Application Note: 1004

Automated Solid-Phase Extraction of Organochlorine Pesticides from Drinking Water

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Key Words

- Organochlorine
- Pesticides
- Extraction
- Water
- Soil

Introduction

Organochlorine pesticides (OCPs) are synthetic chemicals comprising a variety of compounds containing carbon, hydrogen, and chlorine; they are widely used around the world. These compounds can be highly toxic, and some agents—such as DDT—have been banned in the United States because of their unacceptably slow degradation. OCP's are hydrophobic, lipophilic, and extremely stable. Once in air, water, and soil, they are subject to global deposition processes and bioaccumulation in the food chain. Diet is the main source of human exposure, primarily through food consumption where OCPs have bioaccumulated.

Here, twenty chlorinated pesticides were extracted from drinking water using a Thermo Scientific Dionex AutoTrace 280 Solid Phase Extraction Instrument (AT 280). The efficiency of the Dionex AT 280™ method was compared to traditional liquid-liquid phase extraction (LLE). The quantitative determinations of chlorinated pesticides were performed by gas chromatography with Electron Capture Detector (GC-ECD.)

Equipment

Dionex AT 280 6 mL SPE Cartridge System (PN 071385)

Thermo Scientific Dionex SolEx C-18 Extraction Columns (1000 mg/6 mL) (Thermo Fisher PN 075895)

Thermo Scientific Dionex Glass Fiber Filters (Thermo Fisher PN 056781)

Gas Chromatograph with Electron Capture Detector

PCB Column 40 mm × 0.18 mm i.d. × 0.18 µm

Guard Column 5 mm × 0.25 mm i.d.

Milli-Q Water System (Millipore Corporation)

Solvent evaporator

Solvents and Reagents

Dichloromethane (Thermo Fisher Scientific)

Ethyl acetate (Thermo Fisher Scientific)

Methanol (Thermo Fisher Scientific)

Hydrochloric acid (Thermo Fisher Scientific)

Sodium sulfate (Thermo Fisher Scientific)

Screwcap amber vial (Thermo Fisher Scientific PN 033919)

Organochlorine Pesticide Mix AB#

Semivolatile Internal Standard Mix

1 L sample bottle (Thermo Fisher PN 056284)

40 mL collection vial (Thermo Fisher PN 048783)

2 mL screw thread amber vial (Thermo Fisher PN 033919)

Procedure

Sample Preparation for Liquid-Liquid Phase Extraction

Liquid-liquid phase extraction (LLE) was performed according to EPA method 508 Section 11.1.

Sample Preparation for Solid-Phase Extraction

1) Collect 1 L deionized (DI) water.

2) Add Organochlorine Pesticide Mix AB #3.

3) Dechlorinate water with 50 mg/L sodium sulfite

4) Adjust water sample to pH=2 with HCI.

5) Samples are ready for Dionex AT 280

Load six 1 L water samples onto the cartridges using the Dionex AT 280 and elute with ethyl acetate and dichloromethane. Dry the extracts using a solvent-rinse drying column containing approximately 10 cm anhydrous sodium sulfate. Flush two 5 mL portions of dichloromethane through the drying column to elute the remaining sodium sulfate. Concentrate each extract to 1 mL using a slow flow of nitrogen in a water bath using evaporation apparatus. The resulting extracts are ready for analysis by GC-ECD.

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Dionex AutoTrace 280 - Sample Loading Program

Process samples using the following procedure:

Step 1: Condition cartridge with 5 mL ethyl acetate into solvent waste.

Step 2: Condition cartridge with 5 mL dichloromethane into solvent waste.

Step 3: Condition cartridge with 10 mL methanol into solvent waste.

Step 4: Condition cartridge with 10 mL DI water (pH=2) into aqueous waste.

Step 5: Load 1200 mL sample onto column.

Step 6: Dry cartridge with gas for 5 min.

Dionex AutoTrace 280 - Elution Program

Step1: Manually rinse sample container with 20 mL ethyl acetate to collect.

Step2: Manually rinse sample container with 20 mL dichloromethane to collect.

Note: At step 1, add 5 mL ethyl acetate to sample container and at step 2, add 5 mL dichloromethane to sample container.

Step 3: Collect 5 mL of fraction to a second tube using ethyl acetate.

Step 4: Collect 5 mL of fraction to a second tube using dichloromethane.

Dionex AutoTrace 280 Parameters

Flow Rate:	5 mL/min
Condition Flow:	5 mL/min
Load Flow:	10 mL/min
Rinse Flow:	20 mL/min
Elute Flow:	5 mL/min
Condition Air Push:	15 mL/min
Rinse Push:	20 mL/min
Elute Push:	5 mL/min

SPE Parameters

Push delay	5 sec
Air Factor	1.0
Autowash volume	1 mL

Solvent Method

Solvent 1: Ethyl acetate
Solvent 2: Dichloromethane
Solvent 3: Methanol
Solvent 4: DI water (pH=2)
Solvent 5: Unused

GC-ECD Analysis Conditions

Instrument:	GC-ECD
Column:	PCB Column 40 mm × 0.18 mm i.d. × 0.18 µm
Guard Column:	Guard Column 5 mm × 0.25 mm ID
Inj. Port Temp.:	250 °C
Inj. Mode:	Splitless
Inj. Volume:	1 µL
Makeup Gas:	Nitrogen
Flow Rate:	1.5 (mL/min) constant flow
Oven Temp.:	100 °C (hold 1 for min.) to 200 °C at 30°C/min. to 320 °C at 2 °C/min (hold 1min.)

Table 1. The results of the Dionex AutoTrace 280 SPE (N=6) vs LLE (N=3).

Analyte	Spike Level (ng/mL)	SPE % RSD	LLE % RSD	% Recovery SPE vs LLE
Alpha-BHC	50	13	13	113
Gamma-BHC	50	12	12	135
Beta-BHC	50	11	11	113
Heptachlor	50	12	13	64
Delta-BHN	50	12	12	128
Aldrin	50	13	11	134
Heptachlor epoxide	50	11	13	102
Cis-chlordane	50	12	11	138
Endosulfan I	50	11	12	99
4,4′-DDE	50	12	12	135
Dieldrin	50	12	10	107
Trans-chlordane	50	11	13	134
Endrin	50	13	11	125
4,4′-DDD	50	11	15	115
Endosulfate II	50	12	16	134
4,4′-DDT	50	11	11	135
Endrin aldehyde	50	10	11	94
Endosulfan sulfate	50	16	23	131
Methoxychlor	50	9	15	143
Endrin ketone	50	10	26	138

Conclusions

Here, both automated and manual exaction data show good recovery of all compounds. However, the manual extraction required significantly more time compared to the Dionex AutoTrace 280 instrument. As shown in Table 1, analyte recovery was improved using the AT280 Automated SPE instrument for the majority of compounds without sacrificing the precision of analysis. Traditional extraction methods such as liquid/liquid extraction (LLE) are labor intensive and generate large amounts of waste solvent which increases operation and disposal costs. The Dionex AutoTrace 280 is an automated extraction instrument, that allows extraction of multiple compounds from water and significantly reduces laboratory operation costs.

For a detailed description of the LLE method discussed here, follow the link in References.[1]

List of Manufactures

Thermo Fisher Corporation, Sunnyvale, CA USA

Thermo Fisher Scientific International, Pittsburgh, PA USA

Sigma-Aldrich Chemicals, St. Louis, MO USA

Millipore Corporation, Billerica, MA USA

References

1. Method 508, *Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector, Revision 3.0*

   Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency, Cincinnati OH, 45268
   http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_11_06_methods_method_508.pdf

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