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

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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.

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. 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

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 2µg of each internal standard and surrogate. For recovery data, each sample was fortified with 2 µg of each method analyte. The CDS Empore™ 47mm C18-bonded silica disks (Part # 2215, CDS Analytical, Oxford, PA) were used for the extraction with repeated number n=3.

Methods:

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 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. Dry for 10 minutes.

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 $MeCl_2$.

10. Using a disposable pipette, rinse down the sides of the filtration glassware with two 3 mL aliquots of 1:1 EtAc/$MeCl_2$.

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/$MeCl_2$ 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 × 0.25 mm id × 0.25 µm df)
Inlet Temp.:	230 °C
Transfer Line:	250 °C
Injection Mode:	Splitless
Injection Volume:	1 µL
Carrier Gas Flow:	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 on GS-Tek GsBP-5MS column. It can be seen from Figure 1 that these compounds are well separated at the current experimental conditions.

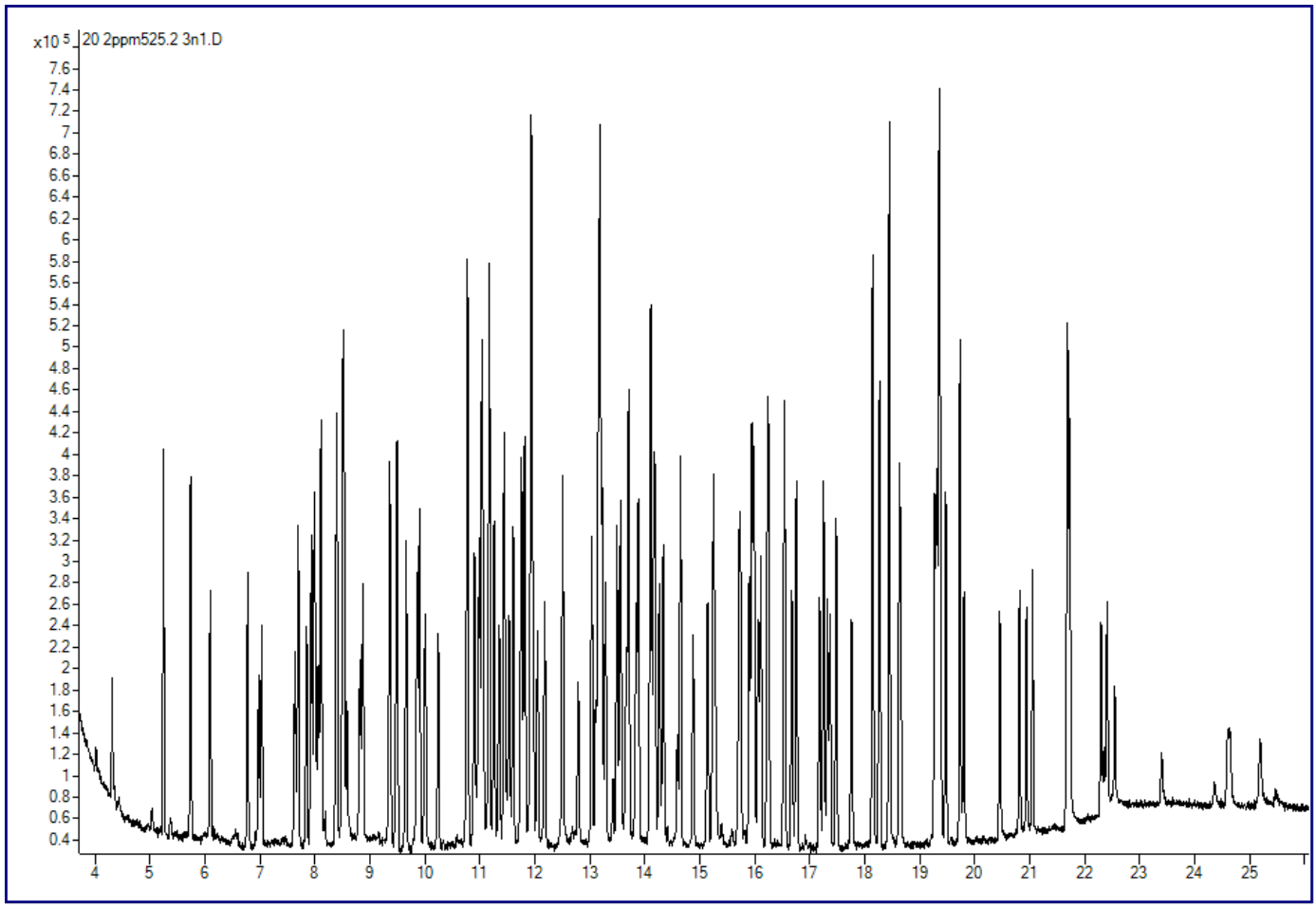

Figure 1. GC Chromatogram of 102 semivolatile compounds from EPA 525.2 method on GsBP-5MS column.

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.

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 credible[3]. 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

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

Analyte	Ave. %R (RSD) (n=3)
Acenaphthylene	86(4.1)
Alachlor	91(3.7)
Aldrin	84(5.2)
Ametryn	85(7.5)
Anthracene	92(3.4)
Atraton	58(15.3)
Atrazine	90(3.8)
Benz[a]anthracene	93(1.9)
Benzo[b]fluoranthene	96(2.8)
Benzo[k]fluoranthene	97(5.9)
Benzo[g,h,i]perylene	121(12.1)
Benzo[a]pyrene	105(2.4)
BHC, alpha	89(5.2)
BHC, beta	87(4.4)
BHC, delta	91(3.2)
BHC, gamma (Lindane)	97(3.3)
Bromacil	81(18.2)
Butachlor	91(3.3)
Butylate	91(3.3)
Butylbenzylphthalate	120(9.4)
Carboxin*	54(12)
Chlordane, alpha	88(3.5)
Chlordane, gamma	87(4.0)
Chlordane, trans nonachlor	87(3.9)
Chlorneb	90(4.2)
Chlorobenzilate	90(6.7)
2-Chlorobiphenyl	92(3.4)
Chlorpropham	93(3.9)
Chlorpyrifos	94(2.4)
Chlorothalonil	89(3.5)
Chrysene	92(1.8)
Cyanazine	89(5.2)
Cycloate	92(3.7)
DCPA	90(4.2)
4,4'-DDD	89(5.6)
4,4'-DDE	88(4.3)
4,4'-DDT	87(2.0)
Diazinon*	109(6.8)
Dibenz[a,h]anthracene	120(9.3)
Di-n-Butylphthalateb	88(8.7)
2,3-Dichlorobiphenyl	94(3.5)
Dichlorvos	81(6.7)
Dieldrin	91(3.3)
Di(2-Ethylhexyl)adipate	108(9.5)
Di(2-Ethylhexyl)phthalate	101(5.3)
Diethylphthalate	80(3.5)
Dimethylphthalate	89(6.4)
2,4-Dinitrotoluene	42(6.7)
2,6-Dinitrotoluene	45(5.6)
Diphenamid	93(2.8)
Disulfoton*	96(9.4)
Disulfoton Sulfone*	164(2.8)
Disulfoton Sulfoxide*	136(8.9)
Endosulfan I	90(9.2)
Endosulfan II	88(2.9)

Analyte	Ave. %R (RSD) (n=3)
Endosulfan Sulfate	86(3.2)
Endrin	91(3.7)
Endrin Aldehyde	88(6.5)
EPTC	91(3.1)
Ethoprop	93(3.6)
Etridiazole	90(3.8)
Fenamiphos	99(4.7)
Fenarimol*	150(5.5)
Fluorene	94(3.7)
Fluridone	113(4.8)
Heptachlor	88(4.6)
Heptachlor epoxide	89(3.6)
2,2',3,3',4,4',6-Heptachlorobiphenyl	91(3.6)
2,2',4,4',5,6'-Hexachlorobiphenyl	93(4.0)
Hexachlorobenzene	94(3.2)
Hexachlorocyclopentadiene	86(3.5)
Hexazinone	92(4.4)
Indeno[1,2,3-cd]pyrene	118(5.8)
Isophorone	88(5.3)
Methoxychlor	90(3.0)
Methyl Paraoxon	91(8.3)
Metolachlor	91(2.1)
Metribuzin	75(8.8)
Mevinphos	80(7.0)
MGK-264	90(3.2)
Molinate	91(4.0)
Napropamide	93(3.5)
Norflurazon	94(3.9)
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	90(5.2)
Pebulate	90(3.4)
2,2',3',4,6-Pentachlorobiphenyl	93(3.0)
Pentachlorophenol	132(7.8)
Permethrin, cis	90(8.2)
Permethrin, trans	91(8.3)
Phenanthrene	95(3.3)
Prometon	84(8.2)
Prometryn	90(7.0)
Pronamide	90(3.2)
Propachlor	92(4.8)
Propazine	91(4.4)
Pyrene	96(4.2)
Simazine	83(6.8)
Simetryn	65(12.2)
Stirofos	93(3.8)
Tebuthiuron	92(5.8)
Terbacil	78(8.7)
Terbufos*	123(4.2)
Terbutryn	89(4.5)
2,2',4,4'-Tetrachlorobiphenyl	94(2.9)
Toxaphene*	ND
Triademefon	97(3.8)
2,4,5-Trichlorobiphenyl	95(3.4)
Tricyclazole	97(7.2)
Trifluralin	85(3.6)
Vernolate	92(3.8)

Spike levels= 2.0 µg/L

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

ND=Not Determined

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 Krigbaum[3]. 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.