Extraction of Semi-volatile Organic Compounds in Drinking Water with NEW Atlantic® ReadyDisk 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 once evaporated to less than 1 mL.
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 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	10	60	2	1	0	45
2. Condition SPE Disk	Methylene Chloride	10	60	2	1	0	45
3. Condition SPE Disk	Methanol	10	60	2	1	60	5
4. Condition SPE Disk	Reagent Water	10	30	2	1	60	5

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	2	60	45
8. Elute Sample Container	Methylene Chloride	5	60	2	Off	2	60	45
9. Elute Sample Container	1:1 EtOAc/MeCl	3	15	2	Off	1	60	45
10. Elute Sample Container	1:1 EtOAc/MeCl	3	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 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.

To demonstrate an Initial Demonstration of Laboratory Accuracy and Precision (IDA and IDP), five 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 percent, per Method 525.2.[1] Results for the five samples are shown in Table 5.

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 C18.

Analyte	Average Recovery (%) n=5	RSD (%) n=5	MDL (µg/L) n=7	Blank (µg/L) n=6
Acenaphthene d10	78.0	8.08	-	4.30
Phenanthrene d10	82.6	7.72	-	4.72
Chrysene d12	81.5	9.59	-	4.72
Isophorone	95.2	6.08	0.13	N.D
2-Nitro-m-xylene	98.1	9.89	-	4.41
Naphthalene	84.6	10.33	0.13	N.D
Dichlorvos	93.8	5.48	0.16	N.D
Hexachlorocyclopentadiene	54.9	20.08	0.15	N.D
EPTC	106.3	5.07	0.08	N.D
Mevinphos	99.2	5.63	0.17	N.D
Butylate	99.1	7.56	0.10	N.D
Vernolate	107.0	6.12	0.10	N.D
Dimethyl phthalate	102.8	7.31	0.13	N.D
Pebulate	106.6	5.33	0.07	N.D
Etridiazole	101.2	8.09	0.06	N.D
2,6-Dinitrotoluene	71.0	7.02	0.18	N.D
Acenaphthylene	97.8	6.47	0.11	N.D
Chloroneb	110.3	7.85	0.11	N.D
Tebuthiuron	110.7	3.65	0.13	N.D
2,4-Dinitrotoluene	70.9	7.60	0.15	N.D
Molinate	111.2	5.98	0.08	N.D
Diethyl phthalate	113.8	7.23	0.20	N.D
Fluorene	103.8	6.91	0.12	N.D
Propachlor	112.2	7.03	0.14	N.D
Ethoprop	112.3	6.14	0.09	N.D
Cycloate	114.7	6.14	0.15	N.D
Chlorpropham	113.3	8.58	0.15	N.D
Trifluralin	102.7	10.39	0.12	N.D
a-BHC	106.7	6.56	0.09	N.D
Atraton	42.0	9.72	0.18	N.D
Hexachlorobenzene	99.9	7.54	0.15	N.D
Prometon	54.6	7.77	0.11	N.D
Lindane (g-BHC)	107.2	9.38	0.12	N.D
Simazine	92.5	6.15	0.22	N.D
Atrazine	102.3	5.99	0.12	N.D
Propazine	101.0	5.37	0.09	N.D
b-BHC	105.2	8.34	0.10	N.D
Pentachlorophenol	101.6	11.08	0.08	N.D
Terbufos	105.7	5.80	0.16	N.D
Pronamide	105.8	5.85	0.09	N.D
Diazinon	92.8	6.19	0.15	N.D
d-BHC	106.5	7.94	0.10	N.D
Phenanthrene	105.8	5.64	0.11	N.D
Disulfoton	105.4	4.66	0.13	0.15
Methyl paraoxon	104.6	6.38	0.11	N.D
Anthracene	95.4	7.30	0.22	N.D
Terbacil	102.3	9.11	0.18	0.30
Chlorothalonil	107.6	7.03	0.06	N.D
Metribuzin	85.8	7.89	0.23	N.D
Simetryn	75.4	9.95	0.17	N.D
Heptachlor	100.6	6.85	0.12	N.D
Ametryn	88.8	9.40	0.19	N.D

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Analyte	Average Recovery (%) n=5	RSD (%) n=5	MDL (µg/L) n=7	Blank (µg/L) n=6
Alachlor	106.8	6.43	0.09	N.D
Prometryn	94.2	8.93	0.18	N.D
Terbutryn	93.6	8.97	0.19	N.D
Di-n-butyl phthalate	107.5	6.81	0.07	N.D
Bromacil	97.0	8.92	0.18	N.D
Cyanazine	103.3	7.60	0.16	N.D
Metolachlor	108.0	6.91	0.08	N.D
Chlorpyrifos	105.6	7.06	0.11	N.D
Aldrin	95.8	7.80	0.28	N.D
Triademefon	104.9	5.85	0.08	N.D
Dacthal	105.0	7.21	0.09	N.D
MGK-264-A	103.4	6.75	0.11	N.D
Diphenamid	110.0	6.21	0.08	N.D
MGK-264-B	103.4	6.75	0.11	N.D
Merphos	108.7	11.42	0.18	N.D
Heptachlor epoxide B	103.1	8.56	0.07	N.D
Heptachlor epoxide A	103.8	8.42	0.18	N.D
Fluoranthene	104.1	6.36	0.09	N.D
g-Chlordane	101.2	7.69	0.10	N.D
Stirofos	115.0	8.56	0.11	N.D
Disulfoton sulfone	112.8	8.77	0.10	N.D
Butaclor	107.5	8.87	0.10	N.D
a-Chlordane	101.7	8.75	0.11	N.D
Endosulfan I	102.9	9.88	0.12	N.D
Fenamiphos	116.6	9.55	0.13	N.D
Pyrene-d10	103.5	9.46	-	4.78
Pyrene	104.6	7.05	0.11	N.D
Napropamide	111.5	6.93	0.14	N.D
trans-Nonachlor	96.3	10.26	0.08	N.D
4,4'-DDE	101.8	7.95	0.09	N.D
Dieldrin	105.5	6.63	0.11	N.D
Tricyclazole	95.0	3.38	0.19	N.D
Terphenyl-d14	120.6	7.49	-	5.29
Carboxin	80.8	10.80	0.21	N.D
Endrin	101.4	8.71	0.14	N.D
Chlorobenzilate	104.5	13.57	0.09	N.D
Endosulfan II	105.6	9.63	0.16	N.D
4,4'-DDD	107.2	6.09	0.09	N.D
Endrin Aldehyde	95.6	4.19	0.14	N.D
Butyl benzyl phthalate	111.5	8.20	0.09	N.D
Norflurazon	109.7	6.91	0.10	N.D
4,4-DDT	107.1	6.18	0.09	N.D
Endosulfan Sulfate	109.8	10.63	0.14	N.D
Bis(2-ethylhexyl)adipate	108.5	7.88	0.10	N.D
Hexazinone	108.4	7.22	0.13	N.D
Triphenylphosphate	111.7	11.64	-	5.00
Endrin Ketone	110.8	10.55	0.11	N.D
Methoxychlor	107.4	10.59	0.08	N.D
Benz(a)anthracene	104.1	6.26	0.14	N.D
Chrysene	106.0	7.88	0.10	N.D
Bis(2-ethylhexyl)phthalate	112.1	11.09	0.22	0.02
Fenarimol	110.5	7.72	0.08	N.D
cis-Permethrin	106.3	7.77	0.10	N.D

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Analyte	Average Recovery (%) n=5	RSD (%) n=5	MDL (µg/L) n=7	Blank (µg/L) n=6
trans-Permethrin	107.6	9.75	0.10	N.D
Di-n-octyl phthalate	107.4	8.48	0.08	N.D
Benzo(b)fluoranthene	106.8	7.28	0.09	N.D
Benzo(k)fluoranthene	105.4	6.50	0.09	N.D
Benzo(a)pyrene	98.4	6.97	0.29	N.D
Fluridone	111.3	6.00	0.09	N.D
Perylene-d12	91.7	11.88	-	3.88
Indeno(1,2,3-cd)pyrene	102.4	6.76	0.10	N.D
Dibenz(ah)anthracene	102.3	6.08	0.12	N.D
Benzo(ghi)perylene	103.7	7.86	0.12	N.D

Conclusion

With the exception of hexachlorocyclopentadiene, 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 low-recovering compounds) recovered at 101.1%. Hexachlorocyclopentadiene's low recovery (54.9%) can be attributed to the compound's sensitivity to thermal and photochemical degradation, as well as its propensity to react with acetone. The low recoveries for atraton and prometon (42.0% and 54.6%, respectively) likely stem from inefficient extractions from the water at pH 2, which causes ionization in solution under acidic conditions.[1] The relative standard deviation for all compounds ranged from 3.38– 20.08%, below the method's RSD criteria of <30%. The NEW Atlantic® ReadyDisk 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
47-6005	Atlantic® ReadyDisk C18	Pk/24
40-705-HT	DryDisk® 65 mm	Pk/50

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