

Solid Phase Microextraction of Organophosphate Insecticides and Analysis by Capillary GC/MS

SPME was used to extract an aquatic sample for analysis of organophosphate insecticides by gas chromatography/mass spectrometry (GC/MS). An SPME fiber coated with 85µm of polyacrylate yielded detection limits ranging from 0.10 to 0.56µg/L. SPME is a quick and highly sensitive sample preparation technique that eliminates the use of solvents.

Key Words:

- organophosphate insecticides
- gas chromatography
- solid phase microextraction
- mass spectrometry

Low levels of organophosphate insecticides in aquatic environments can be toxic to cladoceran species and other organisms. Investigators at The Stover Group (Stillwater, OK, USA) used solid phase microextraction (SPME) to extract organophosphate insecticides from an aquatic sample for analysis by gas chromatography/mass spectrometry (GC/MS).

SPME is a solventless sample preparation technique that eliminates most extraction drawbacks. The SPME unit includes a holder and a length of phase-coated fused silica fiber bonded to a stainless steel plunger. The fiber is introduced into a sample or headspace, and analytes of interest establish equilibrium and adsorb in the phase. The analytes are desorbed from the fiber to a capillary GC column by the heated chromatograph injection port, where they are focused on the front of the column. The technique is quick and highly sensitive. Also, problems associated with solvent use and disposal are largely eliminated.

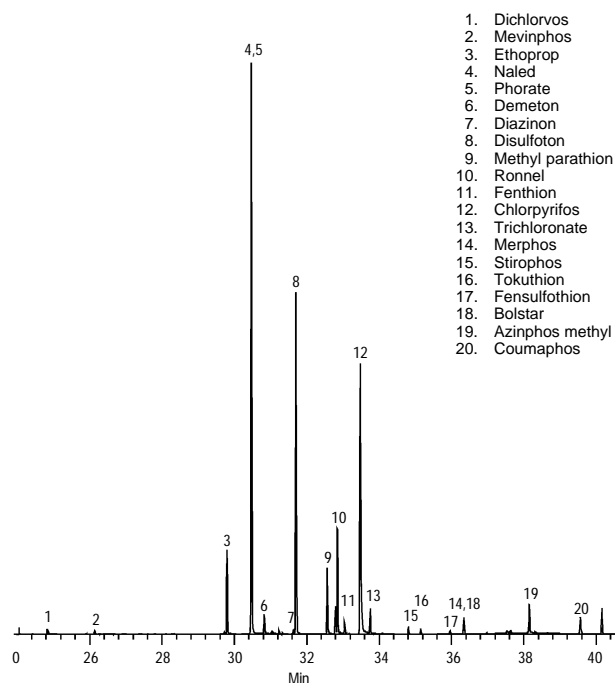
Using a polar SPME fiber, coated with 85µm of polyacrylate, the investigators observed detection limits of 20 insecticides ranging from 0.10 to 0.56µg/L (Table 1). Conditions for the extraction and GC/MS analysis are shown in Figure A.

In subsequent method development, the investigators used GC/MS single ion monitoring to achieve theoretical method detection limits of some insecticides to approximately 0.05µg/L. They have applied this technology to the target list of organophosphate insecticides for method optimization.

SPME analyses of other classes of pesticides are summarized in Supelco literature, available free of charge. Request publication 394058, *Fast Screening for Chlorinated Pesticides by Solid Phase Microextraction/Capillary GC*, and publication 395085, *Solid Phase Microextraction/Capillary GC Analysis of Nitrogen-Containing Herbicides in Water*.

Figure A. Organophosphate Pesticides

Sample: 35mL in 40mL vial (exposed to 4M NaCl, pH 2)
SPME Fiber: 85µm polyacrylate
Cat. No.: 57304 (manual sampling)
Extraction: immersion, 240 min, rapid stirring
Desorption: 5 min, 310°C
Column: crosslinked 5% phenyl methyl silicon, 30m x 0.25mm ID, 0.25µm film
Oven: 35°C (15 min) to 300°C at 10°C/min, hold 5 min
Carrier: helium, 1mL/min
Det.: MS (EM Voltage: relative +700, single ion monitoring)



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This investigation was conducted by D.J. Fort, C.R. Powers, J.K. Delphon, S.L. Burks, and E.L. Stover, The Stover Group, PO Box 2056, Stillwater, OK 74076 USA (phone 405-624-0018).

Additional Literature Relating to SPME of Organophosphate Pesticides

Analysis of Organophosphorus Insecticides from Environmental Samples Using SPME, Magdic, S., Boyd-Boland, A., Jinno, K., Pawliszyn, J., *J. Chromatogr. A* **736**: 219-228 (1996).

Matrix Effects on SPME of Organophosphorus Pesticides from Water, Valor, I., Molto, J., Apraiz, D., Font, G. *J. Chromatogr. A* **767**: 195-203 (1997).

Solid Phase Microextraction of Organophosphorus Pesticides from Water, Sing, M., Lee, F., Lakso, H. *J. Chromatogr. A* **759**: 225-230 (1997).

References not available from Supelco.

Table 1. Method Detection Limits of Organophosphate Insecticides

Peak No.	Compound	Approx. Concentration (µg/L)	Approx. Method Detection Limit (µg/L)
1.	Dichlorvos	3.13	0.11
2.	Mevinphos	3.15	0.10
3.	Ethoprop	2.91	0.10
4.	Naled	2.76	0.10
5.	Phorate	3.12	0.33
6.	Demeton	3.32	0.10
7.	Diazinon	2.96	0.10
8.	Disulfoton	3.09	0.12
9.	Methyl parathion	3.09	0.56
10.	Ronnel	2.93	0.10
11.	Fenthion	3.09	0.21
12.	Chlorpyrifos	2.82	0.10
13.	Trichloronate	2.98	0.10
14.	Merphos	3.37	0.10
15.	Stirophos	3.03	0.34
16.	Tokuthion	3.18	0.10
17.	Fensulfothion	3.09	0.28
18.	Bolstar	3.09	0.10
19.	Azinphos methyl	2.89	0.10
20.	Coumaphos	3.04	0.55

Ordering Information:

Description	Cat. No.
PTE-5 Capillary Column	
30m x 0.25mm ID, 0.25µm film	24135-U
SPME Holder*	
For manual sampling	57330-U
For Varian 8100/8200 AutoSampler (requires Varian SPME upgrade kit)	57331
SPME Fiber Assembly (pk. of 3)	
85µm polyacrylate coating (nonpolar)	
For manual sampling	57304
For Varian 8100/8200 AutoSampler	57305
7µm polydimethylsiloxane coating (nonpolar)	
For manual sampling	57302
For Varian 8100/8200 AutoSampler	57303
100µm polydimethylsiloxane coating (nonpolar)	
For manual sampling	57300-U
For Varian 8100/8200 AutoSampler	57301
30µm polydimethylsiloxane coating (nonpolar)	
For manual sampling	57308
For Varian 8100/8200 AutoSampler	57309
65µm polydimethylsiloxane/divinylbenzene coating (polar)	
For manual sampling	57310-U
For Varian 8100/8200 AutoSampler	57312
65µm Carbowax®/divinylbenzene coating (polar)	
For manual sampling	57311
For Varian 8100/8200 AutoSampler	57313

Description	Cat. No.
SPME Assortment Fiber Pack	
One fiber each of 85µm polyacrylate coating and 100µm and 7µm polydimethylsiloxane coating	
For manual sampling	57306
For Varian 8100/8200 AutoSampler	57307
SPME Sampling Stand	
Supports an SPME holder; includes a rotating puck for eight 4mL vials	57333-U
SPME Inserts and Inlet Liners	
Inserts, Varian SPI Models 1093-94SP1, Series 3000 GC	
each	26364,01
pk. of 5	26364,05
pk. of 25	26364,25
Inlet Liners, Splitless, 0.75mm ID [#]	
For Hewlett-Packard GC - 5700, 5800, 5890	
each	26375,01
pk. of 5	26375,05
pk. of 25	26375,25
For Varian GCs (all)	
each	26358,01
pk. of 5	26358,05
pk. of 25	26358,25
Vials, Hole Caps, Teflon®/Silica Septa	
Screw Top Vials for Varian 8100/8200 AutoSampler	
Clear, 2mL, pk. of 100	27124-U
Amber, 2mL, pk. of 100	27005
Headspace Vials	
Clear, 4mL, pk. of 10	26901
pk. of 100	27136
Amber, 4mL, pk. of 10	26930
pk. of 100	27006
Thermogreen™ LB-2 Septa, Pre-Drilled*	
11mm, pk. of 25	23167
11mm, pk. of 50	23168
9.5mm, pk. of 25	23161
9.5mm, pk. of 50	23162-U
For additional SPME fibers, fiber kits, and SPME accessories, refer to the Supelco catalog.	
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PTE, Thermogreen – Sigma-Aldrich Co.	
Teflon – E.I. du Pont de Nemours & Co., Inc.	
*Technology licensed exclusively to Supelco (US patent 5,691,206; European patent #0523092).	
*First time users must order both holder and fiber assembly. Holder is reusable indefinitely.	
*You can reduce inlet volume by replacing a standard 2mm ID liner with this specially designed liner. This increases sensitivity and provides sharper peaks.	
*Pre-drilled septa reduce septum coring that can cause extraneous peaks.	
Contact our Technical Service Department (phone 800-359-3041 or 814-359-3041, FAX 800-359-3044 or 814-359-5468) for expert answers to your questions.	

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