

Improved Phases for the GC Analysis of Chlorinated and Organophosphorus Pesticides

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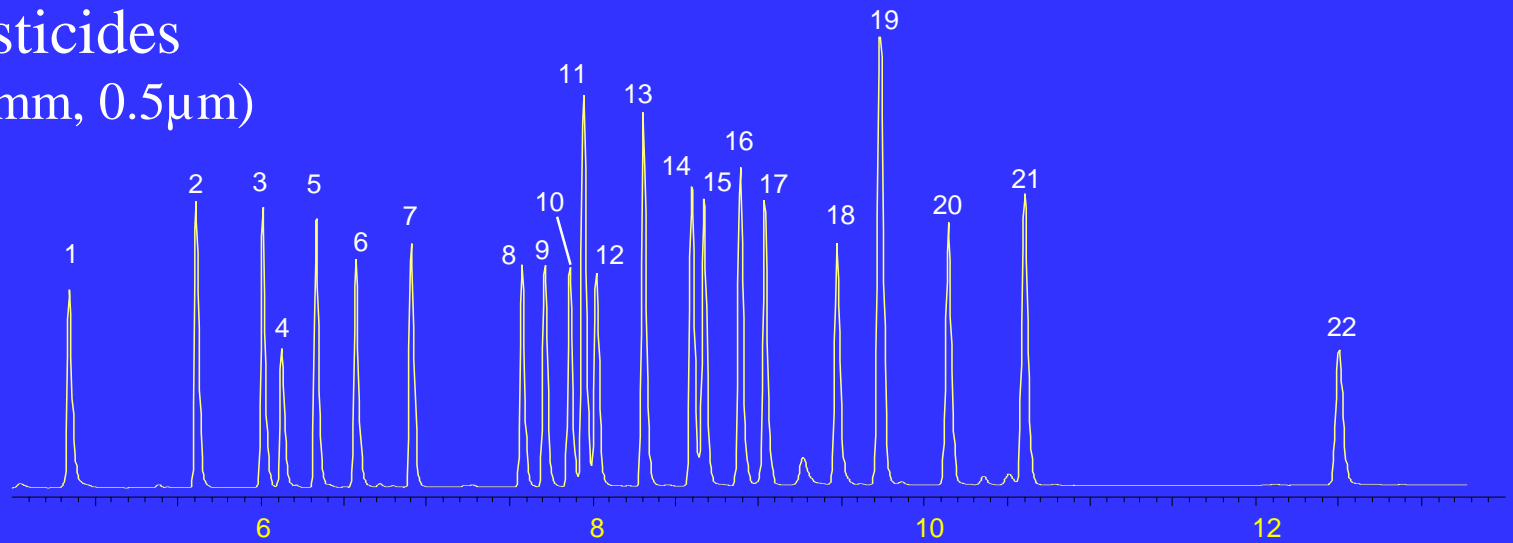
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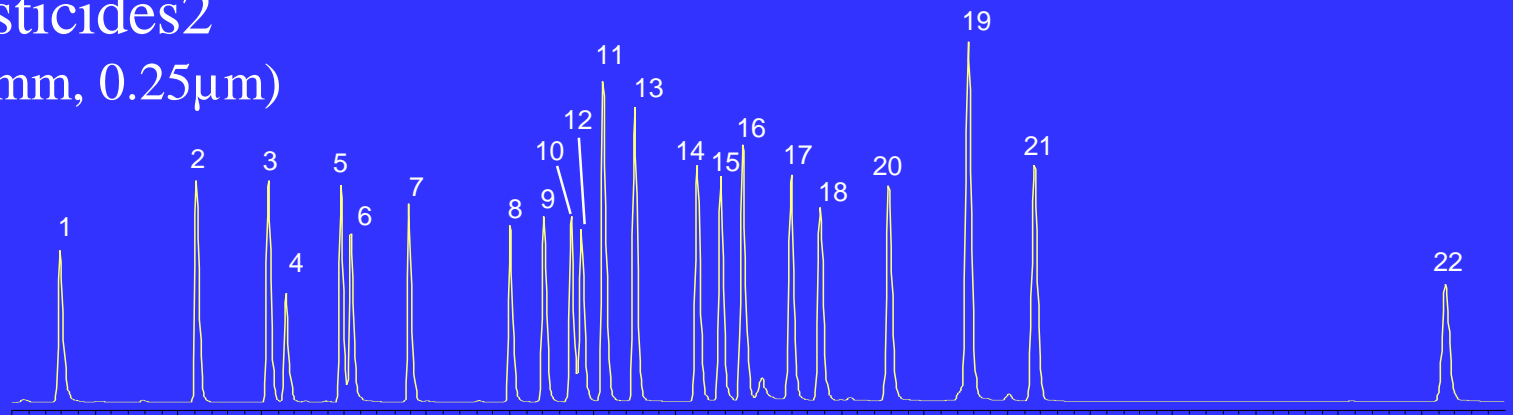
Chlorinated Pesticides

Fast Runs

Rtx-CLPesticides
(30m x 0.32mm, 0.5 μ m)



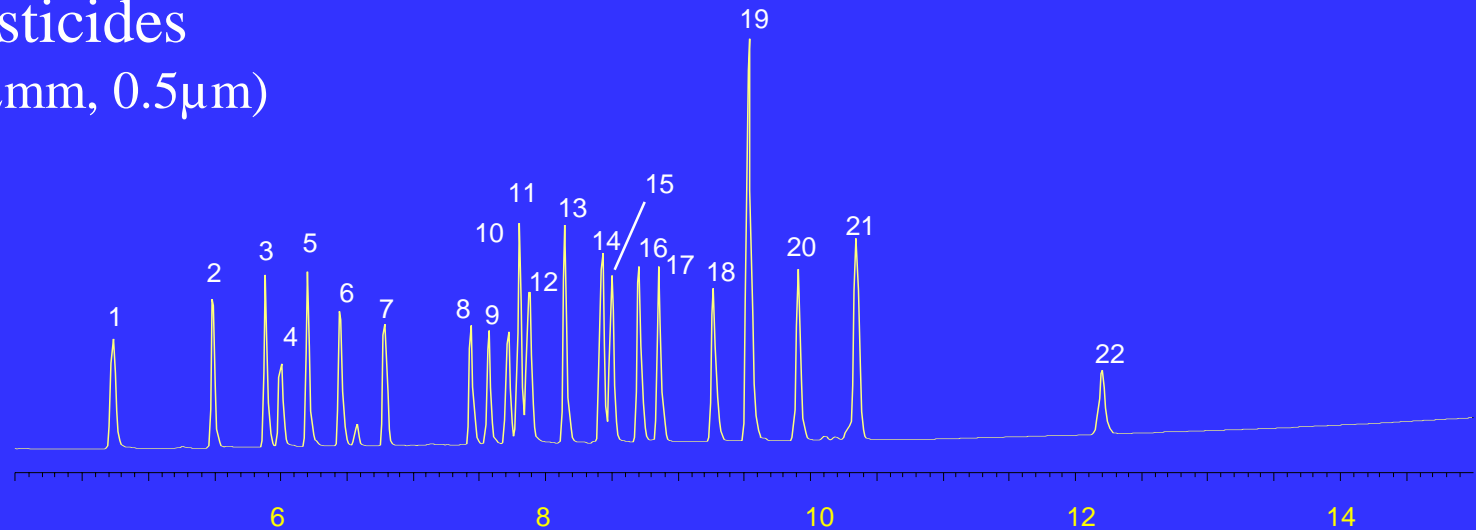
Rtx-CLPesticides2
(30m x 0.32mm, 0.25 μ m)



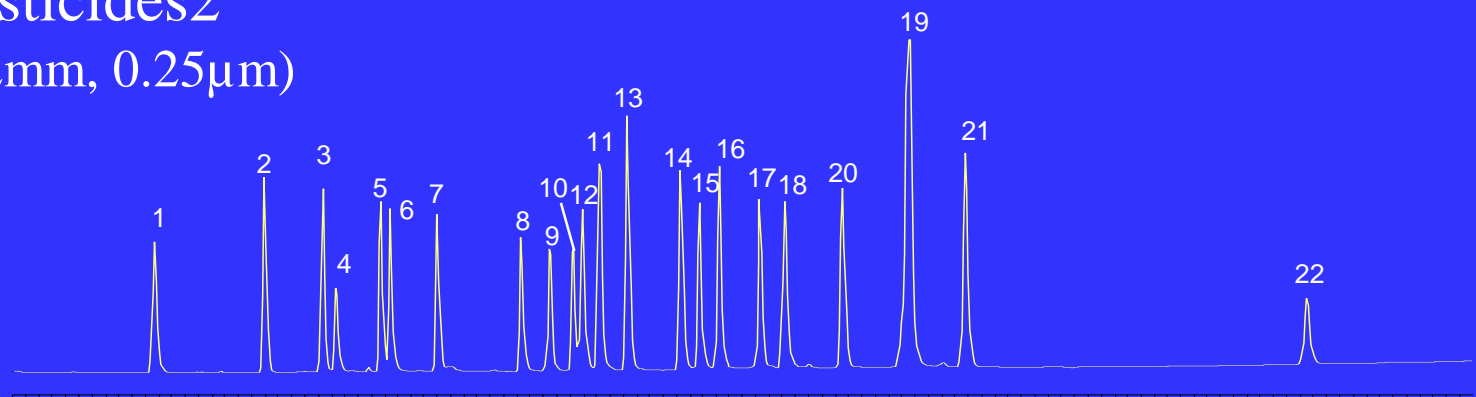
Chlorinated Pesticides

Siltek Deactivation

Stx-CLPesticides
(30m x 0.32mm, 0.5 μ m)



Stx-CLPesticides2
(30m x 0.32mm, 0.25 μ 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

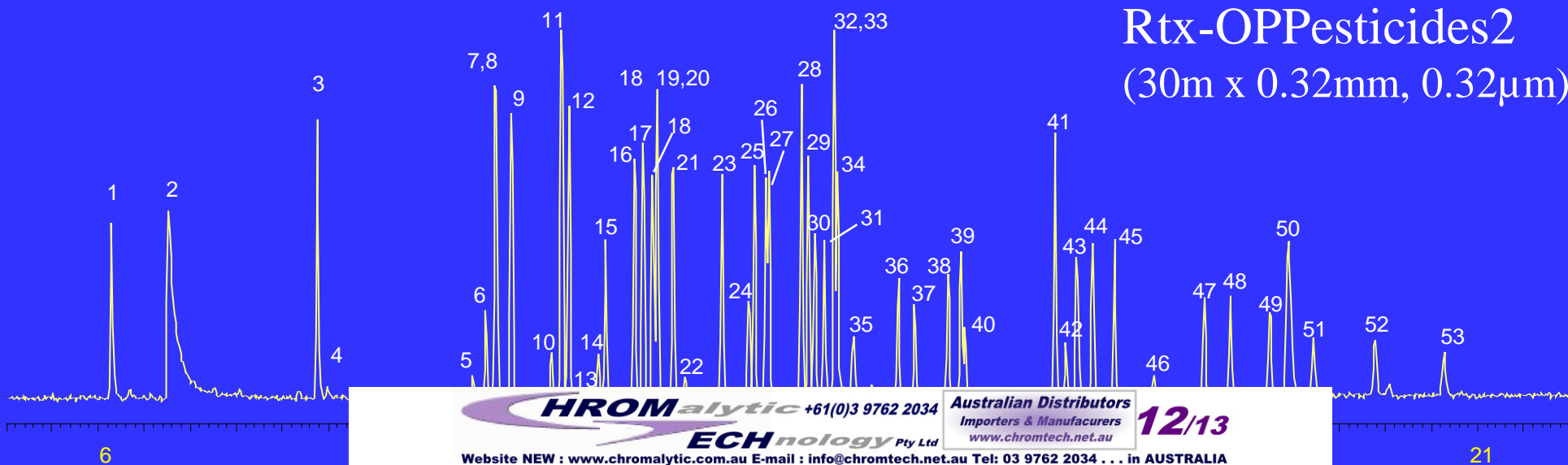
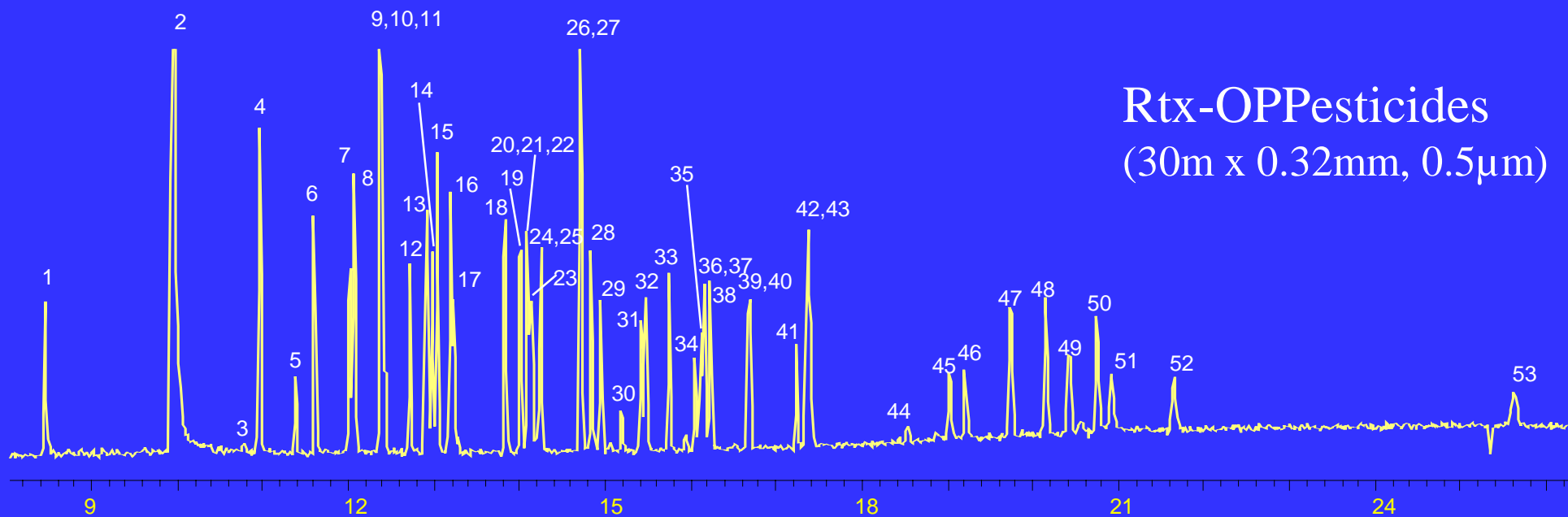
30m x 0.32ID, 0.25µm

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

Organophosphorus Pesticides



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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

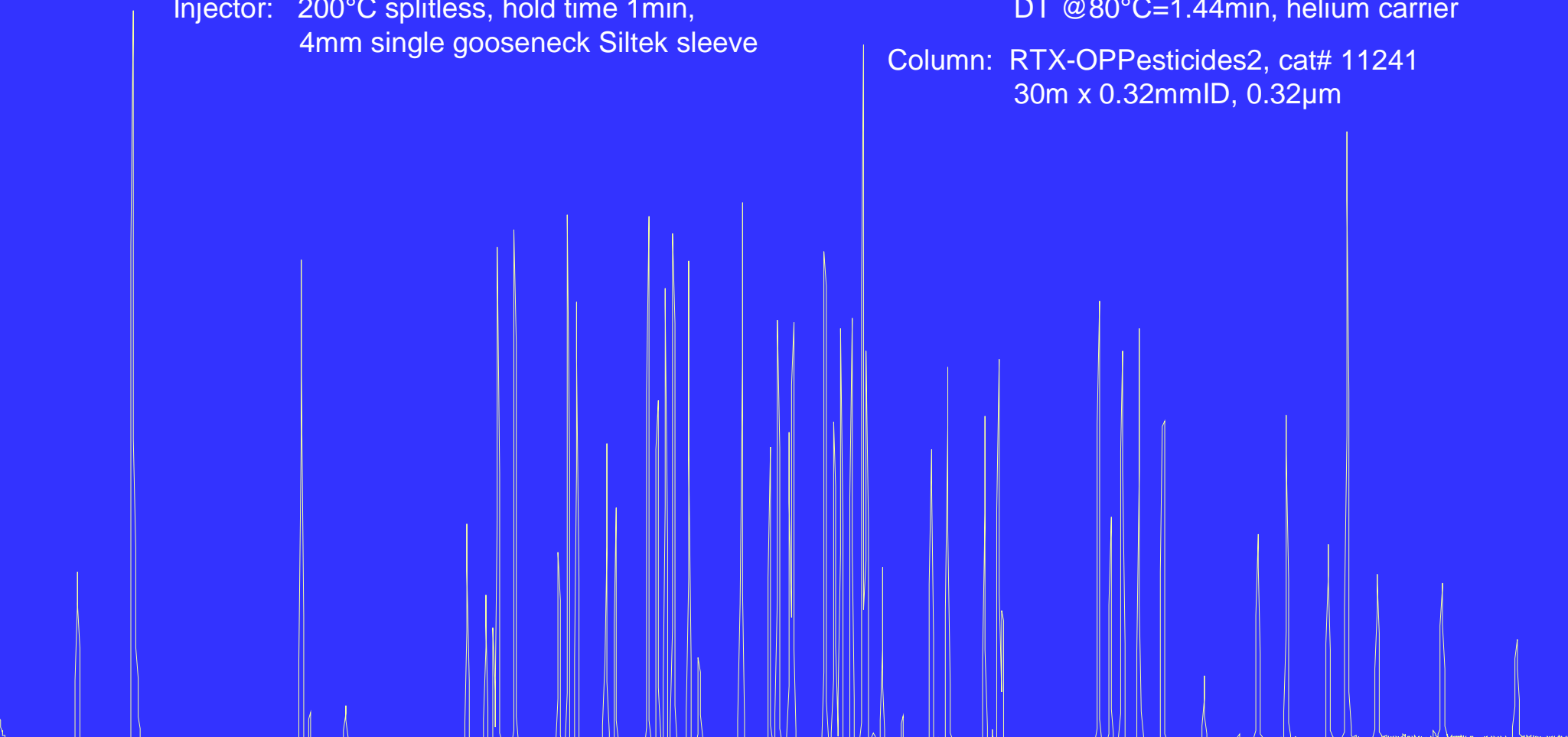
GC oven: 80°C (0.5min) up 12°C/min to 280°C (15min)

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

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

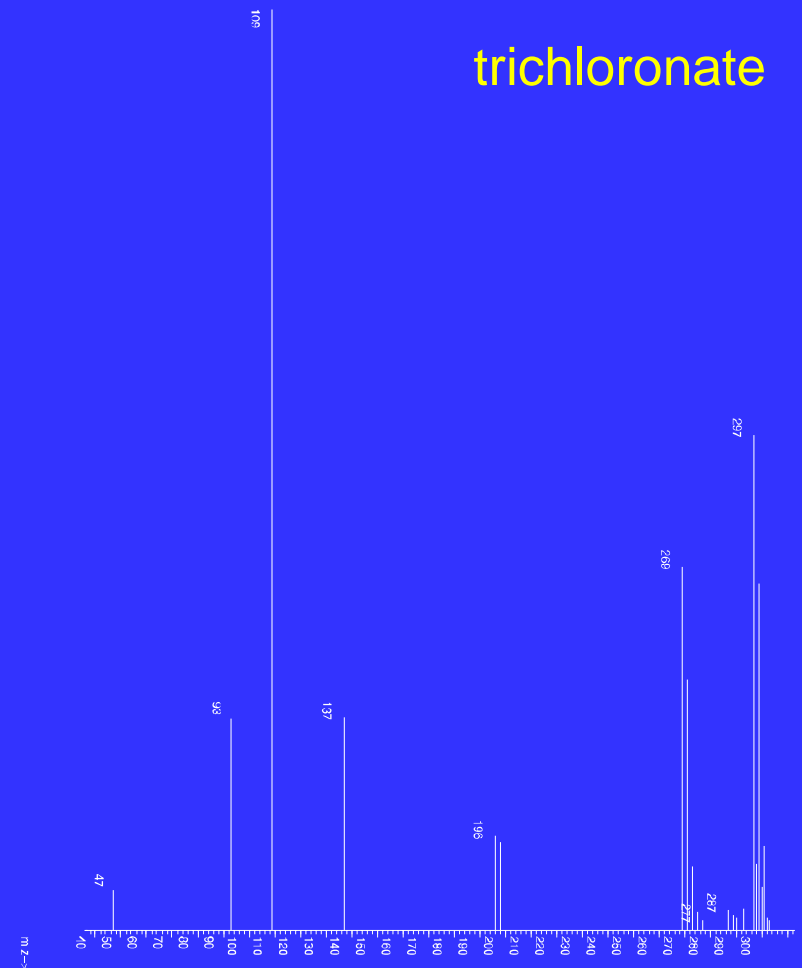
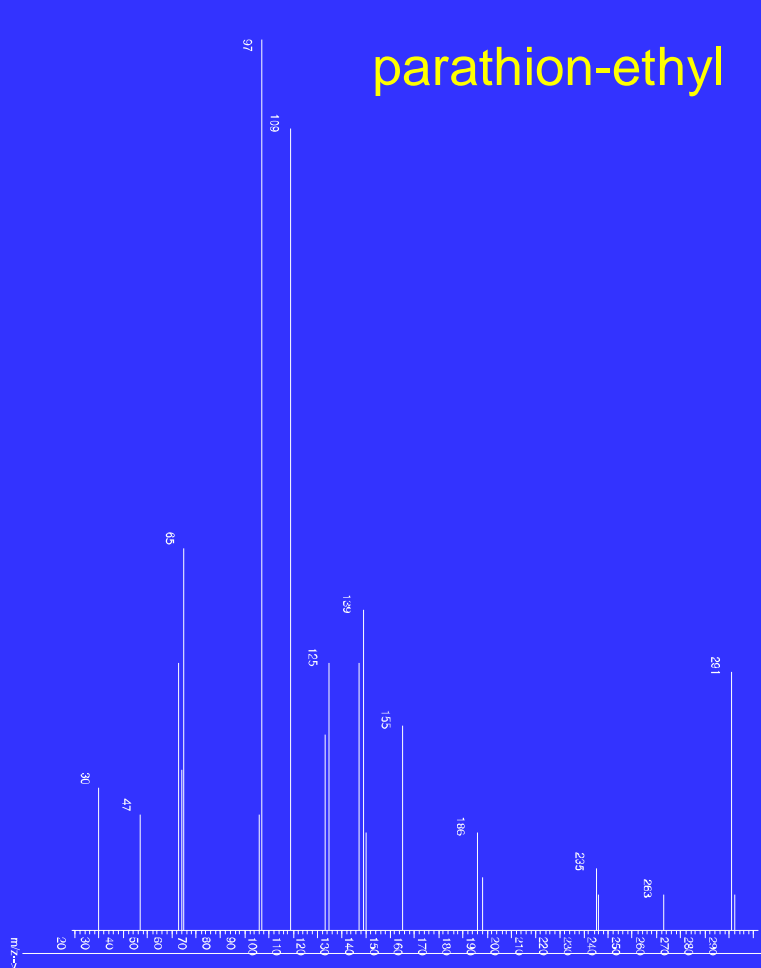
DT @80°C=1.44min, helium carrier

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



Organophosphorus Pesticides MS Spectra

Rtx-OPPesticides2
(30m x 0.32mm, 0.32 μ m)



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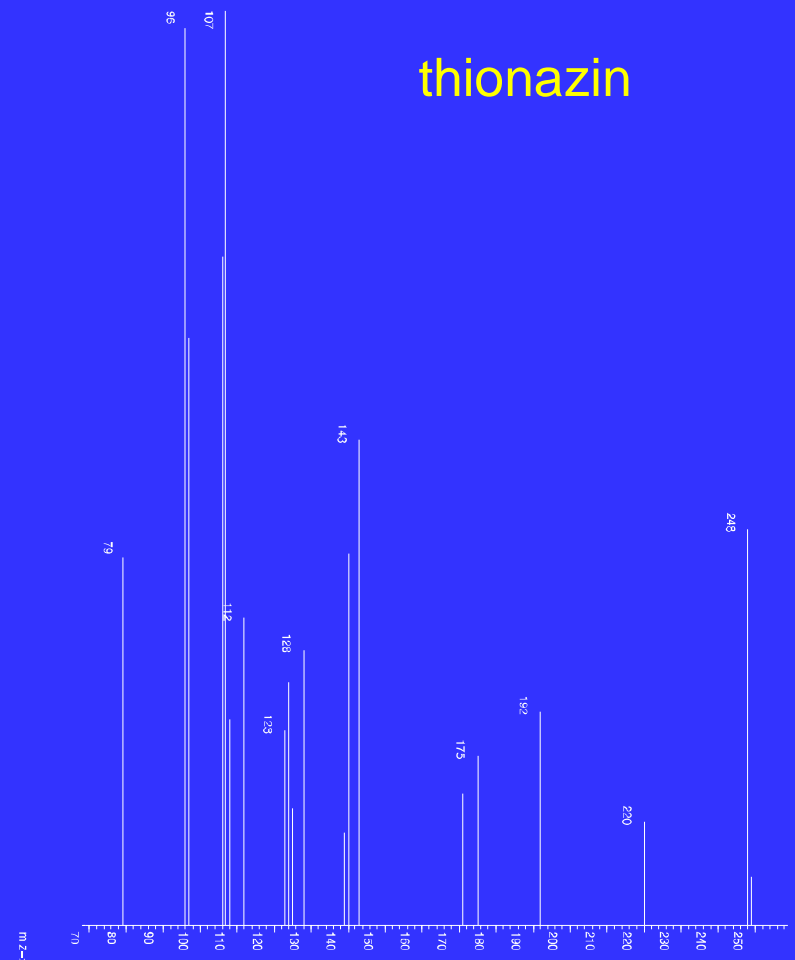
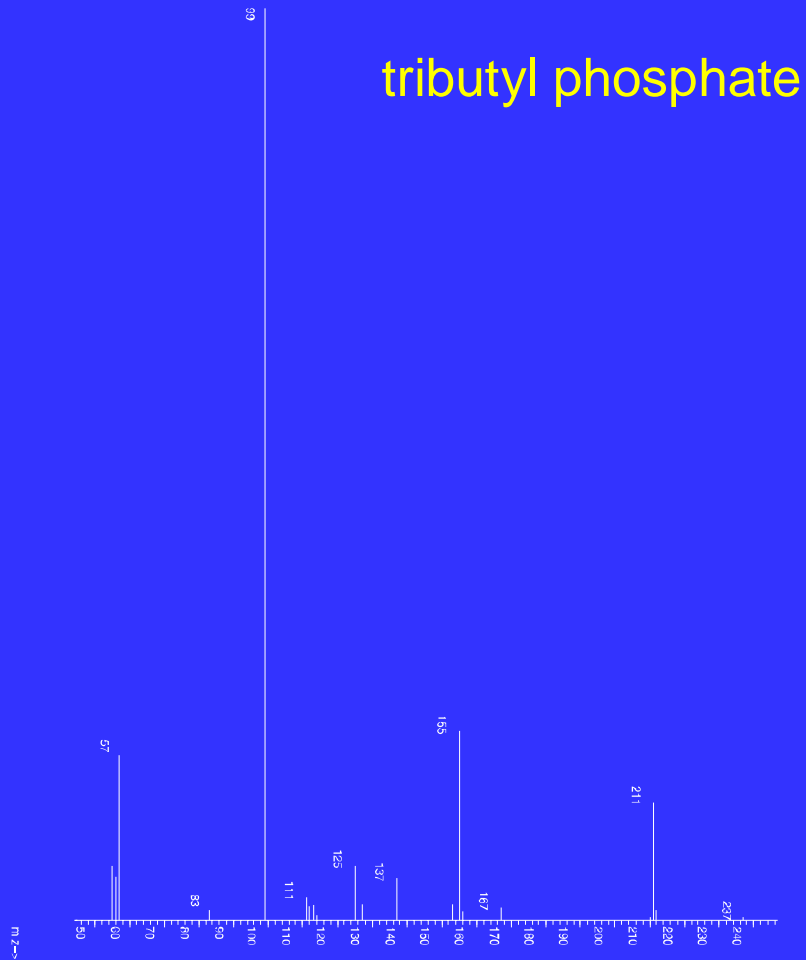
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Organophosphorus Pesticides MS Spectra

Rtx-OPPesticides2
(30m x 0.32mm, 0.32 μ m)



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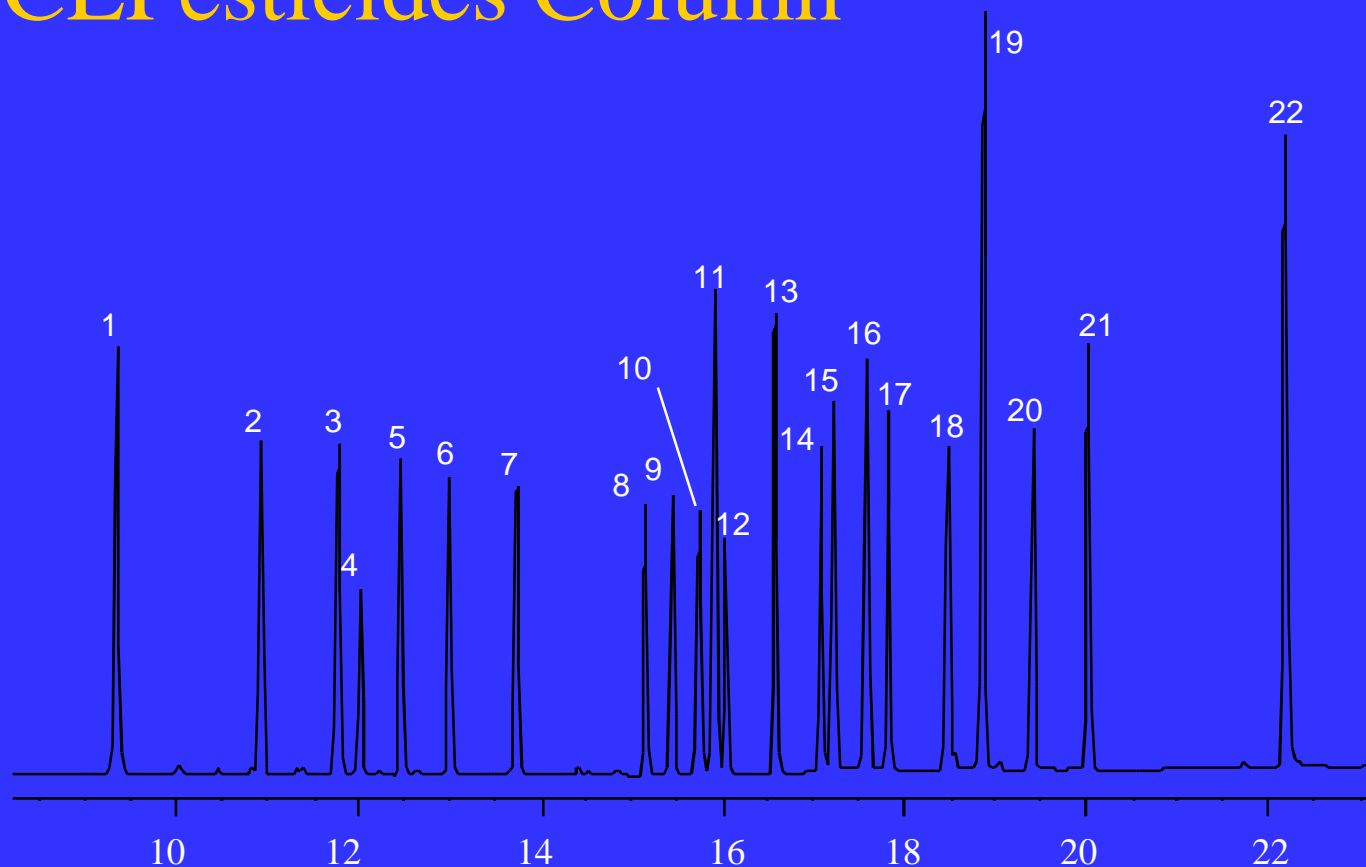
Organochlorine Pesticides

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

Chlorinated Pesticides

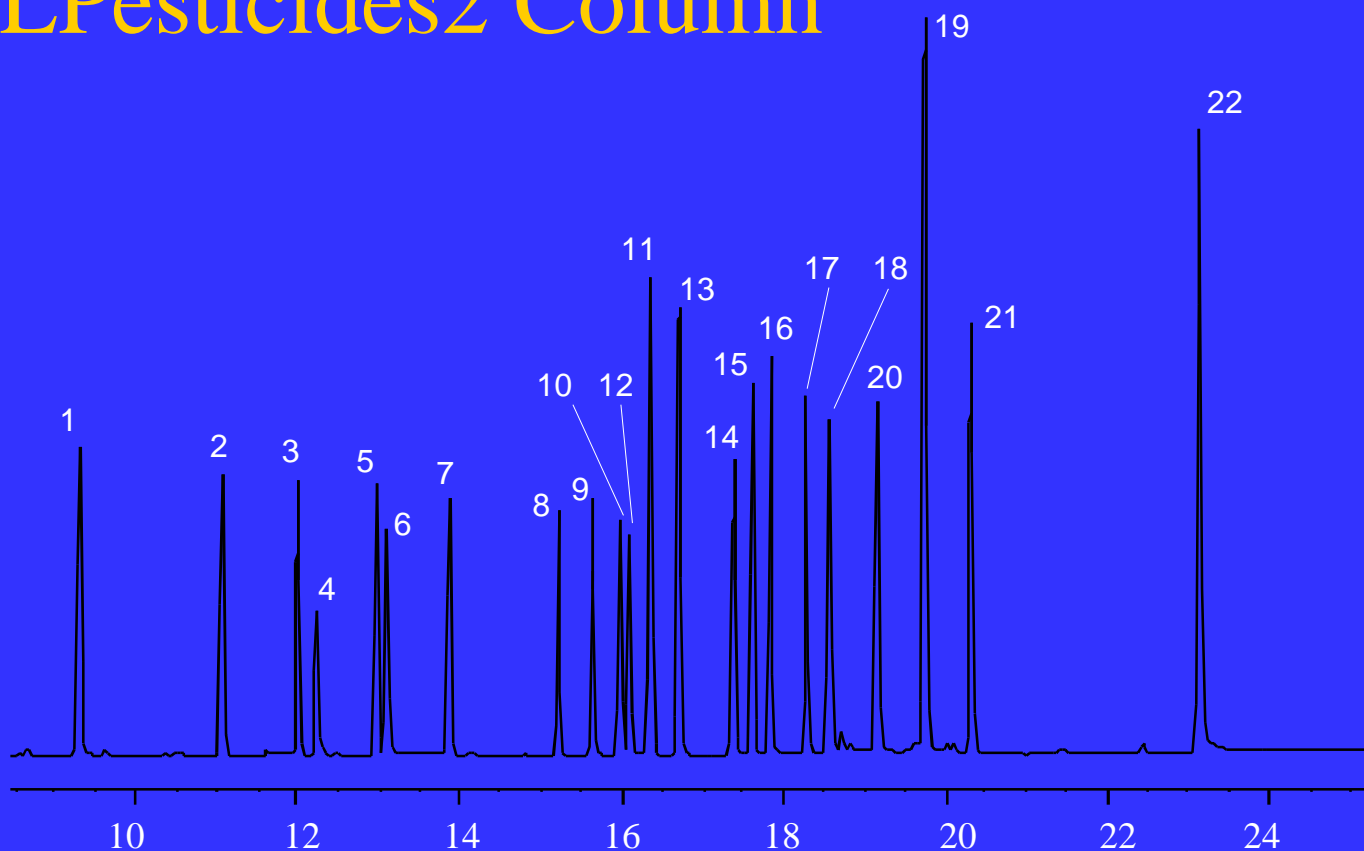
- | | |
|--------------------------------|-----------------------|
| 1 2,4,5,6-tetrachloro-m-xylene | 12 endosulfan I |
| 2 alpha BHC | 13 dieldrin |
| 3 gamma BHC | 14 endrin |
| 4 beta BHC | 15 4,4'-DDD |
| 5 delta BHC | 16 endosulfan II |
| 6 heptachlor | 17 4,4'-DDT |
| 7 aldrin | 18 endrin aldehyde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

Rtx[®]-CLPesticides Column



30m, 0.32mm ID, 0.5 μ m, Rtx[®]-CLPesticides; EPA 8081 list, direct injection, Uniliner[®] 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[®]-CLPesticides2 Column



30m, 0.32mm ID, 0.25 μ m Rtx[®]-CLPesticides2; EPA 8081 list, direct Uniliner[®] 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.

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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

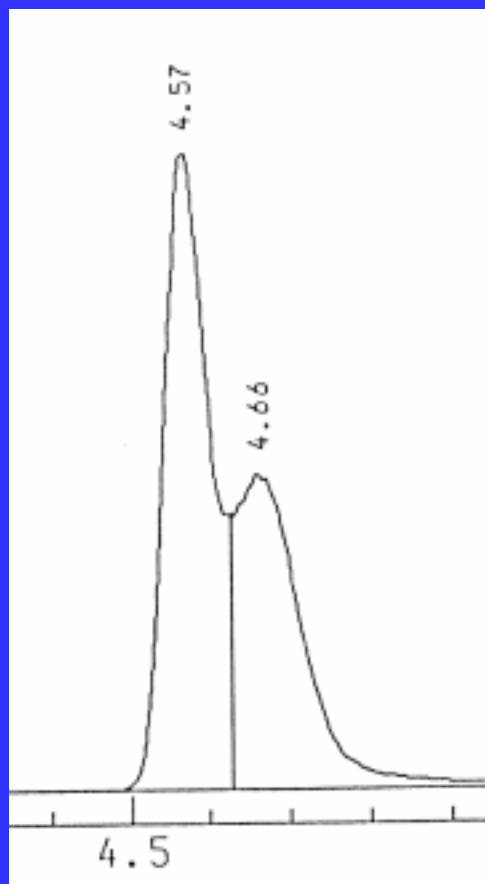
- Columns and stationary phases designed around applications
- Potential for specific phase and column for an individual separation
- Marketing based on real differences
- Requires understanding and ability to model of analyte-phase interactions

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>MeCl₂ & 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:

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

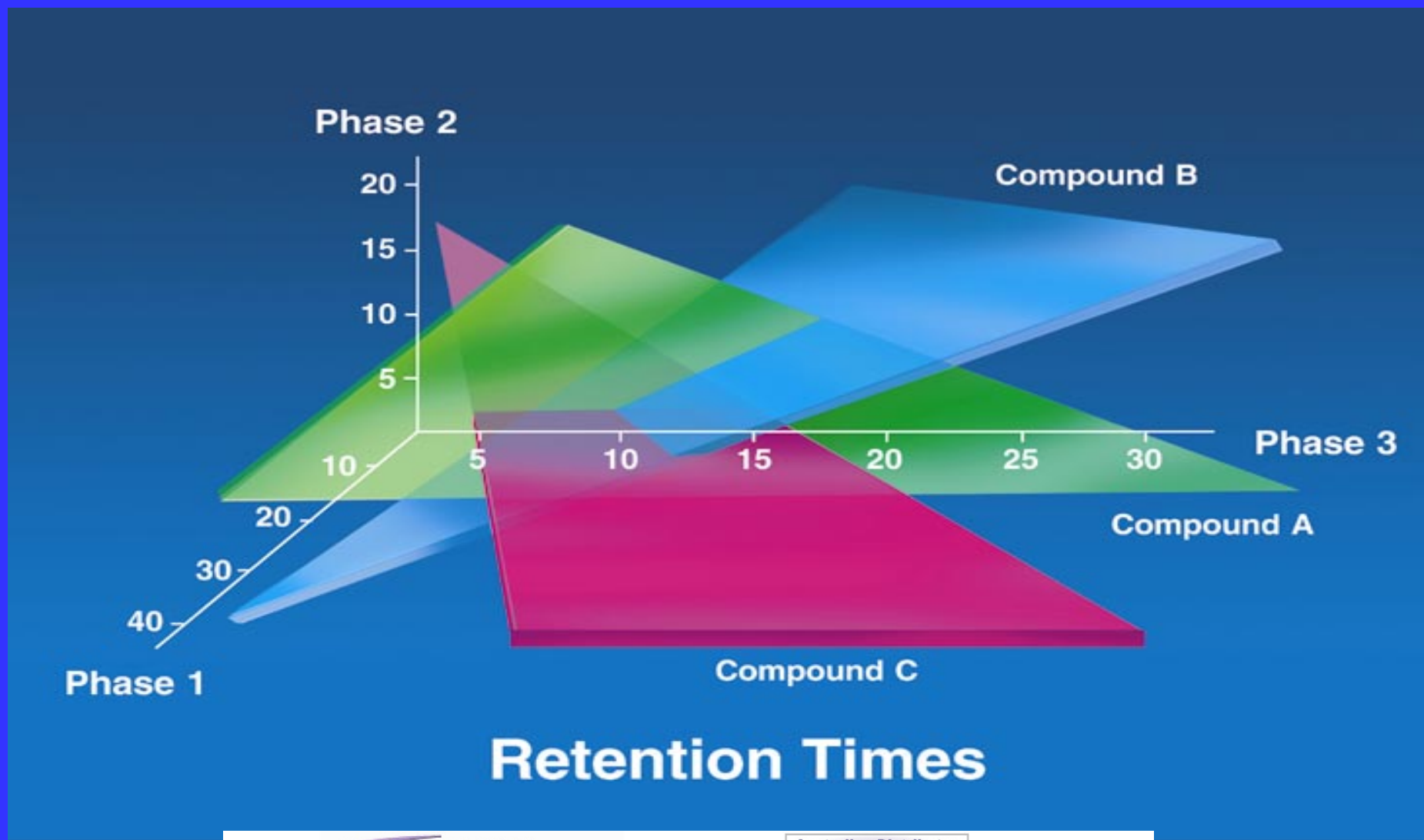
Stationary Phase Optimization

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

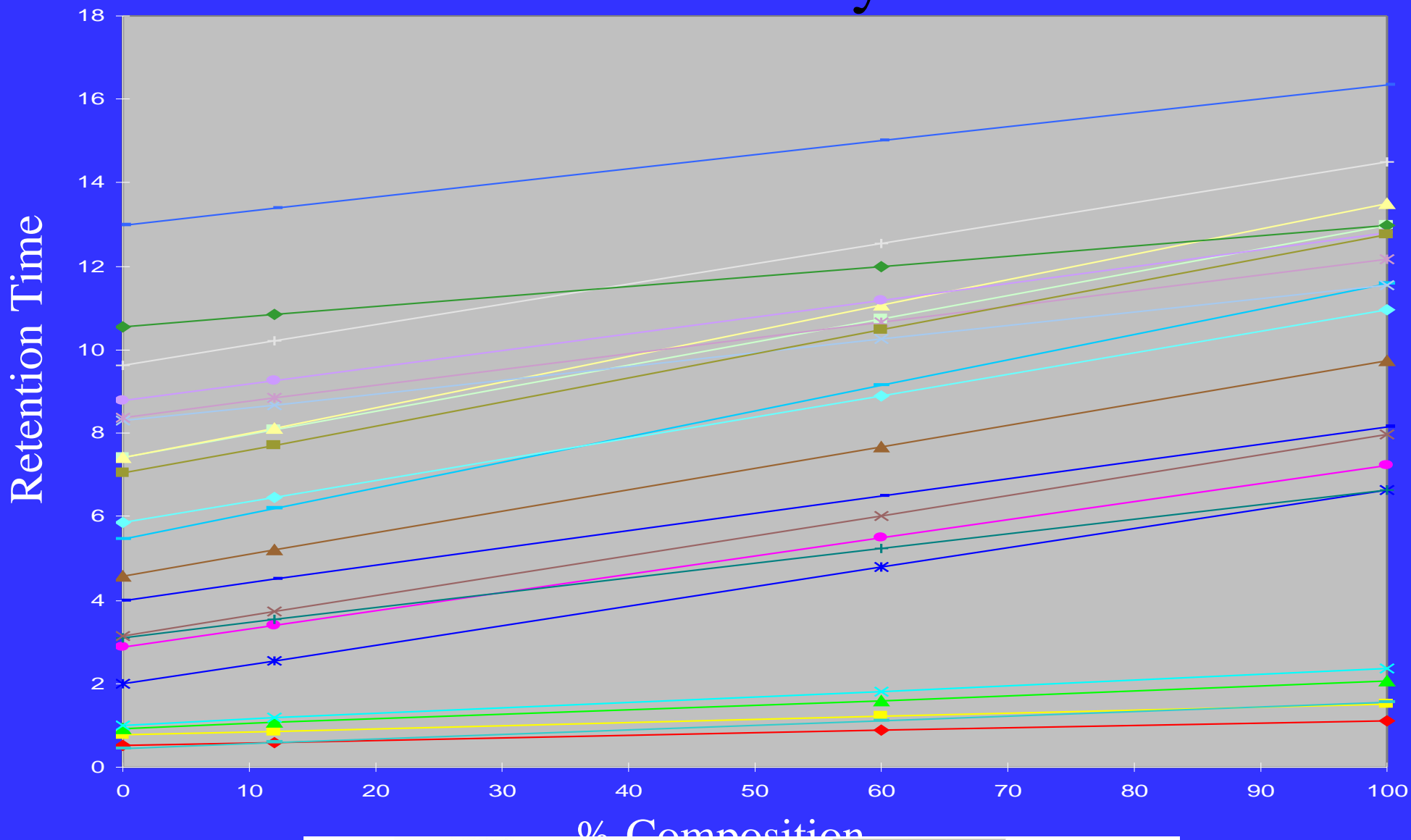
Process for Rtx-OPPesticides2 Column

- Acquire data for target compounds under two temperature programs for functionalities displaying selectivity
- Computer Assisted Stationary Phase Design (CASPD)
 - Calculate ΔH and ΔS 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



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.