Detecting Trace Herbicides in Water Samples by SPE Sample Preparation and GC-MS

Application Note
Environmental

Author:

Guotao Lu
Michael Apsokardu

Abstract
CDS Empore™ SDB-XC SPE cartridges help to extract trace herbicides in water samples by eliminating methylene chloride and greatly reducing organic solvent usage in elution.

Introduction
Organic contaminants are a concern in rivers, streams, and ground water across the whole world. Each year, millions of dollars have been spent to analyze these organic contaminants such as phenols, benzidines, phthalate esters, nitrosamines, organochlorine pesticides, nitroaromatics, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons, and acid-base neutrals. Normally chlorinated solvents are required to extract these contaminants from water samples. Although the methylene chloride needed per water sample is reduced from 150 mL in EPA Method 625,[1] to 15 mL in EPA Method 525,[2] the yearly consumption of methylene chloride for organic contaminant analysis is still as much as 5 to 10 million liters. Methylene chloride can remove ozone from the upper atmosphere and is also a suspected carcinogen. Therefore, the demand to minimize or eliminate the usages of methylene chloride in this analysis is desired.

In this application note, a 15 mL water sample is passed through a 4mm/ 1mL Empore™ SDB-XC Disk SPE cartridge (Cat. #: 4140HD), and eluted with 50 µL ethyl acetate. The extract was then analyzed by GC-MS. The accuracy and precision for the recoveries of 18 analytical standards are determined from the five-point calibration curve of each standard. The validation data presented herein was determined on three replicate measurements for each sample from the same lot of SDB-XC Disk SPE cartridge. MDLs were also determined as part of this validation.

Experiment Setup

Solid phase extraction (SPE) was done with Empore™ SDB-XC 4mm/1mL cartridges (catalog # 4140HD). Reagent-grade methanol, ethyl acetate, and deionized water were used as solvents. The internal standard, terbuthylazine, was present as a solute in methanol at 1.23 ng/µL. The stock solution of herbicide standard contained 1.23 ng/µL of each of the following compounds in HPLC-grade methanol: propachlor obtained from ChemService (West Chester, PA); deethylatrazine and deisopropylatrazine obtained from Ciba Geigy Agricultural Division (Greensboro, NC); and cyanazine amide obtained from Du Pont Experimental Division (Wilmington, DE); ametryn, atrazine, prometon, prometryn, propazine, simazine, and terbutryn obtained from Supelco (Bellefonte, PA); alachlor, cyanazine, metolachlor, and metribuzin obtained from US EPA Pesticide Chemical Repository (Research Triangle Park, NC); and acetochlor obtained from Zeneca-Monsanto (St. Louis, MO).

Standards with concentrations of 0.1, 0.2, 0.5, 1.0, and 2.0 µg/L were prepared in triplicate to generate standard curves for all of the components of the stock solution, except for alachlor-ESA and deethylcyanazine. Three samples each of ground water, river water, and lake water were analyzed with the method and the results compared with a 100-mL method developed in the US Geological Survey laboratory in Lawrence, KS.[3]

Methods

1. A volume of 10 mL of standard or sample was spiked with 50 µL terbuthylazine internal standard solution (equivalent to 61.5 ng of terbuthylazine), and the test tube containing the standard or sample was agitated briefly on a vortex mixer.

2. Cartridges were loaded on a vacuum manifold nine at a time, to which a vacuum of 690 mm Hg was applied. The cartridges were conditioned in batch, first with 200 µL methanol, then with 200 µL ethyl acetate, followed by 200 µL methanol, and 600 µL deionized water.

3. The 10 mL of standard or sample then was loaded in sequential 1-mL aliquots.

4. After loading, the cartridge was dried on the manifold for approximately 10 min (air wash), then removed and cut open with a pair of wire cutters. The plastic case of the cartridge was spread with needle-nose pliers to permit removal of the disk.

5. A volume of 50 µL of ethyl acetate was added to a 100-µL GC vial, and the disk was pushed into the bottom using the tip of a fresh disposable transfer pipette. The vial was capped in preparation for GC-MS. The disks had a tendency to float in the ethyl acetate; sometimes a vial cap had to be removed to push down a disk that had dislodged from the bottom of the vial insert and floated up.

The extract analysis was performed on a Hewlett-Packard Model 5890 Series II Plus GC (Palo Alto, CA) and a 5972 GC mass selective detector (MSD) and a 12-m HP-1 fused silica capillary column of methylsilicone with a film thickness of 0.33 µm and 0.2 mm i.d. (Hewlett-Packard, Palo Alto, CA). The detector was operated in selected ion monitoring (SIM) mode, monitoring three ions of atrazine, including its molecular ion. Each calibration curve was prepared using the base peak of the compound of interest and the base peak of terbuthylazine. Confirmation was based on the presence of the molecular ion peak of the compound of interest and a retention time match. GC-MS parameters are shown in Table 1.

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

GC Parameters	
Column:	Hewlett-Packard HP-1 (12m x 0.2mm x 0.33µm df)
Inlet Temp:	210°C
Transfer Line Temp:	250°C
Injection Mode:	Splitless
Injection Volume:	1 µL
Carrier Gas:	He at 1 mL/min (constant flow)
Oven Program:	50°C hold for 1 min, 50 to 250°C at 6°C min^{-1}, hold 10 min
Mass Spectrometer Parameters	
Solvent Delay:	3.0 min
Threshold:	0
Mass Range:	45-450 m/z
Scan Time:	0.3 s
EM Voltage	870
Sampling Rate	2

Results and Discussion

Table 2 shows detection limits and coefficients of determination (r^2) for the 16 herbicides listed in order of elution from the column (bracketed values are ratios of the number of SIM peaks that passed the detection limit to the total number of SIM peaks used for the compound). As shown in Table 2, the detection limit was 0.1 µg/L or less for all compounds except DIA, acetochlor, and cyanazine, for which it was 0.2 µg/L. As indicated by the r^2 values in Table 2, all of the standard curves were good to excellent.

Atrazine and its two metabolite compounds, DIA and DEA, are more polar than the other triazine herbicides in the mixture. They could cause low recovery rates or even breakthrough on the common reversal SPE phases, like C18, as the data shown by EPA method 525.2.[2] Fig. 1 shows the standard curves for atrazine and two metabolite compounds. The curves were reproducible and demonstrates the advantage of the current 10-mL sample and 50uL elution solvent SPE method to analyze polar herbicides against the regular EPA methods.

Table 2: Detection limit using GC/MS and the Empore™ SDB-XC Disk SPE cartridge.[5]

Compound	Detection limit (µg/l)	Coefficient of determination (r^2)
Propachlor	0.1 [2/3]	0.999
DIA	0.2	0.989
DEA	0.1 [1/3]	0.994
Simazine	0.1 [1/2]	0.995
Prometon	0.1	0.999
Atrazine	0.1	0.999
Propazine	0.1	0.993
Metribuzin	0.1 [1/3]	0.996
Acetochlor	0.2 [1/2]	0.992
Alachlor	<0.1	0.993
Ametryn	<0.1	0.998
Prometryn	<0.1	0.998
Terbutryn	<0.1	0.997
Metolachlor	<0.1	0.997
Cyanazine	0.1–0.2	0.989
Cyanazine amide	0.1	0.956

The number in brackets, such as [2/3], indicates that two of the three SIM ions monitored were detected. A 10-ml sample was used in 1-ml syringe disk.

Table 3 shows the results of a study by comparing the current 10-mL Empore™ SDB-XC Disk SPE cartridge method with an existing 100-mL standard cartridge method for ground water, river, and lake samples. It was shown that the 10-mL method using the SDB-XC disk cartridges demonstrates favorable results compared to the existing 100-mL method using standard cartridges.[4]

Conclusion

A simple and effective method to extract trace herbicides from water samples with the CDS Empore™ SDB-XC 4mm/1mL SPE cartridge has been developed. 16 herbicides listed in EPA Method 525.2 have been studied in this experiment. They have been extracted from ground water, river, and lake samples, and then quantified by GC-MS with concentration from 0.1 to 2.0 µg/L (ppb). 13 of the 16 herbicides in this study have detection limits of 0.1 µg/L or less, whereas the remaining 3 herbicides, DIA, acetochlor, and cyanazine, had a detection limit of 0.2 µg/L. The water sample size was reduced from 100 mL for the standard SPE cartridge method to 10 mL in the current method, and the elution solvent was 50 µL ethyl acetate while the usage of methylene chloride is eliminated. The accuracy and precision for the current 10-mL and SDB-XC 4mm/1mL SPE cartridge method is more favorable than the existing 100-mL and standard cartridge method for ground water, river, and lake samples.

If you are screening water samples to monitor the trace triazine herbicides according to EPA Method 525, CDS Empore™ SDB-XC disk cartridge will help to ensure rapid, economical, and environmentally-friendly sample preparation for you.

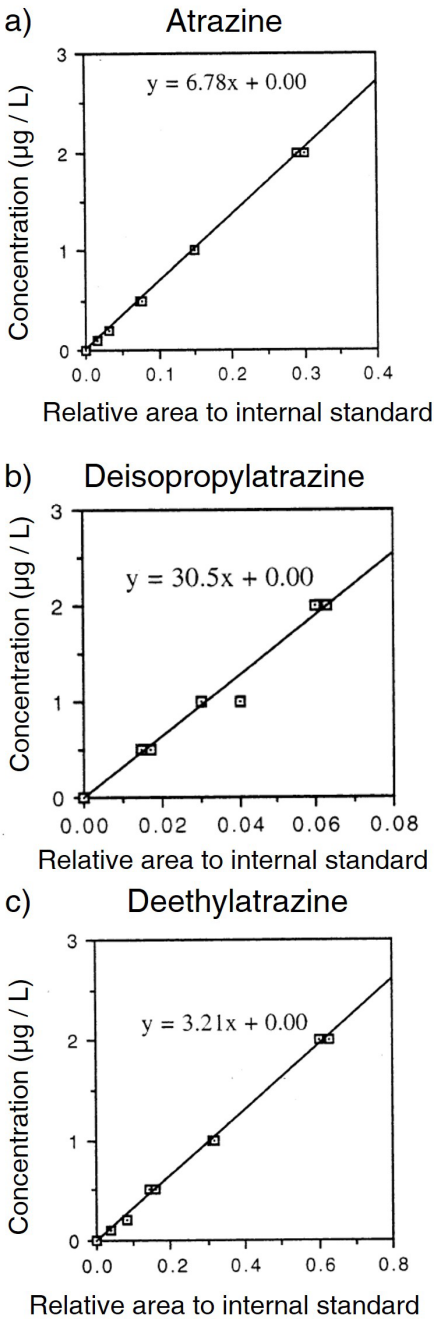

Figure 1. Standard curves using the 10-mL method and SDB-XC disk SPE cartridges for the analysis of (a) atrazine and two metabolites, (b) deisopropylatrazine and (c) deethylatrazine.[5]

Table 3: Slope and r^2 value of concentrations of 10-mL method regressed against 100-mL method.[5]

Compound	No. sample points	Slope	r^2
DIA	5	0.778	0.898
DEA	9	0.753	0.510
Simazine	3	0.580	1.000
Atrazine	9	1.41	0.961
Acetochlor	2	1.39	1.000
Alachlor	2	1.06	1.000
Metolachlor	6	1.61	0.955
Cyanazine	5	1.66	0.763

References:

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3. E.M. Thurman, M. Meyer, M. Pomes, C.A. Perry, A.P. Schwab, Anal. Chem. 62 (1990), 2043.

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