

Automated Solid-Phase Extraction of Organochlorine Pesticides from Drinking Water

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Overview

A new method was developed to automate the capture and elution of Organochlorine pesticides from drinking water. The concentrated analytes were then analyzed by GC with Electron Capture Detection (ECD).



Introduction

Organochlorine pesticides (OCP) are a class of chemicals that were used to control insect pests since the 1940s. The use of OCPs was banned in the later part of last century due to their longevity, a trait that made them effective for long term pest control, but also increased concerns of potential health outcomes such as cancer in humans and ecosystem disruption.

Pesticides are regulated in the U.S. by the Environmental Protection Agency (EPA) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Some states also regulate pesticides under FIFRA, in a more restrictive manner than the EPA. The Stockholm Convention on Persistent Organic Pollutants, a UN treaty, has established global bans on several organochlorine pesticides including DDT, hexachlorobenzene, pentachlorobenzene, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorocyclohexane (alpha-HCH, beta-HCH, and gamma-HCH (lindane)), and chlordecone.

OCPs can be highly toxic, are hydrophobic, lipophilic, and extremely stable. Once in the 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.

In this study twenty chlorinated pesticides were extracted from drinking water using a Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction instrument and the Thermo Scientific™ Dionex™ SolEx™ C 18 cartridges. The recoveries were compared to the traditional liquid-liquid extraction method (LLE). Analysis for both sample preparation methods was performed by gas chromatography with Electron Capture Detection (GC-ECD)

Methods

Equipment

Thermo Scientific™ Dionex™ AutoTrace™ 280 SPE 6mL SPE cartridge system

Dionex SolEx C18 cartridges (6 mL cartridge with 1000 mg of resin)

Sample Preparation for LLE

LLE was performed in accordance with US EPA method 508 section 11.1.

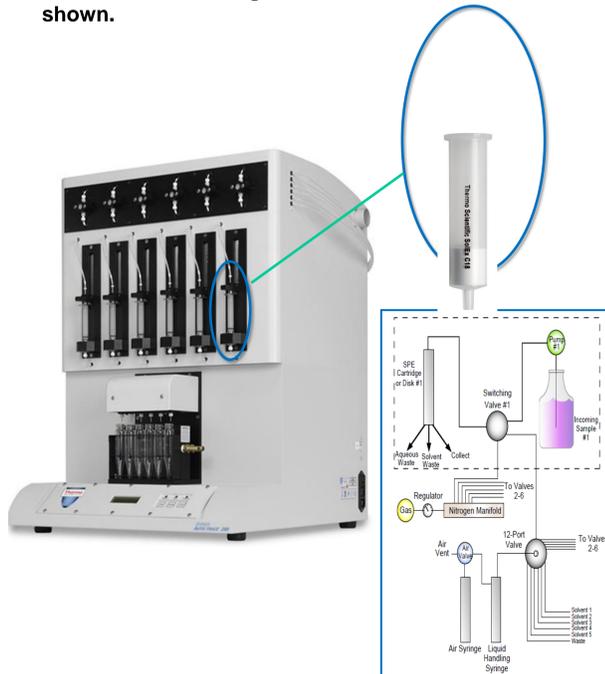
Sample Preparation for Solid-Phase Extraction

Drinking water samples were fortified with a mix of the 20 organochlorine pesticides. The water was dechlorinated using 50 mg/L sodium sulfite, followed by adjusting the pH of the water sample to pH 2 using hydrochloric acid.

Sample Concentration and Elution

Load six 1 L water samples into the cartridges using the Dionex AutoTrace 280 SPE instrument and elute with ethyl acetate and dichloromethane. Dry the extracts to a 1 mL volume. The resulting extract was then analyzed by GC-ECD.

FIGURE 2. Dionex AutoTrace 280 SPE instrument; a Dionex SolEx cartridge and the fluid connections are shown.



Results

Dionex AutoTrace 280 SPE Conditions

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

Method

Step	Step Description	Volume	Solution
1	Condition	5 mL	Ethyl Acetate
2	Condition	5 mL	Dichloromethane
3	Condition	10 mL	Methanol
4	Condition	10 mL	DI Water
5	Load	1200 mL	Sample
6	Dry	5 min	Nitrogen
7	Rinse	20 mL	Ethyl Acetate
8	Rinse	20 mL	Dichloromethane
9	Elute	5 mL	Ethyl Acetate

Note: At Step 9 and 10, add 5 mL Ethylacetate and Dichloromethane to the sample containers respectively.

GC-ECD Analysis Conditions

Instrument	GC-ECD
Column	PCB Analytical Column with Guard
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 for min) to 200 °C at 30 °C/min to 320 °C at 2 °C/min

Both the automated and liquid-liquid phase extraction data show good recovery of all compounds. The LLE extractions required significantly more time when compared to the automated SPE. Table 1. data shows the recoveries were improved when using the Dionex AutoTrace 280 SPE instrument or automated SPE, for most analytes without sacrificing the precision of analysis. Traditional extraction methods such as LLE are labor intensive and generate large amounts of waste, which increases the operation and disposal cost.

FIGURE 1. Structures of Organochlorine Pesticides

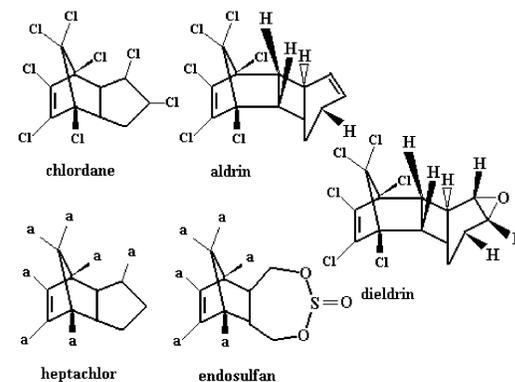


Table 1. The results of the Dionex AutoTrace 280 SPE (N=6) Versus LLE (N=3) at spike levels of 50 ng/mL for all analytes

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

Conclusion

- Automated SPE method followed by GC-ECD analysis was able to concentrate and analyze 20 different Organochlorine pesticides with good recoveries
- The traditional LLE method also showed good recoveries, but was time consuming and labor intensive

References

- Method 508, Determination of chlorinated Pesticides in water by Gas Chromatography with an Electron Capture Detector, Revision 3.0.[Online] http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_11_06_methods_method_508.pdf (accessed June 10, 2014).
- Thermo Scientific Application Note 1004: Automated Solid Phase Extraction of Organochlorine Pesticides from Drinking Water, Sunnyvale, CA. [Online] http://info1.thermoscientific.com/content/CMD_KL_Resources?kl=WAT_#&rid=3356 (accessed June 10, 2014).

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