

Application

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Extract Nonvolatile Pesticides from Drinking Water, Using a Graphitized Carbon Adsorbent

In solid phase extractions of polar analytes from water, recovery rates are higher and show less variation when the extraction is performed with carbon-based Supelclean ENVI-Carb packing, relative to C8- or C18-modified silica packings. The nonporous carbon-based packing also speeds the extraction process without reducing adsorption capacity for these analytes. An effective procedure for extracting carbamate and thiourea pesticides from water is described here.

Key Words:

- carbamates • thioureas • pesticides
- solid phase extraction

Currently, most solid phase extraction (SPE) methods for cleaning, extracting and concentrating pollutants from aqueous environmental samples employ octyl (C8) or octadecyl (C18) phases bonded to a silica support. Using these materials, nonpolar contaminants can be recovered at high rates and with good reproducibility. In most cases, however, polar analytes such as carbamate and thiourea pesticides are recovered at low rates when typical reversed phase extraction conditions are used.

Recovery rates from the carbon-based packing in Supelclean™ ENVI™-Carb solid phase extraction tubes are consistently higher, with less variability, than with liquid-liquid extractions or C8- or C18-silica SPE methods. This study confirmed an SPE method for extracting and concentrating 14 nonvolatile pesticides from drinking water (1), using Supelclean ENVI-Carb tubes. Analyses for these compounds require clean, concentrated samples and quantitative, reproducible pesticide recovery.

Physical characteristics of Supelclean ENVI-Carb carbon and C8- or C18-modified silica are listed in Table 1. Because the carbon-based packing is nonporous, samples can be processed rapidly (adsorption does not require dispersion of analytes into porous regions). Furthermore, although the surface area of the carbon is smaller than that of the porous silica, the carbon's capacity for pesticides is not compromised. The bed weight required is half that needed with the silica packings. The primary surface interaction mechanism is the same for the carbon-based and silica-based packings: nonspecific interaction based on dispersion forces. Supelclean ENVI-Carb carbon also acts as a weak ion exchanger, however (2). This expands the range of analytes it can be used to extract.

The extraction procedure used with Supelclean ENVI-Carb SPE tubes is summarized in Table 2. Sample volumes were 100mL and 1 liter, and pesticide concentrations were 10-50µg/liter.

Table 1. Physical Characteristics of Carbon-Based and Silica-Based Adsorbents

ENVI-Carb Adsorbent	C8- & C18-Modified Silica
graphitized carbon black	silane phase-modified silica gel
hydrophobic	hydrophobic
irregular 40-100µm particles	irregular 40-60µm particles
nonporous	porous (60-300Å)
surface area: 100m ² /g	surface area: 400-600m ² /g

Table 2. Pesticide Extraction from Drinking Water, Using ENVI-Carb Solid Phase Extraction Tubes

SPE Tube:

Supelclean ENVI-Carb, 3mL/0.25g packing

Tube Conditioning:

5mL methylene chloride: methanol (80:20)

1mL methanol

10mL 2% acetic acid in water

Draw solutions through the packing bed consecutively.

Keep packing bed wet until sample is added.

Sample Addition:

100mL-1 liter drinking water (pesticide concentration: 10-50µg/L)

Draw sample through packing at a rate of 5mL/min.

Accelerated rates do not have an adverse effect on recovery.

Drying:

1 minute, vacuum suction

Sample Elution (base-neutral fraction):

0.8-1mL methanol

2 x 3.5mL methylene chloride: methanol (80:20)

Dry eluate under gentle nitrogen purge in a room temperature

water bath to approximately 400-500µL. For best recovery,

wash inside wall of recovery vial with methanol,

again dry to 400-500µL.

Reconstitute samples to a constant volume of 1mL, using methanol.

Inject 20µL for HPLC analysis. Analysis can be automated.

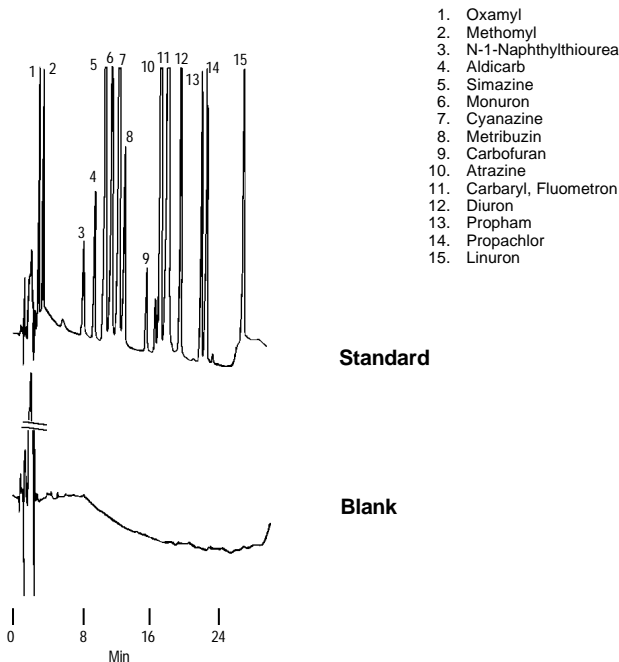
Samples can be passed through Supelclean ENVI-Carb tubes under positive pressure or vacuum. We recommend eluting adsorbed pesticides at a slow (dropwise) rate. To ensure complete removal of dichloromethane, maintain the eluate at room temperature during the drying/vial rinsing/sample re-concentrating process.

Analysis was by HPLC-UV with no derivatization. This approach allows automation of sample preparation with a minimum of cost, equipment, and time. Background in samples extracted with Supelclean ENVI-Carb tubes is negligible (Figure A).

Compared to values from other studies, SPE on ENVI-Carb carbon produced superior recovery and minimum variability for more polar analytes, and comparable results for less polar compounds (Table 3).

Figure A. Nonvolatile Pesticides Extracted from Spiked Water

Column: **SUPELCOSIL LC-18-DB, 25cm x 4.6mm (5µm particles)**
(with Supelguard™ LC-18-DB guard column)
Cat. No.: **58355-U**
Mobile Phase: A - water:acetonitrile, 90:10, B - acetonitrile
20% B (5 min) to 70% B in 30 min
Flow Rate: 1.5mL/min
Det.: UV, 220nm
Inj.: 20µL extract (see Table 2)



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Solid phase extraction of aqueous environmental samples on Supelclean ENVI-Carb tubes offers significant advantages over liquid/liquid extraction or SPE on silica-based packings. Relative to liquid/liquid extractions, SPE eliminates the need for expensive glassware and large volumes of solvent. The technique can also be easily automated, for processing up to 12 or more samples simultaneously. Relative to SPE on silica-based packings, Supelclean ENVI-Carb tubes offer superior, more consistent recovery for a wide range of organic pollutants.

References

- DiCorcia, A. and M. Marchetti, *Anal. Chem.* 63:580 (1991).
- Andreolini, F., et al., *Anal. Chem.* 59:1720 (1987).

References not available from Supelco.

Trademarks

ENVI-Carb, Supelclean, SUPELCOSIL, Supelguard — Sigma-Aldrich Co.

Table 3. Pesticides Recovery is Highest Using Solid Phase Extraction on Carbon-Based Adsorbent

Analyte*	Solid Phase Extraction		Liquid/Liquid
	ENVI-Carb Tubes n=5	C8/C18 Silica* n=4	Extraction** n=4
Oxamyl	95 ±5	53 ±1	55 ±16
Methomyl	97 ±5	43 ±1	74 ±8
Aldicarb	96 ±3	67 ±8	88 ±8
Monuron	97 ±4	90 ±6	90 ±4
Carbaryl	98 ±5	74 ±15	102 ±13
Diuron	98 ±6	90 ±6	94 ±3

*1 liter water samples, HPLC/UV analyses.

**Data from Goodby, *Environmental Lab*, June/July 1990, pp19-58.

Analyte**	Solid Phase Extraction	
	ENVI-Carb Tubes n=5	C8/C18 Silica* n=4
Oxamyl	111 ±9.6	28 ±4.6
Methomyl	105 ±5.0	25 ±4.4
Carbofuran	106 ±6.2	97 ±3.8
Fluometron	106 ±5.7	96 ±4.1
Monuron	99 ±3.2	98 ±6.2
Metribuzin	97 ±3.9	43 ±2.5
Carbaryl	97 ±3.5	90 ±1.2
Propham	95 ±3.2	76 ±2.3
Propachlor	96 ±3.8	90 ±7.5
Aldicarb	96 ±3.5	86 ±1.4
Cyanazine	90 ±5.4	99 ±1.0
Atrazine	89 ±5.7	74 ±1.4
Diuron	88 ±5.7	91 ±7.8
Linuron	88 ±5.4	94 ±4.1

**100mL water samples, 10-50µg/liter (ENVI-Carb extracts) or 20-500µg/liter (C8/C18 silica), HPLC/UV (ENVI-Carb extracts) or HPLC/MS (C8/C18 silica) analysis.

*Data from Bellar & Budde, *Anal. Chem.*, 60: 2076-2083 (1988).

Ordering Information:

Description	Cat. No.
Supelclean ENVI-Carb SPE Tubes	
3mL/0.25g, pk. of 54	57088
6mL/0.25g, pk. of 30	57092
6mL/0.5g, pk. of 30	57094
12mL/1g, pk. of 20	57127-U
12mL/2g, pk. of 20	57128
20mL/5g, pk. of 20	57129
60mL/10g, pk. of 16	57130
SUPELCOSIL™ LC-18-DB HPLC Column	
25cm x 4.6mm	58355-U

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