Determination of Semi-Volatile Organic Compounds in Water Using the Oasis® HLB SPE Disk and Carbon Cartridge for EPA Method 8270D

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Introduction

The purpose of this application note is to demonstrate the use of a fully automated solid phase extraction and concentration system that provides fast extraction while improving the quality and consistency of results for EPA Method 8270D.

EPA Method 8270D is used to determine neutral, acidic, and basic semi-volatile organic compounds that are soluble in methylene chloride. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

The Oasis® HLB (Hydrophilic-Lipophilic Balanced) solid phase extraction disk is able to retain the large list of organic semi-volatile compounds through its unique ratio of hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene sorbent. The Oasis® HLB sorbent has a number of key features that enable it to carry out the extraction, including stability at pH extremes and in a wide range of solvents, extraordinary retention of polar compounds, and a hydrophobic retention capacity 3X higher than that of traditional silica-based SPE sorbents.

The carbon cartridge captures the more volatile compounds that are not able to be retained by the Oasis® HLB disk; such as N-Nitrosodimethylamine (NDMA), Pyridine, 2-Picoline, N-Nitrosomethylethylamine, Methylmethane sulfonate, N-Nitrosodiethylamine and Ethylmethane sulfonate.

The SPE-DEX® 4790 provides automatic extraction of liquid samples by solid phase extraction methods. It can handle samples from 20mL to 4L. The Envision™ Platform provides a user-friendly, web-based controller capable of interacting with up to eight extractors via a standard PC. The DryVap™ Concentrator System provides automatic sample drying with a patented membrane technology (DryDisk™) and automatically concentrates each dried extract by applying heat, vacuum, and sparge flow for up to six samples at one time.

The Reclaimer™ SRS (Solvent Recovery System) is designed to handle the volume of solvent vapor generated from the DryVap™ Concentrator System while in operation. These automated systems are specifically designed to streamline the sample handling required for the preparation and analysis of environmental samples

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, with the Envision Platform Controller, DryVap™ Concentration System, and the Reclaimer™ Solvent Recovery System

Instrumentation

- Horizon Technology SPE-DEX® 4790 Automated Extractor System
- Dual pH Kit
- Carbon Cartridge Kit
- Carbon Cartridge
- Oasis® HLB SPE Disks (47mm)
- Horizon Technology Envision™ Platform (hardware/software system to control extractors)
- Horizon Technology DryVap™ Concentrator System
- DryDisk™ Separation Membranes
- Horizon Technology Reclaimer™ (Solvent Recovery System)
- Agilent 6890 GC
- Agilent 5973 Mass Selective Detector

Method Summary

1) Adjust 1L aqueous sample to pH 2 with HCl, cap the bottle and mix.
2) Spike 8270 surrogate into samples.
3) Spike 8270 compounds into samples (50µg/ml spike was used).
4) Place a small piece of aluminum foil over the opening of the bottle and screw on the bottle cap adaptor.
5) Install a water collection bottle to the water waste line.
6) Remove the original water waste line from the rear panel of the SPE-DEX® 4790.
7) Attach one end to the water collection bottle and the other end to the water waste collection bottle.
8) Attach one end of Teflon tube to the water waste fitting on the rear panel of the SPE-DEX® 4790 and connect the other end to the water collection bottle.
9) Load the disk holder with the Oasis® HLB 47mm disk.

10) Place a clean VOA vial or equivalent receiver onto the extractor.
11) Load the pH 2 sample onto the SPE-DEX® 4790.
12) Start the EPA Method 8270D extraction method and collect extract at high vacuum at -25 in. Hg.
13) Collect extract (approximately 20 mLs.)
14) Cap and label extract as acid portion

pH 12 Extraction

1) Adjust the collected water to pH 12 with NaOH and mix.
2) Mount the carbon cartridge perch to the side of the extractor shelf by tightening the thumbscrew.
3) Then press the cap into the top of the carbon cartridge and place into the perch.
4) Insert the carbon cartridge with the cap into the perch
5) Attach the water waste line with the tube clamp on it to the cap on the carbon cartridge.
6) Attach the other water waste line from the extractor to the tip of the carbon cartridge.
7) Place a clean VOA vial or 125 ml erlenmeyer flask on the extractor.
8) Place a piece of aluminum foil and the bottle cap adaptor onto the pH 12 sample and load onto the SPE-DEX® 4790.
9) Load EPA Method 8270D, and process the sample using the same Oasis® HLB disk as used in the acidic portion. Collect extract at high vacuum at -25 in Hg.
10) Collect extract approximately 20 mLs.
11) Cap and label extract as base portion. If the flask was used the base extract can be combined with the carbon extract.

Cartridge Elution

1) Load EPA Method 8270 carbon onto the SPE-DEX® 4790.
2) Remove the disk holder with the Oasis® HLB disk from the SPE-DEX® 4790.
3) Disconnect the lines from the carbon cartridge and remove it from the perch.
4) Reconnect the waste lines removed from the carbon cartridge.
5) Remove the cap from the carbon cartridge and install the funnel in its place.
6) Install the carbon cartridge / funnel assembly onto the SPE-DEX® 4790 for elution.
7) Elute the carbon cartridge using the EPA Method 8270 carbon method into the 125 mL flask.

Concentration

1) Assemble the DryDisk™ reservoir with a DryDisk™ Separation Membrane and start the concentration process by adding the acid portion into the DryDisk™ tube.
2) Once the acidic portion filters through the DryDisk™ manually rinse the DryDisk™ reservoir with methylene chloride. Once the methylene chloride has filtered into the concentration tube press stop on the Dry Vap™.
3) Clean the DryDisk™ reservoir by emptying out the water and then rinsing the reservoir out with acetone.
4) Then load the DryDisk™ reservoir back onto the DryVap™ Concentration System and start the base/carbon concentration process using the same conditions.
5) Once the basic/carbon portion filters through the DryVap™ manually rinse the DryDisk™ reservoir with methylene chloride.
6) Concentrate the extract to less than 1.0 mL (DryVap™ concentration vessels are graduated to 0.5 mL and 1.0 mL).
7) Rinse the sides of the concentrator tube with methylene chloride and bring the extract up to 1.0 mL.
8) Transfer the extract to a GC vial.
9) Analyze by GC/MS.

GC/MS Method

Agilent 6890 GC with an Agilent 5973 Mass Selective Detector

Column: DB5MS, 30m x 0.25mm ID, 0.25µm

Flow rate: 9 psig helium which is ramped up with the oven temp to maintain a constant flow.

Temp. Ramp

Temp (°C)	Rate (°C/Min)	Hold (Min)
45	0	1.00
270	15	0.00
320	6.0	0.00

Total run time: 24.33 min

Injection Method: Split, Ratio 1:10, 1.0µL injected

Temp (°C)	Rate (°C/Min)	Hold (Min)
280	0	0.00

Table 1. The 8270D Method: Programmable Into the Envision™ Platform Controller.

STEP	SOLVENT	SOAK TIME	DRY TIME
Prewet #1	Acetone	30 Sec	15 Sec
Prewet #2	Acetone	30 Sec	15 Sec
Prewet #3	Reagent Water	10 Sec	2 Sec
Prewet #4	Reagent Water	10 Sec	2 Sec
Sample Process			
Air Dry			30 Sec
Rinse Step #1	Acetone	3:00 Min	20 Sec
Rinse Step #2	Methylene Chloride	3:00 Min	20 Sec
Rinse Step #3	Methylene Chloride	1:00 Min	20 Sec
Rinse Step #4	Methylene Chloride	1:00 Min	20 Sec
Rinse Step #5	Methylene Chloride	1:00 Min	60 Sec

Table 2. The 8270 Carbon Cartridge Method: Programmable Into the Envision™ Platform Controller.

STEP	SOLVENT	SOAK TIME	DRY TIME
Airdry			5:00 Min
Rinse Step #1	Acetone	1:00 Min	0 Sec
Rinse Step #2	Acetone	1:00 Min	1:00 Min
Rinse Step #3	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #4	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #5	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #6	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #7	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #8	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #9	Methylene Chloride	1:00 Min	3 Sec
Rinse Step #10	Methylene Chloride	1:00 Min	1:00 Min

Table 3. Conditions used for the DryVap™ Concentrator System

PARAMETER	SETTING
Dry Volume	20
Heat Power	5
Auto Rinse Mode	OFF
Heat Timer	OFF
Nitrogen Sparge	20 psig Vacuum @ -12 in Hg.

Results

The results for the selected EPA Method 8270D compounds are listed in Table 4, which shows the compound names and percent recovery. Figure 1 is a chromatogram of the selected EPA Method 8270D compounds run on the GC/MS. Horizon Technology's fully automated solid phase extraction system with the Oasis® HLB SPE disk and carbon cartridge had a recovery range between 34-113% for one hundred and five compounds.

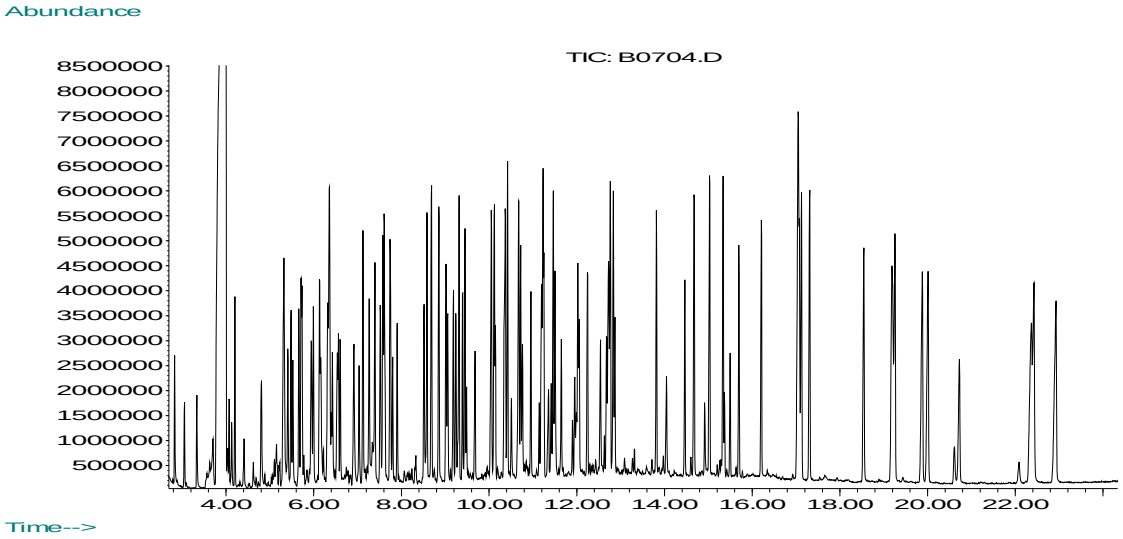
Table 4. Concentration and % Recovery of Compounds:

Compound Name	% Recovery
N-Nitrosodimethylamine (NDMA)	52.04
Pyridine	44.33
2-Picoline	65.11
N-Nitrosomethyl ethylamine	73.32
Methylmethane sulfonate	64.53
2-Flourophenol	79.44
N-Nitrosodiethylamine	76.61
Ethylmethane sulfonate	83.78
Phenol-d6	73.73
Phenol	86.73
Aniline	53.22
Bis(2-chloroethyl)ether	81.39
Pentachloroethane	78.03
2-Chlorophenol	86.55
1,3-Dichlorobenzene	77.94
2,4,6-Trichlorophenol	88.32
2,4,5-Trichlorophenol	85.22
2-Fluorobiphenol	90.19
2-Chloronapthalene	91.75
2-Nitroaniline	90.46
Dimethylphthalate	93.18
2,6-Dinitrotoluene	93.08
Acenaphthylene	89.97
3-Nitroaniline	66.04
Acenaphthene	92.12
2,4-Dinitrophenol	83.30
Pentachlorobenzene	88.28
4-Nitrophenol	94.73
Dibenzofuran	92.81
2,4-Dinitrotoluene	94.18
2,3,4,6-Tetrachlorophenol	89.41
1,4-Dichlorobenzene	78.91
1,2-Dichlorobenzene	80.24
Benzyl alcohol	83.76
2-Methyl phenol	87.04
Bis(2-chloroisopropyl)ether	87.45
Acetophenone	88.32
3+4 Methyl phenol	77.92
N-nitroso-di-n-propylamine	88.40
Hexachloroethane	77.13
o-toluidine	83.04
Nitrobenzene-d5	87.93
Nitrobenzene	85.37
N-Nitrosopiperidine	92.64
Isopherone	91.43
2-Nitrophenol	86.39
2,4-Dimethylphenol	91.04
Bis(2-chlorethoxy)methane	88.59
Benzoic acid	94.45
2,4-Dichlorophenol	85.71
1,2,4-Trichlorobenzene	84.51
Napthalene	87.84
2,6-Dichlorophenol	87.48
4-Chloroaniline	73.18
Hexachloropropene	57.82
Hexachlorobutadiene	80.30
N-nitroso-di-n-butylamine	90.85
4-Chloro-3-methylphenol	91.04
2-Methylnapthalene	89.82
Hexachlorocyclopentadiene	101.81
1,2,4,5 -Tetrachlorobenzene	85.87

Compound Name	% Recovery
2-Napthylamine	49.46
1-Napthylamine	42.32
Diethyl phthalate	95.75
Fluorene	94.80
4-Chlorophenyl phenyl ether	91.72
4-Nitroaniline	78.89
5-nitro-o-toluidine	70.75
4,6-Dinitro-2-methylphenol	90.00
Diphenylamine	93.56
Azobenzene	91.38
2,4,6-Tribromophenol	89.15
1,3,5,-Trinitrobenzene	92.13
Phenacetan	89.71
4-Bromophenyl phenyl ether	89.54
Hexachlorobenzene	87.29
Pentachlorophenol	88.03
Pentachloronitrobenzene	86.83
4-Aminobiphenyl	34.58
Dinoseb	89.05
Phenanthrene	89.78
Anthracene	90.46
Carbazole	89.85

Compound Name	% Recovery
Di-n-butyl phthalate	90.77
4-Nitroquinoline-1-oxide	39.87
Methapyrilene	60.47
Fluoranthene	88.62
Benzidine	113.08
Pyrene	88.89
p-Terphenyl-d14	88.80
Dimethylaminoazobenzene	92.46
3,3`Dimethylbenzidine	45.29
Butyl benzyl phthalate	91.21
3,3'-Dichlorobenzidine	59.29
Benz(a)anthracene	88.72
Chrysene	90.86
Bis(2-ethlyhexyl)phthalate	94.20
Di-n-octyl phthalate	89.90
7,12-Dimethylbenz(a)anthra	77.79
Benzo(b)fluoranthene	85.60
Benzo(k)fluoranthene	89.98
Benzo(a)pyrene	86.29
Indeno(1,2,3-cd)pyrene	87.49
Dibenz(ah)anthracene	87.75
Benzo(ghi)perylene	91.64

Figure 1. Chromatogram of selected 8270D compounds analyzed on a GC/MS after being extracted and concentrated on Horizon Technology fully automated extraction and concentration systems.



Conclusion

This data demonstrates that Horizon Technology automated SPE systems, Oasis® HLB disk, and the carbon cartridge are capable of fully automating selected EPA Method 8270D compounds, resulting in data that is both accurate and precise. Extraction times were typically 30 min for each pH portion and drying and concentrating times were approximately 40 minutes. The SPE-DEX® 4790 Automated Extractor System with the Envision™ Platform, DryVap™ Concentrator System and Reclaimer SRS reduces analyst labor, solvent usage, turnaround time, and improves accuracy and precision.