



Effect of storage on the stability on some organophosphorus formulation and their impurities.

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Abstract:

The present work was carried out to study the persistence of somathion Kz 50% (W/v) EC (Fenitrothion) and malatoxs 57 % (W/V) EC (Malathion) under storage at 54 °C for 28 days. The stability of fenitrothion and malathion active ingredient were 50.43 and 57.17 % before storage for all fenitrothion and malathion become after storage at the end of experiment 39.52 and 36.56% for 28 days storage respectively. The impurities of fenitrothion 50 % EC before storage were UND S-methyl fenitrothion , TMP Tetramethyl pyrophosphorothioat and water become after storage 1.17 % , UND and UND after 28 days from storage at 54 °C respectively . Also, malathion 57 % EC before storage meooops, mooSPs, malaxoin and isomalathion after storage 0.75 , 0.217 , UND and 2.89 % respectively. Fenitrothion and malathion degradation after 28 days product S –methyl Fenitrothion and O,O S triethyl ester , malathion product isomalathion.

Introduction

Organophosphate pesticides (OPs) are used worldwide in agriculture, municipal hygiene, and household pests control (Edwards and Tchounwou, 2005 ; Zheng *et al.*, 2007 and Yang *et al.*, 2008). OPs compounds such as malathion, fenitrothion ,cholrpyrifos, parathion is commonly used as insecticides for over 50 years. OPs work by attacking the nervous system; they are essentially the nerve poisons. Specifically, these compounds inhibit acetylcholinesterase enzyme involved in the hydrolysis of the neurotransmitter, acetylcholine at cholinergic synapses in the central and peripheral nervous systems (cholinergic syndrome) (O'Malley, 1997; Solberg

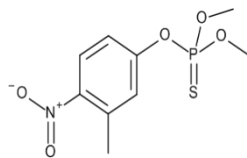

and Belkin, 1997 and Musilek *et al.*, 2005). Malathion and fenitrothion are used in agriculture to control a wide range of sucking and chewing insect pests in a variety of field crops, fruits and vegetables. Malathion can also be used for insect control on livestock, in stables and on stored products.

In this paper, we studied the effect of storage and influence sun light direct and UV lamp of pesticide on (Fenitrothion and malathion) during storage for 28 days at 54 °C .

Materials and methods

1. Source of sample pesticides: Center Agric. Pesticides Laboratory and formulation of pesticides (Table 1).

Table (1): Showed the formulation of pesticides.

Treed name	Active ingredient	Formulation Types	Impurities	Structure
Somathioen (Kz) 50%	Fenitrothion	EC	1- S-methyl fenitrothion Maximum: 2.5% 2- Tetramethyl pyrophosphorothioat (TMPP) Maximum: 0.3 % 3- Water Maximum: 2 g/kg.	
Malatoxs 57 %	Malathion	EC	1- Malaaxon Maximum: 0.1% 2- Isomalathion) Maximum: 2.5% 3- O,O,Strimethyl ester). Maximum: 1.6% 4-MeOOOPS-triester Maximum: 0.5%	 Malathion

2. Sample preparation for tested pesticides:

Accurately weighed enough samples formulation equivalent to 10 mg of standard in a different 25 ml volumetric flask for each sample, and slowly mixed with methanol and the volume was completed with methanol.

3. Sample preparation for impurities:

One g. tested formulation samples in 25 ml volumetric flask for each sample were prepared and slowly mixed with methanol and the volume was completed with methanol.

4. Storage stability tests:

The Previously pesticides (Malathion and fenitrothion) formulation were stored in oven at 54 °C for 14 days according to the (CIPAC Hand book F., 1995 and CIPAC Hand book, 1983) respectively 14 days storage. During the storage period the samples were taken at 0, 1, 3 ,7 , 14 , 21 and 28 days from storage to determine the active ingredient for formulation under testes.

5. Influence of direct sunlight and UV ray:

The pesticides (Malathion and fenitrothion) formulation were influence of direct sunlight .The

samples were taken at 0, 1,5 ,12 , 24 , 36 and 48 hrs. from influence direct sun light to determine the active ingredient and impurities content for formulation under testes if is present .

6. Determiation of pesticides by GC/Ms:

Apparatus Agilent B, 5977 AMSD gas chromatography equipped with an Agilent mass spectrometric detector , with a direct capillary interface and fused silica capacity Colum (30 m x 0.025 mm HP -5 0.25 microm 60 to 325/325 °C). Samples were injected under the following condition; Helium was used as carrier gas at approximately 1 ml /min, pulsed split mode, split ratio (10:1) split flow 10 ml /min. The solvent delay was 4 min and the injection size were 1 UL. Oven temperature program , %0 °C for O<5 min , the 10 /min ramp to 190 °C followed by a 10 °C /min ramp to 210 °C for 1 min followed by a 10 °C /min ramp to 300 °C and held for 2 min, total run time followed by a injection temperature was set at 280 °C. Wiley mass spectral data was used in the identification of the separated peaks .

7. Determination of active ingredient and their impurities by GLC apparatus:

Fenitrothion, malathion and their impurities were determined according to the method of CIPAC Hand Book E. (1993) and CIPAC Hand Book (1983) with some modification using Hewlett-Packard 6890 gas liquid chromatography equipped with flame ionization detector (FID), capillary column HP-50% (15m x 0.53mm i.d. μ m film thickness), and the carrier gas was nitrogen of flow rate 10 ml/min. Oven temperature 100 °C, 160 and 180 °C, respectively for the above pesticides and its impurities, injector temperature was 250°C and detector temperatures, 200°C. Under these conditions the retention times for dimethoate and its impurities were (2.45, 2.86 and 3.72 min), the results of the pesticides and their impurities were quantitatively determined by comparison with the active ingredient standards of known purity under the identical GLC conditions.

8. Determination of water in formulation which contains water impurities:

The water was determined by using isotropic method (Danstark apparatus), the apparatus consists of glass flask connected by a tube to cylindrical tube fitted with graduated receiving tube and reflux condenser. The receiving tube is graduated in 0.1 divisions so that the error of reading does not exceed 0.05 ml. The preferred source of heat is an electric heater with rheostat control. The upper portion of the flask and connecting tube could be insulated. Thoroughly the receiving tube and condenser of the apparatus were cleaned by rinse with water and allowed to dry. 200 ml of toluene and about 2ml of water were introduced into dry flask. The flask was heated until the liquid distillation over period of 2 hours

and allowed to cool for about 30 min and reading off volume of water to an accuracy of 0.05 ml (first distillation). A quantity of the material was weighted accurately to give about 2-3 ml of water for 15 min and transfer to the flask gently. When boiling begins, distillate rate of 2 drops per second until most of the water has still over then the rate of distillation was increase to about 4 drops per second. As soon as the water has been completely distilled, the inside of the condenser tube was rinsed with toluene. The distillation was continued for 15 min, the heat was removed, and the receiving tube could cool to room temperature, and the tube was dislodged by tapping. The water and toluene layer could separate and the volume of water were read off (second distillation) (CIPAC Hand Book F., 1995). The content of water as percentage was calculated using the formula: $\% = 100 (n_1 - n) / W$.

Where: W= the weight of the material being examined.

n= the number of ml water obtained in the first distillation of ml.

n₁= the number of ml water obtained in both distillations.

Results and discussion

1. Effect of storage temperature on stability of soumithion and malatoss active ingredient at 54°C:

The Present data in Table (2) illustrated that the stability of fenitrothion and malathion active ingredient were 50.43 and 57.17 before storage for all fenitrothion and malathion become after storage at the end of experiment 39.52 and 36.56 for 28 storage respectively. According to International Organization WHO specification storage at 54 °C for 3 days and FAO specification storage at 54 °C for 14 days. In general, storage under high temperature above 35 °C show negatively affect the stability if organophosphorus (Fishel, 1993).

Table (2): Effect of storage temperature on stability of soumithion Kz and malatoxs active ingredient at 54°C.

Storage periods (Days)	Soumithion Kz 50 % %		Malatoxs 57 %	
	Fenitrothion 50 %	Loss %	Malathion 57 %	Loss %
0*	50.43	00	57.17	00
1	50.43	00	57.10	0.12
3	50.21	0.43	57.00	0.29
7	49.23	2.37	56.23	1.67
14	47.91	4.99	56.20	1.64
21	40.56	19.33	47.34	17.19
28	39.52	21.16	36.56	36.05

0* One hour before exposure to storage.

2. Influence of direct sunlight and UV ray exposure active ingredients fenitrothion and malathion :

The present date in Table (3) illustrated that the stability of fenitrothion and malathion active ingredient were 50.43% and 57.43% before exposure sun light for all

fenitrothion and malathion become after exposure sun light at the end of experiment 45.77 and 39.11% for 48 hrs. exposure sun light respectively. The percentage loses of fenitrothion and malathion were 24.58 and 22.13% after 48 hrs. of exposure of UV lamp.

Table (3): Influence of direct sunlight and UV ray exposure active ingredients fenitrothion and malathion.

Storage periods (Hours)	Sun light				UV ray			
	Fenitrothion 50 %	Loose	Malatoxs 57%	Loss	Fenitrothion 50 %	Loos	Malatoxs 57%	Loss
0*	50.43	00	57.43	00	57.43	00	57.43	00
1	50.33	0.19	57.12	0.61	57.33	0.17	57.00	0.74
5	49.23	2.38	57.00	0.59	55.86	2.73	57.00	0.74
12	47.50	5.81	55.23	3.83	55.09	4.07	55.34	3.48
24	47.46	5.88	41.45	27.82	48.26	15.96	53.96	6.04
36	46.51	7.58	40.77	29.00	44.82	21.19	53.00	7.71
48	45.77	9.24	39.11	31.89	43.32	24.58	44.72	22.13

3. Effect of storage temperature on stability of impurities fenitrothion and malathion 54 °C:

Data in Table (4) show that the impurities of Fenitrothion 50 % EC before storage were UND S-methyl Fenitrothion , TMPP Tetramethyl pyrophosphorothioat and water become after storage 1.17 , and UND and UND after 28 days from storage at 54 °C respectively this results according to

organization FAO specification maximum level impurities 2.5 % S-methyl fenitrothion . Also, malathion 57 % EC before storage meoops , moosPs , malaxoin and isomalathion after storage 0.75 , 0.217 , UND and 2.89 respectively . The percentage of meoops and isomalathion were more than the (FAO maximum levels 0.5 and 2.5 % , respectively).

Table (4): Effect of storage temperature on stability on impurities Fenitrothion and malathion at 54 °C.

Storage periods (Days)	Soumithion (KZ) (Fenitrothion 50 % EC)			Malatoxs (Malathion 57 % EC)			
	S-methyl fenitrothion	Tetramethyl pyrophospho rothioat (TMPP)	Water	eeoops ester	MooSPs	Malaxoin	ISO malathion
0*	UND	UND	UND	UND	UND	UND	UND
1	UND	UND	UND	UND	UND	UND	UND
3	UND	UND	UND	0.030	0.36 1	UND	0.204
7	0.69	UND	UND	0.036	0.141	UND	0.180
14	0.78	UND	UND	0.44	0.160	UND	1.88
21	1.07	UND	UND	0.519	0.216	UND	1.89
28	1.17	UND	UND	0.751	0.217	UND	2.89

0* One hour before exposure to storage.

4. Effect of storage temperature on stability on impurities fenitrothion and malathion at sun light and UV ray:

The present Tables in (5 and 6) showed that the impurities of Fenitrothion 50 % EC before influence exposure sun light and UV ray were UND S-methyl Fenitrothion , tetramethyl pyrophorothiate and water become after exposure sun light and UV lamp 1.92, UND, UND , 1.83 , UND and UND after 48 hrs. from exposure sun light and UV lamp

respectively . Also, malathion 57 % EC before exposure sun light and UV lamp UND meoooks , mooSPs , malathion and isomalathion after exposure sun light and UV ray 0.80 , 2.32 , UND , 2.80, 0.79 , 2.28, UND and 2.56 respectively . The percentage of meoooks , mooSPs and isomalathion were more than the FAO Maximum levels 0.5 , 1.6 and 2.5 %) .It was notes that isomalathion was increased by the storage period, this could be due the degradation of malathion.

Table (5): Effect of storage temperature on stability on impurities fenitrothion and malathion at sun light.

Storage periods (Days)	Fenitrothion			Malathion			
	S. Methyl fenitrothion	Tetramethyl pyrophorothiate	Water	Meoooks ester	MooSPs	Malaxoin	ISO malathion
0	UND	UND	UND	UND	UND	UND	UND
1	UND	UND	UND	UND	UND	UND	UND
5	UND	UND	UND	0.35	1.10	UND	0.29
12	UND	UND	UND	0.52	1.20	UND	0.34
24	1.02	UND	UND	0.66	1.97	UND	1.18
36	1.09	UND	UND	0.76	2.28	UND	1.38
48	1.92	UND	UND	0. 80	2.32	UND	2.80

0* One hour before exposure to storage.

Table (6): Effect of storage temperature on stability on impurities Fenitrothion and malathion at UV ray.

Storage periods (Days)	Fenitrothion			Malathion			
	S. Methyl fenitrothion	Tetramethyl pyrophorothiate	Water	Meooops ester	MooSPs	Malaxoin	ISO malathion
0	UND	UND	UND	UND	UND	UND	UND
1	UND	UND	UND	UND	UND	UND	UND
5	UND	UND	UND	0.24	1.05	UND	0.20
12	UND	UND	UND	0.56	1.45	UND	0.31
24	0.80	UND	UND	0.77	1.97	UND	1.29
36	1.00	UND	UND	0.79	2.28	UND	2.03
48	1.83	UND	UND	0.79	2.28	UND	2.56

0* One hour before exposure to storage.

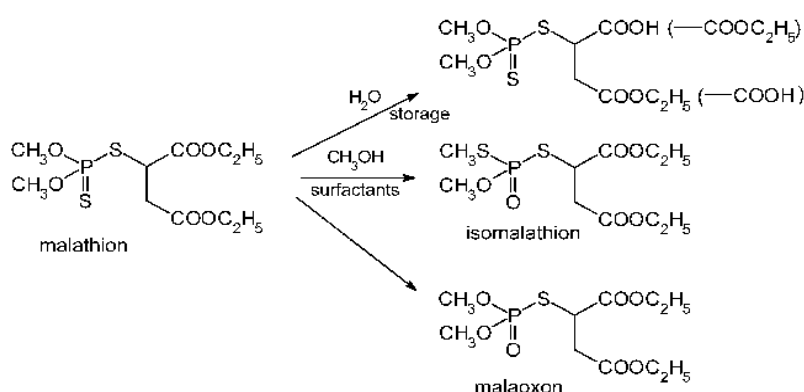


Figure (1): Possible pathways for the formation of impurities of malathion during storage.

5. The degradation product on fenitrothion and malathion By GC/MS:

The data in present in Table (7) showed that fenitrothion and malathion degradation after 28 days product S – methyl fenitrothion and O,O S triethyl ester, malathion product isomalathion. This According to the chemical structure of malathion and metabolism, tow pathway are proposed for malathion photodegradation Figure (1). In the first proposed pathway, the sulphur atom in the P =S bond of malathion will be oxidized into P= O by the ROS attack, such as OH radicals, which leads to the formation of isomalathion. The formation of oxidized derivatives has been documented in the photocatalytic degradation of organophosphorus pesticides containing P=S group (Kraljet *et al.*, 2007 and Liu *et al.*,

2015). In the second proposed pathway, the sulphur atom in P-S or S-C bond could be attacked by positive holes to generate sulfide cation radicals initiate the degradation reaction. Under the sun light, photocatalytic reaction may produce a single electron from the sulfur atom, then initiate P-S or S-C cleavage. The cleavage of P-S bond forms $\text{SCH}_2\text{CONHCH}_3$ radicals and the cleavage of C-S bond forms $(\text{CH}_3\text{O})_2\text{SPS}$ radicals, $\text{SCH}_2\text{C}(\text{O})\text{NHCH}$ Radicals are easier dimerize and led to the formation of 1,2 Bis (Acetyl-N-methyl methane disulfide (Vidal *et al.*, 1999). Similarly, $(\text{CH}_2\text{O})_2\text{SOS}$. Radicals tend to combine with methyl radical (CH_3) to form the reaction mesia O, O, S trimethyl thiophosphorothioate will be generated after oxidization and successively mineralized SO_4 , PO_4 , CO_2 and H_2O

Table (7): The degradation product on Fenitrothion and malathion By GC/Ms.

Pesticides	RT Before	RT After	Compound product after storage 54 C.
Fenitrothion	-----	5.30	Dimethyl benzene
	-----	5.90	1,3 dimethyl
	-----	7.52	Methyl Parathion
	-----	7.97	CarboMethyl Fenitrothion
	-----	8.22	3-methyl 4-nitrophenol
	-----	10.23	S- methyl Fenitrothion*
	24.81	24.81	Fenitrothion
Malathion	-----	5.20	Ethyl benzene
	-----	5.91	Dimethyl benzene
	-----	12.11	O,O S triethyl ester *
	-----	12.23	Isomalathion*
	25.24	25.24	Malathion
	-----	<u>26.26</u>	O,s dimethyl phosphorodith

*Impurities.

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