Journal

J. Biol. Chem. Environ. Sci., 2009, Vol. 4(3): 813-830
www.acepsag.org

EFFECT OF STORAGE TEMPERATURE ON THE STABILITY OF CHEMICAL AND PHYSICAL PROPERTIES WITH DETERMINATION OF MALATHION AND FENITROTHION INSECTICIDES FORMULATIONS RESIDUES IN CUCUMBER FRUITS

Olfat A. Radwan and Atallah I.E.

Pesticides Analysis Dept. Central Agriculture pesticides Lab, Agricultural Res. Center, Dokki, Giza

ABSTRACT

Two insecticides formulation recommended to be used for pest control in Egypt was subjected to storage conditions at the room temperature (25°C), 54°C and sunny place for 14 days and at 72°C for 3 days. The effect of storage on chemical stability and physical properties of malathion and sumithion (fenitrothion) insecticides were considered results showed that the chemical analysis by GC. fenitrothion insecticide was more stable when storage at different temperatures while malathion insecticide formulation was stable when storage at different temperatures than storage at 72°C and the dissipation % in active ingredient was 2.789% according to FAO/WHO meeting (2002) The used formulations become non conformity when storage at 72 °C . GC/MS analysis gives the same separation peaks after and before at all storage conditions except at sunny place its give a new separation peaks after storage. An IR analysis showed that % match of malathion and sumithion insecticides formulations was more than 90 at different storage temperature. On the other hand results showed that physical properties (Emulsification test) were not affected by storage temperature except in case of storage at 72°C whereas, a cream layers 5ml was found at the tap of the containers. So, the best stability for physic-chemical properties could be achieved if the malathion and sumithion formulations stored at room temperature. 54 °C and in sunny place while storage at 72°C were more effective on malathion and sumithion formulations. Cucumber plants were treated with the recommended rate of

malathion and sumithion under the normal field conditions in winter season. Residues analysis showed that the initial deposits (0.5 and0.2ppm) in cucumber fruits. The percentage of loss was (21.9 & 44.10 %) one day after treatment. The residual half life in cucumber was 54.79 and 26.83 hours. For malathion and sumethion respectively. Washing process was effective methods for value 0.42 &0.13 ppm of initial deposits residual of malathion and sumithion respectively on cucumber fruits. The pesticide residues was dissipated to different degrees, with the time elapsed after spraying. The Pre Harvest Interval (PHI) were 14 days post treatment for malathion and sumithion on cucumber fruits, and the residue was low than Acceptable Daily Intake (ADI) after PHI period. These values for malathion and fenitrothion. by CAC/pr 2000 was 0.02 and 0.005 mg/kg (ppm) respectively.

INTRODUCTION

Pesticides may fail to comply with the FAO/WHO meeting specifications 2002 required if is improperly stored. Chemical and physical instability usually lead to the determination of the active ingredient (a.i) content and emulsion stability under the variable climatic conditions as well as several cases (El-Shemy *et al* 1992; El-Deeb *et al* 1991 and Emara & Abdel Aziz 2007). Ministry of Agric. followed FAO and WHO specification and issued a recommendation for local registration in Egyptian market, Centre Agric. Pesticides Laboratory represented by pesticides analysis Res. Division conduct chemical and physical analysis, which involves a.i percentage, fingerprint, and impurities determination by GLC, FT-IR spectra and NMR spectra instruments. In addition, the purpose of this study was to demonstrate the determination of malathion and sumithion in cucumber fruits this will reveal the rate of its persistence in the plants to determine the pre harvest interval (PHI) that should pass after the last treatment and before harvesting for normal the role of human consumption. Washing process to remove surface residues and consequently shortening the safe intervals prior to harvesting was evaluated (Nasr 2002; Hala 2003; Osman *et al* 2004; and Emara 2006).

MATERIALS AND METHODS

Pesticides used:

Malathion (57%EC) insecticide, acaricide from Sumitomo.

Chemical name: diethyl ((dimethoxy phosphinothioyl) thio) butanedioate.

Fenitrothion (50% EC) insecticide from Sumitomo.

Chemical name: *O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate.Fig(1).

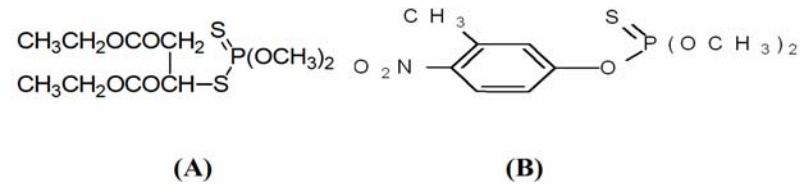

Fig (1): **The chemical structure of (A) malathion and (B). Fenitrothion**

(I)Chemical analysis:

Active ingredients percentage:

Active ingredients percentage were determined before and after storage for tested insecticides malathion and fenitrothion by GLC instrument according to CIPAC hand book (1998) with some modifications.

GLC conditions:

The type of chromatographic system was Hewlett Packard serial 6890 gas chromatograph Fitted with flame ionization detector (FID) , capillary column 15m X 0.53mm and the carrier gas was nitrogen at a flow rate 40 ml / min used under following conditions as shown in table (1) .

Table (1): GLC conditions

Pesticides	Temperature condition °C		
	Oven	Injector	Detector
Malathion	210	250	275
Fenitrothion	200	250	275

The results of tested insecticides were quantitavely determined by comparison with the standards of known purity under the identical GLC conditions.

(B) Absorbance of organophosphorus formulations in infrared (IR spectra) and spectrum of the two tested insecticides by NMR instrument.

The Fourier transform infrared (Avtar 330 Thermo Nicolet) was used to study the effect of storage on the absorbance of function groups and finger print of organophosphorus insecticides formulations according to Barbra (1985) with some modification. Samples were prepared by homogenized 0.01 g. of sample with 0.1 g of dry (KBr) by agatemortar and pestle, and then 0.03g from above mixture was transferred with forceps to a clean stainless steel slide and placed in piston to make at clear and thin film of sample.

(C) Separation and fragmentation of organophosphorus insecticide formulation by gas chromatograph equipped with a mass spectrpmetric detector (GC/MS spectra).

The GC/MS was used to compare the separation and fragmentation of pesticide formulation before and after storage according to the method of Saad *et al.,* (1993).

GC/MS analysis was performed with an Agilent 6890 gas chromatograph equipped with a mass spectrometric detector (MSD) model agilent 5973. Afused silica capillary column 9HP-5MS) , 5 % phenyl poly siloxane as non polar stationary phase (30m X0.25mm i.d) and 0.25 µm film thickness.

Operating condition was as follows:.

Injector port temperature, 250 °C. The helium was used as carrier gas at a flow rate of 1.0ml/min pulsed splitless mode. The column temperature was maintained at 80°C, for 3 min. Then programmed at 8 °C/ min. to 260°C, and held for 20min.

The total analysis time was 43min Al µl volume was injected splitless. The mass spectrometric detector (MSD) was operated in electron impact ionization mode scanning from m/z 50 to 550.

The ion source temperature was 230 °C and the quadrupole temperature 150°C. The electron multiplier voltages (EM Voltage) was maintained 1100 V above autotun , and solvent delay of 3 min

was employed. The instrument was manually turned using Heptacosafluoro Tributylamine (PFTBA).

(II)Physical properties:

Emulsion stability test:.

Five ml of each sample before and after storage was added to a graduated 100 ml cylinder filled with 95ml hard water (prepared according to CIPAC MT36) bymeans of pipette, and then pour the samples onto the water directed to the center . Stopper the cylinder and invert it for 30 times, and then placed in a water bath maintained at 30 °C ±1 for 30 min/ If there is any forming of oily or creamy layer. Either at the top or bottom of the cylinder must be not exceed than 2ml according to WHO (1985 and1979).

(III) Field experimental and sampling:

Cucumber plants were planted at a selected farm at Kafr Shokr Kalyobia Governorate on Oct. 2008 in plots of 1/100 feddan each. The plots received the normal agronomic practices throughout the experimental period. Malathion formulation (57%) was sprayed on Oct.10^{th} 2008 at the recommended rate 250ml/100 L (water)/ feddan. While farm at Kafr Shokr Kalyobia Governorate was sprayed by sumithion formulation 50% EC on Oct. 10^{th} 2008 at recommended rate 1500ml./100L water / feddan. A knapsack sprayer equipped with one nozzle was used.

Besides another blots were left untreated as control in both treatments. Representative samples of mature cucumber fruits (four replicates) were taken at random one hour after application. Subsequent samples were taken 1,3,5,7,and 14 days after treatment. Each sample was divided into two sub samples, the first was washed with tap water for min and the second was left unwashed sub samples were stored in poly ethylene bags until subjected analysis.

Extraction and clean up of tested insecticides:

Residues levels of malathion and fenitrothion in cucumber fruits were determined according to the method of Fytianos *et al*. 1998. Pesticide residues were extracted with 100ml acetone using the warring blender partitioned into n- Hexane .

The extract was carefully decanted and filtered through filter paper watman no.1 then dried through anhydrous sodium sulphate and evaporated on water bath at 40ºC to dryness by using rotary

evaporator. The resulting extract of cucumber fruits were cleared by C18 cartridge column chromatography. The insecticides extracts were evaporated at 30 ºC to dryness residues were dissolved in 1ml acetone and then determined by Agilent GC apparatus at the same conditions was described above.

Results were corrected according to the rate of recovery, which were determined in fortified untreated samples. Following the techniques previously mentioned, the rate recovery was 96.31 and 98.01 % with malathion and fenitrothion respectively. Student's (t) test was used to analyse the statistical significance between the same treatments (Gad and Weil, 1989).

RESULTS AND DISCUSSION

Effect of storage temperature on chemical properties:

(a) Affect of storage temperature on a. i percentage in malathion and fenitrothion insecticide formulations.

The data summarized in table (2) Showed that persistence of active ingredient % of used insecticide was affected by storage conditions and periods. The data indicated that storage at room temperature for 14 days and storage at 72 ºC in two tested insecticides is not affected while, storage at 72° C was the most effective in the chemical decomposition with malathion but fenitrothion was not affected. The malathion and fenitrothion active ingredient percentage as determined one hour before storage were 56.93 and 49.89% for malathion and fenitrothion respectively. Such deposits values were degraded with storage time to reach 55.41 and 49.73 % recording dissipation and loss by 2.789 and 0.54 % after 3 days of storage at 72° C these results are in line with Emara and Abd- El Aziz (2007) who reported that the effect of storage temperatures on the stability of chemical and physical properties of certain local organophosphorus insecticide formulations. Our results are in agreement with those Abdel-Aal *et al.,* (1993a,A&B) and El- Badry and Emara(2006) as they reported that the chemical decomposition of dimethoate , chlopyrifos and profenfos insecticides was higher under tropical storage (54- 72°C) than roof and shelf storage and increased by increasing the storage period. From these results we can observe that the fenitrothion pesticide showed more stability in storage at all treatment, while the malathion pesticide showed more stability in

storage at 54°C than 72°C and indicated that there is correlations between storage temperature and insecticide decomposition.

Table (2): **The effect of storage temperatures on active ingredient percentage in malathion and fenitrothion .**

Type of storage	Storage period (day)	malathion		fenitrothion	
		a.i %	Loss %	a.i %	Loss %
Room temperature 25 ° C	Initial 14	56.93 56.91	0.123 0.158	49.89 49.86	0.22 0.28
In sunny place	14	56.81	0.333	49.67	0.660
54° C	14	56.75	0.439	49.03	1.94
72° C	3	55.41	2.789	49.73	0.54

Initial = One hour before storage
Each value is a mean of three replicates of samples.

B) The effect of storage temperature on the absorbance of malathion and fenitrothion formulation in infrared:

The infrared spectrum of malathion and fenitrothion analysis and effect of different type of storage on the absorbance is presented in table(3,4).The IR spectrum analysis of tested pesticide characteristic by presence of peaks between 2871Cm-1 and 2929Cm-1 supported the present of methyl group (-CH3 , CH2 and CH) , also P=S group was characteristic by IR between 580-750 Cm-1 and P-O-C was characteristic between 970-1050Cm-1.

IR analysis of malathion:

IR analysis of malathion formulation before are shown in table (3) It may be noted that new bands appeared which produced by some shifting of some of the parent function groups and also disappeared some bands. The data showed that –CH3 methyl group absorption bands 2871.99 Cm-1 shifted about 0.11 Cm-1 where malathion storage at 72°C for 3 days. Also P=S absorption bands 699.69 Cm-1 were disappeared in case of malathion storage at 54°C for 14 days. Also P-S-C was pointed out by the band at 1457.82 Cm-1 shifted about 1.48, 0.57 and 0.88 Cm-1 and the % match were 98.21, 98.38

and 98.54 when malathion storage in sunny place , at 54°C and 72°C respectively.

IR analysis of fenitrothion:

The analysis of fenitrothion formulation before and after storage by (IR) spectrum are shown in table (4) It may be noted that new bands appeared which produced by some shifting of some of the parent function groups and also disappeared some bands. The data showed that P=S absorption bands 692.70 Cm-1 shifted about 2.21 Cm-1. Also –CH3 methyl group absorption bands 2872.16 Cm-1 were disappeared in case of fenitrothion storage at 72°C.

Table (3): The effect of storage temperatures on finger print of formulated malathion by using IR spectrum.

Position of bands Cm-1				
Malathion	Room temp.	Sunny place	54 °C	72°C
501.48	501.48	501.45	501.45	501.28
537.56	537.56	437.49	537.11	537.62
656.69	656.69	656.56	656.53	656.74
699.69	699.69	699.06	(I)	699.27
745.64	745.64	745.81	756.54	745.96
821.58	821.58	821.51	821.48	821.46
1016.91	1016.91	1017.01	1016.71	1017.49
1095.97	1095.97	1096.02	1096.12	1096.15
1175.71	1175.71	1175.63	1175.82	1175.88
1207.3	1207.3	1207.25	1207.88	1207.55
1256.07	1256.07	1256.28	1256.62	1257.15
1372.64	1372.64	1372.56	1372.38	1372.27
(I)	(I)	1407.78	1393.37	(I)
1457.82	1457.84	1456.34	1458.39	1465.94
1506.01	1506.04	1505.90	(I)	1505.92
1607.42	1607.42	1607.42	1607.46	1607.37
1736.46	1736.46	1736.47	1736.24	1736.42
2871.99	2871.99	2872.07	2872.19	2871.88
2949.70	2949.72	2949.65	2949.59	2949.71
3457.69	3457.70	3459.64	3457.11	3457.31
Match	100	98.21	98.38	98.54

(I) = Disappearance band.

(C) GC/MS analysis

(1) GC/MS analysis of malathion formulation:

The results summuramized in table(5) and fig(2) showed that storage malathion formulation in sunny place was more shifted than other type of storage which give the same separation. Where disappear and appear' a separation compound like malaoxon which was

appeared at the retention time 9.53min as a primary byproduct due to that organphosphorus insecticides containing P=S were easily degraded and produced oxons P=O (Magara *et al.*, 1994) before storage and different type of storage , while was disappeared from chromatogram of malathion formulation after storage in sunny places shown in Fig (2).

(2) GC/MS analysis of fenitrothion formulation:

The data showed in table (6) and fig(3) indicated that the fenitrothion formulation give the same separation compound before and after different type of storage.

Table (4): The effect of storage temperatures on finger print of formulated fenitrothion by using IR spectrum.

Position of bands Cm-1				
Fenitrothion	**Room temp.**	**Sunny place**	**54 °C**	**72°C**
556.16	556.16	556.14	556.15	(I)
613.90	613.92	613.89	613.90	(I)
642.47	642.47	642.45	642.47	641.81
655.53	655.53	655.53	655.53	655.53
692.70	692.73	692.70	692.70	690.49
746.15	746.15	746.15	746.15	(I)
827.22	827.22	827.22	827.22	825.84
890.83	890.83	890.83	890.83	890.57
971.85	971.85	971.85	971.85	971.51
1037.33	1037.33	1037.33	1037.33	1034.77
1163.21	1163.21	1163.21	1163.21	1163.52
1181.42	1181.42	1181.42	1181.42	1181.71
1239.64	1239.64	1239.64	1239.64	1239.73
1268.87	1268.87	1268.87	1268.87	1269.57
1308.65	1308.65	1308.65	1308.65	1309.28
1345.53	1345.53	1345.53	1345.53	1345.71
1402.56	1402.56	1402.56	1402.56	1402.72
1453.65	1453.65	1453.65	1453.65	1452.65
1523.45	1523.45	1523.45	1523.45	1522.32
1583.26	1583.26	1583.26	1583.26	1583.11
1615.20	1615.20	(I)	1615.20	1615.80
1869.59	1869.59	1869.59	1869.59	1870.79
2872.16	2872.16	2872.16	2872.16	(I)
2953.15	2953.15	2953.15	2953.18	2953.56
3025.67	3025.67	3025.67	3025.67	(I)
Match %	100	96	100	92

(I) = Disappearance band.

The effect of storage temperatures on physical properties (Emulsion stability test):

Data in table (7) indicated that two pesticides passed successfully through emulsion test in different types of storage and comply with WHO Specifications (1979)except in storage at 72 °C malathion and fenitrothion separate 4.6 and 0.6 ml cream later respectively. Similar results are obtained by Abdel-Aal *et al.,* (1993a,A&B) El- Badry & Emara (2006).

Generally , from the previous results a great interest to note the following remarks.

(1) Storage at 72 °C for 3days was the most effective in chemical and physical properties for Malathion but the storage at all types have no effect for fenitrothion .So, malathion formulation in this investigation become nonconformity when storage at 72 °C and become conformity when its storage at room temperature., at 54 °C and in sunny place. Our recommendation, pesticide formulations mainly insecticides must be storage away from high degree of temperature (72 °) to avoid the bad effects on the physical – chemical stability for majority of insecticides formulations.

Table (5): Separation and fragmentation of formulated malathion by GC/MS.

Type of storage	RT	Expected compound name	formula	M.W
Malathion Initial (One hour before storage)	3.7 4.2 4.83 5.75 6.01 6.76 9.53 9.68	Benzene 1,3-dimethyl –P- xylene Benzene 1-ethyl-3- methyl 2-oxa-1,3,3-trimethylbicyclo(2,2,2)octan 2-butenedionic acid diethyl ester Bicyclo(3.3.1)bept-3-en-2-one,4,6,6-trimethyl Diethyl mercapto succinate Malaoxon malation	C8H10 C9H12 C10H18O C8H12O4 C8H14O C814O4S C10H19O7PS C10H19O6PS 2	106 120 154 172 150 206 314 330
In sunny place (14 day)	4.11 4.96 5.8 5.89 6.24 6.48 8.14 9.68	Bicyclo(3.1.1)hepta-2-ene,2,6,6-trimethyl Bicyclo(3.1.1)heptane 3.Butenedioic acid,diethyl ester Bicyclo(3.1.1)hepta-3-en-2-one4,6,6 trimethyl Bicyclo(3.1.1)hepta-3-en-2-one2,6,6 trimethyl 2,6-octadien-1-1,3,7 dimethyl Beta- myrecene Malathion	C10H16 C10H16 C8H12O4 C10-H16 C10-H16 C10H18O C10-H16 C10H19O6PS 2	136 136 172 136 136 154 136 330
Room temp. (14 day)	Like completely			
54°C(14 day)	Like completely			
72°C(3 day)	Like completely			

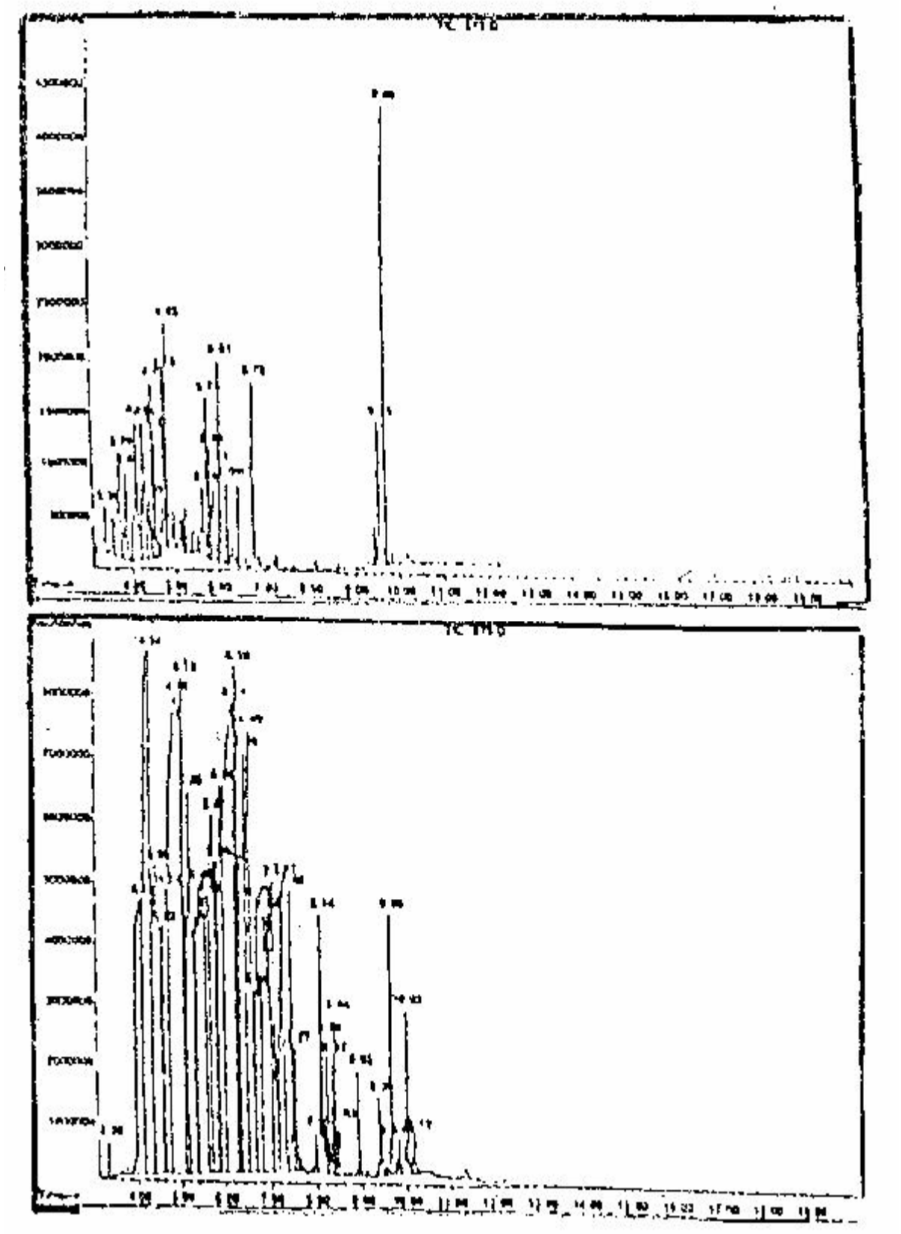

Fig (2): GC/MS Chromatogram of formulated malathion before(1) and after (2) storage in sunny place for 14 days.

Table (6) : Separation and fragmentation of formulated sumithion (fenitrothion) by GC/MS.

Type of storage	RT	Expected compound name	formula	M.W
Sumithion Initial (One hour before storage)	4.62 7.02 13.23 18.56 20.02	Benzene,2,4dimethyl-1-((3-methylphenyl)sulfonyl) 1,2,4- trimethyl benzene Benzene ,4-methoxy-2-methyl-1-nitro 10H-phenothiazine,5,5-dioxide phenothiazine Fenitrothion	C15H19SO2 C9H15 C8H8NO3 C12H9NSO2 C9H12NO2PS	260 105 167 231 277
In sunny place (14 day)	Like completely			
Room temp. (14 day)	Like completely			
54°C(14 day)	Like completely			
72°C(3 day)	Like completely			

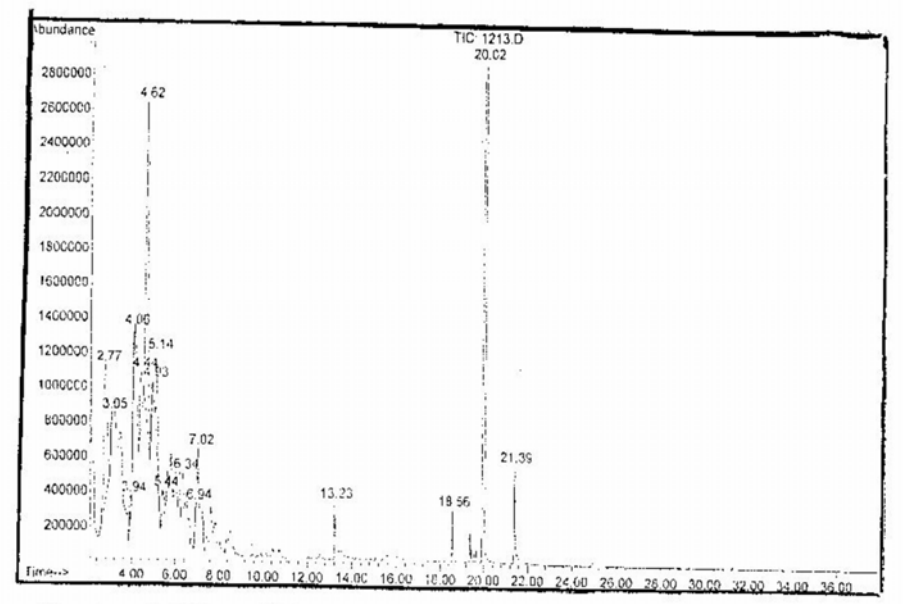

Fig (3) GC/MS Chromatogram of formulated fenitrothion before storage

Table (7): The effect of storage temperatures on emulsion stability for used formulated insecticides.

Types of storage	Period in days	Cream separation (ml)	
		Malathion	Fenitrothion
Initial(I)	(I)	(II)	(II)
Room temp.	14	(II)	(II)
In sunny place	14	(II)	(II)
54°C	14	(II)	(II)
72°C	3	4.6	0.6

(I) = One hour before storage.
(II) = Emulsification complete.

-Total residues in cucumber fruits:

Data in table (8) demonstrate the initial deposits and the residual behavior of malathion and dentition on cucumber fruits after treatment, the initial deposits revealed that the amounts of deposits depended on the nature of the treated surface and relation between the surface treated and its weight (El- Sayed *et al*, 1976).

The indicated that the initial deposits of malathion and fenitrothion residues in cucumber fruits as determined one hour after application(0.5 and 0.2ppm) malathion and fenitrothion respectively. The residues level of initial deposits with malathion and fenitrothion due to many factors ,the ratio of surface to mass area and character of treated surface (smooth or rough and waxy or non waxy) Abo El-Ghar and Ramadan (1992).Moreover , some pesticides were rapidly degraded in open field by sunlight and its stability in some crops which have waxy layer were as described to the diffusion of the active ingredient through the waxy layer of fruits surface that absorbs or reflects the rays, thus , it does not allow its degradation (Carbras et al., 1990). One hour after treatment was (0.5 and 0.2ppm) for malathion and fenitrothion respectively.

These values rapidly declined to 0.39 &0.11 ppm reflecting in the rates of loss 21.9 and 44.1 % malathion and fenitrothion respectively. 24 hours after treatment. Following that period, the

residues decreased to 0.20 ,0.16 ,0.11 ,and 0.02ppm in the cucumber fruits which reported loss of 58.84 , 66.34 , 77.26 ,and 95.9% after 3 , 5 , 7 ,and 14 days resp. with malathion. While the reduced to 0.09 ,0.05 ,0.004 , and 0.002ppm which losses values of fenitrothion rates were 47.75 , 52.25 , 97.90 and 98.85 % after 3,5,7, and 14 days resp. with fenitrothion . This results were similar to that obtained by El – Bouze *et al.*,2005 and Rafa (1998) who's found that the pesticide residues were decreased after treatments by time lapse and the residual half lives (Rl_{50}) of malathion and fenitrothion in cucumber fruits as obtained from persistence curve were (54.79 and 26.83 hour) after treatment resp. Concerning health hazards (MRL,s)for malathion 0.02ppm and not available for fenitrothion as related by codex alimentary committee for pesticide residues (CAC/PR,2000).

Table (8) : Residues of malathion and fenitrothion (µg/g- ppm) on and in unwashed and washed cucumber fruits under field conditions at different time intervals.

Days after treatment	Tested pesticides							
	Malathion				Fenitrothion			
	Washed		unwashed		Washed		unwashed	
	(µg/g) ppm	Loss %	(µg/g) ppm	Loss %	(µg/g) ppm	Loss %	(µg/g) ppm	Loss %
Initial	0.50 ±0.601	-----	0.42 ±0.131	16.00	0.20 ±0.113	-----	0.13 ±0.317	35
1	0.3905 ±0.022	21.90	0.3714 ±0.393	25.72	0.1118 ±0.093	44.10	0.0913 ±0.963	54.35
3	0.2058 ±0.019	58.84	0.1821 ±0.061	63.58	0.0955 ±0.312	47.75	0.0761 ±1.07	61.95
5	0.1683 ±0.033	66.34	0.1316 ±0.017	73.68	0.0526 ±0.132	52.25	0.0291 ±0.081	85.45
7	0.1137 ±0.057	77.26	0.0931 ±0.007	81.38	0.0042 ±0.071	97.90	0.0011 ±0.913	99.45
14	0.0205 ±0.0102	95.90	0.0073 ±0.813	98.54	0.0023 ±0.039	98.85	0.0003 ±0.196	99.85
Rl50	54.79 hour				26.83 hour			

From the previous study we can conclude that the residues of malathion were lower than its Acceptable Daily Intake (ADI)(0.02ppm) in open field . Also residues of fenitrothion were lower than its ADI (0.005ppm) in open field.

REFERENCES

AbdEl- Aal, A.F. ; A. G. El-Sisi ; M.A. El-Hamajy and A. Afify (1993a): Effect of storage conditions and chemical stability of formulations containing pesticide mixtures. Egypt.J.Appl. Sci. 8(10):16-23

AbdEl- Aal, A.F; A.G.EL-Sisi; M.A.El- Hamaky and A.Afify)1993b):The influence of paking and storage conditions on the physical and chemical stability of some pesticide formulations. Egypt J.Appl.Sci.8(9):499-508.

Abo-El- Ghar, M.R and M.M. Ramadan(1962): Studies on residue of certain organophosphorus insecticides on some vegetables. Bull. Soc.Ent. Egypt, pp.359-363.

El- Sayed, M.M.; S. M. Doghiem; S.A.Hindi, A.Shahin and M. Abdel-Salam(1976): Persistence of certain organophosphorus insecticides on some vegetables. Bull. Ent. Soc. Egypt., Econ. Ser. 10:41-49.

Barbara, S. (1985): Modern infrared spectroscopy published on behalf of Acol (University of Greenwich) by John Wiley &Sons Chichester, New Yourk . Brisban. Toranto. Singaore.

Cabras , P.,Spaneda.L; Cabitza F. ; Cubedda M.; Martini G.M. and Brandolini V. (1990): Primicarb abd its metabolite residues in letter influence of culture environment. H. Agric. Food Chem.; 38:879-882.

CIPAC Hand book (1998): Analysis of technical and formulated pesticides. Volume H, P.291.

Codex Alimentaries Committee for pesticide residues (CAC/PR) (2000): List of maximum residue limits for pesticides in food and animal feeds. Part 1.

El- Bouze, M.F.R.; Shereen A. Abd El- Aziz and Nevein S. Ahmed (2005): Residual behavior of some pesticides on vegetable fruits under green house conditions.Egypt.J.Appl.Sci.; 20(2),278-294.

El-Badry, B.M.and Ola M.Y. Emara (2006): Comparative studies on the stability of methomyl , carbofuran and abamectin from different companies under environmental factors. J. Pest. Cont.& Environ. Sci.14(2):207-225.

El-Deeb, W,H.; M.K.El-Shemy ab Y.S. Ebrahim(1991): Effect of storage temperature on the stability biological activity and

phytotoxicity of certain insecticide, Fourth Arab congress of plant protection,Cairo 1-5 Dec., p.399-403.

El- Shemy , M. K. ; S.H. Youssef ; Magdoline A. Saman and Y.S. Ibrahim .(1992): Stability of pesticide formulations under storage conditions. Egypt , J. Appl. Sci., 7(8), 93-106.

Emara, Ola M. Y.(2006): Residual behavior of fenthion and fenpyroximate on orange fruits Egypt. J. of Appl. Sci , 21(613),743-750.

Emara,Ola M. Y. and Shereen A. Abd El- Aziz (2007): Effect of storage temperature on the stability of chemical and physical properties of certain local organophosphorus insecticide formulations. Egypt. J.pf Appl. Sci.,m22(2B):813-828.

FAO/WHO meeting(2002): The tolerance for formulated products. Manual on development and use of FAO and WHO specifications for pesticides. First edition ,P31.

Fytianos , F; J.Konstantinou ; J. Kaidatzis and T.Albanis (1998):Multiresidue determination of insecticides and fungicides in fruits and vegetables by gas chromatography. Bull. Environ. Contam. Toxicol.,61:684-689.

Gad , S.C. and Weil, C .S.(1989): Statistics for toxicologist principles and methods of toxicology. Hayes, AW. (Ed)2nd ed. Raven Press. Ltd., New York, PP. 435-483.

Hala M.I.(2003):Determination of some pesticide residues in fresh agriculture produce available at local market in Egypt. MSc. Thesis Faculty of Science Helwan University.

Magara, Y.; T.Aizawa; N.Matumoto and F.Souna (1994): Degradation of pesticides by chloration during purification. Water science and technology:30(7):119-128.

Nasr, I.N. (2002): Persistence of primiphos-methyl residues on and in pepper and chili fruits and soil. The first Conf. of the central Agric. Pesticide 106,3-5 Sept., P. 1-7. Central Agric. Pesticide Lab., Agric. Res. Center , Dokki, Giza.

Osman,M.A.; Radwan, O.A. ; and Nasr, M.(2004): Determination of chlorphenapyr and abamectin residues in cucumber fruits. The second conf.on the role of biochemistry in environment and agriculture part II February 24-27.P.450-458.

Rafa A.E.A (1998): Determination of certain chlorinated and organophosphorus pesticide residues in vegetables and fruits. Ph.D. Thesis, Fac. Of Agric., Moshtohor, Banha Branch, Zagazig Univ. pp.118.

Saad M.M. Ismail; H.M.Ali and Habiba A. Ramadan(1993): GC-ECD and GC-MS analysis of profenfos residues and its biochemical effects in tomatoes and tomato products. J.Agric. Food Chem.41:610-615.

Shady,M.F.A.;M.E.A. Hegazy; F.A.Adam; M.A.Abd El-Baki and A.S. Shokr (2000): Persistence of malathion and prothiofos organophosphorus insecticides on and in some vegetables crops. Egypt. J. Agric. Res., 78(2): 605-619.

WHO(1985) : Specifications for pesticides used in public health. (6^{th} edition), P.374.

WHO(1979) : Specifications for pesticides used in public health, P.116 Geneva, Switzerland.

تأثير درجة حرارة التخزين على ثبات الخواص الكيميائية و الطبيعية و دراسة المتبقي من مستحضرات الملاثيون و الفنتروثيون الحشرية في ثمار الخيار

الفت عبد اللطيف رضوان و إبراهيم الدسوقي عطا الله
المعمل المركزي للمبيدات –قسم بحوث تحليل المبيدات مركز البحوث الزراعية الدقي-الجيزة-مصر

تتأثر الخواص الكيميائية و الطبيعية لمستحضرات المبيدات بالعديد من العوامل ومن أهمها ظروف التخزين الحرارية و قد اهتمت هذه الدراسة بمعرفة تأثير التخزين على درجة حرارة الغرفة و في مكان مشمس وعلى درجة حرارة 54 و 72 درجة مئوية على كل من الخواص الكيميائية و الطبيعية لأثنين من مبيدات الفسفور العضوية وهى ملاثيون 57% و سوميثيون 50% بصورة مركزات قابلة للاستحلاب. وقد و جدت الدراسة أن أفضل ثبات كان تحت ظروف التخزين على درجة حرارة الغرفة و على درجة 54درجة مئوية و التخزين في مكان مشمس و على 72درجة مئوية في حالة مستحضر السوميثيون بينما اختلف التأثير على مستحضر الملاثيون عند التخزين على درجة حرارة 72 درجة مئوية حيث تأثرت الخواص الطبيعية لمستحضر الملاثيون بينما أوضحت أجهزة التحليل الكروماتوجرافى الغازي وأجهزة التحليل الكروماتوجرافى الغازي المتصل بمطياف الكتلة أن كلا المبيدان تحت الدراسة أظهروا ثبات في الخواص الكيميائية وكذلك لنسبة المادة الفعالة حيث بلغت نسبة الفقد.للملاثيون 2.789% و السوميثيون 0.54%.التحليل في منطقة الأشعة تحت الحمراء قد أعطى بعض الاختلاف الجزئي و منطقة المجاميع الفعالة لكلا المبيدان تحت الدراسة تحت ظروف التخزين عدا في حالة التخزين على درجة حرارة الغرفة.أيضا أظهر اختبار الاستحلاب ثبات السوميثيون في كل حالات التخزين بينما أعطى فصل كريمي علوي مقداره 4.6 سم للملاثيون.

كما اهتمت هذه الدراسة بمعرفة مدى تكسير المبيدان السابقان في الظروف الحقلية حيث تم معاملة الخيار بكل من الملاثيون و سوميثيون بالمعدلات الموصى بها تحت الظروف الحقلية الطبيعية من تحليل المتبقي من هذين المبيدين في فترة ما بعد الرش مباشرة كانت 0.5و 0.2 جزء في المايون لكل من الملاثيون و السوميثيون على التوالي بينما حدث انخفاض بنسبة 21.9%للملاثيون و 44.10%السوميثيون بعد يوم واحد من المعاملة على التوالي ثم توالى تدهور هذه المتبقيات بمضي الوقت بعد الرش وذلك بدرجات مختلفة.عملية الغسيل أزالت 25.72% من الملاثيون و 54.35% من السوميثيون بعد يوم واحد من المعاملة .