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

UCT Part Numbers

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

ECUCTADP
ENVIRO-CLEAN® Glass Cartridge Adaptor

ECUNIBHD
ENVIRO-CLEAN® White Bottle Holder

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

Summary:

EPA methods 8081 (Organochlorine pesticides by GC) and 8082 (Polychlorinated biphenyls by GC) [1-2] are hazardous waste test methods (SW-846) regulated under the Resource Conservation and Recovery Act (RCRA). 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" [3]. 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, which use C18 SPE disk for sample extraction, and elution with methylene chloride (DCM), a toxic chlorinated solvent which needs solvent exchange to n-hexane prior to GC-ECD analysis [4]. Method 3535A is also a performance based SW-846 method that allows for method modifications.

This application note describes an optimized SPE procedure using C18 SPE cartridges to extract target analytes in water samples, and eluting with 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. In addition, sodium sulfate drying can be eliminated when using the acetone:n-hexane elution solvent. Two distinct layers (hexane on top and water on bottom) are formed after evaporative removal of acetone and partial removal of n-hexane, facilitating the easy transfer of the top n-hexane layer into a graduated glass tube for instrumental analysis or continuing concentration to 1 mL for enhanced sensitivity. This step also helps to improve aldrin recovery which could be adversely lost in the sodium sulfate drying step.

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SPE Procedure:

1. **Cartridge Conditioning**
   a) Place the glass adaptor (**ECUCTADP**) onto the 6-station manifold (**ECUCTVAC6**), attach the C18 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 H_2SO_4. Acidifying sample is found to 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 into 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 for GC-ECD or GC/MS analysis.

*: 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 Data of Organochlorine Pesticides in 4 LCS Samples

Compound Name	Spiked at 1 µg/L		Spiked at 10 µg/L	
	Recovery%	RSD% (n=4)	Recovery%	RSD% (n=4)
Alpha lindane	**86.5**	6.8	**90.2**	5.4
Beta lindane	**90.0**	10.3	**93.6**	6.1
Gamma lindane	**92.0**	7.0	**92.0**	5.0
Delta lindane	**89.5**	3.8	**95.5**	5.2
Heptachlor	**87.3**	4.6	**90.5**	3.3
Aldrin	**79.0**	7.6	**90.2**	3.2
Heptachlor epoxide	**86.3**	2.9	**93.2**	5.9
Trans Chlordane	**84.5**	2.3	**91.2**	6.2
Cis Chlordane	**85.3**	2.4	**91.6**	6.1
Endosulfan I	**93.0**	3.2	**94.4**	5.8
4,4'-DDE	**100.3**	3.2	**95.3**	6.0
Dieldrin	**113.0**	2.3	**102.5**	5.1
Endrin	**105.3**	2.8	**106.7**	6.6
Endosulfan II	**104.5**	1.7	**100.4**	6.6
4,4'-DDD	**105.0**	1.1	**100.4**	6.6
Endosulfan sulfate	**102.5**	1.3	**101.2**	7.4
4,4'-DDT	**105.0**	3.0	**101.1**	6.5
Endrin aldehyde	**110.5**	2.3	**101.1**	6.7
Endrin ketone	**102.0**	1.8	**101.3**	6.8
Methoxychlor	**111.3**	3.6	**106.3**	7.6

Conclusion:

An optimized SPE procedure has been demonstrated for the extraction of EPA method 8081 and 8082 analytes in water. 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. The optimized elution requires no sodium sulfate drying or solvent exchange steps, resulting in a more efficient and cost-effective SPE method for such analysis. Excellent recoveries and RSD% have been achieved even for the noticeably troublesome compound, aldrin, which may get lost in the sodium sulfate drying step or degraded on scratched glass surfaces.

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://waste.zendesk.com/hc/en-us/articles/217452058-How-does-EPA-s-Performance-Based-Measurement-System-PBMS-approach-affect-SW-846-

[4] https://www.epa.gov/sites/production/files/2015-06/documents/epa-3535a.pdf

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