

**A Consolidated Method for the Analysis of
Organochlorine Pesticides (OCP) and
Polychlorinated Biphenyls (PCB) in Environmental
Samples
using Automated SPE and GC-MS/MS**

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Pacific Rim Laboratories, Promochrom, ASTM



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1. Comparisons of Methods 608.3 and 625.1
2. Why a new method?
3. Equipment
4. Preliminary Experiments and Results



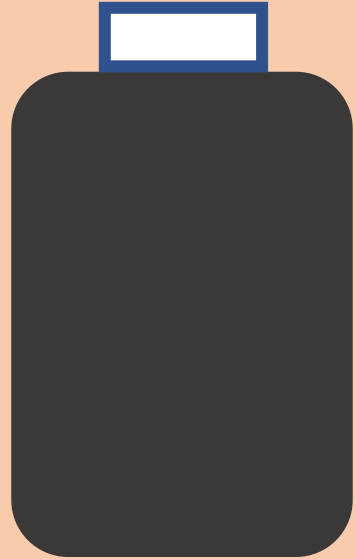
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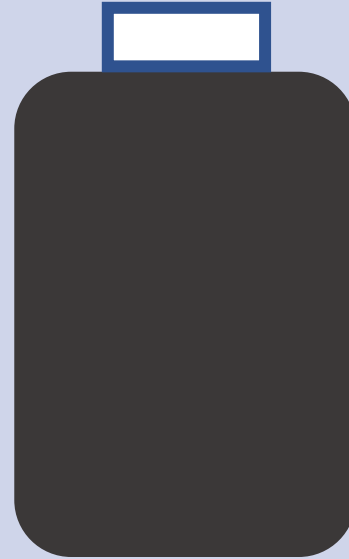
Comparison – Samples

608.3



- Industrial discharges and other environmental samples

625.1



- Municipal and industrial discharges



Comparison – Extraction

608.3

- pH adjustment, Sequential extraction in DCM
- SPE can be used (C18)

625.1

- **Basify** sample, extract into DCM (“base/neutrals”)
- **Acidify** sample, extract into DCM (“acid/neutrals”)



Comparison – Cleanup

608.3

Variety of methods to choose

SPE – C18 phase only

625.1

Variety of methods to choose

SPE – No requirement on phase, stringent QC



Comparison – GC and Detection

608.3

GC/HSD

Halogen-specific
detector (HSD)

625.1

GC/MS

Mass Spectrometer



Comparison – Analytes

608.3

- 86 analytes = 18 pesticides + 68 additional compounds
- **PCB (Aroclors) as additional compounds**

625.1

- 363 analytes = 38 base neutrals + 11 acid neutrals + 314 additional compounds
- **PCB, OCP = Additional compounds (Aroclors)**



Comparison – UPDATES

608.3 (2016)

- PCB = “additional analytes”
- 625.1 GC/MS for qualitative confirmation
- 1668C for PCB
- 1699 for OCP

625.1 (2016)

- OCP, PCB = “additional analytes”
- 608.3 for OCP & PCB
- 1668C for PCB
- 1699 for OCP



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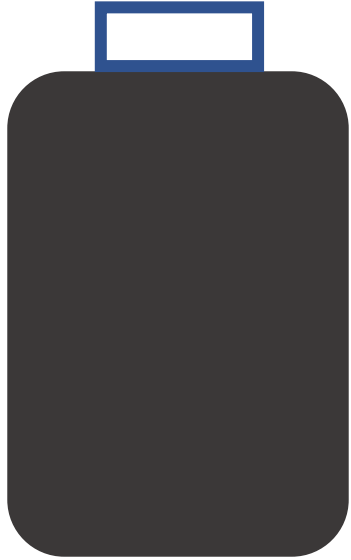
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Why a new Method?

- **Consolidation**
- Understanding **limitations**
- Changes in **analyte scope**
- Changes in **technology**





608.3

EXTRACTION

- DCM
- SPE can be used (C18)

608.3

625.1

CLEANUP

- Variety of methods
- SPE can be used (C18)

625.1

DETECTION

- GC/MS

608.3

ANALYTES

- OCP and PCB (Aroclors)





608.3 (Auto)

EXTRACTION

- DCM
- SPE can be used (C18)

608.3

625.1

CLEANUP

- Variety of methods
- SPE can be used (C18)

625.1

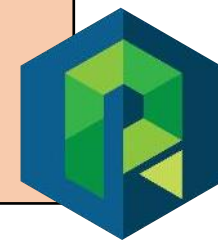
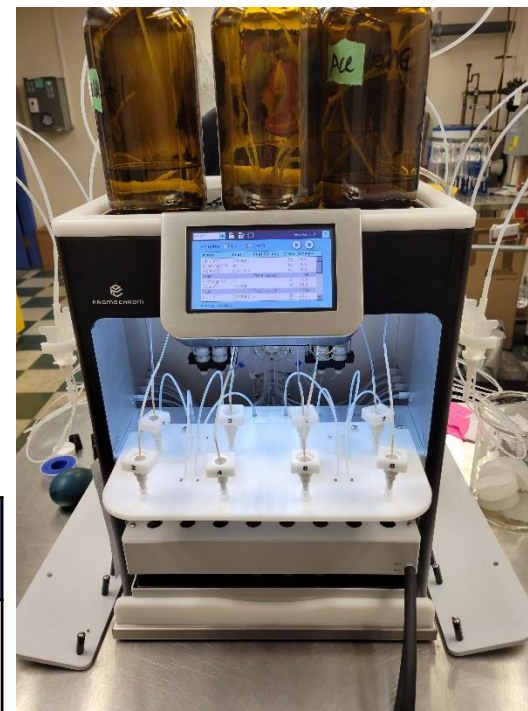
DETECTION

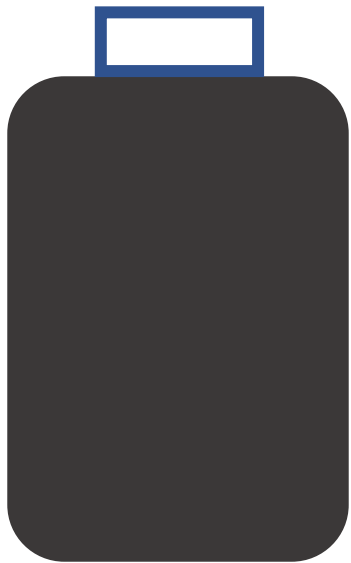
- GC/MS

608.3

ANALYTES

- OCP and PCB





608.3 (Auto)

EXTRACTION

- DCM
- SPE can be used (C18)

608.3

625.1

CLEANUP

- Variety of methods
- SPE can be used (C18)

625.1

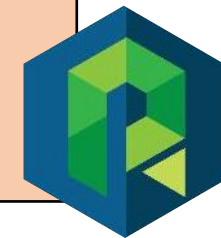
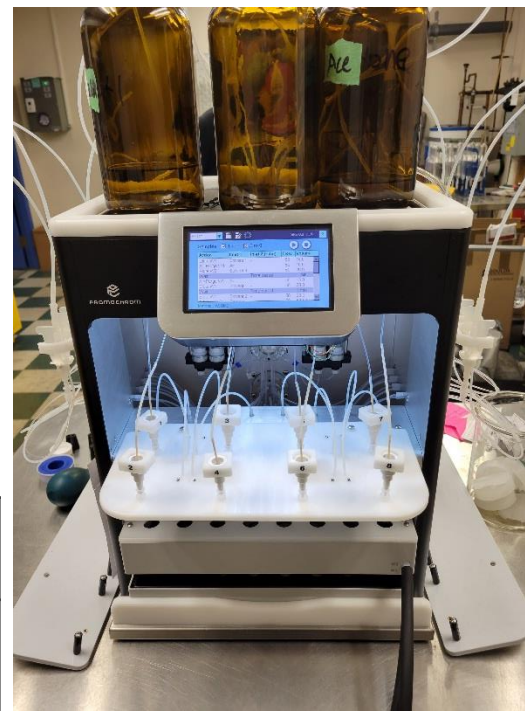
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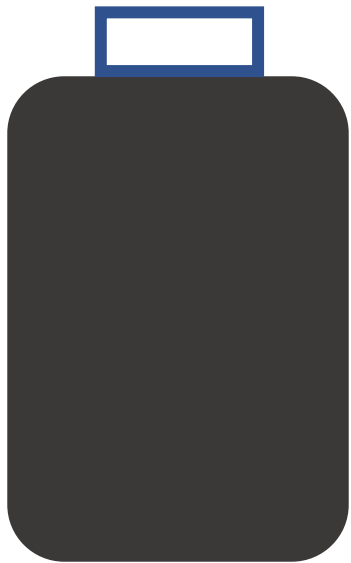
- GC/MS

608.3

ANALYTES

- OCP and PCB

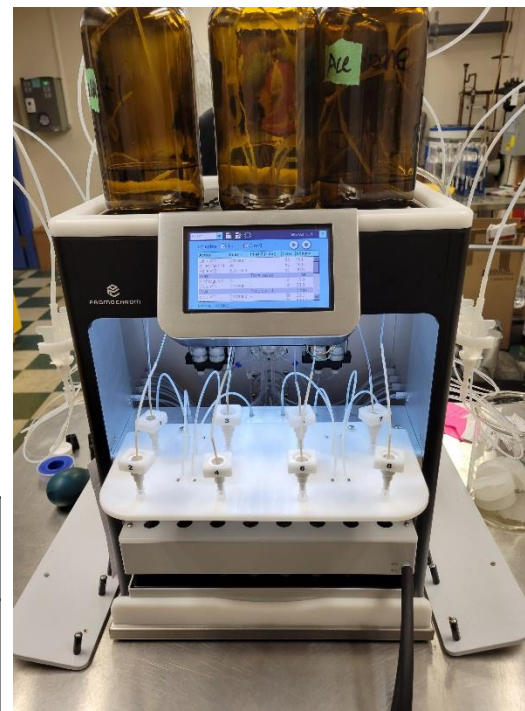




608.3 (Auto)

EXTRACTION

- DCM
- SPE can be used (C18)



608.3

625.1

CLEANUP

- Variety of methods
- SPE can be used (C18)

GC/MS/MS

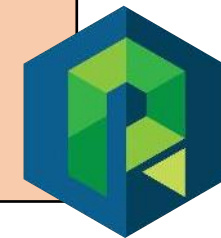
DETECTION

- GC/MS/MS

608.3

ANALYTES

- OCP and PCB

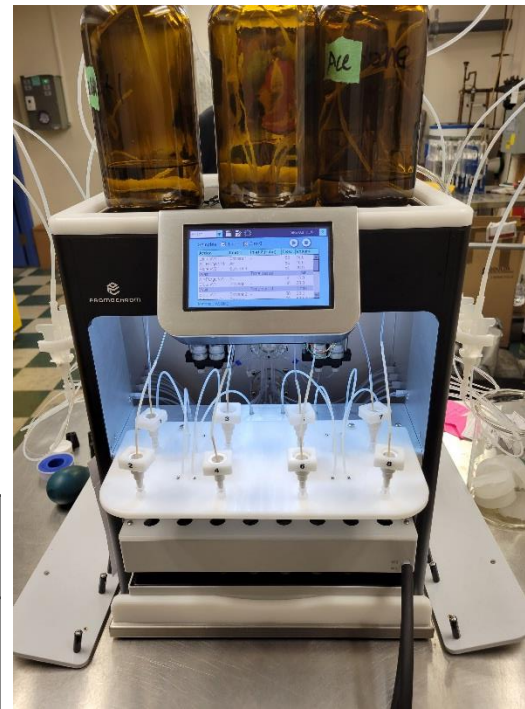




608.3 (Auto)

EXTRACTION

- DCM
- SPE can be used (C18)



608.3

625.1

CLEANUP

- Variety of methods
- SPE can be used (C18)

GC/MS/MS

DETECTION

- GC/MS/MS

608.3

1668C

ANALYTES

- OCP, PCB congeners (GC/MS/MS and HRMS)



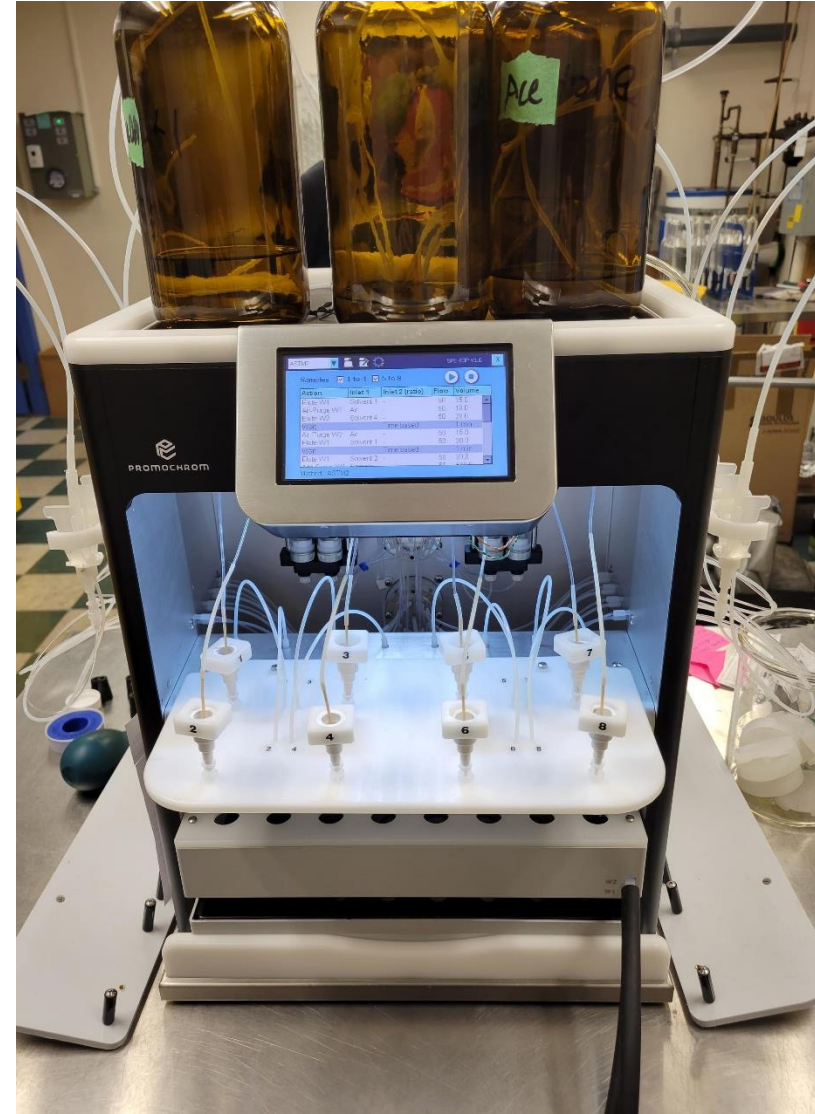
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Automated solid-phase extraction

- “SPE-03” from Promochrom
- Disk cartridges (C18)



Automated Solid-Phase Extraction

- Variety of disk sorbents and formats (C18)



GC/MS/MS and GC/HRMS



GC/MS/MS

and

GC/HRMS



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Method Development Experiments

- Automated Solid-Phase Extraction
 - Drying times
 - Sorbent



SPE Method

- Precondition with Methanol, DCM, Methanol, Water
- Add Sample, N₂ dry
- Collect with acetone, rinse DCM

	Command	Solvent		Speed (mL/min)	Total Volume (mL)
1	Elute W1	Methanol	-	50	15
2	Air-Purge W1	Air	-	50	10
3	Elute W2	DCM	-	50	20
4	Wait			Time based	1 min
5	Air-Purge W2	Air	-	50	15
6	Elute W1	Methanol	-	50	20
7	Wait			Time based	1 min
8	Elute W1	Water	-	50	20
9	Add Samp W1	Sample	-	50	540
10	Air-Purge W1	Air	-	50	10
11	Wait			Manual resume	-
12	N2 Cartridge			Time based	10 min
13	Collect 2	Acetone	-	60	5
14	Rinse	DCM	-	65	20
15	Collect 2	Sample	-	60	10
16	Wait			Time based	1 min
17	Collect 2	Sample	-	60	10
18	Rinse	DCM	-	65	10
19	Air-Purge R	Air	-	65	3
20	Collect 2	Sample	-	60	10
21	Wait			Time based	1 min
22	Collect 2	Sample	-	60	20



Nitrogen drying times experiment – OCP

- Internal Standards only
- Timed nitrogen dry after all sample has gone through SPE disc
- Sodium Sulfate to dry sample

Int Stds	Dry 3 min		Dry 1 min		No Dry	
ALPHA-BHC 13C	41	31	63	63	84	76
BETA-BHC 13C	52	41	77	77	109	95
GAMMA-BHC 13C	46	38	62	55	78	63
DELTA-BHC 13C	51	44	69	61	89	71
HCB 13C	18	16	35	34	33	32
HEPTACHLOR 13C	34	30	63	68	77	67
ALDRIN 13C	53	56	61	73	57	66
CIS-CHLORDANE 13C	102	93	96	144	147	122
TRANS-CHLORDANE 13C	99	100	103	128	129	132
OXYCHLORDANE 13C	104	88	96	110	119	117
CIS-NONACHLOR 13C	78	82	73	77	85	72
TRANS-NONACHLOR 13C	95	87	88	90	99	93
O,P DDE 13C	96	91	87	96	105	97
P,P DDE 13C	83	82	76	81	90	79
O,P DDD 13C	88	78	80	68	78	75
P,P DDD 13C	71	87	72	63	62	43
O,P DDT 13C	69	76	51	123	149	114
P,P DDT 13C	44	92	45	99	102	53
DIELDRIN 13C	94	88	81	87	100	84
ENDRIN 13C	101	88	79	86	90	83
MIREX 13C	57	82	61	66	74	
ENDOSULPHAN 1	109	86	92	95	108	
ENDOSULPHAN 11	102	90	81	85	98	
ENDOSULPHAN SULPHATE	91	89	75	78	95	



Nitrogen drying times experiment – PCB (HRMS)

C13 STD	Dry 3 min		Dry 1 min		No Dry	
PCB 1 13C12 STD	52	50	56	61	56	63
PCB 3 13C12 STD	75	61	72	75	75	74
PCB 4 13C12 STD	54	43	51	52	53	52
PCB 15 13C12 STD	67	56	66	68	70	68
PCB 19 13C12 STD	60	49	57	57	61	54
PCB 37 13C12 STD	83	78	85	79	89	93
PCB 54 13C12 STD	46	42	45	50	51	46
PCB 81 13C12 STD	82	80	74	88	94	78
PCB 77 13C12 STD	85	85	79	85	89	70
PCB 104 13C12 STD	49	45	50	49	49	50
PCB 123 13C12 STD	66	66	66	74	81	79
PCB 118 13C12 STD	64	65	64	71	79	75
PCB 114 13C12 STD	66	68	65	71	78	75
PCB 105 13C12 STD	68	71	69	75	84	73
PCB 126 13C12 STD	79	89	86	84	93	80
PCB 155 13C12 STD	47	44	48	51	52	52
PCB 167 13C12 STD	66	73	69	70	73	63
PCB 156 13C12 STD	69	79	77	71	77	65
PCB 157 13C12 STD	71	77	71	67	72	62
PCB 169 13C12 STD	71	85	77	65	73	58
PCB 188 13C12 STD	38	42	41	43	49	50
PCB 189 13C12 STD	61	73	68	76	81	75
PCB 202 13C12 STD	45	46	45	47	48	44
PCB 205 13C12 STD	52	61	57	61	64	58
PCB 208 13C12 STD	46	55	51	61	63	59
PCB 206 13C12 STD	47	59	51	54	59	53
PCB 209 13C12 STD	41	51	43	46	52	44



Sorbent type experiment

- OCP on GC/MS/MS
- Three disc sorbents were tested
- All three sorbents demonstrated acceptable performance
- Promochrom disc was smaller total mass and size, performing very well (with 3 minutes nitrogen drying)

Int Stds	Atlantic	Empore	Promochrom
ALPHA-BHC 13C	76	80	72
BETA-BHC 13C	95	105	97
GAMMA-BHC 13C	63	87	80
DELTA-BHC 13C	71	101	91
HCB 13C	32	36	23
HEPTACHLOR 13C	67	80	58
ALDRIN 13C	66	55	38
CIS-CHLORDANE 13C	122	119	109
TRANS-CHLORDANE 13C	132	127	119
OXYCHLORDANE 13C	117	104	95
CIS-NONACHLOR 13C	72	87	79
TRANS-NONACHLOR 13C	93	93	87
O,P DDE 13C	97	98	88
P,P DDE 13C	79	90	79
O,P DDD 13C	75	71	69
P,P DDD 13C	43	85	85
O,P DDT 13C	114	110	74
P,P DDT 13C	53	149	123
DIELDRIN 13C	84	102	95
ENDRIN 13C	83	98	95
MIREX 13C	60	87	71
ENDOSULPHAN 1	103	100	96
ENDOSULPHAN 11	84	95	89
ENDOSULPHAN SULPHATE	84	103	92



Sorbent type experiment

- PCB on GC/HRMS
- Three disc sorbents were tested
- All three sorbents demonstrated acceptable performance, however one disc had unacceptably high recoveries
- Promochrom disc performed very well

Int Std	Atlantic	Empore	Promochrom
PCB 1 13C12 STD	63	53	63
PCB 3 13C12 STD	74	75	74
PCB 4 13C12 STD	52	53	52
PCB 15 13C12 STD	68	76	68
PCB 19 13C12 STD	54	66	54
PCB 37 13C12 STD	93	105	93
PCB 54 13C12 STD	46	57	46
PCB 81 13C12 STD	78	89	78
PCB 77 13C12 STD	70	89	70
PCB 104 13C12 STD	50	58	50
PCB 123 13C12 STD	79	101	79
PCB 118 13C12 STD	75	24	75
PCB 114 13C12 STD	75	83	75
PCB 105 13C12 STD	73	96	73
PCB 126 13C12 STD	80	129	80
PCB 155 13C12 STD	52	59	52
PCB 167 13C12 STD	63	131	63
PCB 156 13C12 STD	65	149	65
PCB 157 13C12 STD	62	159	62
PCB 169 13C12 STD	58	505	58
PCB 188 13C12 STD	50	0	50
PCB 189 13C12 STD	75	158	75
PCB 202 13C12 STD	44	94	44
PCB 205 13C12 STD	58	69	58
PCB 208 13C12 STD	59	33	59
PCB 206 13C12 STD	53	249	53
PCB 209 13C12 STD	44	76	44



Summary of Progress

- Automated SPE method implemented
- Drying time appears to affect OCP more than PCB
- Several SPE discs tried – Adequate for OCP, not all adequate for PCB
- Same extract vial:
 - GC/MS/MS for OCP
 - GC/HRMS for PCB



Acknowledgements



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ISO 17025 Accredited | Method Development
POPs | Ultra-trace

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