Summary results using G7000A GC-QQQ for OCPs, Pesticides and PCBs in Marine Sediment and Biota

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PITTCON 2009
Chicago

G7000A GC-QQQ
OCPs and PCBs in Marine Sediment and Biota

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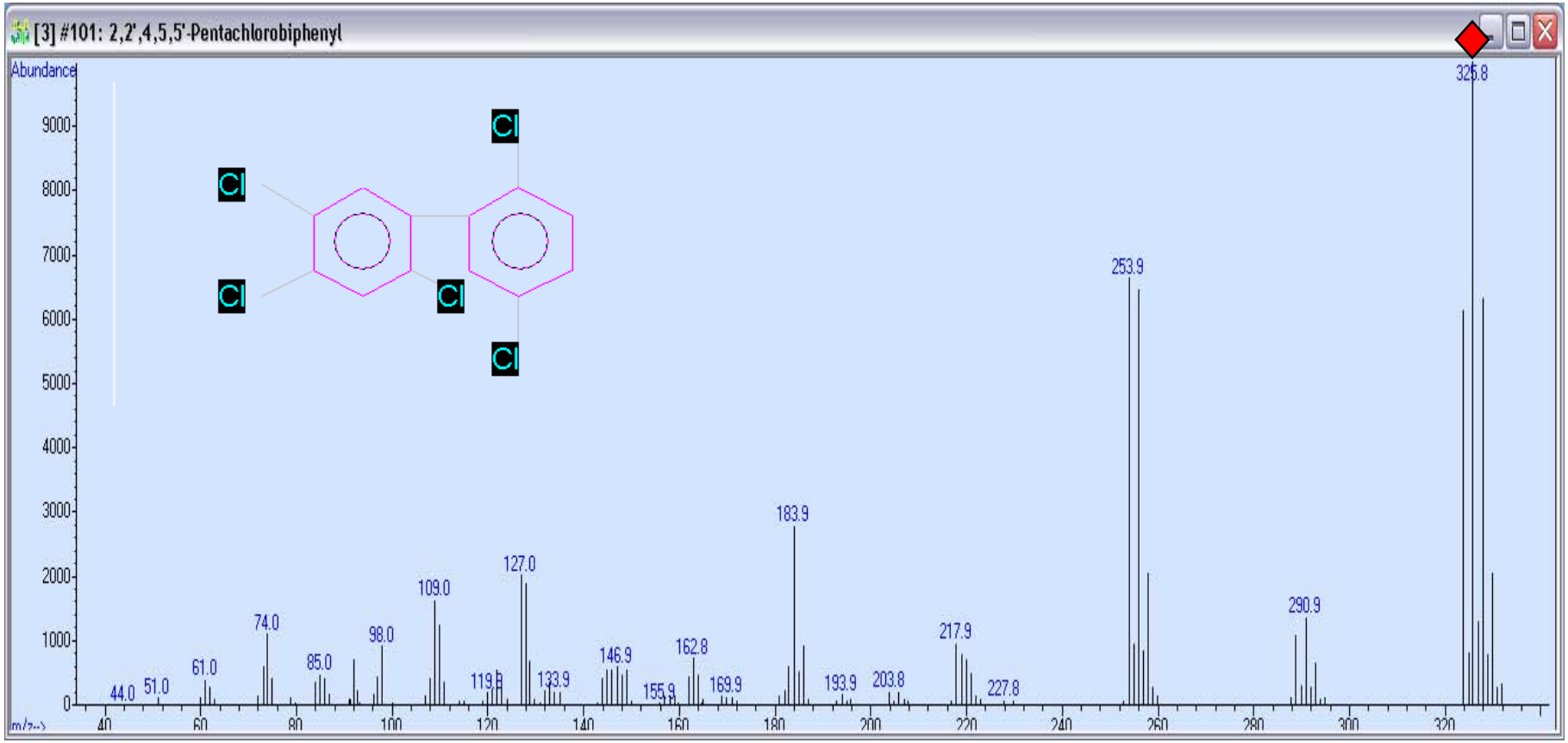
Chicago 2009

EA Evaluation Protocol

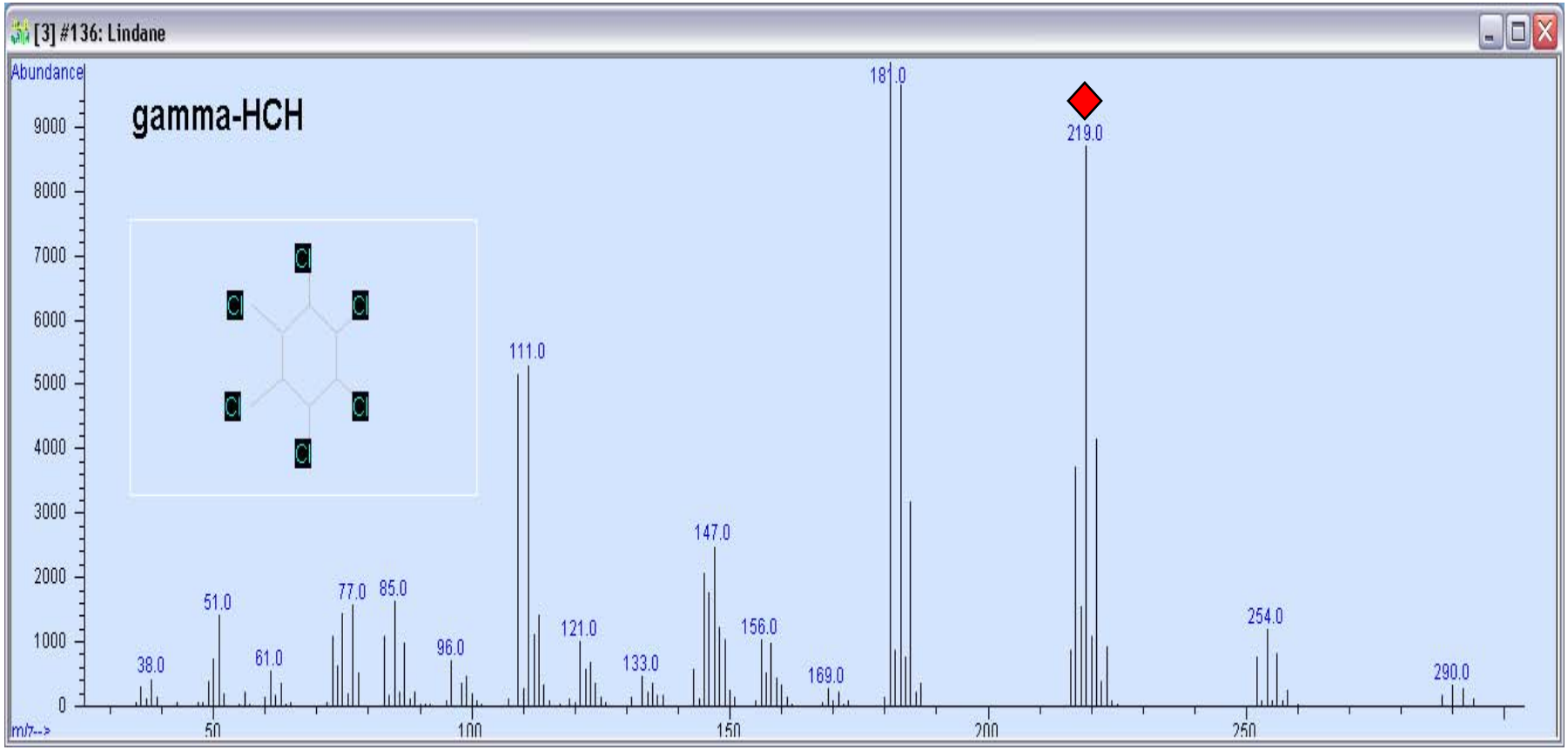
15 Target Analytes, 2 ISTDs

TS	Start Time	Parent Ion		Ret Time
1	2.0	219	a-HCH	6.19
		219	b-HCH	6.76
		219	Lindane	6.89
		219	d-HCH	7.45
2	7.80	256	PCB 28	8.25
3	8.80	292	PCB 52	9.15
4	9.30	263	Aldrin	9.47
5	9.90	193	Isodrin	10.24
6	10.90	360	PCB 155 (ISTD)	11.28
7	11.40	326	PCB 101	11.51
8	11.90	263	Dieldrin	12.18
		263	Endrin	12.56
9	12.70	326	PCB 118	12.84
10	13.00	360	PCB 153	13.25
		360	PCB 138	13.72
11	14.20	394	PCB 180	14.75
12	14.90	272	Mirex (ISTD)	15.09

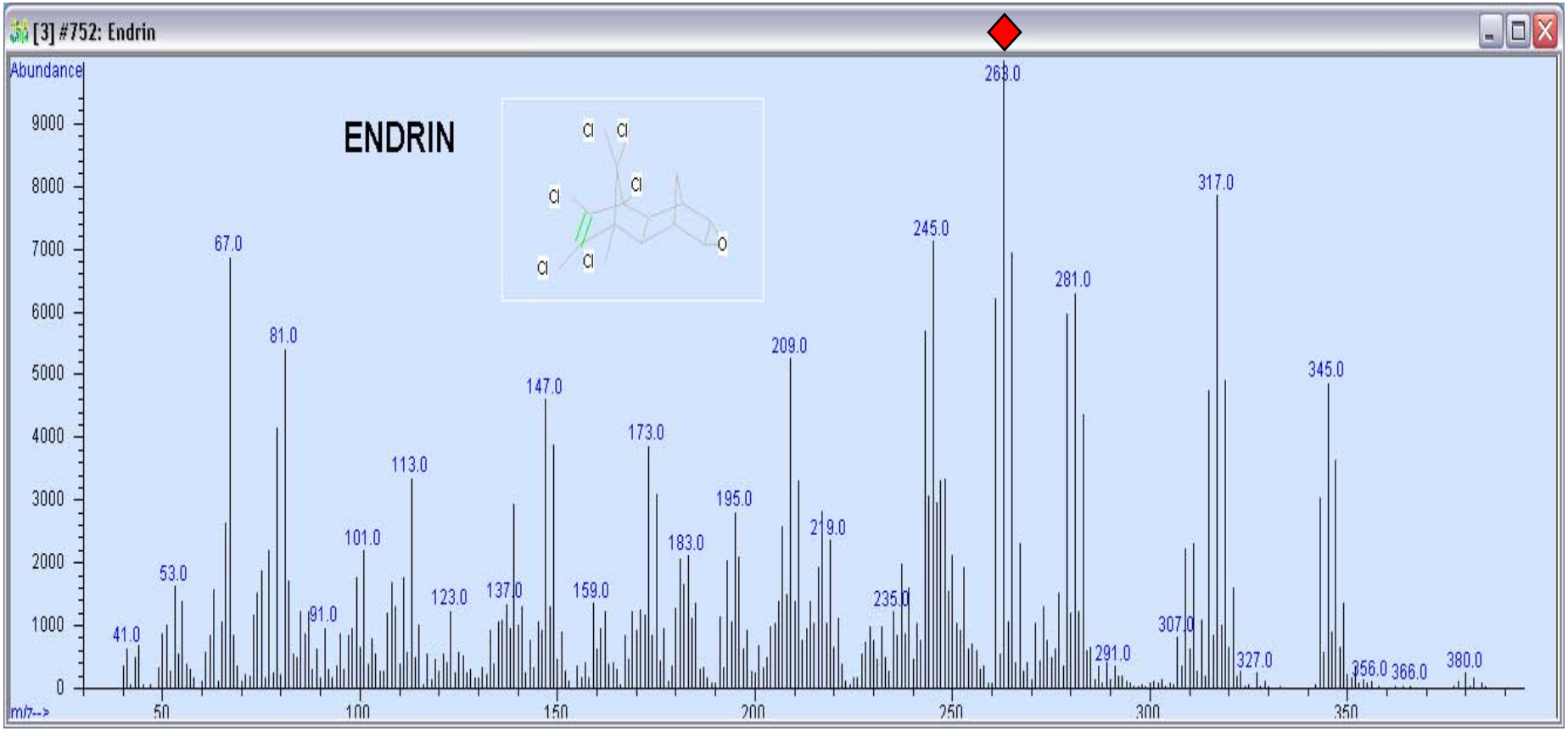
Example EI Spectrum – PCB 101



Example EI Spectrum – g-HCH



Example EI Spectrum - Endrin

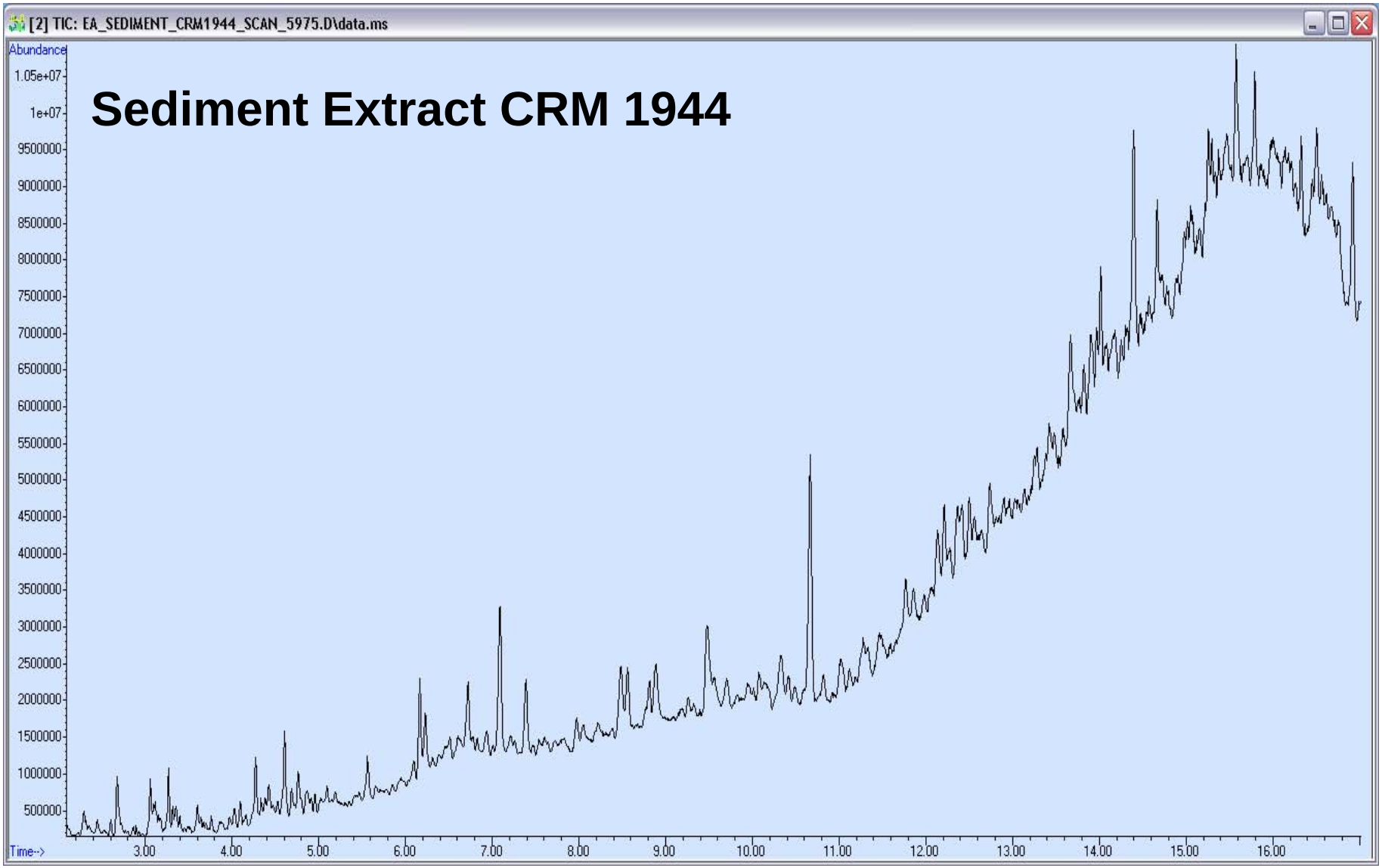


Samples

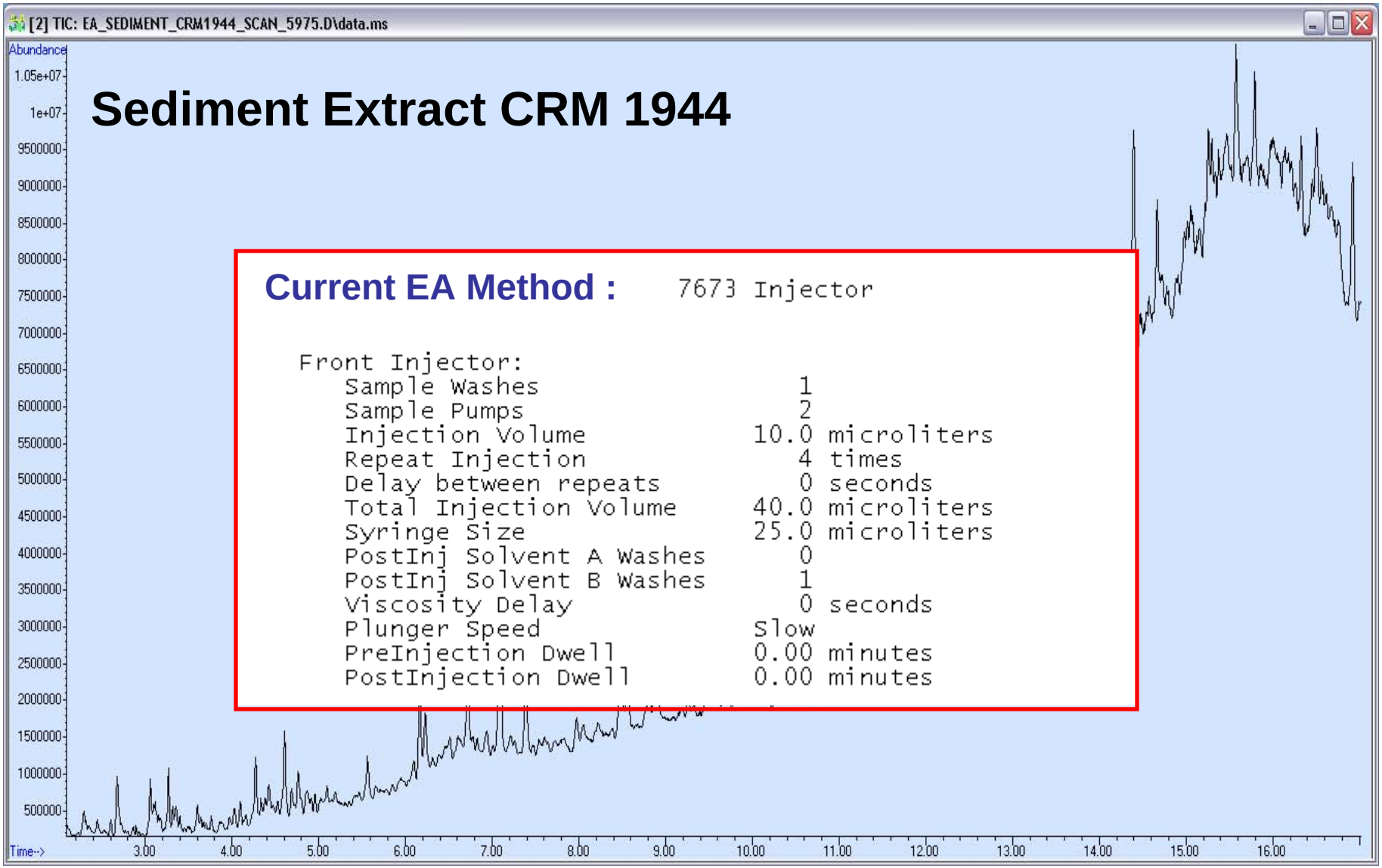
- **NIST SRM 2977 Mussel tissue**
- **NIST SRM 1944 New York / New Jersey Waterway Sediment**

- **The samples (approx 2-5g) are extracted using accelerated solvent extraction (Dionex ASE system) and then purified using size exclusion chromatography followed by alumina clean up.**
  Biota samples are cleaned up using sulphuric acid for PCB analysis .

2ul Splitless Injection Scan Mode – 5975 MSD



2ul Splitless Injection Scan Mode – 5975 MSD



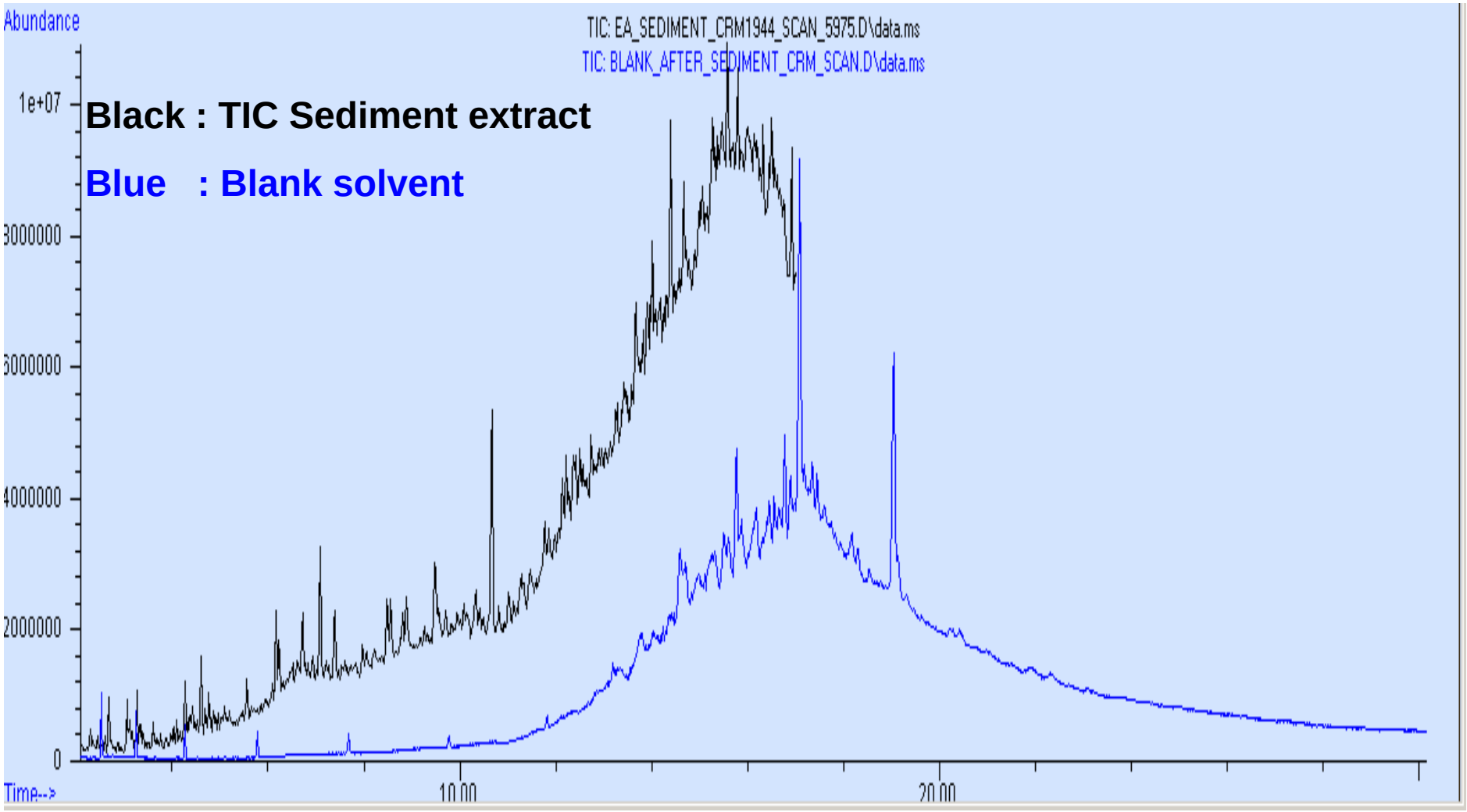
Sediment Extract CRM 1944

Current EA Method : 7673 Injector

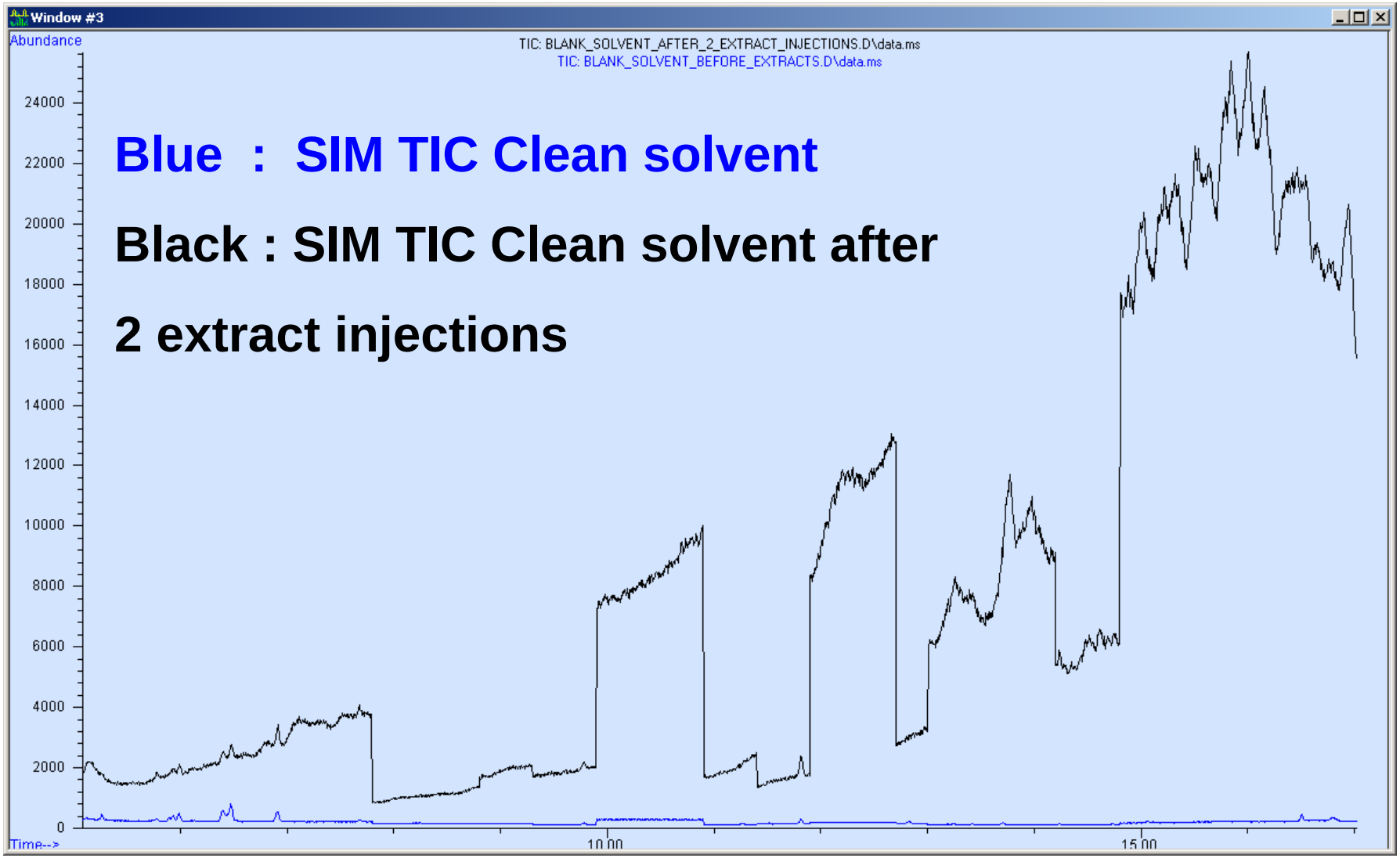
Front Injector:

Sample Washes	1
Sample Pumps	2
Injection Volume	10.0 microliters
Repeat Injection	4 times
Delay between repeats	0 seconds
Total Injection Volume	40.0 microliters
Syringe Size	25.0 microliters
PostInj Solvent A Washes	0
PostInj Solvent B Washes	1
Viscosity Delay	0 seconds
Plunger Speed	Slow
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

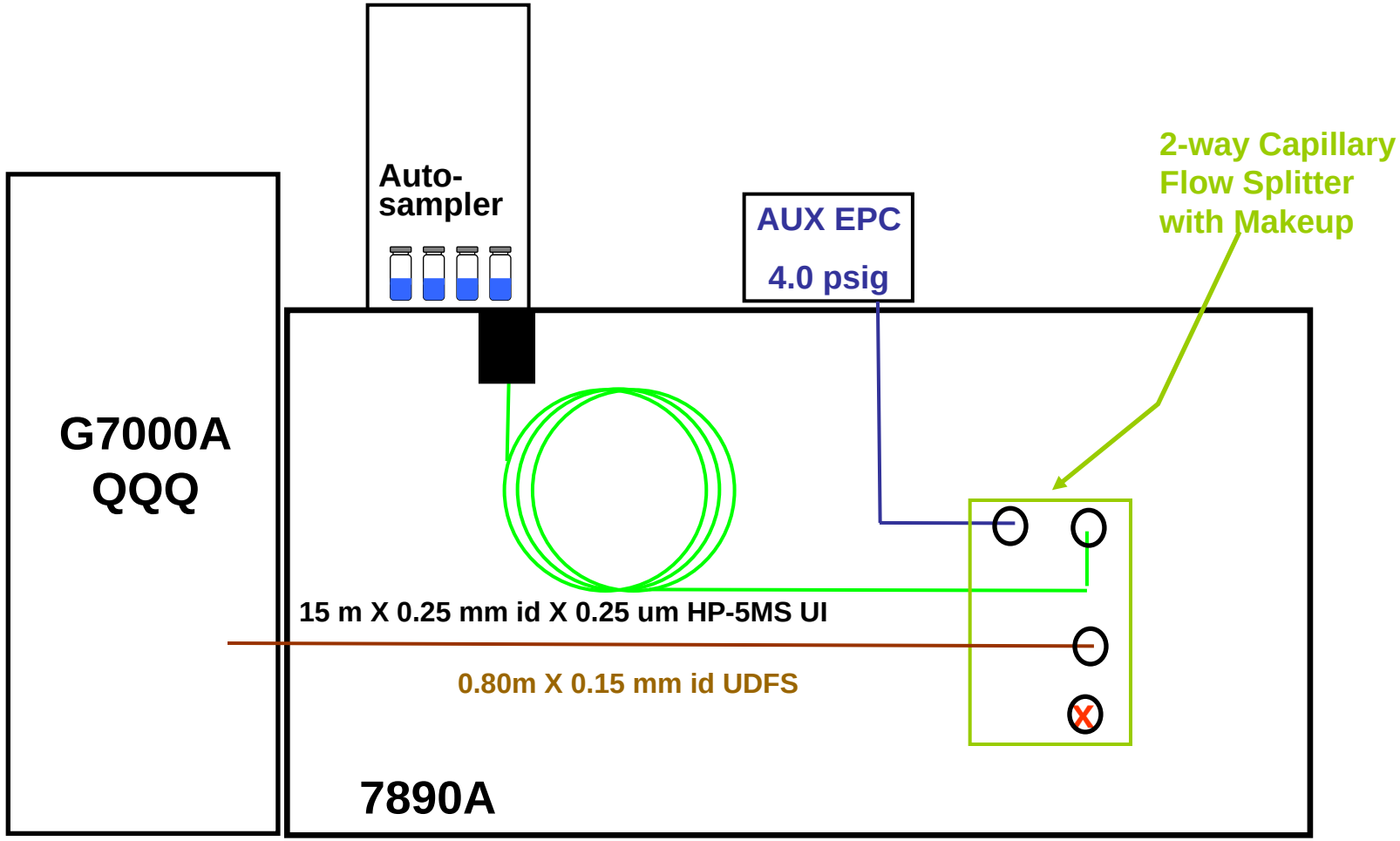
2ul Splitless Injection Scan Mode – 5975 MSD



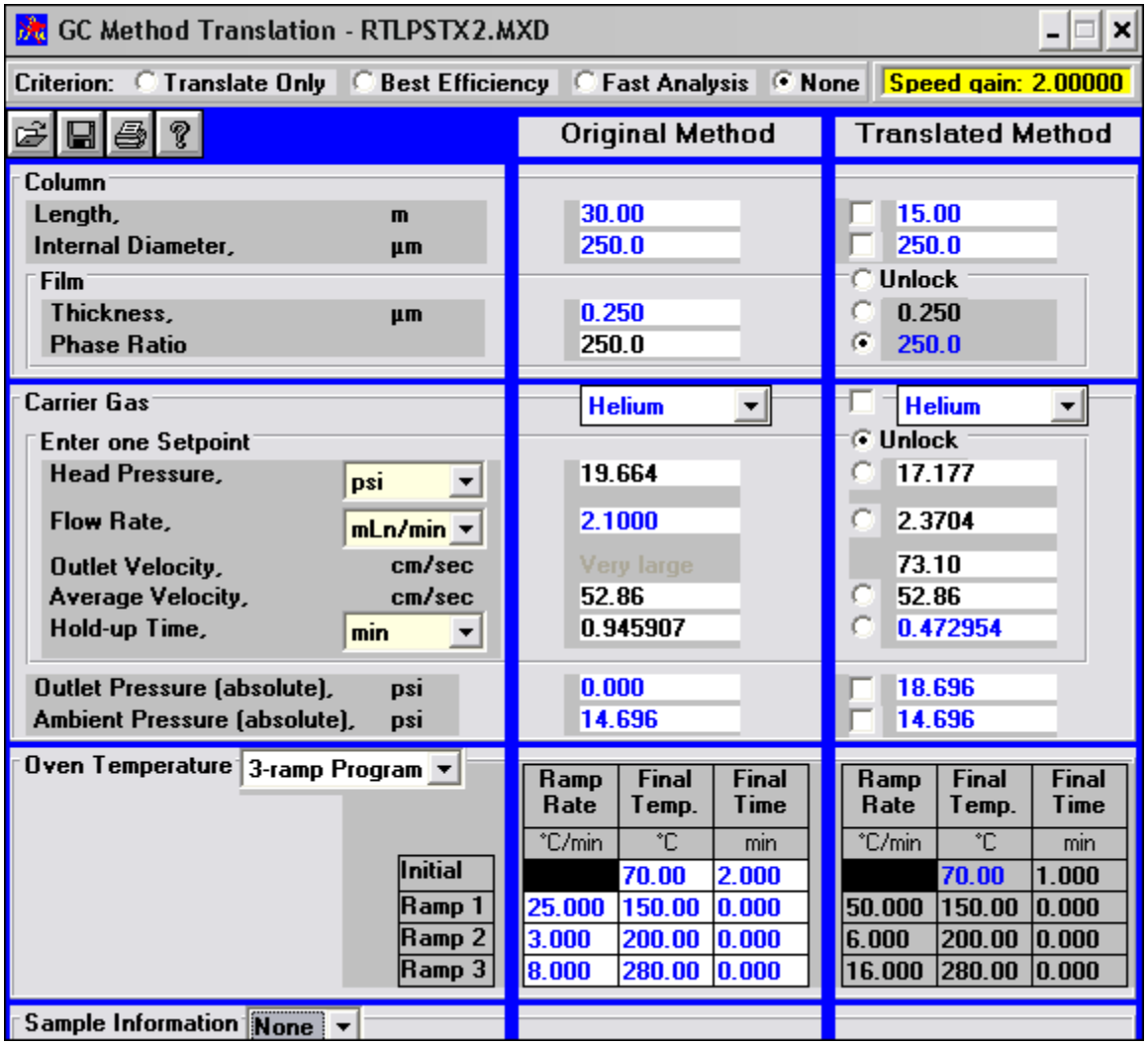
2ul Splitless Injection SIM Mode – 5975 MSD



OCPs / PCBs in Marine Sediments
Agilent RTL Pesticide Method



GC Method Agilent RTL Pest 2x Translated for AUX 4.0 psig



GC Method Translation - RTLPSTX2.MXD

Criterion: ○ Translate Only ○ Best Efficiency ○ Fast Analysis ◉ None Speed gain: 2.00000

		Original Method	Translated Method
Column			
Length,	m	30.00	☐ 15.00
Internal Diameter,	µm	250.0	☐ 250.0
Film			○ Unlock
Thickness,	µm	0.250	○ 0.250
Phase Ratio		250.0	◉ 250.0
Carrier Gas		Helium	☐ Helium
Enter one Setpoint			◉ Unlock
Head Pressure,	psi	19.664	○ 17.177
Flow Rate,	mLn/min	2.1000	○ 2.3704
Outlet Velocity,	cm/sec	Very large	73.10
Average Velocity,	cm/sec	52.86	○ 52.86
Hold-up Time,	min	0.945907	○ 0.472954
Outlet Pressure (absolute),	psi	0.000	☐ 18.696
Ambient Pressure (absolute),	psi	14.696	☐ 14.696

Oven Temperature: 3-ramp Program

	Original Method			Translated Method		
	Ramp Rate °C/min	Final Temp. °C	Final Time min	Ramp Rate °C/min	Final Temp. °C	Final Time min
Initial		70.00	2.000		70.00	1.000
Ramp 1	25.000	150.00	0.000	50.000	150.00	0.000
Ramp 2	3.000	200.00	0.000	6.000	200.00	0.000
Ramp 3	8.000	280.00	0.000	16.000	280.00	0.000

Sample Information: None

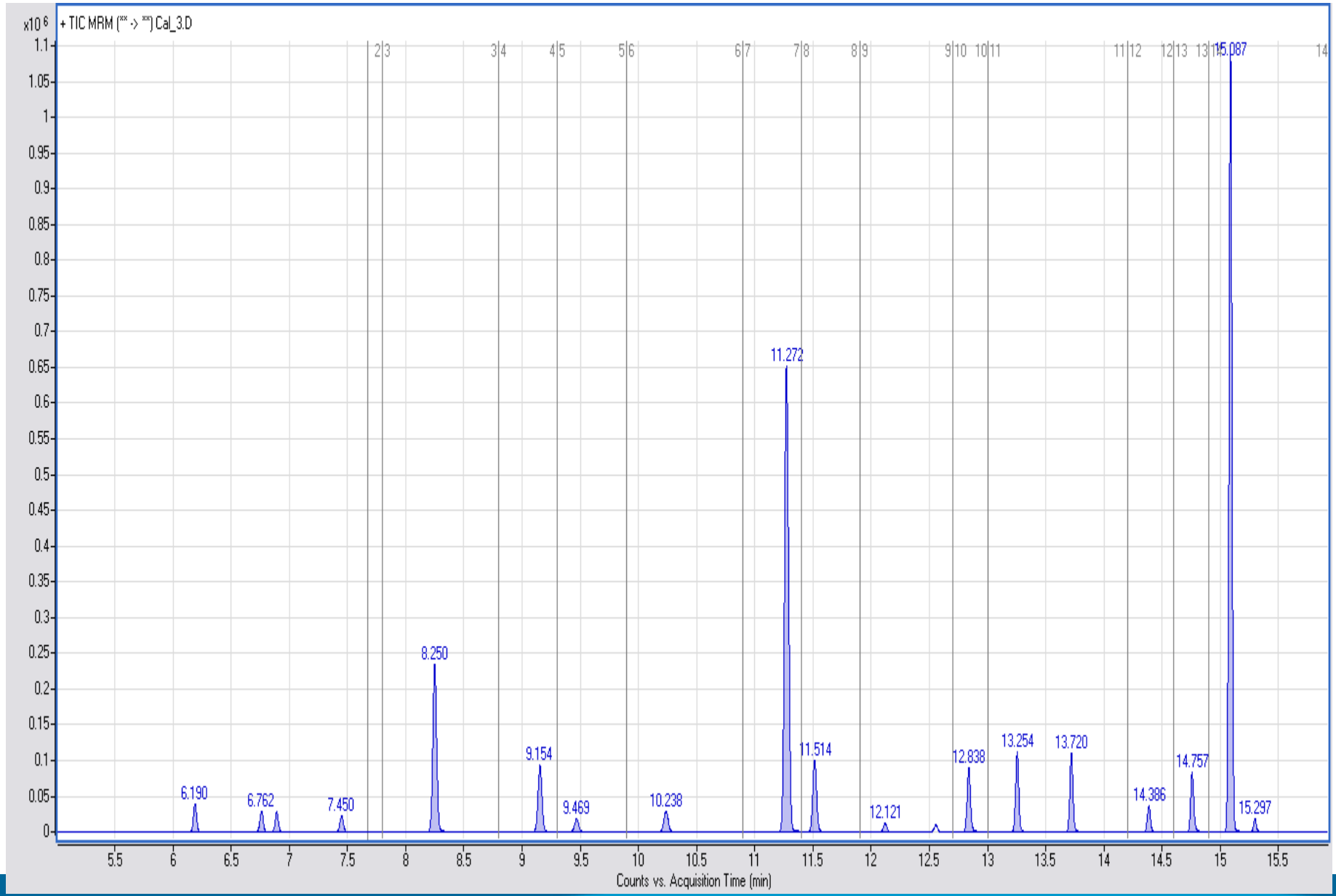
Target RTs and Transitions

TS	Target	Ret Time	Parent Ion m/z	Quant m/z	Qual m/z	CV
1	a-HCH	6.19	219	147	183	20
	b-HCH	6.76	219	147	183	20
	Lindane	6.89	219	147	183	20
	d-HCH	7.45	219	147	183	20
2	PCB 28	8.25	256	186	151	20
3	PCB 52	9.15	292	220	257	20
4	Aldrin	9.47	263	193	228	30
5	Isodrin	10.24	193	123	157	30
6	PCB 155 (ISTD)	11.28	360	290		20
7	PCB 101	11.51	326	256	291	20
8	Dieldrin	12.18	263	193	228	30
	Endrin	12.56	263	193	228	30
9	PCB 118	12.84	326	256		20
10	PCB 153	13.25	360	290	325	20
	PCB 138	13.72	360	290	325	20
11	PCB 180	14.75	394	324	359	20
12	Mirex (ISTD)	15.09	272	237		20

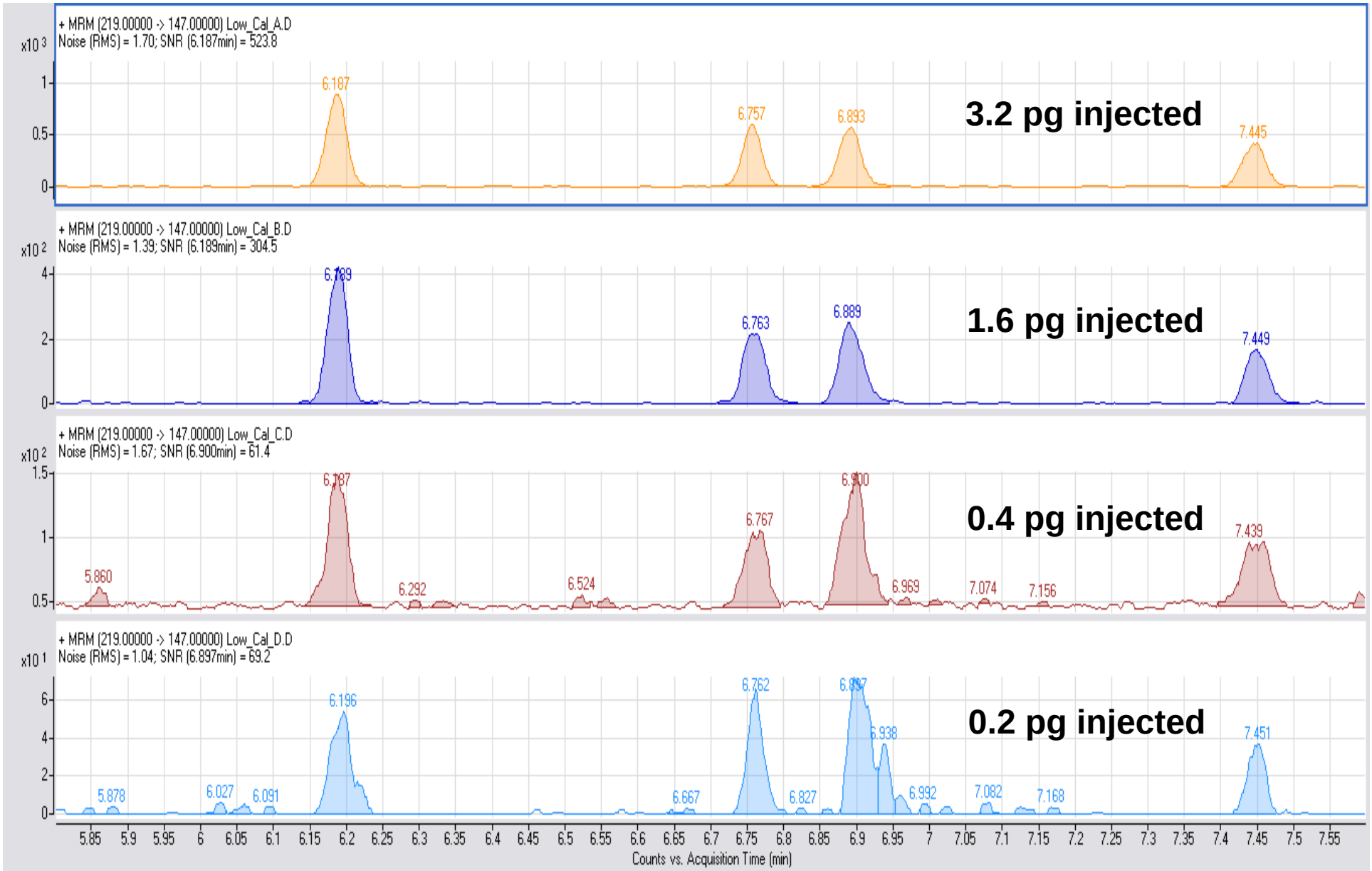
Calibration Range

Std Ref	Conc ppb	uL Injected	pg injected
Cal 5	200	2	400
Cal 4	100	2	100
Cal 3	40	2	80
Cal 2	20	2	40
Cal 1	8	2	16
Low Cal A	1.6	2	3.2
Low Cal B	0.8	2	1.6
Low Cal C	0.2	2	0.4
Low Cal D	0.1	2	0.2

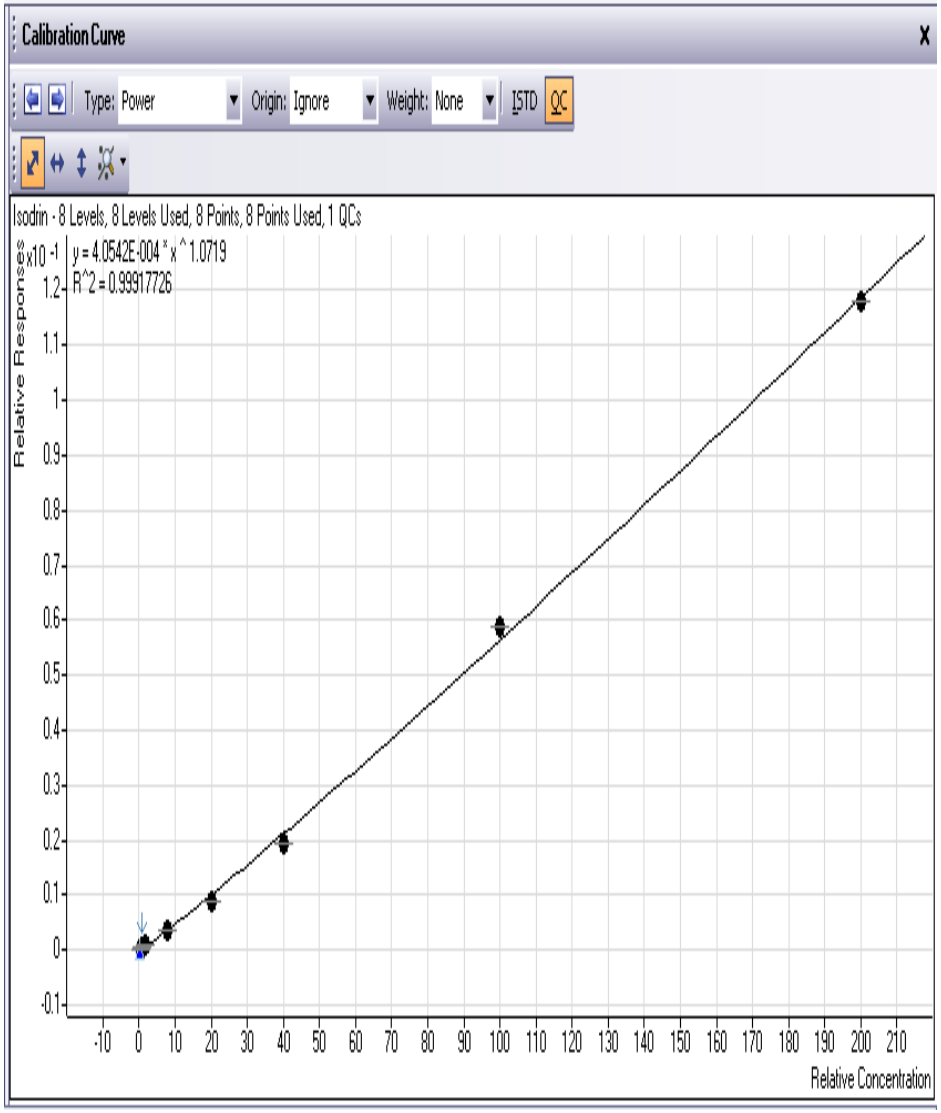
OCs / PCBs TIC MRM

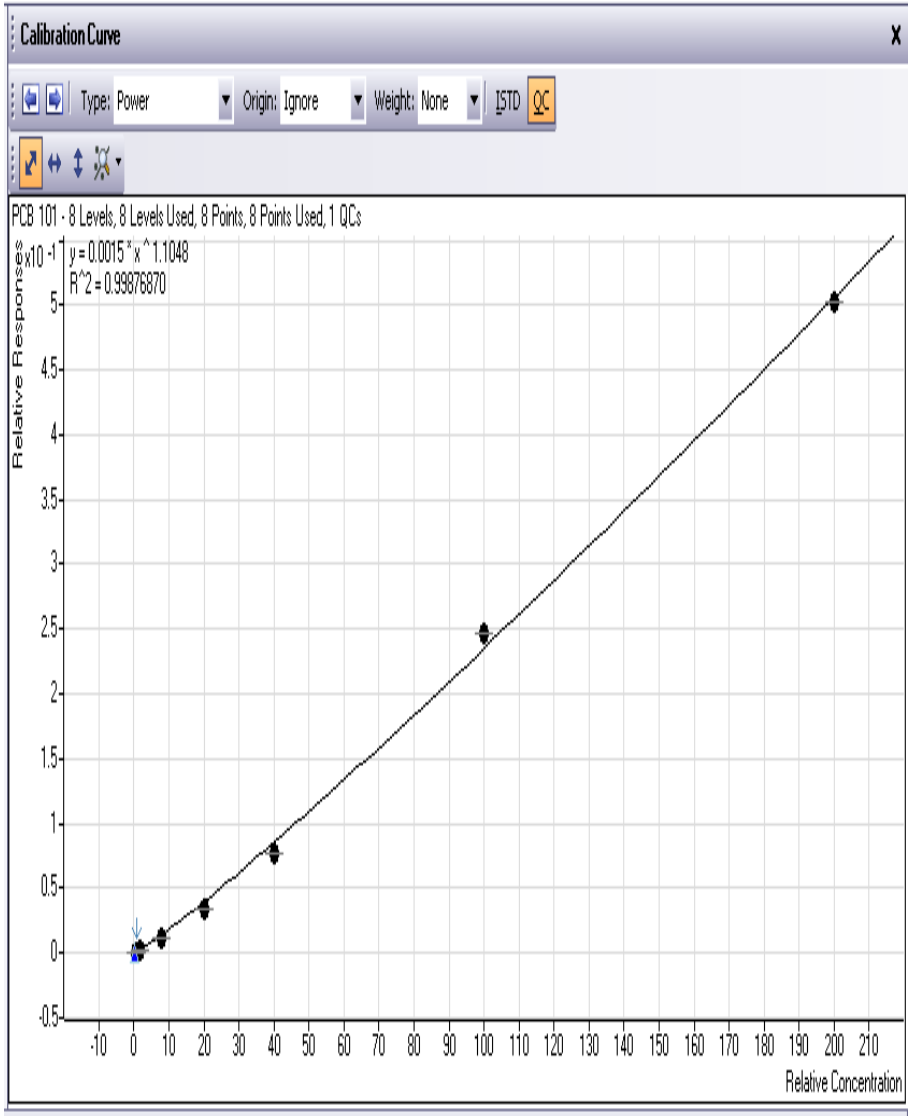


Lindanes : MRM Quant Transition 219 ➡ 147

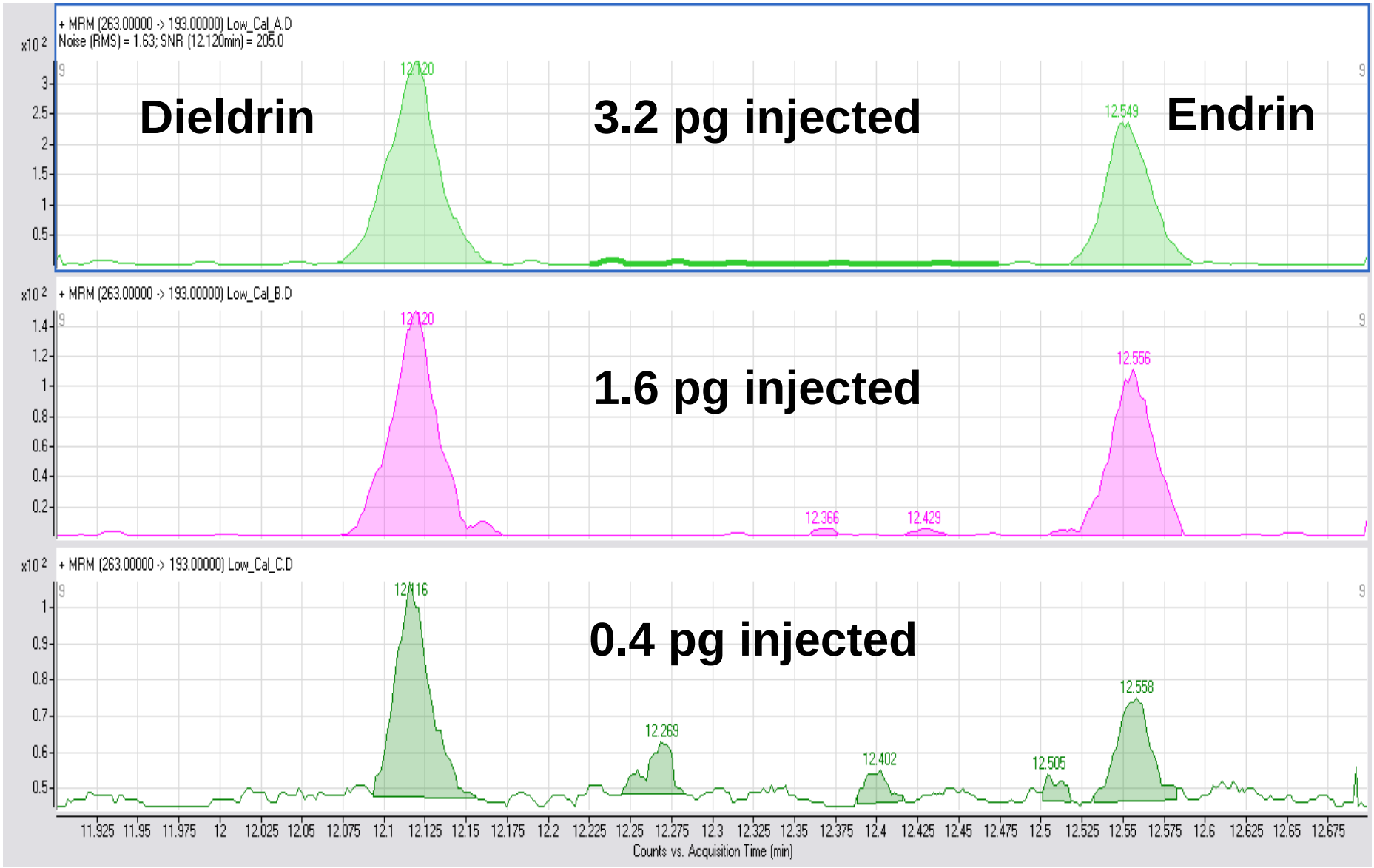


Cal Curves Isodrin, PCB 101

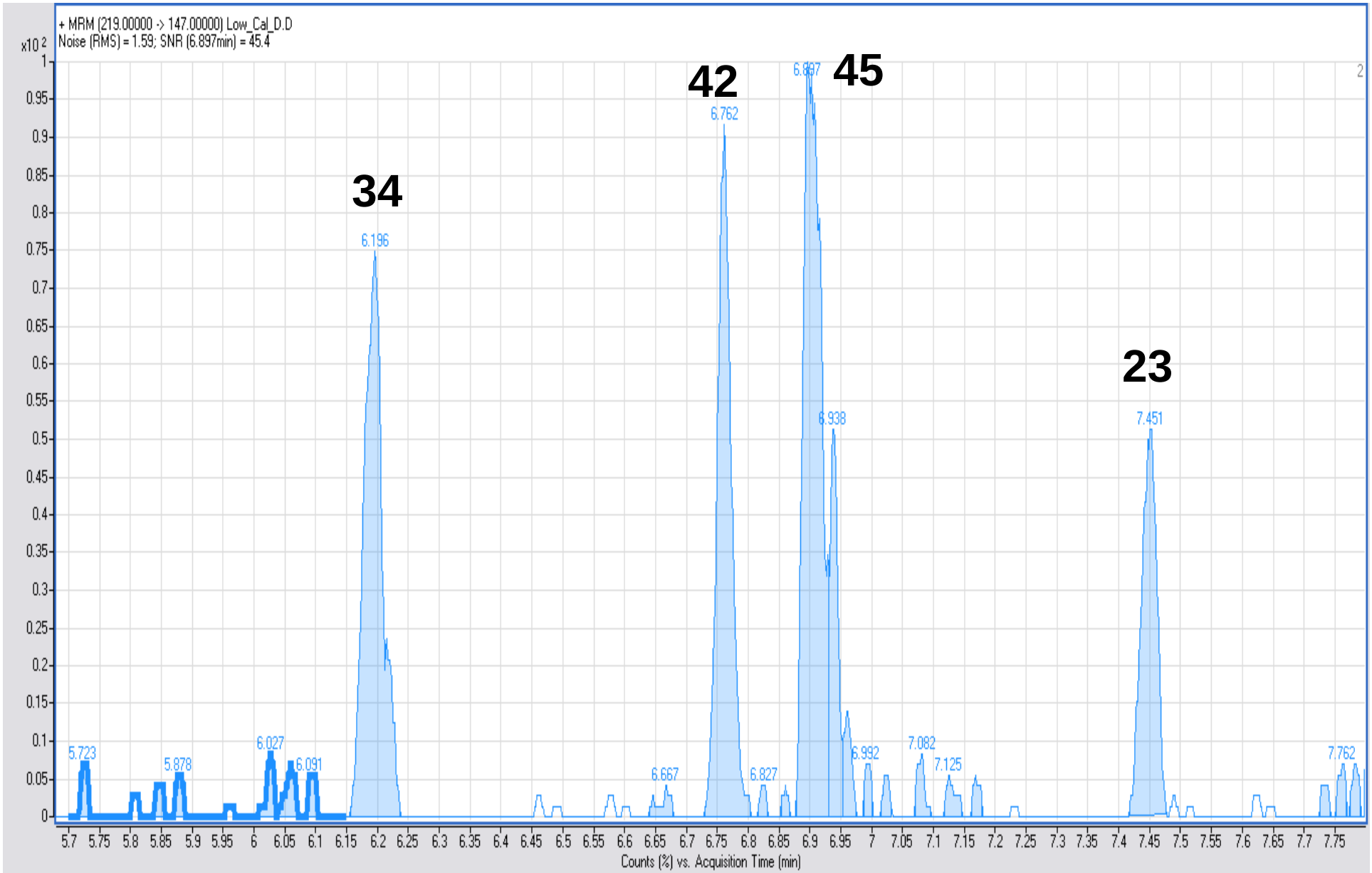




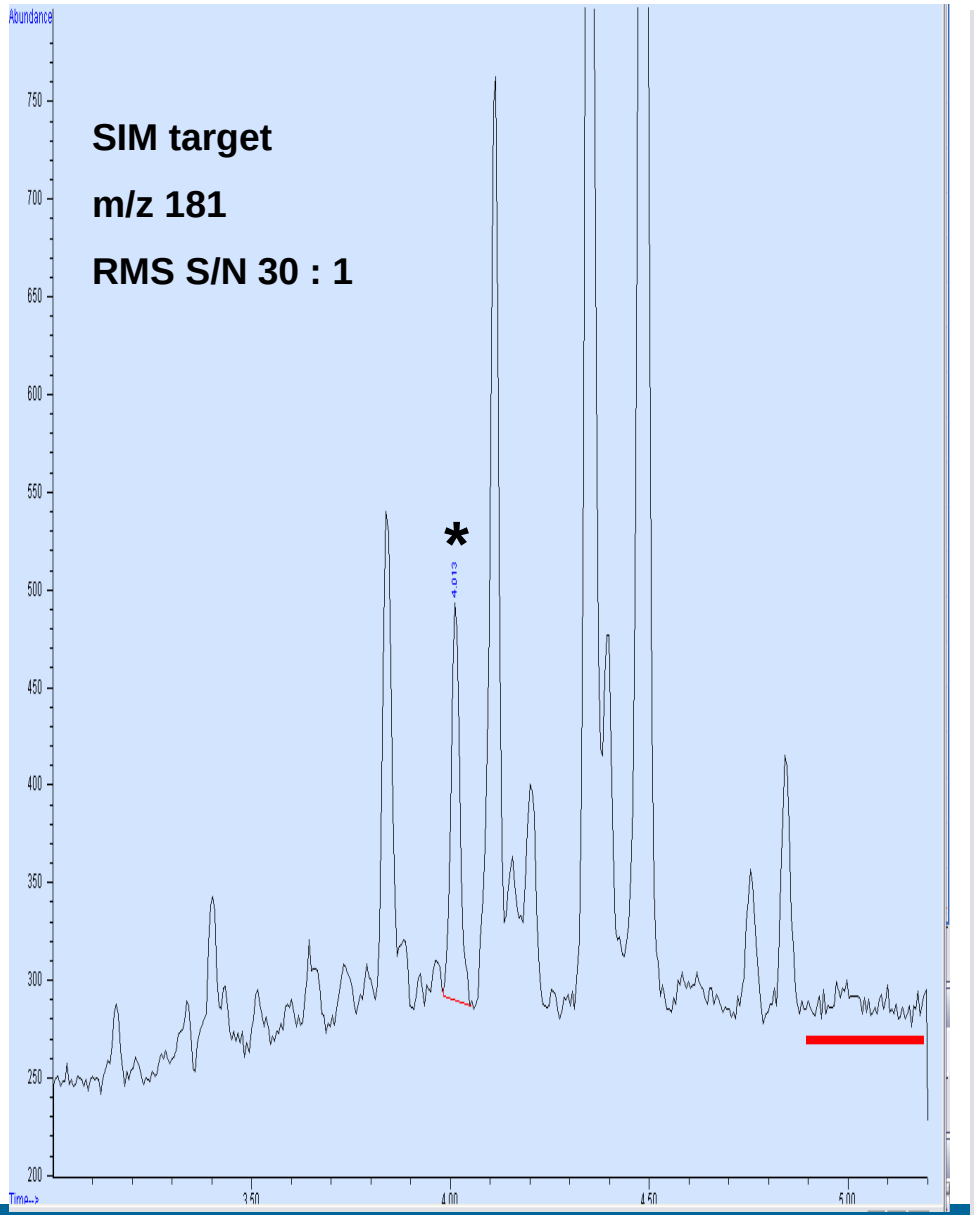
MRM Quant Transition 263 ➡193

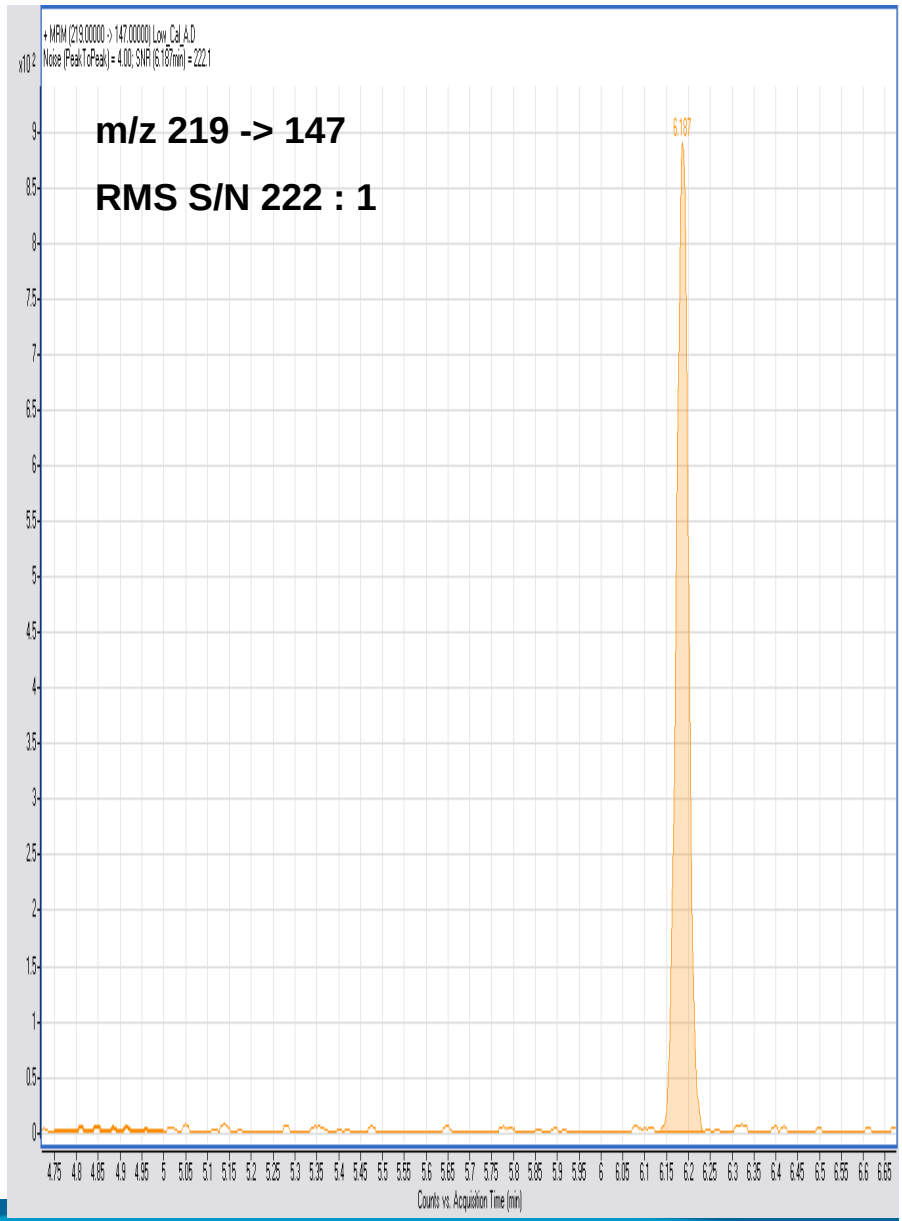


Lindanes : MRM 219 ➡ 147, RMS S/N 200 fg injected

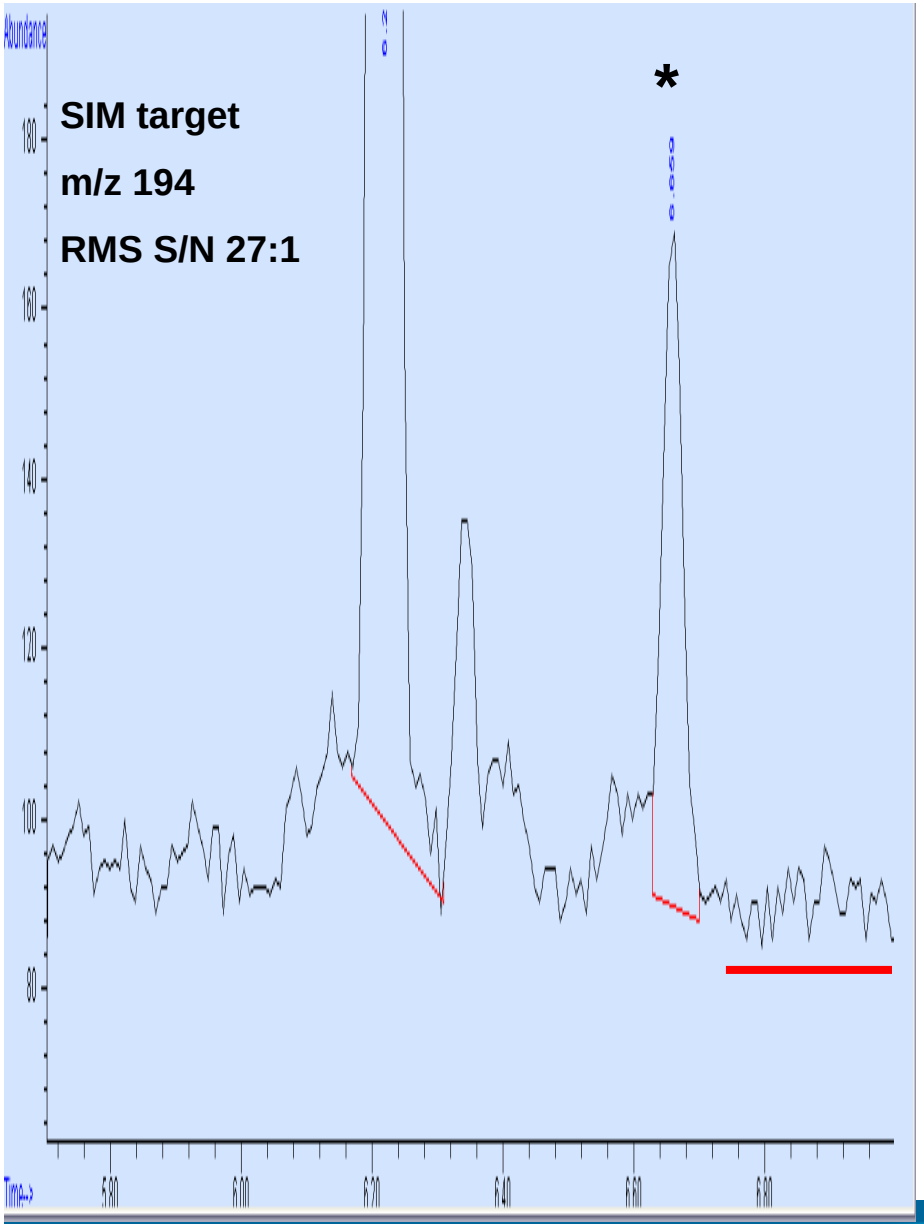


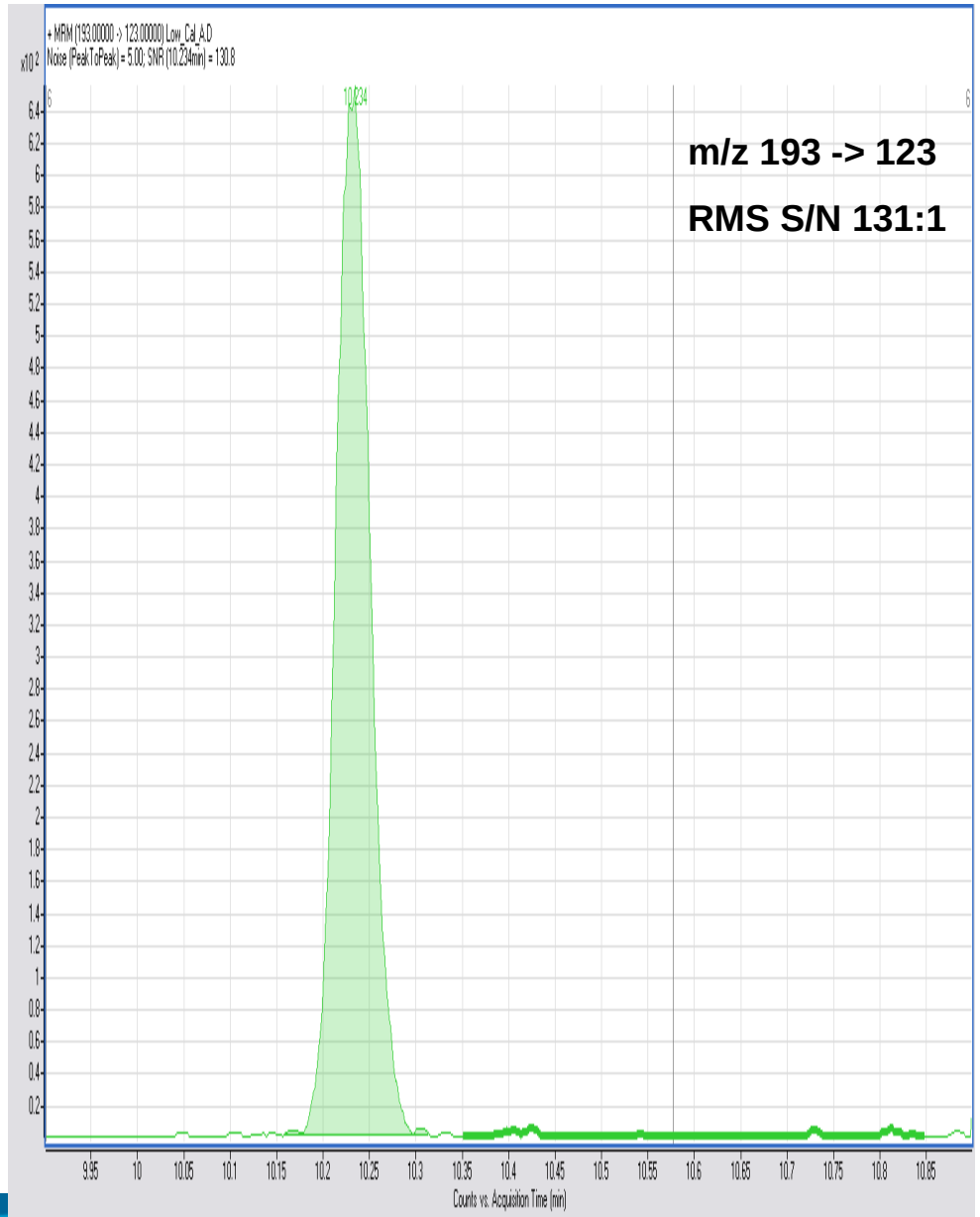
SIM (5973) vs MRM : a-HCH 3.2 pg injected



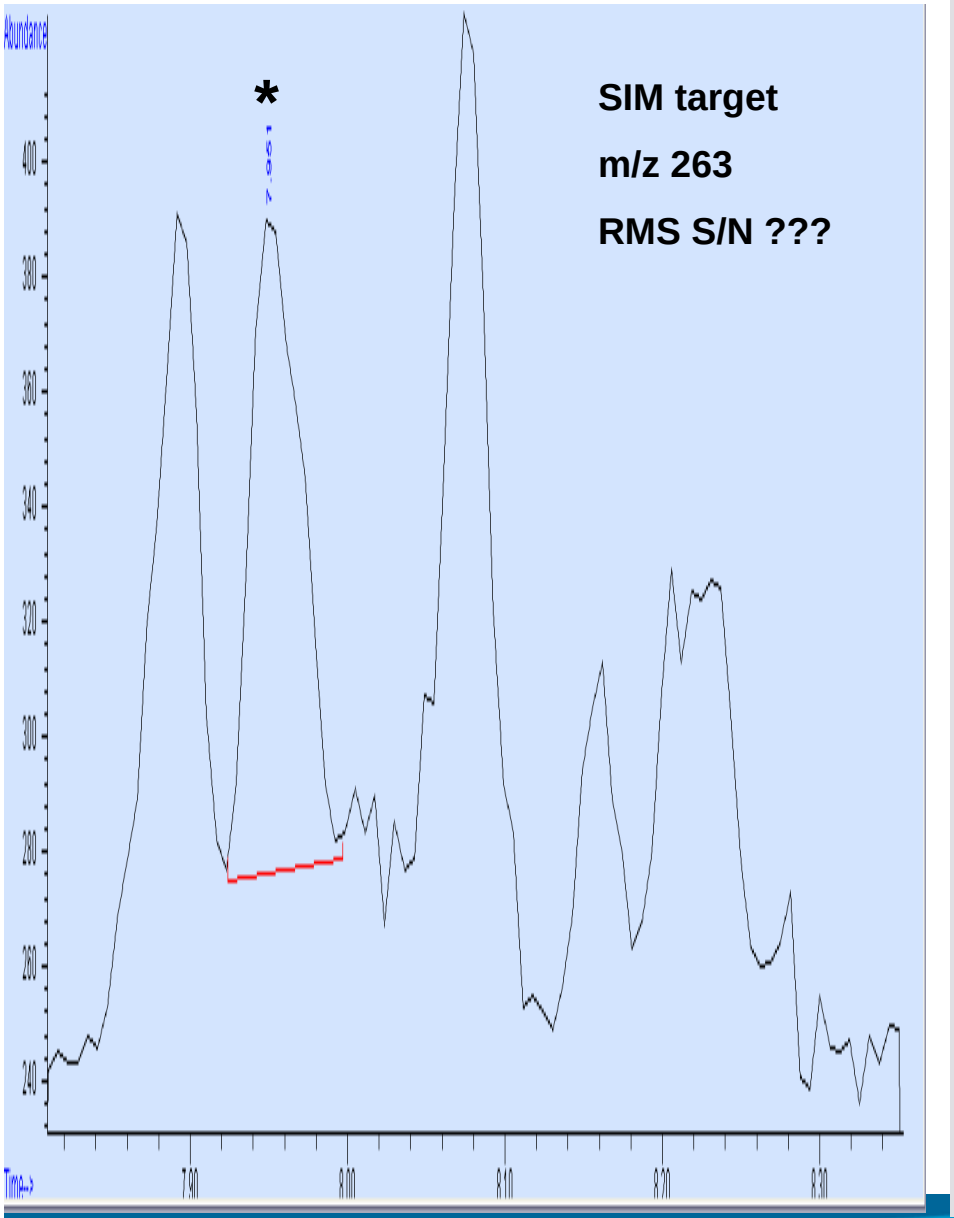


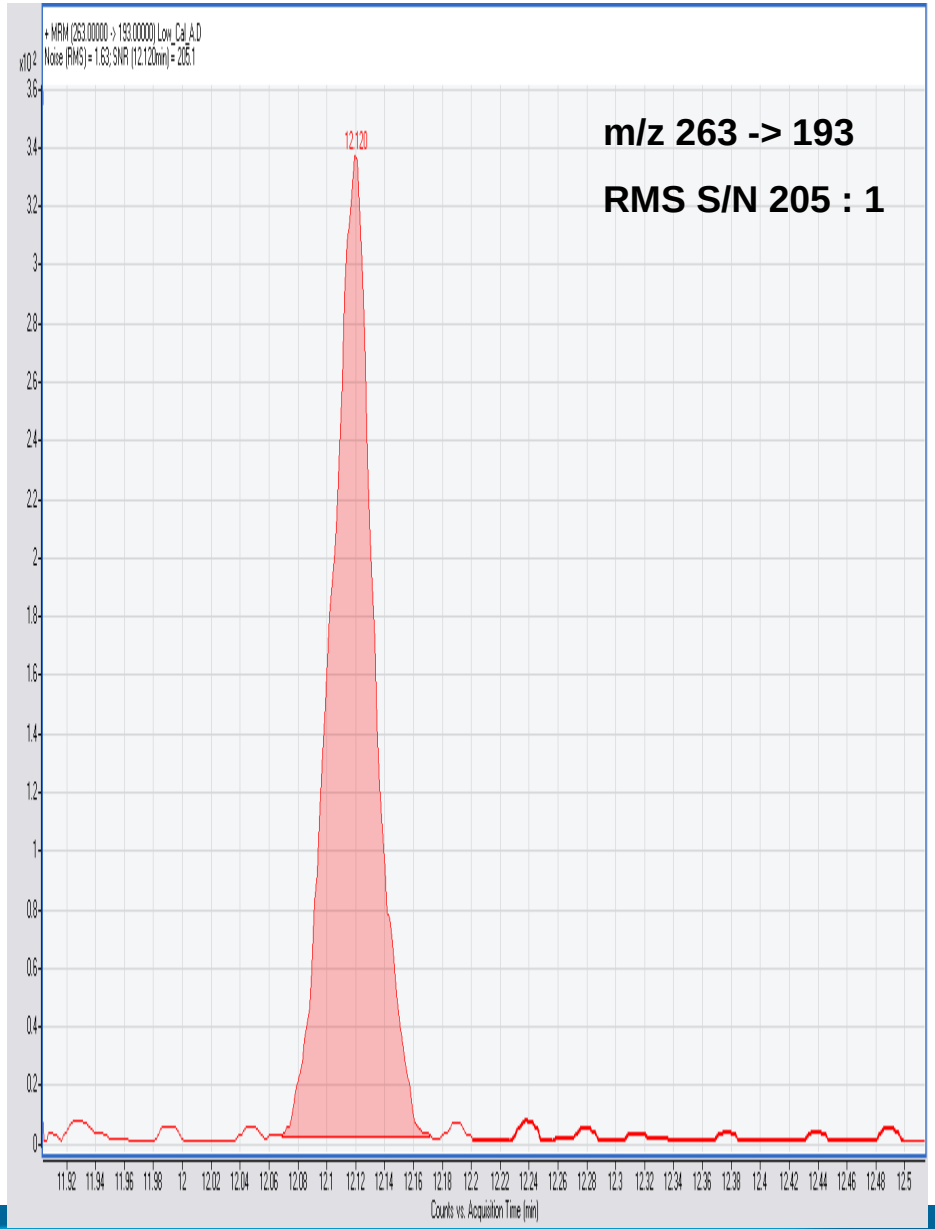
SIM (5973) vs MRM : Isodrin 3.2 pg injected



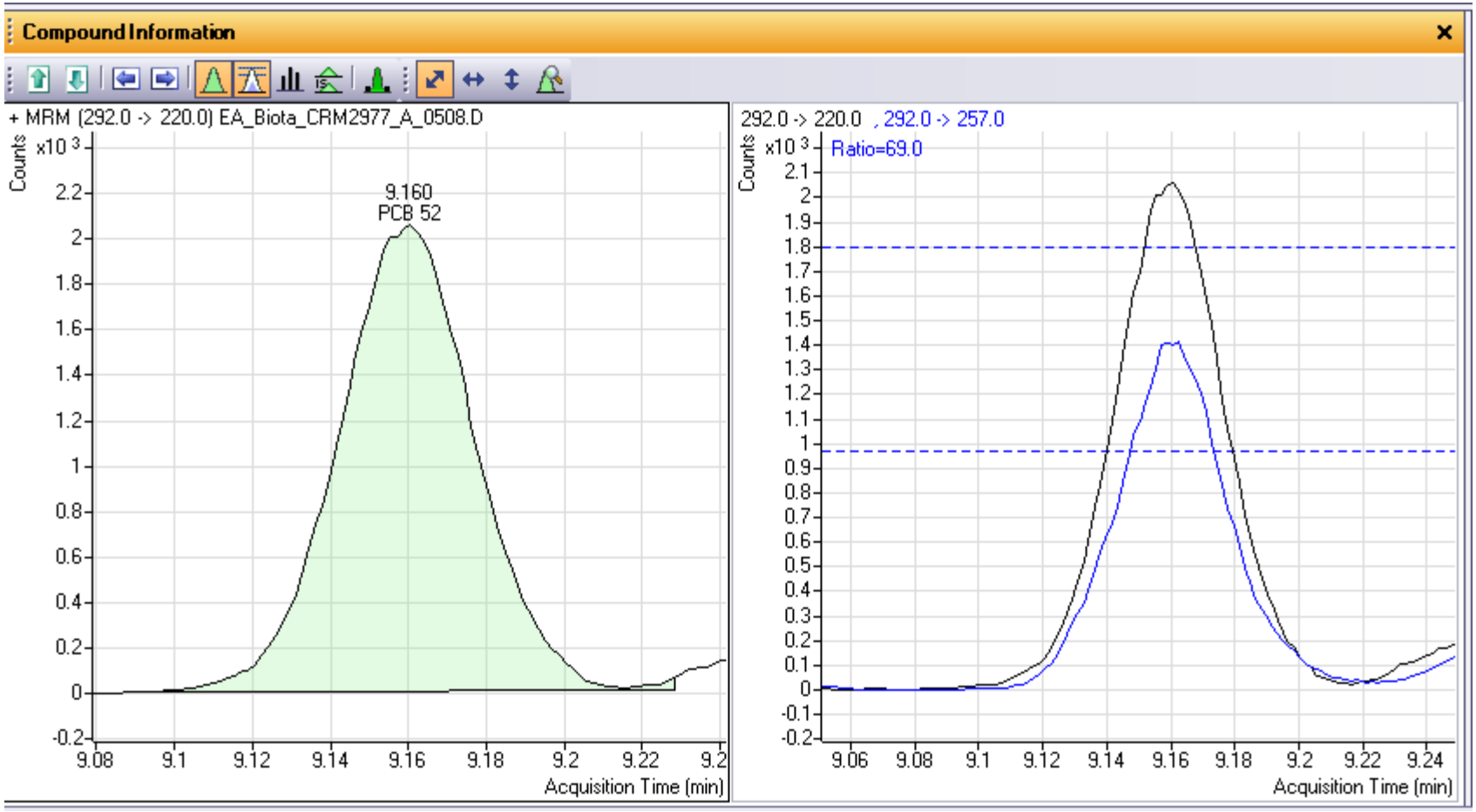


SIM (5973) vs MRM : Dieldrin 3.2 pg injected

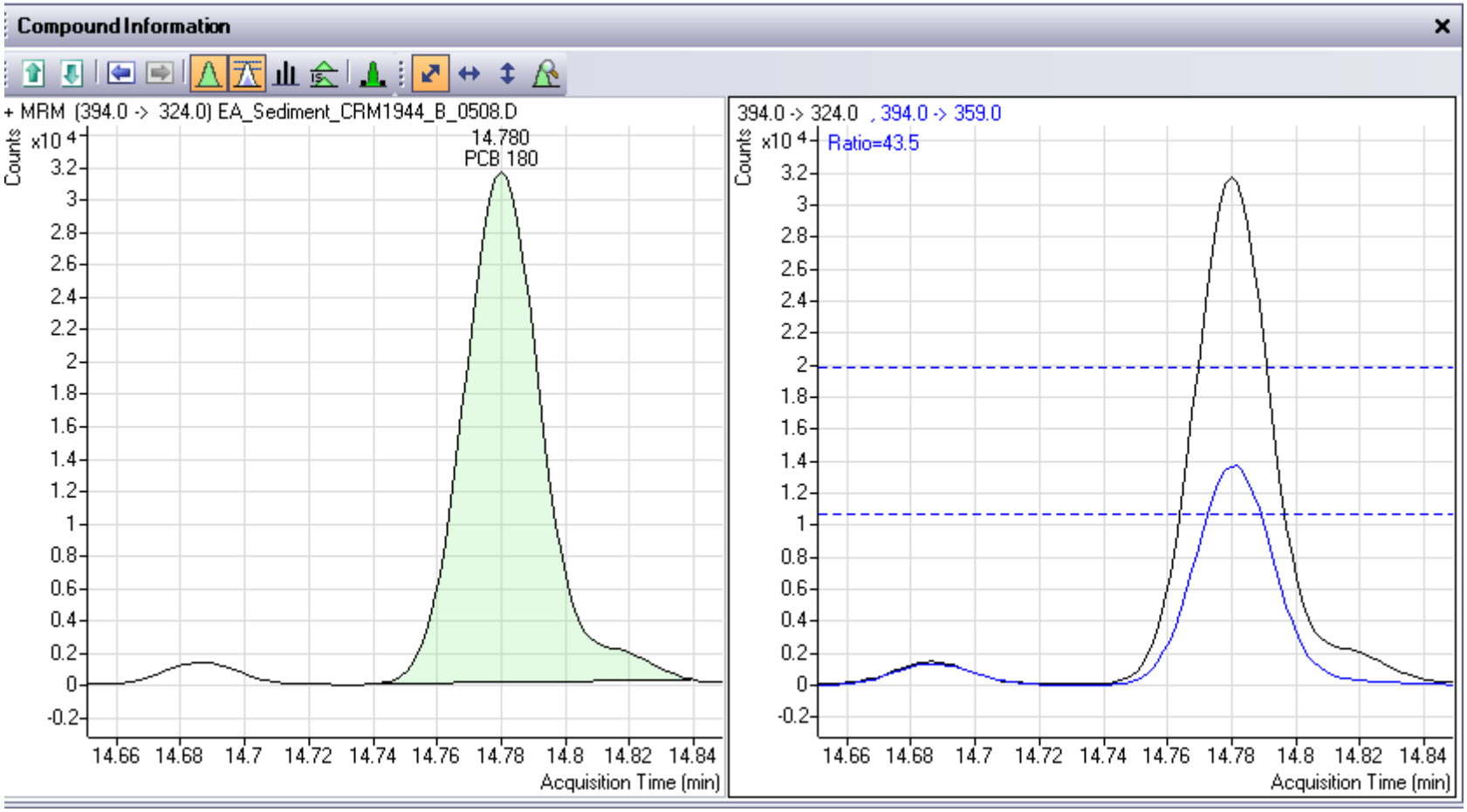




PCB 52 : 0.63 ppb in Biota Extract

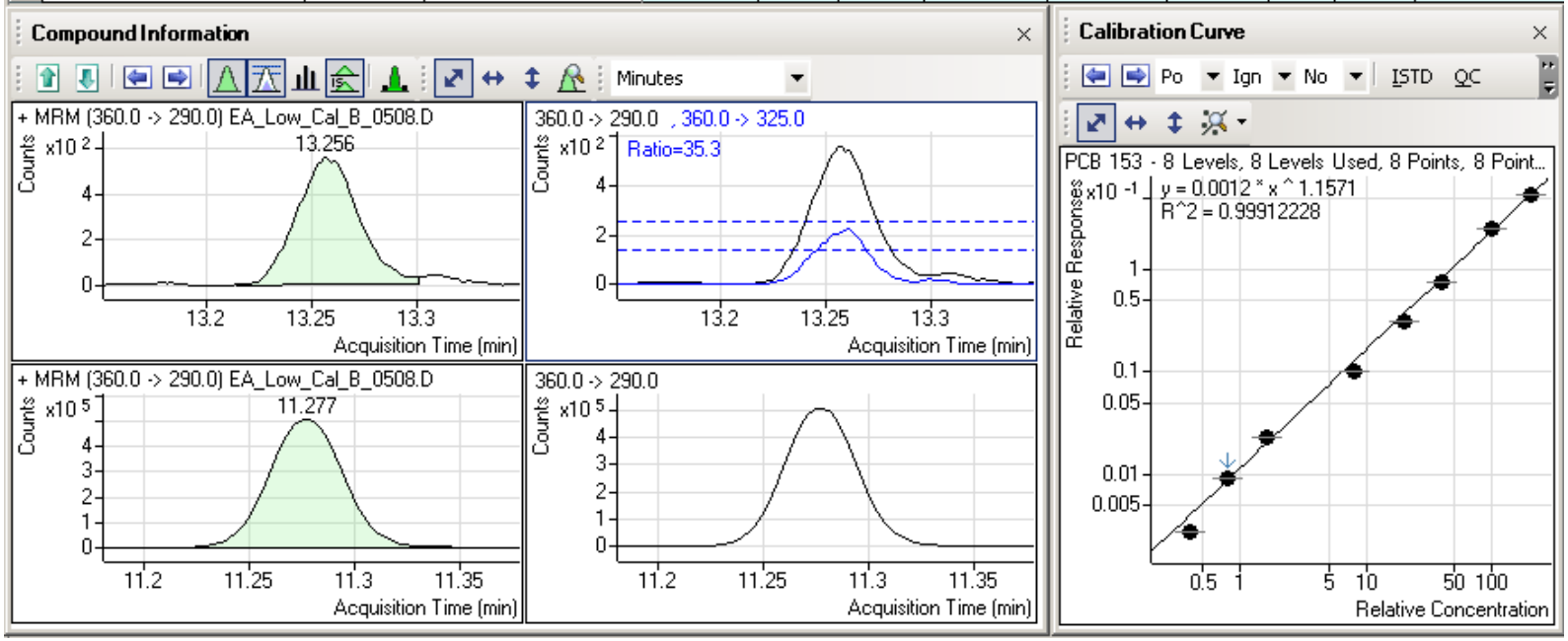


PCB 180 : 19.3 ppb in Sediment Extract



‘Results at a Glance’ – PCB 153

Sample			PCB 153...	PCB 153 Results					Qu...	PCB 155 (ISTD) (IST...	
Name	Type	Acq. Date-Time	Exp. Conc.	RT	Resp.	Calc. Conc.	Final Conc.	Accuracy	Ratio	RT	Resp.
EA Low Cal C	Cal	8/5/2008 3:06 PM	0.4000	13.256	392	0.2905	0.2905	72.6	41.5	11.280	1407548
EA Low Cal B	Cal	8/5/2008 3:23 PM	0.8000	13.256	1153	0.8234	0.8234	102.9	35.3	11.277	1240816
EA Low Cal A	Cal	8/5/2008 3:42 PM	1.6000	13.257	3195	1.7957	1.7957	112.2	34.0	11.277	1394530
EA Cal 01	Cal	8/5/2008 4:01 PM	8.0000	13.257	13772	6.5645	6.5645	82.1	35.1	11.276	1341342
EA Cal 02	Cal	8/5/2008 4:20 PM	20.0000	13.258	44311	16.9417	16.9417	84.7	35.0	11.275	1440849
EA Cal 03	Cal	8/5/2008 4:39 PM	40.0000	13.259	93432	36.7860	36.7860	92.0	34.9	11.277	1238753
EA Cal 04	Cal	8/5/2008 4:58 PM	100.0000	13.259	330146	103.6555	103.6555	103.7	35.9	11.276	1320111
EA Cal 05	Cal	8/5/2008 5:17 PM	200.0000	13.258	781324	199.0773	199.0773	99.5	36.7	11.276	1468188
EA Extract Biota Blank	Sample	8/5/2008 6:53 PM		13.256	409	0.0805	0.0805		69.7	11.277	6486277
EA Biota CRM 2977	Sample	8/5/2008 7:31 PM		13.258	10272	1.5128	1.5128		42.2	11.280	5467023
EA Biota CRM 2977	Sample	8/5/2008 8:09 PM		13.258	9834	1.4803	1.4803		35.1	11.280	5366849
EA Biota CRM 2977	Sample	8/5/2008 8:47 PM		13.261	10925	1.5501	1.5501		41.1	11.284	5652983
EA Extract Sediment Blank	Sample	8/5/2008 9:25 PM		13.261	9597	2.7890	2.7890		35.3	11.283	2516798
EA Sediment CRM 1944	Sample	8/5/2008 10:03 PM		13.275	132267	25.1141	25.1141		43.7	11.295	2727390
EA Sediment CRM 1944	Sample	8/5/2008 10:41 PM		13.278	135023	24.4716	24.4716		43.8	11.300	2868966
EA Sediment CRM 1944	Sample	8/5/2008 11:19 PM		13.279	119553	23.8858	23.8858		28.8	11.301	2612484



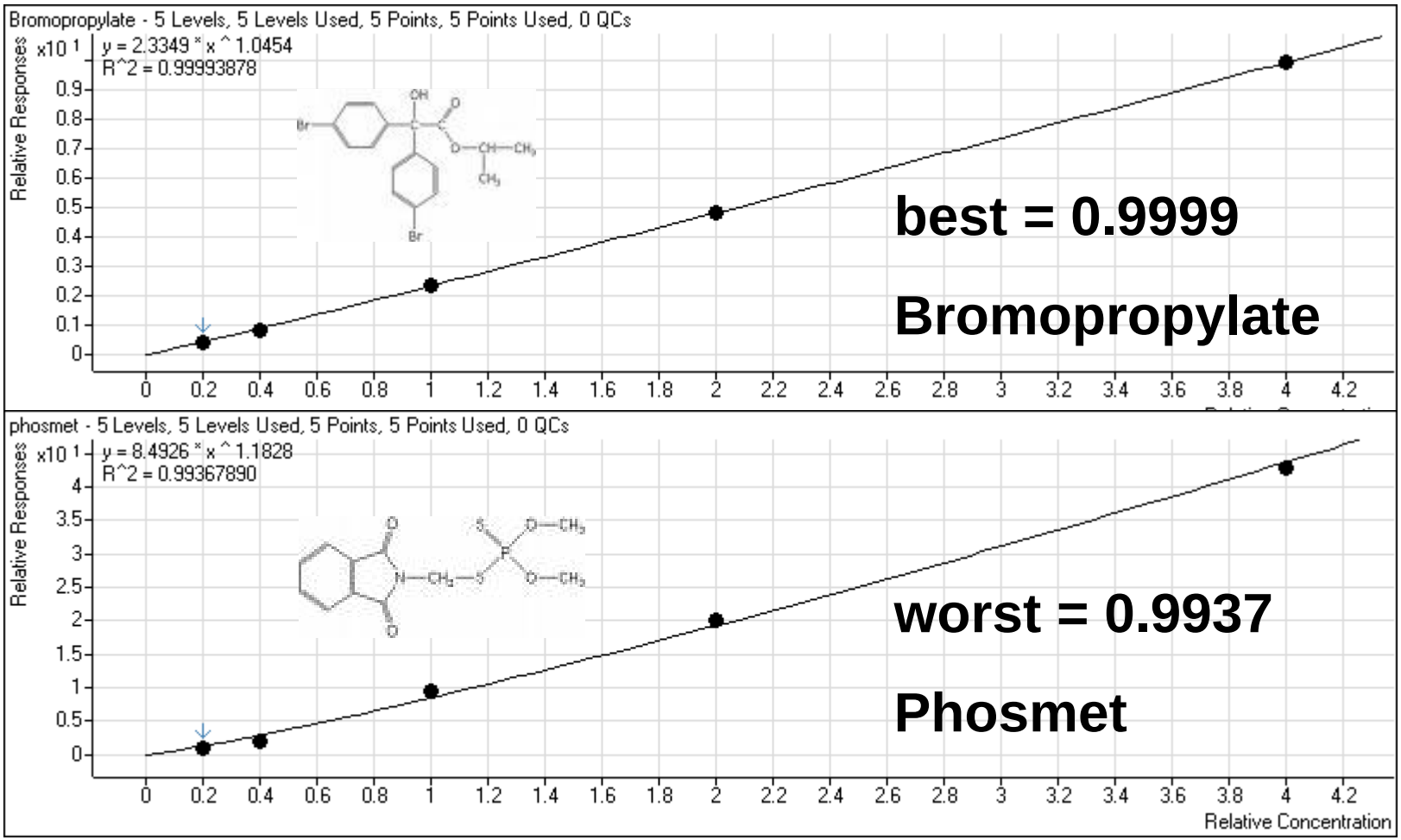
Quant Reproducibility– ppb

	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180
EA Extract Biota Blank	0.03	< 0.01	<0.01	0.04	ND	ND	ND
EA CRM 2977 Biota Extract	0.72	0.63	0.83	1.47	1.51	1.47	1.02
EA CRM 2977 Biota Extract	0.74	0.66	0.84	1.47	1.48	1.46	1.03
EA CRM 2977 Biota Extract	0.76	0.64	0.85	1.55	1.55	1.48	1.14
EA Extract Sediment Blank	0.94	2.93	1.59	2.49	2.79	1.57	4.36
EA 1944 Sediment Extract	46.69	23.29	18.81	23.03	25.11	25.10	19.36
EA 1944 Sediment Extract	44.87	21.83	18.60	23.65	24.47	25.05	19.29
EA 1944 Sediment Extract	45.28	22.28	18.29	22.25	23.88	24.41	18.87

Pesticide/PCB results from the G7000A QQQ-GCMS

Melissa Churley, Santa Clara
Charles Thomson, Santa Clara
Bernhard Rothweiler, WAD
Pasi Vuorinen, Finland
Max Ruemler, WAD

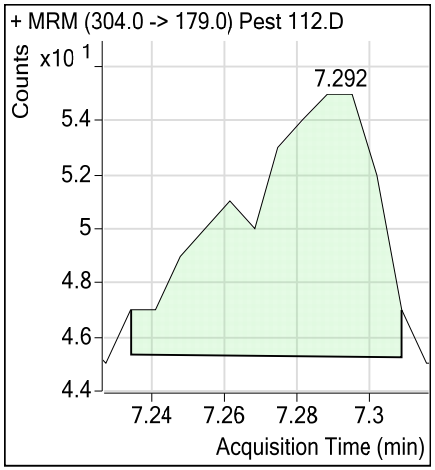
Pesticide STD
5 levels, 10 – 200 ppb

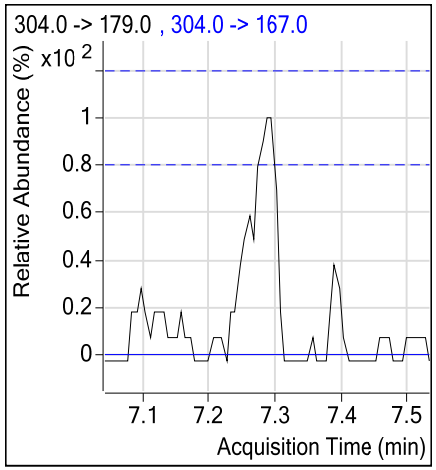


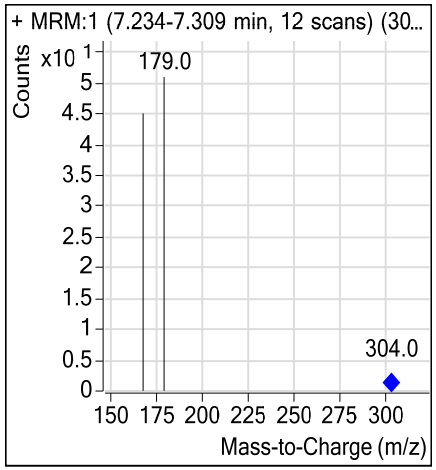
Pesticide STD Results table (ppb)

	QQQ strawberry	Q strawberry	QQQ carrot	Q carrot	QQQ parsley	Q parsley
propoxur					4.0	
chlorpropham			0.4		3.7	
triflualin					22.9	23.6
Carbofuran	1.1		0.5		1.5	
BHC Beta gama					0.2	
diazinon			122.8	112.4	0.1	
vinclozolin			212.1	187.5		
chlorpyriphos methyl			16.6	21.7		
malathion			146.5	139.2	0.3	
fenpropimorph			0.3			
pendimethalin			0.3		26.7	
endosulfan alfa					0.3	
mepanipyrim	64.4	65.2				
kresoxim methyl			10.4	10.8		
Endosulfan beta					0.2	
oxadixyl					4.7	
endosulfan sulfate			20	21.9		
quinoxyfen			65	63.7		
triphenyl phosphate	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD
phosmet			48.4	46.1	5	
cyhalothrin	54.4	49.1			125.8	125.5

Pesticides in the sample
Range detected, 0.1 to 200 ppb

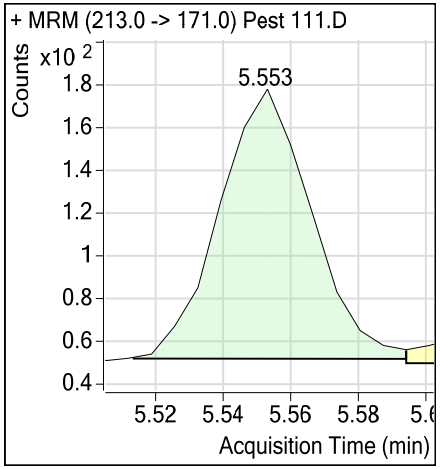


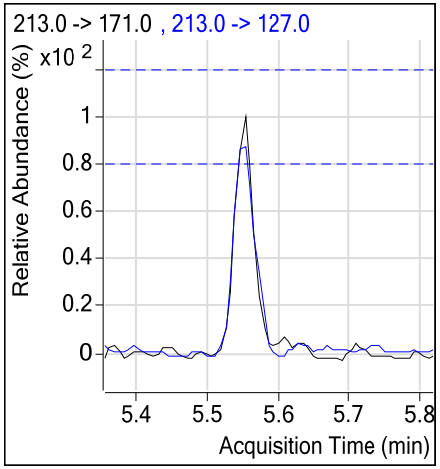


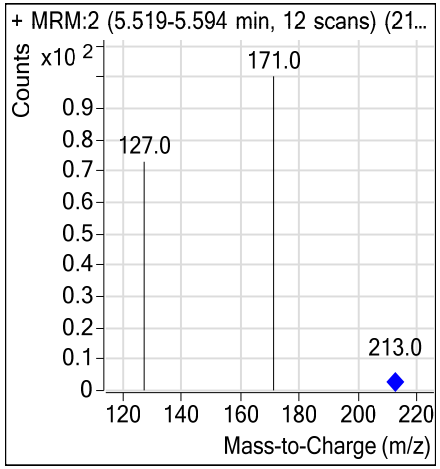


0.1 ppb Diazinon

in parsley matrix



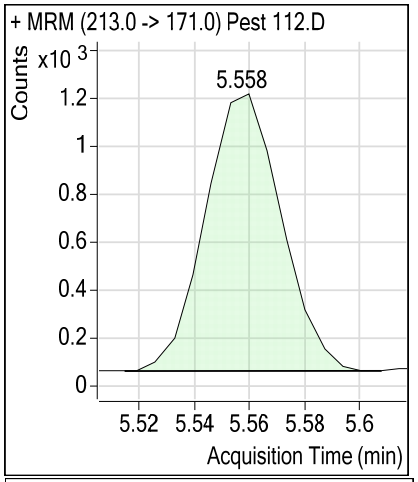


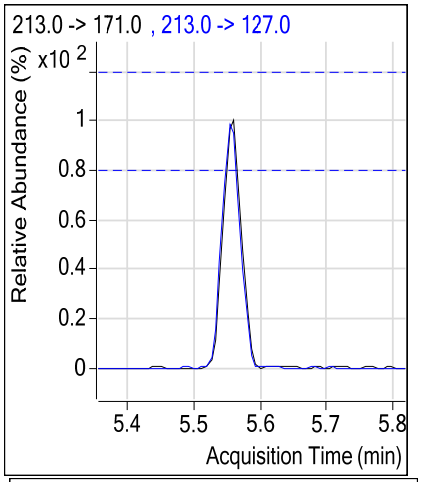


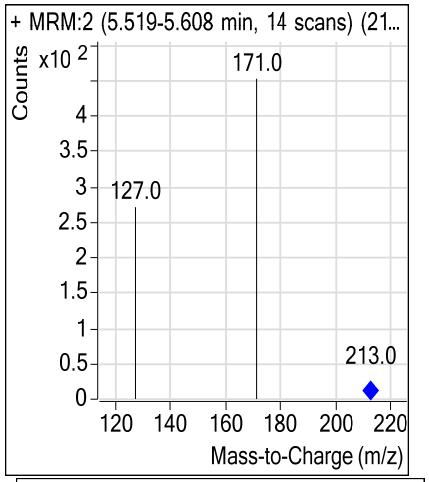
0.4 ppb Chlorpropham

in carrot matrix

Pesticides in the sample
Range detected, 0.1 to 200 ppb

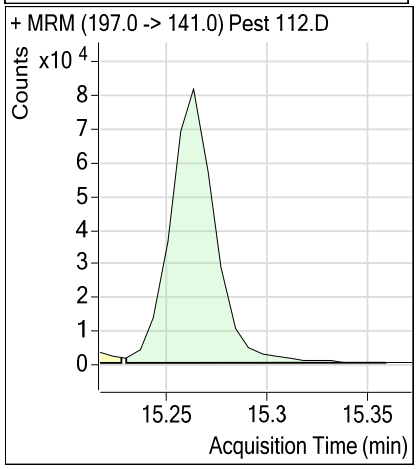


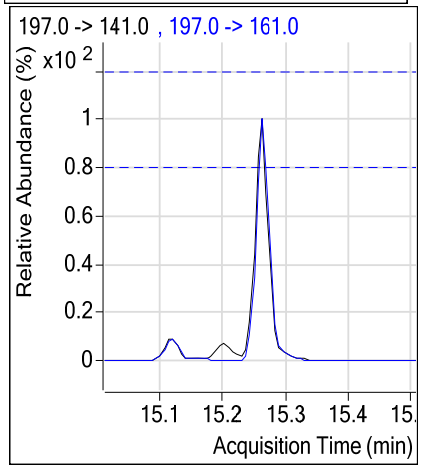


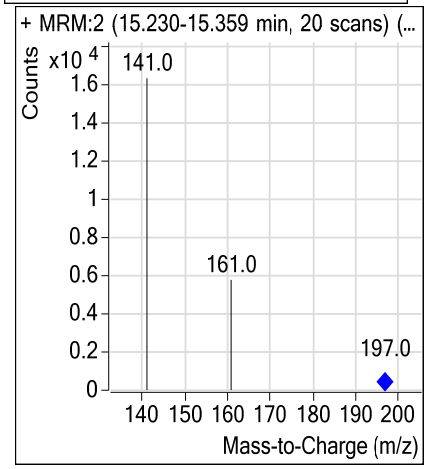


3.7 ppb Chlorpropham

in parsley matrix



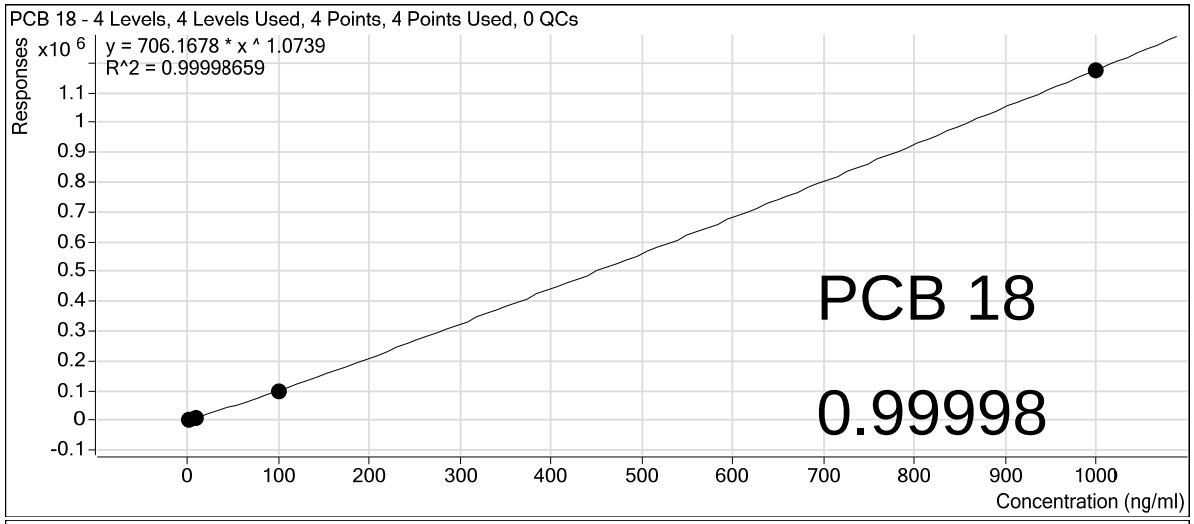


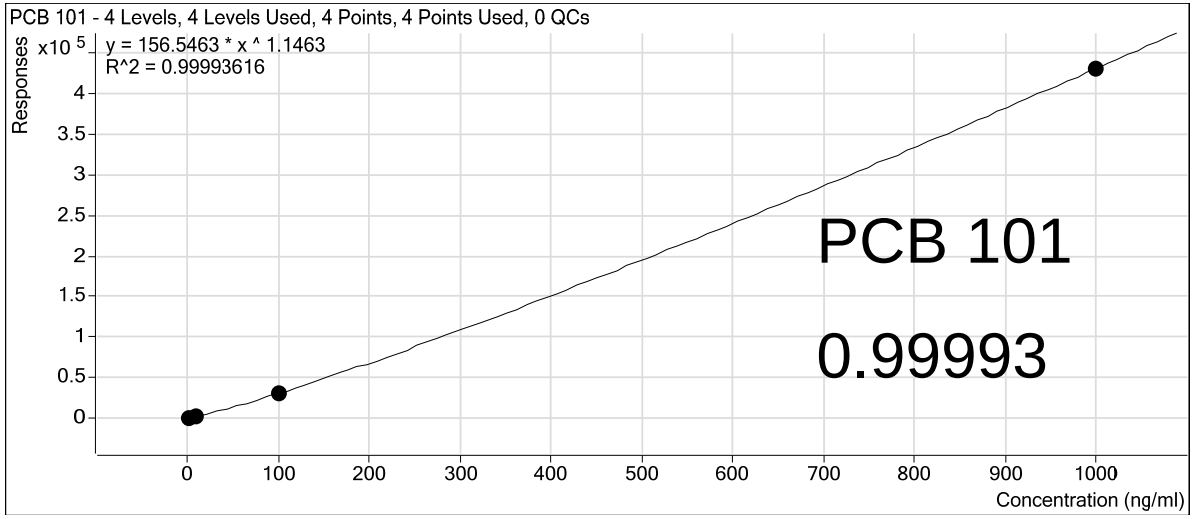


125.8 ppb Cyhalothrin

in parsley matrix

PCB STDs
1 to 1000 ppb

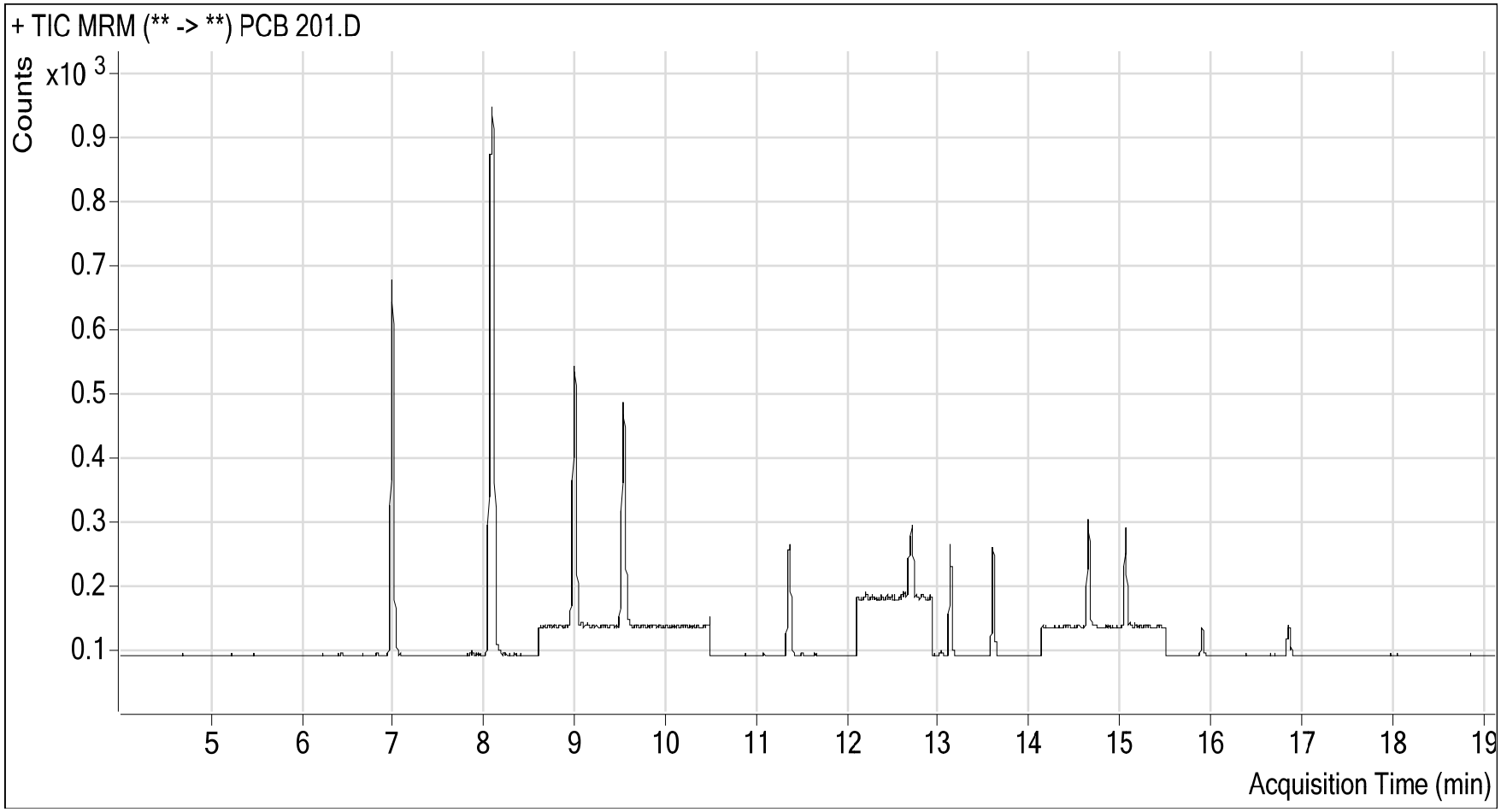




List:

- **PCB18**
- **PCB28+31**
- **PCB52**
- **PCB44**
- **PCB101**
- **PCB149**
- **PCB118**
- **PCB153**
- **PCB138**
- **PCB180**
- **PCB170**
- **PCB194**
- **PCB209**

MRM data from 1 ppb PCB STD



PCBs within fish matrix

	QQQ eel	Q eel	QQQ trout	Q trout
PCB18	0.2		0.3	15.2
PCB28+31	1.1		31.4	
PCB52	6.7	3.8	2.2	0.7
PCB44	4.7	1.3	2.7	0.6
PCB101	18.4	10.7	16.1	7.1
PCB149	54.5	14.3	36.9	10.4
PCB118	34.4	22.6	14.9	9.5
PCB153	148	118.5	52.3	40.8
PCB138	154.8	108.7	54.6	34.1
PCB180	100.9	58.5	46.4	22.5
PCB170	97.1	30.7	43	10.6
PCB194	13.5	3.8	9.1	0.9
PCB209	82.5	56.9	136	88.7

Results summary

Pesticide Standard

- Concentrated on 29 from ~120 Pesticides found
- Compared STD results between single Q and QQQ
  - Scan spectra and SIM data comparable (Collision gas ON!)
  - Over 5 concentration levels (10 – 200 ppb) comparable good results

QQQ benefits

- MRM data are more selective and sensitive (below 1 ppb)
- No matrix effects visible at the QQQ

Results summary

Pesticides in the sample

- Found pesticides in each of the three samples (strawberry, carrot, and parsley) detected compounds in the range of 0.1 to 200 ppb
- Required detection limit is 10 ppb

PCBs in the samples and STD

- STD range 1 – 1000 ppb
- Required detection limit is 1 ppb
- All 14 PCBs detected in matrix (fish)

Results summary

Backflush

- Not running backflush at the Single Quad already effected the chromatographic results after about 20 injections
- Not visible at the QQQ GC/MS system due to backflush

Pesticide STD
Analytical QQQ benefits

- MRM data are more selective and sensitive
  - Found 0.1 to 200 ppb in sample
  - Detected all Pesticide in spiked customer sample
- No matrix effects visible at the QQQ
  - Lower possibility for false positives and negatives