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Solid Phase Extraction of Pesticides from Fruits and Vegetables, for Analysis by GC or HPLC

L. Nolan

Recovery rates for polar analytes such as carbamate and thiourea pesticides are higher, and less variable, with ENVI-Carb carbon-based solid phase extraction tubes than with C8- or C18- silica-based tubes. In an independent study, ENVI-Carb tubes proved to be an effective part of sample cleanup for more than 200 organochlorine, organophosphorus, nitrogen-containing, and carbamate pesticides, from a wide variety of fruits and vegetables. Analysis for most of these pesticides is by GC; 10 carbamate pesticides are analyzed by HPLC.

Concern over pesticide residues in fruits and vegetables has led to the development of many methods for monitoring these compounds. At the same time, regulatory agencies and concerned analysts are attempting to reduce the amounts of organic solvents used in sample preparation. Solid phase extraction has proven very effective for cleaning, extracting, and concentrating pollutants in analyses of environmental samples. Currently, many SPE methods for extracting pollutants from aqueous environmental samples employ octyl (C8) or octadecyl (C18) phases bonded to a silica support. Using these materials, nonpolar analytes can be recovered at high rates and with good reproducibility. Often, however, polar analytes such as carbamate and thiourea pesticides are recovered at low rates when typical reversed phase extraction conditions are used.

Relative to liquid-liquid extraction or SPE with silica-based packings, pesticide extraction using ENVI™-Carb carbon-based packing provides more uniform recovery of a wide variety of nonvolatile analytes. In comparison to values for similar compounds in other studies, SPE on ENVI-Carb carbon produced superior recovery and minimum variability for more polar analytes, such as acids and bases, while maintaining comparable results for less polar compounds (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 nonporous carbon is smaller than that of the porous silica (100m²/g, versus 400-600m²/g), the carbon's capacity for pesticides is not compromised. The bed weight typically required is only one half that needed with the silica-based packings.

Investigators at Agriculture and Agri-Food Canada (Ottawa, Ontario) have developed a multiple-residue cleanup and analysis for monitoring more than 200 organochlorine, organophosphorus, nitrogen-containing, and carbamate pesticides in fruit and vegetable samples. Their flexible system allows quick screening of

Table 1. Pesticide Recovery Is Highest Using ENVI-Carb SPE Tubes

Analyte	Recovery (% ± standard deviation)		
	ENVI-Carb [#] n=5	Solid Phase Extraction C8/C18 Silica* n=4	Liquid/Liquid 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 Supelco laboratories.

*Data from B.E. Goodby, *Environmental Laboratory*, June/July 1990, pp19-58.

“rush” samples as well as thorough cleanup of complex samples. These investigators evaluated the potential value of ENVI-Carb SPE tubes in their procedure, using the process summarized in Table 2. Typical results are summarized in Table 3. (Data for many additional pesticides are available – request Bulletin 900.)

Initially, these authors followed a sample extraction procedure that required preparing and using extraction minicolumns containing a mixture of charcoal and Celite® (1), but with ENVI-Carb tubes they were able to recover several pesticides that were not recoverable on charcoal/Celite minicolumns. This led the investigators to replace the charcoal/Celite minicolumns with ENVI-Carb SPE tubes, and eliminate the labor-intensive minicolumn preparation process.

In the preparation of fruit and vegetable extracts for multiple-residue analysis, additional purification is necessary. Polar interferences from the sample matrix are removed by coupling an aminopropyl-silica-based SPE tube to the ENVI-Carb tube. Under these conditions, recovery of the pesticides is equally good, except for Folpet. In the Canadian group's sample-screening applications, the analysis for organochlorine, organophosphorus, and nitrogen-containing pesticides (more than 200 compounds) is by capillary gas chromatography with mass-specific detection; residues are identified by retention time and ion ratios. Analysis for 10 carbamates is by HPLC with fluorescence detection. Analytes monitored in each GC run (approximately 115 compounds and 80 compounds, respectively) are listed, along with recovery rates and limits of detection, in (1). Postcolumn derivatization and HPLC columns and conditions are described in (2).

Table 2. Extraction of Pesticides from Fruits and Vegetables

1. Homogenize 50g chopped sample with 100mL acetonitrile (e.g., Omni-mixer, half-speed, 5 min).
2. Add 10g sodium chloride (= 8mL in a graduated cylinder). Homogenize 5 min.
3. Transfer ~13mL of acetonitrile (top) layer to 15mL graduated centrifuge tube.
4. Add ~3g sodium sulfate (liquid level to 15mL mark), cap, shake well to remove water.
5. Centrifuge at high speed for 5 min.
6. Transfer 10mL aliquot (= 5g of sample) to a clean 15mL tube. Evaporate to 0.5mL under clean nitrogen (water bath, 35°C).
7. Transfer to ENVI-Carb SPE tube (6mL tube, 500mg packing).
8. Elute pesticides with 20mL acetonitrile/toluene (3:1).
9. Using a rotary evaporator, concentrate sample to ~2mL. Add 2 x 10mL acetone, concentrating the material to ~2mL after each addition, to make a solvent exchange to acetone.
10. Transfer quantitatively to a clean 15mL tube. Add 50µL internal standard (50ng/µL cis-chlordane in acetone), then bring volume to 2.5mL with acetone (final concentrations = 2g/mL extract, 1.0ng/µL cis-chlordane).

GC/mass-specific detection (for organochlorine, organophosphorus, nitrogen-containing pesticides)

1. Set aside 0.5mL final extract for GC/MSD analysis. For chromatography, refer to reference 1.

HPLC/postcolumn derivatization/fluorescence detection (for carbamates)

1. Concentrate remaining 2.0mL final extract to 0.2mL.
2. Add 20µL internal standard (40ng/µL isoprocarb in methanol), then bring volume to 0.8mL with water (pH 3.0 with 36.5–38% HCl/water, 1:4), filter with 0.45µm pore filter (final concentration = 1.0ng/µL isoprocarb). For chromatography, refer to reference 2.

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

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 Adapters	
For using ENVI-Carb tubes with Zymark® AutoTrace unit.	
3mL, pk. of 6	57123
6mL, pk. of 6	57126

References

1. Fillion, J., R. Hindle, M. Lacroix, and J. Selwyn, *Journal AOAC International*, **78**: 1252-1266 (1995).
 2. Chaput, D., *J. Assoc. Official Analytical Chemists*, **71**: 542-546 (1988).
- References not available from Supelco.
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Table 3. Recovery of Pesticides from Fruits and Vegetables, Using ENVI-Carb SPE Tubes

Analyte	Mean % Recov.	Std. Dev.	% C.V.	n=	Commodity/% Recovery						
					Kiwi Fruit	Pine-apple	Beets	Sweet Potato	Squash	Snow Peas	Green Peas
Organochlorine Pesticides											
Aldrin	92.3	5.3	5.7	7	92	95	92	99	97	86	85
α-BHC	93.3	4.4	4.7	7	96	94	88	100	96	89	90
p,p'-DDE	97.7	7.2	7.4	7	103	100	98	105	102	91	85
p,p'-DDT	96.6	9.1	9.4	7	102	97	99	106	102	91	79
Dieldrin	96.9	5.1	5.2	7	97	97	96	104	102	93	89
Endosulfan sulfate	97.4	9.1	9.4	7	106	98	93	110	101	90	84
Endrin	95.0	5.5	5.8	7	88	91	98	103	100	94	91
Heptachlor	92.6	5.0	5.4	7	90	94	92	101	96	89	86
Lindane (γ-BHC)	96.1	5.0	5.2	7	98	98	90	104	99	92	92
Mirex	96.4	8.9	9.2	7	102	98	98	104	102	93	78
Methoxychlor	99.1	5.9	5.9	7	104	98	98	107	103	93	91
Nitrogen-Containing Pesticides/Triazines											
Atrazine	94.7	14.7	15.5	7	67	83	103	109	104	97	100
Cyanazine	96.7	6.5	6.7	6		98	93	108	98	94	89
Cyprazine	95.7	6.8	7.1	6		99	87	104	94	89	101
Prometon	89.6	10.4	11.6	7	75	81	87	104	96	85	99
Simazine	95.1	15.8	16.6	7	67	80	102	110	107	97	103
Organophosphorus Pesticides											
Azinphos-ethyl	92.6	15.0	16.2	7	65	80	95	105	103	95	105
Chlorpyrifos	97.9	5.9	6.0	7	99	99	94	106	104	90	93
Coumaphos	94.9	11.4	12.0	7	78	96	92	101	85	99	113
Diazinon	96.9	5.6	5.8	7	90	95	99	107	99	92	96
Dimethoate	99.3	4.6	4.6	7	105	100	95	104	99	92	100
Disulfoton	71.0	25.4	35.8	7	24	94	57	92	92	64	74
Ethoprophos	92.0	9.8	10.7	7	85	107	83	104	91	83	91
Malathion	97.6	6.3	6.5	7	99	101	92	109	98	91	93
Methamidophos	64.9	8.3	12.7	7	57	72	59	79	57	65	65
Terbufos	89.0	8.7	9.8	7	76	93	84	101	97	83	89

Acknowledgment

The extraction process in Table 2 and data in Table 3 were provided by J. Fillion and J.C. Selwyn, Agriculture and Agri-Food Canada (Laboratory Services Division, Pesticide Laboratory), Ottawa, Ontario.