MONITORING OF COUNTERFEIT SITUATION OF THE MOST DOMINANT PESTICIDES IN EGYPT.

By

GEHAD MOSAD KHATTAB HASAN

B. Sc. Agric. Sc. (pesticides), Ain Shams University, 2006M. Sc. Agric. Sc. (pesticides), Ain Shams University, 2012

A thesis submitted in partial fulfillment

of

the requirements for the degree of DOCTOR OF PHILOSOPHY

in

Agricultural Science (Pesticides)

Department of Plant Protection
Faculty of Agriculture
Ain shams University

ABSTRACT

Gehad Mosad Khattab: Monitoring of Counterfeit Situation of The most Dominant Pesticides in Egypt. Unpublished Ph.D. Thesis, Department of plant protection, Faculty of Agriculture, Ain Shams University, 2021.

This study aims to assess Counterfeit Situation of Pesticides in Egypt through monitoring of the counterfeit of a pesticide widely used in Egypt.

23 samples of different pesticide formulations were collected, which include 9 active ingredients to monitor the Situation of pesticide adulteration in the Egyptian market.

There are 20 unregistered samples through Egyptian Agricultural Pesticides Committee thus representing 86.96% of the total tested samples, four samples of them have registration number and the same name as formulations already registered in Ministry of Agriculture representing 20% of the total unregistered samples, These formulations are (Tinam EC 1.8%), (Mospilan SP 20%), (Score EC 25%) and (Dimethoate EC40 EC 40% code27) the registration numbers of them are (1391), (959), (945) and (1478) respectively. Three samples are Sardo 25% SC), (Chlorofos EC 48%) and (Ictafos EC 48%) were expired representing 13.04% of the total tested samples.

When determination the percentage of the active ingredients in the samples under study, the results were as follows, Only two samples with representing 8.69% of the samples under study were within the permissible limits of % a.i, and these samples are (Tinam EC 1.8%) and (Chlorofos EC 48%) active ingredient content was 1.53 and 50.355% respectively.

Five samples are (Farmactine EC 1.8%), (Occidor WP 50%), (diazinon EC 60%), (dozion EC 60%) and (Dimethoate EC40 EC 40% code28) didn't contain any active ingredient under the condition

analysis. These samples representing 21.74% of the total samples under study.

The percentage of the active ingredient in 16 samples was less than the acceptable limits representing 69.57% of the total tested samples.

The physical properties of the studied samples before and after storage were determined, 17 samples formulated (EC) determined through emulsion characteristics test, six of samples showed good emulsification characteristics before and after storage representing 35.29% of samples formulated (EC) and eleven samples showed poor emulsification characteristics before and after storage representing 64.7% of samples formulated (EC).

Four samples formulated (SP) determined through wet ability characteristics test all samples under testing showed good wet ability characteristics before and after storage representing 17.39% from the total tested samples.

Two samples one of them formulated (WP) and the other formulated (SC), both of them showed good Suspensibility and wet ability characteristics before and after storage representing 8.69% from the total tested samples.

Key words:

Counterfeit Pesticides, Illegal Pesticides, Mass Spectroscopy, IR, Physical properties.

CONTENTS

NO.	Title	Page
	LIST OF TABLES	
	LIST OF FIGURES	
	LIST OF ABBREVIATIONS	
I.	INTRODUCTION	1
II.	REVIEW OF LITERATURE	8
A	The position of counterfeit pesticides around the world.	8
В	The position of counterfeit pesticides in Egypt	16
C.	Threats and risks related to the use of counterfeit	
	pesticides	20
Ш.	MATERIAL AND METHODS	34
1.	Pesticides used	34
1.1.	Abamectin formulations	36
1.2.	Acetamipirid formulations	40
1.3.	Azoxystrobin formulations	42
1.4.	Carbendazim formulations	44
1.5.	Chlorpyrifos formulations	45
1.6.	Cypermethrin formulations	47
1.7.	Diazinon formulations	49
1.8.	Difenoconazole formulation	51
1.9.	Dimethoate formulations	52
2.	Quantitative analysis of active ingredients and	
	impurities of the investigated pesticide formulations	54
2.1.	Standard preparations of the tested pesticides (a.i) and	
	impurities	54
2.2.	Sample preparations of the tested pesticide	
	formulations	54
2.3.	Sample preparations of the impurities of the tested	
	pesticide formulations	55
3.	Determination of active ingredients and impurities	

	contents of the tested pesticides
3.1.	Gas Chromatography
3.2.	High Performance Liquid Chromatography
4.	Determination of other materials present in the
	formulation
4.1.	Gas Chromatography- Mass Spectroscopy
4.2.	Infrared spectroscopy
4.3.	Liquied Chromatography- Mass Spectroscopy
5.	Determination of the main physical criteria
	corresponding to each of investigated formulation
5.1.	Store samples in the oven
5.2	Preparation of standard water
5.3.	Emulsion stability evaluation for formulations (EC)
5.4.	Suspensibility test of (SC and WDG) formulations
6	Questionnaire forms for all workers in the pesticide
	system
6.1.	Farmers
6.2.	Traders
6.3.	Researchers
IV.	RESULTS AND DISCUSSION
1.	Abamectin formulations
1.1.	Abamectin formulation labels
1.2.	Physical Properties of Abamectin formulations
1.3.	Determination of active ingredients content of
	Abamectin formulations by HPLC
1.4.	Identification of other materials present in the samples
1.4.1	LC-Ms analysis of Abamectin formulations
1.4.2	GC-Ms analysis of Abamectin formulations
1.4.3.	Identification of Abamectin by FTIR
2.	Acetamipirid formulations
2.1.	Acetamipirid formulation labels
2.2	Physical Properties of Acetamipirid formulations
2.3	Determination of active ingredients content of

	Acetamipirid formulations
2.4.	Determination of other materials present in the samples
2.4.1.	GC-MS Analysis of Acetamiprid formulations
2.4.2	Identification of Acetamiprid by FTIR
3	Azoxystrobin formulation
3.1	Azoxystrobin formulation label
3.2	Physical Properties of Azoxystrobin formulation
3.3	Determination of active ingredients content of
	Azoxystrobin formulations
3.4.	Determination of other materials present in the samples
3.4.1.	GC-MS Analysis of Azoxystrobin formulation
3.4.2	Identification of Azoxystrobin by FTIR
4	Carbendazim formulation
4.1.	Carbendazim formulation label
4.2.	Physical Properties of Carbendazim formulation
4.3.	Determination of active ingredient content and level of
	impurities in Carbendazim sample
4.3.1.	Determination of active ingredient content of
	Carbendazim formulation
4.3.2.	Level of impurities
4.4.	Determination of other materials present in the samples
4.4.1	GC-MS Analysis of Carbendazim formulation
4.4.2.	Identification of Carbendazim by FTIR
5	Chlorpyrifos
5.1	Chlorpyrifos formulation labels
5.2	Physical Properties of chlorpyrifos formulations
5.3	Determination of active ingredient content and level of
	impurities in Chlorpyrifos samples
5.3.1.	Determination of active ingredient content of
	chlorpyrifos formulations
5.3.2.	Level of impurities
5.4.	Determination of other materials present in the
	samples

5.4.1	GC-MS Analysis of chlorpyrifos formulations
5.4.2	Identification of chlorpyrifos samples by FTIR
6	Cypermethrin
6.1	Cypermethrin formulation labels
6.2	Physical Properties of Cypermethrin formulations
6.3	Determination of active ingredient content in
	Cypermethrin samples
6.4.	Determination of other materials present in the samples
6.4.1.	GC-MS Analysis of cypermethrin formulations.
6.4.2.	Identification of Cypermethrin samples by FTIR
7.	Diazinon
7.1.	Diazinon formulation labels
7.2.	Physical Properties of Diazinon formulations
7.3.	Determination of active ingredient content and level of
	impurities in Diazinon samples
7.3.1.	Determination of active ingredient content of diazinon
	formulations
7.3.2.	Level of impurities
7.4	Determination of other materials present in the
	samples
7.4.1.	GC-MS Analysis of diazinon formulations
7.4.2.	Identification of Diazinon samples by FTIR
8	Difenoconazole formulation
8.1	Difenoconazole formulation label
8.2	Physical Properties of Difenoconazole formulation
8.3	Determination of active ingredients content of
	Difenoconazole formulations
8.4	Determination of other materials present in the samples
8.4.1	GC-MS Analysis of Difenoconazole formulation
8.4.2	Identification of Difenoconazole by FTIR
9	Dimethoate
9.1	Dimethoate formulation labels
9.2	Physical Properties of Dimethoate formulations

9.3	Determination of active ingredient content and level of	
	impurities in Dimethoate samples	134
9.3.1.	Determination of active ingredient content of	
	dimethoate formulations	134
9.3.2.	Level of impurities	135
9.4.	Determination of other materials present in the samples	137
9.4.1.	GC-MS Analysis of dimethoate formulations	137
9.4.2.	Identification of Dimethoate samples by FTIR	139
10	Questionnaires	141
A	- Farmers	141
В	Traders	146
\mathbf{C}	Researchers	157
\mathbf{V}	DISCUSSION	164
VI	SUMMERY	169
VII	REFERANCES	180
	APPENDIX	
	ARABIC SUMMARY	

LIST OF TABLES

Table No.	Title	F
1	Abamectin	
2	Acetamipirid	
3	Azoxystrobin	
4	Carbendazim.	
5	Chlorpyrifos	
6	Cypermethrin	
7	Diazinon	
8	Difenoconazole	
9	Dimethoate	
10	Data from product labels (Abamectin).	
11	Assay for samples of Abamectin formulations using HPLC	
12	Data analysis for samples of Abamectin formulations using LC-Ms	
13	Other pesticides found in the abamectin samples	
14	Design shows IR absorbance of functional groups for	
15	abamectin formulations	
15	Data from product labels (Acetamipirid)	
16	Assay for samples of Acetamipirid formulations using HPLC	
17	Other pesticides found in the acetamiprid samples	
18	IR absorbance of functional groups of acetamiprid	
	formulations	
19	IR absorbance of functional groups of Azoxystrobin	
	formulation	
20	Data from product label (Carbendazim)	
21	IR absorbance of functional groups of Carbendazim	
	formulation	
22	Assay for samples of chlorpyrifos pesticides using GC	
23	Design show IR absorbance of functional groups for	

	chlorpyrifos formulations	114
24	Data from product labels (Cypermethrin)	110
25	Assay for samples of Cypermethrin pesticides using HPLC.	11'
26	Design show IR absorbance of functional groups for	12
	Cypermethrin formulations	14.
27	Data from product labels (Diazinon)	122
28	Design show IR absorbance of functional groups for	
	diazinon formulations	12'
29	Data from product label (difenoconazole)	128
30	IR absorbance of functional groups of difenoconazole	
	formulation	13
31	Data from product labels (Dimethoate)	13
32	Assay for samples of Dimethoate pesticides using GC	13
33	Design show IR absorbance of functional groups for	
	Dimethoate formulations	14
34	The questions about farmer's behavior when purchasing	
	pesticides	14
35	The questions about information about the stores which the	
	farmer buying the pesticides	14
36	The questions about pesticides used by the farmers and	17
	alternative pesticides that they use	14
37	the questions about Procedures, transactions and licenses	
	related to the store	14
20	The questions about Precautions and actions taken in the	14
38	•	
	store	14
39	The questions about the most important problems facing	
	traders in selling and trading pesticides	15
40	The questions about the ways traders can recognize	
	counterfeit pesticides	15
41	The questions about the Specifications and shapes of	
	pesticide packages	15
		10

The questions about Pesticide fraud methods from the	
viewpoint of pesticide traders	154
Questions about The effects of pesticide cheating from the	
viewpoint of pesticide traders	156
Questions about the most important problems facing the	
pesticide industry	158
Questions about methods of pesticide adulteration from the	100
viewpoint of researchers	159
Questions about the reasons for pesticide adulteration from	10)
the viewpoint of researchers	160
Questions about the effects of pesticide fraud from the	100
viewpoint of researchers	162
Questions about the views of pesticide fraud from the	
viewpoint of researchers	163
	viewpoint of pesticide traders Questions about The effects of pesticide cheating from the viewpoint of pesticide traders Questions about the most important problems facing the pesticide industry Questions about methods of pesticide adulteration from the viewpoint of researchers Questions about the reasons for pesticide adulteration from the viewpoint of researchers Questions about the effects of pesticide fraud from the viewpoint of researchers Questions about the views of pesticide fraud from the viewpoint of researchers Questions about the views of pesticide fraud from the

LIST OF FIGURES

Fig.No.		page
1	The Abamectin formulation packages	39
2	The Acetamipirid formulation packages	41
3	The Azoxystrobin formulation packages	43
4	The Carbendazim formulation packages	44
5	The Chlorpyrifos formulation packages	46
6	The Cypermethrin formulation packages	48
7	The Diazinon formulation packages	50
8	The Difenoconazole formulation packages	51
9	The Dimethote formulations packages	54
10	HPLC Chromatograms of Abamectin formulations	79
11	LC-Ms Chromatograms of Abamectin formulations	78
12	GC-MS Chromatograms of abamectin formulations	87
13	FTIR spectrum of Abamectin formulations	89
14	HPLC Chromatograms of acetamiprid formulations	94
15	GC-MS Chromatograms of acetamiprid formulations	96
16	FTIR spectrum of acetamiprid formulations	97
17	HPLC Chromatograms of azoxystrobin formulation	100
18	GC-MS Chromatograms of azoxystrobin formulation	101
19	FTIR spectrum of azoxystrobin formulation	101
20	HPLC chromatogram of carbendazim formulation	104
21	HPLC chromatograms of carbendazim impurities	106
22	GC-MS Chromatograms of carbendazim formulation	106
23	FTIR spectrum of carbendazim formulation	107
24	GC chromatograms of chlorpyrifos formulations	110
25	GC chromatograms of chlorpyrifos impurities	111
26	GC-MS Chromatograms of chlorpyrifos formulation	112
27	Suggested fragmentation pathways of chlorpyrifos	113
28	fragmentation pathways of Sulfotep	113
29	FTIR spectrum of chlorpyrifos formulations	114
30	HPLC chromatograms of cypermethrin formulations	117
31	GC-MS Chromatograms of cypermethrin formulation	120

32	Suggested fragmentation pathways of cypermethrin
33	FTIR spectrum of cypermethrin formulations
34	GC chromatograms of diazinon formulations
35	GC chromatograms of diazinon impurities
36	GC-MS Chromatograms of diazinon formulation
37	FTIR spectrum of diazinon formulations
38	HPLC Chromatogram of difenoconazole formulation
39	GC-MS chromatogram of difenoconazole formulation
40	FTIR spectrum of difenoconazole formulation
41	GC chromatograms of dimethoate formulations
42	HPLC chromatograms of dimethoate impurities
43	GC-MS chromatograms of dimethoate formulation
44	FTIR spectrum of dimethoate formulations
45	The farmer's behavior when purchasing pesticides
46	The information about the stores which the farmer
	buying the pesticides
47	The pesticides used by the farmers and alternative
	pesticides that they use
48	Figure showing The person who consulted the farmer
49	The degree of knowledge of pesticide traders about
	labels
50	The Procedures, transactions and licenses related to the
	store
51	The Precautions and actions taken in the store
52	The most common and counterfeit pesticides
53	The most important problems facing traders in selling
	and trading pesticides
54	Ways traders can recognize counterfeit pesticides
55	Specifications and shapes of pesticide packages
56	Pesticide fraud methods from the viewpoint of pesticide
	traders
57	The effects of pesticide cheating from the viewpoint of
	pesticide traders

58	The most important problems facing the pesticide	
	industry	15
59	Methods of pesticide adulteration from the viewpoint of	
	researchers	15
60	Reasons for pesticide adulteration from the viewpoint of	
	researchers	16
61	The effects of pesticide fraud from the viewpoint of	
	researchers	16
62	Views of pesticide fraud from the viewpoint of	
	researchers	16