



Using Empore™ C18 SPE Disk to Extract SVOCs in Drinking Water Followed by GC-MS Analysis for EPA Method 525.2

Application Note

Environmental

Abstract

CDS Empore™ (formerly 3M™ 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 under EPA Method 525.2.

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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 0.03-2.4 µg/L and the recovery rate varies from 20 – 180% for each individual compound. However, 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 to 1 liter, and (2) low pH around 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 further analyzed by GC/MS.

The validation data presented herein was determined on three repeats of the same lot of C18 disks. MDLs were not determined as part of this validation.

Experimental Setup

Chemicals:

The 525.2 analytes were from AccuStandard (New Heaven, CT). Sodium sulfite was from Sigma-Aldrich (St. Louis, MO). Methylene chloride, Ethyl Acetate and Methanol were all high purity pesticide quality 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 and 5ml of methanol was added as a wetting agent. Each sample was fortified with 2 μ g of each internal standard and surrogate. For recovery data, each sample was fortified with 2 μ g of each method analyte. The CDS Empore™ 47mm C18-bonded silica disks (Part# 2215, Fisher Scientific™ 13-110-018/VWR™ 76333-132, CDS Analytical, Oxford, PA) were used for the extraction with repeated number n=3.

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.

GC/MS Analysis:

The extract analysis was performed on a Shimadzu GC-2010 Gas Chromatograph with a split/splitless injection portal interfaced to a Shimadzu GC-MS QP2010 (Kyoto, Japan) and a 30m x 0.25mm ID GsBP-5MS column with 0.25 micron film (General Separation Technologies, Newark, DE). GC-MS parameters are shown below:

GC Parameters:

Column: GS-Tek GsBP-5MS (30 m x 0.25 mm, ID x 0.25 μ m df)
Inlet Temp: 230 °C
TransferLine: 250 °C
Injection Mode: Splitless
Injection Volume: 1 μ L
Carrier Gas: He at 33 cm/sec (constant flow)
Oven Program: 45°C hold for 1 minute, 45°C to 130°C at 45°C/min, 130°C to 180°C at 12°C/min, 180°C to 240°C at 7°C/min, and 240°C to 320°C at 12°C/min
Hold for 4 minutes.

Mass Spectrometer Parameters

Solvent Delay: 3.0 minutes
Threshold: 0
Scan Range: 45-450
EM Voltage: 870
Sampling Rate: 2
Scans/sec: 3.3

Results and Discussions

Figure 1 showed the GC chromatogram of 102 semi-volatile compounds from EPA Method 525.2. It can be seen from Figure 1 that these compounds are well separated at the current experimental conditions.

Table 1 showed the recovery data of the 102 compounds in EPA Method 525.2 list studied in this experiment. The average recovery for 89 compounds exceeded 85% with average relative standard deviation (RSD) of 4.7%. The other 9 compounds had recovery between 70% to 84%, with average RSD of 7.8%. Together, 98 of 102 compounds in this study have the recovery rates falling into the range of 70% to 130%, required by EPA Method 525.2.

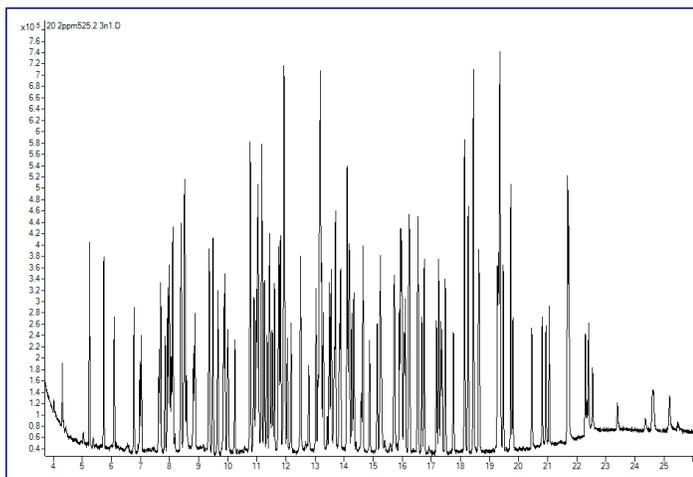


Figure 1. Chromatogram of 102 semi-volatile compounds from EPA 525.2 method.

There are only 4 compounds with recovery less than 70%: Atraton-58%, 2,4-Dinitrotoluene-42%, 2,6-Dinitrotoluene-45%, and Simetryn-65%. For Atraton, the recovery reported from EPA Method 525.2 is 44%, due to the low pH=2 condition for this extraction method. The recovery reported here is a little improved from that of the EPA Method, but to accurately determine its level in water samples, a separated method with pH neutral during the extraction is necessary to get recovery >90%. For 2,4-Dinitrotoluene and 2,6-Dinitrotoluene, the low recoveries are suspected from the breakthrough of C18 phases. Mark Krigbaum has done an excellent investigation on this phenomenon, and his explanation for this issue is credible³. The polarity of both dinitrotoluenes caused their poor retentions on the reversed C18 phases. The exact same extraction conditions in this note have been applied to Empore™ SDB-RPS disks, and both compounds showed recoveries >80% (results not shown here). SDB-RPS is a mixed phase to combine reversed phase and strong cation exchange phase (SCX) together. The SCX portion of the phase has better retention on these polar compounds through ionic interactions, thus improving the recovery dramatically. This result is consistent with the results observed by Mark Krigbaum³. The low recovery of Simetryn is due to the similar reason: the polar groups in diamino-1,3,5-triazine type compounds.

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. 102 organic compounds listed in the method have been effectively extracted from drinking water samples, and then quantified by GC-MS with concentration at 2.0 ppb. 89 compounds spiked into the water samples had the recovery rate exceeded 85% with average RSD of 4.7%, and 9 compounds have the recovery in the range of 70% to 84% with RSD around 7.8%, which are still good for a water quality test method. Together 98 of 102 compounds in this study have recoveries in the range of 70% -

130% per the request of EPA Method 525.2. There are only 4 compounds with recovery less than 70% observed in this study, and the reasons caused the low recovery for each compound have been reasonably explained, respectively.

In summary, excellent analyte recovery and very clean chromatograms can be obtained by using Empore™ C18 disks. The data supports that CDS Empore™ C18 disks are qualified for screening drinking water samples according to EPA Method 525, as well as monitoring phthalates, organochlorine pesticides, triazine herbicides, or PAHs in drinking water.

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)
3. Krigbaum, M., 1997, Evaluation of automated solid phase extractions of agrochemicals and industrial organic compounds from drinking water using U.S. EPA Method 525.2: American Environmental Laboratory, v. 9, no. 4, p. 12-14.

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

Analyte	Ave. %R (RSD) (n=3)	Analyte	Ave. %R (RSD) (n=3)
Acenaphthylene	86(4.1)	Endosulfan Sulfate	86(3.2)
Alachlor	91(3.7)	Endrin	91(3.7)
Aldrin	84(5.2)	Endrin Aldehyde	88(6.5)
Ametryn	85(7.5)	EPTC	91(3.1)
Anthracene	92(3.4)	Ethoprop	93(3.6)
Atraton	58(15.3)	Etridiazole	90(3.8)
Atrazine	90(3.8)	Fenamiphos	99(4.7)
Benz[a]anthracene	93(1.9)	Fenarimol*	150(5.5)
Benzo[b]fluoranthene	96(2.8)	Fluorene	94(3.7)
Benzo[k]fluoranthene	97(5.9)	Fluridone	113(4.8)
Benzo[g,h,i]perylene	121(12.1)	Heptachlor	88(4.6)
Benzo[a]pyrene	105(2.4)	Heptachlor epoxide	89(3.6)
BHC, alpha	89(5.2)	2,2',3,3',4,4',6-Heptachlorobiphenyl	91(3.6)
BHC, beta	87(4.4)	2,2',4,4',5,6'-Hexachlorobiphenyl	93(4.0)
BHC, delta	91(3.2)	Hexachlorobenzene	94(3.2)
BHC, gamma (Lindane)	97(3.3)	Hexachlorocyclopentadiene	86(3.5)
Bromacil	81(18.2)	Hexazinone	92(4.4)
Butachlor	91(3.3)	Indeno[1,2,3-cd]pyrene	118(5.8)
Butylate	91(3.3)	Isophorone	88(5.3)
Butylbenzylphthalate	120(9.4)	Methoxychlor	90(3.0)
Carboxin*	54(12)	Methyl Paraoxon	91(8.3)
Chlordane, alpha	88(3.5)	Metolachlor	91(2.1)
Chlordane, gamma	87(4.0)	Metribuzin	75(8.8)
Chlordane, trans nonachlor	87(3.9)	Mevinphos	80(7.0)
Chlorneb	90(4.2)	MGK-264	90(3.2)
Chlorobenzilate	90(6.7)	Molinate	91(4.0)
2-Chlorobiphenyl	92(3.4)	Napropamide	93(3.5)
Chlorpropham	93(3.9)	Norflurazon	94(3.9)
Chlorpyrifos	94(2.4)	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	90(5.2)
Chlorothalonil	89(3.5)	Pebulate	90(3.4)
Chrysene	92(1.8)	2,2',3',4,6-Pentachlorobiphenyl	93(3.0)
Cyanazine	89(5.2)	Pentachlorophenol	132(7.8)
Cycloate	92(3.7)	Permethrin, cis	90(8.2)
DCPA	90(4.2)	Permethrin, trans	91(8.3)
4,4'-DDD	89(5.6)	Phenanthrene	95(3.3)
4,4'-DDE	88(4.3)	Prometon	84(8.2)
4,4'-DDT	87(2.0)	Prometryn	90(7.0)
Diazinon*	109(6.8)	Pronamide	90(3.2)
Dibenz[a,h]anthracene	120(9.3)	Propachlor	92(4.8)
Di-n-Butylphthalateb	88(8.7)	Propazine	91(4.4)
2,3-Dichlorobiphenyl	94(3.5)	Pyrene	96(4.2)
Dichlorvos	81(6.7)	Simazine	83(6.8)
Dieldrin	91(3.3)	Simetryn	65(12.2)
Di(2-Ethylhexyl)adipate	108(9.5)	Stirofos	93(3.8)
Di(2-Ethylhexyl)phthalate	101(5.3)	Tebuthiuron	92(5.8)
Diethylphthalate	80(3.5)	Terbacil	78(8.7)
Dimethylphthalate	89(6.4)	Terbufos*	123(4.2)
2,4-Dinitrotoluene	42(6.7)	Terbutryn	89(4.5)
2,6-Dinitrotoluene	45(5.6)	2,2',4,4'-Tetrachlorobiphenyl	94(2.9)
Diphenamid	93(2.8)	Toxaphene*	ND
Disulfoton*	96(9.4)	Triademefon	97(3.8)
Disulfoton Sulfone*	164(2.8)	2,4,5-Trichlorobiphenyl	95(3.4)
Disulfoton Sulfoxide*	136(8.9)	Tricyclazole	97(7.2)
Endosulfan I	90(9.2)	Trifluralin	85(3.6)
Endosulfan II	88(2.9)	Vernolate	92(3.8)

Spike levels= 2.0 µg/L

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

ND=Not Determined