Application Note 143

Field Sampling for Pesticides, Using Solid Phase Microextraction/Capillary GC

An SPME Portable Field Sampler can be used to extract analytes from samples in the field, then store them for up to 3 days, or longer, before performing the analysis. A field sampler with a 100µm polydimethylsiloxane-coated fiber extracts chlorinated, organophosphorus, triazine, and other pesticides from water. After 24 hours of storage, analyte loss from storage containers was far greater than loss from a field sampler – more than 70%, versus 10-15%.

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

By optimizing extraction conditions according to the matrix and the class of analytes, solid phase microextraction (SPME)▲ can be used to monitor chlorinated pesticides, organophosphorus pesticides, carbamates, and other pesticides in water, soil, and food samples.*

Figure A. SPME Portable Field Sampler

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The SPME Portable Field Sampler (Figure A) enables environmental analysts to extract samples in the field, store them on the SPME fiber, and analyze the adsorbed analytes without additional processing after returning to the lab. The field sampler is simple to use: expose the fiber to the sample, then retract the fiber within a septum seal. The highly retentive fiber and the sealing mechanism enable you to store the sample for up to three days, or longer. To perform the analysis, simply insert the fiber into the injection port of your GC, for thermal desorption of the analytes to the column. Ultimately, when the fiber loses its analyte-extracting ability (typically 50-100 samples), replace the entire sampler. The field sampler is a simple, reliable sampling unit that can be used at remote locations, without the problems of filling vials or bottles, transporting bulky containers to the laboratory, and ultimately disposing of them – and it provides superior analyte recovery.

Table 1. Negligible Difference in Pesticide Response After 3 Days Storage on 100µm SPME Fiber

Analyte	% Difference▽	Analyte	% Difference▽
Chlorinated Pesticides		*Organophosphorus/Triazine Pesticides*	
α-BHC	- 5.4	TEPP	4
β-BHC	- 3.2	Thionazin	- 5
γ-BHC	- 7.4	Sulfotep	- 4
δ-BHC	- 4.7	Phorate	- 10
Heptachlor	- 2.3	Dimethoate	- 15
Aldrin	1.3	Simazine (triazine)	- 13
Heptachlor epoxide	3.3	Atrazine (triazine)	- 5
Endosulfan I	3.7	Disulfoton	- 9
4,4'-DDE	- 6.3	Methyl parathion	- 7
Dieldrin	3.1	Malathion	4
Endrin	- 11.6	Parathion	- 1
Endosulfan II	- 6.2	Famphur	- 9
4,4'-DDD	14.2	**Mean Difference**	**- 6%**
Endrin aldehyde	- 6.0		
Endosulfan sulfate	- 5.6		
4,4'-DDT	- 7.2		
Endrin ketone	- 5.8		
Methoxychlor	0.1		
Mean Difference	**- 2.6%**		

▽% Difference =
$$\frac{\text{(response after 3 days/4°C) – (response immediately after extraction)}}{\text{response immediately after extraction}}$$

SPME Fiber: 100µm PDMS
Cat. No.: **504823** (portable field sampler)
Sample: Pesticides in water / 25% NaCl, pH = 8
4mL sample in 4mL vial
Extraction: 20 min (direct immersion, constant stirring)
Desorption: 10 min, 260°C

A field sampler containing a 100µm PDMS fiber was developed specifically for extracting pesticides and other semivolatile organic compounds from water. The fiber very effectively retains chlorinated, organophosphorus, and triazine analytes for at least 3 days at 4°C (Table 1). In fact, after 24 hours of storage, analyte losses from whole samples in storage containers were far greater than losses from the field sampler – more than 70%, versus 10-15% (Table 2).

Figure B shows a chromatogram of the extracted pesticides, using an ion trap mass spectrometer. SPME and ion traps are very compatible, because SPME does not introduce a large solvent peak or a large amount of water into the trap. Compared to the extractions summarized in Tables 1 and 2, the extraction time was increased from 20 min to 30 min to improve precision. Salt was

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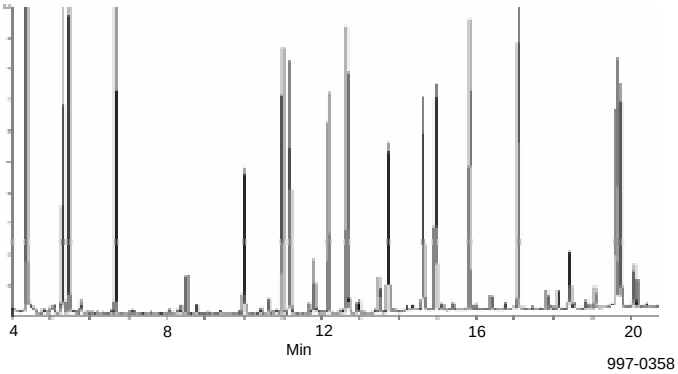
Figure B. Pesticides at 10ppb in Water, Using SPME-GC/MS

SPME Fiber: 100µm PDMS
Cat. No.: **504823** (portable field sampler)
Sample: Pesticides in water / 25% NaCl, pH = 8
4mL sample in 4mL vial
Extraction: 30 min (direct immersion, constant stirring)
Desorption: 10 min, 260°C
Column: Meridian MDN-5, 30m x 0.25mm x 0.25µm
Oven: 50°C (1.5 min) to 150°C at 50°C/min, hold 1 min, to 230°C at 8°C/min, to 300° at 12°C/min, hold 7min
Inj.: splitless/split closed 2 min at 260°C (0.75mm liner, Jade valve)
Det.: Ion trap MS (scan range m/z = 45-450, 0.6sec/scan)

	Analyte	Class
1.	o,o,o-Triethylphosphorothioate	organophos
2.	Thionazin	organophos
3.	Sulfotep	organophos
4.	Phorate	organophos
5.	Simazine	triazine
6.	Atrazine	triazine
7.	Lindane (γ-BHC)	chlorinated
8.	Disulfoton	organophos
9.	Methyl parathion	organophos
10.	Malathion	organophos
11.	Parathion	organophos
12.	Heptachlor epoxide	chlorinated
13.	4,4'-DDE	chlorinated
14.	Famphur	organophos
15.	Endrin ketone	chlorinated
16.	Methoxychlor	chlorinated



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added to improve extraction efficiency, and a pH of 8 appeared to be optimum for most of these pesticides. Recovery of triazines was improved at a slightly acidic pH.

Table 2 shows recovery of extracted analytes stored on the SPME fiber for 24 hours, then analyzed, and recovery of analytes from water samples stored for 24 hours, followed by extraction and analysis. These data show that storing water samples – even at 4°C – can produce unreliable results. The recovery from silanized glass containers was slightly better than from non-silanized glass containers (data not shown), but container deactivation did not improve overall recovery, as expected.

Losses were smaller for analytes stored on the fiber at 4°C than at room temperature (Table 2), but the differences were not great. When possible, an SPME fiber containing extracted analytes should be stored at reduced temperature. Precautions always should be taken to minimize analyte loss on storage.

In summary, the data in Table 2 show that it generally is best to extract samples in the field, rather than store them for later analysis, *but storage on a 100µm PDMS SPME fiber is superior to storage of intact samples in glass or plastic containers.*

Table 2. Difference in Analyte Response after 24 Hours of Storage Compared to Response for Freshly Prepared, Extracted, and Analyzed Samples

	Treatment ▽ / % Difference			
Analyte	**Fiber/4°C**	**Fiber/RT**	**Water/4°C**	**Water/RT**
TEPP	- 8	- 33	- 54	- 67
Thionazin	- 3	9	- 68	- 75
Sulfotep	4	- 23	- 81	- 88
Phorate	- 3	- 27	- 84	- 95
Simazine	- 10	3	- 53	- 50
Atrazine	- 15	1	- 57	- 55
Lindane	- 2	- 12	- 74	- 75
Disulfoton	- 8	- 34	- 93	- 95
Methyl parathion	- 7	- 7	- 68	- 73
Malathion	- 6	- 6	- 74	- 78
Parathion	- 15	- 26	- 83	- 84
Heptachlor epoxide	- 12	- 21	- 83	- 90
DDE	- 12	- 23	- 98	- 94
Famphur	- 3	2	- 60	- 61
Endrin ketone	- 10	- 15	- 82	- 82
Methoxychlor	-14	- 25	- 88	- 89
Mean Difference	**- 8%**	**- 15%**	**- 75%**	**- 78%**

▽RT = room temperature.

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These data show that a single type of SPME fiber – a 100µm PDMS fiber – can be used to extract a variety of pesticides. The extraction technique easily can be adapted to use in the field, with minimal equipment, by the development of the portable field sampler. Analytes stored on the SPME fiber are more stable than in stored water samples. Pesticides are unstable in water, regardless of the type of container used.

Ordering Information:

Description	Cat. No.
SPME Portable Field Sampler, pk. of 2	
with 100µm PDMS fiber	**504823**
with 75µm Carboxen™/PDMS fiber	**504831**
SPME Holder (replaceable fiber, manual version)	
with 100µm PDMS fiber	**57330-U**
Replacement 100µm PDMS fibers, pk. of 3	**57300-U**

For additional SPME products, refer to our catalog or contact your Supelco products distributor.

*For a list of references, request publication 494044.
▲Solid phase microextraction technology is licensed exclusively to Supelco. (US patent pending; European patent #0523092.)

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