

Application

Note
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Solid Phase Extraction/HPLC Analysis of Acidic Herbicides In Drinking Water

Investigators at the Nassau County Department of Health (Hempstead, New York, USA) have developed an analysis for acidic chlorinated herbicides (2,4-D, Dacthal, dicamba, dinoseb, pentachlorophenol, picloram, 2,4,5-T, 2,4,5-TP, tetrachloroterephthalic acid) in water. One-liter samples are extracted using ENVI-Carb solid phase extraction tubes and analyzed by HPLC/photo-diode array. Solvent use is minimal, and the procedure eliminates diazomethane derivatization. The method is quantitative and reproducible. Low background levels in ENVI-Carb tubes make low detection limits possible.

Key Words

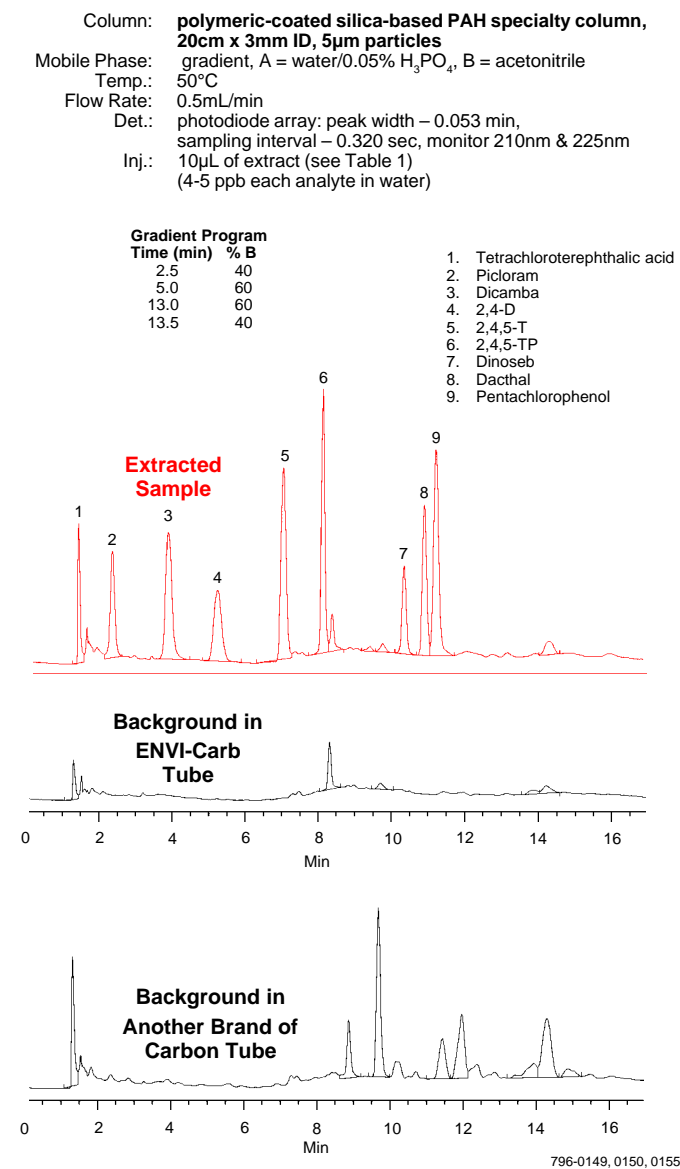
- acidic herbicides
- drinking water
- solid phase extraction
- HPLC

Chlorophenoxyacid herbicides are widely used as a postemergence treatment for agricultural weed control, and to kill aquatic weeds in small bodies of fresh water. Although the highly water-soluble acid and salt forms of these compounds are not very toxic, the ester forms can accumulate in the fat of aquatic and terrestrial organisms, so there is concern about total levels in water sources used for human consumption.

The Nassau County Department of Health (Hempstead, New York, USA) is involved in the routine testing of agricultural monitoring wells and drinking water sources for the presence of organic contaminants, including pesticides and herbicides. The department has developed a method for the extraction and HPLC analysis of acidic chlorinated herbicides: 2,4-D, Dacthal®, dicamba, dinoseb, pentachlorophenol, picloram, 2,4,5-T, 2,4,5-TP, tetrachloroterephthalic acid. The method requires fresh, 1-liter water samples, dechlorinated with sodium thiosulfate when necessary, at ambient pH. The chlorinated acids are extracted using a 6mL, 250mg ENVI™-Carb solid phase extraction tube and analyzed by HPLC/photodiode array. The method can be fully automated, using a Zymark® AutoTrace SPE system which can simultaneously extract six 1000mL samples and the procedure outlined in Table 1. The extracted samples are concentrated to 1mL and the solvent is exchanged to acetonitrile before injection onto the HPLC column. Chromatographic conditions are summarized in Figure A.

This procedure minimizes solvent use, and eliminates cumbersome and dangerous diazomethane derivatization required in an alternative procedure, US Environmental Protection Agency

Figure A. Acidic Herbicides in Water



Figures provided by A. Lichtman, Nassau County Dept. of Health, Hempstead, New York, USA.

Method 515.2. The acids are extracted and analyzed in their free state, so no pH manipulation is needed. The method is quantitative and reproducible (Table 2). ENVI-Carb tubes also produce lower background levels than competing products, which makes even lower detection limits possible.

Table 1. Automated Procedure for Extracting Acidic Herbicides from Water

Zymark AutoTrace Extraction WorkStation 1.20

1. Wash syringe with 8mL water.
 2. Condition 6mL ENVI-Carb SPE tube (250mg packing) with 10mL water.
 3. Pass 900mL sample through tube.
 4. Rinse tube with 10mL water.
 5. Dry tube with clean gas for 10 minutes.
 6. Elute analytes from tube, using 10mL 80% methylene chloride/ 20% methanol/ 0.01% phosphoric acid.
- Liquid Flow: conditioning, sample delivery, rinsing – 20mL/min;
analyte elution – 5mL/min
- Air Flow: conditioning, rinsing – 20mL/min;
analyte elution – 5mL/min

Table 2. Recovery of Acidic Herbicides*

Analyte	Recovery (%)	Std. Dev.
Tetrachloroterephthalic acid	15.7	—
Picloram	91.5	2.3
Dicamba	91	3.4
2,4-D	88.3	7.1
2,4,5-T	78.7	6.2
2,4,5-TP	84.7	9.9
Dinoseb	95.7	5.7
Dacthal	89.3	4.7
Pentachlorophenol	69.5	7.6

*Concentrations: 4-5ppb; n = 4 extractions.

Ordering Information:

Description	Cat. No.
ENVI-Carb Solid Phase Extraction Tubes	
3mL, 250mg packing, pk. of 54	57088
6mL, 250mg packing, pk. of 30	57092
6mL, 500mg packing, pk. of 30	57094
SUPELCOSIL™ LC-PAH Column	
25cm x 4.6mm ID, 5µm particles	58229

Acknowledgment

The information in Figure A, Table 1, and Table 2 was provided by Dr. Andrew Lichtman, Nassau County Department of Health, Hempstead, New York, 11550 USA.

Trademarks

Dacthal — Diamond Shamrock Corp.
ENVI, SUPELCOSIL — Sigma-Aldrich Co.
Zymark — Zymark

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