



## Thermal storage effect on some of non fumigant nematicides

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### Abstract:

The effect of thermal storage on the degradation of fenamiphos ,oxamyl and ethoprophos under trade names nematop 40% EC, hidet star 24% SL and nemavet 20% EC, respectively, were studied .The results showed that the difference of the degradation rate for fenamiphos ,oxamyl and ethoprophos active ingredients in its formulation during storage stability test ,where the calculated half-life  $T_{0.5}$  were 615.6, 744.6 and 350.5 days, respectively. It means that velocity decomposition can be arranged as ethoprophos > fenamiphos > oxamyl . Also, N. nitroamine (impurity) in oxamyl was not detected during 30 days at  $54 \pm 2^\circ\text{C}$ . On the other, gas chromatography/mass spectrometry (GC-MS) was used to compare the fragmentation of three nematicides formulation (fenamiphos ,oxamyl and ethoprophos ) and resultes showed that breakdown of phenol-3-methyl-4-methylthio (fenamiphos phenol) and methyl (2-dimethyl amino)-N-hydroxy-2-oxoethanimidothioate (oximino oxamyl) as main equivalent product for fenamiphos and oxamyl, respectively. While ethoprophos less stability than fenamiphos and oxamyl.

### Introduction

Nematicides is the type of chemical pesticides used to kill nematodes, which are parasitic worms that feed on living material. They can often be harmful to plant growth and health as attack and feed on plant roots Deborah (2001), Lambert and bekal (2002) ,where numbers of eel worm get too high in the soil ,farmers sometimes apply chemicals called fumigant or non fumigant (organophosphate and carbamate) nematicides to the soil control them. However these chemicals are generally

very toxic and hazardous to the health of human and environment. Some nematicides were found to easily leach through the soil and contaminate drinking water in aquifers Barbercheck (2011). Nematicides like aldicarb, caudusfos, fenamiphos and oxamyl one of the most synthetic non fumigant nematicides in the global market .Oxamyl is lipophobic are less adsorbed than more lipophilic compound such as fenamiphos or ethoprophos ,and the former are more effective in a wide range of soil types,

organic contents moisture, soil PH and some environmental parameters such humidity, temperature, sunlight Hugo et al. (2014), Jones and Norris (1998). The aim of this investigation is to study the effect of storage stability tests on the

degradation of fenamiphos, ethoprophos and oxamyl. Also, identification of test nematicides by gas chromatography/mass spectrometry (GC/MS).

## Materials and methods

### 1. Nematicides used:

**Table (1): Name of nematicide, trade name, IUPAC name and molecular formula and mass.**

Name	Trade name	IUPAC name	Molecular formula and mass
Oxamyl 24% SL	Hidet star (Carb)	Methyl-2-(dimethylamino)N-(methyl carbamyl) oxy). 2-Oxo ethanimidothioate.	C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S 219.26 g/mol
Fenamiphos 40% Ec	Nematop (OP)	Ethyl 3-Methyl-4(methyl sulfenyl)phenyl isopropyl phosphoramidate	C <sub>13</sub> H <sub>22</sub> NO <sub>3</sub> PS 303.16g/mol
Ethoprophos 20% Ec	Nemavet (op)	O-ethyl S,S-dipropyl phosphorodithioate	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>2</sub> 242.3g/mol

SL: Solution stability EC: emulsion concentrate

Carb: carbamate Op: organophosphate

### 2. Storage stability test:

The tested samples were stored in oven at 54±2°C for 30 days. During storage period samples were taken at 0, 3, 7, 14, 21 and 30 days to determine the active ingredients for the above nematicides. Also, determine impurity (N-nitrosamine) in oxamyl during storage according to FAO (2008).

### 3. Preparation of sample:

#### 3.1. Standard preparation:

Ten mg of analytical standard from tested nematicides were weighted inside a 25 ml volumetric flask then dissolved and completed to the final volume with methanol.

#### 3.2. Sample preparation for tested nematicides:

Accurately weighed sufficient samples formulation to equivalent 10 mg of standard in different 25 ml volumetric flask for each sample, and weight 1 gm of oxamyl (impurity) was mixed in 25 ml of methanol:

#### 4. Determination of oxamyl, fenamiphos and ethoprophos by GLC instrument:

Hewlett-Packard GC (Model 6890 instrument, equipped with Flame ionization detector (FID), capillary column 15m, 0.55mm. Nitrogen was used as carrier gas at flow rate 40 ml/min. Injector temperature 250°C, Detector temperature 300°C and Oven temperature 200°C, 200°C and 100°C, respectively Mann (1981). At these conditions the retention times (Rt) of fenamiphos, ethoprophos and oxamyl were 3.07, 2.455 and 3.13 minutes, respectively. The results of the above samples were quantitatively determined by comparison with the standards of known purity under the identical GLC conditions.

#### 5. Determination of N. nitrosamines (impurity) in oxamyl by HPLC:

An equipment HPLC (Agilent 1200 series) was used DAD detector. The wavelength detector at 197 nm. A C18 column was used and the flow rate 1.3 ml/min. The mobile phase were acetonitrile : methanol (90:10w/v). At these conditions the retention time (Rt) of N-nitrosamines was illustrated by Gamon *et al.* (1998).

## 6. GC-Chromtography-Mass spectro-metry analysis of the some nematicides before and after storage :

Apparatures Agilent 7980 B, 5977 A MSD gas chromatography equipped with an agilent mass spectrometric detector ,with adirect capillary interface and fused silica capillary column (30mX 0.025 mm) .HP-5-0.25 microm -60 to 325°C was used .Samples were injected under the following conditions .Helium was used as carrier gas approximately 1ml/ min ,pulsed split mode ,splitle ratio (10:1) , split flow 10 ml/ min. The solvent delay was 4 min and the injection size was 1µL,Oven temperature program .50°C for 0.5 min, then 10°C / 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 :29.5 min), the injector temperature was set at 280°C. Wily spectral data base was used in the identification of separated peaks.

## 7. Kinetic study :

The rate of degradtion of the tested active ingredients and half –Life T<sub>0.5</sub> for the nematicides were calculation according to equation Moye *et al.* (1987).

$$T_{0.5} = \ln 2 / K$$

$$K = 1 / T_x \ln A / B_x$$

k. rate of decomposition

A: initial residue

T<sub>x</sub>: time in day

B<sub>x</sub> :residue at time

## Resultes and discussion

### 1. Influnce of storage stability tests on nematicides:

The storage stability test in one of the most important tests which gave attention on the importance of good storage conditions for pesticides, where temperature is known to be one of the most important factors influencing the stability ,persistence and degradation pesticides (Susana and Pieter , 2016).

Data present in Table (2) showed that active ingredient in tested nematicides were affected by storage conditions and periods exposure .The loss percentage of fenamiphos , Ethoprophos and Oxamyl were 2.15,12.2 and 1.87% ,respectively after 30 days of storage at 54±2°C. Decomposition of these materials can be calculating follows first order reaction. However, the half. Lives T<sub>0.5</sub> of these materials of Fenamiphos .Ethoprophos and Oxamyl were 615.6 ,350.5 and 744.6 days , respectively , it means that velocity decomposition can be arranged as Ethoprophos more Fenamiphos more oxamyl .The results in line with Dijksterhuis (1996) and Singh *et al.* (2005) , the degradation of oxamyl and aldicarb were still accelerated 5 years after last application ,while Ethoprophos have low environmental persistence but high toxicity. Genarally ,duration times for carbamate insecticides are usually longer than for organophosphorus insicides according to Smelt *et al.* (1996) and Hay dock *et al.* (2012).

### 2. Influnce of storage at 54 C on N.nitrosamines (impurity) of oxamyl :

N.nitrosamines are chemical compound of the chemical structure R<sub>1</sub>N-(R<sub>2</sub>)-N=O ,where R alkyl or aryl group , it is chemical are used in manufacture of pesticides like oxamyl. Most N.nitrosamines are carcinogenic is especially toxic to human either ingested ,inhalet or contact with skain , it over use can also lead to residue accumulation in food (Rostkowska *et al.* ,1998 and and Park *et al.* , 2015) .It is found that N.nitrosanines was not detected during storage for 30 days at 54±2°C.According to FAO specification (2008) which reported that maximum content of N. nitrosamines was 0.1 mg/kg of oxamyl .

**Table(2) :Effect of storage at 54±2°C on the stability of some nematicides.**

Storage periods (days)	Fenamiphos 40%EC	Loss%	Ethoprophos 20%Ec	Loss%	Oxamyl 24%SI	Loss%
0	39.92	0.00	19.87	0.00	23.98	0.00
3	39.77	0.38	19.81	0.301	23.81	0.71
7	39.39	1.33	19.71	0.81	23.69	1.21
14	39.19	1.83	18.66	6.09	23.52	1.91
21	39.12	2.004	18.04	9.21	23.56	1.75
30	39.06	2.15	17.44	12.2	23.54	1.87
T 0.5	615.6		350.5		744.6	

0. Initial time one hour before storage  $T_{0.5}$  half. life

### 3. Identification of fenamiphos by chemical ionization GC/MS spectroscopy: Fragmentation hypothesized to rationalize through :

Figure (1) described two possible reaction pathways leading to the degradation of fenamiphos M.F  $C_{13}H_{22}O_3NPS$  m/z 303.4.

#### 3.1. First cleavage phosphate ester bond and dealkylation by hydrolysis.

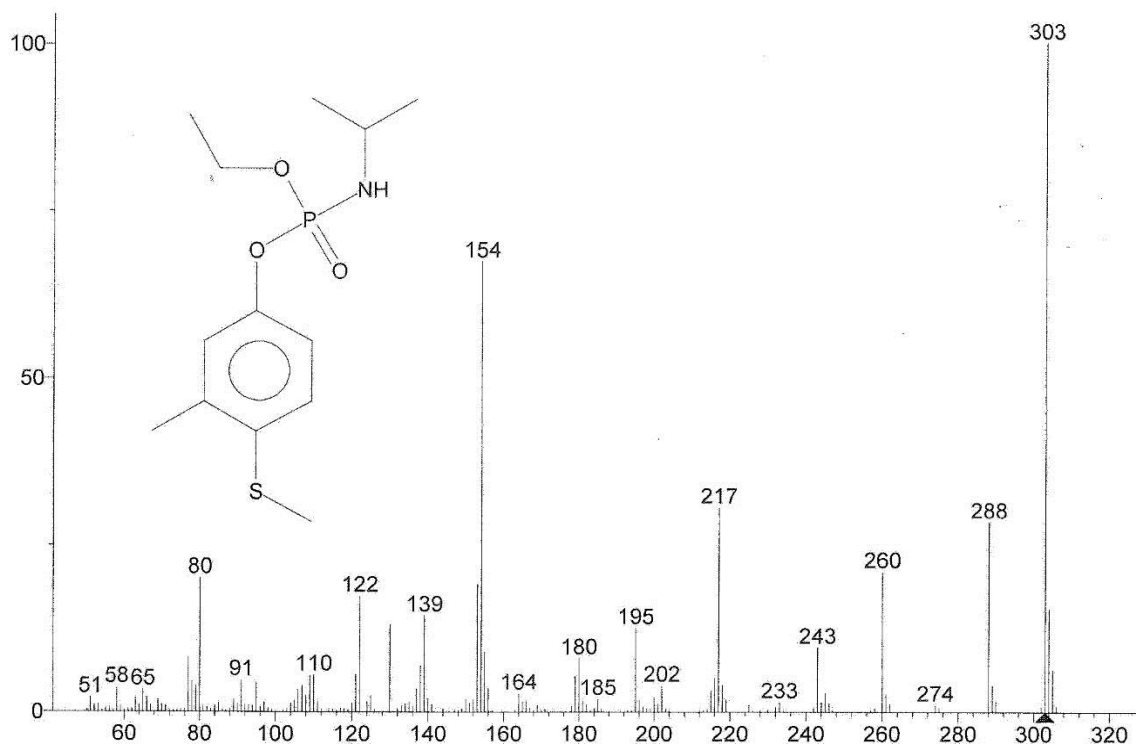
Results in the formation of M.F  $C_{12}H_{19}O_3NPS$  m/z 288 by loss  $CH_3$ , M.F  $C_{10}H_{13}O_3NPS$  m/z 260 by loss  $C_3H_7$  and ,then loss of  $C_3H_{10}N$  to  $C_{10}H_{12}O_3PS$  m/z 243.03 , loss of  $C_5H_{12}N$  to  $C_8H_{10}O_3PS$  m/z 217.08 , loss of  $C_3H_5O_3P$  to  $C_{10}H_{17}NS$  m/z 195, and  $C_9H_{14}NS$  m/z 180 by loss  $CH_3$ .

Second ,oxidation of fenamiphos to fenamiphos sulfoxide phenol  $C_{13}H_{22}O_4NPS$  m/z 319.3 (ethyl-3-methyl-4(methyl sulfenyl) phenyl isopropyl(amidophosphate) .

Fenamiphos phenol (phenol-3-methyl-4 methylthio) M.F  $C_8H_{10}OS$  which is formed by hydrolysis of fenamiphos sulfoxide has also low

detectable .Fenamiphos phenol m/z 154.04 as major degradation and loss  $CH_3$  to phenol -4-methylthio M.F  $C_7H_7OS$  m/z 139.01 .Fragmentation 2-aminopropan-2-yl (hydroxy) phosphinite M.F  $C_3H_9NO_2P$  m/z 122.03 ,phenylthio radical M.F  $C_6H_5S$  m/z 109.01 , methyl phenyl  $C_7H_7$  m/z 91 and phosphoroxyazanium  $H_3NO_2P$  m/z 79.99 gm/mol is described as final product of fenamiphos as shown in Figure (1) .

Data in Table (3) referred that retention time  $R_t$  of fenamiphos was 15.507 minutes before storage and  $R_t$  of breakdown product of fenamiphos , fenamiphos sulfoxide phenol and phenol -3-methyl-4 methylthio were 20.68 ,28.936 and 12.182 minutes ,respectively after storage . The finding is similar by Singh and Walker (2006), Caceres *et al.* (2010) and Kookana *et al.* (1997). Fenamiphos will be oxidation to fenamiphos sulfone ( $FSO_2$ ) The oxidation products are then converted into corresponding phenol by hydrolysis which considered to the most important step in the decontamination process in the environmental conditions.



**Figure (1): Mass Spectrometry (MS) of fenamiphos.**

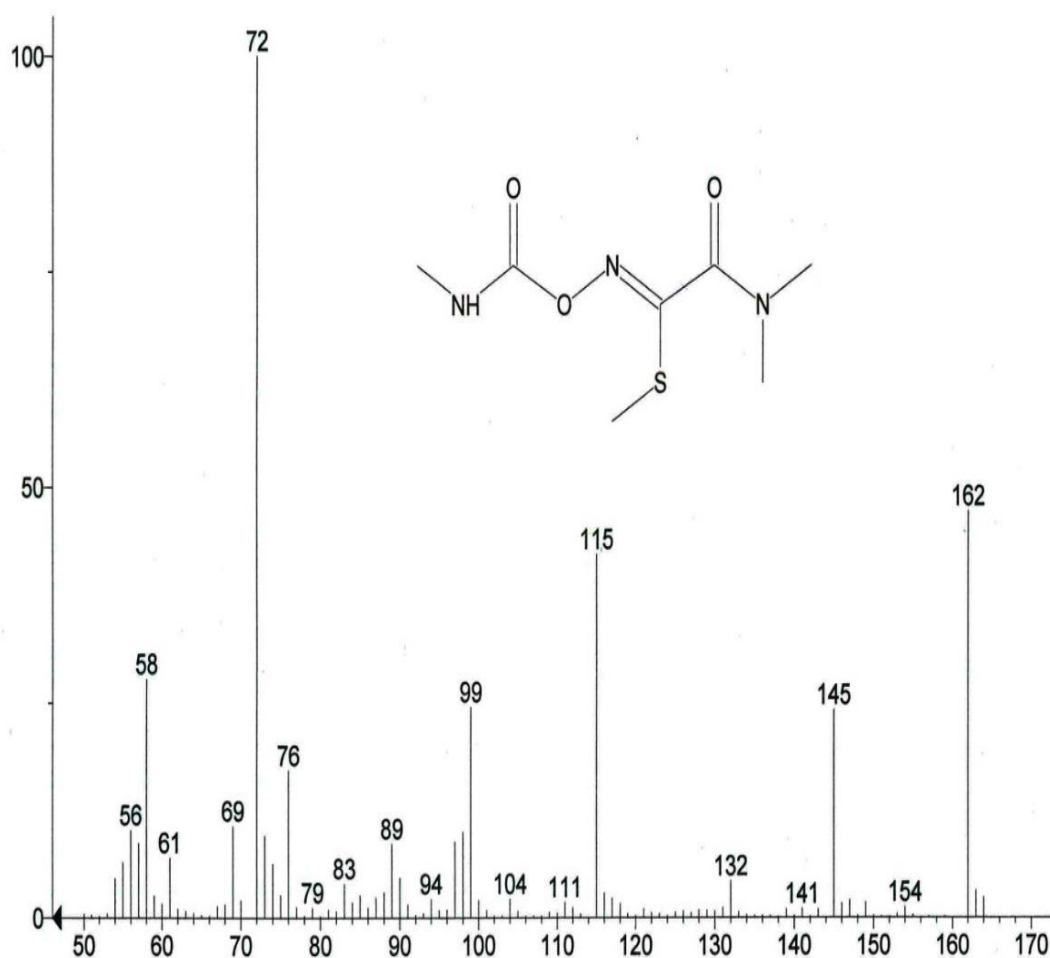
#### 4. Identification of oxamyl by GC-Mass spectroscopy:

Degradation of oxamyl M.F  $C_7H_{13}N_3O_3S$  m/z 219.26 gm/mol proceeded through hydrolysis and cleavage of the methyl carbamoyl bond  $CH_3NH-C=O$  yielded methyl (2-dimethyl amino) -N-hydroxy-2-oxoethanimidothiate known as (oximino oxamyl)  $C_5H_{10}N_2O_2S$  m/z 162.2 as major product. Further hydrolysis yielded by loss of  $CH_3NCO$  and  $CH_3$  to  $C_4H_7N_2O_2S$  m/z 145, loss of  $CH_3NCO$  and  $CH_3S$  to  $C_4H_7N_2O_2$  m/z 115, loss  $CH_3NCO$ ,  $CH_3S$  and  $HO$  to  $C_4H_6N_2O$  m/z 98.04 as minor product. While N,N-dimethyl (oxo) methaniminum  $C_3H_6NO$  m/z 72.1 as major product by GC-Mass as shown in Figure (2).

It is similar that MC Nalley and Wheeler (1988) cleavage of methyl carbamoyl bond to form oxamyl oxime as

the primary hydrolysis product and its geometrical isomer were observed in natural and distilled water exposed to artificial and sunlight. Further hydrolysis yielded (dimethyl amino oxacetic acid) as minor photodegradation product in natural water. Finally, the unstable carbamic acid is rapidly decayed to formaldehyde and  $CO_2$  (Osborn *et al.*, 2010). Table(3) showed that retention time of oxamyl and oxamyl oxime were 12.98 and 18.26 minutes before storage and shift to 12.97 and 18.25 min., respectively after 30 days of storage at  $54 \pm 2^\circ C$ .

Oxamyl oxime was identified as major breakdown product of oxamyl and increasing temperature after last application, total residue for oxamyl and oxamyl oxime reported as oxamyl equivalent (Holt and Pease, 1976).

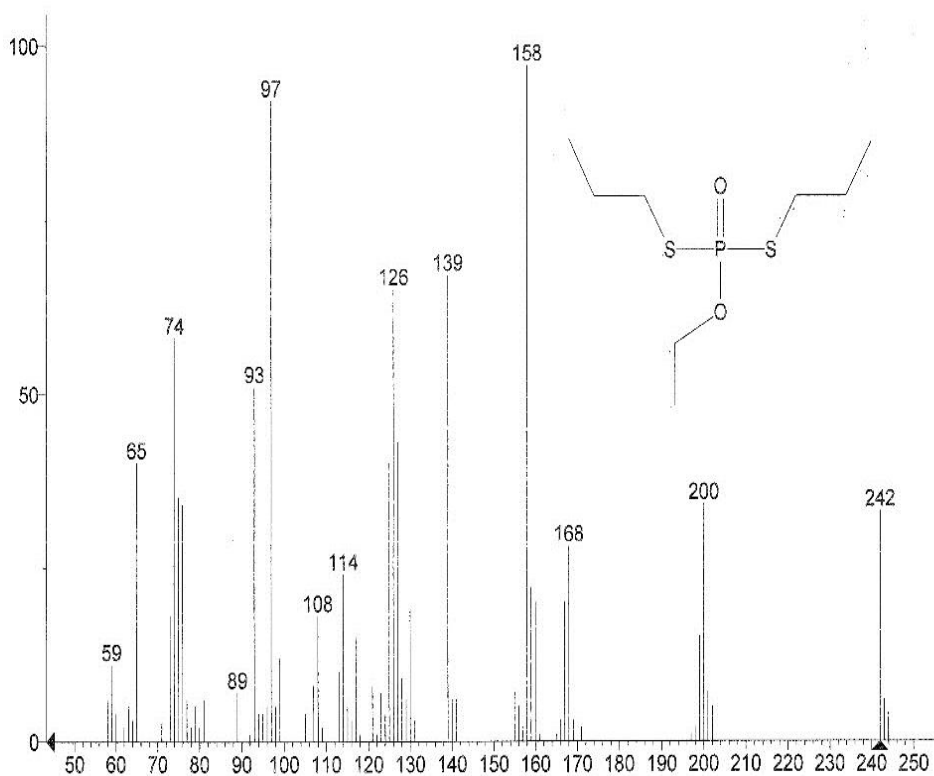


**Figure (2): Mass Spectrometry (MS) of oxamyl.**

### 5. Identification of ethoprophos by GC-Mass spectroscopy :

Mass Chromatogram is described in Figure (3) two possible reaction pathways leading to the fission of C-bond in ethoprophos  $m/z$  242.5 ,M.F  $C_8H_{19}O_2PS_2$  by hydrolysis ,results in the formation  $m/z$  200.2 ,M.F  $C_5H_{13}O_2PS_2$  by loss  $C_3H_6$  and  $C_5H_{12}O_2PS$   $m/z$  168 by loss  $C_3H_7S$  .Dimethylphosphorodithioate M.F  $C_2H_7O_2PS_2$   $m/z$  158 as the major intensity by loss  $2C_3H_6$  groupes in this compound as shown in Figure (3) .Another way by oxidation S is considered to be turned into  $m/z$  139

,M.F  $C_3H_7OPS$  and phosphenoithioic acid M.F  $H_2O_2PS$   $m/z$  97 as the major intensity in chromatogram .Propanethial  $C_3H_6S$  , $m/z$  74.1 and Propanol  $C_3H_6OH$   $m/z$  59.1 is described as final product of ethoprophos as shown in Figure (3) . According to Karpouzas and Walker (2000), it is found that the alkyl group attached to heteroatom S removed and oxidized to an alcohol . Data in Table (3) referred that retention time (Rt) of ethoprophos was 14.022 min before storage and (Rt) of ethoprophos was 14.52 min.after 30 days at  $54 \pm 2^\circ C$ .



**Figure (3): Mass Spectrometry (MS) of ethoprophos**

**Table (3): identification of fenamipho, oxamyl and Ethoprophos by chemical ionization GC/MS.**

Storage period	Nematicides degradation and m/z g/mol	Retention time (min)	Molecular formula their relatively intensity
<b>Initial</b>	Fenamiphos m/z303.4	15.507	C <sub>13</sub> H <sub>22</sub> O <sub>3</sub> NPS 99%
<b>After 30days of storage</b>	Fenamiphos m/z 303.4	16.27	C <sub>13</sub> H <sub>22</sub> O <sub>3</sub> NPS 99%
	Fenamiphos sulfoxide m/z 319.3	28.936	C <sub>13</sub> H <sub>22</sub> O <sub>3</sub> NO <sub>4</sub> PS99% low intensity
	Fenamiphos phenol m/z 154	12.182	C <sub>8</sub> H <sub>10</sub> OS 80%
<b>Initial</b>	Oxamyl m/z 219.26	12.98	C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S 64%
	Oximino oxamyl	12.262	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S 50%
<b>After Storage 30days</b>	Oxamyl m/z 219.26	12.97	C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S 64%
	Oximino oxamyl m/z 162.2	18.255	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S 50%
<b>Initial</b>	Ethoprophos m/z 242.5	14.022	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> S <sub>2</sub> 98%
<b>After Storage 30days</b>	Ethoprophos m/z 242.5	14.52	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>2</sub> 98%

**Initial . One heure before storage.**

It is concluded that half-life of ethoprophos is less than fenamiphos and oxamyl because breakdown of fenamiphos phenol and oxamyl oxime are equivalent active ingredients for fenamiphos and oxamyl, respectively. While breakdown of ethoprophos was not equivalent active ingredient for ethoprophos in environment.

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