a convenient alternative for routine analysis.

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Registry No. Vicine, 152-93-2; convicine, 19286-37-4; raffinose, 512-69-6; stachyose, 470-55-3; verbascose, 546-62-3; sucrose, 57-50-1.

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Rapid Extraction and Gas–Liquid Chromatographic Determination of *d*-Phenothrin in Aqueous Formulations

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A rapid method for extraction and quantitative determination of *d*-phenothrin in aqueous formulations is described. Aliquots of the formulations are mixed with aqueous sodium chloride and acetonitrile and then partitioned with toluene. Interferences are removed by adsorption chromatography on a silica gel column. The *d*-phenothrin is eluted from the column with a mixture of 3% ethyl acetate in pentane. The amount of *d*-phenothrin is determined by gas–liquid chromatography without the need to make sample dilutions by use of the linear flame ionization detector. The minimum detectability of this procedure was 0.10 ppm with a linearity of response for four decades.

Bry et al. (1980) reported on the effectiveness of pyrethroid combination sprays containing *d*-phenothrin [Sumithrin, (3-phenoxyphenyl)methyl *cis,trans*-(+)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate] and tetramethrin [Neo-Pynamin, (1,3,4,5,6,7-hexahydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate]. The pyrethroid combination in aqueous spray formulations effectively protected woolen cloth against damage by larvae of the black carpet bettle, *Attagenus unicolor* (Brahm), the furniture carpet beetle, *Anthrenus flavipes* (LeConte), and the webbing clothes moth, *Tineola bisselliella* (Hummel). These formulations were effective as direct-contact sprays against both larvae and adults. In addition, most of the adult carpet beetles or clothes moths that came in contact with the treated fabric were killed or knocked down. Subsequently, Bry et al. (1981, 1983) reported that pressurized solvent-based *d*-phenothrin formulations alone were effective in protecting woolen cloth against feeding damage by larvae of black and furniture carpet beetles and the webbing clothes moth.

Because *d*-phenothrin showed promise as a useful woolen cloth protectant upon application from aqueous

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treatment baths, a rapid sensitive analytical procedure for its determination was needed. A broad linear range for the analysis was required because the dissipation rate of the *d*-phenothrin formulation from the bath solutions was to be monitored so that an effective deposition of active ingredient could be made. A method for gas chromatographic and high-performance liquid chromatographic determination of *d*-phenothrin in formulations by Sakaue et al. (1981) was not satisfactory because they assayed formulations only at the 1 mg/mL concentration level and did not use any cleanup procedures to remove interferences at the low concentration ranges we needed to measure. Desmarchelier (1980) used a colorimetric procedure to determine residues. Papadopoulou-Mourkidou et al. (1981) analyzed formulations by utilization of an infrared detector for selective liquid chromatographic analysis that did not have sufficient sensitivity. Baker and Bottomly (1982) used a capillary column gas-liquid chromatographic procedure with an electron capture detector that resolved *d*-phenothrin into its two isomer peaks. In addition to the loss in sensitivity because of the presence of two peaks to quantitate, the electron capture detector has a very limited linear range. Baker and Bottomly also described a high-performance liquid chromatography procedure that had a limit of determination of 0.05 mg/kg. This paper describes a rapid sensitive method for the extraction and cleanup of low concentrations of *d*-phenothrin in aqueous formulations or treatment baths that has a broad dynamic linear range.

EXPERIMENTAL SECTION

Instrumentation. A Hewlett-Packard Model 5840 gas chromatograph equipped with an automatic sampler, digital integrator, recorder, and a flame ionization detector (Hewlett-Packard Co., Avondale, PA) was used. The column was a borosilicate tube (1.2-m length by 4-mm i.d.) packed with 5% OV-225 (25% 3-cyanopropyl–25% phenylmethylsilicone) (w/w) on 80/100-mesh Gas-Chrom Q. The newly packed column was conditioned for 24 h at 300 °C. Operating temperatures (°C): column oven, 250; detector, 300; injection port, 300. Gas flows (mL/min): nitrogen carrier, 28; hydrogen, 30; air, 240.

Reagents and Solutions. The adsorbent used for the cleanup was silica gel, Lot 029347, 60/200 mesh (J. T. Baker Chemical Co., Phillipsburg, NJ), used as received (4.81% moisture). The solvents used were pesticide grades of pentane, ethyl acetate, hexane, acetonitrile, and toluene (Fisher Scientific Co., Pittsburgh, PA). The eluant mixture used for the column chromatographic cleanup was ethyl acetate–pentane (3:97). To dry the mixture ca. 25 g of anhydrous sodium sulfate was added to the flask. The *d*-phenothrin analytical standard (94.4% purity) and the emulsifiable concentrate (27% active ingredient) were obtained from the McLaughlin Gormley King Co., Minneapolis, MN.

Sample Preparation and Extraction. A 60 ± 0.1 g portion of thoroughly mixed aqueous emulsifiable concentrate formulation was weighed into a 150-mL beaker. The sample was transferred to a 1-L separatory funnel containing 500 mL of 20% (w/w) aqueous sodium chloride and the beaker rinsed twice with 25 mL of acetonitrile. The washings were added to the separatory funnel, and 50 mL of toluene was added. The separatory funnel was shaken for 1 min and the layers were allowed to separate. The aqueous layer was transferred to a second 1-L separatory funnel and reextracted with 50 mL of toluene. The layers were allowed to separate, and the aqueous phase was drained into a waste container. The two toluene extractions from both 1-L separatory funnels were combined in a 250-mL Erlenmeyer flask by passage through a funnel containing a 2.5-cm plug of anhydrous sodium sulfate. The sodium sulfate plug was washed three times with 20 mL of toluene. The Erlenmeyer flask was placed on a rotary vacuum evaporator in a 40 °C water bath and the extract concentrated just to dryness. The residue was then dissolved in ca. 5 mL of pentane that had been dried by shaking with anhydrous sodium sulfate (ca. 25 g/L).

Table I. Recoveries of *d*-Phenothrin from Aqueous Formulations

sample	concn,[a] μg/g	wt added, μg	wt recd,[b] μg	% recd	std dev[c]
1	0.0993	5.96	5.11	85.7	0.89
2	0.497	29.8	26.9	90.3	0.84
3	0.993	59.6	54.2	90.9	0.27
4	4.97	298	298	100	0.11
5	9.93	596	558	93.6	0.17
6	19.0	1140	1110	97.4	0.20
7	29.8	1790	1610	89.9	0.20
8	49.7	2980	2840	95.3	0.43
9	79.5	4770	4370	91.6	0.29

[a] Weight of samples treated was 60 ± 0.01 g. [b] Value shown is average of five separate analyses. [c] Value shown is for the percent recovered for five separate analyses.

Chromatographic Cleanup. A Chromaflex glass chromatographic column (i.d. = 11.5 mm) (Kontes, Vineland, NJ 08360) was packed with a glass wool plug and 4 g of silica gel used as received. Approximately 1 cm of anhydrous sodium sulfate was added to the top of the packing, and column was wet with pentane that had been dried by shaking with anhydrous sodium sulfate. The sample was quantitatively transferred to the column with dry pentane and the column eluted with 25 mL of dry pentane, followed by 10 mL of dry 3% ethyl acetate in pentane solution. The eluates were discarded. A 125-mL Erlenmeyer flask was placed under the column, which was then eluted with 20 mL of dry 3% ethyl acetate in pentane. The sample was concentrated on a 60 °C water bath under a stream of dry nitrogen just to dryness. The residue was then dissolved in hexane and the resultant mixture transferred to a 1–100-mL volumetric flask, depending on the concentration levels expected. A 2-mL vial was filled ca. two-thirds full with an aliquot of the sample and capped with an aluminum septum cap with a Teflon-coated rubber seal. The vial was stored at −5 °C until ready for gas–liquid chromatographic analysis.

Analytical Procedure. All solutions were brought to room temperature and gas–liquid chromatographic operating conditions adjusted as described.

Instrumentation. With an automatic sampler, 3-μL aliquots of analytical standard solution were injected until the integrator counts varied ±1%. Vials containing analytical standard were placed before and after vials that contain sample solutions. The solution in each vial was injected twice with the automatic sampler, and the integrator counts were averaged and compared with those obtained for similar injections of standard solutions.

RESULTS AND DISCUSSION

For the cleanup procedure described in this paper, a silica gel adsorption chromatographic column was used to separate *d*-phenothrin from impurities in the sample. The *d*-phenothrin was removed from the column by eluting with 3% ethyl acetate–pentane solution. Table I shows the percent *d*-phenothrin recovered from aqueous formulations prepared at nine concentration levels. Each concentration was accurately formulated five times by mixing the weighed emulsifiable concentrate with 60 g of water. Recoveries exceeded 85% for each concentration investi-

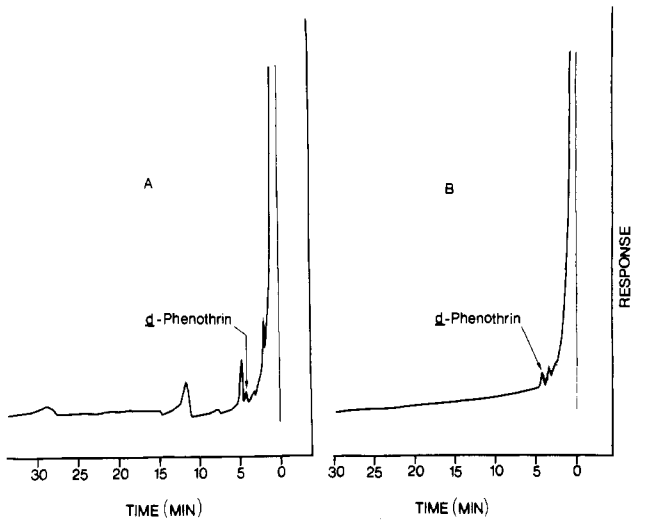

Figure 1. Gas–liquid chromatograms of formulation containing 1.2 ng of *d*-phenothrin (A) before silica gel column cleanup and (B) after silica gel column cleanup.

gated. The method was sensitive to 0.099 ppm active ingredient by weight. In 60 g of formulation this would be a total of 6000 mg of active ingredient, and if the volume of the volumetric flask was 10 mL and the injection volume 3 μL, then 1.8 ng of active ingredient would be injected. The detection limit may be reduced further if a more sensitive analysis is required by reducing the final volume of the solution or by taking a larger sampler aliquot as the background noise level was not due to interferring compounds in the sample. Standard deviations were determined on the five replicates for each of the nine concentration levels studied and are also given in Table I.

Calibration curves of integration counts and of peak height vs concentration were obtained by preparing known concentrations of *d*-phenothrin in hexane that ranged from 0.405 to 2.91 mg/mL and by injecting 3 μL into the gas chromatograph. Linear responses confirmed that the *d*-phenothrin response of the flame ionization detector was linear for the concentrations examined, ranging from 1 to 8700 ng per 3-μL injection volume.

The need for a cleanup to remove or reduce interfering peaks is illustrated by Figure 1. Part A of Figure 1 is a chromatogram obtained for a 3-μL injection of a formulation that contained 4.05 g of *d*-phenothrin in 10 mL of hexane prior to the silica gel cleanup. Part B is the chromatogram obtained for an aliquot of the same 4.05 μg of *d*-phenothrin in 10 mL of hexane after the silica gel column cleanup. *d*-Phenothrin eluted as one peak from 5% OV-225 column with a retention time of ca. 4.9 min.

Aqueous samples carried through the liquid extraction procedure show an unknown peak eluting just prior to the *d*-phenothrin peak (Figure 1). Also, it is shown by a chromatogram of the reagent blank in Figure 2. The exact source of the peak was not determined, but it appears to result from the reagents used in the extraction procedure

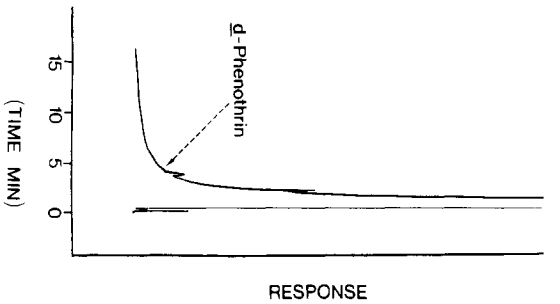

Figure 2. Gas–liquid chromatogram of reagent blank.

as no peak was observed when *d*-phenothrin was placed directly on the silica gel column and eluted as in the procedure described.

The method was used to assay aqueous formulation treating baths that contained 3–800 ppm of active ingredient. The procedure described had more than adequate sensitivity for the residue levels we needed to investigate. Because of the linear response of the detector, there was no need for dilution or concentration of the solutions after a preliminary determination. The gas–liquid chromatographic method described for the analysis of aqueous *d*-phenothrin formulations is simple, rapid, and specific. The cleanup procedure is applicable for the analysis of a wide variety of formulations such as wettable powders, dusts, and other formulations if these substances are water soluble.

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