Application Note 58

Fast Screening for Chlorinated Pesticides by Solid Phase Microextraction/Capillary GC

Fast analysis of environmental samples increases throughput in the lab and is highly desirable for "quick turnaround" screening methods used in the field or prior to GC/MS analysis. Solid phase microextraction is a fast, solventless alternative to conventional sample extraction techniques. Because no solvent is injected, and the analytes are rapidly desorbed onto the column, short, narrow bore columns can be used. This greatly reduces analysis time and improves minimum detection limits, while maintaining resolution. SPME can be effective in screening samples for chlorinated pesticides, or as an alternative extraction method in a formal analysis.

Key Words:
- pesticides • chlorinated pesticides
- solid phase microextraction

In analyses of chlorinated pesticides in wastewater or other environmental samples, the pesticides usually are extracted by liquid-liquid extraction or with solid phase extraction (SPE) cartridges or disks. These methods are time consuming (4-18 hours by liquid-liquid extraction, 1-2 hours by SPE) and labor intensive (20-45 minutes of handling time per sample), and liquid-liquid extractions require large volumes of sample and solvents. In addition, because pesticides generally are present at ppt levels, mixed with other contaminants at higher concentrations, interfering compounds can produce extraneous peaks. Liquid-liquid extraction and SPE can carry contaminants into the final sample, producing a high background. SPE cartridges and, particularly, disks are prone to clogging with samples that contain large amounts of sediment.

In contrast, a new approach to concentrating many analytes, solid phase microextraction (SPME), is faster (15 minutes) and much less labor intensive (about 3 minutes of handling time per sample), and requires only small amounts of sample and no organic solvents. SPME also provides a low background. Less interference makes analyte identification and quantification more reliable.

SPME is a solventless extraction procedure▲ that does not require complex instrumentation. The technique simply involves immersing a phase-coated fused silica fiber into the liquid sample or the headspace above the sample. Pesticides or other compounds of interest adsorb to the phase, then are thermally desorbed in the injection port of the GC and transferred to the capillary column. The time required to reach adsorption equilibrium depends on the distribution constants of the analytes and the thickness of the phase. (Consistent timing is more important than full equilibrium.) Selectivity can be altered by changing the phase type or the coating thickness. Agitation, addition of salt, pH adjustment, and/or immersion of the fiber in the sample, rather than the headspace, improve recovery of difficult-to-extract compounds. Table 1, the relative responses for a series of ten extractions of chlorinated pesticides, shows that SPME is consistent in routine use. The thick film 100µm and 30µm PDMS fibers can be thoroughly cleaned between uses in a Hamilton® heated syringe cleaner (120 VAC; Supelco Cat. No. 20770-U).

Table 1. Precise Relative Responses for Chlorinated Pesticides at 50ppt

Compound	Relative Response (n = 10) Mean	Std. Dev.	% RSD
α-BHC	0.72	0.07	9.2
β-BHC	0.06	0.01	19.1
γ-BHC	0.53	0.06	10.5
δ-BHC	0.28	0.03	11.9
Heptachlor	1.01	0.10	10.2
Aldrin	1.25	0.06	4.8
Heptachlor epoxide	0.92	0.12	13.2
γ-Chlordane	0.97	0.12	9.9
Endosulfan I	0.87	0.10	11.1
α-Chlordane	0.92	0.11	10.1
4,4'-DDE	0.92	0.07	8.1
Dieldrin	0.83	0.08	9.5
Endrin	0.68	0.06	9.1
Endosulfan II	0.72	0.09	13.0
4,4'-DDD	0.69	0.06	8.9
Endrin aldehyde	0.13	0.04	28.6
Endosulfan sulfate	0.54	0.06	11.9
4,4'-DDT	0.51	0.08	15.2
Endrin ketone	0.57	0.06	10.7
Methoxychlor	0.26	0.04	16.2

SPME: **100µm PDMS phase fiber** immersed in 4mL water (15 min, rapid stirring)
Cat. No.: **57300-U**

Column: **SPB-5, 15m x 0.20mm ID, 0.20µm film**
Cat. No.: **24165-U**
Oven Temp.: 120°C (1 min) to 180°C at 30°C/min, then to 290°C at 10°C/min
Carrier: helium, 37cm/sec (set at 120°C)
Det.: ECD, 300°C

Chlorinated pesticides can be analyzed on a 15m x 0.20mm ID x 0.20µm phase film SPB™-5 or SPB-608 column – either will resolve all of the pesticides listed in Table 1. Columns typically used for this analysis are 30 meters long x 0.25mm ID, to accommodate solvent injection. Because SPME does not introduce solvent onto the column, the shorter, narrower column and a higher initial temperature can be used. The short column/high temperature combination reduces analysis time by 10-15 minutes per sample. Figure A shows a dual column analysis of these pesticides following extraction from water by SPME. All analytes were identified and quantified in less than 15 minutes. The 15m x 0.20mm ID columns were easy to install as a pair and it was not difficult to match flow rates. Figure A also shows pesticides from hazardous waste on the SPB-608 column.

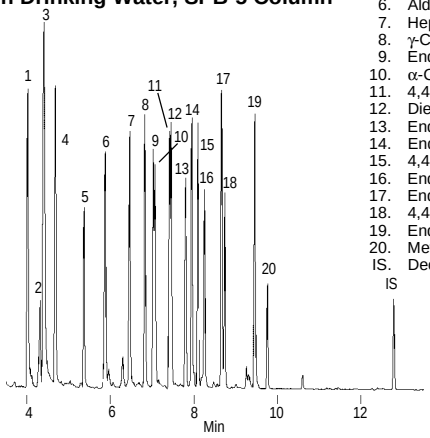
Figure A. Chlorinated Pesticides By SPME/GC

SPME: **100µm PDMS phase fiber**
immersed in 4mL water (15 min)
Cat. No.: **57300-U**

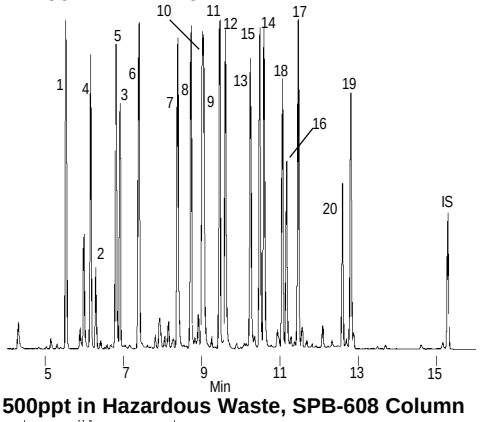
Columns: 15m x 0.20mm ID, 0.20µm film
Cat. Nos.: **SPB-5 — 24165-U; SPB-608 — available on request**
Oven Temp.: 120°C (1 min) to 180°C at 30°C/min, then to 290°C at 10°C/min
Carrier: helium, 37cm/sec (set at 120°C)
Det.: ECD, 300°C
Inj.: 260°C (splitless - closed 3 min)

1. α-BHC
2. β-BHC
3. γ-BHC
4. δ-BHC
5. Heptachlor
6. Aldrin
7. Heptachlor epoxide
8. γ-Chlordane
9. Endosulfan I
10. α-Chlordane
11. 4,4'-DDE
12. Dieldrin
13. Endrin
14. Endosulfan II
15. 4,4'-DDD
16. Endrin aldehyde
17. Endosulfan sulfate
18. 4,4'-DDT
19. Endrin ketone
20. Methoxychlor
IS. Decachlorobiphenyl

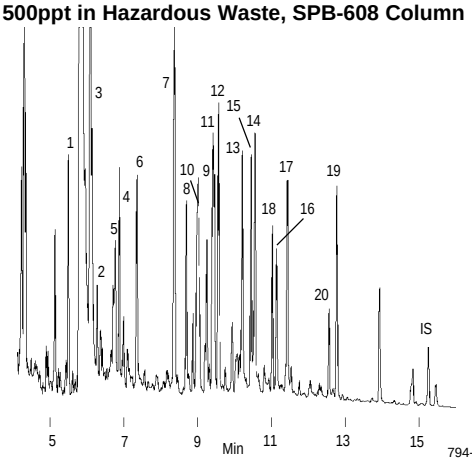
200ppt in Drinking Water, SPB-5 Column



200ppt in Drinking Water, SPB-608 Column



500ppt in Hazardous Waste, SPB-608 Column



794-0441,0442,0443

The combination of extraction by SPME and analysis on short capillary columns can greatly increase the number of samples screened in a day. SPME can be used for screening samples on site or prior to GC/MS analysis. Samples found to be highly concentrated can be diluted prior to the GC/MS analysis. SPME is equally compatible with the conditions required by a GC/MS system, however, and thus can be part of the formal analysis for pesticides.

The results summarized here show that SPME is fast, easy, and compatible with short, narrow bore capillary columns that provide fast analyses. Chlorinated pesticides can be extracted with good accuracy, even from wastewater or hazardous waste samples that contain high concentrations of contaminants. Because the apparatus is portable and easy to use, SPME can be employed in the field for quick turnaround methods, or for screening a sample prior to GC/MS analysis. Precision and accuracy also make SPME effective in quantitative analyses. If your environmental analyses involve these or other analytes, SPME can be the ideal answer to your sample preparation needs.

Ordering Information:

Description	Cat. No.	Cat. No.
SPME Holder		
Initially you must order both holder and fiber assembly. Holder is reusable indefinitely.		
For manual sampling	**57330-U**	
For Varian 8100/8200 AutoSampler (requires Varian SPME upgrade kit)	**57331**	
SPME Fiber Assembly (pk. of 3)		
Polydimethylsiloxane coating	**100µm**	**30µm**
For manual sampling	**57300-U**	**57308**
For Varian 8100/8200 AutoSampler	**57301**	**57309**
Capillary GC Columns		
15m x 0.20mm ID, 0.20µm film		
SPB-5	**24165-U**	
SPB-608	available on request	

For many other SPME fiber types refer to the current Supelco catalog.

▲Technology licensed exclusively to Supelco. US patent 5,691,206; European patent #0523092.

Trademarks

SPB — Sigma-Aldrich Co.
Hamilton — Hamilton Co.

Fused silica columns manufactured under HP US Pat. No. 4,293,415.

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.