EPA 500 Series

Application Notebook

Pulished 2012

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Cartridge-Based

SmartPrep Automated Extractor

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The Extraction of Diquat and Paraquat for EPA Method 549.2 Using the SmartPrep Automated Cartridge Extractor

Alicia Cannon and Brian LaBreque, Horizon Technology, Inc., Salem, NH

Introduction

Diquat and paraquat are some of the most widely used and available herbicides in the world. They are fast-acting, non-selective quaternary amines used mainly in the agricultural industries to control the penetration of invasive plants and increase crop yield.

However, both diquat and paraquat have been proven to be toxic to humans upon exposure. This toxicity and wide availability has led to instances where individuals have issued fatal doses to humans. In turn, this has led to strict guidelines worldwide involving the use of diquat and paraquat in the agricultural community.

This Application Note will outline the process used to extract diquat and paraquat from water samples using the SmartPrep Automated Solid Phase Cartridge Extractor. It will specifically focus on the extraction of the samples needed for an initial demonstration of capability (IDC) according to the procedure outlined by the US Environmental Protection Agency in method 549.2. It will also illustrate that, although method 549.2 recommends that all glassware be silanized, excellent recoveries can be achieved even if the glass syringe barrel on the SmartPrep was not.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 20 mL Tray
- Phenomenex
  - Strata C8 cartridges, 500 mg, 6 mL
  - Spherisorb 3 µm C8 80 Å, 100 x 4.6 mm
- Agilent 1100 Series LC with attached DAD

Method Summary

Preparation of Solvents

1. Conditioning Solution A: Dissolve 0.500 g of cetyl trimethyl ammonium bromide and 5 mL of concentrated ammonium hydroxide in 500 mL of deionized water and dilute to 1000 mL in a volumetric flask.[1] Please note that this solvent may crystallize and should be replaced often to prevent this phenomenon.
2. Conditioning Solution B: Dissolve 10.0 g of 1-hexanesulfonic acid, sodium salt and 10 mL of concentrated ammonium hydroxide in 250 mL of deionized water and dilute to 500 mL in a volumetric flask.[1]
3. Elution Solvent: Add 13.5 mL of orthophosphoric acid and 10.3 mL of diethylamine to 500 mL of deionized water and bring to a final volume of 1000 mL in a volumetric flask.[1]

The Horizon Technology SmartPrep Automated Cartridge Extractor.

4. Ion-Pair Concentrate: Dissolve 3.75 g of 1-hexanesulfonic acid into 15 mL of Elution Solvent and bring to a final volume of 25 mL.[1]
5. Mobile Phase: Add 13.5 mL orthophosphoric acid, 10.3 mL of diethylamine, and 3.0 g of 1-hexanesulfonic acid, sodium salt to 500 mL of deionized water. Bring to a final volume of 1 liter.[1]

Sample Preparation

1. Prepare five aliquots of reagent water measuring 250 mL each (containers were HDPE).
2. Prepare one aliquot as a laboratory fortified blank (LRB).
3. The remaining four aliquots prepare as laboratory fortified blanks (LFBs). Prepare each aliquot by adding 5 µL of a stock standard (at 1000 mg/mL) for a sample concentration of 100 µg/L.
4. Verify the pH and, if needed, adjust the pH to between 7.0 and 9.0 using 10% w/v NaOH or 10% v/v HCl.

SmartPrep Automated Extraction

1. Ensure that all reagents are filled.
2. Ensure that all waste containers are empty.
3. Load a Cleaning Cartridge onto position 21 of the carousel.
4. Load five C8 cartridges onto the carousel into positions 1 through 5.
5. Load five 20 mL HDPE Scintillation vials without their caps onto the tray in positions corresponding to those of the carousel.
6. Place the samples onto the Sample Rack and ensure that a Sip Tube is in place in the lower corner of the sample container.
7. Run the Method given in Table 3 below and collect approximately 4.5 mL of extract at 45 minutes per sample.

8. Add 100 µL of an Ion-Pair Concentrate
9. Bring the sample to a final volume of 5 mL using the Elution Solvent.
10. Analyze the sample by HPLC using the conditions given in Table 1 below.

Table 1: Analysis Conditions

Column Flow: 1.0 mL/min
Solvent: 100% 549.2 Mobile Phase (isocratic)
Spectra Start: 210 nm
Spectra End: 370 nm
Spectra Step: 1 nm
Injection Volume: 20 µL

Results

The minimum quality control requirements set forth in EPA Method 549.2 start with the production of an IDC. To be considered in control, at least four laboratory fortified blanks (LFBs) must be prepared at a concentration of 100 ug/L each. The recoveries and relative standard deviation (RSD) must be within ± 30% and less than 30% respectively for the study.

The results of the extractions performed for this study are given below in Table 2 and a sample spectrum is shown in Figure 1. Both diquat and paraquat were recovered at concentrations higher than 90% and the RSDs were less than 5%. Total extraction times per sample were 2 hours and 20 minutes on average.

Conclusions

The resulting data from the analysis performed proves that the SmartPrep Automated Extractor is an excellent choice for those wishing to extract diquat and paraquat from water matrices regardless of the non-silanized syringe barrel. By using automated extraction techniques, a laboratory can decrease the labor and materials associated with each sample saving both time and money.

References

1. Munch, J.W. and Bashe W.J., **"**Method 549.2-Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection", National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, 45268,1997.

Table 2: Method 549.2 IDC Results

	LRB (ppm)	LFB (%)	LFB (%)	LFB (%)	LFB (%)	Average (%)	RSD (%)
Diaquat	0.01	98.69	92.21	92.30	97.58	95.19	3.60
Paraquat	0.00	95.50	90.96	91.53	92.90	92.72	2.18

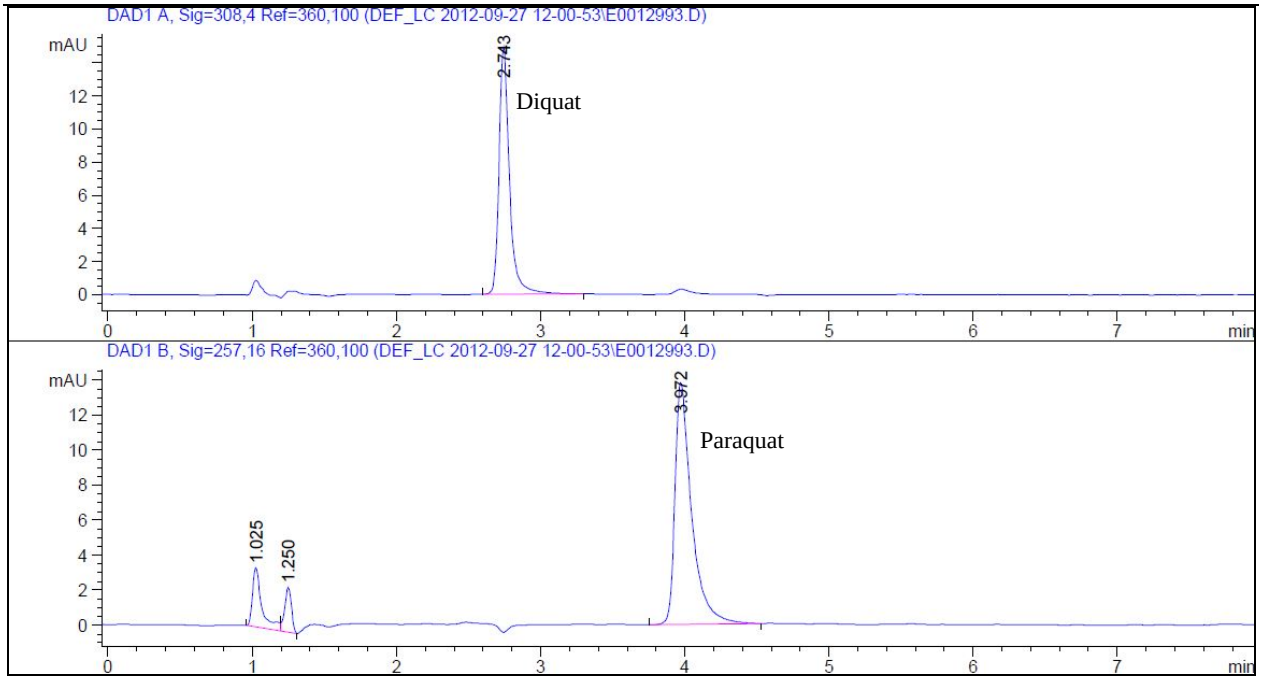

Figure 1: LFB Example Spectrum

Table 3: SmartPrep Extraction Method

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense
1		Reagent Water	5	10	10	0	Yes
2		Methanol	5	10	10	0	Yes
3		Reagent Water	5	10	10	0	Yes
4		Condition Solution A	5	10	10	0	Yes
5		Reagent Water	5	10	10	0	Yes
6		Methanol	10	10	10	0	Yes
7		Reagent Water	5	10	10	0	Yes
8		Condition Solution B	20	10	10	0	Yes
9	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**
		Yes	1	75	3	100	250
10	**Wash Cartridge**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**	**Liquid Sense**
		Methanol	5	10	10	0	Yes
11	**N2 Purge Timer**	**Delay (min)**					
		1					
12	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**
		Eluting Solvent	4.5	1.5	1	10	10

Increasing The Efficiency of EPA Method 549.2 Using the SmartPrep Automated Cartridge Extractor

Alicia Cannon and Brian LaBreque, Horizon Technology, Inc., Salem, NH

Introduction

Within EPA Method 549.2, the suggested rate to load a sample onto a solid phase cartridge is given as 3 to 6 mL/min (Section 11.2.5). However, as advances in the chemistry of the sorbents continue to be made, it may become necessary to re-evaluate this speed. This Application Note will outline the process used to extract diquat and paraquat from water samples using a faster loading rate than given by the EPA in method 549.2. It will specifically focus on the extraction of the samples needed for an initial demonstration of capability (IDC) according to the procedure outlined in the 549.2 method. It will also illustrate that, although method 549.2 recommends that all glassware be silanized, excellent recoveries can be achieved even if the glass syringe barrel on the SmartPrep was not. Lastly, even though the sample load rate is increased by more than a factor of 8 and the syringe barrel was not silanized, the high recoveries required will be maintained.

The Horizon Technology SmartPrep Automated Cartridge Extractor.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 20 mL Tray
- Phenomenex
  - Strata C8 cartridges, 500 mg, 6 mL
  - Spherisorb 3 µm C8 80 Å, 100 x 4.6 mm
- Agilent 1100 Series LC with attached DAD

Method Summary

Preparation of Solvents

1. Conditioning Solution A: Dissolve 0.500 g of cetyl trimethyl ammonium bromide and 5 mL of concentrated ammonium hydroxide in 500 mL of deionized water and dilute to 1000 mL in a volumetric flask.[1] Please note that this solvent may crystallize and should be replaced often to prevent this phenomenon.
2. Conditioning Solution B: Dissolve 10.0 g of 1-hexanesulfonic acid, sodium salt and 10 mL of concentrated ammonium hydroxide in 250 mL of deionized water and dilute to 500 mL in a volumetric flask.[1]
3. Elution Solvent: Add 13.5 mL of orthophosphoric acid and 10.3 mL of diethylamine to 500 mL of deionized water and bring to a final volume of 1000 mL in a volumetric flask.[1]
4. Ion-Pair Concentrate: Dissolve 3.75 g of 1-hexanesulfonic acid into 15 mL of Elution Solvent and bring to a final volume of 25 mL.[1]
5. Mobile Phase: Add 13.5 mL orthophosphoric acid, 10.3 mL of diethylamine, and 3.0 g of 1-hexanesulfonic acid, sodium salt to 500 mL of deionized water. Bring to a final volume of 1 liter.[1]

Sample Preparation

1. Prepare five aliquots of reagent water measuring 250 mL each (containers were HDPE).
2. Prepare one aliquot as a laboratory fortified blank (LRB).
3. The remaining four aliquots prepare as laboratory fortified blanks (LFBs). Prepare each aliquot by adding 5 µL of a stock standard (at 1000 mg/mL) for a sample concentration of 100 µg/L.
4. Verify the pH and, if needed, adjust the pH to between 7.0 and 9.0 using 10% w/v NaOH or 10% v/v HCl.

SmartPrep Automated Extraction

1. Ensure that all reagents are filled.
2. Ensure that all waste containers are empty.
3. Load a Cleaning Cartridge onto position 21 of the carousel.
4. Load five C8 cartridges onto the carousel into positions 1 through 5.
5. Load five 20 mL HDPE Scintillation vials without their caps onto the tray in positions corresponding to those of the carousel.
6. Place the samples onto the Sample Rack and ensure that a Sip Tube is in place in the lower corner of the sample container.
7. Run the Method given in Table 3 below and collect approximately 4.5 mL of extract at 45 minutes per sample.
8. Add 100 µL of an Ion-Pair Concentrate
9. Bring the sample to a final volume of 5 mL using the Elution Solvent.
10. Analyze the sample by HPLC using the conditions given in Table 1 below.

Table 1: Analysis Conditions

Column Flow: 1.0 mL/min
Solvent: 100% 549.2 Mobile Phase (isocratic)
Spectra Start: 210 nm
Spectra End: 370 nm
Spectra Step: 1 nm
Injection Volume: 20 µL

11.

Results

The results of the extractions performed for this study are given below in Table 2 and a sample spectrum is shown in Figure 1. The data was generated using a loading rate of 25 mL/min (compared to the specified rate of 3 mL/min). The average run time was average run time was 36 min. When this is compared to the EPA Method 549.2 specified load rate of 3 mL/min, the time savings were approximately 75%. Both diquat and paraquat were recovered at concentrations higher than 90% and the RSDs were less than 10%.

Conclusions

The resulting data from the analysis performed proves that, even though the sample load rate was increased by more than a factor of 8, the recoveries were still well within the method criteria. It proves that the SmartPrep Automated Extractor is an excellent choice for those wishing to push the limits for the extraction diquat and paraquat from water matrices.

References

1. Munch, J.W. and Bashe W.J., **"**Method 549.2-Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection", National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, 45268,1997.

Table 2: Method 549.2 IDC Results

	LFB (%)	LFB (%)	LFB (%)	LFB (%)	Average (%)	RSD (%)
Diaquat	94.82	96.60	93.00	86.00	92.61	5.01
Paraquat	90.18	94.91	92.00	83.00	90.02	5.63

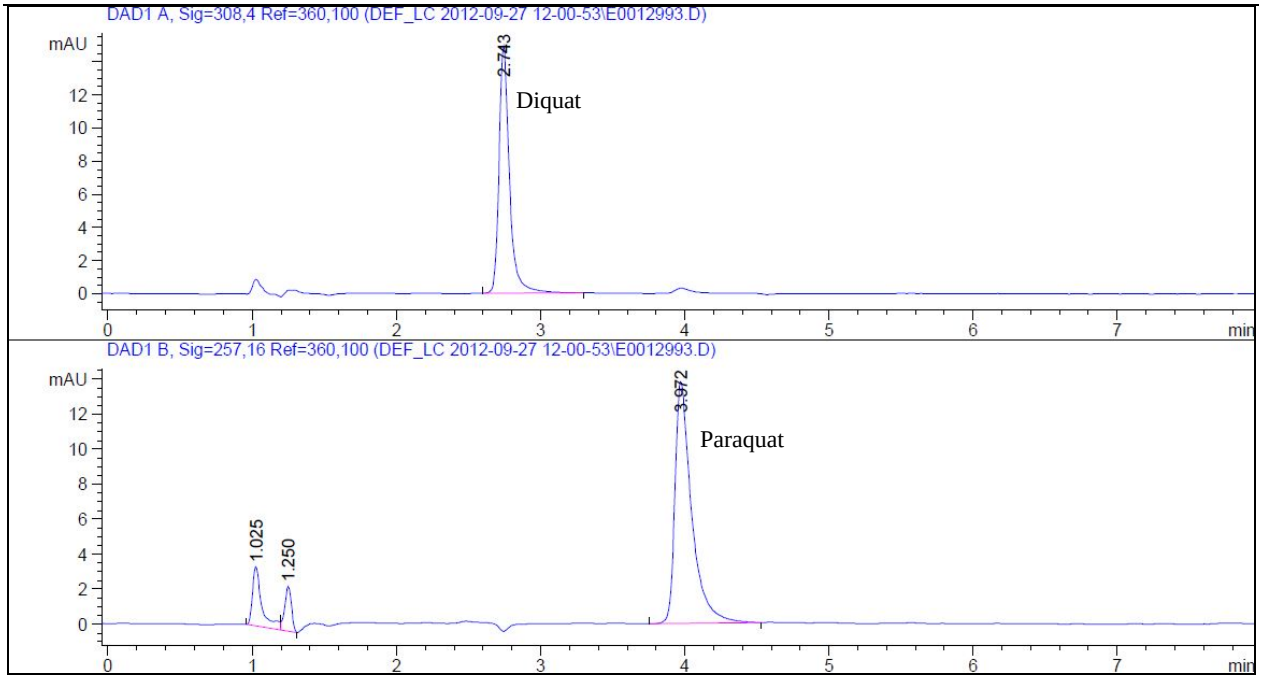

Figure 1: LFB Example Spectrum

Table 3: SmartPrep Extraction Method

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense
1		Reagent Water	5	10	10	0	Yes
2		Methanol	5	10	10	0	Yes
3		Reagent Water	5	10	10	0	Yes
4		Condition Solution A	5	10	10	0	Yes
5		Reagent Water	5	10	10	0	Yes
6		Methanol	10	10	10	0	Yes
7		Reagent Water	5	10	10	0	Yes
8		Condition Solution B	20	10	10	0	Yes
9	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**
		Yes	1	75	25	100	250
10	**Wash Cartridge**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**	**Liquid Sense**
		Methanol	5	10	10	0	Yes
11	**N2 Purge Timer**	**Delay (min)**					
		1					
12	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**
		Eluting Solvent	4.5	1.5	1	10	10

Improving the Efficiency and Accuracy when Extracting Semi-Volatile Organics in Drinking Water by Method 525.2

Brian LaBreque, Horizon Technology, Inc., Salem, NH

Introduction

EPA Method 525 was first promulgated in 1988 and, has since come to be the de-facto standard to measure a wide range of semi-volatile organic compounds in drinking water. In 1995, the EPA issued Revision 2 of the 525 method. With the advances in both chemical knowledge and instrumentation since this time, it has now become possible to improve the recovery of the compounds given in the 525.2 method.

The focus of this Application Note is to illustrate some of the advances which have been made when performing this method using Solid Phase Extraction (SPE). It will make use of the SmartPrep Automated Cartridge Extraction system set up to run in Bottle Rinse Mode with 6 mL SPE cartridges.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 6 mL Cartridge Configuration
  - Bottle Rinse Kit
  - 20 mL VOA Vial Extract Collection Tray
  - DryVap® Concentration System
  - DryDisk® Separation Membrane
- Phenomenex
  - Strata® C18-E, 6 mL Cartridges
  - ZB – Semivolatiles, 30 m x 0.25 mm x 0.25 µm
- Agilent
  - 6890 GC
  - 5975C MSD

Method Summary

1. Prepare six deionized 1 L water samples in amber containers using 1 mL of HCl to lower the pH to 2.
2. Spike samples at 5 µg/L by adding 5 µL of a 1000 µg/mL internal standard solution, 5 µL of a 1000 µg/mL surrogate solution, and 50 µL of a 100 µg/mL spike solution (for blanks, add only internal standards and surrogates).
3. Insert Sip Tubes and attach Bottle Rinse Kits to each sample bottle.
4. Place a 20 mL VOA vial in positions 1-6 of the extract collection tray.
5. Place a 1 g, 6 mL C18-E cartridge in positions 1-6 of the cartridge carousel.
6. Run the extraction method described in Table 4.
7. Place six 200 mL concentrator tubes with a 1 mL endpoint on the DryVap.
8. Place a DryDisk membrane in each DryDisk reservoirs and place on the DryVap.

The Horizon Technology SmartPrep® Automated Cartridge Extractor

9. Pour each extract into a DryDisk reservoir and start the DryVap using the parameters in Table 1.
10. Rinse each VOA vial with methylene chloride and pour the rinsate into the reservoir, repeat 2 times.
11. Rinse down the sides of the reservoir with methylene chloride, repeat 2 times.
12. Upon completion, bring the volume to 1.0 mL with methylene chloride.
13. Transfer 400 µL to a GC vial and add 4 µL of a Terphenyl-d14 solution at 500 µL/mL (the remaining 600 µL should be kept for possible re-analysis).
14. Analyze extracts by GC/MS as shown in Table 2.

Table 1: DryVap Parameters

Parameter	Setting
Dry Volume	20 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	17 psi
Vacuum	-11 in. Hg

Table 2: GC/MS Acquisition Parameters

Injection:
- Inlet Temperature: 345°C
- Mode: Pulsed Splitless
- Amount: 1 µL

Carrier Gas: Helium Constant at 1 mL/min

Oven Program:
- Hold 70°C for 0.5 minutes
- Ramp 16°C/min to 190°C
- Ramp 8°C/min to 290°C
- Ramp 25°C/min, hold for 3 minutes

Detector:
- MSD in scan mode

Results

A six point calibration curve was prepared in ethyl acetate and analyzed using concentrations of 10 µg/mL, 5.0 µg/mL, 2.0 µg/mL, 1.0 µg/mL, 0.5 µg/mL and 0.1 µg/mL.

One Laboratory Reagent Blank and four Laboratory Fortified Blanks (LFB's) were extracted with the Horizon Technology SmartPrep. The rate at which the samples were loaded onto the cartridge was set to 30 mL/min. This resulted in each extraction taking approximately 1.3 hours to process a 1 liter sample. This is a 48% improvement in time over the suggested manual loading rate of 8.3 mL/min. The inline drying and concentration process took approximately 40 minutes. Most target compounds resulted in a percent relative standard deviation (% RSD) of <10%, with only 2 being higher than 10%. All compounds fell within the method criteria for both the average and the RSD regardless of the faster flow rate.

Conclusions

Horizon Technology's SmartPrep Automated Cartridge Extractor and DryVap Drying and Concentration systems were used to extract and concentrate Method 525.2 water samples. Not only was this instrumentation able to pass all the required criteria for an Initial Demonstration of Laboratory Accuracy and Precision, but it was able to save 48% of the total time over the suggested manual loading rate. The improvements made to the extraction method here allow more samples to be processed increased the overall productivity of a laboratory.

Figure 1: LFB Example Chromatogram

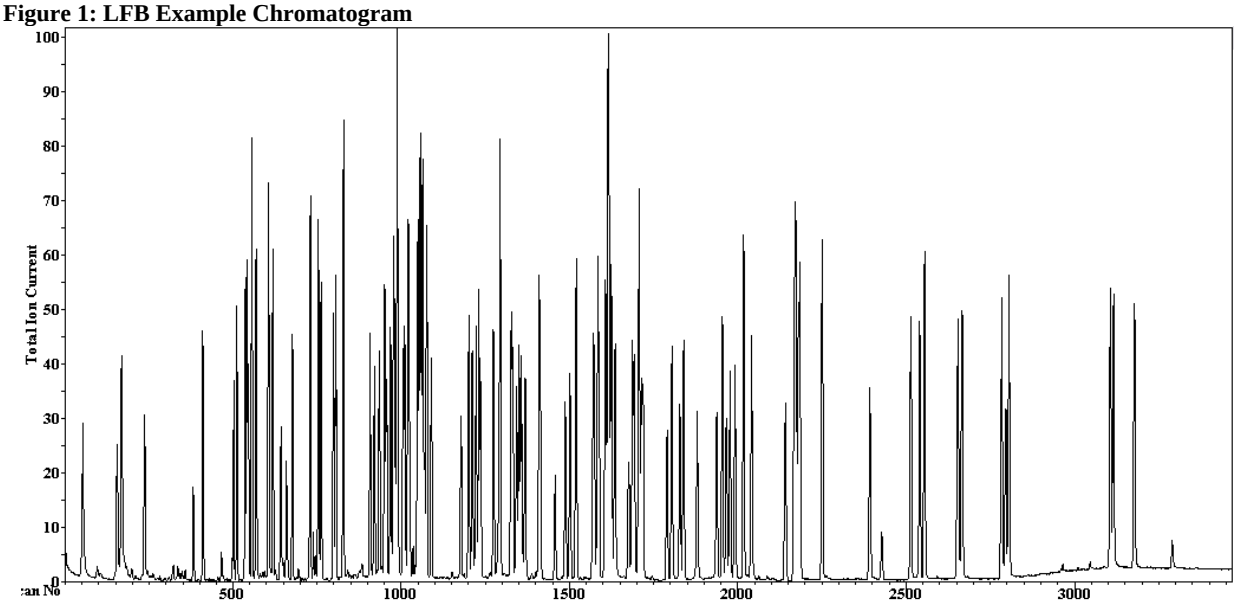

Table 3: EPA 525.2 Recovery Data

		Blank	LFB 1	LFB 2	LFB 3	LFB 4	Avg	RSD
		(ng/uL)	(%)	(%)	(%)	(%)	(%)	(%)
Isophorone		0.03	107.8	103.8	105.6	101.4	104.7	2.6
2-Nitro-m-xylene	S	4.95	101.2	101.4	100.2	96.4	99.8	2.3
Naphthalene		0.00	106.8	105.8	107.2	102.2	105.5	2.2
Dichlorvos		0.00	112.4	110.2	113.2	109.4	111.3	1.6
Hexachlorocyclopentadiene		0.00	86.8	85.8	88.8	85.8	86.8	1.6
EPTC		0.04	110.6	109.2	111.4	107.2	109.6	1.7
Mevinphos		0.00	116.6	108.2	105.2	107.4	109.4	4.6
Butylate		0.00	113.2	111.8	113.0	110.2	112.1	1.2
Vernolate		0.00	114.6	113.4	114.8	111.2	113.5	1.5
Dimethyl phthalate		0.00	120.6	118.6	120.4	116.8	119.1	1.5
Pebulate		0.02	115.2	113.6	116.2	112.2	114.3	1.5
Etridiazole		0.00	116.4	117.8	118.4	113.0	116.4	2.1
2,6-Dinitrotoluene		0.00	92.2	116.4	89.6	81.2	94.9	15.9
Acenaphthylene		0.03	110.6	108.6	110.2	107.2	109.2	1.4
Chloroneb		0.04	121.8	123.2	122.4	118.6	121.5	1.7
Tebuthiuron		0.00	114.4	113.6	116.2	114.6	114.7	0.9
2,4-Dinitrotoluene		0.00	93.6	120.0	91.6	82.6	97.0	16.6
Molinate		0.00	116.6	115.4	115.4	113.0	115.1	1.3
Diethyl phthalate		0.03	122.8	120.2	121.2	118.2	120.6	1.6
Fluorene		0.01	112.0	113.2	113.8	110.8	112.5	1.2
Propachlor		0.00	120.6	119.4	118.6	115.8	118.6	1.7
Ethoprop		0.00	118.6	116.8	118.2	116.0	117.4	1.0
Cycloate		0.04	118.8	116.6	117.4	113.2	116.5	2.0
Chlorpropham		0.00	119.2	118.0	120.0	117.4	118.7	1.0
Trifluralin		0.00	117.2	115.2	118.6	116.6	116.9	1.2
a-BHC		0.03	113.8	110.0	114.4	110.4	112.2	2.0
Atraton		0.00	103.8	103.2	100.8	92.6	100.1	5.2
Hexachlorobenzene		0.00	105.0	104.6	107.4	105.2	105.6	1.2
Prometon		0.00	113.6	109.0	112.0	110.8	111.4	1.7
Lindane (g-BHC)		0.00	116.8	115.2	115.8	113.4	115.3	1.2
Simazine		0.00	114.6	111.2	113.2	111.2	112.6	1.5
Atrazine		0.00	115.0	111.0	113.8	110.8	112.7	1.8
Propazine		0.00	117.2	112.8	115.0	113.0	114.5	1.8
b-BHC		0.00	116.2	112.2	114.2	111.2	113.5	2.0
Pentachlorophenol		0.01	89.0	88.6	90.0	88.2	88.9	0.9
Terbufos		0.00	111.6	111.0	112.2	108.4	110.8	1.5
Pronamide		0.00	114.6	113.8	114.2	111.2	113.5	1.4
Diazinon		0.00	88.4	93.4	91.4	86.2	89.9	3.5
d-BHC		0.00	114.6	111.0	114.0	110.6	112.6	1.8
Phenanthrene		0.00	111.6	110.6	113.0	110.4	111.4	1.1
Disulfoton		0.00	120.4	108.6	120.6	98.0	111.9	9.7
Methyl paraoxon		0.00	115.6	114.6	116.8	116.0	115.8	0.8
Anthracene		0.01	109.4	107.0	110.8	108.4	108.9	1.5
Terbacil		0.00	115.6	113.8	115.6	112.6	114.4	1.3
Chlorothalonil		0.00	116.4	114.0	116.6	115.0	115.5	1.1
Metribuzin		0.00	110.4	109.6	108.4	102.0	107.6	3.6
Simetryn		0.00	111.8	110.6	109.2	103.8	108.9	3.2
Heptachlor		0.00	110.0	109.2	110.0	107.8	109.3	0.9
Ametryn		0.00	112.8	110.6	113.6	111.0	112.0	1.3
Alachlor		0.00	113.8	112.6	113.8	111.6	113.0	0.9
Prometryn		0.00	115.2	111.6	115.8	113.4	114.0	1.7
Terbutryn		0.00	114.0	111.0	114.2	112.8	113.0	1.3
Di-n-butyl phthalate		0.03	114.0	112.8	114.2	111.4	113.1	1.1
Bromacil		0.00	110.0	109.2	109.6	106.4	108.8	1.5
Cyanazine		0.00	114.2	112.4	114.6	112.2	113.4	1.1
Metolachlor		0.00	115.2	112.8	114.8	113.4	114.1	1.0

Table 3: EPA 525.2 Recovery Data (continued):

		Blank	LFB 1	LFB 2	LFB 3	LFB 4	Avg	RSD
		(ng/uL)	(%)	(%)	(%)	(%)	(%)	(%)
Chlorpyrifos		0.00	111.2	109.4	111.4	108.8	110.2	1.2
Aldrin		0.00	107.4	105.0	108.0	105.0	106.4	1.5
Triademefon		0.00	113.0	107.8	110.4	107.0	109.6	2.5
Dacthal		0.00	115.8	113.2	115.4	113.4	114.5	1.2
MGK-264-A		0.00	101.2	99.0	116.8	115.0	108.0	8.5
Diphenamid		0.00	112.2	109.6	112.0	109.0	110.7	1.5
MGK-264-B		0.00	113.0	108.8	112.6	110.2	111.2	1.8
Merphos		0.00	114.4	104.2	109.4	103.2	107.8	4.8
Heptachlor epoxide B		0.00	112.2	109.8	110.8	109.2	110.5	1.2
Heptachlor epoxide A		0.00	114.6	111.6	112.2	108.8	111.8	2.1
Fluoranthene		0.04	109.6	108.6	111.0	108.4	109.4	1.1
g-Chlordane		0.00	106.2	105.2	107.6	106.0	106.3	0.9
Stirofos		0.00	112.6	108.8	111.4	110.8	110.9	1.4
Disulfoton sulfone		0.00	114.4	112.4	114.0	113.6	113.6	0.8
Butaclor		0.00	112.4	109.8	110.4	109.8	110.6	1.1
a-Chlordane		0.00	106.0	105.4	104.6	106.0	105.5	0.6
Endosulfan I		0.00	107.6	108.4	109.0	106.6	107.9	1.0
Fenamiphos		0.00	104.4	100.8	104.8	104.8	103.7	1.9
Pyrene-d10	S	4.89	99.6	96.4	98.2	95.2	97.4	2.0
Pyrene		0.00	107.8	106.6	107.6	106.8	107.2	0.5
Napropamide		0.00	111.0	107.2	108.8	108.4	108.9	1.5
trans-Nonachlor		0.00	112.2	110.8	111.6	110.2	111.2	0.8
4,4'-DDE		0.00	106.4	105.0	107.2	104.8	105.9	1.1
Dieldrin		0.00	107.6	106.2	107.6	104.6	106.5	1.3
Tricyclazole		0.03	100.2	104.4	106.4	102.8	103.5	2.5
Carboxin		0.00	108.0	105.0	106.6	106.2	106.5	1.2
Endrin		0.00	106.2	107.4	105.8	105.2	106.2	0.9
Chlorobenzilate		0.00	110.8	107.6	108.6	108.6	108.9	1.2
Endosulfan II		0.00	107.6	108.4	109.0	106.6	107.9	1.0
4,4'-DDD		0.00	104.0	103.0	104.6	104.0	103.9	0.6
Endrin Aldehyde		0.00	106.8	104.6	104.2	107.2	105.7	1.4
Butyl benzyl phthalate		0.08	110.4	107.6	110.0	108.8	109.2	1.2
Norflurazon		0.00	110.8	107.2	110.8	110.4	109.8	1.6
4,4-DDT		0.00	104.0	103.0	104.6	104.0	103.9	0.6
Endosulfan Sulfate		0.00	108.8	108.0	109.0	107.6	108.4	0.6
Bis(2-ethylhexyl)adipate		0.01	107.6	104.8	108.2	107.4	107.0	1.4
Hexazinone		0.00	110.8	108.4	110.0	109.6	109.7	0.9
Triphenylphosphate	S	4.97	105.4	100.8	102.8	100.6	102.4	2.2
Endrin Ketone		0.00	111.6	111.4	110.6	111.0	111.2	0.4
Methoxychlor		0.00	107.4	105.8	100.8	104.4	104.6	2.7
Benz(a)anthracene		0.07	109.0	108.4	110.2	108.6	109.1	0.7
Chrysene		0.01	111.6	111.6	113.2	111.4	112.0	0.7
Bis(2-ethylhexyl)phthalate		0.07	111.6	108.4	113.4	112.2	111.4	1.9
Fenarimol		0.00	105.4	104.0	105.6	104.8	105.0	0.7
cis-Permethrin		0.00	108.6	105.6	109.2	108.4	108.0	1.5
trans-Permethrin		0.00	108.4	106.2	109.4	108.4	108.1	1.3
Di-n-octyl phthalate		0.07	111.6	108.4	113.4	112.2	111.4	1.9
Benzo(b)fluoranthene		0.01	114.2	114.0	117.0	114.2	114.9	1.3
Benzo(k)fluoranthene		0.01	113.0	112.6	116.2	113.8	113.9	1.4
Benzo(a)pyrene		0.00	111.8	110.6	115.6	112.8	112.7	1.9
Fluridone		0.00	115.6	109.6	116.4	115.6	114.3	2.8
Perylene-d12	S	5.05	109.2	106.2	110.4	104.4	107.6	2.6
Indeno(1,2,3-cd)pyrene		0.00	113.0	111.2	117.6	113.4	113.8	2.4
Dibenz(ah)anthracene		0.00	113.8	113.6	118.6	115.2	115.3	2.0
Benzo(ghi)perylene		0.00	114.6	113.4	120.2	115.0	115.8	2.6

Table 4: SmartPrep Extraction Program

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense	
1		EtOAc	5	10	10	5	No	
2		DCM	5	10	10	5	No	
3		MeOH	10	10	0	0	No	
4		Reagent Water	10	10	0	0	No	
5	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**	
		Yes	2	75	30	1	1000	
6	**N2 Purge Timer**	**Delay (min)**						
		10						
7	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		EtOAc	6	5	5	No		
8	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		12	1	6	30	5	10	5
9	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		EtOAc	5	20				
10	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**	
		Mixing Chamber	5	5	1	10	5	
11	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	6	5	5	No		
12	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		12	1	6	30	5	10	5
13	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		DCM	5	20				
14	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**	
		Mixing Chamber	5	20	1	10	5	

Extracting Semi-Volatile Organics from Drinking Water by EPA Method 525.3 Using the SmartPrep Cartridge Extractor

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Introduction

Since 1988, EPA Method 525 has been the standard in testing for organic compounds in drinking water. While its last version, 525.2, has been in use since 1994, an update to the Federal Register made in 2012 released a new version, 525.3, which contains significant changes when compared to its predecessor.

This application note will outline the extraction of semi-volatile organic compounds from drinking water using the SmartPrep Automated Cartridge Extractor. The extractor, when configured with its optional Bottle Rinse Kit, will process up to 6 samples unattended and will be used to produce a valid Initial Demonstration of Precision (IDP) and Initial Demonstration of Accuracy (IDA).

Additionally, this application note will be used to showcase additional extraction conditions which could be used to decrease sample processing times. This would allow a laboratory to process more samples in less time.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 6 mL Cartridge Configuration
  - 20 mL Tray
  - DryVap® Concentration System
  - DryDisk® Separation Membrane
- J.T.Baker
  - 6 mL H_20-Phobic DVB Speedisk® Column
- Phenomenex
  - Zebron™ ZB-SemiVolatiles
- Agilent
  - 6890 Gas Chromatograph
  - 5975C Inert MSD
  - 7683B Autosampler

Method Summary

1. Sample bottles are prepared using 0.10 g/L L-Ascorbic acid, 0.35 g/L trisodium EDTA, and 9.4 g/L potassium dihydrogen citrate [1].
2. A one liter sample should be collected in this bottle and its pH should be less than or equal to 4.
3. Verify that the sample pH is less than or equal to 4.
4. Add surrogate and spike to each sample.
5. Insert Sip Tubes and attach Bottle Rinse Kits to each sample bottle.
6. Place a 20 mL VOA vial in positions into position of the collection tray relating to the samples loaded.
7. Place cartridges into the corresponding positions on the carousel.
8. Start the extraction process using the method given in Table 2. If the desired sample load rate is 10 mL/min, use a 1 s syringe fill pause. For 30 mL/min, use 2 s.

The Horizon Technology SmartPrep Automated Cartridge Extractor

9. When complete, remove the collected extract (16-20 mL).
10. Place six 200 mL concentrator tubes with a 1 mL endpoint on the DryVap.
11. Place a DryDisk membrane in each DryDisk reservoir and place on the DryVap.
12. Pour each extract into a DryDisk reservoir and start the DryVap using the parameters in Table 1.
13. Rinse each VOA vial with ethyl acetate and pour the rinsate into the reservoir, repeat 2 times.
14. Rinse down the sides of the reservoir with ethyl acetate, repeat 2 times.
15. Upon completion, bring the final volume up to 1 mL using ethyl acetate.
16. Transfer the extract to an autosampler vial, add IS, and analyze by GC/MS.

Table 1: DryVap Parameters

Parameter	Setting
Dry Volume	20 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	17 psi
Vacuum	-11 in. Hg

Results

While EPA Method 525.3 specifies a 10 mL/min flow rate of sample water through a cartridge, it was believed that a higher flow rate may be possible. To prove this, an IDC/IDA study was performed for both the specified 10 mL/min load rate and a higher flow rate of 30 mL/min. By increasing the flow rate, it was hoped that the sample extraction times could be reduced.

Table 3 shows the results of both IDA/IDC studies which were completed using the SmartPrep Extractor and Figure 1 shows a typical chromatogram for this type of sample. The recoveries and deviations for each set of data were excellent with the only compound which was recovered low being hexachlorocyclopentadiene. This compound is known to be problematic, and is called out in section 13.6.3 as being "highly reactive" and degrading "relatively quickly via photolysis and hydrolysis" [1].

When samples were loaded onto the cartridges using a 10 mL/min flow rate, approximately 159 min/sample was needed to complete the full extraction including rinsing the sample container automatically and automatically measuring the original sample volume. By substituting a higher flow rate of 30 mL/min, approximately 86 min/sample is saved without sacrificing recoveries.

Conclusions

The data given in this Application Note illustrates the fact that the combination of Horizon Technology's SmartPrep Automated Extractor, DryVap Concentrator, and DryDisk Separation Membranes represent a complete solution to the preparation of samples for the extraction of semi-volatile organics by EPA Method 525.3. By implementing an automated procedure such as the one outlined here, a laboratory can save much in the way of time and money by freeing up an analyst to perform other, more complicated tasks.

References

[1] Method 525.3: Determination of Semivolatile Organic Chemicals in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS), Version 1.0, February 2012, EPA/600/R-12/010

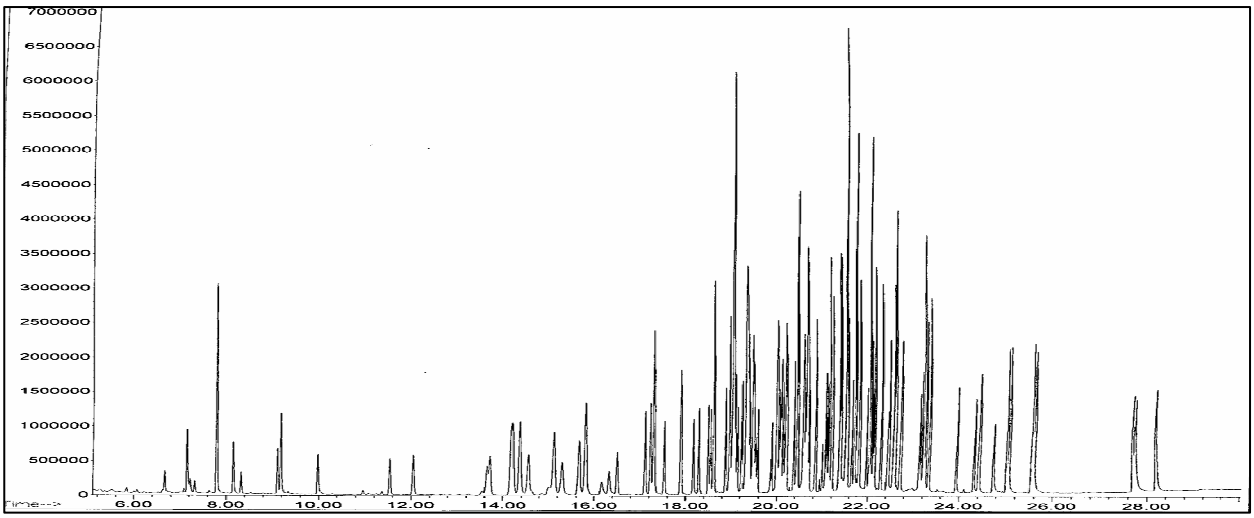

Figure 1: Chromatogram of EPA Method 525.3 Analysis

Table 2: EPA Method 525.3 Extraction Method (both 10 and 30 mL/min)

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense	
1		EtOAc	3	10	60	0	No	
2		EtOAc	2	10	5	0	No	
3		MeOH	10	10	60	0	No	
4		Reagent Water	10	10	5	0	No	
5	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**	
		Yes	1 or 2	75	10 or 30	1	1000	
6	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		Reagent Water	6	5	5	No		
7	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**	
		Yes	1 or 2	75	10 or 30	1	100	
8	**N2 Purge Timer**	**Delay (min)**						
		10						
9	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		EtOAc	6	5	5	No		
10	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**
		6	1	3	30	5	60	0
11	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**
		6	1	3	30	5	0	5
12	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		EtOAc	5	20				
13	**Cartridge Elute**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**N2 Purge** (s)	**Liquid Sense**
		Mixing Chamber	5	5	1	10	5	No
14	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	6	5	5	No		
15	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**
		6	1	3	30	5	60	0
16	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**
		6	1	3	30	5	0	5
17	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		DCM	5	20				
18	**Cartridge Elute**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**N2 Purge** (s)	**Liquid Sense**
		Mixing Chamber	5	5	1	10	5	No

Table 3: Recoveries for both 10 mL/min and 30 mL/min IDC/IDA

	10 mL/min		30 mL/min	
Compound	**Average (%)**	**RSD (%)**	**Average (%)**	**RSD (%)**
Acenaphthylene	92.2	4.9	94.8	3.9
Acetochlor	103.2	4.1	104.4	3.8
Alachlor	101.1	3.9	102.0	4.2
Aldrin	97.7	3.4	98.5	4.7
Ametryn	99.4	7.7	102.6	4.2
Anthracene	95.6	5.3	98.4	4.4
Atraton	97.7	14.2	103.0	4.3
Atrazine	98.1	5.7	100.2	4.0
Benzo(a)anthracene	98.6	5.2	101.3	4.6
Benzo(a)pyrene	98.8	4.2	99.6	4.8
Benzo(b)fluoranthene	97.6	5.0	98.5	5.1
Benzo(g,h,i)perylene	96.6	4.2	95.4	6.0
Benzo(k)fluoranthene	97.8	5.1	98.8	5.5
BHA, 3-	103.0	3.5	105.6	5.3
BHT	94.5	4.8	97.0	4.7
Bis(2-ethylhexyl)adipate	99.1	4.7	100.7	4.8
Bis(2-ethylhexyl)phthalate	99.9	4.9	102.8	5.0
Bromacil	106.6	4.9	108.0	4.3
Butaclor	101.9	3.7	103.2	3.9
Butyl benzyl phthalate	96.4	4.4	98.5	4.0
Butylate	95.4	4.1	97.6	3.4
Captan	113.7	6.8	116.6	3.7
Carboxin	96.0	5.7	98.6	4.8
Chlordane, cis	96.5	4.4	99.9	4.3
Chlordane, trans	98.8	5.4	100.8	5.1
Chlorfenvinphos	106.1	5.0	108.0	4.2
Chlorobenzilate	102.2	4.6	104.1	4.0
Chloroneb	99.3	3.0	100.5	4.2
Chlorothalonil	101.8	4.6	104.2	4.4
Chlorpropham	105.3	3.7	107.4	4.0
Chlorpyrifos	98.7	4.6	100.1	5.0
Chrysene	97.6	5.4	99.6	4.8
Cyanazine	93.8	10.6	100.2	4.6
Cycloate	99.0	3.2	100.6	4.1
Dacthal	99.3	4.0	101.3	4.6
DDD, 4,4'-	105.2	5.3	105.8	4.1
DDE, 4,4'-	96.1	4.4	98.2	4.8
DDT, 4,4'-	95.4	5.0	97.7	5.0
DEET	97.3	4.4	99.6	4.8
Diazinon	92.6	4.7	97.0	5.3
Dibenz(a,h)anthracene	97.4	4.4	96.3	5.7
Dichlorvos	96.8	5.4	99.9	4.3
Dieldrin	97.7	4.0	98.5	4.6
Diethyl phthalate	99.4	3.6	101.2	4.2
Dimethyl phthalate	96.9	3.8	99.5	4.3
DIMP	89.6	6.0	95.9	6.2
Di-n-butyl phthalate	104.0	3.9	104.7	4.1
Dinitrotoluene, 2,4-	105.8	4.2	107.6	4.0
Dinitrotoluene, 2,6-	105.4	5.0	107.5	4.1
Di-n-octyl phthalate	96.3	4.8	98.8	4.9
Diphenamid	101.6	3.4	102.5	4.1
Disulfoton	102.1	2.7	100.5	4.4
Disulfoton sulfone	102.8	3.6	104.5	4.3
Endosulfan I	99.7	3.0	102.7	5.1
Endosulfan II	99.7	3.0	102.7	5.1

Table 3: Recoveries for both 10 mL/min and 30 mL/min IDC/IDA (cont.)

	10 mL/min		30 mL/min	
Compound	**Average (%)**	**RSD (%)**	**Average (%)**	**RSD (%)**
Endosulfan Sulfate	102.0	4.7	103.5	4.0
Endrin	97.7	4.0	98.5	4.6
Endrin Aldehyde	90.6	7.8	98.9	4.5
Endrin Ketone	104.8	3.4	106.6	4.4
EPTC	94.0	5.2	96.9	4.0
Ethion	102.9	5.4	105.2	3.9
Ethoprop	104.4	4.7	107.1	3.7
Ethyl Parithion	107.2	3.2	107.8	5.0
Etridiazole	98.6	4.9	100.1	4.0
Fenamiphos	109.1	4.9	112.6	3.8
Fenarimol	107.2	4.9	111.3	3.7
Fluoranthene	98.2	5.0	100.4	4.5
Fluorene	94.8	4.2	97.9	3.9
Fluridone	108.9	5.0	111.2	4.4
HCH, alpha	102.1	2.2	103.3	4.2
HCH, beta	106.2	4.3	107.1	3.8
HCH, delta	102.7	4.1	103.7	4.2
HCH, gamma	102.9	4.0	103.6	3.6
Heptachlor	102.7	4.1	95.9	8.0
Heptachlor epoxide (A)	100.0	4.4	101.3	4.1
Heptachlor epoxide (B)	99.2	3.3	101.1	3.7
Hexachlorobenzene	90.6	3.9	95.0	4.5
Hexachlorocyclopentadiene	59.5	11.8	65.3	5.8
Hexazinone	101.6	5.9	104.9	3.8
Indeno(1,2,3-cd)pyrene	91.8	4.4	91.1	6.0
Isophorone	90.9	7.2	93.9	4.7
Methoxychlor	95.5	16.0	93.8	7.7
Methyl Paraoxon	107.8	4.9	111.7	4.4
Methyl Parathion	106.9	5.2	108.3	5.2
Metolachlor	102.4	4.2	103.6	4.0
Metribuzin	99.2	5.6	99.4	3.5
Mevinphos	101.5	5.8	107.0	2.8
MGK-264-A	80.5	3.7	101.7	4.5
MGK-264-B	103.2	4.2	105.1	4.1
Molinate	98.0	3.9	99.8	4.1
Naphthalene	88.2	7.0	90.5	4.6
Naproamide	101.1	3.5	102.0	4.0
Nitrofen	103.3	5.0	107.0	4.0
Nonachlor, trans	96.0	4.6	98.8	4.5
Norflurzon	105.1	4.9	108.6	3.4
Oxyfluorfen	103.8	5.5	106.8	3.8
Pebulate	95.3	3.6	97.3	3.6
Pentachlorophenol	99.6	4.7	101.9	6.0
Permethrin, cis	97.9	4.6	99.9	4.8
Permethrin, trans	95.8	4.7	98.1	5.1
Phenanthrene	97.5	4.5	100.0	4.4
Phorate	100.2	5.4	102.7	3.6
Phosphamidon	111.1	5.9	113.9	4.2
Profenofos	102.0	3.4	101.5	4.7
Prometon	98.3	10.3	102.0	4.4
Prometryn	99.7	6.7	102.2	4.7
Pronamide	102.4	3.9	103.5	4.2
Propachlor	101.4	3.8	102.8	3.8
Propazine	99.3	5.6	101.2	4.4
Pyrene	97.0	4.7	99.8	4.6
Simazine	97.2	6.7	101.0	4.1

Table 3: Recoveries for both 10 mL/min and 30 mL/min IDC/IDA (cont.)

	10 mL/min		30 mL/min	
Compound	**Average (%)**	**RSD (%)**	**Average (%)**	**RSD (%)**
Simetryn	98.5	10.2	102.2	4.5
Tebuconazole	101.7	4.6	104.0	5.3
Tebuthiuron	103.5	6.7	107.2	4.0
Terbacil	105.4	5.9	107.6	4.3
Terbufos	95.6	7.2	99.3	3.8
Terbutryn	101.5	7.3	104.8	4.3
Tetrachlorvinphos	106.2	5.6	108.8	4.3
Triademefon	102.2	4.8	103.6	3.5
Tricyclazole	93.6	10.5	98.4	4.3
Trifluralin	102.9	5.1	106.9	3.9
Vernolate	96.7	4.2	98.6	3.8
Vinclozolin	100.9	4.0	103.1	4.6
PCB Congeners				
2-Chlorobiphenyl	93.9	2.1	94.3	3.7
4-Chlorobiphenyl	93.9	2.6	94.9	3.6
2,4-Dichlorobiphenyl	94.2	2.3	95.2	3.9
2,2`,5-Trichlorobiphenyl	94.8	2.8	94.9	3.9
2,2`,4-Trichlorobiphenyl	93.0	3.9	94.4	4.5
2,2`,3,5`-Tetrachlorobiphenyl	95.9	3.2	95.5	4.4
2,2`,5,5`-Tetrachlorobiphenyl	95.0	3.4	94.5	4.3
2,3`,4`,5-Tetrachlorobiphenyl	92.9	3.8	93.1	4.5
2,3,3`,4`,6-Pentachlorobiphenyl	93.4	2.9	93.1	5.0
2,3`,4`,4`,5-Pentachlorobiphenyl	94.2	3.2	93.7	4.2
2,2`,3,4,4`,5-Hexachlorobiphenyl	95.8	3.1	93.7	4.3
2,2`,3,4`,5`,6-Hexachlorobiphenyl	95.4	2.3	93.9	4.5
2,2`,4,4`,5,5`-Hexachlorobiphenyl	95.1	2.6	93.6	4.5
2,2`3,4,4`,5,5`-Heptachlorobiphenyl	97.4	2.1	94.3	5.0
Surrogate Analytes				
2-Nitro-m-xylene	89.2	7.2	91.6	4.6
Benzo(a)pyrene-d12	99.3	4.8	101.0	5.8
Cyanazine-d5	103.4	12.3	110.3	5.0
Triphenylphosphate	100.4	3.2	101.7	5.1

The Extraction of Chlorinated Pesticides, Herbicides, and Organohalides For EPA Method 508.1 Using Automated Cartridge SPE

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Introduction

The initial use of many chlorinated pesticides, herbicides, and organohalides were to aid humanity. DDT was created to control mosquito populations which significantly limited the number of malaria and typhus cases in World War II; while the use of Atrazine has increased the production of corn and sugar cane farms and helped to supply the world with the food it so drastically needs. However, this has given-way to the fact that many of the compounds have been found to be detrimental to either the flora or fauna found in the environment. It is because of their toxicity that many of these compounds have either been banned or are strictly controlled throughout most of the world.

This Application Note will highlight the use of the Horizon Technology SmartPrep Cartridge Extraction System for the extraction of EPA Method 508.1 analytes. This fully automated extractor allows for up to 6 samples in bottle rinse mode or 12 samples without bottle rinse mode to be run unattended. For this application, the instrument will be configured to run 6 mL cartridges and to make use of the optional bottle rinse mode. This will allow for higher recoveries to be obtained while still maintaining a zero-user interface throughout the run.

After the extraction procedure is complete, this study will make use of the Horizon Technology DryVap Concentrator System along with a DryDisk Separation Membrane. The union of these two features provides for automated drying and concentration at the push of a button. The DryDisk is a physical separation membrane which will allow solvent through, but not water. There is no pre-cleaning necessary and very little physical waste. The DryVap allows for up to six samples to be dried and concentrated at a time. It applies heating and sparging while under vacuum for a fast concentration with end point detection.

Instrumentation

- Horizon Technology
  - SmartPrep™ Automated Cartridge Extractor
    - 6 mL Cartridge Configuration
    - Bottle Rinse Kit
    - 20 mL Tray
  - DryVap® Concentration System
  - DryDisk® Separation Membrane
- Phenomenex
  - Strata® C18-E, 6 mL Cartridges
  - Zebron™ – Multiresidue 1:
    - 30 m x 0.32 mm x 0.50 µm
  - Zebron™ - Multiresidue 2:
    - 30 m x 0.25 mm x 0.25 µm
- Hewlett-Packard
  - 5890 Series II GC-ECD
  - 7673 Controller

The Horizon Technology SmartPrep™ Automated Cartridge Extractor

Method Summary

1. Prepare 1 Liter of deionized water using 1 mL of concentrated HCl to lower the pH to approximately 2.
2. After mixing, add 25 µL of a 20 µg/mL surrogate solution and 25 µL of a 20 µg/mL spike solution (for blank samples, add only surrogate solution).
3. Insert Sip Tube number 1 and attach Bottle Rinse Kit 7 to the sample container.
4. Place a 20 mL VOA vial in position 1 of the tray.
5. Place a 6 mL C18-E cartridge in position 1 of the carousel.
6. Run the method given in Table 3.
7. Place a 1 mL endpoint Concentration Tube on the DryVap.
8. Add a DryDisk membrane to the DryDisk reservoir and attach to the DryVap.
9. Transfer the contents of the VOA vial to the DryDisk Reservoir and start the DryVap using the conditions given in Table 1
10. When the extract has processed through the DryDisk, add approximately 2 mL of Ethyl Acetate (EtOAc) to the VOA vial, cap, and shake vigorously.
11. Transfer the rinsate to the DryDisk Reservoir and allow it to process through into the Concentrator Tube.
12. Repeat steps 10 and 11 two additional times.
13. Rinse the DryDisk Reservoir using approximately 2 mL of EtOAc and allow for this rinsate to process through to the Concentrator Tube.
14. Repeat step 13 two additional times.
15. Allow the extract to concentrate to its final volume.
16. Upon completion, use approximately 0.1 mL of EtOAc to rinse the heater and the Concentrator Tube and bring the volume up to the 1 mL mark as indicated on the Tube and transfer to a vial.
17. Add internal and run on a GC-ECD using Table 2.

Table 1: DryVap Parameters

Parameter	Setting
Dry Volume	100 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	20 psi
Vacuum	-10 in. Hg

Table 2: GC-ECD Acquisition Program

Injection:
Inlet Temperature: 1 µL at 250 °C
Carrier Gas:
Helium at a constant flow rate
Oven Program:
120 °C for 0.5 min to 210 °C at 30 °C/min to 230 °C at 6 °C/min hold for 3 min to 300 °C at 6 °C/min hold for 10 min.
Detector:
ECD at 320 °C

Results

Following the 508.1 Method, a calibration curve was prepared and analyzed using the spike concentrations of 0.1 ug/mL, 0.2 ug/mL, 0.5 ug/mL, 1.0 ug/mL, and 2.0 ug/mL. This curve was then used to analyze all the data obtained for this Application Note. A degradation check solution was prepared using DDT and Endrin and was used for every analytical batch to investigate the degradation products of the two analytes.

When using the MR-1 column, it was discovered that there were two sets of co-elutions; one between Simazine, Atrazine, and the other between d-BHC and Metribuzin. Due to this lack of separation, the compounds are not able to be reported on this column.

On the MR-2 column, a similar phenomenon was seen between Heptachlor Epoxide B and the recommended surrogate Dibrophenyl. In this case, a different surrogate, Decachlorobphenyl, was selected to clear up the co-elution.

The average recovery for 12 LCS extracts are given in Table 4 for each column used. With averages of 93% and the highest RSD being 17%, they show excellent results for all the compounds that are able to be reported on each column. For a full list of all the recoveries including blanks, refer to Tables 5a and 5b

Conclusions

The Horizon Technology SmartPrep Automated Cartridge System was used to extract EPA Method 508.1 compounds from water samples. When coupled with the DryVap Concentration System and DryDisk Separation Membranes, both excellent precision and accuracy was demonstrated. The solutions presented will allow a laboratory to streamline their aqueous extraction procedures and minimize the costs associated with labor and solvent while maintain the level of quality required.

Table 3: EPA Method 508.1 Extraction Parameters

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense	
1		EtOAc	5	10	10	2	No	
2		DCM	5	10	10	2	No	
3		DCM	5	10	10	2	No	
4		MeOH	5	10	0	0	No	
5		MeOH	5	10	10	0	No	
6		DI H20	5	10	0	0	No	
7		DI H20	5	10	10	0	No	
8	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**	
		Yes	1	20	10	800	1000	
9	**N2 Purge Timer**	**Delay (min)**						
		5						
10	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		EtOAc	5	5	5	No		
11	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		15*	1	5	10	10	20	1
12	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	5	5	5	No		
13	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		10*	1	5	10	10	20	1
14	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	5	5	5	No		
15	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		10*	1	5	10	10	20	1
16	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		DCM	5	10				
17	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**	
		Mixing Chamber	10	10	1	5	15	

*Sample volumes increased due to sample viscosities.

Table 4: Average Recovery and RSD for 508.1 Blanks and LCS Samples. Like numbered compounds indicate co-elutions.

		Blanks		LCS			
		Average (ug/L) MR-1	Average (ug/L) MR-2	Average (%) MR-1	RSD (%) MR-1	Average (%) MR-2	RSD (%) MR-2
Etridiazole		0.01	0.00	115	12.64	84	8.99
Chloroneb		0.02	0.00	90	5.23	68	6.70
Propachlor		0.03	0.01	92	9.59	86	8.31
Trifluralin		0.01	0.01	83	6.11	92	10.06
a-BHC		0.00	0.00	87	5.67	94	6.89
Lindane (g-BHC)		0.00	0.02	93	5.37	104	6.91
Simazine	1	N/A	0.06	N/A	N/A	94	9.60
Atrazine	1	N/A	0.09	N/A	N/A	95	7.05
b-BHC		0.01	0.00	94	3.99	103	5.74
d-BHC	2	N/A	0.00	N/A	N/A	114	7.75
Chlorothalonil		0.00	0.00	112	8.72	117	10.13
Metribuzin	2	N/A	0.00	N/A	N/A	83	8.44
Heptachlor		0.03	0.01	91	13.83	86	13.64
Alachlor		0.05	0.00	89	11.32	92	10.18
Cyanazine		0.01	0.00	119	8.60	94	4.48
Metolachlor		0.00	N/A	100	5.37	N/A	N/A
Dacthal		0.00	0.00	92	3.75	101	6.13
Heptachlor epoxide B		0.00	0.00	89	4.22	99	6.66
trans-Chlordane		0.00	0.00	84	4.93	91	7.37
Butaclor		0.00	0.00	105	6.81	95	8.19
cis-Chlordane		0.00	0.00	85	4.62	90	6.66
Endosulfan I		0.00	0.00	89	4.01	98	6.76
4,4'-DDE		0.01	0.01	78	7.19	85	9.74
Dieldrin		0.00	0.00	94	4.54	97	6.26
Endrin		0.00	0.00	97	6.56	100	7.74
Chlorobenzilate		0.00	0.00	70	12.60	92	10.99
Endosulfan II		0.00	0.00	92	4.14	99	8.15
4,4'-DDD		0.01	0.00	91	5.00	92	8.40
Endrin Aldehyde		0.01	0.00	90	4.28	92	8.90
4,4-DDT		0.01	0.00	107	6.82	94	8.75
Endosulfan Sulfate		0.00	0.00	96	4.67	96	8.68
Methoxychlor		0.01	0.00	118	10.22	94	10.99
Permethrin		0.05	0.00	107	16.09	106	16.99
Decachlorobiphenyl	S	0.40	0.46	83	6.23	96	10.66

1, 2 - Co-Elutting compounds on MR-1

Table 5a: All EPA Method 508.1 data generated. Like numbered compounds indicate co-elutions.

Sample Name		Blank 1 (ug/L)		Blank 2 (ug/L)		LCS 1 (%)		LCS 2 (%)		LCS 3 (%)		LCS 4 (%)		LCS 5 (%)	
Column ID		MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2
Pentachloronitrobenzene	IS	0.50	0.50	0.50	0.50	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Etridiazole		0.01	0.00	0.01	0.00	86.00	76.00	106.00	82.00	106.00	80.00	106.00	80.00	106.00	78.00
Chloroneb		0.02	0.00	0.01	0.00	86.00	74.00	94.00	72.00	88.00	68.00	88.00	68.00	86.00	60.00
Propachlor		0.02	0.01	0.03	0.00	80.00	86.00	86.00	82.00	84.00	80.00	88.00	84.00	84.00	72.00
Trifluralin		0.00	0.02	0.01	0.00	80.00	82.00	84.00	80.00	80.00	84.00	84.00	86.00	72.00	104.00
a-BHC		0.00	0.00	0.00	0.00	80.00	84.00	86.00	92.00	84.00	88.00	84.00	90.00	80.00	86.00
Lindane (g-BHC)		0.00	0.01	0.00	0.02	86.00	92.00	92.00	98.00	90.00	98.00	90.00	100.00	88.00	98.00
Simazine	1	N/A	0.06	N/A	0.05	N/A	102.00	N/A	90.00	N/A	84.00	N/A	90.00	N/A	84.00
Atrazine	1	N/A	0.07	N/A	0.10	N/A	86.00	N/A	90.00	N/A	96.00	N/A	90.00	N/A	96.00
b-BHC		0.00	0.00	0.01	0.00	88.00	96.00	92.00	96.00	92.00	100.00	94.00	102.00	90.00	98.00
d-BHC	2	N/A	0.00	N/A	0.00	N/A	98.00	N/A	104.00	N/A	106.00	N/A	112.00	N/A	108.00
Chlorothalonil		0.00	0.00	0.00	0.00	98.00	98.00	102.00	104.00	102.00	106.00	108.00	110.00	108.00	114.00
Metribuzin	2	N/A	0.00	N/A	0.00	N/A	94.00	N/A	80.00	N/A	72.00	N/A	90.00	N/A	78.00
Heptachlor		0.02	0.00	0.04	0.02	84.00	82.00	88.00	80.00	76.00	70.00	84.00	80.00	74.00	68.00
Alachlor		0.00	0.00	0.09	0.00	80.00	86.00	82.00	82.00	86.00	96.00	84.00	88.00	84.00	74.00
Cyanazine		0.00	0.00	0.01	0.00	106.00	94.00	110.00	90.00	112.00	94.00	114.00	96.00	112.00	90.00
Metolachlor		0.00	N/A	0.00	N/A	88.00	N/A	96.00	N/A	98.00	N/A	98.00	N/A	98.00	N/A
Dacthal		0.00	0.00	0.00	0.00	86.00	92.00	90.00	96.00	92.00	96.00	92.00	100.00	90.00	94.00
Heptachlor epoxide B		0.00	0.00	0.00	0.00	84.00	N/A	88.00	94.00	88.00	92.00	88.00	96.00	86.00	90.00
trans-Chlordane		0.00	0.00	0.00	0.00	82.00	82.00	86.00	90.00	82.00	86.00	84.00	90.00	80.00	84.00
Butaclor		0.00	0.00	0.00	0.00	88.00	104.00	106.00	86.00	98.00	88.00	102.00	94.00	108.00	86.00
cis-Chlordane		0.00	0.00	0.00	0.00	82.00	82.00	88.00	92.00	84.00	88.00	86.00	92.00	82.00	84.00
Endosulfan I		0.00	0.00	0.00	0.00	84.00	86.00	88.00	96.00	88.00	96.00	88.00	98.00	86.00	92.00
4,4'-DDE		0.01	0.01	0.01	0.01	78.00	80.00	80.00	86.00	74.00	78.00	78.00	86.00	70.00	72.00
Dieldrin		0.00	0.00	0.00	0.00	86.00	88.00	92.00	94.00	92.00	92.00	94.00	98.00	92.00	92.00
Endrin		0.00	0.00	0.00	0.00	86.00	90.00	94.00	92.00	90.00	94.00	94.00	98.00	104.00	92.00
Chlorobenzilate		0.00	0.00	0.00	0.00	84.00	84.00	78.00	86.00	76.00	90.00	66.00	90.00	52.00	76.00
Endosulfan II		0.00	0.00	0.00	0.00	84.00	84.00	90.00	94.00	92.00	96.00	92.00	100.00	90.00	92.00
4,4'-DDD		0.01	0.00	0.01	0.00	84.00	82.00	92.00	90.00	90.00	92.00	90.00	96.00	88.00	84.00
Endrin Aldehyde		0.01	0.00	0.01	0.00	84.00	82.00	90.00	88.00	92.00	94.00	92.00	96.00	92.00	88.00
4,4-DDT		0.01	0.00	0.01	0.00	94.00	82.00	106.00	94.00	106.00	94.00	110.00	100.00	110.00	86.00
Endosulfan Sulfate		0.00	0.00	0.00	0.00	86.00	80.00	94.00	94.00	96.00	96.00	96.00	98.00	96.00	86.00
Methoxychlor		0.00	0.00	0.01	0.00	102.00	86.00	116.00	90.00	116.00	94.00	120.00	100.00	92.00	66.00
Permethrin		0.06	0.00	0.03	0.00	108.00	94.00	94.00	112.00	96.00	104.00	104.00	130.00	94.00	98.00
Decachlorobiphenyl	S	0.41	0.46	0.39	0.45	N/A	N/A	86.00	90.00	84.00	100.00	86.00	104.00	80.00	84.00

1, 2 - Co-Elutting compounds on MR-1

Table 5b: All EPA Method 508.1 data generated. Like numbered compounds indicate co-elutions.

Sample Name		LCS 6 (%)		LCS 7 (%)		LCS 8 (%)		LCS 9 (%)		LCS 10 (%)		LCS 11 (%)		LCS 12 (%)	
Column ID		MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2
Pentachloronitrobenzene	IS	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Etridiazole		110.00	80.00	120.00	78.00	122.00	84.00	118.00	80.00	136.00	92.00	136.00	100.00	128.00	94.00
Chloroneb		82.00	62.00	96.00	72.00	94.00	70.00	88.00	64.00	94.00	74.00	94.00	70.00	84.00	66.00
Propachlor		86.00	80.00	98.00	92.00	98.00	96.00	98.00	86.00	110.00	94.00	100.00	94.00	92.00	90.00
Trifluralin		80.00	82.00	86.00	92.00	90.00	94.00	82.00	92.00	90.00	94.00	88.00	106.00	82.00	104.00
a-BHC		82.00	90.00	92.00	100.00	94.00	104.00	90.00	100.00	92.00	98.00	90.00	100.00	84.00	94.00
Lindane (g-BHC)		88.00	100.00	98.00	106.00	100.00	114.00	98.00	112.00	100.00	110.00	96.00	112.00	92.00	108.00
Simazine	1	N/A	80.00	N/A	90.00	N/A	98.00	N/A	98.00	N/A	102.00	N/A	104.00	N/A	108.00
Atrazine	1	N/A	98.00	N/A	82.00	N/A	94.00	N/A	102.00	N/A	100.00	N/A	100.00	N/A	104.00
b-BHC		90.00	100.00	96.00	106.00	100.00	112.00	96.00	114.00	98.00	108.00	96.00	106.00	90.00	102.00
d-BHC	2	N/A	114.00	N/A	112.00	N/A	126.00	N/A	126.00	N/A	120.00	N/A	122.00	N/A	116.00
Chlorothalonil		100.00	118.00	124.00	112.00	124.00	128.00	114.00	128.00	122.00	124.00	120.00	136.00	116.00	130.00
Metribuzin	2	N/A	80.00	N/A	78.00	N/A	84.00	N/A	82.00	N/A	76.00	N/A	92.00	N/A	90.00
Heptachlor		80.00	76.00	104.00	92.00	106.00	100.00	86.00	84.00	108.00	98.00	106.00	102.00	100.00	96.00
Alachlor		88.00	90.00	116.00	86.00	94.00	98.00	80.00	98.00	98.00	96.00	90.00	96.00	86.00	110.00
Cyanazine		110.00	88.00	130.00	88.00	138.00	100.00	124.00	90.00	132.00	98.00	124.00	98.00	118.00	96.00
Metolachlor		98.00	N/A	104.00	N/A	108.00	N/A	102.00	N/A	106.00	N/A	104.00	N/A	98.00	N/A
Dacthal		90.00	98.00	94.00	98.00	98.00	110.00	92.00	106.00	98.00	106.00	94.00	110.00	90.00	104.00
Heptachlor epoxide B		86.00	94.00	90.00	98.00	96.00	110.00	90.00	104.00	94.00	106.00	94.00	106.00	86.00	100.00
trans-Chlordane		80.00	86.00	82.00	86.00	94.00	106.00	82.00	94.00	88.00	96.00	86.00	96.00	80.00	90.00
Butaclor		102.00	88.00	106.00	88.00	114.00	102.00	106.00	96.00	114.00	100.00	110.00	106.00	108.00	104.00
cis-Chlordane		82.00	86.00	82.00	86.00	94.00	104.00	84.00	92.00	90.00	94.00	88.00	96.00	82.00	88.00
Endosulfan I		86.00	94.00	90.00	96.00	96.00	110.00	88.00	104.00	94.00	104.00	92.00	106.00	86.00	98.00
4,4'-DDE		76.00	80.00	76.00	80.00	92.00	104.00	76.00	88.00	84.00	92.00	80.00	88.00	74.00	80.00
Dieldrin		92.00	94.00	94.00	90.00	102.00	106.00	94.00	100.00	100.00	100.00	98.00	106.00	92.00	102.00
Endrin		94.00	96.00	100.00	96.00	106.00	114.00	90.00	104.00	104.00	108.00	100.00	108.00	98.00	104.00
Chlorobenzilate		60.00	76.00	62.00	90.00	72.00	106.00	72.00	96.00	76.00	104.00	72.00	102.00	68.00	98.00
Endosulfan II		90.00	94.00	92.00	94.00	98.00	112.00	90.00	106.00	98.00	106.00	94.00	108.00	90.00	102.00
4,4'-DDD		92.00	92.00	84.00	78.00	100.00	104.00	90.00	94.00	94.00	96.00	96.00	102.00	92.00	96.00
Endrin Aldehyde		84.00	82.00	88.00	80.00	96.00	104.00	88.00	94.00	94.00	100.00	94.00	102.00	88.00	98.00
4,4-DDT		110.00	94.00	94.00	78.00	120.00	108.00	106.00	96.00	112.00	96.00	112.00	100.00	106.00	94.00
Endosulfan Sulfate		94.00	90.00	96.00	90.00	104.00	108.00	96.00	100.00	102.00	106.00	100.00	104.00	96.00	96.00
Methoxychlor		120.00	92.00	112.00	102.00	134.00	104.00	120.00	92.00	132.00	98.00	130.00	102.00	122.00	98.00
Permethrin		104.00	92.00	98.00	80.00	156.00	132.00	94.00	92.00	114.00	96.00	116.00	106.00	106.00	136.00
Decachlorobiphenyl	S	84.00	96.00	74.00	78.00	90.00	110.00	82.00	96.00	74.00	88.00	88.00	108.00	84.00	104.00

1, 2 - Co-Elutting compounds on MR-1

The Analysis of 1,4-Dioxane for EPA Method 522 and UCMR 3

David Gallagher, Michael Ebitson, Horizon Technology, Inc., Salem, NH

Introduction

1,4-Dioxane is primarily used as an industrial solvent or solvent stabilizer. Its carcinogenic classification by EPA in Group B2 and by California in Proposition 65 along with its more recent detection in multiple groundwater supplies across the US have led to its placement on the UCMR 3 list and has increased the demands for environmental testing.

The main hindrances to the recovery of 1,4-Dioxane is both its high water solubility and its volatility. Over the years, multiple techniques have been employed in an effort to bypass these problems. Purge and Trap analysis is sometimes employed and it does bypass any potential losses due to heating, however it has difficulty due to the high water solubility of the compound. Continuous Liquid-Liquid extraction techniques avoid problems due to solubility, but the large amount of solvent used means that extracts must be concentrated before the final analysis can take place. To avoid these problems, EPA developed Method 522 which involves an extraction process using a solid phase cartridge and very little solvent.

This Application Note will demonstrate the extraction of 1,4-Dioxane from an aqueous matrix using Option 1 of EPA Method 522 for 500 mL initial volume sample. It will make use of the SmartPrep Cartridge Extraction System to produce a valid Initial Demonstration of Precision (IDP) and Initial Demonstration of Accuracy (IDA). The SmartPrep Extraction System can extract 6 samples unattended when using the bottle rinse mode and 12 samples unattended when not in bottle rinse mode. In this case, the SmartPrep will be made to run without the use of the optional bottle rinse mode to maximize sample throughput. All the flow rates were developed and programmed into the SmartPrep to obtain the highest recovery of the target analyte with the highest amount of reproducibility.

Instrumentation

- Horizon Technology
  - SmartPrep™ Automated Cartridge Extractor
    - 6 mL Cartridge Configuration
    - 20 mL Tray
- Restek
  - ResPrep 6 mL, 2 g Coconut Charcoal Cartridges
  - Rxi®-5Sil MS; 30 m x 0.25 mm x 0.25 µm
- Agilent Technologies
  - 6890N GC
  - 5975C MS – Operated in SIM mode

Method Summary

1. Prepare 500 mL of deionized water using 0.5 g of Sodium Bisulfate to lower the pH to approximately 2.
2. Add 2.5 µL of a 2000 µg/mL surrogate solution containing 1,4-dioxane-d_8 and 7.5 µL of a 200 µg/mL spiking solution containing 1,4-dioxane (for blank samples, add only surrogate solution).
3. Attach Sip Tube number 1 to the sample container.
4. Place a 20 mL VOA vial in position 1 of the tray.
5. Place a 6 mL, 2 g Coconut Charcoal cartridge on position 1 of the carousel.
6. Program and run the method given in Table 2 using an N_2P1 pressure of 5 psi and an N_2P2 pressure of 10 psi.
7. Bring the final volume of the extract to 10 mL.
8. Add internal surrogate (tetrahydrofuran-d_8) to the full 10 mL extract and run on a GC-MS using the conditions given in Table 1.

The Horizon Technology SmartPrep Automated Cartridge Extractor.

Table 1: GC-MS Acquisition Program

Injection:
- Inlet Temperature: 200 °C
- Mode: Split (50:1)
- Amount: 1 µL

Carrier Gas:
- Helium at a constant flow rate.

Oven Program:
- 30 °C hold for 2 min to 50 °C at 5 °C/min to 200 °C at 50 °C/min hold for 1 min.

MS Ions Monitored:
- Tetrahydrofuran-d_8 – 46, 78, 80
- 1,4-dioxane-d_8 – 62, 64, 96
- 1,4-dioxane – 58, 88

Results

Once a calibration curve was generated on the GC-MS, the extraction process was programmed into the SmartPrep system as it appears in Method 522. Each extract took approximately 1.5 hr to complete on the SmartPrep. During this time, the SmartPrep delivered all reagents, gases, and sample automatically allowing the user to streamline the preparatory process by performing the extractions overnight.

To obtain a valid IDP and IDA study, four to seven extracts must be prepared near the midrange of the calibration curve. It should be noted that the same extracts may be used for both quality tests. The relative standard deviation (RSD) must be less than 20 % and the average recovery must fall within ± 20 %. The studies performed for this Application Note had the surrogate and internal standards spiked at 10 µg/L while the target analyte was spiked at 3 µg/L. This corresponds to a midrange concentration of the calibration curve that was run on the GC-MS. The data obtained for this study is given in Table 3. With the recovery of both the surrogate and target analyte being 99 and 98 % respectively, and the RSD being less than 10 %, the IDP and IDA studies pass Method 522 criteria.

Conclusions

As many labs investigate 1,4-Dioxane further within the scope of the UCMR 3 program, a reliable technique is needed to extract the target analyte from aqueous sample matrices. The SmartPrep Cartridge Extractor has demonstrated in this Application Note that it can do so with a high amount of both precision and accuracy. In addition to this, the SmartPrep Cartridge Extractor has the ability to extract up to 12 samples automatically while the user is otherwise occupied. These features combine together to streamline the sample preparation process and allow for it to keep up with the rigorous demands of the UCMR 3 program.

Table 2: EPA Method 522 Extraction Program

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense
1		DCM	3	20	10	2	No
2		MeOH	3	20	10	2	No
3		MeOH	3	20	10	0	No
4		DI	3	20	10	0	No
5		DI	3	20	10	0	No
6		DI	3	20	10	0	No
7		DI	3	20	10	0	No
8		DI	3	20	10	0	No
9		DI	3	20	10	0	No
10	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**
		Yes	1	20	10	400	500
11	**N2 Purge Timer**	**Delay (min)**					
		10					
12	**Cartridge Elute**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**N2 Purge** (s)	**Liquid Sense**
		DCM	3	10	1	20	0	No
13	**Cartridge Elute**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**N2 Purge** (s)	**Liquid Sense**
		DCM	3	10	1	20	0	No
14	**Cartridge Elute**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**N2 Purge** (s)	**Liquid Sense**
		DCM	3	10	1	20	20	No

Table 3: Initial Demonstration of Precision and Accuracy for 1,4-Dioxane

	Blank	LCS 1	LCS 2	LCS 3	LCS 4	LCS 5	LCS 6	LCS 7	Average	St Dev	RSD
Recovery as ug/mL											
	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(%)
1,4-Dioxane-d8	8.64	10.81	9.22	9.83	10.39	10.15	9.73	9.49	9.94	0.54	5.47
1,4-Dioxane	ND	3.17	2.60	2.98	3.13	2.94	3.00	2.71	2.93	0.21	7.13
Recovery as %											
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1,4-Dioxane-d8	86.44	108.06	92.16	98.32	103.86	101.48	97.34	94.86	99.44	5.44	5.47
1,4-Dioxane	ND	105.53	86.53	99.40	104.27	98.07	100.00	90.33	97.73	6.97	7.13

SmartPrep SPE Cartridge System: Advanced Fluid Handling Features

Robert Johnson, Horizon Technology, Inc., Salem, NH

Introduction

Solid Phase Extraction (SPE) cartridges have been used for many years, and are well established as a proven extraction, clean-up, and fractionation technique for a wide variety of sample matrices. As such, a diverse set of chemistries are available to handle these various samples. For all of this work, cartridges can be used manually, via a manifold-type setup, or with an automated system, which would simply automate the manual steps. Automated systems are especially preferable when involved with method development and determining the optimal SPE conditions to use.

For any SPE cartridge sample preparation procedure to be successful, especially an automated one, it is essential that several fluid handling steps be performed properly and consistently. Some, but not all, of these steps are listed below:

- Accurate and reproducible volume delivery of the desired reagent(s).
- Delivery of all liquids at a controlled and adjustable flow rate.
- Control of all operations to a desired and precise time interval.
- Handling of a full range of reagents.
- Rinsing the sample container with the eluting reagent.
- Accurate and reproducible mixing of reagent gradients.
- The minimization or elimination of residual air from being introduced into a previously conditioned cartridge.
- Monitoring the presence of all reagents, so the cartridge is never allowed to inadvertently go dry.
- Delivery of all liquids (reagents and samples) directly to the top of the packing material and not simply into the body of the cartridge barrel.
- Purging all parts and lines with an inert gas.
- Compensating for reagent and sample out-gassing.
- Cleaning all flow paths to eliminate carryover and background contamination.
- Uniform treatment of samples.

While the above capabilities are important to ensure successful chemistry, there are other fluid handling steps that are desirable. One of these is the ability to load the entire sample, and to have a system automatically calculate the total volume of the sample that was processed. For large volume environmental samples, this ability would eliminate the operator from either weighing the sample bottle both before and after use or manually marking the sample bottle, using the sample, refilling the bottle to the mark with tap water, and pouring this into a large graduated cylinder to record the starting volume. Both manual operations are time consuming, and because visually reading a mark or graduation line is very subjective, this manual interaction is prone to significant errors. If the wrong initial sample volume is used, then the final calculated analyte concentrations and recovery values will be incorrect.

Horizon Technology SmartPrep™ SPE Cartridge System.

Another desired fluid handling feature is the ability to collect multiple fractions from a single SPE cartridge. Fraction collection is essential for methods like the MA-EPH procedure, where the aliphatic and aromatic compounds must be separated. Also, in method development, the ability to fractionate would allow for the determination of ideal reagent volumes, or reagent ratios to use to provide better separation, or sample cleanup from the cartridge.

Tied with the desire to collect multiple fractions, would be the ability to mix reagent gradients, and use these gradients to elute specific compounds off of the cartridge. For method development work, sometimes the proper reagent ratio is not known, so having the ability to precisely adjust and control the reagent ratios for elution would be extremely useful.

The desire to keep all reagent bottles and lines sealed, so as to minimize, or eliminate any reagent exposures to the operator. This would also allow the SPE operations to be performed on a lab bench, vs. a hood. This last desire would certainly be based on the nature of the reagents and samples being processed, which would dictate their actual place of use.

Another desire, that is well known, is the need to rinse each sample container with the eluting reagent, as many of the analytes of interest do adhere to the container walls. If the walls are not rinsed effectively with the eluting reagent, many of the analytes will not be recovered, resulting in low and inconsistent recovery values.

Instrumentation

- Horizon Technology
  - SmartPrep™ SPE Cartridge System

Conclusions

The SmartPrep SPE Cartridge System has been designed to address and resolve all of the critical and desired fluid handing needs when performing SPE operations.

In addition, the SmartPrep is a modular design, meaning that up to 8 individual modules can be run from a single PC. This module approach allows greater sample handling capacity, the ability to run multiple methods, and the ability to run various cartridge sizes simultaneously. The following points highlight several of the SmartPrep's unique features:

- Ability to handle 1, 3, and 6 mL SPE cartridges.
- Ability to run up to 12 samples on a single module.
- Ability to run multiple methods on a single module.
- Ability to run pre and post run methods to ensure the module is cleaned and prepped before running the actual samples, and to clean and prep the unit for automatic shutdown after the last sample has been processed.
- Ability to handle up to eight reagents for all conditioning, wash, and eluting operations.
- Automatic calculation, based on the methods to be run, of the total volume of reagents required and the total volume of waste reagents that will be generated.
- Separate all waste reagents into one of three identified waste containers; organic, aqueous, and chlorinated. Waste container names can also be customized to the user's specifications.
- Provides accurate and reproducible volume delivery of the desired reagent(s).
- Provides a precise and consistent flow rate through the cartridge.
- Microprocessor maintains and controls all time critical steps.
- Use optical liquid sensors to ensure all reagents are delivered properly.
- Automatically calculate the volume of the sample processed.
- Detect potential errors and pause to notify the operator.
- Utilizes a 10 mL mixing chamber which allows most ratios of reagent mixtures to be created and used for the SPE procedure.
- Allows automatic rinsing of the original sample container to ensure the best chemistry is performed.

The SmartPrep is a very unique and powerful system that can enhance all SPE cartridge operations currently being done manually, freeing up valuable operator time.

SmartPrep SPE Cartridge System: Automatic Sample Volume Calculation

Robert Johnson, Horizon Technology, Inc., Salem, NH

Introduction

Analytical methods which extract aqueous samples require that the initial volume of the sample be determined, as it is necessary to calculate the concentration of the analytes in the sample. Typically, this is done by marking the sample meniscus on the side of the sample bottle before the sample is extracted. Once the sample has been decanted, the sample bottle is filled with water up to the meniscus and decanted into a graduated cylinder, where the sample volume is then recorded. The acts of measuring a meniscus, transferring, and decanting are all very subjective, and can lead to a propagation of errors in the final reported values. The SmartPrep SPE Cartridge System utilizes an optical liquid sensor and sophisticated software, to automatically calculate the volume of sample that has been processed.

Instrumentation

- Horizon Technology
  - SmartPrep™ SPE Cartridge System
    - 6 mL Cartridge Configuration
    - 20 mL VOA Vial Tray

Method Summary

1. Condition a 6 mL SPE C-18 cartridge with 2 mL of Reagent Water.
2. Attach a Sip Tube to the sample container and start the method. The optical liquid sensor will determine when the entire volume of water sample has been processed.
3. Clean the sample line with Vent and nitrogen, in preparation for the next sample run.
4. The sample report will display each samples estimated volume.

The SmartPrep software uses an optical liquid sensor to monitor the presence of the water sample, and determines when the water sample has finished processing. By knowing certain values, which are entered in the Utilities window, the total volume of the sample may be calculated.

For this work, a value of 0.9 seconds was used for the Overhead Time per syringe stroke. This is the time in seconds for the two 12 port valves to rotate between the SPE cartridge port and the sample bottle port.

A value of 36 seconds was used for the Overhead Time for the Load step. This is the time it takes to purge the sample line and a 10 inch Sip Tube of residual air pockets by delivering reagent water down them.

A value of -13 was used for the Calibration Offset, and a volume of 2.85mL was used for the Tubing Dead Volume (Volume between sample line inlet and V1).

The Horizon Technology SmartPrep™ Extraction System.

Results

A total of 7 replicates were run over a 7 day period for five different amounts of water (100, 250, 500, 750, and 1000 mL). These volumes were precisely weighed out and processed using the above values through the SmartPrep. The SmartPrep automatically calculated the volumes shown in Table 1. The SmartPrep consistently and accurately measured the volume every time for each volume set with a maximum error of 2.3 %. This error is less than most Class A graduated cylinders which typically have 3 % error.

Table 1: Estimated Volume Calculations

Replicate	Actual Volume	Extimated Volume	Error
	(g)	(mL)	(%)
1	100	100	0.0
2	250	256	2.3
3	500	507	1.4
4	750	765	2.0
5	1000	1022	2.2

Conclusions

The results clearly indicate the SmartPrep consistently and accurately measures the volume every time for a wide range of volumes to within 2.3 % error or less. This automated feature eliminates the subjective process of the operator marking and refilling a sample bottle, and transferring to a graduated cylinder and replaces it with an absolute process containing less error. The automated volume feature will not only streamline aqueous extraction methods, but will provide more accurate and precise volumes leading to a higher confidence in results.

SmartPrep SPE Cartridge System: Automatic Fraction Collection

Robert Johnson, Horizon Technology, Inc., Salem, NH

Introduction

Based on samples to be processed, the final analytical technique to be employed, or the need to develop and optimize an analytical extraction method, there are times when it is desirable to collect multiple elution fractions from a single sample. One such example would be the separation of aliphatic and aromatic compounds, as required in the Massachusetts method for the determination of Extractable of Petroleum Hydrocarbons (MA-EPH).

For the MA-EPH method, a one mL sample is treated with a fractionation surrogate and loaded onto a silica gel cartridge. The cartridge is then eluted with hexane until all of the aliphatic compounds are collected in one vessel. Then, just before the first aromatic begins to elute off the cartridge, the flow is redirected into a second collection vessel and methylene chloride is used to elute the remaining aromatic compounds retained on the cartridge. Each fraction is then analyzed separately by a gas chromatograph with a flame ionization detector (GC-FID).

While this fraction collection step can be done manually, it is very labor intensive, and prone to errors if the collected elution volumes are not consistent. For the MA-EPH method, a hexane difference of ± 0.5 mL can be significant and, if a problem is encountered, the sample must be re-fractionated. This Application Note will describe how the SmartPrep SPE Cartridge System can be configured and programmed to collect multiple elution fractions accurately and consistently.

Instrumentation

- Horizon Technology
  - SmartPrep™ SPE Cartridge System
    - 6 mL Cartridge Configuration
    - 20 mL VOA Vial Tray
- 6 mL, 2.9 g SPE silica gel cartridge

Method Summary (MA-EPH Fractionation)

1. Attach Sample Line number 1 to the sample container.
2. Place a 20 mL VOA vial in positions 1 and 2 of the tray.
3. Place a 6 mL, 2.9 g silica gel cartridge on position 1 of the carousel.
4. Program and run the method given in Table 1 using an N_2P1 pressure of 5 psi and an N_2P2 pressure of 15 psi (keep in mind that the actual volume of solvents used will be a function of the silica gel cartridge brand and lot used).
5. Analyze both fractions by GC-FID.

Once the SmartPrep has been properly configured with the necessary reagents, desired waste ports, and the MA-EPH method shown, the method is assigned to a position from one to six. For this example, a 6 mL Teflon cartridge filled with 2.9 g of silica gel was used. The cartridge was conditioned with 6 mL of hexane and was sent directly to the organic waste container. The 1 mL sample was then placed onto the head of the cartridge, at a sip and delivery rate of 5 mL/min. This slower rate ensures that the sample can spread evenly and uniformly into the SPE cartridge. Once the sample had been loaded, 4.5 mL of hexane was used to elute the aliphatic compounds into the first collection vessel. The exact amount of hexane needed to elute off only the aliphatic compounds was predetermined by previous work. The aromatic compounds were then eluted into a second vessel using 5.0 mL of methylene chloride (DCM). The extracts are then ready to be concentrated to their final volume of 1 mL and analyzed on a GC-FID.

Horizon Technology SmartPrep™ SPE Cartridge System.

Conclusions

The SmartPrep SPE Cartridge System can be used to collect up to four fractions separately from a single sample. For methods such as MA-EPH where the manual technique is so critical to method performance, the ability to control parameters such as elution volumes and flow rates and to automatically switch between multiple collection vessels will improve the accuracy and precision of that method. It will not only remove some of the error associated with a user's technique, but allow that user to perform other, more complicated, duties within the laboratory once the SmartPrep has been started.

SPE Disk-Based

SPE-DEX 4790 Automated Extractor

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Table 1: MA-EPH Fractionation Method

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense	
1		Hexane	6	10	0	0	No	
2	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		3.5	1	1.5	5	5	0	0
	Cartridge Elute	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**N2 Purge** (s)	**Liquid Sense**
3		Hexane	4.5	5	1	0	0	No
4		DCM	5	5	2	0	0	No
5		VENT	4	20	2	0	10	No
6	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		Hexane	4	10				
7	**Clean Plunger**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Soak (s)**	**Purge (s)**		
		Mixing Chamber	6	10	0	0		

Recovering 1,4-Dioxane for EPA Method 522 Option 1 and UCMR 3 Using the SPE-DEX 4790

David Gallagher, Michael Ebitson, Horizon Technology, Inc., Salem, NH

Introduction

With the promulgation of the third iteration of the Unregulated Contaminant Monitoring Program, testing for the presence of 1,4-Dioxane has become a topic of concern. Primarily used as an industrial solvent or solvent stabilizer, the main hindrances to the recovery of 1,4-Dioxane are both its high water solubility and its volatility. Traditional techniques such as Purge and Trap analysis or Continuous Liquid-Liquid extraction, which requires concentration, may solve one of the issues but are shown to exacerbate the other. To avoid these problems altogether, EPA developed Method 522 which outlines a technique for extraction using a solid phase cartridge and very little solvent.

This Application Note will demonstrate the extraction of 1,4-Dioxane from an aqueous matrix using Option 1 of EPA Method 522 for 500 mL initial volume samples. In this study, the SPE-DEX 4790 will be used to generate a valid Initial Demonstration of Precision (IDP) and Initial Demonstration of Accuracy (IDA). The SPE-DEX 4790 was designed to process large volume aqueous samples in a manner which is both fast and produces accurate results.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790
  - Low Flow Vacuum Regulator
  - 6 mL Cartridge Funnel
  - VOA Vial Collection Adapter
- Restek
  - ResPrep 6 mL, 2 g Coconut Charcoal Cartridges
  - Rxi®-5Sil MS; 30 m x 0.25 mm x 0.25 µm
- Agilent Technologies
  - 6890N GC
  - 5975C MS – Operated in SIM mode

Method Summary

1. Prepare 500 mL of deionized water using 0.5 g of Sodium Bisulfate to lower the pH to approximately 2.
2. Add 2.5 µL of a 2000 µg/mL surrogate solution containing 1,4-dioxane-d_8 and 7.5 µL of a 200 µg/m spiking solution containing 1,4-dioxane (for blank samples, add only surrogate solution).
3. Using a VOA Vial Adapter, attach a 20 mL VOA vial to the SPE-DEX 4790 and secure with a clip.
4. Attach a 6 mL Cartridge Funnel to the Coconut Charcoal Cartridge and load the assembly onto the SPE-DEX 4790.
5. Program and run the method given in Table 2 using the operation conditions of:
   - Main Vacuum: -25” Hg
   - Solvent Waste Vacuum: -15” Hg
   - Water Waste Vacuum: -15”Hg
   - Solvent Bottle Pressure: 15 psi
   - Extractor Pressure: 40 psi

The Horizon Technology SPE-DEX® 4790 and Envision® Controller

6. Bring the final volume of the extract to 10 mL.
7. Add internal surrogate (tetrahydrofuran-d_8) to the full 10 mL extract and run on a GC-MS using the conditions given in Table 1.

Table 1: GC-MS Acquisition Program

Injection:
- Amount: 1 µL
- Inlet Temperature: 200 °C
- Gas type: Helium
- Pressure: 6.47 psi
- Mode: Split (50:1)
- Split flow: 49.9mL/min
- Total flow: 54.1mL/min
- Gas Saver: on
- Saver flow: 20.0mL/mn
- Saver time: 5:00 min

Column Conditions:
- Mode: Consistent flow
- Initial flow: 1.0 mL/min
- Average velocity: 36 cm/sec

Oven Program:
- 30 °C hold for 2 min to 50 °C at 5 °C/min to 200 °C at 50 °C/min hold for 1 min.

MS Ions Monitored:
- Tetrahydrofuran-d_8 – 46, 78, 80
- 1,4-dioxane-d_8 – 62, 64, 96
- 1,4-dioxane – 58, 88

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	DCM	10 sec	30 sec
Prewet 2	MeOH	10 sec	2 sec
Prewet 3	DI Water	10 sec	2 sec
Prewet 4	DI Water	10 sec	2 sec
Prewet 5	DI Water	10 sec	2 sec
Sample Process			
Air Dry 10 min			
Rinse 1	DCM	1 min	1 min
Rinse 2	DCM	1 min	1 min

Results

A calibration curve was generated using the GC-MS and the method given above was used to extract five samples at the concentrations associated with an Initial Demonstration of Precision and an Initial Demonstration of Accuracy. It should be noted that, per EPA Method 522, the same set of samples may be used for both studies as long as the relative standard deviation (RSD) is less than 20 % and the average recovery is within ± 20 %.

The samples run for this study had both the internal standard and surrogate spiked at 10 µg/L and the target analyte spiked at 3 µg/L. The recoveries for these samples are given below in Table 3 and show excellent recoveries and RSD.

Table 3: EPA Method 522 Recoveries

	Recovery as ug/L		Recovery as %	
	1,4-Dioxane-d8	1,4-Dioxane	1,4-Dioxane-d8	1,4-Dioxane
Blank	9.25	ND	92.54	ND
LCS 1	9.30	2.92	93.02	97.40
LCS 2	7.70	2.97	77.00	99.07
LCS 3	7.97	2.95	79.70	98.40
LCS 4	9.29	2.91	92.86	97.07
LCS 5	8.65	2.96	86.50	98.60
Average	8.58	2.94	85.82	98.11
St Dev	0.74	0.03	7.37	0.84
RSD (%)	8.59	0.86	8.59	0.86

Conclusion

With the placement of 1,4-dioxane on the UCMR 3 list more laboratories require a technique which is both fast and reliable. The SPE-DEX 4790 Extractor with the Envision Platform Controller demonstrates that excellent precision and accuracy can be obtained while performing a single sample extraction in approximately 30 minutes. The combination of these features help to streamline the sample preparation process and meet the growing demands of the environmental testing industry.

Analysis of Pharmaceuticals in Water by Automated Solid Phase Extraction

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Introduction

The analytical challenge of measuring emerging contaminants in the environment has been a major research focus of scientists for the last 20 years. Water quality is a critical issue especially for sustainable socioeconomic development. Anthropogenic activities are one of the main causes for water quality damage and, consequently, social concern calls for quality control action. Even after water treatment, it has been demonstrated in many studies that organic contaminants escape conventional wastewater treatment processes and they end up in aquatic systems.

Pharmaceuticals and personal care products are an important group of contaminants that have been targeted, especially in the last decade. For example, EPA Method 1694[1], published in December 2007, is a guiding and screening method for those scientists analyzing pharmaceuticals in environmental samples. The standard EPA protocol uses solid-phase extraction (SPE) for water samples followed by the analysis of extracts by tandem mass spectrometry using a single transition for each compound, with retention time guidelines for identification.

Contaminants are usually present in the environmental samples at very low concentration levels (ng/L) and, for this reason, solid phase extraction techniques are often used to isolate and pre-concentrate the organic compounds of interest. This has led to the development of a method for low concentration level analysis of pharmaceuticals in drinking water samples. The implementation for this method consists of the analysis of 20 analytes which are some of the most common contaminants found in the environment currently.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extraction System
  - Envision® Controller
  - Atlantic™ HLB-M SPE Disk
- Agilent
  - 1200 HPLC and 6220 LC-TOF-MS
  - Zorbax Eclipse XDB-C8 Column
- Caliper Life Sciences
  - Turbovap Concentration Workstation

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, and the Envision® Platform Controller

Method Summary

Drinking water samples were taken from the tap at the Center for Environmental Mass Spectrometry (Boulder, CO). Wastewater samples were collected from several wastewater treatment plants in Denver, Boulder and Estes Park (Colorado, USA). Surface water samples were collected from several locations including rivers and reservoirs in Colorado. A spiking mixture containing the 20 pharmaceutical compounds was used to spike water samples at 0.5 ug/L. No additives were added to water samples, and no filtration of samples was needed.

1. The SPE-DEX 4790 system was purged using a generic method shown in Table 1.
2. Water samples were extracted using the SPE-DEX 4790 system with the method shown in Table 2 resulting in approximately 40 mL of extract.
3. Extracts were transferred to a 45ºC water bath and concentrated with a gentle stream of nitrogen to near dryness.
4. The dry sample was reconstituted in a 1:9 v/v acetonitrile and deionized water solution.

Sample Analysis

The separation of the analytes was carried out using an HPLC system equipped with a reversed phase C_8 analytical column of 150 mm x 4.6 mm and 5 µm particle size.

Column temperature was maintained at 25 ºC. The injected sample volume was 50 µL. Mobile phases A and B were acetonitrile and water with 0.1% formic acid, respectively. The optimized chromatographic method held the initial mobile phase composition (10% A) constant for 5 min, followed by a linear gradient to 100% A after 30 min. The flow-rate used was 0.6 mL/min. A 10-min post-run time was used after each analysis. This HPLC system was connected to a time-of-flight mass spectrometer Agilent 6220 MSD TOF equipped with a dual electrospray source, operating in positive ion mode, using the following operation parameters: capillary voltage: 4000 V; nebulizer pressure: 45 psig; drying gas: 9 L/min; gas temperature: 300 ºC; fragmentor voltage: 190V; skimmer voltage: 60V; octopole RF: 250 V.

Table 1: Purge Method

Step	Solvent	Dry Time
Prewet 1	DI Water	0:15 sec
Prewet 2	Methanol	0:15 sec
Wash 1	DI Water	0:15 sec
Rinse 1	Methanol	0:15 sec

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Methanol	2:00 min	0:15 sec
Prewet 2	DI Water	1:00 min	0:05 sec
Sample Process			
Wash 1	DI Water	1:00 min	0:15 sec
Air Dry 15:00 min			
Rinse 1	Methanol	1:30 min	0:15 sec
Rinse 2	Methanol	1:30 min	1:00 min

Results

The extracts were analyzed by LC-TOF-MS. The compounds were chromatographically separated and detected by accurate mass measurements.

The recoveries and relative standard deviations (RSD) for the selected pharmaceuticals are within EPA's 1694 method criteria for precision and recovery. The results for three replicates are presented in Table 3 and a sample chromatogram for the compounds is given in Figure 1.

Conclusions

The results demonstrated that the SPE-DEX 4790 using Atlantic HLB-M disks can effectively extract pharmaceutical compounds from 1-L water samples in a fraction of time (approx. 40 min). This system allows you to use the original sample bottle which will be rinsed with all of the extraction solvents before the elution step. This rinsing step ensures that all the compounds are rinsed off the glass and retained on the disk.

Acknowledgements

Horizon Technology would like to thank Imma Ferrer and E. Michael Thurman of the Center for Environmental Mass Spectrometry at the University of Colorado in Boulder for their contributions to this Application Note.

References

[1] EPA Method 1694: Pharmaceuticals and personal care products in water, soil, sediment, and biosolids by HPLC/MS/MS, December 2007, EPA-821-R-08-002.
[2] Ferrer, I., Zweingenbaum, J.A., Thurman, E.M., J. Chromatogr. A, 1217 (2010) 5674-5686.

Table 3: Pharmaceutical Recoveries Using SPE TOF

Analyte	Use	Average Recovery (%)	RSD (%)
Acetaminophen	Non-steroidal anti inflammatory	65	8
Albuterol	Bronchodilator	79	5
Atenolol	Antihypertensive	86	3
Caffeine	Cardiac and respiratory stimulant	66	5
Carbamazepine	Anticonvulsant/Antidepressant	101	2
Cotinine	Antidepressant	86	5
DEET	Mosquito repelant	89	6
Dehydronifedipine	Antihypertensive	91	5
Diclofenac	Anti inflammatory	88	9
Diltiazem	Antihypertensive	71	8
Diphenhydramine	Antihistamine	76	5
Gemfibrozil	Non-steroidal anti inflammatory	101	2
Ibuprofen	Non-steroidal anti inflammatory	108	5
Lamotrigine	Antidepressant	95	3
Metoprolol	Antihypertensive	73	5
Naproxen	Non-steroidal anti inflammatory	110	7
Sulfadimethoxine	Antibiotic	85	5
Sulfamethoxazole	Antibiotic	46	8
Triclocarban	Antiseptic	65	5
Trimethoprim	Antibacterial	83	3

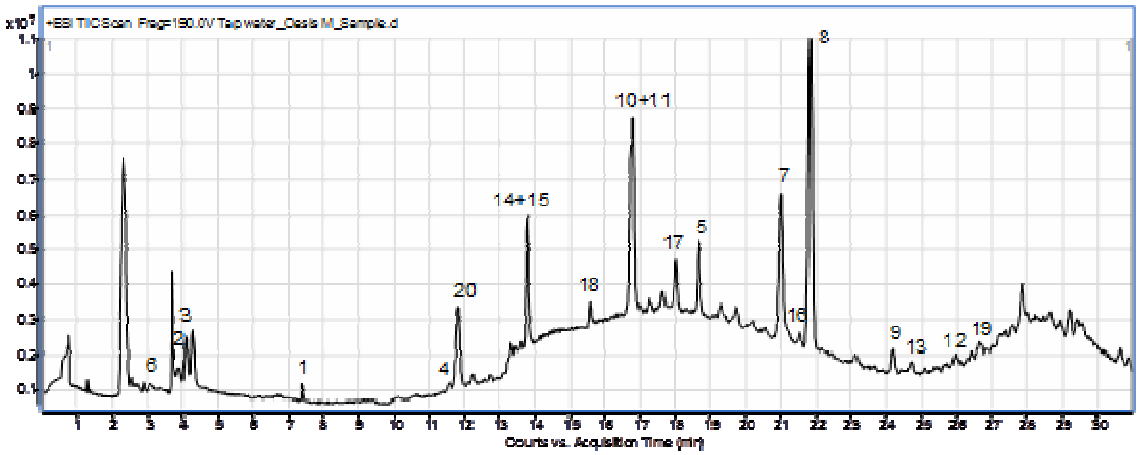

Figure 1: LC-TOF-MS analysis of a spiked tap water sample after extraction with the SPE-DEX 4790

Fast Automated SPE and GC/MS Analysis of PAH Compounds in Tap Water Using the SPE-DEX® 4790 Automated Extractor System

Steve McDonald, Horizon Technology, Inc., Salem, NH

Introduction

Polycyclic aromatic hydrocarbons (PAH) are an important class of environmental contaminants because of their prevalence and demonstrated adverse health effects. PAHs are generated in exhaust from the burning of fossil fuels and other natural products including gasoline, diesel, coal, oil, and wood.

PAHs in tap water are mainly attributed to the presence of PAH-containing materials in water storage and distribution systems. Though few data are available for estimating the potential for PAH release to water from these materials, there are reports that levels can reach as high as 0.01 mg/L with optimum leaching conditions.

The EPA has found that some PAHs can affect health when exposure is at levels above the maximum concentration limit (MCL) for relatively short periods of time. The damage can include suppressed immune systems, or red blood cell damage leading to anemia. Long-term exposure is believed to lead to potential developmental and reproductive effects and some forms of cancer.

EPA Method 3535 provides a general description of solid phase extraction (SPE) for the extraction of semi-volatile contaminants from aqueous samples. This application note uses the Horizon Technology SPE-DEX® 4790 automated extraction system with a DVB SPE disk to extract an aqueous sample for PAH compounds analysis. The extract is dried using the Horizon Technology DryDisk®.

The SPE-DEX® 4790 system was designed to fully automate the SPE process and allow for the extraction of a wide range of compounds from a both effluent and influent samples. The DryDisk® solvent drying system uses a patented membrane to allow solvent through, but not water. Automated SPE is an attractive alternative to liquid-liquid extraction (LLE) techniques because it is safer, faster, generates less solvent waste, and is more cost effective.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extractor System
  - DryDisk® SDS
- JT Baker Speedisk DVB (47 mm, PN 8072-07)
- Agilent 5890 GC/5971 MSD
- Restek
  - Column: 15m X 0.25 mm X 0.25 um Rtx-5 Sil MS
  - Spiking compounds PN 31622
- Water bath capable of maintaining 40 °C

Horizon Technology SPE-DEX® 4790 with Envision™ controller.

Method Summary

1. Adjust a 1000 mL sample of tap water to pH 2.
2. Add spike compounds to the water sample.
3. Place the sample bottle onto the extractor and start the extractor using the method in Table 1.
4. After approx 18 Min, 20 mL of extract are collected in the collection vessel.
5. Dry the extract with the Dry Disk® SDS.
6. Concentrate the extract to 0.8 mL.
7. Add Internal Standards.
8. Analyze by GC/MS using the settings in Table 2.

Table 1: Extractor Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	DCM	1:00 min	1:00 min
Prewet 2	Acetone	1:00 min	1:00 min
Prewet 3	Water	1:00 min	1:00 sec
Prewet 4	Water	30 sec	5 sec
Process Sample			
Air Dry 5 sec			
Rinse 1	Acetone	3:00 min	30 sec
Rinse 2	DCM	1:00 min	30 sec
Rinse 3	DCM	1:00 min	30 sec
Rinse 4	DCM	1:00 min	1:00 min

Table 2: GC Conditions

Mode	Splitless (purge @ 1 min)
Carrier Gas	Helium
Pressure	3 psi at 40 C
Flow	Constant
Inj Temp	280 °C
Inj Amount	2 uL
Interface Temp	300 °C

Temperature Program			
Ramp	**Temp (°C)**	**Rate (°C/min)**	**Hold (min)**
1	40	0	4:00
2	325	10	2:00

Results

One advantage with the extraction equipment is that the drying times are significantly reduced because of the unlimited drying capacity of the DryDisk® membrane. The complete extraction and drying steps were completed in less than 20 min.

The GC/MS analysis was completed in less than 30 min with sufficient resolution of benzo(b)fluoranthene and benzo(k)fluoranthene as well as indeno(1,2,3-c,d)perylene and benz(a,h)anthracene.

Figure 1 below shows a typical chromatogram produced from this method and Table 3 shows the retention times, ions, and percent recovery for each PAH spike. The data indicates that the average recovery from three separate extractions range from 78-109% which are well within the 70–130% range specified in EPA Method 3535.

Conclusions

Automated SPE has been demonstrated to provide fast extraction performance consistent with the specifications set forth in EPA Method 3535. The time required for complete extraction and drying was less than 20 min. The use of automated SPE decreases sample turn-around-time, solvent waste, and solvent exposure to employees, while improving overall efficiency, precision, and accuracy. The cumulative effect leads to lower overhead costs for a laboratory.

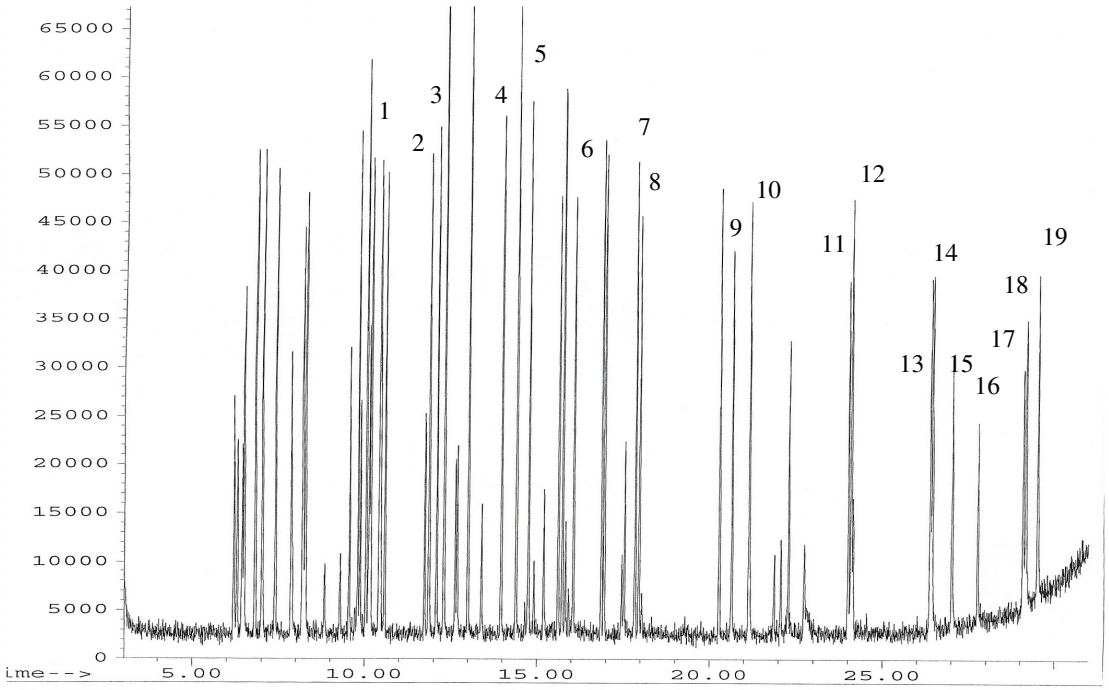

Figure 1: GC/MS chromatogram for PAH compounds in tap water. Numbered peaks are listed in Table 3.

Table 3: Recovery of PAH compounds in tap water.

Peak	Compound	RT (min)	Ion Monitored (amu)	Ave Recovery (n = 3)
1	Naphthalene	10.18	128	88
2	2-methylnaphthalene	11.87	142	89
3	1-methylnaphthalene	12.10	142	90
4	Acenaphthylene	13.97	152	87
5	Acenaphthene	14.41	153	78
6	Fluorene	15.63	166	89
7	Phenanthrene	17.86	178	90
8	Anthracene	17.97	178	86
9	Fluoranthene	20.65	202	92
10	Pyrene	21.15	202	88
11	Benz(a)anthracene	24.02	228	102
12	Chrysene	24.10	228	109
13	Benzo(b)fluoranthene	26.39	252	103
14	Benzo(k)fluoranthene	26.44	252	109
15	Benzo(a)pyrene	27.02	252	105
16	3-methylcholanthrene	27.77	268	97
17	Indeno(1,2,3-c,d)perylene	29.09	276	96
18	Benz(a,h)anthracene	29.17	278	100
19	Benzo(g,h,i)perylene	29.51	276	94

A Dissolved / Particulate Baseline Study of PAH's (Poly-Aromatic Hydrocarbons) in Particulate Laden Water

Horizon Technology, Inc., Salem, NH, USA

Introduction

Poly-Aromatic Hydrocarbons are of great environmental concern due to their carcinogenic impact. When water samples are extracted and analyzed for PAH's, many methods require the water sample to first be filtered, such that the particulate matter is removed. Filtration is also required when conventional Solid Phase Extraction (SPE) cartridges are used to extract samples because SPE cartridges plug easily when any particulate matter is present. With Liquid-Liquid Extraction (LLE) techniques, emulsions typically create problems which could adversely impact the proper extraction of the suspended material. However, compounds such as PCB's and PAH's will come out of the dissolved phase and adsorb onto the surface of the suspended particulate matter in the water column. Therefore, to determine the actual concentration of PAH's in the water sample, the "whole" water sample with the suspended particulate matter should be processed.

As many water samples extracted for PAH's are surface water, river water, ground water, waste water, or water with suspended material, it is desirable to have a analytical method that can handle the "whole" water sample. SPE in a 47 mm "disk" format is a proven extraction method for extracting particulate laden water samples and provides fast flow rates with no breakthrough of analytes. Aqueous samples of one liter and greater can be processed quickly and effectively, providing excellent recoveries of PAH compounds at lower detection limits.

The International Organization for Standardization (ISO), a worldwide federation of national standards solicited their technical committees to develop a new method for analyzing PAH's in particulate laden water. The IWW Water Centre Institute, located in Muelheim an der Ruhr, Germany, offered to participate in the development of a method to explore the possibilities of using SPE disks for the analysis of 16 PAH's in drinking water, ground water, waste water, and surface water. This study conducted by IWW had several goals:

1. Develop an SPE disk method that could handle "whole" water samples (including particulates and suspended matter).
2. Due to possible partitioning of PAH's between the dissolved and particulate phase of the water column, to determine the effectiveness of the extraction technique for PAH's when the particulate matter and the SPE disk are both extracted and eluted with the SPE extracting solvent.
3. Determine the total amount of particulate matter that can be handled by the SPE disk.
4. Determine the best non-halogenated solvent to be used for extracting the SPE disk.
5. Determine if a method could be developed that did not require a solvent concentration step.
6. Develop a fully automated SPE disk method.

Horizon Technology SPE-DEX® 4790 and Envision® Controller

Experiments were carried out using both spiked drinking water and spiked surface water coming from natural water bodies (river water). These experiments would examine the ability of "whole" water samples to be extracted and confirm if SPE would be sufficient to properly extract the sediment particles, and remove any PAH's adsorbed onto the sediment particles.

The best recoveries for this work were achieved with reverse phase C18 JT Baker Speedisks™ and the Horizon SPE-DEX® 4790 Automated Extractor System. This combination worked well for many surface water samples spiked with natural sediments up to a level of 1000 mg/L. Even with this level of suspended material, 1000 mL samples could still be processed in less than 20 minutes, without ever plugging a disk.

Before starting the planned work on surface water samples with natural sediments, the following preliminary work was done:

- The recoveries of PAH spiked drinking water samples not containing any suspended particulate matter (without any solvent concentration step) were calculated.
- The potential adverse effect of extract concentration (i.e. potential losses of target compounds) was explored.
- PAH recoveries from the extraction of certified dried natural sediments (not spiked to the water sample) were determined.

Instrumentation

- Horizon Technology SPE-DEX® 4790 Automated Extractor System
- JT Baker C18 Speedisk™
- Agilent 6890 GC/MS

Method Summary

1) 1000 mL water samples were used.
2) A sample was spiked to a 0.10 ug/L concentration.
3) Place the sample bottle onto the 4790 Extractor and start the method listed in Table 1.
4) After 20 minutes, approximately 9 mL of extract are collected.
5) Some extracts were concentrated and others were not, to determine the impact of the concentration step.
6) Analyze by GC/MS.

Table 1: Extractor Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	20 sec	20 sec
Prewet 2	Acetone	20 sec	20 sec
Prewet 3	Reagent Water	20 sec	20 sec
Prewet 4	Reagent Water	20 sec	20 sec
Process Sample			
Wash 1	Reagent Water	10 sec	10 sec
Air Dry 7:00 min			
Rinse 1	Acetone	1:00 min	30 sec
Rinse 2	Acetone	5:00 min	30 sec
Rinse 3	Acetone	1:00 min	1:00 min

Results

Spiked Drinking Water Samples:
One litre drinking water samples were spiked at a concentration of 0.1 ug/L, and extracted. To maintain consistent conditions, a set water sample flow rate of 50 mL/min was maintained by adjusting the vacuum level. As one of the goals was to examine the impact of solvent evaporation, the rinse solvent volumes were adjusted so each solvent rinse delivered approximately 3 mL of solvent. With three rinses, this gave a final solvent volume of approximately 9 mL. The final volume was adjusted to 10 mL with acetone, and the extract analyzed.

The results from these experiments are shown in Table 2, and indicate high recoveries for the 16 compounds under investigation. Even naphthalene showed recoveries of 75% and a low repeatability coefficient of variation. The minor losses can be traced to the volatilization and oxidation of some compounds due to a long air dry time.

Impact of Solvent Concentration:
To determine if there could be substantial losses of individual analytes during the solvent concentration process, several non-halogenated solvents were spiked with all 16 PAH's. The concentration process was carried out using a sample with an initial volume of 10 mL and initial concentration of 0.005 ug/mL. Using a gentle stream of nitrogen, and temperatures below 20 C, the extract was concentrated to a final volume of 1 mL. Both acetone and hexane containing 5% (v/v) ethyl acetate appeared to provide the best results.

The results of these experiments are shown in Table 3. It can be seen from these results that if concentration to 1.0 mL is necessary, better recoveries are achieved using hexane with 5% ethyl acetate.

Table 2: Recovery of PAH spiked drinking water with no suspended matter.

Substance	Recovery	Repeatability coefficient of variation (n=4)
	(%)	CVr
naphthalene	75	0.8
acenaphthylene	83	5.1
acenaphthene	85	3.2
fluorene	85	1.5
phenanthrene	93	5.1
anthracene	93	4.8
fluoranthene	93	5.1
pyrene	93	6.1
benzo(a)anthracene	88	3.6
chrysene	94	4.1
benzo(b)fluoranthene	89	7.6
benzo(k)fluoranthene	80	3.7
benzo(a)pyrene	81	7.7
indeno(1,2,3,c,d)pyrene	85	7.2
dibenzo(a,h)anthracene	82	7.6
benzo(g,h,i)perylene	91	7.0

Table 3: Recovery for a concentration procedure using different solvents and final volume of 1.0 mL (a: acetone, b: hexane / 5% ethyl acetate).

Substance	- a - Recovery	Repeatability coefficient of variation (n=4)	- b - Recovery	Repeatability coefficient of variation (n=4)
	(%)	CVr	(%)	CVr
naphthalene	58	9.7	76	4.2
acenaphthylene	77	3.0	79	4.5
acenaphthene	82	3.5	81	4.7
fluorene	81	13.4	83	5.1
phenanthrene	67	1.0	92	3.1
anthracene	64	2.0	92	4.0
fluoranthene	83	2.4	101	2.8
pyrene	85	1.8	99	3.4
benzo(a)anthracene	71	1.6	104	1.8
chrysene	79	2.7	99	1.4
benzo(b)fluoranthene	66	1.5	105	2.2
benzo(k)fluoranthene	74	5.9	101	0.7
benzo(a)pyrene	61	2.3	103	3.0
indeno(1,2,3,c,d)pyrene	70	2.1	101	2.6
dibenzo(a,h)anthracene	71	4.3	105	2.3
benzo(g,h,i)perylene	66	3.9	105	3.1

To determine the impact on recoveries of stopping the concentration at a final volume of 5 mL rather than 1.0 mL, another set of experiments were run. Each experiment was carried out four times and the results are shown in Table 4. The results include the repeatability coefficient of variation.

It can be seen from the results of Tables 3 and 4 that high recoveries will be achieved for all analytes under investigation. However, by stopping the concentration at 5 mL, rather than 1.0 mL, there is a significant improvement in the recovery values of lighter compounds. As great care is essential to avoid losses of the readily volatile naphthalene and acenaphthylene during the concentration step, eliminating the solvent concentration step was chosen. In addition, temperatures during the concentration step should not exceed 20 C and the final volume of the concentration step should not go below the 5 mL mark. In those cases, both solvents can be used.

Extraction of Certified Dried Natural Sediments (not spiked into water sample):
Table 5 shows the results of the direct extraction of dried natural sediment by using acetone and hexane with 5% ethyl acetate. The extractions were performed in vessels fitted with a magnetic stirrer, using 0.5 g of sediment and 5 mL of solvent. The sediment used was EC-3 (A Lake Ontario Sediment for Toxic Organics) – National Water Research Institute, Canada 1999 certified reference values (see Table 5). It can be seen from the results that both solvents lead to acceptable recoveries. Most measured values lie exactly within deviations of EC-3 uncertainty limits, or at least within a range of 15% above or below. However, the measured amount of PAH using acetone is a bit higher than when using hexane with 5% ethyl acetate.

Water Samples Spiked with EC-3 Sediment:
The next set of experiments added 500 mg of EC-3 sediment to 1000 mL surface water samples. The experiments were carried out four times, and acetone was used as the extracting solvent. The goal was to explore the use of a strong, water soluble extracting solvent like acetone to sufficiently extract the particulate matter and the SPE disk, even when the SPE disk was still slightly wet with residual water. The results show that the selected seven minute air dry time for the filtered disk was sufficient for sediment amounts up to 750 mg. For greater sediment loadings, a longer air dry time would be better. This will be explained later in this study.

Table 6 shows the results from an experiment where 500 mg of sediment was added to a 1000 mL surface water sample and the final extract was either concentrated or not. The sample with no solvent concentration step had a final extract volume brought to 10 mL, while the other extract was concentrated to 5.0 mL. The results of the two runs show very similar recovery values.

The study then examined the recovery of samples with both 250 mg and 750 mg of certified sediment added to water samples. The results are shown in Table 7, and also indicate good extraction recoveries. It should also be noted that all extracts were concentrated to 5.0 mL final volume.

Table 8 shows the recovery values when a 1000 mL sample was extracted that contained 1000 mg of certified sediment. As can be seen with the recovery data, these values were lower than desired. It was later determined that the 7 minute air dry time, after the water sample had filtered through the SPE disk was insufficient to completely remove most of the residual water from the disk surface. To improve these recoveries, the air dry time should be increased. However, care must be taken to ensure that the dry time is not too long due to the volatility and oxidation likelihood associated with PAH's.

Table 4: Recovery for a concentration procedure using different solvents and final volume of 5.0 mL (a: acetone, b: hexane / 5% ethyl acetate).

Substance	- a - Recovery	Repeatability coefficient of variation (n=4)	- b - Recovery	Repeatability coefficient of variation (n=4)
	(%)	CVr	(%)	CVr
naphthalene	88	2.0	99	2.0
acenaphthylene	90	1.7	102	0.7
acenaphthene	82	2.7	97	1.8
fluorene	84	1.5	95	1.0
phenanthrene	88	2.3	99	0.6
anthracene	91	4.0	99	1.3
fluoranthene	87	2.5	99	1.6
pyrene	87	0.8	97	2.7
benzo(a)anthracene	88	1.2	100	1.6
chrysene	92	3.5	100	3.6
benzo(b)fluoranthene	91	4.2	104	3.3
benzo(k)fluoranthene	88	5.5	97	2.6
benzo(a)pyrene	89	6.4	103	5.1
indeno(1,2,3,c,d)pyrene	94	6.8	96	2.7
dibenzo(a,h)anthracene	101	2.8	102	5.9
benzo(g,h,i)perylene	100	2.8	106	5.7

Table 5: Recoveries of dried certified sediment of Lake Ontario (EC-3) using different solvents.

Substance	EC-3	Acetone		Mixed	
	Informative	Found	Deviation from EC-3 Uncertainty	Found	Deviation from EC-3 Uncertainty
	(ng/g)	(ng/g)	(±%)	(ng/g)	(±%)
naphthalene	35±20	94	+111	48	0
acenaphthylene	25±8	44	+44	28	0
acenaphthene	22±9	20	0	20	0
fluorene	42±21	16	-12	16	-12
phenanthrene	293±33	130	-44	170	-31
anthracene	59±11	45	-5	42	-10
fluoranthene	558±46	455	-10	387	-22
pyrene	436±47	406	0	342	-11
benzo(a)anthracene	312±28	269	-5	215	-22
chrysene	458±59	379	-4	294	-23
benzo(b)fluoranthene	505±88	538	0	411	0
benzo(k)fluoranthene	271±104	270	0	207	0
benzo(a)pyrene	386±50	403	0	311	-6
indeno(1,2,3,c,d)pyrene	359±36	430	+10	259	-18
dibenzo(a,h)anthracene	109±17	69	-21	44	-44
benzo(g,h,i)perylene	348±70	411	0	270	-2

Table 6: Recoveries of surface water spiked with 500 mg of certified sediment (EC-3) using acetone and either concentrated to 5 mL or brought to 10 mL.

Substance	500 mg FV = 10 mL				500 mg FV = 5 mL			
	Concentration	Concentration	Repeatability coefficient of variation (n=4)	Deviation from EC-3 Uncertainty	Concentration	Concentration	Repeatability coefficient of variation (n=4)	Deviation from EC-3 Uncertainty
	(ug/L)	(ng/g)	CVr	(±%)	(ug/L)	(ng/g)	CVr	(±%)
naphthalene	0.036	72	7.9	+49	0.032	64	8.5	+25
acenaphthylene	0.016	31	10.1	0	0.016	33	7.3	0
acenaphthene	0.010	20	9.4	0	0.010	19	2.4	0
fluorene	0.009	18	9.9	-7	0.007	15	4.1	-14
phenanthrene	0.110	220	10.8	-14	0.087	173	2.2	-30
anthracene	0.028	56	6.8	0	0.021	42	5.0	-10
fluoranthene	0.178	356	3.2	-28	0.184	367	1.8	-26
pyrene	0.165	329	7.0	-14	0.160	319	1.9	-16
benzo(a)anthracene	0.110	220	7.8	-21	0.121	243	5.4	-13
chrysene	0.139	279	9.7	-26	0.142	284	3.4	-25
benzo(b)fluoranthene	0.193	385	4.7	-6	0.179	358	7.0	-12
benzo(k)fluoranthene	0.152	304	8.3	0	0.147	294	11.2	0
benzo(a)pyrene	0.220	440	4.8	+1	0.182	363	4.4	0
indeno(1,2,3,c,d)pyrene	0.190	390	8.2	0	0.190	380	3.7	0
dibenzo(a,h)anthracene	0.038	77	5.4	+14	0.029	58	12.8	-31
benzo(g,h,i)perylene	0.147	294	8.2	0	0.150	300	2.5	0

Table 7: Recoveries of surface water spiked with either 250 mg or 750 mg of certified sediment (EC-3) using acetone and concentrated to 5 mL.

Substance	250 mg FV = 5 mL				750 mg FV = 5 mL			
	Concentration	Concentration	Repeatability coefficient of variation (n=4)	Deviation from EC-3 Uncertainty	Concentration	Concentration	Repeatability coefficient of variation (n=4)	Deviation from EC-3 Uncertainty
	(ug/L)	(ng/g)	CVr	(±%)	(ug/L)	(ng/g)	CVr	(±%)
naphthalene	0.015	61	6.1	+17	0.051	68	2.1	+37
acenaphthylene	0.006	24	6.1	0	0.026	35	9.3	+8
acenaphthene	0.004	17	6.2	0	0.014	18	6.1	0
fluorene	0.003	11	9.6	-24	0.011	15	7.1	-14
phenanthrene	0.044	176	2.8	-29	0.131	175	6.2	-29
anthracene	0.009	36	3.4	-20	0.039	52	5.4	0
fluoranthene	0.082	327	3.3	-33	0.277	369	5.8	-26
pyrene	0.073	292	3.4	-22	0.242	323	5.5	-15
benzo(a)anthracene	0.048	193	5.3	-29	0.179	239	10.6	-14
chrysene	0.063	252	4.9	-32	0.216	288	6.9	-24
benzo(b)fluoranthene	0.072	289	1.8	-25	0.268	357	10.1	-12
benzo(k)fluoranthene	0.060	239	8.1	0	0.204	272	6.3	0
benzo(a)pyrene	0.073	293	7.5	-11	0.285	381	8.3	0
indeno(1,2,3,c,d)pyrene	0.052	208	7.1	-32	0.197	263	12.8	-17
dibenzo(a,h)anthracene	0.016	63	4.5	-26	0.042	56	10.8	-33
benzo(g,h,i)perylene	0.061	245	8.1	-9	0.199	265	8.2	-4

Table 8: Recoveries of surface water spiked with either 250 mg or 750 mg of certified sediment (EC-3) using acetone and concentrated to 5 mL.

Substance	Concentration	Concentration	Repeatability coefficient of variation (n=4)	Deviation from EC-3 Uncertainty
	(ug/L)	(ng/g)	CVr	(±%)
naphthalene	0.046	46	4.3	0
acenaphthylene	0.016	16	8.6	-4
acenaphthene	0.011	11	5.7	-9
fluorene	0.010	10	6.9	-26
phenanthrene	0.128	128	7.8	-45
anthracene	0.031	31	8.4	-29
fluoranthene	0.212	212	7.1	-53
pyrene	0.183	183	7.6	-47
benzo(a)anthracene	0.126	126	8	-51
chrysene	0.152	152	6.6	-54
benzo(b)fluoranthene	0.170	170	8.7	-49
benzo(k)fluoranthene	0.124	124	8.3	-16
benzo(a)pyrene	0.203	203	8.9	-34
indeno(1,2,3,c,d)pyrene	0.099	99	6.4	-62
dibenzo(a,h)anthracene	0.030	30	8.3	-57
benzo(g,h,i)perylene	0.116	116	5.5	-47

This problem can be corrected using the Horizon Technology automated SPE systems by first, visually inspecting the sample bottle and estimating the amount of suspended material present. If the amount appears to be less then 1000 mg, use the normal method with the 7 minute air dry time. If the amount appears to be close to or greater than 1000 mg, then use an SPE method that stops the extraction process after the established 7 minute air dry time. The operator would than visually examine the SPE disk with the suspended matter retained on the SPE disk surface, and empirically determine the additional air dry time that might be required. This new method would be downloaded and run. As an example, there could be a series of methods the operator could choose from that would have additional air dry times (2, 4, 6 min etc.) plus the required solvent extraction portion of the method. This type of sample handling would definitely improve the recovery of these compounds.

Conclusions

This study shows that the SPE-DEX® 4790 Automated Extractor system can process water samples containing suspended particulate matter, up to 1000 mg, for the analysis of PAH's. As PAH's are found in both the dissolved and particulate phase of the water sample, it is important to be able to handle "whole" water samples such that the particulate matter in the water sample is retained and extracted with the SPE disk. This filtration method ensures that the PAH's found in the dissolved phase, and those adsorbed onto the particulate matter are properly extracted.

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Determination of Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos from Aqueous Samples Using Atlantic HLB SPE Disks

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Introduction

Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos are commonly used pesticides for the control of insects and aquatic pests in rice production, other agricultural production, and fish aquaculture in parts of the world. Methamidophos in particular is used in great quantities in rice fields in China where rice–fish culture is common as well as in many other rice-producing countries (e.g., Thailand, Malaysia, and the Philippines). Given their prevalent use throughout Asia, residues of Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos show up in many food sources and are commonly monitored in wastewater and drinking water in these regions. As a result many analytical methodologies have been created to monitor these compounds in the environment.

The traditional extraction methods employed use Solid Phase extraction (SPE) for Monocrotophos, Diazinon, Malathion, EPN and a separate liquid liquid extraction (LLE) method for Methamidaphos. Methamidaphos is problematic to extract in traditional SPE and LLE methodologies due to its extreme hydrophilic nature making exchange into a non-polar solvent or absorption onto a solid phase sorbent very difficult resulting in extremely low recoveries of this compound. In the separate LLE method it is necessary to add a quantity of salt (NaCl) in order to decrease Metamidaphos's affinity for the water phase making it partition more easily into the organic phase. This technique, Salting-out Liquid-Liquid Extraction (SALLE)[1], has been employed for many years when trying to extract extremely hydrophilic polar molecules from aqueous matrices. Extraction of all five of these compounds takes time as two separate extraction methodologies must be used.

This application note was developed to demonstrate the extraction of five organophosphate compounds Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos using one solid phase extraction method with one pre-treatment step of sodium chloride NaCl. The method uses the Horizon SPE-DEX 4790 automated SPE extraction system. It will show the efficiency of the extraction while demonstrating excellent recoveries of OPP compounds using Methylene Chloride and minimal amounts of acetone after sample pretreatment with sodium chloride. Methods were developed and results are shown using 47 mm Atlantic HLB-H disks and Carbon Cartridges. Samples used in this study consisted of aqueous samples containing dissolved OPP compounds.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extractor System
  - Envision® Platform Controller
  - 8270 One Pass Hardware Kit (PN 47-2793)

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, Envision® Platform Controller, and DryVap® Automated Drying and Concentrating System.

Instrumentation (continued)

- Horizon Technology (continued)
  - DryVap® Concentrator System
  - 65 mm DryDisks® (PN 40-705-HT)
  - 0.9 mL Concentration Tube (PN 03-1588-04)
  - Atlantic™ HLB-H SPE Disks (PN 47-2346-10)
  - 47 mm Disk Holder (PN 50-0807-01)
  - 8270 Carbon Cartridge 20 CC, Kit (PN 49-2620
  - VOA Vial 40 mL 72 CT. (PN 160-0008)
  - Erlenmeyer Flask, 125 mL (PN 27-0476)
  - Separatory Funnel, 125 mL (PN 27-0834-01)
- Agilent
  - 6890 Gas Chromatograph
  - 5973 Mass Selective Detector in SIM mode
- Phenomenex
  - Zebron™ ZB-5MS, 30 m x 0.25 mm ID, 0.25 µm,

Method Summary

System Setup

1. Install the 8270 One Pass Hardware Kit:
   a. Mount the carbon cartridge perch to the side of the extractor shelf by tightening the thumbscrew.
   b. Disconnect the Water-to-Waste line on the back of the extractor.
   c. Connect one end of the yellow line to the extractor port labeled Water Waste.
   d. Connect one end of the green line to the Water-to-Waste line and the other end to the yellow line connected in step 2 c.

Sample Processing and Elution

1. Adjust a 1 L aqueous sample to pH 2 with HCl, and add 100 grams of NaCl (+ 80 mesh, reagent grade, less than or equal to 98% purity Sigma-Aldrich), cap the bottle and mix.
2. Spike OPP Standard mix (100 µg/mL in MeOH) into samples. 10 µl for 10 µg spike. Place an EZ-Seal over the opening of the bottle and screw on the bottle cap adaptor.

3. Load the disk holder with the Atlantic HLB-H 47 mm disk, and the perch with a 20 cc Carbon Cartridge on the side of disk holder.
4. Place a clean VOA vial or equivalent receiver onto the extractor.
5. Load the sample bottle onto the SPE-DEX 4790.
6. Start the OPP extraction method in Table 1 and collect extract at high vacuum of -25 in. Hg (15.5 in. Hg at the Solvent To Waste bottle) and 15.5 psi Solvent Bottle Pressure.
7. Collect the extract (approximately 30 mL).
8. Cap and label extract as OPP HLB fraction.

Carbon Cartridge Elution

1. Remove the 47 mm Disk Holder from the SPE-DEX 4790.
2. Disconnect the lines from the Carbon Cartridge and remove it from the perch.
3. Reconnect the lines removed from the Carbon Cartridge.
4. Remove the cap from the Carbon Cartridge and install the funnel in its place.
5. Install the Carbon Cartridge / funnel assembly onto the SPE-DEX 4790 for elution.
6. Attach a 125 mL flask onto the extractor.
7. Elute the Carbon Cartridge using the Carbon Elution Method given in Table 2 into the 125 mL flask (Collect approximately 50 to 60 mL of extract).
8. Label the flask to indicate that it contains the carbon fraction.
9. Due to the high salt content, it is necessary to rinse the liquid flow path of the SPE-DEX 4790 extractors to remove the salt residue. This is accomplished by rinsing the flow path with a sample bottle of warm water placed on the SPE-DEX 4790 and running the sample drain method on the envision controller, this is followed by running a purge method with reagent water, acetone, and methylene chloride

Concentration

1. Assemble the DryDisk reservoir with a DryDisk Separation Membrane.
2. Load the DryDisk reservoir onto the DryVap and set the conditions as shown in Table 3.
3. Start the concentration process by adding the OPP HLB fraction into the DryDisk tube.
4. Allow the OPP HLB fraction extract to filter through the DryDisk into the Concentrator tube.
5. Manually rinse the OPP HLB fraction 40 mL VOA vial with methylene chloride adding this to the DryDisk reservoir. Allow the rinse solvent to process through the DryDisk. Do this three times.
6. Follow steps 4 and 5 for the carbon fraction. If DryVap transitions to heat stage press the stop button on the control panel and then press restart.
7. Once the OPP HLB fraction and carbon fractions filter through the DryDisk, manually rinse the DryDisk reservoir with methylene chloride.
8. Once the methylene chloride has filtered into the concentration tube, allow the station to transition to the heat stage.
9. Concentrate the extract to less than 1.0 mL. For enhanced recoveries of Methamidaphos carry out the steps in the optional LLE extraction method following this section.
10. Rinse the sides and heater of the concentrator tube with methylene chloride and bring the extract up to a 1.0 mL final volume.
11. Transfer the extract to a GC vial.
12. Add 5 µg terphenyl-d14 as an internal standard.
13. Analyze by GC/MS using the conditions in the section labeled GC/MS Method.
14. Due to the high salt content, it is necessary to thoroughly rinse the sparge tube of the DryVap to remove all salt residues. Accomplish this by processing 100 mL of warm water followed by acetone and methylene chloride through the DryDisk tube into the evaporator tube.

Table 1: Envision Method for Extraction of Five OPP's from Clean Aqueous Samples using 47 mm Atlantic HLB Disk

Step	Solvent	Soak Time	Dry Time
Prewet 1	MeCl	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 1	Acetone	3:00 min	20 sec
Rinse 2	MeCl	3:00 min	20 sec
Rinse 3	MeCl	1:00 min	20 sec
Rinse 4	MeCl	1:00 min	20 sec
Rinse 5	MeCl	1:00 min	1:00 min

Table 2: Envision Method for Elution of Five OPP's from Carbon Cartridge

Step	Solvent	Soak Time	Dry Time
Air Dry 5 Min			
Rinse 1	Acetone	1:00 min	0 sec
Rinse 2	Acetone	1:00 min	1:00 min
Rinse 3	MeCl	1:00 min	3 sec
Rinse 4	MeCl	1:00 min	3 sec
Rinse 5	MeCl	1:00 min	3 sec
Rinse 6	MeCl	3:00 min	3 sec
Rinse 7	MeCl	1:00 min	3 sec
Rinse 8	MeCl	1:00 min	3 sec
Rinse 9	MeCl	1:00 min	3 sec
Rinse 10	MeCl	1:00 min	1:00 min

Optional LLE extraction method for enhanced recovery of Methamidaphos

1. Transfer the retained water from the top of the DryDisk membrane in the previous concentration step to a 40 mL VOA vial (approximately 10 mL)
2. Add 2 – 2.5 grams of NaCl to each vial.
3. Add 20 mL of 80:20 methylene chloride: acetone to each vial, cap and shake vigorously.
4. Pour the contents into a DryDisk tube and press start on the DryVap control panel until all 20 mL of solvent have been pulled through the DryDisk. When all solvent is through and only residual water remains on the DryDisk press the stop bottom on the DryVap control panel.
5. Transfer the retained water to VOA vial and repeat steps 3, 4, and 5 two more times.
6. Manually rinse the DryDisk reservoir with methylene chloride
7. Once the methylene chloride has filtered into the concentration tube, allow the station to transition to the heat stage.
8. Concentrate the extract to less than 1.0 mL.
9. Rinse the sides and heater of the concentrator tube with methylene chloride and bring the extract up to a 1.0 mL final volume.
10. Transfer the extract to a GC vial.
11. Analyze by GC/MS using the conditions in the section labeled GC/MS Method.
12. Due to the high salt content, it is necessary to thoroughly rinse the sparge tube of the DryVap to remove all salt residues. Accomplish this by processing 100 mL of warm water followed by acetone and methylene chloride through the drydisk tube into the evaporator tube.

Table 3: DryVap Conditions

Parameter	Setting
Dry Volume	20 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	20 psi
Vacuum	-7 in. Hg

GC/MS Method

Oven
Initial Temperature: 60°C, Initial Time: 2 minutes
Ramps:

Rate	Final Temp	Final Time
20.00	270°C	0.00
6.00	320°C	2.00

Run Time: 22.83 minutes

Inlet
Mode: Pulsed Splitless
Initial Temperature: 280°C
Pressure: 8.24 psi
Pulsed Pressure: 25 psi
Pulsed Time: 1.00 minutes
Purge Flow: 50 mL/min
Purge Time: 2.00 minutes

Mass Spectrometer
Acquisition Mode: SIM
Solvent Delay: 5 minutes
Group 1: 5 – 9 minutes, ions 94 and 141
Group 2: 9 – 12 minutes, ions 127, 192, 179, 137, 173, 125
Group 3: 12 minutes – end, ions 244, 122, 157, 169

Results

To demonstrate the loss of analytes due to concentration and drying on the DryVap system, a 30.0 µg mix of OPP analytes was spiked into 25 mL of solvent with an Acetone to Methylene Chloride ratio of 20:80 which represents the final analyte volume for 47 mm disk holder extracts.

The recoveries of these solvent spikes are shown in Table 4 with final end point volumes of 1 mL. Of the five OPP compounds, recoveries were excellent, and resulted in an average recovery range with a low of 89% to a high of 106% for all solvent spikes. This data also demonstrates excellent reproducibility with the RSD's lying between 6.2% and 8.5% for all fractions.

In order to track the extraction efficiency and mobility of the various analytes, extractions of aqueous samples were carried out using a 47 mm HLB-H extraction disk and a 20 cc carbon cartridge arranged on the instrument so that water sample flowed through the HLB disk and carbon cartridge in series. The HLB extraction disk and the carbon cartridge were extracted and analyzed separately and results of this series of extractions are shown in Tables 5, 6, and 7. Extraction results for HLB Disks in Table 5 showed very good recoveries for Monocrotophos, Diazinon, Malathion, and EPN with a low of 73% and a high of 91% and poor recovery of 5% for Methamidaphos. The data in Table 6 shows the results of the carbon cartridge fractions and average recoveries of Methamidaphos were 52% indicating that Methamidaphos is being retained on the carbon cartridge. Data in Table 7 shows the recoveries for Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos for HLB and Carbon Cartridge combined with a low of 56% for Methamidaphos and a high of 98% for Monocrotophos. This data also demonstrates excellent reproducibility with the RSD's lying between 4.2% and 9.1% for all fractions.

Due to the extreme hydrophilic properties of Methamidaphos, it has a tendency to repartition back into the residual water and not transfer with the solvent when extracts are dried using the DryDisk. If higher recoveries of Methamidaphos are desired, an additional extraction of this residual water fraction is required. Data for this additional extraction is shown in Tables 8 and 9. Data in Table 8 indicate excellent recoveries of all five compounds being studied with a low of 83% for Diazinon and a high of 103% for Monocrotophos. The data in Table 9 show the average recoveries and statistics for this additional procédure plus HLB and carbon cartridge fractions combined. Recoveries were excellent for Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos with very good reproducibility ranging between 2.0% and 13.8% for all compounds.

Conclusions

This application note demonstrates an efficient SPE extraction scheme for Monocrotophos, Diazinon, Malathion, EPN, and Methamidaphos. The method demonstrated excellent recoveries for an extraction scheme which uses only SPE as the extraction mechanism. It also demonstrated how, with an additional step, these recoveries can be augmented further. This efficient extraction scheme utilizes Horizon Technology's Atlantic HLB SPE disks and Carbon Cartridges, working on the SPE DEX 4790 automated extraction platform. For the extraction of these five pesticides, this method allows for fast extraction times while yielding excellent recoveries of all five organophosphate pesticides of interest in this study. This method employing a combination of salt addition to the sample matrices as a pre-step followed by SPE extraction can also serve as a model extraction method for other extremely hydrophilic compounds that normally would be difficult to get good extraction recoveries.

Acknowledgements & References

[1] Ronald E Majors LC GC North America , July 1 2009 Salting-out Liquid-Liquid Extraction (SALLE)

Table 4: Recoveries of Analytes Due to Concentration on the DryVap Using 25 mL of Methylene Chloride and 5 mL of Acetone with 1 mL Endpoints

Conc	30 ug				
Final Volume	1.0 mL				
Compound	% Rec	% Rec	% Rec	Ave % Rec	% RSD
Methamidophos	97	106	114	106	8.10
Monocrotophos	97	105	115	106	8.55
Diazinon	82	92	94	89	7.32
Malathion	84	93	96	91	6.85
EPN	88	94	99	94	6.21

Table 5: Recovery Data from Clean Aqueous Samples Using 47 mm HLB Disks

	HLB (H) Disk							
Spiking Concentration	10 ug/L					Ave		
Compound	% Rec	% Rec	% Rec	% Rec	% Rec	% Rec	STDEV	% RSD
Methamidophos	4	5	4	5	5	5	0.24	5.28
Monocrotophos	83	88	89	94	101	91	7.10	7.81
Diazinon	69	74	74	71	77	73	3.09	4.24
Malathion	79	81	88	86	93	85	5.58	6.53
EPN	80	80	92	85	92	86	5.87	6.85

Table 6: Recovery Data from Clean Aqueous Samples Using Carbon Cartridge

	Carbon Cartridge							
Spiking Concentration	10 ug/L					Ave		
Compound	% Rec	% Rec	% Rec	% Rec	% Rec	% Rec	STDEV	% RSD
Methamidophos	53	58	55	50	44	52	5.26	10.13
Monocrotophos	7	8	7	8	7	8	0.40	5.27
Diazinon	0	0	0	0	0	0	0.00	0.00
Malathion	0	0	0	0	0	0	0.00	0.00
EPN	6	6	6	6	6	6	0.11	1.83

Table 7: Recovery Data from Clean Aqueous Samples Total HLB-H And Carbon Cartridge

	Total Recovery HLB and Carbon Cartridge							
Spiking Concentration	10 ug/L							
						Ave		
Compound	% Rec	% Rec	% Rec	% Rec	% Rec	% Rec	STDEV	% RSD
Methamidophos	57	63	59	54	49	56	5.16	9.13
Monocrotophos	90	96	96	101	109	98	6.99	7.10
Diazinon	69	74	74	71	77	73	3.09	4.24
Malathion	79	81	88	86	93	85	5.58	6.53
EPN	87	86	98	91	98	92	5.86	6.36

Table 8: Recovery Data from Clean Aqueous Samples Total HLB-H ,Carbon Cartridge and LLE of Residual Water

	HLB-H	Carbon	LLE	Total	HLB-H	Carbon	LLE	Total	HLB-H	Carbon	LLE	Total
Compound												
Methamidophos	5	61	35	101	5	56	15	77	7	55	30	93
Monocrotophos	96	0	0	96	104	0	0	104	109	0	0	109
Diazinon	83	0	0	83	82	0	0	82	85	0	0	85
Malathion	94	0	0	94	96	0	0	96	101	0	0	101
EPN	91	0	0	91	93	0	0	93	97	0	0	97

Table 9: Total Recovery Data HLB Disk, Carbon Cartridge and LLE of Residual Water

	Total recovery HLB Disk + Carbon Cartridge + LLE of Residual Water					
Spiking Concentration	10 ug/L					
				Ave		
Compound	% Rec	% Rec	% Rec	% Rec	STDEV	% RSD
Methamidophos	101	77	93	90	12.45	13.83
Monocrotophos	96	104	109	103	6.72	6.50
Diazinon	83	82	85	83	1.67	2.00
Malathion	94	96	101	97	3.52	3.65
EPN	91	93	97	94	3.12	3.33

Development of a Method for Neutral Herbicides and Pesticides Using a SPE-DEX® 4790 Automated SPE Extraction System

Susan Petitti, Horizon Technology, Inc., Salem, NH

Introduction

The Minnesota Dept. of Agriculture conducted a preliminary evaluation of the SPE-DEX® 4790 Automated Extractor manufactured by Horizon Technology, Inc. The purpose of the evaluation was to determine the feasibility of the system for the extraction of herbicides and pesticides in river water using an in-house method. De-ionized (DI) water was spiked with the selected analytes and the extraction performed using a DVB disk and a C18 disk for comparison. A matrix spike was also performed using river water. Final analysis for the determination of the analytes is by GC/MS.

Instrumentation

- Horizon Technology SPE-DEX® 4790 Automated Extractor System
- Bakerbond Speedisk™
  - DVB Disk (8067-06)
  - C18 Disk (8055-06)
- HPGC 6890, APEX PTV, MS 5973

Method Summary

1) Two liters of DI water and one of river water are used.
2) The water samples are spiked with 1.00 ppb of the selected analytes.
3) Run one liter of DI water using a DVB disk and another liter using a C18 disk.
4) Run one liter of river water using a DVB.
5) The extracts are dried using sodium sulfate.
6) The samples are concentrated.
7) Final analysis is by GC/MS.

Table 1: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Ethyl Acetate	1:30 min	1:30 min
Prewet 2	$MeCl_2$	1:30 min	1:30 min
Prewet 3	Methanol	3 min	0 min
Prewet 4	Reagent Water	1:30 min	0 min
Process Sample			
Air Dry 8 min			
Rinse 1	Ethyl Acetate	1 min	1 min
Rinse 2	Ethyl Acetate	1 min	1 min
Rinse 3	$MeCl_2$	1:30 min	1 min
Rinse 4	$MeCl_2$	1:30 min	1 min
Rinse 5	$MeCl_2$	1:30 min	1 min
Rinse 6	$MeCl_2$	1:30 min	1 min

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, and the Envision® Platform Controller.

Results

Table 1 shows the parameters programmed into the Horizon Technology SPE-DEX® 4700 Controller for the extraction process. All steps of the extraction process are automated.

The results of the analysis of DI water spiked at a concentration of 1.00 ppb are given in Table 2. Both a DVB and C18 Bakerbond Speedisk™ were used for the extraction process. The recovery obtained for Deisopropylatrazine is low due to its solubility in water. The solubility issues would also be relevant for Deethylatrazine, but the DVB disk showed excellent recovery for this compound.

For the second round of testing, a spiked river sample was extracted. There are two reasons for this. First, to determine if the DVB Bakerbond Speedisk® could filter this sample matrix without clogging. Secondly, it must also be determined what kind of role the matrix effects must play in the extraction of influent samples. The results are shown below in Table 3 and indicate that the presence of an influent matrix has very little effect on the recovery of neutral herbicides and pesticides.

Conclusions

This evaluation study was conducted to determine the feasibility of the Horizon Technology SPE-DEX® 4790 Automated Extraction System for the extraction of herbicides and pesticides. The preliminary results demonstrate the capability of this method for the automated SPE extraction of organic compounds. With further method development, the Minnesota Department of Agriculture is confident that the recovery results can be improved.

Using the Horizon Technology SPE-DEX® 4790 to extract samples reduces the total cost a company incurs per sample by reducing analyst labor, solvent usage, and turn-around-times, while still managing to improve accuracy and precision.

Table 2: Recovery of spike in DI water (NR = Not Reported)

Analyte	DVB Disk Recovery (%)	C18 Disk Recovery (%)
Deisopropylatrazine	33	20
Deethylatrizine	105	40
Prometon	72	33
Atrazine	115	98
Chlorothalonil	94	84
Dimethenamid	119	105
Acetochlor	113	105
Alachlor	114	103
Metolachlor	118	107
Cyanazine	172	150
Metazachlor	117	102
EPTC	75	70
Propachlor	95	84
Ethafluralin	93	79
Trifluralin	88	73
Phorate	35	62
Dimethoate	99	35
Simazine	100	90
Propazine	102	92
Terbufos	34	60
Fonofos	53	81
Diazinon	97	90
Triallate	96	84
Metribuzin	122	88
Methyl parathion	119	102
Malathion	109	99
Chlorpyrifos	98	88
Pendimethalin	99	82
Metribuzin DADK	293	NR
Metribuzin DK	118	NR
Clomazone	123	NR
Metribuzin DA	136	NR

Table 3: Recovery of spike in river water.

Analyte	DVB Disk Recovery (%)
Deisopropylatrazine	42
Deethylatrizine	106
Prometon	53
Atrazine	110
Chlorothalonil	73
Dimethenamid	117
Acetochlor	135
Alachlor	108
Metolachlor	117
Cyanazine	148
Metazachlor	104
EPTC	64
Propachlor	96
Ethafluralin	95
Trifluralin	85
Phorate	88
Dimethoate	119
Simazine	101
Propazine	104
Terbufos	90
Fonofos	93
Diazinon	102
Triallate	91
Metribuzin	119
Methyl parathion	118
Malathion	110
Chlorpyrifos	102
Pendimethalin	97
Metribuzin DADK	171
Metribuzin DK	126
Clomazone	106
Metribuzin DA	101

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EPA Method 506: Phthalate and Adipate Esters

Horizon Technology, Inc., Salem, NH

Introduction

EPA Method 506 is used to determine Phthalate and Adipate Esters in drinking water. The analytes are extracted from the water using a Horizon Technology 47 mm C18 disk. The disk is extracted with Acetonitrile and Methylene Chloride. The extract is then dried and concentrated to a final volume of 1.0 mL using the Horizon Technology DryVap® with DryDisk® technology. Final analysis is by GC/PID.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extractor
  - DryVap® Concentrator System
  - DryDisk®
  - Atlantic™ C18 Disk
- GC with PID

Method Summary

1. Purge the SPE-DEX® 4790 extractor using the method from Table 1.
2. Load the sample onto the extractor.
3. Run the method listed in Table 2.
4. Using the DryVap® with a DryDisk®, dry the extract and concentrate it down to 1.0mL final volume
5. Analyze the extract using a GC with PID.

Table 1: Purge Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Reagent Water	0 sec	10 sec
Air Dry 5 sec			
Rinse 1	Methylene Chloride	0 sec	15 sec
Rinse 2	Acetonitrile	0 sec	15 sec

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, Envision® Platform Controller, and DryVap® Automated Drying and Concentrating System.

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Methylene Chloride	1:00 min	1:00 min
Prewet 2	Methanol	1:00 min	0 sec
Prewet 3	Reagent Water	1:00 min	0 sec
Process Sample			
Air Dry 5:00 min			
Rinse 1	Acetonitrile	1:00 min	1:00 min
Rinse 2	Methylene Chloride	1:00 min	1:00 min
Rinse 3	Methylene Chloride	1:00 min	1:30 min

The Extraction of Chlorinated Pesticides, Herbicides, and Organohalides For EPA Method 508.1 Using Automated Cartridge SPE

David Gallagher, Michael Ebitson, Horizon Technology, Inc., Salem, NH

Introduction

The initial use of many chlorinated pesticides, herbicides, and organohalides were to aid humanity. DDT was created to control mosquito populations which significantly limited the number of malaria and typhus cases in World War II; while the use of Atrazine has increased the production of corn and sugar cane farms and helped to supply the world with the food it so drastically needs. However, this has given-way to the fact that many of the compounds have been found to be detrimental to either the flora or fauna found in the environment. It is because of their toxicity that many of these compounds have either been banned or are strictly controlled throughout most of the world.

This Application Note will highlight the use of the Horizon Technology SmartPrep Cartridge Extraction System for the extraction of EPA Method 508.1 analytes. This fully automated extractor allows for up to 6 samples in bottle rinse mode or 12 samples without bottle rinse mode to be run unattended. For this application, the instrument will be configured to run 6 mL cartridges and to make use of the optional bottle rinse mode. This will allow for higher recoveries to be obtained while still maintaining a zero-user interface throughout the run.

After the extraction procedure is complete, this study will make use of the Horizon Technology DryVap Concentrator System along with a DryDisk Separation Membrane. The union of these two features provides for automated drying and concentration at the push of a button. The DryDisk is a physical separation membrane which will allow solvent through, but not water. There is no pre-cleaning necessary and very little physical waste. The DryVap allows for up to six samples to be dried and concentrated at a time. It applies heating and sparging while under vacuum for a fast concentration with end point detection.

Instrumentation

- Horizon Technology
  - SmartPrep™ Automated Cartridge Extractor
    - 6 mL Cartridge Configuration
    - Bottle Rinse Kit
    - 20 mL Tray
  - DryVap® Concentration System
  - DryDisk® Separation Membrane
- Phenomenex
  - Strata® C18-E, 6 mL Cartridges
  - Zebron™ – Multiresidue 1:
    - 30 m x 0.32 mm x 0.50 µm
  - Zebron™ - Multiresidue 2:
    - 30 m x 0.25 mm x 0.25 µm
- Hewlett-Packard
  - 5890 Series II GC-ECD
  - 7673 Controller

The Horizon Technology SmartPrep™ Automated Cartridge Extractor

Method Summary

1. Prepare 1 Liter of deionized water using 1 mL of concentrated HCl to lower the pH to approximately 2.
2. After mixing, add 25 µL of a 20 µg/mL surrogate solution and 25 µL of a 20 µg/mL spike solution (for blank samples, add only surrogate solution).
3. Insert Sip Tube number 1 and attach Bottle Rinse Kit 7 to the sample container.
4. Place a 20 mL VOA vial in position 1 of the tray.
5. Place a 6 mL C18-E cartridge in position 1 of the carousel.
6. Run the method given in Table 3.
7. Place a 1 mL endpoint Concentration Tube on the DryVap.
8. Add a DryDisk membrane to the DryDisk reservoir and attach to the DryVap.
9. Transfer the contents of the VOA vial to the DryDisk Reservoir and start the DryVap using the conditions given in Table 1
10. When the extract has processed through the DryDisk, add approximately 2 mL of Ethyl Acetate (EtOAc) to the VOA vial, cap, and shake vigorously.
11. Transfer the rinsate to the DryDisk Reservoir and allow it to process through into the Concentrator Tube.
12. Repeat steps 10 and 11 two additional times.
13. Rinse the DryDisk Reservoir using approximately 2 mL of EtOAc and allow for this rinsate to process through to the Concentrator Tube.
14. Repeat step 13 two additional times.
15. Allow the extract to concentrate to its final volume.
16. Upon completion, use approximately 0.1 mL of EtOAc to rinse the heater and the Concentrator Tube and bring the volume up to the 1 mL mark as indicated on the Tube and transfer to a vial.
17. Add internal and run on a GC-ECD using Table 2.

Table 1: DryVap Parameters

Parameter	Setting
Dry Volume	100 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	20 psi
Vacuum	-10 in. Hg

Table 2: GC-ECD Acquisition Program

Injection:
Inlet Temperature: 1 µL at 250 °C
Carrier Gas:
Helium at a constant flow rate
Oven Program:
120 °C for 0.5 min to 210 °C at 30 °C/min to 230 °C at 6 °C/min hold for 3 min to 300 °C at 6 °C/min hold for 10 min.
Detector:
ECD at 320 °C

Results

Following the 508.1 Method, a calibration curve was prepared and analyzed using the spike concentrations of 0.1 ug/mL, 0.2 ug/mL, 0.5 ug/mL, 1.0 ug/mL, and 2.0 ug/mL. This curve was then used to analyze all the data obtained for this Application Note. A degradation check solution was prepared using DDT and Endrin and was used for every analytical batch to investigate the degradation products of the two analytes.

When using the MR-1 column, it was discovered that there were two sets of co-elutions; one between Simazine, Atrazine, and the other between d-BHC and Metribuzin. Due to this lack of separation, the compounds are not able to be reported on this column.

On the MR-2 column, a similar phenomenon was seen between Heptachlor Epoxide B and the recommended surrogate Dibrophenyl. In this case, a different surrogate, Decachlorobphenyl, was selected to clear up the co-elution.

The average recovery for 12 LCS extracts are given in Table 4 for each column used. With averages of 93% and the highest RSD being 17%, they show excellent results for all the compounds that are able to be reported on each column. For a full list of all the recoveries including blanks, refer to Tables 5a and 5b

Conclusions

The Horizon Technology SmartPrep Automated Cartridge System was used to extract EPA Method 508.1 compounds from water samples. When coupled with the DryVap Concentration System and DryDisk Separation Membranes, both excellent precision and accuracy was demonstrated. The solutions presented will allow a laboratory to streamline their aqueous extraction procedures and minimize the costs associated with labor and solvent while maintain the level of quality required.

Table 3: EPA Method 508.1 Extraction Parameters

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense	
1		EtOAc	5	10	10	2	No	
2		DCM	5	10	10	2	No	
3		DCM	5	10	10	2	No	
4		MeOH	5	10	0	0	No	
5		MeOH	5	10	10	0	No	
6		DI H20	5	10	0	0	No	
7		DI H20	5	10	10	0	No	
8	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**	
		Yes	1	20	10	800	1000	
9	**N2 Purge Timer**	**Delay (min)**						
		5						
10	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		EtOAc	5	5	5	No		
11	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		15*	1	5	10	10	20	1
12	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	5	5	5	No		
13	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		10*	1	5	10	10	20	1
14	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	5	5	5	No		
15	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		10*	1	5	10	10	20	1
16	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		DCM	5	10				
17	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**	
		Mixing Chamber	10	10	1	5	15	

*Sample volumes increased due to sample viscosities.

Table 4: Average Recovery and RSD for 508.1 Blanks and LCS Samples. Like numbered compounds indicate co-elutions.

		Blanks		LCS			
		Average (ug/L) MR-1	Average (ug/L) MR-2	Average (%) MR-1	RSD (%) MR-1	Average (%) MR-2	RSD (%) MR-2
Etridiazole		0.01	0.00	115	12.64	84	8.99
Chloroneb		0.02	0.00	90	5.23	68	6.70
Propachlor		0.03	0.01	92	9.59	86	8.31
Trifluralin		0.01	0.01	83	6.11	92	10.06
a-BHC		0.00	0.00	87	5.67	94	6.89
Lindane (g-BHC)		0.00	0.02	93	5.37	104	6.91
Simazine	1	N/A	0.06	N/A	N/A	94	9.60
Atrazine	1	N/A	0.09	N/A	N/A	95	7.05
b-BHC		0.01	0.00	94	3.99	103	5.74
d-BHC	2	N/A	0.00	N/A	N/A	114	7.75
Chlorothalonil		0.00	0.00	112	8.72	117	10.13
Metribuzin	2	N/A	0.00	N/A	N/A	83	8.44
Heptachlor		0.03	0.01	91	13.83	86	13.64
Alachlor		0.05	0.00	89	11.32	92	10.18
Cyanazine		0.01	0.00	119	8.60	94	4.48
Metolachlor		0.00	N/A	100	5.37	N/A	N/A
Dacthal		0.00	0.00	92	3.75	101	6.13
Heptachlor epoxide B		0.00	0.00	89	4.22	99	6.66
trans-Chlordane		0.00	0.00	84	4.93	91	7.37
Butaclor		0.00	0.00	105	6.81	95	8.19
cis-Chlordane		0.00	0.00	85	4.62	90	6.66
Endosulfan I		0.00	0.00	89	4.01	98	6.76
4,4'-DDE		0.01	0.01	78	7.19	85	9.74
Dieldrin		0.00	0.00	94	4.54	97	6.26
Endrin		0.00	0.00	97	6.56	100	7.74
Chlorobenzilate		0.00	0.00	70	12.60	92	10.99
Endosulfan II		0.00	0.00	92	4.14	99	8.15
4,4'-DDD		0.01	0.00	91	5.00	92	8.40
Endrin Aldehyde		0.01	0.00	90	4.28	92	8.90
4,4-DDT		0.01	0.00	107	6.82	94	8.75
Endosulfan Sulfate		0.00	0.00	96	4.67	96	8.68
Methoxychlor		0.01	0.00	118	10.22	94	10.99
Permethrin		0.05	0.00	107	16.09	106	16.99
Decachlorobiphenyl	S	0.40	0.46	83	6.23	96	10.66

1, 2 - Co-Elutting compounds on MR-1

Table 5a: All EPA Method 508.1 data generated. Like numbered compounds indicate co-elutions.

Sample Name		Blank 1 (ug/L)		Blank 2 (ug/L)		LCS 1 (%)		LCS 2 (%)		LCS 3 (%)		LCS 4 (%)		LCS 5 (%)	
Column ID		MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2
Pentachloronitrobenzene	IS	0.50	0.50	0.50	0.50	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Etridiazole		0.01	0.00	0.01	0.00	86.00	76.00	106.00	82.00	106.00	80.00	106.00	80.00	106.00	78.00
Chloroneb		0.02	0.00	0.01	0.00	86.00	74.00	94.00	72.00	88.00	68.00	88.00	68.00	86.00	60.00
Propachlor		0.02	0.01	0.03	0.00	80.00	86.00	86.00	82.00	84.00	80.00	88.00	84.00	84.00	72.00
Trifluralin		0.00	0.02	0.01	0.00	80.00	82.00	84.00	80.00	80.00	84.00	84.00	86.00	72.00	104.00
a-BHC		0.00	0.00	0.00	0.00	80.00	84.00	86.00	92.00	84.00	88.00	84.00	90.00	80.00	86.00
Lindane (g-BHC)		0.00	0.01	0.00	0.02	86.00	92.00	92.00	98.00	90.00	98.00	90.00	100.00	88.00	98.00
Simazine	1	N/A	0.06	N/A	0.05	N/A	102.00	N/A	90.00	N/A	84.00	N/A	90.00	N/A	84.00
Atrazine	1	N/A	0.07	N/A	0.10	N/A	86.00	N/A	90.00	N/A	96.00	N/A	90.00	N/A	96.00
b-BHC		0.00	0.00	0.01	0.00	88.00	96.00	92.00	96.00	92.00	100.00	94.00	102.00	90.00	98.00
d-BHC	2	N/A	0.00	N/A	0.00	N/A	98.00	N/A	104.00	N/A	106.00	N/A	112.00	N/A	108.00
Chlorothalonil		0.00	0.00	0.00	0.00	98.00	98.00	102.00	104.00	102.00	106.00	108.00	110.00	108.00	114.00
Metribuzin	2	N/A	0.00	N/A	0.00	N/A	94.00	N/A	80.00	N/A	72.00	N/A	90.00	N/A	78.00
Heptachlor		0.02	0.00	0.04	0.02	84.00	82.00	88.00	80.00	76.00	70.00	84.00	80.00	74.00	68.00
Alachlor		0.00	0.00	0.09	0.00	80.00	86.00	82.00	82.00	86.00	96.00	84.00	88.00	84.00	74.00
Cyanazine		0.00	0.00	0.01	0.00	106.00	94.00	110.00	90.00	112.00	94.00	114.00	96.00	112.00	90.00
Metolachlor		0.00	N/A	0.00	N/A	88.00	N/A	96.00	N/A	98.00	N/A	98.00	N/A	98.00	N/A
Dacthal		0.00	0.00	0.00	0.00	86.00	92.00	90.00	96.00	92.00	96.00	92.00	100.00	90.00	94.00
Heptachlor epoxide B		0.00	0.00	0.00	0.00	84.00	N/A	88.00	94.00	88.00	92.00	88.00	96.00	86.00	90.00
trans-Chlordane		0.00	0.00	0.00	0.00	82.00	82.00	86.00	90.00	82.00	86.00	84.00	90.00	80.00	84.00
Butaclor		0.00	0.00	0.00	0.00	88.00	104.00	106.00	86.00	98.00	88.00	102.00	94.00	108.00	86.00
cis-Chlordane		0.00	0.00	0.00	0.00	82.00	82.00	88.00	92.00	84.00	88.00	86.00	92.00	82.00	84.00
Endosulfan I		0.00	0.00	0.00	0.00	84.00	86.00	88.00	96.00	88.00	96.00	88.00	98.00	86.00	92.00
4,4'-DDE		0.01	0.01	0.01	0.01	78.00	80.00	80.00	86.00	74.00	78.00	78.00	86.00	70.00	72.00
Dieldrin		0.00	0.00	0.00	0.00	86.00	88.00	92.00	94.00	92.00	92.00	94.00	98.00	92.00	92.00
Endrin		0.00	0.00	0.00	0.00	86.00	90.00	94.00	92.00	90.00	94.00	94.00	98.00	104.00	92.00
Chlorobenzilate		0.00	0.00	0.00	0.00	84.00	84.00	78.00	86.00	76.00	90.00	66.00	90.00	52.00	76.00
Endosulfan II		0.00	0.00	0.00	0.00	84.00	84.00	90.00	94.00	92.00	96.00	92.00	100.00	90.00	92.00
4,4'-DDD		0.01	0.00	0.01	0.00	84.00	82.00	92.00	90.00	90.00	92.00	90.00	96.00	88.00	84.00
Endrin Aldehyde		0.01	0.00	0.01	0.00	84.00	82.00	90.00	88.00	92.00	94.00	92.00	96.00	92.00	88.00
4,4-DDT		0.01	0.00	0.01	0.00	94.00	82.00	106.00	94.00	106.00	94.00	110.00	100.00	110.00	86.00
Endosulfan Sulfate		0.00	0.00	0.00	0.00	86.00	80.00	94.00	94.00	96.00	96.00	96.00	98.00	96.00	86.00
Methoxychlor		0.00	0.00	0.01	0.00	102.00	86.00	116.00	90.00	116.00	94.00	120.00	100.00	92.00	66.00
Permethrin		0.06	0.00	0.03	0.00	108.00	94.00	94.00	112.00	96.00	104.00	104.00	130.00	94.00	98.00
Decachlorobiphenyl	S	0.41	0.46	0.39	0.45	N/A	N/A	86.00	90.00	84.00	100.00	86.00	104.00	80.00	84.00

1, 2 - Co-Elutting compounds on MR-1

Table 5b: All EPA Method 508.1 data generated. Like numbered compounds indicate co-elutions.

Sample Name		LCS 6 (%)		LCS 7 (%)		LCS 8 (%)		LCS 9 (%)		LCS 10 (%)		LCS 11 (%)		LCS 12 (%)	
Column ID		MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2	MR-1	MR-2
Pentachloronitrobenzene	IS	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Etridiazole		110.00	80.00	120.00	78.00	122.00	84.00	118.00	80.00	136.00	92.00	136.00	100.00	128.00	94.00
Chloroneb		82.00	62.00	96.00	72.00	94.00	70.00	88.00	64.00	94.00	74.00	94.00	70.00	84.00	66.00
Propachlor		86.00	80.00	98.00	92.00	98.00	96.00	98.00	86.00	110.00	94.00	100.00	94.00	92.00	90.00
Trifluralin		80.00	82.00	86.00	92.00	90.00	94.00	82.00	92.00	90.00	94.00	88.00	106.00	82.00	104.00
a-BHC		82.00	90.00	92.00	100.00	94.00	104.00	90.00	100.00	92.00	98.00	90.00	100.00	84.00	94.00
Lindane (g-BHC)		88.00	100.00	98.00	106.00	100.00	114.00	98.00	112.00	100.00	110.00	96.00	112.00	92.00	108.00
Simazine	1	N/A	80.00	N/A	90.00	N/A	98.00	N/A	98.00	N/A	102.00	N/A	104.00	N/A	108.00
Atrazine	1	N/A	98.00	N/A	82.00	N/A	94.00	N/A	102.00	N/A	100.00	N/A	100.00	N/A	104.00
b-BHC		90.00	100.00	96.00	106.00	100.00	112.00	96.00	114.00	98.00	108.00	96.00	106.00	90.00	102.00
d-BHC	2	N/A	114.00	N/A	112.00	N/A	126.00	N/A	126.00	N/A	120.00	N/A	122.00	N/A	116.00
Chlorothalonil		100.00	118.00	124.00	112.00	124.00	128.00	114.00	128.00	122.00	124.00	120.00	136.00	116.00	130.00
Metribuzin	2	N/A	80.00	N/A	78.00	N/A	84.00	N/A	82.00	N/A	76.00	N/A	92.00	N/A	90.00
Heptachlor		80.00	76.00	104.00	92.00	106.00	100.00	86.00	84.00	108.00	98.00	106.00	102.00	100.00	96.00
Alachlor		88.00	90.00	116.00	86.00	94.00	98.00	80.00	98.00	98.00	96.00	90.00	96.00	86.00	110.00
Cyanazine		110.00	88.00	130.00	88.00	138.00	100.00	124.00	90.00	132.00	98.00	124.00	98.00	118.00	96.00
Metolachlor		98.00	N/A	104.00	N/A	108.00	N/A	102.00	N/A	106.00	N/A	104.00	N/A	98.00	N/A
Dacthal		90.00	98.00	94.00	98.00	98.00	110.00	92.00	106.00	98.00	106.00	94.00	110.00	90.00	104.00
Heptachlor epoxide B		86.00	94.00	90.00	98.00	96.00	110.00	90.00	104.00	94.00	106.00	94.00	106.00	86.00	100.00
trans-Chlordane		80.00	86.00	82.00	86.00	94.00	106.00	82.00	94.00	88.00	96.00	86.00	96.00	80.00	90.00
Butaclor		102.00	88.00	106.00	88.00	114.00	102.00	106.00	96.00	114.00	100.00	110.00	106.00	108.00	104.00
cis-Chlordane		82.00	86.00	82.00	86.00	94.00	104.00	84.00	92.00	90.00	94.00	88.00	96.00	82.00	88.00
Endosulfan I		86.00	94.00	90.00	96.00	96.00	110.00	88.00	104.00	94.00	104.00	92.00	106.00	86.00	98.00
4,4'-DDE		76.00	80.00	76.00	80.00	92.00	104.00	76.00	88.00	84.00	92.00	80.00	88.00	74.00	80.00
Dieldrin		92.00	94.00	94.00	90.00	102.00	106.00	94.00	100.00	100.00	100.00	98.00	106.00	92.00	102.00
Endrin		94.00	96.00	100.00	96.00	106.00	114.00	90.00	104.00	104.00	108.00	100.00	108.00	98.00	104.00
Chlorobenzilate		60.00	76.00	62.00	90.00	72.00	106.00	72.00	96.00	76.00	104.00	72.00	102.00	68.00	98.00
Endosulfan II		90.00	94.00	92.00	94.00	98.00	112.00	90.00	106.00	98.00	106.00	94.00	108.00	90.00	102.00
4,4'-DDD		92.00	92.00	84.00	78.00	100.00	104.00	90.00	94.00	94.00	96.00	96.00	102.00	92.00	96.00
Endrin Aldehyde		84.00	82.00	88.00	80.00	96.00	104.00	88.00	94.00	94.00	100.00	94.00	102.00	88.00	98.00
4,4-DDT		110.00	94.00	94.00	78.00	120.00	108.00	106.00	96.00	112.00	96.00	112.00	100.00	106.00	94.00
Endosulfan Sulfate		94.00	90.00	96.00	90.00	104.00	108.00	96.00	100.00	102.00	106.00	100.00	104.00	96.00	96.00
Methoxychlor		120.00	92.00	112.00	102.00	134.00	104.00	120.00	92.00	132.00	98.00	130.00	102.00	122.00	98.00
Permethrin		104.00	92.00	98.00	80.00	156.00	132.00	94.00	92.00	114.00	96.00	116.00	106.00	106.00	136.00
Decachlorobiphenyl	S	84.00	96.00	74.00	78.00	90.00	110.00	82.00	96.00	74.00	88.00	88.00	108.00	84.00	104.00

1, 2 - Co-Elutting compounds on MR-1

EPA Method 508.1: Chlorinated Pesticides, Herbicides, and Organohalides

Horizon Technology, Inc., Salem, NH

Introduction

Method 508.1 is used to determine twenty-nine chlorinated pesticides, three herbicides, and four organohalides in ground water, drinking water, and water in any treatment stage. The analytes are extracted from the water using a 47 mm C18 disk. The disk is extracted on the Horizon Technology SPE-DEX® 4790 Automated Extraction System using Ethyl Acetate and Methylene Chloride (DCM). The extract is then dried and concentrated using the Horizon Technology DryVap® with DryDisk® technology. Final analysis is by GC/ECD.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extractor
  - DryVap® Concentrator System
  - DryDisk® Solvent Drying System
  - Atlantic™ C18 SPE Disk (47 mm)
- GC equipped with ECD

Method Summary

1. Prepare a one liter sample.
2. Run the purge method shown in Table 1.
3. Run the sample on SPE-DEX® 4790 Automated Extractor using the method in Table 2.
4. Load a DryDisk® holder onto the DryVap® concentrator.
5. Pour the extract into the DryDisk® holder and run the DryVap® to concentrate the sample to 1 mL.
6. Analyze the extract using a GC with ECD.

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, Envision® Platform Controller, and DryVap® Automated Drying and Concentrating System.

Table 1: Purge Method

Step	Solvent	Soak Time	Dry Time
Wash 1	DCM	0 sec	15 sec
Wash 2	Ethyl Acetate	0 sec	15 sec

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	1:1 Ethyl Acetate / DCM	1:00 min	1:00 min
Prewet 2	Methanol	1:00 min	0 sec
Prewet 3	Reagent Water	1:00 min	0 sec
Process Sample			
Air Dry 8:00 min			
Rinse 1	Ethyl Acetate	1:30 min	1:00 min
Rinse 2	DCM	1:30 min	1:00 min
Rinse 3	DCM	1:30 min	2:00 min

Method Detection Limits For EPA Method 515.2: Chlorinated Acids

Susan Petitti, Horizon Technology, Inc., Salem, NH

Introduction

EPA Method 515.2 is applicable to the determination of chlorinated acids in ground water and finished drinking water. The form of each acid is not distinguished by this method. Results are calculated and reported for each listed analyte as the total free acid. The analytes are extracted from the water using a DVB-Hydrophobic disk and the Horizon Technology SPE-DEX® 4770 Automated Extraction System. The disk is extracted with Methylene Chloride and the extract dried with sodium sulfate. The extract is derivatized with diazomethane. Final analysis is by GC/ECD.

Instrumentation

- Horizon Technology SPE-DEX® 4770 Automated Extraction System
- DVB-Hydrophobic disk (Bakerbond Speedisk™, 8068-06).
- HP GC with ECD

Method Summary

1) Seven, 250 mL aliquots of reagent water are used to calculate the MDL.
2) Sodium chloride is pre-washed with methylene chloride and acetone.
3) 50 g of the pre-washed sodium chloride is dissolved into the 250 mL sample.
4) The pH is adjusted to 12 using 6 N NaOH to hydrolyze derivatives.
5) Let sample stand for 1 hour.
6) Extraneous organic material is removed by a solvent wash using methylene chloride.
7) The sample is adjusted to pH 1 using concentrated sulfuric acid.
8) Chlorinated acids are extracted using the SPE-DEX® 4770 with a DVB disk and the method in Table 1.
9) The extract is dried using sodium sulfate.
10) The acids are converted to their methyl esters using diazomethane.
11) Excess derivatizing reagent is removed, and the esters are determined by capillary GC using an electronic capture detector (ECD).

Results

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An estimate of the MDL is made first; then seven 250 mL aliquots of reagent water are spiked with known concentrations of the analytes of interest. The sample is then extracted and analyzed.

Table 1: Extraction method.

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	5 sec	5 sec
Prewet 2	Methanol/MTBE	3:00 min	5:00 min
Prewet 3	Acetone	3:00 min	5 sec
Prewet 4	$MeCl_2$	3:00 min	5 sec
Prewet 5	Methanol	1:00 min	0 sec
Prewet 6	Methanol	3:00 min	0 sec
Prewet 7	Reagent Water	5 sec	0 sec
Prewet 8	Reagent Water	5 sec	0 sec
Process Sample			
Wash 1	Reagent Water	10 sec	10 sec
Wash 2	Reagent Water	10 sec	0 sec
Air Dry 5:00 min			
Rinse 1	Acetone	3:00 min	30 sec
Rinse 2	$MeCl_2$	1:00 min	5 sec
Rinse 3	$MeCl_2$	1:00 min	5 sec
Rinse 4	$MeCl_2$	1:00 min	30 sec

Table 2 shows a summary of the MDL generated for the 515.2 analytes (a complete list can be found in Table 3).

Table 2: MDL for EPA Method 515.2

Analyte	Spike Value (ug/L)	Mean	RSD (%)	Recovery (%)	MDL (ug/L)
DCPAA-SS	0.5	0.44	7.09	87	0.08
DICAMBA	4	4.22	15.27	105	2.42
24-D	4	4.78	8.68	120	1.47
PCP	0.16	0.14	12.38	86	0.03
SILVEX	0.8	0.77	6.68	96	0.09
245-T	4	4.12	7.49	103	1.04
DINOSEB	0.8	0.75	15.41	94	0.41
BENTAZON	4	30.7	17.42	77	0.49
DCPA, MONO-ACID	4	4.18	18.67	104	1.99
PICLORAM	4	3.9	13.87	97	1.84
ACIFLUORFEN	4	3.8	10.69	95	1.54

Conclusions

This work on the determination of MDLs for chlorinated acids demonstrates the capability of the Horizon Technology SPE-DEX® 4770 for the automated SPE extraction of organic compounds. This system reduced analyst labor, solvent usage, and turn-around-time, while still improving accuracy and precision.

Acknowledgements

Horizon Technology would like to thank the Michigan Department of Environmental Quality.

Table 3: Complete list of MDL data.

Analyte	Spike Value (ug/L)	Rep. 1 (ug/L)	Rep. 2 (ug/L)	Rep. 3 (ug/L)	Rep. 4 (ug/L)	Rep. 5 (ug/L)	Rep. 6 (ug/L)	Rep. 7 (ug/L)	Student t-value	Standard Deviation	Mean (ug/L)	RSD (%)	Recovery (%)	MDL (ug/L)
DCPAA-SS	0.5	0.461	0.447	0.458	0.406	0.409	0.495	0.444	3.143	0.03	0.45	6.94	89	0.10
DICAMBA	4.0	3.806	4.183	3.719	5.558	3.829	4.585	4.405	3.143	0.64	4.30	14.99	107	2.03
24-D	4.0	4.973	5.145	4.924	3.960	4.906	4.553	5.101	3.143	0.41	4.79	8.65	120	1.30
PCP	0.2	0.123	0.138	0.144	0.138	0.144	0.163	0.174	3.143	0.02	0.15	11.63	91	0.05
SILVEX	0.8	0.770	0.779	0.803	0.779	0.723	0.869	0.859	3.143	0.05	0.80	6.46	100	0.16
245-T	4.0	4.477	4.100	4.321	4.102	3.599	4.513	4.245	3.143	0.31	4.19	7.36	105	0.97
DINOSEB	0.8	0.595	0.666	0.798	0.780	0.932	0.874	0.819	3.143	0.12	0.78	14.89	98	0.37
BENTAZON	4.0	2.822	3.224	3.177	3.042	3.101	4.035	4.230	3.143	0.54	3.38	15.86	84	1.68
DCPA, MONO-ACID	4.0	3.632	3.744	3.785	4.985	4.732	5.539	5.165	3.143	0.78	4.51	17.28	113	2.45
PICLORAM	4.0	3.035	4.522	3.595	4.185	4.159	3.313	4.128	3.143	0.54	3.85	14.05	96	1.70
ACIFLUORFEN	4.0	3.977	4.362	3.887	3.729	3.022	3.925	3.713	3.143	0.41	3.80	10.67	95	1.28

Determination of Organic Compounds in Drinking Water Using Atlantic™ C18 SPE Disks for EPA Method 525.2

Michael Ebitson, Horizon Technology, Inc., Salem, NH

Introduction

Method 525.2 describes the procedure to determine low ppb levels of semi-volatile organic material in drinking water using solid phase extraction (SPE) or liquid–solid extraction (LSE) techniques. The City of Fort Worth, Water Department implemented an automated SPE process for the analysis of semi-volatiles by EPA Method 525.2 using the Atlantic™ C18 solid phase extraction disk. Ethyl acetate, methanol and water were used to condition the Atlantic™ C18 disk prior to the extraction step. The extraction solvents used were a 1:1 mixture of methylene chloride and ethyl acetate. Extracts were then analyzed by GC/MS using a splitless injection technique.

Automated sample handling equipment manufactured by Horizon Technology, Inc. was used in this method, including the SPE-DEX® 4790 Automated Extraction System, the Envision® Platform Controller, and the DryVap® Automated Drying and Concentration System. These units are designed to streamline the sample handling required for analyzing environmental samples.

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

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extractor System
  - Envision® Platform Controller
  - DryVap® Concentrator System
  - DryDisk® Separation Membranes
  - Atlantic™ C18 Disks (47mm)
- Agilent
  - 6890 GC
  - 5973 inert MSD
  - 7683B Autosampler
  - Column A: HP-5ms, 30m x 0.250mm x 0.25um
- Liner: 4mm single taper, deactivated, splitless
- Merlin MicroSeal® High Pressure Septum

Method Summary

1. A one liter aliquot of sample is used.
2. Adjust the samples a pH less than two.
3. Spike surrogate and internal standard compounds into samples.

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, Envision® Platform Controller, and DryVap® Automated Drying and Concentrating System.

4. Spike analyte standards into samples.
5. Start extraction method in Table 1, collect extract (approximately 30 mL).
6. Add extract to the DryDisk® holder and start concentration process (Table 2) on the DryVap® system.
7. Concentrate the extract to less than 1.0 mL and quantitatively bring the extract volume to 1.0ml (DryVap® concentration vessels are graduated to 0.5 mL and 1.0 mL).
8. Transfer a portion of the extract to a GC vial with insert.
9. Analyze by GC/MS.

Table 1: Extractor Program

STEP	SOLVENT	SOAK TIME	DRY TIME
Prewet #1	Ethyl Acetate	1:30 min	1:30 min
Prewet #2	Methanol	1:30 min	0 min
Prewet #3	DI Water	1:30 min	0 min
Sample Process			
Air Dry 8:00 min			
Rinse Step #1	Ethyl Acetate	1:30 min	1:00 min
Rinse Step #2	Methylene Chloride	1:30 min	1:00 min
Rinse Step #3	MeCl2:EtAc (1:1)	1:30 min	2:00 min
Rinse Step #4	MeCl2:EtAc (1:1)	1:30 min	2:00 min

Table 2: DryVap® Concentrator System Conditions.

PARAMETER	SETTING
Dry Volume	20
Heat Power	5
Auto Rinse Mode	OFF
Heat Timer	OFF

Results

Ultra-Pure (UP) water was spiked with 525.2 standard at a theoretical concentration of 5.0 ppb. The results for the Atlantic™ C18 disks are listed in Table 3 and a typical chromatogram is shown in Figure 1. Forty two compounds were included in the target compound list. The table shows the compound names, amount recovered, and percent recovery.

The Atlantic™ C18 disk had a recovery range of 61-122%. Twenty seven compounds fell within the 100-122% recovery range and twelve compounds fell within the 90-100% recovery range. One compound fell within each of the following ranges: 80-90%, 70-80%, and 60%-70%. Atlantic™ C18 disk 2 had a recovery range of 58-119%. Twenty eight compounds fell within 100-119%. Nine compounds fell within 90-100%. Three compounds fell between the 80-90%. One compound fell within each of the following ranges: 70-80% and 50-60%.

One thing of particular merit is the excellent recovery for Prometon with an acidic extraction (pH<2). This analyte usually requires a separate extraction under neutral pH conditions.

Conclusions

This data demonstrates that the equipment used in this study is capable of fully automating EPA method 525.2 and that the resulting data is both accurate and precise.

The Horizon Technology SPE-DEX® 4790 Automated Extractor System with the Envision™ Platform Controller and DryVap® Concentrator System with DryDisk® technology reduces analyst labor, solvent usage, turnaround time, and improves accuracy and precision. All of these qualities serve to reduce the total cost of a sample to a laboratory.

Acknowledgements

We would like to thank Dr. Johnny Skelton, PhD, from the City of Fort Worth, Water Department, Centralized Laboratory Services for his time and assistance with the set-up and running of the samples used in this study.

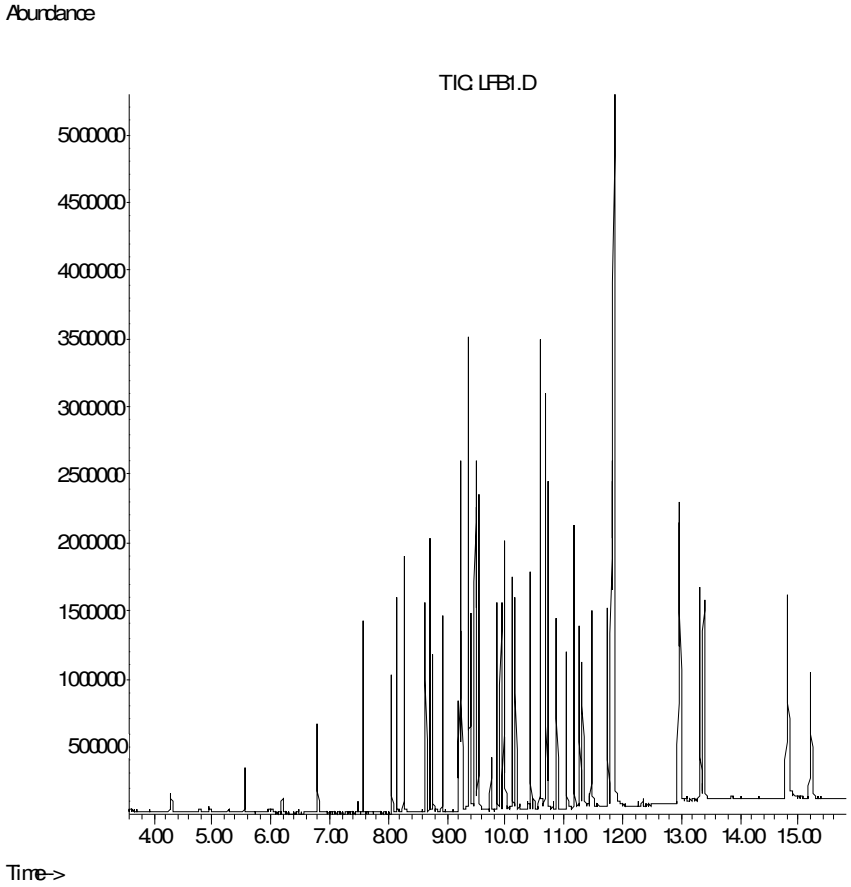

Figure 1: EPA Method 525.2 Chromatogram

Table 3: Recoveries for EPA Method 525.2

Analyte	(ppb) Atlantic Disk 1	% Recovery	(ppb) Atlantic Disk 2	% Recovery
Hexachlorocyclopentadiene	4.92	98	5.27	105
Dimethylphthalate	4.7	94	4.56	91
Acenaphthylene	5.07	101	4.87	97
Diethylphthalate	6.11	122	5.86	117
Fluorene	5.49	110	5.34	107
Propachlor	5.73	115	5.53	111
Trifluralin	6.07	121	5.89	118
Hexachlorobenzene	5.35	107	5.12	102
Atrazine	5.37	107	4.96	99
Prometon	3.93	79	4.16	83
Simazine	4	80	3.96	79
gamma-BHC	5.34	107	5.25	105
Phenanthrene	4.82	96	4.86	97
Anthracene	4.74	95	4.75	95
Pentachlorophenol	19.74	99	20.03	100
Metribuzin	3.06	61	2.92	58
Alachlor	5.35	107	5.34	107
Heptachlor	5.67	113	5.52	110
Di-n-butylphthalate	5.36	107	5.27	105
Bromacil	4.57	91	4.46	89
Metalachlor	5.43	109	5.4	108
Aldrin	4.58	92	4.24	85
Heptachlor Epoxide	5.4	108	5.5	110
gamma-Chlordane	5.36	107	5.16	103
Butachlor	5.55	111	5.55	111
alpha-Chlordane	5.37	107	5.22	104
trans-Nonachlor	5.34	107	5.14	103
Pyrene	5.45	109	5.29	106
Dieldrin	5.74	115	5.65	113
Endrin	5.5	110	5.16	103
cis-Nonachlor	4.8	96	4.86	97
Butylbenzylphthalate	5.51	110	5.59	112
Di-(2-ethylhexyl) Adipate	5.75	115	5.95	119
Methoxychlor	5.67	113	5.8	116
Benzo (a) Anthracene	5.03	101	5.02	100
Chrysene	5.19	104	5.11	102
Di-(2-ethylhexyl) Phthalate*	10.24	205	8.01	160
Benzo (b) Fluoranthene	5.24	105	5.59	112
Benzo (k) Fluoranthene	5.08	102	4.83	97
Benzo (a) Pyrene	4.75	95	4.81	96
Indeno (1,2,3-cd) Pyrene	4.75	95	4.92	98
Dibenz (a,h) Anthracene	4.87	97	5.09	102
Benzo (g,h,i) Perylene	4.79	96	5.01	100

*High recovery due to a contaminant in the UP water system and not the disks or equipment. DI water is recommended.

Determination of Organic Compounds in Drinking Water Using Atlantic DVB Disks for EPA Method 525.3

Bob Johnson, Horizon Technology, Inc., Salem, NH

Introduction

In the June 28, 2012 issue of the Federal Register, the EPA announced the approval of alternate testing methods for use in measuring the levels of contaminates in drinking water and for determining compliance with national primary drinking water regulations. The Safe Drinking Water Act (SDWA) authorizes the EPA to approve the use of alternative testing methods through publication in the Federal Register. The EPA used this streamline authority to make 10 additional methods available for analyzing drinking water samples required by regulation. This expedited approach provides public water systems, laboratories, and primacy agencies with more timely access to new measurement techniques and greater flexibility in the selection of analytical methods. This authority and flexibility helps reduce monitoring costs while maintaining public health protection.

One of the methods approved by this action is Method 525.3 for the determination of semi-volatile organic compounds in finished drinking water. The method analytes are extracted and concentrated from the water using solid phase extraction. Extracts are injected onto a capillary GC column and analyzed using mass spectrometry. Method 525.3 is similar in many ways to its predecessor, method 525.2 (Rev 2.0 – 1995), however there are significant changes which make the newer 525.3 a vastly improved method. Several of the major changes are as follows:

- The sorbent material has been changed from C18 to DVB (divinylbenzene). This yields better recoveries over a wider pH range.
- The preservation/dechlorination scheme has changed from HCl and sodium sulfite, to ascorbic acid, EDTA, and citric acid. This is safer for field sampling crews, and allows bottles to be shipped with preservatives pre-added.
- The internal standard is added to the final extract, not prior to the extraction as with 525.2.
- The use of SIM mode is an option for regulated compounds that have difficulty reaching detection limits.
- The surrogate perylene-d12 has been dropped.
- Pentachlorophenol-C13 is now used as an internal standard for pentachlorophenol.

One of the key points to be aware of with method 525.3, is that during the development of the method, the EPA found that several brands of styrene-divinylbenzene (SDVB) and modified SDVB media in cartridge format did not provide satisfactory performance. Therefore, this method specifically identifies those sorbent materials which can be used. Where method modifications are proposed, the analyst must perform the procedures outlined in the initial demonstration of capability (IDC, Sect 9.2), verify that all QC acceptance criteria in this method (Sect. 9) are met, and that method performance in real samples matrices is equivalent to that demonstrated for Laboratory Fortified Sample Matrices (LFSMs) in Sect. 17.

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, and the Envision® Platform Controller.

This application note will describe the use of the Horizon Technology SPE-DEX 4790 automated extractor system, and the Atlantic DVB SPE disk for the extraction of water samples, as specified in method 525.3.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extraction System
  - Envision® Platform Controller
  - Atlantic™ DVB 50 mm SPE Disk
- Organomation
  - N-Evap Concentrator
- Restek
  - Rxi-5Sil MS 30 m, 0.25 mm ID, 0.25 um df
- Agilent
  - 6890 Gas Chromatograph
  - 5973 Inert MSD
  - 7683B Autosampler

Method Summary

Preservation and Declorination

1. Sample bottles are prepared using 0.10 g/L L-Ascorbic acid, 0.35 g/L trisodium EDTA, and 9.4 g/L potassium dihydrogen citrate (Section 8).

2. A one liter sample should be collected in this bottle and its pH should be less than or equal to 4.

Extraction

1. Verify that the sample pH is less than or equal to 4.
2. Add surrogate to each sample.
3. Load the sample onto the SPE-DEX 4790 extractor and start the extraction process using the method given in Table 1.
4. When complete, remove the collected extract (16-20 mL).
5. Pour the extract through a tube containing 10 g of anhydrous sodium sulfate.
6. Rinse the sodium sulfate using 5 mL of DCM.
7. Using the N-Evap Concentrator, concentrate the extract to a volume of 0.7 mL using a gentle stream of nitrogen and a water bath temperature of 40ºC.
8. Bring the final volume up to 1 mL, making sure to rinse the concentrator tube with EtOAc
9. Transfer the extract to an autosampler vial and analyze by GC/MS.

Table 1: Extraction Method*

Step	Solvent	Soak Time	Dry Time
Prewet 1	EtOAc	1:00 min	30 sec
Prewet 2	DCM	1:00 min	30 sec
Prewet 3	MeOH	1:00 min	0 sec
Prewet 4	Reagent Water	5 sec	0 sec
Sample Process			
Air Dry 1:00 min			
Rinse 1	EtOAc	1:30 min	30 sec
Rinse 2	DCM	1:30 min	30 sec
Rinse 3	DCM	1:30 min	30 sec
Rinse 4	DCM	1:00 min	20 sec

*The Data given in EPA Method 525.3 and this Application Note was generated using this method. However, EPA recommends the addition of two reagent water wash steps each with 10 sec soak times and 30 sec dry times.

Results

Table 2 shows the precision and accuracy data obtained from method analytes fortified in reagent water at three concentrations and extracted using the SPE-DEX 4790 Extractor System and the Atlantic DVB SPE disk. The concentrations were 0.25, 2.0, and 5.0 ug/L. The mean recovery values and RSD's are shown.

Table 3 shows the precision and accuracy data obtained for method analytes fortified in finished drinking water from ground and surface water sources and extracted using the same setup, as above. The fortified concentration was 2.0 ug/L. The mean recovery values and RSD's are shown for both synthetic hard water and for surface water.

Recoveries and deviations from both sets are excellent, indicating the SPE-DEX 4790 and Atlantic disk are a viable option for those laboratories looking to increase sample throughput, and reduce labor costs.

Conclusions

The recently promulgated method 525.3 addresses many of the subtle chemistry issues that have plagued method 525.2. In keeping with advances in sorbent technology, method 525.3 now uses polymeric DVB material in place of the conventional C18. With these changes, method 525.3 will now be the preferred method of choice for the analysis of semi-volatile compounds in drinking water.

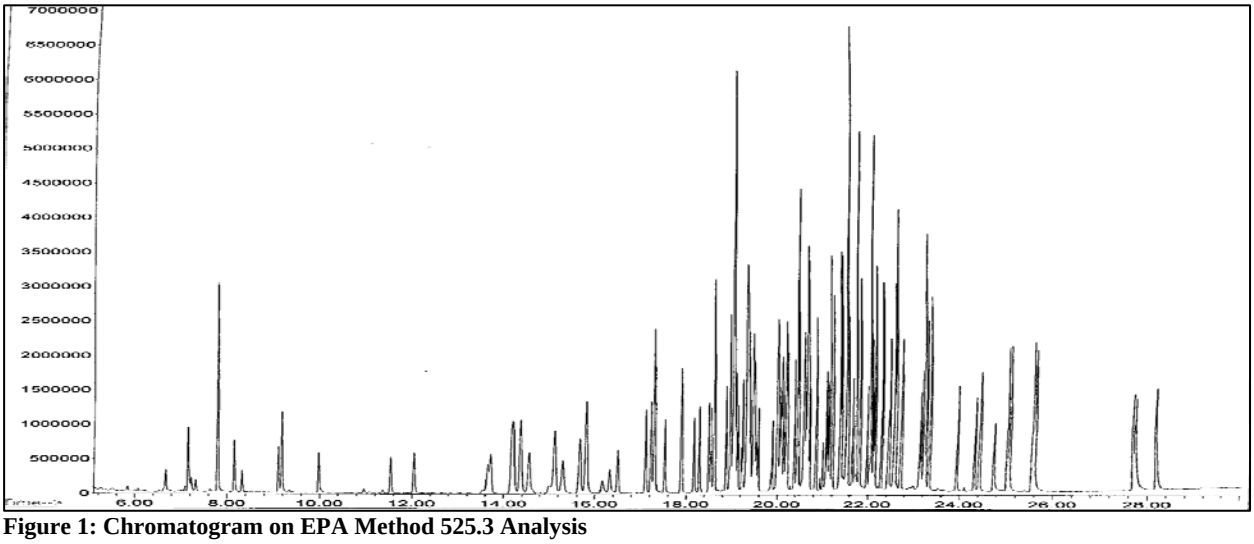

Figure 1: Chromatogram on EPA Method 525.3 Analysis

Table 2: Precision and Accuracy Data for Method Analytes Fortified in Reagent Water at Three Concentrations and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Concentration; Full Scan GC/MS Analysis[a].

	Fortified Conc. 0.25 µg/L		Fortified Conc. 2.0 µg/L		Fortified Conc. 5.0 µg/L	
Analytes	**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**
acenaphthylene	87.3	3.4	86.6	1.1	90.5	1.3
acetochlor	92.3	4.0	93.9	2.6	95.2	1.4
alachlor	95.6	8.0	93.4	2.0	94.6	1.4
aldrin	85.6	1.2	84.7	5.7	90.4	1.2
ametryn	91.4	3.5	93.9	2.9	95.8	1.5
anthracene	87.2	4.6	90.2	2.2	92.9	1.4
atraton	93.2	5.2	94.9	5.3	98.5	2.4
atrazine	94.5	7.4	92.9	2.9	95.0	1.9
benzo[*a*]anthracene	93.6	2.5	90.6	2.1	91.3	1.7
benzo[*a*]pyrene	88.9	3.5	85.8	3.0	88.2	3.9
benzo[*b*]fluoranthene	87.9	3.6	85.1	3.0	89.0	4.0
benzo[*g,h,i*]perylene	88.3	4.2	79.8	3.9	84.5	3.8
benzo[*k*]fluoranthene	91.1	3.8	85.9	2.7	87.2	3.9
BHT	89.8	5.0	84.9	1.5	87.6	1.2
bromacil	96.9	1.9	94.3	2.8	96.6	3.6
butachlor	94.9	5.0	91.5	2.8	93.0	2.4
butylate	86.9	2.4	88.0	2.4	91.5	1.5
butylbenzylphthalate	104.0	19.0	94.5	3.9	93.6	1.2
chlordane, cis	92.1	6.5	89.2	4.9	89.7	2.5
chlordane, trans	91.2	5.0	89.4	4.2	88.9	2.3
chlorfenvinphos	89.1	7.7	94.0	4.3	95.3	2.4
chlorobenzilate	96.0	4.0	93.8	4.4	92.4	1.9
chloroneb	89.7	4.2	90.9	1.4	93.6	1.3
chlorothalonil	89.0	4.8	94.3	1.6	97.3	2.3
chlorpropham	93.7	7.7	92.5	2.3	95.8	0.8
chlorpyrifos	89.1	2.6	91.3	3.2	94.4	2.1
chrysene	90.7	2.3	92.0	2.6	90.9	1.4
cyanazine	101.0	8.6	108.0	3.3	114.0	3.7
cycloate	90.0	4.9	89.6	1.7	92.4	0.3
dacthal (DCPA)	93.9	3.3	94.3	2.1	96.0	1.2
DDD, 4,4′-	91.0	3.4	91.8	3.4	88.3	1.8
DDE, 4,4′-	83.9	4.3	87.9	6.8	85.6	3.0
DDT, 4,4′-	88.8	6.0	88.3	4.2	86.4	2.4
DEET	91.6	5.5	92.9	2.0	94.5	0.8
di(2-ethylhexyl)adipate	84.1	8.6	76.2	3.3	76.5	3.1
di(2-ethylhexyl)phthalate	ND[e]	11.0	77.0	2.7	72.7	2.8
dibenzo[*a,h*]anthracene	85.3	5.0	76.7	3.7	81.5	4.5
dibutyl phthalate	ND	6.4	111.0	2.2	95.0	1.0
dichlorvos	93.2	4.4	86.7	1.0	89.3	2.3
dieldrin	93.6	9.2	91.3	6.2	91.1	2.8
diethylphthalate	93.6	5.4	91.4	2.2	94.2	0.9
dimethipin	36.0	13.0	32.8	25.0	28.4	9.6
dimethylphthalate	89.4	5.3	90.0	1.0	92.6	1.0
DIMP	89.9	5.3	83.9	2.7	86.8	1.8
dinitrotoluene, 2,4-	88.6	5.8	92.1	1.4	97.0	1.3
dinitrotoluene, 2,6-	89.3	5.7	89.1	2.1	94.0	0.7
diphenamid	93.8	3.2	94.7	2.1	96.2	1.4
disulfoton	71.0	5.0	77.4	4.9	77.8	4.8
endosulfan I	87.9	9.2	89.6	3.3	91.1	1.4
endosulfan II	94.8	5.8	91.5	6.7	90.6	3.0
endosulfan sulfate	95.1	4.8	93.4	2.7	93.4	1.7
endrin	88.1	2.1	92.5	4.7	93.0	2.3
EPTC	85.8	3.5	86.2	1.0	90.5	1.8
ethion	96.1	4.3	93.5	3.9	92.7	2.8

Table 2: Precision and Accuracy Data for Method Analytes Fortified in Reagent Water at Three Concentrations and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Concentration; Full Scan GC/MS Analysis[a] (continued).

	Fortified Conc. 0.25 µg/L		Fortified Conc. 2.0 µg/L		Fortified Conc. 5.0 µg/L	
Analytes	**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**
ethoprop	91.9	4.1	92.1	2.7	95.7	0.7
ethyl parathion	92.9	7.8	88.8	3.1	93.4	2.8
etridiazole	84.6	6.7	88.8	1.4	92.3	1.1
fenamiphos	90.4	13.0	89.1	2.8	92.4	1.7
fenarimol	99.8	5.9	95.9	3.7	100.0	3.4
fluorene	86.6	4.4	88.1	1.2	92.5	0.5
fluridone	95.4	8.2	96.1	5.9	101.0	4.6
HCCPD	72.6	6.9	73.5	2.4	76.5	4.4
HCH, alpha	91.5	5.9	91.1	1.3	93.3	0.7
HCH, beta	96.1	6.1	94.4	2.8	97.0	2.3
HCH, delta	88.5	5.7	90.6	3.4	93.4	1.5
HCH, gamma (lindane)	89.4	4.0	92.1	3.0	92.3	0.9
heptachlor	91.9	9.9	89.8	3.2	92.6	0.3
heptachlor epoxide	86.8	3.3	91.3	5.7	92.8	2.4
hexachlorobenzene	86.8	6.1	89.5	1.9	90.5	1.1
hexazinone	95.0	3.8	97.8	1.8	100.0	1.7
indeno[1,2,3-*c*,*d*]pyrene	85.3	5.5	80.2	3.7	86.1	4.3
isophorone	88.2	6.0	87.4	1.3	87.1	1.5
methoxychlor	94.1	4.0	93.0	2.6	92.2	1.3
methyl parathion	90.3	3.8	93.6	3.1	95.4	0.4
metolachlor	90.3	5.0	93.9	3.2	96.6	1.6
metribuzin	93.3	4.7	94.8	1.5	95.4	2.0
mevinphos	90.1	4.7	89.4	1.6	93.2	0.9
MGK 264(a)	87.5	4.0	92.3	2.6	94.5	1.5
MGK 264(b)	86.3	7.9	94.4	3.9	96.3	2.5
molinate	90.5	6.9	89.2	1.1	91.6	1.4
napropamide	97.3	7.6	93.3	3.8	92.9	1.2
nitrofen	90.4	5.1	94.4	3.3	94.0	1.3
nonachlor, trans	86.7	4.2	86.8	2.4	86.0	3.3
norflurazon	97.0	3.8	95.1	2.3	98.9	3.3
oxyfluorfen	94.3	5.2	93.2	4.5	92.9	1.9
pebulate	90.5	3.7	88.4	1.6	90.9	2.0
pentachlorophenol	93.0	4.4	97.4	3.9	94.8	3.4
permethrin, cis	87.7	2.0	79.8	1.3	80.9	3.5
permethrin, trans	89.3	3.2	82.3	2.2	83.2	2.0
phenanthrene	88.6	3.9	90.1	2.4	92.6	1.7
phorate	83.7	4.2	88.8	2.3	91.1	1.0
phosphamidon	98.3	6.5	95.2	2.9	95.5	2.0
profenofos	92.0	8.6	93.7	2.8	94.7	4.2
prometon	90.0	3.8	93.9	3.2	96.0	0.8
prometryn	94.0	2.0	98.9	3.9	102.0	2.2
pronamide	92.3	4.0	93.5	1.7	96.1	1.9
propachlor	88.8	5.2	91.5	2.8	94.7	0.9
propazine	95.5	3.3	93.5	2.6	95.7	0.6
pyrene	92.2	4.3	91.8	3.8	92.3	2.1
simazine	93.9	3.8	94.2	1.8	98.7	2.9
simetryn	95.1	2.1	93.8	2.8	95.4	1.0
tebuconazole	93.2	5.3	94.7	2.0	97.0	2.3
tebuthiuron	95.4	11.0	91.3	9.5	99.6	8.9
terbacil	91.4	6.1	94.5	1.9	96.2	2.9
terbutryn	96.5	5.1	93.7	3.0	95.5	1.5
tetrachlorvinphos	95.6	4.9	92.3	3.1	93.0	2.8
triadimefon	94.5	2.4	96.1	3.3	96.7	2.6
tribufos	82.0	5.2	95.8	4.4	93.7	1.6

Table 2: Precision and Accuracy Data for Method Analytes Fortified in Reagent Water at Three Concentrations and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Concentration; Full Scan GC/MS Analysis[a] (continued).

	Fortified Conc. 0.25 µg/L		Fortified Conc. 2.0 µg/L		Fortified Conc. 5.0 µg/L	
Analytes	**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**
trifluralin	91.0	5.8	91.2	2.1	95.9	0.8
vernolate	87.3	2.5	87.0	1.1	90.7	1.8
vinclozolin	94.3	8.5	94.7	4.6	94.9	2.2
PCB congeners (by IUPAC#)						
2-chlorobiphenyl (1)	85.3	5.2	87.2	1.8	90.0	0.5
4-chlorobiphenyl (3)	88.2	4.0	88.1	1.3	92.0	1.1
2,4′-dichlorobiphenyl (8)	87.1	5.8	90.8	2.0	92.5	0.4
2,2′,5-trichlorobiphenyl (18)	89.4	2.5	91.0	2.9	92.0	0.5
2,4,4′-trichlorobiphenyl (28)	84.4	6.8	90.6	3.1	90.8	0.4
2,2′,3,5′-tetrachlorobiphenyl (44)	87.2	7.5	89.6	2.8	90.3	1.7
2,2′,5,5′-tetrachlorobiphenyl (52)	89.4	5.4	88.8	2.2	89.4	2.7
2,3′,4′,5-tetrachloroobiphenyl (70)	87.8	8.3	88.3	5.0	89.4	1.7
2,3,3′,4′,6-pentachlorobiphenyl (110)	87.1	3.2	90.5	4.1	88.5	3.4
2,3′,4,4′,5-pentachlorobiphenyl (118)	85.5	3.4	89.0	4.3	84.3	4.1
2,2′,3,4,4′,5′-hexachlorobiphenyl (138)	85.9	5.7	88.6	3.9	86.4	2.8
2,2′,3,4′,5′,6-hexachlorobiphenyl (149)	84.3	6.6	88.0	4.5	86.7	3.6
2,2′,4,4′,5,5′- hexachlorobiphenyl (153)	83.1	4.4	87.7	4.7	85.1	4.6
2,2′,3,4,4′,5,5′-heptachlorobiphenyl (180)	81.9	6.0	87.1	4.5	86.5	2.9
Surrogate Analytes						
1,3-dimethyl-2-nitrobenzene	86.4	4.0	86.2	1.9	88.0	0.9
benzo[*a*]pyrene-d_{12}	89.6	3.5	93.5	5.1	98.9	4.2
triphenyl phosphate	87.8	2.6	93.3	2.9	99.9	1.8

Table 3: Precision and Accuracy Data for Method Analytes Fortified in Finished Drinking Water From Ground and Surface Water Sources, and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Matrix; Full Scan GC/MS Analysis[a].

	Fortified Conc. (µg/L)	Synthetic Hard Water		Surface Water	
Analytes		**Mean % Recovery**	**RSD**	**Mean % Recovery**	**RSD**
acenaphthylene	2.0	90.9	2.2	92.1	1.8
acetochlor	2.0	98.7	0.5	97.0	2.6
alachlor	2.0	96.9	1.2	95.0	1.6
aldrin	2.0	93.3	3.4	93.2	2.9
ametryn	2.0	90.8	4.2	90.0	3.2
anthracene	2.0	95.3	2.2	94.8	1.6
atraton	2.0	85.8	5.7	88.2	4.5
atrazine	2.0	92.2	3.2	93.3	0.8
benzo[*a*]anthracene	2.0	92.1	2.4	91.9	1.7
benzo[*a*]pyrene	2.0	87.4	2.3	86.8	2.4
benzo[*b*]fluoranthene	2.0	85.7	3.6	85.8	3.0
benzo[*g,h,i*]perylene	2.0	79.1	1.6	78.4	6.1
benzo[*k*]fluoranthene	2.0	87.9	3.3	85.1	3.5
BHT	2.0	92.6	1.6	93.8	2.4
bromacil	2.0	95.4	4.2	96.1	2.7
butachlor	2.0	93.5	3.6	93.4	2.1
butylate	2.0	95.0	2.0	95.8	3.4
butylbenzylphthalate	2.0	92.8	3.2	92.5	1.9

Table 3: Precision and Accuracy Data for Method Analytes Fortified in Finished Drinking Water From Ground and Surface Water Sources, and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Matrix; Full Scan GC/MS Analysis[a] (continued).

Analytes	Fortified Conc. (µg/L)	Synthetic Hard Water		Surface Water	
		Mean % Recovery	RSD	Mean % Recovery	RSD
chlordane, cis-	2.0	89.0	1.7	89.8	2.3
chlordane, trans	2.0	89.7	1.6	90.3	1.3
chlorfenvinphos	2.0	95.2	4.1	95.1	2.3
chlorobenzilate	2.0	94.3	4.1	93.2	1.7
chloroneb	2.0	95.6	1.2	95.6	1.5
chlorothalonil	2.0	97.1	1.9	97.8	1.6
chlorpropham	2.0	97.1	1.4	97.4	2.0
chlorpyrifos	2.0	95.2	2.5	95.0	2.2
chrysene	2.0	94.8	2.7	91.8	2.3
cyanazine	2.0	98.7	7.1	97.4	5.4
cycloate	2.0	94.4	2.3	94.5	2.0
dacthal (DCPA)	2.0	97.5	1.7	98.0	0.6
DDD, 4,4′-	2.0	86.5	3.5	87.5	1.4
DDE, 4,4′-	2.0	83.6	1.7	84.2	2.6
DDT, 4,4′-	2.0	82.4	2.1	82.5	0.6
DEET	2.0	99.3	2.4	99.3	2.9
di(2-ethylhexyl)adipate	2.0	72.1	1.4	73.4	2.0
di(2-ethylhexyl)phthalate	2.0	73.0	3.6	74.7	3.1
dibenzo[*a,h*]anthracene	2.0	75.8	2.1	75.2	6.3
dibutyl phthalate	2.0	116.0	2.3	114.0	1.0
dichlorvos	2.0	90.0	3.6	91.4	2.2
dieldrin	2.0	90.4	4.9	88.3	1.8
diethylphthalate	2.0	96.7	2.3	96.4	1.1
dimethipin	2.0	45.0	24.0	34.8	17.0
dimethylphthalate	2.0	94.3	1.8	95.2	1.9
DIMP	2.0	84.6	3.5	88.3	5.1
dinitrotoluene, 2,4-	2.0	93.4	5.6	98.2	3.0
dinitrotoluene, 2,6-	2.0	92.9	3.3	95.5	1.1
diphenamid	2.0	95.5	2.6	95.2	1.8
disulfoton	2.0	80.0	5.1	73.4	10.0
endosulfan I	2.0	68.1	2.7	59.4	7.7
endosulfan II	2.0	90.6	6.2	89.7	4.8
endosulfan sulfate	2.0	92.6	3.2	92.1	2.4
endrin	2.0	90.6	3.4	93.0	2.5
EPTC	2.0	93.0	2.0	94.6	2.0
ethion	2.0	92.8	3.2	89.3	1.1
ethoprop	2.0	99.1	2.1	98.7	2.6
ethyl parathion	2.0	95.4	1.9	96.3	6.8
etridiazole	2.0	96.1	2.6	95.1	2.8
fenamiphos	2.0	90.3	4.4	91.8	2.9
fenarimol	2.0	98.7	4.5	94.4	1.8
fluorene	2.0	93.3	1.7	93.0	2.4
fluridone	2.0	89.1	6.1	87.0	10.0
HCCPD	2.0	83.8	2.7	85.4	3.8
HCH, alpha	2.0	95.2	2.6	96.4	3.6
HCH, beta	2.0	99.6	3.1	98.5	2.9

Table 3: Precision and Accuracy Data for Method Analytes Fortified in Finished Drinking Water From Ground and Surface Water Sources, and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Matrix; Full Scan GC/MS Analysis[a] (continued).

Analytes	Fortified Conc. (µg/L)	Synthetic Hard Water		Surface Water	
		Mean % Recovery	RSD	Mean % Recovery	RSD
HCH, delta	2.0	94.8	3.3	94.2	2.4
HCH, gamma (lindane)	2.0	92.8	1.8	94.1	2.8
heptachlor	2.0	90.5	3.7	91.4	3.7
heptachlor epoxide	2.0	95.4	4.5	92.3	3.0
hexachlorobenzene	2.0	93.6	1.3	92.8	1.8
hexazinone	2.0	95.1	1.6	94.9	4.4
indeno[1,2,3-*c*,*d*]pyrene	2.0	80.6	2.7	80.6	6.3
isophorone	2.0	90.9	2.3	91.9	1.4
methoxychlor	2.0	93.4	3.6	93.8	1.8
methyl parathion	2.0	95.4	2.6	98.3	4.9
metolachlor	2.0	97.0	1.6	98.0	1.6
metribuzin	2.0	93.7	1.0	93.6	1.5
mevinphos	2.0	95.0	2.5	95.6	1.3
MGK 264(a)	1.6	95.7	2.3	93.9	2.2
MGK 264(b)	0.4	98.4	3.6	98.1	4.0
molinate	2.0	93.9	2.2	94.5	1.7
napropamide	2.0	91.3	4.4	93.1	1.9
nitrofen	2.0	93.2	3.3	95.6	1.8
nonachlor, trans	2.0	86.7	3.7	86.3	2.9
norflurazon	2.0	97.1	3.1	96.0	1.5
oxyfluorfen	2.0	93.5	3.2	95.3	0.8
pebulate	2.0	92.8	2.3	94.3	2.4
pentachlorophenol	8.0	96.8	2.7	96.6	2.2
permethrin, cis	2.0	77.7	3.1	77.3	2.1
permethrin, trans	2.0	80.1	2.9	79.1	1.8
phenanthrene	2.0	93.8	1.2	94.3	2.3
phorate	2.0	92.0	1.5	93.0	4.1
phosphamidon	2.0	92.7	5.3	94.6	1.7
profenofos	2.0	94.2	2.9	95.7	2.0
prometon	2.0	87.4	6.1	86.1	3.6
prometryn	2.0	93.3	4.5	91.5	2.8
pronamide	2.0	95.7	2.3	96.4	1.7
propachlor	2.0	97.1	2.8	96.3	1.3
propazine	2.0	93.8	1.8	93.0	3.0
pyrene	2.0	93.0	2.5	93.7	1.4
simazine	2.0	91.8	2.7	92.9	2.7
simetryn	2.0	88.4	3.8	89.6	3.4
tebuconazole	2.0	97.0	2.3	96.8	2.4
tebuthiuron	2.0	97.7	6.1	98.8	8.0
terbacil	2.0	96.1	2.0	96.5	2.6
terbutryn	2.0	92.4	5.4	89.6	4.2
tetrachlorvinphos	2.0	91.7	3.9	91.8	3.1
triadimefon	2.0	97.6	3.9	93.8	4.2
tribufos	2.0	95.2	3.7	93.5	2.3
trifluralin	2.0	100.0	1.8	99.1	2.0

Table 3: Precision and Accuracy Data for Method Analytes Fortified in Finished Drinking Water From Ground and Surface Water Sources, and Extracted Using Horizon Atlantic DVB Disks; N=5 for Each Matrix; Full Scan GC/MS Analysis[a] (continued).

Analytes	Fortified Conc. (µg/L)	Synthetic Hard Water		Surface Water	
		Mean % Recovery	RSD	Mean % Recovery	RSD
vernolate	2.0	92.6	2.4	94.0	2.5
vinclozolin	2.0	97.5	1.1	97.6	3.9
PCB congeners (by IUPAC#)					
2-chlorobiphenyl (1)	2.0	90.8	2.0	92.0	2.4
4-chlorobiphenyl (3)	2.0	91.8	2.3	92.4	3.2
2,4′-dichlorobiphenyl (8)	2.0	94.9	2.0	95.0	2.7
2,2′,5-trichlorobiphenyl (18)	2.0	95.2	2.2	94.4	1.8
2,4,4′-trichlorobiphenyl (28)	2.0	93.6	1.9	92.9	3.4
2,2′,3,5′-tetrachlorobiphenyl (44)	2.0	94.4	3.8	92.1	2.1
2,2′,5,5′-tetrachlorobiphenyl (52)	2.0	91.1	3.6	91.4	2.5
2,3′,4′,5-tetrachloroobiphenyl (70)	2.0	87.8	1.2	89.4	1.2
2,3,3′,4′,6-pentachlorobiphenyl (110)	2.0	86.6	1.3	88.0	1.8
2,3′,4,4′,5-pentachlorobiphenyl (118)	2.0	83.3	2.9	86.9	1.7
2,2′,3,4,4′,5′-hexachlorobiphenyl (138)	2.0	82.6	1.8	84.7	2.2
2,2′,3,4′,5′,6-hexachlorobiphenyl (149)	2.0	82.5	2.0	85.9	2.8
2,2′,4,4′,5,5′- hexachlorobiphenyl (153)	2.0	81.5	1.8	83.4	2.9
2,2′,3,4,4′,5,5′-heptachlorobiphenyl (180)	2.0	79.3	2.6	81.3	1.6
Surrogate Analytes					
1,3-dimethyl-2-nitrobenzene	2.0	88.7	2.9	90.6	3.8
benzo[*a*]pyrene-d_{12}	2.0	94.1	2.4	93.4	3.2
triphenyl phosphate	2.0	92.2	1.8	92.4	1.7

EPA Method 526: Selected Semi-Volatile Organics by GC/MS

Horizon Technology, Inc., Salem, NH

Introduction

Method 526 is a gas chromatography / mass spectrometry (GC/MS) method for the determination of selected semi-volatile compounds in raw and finished drinking waters. This method efficiently extracts analytes using the SPE-DEX® 4790 with an Atlantic® 47 mm polystyrene divinylbenzene (DVB) disk. The disk is extracted with using Ethyl Acetate (EtAc) and Methylene Chloride (DCM). The extract is then dried and concentrated using the DryVap® concentrator system coupled with DryDisk® technology to a final volume of 1.0 mL. Final analysis is done by GC/MS.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated SPE Extractor
  - Atlantic® DVB disk (47 mm)
  - DryVap® solvent concentration system
  - DryDisk® solvent drying membrane
- GC/MS system

Method Summary

1. A one liter sample is prepared.
2. Purge the SPE-DEX® 4790 system using the method listed in Table 1.
3. Extract the sample using the method in Table 2.
4. Pour the extract into the DryDisk® reservoir and start the DryVap®.
5. Final analysis is done by GC/MS

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, Envision® Platform Controller, and DryVap® Automated Drying and Concentrating System.

Table 1: Purge Method

Step	Solvent	Soak Time	Dry Time
Wash 1	Methylene Chloride	0 sec	5 sec
Wash 2	Ethyl Acetate	0 sec	10 sec

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	EtAc/DCM (1:1)	1:30 min	1:30 min
Prewet 2	Methanol	1:30 min	0 sec
Prewet 3	Reagent Water	1:30 min	0 sec
Process Sample			
Air Dry 8:00 min			
Rinse 1	Ethyl Acetate	1:30 min	1:00 min
Rinse 2	Methylene Chloride	1:30 min	1:00 min
Rinse 3	EtAc/DCM (1:1)	1:30 min	2:00 min

Improving the Efficiency and Accuracy when Extracting Semi-Volatile Organics in Drinking Water by Method 525.2

Brian LaBreque, Horizon Technology, Inc., Salem, NH

Introduction

EPA Method 525 was first promulgated in 1988 and, has since come to be the de-facto standard to measure a wide range of semi-volatile organic compounds in drinking water. In 1995, the EPA issued Revision 2 of the 525 method. With the advances in both chemical knowledge and instrumentation since this time, it has now become possible to improve the recovery of the compounds given in the 525.2 method.

The focus of this Application Note is to illustrate some of the advances which have been made when performing this method using Solid Phase Extraction (SPE). It will make use of the SmartPrep Automated Cartridge Extraction system set up to run in Bottle Rinse Mode with 6 mL SPE cartridges.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 6 mL Cartridge Configuration
  - Bottle Rinse Kit
  - 20 mL VOA Vial Extract Collection Tray
  - DryVap® Concentration System
  - DryDisk® Separation Membrane
- Phenomenex
  - Strata® C18-E, 6 mL Cartridges
  - ZB – Semivolatiles, 30 m x 0.25 mm x 0.25 µm
- Agilent
  - 6890 GC
  - 5975C MSD

Method Summary

1. Prepare six deionized 1 L water samples in amber containers using 1 mL of HCl to lower the pH to 2.
2. Spike samples at 5 µg/L by adding 5 µL of a 1000 µg/mL internal standard solution, 5 µL of a 1000 µg/mL surrogate solution, and 50 µL of a 100 µg/mL spike solution (for blanks, add only internal standards and surrogates).
3. Insert Sip Tubes and attach Bottle Rinse Kits to each sample bottle.
4. Place a 20 mL VOA vial in positions 1-6 of the extract collection tray.
5. Place a 1 g, 6 mL C18-E cartridge in positions 1-6 of the cartridge carousel.
6. Run the extraction method described in Table 4.
7. Place six 200 mL concentrator tubes with a 1 mL endpoint on the DryVap.
8. Place a DryDisk membrane in each DryDisk reservoirs and place on the DryVap.

The Horizon Technology SmartPrep® Automated Cartridge Extractor

9. Pour each extract into a DryDisk reservoir and start the DryVap using the parameters in Table 1.
10. Rinse each VOA vial with methylene chloride and pour the rinsate into the reservoir, repeat 2 times.
11. Rinse down the sides of the reservoir with methylene chloride, repeat 2 times.
12. Upon completion, bring the volume to 1.0 mL with methylene chloride.
13. Transfer 400 µL to a GC vial and add 4 µL of a Terphenyl-d14 solution at 500 µL/mL (the remaining 600 µL should be kept for possible re-analysis).
14. Analyze extracts by GC/MS as shown in Table 2.

Table 1: DryVap Parameters

Parameter	Setting
Dry Volume	20 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	17 psi
Vacuum	-11 in. Hg

Table 2: GC/MS Acquisition Parameters

Injection:
- Inlet Temperature: 345°C
- Mode: Pulsed Splitless
- Amount: 1 µL

Carrier Gas: Helium Constant at 1 mL/min

Oven Program:
- Hold 70°C for 0.5 minutes
- Ramp 16°C/min to 190°C
- Ramp 8°C/min to 290°C
- Ramp 25°C/min, hold for 3 minutes

Detector:
- MSD in scan mode

Results

A six point calibration curve was prepared in ethyl acetate and analyzed using concentrations of 10 µg/mL, 5.0 µg/mL, 2.0 µg/mL, 1.0 µg/mL, 0.5 µg/mL and 0.1 µg/mL.

One Laboratory Reagent Blank and four Laboratory Fortified Blanks (LFB's) were extracted with the Horizon Technology SmartPrep. The rate at which the samples were loaded onto the cartridge was set to 30 mL/min. This resulted in each extraction taking approximately 1.3 hours to process a 1 liter sample. This is a 48% improvement in time over the suggested manual loading rate of 8.3 mL/min. The inline drying and concentration process took approximately 40 minutes. Most target compounds resulted in a percent relative standard deviation (% RSD) of <10%, with only 2 being higher than 10%. All compounds fell within the method criteria for both the average and the RSD regardless of the faster flow rate.

Conclusions

Horizon Technology's SmartPrep Automated Cartridge Extractor and DryVap Drying and Concentration systems were used to extract and concentrate Method 525.2 water samples. Not only was this instrumentation able to pass all the required criteria for an Initial Demonstration of Laboratory Accuracy and Precision, but it was able to save 48% of the total time over the suggested manual loading rate. The improvements made to the extraction method here allow more samples to be processed increased the overall productivity of a laboratory.

Figure 1: LFB Example Chromatogram

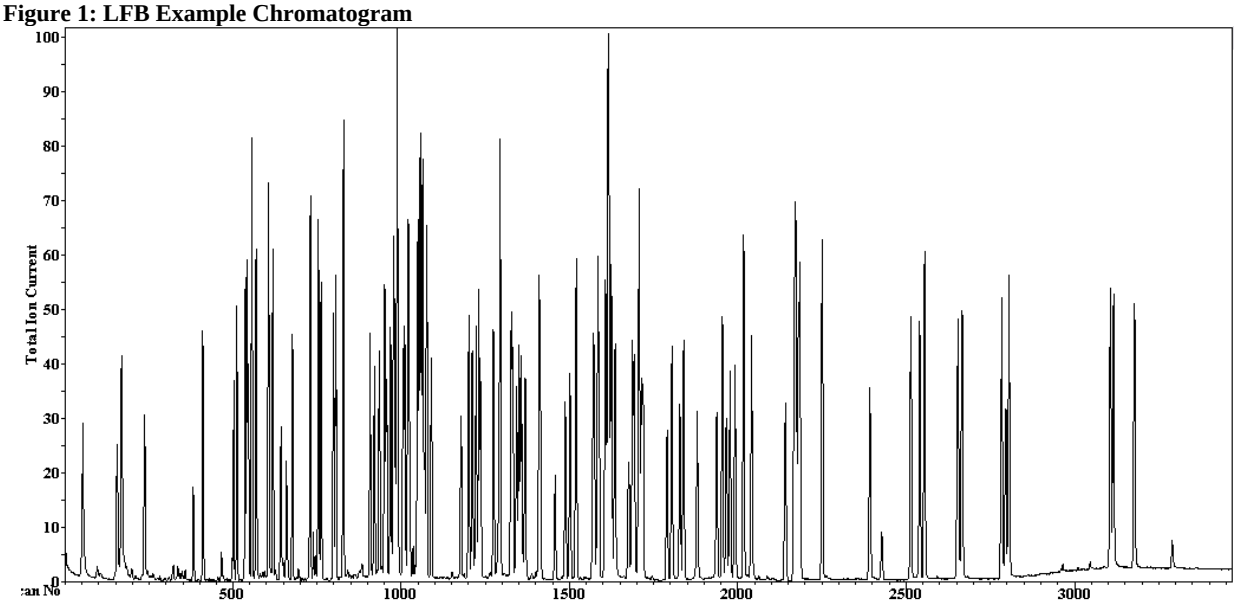

Table 3: EPA 525.2 Recovery Data

		Blank	LFB 1	LFB 2	LFB 3	LFB 4	Avg	RSD
		(ng/uL)	(%)	(%)	(%)	(%)	(%)	(%)
Isophorone		0.03	107.8	103.8	105.6	101.4	104.7	2.6
2-Nitro-m-xylene	S	4.95	101.2	101.4	100.2	96.4	99.8	2.3
Naphthalene		0.00	106.8	105.8	107.2	102.2	105.5	2.2
Dichlorvos		0.00	112.4	110.2	113.2	109.4	111.3	1.6
Hexachlorocyclopentadiene		0.00	86.8	85.8	88.8	85.8	86.8	1.6
EPTC		0.04	110.6	109.2	111.4	107.2	109.6	1.7
Mevinphos		0.00	116.6	108.2	105.2	107.4	109.4	4.6
Butylate		0.00	113.2	111.8	113.0	110.2	112.1	1.2
Vernolate		0.00	114.6	113.4	114.8	111.2	113.5	1.5
Dimethyl phthalate		0.00	120.6	118.6	120.4	116.8	119.1	1.5
Pebulate		0.02	115.2	113.6	116.2	112.2	114.3	1.5
Etridiazole		0.00	116.4	117.8	118.4	113.0	116.4	2.1
2,6-Dinitrotoluene		0.00	92.2	116.4	89.6	81.2	94.9	15.9
Acenaphthylene		0.03	110.6	108.6	110.2	107.2	109.2	1.4
Chloroneb		0.04	121.8	123.2	122.4	118.6	121.5	1.7
Tebuthiuron		0.00	114.4	113.6	116.2	114.6	114.7	0.9
2,4-Dinitrotoluene		0.00	93.6	120.0	91.6	82.6	97.0	16.6
Molinate		0.00	116.6	115.4	115.4	113.0	115.1	1.3
Diethyl phthalate		0.03	122.8	120.2	121.2	118.2	120.6	1.6
Fluorene		0.01	112.0	113.2	113.8	110.8	112.5	1.2
Propachlor		0.00	120.6	119.4	118.6	115.8	118.6	1.7
Ethoprop		0.00	118.6	116.8	118.2	116.0	117.4	1.0
Cycloate		0.04	118.8	116.6	117.4	113.2	116.5	2.0
Chlorpropham		0.00	119.2	118.0	120.0	117.4	118.7	1.0
Trifluralin		0.00	117.2	115.2	118.6	116.6	116.9	1.2
a-BHC		0.03	113.8	110.0	114.4	110.4	112.2	2.0
Atraton		0.00	103.8	103.2	100.8	92.6	100.1	5.2
Hexachlorobenzene		0.00	105.0	104.6	107.4	105.2	105.6	1.2
Prometon		0.00	113.6	109.0	112.0	110.8	111.4	1.7
Lindane (g-BHC)		0.00	116.8	115.2	115.8	113.4	115.3	1.2
Simazine		0.00	114.6	111.2	113.2	111.2	112.6	1.5
Atrazine		0.00	115.0	111.0	113.8	110.8	112.7	1.8
Propazine		0.00	117.2	112.8	115.0	113.0	114.5	1.8
b-BHC		0.00	116.2	112.2	114.2	111.2	113.5	2.0
Pentachlorophenol		0.01	89.0	88.6	90.0	88.2	88.9	0.9
Terbufos		0.00	111.6	111.0	112.2	108.4	110.8	1.5
Pronamide		0.00	114.6	113.8	114.2	111.2	113.5	1.4
Diazinon		0.00	88.4	93.4	91.4	86.2	89.9	3.5
d-BHC		0.00	114.6	111.0	114.0	110.6	112.6	1.8
Phenanthrene		0.00	111.6	110.6	113.0	110.4	111.4	1.1
Disulfoton		0.00	120.4	108.6	120.6	98.0	111.9	9.7
Methyl paraoxon		0.00	115.6	114.6	116.8	116.0	115.8	0.8
Anthracene		0.01	109.4	107.0	110.8	108.4	108.9	1.5
Terbacil		0.00	115.6	113.8	115.6	112.6	114.4	1.3
Chlorothalonil		0.00	116.4	114.0	116.6	115.0	115.5	1.1
Metribuzin		0.00	110.4	109.6	108.4	102.0	107.6	3.6
Simetryn		0.00	111.8	110.6	109.2	103.8	108.9	3.2
Heptachlor		0.00	110.0	109.2	110.0	107.8	109.3	0.9
Ametryn		0.00	112.8	110.6	113.6	111.0	112.0	1.3
Alachlor		0.00	113.8	112.6	113.8	111.6	113.0	0.9
Prometryn		0.00	115.2	111.6	115.8	113.4	114.0	1.7
Terbutryn		0.00	114.0	111.0	114.2	112.8	113.0	1.3
Di-n-butyl phthalate		0.03	114.0	112.8	114.2	111.4	113.1	1.1
Bromacil		0.00	110.0	109.2	109.6	106.4	108.8	1.5
Cyanazine		0.00	114.2	112.4	114.6	112.2	113.4	1.1
Metolachlor		0.00	115.2	112.8	114.8	113.4	114.1	1.0

Table 3: EPA 525.2 Recovery Data (continued):

		Blank	LFB 1	LFB 2	LFB 3	LFB 4	Avg	RSD
		(ng/uL)	(%)	(%)	(%)	(%)	(%)	(%)
Chlorpyrifos		0.00	111.2	109.4	111.4	108.8	110.2	1.2
Aldrin		0.00	107.4	105.0	108.0	105.0	106.4	1.5
Triademefon		0.00	113.0	107.8	110.4	107.0	109.6	2.5
Dacthal		0.00	115.8	113.2	115.4	113.4	114.5	1.2
MGK-264-A		0.00	101.2	99.0	116.8	115.0	108.0	8.5
Diphenamid		0.00	112.2	109.6	112.0	109.0	110.7	1.5
MGK-264-B		0.00	113.0	108.8	112.6	110.2	111.2	1.8
Merphos		0.00	114.4	104.2	109.4	103.2	107.8	4.8
Heptachlor epoxide B		0.00	112.2	109.8	110.8	109.2	110.5	1.2
Heptachlor epoxide A		0.00	114.6	111.6	112.2	108.8	111.8	2.1
Fluoranthene		0.04	109.6	108.6	111.0	108.4	109.4	1.1
g-Chlordane		0.00	106.2	105.2	107.6	106.0	106.3	0.9
Stirofos		0.00	112.6	108.8	111.4	110.8	110.9	1.4
Disulfoton sulfone		0.00	114.4	112.4	114.0	113.6	113.6	0.8
Butaclor		0.00	112.4	109.8	110.4	109.8	110.6	1.1
a-Chlordane		0.00	106.0	105.4	104.6	106.0	105.5	0.6
Endosulfan I		0.00	107.6	108.4	109.0	106.6	107.9	1.0
Fenamiphos		0.00	104.4	100.8	104.8	104.8	103.7	1.9
Pyrene-d10	S	4.89	99.6	96.4	98.2	95.2	97.4	2.0
Pyrene		0.00	107.8	106.6	107.6	106.8	107.2	0.5
Napropamide		0.00	111.0	107.2	108.8	108.4	108.9	1.5
trans-Nonachlor		0.00	112.2	110.8	111.6	110.2	111.2	0.8
4,4'-DDE		0.00	106.4	105.0	107.2	104.8	105.9	1.1
Dieldrin		0.00	107.6	106.2	107.6	104.6	106.5	1.3
Tricyclazole		0.03	100.2	104.4	106.4	102.8	103.5	2.5
Carboxin		0.00	108.0	105.0	106.6	106.2	106.5	1.2
Endrin		0.00	106.2	107.4	105.8	105.2	106.2	0.9
Chlorobenzilate		0.00	110.8	107.6	108.6	108.6	108.9	1.2
Endosulfan II		0.00	107.6	108.4	109.0	106.6	107.9	1.0
4,4'-DDD		0.00	104.0	103.0	104.6	104.0	103.9	0.6
Endrin Aldehyde		0.00	106.8	104.6	104.2	107.2	105.7	1.4
Butyl benzyl phthalate		0.08	110.4	107.6	110.0	108.8	109.2	1.2
Norflurazon		0.00	110.8	107.2	110.8	110.4	109.8	1.6
4,4-DDT		0.00	104.0	103.0	104.6	104.0	103.9	0.6
Endosulfan Sulfate		0.00	108.8	108.0	109.0	107.6	108.4	0.6
Bis(2-ethylhexyl)adipate		0.01	107.6	104.8	108.2	107.4	107.0	1.4
Hexazinone		0.00	110.8	108.4	110.0	109.6	109.7	0.9
Triphenylphosphate	S	4.97	105.4	100.8	102.8	100.6	102.4	2.2
Endrin Ketone		0.00	111.6	111.4	110.6	111.0	111.2	0.4
Methoxychlor		0.00	107.4	105.8	100.8	104.4	104.6	2.7
Benz(a)anthracene		0.07	109.0	108.4	110.2	108.6	109.1	0.7
Chrysene		0.01	111.6	111.6	113.2	111.4	112.0	0.7
Bis(2-ethylhexyl)phthalate		0.07	111.6	108.4	113.4	112.2	111.4	1.9
Fenarimol		0.00	105.4	104.0	105.6	104.8	105.0	0.7
cis-Permethrin		0.00	108.6	105.6	109.2	108.4	108.0	1.5
trans-Permethrin		0.00	108.4	106.2	109.4	108.4	108.1	1.3
Di-n-octyl phthalate		0.07	111.6	108.4	113.4	112.2	111.4	1.9
Benzo(b)fluoranthene		0.01	114.2	114.0	117.0	114.2	114.9	1.3
Benzo(k)fluoranthene		0.01	113.0	112.6	116.2	113.8	113.9	1.4
Benzo(a)pyrene		0.00	111.8	110.6	115.6	112.8	112.7	1.9
Fluridone		0.00	115.6	109.6	116.4	115.6	114.3	2.8
Perylene-d12	S	5.05	109.2	106.2	110.4	104.4	107.6	2.6
Indeno(1,2,3-cd)pyrene		0.00	113.0	111.2	117.6	113.4	113.8	2.4
Dibenz(ah)anthracene		0.00	113.8	113.6	118.6	115.2	115.3	2.0
Benzo(ghi)perylene		0.00	114.6	113.4	120.2	115.0	115.8	2.6

Table 4: SmartPrep Extraction Program

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense	
1		EtOAc	5	10	10	5	No	
2		DCM	5	10	10	5	No	
3		MeOH	10	10	0	0	No	
4		Reagent Water	10	10	0	0	No	
5	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**	
		Yes	2	75	30	1	1000	
6	**N2 Purge Timer**	**Delay (min)**						
		10						
7	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		EtOAc	6	5	5	No		
8	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		12	1	6	30	5	10	5
9	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		EtOAc	5	20				
10	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**	
		Mixing Chamber	5	5	1	10	5	
11	**Sample Bottle Rinse**	**Reagent**	**Volume (mL)**	**Vent Volume (mL)**	**Spray Time (s)**	**Liquid Sense**		
		DCM	6	5	5	No		
12	**Sample Bottle Elute**	**Volume (mL, to Mixer)**	**Destination (Tube)**	**Volume (mL, to elute)**	**Sip Rate (mL/min)**	**Delivery Rate (mL/min**	**Soak (s)**	**N2 Purge (s)**
		12	1	6	30	5	10	5
13	**Add to Mixing Chamber**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**				
		DCM	5	20				
14	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**	
		Mixing Chamber	5	20	1	10	5	

EPA Method 548.1: Determination of Endothall by Automated Solid Phase Extraction (SPE)

Susie Petitti, Horizon Technology, Inc., Salem, NH, USA

Introduction

Endothall is an organic solid of white odorless crystals used as a defoliant for a wide range of crops and as a herbicide for both terrestrial and aquatic weeds. The EPA has found that short-term exposure to levels above 0.1 ppm (MCL = Maximum Contaminant Level) can potentially cause depressed breathing and heart rate. Long-term exposure above the MCL has the potential to cause an increase in size of some internal organs, particularly the stomach and intestine.

EPA Method 548.1 details the procedure for the determination of endothall in drinking water by ion-exchange solid phase extraction (SPE), acidic methanol methylation, and gas chromatography / mass spectrometry. This note presents data from the State of Idaho Bureau of Labs for the initial demonstration of capability using the Horizon Technology SPE-DEX® 4790 Automated Extractor System. Automated SPE provides the benefits of high sample throughput, low solvent consumption, safe working conditions, and consistent and reliable data.

Instrumentation

- Horizon Technology SPE-DEX® 4790 Extraction System
- SPE Disk: Empore™ Anion-SR, 47 mm
- GC/MS unit

Method Summary

1) IPR samples: Four replicates prepared using 100 mL of 18.2 ohm DI water at neutral pH, spiked at 25 µg/L.
2) MDL samples: Seven replicates prepared using 100 mL of 18.2 ohm DI water at neutral pH, spiked at 4 µg/L.
3) SPE-DEX® 4790 Extractors prepared for extraction by running the purge method in Table 1 three times to flush the system.
4) Two Empore™ Anion-SR disks stacked in the Disk Holder Assembly and loaded unto the extractors.
5) Sample bottles are loaded onto the extractor bottle holders and the collection vessels attached to the extractors.
6) IPR and MDL samples extracted using Horizon Technology's SPE-DEX® 4790 Automated Extractor System using the method in Table 2.
7) At the end of the extraction run, the derivatization, partition, and analysis is performed on solvent extracts according to EPA Method 548.1 section 11.4.
8) The top disk in the disk holder is discarded. The bottom disk is saved for the next run. All disk holders are rinsed with DI water.
9) Purge the extractors twice between sample runs. Rinse the bottle holders and sample inlet areas with DI water using a squeeze bottle.

Horizon Technology SPE-DEX® 4790 and Envision® Controller

10) For the next run, placed a new disk on the support screen in the Disk Holder Cup. Placed the bottom disk from the previous run on top of the new disk.
11) Analyze the samples using the GC method in Table 3.

Table 1: Purge Method

Step	Solvent	Soak Time	Dry Time
Wash 1	Methanol	0 s	10 s
Wash 2	Methanol	0 s	10 s

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	$MeCl_2$	1:00 min	30 s
Prewet 2	MeOH	2:00 min	30 s
Prewet 3	1N HCl/MeOH	0:30 min	6 s
Prewet 4	Reagent Water	30 min	6 s
Prewet 5	1N NaOH	1:30 min	6 s
Prewet 6	1N NaOH	0:30 min	6 s
Prewet 7	Reagent Water	1:00 min	6 s
Prewet 8	Reagent Water	0:30 min	0 s
Process Sample			
Wash 1	MeOH	0:30 min	1:00 min
Wash 2	MeOH	0:30 min	1:00 min
Air Dry 3:00 min			
Rinse 1	10% H_2SO_4/MeOH	2:00 min	0:30 min
Rinse 2	10% H_2SO_4/MeOH	2:00 min	0:30 min
Rinse 3	10% H_2SO_4/MeOH	2:00 min	0:30 min
Rinse 4	$MeCl_2$	1:00 min	1:00 min

Table 3: GC/MS Conditions

Mode	Splitless
Carrier Gas	Helium
Linear Velocity	45 cm/min (100.1 kPa)
Pulsed	300 kPa for 1 min
Inj Temp	200 °C
Inj Amount	2 uL
MS Scan	45-450 at 0.27 s interval
Interface Temp	290 °C
Ion Source	290 °C

Temperature Program			
Ramp	**Temp (°C)**	**Rate (°C/min)**	**Hold (min)**
1	70	0	3:00
2	290	20	4:00

Results

The Initial Precision and Recovery (IPR) samples were spiked with 25 ug/L and the recovery data is shown in Table 4. The average recovery for the IPR data is 87.7% with an RSD value of 8.76. Both these values are within the acceptable range as per the EPA Method.

Table 4: Initial Precision & Recovery (IPR)

	Conc. (ug/L)	**Rec. (%)**
IPR 1	21.46	85.8
IPR 2	20.42	81.7
IPR 3	21.08	84.3
IPR 4	24.73	98.9
Average	21.92	87.7
RSD	8.76	7.67

The Method Detection Limit (MDL) data is shown in Table 5. They were spiked with 4 ug/L of solution and were calculated by multiplying the standard deviation from the replicate study by the student t-value of 3.143.

Table 5: Method Detection Limit (MDL)

Analyte	**Rec. (ug/L)**
MDL 1	3.89
MDL 2	4.41
MDL 3	3.51
MDL 4	3.49
MDL 5	3.69
MDL 6	4.25
MDL 7	3.8
STD DEV	0.353
MDL	1.109
RL	2.5

It is important to purge on the extractors between sample extractions. The purge uses methanol washes to remove any traces of acid left behind from the previous run. The sulfate ion is a strong competing ion that will bind to the disk and interfere with the extraction of endothall. In addition to purging, the bottle holder and disk holders should be rinsed with DI water to remove residual acid and aid recovery.

Conclusions

Results presented in this paper from an independent laboratory indicate that automated SPE using Horizon Technology's SPE-DEX® 4790 extractors provide accurate and precise results for the determination of endothall in drinking water following EPA Method 548.1. Automated SPE uses less volume of solvents, eliminates emulsions, reduces exposure to solvents, improves recoveries and consistency of results, increases productivity, and reduces labour costs.

Acknowledgements

Horizon Technology would like to thanks Renea Anglin and the State of Idaho Bureau of Labs in Boise, ID for their help.

EPA Method 549.2: Diquat and Paraquat

Horizon Technology, Inc., Salem, NH

Introduction

Method 549.2 is used to determine diquat and paraquat in drinking water and drinking water sources. The analytes are extracted from the water using a SPE-DEX® 4790 47 mm C8 disk. The disk is extracted with acidic aqueous solvent "Disk Eluting Solvent" (DES) and analyzed by HPLC with UV detection.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extraction System
- C8 disk (47 mm)
- Conditioning solvents
  - CS A: cetyltrimethylammonium bromide
  - CS B: 1-hexanesulfonic acid
- Disk Eluting Solvent (DES)
- HPLC with UV detector

Method Summary

1. Prepare the sample according to EPA Method 549.2.
2. Run the purge method given in Table 1.
3. Extract the sample using the method in Table 2.
4. Run the extract on an HPLC with UV detector.

Table 1: Purge method

Step	Solvent	Soak Time	Dry Time
Wash 1	Methanol	0 sec	15 sec
Wash 2	Methanol	0 sec	15 sec

The Horizon Technology SPE-DEX® 4790 and Envision® Controller

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Methanol	1:00 min	2 sec
Prewet 2	Reagent Water	10 sec	2 sec
Prewet 3	Reagent Water	10 sec	2 sec
Prewet 4	CS A	1:00 min	2 sec
Prewet 5	Reagent Water	10 sec	2 sec
Prewet 6	Reagent Water	30 sec	2 sec
Prewet 7	CS B	30 sec	2 sec
Process Sample			
Air Dry 2:00 min			
Rinse 1	Methanol	1:00 min	10 sec
Rinse 2	DES	1:00 min	30sec
Rinse 3	DES	1:00 min	1:00 min

The Extraction of Diquat and Paraquat for EPA Method 549.2 Using the SmartPrep Automated Cartridge Extractor

Alicia Cannon and Brian LaBreque, Horizon Technology, Inc., Salem, NH

Introduction

Diquat and paraquat are some of the most widely used and available herbicides in the world. They are fast-acting, non-selective quaternary amines used mainly in the agricultural industries to control the penetration of invasive plants and increase crop yield.

However, both diquat and paraquat have been proven to be toxic to humans upon exposure. This toxicity and wide availability has led to instances where individuals have issued fatal doses to humans. In turn, this has led to strict guidelines worldwide involving the use of diquat and paraquat in the agricultural community.

This Application Note will outline the process used to extract diquat and paraquat from water samples using the SmartPrep Automated Solid Phase Cartridge Extractor. It will specifically focus on the extraction of the samples needed for an initial demonstration of capability (IDC) according to the procedure outlined by the US Environmental Protection Agency in method 549.2. It will also illustrate that, although method 549.2 recommends that all glassware be silanized, excellent recoveries can be achieved even if the glass syringe barrel on the SmartPrep was not.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 20 mL Tray
- Phenomenex
  - Strata C8 cartridges, 500 mg, 6 mL
  - Spherisorb 3 µm C8 80 Å, 100 x 4.6 mm
- Agilent 1100 Series LC with attached DAD

Method Summary

Preparation of Solvents

1. Conditioning Solution A: Dissolve 0.500 g of cetyl trimethyl ammonium bromide and 5 mL of concentrated ammonium hydroxide in 500 mL of deionized water and dilute to 1000 mL in a volumetric flask.[1] Please note that this solvent may crystallize and should be replaced often to prevent this phenomenon.
2. Conditioning Solution B: Dissolve 10.0 g of 1-hexanesulfonic acid, sodium salt and 10 mL of concentrated ammonium hydroxide in 250 mL of deionized water and dilute to 500 mL in a volumetric flask.[1]
3. Elution Solvent: Add 13.5 mL of orthophosphoric acid and 10.3 mL of diethylamine to 500 mL of deionized water and bring to a final volume of 1000 mL in a volumetric flask.[1]

The Horizon Technology SmartPrep Automated Cartridge Extractor.

4. Ion-Pair Concentrate: Dissolve 3.75 g of 1-hexanesulfonic acid into 15 mL of Elution Solvent and bring to a final volume of 25 mL.[1]
5. Mobile Phase: Add 13.5 mL orthophosphoric acid, 10.3 mL of diethylamine, and 3.0 g of 1-hexanesulfonic acid, sodium salt to 500 mL of deionized water. Bring to a final volume of 1 liter.[1]

Sample Preparation

1. Prepare five aliquots of reagent water measuring 250 mL each (containers were HDPE).
2. Prepare one aliquot as a laboratory fortified blank (LRB).
3. The remaining four aliquots prepare as laboratory fortified blanks (LFBs). Prepare each aliquot by adding 5 µL of a stock standard (at 1000 mg/mL) for a sample concentration of 100 µg/L.
4. Verify the pH and, if needed, adjust the pH to between 7.0 and 9.0 using 10% w/v NaOH or 10% v/v HCl.

SmartPrep Automated Extraction

1. Ensure that all reagents are filled.
2. Ensure that all waste containers are empty.
3. Load a Cleaning Cartridge onto position 21 of the carousel.
4. Load five C8 cartridges onto the carousel into positions 1 through 5.
5. Load five 20 mL HDPE Scintillation vials without their caps onto the tray in positions corresponding to those of the carousel.
6. Place the samples onto the Sample Rack and ensure that a Sip Tube is in place in the lower corner of the sample container.
7. Run the Method given in Table 3 below and collect approximately 4.5 mL of extract at 45 minutes per sample.

8. Add 100 µL of an Ion-Pair Concentrate
9. Bring the sample to a final volume of 5 mL using the Elution Solvent.
10. Analyze the sample by HPLC using the conditions given in Table 1 below.

Table 1: Analysis Conditions

Column Flow: 1.0 mL/min
Solvent: 100% 549.2 Mobile Phase (isocratic)
Spectra Start: 210 nm
Spectra End: 370 nm
Spectra Step: 1 nm
Injection Volume: 20 µL

Results

The minimum quality control requirements set forth in EPA Method 549.2 start with the production of an IDC. To be considered in control, at least four laboratory fortified blanks (LFBs) must be prepared at a concentration of 100 ug/L each. The recoveries and relative standard deviation (RSD) must be within ± 30% and less than 30% respectively for the study.

The results of the extractions performed for this study are given below in Table 2 and a sample spectrum is shown in Figure 1. Both diquat and paraquat were recovered at concentrations higher than 90% and the RSDs were less than 5%. Total extraction times per sample were 2 hours and 20 minutes on average.

Conclusions

The resulting data from the analysis performed proves that the SmartPrep Automated Extractor is an excellent choice for those wishing to extract diquat and paraquat from water matrices regardless of the non-silanized syringe barrel. By using automated extraction techniques, a laboratory can decrease the labor and materials associated with each sample saving both time and money.

References

1. Munch, J.W. and Bashe W.J., **"**Method 549.2-Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection", National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, 45268,1997.

Table 2: Method 549.2 IDC Results

	LRB (ppm)	LFB (%)	LFB (%)	LFB (%)	LFB (%)	Average (%)	RSD (%)
Diaquat	0.01	98.69	92.21	92.30	97.58	95.19	3.60
Paraquat	0.00	95.50	90.96	91.53	92.90	92.72	2.18

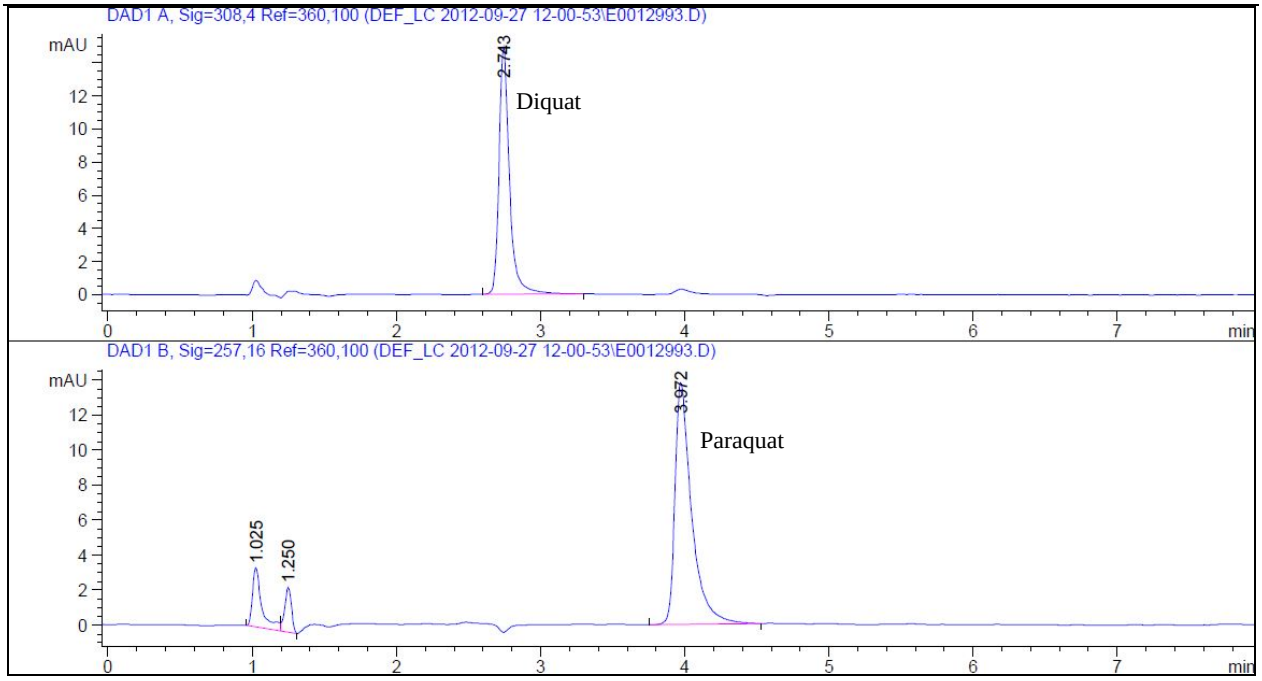

Figure 1: LFB Example Spectrum

Table 3: SmartPrep Extraction Method

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense
1		Reagent Water	5	10	10	0	Yes
2		Methanol	5	10	10	0	Yes
3		Reagent Water	5	10	10	0	Yes
4		Condition Solution A	5	10	10	0	Yes
5		Reagent Water	5	10	10	0	Yes
6		Methanol	10	10	10	0	Yes
7		Reagent Water	5	10	10	0	Yes
8		Condition Solution B	20	10	10	0	Yes
9	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**
		Yes	1	75	3	100	250
10	**Wash Cartridge**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**	**Liquid Sense**
		Methanol	5	10	10	0	Yes
11	**N2 Purge Timer**	**Delay (min)**					
		1					
12	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**
		Eluting Solvent	4.5	1.5	1	10	10

Increasing The Efficiency of EPA Method 549.2 Using the SmartPrep Automated Cartridge Extractor

Alicia Cannon and Brian LaBreque, Horizon Technology, Inc., Salem, NH

Introduction

Within EPA Method 549.2, the suggested rate to load a sample onto a solid phase cartridge is given as 3 to 6 mL/min (Section 11.2.5). However, as advances in the chemistry of the sorbents continue to be made, it may become necessary to re-evaluate this speed. This Application Note will outline the process used to extract diquat and paraquat from water samples using a faster loading rate than given by the EPA in method 549.2. It will specifically focus on the extraction of the samples needed for an initial demonstration of capability (IDC) according to the procedure outlined in the 549.2 method. It will also illustrate that, although method 549.2 recommends that all glassware be silanized, excellent recoveries can be achieved even if the glass syringe barrel on the SmartPrep was not. Lastly, even though the sample load rate is increased by more than a factor of 8 and the syringe barrel was not silanized, the high recoveries required will be maintained.

The Horizon Technology SmartPrep Automated Cartridge Extractor.

Instrumentation

- Horizon Technology
  - SmartPrep® Automated Cartridge Extractor
  - 20 mL Tray
- Phenomenex
  - Strata C8 cartridges, 500 mg, 6 mL
  - Spherisorb 3 µm C8 80 Å, 100 x 4.6 mm
- Agilent 1100 Series LC with attached DAD

Method Summary

Preparation of Solvents

1. Conditioning Solution A: Dissolve 0.500 g of cetyl trimethyl ammonium bromide and 5 mL of concentrated ammonium hydroxide in 500 mL of deionized water and dilute to 1000 mL in a volumetric flask.[1] Please note that this solvent may crystallize and should be replaced often to prevent this phenomenon.
2. Conditioning Solution B: Dissolve 10.0 g of 1-hexanesulfonic acid, sodium salt and 10 mL of concentrated ammonium hydroxide in 250 mL of deionized water and dilute to 500 mL in a volumetric flask.[1]
3. Elution Solvent: Add 13.5 mL of orthophosphoric acid and 10.3 mL of diethylamine to 500 mL of deionized water and bring to a final volume of 1000 mL in a volumetric flask.[1]
4. Ion-Pair Concentrate: Dissolve 3.75 g of 1-hexanesulfonic acid into 15 mL of Elution Solvent and bring to a final volume of 25 mL.[1]
5. Mobile Phase: Add 13.5 mL orthophosphoric acid, 10.3 mL of diethylamine, and 3.0 g of 1-hexanesulfonic acid, sodium salt to 500 mL of deionized water. Bring to a final volume of 1 liter.[1]

Sample Preparation

1. Prepare five aliquots of reagent water measuring 250 mL each (containers were HDPE).
2. Prepare one aliquot as a laboratory fortified blank (LRB).
3. The remaining four aliquots prepare as laboratory fortified blanks (LFBs). Prepare each aliquot by adding 5 µL of a stock standard (at 1000 mg/mL) for a sample concentration of 100 µg/L.
4. Verify the pH and, if needed, adjust the pH to between 7.0 and 9.0 using 10% w/v NaOH or 10% v/v HCl.

SmartPrep Automated Extraction

1. Ensure that all reagents are filled.
2. Ensure that all waste containers are empty.
3. Load a Cleaning Cartridge onto position 21 of the carousel.
4. Load five C8 cartridges onto the carousel into positions 1 through 5.
5. Load five 20 mL HDPE Scintillation vials without their caps onto the tray in positions corresponding to those of the carousel.
6. Place the samples onto the Sample Rack and ensure that a Sip Tube is in place in the lower corner of the sample container.
7. Run the Method given in Table 3 below and collect approximately 4.5 mL of extract at 45 minutes per sample.
8. Add 100 µL of an Ion-Pair Concentrate
9. Bring the sample to a final volume of 5 mL using the Elution Solvent.
10. Analyze the sample by HPLC using the conditions given in Table 1 below.

Table 1: Analysis Conditions

Column Flow: 1.0 mL/min
Solvent: 100% 549.2 Mobile Phase (isocratic)
Spectra Start: 210 nm
Spectra End: 370 nm
Spectra Step: 1 nm
Injection Volume: 20 µL

11.

Results

The results of the extractions performed for this study are given below in Table 2 and a sample spectrum is shown in Figure 1. The data was generated using a loading rate of 25 mL/min (compared to the specified rate of 3 mL/min). The average run time was average run time was 36 min. When this is compared to the EPA Method 549.2 specified load rate of 3 mL/min, the time savings were approximately 75%. Both diquat and paraquat were recovered at concentrations higher than 90% and the RSDs were less than 10%.

Conclusions

The resulting data from the analysis performed proves that, even though the sample load rate was increased by more than a factor of 8, the recoveries were still well within the method criteria. It proves that the SmartPrep Automated Extractor is an excellent choice for those wishing to push the limits for the extraction diquat and paraquat from water matrices.

References

1. Munch, J.W. and Bashe W.J., **"**Method 549.2-Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection", National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, 45268,1997.

Table 2: Method 549.2 IDC Results

	LFB (%)	LFB (%)	LFB (%)	LFB (%)	Average (%)	RSD (%)
Diaquat	94.82	96.60	93.00	86.00	92.61	5.01
Paraquat	90.18	94.91	92.00	83.00	90.02	5.63

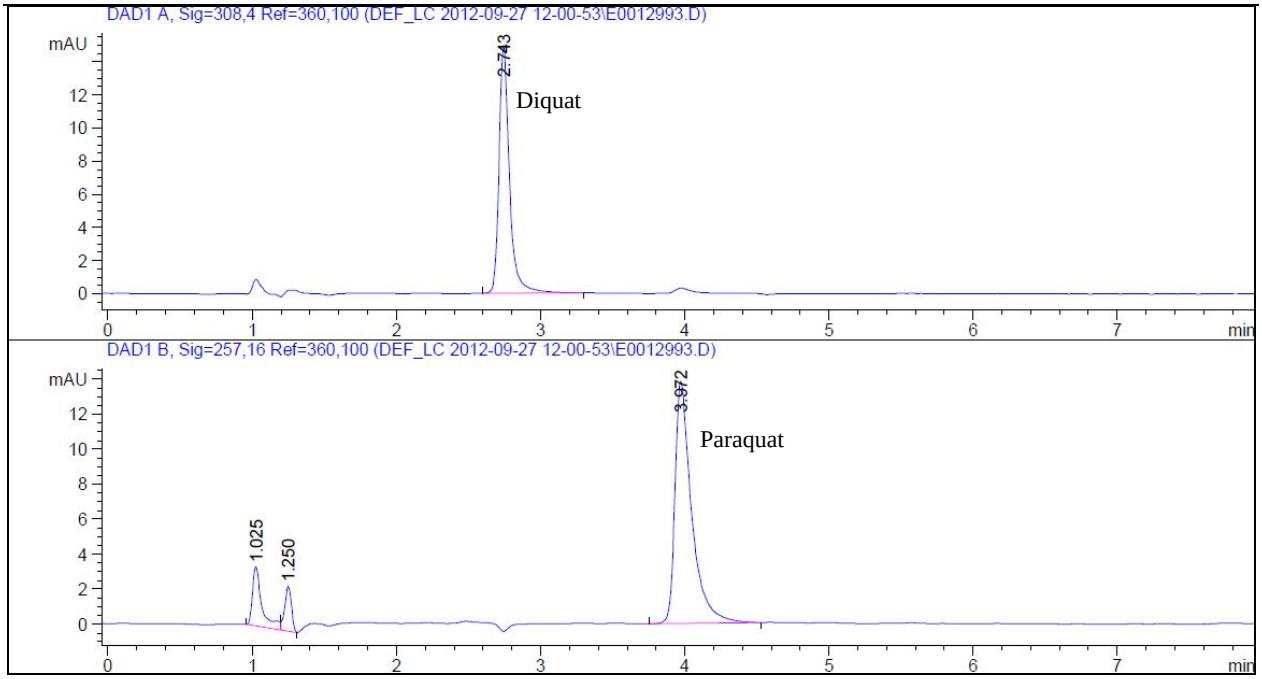

Figure 1: LFB Example Spectrum

Table 3: SmartPrep Extraction Method

Step	Conditioning	Reagent	Volume (mL)	Rate (mL/min)	Soak (s)	N2 Purge (s)	Liquid Sense
1		Reagent Water	5	10	10	0	Yes
2		Methanol	5	10	10	0	Yes
3		Reagent Water	5	10	10	0	Yes
4		Condition Solution A	5	10	10	0	Yes
5		Reagent Water	5	10	10	0	Yes
6		Methanol	10	10	10	0	Yes
7		Reagent Water	5	10	10	0	Yes
8		Condition Solution B	20	10	10	0	Yes
9	**Load Sample**	**Load Until Empty (mL)**	**Syringe Fill Pause (s)**	**Sample Sip Rate (mL/min)**	**Sample Deliver Rate (mL/min)**	**Minimum Volume (mL)**	**Expected Volume (mL)**
		Yes	1	75	25	100	250
10	**Wash Cartridge**	**Reagent**	**Volume (mL)**	**Delivery Rate (mL/min)**	**Soak (s)**	**N2 Purge (s)**	**Liquid Sense**
		Methanol	5	10	10	0	Yes
11	**N2 Purge Timer**	**Delay (min)**					
		1					
12	**Elute Cartridge**	**Reagent**	**Volume (mL)**	**Rate (mL/min)**	**Destination (Tube)**	**Soak (s)**	**Purge (s)**
		Eluting Solvent	4.5	1.5	1	10	10

EPA Method 552.1: Haloacetic Acid and Dalapon Using the SPE-DEX® 4790 Automated Extraction System

Susan Petitti, Horizon Technology, Inc., Salem, NH

Introduction

EPA Method 552.1 is an ion exchange procedure used for determining haloacetic acids and dalapon in drinking water and drinking water sources. Since this is an ion exchange procedure, other naturally occurring ions in water sources can potentially interfere. Sulfate and thiosulfate are effective counter ions that compete with the analytes for the ion exchange sites on the solid phase extraction (SPE) disk. Sulfate ions in concentrations greater than 200 mg/L will effectively displace the haloaceteic acids from the SPE disk during the extraction process results in reduced recoveries. Reduced recoveries may also be observed in very high ionic strength waters (i.e. 400 mg/L NaCl). Therefore, the success of the extraction depends on the sample being relatively free of ionic species.

This purpose of this application note is to present data demonstrating the capability of the Horizon Technology SPE-DEX® 4790 Automated Extraction System to perform the sample extraction required for this method.

The SPE-DEX® 4790 Automated Extractor was designed to allow fully automated extraction of a wide range of samples. When used, the system reduces the amount of solvent used, reduces human exposure to solvents, eliminates the formation of emulsions, and improves recoveries and consistency of results. The combination of these effects allows for a reduction in both turn-around-times and production costs for a laboratory.

Instrumentation

- Horizon Technology SPE-DEX® 4790 Automated Extraction System
- Heating Block
- Empore™ 47 mm Anion Exchange Disk
- HP 5890 GC with ECD
- HP 7673A Autosampler
- AccuStandard Solutions: M-552.1A, M-552.1-SS

Method Summary

I. Calibration Standards

1. Six different calibration levels for each analyte were prepared from the AccuStandard standard solutions.
2) Extract all levels using SPE-DEX® 4790 Extraction System and the method in Table 1.
3) After extraction, the solvent partition step is performed on all standards.
4) Run calibration samples on GC.

II. Initial Demonstration of Capability (IDC)

1) Five replicate volumes at 100 mL of DI water were acidified to a pH of 5 using HCl.
2) 200 uL of the primary dilution solution were added to each bottle to obtain Level 2 analyte concentrations.
3) Spiked DI water samples were extracted with the Horizon Technology SPE-DEX® 4790 Automated Extractor Systems and the method in Table 1.
4) After extraction, perform solvent partition.
5) Analyze on GC.

Horizon Technology SPE-DEX® 4790 and Envision® Controller

III. Method Detection Limit (MDL)

1) Nine replicate volumes at 100 mL of DI water acidified to pH 5 with HCl.
2) 100 uL of the primary dilution solution were added to each bottle to obtain Level 1 analyte concentrations.
3) The samples were then extracted with the Horizon Technology SPE-DEX® 4790 Automated Extractor Systems and the method in Table 1.
4) After extraction, perform solvent partition.
5) Analyze on GC.

Table 1: Extraction Method.

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	3:00 min	30 sec
Prewet 2	HCl / Methanol	1:30 min	1 sec
Prewet 3	Reagent Water	30 sec	1 sec
Prewet 4	NaOH / Reagent Water	1:30 min	1 sec
Prewet 5	Reagent Water	30 sec	2 sec
Prewet 6	Reagent Water	30 sec	0 sec
Process Sample			
Wash 1	Methanol	30 sec	1:00 min
Wash 2	Methanol	30 sec	1:00 min
Air Dry 2:00 min			
Rinse 1	H_2SO_4 / Methanol	4:00 min	2:00 min
Rinse 2	H_2SO_4 / Methanol	2:00 min	2:00 min

Results

The pH of the DI water was adjusted using HCl rather than H_2SO_4, to avoid the introduction of sulfate ions. It is also recommended to use a 1% solution of ammonium chloride, NH_4Cl (1 g / 100 mL), rather than granular ammonium chloride because the chloride ions will compete with the active sites of the SPE disk and reduce the recoveries of the haloacetic acids. The Horizon Technology SPE-DEX® 4790 Automated Extraction System was also flushed with DI water between samples to remove any traces of acid left behind from the previous extraction run.

Each laboratory is responsible for operating a formal quality assurance program. For Method 552.1, the minimum requirements include an initial demonstration of laboratory capability (IDC), method detection limit (MDL) study, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrices.

The capability of the Horizon Technology SPE-DEX® 4790 Automated Extraction Systems for the extraction of haloacetic acids and dalapon in drinking water was demonstrated by extracting the calibration standards, the IDC, the MDL study, and tracking the surrogate and internal standard recoveries.

The results of the IDC are presented in Table 2 and clearly show that the recoveries are within the specified tolerances dictated by method 552.1.

The recoveries for an MDL study conducted using the SPE-DEX® 4790 are presented in Table 3. The MDL was calculated using a Student t-value of 2.896. This is the t-value based on a 99 % confidence interval using the appropriate degrees of freedom.

The last study done was to monitor the peak area for the internal standard used, namely 1,2,3-trichloropropane. The recorded values are listed in Table 4.

Conclusions

The data collected and presented in this study meet the EPA criteria for Method 552.1 and demonstrate the capability of the Horizon Technology SPE-DEX® 4790 Automated Extractor Systems to perform the extraction process.

Automated SPE reduces solvents by eliminating emulsions, reduces worker exposure to solvents, improves recoveries and consistency of results, and increases a worker's productivity. The combination of these effects allows a laboratory to decrease the turn-around-times and overhead associated with a sample run thereby saving them money.

Acknowledgements

Horizon Technology would like to thank Joe Poland and the Connecticut Department of Health in Hartford for their help.

Table 2: IDC Recoveries

	Monochloroacetic Acid (5.94 ug/L)		Monobromoacetic Acid (4.00 ug/L)		Dalapon (4.00 ug/L)		Dichloroacetic Acid (5.95 ug/L)		2-Bromopropionic Acid* (8.22 ug/L)		Trichloroacetic Acid (1.98 ug/L)		Bromochloroacetic Acid (3.97 ug/L)		Dibromoacetic Acid (1.97 ug/L)	
	ppb	**%**	**ppb**	**%**	**ppb**	**%**	**ppb**	**%**	**ppb**	**%**	**ppb**	**%**	**ppb**	**%**	**ppb**	**%**
IDC 1	4.63	78	3.38	85	3.65	91	4.99	84	7.16	87	1.73	87	3.18	80	1.59	81
IDC 2	4.86	82	3.58	90	3.97	99	5.48	92	7.45	91	1.88	95	3.44	87	1.69	86
IDC 3	5.33	90	3.91	98	4.33	108	5.89	99	8.21	100	1.96	99	3.34	84	1.62	82
IDC 4	5.23	88	3.99	100	4.13	103	5.68	95	7.78	95	1.86	94	2.76	70	1.43	73
IDC 5	5.42	91	3.96	99	4.1	103	5.84	98	8.07	98	1.83	92	2.76	70	1.43	73
Mean		86		94		101		94		94		93		78		79
Std Dev		5.6		6.6		6.3		6.0		5.3		4.4		7.9		5.8

*Includes Level 2 standard of 1.97 ppb plus the surrogate's 6.25 ppb

Table 3: MDL Recoveries

	Monochloroacetic Acid (2.97 ug/L)	Monobromoacetic Acid (2.00 ug/L)	Dalapon (2.00 ug/L)	Dichloroacetic Acid (2.98 ug/L)	2-Bromopropionic Acid (0.984 ug/L)	Trichloroacetic Acid (0.990 ug/L)	Bromochloroacetic Acid (1.99 ug/L)	Dibromoacetic Acid (0.985 ug/L)
MDL 1	2.84	2.01	1.93	2.91	0.95	1.05	2.30	1.36
MDL 2	1.91	1.53	1.25	1.94	0.66	0.83	1.88	1.21
MDL 3	2.81	2.02	1.76	2.96	0.94	1.02	2.36	1.37
MDL 4	2.59	1.87	1.73	2.80	0.89	1.01	2.34	1.39
MDL 5	2.41	1.74	1.26	2.56	0.79	0.84	2.21	1.34
MDL 6	2.70	2.16	2.10	2.93	0.99	1.10	2.15	1.25
MDL 7	2.62	1.91	1.79	2.69	0.91	1.05	2.24	1.29
MDL 8	2.05	1.73	1.68	2.32	0.73	0.98	2.19	1.28
MDL 9	2.34	1.83	1.59	2.30	0.81	0.92	1.70	1.04
Mean	2.47	1.87	1.68	2.60	0.85	0.98	2.15	1.28
STDEV	0.33	0.19	0.28	0.35	0.11	0.10	0.22	0.11
MDL	0.95	0.54	0.81	1.02	0.32	0.28	0.64	0.31

Table 4: Internal Standard Peak Area Monitoring Results

Run Designation	1,2,3-Trichloropropane Peak Area
Callibration Standards	
Level 1	137,081
Level 2	127,034
Level 3	127,374
Level 4	124,712
Level 5	127,111
Level 6	126,997
Initial Demonstration of Capability	
IDC1	138,606
IDC2	133,971
IDC3	123,594
IDC4	119,016
IDC5	115,416
Method Detection Limit Study	
MDL1	122,805
MDL2	124,255
MDL3	121,991
MDL4	115,357
MDL5	126,295
MDL6	120,202
MDL7	134,567
MDL8	137,852
MDL9	137,188

Analysis of Pharmaceuticals in Water by Automated Solid Phase Extraction

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University of Colorado, Boulder, CO, USA

Introduction

The analytical challenge of measuring emerging contaminants in the environment has been a major research focus of scientists for the last 20 years. Water quality is a critical issue especially for sustainable socioeconomic development. Anthropogenic activities are one of the main causes for water quality damage and, consequently, social concern calls for quality control action. Even after water treatment, it has been demonstrated in many studies that organic contaminants escape conventional wastewater treatment processes and they end up in aquatic systems.

Pharmaceuticals and personal care products are an important group of contaminants that have been targeted, especially in the last decade. For example, EPA Method 1694[1], published in December 2007, is a guiding and screening method for those scientists analyzing pharmaceuticals in environmental samples. The standard EPA protocol uses solid-phase extraction (SPE) for water samples followed by the analysis of extracts by tandem mass spectrometry using a single transition for each compound, with retention time guidelines for identification.

Contaminants are usually present in the environmental samples at very low concentration levels (ng/L) and, for this reason, solid phase extraction techniques are often used to isolate and pre-concentrate the organic compounds of interest. This has led to the development of a method for low concentration level analysis of pharmaceuticals in drinking water samples. The implementation for this method consists of the analysis of 20 analytes which are some of the most common contaminants found in the environment currently.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 Automated Extraction System
  - Envision® Controller
  - Atlantic™ HLB-M SPE Disk
- Agilent
  - 1200 HPLC and 6220 LC-TOF-MS
  - Zorbax Eclipse XDB-C8 Column
- Caliper Life Sciences
  - Turbovap Concentration Workstation

The Horizon Technology SPE-DEX® 4790 Automated Extraction System, and the Envision® Platform Controller

Method Summary

Drinking water samples were taken from the tap at the Center for Environmental Mass Spectrometry (Boulder, CO). Wastewater samples were collected from several wastewater treatment plants in Denver, Boulder and Estes Park (Colorado, USA). Surface water samples were collected from several locations including rivers and reservoirs in Colorado. A spiking mixture containing the 20 pharmaceutical compounds was used to spike water samples at 0.5 ug/L. No additives were added to water samples, and no filtration of samples was needed.

1. The SPE-DEX 4790 system was purged using a generic method shown in Table 1.
2. Water samples were extracted using the SPE-DEX 4790 system with the method shown in Table 2 resulting in approximately 40 mL of extract.
3. Extracts were transferred to a 45ºC water bath and concentrated with a gentle stream of nitrogen to near dryness.
4. The dry sample was reconstituted in a 1:9 v/v acetonitrile and deionized water solution.

Sample Analysis

The separation of the analytes was carried out using an HPLC system equipped with a reversed phase C_8 analytical column of 150 mm x 4.6 mm and 5 µm particle size.

Column temperature was maintained at 25 ºC. The injected sample volume was 50 µL. Mobile phases A and B were acetonitrile and water with 0.1% formic acid, respectively. The optimized chromatographic method held the initial mobile phase composition (10% A) constant for 5 min, followed by a linear gradient to 100% A after 30 min. The flow-rate used was 0.6 mL/min. A 10-min post-run time was used after each analysis. This HPLC system was connected to a time-of-flight mass spectrometer Agilent 6220 MSD TOF equipped with a dual electrospray source, operating in positive ion mode, using the following operation parameters: capillary voltage: 4000 V; nebulizer pressure: 45 psig; drying gas: 9 L/min; gas temperature: 300 ºC; fragmentor voltage: 190V; skimmer voltage: 60V; octopole RF: 250 V.

Table 1: Purge Method

Step	Solvent	Dry Time
Prewet 1	DI Water	0:15 sec
Prewet 2	Methanol	0:15 sec
Wash 1	DI Water	0:15 sec
Rinse 1	Methanol	0:15 sec

Table 2: Extraction Method

Step	Solvent	Soak Time	Dry Time
Prewet 1	Methanol	2:00 min	0:15 sec
Prewet 2	DI Water	1:00 min	0:05 sec
Sample Process			
Wash 1	DI Water	1:00 min	0:15 sec
Air Dry 15:00 min			
Rinse 1	Methanol	1:30 min	0:15 sec
Rinse 2	Methanol	1:30 min	1:00 min

Results

The extracts were analyzed by LC-TOF-MS. The compounds were chromatographically separated and detected by accurate mass measurements.

The recoveries and relative standard deviations (RSD) for the selected pharmaceuticals are within EPA's 1694 method criteria for precision and recovery. The results for three replicates are presented in Table 3 and a sample chromatogram for the compounds is given in Figure 1.

Conclusions

The results demonstrated that the SPE-DEX 4790 using Atlantic HLB-M disks can effectively extract pharmaceutical compounds from 1-L water samples in a fraction of time (approx. 40 min). This system allows you to use the original sample bottle which will be rinsed with all of the extraction solvents before the elution step. This rinsing step ensures that all the compounds are rinsed off the glass and retained on the disk.

Acknowledgements

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References

[1] EPA Method 1694: Pharmaceuticals and personal care products in water, soil, sediment, and biosolids by HPLC/MS/MS, December 2007, EPA-821-R-08-002.
[2] Ferrer, I., Zweingenbaum, J.A., Thurman, E.M., J. Chromatogr. A, 1217 (2010) 5674-5686.

Table 3: Pharmaceutical Recoveries Using SPE TOF

Analyte	Use	Average Recovery (%)	RSD (%)
Acetaminophen	Non-steroidal anti inflammatory	65	8
Albuterol	Bronchodilator	79	5
Atenolol	Antihypertensive	86	3
Caffeine	Cardiac and respiratory stimulant	66	5
Carbamazepine	Anticonvulsant/Antidepressant	101	2
Cotinine	Antidepressant	86	5
DEET	Mosquito repelant	89	6
Dehydronifedipine	Antihypertensive	91	5
Diclofenac	Anti inflammatory	88	9
Diltiazem	Antihypertensive	71	8
Diphenhydramine	Antihistamine	76	5
Gemfibrozil	Non-steroidal anti inflammatory	101	2
Ibuprofen	Non-steroidal anti inflammatory	108	5
Lamotrigine	Antidepressant	95	3
Metoprolol	Antihypertensive	73	5
Naproxen	Non-steroidal anti inflammatory	110	7
Sulfadimethoxine	Antibiotic	85	5
Sulfamethoxazole	Antibiotic	46	8
Triclocarban	Antiseptic	65	5
Trimethoprim	Antibacterial	83	3

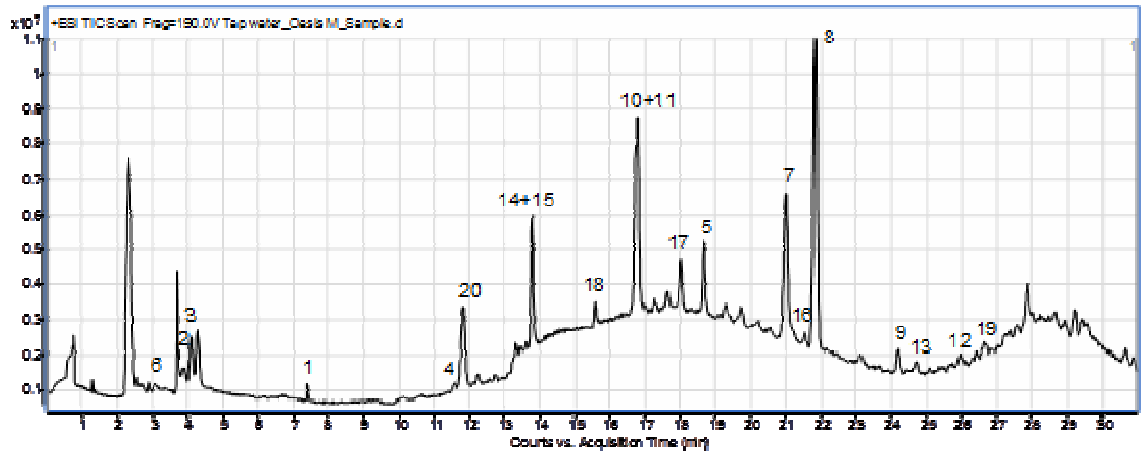

Figure 1: LC-TOF-MS analysis of a spiked tap water sample after extraction with the SPE-DEX 4790