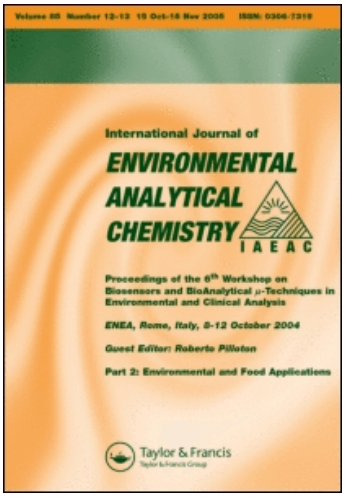

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Gas Chromatographic Determination of Cypermethrin and Fenvalerate Residues in Wheat and Milled Fractions

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A method to determine cypermethrin and fenvalerate residues in wheat and milled fractions was developed. The method involved extraction of residues with acetone-hexane and partitioning residues into hexane using aqueous sodium chloride solution. After concentrating hexane extracts, column chromatography cleanup was performed on Pasteur pipette micro columns containing Florisil, using benzene as the elution solvent, and packed column electron-capture GC was used for analysis. The limits of detection with this method were 0.02 mg kg^{-1} for cypermethrin and 0.04 mg kg^{-1} for fenvalerate. Average recoveries of 82 to 98% of cypermethrin and 80–86% of fenvalerate were obtained from wheat and milled fractions fortified at 0.41 to 3.80 mg kg^{-1}. No interference was observed from co-extractives.

KEY WORDS: GC analysis, fenvalerate, cypermethrin, stored wheat, milled fractions, insecticide residues.

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INTRODUCTION

Cypermethrin (RS)-α-cyano-3 phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylate, and fenvalerate, α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methyl butyrate, are effective insecticides against a number of phytophagous insect pests.[1–5] To date, these insecticides have been evaluated against stored product insects only on a limited scale[6,7] but they appear to be potential grain protectant candidates.

Methods to determine residues of cypermethrin and fenvalerate in vegetables,[8–11] soil[12,13] and animal tissues[14] have been developed. Simonaitis and Cail[15] also described a gas chromatographic method for the determination of permethrin in wheat and corn. Noble *et al.*[16] and Hargreaves *et al.*[17] used a high pressure liquid chromatographic method to determine residues of deltamethrin, fenvalerate, permethrin, and phenothrin in stored wheat. To the best of our knowledge, there is no published analytical method for cypermethrin in wheat.

Before any insecticide can be tested intensively as a grain protectant, analytical methodology is required to enable insecticide loss to be studied in grain and its milled fractions; e.g., bran, flour (endosperm) and germ. A rapid and inexpensive method for the determination of cypermethrin and fenvalerate was developed and used to determine residues of these two pyrethroids in stored wheat and milled fractions.

EXPERIMENTAL

Reagents

Glass distilled acetone, hexane, and benzene were obtained from Caledon Laboratories, Georgetown, Ontario (caution: benzene is a potential carcinogen). Analytical standards of cypermethrin and fenvalerate were supplied by Shell International Chemical Co., Toronto, Ontario, Canada. Reagent grade anhydrous sodium sulfate was obtained from Fisher Scientific Co., Winnipeg, Manitoba, Canada. Florisil (80–100 mesh) was obtained from Floridin Co., Hancock, WV, U.S.A., activated for 3 h at 250°C, and deactivated

with 8% water. Silanized glass wool was obtained from Applied Science Laboratories, Inc., State College, PA, U.S.A.

Gas Chromatograpy

A Varian 1800 gas chromatograph was fitted with a 0.6 m × 4 mm i.d. silanized glass column packed with 3% OV-210 on Gas Chrom Q, 80–100 mesh and a tritium foil electron capture detector. Temperatures (°C): inlet 250, column 200, detector 225. Nitrogen carrier gas flow rate, 80 mL/min.

Procedure

Five-gram samples of hard red spring wheat, var. Neepawa, were ground (GS Iona Model CG8-General Signal Appliances Ltd., Canada) and placed in 50 mL stainless steel extraction tubes.[18] In addition, 5-g samples (3-g for bran) of milled fractions (Ottawa micro mill No. 6012—Engineering Research Service, Agriculture Canada, Ottawa) were also used. The samples were spiked with cypermethrin or fenvalerate in hexane to give three levels (see Table I); the hexane was evaporated under dry nitrogen and the samples were allowed to stand for 24 h and one stainless steel ball (1.75 cm dia.) was placed in each tube.

The extraction was carried out using 25 mL acetone-hexane (1:1) on a wrist action shaker for 1 h.[19] The tubes were centrifuged at 1000 rpm for 10 min, and a 5.00 mL aliquot placed in a 15-mL centrifuge tube; 6 mL of 2% aqueous NaCl was added and agitated for *ca.* 15 sec. The hexane layer was removed and the aqueous layer reextracted twice with 2 mL hexane. The combined hexane extract was dried over anhydrous sodium sulfate and concentrated to *ca.* 1 mL at 40° under a stream of dry nitrogen.

A disposable Pasteur pipet (22.5 × 0.5 cm) was packed with 500 mg deactivated Florisil, topped with *ca.* 0.5 g anhydrous sodium sulfate, and prewashed with 3 mL hexane. The concentrated extract was cleaned up on this column using 1 mL hexane and 5 mL benzene. The hexane eluate (containing largely lipid coextractives) was discarded; the benzene eluate was collected and 2–8 μL analyzed by EC-GC.

TABLE 1

Percent recovery[a] of cypermethrin and fenvalerate from wheat and its milled fractions.

Fraction	Cypermethrin		Fenvalerate	
	Fortification level $mg\,kg^{-1}$	Percent recovery (Means ± S.D.)	Fortification level $mg\,kg^{-1}$	Percent recovery (Means ± S.D.)
Whole grain[b]	0.46	83.9 ± 5.3	0.46	77.6 ± 3.1
	1.14	95.3 ± 1.2	0.82	90.0 ± 4.5
	2.28	91.1 ± 4.5	2.04	90.5 ± 8.7
Flour	0.46	103.9 ± 1.7	0.41	81.8 ± 2.0
	0.91	97.5 ± 5.3	0.82	81.5 ± 7.2
	2.28	91.1 ± 0.3	2.04	86.3 ± 3.0
Middlings	0.46	74.7 ± 1.3	0.41	82.3 ± 1.2
	0.91	84.9 ± 4.7	0.82	77.2 ± 3.2
	2.28	85.0 ± 1.7	2.04	86.5 ± 1.6
Bran	0.76	86.4 ± 1.5	0.68	80.3 ± 4.2
	1.52	85.3 ± 2.8	1.36	76.2 ± 0.5
	3.80	82.8 ± 1.4	3.39	82.1 ± 3.6

[a]Mean of 3 replications.
[b]Ground wheat.

RESULTS AND DISCUSSION

Under the GC conditions described, fenvalerate and cypermethrin each eluted as a single peak. The retention times were 3.3 min for cypermethrin and 4.8 min for fenvalerate (Figure 1). The blank extracts showed no interfering peaks from wheat or milled fractions. Quantitation was done using external standards. Each of the extracts was injected twice. Excellent recoveries of cypermethrin and fenvalerate were obtained from fortified samples (Table I). Cypermethrin recoveries ranged from 83.9 to 95.2, 91.1 to 104.0, 82.8 to 84.6, and 74.7 to 85.0 percent from spiked whole grain, flour, bran, and middlings, respectively (Table I). The percent range of recoveries for fenvalerate was 77.6 to 90.5, 81.5 to 86.3, 76.2 to 82.1, and 77.2 to 86.5, respectively (Table I). The lower limits of detection were 0.02 mg kg^{-1} for cypermethrin and 0.04 mg kg^{-1} for fenvalerate.

The method described is rapid and more economical than the method of Simonaitis and Cail (1977) for permethrin, and than that used by Noble *et al.*, (1982) and Hargreaves *et al.*, (1982) for deltamethrin, fenvalerate, permethrin, and phenothrin. Less than 40 mL of solvents is required to extract and clean up a 5-g sample. Similarly, only 0.5 g of Florisil is needed for cleanup of each sample.

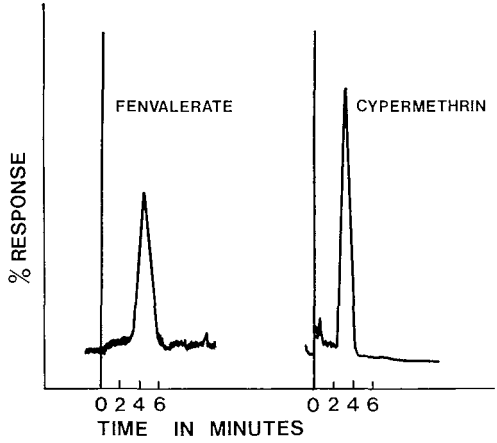

FIGURE 1 Retention times of fenvalerate and cypermethrin.

The use of ball-mill extraction makes it possible to extract 12 samples in 1 h. Thus, the method developed is rapid and inexpensive and can be used routinely to determine residues of cypermethrin and fenvalerate in wheat.

Although in some instances it may be necessary to quantify individual isomers, usually the determination of total cypermethrin and fenvalerate is feasible and within the capabilities of most laboratories. The method described here was used for the determination of residues of cypermethrin and fenvalerate in wheat and milled fractions.

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