Extractions of Phenols in Water Using the Empore™ HLB SPE EZ-Disk

Application Note
Environmental

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Abstract
This application note demonstrates the performance of the CDS Empore™ HLB 25mm EZ-Disk to extract 19 different species of phenols from reagent grade water. Water samples were processed with the assistance of the EZ-Trace SPE workstation. The recovery is determined for all 19 phenols for this method and demonstrates that the Empore™ HLB EZ-Disk is effective for extraction small polar molecules such as phenols.

Introduction
Phenolic compounds are widely used throughout industry as flavoring agents, antioxidants, and other applications providing health benefits. Due to the prominence of phenolic compounds in industrial processes, phenols are some of the most common organic pollutants in waterways. Concentrations of phenols are strictly regulated due to their toxicity to both humans and aquatic life. Additionally, during the chemical treatment process, phenols further react to form by-products that can have potentially mutagenic or carcinogenic effects on humans. Due to both solubility and volatility, phenols are difficult to extract and quantify from water samples.[1]

Previously, the EPA had released Method 528 describing a method for the extraction of 11 phenols from water.[2] This application note extends this list to 19 phenolic compounds of interest and presents a method for extraction using the Empore™ HLB 25mm EZ-Disk, which is a syringe-type SPE cartridge.

The validation data presented herein was determined on four replicate measurements for each sample from the same lot of HLB EZ-Disks. MDLs were not determined as part of this validation.

Experiment Setup
SPE disk:
Solid phase extraction (SPE) was done with Empore™ HLB 25mm EZ-Disk (CDS Analytical PN 98-0706-0110-9; Model No. 7280SD).

Extraction System:
Four extractions were performed simultaneously with the Empore™ EZ-Trace SPE vacuum system (catalog # 8000; VWR part # 76449-580).

Chemicals:
The phenols 8270 Calibration Mix (cat. 31618), Acids Surrogate Mix (cat. 31003), and Internal Standards Mix, EPA 528 (cat. 31696) were all purchased from Restek (Bellefonte, PA). The GC-MS calibration standard decafluorotriphenylphosphine (DTFPP) was also purchased from Restek. Methanol, dichloromethane, and methyl tert-butyl ether (MTBE) were purchased from Sigma Aldrich (St. Louis, MO) and ethyl acetate from EMD Millipore (Darmstadt, Germany). Water was treated in house using a Milli-Q Water Treatment System.

Preparartion of Standards:
Water samples were spiked to 10 and 20 ppb using the calibration standards.

Methods:
1. A 250 mL water sample was adjusted to pH 2 using chloric acid and was then spike with the standard mixtures of analytes and surrogates.

2. Four 25mm HLB EZ-Disks were mounted onto the four positions of the EZ-Trace.

3. An empty, 6mL cartridge was placed on the top of each holder. The disks were conditioned with 3 mL of MTBE, soaked for 1 minute, and then dried thoroughly. The disks were then washed first with 3 mL of methanol and then with 5 mL of reagent grade water.

4. The cartridge was then replaced by a conical water sample adapter and the water sample bottles were loaded from the top. The EZ-Trace was adjusted so that the flow rate would be between 10 and 15 mL/min.

5. The disks were rinsed with 3 mL of reagent grade water and then dried under vacuum for 15 minutes.

6. Elution was performed with 3 mL of 10:90 methanol:MTBE and then 3 mL of methylene chloride. The extract was dried with 3 g of anhydrous sodium sulfate.

7. The sample was then dried to a volume of 0.5 mL under a gentle nitrogen stream using the LabTech ET concentrator. The internal standard was then added to the sample, and the sample was adjusted to 1 mL using methylene chloride in preparation for GC-MS analysis. The parameters for the GC-MS analysis are provided in Table 1.

Results and Discussion

The recoveries for all phenolic compounds were determined by GC-MS analysis. A chromatogram resulting from the GC-MS analysis is shown in Figure 1. The recoveries of the phenolic compounds is graphically shown in Figure 2, and the detailed data can be found in Table 2. Percent recoveries ranged between 70% and 104% with an average RSD of 5% for both concentration levels of 10 and 20ppb. A few notable exceptions with a high RSD at both concentration levels were 2,4-dimethylphenol and 2,4-dinitrophenol.

Conclusions

In this application note, a method was developed using the Empore™ HLB 25mm EZ-Disk for the extraction of a broad phenolic compounds. This method provides the framework obtaining suitable recoveries (>70%). The RSD was suitable most of the analytes as well.

Table 1: Overview of the GC and MS parameters and methods.

GC Parameters	
Column:	Restek RXI-5sil-MS (30m x 0.25mm x 0.25µm)
Inlet Temp:	200°C
Injection Mode:	Splitless
Carrier Gas:	He at 44.5 cm s^{-1} (constant flow)
Oven Program:	35°C hold for 6 min, 35 to 250°C at 8°C min^{-1}
Mass Spectrometer Parameters	
Ion Source Temp:	200°C
Transfer Line Temp:	220°C
Solvent Delay:	10 min
Threshold:	0
Mass Range:	45-350 m/z
Scan Time:	0.3 s

References

1. Mu'azu N. D.; et. al.; Removal of Phenolic Compounds from Water Using Sewage Sludge-based Activated Carbon Adsorption: A Review; Int. J. Environ. Res. Public Health; 2017.
2. Environmental Protection Agency. Method 528.
Determination of Phenols in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS); 2000.

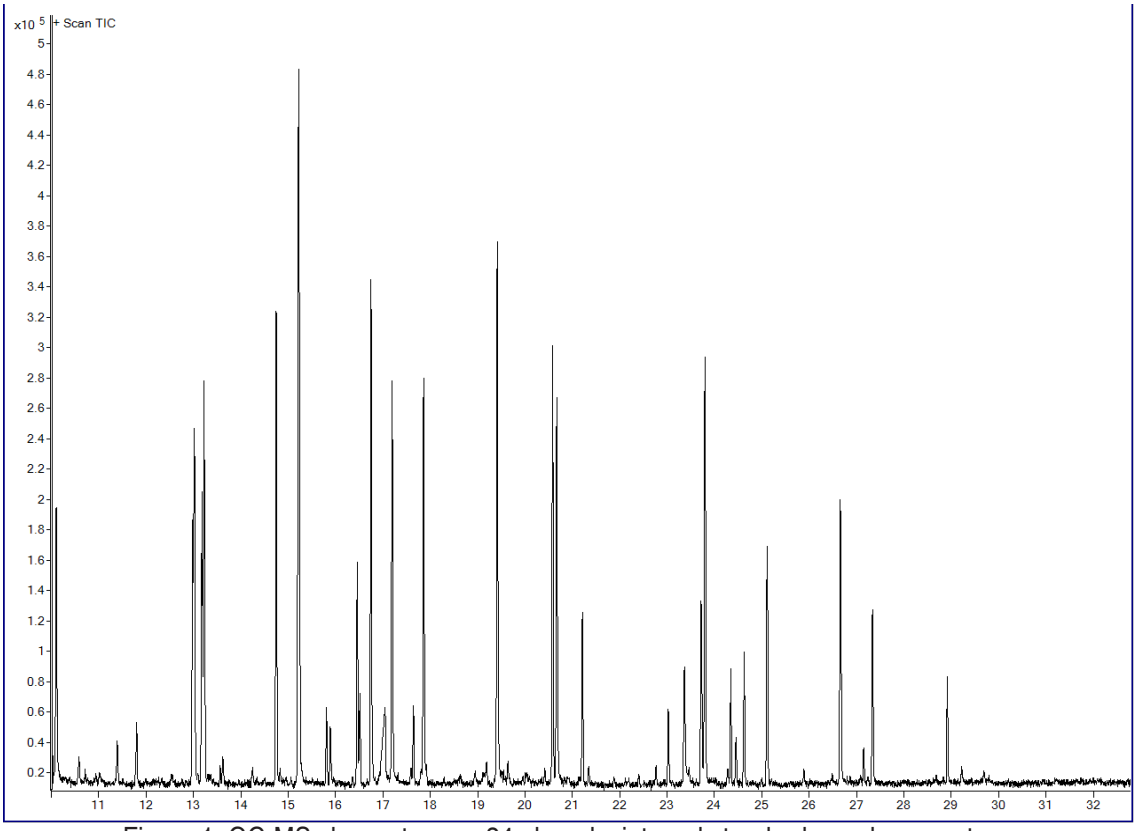

Figure 1. GC-MS chromatogram 24 phenols, internal standards, and surrogates.

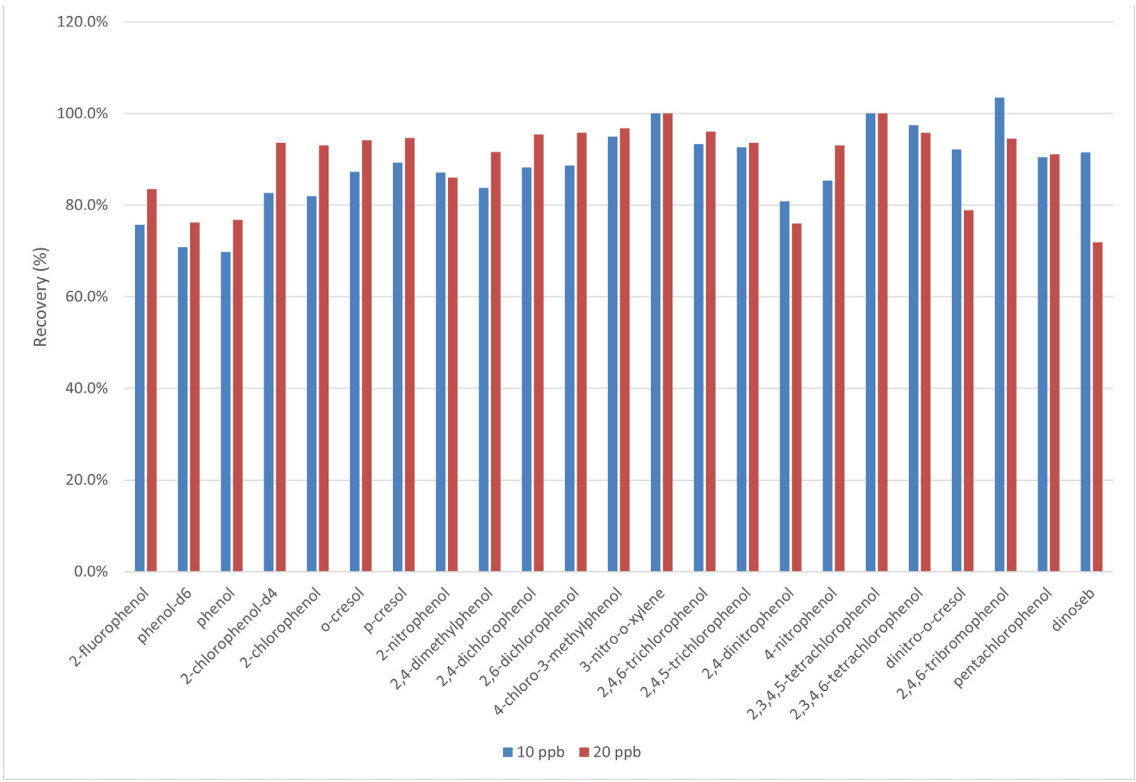

Figure 2. Percent recoveries of phenolic compounds in reagent grade water when spiked at concentrations of 10 ppb (blue) and 20 ppb (red).

Table 2. Retention time, recoveries, and RSD of phenolic compounds and spiked concentration levels of 10 and 20 ppb (n=4).

		10 ppb		20 ppb	
	Retention Time (min)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2-fluorophenol	10.11	75.7	4.2	78.1	3.3
phenol-d6	13.00	70.9	5	70.2	3.8
phenol	13.02	69.8	6.9	71.9	3.1
2-chlorophenol-d4	13.2	82.7	5.4	88.4	1
2-chlorophenol	13.25	82	5.4	88.3	0.9
o-cresol	14.75	87.3	4	86.8	1.9
p-cresol	15.25	89.3	4	88.2	1.6
2-nitrophenol	16.48	87.1	2.9	83.8	1
2,4-dimethylphenol	16.77	83.8	10	74.6	12.1
2,4-dichlorophenol	17.21	88.2	4.3	92.6	1.2
2,6-dichlorophenol	17.88	88.7	4.1	91.6	0.9
4-chloro-3-methylphenol	19.43	95	3.1	91.1	1
3-nitro-o-xylene (IS)	19.44	100	0	100	0
2,4,6-trichlorophenol	20.61	93.3	3.3	90.5	2.3
2,4,5-trichlorophenol	20.69	92.7	3.6	86.2	4.5
2,4-dinitrophenol	23.05	80.9	18.2	74.2	22.7
4-nitrophenol	23.39	85.3	8.1	86.5	8.7
2,3,4,5-tetrachlorophenol (IS)	23.74	100	0	100	0
2,3,4,6-tetrachlorophenol	23.83	97.5	3.5	101	5.1
dinitro-o-cresol	24.65	92.1	5.9	83.7	11.6
2,4,6-tribromophenol	25.14	103.5	3.9	102.7	4.6
pentachlorophenol	26.68	90.5	4.1	88.3	8.5
dinoseb	27.36	91.5	6.5	80.8	12.8