Improved Phases for the GC Analysis of Chlorinated and Organophosphorus Pesticides

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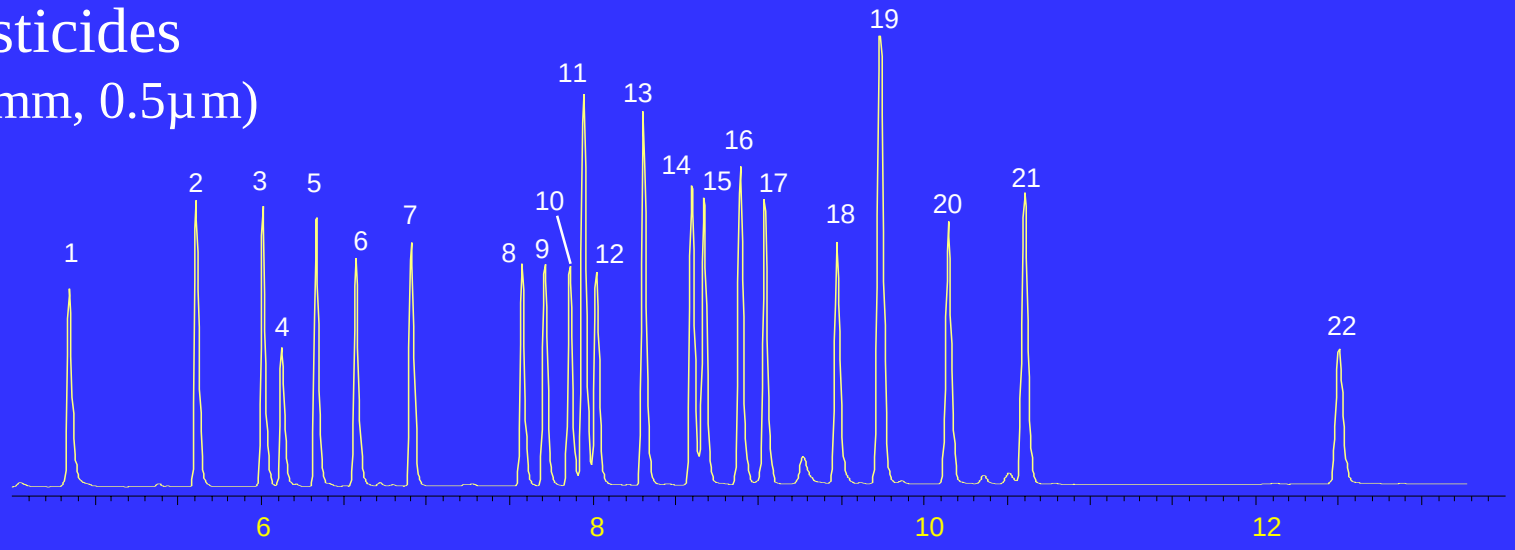
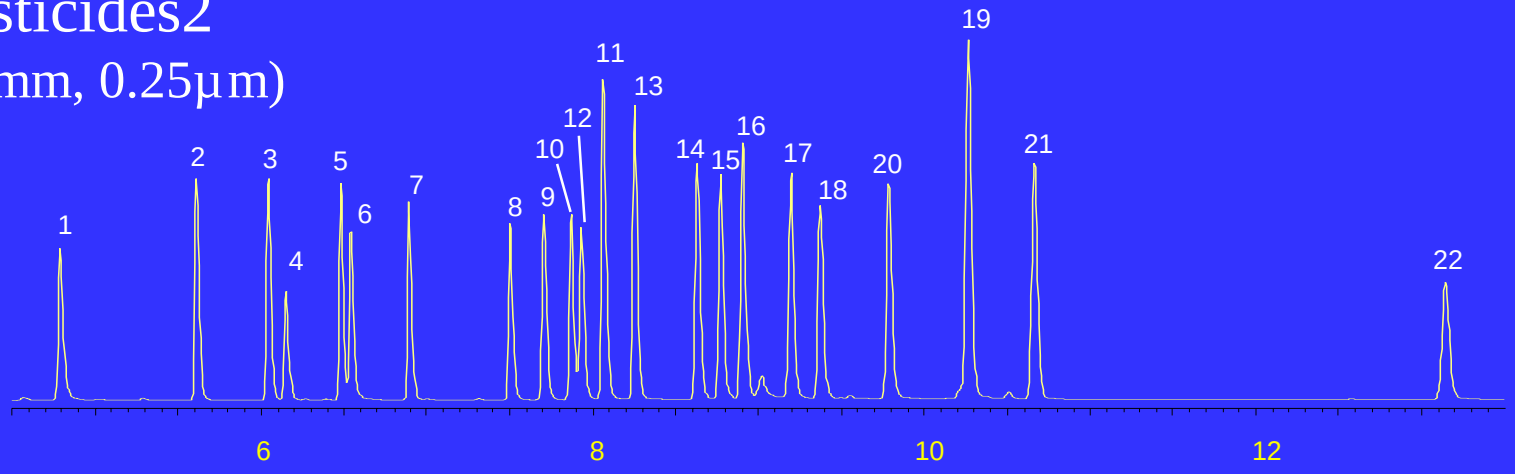
Chlorinated Pesticides
Fast Runs

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

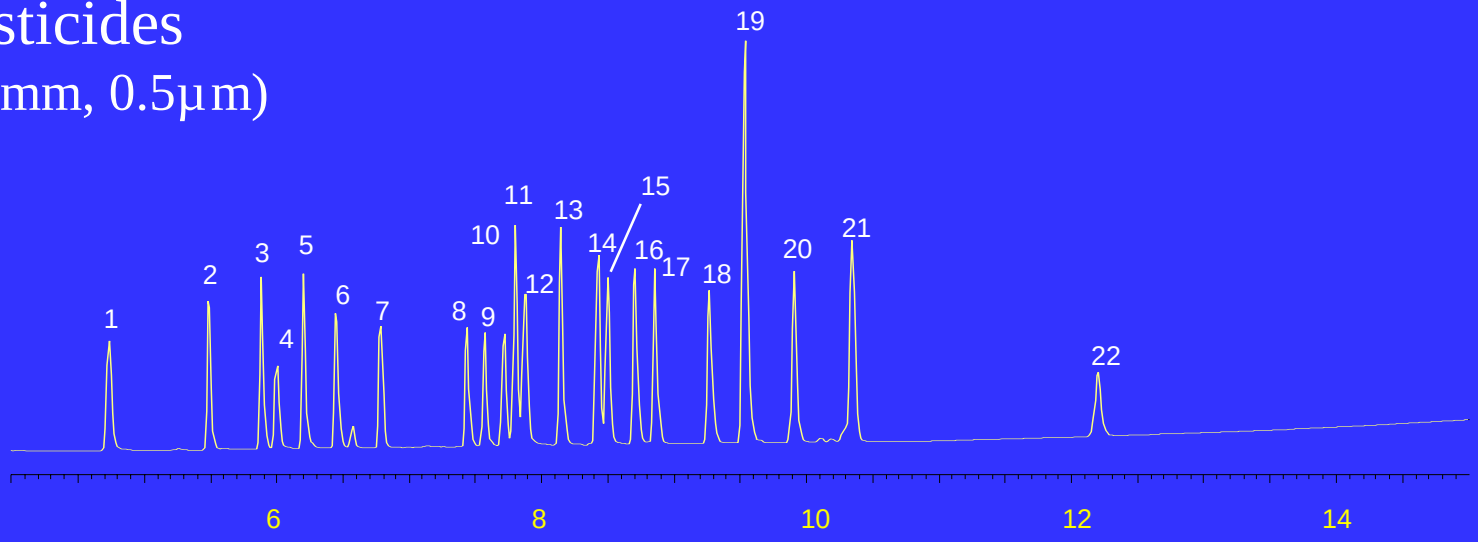


Rtx-CLPesticides2
(30m x 0.32mm, 0.25µm)

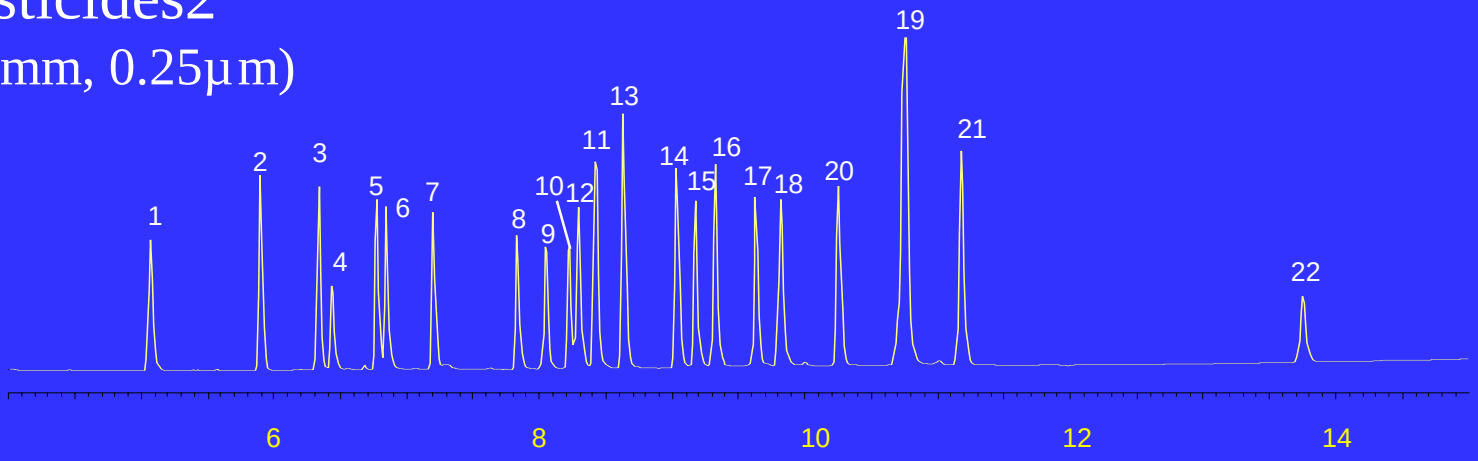


Chlorinated Pesticides
Siltek Deactivation

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



Stx-CLPesticides2
(30m x 0.32mm, 0.25µm)



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

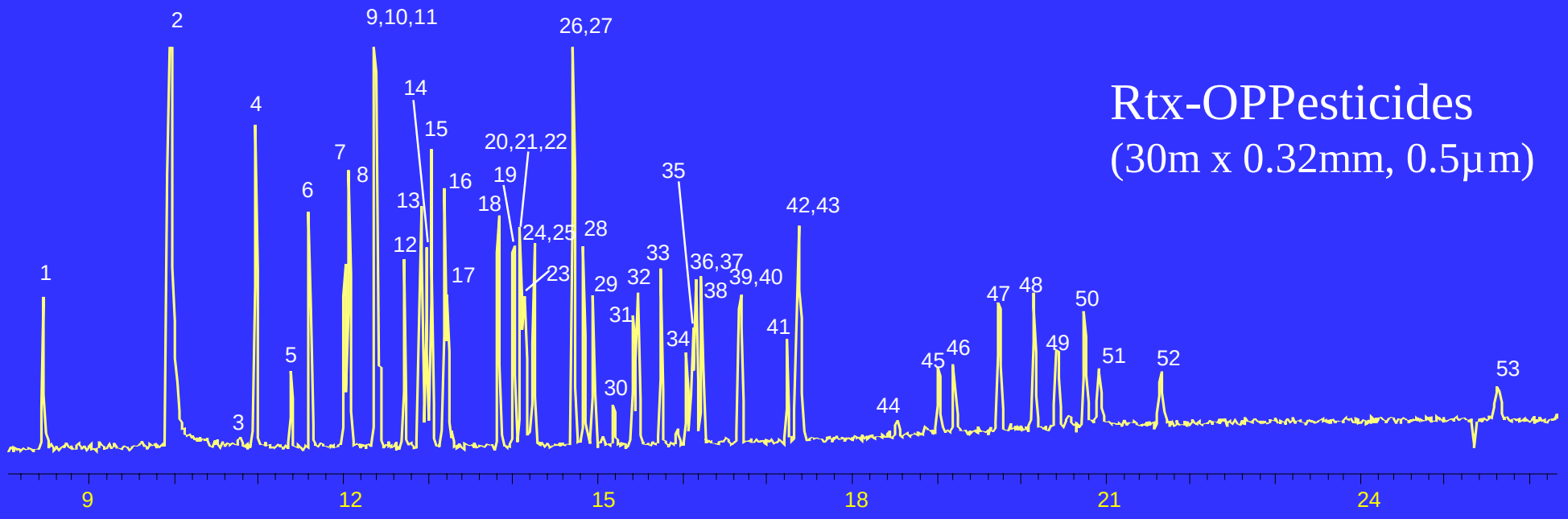
30m x 0.32ID, 0.25µm

Rtx-CLPesticides 2, cat#11324

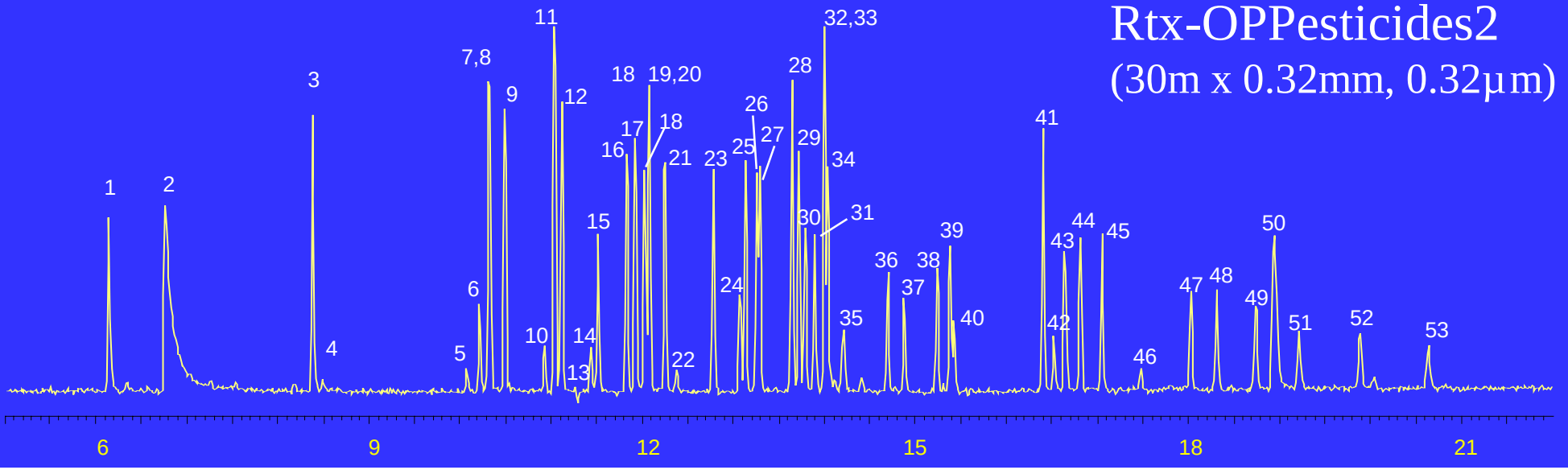
30m x 0.32mmID, 0.25µm

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, 0.5µm)



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

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

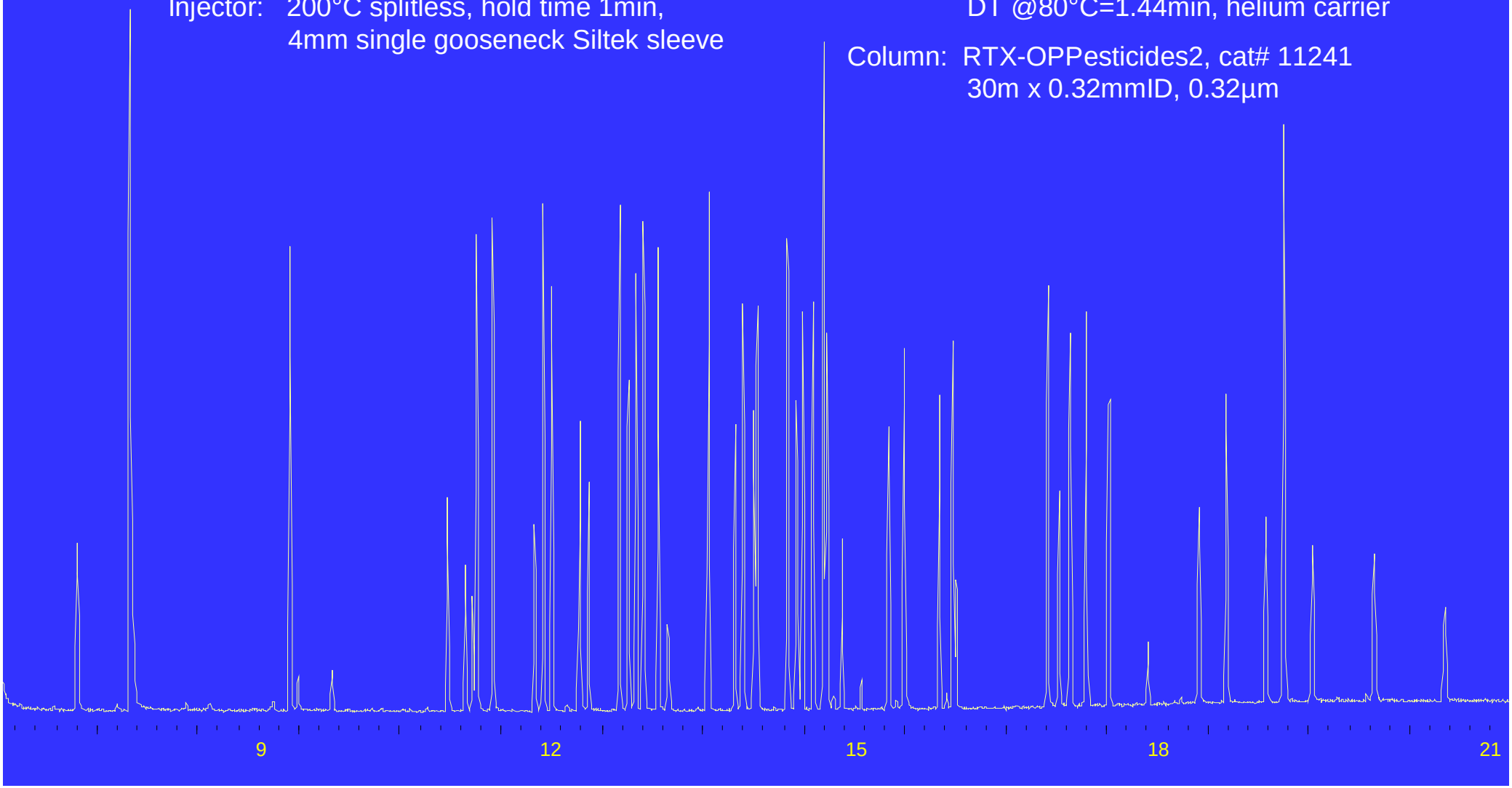
GC oven: 80°C (0.5min) up12°C/min to 280°C (15min)

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

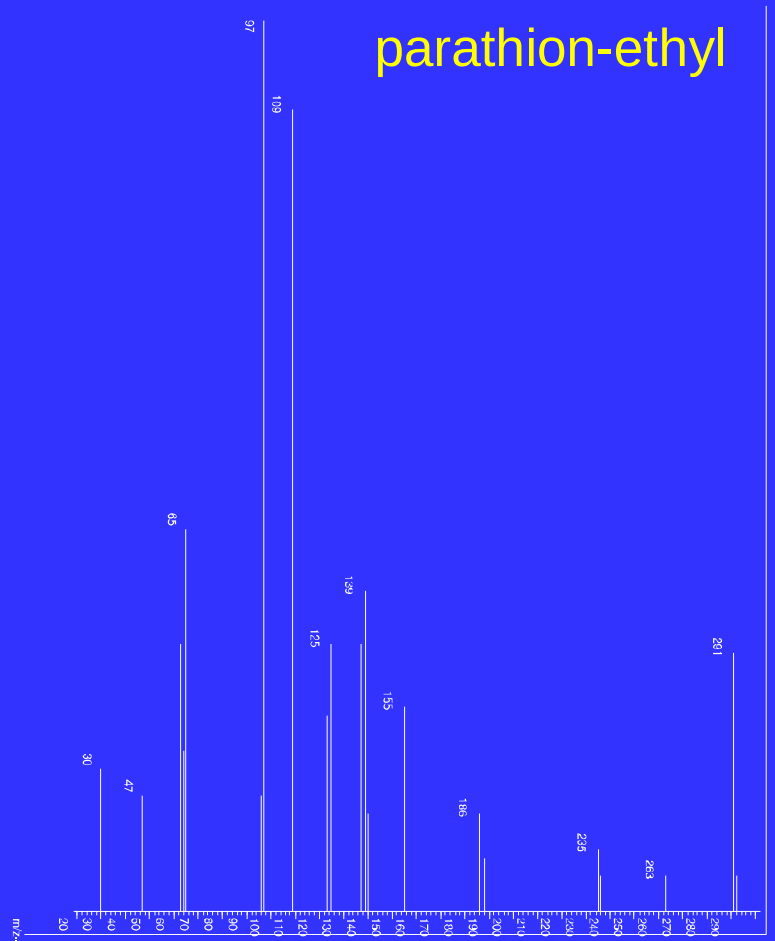
Column: RTX-OPPesticides2, cat# 11241
30m x 0.32mmID, 0.32µm



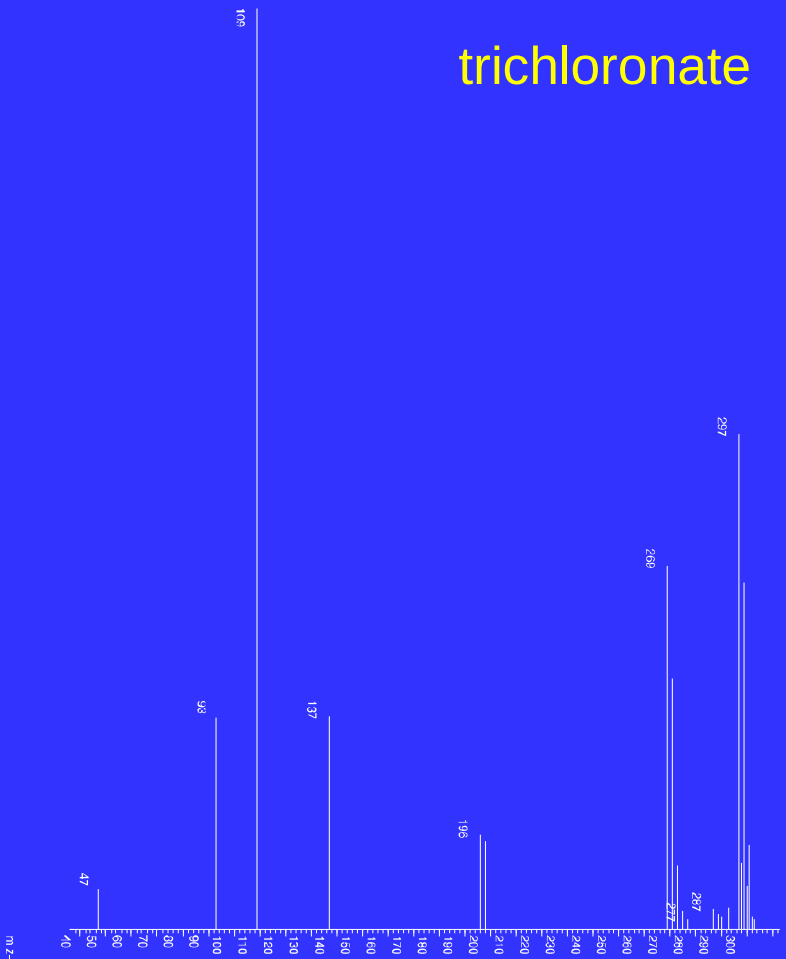
Organophosphorus Pesticides
MS Spectra

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

parathion-ethyl



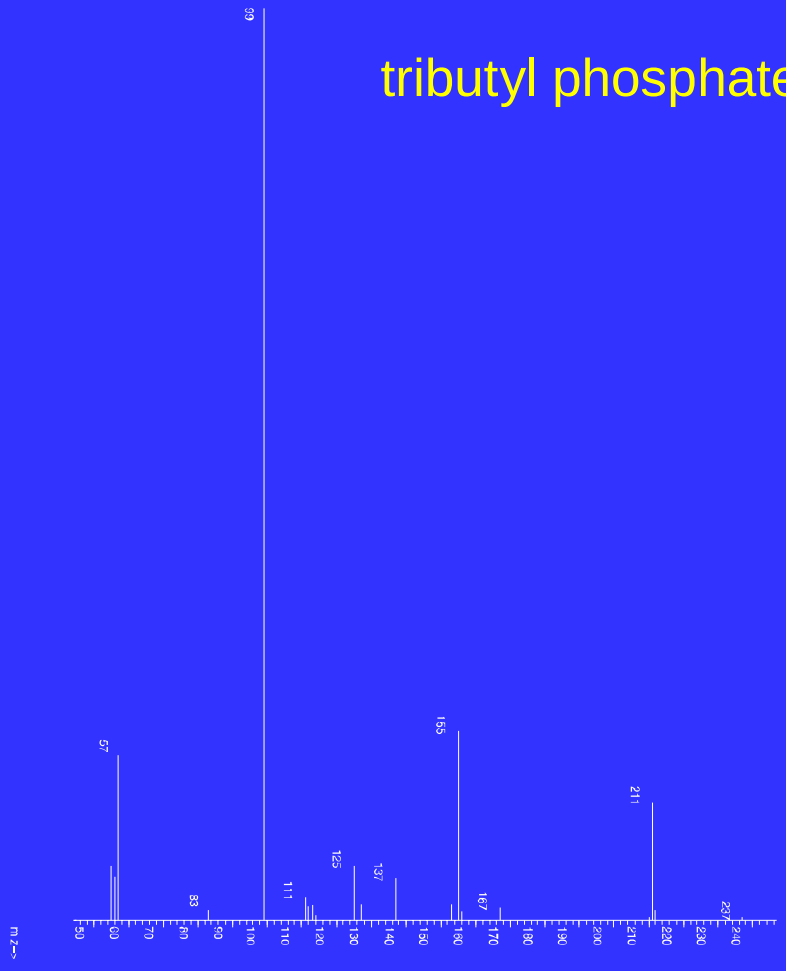
trichloronate



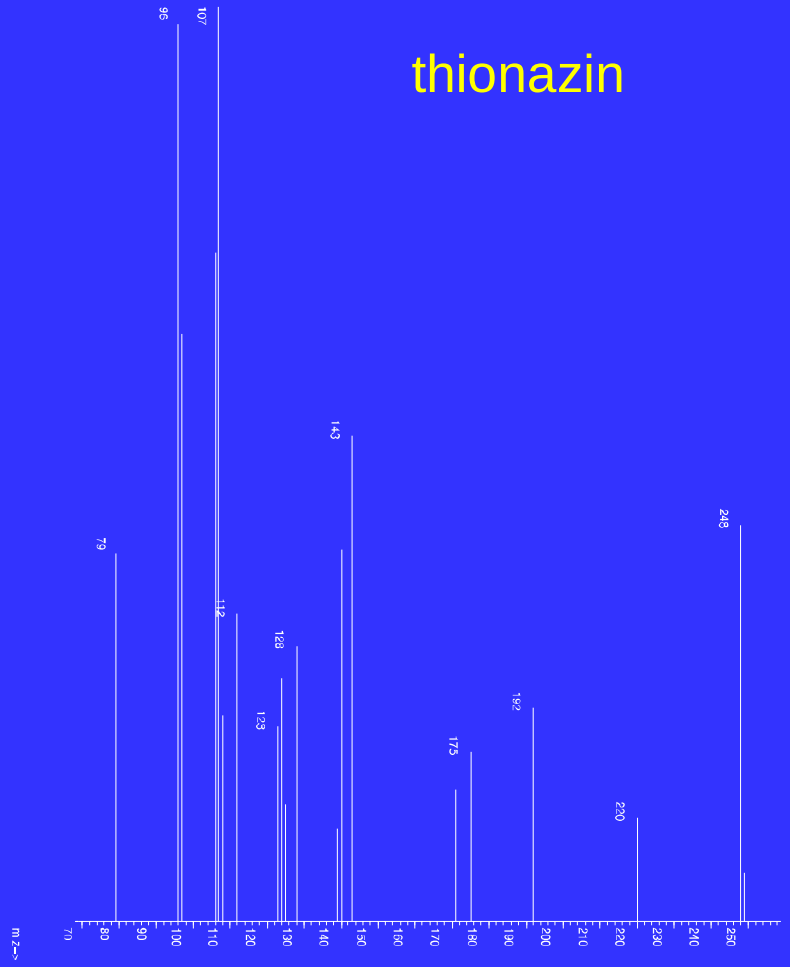
Organophosphorus Pesticides MS Spectra

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

tributyl phosphate



thionazin



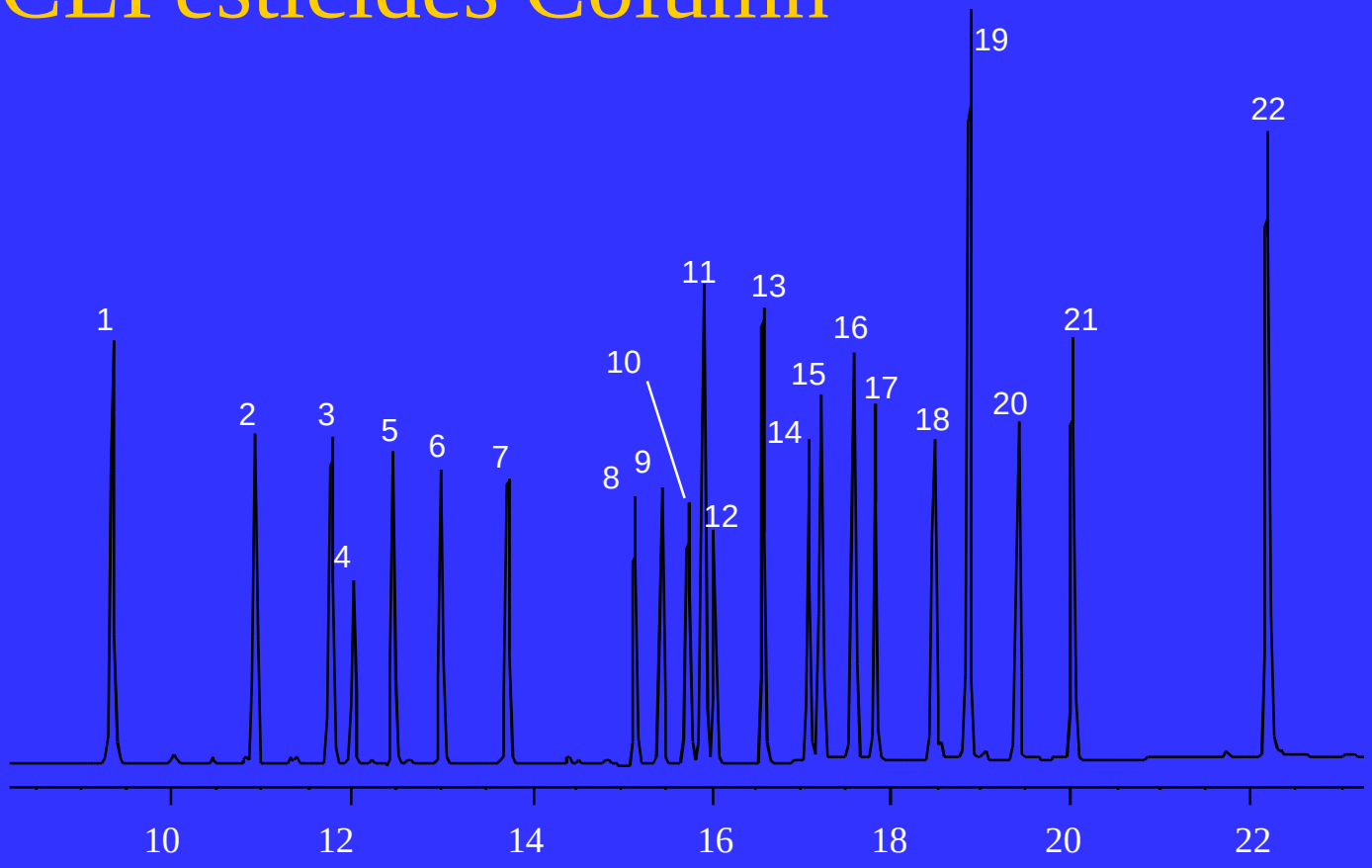
Organochlorine Pesticides

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

Chlorinated Pesticides

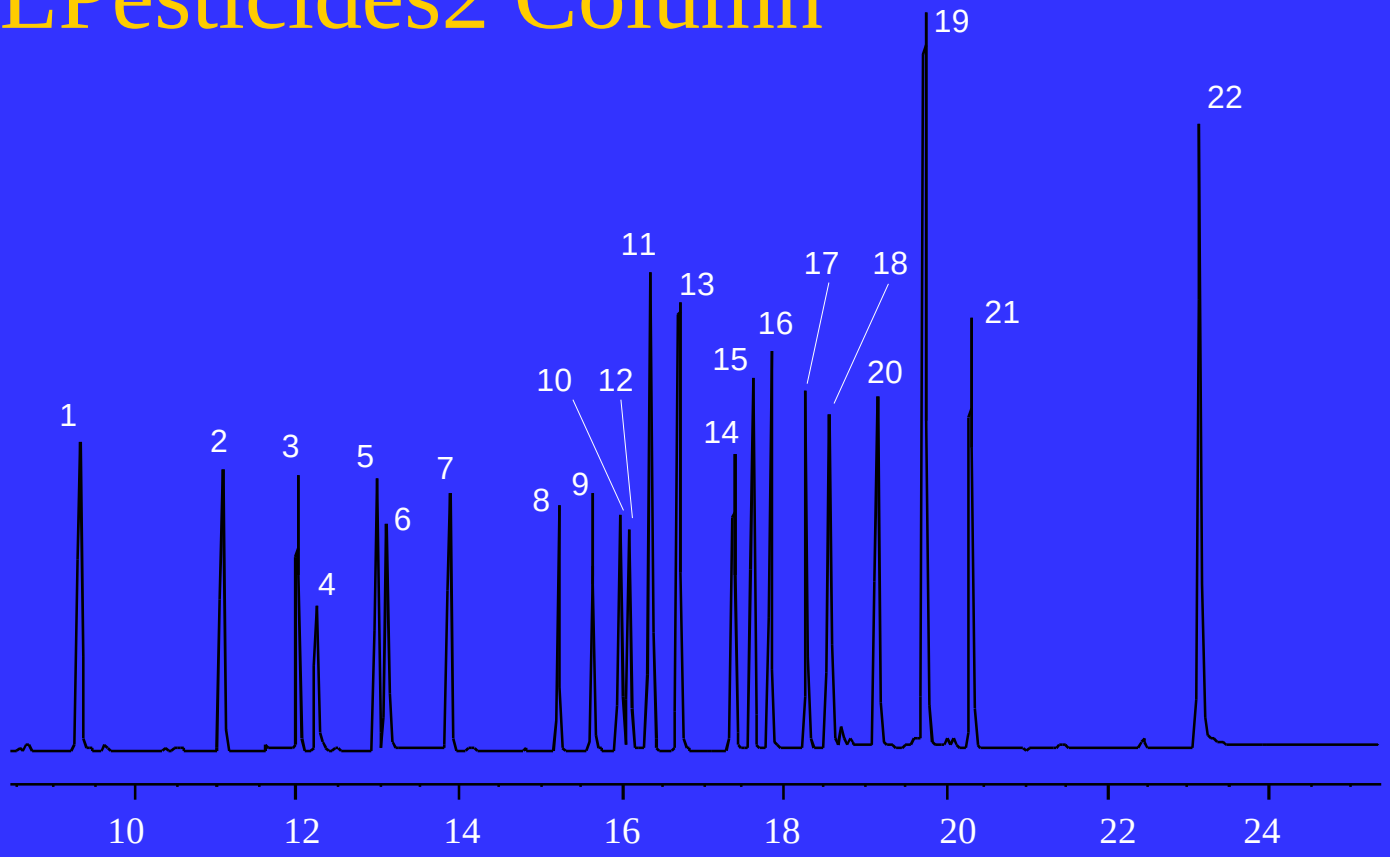
1 2,4,5,6-tetrachloro-m-xylene
2 alpha BHC
3 gamma BHC
4 beta BHC
5 delta BHC
6 heptachlor
7 aldrin
8 heptachlor epoxide
9 gamma chlordane
10 alpha chlordane
11 4,4'-DDE
12 endosulfan I
13 dieldrin
14 endrin
15 4,4'-DDD
16 endosulfan II
17 4,4'-DDT
18 endrin aldehyde
19 methoxychlor
20 endosulfan sulfate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

Rtx®-CLPesticides Column



30m, 0.32mm ID, 0.5µm, 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, 0.25µm 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.

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

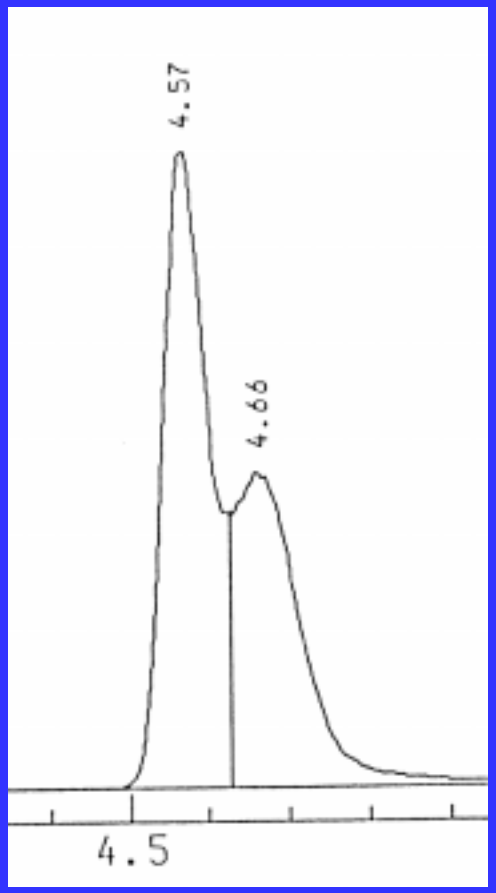
Future of GC

- 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 Rt 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

$MeCl_2$ & Freon 113	*Rep 1*	*19.85*	*18.48*
	Rep 2	*19.29*	*18.48*
	Rep 3	*19.36*	*18.52*
Methylene Chloride	*Rep 1*	*21.48*	
	Rep 2	*20.79*	
	Rep 3	*20.95*	
Freon 113	*Rep 1*		*16.3*
	Rep 2		*16.46*
	Rep 3		*16.25*

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:

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

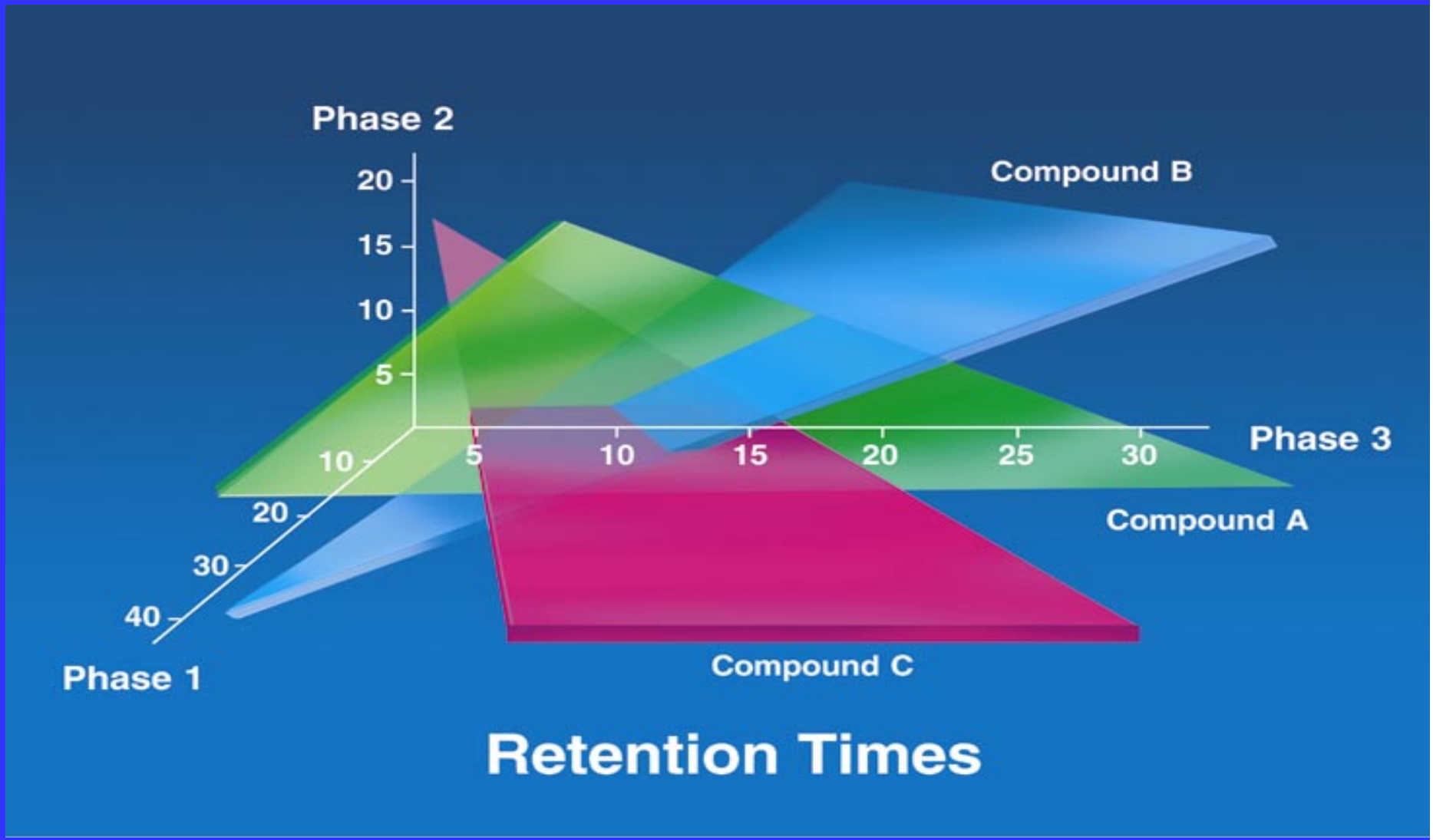
Stationary Phase Optimization

- Window diagramming
- Computer simulation of Rt 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

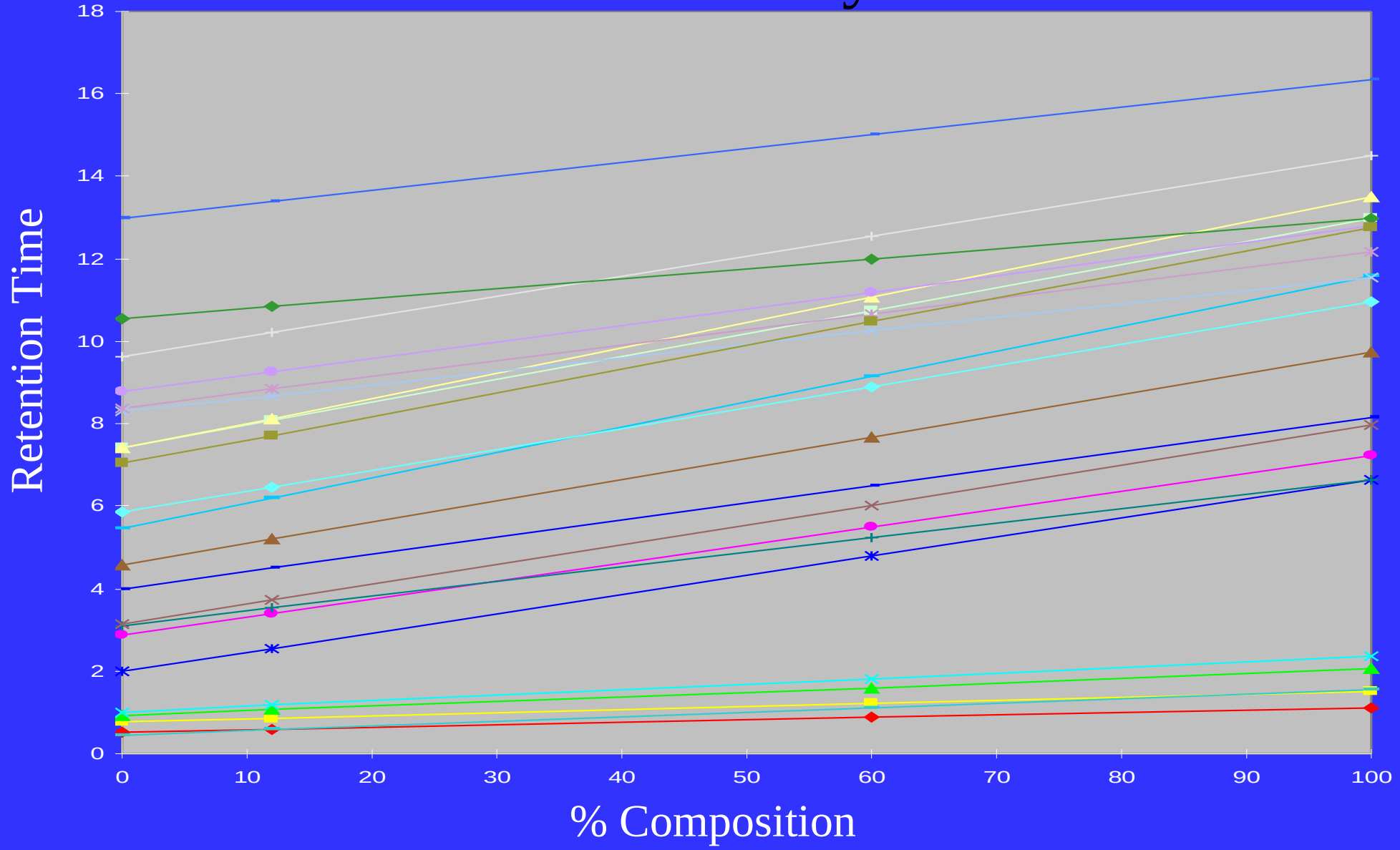
Process for Rtx-OPPesticides2 Column

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