

# New Analytical Method of Aroclor and Organochlorine Pesticides in Ground Water

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## 1. Introduction

Polychlorobiphenyl (PCB) mixture, Aroclor, and organochlorine pesticides are known as Persistent Organic Pollutants (POPs). The United States Environmental Protection Agency (USEPA) requires the use of a gas chromatograph with electron capture detector (GC-ECD) to measure them in environmental samples. The GC-ECD method uses pattern recognition to determine the type of Aroclor. This method also requires confirmation of every detected component on a separate, dissimilar stationary phase GC column due to less selectivity of the ECD detector. Because pesticides co-elute with many of the PCB peaks, the accurate quantitation of target compounds is a challenging task.

A new method using triple quadrupole GC-MS/MS can measure all targeted pesticides and PCBs in single run due to its high selectivity. Additionally, the type of Aroclor can be determined with a simple mathematical algorithm. In this poster, the performance of this new analytical method is demonstrated using environmental samples.

## 2. Method

### 2-1. Sample Preparation

Calibration standards (0.5 to 200 ng/mL) were made of the pesticides standards and nine PCB standards (mono: #1, di: #4, tri: #18, tetra: #52, penta: #101, hexa: #149, hepta: #187, octa: #199, nona: #208).

River water and wastewater effluent were spiked at 10 and 100 ng/L with the pesticide standards and Aroclor 1232. The samples were extracted with methylene chloride under acid and base conditions, then concentrated to 1 mL using a vacuum vortex evaporation system.

### 2-2. Analytical Conditions

[System Configuration]  
 GC-MS/MS: GCMS-TQ8040 (Shimadzu)  
 Auto Injector: AOC-20i+s (Shimadzu)  
 Column: SH-Rxi-5MS 30 m x 0.25 mm I.D., df=0.25 μm (Shimadzu)  
 Glass Liner: Topaz, Splitless Liner with Wool (Restek)

[GC]  
 Injection Temperature: 275 °C  
 Injection Mode: Splitless (High Press. Injection, 250 kPa, 1.5 min)  
 Flow Control: Constant Linear Velocity (43.5 cm/sec)  
 Oven Temperature: 60 °C (0.5min), 40 °C/min to 180 °C, 4 °C/min to 280 °C, 20 °C/min to 330 °C (1 min)

Injection Volume: 2 μL  
 Carrier Gas: Helium

[MS]  
 Interface Temperature: 290 °C  
 Ion Source Temperature: 230 °C  
 Ionization Mode: EI  
 Ionization Voltage: 70 eV  
 Emission Current: 60 μA  
 Acquisition Mode: MRM  
 Loop Time: 0.5 sec



Figure 1 GCMS-TQ8040 and AOC-20i+s

## 2-3. Determination Procedure of Aroclors

A new Aroclor determination method was evaluated. This method is suitable for 1) identifying the type of Aroclor and 2) quantifying its concentration using only nine PCB congeners. The need of visual chromatograph comparison for 1) assessing Aroclors pattern recognition and 2) subsequent reanalysis of calibration standards for quantitation are eliminated in this method. Pesticides were quantified by means of the internal standard method. All calibration curves were built with mean response factor curve fit type, and RF % less than 30 %.

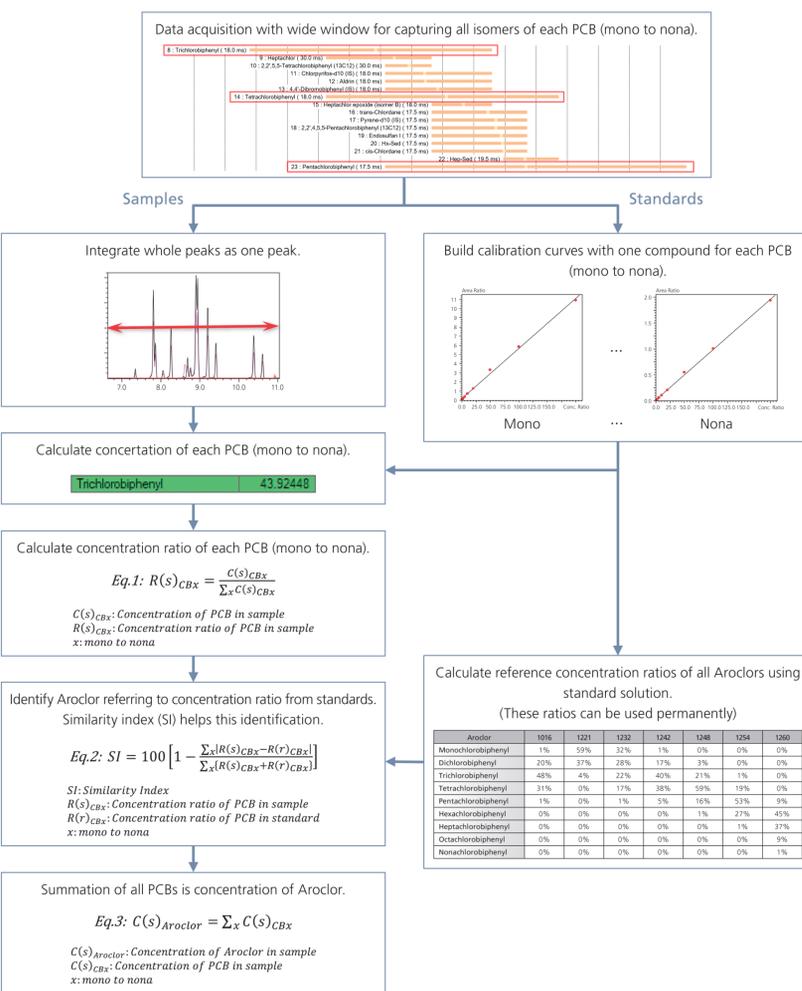


Figure 2 Aroclor determination procedure

## 3. Results

### 3-1. Calibrations

Calibration curves for the majority of compounds ranged 0.5 to 200 ng/mL with less than 30 % of RF %RSD. Responses of internal standards remained for the duration of this study and helped to get good calibration results.

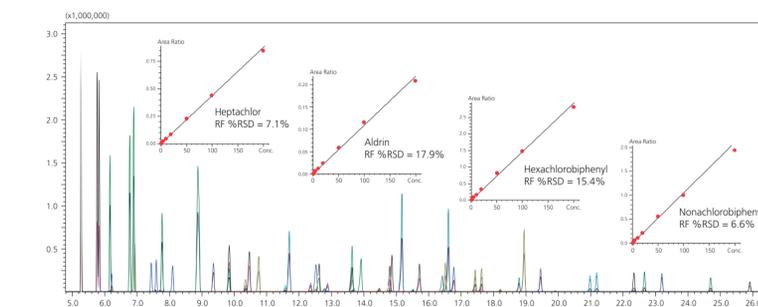


Figure 3 MRM chromatogram (200 ng/mL standard) and calibration

### 3-2. Recoveries of Pesticides

Most pesticides showed recoveries within 70 to 120 % even at low concentration level, 10 ng/mL. For the majority of toxaphenes, the calibration curves started from 20 ng/mL. Therefore their recoveries were available at only 100 ng/mL.

Although same amount of Aroclor 1232 was spiked in the samples, the recoveries of pesticides were not affected because MRM method eliminated the interfering signal that occurs in the ECD.

Table 1 Recovery rates (%) of organochlorine pesticides

Compound	Calibration range (ng/mL)	RF %RSD	Effluent		River Water	
			Spiked 10 ng/L	Spiked 100 ng/L	Spiked 10 ng/L	Spiked 100 ng/L
alpha-BHC	0.5 - 200	14.7	70.2	65.6	68.1	68.1
gamma-BHC	0.5 - 200	28.6	69.2	66.2	69.7	67.9
beta-BHC	0.5 - 200	14.0	67.4	66.9	71.7	68.0
delta-BHC	0.5 - 200	24.7	67.8	64.6	70.7	66.9
Heptachlor	0.5 - 200	7.1	88.1	82.5	75.3	82.3
Heptachlor epoxide	0.5 - 200	12.5	93.8	86.1	81.2	92.6
Aldrin	0.5 - 200	17.9	125.5	76.2	64.1	74.4
Dieldrin	1 - 200	28.3	82.6	86.1	68.3	91.1
Endrin	0.5 - 200	29.3	102.9	118.1	96.0	119.3
trans-Chlordane	0.5 - 200	17.6	75.8	82.6	84.1	88.5
cis-Chlordane	0.5 - 200	21.9	84.4	83.6	83.3	87.1
Heptachlorobiphenyl	0.5 - 200	23.6	91.4	85.1	73.1	87.5
Octachlorobiphenyl	0.5 - 200	27.3	72.8	84.6	73.7	91.0
Endosulfan II	0.5 - 200	24.6	70.2	71.3	74.0	73.1
Endosulfan sulfate	0.5 - 200	25.5	67.3	67.1	72.4	69.0
4,4'-DDE	0.5 - 200	26.4	83.4	82.5	96.9	97.1
4,4'-DDD	0.5 - 200	25.5	91.9	87.4	71.2	67.0
4,4'-DDT	0.5 - 200	27.6	97.3	93.9	68.7	69.7
Methoxychlor	5 - 200	28.1	64.0	93.6	67.1	95.6
Hx-Sed	10 - 200	28.2	N/A	95.0	N/A	98.4
Hep-Sed	20 - 200	22.7	N/A	92.0	N/A	102.4
Parlar-26	10 - 200	27.0	N/A	99.0	N/A	102.8
Parlar-40, 41	20 - 200	26.4	N/A	105.5	N/A	94.8
Parlar-44	20 - 200	28.4	N/A	86.7	N/A	94.8
Parlar-50	10 - 200	25.9	N/A	124.1	N/A	77.1

### 3-3. Determination of Aroclor

Firstly, the type of Aroclor was identified using chlorobiphenyl concentration ratios. All spiked samples showed the highest similarity indices on Aroclor 1232 (Fig. 4). Type of Aroclor was identified correctly without visual chromatogram comparison. Secondary, concentrations were determined by summation of all chlorobiphenyls. Acceptable recoveries (100.2 to 128.1 %) were obtained without building additional calibration curves using Aroclor standard solutions.

Table 2 Concentration and ratios of chlorobiphenyls in samples

Sample	Effluent Water				River Water			
	Conc.	Spiked 10 ng/L	Spiked 100 ng/L	Ratio	Conc.	Spiked 10 ng/L	Spiked 100 ng/L	Ratio
PCB								
Monochlorobiphenyl	3.44	27%	30.55	29%	2.40	23%	30.82	29%
Dichlorobiphenyl	3.24	25%	27.58	26%	3.35	33%	28.07	26%
Trichlorobiphenyl	2.82	22%	23.75	23%	1.74	17%	24.18	22%
Tetrachlorobiphenyl	2.01	16%	21.39	20%	1.79	18%	21.44	20%
Pentachlorobiphenyl	0.42	3%	1.71	2%	0.96	9%	2.86	3%
Hexachlorobiphenyl	0.87	7%	0.00	0%	0.00	0%	0.22	0%
Heptachlorobiphenyl	0.00	0%	0.00	0%	0.00	0%	0.00	0%
Octachlorobiphenyl	0.00	0%	0.00	0%	0.00	0%	0.00	0%
Nonachlorobiphenyl	0.00	0%	0.00	0%	0.00	0%	0.34	0%
Sum	12.81	-	104.98	-	10.24	-	107.94	-

Table 3 Reference concentration ratios of Aroclors

Aroclor	1016	1221	1232	1242	1248	1254	1260
Monochlorobiphenyl	1%	59%	32%	1%	0%	0%	0%
Dichlorobiphenyl	20%	37%	28%	17%	3%	0%	0%
Trichlorobiphenyl	48%	4%	22%	40%	21%	1%	0%
Tetrachlorobiphenyl	31%	0%	17%	38%	59%	19%	0%
Pentachlorobiphenyl	1%	0%	1%	5%	16%	53%	9%
Hexachlorobiphenyl	0%	0%	0%	0%	1%	27%	45%
Heptachlorobiphenyl	0%	0%	0%	0%	0%	1%	37%
Octachlorobiphenyl	0%	0%	0%	0%	0%	0%	9%
Nonachlorobiphenyl	0%	0%	0%	0%	0%	0%	1%

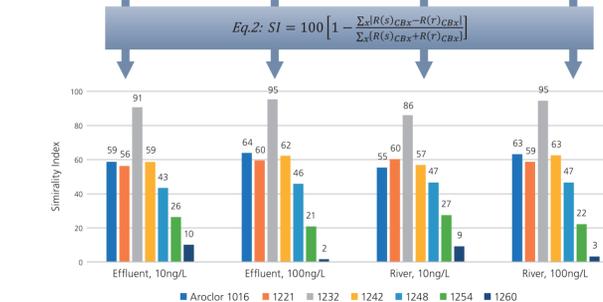


Figure 4 Similarity indices of samples

## 4. Conclusions

This new methodology leads to a simple and rapid determination of Aroclors and organochlorine pesticides using MRM analysis by triple quadrupole GC-MS/MS. All of compounds can be analyzed in single run without interferences from each other because of the high selectivity of MRM analysis. It does not require second column confirmation, required in GC-ECD methods. In addition, the type of Aroclor can be identified with a mathematical calculation which is more traceable and reliable than visual pattern recognition. This method can reduce data acquisition, processing time and error introduction, therefore, increase the laboratory throughput for ground and wastewater analysis.