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Analysis of Full Scan Method 625 Semi-Volatiles and MRM Method 608 Pesticides by GCMSMS in a Single Extract

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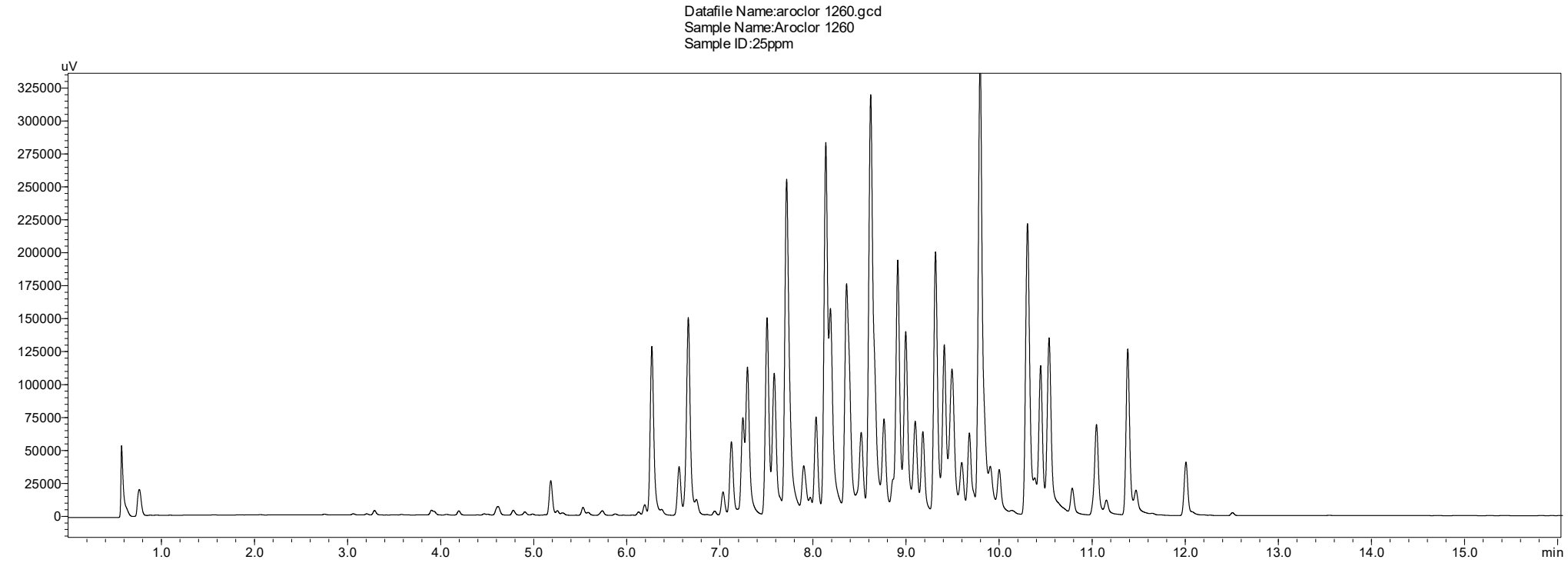
August 2016

Pesticide and Semi-volatile analysis requires two extractions and two analyses

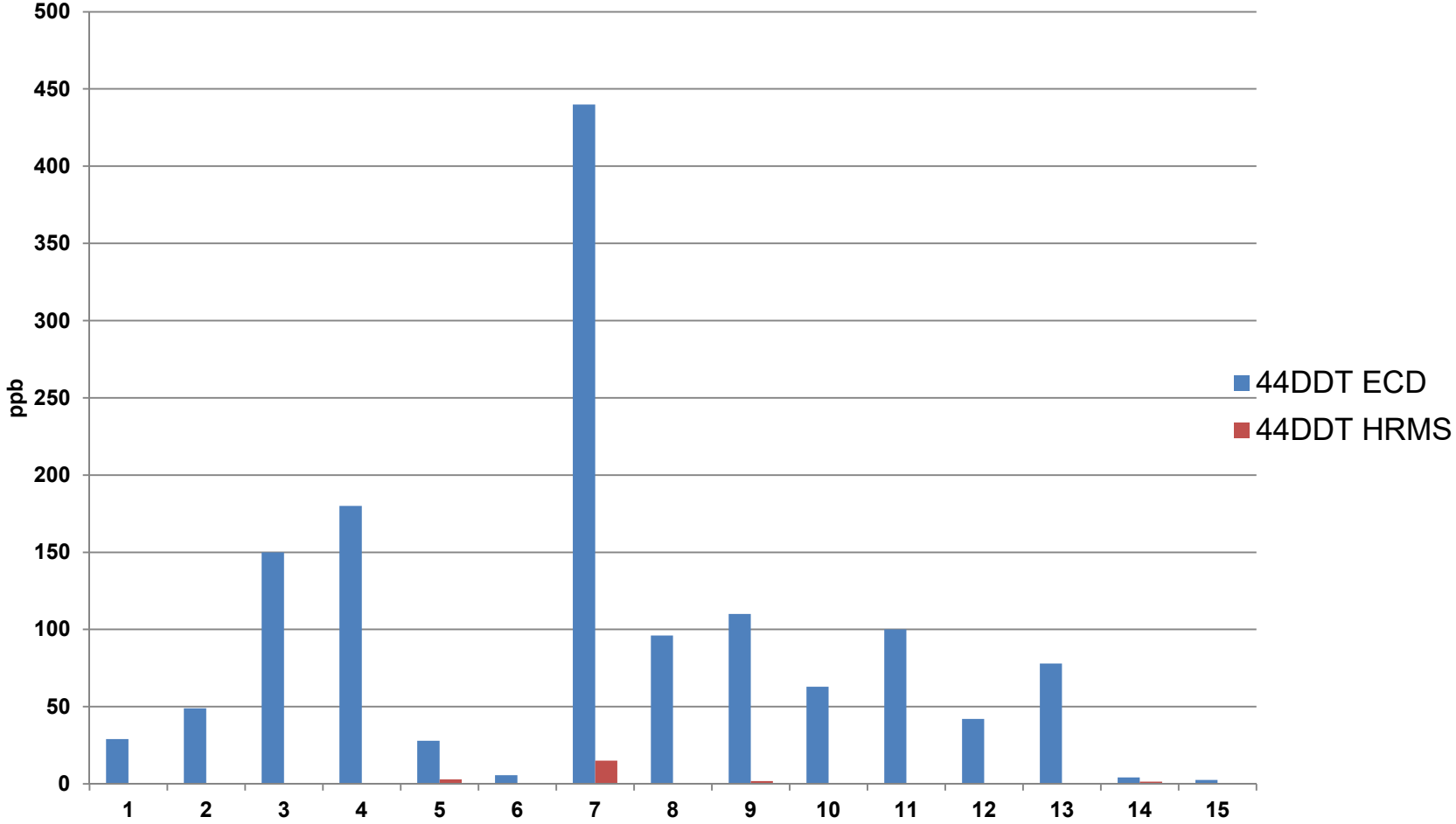
- Pesticides → 1000 ml → $MeCL_2$ → Hexane
  - 608
  - 8080

- Semi-Volatiles → 1000 ml → $MeCL_2$
  - 625
  - 8270

Pesticide requires GC-ECD with dual column confirmation, PCB require pattern recognition

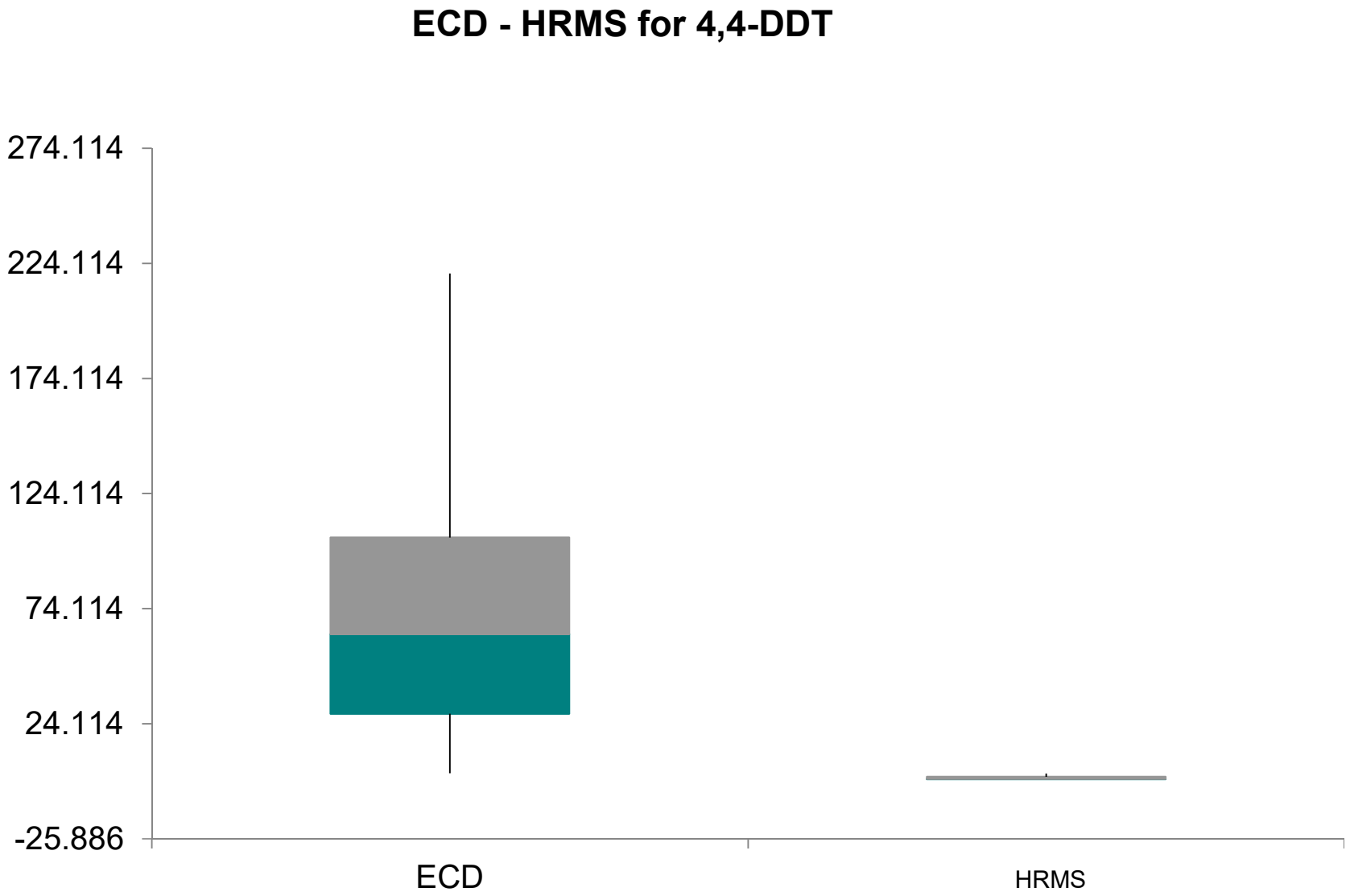


Interference of 4,4 DDT in PCB contaminated Soil using Method 8081

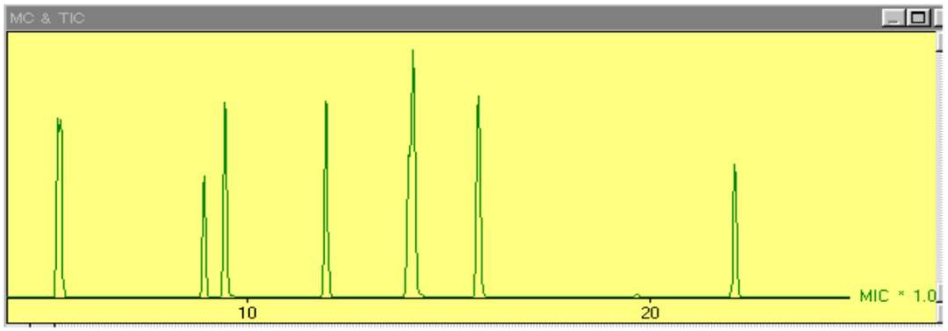


James J McAteer, Jr., and Erin Carroll Hughes; Bias in Organochlorine Pesticide Data, Comparison of Analysis by GC/ECD and HRGC/MSMS; NEMC 2014

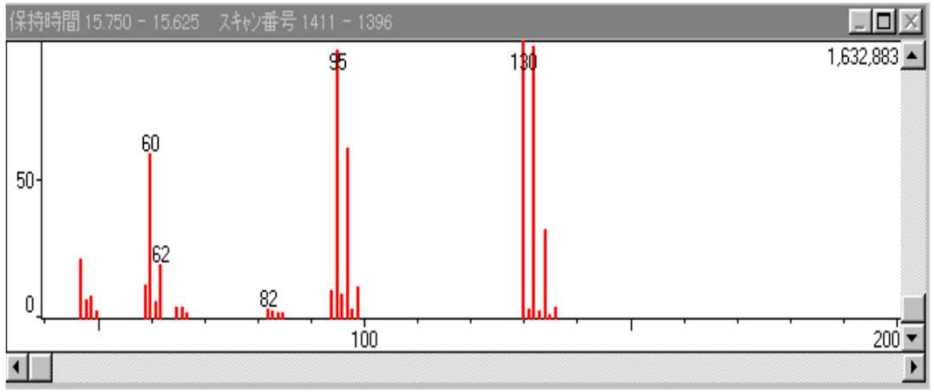
Significant positive bias for DDT by GC-ECD



Single quadrupole GCMS (full scan) is used for semi-volatile analysis

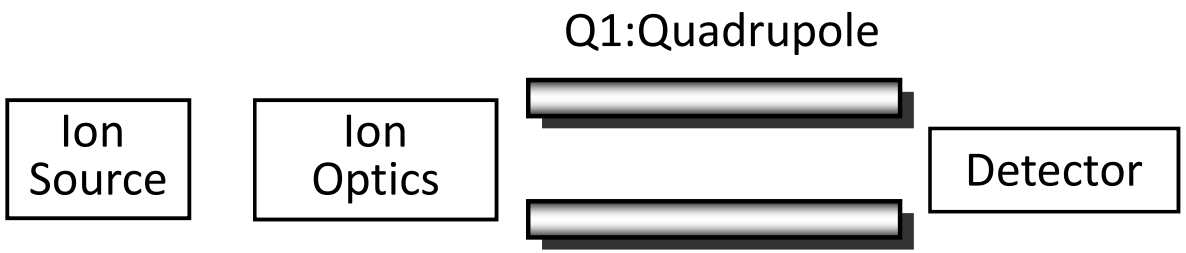


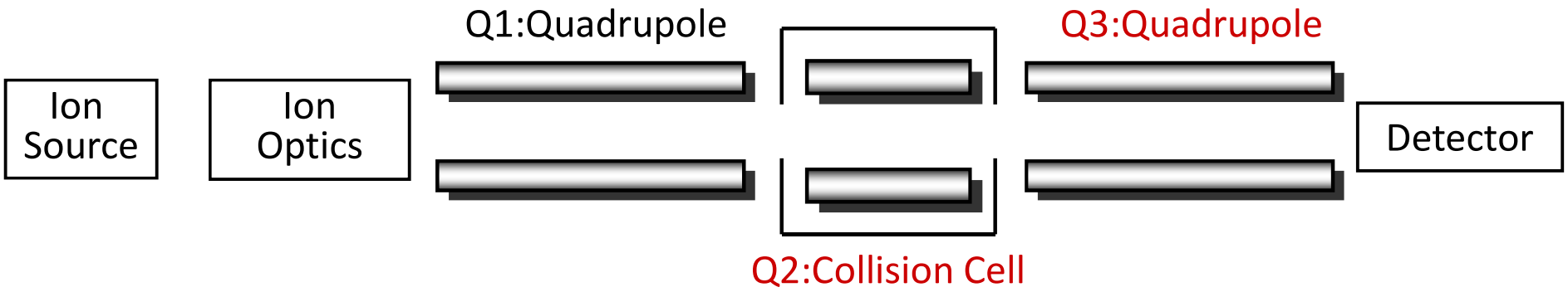
Gas Chromatograph: separation on a capillary column, identification by RT, and quantitation



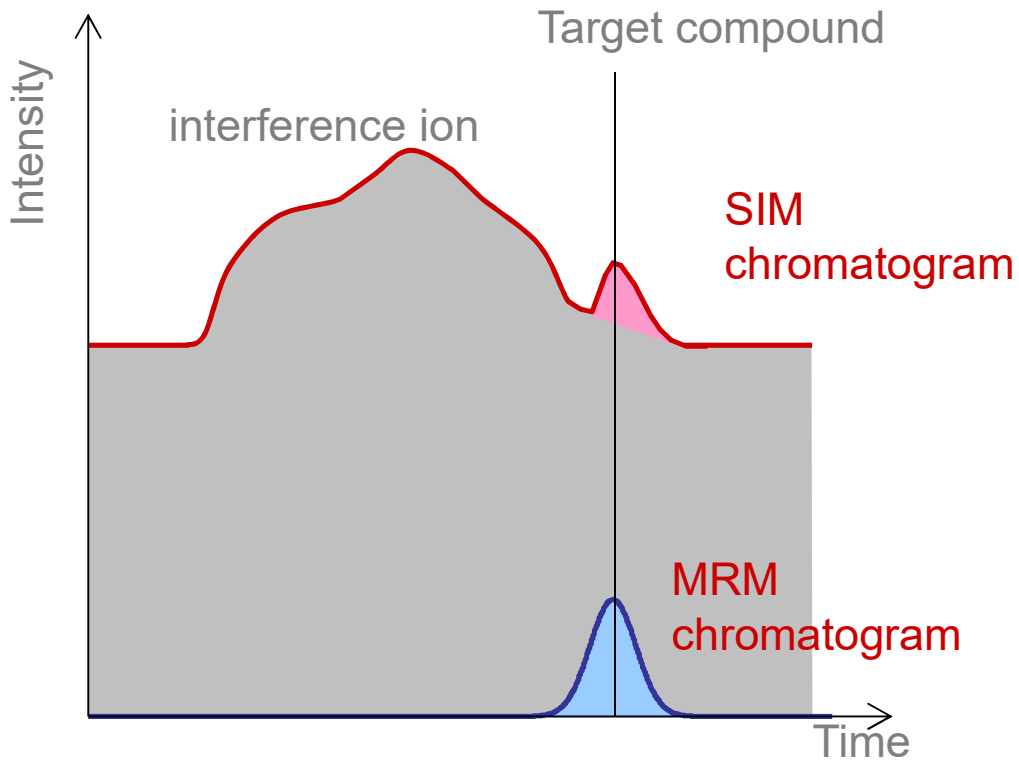
Mass Spectrometer: positive identification by matching to a library

A triple Quadrupole adds a collision cell and another quadrupole



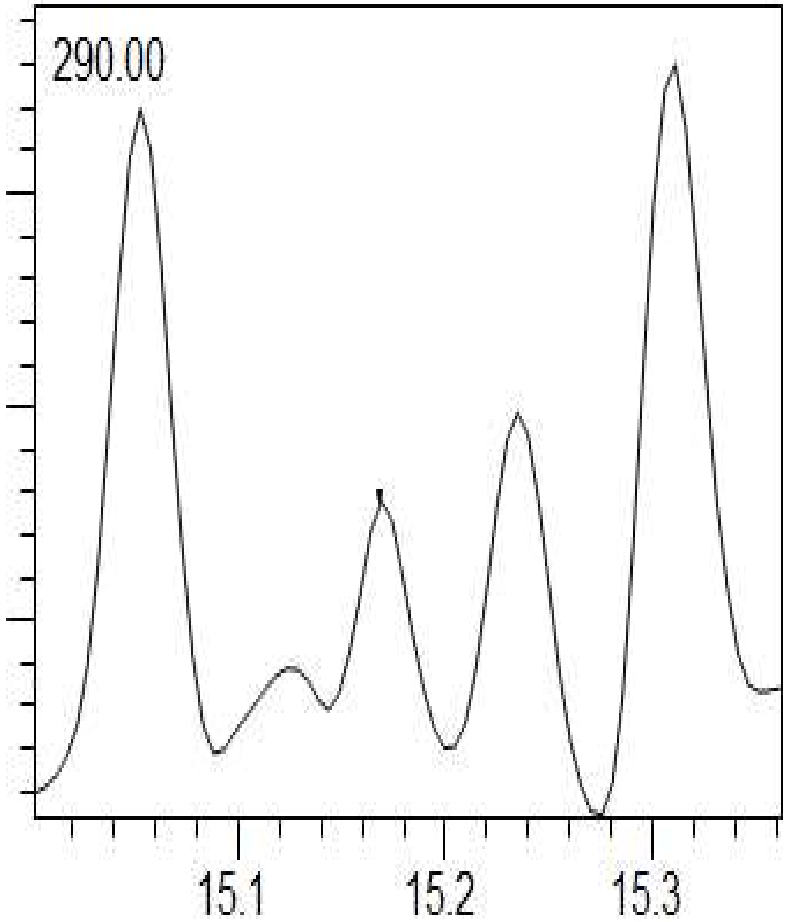


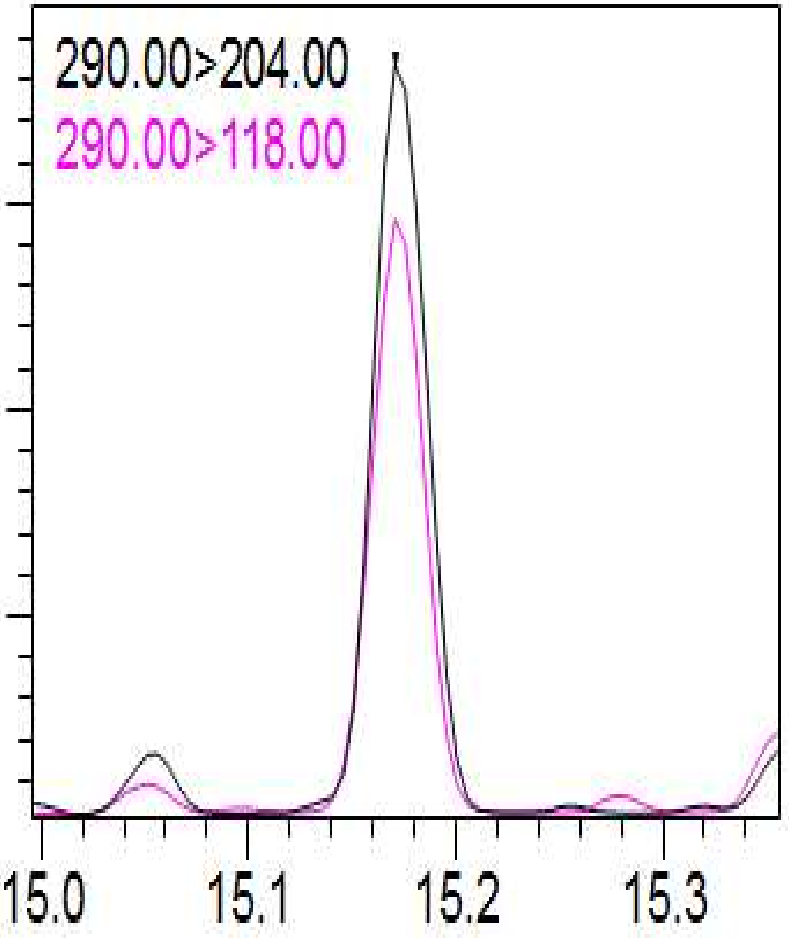
Triple Quad is ideal for GCMS analysis in complex matrices



- **S/N ratio is enhanced**
- **Extremely selective for quantitation**
- **10x lower MDL than SIM**
- **Extended linear range**

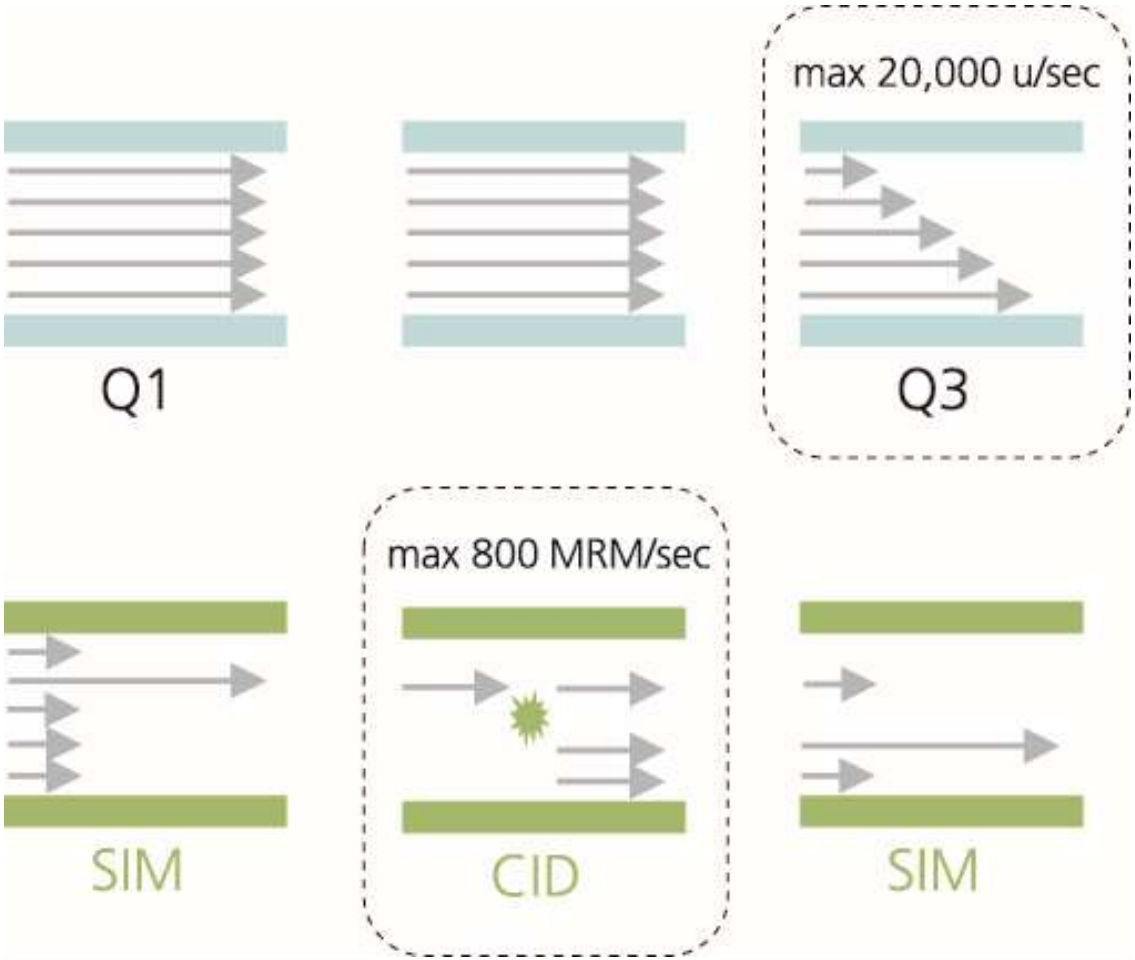
SIM and MRM data showing better detection and selectivity by MRM



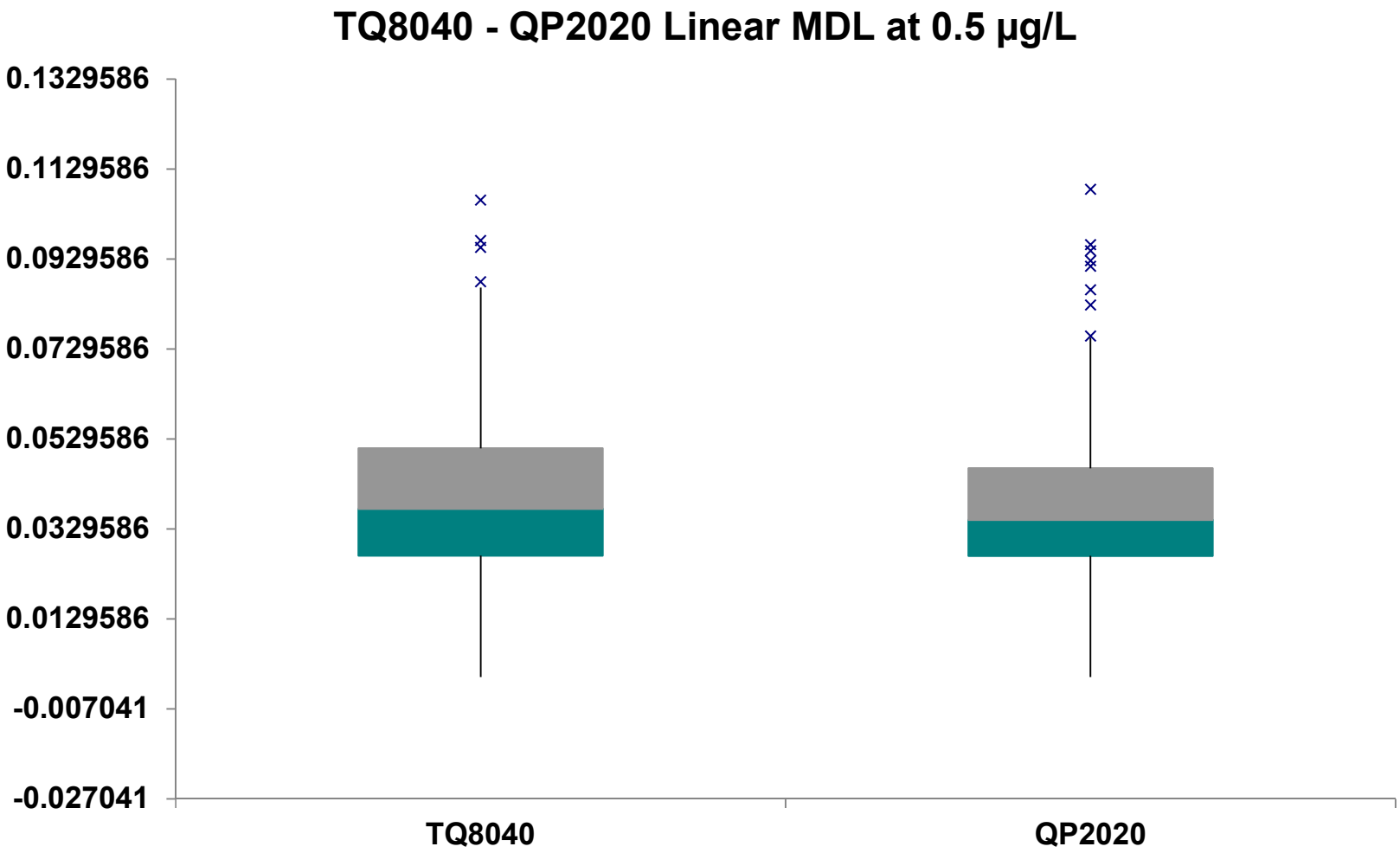


GCMSMS Multiple Reaction Monitoring allows us to see lower concentrations with large dynamic range with less interference

The triple quad can operate in single quad mode and MRM, allowing us to run Method 625

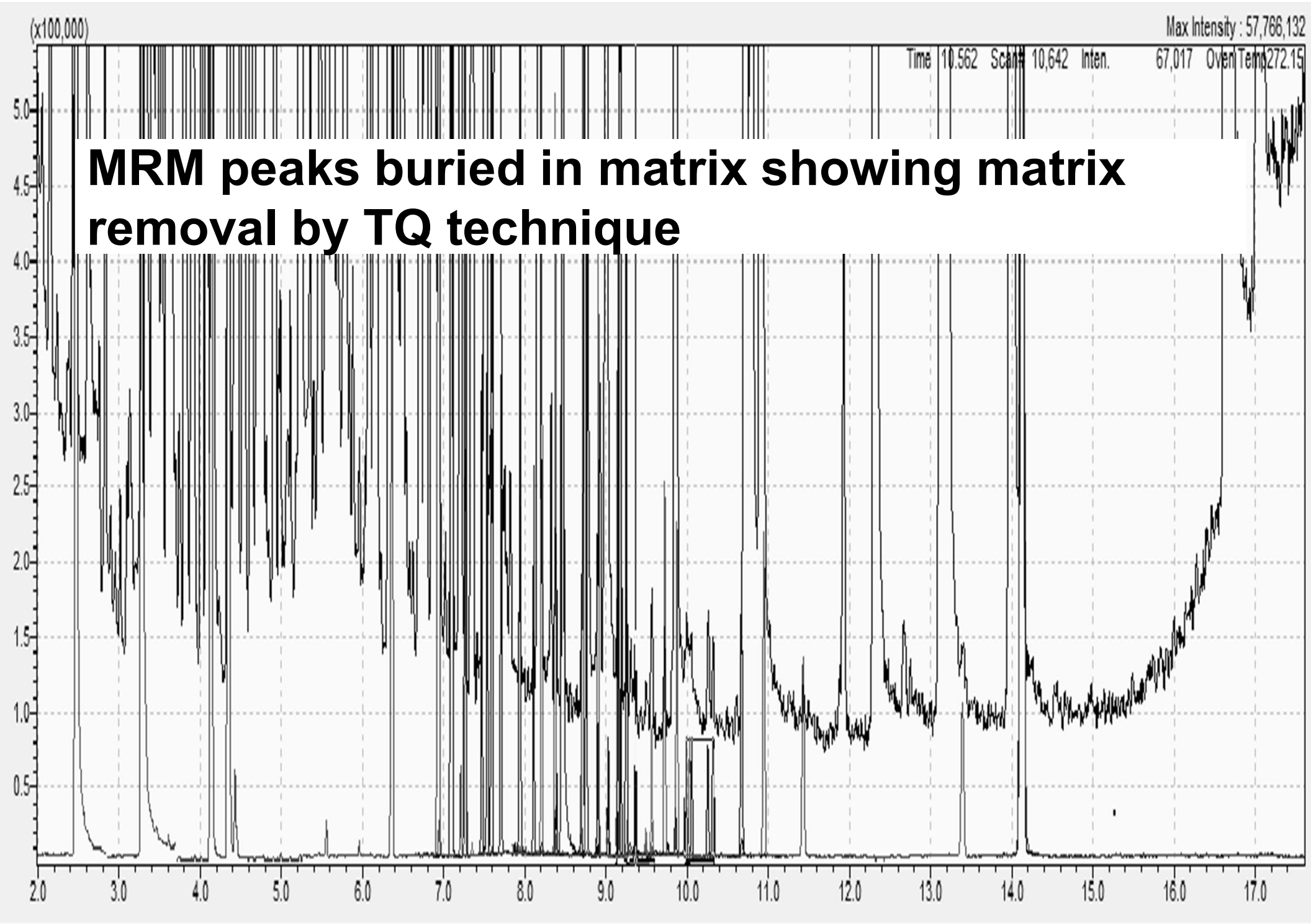


TQ in SQ mode obtains near equivalent results to a SQ only instrument, no loss in sensitivity



Advantages and disadvantages for MRM analysis of pesticides

Advantages	Disadvantages
Sensitive enough for pesticides analysis	<u>Not approved</u>
Low detection limits	No ILS data
Run Pesticides from Semi-volatile extract?	Do all pesticides extract?



MRM peaks buried in matrix showing matrix removal by TQ technique

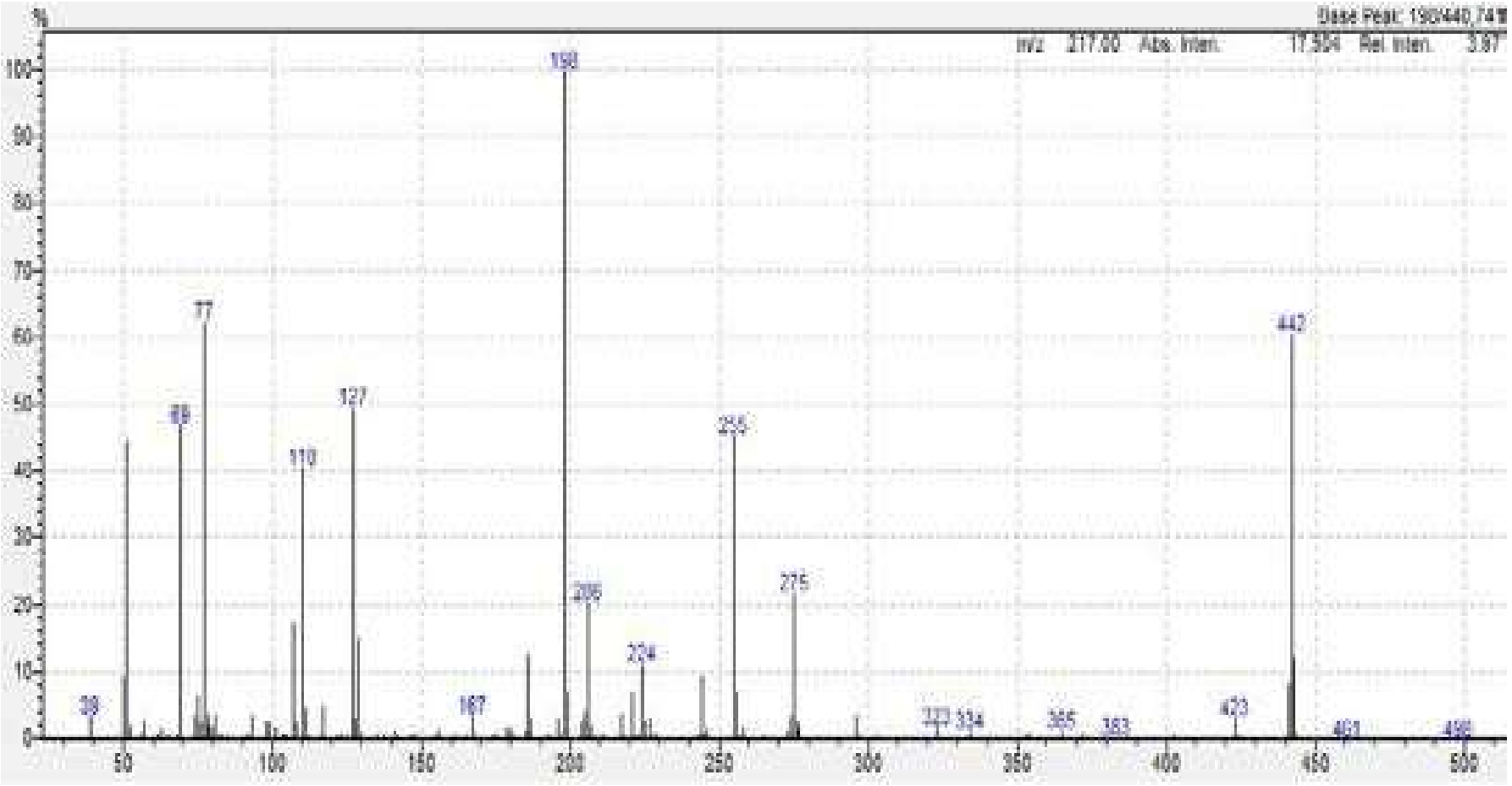
WK54549 Determination of organochlorine pesticides and PCB congeners in aqueous solutions by gas chromatography triple quadrupole mass spectrometry

Eliminate solvent exchange into hexane, if possible use the acid-base neutral extraction

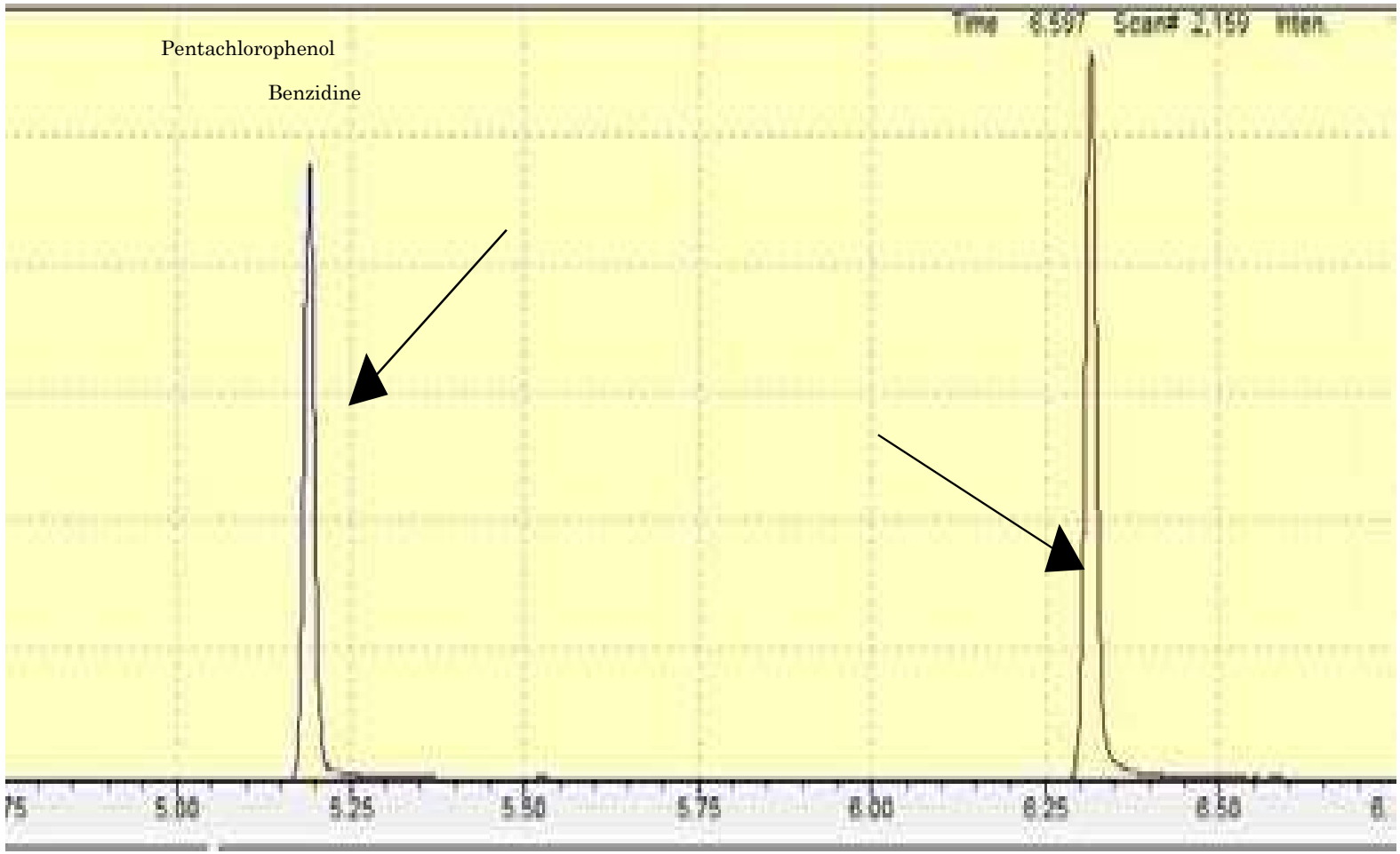
Increase throughput and lower costs

“twin-line” capability connects the semi-volatile and pesticide column to the detector, enables Method 625 and pesticides on one instrument

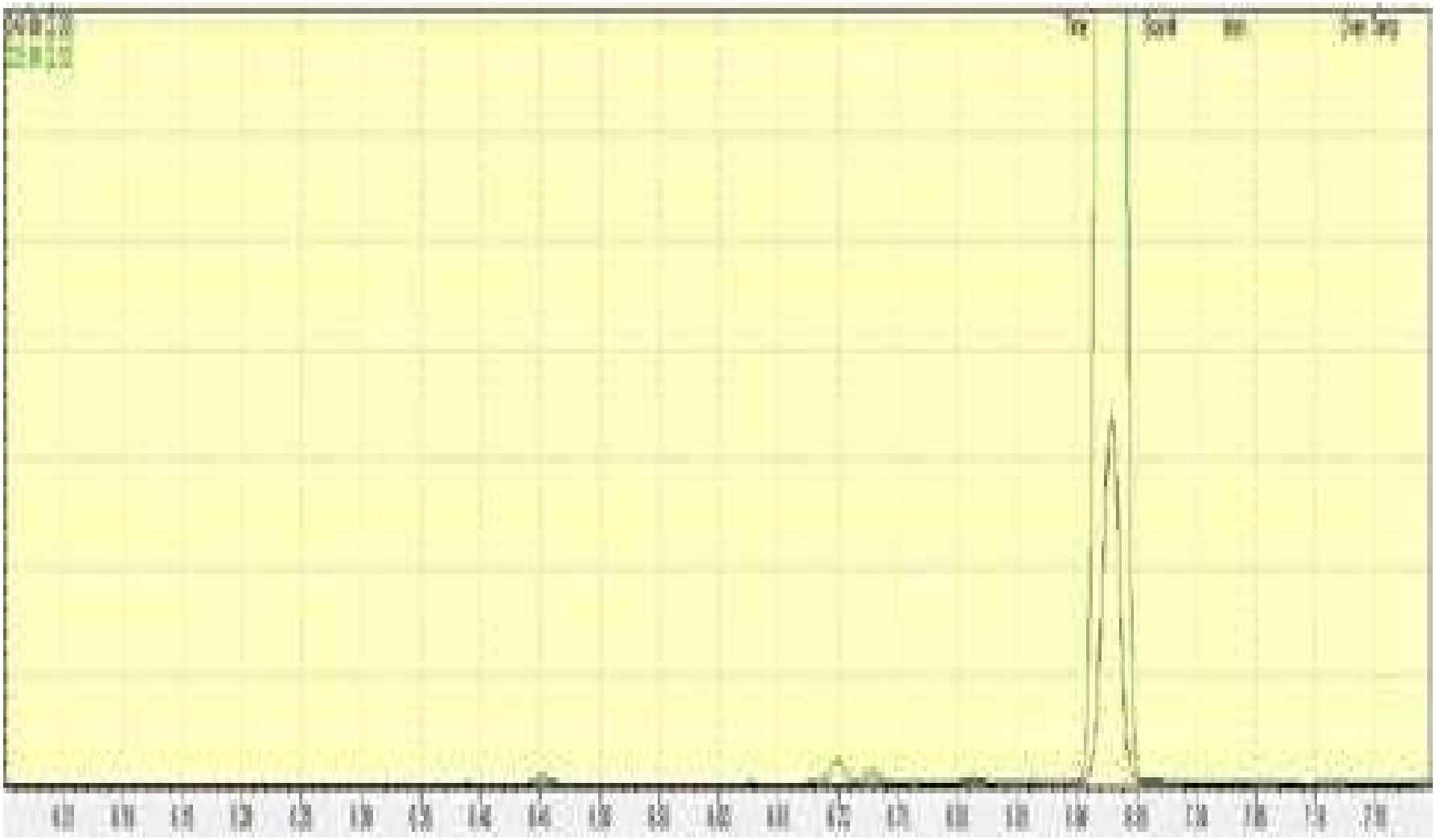
Method 625 (GCMS) on the TQ in SQ mode must meet all QC including DFTPP tune



Peaks must not tail



DDT must not breakdown



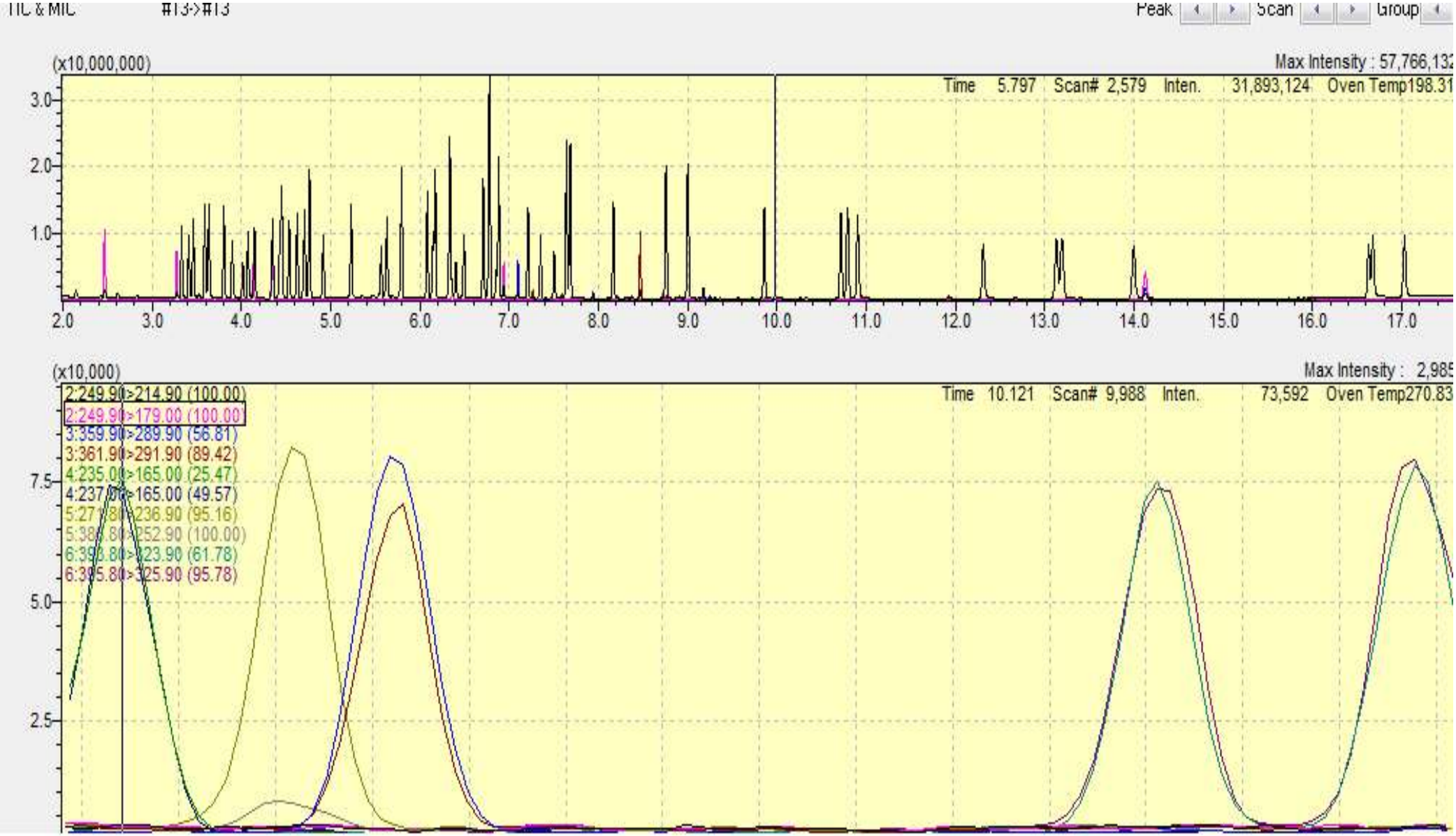
ASTM will validate MRM analysis of pesticides in $MeCL_2$, and compare to Method 608

1. Minimum 9 matrices
2. MS/MSD
3. MDL
4. Comparison to ECD

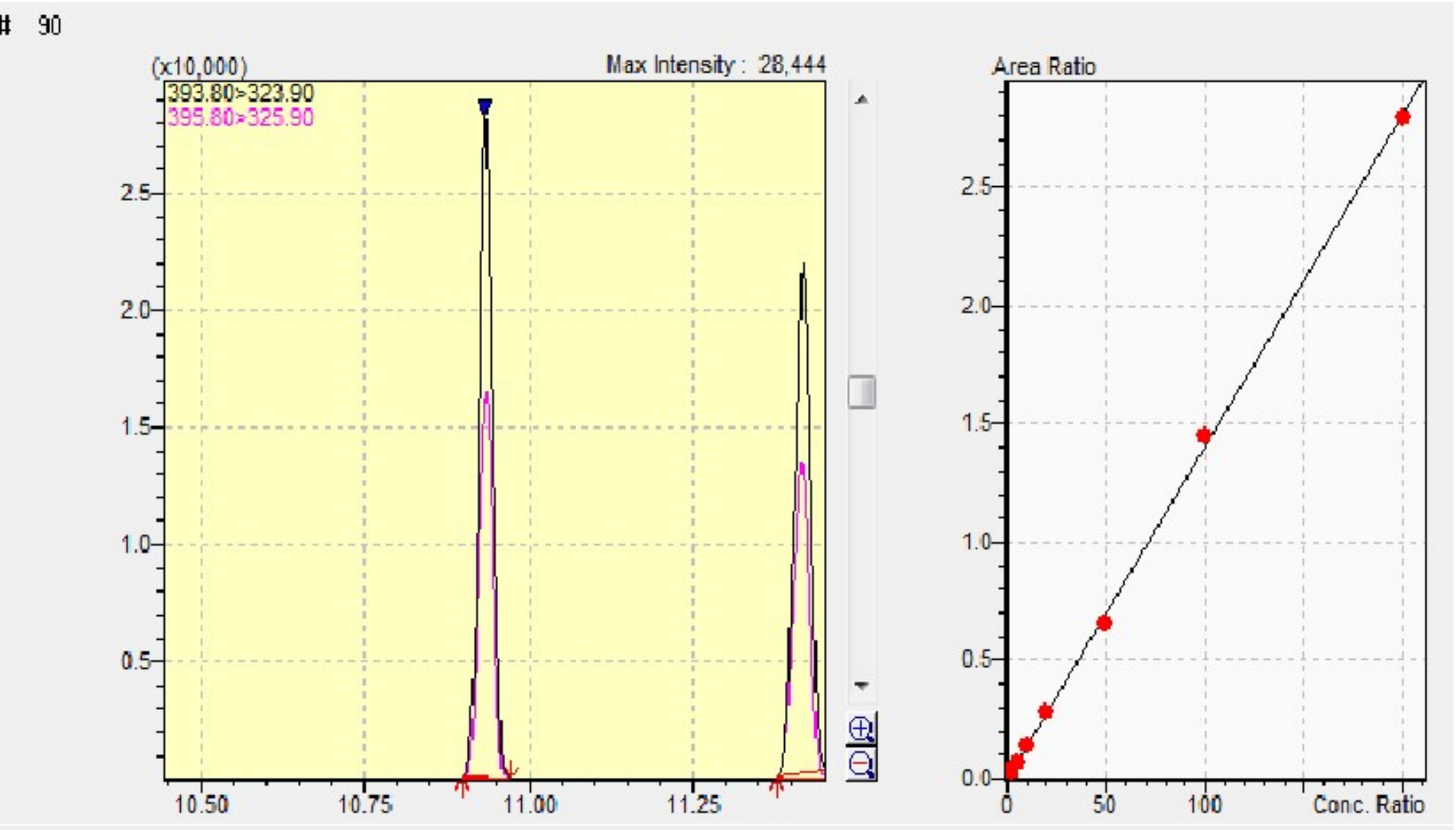
5. See if acid-base neutral recoveries equal as received recoveries.
6. Multiple laboratory study of 608 list + PCBs and congeners

Proof of concept, instrument method

Chromatogram showing MRM Quantitation of 0.005 ppb DDT



Chromatogram showing 0.005 ppb PCB congener and MRM Quantitation with curve



Component	Estimated MDL (assumes 1000ml/1ml) µg/L			
	1 ppb standard	2 ppb standard	5 ppb standard	Method 608 MDL (µg/L)
Alpha-BHC	0.0002	0.0005	0.0004	0.003
Gamma-BHC (Lindane)	0.0003	0.0005	0.0004	0.004
Beta-BHC	0.0002	0.0004	0.0005	0.006
Delta- BHC	0.0003	0.0004	0.0007	0.009
Heptachlor	0.0003	0.0004	0.0007	0.003
Aldrin	0.0004	0.0007	0.001	0.004
Heptachlor Epoxide (isomer B)	0.0004	0.0007	0.0014	0.083
Trans-Chlordane	0.0002	0.0007	0.0011	0.014
Cis-Chlordane		0.0009	0.0016	0.014
Endosulfan I	0.0003	0.0006	0.0013	0.014
4,4’-DDE	0.0003	0.0003	0.0005	0.004
Diledrin		0.0009	0.0022	0.002
Endrin		0.0008	0.0012	0.006
4,4’-DDD	0.0002	0.0003	0.0004	0.011
Endosulfan II		0.0009	0.0013	0.004
Endrin Aldehyde			0.0026	0.023
4,4’-DDT	0.0001	0.0003	0.0004	0.012
Endosulfan Sulfate	0.0002	0.0004	0.0005	0.066

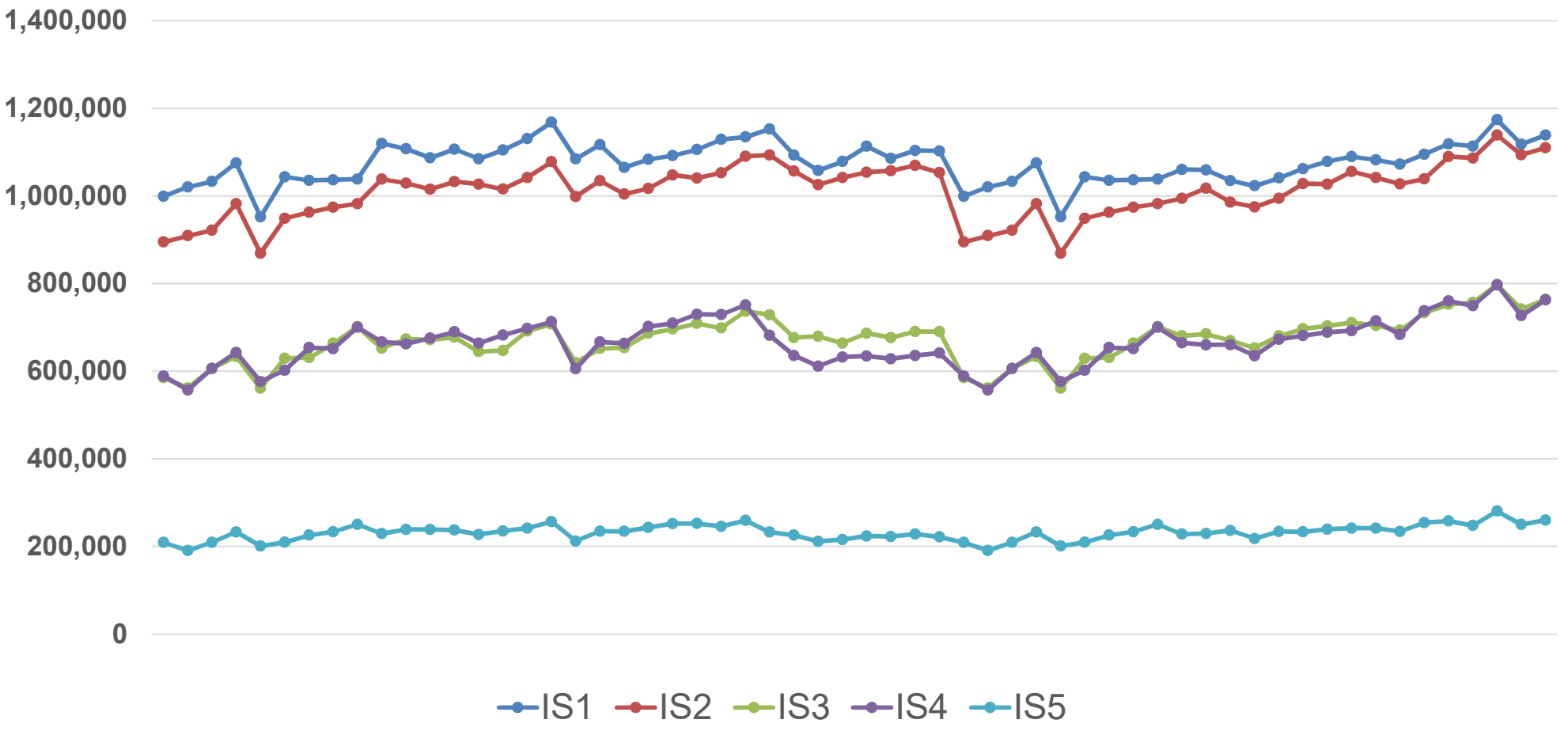
2-Chlorobiphenyl (#1)	0.0002	0.0004	0.0005	0.065*
2,3-Dichlorobiphenyl (#5)		0.0004	0.0004	
2,2',5-Trichlorobiphenyl (#18)		0.0003	0.0006	
2,2',5,5'-Tetrachlorobiphenyl (#52)	0.0002	0.0003	0.0004	
2,2'3,5'-Tetrachlorbiphenyl (#44)	0.0002	0.0002	0.0006	
2,3'4,4'-Tetrachlorobiphenyl (#66)	0.0002	0.0003	0.0004	
2,2',4,5,5'-Petachlorobiphenyl (#101)	0.0003	0.0004	0.0008	
2,2',3,4,5'-Pentachlorbiphenyl (#87)	0.0003	0.0004	0.0007	
2,3,3'4',6-Pentachlorobiphenyl (#110)	0.0003	0.0004	0.0008	
2,2',3,5,5',6-Hexachlorobiphenyl (#151)	0.0003	0.0004	0.0008	
2,2',4,4',5,5'-Hexachlorobiphenyl (#153)	0.0005	0.0002	0.0006	
2,2',3,4,5,5'-Hexachlorbiphenyl (#141)	0.0006	0.0004	0.0006	
2,2',3,4,4',5'-Hexachlorobiphenyl (#138)		0.0003	0.0006	
2,2',3,4',5,5',6-Heptachlorobiphenyl (#187)		0.0004	0.0009	
2,2'3,4,4'5',6- Heptachlorobiphenyl (#183)	0.0002	0.0003	0.0008	
2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)	0.0003	0.0003	0.0005	
2,2'3,3'4,4'5- Heptachlorobiphenyl (#170)	0.0001	0.0001	0.0004	
2,2'3,3'4,4'5,5',6-Nonachlorobiphenyl (#206)	0.0004	0.0003	0.0004	

IDL's are low enough that bigger split or less sample may be extracted – increasing life of liner and column.

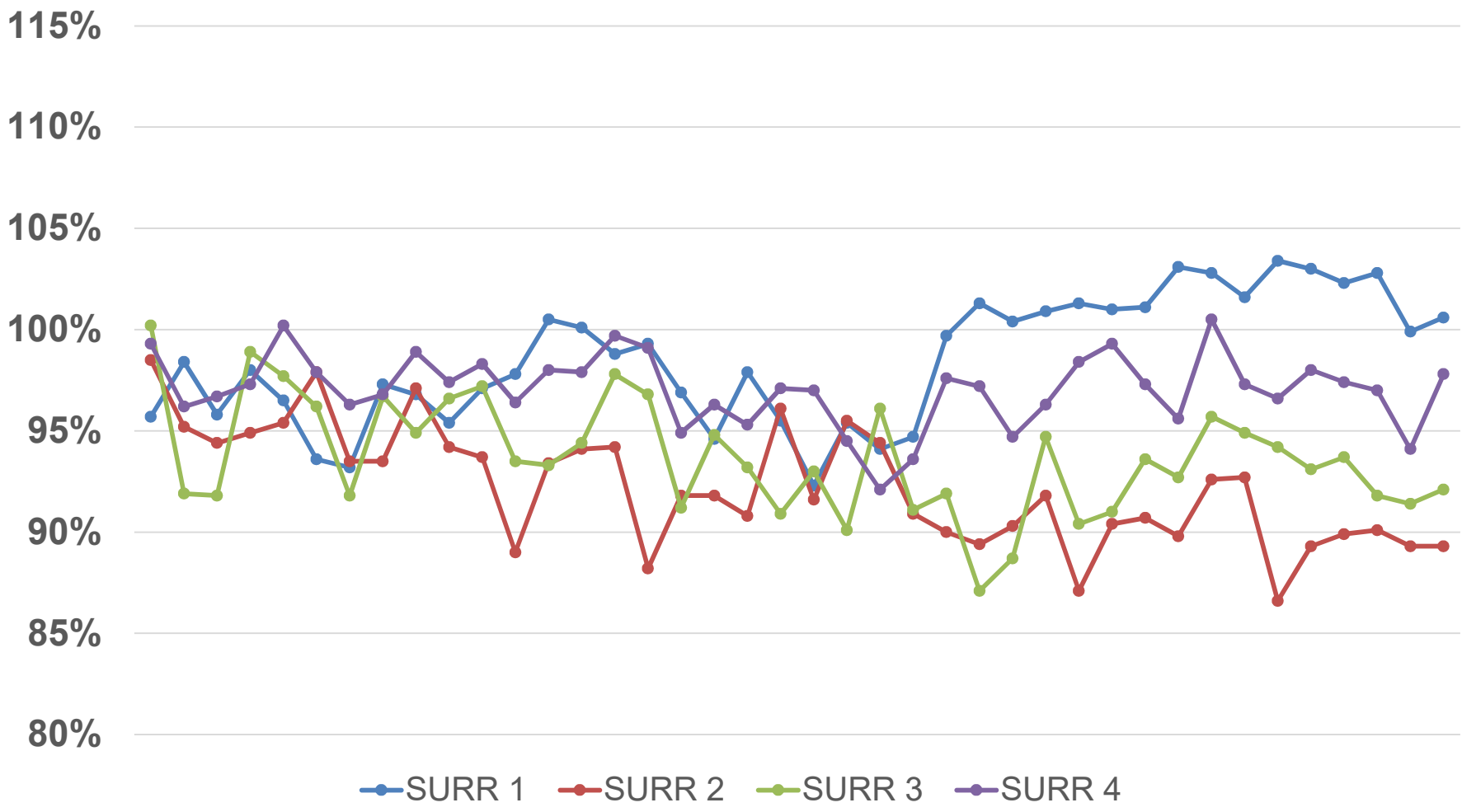
Component	Precision and Accuracy			
	10 ppb Standard		20 ppb standard	
	% REC	%RSD	%REC	%RSD
Alpha-BHC	96	2.3	87	2.7
Gamma-BHC (Lindane)	102	3.7	94	2.0
Beta-BHC	97	1.9	89	1.5
Delta- BHC	99	2.1	92	2.3
Heptachlor	107	4.8	104	2.0
Aldrin	114	6.0	110	1.6
Heptachlor Epoxide (isomer B)	122	7.1	118	3.7
Trans-Chlordane	108	4.8	101	5.2
Cis-Chlordane	128	5.4	124	4.8
Endosulfan I	113	13.0	112	2.9
4,4’-DDE	105	1.9	96	2.2
Diledrin	110	13.3	113	5.3
Endrin	127	10.0	124	4.7
4,4’-DDD	102	2.3	99	1.9
Endosulfan II	129	10.3	131	5.4
Endrin Aldehyde	124	16.7	134	5.8
4,4’-DDT	119	1.9	115	1.7
Endosulfan Sulfate	116	2.2	115	1.6
Methoxychlor	126	2.7	122	1.8
Endrin Ketone	90	14.5	107	8.8
2-Chlorobiphenyl (#1)	96	1.8	86	3.1
2,3-Dichlorobiphenyl (#5)	97	1.9	87	1.3

2-Chlorobiphenyl (#1)	96	1.8	86	3.1
2,3-Dichlorobiphenyl (#5)	97	1.9	87	1.3
2,2',5-Trichlorobiphenyl (#18)	97	1.2	87	1.2
2,4',5-Trichlorobiphenyl (#31)	98	1.7	88	1.3
2,2',5,5'-Tetrachlorobiphenyl (#52)	97	2.2	87	2.6
2,2'3,5'-Tetrachlorbiphenyl (#44)	101	3.1	90	2.0
2,3'4,4'-Tetrachlorobiphenyl (#66)	99	1.7	90	1.9
2,2',4,5,5'-Petachlorobiphenyl (#101)	102	2.6	94	2.4
2,2',3,4,5'-Pentachlorbiphenyl (#87)	99	2.5	89	3.0
2,3,3'4',6-Pentachlorobiphenyl (#110)	96	1.9	88	1.8
2,2',3,5,5',6-Hexachlorobiphenyl (#151)	106	3.2	97	3.6
2,2',4,4',5,5'-Hexachlorobiphenyl (#153)	106	2.9	96	2.6
2,2',3,4,5,5'-Hexachlorbiphenyl (#141)	104	2.1	97	1.3
2,2',3,4,4',5'-Hexachlorobiphenyl (#138)	111	3.3	105	1.3
2,2',3,4',5,5',6-Heptachlorobiphenyl (#187)	109	4.8	103	2.1
2,2'3,4,4'5',6- Heptachlorobiphenyl (#183)	110	3.1	102	2.7
2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)	102	2.9	94	1.8
2,2'3,3'4,4'5- Heptachlorobiphenyl (#170)	106	1.4	98	1.5
2,2'3,3'4,4'5,5',6-Nonachlorobiphenyl (#206)	101	1.7	95	1.5

Internal Standard Area for 58 injections



Surrogate Recovery for 58 injections



Advantages of MRM quantitation of Method 608 Pesticides and PCBs

- Fewer interferences
- Detection limits similar to GC-ECD
- No need to exchange to hexane
- Can run 625 and pesticides/PCB on one instrument
- May be possible to use acid / BN extraction for pesticides

Thank You, for more information contact me

- wclipps@shimadzu.com
- Come by our booth, or visit www.ssi.shimadzu.com