Extraction of Semi-volatile Organic Compounds in Drinking Water with NEW Atlantic® ReadyDisk High Capacity C18 Solid Phase Extraction Disks

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Introduction

Drinking water is one of the primary sources of human exposure to toxic chemicals. The U.S. EPA identifies and regulates a number of compounds in drinking water that could pose health risks, and outlines methods for properly quantifying them. Contaminants can be biological, physical, chemical or radiological, and can exist in a wide range of concentrations. Therefore, the list of EPA methods that are approved for use in testing drinking water is extensive and each method presents its own challenges, based on the specific compounds being quantified.

EPA Method 525.2 is used to quantitate organic compounds found in drinking and source waters. Method 525.2 uses a reversed phase separation mechanism to isolate a large variety of compounds from the sample matrix. The reversed phase separation is achieved using a C18 bonded silica stationary phase which is packed into an SPE cartridge or disk. The C18 stationary phase allows for the extraction of semi-volatile compounds from the sample matrix which are then analyzed by gas chromatography-mass spectrometry (GC-MS).[1]

Instrumentation

All samples were analyzed using the instrumentation listed in Table 1 below.

Experimental

The organic compounds were eluted from the ReadyDisk with small quantities of ethyl acetate, followed by methylene chloride, followed by a 1 to 1 (v/v) mixture of ethyl acetate to methylene chloride. The extracted solution was dried and concentrated via solvent evaporation using the DryVap® with DryDisk® Separation Membranes.

The sample components were separated, identified, and measured using the gas chromatography/mass spectrometry (GC/MS) system listed in Table 1.

A summary of the overall sample preparation, extraction, drying and concentration procedure is listed below. A detailed overview of the method that was run on the Biotage® Horizon 5000 is listed in Table 2. The DryVap® and Agilent GC/MS parameters are listed in Table 3 and 4, respectively.

1. Obtain 1-liter samples of drinking water.
2. Add dechlorinating agent to each 1-liter sample.
3. Acidify each sample to pH <2 using concentrated HCl.
4. Add surrogate and internal standard compounds to each sample.
5. Start extraction method shown in Table 2 and collect all extracts (~20 mL each).
6. Add each extract to the DryDisk® holder and start automated drying and concentration process on the DryVap® system. Evaporate each extract to 0.9 mL using the method listed in Table 3.
7. Quantitatively, bring each extract volume to 1.0 mL using ethyl acetate.
8. Add external standard to each extract.
9. Transfer the extract to a 2.0 mL GC vial.

Table 1. Sample preparation and analysis systems and consumables.

Sample Preparation	
Solid Phase Extraction Disk	Atlantic® ReadyDisk HC-C18
Extraction System	Biotage® Horizon 5000
Drying/Concentration System	Biotage® Horizon DryVap® with DryDisk® Separation Membranes
Analysis	
GC/MS Instrument	Agilent 6890 with 5975C Inert GC/MSD

Table 2. Biotage® Horizon 5000 Extraction Program.

Step	Solvent	Solvent Volume (mL)	Purge Time (s)	Pump Rate (#)	Saturation Time (s)	Soak Time (s)	Drain Time (s)
1. Condition SPE Disk	Ethyl Acetate	20	60	2	1	0	45
2. Condition SPE Disk	Methylene Chloride	20	60	2	1	0	45
3. Condition SPE Disk	Methanol	20	60	2	2	60	10
4. Condition SPE Disk	Reagent Water	20	30	2	1	60	10

Step	Sample Flow Rate (#)	Done Loading Sample Delay (s)
5. Load Sample	2 (approximately 70 mL/min)	45

Step	Dry Time (s)	Pump Speed (#)	N_2 Blanket
6. Air Dry Disk Timer	600	6	OFF

Step	Solvent	Solvent Volume (mL)	Purge Time (s)	Pump Rate(#)	N_2 Blanket	Saturation Time (s)	Soak Time (s)	Drain Time (s)
7. Elute Sample Container	Ethyl Acetate	5	60	2	Off	1	60	45
8. Elute Sample Container	Methylene Chloride	5	60	2	Off	1	60	45
9. Elute Sample Container	1:1 EtOAc/MeCl	5	15	2	Off	1	60	45
10. Elute Sample Container	1:1 EtOAc/MeCl	5	15	6	Off	1	60	60

Table 3. DryVap® Conditions.

Parameters	Value
Drying Mechanism	DryDisk® (PN: 40-705-HT)
Dry Volume	100 mL
Heater Power	5
Heater Timer	Off (automatic endpoint mode used)
Auto Rinse	Off

Table 4. GC/MS Parameters.

Parameter	Value
Injection Volume	1 µL
Inlet Temperature	280 °C
Mode	Splitless
Gas Type	Helium
Column Conditions	ZB-SemiVol (Phenomenex), 30 m, 0.25 mm, 0.25 µm
Mode	Constant Flow 1 mL/min
Oven Program	60 °C hold for 2 minutes Ramp 20 °C/min to 270 °C Ramp 6 °C/min to 320 °C Hold for 3 minutes

Results and Discussion

Per EPA Method 525.2, a series of laboratory reagent blanks (LRBs) were measured to demonstrate a lack of contamination from the extraction system and the Atlantic® ReadyDisk HC-C18, prior to analyzing any samples. Six replicate LRBs were prepared and extracted as described in EPA Method 525.2, following the procedure in the method summary in this note. All blanks were spiked with internal standards such that their final concentration in solution was 5 µg/L. The results for the six LRBs are shown in Table 5 below.

To demonstrate an Initial Demonstration of Laboratory Accuracy and Precision (IDA and IDP), six replicates of a laboratory fortified blank (LFB) were prepared and extracted as described in EPA Method 525.2. Each replicate contained all analytes of interest, including internal standards and surrogates, at 5 µg/L. For each measured analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130 % and the RSD should be less than 30 %, per Method 525.2.[1] Results for the six samples are shown in Table 5 below.

Seven additional laboratory fortified blanks were prepared such that all analytes of interest were present at approximately 0.5 µg/L. All seven replicates were analyzed on three consecutive days to produce data for calculating method detection limits (MDLs).

Method Detection Limits (MDLs) were calculated based on the measured LFB solutions and are reported in Table 5 below. Results are based on the standard deviation of the replicate measurements, multiplied by the appropriate Student's t value for the 99 % confidence interval. Results are reported Not Detected (ND) if the measured concentration for all samples were below the lowest calibration point of 0.1 µg/L.

The method detection limits (MDL) were calculated using the formula[1]:

$$MDL = S \times t_{(n-1,\ 1\ alpha\ 0.99)}$$

Where:

t = Student's t value for the 99% confidence level (n-1,1-alpha = 0.99) with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses

Table 5. IDA and IDP, MDLs and LRB results for the Atlantic® ReadyDisk HC-C18.

Analyte	Average Recovery (%) n=6	RSD (%) n=6	MDL (µg/L) n=7	Blank (µg/L) n=6
Acenaphthene d10	78.8	4.44	-	4.06
Phenanthrene d10	82.2	4.44	-	4.31
Chrysene d12	79.3	8.09	-	3.94
Isophorone	106.3	1.96	0.04	ND
2-Nitro-m-xylene	90.2	3.91	0.09	ND
Naphthalene	78.9	8.42	0.09	ND
Dichlorvos	109.1	1.71	0.07	ND
Hexachlorocyclopentadiene	27.6	23.07	ND	ND
EPTC	105.8	1.70	0.04	ND
Mevinphos	111.5	1.09	0.10	ND
Butylate	101.0	2.18	0.05	ND
Vernolate	105.9	1.47	0.05	ND
Dimethyl phthalate	113.5	1.91	0.06	ND
Pebulate	105.5	1.51	0.04	ND
Etridiazole	97.1	2.38	0.07	ND
2,6-Dinitrotoluene	110.6	1.41	0.08	ND
Acenaphthylene	98.9	2.10	0.05	ND
Acenaphthene	109.0	2.51	0.06	ND
Chloroneb	111.5	2.00	0.10	ND
Tebuthiuron	101.4	1.68	0.10	ND
2,4-Dinitrotoluene	106.5	1.42	0.05	ND
Molinate	108.6	1.63	0.05	ND
Diethyl phthalate	114.7	1.83	0.21	0.04
Fluorene	104.1	1.30	0.06	ND
Propachlor	111.9	1.50	0.09	ND
Ethoprop	110.2	1.55	0.08	ND
Cycloate	110.5	1.59	0.05	ND
Chlorpropham	113.4	1.73	0.09	ND
Trifluralin	101.7	5.10	0.08	ND
a-BHC	110.7	1.46	0.05	ND
Atraton	25.3	28.64	ND	ND
Hexachlorobenzene	96.9	6.67	0.08	ND
Dimethoate	80.0	11.81	0.09	ND
Prometon	37.6	19.63	ND	ND
Lindane (g-BHC)	110.4	1.39	0.06	ND
Simazine	104.9	1.23	0.05	ND
Atrazine	104.7	1.82	0.07	ND
Propazine	108.3	1.18	0.04	ND
b-BHC	110.6	1.38	0.04	ND
Pentachlorophenol	98.2	2.04	0.04	ND
Terbuthylazine	104.9	2.31	0.04	ND
Terbufos	91.0	6.94	0.03	ND
Pronamide	106.3	1.36	0.03	ND
Diazinon	95.7	1.77	0.07	ND
d-BHC	107.8	1.81	0.02	ND
Phenanthrene	105.0	1.62	0.03	ND
Disulfoton	82.4	8.00	0.06	0.12
Methyl paraoxon	107.1	0.88	0.16	ND
Anthracene	78.4	11.40	0.07	ND
Terbacil	97.6	4.56	0.10	0.37
Chlorothalonil	109.8	2.99	0.05	ND
Caffeine	85.9	10.85	0.07	ND

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Analyte	Average Recovery (%) n=6	RSD (%) n=6	MDL (µg/L) n=7	Blank (µg/L) n=6
Acetochlor	103.3	2.39	0.07	ND
Metribuzin	110.6	1.62	0.08	ND
Simetryn	79.0	13.56	0.17	ND
Heptachlor	96.3	5.80	0.08	ND
Ametryn	89.5	9.39	0.20	ND
Alachlor	105.9	1.08	0.04	ND
Prometryn	95.3	6.61	0.21	ND
Terbutryn	92.8	7.42	0.18	ND
Di-n-butyl phthalate	105.4	1.78	0.06	ND
Bromacil	108.5	2.05	0.13	ND
Malathion	103.4	2.04	0.10	ND
Cyanazine	104.1	1.57	0.10	ND
Metolachlor	108.3	1.48	0.04	ND
Chlorpyrifos	101.6	4.05	0.08	ND
Thiobencarb	102.2	1.90	0.02	ND
Aldrin	96.5	7.04	0.09	ND
Triademefon	107.7	1.80	0.05	ND
Dacthal	104.3	1.73	0.04	ND
MGK-264-A	104.2	1.87	0.06	ND
Diphenamid	108.5	1.51	0.03	ND
MGK-264-B	104.2	1.87	0.06	ND
Merphos	110.2	2.08	0.61	ND
Heptachlor epoxide B	104.8	2.81	0.07	ND
Heptachlor epoxide A	102.1	4.64	1.07	0.07
Fluoranthene	101.6	4.42	0.04	ND
g-Chlordane	106.8	1.59	0.06	ND
Stirofos	113.2	5.49	0.11	ND
Disulfoton sulfone	113.9	5.80	0.10	ND
Butaclor	109.4	4.64	0.09	ND
a-Chlordane	106.2	1.58	0.06	ND
Endosulfan I	113.1	2.93	0.11	ND
Fenamiphos	113.2	5.15	0.12	ND
Pyrene-d10	105.5	1.59	-	ND
Pyrene	107.1	1.22	0.07	ND
Napropamide	119.8	5.79	0.10	ND
trans-Nonachlor	99.2	2.06	0.07	ND
4,4'-DDE	105.7	1.65	0.07	ND
Dieldrin	108.2	2.05	0.07	ND
Tricyclazole	97.0	5.88	0.12	ND
Terphenyl-d14	126.8	7.93	-	6.35
Carboxin	78.6	8.09	0.17	ND
Endrin	104.1	1.46	0.06	ND
Chlorobenzilate	108.9	5.29	0.10	ND
100) Endosulfan II	111.4	3.48	0.13	ND
4,4'-DDD	108.4	1.67	0.05	ND
Endrin Aldehyde	106.0	5.13	0.16	ND
Butyl benzyl phthalate	110.1	3.54	0.05	ND
Norflurazon	106.9	5.95	0.08	ND
4,4-DDT	108.4	1.67	0.05	ND
Endosulfan Sulfate	112.8	4.00	0.09	ND
Bis(2-ethylhexyl)adipate	103.6	2.16	0.14	ND
Hexazinone	111.4	4.51	0.07	ND
Triphenylphosphate	108.9	3.92	-	ND

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Analyte	Average Recovery (%) n=6	RSD (%) n=6	MDL (µg/L) n=7	Blank (µg/L) n=6
Endrin Ketone	117.6	3.92	0.09	ND
Methoxychlor	100.8	1.63	0.17	ND
Benz(a)anthracene	95.0	3.12	0.05	ND
Chrysene	102.6	2.11	0.04	ND
Bis(2-ethylhexyl)phthalate	104.2	2.06	0.11	ND
Fenarimol	111.0	6.23	0.11	ND
cis-Permethrin	99.5	2.27	0.13	ND
trans-Permethrin	102.3	1.91	0.12	ND
Di-n-octyl phthalate	106.4	2.05	0.07	0.17
Benzo(b)fluoranthene	100.5	2.36	0.07	ND
Benzo(k)fluoranthene	101.0	3.34	0.04	ND
Benzo(a)pyrene	83.5	6.57	0.11	ND
Fluridone	103.1	4.64	0.09	ND
Perylene-d12	79.1	8.55	-	ND
Indeno(1,2,3-cd)pyrene	86.7	5.29	0.16	ND
Dibenz(ah)anthracene	77.9	5.72	0.05	ND
Benzo(ghi)perylene	93.4	5.20	0.11	ND

Conclusion

With the exception of hexachlorocyclopentadiene, carboxin, atraton and prometon, all analytes were recovered within 70–130 % of the known value, in compliance with Method 525.2 criterion for spike recoveries. The average spike (including the problem compounds) recovered at 100.9 %.

Hexachlorocyclopentadiene's low recovery (27.6 %) can be attributed to the compound's sensitivity to thermal and photochemical degradation, as well as its propensity to react with acetone. The recovery of carboxin (78.6 %) can be attributed to its significant instability in water. The low recoveries for atraton and prometon of (25.3 % and 37.6 % respectively) likely stem from inefficient extraction from the water at pH 2, which causes ionization in solution under acidic conditions.[1]

The relative standard deviation for all compounds ranged from 0.88–28.6 %, below the method's RSD criteria of ‹30 %. The NEW Atlantic® ReadyDisk HC-C18 provided excellent analyte accuracy and precision in an easy-to-use, plug-n-play format.

References

1. United States Environmental Protection Agency, Method 525.2, Revision 2.0: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry.

Ordering Information

Part Number	Description	Quantity
47-6006	Atlantic® ReadyDisk HC-C18	Pk/24
40-705-HT	DryDisk® 65 mm	Pk/50

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