

## Determination of Endothall by Automated Solid Phase Extraction (SPE) - Initial Demonstration of Capability

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### 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. 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 short note presents data from the State of Idaho Bureau of Labs for the initial demonstration of capability using the Horizon Technology automated SPE-DEX<sup>®</sup> 4790 Extractor System. Automated SPE provides the benefits of high sample throughput, low solvent consumption, safe working conditions and consistent, reliable data.

### Instrumentation

- SPE-DEX<sup>®</sup> 4790 Extractor System (Horizon Technology, Salem, NH).
- SPE Disk: Empore<sup>™</sup> Anion-SR, 47 mm
- Gas chromatography Conditions:
  - Front Inlet:
    - Mode – Splitless
    - Initial Temp. 200°C
    - Column Flow: Linear velocity 45 cm/min (100.1 kpa)  
Pulsed – 300 kpa for 1.00 min.
  - Oven: Initial temp. 70°C for 3.0 min.  
Ramp 1- 290°C @ 20°C/min. hold 4.0 min
  - MS: Scan 45 – 450 @ 0.27 sec interval, scan Speed 1666
  - Carrier gas: Helium
  - Interface Temp. 290°C
  - Ion Source: 290°C
  - 2µL injection

### Method Summary

- 1) IPR samples: Four replicates prepared using 100 mL of 18.2 ohms DI water at neutral pH, spiked at 25 µg/L.
- 2) MDL samples: Seven replicates prepared using 100 mL of 18.2 ohms DI water at neutral pH, spiked at 4 µg/L.
- 3) SPE-DEX<sup>™</sup> 4790 Extractors prepared for extraction by running Purge Method 548.9 (Table 1) three times to flush the system.
- 4) Two Empore<sup>™</sup> Anion-SR disks stacked in the Disk Holder Assembly and loaded onto 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<sup>™</sup> 4790 Automated Extractor System using Controller Method 548.1.
- 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) Top disk in the Disk Holders is discarded. Bottom disk is saved for the next run. All Disk Holders rinsed with DI water.
- 9) Purged Extractors twice using 548.9 between sample runs and rinse the Bottle Holders and sample inlet areas with DI water using a squeeze bottle and Controller Method 15 twice.
- 10) For the next run, placed a fresh 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.

### Results

The Initial Precision and Recovery (IPR) data are shown in Table 3. The Method Detection Limit (MDL) data are shown in Table 4. The average recovery for the IPR data is 87.7 % with % RSD value of 8.76. Both these values are within the acceptable range as per the EPA Method. The MDL is 1.1 ppb and was calculated by multiplying the STD DEV from the replicate study by the student t value of 3.143. The method states that reagent water MDLs should be 2 ppb or lower (sec. 11.2.4, EPA Method 548.1).

It is important to run a Purge Method on the Extractors between sample extractions. The Purge Method 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, the Bottle Holders and Disk Holders should be rinsed with DI water to remove residual acid.

### ***Conclusions***

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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.

**Table 1: Purge Method 548.9**

Step	Solvent	Soak Time	Dry Time
No Prewets			
Wash 1	Methanol	0	10 sec
Wash 2	Methanol	0	10 sec
Wash 3	Methanol		
Air Dry			0
No Rinses			

**Table 2: Extraction Method 548.1**

Step	Solvent	Soak Time	Dry Time
Prewet 1	MeCl <sub>2</sub>	1:00 min	30 sec
Prewet 2	MeOH	2:00 min	30 sec
Prewet 3	1N HCl/MeOH	30 sec	6 sec
Prewet 4	Reagent Water	30 min	6 sec
Prewet 5	1N NaOH	1:30 sec	6 sec
Prewet 6	1N NaOH	30 sec	6 sec
Prewet 7	Reagent Water	1:00 min	6 sec
Prewet 8	Reagent Water	30 sec	0 sec
Process Sample			
Wash 1	MeOH	30 sec	1:00 min
Wash 2	MeOH	30 sec	1:00 min
Air Dry			3:00 min
Rinse 1	10% H <sub>2</sub> SO <sub>4</sub> /MeOH	2:00 min	30 sec
Rinse 2	10% H <sub>2</sub> SO <sub>4</sub> /MeOH	2:00 min	30 sec
Rinse 3	10% H <sub>2</sub> SO <sub>4</sub> /MeOH	2:00 min	30 sec
Rinse 4	MeCl <sub>2</sub>	1:00 min	1:00 min

Note: The 6 second Dry Time for the Prewets may need to be adjusted for your specific system. This is a critical step; Prewets should pull most of the way through the disk before adding the next reagent.

**Table 3. Initial Precision & Recovery (IPR)**

Analyte	Endothall	% Recovery
Spike Level	25 ug/L	
IPR 1	21.46	85.8
IPR 2	20.42	81.7
IPR 3	21.08	84.3
IPR 4	24.73	98.9
<b>Average</b>	<b>21.92</b>	<b>87.7</b>
<b>RSD</b>	<b>8.76</b>	<b>7.67</b>

**Table 4. Method Detection Limit (MDL)**

Analyte	Endothall
Spike Level	4 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	3.80
<b>STD DEV</b>	<b>0.353</b>
<b>MDL</b>	<b>1.109</b>
<b>RL (Reporting Limit)</b>	<b>2.5</b>