

# Determination of Organophosphorus Pesticides in Ground Water Using EPA Method 8141B by Empore™ SDB-RPS SPE Disk and GC-MS Analysis

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## Abstract:

CDS Empore™ (formerly 3M™ Empore™) SDB-RPS Solid Phase Extraction (SPE) disks facilitate rapid and reliable sample preparation and provide excellent analyte recovery for hydrophilic compounds with clean chromatograms. This application note demonstrates the performance of such disks in the monitoring of Organophosphorus (OP) pesticides in ground water samples using EPA Method 8141B.

## Introduction

OP pesticides are the most widely used pesticides in the world to control agricultural, household, and structural pests, because such pesticides do not persist in the environment for prolonged period of time, and also do not accumulate in the body fat of humans and other animals due to their readily hydrolysis property. However, the readily hydrolysis nature of OP pesticides is sometimes misleading to the public and potentially decrease people's awareness of the hazards from such compounds. As a matter of fact, without enough precautions, people could be in routine exposure through multiple ways of contact, such as the consumption of fresh and processed vegetables, direct touching pesticides-contaminated surfaces, breathing air near pesticide application, and drinking pesticide contaminated water. On the toxicology side, the primary mechanism of OP pesticides is the inhibition of the enzyme acetylcholinesterase mainly targeting to central nervous system, respiratory tract, and cardiovascular system. To bring up the public awareness as well as increase public safety, EPA classifies most OP pesticides as either toxicity class I (highly toxic) or toxicity class II (moderately toxic) and also regulates these compounds by mandatory EPA methods.

EPA Method 3535A includes OP pesticides as the target compound to be cleaned and concentrated by SPE method with Empore™ SDB-RPS disks, and Method 8141B defined the quantification of OP contaminants from ground water samples<sup>1,2</sup> by GC/MS instrument. A few major challenges in these methods in the sample preparation side include (1) large sampled volume at 1 liter, (2) unstable chemical structure by readily hydrolysis and oxidation to result in coelution in GC analysis. Empore™ SDB-RPS disks can consistently tackle with these challenges with the best suitable extraction results among all the SPE disks and cartridges from different vendors.

In this application note, a one-liter water sample was passed through a 47mm SDB-RPS Empore™ disk and eluted with acetone and methyl tert-butyl ether (MTBE) under negative pressure. Then the solvent was changed to hexane, and the extract was dried and reduced in volume down to 1.0 mL to be further analyzed by GC/MS. The validation data presented herein was determined from three runs of SDB-RPS disks from the same lot.

## Experimental

### Chemicals:

The 8140/41 analytes (26 compounds) were purchased from Restek (Bellefonte, PA). Sodium sulfite was from Sigma-Aldrich (St. Louis, MO). Water, Acetone, Hexane, MTBE, and Methanol were all high purity pesticide quality from Burdick & Jackson (Muskegon, MI).

### Sample Pre-treatment:

40 mg of sodium sulfite was added to 1 L of purified water (by Millipore Mill-Q™ system) to reduce free chlorine. 5ml of methanol was added into the water sample as a wetting agent. Each sample was fortified with 5 µg of each internal standard. For recovery data, each sample was fortified with 5 µg of each method analyte. The CDS Empore™ 47mm SDB-RPS disks (Part # 2241, Fisher Scientific™ 13-110-022 /VWR™ 76133-140, CDS Analytical, Oxford, PA) were used for the extraction with repeated number n=3.

### Methods:

1. Assemble an all glass filtration assembly using a 47 mm SDB-RPS Empore™ disk. Use of a manifold for multiple extractions is acceptable.
2. Wash the extraction apparatus and disk by adding 5 ml of acetone to the reservoir. Pull a small amount through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry. Add 5 ml of methanol as the 2<sup>nd</sup> washing step, and repeat the previous washing steps one more time.
3. Condition the disk by adding approximately 5 ml of methanol to the reservoir, pulling a small amount through the disk then letting it soak for about one minute. Pull most of the remaining methanol through the disk, leaving 3 to 5mm of methanol on the surface of the disk.
4. Add 20 ml of reagent water to the disk and using the vacuum pull most through, again leaving 2 to 3 mm of water on the surface of the disk.
5. Add the water sample to the reservoir and, under vacuum, filter as quickly as the vacuum will allow. Drain as much water from sample bottle as possible. Dry for 3 minutes under vacuum.
6. Remove filter assembly and insert suitable sample tube for eluate collection.
7. Add 0.6 ml of acetone to the disk, soak 1 minute.
8. Add 5 ml of MTBE to the sample bottle. Rinse bottle thoroughly and transfer solvent to the disk with dispo-pipet, rinsing sides of filtration reservoir in the process.
9. Pull half of solvent through disk then release the vacuum. Allow the remaining solvent to soak the disk for about one minute, then draw remainder through under vacuum.
10. Repeat the solvent rinse of the sample bottle and apparatus using 5 mL of MTBE twice more.

10. Using a disposable pipette, rinse down the sides of the filtration glassware with two 3 mL aliquots of MTBE.

11. Dry the combined eluant with 10 grams granular anhydrous sodium sulfate. Rinse the collection tube and sodium sulfate with two 3 mL portions of MTBE and place combined solvent into a concentrator tube. The solvent is exchanged to hexane.

12. Concentrate extract to 1 ml under gentle stream of nitrogen (may be warmed gently). Do not concentrate to <0.5 ml or loss of analytes could occur.

### **GC-MS Analysis:**

The quantification analysis was performed on a Shimadzu GC-2010 Gas Chromatograph with a split/splitless injection portal interfaced to a Shimadzu GC-MS QP2010 (Kyoto, Japan) and a 30m x 0.25mm ID GsBP-5MS column with 0.25 micron film (General Separation Technologies, Newark, DE). GC-MS parameters are shown below.

#### **GC Parameters:**

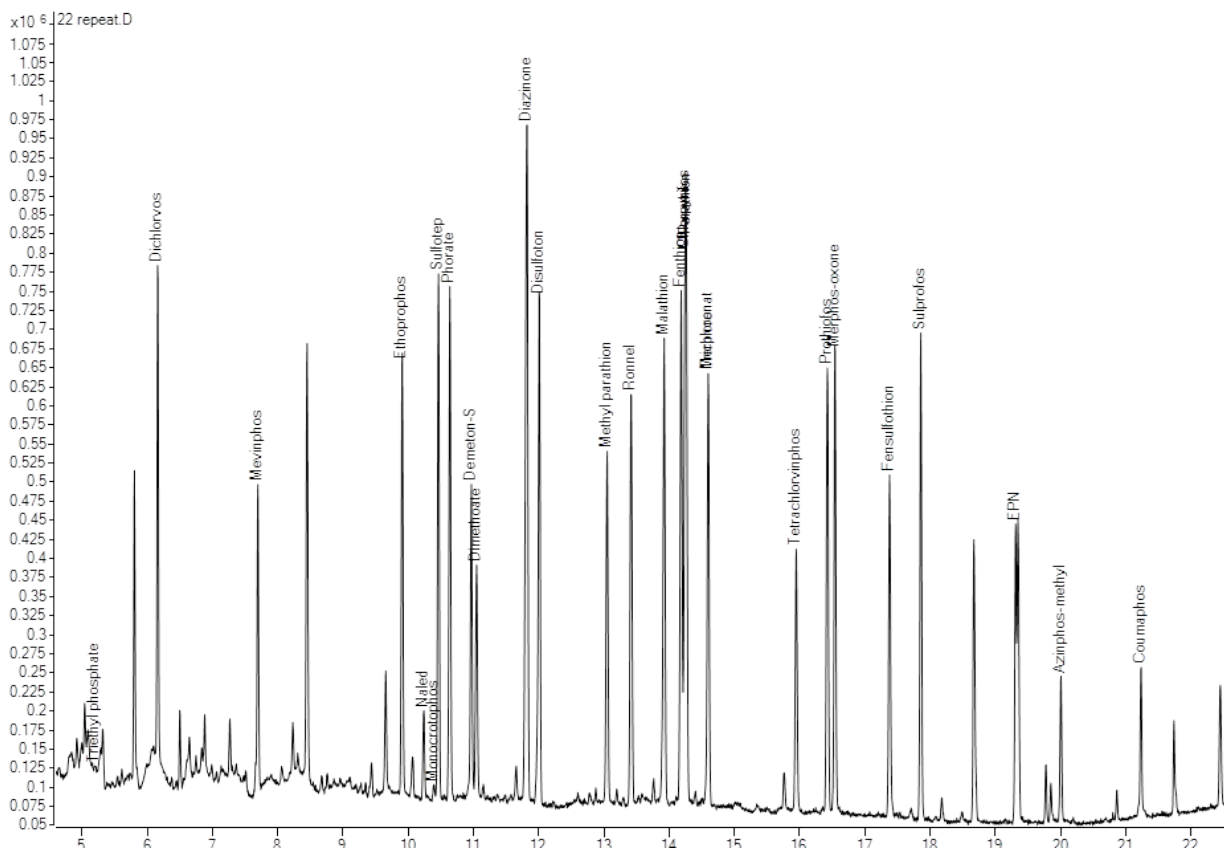
Column: GS-Tek GsBP-5MS (30 m × 0.25 mm id × 0.25 μm df)  
Inlet Temp.: 230 °C  
Transfer Line: 250 °C  
Injection Mode: Splitless  
Injection Volume: 1 μL  
Carrier Gas Flow: He at 33 cm/sec (constant flow)  
Oven Program: 45°C hold for 1 minute, 45°C to 130°C at 45°C/min, 130°C to 180°C at 12°C/min, 180°C to 240°C at 7°C/min, and 240°C to 320°C at 12°C/min. Hold for 6 minutes.

#### **Mass Spectrometer Parameters**

Solvent Delay: 3.0 minutes  
Threshold: 0  
Scan Range: 45-450  
EM Voltage: 910  
Sampling Rate: 2  
Scans/sec: 3.3

## **Results and Discussions**

Figure 1 showed the GC chromatogram of 26 OP pesticide compounds from the 8140/41 analytes standard. Among the 26 compounds, only 24 are on the EPA Method 8141B list. It can be concluded from the chromatogram that these compounds were well separated by the current experimental conditions.



**Figure 1.** GC chromatogram of 26 compounds from 8140/41 analytes standard.

Table 1 listed the comparison data of the 24 compounds listed in the EPA Method 8141B. The average recovery was 89.6% with an averaged relative standard deviation (RSD) at 3.3%. In contrast, the average recovery for the same 24 compounds from EPA 8141B guideline was 82.3% with averaged RSD at 6.4%. In the 24 compounds, 16 had better recovery rates than the EPA 8141B guideline, 4 of them had equivalent recovery rates, and the rest 4 of them had less recovery rates. As a summary, 23 of 24 compounds in this study had the recovery rates falling into the range between 70% to 130%, passing the EPA Method 8141B.

The only compound with recovery less than 70% was Dimethoate, whose recovery rate was calculated as 67.2%. This recovery rate could be improved by minimizing hydrolysis and oxidation by different optimized experiment conditions, which is not the focus of this application.

The 3.3% RSD from only three runs was showing great consistency on the performance Empore™ SDB-RPS disks, which makes the redundant runs aiming to improve RSDs unnecessary.

**Table 1. Average recovery and RSD comparisons for compounds in EPA 8141B**

<b>Analyte</b>	<b>Average %R (RSD) (n=3)* (From current method)</b>	<b>Average %R (RSD) (n=7)** (From EPA 8141B)</b>
Azinphos-methyl	95.4(7.1)	109.7(7.0)
Chlorpyrifos	92.5(2.4)	77.5(5.2)
Coumaohos	97.0(10.0)	100.8(13.5)
Demeton-S	84.3(1.5)	73.8 (5.1)
Diazinone	88.8(2.8)	70.0(5.0)
Dichlorvos	89.6(6.4)	90.1(7.9)
Dimethoate	67.2(5.2)	76.7(9.5)
Disulfoton	86.0(2.3)	79.5(6.1)
EPN	90.4(4.1)	67.9(7.9)
Ethoprophos	90.6(1.8)	81.4(3.7)
Fensulfothion	87.6(1.0)	97.2(6.0)
Fenthion	92.7(2,8)	79.5 (4.3)
Malathion	98.3(3.7)	78.0(8.7)
Methyl parathion	92.2(3.2)	83.6(4.7)
Mevinphos	84.8(5.8)	96.8(6.7)
Naled	78.6(1.8)	88.1(7.9)
Parathion	93.6(3.3)	69.6(5.8)
Phorate	86.8(2.5)	70.8(6.7)
Prothiofos	92.2(0.5)	77.8(5.6)
Ronnel	91.2(1.2))	77.8(4.7)
Sulfotepp	91.0 (2.6)	68.9(8.6)
Sulprofos	92.3(2.4)	78.2(4.3)
Tetrachlorvinphos	97.0(3.0)	106.3(5.9)
Trichloronate	91.7(1.4)	75.7(3.9)

\*Spike levels= 5.0 µg/L. Data from the current validation method.

\*\*Spike levels= 10.0 µg/L. Data from EPA Method 8141B guidelines.

## Conclusions

A simple and effective method to extract organophosphorus pesticide compounds from large volume of 1L water sample by Empore™ SDB-RPS 47mm disks had been validated per EPA Method 8141B. 24 OP pesticide compounds listed in the method had been separated from water samples, and then quantified by GC-MS with concentration at 5.0 ppb. 23 of these 24 compounds had recoveries in the range of 70%-130%, which exceeds the requirement in EPA Method 8141B. The average recovery rate was higher than that the EPA 8141B guidelines at a much lower 3.3% RSD.

In summary, excellent analyte recovery and clean chromatograms could be obtained by Empore™ SDB-RPS disks. The data supported the claim that CDS Empore™ SDB-RPS disks are well qualified for screening ground water samples according to EPA Method 8141B on monitoring OP pesticides.

## References

1. EPA Method 3535A: Solid-Phase Extraction (SPE), part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.
2. EPA Method 8141B: Organophosphorus Compounds by Gas Chromatography, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.