



Chlorinated Pesticides and PCB Analysis

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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

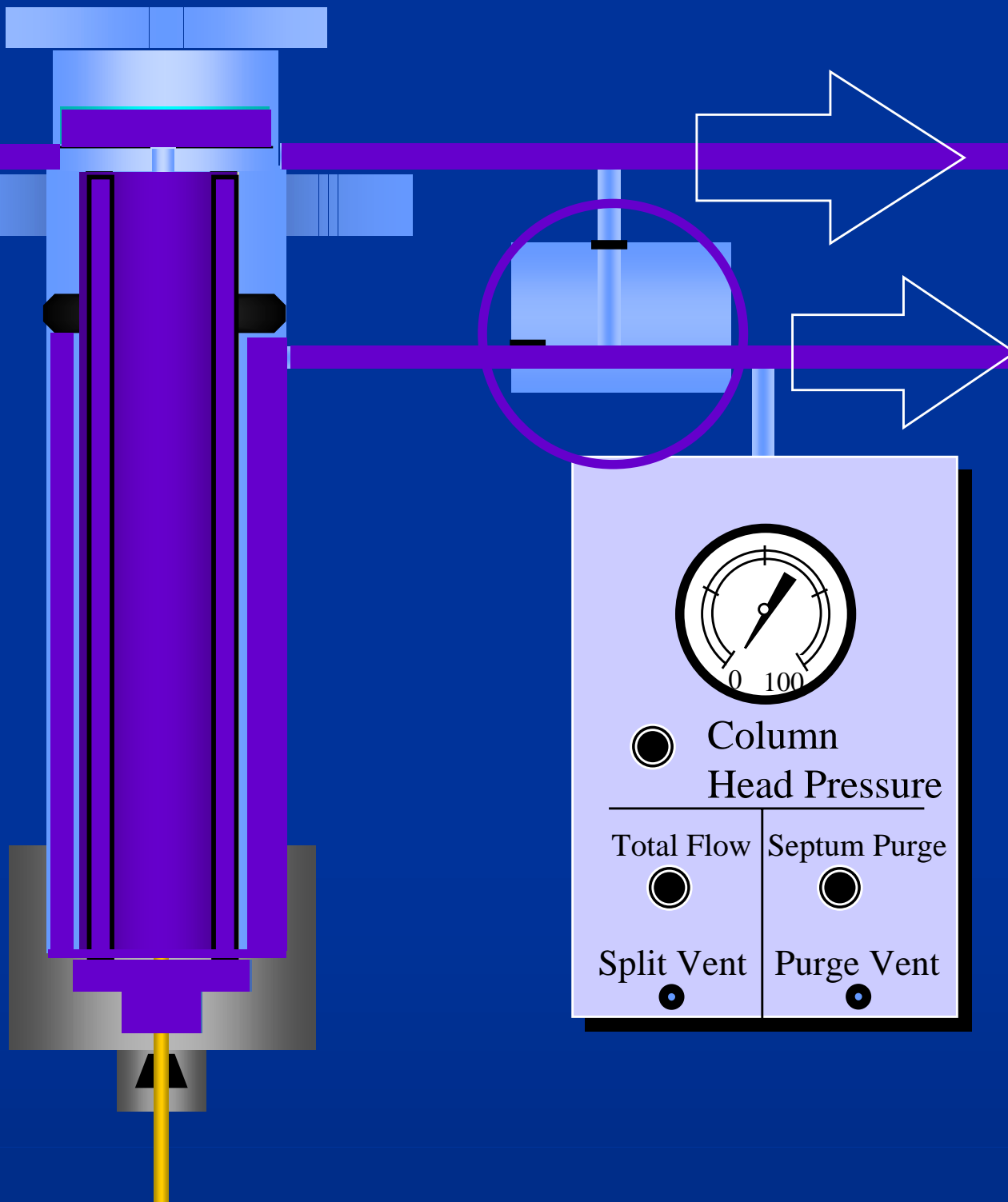
- Important aspects of injector
 - Flow pattern
 - Hold time
 - Sample Vaporization
 - Liners
 - Activity
 - Endrin/DDT breakdown

Split/Splitless Injection Port



Injection Port
Components

Splitless
Injection



Factors Affecting Splitless Injection

1. Hold Times

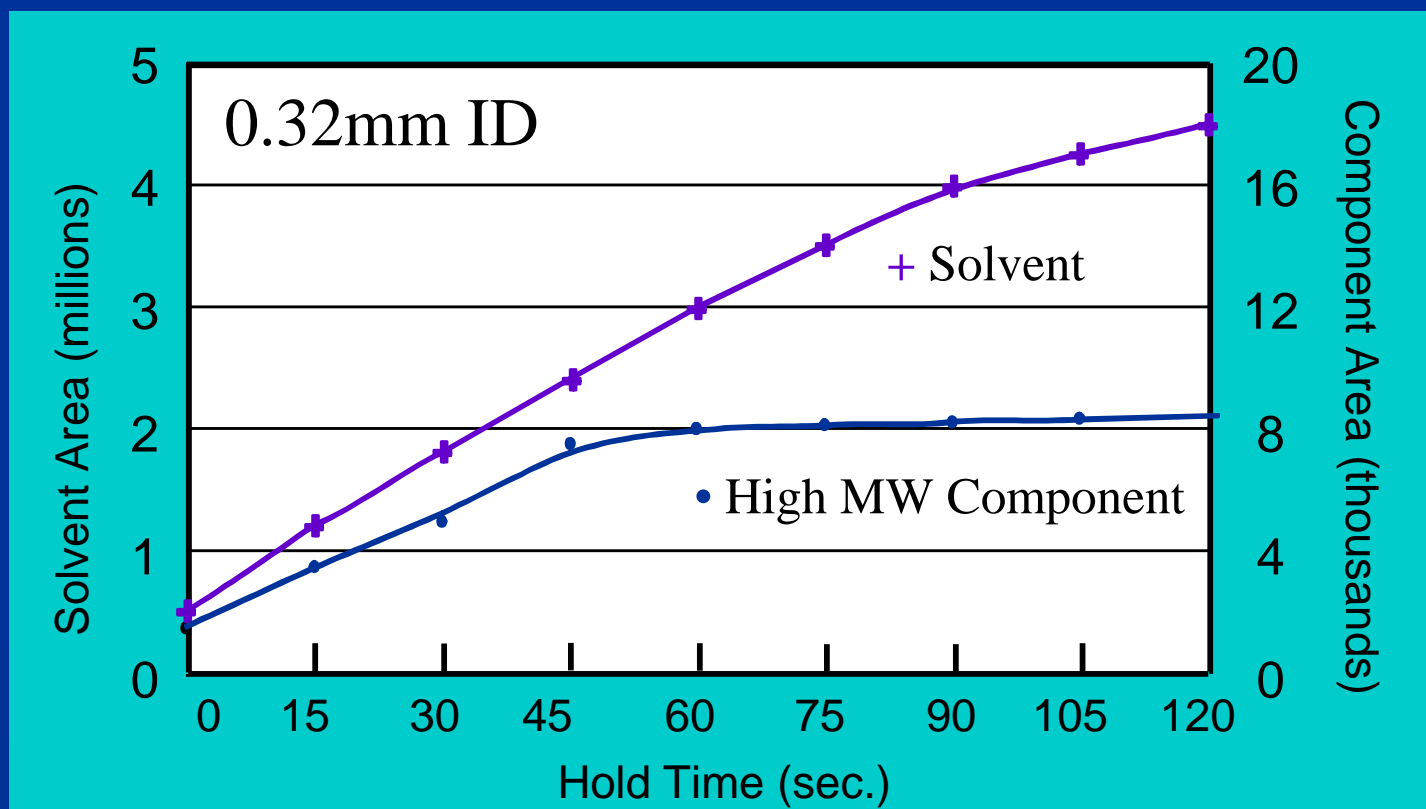
Column ID (mm)	Column Flow Rate (cc/min.) He	Approx. Hold Time
0.18	0.3	3 min
0.25	0.7	1.5 min
0.32	1.2	45 sec
0.53	2.6	30 sec

*Determine
this
empirically*

Note: based on a 2 μ L injection volume of CH₂Cl₂ = 0.8 mL sample expansion value @ 250°C & 10 psig.

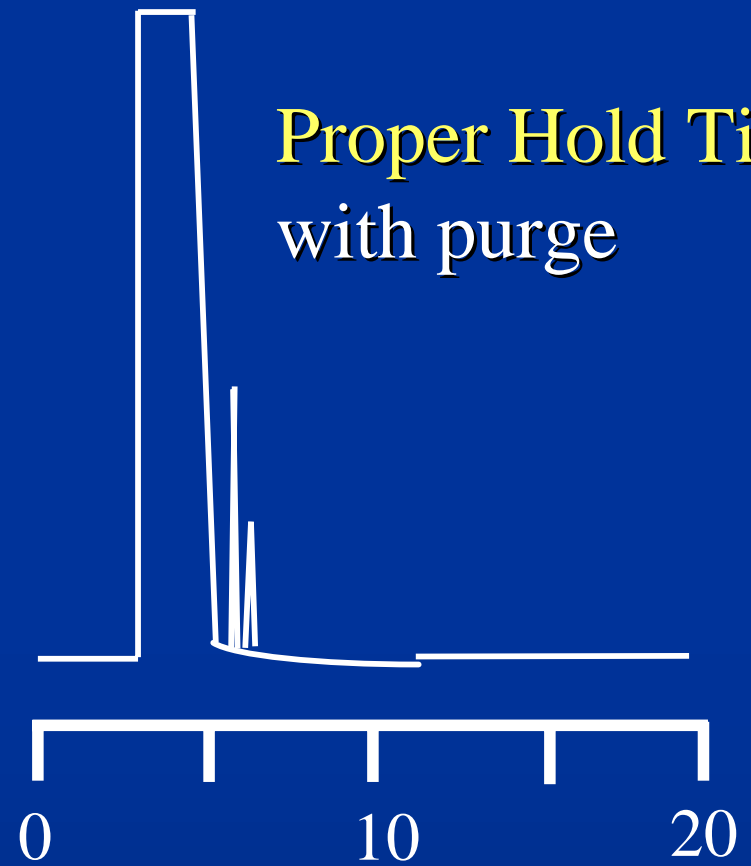
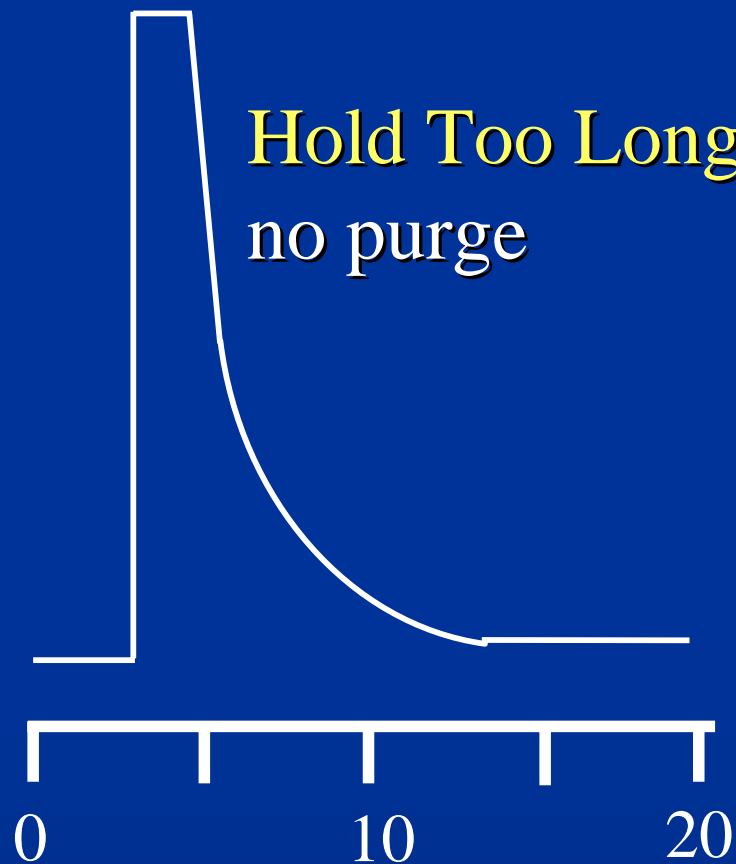
Factors Affecting Splitless Injection

1. Hold Time Optimization



Factors Affecting Splitless Injection

1. Hold Times



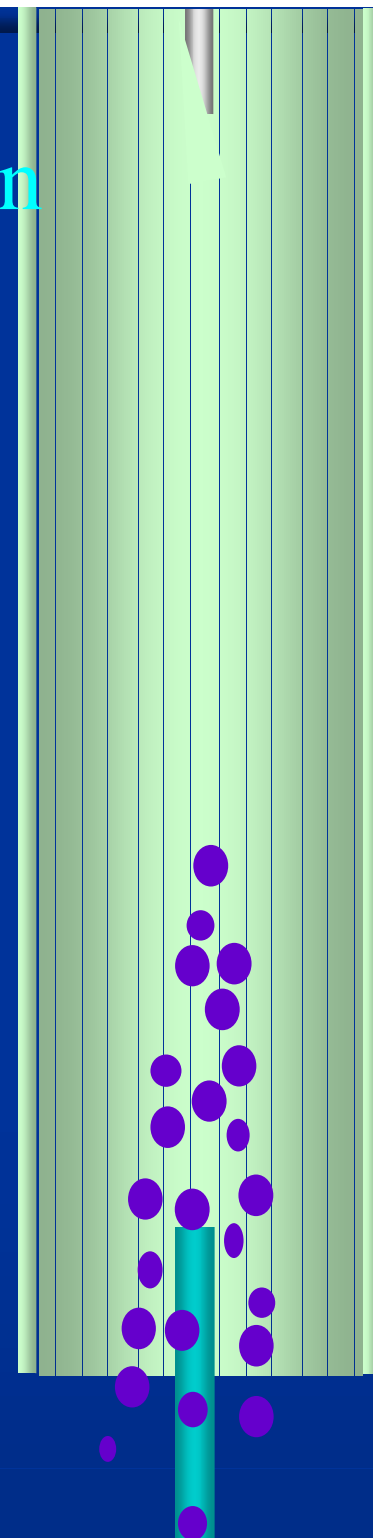
Time (min)

Factors Affecting Splitless Injection

3. Sample Vaporization

Fast Autosampler :
Incomplete vaporization

Aerosols or droplets reach the
column instead of vapors



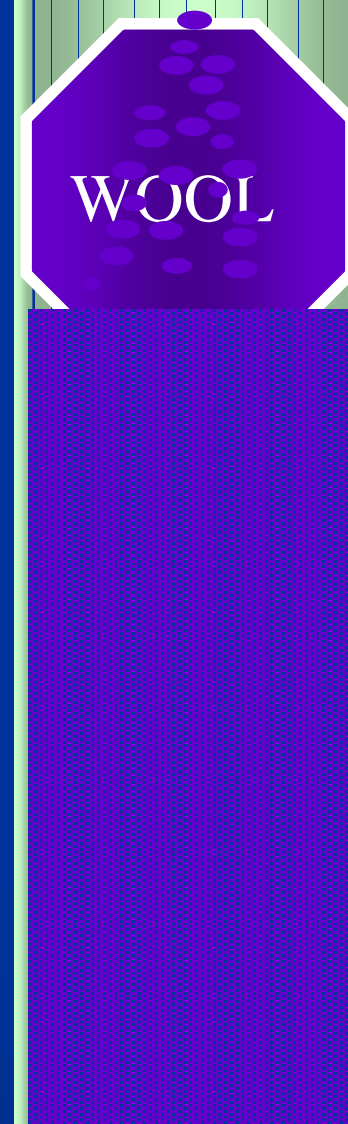
Factors Affecting Splitless Injection

3. Sample Vaporization

Fast Autosampler :

Pack with wool or CarboFrit™

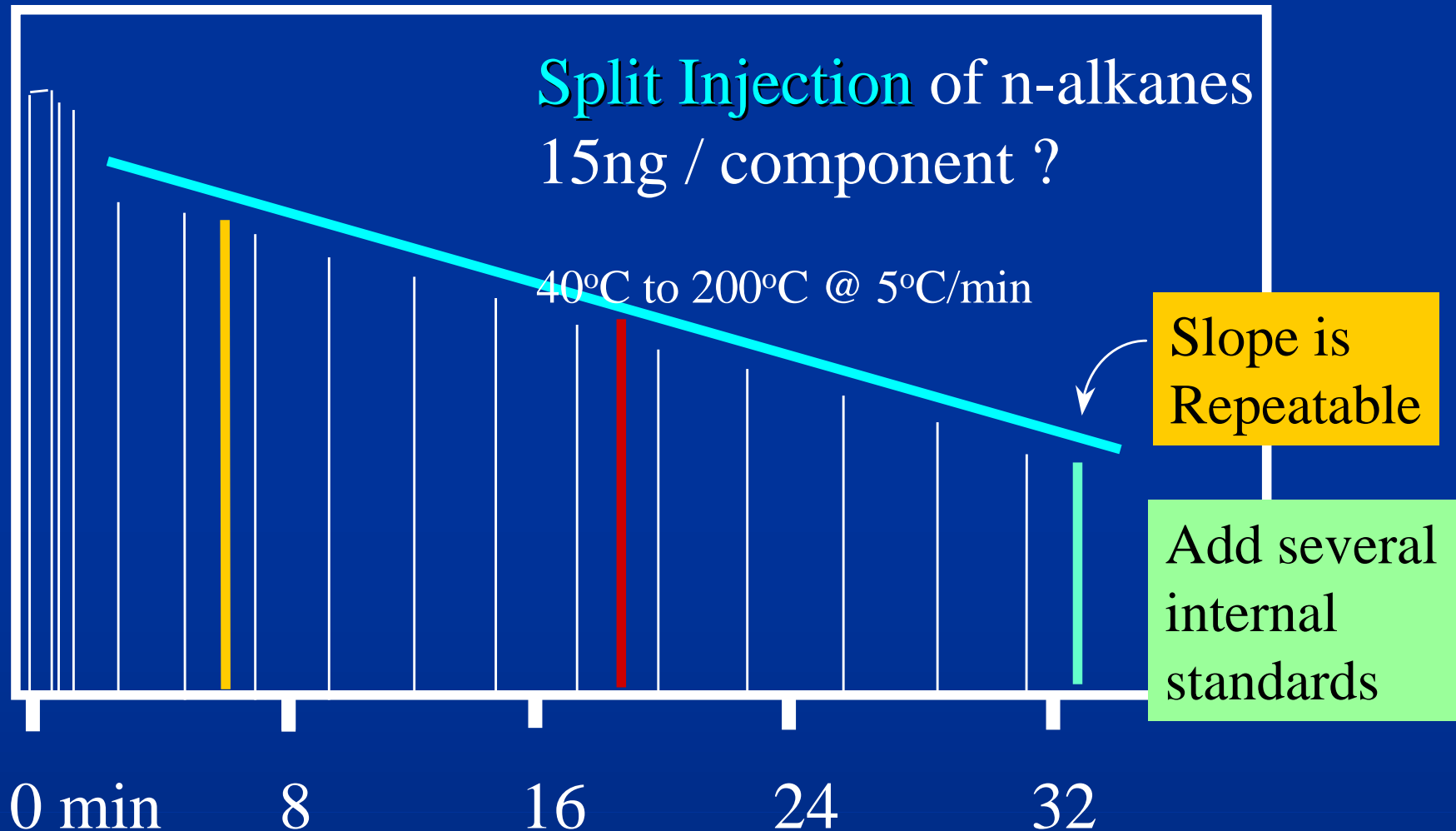
STOPS AEROSOLS COMPLETELY



II. Splitter Discrimination

Molecular Weight Discrimination

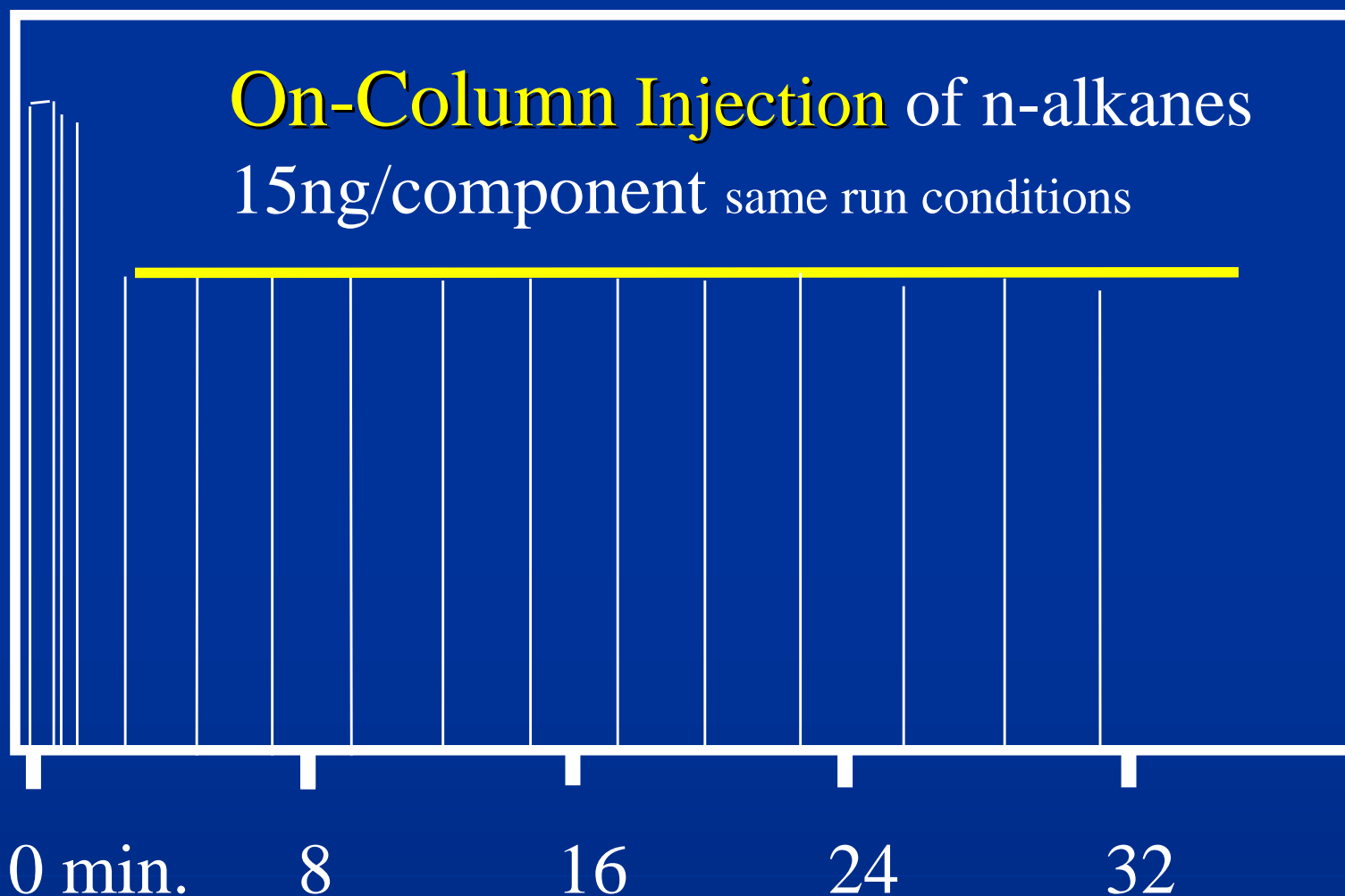
Rtx-1: 30m, 0.32mm ID, 0.25 μ m



II. Splitter Discrimination

No Molecular Weight Discrimination

Rtx-1: 30m, 0.32mm ID, 0.25 μ m



Splitless Liner Designs

Straight



Gooseneck



Double
Gooseneck



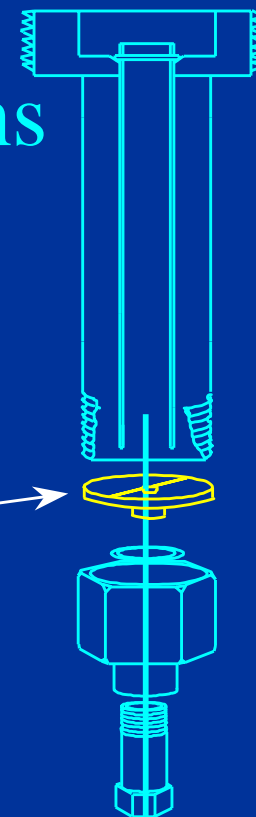
Cyclo Double-
Gooseneck



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

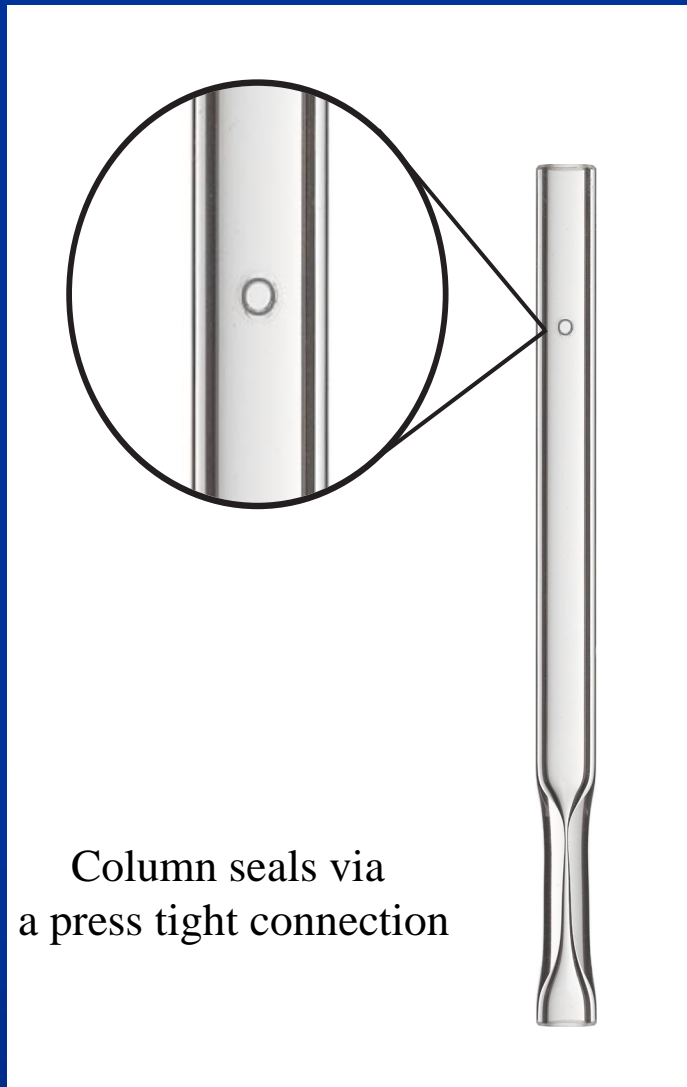
Types of Surface Treatments



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

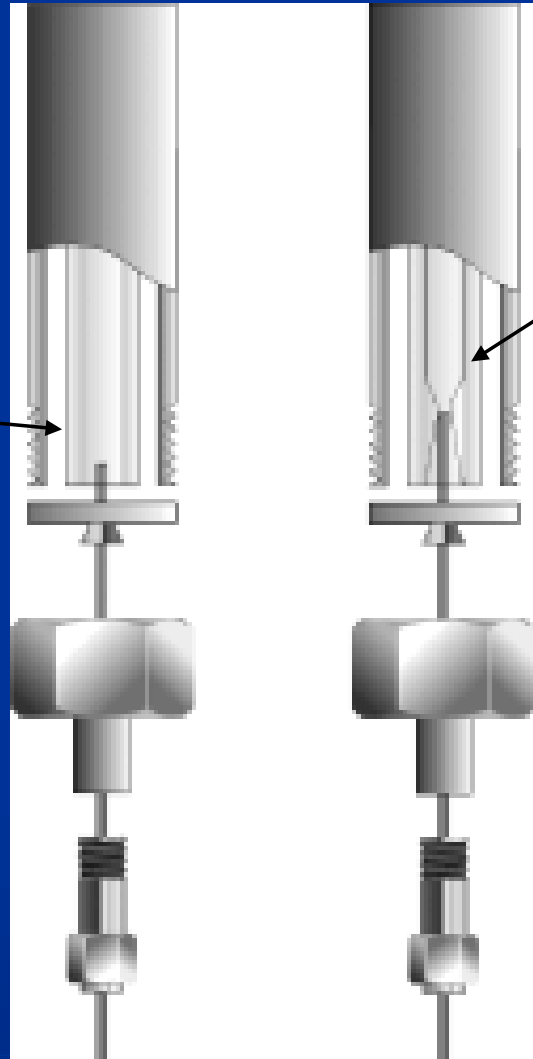
Drilled Uniliner



- 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

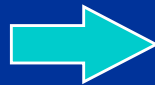
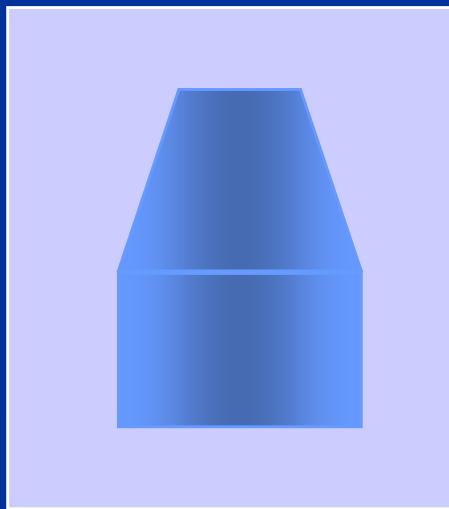
Press-fit
connection

Direct Injection Mode

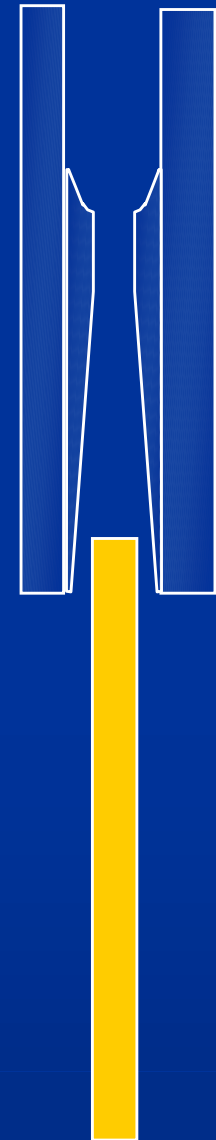
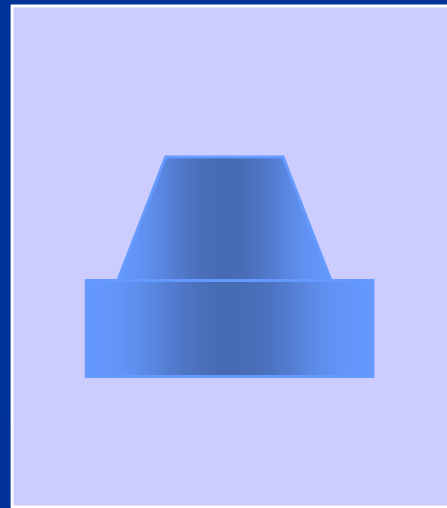
Making the proper press-fit connection

1. Pre-seat or pre-crush new ferrules

New Ferrule



Pre-seated Ferrule

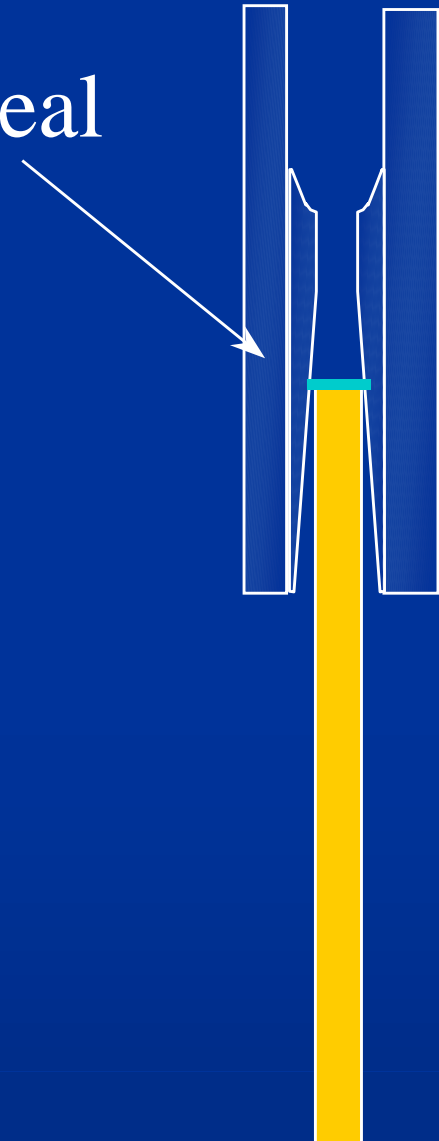


Direct Injection Mode

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



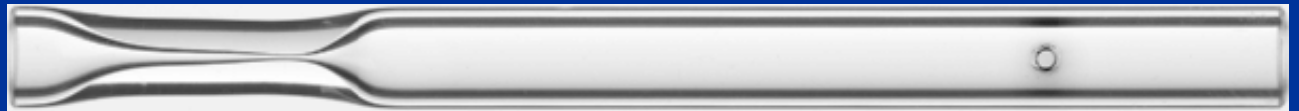
Cyclo
Uniliner®



Standard
Uniliner®

Drilled Uniliners

4mm
IP deactivated



4mm
Siltek deactivated



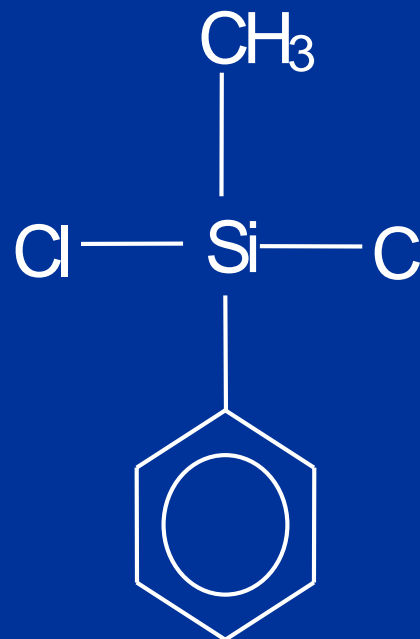
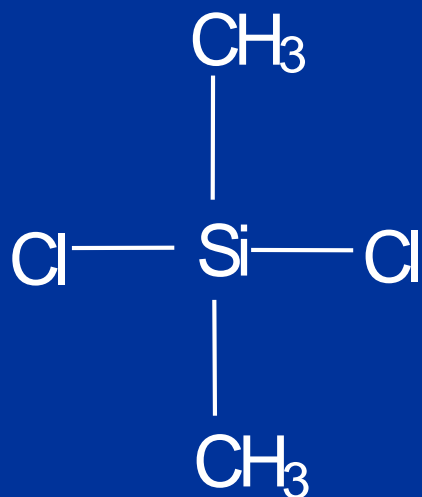
2mm
Siltek deactivated



Inlet Liner Deactivation

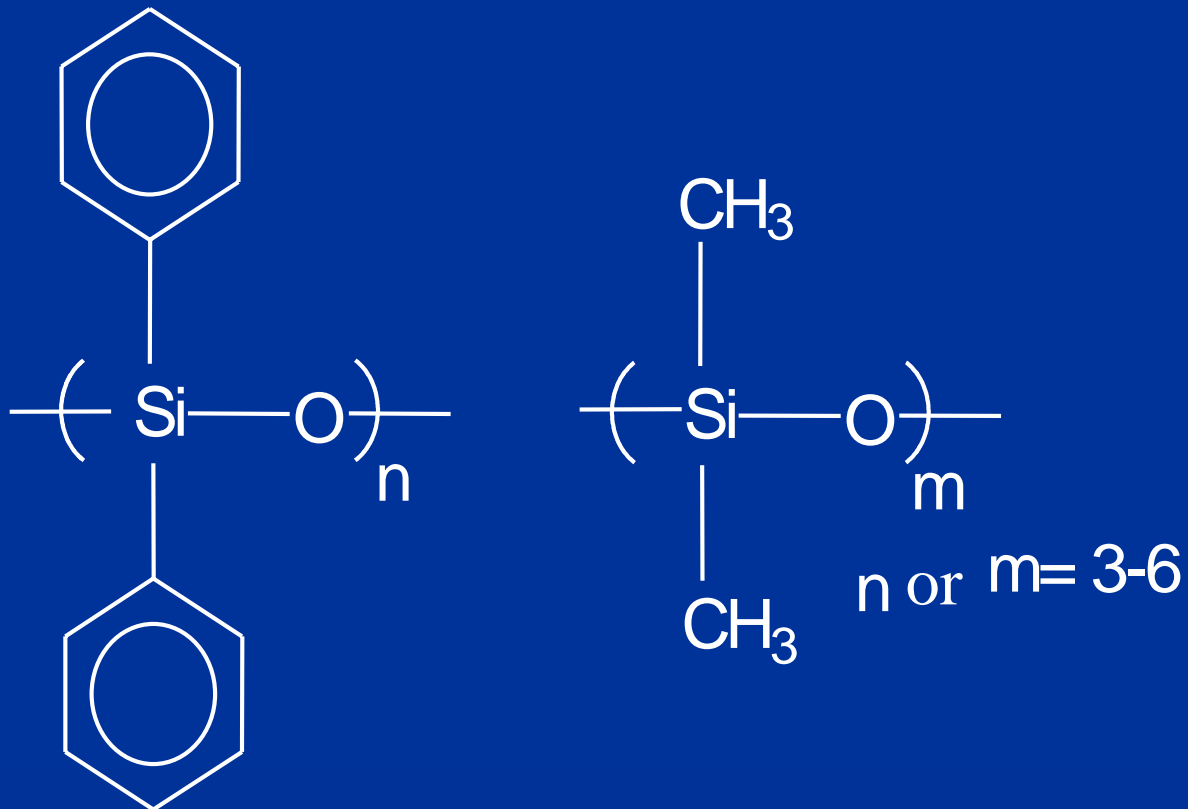
- “Pinpoint” deactivation
 - Chloro-silanes
- Polymeric deactivation
 - “IP” deactivation
- Surface modification
 - Siltek

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

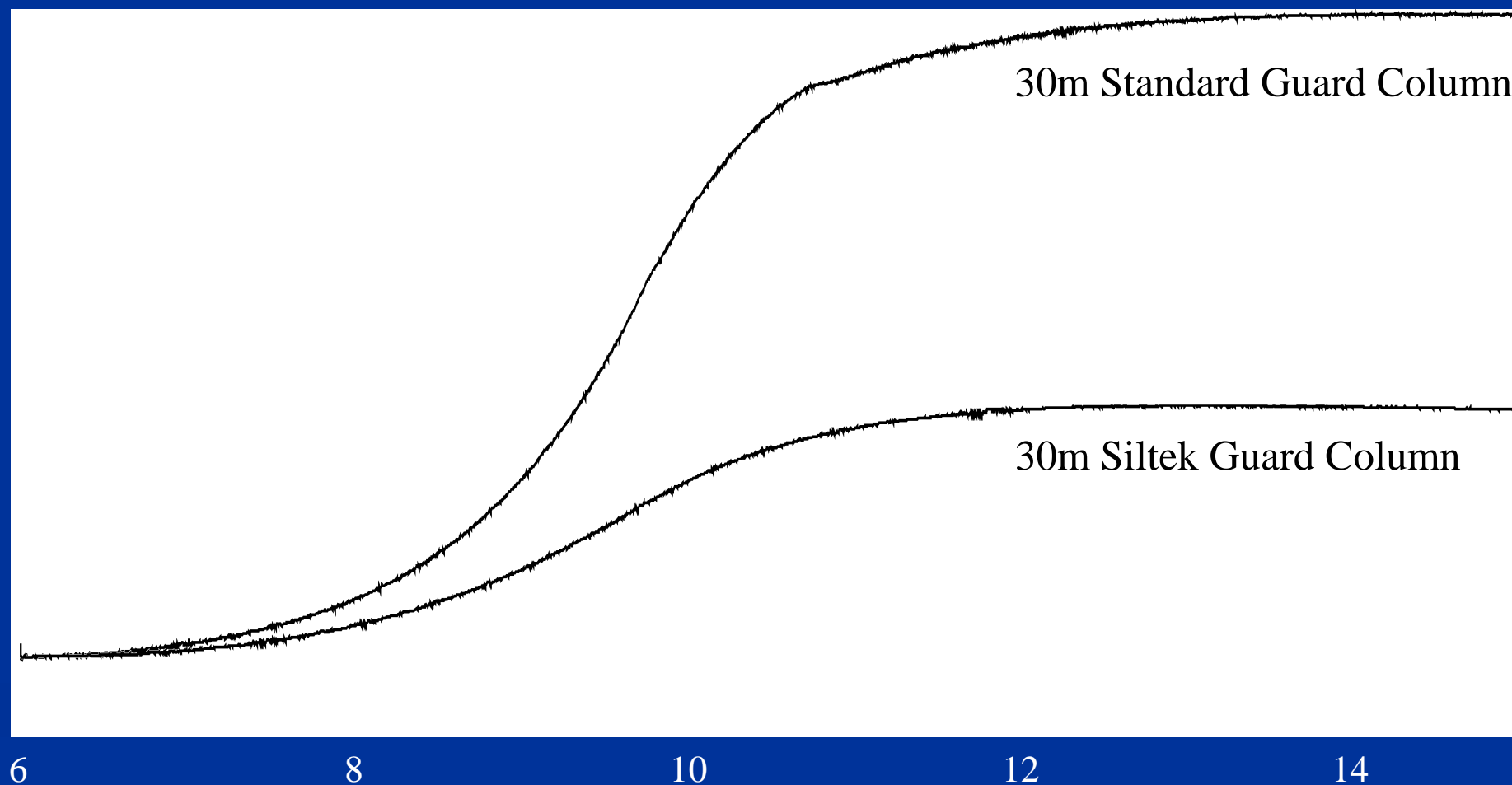
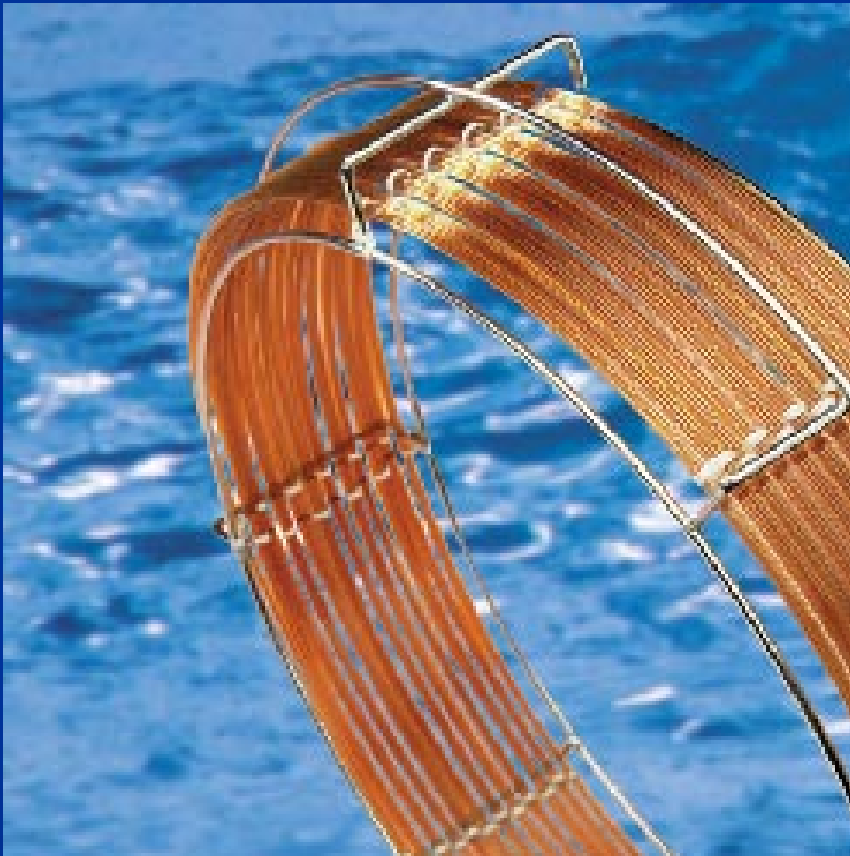


Figure 8

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



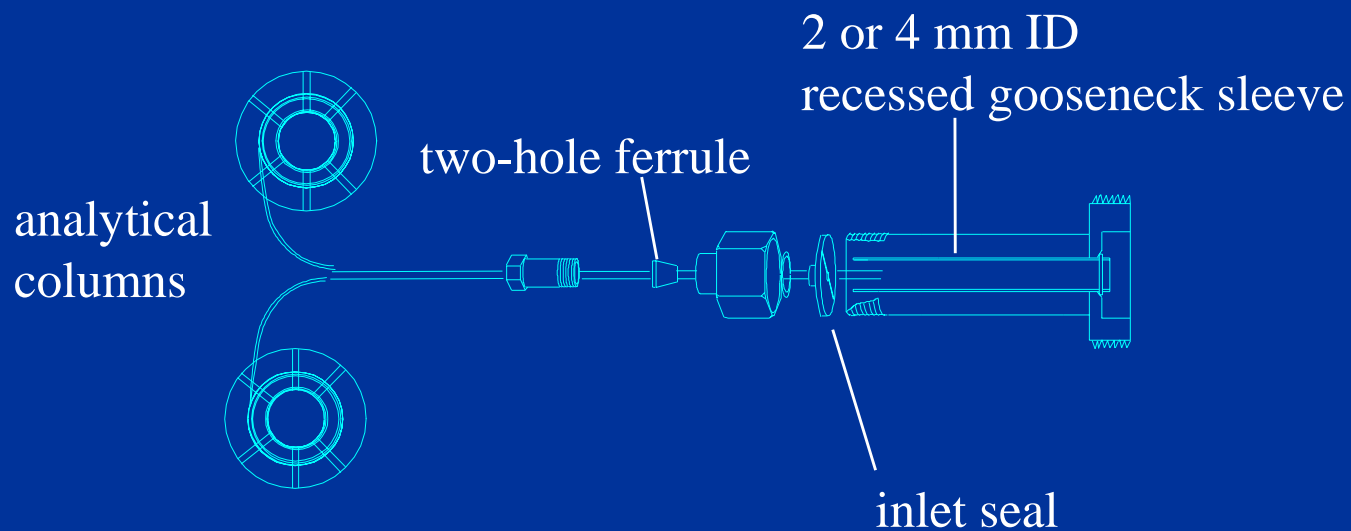
- Utilizes columns of different selectivity
- Changes elution order and retention times for components
- Improves qualitative reliability
- Can be done simultaneously to increase sample throughput

Typical Column Pairings

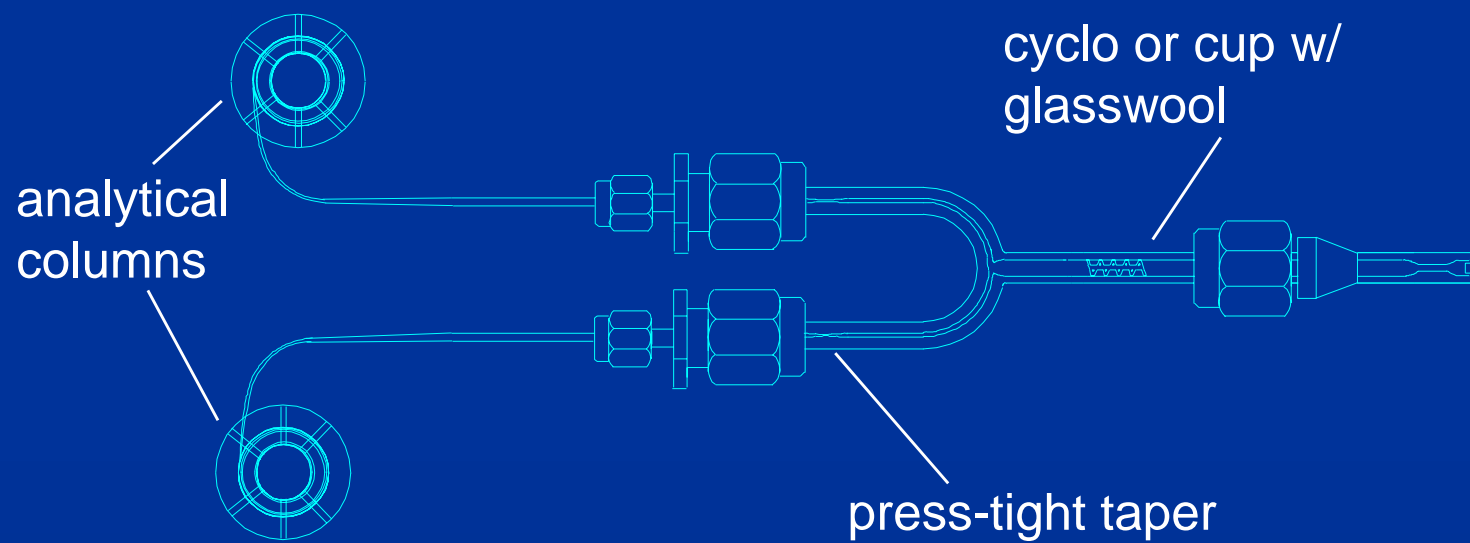
- Rtx-5 and Rtx-50
 - Good resolution, runs typically greater than 25 minutes
- Rtx-1701 and Rtx-35
 - Good resolution, activity problems on 1701 polymer, runs typically greater than 25 minutes
- Rtx-CLP1 and Rtx-CLP2
 - Best resolution and run times less than 15 minutes
- Dimensions
 - Length: 15, 30,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

Dual Column Fitting

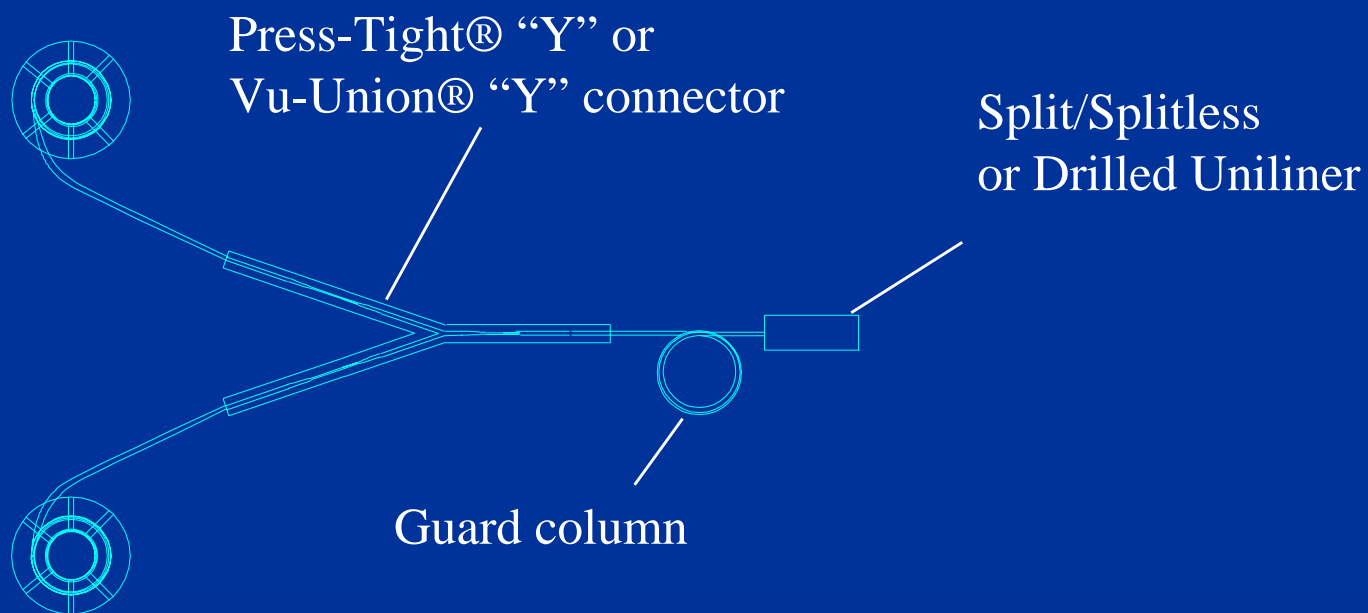
With a Two-Hole Ferrule for Split Inlets



Dual Column "T"



Dual Column Injection



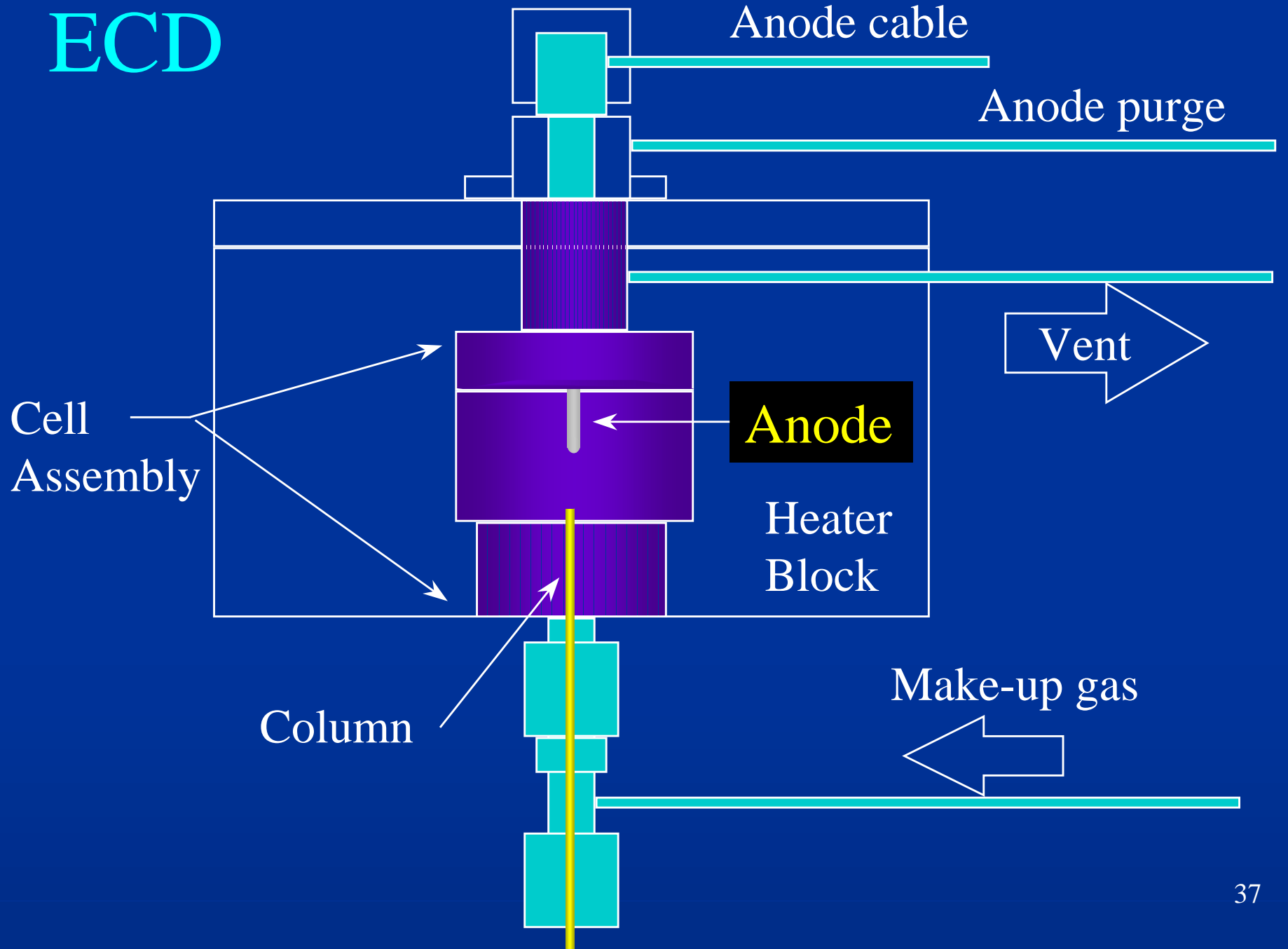
ECD – General Information

- 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

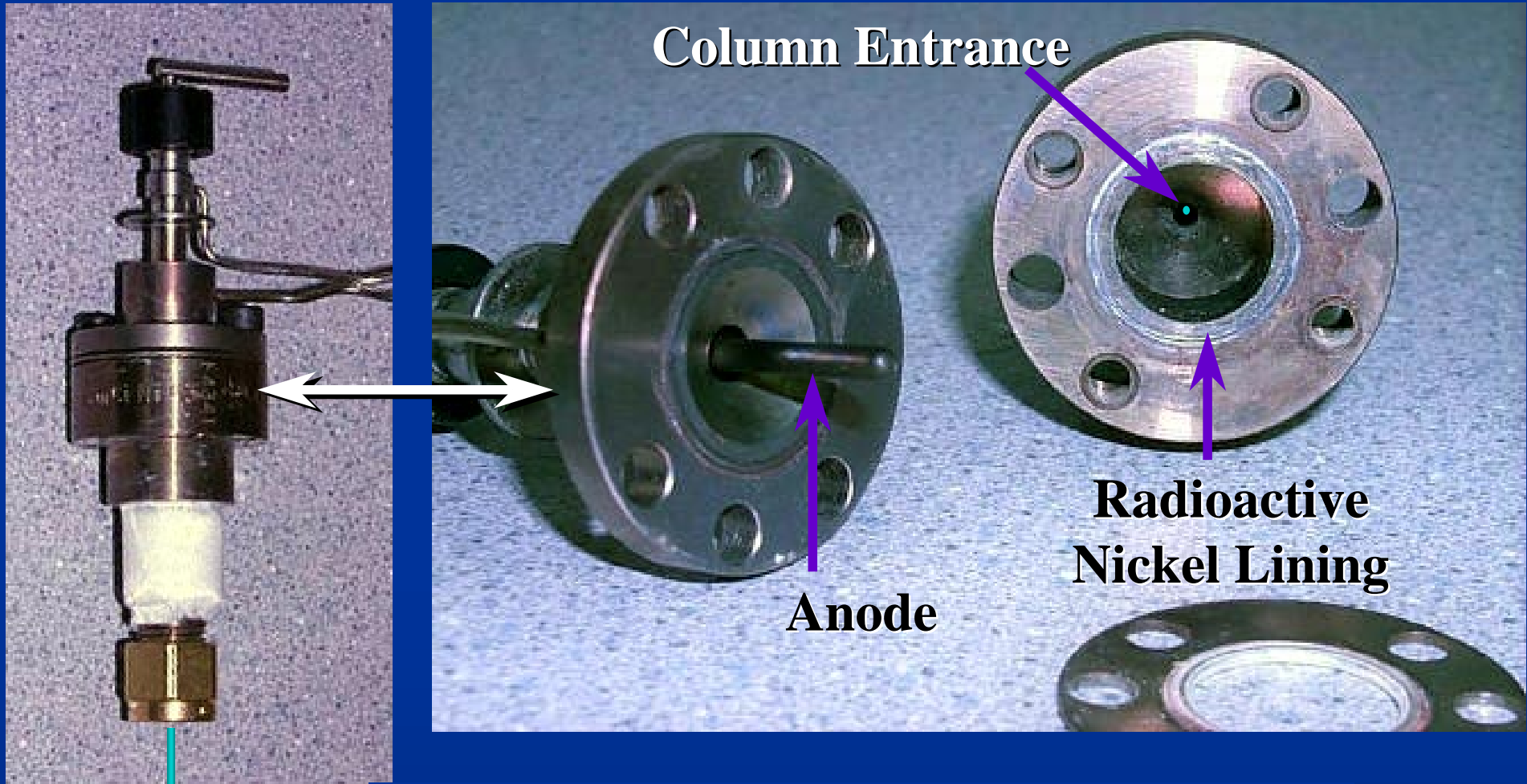
ECD Response Relative to Hydrocarbons

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

ECD



ECD – Cell Disassembly



Do not disassemble without proper permit.

ECD

- 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

Rtx-CLPesticides2

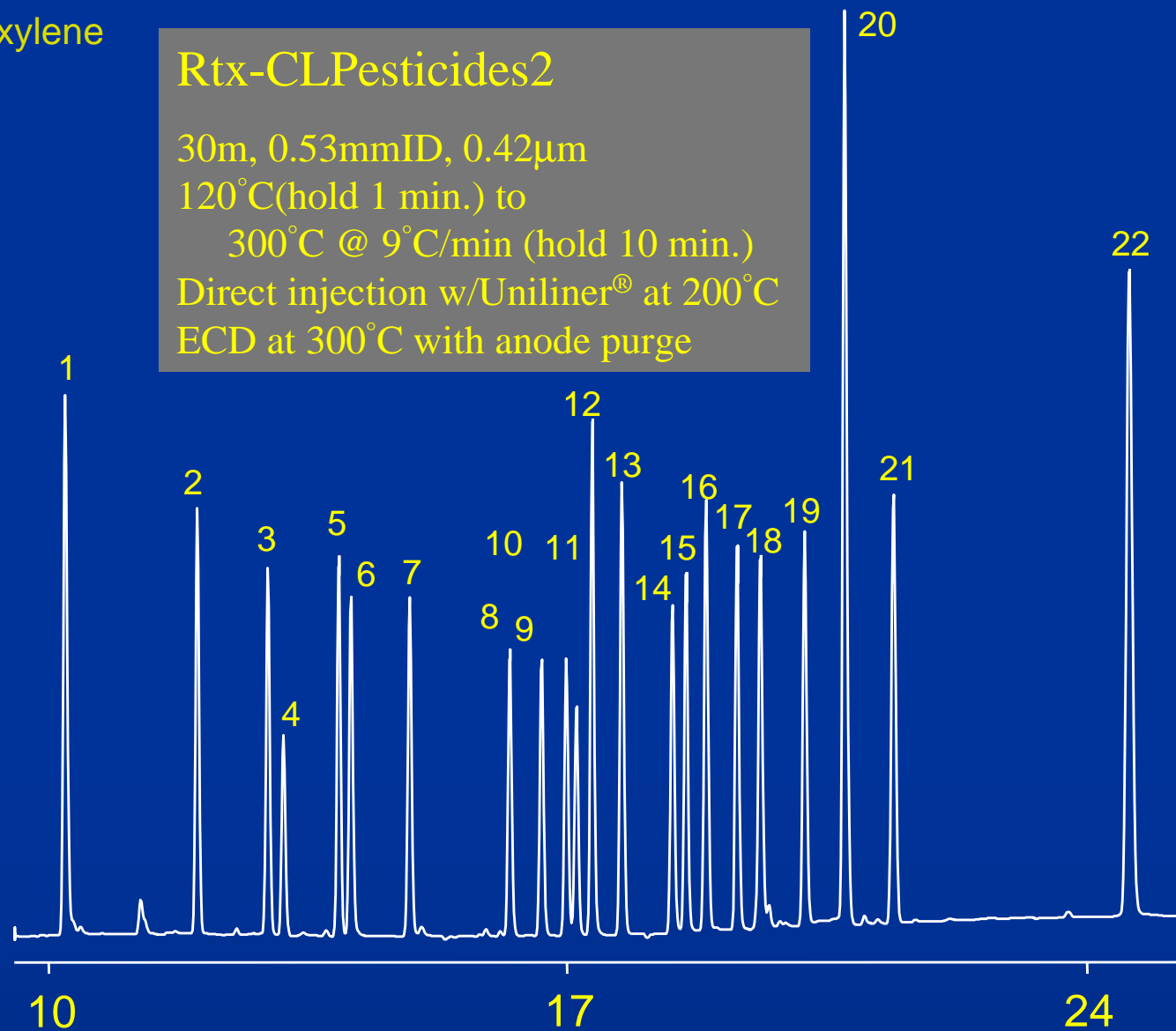
30m, 0.53mmID, 0.42 μ m

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

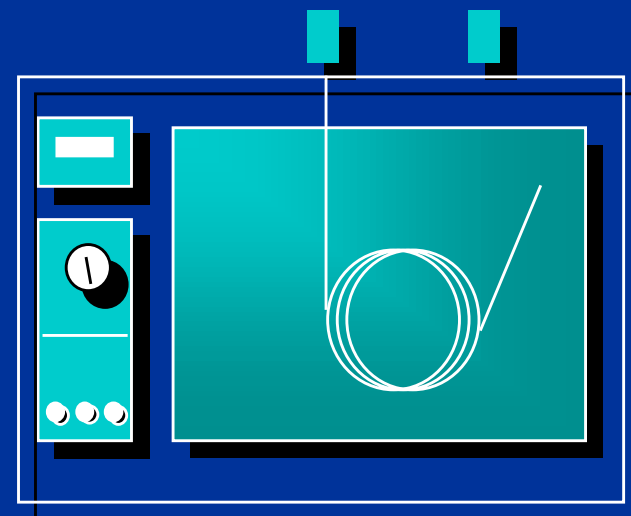
ECD Operating Briefs

- 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!



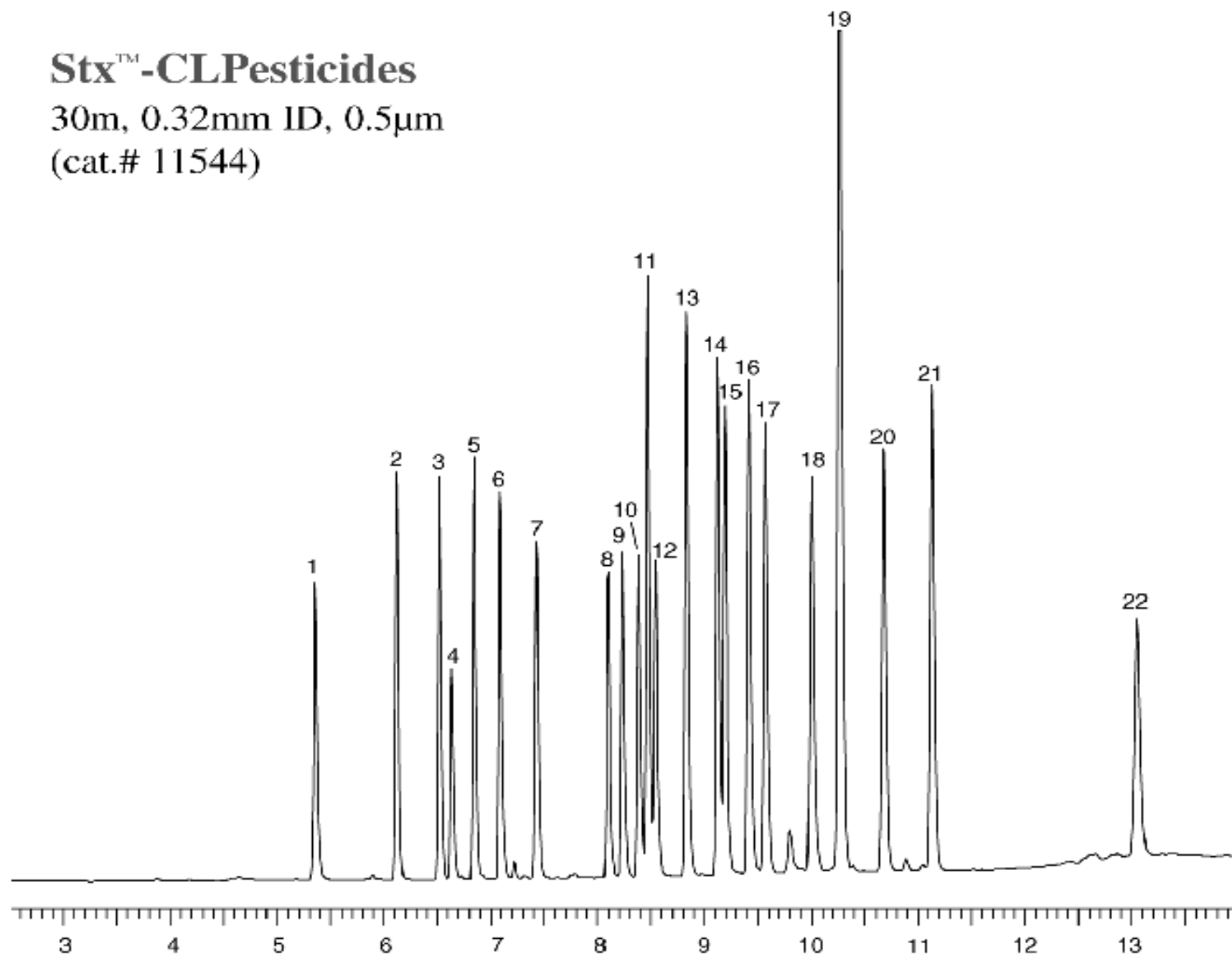
ECD Maintenance

- 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

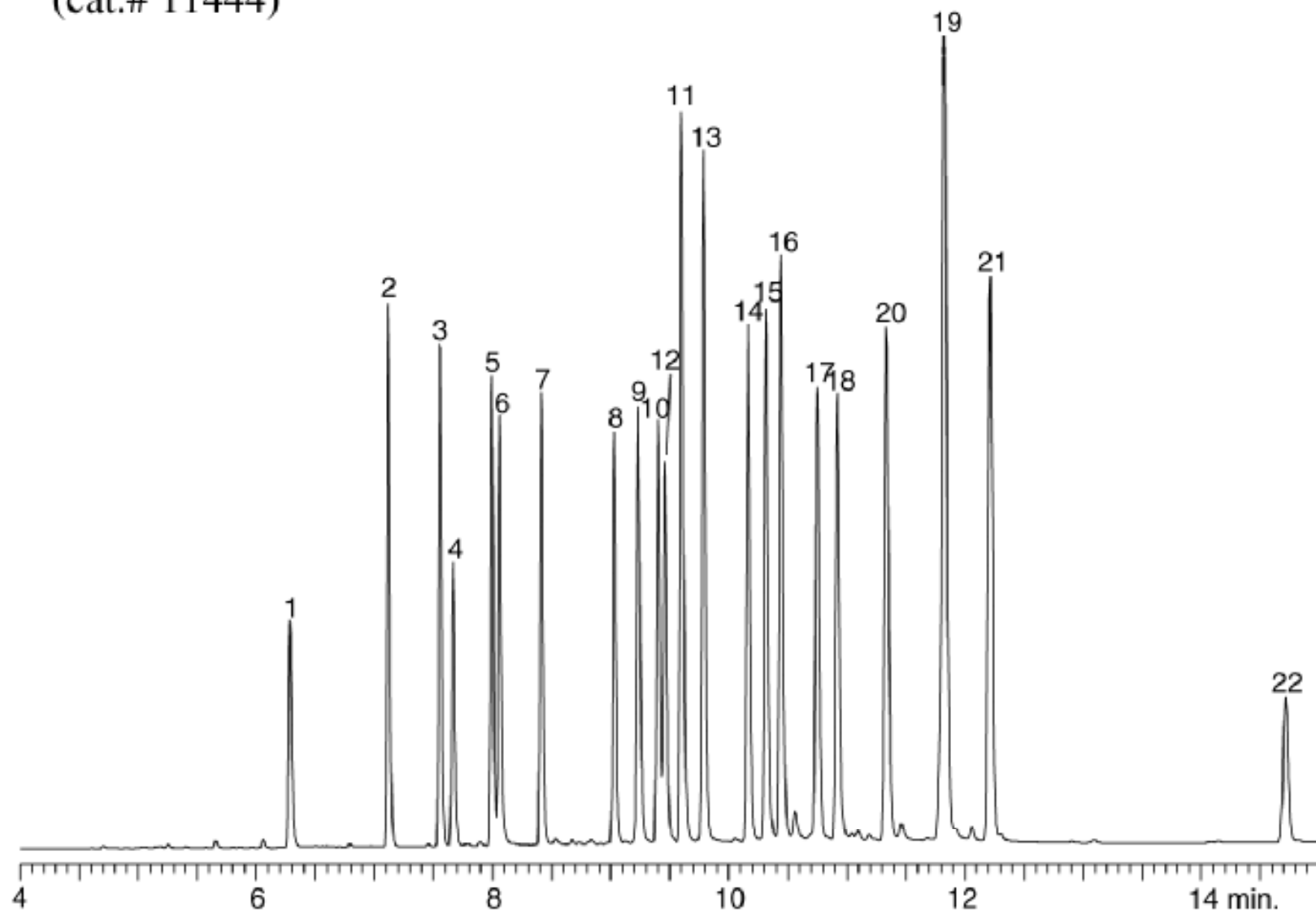
(cat.# 11544)



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

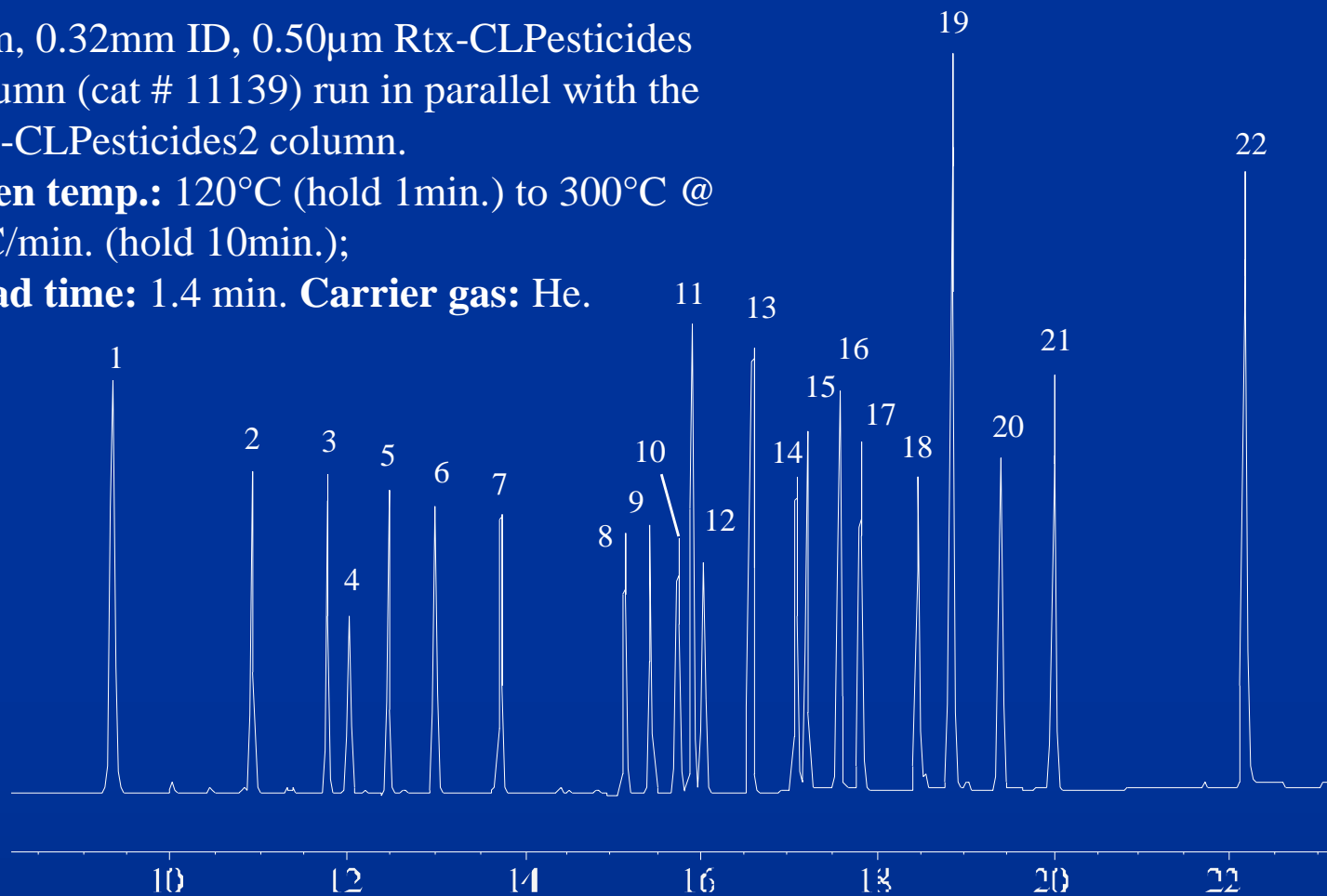
Make-up gas: nitrogen

Rtx-CLPesticides

30m, 0.32mm ID, 0.50 μ 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.

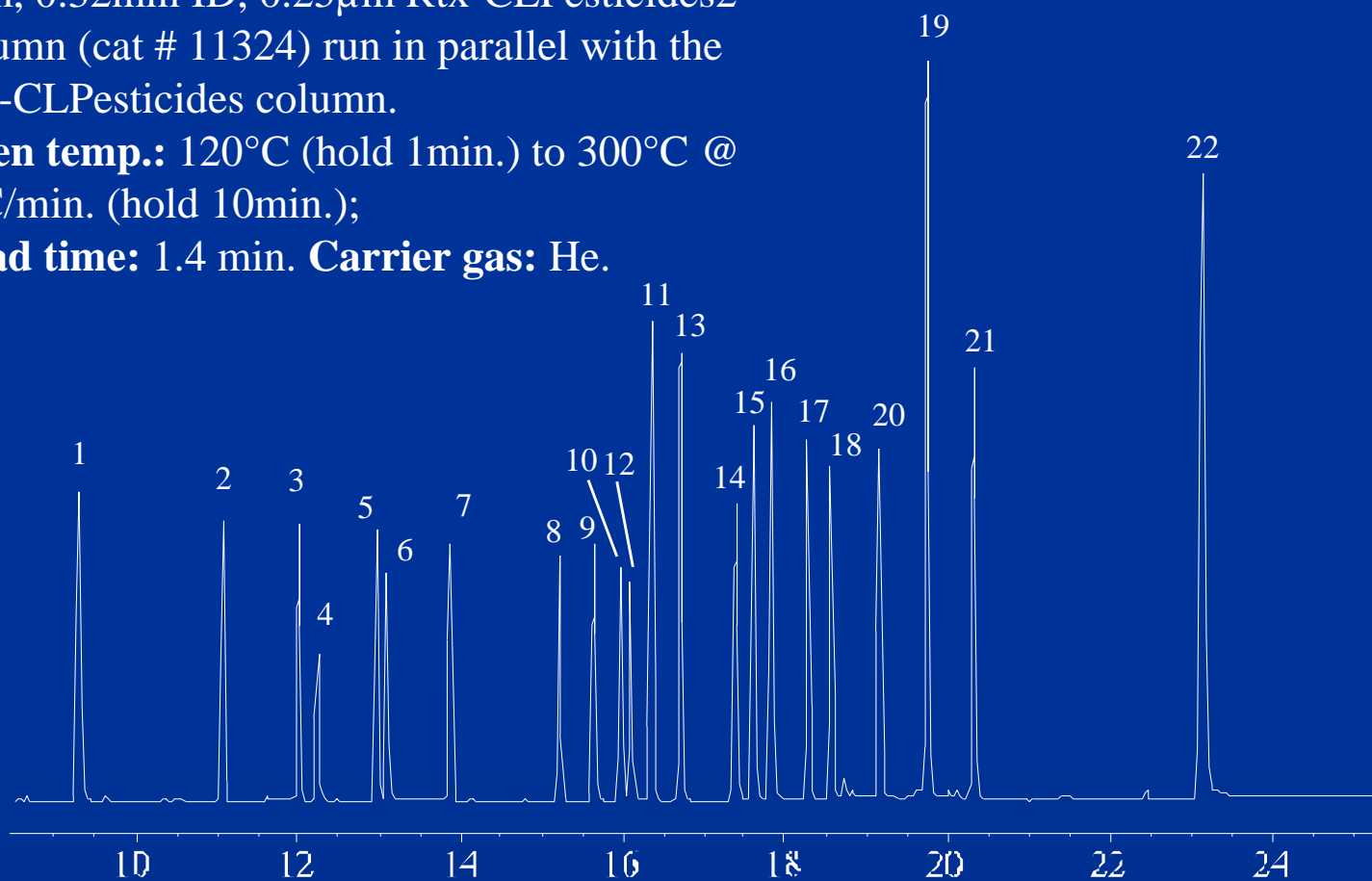


Rtx-CLPesticides2

30m, 0.32mm ID, 0.25 μ 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.

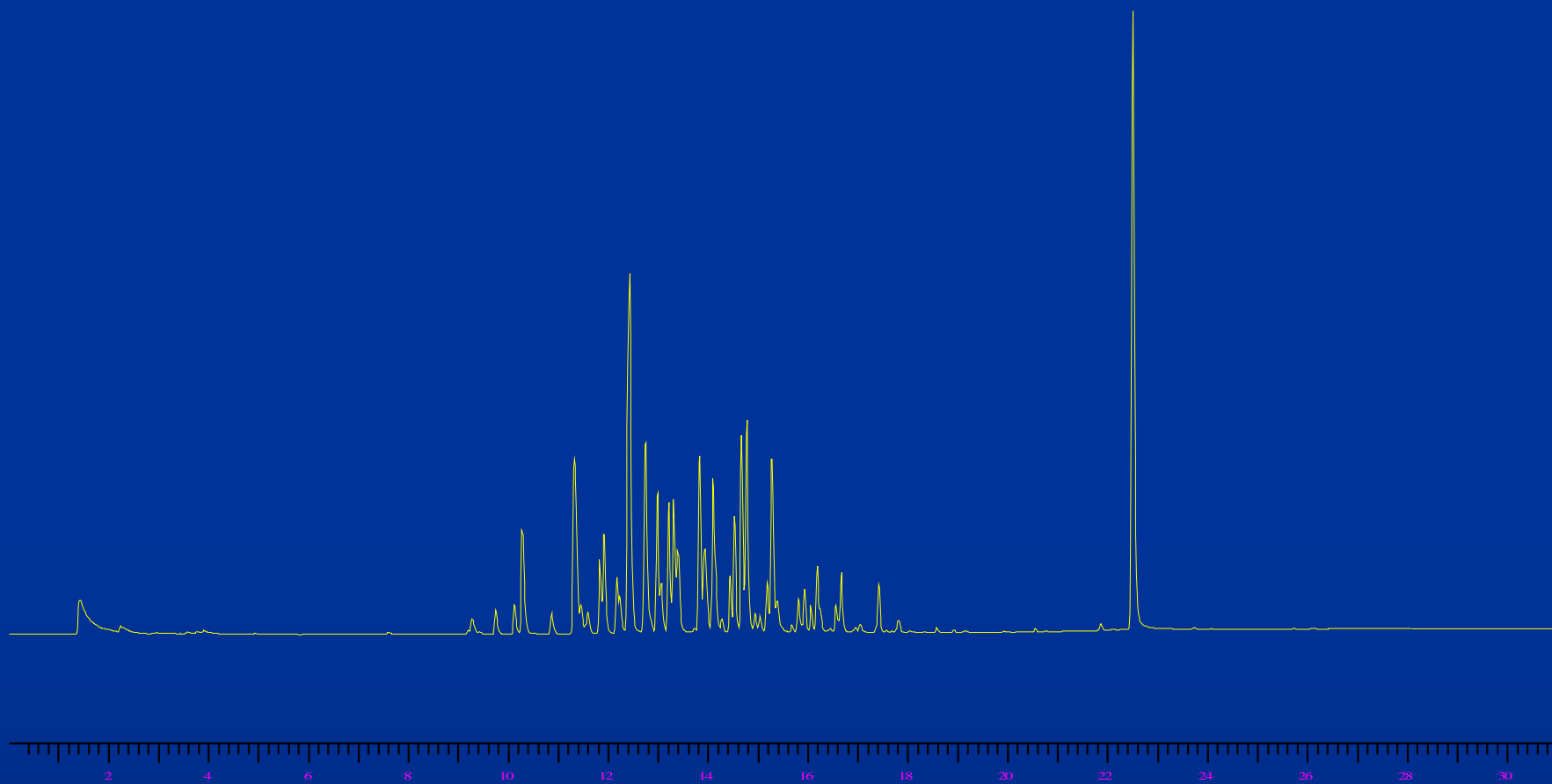


EPA Method 8080 Pesticides

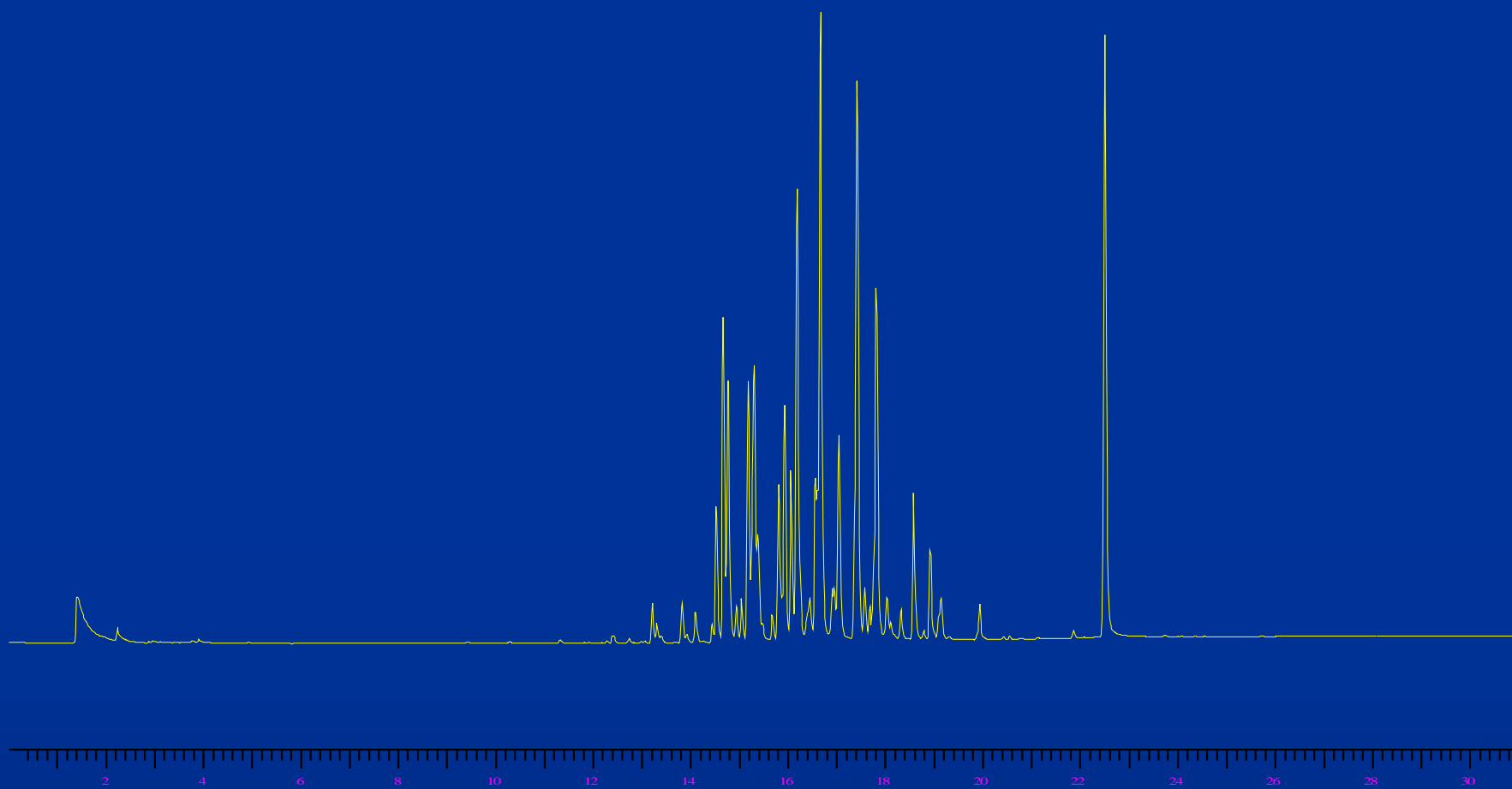
1. 2,4,5,6-tetrachloro-m-xylene
2. α -BHC
3. γ -BHC
4. β -BHC
5. δ -BHC
6. heptachlor
7. aldrin
8. heptachlor epoxide
9. γ -chlordane
10. α -chlordane
11. 4,4'-DDE
12. endosulfan I
13. dieldrin
14. endrin
15. 4,4'-DDD
16. endosulfan II
17. 4,4'-DDT
18. endrin aldehyde
19. methoxychlor
20. endosulfan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

Lit. #59547 — 8081A

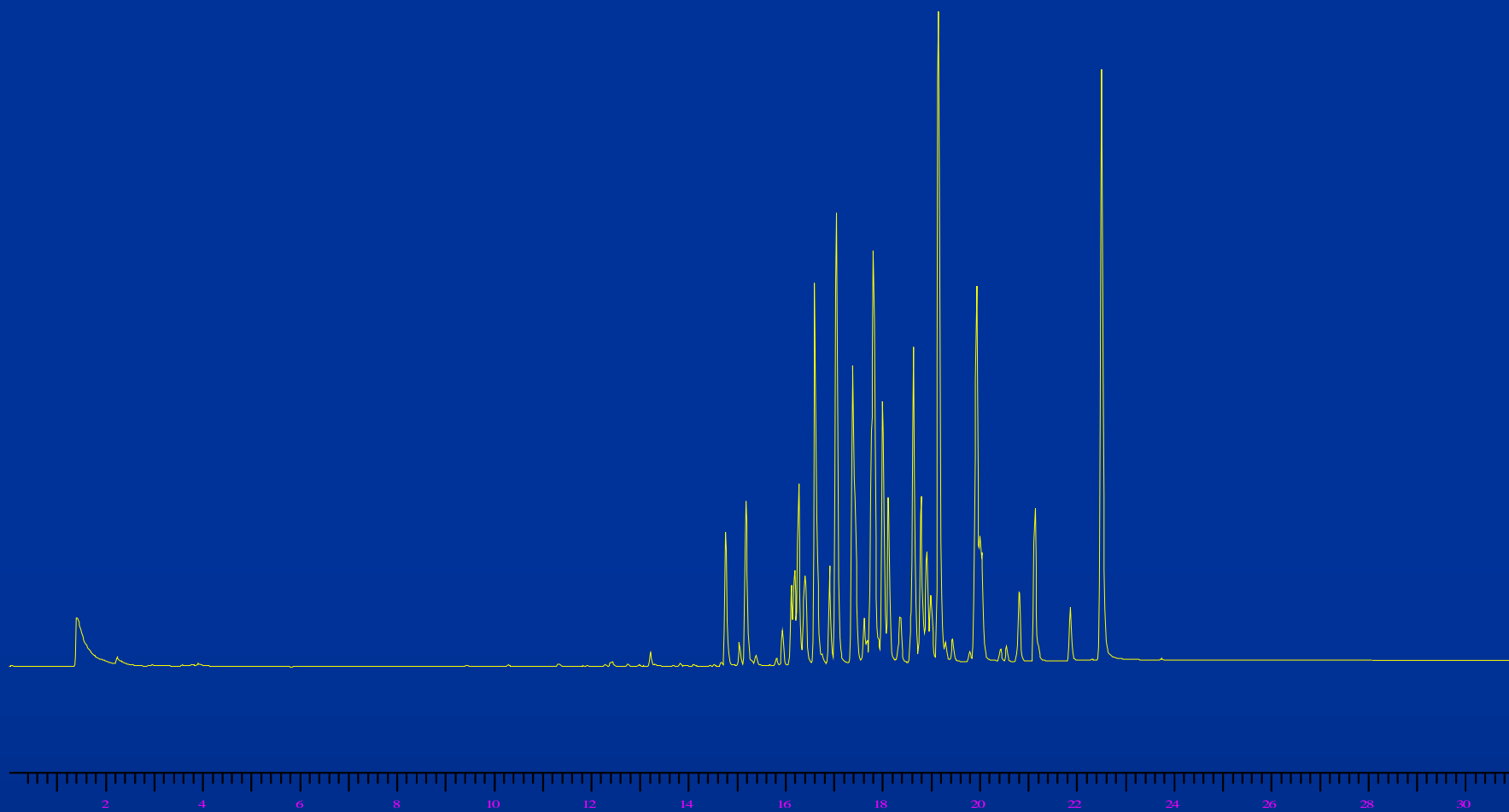
Aroclor 1242



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