



High Throughput Solid Phase Extraction of Pesticides and Flame Retardants in Drinking Water using EPA Method 527

Application Note

Environmental

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Abstract

CDS Empore™ (formerly 3M™ Empore™) EZ-Trace is an extraction system allowing for simultaneous extractions and significantly reducing preparation time of multiple samples. This application note demonstrates the performance of the EZ-Trace using the Empore™ SDB-XC disk under EPA Method 527.1 for reagent grade water samples. The recovery is determined for 26 analytes, consisting of pesticides and flame retardants, and demonstrates that the Empore™ EZ-Trace system provides a clean and efficient extraction with the Empore™ SDB-XC disk.

Introduction

EPA Method 527.1 is a targeted list of 26 semi-volatile organic compounds in drinking water designed to detect and quantify various pesticides and chemical additives in flame retardants.¹ For example, numerous pesticides appearing in EPA 527.1 are classified as pyrethroids, which are a chemical class of pesticides that are highly effective insecticides. While pyrethroids generally have low mammalian toxicity, they are known to be toxic to aquatic organisms including fish. Examples of herbicides and organophosphate pesticides can also be found within the list of target compounds. Other major chemical classes of interest in EPA 527.1 are polybrominated biphenyls (PBB's) and polybrominated diphenyl ethers (PDBE's). Chemical species belonging to these classes are often used as additives in flame retardants and are also known carcinogens to humans.²

In this application note, multiple extractions are performed simultaneously by the Empore™ EZ-Trace to extract pesticide and flame retardant compounds from reagent grade water samples using the 47 mm Empore™ SDB-XC, polymeric-based SPE disks. Extractions are performed on the EZ-Trace under the negative pressure of a vacuum pump. The extract is evaporated, diluted, and then analyzed via GC-MS. The accuracy and precision for the recoveries of 26 analytical standards are determined from the four-point calibration curve of each standard. The results are assessed by the efficiency, reproducibility, and cleanliness of the extraction in combination with the accuracy and precision of the SDB-XC disk. The validation data presented herein was determined on four replicate measurements for each sample from the same lot of SDB-XC disks. MDLs were not determined as part of this validation.

Experiment Setup:

Solid phase extraction (SPE) was done with Empore™ SDB-XC 47mm disks (catalog # 2240). Four extractions were performed simultaneously with the Empore™ EZ-Trace SPE channel vacuum system (catalog # 8000).



EPA Method 527.1 internal standards were acquired from Sigma Aldrich (St. Louis, MO). The remainder of the target analytes and surrogate molecules were obtained from AccuStandard (New Haven, CT) as pre-mixed solutions. The GC-MS calibration standard decafluorotriphenylphosphine (DTFPP) was also purchased from Restek. Reagents potassium dihydrogen citrate, L-ascorbic acid, and ethylenediaminetetraacetic acid (EDTA) trisodium were all purchased from Sigma Aldrich (St. Louis, MO). Methanol, ethyl acetate, and dichloromethane were also purchased from Sigma Aldrich (St. Louis, MO). Water was treated in house using a Milli-Q Water Treatment System.

The primary dilution standard (PDS) was prepared at a concentration of $50 \mu\text{g L}^{-1}$. This solution was refrigerated until ready for use. Reagent grade water samples were first treated with approximately 0.1 g L-ascorbic acid, 0.35 g EDTA, and 9.4 g potassium dihydrogen citrate. Each water sample was buffered to pH 3.8 to prevent microbial growth and analyte degradation.

Methods:

1. Spike the first 1 liter reagent water sample with 20 μL of PDS and 10 μL of surrogate. The concentration of PDS in the water sample is $1 \mu\text{g L}^{-1}$.
2. Assemble all 4 disk adapter and glass filtration assemblies on the Empore™ EZ-Trace using a 47 mm Empore™ SDB-XC Solid Phase Extraction (SPE) disk.
3. Wash each disk with 5 mL of 1:1 ethyl acetate : methylene chloride. Pull a small amount of solvent through the disk and soak for 1 minute. Draw the remainder of the solvent through the disk and allow the disk to dry.
4. Then wash each disk with 10 mL of methanol and then soak for one minute. Leave a layer of methanol remaining above the disk.
5. Condition each disk by adding two 10 mL aliquots of water to the disk. Do not let the disk dry leaving a layer of water above the disk.
6. Add each 1 L water sample to a filtration reservoir. Under vacuum, filter as quickly as the vacuum will allow. Before all the water samples have filtered through their SPE disks, wash each bottle with 10 mL of water and add to the filtration reservoirs.
7. Before disk drying, wash each SPE disk with another 5-10 mL of water to wash any salts off the disks. Dry the disks for 10 minutes under vacuum.

8. Rinse the sample bottle with 5 mL of ethyl acetate and add to the reservoir. Let the disk soak for one minute.

9. Repeat step 9 using 5 mL dichloromethane.

10. Pre-rinse a filtration reservoir with 5 mL of 1:1 ethyl acetate : dichloromethane. Dry the combined eluant with 10 g of granular anhydrous sodium sulfate and collect in an evaporation vial. Rinse the collection tube and sodium sulfate each with a 5 mL portion of dichloromethane into the evaporation vial.

11. Dry the extract to just below 1 mL under a gentle stream of nitrogen (warm gently). Allow the eluate to come back to room temperature and adjust to 1 mL mark with ethyl acetate.

12. Dilute the eluate with ethyl acetate back to the 1 mL mark on the evaporation vial. Transfer this solution to a 1 mL GC-MS vial. Add 10 μL IS to the vial.

13. Repeat this procedure for the other reagent water samples by adding 40 μL of PDS to the sample. For all samples, add 10 μL of surrogate. Determine the recovery of each analytical calibration standard using GC-MS.

GC-MS Analysis

The extract analysis was performed on a Shimadzu GC-2010 Gas Chromatograph with a splitless injection port interfaced to a Shimadzu GC-MS QP2010 (Kyoto, Japan) and a 30m x 0.25mm x 0.25 μm MilliporeSigma GC column. GC-MS parameters are shown in Table 1.

The GC-MS method described in Table 1 was used on the recommendation of EPA Method 527.1. The mass spectrometry method was modified based on the needs of these experimental conditions. Modifications to mass spectrometry methods are permitted by EPA method 527.1. Ions used for quantification of each standard were selected by those recommended by EPA Method 527.1. A four-point calibration curve was constructed for the calibration of each analytical standard. The MS was tuned successfully using DTFPP.

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

GC Parameters

Column: SLB®-5ms (30m x 0.25mm x 0.25µm)
 Inlet Temp: 250°C
 Transfer Line Temp: 250°C
 Injection Mode: Splitless
 Injection Volume: 2 µL
 Carrier Gas: He at 42.7 cm/s (constant flow)
 Oven Program: 55°C hold for 0 min, 55 to 200°C at 20°C min⁻¹, hold 2 min, 200 to 300°C at 4°C min⁻¹, hold 0.75 min

Mass Spectrometer Parameters

Solvent Delay: 4.4 min
 Threshold: 0
 Mass Range: 4.4-19.0min: 45-450 m/z
 19.0-35.0min: 45-670 m/z
 Scan Time: 0.3 s

Results and Discussion:

Figure 1 shows the chromatogram of the 26 standards, 3 surrogates, and 3 internal standard compounds under EPA Method 527.1. The compounds are well-separated under the conditions of the GC method described in Table 1.

For the both samples of the reagent grade water, the average recovery was 103% with 16% and 13% RSD for 1 and 2 µg L⁻¹ respectively. A summary of this data is located in Table 2. As allowed by EPA Method 527.1, the permissible recovery range is between 70% and 130% with ≤ 20% RSD. In the case of each sample, more than 92% of analytes were within the acceptable recovery limit, while more than 96% had sufficient RSDs.

The complete recovery data of all 26 compounds is listed in Table 3 for two different concentrations of PDS in reagent grade water. Compounds yielding notably high recoveries include kepone and bromacil. Kepone is noted by the EPA as being problematic for measurements under method 527.1. Quantification of bromcil is also expected to show high recoveries due to interferences from the SDB-XC disk.

Other problematic analytes of note include esfenvalerate, fenvalerate, norflurazon, nitrophen, and parathion, which can

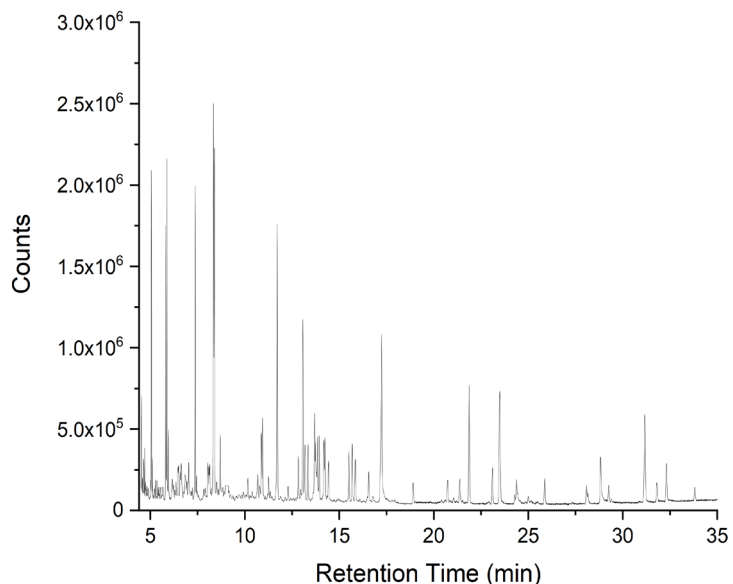


Figure 1: Chromatogram of 26 analytes, 3 surrogates, and 3 internal standards. Analytes have a concentration of 2 µg L⁻¹ in the water sample.

Table 2: Summary of results for two different concentrations of PDS in reagent grade water.

Water	Reagent Grade Water	
µg L ⁻¹	1.0	2.0
# 70-130%	24	26
avg Rec. (%RSD)	102.7 (15.8)	102.6 (12.7)

exhibit a matrix-induced enhanced chromatographic response causing recoveries greater than 100%. These analytes are susceptible to inlet adsorption and thermal degradation. This effect is typically most prominent in pristine calibration solutions and less noticeable in dirtier water samples. The final result is that the recoveries from the water sample appear to be larger. The procedures recommended by the EPA minimize this effect have been followed. Dimethoate also produced low recovery in the 2 µg L⁻¹ sample. This compound is known to produce low recoveries, according the EPA method.

Conclusions:

The performance of the Empore™ EZ-Trace was demonstrated as part of this experimental work, performing 4 extractions of 26 pesticide and flame retardant compounds simultaneously on the Empore™ SDB-XC SPE disk. Recoveries for both samples were within the acceptable limits for 92% of analytes while 96% of analytes were within the acceptable RSD limit. Specifically, or

the five compounds known to produce high recoveries, their accuracy and precision were all within the limits set by the EPA method.

In summary, the CDS Empore™ EZ-Trace, combined with the Empore™ SDB-XC SPE disk, provide a clean and efficient screening method while still produced high analyte recoveries for the compounds listed by EPA Method 527.1.

References:

1. Environmental Protection Agency. Method 527.1. Determination of Selected Pesticides and Flame Retardants in Drinking Wwater by Solid Phase Extraction and Capillary Column Gas Chromatography/ Mass Spectrometry (GC/MS), 2005.
2. Pepich, B. V.; Prakash, B.; Domino, M. M.; and Dattilio, T. A.; Development of U.S. EPA Method 527 for the analysis of selected pesticides and flame retardants in UCMR Survey, *Environ. Sci. Tech.*, 2005.

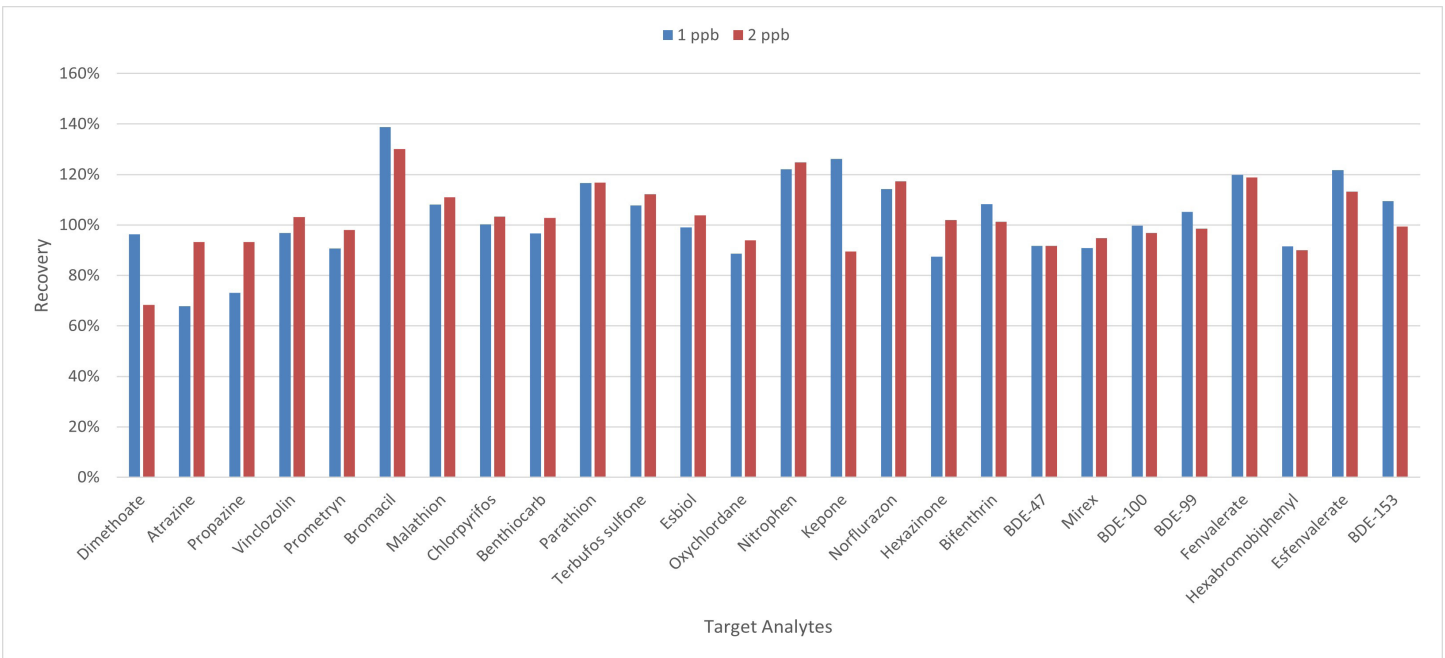


Figure 2: Recovery of 26 target analytes in two reagent water samples having concentrations of 1 ppb (blue) and 2 ppb (red).

Table 3: Average recovery of 25 analytical calibration standards for 2 samples of reagent water containing different concentrations of standards. Shown in parentheses are the relative standard deviations. For each water sample, there are four replicate measurements. Concentrations are representative of a 1 liter water sample.

Concentration ($\mu\text{g L}^{-1}$)	Reagent Grade Water	
	1.0	2.0
	%Rec. (RSD)	%Rec. (RSD)
Dimethoate	88.7 (13.8)	68.4 (10.4)
Atrazine	67.8 (29.8)	93.2 (5)
Propazine	73.1 (23.3)	93.2 (4.5)
Vinclozolin	96.9 (11.4)	103.1 (2.7)
Prometryn	90.1 (9.4)	98.1 (5)
Bromacil	138.9 (11.1)	130.0 (5.3)
Malathion	108.1 (10.4)	110.9 (2.7)
Chlorpyrifos	100.3 (11.5)	103.3 (2.2)
Thiobencarb	96.6 (10.6)	102.7 (2.3)
Parathion	116.6 (14.1)	116.8 (3)
Terbufos-Sulfone	107.8 (10.5)	112.2 (3.1)
Oxychlorane	99.0 (8.6)	103.8 (2.4)
Esbiol	88.7 (10.5)	93.9 (2.7)
Nitrophen	122.1 (16.3)	124.8 (6.4)
Kepone	126.1 (7.2)	89.5 (29.2)
Norflurazon	114.3 (12.7)	117.2 (6.4)
Hexazinone	87.5 (9.1)	101.9 (7.7)
Bifenthrin	108.2 (5.6)	101.3 (2.8)
2,2',4,4'-Tetrabromodiphenyl Ether (BDE-47)	91.7 (5.1)	91.7 (2.7)
Mirex	90.8 (5.7)	94.7 (2.1)
2,2',4,4',6-Pentabromodiphenyl Ether (BDE-100)	99.8 (5.2)	96.9 (1.7)
2,2',4,4',5-Pentabromodiphenyl Ether (BDE-99)	105.2 (6.9)	98.6 (2.3)
Hexabromobiphenyl	119.8 (5.1)	118.9 (5.3)
Fenvalerate	91.6 (19.4)	90.0 (1.8)
Esfenvalerate	121.7 (2.6)	113.2 (4.5)
2,2',4,4',5,5'-Hexabromodiphenyl Ether (BDE-153)	109.4 (4.5)	99.5 (5.1)