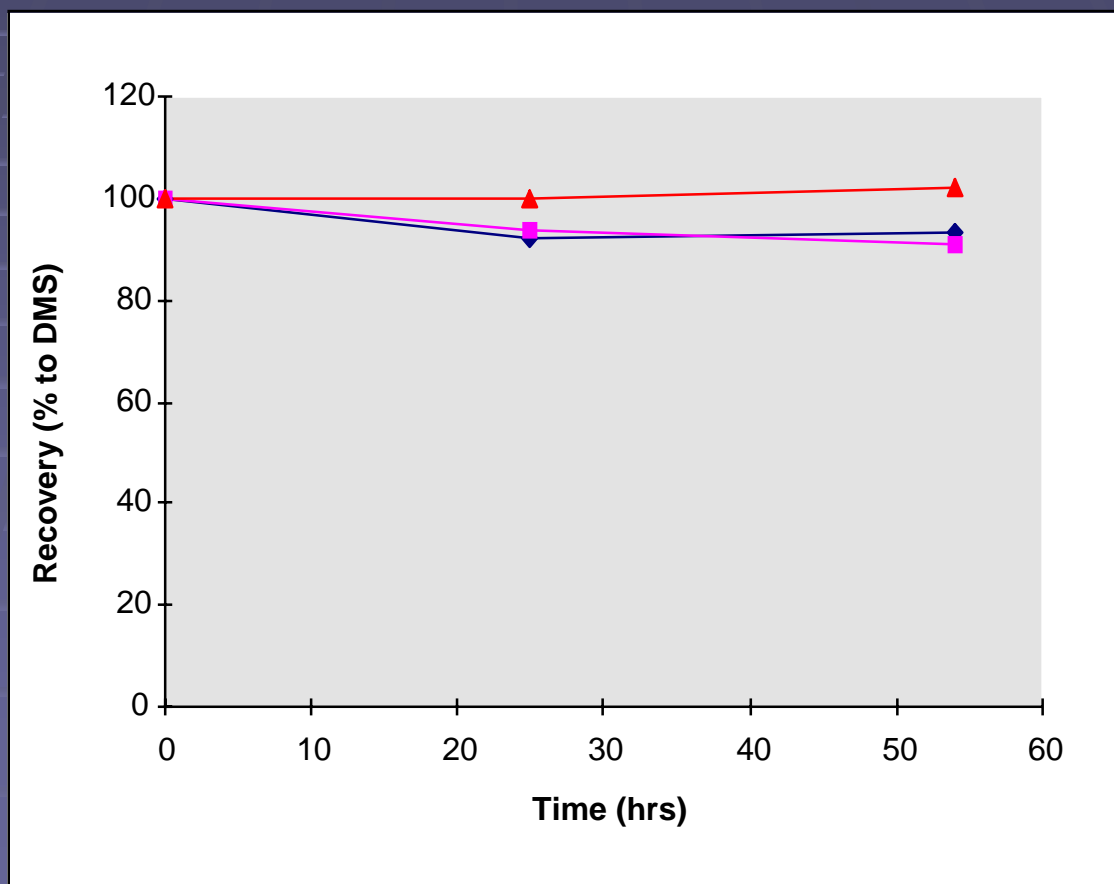
# H<sub>2</sub>S at 27.57ppbv in 300ml Sulfinert™ Cylinders



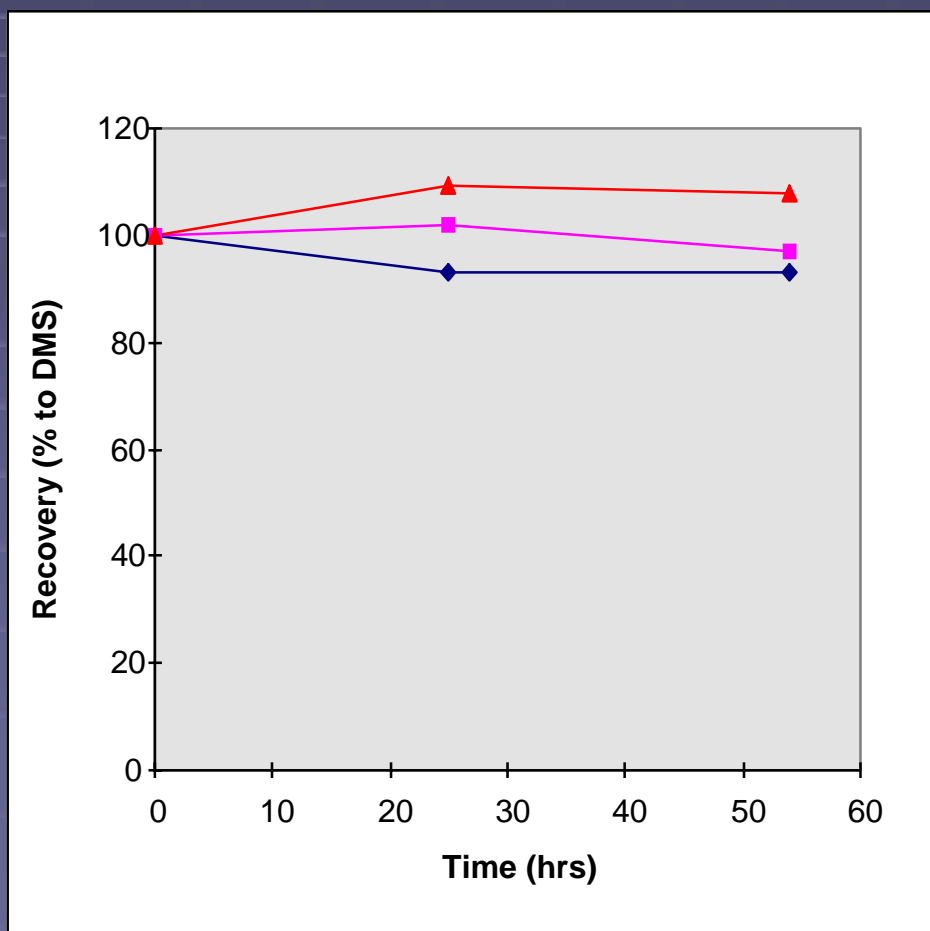
# COS at 14.59ppbv in 300ml Sulfinert™ Cylinders



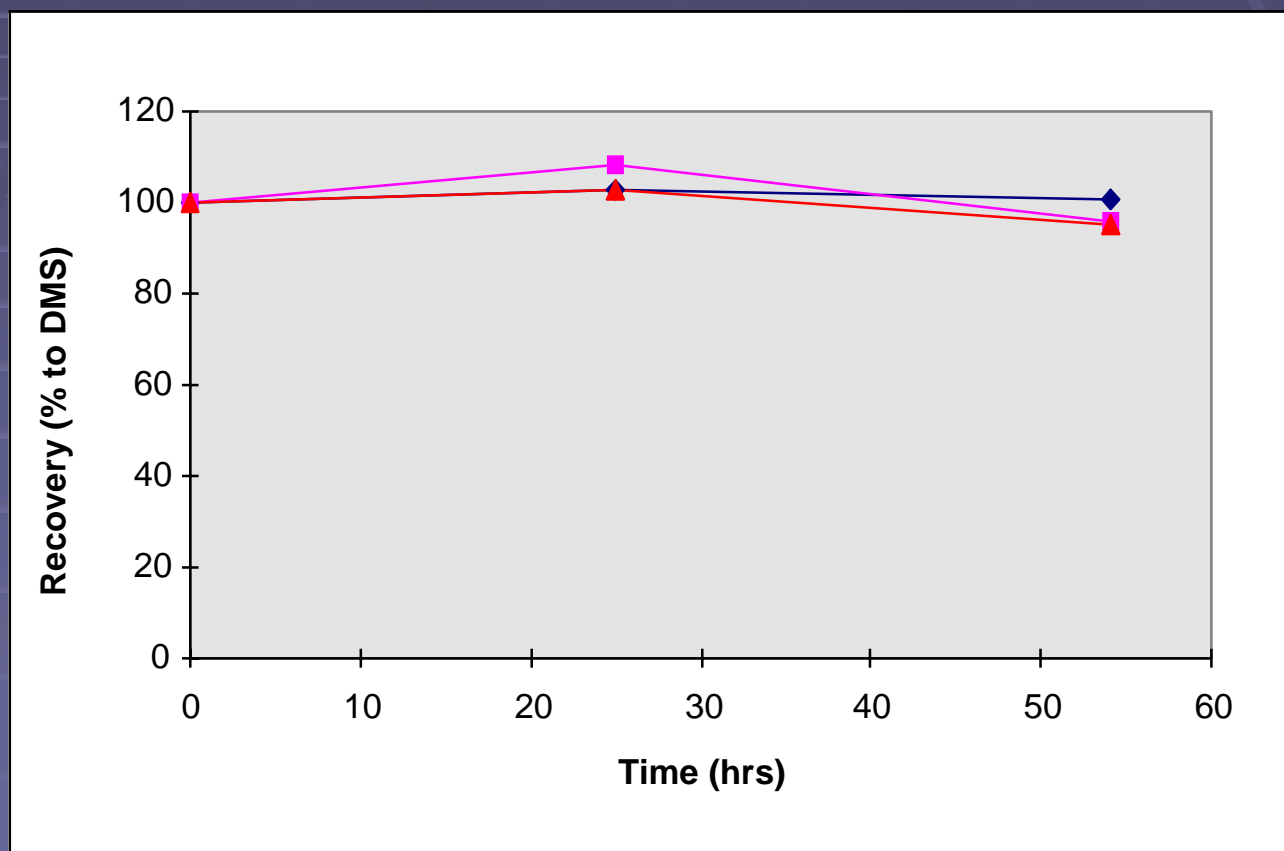
# Ethyl Mercaptan at 14.53ppbv in 300ml Sulfinert™ Cylinders



# Methyl Mercaptan at 18.8ppbv in 300ml Sulfinert™ Cylinders



# Dimethyl Disulfide at 18.99ppbv in 300ml Sulfinert™ Cylinders

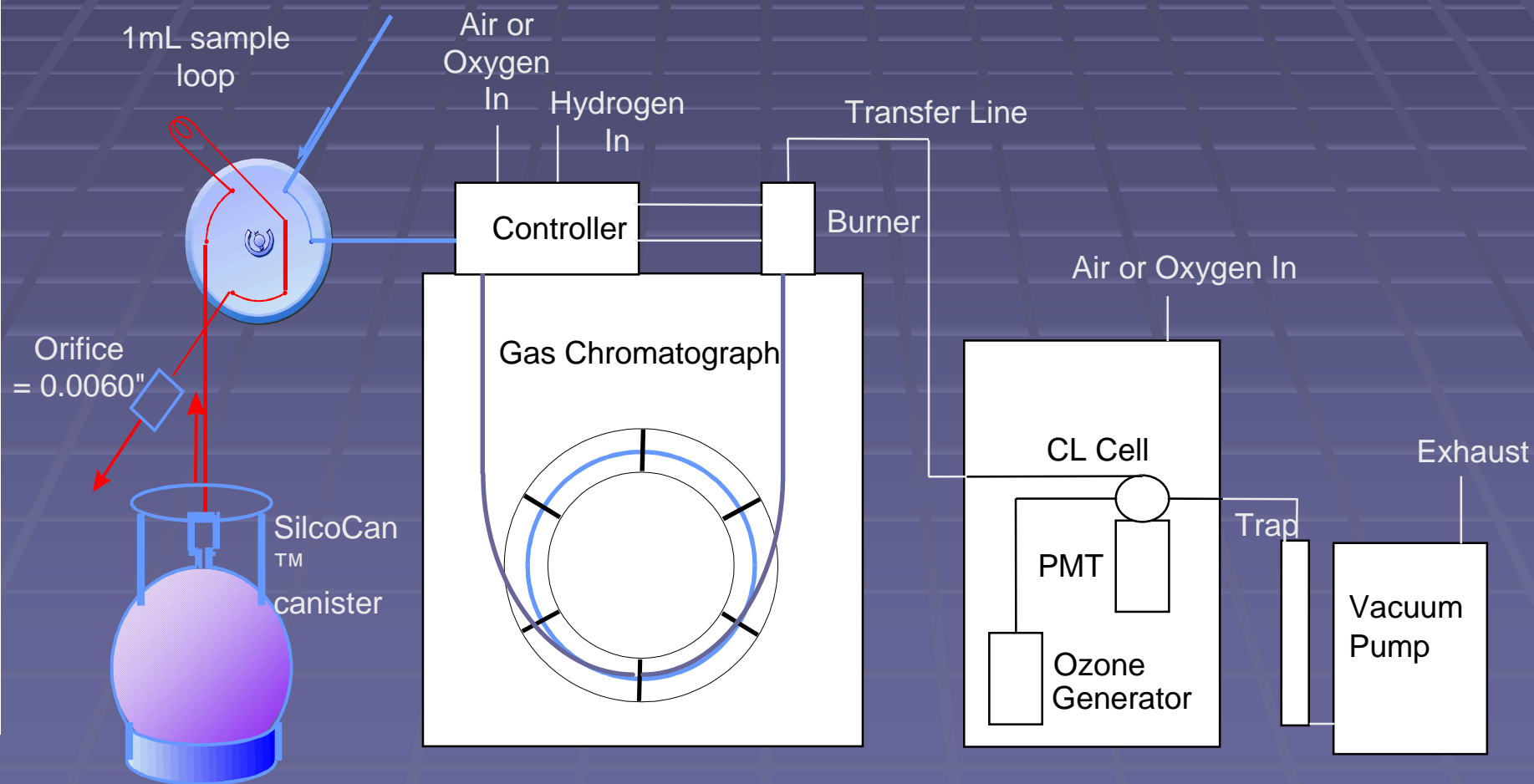


# Ambient Air Sampling Canisters Objective

- Demonstrate suitability for storage of low level (1-20ppbv) sulfurs in SilcoCan™ canisters.



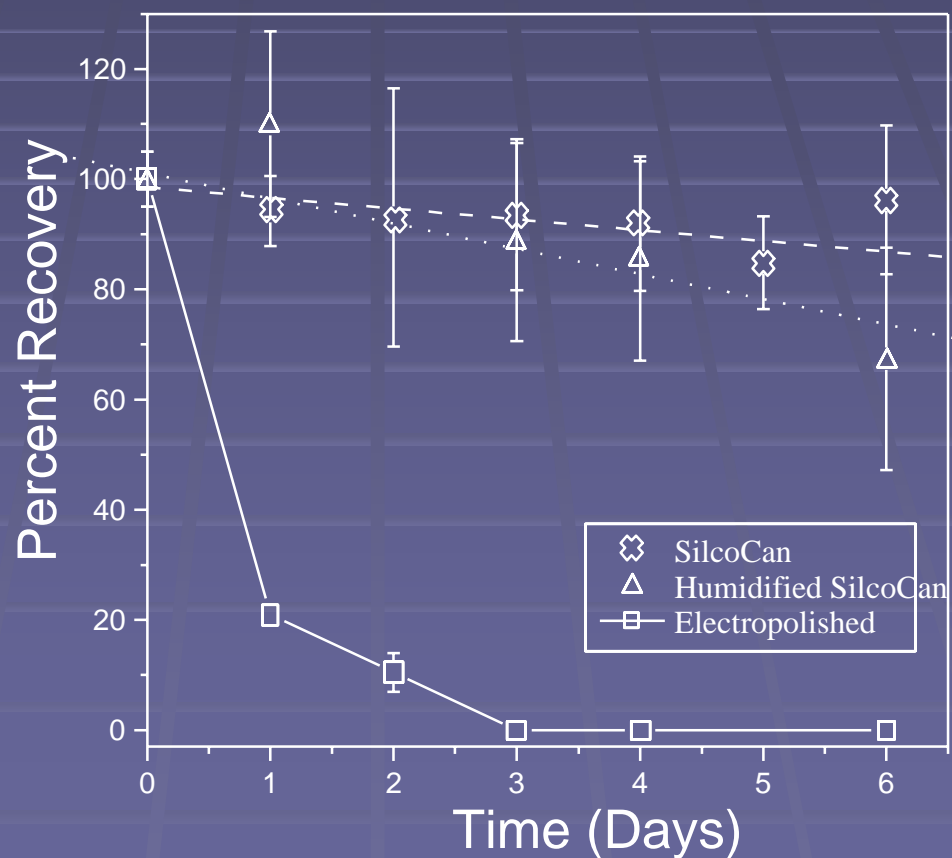
# Block diagram of Analytical System



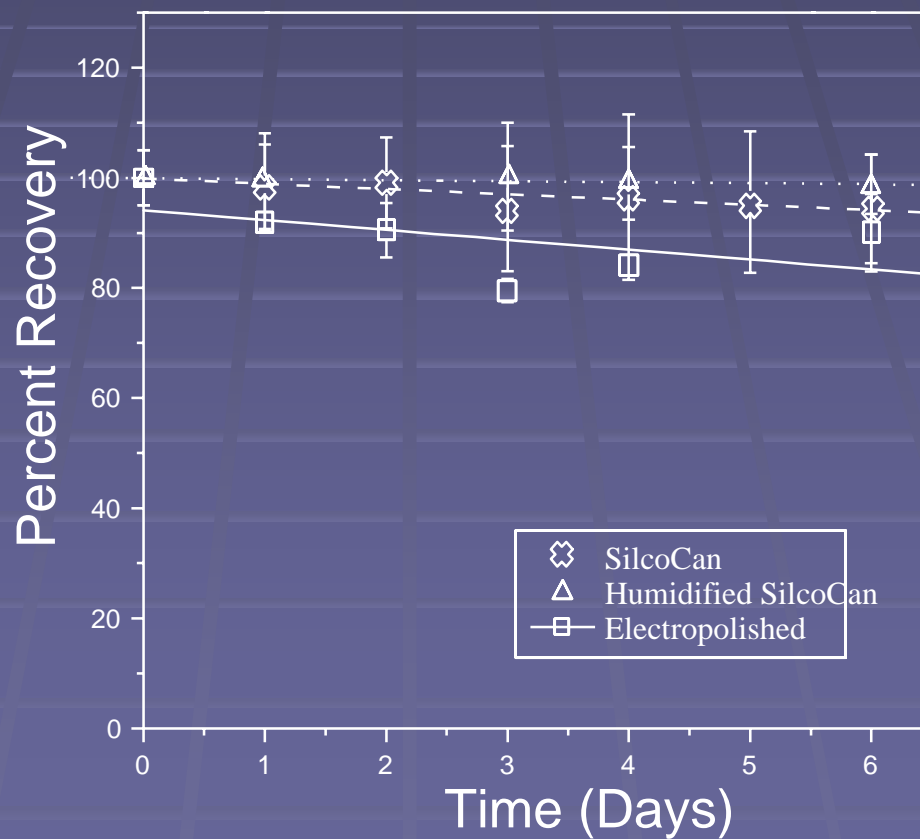
# Stability Study Test

- 11ppbv
- 6 days stability study
- Reference std is at 55ppbv
- Dimethyl sulfide as internal standard
- SilcoCans (n=18)
- Humidified (rh=50%) SilcoCans (n=5)
- Electropolished Cans (n=2)

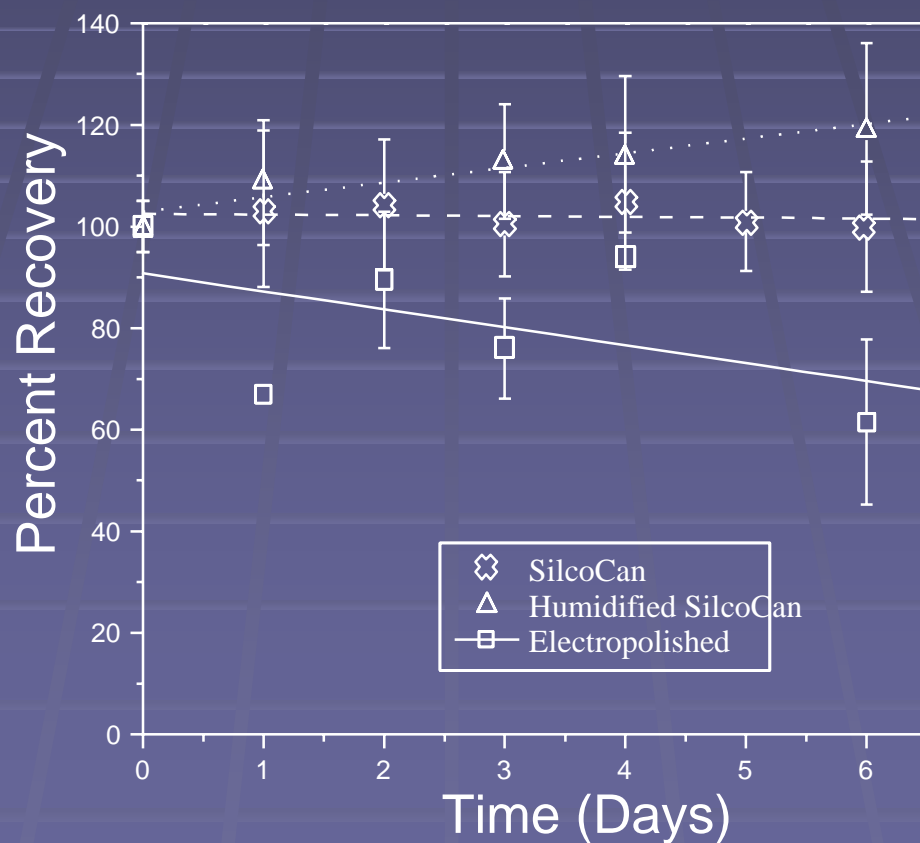
# H<sub>2</sub>S at 11ppbv in 6l Air Sampling Cans



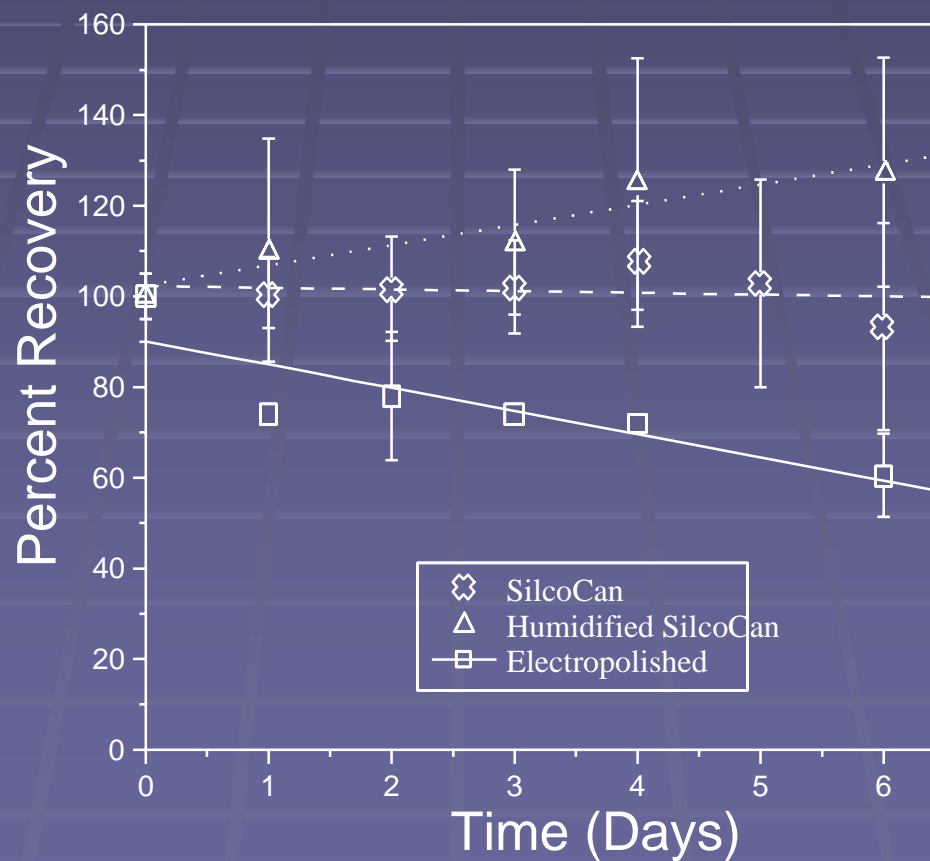
# COS at 10ppbv in 6l Air Sampling Cans



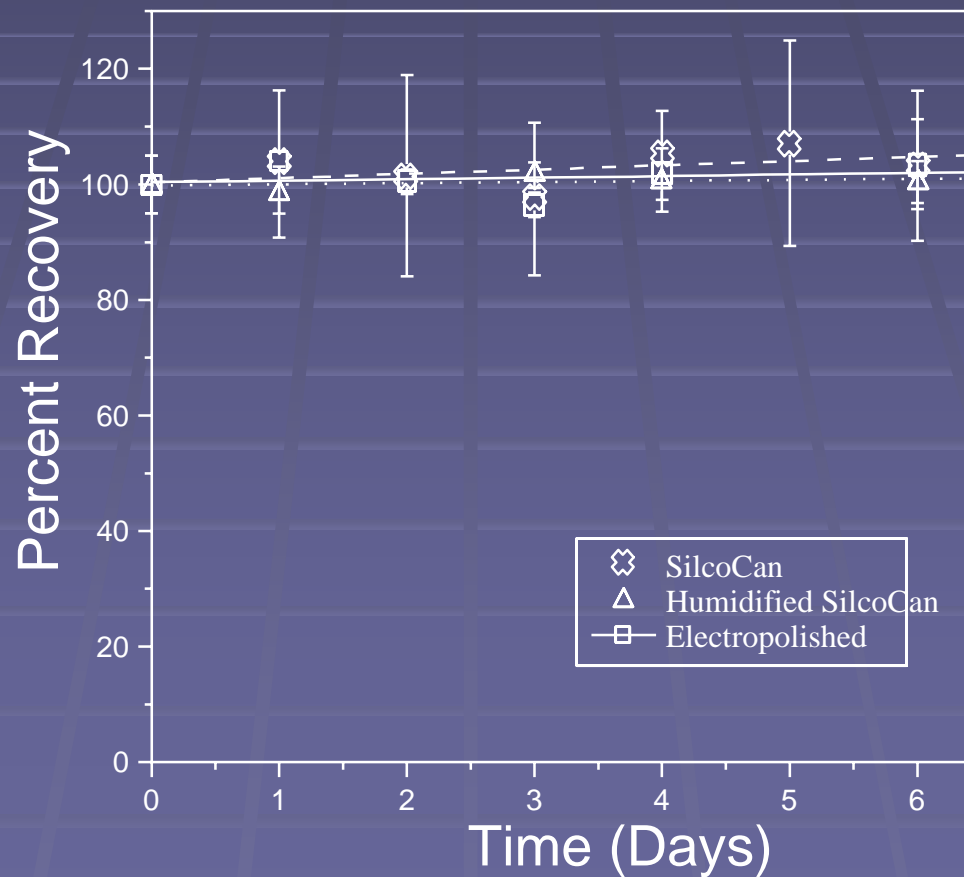
# Methyl Mercaptan at 11ppbv in 6l Air Sampling Cans



# Ethyl Mercaptan at 11ppbv in 6l Air Sampling Cans



# Dimethyl Disulfide at 11ppbv in 6l Air Sampling Cans



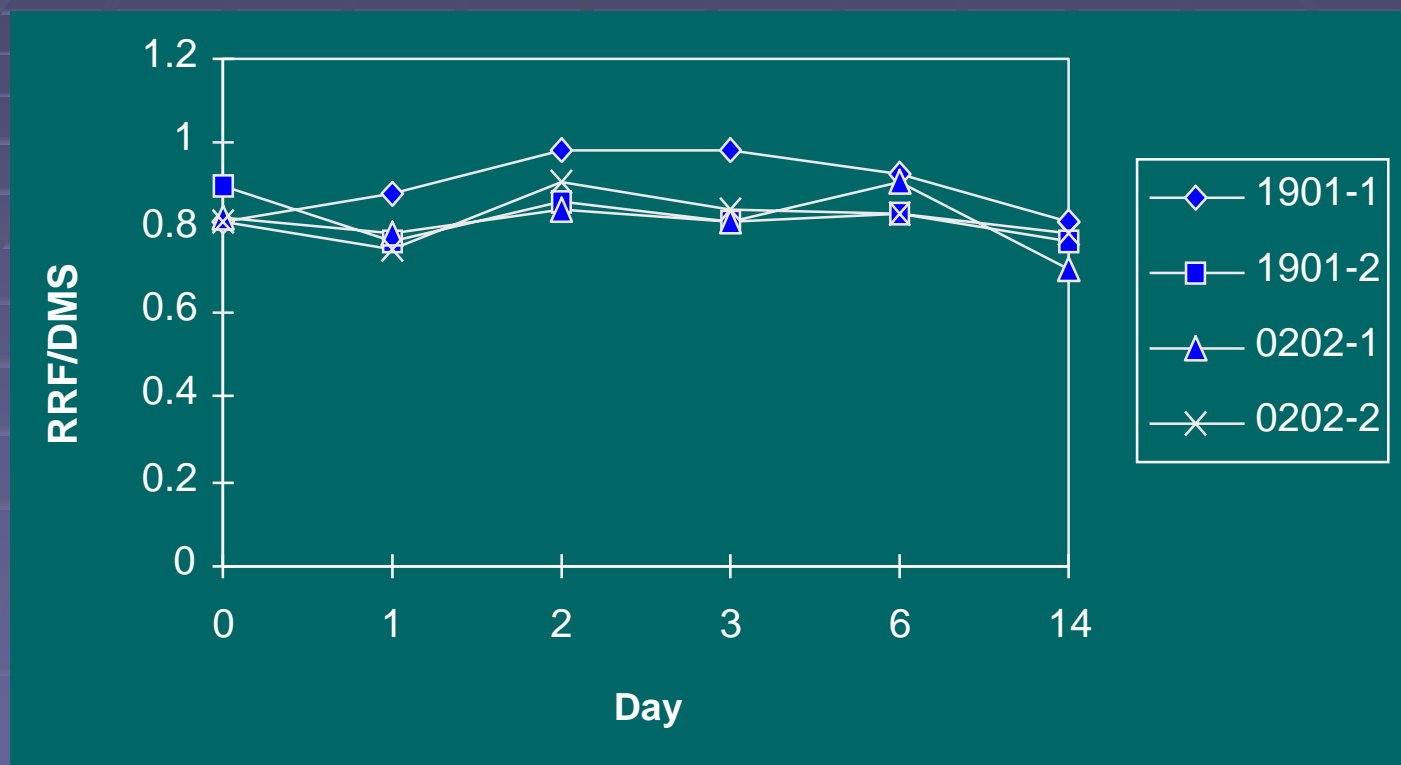


# Extended Stability Study

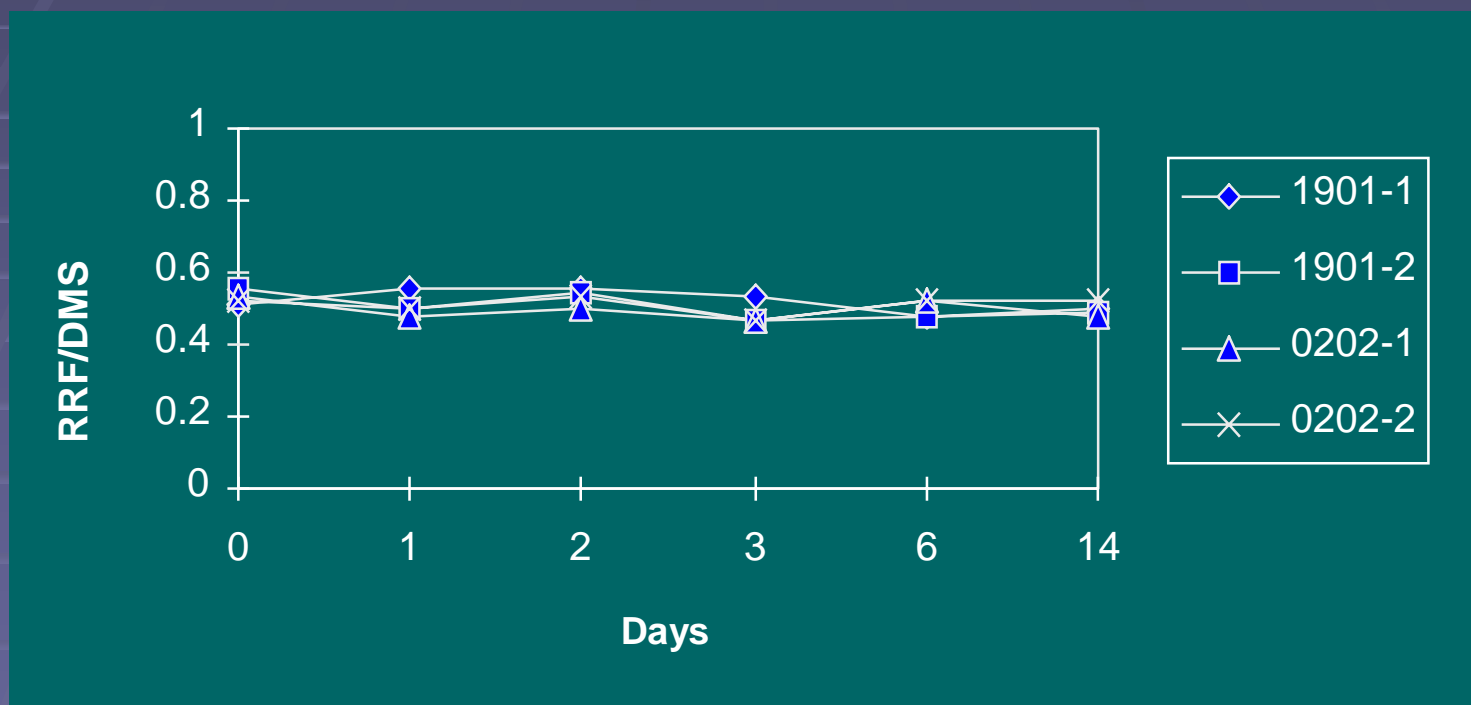
- Is the SilcoCan capable of storing 11ppbv sulfurs longer than 6 days?
- Tested 4 SilcoCans on Day 14



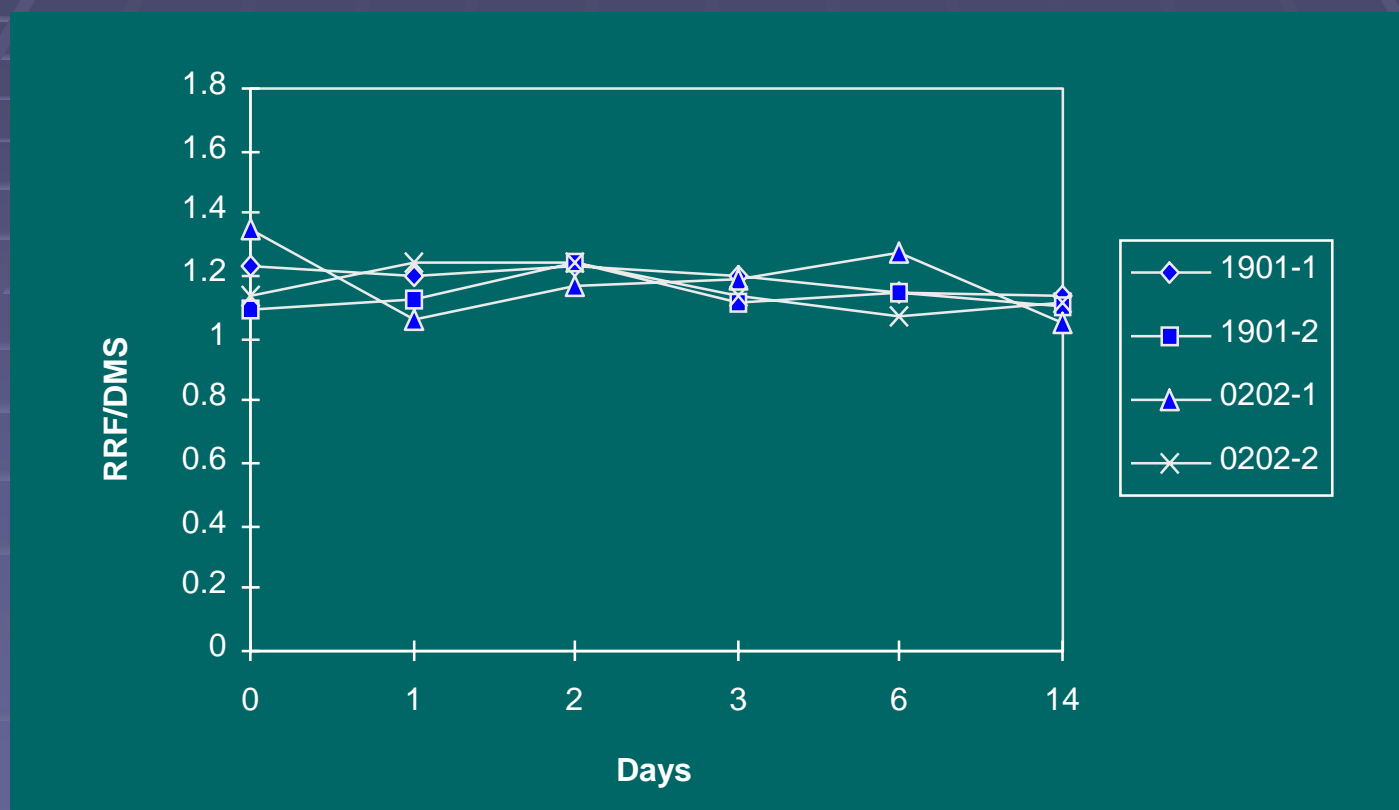
# H<sub>2</sub>S at 11ppbv for 14 days



# COS at 10ppbv for 14 Days



# Methyl Mercaptan 11ppbvfor 14 Days



# Performance of Silcosteel® Coating for transfer of NO<sub>x</sub> & Ammonia containing streams

- Study conducted by University of California Center for Environmental Research and Technology (October 2001)
- Study focused on quantifying uncertainties in continuous emission monitoring systems
- Study tried to simulate exhaust gas
- Total NO<sub>x</sub> levels in study were 0.4ppm, 2ppm and 9.5ppm total
- Dry, wet, and with ammonia

# NO<sub>x</sub> Study Conditions

- 100' section of 1/4" Silcosteel<sup>®</sup> coated tubing used to transfer Simulated Exhaust Streams
- Looking at recovery of components through the transfer system and relative standard deviation

# NO<sub>x</sub> Containing Sample Streams Studied

- Variety of components and concentrations studied:
- Each Condition tested with 3 NO<sub>x</sub> concentrations 0.4ppm, 2ppm and 9.5ppm total NO<sub>x</sub>
  - Dry Simulated Exhaust
  - Wet (13%H<sub>2</sub>O) Simulated Exhaust
  - Wet (13% H<sub>2</sub>O) Simulated Exhaust + 6ppm Ammonia
  - Wet (13% H<sub>2</sub>O) Simulated Exhaust + 10ppm Ammonia
  - Wet (6% H<sub>2</sub>O) Simulated Exhaust
  - Wet (6% H<sub>2</sub>O) Simulated Exhaust + 10ppm Ammonia



# Results from Study

- Silcosteel® coated tubing showed good transfer properties for entire experimental matrix
- Performed at the same level as Teflon lined tubing.
- Both performed better than a standard stainless steel transfer line
- Study noted that results warranted further study

# Examples of applications

- Purge and Trap systems manufactured to test water quality use Restek treated tubing to insure transfer
- Varian Ion trap mass spectrometer elements are coated to eliminate adsorption of ions
- Sulfur sampling and transfer equipment is coated to eliminate loss of active compounds
  - Testing of Ethylene and Propylene
  - Testing of Beverage grade CO<sub>2</sub> for sulfur
  - Testing of Sulfur compounds in beer
  - Natural Gas; LPG; Gasoline; Diesel

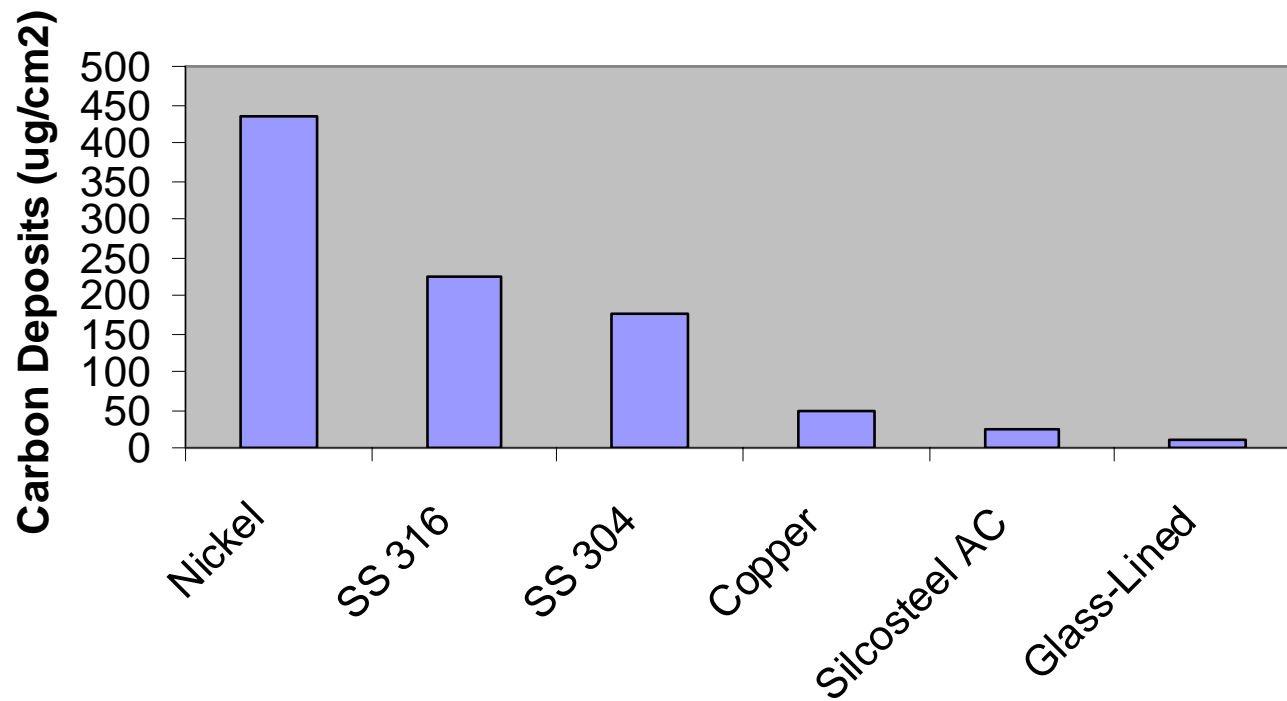


# Anti-Coking

- In applications of heated hydrocarbon transfer, carbon deposits can form
- Carbon deposits are catalyzed by nickel, sulfur and carbon in steel lattice
- The Silcosteel-AC coating produces a barrier that eliminates catalytic carbon buildup

# Anti-Coking Data

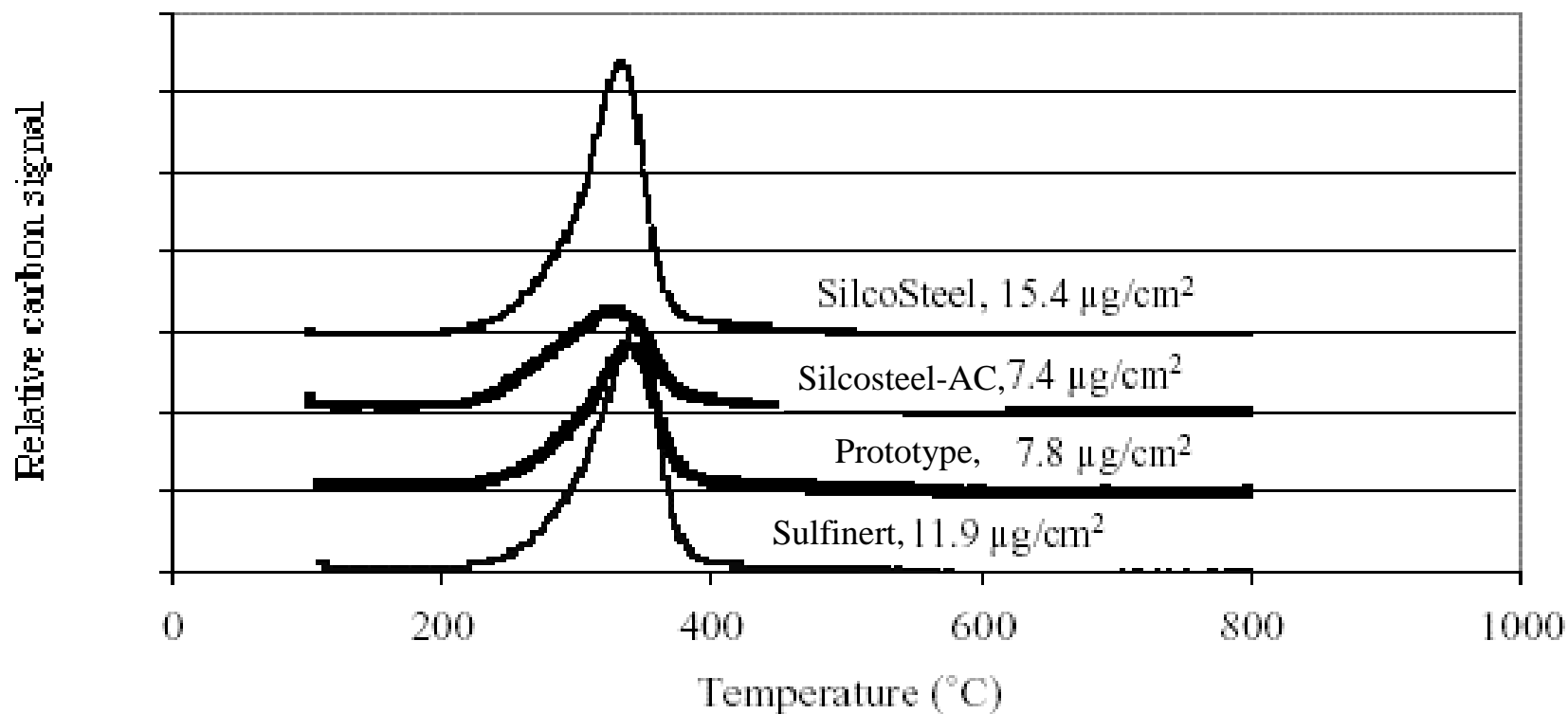
**Carbon Deposits from JP-8 Fuel on Various Types of Tubing**



- Semih Eser; PSU Prof. Fuel Sciences
- 8x improvement over raw 316L

# Anti-Coking Data (cont.)

**Different coatings, SEGMENT-2, JP5,  
350°C, 4 mL/min. 24h**



# Example Applications

- Coating fuel injector nozzles to decrease buildup
- Increasing lifetimes of Ethylene and Propylene Plug Flow reactors
- Increasing reliability of valves used in internal combustion engines
- Reduces fouling in heat exchangers

# Corrosion Resistance

- Stainless steel surfaces susceptible to attack from hydrochloric acid, sulfuric acid and nitric acid
- Silcosteel-CR treatment produces a layer of amorphous silicon
- Amorphous silicon is insoluble in hydrochloric acid, sulfuric acid and nitric acid

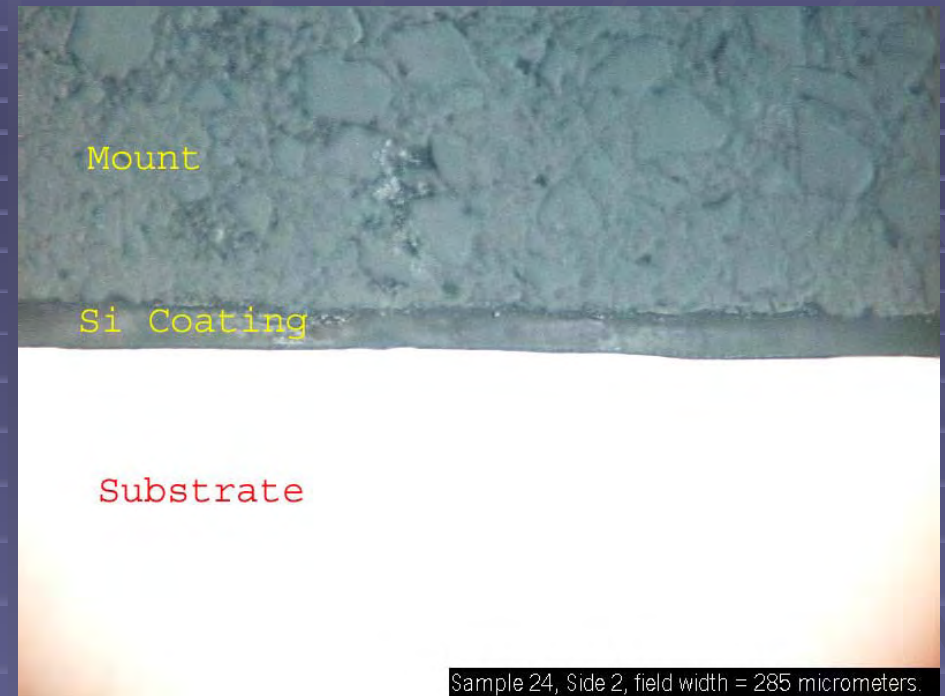
# Corrosion Data (cont.)

- Evaluation

- Certified corrosion engineers
- Spectroscopic analysis
- Mechanical testing
- Electrochemical

Cyclic Polarization in neutral, acidic, alkaline

- Atmospheric corrosion
  - ASTM moisture condensation
  - Salt spray ASTM B117
- Stress corrosion cracking (MgCl; ASTM G36)





# ASTM G45 B Data

- ASTM G45 method B; Pitting and Crevice Corrosion
  - 6% Ferric Chloride solution
  - 72hrs, 20°C
  - Gasket wrap

Sample	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Weight Loss (g/m <sup>2</sup> )
Silco-CR Sample 17	10.4105	10.3710	0.0395	19
Silco-CR Sample 28	10.1256	10.0743	0.0513	25
Silco-CR Sample 47	10.1263	10.0742	0.0521	25
Bare Sample 27	10.0444	9.5655	0.4789	231
Bare Sample 34	10.1265	9.6923	0.4342	209
Bare Sample 37	10.1007	9.6276	0.4731	228

# ASTM G45 B (cont.)

- Silcosteel<sup>®</sup>-CR treated sample showing no crevice corrosion only slight pitting corrosion

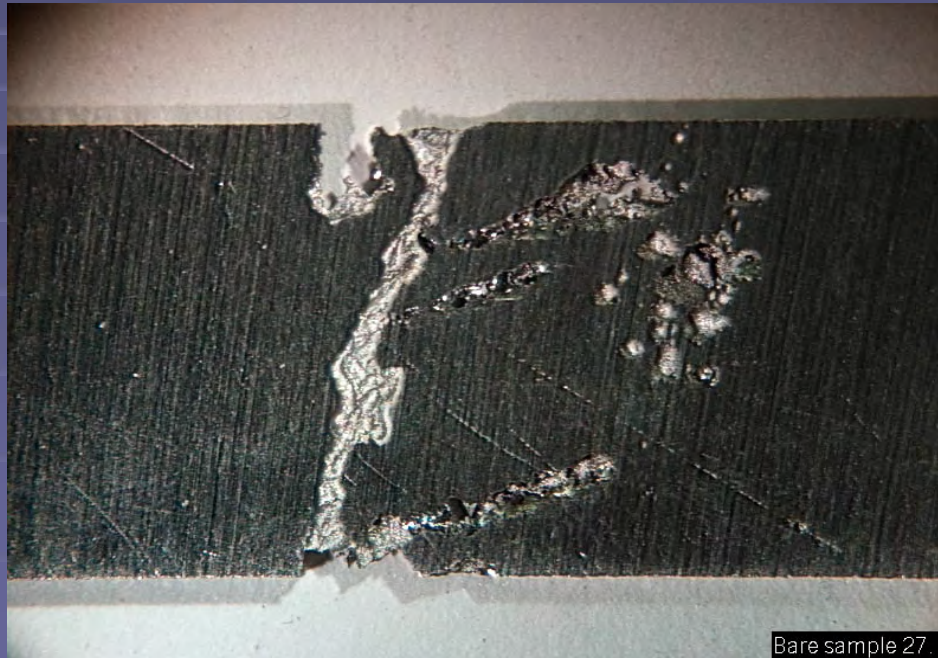


CVD siliconized sample 17.



# ASTM G45 B (cont.)

- Bare 316L Stainless Steel coupon showing severe crevice corrosion



Bare sample 27.

# ASTM G-61 Data

- ASTM G-61; Cyclic Polarization Electrochemical Corrosion Testing
  - Acid, neutral, basic aqueous solutions with varying Cl<sup>-</sup> ion concentrations (100, 3000, 5000ppm)
  - EG&G VersaStat System, 23°C
  - 316L vs. Silcosteel®-CR on 316L, 304L

Neutral solution;  
3000ppm Cl<sup>-</sup>

-CR vs 316L Raw: **50x** improvement

Sample	Ec, mV	Ic, uA/cm^2	Eb, mV	CR, mpy
316 L	-418	0.096	370	0.04
Silcosteel-CR 316 L	-533	0.002	1460	0.0009
304 L	-435	0.145	361	0.06

Ec = corrosion potential  
Ic = current density at Ec  
Eb = pitting potential  
CR = corrosion rate

# ASTM-G61 (cont.)

Acidic Solution; 1N H<sub>2</sub>SO<sub>4</sub>;  
3000ppm Cl<sup>-</sup>

-CR vs 316L Raw: **10x** improvement

Sample	Ec, mV	Ic, uA/cm <sup>2</sup>	Eb, mV	CR, mpy
316 L	-662	1.920	370	0.83
Silcosteel-CR 316 L	-843	0.123	927	0.05
304 L	-639	2.650	587	1.14

Basic Solution; 1N NaOH;  
3000ppm Cl<sup>-</sup>

-CR vs 316L Raw: **4x** improvement\*

Sample	Ec, mV	Ic, uA/cm <sup>2</sup>	Eb, mV	CR, mpy
316 L	-419	0.193	265	0.08
Silcosteel-CR 316 L	-816	0.036	618	0.02
304 L	-388	1.120	668	0.48

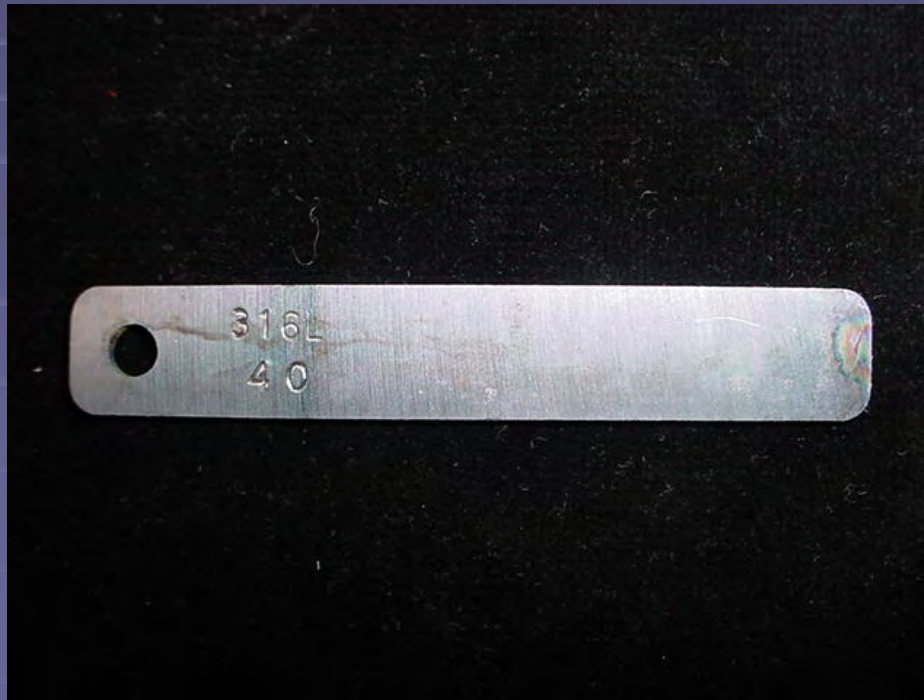
# ASTM B117 Data

- ASTM B 117 – “Practice for Operating Salt Spray (Fog) Apparatus.”
  - 1000 hour exposure
  - 100 degree Fahrenheit
  - 3.5% by weight sodium chloride
- Reproduces exposure to marine environments.



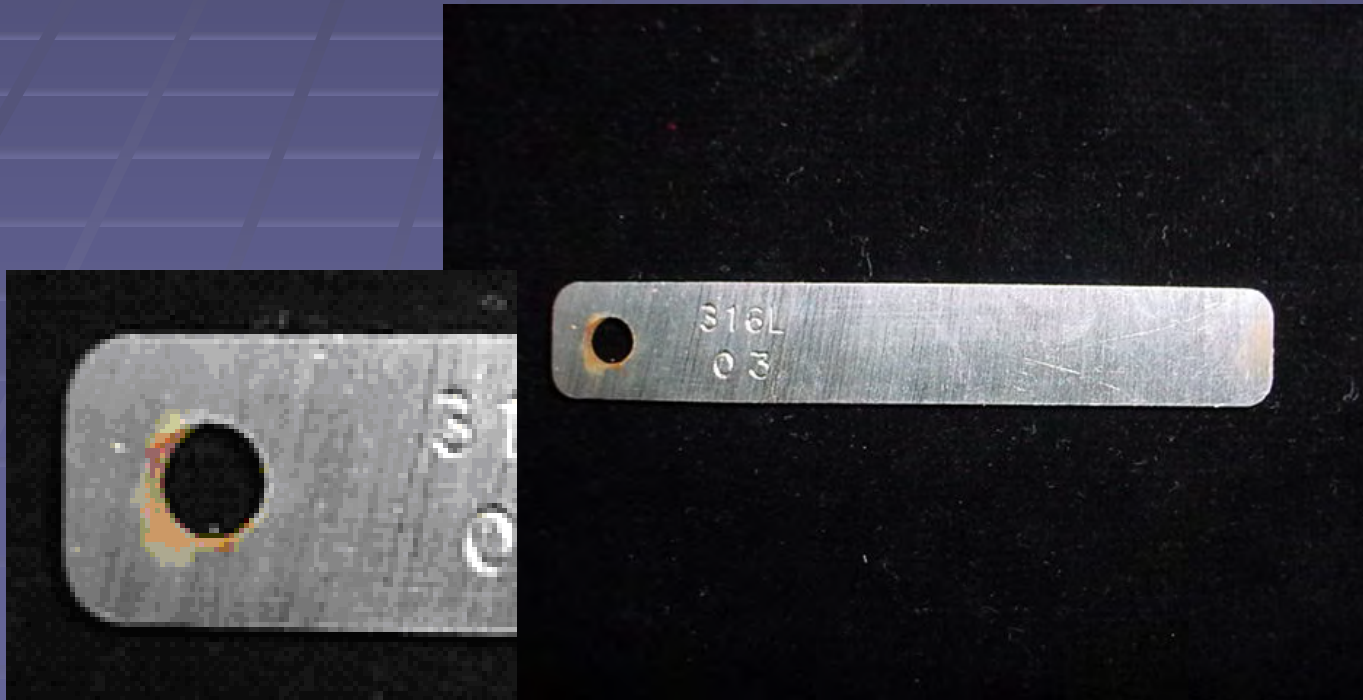
# ASTM B117 Data (cont.)

- Silcosteel®-CR treated samples showed no signs of bleeding, rusting, or pitting corrosion



# ASTM B117 Data (cont.)

- The non-treated samples showed some light surface rusting, but no signs of pitting corrosion.



# ASTM D4585 Data

- ASTM D 4585, "Practice for Testing the Water Resistance of Coatings Using Controlled Condensation."
  - 1000 hour study
  - 100 degrees Fahrenheit
  - Distilled water
- Reproduces exposure to atmospheric conditions

# ASTM D4585 (cont.)

- Silcosteel<sup>®</sup>-CR treated samples showed no signs of bleeding, rusting, or pitting corrosion





# ASTM D4585 (cont.)

- Only a very light surface oxide film was seen on the bare samples.



# Examples Applications

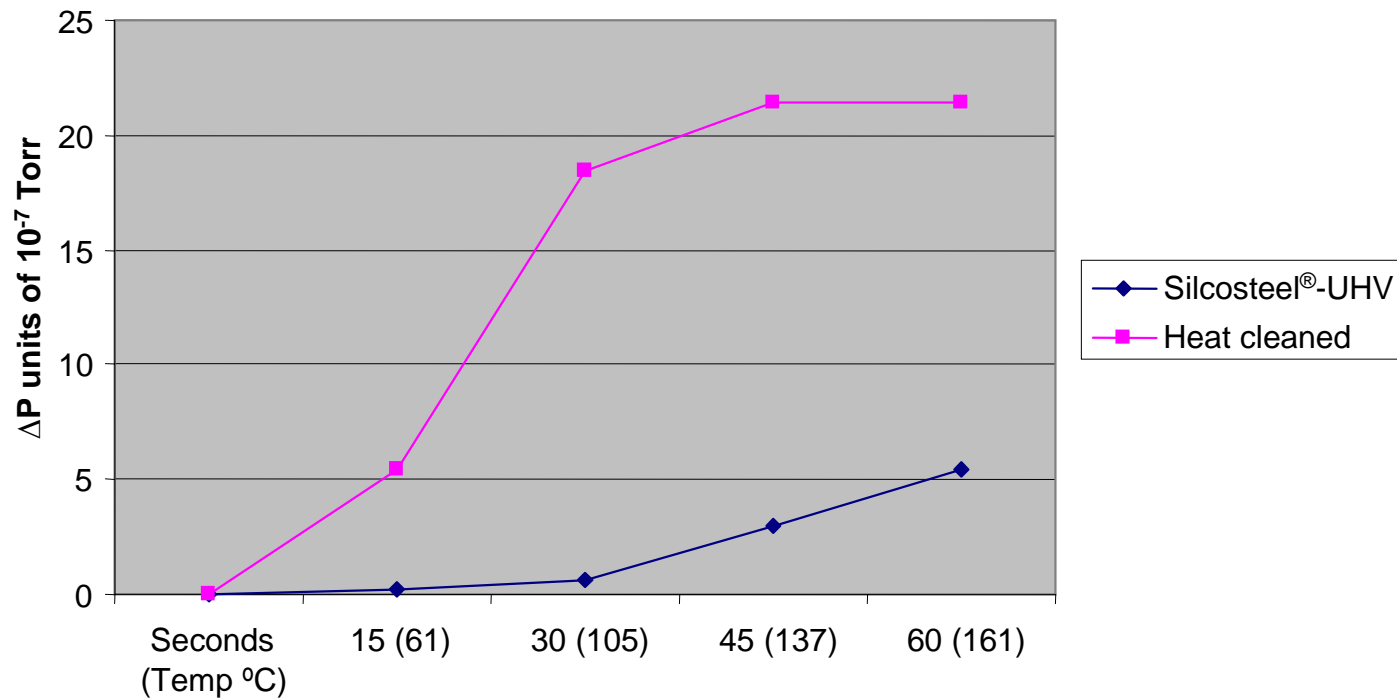
- Using Silcosteel-CR treated 316L stainless steel instead of items made from Hastelloy or Inconel in corrosive environments
- Protecting the value and extending the life of expensive existing equipment in corrosive environments by use of protective coating
- Increase cycle lifetime of equipment

# Ultra-High-Vacuum (UHV)

- UHV environments are characterized as having a vacuum of  $1 \times 10^{-7}$  Torr or better
- In these conditions, materials trapped to the surface of and inside the steel outgas into the vacuum environment
- The outgassing of material increases pressure in the environment
- Large pumps and long “pump down” times are required to achieve UHV environments
- Silcosteel-UHV treatment produces a barrier that blocks materials from outgassing into the vacuum environment.

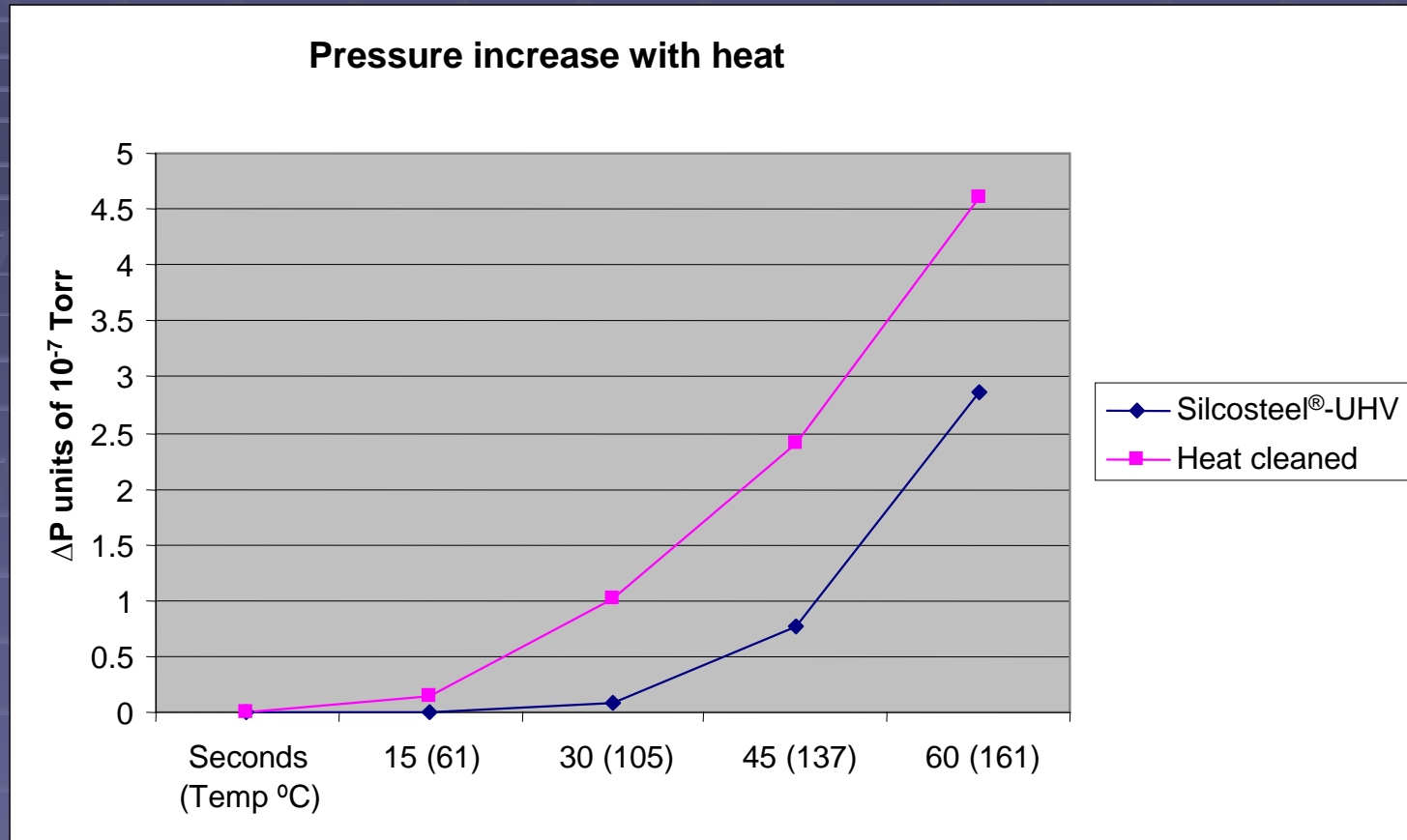
# Ultra-High Vacuum Data

Pressure increase with heat



- Bruce Kendall: Elvac Labs, PSU Physics prof. (ret.)
- Turbopump,  $4.6 \times 10^{-7}$  Torr base pressure
- 1hr under vacuum ( $\Delta P_1$ )
- 27x improvement at 61°C

# Ultra-High Vacuum Data (cont.)



- Turbopump,  $7.5 \times 10^{-8}$  Torr base pressure
- 10hr under vacuum ( $\Delta P_2$ )
- 14x improvement at 61 $^{\circ}\text{C}$



# Example Applications

- Coating of accelerator chambers to create higher vacuum environment
- Use in coating of semi-conductor manufacturing equipment to decrease defect rate
- Reducing time needed to achieve high vacuum environments in analytical equipment (SEM, XPS, etc.,.)

# Future

- Currently renovating for expansion
- New process oven (31" ID x 24" deep)
- Continual process improvement and new product development
  - Hardness
  - Improved corrosion resistance
  - Customized surfaces

# Sample Preparation and Confirmation Column for Phenoxyacid Herbicides by HPLC

Julie Kowalski, Kristi Sellers, Lydia Nolan, and  
Rebecca Wittrig

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823





# Introduction

Phenoxyacid herbicides, such as 2,4-D, dicamba, picloram, and Silvex, are used to control agricultural and aquatic weeds. These compounds can be found in the acid form, or as the salts or esters. While not considered highly toxic, phenoxyacid herbicides are monitored in agricultural monitoring wells and drinking water sources. Traditionally, these compounds have been analyzed by gas chromatography (GC), for example by US EPA Method 8151. To make these compounds amenable to GC, they must first be converted to the methyl esters using a derivatizing agent such as diazomethane, a time-consuming procedure.

An optimized HPLC method for analyzing phenoxyacid herbicides using a C18 column and gradient procedure was previously presented. In order to perform confirmation analysis, a second column producing retention time and elution order changes is needed. A confirmation column has been developed that has a different selectivity for the phenoxyacid herbicides than a C18 stationary phase using the same gradient procedure.

A solid phase extraction (SPE) method has been verified to extract and concentrate water samples up to 1L volume and to quantitatively recover at least 16 of the common underivatized herbicides in Table 1. This simple sample preparation step provides cleaner analytical samples and lower HPLC detection limits, making this a suitable replacement for GC analysis.

Table I. Chlorophenoxyacid Herbicides included in this study.

Mix A	Mix B	
picloram	4-nitrophenol	1,4-dichlorobenzene (IS)
chloramben	MCPA	2,4-dichlorophenyl acetic acid (surrogate)
dicamba	3,5-dichlorobenzoic acid	
bentazon	MCPP	
2,4-D	2,4,5-T	
dichlorprop	2,4-DB	
2,4,5-TP (Silvex)	dinoseb	
acifluorfen	pentachlorophenol	

# Confirmation Column Selection

Previous work indicated that the Ultra Aqueous C18 stationary phase provided enhanced selectivity for the target herbicides. Many different types of HPLC stationary phases were evaluated as possible confirmation columns; such as the Ultra PFP (pentafluorophenyl), and IBD (intrinsically base deactivated), as well as the Pinnacle II™ PAH and Phenyl phases. These were all tested to establish if they provided adequate separation, rapid analysis times and sufficient elution order changes to qualify as a reliable confirmation column. Results of these studies indicated that the Allure™ Basix phase met all the necessary requirements.

Figure 1 demonstrates the problems when using either a standard C18 or even a base deactivated C18 phase for the analysis of these acidic herbicides. Figure 2 shows the significant analytical improvement when using the Ultra Aqueous C18 and the HPLC conditions listed in Table II. The chromatograms for Mix A and B are overlayed for clarity. Figure 3 chromatograms were generated using these same analytical conditions and the Allure Basix column. All of the runs were completed in less than 17 minutes and still provided adequate separations. The Ultra Aqueous stationary phase contains a polar embedded group in addition to the C18 functionality, while the Allure's highly retentive propyl cyano phase demonstrates a very different selectivity for the target herbicides under the same analytical conditions. Table III highlights both the differences in elution order and the shift in retention times that are critical to obtaining good confirmation of the identified underivatized analytes.

Figure 1. Analysis of phenoxyacid herbicides using standard C18 columns: non-base deactivated (upper) and base deactivated stationary phases (lower).

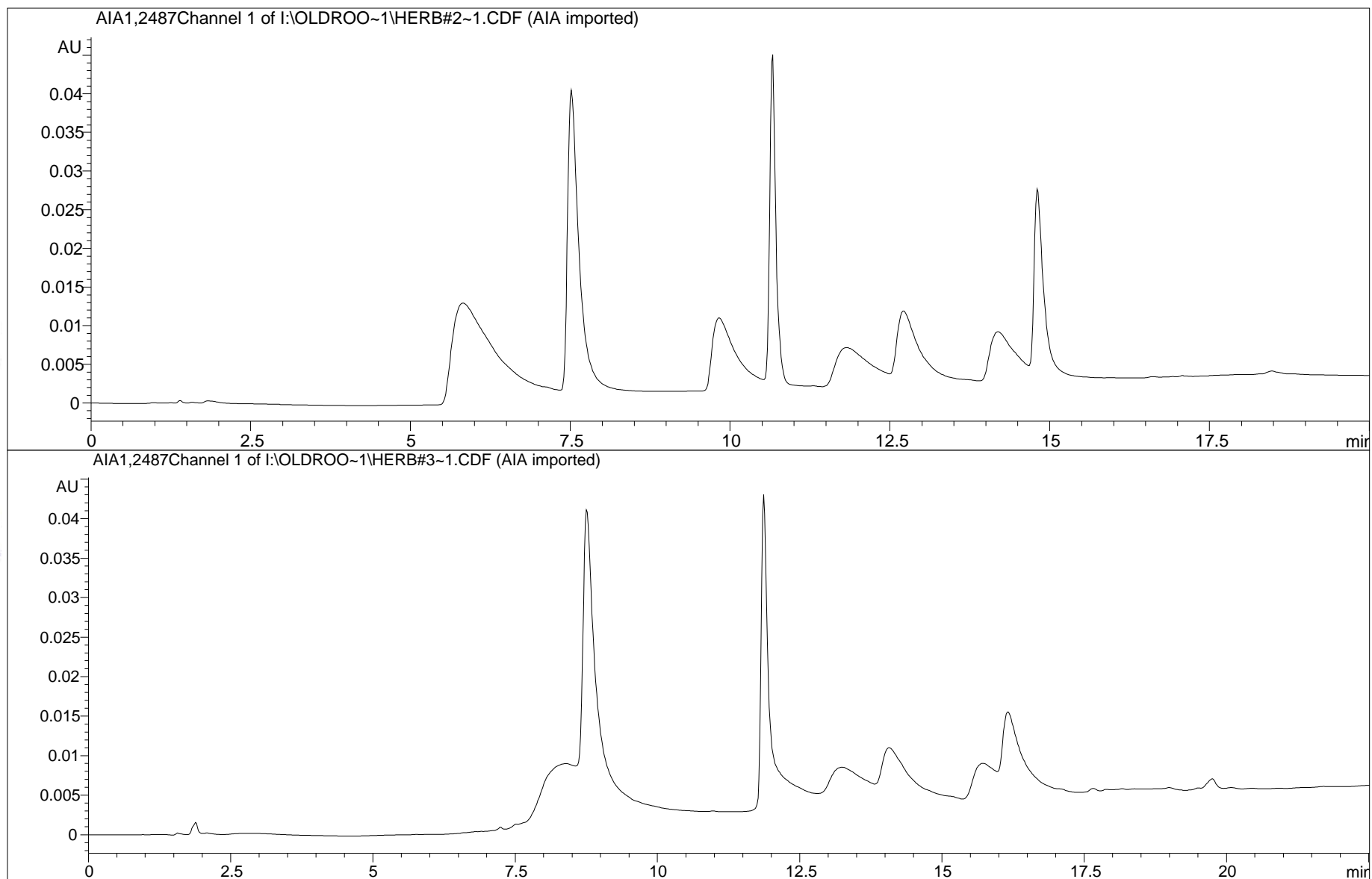
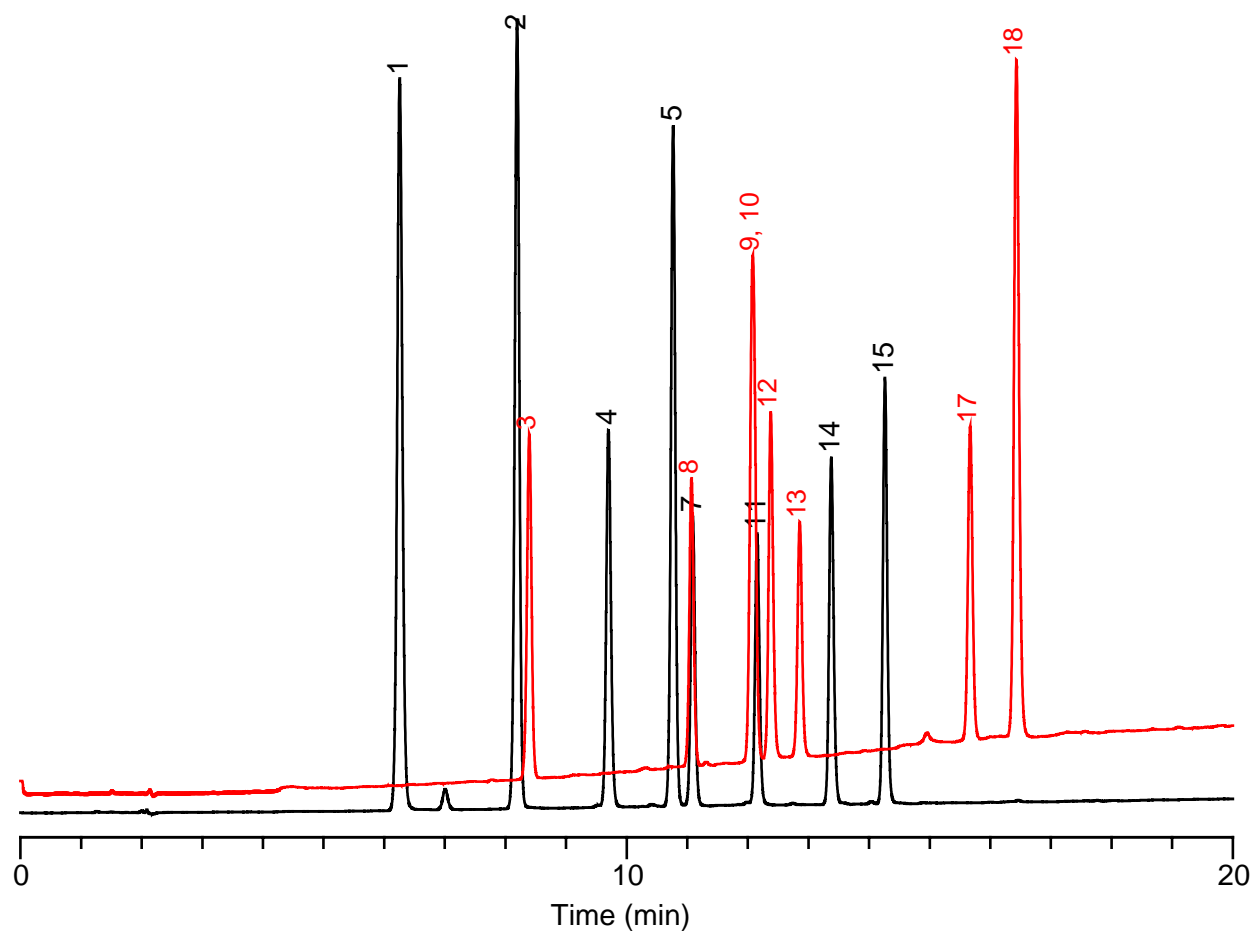


Table II. Improved chromatographic conditions for separation and confirmation of phenoxyacid herbicides.

<b>HPLC Columns</b>	Ultra Aqueous C18, 150x4.6mm, 5µm Allure™ Basix, 150x4.6mm, 5µm
<b>Mobile Phase</b>	A: 0.05% H <sub>3</sub> PO <sub>4</sub> B: acetonitrile
<b>Gradient Program</b>	0 min          20%B 28 min        80%B 33 min        90%B 34 min        20%B
<b>Flow Rate</b>	1.0 mL/min
<b>Detection</b>	UV @ 225nm
<b>Injection</b>	10µL
<b>Concentration</b>	10 ppm each

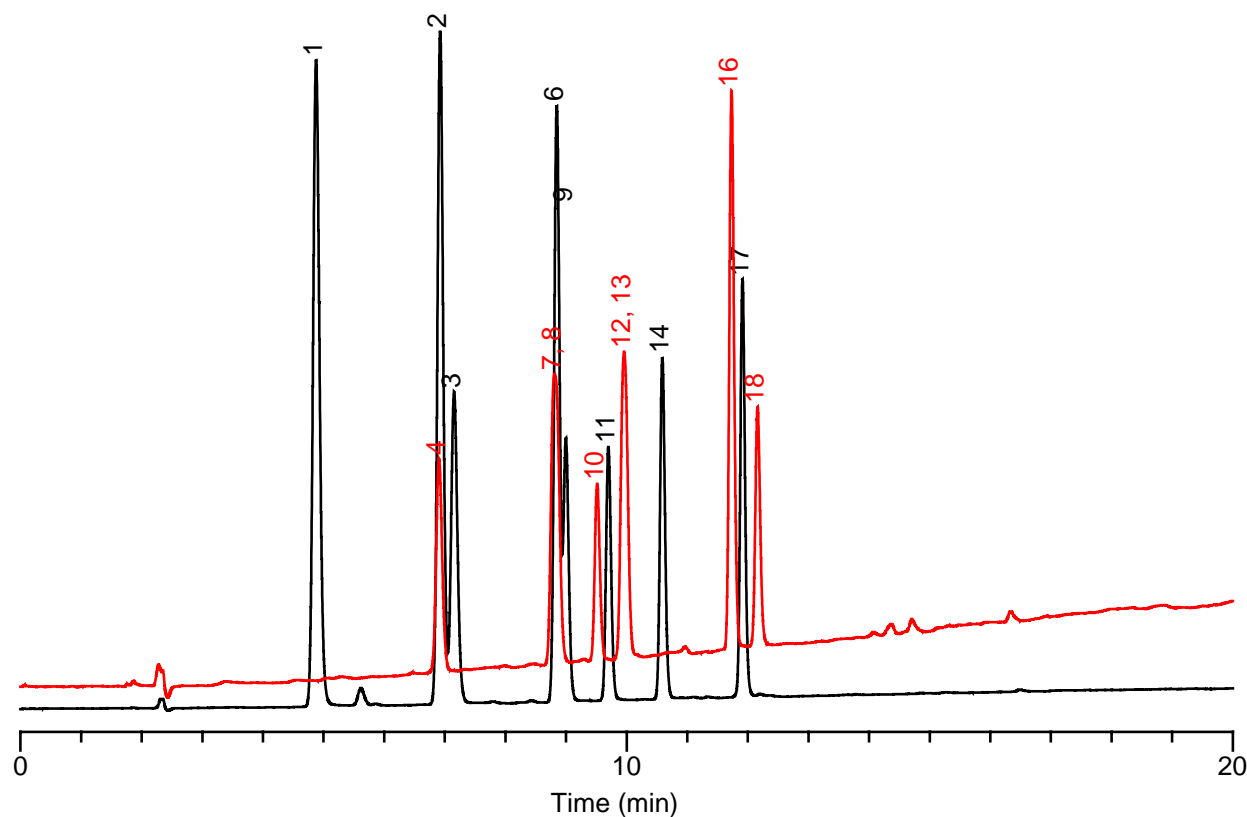
Figure 2. Separation of phenoxyacid herbicide mix A and B, using an Ultra Aqueous C18 column and the conditions in Table II.



Peak List:

1. Pichloram
2. Chloramben
3. 4-nitrophenol
4. Dicamba
5. Bentazon
6. DCAA (Surr) (not shown)
7. 2,4-D
8. MCPA
9. 3,5-DCBA
10. MCPP
11. Dichlorprop
12. 2,4,5-T
13. 2,4-DB
14. 2,4,5-TP (Silvex)
15. Acifluorfen
16. 1,4-DCB (IS) (not shown)
17. Dinoseb
18. Pentachlorophenol

Figure 3. Separation of phenoxyacid herbicide mix A and B, using an Allure Basix column and the conditions in Table II.



### Peak List

1. Pichloram
2. Chloramben
3. Dicamba
4. 4-nitrophenol
5. DCAA (Surr) (not shown)
6. Bentazon
7. 3,5-DCBA
8. MCPA
9. 2,4-D
10. MCPP
11. Dichlorprop
12. 2,4-DB
13. 2,4,5-T
14. 2,4,5-TP (Silvex)
15. 1,4-DCB (IS) (not shown)
16. Pentachlorophenol
17. Acifluorfen
18. Dinoseb



Table III. Comparison of retention times and elution orders for chlorophenoxy herbicides on Ultra Aqueous C18 and Allure Basix columns. Coelution groups are highlighted.

Compound	Ultra Aqueous C18
Pichloram	6.24
Chloramben	8.16
4-nitrophenol	8.38
Dicamba	9.64
Bentazon	10.69
DCAA (Surr)	10.83
2,4-D	11.03
MCPA	11.04
3,5-DCBA	12.05
MCPP	12.07
Dichlorprop	12.09
2,4,5-T	12.34
2,4-DB	12.82
2,4,5-TP (Silvex)	13.30
Acifluorfen	14.05
1,4-DCB (IS)	15.23
Dinoseb	15.62
Pentachlorophenol	16.39

Compound	Allure Basix
Pichloram	5.93
Chloramben	8.54
Dicamba	9.02
4-nitrophenol	9.08
DCAA (Surr)	10.62
Bentazon	11.07
3,5-DCBA	11.07
MCPA	11.19
2,4-D	11.32
MCPP	12.03
Dichlorprop	12.18
2,4-DB	12.55
2,4,5-T	12.65
2,4,5-TP (Silvex)	13.32
1,4-DCB (IS)	13.61
Pentachlorophenol	15.11
Acifluorfen	15.19
Dinoseb	15.84



# Solid Phase Extraction

To meet required detection limits for these herbicides, a concentration step is necessary. Solid phase extraction (SPE) can be used to extract the herbicides as free acids from a water matrix, before elution with suitable solvents. Several types of beds were previously tested for this application, including C18, and graphitized carbon. We have confirmed that a specialty divinylbenzene material, the Resprep AH SPE 6mL/500mg tube, gave the best overall recoveries.

Analytical conditions are the same as in Table II. The SPE preparation method is detailed in Table IV. Water sample volumes from 500milliliters to 1liter must be adjusted to a pH of 2 for best recovery results. Results of a final study for all 16 herbicides, internal and surrogate standards are summarized in Tables V and VI. When using a 1L sample size, recoveries of the herbicides were 92-100%, with the exception of the internal standard 1,4 dichlorobenzene. This analyte is not well retained on the packing and reduced recovery is due to breakthrough during the sample extraction step. The 1L samples were spiked with 10ppb of each herbicide and the SPE method overall produced a 200-fold concentration of the analytes. The use of MTBE during elution is optional. Most recoveries improved only slightly, but it is required for quantitative recovery of pentachlorophenol.

Table IV. Conditions for the solid phase extraction of phenoxyacid herbicides.

SPE tube	6mL, 500mg Resprep AH tube, 6mL/500mg cat#26029
Tube conditioning	<ol style="list-style-type: none"> <li>1. 4mL acidified methanol (0.01% phosphoric acid)</li> <li>2. 4mL deionized water (pH=2)</li> </ol>
Sample	500mL or 1L water, pH adjusted to 2
Sample flow rate	Sample passed through tube at rapid vacuum flow rate
Wash	Inner surface of tube rinsed with small amount of acidified water, if necessary
Dry	Tube dried for less than 1 minute
Extraction	<ol style="list-style-type: none"> <li>1. 3 x 2mL acidified methanol</li> <li>2. Additional 2mL methyl t-butyl ether (optional)</li> <li>3. Sample concentrated to 5mL (ambient temperature, nitrogen purge)</li> </ol>

Table V. Recoveries of phenoxyacid herbicides after solid phase extraction.

Analyte	% Recovery 500mL sample	%RSD n=4	% Recovery 1L sample
pichloram	89.9	5.8	97.5
chloramben	90.6	5.9	99.1
dicamba	89.2	5.5	98.4
bentazon	89.0	5.7	97.5
2,4-D	88.7	5.7	98.3
dichloroprop	91.9	6.9	100.4
2,4,5-TP	89.0	5.5	98.0
acifluorfen	82.9	5.6	91.9
1,4 dichlorobenzene (IS)	60.5	4.4	77.3

Table VI. Recoveries of additional phenoxyacid herbicides after solid phase extraction.

Analyte	% Recovery 500mL sample	% RSD n=3	% Recovery 1L sample	% RSD n=3
4-nitrophenol	97.2	2.4	92.3	0.9
2,4 DCAA (surrog)	100.7	6.3	97.4	0.9
MCPA	99.7	2.4	96.5	1.5
3,5 dichlorobenzoic acid	99.8	2.2	95.2	1.1
MCPP	100.6	2.8	96.6	1.5
2,4-T	96.2	2.3	96.2	1.5
2,4-DB	99.1	2.4	97.7	1.7
1,4 dichlorobenzene (IS)	73.2	1.3	72.0	3.0
Dinoseb	93.4	1.0	95.0	1.4
pentachlorophenol	93.0	1.3	93.5	2.5

# Conclusions

Based on this study, HPLC analysis of phenoxyacid herbicides after solid phase extraction is a viable alternative to the gas chromatographic procedure. The chromatographic separation of the herbicides was optimized using an Ultra Aqueous C18 column, a C18 stationary phase with a polar embedded group, and confirmed using an Allure Basix column, a propyl cyano stationary phase. These phases have enhanced selectivity for the acidic compounds when analyzed at low pH. This HPLC technique does not require derivitization of the acidic analytes, a step which requires experienced laboratory personnel and a significant preparation time commitment for each sample.

In order to meet the required detection limits, a solid phase extraction method was developed which resulted in a 200-fold concentration of the analytes during cleanup. The SPE method, using a substituted divinylbenzene packing material, showed excellent recoveries for all 16 acid herbicides and 1 surrogate, even with 1 liter samples. The internal standard shows lower recoveries than the target herbicides; other options for the internal standard will be explored. The SPE method allows for rapid and quantitative recovery of these herbicides in their free acid form.

# A Comparison of Liner Geometries and Their Effect on Gas Chromatographic Performance.

Michael A. Goss and Brad Rightnour

Restek Corporation, 110 Benner Circle,  
Bellefonte, PA 16823



# Abstract

When using Split/Splitless injection ports, analysts have a wide variety of liner geometries to choose from. Split liners are designed with mixing chambers and tortuous flow paths to fully vaporize the sample into a homogeneous vapor cloud before it reaches the split point. Splitless liners usually are designed as straight tubes, with alternate designs, such as a gooseneck restriction, which help contain the sample cloud in the injector and minimize the breakdown of compounds sensitive to catalytic decomposition from contact with metal inlet parts. The residence time of the sample in a splitless liner is dependent on liner geometry, gas velocity, and sample vaporization time.



# Introduction

With so many inlet liner designs on the market today, how do you determine which one is best suited for your analysis? Each liner geometry offers the analyst a unique sample flow, through the liner onto the analytical column, through cups, cyclos, and packings designed in the inner bore of the liner. How does each design affect sample flow? How does the internal volume of the liner affect chromatography?

We will look at these questions to determine which is the best liner for your analysis.



# Basic Liner Characteristics

When choosing a liner for your analysis you should always consider the expansion volume of the sample that you are introducing into the liner. Expansion volumes can vary with the solvent that you are using.

Back flash can occur when the expansion volume of the solvent in the sample is greater than that of the expansion volume of the liner. This can cause poor peak area reproducibility, tailing solvent peaks and ghost peaks.

# Backflash Liner Volumes

	<u>Theoretical*</u>	<u>Effective</u>
1.0mm ID	= 59 $\mu$ L	30 $\mu$ L
2.0mm ID	= 236 $\mu$ L	118 $\mu$ L
3.0mm ID	= 530 $\mu$ L	265 $\mu$ L
4.0mm ID	= 942 $\mu$ L	471 $\mu$ L

\* Liner volume actually available for vaporization with carrier gas present is  $\leq \frac{1}{2}$  theoretical!

*From Grob, Split and Splitless Injection, 3<sup>rd</sup> ed.*

# Backflash

## Solvent Expansion Volumes

Injection volume (liquid)	Expansion volume (vaporized)				
	H <sub>2</sub> O	CS <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	Hexane	Isooctane
0.5µL	<del>710µL</del>	212µL	200µL	98µL	78µL
1.0µL	<del>1420µL</del>	423µL	401µL	195µL	155µL
2.0µL	<del>2840µL</del>	<del>846µL</del>	<del>802µL</del>	390µL	310µL
5.0µL	<del>7100µL</del>	<del>2120µL</del>	<del>2000µL</del>	<del>975µL</del>	<del>775µL</del>

\*Based on liner ID of 4mm, injection port temperature of 250°C and 10psig head pressure.

~~X~~ = Too large

# Splitless Liners

Splitless liners are designed to hold the sample in the liner between 0.5 and 2.0 minutes. A large surface area for sample vaporization is not a factor in splitless injections.

It is common to use packing materials whenever dirty samples are analyzed. Liners packed with wool help promote sample vaporization, as well as trap non-volatile residue to prevent column contamination which ultimately increases column life.

# Splitless Liner Designs

Straight

Gooseneck

Double  
Gooseneck

Cyclo Double-  
Gooseneck

## Benefits:

Low cost.

## Drawbacks:

Prone to high molecular weight distribution.

Sample exposed to metal surface below liner.

## Benefits:

Decrease sample contact with metal inlet parts.

Improves sample transfer to column.

## Drawbacks:

More sample backflash than with the double gooseneck.

## Benefits:

Decrease sample backflash.

Decrease injection port discrimination.

## Drawbacks:

Cannot be packed with wool.

Difficult to clean.

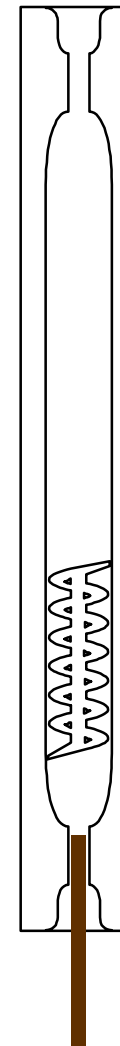
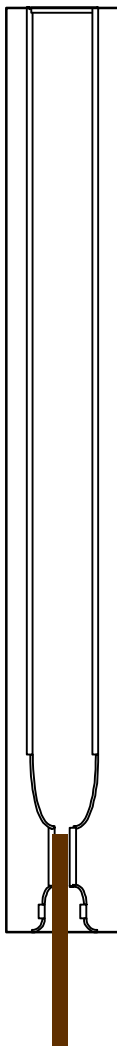
## Benefits:

Extends column lifetime by trapping non-volatile residue.

## Drawbacks:

Cannot be packed with wool.

Difficult to clean.



# Straight Tube Design

The straight tube design is the most common splitless liner design. This liner is ideal for low molecular weight samples that are prone to thermal decomposition. If used for high molecular weight sample analysis, packing material such as glass wool or CarboFrit™ material is recommended to aid in sample vaporization.

# Gooseneck Liners

The gooseneck liner helps isolate the sample from the metal injection port parts situated at the base of the injector. This design funnels the sample onto the analytical column for increased splitless efficiency and decreased breakdown of highly active compounds, such as Endrin and DDT. The double gooseneck design helps to contain the sample cloud in the liner, for increased performance with larger sample introductions, but cannot be packed with wool.

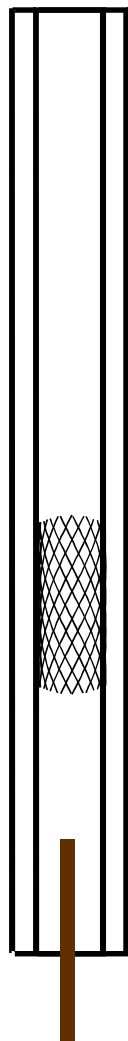
# Split Liners

Split liners are designed to help vaporize the sample by using mixing chambers and tortuous flow paths to help vaporize the sample before it enters the analytical column. Materials such as deactivated fused silica wool or beads, CarboFrit™ packing, and other packings are used to increase sample vaporization.



# Split Injection Liner Designs

Split with wool or  
CarboFrit™



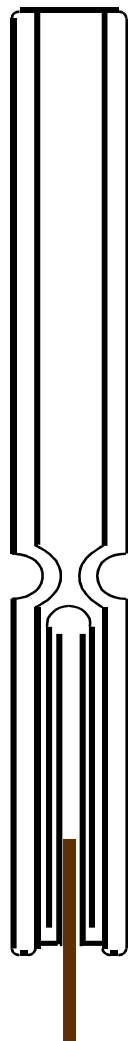
## Benefits:

Low cost.  
Reproducible performance.

## Drawbacks:

Wool can be adsorptive, especially if fibers are broken.

Laminar Cup



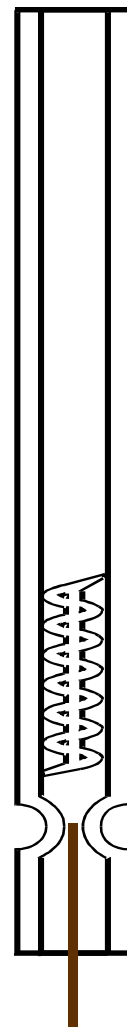
## Benefits:

Best splitter for high molecular weight compounds.  
High resolution.

## Drawbacks:

Costly.

Cyclosplitter®



## Benefits:

Ideal for dirty samples.  
Allows many injections of dirty samples before cleaning is required.

## Drawbacks:

Not recommended for large volume injections.

# Straight Tube Design

The most common liner for split analysis is the straight liner with deactivated wool, which offers the analyst a wide variety of options. The wool has a high surface area for more sample evaporation to occur, and promotes a uniform vapor cloud to enter the split point. The drawback of this design is that the wool increases breakdown of highly active compounds. When using this liner, the wool needs to be changed frequently. The position of the wool inside the liner and the quantity of the wool used is critical to reproducibility.

# Cup Splitter Designs

Cup splitter liners offer a more homogenous vaporization through increased sample residence time in the liner. The sample passes through a series of tortuous flow paths, which aids in sample vaporization. These liners are best suited for high molecular weight compounds.

The Cyclosplitter<sup>®</sup> liner incorporates a cylindrical glass screw in the sample pathway. The screw helps to mix and vaporize the sample. The increased surface area in the glass screw also helps to trap non-volatile residue, therefore, making it ideal for dirty samples.

# Uniliner® for Direct Injection

A Uniliner® is designed with a “press tight” fit between the glass surface of the liner and the analytical column. This prevents the sample from contacting metal inlet parts at the base of the splitless injection port. It also eliminates many problems associated with splitless hold times, such as reduced response and adsorption of high molecular weight compounds in the inlet, providing overall higher sensitivity.

## Drilled Uniliner<sup>®</sup> design

The drilled Uniliner<sup>®</sup> is ideal for use with EPC equipped GC systems. The hole equalizes pressure and maximizes sensitivity. The drilled Uniliner<sup>®</sup> with the hole near the bottom is recommended for analysis in which compounds of interest could be affected by a tailing solvent peak. The drilled Uniliner<sup>®</sup> with the hole near the top is recommended for analysis where compounds of interest elute away from the solvent peak.

# Direct Injection Liners

## Open-top Uniliner® w/ wool

### Benefits:

Easy to clean.  
No contact with metal inlet parts.  
Simulates on-column sample introduction.

### Drawbacks:

Wool can be adsorptive, especially if fibers are broken.

## Cyclo Uniliner®

### Benefits:

Excellent vaporization for high and low molecular weight samples.  
Traps non-volatile residue.

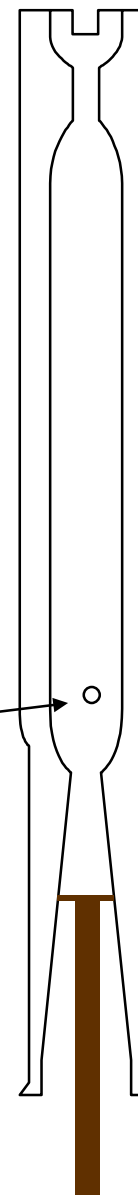
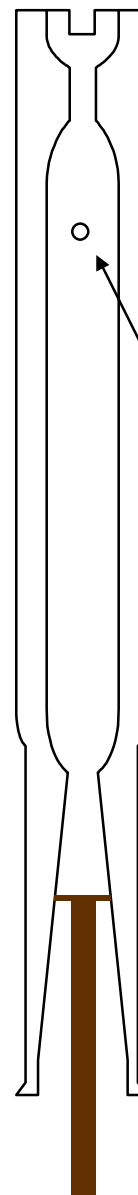
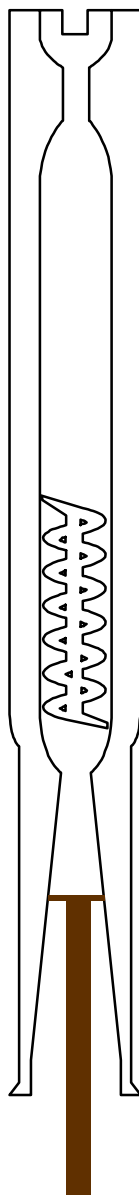
### Drawbacks:

Cannot be packed with wool.  
Difficult to clean.

## Standard Uniliner® with hole

### Benefits:

Ideal for EPC equipped GC's.  
The hole at the top is ideal for analysis in which the compounds of interest elute away from the solvent peak.  
The hole at the bottom is ideal for analysis in which the compounds of interest could be affected by a tailing solvent peak.



# Summary

When choosing a liner for your analysis, there are several key factors that will affect how the sample travels through the liner and onto the column. Choose a liner for the type of injection you will be performing and the type of compounds that are in the sample. Each liner offers a unique sample pathway and is designed to work best with a particular type of injection mode. Be sure to review all the variables, so your results are accurate and your downtime is decreased.

# A Novel Approach to Ensuring a Leak Free Injection Port.

Michael A. Goss and Brad Rightnour

Restek Corporation, 110 Benner Circle,  
Bellefonte, PA 16823





# Abstract

In Split/Splitless injection ports, it can be difficult to make and maintain a good seal with a conventional metal inlet disk. The metal to metal seal dictates that you apply considerable torque to the reducing nut, but this does not always ensure a leak-tight seal. Over-tightening of the reducing nut can cause the critical seal on the bottom of the injector to become damaged or flattened. Over the course of oven temperature cycling, metal seals are prone to leaks, which ultimately can degrade the capillary column and cause other analytical difficulties.

# Introduction

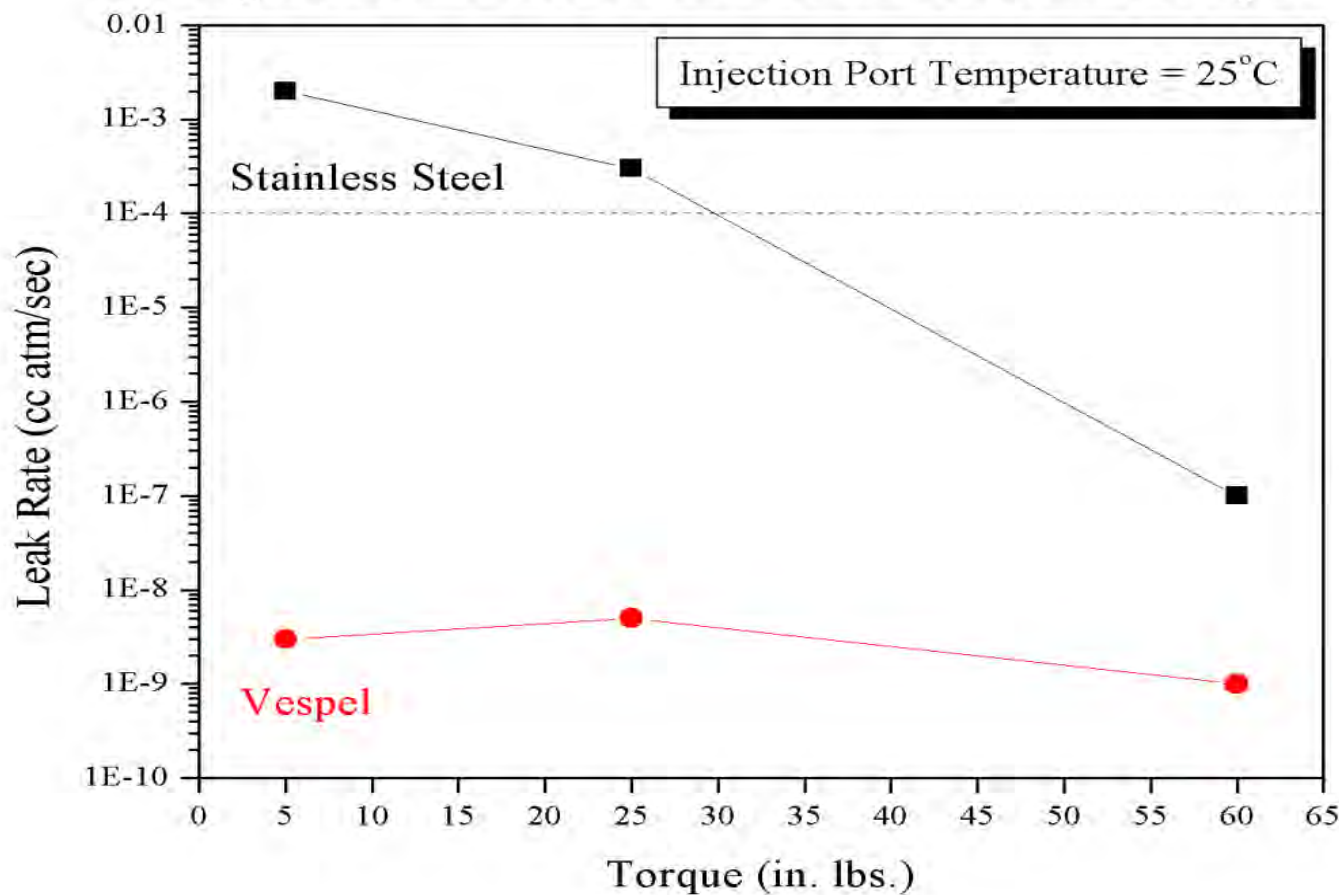
A new type of inlet seal has been developed that will greatly improve injection port performance by maintaining a reliable seal after repeated temperature cycles, without retightening the reducing nut. This new inlet seal features two soft rings, one embedded in its top surface and the other embedded in its bottom surface. These rings eliminate the need for a washer, ensure very little torque is needed to make a leak-tight seal, and will not harm the critical seal at the bottom of the injector. The Vespel<sup>®</sup> rings are outside the sample flow path for worry free chromatography.

# Experiment #1

The standard metal inlet seals are troublesome to get a leak-free seal even under ideal conditions. Several different inlet seals were tested using a high sensitivity leak detector with a Helium leak rate range of  $1 \times 10^{-1}$  to  $2 \times 10^{-10}$  (atm cc/sec.). The inlet seals were tested at various torques to determine the affect of tightening on the new inlet seal and a conventional standard metal inlet seal. Several seals of each type were tightened at 5, 25, and 60 pounds and the leak rates were measured at each setting. The following data shows the differences between the two types of inlet seals.

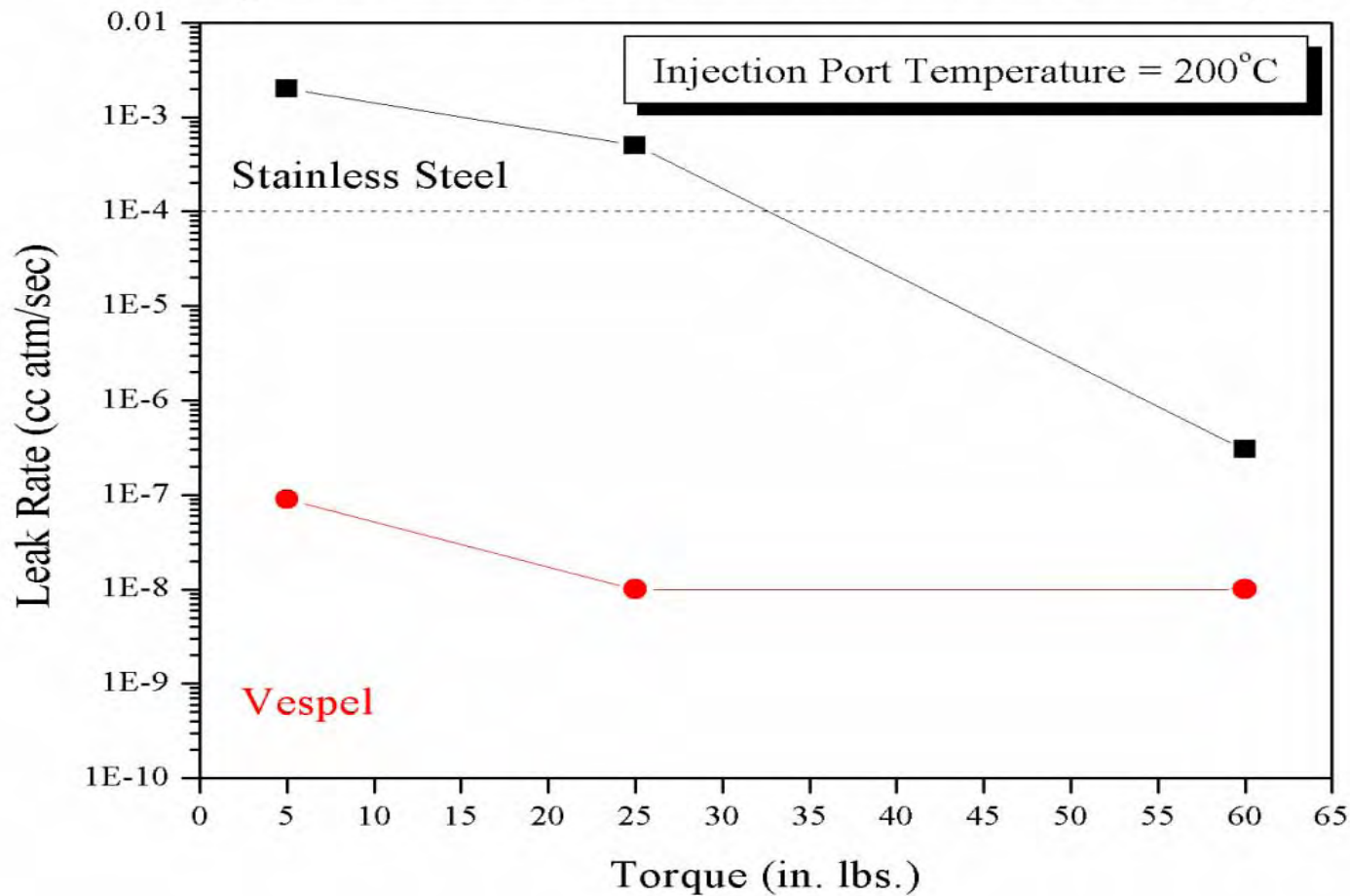
# Dual Vespel® Ring Inlet Seal at Various Torques at 25° C.

Injection Port Leak Rate *versus* Torque



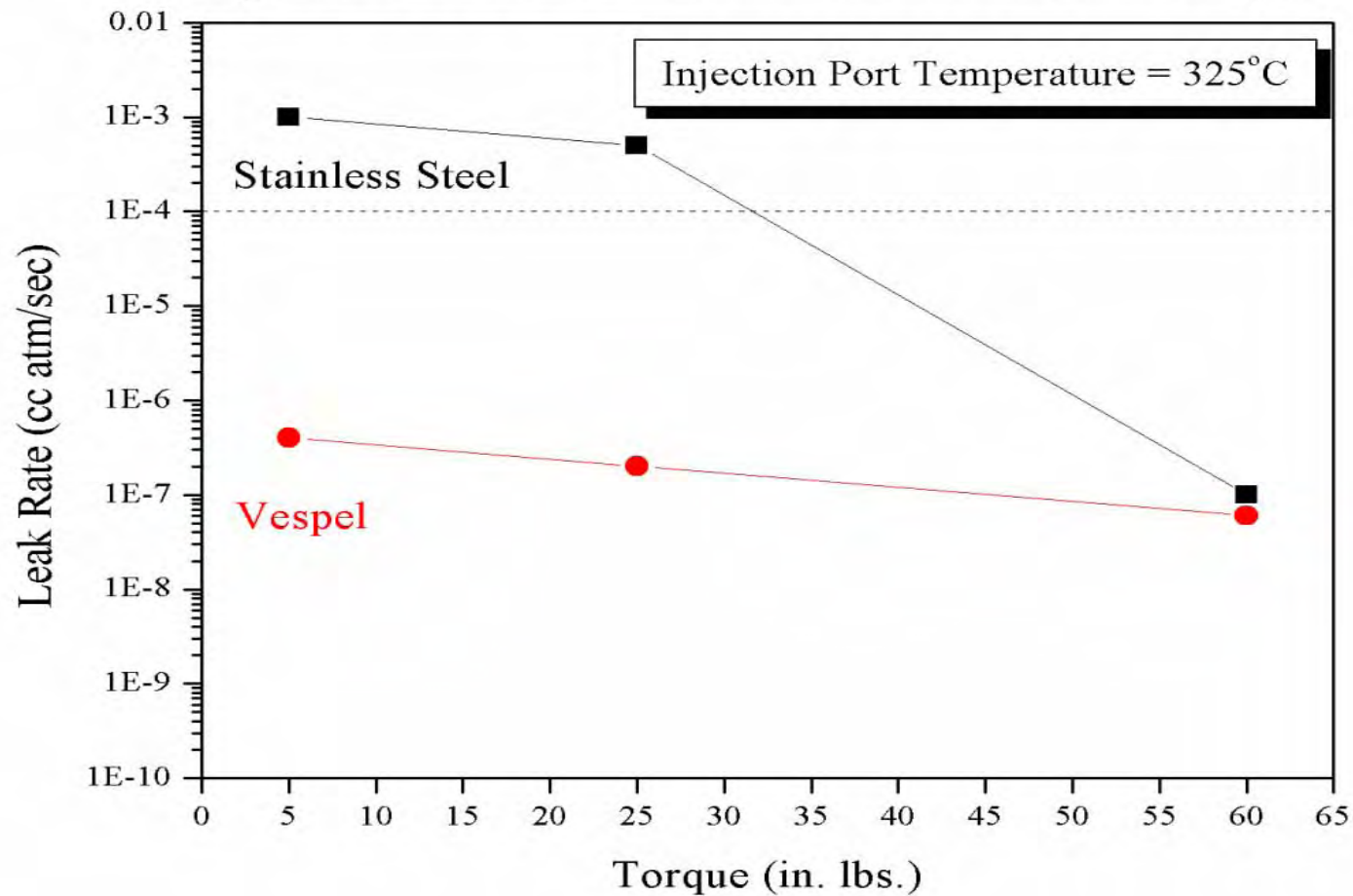
# Dual Vespel® Ring Inlet Seal at Various Torques at 200° C.

Injection Port Leak Rate *versus* Torque



# Dual Vespel® Ring Inlet Seal at Various Torques at 325° C.

Injection Port Leak Rate *versus* Torque





# Summary of Experiment #1

The Dual Vespel® Ring Inlet Seal has a much lower overall leak rate than standard all-metal inlet seals at torques of 5 to 60 pounds with varying injection port temperatures.

This lower leak rate results in extended column lifetime by reducing Oxygen permeation into the carrier gas and reduces detector noise, especially with sensitive detectors such as ECDs and MSDs. The soft seal will not harm the critical seal at the bottom of the injector, increasing the lifetime of the injection port.

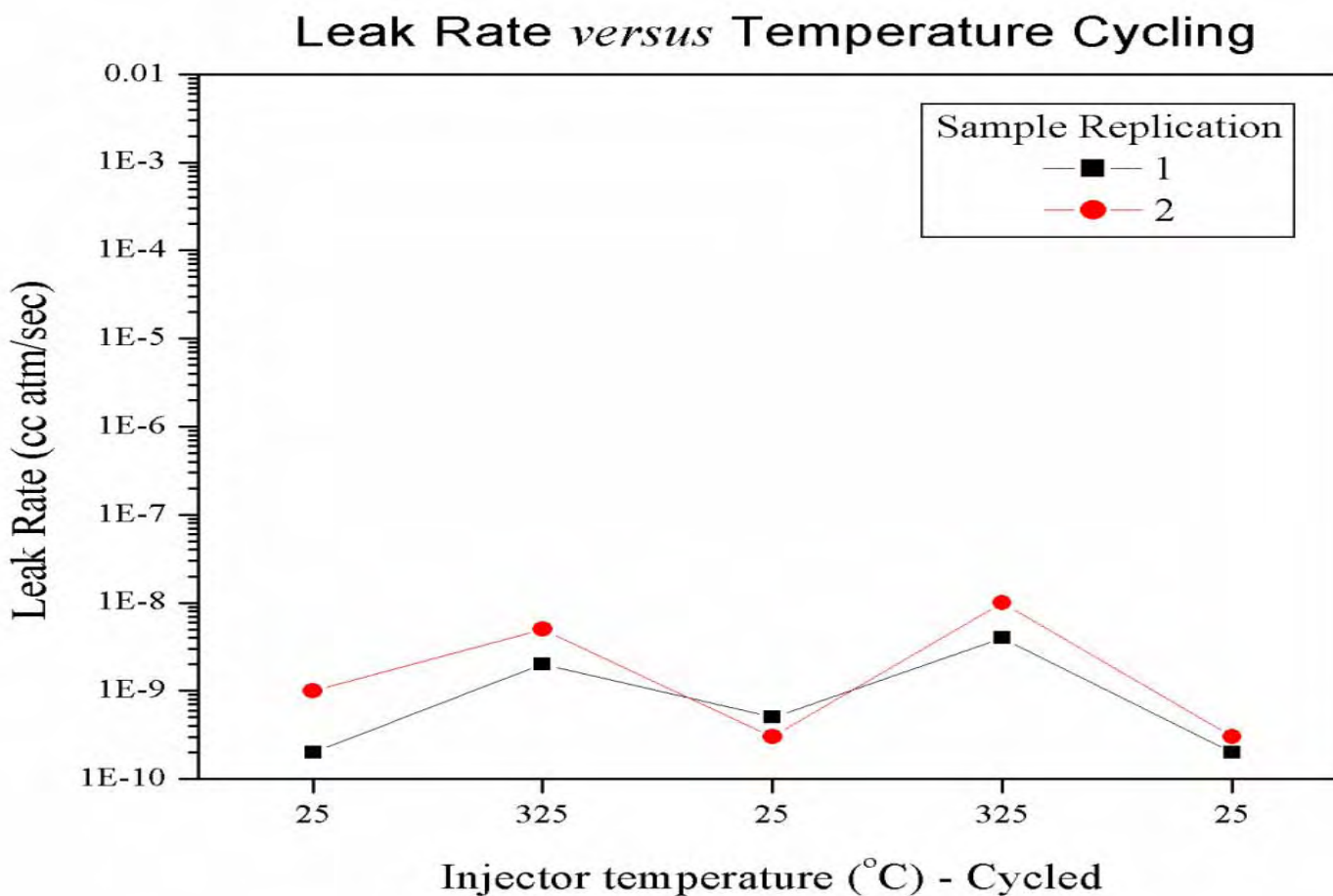
## Experiment #2

In order to ensure that the Vespel<sup>®</sup> material embedded in the surface of the inlet seal would not deform and cause leaks at various oven temperature cycles, the following tests were performed:

The reducing nut with the new inlet seal was tightened to a torque of 25 pounds. The injection port temperature was heated to 325° C., then cooled to 25° C. several times. The leak rate was then measured at temperatures of 25° C. and 325° C. The test was performed twice to verify the results. The following data was collected.



# Dual Vespel® Ring Inlet Seal Leak Rate After Various Oven Temperature Cycles (Torque set at 25 pounds)

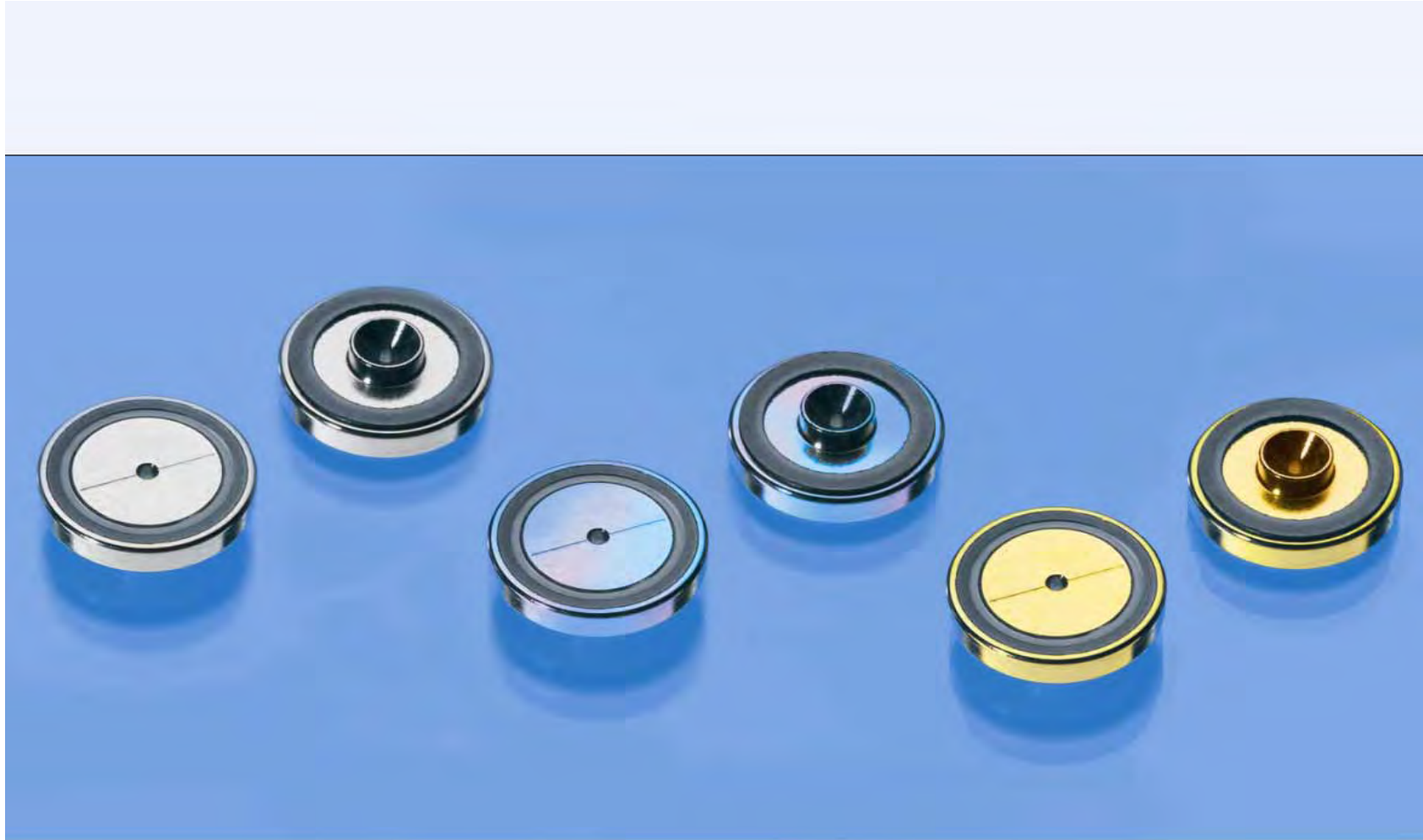


# Summary of Experiment #2

The test was performed with two different inlet seals on different injection ports.

The test results show that the Duel Vespel<sup>®</sup> Ring Inlet Seal greatly improves injection port performance by retaining its sealing capability, even after repeated temperature cycles, at a very low torque (25 pounds), without re-tightening the reducing nut.

# Dual Vespel® Ring Inlet Seal



# Summary

The Duel Vespel® Ring Inlet Seal out performed the standard metal inlet seal in all of the testing.

The Duel Vespel® Ring Inlet Seal will not harm the critical seal at the bottom of the injection port, which will increase the lifetime of the injection port.

The Duel Vespel® Ring Inlet Seals will reduce operator variability by sealing at a wide range of torques, and will not be affected by temperature changes in the oven or the injection port. The Vespel® rings are outside the sample flow path for worry free chromatography.

# A New Split/Splitless Injection Port Eliminates Sealing Problems and Offers Improved Inertness

Brad Rightnour, Mike Goss, and Jonathan  
Kaufmann

Restek Corporation, 110 Benner Circle,  
Bellefonte, PA 16823



# Abstract

Common problems associated with split/splitless injection ports include analyte breakdown or adsorption to the hot metal surfaces of the inlet body and difficulty in obtaining a reliable seal at the liner and base of the injection port. Further, split/splitless injection ports have been costly to maintain; traditionally, users have had to use special and often expensive parts to maintain these ports.



# Introduction

A new split/splitless injection port eliminates the trouble areas associated with this type of injector, improving inertness and ensuring reliable sealing. An inert coating on the metal surfaces reduces sample breakdown when the surfaces are heated, ensuring more accurate data and allowing greater productivity. The new injection port eliminates critical sealing problems associated with metal-to-metal seals, and requires only inexpensive standard components for maintenance. In combination, these features make the new injection port easier, more reliable, and more economical to operate and maintain.

# New Split/Splitless Injection Port

Design 1

Design 2



Hex design aligns every time for easy installation and removal  
Uses specially designed 1/4" V/G ferrules



Injection port remains leak-tight at 400°C

Redesigned injector base improves seal and simplifies column installation

Base screw supports liner

Base seals with standard 1/4" ferrule

Uses standard OEM inlet seal

Base fitting uses standard 1/16" ferrule to seal column



# Experimental

Several criteria were selected to determine the inertness and reproducibility of the new injection port design and ensure that proper vaporization and flow characteristics were maintained. The first experiment was to investigate if injection port discrimination existed in the new injection port.

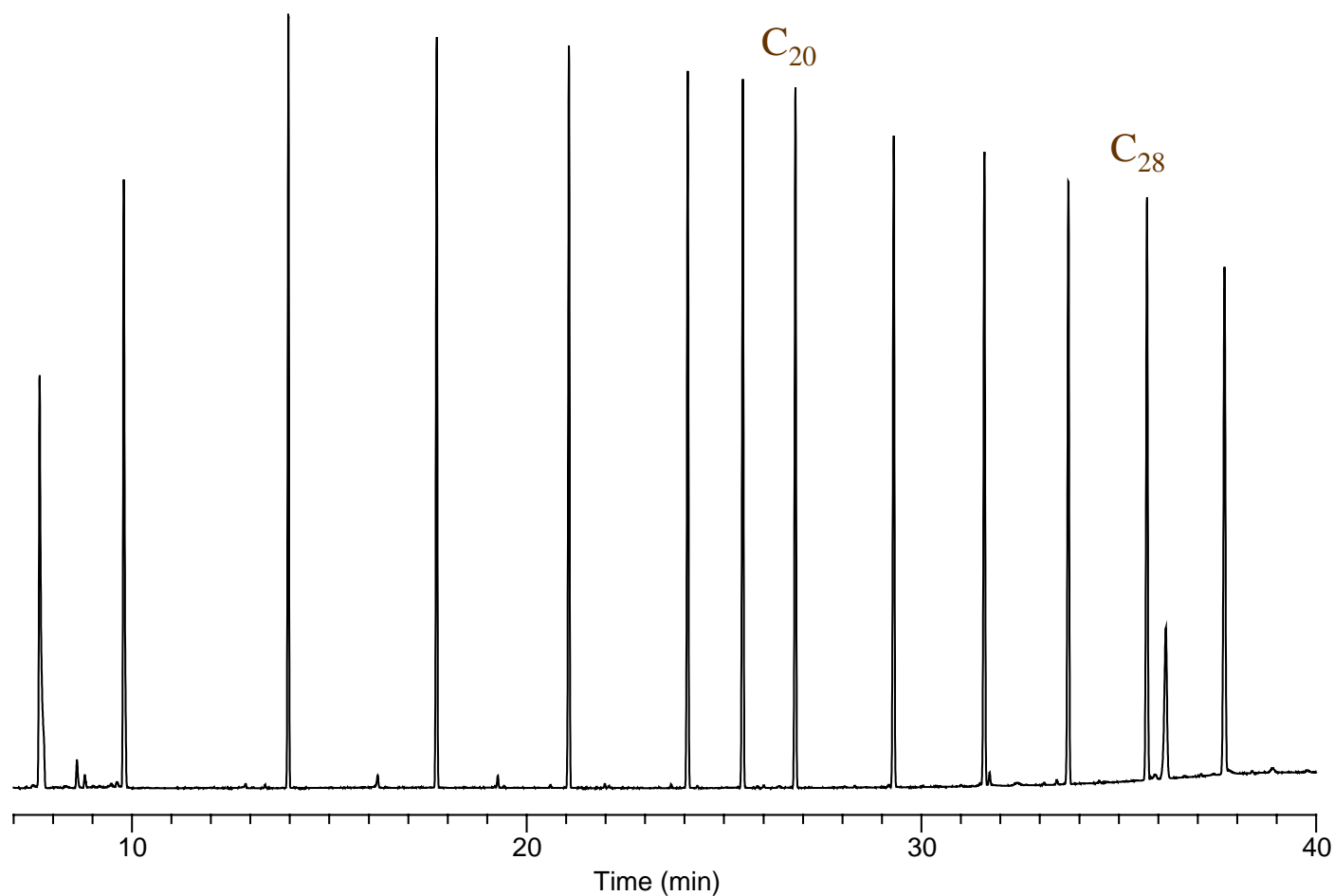
To demonstrate the absence of aliphatic mass discrimination the MA EPH method<sup>1</sup> reference mix was used to determine if the  $C_{28}$  to  $C_{20}$  response ratio meet the required  $>0.85$ .

The test was conducted on an Agilent 5890 Series II GC with an FID. The calculated results (Figure 1) show that the response ratio for  $C_{28}$  to  $C_{20}$  is 1.0. The response ratio meets the required standard of  $>0.85$ .

1. Method for the Determination of Extractable Petroleum Hydrocarbons: Commonwealth of Massachusetts, May 2004, Revision 1.1

# Figure 1

$C_{28}:C_{20}$  response ratio indicates no mass discrimination in the new port.



XTI®-5 30m, 0.25mm ID, 0.25 $\mu$ m (cat# 12223)

Injection: splitless  
Agilent 5890 Series II  
Oven temp.: 320°C  
Carrier gas: helium, constant pressure  
Flow rate: 20 cm/sec.  
Initial temp.: 40°C (hold 1.5 min) to 320°C @ 15°C/min (hold 5 min).  
FID @ 340°C  
Sample: MA EPH reference mix (31459)

The second experiment was to determine the reproducibility of peak area ratios between injection ports and whether active sites or dead volume existed inside the new injection port. A mixture of hydrocarbons and phenols was injected; the peak area ratio was calculated using 2,4-dinitrophenol and C14 (Table 1).

The XTI® injection mix with an on-column concentration of 7-17ng also was used. Responses were excellent for all probes, including the active compounds 2,4-dinitrophenol, 1,2-hexanediol, and benzoic acid (Figure 2).

# Table 1

ivalent peak area values show there is no adsorption and no dead volume in the new injection port.

Conventional Injector	New Sure Fit™ Injector
2,4-dinitrophenol/C14	2,4-dinitrophenol/C14
Peak Area ratio %	Peak Area ratio %
0.69	0.74
0.66	0.70
0.70	0.66
0.71	0.88
0.65	0.70
<b>Mean = 0.68</b>	<b>Mean = 0.74</b>

# Figure 2

Excellent responses for active probes.

Australian Distributors  
Importers & Manufacturers  
www.chromtech.net.au  
Tel: 03 9762 2034 . . . in AUSTRALIA

CHROMALYTIC  
ECHNOLOGY Pty Ltd  
Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au  
Tel: +61(0)3 9762 2034

Injection: split

GC: Agilent 5890 Series II

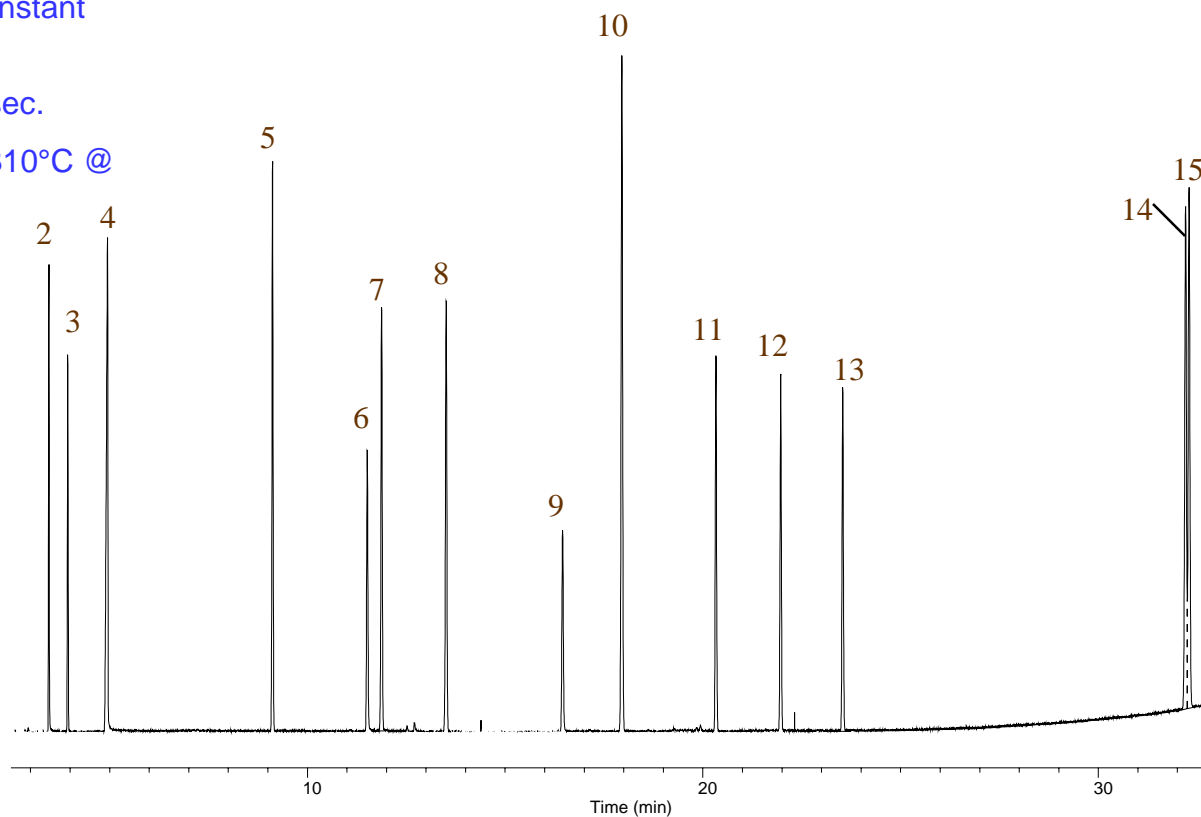
Inj. temp.: 325°C

Carrier gas: helium, constant  
pressure

Linear velocity: 20 cm/sec.

Oven temp.: 100°C to 310°C @  
5°C/min.

Detector: FID @325°C



- 2. 1,2-hexanediol
- 3. Nitro-di-n-Propylamine
- 4. Benzoic Acid
- 5. C-14
- 6. 2,4-Dinitrophenol
- 7. Nitrophenol
- 8. Nitroaniline
- 9. Pentachlorophenol
- 10. Carbazole
- 11. C-20
- 12. C-21
- 13. C-22
- 14. Benzo b Fluoranthene
- 15. Benzo k Fluoranthene

XTI®-5 30m, 0.25mm ID, .25µm (cat# 12223)

# Conclusion

The new Sure Fit™ injection port incorporates an innovative hex design which makes aligning the split/splitless weldment and shell weldment easy and makes installation and removal of liners trouble free. One Sure Fit™ shell weldment design allows the use of an inexpensive replacement to the standard OEM inlet seals, and can be easily cleaned and replaced when severely contaminated. An alternative Sure Fit™ shell weldment with a specially designed fitting uses a standard 1/4" ferrule to seal the base of the weldment.

The new Sure Fit™ injection port uses a specially designed Vespel®/graphite tapered ferrule to seal the liner inside the weldment. The new ferrule design eliminates the need for multiple graphite or fluorocarbon o-rings for different liners and conditions to minimize chance of leaks.

The Sure Fit™ injector is Siltek® treated to provide optimal inertness and resistance to temperature and pH extremes inside the GC system.

# Gas Chromatographic Analysis of Volatile Organic Compounds Using a Unique Stationary Phase

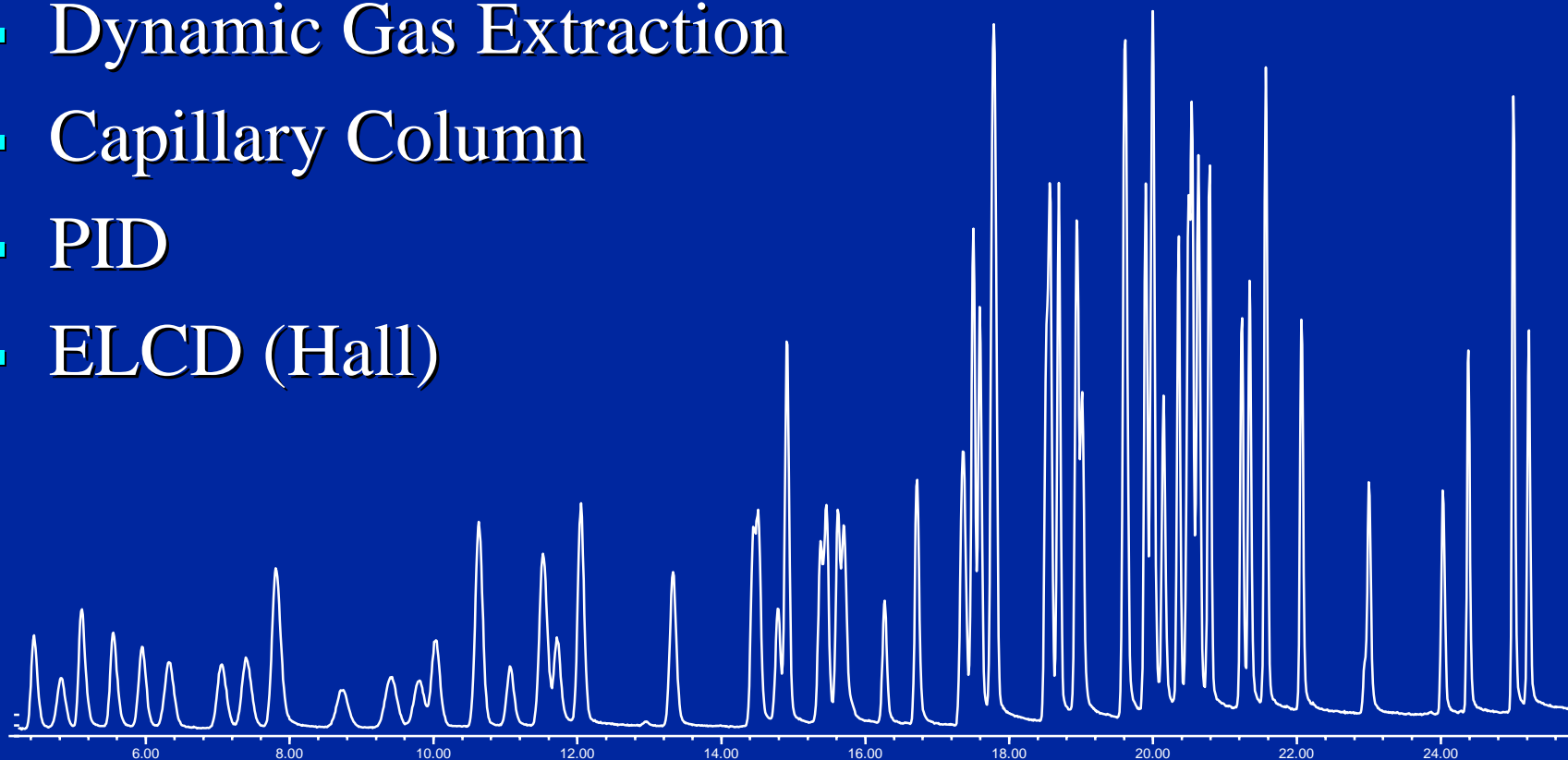
CHRIS M. ENGLISH, FRANK L. DORMAN,  
MARK LAWRENCE & DINESH PATWARDHAN.

Restek Corporation  
110 Benner Circle  
Bellefonte, PA, 16823  
(800) 356-1688  
<http://www.restekcorp.com>

CHROMATOGRAPHY  
**RESTEK** resolutions

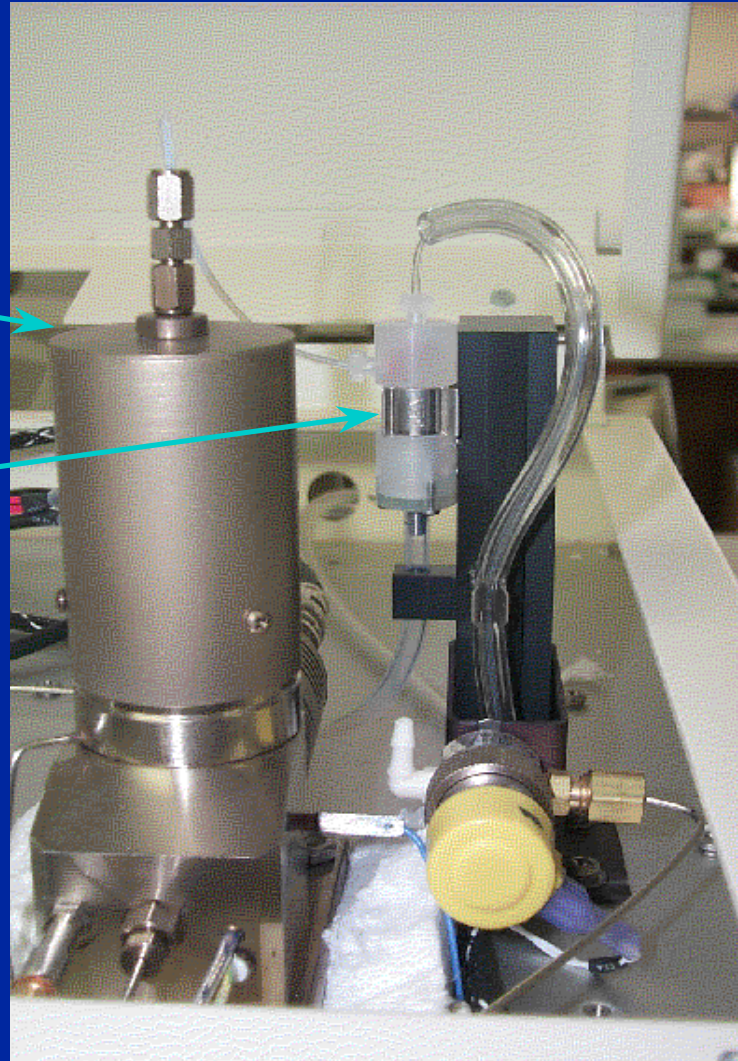
# GC Volatiles Analysis EPA Methodology

- Dynamic Gas Extraction
- Capillary Column
- PID
- ELCD (Hall)





# ELCD Detector



Reactor

Conductivity  
Cell

# Target List 8021A

Benzene  
Bromobenzene  
Bromochloromethane  
Bromodichloromethane  
Bromoform  
Bromomethane  
n-butylbenzene  
sec-butylbenzene  
tert-butylbenzene  
Carbontetrachloride  
Chlorobenzene  
Chloroethane  
Chloroform  
Chloromethane  
2-Chlorotoluene  
4-Chlorotoluene  
Dibromochloromethane  
1,2-Dibromo-3-chloropropane  
1,2-Dibromoethane  
Dibromoethane  
1,2-Dichlorobenzene

1,3-Dichlorobenzene  
1,4-Dichlorobenzene  
Dichlorodifluoromethane  
1,1-Dichloroethane  
1,2-Dichloroethane  
1,1,-Dichloroethene  
cis-1,2-dichloroethene  
trans-1,2-dichloroethene  
1,2-Dichloropropane  
1,3-Dichloropropane  
2,2-Dichloropropane  
1,1-Dichloropropene  
cis-1,3-dichloropropene  
trans-1,3-dichloropropene  
Ethylbenzene  
Hexachlorobutadiene  
Isopropylbenzene  
4-Isopropyltoluene  
Methylene chloride  
Naphthalene  
Propylbenzene  
Styrene  
1,1,1,2-Tetrachloroethane  
1,1,2,2-Tetrachloroethane  
Tetrachloroethene

Toluene  
1,2,3-Trichlorobenzene  
1,2,4-Trichlorobenzene  
1,1,1-Trichloroethane  
1,1,2-Trichloroethane  
Trichloroethene  
Trichlorofluoromethane  
1,2,3-Trichloropropane  
1,2,4-Trimethylbenzene  
1,3,5-Trimethylbenzene  
Vinyl Chloride  
o-Xylene  
m-Xylene  
p-Xylene  
  
Fluorobenzene  
2-Bromo-1-chloropropane  
4-Bromo-1-Chlorobenzene  
1-Chloro-2-fluorobenzene  
1,4-Dichlorobutane  
  
Freon-113  
Methyl-tert-butyl-ether  
Tert-Butanol  
Choroethylvinylether

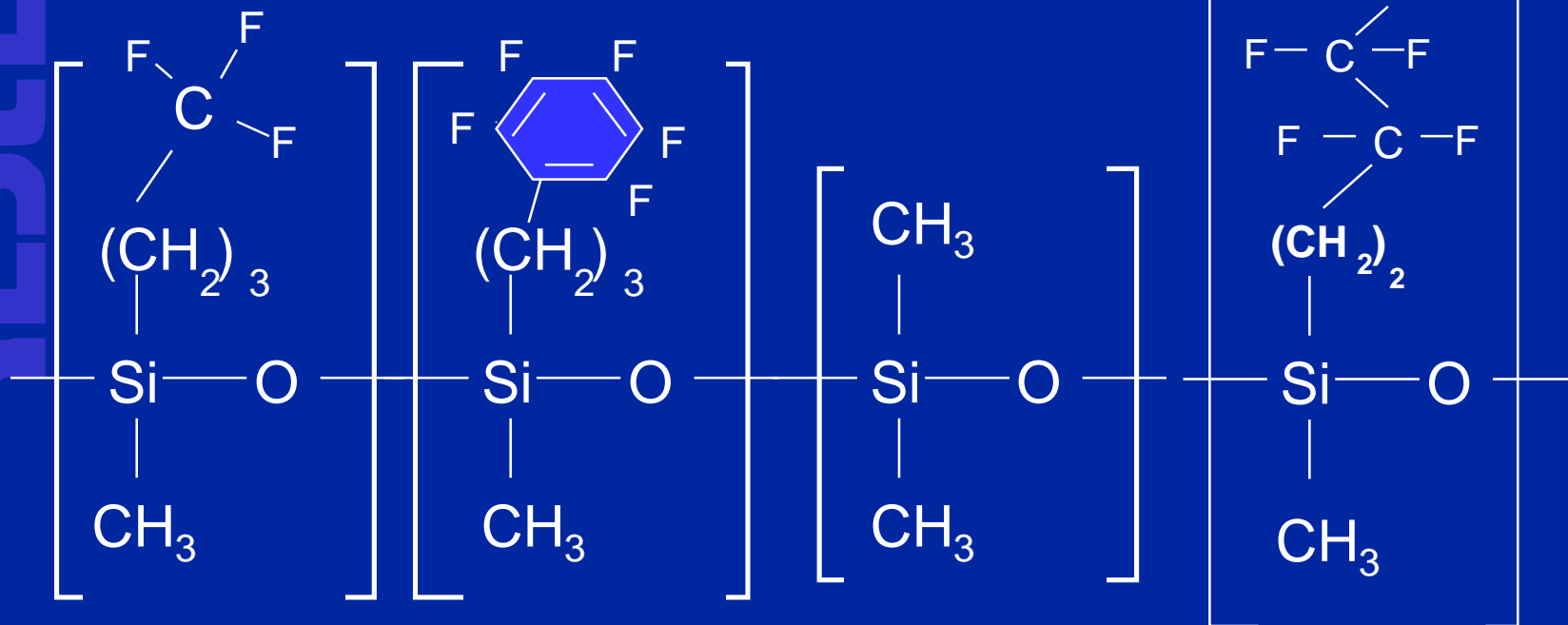
# Design Criteria

- Column length
- Analysis Time
- Low Bleed
- Critical Resolution
- No Cryofocusing
- PID ELCD

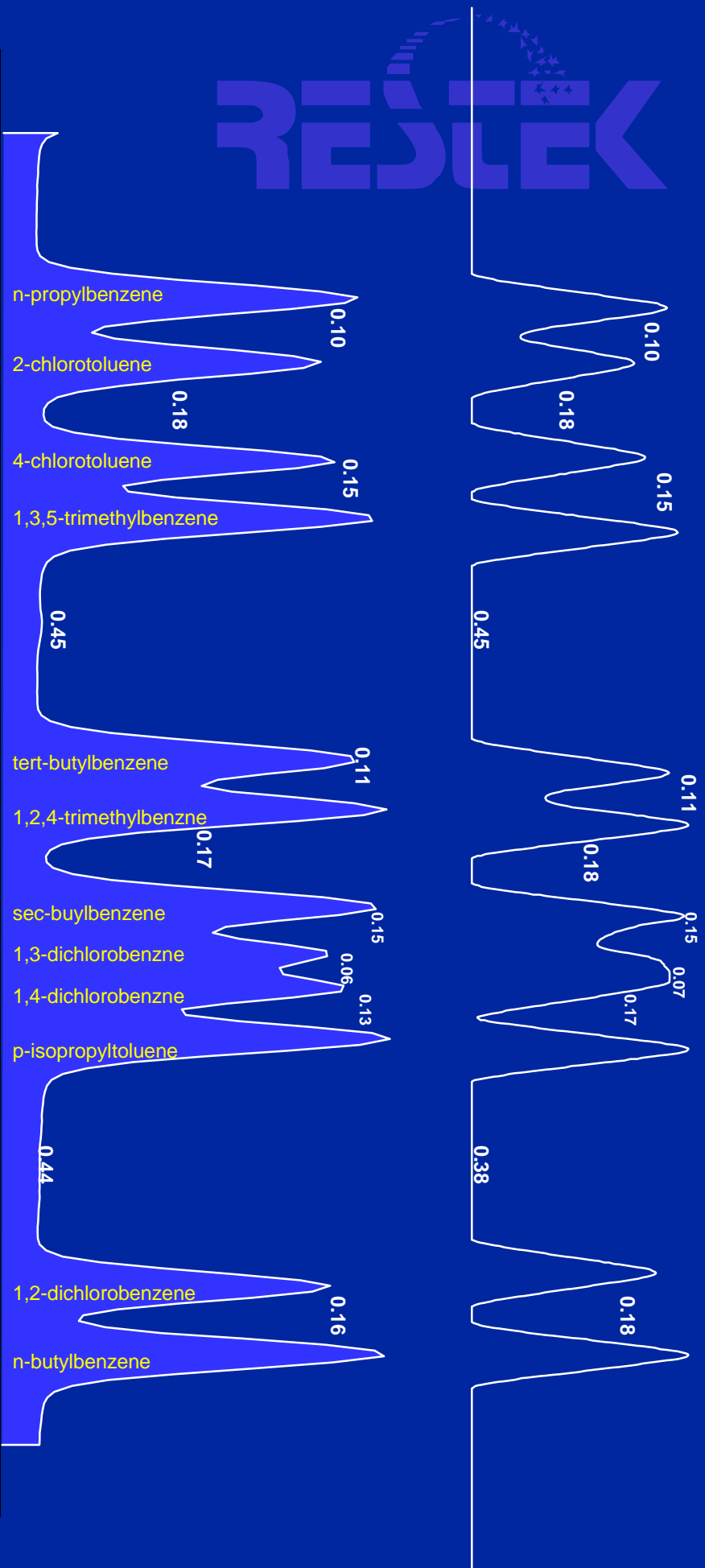


# Experimental Fluorinated Phase

## Bonded Polymer Examined for GC Applications.



# Predicted vs. Actual 4 Dimensional Phase





## Application #1 US EPA METHOD 502.2/8021

Column #1: Rtx-VGC 75m x 0.45mm x 2.55df

Column #2: Rtx-VRX 75m x 0.45mm x 2.55df

GC Program: 35°(4) 3/75 (2) 21/175 (0) 35/205 (5)

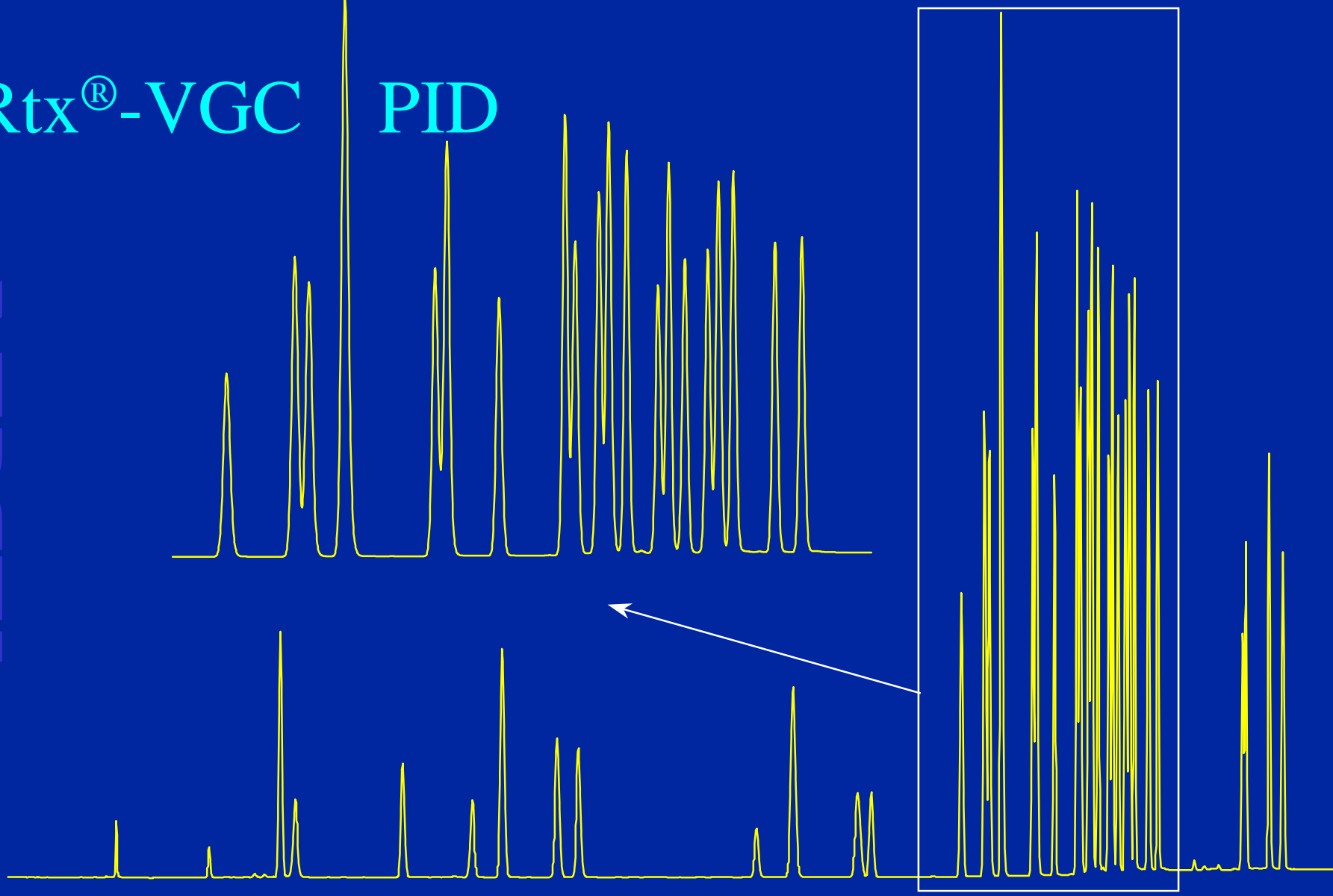
He Flow: ~11 ml/min (Adjust Cl<sub>2</sub>F<sub>2</sub>me to 2.24 min. @ 35°C)

Total Runtime: 29 minutes

Added Cmpds: Freon®113, MTBE

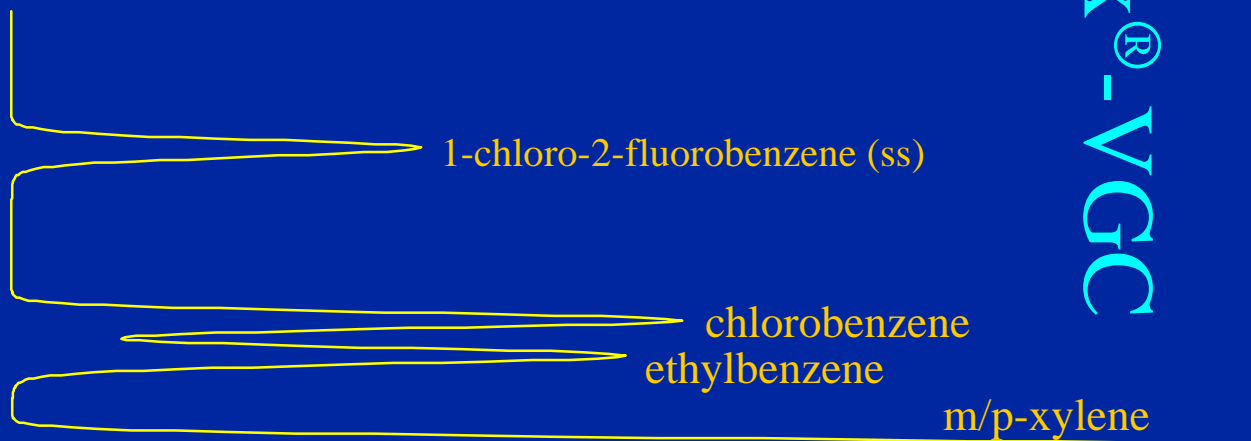
Surrogates: fluorobenzene, 1-bromo-2-chloroethane,  
1-chloro-3-fluorobenzene

# Rtx<sup>®</sup>-VGC PID

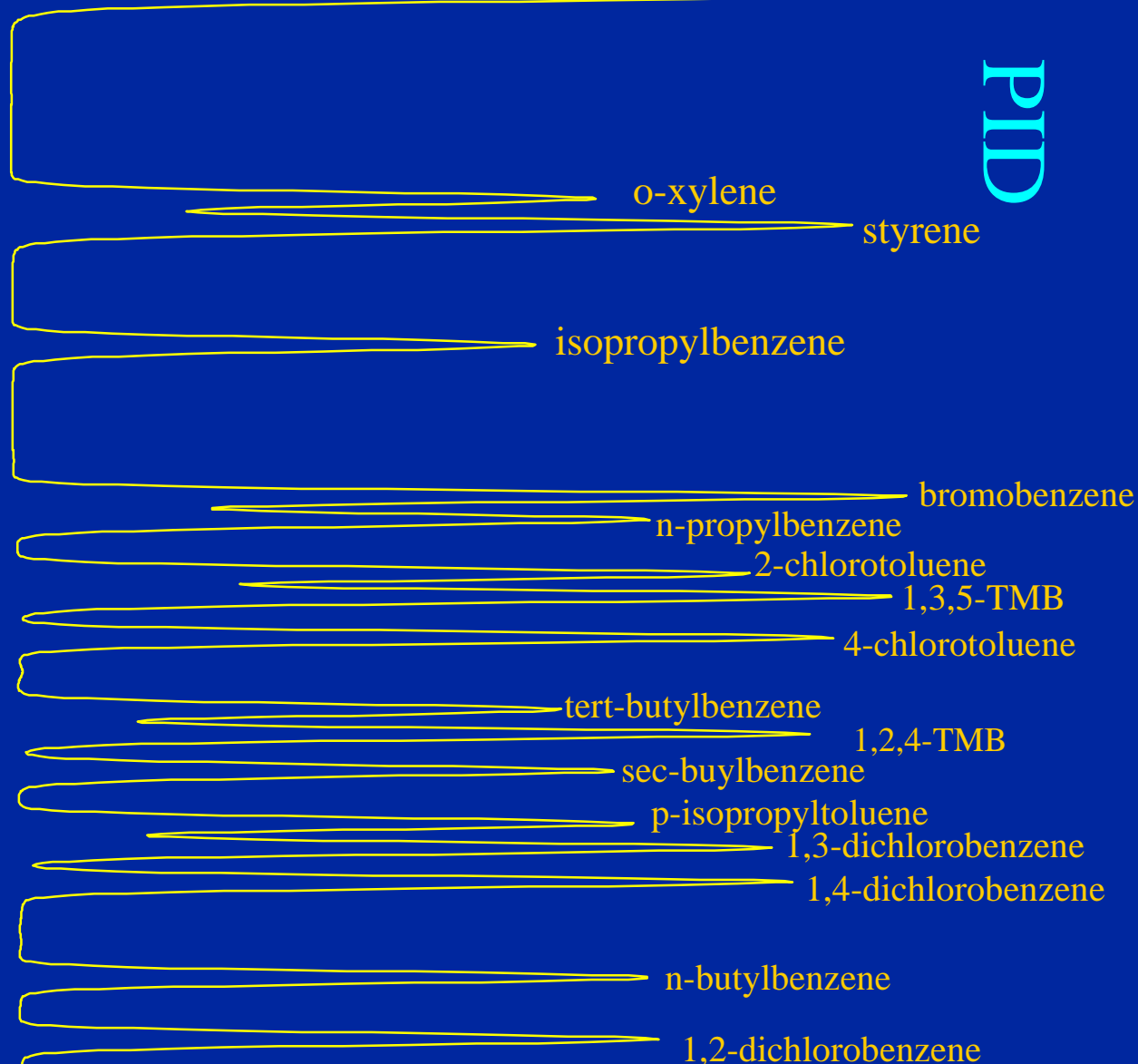




Rtx<sup>®</sup>-VGC



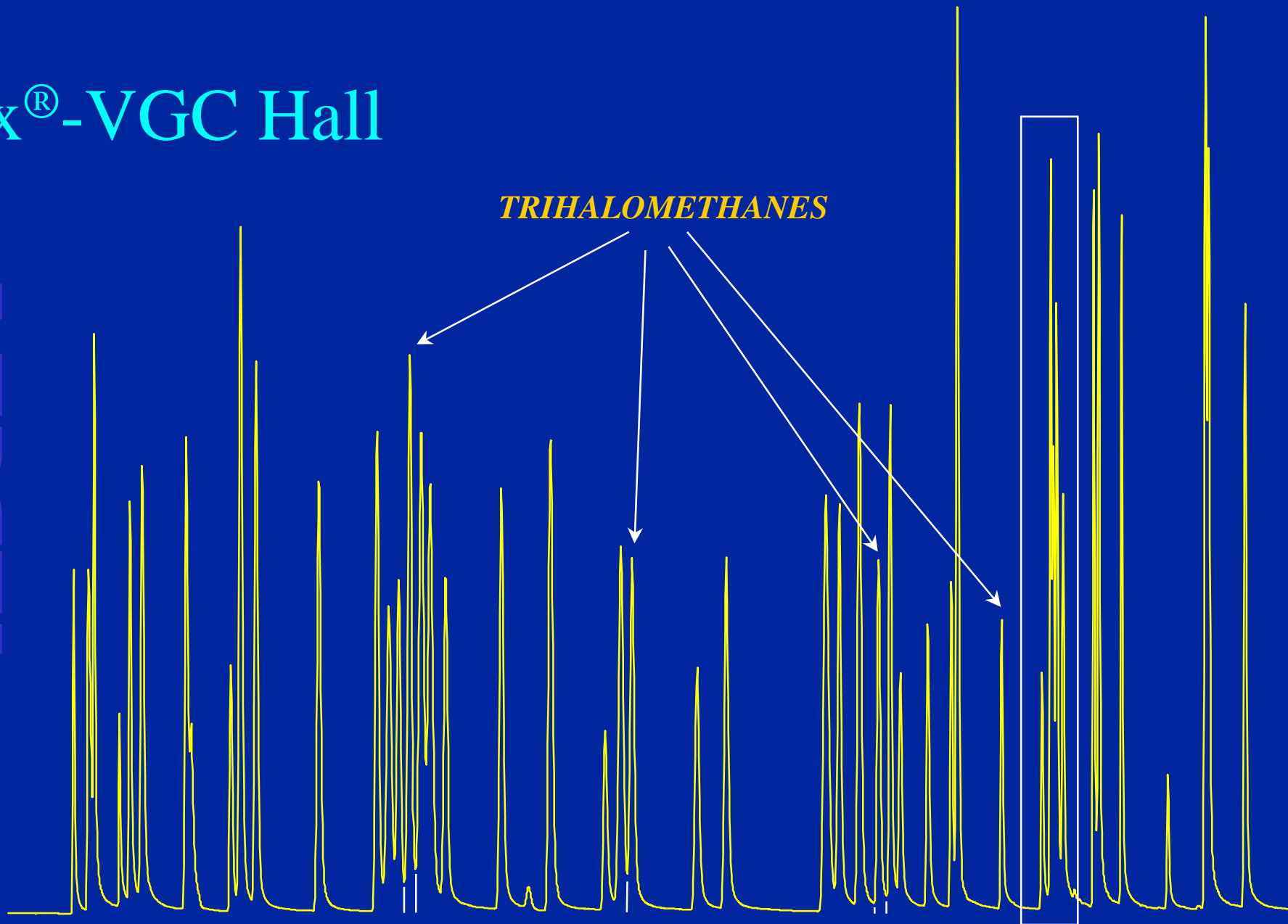
PID



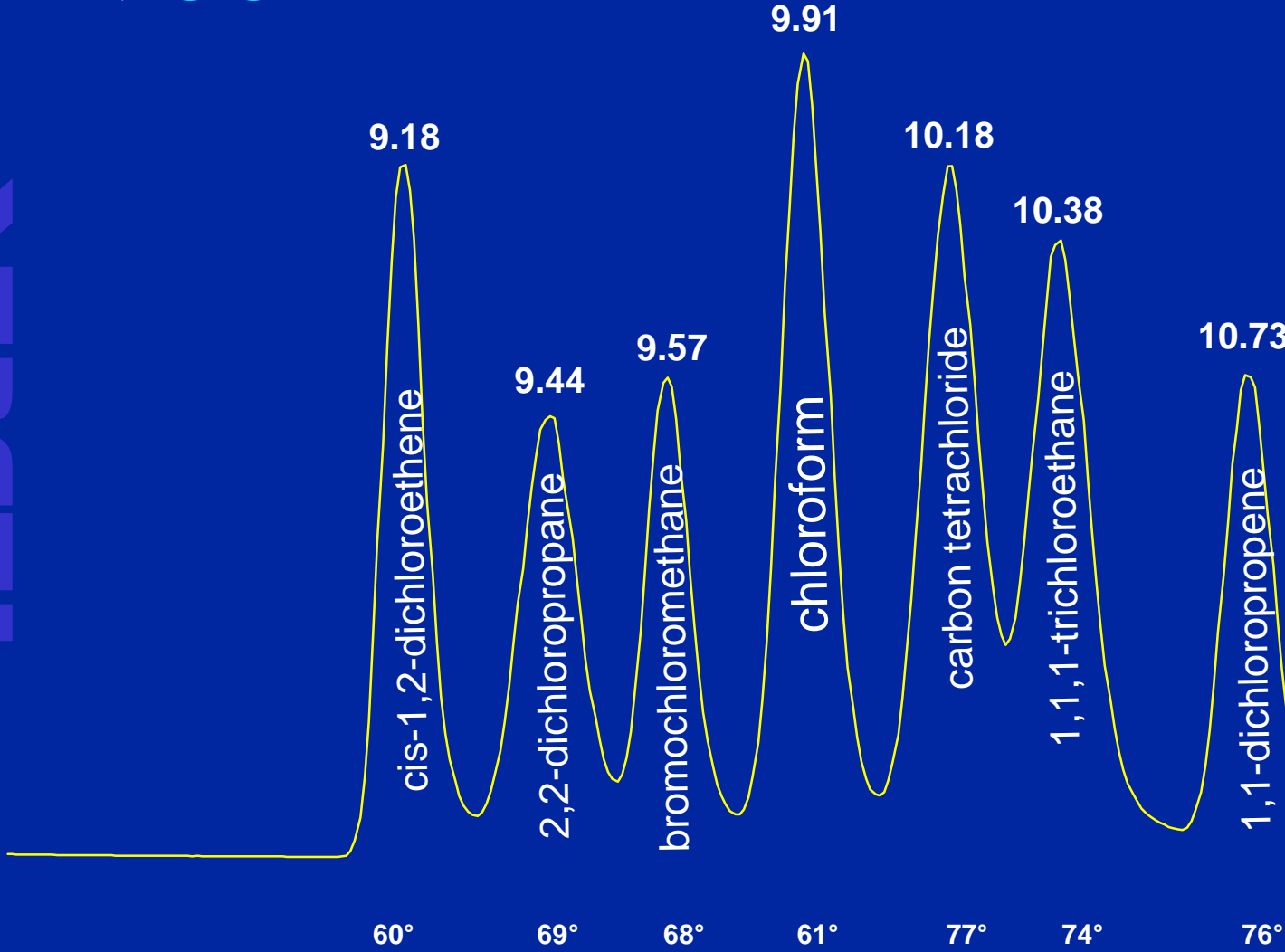


# Rtx<sup>®</sup>-VGC Hall

## TRIHALOMETHANES



# Rtx<sup>®</sup>-VGC





# Rtx<sup>®</sup>-VGC Hall

**bromobenzene**

**1,1,2,2-tetrachloroethane**

**2-chlorotoluene**

**1,2,3-trichloropropane**

**4-chlorotoluene**

Application #2      US EPA METHOD 502.2/8021  
Column #1: Rtx-VGC 75m x 0.45mm x 2.55df  
Column #2: Rtx-502.2 75m x 0.45mm x 2.55df

GC Program: 50°(2) 2/70 (0) 9/130 (0) 40/200 (5)

He Flow: 10ml/min (Adjust Cl<sub>2</sub>F<sub>2</sub>me to 2.28 min. @ 50°C)

Total Runtime: 25 minutes

Added Cmpds: allyl chloride, MTBE

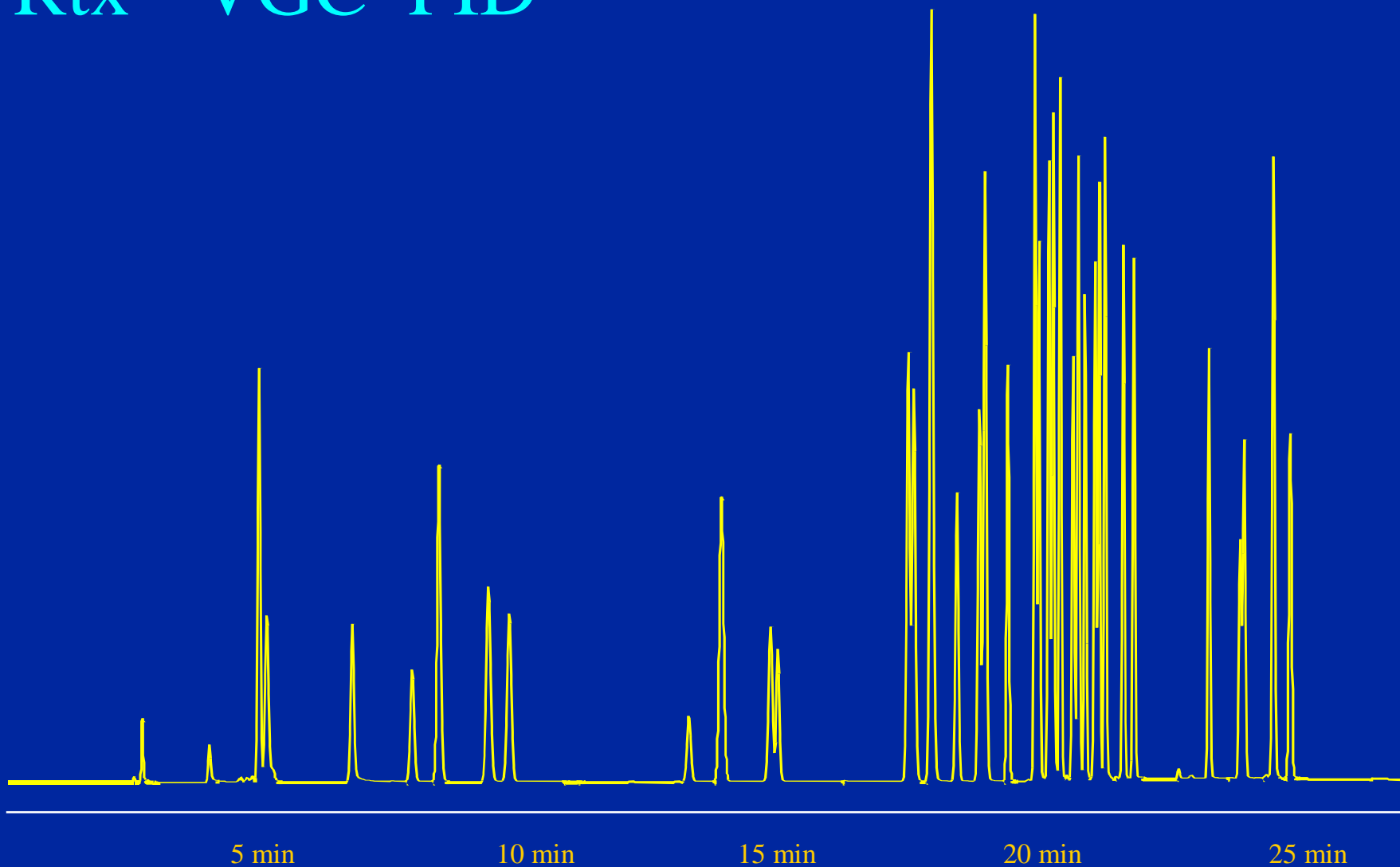
Surrogates: fluorobenzene, 1-bromo-2-chloroethane,  
1-chloro-2-fluorobenzene

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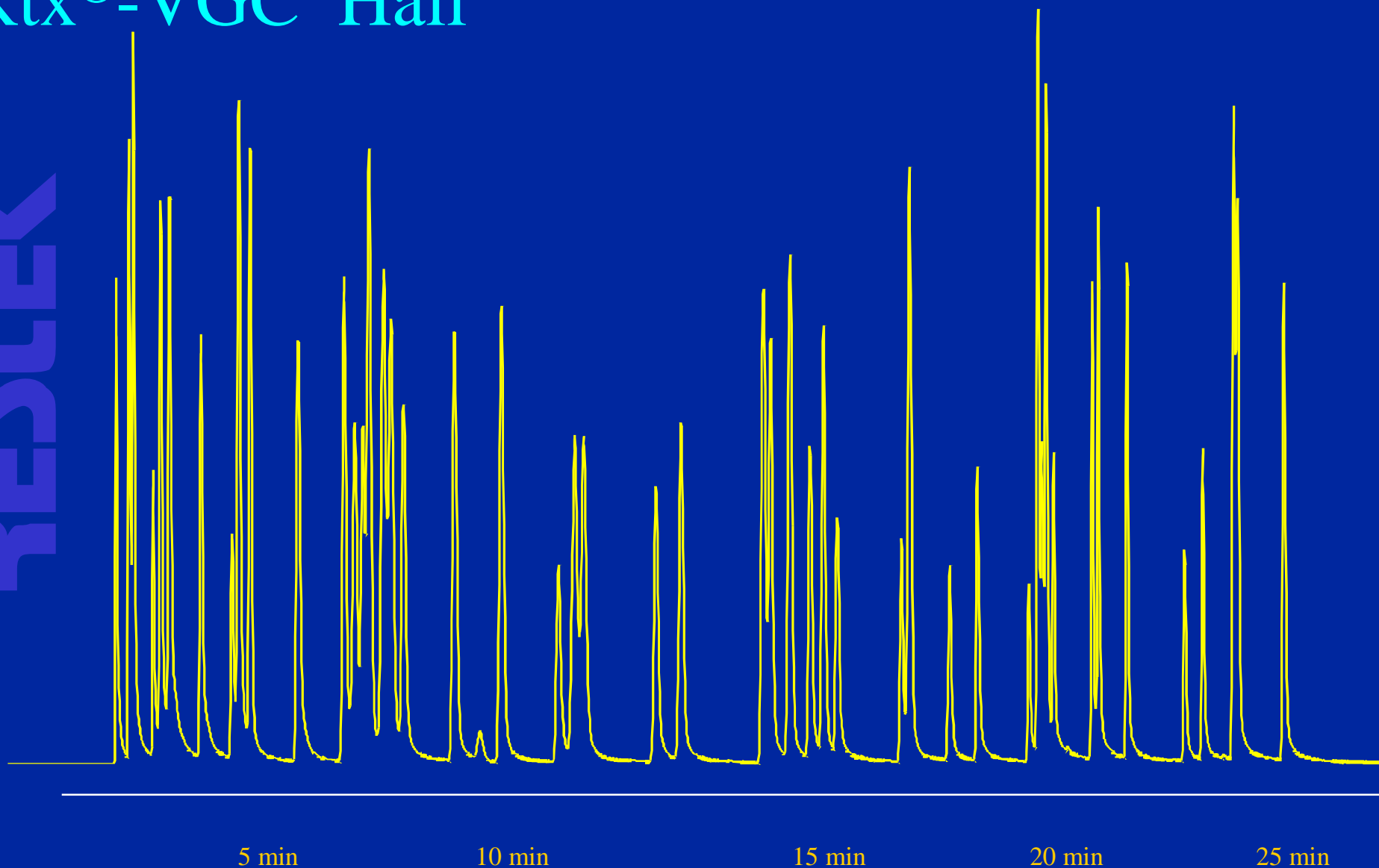
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# Rtx<sup>®</sup>-VGC PID



# Rtx<sup>®</sup>-VGC Hall



### Application #3 US EPA METHOD 601/602

Column #1: Rtx-VGC 75m x 0.45mm x 2.55df

Column #2: Rtx-VRX 75m x 0.45mm x 2.55df

GC Program: 40°(2) 4/58 (0) 10/90 (5) 40/220 (5)

He Flow: ~10 ml/min (Adjust Cl<sub>2</sub>F<sub>2</sub>me to 2.47 min. @ 40°C)

Total Runtime: 20 minutes

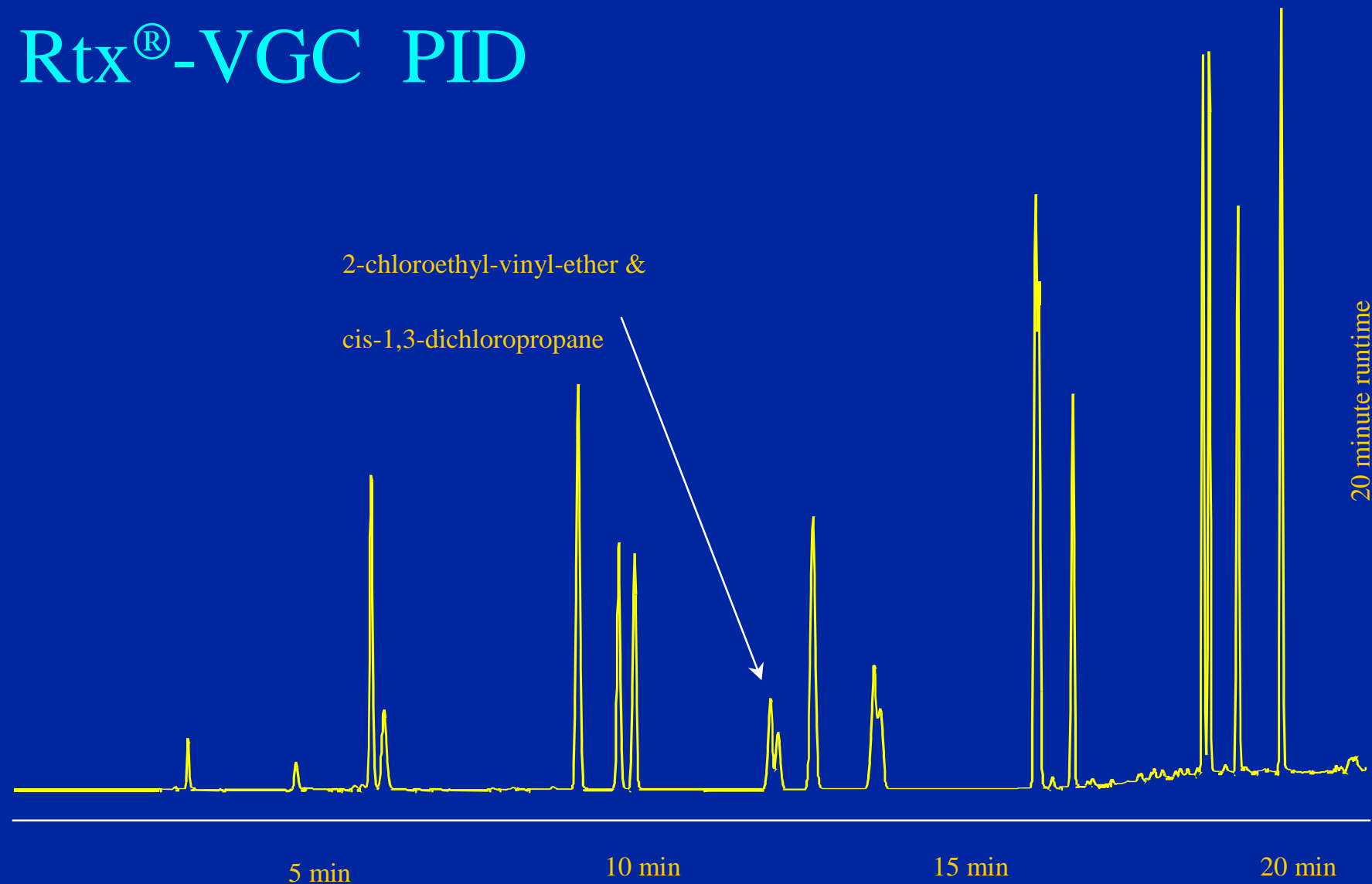
Added Cmpds: MTBE, 2-chloroethyl-vinyl-ether

Surrogates: fluorobenzene, 1-chloro-2-fluorobenzene,  
4-bromo-1-chlorobenzene, bromochloromethane

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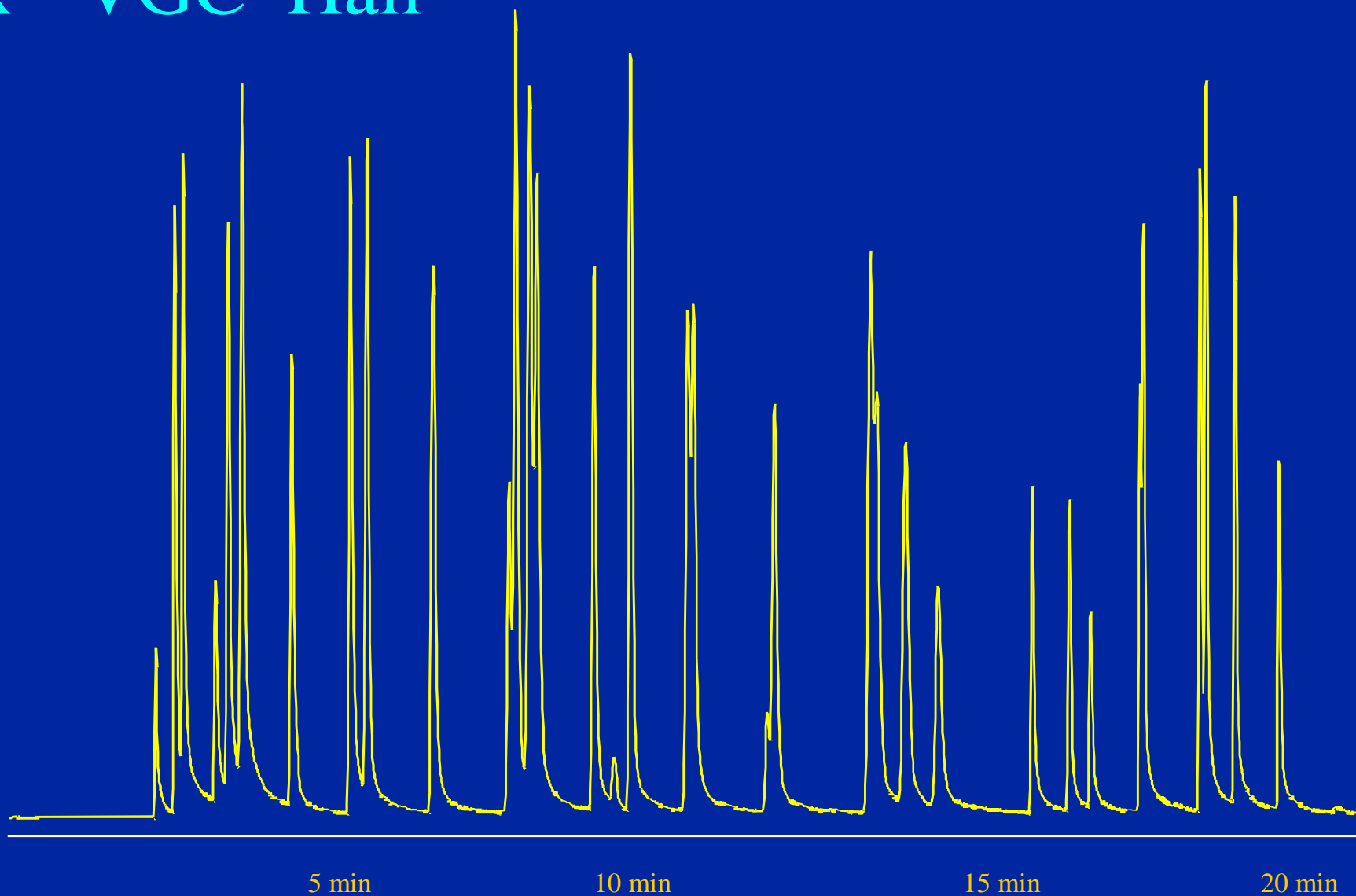
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# Rtx<sup>®</sup>-VGC Hall



## Application #4 US EPA METHOD 8021B

**Column #1: Rtx-VGC 75m x 0.45mm x 2.55df**

**Column #2: Rtx-502.2 75m x 0.45mm x 2.55df**

GC Program: 45°(4) 2/70 (0) 20/210 (10)

He Flow: ~10 ml/min (Adjust Cl<sub>2</sub>F<sub>2</sub>me to 2.40 min. @ 45°C)

Total Runtime: 29 minutes

Added Cmpds: MTBE, 2-chloroethyl-vinyl-ether, Freon®113, iodomethane, tert-butyl alcohol, pentachloroethane, 1&2-methylnaphthalene.

Missing Cmpds: bis(2-chloroisopropyl)ether, bromoacetone, 2-chloroethanol, 1,3-dichloro-2-propanol, epichlorhydrin

Surrogates: fluorobenzene, 1-bromo-2-chloroethane, 1-chloro-2-fluorobenzene, 2-bromo-1-chlorobenzene

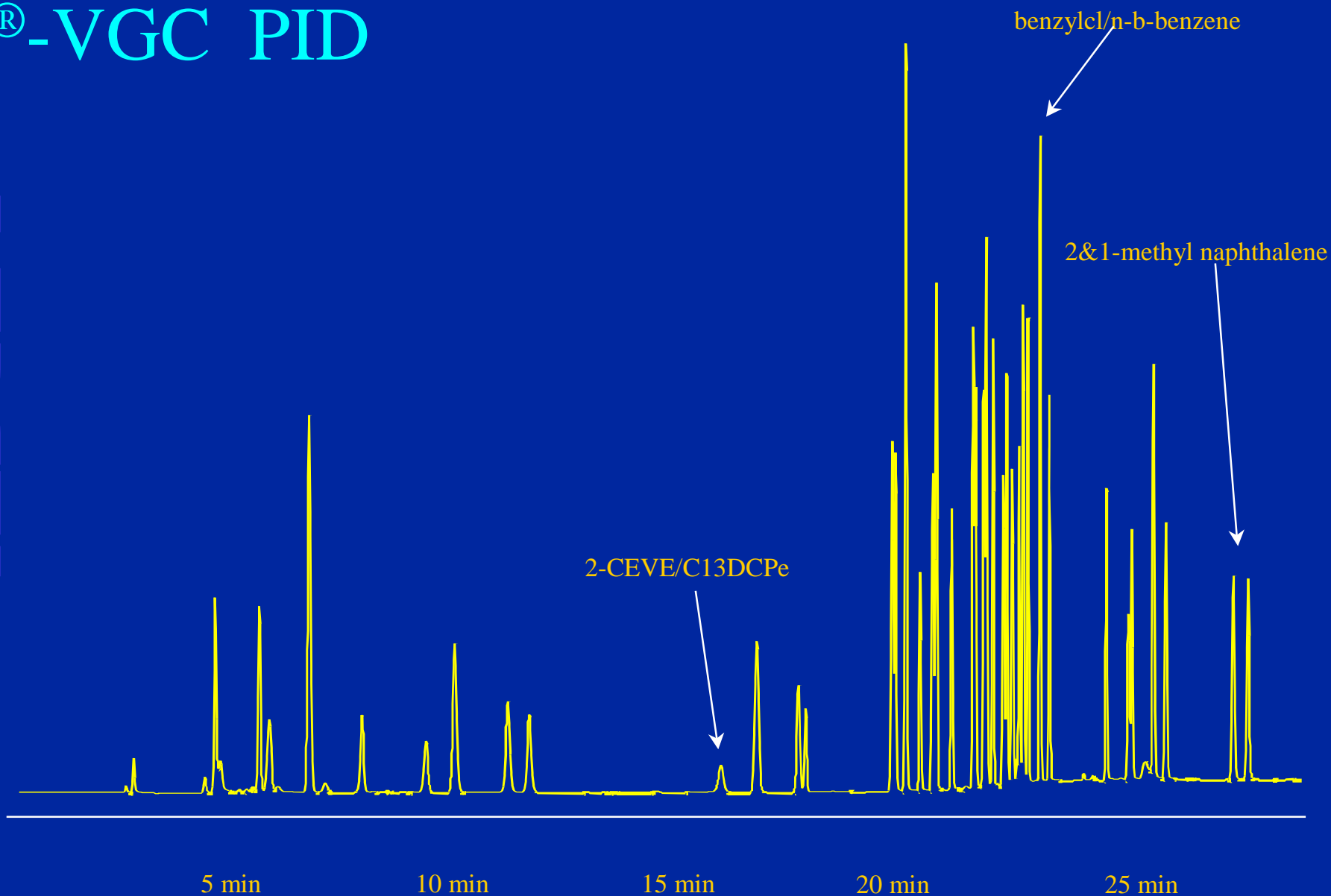
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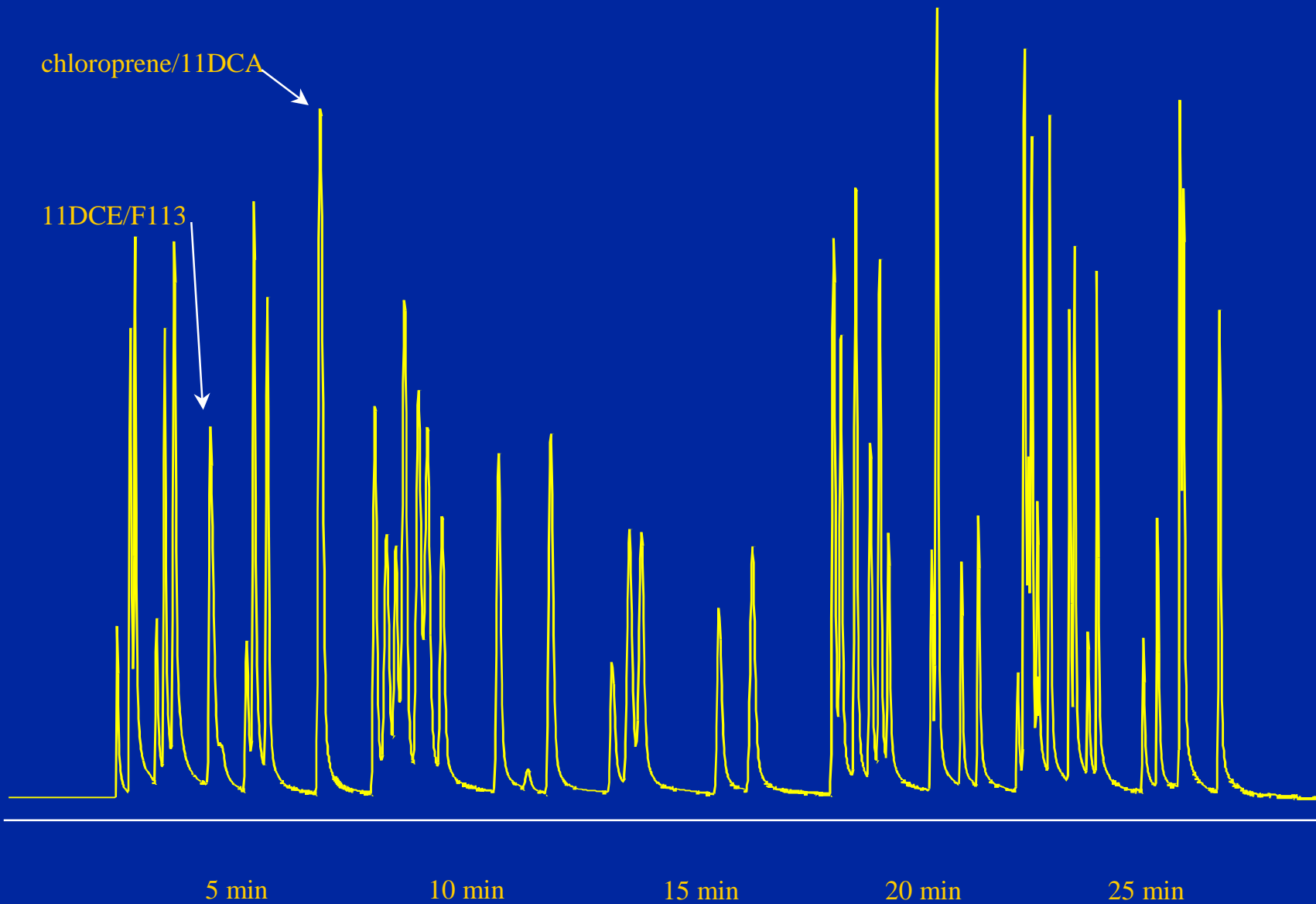
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# Rtx<sup>®</sup>-VGC Hall



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# Rtx<sup>®</sup>-VGC Column

- Excellent gas resolution
- 25 minute run time
- 40°C starting temperature possible
- Separates all compounds in US EPA Methods 502.2 & 8021





# Finnigan 9001 GC

Instrument Courtesy of Thermoquest



# Conclusions

- Application-specific column
- Computer modeling
- Resolution of critical compounds

# For More Information...

Author e-mail: [cenglish@restekcorp.com](mailto:cenglish@restekcorp.com)

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# DESIGN OF NEW LOW-BLEED GAS CHROMATOGRAPHIC STATIONARY PHASES AND CAPILLARY COLUMNS

Frank L. Dorman, Gary B. Stidsen, Chris M.  
English, Rick Morehead, Jack Cochran, Eric  
J. Reiner, and Karen MacPherson

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# When is a Low-Bleed Column Important?

- Low concentration GC-MS analyses
  - Full scan
  - SIM
  - High-resolution
- When detector is especially sensitive to bleed
  - ECD
- When bleed directly interferes with quantitation
  - Bleed and analyte share the same ions (rare)

# How Do You Make a Low-Bleed Column ?

- Thinner stationary phase thickness
  - Not really purchasing what you think...
- Higher conditioning temperatures
  - Can lead to higher reactivity and phase loss
- Improve deactivation chemistry
  - Phase has more “affinity” for tubing
- Move polymer functionality from side chain to backbone

# Considerations for Backbone-modified Polysiloxane Stationary Phases:

- By using a “low-bleed” column, you do not want to give up selectivity.
  - Many “low bleed” columns are dimethyl or phenyl/methyl-type
- Computer Assisted Stationary Phase Design (CASPD) utilized to optimize selectivity of backbone-stabilized polymers for specific applications
  - *Anal. Chem.* **74**(9), 2133-2138 2002.
  - *LC\*GC* **18**(9), 928, 2000.
  - *American Laboratory*, **31**(6), 20-26, 1999.

# Applications

## Rtx-PCB Capillary GC Column

- Proprietary polysiloxane designed for PCB congener separation for GC-MS analysis
- 380 maximum operating temperature in standard high-temperature fused silica tubing
- Standard column dimensions, standard film thickness
- Generally increased retention for aromatics over “5”, “5Si1 MS” and “XLB” type phases

# Analysis of PCB Congeners – GC-MS

- European congener list:
  - BZ # 28,52,101,118,153,138 and 180 resolved by Cl level or chromatographically from all others
- 1668
  - All 13 congeners resolved
- McFarland and Clarke congeners:
  - 33 of 36 resolved (1 more than best previous column – XLB )
- Aroclor congeners out of 139:
  - 127 resolved (3 more than XLB)
  - 9 pairs are unresolved
- 209 Congeners:
  - 168 resolved (same number but different congeners as XLB)



# GC-ToF Analysis

- Pyrethroids analysis
  - Late-eluting pyrethroids can be difficult to keep well resolved on standard columns due to limited maximum operating temperature.
  - Peak width is narrower if the compounds are eluted during the temperature program, not on an isothermal hold
    - Preference is for column with high maximum operating temperature
  - Selectivity must be appropriate to achieve separation between the target compounds which can have similar mass spectra



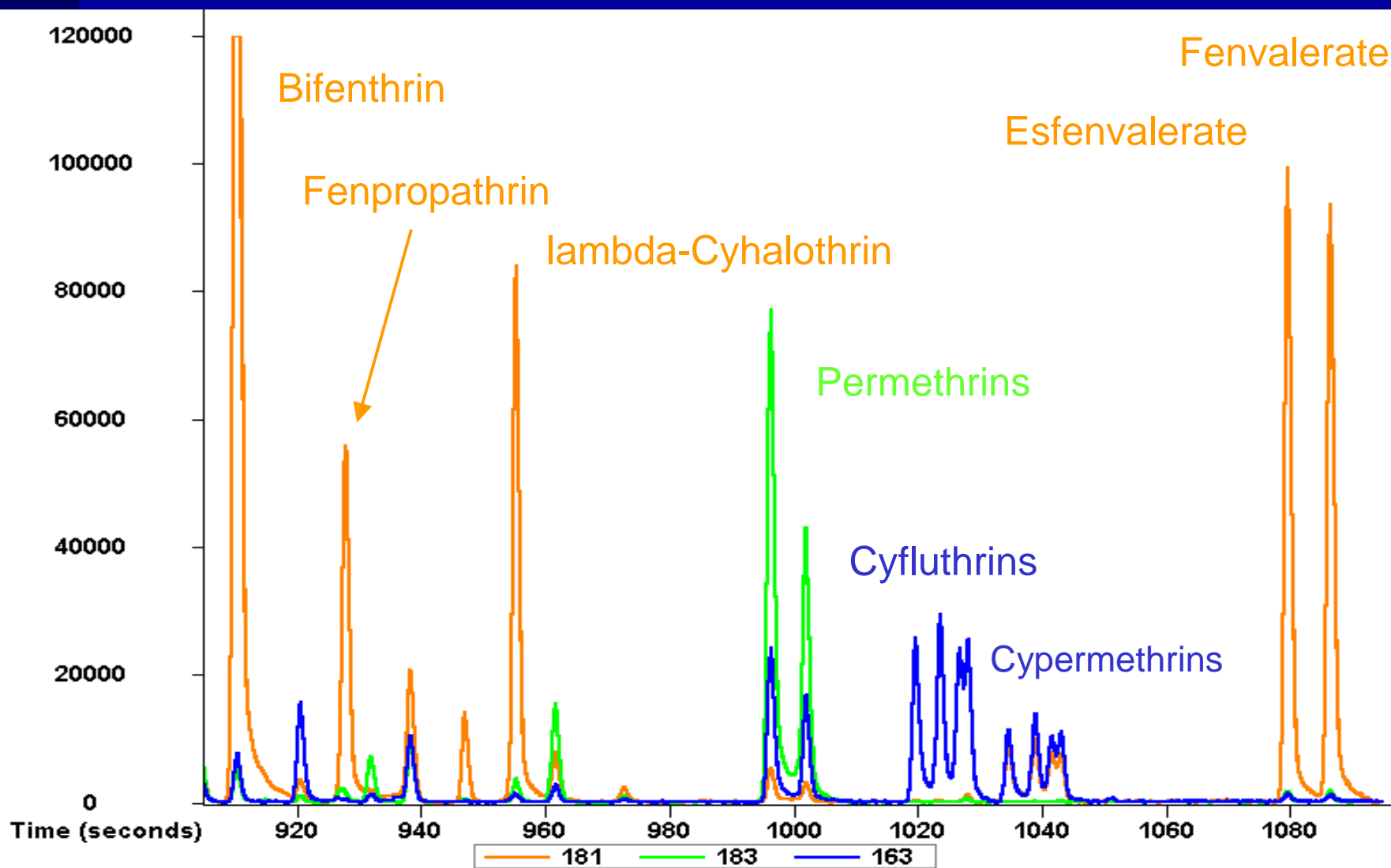
# GC Conditions

- Splitless injection
  - One microliter at 250°C
  - 60 sec valve time
  - 30 m x 0.25 mm x 0.25  $\mu$ m Restek Rtx-PCB column
  - Constant flow helium, 1 mL/minute
- GC oven program
  - 60°C (1 min), 30°/min to 120°, 15°/min to 360° (1 min)
  - Total run time: 20 min

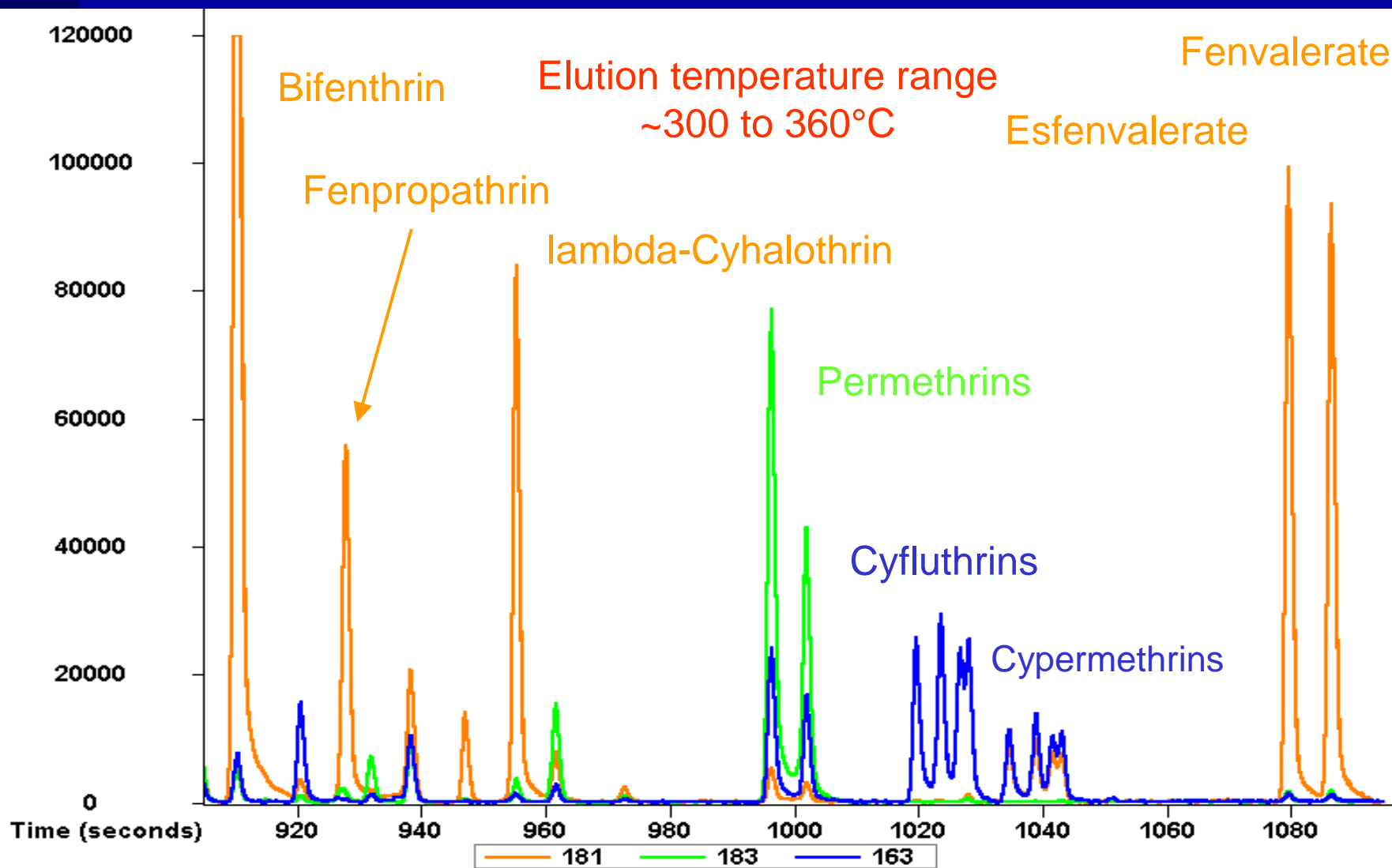
# MS Conditions

- Source temperature: 225°C
- Electron ionization: 70 eV
- Stored mass range: 45 to 550 u
- Acquisition rate: 10 spectra/sec

# Pyrethroids on Rtx-PCB



# Pyrethroids on Rtx-PCB

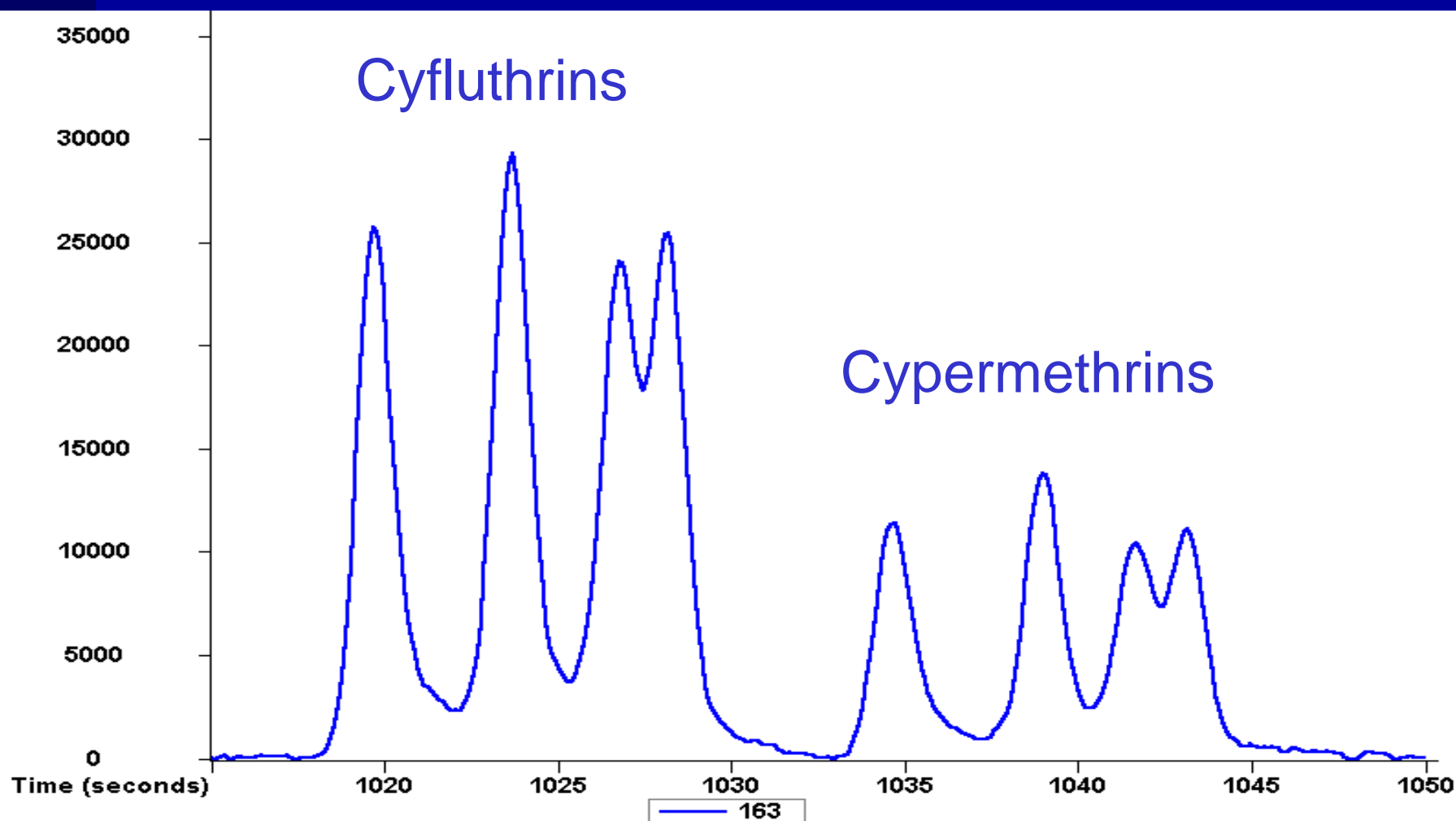


# Separation of Cyfluthrins and Cypermethrins on Rtx-PCB

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# Pyrethroids on Rtx-PCB

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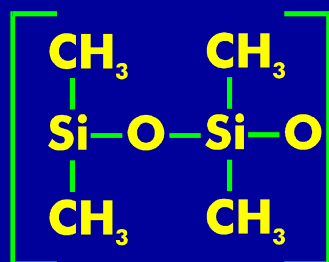
Pesticide	RT sec	RT min	RRT	Elution Temp °C	MW	Formula	CAS#	1	2 Ions	3
Pentachloronitrobenzene	680.5	11.34	1.000	245	293	C6Cl5NO2	82-68-8	237	249	295
Bifenthrin	916.0	15.27	1.346	304	410	C22H22O2ClF3	82657-04-3	165	166	181
Fenpropathrin	933.5	15.56	1.372	308	349	C22H23NO3	39515-41-8	97	181	265
lambda-Cyhalothrin	961.0	16.02	1.412	315			91465-08-6	181	197	208
cis-Permethrin	1002.2	16.70	1.473	326	390	C21H20Cl2O3	54774-45-7	127	163	183
trans-Permethrin	1007.9	16.80	1.481	327	390	C21H20Cl2O3	61949-77-7	127	163	183
Cyfluthrin	1025.5	17.09	1.507	331	433	C22H18Cl2FNO3	68359-37-5	163	206	226
Cyfluthrin	1029.4	17.16	1.513	332	433	C22H18Cl2FNO3	68359-37-5	163	206	226
Cyfluthrin	1032.5	17.21	1.517	333	433	C22H18Cl2FNO3	68359-37-5	163	206	226
Cyfluthrin	1033.9	17.23	1.519	333	433	C22H18Cl2FNO3	68359-37-5	163	206	226
Cypermethrin	1040.5	17.34	1.529	335	415	C22H19Cl2NO3	52315-07-8	163	181	209
Cypermethrin	1044.8	17.41	1.535	336	415	C22H19Cl2NO3	52315-07-8	163	181	209
Cypermethrin	1047.5	17.46	1.539	337	415	C22H19Cl2NO3	52315-07-8	163	181	209
Cypermethrin	1048.9	17.48	1.541	337	415	C22H19Cl2NO3	52315-07-8	163	181	209
Esfenvalerate	1085.6	18.09	1.595	346	419	C25H22ClNO3	66230-04-4	167	225	419
Fenvalerate	1092.5	18.21	1.605	348	419	C25H22ClNO3	51630-58-1	167	225	419

# Rtx-500 Capillary GC Column

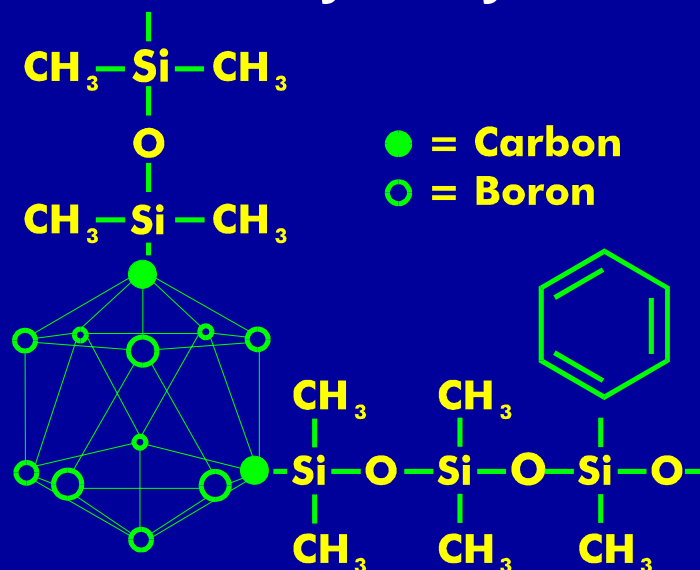
- Carborane-stabilized stationary phase
  - Maximum temperature of 380 C in “standard high-temperature” tubing
  - Maximum temperature of 440 C in passivated metal columns (Mxt-500)
- Extremely low bleed levels
  - Surpasses phenyl/methyl phases, and silphenylene stationary phases
- Common dimensions available

# Carborane-polysiloxane Stationary Phase

## Dimethyl Polysiloxane



## Carborane Dimethyl Polysiloxane





# Analysis of PCB Congeners by GC-MS

- Toxic PCB's by USEPA method 1668 commonly run on “octyl” phases
  - Very high background from bleed decreases sensitivity
  - Phase loss can cause retention order changes
  - “5” phases can have coelution issues
    - 118/123
    - 156/157
  - Rtx-500 Column can improve upon these...

# Toxic PCB Congeners

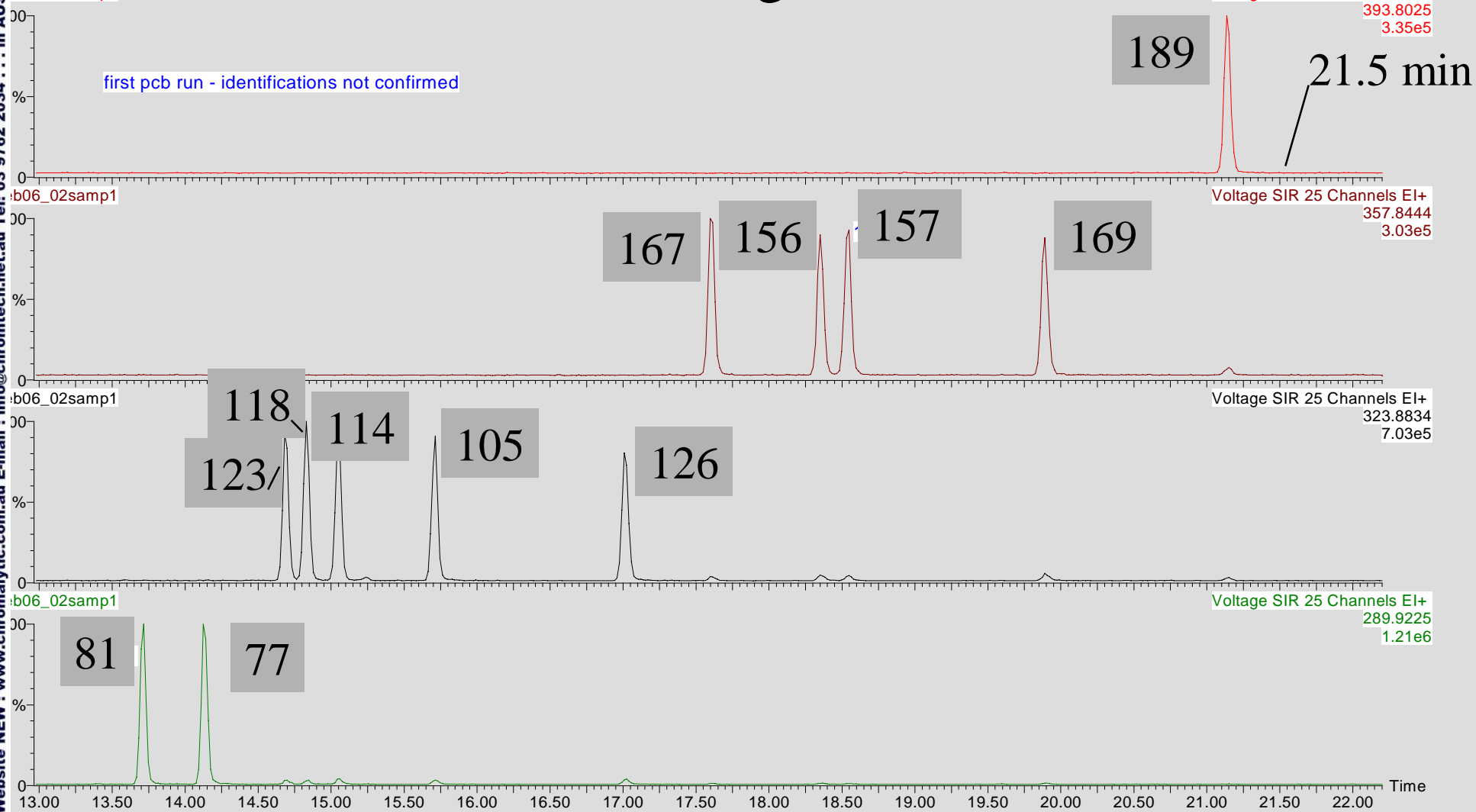
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p-cs5 on htc  
b06\_02samp1

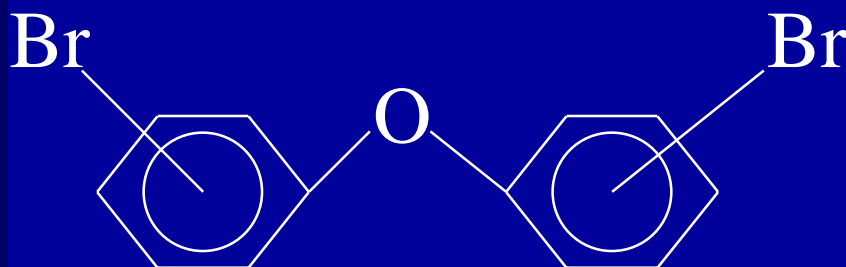
first pcb run - identifications not confirmed



# Analysis of Siloxanes in the Environment

- Rare case, but becoming important
- Since most all GC phases are siloxanes, bleed ions directly interfere with quantitation ions for GC-MS analyses
- Rtx-500 Carborane-based capillary column does not have any siloxane character in its bleed spectrum
- Rtx-500 also useful for PBDE flame retardant analyses (Pittcon 2003 Workshop)

# Polybrominated Diphenylethers



## Br 1-10

- Named similarly to PCB congeners (BDE 1-209)  
J. High Resolut Chromatogr **15**:260
- Human exposure via the food chain is 0.2 – 0.7 mg/day  
Organohalogen Compounds **35**:411
- Listed as Endocrine Disruptors  
Environ Health Perspect **101**:378

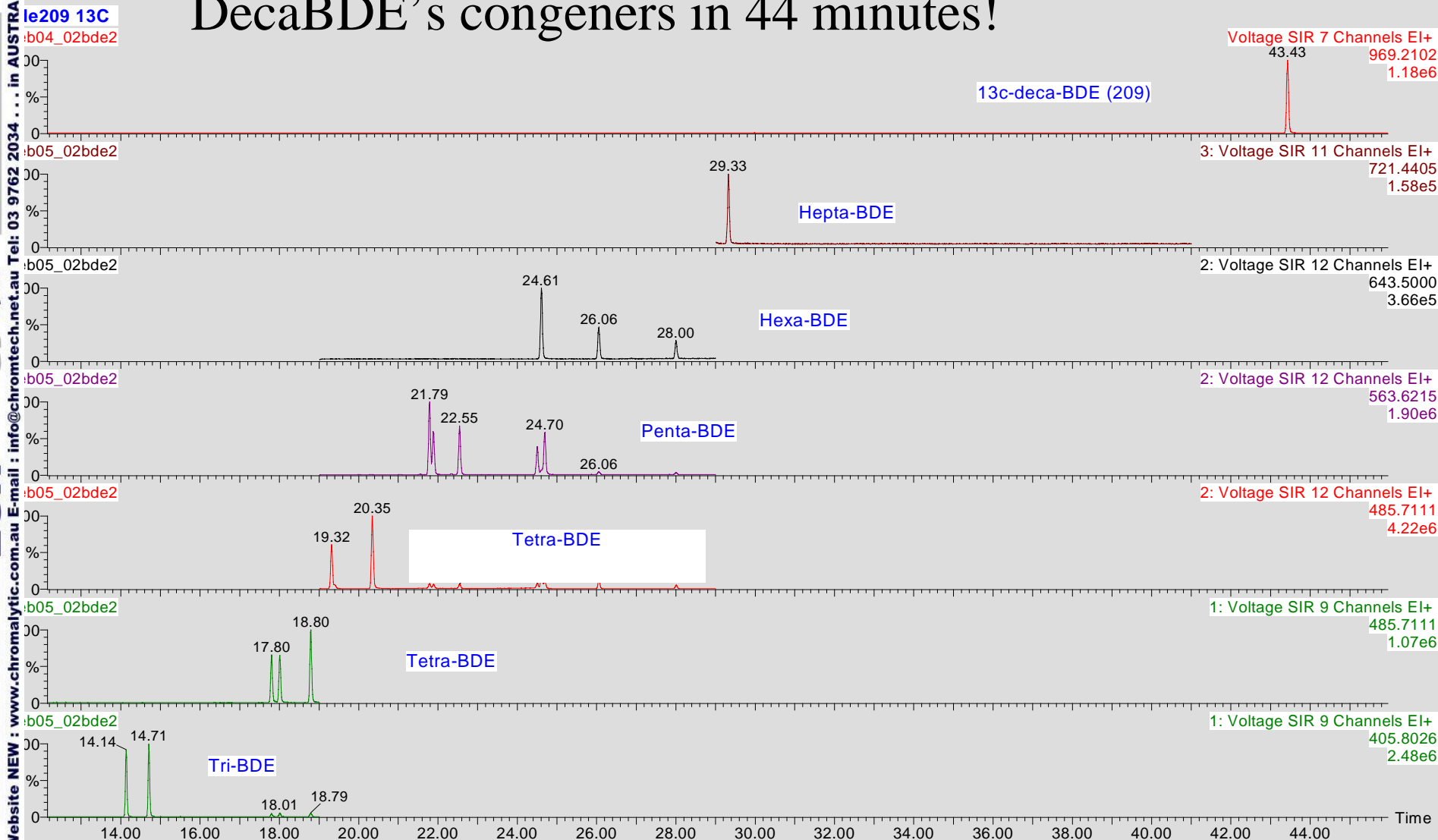
# Wellington Laboratories BDE Mix-C

4-bromodiphenyl ether (3)	250	141,115
2,4-Dibromodiphenyl ether (7)	168	328,139
4,4'-dibromodiphenyl ether (15)	328	168,221
2,2',4-tribromodiphenyl ether (17)	248	408,406
2,4,4'-tribromodiphenyl ether (28)	406	248,246
2,2',4,5'-tetrabromodiphenyl ether (49)	326	486,328,324
2,3',4',6-tetrabromodiphenyl ether (71)	326	486,324,328
2,2',4,4'-tetrabromodiphenyl ether (47)	326	486,328,324
2,3',4,4'-tetrabromodiphenyl ether (66)	326	486,328,324
3,3',4,4'-tetrabromodiphenyl ether (77)	326	486,328,324
2,2',4,4',6-pentabromodiphenyl ether (100)	406	564,566
2,3',4,4',6-pentabromodiphenyl ether (119)	404	406,564
2,2',4,4',5-pentabromodiphenyl ether (99)	406	564,566
2,2',3,4,4'-pentabromodiphenyl ether (85)	406	564,566
3,3',4,4',5-pentabromodiphenyl ether (126)	566	564,568,406
2,2',4,4',5,6'-hexabromodiphenyl ether (154)	484	644,486
2,2',4,4',5,5'-hexabromodiphenyl ether (153)	644	484,486,482
2,2',3,4,4',5'-hexabromodiphenyl ether (138)	642	484
2,2',3,4,4',5',6-heptabromodiphenyl ether (183)	722	564
decabromodiphenyl ether (209)	956	

# Baseline separation of Tri, Tetra, Penta, Hexa, Hepta, and DecaBDE's congeners in 44 minutes!

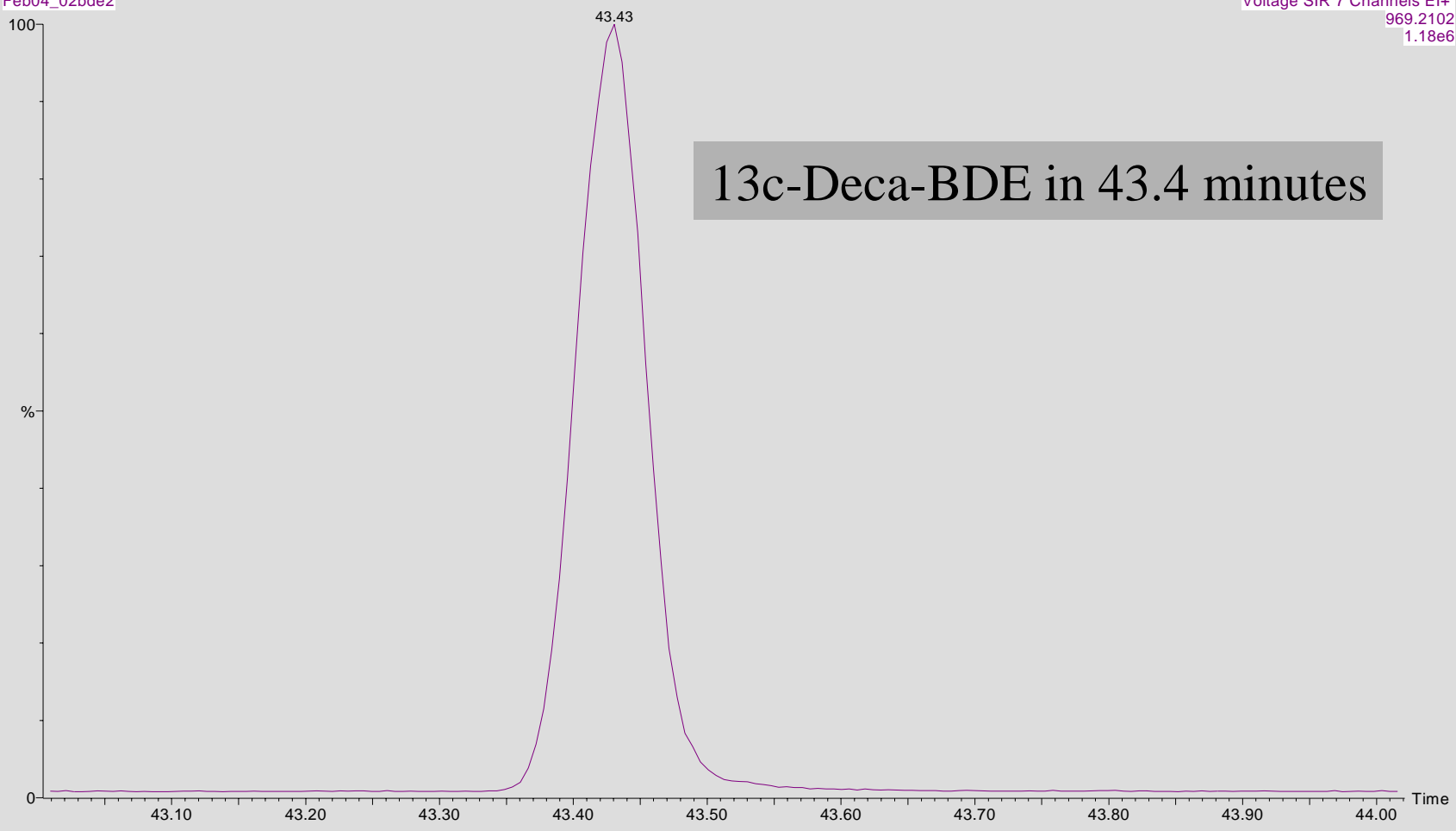
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bde209 13C  
Feb04\_02bde2

Voltage SIR 7 Channels EI+  
969.2102  
1.18e6



13c-Deca-BDE in 43.4 minutes

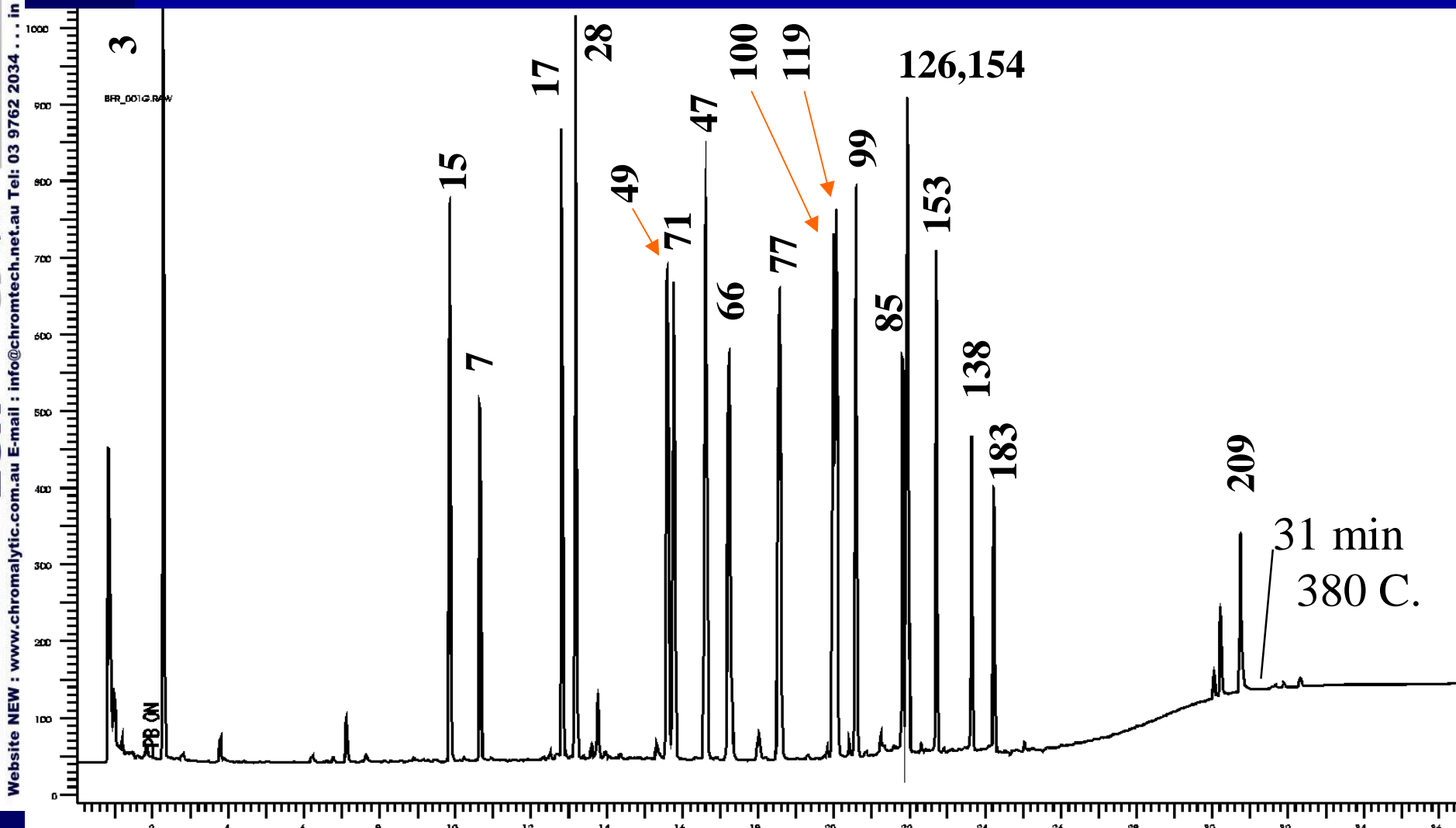
BROMINATED FLAME RETARDANT GC PROGRAM				
INSTRUMENT CONFIGURATION				
Micromass Autospec-UltimaNT (High Resolution Mass Spectro				
Source Temperature = 300°C				
GC CONDITIONS (HP 6890 +)				
Constant flow @ 1.5mL/min				
Injector Temp. 300°C				
Temp. Ramp Temp. Hold Time				
Start Temp. 100 1 min				
10 110 0.64				
80 180 0				
5 350 23				
TOTAL RUN TIME = 60.51				
**NB: DecaBDE (last elutor) elutes at ~43 min.				



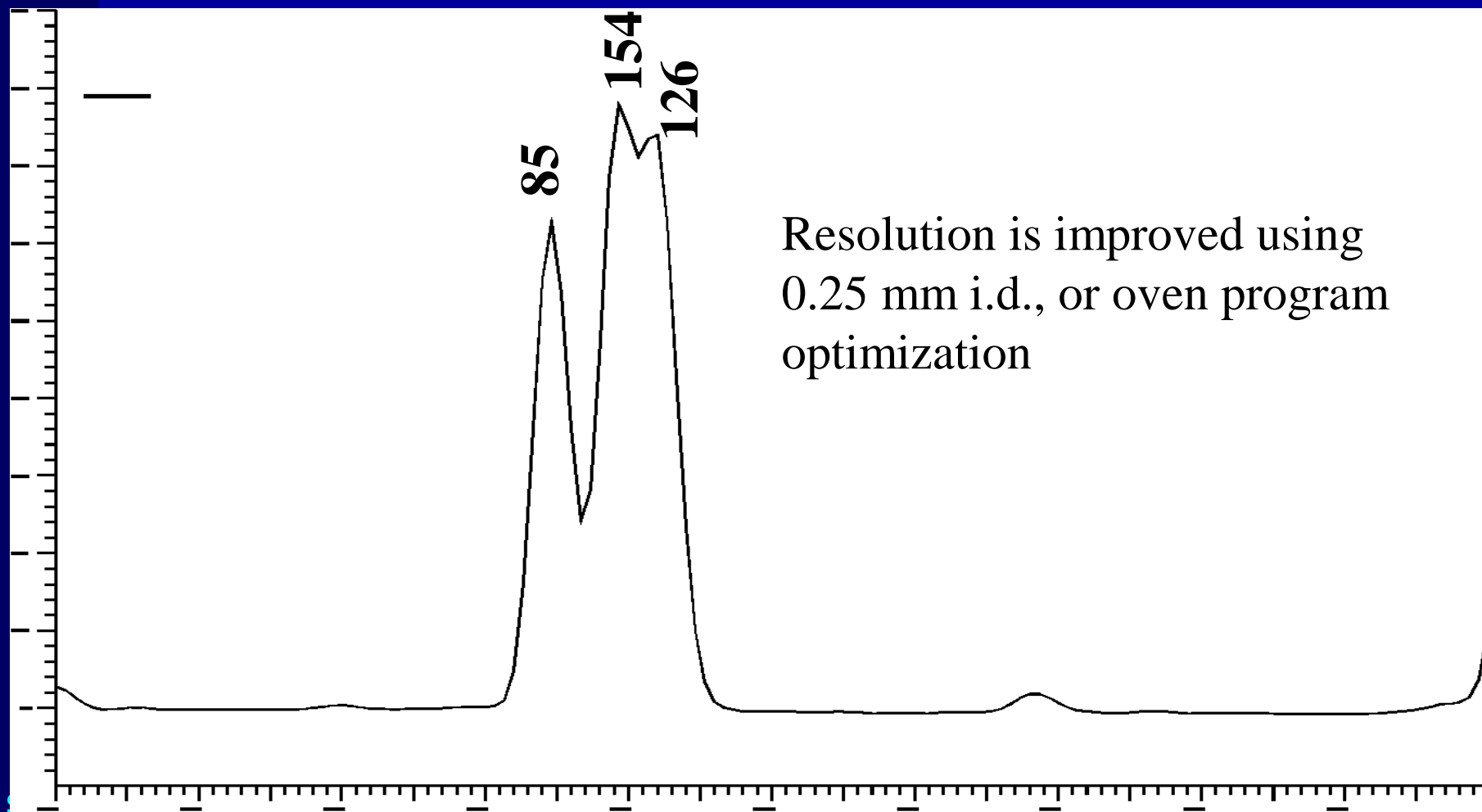
# GC-ECD Analysis

- Electron capture detector is common to many laboratories
- Compounds have excellent response by ECD
- Higher flow rates may allow for more rapid separation using larger-diameter columns
- Instrumentation less expensive than HRMS
- Instrumentation is also field portable

# Wellington Laboratories BDE Mix-C



# 0.53 mm i.d. column partially resolves BDE 154 and 126 under these conditions



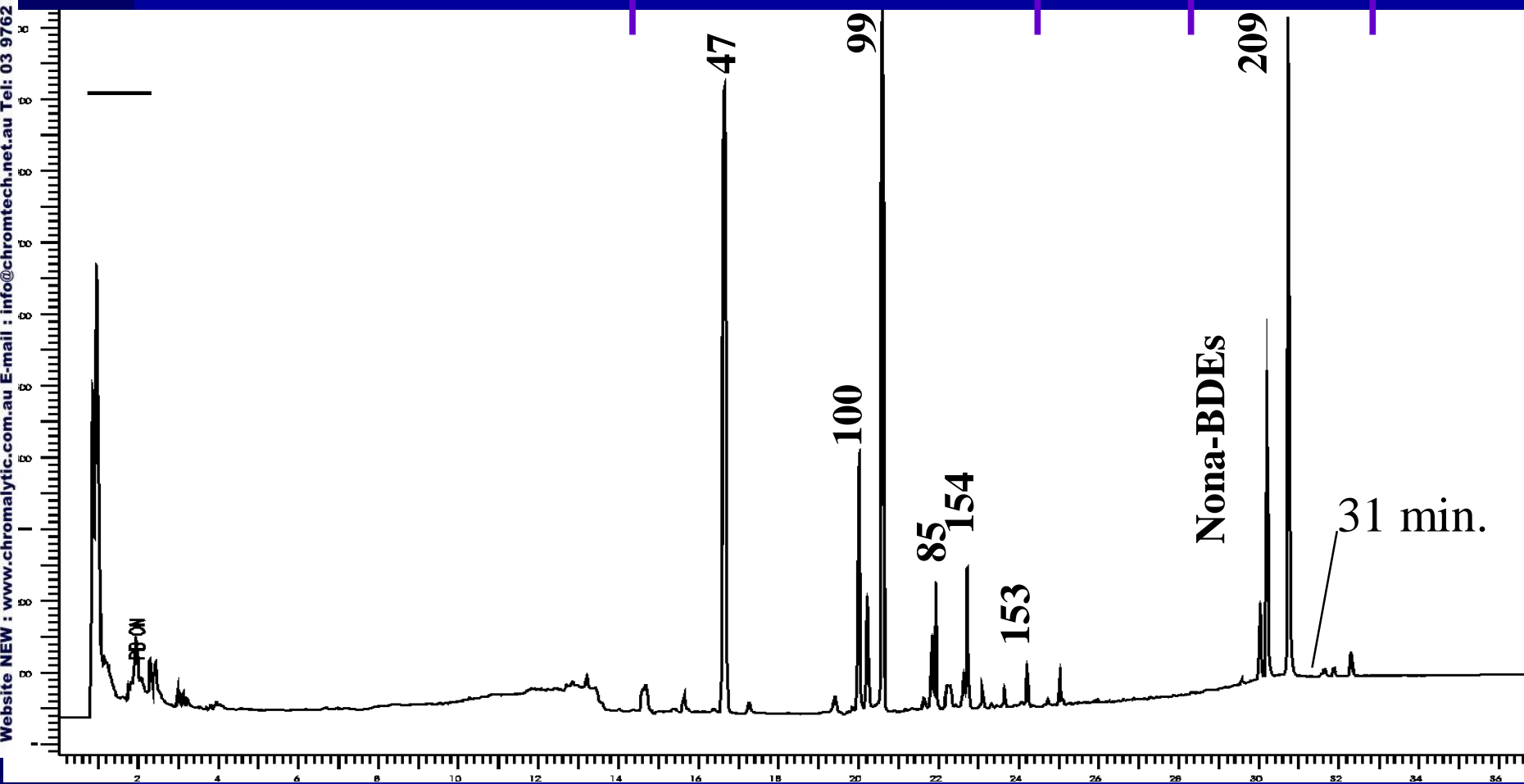
Resolution is improved using  
0.25 mm i.d., or oven program  
optimization

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# Commercially Available PBDE Mixes

DE-71<sup>TM</sup>

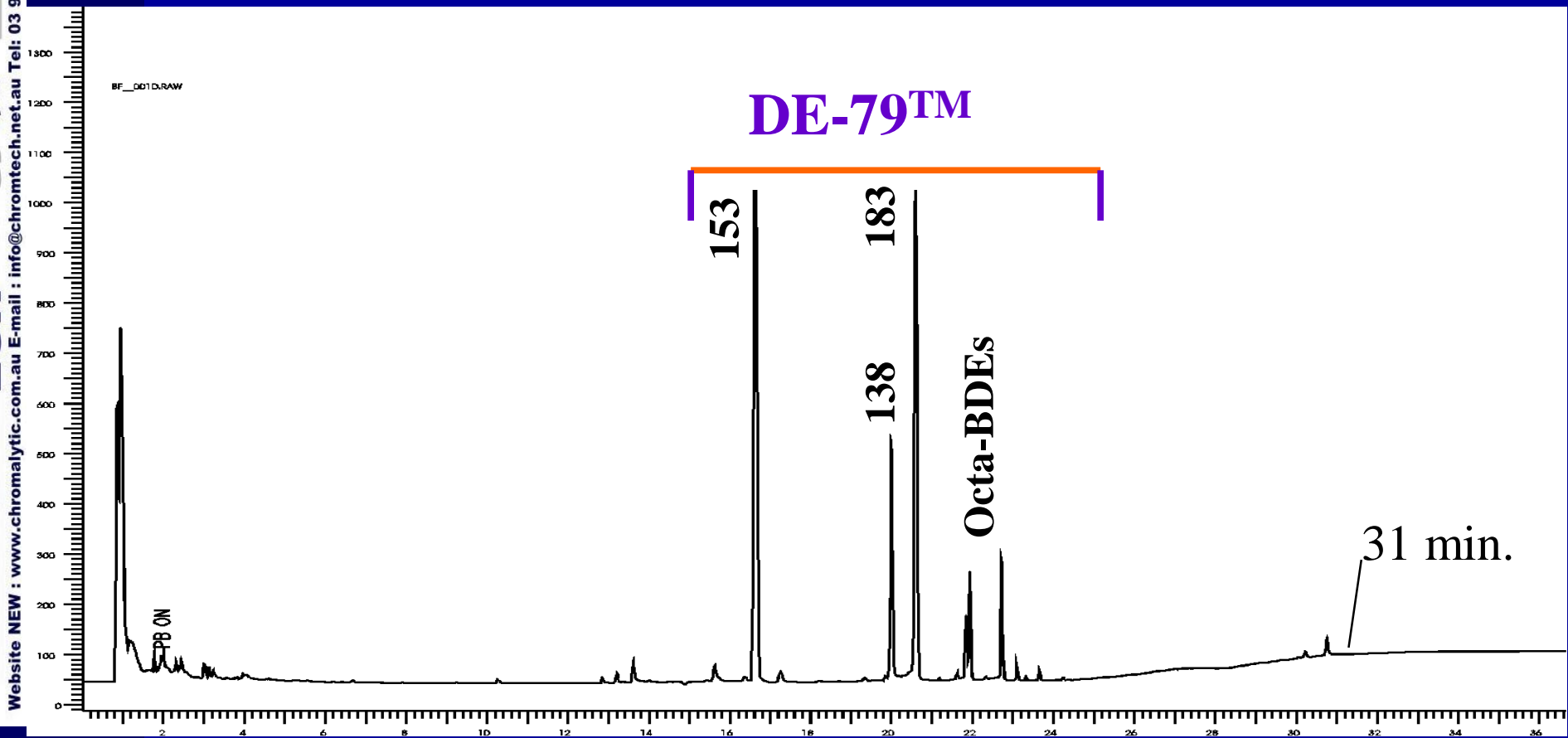
DE-83<sup>TM</sup>



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# Commercially Available PBDE Mixes



# Conditions

**Column:** Rtx-500 30m x 0.53mm x 0.15 Ser# 233548  
**Flows:** Hydrogen 7.69ml/min (66.7cm/sec) @ 100°C  
**Dead Time:** MeCl2 Headspace 0.76min @ 100°C  
**Oven:** 100(1) 15/260(5) 15/380 (15) ~ 40 min runtime  
**Standards:** Wellington Laboratory BDE-Mix C  
1ul injection 30pg on column.  
**Injection:** Drilled Press-Tight Uniliner.

Restek [www.restekcorp.com](http://www.restekcorp.com)

# Rtx-Dioxin Capillary Column

- Proprietary polysiloxane designed for replacement of “5”-type columns as primary, or high-cyano secondary columns for toxic dioxin and furan analysis by GC-HRMS
- 380 maximum operating temperature in standard high-temperature fused silica tubing

# Dioxin and Furan Analysis

- Dual column method
  - Usually 5% diphenyl column and a high-cyano column (eg Rtx-225)
  - Cyano columns have poorer lifetimes and lower maximum operating temperatures
  - 5% diphenyl phases do not have the selectivity to accurately quantitate most samples
    - USEPA requires 2,3,7,8-tcdf to be confirmed on a X-225
- Desirable to have both columns in the same oven, and to improve the separation of the “5”



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Feb06\_0

TCDD Resolution Mix

RTX-DIOXIN  
40m x .18 x .10

\*\*\*\*\*  
2378-TCDD

Voltage SIR 14 Channels EI+  
321.8936  
3.53e5

21.03

21.96

1234-TCDD

JUL26\_QCS003

TCDD Resolution Mix

DB5  
60m x .25 x .25

\*\*\*\*\*  
2378-TCDD

2: SIR of 20 Channels EI+  
321.894  
2.35e5

1237/1238-TCDD

1239-TCDD

21.13

21.40

22.22

1234-TCDD

\*\*\*\*\*  
2378-TCDD

22.71

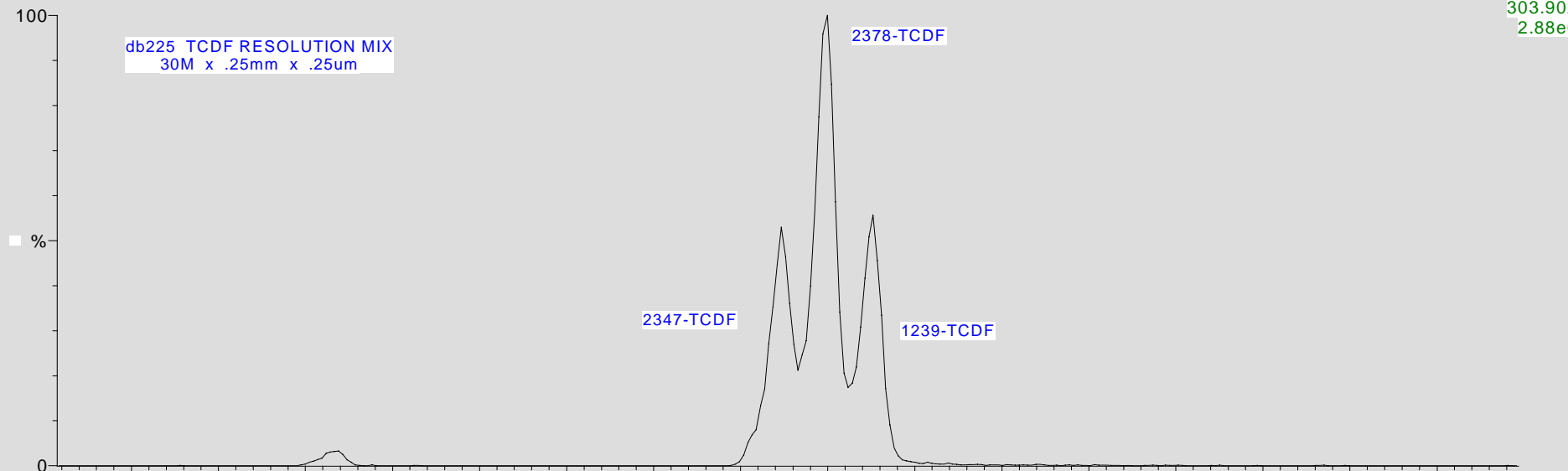
22.92

Time

OCT24\_QCS001

SIR of 12 Channels EI+  
303.902  
2.88e6

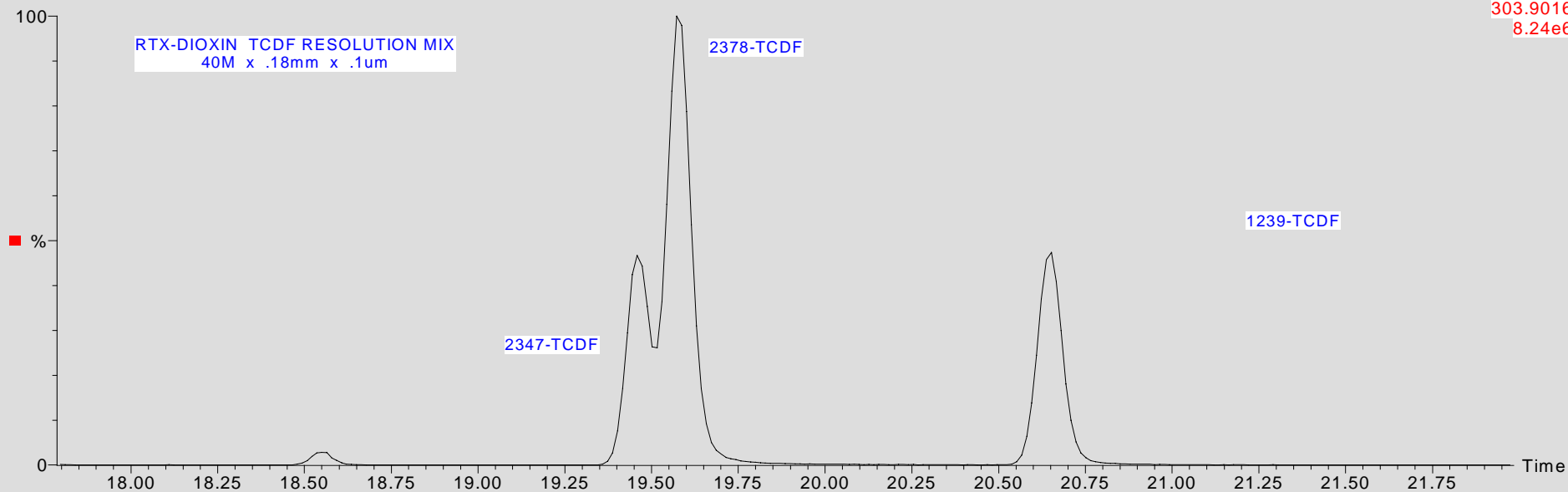
db225 TCDF RESOLUTION MIX  
30M x .25mm x .25um



feb18\_37

2: Voltage SIR 20 Channels EI+  
303.9016  
8.24e6

RTX-DIOXIN TCDF RESOLUTION MIX  
40M x .18mm x .1um



# Fly Ash Round Robin Samples

## >110 laboratories participating

	DB-5	DB-225	RTX-DIOXIN	MEDIAN	MEAN
Ash A	250	21	30	28	32
Ash B	2100	300	378	390	390
Ash C	170	19	28	27	32
All results reported as pg/g					

Median and Mean agreement gives good confidence in “true” value

[www.restekcorp.com](http://www.restekcorp.com)

# Rtx-Dioxin Conditions

Micromass Altima High Resolution GC-MS

Rtx-Dioxin 40m x .18 x .1

Initial Temp 130 C

	Time	Rate C/min	Temp	
	0	52	200	
	10.2	2.9	235	
	10	6.9	300	
	24			

Constant Pressure of 1.2 mL/min

Injector Temp = 270C

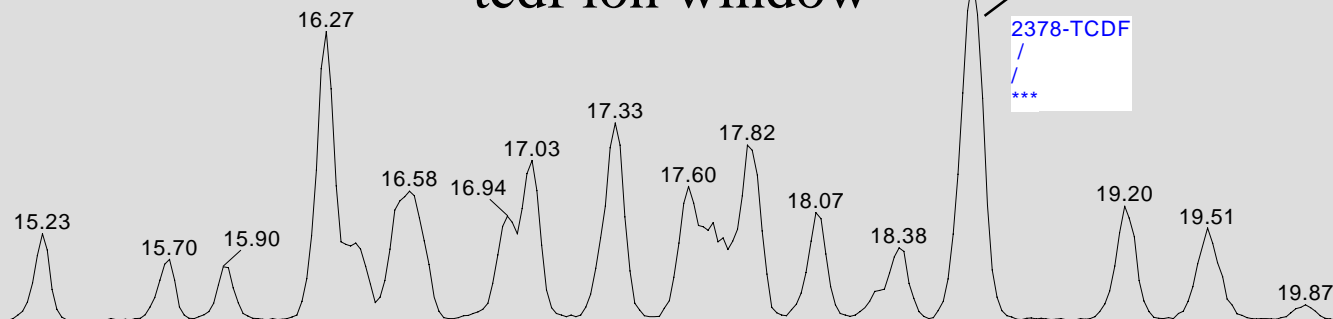
JUN18 Flyash extract  
DB5  
60M x .25mm x .25um

tcdf ion window

Up to 6 congeners coeluting

2: SIR of 20 Channels EI+  
303.902  
2.28e6

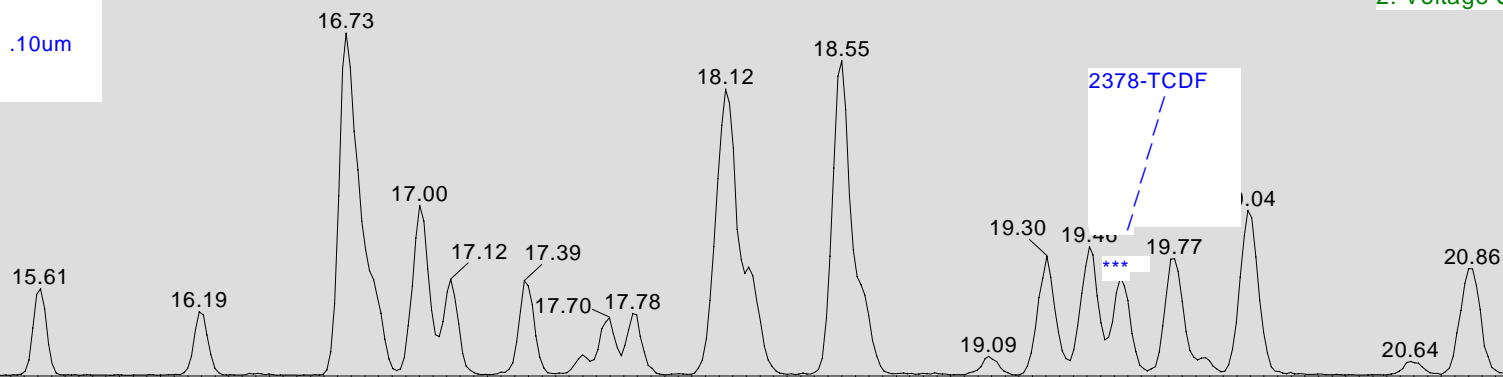
2378-TCDF  
\*\*\*



3 Flyash extract  
RTX-DIOXIN  
40M x .18mm x .10um

2: Voltage SIR 20 Channels EI+  
303.9016  
7.01e5

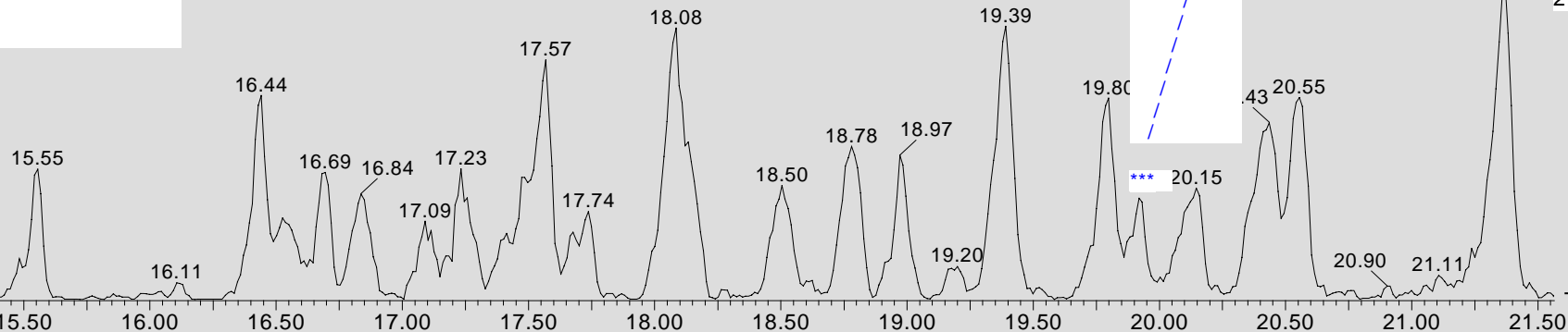
2378-TCDF  
\*\*\*



24 Flyash extract  
DB225  
30M x .25mm x .25um

SIR of 12 Channels EI+  
303.902  
2.31e4

2378-TCDF  
\*\*\*



Time

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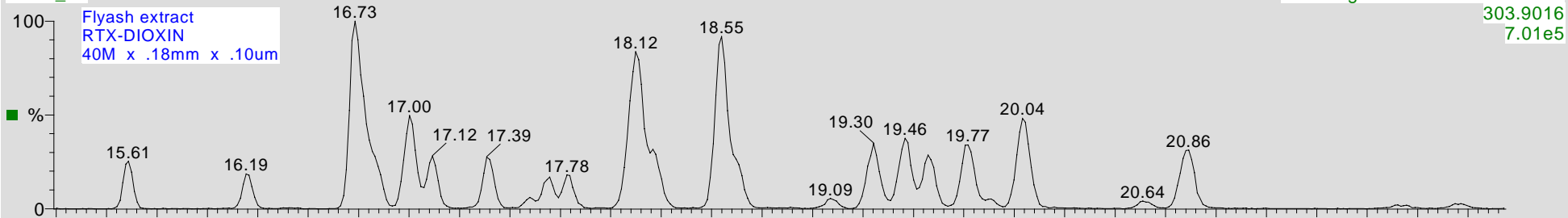
Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034  
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+61(0)3 9762 2034

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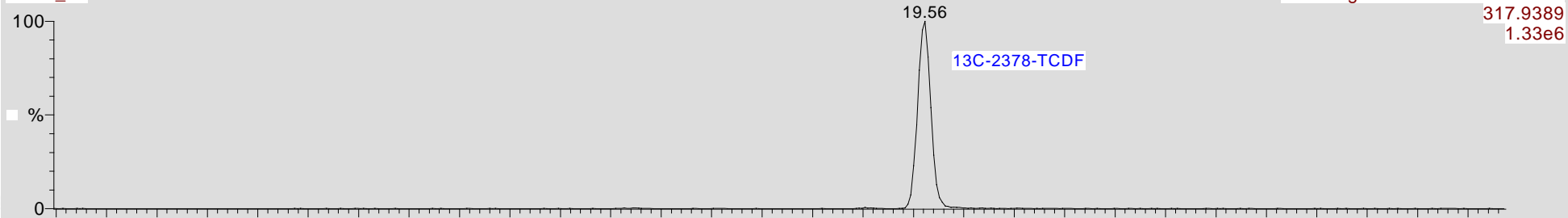
feb18\_33

Flyash extract  
RTX-DIOXIN  
40M x .18mm x .10um



2: Voltage SIR 20 Channels EI+  
303.9016  
7.01e5

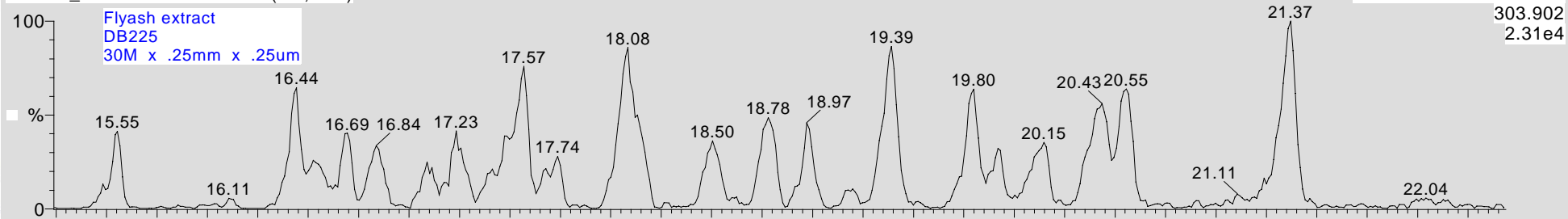
feb18\_33



2: Voltage SIR 20 Channels EI+  
317.9389  
1.33e6

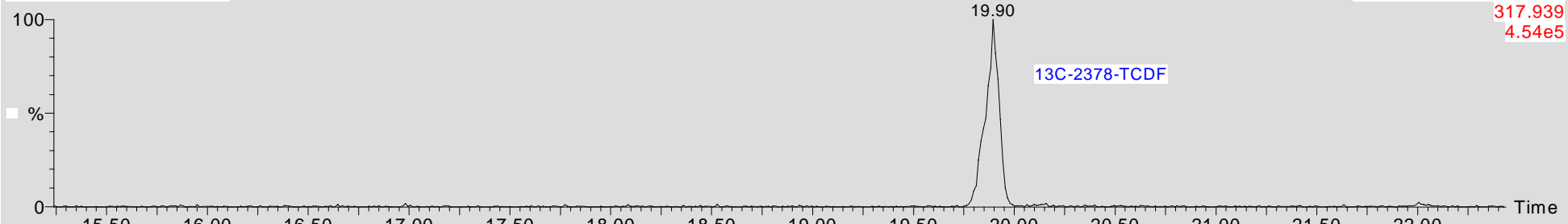
OCT24\_CONFIRM2S019 Sm (Mn, 1x1)

Flyash extract  
DB225  
30M x .25mm x .25um



SIR of 12 Channels EI+  
303.902  
2.31e4

OCT24\_CONFIRM2S019



SIR of 12 Channels EI+  
317.939  
4.54e5

Time

# Rtx-Dioxin Column

- Replaces a 5% diphenyl column for high-resolution dioxin and furan analyses
  - Improves sensitivity due to lower bleed levels
  - Improves separation of many congeners
- May replace high-cyano columns as confirmation column to the 5% diphenyl
  - All but 2 congeners were within 10% of the fly ash median values
    - These 2 can be quantitated using the 5% diphenyl column
  - May eliminate the need for –2330, -2331, -225 confirmation columns
  - Final characterization currently underway

# Low-Bleed Columns Summary:

- **Rtx-XLB**
  - Low bleed column for pesticides and PCB Congeners, similar to DB-XLB
- **Rtx-PCB**
  - Low bleed column for pesticides and PCB Congeners, resolves a few more congeners than XLB phases
  - Unbiased GC-MS results for European PCB congener method
- **Rtx-500**
  - Carborane-based column, exceptionally high thermal stability
- **Rtx-Dioxin**
  - Improvement over the 5% diphenyl columns, and possible replacement for high-cyano confirmation phases



# Acknowledgements

- Reference materials courtesy of Wellington Laboratories – Guelph, Ontario
- Dr. Eric Reiner and Karen MacPherson of the Ontario Ministry of the Environment – Etobicoke, Ontario provided the HRMS analyses, and guidance.
- Jack Cochran of LECO Corporation – Pesticide and PCB analyses

# Rtx 1HT SimDist Packed Column

Barry Burger, Dinesh Patwardhan, Kristi Sellers, Gary  
Stidsen and Chris Cox

Restek Corp.

110 Benner Circle

Bellefonte, Pa.

# Project Objective

- Develop a PDMS polymer and column that is thermally stable, possess low bleed characteristics, yields symmetrical hydrocarbon peak shape and elutes hydrocarbons according to boiling point. The polymer should be acceptable for use in both GC packed columns, metal capillary tubing and fused silica and meet all ASTM method D-2887-93 and D3710-93 criteria.

# Polymer Characteristics

- Low bleed at 430 c thus mitigating baseline subtraction which leads to errors if the baseline is not reproducible.
- Non-polar so as not to affect the elution of the hydrocarbons.
- Ability to be cross-linked with diatomaceous earth solid supports, fused silica and metal capillary tubing.
- Must elute hydrocarbons in order of increasing boiling point and conform to ASTM method D-2887-93 and D 3710-93 criteria.
- Out of the box and running in under 30 minutes.

# Solid Support Characteristics

- Low trace metal content to prevent sample interaction.
- Classified to a narrow particle size distribution.
- Non-polar deactivation so as not to effect the elution of the hydrocarbons.

# Tubing Characteristics

- The tubing ID must be free of oils associated with the manufacturing process so as not to contribute to peak tailing or artifacts in the baseline during temperature programming.
- Sulfinert deactivated to prevent any interaction with the petroleum sample.

# Column Reproducibility Data

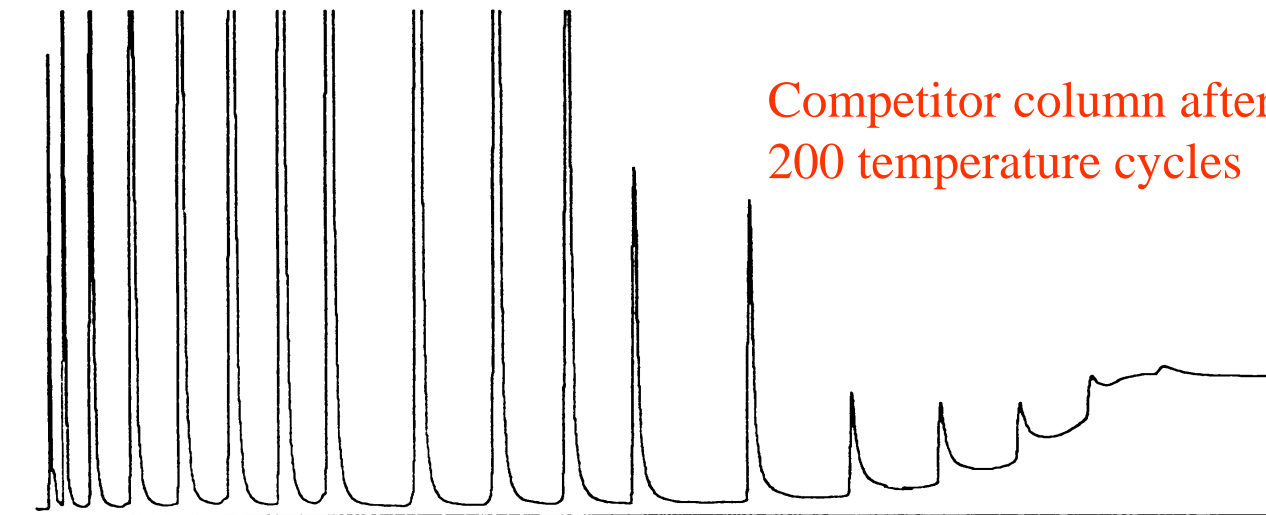
	Min. Rt.	Max. Rt.	Ave Rt.	Std. Dev.
●				
● C5	0.241	0.243	0.242	0.001
● C6	0.493	0.497	0.495	0.002
● C10	5.746	5.765	5.752	0.005
● C20	18.482	18.491	18.486	0.004
● C28	25.093	25.103	25.098	0.004
● C40	32.160	32.171	32.166	0.004
● C44	34.316	34.328	34.326	0.007

# Reference Gas Oil #1 Data

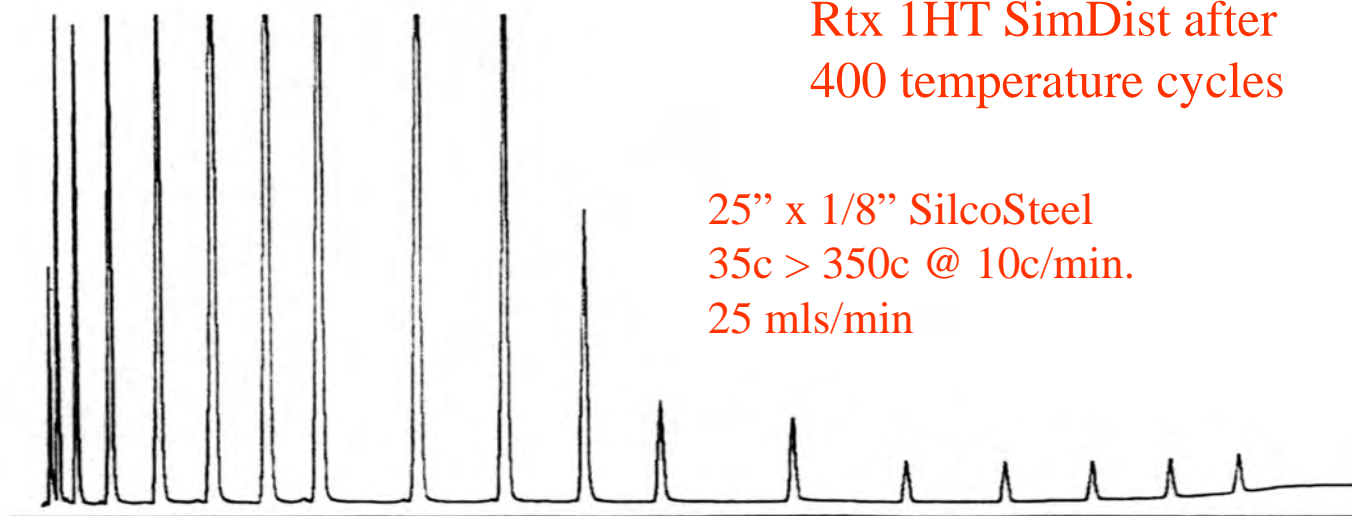
	<u>ASTM consensus</u>	<u>ASTM</u>	<u>Rtx-1HT</u>	<u>Std. Dev.</u>
<u>IBP</u>	<u>Range</u>	<u>Avg.</u>	<u>Avg.</u>	
5	140-146	143	141.2	0.29
10	165-173	169	167.3	0.29
20	217-225	221	218.0	0.87
30	254-262	258	255.7	0.58
50	307-317	312	310.5	0.50
70	349-359	354	353.7	0.29
80	371-382	376	375.7	0.29
90	399-409	404	403.5	0.00
FBP	462-488	475	466.8	0.58



# Column Longevity Data



Competitor column after  
200 temperature cycles

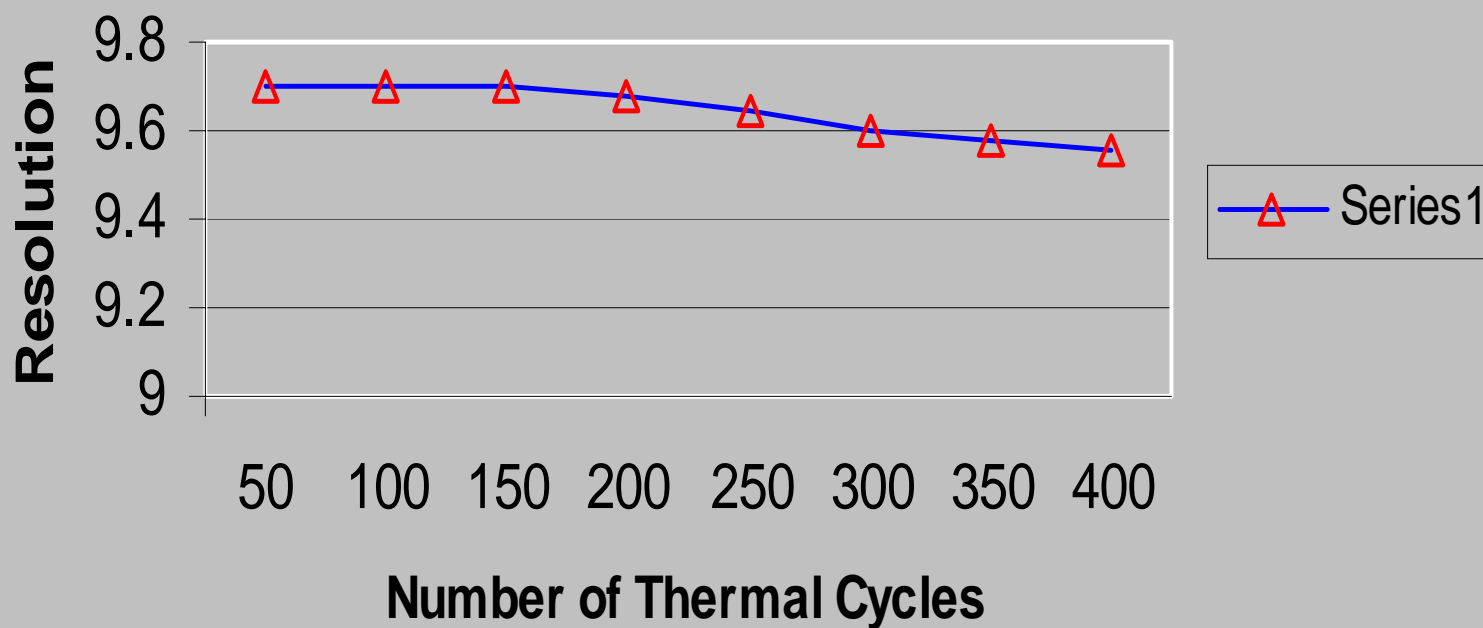


Rtx 1HT SimDist after  
400 temperature cycles

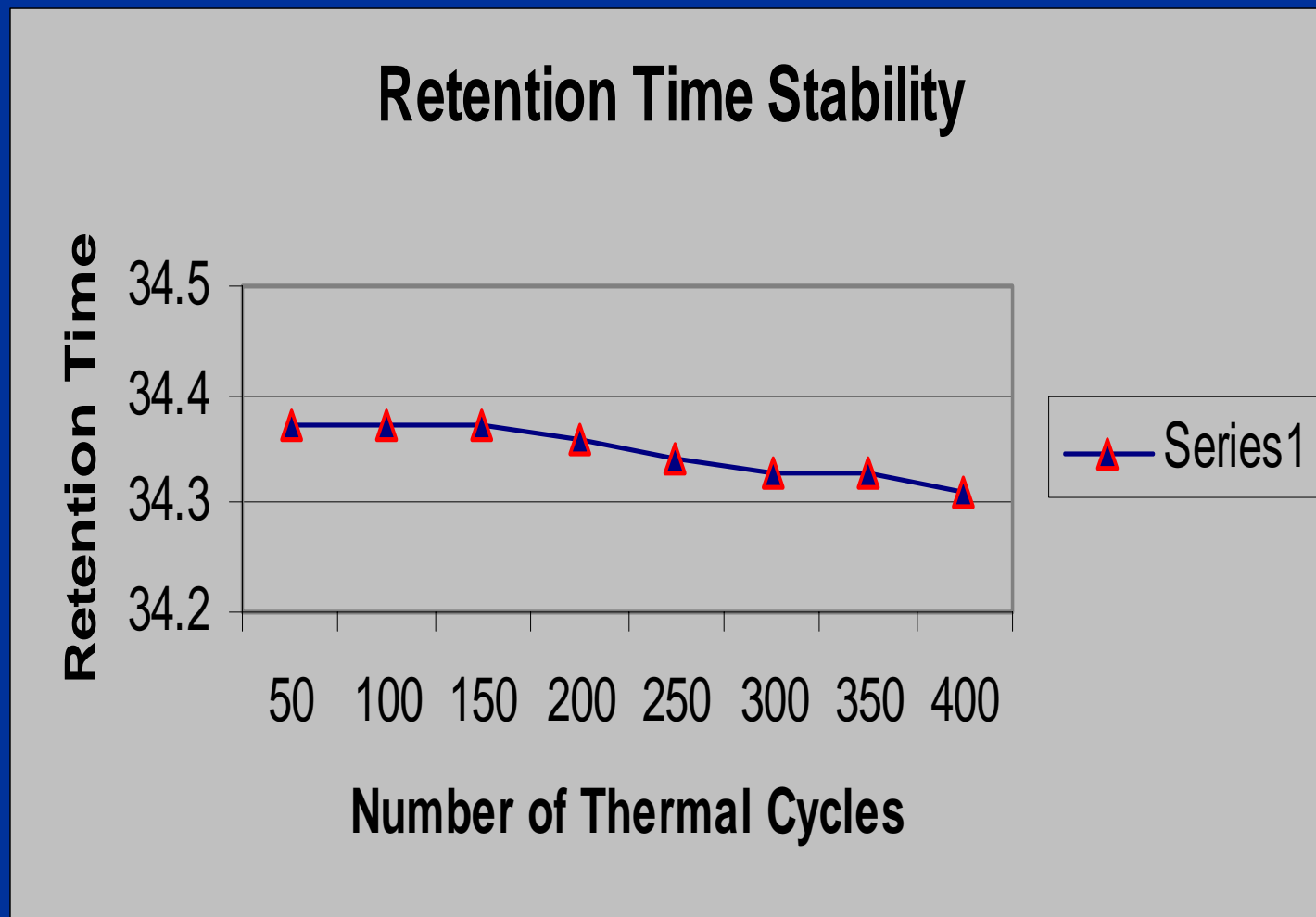
25" x 1/8" SilcoSteel  
35c > 350c @ 10c/min.  
25 mls/min

# Performance After 400 Thermal Cycles to 350 C

## C16 / C18 Resolution



# C44 Retention Time Stability



# Conclusion

Simulated distillation is the most common analysis performed in petroleum laboratories. D-2887 and D-3710 can be done using either a packed or capillary column. The new Rtx 1HT column is 100 % PDMS, totally immobilized, thermally stable to 430 c and exceeds all ASTM method D-2887-93 and D-3710-93 criteria. The Rtx 1HT SimDist packed column is the perfect choice, requiring minimal conditioning (< 30 min.) and yielding a stable baseline, excellent peak symmetry and reproducible retention times right out of the box.

# Mtx 1HT SimDist

Barry Burger, Dinesh Patwardhan, Kristi Sellers, Gary  
Stidsen and Chris Cox

Restek Corp.

110 Benner Circle

Bellefonte, Pa.

# Project Objective

- Develop a 100% PDMS polymer with the following characteristics:
  - - Thermally stable
  - - Low Bleed
  - - Symmetrical hydrocarbon peaks
  - - Boiling point elution of hydrocarbons

# Polymer Characteristics

- Thermally stable to 450c
- Requires minimal conditioning
- Longevity (>350 temperature cycles)
- 100 % cross-linked
- Polarity equivalent to existing liquid phases

# Column Characteristics

- Reproducible retention times
- Boiling point elution of hydrocarbons
- Meets resolution criteria of C 50 & C 52
- Meet skewing criteria for polywax 1000 after 10 cycles/day for three weeks.
- No breakage problem



# Tubing Characteristics

- ID free of any petroleum based residue during tubing manufacture.
- ID surface roughness <50 RMS units

# Sulfinert Deactivation

- The next generation of metal passivation.
- Non-polar surface, therefore no selectivity effects toward aromatics.
- Durable deactivation layer will not fracture.
- Deactivation layer is incorporated into the framework of atoms on the surface of the stainless steel.
- Thermally stable at 450 c.

# Column installation and Conditioning

- Connect the column to the injector and detector using graphite ferrules.
- Turn on the carrier gas pressure.
- If using He adjust pressure to 1.0 psig
- If using H2 adjust pressure to 2.0 psig
- Check the system for leaks using an electronic leak detector.
- If system is leak free ramp the column through one program cycle.

# Analytical System

- Equipped with cool on-column injection
- Instrument capable of linear temperature programming from ambient to 430c.
- Detector range to 430c
- Integration system capable of converting the detector signal into peak area slices.
- Accurate recording of retention times.

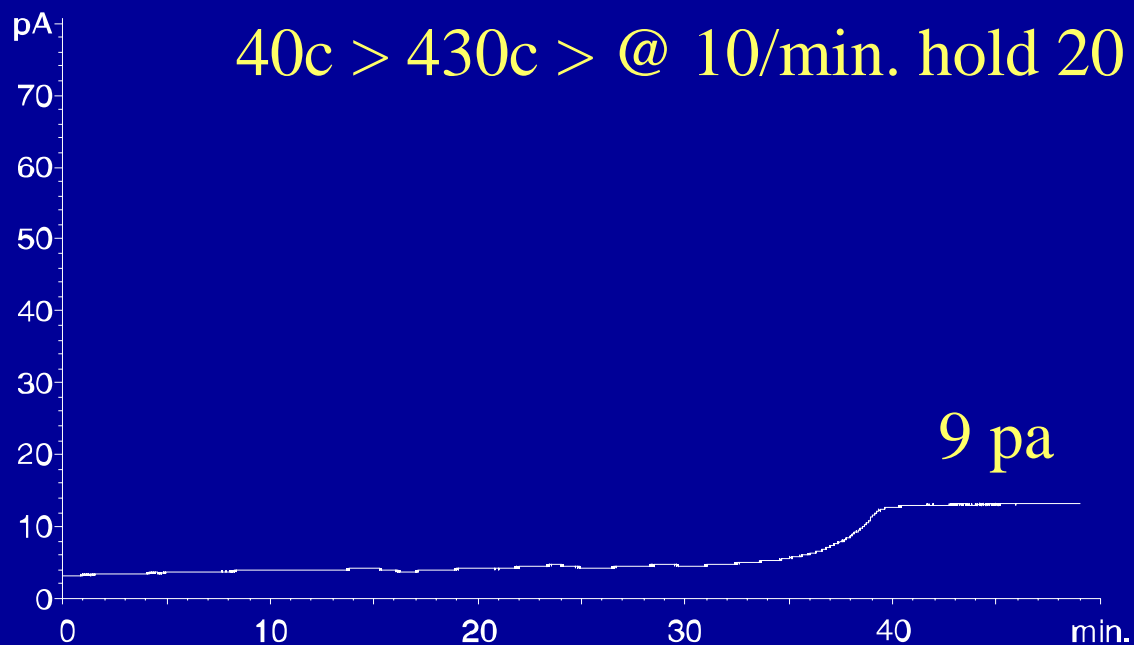
# Carrier Gas Considerations

- Gas of choice must be O<sub>2</sub> free to prevent oxidation at high temperatures
- Recommend the use of O<sub>2</sub>/ moisture scrubber regardless of the purity of carrier gas being used.
- Use He or H<sub>2</sub> for optimum efficiency

# GC Parameters Polywax 1000

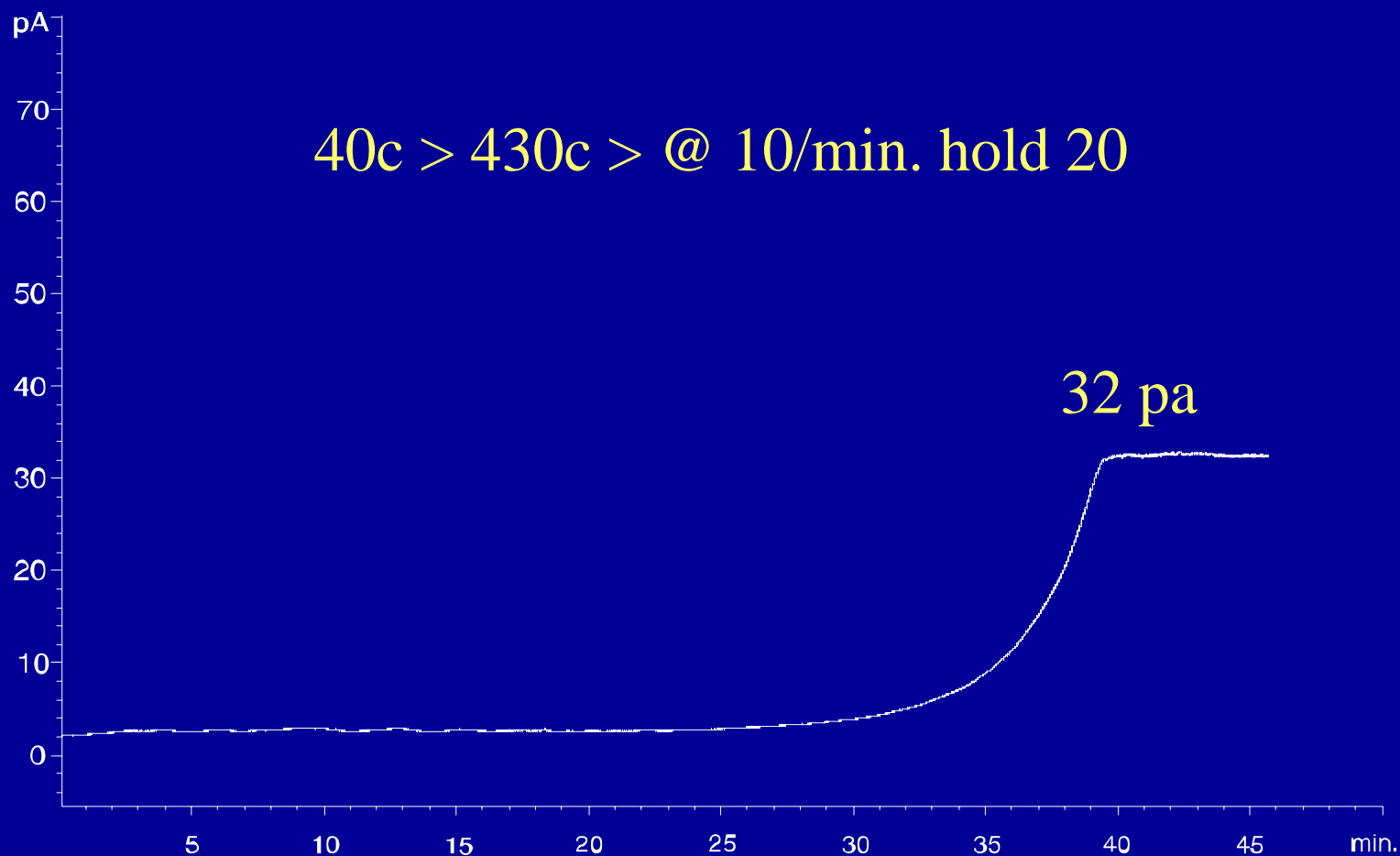
- Oven temperature: programmed 40c > 430c @ 10c/minute hold 10 minutes
- Carrier gas: He
- Inlet pressure: 1.0 psig
- Detector temp: 430c
- Injector temp: Cold on column. Oven track mode

# MXT-1HT Bleed Profile



# Competitor Bleed Profile

40c > 430c > @ 10/min. hold 20

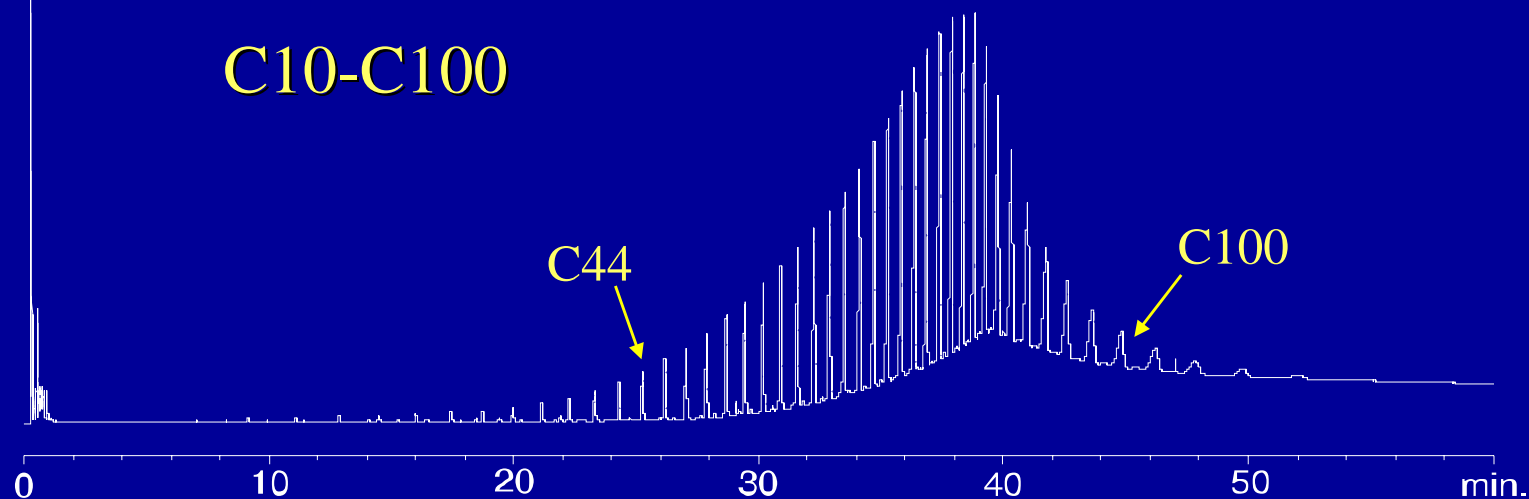




# MXT-1HT Polywax 1000 C<sub>10</sub>-C<sub>100</sub>

40c > 430c > @ 10/min. hold 20

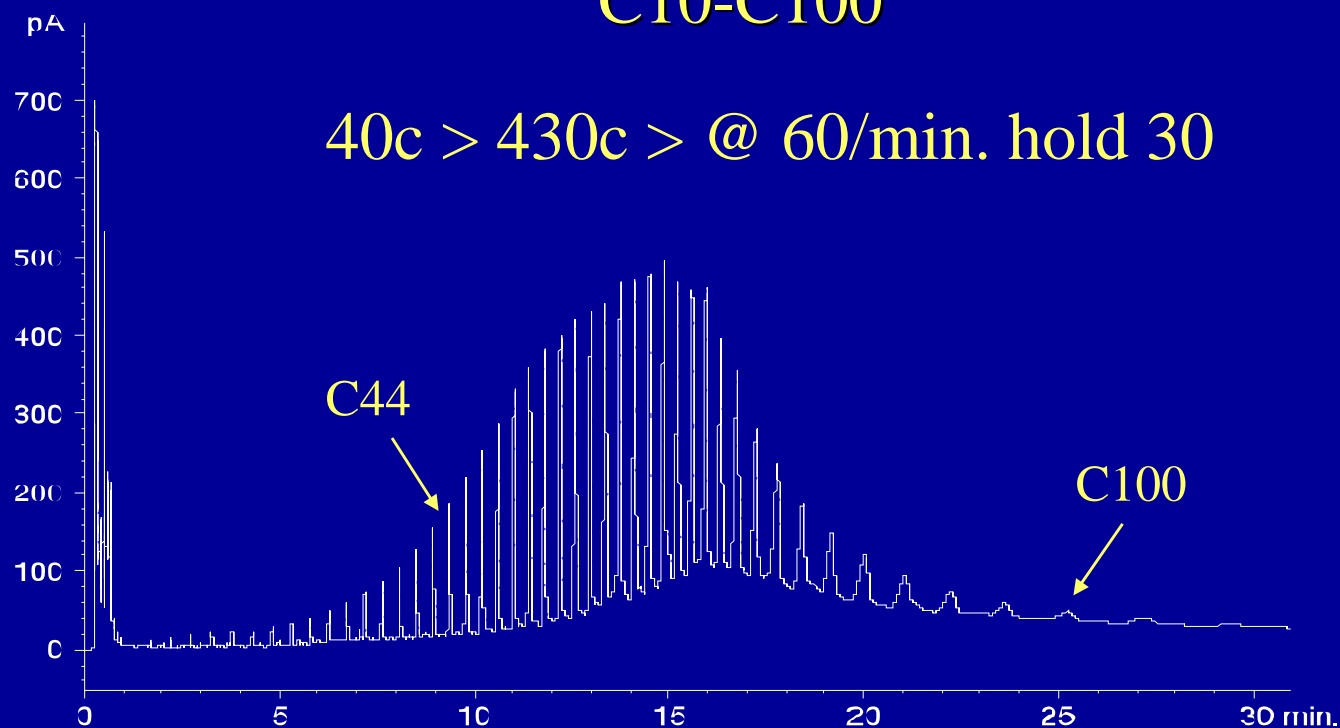
C<sub>10</sub>-C<sub>100</sub>



# Polywax 1000 60°C/ minute ramp rate

C10-C100

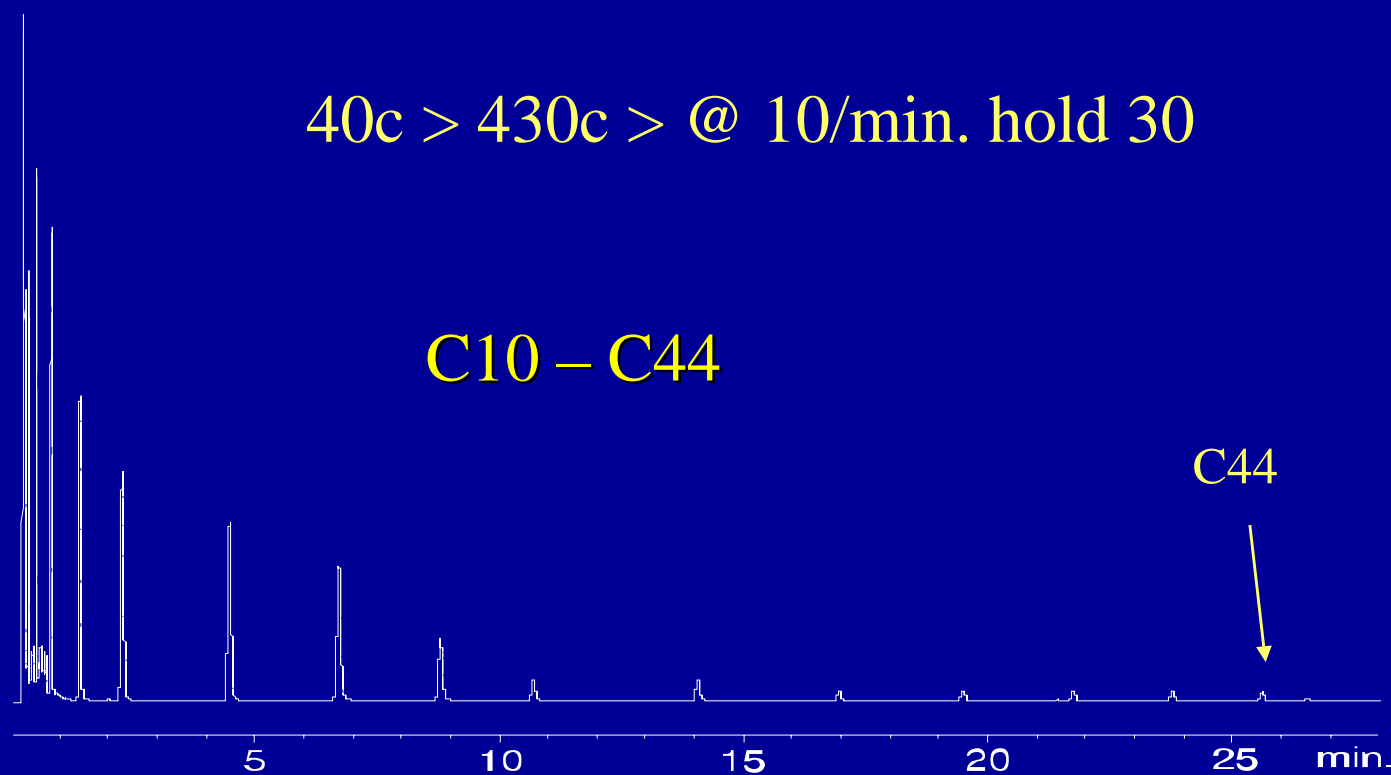
40c > 430c > @ 60/min. hold 30



# MXT-1HT

40c > 430c > @ 10/min. hold 30

C10 – C44



# MXT-1HT Strengths

- Advanced polymer manufacturing technology assures future reproducibility
- Column will not break
- Passive OD scoring will not weaken the column
- Column end will not fracture while inserting into cool on-column injectors, as with metal clad fused silica columns.

# Conclusion

- Boiling point resolution
- Out of the box technology
- 100% non-polar
- Retention time reproducibility
- Symmetry hydrocarbon peaks
- Low Column bleed
- Superior column longevity

# The Design of High Temperature Metal Capillary Gas Chromatography Column Based on Polydimethylsiloxane

Dinesh V. Patwardhan Ph. D., Barry Burger,  
Rick Morehead, Jarl Snider, Kristi Sellers,  
Chris Cox

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# Outline

Background

Column Bleed

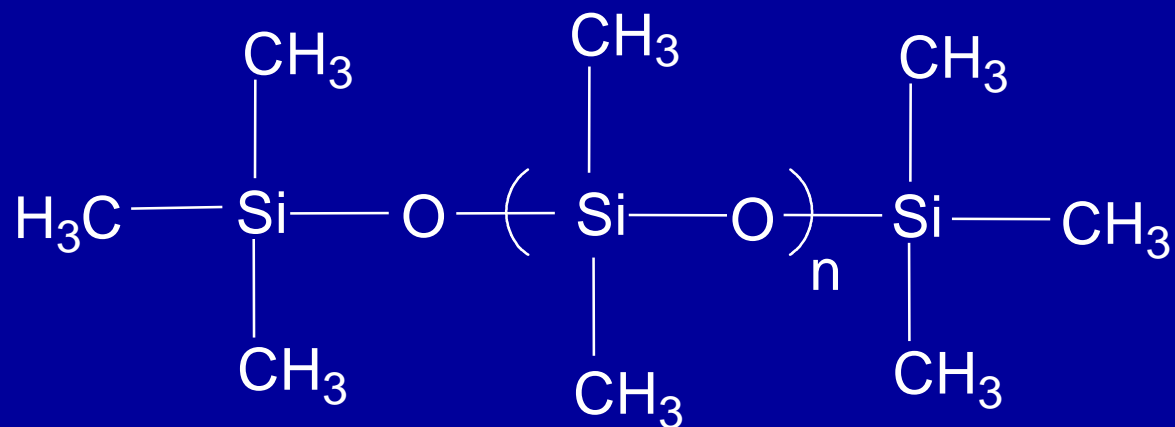
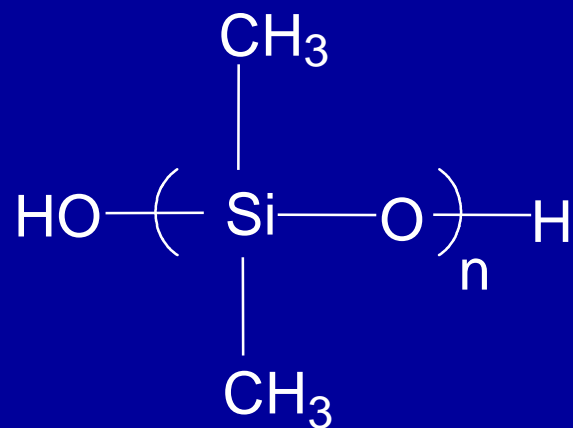
Column Selectivity

Unique Attributes of High Temperature Column

Applications

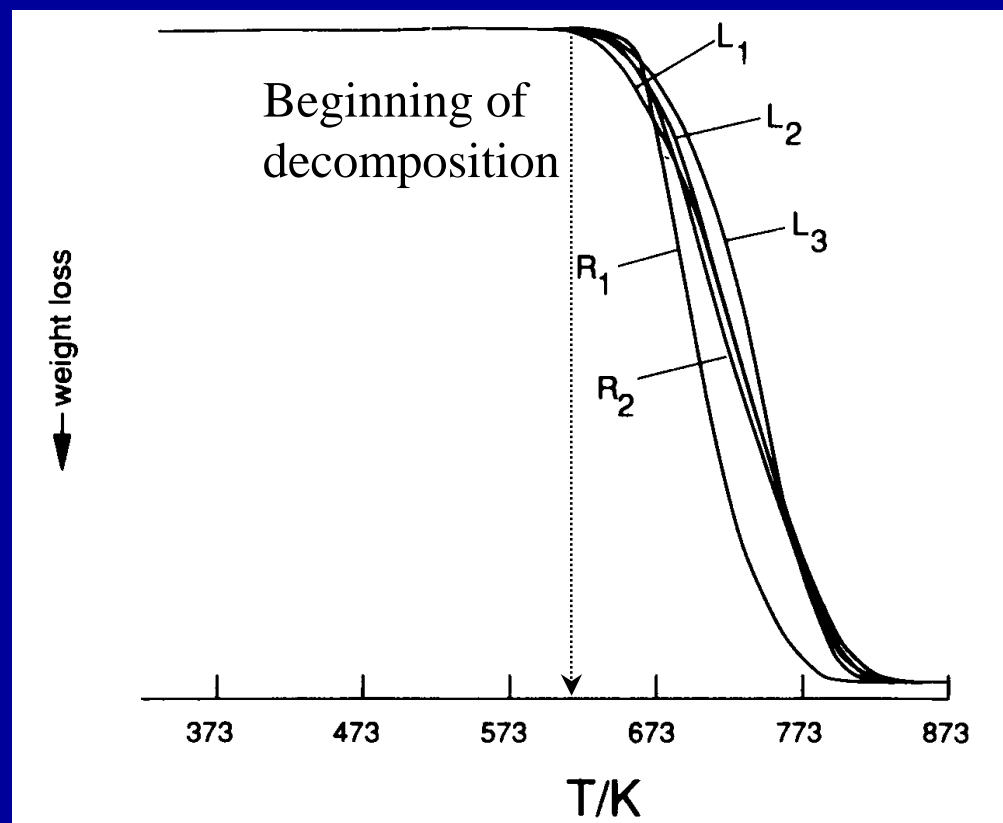
Conclusions

# Polydimethylsiloxane



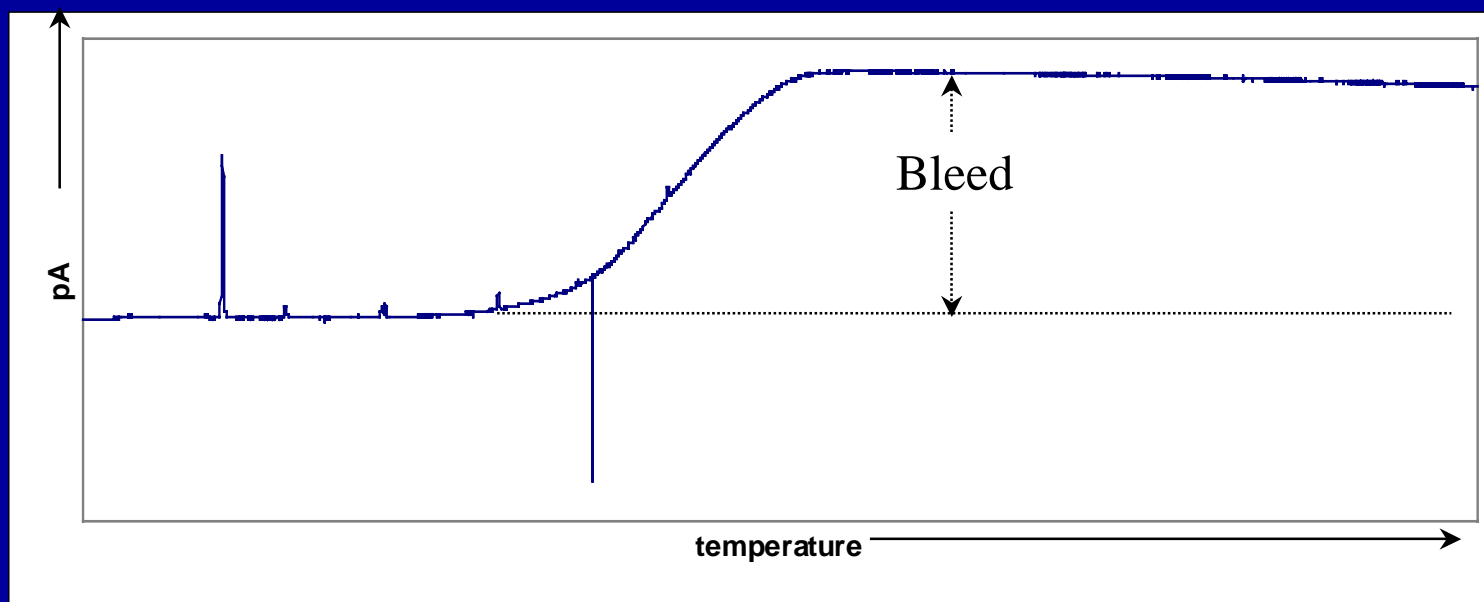


# Thermal Stability of PDMS



Adapted from Siloxane Polymers, ed. Clarson & Semlyen, 1993.

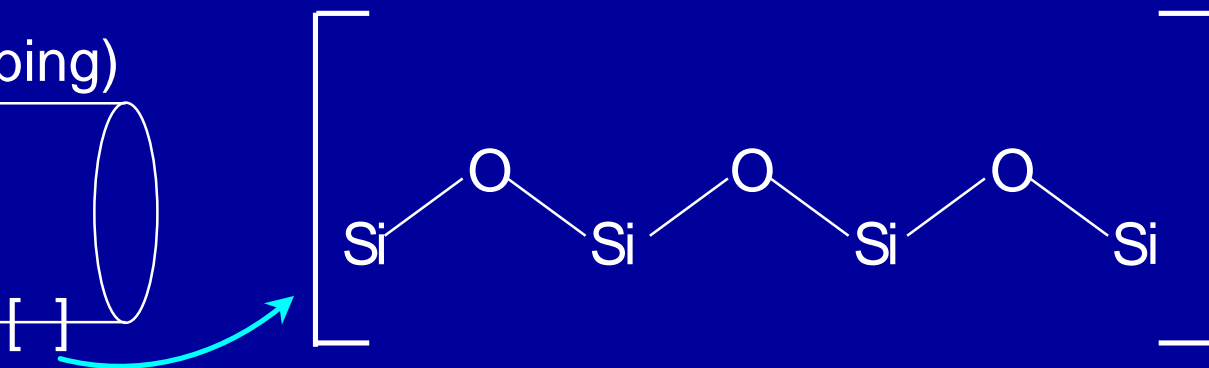
# Bleed



# Origin of Bleed

- Oligomers that are created in a column's lifetime

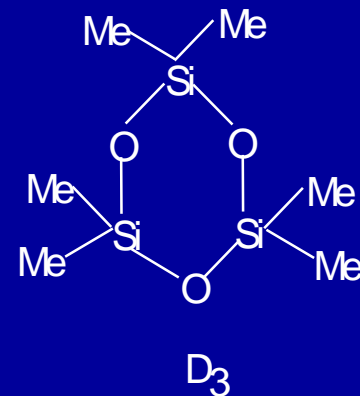
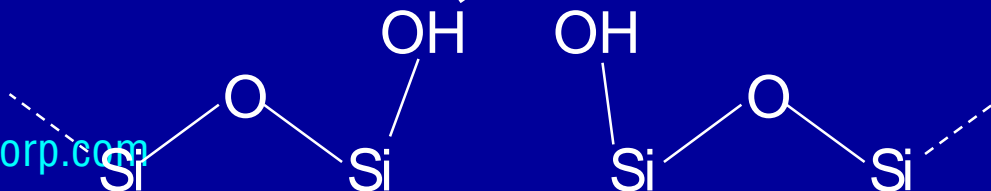
(FS tubing)



(polymer coating)

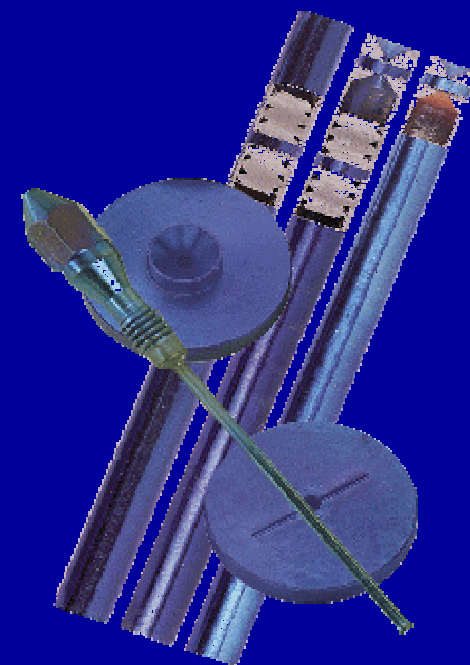
D<sub>3</sub>/D<sub>4</sub> bleed

PDMS



# Deactivation of Metal Columns

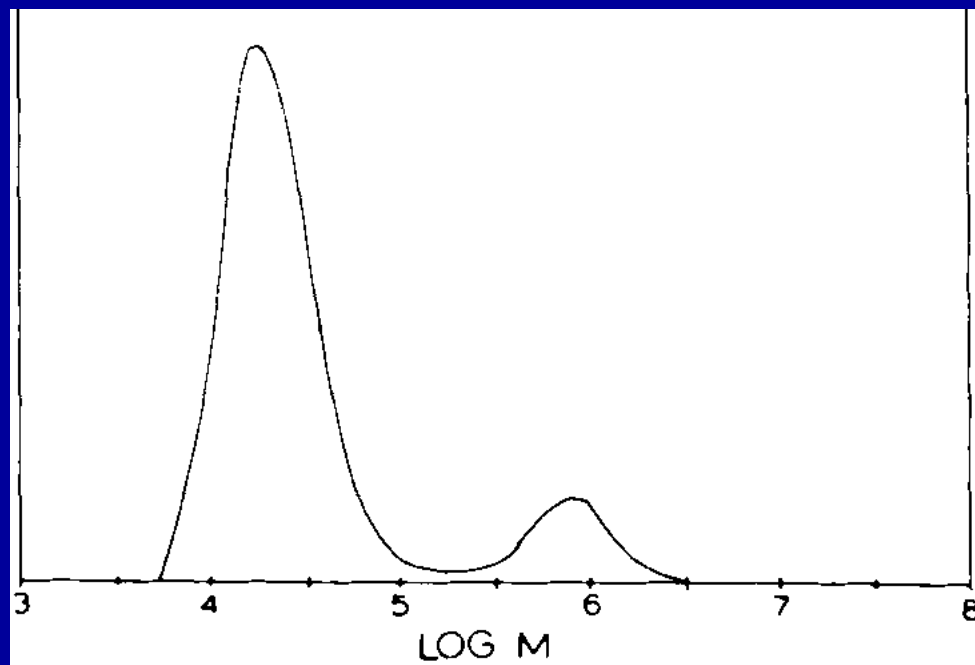
- We are using an advanced deactivation called Siltek™. It is a deposition process, unlike silazane or silicone deactivation.



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# Origin of Bleed

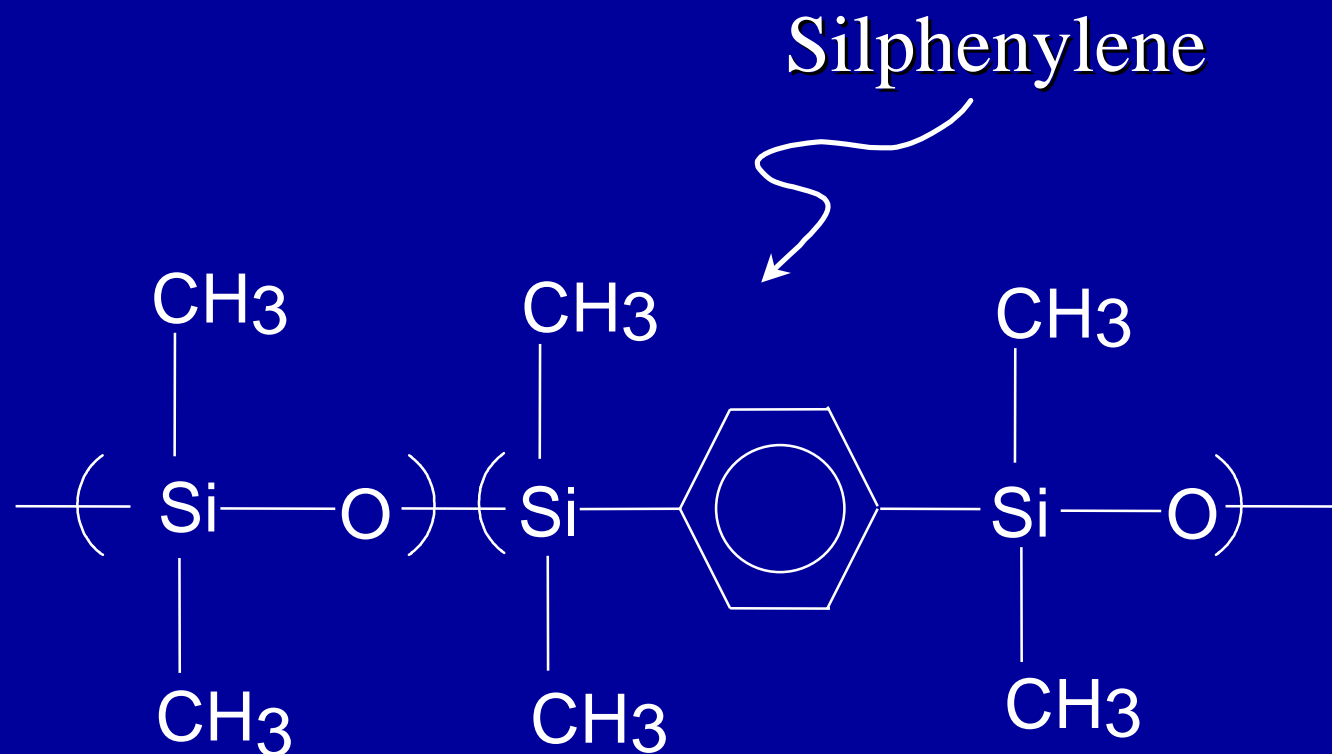
- Polymer Synthesis



Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.

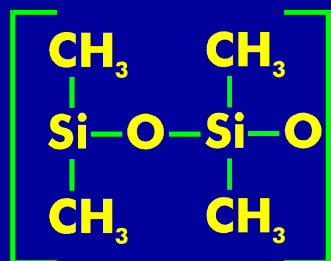
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# Enhancement of Thermal Stability by Using Additives

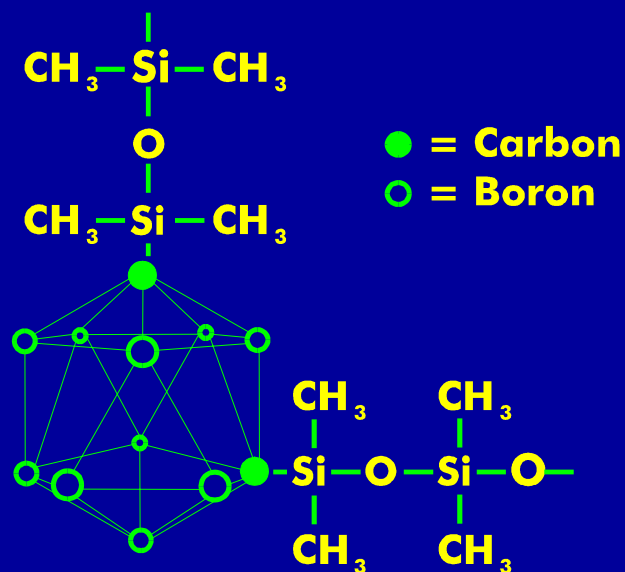


# Stationary Phases for High Temperature Simulated Distillation

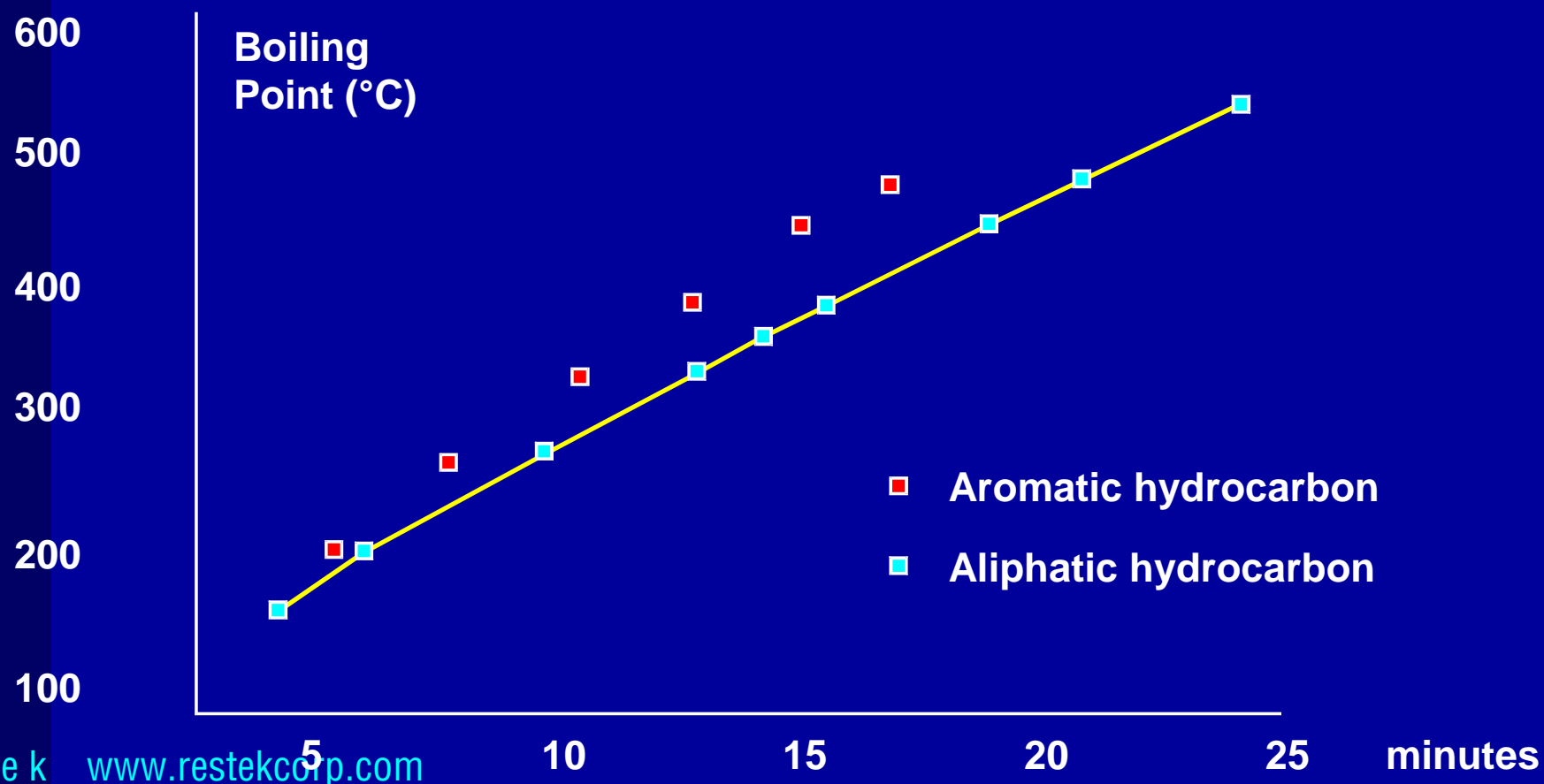
## Dimethyl Polysiloxane



## Carborane Dimethyl Polysiloxane

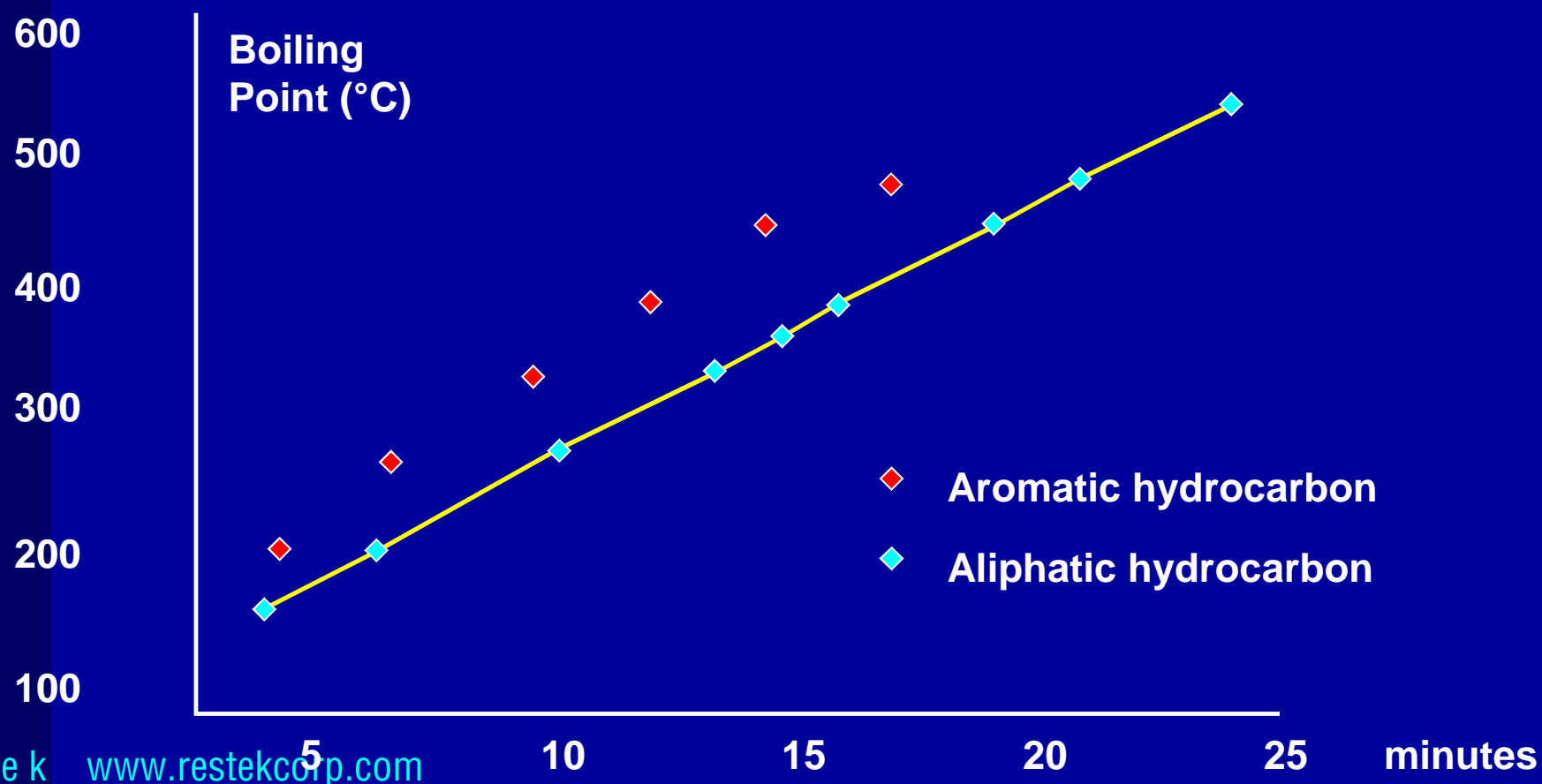


# Retention According to BP methyl silicone





# Retention According to BP carborane



# Published vs Calculated BP for Aromatics

Compound	Published BP (°C)	Calculated BP	
		Dimethyl <u>Polysiloxane</u>	Carborane Dimethyl <u>Polysiloxane</u>
naphthalene	217	201	180
acenaphthalene	279	249	222
phenanthrene	340	300	275
anthracene	340	302	277
pyrene	393	342	321
chrysene	448	382	363
benzo-a-pyrene	477	414	410

# High Temperature Simulated Distillation

- ASTM Method D 6352-02 is used for the determination of the boiling range distribution of petroleum distillate fractions.
- The method specifies the use of a short, wide bore, thin film capillary column.
- The upper temperature of the analysis is set at 400°C.

# Column Design

- Method criteria: 5 m x 0.53mm ID x 0.10um
- Stainless steel tubing
- Treated with Siltek Deactivation
- A high temperature, non-polar stationary phase was developed that was able to withstand 430°C while producing minimal bleed.
- Matching the McReynolds requirements of the method.

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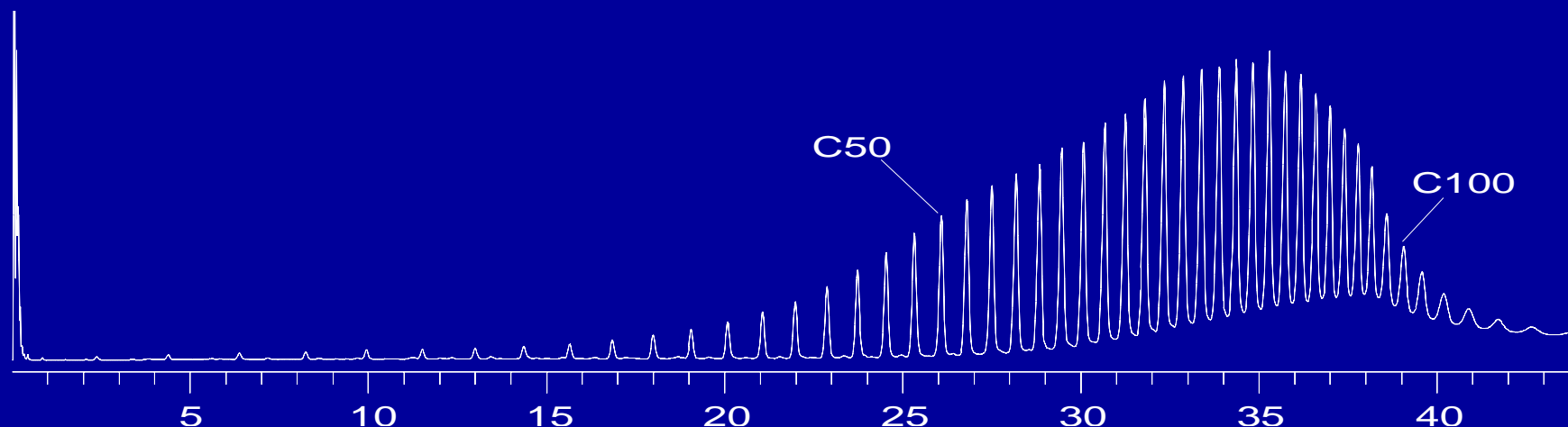
# Experimental Design

- A lifetime study was performed by repetitively injecting a standard mixture designed for ASTM D2887 calibration.
- A Polywax 1000 sample was injected and resolution between C50 and C52 was calculated according to the method.
- Record kept of the retention time for C52 and the bleed at 430°C over the course of the experiment.
- Repeated until the column resolution fell below ASTM D6352-02 specifications.

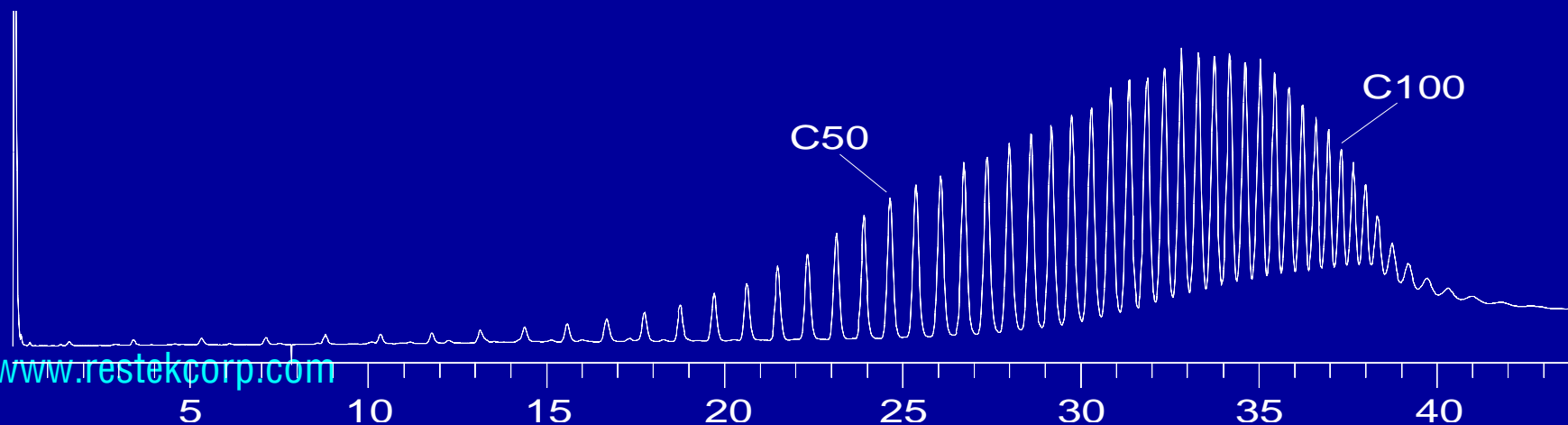
# GC Conditions

- D2887 sample
  - 40°C to 430°C at 70°C/minute
  - Hold at 430°C for 10 minutes
- Polywax 1000 sample
  - 50°C to 430°C at 10°C/ minute
  - Hold at 430°C for 6 minutes
- Carrier Gas – Helium, 1.8psi (14ml/min)
- Sample – 0.2uL, 2% sample in Carbon Disulfide
- Cold On Column Injection with Oven Tracking

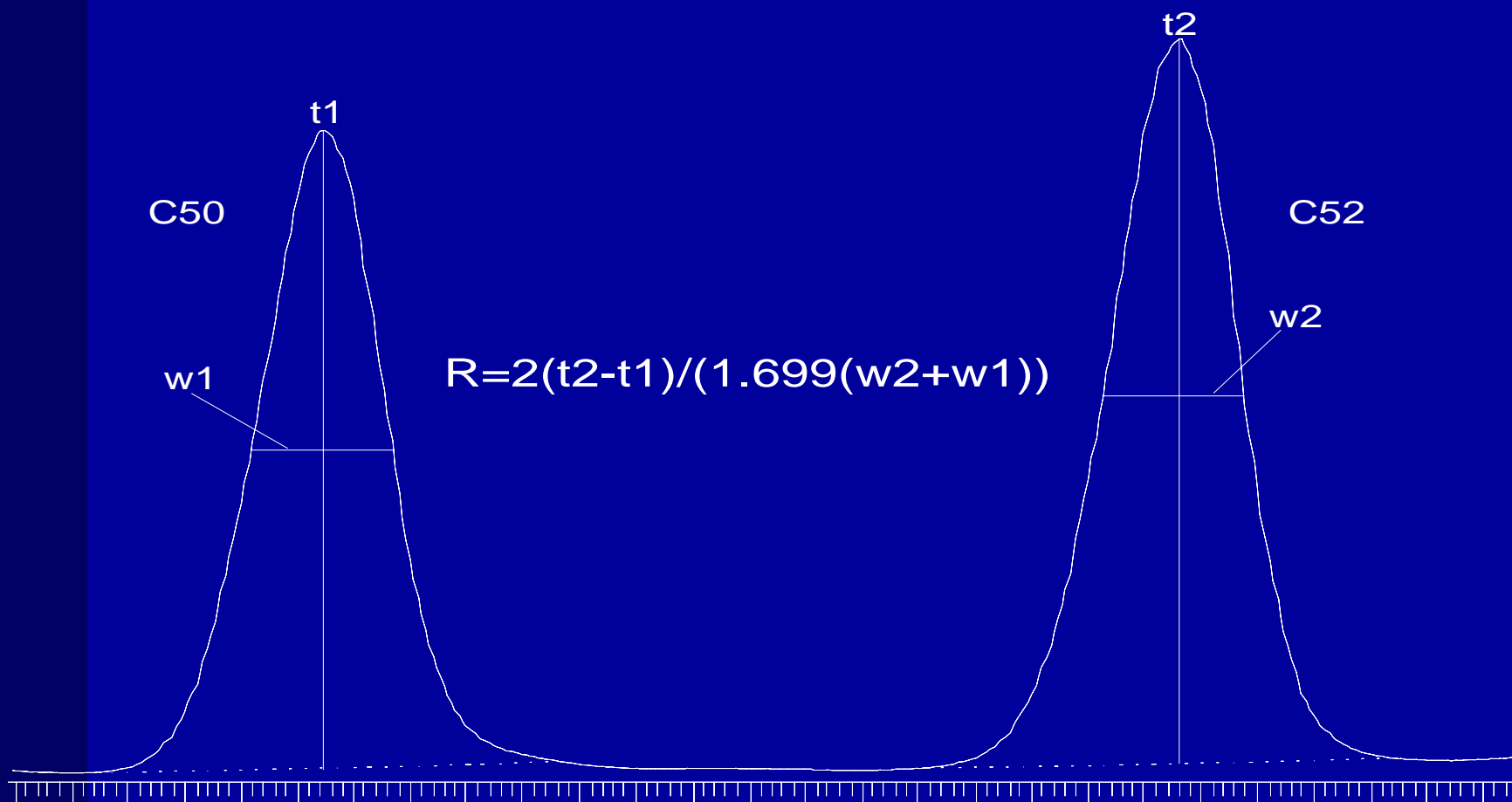
## Polywax 1000 – Run #1



## Polywax 1000 – Run #400



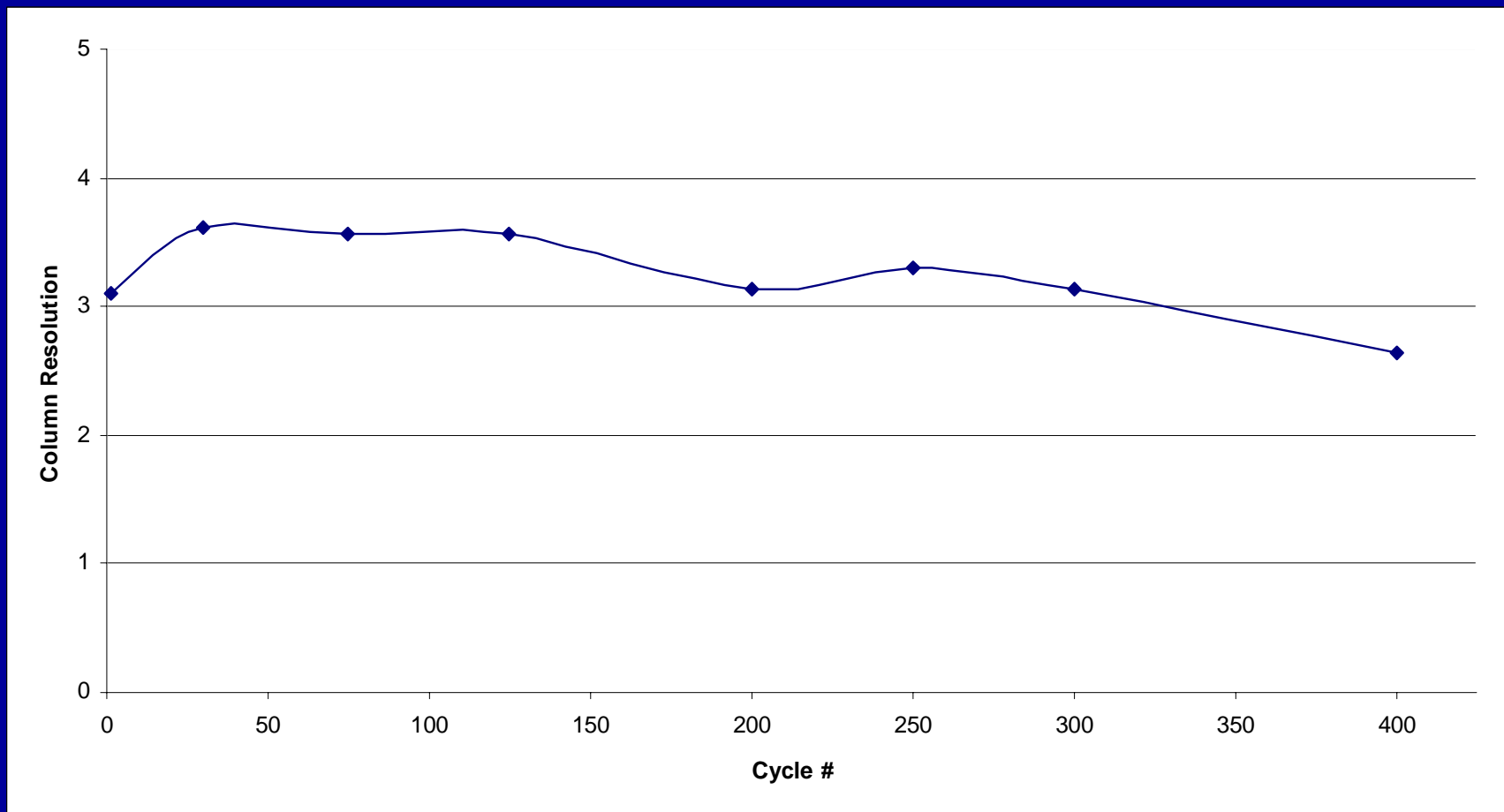
# C50 / C52 Resolution – Run #1



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# C50 / C52 Resolution

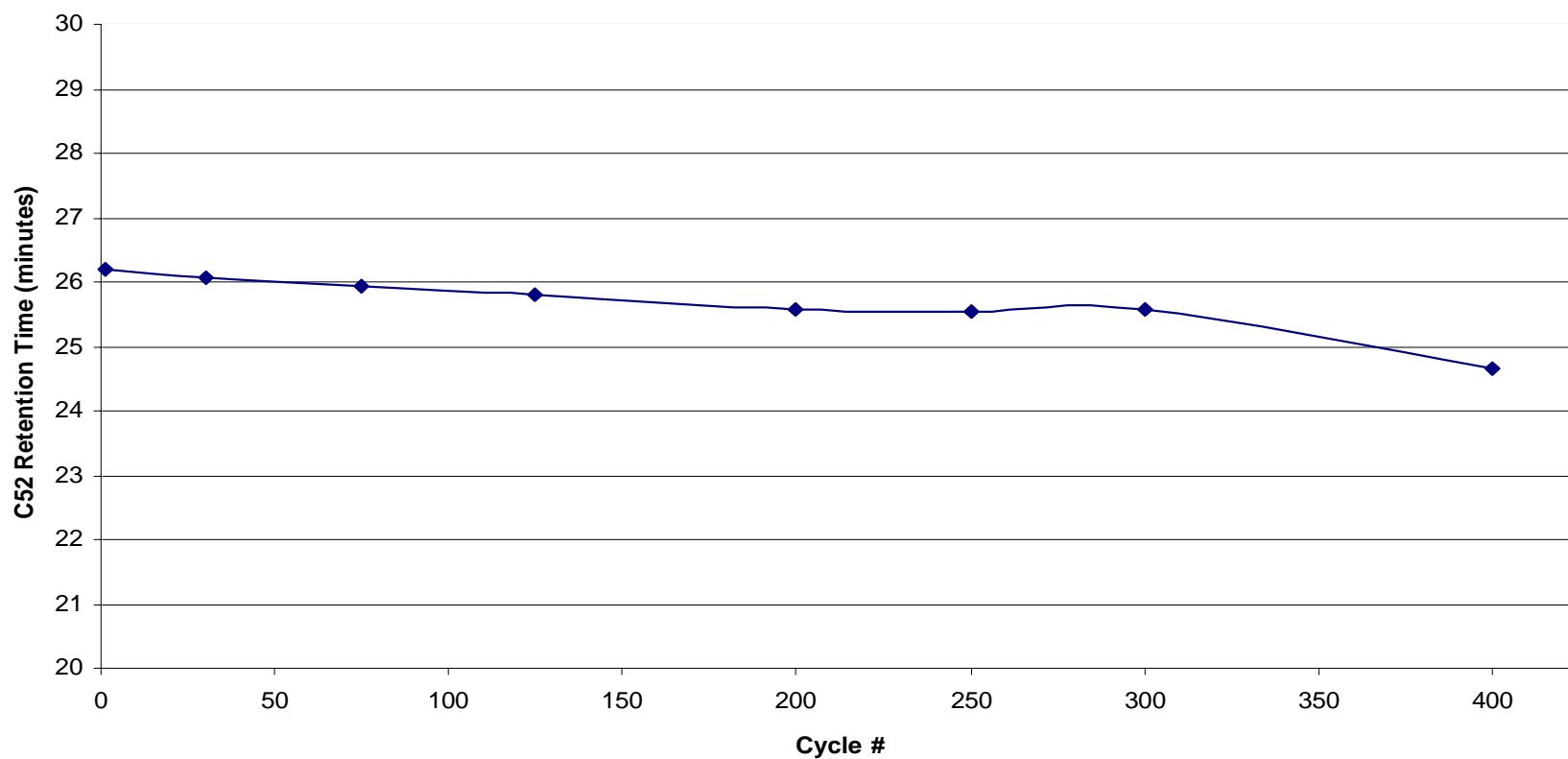


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# C52 Retention Time Stability



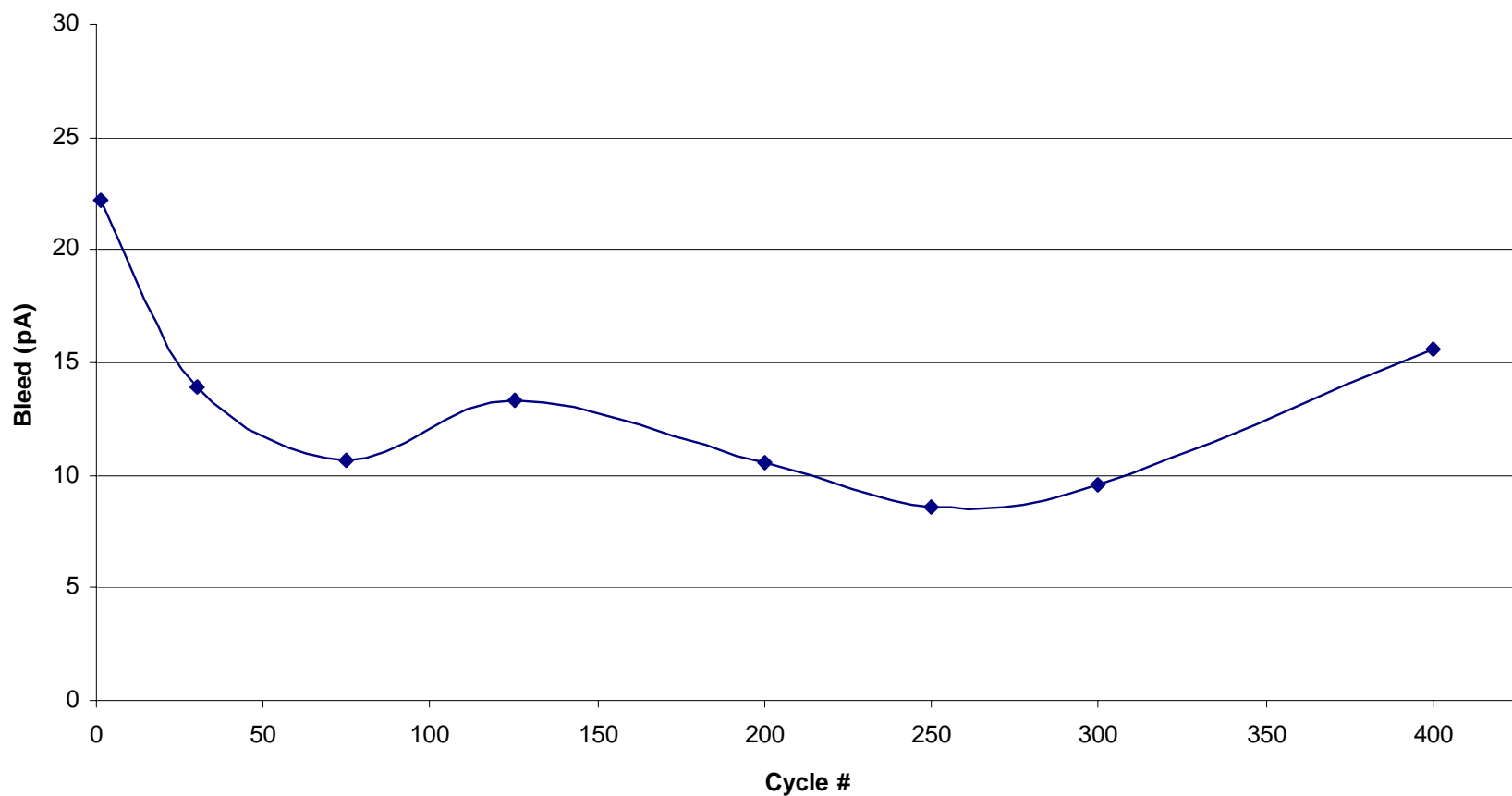
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# Column Bleed Stability



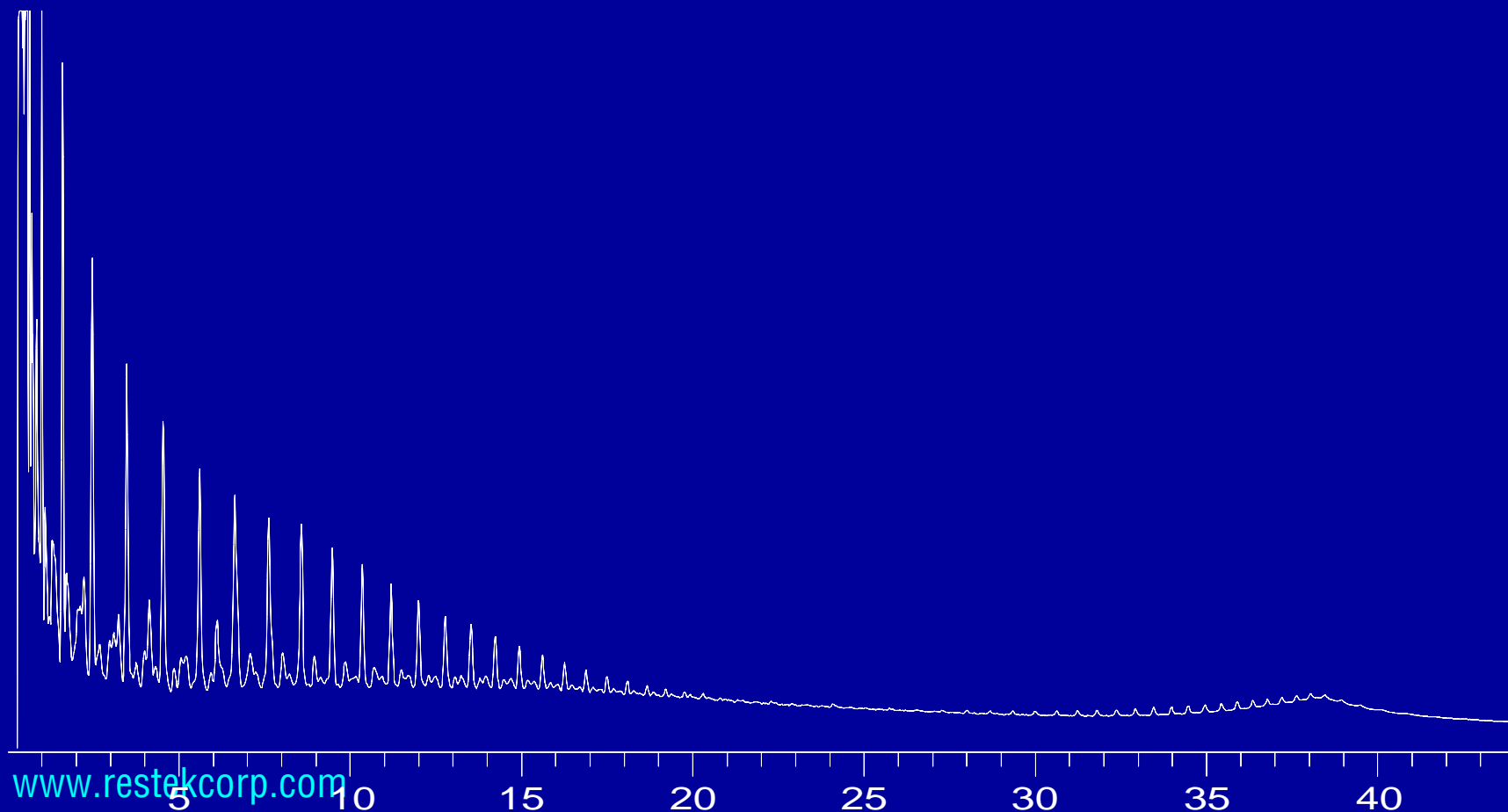
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# Pennsylvania Light Crude Oil



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## Summary

- The MXT-1HT column demonstrates superior performance due to Siltek Deactivation and our in-house polymer synthesis.
- The MXT-1HT has the selectivity of polydimethylsiloxane.
- Able to withstand 400 cycles at 430°C and still retain good column efficiency and low bleed.
- Column demonstrated low bleed and adequate separating efficiency to resolve hydrocarbons in a crude oil sample.

# A NEW APPROACH TO CONFIRMING ORGANIC VOLATILE IMPURITY TESTING IN PHARMACEUTICAL PRODUCTS.

BECKY WITTRIG, Ph.D., CHRIS M.  
ENGLISH, & FRANK L. DORMAN, Ph.D.



# Application: Residual Solvents

- Pharmaceutical Formulations
- Guidelines for Testing
  - ◆ International Conference on Harmonization
  - ◆ European Pharmacopoeia
- Compound Lists Vary
  - ◆ Over 60 compounds of regulatory interest
  - ◆ Classes based on toxicities
  - ◆ Resolution of large lists on a single stationary phase can be extremely difficult

# The Three Approaches:

- Existing Phases Evaluated
- Modeling for a New Stationary Phase
- Stop-Flow GC Technology
  - ◆ Using Existing RT Data
  - ◆ Applying RT Data for Stop-Flow



# Existing Phases Evaluated

- Change in selectivity
- Low bleed
- Critical resolution
- FID or MS detection

u Column Design.



# GC Analysis of OVI by USP <467>

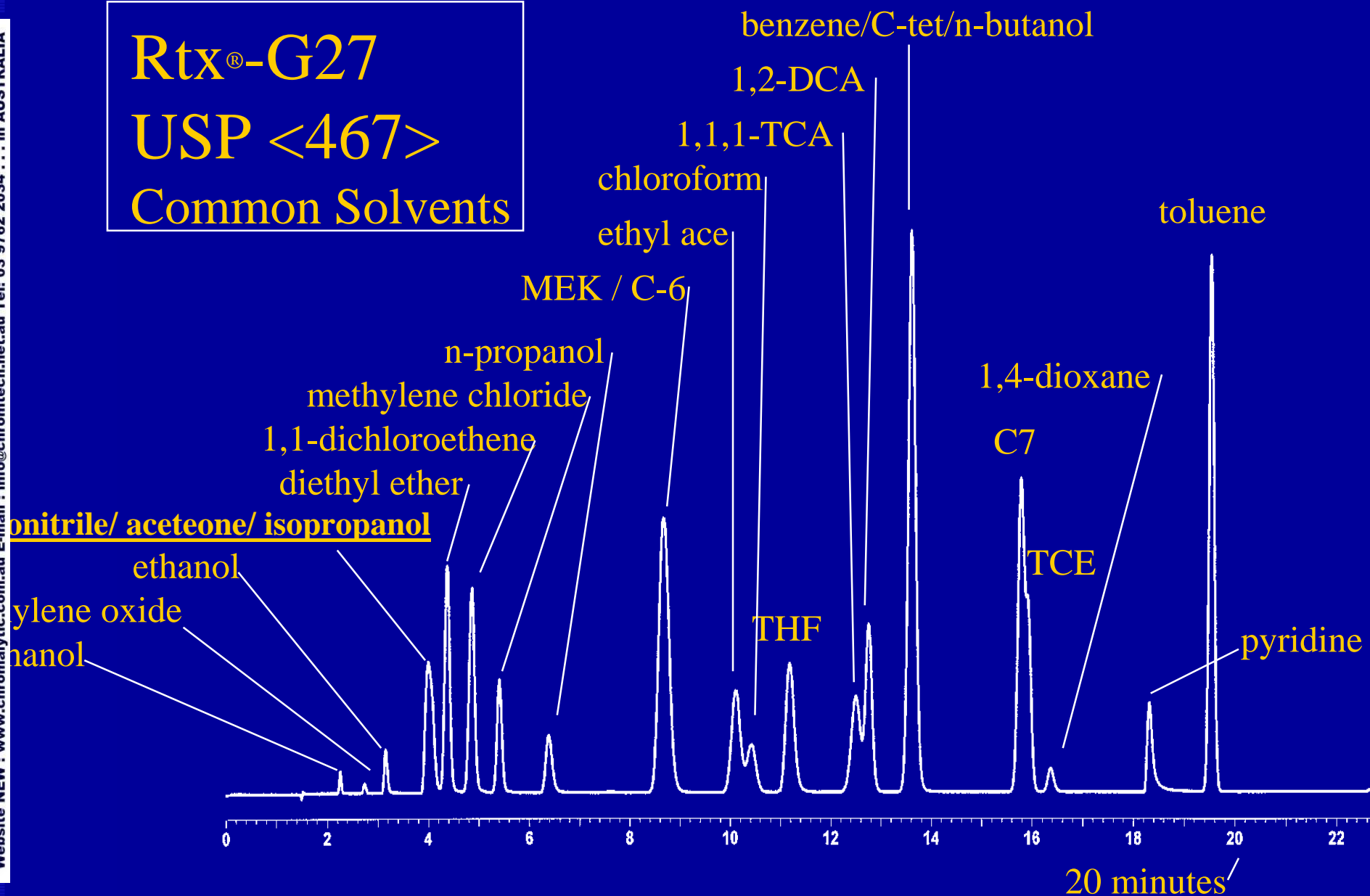
- Method I: G27 30m x 0.53mm x 5.0 df
  - ◆ Direct Aqueous
- Method IV: G43 30m x 0.53mm x 3.0 df
  - ◆ Static Headspace
- Method V: G43 30m x 0.53mm x 3.0 df
  - ◆ Direct Aqueous
- Method VI: choice of 9 columns, depending on monograph

# Rtx®-G27 USP <467> Common Solvents

Australian Distributors  
Importers & Manufacturers  
www.chromtech.net.au

Website NEW : www.chromalytic.com.au E-mail : info@chromtech.net.au Tel: 03 9762 2034 . . . in AUSTRALIA

CHROMALYTIC  
EChnology Pty Ltd

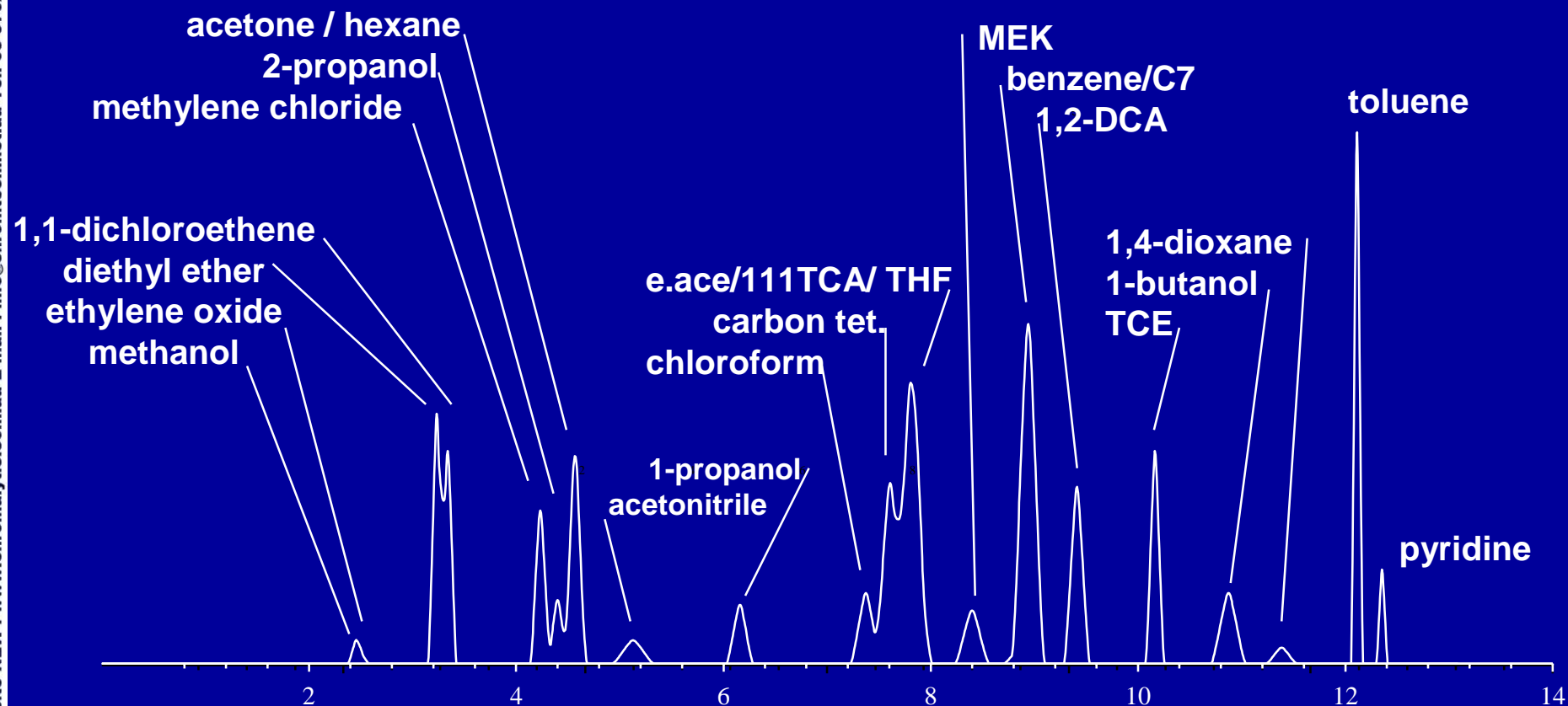


# The Rtx-G27 Unresolved

- acetonitrile (II), acetone (III), IPA (III)
- MEK (III), C6 (II)
- benzene (I), carbon tet. (I), n-butanol (III)
- C7 (III), TCE (II)

# Rtx<sup>®</sup>-VGC

## USP <467> Common Solvents

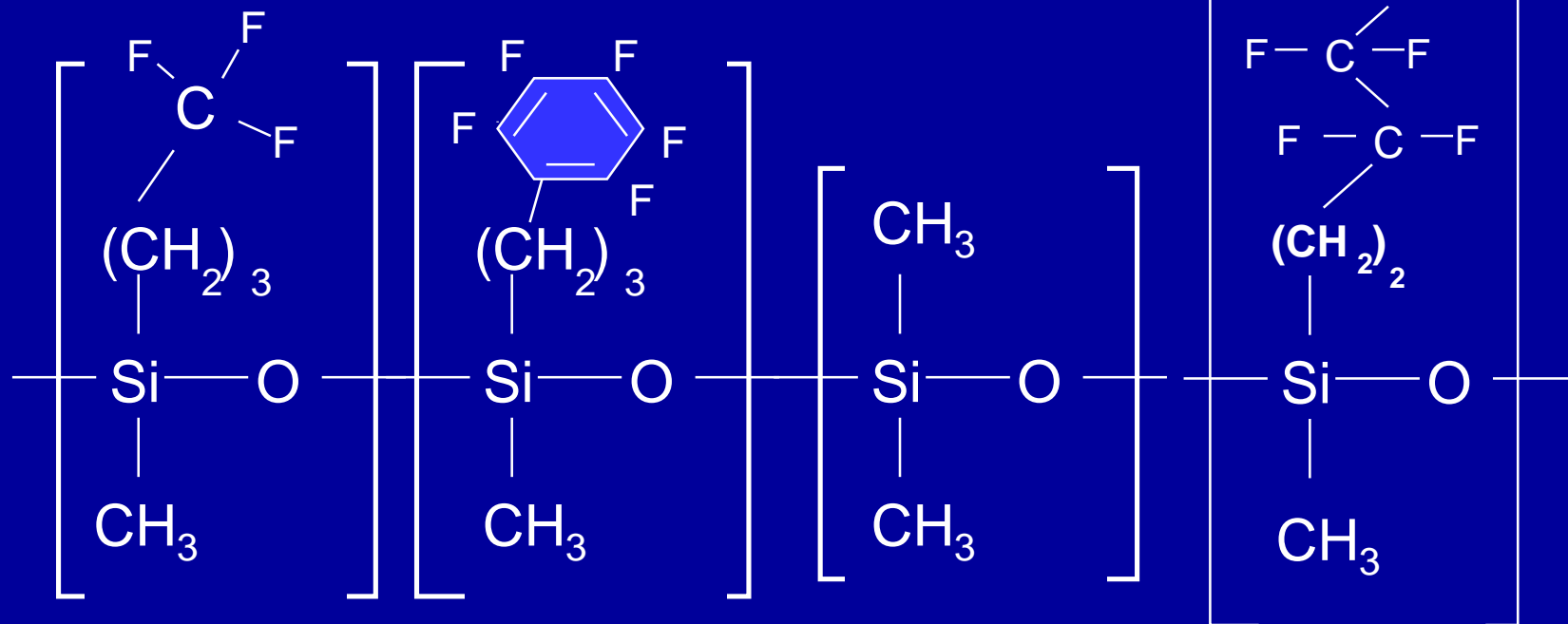


# The Rtx-VGC Unresolved

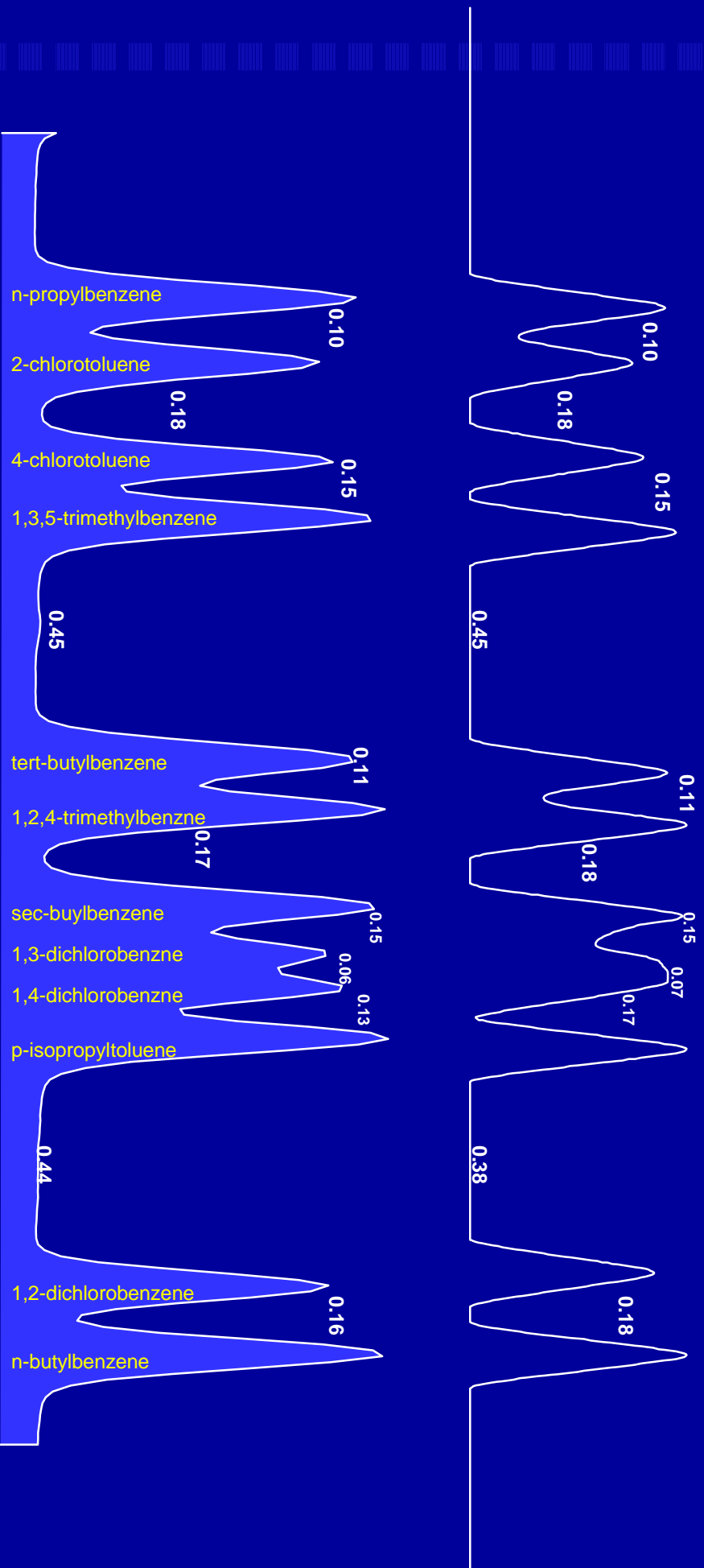
- acetone (III), C6 (II)
- E.ace (III), 111TCA (I), THF (III)
- benzene (I), C7 (III)

# Experimental Fluorinated Phase

## Bonded Polymer Examined for GC Applications.



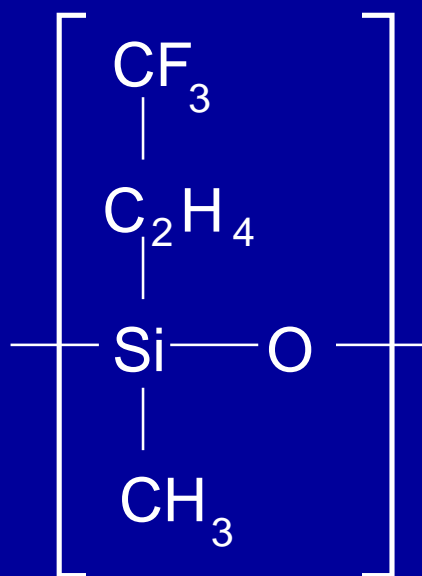
# Modeling for a New Bonded Phase



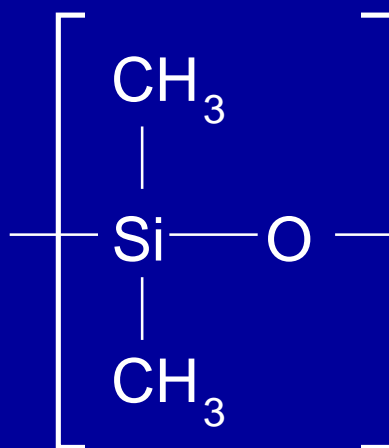


# Stationary Phases Used for Modeling

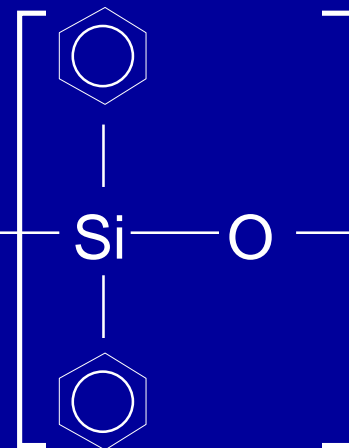
trifluoropropylmethyl  
polysiloxane



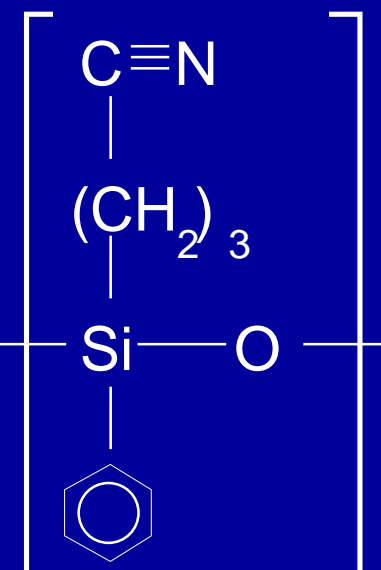
dimethyl  
polysiloxane



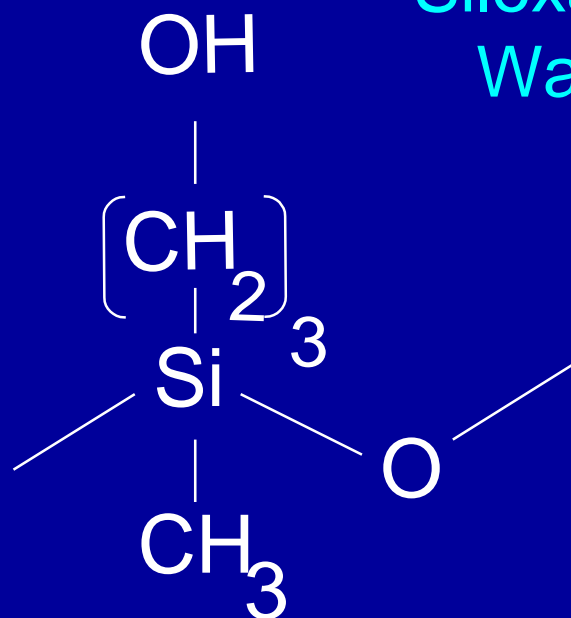
diphenyl  
polysiloxane



cyanopropylphenyl  
polysiloxane

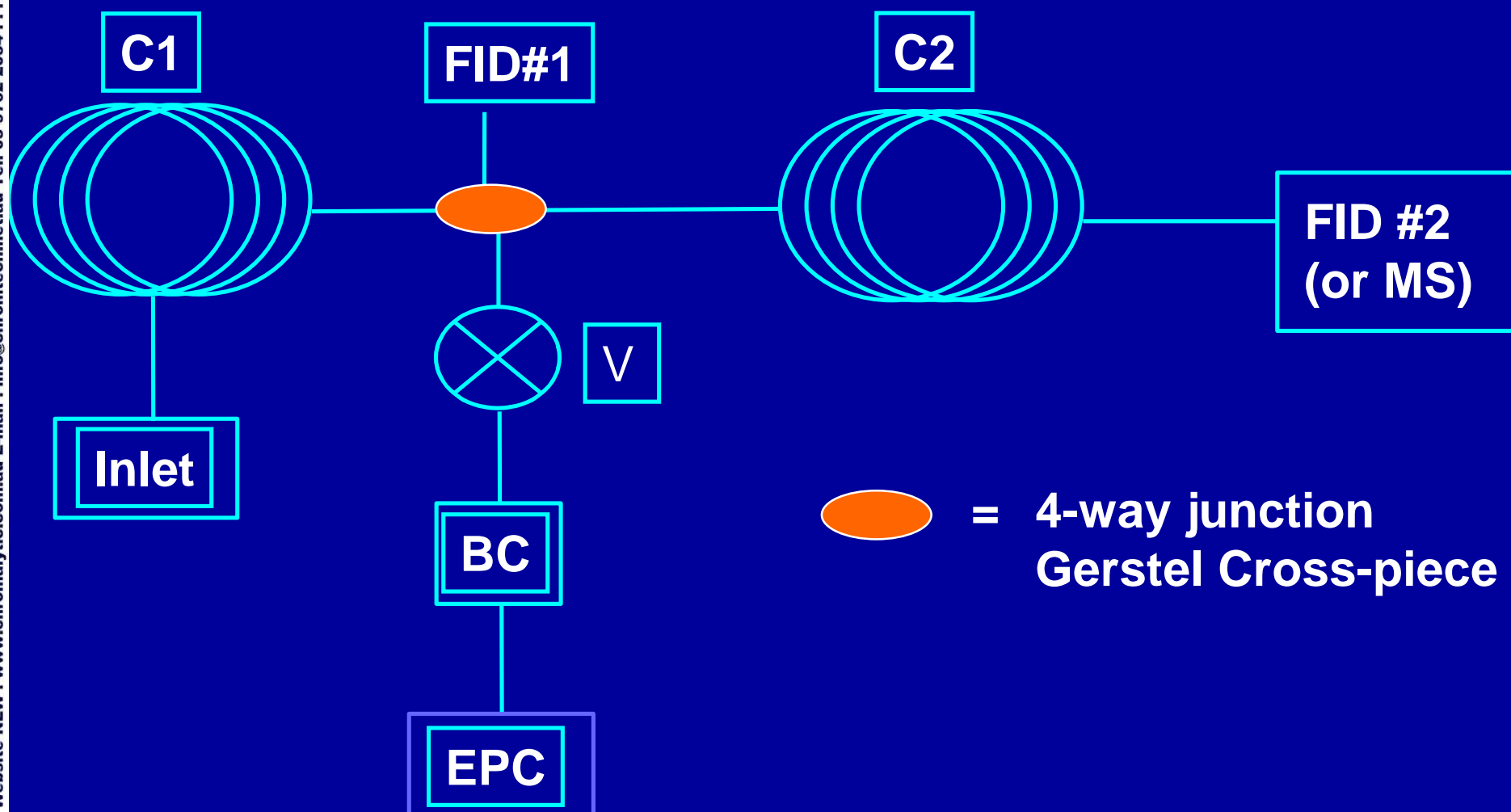


# 1-hydroxypropyl-methyl



Experimental  
Siloxane-based  
Wax Phase

# Stop Flow GC System: Sacks, et. al.\*



\*Richard Sacks, University of Michigan

# Summary of Stop-Flow GC

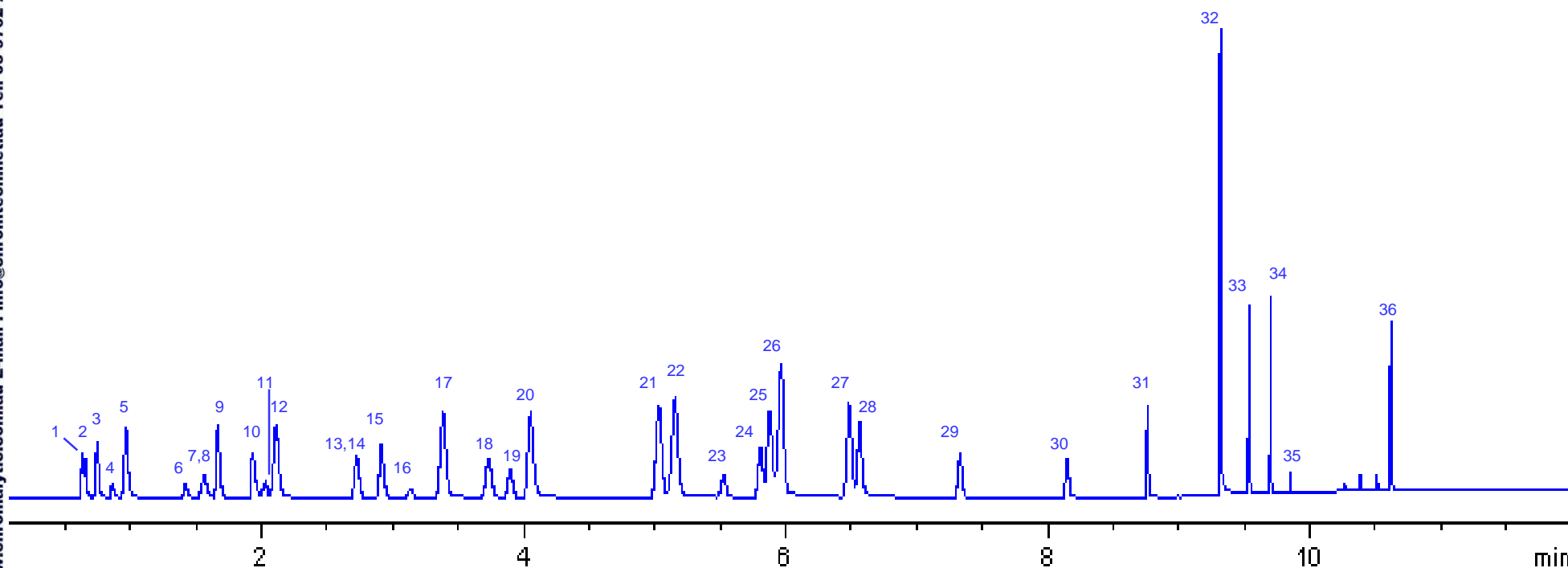
- Ability to “Tune” the Selectivity
- Flexibility
  - ◆ Standard dimension columns
  - ◆ Can vary the pulse sequences
- Significant Improvements in Analysis Times Possible
  - ◆ Fast oven programs, high flow rates

# Class I & II Residual Solvents

Peak #	Compound	Peak #	Compound
1	2-methylpentane	19	1,2-dichloroethane (1,2-DCA)
2	hexane	20	2-hexanone (MBK)
3	methyl cyclopentane	21	p-xylene
4	1,1-dichloroethene (1,1-DCE)	22	m-xylene
5	methyl cyclohexane	23	nitromethane
6	<i>trans</i> -1,2-dichloroethene	24	2-methoxyethanol
7	carbon tetrachloride (CCl <sub>4</sub> )	25	pyridine
8	1,1,1-trichloroethane (1,1,1-TCA)	26	o-xylene
9	methanol	27	chlorobenzene
10	1,2-dimethoxyethane	28	2-ethoxyethanol
11	methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	29	1,1,2-trichloroethane (1,1,2-TCA)
12	benzene	30	dimethyl formamide (DMF)
13	<i>cis</i> -1,2-dichloroethene	31	N,N-dimethylacetamide (DMA)
14	trichloroethene (TCE)	32	1,2,3,4-tetrahydronaphthalene (THN)
15	acetonitrile (MeCN)	33	ethylene glycol (EG)
16	chloroform	34	1-methyl-2-pyrrolidinone (1-MP)
17	toluene	35	formamide
18	1,4-dioxane	36	sulfolone

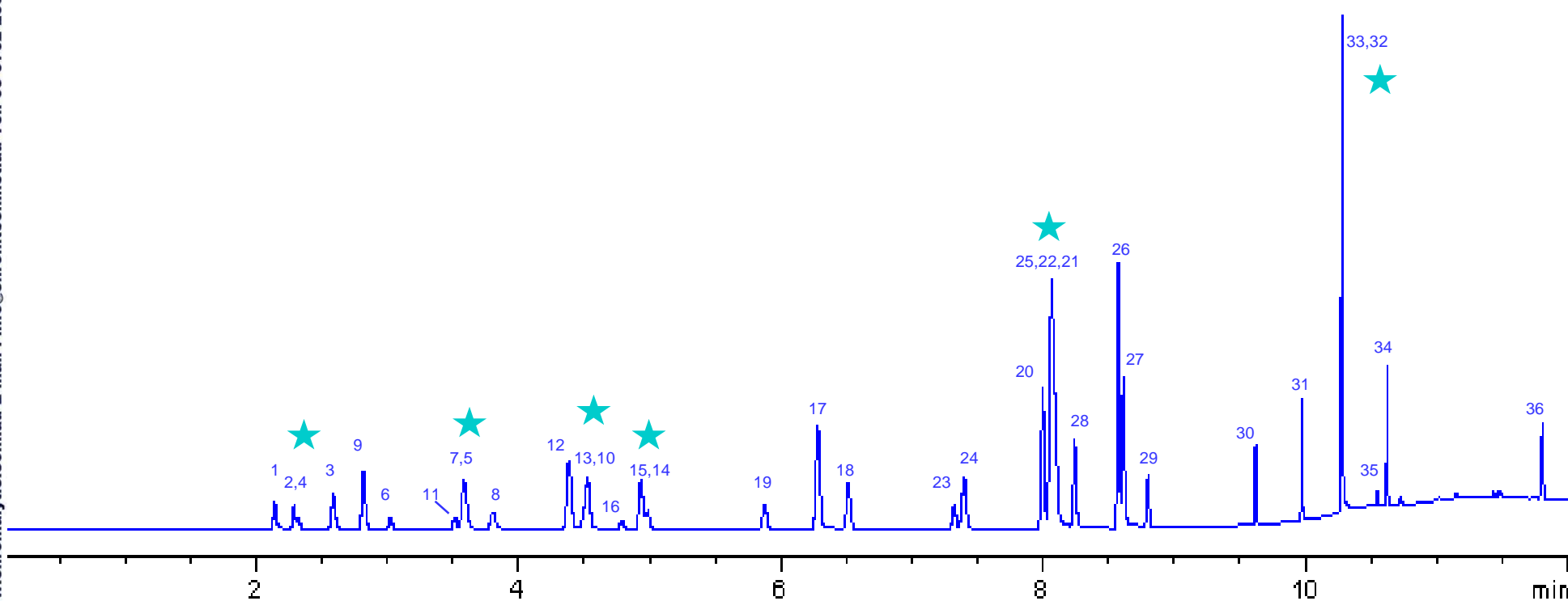
# Fast Run Conditions: 1<sup>st</sup> FID

After Rtx-Stabilwax, 15m x 0.25mm x 0.5 $\mu$ m



# Fast Run Conditions: 2<sup>nd</sup> FID

## After Rtx-Stabilwax + Rtx-200 (30m x 0.25mm x 1.0 $\mu$ m)



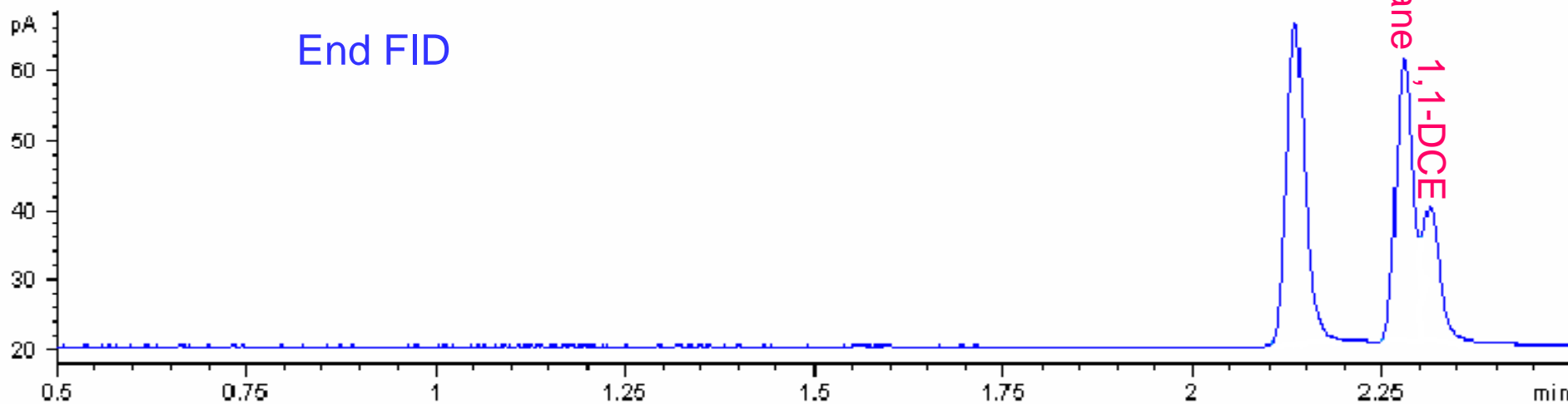
## Residual Solvents: Run Conditions

	<i>Standard Procedure</i>	<i>Fast Procedure</i>
<b>Analytical Columns</b>	<b>Stabilwax</b> 15m x 0.25mm, 0.5 $\mu$ m Rtx-200 30m x 0.25mm, 1 $\mu$ m	<b>Stabilwax</b> 15m x 0.25mm, 0.5 $\mu$ m Rtx-200 30m x 0.25mm, 1 $\mu$ m
<b>Oven Program</b>	40°C (6 min. hold) to 100°C at 4°C/min., to 220°C at 15°C/min., 5 min. hold	40°C (1 min. hold) to 65°C at 6°C/min., to 100°C at 12°C/min., to 250°C at 70°C/min., 1.8 min. hold
<b>Column Flow</b>	1.5 mL/min. constant flow	2.5 mL/min. to 9.5 min. 3.5 mL/min. at 10 min.
<b>Injector</b>	230°C	230°C
<b>Injection</b>	0.2 $\mu$ L HS, 200:1 split	0.2 $\mu$ L HS, 200:1 split
<b>Detectors</b>	Dual FIDs @ 250°C	Dual FIDs @ 250°C

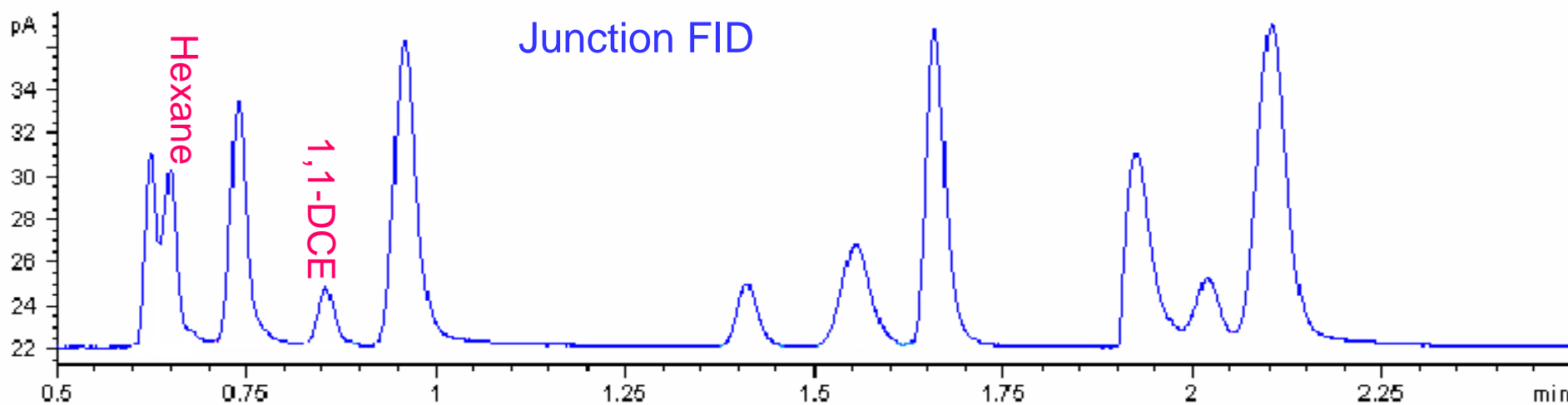


# Class I & II Residual Solvents: No Pulses

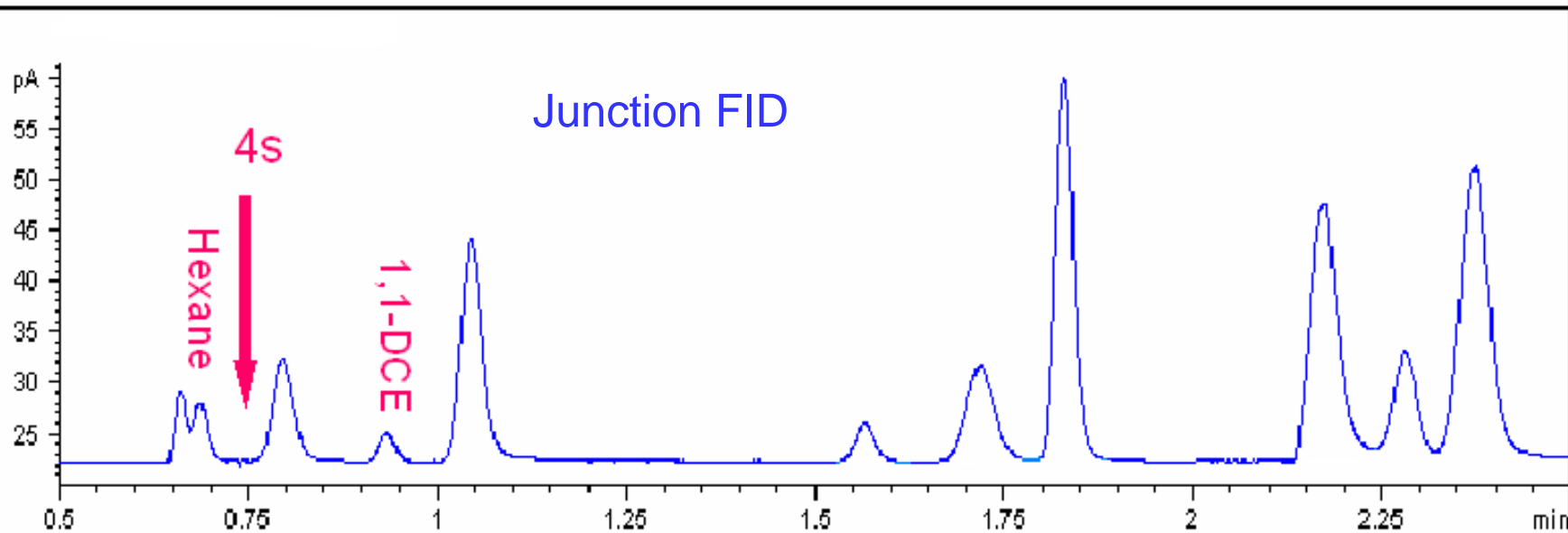
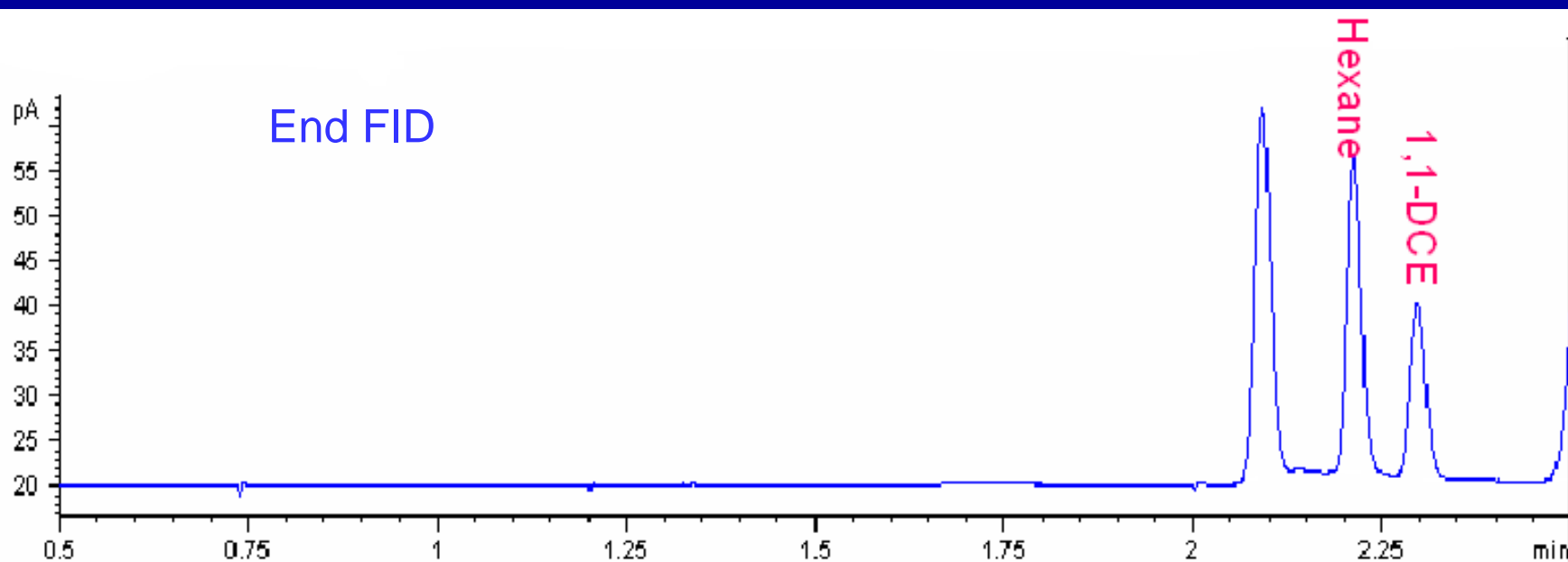
End FID



Junction FID



## Residual Solvents: Pulse @ 44 sec.



# Residual Solvents: No Pulses

End FID

CCl<sub>4</sub> + methylcyclohexane

1,1,1-TCA

CH<sub>2</sub>Cl<sub>2</sub>

methylcyclohexane

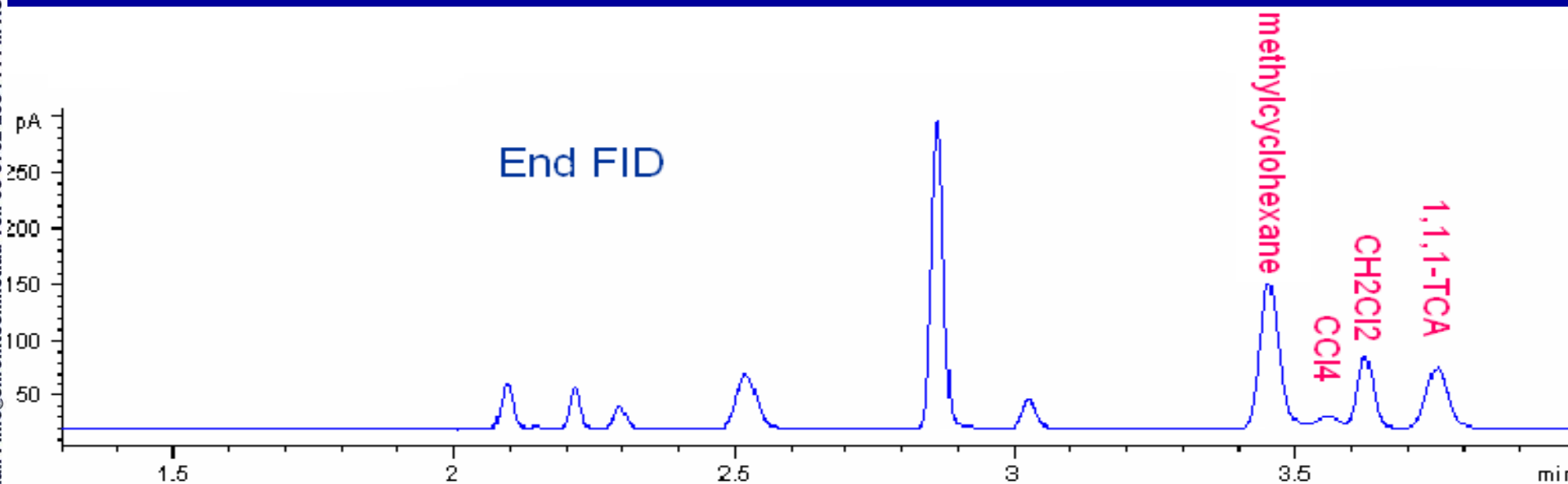
Junction FID

CCl<sub>4</sub> + 1,1,1-TCA

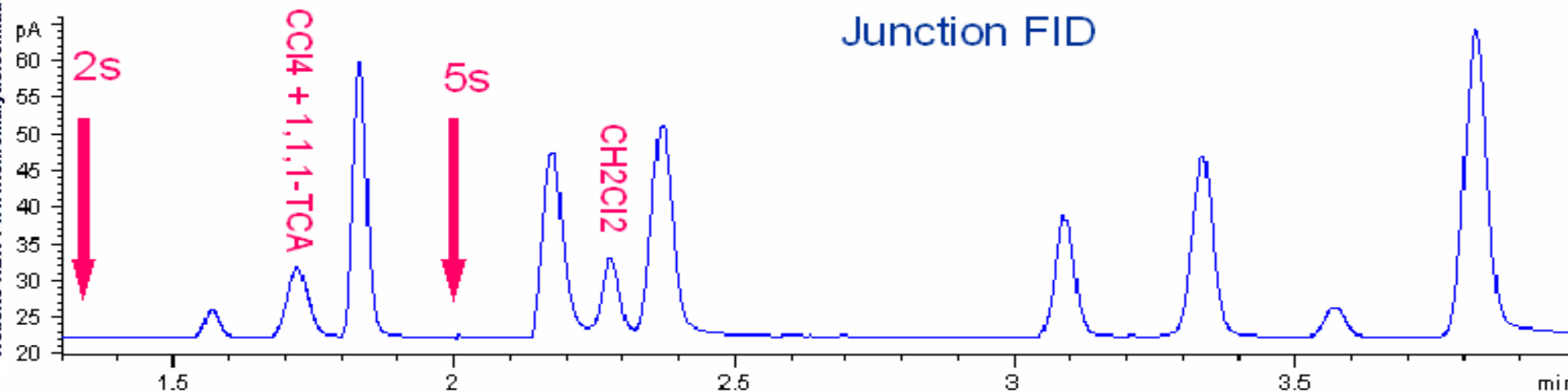
CH<sub>2</sub>Cl<sub>2</sub>

## Residual Solvents: Pulses @ 72 & 120 sec.

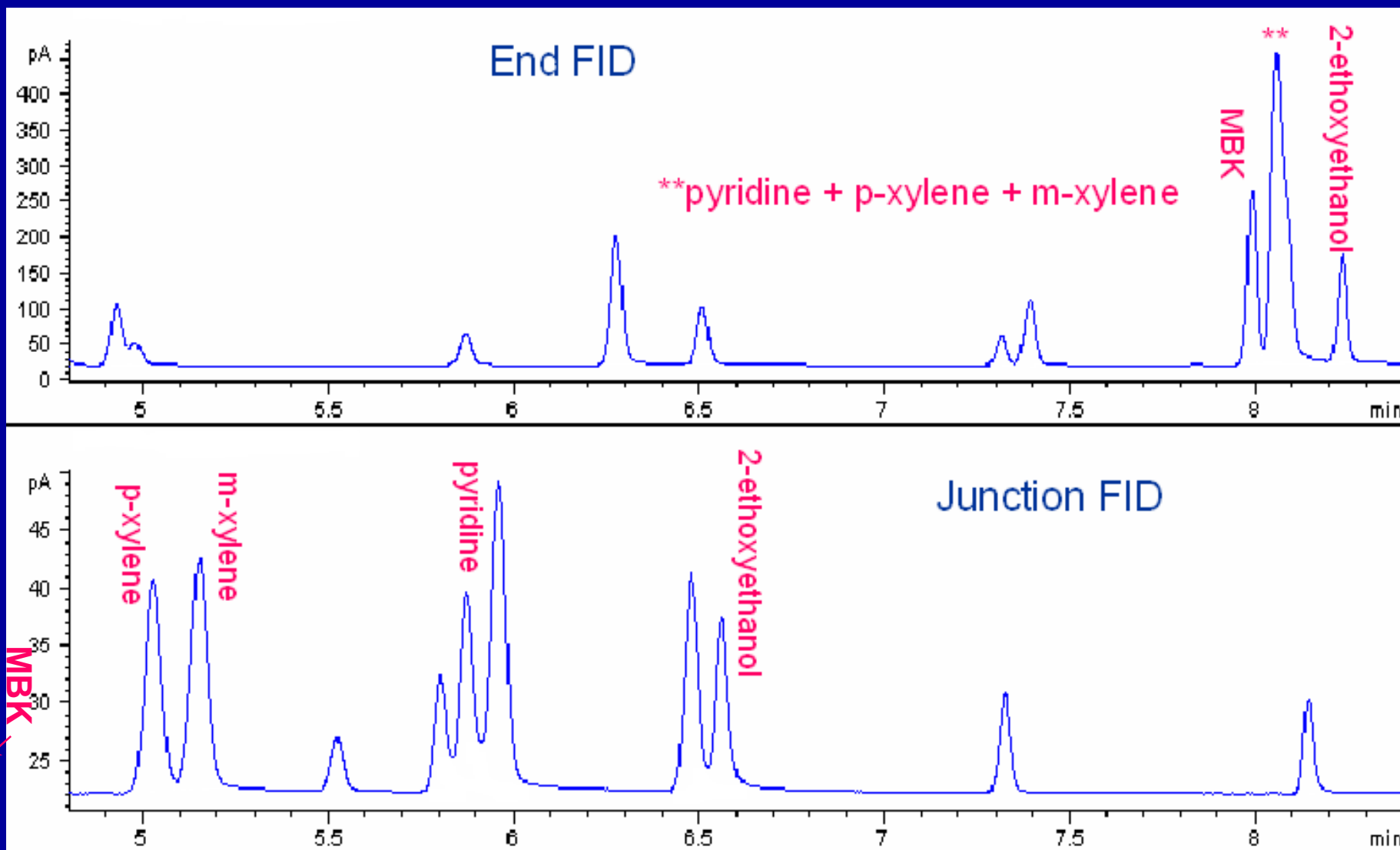
End FID



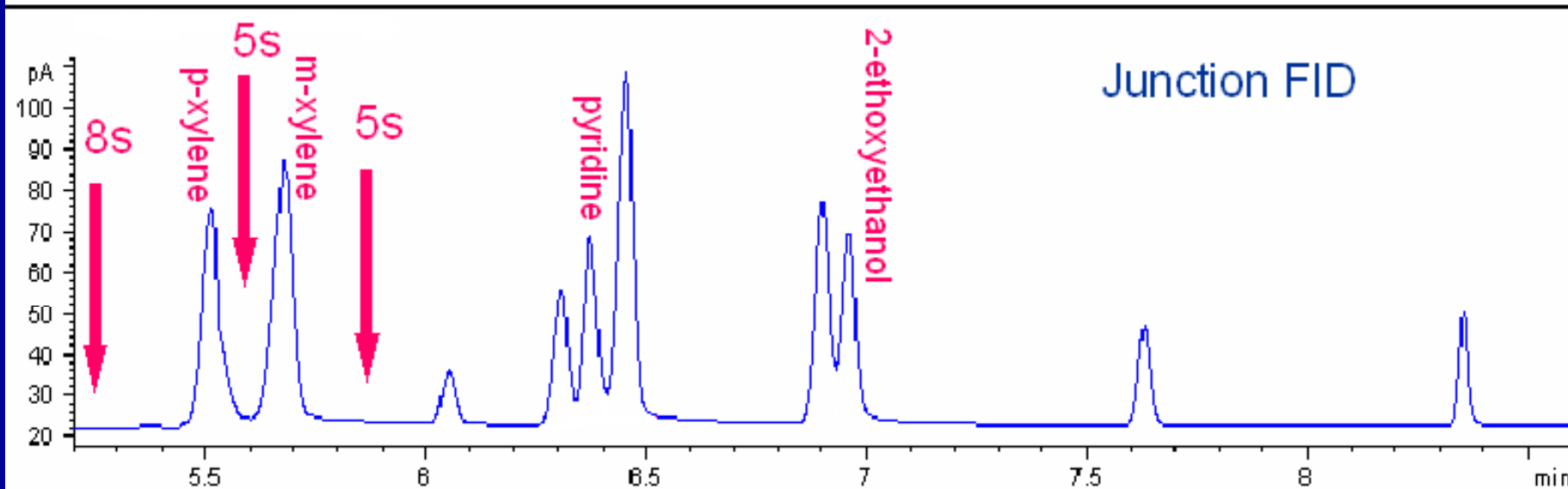
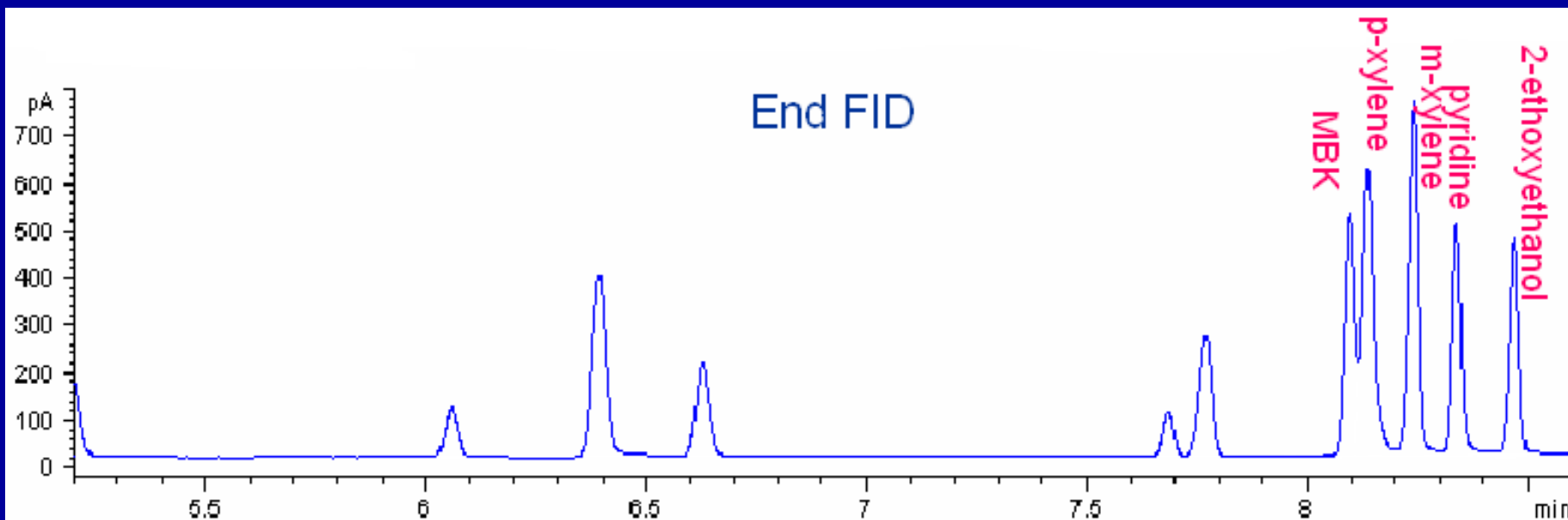
Junction FID



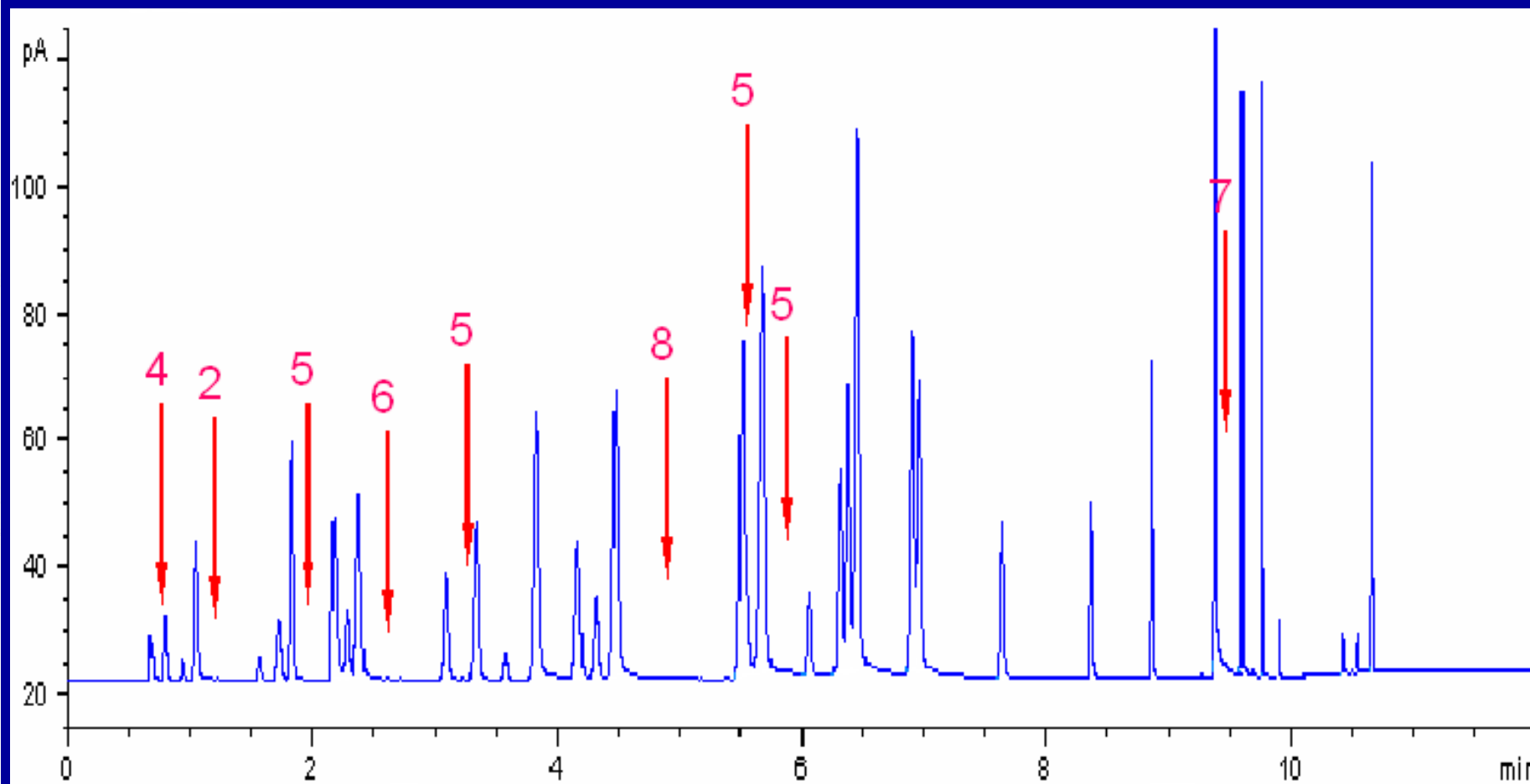
# Residual Solvents: No Pulses



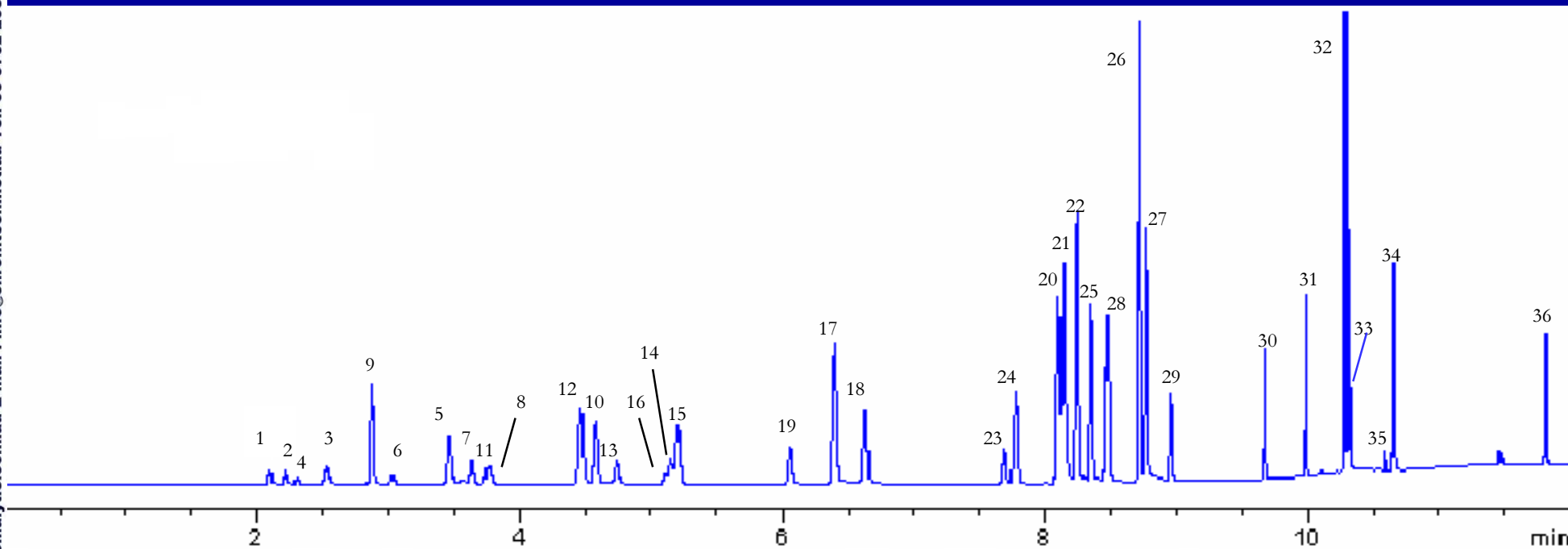
## Residual Solvents: Pulses @ 290, 330, & 346 sec.



# Class I & II OVIs: Total of 9 Pulses *At the Junction*



# Class I & II OVIs: Total of 9 Pulses *At the End Detector – all 36 resolved*





# Summary of Stop-Flow GC

- Ability to “Tune” the Selectivity
- Flexibility
  - ◆ Standard dimension columns
  - ◆ Can vary the pulse sequences
- Significant Improvements in Analysis Times Possible
  - ◆ Fast oven programs, high flow rates

# Conclusions

- Completed evaluation of current phases
- Continue work on a new stationary phases
  - ◆ Using computer modeling
  - ◆ Goal: resolve 76 compounds
- Continue with Stop-Flow technology

# For More Information...

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# Improving Method Performance through Fast LC

C. Vernon Bartlett, B.A.; Terrence S. Reid,  
M.S.; Rebecca E. Wittreg, Ph.D

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# Abstract

The analysis time needed for many separations can be drastically reduced by the use of fast HPLC techniques. Several separations were converted using fast HPLC techniques. Analysis times for some separations that previously took over 35 minutes were reduced to less than 12 minutes with improvement in selectivity between the components. Qualitative TLC techniques can be converted to truly quantitative HPLC. Since columns employed in the fast LC analysis were typically less than 100mm in length, the reduction in analysis time also resulted in increased sensitivity due to reduction of band spreading.

In addition to improving performance through reduction of particle size and column length, performance gains may also be realized by using columns equipped with an appropriately optimized and highly selective stationary phase. These phases allow improved separation of the components without the drastic increase in  $k$  that often results when reduction in mobile phase strength is used to improve selectivity.

# Fast LC Technique

- Highly selective stationary phase is desired to maximize alpha values.
- Elution of components is typically accomplished through the use of gradients to reduce retention of highly retained components.
- Simple resolution of methylene substitutions /additions may be accomplished isocratically.
- Good screening technique for unknowns.

# Fast LC Technique – Advantages

- Fast re-equilibration (when using gradients)
- Sensitivity improvements.
- Older qualitative techniques can be adapted to a highly automated quantitative technique.
- Allows potentially high increases in sample throughput.
- Great technique when performed by LC-MS
- Shorter analysis times reduce solvent consumption and waste.

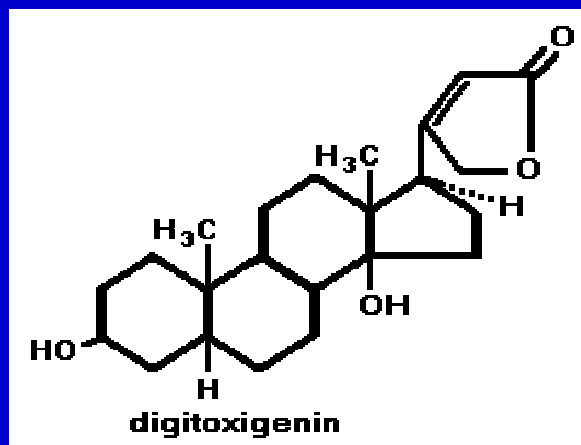
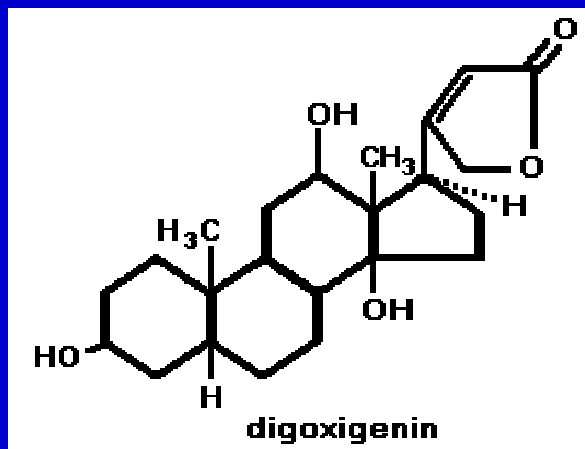
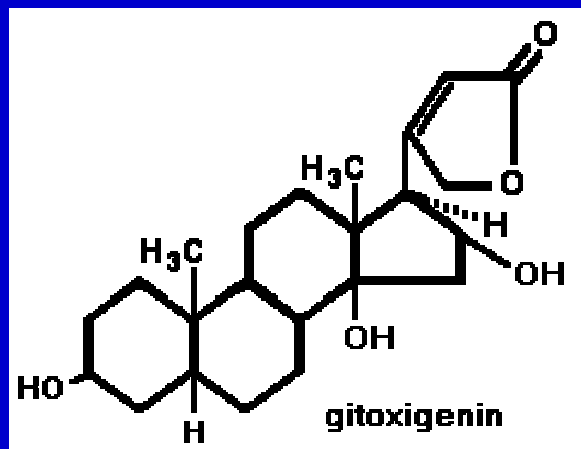
# Fast LC Technique – Disadvantages

- Critical separations are more sensitive to extra-column volume (as post column reactors).
- Extremely selective stationary phase must be used to maximize selectivity – especially for structural isomers.
- May not be well suited to normal phase or ion pairing separations (with gradients).



# Fast LC improvement of USP TLC and HPLC Method

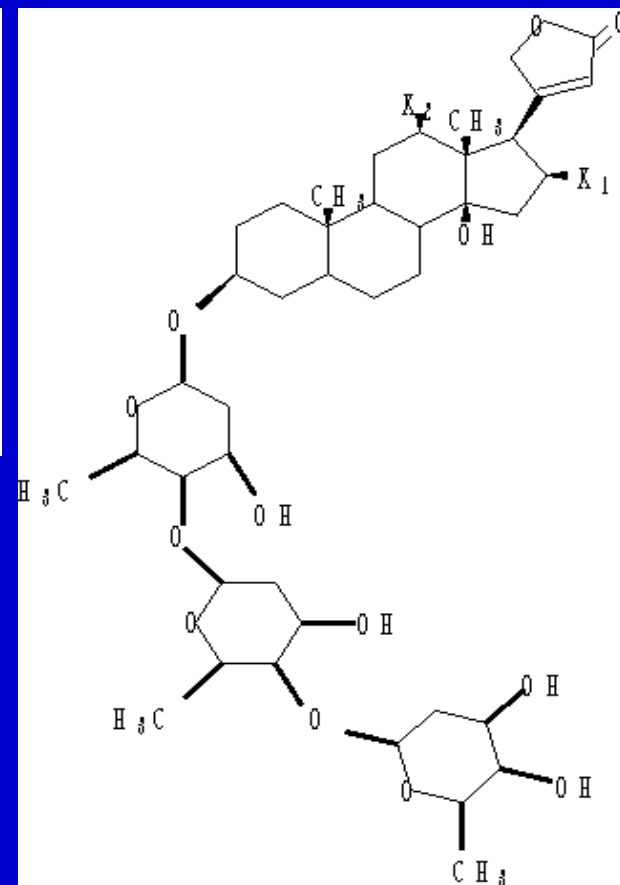
## Digitalis Extracts and Derivatives



Digitoxin:  $X_1=X_2=H$

Digoxin:  $X_1=H; X_2=OH$

Gitoxin:  $X_1=OH; X_2=H$



Digitoxin Substitutions

Figure 1

# Fast LC Separation of Digitalis Derivatives (3 minutes)

## Digitalis Extracts/Derivatives on Ultra Alkaloids Cartridge Column: Fast LC

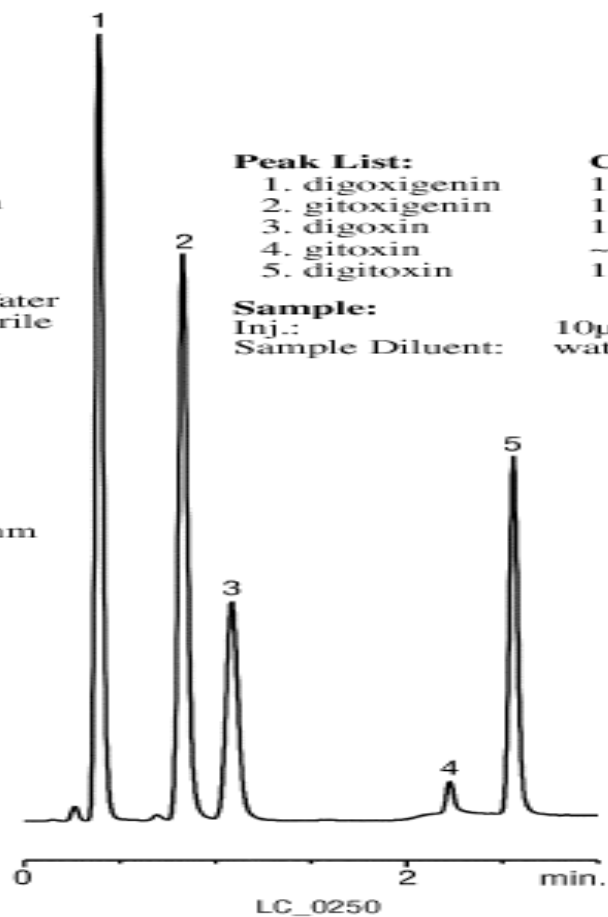
**Column:**  
Catalog #: 30 x 4.0mm  
Dimensions:  
Particle Size: 3µm  
Pore Size: 100Å

**Conditions:**  
Mobile Phase:  
A: 100% Water  
B: Acetonitrile  
Time (min.) %B  
0.0 20  
1.5 20  
1.51 35  
3.0 35  
3.1 20

Flow: 2.0mL/min  
Temp.: 27°C  
Det.: UV @ 230nm

Peak List:	Conc.	Ret. Time (min.)
1. digoxigenin	100µg/mL	0.40
2. gitoxigenin	100µg/mL	0.80
3. digoxin	100µg/mL	1.10
4. gitoxin	~10µg/mL	2.20
5. digitoxin	100µg/mL	2.60

**Sample:**  
Inj.: 10µL  
Sample Diluent: water:acetonitrile (80:20 v/v)



# Advantages of Digitalis Fast LC over Current Methods

- Improved automation and analysis throughput.
- Reduction of analysis time – previously a 30cm length C18 column was required for resolution.
- Ability to analyze all materials by HPLC.
- Ability to precisely quantitate materials vs TLC.
- Highly selective stationary phase.
- Technique can also be applied to purification and analysis of digoxin labeled materials for biological activity.
- Perfect technique for use in high speed cleaning validations.

# Fast LC Analysis of Carbamates

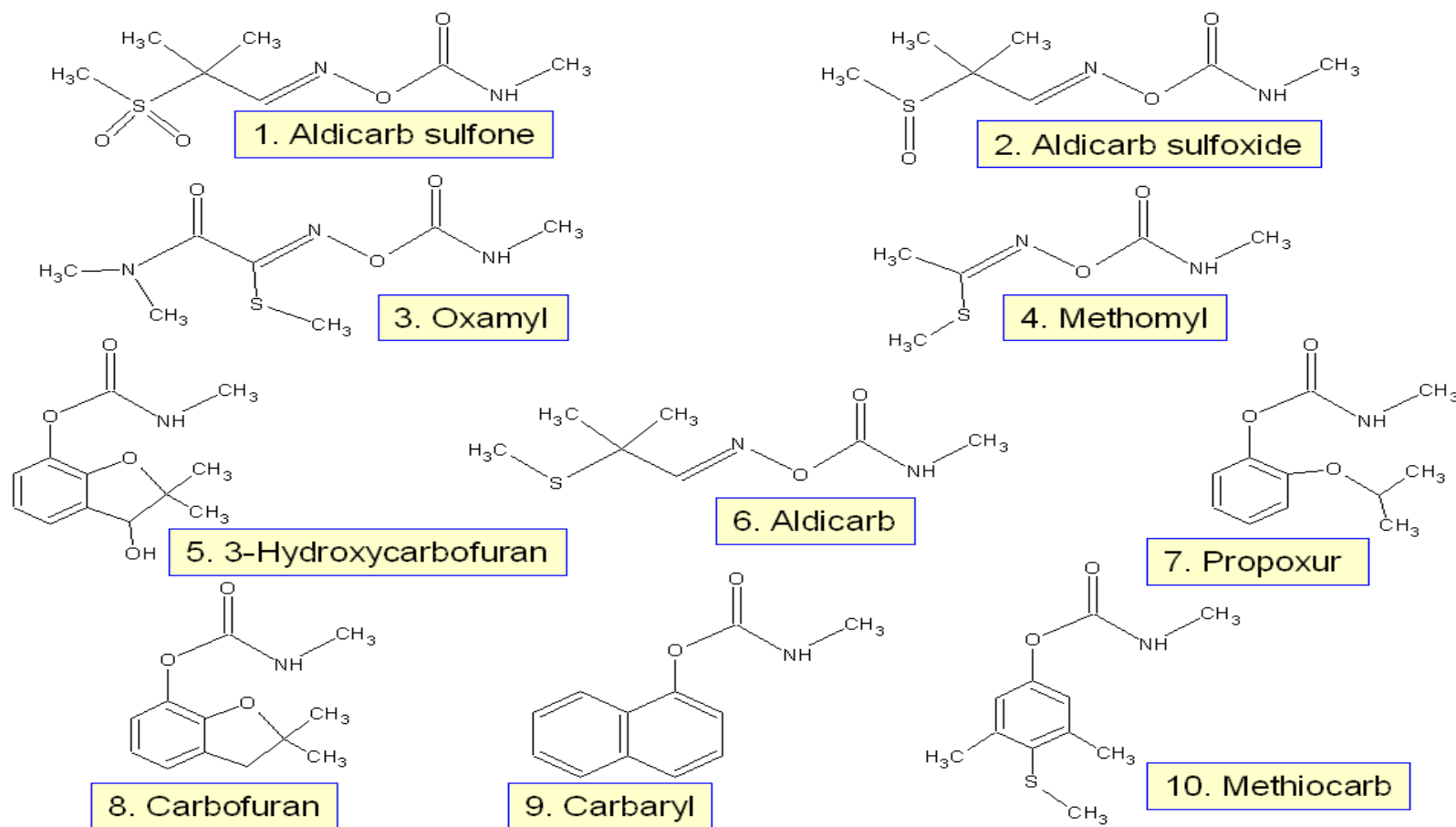


Figure 3-Structures of Commonly Analyzed Carbamates

# Carbamate Analysis using Standard HPLC Methodology (About 40 minutes)

## Carbamate Pesticides on Pinnacle Carbamate

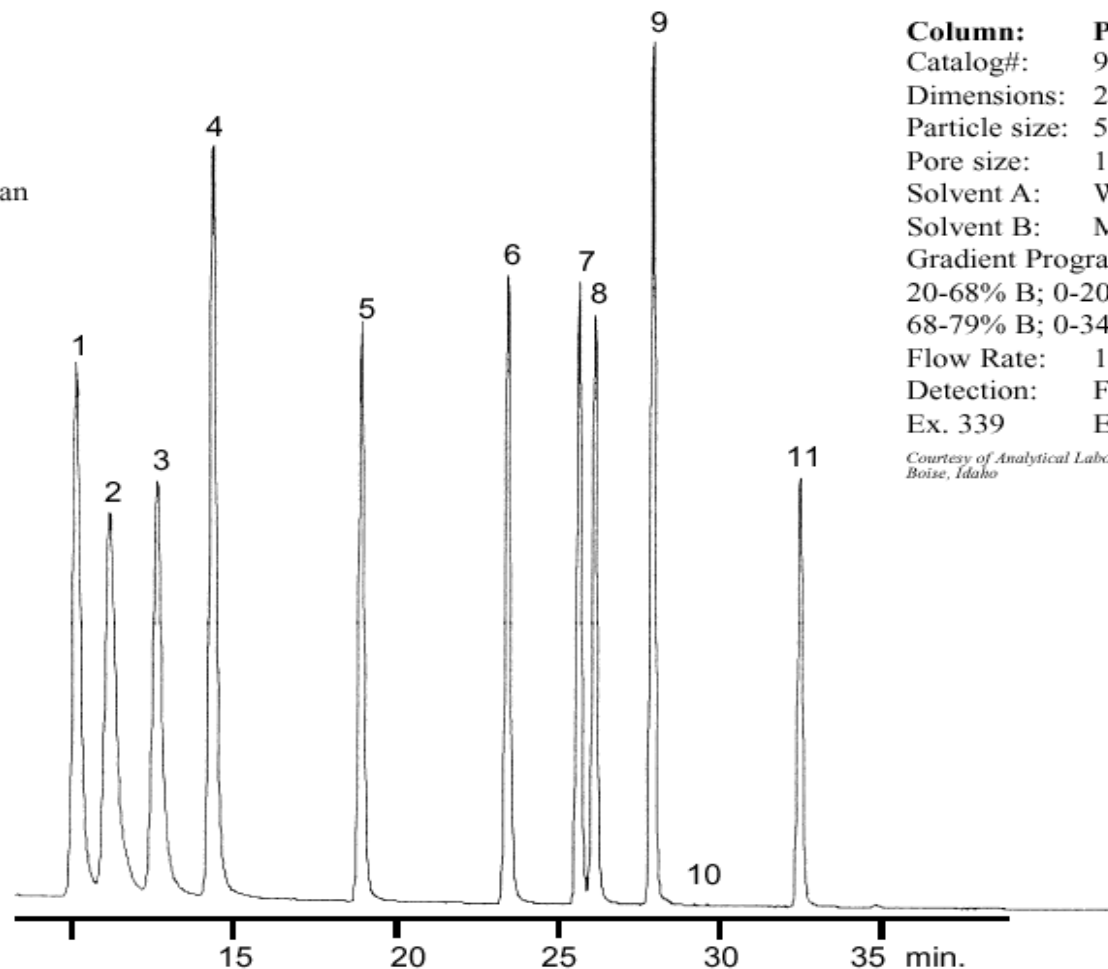
Applications Note: LC\_0192

### Peak List:

1. aldicarb sulfoxide
2. aldicarb sulfone
3. oxamyl
4. methomyl
5. 3-hydroxycarbofuran
6. aldicarb
7. propoxur
8. carbofuran
9. carbaryl
10. 1-naphthol
11. methiocarb

**Column:** Pinnacle Carbamate  
**Catalog#:** 9173575  
**Dimensions:** 250 x4.6mm  
**Particle size:** 5µm  
**Pore size:** 120Å  
**Solvent A:** Water  
**Solvent B:** Methanol  
**Gradient Program:**  
20-68% B; 0-20 min.  
68-79% B; 0-34 min.  
**Flow Rate:** 1.0mL/min  
**Detection:** Fluorescence  
**Ex. 339** **Em. 445nm**

*Courtesy of Analytical Laboratories, Inc.  
Boise, Idaho*



# Fast LC Separation of Carbamates (About 13 minutes)

## Fast LC Separation of 11 Carbamates on Ultra Carbamate

### Peak List:

1. aldicarb
2. aldicarb sulfoxide
3. oxamyl
4. methomyl
5. 3-hydroxycarbofuran
6. aldicarb
7. propoxur
8. carbofuran
9. carbaryl
10. methiocarb
11. 4-bromo-3,5-dimethylcarbamate

### Sample:

Inj.: 5 $\mu$ L  
Conc.: 50 $\mu$ g/mL  
Solvent: methanol

### Restek standards:

Catalog# 32274 and 32273 mixed 50:50

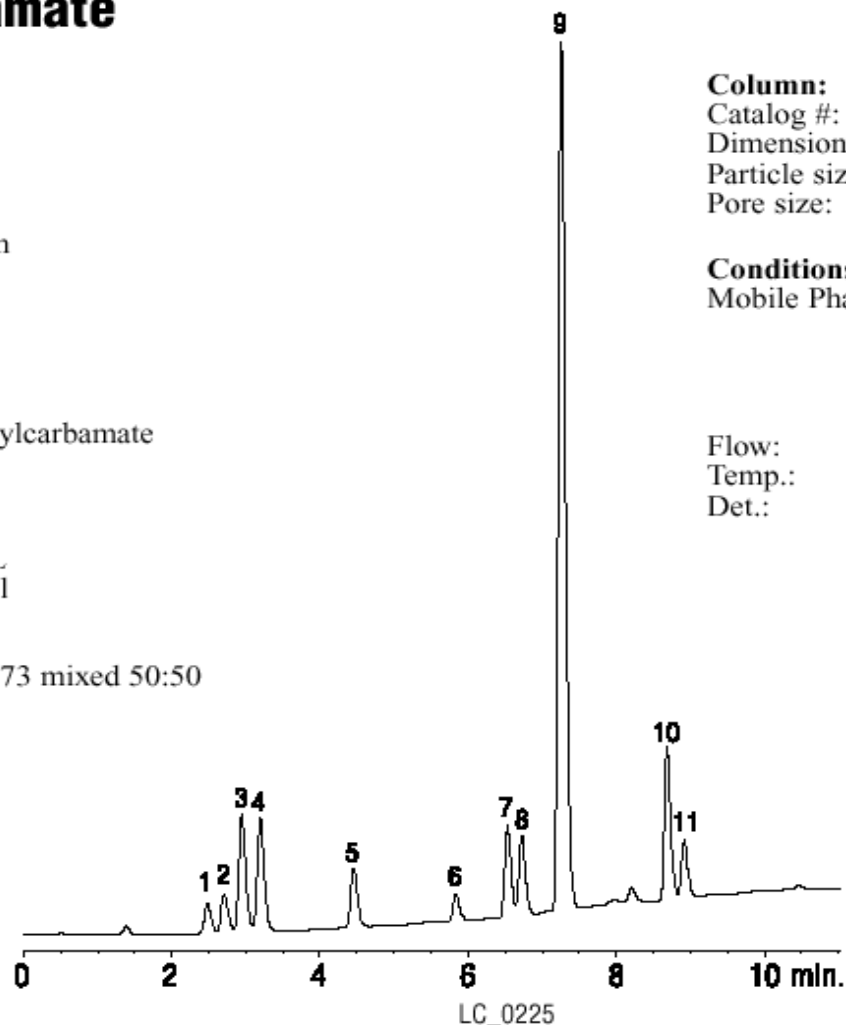
### Column:

Catalog #: 9177355  
Dimensions: 50 x 4.6mm  
Particle size: 3 $\mu$ m  
Pore size: 100Å

### Conditions:

Mobile Phase: A: 90:10 water:methanol  
B: 90:10 methanol:acetonitrile  
Time (min): %B  
0 10  
10 90

Flow: 1.5mL/min  
Temp.: 27°C  
Det.: UV @ 220nm





# Fast LC Analysis of Carbamates with MS Detection

Table II. Experimental conditions for the LC/MS analysis of carbamate compounds.

## HPLC Conditions

Column: Ultra Carbamate, 100 mm x 4.6 mm, 3  $\mu$ m  
 Mobile Phase A: 90% water:10% methanol with 10mM ammonium formate  
 Mobile Phase B: 10% acetonitrile:90% methanol with 10mM ammonium formate  
 Gradient: 90%A:10%B to 10%A:90%B from 0-15 minutes  
 Inj. Volume: 10  $\mu$ L  
 Flow Rate: 0.75 mL/min to UV detector, 0.25 mL/min to MSD

## MSD Conditions

Detector: Micromass ZMD  
 Mode: ESI+  
 Capillary V: 3.50  
 Extractor: 4.0  
 Ion Energy: 0.4  
 Multiplier: 650  
 Source Temp: 100°C  
 Desolv. Temp: 250°C  
 Gas Flow: 490 L/hr.

Compound	Ion	Cone V
1	223.3	25V
2	207.3	18V
3	237.2*	10V
4	163.2	15V
5	238.3	15V
6	191.2	8V
7	210.2	18V
8	222.3	22V
9	202.2	18V
10	226.3	19V

\*Ammonium adduct (all other are [M+H]<sup>+</sup> ions)

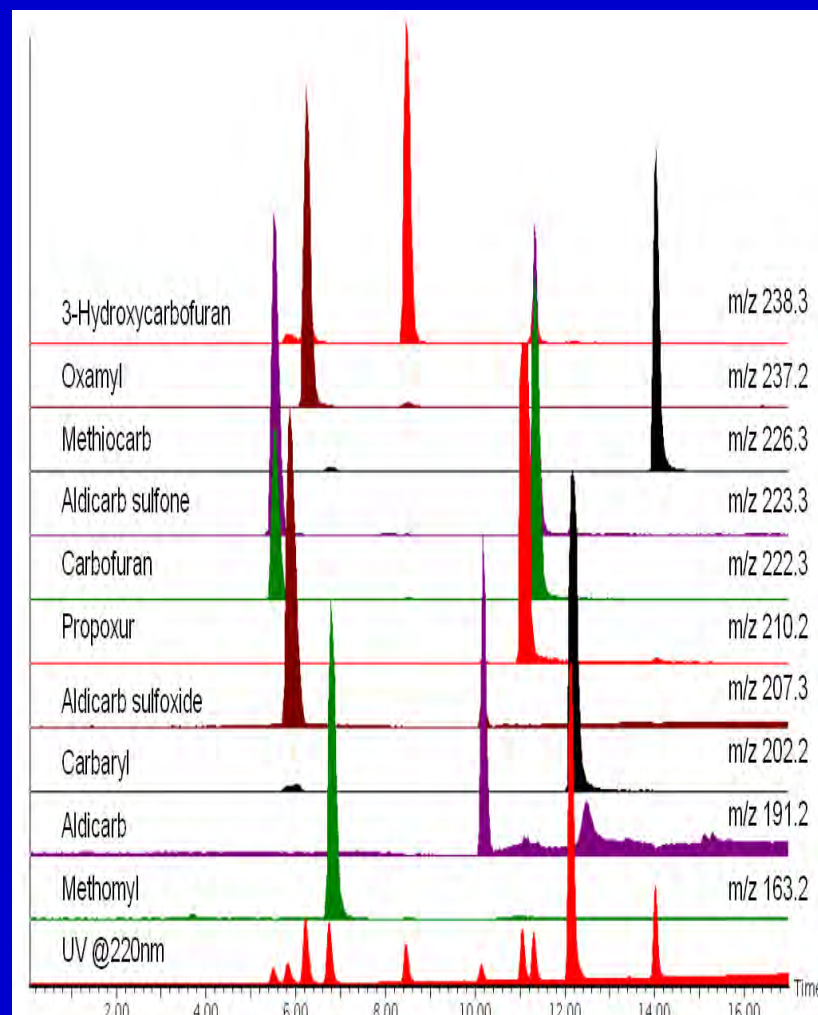


Figure 6

# Fast LC Analysis – Carbamate Separation Loss

- Post Column Volumes produced by external reactors can be detrimental to critical separations – especially to smaller bore columns.

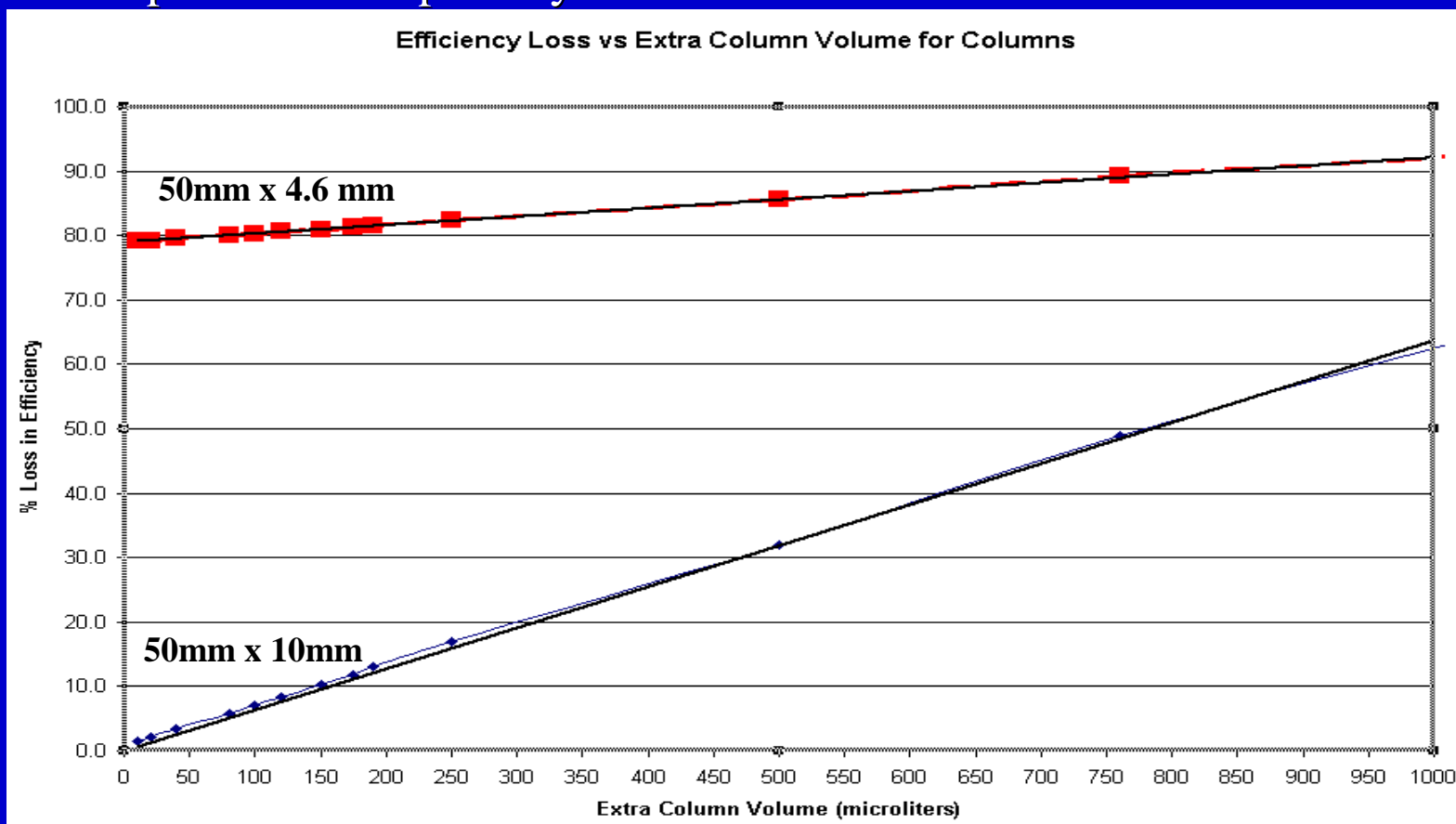


Figure 7



# Conventional Vanilla Flavoring Analysis (About 20 minutes with gradient)

## Vanillin and Ethyl Vanillin on Ultra C8

Applications Note: LC\_0148

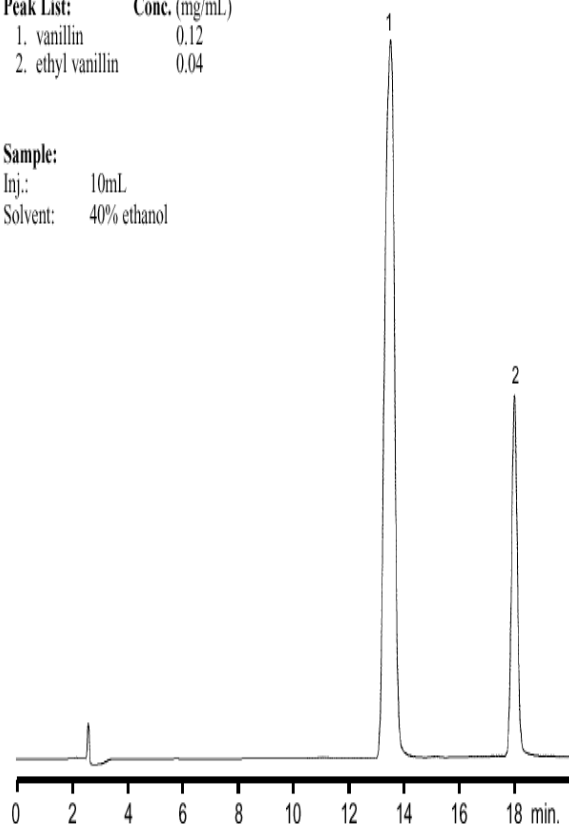
Peak List:	Conc. (mg/mL)
1. vanillin	0.12
2. ethyl vanillin	0.04

Sample:  
Inj.: 10mL  
Solvent: 40% ethanol

Column: Ultra C8  
Catalog#: 9103565  
Dimensions: 150x4.6mm  
Particle size: 5µm  
Pore size: 100Å

Conditions:  
Mobile phases: A: 1.2% acetic acid  
B: methanol  
Gradient: Minutes %B  
0.0 20.0  
5.0 20.0  
15.0 40.0  
20.0 40.0  
25.0 20.0

Flow: 1.0mL/min.  
Temp.: 28°C  
Det.: UV @ 254nm



## Vanillin on Ultra C8

Application Note: LC\_0149

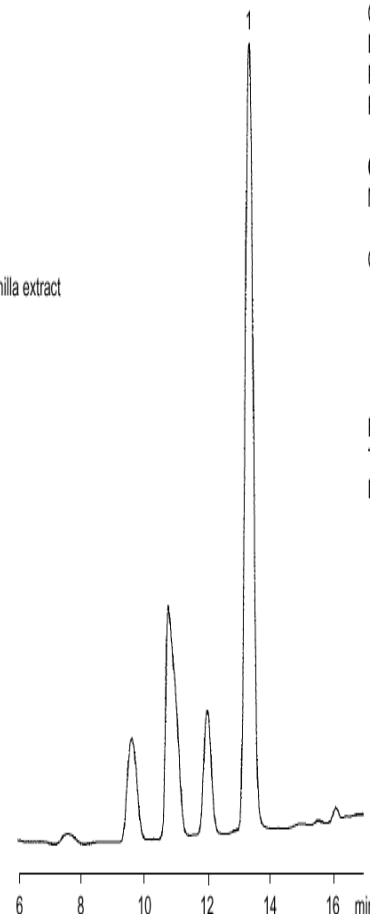
Column: Ultra C8  
Catalog#: 9103565  
Dimensions: 150x4.6mm  
Particle size: 5µm  
Pore size: 100Å

Conditions:  
Mobile phases: A: 1.2% acetic acid  
B: methanol  
Gradient: Minutes %B  
0.0 20.0  
5.0 20.0  
15.0 40.0  
20.0 40.0  
25.0 20.0

Flow: 1.0mL/min.  
Temp.: 28°C  
Det.: UV @ 254nm

Peak List:  
1. vanillin

Sample:  
Inj.: 10mL  
Conc.: 5% solution of vanilla extract  
Solvent: 40% ethanol



# Highly Selective Fast LC Vanillin Analysis (Less than 5 minutes and isocratic)

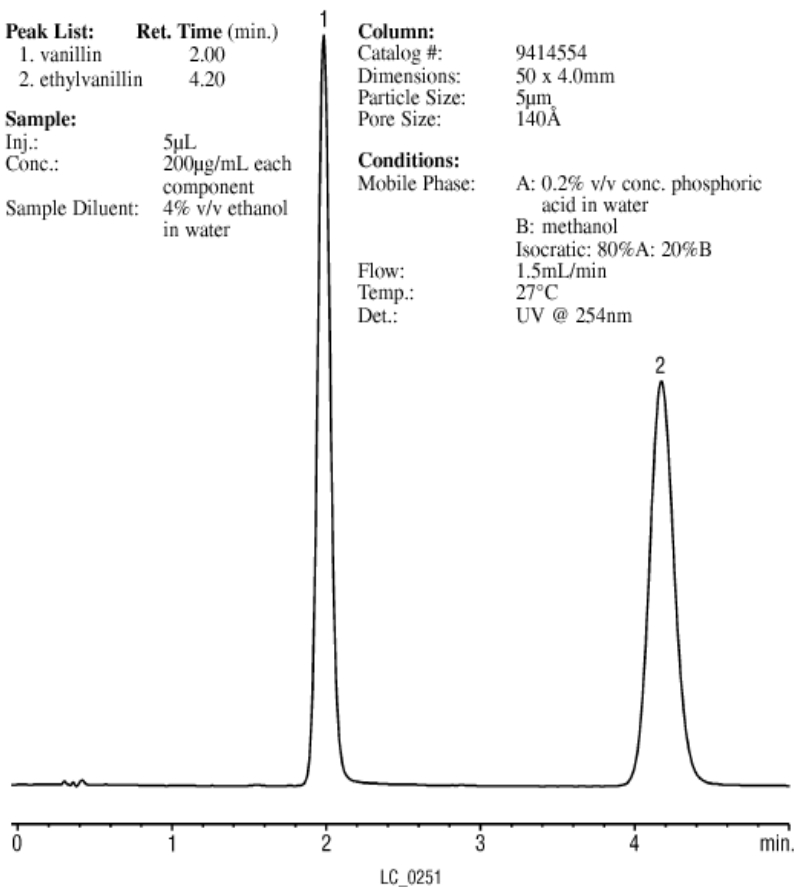
## Vanillin and Ethylvanillin on Pinnacle™ DB C18: Fast LC

Peak List:	Ret. Time (min.)
1. vanillin	2.00
2. ethylvanillin	4.20

**Sample:**  
Inj.: 5µL  
Conc.: 200µg/mL each component  
Sample Diluent: 4% v/v ethanol in water

**Column:**  
Catalog #: 9414554  
Dimensions: 50 x 4.0mm  
Particle Size: 5µm  
Pore Size: 140Å

**Conditions:**  
Mobile Phase: A: 0.2% v/v conc. phosphoric acid in water  
B: methanol  
Isocratic: 80%A: 20%B  
Flow: 1.5mL/min  
Temp.: 27°C  
Det.: UV @ 254nm



## Vanilla Bean Extract on Pinnacle™ DB C18: Fast LC

**Column:**  
Catalog #: 9414554  
Dimensions: 50 x 4.0mm  
Particle Size: 5µm  
Pore Size: 140Å

**Conditions:**  
Mobile Phase: A: 0.2% v/v conc. phosphoric acid in water  
B: methanol  
Isocratic: 80% A: 20% B  
Flow: 1.5mL/min  
Temp.: 27°C  
Det.: UV @ 254nm

**Peak List:** Ret. Time (min.)  
1. Vanillin 2.00

**Sample:**  
Inj.: 5µL  
Conc.: unknown  
Sample Diluent: 20% v/v commercial extract in water

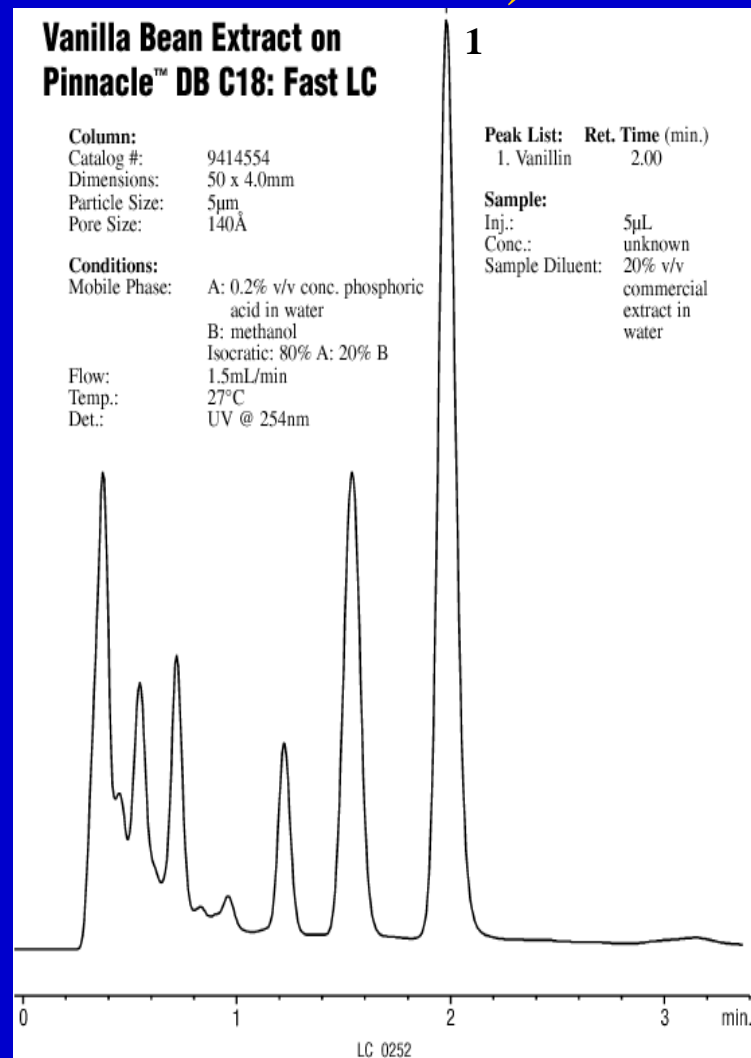


Figure 9

# Vanillin Fast LC Analysis Advantages

- Takes advantage of improved methylene selectivity by the use of C18 phase versus a C8
- Analysis can be conducted in 3 to 5 minutes versus older 15 minute methods.
- High but not excessive selectivity of C18 phases toward simple methylene substitutions allow the use of an isocratic mobile phase.
- Reduction of column length also reduces the time needed for more hydrophobic analytes to elute from system.

# Conclusion

- Fast LC techniques applied upon highly selective stationary phases create a viable, precise quantitative alternative for analyses previously performed by Thin Layer Chromatography. In addition, these techniques can be used to improve method sensitivity, reduce solvent waste, and enhance laboratory throughput. Simplification of methods from gradient elution to isocratic elution can also occur when the proper stationary phase is used with a drastic reduction in analysis time, however, extraneous column volume caused by items as post column reactors can have a greater adverse effect when using fast columns.

# Acknowledgements

- The authors would like to thank Randy Romesberg, Larry Peters, and Rahul Patil of Restek Corporation for their participation in creating columns and hardware.

# Advances in Capillary Column Technology, and Separation Modeling for Comprehensive 2-Dimensional Gas Chromatography

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# Is Comprehensive 2-D Ready for Industrial Use?

- There is not an “agreed” upon method
  - Heated zone modulation
  - Valve-type modulation
  - Cryo-jet modulation
- Technique is confused by other “2-D techniques”
  - Heart-cutting
  - Dean-switching
  - Coupled column techniques
- Limited manufacturers and supplies
  - Technique was considered “research-only tool”
  - Consumables are now behind instrumentation
- Lets not follow 1-D technology.....

## State of Affairs in 1-D GC

- Many users view GC as “separation by boiling point”
- Most of the rest view it as a “black box”
- Column choice has been either mandated or is based on history
- Column choices are few
- Most popular phases are similar in terms of selectivity
- Users look to column manufacturers, and manufacturers are staffed by former users.....



# The Reality of the GC Marketplace (the dark side)

- Most Frequent calls/complaints:
  - Installation issues:
    - “Column has one end”
    - “Which side goes into the injector”
    - Improper installations into inlet or detector
    - Leaks and or flow-related issues
    - Press-tight issues!
  - “Which column do you recommend for...\_\_\_\_\_?”
  - “What conditions do you recommend for...\_\_\_\_\_?”
- Most users do not fully understand the variables that effect separation and how to optimize them.

# Can Comprehensive 2-D GC be Successful in the Marketplace?

- A Few Commercial Manufacturers Now Exist
- Quantitation Software is Available
- Continued Need for:
  - Optimization Software
    - What is the best set of conditions?
  - Support by Consumables Manufacturers
    - What columns do I use?
  - Understanding Where it is/isn't Needed
    - Is this a niche technique?
  - **Ease of Use**

# Chromatographic Columns

- Press-tight connectors
  - Allow use of dissimilar i.d. columns
  - More flexible
  - Prone to leaks, many customers do not like them
  - Best connection device is glass
- Continuous columns
  - Both columns must be same i.d.
  - Easier to handle and install
  - Can use a restrictor if necessary
  - Can have an uncoated section where modulator is placed

# Typical GCxGC Column Assembly

- First dimension column
- Inter-column transfer line (modulator tube)
- Second dimension column
- Detector transfer line
- Typically requires up to 3 press-fit connections

# Press-tight connectors

- Standard press-tights fittings
  - Low cost
  - Low thermal mass
  - Low dead volume
- Metal press tights and unions
  - Higher cost
  - Higher thermal mass
- Vu 2 Union
  - Low thermal mass for chromatographic portion
  - Uses standard press-tights in a housing with back-up ferrules
  - Low cost once holder is purchased

## GCxGC Column Assembly

- For R&D purposes, it is preferable to have the ability to change column dimensions at will, and the time involved in preparing the column set is part of the overall task
- For routine laboratory analysis, it is preferable to have ready-made column ensembles, such as is the case in 1D GC. This insures good column quality and reproducibility

# Goal

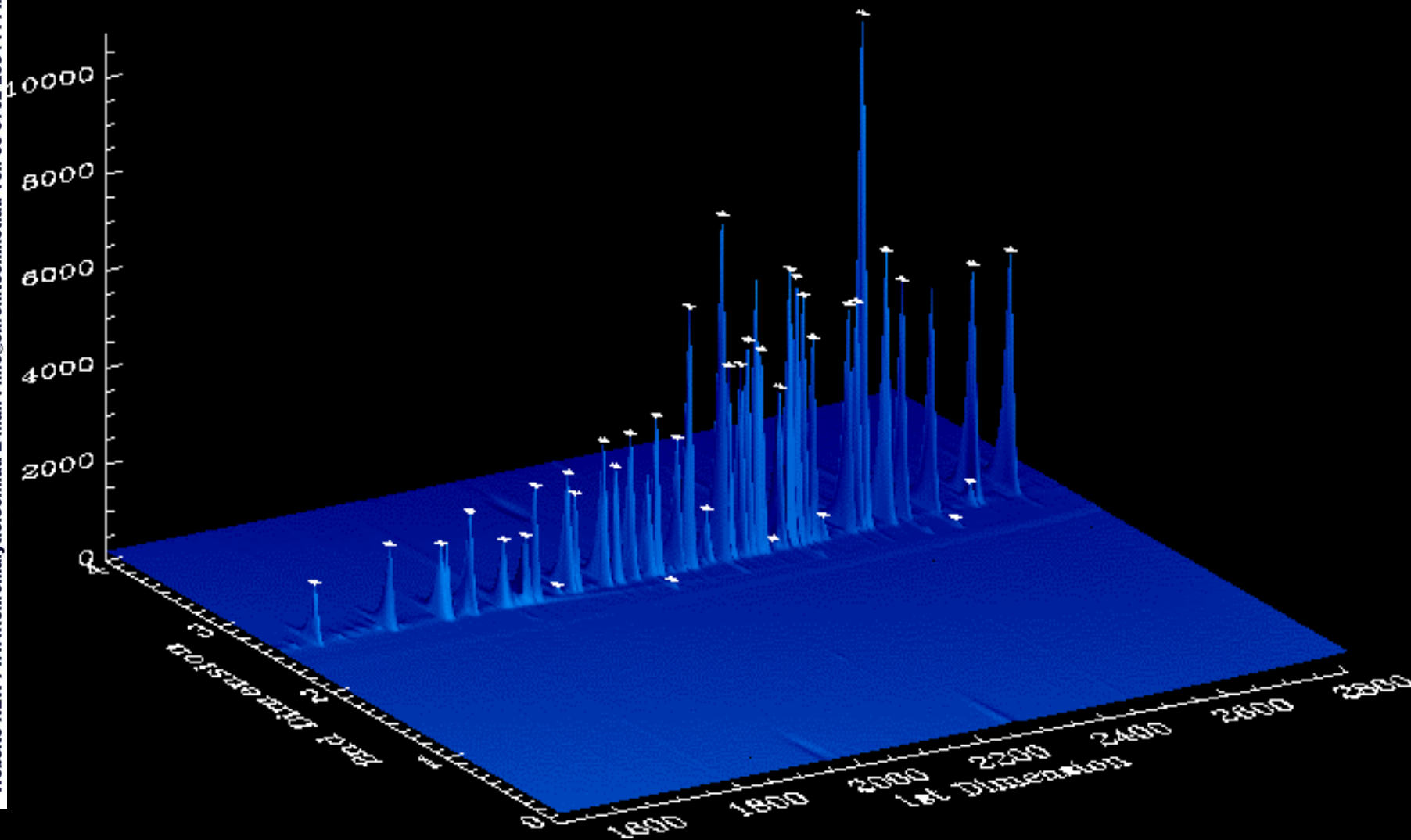
- Investigation of a set of continuous column sets for a Jet modulator GCxGC system

# Experimental

- Columns
  - 100  $\mu\text{m}$  set (3m Rtx-1, 1m Rtx-1701)
  - 250  $\mu\text{m}$  set (6m Rtx-1, 2m Rtx-1701)
- Modulator
  - Type: Quad Jet system (Zoex Corporation)
  - Period: 4 seconds
- Detectors
  - FID
  - $\mu$ -ECD

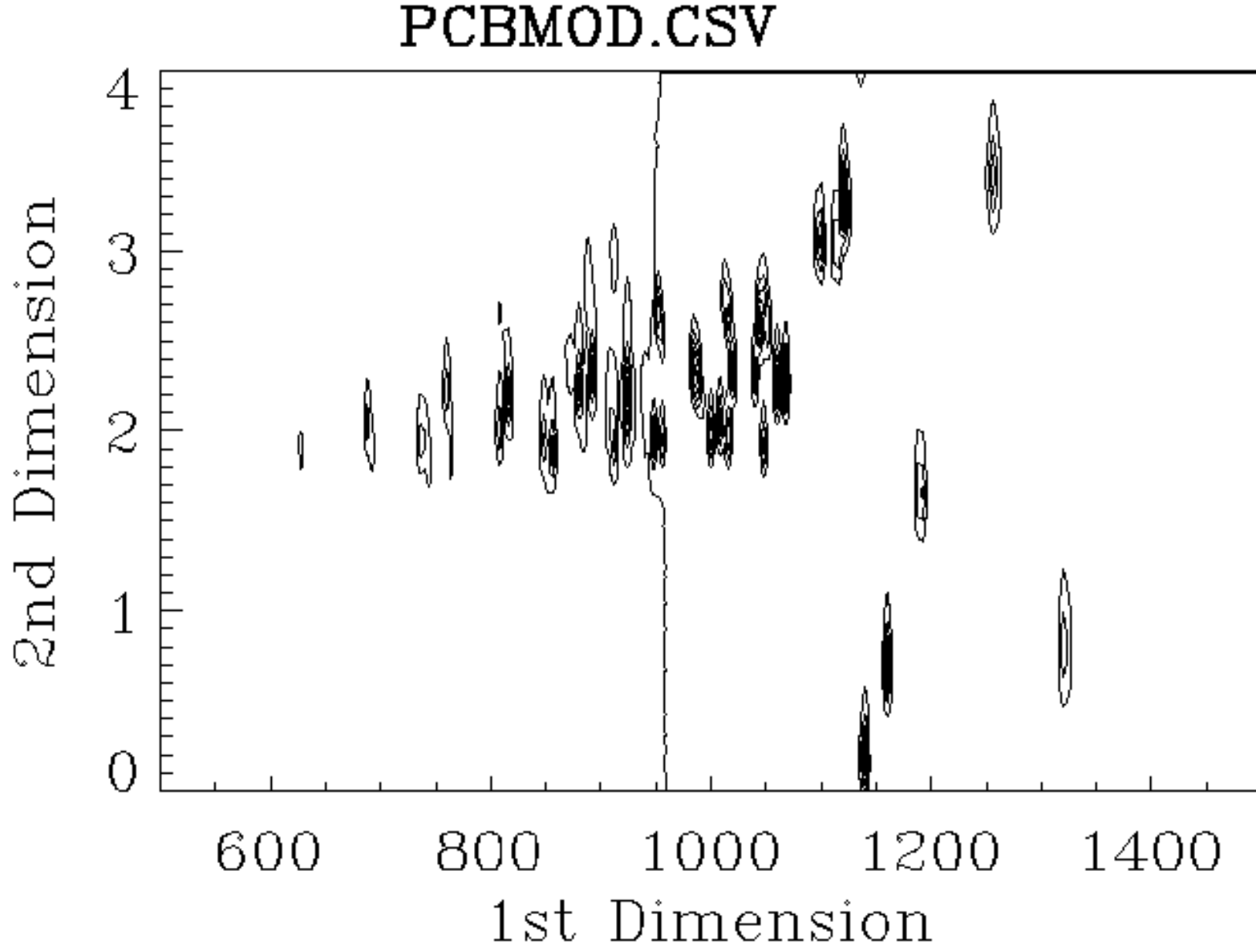


# STRIPMOD.CSV



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## Current continuous 2-D columns

0.25 mm i.d.:

Rtx-1/Rtx-1701 1.0 X 0.1  $\mu$ m d.f. 30 X 5 M

Rtx-1/Rtx-200 1.0 X 0.1  $\mu$ m d.f. 30 X 5 M

Rtx-1/Rtx-50 1.0 X 0.1  $\mu$ m d.f. 30 X 5 M

Rtx-1/Deactivated tubing 1.0 X 0  $\mu$ m d.f. 30 X 5 M

0.18 mm i.d.:

Rtx-1/Rtx-1701 1.0 X 0.1  $\mu$ m d.f. 10 X 2 M

Rtx-1/Rtx-200 1.0 X 0.1  $\mu$ m d.f. 10 X 2 M

Rtx-1/Rtx-50 1.0 X 0.1  $\mu$ m d.f. 10 X 2 M

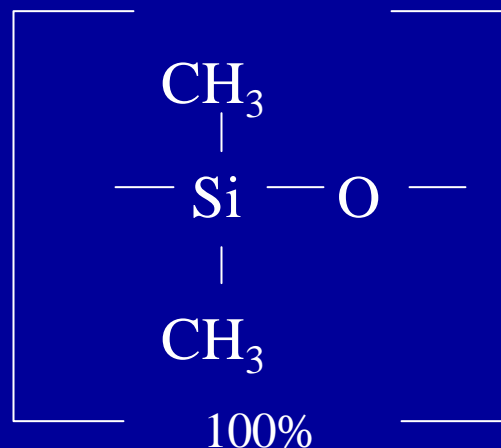
Rtx-1/Deactivated tubing 1.0 X 0  $\mu$ m d.f. 10 X 5 M

0.10 mm i.d.:

Rtx-1/Rtx-1701 1.0 X 0.1  $\mu$ m d.f. 10 X 2 M

Rtx-1/Rtx-200 1.0 X 0.1  $\mu$ m d.f. 10 X 2 M

# Rtx<sup>®</sup>-1



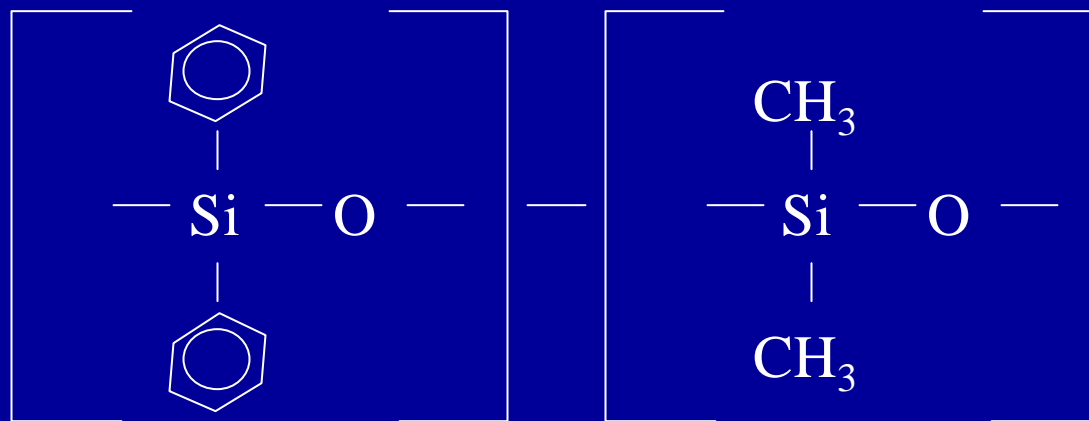
Polarity: least polar bonded phase

Uses: boiling point separations (solvents,  
petroleum products, and pharmaceuticals)

Properties: min. temp. (-60°C), max. temp. (360°C to  
430°C), helix structure

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# Rtx<sup>®</sup>-5, 20, 35, 65



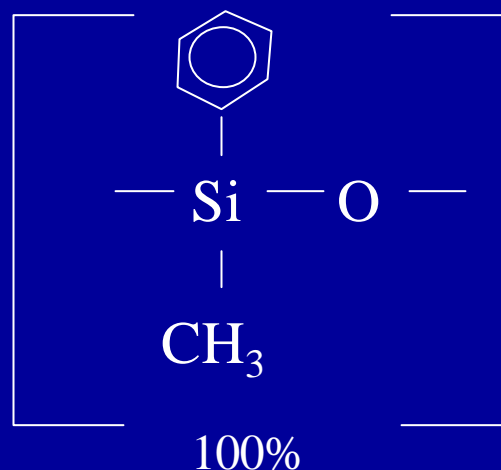
e.g., Rtx-5: 5% diphenyl 95% dimethyl

Polarity: non-polar

Uses: boiling point separations (aromatics, flavors, environmental samples, and aromatic hydrocarbons)

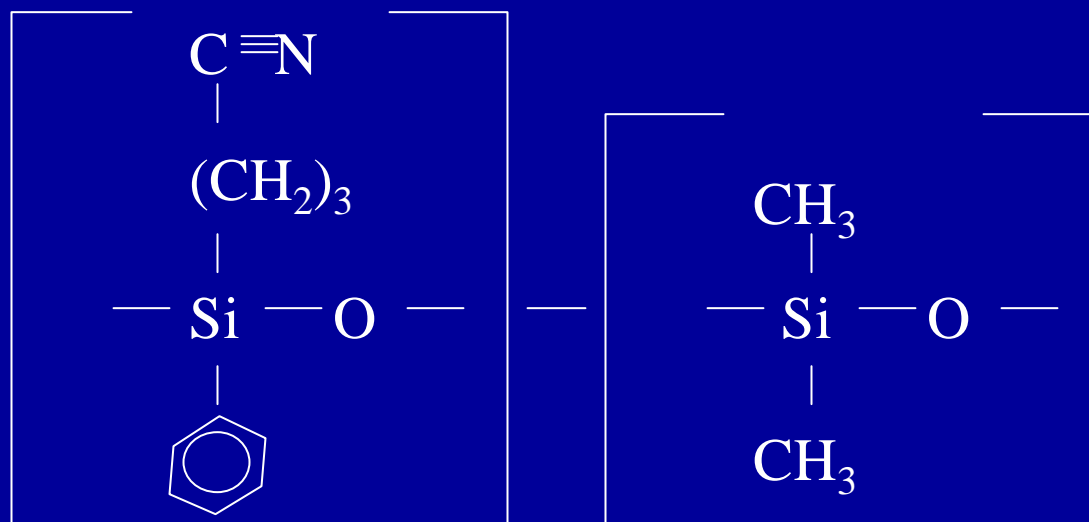
Properties: min. temp. (-60°C), max. temp. (340°C)

# Rtx<sup>®</sup>-50



Polarity: intermediate polarity  
 Uses: triglycerides and phthalate esters  
 Properties: min. temp. (0°C), max. temp. (340°C)

# Rtx<sup>®</sup>-1301, 624, 1701



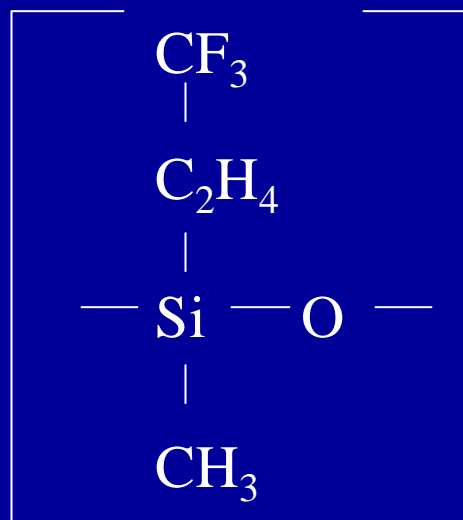
Polarity: intermediate polarity

Uses: pesticides, Aroclor<sup>®</sup>, alcohols, and  
oxygenates

Properties: min. temp. (-20°C), max. temp. (280°C)

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# Rtx<sup>®</sup>-200



Polarity: selective for lone pair electrons  
Uses: environmental samples, solvents, and Freon<sup>®</sup>

Properties: min. temp. (-20°C), max. temp. (360°C)

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# What Phases Do We Need??

Wax Like Phases

Chiral Phases

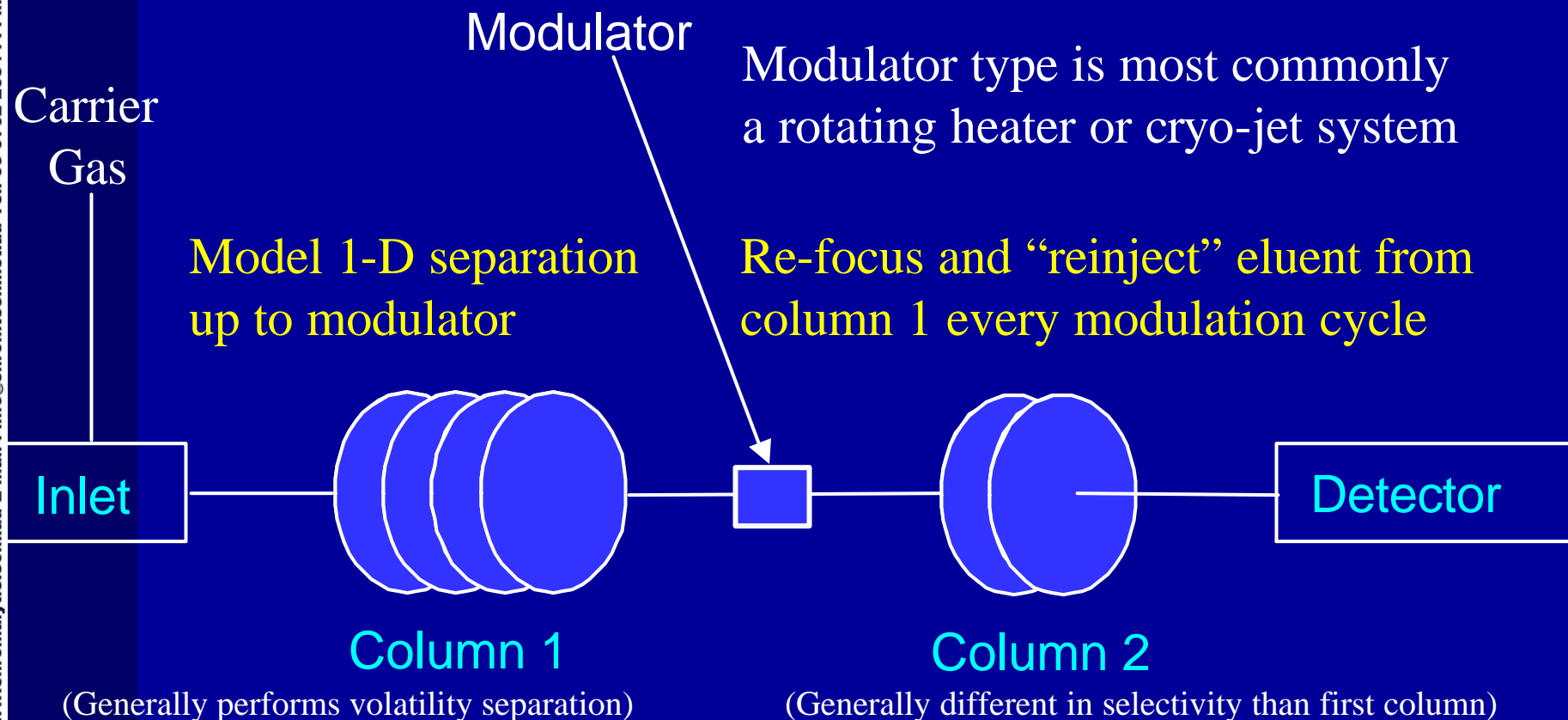
Liquid Crystal Phases

Others....

# Optimization/Modeling of Separations

- Several approaches have been used for conventional separations
- Allows prediction of optimal conditions for a users column (Pro EZ-GC)
- Allows prediction of optimal stationary phase chemistry and conditions (*Anal. Chem.* 74(9), 2133-2138 2002)
- Can these be applied to Comprehensive 2-D separations?

# Comprehensive 2D-GC System



# 1-D Modeling

## General Equation for Resolution:

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (a-1 / a)$$

Selectivity Factor ( $\alpha$ ) – addressed by  
stationary phase modeling  
not commonly done by end user

Capacity Factor (k), and Column Factor –  
addressed by physical modeling  
can be simultaneous with, or independent of  
stationary phase modeling

# Stationary Phase Optimization Techniques

- Empirical Modeling:
  - Window diagramming approach
  - Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
  - Computer prediction of optimized stationary phase composition and column dimensions, with specific resolution factors (times and peak widths)
- Molecular Modeling:
  - Computer prediction of solute/stationary phase interactions for new polymer designs

# Stationary Phase Optimization

- Window diagramming (Rtx-502.2)
- Computer simulation of selectivity, independent of column dimensions (ezGC™)
  - Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx-TNT, Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

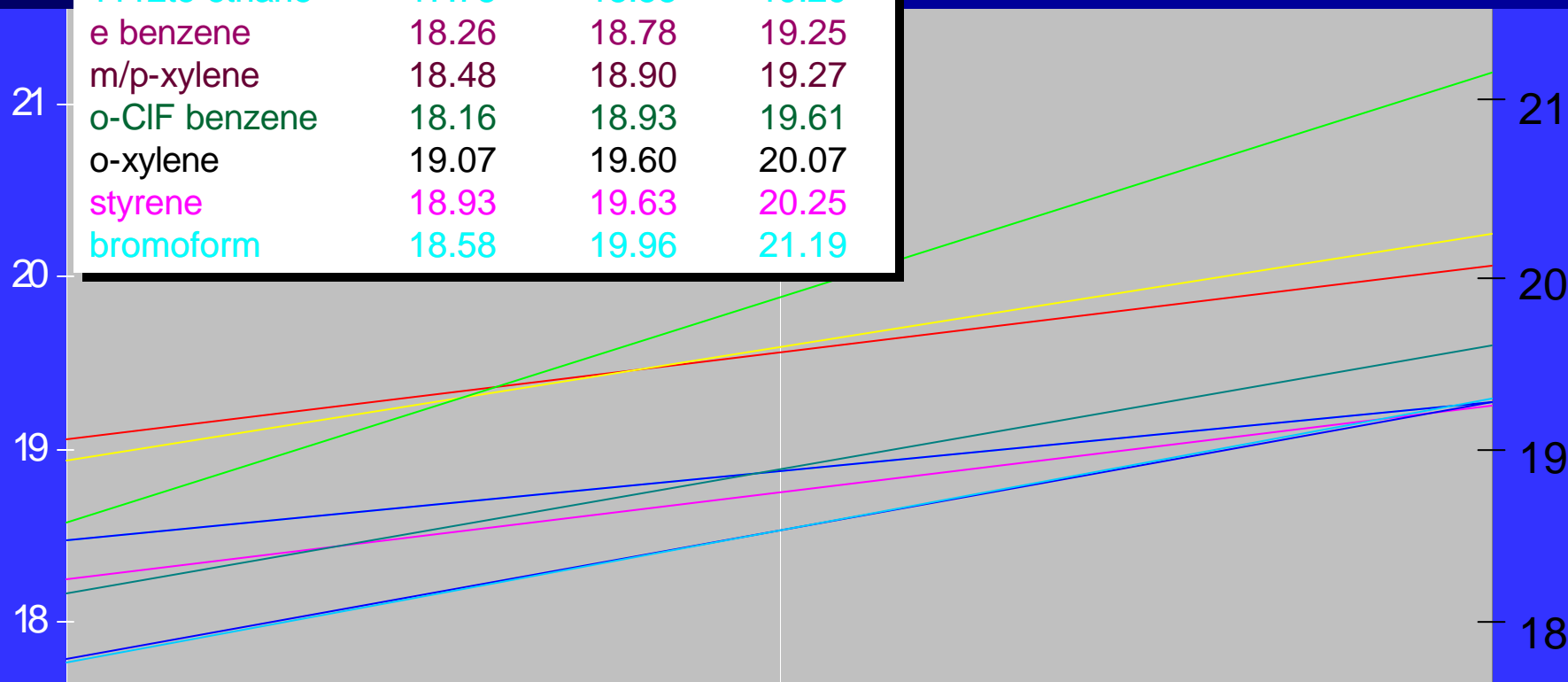
# Window Diagrams

- Maier and Karpathy ('60's):
  - Demonstrated that mixing phases together could yield unique selectivity for packed column applications
- Laub and Purnell (70's)
  - Mixed phase packed column applications
- Jennings et al (80's)
  - Packed column applications, and capillary work based on lengths of dissimilar columns
  - DB<sup>TM</sup>-1301 developed using DB<sup>TM</sup>-1 and DB<sup>TM</sup>-1701



# Window Diagramming

	Rtx <sup>®</sup> -1	Rtx <sup>®</sup> -502	Rtx <sup>®</sup> -35
chlorobenzene	17.79	18.57	19.27
1112te ethane	17.78	18.58	19.29
e benzene	18.26	18.78	19.25
m/p-xylene	18.48	18.90	19.27
o-ClF benzene	18.16	18.93	19.61
o-xylene	19.07	19.60	20.07
styrene	18.93	19.63	20.25
bromoform	18.58	19.96	21.19



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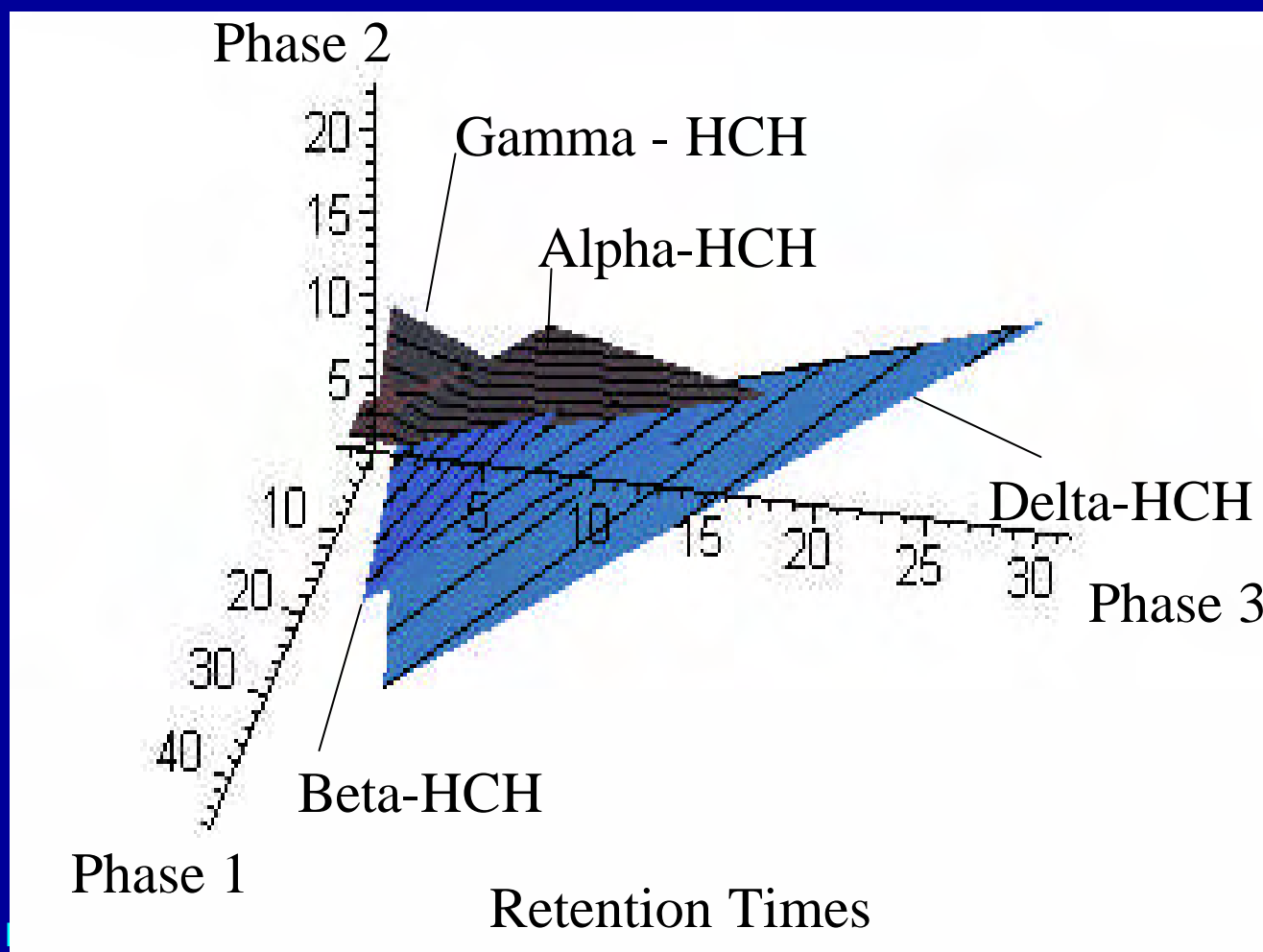
# Stationary Phase Optimization

- Window diagramming
- Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
  - Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition and column dimensions
  - Rtx®-CLPesticides, Rtx-CLPesticides2, Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX
- Computer prediction of solute/stationary phase interactions for new polymer designs

## Computer simulation of phase selectivity, independent of column dimensions (ezGC™)

- “Fix” Run Conditions
- Input data is normalized for column and program parameters
- Search for optimum solution by varying the stationary phase composition
- Program tracks up to 8 dimensions of phase functionalities.
- No solution requires separate re-optimization of input data

# 3-Space Selectivity Surface for 4 Pesticide Compounds

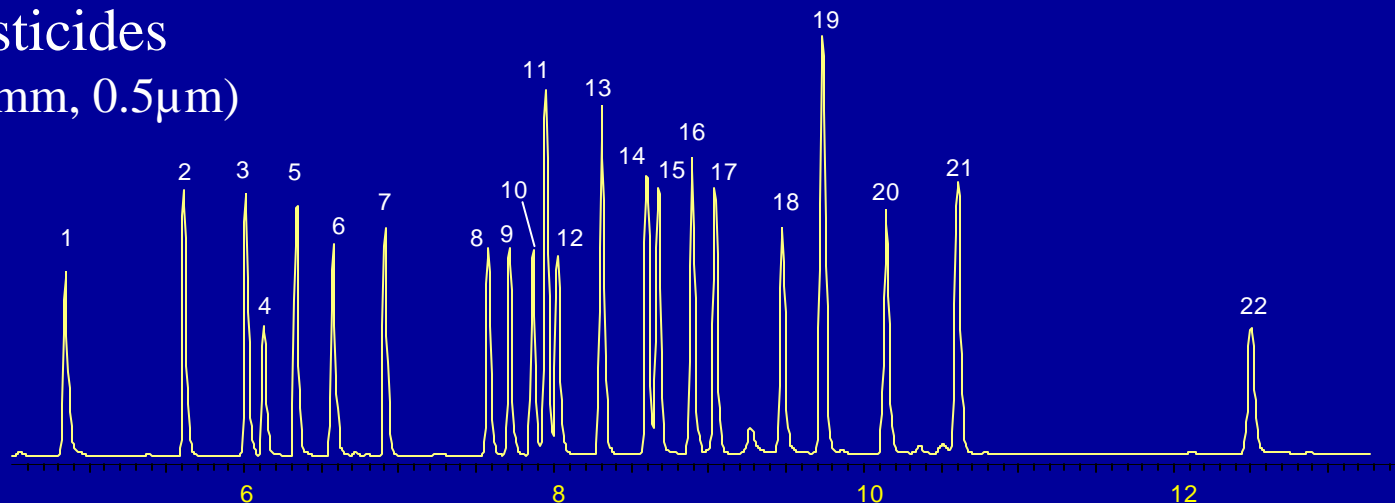


## Rtx<sup>®</sup>-CLPesticides Column Benefits

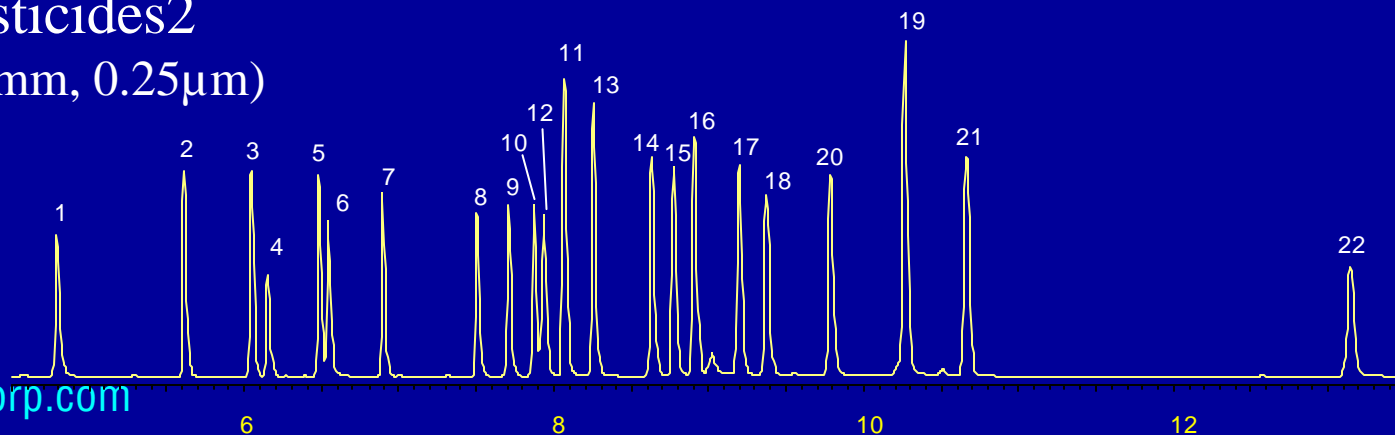
- Baseline resolution of all 22 compounds
- < 25 minute analysis time
- Available in all common dimensions
  - 0.18, 0.25, 0.32 and 0.53mm ODs
- Very low electron capture detector (ECD) bleed levels
- High thermal stability
  - 330°C maximum temperature

# Chlorinated Pesticides Fast Runs

Rtx-CLPesticides  
(30m x 0.32mm, 0.5 $\mu$ m)



Rtx-CLPesticides2  
(30m x 0.32mm, 0.25 $\mu$ m)



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Website NEW : [www.chromalytic.com.au](http://www.chromalytic.com.au) E-mail : [info@chromtech.net.au](mailto:info@chromtech.net.au)

# Chlorinated Pesticides

- 1 2,4,5,6-tetrachloro-m-xylene
- 2 alpha BHC
- 3 gamma BHC
- 4 beta BHC
- 5 delta BHC
- 6 heptachlor
- 7 aldrin
- 8 heptachlor epoxide
- 9 gamma chlordane
- 10 alpha chlordane
- 11 4,4'-DDE

- 12 endosulfan I
- 13 dieldrin
- 14 endrin
- 15 4,4'-DDD
- 16 endosulfan II
- 17 4,4'-DDT
- 18 endrin aldehyde
- 19 methoxychlor
- 20 endosulfan sulfate
- 21 endrin ketone
- 22 decachlorobiphenyl

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# Stationary Phase Optimization

- Window diagramming
- Computer simulation of phase selectivity, independent of column dimensions (ezGC™)
- Rtx®-CLPesticides, Rtx-CLPesticides2
- Computer prediction of optimized stationary phase composition AND column dimensions
  - Rtx-TNT Rtx-TNT2, Rtx-VMS, Rtx-VGC, Rtx-5SilMS, Rtx-VRX, Rtx-OPPesticides2, Customer-specific columns
- Computer prediction of solute/stationary phase interactions for new polymer designs



# Achieving Analyte Separation

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (a-1 / a)$$

## Capacity Factor

$$k = (t_R - t_0) / t_0$$

## Selectivity

$$a = k_2 / k_1$$

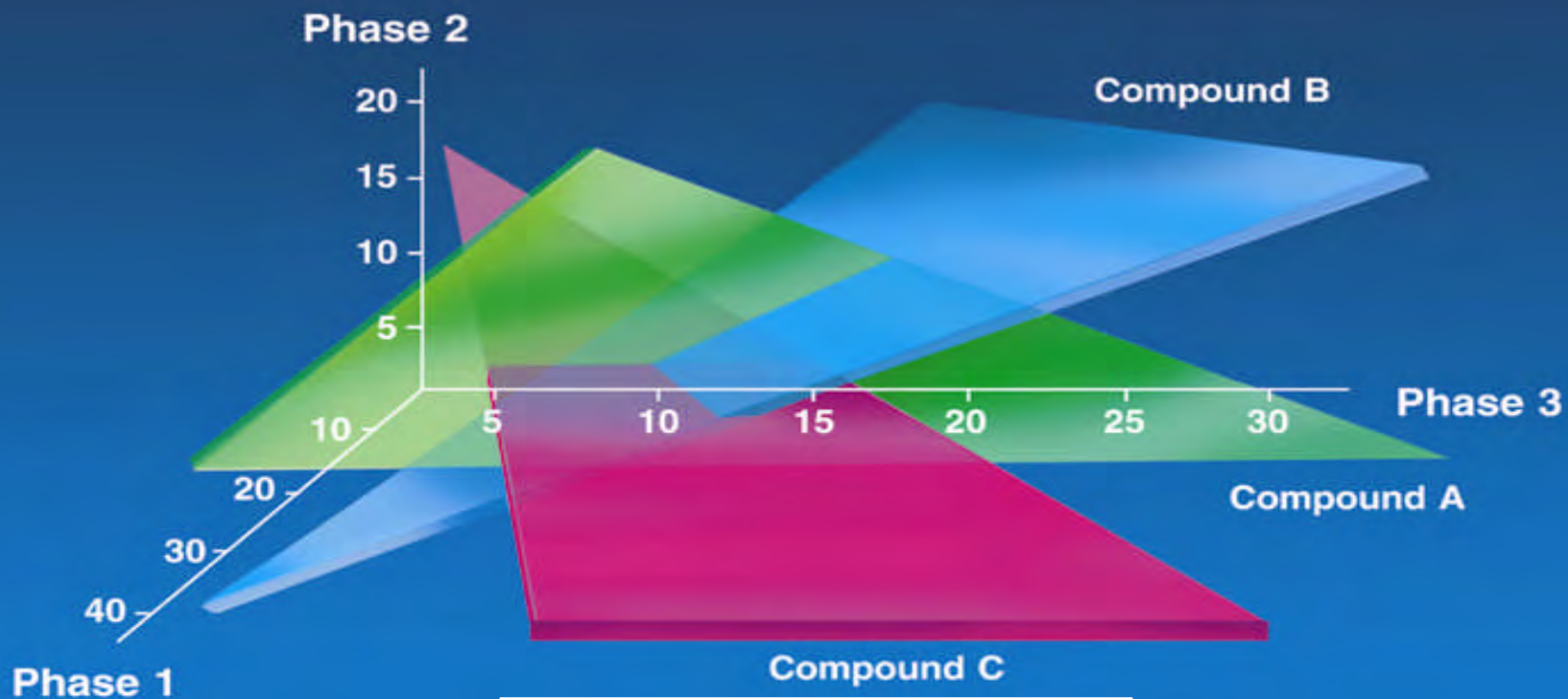
## Thermodynamics:

$$DG = DH - TDS$$

$$DG = -RT \ln K_D$$

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# 3-Space Selectivity Model for 3 Compounds

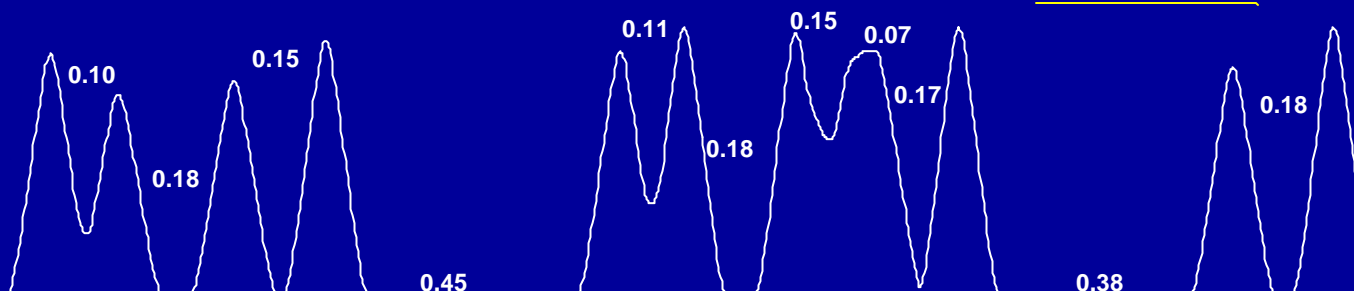


$$\text{Surface} = F \Delta H \Delta S$$

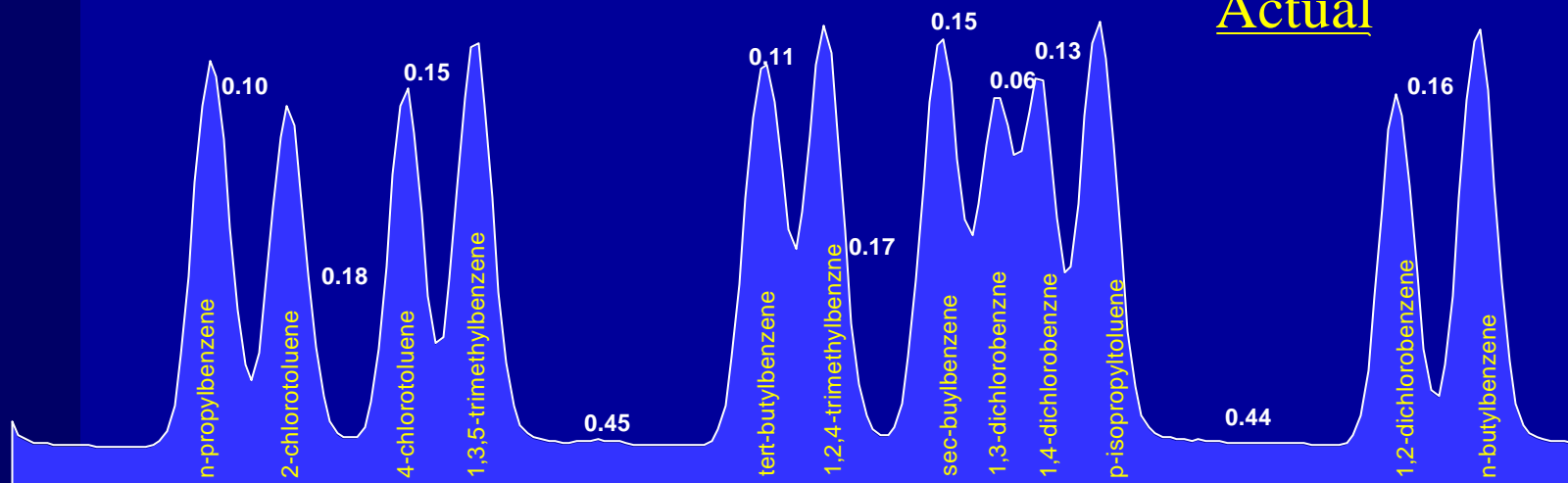
# Volatiles Analysis: Predicted vs. Actual 4 Dimensional Phase

Anal. Chem. 74(9), 2133-2138 2002

Predicted



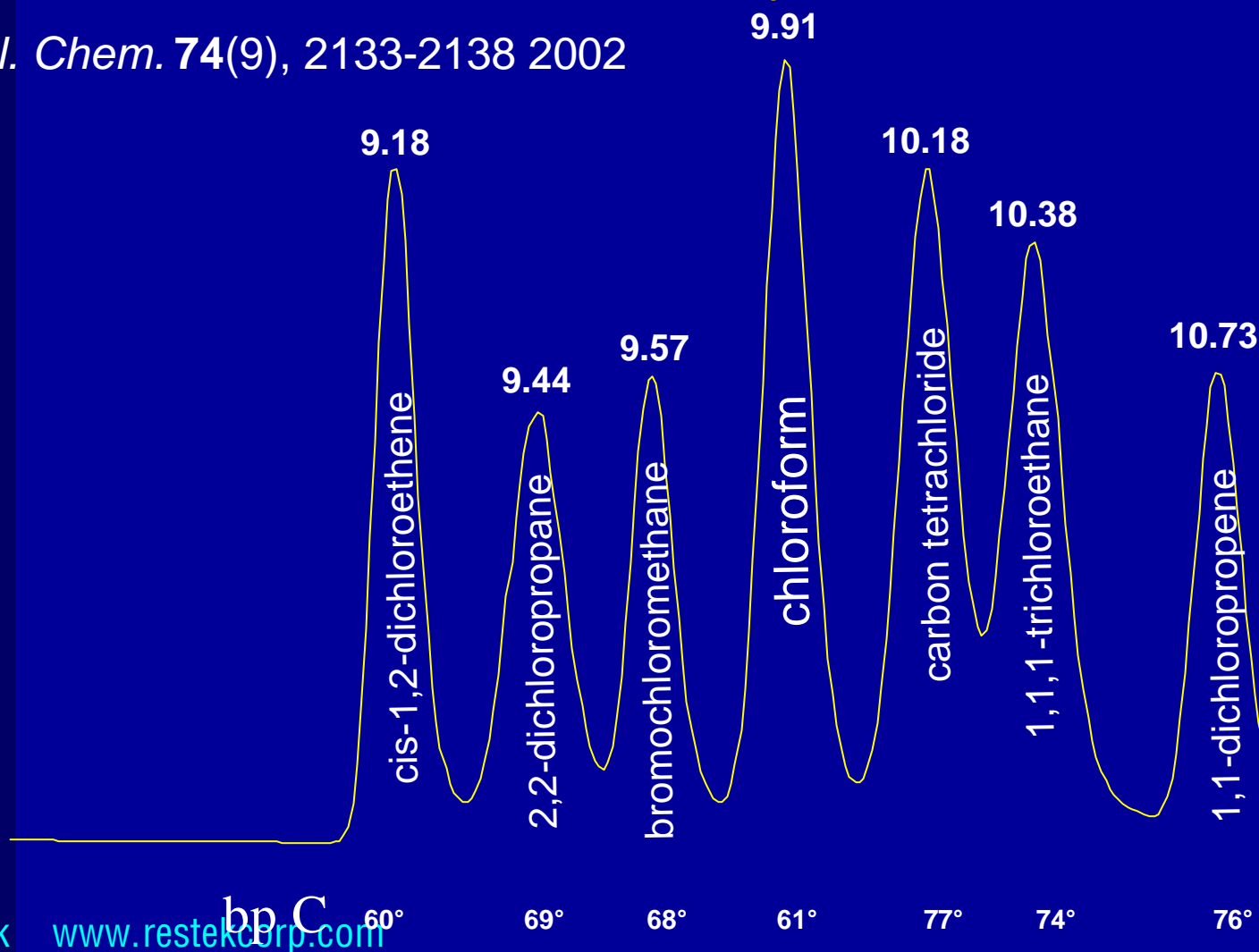
Actual



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# Volatiles Analysis: Rtx<sup>®</sup>-VGC

*Anal. Chem.* 74(9), 2133-2138 2002



## Design Criteria of 2-D Column

- Continuous section of tubing with no press-tight
- Volatility separation 1<sup>st</sup>
- Alternate selectivity 2<sup>nd</sup>
- Same i.d. for both columns
- Thicker film on 1<sup>st</sup> ?
- Maintain higher efficiency on 2<sup>nd</sup> ?
- Will also work for press-fit columns



# Simultaneous 2-D Modeling

---or---

## Why 2D is not 2X 1D GC

- 1.) Calculation of the pressure at the modulation point is not as straight forward during a “desorption”
- 2.) Not a normal “injection” onto second column  
there is a selective retention of analyte in the phase
- 3.) There is no “buffer volume” at the modulation point, or a pressure controller to adjust for any pressure surges  
at 1 atm a liquid expands 1000X as it vaporizes



## Input Data

- Compounds of interest analyzed in 1-D mode on each stationary phase of interest at two different temperatures or temperature programs
- A separate  $\Delta H$  and  $\Delta S$  are calculated for each compound on each stationary phase independent of physical parameters
- Separation is modeled on conditions of 1<sup>st</sup> column
- Eluent is re-focused (peak width is re-calculated) and injected onto 2<sup>nd</sup> column
- Final elution from second column is reported as a function of both 1<sup>st</sup> and 2<sup>nd</sup> dimension – tabular report

# Modeling Accuracy on Continuous 2D column - LECO Pegasus 4D system Conditions

180 um i.d. continuous 2D column:

10M Rtx-1, 1.0 um d.f.

50C (0.2 min), 5C/min to 200C (0.8 min)

0.8M Rtx-1701, 0.1 um d.f.

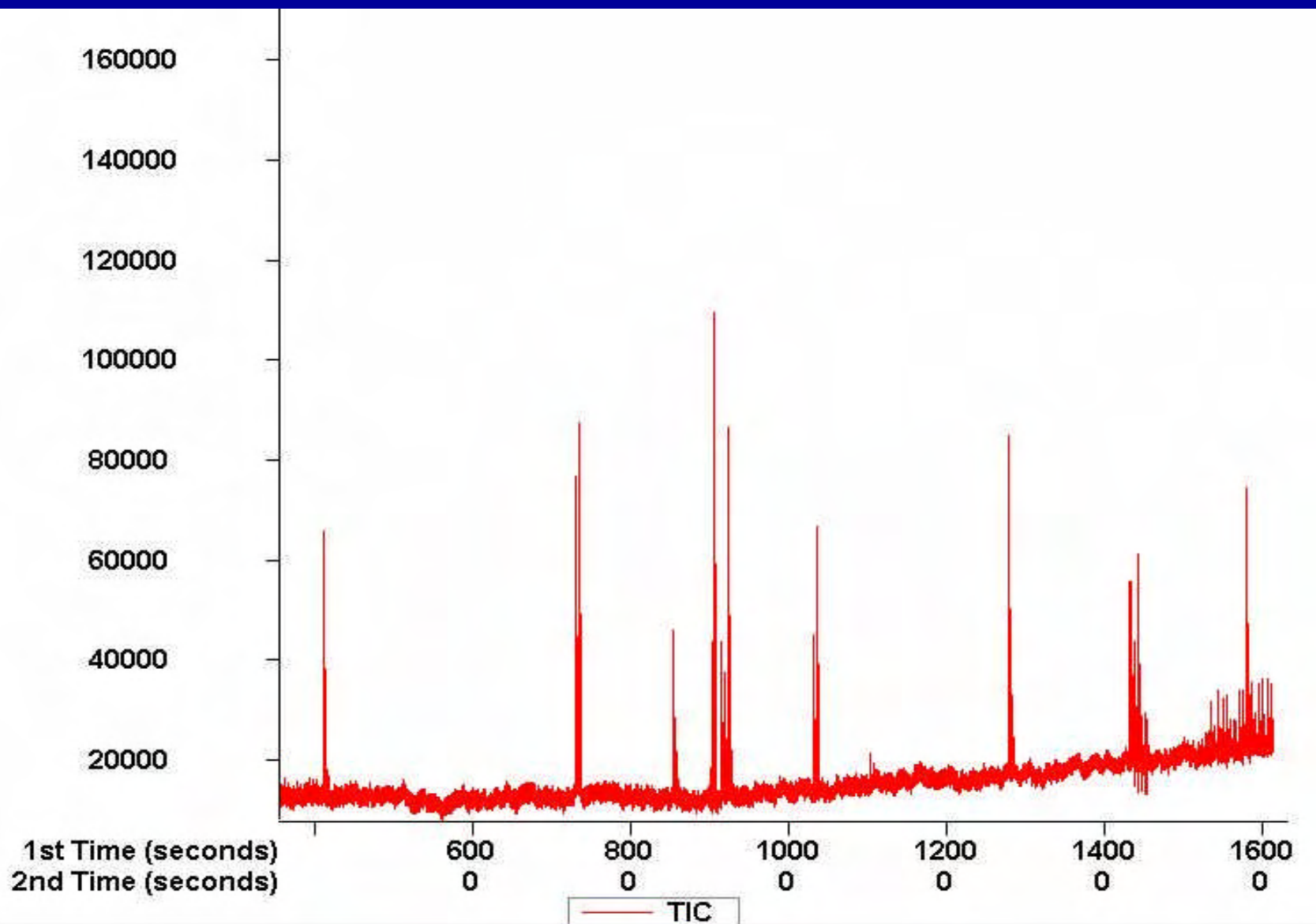
55C (0.2 min), 5C/min to 205C (0.8 min)

Helium Carrier, 1mL/min constant flow

1uL injection, 200/1 split

Modulator Period = 4 sec





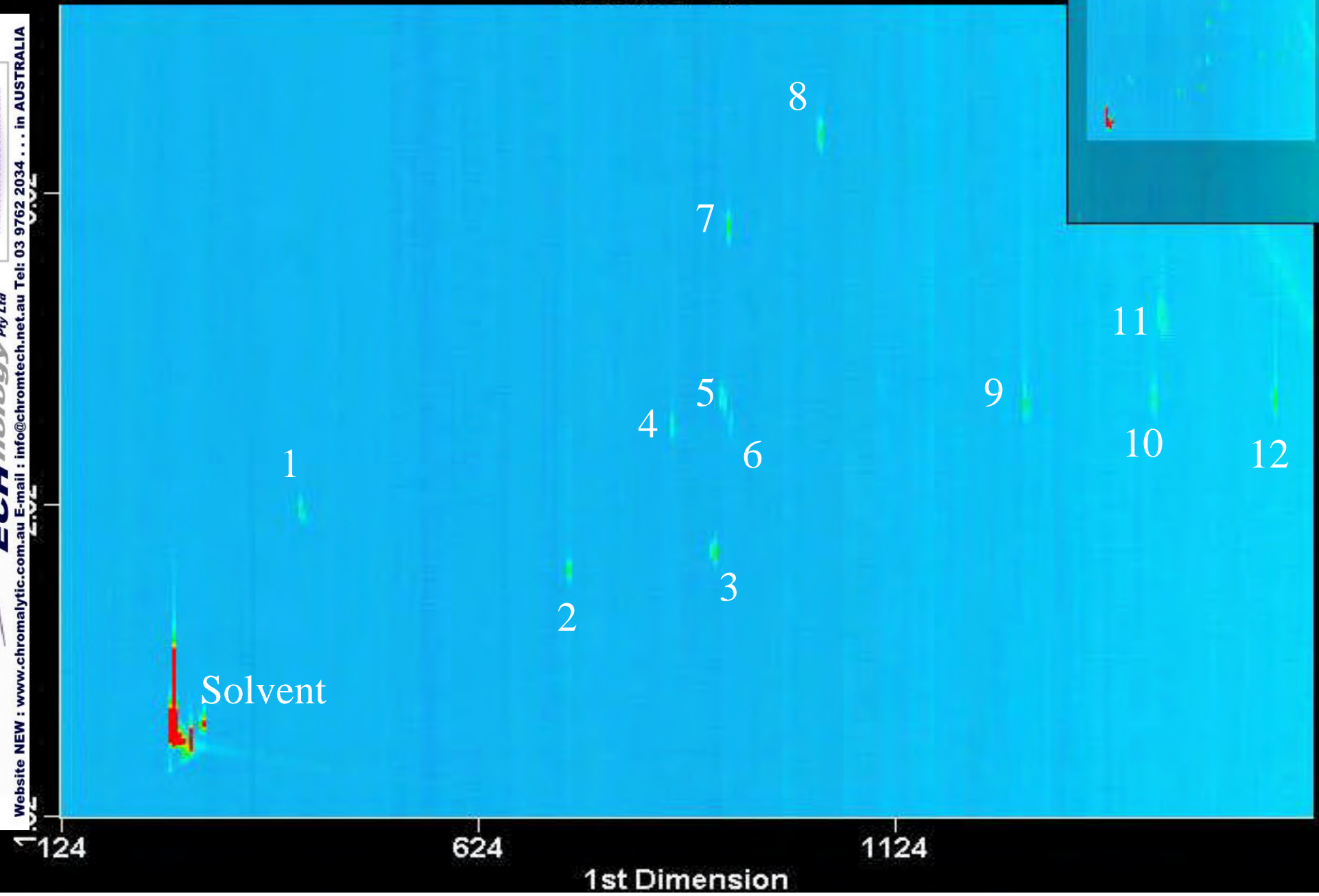
# Grob Test Mixture

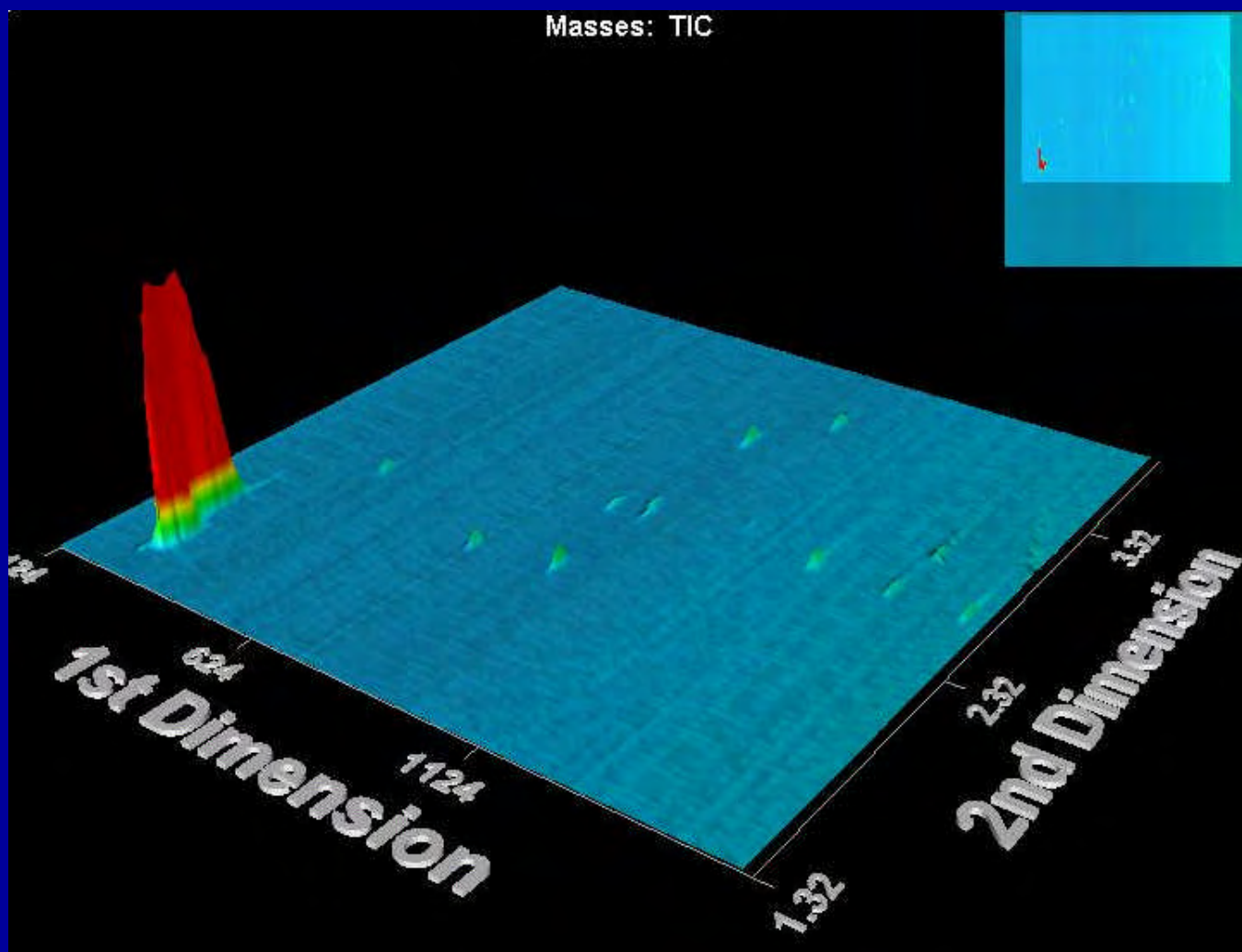
## As numbered on 2D Chromatogram

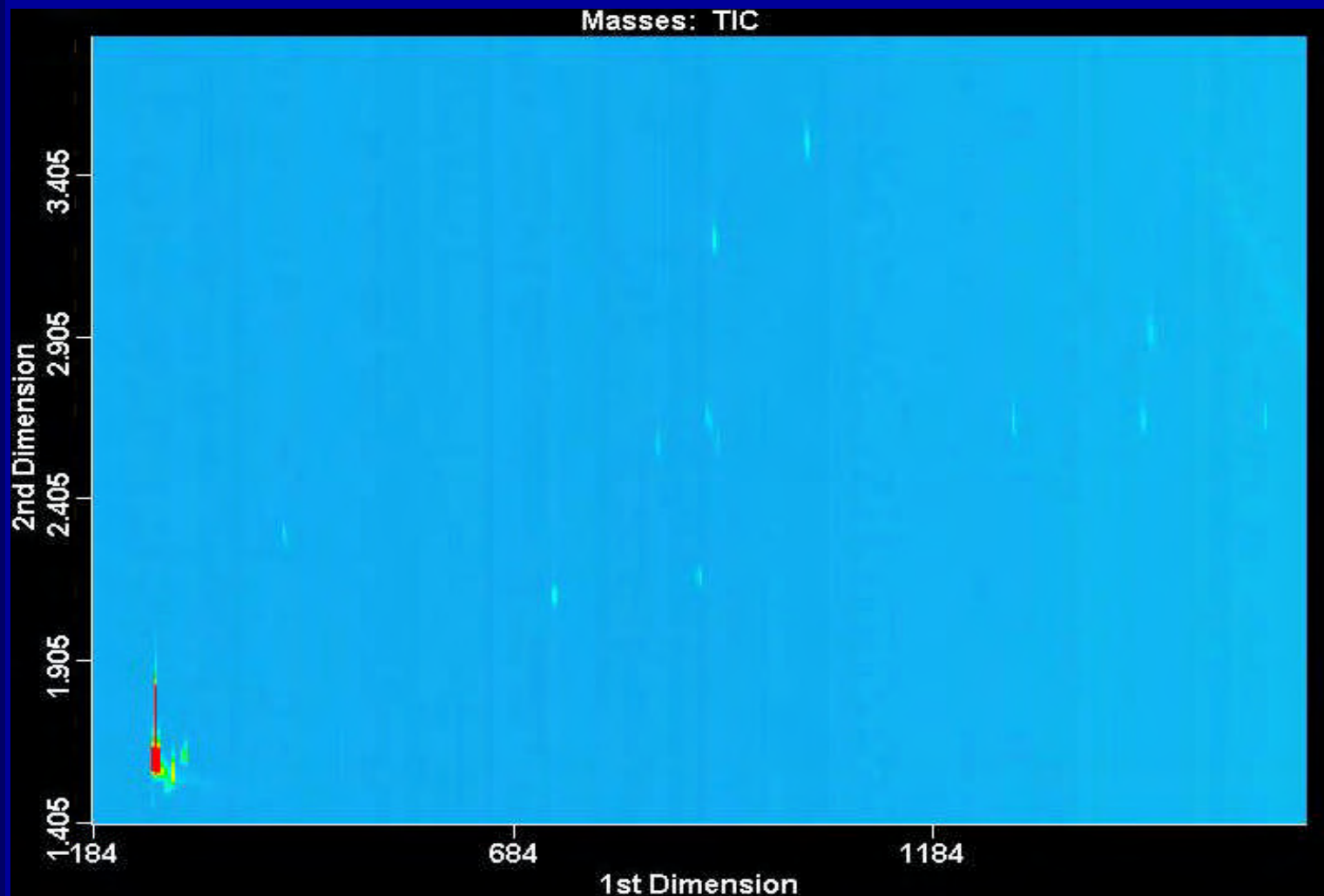
- 1.) 2,3-butanediol
- 2.) decane
- 3.) undecane
- 4.) 1-octanol
- 5.) 1-nonanol
- 6.) 2-ethylhexanoic acid
- 7.) 2,6-dimethylphenol
- 8.) 2,6-dimethylaniline
- 9.) C10 FAME
- 10.) C11 FAME
- 11.) dicyclohexylamine
- 12.) C12 FAME

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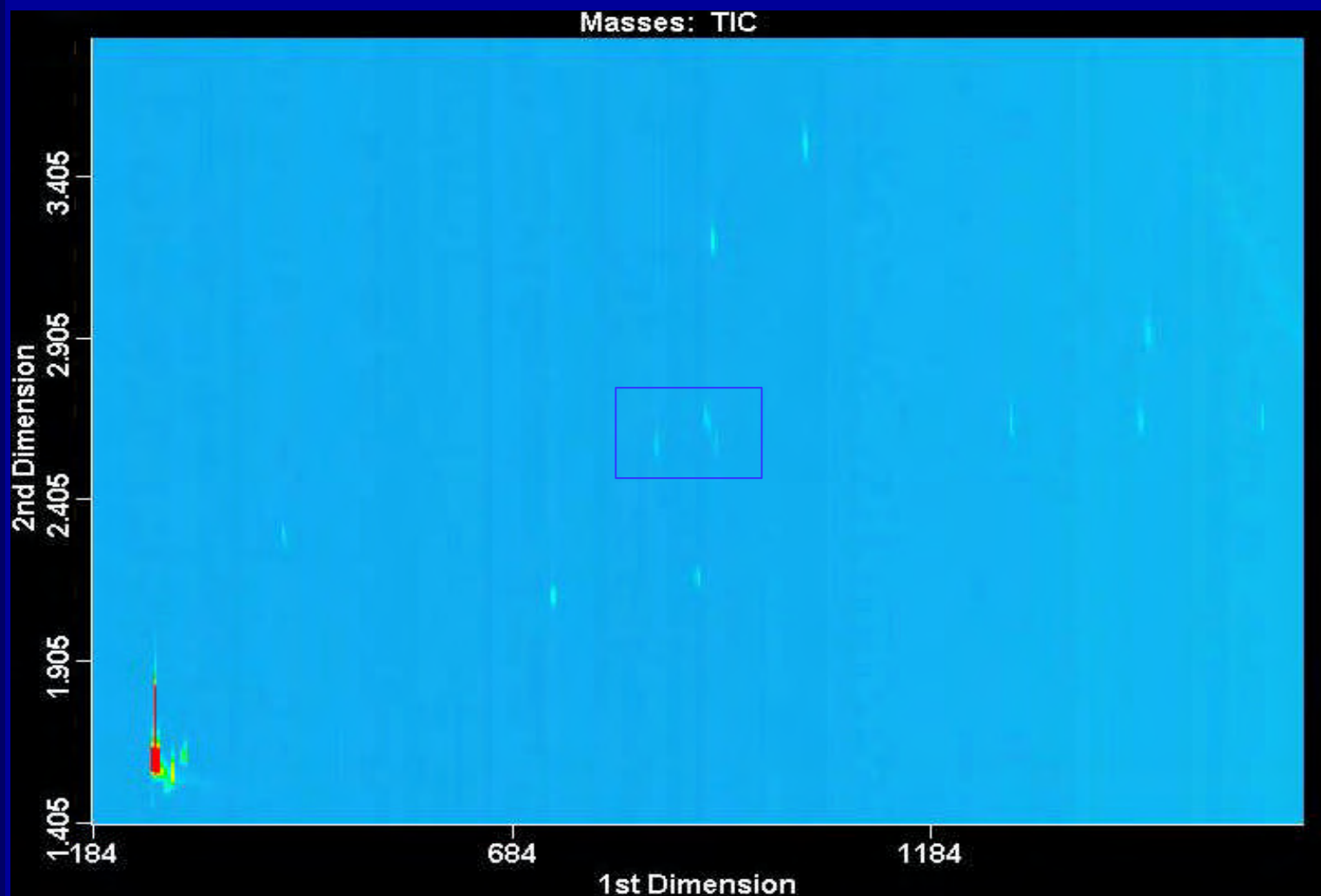
Masses: TIC

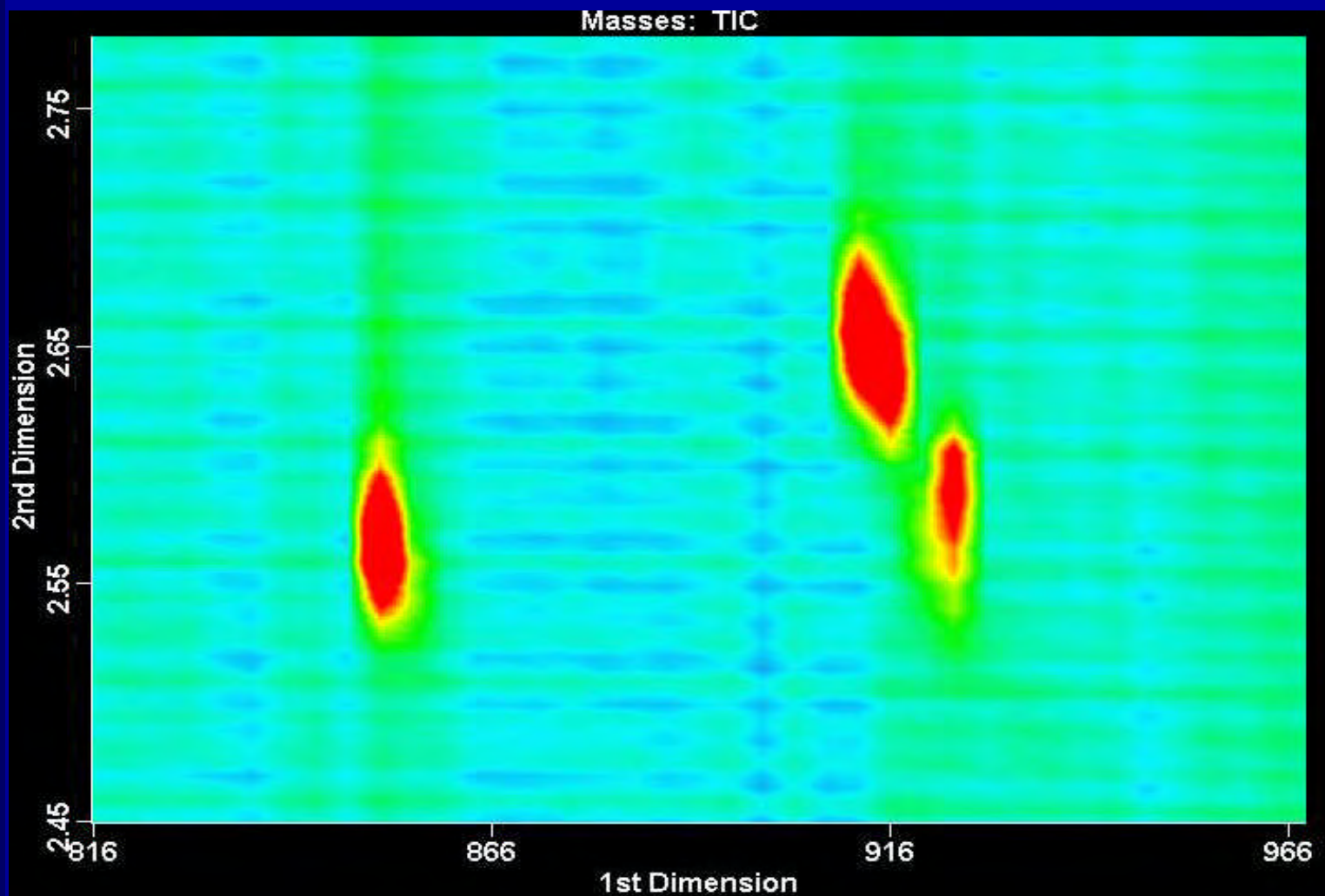


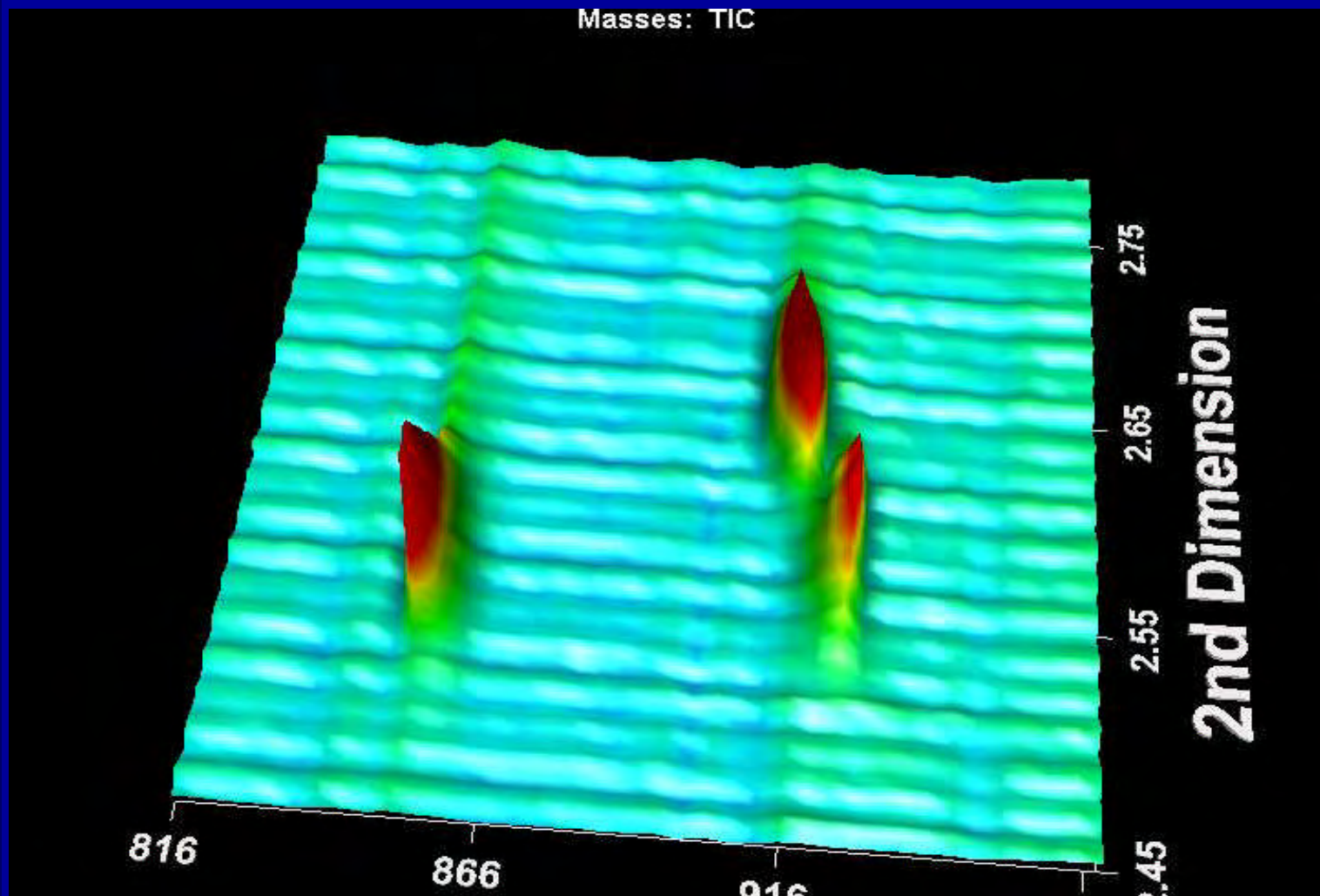




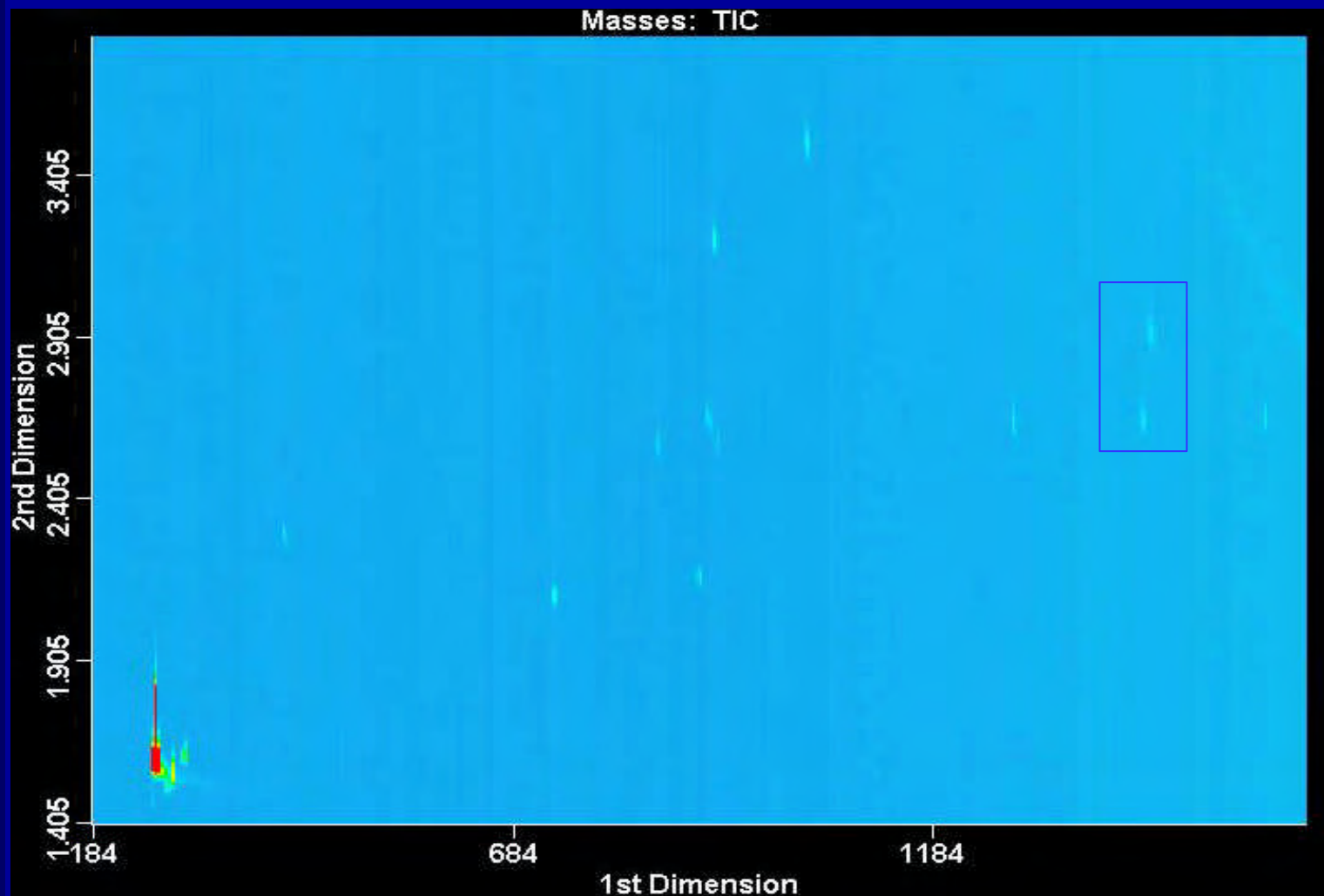


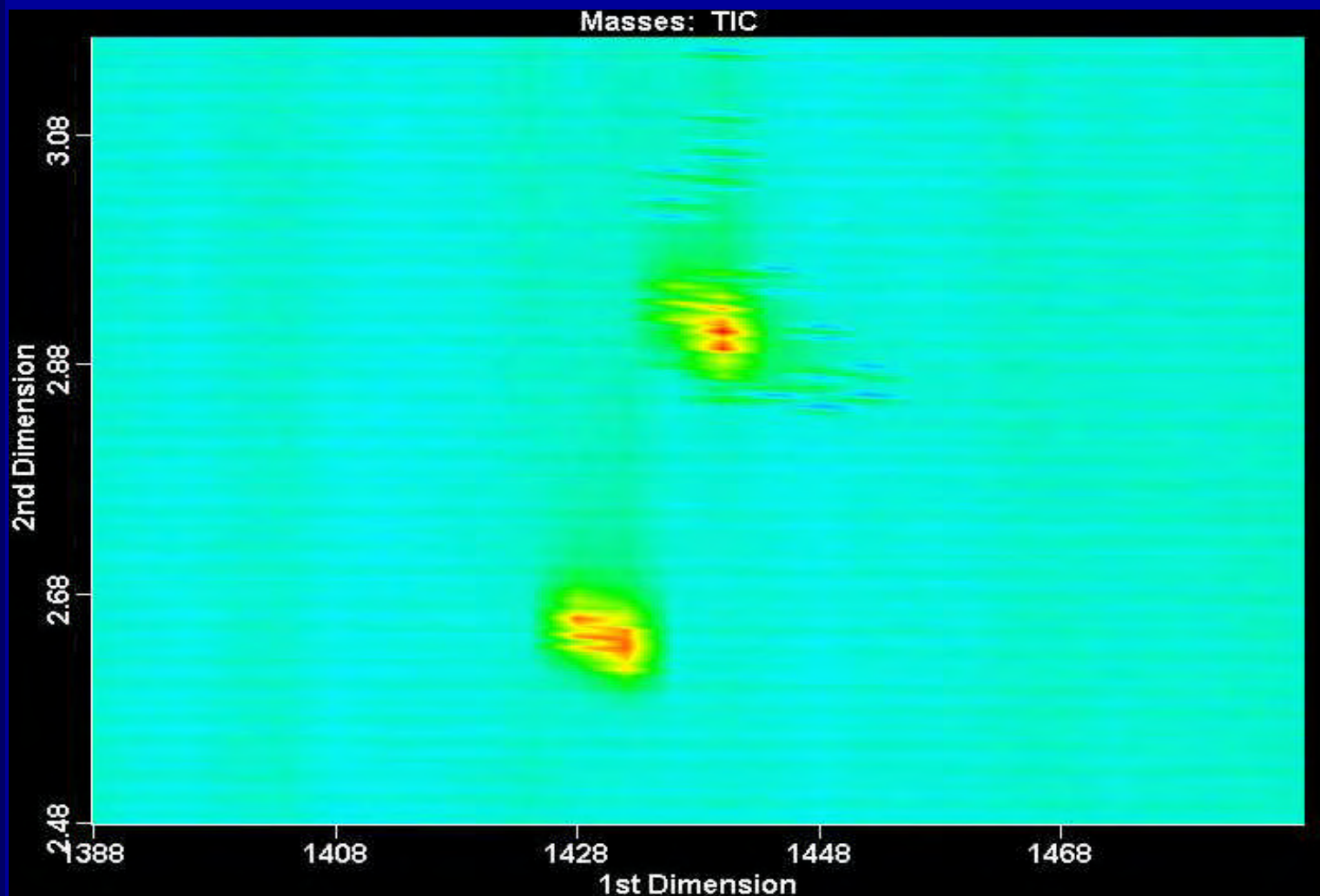






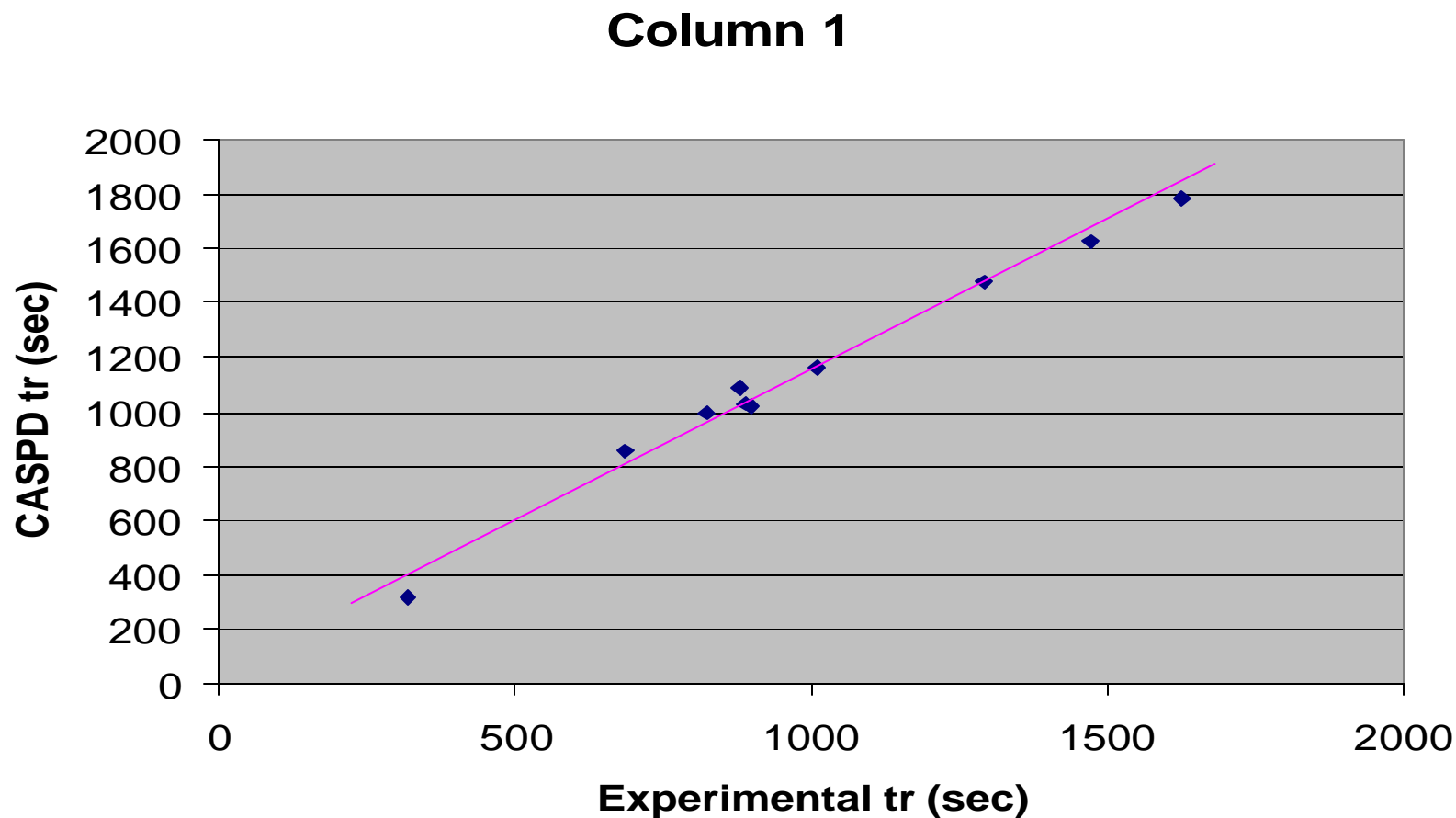




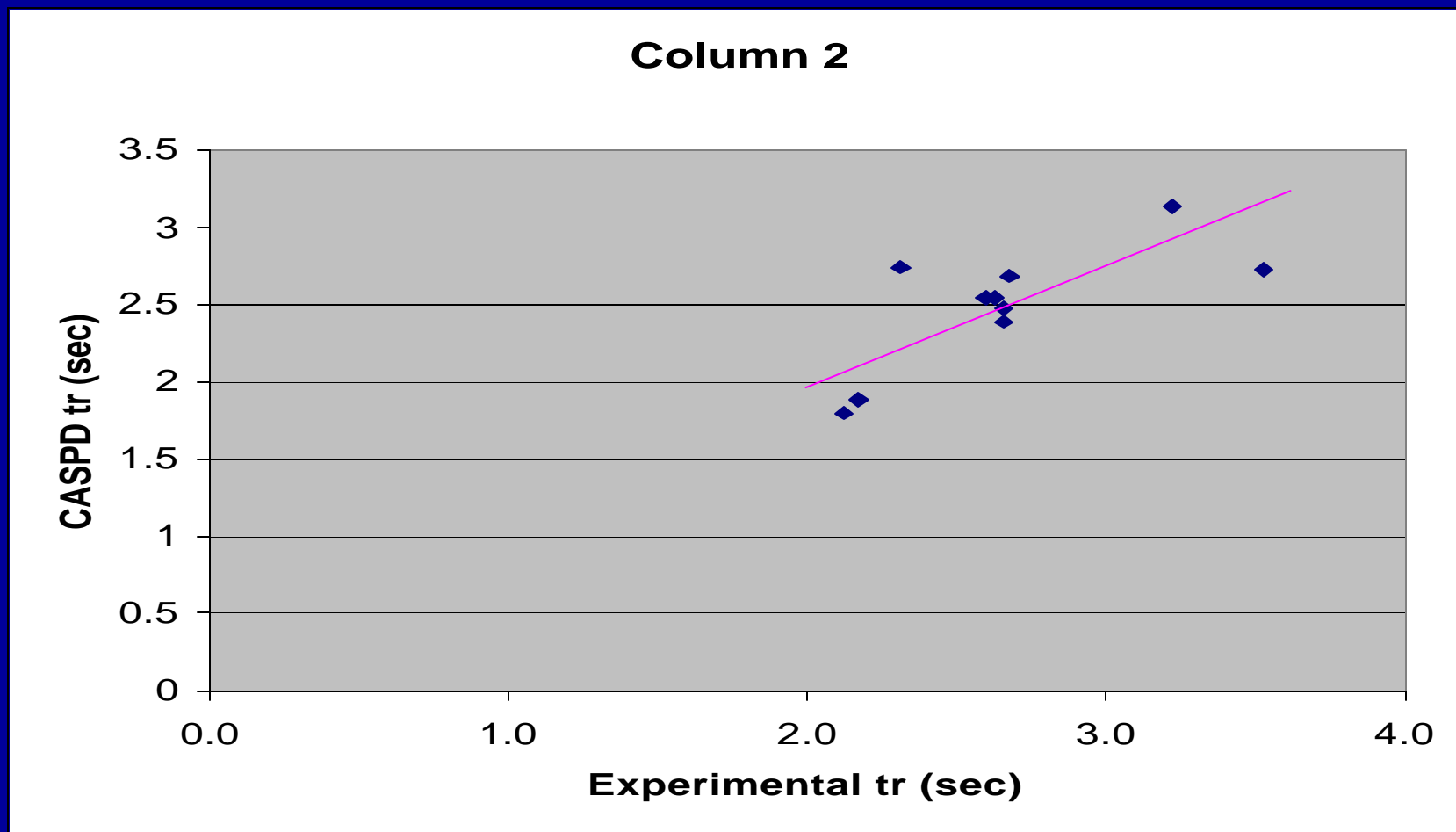


			Column 1			Column 2	
			Exp	Model		Exp	Model
Compound Name	#	tr1 cm	tr1 sec	tr1 sec	tr2 cm	tr2 sec	tr2 sec
Calibration	0	17.35	1124		12.85	2	
2,3 Butanediol	1	4.9	317	318	6.4	2.3	2.74
decane	2	10.55	683	858	5.15	2.1	1.8
undecane	3	13.55	878	1088	5.5	2.2	1.89
1-octanol	4	12.75	826	995	8.2	2.6	2.54
1-nonanol	5	13.75	891	1032	8.7	2.7	2.68
2-ethylhexanoic acid	6	13.9	900		8.25	2.6	
2,6 dimethylphenol	7	13.85	897	1018	12.25	3.2	3.13
2,6-dimethylaniline	8	15.55	1007	1160	14.2	3.5	2.73
C10-FAME	9	19.95	1292	1476	8.6	2.7	2.39
C11-FAME	10	22.7	1471	1627	8.6	2.7	2.47
dicyclohexylamine	11	22.85	1480		10.25	2.9	
C12-FAME	12	25.1	1626	1784	8.4	2.6	2.55

# Actual –vs.- Theoretical for Column 1



# Actual –vs.- Theoretical for Column 2



# Conclusions

- Columns performed successfully
- Modeling is not yet correct
- Future work
  - Investigation of the best column ratios for general use
  - Vu-2 Union developed for applications requiring press-tight connections
  - Role of modulator in “injection” onto second column
  - Modeling refinements for column ensemble developments and technical service
  - Commercially-available Optimization program?

## Summary

- Continuous 2-D columns eliminate need for press tight.
  - Distinct advantage for commercial users
- Modeling optimization software can save large amount of R&D time for column ensemble development
- Physical optimization work on hold
- Additional research needs to be done for prediction of second column elution



# Acknowledgements

- Jack Cochran – LECO Corporation
- Ed Ledford – Zoex Corporation
- Jean-Marie D. Dimandja – Spelman College



# Analysis of Browning Reaction Products in Foods, Using High Performance Liquid Chromatography

**Rebecca E. Wittrig, Ph.D. and Lydia Nolan**  
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Bellefonte, PA 16823



# Introduction

In food systems, perceived flavor is based not only on individual ingredients that make up the product, but also on interactions between these components. Browning is an important reaction in food systems, and affects both the flavor and the color of the product. One type of non-enzymatic browning reaction that occurs in products such as baked goods and soy sauce is the Maillard reaction. When reducing sugars such as glucose are heated in the presence of a free amino acid or a free amino group in a protein chain, a variety of products, including 5-hydroxymethyl-2-furaldehyde (HMF), result. To monitor the progress of a Maillard browning reaction, HPLC with a UV-visible detector can be used to quantitate products such as HMF.<sup>1</sup> In systems containing a number of reaction products, LC with a mass selective detector (LC/MS) would provide more specific information about the reaction products. The application of LC and LC/MS to the study of HMF will be presented.

# The Maillard Reaction

The Maillard reaction is one of four primary non-enzymatic browning reactions. This reaction requires the presence of an amino-bearing compound, a reducing sugar, and water. Basic amino acids, such as lysine, are especially susceptible. When the reducing sugar is a hexose, 5-hydroxymethyl-2-furaldehyde, or HMF, is one of the intermediate reaction products, especially at lower pH. The structure of HMF is shown below, and a simplified Maillard reaction scheme is shown in Figure 1.<sup>2</sup> The formula weight of HMF is 126.1, and the  $UV_{\max}$  is 283nm. On further reaction, a number of high molecular weight polymeric materials are formed, resulting in color and flavor changes. These changes may or may not be desirable; some of the negative effects include off-flavors or off-colors, and the potential loss of essential amino acids such as lysine.

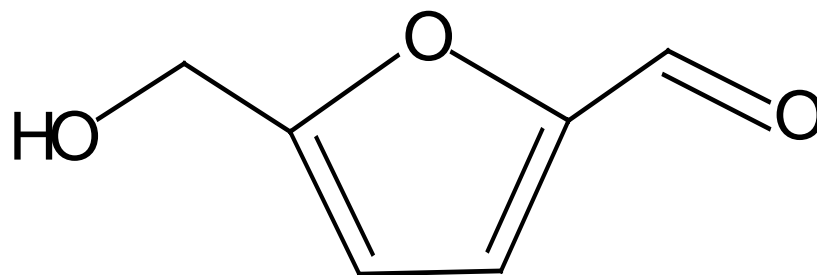
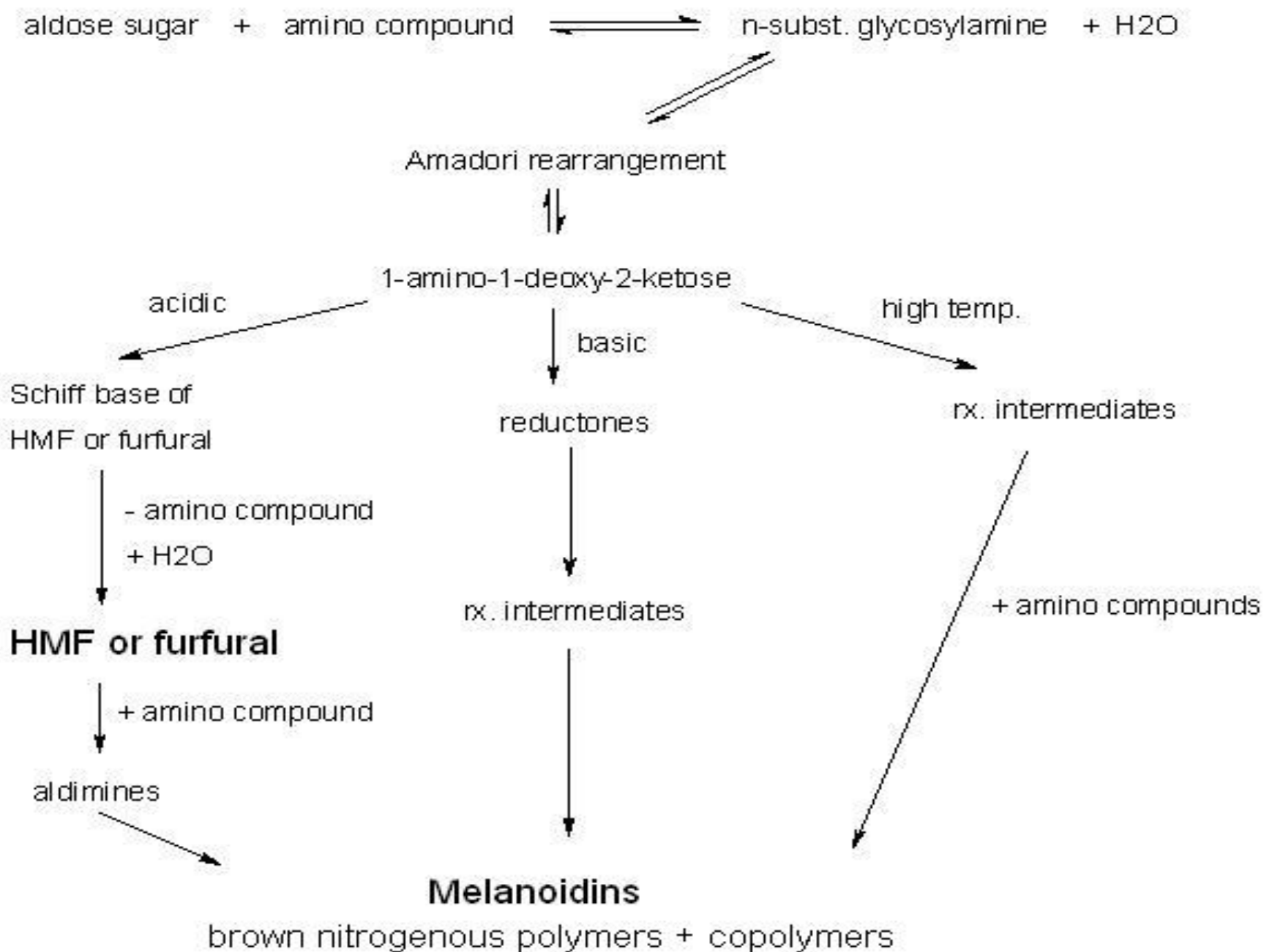


Figure 1. Simplified Maillard reaction scheme.



# Liquid Chromatographic Analysis of HMF

Liquid chromatography (LC) provides a powerful tool for monitoring reaction products such as HMF in a variety of food and beverage products. Compared to the traditional spectrophotometric methods, LC is a much more specific assay and is less susceptible to interferences. A number of LC procedures have been published,<sup>3-5</sup> most using a reversed phase separation with a C18 or C8 stationary phase and water:methanol or water:acetonitrile as the mobile phase. In order to make the separation compatible with MS detection, water:methanol with 10 mM ammonium formate was used in this work.

The analysis of an HMF standard is shown in Figure 2, with the LC conditions given in Table I. The method is linear over the range of 0.014–213 ppm, as shown in Figure 3. Several types of fruit juice were tested using this method. A grape juice assay is shown in Figure 4. There is at least one compound that interferes with the HMF when using UV detection at 280nm; therefore, some type of sample treatment will be needed.

Figure 2. Analysis of an HMF standard solution by HPLC. Run conditions are given in Table I.

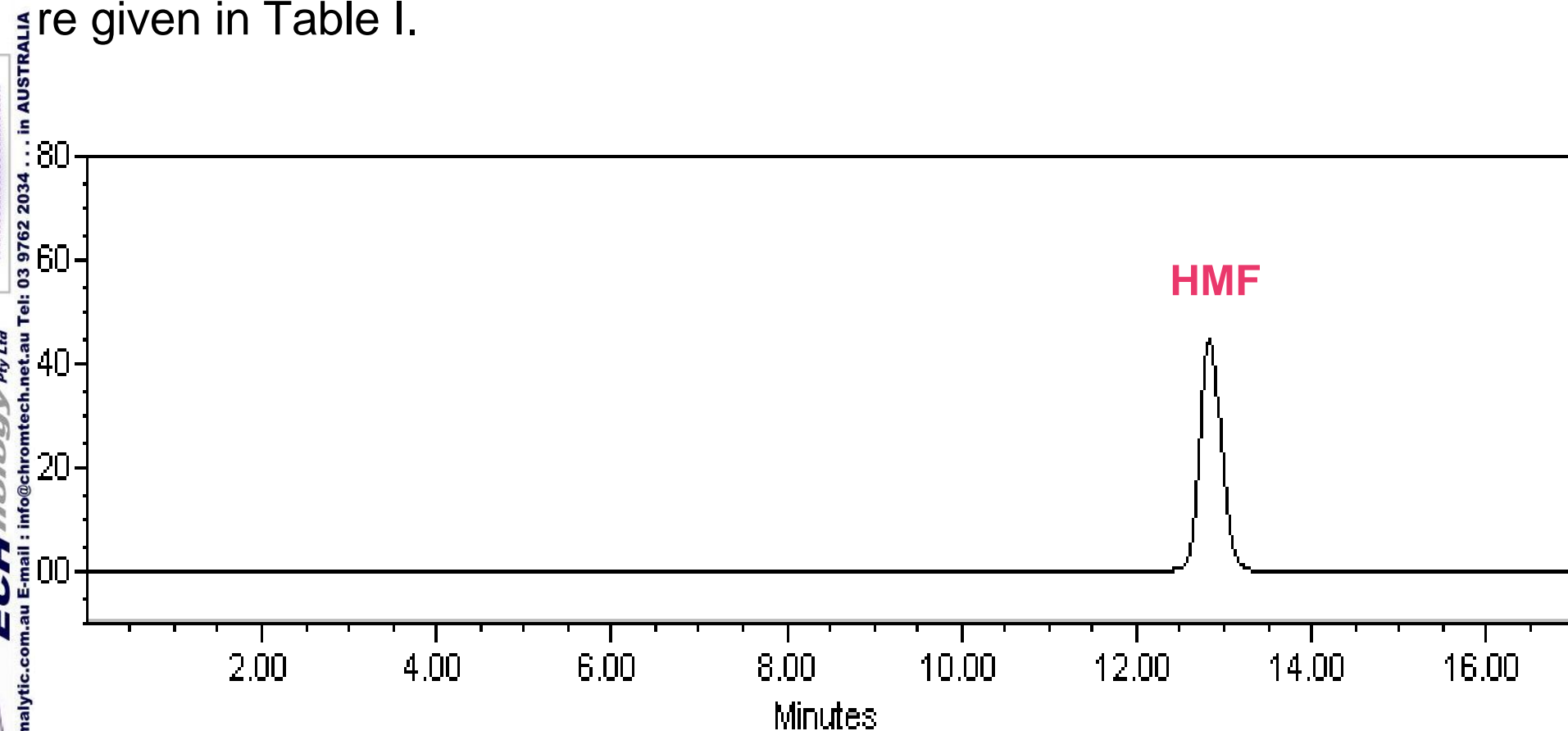


Table I. Chromatographic conditions for HMF analysis by LC.

Column: Ultra C18 (Restek Corp.), 250 mm x 4.6 mm, 5  $\mu$ m

Mobile Phase A: 90:10 water:methanol, 10 mM ammonium formate

Mobile Phase B: 10:90 water:methanol, 10 mM ammonium formate

<u>Time (minutes)</u>	<u>% B</u>
0	0
5	0
10	100
20	100
21	0

Flow: 0.5 mL/min.

Temperature: ambient

Detector: UV @ 280 nm

Injection Volume: 10  $\mu$ L

Figure 3. Linearity plot for HMF, using LC-UV. Over a concentration range of 14 ppb - 213 ppm,  $R^2 = 0.9994$ .

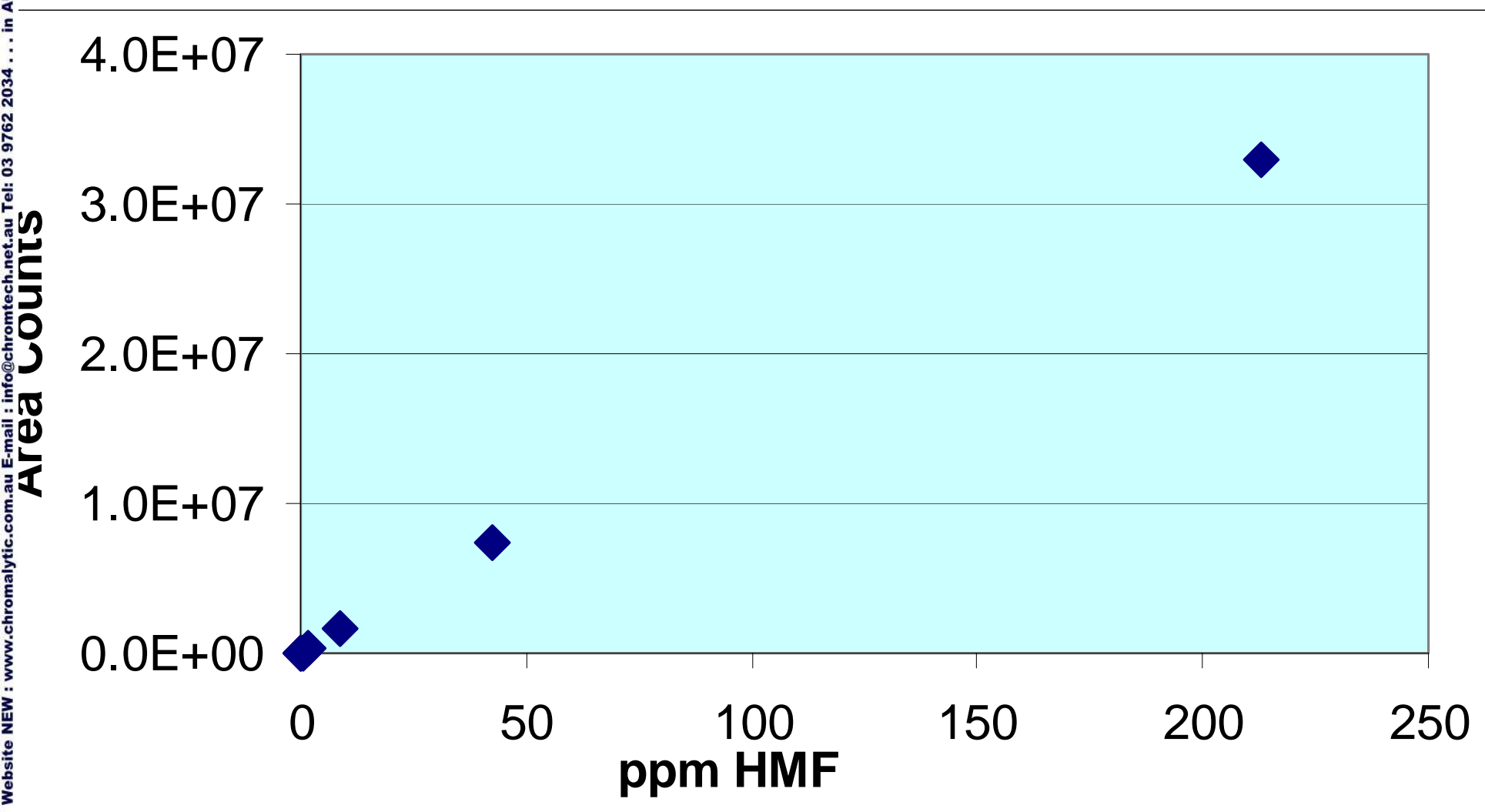
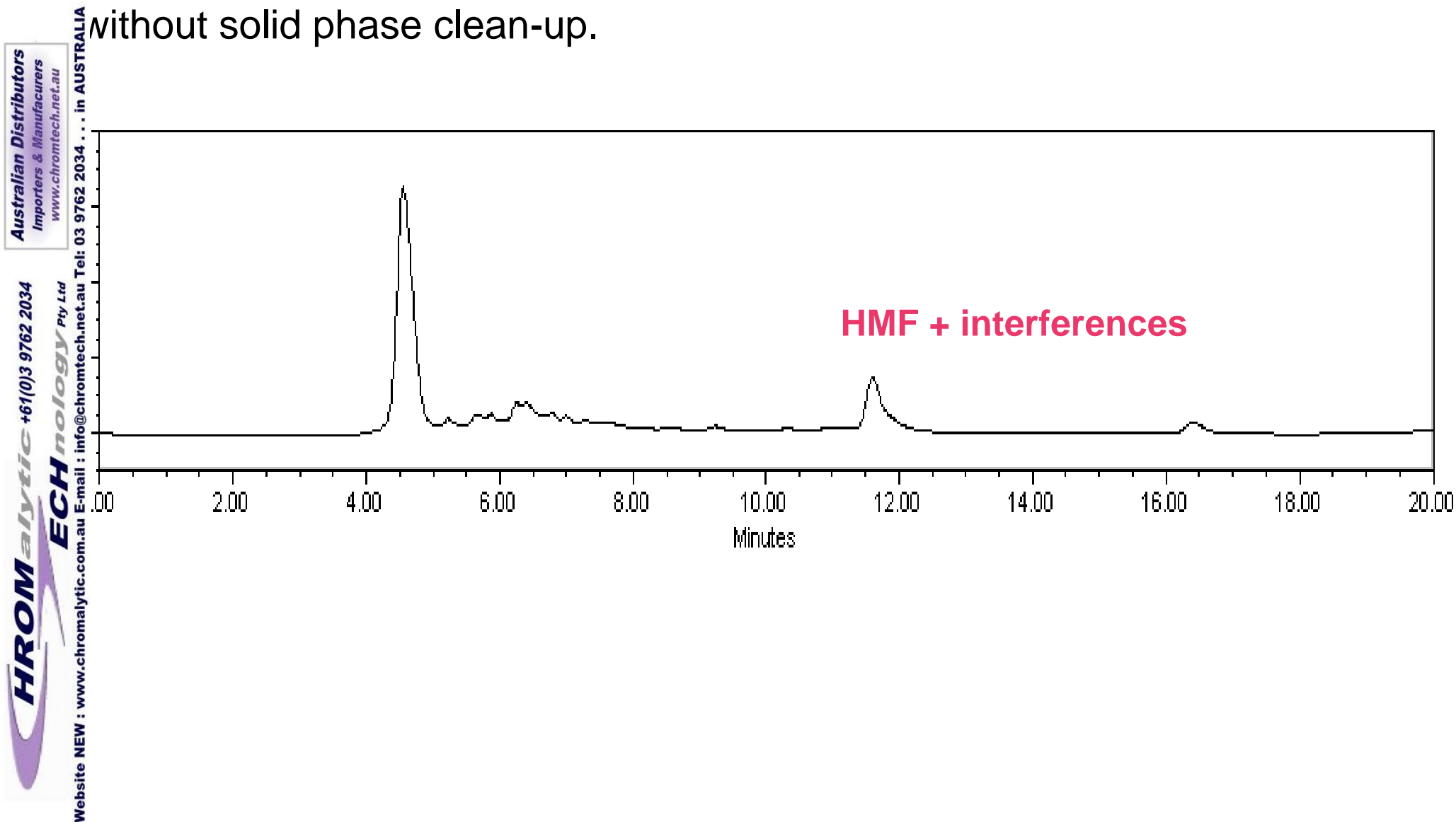




Figure 4. Analysis of HMF in grape juice. The juice was analyzed neat, without solid phase clean-up.



# Solid Phase Extraction of HMF from Juice Samples

Because of the interferences present in grape juice, sample treatment was necessary. Previous reports of solid phase extraction (SPE) used C18 cartridges with 15-20% acetonitrile as the final extraction solvent.<sup>6,7</sup> To match the mobile phase in this analysis, methanol was used at concentrations of 20%, 50%, and 100%. Both C18 tubes and carbon molecular sieve (Carboprep™) tubes were tested. Good recoveries were obtained using either 20% or 50% methanol and the C18 phase; however, the lower concentration of methanol resulted in a cleaner final extract. Good recoveries were obtained with the Carboprep™ tubes as well, with 100% methanol.

## Extraction Procedure

### Conditioning

- a. Apply 3 mL methanol
- b. Apply 3 mL deionized water

### Sample Application

- a. Apply 4 mL sample to moist SPE tube, gravity feed

### Wash

- a. Pull remaining sample through tube, using vacuum
- b. Apply 3 mL water
- c. Remove excess water from bed under vacuum

### 4. Elution

- a. Apply 2 mL elution solvent, gravity feed, dilute to volume

Figure 5. Analysis of HMF in grape juice, following extraction using a C18 SPE tube. HMF was eluted with 20% methanol.

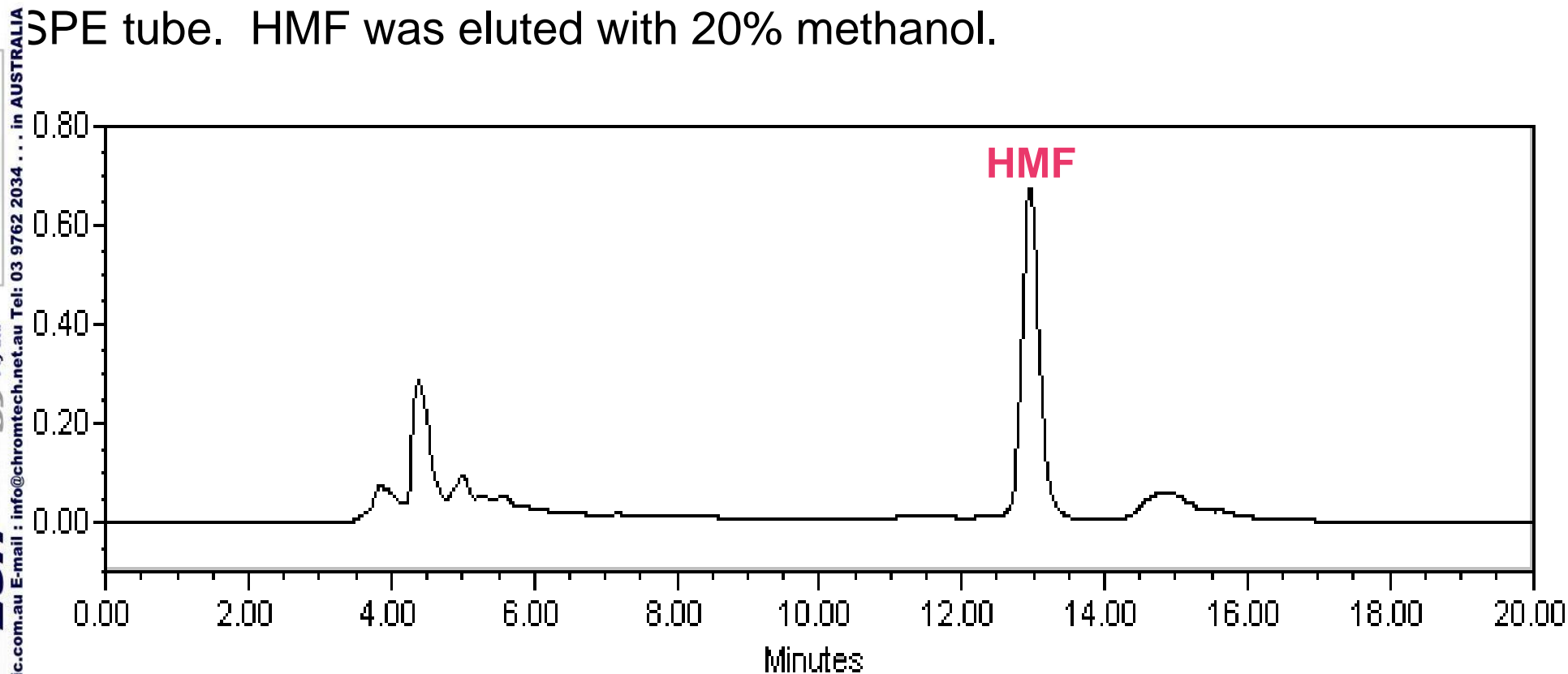


Figure 6. Analysis of HMF in grape juice, following extraction using a C18 SPE tube. HMF was eluted with 50% methanol.

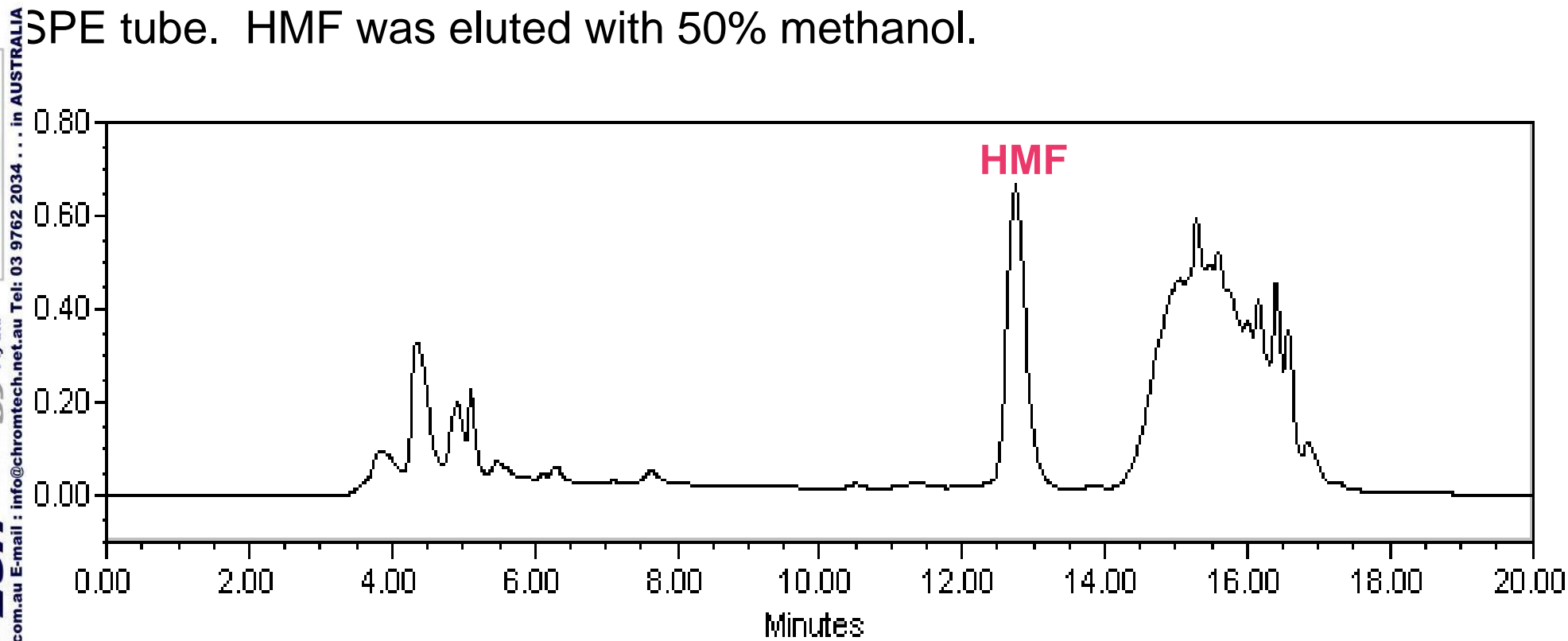
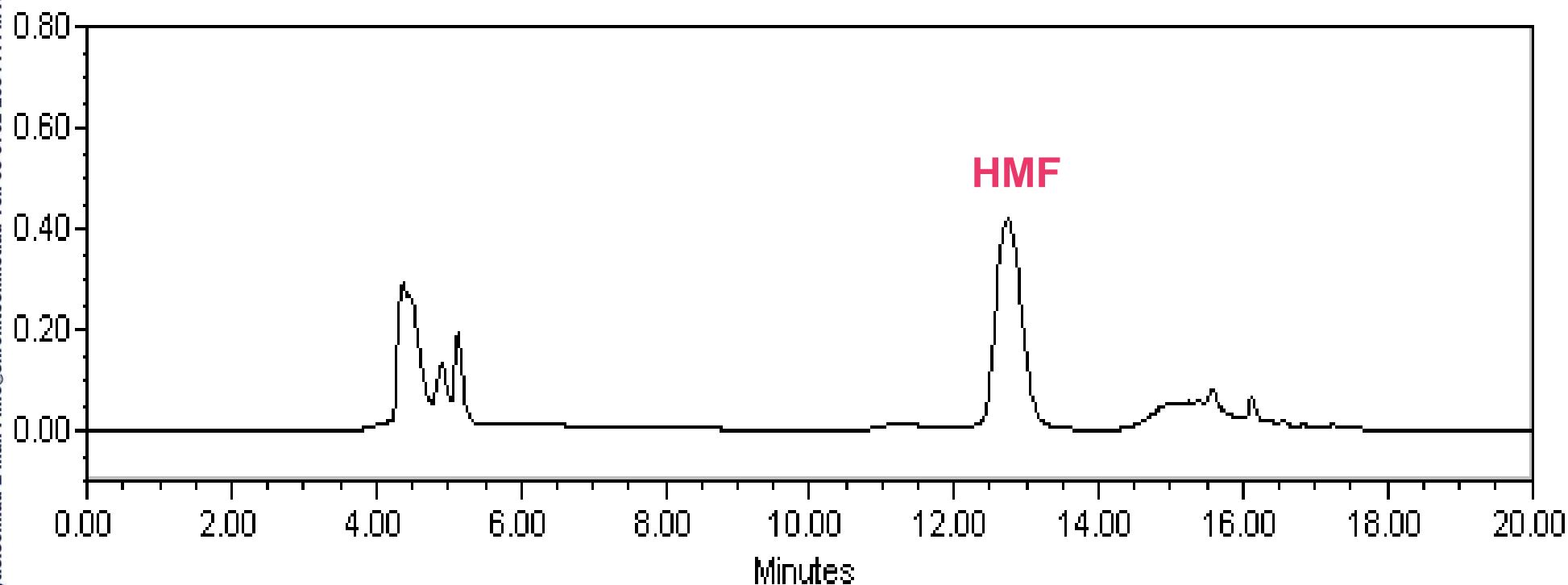


Figure 7. Analysis of HMF in grape juice, following extraction using a Carboxyprep™ SPE tube. HMF was eluted with 100% methanol.



# I C/MS Analysis of HMF

For specific detection of HMF, a mass spectrometric (MS) detector can be used, in a scanning or selected ion mode (SIM). In addition to monitoring the HMF (M+H)<sup>+</sup> ion at m/z 127, a wider mass range can be scanned to identify other components in the sample extract. This method is not as sensitive as the UV assay; however, it does provide more information about the composition of the sample, and may allow identification of other reaction products.

Figure 8. Detection of HMF, using a mass spectrometer.

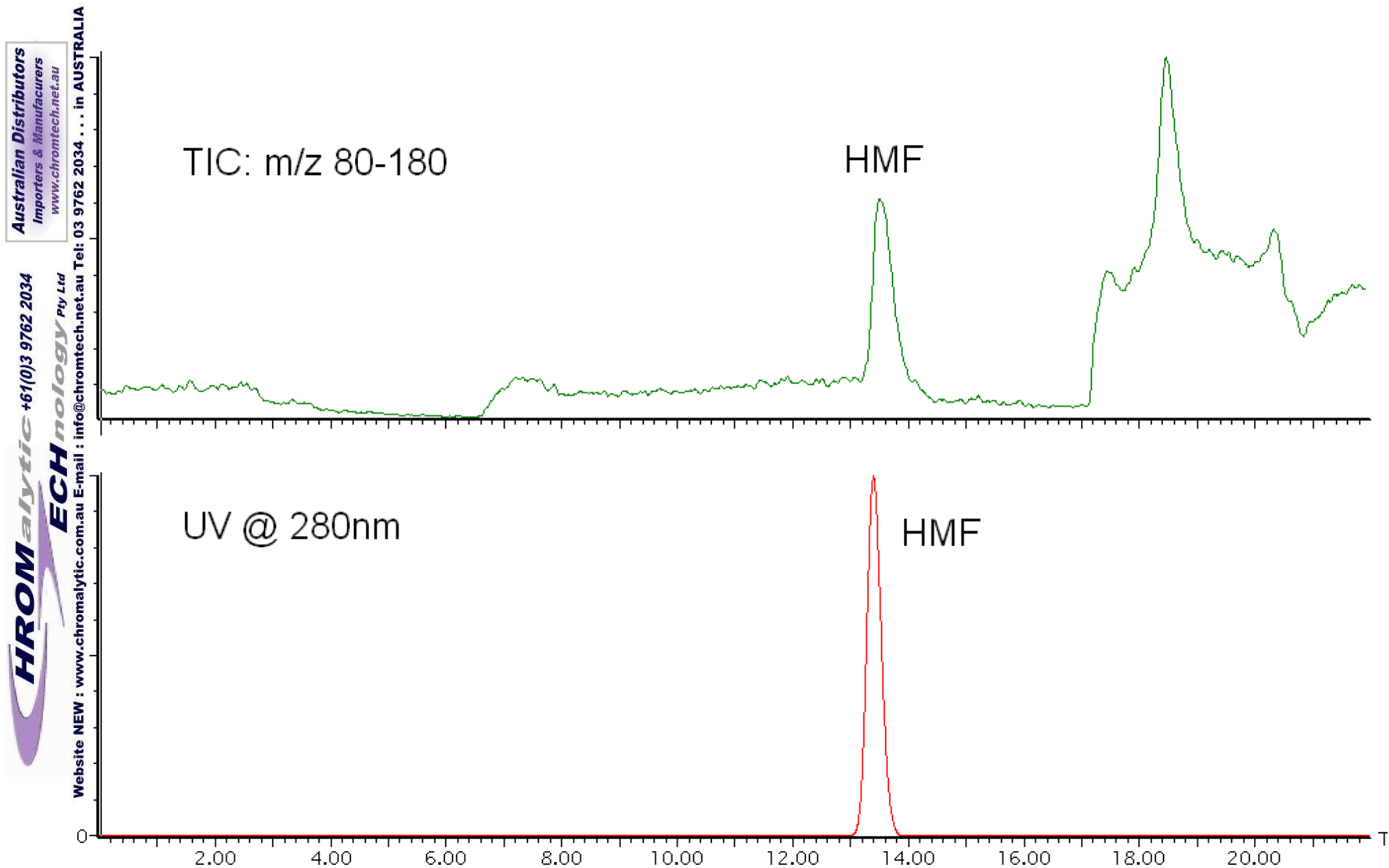


Table II. Experimental conditions for the LC/MS analysis of HMF.

### **HPLC Conditions**

Column:	Ultra C18 (Restek Corp.), 250 mm x 4.6 mm, 5 $\mu$ m
Mobile Phase A:	90:10 water:methanol, 10 mM ammonium formate
Mobile Phase B:	10:90 water:methanol, 10 mM ammonium formate
Gradient:	Same as in Table I
inj. Volume:	10 $\mu$ L
Flow Rate:	0.3 mL/min to UV detector, 0.2 mL/min to MSD

### **MSD Conditions**

Detector:	Micromass ZMD
Mode:	ESI+
Capillary V:	3.08V
Extractor V:	13V
ion Energy:	0.5
Multiplier:	650
Source Temp:	100°C
Desolv. Temp:	200°C
Gas Flow:	500 L/hr.
SIM ion:	m/z = 127
TIC range:	m/z = 80 – 180



# Summary

liquid chromatography provides a sensitive tool for monitoring products from the Maillard browning reaction in foods, such as HMF. Compared to additional spectrophotometric assays, compounds such as HMF can be selectively determined. Because of the potential for interferences when using UV detection, samples should be prepared by solid phase extraction. Good recoveries of HMF from grape juice were obtained using either C18 SPE tubes or Carboprep™ tubes. An MS detector can be used to monitor the reaction products. Because the MS provides molecular weight information, it is possible to obtain more detailed information about the reaction.

# References

1. Monti, Simona M. et. al., *Food Chem.* **1998**, 62, 369.
2. Davies, C.G.A., Labuza, T.P., *The Maillard Reaction: Application to Confectionary Products*, Dept. of Food Science, University of Minnesota.
3. Li, Z.F. et. al., *Agric. and Biol. Chem.* **1988**, 52(9), 2231.
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# Application of High Speed Gas Chromatographic Techniques to Flavor Systems

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# Introduction

Flavor systems, in general, are complex mixtures of organic compounds. Since many of the components are volatile, they often can be analyzed using gas chromatography (GC). Flavor systems are evaluated by GC for a number of reasons. Flavor extracts might be tested for quality control purposes, or to determine if a new material matches a desired flavor profile; or, flavor systems can be “reverse engineered” to estimate the volatile composition. With a wide range of compound types, boiling points and concentrations, the analysis times can be quite long. Additionally, complete resolution of all components might require two different stationary phases. For routine analyses, an ideal separation would involve a single, rapid run with complete resolution of all target components. Two approaches for achieving high speed GC separations will be discussed.

One approach to reduced analysis times utilizes fast oven temperature programs, particularly useful if a wide range of boiling points are represented. To ensure fast, reproducible temperature gradients an auxiliary heating unit can be introduced into the GC oven. For complex systems that require a dual column analysis for complete characterization, two-dimensional GC techniques can significantly reduce analysis times. Flow-modified selectivity tuning using two dissimilar stationary phases in series will be discussed. In this technique, the columns are joined at a junction point connected to a source of carrier gas. The flow through the first column can be stopped for short periods of time, enhancing the separation of target compounds.

# Fast GC Using Rapid Temperature Programs

Fast temperature programs can be used in GC to speed up the elution of high boiling point compounds and late eluters. This is especially useful if compounds with widely varying boiling points are present in the sample. While many GCs can be temperature programmed at rates 70°C/min. or higher, at higher temperatures these programs can be difficult to maintain. The temperature profile also tends to become less reproducible as the temperature and the programmed ramp rate increases.

Auxiliary heaters, such as the GC Racer temperature programmer, can be used to maintain the desired temperature gradient. The GC Racer consists of a resistive heating element that is placed on the floor of the GC oven, and a controller that connects with the main PC board of the GC. In Figures 1 and 2, the actual temperature in the oven of an Agilent 6890 GC, with and without the GC Racer, is shown at two different temperature programs. In Figure 3, a high-speed GC separation of volatile compounds is shown. This was done with and without the GC Racer, using the instrument conditions given in Table I.

Figure 1. Actual temperature vs. time for an Agilent 6890 GC, using a temperature program of 20°C/min.

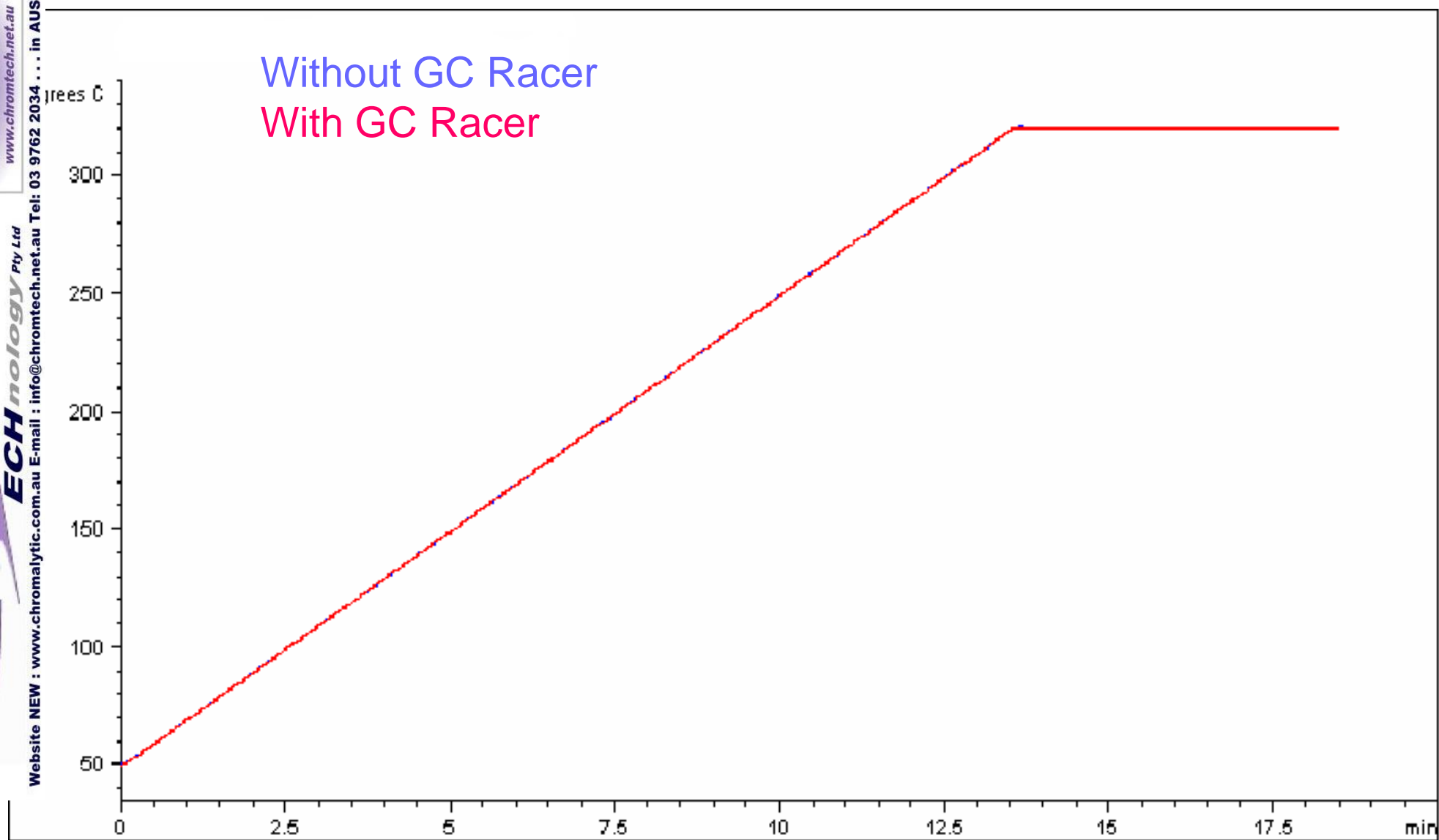


Figure 2. Actual temperature vs. time for an Agilent 6890 GC, using a temperature program of 60°C/min.

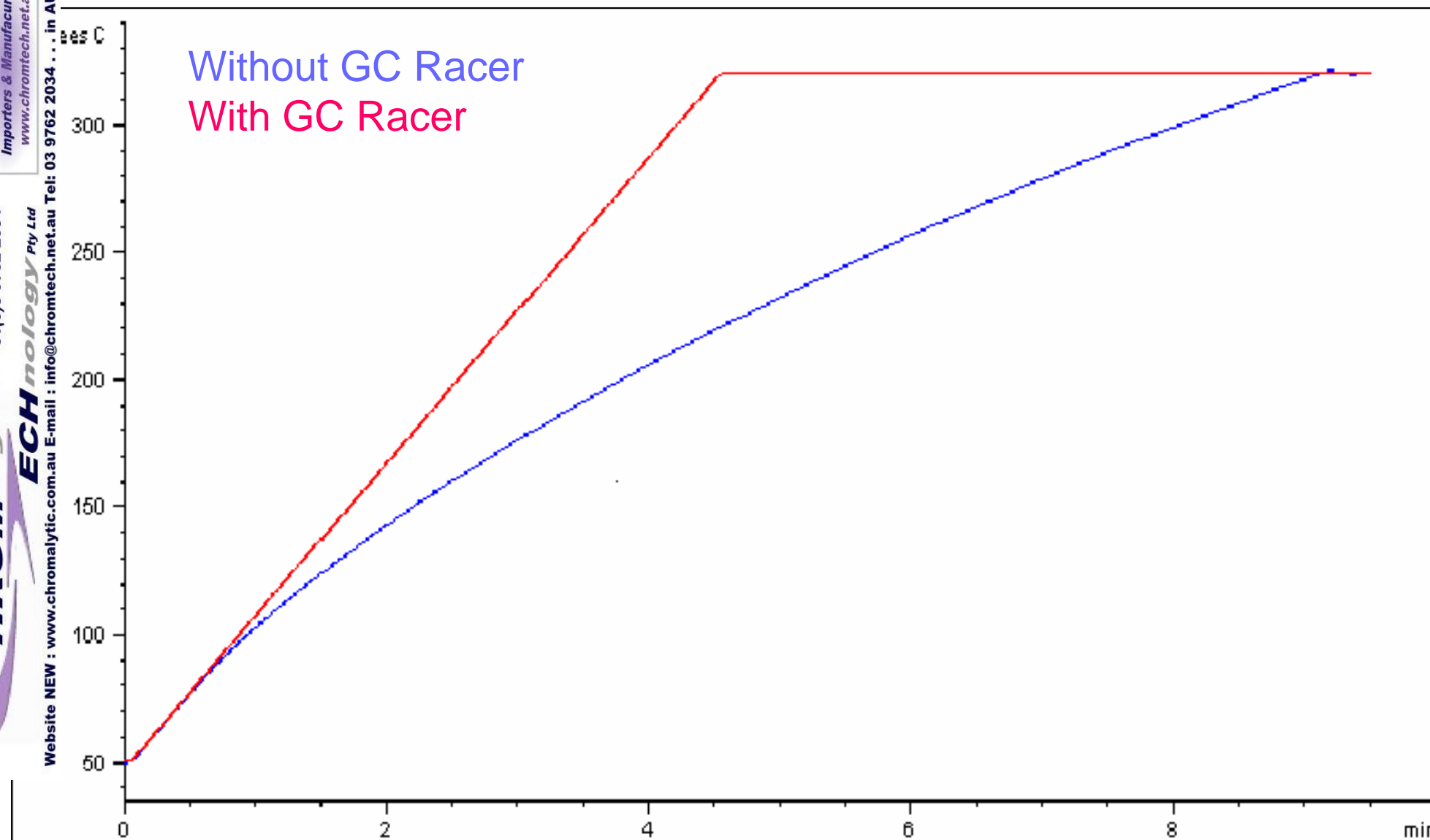


Figure 3. Separation of volatile compounds, with and without the GC Racer system.

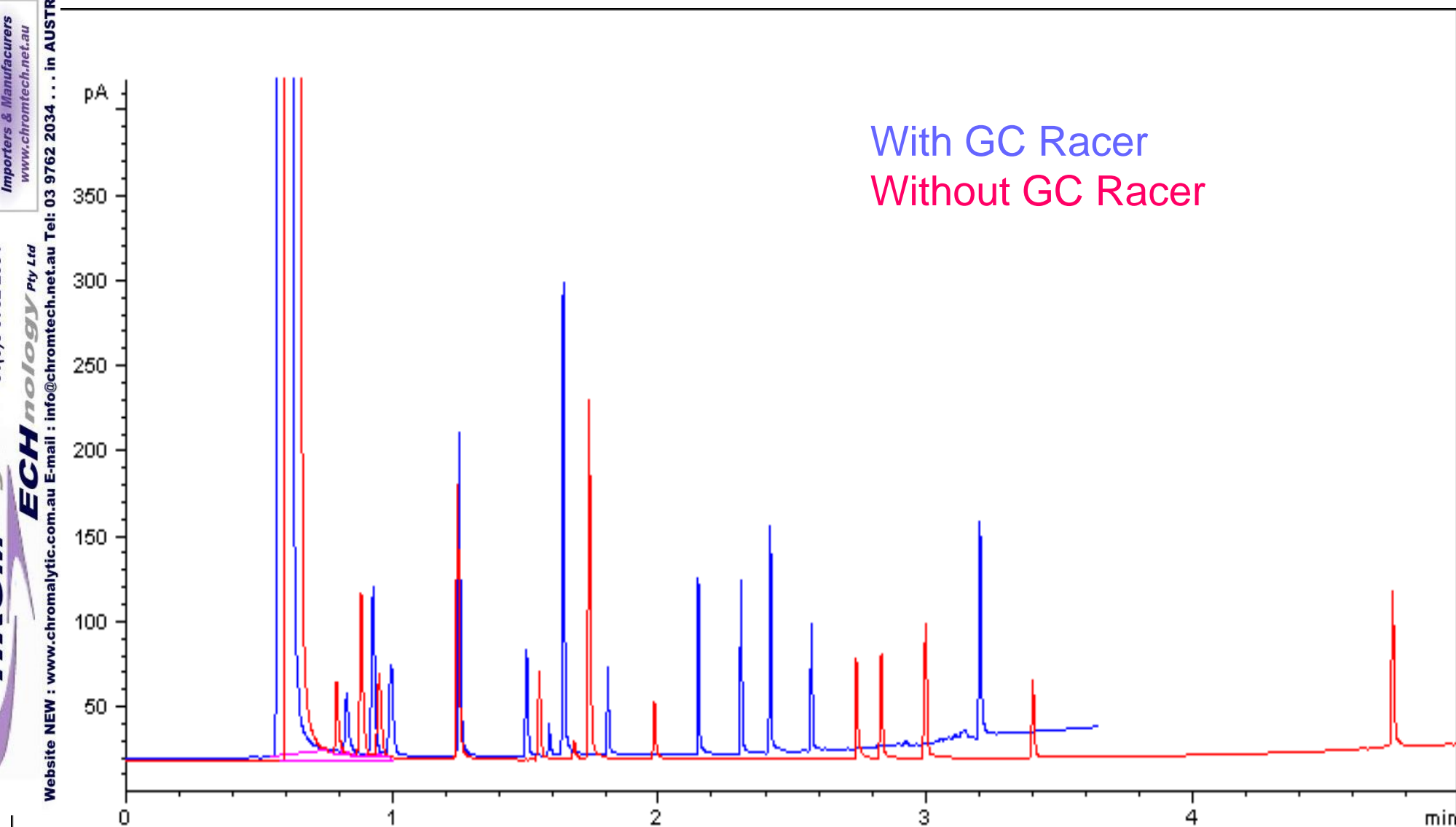




Table I. GC program for the volatile compounds analyzed in Figure 3.

Columns:	Rtx®-VMS, 10m x 0.18mm x 1.0µm Stabilwax®-DA, 10m x 0.18mm x 0.18µm
Injector:	250°C, 1 µL split injection (150:1)
Carrier Gas:	hydrogen at 25 psi, constant pressure
Oven:	35°C (0.5 min. hold) to 45°C at 20°C/min. to 210°C at 100°C/min. (1-4 min. hold)
Detector:	FID @ 250°C Air @ 400cc/min. H2 @ 40cc/min. N2 @ 40cc/min.

# Fast GC Using Pressure Tunable Selectivity

A powerful technique for separating complex mixtures, developed by Sacks, et. al.<sup>1,2</sup> at the University of Michigan, uses pressure-tunable selectivity and a series-coupled column ensemble. In this technique (Stop-Flow GC), two standard-dimension capillary columns with dissimilar stationary phases are connected in series, using a 4-way junction. At this junction point, a source of carrier gas also is connected, with the pressure controlled by an external Electronic Pressure Control (EPC) unit. An external valve controls the flow of the carrier gas to the junction point. A detector is connected to the fourth port of the junction, and monitors the components as they elute from the first column.

When an injection is made, the sample components move through the first and second columns. There are 4 possible scenarios for closely-eluting compounds A and B:

- (1) A and B are resolved after passing through both columns
- (2) A and B are not resolved after the first column, but are resolved after the second column
- (3) A and B are resolved after the first column, but not after the second column
- (4) A and B are not resolved after either column

In the first two scenarios, the separation can be allowed to proceed normally. In the 4<sup>th</sup> scenario, different column chemistries should be selected. Stop-Flow GC can be used to significantly improve the resolution described in the 3<sup>rd</sup> scenario.

For compounds that resolve on the first column, but coelute at the end of the second column, a stop-flow pulse can be introduced between the two compounds as they elute from the first column. This is done by opening the valve to the external gas source after the first compound has passed the junction point. The first compound continues on through the second column, while the second compound is stopped (or moved slightly backward) on the first column. In this way, the separation between the two components can be increased, as demonstrated in Figure 5. In Figure 5a, no stop-flow pulses have been applied, resulting in the coelution of A and B, as well as C and D. In Figure 5b, one pulse at 28 seconds has been applied, effectively resolving A and B at the outlet of the second column. In Figure 5c, both sets of coeluting compounds have been resolved by using stop-flow pulses at 28 and 43 seconds.

In Figures 6 and 7, the stop-flow technique was applied to a mixture of volatile organic compounds. In particular, pyridine, p-xylene, and m-xylene were difficult to resolve on the selected stationary phases. Using a series of 3 stop-flow pulses, the resolution of these compounds can be greatly improved. The timing and duration of the stop-flow pulses, as well as the resulting chromatogram, are shown in Figure 7.

Figure 4. Diagram of the Stop-Flow GC system, originally described by Sacks, et. al.<sup>1,2</sup>

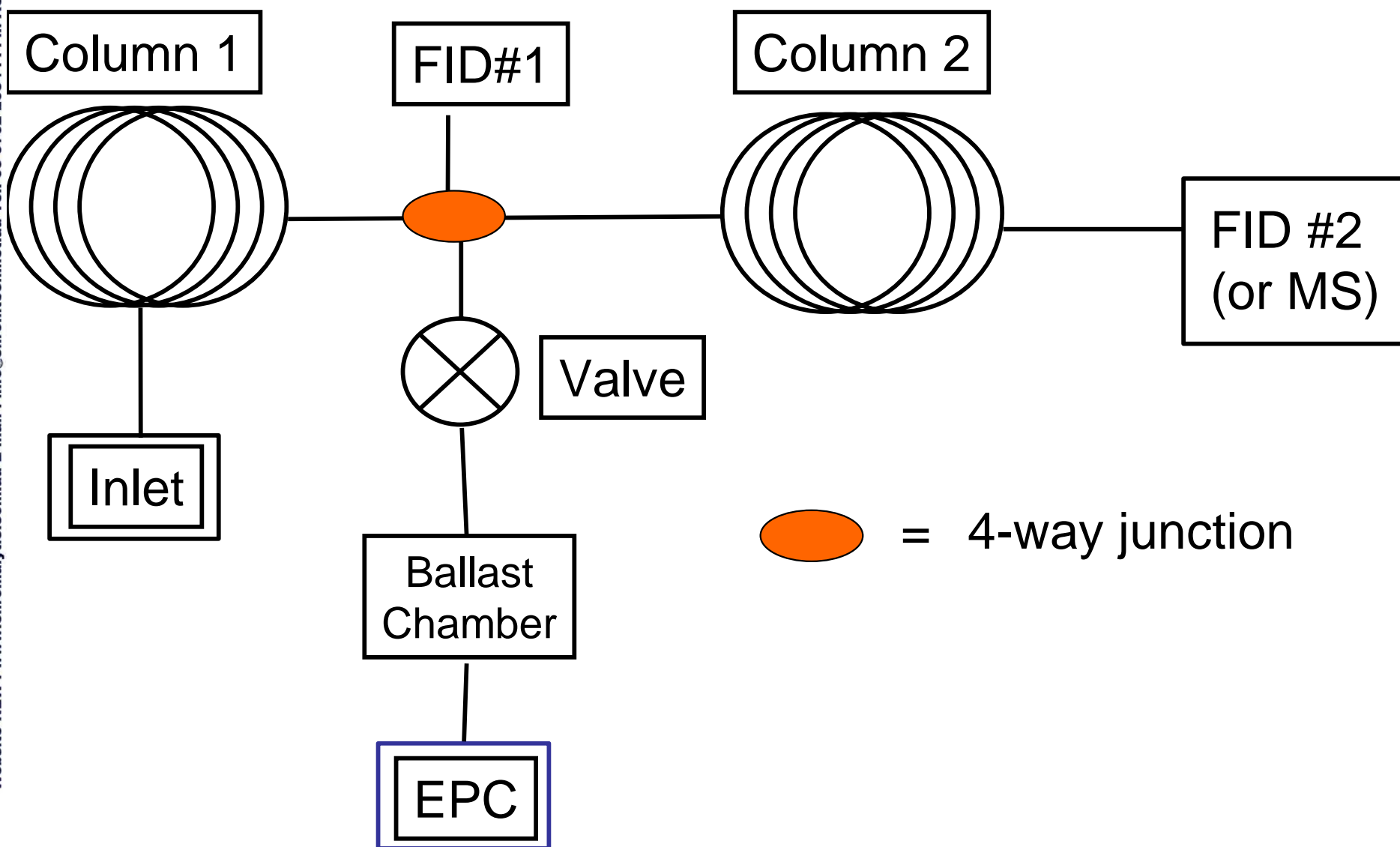


Figure 5. Stop-Flow GC for optimizing the separation of coeluting compounds: (a) no stop-flow pulses; (b) pulse at 28s; (c) pulses at 28s & 43s.

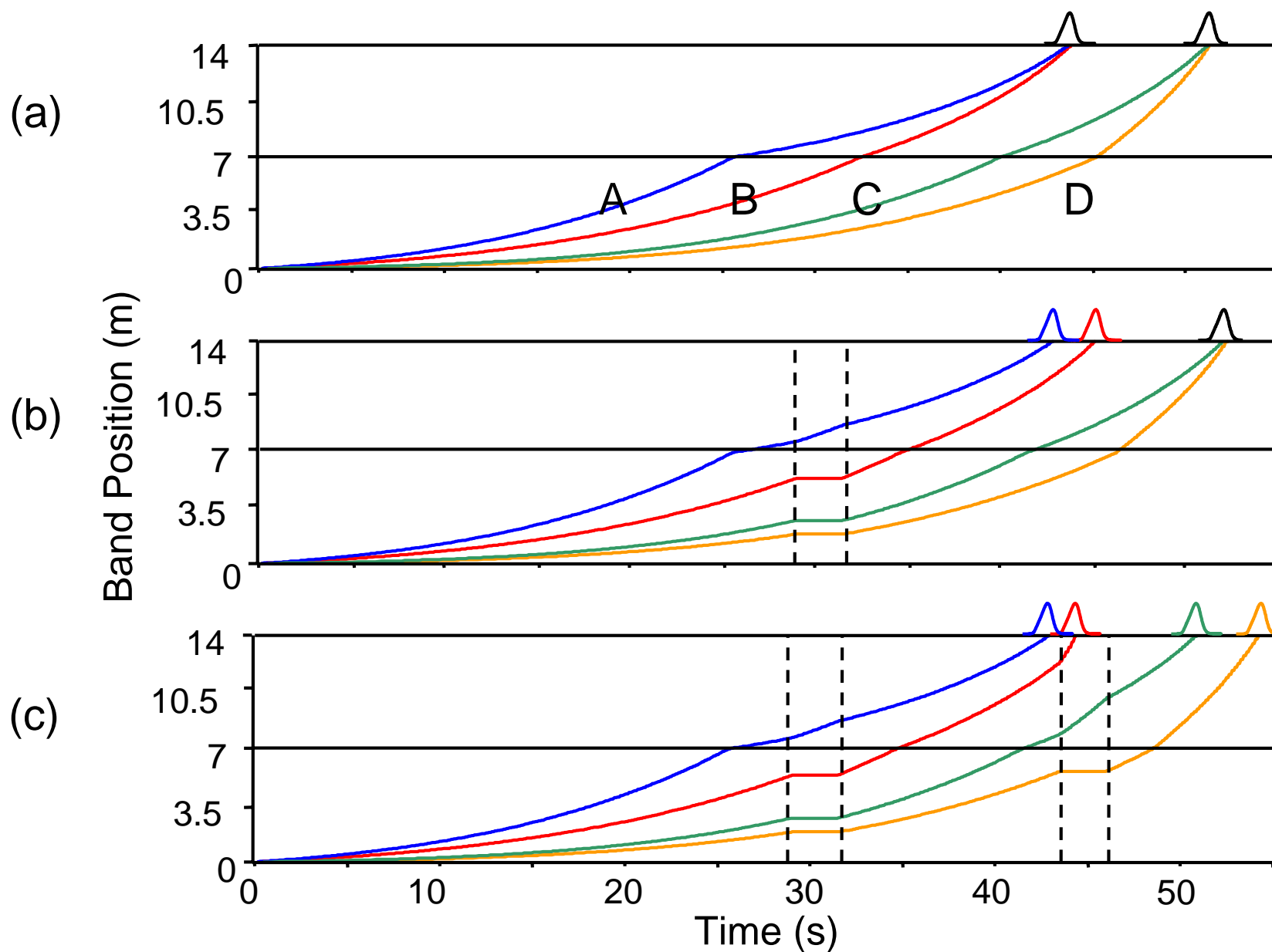


Figure courtesy of R. Sacks, University of Michigan

Figure 6. Volatile organic compounds, no stop-flow pulses.

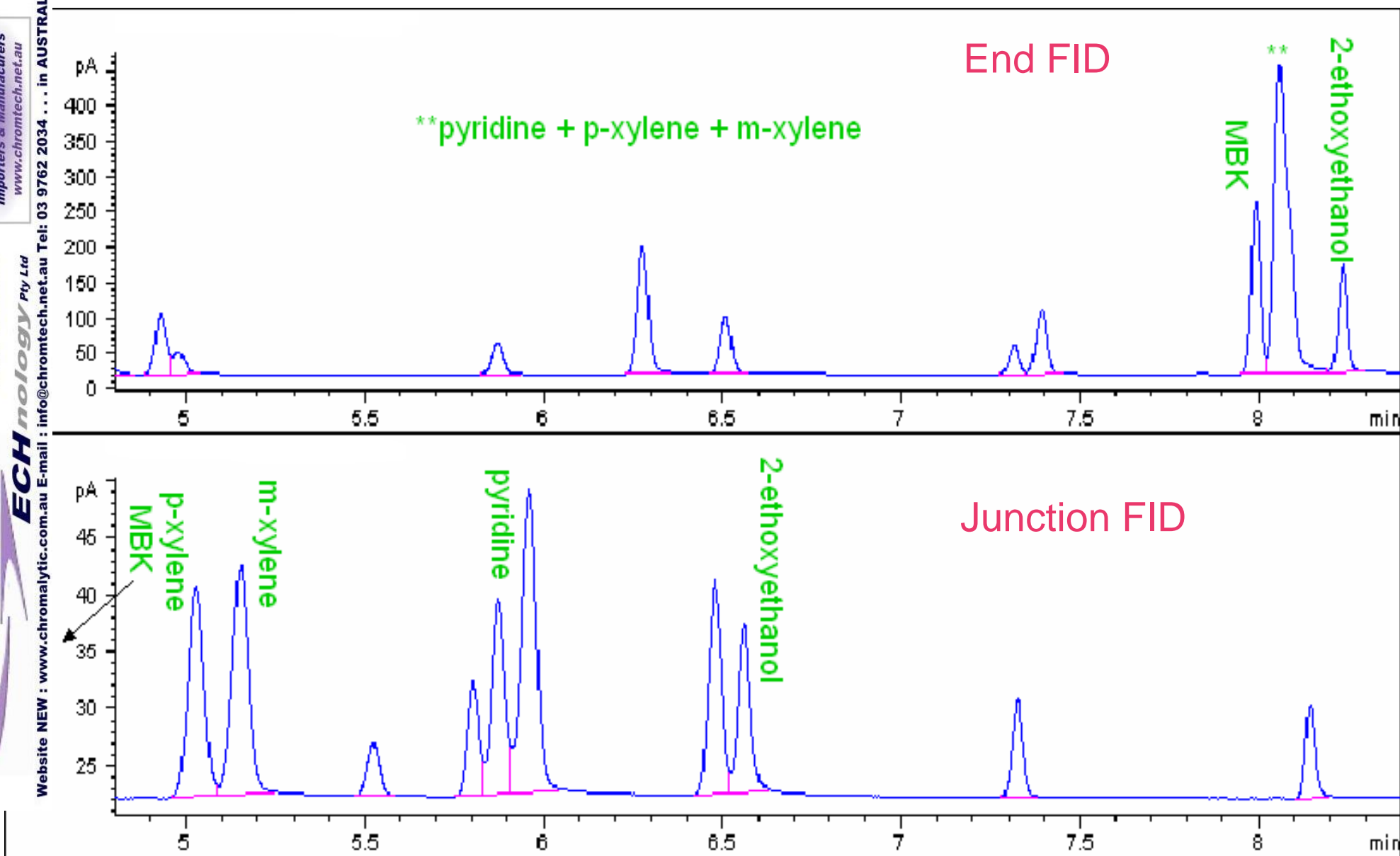


Figure 7. Volatile organic compounds, stop-flow pulses at 290, 330, & 346 °C.

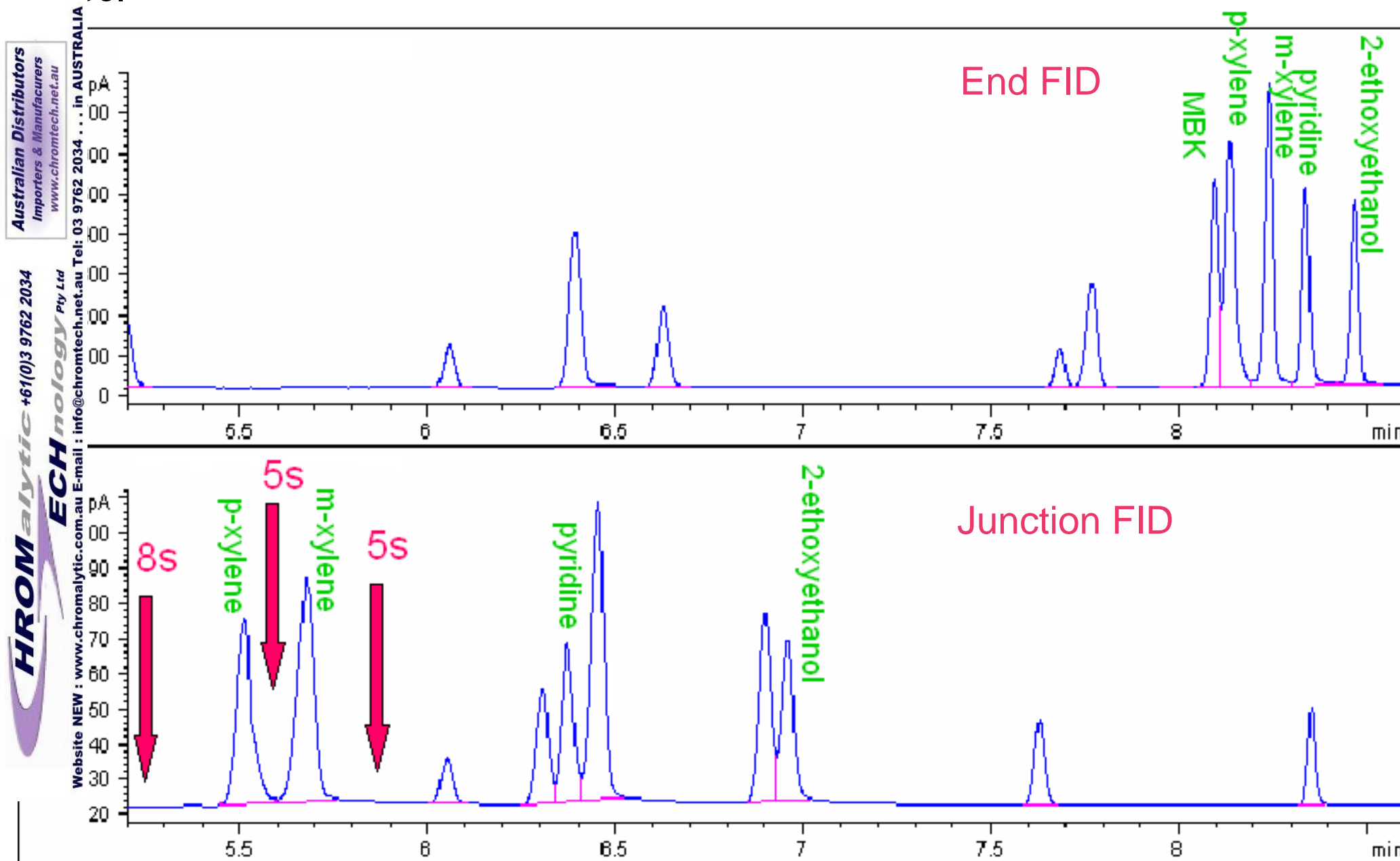




Table II. GC operating conditions for the volatile organic compound analysis in Figures 6-7.

Columns:	Rtx®-Stabilwax, 15m x 0.25mm x 0.5µm Rtx®-200, 30m x 0.25mm x 1.0mm
Injector:	230°C, 200:1 split 0.2 µL injection
Carrier Gas:	hydrogen at 2.5 mL/min. (constant flow), 0-9.5 min. to 3.5 mL/min. at 10 min.
Oven:	40°C (1 min. hold) to 65°C at 6°C/min. to 100°C at 12°C/min. to 250°C at 70°C/min. (1.8 min. hold)
Detectors:	Dual FIDs @ 250°C Air @ 400cc/min. H2 @ 40cc/min. N2 @ 40cc/min.
Junction Pressure:	74 psig (59 psi headpressure)



# Stop-Flow GC of an Essential Oil Standard

Essential oil samples are complex mixtures of organic compounds. A wide range of concentrations and boiling points typically are represented. The Fragrance Material Association (FMA) has proposed a test mix representative of the variety of compounds found in essential oil samples (see Table III). This mix was used to test the applicability of the stop-flow technique to this type of sample.

In Figure 8, the dual column analysis of the FMA test mix is shown, with no stop-flow pulses applied. The first column contains a polar polyethylene glycol stationary phase; the second column contains a non-polar 100% dimethylpolysiloxane stationary phase. GC conditions have been optimized to reduce the run time to approximately 10 minutes. At the end of the first column, thymol and cinnamyl acetate coelute; these compounds resolve at the end of the second column. Limonene and eucalyptol are adequately resolved on the first column; however, these compounds are not well resolved at the end of the second column. A 6 second stop-flow pulse at 187 seconds gives significantly better resolution of limonene and eucalyptol, as shown in Figure 9. In Figure 10, the effect of the length of the stop-flow pulse is shown.

Table II. GC operating conditions for the essential oil compounds analyzed in Figures 8-9.

Columns:	Rtx®-Stabilwax, 15m x 0.25mm x 0.5µm Rtx®-1, 30m x 0.25mm x 0.25µm
Injector:	230°C, 200:1 split 0.2 µL injection
Carrier Gas:	hydrogen at 2.5 mL/min. (constant flow), 0-7 min. to 4.0 mL/min. at 7.4 min.
Oven:	40°C to 120°C at 20°C/min. to 250°C at 100°C/min. (4 min. hold)
Detectors:	Dual FIDs @ 250°C Air @ 400cc/min. H2 @ 40cc/min. N2 @ 40cc/min.
Injection Pressure:	87 psig (72 psi headpressure)

Figure 8. Analysis of an essential oil standard, using a dual column ensemble and no stop-flow pulses.

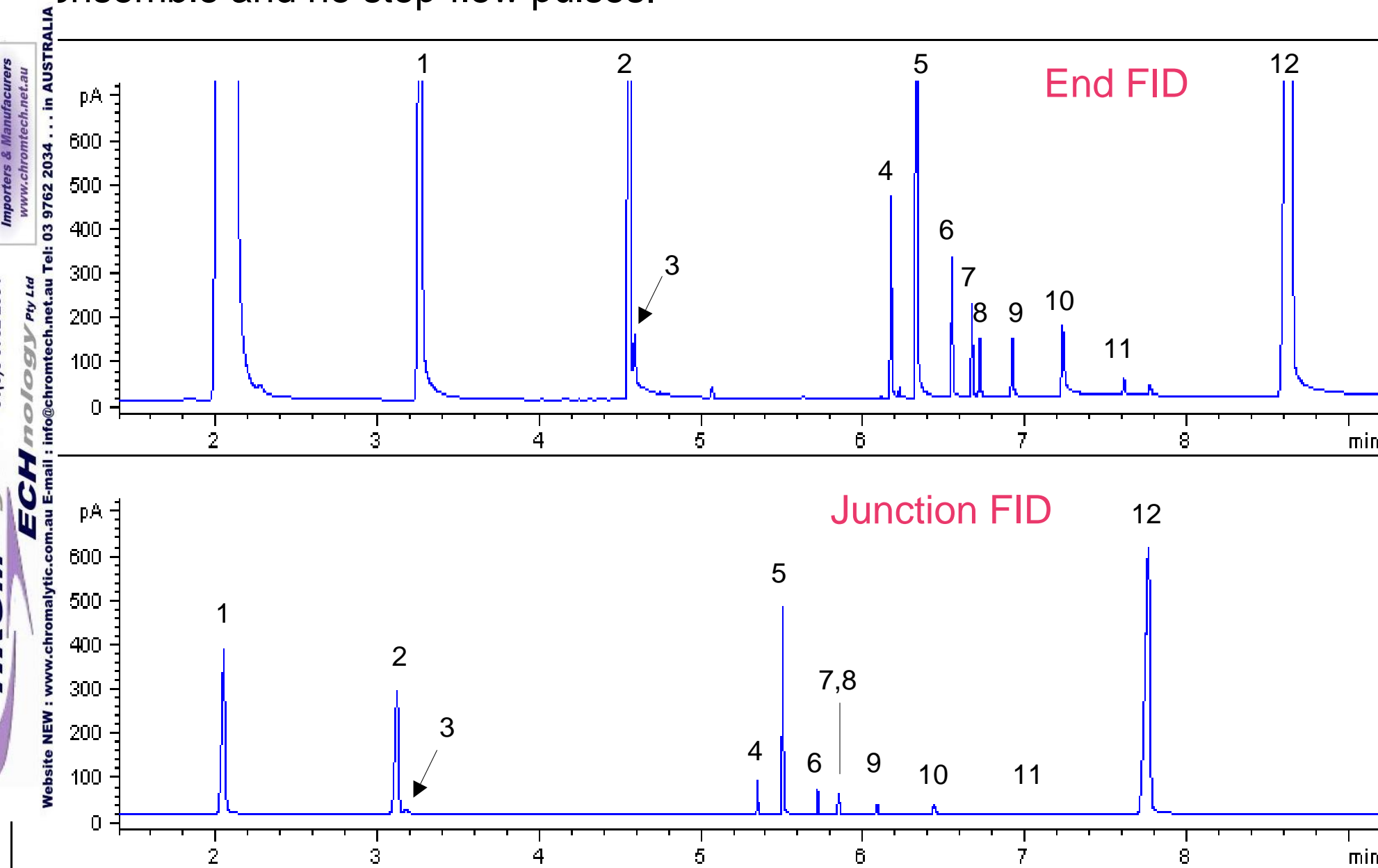


Table III. Compound list for the essential oil standard.

<i>Compound #</i>	<i>Compound Name</i>
1	Ethyl butyrate
2	Limonene
3	Eucalyptol
4	Geraniol
5	Hydroxycitronellal
6	Cinnamic aldehyde
7	Thymol
8	Cinnamyl acetate
9	Cinnamyl alcohol
10	Benzoic acid
11	Vanillin
12	Benzyl salicylate

Figure 9. Essential oil standard, with a 6 second pulse at 187 seconds. Note the improved resolution between limonene and eucalyptol.

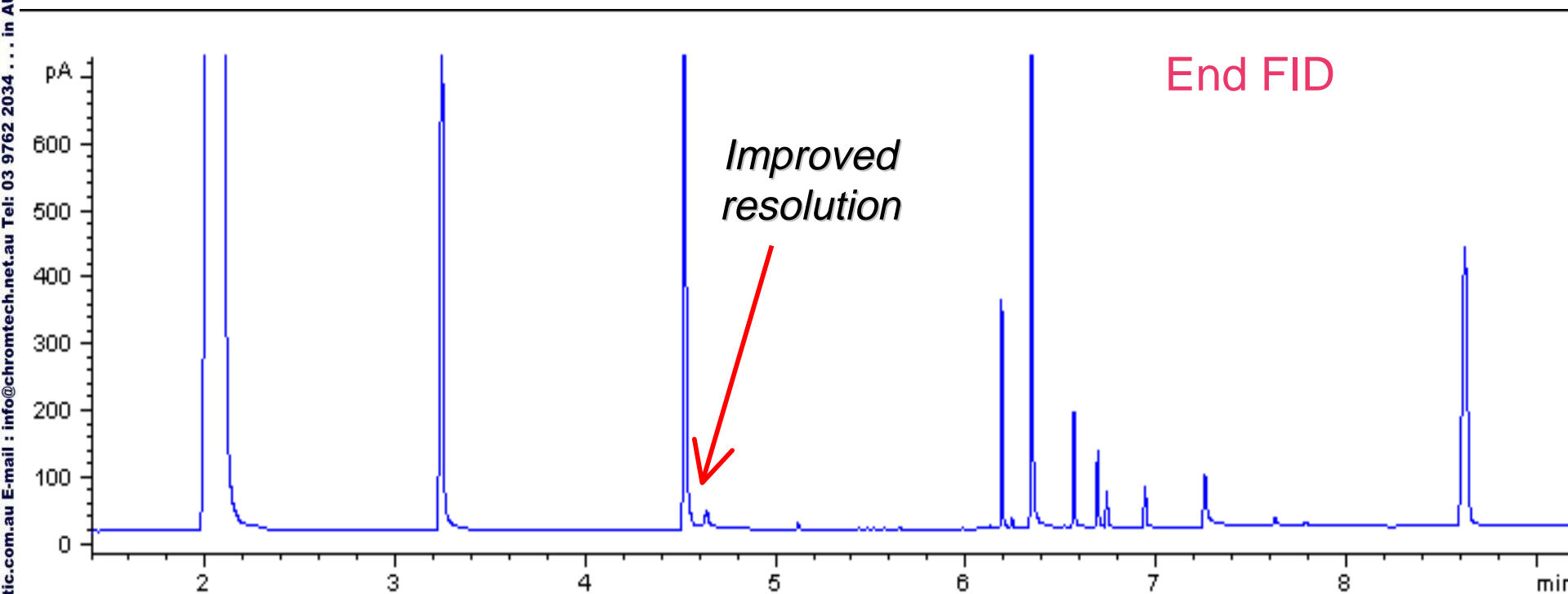
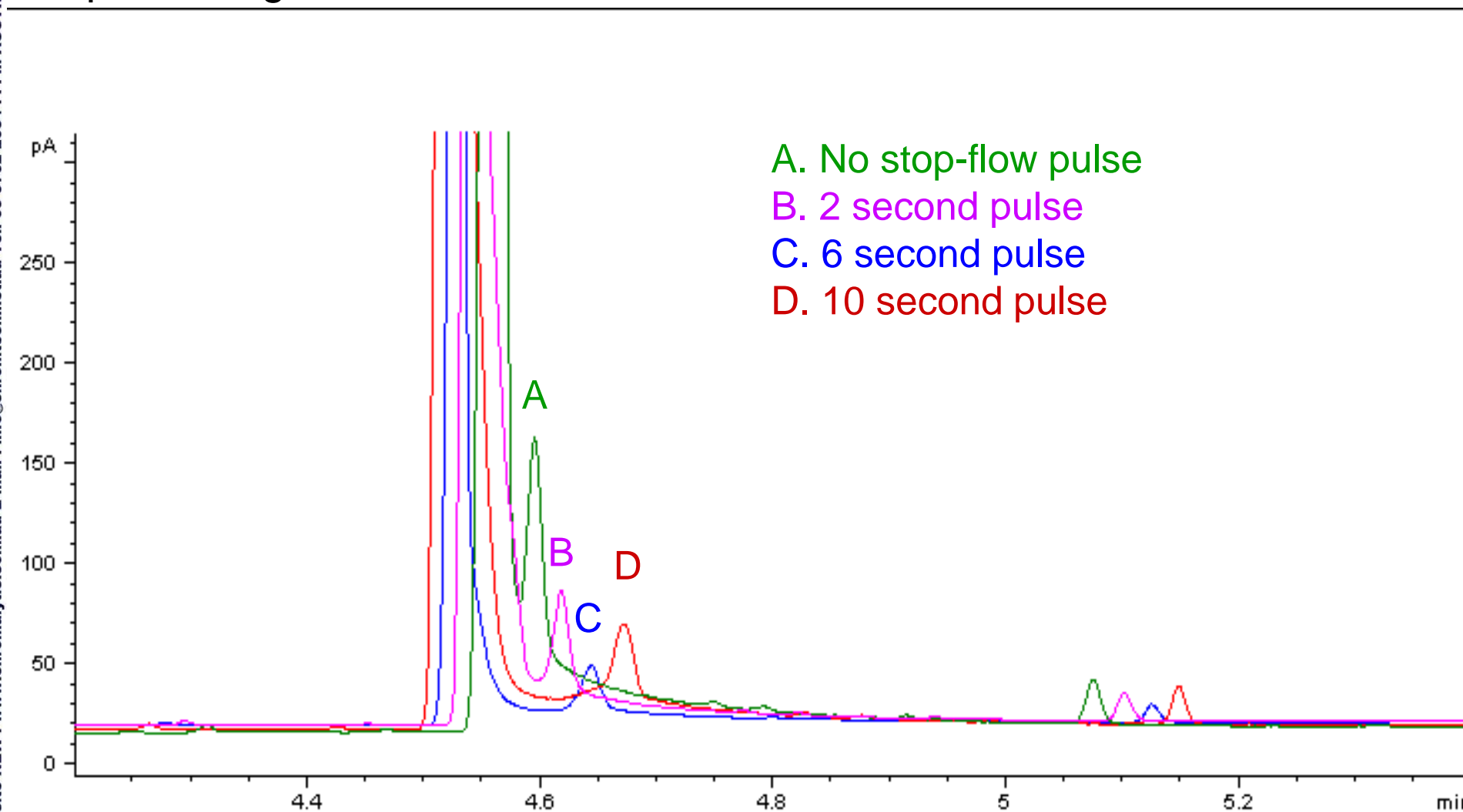


Figure 10. Separation of limonene and eucalyptol with increasing stop-flow pulse lengths.



A. No stop-flow pulse

B. 2 second pulse

C. 6 second pulse

D. 10 second pulse

# Summary

GC analysis of flavor systems can be a time-consuming task. Because of the complexity of the separations, dual column systems often are required to resolve all of the target components. In addition, because of the wide range of boiling points, oven programs covering a wide range of temperatures often must be used. This work shows two approaches used to speed up chromatographic separations. Fast oven programs can be reproducibly maintained using an auxiliary heating unit. This can result in significant reductions in run time, as long as the resolution of critical component pairs can be maintained. For more complex systems that are difficult to completely separate on one type of stationary phase, Stop-Flow GC can be a powerful means of “tuning” the separations, with minimal hardware modifications required.

# References

1. T. Veriotti and R. Sacks, *Anal. Chem.*, **2001**, 73, 3045.
2. T. Veriotti and R. Sacks, *Anal. Chem.*, **2001**, 73, 4395.



# Reduction of Mass Spectrometer Downtime During Column Change Using A Critical Orifice Connection Device

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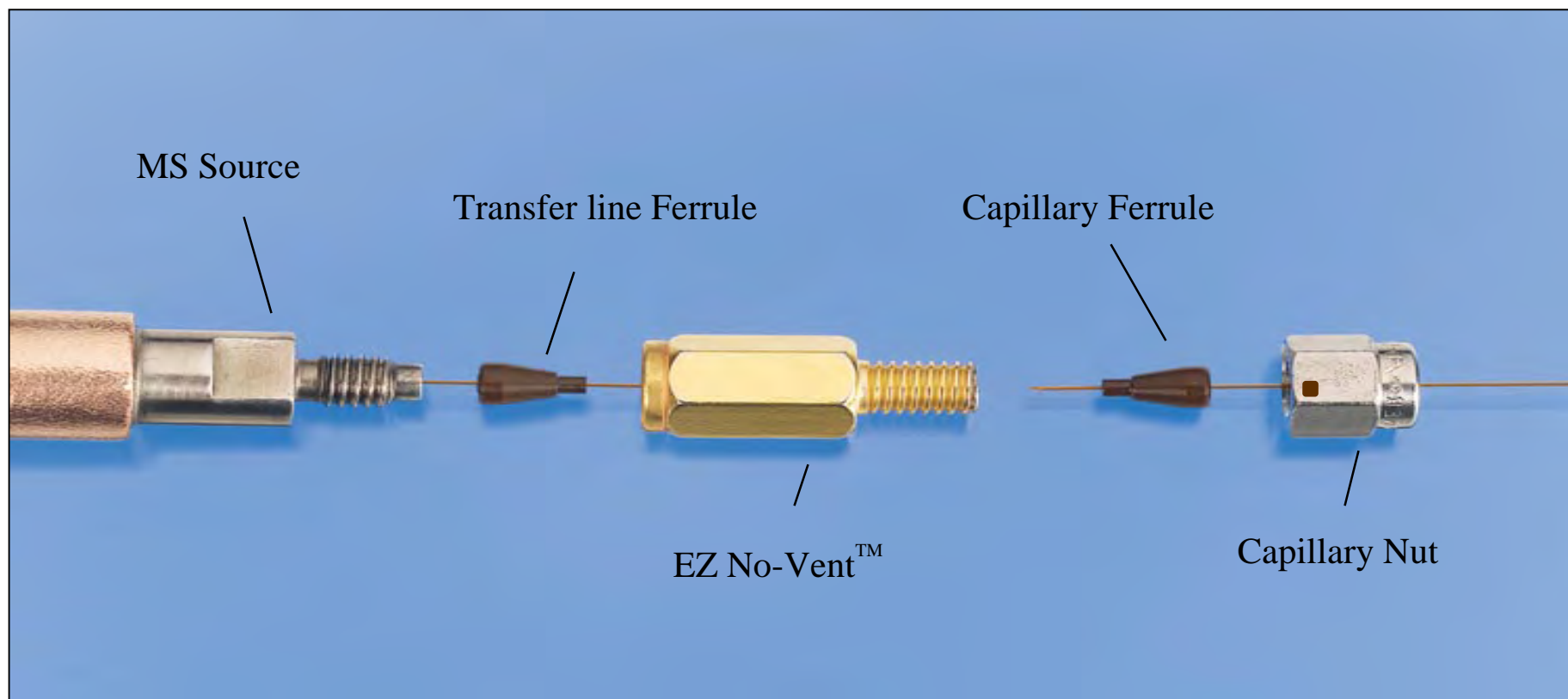
# Abstract

A common problem with the use of mass spectrometers is the amount of time needed to change a capillary column. Prior to removing the column it is necessary to vent the MS system. After installation of a new column the MS must be pumped down to a high level of vacuum prior to use. Overall this process can take as long as 5 hours, during which time the instrument is non-productive. A new mass spectrometer connector allows analyst to easily change the capillary column without the need to vent the instrument.

# Introduction

Changing a column in a GC/MS is a lengthy process and can take valuable time away from productivity. The new EZ No-Vent™ connector was designed to allow the analyst to change columns in the MS without venting. The EZ No-Vent™ connector utilizes a critical orifice to minimize the introduction of oxygen, and thus eliminates the need to use a purge gas. The EZ No-Vent™ connector easily attaches to the MS source with a standard ferrule, and without the need for special tools or plumbing. It also does not require secondary flow or pressure controllers, connection to the GC electronics, or additional gas lines.

# EZ No-Vent™ Connector



# Experiment #1

The EZ No-Vent™ connector was tested using highly volatile gases that are very susceptible to tailing from the presence of dead volume in the sample pathway. The chromatographic system initially was configured using a purge-and-trap concentrator connected to the capillary column by a split injection port. The column was directly inserted into the MS interface (Figure 1). The same configuration was then evaluated with the EZ No-Vent™ connector at the MS interface. Any dead volume in this fitting would result in significant tailing and broader peaks. As shown the peak shape was excellent using this new fitting (Figure 2).

# Figure 1:

## Before Using EZ No-Vent™ Connector

1. dichlorodifluoromethane
2. 1,2-dichlorotetrafluoroethene (Freon® 114)
3. chloromethane
4. vinyl chloride
5. bromomethane
6. chloroethane
7. trichlorofluoromethane

Inj.:Purge & Trap

GC: Agilent 6890

Inj. temp.: 300°C

Carrier gas: helium, constant flow

Flow rate: 1.0mL/min.

Oven temp.: 60°C isothermal

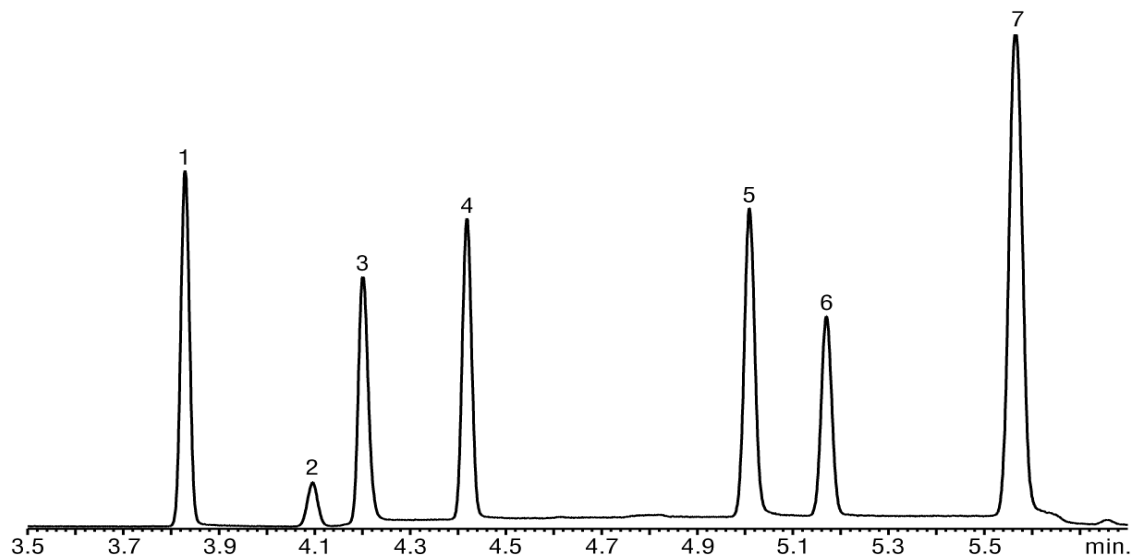
Det:Agilent 5973 GC/MS

Transfer line temp.: 280°C

Scan range: 35-550 amu

Tune: BFB

Ionization: EI



Rtx®-624 60m, 0.25mm ID, 1.4µm (cat# 10969), column connected directly to MS source.

Volatile Gas Mix 502.2 Calibration Mix#1 (gases) cat# 30042

# Figure 2:

## Column Connected to EZ No-Vent™ Connector

1. dichlorodifluoromethane
2. 1,2-dichlorotetrafluoroethene (Freon® 114)
3. chloromethane
4. vinyl chloride
5. bromomethane
6. chloroethane
7. trichlorofluoromethane

Inj.:Purge & Trap

GC: Agilent 6890

Inj. temp.: 300°C

Carrier gas: helium, constant flow

Flow rate: 1.0mL/min.

Oven temp.: 60°C isothermal

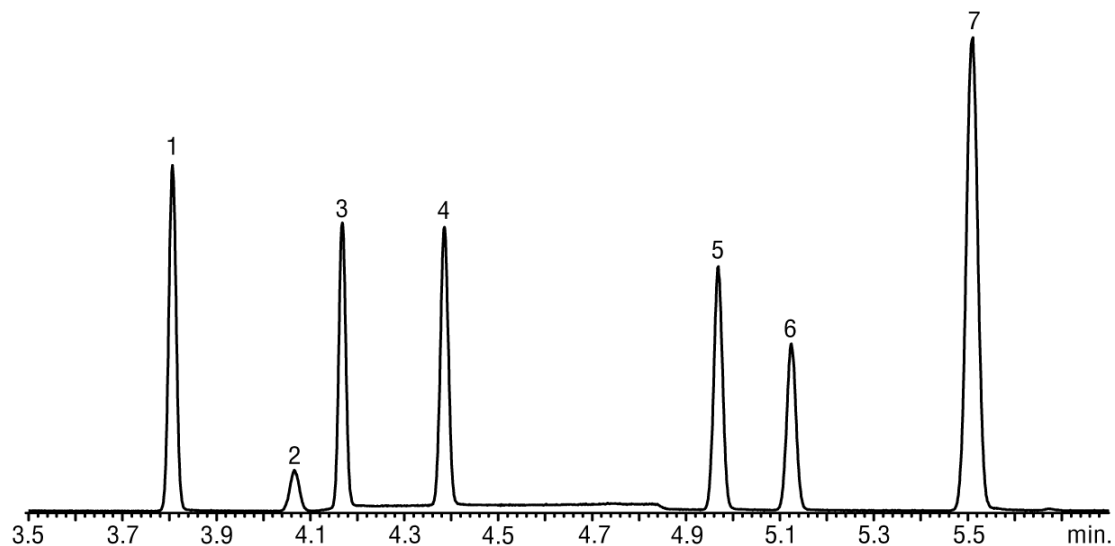
Det:Agilent 5973 GC/MS

Transfer line temp.: 280°C

Scan range: 35-550 amu

Tune: BFB

Ionization: EI



Rtx®-624 60m, 0.25mm ID, 1.4µm (cat# 10969) column connected to EZ No-Vent™ connector.

Volatile Gas Mix 502.2 Calibration Mix#1 (gases) cat# 30042



## Experiment #2

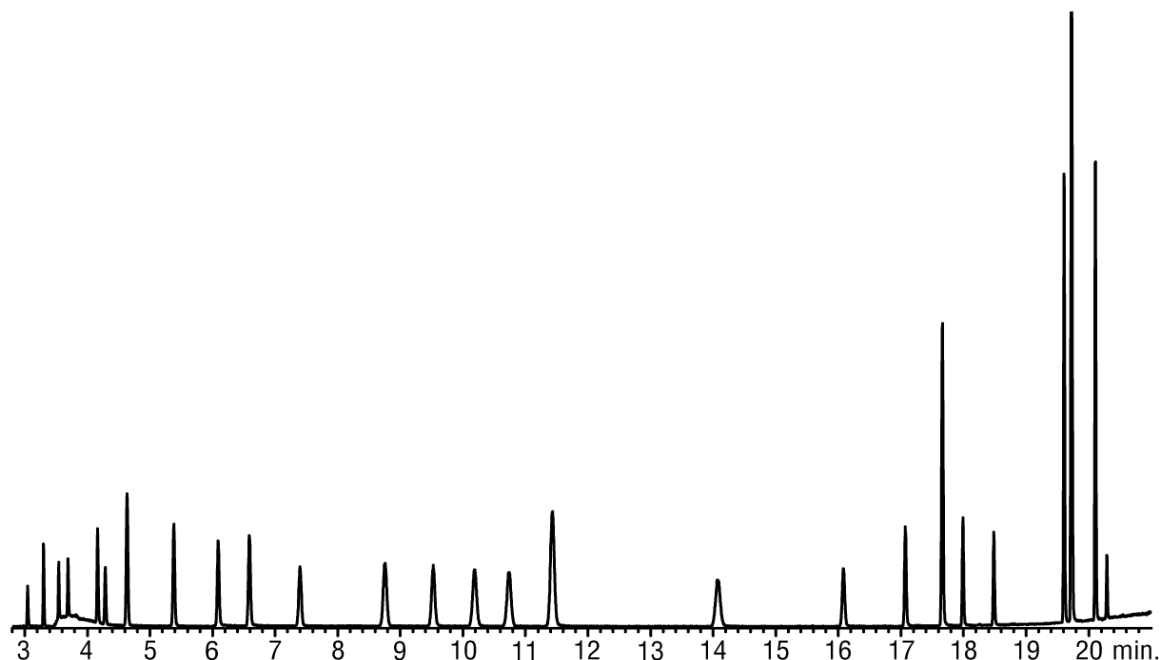
The EZ No-Vent™ connector allows columns to be changed without venting the MS, which can save a day of downtime. An application specific test was used to evaluate the ability of the MS to stabilize after a column change and without venting the MS. Again, purge-and-trap was used with halogenated volatiles. The first chromatogram (Figure 3) was run using an Rtx-624 phase and was acquired at 08:12 AM. A different column was installed and chromatogram acquired at 09:28 AM, with excellent peak shape and response (Figure 4) . Between runs the tune was verified and passed bromofluorobenzene (BFB) criteria. EZ No-Vent™ technology allows several column changes in a single day, without harm to the MS.



## Figure 3:

### 1<sup>st</sup> Column, Equilibrated System

Inj.:Purge & Trap  
 GC: Agilent 6890  
 Inj. temp.: 300°C  
 Carrier gas: helium, constant flow  
 Flow rate: 1.0mL/min.  
 Oven temp.: 60°C (hold 15 min)  
               to 220°C @ 30°C/min (hold 1 min)  
 Det: Agilent 5973 GC/MS  
 Transfer line temp.: 280°C  
 Scan range: 35-550 amu  
 Tune: BFB  
 Ionization: EI



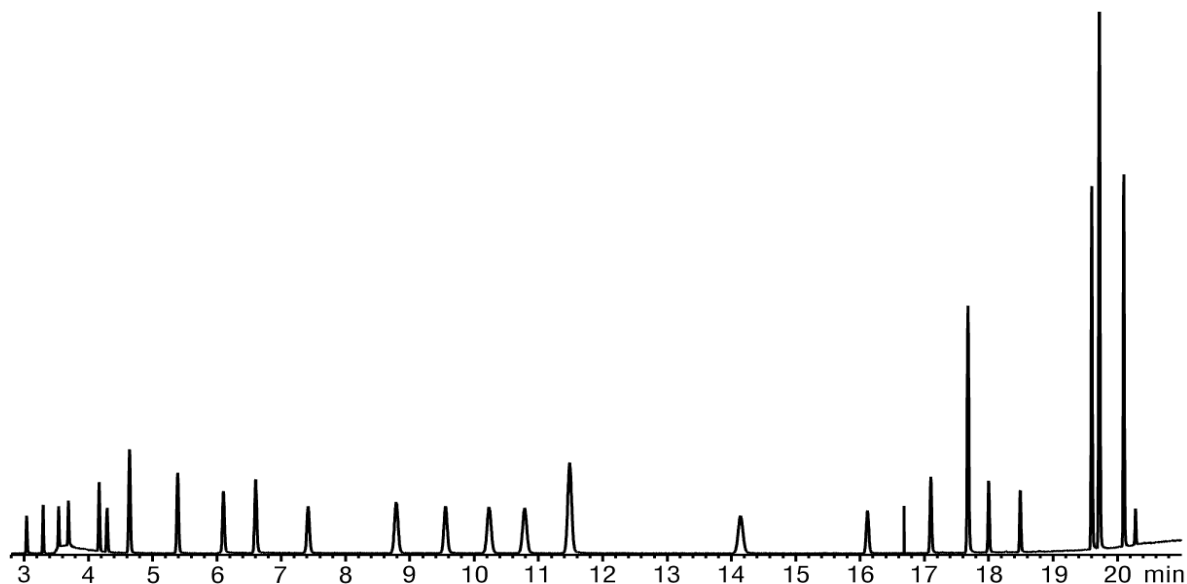
Rtx®-624 60m, 0.25mm ID, 1.4µm (cat# 10969),  
 EZ No-Vent™ connector, equilibrated system.  
 Halogenated Volatiles @ 200 ppb in 5mL/RO water.

502.2 Calibration Mix#1 (gases)	cat# 30042
502.2 Calibration Mix#2	cat# 30043
BTEX standard	cat# 30213

# Figure 4:

## Acquired 76 minutes after Installing 2<sup>nd</sup> Column, without venting

Inj.:Purge & Trap  
 GC: Agilent 6890  
 Inj. temp.: 300°C  
 Carrier gas: helium, constant flow  
 Flow rate: 1.0mL/min.  
 Oven temp.: 60°C (hold 15 min)  
 to 220°C @ 30°C/min (hold 1 min)  
 Det: Agilent 5973 GC/MS  
 Transfer line temp.: 280°C  
 Scan range: 35-550 amu  
 Tune: BFB  
 Ionization: EI



Rtx®-624 60m, 0.25mm ID, 1.4µm (cat# 10969) EZ No- Vent™ connector,  
 acquired 76 min. after installing new column.

Halogenated Volatiles @ 200 ppb in 5mL/RO water.

502.2 Calibration Mix#1 (gases)	cat# 30042
502.2 Calibration Mix#2	cat# 30043
BTEX standard	cat# 30213

# Conclusion

The EZ No-Vent™ connector allows the analyst to easily change capillary columns in the MS without the time consuming need to vent the system. The EZ No-Vent™ connector allows the analyst to acquire a maximum number of runs, and make more efficient use of time, for higher productivity. The EZ No-Vent™ connector is easy to install and does not require additional plumbing or special tools. A critical orifice minimizes the introduction of oxygen into the MS during column changes, which eliminates the need for additional purge gases. The EZ No-Vent™ connector is gold-plated for maximum inertness and worry-free operation.

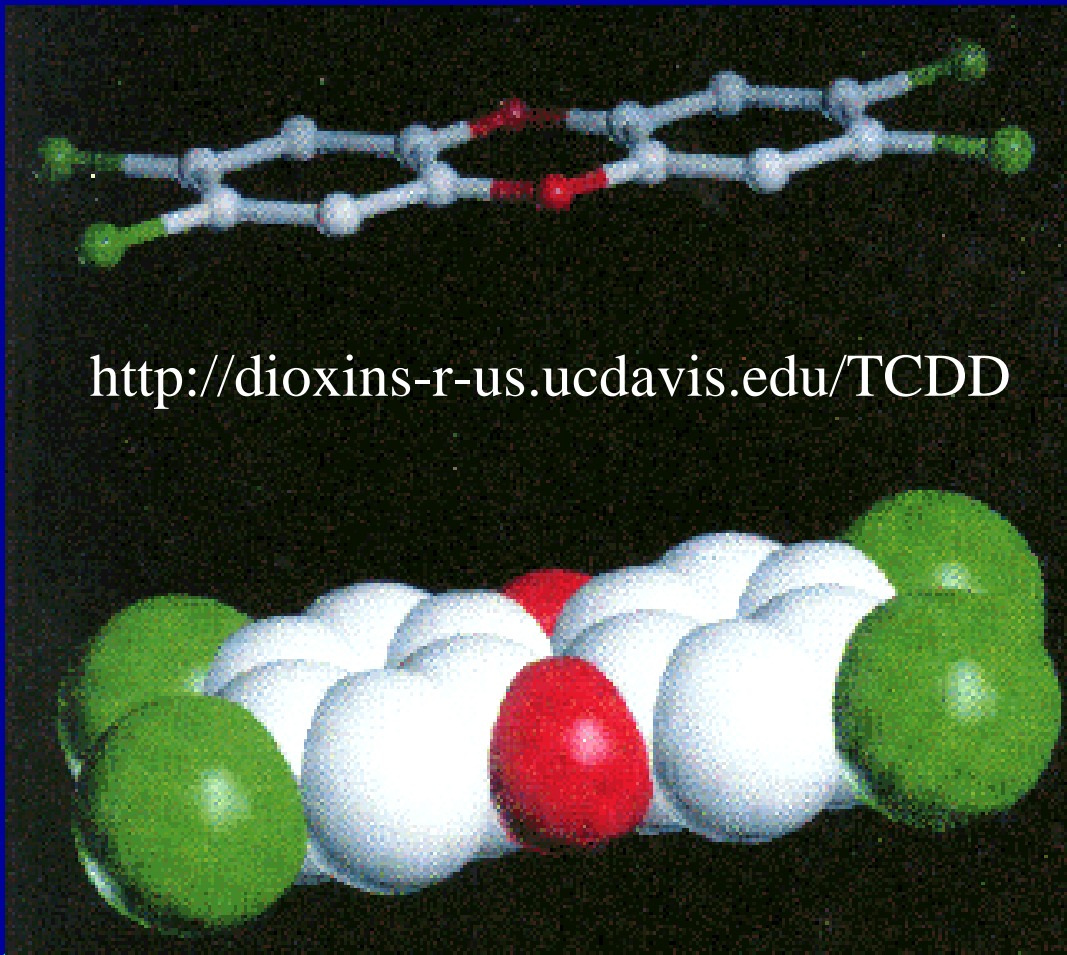
# Introducing the Rtx-Dioxin Capillary Column

Frank L. Dorman, Rick Morehead, Eric J.  
Reiner, and Karen MacPherson

Restek Corporation  
[www.restekcorp.com](http://www.restekcorp.com)



# Analysis of Dioxins and Furans



restek [www.restekcorp.com](http://www.restekcorp.com)

# PCDD and PCDF Target List

# of Chlorine	#Dioxins	#Furans
tetra	22(1)	38(1)
penta	14(1)	28(2)
hexa	10(3)	16(4)
hepta	2(1)	4(2)
octa	1(1)	1(1)

( ) numbers are 2,3,7,8-substituted congeners

# Dioxin and Furan Analysis

- Primary column commonly “5-type”
  - Significant number of coelutions of non-toxic congeners with 2,3,7,8-substituted congeners
- Confirmation column usually 225 or 2331
  - Poor thermal stability and lifetime
  - High baseline reduces sensitivity
  - Improved quantitation accuracy due to better resolution of toxic for non-toxic congeners

# Desired Attributes of New Column/s

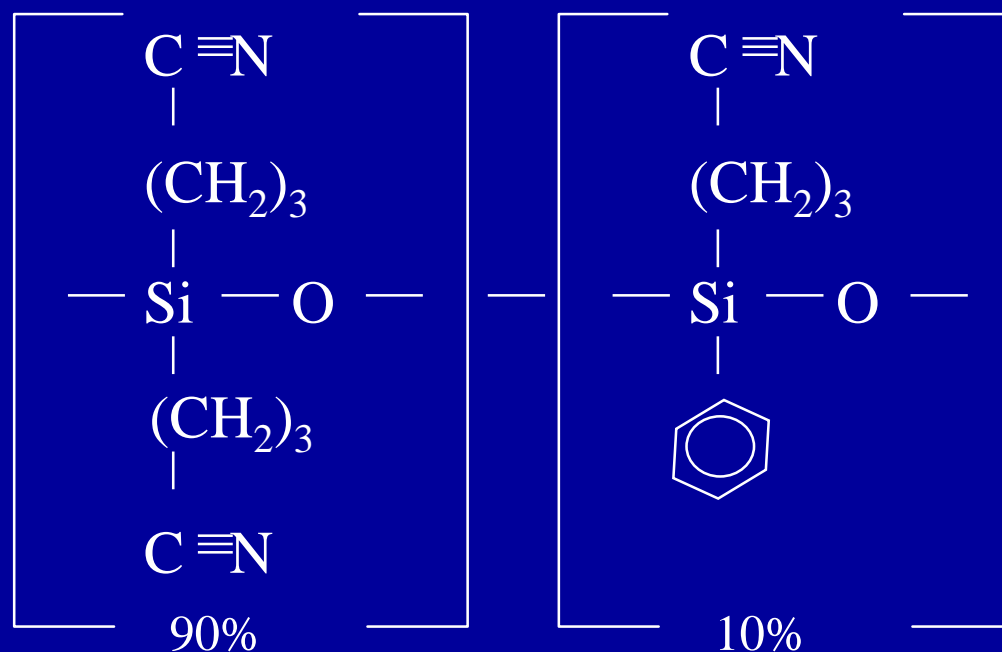
- To replace primary 5-type column
  - Improved separation of toxic congeners
  - Improved thermal stability?
  - Improved bleed levels?
  - Same or shorter run times
  - Fused silica column



# Desired Attributes of New Column/s

- To replace 225 or 2331 confirmation column
  - Improved thermal stability
  - Improved lifetime
  - Compatible to primary column
    - Same oven for both columns
  - Less bleed
    - Improved sensitivity
  - Less reactive
    - Cyano-containing columns are prone to acid/base reactions

# Rtx<sup>®</sup>-2330

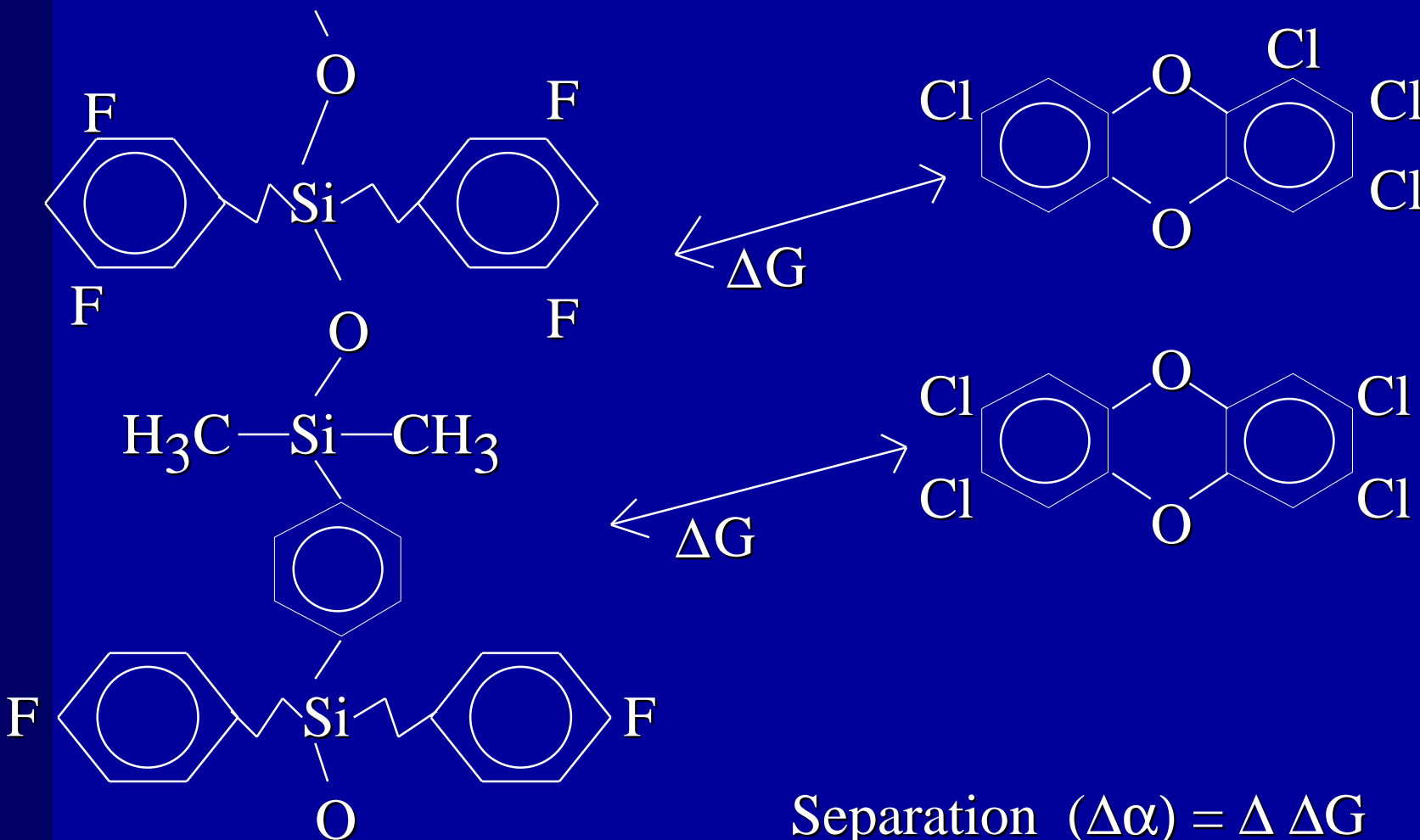


Polarity: very polar

Uses: cis/trans isomers

Properties: min. temp. (0°C), max. temp. (275°C)

# Why Stationary Phase Selectivity Can Be Difficult....



Separation ( $\Delta\alpha$ ) =  $\Delta\Delta G$

# Column Requirements

- Separate 2,3,7,8-substituted PCDDs/PCDFs from all other isomers
- High thermal stability (330°C +)
- High resolution GC-MS
  - 0.0001 mass resolution, PFK mass lock
- Reasonable run time (40-60 min.)
- Separate co-planar and mono-ortho PCBs
- Separation by chlorination level

# Rtx-Dioxin Capillary Column

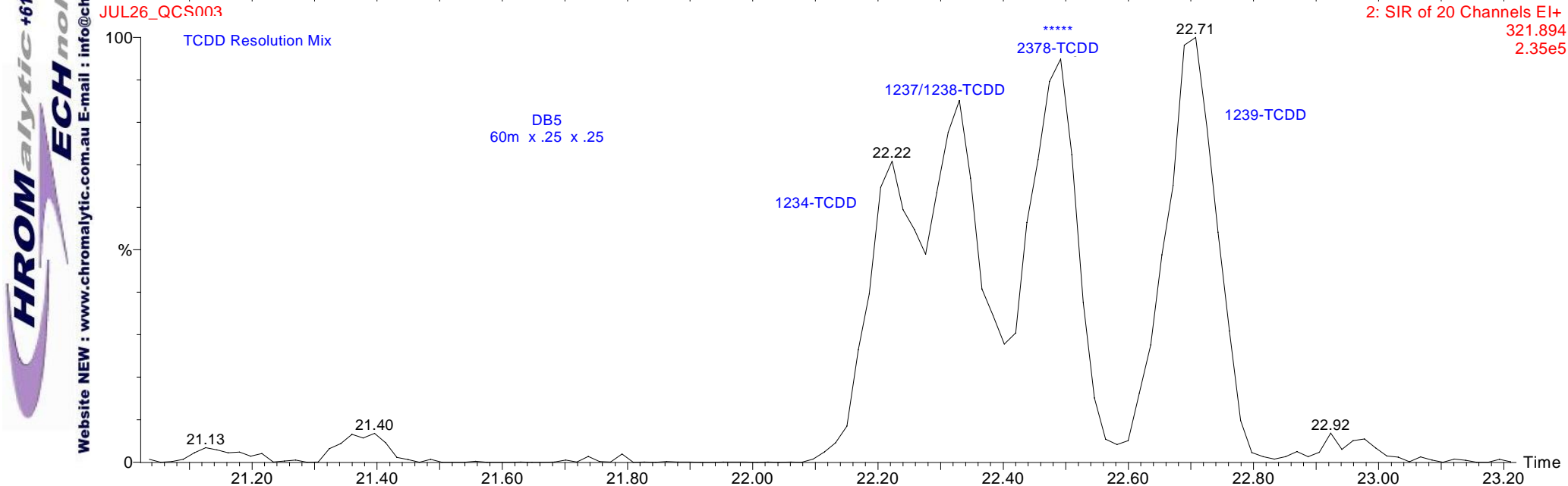
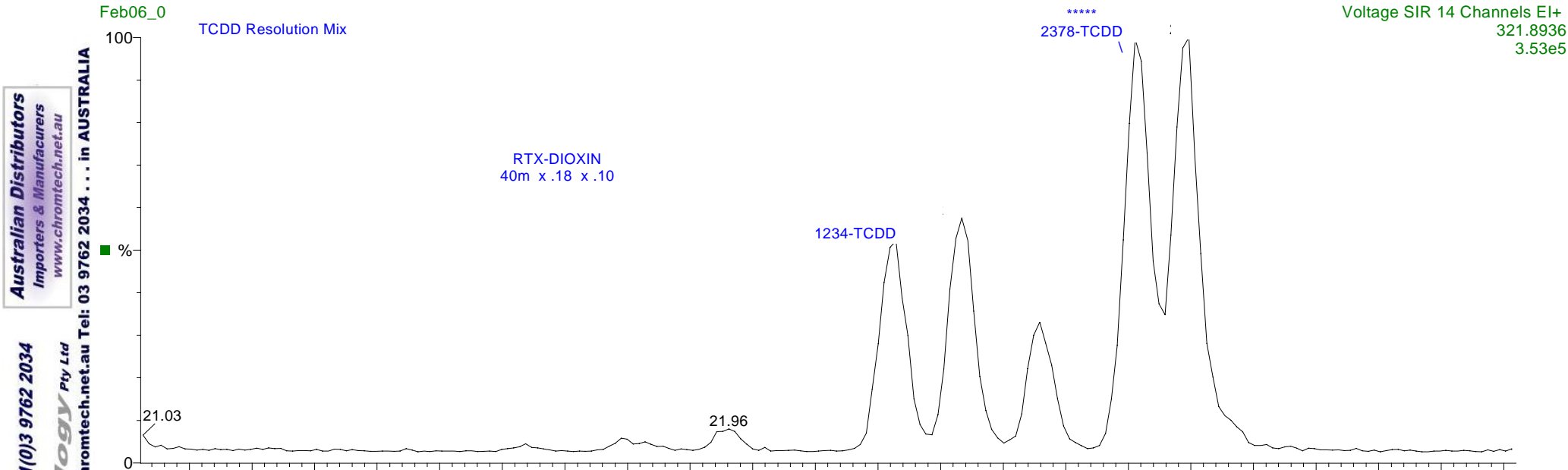
- Proprietary polysiloxane designed for replacement of “5”-type columns as primary, or high-cyano secondary columns for toxic dioxin and furan analysis by GC-HRMS
- 380 maximum operating temperature in standard high-temperature fused silica tubing

# Dioxin and Furan Analysis

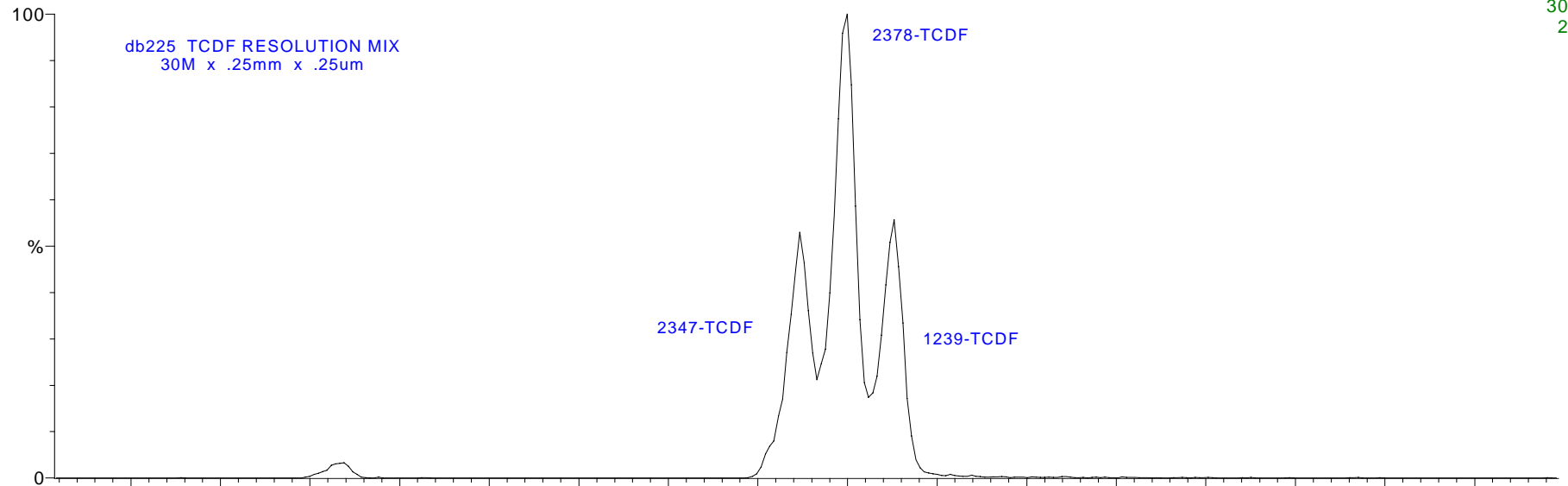
- Dual column method
  - Usually 5% diphenyl column and a high-cyano column (eg Rtx-225)
  - Cyano columns have poorer lifetimes and lower maximum operating temperatures
  - 5% diphenyl phases do not have the selectivity to accurately quantitate most samples
    - USEPA requires 2,3,7,8-tcdf to be confirmed on a X-225
- Desirable to have both columns in the same oven, and to improve the separation of the “5”

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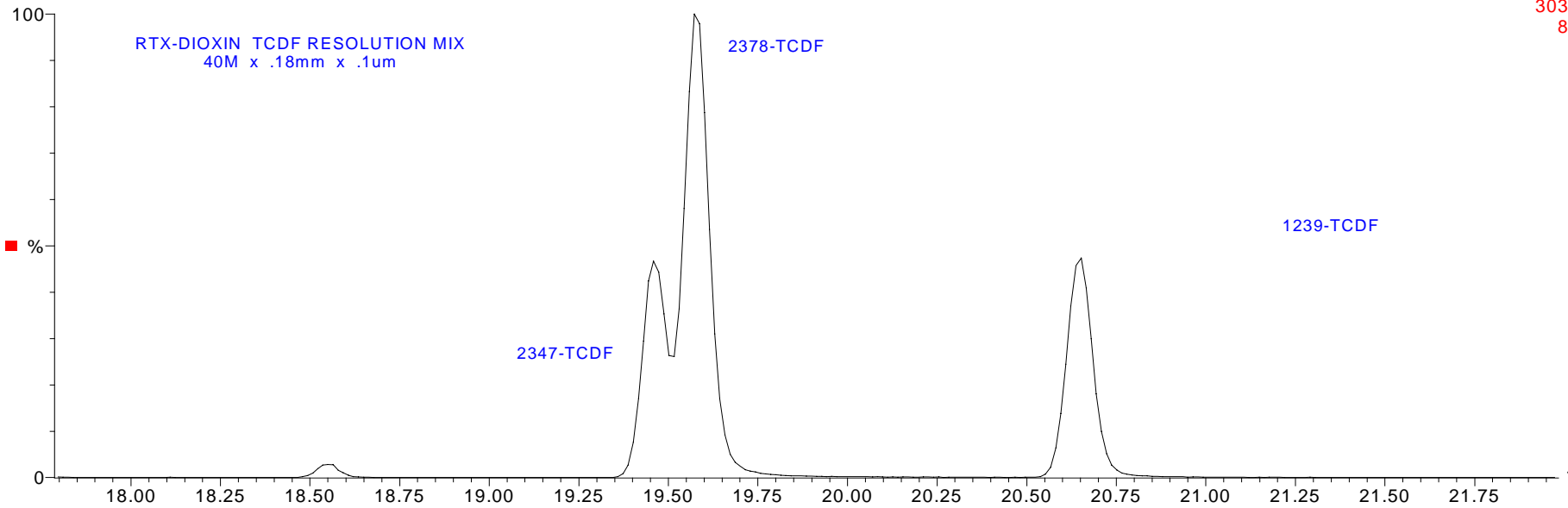


OCT24\_QCS001



SIR of 12 Channels EI+  
303.902  
2.88e6

feb18\_37



2: Voltage SIR 20 Channels EI+  
303.9016  
8.24e6



# Fly Ash Round Robin Samples

## >110 laboratories participating

	DB-5	DB-225	RTX-DIOXIN	MEDIAN	MEAN
Ash A	250	21	30	28	32
Ash B	2100	300	378	390	390
Ash C	170	19	28	27	32
All results reported as pg/g					

Median and Mean agreement gives good confidence in “true” value

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# Rtx-Dioxin Conditions

Micromass Altima High Resolution GC-MS

Rtx-Dioxin 40m x .18 x .1

Initial Temp 130 C

	Time	Rate C/min	Temp	
	0	52	200	
	10.2	2.9	235	
	10	6.9	300	
	24			

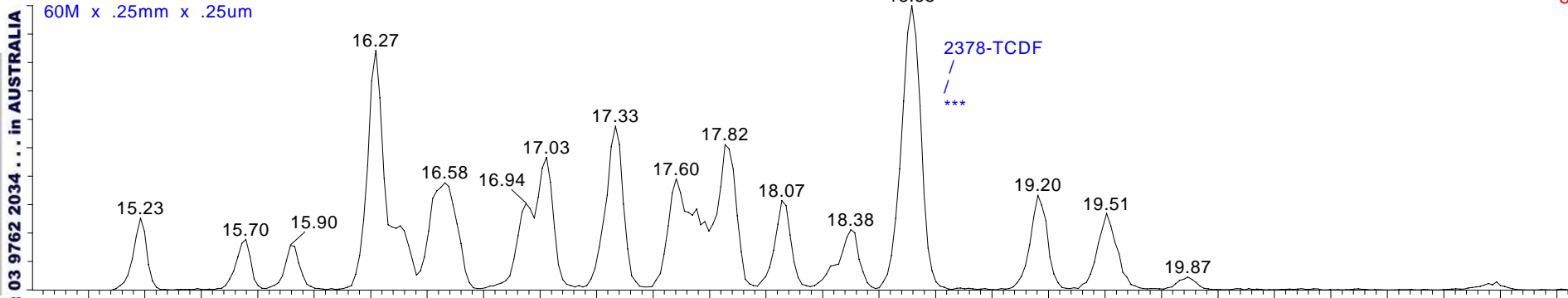
Constant Pressure of 1.2 mL/min

Injector Temp = 270C

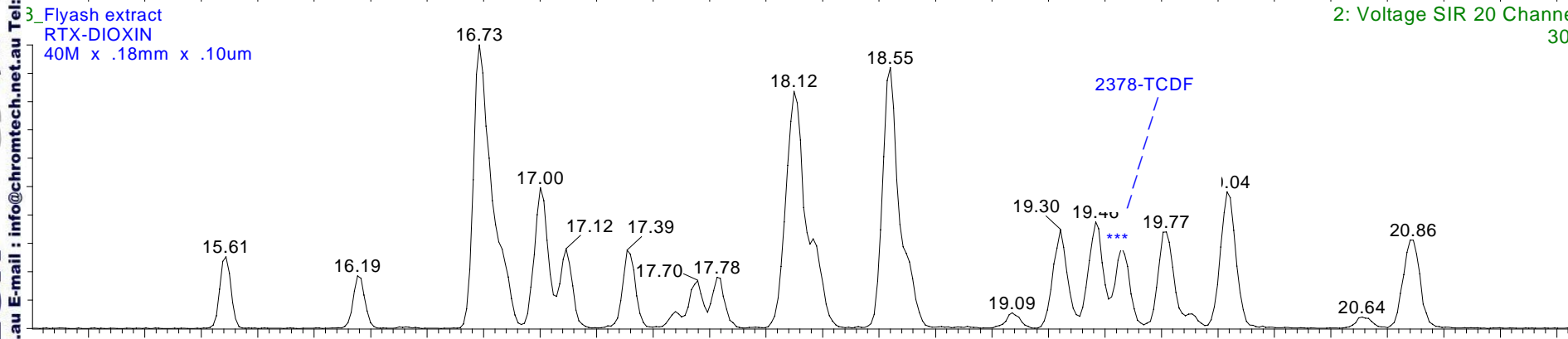
JUN18 Flyash extract  
DB5  
60M x .25mm x .25um

2: SIR of 20 Channels EI+  
303.902  
2.28e6

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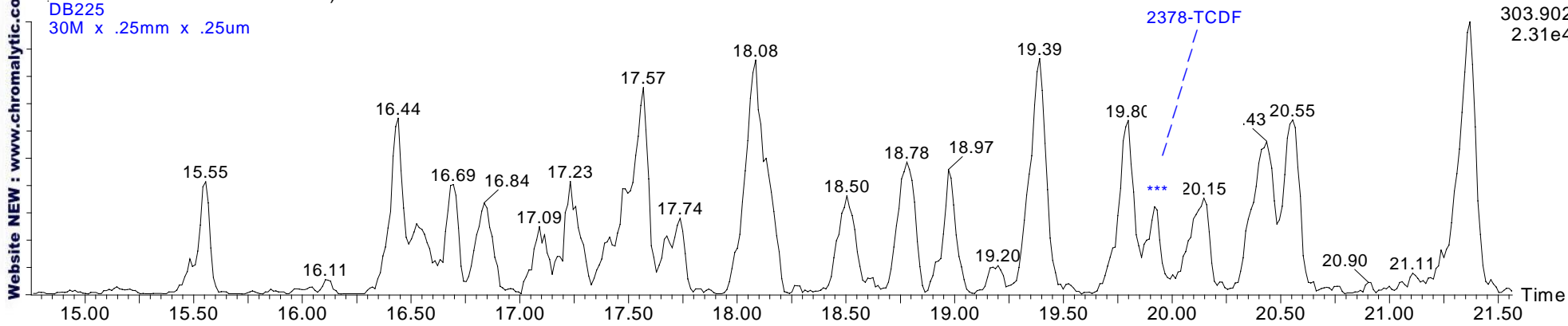
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2: Voltage SIR 20 Channels EI+  
303.9016  
7.01e5

24 Flyash extract  
DB225  
30M x .25mm x .25um

SIR of 12 Channels EI+  
303.902  
2.31e4



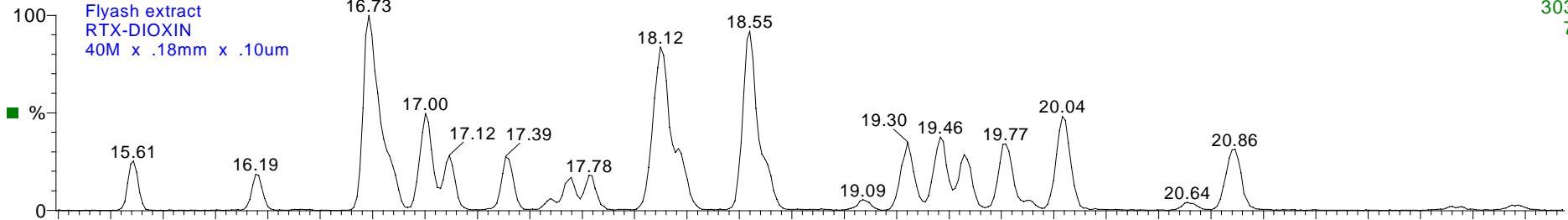
Time

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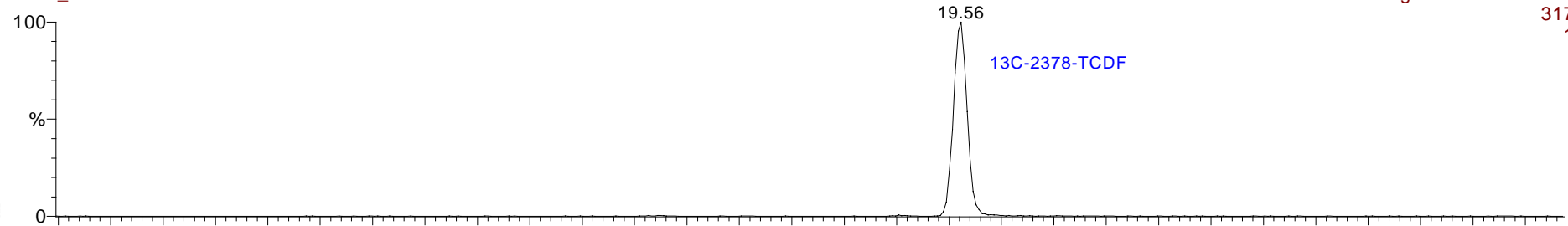
feb18\_33

Flyash extract  
RTX-DIOXIN  
40M x .18mm x .10um



2: Voltage SIR 20 Channels EI+  
303.9016  
7.01e5

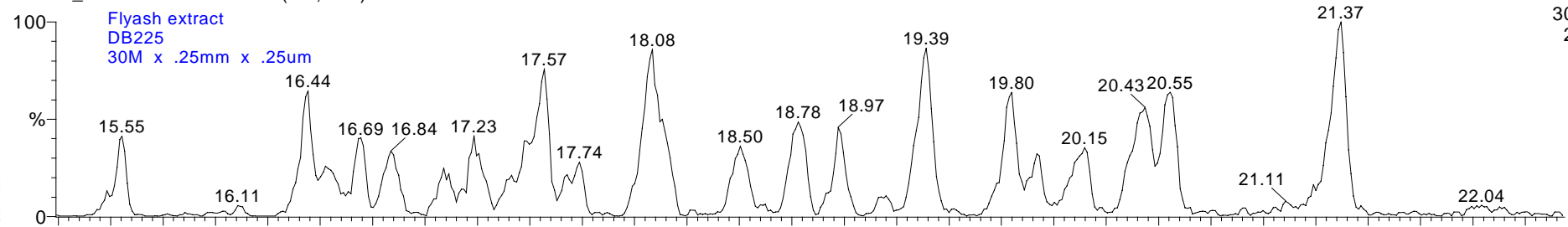
feb18\_33



2: Voltage SIR 20 Channels EI+  
317.9389  
1.33e6

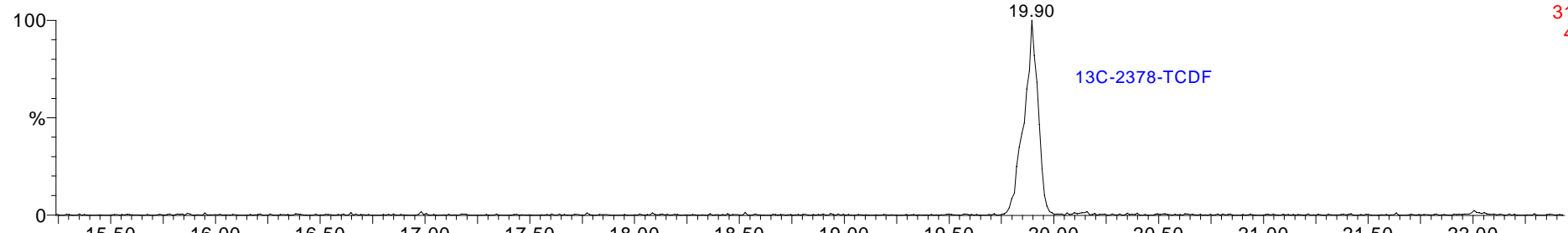
OCT24\_CONFIRM2S019 Sm (Mn, 1x1)

Flyash extract  
DB225  
30M x .25mm x .25um



SIR of 12 Channels EI+  
303.902  
2.31e4

OCT24\_CONFIRM2S019



SIR of 12 Channels EI+  
317.939  
4.54e5

Time

## Rtx-Dioxin Column

- Replaces a 5% diphenyl column for high-resolution dioxin and furan analyses
    - Improves sensitivity due to lower bleed levels
    - Improves separation of many congeners
  - May replace high-cyano columns as confirmation column to the 5% diphenyl
    - All but 2 congeners were within 10% of the fly ash median values
      - These 2 can be quantitated using the 5% diphenyl column
    - May eliminate the need for –2330, -2331, -225 confirmation columns
    - Final characterization currently underway complete for Dioxin
- 2003 August 24-29 in Boston

# Acknowledgements

- Reference materials courtesy of Wellington Laboratories – Guelph, Ontario
- Dr. Eric Reiner and Karen MacPherson of the Ontario Ministry of the Environment – Etobicoke, Ontario provided the HRMS analyses, and guidance.
- Jack Cochran of LECO Corporation – Pesticide and PCB analyses

# Improving Method Performance through Fast LC

C. Vernon Bartlett, B.A.; Rebecca E. Wittrig, Ph.D.

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# Abstract

Fast LC methods can be created by taking advantage of a wide range of separation variables to optimize resolution. Increases in resolution are created through increases in theoretical plates, selectivity, and retention. Alpha, the selectivity variable, is the greatest factor in separation optimization. Sometimes a simple phase change is all that is needed to convert a method to a Fast LC separation. Optimization of alpha through stationary phase selection can change a gradient system to a faster isocratic system, allow creation of a single method in lieu of multiple analysis methods, and reduce analysis times to a fraction of the original. This study examines the variables of the resolution equation and gives significant attention to the optimization of alpha in HPLC separations.



# Fast LC Methods

- Use of columns that can operate at high flow rates with reduced pressures (increased  $k'$ )
- Use of a reduced particle size substrate ( $<3\mu\text{m}$ ) to force higher theoretical plate counts (increased  $N$ )
- Use of shortened standard packed columns with optimized and possibly unique stationary phases (increased  $\alpha$ )

# Fast LC Technique

- Highly selective stationary phase is desired to maximize alpha values.
- Elution of components is typically accomplished through the use of gradients to reduce retention of highly retained components.
- Simple resolution of methylene substitutions /additions may be accomplished isocratically.
- Good screening technique for unknowns.

# Fast LC Technique – Advantages

- Faster re-equilibration (when using gradients).
- Sensitivity improvements.
- Older qualitative techniques can be adapted to a highly automated quantitative technique.
- Significant increases in sample throughput possible.
- Great technique when performed by LC-MS.
- Shorter analysis times reduce solvent consumption and waste.

# Fast LC Technique – Disadvantages

- Critical separations are more sensitive to extra-column volume (as post column reactors).
- Extremely selective stationary phase must be used to maximize selectivity – especially for structural isomers.
- May not be well suited to normal phase or ion pairing separations (with gradients).

# Principles and Theory of HPLC

## General Resolution Equation

$$R = \frac{1}{4} \left( \frac{a-1}{a} \right) \sqrt{N} \left( \frac{k'}{k'+1} \right)$$


### Selectivity

- stationary phase
- mobile phase composition
- additives

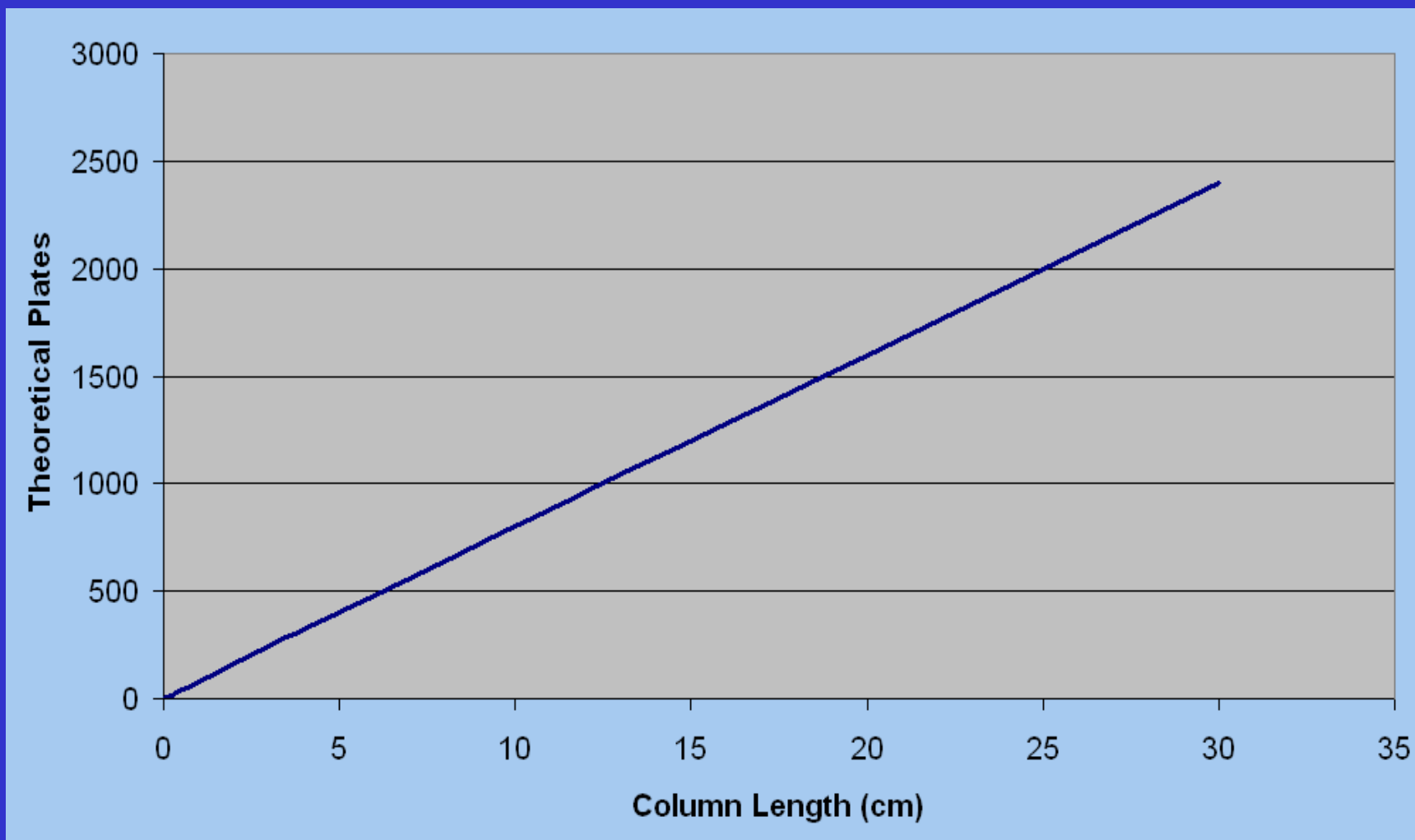
### Efficiency

- particle size
- column length

### Retention

- chain length
- mobile phase strength

# Column Length vs Theoretical Plates

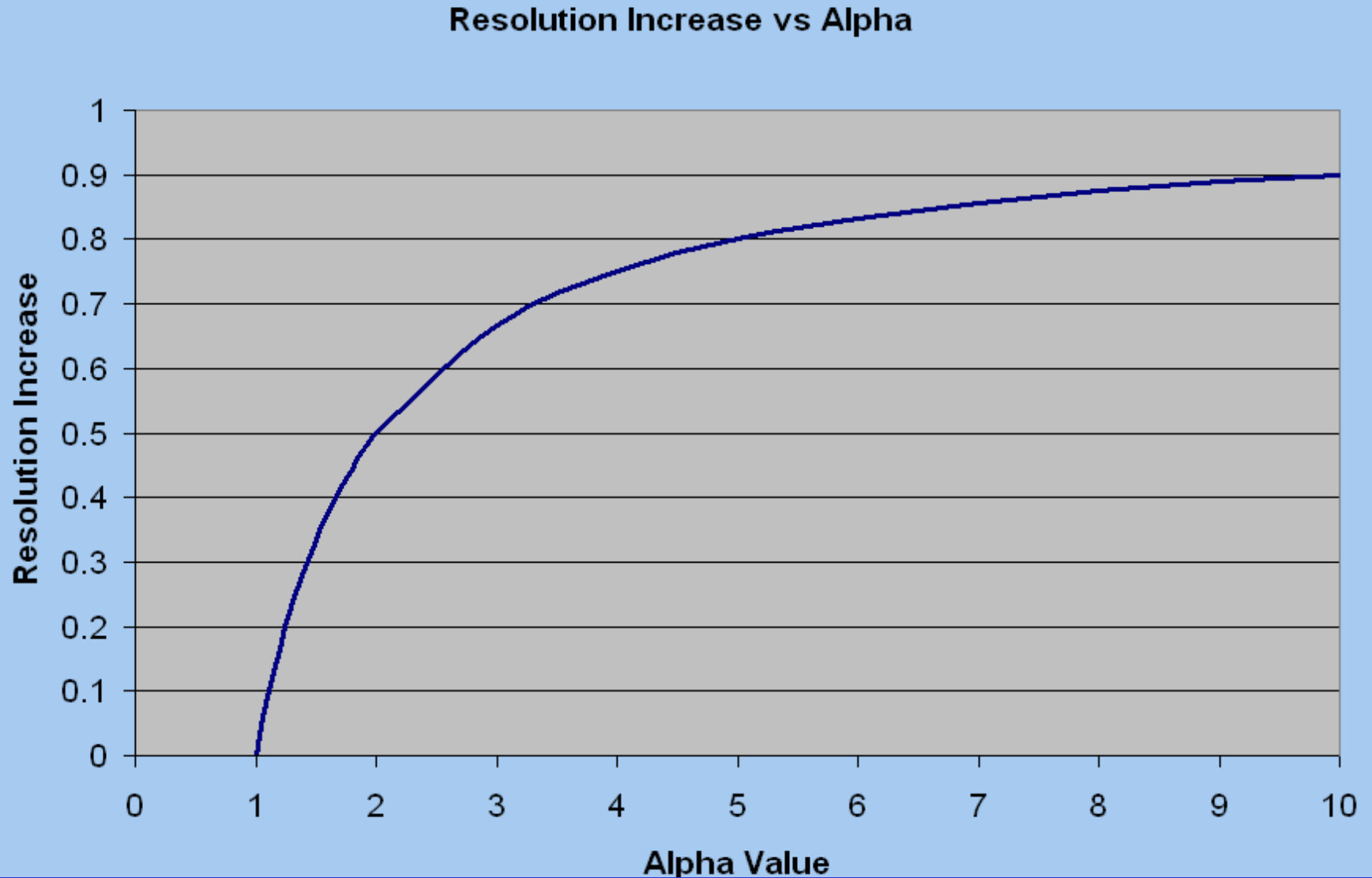


# Theoretical Plates and Fast LC

- The longer the column, the more theoretical plates the column is capable of providing.
- Shortening columns will reduce runtime at the expense of resolution.
- The loss in resolution can sometimes be compensated by the use of smaller particles.
- To achieve the separation with a shorter column, the important factor is to maintain the number of theoretical plates necessary for the resolution.



# Resolution Increase vs Alpha



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# Alpha (Selectivity) in Fast LC

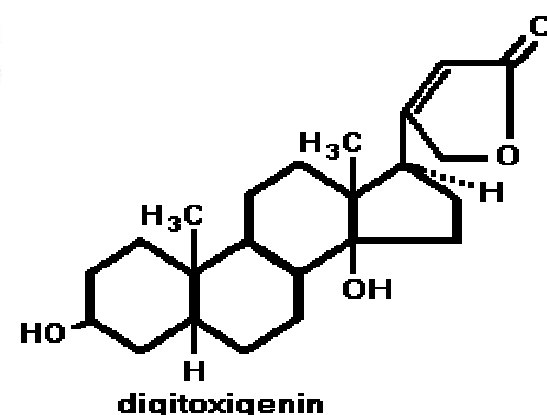
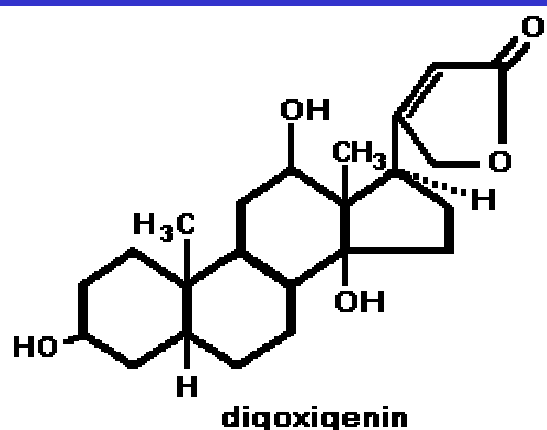
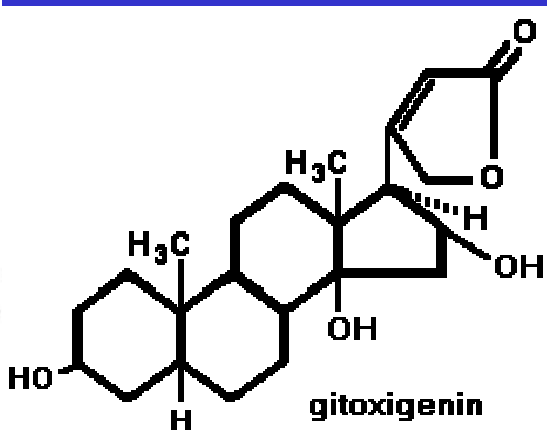
- Alpha has the greatest influence over the separation efficiency.
- Small changes in Alpha can lead to dramatic increase in resolution.
- Small changes in Alpha from 1-2 have the greatest influence on resolution.
- Additional increases in Alpha can be realized by taking advantage of other chemical and physical properties of the analyte, mobile phase composition, and the stationary phase.

# Alpha (Selectivity) in Fast LC

- Taking advantage of mixed mode interactions, size exclusion, shape selectivity, and other properties will lead to further increases in Alpha.
- High increases in Selectivity mean shorter HPLC columns can be used to achieve the desired resolution, while reducing analysis time.

# Fast LC improvement of USP TLC and HPLC Method

## Digitalis Extracts and Derivatives



Digitoxin:  $X_1=X_2=H$

Digoxin:  $X_1=H; X_2=OH$

Gitoxin:  $X_1=OH; X_2=H$

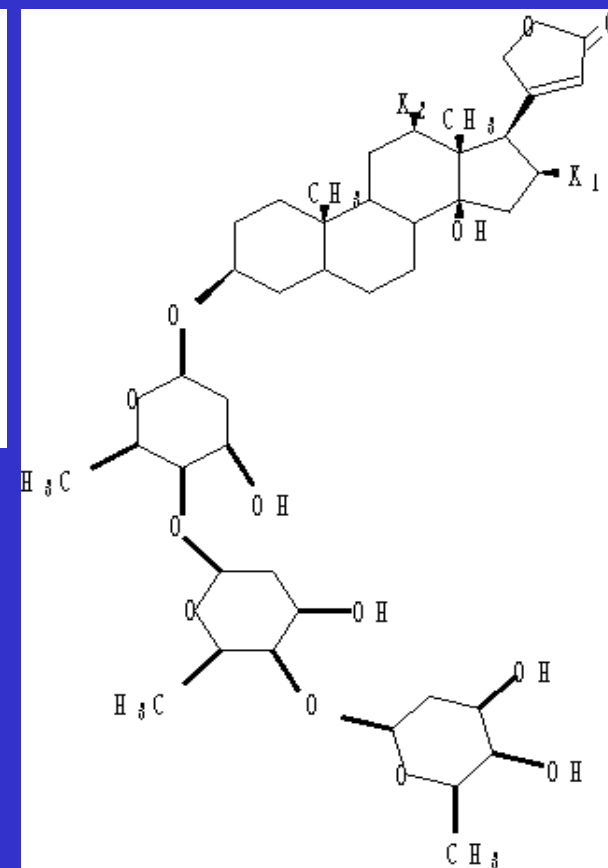
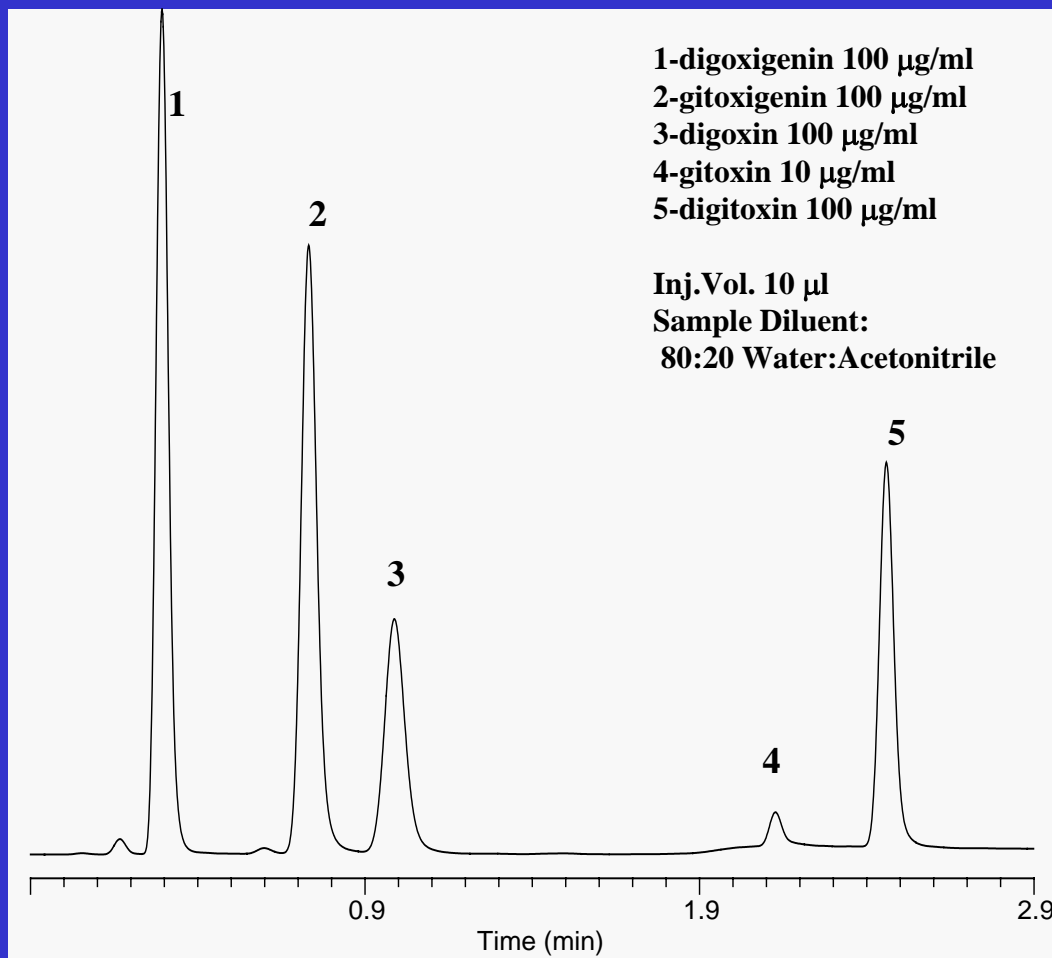


Figure 1

# Fast LC Separation of Digitalis Derivatives on Ultra PFP Propyl (3 minutes)

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Part number: 5179335

Particle Size: 3µm

Pore Size: 100 Å

Dimensions: 30mm x 4.0 mm

Flow Rate: 2.0 ml/min

Temp: 27° C

Detection: UV @ 230 nm

Mobile Phase:

A: 100% Water

B:Acetonitrile

Time (min): %B

0.0 20

1.5 20

1.51 35

3.0 35

3.01 20

LC\_250

# Advantages of Digitalis Fast LC over Current Methods

- Improved automation and analysis throughput.
- Reduction of analysis time – previously a 30 cm length C18 column was required for resolution.
- Ability to analyze all materials by HPLC.
- Ability to precisely quantitate materials vs TLC.
- Highly selective stationary phase.
- Technique can also be applied to purification and analysis of digoxin labeled materials for biological activity.
- Perfect technique for use in high speed cleaning validations.

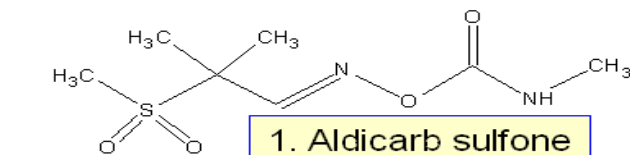
# Fast LC Analysis of Carbamate Insecticides

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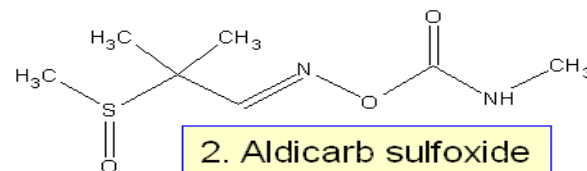
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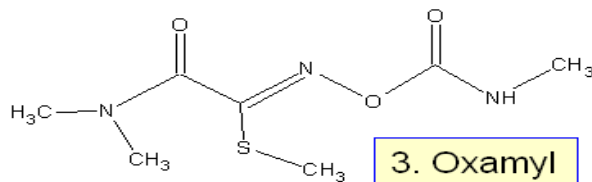
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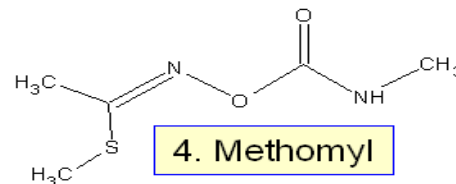
1. Aldicarb sulfone



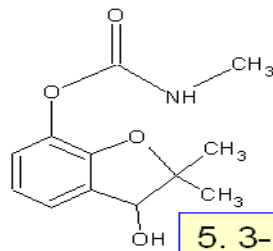
2. Aldicarb sulfoxide



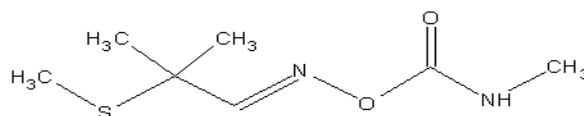
3. Oxamyl



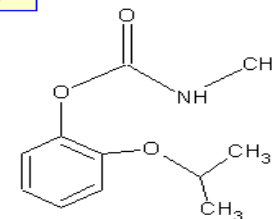
4. Methomyl



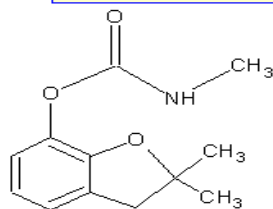
5. 3-Hydroxycarbofuran



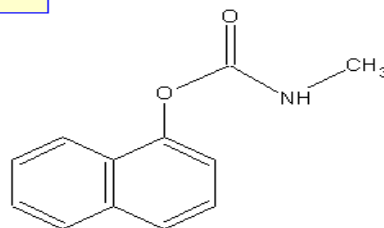
6. Aldicarb



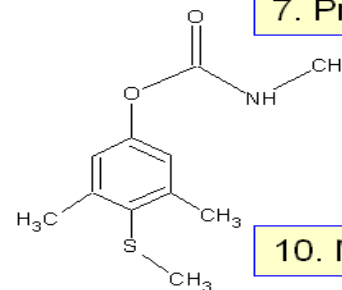
7. Propoxur



8. Carbofuran



9. Carbaryl



10. Methiocarb

Figure 3-Structures of Commonly Analyzed Carbamates

# Carbamate Analysis using Standard HPLC Methodology (About 40 minutes)

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## Carbamate Pesticides on Pinnacle Carbamate

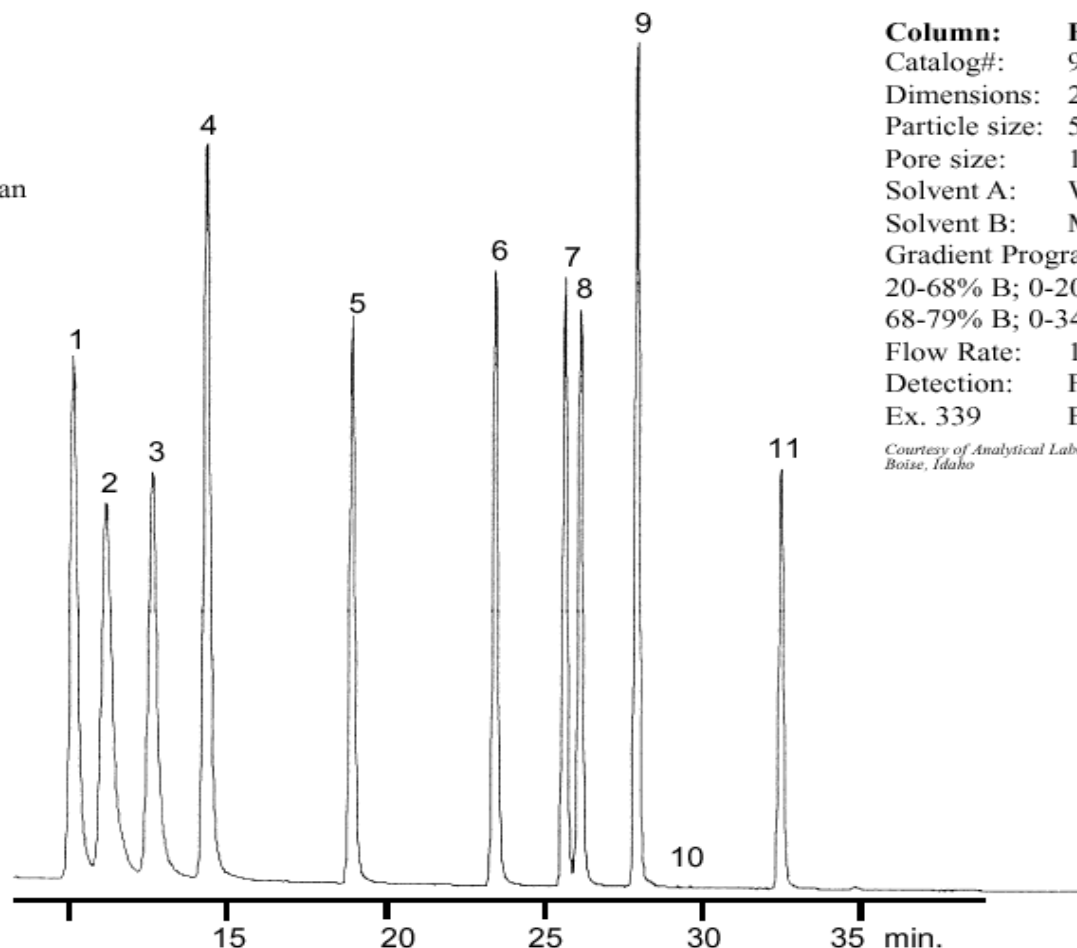
Applications Note: LC\_0192

### Peak List:

1. aldicarb sulfoxide
2. aldicarb sulfone
3. oxamyl
4. methomyl
5. 3-hydroxycarbofuran
6. aldicarb
7. propoxur
8. carbofuran
9. carbaryl
10. 1-naphthol
11. methiocarb

**Column:** Pinnacle Carbamate  
**Catalog#:** 9173575  
**Dimensions:** 250 x4.6mm  
**Particle size:** 5µm  
**Pore size:** 120Å  
**Solvent A:** Water  
**Solvent B:** Methanol  
**Gradient Program:**  
20-68% B; 0-20 min.  
68-79% B; 0-34 min.  
**Flow Rate:** 1.0mL/min  
**Detection:** Fluorescence  
**Ex. 339** **Em. 445nm**

*Courtesy of Analytical Laboratories, Inc.  
Boise, Idaho*





# Fast LC Separation of Carbamates (About 13 minutes)

## Fast LC Separation of 11 Carbamates on Ultra Carbamate

### Peak List:

1. aldicarb sulfone
2. aldicarb sulfoxide
3. oxamyl
4. methomyl
5. 3-hydroxycarbofuran
6. aldicarb
7. propoxur
8. carbofuran
9. carbaryl
10. methiocarb
11. 4-bromo-3,5-dimethylcarbamate

### Sample:

Inj.: 5 $\mu$ L  
Conc.: 50 $\mu$ g/mL  
Solvent: methanol

### Restek standards:

Catalog# 32274 and 32273 mixed 50:50

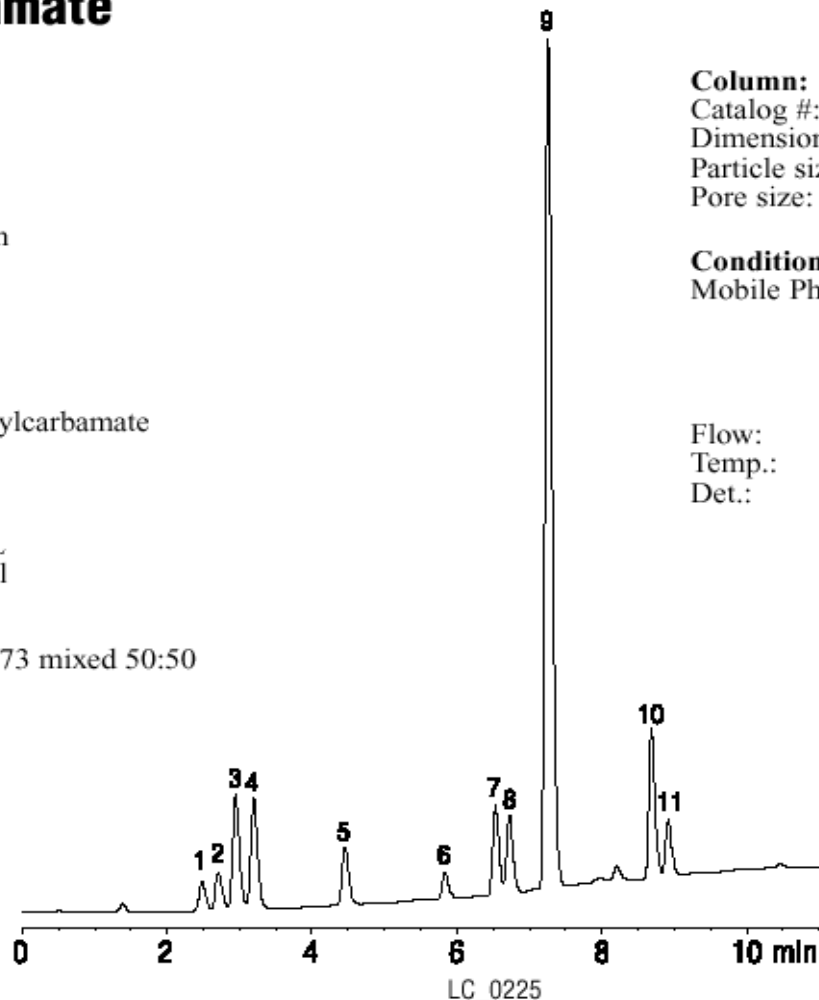
### Column: Ultra Carbamate

Catalog #: 9177355  
Dimensions: 50 x 4.6mm  
Particle size: 3 $\mu$ m  
Pore size: 100Å

### Conditions:

Mobile Phase: A: 90:10 water:methanol  
B: 90:10 methanol:acetonitrile  
Time (min): %B  
0 10  
10 90

Flow: 1.5mL/min  
Temp.: 27°C  
Det.: UV @ 220nm



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# Fast LC Analysis of Carbamates with MS Detection

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Table II. Experimental conditions for the LC/MS analysis of carbamate compounds.

## HPLC Conditions

Column: Ultra Carbamate, 100 mm x 4.6 mm, 3  $\mu$ m  
Mobile Phase A: 90% water:10% methanol with 10mM ammonium formate  
Mobile Phase B: 10% acetonitrile:90% methanol with 10mM ammonium formate  
Gradient: 90%A:10%B to 10%A:90%B from 0-15 minutes  
Inj. Volume: 10  $\mu$ L  
Flow Rate: 0.75 mL/min to UV detector, 0.25 mL/min to MSD

## MSD Conditions

		Compound	Ion	Cone V
Detector:	Micromass ZMD	1	223.3	25V
Mode:	ESI+	2	207.3	18V
Capillary V:	3.50	3	237.2*	10V
Extractor:	4.0	4	163.2	15V
Ion Energy:	0.4	5	238.3	15V
Multiplier:	650	6	191.2	8V
Source Temp:	100°C	7	210.2	18V
Desolv. Temp:	250°C	8	222.3	22V
Gas Flow:	490 L/hr.	9	202.2	18V
		10	226.3	19V

\*Ammonium adduct (all other are [M+H]<sup>+</sup> ions)

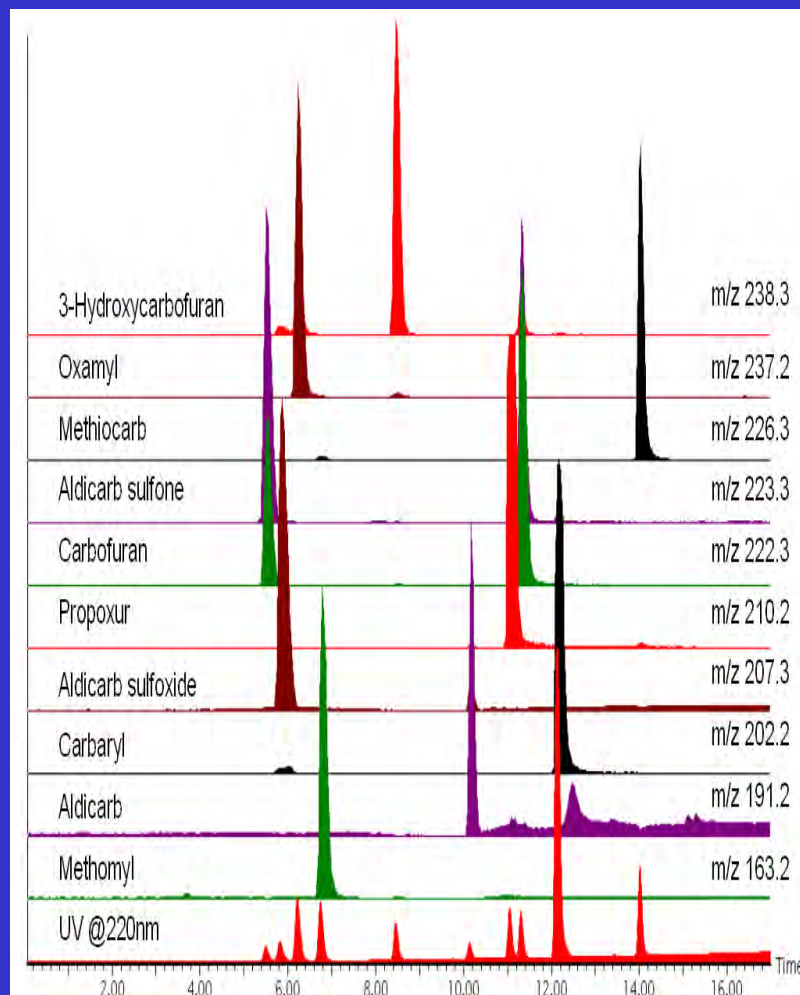
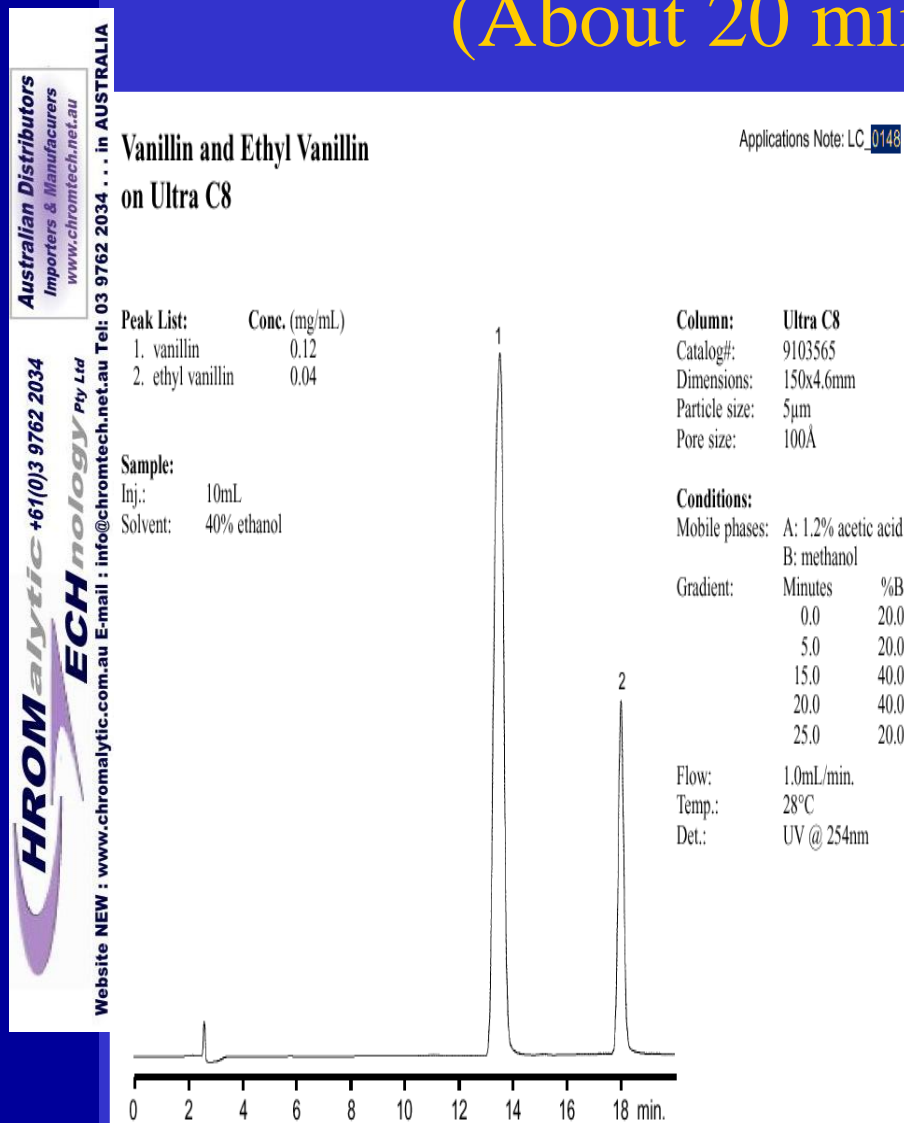
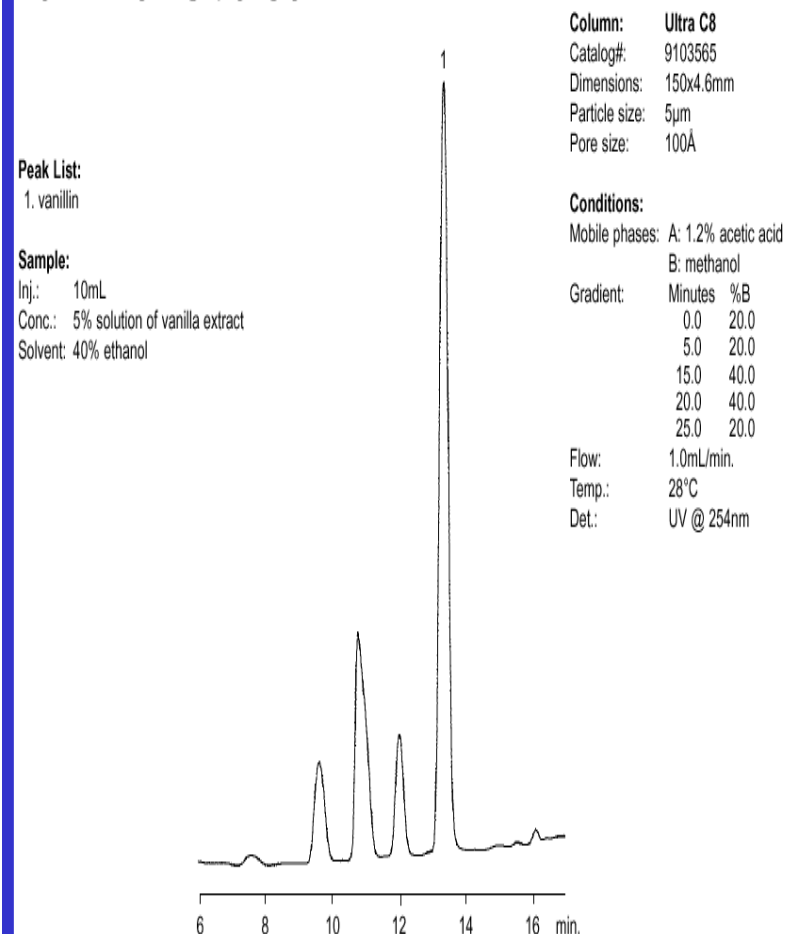


Figure 6

# Conventional Vanilla Flavoring Analysis (About 20 minutes with gradient)



## Vanillin on Ultra C8



# Highly Selective Fast LC Vanillin Analysis (Less than 5 minutes and isocratic)

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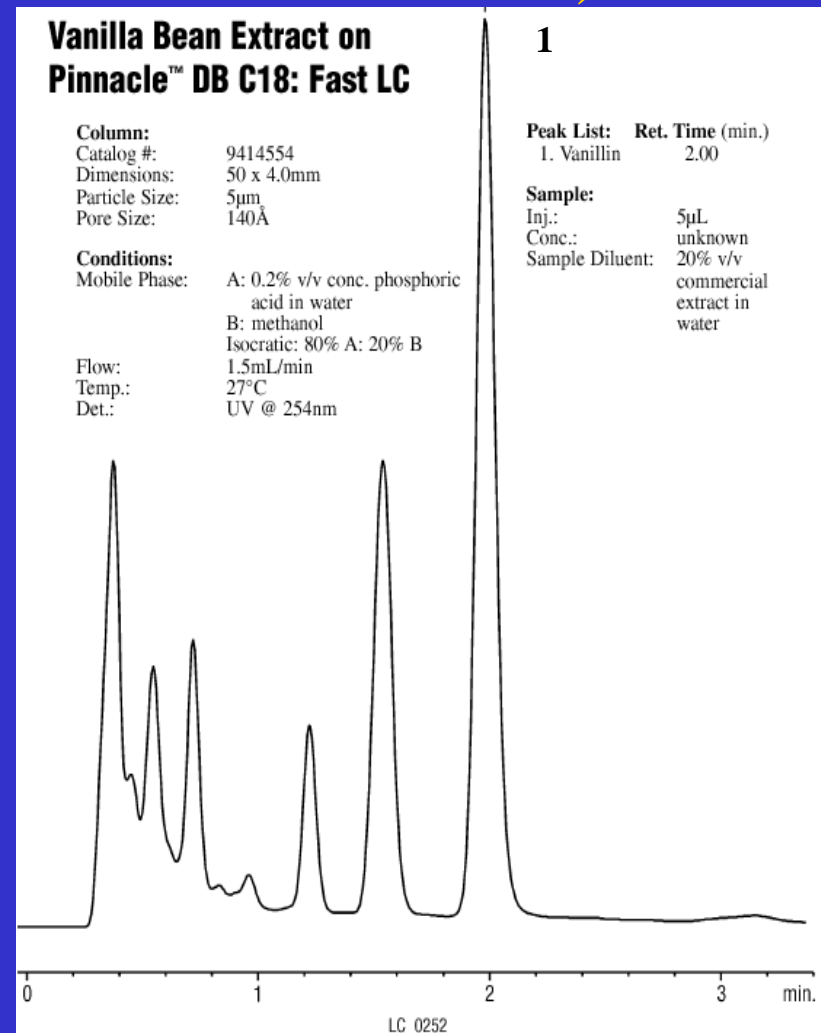
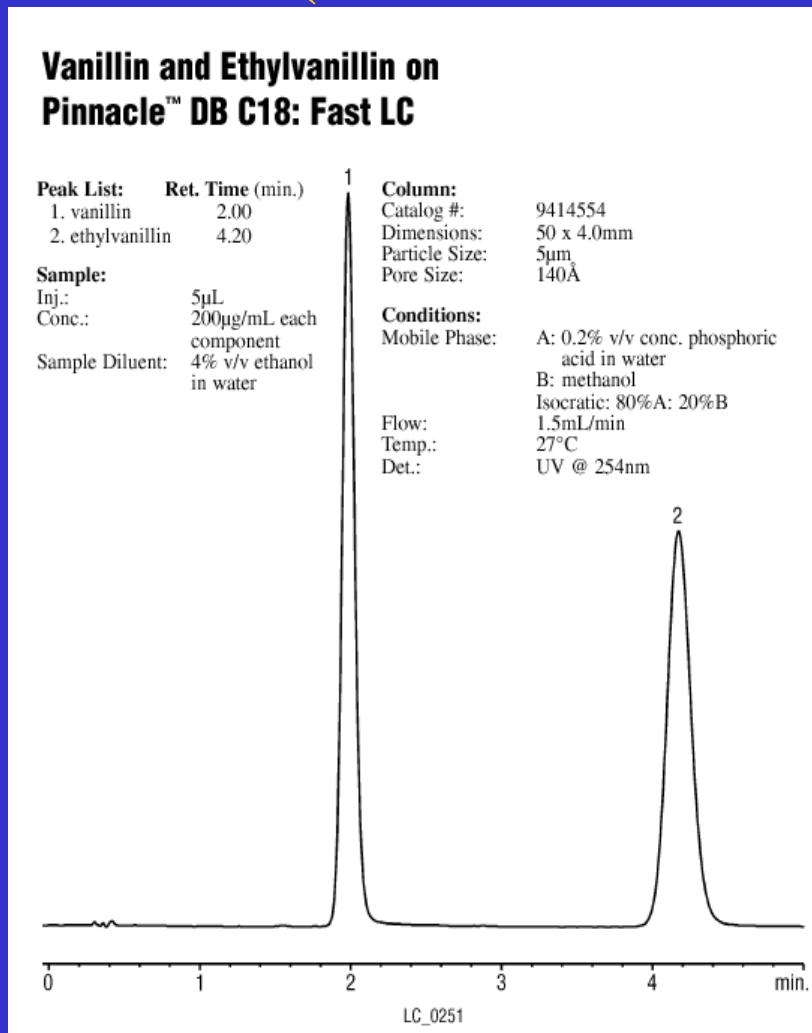


Figure 9

# Vanillin Fast LC Analysis Advantages

- Takes advantage of improved methylene selectivity by the use of C18 phase versus a C8
- Analysis can be conducted in 3 to 5 minutes versus older 20-25 minute methods requiring re-equilibration.
- High but not excessive selectivity of C18 phases toward simple methylene substitutions allow the use of an isocratic mobile phase.
- Reduction of column length also reduces the time needed for more hydrophobic analytes to elute from system.

# EPA Method 610 – PAHs on Pinnacle II PAH

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## Peak List:

1. naphthalene
2. acenaphthylene
3. acenaphthene
4. fluorene
5. phenanthrene
6. anthracene
7. fluoranthene
8. pyrene
9. benzo(a)anthracene
10. chrysene
11. benzo(b)fluoranthene
12. benzo(k)fluoranthene
13. benzo(a)pyrene
14. dibenzo(a,h)anthracene
15. benzo(ghi)perylene
16. indeno(1,2,3-cd)pyrene

## Sample:

Inj.: 5µL  
Sample Diluent: methylene chloride:acetonitrile (1:9, v/v)

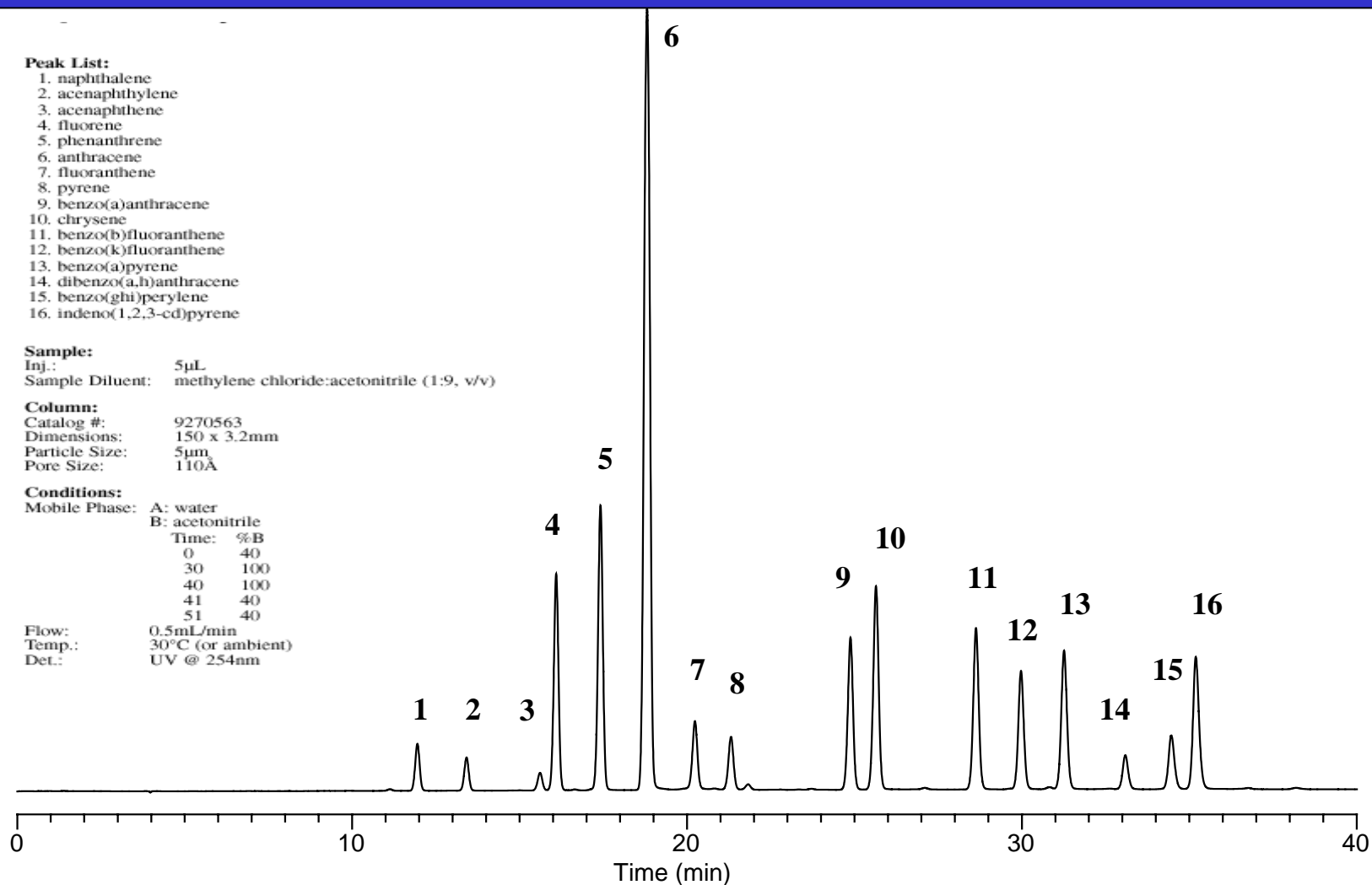
## Column:

Catalog #: 9270563  
Dimensions: 150 x 3.2mm  
Particle Size: 5µm  
Pore Size: 110Å

## Conditions:

Mobile Phase: A: water  
B: acetonitrile  
Time: %B  
0 40  
30 100  
40 100  
41 40  
51 40

Flow: 0.5mL/min  
Temp.: 30°C (or ambient)  
Det.: UV @ 254nm



# PAHs on Pinnacle II PAH- Fast LC

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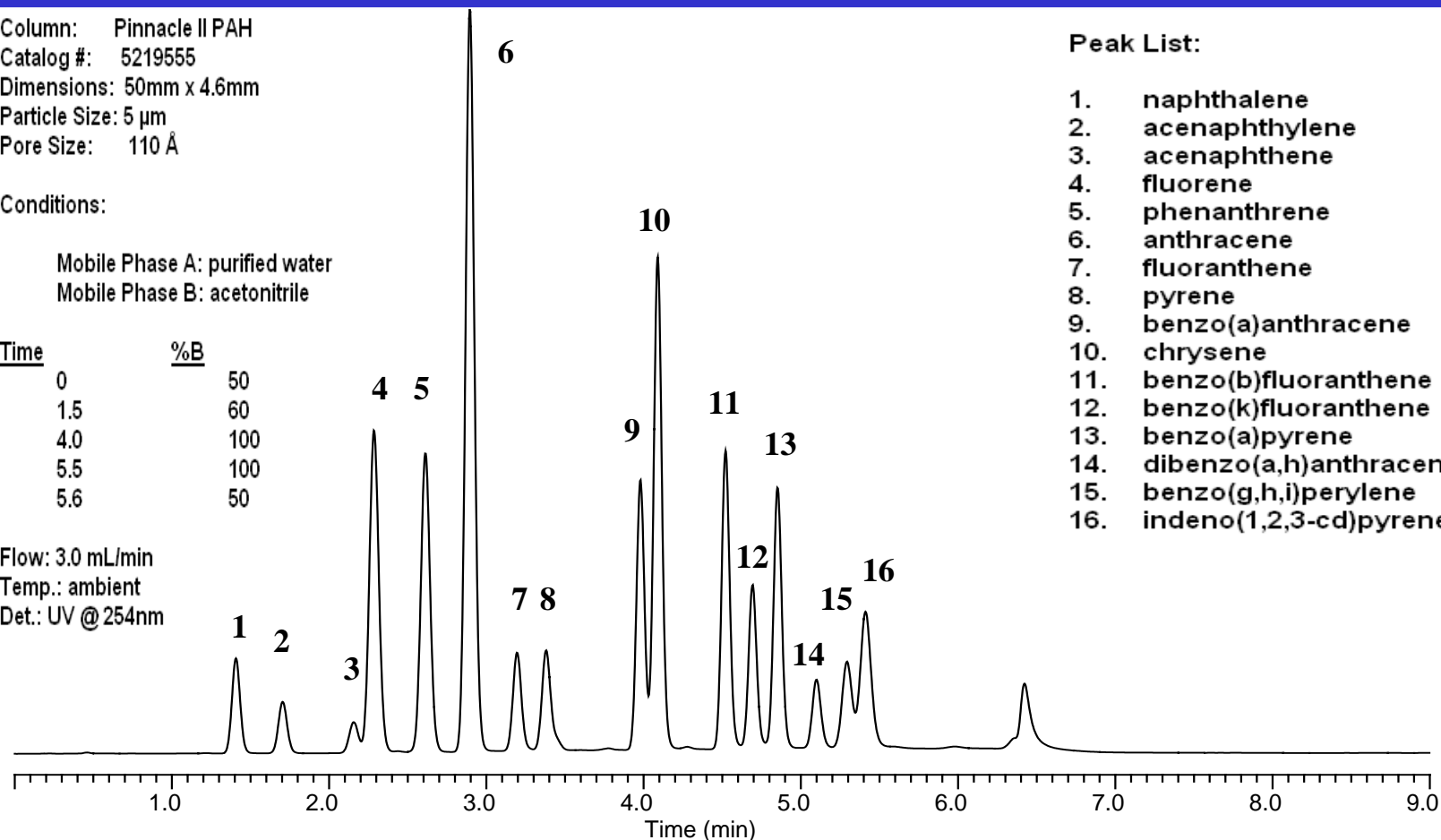
Column: Pinnacle II PAH  
Catalog #: 5219555  
Dimensions: 50mm x 4.6mm  
Particle Size: 5  $\mu$ m  
Pore Size: 110 Å

Conditions:

Mobile Phase A: purified water  
Mobile Phase B: acetonitrile

Time	%B
0	50
1.5	60
4.0	100
5.5	100
5.6	50

Flow: 3.0 mL/min  
Temp.: ambient  
Det.: UV @ 254nm



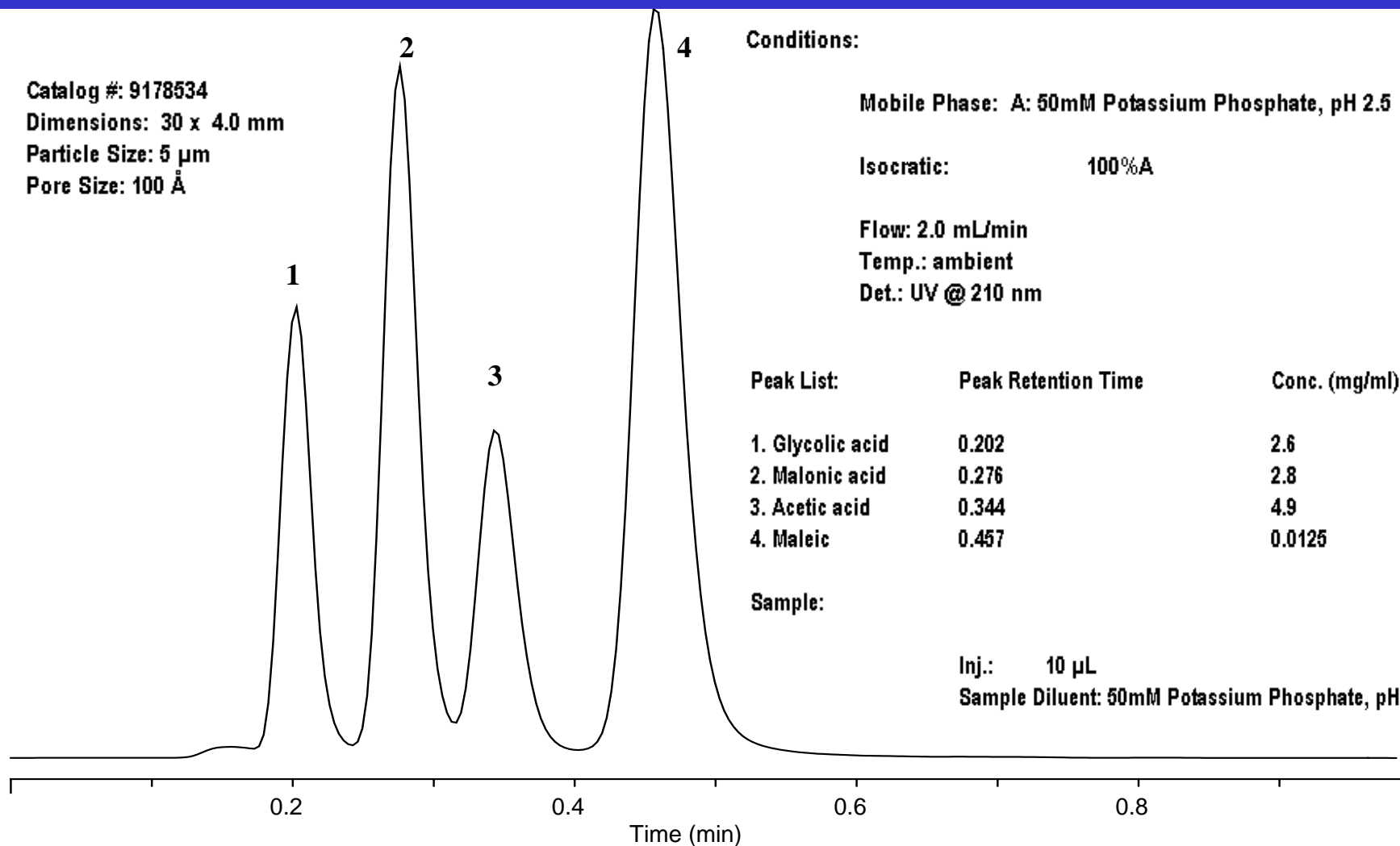


# Fast LC Analysis of Carboxylic Acids on Ultra Aqueous C18

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Catalog #: 9178534  
Dimensions: 30 x 4.0 mm  
Particle Size: 5  $\mu$ m  
Pore Size: 100 Å



# Fast LC Analysis of Aromatic Amino Acids on Ultra Aqueous C18

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Column:

Catalog #: 9178535  
Dimensions: 30 mm x 4.0 mm  
Particle Size: 5  $\mu$ m  
Pore Size: 100 Å

Conditions:

Mobile Phase: A: 50mM Potassium Phosphate, pH 2.5

B: Acetonitrile

Time:	%B
0.0	0%
1.0	40%
1.2	0
5.0	0

Flow: 1.0 mL/min  
Temp.: 50 °C  
Det.: UV @ 254 nm

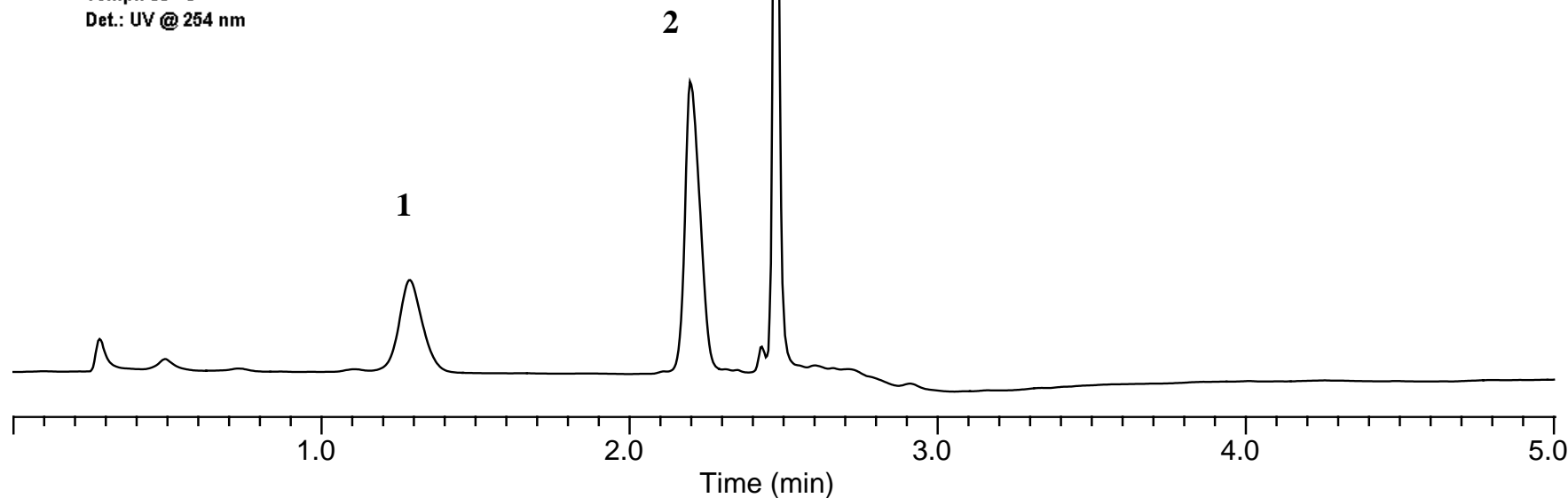
3

Peak List:	Peak Retention Time	Conc. (mg/ml)
1. Tyrosine	1.286	1.25
2 Phenylalanine	2.197	0.55
3. Tryptophan	2.475	0.035

Sample:

Inj.: 10  $\mu$ L

Sample Diluent: 50mM Potassium Phosphate, pH 2.5





# Conclusions

- Highly selective and sometimes unique stationary phases make Fast LC a reality using conventional hardware and techniques.
- Fast LC is viable, precise quantitative alternative for analyses previously performed by Thin Layer Chromatography.
- Fast LC can improve method sensitivity, reduce solvent waste, and enhance laboratory throughput.

# Conclusions

- The proper stationary phase selection can change a gradient system to a faster isocratic system.
- Sometimes only a simple phase change is needed to convert a method to a Fast LC separation.
- Selectivity is still the greatest factor in separation optimization.

# Acknowledgements

- The authors would like to thank Randy Romesberg, Larry Peters, and Rahul Patil of Restek Corporation for their participation in creating columns and hardware.

# Headspace Analysis of Residual Solvents in Pharmaceuticals, Using Flow-Modulation Chromatography.

CHRISTOPHER M. ENGLISH, Rebecca E.  
Wittrig, Frank L. Dorman.

# Application: Residual Solvents

- Pharmaceutical Formulations
- Guidelines for Testing
  - International Conference on Harmonization
  - European Pharmacopoeia
- Compound Lists Vary
  - Over 60 compounds of regulatory interest
  - Classes based on toxicities
  - Resolution of large lists on a single stationary phase can be extremely difficult

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# The Three Approaches:

- Evaluate Existing Phases
- Develop a New Stationary Phase
- Stop-Flow GC Technology
  - Using Existing RT Data
  - Applying RT Data for Stop-Flow

# Existing Phases Evaluated

- Change in selectivity
- Low bleed
- Critical resolution
- D or MS detection

- Column Design.





Rtx®-G27

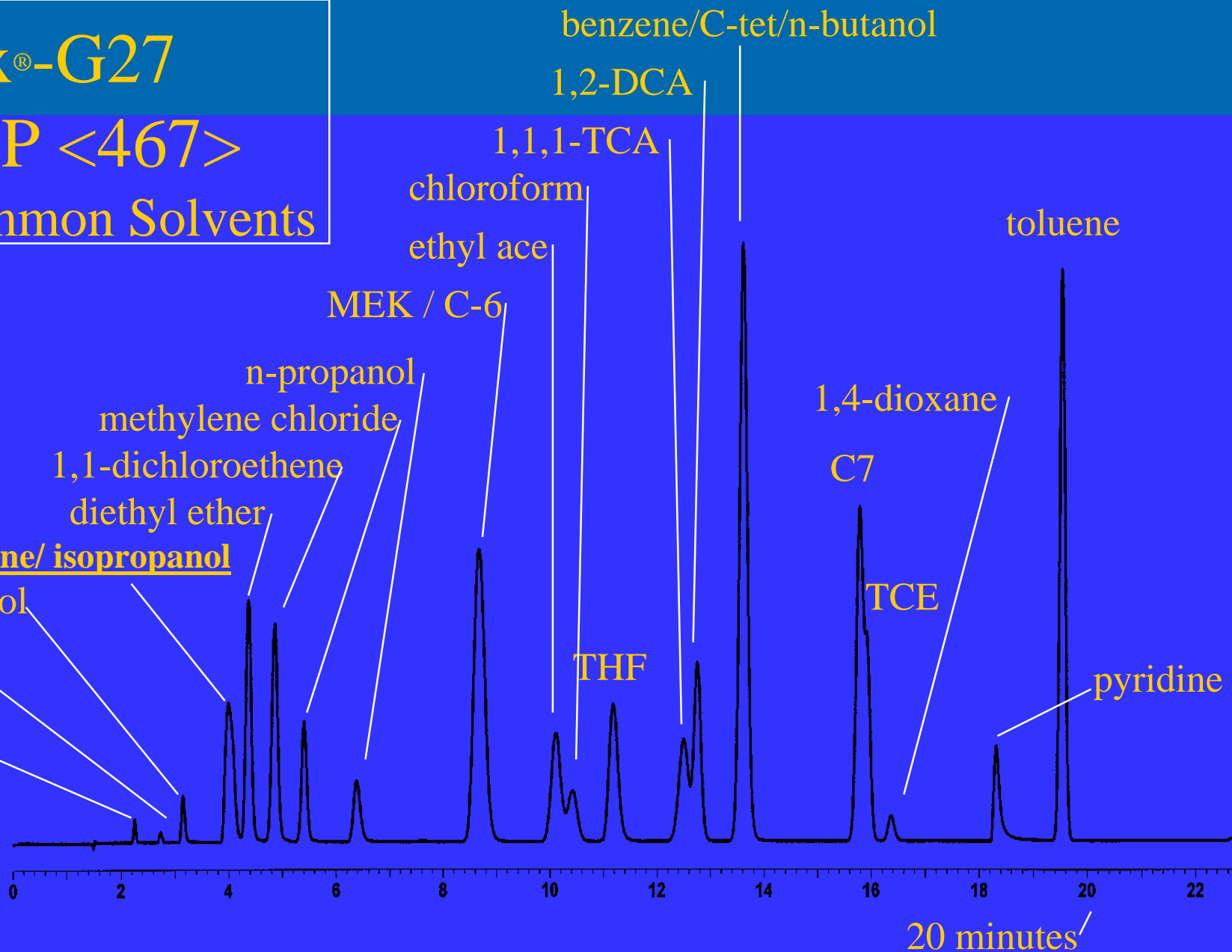
USP <467>

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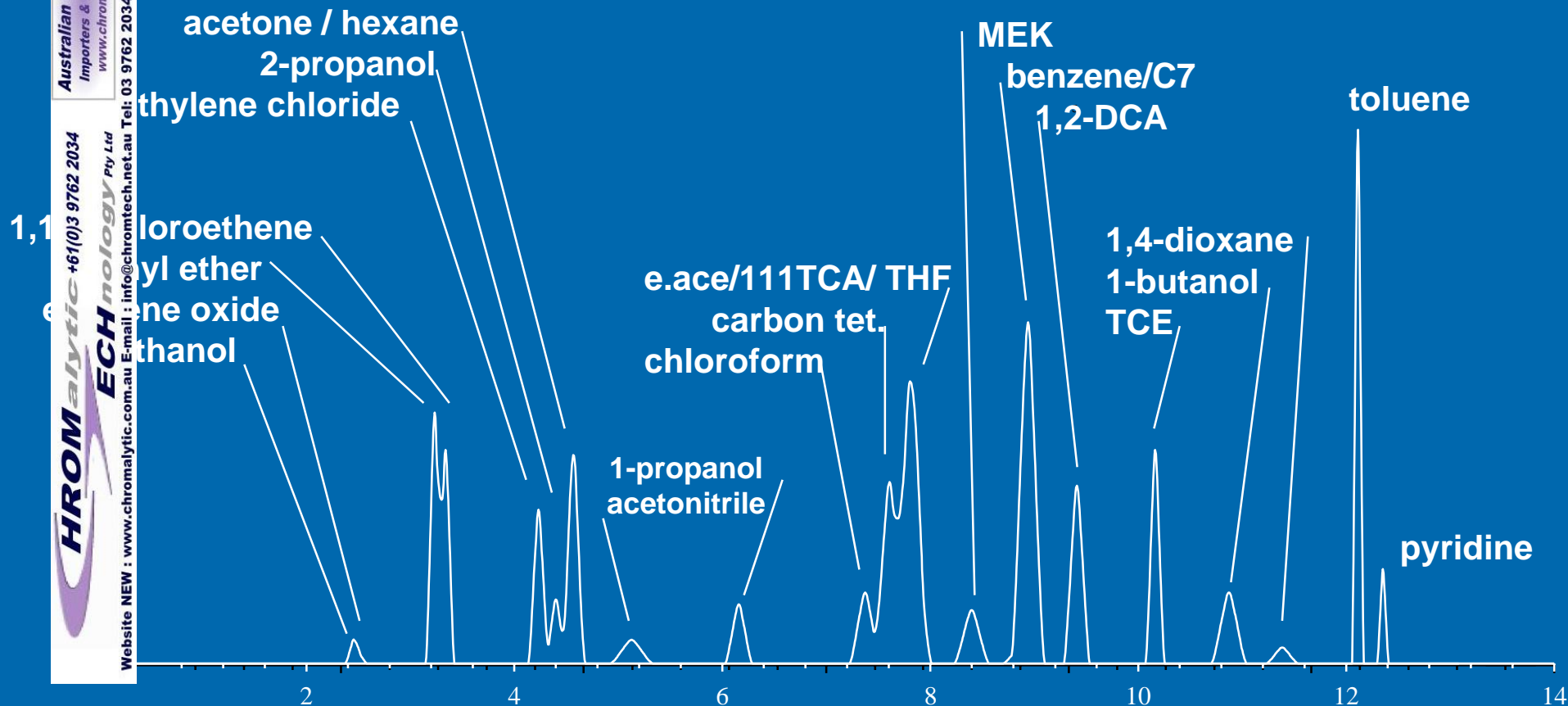


# The Rtx-G27 Unresolved

- acetonitrile (II), acetone (III), IPA (III)
- MEK (III), C6 (II)
- benzene (I), carbon tet. (I), n-butanol (III)
- C7 (III), TCE (II)

# Rtx<sup>®</sup>-VGC

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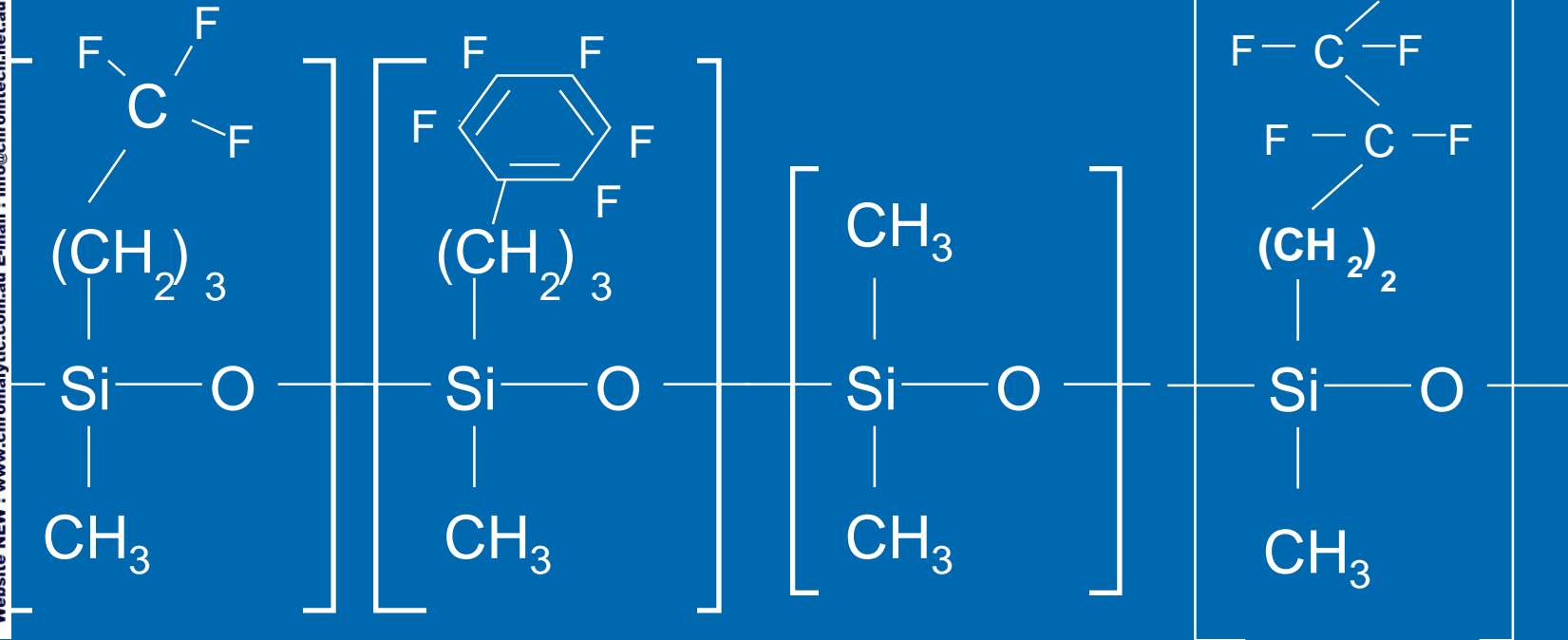
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# The Rtx-VGC Unresolved

- acetone (III), C6 (II)
- E.ace (III), 111TCA (I), THF (III)
- benzene (I), C7 (III)

# Experimental Fluorinated Phase

## Bonded Polymer Examined for GC Applications.



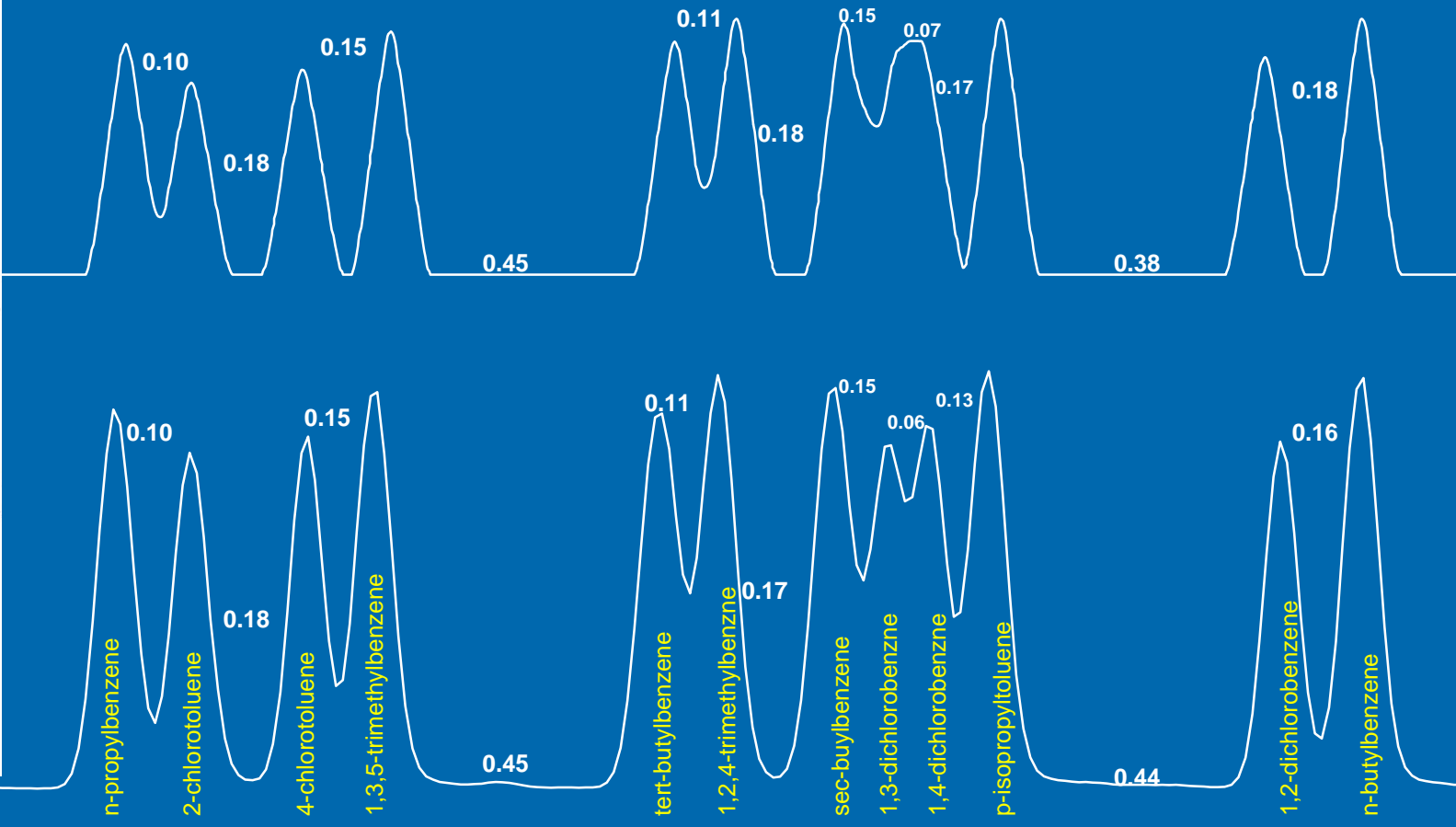
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# Modeling for a New Bonded Phase

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# Stationary Phases Used for Modeling

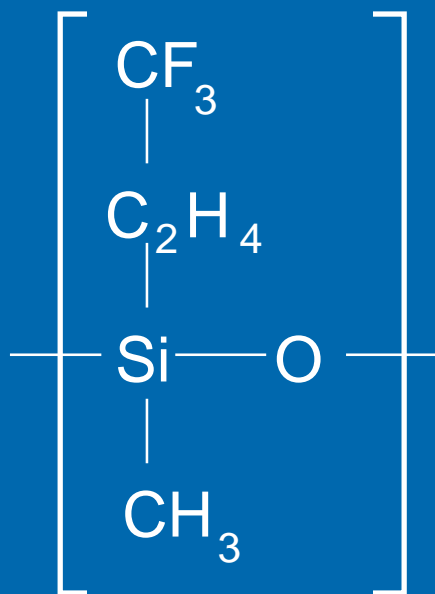
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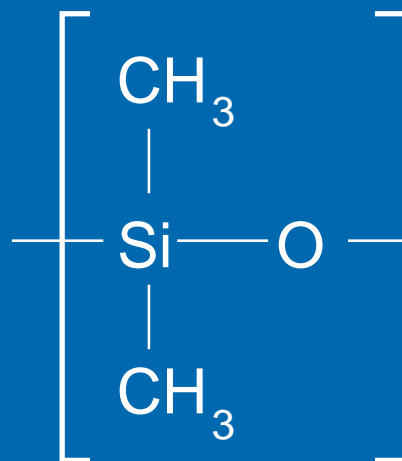
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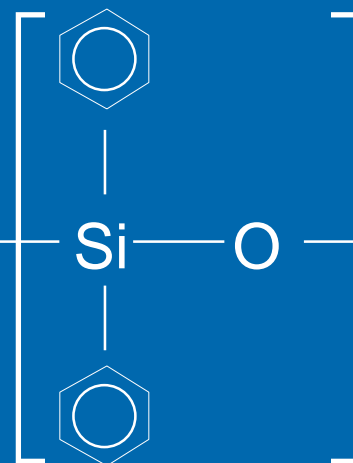
trifluoropropylmethyl  
polysiloxane



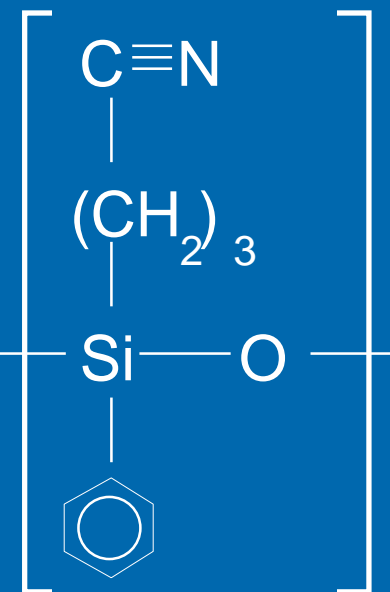
dimethyl  
polysiloxane



diphenyl  
polysiloxane



cyanopropylphenyl  
polysiloxane



# Current Issues with the ICH Compounds.

Separation  
Concentration

# Headspace & Stop Flow

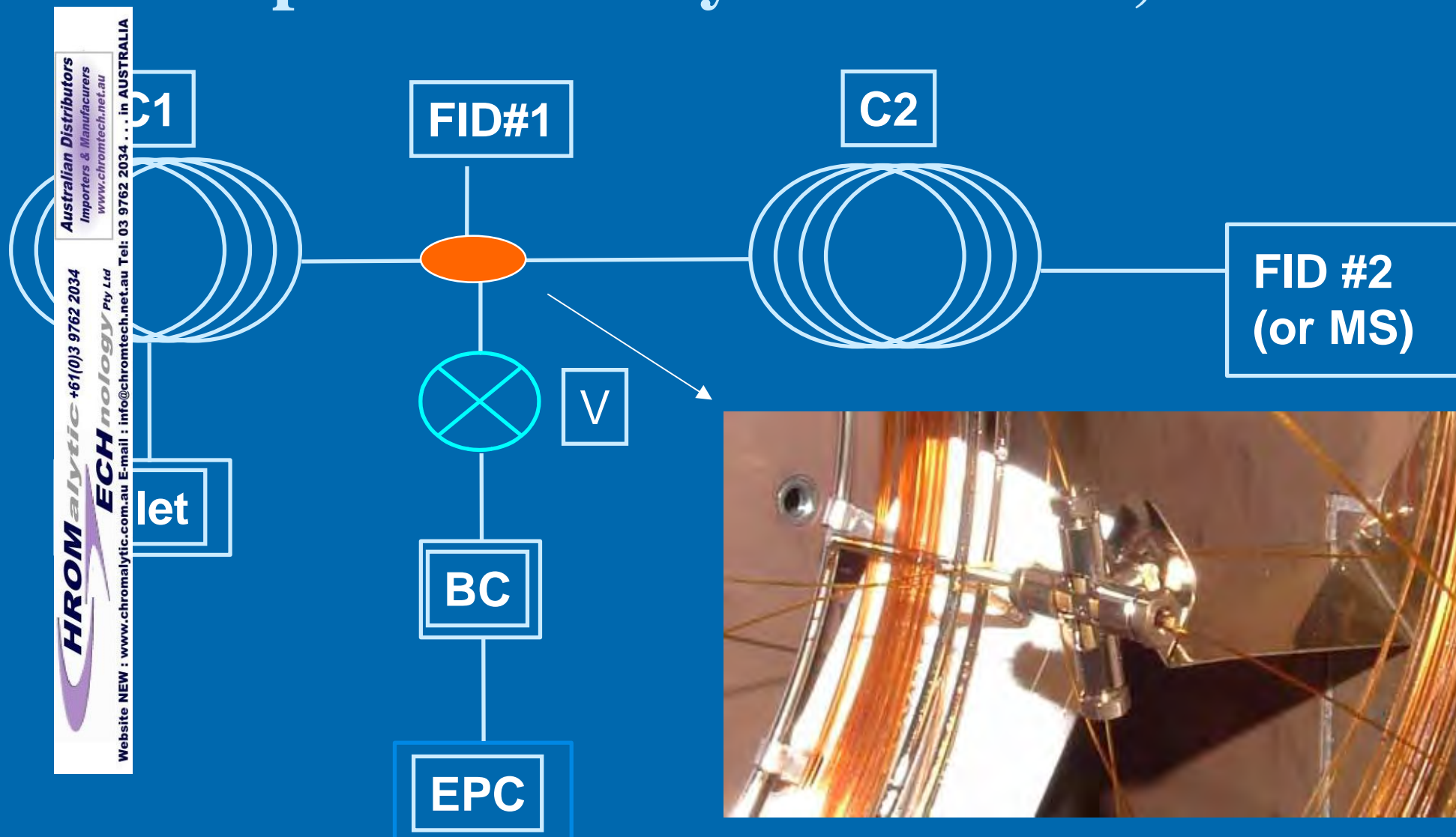


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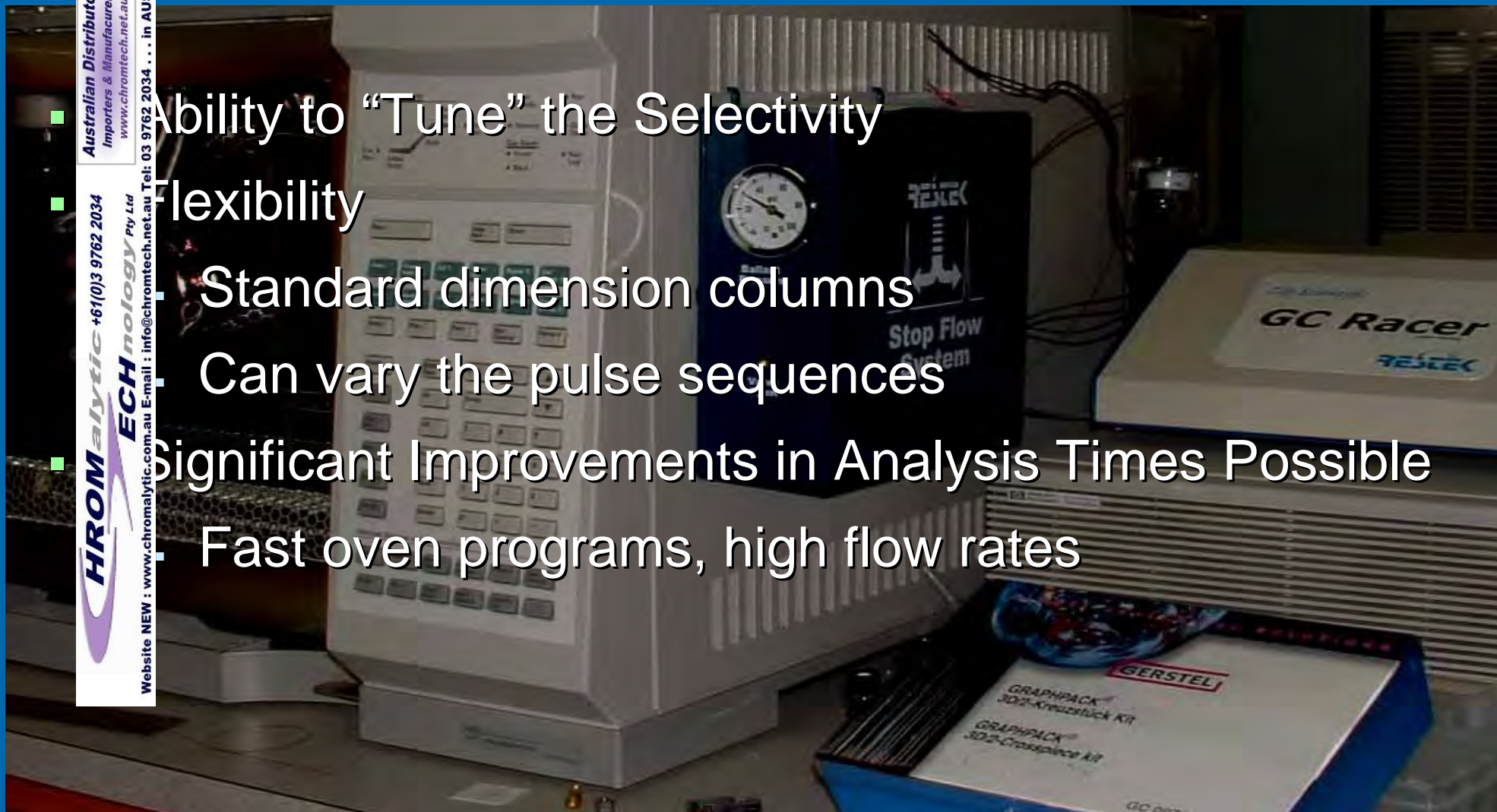
# Stop Flow GC System: Sacks, et. al.\*



\*Richard Sacks, University of Michigan

# Summary of Stop-Flow GC

- Ability to “Tune” the Selectivity
- Flexibility
- Standard dimension columns
- Can vary the pulse sequences
- Significant Improvements in Analysis Times Possible
- Fast oven programs, high flow rates



# Class I & II Residual Solvents

Peak #	Compound	Peak #	Compound
1	2-methylpentane	19	1,2-dichloroethane (1,2-DCA)
2	hexane	20	2-hexanone (MBK)
3	methyl cyclopentane	21	p-xylene
4	1,1-dichloroethene (1,1-DCE)	22	m-xylene
5	methyl cyclohexane	23	nitromethane
6	<i>trans</i> -1,2-dichloroethene	24	2-methoxyethanol
7	carbon tetrachloride (CCl <sub>4</sub> )	25	pyridine
8	1,1,1-trichloroethane (1,1,1-TCA)	26	o-xylene
9	methanol	27	chlorobenzene
10	1,2-dimethoxyethane	28	2-ethoxyethanol
11	methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	29	1,1,2-trichloroethane (1,1,2-TCA)
12	benzene	30	dimethyl formamide (DMF)
13	<i>cis</i> -1,2-dichloroethene	31	N,N-dimethylacetamide (DMA)
14	trichloroethene (TCE)	32	1,2,3,4-tetrahydronaphthalene (THN)
15	acetonitrile (MeCN)	33	ethylene glycol (EG)
16	chloroform	34	1-methyl-2-pyrrolidinone (1-MP)
17	toluene	35	formamide
18	1,4-dioxane	36	sulfolone

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# Coelutions by Phase

## Class I & II

### Rtx-1

1,2-dichloroethane / methyl cyclopentane  
1,4-dioxane / trichloroethene  
p-xylene / m-xylene

### Rtx-200

hexane / methylene chloride  
1,2-dichloroethane / trichloroethene  
2-ethoxyethanol / toluene

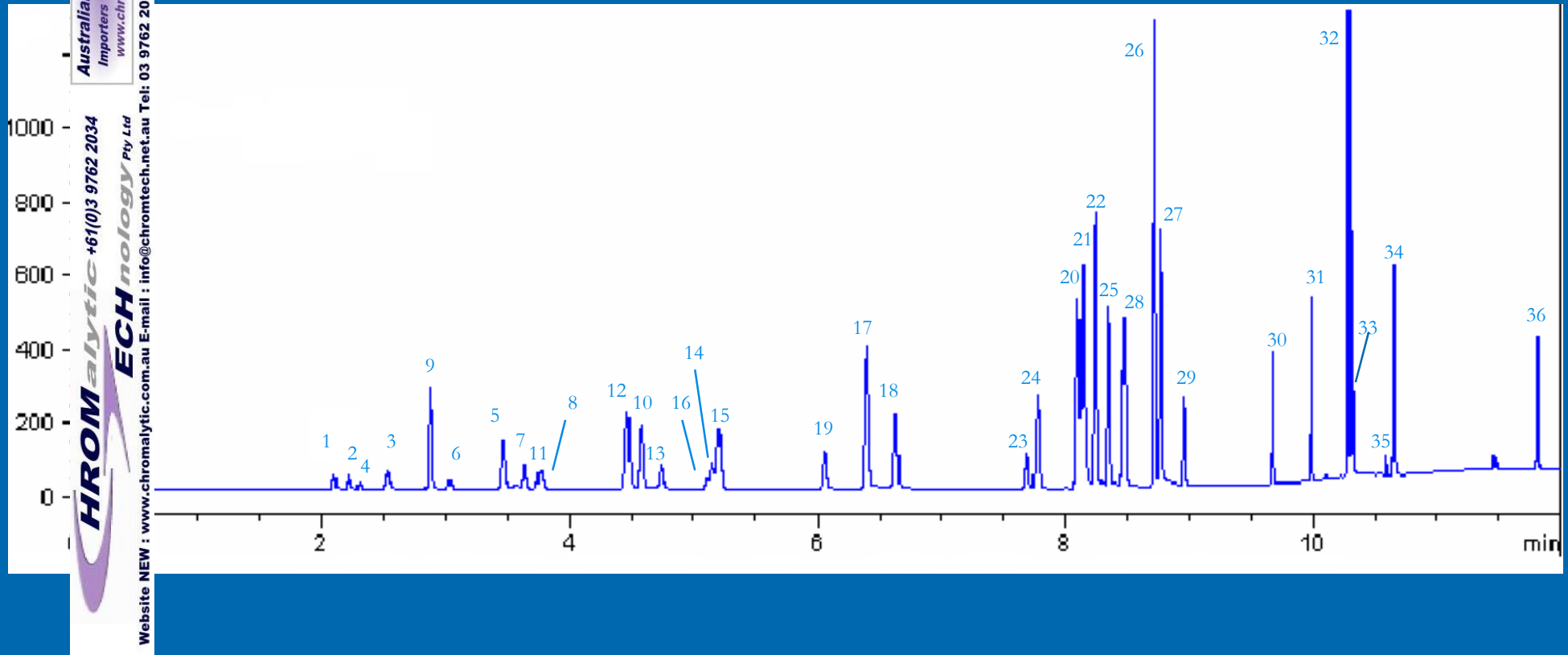
### Stabilwax

carbon tetrachloride / 1,1,1-trichloroethane  
cis-1,2-dichloroethene / trichloroethene

### Rtx-VMS


Carbon tetrachloride / 1,1,1-trichloroethane (close pair)  
Trichloroethene / methyl cyclohexane  
p-xylene / m-xylene

# Class I & II OVIs: Total of 9 Pulses *At the End Detector – all 36 resolved*





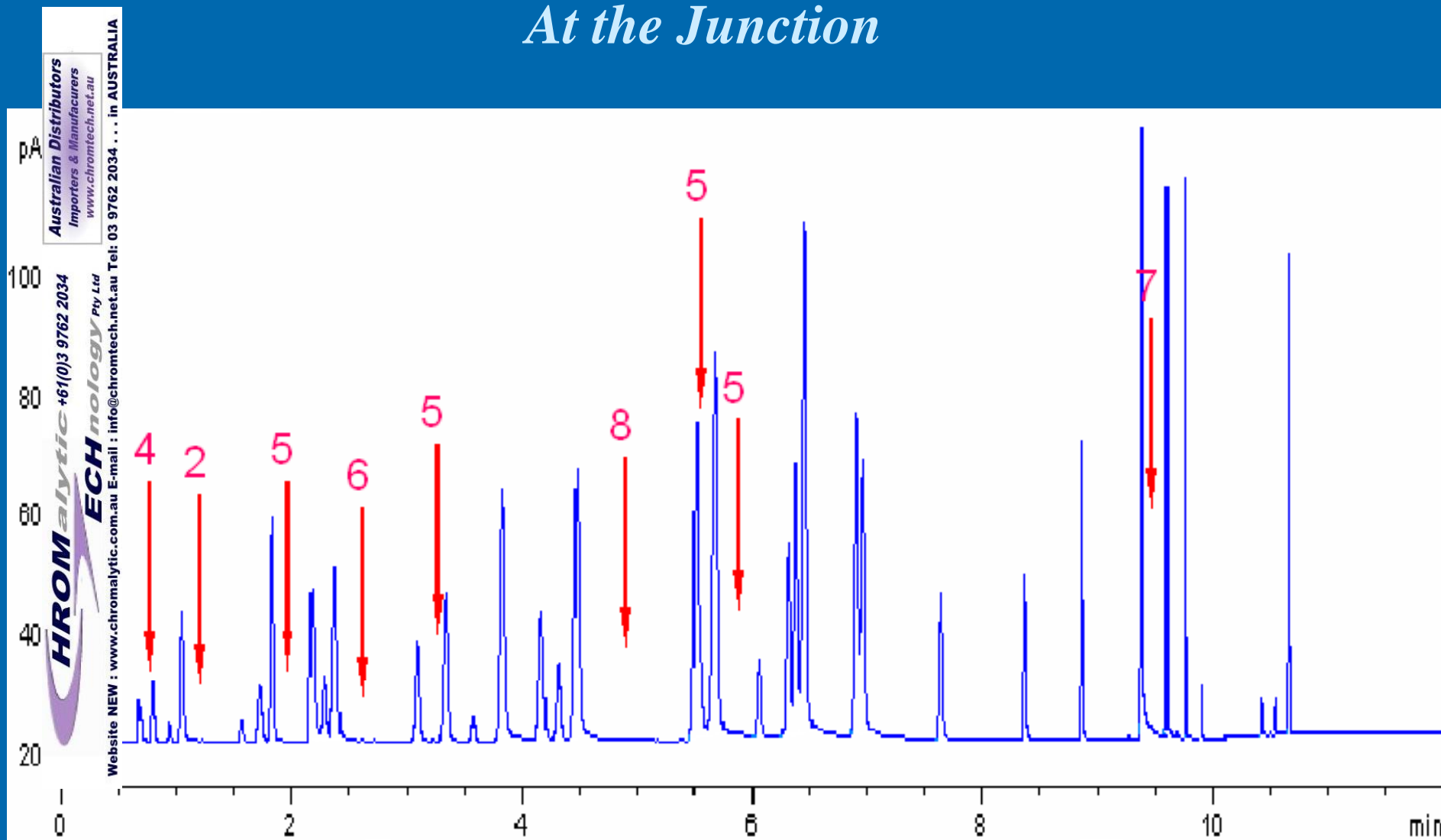
# Residual Solvents: Run Conditions

		<i>Standard Procedure</i>	<i>Fast Procedure</i>
 <b>HROMalytic</b> Pty Ltd Website NEW : <a href="http://www.chromalytic.com.au">www.chromalytic.com.au</a> E-mail : <a href="mailto:info@chromtech.net.au">info@chromtech.net.au</a> Tel: 03 9762 2034	<b>Analytical Columns</b>	<b>Stabilwax</b> 15m x 0.25mm, 0.5µm <b>Rtx-200</b> 30m x 0.25mm, 1µm	<b>Stabilwax</b> 15m x 0.25mm, 0.5µm <b>Rtx-200</b> 30m x 0.25mm, 1µm
	<b>Program</b>	40°C (6 min. hold) to 100°C at 4°C/min., to 220°C at 15°C/min., 5 min. hold	40°C (1 min. hold) to 65°C at 6°C/min., to 100°C at 12°C/min., to 250°C at 70°C/min., 1.8 min. hold
	<b>Column Flow</b>	1.5 mL/min. constant flow	2.5 mL/min. to 9.5 min. 3.5 mL/min. at 10 min.
	<b>Detector</b>	<b>230°C</b>	<b>230°C</b>
	<b>Injection</b>	0.2 µL HS, 200:1 split	0.2 µL HS, 200:1 split
	<b>Detectors</b>	<b>Dual FIDs @ 250°C</b>	<b>Dual FIDs @ 250°C</b>

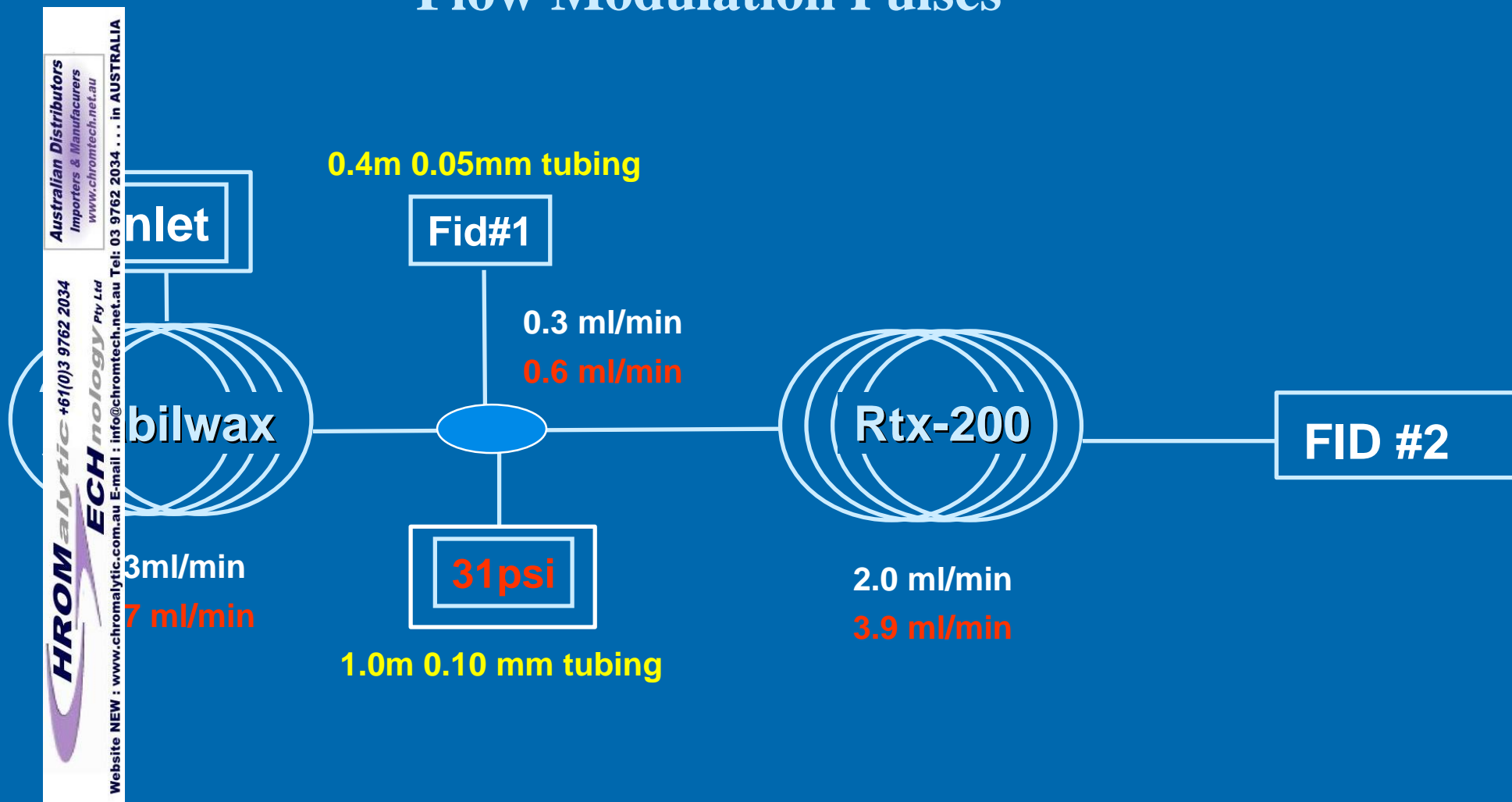
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# Class I & II OVIs: Total of 9 Pulses *At the Junction*



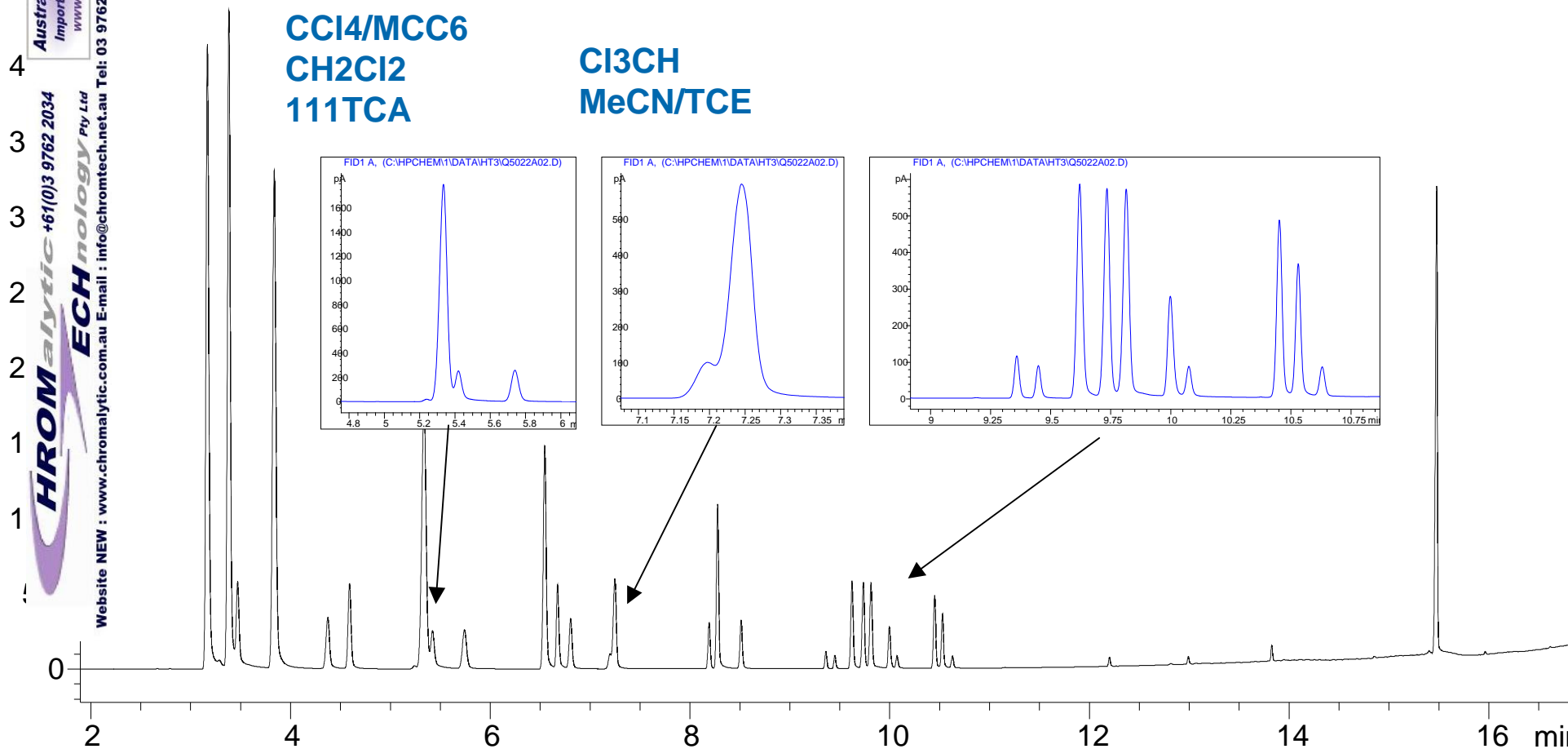
# Flow Modulation Pulses



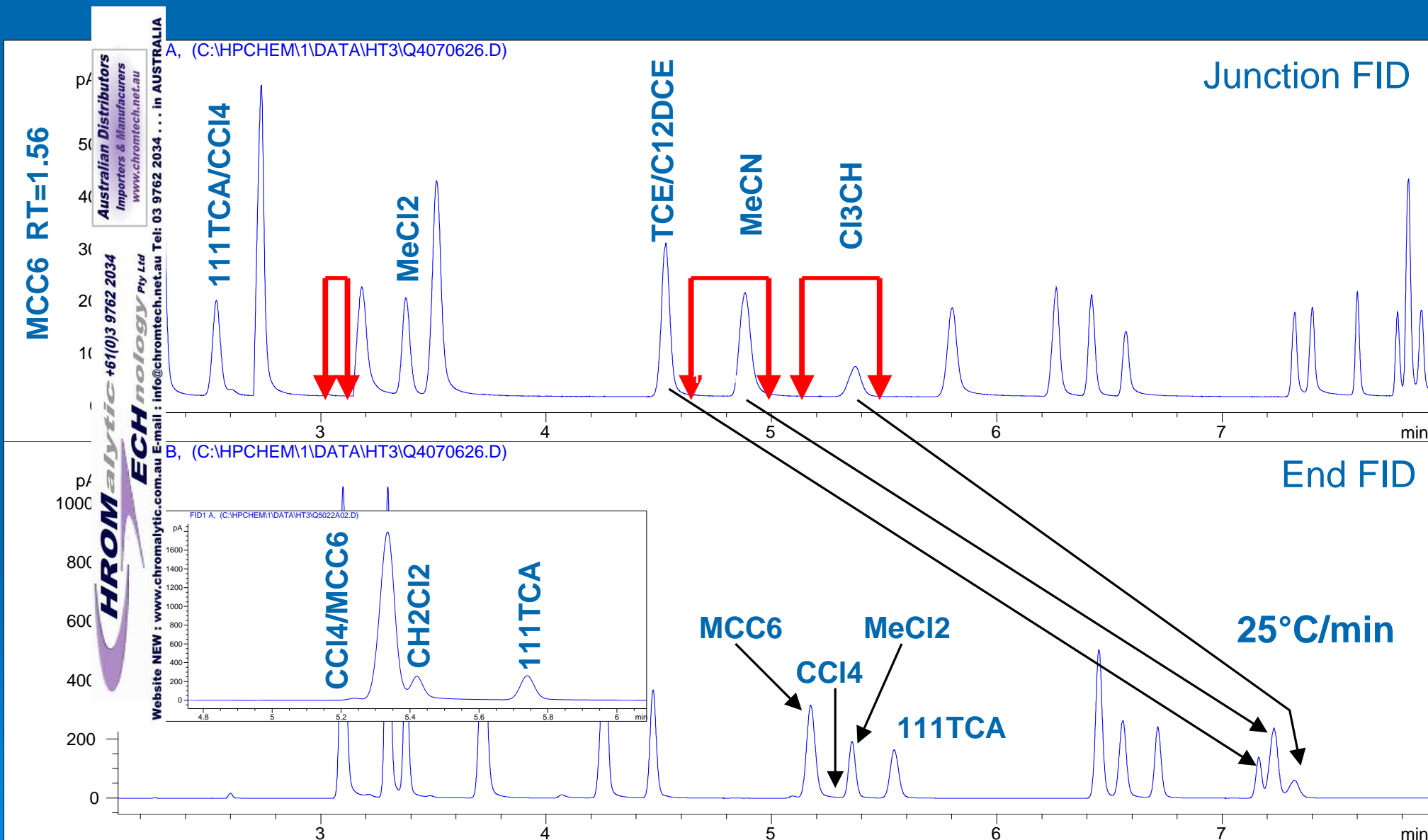


# Stabilwax 15m x 0.25mm x 0.5df Rtx-200 30m x 0.25mm x 1.0df Analysis without Pulses 2<sup>nd</sup> FID

D1 A, (C:\HPCHEM\1\DATA\HT3\Q5022A02.D)



# Three Flow Modulation Pulses



# Teledyne Tekmar HT7000

Platen Temperature:	140°C
Sample Equilibration Time:	5 minutes
Washing Time:	10 minutes
Washing Power:	2
Temperature Stabilization Time:	1
Pressure Time:	0.2 minutes
Pressure Equilibrium:	0.3 minutes
Loop Fill Time:	0.1 minutes
Loop Equilibration Time:	0.05 minutes
Injection Time:	1.0 minutes
Loop/Line Temperature:	250°C
Vial Size:	22ml high temperature vials
Sample Loop Size:	Silcosteel 1ml Standard Size.
Static Vial Pressure:	3.5 PSI Helium
Pressurization:	8 PSI Helium
Variable Injection Pressure (VIPR)	5 PSI Helium
Concentration:	200ppm each component.
Solvent:	1,3-dimethyl-2-imidazolidinone (DMI)
Interface:	plumbed through injection port 1:20 split

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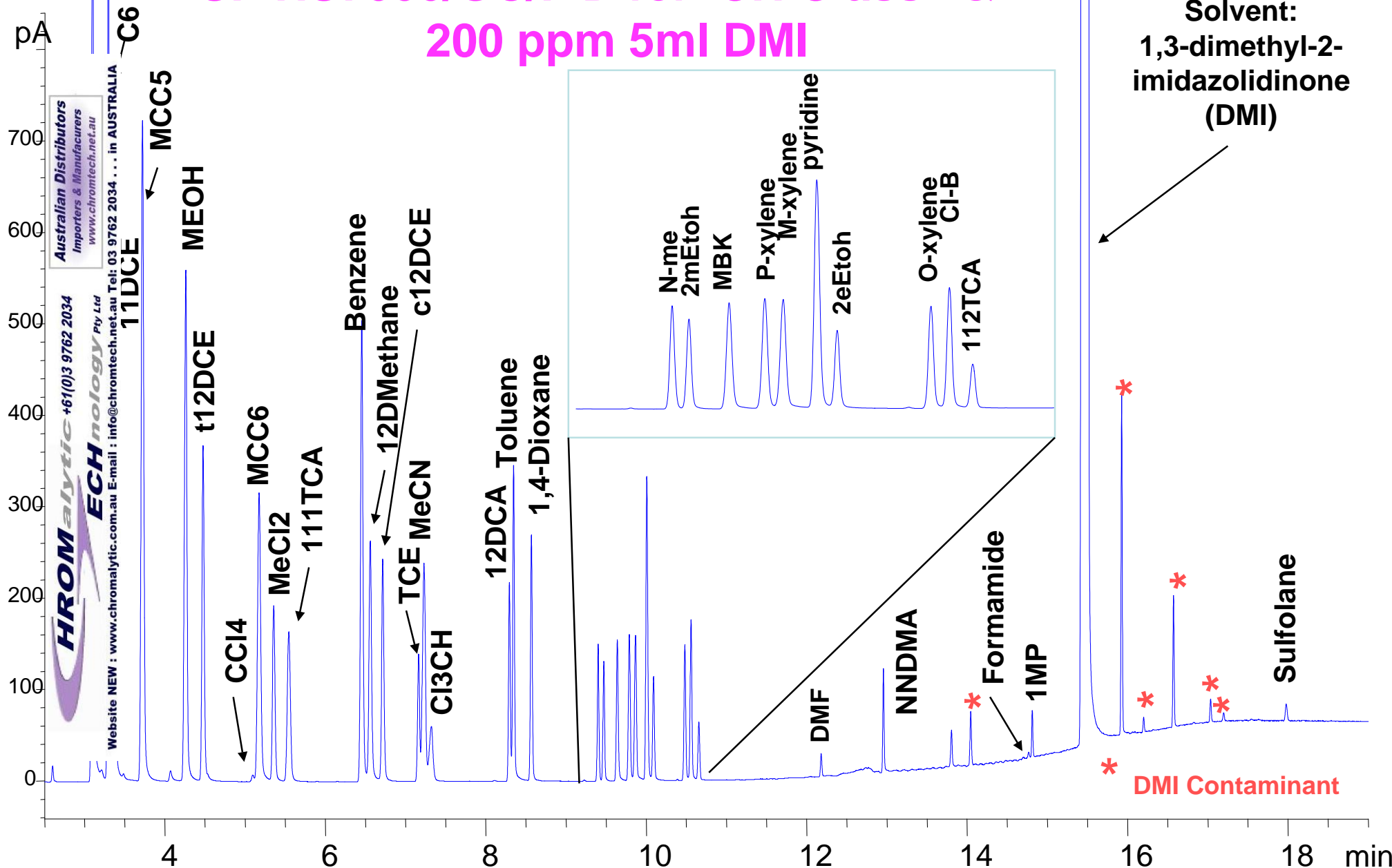
GC Agilent 6890  
Injection Port Temperature: 250°C  
Carrier gas: helium, constant flow  
Flow rate: 2.3 ml/min, 25.6psi @ 40°C.  
Oven temperature: 40°C (hold 2 min.) to 55°C @ 4°C/min. (no hold)  
to 110°C @ **25°C/min.** (hold 2 min.) to 250°C @  
25°C/min (hold 5 minutes)  
Total Runtime: 20.55 minutes  
Agilent Dual Flame Ionization Detectors

Reactor's Stop-Flow Unit Pulse Settings:  
Injection Port Connection: cool-on-column injector.  
Pressure: 31.0 PSI constant pressure  
Pulse:  
Valve Closed 0.00 minutes.

Valve Open	3.00 minutes
Valve Closed	3.15 minutes
Valve Open	4.65 minutes
Valve Closed	5.02 minutes
Valve Open	5.10 minutes
Valve Closed	5.40 minutes

# SF-HS7000/GC/FID for ICH Class I & II

## 200 ppm 5ml DMI



# Teledyne Tekmar HT3 HS/HS-Trap



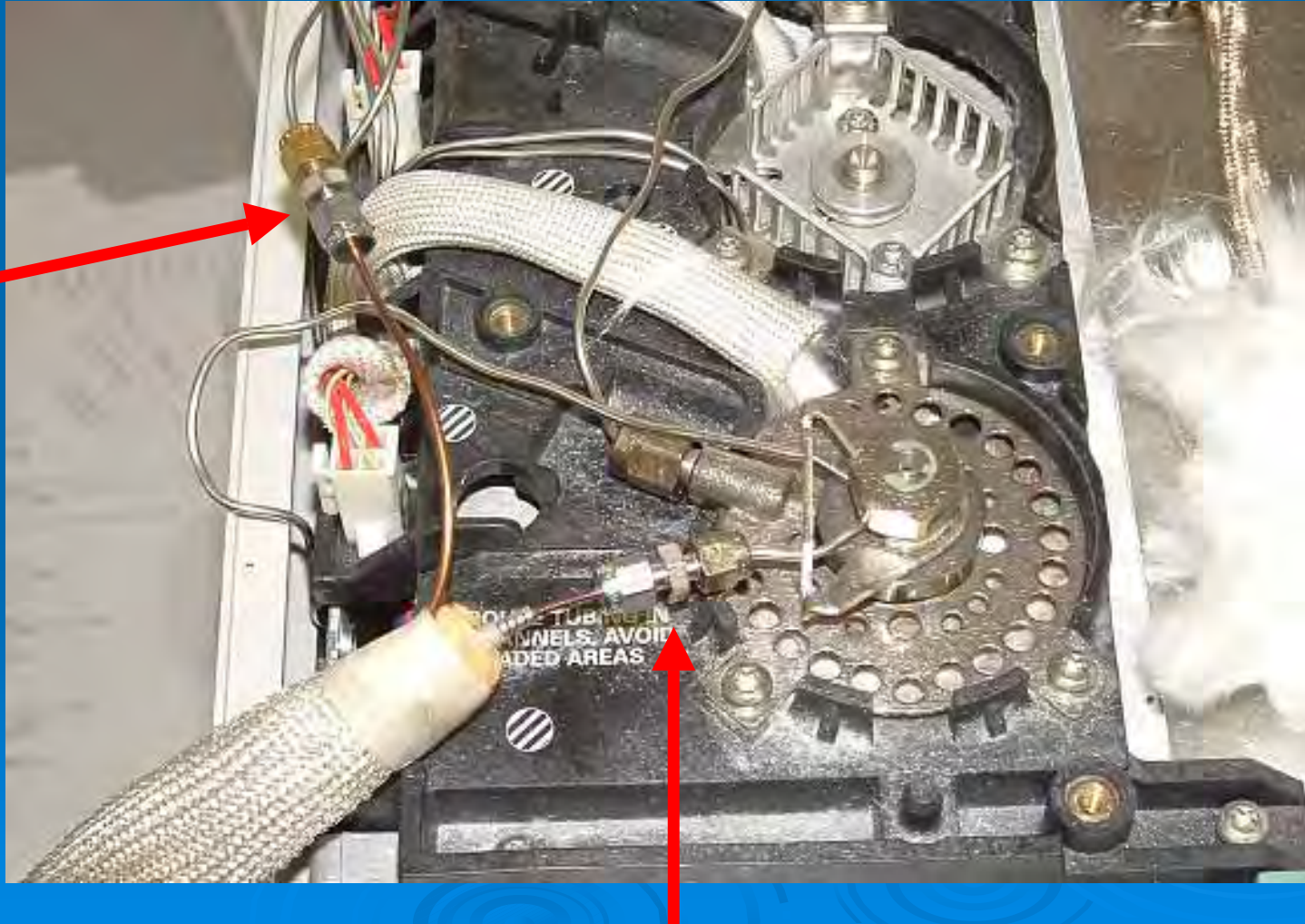
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# Instrument Setup

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# HT3 Conditions Using DMI

Constant Heat Time	ON
G.C. Cycle Time	23.00 min
Valve Oven Temp	150 C
Transfer Line Temp	150 C
Standby Flow Rate	50mL/min
Platen / Sample Temp	150 C
Platen Temp Equil. Time	0.10 min
Sample Equil. Time	1.00 min
Mixer	ON
Mixing Time	10.00 min
Mixing Level	Level 5
Mixer Stabilize Time	0.50 min
Pressure	8 PSIG
Pressure Time	2.00 min
Pressure Equil. Time	0.50 min
Loop Fill Pressure	5 PSIG
Loop Fill Time	2.00 min
Loop Fill Equil. Time	0.50 min
Inject Time	1.00 min



# Class I & II Residual Solvents

Peak #	Compound	Peak #	Compound
1	2-methylpentane	19	1,2-dichloroethane (1,2-DCA)
2	hexane	20	2-hexanone (MBK)
3	methyl cyclopentane	21	p-xylene
4	1,1-dichloroethene (1,1-DCE)	22	m-xylene
5	methyl cyclohexane	23	nitromethane
6	<i>trans</i> -1,2-dichloroethene	24	2-methoxyethanol
7	carbon tetrachloride (CCl <sub>4</sub> )	25	pyridine
8	1,1,1-trichloroethane (1,1,1-TCA)	26	o-xylene
9	methanol	27	chlorobenzene
10	1,2-dimethoxyethane	28	2-ethoxyethanol
11	methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	29	1,1,2-trichloroethane (1,1,2-TCA)
12	benzene	30	dimethyl formamide (DMF)
13	<i>cis</i> -1,2-dichloroethene	31	N,N-dimethylacetamide (DMA)
14	trichloroethene (TCE)	32	1,2,3,4-tetrahydronaphthalene (THN)
15	acetonitrile (MeCN)	33	ethylene glycol (EG)
16	chloroform	34	1-methyl-2-pyrrolidinone (1-MP)
17	toluene	35	formamide
18	1,4-dioxane	36	sulfolone

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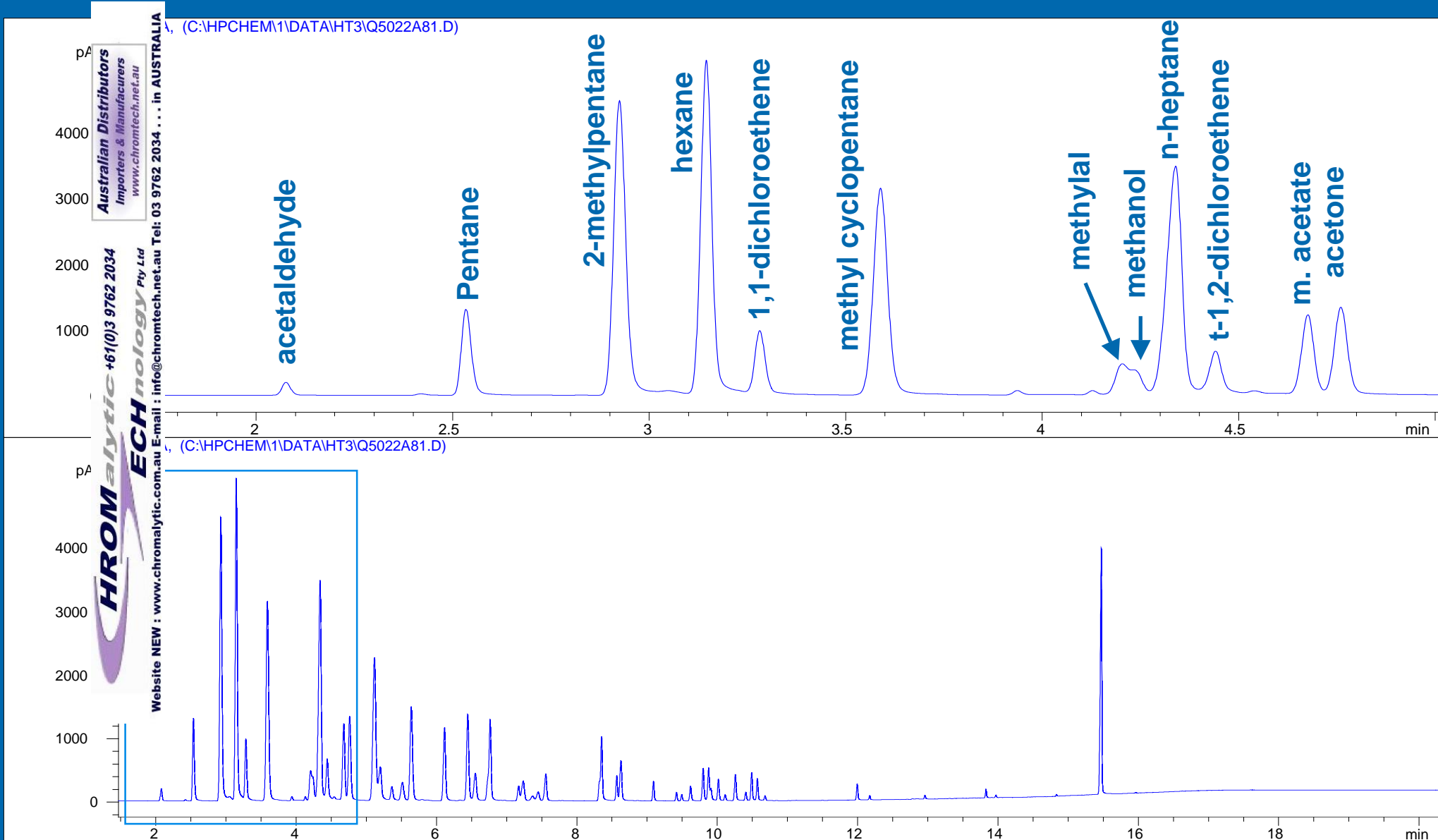
# Class III Added Residual Solvents



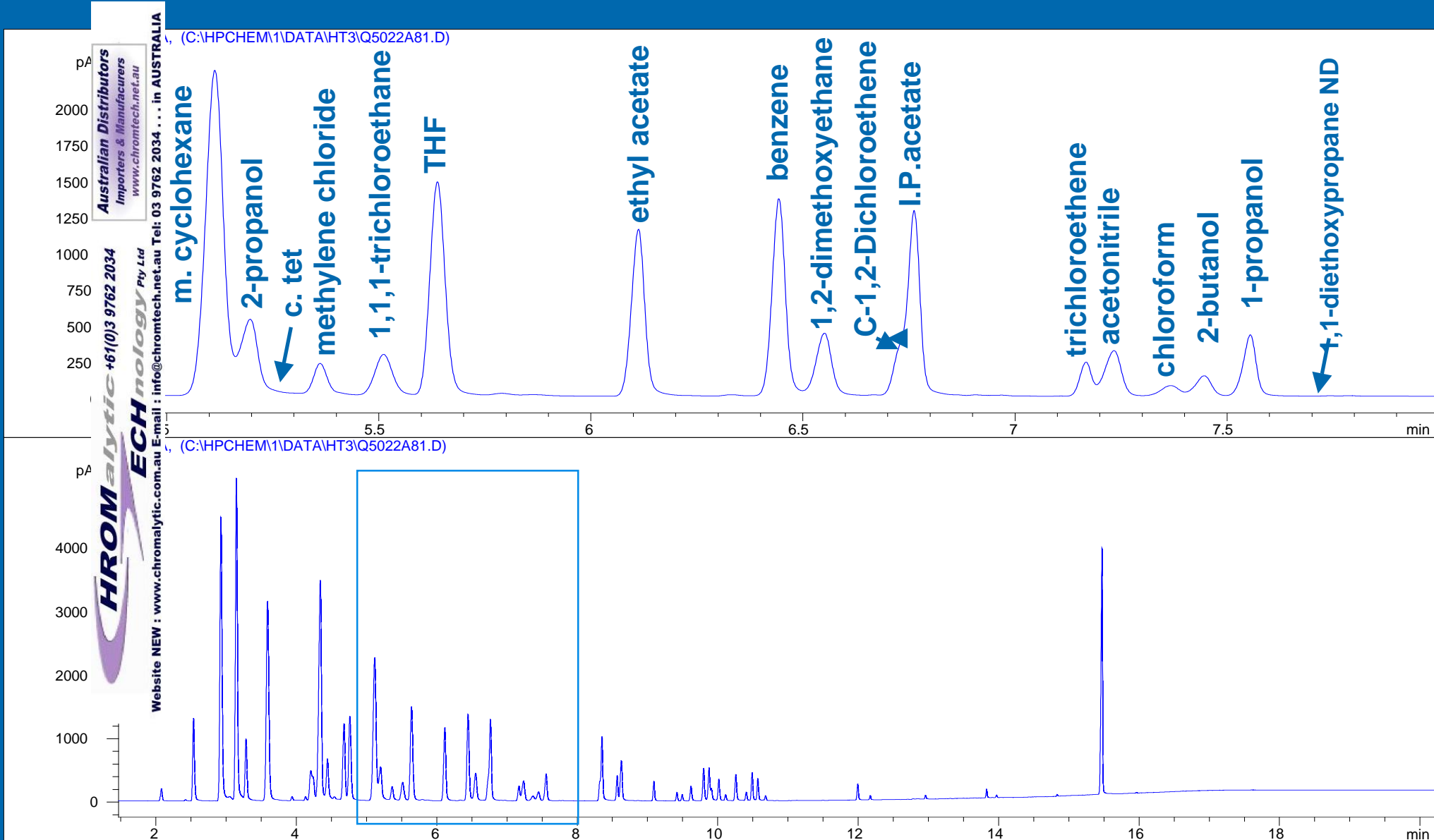
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<u>compound</u>	<u>class</u>
pentane	3
methylal	4
pentane	3
n-heptane (C7)	3
methyl acetate	3
acetone	3
2-propanol	3
tetrahydrofuran	3
ethyl acetate	3
isopropyl acetate	3
2-butanol	3
1-propanol	3
1,1-diethoxypropane	4
hexanone (MIBK)	3
1-butanol	3
isoamyl alcohol	3
isoamyl acetate	s
1-pentanol	3
anisole	3
dimethyl sulfoxide	3

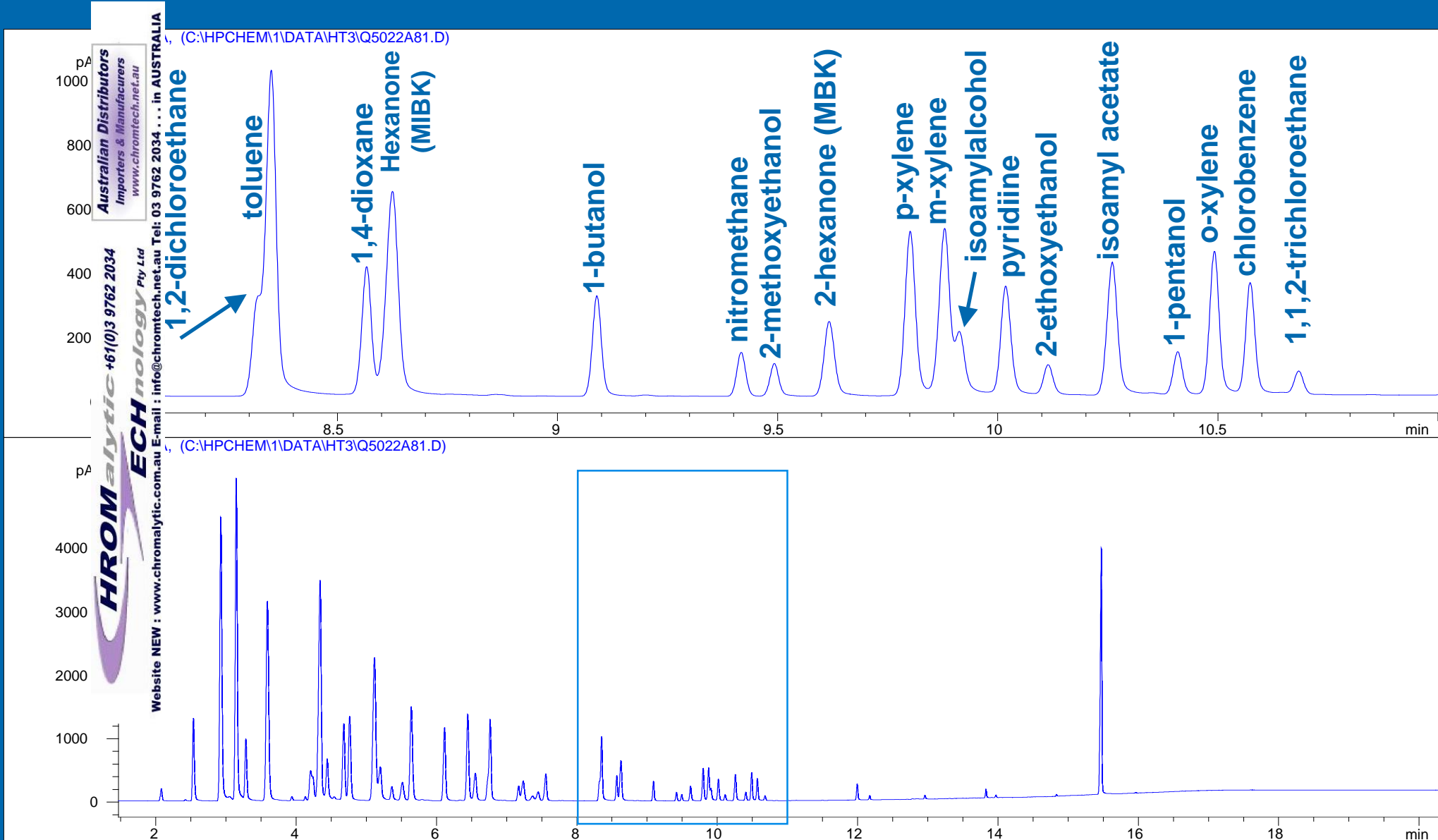
# Class I,II,III 2<sup>nd</sup> FID by HS



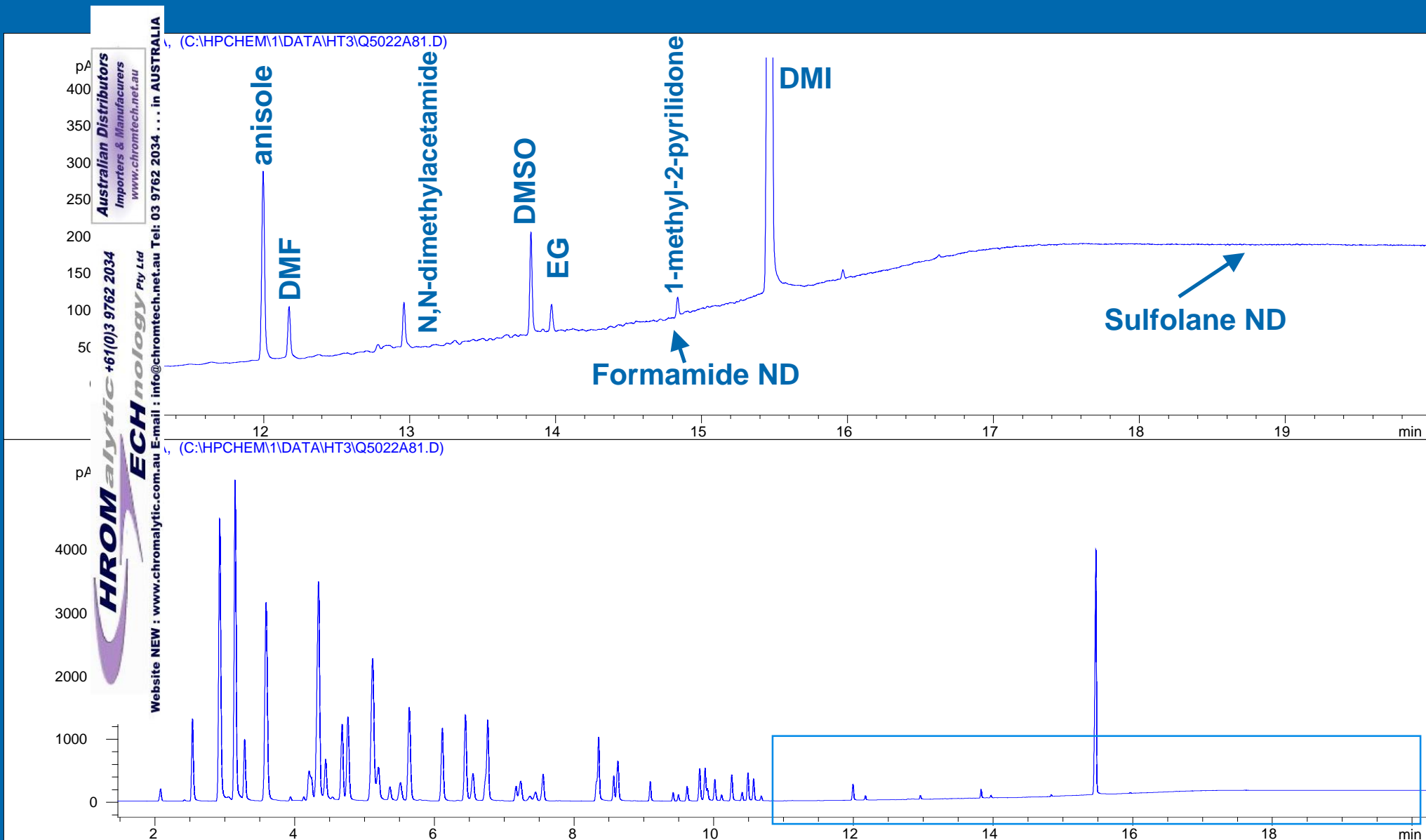
# Class I,II,III 2<sup>nd</sup> FID by HS



# Class I,II,III 2<sup>nd</sup> FID by HS



# Class I,II,III 2<sup>nd</sup> FID by HS (spiked @ 400ppm)



# Stabilwax / Rtx-200 Unresolved

## Under Current Conditions

- methylal (s) / methanol (II)
- n-heptane (III) / isooctane (s)
- t-1,2-DCE (II) / ethyl formate (III)
- ethanol (III) / methyl cyclohexane (II)
- 2-butanone (III) / 1,2-dimethoxyethane (II)
- isobutyl acetate (III) / hexanone (III)
- 1-pentanol (III) / isopropylbenzene (III)
- c-1,2-dichloroethene (II) / isopropyl acetate (III)

# Summary of Stop-Flow GC

- Ability to “Tune” the Selectivity
- Flexibility
  - Standard dimension columns
  - Can vary the pulse sequences
- Significant Improvements in Analysis Times Possible
  - Fast oven programs, high flow rates



# Conclusions

- continue evaluation of current phases
- continue work on a new stationary phases
  - Using computer modeling
  - Goal: resolve Class I, II, III, other solvents.
- continue with Stop-Flow technology

Special Thanks to Ed  
ce, Eric Heggs,  
an Wallace & Terry  
fers of Teledyne  
kmar for their  
sistance in setup  
d operation of the  
3 Headspace unit.

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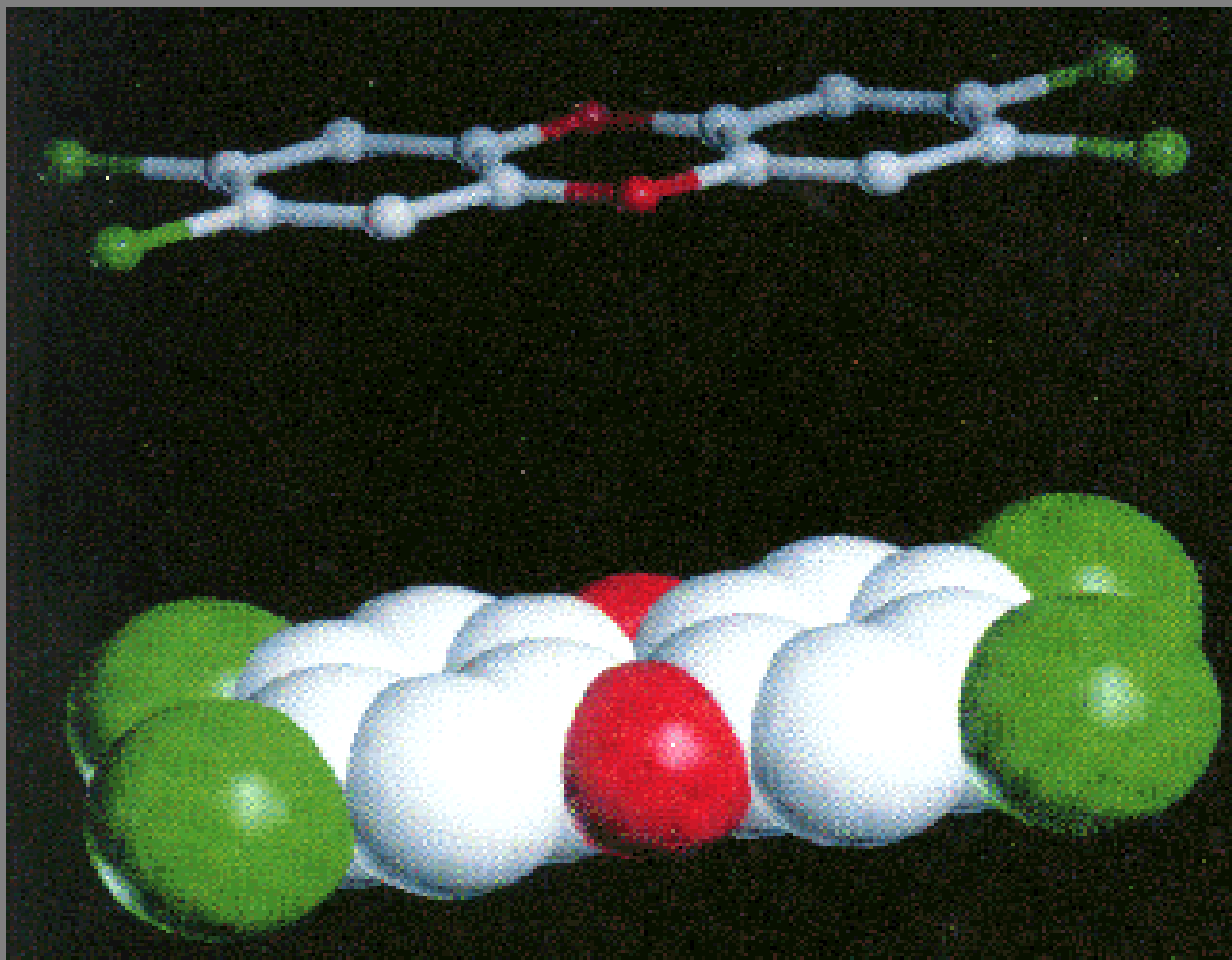
# Improved Separation and Quantification of Dioxin and Furan Congeners Using an Application-Specific Capillary Gas Chromatographic Column and GC-HRMS

Frank Dorman, Shawn Reese, Gary Stidsen  
Restek Corporation, Bellefonte, Pennsylvania

Jack Cochran  
LECO Corporation, Las Vegas, Nevada

Eric Reiner, Karen MacPherson, Terry Kolic  
Ministry of Environment, Etobicoke, Ontario

# Analysis of Dioxins and Furans



<http://dioxins-r-us.ucdavis.edu/TCDD>

# History

## GC Analytical Methods

All isomers/congeners can be separated from each other with a minimum of two columns (Ryan, J., 1991) and GC HRMS

**Typically used:** 60-M GC column, 5% phenyl liquid phase, separates many congeners, but not with complete resolution

HOWEVER..

Confirmation still required, generally with “high-cyano” liquid phases

ex. for 2,3,7,8-TCDF Method 1613 suggests a 225-phase

# Dioxin and Furan Analysis

## Dual column method

- Usually 5% diphenyl column and a high-cyano column (eg Rtx-225)
- Cyano columns have poorer lifetimes and lower maximum operating temperatures
- 5% diphenyl phases do not have the selectivity to accurately quantitate most samples
  - USEPA requires 2,3,7,8-tcdf to be confirmed on a X-225

Desirable to have both columns in the same oven, and to improve the separation of the “5”, or **employ a single column which achieves the necessary separation**

# PCDD and PCDF Target List

# of Chlorine	#Dioxins	#Furans
tetra	22(1)	38(1)
penta	14(1)	28(2)
hexa	10(3)	16(4)
hepta	2(1)	4(2)
octa	1(1)	1(1)

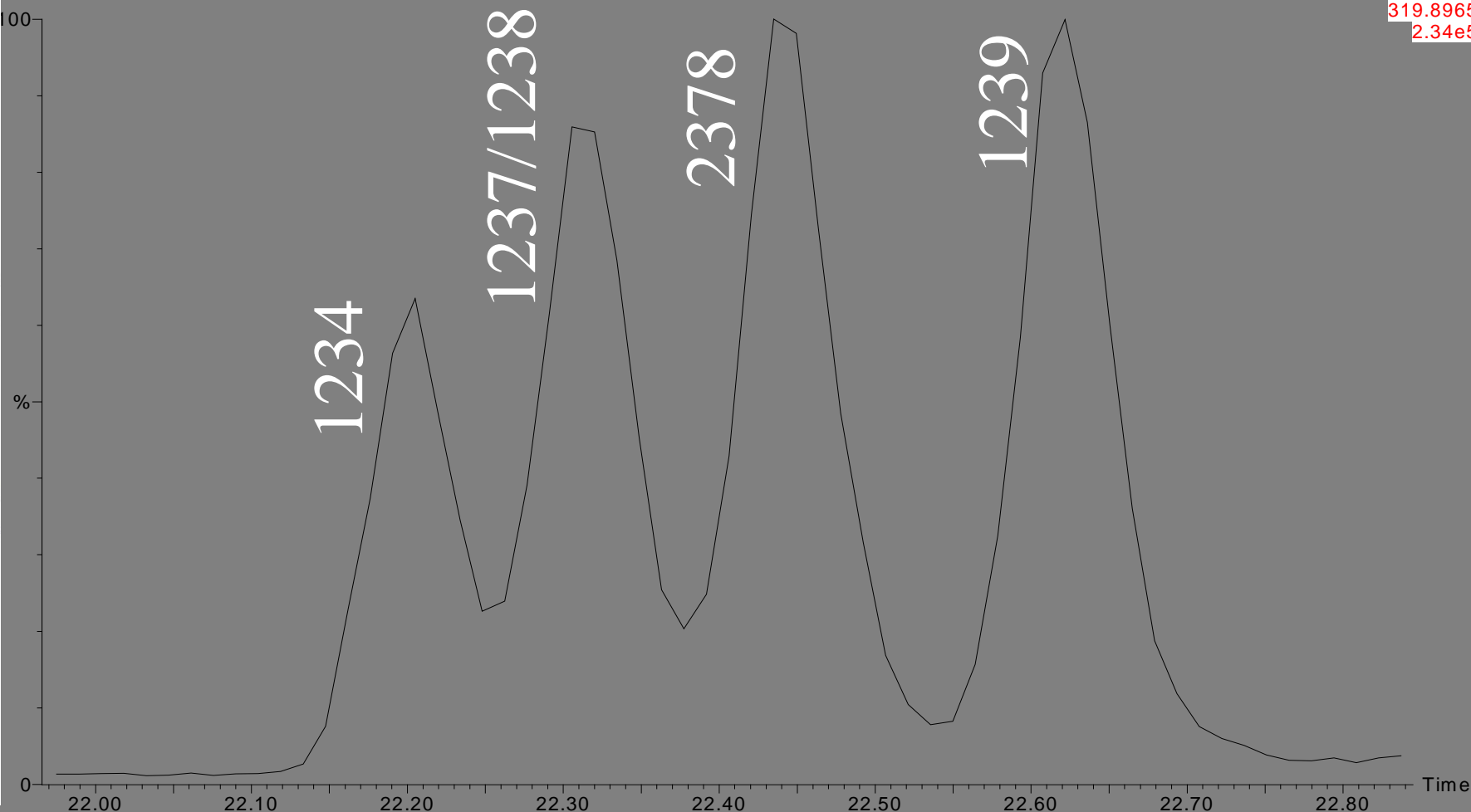
( ) numbers are 2,3,7,8-substituted congeners



# Tetra-dioxin resolution check standard on 5% diphenyl / 95% dimethyl stationary phase

ul21\_23

2: Voltage SIR 20 Channels EI+  
319.8965  
2.34e5

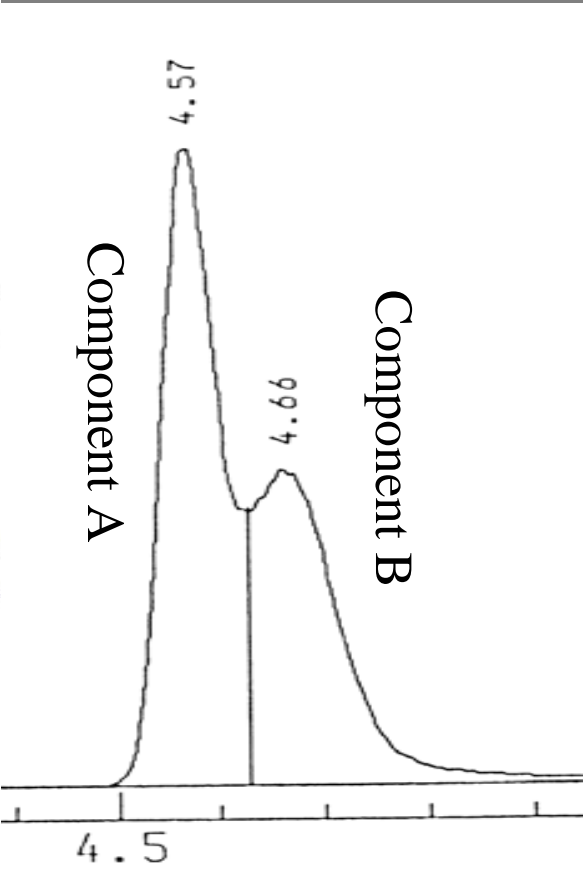


60-M X 0.25 mm i.d. X 0.25 um d.f.



# How Resolution Affects Quantitation

## Quantification of 20 ng/uL Reference Standard (Results Based on Multi-level/Multi-component Calibration):



<i>Component A &amp; B</i>	<i>Rep 1</i>	<i>19.85</i>	<i>18.48</i>
	<i>Rep 2</i>	<i>19.29</i>	<i>18.48</i>
	<i>Rep 3</i>	<i>19.36</i>	<i>18.52</i>
<i>Component A</i>	<i>Rep 1</i>	<i>21.48</i>	
	<i>Rep 2</i>	<i>20.79</i>	
	<i>Rep 3</i>	<i>20.95</i>	
<i>Component B</i>	<i>Rep 1</i>		<i>16.3</i>
	<i>Rep 2</i>		<i>16.46</i>
	<i>Rep 3</i>		<i>16.25</i>

# Achieving Analyte Separation

## Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha-1 / \alpha)$$

## Capacity Factor

$$k = t_R - t_0 / t_0$$

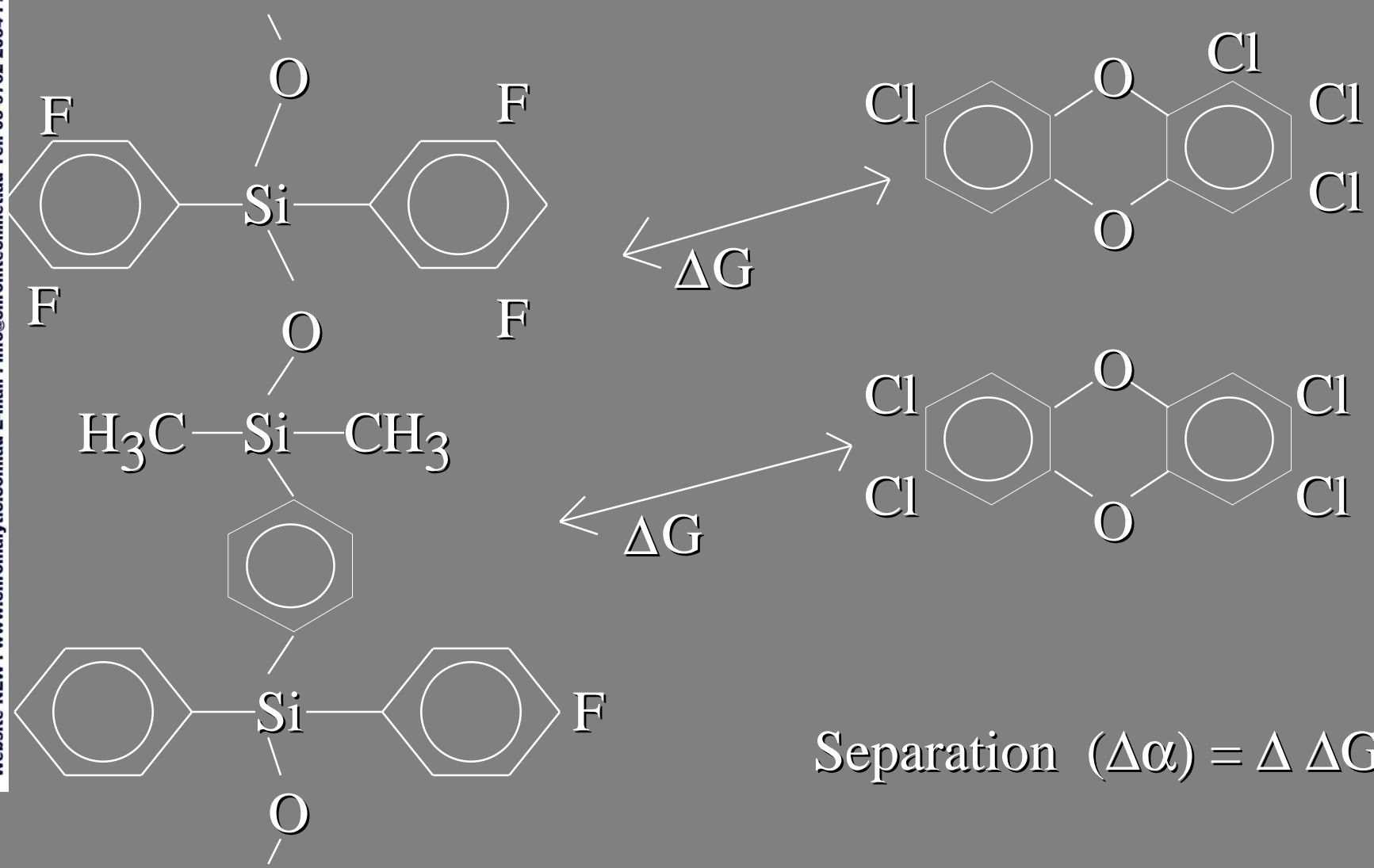
## Selectivity

$$\alpha = k_2 / k_1$$

## Thermodynamics:

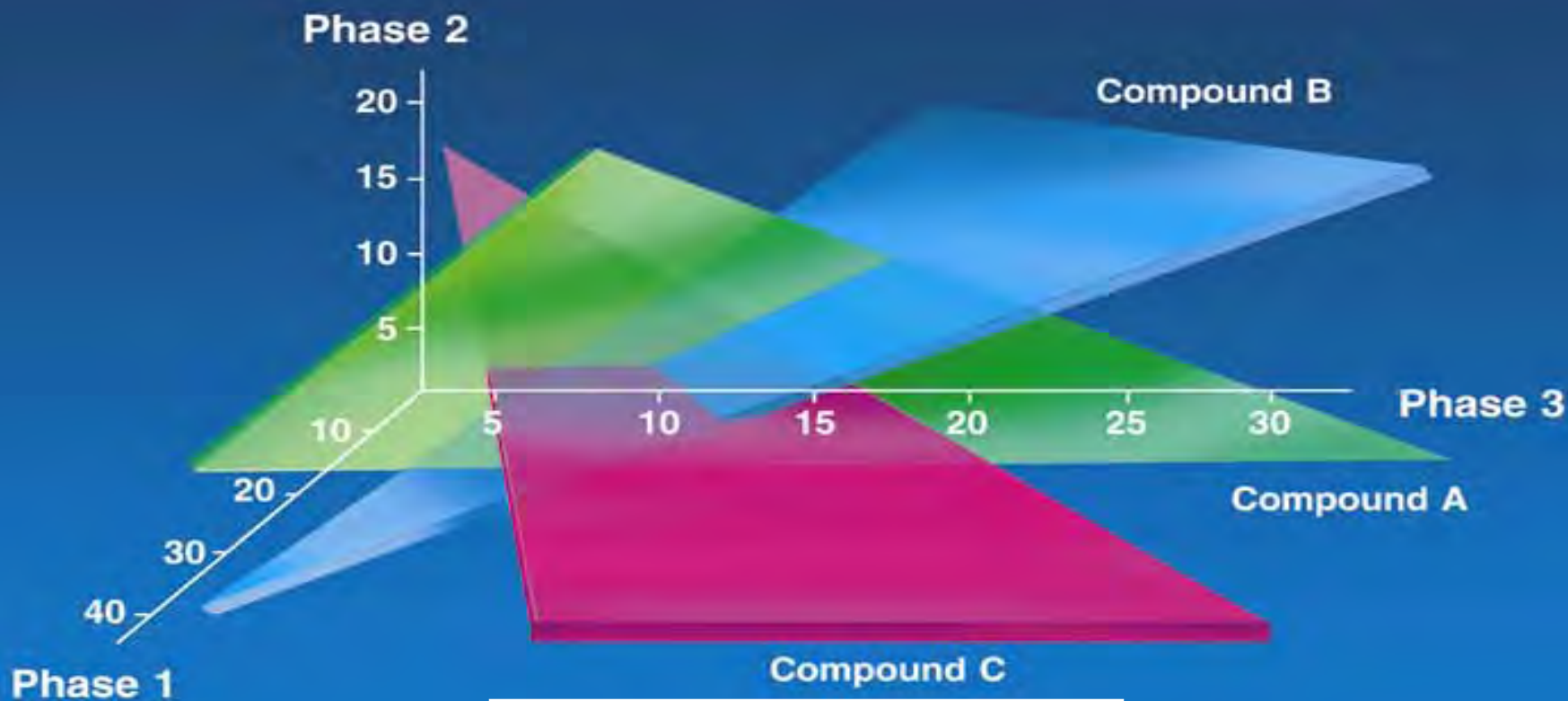
$$\Delta G = \Delta H - T\Delta S \quad \Delta G = - RT \ln K_D$$

# Modeling - Energies of Interaction

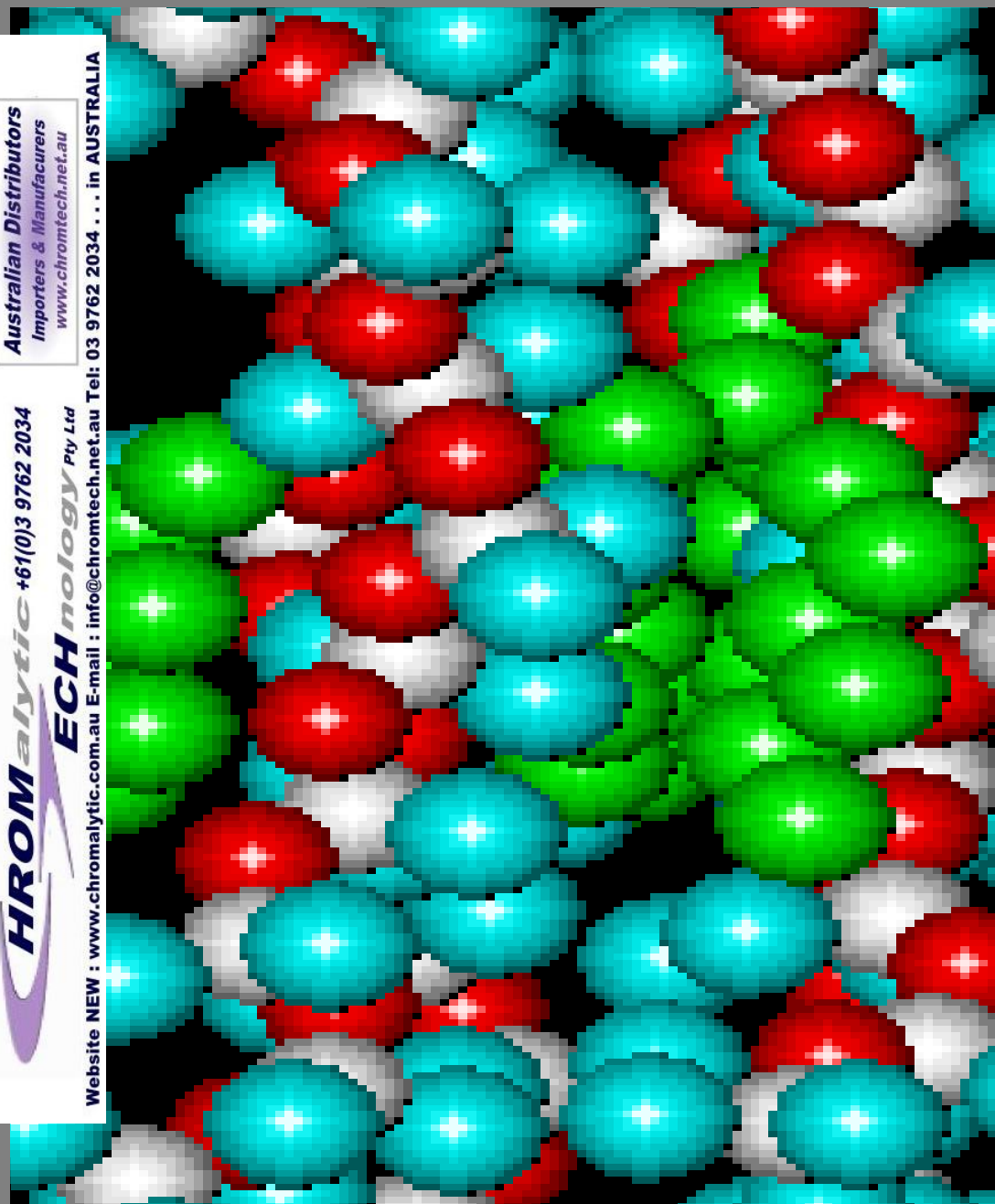


Separation ( $\Delta\alpha$ ) =  $\Delta \Delta G$

# 3-Space Selectivity Model for 3 Compounds



$$\text{Surface} = F \Delta H \Delta S$$



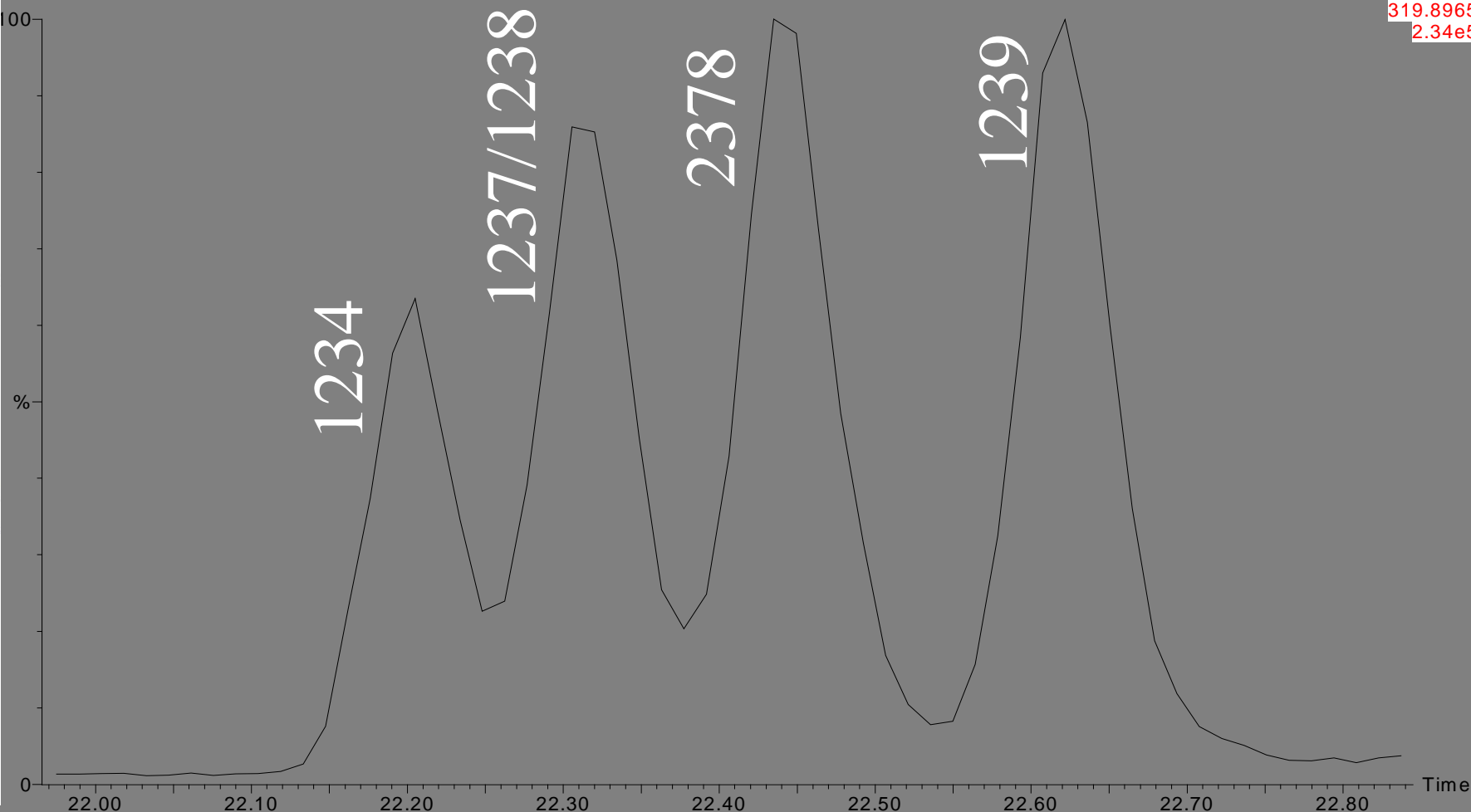
Example Result:  
Demeton-O on  
PDMS:

Observed  $\Delta G =$   
-1.14E4 J/mol  
Calculated  $\Delta G =$   
-1.13E4 J/mol

# Tetra-dioxin resolution check standard on 5% diphenyl / 95% dimethyl stationary phase

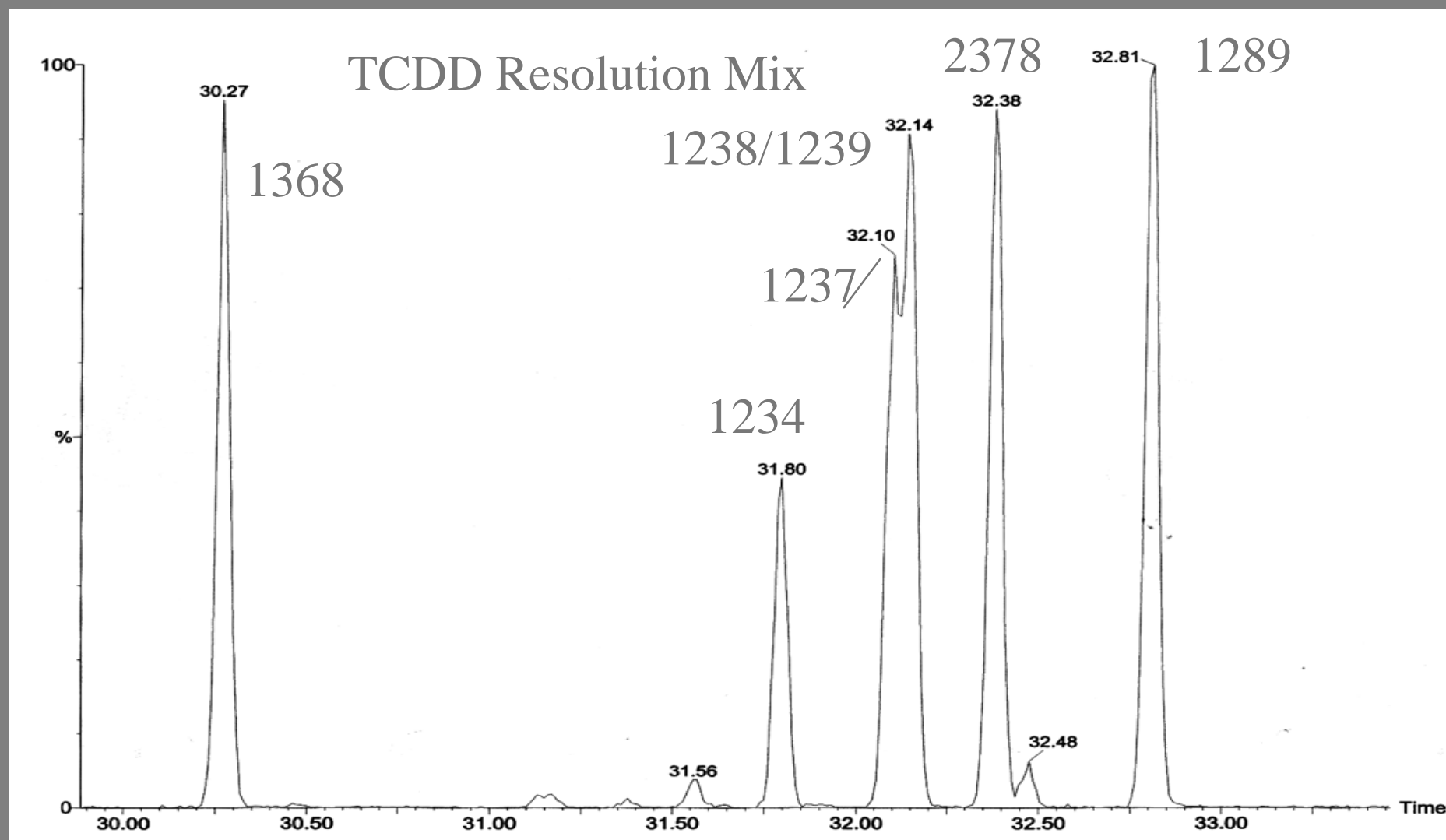
ul21\_23

2: Voltage SIR 20 Channels EI+  
319.8965  
2.34e5



60-M X 0.25 mm i.d. X 0.25 um d.f.

# Rtx-Dioxin2 Capillary GC Column



may06\_cs5

x4

# Dioxin Window

Voltage SIR 14 Channels EI-

321.893

1.90e

Voltage SIR 14 Channels EI-

355.854

2.77e

Voltage SIR 14 Channels EI-

389.815

2.02e

Voltage SIR 14 Channels EI-

423.776

6.58e

Voltage SIR 14 Channels EI-

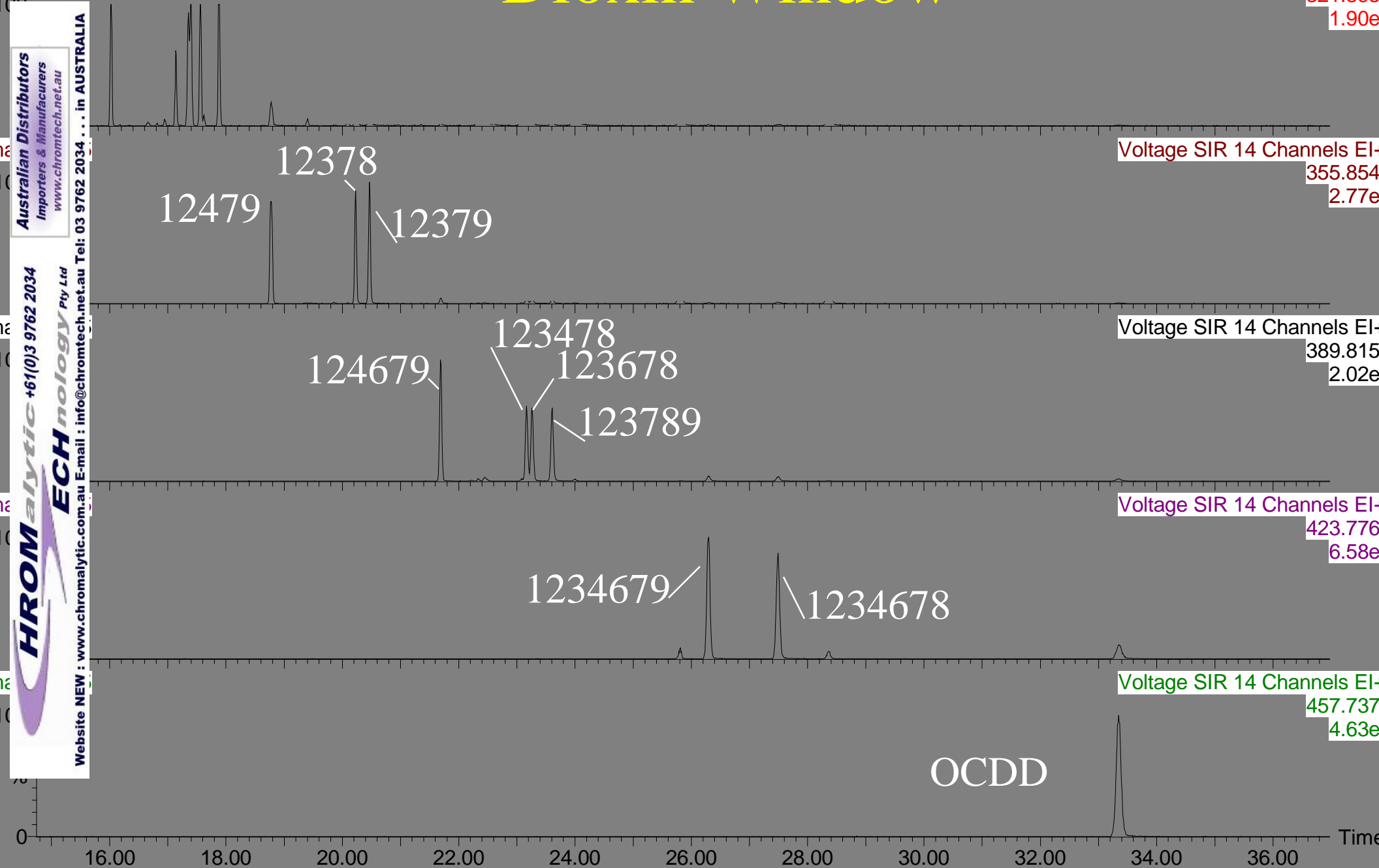
457.737

4.63e

OCDD

Time

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may06\_cs5

# Furan Window

Voltage SIR 14 Channels EI-  
303.901  
8.57e

Voltage SIR 14 Channels EI-  
341.856  
3.09e

Voltage SIR 14 Channels EI-  
375.817  
2.52e

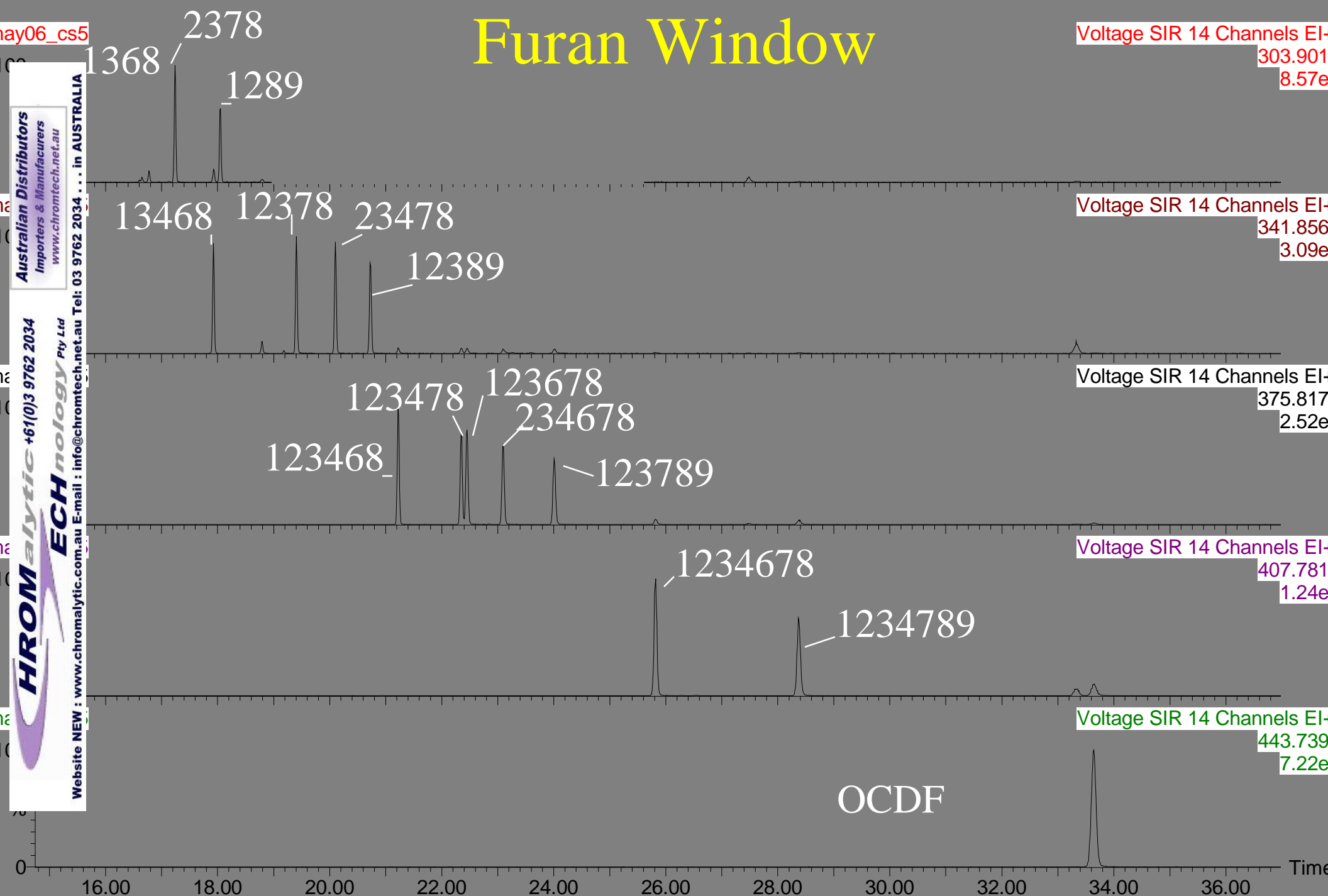
Voltage SIR 14 Channels EI-  
407.781  
1.24e

Voltage SIR 14 Channels EI-  
443.739  
7.22e

OCDF

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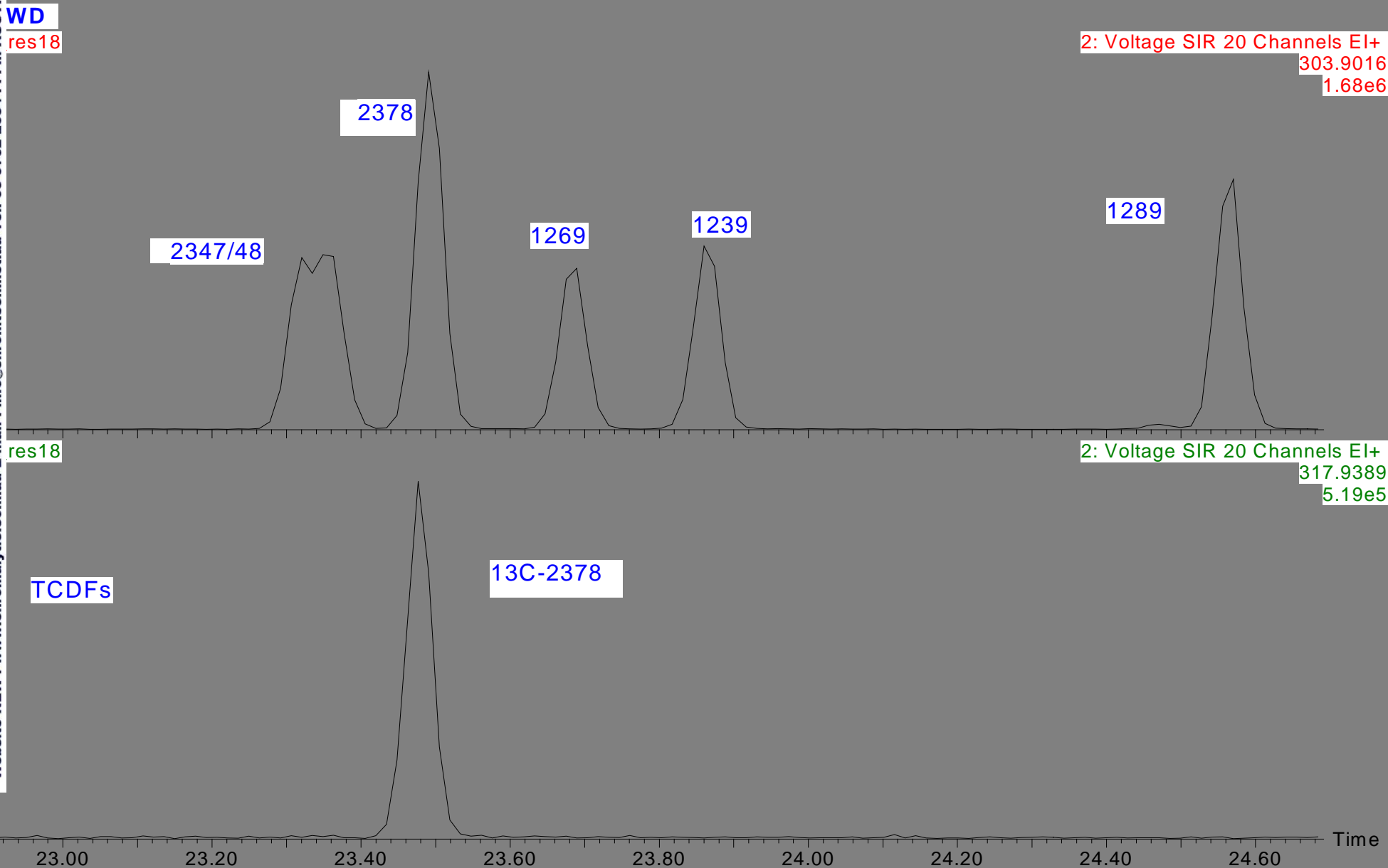


# GC program for RTX-Dioxin2<sup>®</sup>

	<b>60m x 0.25mm x 0.25µm</b>
Gas Flow - constant	1.5mL/min
Initial Temp.	130 °C - hold 1min
1st Temp. Ramp	40 °C/min to 200 °C, 0 hold
2nd Temp. Ramp	3.0 °C/min to 235 °C, 0 hold
3rd Temp. Ramp	5 °C /min to 300 °C, hold ~5-10min.
Total Run Time	~43 min

# TCDF Resolution on RTX-Dioxin2®

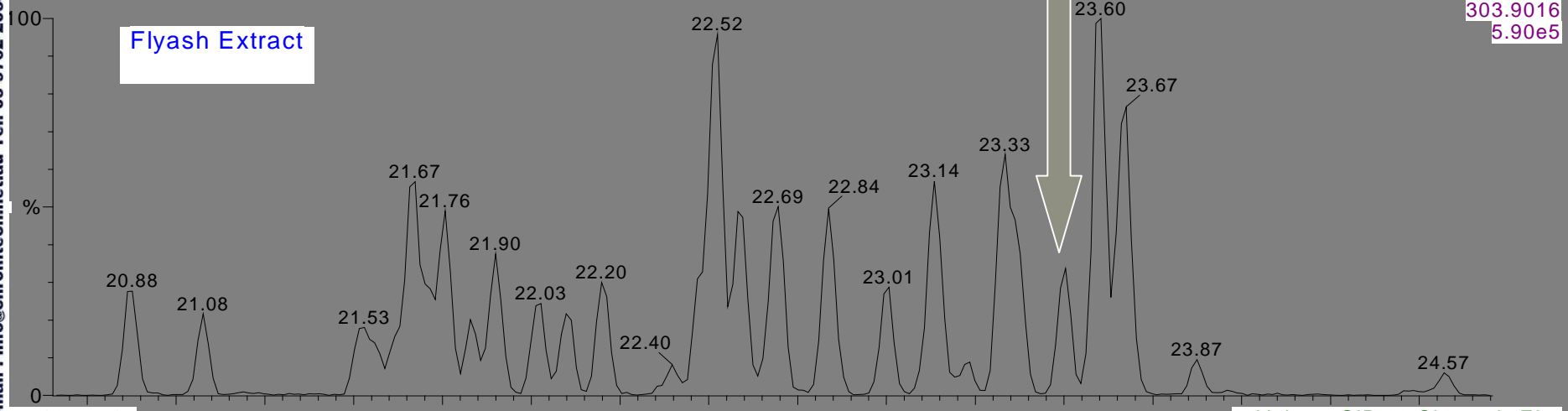
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# TICDF ion channel for flyash extract

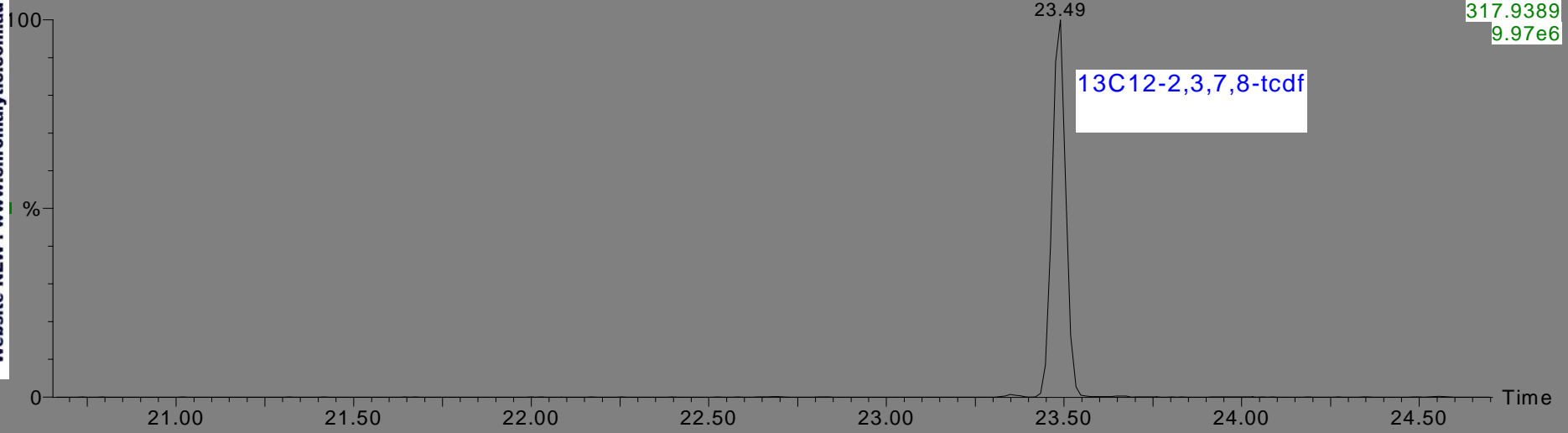
101863-0004  
 day12\_res15

Flyash Extract



2: Voltage SIR 20 Channels EI+  
 303.9016  
 5.90e5

day12\_res15



2: Voltage SIR 20 Channels EI+  
 317.9389  
 9.97e6

13C12-2,3,7,8-tcdf

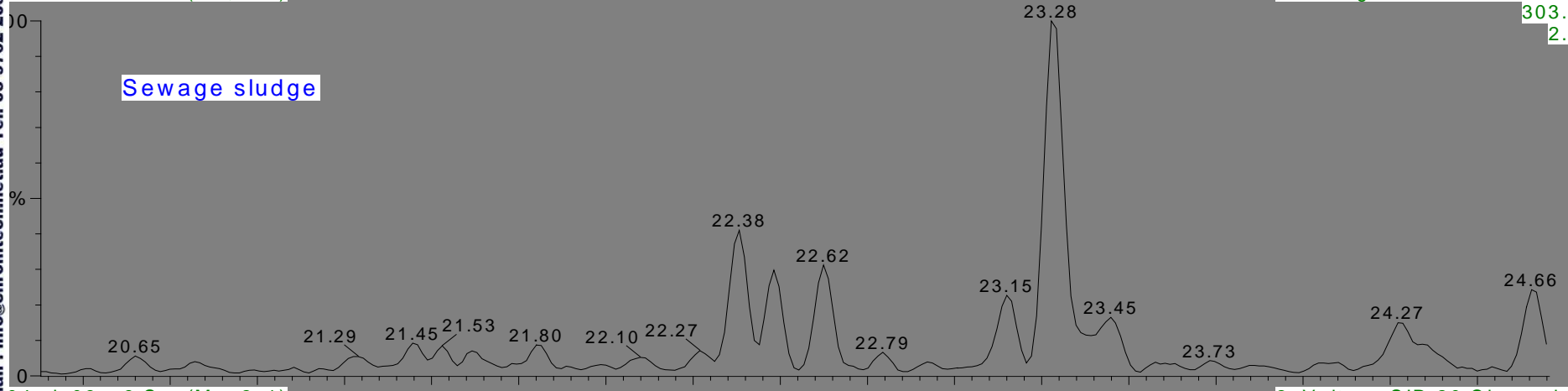
# TCDF ion channel for sewage sludge

1917-0004 .5/10

04\_dx03\_s3 Sm (Mn, 2x1)

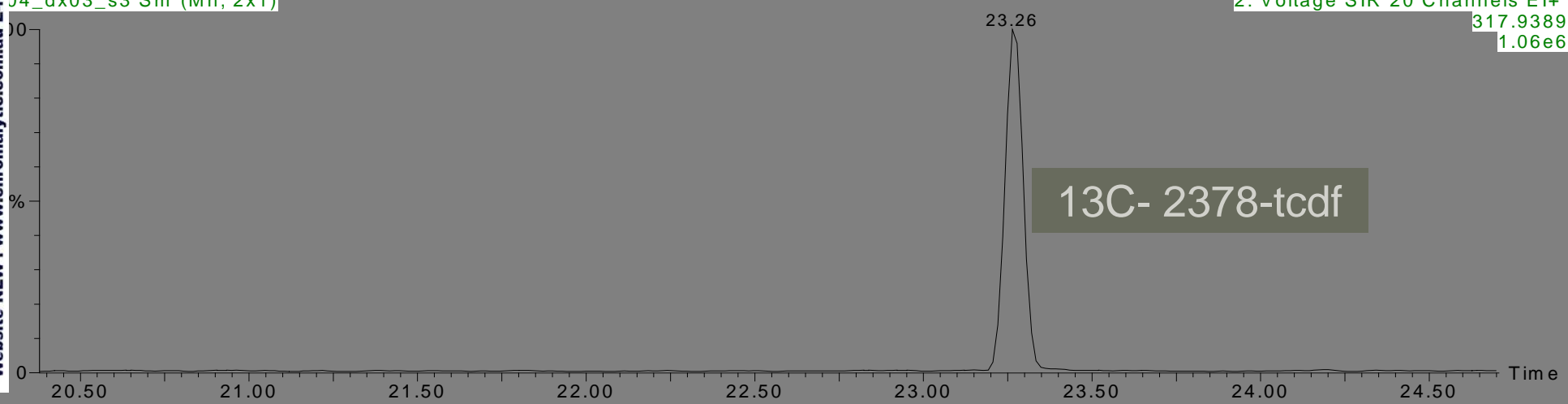
Sewage sludge

2: Voltage SIR 20 Channels EI+  
303.9016  
2.17e4



04\_dx03\_s3 Sm (Mn, 2x1)

2: Voltage SIR 20 Channels EI+  
317.9389  
1.06e6



13C- 2378-tcdf

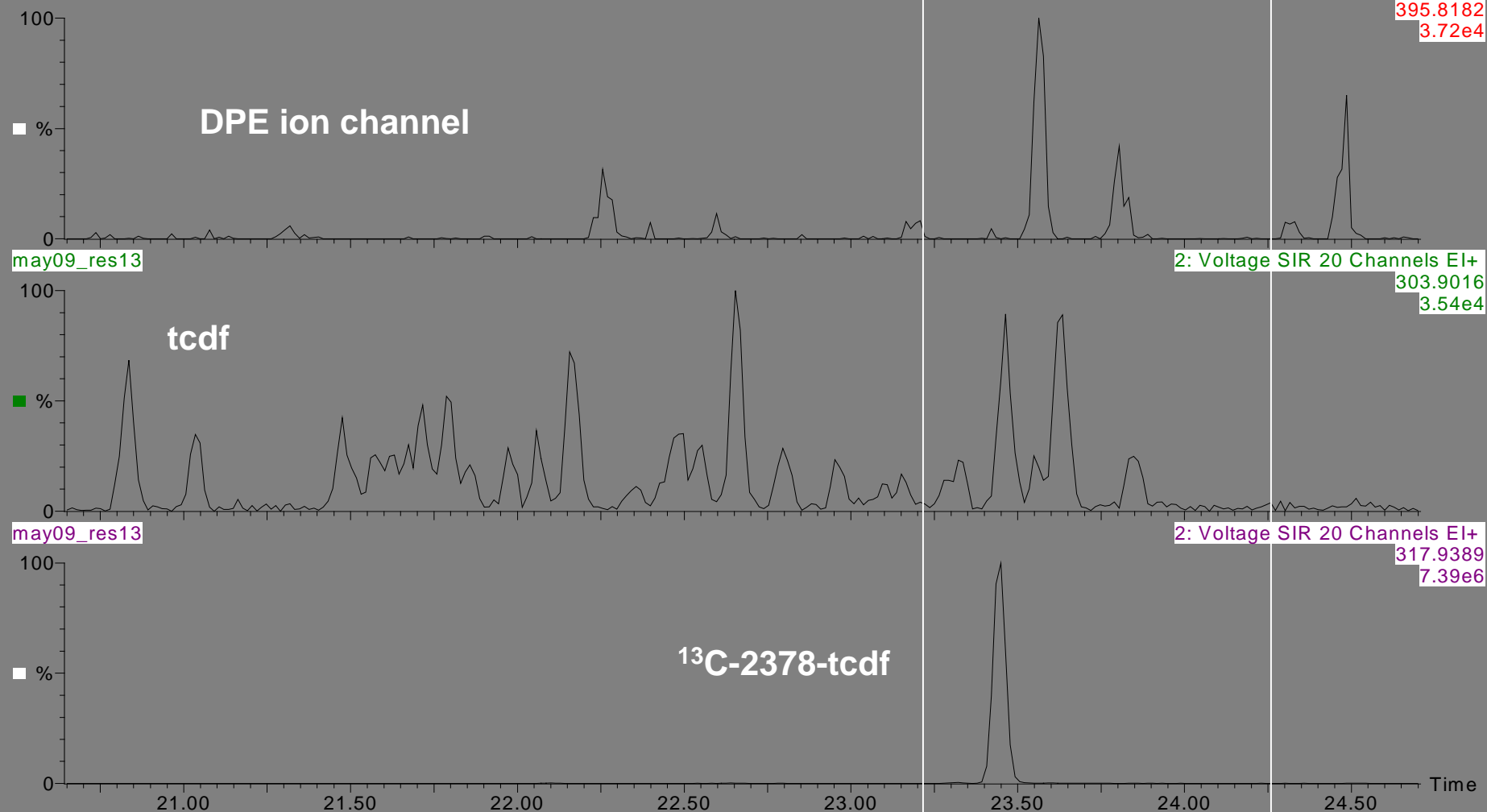
# Table I - 2,3,7,8-TCDF (pg/g)

	5% phenyl	X-225	Rtx-DIOXIN2 <sup>®</sup>	Certified Value
MS-01	78	46	47	52.5 ± 16
-2(DX-1)	88	n/a	37	89 (±44)
diment	37	19	19	23
ST 1974	4.7	n/a	3.3	-
wash	240	38	32	31
wash-2	250	40	32	28
ota-1	1	1.3	0.8	1.25
ota-2	4.3	4.3	2.2	1.45

# TCDF ion channel for Biota sample

c101775-0003

may09\_res13



# Potential resolution between DPEs and Furans

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01775-0003

ay09\_res13

DPE ion channel

2: Voltage SIR 20 Channels EI+  
395.8182  
3.72e4

ay09\_res13

tcdf

2: Voltage SIR 20 Channels EI+  
303.9016  
3.16e4

ay09\_res13

$^{13}\text{C}$ -2378-tcdf

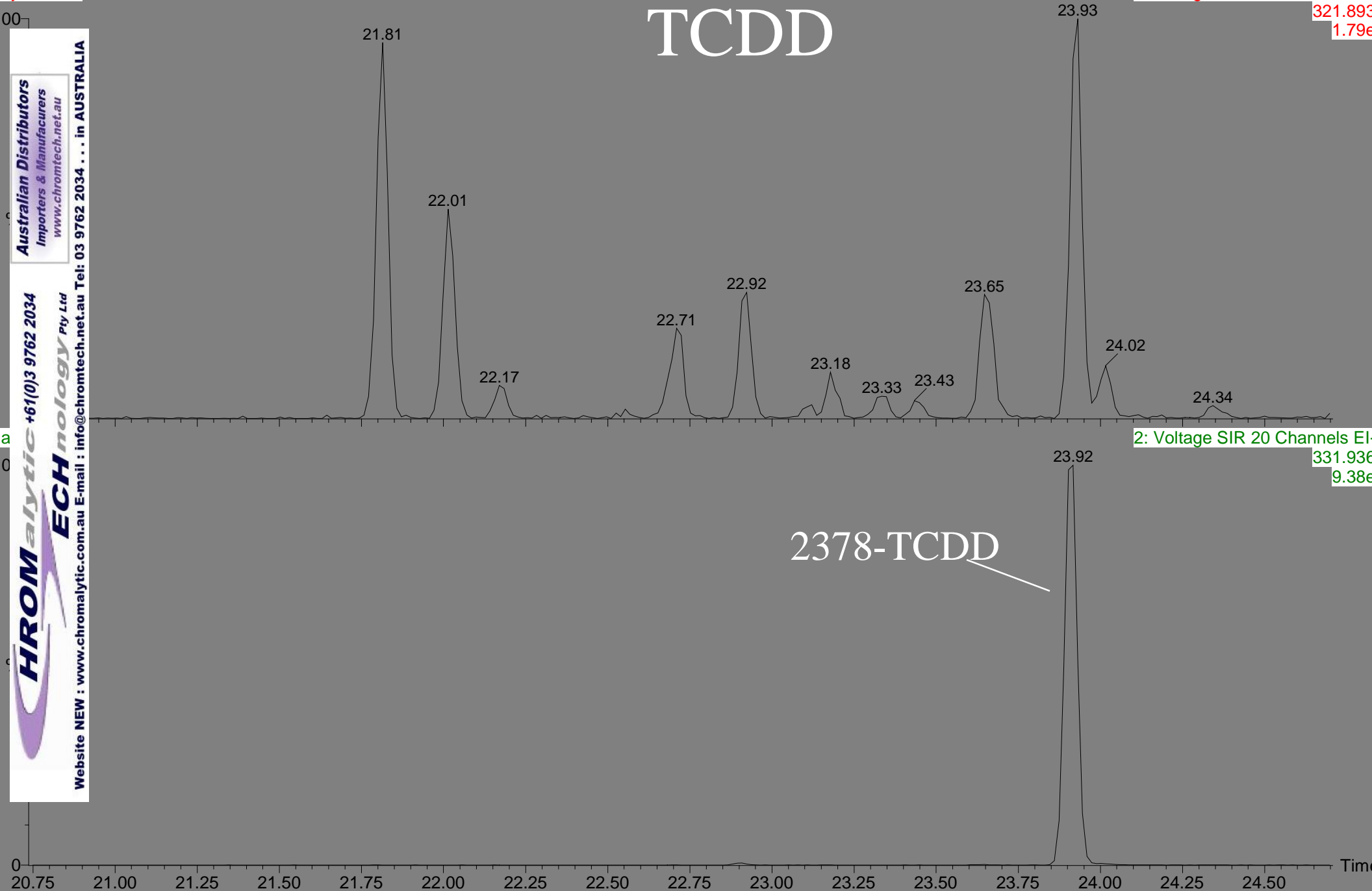
2: Voltage SIR 20 Channels EI+  
317.9389  
7.39e6

Time

23.10 23.20 23.30 23.40 23.50 23.60 23.70 23.80 23.90 24.00 24.10 24.20 24.30 24.40



TCDD



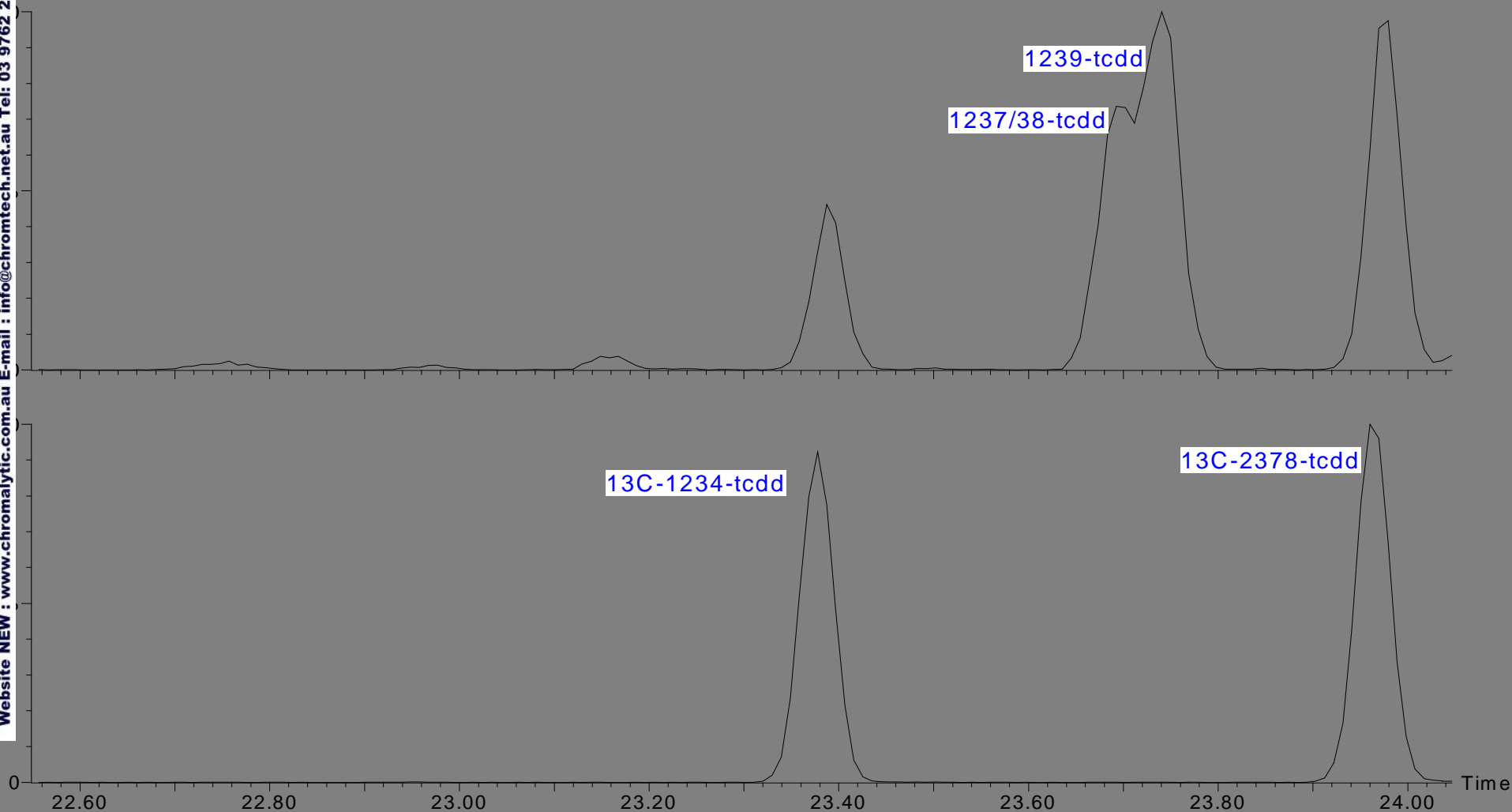
2378-TCDD

# 5% Phenyl Column Resolution Mix

## Rtx-DIOXIN2<sup>®</sup>

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# Table II - 2,3,7,8-TCDD (pg/g)

	5% phenyl	X-225 <sup>®</sup>	Rtx-Dioxin2 <sup>®</sup>	Certified Value
VMS-01	21	23	14	17.7±5.6
C-2 (DX-1)	240	n/a	284	263(± 53)
ediment	8.5	8.1	9	6
lyash	5.6	6.7	4.4	5
lyash-2	<3	3.1	4.4	4.0

# PCDF



## 12378-PCDF

26.39

## 23478-PCDF

27.28



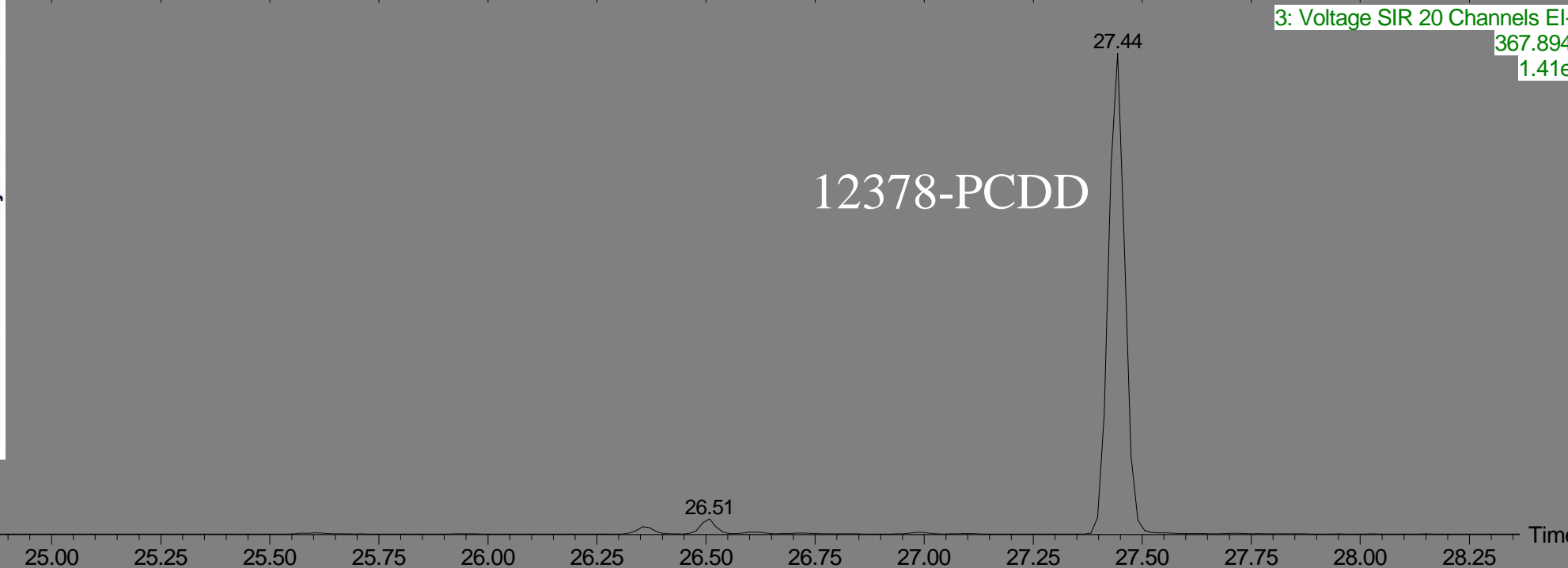
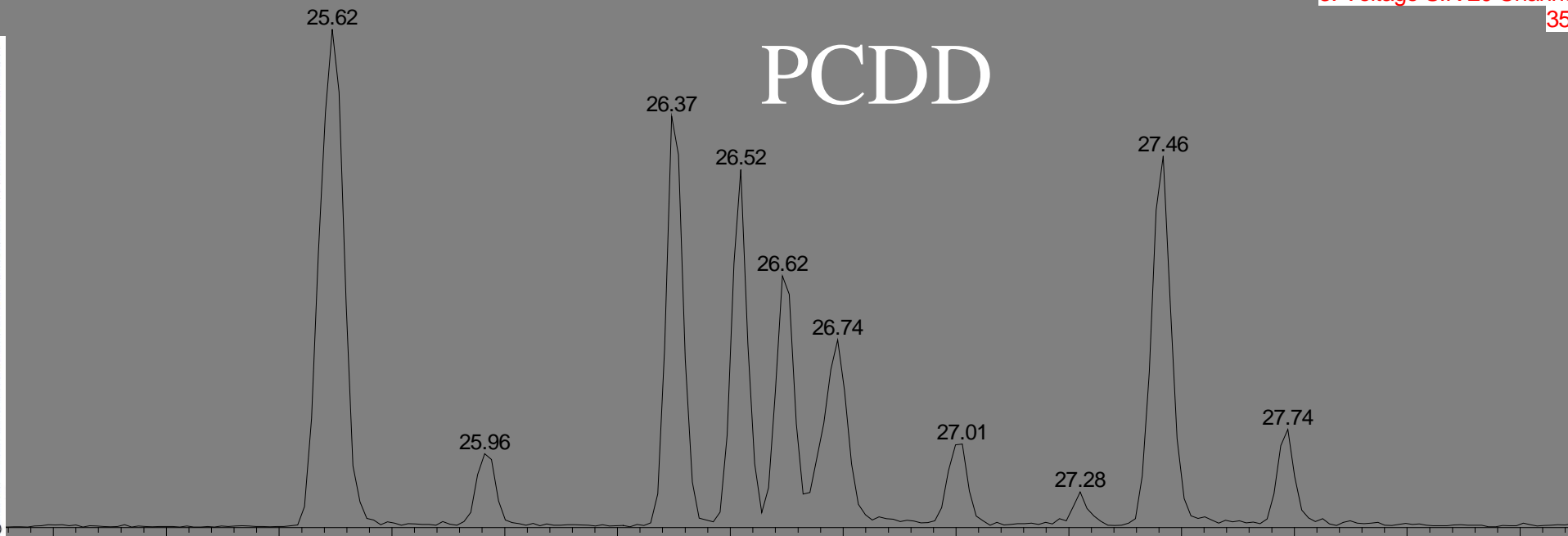
# Table III - 1,2,3,7,8-PCDF (pg/g)

	5% phenyl	Rtx-Dioxin2 <sup>®</sup>	Certified Value
WMS-01	13	11	12.6 ± 5
EC-2(DX-1)	33	30	39 ± 14
Sediment	42	40	49
Flyash	72	72	73
Flyash-2	86	68	70

# Table IV- 2,3,4,7,8-PCDF (pg/g)

	5%phenyl	Rtx-Dioxin2 <sup>®</sup>	Certified Value
WMS-01	26	15	18.5 ± 6.1
EC-2(DX-1)	63	55	62 ± 32
Sediment	23	18	21
Flyash	170	140	120
Flyash-2	160	130	110

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# HxCDF ion channel in Flyash sample

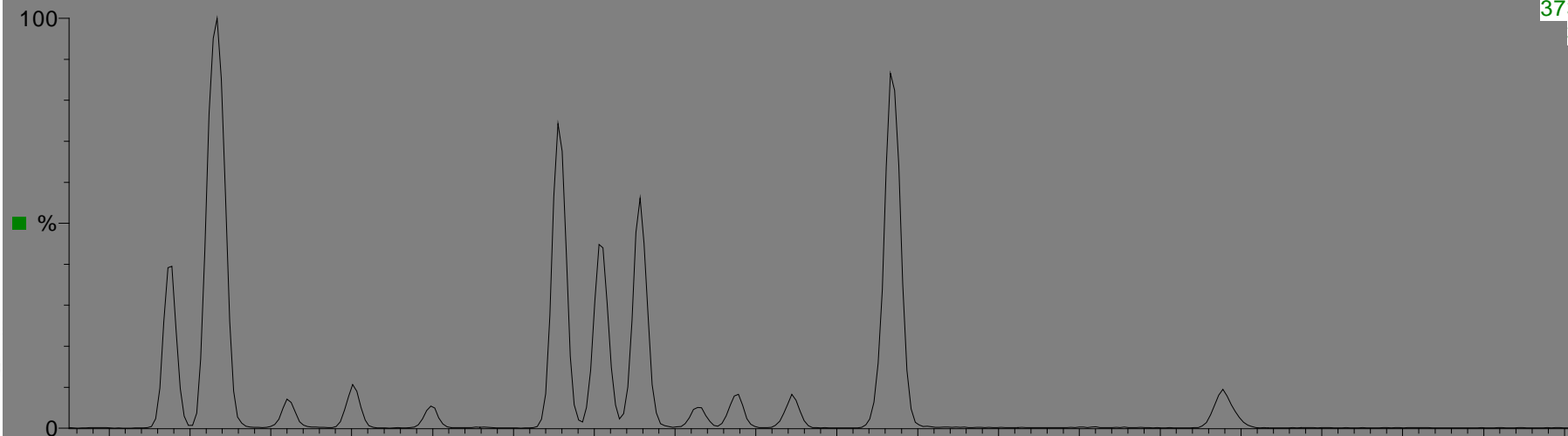
c101863-0004

may12\_res15

4: Voltage SIR 16 Channels EI+

373.8207

3.19e6



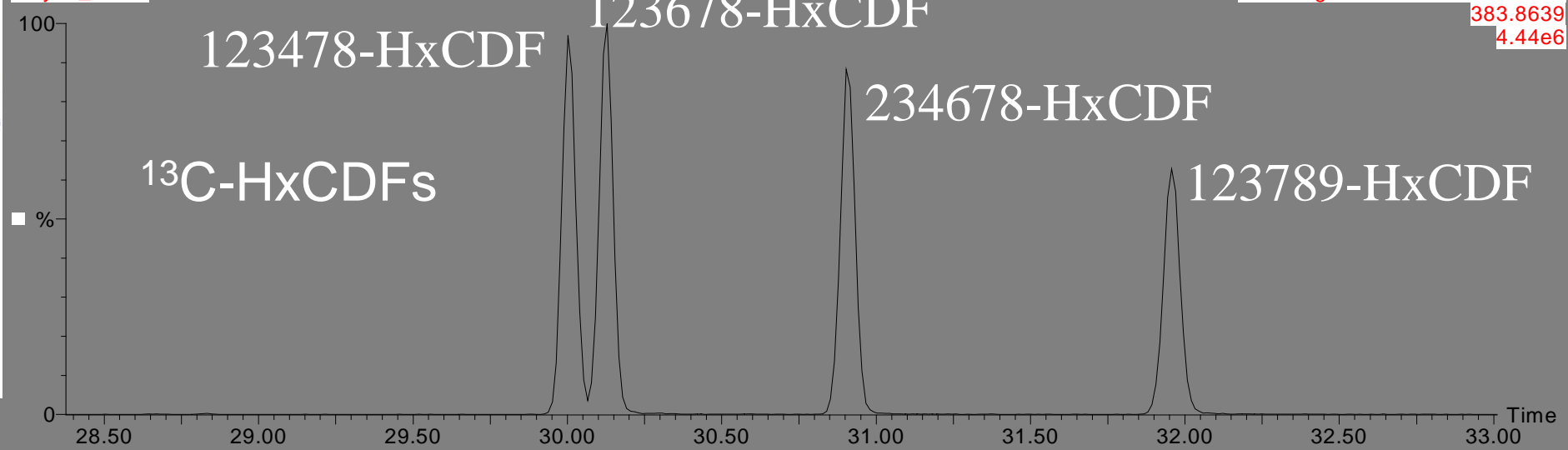
may12\_res15

4: Voltage SIR 16 Channels EI+

383.8639

4.44e6

123478-HxCDF  
123678-HxCDF  
234678-HxCDF  
<sup>13</sup>C-HxCDFs  
123789-HxCDF





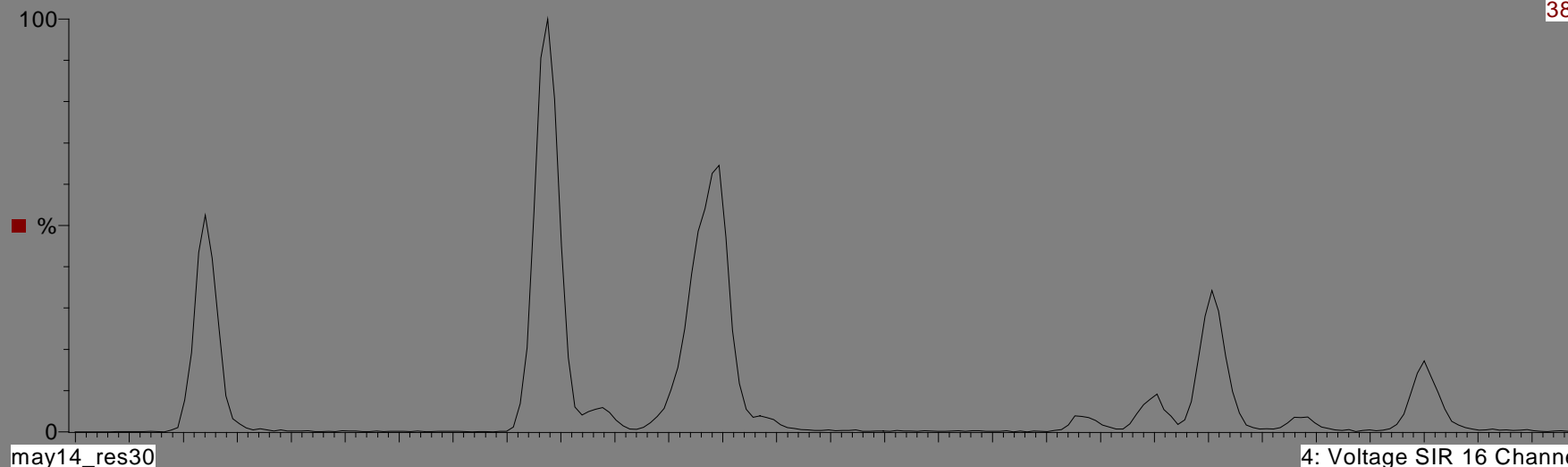
# Table V - 1,2,3,4,7,8-HxCDF (pg/g)

	5% phenyl	Rtx-Dioxin2 <sup>®</sup>	Certified Value
<b>WMS-01</b>	80	50	67 ± 24
<b>EC-2 (DX-1)</b>	780	630	714 (± 276)
<b>Sediment</b>	290	210	230
<b>Flyash</b>	570	200	190
<b>Flyash-2</b>	520	190	180

# HxCDD ion channel for sediment

EC-2 10uL  
may14\_res30

4: Voltage SIR 16 Channels EI+  
389.8156  
8.26e5



4: Voltage SIR 16 Channels EI+  
401.8559  
3.82e6

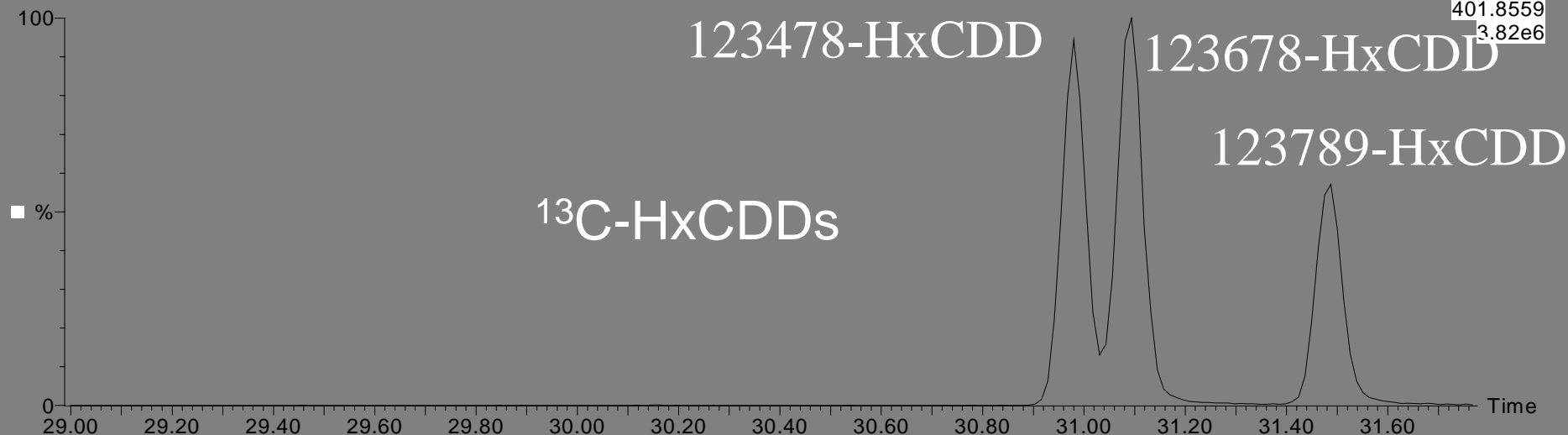
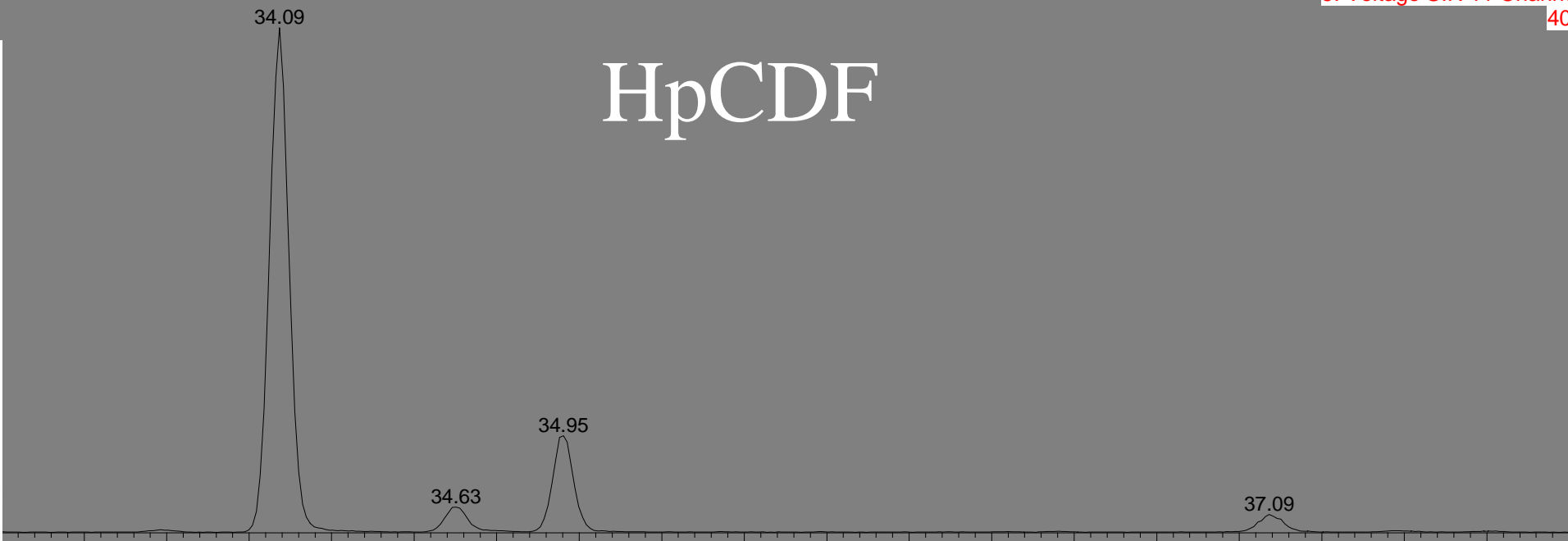


Table VI - 1,2,3,7,8,9-HxCDD (pg/g)

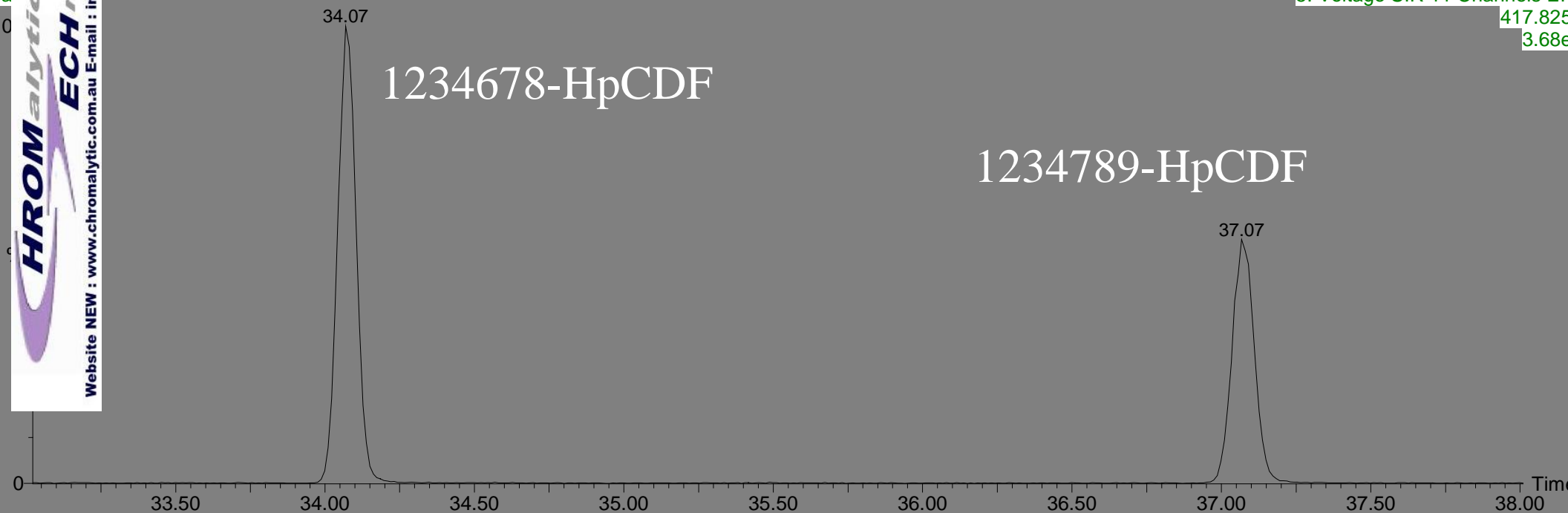
	5% phenyl	Rtx-Dioxin2 <sup>®</sup>	Certified Value
WMS-01	27	29	17.3 ± 8
EC-2 (DX-1)	65	38	53 (± 24)
Sediment	5	6.3	3
Flyash	40	38	40
Flyash-2	39	29	33

## HpCDF

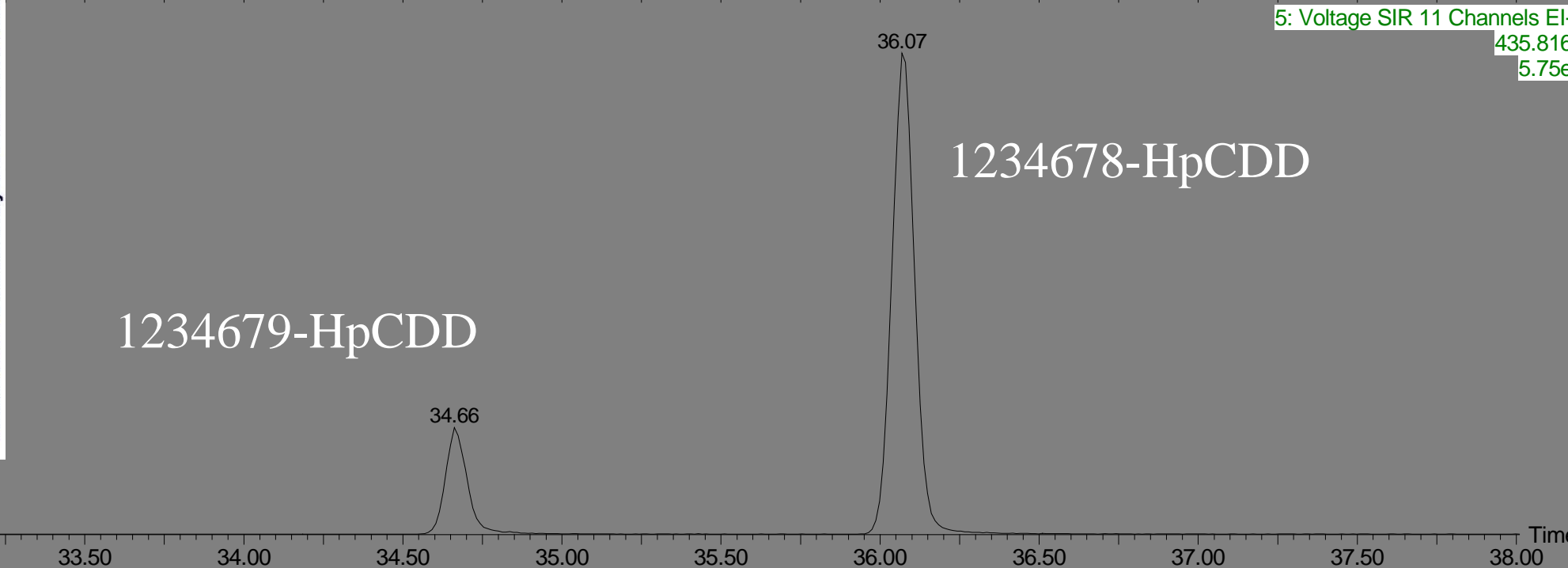
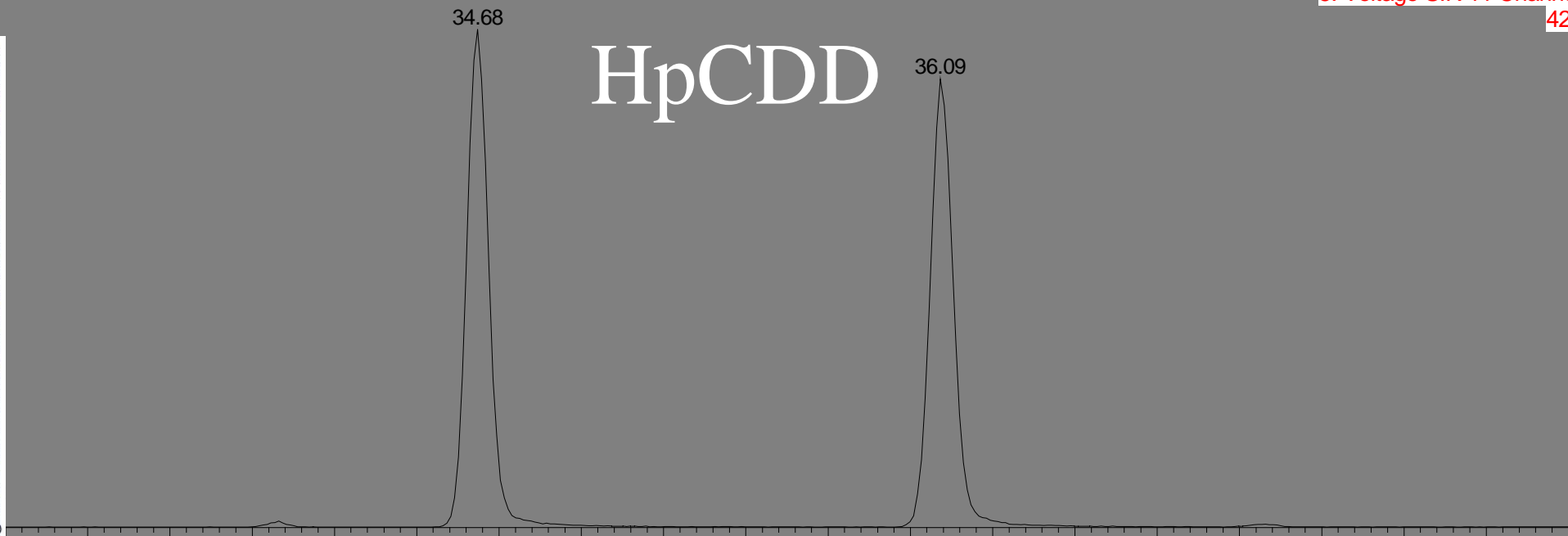


## 1234678-HpCDF

## 1234789-HpCDF



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# OCDD/OCDF

OCDF

43.33

6: Voltage SIR 9 Channels EI

441.742

6.96e

OCDD

43.03

6: Voltage SIR 9 Channels EI

457.737

3.15e

43.00

6: Voltage SIR 9 Channels EI

469.778

2.59e

# Rtx-Dioxin2 Capillary Column

Proprietary backbone stabilized polysiloxane designed for toxic dioxin and furan analysis by GC-HRMS

340 maximum operating temperature in standard fused silica tubing

Can be used as secondary confirmation column for Rtx-Dioxin, or other primary columns like 5% diphenyl phases

Can function as single column for stand-alone dioxin and furan analysis – and has been accredited for use as such

- Clive Robinson ALS Environmental –Queensland Australia

Chromatographically separates the chlorinated diphenylethers from the furans – especially important in biota matrices

Columns available:

- Cat # 10758 - 60 M X 0.25 mm i.d. X 0.25 um d.f.
- Cat # 10759 - 40 M X 0.18 mm i.d. X 0.18 um d.f.

# Evaluation of a Variety of GC Stationary Phases for the Analysis of Volatile Organics by US EPA Method 8260.

CHRISTOPHER M. ENGLISH,

Christine Stewart, Frank L. Dorman &  
Gary Stidsen.



# Abstract

Many GC stationary phases have been used for the analysis of volatile organic compounds by US EPA Method 8260. With an ever-expanding target list, and the availability of many stationary phases, choosing the correct column can be difficult.

Every stationary phase has limitations, whether related to temperature range, stability, or selectivity. Selectivity limitations can be a function of sample-specific compounds that share common ions for quantification.

This paper will examine the performance of various stationary phases, with varied sample concentrations, in volatiles analysis, and will include example chromatograms for situations for which each column is best suited. Compound identifications, purge and trap conditions, interfering ions, and other factors specific to the GC/MS analysis will be presented.

# Introduction

Qualitative identification of a target compound by GC/MS is based on retention time and on the comparison of the sample mass spectrum to a reference mass spectrum. Identification of compounds uses three ions of the greatest intensity. The quantitation ion is usually the highest  $m/z$  fragment and is used for determining concentrations of a particular analyte. It is important that there be no coelution between compounds sharing ions used for quantitation. As long as unique quantitation ions can be selected for compounds that share retention time, chromatographic coelution is acceptable. When using any column for GC/MS, attention must be given to coeluting compounds to determine if acceptable quantitation ions can be found. This paper will examine optimized conditions on four different stationary phases for suitability by EPA Method 8260.

Purge and trap used for this work was the  
O.I. 4560 & 4660 Eclipse.



Instrument Courtesy of O.I.Analytical.

# Coelutions by Phase:

Calibration curves for the four columns evaluated passed EPA 8260 criteria (SPCC & CCC) for response factors and relative standard deviations. Two compounds in the test set showed poor response, acetone and TBA. The Rtx-VMS, Rtx-VRX, Rtx-Volatiles and Rtx-624 were tested in the 30m x 0.25mm x 1.4df column dimensions. The compounds are listed by quantification ion and retention time (see Table 1).



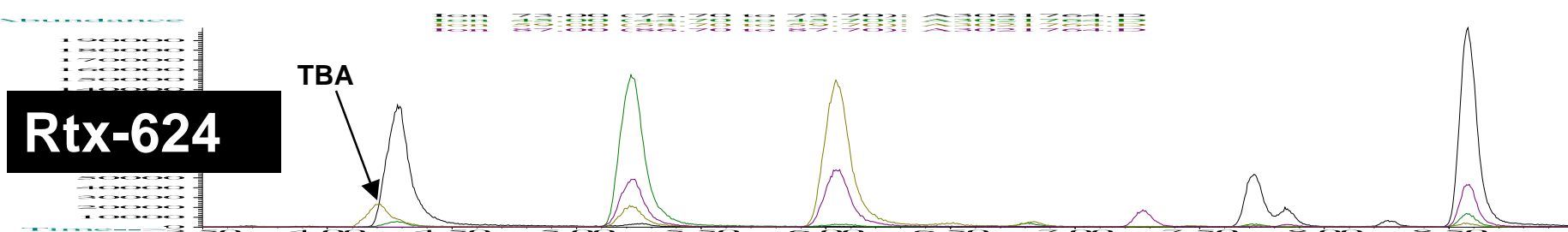
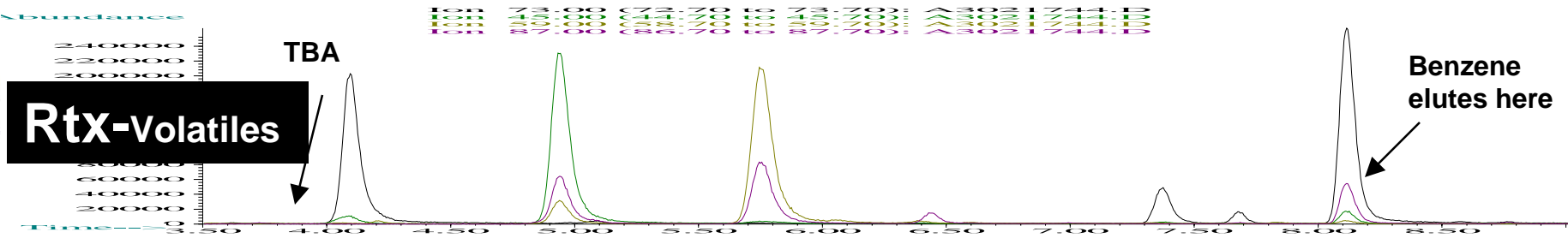
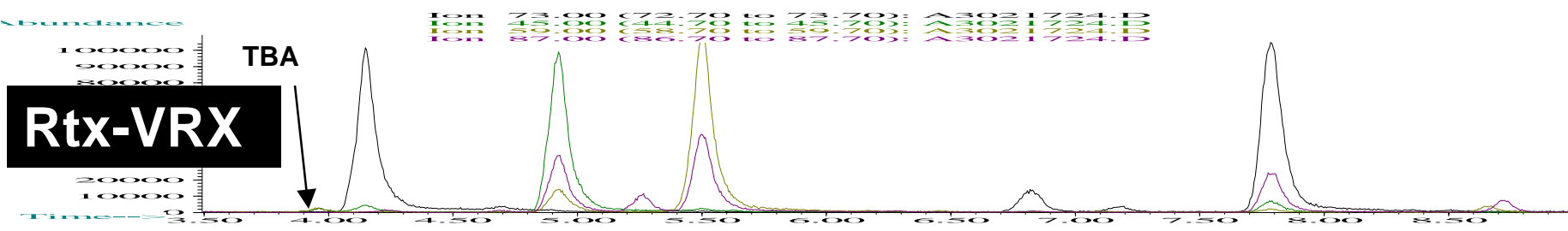
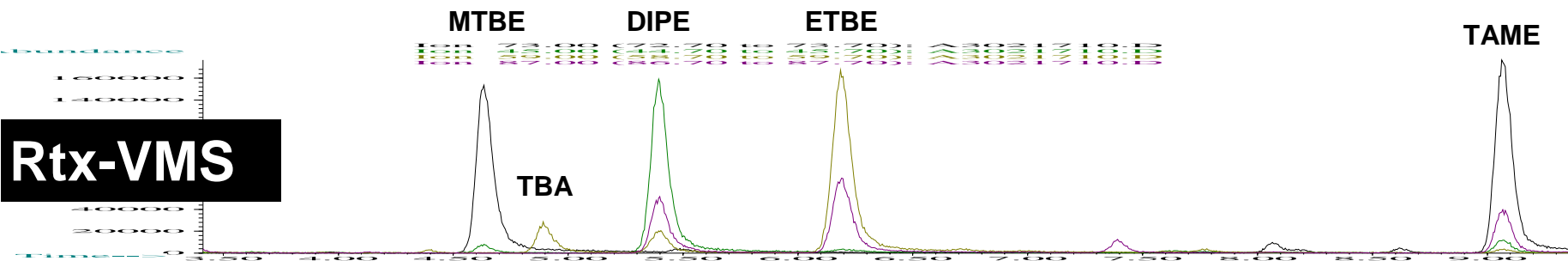
Compound	SigMS	Char. Ion	Rtx-VMS	Rtx-VRX	Rtx-VOLATILES	Rtx-624
dichlorodifluoromethane	85	85 87	1.65	1.74	1.69	1.52
chloromethane	50	50 52	1.84	1.80	1.84	1.69
vinyl chloride	62	62 64	1.95	1.94	1.95	1.81
bromomethane	94	94 96	2.30	2.20	2.27	2.16
chloroethane	64	64 66	2.46	2.31	2.34	2.27
trichlorofluoromethane	101	151 101 153	2.63	2.72	2.63	2.51
diethylether	59	74 45	3.03	2.92	2.89	2.86
1,1-dichloroethene	96	96 61 63	3.26	3.17	3.20	3.14
carbon disulfide	76	78 76	3.28	3.47	3.73	3.37
Freon 113	101	151 101 85	3.35	3.38	3.11	3.14
iodomethane	142	127 141	3.44	3.17	3.49	3.37
allyl chloride	76	41 39 78	3.95	2.66	3.62	3.69
methylene chloride	84	49	4.12	3.30	3.73	3.93
acetone	43	43 58	4.23	2.81	3.04	3.38
trans-1,2-dichloroethene	96	96 61 98	4.38	3.95	4.21	4.29
methyl-d3-tert-butyl-ether	76		4.59	4.07	4.08	4.18
methyl-tert-butyl-ether	73	73 57	4.62	4.15	4.08	4.45
tert-butyl alcohol	59	59 84	4.87	3.21	3.31	4.14
acetonitrile	41	40 39	5.00	3.33	3.61	3.60
diisopropyl ether	45	43 87	5.38	4.88	4.94	5.22
chloroprene	64	(53) 88 90 51	5.50	4.70	5.08	5.23
1,1-dichloroethane	63	63 65 83	5.52	4.24	4.87	5.23
acrylonitrile	53	52 51	5.63	4.70	3.82	4.29
ethyl-tert-butyl ether	59	57 87	6.17	5.49	5.75	6.04
cis-1,2-dichloroethene	96	96 61 98	6.70	4.93	6.06	6.51
2,2-dichloropropane	77	77 97	6.93	5.38	11.96	6.51
bromochloromethane	128	128 49 130	7.13	5.17	6.68	7.05
chloroform	83	83 85	7.28	5.26	6.44	7.27
carbon tetrachloride	117	117 119	7.59	7.11	7.84	7.73
tetrahydrofuran	42	72 71 41	7.72	5.80	5.60	7.60
methyl acrylate	55	85	7.76	5.40	6.44	6.82
1,1,1-trichloroethane	97	97 99 61	7.76	6.46	7.34	7.48
dibromofluoromethane	111	111 192	7.78	5.41	6.86	7.64
1,1-dichloropropene	75	75 77 39	8.06	6.84	7.68	7.86
2-butanone	72	43 57 (use 43)	8.13	4.80	5.68	6.67
benzene	78	78	8.62	7.17	8.10	8.26
propionitrile	54	54 52 55 40	8.74	ND	ND	6.96
methacrylonitrile	41	41 67 39 52 66	8.79	4.95	6.22	7.27
1,2-dichloroethane-d4	65		8.95	6.14	8.10	8.26
pentafluorobenzene	168	99 137 117	9.02	6.27	7.00	7.88
tert-amyl-methyl ether	73	87 55	9.06	7.79	8.12	8.57
1,2-dichloroethane	62	62 98	9.10	6.27	8.10	8.57
trichloroethene	95	95 97 139 132	10.02	8.67	9.31	9.64
1,4-difluorobenzene	114	88 63	10.17	7.81	8.77	9.27
dibromomethane	93	93 95 174	10.95	8.38	9.93	10.39
1,2-dichloropropane	63	63 112	11.21	8.52	9.57	10.17
bromodichloromethane	83	83 85 127	11.45	8.67	9.91	10.75

toluene-d8	98			13.42	12.75	11.34	12.00
toluene	92	92 91		13.54	12.97	11.47	12.11
2-nitropropane	43	41 39 27		14.12	14.26	10.07	11.37
tetrachloroethene	166	(164) 129 131		14.43	15.61	12.53	13.05
2-bromo-1-chloropropane	77	77 107 41 158		14.50	12.75	11.96	12.57
4-methyl-2-pentanone	43	(100) 58 85		14.62	11.19	10.72	11.99
trans-1,3-dichloropropene	75	75 110 77		14.85	12.01	11.76	12.75
1,1,2-trichloroethane	83	83 97 85		15.00	12.37	11.96	13.05
ethyl methacrylate	69	41 99 86 114		15.25	14.03	11.96	12.91
dibromochloromethane	129	129 127		15.38	13.84	12.68	13.73
1,3-dichloropropane	76	76 78		15.63	13.23	12.37	13.37
1,2-dibromoethane	107	107 109 188		15.85	14.67	12.99	13.93
2-hexanone	43	58 57 100		16.77	14.26	12.14	13.60
chlorobenzene-D5	117	82 54		17.22	18.25	13.65	14.83
chlorobenzene	112	112 77 114		17.26	18.38	13.72	14.88
ethylbenzene	91	91 106		17.41	19.38	13.89	15.07
1,1,1,2-tetrachloroethane	131	131 133 119		17.45	18.16	13.81	15.07
m-xylene	108	106 91		17.70	19.96	14.02	15.07
p-xylene	108	106 91		17.70	19.96	14.02	15.07
o-xylene	108	106 91		18.31	20.70	16.65	15.92
bromoform	173	173 175 254		18.36	19.78	15.02	16.24
styrene	104	104 78		18.38	20.57	14.68	15.97
isopropylbenzene	105	105 120		18.70	21.34	15.24	16.47
4-bromo-1-fluorobenzene	95	95 174 176		18.97	21.30	15.52	16.73
bromobenzene	156	156 77 158		19.04	21.52	15.75	16.88
cis-1,4-dichloro-2-butene	53	(75) 53 77 124		19.07	20.49	15.19	16.73
1,4-dichlorobutane	55	55 90 75		19.12	20.64	15.29	16.73
n-propylbenzene	91	91 120		19.13	21.86	15.84	17.04
1,1,2,2-tetrachloroethane	83	83 131 85		19.21	16.18	15.40	17.04
2-chlorotoluene	91	91 126		19.24	21.99	16.02	17.16
1,2,3-trichloropropane	75	75 77 97 110		19.30	20.92	15.60	17.04
1,3,5-trimethylbenzene	105	105 120		19.32	22.37	16.65	17.27
trans-1,4-dichloro-2-butene	53	88 75		19.36	21.10	15.75	17.15
4-chlorotoluene	91	91 126		19.40	22.10	16.10	17.15
tert-butylbenzene	119	119 91 134		19.58	22.62	16.61	17.68
pentachloroethane	167	130 132 165		19.59	22.28	16.61	17.76
1,2,4-trimethylbenzene	105	105 120		19.64	22.77	16.61	17.30
sec-butylbenzene	105	105 134		19.73	22.86	16.93	17.95
p-isopropyltoluene	119	119 134 91		19.85	23.09	17.13	18.14
1,3-dichlorobenzene	146	146 111 148		19.87	22.86	17.13	18.05
1,4-dichlorobenzene-d4	152		150	19.93	22.94	17.24	18.22
1,4-dichlorobenzene	146	146 111 148		19.94	22.94	17.28	18.22
n-butylbenzene	91	91 92 134		20.15	23.47	17.66	18.62
1,2-dichlorobenzene	146	146 111 148		20.24	23.28	17.72	18.65
1,2-dibromo-3-chloropropane	75	75 155 157		20.79	23.70	18.60	19.55
nitrobenzene	123	51 77		21.19	23.92	18.69	19.80
hexachlorobutadiene	225	225 223 227		21.24	25.10	19.77	20.51
1,2,4-trichlorobenzene	180	180 182 145		21.27	24.84	19.57	20.38
naphthalene	128		128	21.52	25.01	19.77	20.64
1,2,3-trichlorobenzene	180	180 182 145		21.66	25.18	20.04	20.38

## Oxygenate Extracted Ions by EPA Method 8260.

Adding compounds such as the oxygenates to the 8260 compound list can result in critical coelutions. Several examples are given. The Rtx-624 30 meter x 0.25mm x 1.4df column does not resolve the TBA from MTBE. These compounds share 59 ion. The Rtx-Volatiles phase has a coelution of TAME/Benzene m/z 73.

# Oxygenate Extracted Ions by EPA Method 8260.



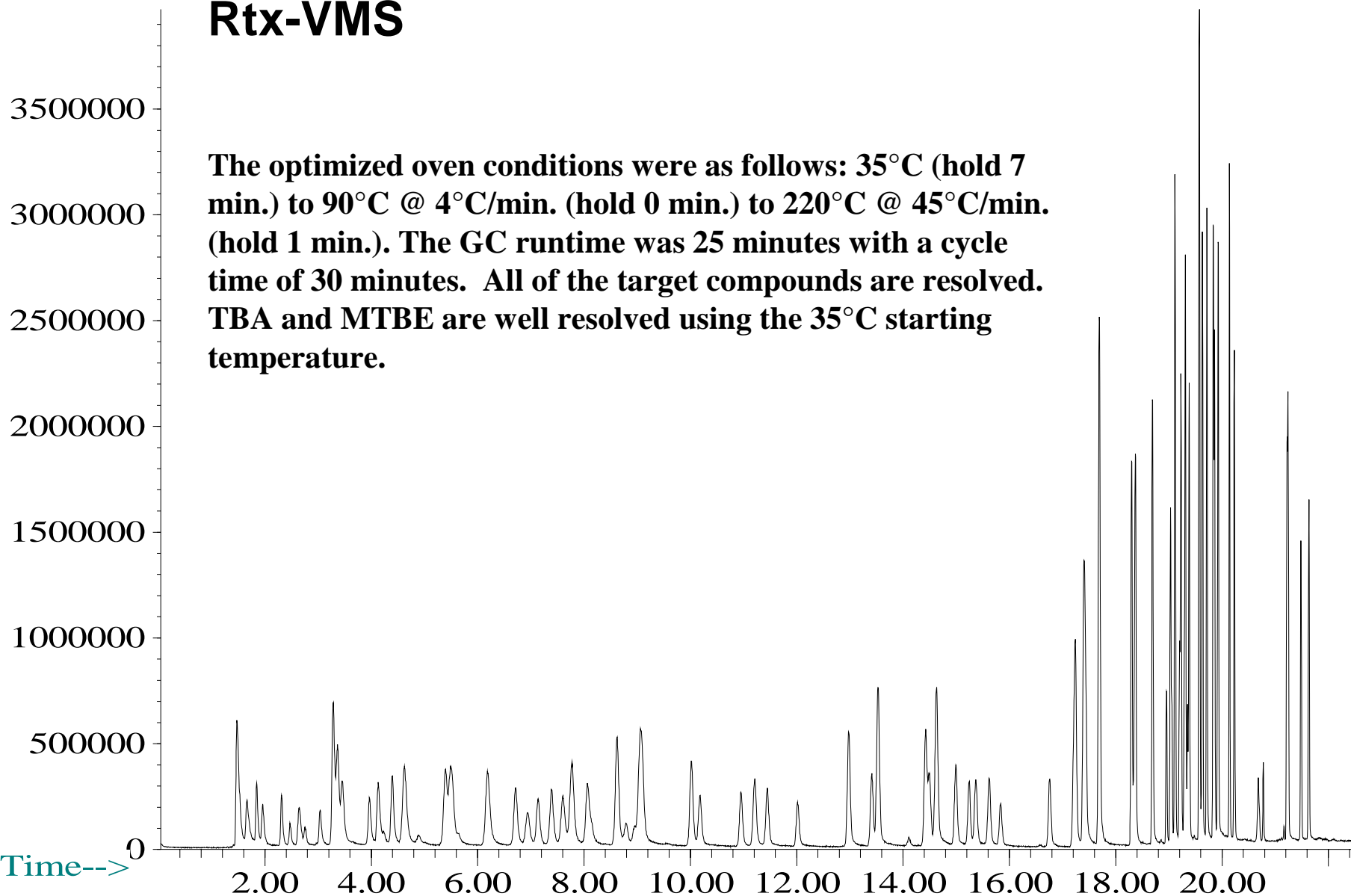


Abundance

## Rtx-VMS

The optimized oven conditions were as follows: 35°C (hold 7 min.) to 90°C @ 4°C/min. (hold 0 min.) to 220°C @ 45°C/min. (hold 1 min.). The GC runtime was 25 minutes with a cycle time of 30 minutes. All of the target compounds are resolved. TBA and MTBE are well resolved using the 35°C starting temperature.

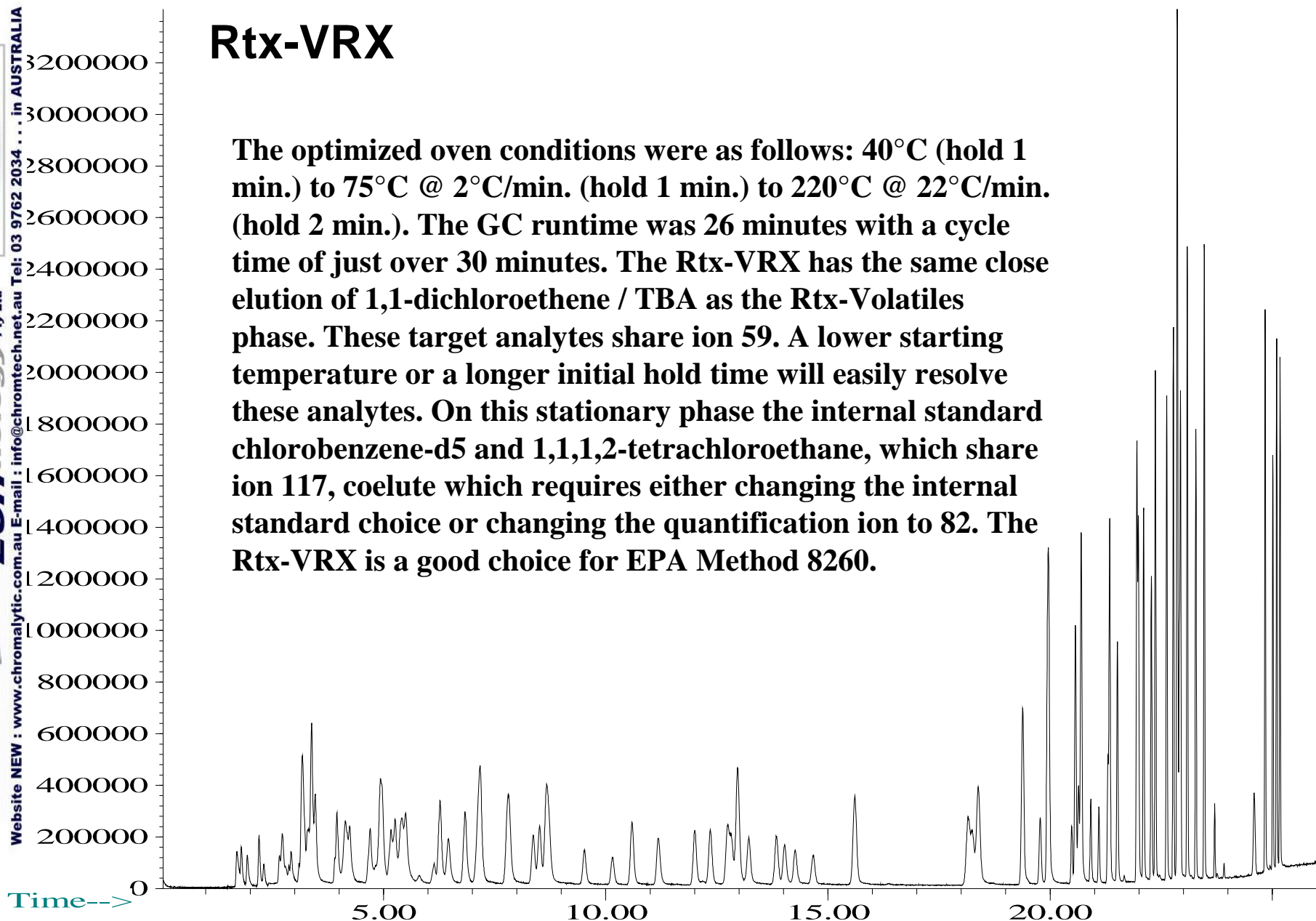
Time-->



Abundance

## Rtx-VRX

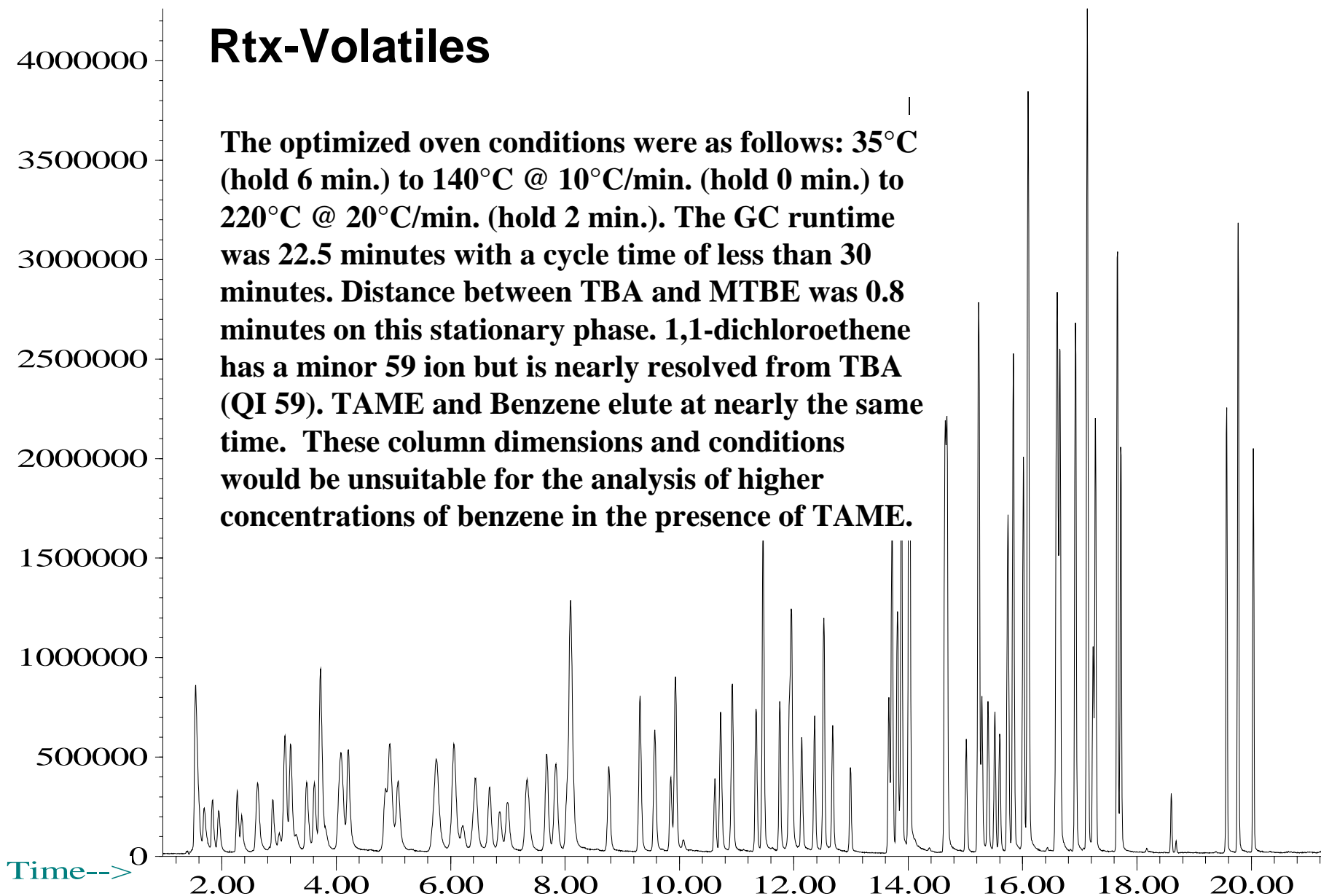
The optimized oven conditions were as follows: 40°C (hold 1 min.) to 75°C @ 2°C/min. (hold 1 min.) to 220°C @ 22°C/min. (hold 2 min.). The GC runtime was 26 minutes with a cycle time of just over 30 minutes. The Rtx-VRX has the same close elution of 1,1-dichloroethene / TBA as the Rtx-Volatiles phase. These target analytes share ion 59. A lower starting temperature or a longer initial hold time will easily resolve these analytes. On this stationary phase the internal standard chlorobenzene-d5 and 1,1,1,2-tetrachloroethane, which share ion 117, coelute which requires either changing the internal standard choice or changing the quantification ion to 82. The Rtx-VRX is a good choice for EPA Method 8260.



Abundance

## Rtx-Volatiles

The optimized oven conditions were as follows: 35°C (hold 6 min.) to 140°C @ 10°C/min. (hold 0 min.) to 220°C @ 20°C/min. (hold 2 min.). The GC runtime was 22.5 minutes with a cycle time of less than 30 minutes. Distance between TBA and MTBE was 0.8 minutes on this stationary phase. 1,1-dichloroethene has a minor 59 ion but is nearly resolved from TBA (QI 59). TAME and Benzene elute at nearly the same time. These column dimensions and conditions would be unsuitable for the analysis of higher concentrations of benzene in the presence of TAME.



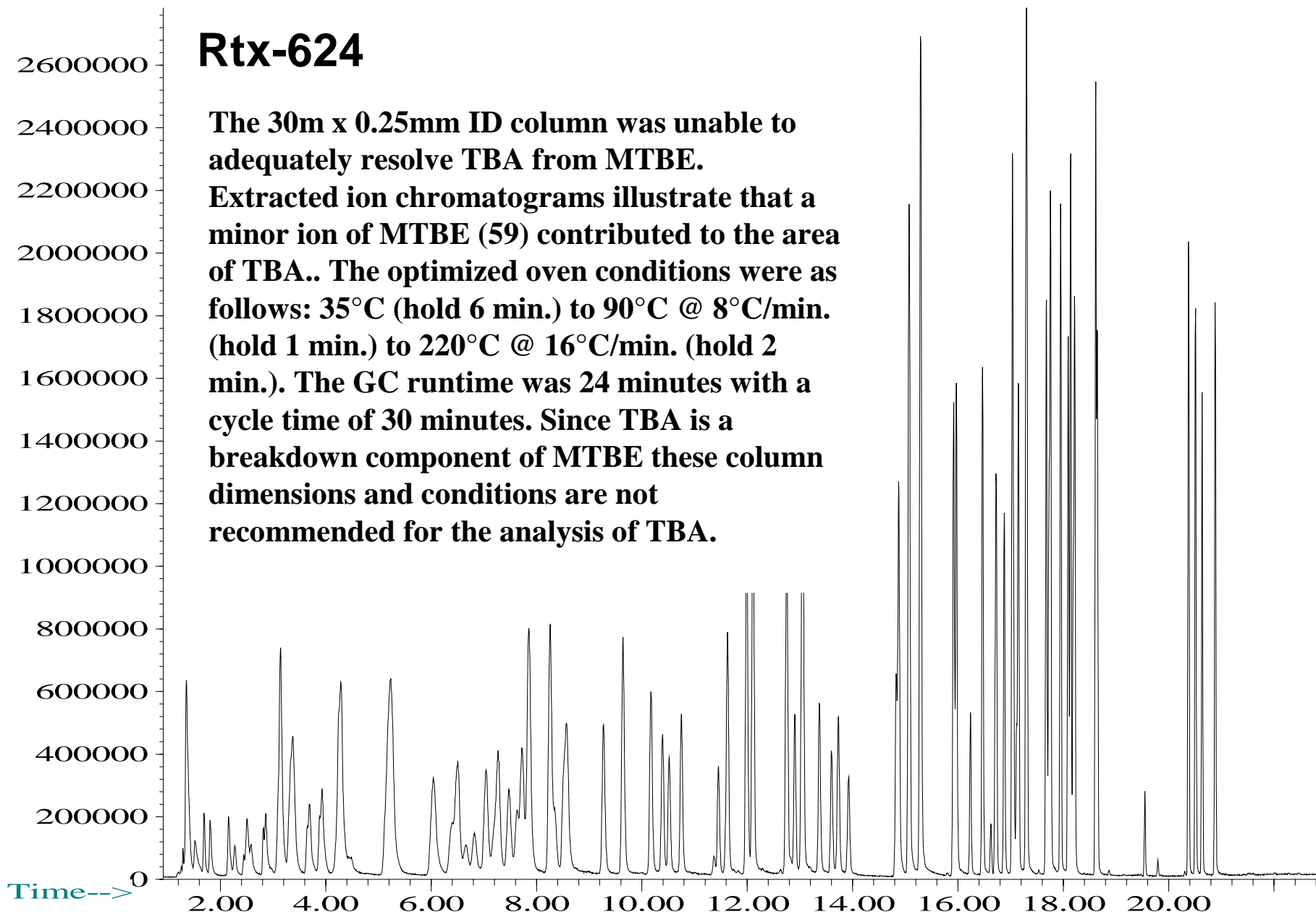
Time--&gt;

Abundance

## Rtx-624

The 30m x 0.25mm ID column was unable to adequately resolve TBA from MTBE.

Extracted ion chromatograms illustrate that a minor ion of MTBE (59) contributed to the area of TBA.. The optimized oven conditions were as follows: 35°C (hold 6 min.) to 90°C @ 8°C/min. (hold 1 min.) to 220°C @ 16°C/min. (hold 2 min.). The GC runtime was 24 minutes with a cycle time of 30 minutes. Since TBA is a breakdown component of MTBE these column dimensions and conditions are not recommended for the analysis of TBA.



Time--&gt;

## Conclusions

The Rtx-VRX and Rtx-VMS had the best performance given the compound list and column dimensions. Incomplete resolution of TAME and benzene make the Rtx-Volatiles a poor choice for an extended list of volatiles. The Rtx-624 also suffers from a coelution of TBA/MTBE, but with a longer column this pair is able to be resolved. With an expanding target list and difficult sample matrixes, care must be taken to assure correct compound identification in the presence of interfering analytes.

# A New, Unique Stationary Phase for the Rapid Analysis of Organochlorine Pesticides

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France.

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823

# Abstract

Many organochlorine pesticides are known or suspected mutagens and/or carcinogens. Due to the nature of these compounds, along with their long-term persistence in the environment, organochlorine pesticides continue to be some of the most widely monitored analytes for the environmental industry. The ability to rapidly and accurately analyze samples, without the need to invest in new, complex equipment can create a competitive advantage.

This poster discusses the use of a new, unique stationary phase for the rapid analysis of organochlorine pesticides. This phase allows a sub 10-minute analysis time for the 20 common pesticides and 2 surrogates analyzed by US EPA Method 8080. This is accomplished in the constant pressure mode, without need for constant flow or pressure pulses to achieve separation. In addition, this phase can be used in conjunction with a second stationary phase, CLPesticides2, to create a dual column confirmation system for analyzing the 22 components in less than 10 minutes, with the two columns exhibiting differing selectivity.



# Introduction

In the environmental industry, the chlorinated pesticides analytical methods often are the most challenging to perform. Analysts struggle with linearity, breakdown, and lengthy calibrations; as well as column bleed, column reactivity and poor separation. Advancements have been made to address these issues with the development of new columns that are designed specifically for the separation of chlorinated pesticides, to be used in parallel for simultaneous quantification and confirmation by gas chromatography/electron capture detection (GC/ECD). This paper will show applications using the new Rtx-440 column with three different confirmation columns. The advantages and disadvantages will be discussed with each column pair.

The three column pairs evaluated:

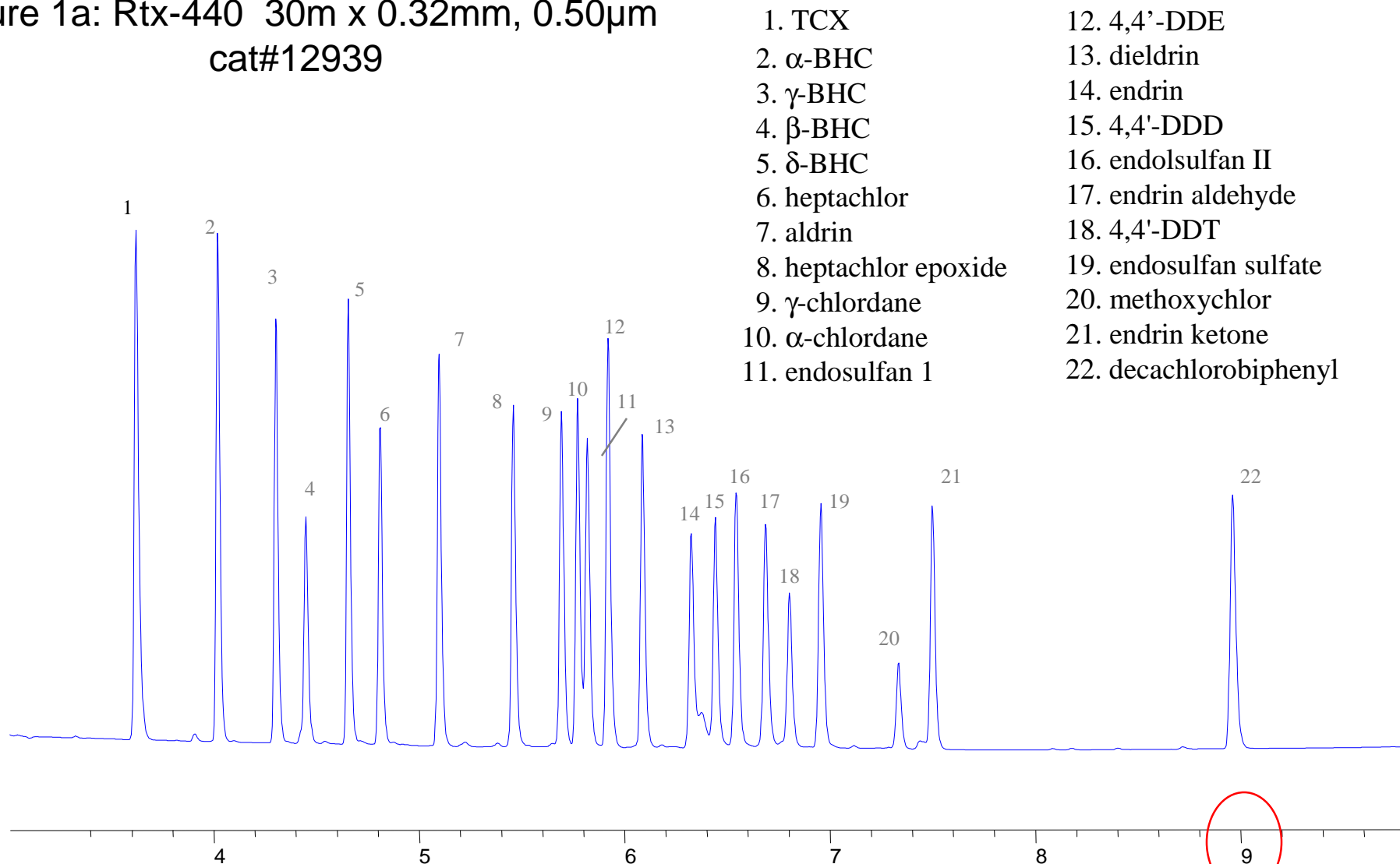
- 1.) Rtx-440 & Rtx-XLB
- 2.) Rtx-440 & Rtx-CLPesticides
- 3.) Rtx-440 & Rtx-PCB



# Rtx-440 & Rtx-XLB: Low Bleed and Excellent Resolution in Less Than 12 Minutes (Figures 1a & 1b).

Decachlorobiphenyl elutes off of the "XLB" phase in 11.5 minutes, while the target compounds listed in EPA Method 8080 are 80% resolved on both columns. Optimization of the expanded list of compounds found in EPA Method 8081A resulted in 80% resolution of the 32 target compounds (plus the surrogates) on the Rtx-440, with the exception of kepone and endrin aldehyde. The Rtx-XLB phase under the same conditions has two poorly resolved pairs: endrin/2,4'-DDT & endosulfan II & kepone. The clear advantage of this column pair is the rapid analysis and low bleed without a sacrifice in resolution. These columns have the same elution order for the EPA 8080 pesticides, which is a disadvantage of this application. Although there are elution order differences for the expanded list and the retention times are different for all of the chlorinated pesticides there is still a need to find a more dissimilar stationary phase as a confirmation column.

Figure 1a: Rtx-440 30m x 0.32mm, 0.50µm  
 cat#12939

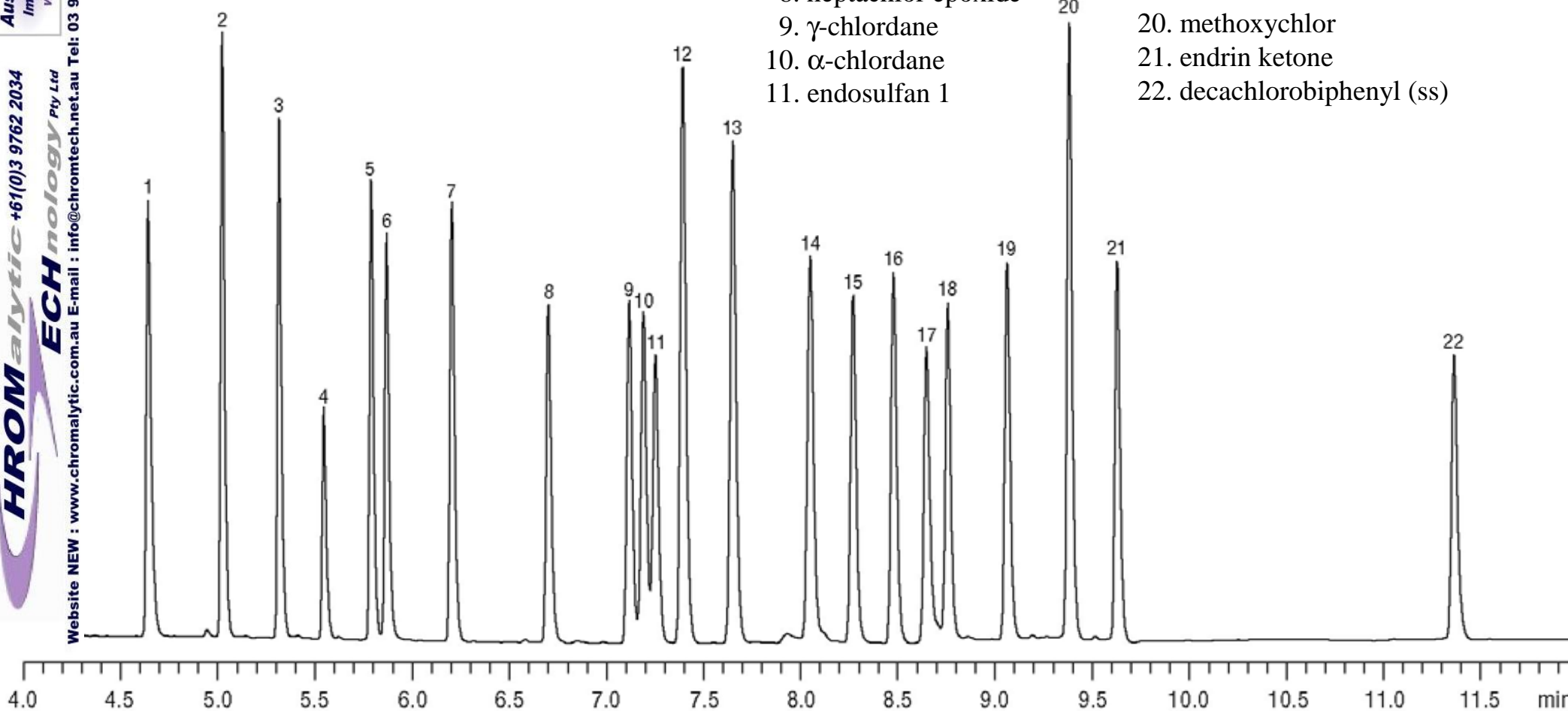


- |                       |                        |
|-----------------------|------------------------|
| 1. TCX                | 12. 4,4'-DDE           |
| 2. α-BHC              | 13. dieldrin           |
| 3. γ-BHC              | 14. endrin             |
| 4. β-BHC              | 15. 4,4'-DDD           |
| 5. δ-BHC              | 16. endosulfan II      |
| 6. heptachlor         | 17. endrin aldehyde    |
| 7. aldrin             | 18. 4,4'-DDT           |
| 8. heptachlor epoxide | 19. endosulfan sulfate |
| 9. γ-chlordane        | 20. methoxychlor       |
| 10. α-chlordane       | 21. endrin ketone      |
| 11. endosulfan 1      | 22. decachlorobiphenyl |

Conditions for Both Columns: Inj: 1.0 uL splitless (0.5 min hold), 4mm Drilled Uniliner inlet sleeve  
 Inj. Temp: 225°C Carrier gas: hydrogen, constant pressure, 71cm/sec @ 140°C  
 Oven temp: 140°C(0.5min) to 268°C @ 30°C/min (0min), to 290°C @ 11°C/min (0min), to 330°C @ 25°C/min (5min)

ure 1b: Rtx-XLB 30m x 0.32mm,  
 0.50µm film cat#12839

- |                       |                             |
|-----------------------|-----------------------------|
| 1. TCX                | 12. 4,4'-DDE                |
| 2. α-BHC              | 13. dieldrin                |
| 3. γ-BHC              | 14. endrin                  |
| 4. β-BHC              | 15. 4,4'-DDD                |
| 5. δ-BHC              | 16. endosulfan II           |
| 6. heptachlor         | 17. endrin aldehyde         |
| 7. aldrin             | 18. 4,4'-DDT                |
| 8. heptachlor epoxide | 19. endosulfan sulfate      |
| 9. γ-chlordane        | 20. methoxychlor            |
| 10. α-chlordane       | 21. endrin ketone           |
| 11. endosulfan 1      | 22. decachlorobiphenyl (ss) |



# Rtx-440 & Rtx-CLPesticides2 Columns: A Sub-10-Minute Analysis Time (figures 2a & 2b).

Figure 2a shows a separation of 20 commonly analyzed organochlorine pesticides obtained less than 10 minutes by using an Rtx-440 column. Only alpha-chlordane and endosulfan (peaks 10 & 11) are not separated to baseline. The advantage of this column pair is the difference in selectivity. This Rtx-CLPesticides2 column when run under the given conditions (figure 2b) that achieve a sub-7-minute analysis time result in 60% resolution versus the 80% peak resolution of the Rtx-440/Rtx-XLB pair. The column exhibits good thermal stability as indicated by the baseline between the initial temperature and the maximum temperature of the program, 330°C. In a dual-column approach to this application, an Rtx-440 column can be paired with an Rtx-CLPesticides2 column. The latter column will provide an equally fast separation (figure 2b) and near equivalent resolution, with a reverse in elution order for endrin aldehyde and 4,4'-DDT (peaks 17 & 18).

Figure 2a: Rtx-440 30m x 0.32mm, 0.50µm

Conditions for both columns:

Inj.: 1.0µL splitless (hold 0.75 min.), 4mm Drilled Uniliner® inlet liner (cat.# 21055)

Inj. temp.: 225°C Det.: ECD @ 320°C

Carrier gas: hydrogen, constant pressure

Linear velocity: 73cm/sec. @ 140°C

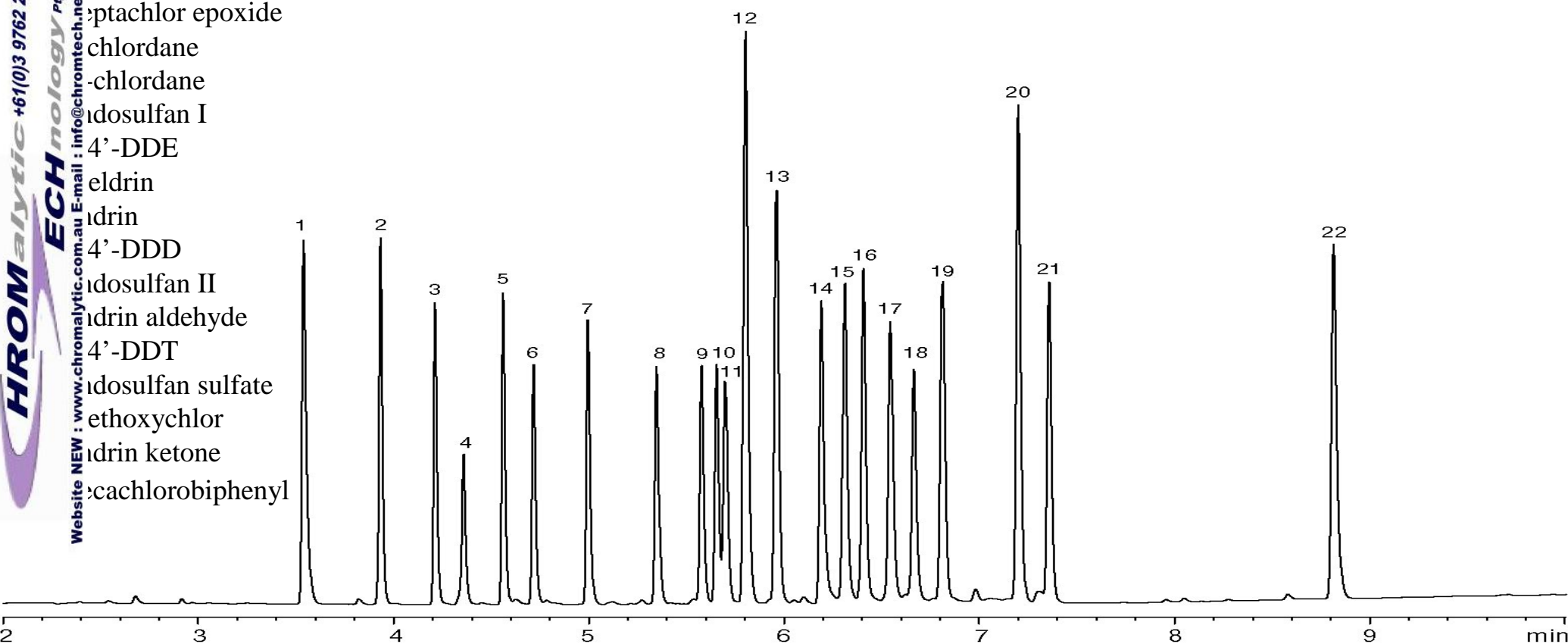
Oven temp.: 140°C (hold 0.5 min.) to 268°C @ 30°C/min., to 290°C @ 11°C/min., to 330°C @ 25°C/min. (hold 5 min.)

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ptachlor epoxide  
chlordane  
-chlordane  
idosulfan I  
4'-DDE  
eldrin  
drin  
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drin aldehyde  
4'-DDT  
idosulfan sulfate  
ethoxychlor  
drin ketone  
cachlorobiphenyl

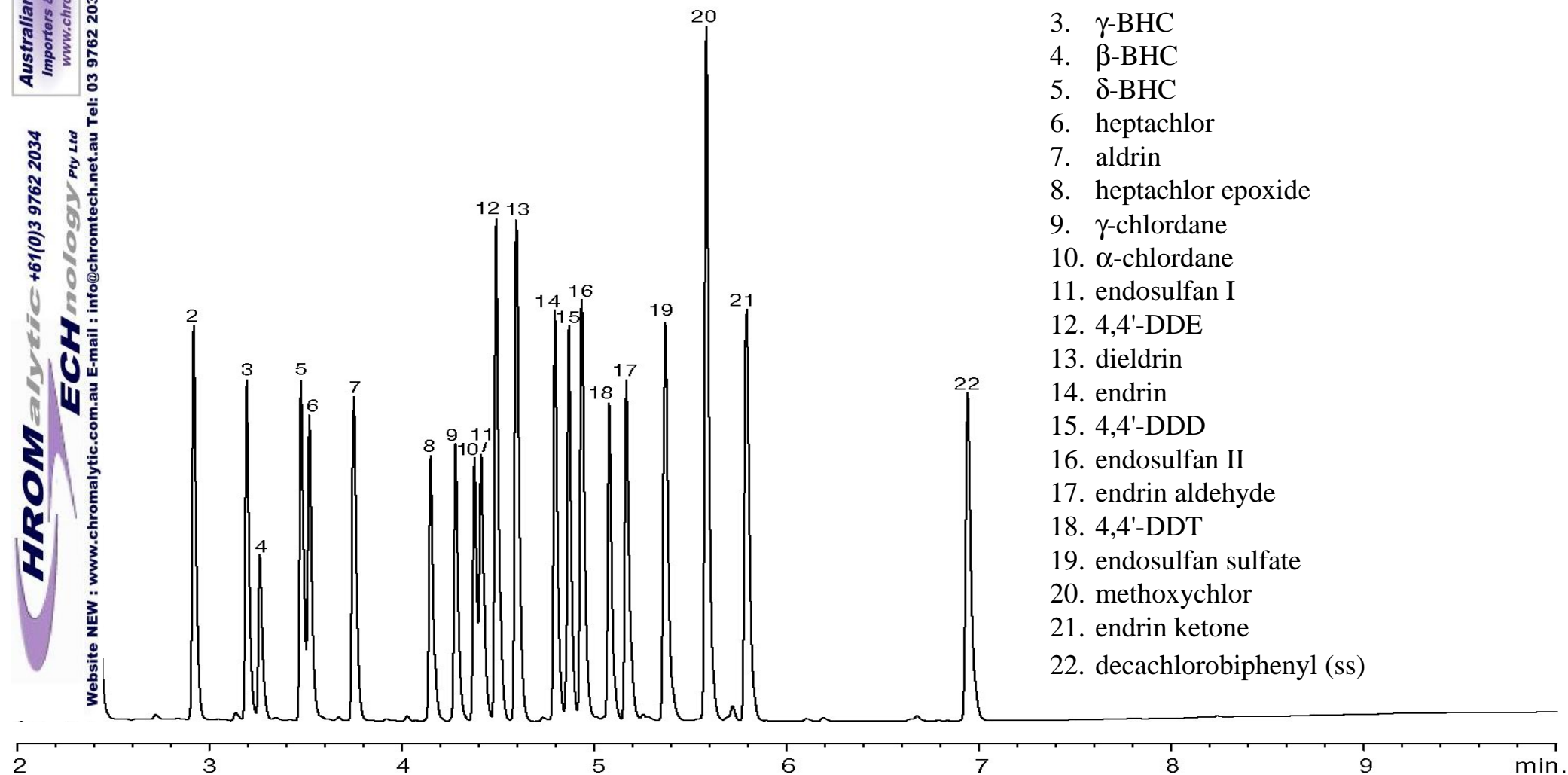


File 2b: Rtx-CLPesticides 30m x 0.32mm, 0.25µm Cat#11324

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1. 2,4,5,6-tetrachloro-m-xylene (ss)
2.  $\alpha$ -BHC
3.  $\gamma$ -BHC
4.  $\beta$ -BHC
5.  $\delta$ -BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9.  $\gamma$ -chlordane
10.  $\alpha$ -chlordane
11. endosulfan I
12. 4,4'-DDE
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endosulfan II
17. endrin aldehyde
18. 4,4'-DDT
19. endosulfan sulfate
20. methoxychlor
21. endrin ketone
22. decachlorobiphenyl (ss)



# Rtx-440 & Rtx-PCB Columns: Two New Low Bleed Columns with Unique Selectivity (figures 3a & 3b).

This column pair allows the accurate determination of organochlorine pesticides or polychlorinated biphenyls (PCBs). The Rtx-PCB column is well suited for congener-specific analysis where greater PCB information is necessary versus the more commonly performed Arochlor test. The analysis of the 20 chlorinated pesticides is shown in less than 20 minutes but separation is the least optimal of the choices presented in this paper. This column pair can produce 80% resolution for EPA Method 8080 with a longer runtime (20 minutes). The selectivity between these columns is unique; there are two column pair changes: heptachlor/d-BHC (peaks 5/6) & 4,4'-DDT/endrin aldehyde (peaks 17/18). These two columns also have excellent bleed characteristics minimizing detector contamination, allowing intervals between cleanings and thus increasing throughput over time.



Figure 3a: Rtx-440 30m x 0.32mm, 0.50µm

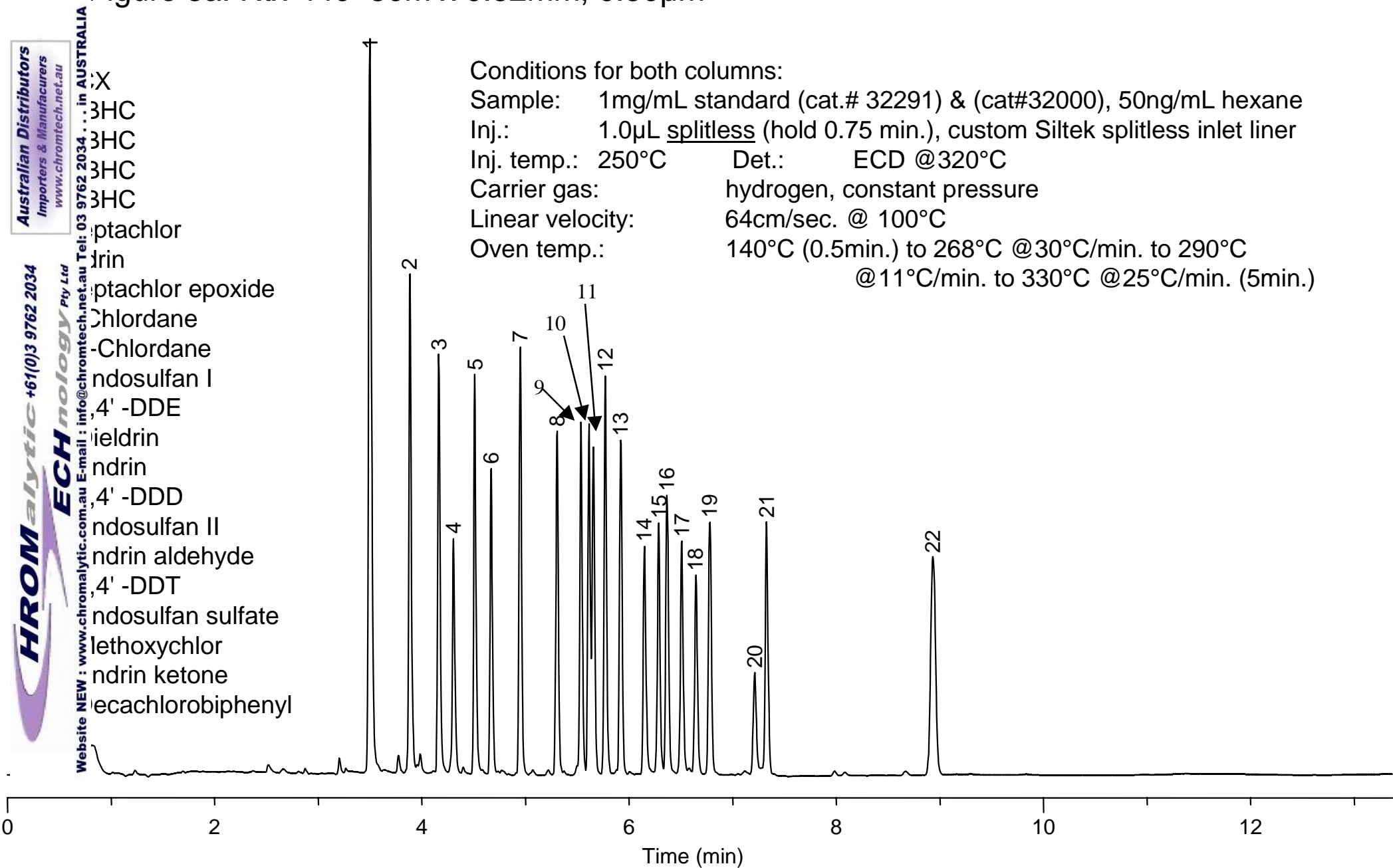
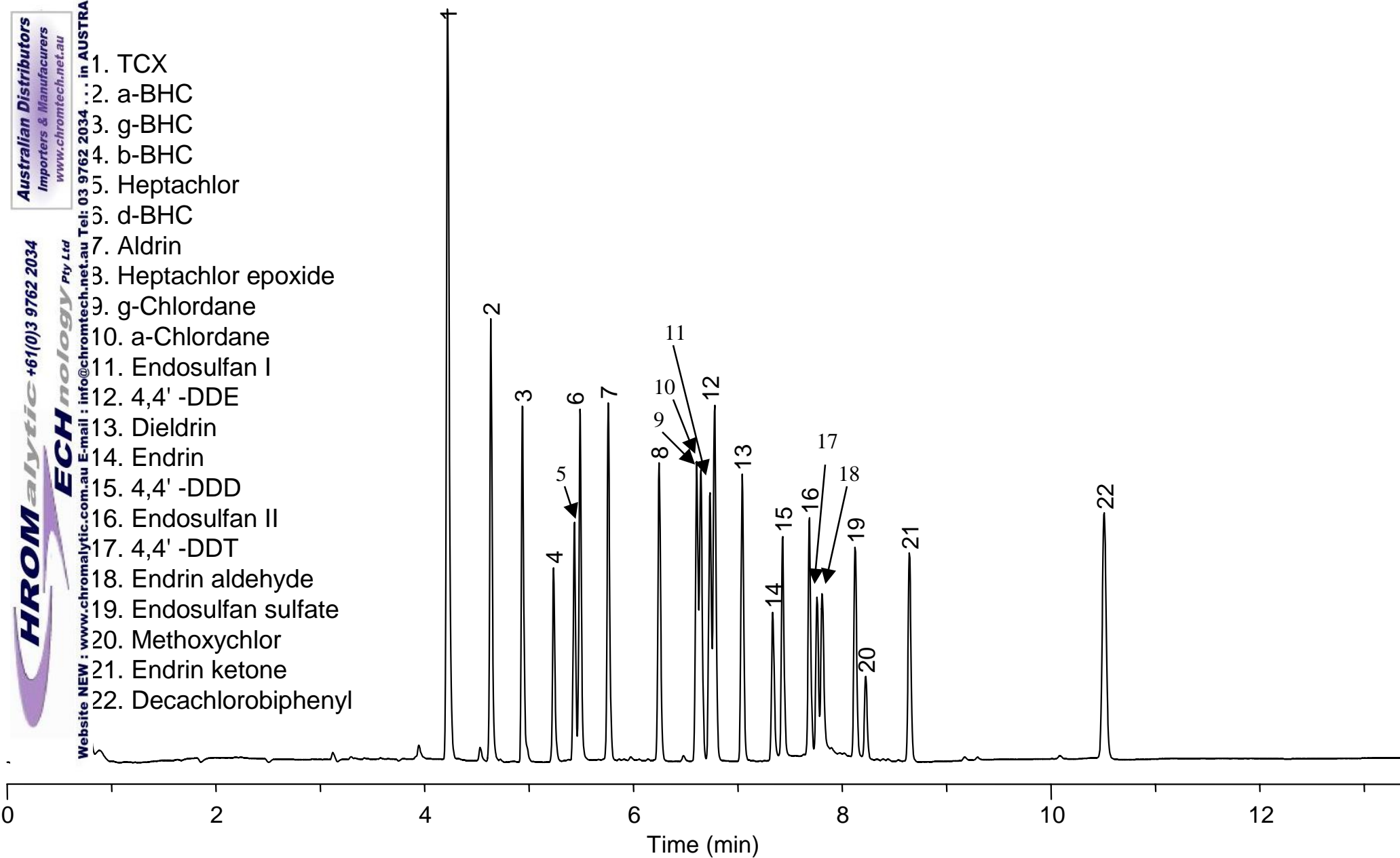




Figure 3b: Rtx-PCB 30m x 0.32mm, 0.50µm (Cat# 13239)



# Conclusion

Although the analysis of chlorinated pesticides historically has been one of the more difficult tasks performed by environmental testing laboratories, using any combination of the above columns for EPA pesticide methodologies will improve laboratory results and increase throughput. Laboratories using cyanopropyl-phase or phenyl-phase columns must calibrate using 5-point curves, injecting mix A and mix B compounds separately because target compounds coelute. Since there are no coelutions using the columns presented the mixes can be combined. This eliminates the need for 5 injections per calibrations and will free up a minimum of 2.5 hours a day to analyze more samples.

Three confirmation columns were examined in this paper: Rtx-XLB, Rtx-CLPesticides2 and the Rtx-PCB. The Rtx-XLB provides excellent resolution, but lacks differences in retention order to the Rtx-PCB. The Rtx-CLPesticides2 has a reverse in elution order between endrin and 4,4'-DDT with nearly equivalent resolution to the Rtx-440 primary column. The Rtx-PCB column exhibits two compound retention order changes but lacks the resolution of the Rtx-CLPesticides2 & Rtx-XLB. The Rtx-440 easily resolves the 20 chlorinated pesticides in less than 10 minutes. Determining the best confirmation column is a matter of preference. The information presented in this paper will allow laboratories to make informed decisions based upon the requirements of their clients and their specific methods.