Application Note 20579

Analysis of Low Level Pyrethroid Pesticides in Water

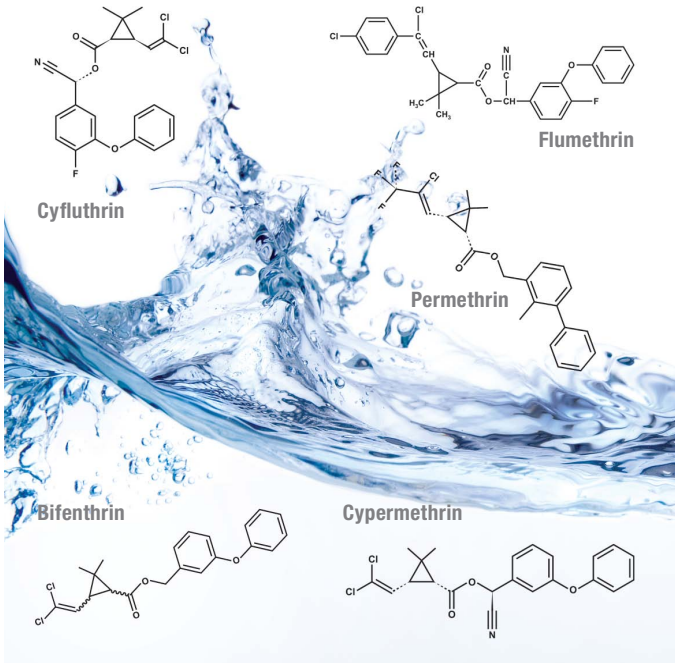
Anila I. Khan, Thermo Fisher Scientific, Runcorn, Cheshire, UK

Key Words

Pyrethroid pesticides, SPE extraction, 5% silarylene phenyl polysiloxane, adsorption effect of pyrethroids

Abstract

A method for the determination of pyrethroids in water at ultra-low-level concentrations of 0.02 and 0.10 ng/mL was developed using solid-phase extraction (SPE) for pre-concentration and subsequent analysis by GC with PTV injection. Careful selection of the autosampler vial type was needed to minimize adsorption effects.



Introduction

Pyrethroids are a class of synthetically produced insecticides that are mainly used for domestic purposes to control insects such as mosquitoes. They behave very similarly to natural pyrethrins, which are derived from chrysanthemum flowers and are extremely toxic to fish and aquatic organisms, but have low toxicity towards humans. However, repeated exposure increases the risk of anaphylaxis and allergic reaction at very low concentrations and should be monitored.

In this study, a simple method for isolating pyrethroids from water at low ng/mL levels was performed using solid-phase extraction (SPE) followed by GC/MS utilizing a programmable temperature vaporizer (PTV) operated in simulated on-column injection mode.

The separation of the pyrethroid (bifentrin, permethrin, cyfluthrin, cypermethrin and flumethrin) extracts was carried out using a Thermo Scientific™ TraceGOLD™ TG-5SilMS column and GuardGOLD™ pre-column. The TraceGOLD column is based on a silarylene chemistry, which provides more stability and lower bleed than standard 5% phenyl dimethylpolylsiloxane phase GC columns. This in turn gives rise to better sensitivity due to a lower background signal and can also partially resolve complex mixtures of cyfluthrin and cypermethrin isomers.

Thermo SCIENTIFIC

Experimental Details

Consumables		Part Number
Columns:	TraceGOLD TG-5SilMS, 30 m x 0.25 mm x 0.25 µm GuardGOLD 2 m x 0.53 mm ID Press-Fit union	26096-1420 26050-0253 64000-001
Injection port septum:	Thermo Scientific BTO septum, 12.7 mm	31303228
Liner:	Thermo Scientific PTV Silcosteel liner for PTV simulated on-column injection, 1 x 2.75 x 120 mm	45322052
Column ferrules:	100% graphite ferrules for Thermo Scientific TRACE™ injector, 0.53 mm ID	29053486
Colum ferrules:	Graphite/Vespel® for transfer line, 0.1–0.25 mm ID	29033496
Injection syringe:	85 mm 26s gauge, 10 µL fixed needle syringe for a Thermo Scientific TriPlus™ RSH Autosampler	365D0321
Vial:	Thermo Scientific National™ 9 mm Target DP Vial, 300 µL	C4000-11
Vial closure:	Thermo Scientific Chromacol™ 9 mm Open Top Short Screw Cap, 6 mm hole, with silicone/PTFE septa	9-SC(B)-ST101
Solvent:	Fisher Scientific™ LC-MS grade water	W/0112/17

Preparation of Calibration Standards

A stock standard solution of 1 mg/mL of bifenthrin, permethrin, cyfluthrin, cypermethrin and flumethrin was prepared in ethyl acetate.

The stock solution was then used to prepare calibration standard solutions in ethyl acetate of 50, 100, 200, 500, 1000 and 2000 ng/mL. A 100 µL aliquot of each calibration standard was then placed into an autosampler vial and 10 µL of 10 µg/mL of internal standard was added to each vial.

Sample Preparation: SPE Extraction Protocol		Part Number
SPE cartridge:	Thermo Scientific HyperSep™ C18 SPE column, 2000 mg/15 mL	60108-701
Compound:	(i) Bifenthrin, (ii) cis/trans permethrin, (iii) cyfluthrin, (iv) cypermethrin and (v) flumethrin (a) 1 L at 0.02 ng/mL of compounds (i)–(v) (b) 1 L at 0.10 ng/mL of compounds (i)–(v) in water	
Matrix:	LC/MS water	
Conditioning stage:	10 mL ethyl acetate, 10 mL acetone, 2 x 10 mL aliquots water applied sequentially to the SPE cartridge and then pulled through under vacuum at 4-5mL/min.	
Application stage:	1 L of sample applied to the SPE cartridge under vacuum at 4–5 mL/min	
Washing stage:	10 mL of water was added to the sample vessel, swirled and applied onto the SPE cartridge. The cartridge was dried for 20 min under vacuum.	
Elution stage:	10 mL ethyl acetate was added to the sample vessel, swirled and applied onto the SPE cartridge. Then 10 mL ethyl acetate was applied directly onto the cartridge.	
Additional stages:	Solvent was evaporated to dryness at 40 °C and the residue was reconstituted in 100 µL of ethyl acetate to give the final concentration of pyrethroids at 200 and 1000 ng/mL. Then 10 µL of 10 µg/mL of internal standard was added to the vial.	

Separation Conditions	
Instrumentation:	Thermo Scientific TRACE GC Ultra
Carrier gas:	Helium
Split flow:	50 mL/min
Column flow:	1.2 mL/min, constant flow
Oven temperature:	80 °C (0.5 min), 30 °C/min ramp, 220 °C (4 min), 10 °C/min ramp, 320 °C (10 min)
Injector type:	PTV simulated on-column
Injector mode:	Splitless (10 min) 30 mL/min flow rate, constant septum purge
Injector temperature phases:	40 °C (0.10 min), transfer 12 °C/s, 330 °C (10 min)
Detector type:	Thermo Scientific ISQ™ mass spectrometer
Transfer line temperature:	260 °C
Source temperature:	220 °C
Ionization conditions:	EI
Electron energy:	70 eV
Emission current:	25 µA

Scan Start Time (min)	Compound Name	Mass List (Quan), Qual ions	Total Scan Time (s)
5.50	1,2,3,4-tetrachloro-naphthalene (IS)	(264), 268, 266,	0.222
9.50	Bifenthrin	(181), 165, 166, 182	0.216
14.00	*cis*/*trans* permethrin	(183), 184, 163, 165	0.216
15.40	Cyfluthrin/cypermethrin	(226), (181), 182, 163, 165, 166,	0.234
17.00	Flumethrin	(239), 241, 283, 285	0.216

Table 1: SIM Scan parameters

Injection Conditions	
Instrumentation:	TriPlus RSH Autosampler
Injection volume:	2 µL
Injection depth:	70 mm
Penetration speed:	10 mm/s
Injection speed:	50 µL/s

Results

The analysis was performed in selected ion monitoring (SIM) mode. Figure 1 shows the total ion chromatogram (TIC) of spiked pyrethroids in water at 0.10 ng/mL after the pre-concentration step. Peak identification is shown in Table 2. To assess method linearity for spiked pyrethroids at 0.02 and 0.10 ng/mL (pre-concentrated to 200 and 1000 ng/mL using SPE), a calibration curve (50–2000 ng/mL) was constructed for each compound using 1,2,3,4-tetrachloronaphthalene as the internal standard (IS). The coefficients of determination (R^2) between the area ratios of sample and internal standard for all pyrethroids were greater than 0.99 (Table 3), demonstrating good method linearity.

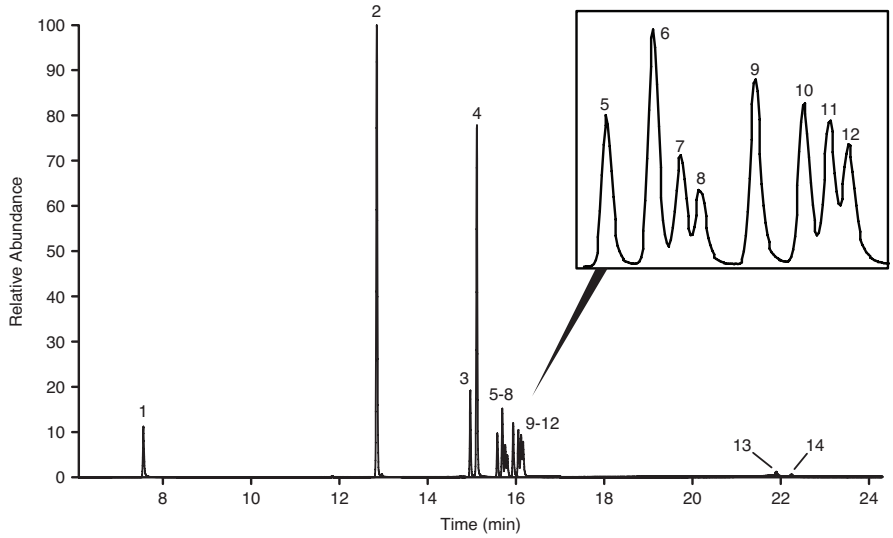


Figure 1: SIM chromatogram of 1000 ng/mL of pyrethroid pesticides separated on a TraceGOLD TG-5SilMS column after SPE extraction using a HyperSep C18 SPE cartridge

Peak Number	Compound	t_R (min) TG-5SilMS
1	1,2,3,4-Tetra Chloronaphthalene (IS)	7.56
2	Bifentrin	12.84
3	Permethrin isomer a	14.97
4	Permethrin isomer b	15.11
5	Cyfluthrin isomer a	15.58
6	Cyfluthrin isomer b	15.69
7	Cyfluthrin isomer c	15.76
8	Cyfluthrin isomer d	15.81
9	Cypermethrin isomer a	15.94
10	Cypermethrin isomer b	16.06
11	Cypermethrin isomer c	16.12
12	Cypermethrin isomer d	16.16
13	Flumethrin isomer a	21.90
14	Flumethrin isomer b	22.25

Table 2: Peak identification

Three extractions of each pyrethroid spiked at two concentrations of 0.02 and 0.10 ng/mL in water were carried out using a HyperSep C18 SPE cartridge. The pyrethroids recoveries were measured to be 71%–111%, with relative standard deviations (RSD) of 4%–22%. See Table 3 for individual pyrethroids measured at each concentration.

Analyzing pyrethroids at low concentration levels can be challenging because they adsorb readily onto glass surfaces, such as sample bottles, GC inlet liners and vials. To eliminate the glass adsorption effect, plastic vials were used instead of glass vials with a GC method utilizing a programmable temperature vaporizer (PTV) in simulated on-column mode. The contact time between the solvent and plastic vials was kept to a minimum to avoid introduction of polypropylene extractables into the mass spectrometer. However, studies have also shown that good recovery can be achieved with vials manufactured from high purity clear neutral borosilicate glass. [1,2]

Compound	Linearity R^2	% Recovery for 0.02 ng/mL	% RSD (n=3)	% Recovery for 0.10 ng/mL	% RSD (n=3)
Bifenthrin	0.9995	108	14.7	82	7.2
Permethrin Isomer a	0.9984	107	9.1	86	12.1
Permethethrin Isomer b	0.9979	111	12.5	86	5.7
Cyfluthrin Total Isomers	0.9953	111	10.9	102	6.0
Cypermethrin Total Isomers	0.9957	102	11.2	85	4.5
Flumethrin Isomer a	0.9975	71	17.7	89	7.6
Flumethrin Isomer b	0.9945	73	22.2	94	17.3

Table 3: Linearity (50–2000 ng/mL) and recovery data for pyrethroids in water at 0.02 and 0.10 ng/mL

Conclusion

- The SPE-GC/MS method utilizing HyperSep C18 SPE cartridges demonstrated high recovery for synthetic pyrethroids in water at the levels of 0.02 and 0.10 ng/mL.
- The GC/MS method was found to be linear over the range of 50 to 2000 ng/mL.
- Studies showed plastic and high purity, clear, neutral, borosilicate glass vials reduce adsorption of pyrethroids at low concentration.

References

1. The Effect of the Autosampler Vial's Glass Surface on GC-MS Analysis of Pyrethroid Pesticides at ppb Levels. Brian W King and Anila I Khan, Thermo Fisher Scientific, Runcorn, UK. Poster Reference number PSCCS 0512 588.

2. Application Note 20642: The Effect of the Autosampler Vial's Glass Surface on GC-MS Analysis of Pyrethroid Pesticides at Low Concentration. Anila I Khan, Thermo Fisher Scientific, Runcorn, UK.

thermoscientific.com/crc

USA and Canada +1 800 332 3331
France +33 (0)1 60 92 48 34
Germany +49 (0) 2423 9431 20 or 21
United Kingdom +44 (0)1928 534110
Japan +81 3 5826 1615

China +86 21 68654588 +86 10 84193588
+86 20 83145199 800 810 5118
India +91 22 6742 9494 +91 27 1766 2352
Australia 1 300 735 292 (free call domestic)
New Zealand 0800 933 966 (free call domestic)
All Other Enquiries +44 (0) 1928 534 050

Technical Support
North America +1 800 332 3331
Outside North America +44 (0) 1928 534 440

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific

AN20579_E 08/12S