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Document Name: 3M 0222: Organochlorine Pesticides and PCBs in Wastewater Using Empore Disk

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Standards Body: 3M Corporation

APPROVED

Official Incorporator:

THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Empore™
Extraction Disks

November 1995

Method Summary

EPA Method 608
Alternate Test Method 3M0222

Organochlorine Pesticides and PCBs in Wastewater Using 3M Empore™ Extraction Disks

This method approval was announced in the Federal Register/Vol. 60, No. 148 on August 2, 1995. Its use is appropriate for effluent testing in support of NPDES permit applications, discharge monitoring reports, state certification, and other requests from the permitting authority for quantitative or qualitative effluent data. A copy of the method can be obtained from 3M: (800) 440-2966, ext. 67.

Summary of Method

This method describes a Nationwide Alternate Test Procedure (ATP) for Method 608, using 3M Empore Extraction Disks to extract certain organochlorine pesticides and PCBs from aqueous samples. A measured volume of sample, approximately one liter, is extracted with a 90 mm C18 Empore disk. The disk is eluted with acetone followed by methylene chloride. The eluent is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The eluant is analyzed by GC/ECD.

Performance Data

Validation studies for the Alternative Test Procedure were performed on the organochlorine pesticides and representative PCBs from EPA Method 608. Validation data were generated in a single laboratory with less extensive confirmation in two additional labs. The study was performed on triplicate samples of reagent water and industrial wastewaters spiked at three concentrations. The samples were also prepared by the standard liquid extraction for equivalency determinations. Matrices provided for the validation included effluents from five industrial classifications.

Matrix Profiles

Waste Water Sources:	Chemical Manufacturing Pharmaceutical Manufacturing Pulp & Paper Sewage Treatment Refuse Plant	
Solids Profiles Range (mg/L):	TSS TDS TS	3-120 360-48,300 560-50,500
Sample pH Range:	3.1-12.0	

Equivalency Study

Analyte	Empore MDL µg/L	Low Level		Mid Level		High Level	
		Empore %R(RSD)	LLE %R(RSD)	Empore %R(RSD)	LLE %R(RSD)	Empore %R(RSD)	LLE %R(RSD)
Aldrin[1]	0.008	121(19)	123(17)	72(8)	73(20)	76(9)	76(23)
BHC, alpha[1]	0.005	134(17)	133(14)	89(21)	92(20)	93(8)	96(4)
BHC, beta[1]	0.021	116(39)	126(26)	95(15)	96(6)	95(8)	97(5)
BHC, delta[1]	0.011	162(32)	158(26)	99(20)	101(15)	106(15)	109(11)
BHC, gamma[1]	0.004	135(27)	134(30)	87(9)	97(22)	96(11)	98(6)
p,p'-DDD[2]	0.083	91(18)	90(29)	92(16)	92(29)	90(12)	86(26)
p,p'-DDE[1]	0.022	150(38)	148(33)	83(12)	76(15)	86(11)	81(26)
p,p'-DDT[2]	0.071	84(10)	83(19)	81(12)	78(25)	84(11)	76(25)
Dieldrin[1]	0.008	111(22)	112(19)	77(11)	78(10)	85(8)	82(16)
Endosulfan I[1]	0.008	98(14)	92(19)	73(17)	72(20)	82(16)	78(20)
Endosulfan II[2]	0.043	74(8)	73(13)	77(11)	78(15)	90(9)	88(15)
Endosulfan sulfate[2]	0.048	97(8)	97(13)	97(8)	98(16)	98(8)	96(14)
Endrin[2]	0.068	96(9)	95(19)	94(9)	96(22)	96(8)	92(22)
Endrin aldehyde[1]	0.015	95(21)	90(28)	75(26)	73(27)	73(26)	68(35)
Heptachlor[1]	0.020	128(28)	128(35)	98(30)	101(32)	89(20)	88(31)
Heptachlor epoxide[1]	0.010	110(16)	123(31)	100(29)	91(13)	92(10)	88(18)
Methoxychlor[1]	0.027	172(49)	169(52)	113(18)	111(34)	105(16)	100(31)
Chlordane[3]	0.07	96(23)	97(27)	73(19)	66(35)	79(15)	82(27)
Toxaphene[4]	0.61	136(55)	128(34)	93(19)	92(22)	80(11)	81(23
PCB 1254[3]	0.26	80(42)	65(35)	88(6)	79(25)	83(7)	77(27)
Average:		114	113	88	87	89	86

n=30 Spiking levels: [1] low 0.2, mid 1.0, high 5.0 µg/L
[2] low 1.0, mid 5.0, high 15 µg/L
[3] low 2.0, mid 10, high 100 µg/L
[4] low 10, mid 50, high 250 µg/L

Method

1. Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample.

2. Assemble an all glass filtration assembly using a 90 mm C18 3M Empore Extraction Disk. Use of a manifold for multiple extractions is acceptable.

   Note: If samples contain significant quantities of particulates, the use of an in-situ glass micro-fiber prefilter (Whatman GMF 150, 1 micron pore size or equivalent) and/or an inert depth filter such as Empore Filter Aid 400 is advisable. The glass fiber prefilter is placed on top of the Empore disk prior to placement of the glass reservoir and clamp. When using Filter Aid 400, assemble the glassware with the disk (and glass fiber prefilter) and clamp in place. Pour about 40 grams (large end of provided scoop) of the Filter Aid onto the surface of the disk.

3. **Prewash** – Wash the extraction apparatus and disk by adding 20 mL of methylene chloride ($MeCl_2$) to the reservoir washing down the sides of the glass reservoir in the process. Pull a small amount through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.

   Note: When using Filter Aid, adjust the volume of all solvents so the volumes used are sufficient to submerge the bed. In subsequent steps volumes should be adjusted so the liquid level is maintained above the depth filter bed for ease of observation.

4. **Condition** – Pre-wet the disk by adding 20 mL methanol (MeOH) to the reservoir, pulling a small amount through the disk, then letting it soak for about one minute. Pull most of the remaining MeOH through the disk, leaving 3-5 mm on the surface of the disk, which should not be allowed to go dry from this point until the sample extraction has been completed. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY. The disk is composed of hydrophobic materials. To make it amenable to a water solution, it must be pre-wet with a water miscible solvent (MeOH) or it wil1 not allow water to pass through the materials. Should the disk accidentally dry, simply repeat the pre-wetting step.

5. Rinse the disk by adding 20 mL of reagent water to the disk and drawing most through, again leaving 3-5 mm of water on the surface of the disk.

6. **Extraction** – Add the water sample to the reservoir and, under full vacuum, filter as quickly as the vacuum will allow. Drain as much water from the sample bottle as possible. Particulate-free water may pass through the disk in as little as 10 minutes without reducing analyte recoveries. Allow the entire sample to pass through the disk, then dry the disk by maintaining vacuum for about 3 minutes.

   Note: With heavily particle-laden samples, allow the sediment to settle; decant as much liquid as is practical into the reservoir. Allow most of the liquid to filter, then swirl the sediment portion and add it to the reservoir. Before the entire sample has filtered, rinse the sample bottle with reagent water and add to the reservoir to transfer any particulates remaining in the bottle to the extraction. Drain as much water as possible from the sample bottle.

7. Remove the entire filter assembly (do not disassemble) and insert suitable sample tube for eluent collection. The sample tube should have sufficient capacity to contain the elution solvent volume and should fit around the drip tip of the extraction glassware base unit. The tube should be seated so that the drip tip is below the neck of the sample tube to prevent splattering (and subsequent analyte loss) when the vacuum is applied. If using a filter flask, empty the water filtrate before inserting the collection tube.

8. **Elution** – Add 5.0 mL acetone to the disk. Allow the acetone to spread evenly across the disk, then quickly turn the vacuum on and off again to pull a fraction of a milliliter through the disk. Allow the disk to soak for 15 to 20 seconds. This water-miscible solvent penetrates the water-filled pores of the sorbent and improves the recovery of compounds adsorbed to intrastitial surfaces.

9. Add 20 mL of $MeCl_2$ to the sample bottle. Rinse the bottle thoroughly and, with the acetone still on the disk, transfer the solvent to the disk with a dispo-pipette, rinsing down the sides of filtration reservoir in the process. Draw about half of the solvent through disk, then release the vacuum. Allow the remaining $MeCl_2$ to soak the disk for about one minute, then draw remainder through under vacuum.

10. Repeat the bottle rinse and elution in step 9 with a 10 mL aliquot of $MeCl_2$.

11. Dry the combined eluates by slowly adding about 10 grams anhydrous sodium sulfate to the collection tube (this helps prevent the drying column from plugging due to excess water) and then pouring through a drying column containing about 10 cm anhydrous sodium sulfate. Rinse the collection tube and sodium sulfate with 20 - 30 mL $MeCl_2$ and place combined solvent into a 500 mL KD flask fitted with a 10 mL receiving tube. Add 10 mL hexane and silicon carbide boiling chips and place a 3 ball Snyder column on the KD flask.

12. Concentrate to desired final volume. Sample cleanup procedures may not be necessary for relatively clean matrices; however, if circumstances require additional clean-up, the procedure does not vary from the standard 608 methodology.

13. Analyze by GC/ECD.

3M

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