

An Optimized Solid Phase Extraction Procedure for EPA Method 8081 and 8082 Analytes in Water



UCT Part Numbers

ECUNIC18
ENVIRO-CLEAN® Universal C18
1100 mg/Universal Cartridge

HYDFLW01
HydraFlow® 4 Channel
Cartridge Manifold

ECUNIBHD
Universal Cartridge
Bottle Holder Adapter

ECUCTRAP20
20 L Waste Trap

VMFSPEVAP-32
SPeVAP® 32 Position
Multi-Function Solvent
Evaporator

VMFSPEVAPCR-3252
SPeVAP® 32 Position 27-29 mm
VOA Vial Collection Rack

ECROCKER400
Vacuum Pump – 110 Volt

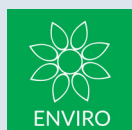
ECUCTRAP20-ADPT
20 L Waste Trap Adapter

ECSS01K
Sodium Sulfate Anhydrous, ACS
Grade Granular 60 Mesh, 1.0 KG

Summary:

EPA methods 8081, organochlorine pesticides (OCPs) by GC, and 8082, polychlorinated biphenyls by GC (PCBs), are hazardous waste test methods (SW-846) regulated under the Resource Conservation and Recovery Act (RCRA)[1, 2]. These methods are performance based which allow analysts to modify the sampling and analytical approaches to meet the measurement requirements. In other words, these methods convey “what” needs to be accomplished but not prescriptively “how”. For water samples in methods 8081 and 8082, liquid-liquid extraction and solid phase extraction (SPE) are allowed to extract the target analytes from various aqueous samples. EPA method 3535A outlines several solid phase extraction methods for different EPA methods including 8081 and 8082. Use of C18 SPE disk for sample extraction and elution with methylene chloride (DCM), a toxic chlorinated solvent which needs to be solvent exchanged to n-hexane prior to GC-ECD analysis. Method 3535A is also a performance-based SW-846 method that allows for method modifications[3].

In this application note, a new elution solvent approach was explored, in order to eliminate DCM from the extraction protocol. The extraction was optimized using the UCT HydraFlow and ECUNIC18 cartridges resulting in a final elution volume of 65 mL.



SPE Procedure:

1. Sample Preparation

- Fill sample bottles with 1 liter of water and spike with 5 mL of concentrated sulfuric acid to adjust the pH to less than 2
- Add 100 µl of standard to the samples

2. Cartridge Conditioning

- Setup the HydraFlow®
- Place the UCT **ECUNIC18** cartridges on the HydraFlow®
- Add 10 mL of acetone to the cartridges and allow them to soak for 2 minutes
- Turn on the vacuum pump
- Turn the side knob on the Hydraflow to organic, open the waste knob on the side, and turn the knobs on the front to the right to "Waste Flow" to pull the solvent through
- Repeat (c and e) with 10 mL of hexane and allow the hexane to completely dry out
- Repeat (c and e) with 10 mL of methanol
- Before all the methanol is pulled through the cartridges, close the valves, add 30 mL of DI water, and soak for 2 minutes
- Change the side knob to Aqueous then pull to waste down to 20 mL

3. Sample Loading

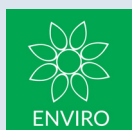
- Close all valves and add samples bottles to the bottle holders
- Slowly run the samples through the cartridges at a rate no faster than 30 mL/minute
- Once the entire sample is run through, allow the cartridges to dry under full vacuum for 15 minutes
- While drying, shake/tap the cartridges to remove excess water
- Once fully dry, analyte elution can begin

4. Analyte Elution

- Rinse the sample bottles with 5 mL of acetone, and slowly turn the front knobs to the left to "Elution Flow" collecting the eluate in the collection vials
- Eluate should be collected slowly at a drop-wise rate
- Repeat (a and b) 3 more times rinsing the sample bottles with 10 mL of hexane and collecting the eluate
- The final elution volume should be 5 mL of acetone and 30 mL of hexane, 35 mL total
- Pack Pyrex funnels with glass wool and add 15 grams of sodium sulfate
- Rinse the sodium sulfate with 10 mL of hexane and collect as waste
- Insert the funnels into new 70 mL collection vials
- Pour the sample over the sodium sulfate and break up any clumping with a glass stir rod
- Rinse the collection vial with 10 mL of hexane and pour over the sodium sulfate
- Repeat (i) 2 more times, breaking up clumping between each rinse, for a total solvent volume of 65 mL

5. Eluate Evaporation

- Insert collection vials into the UCT SPeVAP
 - Dry samples down to 1 mL at 40°C with a gentle nitrogen stream
- Note:** Do not let the samples evaporate to dryness. This will result in analyte recovery loss.
- Transfer the sample to an autosampler vial to analyze on GC-ECD or GC-MS



Instrument Parameters - PCB Analysis:

GC-ECD Instrument Parameters for PCB Analysis		
Column		RTX-PCB
Front Inlet		
Mode		Split
Initial Temperature		250°C
Pressure		3.54 psi
Split Ratio		10:1
Split Flow		10.7 mL/min
Gas Type		Hydrogen
Detector (μECD)		
Temperature		250°C
Makeup Flow		60.0 mL/min
Makeup Gas Type		Nitrogen
Temperature Program		
Rate (°C/min)	Final Temperature (°C)	Hold Time (min)
Initial	100	1
10	320	5

Results - PCB Analysis:

Fig 1. PCBs GC-MS Chromatogram – 1 μg/L

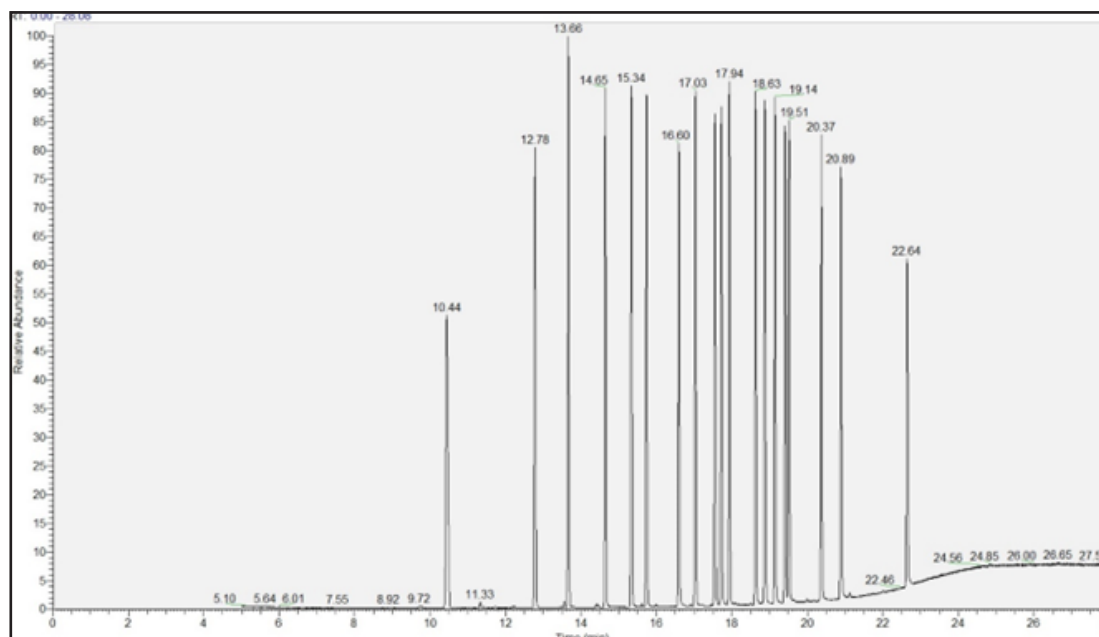


Fig 2. PCBs GC-MS Chromatogram – 1 µg/L (Zoomed In)

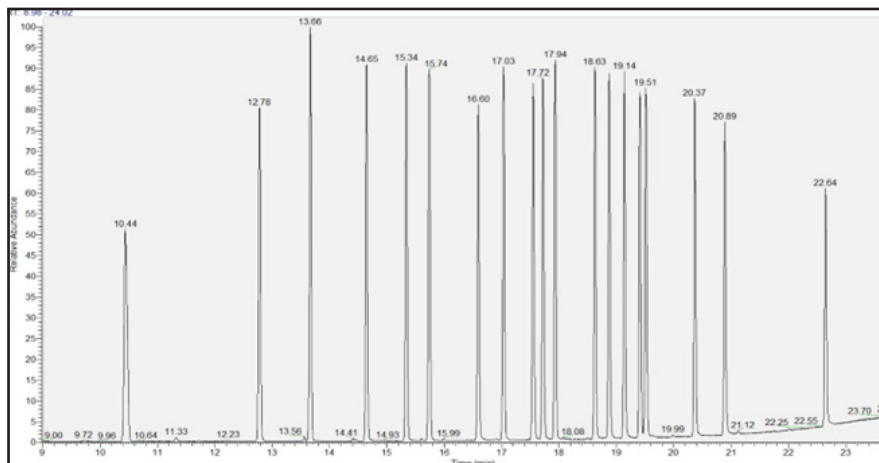


Fig 3. PCBs GC-ECD Chromatogram – 1 µg/L

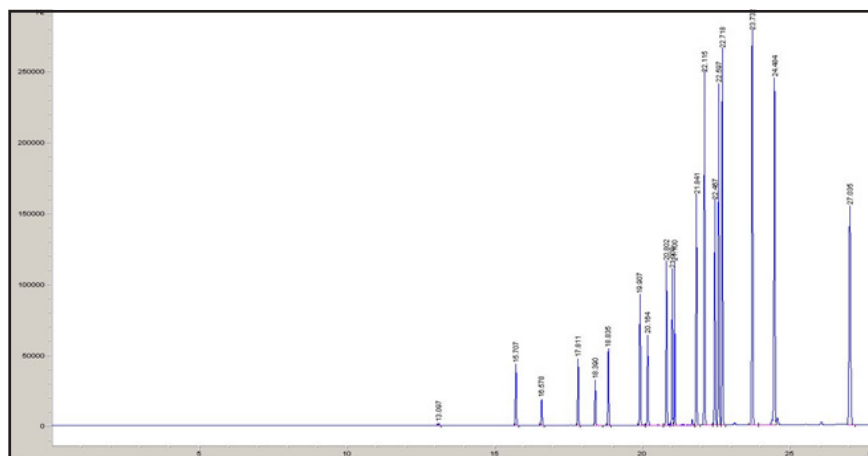
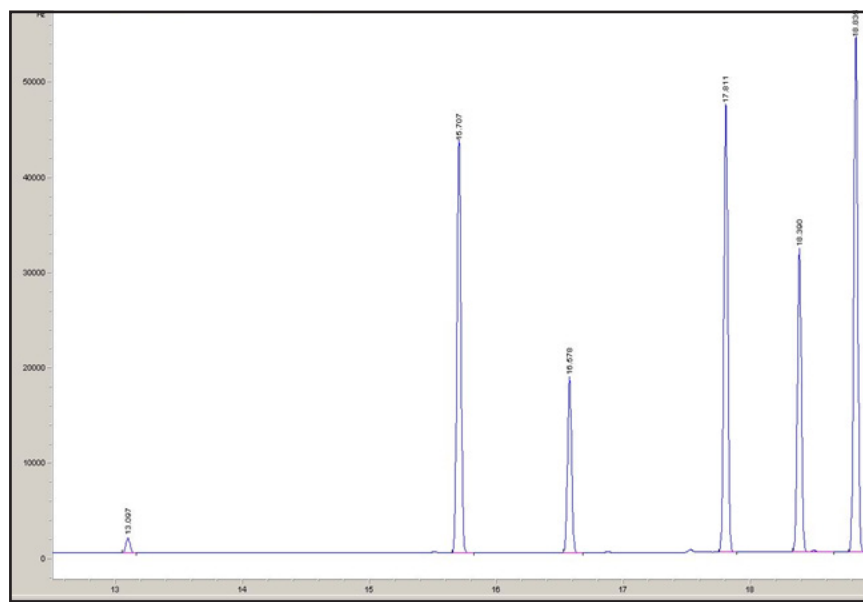


Fig 4. PCBs GC-ECD Chromatogram – Early eluting analytes 1 µg/L (Zoomed In)



PCB Data					
	Analyte	GC-ECD-RT	GC-MS-RT	Recovery %	RSD %
1	2-Chlorobiphenyl	13.09	10.44	104.3	6
2	2,3-Dichlorobiphenyl	15.71	12.78	87.2	10
3	2,2',5-Trichlorobiphenyl	16.59	13.66	118.2	9
4	2,4',5-Trichlorobiphenyl	17.82	14.65	126.3	7
5	2,2',5,5'-Tetrachlorobiphenyl	18.40	15.34	112.1	6
6	2,2',3,5'-Tetrachlorobiphenyl	18.84	15.74	108.3	6
7	2,3',4,4'-Tetrachlorobiphenyl	19.92	16.60	94.6	4
8	2,2',4,5,5'-Pentachlorobiphenyl	20.17	17.03	100.1	6
9	2,2',3,4,5'-Pentachlorobiphenyl	20.81	17.55	97.6	6
10	2,3,3',4',6-Pentachlorobiphenyl	21.01	17.72	98.4	6
11	2,2',3,5,5',6-Hexachlorobiphenyl	21.11	17.94	100.3	6
12	2,2',4,4',5,5'-Hexachlorobiphenyl	21.85	18.63	90.2	4
13	2,2',3,4,5,5'-Hexachlorobiphenyl	22.12	18.87	95.5	6
14	2,2',3,4,4',5'-Hexachlorobiphenyl	22.48	19.14	95.3	5
15	2,2',3,4',5,5',6-Heptachlorobiphenyl	22.61	19.40	95.1	5
16	2,2',3,4,4',5',6-Heptachlorobiphenyl	22.73	19.51	107.0	6
17	2,2',3,4,4',5,5'-Heptachlorobiphenyl	23.74	20.37	95.7	6
18	2,2',3,3',4,4',5-Heptachlorobiphenyl	24.49	20.89	93.7	7
19	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	27.05	22.64	93.2	5



Instrument Parameters - OCP Analysis:

GC-ECD Instrument Parameters for OCP Analysis		
Column		RTX-PCB
Front Inlet		
Mode		Split
Initial Temperature		250°C
Pressure		4.28 psi
Split Ratio		10:01
Split Flow		10.7 mL/min
Gas Type		Hydrogen
Detector (μECD)		
Temperature		250°C
Makeup Flow		60.0 mL/min
Makeup Gas Type		Nitrogen
Temperature Program		
Rate (°C/min)	Final Temperature (°C)	Hold Time (min)
Initial	150	1
10	220	6
2	250	1
10	320	5

Results - OCP Analysis:

Fig 1. OCPs GC-MS Chromatogram – 1 µg/L

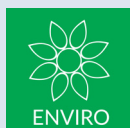
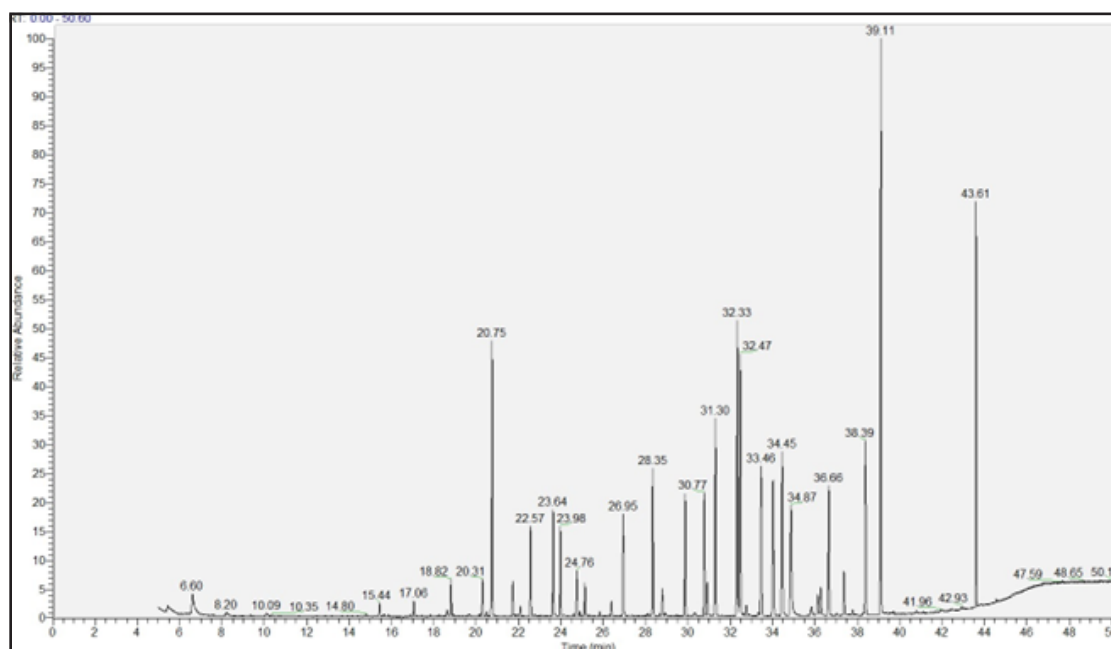


Fig 2. OCPs GC-MS Chromatogram – 1 µg/L (Zoomed in)

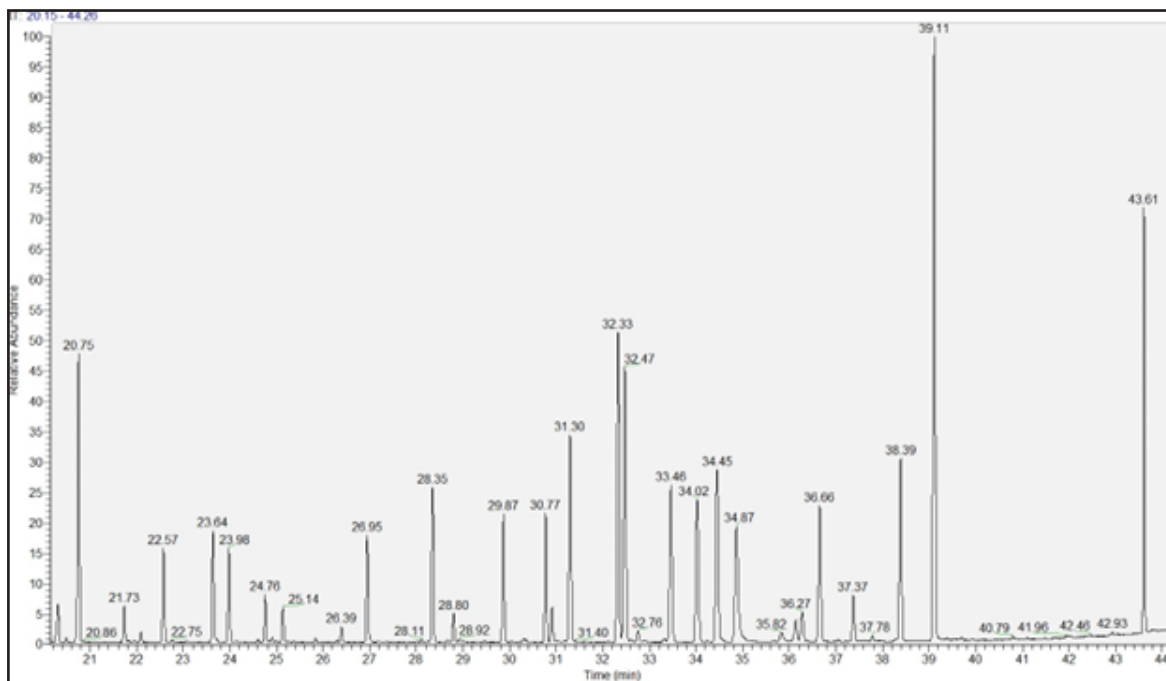
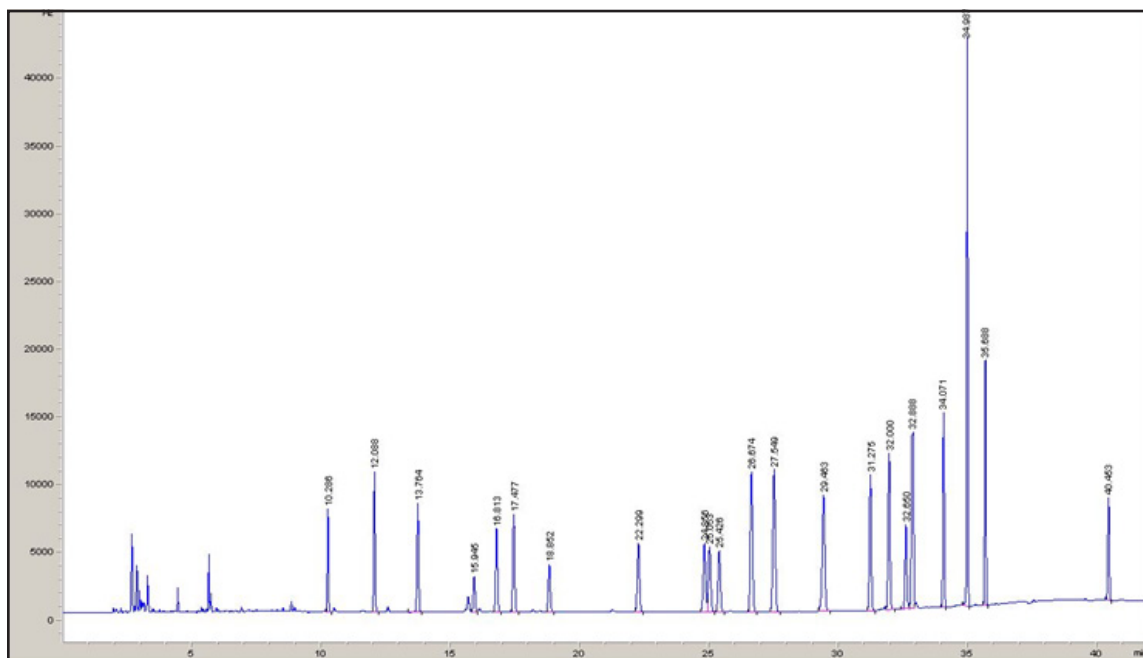
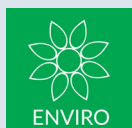


Fig 3. OCPs GC-ECD Chromatogram – 1 µg/L Extracted Standard



OCP Data					
	Analyte	GC-ECD-RT	GC-MS-RT	Recovery %	RSD %
1	2,4,5,6-tetrachloro-m-xylene	10.28	20.75	83.1	12
2	α -BHC	12.08	25.10	106.0	10
3	γ -BHC	13.76	22.58	113.9	10
4	β -BHC	15.94	23.59	108.7	9
5	δ -BHC	16.81	23.97	108.4	11
6	Heptachlor	17.47	26.95	108.5	11
7	Aldrin	18.85	28.36	123.8	21
8	Heptachlor epoxide	22.29	29.88	106.7	11
9	cis-Chlordane	24.85	30.79	107.3	10
10	trans-Chlordane	25.05	31.31	106.2	10
11	4,4'-DDE	25.42	32.38	100.9	10
12	Endosulfan I	26.67	31.42	102.3	11
13	Dieldrin	27.55	32.48	110.3	11
14	Endrin	29.46	33.48	97.3	29
15	4,4'-DDD	31.27	34.44	104.5	12
16	Endosulfan II	32.00	34.02	109.5	11
17	4,4'-DDT	32.65	36.66	103.3	10
18	Endrin aldehyde	32.89	34.86	102.6	12
19	Methoxychlor	34.07	39.10	99.0	10
20	Endosulfan sulfate	34.99	36.26	102.2	11
21	Endosulfan sulfate	35.69	38.38	96.8	3
22	Decachlorobiphenyl	40.45	43.60	83.6	15



Conclusion:

This application note describes an optimized SPE procedure using ECUNIC18 SPE cartridges to extract PCB and OCP target analytes in water samples. This procedure employs acetone and n-hexane mixture instead of DCM. After evaporation, the analytes are enriched in n-hexane thus no solvent exchange is needed for GC-ECD detection. The modified method uses non-chlorinated solvents (acetone and n-hexane) to elute the target analytes and surrogates that are retained on the C18 sorbent. Using sodium sulfate and then rinsing it a few times substantially improved Aldrin recoveries. Solvent accumulation was also reduced to just 65 mL. The result was excellent recoveries >85% and RSDs <10% for most analytes. This is a very good method for a high-volume production lab that would like to streamline an SPE extraction. The method was carried out using UCT's new extraction manifold, the Hydraflow®. Many advantages were gained from employing this manifold, one of which is the high vacuum pressure which allows for drying the cartridges. This step is very critical in obtaining acceptable recoveries. Any moisture left in the cartridges can be the root cause behind lower recoveries.

References:

- [1] <https://www.epa.gov/sites/production/files/2015-12/documents/8081b.pdf>
- [2] <https://www.epa.gov/sites/production/files/2015-07/documents/8082a.pdf>
- [3] <https://www.epa.gov/sites/default/files/2015-12/documents/3535a.pdf>

UCT, LLC • 2731 Bartram Road • Bristol, PA 19007 800.385.3153 • 215.781.9255
www.unitedchem.com Email: methods@unitedchem.com

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