

TheReporter

Reprinted from Volume 15, No. 4, 1996

T296044

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Single Solid Phase Extraction Procedure Yields Base/Neutral and Acid Fractions, for HPLC Analysis of Pesticides in Groundwater

C.L. Ritland, S. Cohen, C.J. Mason, Nevada Division of Agriculture
L. Nolan, Supelco

Investigators at the Nevada Division of Agriculture have developed a fast, solvent-conserving, automation-compatible solid phase extraction for concentrating pesticides from 400mL–2-liter samples of groundwater. Base/neutral and acidic pesticides are extracted simultaneously in an ENVI-Carb SPE tube, then are eluted as separate groups. Each fraction is concentrated and analyzed by reversed phase HPLC with diode array detection. Low background in the carbon-based adsorbent allows detection limits of 0.1–5.0µg/liter for 29 monitored compounds.

Under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), the United States Environmental Protection Agency requires states to develop State Management Plans (SMP) for pesticides considered to endanger groundwater. The Nevada Division of Agriculture laboratory (Reno, Nevada, USA) is to assist in monitoring groundwater for those pesticides used in Nevada.

In use at the Nevada laboratory, official methods of sample extraction proved time-consuming and required large amounts of expensive, hazardous solvent that then had to be disposed of. To better serve their needs, these investigators developed a solid phase extraction (SPE) method that is quick, uses minimal solvent, and can be automated. (The Nevada investigators use a Zymark® AutoTrace automated solid phase extraction workstation.) The investigators follow this method in monitoring water samples for 29 base/neutral and acidic pesticides.

The method calls for processing water samples through ENVI™-Carb SPE tubes. In investigations elsewhere, the carbon-based packing in ENVI-Carb tubes has provided superior recovery and less variability for polar analytes, such as acids and bases, while maintaining comparable results for less polar compounds (1–4). In the Nevada analysts' method, base/neutral pesticides and acidic pesticides adsorb to the packing in the ENVI-Carb tube, then are eluted as separate groups by using selective elution steps. Each extract is concentrated, then analyzed by reversed phase HPLC with diode array detection. Chromatograms for representative base/neutral and acidic pesticides, in Figures A and B, respectively, show the analytes are well resolved, and that low background helps to ensure reliable quantification. In developing the procedure, the analysts determined recovery rates for each analyte at 3 times and at 10 times the estimated detection limit (EDL). Recovery rates at the 3x EDL level are summarized in Table 2. Detection limits for 29 monitored compounds ranged from 0.1 to 5.0µg/liter. Sensitivity can be increased by increasing the sample volume from 400mL to

Figure A. Base/Neutral Pesticides in Water, Using SPE/HPLC

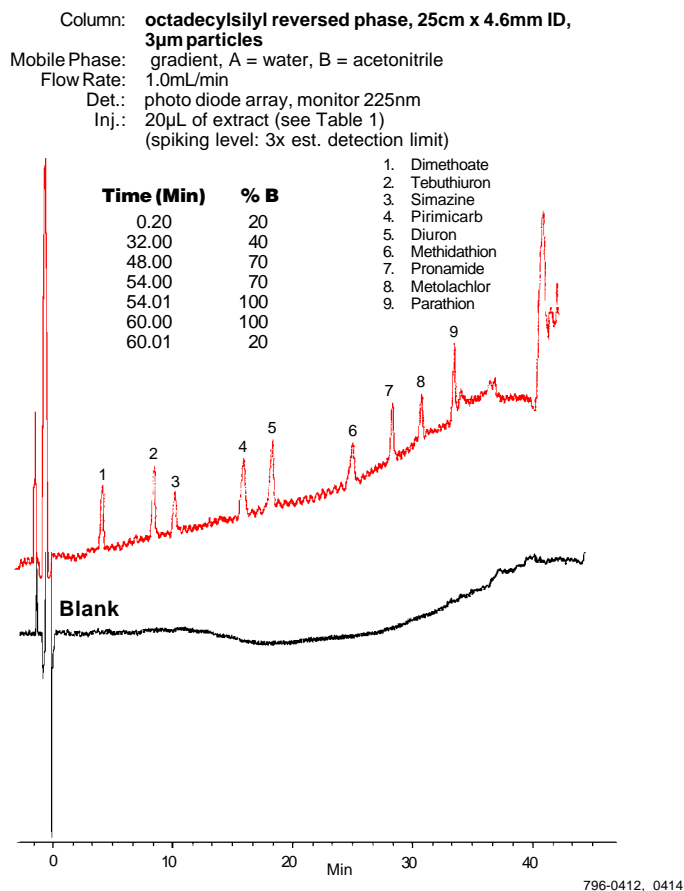


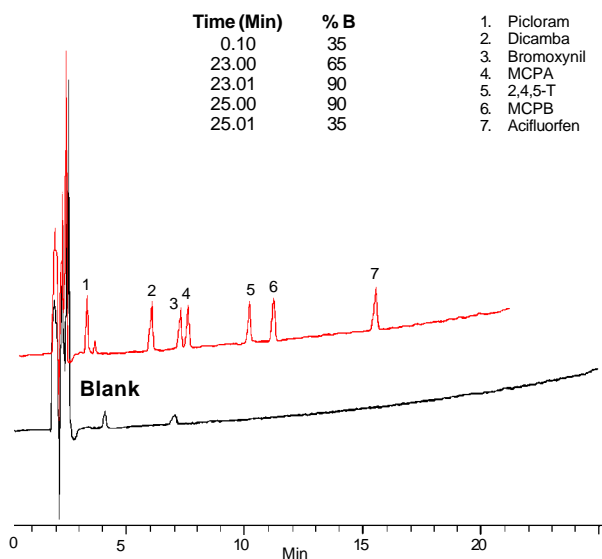
Figure provided by C.L. Ritland, S. Cohen, C.J. Mason, Nevada Div. Agriculture, Reno, Nevada, USA.

2 liters. HPLC with diode array detection showed excellent linearity for all analytes, from 1x EDL to 50x EDL.

The results of this work show that automated solid phase extraction is a viable alternative to time-consuming liquid-liquid extractions for monitoring pesticides in water. The graphitized carbon-based adsorbent medium in ENVI-Carb SPE tubes and a selective elution process effectively separate base/neutral analytes from acidic analytes while ensuring high recovery rates.

Figure B. Acidic Pesticides in Water, Using SPE/HPLC

Column: octadecylsilyl reversed phase, 30cm x 3.9mm ID, 4µm particles
 Mobile Phase: gradient, A = water/0.05% trifluoroacetic acid, B = acetonitrile/0.025% trifluoroacetic acid
 Flow Rate: 1.0mL/min
 Det.: photo diode array, monitor 230nm
 Inj.: 20µL of extract (see Table 1)
 (spiking level: 3x est. detection limit)



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Figure provided by C.L. Ritland, S. Cohen, C.J. Mason, Nevada Div. Agriculture, Reno, Nevada, USA.

Table 1. Procedure for Extracting Pesticides from Water

- Condition ENVI-Carb SPE tube (3mL, 250mg packing) with 5mL methylene chloride:methanol, 4:1, followed by 2mL methanol, followed by 10mL 2% acetic acid.
- Pass 400mL water sample through tube.
- Rinse tube with 10mL water.
- Dry tube with clean nitrogen for 5 minutes.
- Recovery of Base/Neutral Pesticides**
Pass 1mL methanol, then 2 x 2mL methylene chloride:methanol, 4:1 through tube.
Collect all 3 eluates (5mL total) in same recovery vessel.
- Recovery of Acidic Pesticides**
Pass 2 x 2mL methylene chloride:methanol, 3:2 (made basic with 0.016mol/liter KOH) through same tube.
Collect both eluates (4mL total) in same recovery vessel.
Add 350µL 2% trifluoroacetic acid in water (acids eluate only).
- Dry recovered eluates, then reconstitute each with 1mL methanol. Filter. Analyze by RP-HPLC.

Table 2. Recovery of Acidic and Base/Neutral Pesticides

(3x Estimated Detection Limit)

Analyte	Concentration EDL	Concentration (µg/L) in Sample	Recovery (%)	Mean % RSD
Dimethoate	5.0	15.0	89.2	8.0
Tebuthiuron	2.5	7.5	88.7	8.3
Simazine	0.1	0.3	86.2	7.4
Pirimicarb	1.3	3.7	83.4	9.4
Diuron	1.3	3.7	94.9	6.2
Methidathion	1.3	3.7	86.0	18.4
Pronamide	0.8	2.3	85.3	11.9
Metolachlor	0.8	2.3	88.4	18.8
Parathion	2.5	7.5	71.8	13.3
Bromacil	1.3	3.7	98.5	14.1
Cyanazine	0.2	0.6	93.9	18.9
Atrazine	0.2	0.6	95.1	17.4
Prometon	0.3	0.7	98.8	18.1
Chlorpropham	0.4	1.2	50.7	36.9
Alachlor	1.7	5.2	84.5	17.9
Dacthal	1.0	1.9	93.1	29.6
Picloram*	0.5	1.5	99.8	3.6
Dicamba*	1.3	3.7	128.8	12.0
Bromoxynil*	1.0	3.0	89.0	4.6
MCPA*	1.3	3.7	100.3	6.2
2,4,5-T*	1.5	4.5	102.0	6.2
MCPB*	1.2	3.6	93.8	5.4
Acifluorfen*	1.5	4.5	97.7	6.1
Bentazon	1.5	4.5	85.0	2.9
2,4-D	1.5	4.5	98.0	4.0
MCPB	1.3	3.7	92.3	3.2
2,4-DB	1.5	4.5	91.6	4.2
2,4,5-TP	1.5	4.5	95.7	4.0
Dinoseb	2.0	6.0	47.1	31.9

*n = 8, all others n = 9.

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
AutoTrace SPE Tube Adaptors	
Prevent damage to packing bed in SPE tube	
3mL, pk. of 6	57123
6mL, pk. of 6	57126

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Acknowledgment

Information and figures in this article were provided by Christopher Ritland, Sharryn Cohen, and Christopher Mason, Nevada Division of Agriculture, 350 Capitol Hill Avenue, Reno, Nevada USA 89502.

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Reprinted from Volume 15, No. 4, 1996