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Effects of the High Temperature on the Physical and Chemical Properties of Some Public Health Insecticide Formulations

ABDURRAHMAN AKSOY*, OGUZHAN YAVUZ, DILEK GUVENC and YAVUZ KURSAD DAS
Department of Pharmacology-Toxicology, Faculty of Veterinary Medicine
Ondokuz Mayis University, 55139 Samsun, Turkey
Fax: (90)(362)4576922; Tel: (90)(362)3121919-2816
E-mail: abaksoy@gmail.com

Insecticides are manufactured, formulated and packaged to specific standards for safe and effective vector control. Sometimes the insecticide products can break down and lose their active ingredients under storage conditions (especially high temperature). In this study, 11 different insecticide formulations were stored in 50 mL coex bottles (same as an original package) at 54ºC during 14 d. The formulations contained 1 organophosphate (temephos) and 6 synthetic pyrethroids (α-cypermethrin, δ-methrin, cypermethrin, cyfluthrin, cyphenothrin and permethrin) alone or combined with knock down agent tetramethrin and synergist agent piperonyl butoxide. Formulation type of all formulations was emulsifiable concentrate. Density, appearance, colour and pH of the formulations were determined as the physical parameters at the beginning and end of the storage period. The chemical analysis of the samples was made by gas chromatography equipped with flame ionization detector at the beginning and 14th day. At the end of the study, physical and chemical features of the used formulations did not change under the high temperature (54ºC) during 14 d. The formulations used in the study are resistant to high temperature and they may safely use for a long time under the normal storage conditions. Also, the formulations can be effective to the target organisms in the tropics or in temperate climates. But, we defined that, accelerated stability tests are not satisfactory in the field conditions and long term stability tests, especially 2 years or more and biological efficacy tests should be performed additionally.

Key Words: Insecticide, Formulation, Gas chromatography.

INTRODUCTION

Today, insecticide usage is the most important element in the integrated approach to control of vectors and pests of agriculture and public health importance[1,2]. Diseases such as malaria, Chagas disease, dengue and dengue haemorrhagic fever, onchocerciasis and leishmaniasis affect the health and well-being of millions of people worldwide and are an impediment to social and economic development. The proper use of insecticides play an important global role in the prevention and control of these diseases[2].

Insecticides are manufactured, formulated and packaged to specific standards. Because, one of the critical issues of the vector control programmes is good quality of insecticide active ingredients. But, sometimes insecticides can break down and lose their active ingredients under storage conditions. Some insecticides become more toxic, flammable or explosive as they break down and may cause unacceptable effects on non-target organisms. The insecticides also become ineffective in this situation[3-6].

Because of these, storage stability tests are performed to determine how the quality of a insecticide product varies with time under the influence of environmental factors, such as temperature and humidity. The test requirement for stability during storage can normally be established in one or more ways, such as accelerated testing, ambient testing, cold stability testing, testing for reactivity towards container material. An accelerated stability study is used to indicate ageing of a product by elevated temperatures[7,8]. In the present study, changes of physical and chemical characteristics of the public health insecticide formulations under the high temperature condition for 14 d were investigated. The obtained data was used for evaluation of quality and safety of the used insecticide formulations.

EXPERIMENTAL

11 Public health pesticide formulations were stored at 54 ± 2ºC during 14 d. These conditions are accepted to the accelerated storage stability studies by the Collaborative International Pesticide Analytical Council[9]. Chemical analysis of the samples was made with gas chromatography method at the beginning and 14th day. Samples were kept in 50 mL coex bottle (same as an original packages) for each analysis.

The formulations contained one organophosphate (temephos) and six synthetic pyrethroids (α-cypermethrin, δ-methrin, cypermethrin, cyfluthrin, cyphenothrin and permethrin) alone or combined with knock down agent tetramethrin and synergist agent piperonyl butoxide (PBO). Formulation type of all formulations was emulsifiable concentrate. Specifications of the formulations are shown in Table-1.

Certified insecticide standards were used for chemical analysis. Temephos (90.8 %) was purchased from Ficom Organics Ltd. (Mumbai, India), δ-methrin (98 %), α-cypermethrin (97.8 %) and cypermethrin (92.3 %) were purchased from Tagros Chemicals Ltd. (Chennai, India), cyphenothrin (93.1 %) was purchased from Changzhou Ltd. (Changzhou, China), permethrin (94.5 %) and cyfluthrin were purchased from Shenzen Oct Production Materials Co. Ltd. (Shenzen, China), tetramethrin (97.6 %) and PBO (94.2 %) were purchased from Aestar Zhongshan Fine Chemicals Inc. Ltd. (Zhongshan, China). Aceton (GC analysis gradient) was obtained from Merck (Darmstadt, Germany).

TABLE-1
SPECIFICATIONS OF THE USED INSECTICIDE FORMULATIONS

Formulation	Active ingredients (a.i.)	a.i. in the formulation (g/L)	Ratio (%)
1	Temephos	500	50
2	Temephos	500	50
3	Temephos	500	50
4	α-Cypermethrin	100	10
5	δ-Methrin	50	5
6	Cypermethrin	100	10
7	Cypermethrin	100	10
	Tetramethrin	15	1.5
	Piperonyl butoxide	60	6
8	Cyfluthrin	50	5
	Tetramethrin	25	2.5
	Piperonyl butoxide	100	10
9	Cyphenothrin	200	20
	Tetramethrin	50	5
	Piperonyl butoxide	150	15
10	Permethrin	109	10.9
	Tetramethrin	24	2.4
	Piperonyl butoxide	133	13.3
11	Permethrin	250	25
	Tetramethrin	50	5
	Piperonyl butoxide	150	15

A Shimadzu GC-17A with flame ionization detector (FID) and Shimadzu AOC 20i autoinjector was used for gas chromatographic analysis. Nuve EN 500 incubator (Ankara, Turkey) was used for 54 ± 2ºC condition. Thermo, Orion 710A+ pH meter was used for pH measurements.

Analysis was carried out on 30 m × 0.32 mm i.d. fused silica capillary column with 0.25 µm film of 95 % dimethylpolysiloxane 5 % diphenyl (Teknokroma, Spain). The standards and the formulations were dissolved in acetone and 1 microliter delivery volume at fast injection speed was injected with an auto injector system. Different test methods were applied for temephos and synthetic pyrethroids. For the analysis of temephos, the detector temperature was set at 300ºC, the injector temperature was set at 300ºC and the column oven temperature program was as follows; initial temperature 130ºC, hold for 1 min; ramp to 200ºC at 15ºC/min, hold for 1 min.; ramp to 300ºC at 15ºC/min, hold for 15 min. Carrier gas was nitrogen. Total analysis time was 28.33 min. For the analysis of synthetic pyrethroids; the detector was set at 300ºC, injector temperature was set at 280ºC, the column oven temperature program was as follows; initial temperature 100ºC, hold for 1 min; ramp to 205ºC at 15ºC/min; ramp to 275ºC at 15ºC/min, hold for 25 min. Carrier gas was nitrogen. Total analysis time was 38.67 min.

Density (g/mL), appearance, colour and pH of the formulations were determined at the beginning and end of the storage period.

Tolerance limits on content of active ingredients of WHO and FAO were used in the chemical analysis (Table-2)[1,10].

TABLE-2
TOLERANCE LIMITS ON CONTENT OF ACTIVE INGREDIENT IN FORMULATED PRODUCTS

Declared content in g/kg or g/L at 20° C*	Tolerance limits of the declared content
up to 25	± 15 % (for homogeneous formulations; EC, SC, …) ± 25 % (for non-homogeneous formulations; Granule. Wettable granule...)
above 25 up to 100	± 10 %
above 100 up to 250	± 6 %
above 250 up to 500	± 5 %
above 500	± 2.5 %

*In each range, the upper limit is included.

RESULTS AND DISCUSSION

Any changes on the appearance and colour of the formulations were not determined at the end of the study. Furthermore, density and pH values were not significantly changed during storage (Table-3). Namely, all formulations protected their physical characteristics at the high temperature condition.

In the gas chromatographic analysis, retention times of the synthetic pyrethroids were determined between 16.050 and 27.748 min. Also, the retention time of temephos was 19.915 min.

Chemical analysis results were made at the beginning of the study and end of the storage period, are shown in Table-4. Active ingredients of the all formulations were found suitable according to the tolerance limits at the beginning and 14th day of chemical analysis.

Information on the physical and chemical characteristics of an insecticide product is directly used in hazard assessment and the safe and proper storage of insecticide is an important component of good pest management[8,11]. Sometimes, public health insecticide formulations can break down, especially under conditions of high temperature and humidity. In this situation, insecticides can become more toxic and hazardous to animal and

TABLE-3
DENSITY AND pH OF THE FORMULATIONS

For.	Active ingredients (a.i.)	a.i. in the formulation (g/L)	Density (g/mL)		pH (25ºC)	
			Begin.	14th day	Begin.	14th day
1	Temephos	500	1.2404	1.2095	1.6	1.5
2	Temephos	500	1.0100	1.0900	1.5	1.5
3	Temephos	500	1.0185	1.0568	5.3	5.3
4	α-Cypermethrin	100	0.9050	0.9027	5.8	5.7
5	δ-Methrin	50	0.9680	0.9114	4.3	4.7
6	Cypermethrin	100	0.9007	0.9800	4.6	4.7
7	Cypermethrin Tetramethrin Piperonyl butoxide	100 15 60	0.8241	1.0270	2.5	3.2
8	Cyfluthrin Tetramethrin Piperonyl butoxide	50 25 100	0.9210	0.9311	4.6	4.6
9	Cyphenothrin Tetramethrin Piperonyl butoxide	200 50 150	0.9600	0.9800	3.8	3.9
10	Permethrin Tetramethrin Piperonyl butoxide	109 24 133	0.9091	0.8775	3.5	3.5
11	Permethrin Tetramethrin Piperonyl butoxide	250 50 150	0.9800	0.9900	4.0	4.0

human health. The formulations also become ineffective and vector control programmes become unsuccessful[11-14].

Because of these, storage stability studies are performed to provide data on change (or lack of change) in product composition over time. If certain ingredients decompose under conditions of high temperature, then other new chemicals may be formed whose toxicity may need to be considered. The results are also used to establish storage conditions and determine a suitable shelf life for the product[7,8].

In the present study, physical and chemical properties did not change under the high temperature (54 ± 2ºC) during 14th day. This storage condition is accepted for the accelerated storage stability tests[2,8,9] and the accelerated stability tests provide a useful guide on performance and safety after storage in hot or temperate climates[7].

TABLE-4
CHEMICAL ANALYSIS RESULTS OF THE FORMULATIONS
AT 54 ± 2ºC TEMPERATURE

For.	Active ingredients (a.i.)	a.i. in the formulation (g/L)	T.L.* (%)	Beginning		14th day	
				F.C.** (g/L)	Variety (%)	F.C.** (g/L)	Variety (%)
1	Temephos	500	±5	485.7	2.86	486.7	2.66
2	Temephos	500	±5	509.9	1.98	519.5	3.90
3	Temephos	500	±5	507.9	1.58	514.9	2.98
4	α-Cypermethrin	100	±10	104.3	4.30	100.5	0.50
5	δ-Methrin	50	±10	47.8	4.40	51.2	2.40
6	Cypermethrin	100	±10	97.0	3.00	99.9	0.10
7	Cypermethrin	100	±10	93.1	6.90	92.2	7.80
	Tetramethrin	15	±15	13.4	10.67	14.3	4.67
	Piperonyl butoxide	60	±10	57.0	5.00	61.6	2.67
8	Cyfluthrin	50	±10	46.4	7.20	54.1	8.20
	Tetramethrin	25	±10	25.3	1.20	26.4	5.60
	Piperonyl butoxide	100	±10	93.8	6.20	104.5	4.50
9	Cyphenothrin	200	±6	195.0	2.50	209.0	4.50
	Tetramethrin	50	±10	53.0	6.00	52.0	4.00
	Piperonyl butoxide	150	±6	151.0	0.67	153.0	2.00
10	Permethrin	109	±6	104.5	4.13	110.9	1.74
	Tetramethrin	24	±15	26.7	11.25	25.3	5.42
	Piperonyl butoxide	133	±6	132.9	0.08	130.7	1.73
11	Permethrin	250	±6	262.2	4.88	264.3	5.72
	Tetramethrin	50	±10	49.7	0.60	53.7	7.40
	Piperonyl butoxide	150	±6	153.4	2.27	154.7	3.13

*T.L.: Tolerance limit (Table-2), **F.C.: Found concentration.

The findings of this study may indicate that, the formulations, used in the study, are resistant to high temperature and may safely use for a long time under the normal storage conditions. The formulations can also be effective to target organisms in the tropics or in temperate climates. But, it should be noted that the insecticide formulations may also pass the accelerated tests and yet still be unsatisfactory in the field. Because of this, long term stability tests, especially 2 years or more and biological efficacy tests should be performed additionally[7-9].

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