



Solid Phase Extraction of Organochlorine Pesticides and PCBs by EPA Method 608.3

UCT Part Numbers

ECUNIC18
ENVIRO-CLEAN®
1100mg C18/
Universal Cartridge (83mL)

ECUCTADP
ENVIRO-CLEAN®
Glass Cartridge Adaptor

ECUNIBHD
ENVIRO-CLEAN®
White Bottle Holder

ECUCTVAC6
ENVIRO-CLEAN®
6 Station Vacuum Manifold
Stainless Steel System



Summary:

The U.S. EPA has recently updated method 608.2 to 608.3, for the determination of organochlorine pesticides and PCBs in water by GC/HSD, which allows both liquid-liquid extraction (LLE) and solid phase extraction (SPE) techniques to be used in sample extractions [1]. The updated method specifies that samples can be extracted using LLE or disk-based SPE procedures developed by 3M Corporation; however, it also clearly states that the method is performance based, and may be modified to improve performance provided that all necessary performance requirements are met (Section 1.8). The allowable modifications and changes are described in 40 CFR 136.6 [2]. If the underlying chemistry and determinative technique in the modified method are essentially the same as an approved method, then the modified method is an equivalent and acceptable alternative to the approved one. On account of the similarities in retention chemistry for a C18 phase in either a disk or cartridge format, SPE using C18 cartridges should be deemed as an equivalent and acceptable alternative to using C18 disks, if all performance requirements are met. Large ID C18 SPE cartridges (83 mL) are employed in this study to overcome the clogging issue typically encountered using small ID cartridges (such as 6-mL ones) when handling samples containing high particulate levels. Alternate reagents are also allowed if equal or better performance can be obtained [2].

An SPE procedure using large ID C18 SPE cartridges and elution with acetone and n-hexane instead of acetone and dichloromethane (DCM) is presented. With the optimized elution solvents, no solvent exchange is needed as the final solvent after evaporation would be n-hexane instead of DCM, which can be injected directly to GC-ECD. In addition, sodium sulfate drying can be eliminated as two distinct layers, hexane on top and water on bottom, are formed after evaporation. It's quite easy transferring the top hexane layer to a 10-mL glass container for instrumental detection or continuing to evaporate to 1 mL if enhanced method sensitivity is desired.



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SPE Procedure:

1. Cartridge Conditioning

- a) Place the glass adaptor (**ECUCTADP**) onto the 6-station manifold (**ECUCTVAC6**), attach the C18 Universal SPE cartridge (**ECUNIC18**) to the glass adaptor, then attach the bottle holder (**ECUNIBHD**) to the top of the SPE cartridge.
- b) Add 10 mL DCM to the SPE cartridge by rinsing the bottle holder and the SPE cartridge, let DCM wet and soak the SPE sorbent for 1 min before drawing to waste and leave full vacuum on for 1 min.
- c) Add 10 mL methanol (MeOH) to the SPE cartridge, let MeOH wet and soak the SPE sorbent for 2 min, then pull MeOH through (or by gravity) leaving a thin layer above the frit.
- d) Add 20 mL reagent water to the SPE cartridge, pull water through leaving a water layer of about 1 cm above the frit.

2. Sample Extraction

- a) Adjust 1 L sample to pH < 2 using 6 N HCl or H₂SO₄. Acidifying sample is optional, however it can improve the recovery of decachlorobiphenyl (surrogate).
- b) Add surrogate and target analyte spiking solutions (prepared in MeOH or acetone) to the sample.
- c) Add 5 mL MeOH to the sample and mix well.
- d) Load the sample bottle to the bottle holder, adjust vacuum for a fast dropwise flow (about 30 mL/min).

3. Cartridge Drying

- a) Dry the SPE cartridge under full vacuum for 10 min. Move the cartridge from the manifold during drying, and shake the cartridge to remove excess water from the bottom of the SPE cartridge.

4. Analyte Elution

- a) Insert glass vial* (40 or 50 mL) into the SPE manifold to collect the eluate.
- b) Rinse the sample bottle with 10 mL of 1:1 acetone:n-hexane solution, add the bottle rinse to the SPE cartridge, let elution solvent wet and soak the sorbent for 1 min before drawing it slowly to the collection vial. Leave full vacuum on for 1 min.
- c) Repeat the elution with 10 mL of 1:9 acetone:n-hexane solution (sample bottle rinse), and an additional 10 mL of 1:9 acetone:n-hexane solution (bottle holder rinse).

5. Eluate Evaporation

- a) Remove the glass vial from the manifold. Evaporate to about 5 mL using TurboVap under a gentle stream of nitrogen (9 - 10 psi) at 40°C.
- b) Transfer the upper n-hexane layer (bottom layer is water residue that is immiscible with n-hexane) to a graduated glass tube*, rinse the eluate vial with 4 - 5 mL n-hexane, transfer the rinsate to the graduated tube, adjust the final volume to 10 mL** with n-hexane, and mix well.
- c) Transfer 1 mL extract to 2-mL autosampler vial for GC-ECD analysis or GC/MS confirmation.

*: Use new sample bottles, glass vials and graduated tubes as aldrin may degrade on the active sites of the old/used glassware.

** : Continue evaporating to 1 mL if higher sensitivity is desired.



Results:

Accuracy and Precision in Comparison to QC Acceptance Criteria in Method 608.3

Compound Name	Spiked at 1 µg/L (n=4)		Spiked at 10 µg/L (n=4)		QC Acceptance Criteria	
	Recovery%	RSD%	Recovery%	RSD%	Recovery%	RSD%
alpha lindane	87	7	90	5	49-130	28
beta lindane	90	10	94	6	39-130	38
gamma lindane	92	7	92	5	43-130	29
delta lindane	90	4	95	5	51-130	43
Heptachlor	87	5	91	3	43-130	28
Aldrin	79	8	90	3	54-130	25
Heptachlor epoxide	86	3	93	6	57-132	22
trans Chlordane	85	2	91	6	55-130	24
cis Chlordane	85	2	92	6	55-130	24
Endosulfan I	93	3	94	6	57-141	25
4,4'-DDE	100	3	95	6	54-130	30
Dieldrin	113	2	103	5	58-130	42
Endrin	105	3	107	7	51-130	42
Endosulfan II	105	2	100	7	22-171	63
4,4'-DDD	105	1	100	7	48-130	32
Endosulfan sulfate	103	1	101	7	38-132	32
4,4'-DDT	105	3	101	6	46-137	39
Endrin aldehyde	111	2	101	7	NA	NA
Endrin ketone	102	2	101	7	NA	NA
Methoxychlor	111	4	106	8	NA	NA

Conclusion:

A modified SPE method using UCT's large ID C18 cartridges has been demonstrated for the extraction of organochlorine pesticides in water. The modified method did not change the underlying chemistry or the determinative technique of the approved SPE procedure using C18 disks. The change of elution solvent from acetone/DCM to acetone/n-hexane is an allowable change [2], which resulted in a more efficient and cost-effective method requiring no sodium sulfate drying or solvent exchange steps. The accuracy and precision obtained by this method have easily passed the QC acceptance criteria set by method 608.3 (Table 4), and the results are comparable or better than those that were obtained by 3M C18 disks [3], making the presented method a successful extraction alternative for EPA method 608.3.

References:

- [1] Method 608.3 – Organochlorine Pesticides and PCBs by GC/HSD, U.S. EPA, Office of Water, Office of Science and Technology, Washington, DC
- [2] <https://www.gpo.gov/fdsys/pkg/CFR-2015-title40-vol23/xml/CFR-2015-title40-vol23-sec136-6.xml>
- [3] EPA Method 608 ATP 3M0222, An alternative test procedure for the measurement of organochlorine pesticides and polychlorinated biphenyls in waste water. Federal Register/Vol. 60, No. 148 August 2, 1995

