CHROM. 6167

ANALYTICAL STUDIES OF PYRETHRIN FORMULATIONS BY GAS CHROMATOGRAPHY

II. ISOLATION OF THE PYRETHRINS FROM WATER-BASED FORMULATIONS*

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SUMMARY

The extraction of pyrethrins and synergists from water-base aerosol formulations is improved and simplified by the use of acetone in the extraction procedure. The procedure minimizes interferences from extraneous substances previously encountered in the subsequent analysis of the pyrethrins by gas chromatography.

INTRODUCTION

The majority of commercial insecticide formulations for household use are now packaged in aerosol form which contain either petroleum distillates or water as the carrier for the toxicants enclosed in the aerosol container. Water-base pressurized products represent a large part of the present market for pesticide aerosols, because of the economical advantage over petroleum-base mixtures[1-5]. However, they have created a sampling problem in the analysis of the formulations for the active insecticide ingredients. Emulsifiers and corrosion inhibitors are usually included in the water-base formulations, the former to produce a homogeneous mixture of active and inactive ingredients, and the latter to protect the interior of the aerosol container. Contrary to the petroleum distillate aerosol mixtures, the water-base formulations are not wholly compatible with the analytical procedure recently suggested for pyrethrin analyses[6].

Methods of sampling water-base aerosols by commercial laboratories have included the following procedures:

(1) The aerosol container is punctured, the volatile propellant is evaporated, the water fraction is removed via a rotary evaporator and the residue is examined either by infrared spectrophotometry or by gas chromatography. The analyst, unless he is certain of the nature of the propellant, is advised to chill the container prior to application of the puncture.

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(2) The aerosol container is opened, the entire contents are removed and exposed to the laboratory atmosphere for a period of time; during this period, the emulsified foamy matrix disintegrates and the entrapped propellant is completely dissipated. The residue is dissolved in acetone and analyzed by gas chromatography. This procedure is too lengthy and it may cause analytical errors, because of degradation and/or volatilization of the active ingredients during the extensive exposure period to the atmosphere.

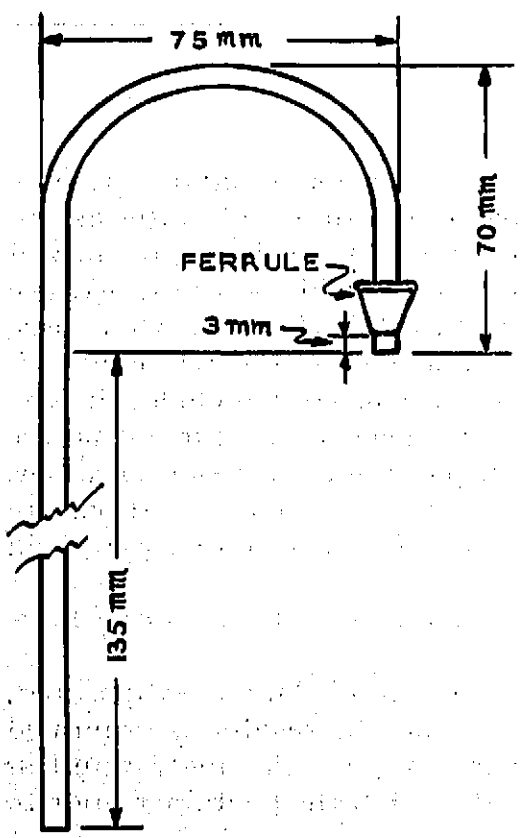
(3) Some laboratories have used biological assay techniques instead of chemical analyses of formulations of this type.

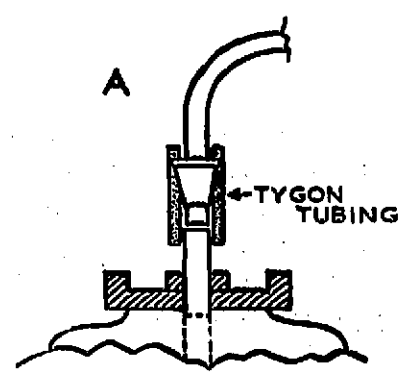
The above methods are tedious, time consuming, subject to error, or non-specific for the active pesticide ingredients. A proposed method that circumvents these problems and eliminates the formation of emulsions during the extraction process includes the use of acetone to isolate the active pesticide components from the water-base mixture for subsequent analysis, and is described in this paper.

MATERIALS AND METHODS

Gas chromatograph

An F&M Model 810 instrument with a flame ionization detector was used. The column temperature was 190° and the injector port and detector block temperatures were 205°. The gas flow-rates were: nitrogen, 40 ml/min; hydrogen, 30 ml/min; air, 210 ml/min. The spiral borosilicate gas chromatograph column was 1/4 in. I.D. by





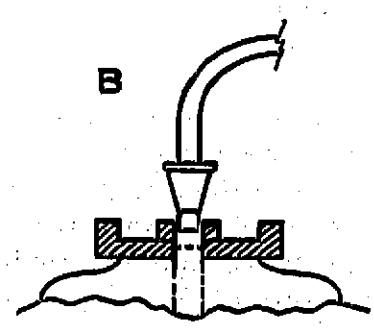


Fig. 1. Details of design for stainless-steel sampling tube.

Fig. 2. Method of attaching sampling tube to aerosol containers fitted with (A) a male-type outlet and (B) a female-type outlet.

Fig. 3. Example of sampling aerosol container for sample analysis.

4 ft., packed with 5 % SE-30 silicone coated on Chromosorb W, AW, DMCS, 60–80 mesh. A Leeds and Northrup Speedomax H recorder, 1 mV full-scale, chart speed 0.5 in./min, was used.

Chromatographic columns for Florisil clean-up

The columns were 20 × 400 mm borosilicate glass with Ultramax stopcocks and 250 ml reservoirs.

U-tubes for aerosol sampling

The sampling tube was constructed from 1/8 in. I.D. stainless-steel tubing (Fig. 1). With a male-type aerosol outlet, a short piece of Tygon tubing is attached between the stainless-steel tube and the aerosol outlet (Fig. 2A). With a female-type outlet, the stainless-steel tube is inserted directly into the aerosol outlet (Fig. 2B). Hand pressure is applied to the assembly to release an aliquot sample from the aerosol container (Fig. 3).

Florisil

This was 60–100 mesh and was heated at 130° for 16 h prior to use.

Reagents

Anhydrous sodium sulfate was heated at 200° for 16 h prior to use. Reagent grade hexane, acetone and carbon disulfide were distilled in an all-glass system prior to use.

Pyrethrin and synergists standard solutions

Premium pyrocide (20 % pyrethrin assay), technical piperonyl butoxide (PBO), MGK 264 (N-octylbicycloheptenedicarboximide, NOBD), Pyrocide intermediate No. 6788 (for formulated mixtures of pyrethrin 0.25 %, piperonyl butoxide 0.80 % and MGK 264 0.40 %), and X-2597-71 (emulsifier and corrosion inhibitor mixture) were kindly supplied by Mr. DEAN C. KASSERA of the McLaughlin Gormley King Co., Minneapolis, Minn., U.S.A. Standard solutions in carbon disulfide were prepared, which contained 0.6 μg/ml of pyrethrin I (assuming a 1:1 ratio of Py I–Py II in the Premium pyrocide), 1.2 μg/ml of PBO and 0.6 μg/ml of NOBD. Aliquots of 2 μl were used for gas chromatographic analysis. With a gas chromatograph setting of range 10 and attenuation 16, the linearity detector range was 0.2–2.2 μg for pyrethrin I, 0.6–5.6 μg for PBO and 0.6–1.8 μg for NOBD. The minimum detectability was approximately 0.06 μg for each of the three active components at a range setting of 10 and attenuation 2.

Preparation of samples for analysis

The cap and spray head are removed from the aerosol container. The container plus the sampling tube (Fig. 1) are weighed together. The aerosol can is shaken vigorously for 1 min, the sampling tube is immediately attached to the outlet of the can, the opposite end of the tube is immersed into 100 ml of hexane contained in a 250 ml pear-shaped separating funnel and the tube is depressed (Fig. 3) to deliver approximately a 10 g sample into the hexane. The can is again shaken and a second 10 g sample is added to the hexane, making a total of about 20 g of sample. The hexane–pesticide solution is quantitatively transferred to a 1-l separatory funnel, using five rinses of 10 ml portions of acetone to effect the complete transfer. Distilled water (450 ml) and saturated aqueous sodium chloride solution (50 ml) are added, the funnel is stoppered and shaken vigorously for 3 min with intermittent release of the stopper to remove excess internal pressure. The organic and aqueous phases are allowed to separate. The aqueous layer will resemble a soap solution owing to emulsifier ingredients extracted from the original sample. The aqueous layer is removed from the funnel and discarded. Saturated sodium chloride solution (25 ml) is added to the remaining organic phase in the funnel, the mixture is agitated gently and the two phases are allowed to separate. The aqueous phase is removed and discarded. The organic phase is passed through a column (80 × 15 mm) containing 5–10 g of anhydrous sodium sulfate, followed by several rinses of the column with 5 ml aliquots of hexane, and collected in a beaker. The solution is concentrated to about 50 ml on a warm steam bath aided by a gentle stream of air or nitrogen. The sample is cleaned up on a Florisil column as previously described[6]. The acetone eluate from the Florisil column is evaporated nearly to dryness by means of a stream of air. The residue is diluted to

about 10 ml with carbon disulfide and passed through an anhydrous sodium sulfate column; the eluate, plus several column washings of carbon disulfide, are made up to a definite volume with carbon disulfide, and aliquots (2–3 μl) of the solution are applied to the gas chromatograph for analysis.

RESULTS AND DISCUSSION

The experiments were designed to (1) determine the effect, if any, of the proposed acetone technique on the recovery efficiency of each pesticide ingredient at three different concentration levels (in the amounts ordinarily found in household formulations); (2) determine what concentration within the acceptable range of analysis might be significantly influenced by the use of acetone; and (3) determine the effect, if any, of the proposed procedure on the quantitative recovery of one or more of the active pesticide components in a mixed formulation containing the pyrethrins and the synergists PBO and NOBD.

A series of recovery tests were made with the individual active ingredients pyrethrin, PBO and NOBD. The pesticide component in each series was mixed with deionized water, corrosion inhibitor, kerosene and surfactant mixture, simulating a commercial formulation mixture, but with the omission of the propellant ingredient. In the routine analysis of aerosol pesticide formulations, it is common practice to remove the propellant ingredient prior to analysis. Therefore, the procedure applied to the simulated commercial mixtures described herein are comparable to commercial preparations at the time of analysis. The results of the tests are tabulated in Tables I, II and III.

TABLE I

PERCENTAGE RECOVERY OF PYRETHRIN FROM SIMULATED COMMERCIAL MIXTURES CONTAINING KEROSENE, DEIONIZED WATER AND CORROSION INHIBITOR

Propellant ingredient was not included in the mixture.

Pyrethrin concentration (%)	*Pyrethrin added* (*mg*)	*Pyrethrin recovered* (*mg*)	*Recovery* (%)	*Average recovery* (%)
0.25	84.0	72.0	86	92
	68.0	65.0	96	
	76.0	72.0	95	
	61.0	56.0	92	
	70.0	63.0	90	
0.30	75.4	73.0	97	95
	75.4	73.0	97	
	75.4	72.0	95	
	75.4	72.0	95	
	75.4	70.0	93	
0.50	126.0	121.0	96	94
	123.0	116.0	94	
	124.0	108.0	87	
	145.0	138.0	95	
	110.0	106.0	96	

TABLE II

PERCENTAGE RECOVERY OF PIPERONYL BUTOXIDE (PBO) FROM SIMULATED COMMERCIAL MIXTURES CONTAINING KEROSENE, DEIONIZED WATER AND CORROSION INHIBITOR

Propellant ingredient was not included in the mixture.

PBO concentration (%)	*PBO added* (*mg*)	*PBO recovered* (*mg*)	*Recovery* (%)	*Average recovery* (%)
0.5	100.9	92.3	91	92
	100.9	93.0	92	
	100.9	92.0	91	
	100.9	93.0	92	
	100.9	93.0	92	
0.8	169.6	166.0	98	95
	169.6	163.0	96	
	169.6	164.0	97	
	169.6	156.0	92	
	169.6	153.0	90	
1.25	252.0	240.0	95	94
	252.0	235.0	93	
	252.0	239.0	95	
	252.0	239.0	95	
	252.0	234.0	93	

TABLE III

PERCENTAGE RECOVERY OF *n*-OCTYLBICYCLOHEPTENEDICARBOXIMIDE (NOBD) FROM SIMULATED COMMERCIAL MIXTURES CONTAINING KEROSENE, DEIONIZED WATER AND CORROSION INHIBITOR

Propellant ingredient was not included in the mixture.

NOBD concentration (%)	*NOBD added* (*mg*)	*NOBD recovered* (*mg*)	*Recovery* (%)	*Average recovery* (%)
0.4	80.5	74.0	92	93
	80.5	76.0	94	
	80.5	73.0	91	
	80.5	77.0	96	
	80.5	76.0	94	
0.5	109.4	102.0	93	92
	109.4	106.0	97	
	109.4	100.0	91	
	109.4	98.0	90	
	109.4	98.0	90	
1.0	207.0	192.0	93	94
	207.0	199.0	96	
	207.0	192.0	93	
	207.0	200.0	97	
	207.0	192.0	93	

Pyrocide intermediate No. 6788 was used in another series of tests, simulating a commercial formulation mixture of pyrethrins 0.25%, PBO 0.80% and NOBD 0.40%, and the inactive ingredients described above. The results of the tests are given in Table IV.

Statistical analysis of the results (Table V) showed that neither the variation of

TABLE IV

PERCENTAGE RECOVERY OF A MIXTURE OF PYRETHRINS, PBO AND NOBD FROM SIMULATED MIXTURES CONTAINING KEROSENE, DEIONIZED WATER AND CORROSION INHIBITOR

Pyrocide intermediate No. 6788 used for active pesticide ingredients. Propellant ingredient was not used in the mixture.

Sample No.	*Component*	*Concentration (%)*	*Amount added (mg)*	*Amount found (mg)*	*Recovery (%)*	*Average recovery (%) of individual components (5 values)*
1	Pyrethrin	0.25	50.0	46.6	93	
	PBO	0.80	160.0	149.0	93	
	NOBD	0.40	80.0	75.0	94	
2	Pyrethrin	0.25	50.0	48.4	97	
	PBO	0.80	160.0	152.0	95	
	NOBD	0.40	80.0	76.0	95	
3	Pyrethrin	0.25	50.0	47.0	94	
	PBO	0.80	160.0	149.0	93	
	NOBD	0.40	80.0	74.0	92	
4	Pyrethrin	0.25	50.0	47.0	94	
	PBO	0.80	160.0	148.0	92	
	NOBD	0.40	80.0	76.0	95	
5	Pyrethrin	0.25	50.0	46.2	92	
	PBO	0.80	160.0	151.0	94	
	NOBD	0.40	80.0	74.0	92	
	Pyrethrin					94
	PBO					93
	NOBD					94

TABLE V

ANALYSIS OF VARIANCE

Type of sample [a]	*Source of variation*	*Degrees of freedom*	*Mean square*	*F-value*
(A) Pyrethrin	Concentration level	2	16.20	1.45
	samples	12	11.10	$F_{0.05} = 5.10$
(B) PBO	Concentration level	2	13.26	2.99
	samples	12	4.43	$F_{0.05} = 5.10$
(C) NOBD	Concentration level	2	6.07	1.12
	samples	12	5.43	$F_{0.05} = 5.10$
(D)[b] Pyrethrin	Component	2	0.27	0.04
PBO, NOBD	samples	42	7.68	$F_{0.05} = 3.22$

[a] Active pesticide ingredient.

[b] No significant differences were noted in the recovery tests at the different concentration levels of pesticide components A, B and C. Therefore, the concentration level of each component was ignored and the analysis of variance was applied to the mixture (D) of the three components, pyrethrin, PBO and NOBD.

the concentration level of the individual pesticide components nor a mixture of the pesticide components in the presence of the inert ingredients affected the desired analytical results of the proposed procedure. The percentage recoveries fell within a relatively consistent range and were statistically acceptable as the desired analytical values for the pesticide.

Commercially available water-base pesticide aerosols (38 samples) were also

TABLE VI

ANALYTICAL RESULTS ON WATER-BASE AEROSOL SAMPLES OBTAINED BY ACETONE PRE-TREATMENT PROCEDURE

Sample code	*Pesticide components*					
	Pyrethrin (%)		*PBO (%)*		*NOBD (%)*	
	Label guarantee	*Found*	*Label guarantee*	*Found*	*Label guarantee*	*Found*
A	0.25	0.27	0.625	0.66	0.625	0.67
	0.25	0.26	0.625	0.66	0.625	0.68
	0.25	0.26	0.625	0.67	0.625	0.68
	0.25	0.26	0.625	0.70	0.625	0.67
	0.25	0.26	0.625	0.68	0.625	0.68
	0.25	0.26	0.625	0.68	0.625	0.68
	0.25	0.27	0.625	0.68	0.625	0.67
	0.25	0.26	0.625	0.66	0.625	0.66
	0.25	0.26	0.625	0.68	0.625	0.68
	0.25	0.27	0.625	0.68	0.625	0.66
	0.25	0.27	0.625	0.66	0.625	0.66
	0.25	0.27	0.625	0.66	0.625	0.66
B	0.20	0.20	1.00	0.94		
	0.20	0.19	1.00	0.97		
	0.20	0.20	1.00	0.89		
	0.20	0.19	1.00	0.92		
	0.20	0.20	1.00	0.91		
	0.20	0.20	1.00	0.93		
	0.20	0.20	1.00	0.93		
	0.20	0.20	1.00	0.93		
	0.20	0.20	1.00	0.92		
	0.20	0.20	1.00	0.93		
	0.20	0.19	1.00	0.91		
	0.20	0.20	1.00	0.93		
C	0.30	0.28	1.25	1.13	0.50	0.49
	0.30	0.27	1.25	1.06	0.50	0.46
	0.30	0.28	1.25	1.13	0.50	0.44
	0.30	0.27	1.25	1.10	0.50	0.45
D	0.40	0.47	4.00	3.96		
E	0.25	0.23	1.25	0.80		
	0.25	0.19	1.25	0.84		
	0.25	0.21	1.25	0.75		
	0.25	0.22	1.25	0.87		
	0.25	0.21	1.25	0.83		
F	0.25	0.23	0.90	0.80	0.50	0.48
G	0.25	0.29	0.62	0.60	0.62	0.53
H	0.25	0.27	0.80	0.88		
I	0.25	0.23	0.62	0.61	0.62	0.68

analyzed for pyrethrins and the synergists by using the proposed procedure. The results of the tests are given in Table VI; each analytical result was obtained from a separate can of aerosol mixture. The tangible differences noted between the label guarantee values and the analytical values for the PBO component of sample E were due to faulty composition of the commercial aerosol and not to a problem in analytical technique.

The advantages of incorporating acetone in the extraction procedure of an aerosol water-base pesticide formulation prior to gas chromatographic analysis of the pesticide ingredients are:

(1) the elimination of potential losses of volatile components during the sampling procedure, thereby minimizing sampling errors;

(2) the elimination of the problem of removing the foam reactants (emulsifier ingredients) prior to analysis;

(3) the elimination of the prior removal of the propellant ingredient;

(4) the aerosol can be sampled under actual spraying conditions;

(5) preliminary puncture of the aerosol can to remove all of the propellant is unnecessary and therefore numerous subsequent samples can be made from the same container under the same original conditions; and

(6) extraneous ingredients are removed more efficiently from the sample, thereby eliminating background interferences on the recorded gas chromatograph chart data and minimizing the problems of contamination of the gas chromatograph column and detector.

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