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Note

Determination of fenitrothion, bioresmethrin and piperonyl butoxide in aerosol concentrates by high-performance liquid chromatography

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Formulations consisting of fenitrothion [O,O-dimethyl-O-(4-nitro-*m*-tolyl) phosphorothioate], bioresmethrin [5-benzyl-3-furylmethyl(±)-*trans*-chrysanthemate] and piperonyl butoxide {5-[2-(2-butoxyethoxy)ethoxymethyl]-6-propyl-1,3-benzodioxole} in various ratios have been evaluated and proposed for use as grain protectants[1,2]. Methods published to date for the determination of fenitrothion include infra-red analysis[3], gas–liquid chromatography[4–6] and reversed-phase high-performance liquid chromatography (RP-HPLC)[7]. Bioresmethrin has been determined by gas chromatography–mass spectrometry (GC–MS)[8] and GC[9,10]. Several methods have also been described for the determination of piperonyl butoxide (Pip. But.) including GC–MS[8] and HPLC[11]. Although several methods have been described for the determination of the individual technical materials and their determination at the residual level in various matrices, little has been published on the analysis of formulations containing all three components.

The method described here was developed for the rapid determination of all the above three pesticides in aerosol concentrate formulations. Determination of the three components is achieved by RP-HPLC separation, followed by UV detection at 240 nm.

EXPERIMENTAL

Apparatus

The analyses were performed on a Waters Model 6000A pump, equipped with a U6K injector and Model 450 variable-wavelength UV detector (Waters Assoc., Sydney, Australia). A Brownlee Labs. RP-8 (10 μm), 25 cm × 4.6 mm I.D. reversed-phase column was used (Activon Scientific Services, Granville, Australia). The detector was coupled to a Curken 250-1 recorder (Varian, Sydney, Australia) and injections were made with a Hamilton 25-μl syringe (Waters).

Reagents and standards

Fenitrothion (99.5%), bioresmethrin (93.7%) and piperonyl butoxide (97.0%)

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were obtained from Cooper Australia (N.S.W., Australia), acetonitrile and methanol (HPLC grade, Burdick & Jackson) from Alltech (N.S.W., Australia).

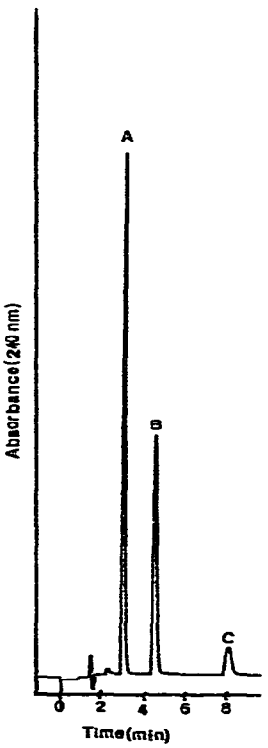
Preparations of standard

A solution of 0.65 g fenitrothion, 0.40 g piperonyl butoxide and 0.10 g bioresmethrin in 100 g methanol was prepared and diluted 1 ml to 10 ml in methanol to

TABLE I

SAMPLES OF AEROSOL CONCENTRATES ANALYSED

Sample	*Component (g/100 g dichloromethane)*		
	Bioresmethrin	*Pip./But.*	*Fenitrothion*
1	0.75	3.50	6.00
2	1.00	4.00	6.50
3	1.25	4.50	7.00



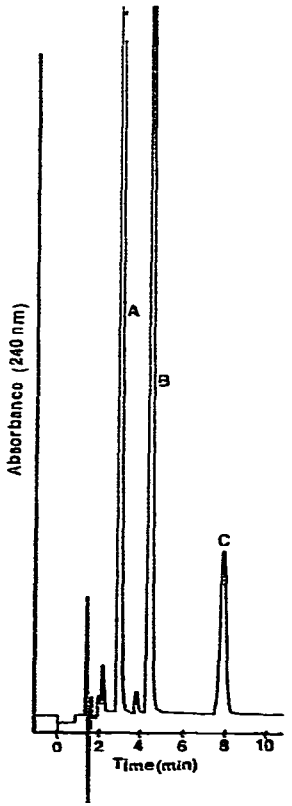


Fig. 1. Chromatogram of a standard solution of fenitrothion (A), piperonyl butoxide (B) and bioresmethrin (C). Retention times are 3.0, 4.4 and 7.8 min respectively. Detector set at 0.2 a.u.f.s. Conditions as in Experimental.

Fig. 2. Chromatogram of standard solution as in Fig. 1 but with detector set at 0.04 a.u.f.s.

TABLE II

RECOVERY OF BIORESMETHRIN, PIPERONYL BUTOXIDE AND FENITROTHION FROM AEROSOL CONCENTRATES

Bioresmethrin			*Pip./But.*			*Fenitrothion*		
Added (%)	*Found (%)*	*Recovery (%)*	*Added (%)*	*Found (%)*	*Recovery (%)*	*Added (%)*	*Found (%)*	*Recovery (%)*
0.75	0.76	101.3	3.5	3.60	102.9	6.0	6.21	103.5
0.75	0.76	101.3	3.5	3.70	105.7	6.0	6.24	104.0
0.75	0.77	102.7	3.5	3.60	102.9	6.0	6.21	103.5
1.0	1.02	102.0	4.0	3.97	99.3	6.5	6.51	100.2
1.0	1.00	100.0	4.0	3.99	99.8	6.5	6.48	99.7
1.0	1.03	103.0	4.0	4.06	101.5	6.5	6.59	101.4
1.25	1.24	99.2	4.5	4.58	101.8	7.0	7.00	100.0
1.25	1.27	101.6	4.5	4.53	100.7	7.0	7.08	101.1
1.25	1.28	102.4	4.5	4.51	100.2	7.0	7.12	101.7
	Mean	101.5		Mean	101.6		Mean	101.7

give an analytical standard consisting of 0.065% fenitrothion, 0.040% piperonyl butoxide and 0.010% bioresmethrin.

Preparation of samples

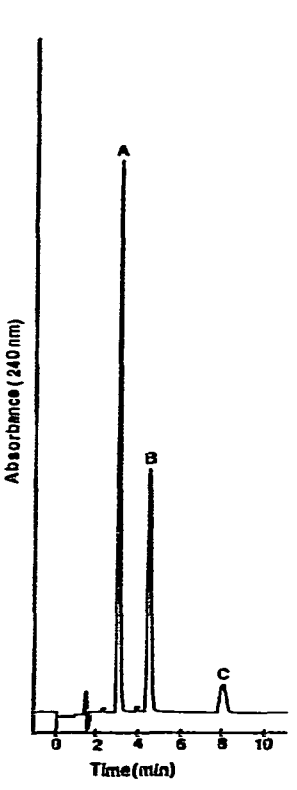
A 1-ml sample of each of the concentrates containing the three components in methylene chloride, as shown in Table I, was separately diluted to 100 ml in methanol.

Preparation of mobile phase

The mobile phase was prepared by adding 700 ml of acetonitrile to 300 ml distilled water and degassing under vacuum.

Chromatographic conditions

Flow-rate: 2.0 ml/min. Detector settings: 240 nm and 0.2 a.u.f.s. for fenitrothion and piperonyl butoxide; 0.04 a.u.f.s. for bioresmethrin. Chart speed: 0.5 cm/min. Injection volume: 20 μl, each in triplicate.



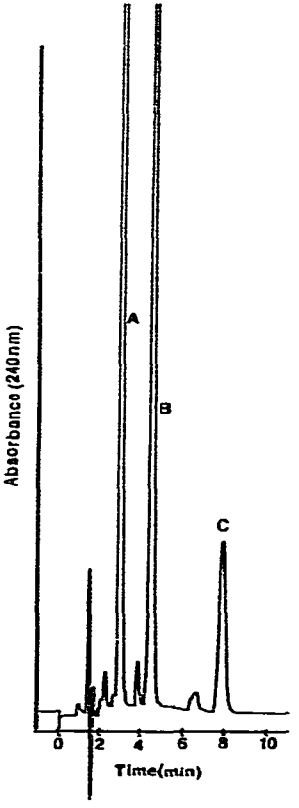


Fig. 3. Chromatogram of aerosol concentrate containing fenitrothion (A), piperonyl butoxide (B) and bioresmethrin (C) with detector set at 0.2 a.u.f.s. Conditions as in Experimental.

Fig. 4. Chromatogram of aerosol concentrate as in Fig. 3 but with detector set at 0.04 a.u.f.s.

RESULTS AND DISCUSSION

Figs. 1 and 2 show typical chromatograms for the standard solution with the detector set at 0.2 a.u.f.s. and 0.04 a.u.f.s. respectively. The retention times under the chromatographic conditions used are 3 min (1.5 cm), 4.4 min (2.2 cm) and 7.8 min (3.9 cm) for fenitrothion, piperonyl butoxide and bioresmethrin respectively. Figs. 3 and 4 show chromatograms of an aerosol concentrate containing a nominal 0.010% bioresmethrin, 0.040% piperonyl butoxide and 0.065% fenitrothion.

As can be seen in Table II, the average recoveries of each component for the three concentration ranges investigated are: bioresmethrin, 101.5% (range 99.2–102.4%); piperonyl butoxide, 101.6% (range 99.3–105.7%) and fenitrothion, 101.7% (range 100.0–104.0%).

Due to the large differences in the concentrations of the three components it is necessary to perform two chromatographic runs for each solution; in one run the detector is set at 0.2 a.u.f.s. to quantitate fenitrothion and piperonyl butoxide, in the second run the detector is set at 0.04 a.u.f.s. to quantitate bioresmethrin. The complete analysis time is approximately 30 min.

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