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APPLICATION NOTE

Extraction of a Full Suite of Semivolatile Compounds from Drinking Water using Automated Disk Solid Phase Extraction following Chinese Method SL 392-2007

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Key Words

SL 392-2007, SPE, solid phase extraction, drinking water

Introduction

Drinking water is a significant source of environmental exposure, especially for small children. Countries around the world have put regulations in place to monitor drinking water quality for a wide range of hazardous compounds. Methods such as SL 392-2007 in China, the EN methods in Europe and US methods such as method 525.2 cover a large suite of analytes of concern. They can be effectively extracted using solid phase extraction (SPE) disks and using GC/MS for detection.

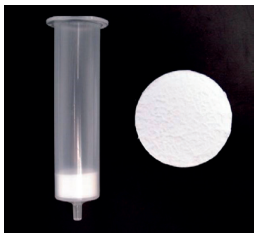

Figure 1. Disk and Cartridge formats next to each other

Chinese Method SL-392-2007 describes a procedure to determine a full suite of low concentration semivolatile organic compounds in drinking water using solid phase extraction (SPE) using a cartridge format.[1] The same sorbent material is available in disk format and provides advantages for larger water volumes and whole water, which may contain particulates. Because of the increased surface area as shown in Figure 1, the water passes through the disk more quickly and particles do not clog the system as easily. This application note will demonstrate the performance that can be obtained using a disk-based SPE method and following the requirement's of method SL 392-2007.

Instrumentation

- Horizon Technology, Inc.
  - SPE-DEX® 5000 Automated Extractor
  - DryVap® Concentration System
  - DryDisk® Separation Membranes
  - Atlantic® C18 High Capacity Disk

SPE-DEX 5000 Automated Extractor

The SPE-DEX 5000 was used for extraction of the analytes from the water samples. The SPE-DEX 5000 is an automated system that conditions the solid phase extraction disk, loads the sample through the disk, rinses the sample bottle and elutes the sample all without user intervention. The 47-mm disk holder was used with C18 disks . High capacity disks were used

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because some of the more water soluble compounds are better retained and suffer less breakthrough with this disk. Ethyl acetate and methylene chloride were used for elution.

The method run on the SPE-DEX 5000 is shown in Table 1. The method information, run time, sample identification and other information are stored in a file when the sample is run. This can be printed in a report or exported to the laboratory LIMS for archiving.

Method Summary

1. Obtain six 1-liter samples of drinking water.
2. Add dechlorinating agent to each 1-liter sample.
3. Acidify each 1-liter water sample to pH <2 using concentrated HCl.
4. Add surrogate and internal standard compounds into samples.
5. Start extraction method shown in Table 1 and collect extract (≈32 mL).
6. Add extract to the DryDisk holder and start automated drying and concentration process on the DryVap system (the DryVap system automatically dries and concentrates extract to 0.9 mL).
7. Quantitatively bring extract volume to 1.0 mL using methylene chloride once the extracts are evaporated to less than 1 mL.

Table 1. Extraction Method

Step	Solvent	Solvent Volume (mL)	Purge Time (s)	Pump Rate (#)	Sat. Time (s)	Soak Time (s)	Drain Time (s)	
1. Condition SPE Disk	Methylene Chloride	15	60	2	1	20	30	
2. Condition SPE Disk	Ethyl Acetate	11	60	2	1	20	30	
3. Condition SPE Disk	Methanol	11	60	2	1	60	2	
4. Condition SPE Disk	Reagent Water	9	30	2	1	5	5	
5. Condition SPE Disk	Reagent Water	9	60	2	1	30	0	
Step	Sample Flow Rate (#)			Done Loading Sample Delay (s)				
6. Load Sample	2			45				
Step	Dry Time (s)		Pump Rate (#)			N_2 Blanket		
7. Air Dry Disk Timer	60		6			Off		
Step	Solvent	Solvent Volume (mL)	Purge Time (s)	Pump Rate (#)	N2 Blanket	Sat. Time (s)	Soak Time (s)	Elute Time (s)
8. Elute Sample Container	Ethyl Acetate	8	60	2	Off	1	30	45
9. Elute Sample Container	Methylene Chloride	8	15	2	Off	1	30	45
10. Elute Sample Container	Methylene Chloride	8	15	2	Off	1	30	45
11. Elute Sample Container	Methylene Chloride	8	15	6	Off	2	30	60

8. Add external standard into the 1-milliliter extract.
9. Transfer the extract to a 2.0 mL GC vial.
10. Analyze by GC/MS.

Column	ZB Semi-volatiles, 30 m x 0.35 mm i.d., 0.25 µm film thickness (Phenomenex)		
Flow Rate	9 psig helium ramped up with the oven temperature to maintain a constant flow		
Temperature Ramp			
	Temperature (^{o}C)	Rate (^{o}C/min)	Hold (min)
	60	0	2.00
	270	20	0.00
	320	6	3.00

Gas Chromatography Mass Spectrometry System

The GC/MS used was a 6890 GC with a 5973 MSD (Agilent).
Total Run Time: 23.83 minutes
Injection Method: 1.0 µL injected, Temperature 280^{o}C , Pulsed splitless

- Inlet pulse pressure 25.0 psi for 1.00 min
- Purge flow to split vent 50 mL/min for @2.00 min

Results and Discussion

Six replicate laboratory fortified blanks (LFBs) were extracted as described in Chinese method SL 392-2007, following the procedure in the method summary in this note. Drinking water was spiked with standards and surrogates at a concentration of 5 µg/L.

The results are shown in Table 2 for each of the six replicate samples.

Table 2. Recoveries of Spiked Analytes in Drinking Water

Compound	Sample 1 (% Rec)	Sample 2 (% Rec)	Sample 3 (% Rec)	Sample 4 (% Rec)	Sample 5 (% Rec)	Sample 6 (% Rec)	AVG	RSD
Acenaphthene d10	70.0	73.0	77.6	81.0	75.0	76.8	75.6	5.06
Phenanthrene d10	75.6	84.2	88.0	95.4	84.4	85.8	85.6	7.49
Chrysene d12	77.0	83.8	90.2	98.2	84.0	86.0	86.5	8.25
2,4-Dinitrotoluene	113	112	109	110	112	109	111	1.44
2,6-Dinitrotoluene	113	112	108	109	113	107	110	2.49
2-Nitro-m-xylene	95.6	95.6	90.0	87.0	98.0	94.6	93.5	4.41
4,4'-DDD	94.4	93.8	94.0	90.4	94.0	93.6	93.4	1.58
4,4'-DDE	91.4	89.8	92.8	87.2	90.4	89.6	90.2	2.09
4,4-DDT	94.4	93.8	94.0	90.4	94.0	93.6	93.4	1.58
a-BHC	99.2	95.2	97.8	93.8	98.4	96.6	96.8	2.11
Acenaphthene	110	109	101	105	109	106	107	3.08
Acenaphthylene	95.6	95.6	93.8	90.2	98.0	97.0	95.0	2.91

Compound	Sample 1 (% Rec)	Sample 2 (% Rec)	Sample 3 (% Rec)	Sample 4 (% Rec)	Sample 5 (% Rec)	Sample 6 (% Rec)	AVG	RSD
Acetochlor	108	109	104	103	107	108	106	2.11
a-Chlordane	92.8	91.4	93.4	88.8	93.0	92.0	91.9	1.83
Alachlor	99.8	97.0	99.0	95.2	98.8	98.4	98.0	1.70
Aldrin	85.0	81.6	84.6	81.2	82.4	83.6	83.1	1.90
Ametryn	98.6	95.2	96.8	93.8	98.0	96.4	96.5	1.84
Atrazine	104	98.0	100	96.6	98	100	99.4	2.48
b-BHC	99.0	96.8	98.6	96.0	99.6	97.0	97.8	1.46
Benz(a)anthracene	89.2	87.6	89.0	85.4	88.6	88.8	88.1	1.63
Benzo(a)pyrene	73.8	74.0	76.2	70.4	74.8	75.4	74.1	2.72
Benzo(b)fluoranthene	95.0	93.8	95.4	89.0	92.0	92.0	92.9	2.56
Benzo(ghi)perylene	95.0	93.0	95.2	91.4	93.0	93.2	93.5	1.52
Benzo(k)fluoranthene	91.0	88.8	91.8	89.0	92.2	92.4	90.9	1.76
Bis(2-ethylhexyl)adipate	95.4	92.6	93.4	90.8	94.4	94.2	93.5	1.73
Bis(2-ethylhexyl)phthalate	96.0	94.0	95.0	92.4	94.8	95.4	94.6	1.34
Bromacil	105	103	104	100	104	102	103	1.81
Butaclor	98.0	98.4	97.6	92.6	100	97.4	97.4	2.61
Butyl benzyl phthalate	100	99.0	98.6	93.4	101	99.0	98.5	2.69
Butylate	103	101	101	97.0	104	101	101	2.41
Caffeine	82.4	88.8	77.2	78.0	84.8	79.0	81.7	5.52
Chlorobenzilate	101	101	99.2	95.4	104	102	100	2.84
Chloroneb	112	110	114	111	113	109	111	1.62
Chlorothalonil	107	105	106	101	107	105	105	1.91
Chlorpropham	125	122	119	122	122	121	122	1.56
Chlorpyrifos	101	95.0	101	96.2	98.6	98.2	98.3	2.45
Chrysene	92.8	90.8	92.8	89.2	91.8	91.6	91.5	1.49
cis-Permethrin	97.8	96.4	96.4	94.4	95.8	96.0	96.1	1.14
Cyanazine	104	99.4	101	98.2	101	100	101	1.93
Cycloate	113	111	110	110	113	110	111	1.32
Dacthal	99.0	96.4	98.6	95.2	99.6	97.8	97.8	1.71
d-BHC	99.6	97.6	101	96.0	100.2	97.4	98.6	1.86
Diazinon	92.8	89.8	90.2	88.0	91.6	91.0	90.6	1.82
Dibenz(ah)anthracene	92.2	91.6	92.2	92.8	91.6	95.6	92.7	1.62
Dichlorvos	119	115	110	112	119	115	115	3.11
Dieldrin	95.6	95.2	95.0	90.2	95.8	93.6	94.2	2.25
Diethyl phthalate	115	114	113	112	114	111	113	1.34
Dimethoate	81.0	90.0	72.8	77.2	82.2	80.0	80.5	7.11
Dimethyl phthalate	109	107	107	106	109	105	107	1.32

Compound	Sample 1 (% Rec)	Sample 2 (% Rec)	Sample 3 (% Rec)	Sample 4 (% Rec)	Sample 5 (% Rec)	Sample 6 (% Rec)	AVG	RSD
Di-n-butyl phthalate	101	98.8	100	95.0	99.6	98.2	98.9	2.20
Di-n-octyl phthalate	99.6	96.0	98.6	94.8	97.6	97.4	97.3	1.78
Diphenamid	101	98.0	98.8	95.4	100	97.6	98.5	2.05
Disulfoton	96.4	92.8	96.2	91.8	97.4	97.4	95.3	2.54
Disulfoton sulfone	102	103	99.6	97.4	105	102	102	2.64
Endosulfan I	97.8	92.8	97.0	93.4	97.0	93.4	95.2	2.37
Endosulfan II	96.6	97.6	98.8	92.2	98.6	95.2	96.5	2.58
Endosulfan Sulfate	99.2	99.8	98.8	95.4	101	100	99.1	2.06
Endrin	115	111	110	105	114	111	111	3.13
Endrin Aldehyde	88.8	88.4	84.4	81.6	89.4	84.8	86.2	3.60
Endrin Ketone	97.6	97.6	98.8	91.8	101	98.2	97.5	3.19
EPTC	107	104	99.4	99.4	107	104	103	3.24
Ethoprop	119	119	112	116	118	115	117	2.28
Etridiazole	107	107	105	103	110	106	106	2.27
Fenamiphos	116	119	108	109	119	117	115	4.45
Fenarimol	104	104	96.6	96.8	102	103	101	3.28
Fluoranthene	98.2	95.2	97.8	93.8	96.6	95.2	96.1	1.77
Fluorene	104	104	102	100	105	103	103	1.73
Fluridone	110	113	103	104	112	110	109	3.65
g-Chlordane	90.6	89.4	90.8	88.2	91.4	90.2	90.1	1.27
Heptachlor	96.4	91.0	95.6	92.6	94.2	94.8	94.1	2.12
Heptachlor epoxide A	96.8	92.2	95.2	91.0	93.8	92.4	93.6	2.29
Heptachlor epoxide B	96.2	95.2	98.0	92.6	96.8	94.0	95.5	2.05
Hexachlorobenzene	92.0	87.2	91.0	87.2	89.8	91.0	89.7	2.29
Hexazinone	100	100	98.0	94.6	101	100	99.1	2.49
Indeno(1,2,3-cd)pyrene	94.0	94.4	95.2	91.0	92.6	93.4	93.4	1.59
Isophorone	109	101	96.6	97.4	107	100	102	4.91
Lindane (g-BHC)	99.4	95.6	99.8	95.2	99.4	96.4	97.6	2.17
Malathion	117	116	108	110	115	117	114	3.43
Merphos	93.4	90.6	104	101	108	108	101	7.32
Methoxychlor	100	99.8	98.6	94.2	99.2	97.8	98.3	2.22
Methyl paraoxon	98.8	97.2	97	93.8	94.6	93.4	95.8	2.27
Metolachlor	102	99.4	100	97	102	99.4	100	1.98
Metribuzin	100	96.4	96.2	94.6	99.4	97	97.3	2.22
Mevinphos	127	124	116	122	126	122	123	3.24
MGK-264-A	96.0	94.6	95.8	92.6	97.2	96.0	95.4	1.66
MGK-264-B	96.0	94.6	95.8	92.6	97.2	96.0	95.4	1.66

Compound	Sample 1 (% Rec)	Sample 2 (% Rec)	Sample 3 (% Rec)	Sample 4 (% Rec)	Sample 5 (% Rec)	Sample 6 (% Rec)	AVG	RSD
Molinate	111	109	108	107	111	107	109	1.64
Naphthalene	89.6	89.8	86.8	80.2	92.0	90.4	88.1	4.81
Napropamide	102	101	98.6	94.2	103	100	99.8	3.09
Norflurazon	99.6	100	96.8	93.8	102	99.6	98.7	2.93
Pebulate	108	106	104	102	109	105	105	2.50
Pentachlorophenol	106	104	105	102	108	107	105	1.98
Perylene-d12	79.2	78.4	81.4	76.6	79.4	80.6	79.3	2.13
Phenanthrene	97.4	94.2	96.0	91.4	97.4	95.8	95.4	2.39
Prometon	79.2	76.6	79.8	73.4	75.2	77.6	77.0	3.15
Prometryn	99.4	95.6	97.4	94.4	97.8	97.0	96.9	1.80
Pronamide	100	96.6	98.8	95.4	99.4	98.0	98.0	1.79
Propachlor	115	112	112	112	113	110	112	1.37
Propazine	103	100	100	98	101	100	101	1.76
Pyrene	96.2	95.2	95.8	90.8	96.4	95.4	95.0	2.20
Pyrene-d10	95.8	94.6	95.6	90.2	96.8	93.8	94.5	2.47
Simazine	98.8	95.8	98.0	95.0	97.4	94.0	96.5	1.93
Simetryn	99.8	97.0	102	99.6	98.4	102	99.9	2.07
Stirofos	112	111	105	104	114	114	110	3.96
Tebuthiuron	120	121	110	118	120	118	118	3.25
Terbacil	119	117	112	111	118	116	115	2.96
Terbufos	122	114	121	110	113	106	115	5.43
Terbuthylazine	101	98.4	98.0	96.0	99.4	98.0	98.5	1.81
Terbutryn	101	98.4	100	96.2	100.6	99.6	99.3	1.74
Terphenyl-d14	130	119	111	102	119	116	116	7.97
Thiobencarb	101	99.6	95.4	96.8	98.6	99.8	98.6	2.16
trans-Nonachlor	92.6	92.0	92.6	89.4	92.8	91.2	91.8	1.42
trans-Permethrin	94.4	92.0	94.2	90.0	93.2	92.4	92.7	1.76
Triademefon	102	99.4	97.2	92.6	98.6	97.0	97.8	3.25
Tricyclazole	99.6	98.4	88.8	89.6	97.6	95.2	94.9	4.88
Trifluralin	110	108	107	107	108	107	108	1.11
Triphenylphosphate	101	101	99.0	95.0	102	101	99.8	2.58
Vernolate	106	105	101	100	109	104	104	3.09

The recoveries are within 70—130% in all cases for the more than 100 compounds measured. The precision was excellent and the relative standard deviations ranged between 2-3% for most of the analytes. Table 3 compares selected analyte data from method SL 392-2007 with the data obtained in this work. It can be seen that the data obtained with the SPE-DEX 5000 and the C18 disk are equivalent or better in terms of spike recoveries and relative standard deviation.

Table 3. Comparison of Data from the Method to that Acquired Here

	SL 392-2007		C18 HC Disk SPE-DEX 5000	
	% Recovery	%RSD	% Recovery	%RSD
2,4-Dinitrotoluene	99.3	2.94	111	1.44
Benzo(k)fluoranthene	83.1	2.17	90.9	1.76
Chrysene	85.8	1.00	91.5	1.49
Dichlorvos	121	3.01	115	3.11
Dieldrin	81.9	7.37	94.2	2.25
Heptachlor epoxide B	77.7	7.87	95.5	2.05
Pyrene	80.2	6.02	95.0	2.20

Conclusion

The Atlantic high-capacity C18 disks provided excellent recovery of the large suite of compounds extracted in water. The compounds included in the method had excellent performance and an average recovery of 98.8% was achieved with a 5 µg/L spike. The spike recovery criterion of 70-130% was achieved in all cases.

The SPE-DEX 5000 system provided uniform performance and a hands-off approach to the extraction step. The reproducibility of the six runs was excellent and the average of the relative standard deviation values was 2.6%. The Atlantic high-capacity C18 disk allowed even more water soluble compounds, such as caffeine, to be successfully retained with good recovery, further demonstrating the utility of solid phase extraction. In combination with the SPE-DEX 5000, the samples were reliably extracted with excellent precision. This data demonstrates that the equipment used in this study is capable of fully automating disk SPE technology for Chinese Environmental Method SL 392-2007 and that the resulting data is both accurate and precise.

References:

1. China Method SL 392-2007, Determination of Semivolatile Organic Compounds in Water by Solid Phase Extraction- Gas Chromatography (GC/MS).

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