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ANALYTICAL STUDIES OF PYRETHRIN FORMULATIONS BY GAS CHROMATOGRAPHY*

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SUMMARY

Commercial formulations of mixtures of pyrethrins, piperonyl butoxide, and *n*-octyl bicycloheptene dicarboximide were quantitatively measured by gas chromatography. The three active ingredients of the formulations were measured simultaneously using gas chromatographic columns containing the support Chromosorb W coated with either 3% or 5% SE-30 silicone. The individual pesticide components present in the formulations, ranging in amounts of 0.05 to 50.0% of the mixtures, could be measured within a reasonable degree of accuracy.

INTRODUCTION

Pesticide chemists generally agree that the AOAC method[1] for the analysis of pyrethrin formulations is tedious, time-consuming, and lacks precision and accuracy; the latter is evident in the collaborative report by KELSEY[2]. The British Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry on Methods of Assay for Crude Drugs made a comparative detailed study of the method with the PBK (Pyrethrum Board of Kenya) procedure[3] and concluded that the AOAC procedure was "inherently unsatisfactory", that it also measured "false materials", but they recommended its use as an interim measure.

The AOAC procedure measures the hydrolysis products of the pyrethrums, considered to be chrysanthemum monocarboxylic acids which are derived from pyrethrin I and cinerin I components of the pyrethrum mixture and are reported as pyrethrin I (ref. 4); the measured dicarboxylic acids are derived from the pyrethrin II and cinerin II components and are reported as pyrethrin II. Recent reports[5] indicate that jasmolin I would also be included in the pyrethrin I fraction and jasmolin

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II would be included in the pyrethrin II fraction. Pyrethrins are subject to degradation by air oxidation, exposure to light, and possibly by enzymatic activity[6], and the degraded components most probably yield acids on hydrolysis which would be measured and reported as true pyrethrins.

To facilitate process and formulation procedures, WACHS AND HANLEY[7] utilized the principle of the selective reaction of ethylenediamine with the cyclopentenolone esters of pyrethrums. The amine salts of the carboxylic acids are titrated with sodium methylate. The esters of cinerin II and pyrethrin II were not measured in this procedure and a molecular weight factor was used to calculate total pyrethrins, which assumed a 1:1 ratio of pyrethrins I and II. FURMANEC *et al.*[8] employed thin-layer chromatography for the separation of pyrethrins I and II, followed by treatment of the separated fractions with orthophosphoric acid and heat and the measurement of the reaction products by colorimetry at 550 mμ. In the latter procedure, decomposition problems could arise unless elaborate precautions were taken[9].

The most promising procedure for the screening of pyrethrum formulations, especially for the ones that contain small amounts (in the range of 0.05–0.50% pyrethrin concentrations) of the pesticide, includes the use of gas chromatography[9–16]. Further, if the synergist piperonyl butoxide (PBO) or *n*-octyl bicycloheptene dicarboximide (NOBD) are present in the pyrethrin formulation, all of the components can be measured simultaneously under the conditions reported in this study. It is conceded[5] that a pyrethrin primary standard or an accurately assayed pyrethrum extract must be available as a frame of reference for quantitation purposes. This report presents data on the analysis of pyrethrins and synergists by gas chromatography wherein the only variable parameter was the gas chromatographic column. The cleanup reagent Florisil was used with all samples to remove oil-based materials and other substances that would otherwise interfere with the gas chromatographic analysis of the NOBD component of the formulation.

MATERIALS AND METHODS

Materials

Gas chromatograph. A Varian Aerograph Series 1200, flame-ionization detector was employed. The column temperature was 190°, the injector and detector temperatures were 205°. Gas flow rates were nitrogen, 25 ml/min; hydrogen, 25 ml/min; air 200 ml/min. Three of the gas chromatographic columns used contained packings of 3%, 5%, and 7% SE-30 silicone, respectively, coated on a Chromosorb W support. A fourth column contained 5% SE-30 silicone coated on Gas-Chrom Q support. All supports were 60–80 mesh, acid-washed and treated with dimethyldichlorosilane. The gas chromatographic columns were $\frac{1}{8}$ in. I.D. by 5-ft. spiral borosilicate glass. A Leeds and Northrup Speedomax H recorder, 1 mV full scale, chart speed 0.5 in./min was used.

Chromatographic columns for Florisil cleanup. The columns consisted of 20 × 400 mm borosilicate glass with Ultramax stopcock and 300-ml reservoir.

Glass U-tubes for aerosol sampling. Two types of tubes were applied: (1) 1.5 mm I.D. × 7 mm O.D. capillary tubing with one end expanded to accept a 3-mm ($\frac{1}{8}$-in.) silicone 'O' ring. (2) 3-mm ($\frac{1}{8}$-in.) glass tubing fused inside 5 mm O.D. glass tubing

with an extension of about 12 mm of the $\frac{1}{8}$-in. tubing. A $\frac{1}{8}$-in. 'O' ring will seal the connection when the sample is withdrawn from the aerosol container.

Florisil. Florisil (Floridin Co., Pittsburgh, Pa.), 60–80 mesh, was heated for 16 h at 130° prior to use.

Reagents. Anhydrous sodium sulfate was heated for 16 h at 280° prior to use. Hexane, acetone, and carbon disulfide were redistilled in an all-glass system.

Pyrethrin and synergists standard solutions. Pyrethrin concentrate (20% assay) was supplied by Niagara Chemical Division, FMC Corp., 100 Niagara St., Middleport, N.Y. 14105; piperonyl butoxide, 100% (PBO) by Fairfield Chemical Division, FMC Corp., 441 Lexington Avenue, New York, N.Y.; and *n*-octyl bicycloheptene dicarboximide (NOBD) by McLaughlin Gormley King Co., 1715 Fifth St., S. E., Minneapolis, Minn.

Solutions of mixtures of the above compounds were prepared for gas chromatography standards as follows. The concentration of the compounds in carbon disulfide solution was 0.4 μg/μl for pyrethrin I, and 1.1 μg/μl each for PBO and NOBD; 2-μl or 3-μl aliquots were applied to the gas chromatographic column. A range setting of 10 and a variable attenuation setting of 16, 32, or 64 were used with the instrument. To quantitate the NOBD in the standard mixture, either a smaller aliquot, a change in attenuation setting, or an additional dilution of the standard solution was necessary to bring the NOBD curve within the linear range on the recorder chart (see Fig. 1).

The linearity range was 0.2 to 2.2 μg for pyrethrin I, 0.6 to 5.6 μg for PBO, and 0.3 to 1.7 μg for NOBD, with a minimum detectability of about 0.06 μg for each of the three components.

Preparation of samples

Aerosols. The cap and spray head are removed from the container. The remainder of the container and the appropriate U-tube are weighed. The U-tube is attached to the spray tube of the aerosol container. The aerosol container is shaken vigorously for at least 30 sec, the open end of the U-tube is plunged into 125 ml hexane contained in a separatory funnel and the U-tube is immediately depressed to remove 10–20 g of the sample from the container. The container and U-tube are again weighed to determine, by difference, the weight of the sample to be analyzed. If the sample is miscible with hexane, it is transferred to the Florisil column for cleanup. If the sample is a water–oil base emulsion, the pyrethrins are partitioned into a hexane layer and the hexane is concentrated to a small volume by evaporation on a steam bath with a stream of air. The residue is then transferred to the Florisil column with hexane.

Liquids (oil based). An appropriate amount of sample is weighed, diluted with 10 ml hexane, and transferred to the Florisil column for cleanup.

Dusts. Although dusts were not included in this study, if such materials are analyzed for the pyrethrins, the sample is extracted with either acetonitrile or chloroform (dust:solvent = 1:5) by shaking for 1 h on a mechanical shaker. The mixture is filtered, the solvent is removed by evaporation, and the residue is transferred to the Florisil column with hexane for cleanup.

Sample cleanup

The chromatographic column is packed with 5 g anhydrous sodium sulfate, followed by 20 g Florisil, and topped with 5 g anhydrous sodium sulfate. The column

TABLE I

ANALYTICAL DATA ON COMMERCIAL PYRETHRUM SAMPLES OBTAINED WITH VARIOUS GAS CHROMATOGRAPHIC COLUMNS[a]

Gas chromatographic column	*Sample*[b]								
	Py			*PBO*			*NOBD*		
	Range	*Average (%)*	*Label guarantee*	*Range*	*Average (%)*	*Label guarantee*	*Range*	*Average (%)*	*Label guarantee*
3% SE-30 on Chromosorb W									
Aerosol A[c]	0.18–0.21	0.19	0.20	0.42–0.56	0.50	0.50	0.43–0.57	0.51	0.50
Aerosol B	0.16–0.23	0.20	0.20	0.47–0.64	0.53	0.50	0.47–0.69	0.53	0.50
Aerosol C	0.19–0.22	0.20	0.20	0.46–0.53	0.49	0.50	0.46–0.66	0.54	0.50
Py 2.5	2.27–2.68	2.49	2.50	—	—	—	—	—	—
Py 53	4.80–5.69	5.11	5.00	49.0–56.1	52.4	53.1	—	—	—
65404	0.038–0.049	0.044	0.05	0.078–0.086	0.082	0.10	0.14–0.16	0.14	0.16
5% SE-30 on Chromosorb W									
Aerosol A	0.20–0.24	0.22	0.20	0.43–0.54	0.49	0.50	0.44–0.54	0.47	0.50
Aerosol B	0.20–0.24	0.21	0.20	0.48–0.59	0.51	0.50	0.45–0.58	0.51	0.50
Aerosol C	0.19–0.21	0.20	0.20	0.41–0.50	0.46	0.50	0.41–0.53	0.47	0.50
Py 2.5	2.30–2.58	2.42	2.50	—	—	—	—	—	—
Py 53	4.95–5.20	5.03	5.00	50.2–53.0	51.7	53.1	—	—	—
65404	0.041–0.050	0.045	0.05	0.075–0.085	0.079	0.10	0.13–0.15	0.14	0.16
7% SE-30 on Chromosorb W									
Aerosol A	0.17–0.25	0.20	0.20	0.38–0.53	0.45	0.50	0.48–0.60	0.55	0.50
Aerosol B	0.19–0.25	0.21	0.20	0.41–0.56	0.49	0.50	0.47–0.60	0.54	0.50
Aerosol C	0.16–0.21	0.19	0.20	0.46–0.64	0.54	0.50	0.41–0.50	0.45	0.50
Py 2.5	1.90–3.45	2.39	2.50	—	—	—	—	—	—
Py 53	3.85–4.65	4.33	5.00	43.5–54.0	48.8	53.1	—	—	—
65404	0.040–0.055	0.044	0.05	0.070–0.075	0.073	0.10	0.13–0.16	0.15	0.16
5% SE-30 on Gas-Chrom Q									
Aerosol A	0.17–0.22	0.19	0.20	0.45–0.58	0.50	0.50	0.46–0.53	0.49	0.50
Aerosol B	0.17–0.23	0.20	0.20	0.43–0.59	0.51	0.50	0.36–0.54	0.47	0.50
Aerosol C	0.17–0.21	0.18	0.20	0.44–0.62	0.51	0.50	0.34–0.52	0.46	0.50
Py 2.5	2.28–2.71	2.47	2.50	—	—	—	—	—	—
Py 53	4.55–5.40	4.70	5.00	50.0–54.2	51.7	53.1	—	—	—
65404	0.043–0.052	0.047	0.05	0.087–0.092	0.089	0.10	0.13–0.15	0.14	0.16

[a] Acid-washed, dimethyldichlorosilane-treated support, 60–80 mesh.

[b] Commercially available formulations which contained pyrethrins (Py), piperonyl butoxide (PBO) and *n*-octyl bicycloheptene dicarboximide (NOBD).

[c] Aerosols A, B, and C were samples of the same shipment of the type designed for household use. The remainder of the samples were oil-based formulations. The analytical range represents nine samplings of each sample for analysis, except No. 65404, which was four samplings.

TABLE II

OBSERVED VARIATIONS IN ANALYTICAL DATA FROM REPLICATE SAMPLINGS OF THE PYRETHRIN FORMULATIONS

Gas chromatographic column	*Sample component*[a]								
	Py			*PBO*			*NOBD*		
	Range	*Maximum variation (%)*	*Maximum variation from label guarantee (%)*	*Range*	*Maximum variation (%)*	*Maximum variation from label guarantee (%)*	*Range*	*Maximum variation (%)*	*Maximum variation from label guarantee (%)*
Aerosols A, B and C[b]									
3% SE-30 on Chromosorb W	0.16–0.23	0.07	35	0.42–0.64	0.22	44	0.43–0.69	0.26	52
5% SE-30 on Chromosorb W	0.19–0.24	0.05	25	0.41–0.59	0.18	36	0.41–0.58	0.17	34
7% SE-30 on Chromosorb W	0.17–0.25	0.09	45	0.38–0.64	0.26	52	0.41–0.60	0.19	38
5% SE-30 on Gas-Chrom Q	0.17–0.23	0.06	30	0.43–0.62	0.19	38	0.34–0.54	0.20	40
Py 2.5									
3% SE-30 on Chromosorb W	2.27–2.68	0.41	16.4	—	—	—	—	—	—
5% SE-30 on Chromosorb W	2.30–2.58	0.28	11.2	—	—	—	—	—	—
7% SE-30 on Chromosorb W	1.90–3.45	1.55	62.0	—	—	—	—	—	—
5% SE-30 on Gas-Chrom Q	2.28–2.71	0.43	17.2	—	—	—	—	—	—
Py 53									
3% SE-30 on Chromosorb W	4.80–5.69	0.89	17.8	49.0–56.1	7.1	13.4	—	—	—
5% SE-30 on Chromosorb W	4.95–5.20	0.25	5.0	50.2–53.0	2.8	5.3	—	—	—
7% SE-30 on Chromosorb W	3.85–4.65	0.80	16.0	43.5–54.0	10.5	19.8	—	—	—
5% SE-30 on Gas-Chrom Q	4.55–5.40	0.85	17.0	50.0–54.2	4.2	7.9	—	—	—
65404									
3% SE-30 on Chromosorb W	0.038–0.049	0.011	22.0	0.078–0.086	0.008	8.0	0.14–0.16	0.02	12.5
5% SE-30 on Chromosorb W	0.041–0.050	0.009	18.0	0.075–0.085	0.010	10.0	0.13–0.15	0.02	12.5
7% SE-30 on Chromosorb W	0.040–0.055	0.015	30.0	0.070–0.075	0.005	5.0	0.13–0.16	0.03	18.8
5% SE-30 on Gas-Chrom Q	0.043–0.052	0.009	18.0	0.087–0.092	0.005	5.0	0.13–0.15	0.02	12.5

[a] Py = pyrethrins; PBO = piperonyl butoxide; NOBD = *n*-octyl bicycloheptene dicarboximide.
[b] Aerosols, twenty-seven samplings; Py 2.5 and Py 53, nine samplings each; 65404, four samplings.

is prewashed with 100 ml hexane, leaving enough of the solvent in the column to cover the packed contents of the column. The sample residue is transferred to the column with 5–10 ml hexane, the column is then washed with 75 ml hexane; the hexane eluate is discarded. The pyrethrins and the synergistic compounds are then eluted from the column with 125 ml acetone. The acetone eluate is evaporated nearly to dryness by means of a stream of air and a warm steam bath. The residue is diluted to about 10 ml with carbon disulfide and passed through a small column of anhydrous sodium sulfate. The sodium sulfate column is washed with a small amount of carbon disulfide and the combined eluates are made to a definite volume for gas chromatographic analysis.

RESULTS AND DISCUSSION

The data shown in Tables I and II on the pyrethrins (Py) were obtained from the pyrethrin I fraction of the gas chromatographic curve. The calculated amount of

TABLE III

ANALYSIS OF PYRETHRIN CONTENT OF AEROSOL FORMULATIONS[a]

Sample	*Gas chromatographic column*			
	3% SE-30 on Chromosorb W (%)	*5% SE-30 on Chromosorb W (%)*	*7% SE-30 on Chromosorb W (%)*	*5% SE-30 on Gas-Chrom Q (%)*
	0.19	0.20	0.20	0.19
	0.19	0.21	0.17	0.18
	0.21	0.20	0.21	0.17
	0.19	0.20	0.19	0.17
A	0.19	0.20	0.25	0.18
	0.20	0.24	0.21	0.19
	0.21	0.24	0.21	0.19
	0.18	0.24	0.19	0.21
	0.19	0.22	0.19	0.22
	0.20	0.21	0.25	0.21
	0.16	0.18	0.19	0.18
	0.18	0.23	0.20	0.20
	0.21	0.21	0.21	0.19
B	0.23	0.21	0.22	0.20
	0.22	0.23	0.21	0.21
	0.22	0.24	0.20	0.23
	0.19	0.21	0.19	0.20
	0.20	0.20	0.19	0.17
	0.20	0.20	0.21	0.17
	0.20	0.19	0.19	0.18
	0.19	0.19	0.16	0.17
	0.19	0.21	0.17	0.17
C	0.19	0.21	0.21	0.17
	0.22	0.19	0.21	0.18
	0.19	0.20	0.21	0.21
	0.20	0.20	0.19	0.20
	0.19	0.20	0.20	0.21

[a] Pyrethrin I values, determined by gas chromatography, were multiplied by a factor of 2. Nine analyses were made on each of three aerosol formulations (all three aerosols of identical label; pyrethrin content 0.20%), on four gas chromatographic columns as described above.

pyrethrin I was multiplied by a factor of 2, since it is known that the two major components present in pyrethrums are pyrethrin I and pyrethrin II and normally occur in approximately equal amounts[6,14]. With one possible exception, the data in the tables and Fig. 1 indicate that a gas chromatographic column containing a 5% SE-30 silicone on Chromosorb W (AW-DMCS), 60–80 mesh, was preferable for the separation and quantitation of pyrethrin I, NOBD, and PBO. The exception was the samples packed in the aerosol containers, where statistical analysis (Tables III and IV) indicated that the 3% SE-30 silicone column was the preferred one.

TABLE IV

STATISTICAL DATA ON PYRETHRIN AEROSOL FORMULATION ANALYSIS[a]

Gas chromatographic column	*Mean value*	*Standard deviation*	*Coefficient of variation*
3% SE-30 on Chromosorb W	0.197	0.014	7.51
5% SE-30 on Chromosorb W	0.209	0.016	8.08
7% SE-30 on Chromosorb W	0.201	0.020	9.94
5% SE-30 on Gas-Chrom Q	0.190	0.017	9.28

[a] Based on nine samplings from each of three aerosols, or a total of 27 samplings.

ANALYSIS OF VARIANCE[b]

Source of variation	*Degrees of freedom*	*Sum of squares*	*Mean square*
Gas chromatographic column	3	50.2	16.73
Aerosol sample	2	23.7	11.85
Column × sample	6	209.9	34.94[c]
Determination within sample within column	96	85.1	0.89
Total	107	368.9	

[b] Calculations based on % values (see Table III) × 100 for simplicity.
[c] Significant level at 1%.

Under the experimental conditions specified in this report, the pyrethrin I component of the pyrethrum fraction (Fig. 1, curves A and B, peak 2) of the formulation was the only predominant peak of the pyrethrum fraction in the curve recorded by the gas chromatograph; the other pyrethrum components did not interfere with the simultaneous recording of the NOBD and PBO components of the mixture. The identity of the pyrethrin I fraction, collected from the gas chromatographic column, was confirmed by IR spectroscopy (see Fig. 2); the spectrum was in excellent agreement with the one reported by ELLIOTT[17].

The manipulative errors that may accumulate during the period of sampling, cleanup, and final concentration, prior to the sample reaching the gas chromatographic analysis stage must be considered in any comparative analytical techniques. One must assume that such errors will be minimal in the hands of an experienced analyst and, therefore, any major differences in the comparative data will be related to the gas chromatographic column performance. Visual evidence of this factor is apparent

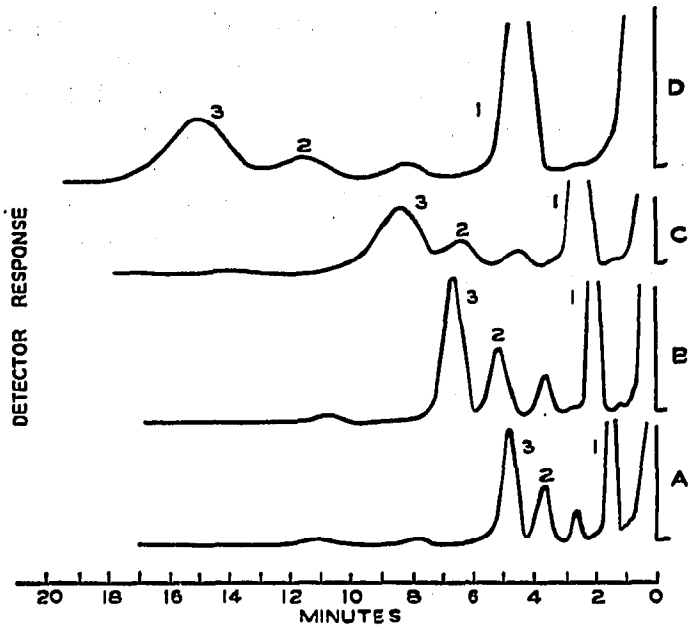

Fig. 1. Gas chromatographic curves of pyrethrin–synergist formulations. Curves A, B, and D from gas chromatographic columns of 3%, 5%, and 7% SE-30 silicone on Chromosorb W, respectively; curve C from a column of 5% SE-30 silicone on Gas-Chrom Q. Peaks 1, 2, and 3 are NOBD, pyrethrin I, and PBO, respectively.

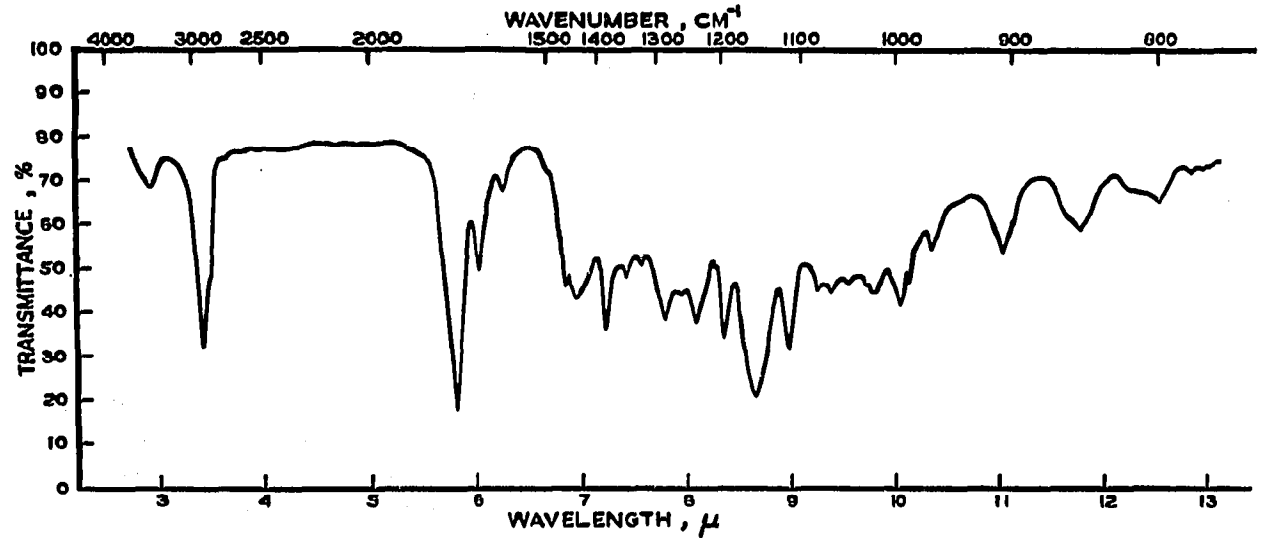

Fig. 2. IR spectrum of the pyrethrin I fraction obtained from the gas chromatographic column.

in curves C and D of Fig. 1; arithmetic recovery data (Table V) does not readily show this distinction. The proper sampling of aerosols is always difficult, as illustrated in Tables I, II, and VI.

The data indicate that the label guarantee of a commercial formulation which contains pyrethrins and synergists can be verified by analysis of the mixture by gas chromatography. If it becomes necessary to adhere to the conditions for the "permissive guarantee variations" or a "passed" judgment decision on the label guarantee

TABLE V

RECOVERY OF PYRETHRIN FORMULATION COMPONENTS FROM FLORISIL COLUMNS

Gas chromatographic column		*Pyrethrin I (%)*	*Piperonyl butoxide (%)*
3% SE-30 on Chromosorb W		87	90
		88	92
		94	94
	Average	90	92
5% SE-30 on Chromosorb W		90	95
		89	95
		96	95
	Average	92	95
7% SE-30 on Chromosorb W		91	93
		89	90
		84	86
	Average	88	90
5% SE-30 on Gas-Chrom Q		94	95
		92	93
		90	95
	Average	92	94

TABLE VI

EFFECT OF SAMPLING TECHNIQUE ON ANALYTICAL VALUES OF PYRETHRIN FORMULATIONS FROM AEROSOL CONTAINERS[a]

Sampling date	*Sample weight (g)*	*Sampling procedure*[b]		*Pyrethrins (%)*	*Piperonyl butoxide (%)*
May 21st	13.1	No shaking		0.19	0.47
	15.7			0.14	0.37
			Average	0.17	0.42
May 23rd	16.6	No shaking		0.23	0.58
	11.7			0.18	0.49
	17.3			0.27	0.73
	18.6			0.22	0.58
			Average	0.23	0.60
May 28th	18.0	Shaken		0.22	0.51
	18.0			0.20	0.51
	13.5			0.23	0.56
	15.5			0.21	0.47
	16.0			0.21	0.50
	27.0			0.17	0.45
			Average	0.21	0.50
Label guarantee				0.20	0.50

[a] The aerosol samples were a mosquito and fly spray containing an emulsion of water and oil base and isobutane propellant.

[b] No shaking means: the sample was taken with no prior mixing.
Shaken means: the aerosol can was shaken vigorously for 30 sec prior to each sampling.

of a commercial sample, prescribed by the Association of American Pesticide Control Officials (AAPCO)[18] as follows:

Pesticide active ingredient guarantee (%)	*Allowable deviation below guarantee*
<1.00	15% of guarantee
1.00– 19.99	0.1 plus 5% of guarantee
20.00– 49.99	0.5 plus 3% of guarantee
50.00–100.00	1.0 plus 2% of guarantee

It is possible that aerosol formulations with individual active ingredients of less than 1.00% could be analyzed within their prescribed limitations. It may also be possible to retain this degree of precision with oil-based formulations within the label guarantee range of 1 to 49.99%. However, when the active ingredient is $\geqslant 50\%$, such as piperonyl butoxide, it may be somewhat difficult to adhere to the AAPCO analytical restrictions.

REFERENCES

1 *Official Methods of Analysis of the Association of Official Agricultural Chemists*, 10th Ed., Association of Official Agricultural Chemists, Washington, 1965, pp. 50–52.
2 D. KELSEY, *J. Assoc. Offic. Agr. Chemists*, 43 (1960) 354.
3 Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry on Methods of Assay of Crude Drugs, *Analyst*, 89 (1964) 689.
4 *Specifications for Pesticides*, World Health Organization, Geneva, 1967, pp. 34–39.
5 S. W. HEAD, *Pyrethrum Post*, 9 (1968) 31.
6 S. W. HEAD AND G. D. BLYNNE JONES, *Pyrethrum Post*, 8 (1965) 14.
7 H. WACHS AND A. V. HANLEY, *Soap Chem. Specialties*, 43 (1967) 78.
8 D. FURMANEC, F. A. E. SCHILLING AND B. B. BROWN, *Pyrethrum Post*, 10 (1969) 21.
9 H. BECKMAN AND P. T. ALLEN, in R. F. GOULD (Editor), *Advances in Chemistry, Series 53*, American Chemical Society, Washington, 1966, pp. 51–64.
10 L. DONEGAN, P. J. GODIN AND E. M. THAIN, *Chem. Ind. (London)*, (1962) 1420.
11 H. BECKMAN, P. T. ALLEN AND P. BERKENKOTTER, *J. Gas Chromatog.*, 8 (1963) 21.
12 S. W. HEAD, *Pyrethrum Post*, 7 (1964) 12.
13 B. J. GUDZINOWICZ, *Anal. Chem.*, 37 (1965) 1068.
14 S. W. HEAD, *Pyrethrum Post*, 8 (1966) 3.
15 S. W. HEAD, *Pyrethrum Post*, 9 (1967) 12.
16 VON WOLFRAM-DIETRICH WEINMANN AND C. RODER, *Nachrbl. Deut. Pflanzenschutzdienst (Berlin)*, 20 (1968) 184.
17 M. ELLIOTT, *J. Appl. Chem.*, 11 (1961) 19.
18 *Permissive Guarantee Variations Committee Report*, in R. H. GUNTERT (Editor), *Official Publication Association of American Pesticide Control Officials Inc.*, State Board of Agriculture, Topeka, 1968–1969, p. 83.