Application Brief

Water Analysis

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Analysis of Parathion-Ethyl in Water with 85 µm Polyacrylate SPME Fibers

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Introduction

As many of the organochlorine pesticides became banned in the 1970s, the agrochemical industry turned to the less persistent, but more acutely toxic, organophosphorus pesticide (OPP) compounds to control insect pests.[1] OPPs are among the most widely used pesticides. As a result of this widespread use, their residues have been detected in samples such as surface waters, soil, and agricultural products.[2]

Organophosphates (OPs) are a class of insecticides, several of which are highly toxic. Thirty-six of them are registered for use in the United States, and all can potentially cause acute and subacute toxicity.[3] Over the past decade, several notable OPs have been discontinued for use, including parathion (also known as parathion-ethyl), which is no longer registered for use. A broad spectrum OP used to control many insects and mites, parathion is a polar compound that is extremely soluble in water.

The extraction of polar compounds from polar matrices is possible with the use of the polyacrylate (PA) SPME fiber. SPME extractions can be performed in one of two ways:

1. By direct immersion (DI), in which the fiber is fully immersed in an aqueous matrix, or
2. By headspace (HS), where the fiber is positioned in the headspace over the matrix

This Application Note used direct immersion solid phase microextraction (DI-SPME), which provides enhanced extraction of polar compounds that are extremely soluble in many sample matrices.

Experimental

Fifteen milliliters of water (18.2 Ω) were added to a 20 mL headspace sample vial containing ~5.4 g of NaCl (to achieve saturation of the sample volume). The water samples were then spiked with 50 µL of 100 ppm organophosphorus pesticides standard (part number SPM-834-1) and 50 µL of the internal standard (containing simazine-D10, atrazine-D5, terbutryn-(S-methyl-D3), and fenthion-(S-methyl-D3) at 100 ppm). The samples were vortexed prior to placement on the sample rack.

DI-SPME

The DI-SPME extraction technique was used for this study. In DI-SPME, the fiber is fully immersed in the aqueous sample, allowing isolation of more nonvolatile compounds, such as organophosphorus pesticides.

GC/MS analysis

Selected organophosphorus pesticides in water were extracted using DI-SPME with a PAL RTC rail system. This was combined with an Agilent 7890B GC system coupled with an Agilent 5977B High Efficiency Source GC/MSD (Figure 3).

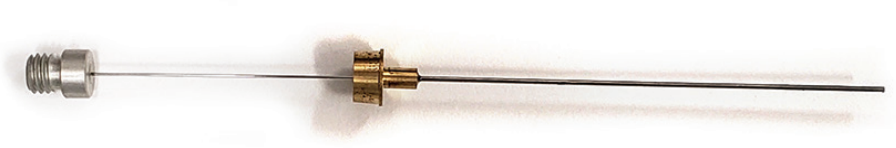

Figure 1. 85 µm Polyacrylate (PA) SPME fiber (p/n 5191-5876).

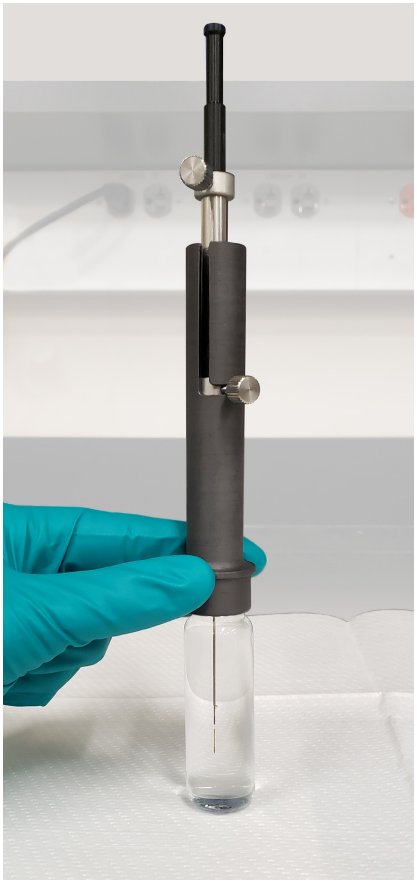

Figure 2. DI sampling with an SPME fiber.

Figure 3. The PAL RTC rail system combined with an Agilent 7890B GC and an Agilent 5977B GC/MSD.

Table 1. SPME headspace parameters.

Parameter	Value
Script Name	ARROW-STD-V2.0
Tool	SPME 1
SPME Fiber Phase	85 µm Polyacrylate (PA) (p/n 5191-5876)
Incubation Time	0 minutes
Stirrer	Heatex Stirrer 1
Heatex Stirrer Speed (Agitation)	1,000 rpm
Heatex Stirrer Temperature (Extraction Temperature)	60 °C
Agitator	None
Sample Extract Time	45 minutes
Extraction Temperature	60 °C
Sample Vial Penetration Depth	40 mm
Sample Vial Penetration Speed	20 mm/s
Inlet Penetration Depth	40 mm
Inlet Penetration Speed	100 mm/s
Injection Signal Mode	Before fiber expose
Sample Desorption Time	3 minutes
Conditioning Port	SPMEArrowCond 1
Predesorption Conditioning Time	5 minutes (analytical run)/30 minutes (precondition)
Fiber Conditioning Station Temperature	280 °C
Post Desorption Conditioning Time	0 minutes
GC Cycle Time	5 minutes (set for sequence overlap)

Table 2. Agilent 7890B GC settings.

Parameter	Value
Inlet Liner	Inlet liner, Ultra Inert, splitless, straight, 0.75 mm id (p/n 5190-4048)
Injection Mode/Temperature	Splitless/275 °C
Oven Program	60 °C (hold 1 minute), 30 °C/min to 180 °C (hold 3 minutes), 5 °C/min to 280 °C (hold 3 minutes)
Equilibration Time	0.5 minutes
Control Mode	Constant flow (1 mL/min)
Column	Agilent J&W DB-5ms Ultra Inert Intuvo GC column module, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI)
Septum Purge Flow Mode	Standard at 3 mL/min
Purge Flow to Split Vent	15 mL/min at 0.35 minutes
Agilent 5977B GC/MS Conditions	
Transfer Line	280 °C
Acquisition Mode	SCAN
Solvent Delay	6 minutes
Tune File	atune.u
Gain	1
MS Source Temperature	280 °C
MS Quad Temperature	150 °C

Results and discussion

Polyacrylate fiber reproducibility

Six replicate injections of spiked water samples were performed to collect data for PA fiber reproducibility. Percent RSDs were calculated for each fiber, then averaged together. Each set of replications maintained a percentage of RSDs lower than 30%. Table 3 shows the averaged results; Figure 4 shows a chromatogram of the selected OPs.

Table 3. Compound %RSD results per DVB/PDMS fiber.

Compound	Fiber 01	Fiber 02	Fiber 03	Average
Sulfotepp	18.71	26.28	8.56	17.85
Parathion-ethyl	19.35	22.28	20.05	20.56
EPN	17.13	28.61	23.84	23.19

Conclusion

DI-SPME was used with an Agilent 85 µm PA SPME fiber (p/n 5191-5876) followed by gas chromatographic-mass spectrometry analyses (GC/MS) for the analysis of selected organophosphorus pesticides, specifically parathion in water.

References

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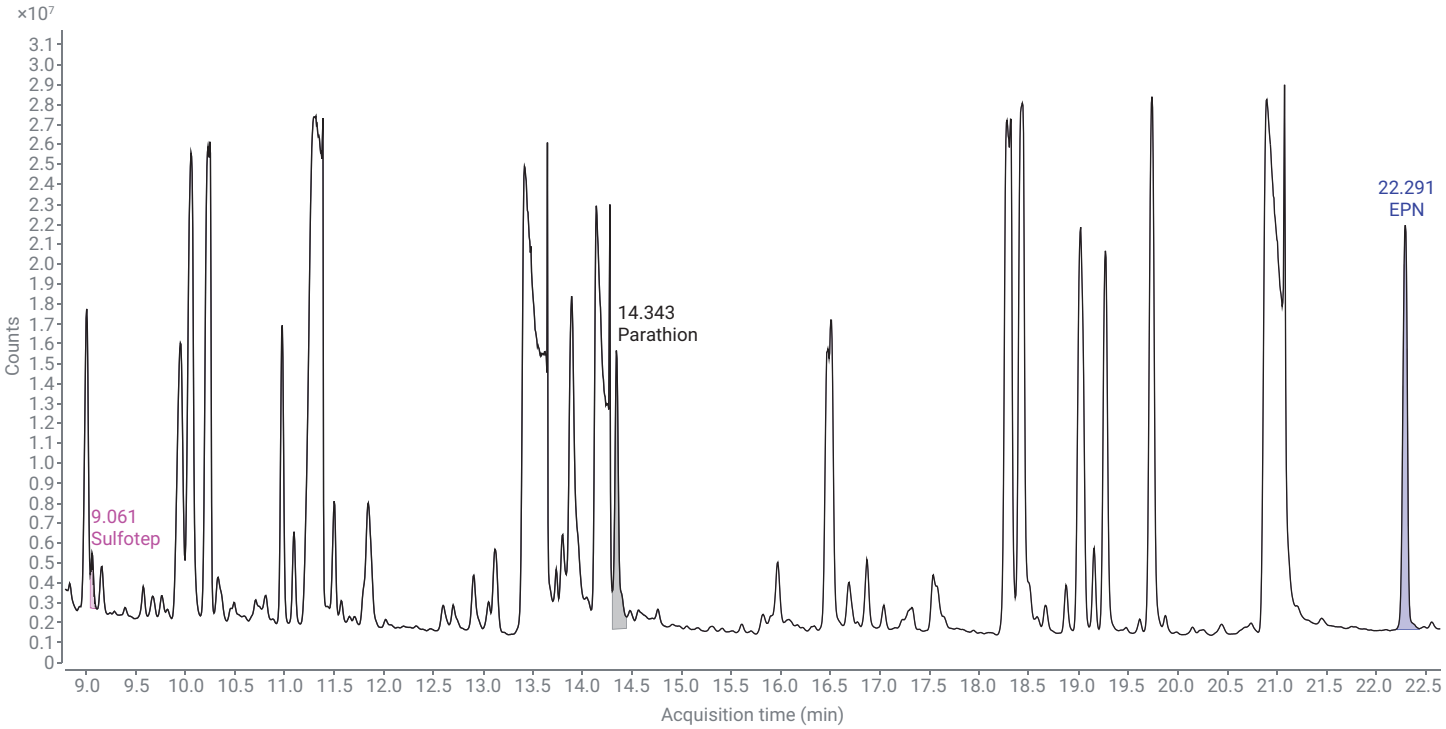

Figure 4. Total ion chromatogram of spiked OPs in water.

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