

# Technical Report

## Analysis of Aroclor and Organochlorine Pesticides in Ground Water using Triple Quadrupole GC-MS/MS

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### Abstract:

USEPA method 608 is GC-ECD method to determine Aroclor and organochlorine pesticides. This method requires the use of second column for confirming the detected compounds due to the low selectivity of the ECD detector comparing with GC-MS/MS. Also pattern recognition is required for accurate identification of Aroclors. Triple quadrupole GC-MS/MS based method offers a solution for the GC-ECD method's drawbacks by providing high selective analysis. In addition, the type and concentration of Aroclor can be simultaneously determined.

**Keywords:** Aroclor, Polychlorobiphenyl, Pesticides, GC-MS/MS, EPA

### 1. Introduction

Polychlorobiphenyl (PCB) mixture, Aroclor, and organochlorine pesticides are known as Persistent Organic Pollutants (POPs) and 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. Pesticides also co-elute with many of the PCB peaks, making it difficult to accurately quantitate the compounds. This GC-ECD method also requires confirmation of every detected component on a separate, dissimilar stationary phase GC column due to less selectivity of the ECD detector.

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

### 2. Materials and Methods

Calibration standards (0.5 to 200 ng/mL) were made of the two pesticides standards and nine PCB standards listed below.

- Organochlorine pesticides (RESTEK)
- Toxaphene (Cambridge Isotope Laboratory)
- 2-Chlorobiphenyl (Accustandard for all PCBs)
- 2,2'-Dichlorobiphenyl
- 2,2',5'-Trichlorobiphenyl
- 2,2',5,5'-Tetrachlorobiphenyl
- 2,2',4,5,5'-Pentachlorobiphenyl
- 2,2',3,4',5',6'-Hexachlorobiphenyl
- 2,2',3,4',5,5',6'-Heptachlorobiphenyl
- 2,2',3,3',4,5,5',6'-Octachlorobiphenyl
- 2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl

For samples, above organochlorine pesticides, toxaphene standards and Aroclor 1232 standard (RESTEK) were spiked in at 10 and 100 ng/L.

Then samples were extracted according to the procedure described in section 2-1.

The two internal standards listed below were spiked to all vials at 100 ng/mL.

- Pyrene-d10 (for pesticides, Sigma Aldrich)
- Decachlorobiphenyl (for mono to nona chlorobiphenyl, RESTEK)

#### 2-1. Sample Preparation

In this study, river water and wastewater effluent were used. This procedure assumes an extraction volume of 1L. Mark the meniscus on the sample bottle for later determination of volume. The samples were prepared as follows:

1. Pour entire sample into a separatory funnel.
2. For the spiked sample, pipet standard solutions to the separatory funnel.
3. Adjust pH to less than 2 using sulfuric acid solution.
4. Add 60 mL methylene chloride (DCM) to the sample bottle, seal, and shake for about 30 seconds.
5. Transfer DCM to the separatory funnel and shake the funnel for 2 min with periodic venting to relieve pressure.
6. Allow for phases separation for 10 minutes. If an emulsion forms, apply mechanical means to break the emulsion.
7. Collect DCM layer through a drying column containing approximately 30g anhydrous sodium sulfate.
8. Repeat step 4 to 7 twice more and combine DCM fractions.
9. Adjust pH in the sample to 11 – 13 using sodium hydroxide solution.
10. Repeat step 4 to 7 three times.
11. Concentrate the extract solution to 1mL using a vacuum vortex evaporation system. The bottom part, collection part, must be cooled down to 4°C to prevent losing target compounds.
12. Transfer the extract to a GC vial and spike the internal standard solution.

## 2-2. Analytical Conditions

System Configuration	
GC-MS/MS	: GCMS-TQ8040 (Shimadzu)
Auto Injector	: AOC-20i+s (Shimadzu)
Column	: SH-Rxi-5MS 30m x 0.25mmI.D., df=0.25µm (Shimadzu, P/N:221-75940-30)
Glass Liner	: Topaz, Splitless Liner with Wool (Restek, Cat.# 23336)
GC	
Injection Temp.	: 275°C
Oven Temp.	: 60°C (0.5min), 40°C/min to 180°C, 4°C/min to 280°C, 20°C/min to 330°C (1min)
Flow Control	: Linear Velocity (43.5cm/sec)
Injection Mode	: Splitless with high pressure injection (250kPa, 1.5min)
Injection Volume	: 2µL

MS	
Interface Temp.	: 290°C
Ion Source Temp.	: 230°C
Ionization Mode	: EI
Ionization voltage	: 70eV
Emission Current	: 60µA
Acquisition Mode	: MRM (See Table 1)
Resolution	: Unit (Q1) – Unit (Q3)
Loop Time	: 0.5sec

Table 1 MRM transitions

ID	Compounds	Retention Index	Quantitation		Qualification	
			m/z	CE	m/z	CE
1	Monochlorobiphenyl	1573	188.0>152.0	24	190.0>152.0	24
2	Dichlorobiphenyl	1735	222.0>152.0	24	224.0>152.0	24
3	Trichlorobiphenyl	1893	255.9>186.0	26	257.9>186.0	26
4	Tetrachlorobiphenyl	2045	289.9>219.9	26	291.9>221.9	26
5	Pentachlorobiphenyl	2197	323.9>253.9	26	325.9>255.9	26
6	Hexachlorobiphenyl	2345	359.9>289.9	28	361.9>291.9	28
7	Heptachlorobiphenyl	2477	393.8>323.9	28	395.8>325.9	28
8	Octachlorobiphenyl	2614	427.8>357.8	28	429.8>359.8	28
9	Nonachlorobiphenyl	2754	461.7>391.8	30	463.7>393.8	30
10	alpha-BHC	1736	180.9>144.9	16	218.9>182.9	8
11	beta-BHC	1800	180.9>144.9	16	218.9>182.9	8
12	delta-BHC	1839	180.9>144.9	16	218.9>182.9	8
13	gamma-BHC	1784	180.9>144.9	16	218.9>182.9	8
14	trans-Chlordane	2126	372.8>263.9	28	374.8>265.9	26
15	cis-Chlordane	2156	372.8>263.9	28	374.8>265.9	26
16	4,4'-DDD	2286	235.0>165.0	24	237.0>165.0	28
17	4,4'-DDE	2199	246.0>176.0	30	317.9>248.0	24
18	4,4'-DDT	2366	235.0>165.0	24	237.0>165.0	28
19	Endosulfan I	2151	194.9>160.0	8	194.9>125.0	24
20	Endosulfan II	2266	194.9>160.0	8	194.9>125.0	24
21	Endosulfan sulfate	2355	271.8>236.9	18	386.8>252.9	16
22	Aldrin	2003	262.9>191.0	34	262.9>193.0	28
23	Dieldrin	2203	276.9>241.0	8	262.9>193.0	34
24	Endrin	2247	262.9>191.0	30	262.9>193.0	28
25	Heptachlor	1935	271.8>236.9	20	273.8>238.9	16
26	Heptachlor epoxide	2079	352.8>262.9	14	354.8>264.9	20
27	Methoxychlor	2494	227.1>169.1	24	227.1>212.1	14
28	Hx-Sed	2153	294.9>258.9	6	296.9>260.9	6
29	Hep-Sed	2195	306.9>270.9	4	308.9>272.9	4
30	Parlar-26	2245	328.9>292.9	8	330.9>294.9	8
31	Parlar-40	2367	340.9>304.9	6	342.9>306.9	6
32	Parlar-41	2367	340.9>304.9	6	342.9>306.9	6
33	Parlar-44	2389	376.9>340.9	4	378.9>342.9	4
34	Parlar-50	2435	374.9>338.9	6	376.9>340.9	6
35	Parlar-62	2548	338.9>302.9	6	340.9>304.9	6
36	Pyrene-d10 (IS)	2141	212.2>208.2	30	208.2>204.2	30
37	Decachlorobiphenyl (IS)	2897	497.7>427.8	30	499.7>429.8	30

Note: Retention indices of PCBs show the center of acquisition window.

## 2-3. Determination Procedure of Aroclors

A new Aroclor determination method was evaluated. This method can identify the type of Aroclor and quantify its concentration using just nine PCB congeners. Thus, pattern recognition by visually chromatogram comparison to identify Aroclors and subsequent reanalysis of calibration standards for quantitation are not needed.

Pesticides were determined with the normal internal standard method.

All calibration curves were built with mean response factor curve fit type, and RF %RSD should be less than 30%.

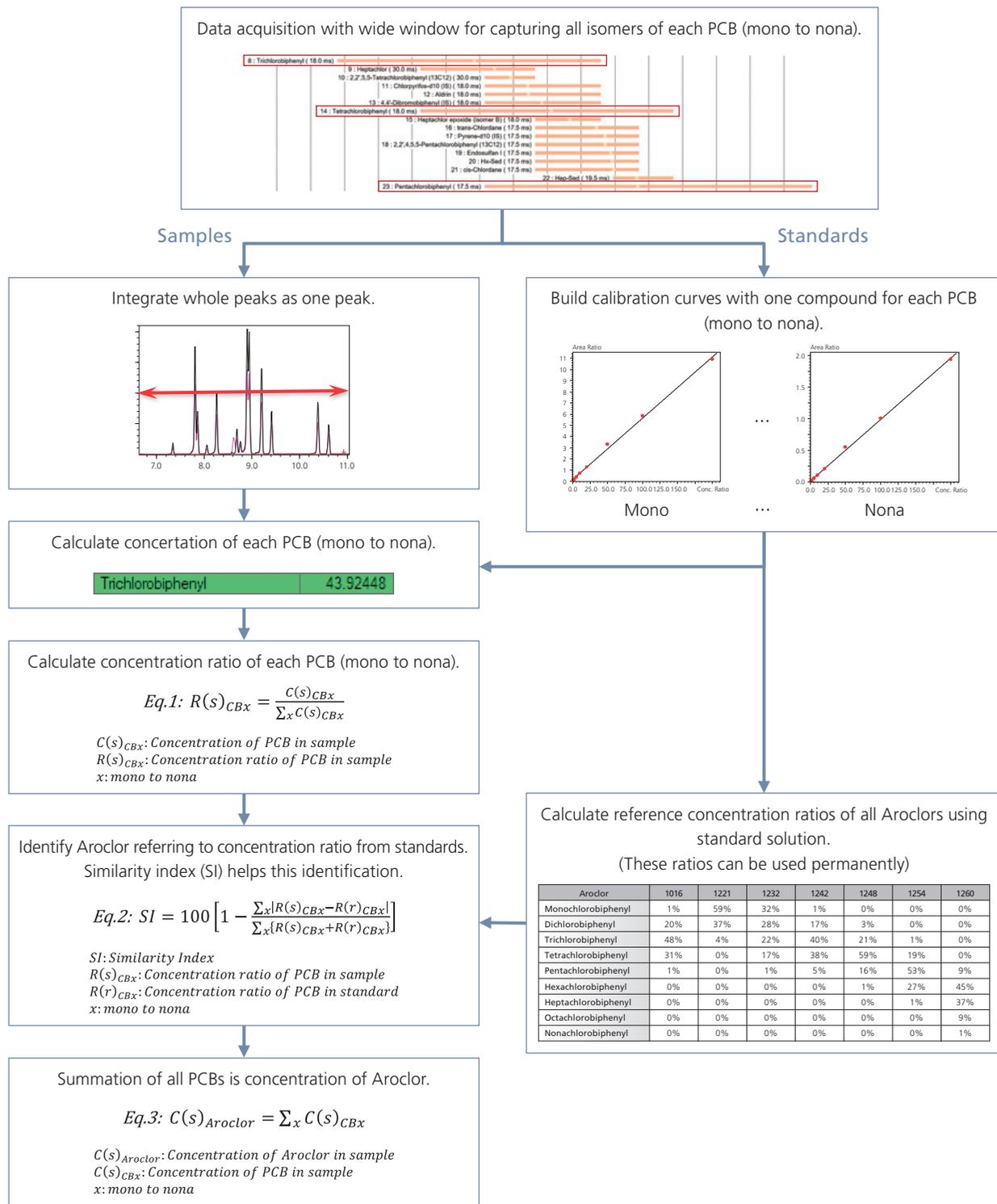


Fig. 1 Aroclor determination procedure

### 3. Results

#### 3-1. Calibrations

Calibration curves for the majority of compounds ranged 0.5 to 200ng/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.

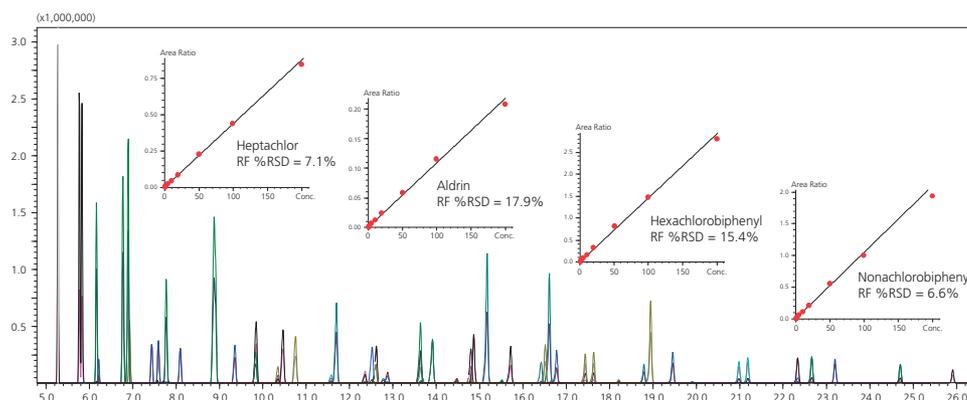


Fig. 2 MRM chromatogram (200ng/mL standard) and calibration

#### 3-2. Recoveries of Pesticides

Most pesticides showed recoveries within 70 to 120% even at low concentration level, 10ng/mL. Lower recoveries were assumed to occur due to losses during evaporation or degradation (e.g. gamma-BHC, 4,4'-DDE).

All of those recoveries were greater than 77%.

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.

Regarding some toxaphenes, the calibration curves started from 20ng/mL. Therefore recoveries were available at only 100ng/mL.

Table 2 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	65.8	65.6	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
Endosulfan I	0.5 - 200	23.6	91.4	85.1	73.1	87.5
Endosulfan II	0.5 - 200	27.3	72.8	84.6	73.7	91.0
Endosulfan sulfate	0.5 - 200	24.6	70.2	71.3	74.0	73.1
4,4'-DDE	0.5 - 200	25.5	67.3	67.1	72.4	69.0
4,4'-DDD	0.5 - 200	26.4	83.4	82.5	96.9	97.1
4,4'-DDT	0.5 - 200	25.5	91.9	87.4	71.2	67.0
Methoxychlor	0.5 - 200	27.6	97.3	93.9	68.7	69.7
Hx-Sed	5 - 200	28.1	64.0	93.6	67.1	95.6
Hep-Sed	10 - 200	28.2	N/A	95.0	N/A	98.4
Parlar-26	20 - 200	22.7	N/A	92.0	N/A	102.4
Parlar-40, 41	10 - 200	27.0	N/A	99.0	N/A	102.8
Parlar-44	20 - 200	26.4	N/A	105.5	N/A	94.8
Parlar-50	20 - 200	28.4	N/A	86.7	N/A	94.8
Parlar-62	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 calibration curves of chlorobiphenyls started from 0.5ng/mL and those of RF %RSD were less than 16.2%. Table 3 shows those ratios in samples. Then similarity indices were calculated using the equation 2 in Fig. 1. To calculate similarity indices, reference ratios must be prepared with standard solutions (Table 4). These ratios can be used permanently unless PCB components of calibration standard solutions changes. All spiked samples showed the highest similarity indices on Aroclor 1232 (Fig. 3). Type of Aroclor was identified correctly without visual chromatogram comparison.

Secondary, concentrations were determined by summation of all chlorobiphenyls. Recoveries were 100.2 to 128.1%. Acceptable recoveries were obtained without building additional calibration curves using Aroclor standard solutions.

Quantification of chlorobiphenyls in samples with and without pesticides showed no relevant differences. Hence, potential interferences from pesticides were eliminated by using MRM (data not shown.).

Table 3 Concentration and ratios of chlorobiphenyls in samples

Sample	Effluent Water				River Water			
	Spiked 10 ng/L		Spiked 100 ng/L		Spiked 10 ng/L		Spiked 100 ng/L	
	Conc.	Ratio	Conc.	Ratio	Conc.	Ratio	Conc.	Ratio
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 4 Reference concertation 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%

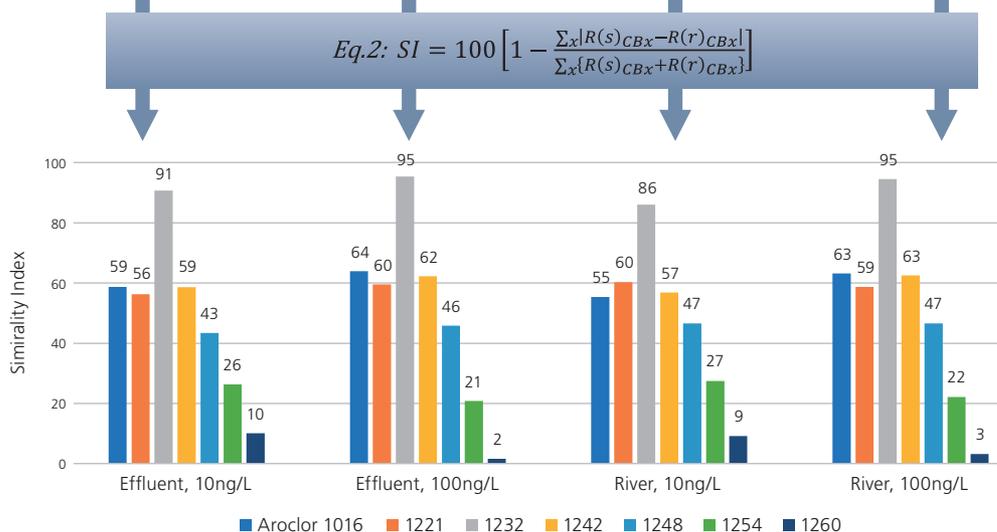


Fig. 3 Similarity indices of samples

## 4. Conclusion

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 like a GC-ECD technique. In addition, the type of Aroclor can be identified with mathematical calculation which is more traceable and reliable than visual pattern recognition.

This method can reduce data acquisition and processing time and increasing laboratory throughput for ground and wastewater analysis.

## Reference

- 1) USEPA Method 608, Organochlorine Pesticides and PCBs
- 2) ASTM International Collaboration Areas, WK54549, New Test Method for Determination of organochlorine pesticides and PCB congeners in aqueous solutions by gas chromatography triple quadrupole mass spectrometry

### Smart Performance That Boosts Routine Analytical Work

## GCMS-TQ8040 NX

**Smart Performance**—Enabling highly sensitive simultaneous analysis of multiple components

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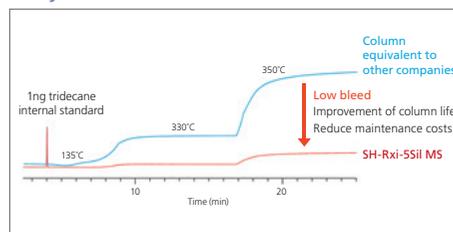


## GC Capillary Column SH Series



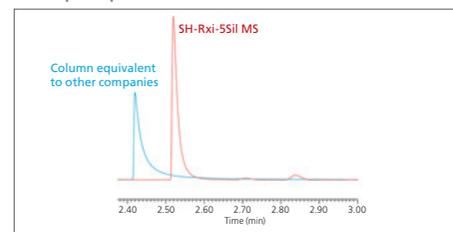
SH-Rxi-5MS (P/N:221-75940-30)  
was used for this application.

### Very low bleed!



Column : SH-Rxi-5SII MS  
 Column Volume : 30m, 0.25mm ID, 0.25µm  
 Sample : 40µg/mL n-tridecane in methylene chloride  
 Injector : 1.0µL split (split ratio 40:1), 4mm single gooseneck splitless liner w/wool  
 Injection Temp. : 250°C  
 Carrier Gas : helium, constant flow  
 Flowrate : 1.4mL/min.  
 Column Oven Temp. : 135°C (hold 4min.) to 330°C (hold 10min.) @ 70°C/min. to 350°C (hold 10min.) @ 70°C/min.  
 Detector : FID @ 330°C

### Sharper peaks!



Column : SH-Rxi-5SII MS  
 Column Volume : 30m, 0.25mm ID, 0.25µm  
 Sample : 40µg/mL 1,4-dioxane, pyridine, 2,4-dinitrophenol 100µg/mL phenanthrene in methanol  
 Injector : 1.0µL split (split ratio 20:1), 4mm single gooseneck splitless liner w/wool  
 Injection Temp. : 250°C  
 Carrier Gas : helium, constant flow  
 Flowrate : 2.5mL/min.  
 Column Oven Temp. : 50°C (hold 4min.) to 180°C (hold 8min.) @ 25°C/min.  
 Detector : FID @ 300°C

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