Determination of Organic Compounds in Drinking Water by Empore™ C18 SPE Disks and GC-MS with EPA Method 525.2

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Application Note
Environmental

Abstract
3M™ Empore™ (now CDS Empore™) C18 Solid Phase Extraction (SPE) disks facilitate rapid and reliable sample preparation and provide excellent analyte recovery for clean chromatograms. This application note demonstrates the performance of such disk in the monitoring of drinking water samples by EPA Method 525.2.

Introduction
The target analyte list for EPA Method 525.2 is comprised of 110 compounds that are representative of four organic compound classes as pesticides, polynuclear aromatic hydrocarbons, PCBs, phthalates and adipates. Method detection limits (MDLs), as published in the method, ranges from 0.03-2.4μg/L and the recovery rate varies from 20 – 180% for each individual compound. Furthermore, after averaging each compound within the four compound classes, the averaged recovery rate for each class is:

Pesticides	108%
PCBs	108%
Phthalates & Adipates	116%
PAHs	112%

EPA Method 525.2 specified SPE disks as the sample preparation tool for the cleanup and concentration of organic contaminants from drinking water samples[1,2]. There are two challenges in the methods in the sample preparation as (1) large sampled volume at 1 liter, and (2) low pH at 2. Empore™ C18 disks can consistently tackle with these challenges without loss of C18 phase from the silica support in the disks. EPA Method 525.2 specially warned that stripping C18 phase in the extraction disk packing will complicate the chromatographic analysis with high background, which could obscure the testing results on compounds of interests.

In this application note, a one-liter water sample was passed through a 47mm C18 Empore™ disk and eluted with ethyl acetate and methylene chloride under negative pressure. Then the extract was dried and reduced in volume down to 1.0 mL and future analyzed by GC/MS.

The validation data presented herein was determined on three separate lots of C18 disks. MDLs were not discussed as it relies on the GC/MS instrument setup. The recovery rate and RSDs were the key focus. In addition to the analytes listed in EPA Method 525.2, recovery data for an extended list of analytes is also studied.

Experimental Setup

Chemicals:
99 compounds in Table 1 plus 31 compounds in Table 2 were individually purchased from AccuStandard (New Heaven, CT), then mixed to a final 1000ppm concentration for each compound. Sodium sulfite was obtained from Sigma-Aldrich (St. Louis, MO). Methylene chloride, Ethyl Acetate and Methanol were GC grade and acquired from Burdick & Jackson (Muskegon, MI).

Sample Pre-treatment:
40 mg of sodium sulfite was added to 1 L of tap water to reduce free chlorine. The water sample was adjusted to pH=2 by using 6M HCl. 5ml of methanol was added as a wetting agent. For recovery data, each water sample was spiked with 2 μl of 130 compounds mix. Internal standard and surrogate were also added for GC/MS detection. The Empore™ 47mm C18-bonded silica disks (Fisher Scientific™ 13-110-018/VWR™ 76333-132, CDS Analytical, Oxford, PA) were used for the extraction from 3 different lots and repeated number n=9.

Method:
1.Assemble an all glass filtration assembly using a 47 mm C18 Empore™ disk. Use of a manifold for multiple extractions is acceptable.

2. Wash the extraction apparatus and disk by adding 5 ml of a 1:1 mixture of ethyl acetate (EtAc): methylene chloride (MeCl2) to the reservoir. 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.

3. Condition the disk by adding approximately 5 ml of methanol to the reservoir, pulling a small amount through the disk then letting it soak for about one minute. Pull most of the remaining methanol through the disk, leaving 3 to 5mm of methanol on the surface of the disk.

4. Add 5 ml of reagent water to the disk and using the vacuum pull most through, again leaving 3 to 5 mm of water on the surface of the disk.

5. Add 5 ml of methanol to the water sample and mix well. Add the water sample to the reservoir and, under vacuum, filter as quickly as the vacuum will allow. Drain as much water from sample bottle as possible.

6. Remove filter assembly and insert suitable sample tube for eluate collection.

7. Add 5 ml of EtAc to the sample bottle. Rinse bottle thoroughly and transfer solvent to the disk with dispo-pipet, rinsing sides of filtration reservoir in the process.

8. Pull half of solvent through disk then release the vacuum. Allow the remaining solvent to soak the disk for about one minute, then draw remainder through under vacuum.

9. Repeat the solvent rinse of the sample bottle and apparatus using 5 mL of MeCl2.

10. Using a disposable pipette, rinse down the sides of the filtration glassware with two 3 mL aliquots of 1:1 EtAc/MeCl2.

11. Dry the combined eluant with 5-7 grams granular anhydrous sodium sulfate. Rinse the collection tube and sodium sulfate with two 3 mL portions of 1:1 EtAc/MeCl2 and place combined solvent into a concentrator tube.

12. Concentrate extract to 1 ml under gentle stream of nitrogen (may be warmed gently). Do not concentrate to <0.5 ml or loss of analytes could occur.

13. Analyze by GC/MS.

Results

Table 1 summarized 99 compounds on the EPA Method 525.2 list. The average recovery for 95 compounds exceeded 90% with average Relative Standard Deviation (RSD) = 4.3%. The other 4 compounds had recovery between 77% to 89% with an average RSD = 10%. Additional 31 organic compounds have been validated, and the results were shown in Table 2. 29 of these 31 compounds exceeded 90% with average RSD = 5.7%. These results showed the organic compounds in drinking water samples had been effectively extracted by Empore™ C18 disks.

Conclusions

A simple and effective method to extract organic compounds from large volume 1L drinking water sample by Empore™ C18 47mm disks has been validated per EPA Method 525.2. The results are showing excellent analyte recovery and RSDs using Empore™ C18 disks, ensuring a rapid, economical, reliable sample preparation.

References

1. Method 525. Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (Revision 2.1), Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH USA 45268.

2. National Primary Drinking Water Regulations; Analytical Techniques 40 CFR Parts 141 and 143 (Final Rule), Federal Register 53 (No. 33), 5142-5147 (Feb. 19, 1988)

Table 1. Average recovery and RSD for compounds in EPA 525.2

525.2 METHOD PERFORMANCE

Analyte	Ave %R(RSD) (n=9)
Acenaphthylene	109(3.2)
Alachlor	113(2.3)
Aldrin	113(3.7)
Ametryn	123(6.5)
Anthracene	120(3.4)
Atraton1	44(22)
Atrazine	123(4.6)
Benz[a]anthracene	105(3.4)
Benzo[b]fluoranthene	112(4.8)
Benzo[k]fluoranthene	109(10)
Benzo[g,h,i]perylene	120(3.9)
Benzo[a]pyrene	106(2.8)
BHC, alpha	122(4.2)
BHC, beta	112(4.3)
BHC, delta	119(3.4)
BHC, gamma (Lindane)	118(2.7)
Bromacil	115(7.1)
Butachlor	105(2 7)
Butylate	115(6.0)
Butylbenzylphthalate	121 (3.4)
Carboxin	100(4.9)
Chlordane, alpha	97(3.1)
Chlordane, gamma	119(3.5)
Chlordane, bans nonachlor	98(4.2)
Chlorneb	123(4.7)
Chlorobenzilate	107(2 8)
Chlorpropham	100(3 2)
Chlorpyrifos	120(5.9)
Chlorthalonil	110(3.2)
Chrysene	104(3.1)
Cyanazine	77(3.2)
Cycloate	124(3.1)
DCPA	122(4 1)
4,4'-DDD	112(3.8)
4,4'-DDE	99(7 0)
4,4'-DDT	110(7.4)
Diazinon	98(13)
Dibenz[a,h]anthracene	124(3.7)
di-n-butylphthalate	125(4.4)
Dichlorvos	109(10)
Dieldrin	98(2.9)
di(2-ethylhexyl)adipate	111 (4.0)
di(2-ethylhexyl)phthalate	122(3.7)
Diethylphthalate	106(3.5)
Dimethylphthalate	113(4.8)
2,4-dinitrotoluene	79(11)
2,6-dinitrotoluene	84(9.8)
Diphenamid	1 08(2.8)
Disulfoton	115(7.6)
Disulfoton sulfone2	164(2.8)
Disulfoton sulfoxide2	136(8.9)

Analyte	Ave %R(RSD) (n=9)
Endosulfan I	102(5.2)
Endosulfan II	118(3.4)
Endosulfan sulfate	117(3.3)
Endrin	126(3.0)
Endrin aldehyde	119(9.2)
EPTC	112(8.4)
Ethoprop	110(4.2)
Etridiazole	116(3.7)
Fenamiphos	99(2.2)
Fenarimol2	150(5.5)
Fluorene	108(3.0)
Fluridone2	114(4.5)
Heptachlor	112(4.1)
Heptachlor epoxide	109(2.9)
Hexachlorobenzene	104(4.1)
Hexachlorocyclopentadiene	103(7.5)
Hexazinone	125(4.6)
Indeno [I,2,3, c, d] pyrene	121 (3.7)
Isophorone	87(11)
Methoxychlor	107(2 1)
Methyl paraoxon	106(4 2)
Metolachlor	109(2 2)
Metribuzin1	81 (6.0)
Mevinphos	108(7.9)
MGK 264	116(4.0)
Molinate	121(5.6)
Napropamide	97(3.2)
Norflurazon2	141(4.2)
Pebulate	119(5.4)
Pentachlorophenol	81 (4.9)
Permethnn, cis	110(4.4)
Permethrin, trans	114(3.8)
Phenanthrene	113(1.9)
Prometon1	49(37)
Prometryn	110(5.2)
Pronamide	120(4.7)
Propachlor	120(5.6)
Propazine	118(4.4)
Pyrene	109(2.4)
Simazine	92(7.3)
Simetryn	103(15)
Stirofos	106(4.3)
Tebuthiuron2	100(11)
Terbacil	108(6 8)
Terbufos1	124(3.0)
Terbutryn	113(5.5)
Triademefon	117(13)
Tricyclazole2	137(12)
Trifluralin	113(5.6)
Vernolate	102(4.8)

PCB Congeners	
2,3-Dichlorobiphenyl	116(3.6)
2-Chlorobiphenyl	99(2.3)
2,2',3,3',4,4',6-heptachlorobiphenyl	110(5.6)
2,2',4,4',5,6'-hexachlorobiphenyl	106(3.3)
2,2',3,3',4,5',6,6'-octachlorobiphenyl	106(6.2)
2,2',3',4,6-pentachlorobiphenyl	105(3.2)
2,2',4,4'-tetrachlorobiphenyl	114(2.9)
2,4,5-trichlorobiphenyl	114(3.1)

1 n=3

2 Analyte recovery reported is from EPA published method. It was not included in the independent validation.

Spike levels = 2.0 µg/L

Table 2. Additional compounds validated by this method

Analyte	Ave %R (RSD)[1]	Analyte	Ave %R (RSD)[1]
Aspon	121(3.8)	Famphur	107(5.3)
Azinphos-methyl	93(3.2)	Fenthion	124(4.1)
Benfluralin	115(4.5)	Fluazifop-butyl	123(3.1)
Bolstar	117(4.1)	Fluchloralin	123(3.5)
Chloropropylate	103(3.0)	Fluometuron	99(3.9)
Clomazone	104(4.1)	Malathion	113(3.9)
Coumaphos	100(2.3)	Merphos	100(17)
Demeton	61(4.5)	1-methyl Naphthalene	93(4.5)
Desethylatrazine	26(3.0)	MGK-326	120(5.1)
Desisopropylatrazine[2]	102(NA)	Oxadiazon	115(2-9)
Dichlobenil	99(7.2)	Pendimethalin	123(7.1)
Dichlofenthion	123(3.2)	Phorate	97(4.1)
Dichloran	114(12)	Profluralin	127(11)
Dyfonate	104(3.5)	Propanil	100(4.2)
Ethelfluralin	97(2.3)	Tribufos (DEF)	107(3.8)
Ethion	115(3.6)		

1 Spike levels 2.0 µg/L, n=9

2 n=2