

# Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

**Pittcon 2016** 1110-2

Brahm Prakash, William Lipps, Di Wang, Shilpi Chopra,  
Nicole Lock and Laura Chambers  
Shimadzu Scientific Instruments, Columbia, MD, USA

# Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

## Introduction

This poster describes use of a triple quadrupole GC/MS/MS method using Multiple Reaction Monitoring (MRM) mode for sensitive and selective detection and quantitation of Organochlorine pesticides and PCBs. A database with optimized MRM transitions for all of the OCPs and PCBs, including relative retention times for all components, makes method setup possible within minutes. The use of GC/MS/MS MRM mode provides enhanced selectivity, specificity and sensitivity in complex matrices with potential co-eluting interferences<sup>1</sup>.

This poster presents all instrument operating conditions and instrument method performance statistics, including method linearity, accuracy, precision, and instrument detection limits for all compounds.

Chlorinated pesticides and polychlorinated biphenyl (PCB) congeners (known collectively as Aroclor) are among the most difficult to measure environmental organic compounds.

The sensitivity of GCMS has increased dramatically since

Method 608 was written. New GCMS technology can be run in selected ion monitoring mode (SIM), greatly increasing the sensitivity. In addition, newer tandem GCMS technology eliminates almost all noise, increasing the sensitivity of the detector 5 - 10 times more than that of SIM.

Triple quadrupole mass spectrometry is the linking together of two quadrupoles. Ions are separated in the first quadrupole, fragmented further in a collision cell, and the product ions are separated and analyzed by a second quadrupole. This technique eliminates matrix interferences, making it highly selective and extremely sensitive. Faster scanning analyzers, such as the Shimadzu GCMS-TQ8040, are capable of Scan/MRM and/or Scan/SIM all in a single method.

Figure 1 shows a SIM and MRM chromatogram showing the decrease in noise and signal and the corresponding increase in the MRM signal-to-noise ratio. MRM detection limits are usually 5-10 times lower than SIM detection limits.

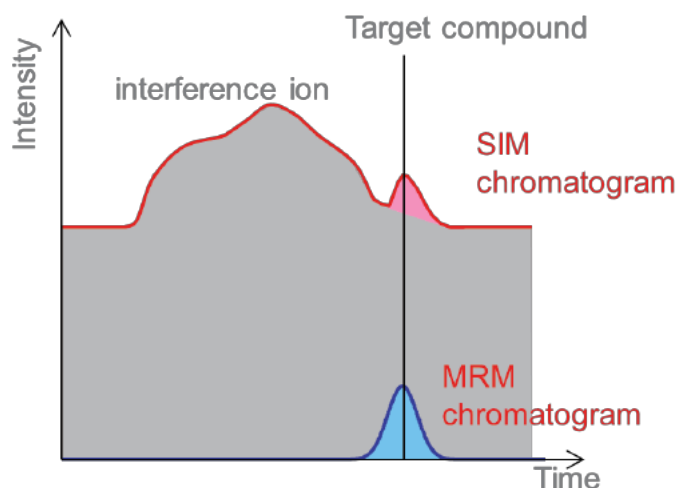


Figure 1: Example of a SIM and MRM chromatogram showing improvement of MRM S/N ratio

# Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

## Experimental

This study was conducted using a Shimadzu GCMS-TQ8040 configured with a Restek capillary column designed specifically for the analysis of semi-volatile analytes. The GC was operated in constant linear velocity mode, providing the best chromatographic resolution, symmetrical peak shapes, and enhanced sensitivity for the target compounds. A commercial mixture of 19 PCB congeners, 20 Organochlorine pesticides, five internal

standards, and four surrogates was used to prepare calibration curves ranging from 0.5 - 200 ppb. The standards were prepared in a mixture of EPA method 625 acids and base-neutral target analytes to provide a better, more realistic, synthetic matrix. Chromatographic conditions were established and the MRM method was optimized for each component. The instrument operating conditions are shown in Table 1.

Table 1: GCMS-TQ8040 operating conditions

<b>Instrument</b>	<b>: GCMS-TQ8040</b>
Column	: SH-Rxi-5 MS, 30 m x 0.25 mm x 0.25 µm (Shimadzu PN 221-75940-15)
Oven Program	: 50 °C, hold 0.5 minute, 28 °C/minute to 265 °C, 3 °C/minute to 285 °C, 25 °C/minute to 330 °C, hold 1.0 minute
Injector	: Pulse Splitless (250kPa for 1.50 minutes, 2µL 275 °C)
Carrier Gas	: Helium Constant linear velocity mode, 43.5 cm/sec Total Flow 30 mL/min, Column Flow = 1.0 mL/min Purge Flow 3.0 mL/min
Interface Temperature	: 290 °C
<b>Mass Spectrometer</b>	<b>: GCMS-TQ8040</b>
Ion Source Temperature	: 230 °C
MS Operating Mode	: Acquisition Mode, MRM CID gas, Argon Solvent cut Time, 1.35 minutes Detector voltage absolute, 1.90kV Threshold = 0, Event time 0.200 sec
<b>Analysis Times</b>	<b>: 17.65 minutes</b>
GC Cycle Time	: 22.00 minutes

## MRM Method Development

MRM transitions were monitored for each component. Quantitative and qualitative transitions were selected to provide maximum sensitivity and as independent confirmation of the compounds identity. The Ion Shield High Efficiency source minimized fragmentation even at 70 eV, providing an optimum abundance and

transmission of ions into the quadrupoles. Method settings were made to provide enough sensitivity to easily detect and quantify the target analytes at concentrations equal to or better than Method 608. MRM transitions and collision energies (CE) for each compound are shown in Table 2.

# Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

## Calibration

A 9-point calibration curve of 0.5 - 200 ppb was analyzed using the conditions described in Table 1. The curves of all 48 components were evaluated using linear regression and %RSD of the calculated Response factors. A MRM chromatogram from a mid-point standard is shown in Figure 2.

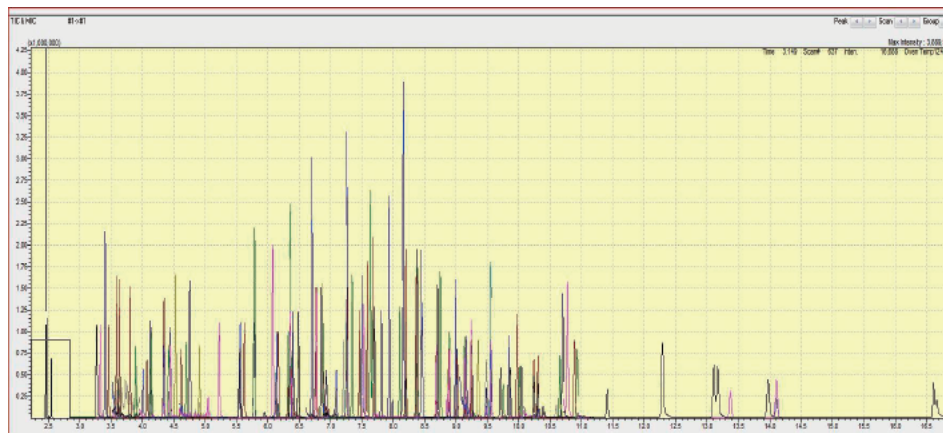


Figure 2: Mid-point standard MRM chromatogram from the 50ug/L calibration standard

# Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

Table 2: GCMS-TQ8040 MRM transitions and collision energies; estimated MDL compared to method 608 MDL; precision and accuracy for pesticides and PCB congeners

Compound	Quantitative			Qualitative			Estimated MDL (assumes 1000ml/1ml) µg/L			Precision and Accuracy			
	Precursor	Product	CE (V)	Precursor	Product	CE (V)	1 ppb standard	2 ppb standard	5 ppb standard	10 ppb Standard		20 ppb standard	
										%REC	%RSD	%REC	%RSD
2-Fluorophenol (IS)	112.00	64.20	18.0	92.00	64.20	6.0							
Pentafluorophenol (SURR)	136.00	117.20	15.0	184.00	117.20	27.0							
Nitrobenzene-d5 (IS)	82.00	54.20	15.0	128.00	82.30	15.0							
2,4,5,6-tetrachloro-m-xylene (SURR)	244.00	209.10	15.0	171.00	136.20	15.00							
4,4'-Dibromooctafluorobiphenyl (SURR)	456.00	296.00	27.0	296.00	246.10	24.0							
Alpha-BHC	180.90	144.90	16.0	218.90	182.90	8.0	0.0002	0.0005	0.0004	96	2.3	87	2.7
Gamma-BHC (Lindane)	180.90	144.90	16.0	218.90	182.90	8.0	0.0003	0.0005	0.0004	102	3.7	94	2.0
Beta-BHC	180.90	144.90	16.0	218.90	182.90	8.0	0.0002	0.0004	0.0005	97	1.9	89	1.5
Delta- BHC	180.90	144.90	16.0	218.90	182.90	8.0	0.0003	0.0004	0.0007	99	2.1	92	2.3
Heptachlor	271.80	236.90	20.0	273.80	238.90	16.0	0.0003	0.0004	0.0007	107	4.8	104	2.0
Aldrin	269.90	191.00	34.0	262.90	193.00	28.0	0.0004	0.0007	0.001	114	6.0	110	1.6
4,4'Dibromobiphenyl (SURR)	312.00	152.30	14.0	152.30	126.20	24.0							
Heptachlor Epoxide (isomer B)	352.80	262.90	14.0	354.80	264.90	20.0	0.0004	0.0007	0.0014	122	7.1	118	3.7
Trans-Chlordane	372.80	263.90	28.0	374.80	265.90	26.0	0.0002	0.0007	0.0011	108	4.8	101	5.2
Cis-Chlordane	372.80	263.90	28.0	374.80	265.90	26.0		0.0009	0.0016	128	5.4	124	4.8
Endosulfan I	194.90	160.00	8.0	194.90	125.00	24.0	0.0003	0.0006	0.0013	113	13.0	112	2.9
4,4'-DDE	246.00	176.00	30.0	317.90	248.00	24.0	0.0003	0.0003	0.0005	105	1.9	96	2.2
p-Terphenyl-d14 (IS)	244.00	240.30	30.0	244.00	242.20	18.0							
Dieldrin	276.90	241.00	8.0	262.90	193.00	34.0		0.0009	0.0022	110	13.3	113	5.3
Endrin	262.90	191.00	30.0	262.90	193.00	28.0		0.0008	0.0012	127	10.0	124	4.7
4,4'-DDD	235.00	165.00	24.0	237.00	165.00	28.0	0.0002	0.0003	0.0004	102	2.3	99	1.9
Endosulfan II	194.90	160.00	8.0	194.90	125.00	24.0		0.0009	0.0013	129	10.3	131	5.4
Endrin Aldehyde	249.90	214.90	18.0	249.90	179.00	16.0			0.0026	124	16.7	134	5.8
4,4'-DDT	235.00	165.00	24.0	237.00	165.00	28.0	0.0001	0.0003	0.0004	119	1.9	115	1.7
Endosulfan Sulfate	271.80	236.90	18.0	386.80	252.90	16.0	0.0002	0.0004	0.0005	116	2.2	115	1.6
Methoxychlor	227.10	169.10	24.0	227.10	212.10	14.0	0.0002	0.0004	0.0007	126	2.7	122	1.8
Endrin Ketone	281.00	244.90	12.0	281.00	208.90	24.0			0.0014	90	14.5	107	8.8
Decachlorobiphenyl (BZ#209) (IS)	497.70	427.80	30.0	499.70	429.80	30.0							
Decafluorobiphenyl (IS)	214.00	179.10	18.0	178.00	160.60	9.0							
2-Chlorobiphenyl (#1)	188.00	152.00	24.0	190.00	152.00	24.0	0.0002	0.0004	0.0005	96	1.8	86	3.1
2,3-Dichlorobiphenyl (#5)	222.00	152.00	24.0	224.00	152.00	24.0		0.0004	0.0004	97	1.9	87	1.3
2,2',5-Trichlorobiphenyl (#18)	255.90	186.00	26.0	257.90	186.00	26.0		0.0003	0.0006	97	1.2	87	1.2
2,4',5-Trichlorobiphenyl (#31)	255.90	186.00	26.0	257.90	186.00	26.0				98	1.7	88	1.3
2,2',5,5'-Tetrachlorobiphenyl (#52)	289.90	219.90	26.0	291.90	221.90	26.0	0.0002	0.0003	0.0004	97	2.2	87	2.6
2,2',3,5'-Tetrachlorobiphenyl (#44)	289.90	219.90	26.0	291.90	221.90	26.0	0.0002	0.0002	0.0006	101	3.1	90	2.0
2,3',4,4'-Tetrachlorobiphenyl (#66)	289.90	219.90	26.0	291.90	221.90	26.0	0.0002	0.0003	0.0004	99	1.7	90	1.9
2,2',4,5,5'-Petachlorobiphenyl (#101)	323.90	253.90	26.0	328.90	255.90	26.0	0.0003	0.0004	0.0008	102	2.6	94	2.4
2,2',3,4,5'-Pentachlorobiphenyl (#87)	323.90	253.90	26.0	325.90	255.90	26.0	0.0003	0.0004	0.0007	99	2.5	89	3.0
2,3,3',4',6-Pentachlorobiphenyl (#110)	323.90	253.90	26.0	325.90	255.90	26.0	0.0003	0.0004	0.0008	96	1.9	88	1.8
2,2',3,5,5',6-Hexachlorobiphenyl (#151)	359.90	289.90	28.0	361.90	291.90	28.0	0.0003	0.0004	0.0008	106	3.2	97	3.6
2,2',4,4',5,5'-Hexachlorobiphenyl (#153)	359.90	289.90	28.0	361.90	291.90	28.0	0.0005	0.0002	0.0006	106	2.9	96	2.6
2,2',3,4,5,5'-Hexachlorobiphenyl (#141)	359.90	289.90	28.0	361.90	291.90	28.0	0.0006	0.0004	0.0006	104	2.1	97	1.3
2,2',3,4,4',5'-Hexachlorobiphenyl (#138)	359.90	289.90	28.0	361.90	291.90	28.0		0.0003	0.0006	111	3.3	105	1.3
2,2',3,4',5,5',6-Heptachlorobiphenyl (#187)	393.80	323.90	28.0	395.80	325.90	28.0		0.0004	0.0009	109	4.8	103	2.1
2,2',3,4,4',5',6-Heptachlorobiphenyl (#183)	393.80	323.90	28.0	395.80	325.90	28.0	0.0002	0.0003	0.0008	110	3.1	102	2.7
2,2',3,4,4',5,5',6-Heptachlorobiphenyl (#180)	393.80	323.90	28.0	395.80	325.90	28.0	0.0003	0.0003	0.0005	102	2.9	94	1.8
2,2',3,3',4,4',5'-Heptachlorobiphenyl (#170)	393.80	323.90	28.0	395.80	325.90	28.0	0.0001	0.0001	0.0004	106	1.4	98	1.5
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (#206)	461.70	391.80	30.0	463.70	393.80	30.0	0.0004	0.0003	0.0004	101	1.7	95	1.5

# Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

## Method Detection Limit (MDL)

An instrument detection limit (IDL) study was made using eight replicate injections at 1.0, 2.0 and 5.0 ppb standards but with concentrations divided by 1000 to approximate MDLs for 1000 ml samples extracted and concentrated to 1 ml. These estimated MDL results were compared to Method 608 detection limits and are shown in Table 2.

## Precision and Accuracy

Eight replicates of 10 ppb and 20 ppb were made to determine precision and accuracy. Table 2 lists the results of the precision and accuracy study, reporting the % recovery and the %RSD for all compounds at both concentrations.

## Internal Standard and Surrogate Study

Five internal standards were used for calibration and four surrogate standards to measure recovery. Table 3 lists the components. Figure 3 and Figure 4 plot the internal standard area and the surrogate standard recovery, respectively. The small variance (< 6 %RSD for all compounds) in the data demonstrates the long-term stability of the instrumental method.

Table 3: Internal and surrogate standards

IS 1	2-Fluorophenol
IS 2	Nitrobenzene-d5
IS 3	p-Terphenyl-d14(IS)
IS 4	Decachlorobiphenyl (BZ #209)
IS 5	Decafluorobiphenyl
SURR 1	Pentafluorophenol
SURR 2	2,4,5,6-tetrachloro-m-Xylene
SURR 3	4,4'-Dibromooctafluorobiphenyl
SURR 4	4,4'-Dibromobiphenyl(SURR)

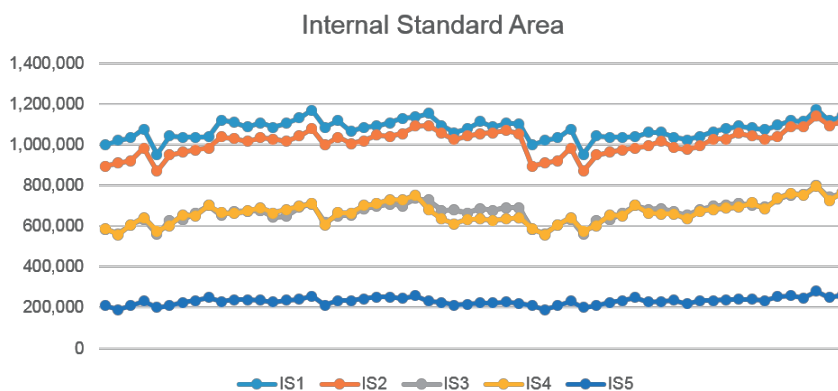


Figure 3: Internal standard area

## Determination of Organochlorine Pesticides and Polychlorinated Biphenyls Using GC/MS/MS Operated in the MRM Mode

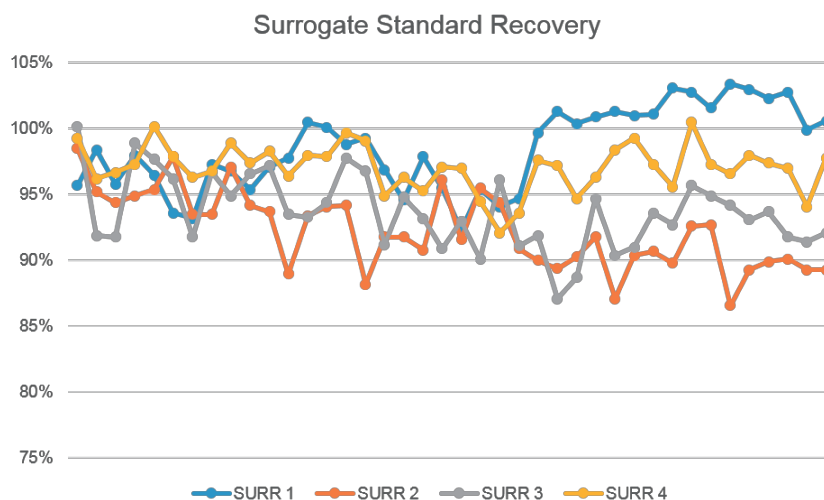


Figure 4: Surrogate standard recovery

## Conclusion

Triple quadrupole GCMS analysis simplifies detection and quantitation of pesticides and PCBs. Detection limits are equal to or better than Method 608 detection limits. Triple quadrupole GCMS does not suffer from interferences nor does it require dual columns to confirm the identity of peaks. PCB analysis by Method 608 is difficult because the Aroclor pattern changes with weathering often resulting in

samples containing PCBs being reported as not detected. Using a triple quadrupole GCMS, such as the Shimadzu GCMS-TQ8040, for pesticides and PCB analysis is a viable alternative to EPA Method 608. This paper evaluated standards only. Our evaluation indicates that triple quadrupole GCMS is a suitable alternative to pesticide and PCB analysis by GC-ECD.

## References

1. Technical Report C146-E230, Analysis of Pesticides in Food Matrix using QuEChERS by Triple Quadrupole GC/MS/MS and LC/MS/MS, Shimadzu Corporation, Japan, June 2013
2. US EPA Method 608, Organochlorine pesticides and PCBs, CFR40 Part 136 Appendix A
3. Technical Guide, Analysis of Halogenated Environmental Pollutants Using Electron Capture Detection, Restek Lit # EVTG1648-UNV, 2014

First Edition: March, 2016