

# Analysis of Semi-Volatile Organic Compounds by Shimadzu GCMSMS with Reduced Methylene Chloride Usage



ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 751 [

EPA-HQ-OPPT-2020-0465; FRL-8155-01-  
OCSPP]

RIN 2070-AK70

Methylene Chloride; Regulation Under the Toxic  
Substances Control Act (TSCA)

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

## Summary:

- **Applies to approximately 47 entities**
  - **Includes NAICS Code 541380 Testing Laboratories and Services**
- **Finalized an ECEL under TSCA section 6(a) of 2 ppm (8 mg/m<sup>3</sup>) as an 8-hour TWA**
- **Finalized an ECEL action level at half of the 8-hour ECEL, or 1 ppm (4 mg/m<sup>3</sup>) as an 8-hour TWA.**

**Air Conc Condition Initial Monitoring**

**Periodic Monitoring Requirement**

< ECEL action level < EPA STEL.

ECEL and EPA STEL every 5 yrs

< ECEL action level and > EPA STEL.

ECEL every 5 yrs,  
EPA STEL every 3 months

> ECEL action level < ECEL; and < EPA STEL.

ECEL every 6 months

> ECEL action level and < ECEL; and > EPA STEL

ECEL every 6 months  
EPA STEL every 3 months

>ECEL

ECEL every 3 months  
EPA STEL every 3 months

# Current Laboratory Methylene Chloride Concerns

Primary Extraction Solvent for EPA methods for Semivolatile Organics, Chlorinated and Organophosphorus Pesticides, Total Petroleum Hydrocarbons, Herbicides, Disinfection Byproducts (i.e., HAA's)

Methods generally written for large volume extractions of 100-1000 ml of sample using up to 360 ml Methylene Chloride or greater

# Current Laboratory Methylene Chloride Concerns

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**Typical AVG Laboratory exposure levels at 2 - 4 X ECEL (2 ppm) with full volume extraction**

**With minimal 100 ml sample volume extraction, AVG Laboratory exposure exceeds ECEL Action Level (1 ppm)**

# Potential Laboratory Methylene Chloride Reduction Remedies

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- 1. Use of method minimum sample volume**
  - a. For full Semivolatile Organic extraction a reduction from 360 ml to 36 ml**
  - b. Requires sequential extraction processes**
- 2. Combination of multiple historical extractions into a single extraction using method minimum sample volume of 100 ml (SW846 3510C Reduced Volume (RV))**
  - a. Combination of Organochlorine Pesticides and Semivolatile Organics into a single extraction**
  - b. Reduces solvent usage from maximum 540 ml to 36 ml using sequential extractions**

# Study Design

## Target Analyte List

- 49 Acid and Base Neutral Extractable Compounds listed in 40 CFR 136 Method 625.1 Tables 1 and 2
- 9 additional analytes from 40 CFR 136 Method 625.1 Table 3
- All analytes from 40 CFR 136 Method 608.3 Table 1
- Toxaphene

Table 2--Acid Extractables

Analyte	CAS Registry
4-Chloro-3-methylphenol	59-50-7
2-Chlorophenol	95-57-8
2,4-Dichlorophenol	120-83-2
2,4-Dimethylphenol	105-67-9
2,4-Dinitrophenol	51-28-5
2-Methyl-4,6-dinitrophenol	534-52-1
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
Pentachlorophenol 2	87-86-5
Phenol	108-95-2
2,4,6-Trichlorophenol	88-06-2

# Instrument Parameters

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<u>Parameter</u>	<u>Value</u>
MS	Shimadzu GC-2030 TQ
Column	Agilent J&W DB-5ms UI, 30 m, 0.25 mm, 0.25
Inlet	Split/Splitless
Injection volume	2 $\mu$ L
Injection mode	Splitless
Inlet temperature program	280 °C
Oven temperature program	40 °C for 1.5 min; 20 °C/min to 280 °C, 5 °C/min to 320 °C; 1.0 min hold
Carrier gas	Helium
Column flow	1.2 mL/min
Transfer line temperature	300 °C
Quadrupole temperature	150 °C
Source temperature	230 °C
TQ mode	dMRM

## Initial Calibration Summary

### • Calibration Range:

- Base Neutral / Acid Extractable compounds 0.5 ug/L to 100 ug/L
  - 2 analytes calibrated linear regression with  $r^2 > 0.99$ 
    - Bis-2-ethylhexyl phthalate and 2,6-Dinitrotoluene
  - 5 analytes calibrated using quadratic fit with  $r^2 > 0.99$ 
    - 2,4-Dinitrophenol, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, Pentachlorophenol, and Benzidine
  - 57 analytes calibrated using average RF with % RSD  $\leq 35\%$
- Organochlorine Pesticide compounds 0.025 ug/L to 10.0 ug/L
  - All analytes calibrated using average RF with % RSD  $\leq 35\%$

Name	RF %RSD
N-Nitrosodimethylamine	7.820749
2-Fluorophenol	5.749316
Phenol-d6	12.994588
Phenol	20.703211
Bis(2-chloroethyl)ether	7.807961
2-Chlorophenol	7.353414
N-Nitrosodi-n-propylamine	8.478713
4-Nitrophenol	57.128463

# MDL Summary - Semivolatile Organics SW846 3510C RV

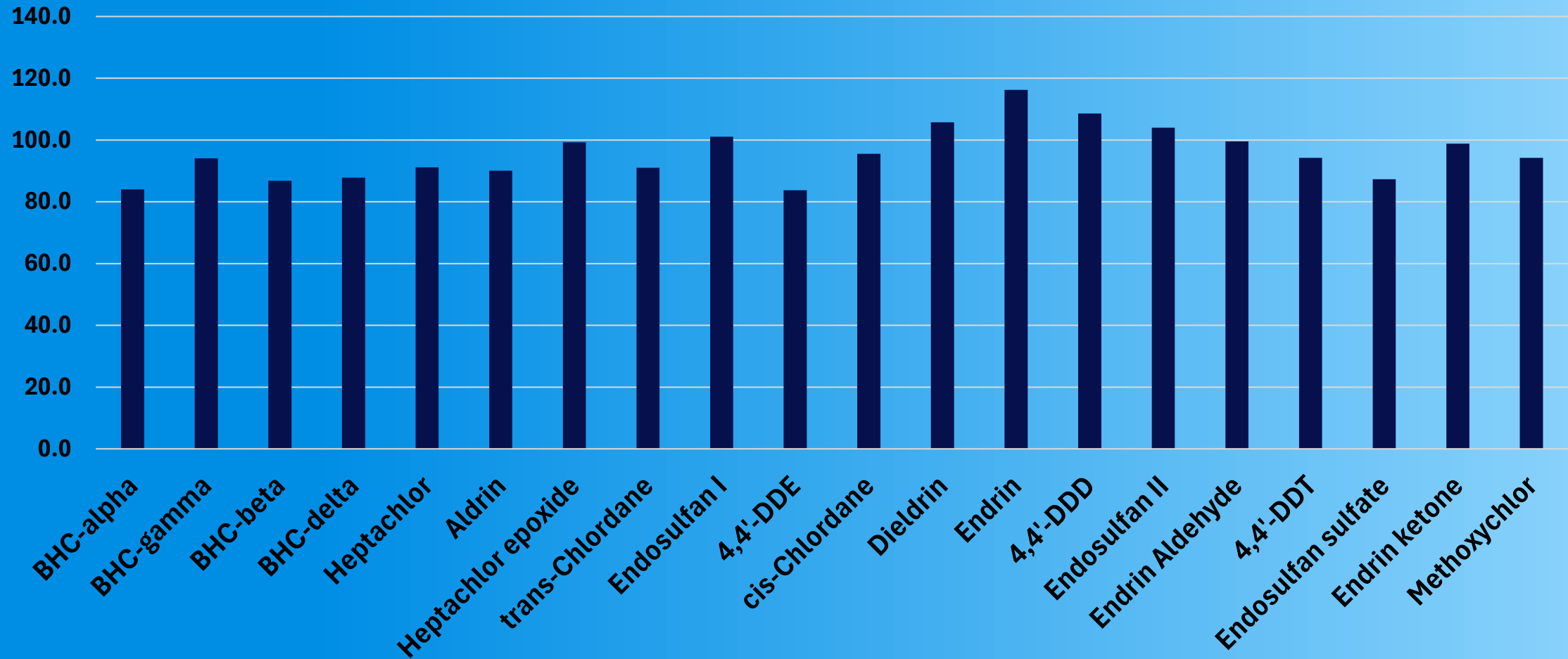
	<b>Conc. PPB</b>	<b>% Ave Rec</b>	<b>LOD ug/L</b>	<b>MDL ug/L</b>
Compound Name				
Phenol	0.1	86.7	0.5	0.0701
4-Chloro-3-methylphenol	0.1	60.0	0.5	0.0567
Hexachlorocyclopentadiene	0.1	58.6	0.5	0.0703
2,4,6-Trichlorophenol	0.1	61.8	0.5	0.0415
2,6-Dinitrotoluene	0.1	117.9	0.5	0.1530
Benzo[a]anthracene	0.1	102.0	0.5	0.0215
Chrysene	0.1	96.4	0.5	0.0267
Benzo(b)fluoranthene	0.1	87.9	0.5	0.0161
Benzo(k)fluoranthene	0.1	90.7	0.5	0.0114
Benzo(a)pyrene	0.1	79.2	0.5	0.1104
Indeno(1,2,3-cd)pyrene	0.1	104.9	0.5	0.0180
Dibenzo(a,h)anthracene	0.1	90.3	0.5	0.0223
Benzo(g,h,i)pyrene	0.1	98.8	0.5	0.0204

# MDL Summary – Organochlorine Pesticides SW846 3510C RV

	<b>Conc. PPB</b>	<b>% Ave Rec</b>	<b>LOD ug/L</b>	<b>MDL ug/L</b>
Compound Name				
alpha-BHC	0.0100	89.6	0.025	0.0061
Gamma-BHC	0.0100	117.0	0.025	0.0202
beta-BHC	0.0100	88.0	0.025	0.0055
Delta-BHC	0.0100	94.9	0.025	0.0076
Heptachlor	0.0100	98.1	0.025	0.0065
Aldrin	0.0100	108.7	0.025	0.0140
Heptachlor-exo-epoxide	0.0100	111.4	0.025	0.0083
trans-Chlordane	0.0100	93.0	0.025	0.0066
alpha-Endosulfan	0.0100	114.9	0.025	0.0047
p,p'-DDE	0.0100	94.4	0.025	0.0052
cis-Chlordane	0.0100	79.4	0.025	0.0119
Dieldrin	0.0100	117.7	0.025	0.0076
Endrin	0.0100	115.0	0.025	0.0173
p,p'-DDD	0.0100	68.9	0.025	0.0165
beta-Endosulfan	0.0100	281.0	0.025	0.0651
Endrin aldehyde	0.0100	130.7	0.025	0.0309
p,p'-DDT	0.0100	133.1	0.025	0.0163
Endosulfan sulfate	0.0100	110.3	0.025	0.0053
Endrin ketone	0.0100	108.3	0.025	0.0062
Methoxychlor	0.0100	110.0	0.025	0.0047

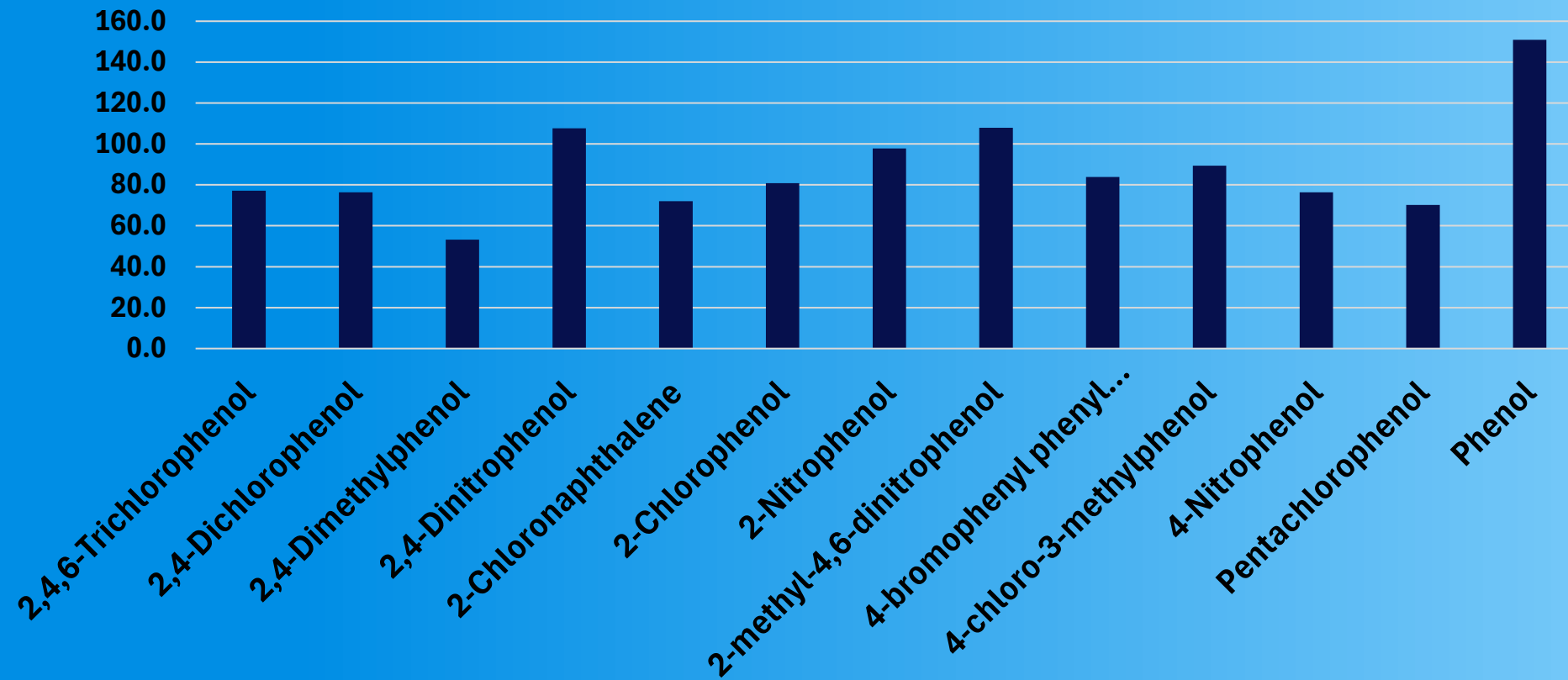
# Target EPA Pesticides by GCMSMS SW846 3510C RV

Precision and Accuracy: AVE % REC 4 Replicates



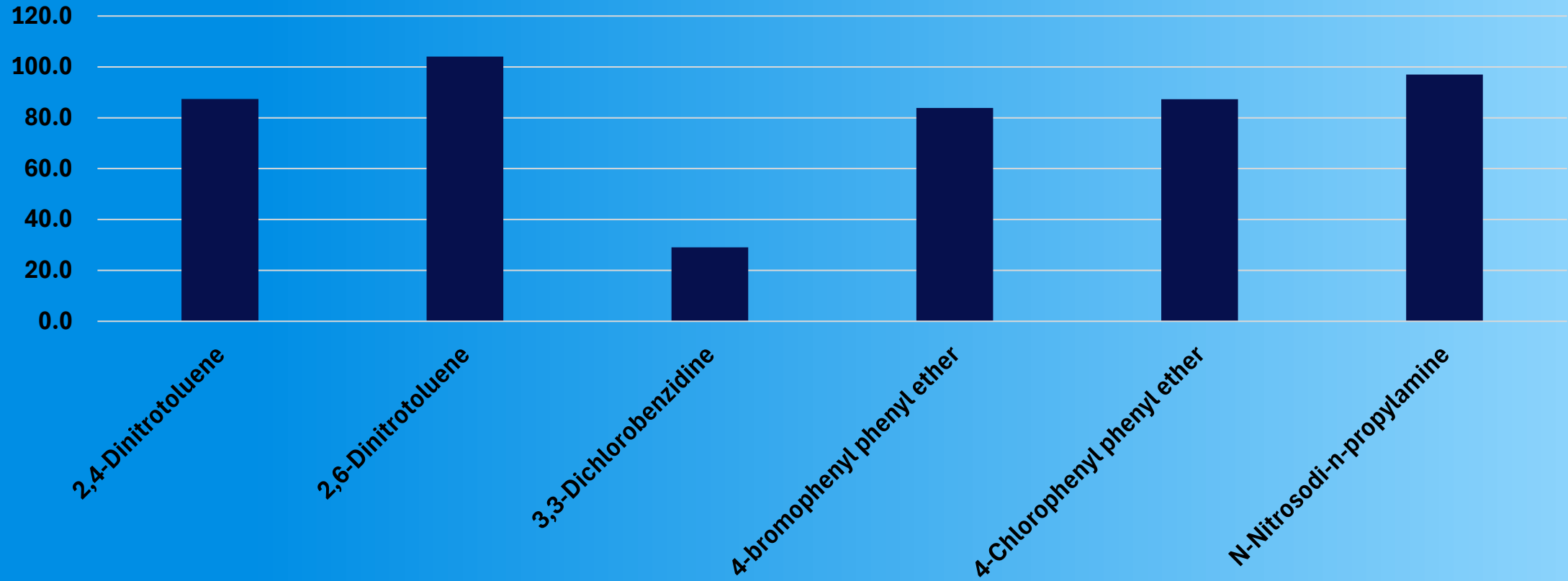
# Chlorinated Phenols by GCMSMS SW846 3510C RV

## Precision and Accuracy: AVE % REC 4 Replicates



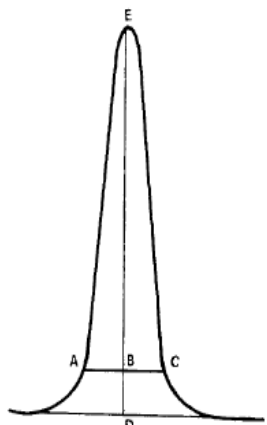
# Precision and Accuracy Study SW846 3510C RV

## Precision and Accuracy: AVE % REC 4 Replicates



# Performance Measurements

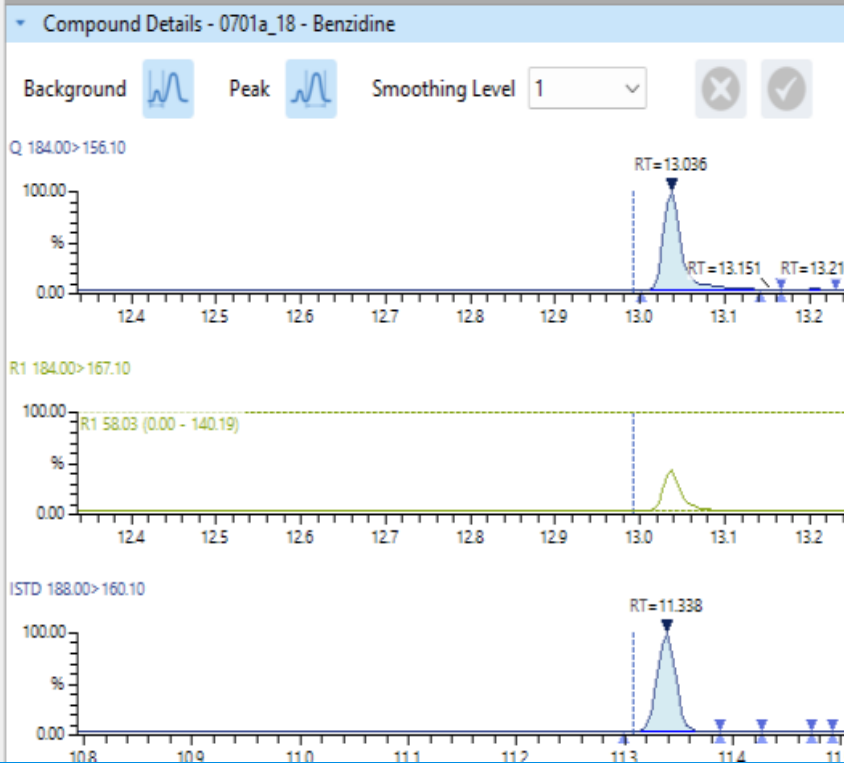
## USEPA Requirements for Peak Tailing



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

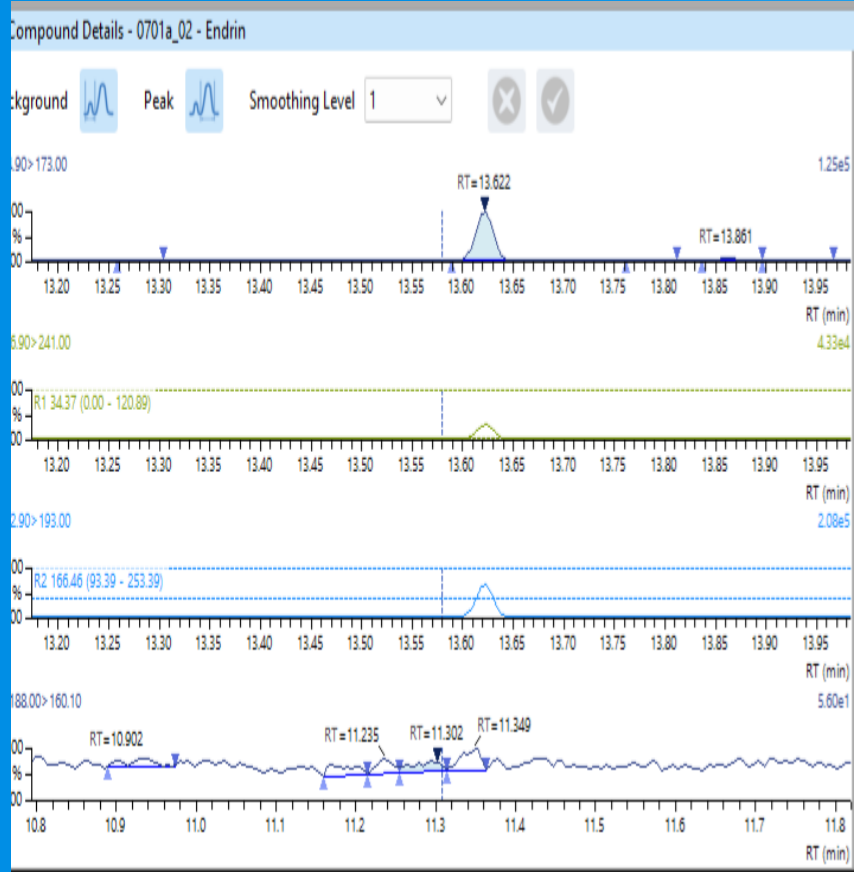
Example calculation: Peak Height = DE = 100 mm  
 10% Peak Height = BD = 10 mm  
 Peak Width at 10% Peak Height = AC = 23 mm  
 AB = 11 mm  
 BC = 12 mm  
 Therefore: Tailing Factor =  $\frac{12}{11} \approx 1.1$

Compound Results - 0701a_18										
#	Name	Comment 1	Tailing F.	RT	Foun...	Area	Conc.	RF %RS...	RF RSE ...	DDT Bkdw
34	2,4-Dinitrotoluene	Table 4	1.404	9.708	9.721	21883	85.4085	15.986549	12.162...	65.2197
35	Diethyl Phthalate	Table 4	1.005	10.020	10.037	63019	115.2635	9.266385	9.266385	65.2197
36	Fluorene	Table 4	1.030	10.147	10.167	37632	89.1105	7.960794	7.960794	65.2197
37	4-Chlorophenyl-phenyl et...	Table 4	1.012	10.135	10.175	89485	87.7381	11.707055	11.707...	65.2197
38	4,6-Dinitro-2-methylphenol	Table 5	1.451	10.207	10.229	9147	91.6907	79.285985	15.279...	65.2197
39	Azobenzene	Table 4 (N...	1.121	10.355	10.371	82626	87.4914	15.399696	15.399...	65.2197
42	4-Bromophenyl phenyl et...	Table 4	1.006	10.745	10.786	52147	87.9288	10.220070	10.220...	65.2197
44	Hexachlorobenzene	Table 4	0.992	10.828	10.855	44011	81.1369	22.168450	21.056...	65.2197
47	Pentachlorophenol	Table 5	1.467	11.076	11.104	42165	435.4691	84.358017	18.573...	65.2197
52	Anthracene	Table 4	1.027	11.330	11.368	59922	84.1490	16.146331	16.146...	65.2197
53	Phenanthrene	Table 4	1.056	11.398	11.432	55119	93.1815	9.353981	9.353981	65.2197
56	Di-n-butyl phthalate	Table 4	0.999	12.073	12.095	141098	114.7331	10.458489	10.458...	65.2197
59	Fluoranthene	Table 4	1.084	12.836	12.859	72122	89.3713	6.726572	6.726572	65.2197
61	Pyrene	Table 4	1.028	13.095	13.142	68616	87.1880	9.101510	9.101510	65.2197
62	<b>Benzidine</b>	Table 4	<b>1.625</b>	12.991	13.036	105692	175.3658	77.127596	19.033...	65.2197
75	Butyl benzyl phthalate	Table 4	0.999	13.969	13.991	58677	89.2642	8.696985	8.696985	65.2197
79	3,3'-Dichlorobenzidine	Table 4	1.203	14.692	14.746	180739	191.2803	14.164296	14.164...	65.2197
80	Benzo[a]anthracene	Table 4	0.000	14.730	14.773	98539	84.4514	13.227483	13.227...	65.2197
83	Chrysene	Table 4	0.000	14.835	14.828	110816	85.3006	14.739181	14.739...	65.2197
84	Bis(2-ethylhexyl) phthalate	Table 4	0.992	14.842	14.858	76981	87.6710	93.532839	7.845166	65.2197
85	Di-n-octyl phthalate	Table 4	1.015	15.944	15.995	131178	84.1470	13.314380	13.314...	65.2197



# Instrument Performance Measurements

## USEPA Requirements for Degradation – Endrin and DDT Breakdown



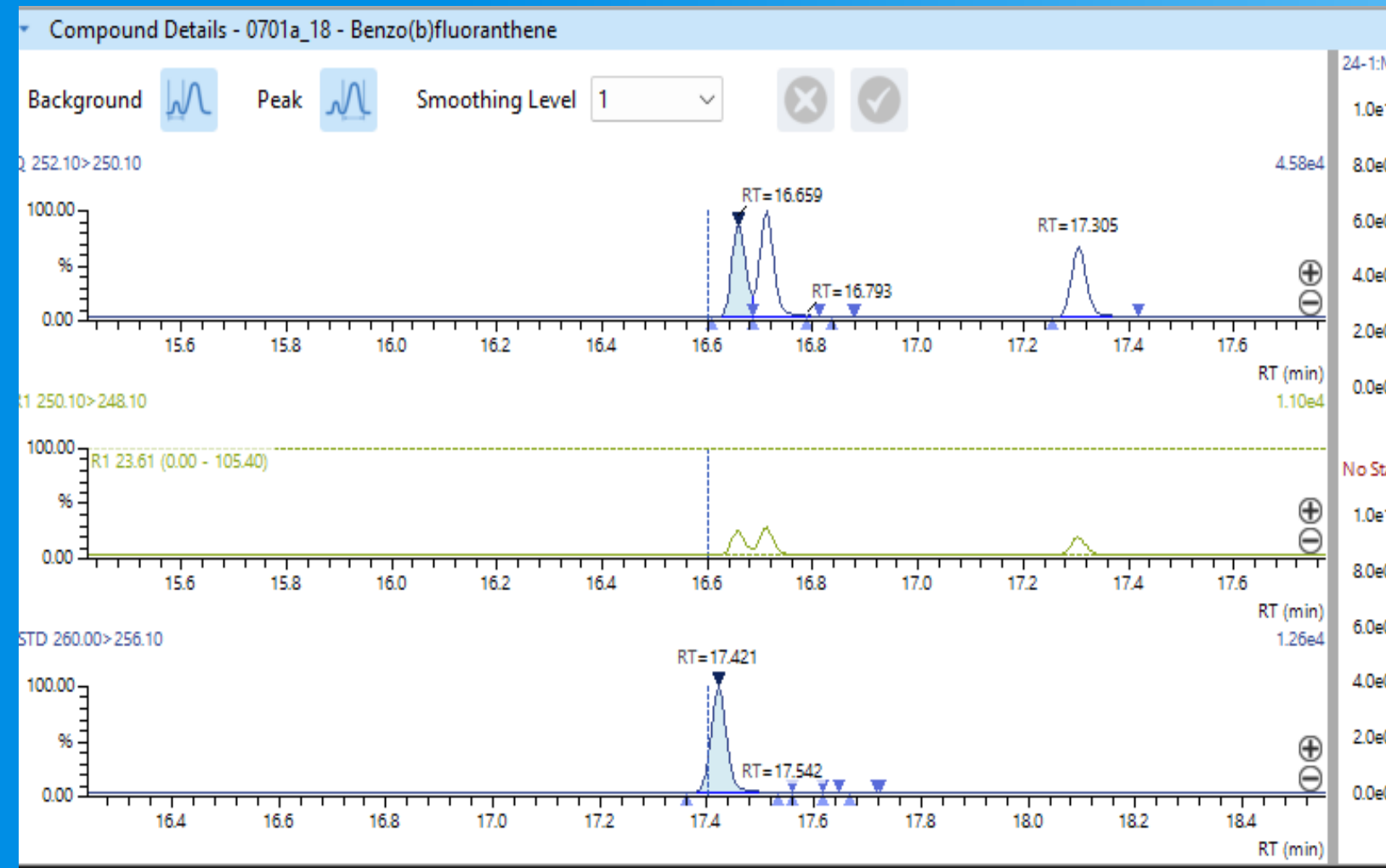
Compound Results - 0701a_02											
#	Name	Comment 1	RT	Foun...	Area	Conc.	RF %RS...	RF RSE ...	DDT Bkdown	Endrin ...	IST
43	alpha-BHC	OCP	10.762	10.553	51	136.7277	11.025821	11.025...	100.00000	4.55709	
46	beta-BHC	OCP	11.130	11.165	61	200.9647	10.191828	10.191...	100.00000	4.55709	
48	Gamma-BHC	OCP	11.016	11.062	42	156.0075	12.515328	12.515...	100.00000	4.55709	
50	Delta-BHC	OCP	11.410	11.455	63	240.6111	8.830364	8.830365	100.00000	4.55709	
55	Heptachlor	OCP	11.932	11.969	194	328.3025	10.433915	10.433...	100.00000	4.55709	
57	Aldrin	OCP	12.324	12.252	227	1490.5731	8.187691	8.187691	100.00000	4.55709	
58	Heptachlor-exo-epoxide	OCP	12.703	12.738	77	474.6109	17.217511	17.217...	100.00000	4.55709	
60	trans-Chlordane	OCP	12.967	13.119	76	550.8641	7.729069	7.729069	100.00000	4.55709	
63	alpha-Endosulfan	OCP	13.117	----	----	----	12.671025	12.671...	----	----	
64	p,p'-DDE	OCP	13.273	13.280	5954	10523.1658	13.108504	13.108...	100.00000	4.55709	
68	cis-Chlordane	OCP	13.260	13.119	76	561.3690	15.643190	15.643...	100.00000	4.55709	
70	Dieldrin	OCP	13.383	----	----	----	17.850940	17.850...	----	----	
71	Endrin	OCP	13.579	13.622	158442	2796991.03...	21.036029	21.036...	100.00000	4.55709	
72	Endrin aldehyde	OCP	13.865	13.861	7465	164304.5980	5.924313	5.924313	100.00000	4.55709	
73	p,p'-DDD	OCP	13.660	13.621	2069	1825.0289	20.247834	20.247...	100.00000	4.55709	
74	beta-Endosulfan	OCP	13.706	13.622	38294	342272.2707	19.434001	19.434...	100.00000	4.55709	
76	p,p'-DDT	OCP	14.102	14.102	3795787	7224692.67...	8.037743	8.037744	0.21093	4.55709	
77	Endosulfan sulfate	OCP	14.066	14.091	108	216.5503	19.577864	19.577...	100.00000	4.55709	
78	Endrin ketone	OCP	14.640	14.601	101	1196.4148	19.607135	19.607...	100.00000	4.55709	
82	Methoxychlor	OCP	14.654	14.692	109	632.3251	11.416339	11.416...	100.00000	4.55709	

Breakdown for Endrin and DDT should be < 15%

# Instrument Performance Measurements

## USEPA Requirements for Isomer Separation

The resolution should be verified on the mid-point concentration of the ICAL as well as the laboratory-designated CCV level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene)



# Potential Laboratory Methylene Chloride Reduction Remedies

## (Continued)

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- 3. Use of Micro-extraction methods (EPA 3511)**
  - a. Reduction to minimal 3-5 ml solvent**
  - b. Allows single-increment extraction process**
  - c. Total solvent reduction at 99%**
  - d. Total extraction time reduction from 7-8 hrs. total to 2.5 hrs.**

# Additional Study – Microextraction

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- **Extraction using SW846 Method 3511**
  - **Single extraction**
  - **pH 3**
  - **4 ml methylene chloride**
  - **Final extract volume 4 ml**
- **Analytes listed in 40 CFR 136 Method 625.1**
  - **Tables 1 and 2**
- **Final LOQ 2.0 ug/L with select phenolics at 10 ug/L**

# Additional Study – Calibration from 5 u/L to 100 ug/L Method 3511

	Concentration ug/L	Avg	%RSD	Correlation Coefficient
<b>Compound</b>				
Benz[a]anthracene	Average RF	1.060	13.400	
Nitrobenzene	Average RF	1.790	16.800	
2-Nitrophenol	Average RF	0.064	9.150	
2,4-Di methylphenol	Average RF	0.280	10.300	
2,4-Dichlorophenol	Average RF	0.240	15.500	
Benzo[b]fluoranthene	Average RF	1.980	4.990	
Benzo[k]fluoranthene	Average RF	1.920	15.000	
Benzo[a]pyrene	Average RF	0.960	7.150	
Pentachlorophenol	Quadratic	0.075	29.700	0.9997
Naphthalene	Average RF	0.740	4.750	
Hexachlorobutadiene	Average RF	0.380	2.560	
4-chloro-3-	Average RF	0.220	11.900	
Phenol	linear			0.9991



Thank you