Excellence in Science

A New Method for the Analysis of Pesticides in Water Samples

William Lipps

Shimadzu Scientific Instruments

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Pesticide and PCBs Analysis Overview

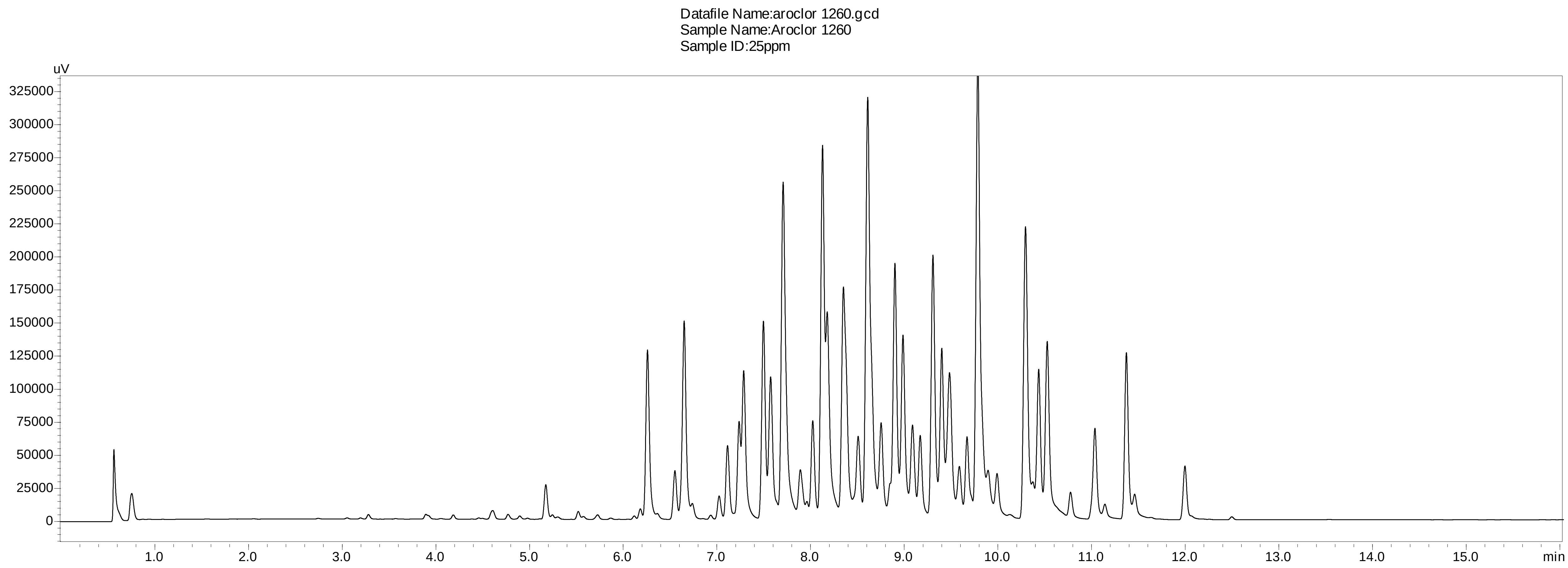
- Currently, organochlorine (OC) pesticides and PCBs target list are run by Method 8081 and Method 608 on GC/ECD.

- ECD is a highly sensitive detector for compounds containing electronegative atoms or functional groups (halogens, organometallics, nitrites, nitro groups), and is capable of achieving (and exceeding) the low reporting limits required for target list OC pesticides.

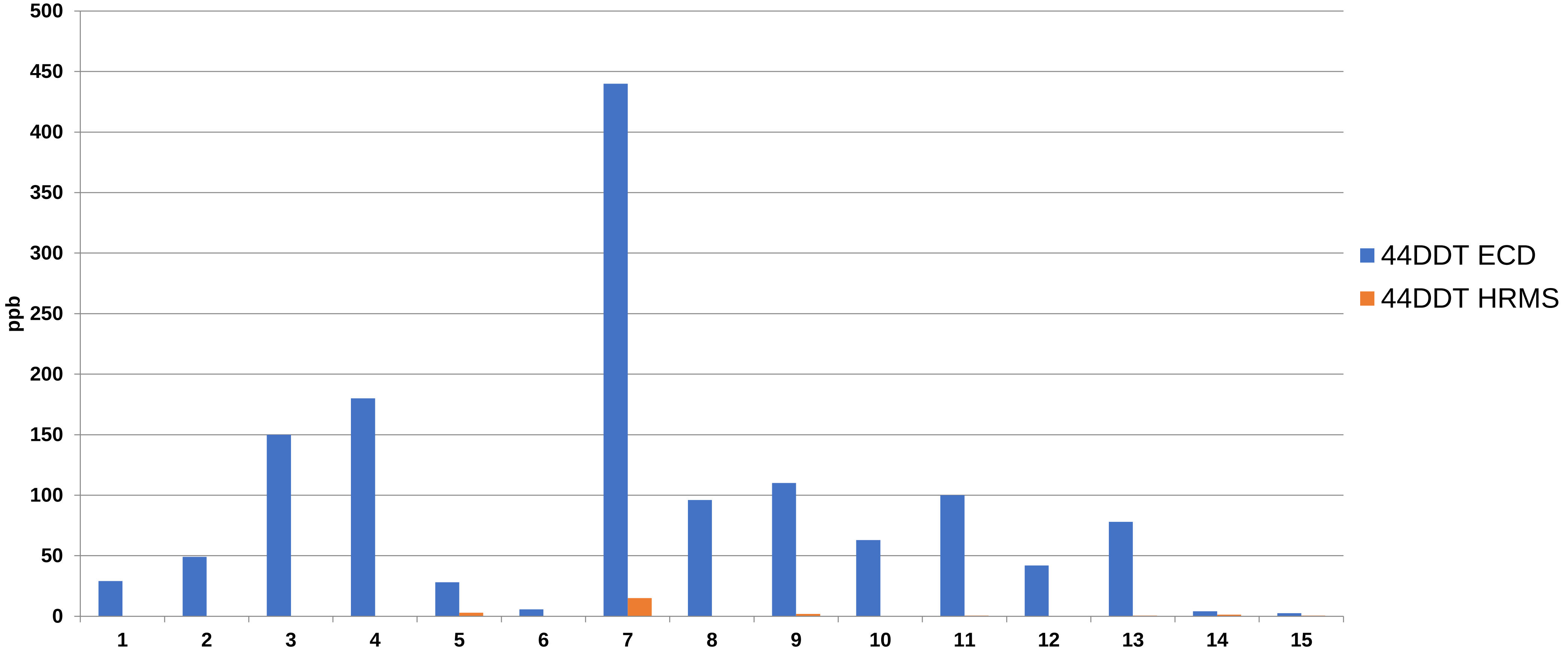
- These methods perform very well if sample extracts are relatively free of interferences. Unfortunately, environmental sample extracts rarely meet this criterion.

- As a non-specific detector, target compound identification is achieved via agreement between sample chromatographic peak retention time (RT) and its expected retention time as determined during calibration. This must be confirmed by a second dissimilar stationary phase column or other qualitative technique (e.g. GC/MS).

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

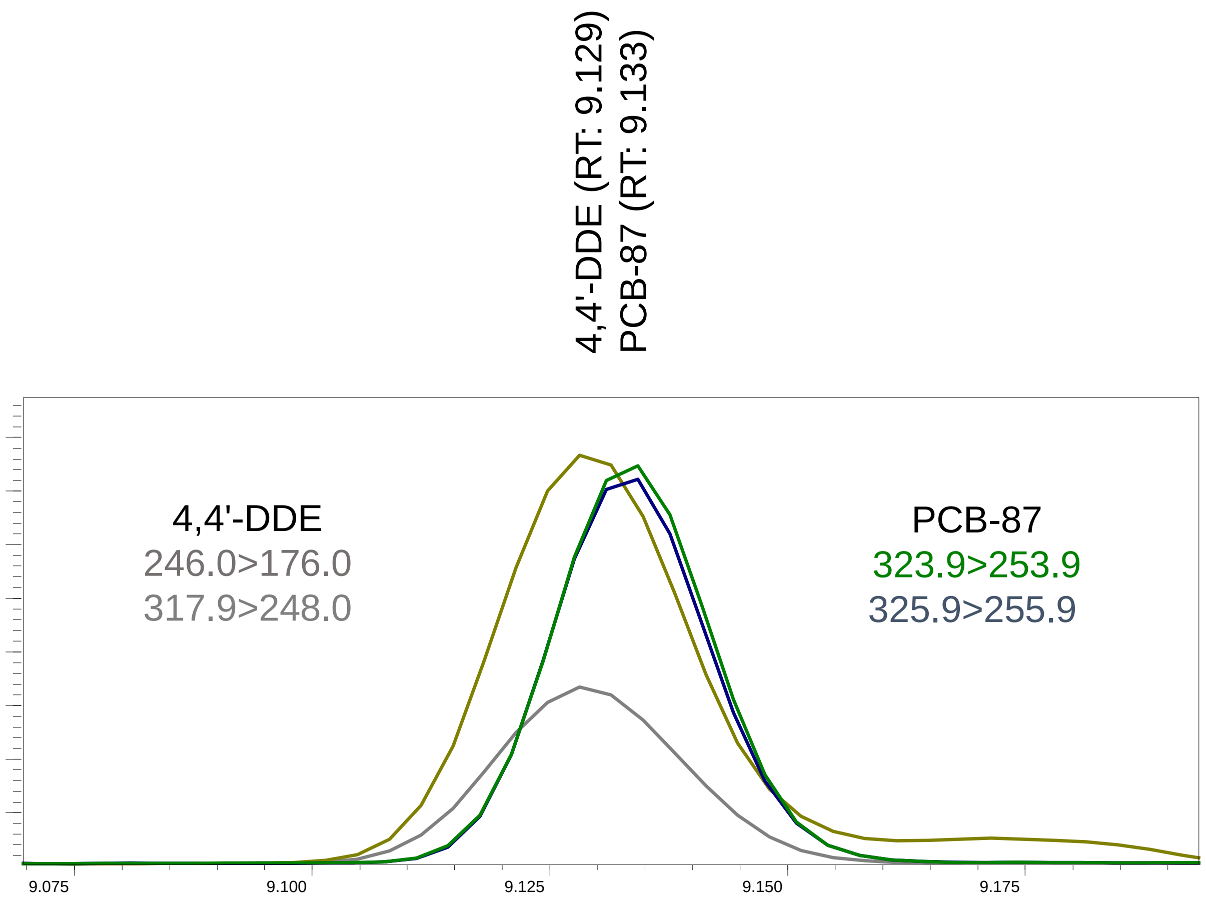


PCB containing samples may interfere significantly with pesticide analysis by GC-ECD



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

Some pesticides and PCBs coelute but each peak could be identified by high selectivity of GC-MS/MS.



- In this case, GC-ECD could be problem
- EPA 608 requires second column confirmation.

A comparison of Pesticides by GC-ECD and GC-HRMS showing interferences with GC-ECD

Compound	Instrument	Sample C1	Sample C2	Sample C3	Sample C4	Sample C5	Sample C6	Sample C7
4,4 - DDT	GC-ECD	29	49	150	180	28	5.7	440
	GCMSMS	0.014	0.014	0.014	0.014	3	0.014	0.5
4,4 - DDD	GC-ECD	14	33	2.9	4.9	5.1	0.43	17
	GCMSMS	28	35	12	9.7	18	0.51	31
4,4 - DDE	GC-ECD	3.2	1.2	1.1	1.6	4.4	0.42	6.5
	GCMSMS	2.4	6.7	9.3	5.6	5.0	0.13	6.3
Arachlors	GC-ECD	300	950	6500	1500	650	186	216
TPH	GC-FID	5700	5800	1500	1010	1010	96	1500

ASTM D8543, a new method for the analysis of pesticides, and PCBs in water samples using GC-MS/MS.

- Why not just use method 625.1 modified?
  - Method 608.3 **should** be used for determination of pesticides and PCBs. However, if pesticides and/or PCBs are to be determined, an additional sample must be collected and extracted using the pH adjustment and extraction procedures specified in Method 608.3.

What is the meaning of the word “should”?

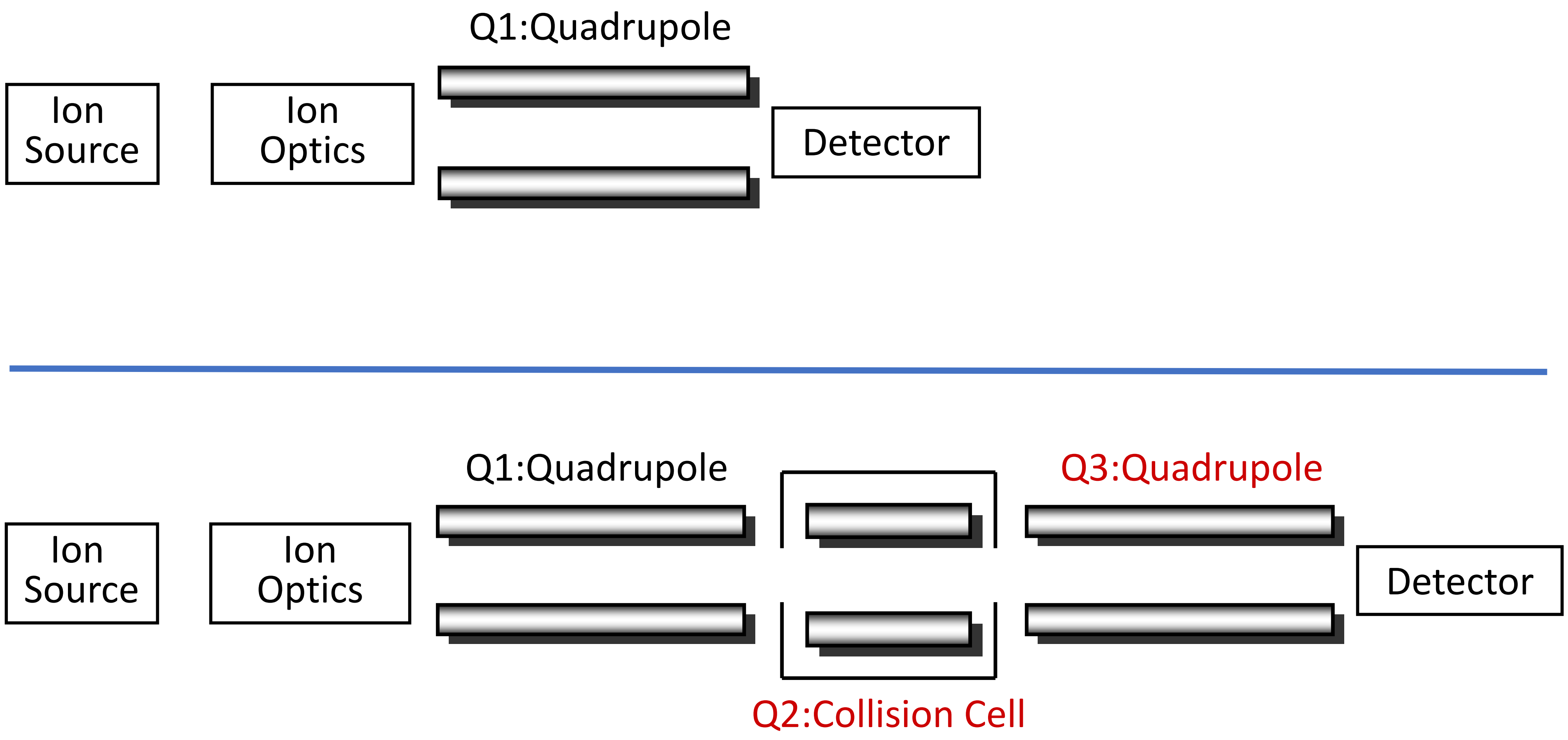
Should is the past tense of shall and means must

- The Supreme Court of the United States ruled that “shall” really means “may” – quite a surprise to attorneys who were taught in law school that “shall” means “must”. In fact, “must” is the only word that imposes a legal obligation that something is mandatory. ... Black's Law Dictionary.

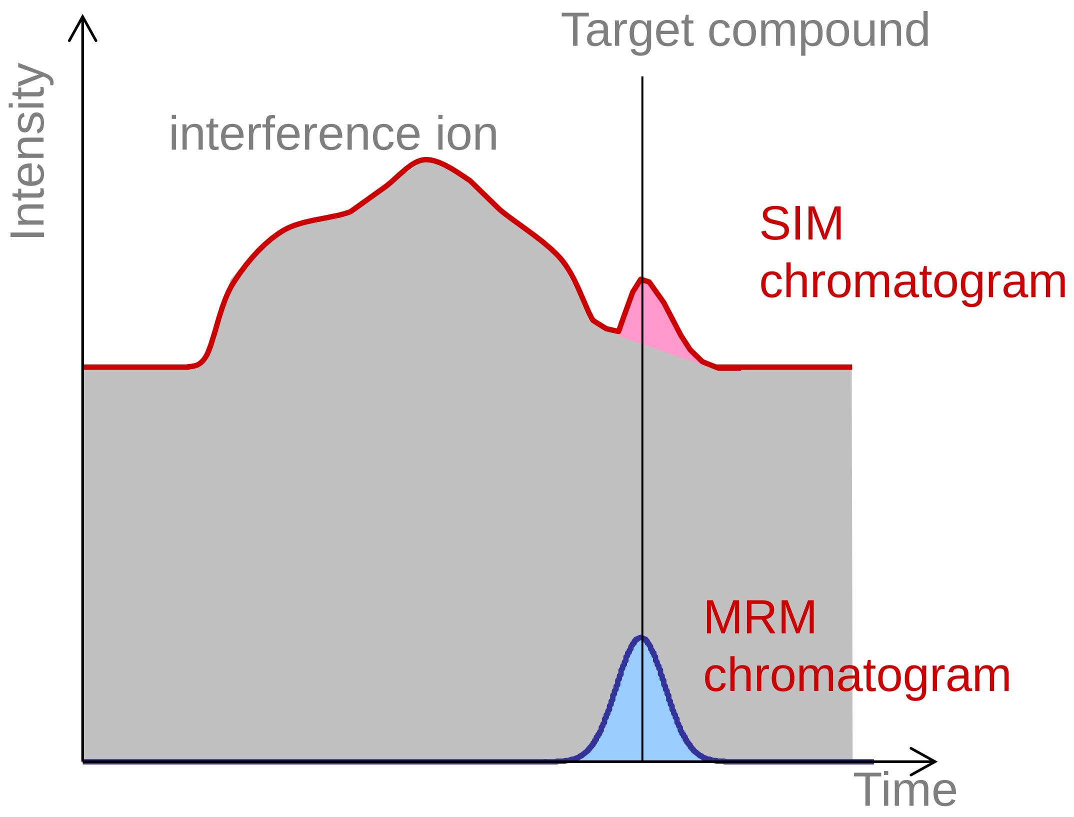
- 'Should' was found to be the past tense form of 'Shall', but the two cannot be used in place of each other. ... 'Shall' is used in formal writing and expresses future tense. 'Should' is used in informal writing mainly, and as the past tense of 'Shall'.

- **Will you risk your lab on the word “should”?**

The triple Quadrupole adds a collision cell and another quadrupole

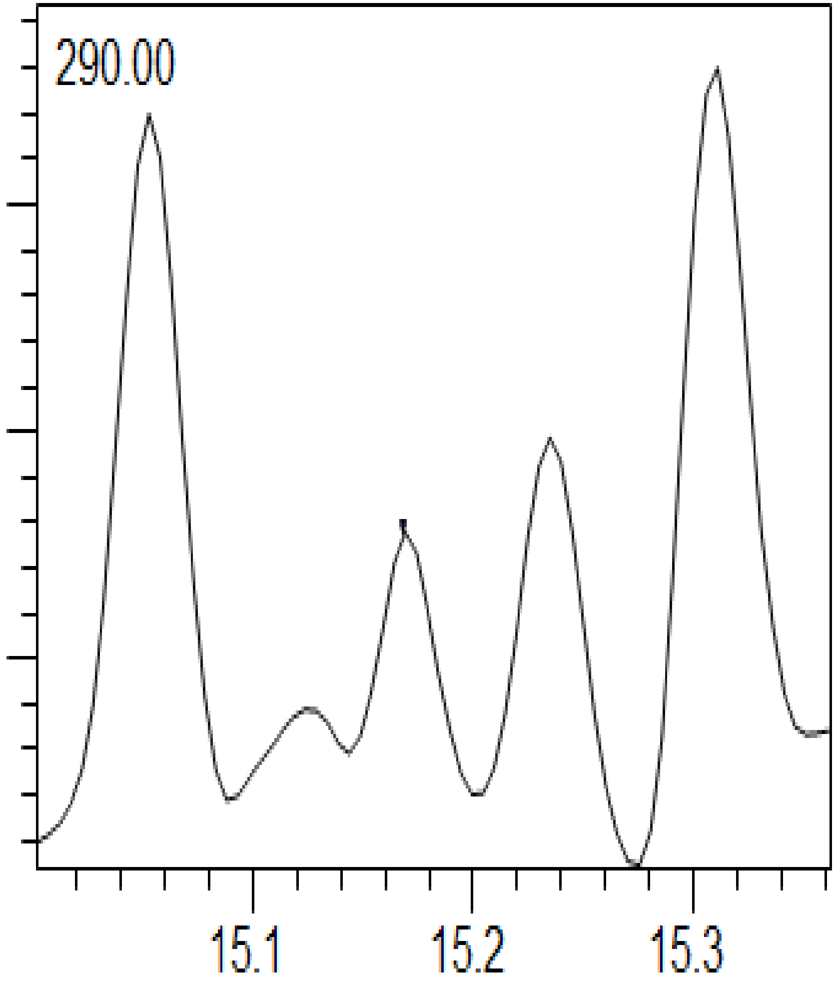


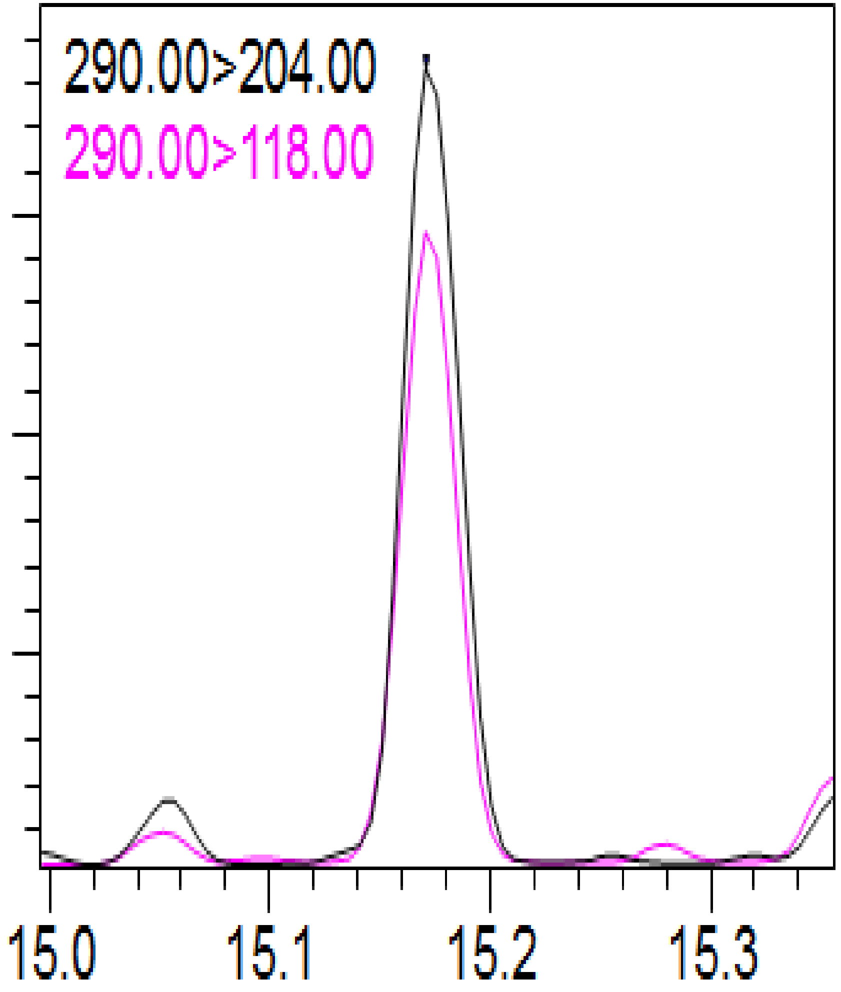
Triple Quad is ideal for GCMS analysis in complex matrices



- **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

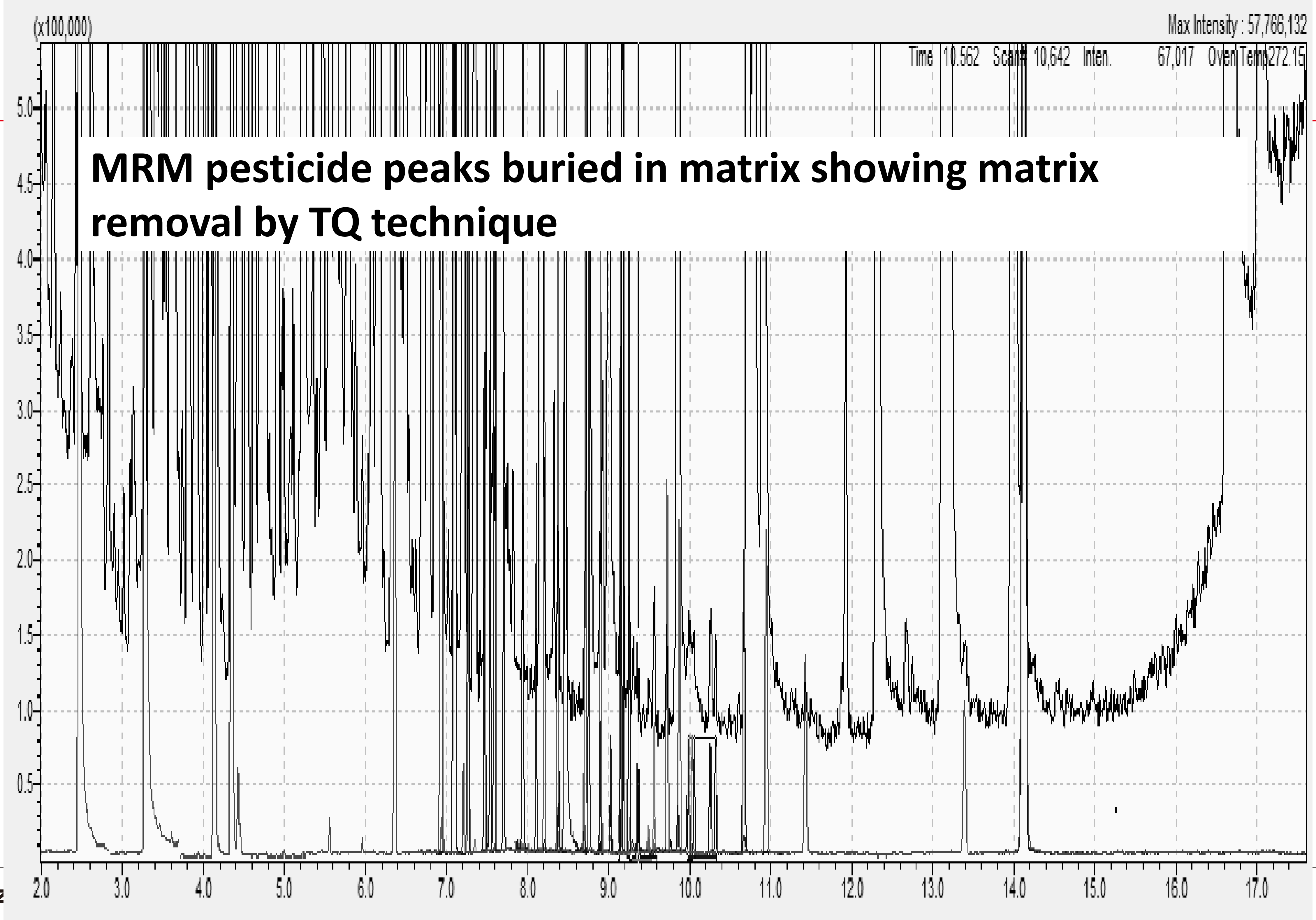




GCMSMS Multiple Reaction Monitoring allows us to see lower concentrations with large dynamic range with less interference

Perfect for analysis of pesticides and PCBs

MRM pesticide peaks buried in matrix showing matrix removal by TQ technique



Advantages and disadvantages for MRM analysis of pesticides

Advantages	Disadvantages
Sensitive enough for pesticides analysis	**Not approved to replace ECD**
Low detection limits	No ILS data
Run Pesticides from Semi-volatile extract, smaller volume and different solvents?	Do all pesticides extract? Need to validate.

A triple quadrupole method for the analysis of pesticides and PCB's

ASTM D8543 Standard Test Method for Determination of Pesticides and Polychlorinated Biphenyls (PCBs) in Aqueous Solution by a Tandem Gas Chromatography/Mass Spectrometry/Mass Spectrometry (GC/MS/MS)

- Same extraction as EPA Method 608.3 (for now)
- Text exactly as Method 608.3 except GC-MS/MS part
- ATP validation for new detector – compare ECD to MS/MS on same extracts

ASTM validating MRM analysis of pesticides in $MeCL_2$, and comparing to Method 608

1. Minimum 9 matrices
2. MS/MSD
3. MDL
4. Comparison to ECD
5. Multiple laboratory study of 608 list + PCBs and congeners

All pertinent QC for the method, such as DDT and Endrin breakdown, must be retained

ID	Compound	Area	50ppb Area	Conc
42	4,4'-DDE	28348	4607627	0.307620387
47	Endrin	407073	313722	64.87798114
51	4,4'-DDD	75560	7184896	0.525825287
54	EndrinAldehyde	2105	902890	0.116570125
58	4,4'-DDT	6230621	5945508	52.39771774
62	EndrinKetone	6939	313722	1.105915428
		% breakdown		% breakdown
	DDT	1.64		1.57
	Endrin	2.17		1.85

Proof of concept, instrument method

MDL compared to method 608 MDL For Organochlorine Pesticides

Compound	Single Lab MDL, ng/L	Method Required MDL, ng/L	Method Required MRL, ng/L
Alpha-BHC[A]	0.2	3	9
Gamma-BHC[A]	0.2	4	12
Beta-BHC[A]	0.3	6	18
Delta-BHC[A]	0.2	9	27
Heptachlor[A]	0.3	3	9
Aldrin[A]	0.5	4	12
cis-Heptachlor Epoxide[A]	3	83	249
trans-Heptachlor Epoxide	2	83	129
cis-Chlordane (alpha)[A]	0.3	14	42
Endosulfan I[A]	6	14	42
trans-Chlordane (gamma)[A]	0.5	14	42
4,4'-DDE[A]	0.3	4	12
Dieldrin[A]	3	2	6
Endrin[A]	5	6	18
Endosulfan II[A]	3	4	12
4,4'-DDD	0.4	5	15
Endrin Aldehyde[A]	0.5	23	70
Endosulfan Sulfate[A]	0.3	7	21
4,4'-DDT[A]	0.3	11	33

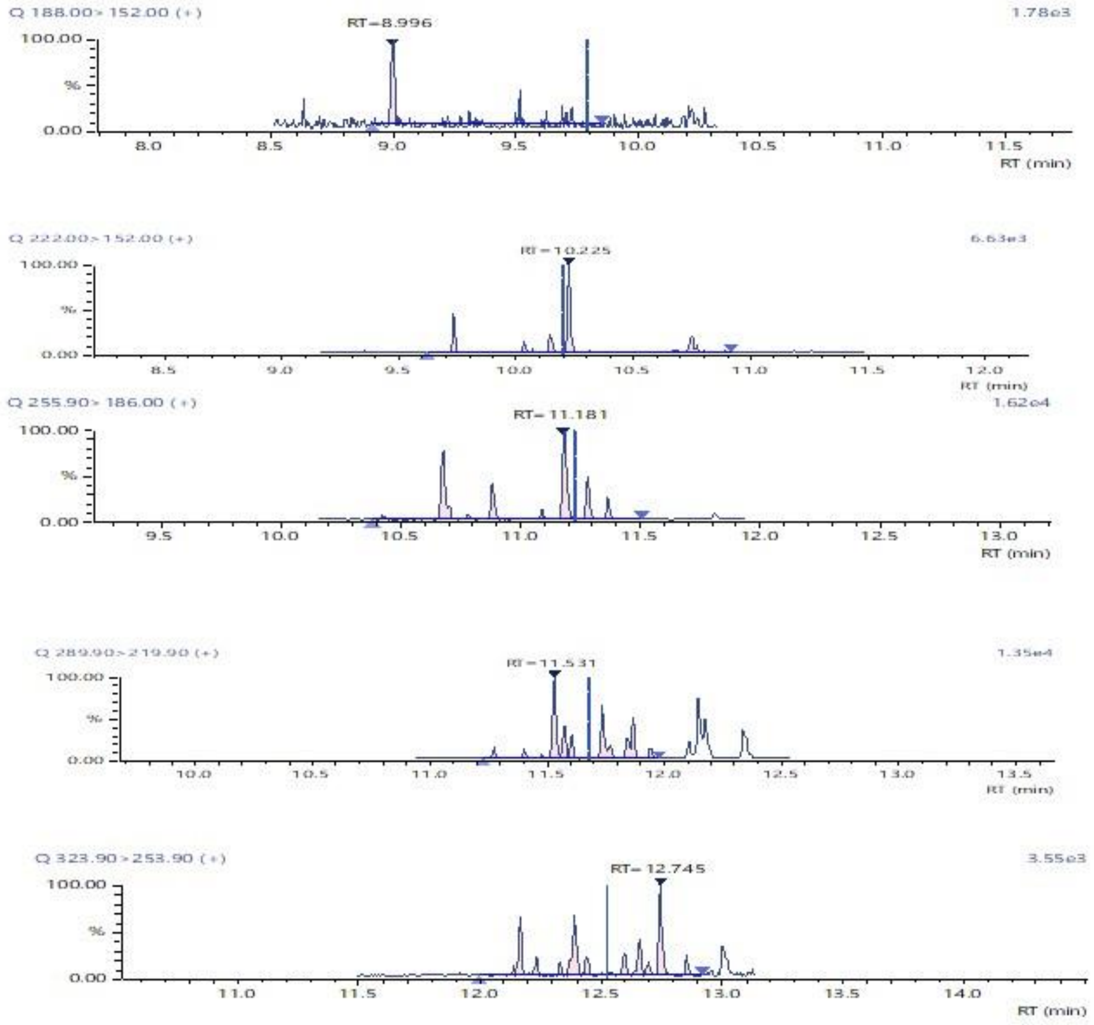
% Recovery of Spiked Organochlorine Pesticides by SPE

Component	50 ng/L		5 ng/L		EPA Method 608.3 QC Acceptance Criteria	
	Recovery (%)	RSD (n=3)	Recovery (%)	RPD (n=2)	Recovery Range (%)	RSD
Pesticides						
alpha-BHC	77.0	15%	74.7	6.2%	37-140	36
gamma-BHC	89.5	12%	85.7	5.1%	32-140	39
beta-BHC	81.3	12%	82.0	6.4%	17-147	44
delta-BHC	89.5	13%	85.9	5.0%	19-140	52
Heptachlor	91.3	13%	92.8	9.0%	34 - 140	43
Aldrin	89.8	11%	91.7	16%	42-140	35
cis-Heptachlor Epoxide	115	18%	96.2	25%	37 - 142	26
trans-Heptachlor Epoxide	108	16%	68.3	13%	37 - 142	26
cis-Chlordane	58.8	17%	53.9	8.7%	45-140	35
Endosulfan I	69.9	11%	49.0	42%	45-153	28
trans-Chlordane (gamma)	60.9	18%	50.4	16%	45-140	35
4,4'-DDE	62.6	18%	61.3	8.2%	30-145	35
Dieldrin	75.5	18%	61.2	45%	36-146	49
Endrin	82.5	17%	61.0	2.3%	30 - 147	48
Endosulfan II	74.4	14%	58.1	22%	D-202	53
4,4'-DDD	69.0	19%	68.8	13%	31-141	39
Endosulfan Sulfate	62.7	16%	59.7	18%	26-144	38
4,4'-DDT	67.5	20%	73.1	10%	25-160	42

% Recovery of Spiked Organochlorine Pesticides by LLE

Component	1 ppb	2 ppb	25 ppb	50 ppb
alpha-BHC	88	92	94	87
gamma-BHC (Lindane)	82	88	102	93
beta-BHC	86	91	97	90
delta-BHC	87	95	104	95
Heptachlor	90	100	99	92
Aldrin	100	90	89	79
Heptachlor epoxide (isomer B)	96	99	104	94
trans-Chlordane	99	93	97	92
cis-Chlordane	97	82	93	85
Endosulfan I	98	84	104	90
4,4'-DDE	78	96	96	91
Dieldrin	104	65	96	92
Endrin	108	97	96	87
4,4'-DDD	86	85	91	86
Endosulfan II	105	78	100	94
Endrin aldehyde	106	62	102	101
4,4'-DDT	76	84	96	91
Endosulfan sulfate	84	100	108	98
Methoxychlor	80	83	102	100
Endrin ketone	50	91	106	97

Recognition of Aroclor by analysis of PCB congeners



Area 1046
Monochlorobiphenyl

Area 13119
Dichlorobiphenyl

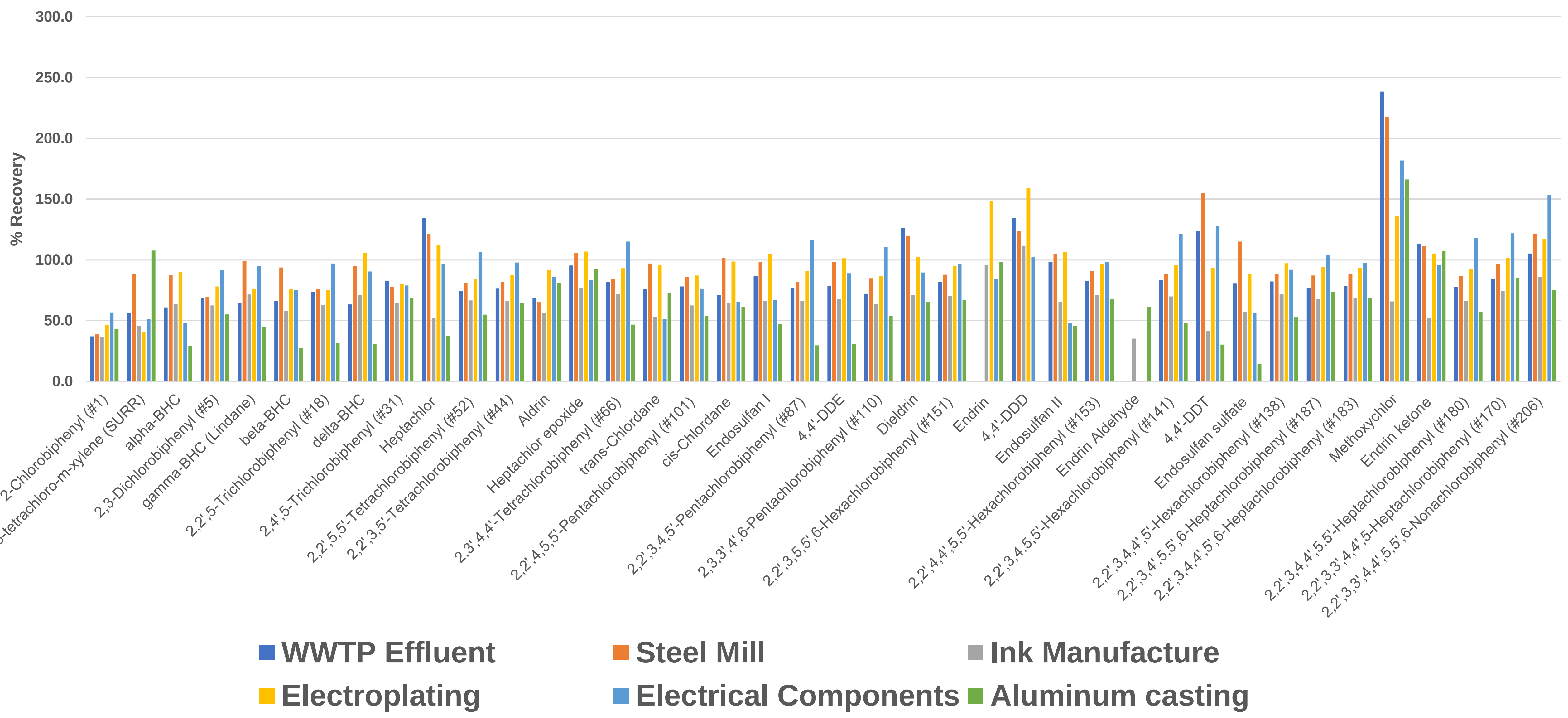
Area 58451
Trichlorobiphenyl

Area 49523
Tetrachlorobiphenyl

Area 12703
Pentachlorobiphenyl

Looks 1242 or 1248

Preliminary Matrix Spike recovery in various matrices



Pesticide CCV Recovery and Precision from 21 different runs

Compound	CCV Average % Recovery	Standard Deviation
alpha-BHC	85.72	14.49
gamma-BHC (Lindane)	86.45	14.81
beta-BHC	85.60	14.17
delta-BHC	85.14	14.00
Heptachlor	94.26	16.86
Aldrin	85.99	13.80
Heptachlor epoxide (isomer B)	94.59	10.65
trans-Chlordane	90.20	10.60
cis-Chlordane	86.48	17.71
Endosulfan I	100.77	11.23
4,4'-DDE	98.48	21.80
Dieldrin	104.03	10.03
Endrin	102.67	25.16
4,4'-DDD	102.81	19.70
Endosulfan II	100.97	11.15
Endrin aldehyde	108.02	20.58
4,4'-DDT	104.64	22.48
Endosulfan sulfate	94.29	13.27
Methoxychlor	114.92	27.73
Endrin ketone	101.54	19.24

Congener CCV Recovery and Precision from 21 different runs

Compound	CCV Average % Recovery	Standard Deviation
2-Chlorobiphenyl (#1)	92.35	12.75
2,3-Dichlorobiphenyl (#5)	93.63	11.21
2,2',5-Trichlorobiphenyl (#18)	93.08	9.54
2,4',5-Trichlorobiphenyl (#31)	92.77	8.70
2,2',5,5'-Tetrachlorobiphenyl (#52)	93.94	7.01
2,2',3,5'-Tetrachlorobiphenyl (#44)	94.53	6.83
2,3',4,4'-Tetrachlorobiphenyl (#66)	96.03	5.86
2,2',4,5,5'-Pentachlorobiphenyl (#101)	93.67	6.37
2,2',3,4,5'-Pentachlorobiphenyl (#87)	94.45	7.41
2,3,3',4',6-Pentachlorobiphenyl (#110)	92.55	6.06
2,2',3,5,5',6-Hexachlorobiphenyl (#151)	93.00	7.21
2,2',4,4',5,5'-Hexachlorobiphenyl (#153)	95.44	6.60
2,2',3,4,5,5'-Hexachlorobiphenyl (#141)	95.61	5.46
2,2',3,4,4',5'-Hexachlorobiphenyl (#138)	97.30	5.48
2,2',3,4',5,5',6-Heptachlorobiphenyl (#187)	97.53	6.03
2,2',3,4,4',5',6-Heptachlorobiphenyl (#183)	95.76	6.06
2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)	97.01	5.33
2,2',3,3',4,4',5-Heptachlorobiphenyl (#170)	101.30	5.15
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (#206)	91.26	10.32

Advantages of MRM quantitation of Method 608 Pesticides and PCBs

- **Fewer interferences**
- **Detection limits similar to GC-ECD**
- **Long-term stability of response**
- **No need to exchange to hexane**
- **No second column confirmation**

Thank You, for more information on this new ASTM method, contact:

- wclipps@shimadzu.com

- Or visit www.ssi.shimadzu.com