Determining PCB Aroclors in Matrix by GC MSMS Tandem Mass Spectrometry

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Introduction

Poly chlorinated biphenyls or PCB Aroclors are ubiquitous synthetic entities not known to naturally occur in the environment. These compounds were synthesized primarily for use as coolants and insulating fluids in electrical equipment. Initially PCB Aroclors were valued for their chemical stability however, the fact that they are so stable resulted in environmental persistence and ultimately, a ban on PCB production

Aroclors are PCB mixtures that were produced from approximately 1930 to 1979. Aroclor is one of the most commonly known trade names for PCB mixtures. There are many types of Aroclors and each has a distinguishing suffix number that indicates the degree of chlorination. The numbering standard for the different Aroclors is as follows:

The first two digits generally refer to the number of carbon atoms in the phenyl rings (for PCBs this is 12), the second two numbers indicate the percentage of chlorine by mass in the mixture. For example, the name **Aroclor 1254** means that the mixture contains approximately 54% chlorine by weight.

Herein is a presentation of Data collected on Agilent's GC-tandem mass spectrometer GCMS/MS 7000B which offers both superior sensitivity and selectivity for the analysis of PCB Aroclors in matrices The purpose of the analysis is to quantitatively identify the amount of PCB Aroclors present in the matrix



Instrument Parameters										
Deca	497.7	Wide	427.7	Wide	20	25				
Nona	461.7	Wide	391.8	Wide	20	25				
Octa	427.8	Wide	357.8	Wide	20	25				
Hepta	393.8	Wide	323.9	Wide	20	25				
Hexa	359.8	Wide	289.9	Wide	20	25				
Penta	325.9	Wide	255.9	Wide	20	25				
Tetra	291.9	Wide	222	Wide	20	25				
Tri	258	Wide	186	Wide	20	25				
Di	222	Wide	152	Wide	20	25				
Mono	188	Wide	152	Wide	20	25				
Acenaphtene D10	164	Wide	160	Wide	20	50				
Acenaphtene D10	164	Wide	82	Wide	20	50				

GC-MS/MS Conditions MMI Inlet (He) Injection Volume: 1 µL Mode: splitless injection Injector split/splitless: 250 °C

Column #1 HP5MSUI (30 m x 250 µm x 0.25 µm) Constant Flow: 0.72 mL/min

Oven Program: 70 °C for 1.5 min 16 °C/min to 200 °C for 1.5 min

MS Transfer Line: 280 °C

El Mode, Source: 280 °C

Run Time: 10.125 min

Results and Discussion

Analytical Method

A Multi point calibration curve was used for unknown's analysis and quantification. The PCB Aroclor calibration concentrations are as follows: 5ng/ml, 10ng/ml, 20ng/ml, 40ng/ml, 50ng/ml

A single time segment was used to monitor the Mono through Nona transitions.

For Mass Quantification the Relative Response Factor (RRF) method was used to determine the amount of each Aroclor present in the sample. Mass quantification was on the sum of all relevant transitions for the particular Aroclor

Quantification is based on the following:

(Formula based on injection and quantification of a known mass of Internal Standard (IS) and a calibration standard containing individual Aroclors of interest, an RRF was calculated for each Aroclor.

All individual Aroclors were then combined into a single calibration curve Table which is used in the analysis of unknowns) the assumption used is that the RRF stays the same between the calibration standard and sample. **Example RRF calculations are as follows:**

From the calibration standard data:

RRF Aroclor 1260 = (mass 1260 in calibration)standard/area 1260 in calibration standard) /(mass IS in calibration standard/area IS in calibration standard) From the sample, data rearranging the RRF equation to solve for Aroclor mass and plugging in the RRF calculated above: Mass Aroclor 1260 = (RRF Aroclor 1260)x(areaAroclor1260 in sample)x(mass IS in sample/area IS insample



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		8	Name	Data File	Туре	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	M	Calc. Conc.	Accuracy	Ratio	MI	Ratio	MI
•	0		1016 ICAL 0.4 ppm 2012407	1016 ICAL CS5 2012407.D	Cal	1016-5	2/2/2012 9:13 AM		6.278	6429579		0.6423		61.9		26.9	
			1016 ICAL 0.2 ppm 2012406	1016 ICAL CS4 2012406.D	Cal	1016-4	2/2/2012 9:29 AM		6.279	2718447		0.2734		64.0		25.8	
	0		1016 ICAL 0.1 ppm 2012405	1016 ICAL CS3 2012405.D	Cal	1016-3	2/2/2012 9:45 AM		6.278	1296080		0.1320		63.3		25.0	
			1016 ICAL 0.05 ppm 2012404	1016 ICAL CS2 2012404.D	Cal	1016-2	2/2/2012 10:01 AM		6.279	609491		0.0638		64.1		25.8	
	9		1016 ICAL 0.025 ppm 2012403	1016 ICAL CS1 2012403.D	Cal	1016-1	2/2/2012 10:18 AM		6.278	275566		0.0306		65.3		24.7	
	9	٣	1221 ICAL 0.4 ppm 2012412	1221 ICAL CS5 2012412.D	Cal	1221-5	2/2/2012 10:34 AM		6.279	3655919		0.3666		1820.1		7.5	
		٣	1221 ICAL 0.2 ppm 2012411	1221 ICAL CS4 2012411.D	Cal	1221-4	2/2/2012 10:50 AM		6.278	1748234		0.1770		1836.7		8.5	
	9	٣	1221 ICAL 0.1 ppm 2012410	1221 ICAL CS3 2012410.D	Cal	1221-3	2/2/2012 11:06 AM		6.279	777		0.0033		694.6		34.0	
		٣	1221 ICAL 0.05 ppm 2012409	1221 ICAL CS2 2012409.D	Cal	1221-2	2/2/2012 11:23 AM		6.278	416708		0.0446		1928.5		8.9	
	0	٣	1221 ICAL 0.025 ppm 2012408	1221 ICAL CS1 2012408.D	Cal	1221-1	2/2/2012 11:39 AM		6.279	199670		0.0230		1801.7		10.7	
	0	٣	1232 ICAL 0.4 ppm 2012417	1232 ICAL CS5 2012417.D	Cal	1232-5	2/2/2012 11:55 AM		6.278	3611334		0.3621		235.0		20.0	
	0	٣	1232 ICAL 0.2 ppm 2012416	1232 ICAL CS4 2012416.D	Cal	1232-4	2/2/2012 12:11 PM		6.279	1608051		0.1630		230.3		21.3	
	0	٣	1232 ICAL 0.1 ppm 2012415	1232 ICAL CS3 2012415.D	Cal	1232-3	2/2/2012 12:28 PM		6.278	696772		0.0725		213.8		21.0	
	0	٣	1232 ICAL 0.05 ppm 2012414	1232 ICAL CS2 2012414.D	Cal	1232-2	2/2/2012 12:44 PM		6.279	360004		0.0390		221.3		20.0	
	0	٣	1232 ICAL 0.025 ppm 2012413	1232 ICAL CS1 2012413.D	Cal	1232-1	2/2/2012 1:00 PM		6.278	164115		0.0195		245.4		22.8	
	0		1242 ICAL 0.4 ppm 2012422	1242 ICAL CS5 2012422.D	Cal	1242-5	2/2/2012 1:16 PM	0.4000	6.279	3997882		0.4006	100.1	65.4		25.8	
	0		1242 ICAL 0.2 ppm 2012421	1242 ICAL CS4 2012421.D	Cal	1242-4	2/2/2012 1:32 PM	0.2000	6.278	1982036		0.2002	100.1	67.3		25.2	
	0		1242 ICAL 0.1 ppm 2012420	1242 ICAL CS3 2012420.D	Cal	1242-3	2/2/2012 1:49 PM	0.1000	6.279	935452		0.0962	96.2	68.7		24.5	
	0		1242 ICAL 0.05 ppm 2012419	1242 ICAL CS2 2012419.D	Cal	1242-2	2/2/2012 2:05 PM	0.0500	6.278	486831		0.0516	103.2	69.6		25.1	
	9		1242 ICAL 0.025 ppm 2012418	1242 ICAL CS1 2012418.D	Cal	1242-1	2/2/2012 2:21 PM	0.0250	6.279	234187		0.0265	105.9	69.1		23.0	
		٣	1248 ICAL 0.4 ppm 2012606	1248 ICAL CS5 2012606.D	Cal	1248-5	2/2/2012 2:37 PM		6.278	2675539		0.2691		21.8		82.7	
		٣	1248 ICAL 0.2 ppm 201205	1248 ICAL CS4 201205.D	Cal	1248-4	2/2/2012 2:54 PM		6.279	1169273		0.1194		21.8		80.3	
		٣	1248 ICAL 0.1 ppm 2012604	1248 ICAL CS3 2012604.D	Cal	1248-3	2/2/2012 3:10 PM		6.278	573827		0.0602		22.2		78.4	
		٣	1248 ICAL 0.05 ppm 2012603	1248 ICAL CS2 2012603.D	Cal	1248-2	2/2/2012 3:26 PM		6.279	278526		0.0309		22.5		79.5	
		٣	1248 ICAL 0.025 ppm 2012602	1248 ICAL CS1 2012602.D	Cal	1248-1	2/2/2012 3:42 PM		6.278	159913		0.0191		21.4		77.9	
		٣	1254 ICAL 0.4 ppm 2012611	1254 ICAL CS5 2012611.D	Cal	1254-5	2/2/2012 3:58 PM		6.279	352363		0.0382		40.8		1368.4	
		٣	1254 ICAL 0.2 ppm 2012610	1254 ICAL CS4 2012610.D	Cal	1254-4	2/2/2012 4:15 PM		6.278	168893		0.0200		42.4		1337.3	
	0	٣	1254 ICAL 0.1 ppm 2012609	1254 ICAL CS3 2012609.D	Cal	1254-3	2/2/2012 4:31 PM		6.279	100684		0.0132		40.2		1290.4	
		٣	1254 ICAL 0.05 ppm 2012608	1254 ICAL CS2 2012608.D	Cal	1254-2	2/2/2012 4:47 PM		6.278	46594		0.0078		54.8		1283.9	
	0	٣	1254 ICAL 0.025 ppm 2012607	1254 ICAL CS1 2012607.D	Cal	1254-1	2/2/2012 5:03 PM		6.279	22379		0.0054		58.2		1449.8	
		٣	1260 ICAL 0.4 ppm 2012616	1260 ICAL CS5 2012616.D	Cal	1260-5	2/2/2012 5:19 PM		6.278	47942		0.0080		79.9		72.4	
		٣	1260 ICAL 0.2 ppm 2012615	1260 ICAL CS4 2012615.D	Cal	1260-4	2/2/2012 5:36 PM		6.279	22268		0.0054		79.3		72.4	

9 unique Aroclor standards were used for acquiring the calibration curves. When analyzing unknown samples there is often co-eluting Aroclors. In these instances a subset of the Aroclors total areas is used to isolate and identify the Aroclor from other Aroclors.

In these instances it is necessary to use both the Quantitative and Qualitative program in Mass Hunter to make the appropriate determination as to what coelution's exist and the effect that it has on the concentration of a particular Aroclor.

Based on previous work by Dr. Frame⁽¹⁾ the following table shows the predicted ratios of 5 individual Aroclors.

Table 3. Typical					
PCB Homologue					
wt) of Five PCB					
Aroclors PCB	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
Homologue	(%)	(%)	(96)	(96)	(%)
Mono-CB	0.7	0.8	0	0	0
DI-CB	17.5	15.0	0.4	0.2	0.1
Tri-CB	54.7	44.9	22.0	1.3	0.2
Tetra-CB	26.6	32.6	56.6	16.4	0.5
Penta-CB	0.5	6.4	18.6	53.0	8.6
Hexa-CB	0	0.3	2.0	26.8	43.4
Hepta-CB	0	0	0.6	2.7	38.5
Octa-CB	0	0	0	0	8.3
Nona-CB	0	•	0	0	0.7
Deca-CB	0	0	0	0	0
	40.00	64.70	0.70	45.72	10.61





Results and Discussion



PCB Aroclors are persistent environmental pollutants. In the United States and other countries around the world. PCBs were widely used as dielectric fluids in transformers and capacitors and also used as coolants. In 1979, PCB production was banned in the late twentieth century.

The work presented herein demonstrates the applicability of GC tandem mass spectrometry to monitor exposure to PCB Aroclors in matrix. The same methodology is also applied to matrices such as gas-phase air, particulate phase air, sediment and sediment pore water. Human health studies concluded that PCB Aroclors are probable carcinogens and exposure can also result in deleterious effects on the immune. reproductive and endocrine systems.

Traditionally the analysis for PCB Aroclors is done by GC Electron Capture Detector (ECD) methodology. Historically a traditional single stage GCMS system has lacked the ability to achieve the detection limits of an ECD due to matrix interferences.

In this study we employed the use of a GC-tandem mass spectrometry (GC-MS/MS) The GC-MS/MS not only achieved but surpassed the required detection limits of the traditional GC ECD detector. In addition to achieving the detection limits the system also offers confirmation of the compound by using the individual Congener groups to positively identify the compounds by utilizing both the GC retention times and the MRM transition for the Aroclor. Comparing the data with that obtained via GC-ECD suggests that GC-MS/MS is an appropriate tool and offers a confirmatory technique. Labs may now expand GC-MS/MS for the analysis of PCB Aroclors in matrix.



Bibliography

1. Frame et al. (1996) has reported on the detailed analyses of the PCB congener distributions present in Aroclors 1016, 1242, 1248, and 1254. Because of variation to the chlorination process during chemical synthesis, no two batches of the same Aroclor had identical PCB congener distributions. In fact, substantial differences in congener profiles between batches of the same Aroclor could lead to significant differences in biological effects (Kodavanti et al., 2001).