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Note

Simultaneous determination of pynamin forte, resmethrin and piperonyl butoxide in insecticide formulations by gas chromatography

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The pesticide resmethrin has been employed as a grain protectant and for household use either alone or combined with the synergist piperonyl butoxide for many years. Currently, there is a need to determine the level of each component in formulations for product registration. In addition, the level of active constituents must be monitored for quality assurance and stability purposes.

The gas chromatographic (GC) separation of resmethrin and piperonyl butoxide in the same product has been a challenge. Chromatographers have used various techniques to isolate the components so each could be quantitated.

Open column chromatographic separations on alumina[1] have been applied to isolate bioresmethrin and piperonyl butoxide as separate fractions prior to GC analysis. GC–mass spectrometry using chemical ionization[2] was employed to monitor fragments of a specific *m/e* which are unique for each component even though they elute as a single peak. High-performance liquid chromatography[3] has been successfully used to separate these insecticides. A mixture of the active constituents was subjected to alkaline hydrolysis[4] producing an alcohol from the resmethrin which can be separated from piperonyl butoxide by GC. A GC method[5] has been reported which allows for the direct determination of both active constituents. However, the components are not completely resolved. In addition, the method requires a longer column, higher operating temperature and longer analysis time than the method reported here. The procedure reported here separates these commonly used insecticides on a relatively new, highly polar stationary phase and allows the simultaneous quantitation of each. This method has also been successfully applied to the analysis of aerosol insecticide formulations.

EXPERIMENTAL

Materials

Reagent-grade isopropanol from Sargent Welch was used without further purification. Dipentyl phthalate (DPP) was obtained from Eastman-Kodak. Pynamin forte 92% certified was purchased from Sumitomo (Osaka, Japan). Resmethrin 40% certified standard was supplied by Penick (Lyndhurst, NJ, U.S.A.). Technical piperonyl butoxide (93% active) was procured from FMC (Philadelphia, PA, U.S.A.).

A Tracor Model 560 gas chromatograph with a flame ionization detector was

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used. A 1.8 m × 2 mm I.D. silanized glass column was packed with 3% OV-275 on 80–100 mesh Chromasorb W AW (Supelco). The number of theoretical plates should be approximately 1600 plates per column (see Fig. 1). Supplier's recommendations for column maintenance were followed. Peak areas were integrated on a Spectra-Physics Model 4270 electronic integrator.

METHOD

Test solution. Weigh 2.5 g of 40% resmethrin and 1 g of piperonyl butoxide into separate 100-ml volumetric flasks. Dilute each to volume with isopropanol and mix thoroughly. Pipette 10 ml of each solution into a 25-ml volumetric flask. Pipette 2.0 ml of 5% (w/v) dipentyl phthalate in isopropanol into the flask. Dilute to volume with isopropanol and mix. This test solution is used to determine column efficiency (see Fig. 1).

Standard preparation. Weigh to the 4th decimal 0.15 g Pynamin Forte, 0.15 g resmethrin and 0.50 g piperonyl butoxide into a 100-ml volumetric flask. These weights represent active ingredient and adjustment will be necessary in order to account for percent purity of raw materials used (*i.e.*, 0.375 g of 40% resmethrin is 0.15 g resmethrin active ingredient, etc.). Dilute to volume with isopropanol and mix. Pipette exactly 10 ml into a 50-ml glass stoppered graduate mixing cylinder. Then pipette exactly 3.0 ml of 0.5% (w/v) DPP internal standard solution into the graduate, dilute to 50 ml with isopropanol and mix. This is the standard.

Sample preparation. Remove the actuator from the aerosol valve and weigh the full container. Shake the container vigorously for 2 min. Connect an actuator equipped with a delivery tube to the container valve. Immerse the end of the tube into 300 ml of isopropanol in a 1-l volumetric flask. Actuate the valve to deliver the product into the flask, continue until all the pressure is dissipated. Carefully, remove the bottom of the container with a can opener and pour the remaining depressurized contents into the flask. Wash the interior of the container and rinse the delivery tube with isopropanol, adding the washings to the flask, then dilute to volume with isopropanol and mix. Dry the container and reweigh to determine the weight of product in the flask. Pipette a 25-ml aliquot into a 50-ml glass stoppered graduate mixing cylinder. Add by pipette 3.0 ml of 0.5% DPP internal standard solution, dilute to 50 ml with isopropanol and mix. This is the sample.

GC conditions. Inject a 1.0-μl portion of each solution into the gas chromatograph at the following parameters: column, 1.8 m × 2 mm I.D. 3% OV-275 on 80–100 mesh Chromosorb W AW; column temperature, 185°C; injector temperature, 210°C; detector temperature, 300°C; carrier gas flow-rate, nitrogen at 30 ml/min.

Calculation

$$\text{Area ratio} = \frac{\text{area of component of interest}}{\text{area of internal standard peak}}$$

$$\text{Factor} = \frac{(\text{standard weight in g}/10)^* \times \%\ \text{purity}/100}{\text{area ratio of standard}}$$

* g of component in standard equals g weighed/10 since a 10-ml aliquot was taken from the 100-ml standard solution.

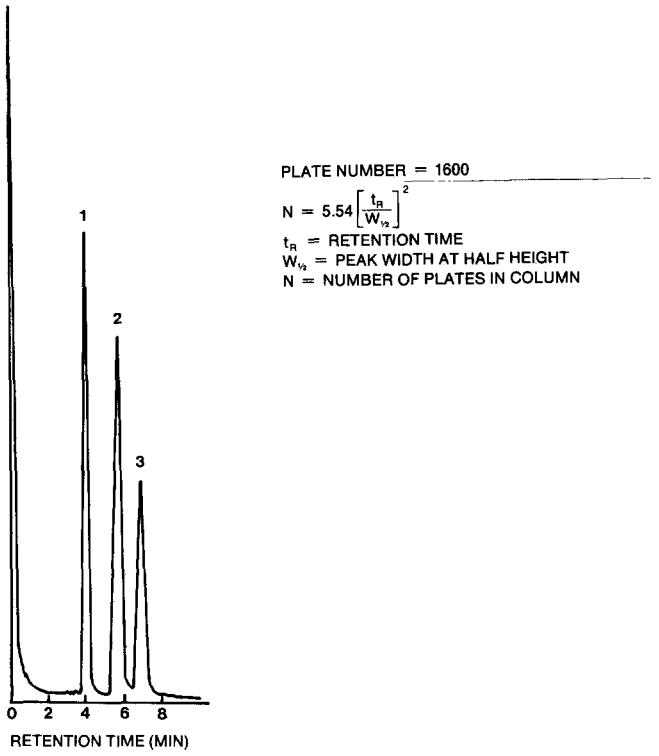

Fig. 1. Gas chromatogram of a test solution of resmethrin and piperonyl butoxide with dipentyl phthalate used as the internal standard. For chromatographic conditions, see Experimental. Peaks: 1 = dipentyl phthalate (internal standard); 2 = resmethrin; 3 = piperonyl butoxide.

$$\% \text{ Component} = \frac{\text{area ratio of sample} \times \text{factor} \times 100}{\text{wt of sample in g} \times 0.025^*}$$

Separate factors are calculated for each active constituent.

RESULTS AND DISCUSSION

An internal standard method for the simultaneous determination of piperonyl butoxide and resmethrin was developed. A chromatogram of a test solution illustrating this separation is shown in Fig. 1.

The resolution calculated for these components is greater than 1.8, which indicates complete separation and allows for the satisfactory quantitation of each. The reproducibility of the chromatographic method for ten injections of the test solution is excellent. Less than 1.5% relative standard deviation for each component was achieved.

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* g of sample in final solution — sample wt × 25/1000 since a 25-ml aliquot was taken from the 1000-ml initial solution.

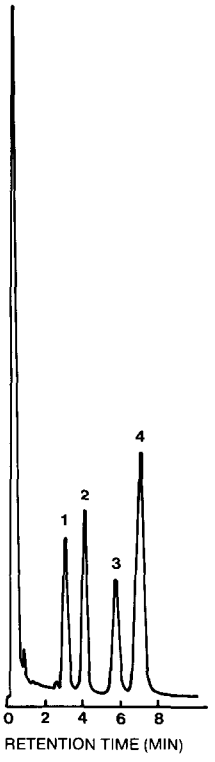

Fig. 2. Gas chromatogram obtained from an insecticide formulation. For chromatographic conditions, see Experimental. Peaks: 1 = pynamin forte; 2 = dipentyl phthalate (internal standard); 3 = resmethrin; 4 = piperonyl butoxide.

This chromatographic procedure was applied to the determination of active constituents in an aerosol insecticide formulation. Pynamin forte, resmethrin and piperonyl butoxide were determined simultaneously. A typical chromatogram is shown in Fig. 2. The chromatographic reproducibility was as good as stated above. The linearity of response of each component at 0.5 to 1.5 times the recommended concentrations was checked and correlation coefficients of 0.999 were attained. The

TABLE I

RESULTS FROM THE GAS CHROMATOGRAPHIC ANALYSIS OF AN AEROSOL INSECTICIDE FORMULATION

Component	*% Active ingredient*		
	*Experimental**	*Theoretical*	*R.S.D. (%)*
Pynamin forte	0.15	0.15	1.5
Resmethrin	0.13	0.15	1.6
Piperonyl butoxide	0.44	0.46	1.4

* Represents the average of 8 injections of a sample solution.

experimental results are given in Table I. Good agreement between the experimental and theoretical values for each active constitutent was obtained.

The described chromatographic method allows for the direct determination of resmethrin and piperonyl butoxide. It also has the advantages of a shorter analysis time than previously reported GC methods[4,5], is simpler, not requiring any sample pre-treatment[1,4], and does not require expensive instrumentation for detection[2]. The procedure has been successfully applied to aerosol insecticide formulations and is reproducible.

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